

RILEM State-of-the-Art Reports

John L. Provis

Jannie S.J. van Deventer *Editors*

Alkali Activated Materials

State-of-the-Art Report,
RILEM TC 224-AAM



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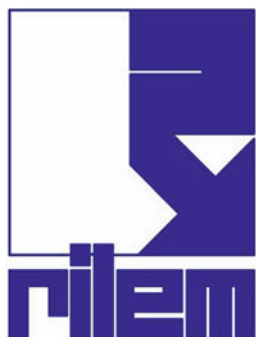
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Alkali Activated Materials

RILEM State-of-the-Art Reports

Volume 13

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Editors

Alkali Activated Materials

State-of-the-Art Report, RILEM
TC 224-AAM

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Preface

The concept of alkali activated materials (AAM) as an alternative to Portland cement has been known since at least 1908. Also, the durability of AAM in-service has been demonstrated over several decades in Belgium, Finland, the former USSR and China, and more recently in Australia. Nevertheless, fundamental research on AAM has blossomed internationally only since the 1990s, and most of this work has been focused on AAM microstructure with little emphasis on the prediction of service life, durability and engineering properties. Until recently, the field of AAM has been viewed as an academic curiosity with potential in niche applications, but not as a substitute for Portland cement in bulk applications.

There are several reasons why AAM technology has not received the same traction in the marketplace as has Portland cement. Firstly, limestone is available almost everywhere, so Portland cement can be produced in close proximity to markets. In contrast, precursors for AAM like fly ash and metallurgical slag are not available everywhere, or the supply chain for their distribution has not been established in local markets, as a supply chain has an interdependency with the existence of a ready market. Secondly, rapid advances in polymer admixtures since the 1970s have vastly improved the wet and cured properties of modern Portland based concrete. Advanced admixtures are not yet available for AAM, so it is a challenge for AAM to compete against modern Portland concrete from a placement perspective. Thirdly, Portland concrete has an extensive track record of more than 150 years, while AAM technology has featured in limited applications, with the early examples in the USSR not readily accessible to the wider market. Fourthly, all standards for concrete products in different jurisdictions have a cascading dependence on the assumption that Portland cement is used as the key binder, even when supplementary cementitious materials such as fly ash and blast furnace slag are included. When an AAM mix design not including Portland cement is introduced into a market, it does not comply with the existing standards, which has huge implications for decision-makers, especially consulting engineers and asset owners, regarding risk and liability. Fifthly, a series of durability tests, albeit not perfect, linked with the standards regime for Portland concrete has been accepted by the market as a means to predict

in-service life, mainly supported by Portland concrete's extensive track record. The absence of a long track record linked with uncertainty in the prediction of in-service life based on laboratory durability tests compounds the challenge to get AAM into the market. Sixthly, the existing engineering design codes for Portland concrete are based on a set of implicit assumptions relating microstructure to macro behaviour of the concrete under different environmental conditions. These assumptions may not be valid in the case of AAM, and inadequate research has been done to revise the design codes for AAM.

Clearly, the obstacles facing AAM in the marketplace are formidable. The substantial progress that has been made so far in the development and commercialisation of AAM bears testimony to the vision and determination of several individuals over many years. Nevertheless, the key driver for the wider adoption of AAM over recent years is the substantial reduction in CO₂ emissions compared with Portland cement. It is a CO₂ conscious market rather than present or anticipated legislation on CO₂ reduction that has provided the impetus for the use of AAM in carefully selected commercial projects. Operational experience of AAM in large scale demonstration projects has stimulated further fundamental research, especially with the aim to understand the durability and engineering properties of AAM. Equally importantly, local markets have become more comfortable with a concrete not based on Portland cement, including in structural applications, which is a giant step forward. Consequently, around the world the level of confidence in AAM has grown as a result of progress at a commercial level linked with key advances in research. Today there is a body of solid science underpinning AAM technology, and the number of research papers in the field has grown exponentially, fortunately with more papers appearing in top ranked journals.

I wish to thank Prof. Angel Palomo of the Instituto de Ciencias de la Construcción Eduardo Torroja in Madrid, Spain, for his foresight when he suggested in late 2006 that a RILEM Technical Committee (TC) be established in the field of AAM. Professor Palomo was also the inaugural Secretary of this TC; his contributions to this TC and the field of AAM in general are gratefully acknowledged. It was symbolically an important step along the path of establishing confidence in a new construction material when RILEM approved TC 224-AAM in early 2007. Notably, TC 224-AAM was the first international committee in this field and its membership constituted the key players active in AAM from a concrete perspective. The membership changed marginally during the 6 years of the life of the TC, with the final 36 members contributing to this State of the Art Report representing 15 countries.

In line with the scope of RILEM as an organisation, the TC focused its activities on the application of AAM in construction materials, including concrete, mortars and grouts, with the exclusion of AAM as ceramic-type materials for high-temperature applications. The TC had three key objectives: (1) To review the state of the art of research on the chemistry and material science of AAM, as well as the performance of AAM concrete in-service; (2) To assess the existing standards regime, and to develop a framework to be used by standards bodies in different jurisdictions for the regulation of AAM; (3) To review published information on physical and chemical

test procedures to evaluate the durability of AAM, and to develop appropriate testing methods to be incorporated into a new standards framework. From the start it has been evident that a prescriptive standard would not be appropriate for the wide variety of source materials and activation conditions that could be used in AAM. A performance standard framework is required, which places renewed emphasis on performance testing of concrete, which in itself has been identified as a complex area that requires further work.

To a large extent the TC has met the above three objectives. At the same time, the activities of the TC have been invaluable in identifying the gaps in our understanding of AAM, so that more work is required in the following areas: (1) The mechanism of phase formation when low and high calcium precursor materials are combined requires improved understanding, in order to design practical mixing and curing conditions resulting in a stable binder gel not susceptible to desiccation; (2) Very little progress has been made on the development of chemical admixtures to manipulate gel setting times, to control rheology and workability of wet concrete, and to assist with the ambient curing of placed concrete; (3) Despite promising signs that alkali-aggregate reactions are less problematic in AAM than in Portland concrete, the expansive reactions in AAM concrete remain poorly understood; (4) AAM concrete appears to perform well under aggressive chemical and physical exposure conditions, but there is insufficient work relating laboratory test data to in-service performance; (5) Existing test methods for carbonation of AAM concrete appear inadequate; (6) The creep behaviour of AAM concrete lacks thorough investigation, which is an impediment to structural design. It is hoped that this State of the Art Report will enhance the confidence in AAM as a construction material, stimulate further research, promote commercialisation of AAM, and in the broader sense serve to educate the construction community about AAM.

TC 224-AAM was organised in the following three Working Groups (WG): (1) WG 1, led by Prof. John Provis (formerly of the University of Melbourne, Australia, and more recently of the University of Sheffield, UK), compiled a comprehensive review of research on AAM and industrial applications; (2) WG 2, led by Dr. Lesley Ko of Holcim in Switzerland, reviewed the existing standards in different jurisdictions and developed a framework for a performance standard for AAM; (3) WG 3, led by Dr.-Ing. Anja Buchwald (formerly of Bauhaus-Universität Weimar in Germany, and since 2009 of ASCEM in the Netherlands), focused on the development of testing methods for AAM with the aim to underpin a framework for a performance standard. Membership of the three WGs overlapped, and as the TC approached the drafting of this State of the Art Report during 2011, the foci of WGs merged in joint TC meetings with all members present, supplemented by extensive electronic communication between members. I am sincerely grateful to Prof. John Provis, Dr. Lesley Ko and Dr.-Ing. Anja Buchwald for the effective way in which they have facilitated the activities of the WGs. I also wish to acknowledge the contributions, guidance and advice by many of the TC members to the activities of the WGs, which are not necessarily fully reflected in a written report.

The inaugural meeting of TC 224-AAM was held on 5 September 2007 in Ghent, Belgium. WG 2 held specialist workshops in Zürich, Switzerland, on 27–28 March 2008, and also in València, Spain, on 2–3 October 2008. The second joint meeting of TC 224-AAM was held on 9 June 2008 in Brno, Czech Republic, in conjunction with the 3rd International Symposium on Non-Traditional Cement and Concrete, held in Brno from 10 to 12 June 2008, and in which several TC members participated. The TC held a workshop on AAM on 28 May 2009 in Kiev, Ukraine, during which 15 technical papers were presented. This workshop was followed by the third joint TC meeting on 29 May 2009. The fourth TC meeting was held on 9 May 2010 in Jinan, Shandong, China, in conjunction with the First International Conference on Advances in Chemically-Activated Materials (CAM' 2010) as part of the 7th International Symposium on Cement & Concrete. The proceedings of CAM' 2010 were edited by Caijun Shi and Xiaodong Shen and published as Proceedings 72 by RILEM Publications S.A.R.L., Bagneux in 2010. Many TC members contributed to CAM' 2010 during which 6 keynote talks and 23 general papers were presented.

The fifth joint meeting of TC 224-AAM was held on 1 July 2011 in Madrid, Spain, in conjunction with the XIII International Congress on the Chemistry of Cement (XIII ICC), in which many TC members participated. The TC also held a pre-congress training course on AAM, co-sponsored by RILEM and hosted by XIII ICC, in Madrid on 2 July 2011, which was attended by 60 delegates. The sixth and final joint meeting of TC 224-AAM was held on 7 September 2011 in Hong Kong as part of RILEM week. The TC Chair and Secretary presented a detailed report on the outcomes of TC224-AAM to the RILEM Week attendees. I wish to thank the many TC members who acted as hosts for TC and WG meetings for their professionalism, generosity, hospitality and above all, friendship. We worked hard together as a TC, but we also had lots of fun and good times which I hope everyone will cherish as I do.

All of 2012 and the first part of 2013 were devoted to the finalisation of this State of the Art Report. I wish to sincerely thank the authors of the 13 chapters for their hard work, dedication and collaborative spirit in producing an integrated document. Many authors have devoted large amounts of time and effort in drafting what is hoped will be a valuable reference publication in the field of AAM. It should be noted that chapter authors are in each case generally listed in alphabetical order, except where the majority of a chapter has been written by one author; in such cases, that author is listed first and the others are given in alphabetical order. I especially wish to express my gratitude to Prof. Arie van Riessen of Curtin University in Perth, Australia, and Dr. Frank Winnefeld of Empa, Switzerland, for the time that they have so generously devoted to reading and correcting the drafts of the various chapters.

I am convinced that all TC members, especially the authors, would like to join me in specifically acknowledging the tremendous efforts and contribution of Prof. John Provis to the operation of TC224-AAM. As Secretary for most of the life of the TC, he ensured that meetings were organised smoothly, minutes were kept meticulously, and communication with the RILEM Bureau as well as within the TC was effective. Moreover, Prof. Provis as joint Editor went well beyond the call of duty in ensuring that this State of the Art Report is a document that we could all be proud of. On behalf of all TC members I extend my deep appreciation to him for this selfless contribution.

Prof. Jannie S.J. van Deventer (Zeobond Pty. Ltd., Melbourne, and The University of Melbourne, Australia)

Chair of RILEM Technical Committee TC 224-AAM

Editors: John L. Provis^{1,2} and Jannie S. J. van Deventer^{2,3}

Title of State of the Art Report: “Alkali Activated Materials: State-of-the-Art Report, RILEM TC 224-AAM”

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Chapter 1

Introduction and Scope

John L. Provis

1.1 Report Structure

This report has been prepared by the RILEM Technical Committee on Alkali Activated Materials (TC 224-AAM). The objectives of this Technical Committee are threefold: to analyse the state of the art in alkali activation technology, to develop recommendations for national Standards bodies based on the current state of understanding of alkali-activated materials, and to develop appropriate testing methods to be incorporated into the recommended Standards. TC 224-AAM was formed in 2007, and was the first international Technical Committee in the area of alkaline activation. The focus of the TC has been specifically in applications related to construction (concretes, mortars, grouts and related materials), and thus does not encompass the secondary field of application of alkali-activated binders as low-cost ceramic-type materials for high-temperature applications at a comparable level of detail.

This State of the Art report will be structured in five main sections, as follows:

- Chapters 1 and 2 contain a historical overview of the development of alkali activation technology in different parts of the world, providing a basis from which to understand why the field has developed in the ways it has
- Chapters 3, 4, 5 and 6 focus on the discussion and analysis of alkali activation chemistry, and the nature of the binding phases in different alkali-activated systems:

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- high-calcium alkali-activated systems, in particular those based on metallurgical slags
 - low-calcium alkali-activated systems, predominantly dealing with alkali aluminosilicates and including those materials which are now widely known as ‘geopolymers’
 - a discussion of the intermediate compositional region, which is accessible by blending calcium-based and aluminosilicate-based precursors, as well as through the use of some sole precursor materials
 - the role of chemical admixtures in developing alkali-activated binders and concretes with desirable properties
- Chapters 7, 8, 9 and 10 contain the technical heart of the work conducted by TC 224-AAM, addressing issues of durability and engineering properties, standards compliance, and testing methods.
- Chapters 11 and 12 outline some of the applications (historical and ongoing) and potential areas for implementation of alkali activation technology.
- Chapter 13 concludes the Report by outlining the most important future needs in research, development and standardisation in the alkali activation field.

1.2 Background

The reaction of an alkali source with an alumina- and silica-containing solid precursor as a means of forming a solid material comparable to hardened Portland cement was first patented by the noted German cement chemist and engineer Kühl in 1908 [1] (Fig. 1.1a), where the combination of a vitreous slag and an alkali sulfate or carbonate, with or without added alkaline earth oxides or hydroxides as ‘developing material’, was described as providing performance “*fully equal to the best Portland cements*”. The scientific basis for these binders was then developed in more detail by Purdon [2, 3], who in an important journal publication in 1940 [2] (Fig. 1.1b) tested more than 30 different blast furnace slags activated by NaOH solutions as well as by combinations of Ca(OH)₂ and different sodium salts, and achieved rates of strength development and final strengths comparable to those of Portland cements. He also noted the enhanced tensile and flexural strength of slag-alkali cements compared to Portland cements of similar compressive strength, the low solubility of the hardened binder phases, and low heat evolution. Purdon also commented that this method of concrete production is ideal for use in ready-mixed and precast applications where activator dosage can be accurately controlled. However, sensitivity of the activation conditions to the amount of water added, and the difficulties inherent in handling concentrated caustic solutions, were noted as potential problems. Experience over the subsequent 70 years has shown that Purdon was correct in identifying these as issues of concern – see the comparable listing of difficulties presented by Wang et al. [4] in 1995, for example – but it has also been shown that each is able to be remedied by correct application of scientific understanding to the problems at hand.

a UNITED STATES PATENT OFFICE.

HANS KÜHL, OF BLANKENESE, NEAR HAMBURG, GERMANY, ASSIGNOR, BY MESNE ASSIGNMENTS, TO THE ATLAS PORTLAND CEMENT COMPANY, OF NEW YORK, N. Y., A CORPORATION OF PENNSYLVANIA.

SLAG CEMENT AND PROCESS OF MAKING THE SAME.

No. 800,939.

Specification of Letters Patent.

Patented Oct. 13, 1908.

Application filed July 3, 1907. Serial No. 381,860.

b

THE ACTION OF ALKALIS ON BLAST-FURNACE SLAG

By A. O. PURDON

Although slag may be considered to be a cement in itself, hydration proceeds with such extreme slowness that it cannot be used alone as such. The reactions are usually accelerated by incorporation with the slag of lime, Portland cement clinker, or anhydrite. The resulting cements, compared with Portland, are characteristically slow-hardening but attain great strength with time. A relatively small quantity of an alkali is a much more efficient accelerator. The resulting cement has greater strength, both initial and final, than Portland. The optimum quantity of caustic soda is 5–8% of the mixing water. The same effect is produced by incorporation of lime plus a sodium salt in such quantities as to produce a like quantity of nascent soda. Cements made in this way, apart from their characteristically high early strength, have the following advantages over Portland: (a) Heat of hydration is extremely low. (b) Concrete is practically watertight. (c) Low solubility in pure or aggressive waters.



Fig. 1.1 Early publications relating to slag activation: (a) the 1908 patent of Kühl; (b) the 1940 paper of Purdon, “*The action of alkalis on blast furnace slag*”; (c) the 1959 book of Glukhovsky, “*Gruntosilikaty*”

Following the initial investigations in Western Europe, research into alkali activation technology then moved eastward for several decades. Both the former Soviet Union and China experienced cement shortages which led to the need for alternative materials; alkali activation was developed in both regions as a means of overcoming this problem by utilising the materials at hand, specifically metallurgical slags. In particular, work in the former Soviet Union was initiated by Glukhovsky [5] (Fig. 1.1c) at the institute in Kiev which now bears his name, and focused predominantly on alkali-carbonate activation of metallurgical slags.

After the work of Purdon, alkali activation research in the Western world was quite limited until the 1980s, as highlighted in the timeline published in a review by

Roy [6]. Davidovits, working in France, patented numerous aluminosilicate-based formulations for niche applications from the early 1980s onwards [7], and first applied the name ‘geopolymer’ to these materials [8]. The United States Army published a report in 1985 discussing the potential value of alkali activation technology in military situations, particularly as a repair material for concrete runways [9]. This report was prepared in conjunction with the commercial producers of an alkali-activated binder which was at the time sold under the name Pyrament.

1.3 Combining Activators with Solid Precursors

Since the 1990s, alkali activation research has grown dramatically in all corners of the globe, with more than 100 active research centres (academic and commercial) now operating worldwide, and detailed research and development activity taking place on every inhabited continent. Much of this work has been based around the development of materials with acceptable performance, based on the particular raw materials which are available in each location; there are a very large number of technical publications available in the literature which report the basic physical and/or microstructural properties of alkali-activated binders derived from specific combinations of raw materials and alkaline activators. Rather than recapitulating these results in detail, the general outcomes of the work which has been published over the past several decades regarding the amenability of different precursors to activation by different alkali sources are summarised in Table 1.1.

1.4 Notes on Terminology

Some comments on terminology are also necessary as a part of this State of the Art Report, as this is a contentious point in the field of alkali activation in general. The discussion here follows in general terms the presentation of van Deventer et al. [10]; it should be noted that the Technical Committee is not necessarily in complete agreement regarding all of the points raised here.

There exists a plethora of names applied to the description of very similar materials, including ‘mineral polymers,’ ‘inorganic polymers,’ ‘inorganic polymer glasses,’ ‘alkali-bonded ceramics,’ ‘alkali ash material,’ ‘soil cements,’ ‘soil silicates,’ ‘SKJ-binder,’ ‘F-concrete,’ ‘hydroceramics,’ ‘zeocements,’ ‘zeoceramics,’ and a variety of other names. The major impact of this proliferation of different names describing essentially the same material is that researchers who are not intimately familiar with the field will either become rapidly confused about which terms refer to which specific materials, or they will remain unaware of important research that does not appear upon conducting a simple keyword search on an academic search engine. In the context of this Report, the terms ‘alkali-activated material (AAM)’ and ‘geopolymer’ are at least worthy of some comment:

Table 1.1 Summary of the different combinations of solid precursor and alkaline activator which have been shown to be feasible and/or desirable

	MOH	$M_2O_7SiO_2$	M_2CO_3	M_2SO_4	Other
Blast furnace slag	Acceptable § 3.2, § 3.3.1	Desirable § 3.2, § 3.3.2	Good § 3.3.3	Acceptable § 3.3.4	
Fly ash	Desirable § 4.2.1, § 4.3, § 5.4.1	Desirable § 4.2.2, 4.3, § 5.4.1	Poor – becomes acceptable with cement/clinker addition § 5.5.5	Only with cement/ clinker addition § 5.5.4	$NaAlO_2$ – acceptable § 4.2.3
Calcined clays	Acceptable § 4.2.1, § 4.4.1, § 4.4.2	Desirable § 4.2.2, § 4.4.1, § 4.4.2	Poor § 5.5.5	Only with cement/ clinker addition § 5.5.5	
Natural pozzolans and volcanic ashes	Acceptable/Desirable § 4.5	Desirable § 4.5			
Framework aluminosilicates	Acceptable § 4.4.3	Acceptable § 4.4.3	Only with cement/ clinker addition	Only with cement/ clinker addition	
Synthetic glassy precursors	Acceptable/Desirable (depending on glass composition) § 4.7	Desirable § 4.7			
Steel slag		Desirable § 3.7.1			
Phosphorus slag		Desirable § 3.7.2			
Ferronickel slag		Desirable § 3.7.3, § 4.6			

(continued)

Table 1.1 (continued)

	MOH	$M_2O \cdot rSiO_2$	M_2CO_3	M_2SO_4	Other
Copper slag		Acceptable (grinding of slag is problematic) § 3.7.3			
Red mud		Acceptable (better with slag addition) § 5.5.4			
Bottom ash and municipal solid waste incineration ash		Acceptable § 3.7.4			

The section numbers of this report where these different combinations are analysed in detail are also given

Notes:

1. Classifications are as follows:

Desirable: the synthesis of high-performance (high strength, durable) binders and concretes can be achieved by the use of this activator

Good: performance is generally slightly below that which is achieved with the optimal activator, but good results can still be achieved

Acceptable: the generation of valuable alkali-activated binders is possible, but there are significant drawbacks in terms of strength development, durability, and/or workability

Poor: strength development is generally insufficient for most applications; systems where it is noted that the addition of significant levels of Portland cement clinker is required would otherwise fall in this category

2. M represents an alkali metal cation; activation under high-pH conditions but in the absence of alkali metal compounds (e.g. lime-pozzolan cements) is beyond the scope of this Report

3. Blends of various raw materials are not described explicitly in this Table

4. The column headed $M_2O \cdot rSiO_2$ describes the full range of alkali metal silicate compositions, regardless of modulus (r)

5. Blank cells describe systems which have not been characterised in the open scientific literature

- Alkali activated material (AAM) is the broadest classification, encompassing essentially any binder system derived by the reaction of an alkali metal source (solid or dissolved) with a solid silicate powder [11, 12]. This solid can be a calcium silicate as in alkali-activation of more conventional clinkers, or a more aluminosilicate-rich precursor such as a metallurgical slag, natural pozzolan, fly ash or bottom ash. The alkali sources used can include alkali hydroxides, silicates, carbonates, sulfates, aluminates or oxides – essentially any soluble substance which can supply alkali metal cations, raise the pH of the reaction mixture and accelerate the dissolution of the solid precursor. Note that acidic phosphate chemistry in ceramic production [13] is not covered by this definition; in spite of occasional tendencies towards describing chemically bonded phosphate ceramics using ‘geopolymer’ terminology [14], this serves only to confuse the issue even further. This report also specifically excludes the analysis of lime-pozzolan based systems and other materials where an elevated pH is generated through the supply of alkaline earth compounds. The reactions which can take place between some (usually Class C) fly ashes and water [15], or (over an extended period of time) between slag and water [16], are also not incorporated into this definition, although a brief discussion of each of these classes of material is included in the report for the sake of comparison and completeness.
- Geopolymers [17] are in many instances viewed as a subset of AAMs, where the binding phase is almost exclusively aluminosilicate and highly coordinated [18, 19]. To form such a gel as the primary binding phase, the available calcium content of the reacting components will usually be low, to enable formation of a pseudo-zeolitic network structure [20] rather than the chains characteristic of calcium silicate hydrates. The activator will usually be an alkali metal hydroxide or silicate [21]. Low-calcium fly ashes and calcined clays are the most prevalent precursors used in geopolymer synthesis [22]. It is also noted that the term ‘geopolymer’ is also used by some workers, both academic and commercial, in a much broader sense than this; this is often done for marketing (rather than scientific) purposes.

The distinction between these classifications is shown schematically in Fig. 1.2. This is obviously a highly simplified view of the chemistry of concrete-forming systems; any attempt to condense the chemistry of a system such as $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-M}_2\text{O-Fe}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$ (to list only the most critical components) into a single three-dimensional plot is inevitably fated to make significant omissions. However, as a means of illustrating the classification of AAMs and their position with respect to OPC and sulfoaluminate cementing systems, it does serve a useful purpose. Geopolymers are shown here as a subset of AAMs, with the highest Al and lowest Ca concentrations.

We note also that the general classification of blast furnace slag (BFS) will be used throughout this Report; this will be used to encompass slags which have been cooled and pelletised or granulated by any of the variety of available processes. This review will not enter in detail into the discussion of the details of slag processing and chemistry; some of the information presented will relate specifically to pelletised slags and some to ground granulated slags, but they will be addressed under the general heading of BFS.

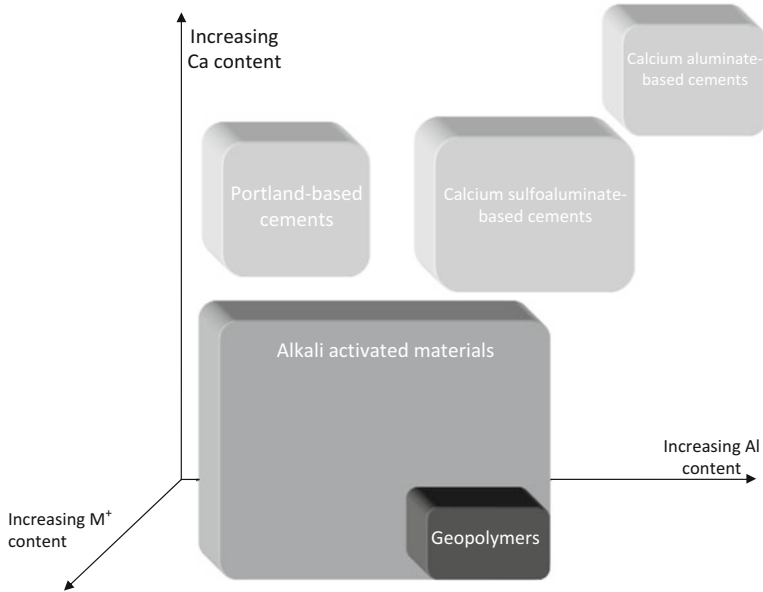


Fig. 1.2 Classification of AAMs, with comparisons to OPC and calcium sulfoaluminate binder chemistry. *Shading* indicates approximate alkali content; *darker shading* corresponds to higher concentrations of Na and/or K (Diagram courtesy of I. Beleña)

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Chapter 2

Historical Aspects and Overview

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2.1 Why Alkali Activation?

2.1.1 *The Global Perspective: Greenhouse Emission Drivers*

Cement and concrete are critical to the world economic system; the construction sector as a whole contributed US\$3.3 trillion to the global economy in 2008 [1]. The fraction of this figure which is directly attributable to materials costs varies markedly from country to country – particularly between developing and developed

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countries. Worldwide production of cement in 2008 was around 2.9 billion tonnes [2], making it one of the highest-volume commodities produced worldwide. Concrete is thus the second-most used commodity in the world, behind only water [3]. It is noted that there are certainly applications for cement-like binders beyond concrete production, including tiling grouts, adhesives, sealants, waste immobilisation matrices, ceramics, and other related areas; these will be discussed in more detail in Chaps. 12 and 13, while the main focus of this chapter will be large-scale concrete production.

Such an enormous volume of production is also associated with a very significant environmental penalty; cement production contributes at least 5–8 % of global carbon dioxide emissions [4], mainly because cement production requires the high-temperature decomposition of limestone (calcium carbonate) to generate reactive calcium silicate and aluminate phases. Demand for cement is growing rapidly worldwide, particularly in the developing world [5], meaning that there is an urgent need for alternative binders to meet the housing and infrastructure needs of billions of people without further compromising the Earth's atmospheric CO₂ levels.

Ordinary Portland cement (OPC) is normally made by heating a mixture of raw materials in a rotary kiln to about 1,450 °C, cooling this semi-molten material to form a solid clinker, then intergrinding with calcium sulfate to generate a fine powder. The major raw material used is limestone (mostly CaCO₃), which is blended with materials such as shales or clays to provide the necessary alumina and silica. The clinker is predominantly calcium silicate, which is rapidly cooled to stabilise a mixture of alite (3CaO·SiO₂) and belite (2CaO·SiO₂), with minor (but important) CaO-rich aluminate and aluminoferrite phases. However, when limestone is heated in the kiln, it decomposes according to reaction (2.1) to release 0.78 t CO₂ per tonne of CaO produced.



Gartner [6] calculated the total raw-materials CO₂ emissions (i.e. CO₂ released from the carbonate precursor) associated with each of the main cement-forming phases. Summing these values for the phase composition of a typical CEM I cement, around 0.5 t CO₂ per tonne of clinker is released by limestone decomposition, depending on the precise clinker composition. A value of 0.53 t CO₂ per tonne of clinker was given by Damtoft et al. [7], along with an average of 0.34 t CO₂ per tonne cement associated with energy consumption.

It is estimated by industry leaders that the current best-available technological strategies in Portland cement production (including the use of alternative fuels, optimised use of cement in concrete, recycling, and blending with pozzolans) could reduce CO₂ emissions from cement manufacturing and use by about 17 % [7].

One of the often-claimed, although rarely sufficiently substantiated, advantages of alkali activated materials (AAMs) over traditional Portland cements is the much lower CO₂ emission associated with AAM production. AAMs are among several alternative binders which are being discussed at present with a view towards obtaining environmental savings in the construction industry; others include calcium

aluminates, sulfoaluminates, supersulfated cements, and magnesium-based binders [8]. The CO₂ savings in the case of alkali-activated binders are mainly due to the avoidance of a high-temperature calcination step in AAM synthesis from ashes and/or slags. The use of an alkaline activating solution does reintroduce some Greenhouse cost, which is the key point requiring quantification and optimisation. Duxson et al. [9] presented a calculation of the CO₂ emissions due to various alkali-activated fly ash and/or metakaolin binders as a function of the dissolved solids (Na₂O + SiO₂) content of the activating solution. The CO₂ evolved during the production of Na₂O in the chlor-alkali process and SiO₂ as aqueous sodium silicate were used as the primary inputs, and this calculation showed CO₂ savings on the order of 80 % when compared to Portland cement on a binder-to-binder basis. The definition of the functional unit in an analysis such as this is of course important. When binder performance is taken into consideration, a ‘good’ alkali-activated binder may provide further advantages over a standard-performance Portland cement, but the converse is also true, and the environmental advantages which may be gained by the use of a novel binder could be negated, on a life-cycle basis by either lower strength (necessitating the use of more material for the same structural performance) or poor durability (necessitating more regular replacement).

Discussions around the life-cycle analysis of alkali-activated binders have provided results which vary dramatically between mix designs and binder types; it is not the role of this Report to provide commentary on the validity of the different lifecycle approaches adopted by different authors. The estimated CO₂ savings (comparing AAM to Portland cement) quoted in the literature from life-cycle studies range from 80 [10] to 30 % [11], with other studies providing values intermediate between these extremes [12–16]. Another recent study [17] provided a detailed emissions breakdown across a number of categories, but assumed the use of a rather inefficient process for the production of sodium silicate as an activator. This resulted in a calculated global warming potential for AAMs based on these materials which exceeded that of OPC concretes, in addition to significantly unfavourable outcomes in terms of other aspects of sustainability, particularly in terms of environmental toxicity. It is clear that further work and consistency is required in understanding LCA methodology before a consensus can be reached between the scientific and engineering communities and experts in Life Cycle Analysis. Consistency and defensibility of methodology and inputs is required to provide the firm scientific (and, in the current era of carbon taxation, economic) arguments which may eventually support wider uptake of AAMs in the marketplace.

2.1.2 The Global Perspective: Other Environmental Drivers

Despite visible and continuing progress in reducing the environmental impact of cement manufacturing, this industry does contribute very significantly to the environmental footprint of the world’s industrial sector, in several areas in addition to CO₂ emissions.

Firstly, this is connected with exhaustion of mineral reserves, especially with regard to relatively small European and East Asian countries, where cement consumption is rather high but natural resources are limited. Governments, facing societal pressures, are increasingly regulating the extraction of natural raw materials and the landfilling of high-volume wastes. This is in part for environmental protection reasons and partly for aesthetic reasons; having a large quarry or fly ash dump nearby is not attractive for residents or voters. While quarrying of aggregates is required for AAM concretes in an essentially identical manner to OPC concretes, the replacement of quarried raw materials by fly ash and/or slags provides advantages in both areas. Western Europe is certainly leading the world in this area at present in terms of blending waste ashes and slags into OPC-based concretes and in other methods of utilisation, with 100 % utilisation of fly ash, bottom ash and boiler slags reported in several European countries for more than a decade now [18, 19]. The main limitation on slag utilisation in binder production at present is the availability of sufficiently finely ground and glassy slags, as slow-cooled slag tends to crystallise and is used mainly as aggregate due to its low reactivity. In much of the developed world, ground granulated blast furnace slag is essentially fully utilised due to its beneficial properties in Portland cement concretes [20], being blended with cement either during or after grinding, or added during concrete mixing [21].

A second significant problem in cement manufacture is the issue of the emission of hazardous substances into the atmosphere from cement kilns. Major advances have been made in the ability to capture and recycle cement kiln dust and other potential emissions over the past several decades [22], but even so, there may be non-negligible emissions of hazardous components in the flue gas streams, particularly where older kiln types with limited gas scrubbing/cleaning capabilities are in operation, as in many parts of the developing world, and/or where wastes are being reused as fuels. It should be noted that the production of sodium silicate or hydroxide activators for alkali activation also introduces non-Greenhouse gas emissions (SO_x , NO_x , phosphate, and others) into lifecycle calculations [16, 17]; it is important to continue to develop rigorous methods for quantifying these emissions from different sodium silicate production routes, as initial computations are showing that these issues may prove more problematic for alkali-activated binders than is the case for Portland cement.

Conversely, the emissions of heavy metals (other than possibly mercury from some forms of the chlor-alkali process) are likely to be lower for AAMs than for Portland cement due to the removal of a kiln-based processing step. It could in some cases be argued that the alkali-activation of waste materials which would otherwise be landfilled is reducing the net heavy metals emission to the environment by solidifying these metals within the alkali-activated matrix.

Alkali activation technology also provides the opportunity for the utilisation of waste streams that may not be of significant benefit in OPC-blending applications. For example, work on magnesia-iron slags [23], ferronickel [24] slags, and tungsten mine waste [25], has shown that these materials can be effectively converted to valuable materials by alkali activation, while they are of little or no benefit as mineral additions to OPC. These may turn out to be minor niche applications for

alkali activation technology, but they do provide additional environmental drivers for these materials in certain scenarios and in certain regions where these wastes are available and/or problematic.

The basic aims and principles of European environmental policy are specified in Article 130r of the Treaty of Rome, and are directed towards the prevention, reduction and the elimination of environmental damage, preferably at source, and careful management of raw materials reserves. The most advanced building materials producing countries and companies are predominantly located in Europe, and are working actively to be on the leading edge of technologies, including looking ahead into the future for the development of new types of progressive building materials [8, 26, 27]. The introduction of the ideas of the European environmental policy has resulted in an attempt to introduce concepts such as the “best available technology” in order to limit emissions and meet environmental quality standards, and technological innovations in the cement and concrete industry are predominantly focused on achieving such goals, for both environmental and economic reasons. Further moves towards the development of energy-saving and environmental safety policies in the cement industry will almost certainly include development and commercial-scale application of binding systems with minimum Portland clinker content. An alkali-activated, or hybrid alkali-activated, cement can be considered as one such cementitious material.

2.1.3 Commercial Drivers

While at this time the environmental drivers may not be solely sufficient to induce widespread adoption of geopolymer technology, anticipated increases in the financial cost of CO₂ emission via national and international carbon credits trading schemes or ‘carbon tax’ regimes, and/or increases in the cost of potable water (which may be important in very dry regions), would mean that these factors would become commercial drivers which may take on some significance in the construction products industry.

The market competitiveness of different cements has traditionally been dominated by hardened binder performance properties, fresh concrete properties (workability), price, standardisation, and traditional work practises in the construction industry. Generations of engineers have been trained to select binder formulations and concrete mix designs which give the desired performance at the lowest possible economic cost, and Portland cement-based binders have overwhelmingly been the material system of choice due to ease of use and generally good performance. However, with the current focus on environmental issues as discussed in Sect. 2.1.2 above, priorities have changed greatly. Environmental performance (including energy consumption) is now of paramount importance in the selection of materials for construction in the developed world, and also increasingly in middle-income developing nations with a view towards future sustainability issues. The recent focus on global warming, public and consumer

preference for “green” products, and the associated market in carbon credits, have all now combined to make AAMs for the first time a viable large-scale proposition in the conservative cement and concrete industry.

Concern over Greenhouse gas emissions will obviously not be sufficient in itself to drive AAM uptake in all parts of the world, in particular in many developing nations where cement is relatively inexpensive, margins are low, and cost-effectiveness is paramount. In these regions, supply chains and economies of scale will need to be developed for AAM concretes to compete with cement producers for a share of a rapidly growing market [5]. The ability to utilise local naturally occurring raw materials (pozzolanic soils and clays) as AAM precursors will be highly desirable in these regions, with the main challenge being the sourcing of appropriate activators. The supply of raw materials is also likely to be an issue in some developed nations, where BFS and fly ash are extensively utilised in blending with Portland cements and are thus not available in sufficient quantities to launch a large industry sector dedicated to the alkaline activation of such materials. Again in these parts of the world, the development of alkali-activated binders based on materials which would not otherwise be utilised, and in particular materials derived from naturally-occurring soils, appears to be a potentially profitable way forward.

Recent commercial history in the developed world has shown that two of the major barriers to the introduction of a new material into the construction industry are:

1. the need for standards in each governmental jurisdiction, given that the development and introduction of such documents is at best a gradual process, and
2. the unanswerable questions relating to durability of concrete, considering the requirement for structural concretes to last for at least several decades, where data on such time scales are simply not available for a newly developed material.

The work program of RILEM TC 224-AAM has been specifically dedicated to addressing these two points. The issues of standards, durability testing, and in particular accelerated testing for durability in a way that can sensibly and rapidly be applied to the prediction of AAM concrete and binder performance, lie at the heart of the work outlined in this Report.

In the developed world, there are very specific standards for what is considered ‘acceptable’ performance for a cementitious binder. These have been developed over many years with benchmarks often set with the chemistry and behaviour of OPC-based concretes specifically in mind – but despite this, standards containing constraints such as ‘minimum cement content’ are beginning to be seen as excessively prohibitive, even for OPC-based systems [28]. Products such as AAM concrete or other alternative binders, and even some high-performance cement-based systems, may not simply be an evolution of existing OPC technology but instead may require a different chemical and engineering viewpoint to understand their behaviour, and may perform entirely acceptably but without conforming exactly to the established OPC-based benchmarks, particularly with regard to rheology and chemical composition. This has long been believed by cement producers and potential

AAM market entrants to be a significant hindrance to the acceptance of AAM technology in the developed world. However, ongoing experience in Australia and the USA is showing that by working with all stakeholders (including regulators, architects, insurers, structural engineers, construction companies and end users) to explain the product, these barriers can be overcome, so long as the intent of the regulatory standards is met.

Provided that a practical mechanism can be put in place to achieve regulatory acceptance of AAM concrete in the market, the key question in the minds of many specifiers and end-users still remains the issue of durability. Most standard methods of testing cement and concrete durability involve exposing small samples to very extreme conditions for reasonably short periods of time. These results are then used to predict how the material will perform in normal environmental conditions over a period of decades or more [29]. The major problem with this approach to testing durability is that it can only ever give indications of the expected performance, rather than definitive proof. There has therefore been a process of very slow adoption of new materials, as one may need to wait up to 20–30 years for the real-world verification which is required, or at least requested, by most design engineers.

However, the developing world does not have the same entrenched standards, and is generally more willing to accept an innovative solution to a problem such as the use of alternative binders in concretes, as market demand is projected to markedly exceed the currently available supply in the next several decades. This was the original driver for the development of alkali-activated binders in the former Soviet Union, as cement demand outstripped supply, and the increasing problems being faced by developing regions in terms of ‘counterfeit’ cement products in recent years speak to a similar additional driver for the development of alternative, low-cost technologies in the current economic climate. Developing markets, particularly China and India where fly ash is widely available due to coal-fired electricity generation, and where CO₂ emission is likely to become an increasingly significant political issue, may prove to be the primary areas in which alkali-activation technology becomes increasingly accepted on a regulatory level.

It is also notable that there are certain, usually relatively isolated, geographic regions in which AAM binders derived from local materials may provide a distinct cost advantage over importation of Portland cement. A particular example of this is Alaska, which currently relies entirely on cement imports but has a high domestic rate of production of fly ashes; a cost comparison between AAM and OPC in that particular market shows the costs associated with the two technologies are comparable for low-performance concreting, with AAM gaining an advantage where higher performance is specified, due to the specific cost conditions existing in that market [30]. This may be the case in other regions worldwide where coal-fired power generation is utilised but local production of Portland cement is limited, although detailed studies are required in each location and with an understanding of local conditions and attitudes to determine the likelihood of uptake of AAMs.

2.1.4 *Technical Drivers*

Following the discussion presented in Sect. 2.1.3 above, and as will be outlined in detail in the later chapters of this Report, it should also be noted that alkali-activated cements and concretes are capable of meeting or exceeding the vast majority of existing performance requirements commonly specified in construction applications, especially where acid, chemical and/or fire resistance may be required. Situations where standards for concretes used in construction exclude alkali-activation technology mainly exist due to the lack of commercial push for the technology from major industry and regulatory stakeholders. Naturally, the nature and push of the economic and environmental drivers will determine the rate and nature of the changes in this respect. Concurrent with changes in the value proposition (economic and/or environmental) of using AAM over time, there is also a growth in the quality and quantity of data proving the durability of the material, and the development of appropriate standards for these materials. Progress in this regard is addressed in detail in Chaps. 8, 9, and 10 of this Report specific to areas of durability; the discussion presented in this section is framed in more general and philosophical terms.

One of the fundamental principles which guided the development of alkali-activated binders in the former Soviet Union was the concept of the synthesis of analogues to the natural alkali/alkaline earth-aluminosilicate minerals which dominate much of the Earth's crust [31]. The possibility of the approximation to such phase formation under concrete production conditions is supported by the work which has been conducted by scientific researchers in this area since the 1950s [32, 33]. This work has led to the following conclusions:

- the physico-chemical processes taking place during hardening of conventional calcium silicate-based cementitious materials are analogous to a certain extent to the process of chemical weathering of rocks and formation of structure of stone-like substances of sedimentary and metamorphous origin; however, these processes take place with very different rates, since the starting materials differ in basicity and physical state;
- the hydration processes in calcium-based cements take place more actively due to the higher basicity and metastability of the constituent minerals compared to alkaline rocks of stable structure. Their hydration products are water resistant hydrous silicates and aluminates, as well as soluble calcium hydroxide;
- to accelerate these processes in natural rocks or artificial alkaline and alkaline/alkali-earth aluminosilicates which are sufficiently similar in composition that it becomes possible to use them to form hydraulic cementitious materials, this may be achieved through conversion of the substance from a stable crystalline state into a more active metastable state, including a glassy one, and when necessary, by introduction of alkaline oxides or hydroxides. As a result, the hydration processes of highly basic alkaline substances will be similar in their fundamental character to the natural processes of weathering of feldspar and nepheline rocks;
- the hydration products of high-basic and low-basic substances are similar to natural mineral formations, particularly low-solubility classes of hydroalu-

minosilicates – including layered double hydroxides, zeolites and low-basic calcium hydrosilicates, as well as soluble hydroxides or silicates of sodium and potassium. By precipitation of nanosized, disordered grains which crystallographically resemble these minerals, forming a hardened gel, binding of aggregates can result in a monolithic alkali-activated concrete. The chemical and thermodynamic durability of the binder phases in this concrete will in general tend to increase as the structure of the hydration products becomes more and more stable.

Many of these concepts were initially proposed on the basis of pure chemical and geochemical arguments; detailed characterisation of reaction mechanisms and gel nanostructures has become available more recently with advances in analytical techniques, and both the description of alkali-activation as a process resembling chemical weathering of aluminosilicate minerals [34] and the identification of nanoscale layered double hydroxides [35–37], siliceous hydrogarnets [38], and either nanoscale or crystallographically distinct zeolites [39, 40], has been directly confirmed.

The successful introduction of alkali metals into the binding compounds in considerably larger quantities than is allowed in compliance with the prescriptive composition-based standards applied to traditional Portland cements has led to the suggestion that it is necessary to consider the alkaline metals not only as activators to accelerate hardening, but rather as essential and independently functioning components of an aluminosilicate binding system. The reaction products of low-Ca systems may be represented as disordered zeolite-like compounds [39, 41, 42], while the hydration of higher-Ca systems results in a product which is predominantly a calcium silicate hydrate gel containing significant degrees of substituent elements (particularly Al), and which coexists with (predominantly disordered) particulates of other compounds whose nature depends on the exact chemistry of the aluminosilicate precursor and the activator [37, 43–48]. The role of alkalis within the binding products appears more essential in lower-calcium systems, where it is able to form part of the pseudozeolitic gel structure, as well as being present at elevated levels in the pore solution. Its structural role in the solid reaction products of high-calcium systems including alkali-activated BFS has been proposed by some authors to be more restricted [49, 50], but the presence of Na-containing solid phases has been identified under certain conditions, particularly where low Mg levels restrict the formation of hydrotalcite-like products to consume Al released by the aluminosilicate precursor [51].

Figure 2.1 shows the proposed relationship between binder phase chemistry, structure, stability and durability which has been developed through 50 years of research in the area of academic and development work in this field in the research group led by Glukhovskiy and Krivenko [52]. A critical point associated with this Figure is the issue of the solubility of the reaction products as a function of composition. High-basic hydrates are more subject to corrosion action than their low-basic counterparts; this trend is well-known in the area of geochemistry [53, 54] in relation to mineral weathering resistance, and is able to be utilised here to

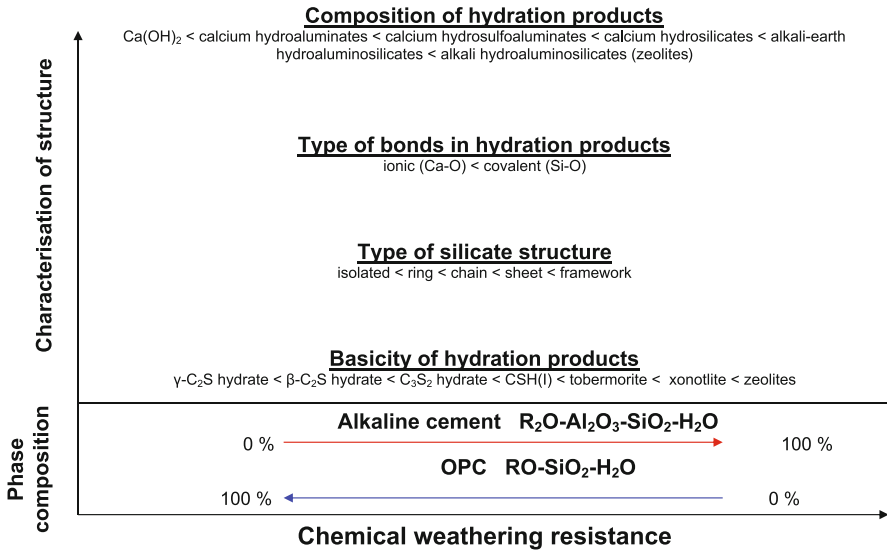


Fig. 2.1 Proposed relationship between mineralogical durability, phase compositions of hydration products, and their structure (Adapted from Krivenko [52])

provide a thermodynamic basis for the stability of alkali-activated binders, which in general have a lower calcium content (and thus lower overall basicity and higher degree of silicate connectivity) than the hydration products of Portland cement. The physicochemical importance of these thermodynamic processes in the context of binder synthesis reaction mechanisms has recently been discussed in detail by Gartner and Macphee [26]. The relative bond-forming and bond-breaking tendencies of different alkali and alkaline-earth cations, as well as Al and Si, are seen to show a profound influence on the reaction mechanisms and binder structures formed in these systems. The development of a detailed understanding of the chemical thermodynamics of binder formation is certainly a necessary, but by no means a sufficient, condition for the widespread acceptance of AAM binders, and research activities in this area are ongoing in several parts of the world. The availability of good thermodynamic data will never *per se* convince an end-user or specifier of the value of a new material, but its absence may have a strong deterrent effect, and so scientific advances in this area are critical to the uptake of AAM concretes in key applications.

Other areas in which technical drivers for AAM concrete uptake have been proposed to exist include [9]:

- Strength (compressive, flexural and abrasion resistance), including rapid and controllable strength gain in some mixes under specific curing conditions
- Resistance to high temperature and fire; low thermal conductivity
- Resistance to acid and chemical attack

- Low susceptibility to degradation by alkali-silica reaction
- Good volumetric stability after hardening
- Adhesion and binding to cement/concrete, ceramic, glass and some metallic substrates
- High initial internal pH leading to passivation of reinforcing steel
- Low permeability
- Low cost

Each of these points will be addressed in detail in Chaps. 8, 9, and 10 of this report. It is sufficient at this point to say that each advantageous characteristic listed above is undoubtedly achievable by the use of a correctly designed alkali-activated binder system, but that no single formulation will achieve all of these characteristics simultaneously. Alkali-activated aluminosilicate binders have been used in applications ranging from aerospace to construction to hazardous waste management. The highest-volume application is certainly related to use as a construction material, and this is the primary focus of this Report, but it should be remembered that the potential for higher profit margins in some niche applications is likely to lead commercial development in areas other than high-volume concrete production.

2.2 Alkaline Activation Throughout History

2.2.1 Alkalis in Ancient Cements

There has in the past three decades been high-profile discussion, from both scientific/engineering and historical perspectives, regarding the possible role of alkali-containing cements in ancient Egyptian and Roman constructions, in addition to possibly some of the materials used in earlier civilisations in the Middle East region, particularly the Syrian and Greek constructions which preceded the rise of the Roman Empire and potentially influenced their selection of construction materials. The connection between ‘geopolymer’ materials and a potential role in the construction of Egyptian pyramids has most prominently been promoted by Davidovits [55, 56], who has proposed a number of detailed theories whereby the large building blocks comprising the pyramids are suggested to have been poured in-place, utilising chemistry resembling that of alkali activation. More detailed scientific analysis of pyramid stone samples, published in the peer-reviewed academic literature [57, 58], has not upheld the suggestions of elevated alkali or aluminium contents in pyramid stones, but does show the presence of amorphous silica and other components which could potentially be consistent with the reagglomeration of limestone in a poured-in-place manner. Scientific and historical investigation have to date not been able to produce fully complete evidence either in favour of this theory or to entirely refute it; it is mentioned in this Report due to the publicity which has been raised in this area, which means that this discussion is necessary (although peripheral) in a report on the State of the Art in this area.

There has also been significant discussion surrounding the potential connections between ancient Roman concretes [59] and modern alkali-activated binders [31]. Roman concretes differ widely in composition, performance and durability; of specific interest in the context of this Report are the concretes which were based on the activation of pozzolanic materials (volcanic ash sourced from areas including what is now the Pozzuoli (formerly Puteoli) region of southern Italy [60]) with calcium compounds, particularly lime, where the elevated pH generated by the reaction of the lime initiated the reaction of the pozzolanic material. The volcanic ashes used in these concretes often included significant contents of alkalis [61], and the final concrete products, when examined after 2,000 years in service, often contain evidence of the presence of zeolites including analcime. It is known that analcime in particular is often present in volcanic ashes; examinations of Roman mortars with unreacted pozzolana embedded within the mortar have found elevated analcime concentrations in the mortar regions compared to the unreacted pozzolana [62], indicating that it is possible that the alkaline environment within the concretes has led to the formation of additional zeolites, as is known to be the case when volcanic ashes are exposed to alkaline geological conditions [63], although the difficulties associated with accurately separating the reacted and unreacted materials for analyses such as this have also been noted [64].

The interest in the comparison with Roman concrete, and the relevance to the discussion presented here, is primarily derived from arguments related to durability and the retention of strength. Over a period of 2,000 years, these concretes have remained in service in environments including immersion in seawater, while others including the Pantheon in Rome have withstood significant seismic activity. Similarly interesting from this point of view are the hydro-engineering structures, concrete-based roads, multi-layered floors, vaults, and domes which remain to this day. Although it is undoubted that some Roman concrete structures have degraded over the centuries, the fact that so many remain intact does provide some potential lessons in terms of construction materials chemistry and design. A further point to mention is that much of the degradation observed in modern concretes is due to the corrosion of embedded steel reinforcing, while the unreinforced Roman structures are not subject to this mode of decay.

Early Roman mortars appear to be predominantly based on the development of hardness and strength by carbonation of lime, until it was discovered (either by experimentation or by implementation of knowledge gained from surrounding civilisations) that the formation of aluminosilicate binding phases by the inclusion of volcanic silica-containing ash and/or fired clay gave improvements; that is, changing their mineralogical composition gave an increase in durability. The mineralogical composition of ancient cements is not the same as that of modern Portland cements; the ancient binders tend to be lower in Ca and richer in alkalis, Si and Al [31, 60, 64]. The presence of analcime in various ancient cements supports the idea that such a zeolite is a more stable phase formed as a result of long-term hydrothermal transformation of the initial phases, consistent with the schemes presented in Fig. 2.1.

It is also notable that, although modern cements have often been used to repair ancient structures, the modern repairs have only rarely proven to be as durable as the ancient cements under identical exposure conditions. This may indicate that the binder structures formed with a lower calcium and higher aluminosilicate content could provide advantages in terms of binder stability over extended time periods, or may be related to incompatibility in material (chemical and mechanical) properties between the existing and new materials if the repair material is not well selected. Although C-S-H gel is a major constituent of both Portland cement paste and many ancient cements, it is not quite correct to conclude that its presence is responsible for durability. The resistance to environmental exposure appears to be related to the degree of gel cross-linking, as outlined in Fig. 2.1, and the presence of reduced quantities of calcium and elevated levels of tetrahedral aluminium (often charge-balanced by alkalis, as in the case of zeolites) is strongly advantageous in this area. This is thus the key outcome of the discussion of ancient and modern cements in the context of this Report; it is possible to draw implications related to the durability of modern cements from the analysis of certain ancient materials, and these trends appear to comment favourably upon the inherent chemical durability of aluminosilicate-based (as opposed to calcium silicate-based) binders.

2.2.2 Use of Alkali in Contemporary Cements

Most modern cement standards contain regulations describing the maximum allowable alkali content of the cement, in an attempt to minimise the likelihood of alkali-aggregate reactions, and queries are sometimes raised regarding whether these limits (often around 0.6 wt.% $\text{Na}_2\text{O}_{\text{eq}}$) are sufficiently restrictive [65]. The presence of alkalis in Portland cement, either as a high-alkali clinker or as NaOH in the mix water, has also been shown to influence mechanical, elastic, and various other properties of the resulting concretes in a generally (but not uniformly) deleterious manner, and can reduce shrinkage [66]. The importance of the provision of at least some alkali content has been highlighted in the context of development and retention of pore solution alkalinity [67], admixture-cement compatibility [68], and in the role played by alkalis in determining the initial reaction mechanism and hydration products of the silicate [69, 70] and aluminate [71] phases in the clinker.

It is also well known that the addition of pozzolanic materials can reduce the likelihood of deleterious alkali-silica reactions, as the additional available Al and Si react with the alkalis to form non-expansive gel products which do not damage the concrete structure [72–75]. The availability of a highly alkaline pore solution environment is also well known to be important in preserving the passive state of embedded steel within a reinforced concrete.

Combining these points, and building from the discussion presented in Sect. 2.1 above, there appears to be relatively strong technical justification for research and development in combining alkalis with pozzolan-like materials to generate alkali-aluminosilicate binders for use in concretes. The presence of at least some quantity of

calcium appears likely to be beneficial; a basic pre-requisite for the chemical mechanisms in all of the cements (Portland and non-Portland) discussed above is the presence of an alkaline medium. The evidence for a certain degree of similarity of the reaction processes of traditional and non-traditional silicate binder systems enables researchers to make use of the state-of-the-art data regarding the processes of hydration and hardening of the calcium-based cementitious materials in establishing the theoretical background for production of concretes from alkali-activated cements. There are, of course, limitations regarding the fundamental depth of the analogies which can be drawn, and some analogies may in fact turn out to be actively misleading (this must remain a point of caution in this research field, as in all complex areas of research), but the fact remains that it is certainly possible to obtain valuable data from the extensive literature on Portland cement and its blends to provide understanding of AAM binders and concretes.

2.3 Chemistry of Alkaline Activating Solutions

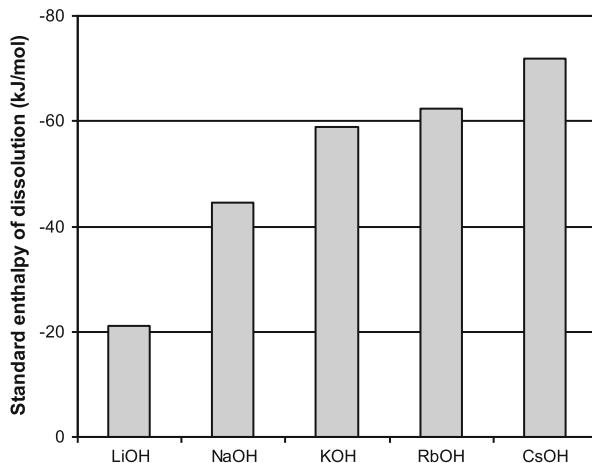
At this point, it is necessary to provide a very brief discussion of the chemistry of the alkaline activating solutions which are able to be combined with aluminosilicate precursors to generate novel cementing materials. This discussion will not be exhaustive, but will provide sufficient background to lead into the more detailed analysis which will follow in Chaps. 3, 4, and 5 based on the discussion of the different possible combinations of activators and solid precursors. For an overview of silicate and hydroxide solution chemistry, the reader is also referred to reference [76], and for reaction processes involving carbonate or sulfate activating solutions, to the book by Shi, Krivenko and Roy [77].

2.3.1 Alkali Hydroxides

The alkali hydroxides most commonly used as alkali activators are those of sodium and/or potassium; lithium, rubidium and caesium hydroxides are of limited large-scale application due to their cost and scarcity, as well as the relatively low solubility of LiOH in water (just under 5.4 mol/kg H₂O at 25 °C [78]). By comparison, both sodium and potassium hydroxides are soluble in water up to concentrations exceeding 20 mol/kg H₂O at 25 °C [79, 80], and concentrations exceeding 5 mol/kg H₂O are widely used in studies related to alkali-activation, particularly when using class F fly ash precursors.

Sodium hydroxide is predominantly produced via the chlor-alkali process, in parallel with Cl₂. This has important environmental implications for its use in alkali activation, both in terms of Greenhouse emissions (via electricity consumption) and in terms of emissions of other components such as mercury which are sometimes utilised in this process; modern membrane cells are more efficient in this regard. Similarly, potassium hydroxide is produced by electrolysis of KCl solutions.

Fig. 2.2 Standard enthalpies of dissolution of MOH (M: alkali metal) to infinite dilution at 25 °C (Data from the reviews of Gurvich et al. [81, 82])



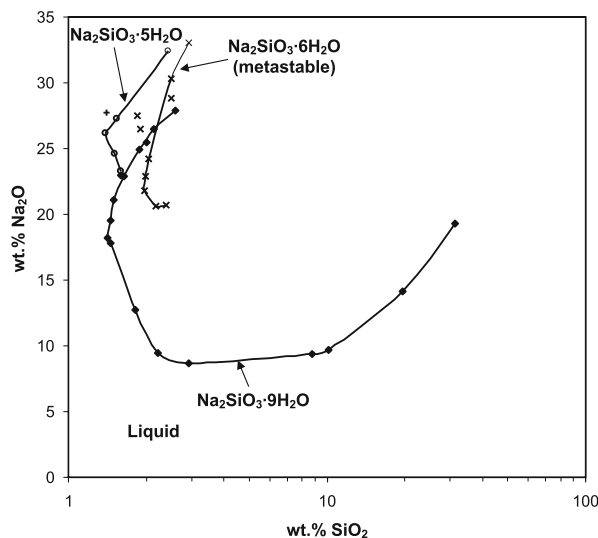
In a processing context, aside from their obviously highly corrosive nature, the most important properties of concentrated hydroxide solutions that must be considered are viscosity, and the heat released by the dissolution of the solid alkali hydroxide compounds during preparation of the solutions. The viscosity of even highly concentrated alkali hydroxide solutions rarely exceeds that of water by more than a factor of 10 [76], and this is a marked advantage over comparable alkali silicate solutions, as will be discussed in Sect. 2.3.2 below.

Figure 2.2 depicts the standard enthalpy of dissolution to infinite dilution, $\Delta_{\text{aq}}H^{\circ}_{298.15\text{K}}$, of the alkali hydroxides as a function of cation size. The importance of this is that, in preparing a concentrated hydroxide solution, a significant temperature increase will take place, which may be problematic in an industrial context. The actual heat released by dissolution into a concentrated solution will be slightly less than the infinite-dissolution values, as the additional heat of dilution incurred by moving to infinite dilution will not be a factor. However, the enthalpy of dissolution dominates over the dilution effects, accounting for around 90 % of the total enthalpies plotted in Fig. 2.2 [76].

The data in Fig. 2.2 can then be used to calculate the approximate temperature increase expected when dissolving solid alkali hydroxides at high concentrations. If it is assumed that dissolving 10 mol of NaOH into a litre of water releases 90 % of the heat that would be released in moving to infinite dissolution, then this will be around 400 kJ. Taking the mean heat capacity of NaOH solution to be approximately equal to that of water [83], this quantity of heat will be sufficient to raise the temperature of the water by over 90 °C. In most cases, heat will be lost to the surroundings and/or expended by vapourisation of some of the solution. However, such a temperature rise taking place in a highly caustic solution will need to be very carefully considered and monitored in an industrial production setting.

Efflorescence (particularly due to the formation of white carbonate or bicarbonate crystals) is also a known issue in binders activated with too high a concentration

Fig. 2.3 Crystallisation isotherms for hydrated sodium metasilicate phases at 25 °C and ambient pressure, plotted from the tabulated data of Wills [86]. The phase $\text{Na}_3\text{HSiO}_4 \cdot 5\text{H}_2\text{O}$, which is reported at relatively high Na_2O and low SiO_2 concentrations, is not depicted (Plot adapted from [76])



of hydroxide solutions, where the excess alkali reacts with atmospheric CO_2 . This is unsightly, but not always harmful to the structural integrity of the material. Efflorescence is generally more marked in the presence of Na than K in hydroxide-activated binders.

2.3.2 Alkali Silicates

As for the case of hydroxides, the silicates of sodium and potassium are those with the greatest industrial relevance in alkali activation [76], and will be the primary focus of the discussion here. Lithium silicate is insufficiently soluble for use in most alkali-activated binder systems, and the high costs and currently limited production volumes of rubidium and caesium silicates restrict their large-scale usage. Alkali silicates are generally produced from carbonate salts and silica via calcination then dissolution in water at the desired ratios, which brings associated energy consumption and CO_2 emissions. However, due to the relatively low content (by mass) of activator in most alkali-activated binders, the process CO_2 emission rate induced by the calcination of carbonates here is much lower per tonne of binder than the process CO_2 emissions associated with Portland cement production [6]; this is an area of ongoing discussion in the literature at present.

Figure 2.3 shows a portion of the Na_2O - SiO_2 - H_2O composition space with crystallisation isotherms at 25 °C [76]; a diagram showing more detail of the complex phase relationships at lower Si contents is also available in the work of Brown [84], along with discussion of the potential formation of more siliceous phases which are observed in hydrothermal geological deposits, but whose role and stability regions

in the phase diagram remains unknown [84]. The full phase diagram for this system has never in fact been determined, mainly due to the predominance of metastable aqueous silicate solutions which, if they will ever precipitate, will do so very slowly [84]. This is highlighted by the observation that in the table of ‘typical commercial sodium silicates’ given by Weldes and Lange [85], all of the compositions given for common sodium silicate solutions actually fall in the region of the phase diagram in which precipitation of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ would be expected.

According to the classifications of Vail [87], describing the nature of the products formed in different regions of the full ternary $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$ system, most of the silicate compositions which are of primary interest in alkali-activated binder synthesis are in the regimes noted as being partially crystalline mixtures, highly viscous solutions, and/or prone to crystallisation as hydrated sodium metasilicates. This necessitates care in the handling and storage of such solutions; the stockpiling of silicate solutions for extended periods prior to use (either in laboratory experiments or in larger-scale production runs) can lead to unexpected and/or unfavourable outcomes. Similar issues are not generally encountered with potassium silicate solutions, as the precipitation of hydrated potassium silicate phases is much less prevalent than in the sodium case, and the stability range of the homogeneous aqueous solution is much wider.

The chemistry (aqueous and solid-state) of silica is probably more complex than that of any other element other than carbon, and remains relatively poorly understood from a fundamental standpoint. In concentrated alkaline solutions, silica polymerises into an array of small species [88, 89], the identities and structures of several of which are only now being resolved through the careful application of ^{29}Si NMR [88, 90–93], and mass spectroscopy [94, 95]. Infrared spectroscopy has also been applied [96–98], but the interpretation of spectral features does not always correlate well with the results of NMR experiments.

In the context of geopolymerisation, the most important aspect of the existence of a distribution of silicate species is the variability in lability (and thus also reactivity) between the different species present. Operating in parallel with the effects of silicate oligomer formation in concentrated solutions are acid-base reactions; monomeric silica, $\text{Si}(\text{OH})_4$, is also known as ‘orthosilicic acid,’ and behaves as a polyprotic weak acid under alkaline conditions.

The majority of the silicate sites present in the activating solutions used in AAMs will be deprotonated either once or twice [99]. Taking into account the distribution of species present and their respective pK_a values, most silicate activating solutions are buffered at approximately pH 11–13.5 by the silicate deprotonation equilibria [100, 101], and yet can provide a much higher level of ‘available alkalinity’ when compared to hydroxide solutions at the same pH due to the buffering effect providing a ready source of basic species. Obviously, hydroxide activating solutions will have a higher pH than this prior to mixing with solid aluminosilicates, but the dissolution of a moderate amount of silica from the solid precursor into such a solution will rapidly bring the pH into this region during the reaction process.

Figures 2.4 and 2.5 present the viscosities of sodium and potassium silicate solutions, respectively, as a function of composition, at room temperature; data were

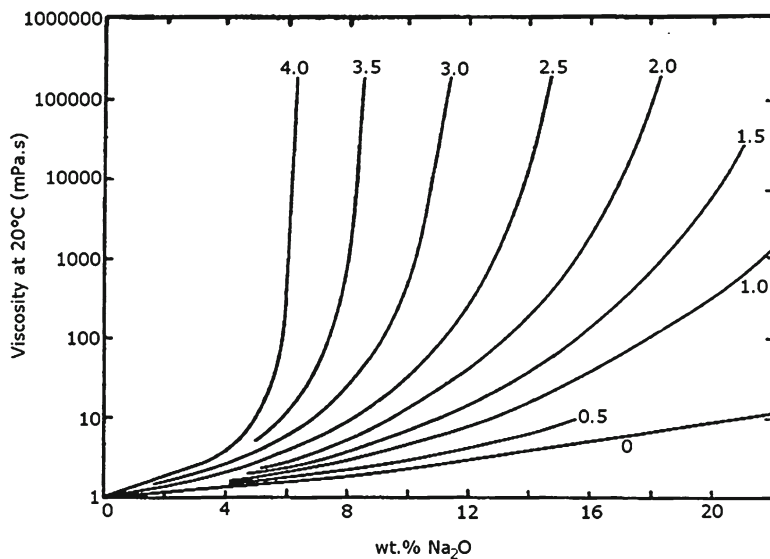


Fig. 2.4 Viscosities of sodium silicate solutions with mass ratio $\text{SiO}_2/\text{Na}_2\text{O}$ as marked. Mole ratios are 3 % greater than the mass ratios shown (Data from Vail [87])

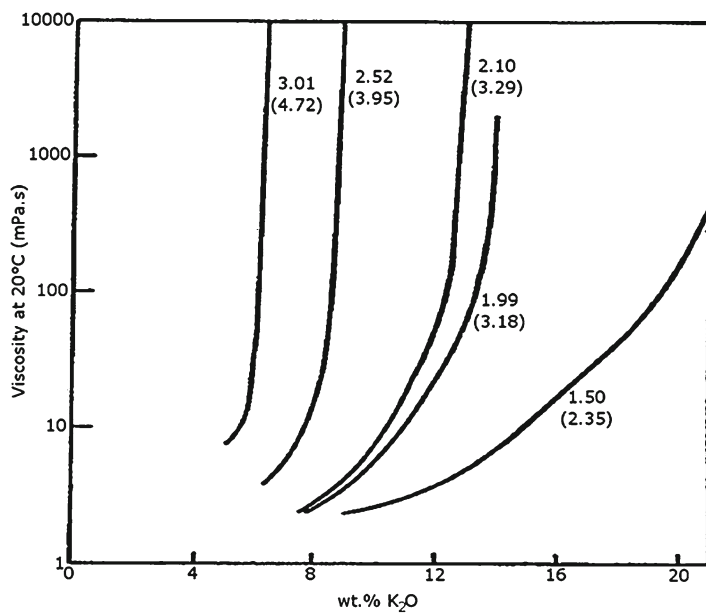


Fig. 2.5 Viscosities of potassium silicate solutions with mass ratio (mole ratio) $\text{SiO}_2/\text{K}_2\text{O}$ as marked (Data from Vail [87])

obtained from [87]. In both Figures, viscosities are plotted on a logarithmic scale, and increase dramatically at higher silica content. Importantly, potassium silicate solutions show a much lower viscosity than sodium silicates of comparable composition. Sodium silicates are also very much more sticky than potassium silicates [85]. Finishing freshly placed sodium silicate-activated concretes can thus be problematic, because the sodium-containing AAM pastes tend to stick to concrete finishing equipment, and also to the sand and aggregate particles.

Yang et al. [102] showed that the viscosities of sodium silicate solutions decrease markedly with increasing temperature. However, the solubility of some sodium metasilicate phases does begin to decrease at elevated temperature [87], meaning that heating is not in fact guaranteed to enhance the preparation of activating solutions from solid metasilicates. The enthalpy of solution of solid anhydrous sodium metasilicate into concentrated solutions also decreases as a function of concentration [87] due to the inability to achieve full hydration of dissolved species at very high concentrations.

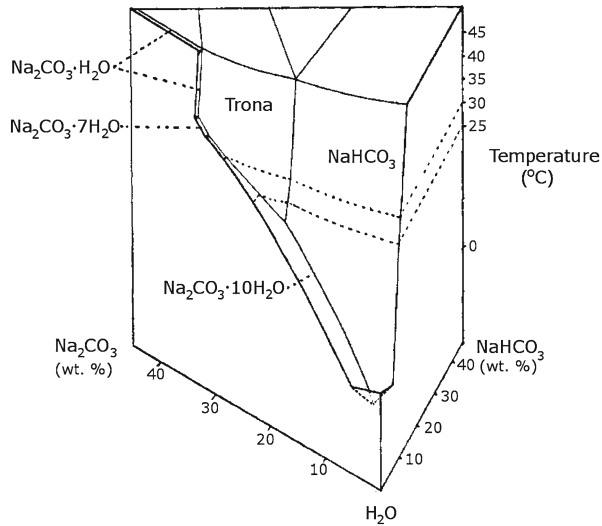
2.3.3 Alkali Carbonates

Activation of aluminosilicates with carbonate solutions has also been undertaken. Alkali carbonates are produced either by the Solvay process or directly from mining of carbonate salt deposits (of which there are an estimated 5×10^{10} tonnes in a single deposit in the Green River Basin of Wyoming, USA, in addition to plentiful deposits elsewhere around the world [103]). The direct Greenhouse impact of these processes is somewhat less than the impact of the production of hydroxide or silicate solutions, but the alkalinity of carbonate solutions is lower than that of the other activating solutions, meaning that the selection of aluminosilicate raw materials with which carbonate activators may be used is narrower, as will be discussed in detail in Chaps. 3, 4, and 5. Potassium carbonates, or the carbonates of other alkali metals, have not often been used in preparation of alkali-activated binders.

Figure 2.6 presents a phase diagram for the ternary system Na_2CO_3 - NaHCO_3 - H_2O , which is of relevance both to the use of carbonate activators and also to the carbonation-related chemistry of alkali-activated binder pore solutions. It is necessary to consider the potential formation of bicarbonate, even in systems where solid Na_2CO_3 is combined with water to form the activating solution, because even a small extent of carbonate hydrolysis or additional atmospheric carbonation will lead to bicarbonate formation. A point of particular interest in this diagram is the formation of hydrous sodium carbonate salts, including the decahydrate $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ which will bind a large amount of water if it is allowed to form, which may cause difficulties related to the water demand of mix designs if it forms during mixing, but also potentially providing pore-filling capabilities if it develops later as a product of atmospheric carbonation of the binder or its pore solution.

The viscosities of Na_2CO_3 and NaHCO_3 solutions are unlikely to be problematic in handling or production; these do not exceed the viscosity of water by more

Fig. 2.6 Ternary phase diagram for the system $\text{Na}_2\text{CO}_3\text{-NaHCO}_3\text{-H}_2\text{O}$ (Adapted from Hill and Bacon [104]). The ternary eutectic is shown at $-3.3\text{ }^\circ\text{C}$, the $\text{Na}_2\text{CO}_3\cdot 10\text{H}_2\text{O}\text{-NaHCO}_3\text{-trona}$ invariant point at $21.3\text{ }^\circ\text{C}$, and the lower and upper temperature points on the $\text{Na}_2\text{CO}_3\cdot 7\text{H}_2\text{O}\text{-trona}$ coexistence line are at 32.0 and $35.2\text{ }^\circ\text{C}$ respectively [104]. *Dashed lines* show the isotherms at 25 and $30\text{ }^\circ\text{C}$

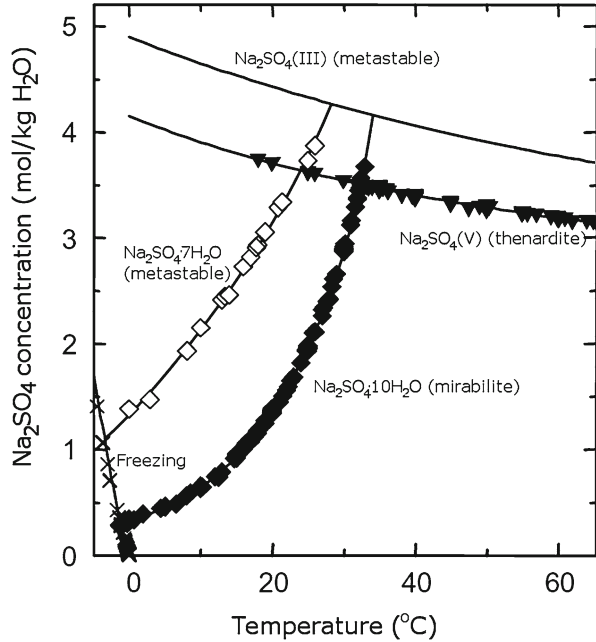


than a factor of 5 up to saturation concentrations [105]. A more likely issue relates to precipitation and/or carbonation in these solutions, as Fig. 2.6 shows – the absorption of CO_2 into an Na_2CO_3 solution will lead to NaHCO_3 precipitation (and this process is relatively rapid, as evidenced by the use of alkali carbonates as solvents for CO_2 in gas-cleaning processes), and the solubility of Na_2CO_3 is also strongly temperature-dependent. Cooling of a concentrated sodium carbonate solution is likely to lead to precipitation, and the solubility of hydrous sodium carbonates above $35\text{ }^\circ\text{C}$ is also slightly retrograde (decreasing with increasing temperature). The use of sodium carbonates rather than silicates as activators also does not fully remove the issue of the stickiness of these materials [106], because the silica released by dissolution of raw materials contributes to this in the early stages of reaction.

2.3.4 Alkali Sulfates

Similar to the case for carbonate solutions, it is also possible to achieve alkali activation of some aluminosilicate materials by addition of sodium sulfate. Sodium sulfate activation provides significant scope for Greenhouse savings in binder production, if the binder properties are able to reach satisfactory levels, as the salt is obtained either directly from mining (natural resources of over 10^9 tonnes are estimated to exist worldwide [107]), or as a byproduct from the manufacture of many other industrial chemicals. The performance of the binder products is the main query surrounding the use of sodium sulfate in activation of most combinations of clinker-free aluminosilicate materials; the addition of clinker is usually required for

Fig. 2.7 Phase diagram for the system $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ (Adapted from [109]); points are experimental data and lines are computed from the thermodynamic model developed by those authors. Both metastable and stable phase equilibria are shown



sufficient strength generation, as discussed in detail in Sect. 3.6 of this Report. The viscosities of aqueous sodium sulfate solutions are also not more than a factor of ~ 5 higher than that of water in the temperature and concentration range of interest [108]. Potassium sulfates, or the sulfates of other alkali metals, have not often been used in the preparation of alkali-activated binders.

Figure 2.7 presents a phase diagram for the $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ system, adapted from the detailed study of Steiger and Asmussen [109]. This system is also of importance in the study of cement and concrete durability due to the formation of sodium salts during some instances of sulfate attack on hydraulic binders. In the phase diagram of relevance to alkali-activation chemistry, there are various phases of interest. The anhydrous salt, thenardite, is one of five polymorphs of Na_2SO_4 (another, $\text{Na}_2\text{SO}_4(\text{III})$ is observed metastably within the temperature range of interest), and the other key stable phase is mirabilite (Glauber's salt), which is the decahydrate and thermally decomposes at 32.4°C . The formation of the metastable heptahydrate phase is also possible, particularly under conditions of rapid cooling or evaporation [109].

2.4 Global Development of Alkali Activation Technology

The sections to follow will address the development of alkali-activated binders from a technological, historical and societal perspective in different regions of the world. There have been different factors motivating the scientific developments in this area

depending on economic, regulatory and climatic factors in different parts of the world, and this is reflected to some extent in the ways in which the technology has evolved. To fully understand the state of the art of developments in this area of technology at present, it is essential to understand the background and context within which this state of the art exists, and thus such information comprises an essential aspect of this Report.

It must also be noted that this brief review does not aim to be an exhaustive listing of all the contributions made by scientists and engineers in each specific region to the study and development of alkaline cements and concretes. Such an endeavour would take up too much space, and would necessarily risk significant oversights. The intention, rather, is to highlight the research groups who, through the progress of time, have contributed to a fuller understanding of these materials. Hence, while some relevant names may have been inadvertently omitted, none of the names included is irrelevant.

2.5 Development of Alkali-Activated Materials in Northern, Eastern and Central Europe

In the mid 1950s, and in the context of a demand for Portland cement alternatives in the former Soviet Union, Professor V.D. Glukhovsky began to investigate the binders used in ancient Roman and Egyptian structures [31], and discovered the possibility of producing binders using low basic calcium or calcium-free aluminosilicate (clays) and solutions containing alkali metals [41]. He called the binders “soil cements” and the corresponding concretes “soil silicates”. Depending on the compositions of the starting materials, these binders can be divided into two groups: alkaline binding systems $\text{Me}_2\text{O}-\text{Me}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ and alkaline-earth alkali binding systems $\text{Me}_2\text{O}-\text{MeO}-\text{Me}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. Based on these observations, he combined aluminosilicate wastes such as various types of slags and clays with alkaline industrial waste solutions to form a family of cement-alternative binders. These materials are often described in terms of analogies with natural zeolites and low-basic calcium hydroaluminosilicates, and are able to be processed and placed using equipment and expertise which does not differ very greatly from that which is used in the placement of Portland cement concretes.

From the 1960s onwards, the research institute in Kiev, Ukraine which is now named in honour of Professor Glukhovsky has been involved in the construction of apartment buildings, railway sleepers, road sections, pipes, drainage and irrigation channels, flooring for dairy farms, pre-cast slabs and blocks, using alkali activated blast furnace slag [77, 110]. Subsequent studies of sections taken from these original structures have shown that these materials have high durability and compact microstructure [111]. A vast number of patents and standards were produced on the earlier slag mixes, but this documentation has been largely inaccessible in the West. The Kiev team has continued under the supervision of Kryvenko to develop mix designs for different raw materials and applications [32, 112, 113]. Details of

several of the applications in which their materials have been utilised are provided in Chaps. 11 and 12 of this Report; it is reported that more than $3 \times 10^6 \text{ m}^3$ of alkali-activated concretes were poured in the former Soviet Union prior to 1989 [114]. Although this quantity may not be large as a percentage of the total construction materials market, it is certainly a large volume of material production, and demonstrates the viability of the technology at scale.

Kiev National University of Civil Engineering and Architecture has also organised international conferences on alkali-activated cements and concretes in 1994 and 1999 in Kiev, Ukraine [115, 116], and in 2007 in Prague, Czech Republic (sponsored by the EU, the Government of the Czech Republic and the City Government of Prague) [117]. The Proceedings of these conferences provide particularly valuable and rare insight into much of the work which has been conducted in the former Soviet Union, which has not been made readily accessible in the English language in any other formats.

Much of the early work conducted elsewhere in the eastern regions of Europe is detailed by Talling and Brandstetr [118]. The expertise which was developed in Poland from the 1970s onwards [119–125] has led to alkali-activated binders finding use as grouts and mortars in dams [126], in waste immobilisation [127], as railway sleepers and other prestressed elements [125], and in a variety of other applications, with more than $100,000 \text{ m}^3$ of concrete produced from 1974 to 1979 alone [125]. Alkali-carbonate activated BFS concretes poured in 1974 as the flooring slab and external walls of an industrial storehouse were analysed after 27 years in service, and showed excellent durability performance and serviceability [124].

Other groups in northern and eastern Europe also made significant advances in the initial period of development of alkali-activated material systems. In the 1980s and early 1990s, prominent papers were also written in Finland [128–133], especially focused on the superplasticised alkali-activated BFS system known as F-concrete, and in Sweden [134]. However, developments in this region have not appeared to continue as prominently as in this early time period. In today's Czech Republic, several reputed groups of researchers have been working on alkali-activated systems for a number of years; work in this region was initiated by Brandstetr [118], including work published in collaboration with colleagues in Canada [135, 136]. Currently, one of the foremost teams is the group in Prague led by Škvára [137–141] who have studied the alkali activation processes taking place in BFS, fly ash and blends of the two materials, as well as key aspects of durability. Teams specialising in AAM are also working on commercial-scale development of alkali-activated BFS concretes at the company ZPSV A.S. [142–144] and on AAM fire resistance [145, 146]. In the Czech and Slovak Republics, alkali-activated aluminosilicate binders developed by the company ALLDECO have found utilisation in the immobilisation of nuclear wastes [147]. A range of systems based on metallurgical slags have also been analysed in Romania since the 1980s [148] for construction purposes.

Interest in alkali-activated materials in the central European region has also materialised in the organisation of four international congresses on Non-Traditional Cement and Concrete [149–152], and one specifically on alkali-activated binders

[117], which have served as platforms for the presentation of the latest scientific advances in the area. Many of the nations in this region have the desire to make use of the by-products of metallurgical processes, which has combined with the need for inexpensive construction materials to provide a strong driver for developments in alkali-activation technology.

2.6 Development of Alkali-Activated Materials in China

The products resulting from alkaline activation of metallurgical slags have been marketed as “JK cement” in China for many years [153], and the early developments in alkali-activation technology in China were summarised in a review article by Wang [154]. The key driver in the initial stages of the development of this technology was the demand for high-strength (>80 MPa) concretes with low energy requirements during production, and the plentiful by-products available from China’s metallurgical industries provided opportunities for the generation of binders from slags from ferrous and non-ferrous metallurgy, in particular BFS and phosphorus slags. Issues with rapid setting of alkali-activated BFS concretes were identified, and admixture development was highlighted as a key area requiring attention. A review published in 1995 [114] compared developments up to that time in China, the former USSR and in the USA, and showed that comparable performance results were being obtained in all three regions. More recent developments have been outlined in some detail by Pan and Yang [155], and the discussion here follows from that presentation.

Two major non-technical factors have also influenced the development of alkali-activated binders in China. One is related to the historical development of the science and technology globally, and the other, more recent driver is related to the protection of the environment and the sustainable development of industrial production of binding materials in China. Much of the early research was led by intellectual curiosity and the possibility to develop interesting new materials, as in many other countries. However, in recent years, with rapid industrial development in China, many environmental problems have emerged, which have received more and more attention from the Chinese government; this has become the most important driver for the active and extensive research activities on AAMs in China. The development of more durable cements and concretes is also an important aim which is driving developments in some aspects of the technology, mainly for niche applications including coatings for marine concretes [156, 157].

2.6.1 Industrial Solid Waste Generation in China

Due to rapid industrial development and high output in its manufacturing sectors, China provides opportunities for the development of AAMs from a wide range of

Table 2.1 Annual production of industrial solid wastes in China with relevance to alkali-activation, either as raw material or to supply sulfate for activation

Solid waste	Production, Mt p.a.
Blast furnace slag	230
Steel slag	100
Phosphorus slag	10
Fly ash	300
Red mud	3
Coal gangue	100
Calcium carbide residue	20
Soda residue	15
Phosphogypsum	20
Flue gas desulfurisation gypsum	5

solid waste materials. Potentially suitable industrial solid wastes generated in China include blast-furnace slags, steel slag, phosphorus slag, fly ash, red mud, coal gangue, calcium carbide residue, soda residue, phosphogypsum, and flue gas desulfurisation gypsum, among others. Based on information reported in the literature, estimated annual production of these wastes is listed in Table 2.1 [155].

There is also reported, as of 2009, to be stockpiled about 1,300 million tonnes of accumulated unused fly ash, and 3,600 million tonnes of accumulated unused coal gangue, awaiting further industrially and/or environmentally beneficial treatment and/or reutilisation [155]. For the purposes of comparison, the production of Portland cement in China in 2009 was 1,650 million tonnes, with a mean annual growth rate exceeding 9 % between 2006 and 2010 [158].

Among the materials listed in Table 2.1, BFS is almost totally utilised as a mineral admixture for cement and concrete in China, so that it is now commonly considered as a secondary product rather than as a waste, similar to the scenario in Europe. Around 40 % of the fly ash, and some of the phosphorus slag and gypsum byproducts, are used in the construction industry, while the others listed are not widely used in beneficial applications at present [155]. This provides a wealth of potential precursors for alkali activation, although suitable methods of treatment and industrial-scale production must still be developed. Chinese research has made extensive use of fly ash, blast furnace and phosphorus slags, metakaolin and other calcined clays, red mud, and coal gangues in alkali activation, in addition to development work in the areas of admixtures and fundamental chemistry applicable to many of these systems.

The reuse of industrial solid waste in China is encouraged by government and taxation policy [159, 160]; products in which the content of industrial solid waste (excluding BFS) is more than 30 % are able to be sold tax-free [155]. There are also major national policy frameworks related to energy savings and waste reduction in manufacturing, designed to enhance environmental protection and sustainable development. Thus, research and development related to AAM chemistry and manufacture are generally in good coincidence with national policies in China. This has provided a strong driver for activities and development in this area over the past two decades, and advances which have been made in the area of alkali-activation

technology in China have been important in proving the value of this technology on a worldwide basis [77].

Currently, about 50 universities or research institutes in China are engaged in AAM research activity [155]. National scientific meetings in this area have been held since 2004, and a national technical committee has been established through the Chinese Ceramic Society to provide organisation and information exchange.

2.6.2 Financial Aspects of Alkali and Raw Materials Supply in China

The main issue related to the uptake of AAM binders and concretes in China, in common with many areas in which the price of Portland cement is relatively low, is the relatively higher cost associated with the production of alkali-activated concretes. The average commercial price of Portland cement in China as of 2009 was around CNY300-350/tonne (EUR1 \approx CNY8), the cost of BFS is around CNY200/tonne, and commercial liquid waterglass costs about CNY4500/tonne. Thus, the price of an alkali-activated BFS binder would be expected to be around CNY500/tonne, which is much more expensive than Portland cement [155], and this is currently providing a hindrance to the uptake of alkali-activation technology in China. The cost situation with respect to the use of fly ash or metakaolin as the main binder components is likely to be less restrictive, but some of the technical and durability challenges associated with the development of binders based on these materials remain to be overcome in the Chinese context.

2.7 Development of Alkali-Activated Cements in Western Europe and North America

Metallurgical, and particularly blast furnace, slags have long been used as cementitious constituents in concretes in western Europe, with developments in this area dating as far back as at least the 1860–1870s in France and Germany [161], and 1905 in the USA [162]. Fly ash was first used in concrete in the USA in the 1930s [163]. The first use of alkalis along with hydraulic or latent hydraulic components to form a binder dates to the early 1900s, when the German scientist Kühl reported [164] studies on the setting behaviour of mixtures of ground slag and alkaline components. Chassevent [165] measured the reactivity of slags using caustic potash and soda solutions in 1937, although this work was aimed at analysis of the slags, rather than specifically aiming to develop binders from them. Purdon [166] performed the first extensive laboratory study on cements consisting of slag and caustic soda, with and without lime, in 1940. However, there was only very limited activity in this area in the succeeding decades, as the focus of research and development remained in the production and optimisation of Portland cements and the concretes synthesised from them.

In the late 1970s, the French chemical engineer Davidovits reignited interest in this area with the development of alkali-activated binders based on metakaolin, and coined the term “geopolymer” to describe his products [167–171]. These were initially marketed for reasons related to fire resistance, but the high early strength gain achievable through certain combinations of alkali-activation chemistry with set-controlling additives soon gained interest from government and industrial organisations in the USA [172]. Davidovits’ benchmark contributions [171] to AAM research include discussion of what he considered to be the ideal conditions for synthesising geopolymers, the characterisation of the reaction products obtained, and the study of end product characteristics, properties and possible applications. Through the 1980s and 1990s, a hybrid OPC/AAM concrete called Pyrament® was developed and marketed, among a range of products developed through the French ‘Geopolymer Institute’ [171, 173]. The Geopolymer Institute also hosted a conference series with events held in France [174–176] and Australia [177]; this series has in recent years been continued as the annual GeopolymerCamp event in France, and Davidovits has continued to actively promote geopolymer technology through this Institute.

The Pyrament concrete which was marketed in the 1980s–1990s achieved a compressive strength of 20 MPa at 4 h under standard curing conditions, or sufficient 4-h strength development at temperatures as low as -2°C to accept the load of a taxiing military aircraft [178], and was used in the 1991 Gulf War for the rapid placement of runways. By 1993, Pyrament was applied in 50 industrial facilities in the USA, 57 US military installations, and in seven other countries [173, 179], and was provided with strong endorsement from the U.S. military [180]. However, in 1996, the marketing of Pyrament was terminated by the parent company of its manufacturer, and much of the operational experience gained with Pyrament was lost. Pyrament was approximately twice as expensive as Portland cement concrete [181] and had a high clinker content rather than being a pure alkali-activated aluminosilicate system, as its aim was technical performance rather than lower CO_2 emissions or cost reduction. There has not been a systematic survey of the long-term performance of Pyrament structures in the open literature, although online reports released by the Geopolymer Institute [182] indicate good performance as a commercial airport taxiway construction material over a 25-year timespan.

Researchers in the UK [183] and the Netherlands [184] also provided some of the first contributions to the literature on alkali activation of BFS-fly ash blends; both groups published data for a 60 % BFS/40 % fly ash blend activated by 7 % NaOH by binder mass, and noted good strength development but problems with efflorescence and carbonation. These experimental programmes were explicitly stated to be an investigation of simulants of the Trief process for cement production from waste materials, but what is of more relevance to this Report is that they produced some of the first publicly available data on fly ash-BFS AAM systems.

In the 1980s, as discussed in the preceding sections of this chapter, Roy and collaborators in the USA began to develop analogies between alkali-activated binders and ancient cements, and used some of this knowledge to engineer AAM binders and concretes with a view towards the development of a more durable alternative to

Portland cement [64, 185–187]. Separately, work at Louisiana State University led to the development of alkali-activated materials based on class C fly ash [188], and contributions to the understanding of alkali-activated BFS chemistry [189].

Also in the 1990s, researchers throughout western Europe began to develop more detailed scientific foundations for the understanding of alkali-activation technology, with a collaboration between Palomo in Spain and Glasser in the UK providing a key early paper in this area [190] related to the alkaline activation of metakaolin. Around the same time, research and development work in Canada [135, 136, 191–198] provided some strong basis for engineering and scientific research in this area. However, the focus of much of the Canadian research community appears to have since moved to focus on high-SCM OPC blends, and the initially high level of output did not grow after this time, although some important outcomes have continued to be published [199–201].

In Spain, research on AAM has been underway since 1995 at the Eduardo Torroja Institute for Construction Science (a Spanish National Research Council body) in Madrid. The driving force behind research in Spain to develop alternative cements based on the alkali activation of industrial waste (blast furnace slag, fly ash, mining debris and so on), as in many other European countries, is essentially the pursuit of new construction materials able to compete in performance with OPC, but with a much lower environmental impact. These studies are undertaken within the framework of “sustainable” construction, where materials were and continue to be a fundamental part of the building process. The aim has been to find materials (cements and concretes) whose manufacture would be less energy-intensive and at the same time involve the re-use of industrial waste and by-products. Such new materials are also expected to exhibit strength and durability at least comparable, if not higher, when compared with OPC.

Working within this framework since the early 1990s, two teams, headed by Palomo and Puertas, continue to study the alkali activation of fly ash and blast furnace slag, respectively. In their research, both groups have aimed to establish the effect of the factors involved in activation, identify the mechanisms governing the process on chemical and microstructural levels [46, 202–207] and characterise the nature of the hydration products. They also reported the formation of a laminar C-S-H gel in alkali activation of BFS, as opposed to the characteristic chain-type structure exhibited by this gel in OPC systems [208, 209]. These workers were also the first to identify and characterise the gels which have been termed “N-A-S-H gels” [210, 211], as the alkali aluminosilicate analogue of the C-S-H gels which dominate Portland cement hydration products. These teams have also conducted thorough studies of the strength and durability of AAMs, and explored the behaviour of different (superplasticiser, shrinkage reducing) organic admixtures in such systems [212], as discussed in detail in Chap. 6 of this Report.

From the early 1990s onwards, researchers in the UK also provided detailed information in this field, particularly related to BFS hydration in the presence and absence of added alkali sources. Wang and Scrivener published a number of articles [35, 114, 213, 214] in which they addressed what, at the time, was the state of the art of the factors affecting the bearing strength of activated slag systems and the

Fig. 2.8 An AAM construction unit (75 MPa compressive strength after vibrocompaction) developed in Belgium in the 1990s (Image courtesy of J. Wastiels, Vrije Universiteit Brussel)



nature of the hydration products formed. The contributions of Richardson [37, 43, 215, 216] to the morphological characterisation and micro- and nano-structural analysis of the C-S-H gel forming in systems with a high blast furnace slag content also merit special attention.

In Belgium, the team led by Wastiels and Rahier published a very important early series of papers on the reaction mechanisms and products associated with the interaction between metakaolin and sodium silicate solutions, forming products which were described as ‘inorganic polymer glasses’ [217–220], and this work has continued to produce valuable mechanistic understanding since that time [221]. These reaction products resemble closely the ‘geopolymers’ of Davidovits, and were described in terms of glassy polymer structures rather than as a cement-like material; this terminology has appeared to hinder the uptake of the knowledge generated by these authors into the wider alkali-activation community, but the information presented in those papers is certainly valuable in understanding AAM binder structures. A joint academic-commercial research program in the same institution through the 1980s–1990s also resulted in the development of high-strength fly ash-based AAM binders and fibre-reinforced composites [222–224], and building units (Fig. 2.8). These products were technically successful in terms of the development of the desired physical properties, but eventually did not reach large-scale production due to fly ash supply constraints.

Since 2000, there has been a proliferation of research interest in Europe. In Germany, a multi-institutional collaborative team has engaged in the study of AAM binders for several years [12, 225–229], including important initial work in areas related to lifecycle analysis and sustainability accounting [12–14]. In the Netherlands, the company ASCEM has been developing proprietary cements based on alkali-activation of synthetic glasses for more than 15 years, with success in production methods, strength development and durability performance having been demonstrated [230]. In Switzerland, key advances have been made in the area of characterisation and thermodynamic modelling of cementing systems, including specific application to hydrating BFS systems [50, 231–236]. The Construction Technology Institute in Valencia, Spain, which also engages in AAM research, has

made interesting contributions to the alkaline activation of clays [237]. Significant advances in the area of binder and zeolite formation based on the alkali activation of fly ash [238, 239] have also been made by Querol in Barcelona, and a group of researchers in Italy have contributed to the understanding of alkali-activation of volcanic ashes [240]. In Portugal, the desire for utilisation of clay-rich tungsten mining wastes has driven a research program in this area to produce some interesting outcomes and a number of journal papers [25, 241, 242]. It seems that the main hurdle facing AAM producers in the EU at present is the apparently restrictive standards regime, although detailed discussion of some concepts in this area will be presented in Chap. 7 of this Report.

For several years from the mid-1990s, developments in AAMs in the USA were led by Balaguru and colleagues at Rutgers University, working in collaboration with government agencies and with a focus on composites and coatings [243–246]. After 2000, the Kriven group at the University of Illinois began an extensive program of work, sponsored in part by the U.S. Air Force, investigating the alkali activation of calcined clays and synthetic aluminosilicate precursors as a low-cost option for high-temperature ceramic-type applications [42, 247–251]. A group based at Penn State University also developed ‘hydroceramics’ (alkali-activated clays cured hydrothermally) as a potential material for the immobilisation of caesium and strontium-bearing nuclear waste streams [252–255]. More recently, important advances in fly ash utilisation, chemistry and engineering properties have resulted from work in Pennsylvania [256–258], Louisiana [259–261], Texas [262] and elsewhere; it appears that there is a stronger focus on alkaline activation of fly ash than slag-based systems in the USA at present. The availability of performance-based standards for cements in the USA seems to be beneficial for the uptake of AAMs in this market, although the currently limited acceptance of these standards provides some restrictions at present.

In short, the many significant breakthroughs and the prolific production of relevant papers speak to the importance of European and North American scientists’ contribution to AAM research and development. The particular drivers for the technology in these parts of the world, and the generally more constrained regulatory environments under which industry operates, have led to a scientific focus which is somewhat distinct from the engineering/applications focus which has led research in eastern Europe and China in particular.

2.8 Development of Alkali-Activated Cements in Australasia

Research activity in AAMs in Australia was initiated in the mid-1990s, with the primary aim of developing methods of treating and immobilising mining wastes containing elevated levels of heavy metal contaminants [263–265]. Since this time, the research program at the University of Melbourne, led first by Van Deventer and more recently by Provis, has published in excess of 100 journal papers in this area. Given that Australia has a plentiful supply of underutilised fly

ash, applied research has been focused to a large extent in this area [266–270], although fundamental studies of systems based on metakaolin [34, 271–273] have also been utilised to provide basic information. This group has particularly focused on nanostructural characterisation methods, and has introduced the use of a variety of computational methods, advanced in situ characterisation techniques, synchrotron and neutron beamline-based methods to the area of AAMs [34, 42, 89, 99, 273–279].

Another long-running Australian research program is the group led by Sanjayan, who have published a number of key papers related to concretes obtained by the alkali-activation of slags [280–284], and also some detailed studies on alkali-activated fly ash concretes [285] and high-temperature properties of AAMs [286]. This work provides particular value in combining structural engineering and materials science approaches to the analysis of problems related to larger-scale structures and structural materials.

At Curtin University in Western Australia, two research groups have produced results related to structural [287–290] and physicochemical [291–294] aspects of AAM technology respectively. This research program also led to some pilot-scale concrete production in collaboration with cement and resources companies through the Centre for Sustainable Resource Processing research and development organisation, but full-scale commercial production has not yet been implemented in Western Australia. The Australian national research organisations CSIRO [295–297] and ANSTO [298, 299] have also contributed significantly in this research field. Australia is a developed nation with a resource-based economy, which means that the availability of raw materials is mainly determined by supply-chain constraints rather than limited generation rates; if these issues can be resolved, it does appear to provide good scope for the up-scaling of alkali-activation technology, subject to corresponding developments in its standards regime.

In New Zealand, a long-running research program led by MacKenzie has contributed to the development of fundamental scientific understanding of alkali-activated clays [300–303]; the supply of fly ash in New Zealand is reasonably limited, and the available Class C ash tends to present challenges related to setting rates and rheology [304].

In parallel to the above Australian and New Zealand research activities, commercial developments have been driven by Melbourne-based companies Siloxo (1999–2005) and Zeobond (2005–ongoing) [10, 305–308]. Siloxo was closely related to activities to successfully utilise New Zealand-sourced Class C fly ash in pre-mixed concrete with local cement companies. More recently, the commercialisation activities and portfolio of project applications of Zeobond's technology (branded as E-Crete nation-wide and also as 'Earth Friendly Concrete' under license to Wagners group in Queensland) have led to advances in the regulatory acceptance of AAMs in Australia, leading most other jurisdictions in the developed world in terms of acceptance of alkali-activated binders in civil infrastructure applications.

2.9 Development of Alkali-Activated Cements in Latin America

The development of alkali activation in Latin America has been based mainly around the valorisation of the BFS and metakaolin sources which are plentiful in that region. Research has been ongoing since the 1990s in Brazil [309–311] and the 2000s in Colombia [51, 312–314] and Mexico [315–317]. This region has a high demand for construction materials, a ready supply of raw materials, and a relatively strong degree of environmental consciousness related to the preservation of unique environments and biodiversity; this appears to provide good prospects for the wider uptake of AAMs technology in the region in general.

2.10 Development of Alkali-Activated Cements in India

India is an area in which fly ashes are particularly plentiful, with generation exceeding 150 million tonnes by 2011 [318], but there is a tendency, due to the coal prevalent coal geology and combustion conditions, for the reactivity of the ashes to be relatively low [318, 319]. This has led to significant research progress in the area of mechanochemical activation of ashes for use in AAMs [318, 320–322], and following from this as well as some empirical academic studies addressing mix design issues in alkali-activated fly ash concretes, the commercialisation of fly ash-derived AAM paving tiles has commenced in India [323]. With the level of utilisation of fly ash in India currently lower than in most other parts of the world, and a growing demand for construction products, this market would seem to provide opportunities for AAM uptake to expand.

2.11 Conclusions

Research and development activities in alkali-activated binders and concretes are motivated by a number of technical, economic and environmental drivers, with the prevailing market conditions in different parts of the world having led development in different directions and for different reasons over the past decades. The scientific foundations of alkali-activation technology are reasonably well established, and analogies with ancient cements as well as more recent analysis of decades-old structures have shown promising results in terms of durability. A need for developments in the area of standardisation has been identified, which history has shown will largely be driven by market advancement. These key areas, identified from a historical perspective here, will now become the focus of the remaining chapters of this Report.

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Chapter 3

Binder Chemistry – High-Calcium Alkali-Activated Materials

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3.1 Introduction

As mentioned in Chap. 2, the development and assessment of alkali-activated binders based on calcium-rich precursors such as blast furnace slag (BFS) and other Ca-rich industrial by-products have been conducted for over a century [1–3]. However, an increase in interest in the understanding of the microstructure of alkali-activated binders has taken place in the past decades. This has been driven by the need for scientific methods to optimise the activation conditions which give a strong, stable binder from a particular raw material, and consequently a high-performance alkali-activated material (AAM) concrete, while achieving acceptable workability and a low environmental footprint. A detailed scientific understanding of the structure of these materials is required to generate the technical underpinnings for standards which will facilitate their wider commercial adoption [4, 5].

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The chemistry and basic engineering aspects of alkali-activated BFS-based binders have been discussed in detail in a number of reviews in the scientific literature, including (but by no means limited to) [6–18]. Literature on Ca-rich precursors other than BFS is relatively less abundant, but will also be summarised in the latter sections of this chapter.

The structure of the binding gels formed through the activation of BFS is strongly dependent on various chemical factors which control the reaction mechanism, and consequently also mechanical strength development and durability performance. These factors can be classified broadly into two categories: those directly related to the activator used, and those associated with the characteristics of the raw materials. These two types of factors will be addressed in detail in the following sections.

3.2 Structure and Chemistry of the Binder – BFS-Based Systems

The structural development of AAMs based on BFS is a highly heterogeneous reaction process that is mainly governed by four mechanisms: dissolution of the glassy precursor particles, nucleation and growth of the initial solid phases, interactions and mechanical binding at the boundaries of the phases formed, and ongoing reaction via dynamic chemical equilibria and diffusion of reactive species through the reaction products formed at advanced times of curing [19–21].

There is a consensus, in studies reporting the assessment of the reaction products formed by alkaline activation of BFS, that the main reaction product is an aluminium-substituted C-A-S-H type gel [8, 22–27], with a disordered tobermorite-like C-S-H(I) type structure. This is accompanied by the formation of secondary reaction products such as AFm type phases (mainly identified in NaOH-activated binders [23, 28, 29], and also the Si-containing AFm phase strätlingite in silicate-activated binders [30, 31]), hydrotalcite (identified in activated BFS with relatively high contents of MgO [25, 32, 33]), and zeolites such as gismondine and garronite (formed in activated BFS binders with high Al_2O_3 and low (<5 %) MgO [21, 34, 35]).

The structure and composition of the C-A-S-H type product forming upon activation of BFS is strongly dependent on the nature of the activator used. The C-A-S-H product formed in NaOH-activated BFS presents a higher Ca/Si ratio and a more ordered structure than the C-A-S-H type gel formed in silicate-activated BFS binders [23, 24], as a consequence of the increased availability of silicate species in the pore solution in silicate-activated systems. Puertas et al. [36] identified that C-A-S-H type gels in alkali silicate-activated BFS binders are likely to have a structure comparable to coexisting 11 and 14 Å tobermorite-like phases. Myers et al. [27] developed a structural model to describe these gels based on the constraints inherent in the crosslinked and non-crosslinked structures of the different tobermorite-like units (Fig. 3.1), which enables calculation of the chain length, Al/Si ratio and degree of crosslinking for these more complex structures which cannot be fully described by standard models for non-crosslinked tobermorite-like C-S-H gels.

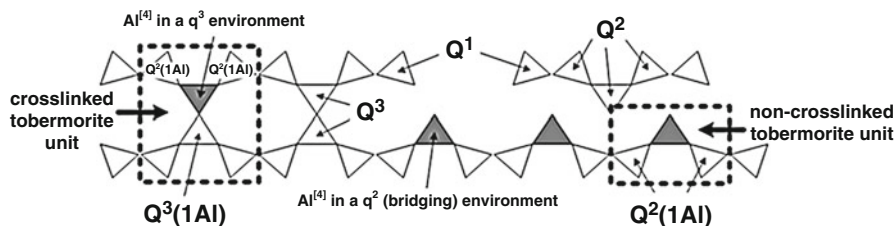
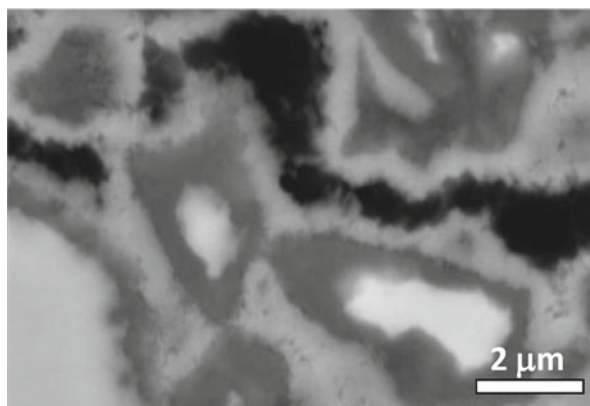


Fig. 3.1 Schematic representation of cross linked and non-cross linked tobermorite structures which represent the generalised structure of the C-(N)-A-S-H type gel (Image courtesy of R.J. Myers, University of Sheffield)

Fig. 3.2 Backscattered electron image of NaOH activated BFS after 180 days of curing. The dark rim around *light grey* unreacted BFS particles contains high Na, and the bright rim contains relatively low Na (Adapted from [37])



Recent studies have also revealed [37] that it is possible that some of the chemically bound Ca^{2+} in C-A-S-H is replaced by Na^+ , leading to the formation of a C-(N)-A-S-H inner type gel in both NaOH-activated (Fig. 3.2) and silicate-activated BFS binders (Fig. 3.3). C-(N)-A-S-H type gels have also been observed in the interfacial transition zone between siliceous aggregates and silicate-activated BFS binders [38, 39], with a lower Ca/Si ratio than is observed in the binding gel formed in the bulk gel.

In analysing the structure of alkali-activated BFS binders, it is also instructive to understand the chemistry of binders formed through the reaction of BFS with water in the absence of alkaline activators. Such pastes do harden, given sufficient time (22 % reaction of a rather coarsely-ground BFS was reported after 20 years of hydration, providing sufficient reactive components for binder gel formation), and form a rather highly Al-substituted C-S-H phase mixed with an Mg-Al layered double hydroxide and disordered layered Al hydroxide phases [41]. The C-S-H has a limited capacity to take up Al, which is restricted by the geometry of the silicate chains and the thermodynamics of ionic substitution to a maximum Al/Si ratio slightly less than 0.20 [27, 42–45].

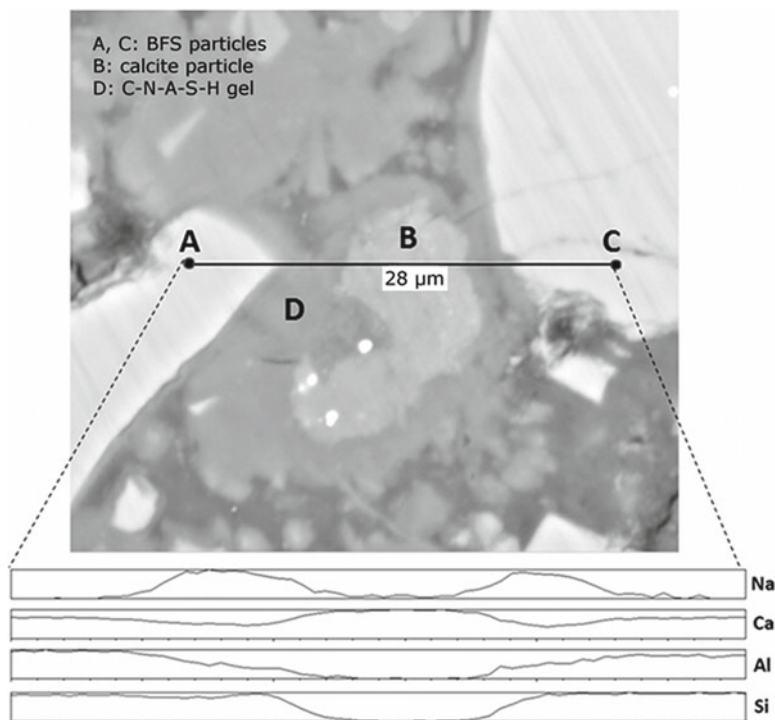


Fig. 3.3 Scanning electron micrograph and elemental distribution between two unreacted BFS particles of a polished 28 days sodium silicate-activated binder (80 wt.% BFS/20 wt.% metakaolin) (Adapted from [40])

However, beyond the identification of hydrotalcite, AFm and zeolitic-type phases in binders of different compositions, the exact chemistry controlling the formation (kinetics and equilibria) of the secondary phases in alkali-activated BFS systems is not yet particularly well understood. There have been numerous studies published in which one or more of these types of secondary phase are identified through x-ray diffraction (XRD) and/or nuclear magnetic resonance (NMR) analysis of the products of reaction of a particular BFS with an activator, but systematic studies across a wider range of BFS compositions are rare. Such studies have appeared in the literature based on industrial slags [32, 46, 47], but slags from a particular geographical region tend to fall within a fairly limited compositional range due to similarities in iron ore mineralogy and blast furnace operations, and so analysis of the products of alkaline activation of synthetic slags which can be designed across a wider compositional range [46, 48] would appear to provide greater opportunities for the systematic analysis of the influence of BFS chemistry on the formation of the binder.

However, the effects of activator selection on binder chemistry are significantly better described in the literature, and will be addressed in the following section.

3.3 Activators for BFS Systems

As was mentioned in Sect. 3.2, the reaction of BFS with water will, over a very extended period of time, lead to the formation of a hardened binder. The most critical role of the alkaline activator in an AAM is therefore to accelerate this reaction to take place within a reasonable timeframe for the production of an engineering material, and this is most readily achieved by the generation of an elevated pH. The chemistry of the most common alkaline activators used in AAMs was outlined in Chap. 2 of this report. Alkali silicates and hydroxides generate the highest pH among these common activators, while carbonates and sulfates generate moderately alkaline conditions, and generate free hydroxide for the activation process through reactions involving calcium from the BFS.

In the early part of the reaction process (the first 24–48 h), the kinetics of reaction of alkali silicate-, carbonate- or hydroxide-activated BFS binders have been evaluated using isothermal calorimetry, identifying that the structural development occurs in five stages (induction, pre-induction, acceleration, deceleration and finalisation), producing a heat flow curve broadly similar to what is expected for conventional Portland cement [19, 22]. However, the duration and intensity of each of the heat release processes identified during the first hours of setting of alkali-activated BFS specimens depends on the type of activator used (Fig. 3.4).

In a broader study addressing the effect of the type of activator, Shi and Day [50–52] proposed three reaction models for AAM: one where a sole peak is identified in the first minutes of reaction, typically observed in hydration of BFS with water or Na_2HPO_4 . The second model presents a pre-induction peak, followed by

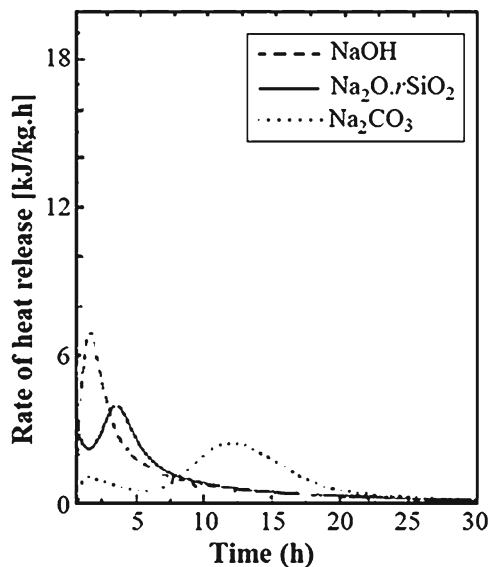


Fig. 3.4 Isothermal calorimetry curves of activated BFS binders, as a function of the nature of the alkaline activator (Adapted from [49])

an induction period and a second peak associated with the acceleration and consequent precipitation of reaction products. This behaviour is typically observed in NaOH-activated BFS binders, suggesting some mechanistic comparisons to the hydration of Portland cement, where the initial and final setting times can be directly affected by the acceleration period of the heat evolution and the consequent formation of reaction products [33]. The third model involves an initial double peak, followed by the induction period, then a third peak assigned to the acceleration period of the reaction. This behaviour is expected when the BFS is activated by weak salts including silicates, carbonates, phosphates and fluorides [50]. Activation of BFS with NaOH or Na_2CO_3 generally leads to a lower total heat release over the first 24 h of reaction compared to silicate-activated binders, associated with a slower reaction process [19].

The reaction products, and therefore the performance, of activated BFS binders are strongly dependent on the nature and concentration of the activator used [53]. The possible activating solutions include alkaline hydroxides (ROH , $\text{Ca}(\text{OH})_2$), weak salts (R_2CO_3 , R_2S , RF), strong acid salts (Na_2SO_4 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and alkali silicate salts $\text{R}_2\text{O} \cdot r\text{SiO}_2$, where R is Na^+ , K^+ , or less commonly Li^+ , Cs^+ or Rb^+ . Among these, the commonly used activators for the production of activated BFS binders are sodium hydroxide (NaOH), sodium silicates ($\text{Na}_2\text{O} \cdot r\text{SiO}_2$), sodium carbonate (Na_2CO_3) and sodium sulfate (Na_2SO_4), as discussed in Chap. 2 [18, 46, 53, 54]. Shi and Day [55] identified that all caustic alkalis, and alkali compounds whose anions can react with Ca^{2+} to produce Ca-rich compounds that are less soluble than $\text{Ca}(\text{OH})_2$, can act as activators for BFS. The anionic component of an alkaline activator reacts with Ca^{2+} dissolving from the BFS to form Ca-rich products during the initial reaction period. Roy et al. [56], activating BFS with different hydroxide solutions (LiOH , NaOH , KOH , $\text{Ca}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, and $\text{Ba}(\text{OH})_2$), identified similar reaction products in each of these systems independent of the ionic radius or valence of the cation present, when the activators were all formulated with the same pH. The compressive strength developed by activated BFS binders as a function of the type of activator is shown in Fig. 3.5.

The efficiency of the activator is strongly influenced by the pH, as this controls the initial dissolution of the precursor and the consequent condensation reactions [33, 50, 55–57]. The effect of the pH on the activation of BFS is also strongly dependent on the type of activator, because calcium solubility decreases at higher pH while silica and alumina solubilities increase. Although NaOH activating solutions have a much higher pH than sodium silicate solutions of similar alkali concentration, comparable amounts of BFS react in the presence of each of the types of activator, and the silicate-activated binders usually develop higher mechanical strength than NaOH-activated BFS [37, 53, 58, 59]. This is a consequence of the additional supply of silicate species in the systems to react with the Ca^{2+} cations derived from the dissolved BFS, forming dense C-A-S-H reaction products [24], and also driving further Ca dissolution by removing it from the solution phase. Therefore, the selection of the most appropriate alkaline activator needs to include consideration of the solubility of calcium species at the pore solution pH in the fresh paste, as well as the interactions involving the cations supplied by the activator, which can promote the formation of specific reaction products.

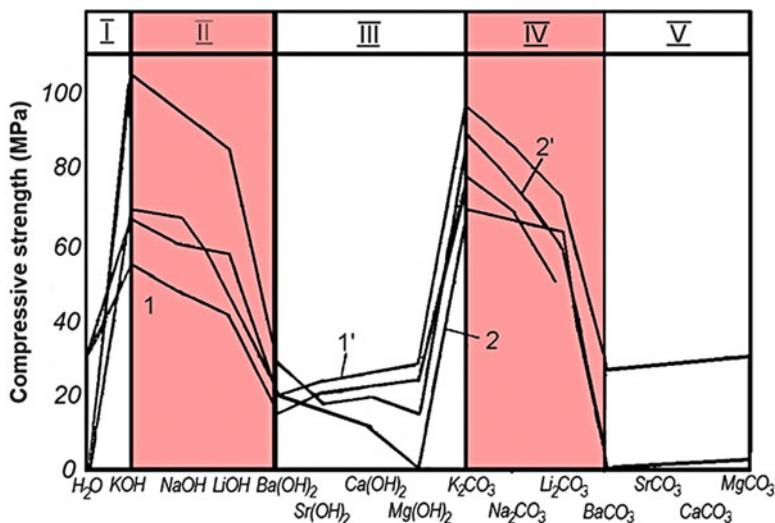


Fig. 3.5 Compressive strengths of cement compositions as a function of the type of alkaline activator and composition of the BFS precursor: samples marked 1 and 1' are based on a BFS with $M_b=1.13$ (6.75 wt.% Al_2O_3); samples marked 2 and 2' are based on a BFS with $M_b=0.85$ (15.85 wt.% Al_2O_3). Samples 1 and 2 were steam-cured ($T=90\pm 5$ °C, 3+7+2 h), and 1' and 2' were cured in an autoclave ($T=173$ °C, 3+7+2 h) (Data courtesy of P.V. Krivenko)

Fernández-Jiménez et al. [58], following a statistical experimental design, identified that the nature of the activator is the main factor controlling the mechanical properties of activated BFS materials. The activation of a BFS with moderate specific surface area ($450\text{ m}^2/\text{kg}$) led to the development of higher mechanical strength when using sodium silicate activators, consistent with the results obtained in other studies (e.g. [53]). Improved mechanical strengths can be achieved when using NaOH and Na_2CO_3 as activators with more finely ground BFS [55, 58].

The mechanical strength development of silicate-activated BFS materials is dependent on the modulus of the activator solution ($M_s = \text{molar ratio } SiO_2/Na_2O$; see detailed discussion in Chap. 2), and the nature of the BFS used, as shown in Fig. 3.6 [53]. In NaOH-activated and Na_2CO_3 -activated BFS binders, the activator dosage and water to binder ratio seem to have less influence on the kinetics of reaction than in silicate activated BFS binders [52]. Palacios and Puertas [60] identified that the mixing time also has a remarkable effect on the mechanical strength development of silicate-activated BFS binders, so that longer times of mixing (up to 30 min) can lead to the enhancement of the strength up to 11 %, as well as reduction of the permeability of the system, associated with a reduction of the volume of small pores.

It has also been identified that a sodium silicate-lithium carbonate composite activator promotes a higher extent of reaction than solely using $Na_2O.rSiO_2$ based activators, attributed in part to the presence of a retarding effect [61, 62].

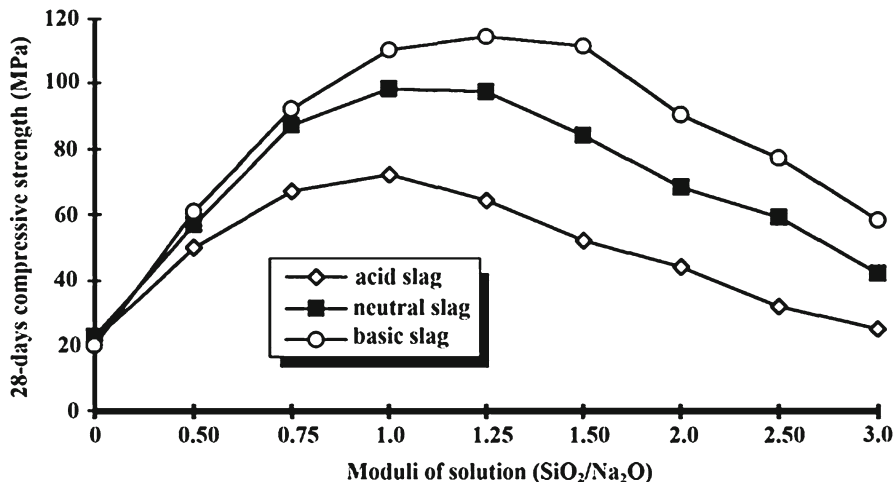


Fig. 3.6 Twenty-eight-day compressive strengths of silicate-activated BFS mortars, cured at 20 °C, as a function of the modulus of the activating solution. The BFS had a fineness of $4,500 \pm 300 \text{ cm}^2/\text{g}$, with an alkaline solution/BFS ratio of 0.41 and a sand/BFS ratio of 2.0 (Data from [53])

The activation of BFS using Na_2SO_4 has attracted less attention than NaOH -activated and $\text{Na}_2\text{O} \cdot r\text{SiO}_2$ -activated systems, mainly as a consequence of the low mechanical strength development observed at early times of curing. However, the relatively low pH of the pore solution achieved in these systems, along with the formation of larger amounts of ettringite, gives properties which are desirable for applications such as the immobilisation of nuclear wastes. In such applications, the mechanical strength requirements are much lower than in conventional civil infrastructure applications, while the ettringite chemically binds large amounts of free water, and therefore reduces the risk of metal corrosion [63, 64]. The use of finely ground BFS, plus the inclusion of small amounts of lime or Portland clinker, can give much higher mechanical strength in sulfate-activated BFS binders [53, 65, 66]. These hybrid binders are discussed in detail in Chap. 5.

3.3.1 Binder Structure – Hydroxide Activation

The binder in a hydroxide-activated BFS system is dominated by a C-A-S-H gel, with closely intermixed Al-rich secondary phases such as layered double hydroxides (often resembling the hydrotalcite group) and/or calcium (silico)aluminate hydrates [28, 56, 57, 67–69], depending mainly on the Al and Mg content of the BFS source. The degree of structural ordering of the C-A-S-H gel tends to be relatively high compared to most Portland cement hydration products [67], and this gel phase shows structural features resembling a 14 Å tobermorite [70]. The inner

product and outer product regions of the gel (i.e., the gel formed in the areas initially occupied by BFS particles or by the solution, respectively) tend to have similar compositions [70]. As in Portland cement systems, the C-A-S-H gel includes layers of tetrahedrally coordinated silicate chains with a dreierketten structure (Fig. 3.1), each chain containing $(3n-1)$ tetrahedra for an integer value of n . The interlayer region is rich in Ca, and also contains the water of hydration. The aluminium in the C-A-S-H gels is mostly present in tetrahedral bridging sites within the chains, as has been identified in blended Portland cement systems [45, 71, 72], and Na^+ cations can balance the negative charge generated when Al^{3+} replaces Si^{4+} . This tetrahedrally coordinated aluminium is the main site at which crosslinking between the silicate chains takes place [73–75]. The observation that the Al only becomes substituted into these bridging sites leads to compositional restrictions within the C-A-S-H structure, limiting the maximum degree of Al substitution (although the exact upper bound depends on the chain length and degree of crosslinking [27]), thus leading to the formation of the Al-rich secondary phases as noted above.

The C-A-S-H type gels formed in NaOH-activated BFS tend to have a relatively low degree of crosslinking [24, 76], although Palacios and Puertas [77] did also identify a small content of Q^3 units in the gel. The type of activator used also affects the chemical composition of the gels; because there is no extra Si supplied by a hydroxide activator, the $\text{Ca}/(\text{Si} + \text{Al})$ ratio of the system (and thus of the C-A-S-H gel itself) will be higher than in silicate-activated binders. However, independent of the activator used, the C-A-S-H type gel formed through the activation of BFS has a lower Ca content than a hydrated Portland cement system, whose Ca/Si ratio is usually between 1.5 and 2.0 [9].

3.3.2 Binder Structure – Silicate Activation

Since the initial work of Purdon [3], silicate activation has been the most widespread method for production of BFS-based AAMs, due to the versatility of the method and the generally high performance of the binders produced. The silicate activators used in the production of BFS-based binders are most commonly commercially-supplied sodium silicate solutions or spray-dried powders. The activator is usually included in the mix as a solution; however, it can also be incorporated in the solid state, blended or interground with the BFS [53]. The addition of the activator as a solid can result in lower and more variable early strength, as a consequence of the slower availability of alkalinity during the progress of the reaction [53, 78–80]. Also, the fact that the activators are hygroscopic might cause partial reaction before addition of the mix water [53].

However, there are alternative sources of activators which may provide advantages in terms of price and/or environmental footprint in some circumstances. Živica and colleagues [81–83] have used chemically modified silica fume combined with NaOH as an alkaline activator in the production of high performance activated BFS binders, identifying a highly densified structure and enhanced mechanical strength

compared to binders produced using commercial sodium silicate solutions. Bernal et al. [84] also identified improved mechanical strengths, along with comparable structural features, in BFS/metakaolin binders activated by chemically modified silica fume. Alternative sources of silicon such as rice husk ash [84] and nanosilica [85] have also been assessed as substitute silica sources in these alternative activators, showing that the combination of alkalis with highly amorphous Si-containing precursors can be successfully used as activators in the production of AAMs.

It is well known that the main reaction product in alkali silicate-activated BFS binders is a poorly crystalline C-A-S-H type gel [36, 68, 86, 87], whose structure is strongly influenced by the chemistry of the BFS source and the composition of the activator [32, 47]. The outer product forms rapidly, with its formation enhanced by the presence of high concentrations of silica (and thus a strong tendency towards supersaturation) in the initially fluid-filled regions [25, 88]. The pore structure is variously reported to be either very impermeable or rather open, depending on both the mix design and the methods of sample preparation and measurement, as the application of either a high intrusion pressure or an unsuitable drying regime will lead to damage in the samples prior to (or during) analysis [89, 90]. An increasing activator dose generally leads to a more refined pore network [91].

^{29}Si and ^{27}Al MAS NMR results have proved that the use of silicate type activators induces the formation of a C-A-S-H gel with a relatively high content of Q^2 and Q^3 sites, which is an indication of a high degree of crosslinking and high densification of the gel [24, 25, 77, 87, 92]. Fernández-Jiménez [73] observed reductions in the Al concentration in bridging positions, along with an increment in the Si bridging units, with a decrease in the sodium silicate activator concentration. Curing at 45 °C leads to the formation of a highly uniform C-S-H product with a reduced degree of crosslinking (Q^3 and $\text{Q}^3(1\text{Al})$ sites are not observed) than in binders cured at 25 °C [73]. Heat-curing of silicate-activated BFS can accelerate setting, but is not always beneficial for long-term properties, particularly if thermal incompatibilities lead to microcracking, or if the water required to mediate the reaction is lost from the material and thus the ongoing reaction is restricted [93].

Hydrotalcite-like Mg-Al layered double hydroxides are also observed as a reaction product when the BFS used contains sufficient Mg [24, 25, 32, 67, 68, 87]. Zeolitic products are also sometimes observed in samples with lower Mg content, commonly in the gismondine type structure family with varying degrees of Na/Ca substitution [21, 34], while thomsonite has also been observed in aged activated BFS pastes [94]. Additional products which have been observed in silicate-activated BFS include siliceous hydrogarnets such as katoite [87], and sometimes also distinct crystalline AFm phases including strätlingite [30, 31].

However, the AFm phases are not always identifiable by XRD, as it has been proposed that some of the aluminium within the binding gel exists as AFm-like layers, intimately intermixed into the C-S-H structure and thus not distinguishable by XRD [29, 68, 87]. The literature provides very little detailed analysis of the mechanism of formation of AFm phases in alkali-activated BFS binders, although from stoichiometric arguments, these phases are likely to be linked to high concentrations of available Ca and Al [30, 86]. Figure 3.7 shows an example of a phase assemblage calculated from a thermodynamic model of the alkali-activation of BFS with a

Fig. 3.7 Results of thermodynamic modelling of the phase assemblage formed by activation of BFS with sodium silicate, as a function of the fraction of BFS hydrated (Adapted from [30])

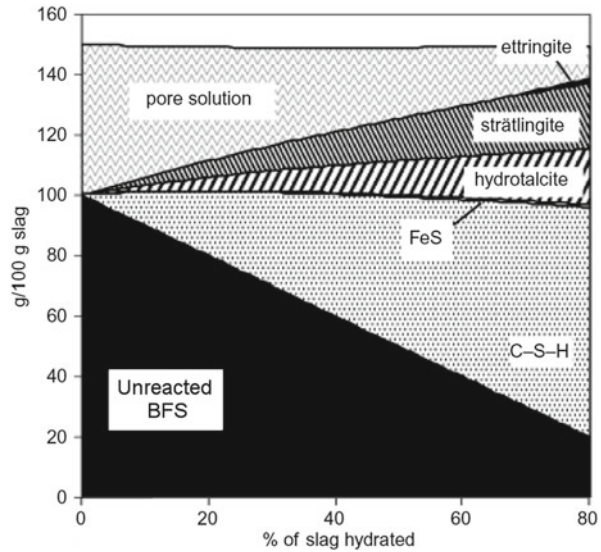
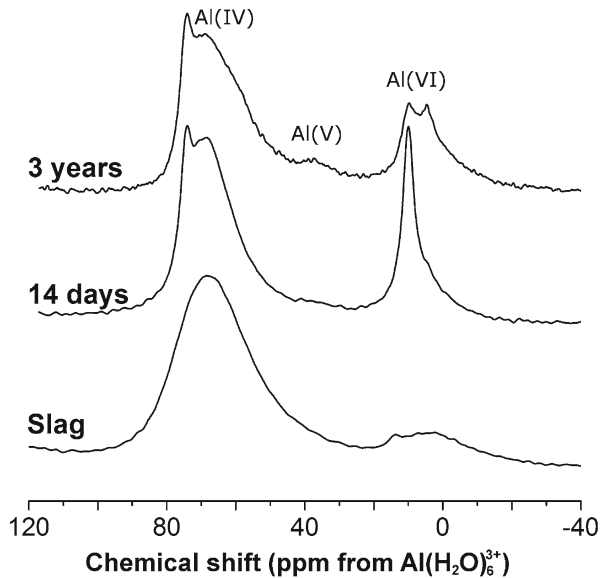


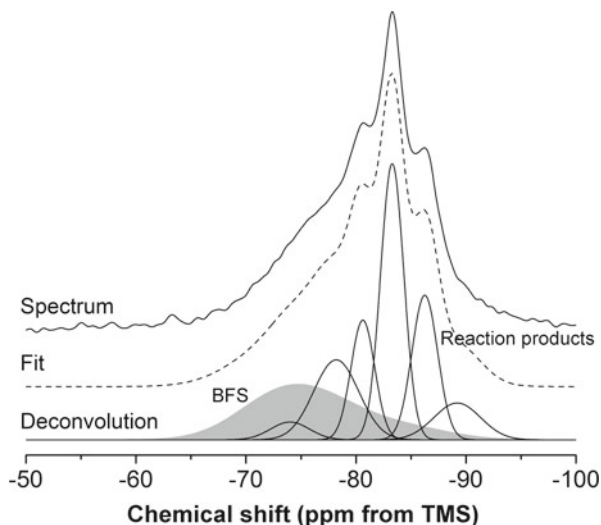
Fig. 3.8 ^{27}Al MAS NMR spectra of BFS, and the products of its alkali-activation with sodium silicate of modulus 1.0, after 14 days and 3 years of curing (Data from [87])



low-modulus sodium silicate solution, where the phases predicted to form generally align closely with the experimental observations as noted above [30].

Figure 3.8 shows ^{27}Al MAS NMR spectra of BFS, and alkali silicate-activated BFS binders. The spectrum of the unreacted BFS exhibits a broad resonance between 50 and 80 ppm, centred around 68 ppm, assigned to the tetrahedral Al in the glassy BFS. Upon activation, samples cured for 14 days and for 3 years show a sharper Al(IV) band than the unreacted BFS, along with the formation of a somewhat narrower resonance centred at 74 ppm. The peak at ~68 ppm is

Fig. 3.9 Deconvoluted ^{29}Si MAS NMR spectra of alkali-activated BFS cured for 14 days. The *dark grey* band represents the contribution of the remnant anhydrous BFS (Data from [87])



associated both with remnant unreacted BFS, and also potentially with cross linking bridging tetrahedra within the C-A-S-H gel [45]. The sharp peak at 74 ppm is assigned to Al(IV) incorporated in non-crosslinking bridging tetrahedra bonded to $Q^2(1Al)$ sites [44, 45, 95, 96].

In the octahedral Al region (from -10 to 20 ppm), the alkali-activated BFS sample cured for 14 days activated shows a high intensity narrow peak centred at 10 ppm, along with a small shoulder centred at 4.5 ppm, which can be assigned to both AFm and hydrotalcite-type phases [28, 86, 87], as the peak locations for these types of phases overlap and depend on the precise nature and degree of ionic substitution within the phases.

In the 3 year old sample in Fig. 3.8, the increase in the intensity of the 3 ppm peak is consistent with the development of a disordered phase such as the ‘third aluminate hydrate’ of Andersen et al. [96, 97], which is a hydrous amorphous alumina structure and can be closely intermixed with layered Mg-Al phases [41].

Figure 3.9 shows the ^{29}Si MAS NMR spectrum of the same 14-day cured alkali silicate-activated BFS sample as shown in Fig. 3.8 [87]. Deconvolution into component sub-peaks and identification of the contribution of unreacted BFS enables direct calculation of the extent of reaction of the BFS [87, 98], which is around 75% in the sample shown here [87]. The positions and relative intensities of the reaction product sub-peaks shown in Fig. 3.9 are consistent with the chemistry of tobermorite-like C-A-S-H gels, with site connectivities ranging from Q^1 to Q^3 , and varying degrees of Al substitution and different charge-balancing species leading to the presence of multiple peaks for each connectivity type [87].

The combination of alkali silicate-activated BFS and finely-ground limestone has also been demonstrated to provide acceptable strength development and durability performance, and limestone is generally available at a lower cost than either BFS or sodium silicate, meaning that this provides a potentially cost-effective route to AAMs [99].

3.3.3 Binder Structure – Carbonate Activation

Sodium carbonate activation of BFS has been applied for more than 50 years in eastern and central Europe [16, 46, 100], as a lower cost and more environmentally friendly alternative to hydroxide or silicate activators. The use of this activator promotes the development of a lower pH compared to many alkali-activated binder systems, which is potentially beneficial in terms of occupational health and safety considerations. Niche applications such as immobilisation of reactive metals, which is important in the disposal of nuclear wastes, can also benefit from the reduced susceptibility to corrosive processes [64]. However, the understanding of the structural development of carbonate-activated BFS is very limited, as carbonate-activated binders have attracted less attention from academia and industry than other activated-BFS systems, because of the generally delayed hardening and strength development [59, 101, 102], when compared with NaOH or sodium silicate activators. The incorporation of finely ground limestone in Na₂CO₃-activated binders can also give some benefits in terms of performance and cost [103, 104], where binders with 97 % reduction in Greenhouse emissions compared to Portland cement have been developed, with 3-day strengths exceeding 40 MPa.

Studies assessing sodium carbonate-activated materials [24, 33, 54, 58, 59, 101] generally report higher mechanical strength development of BFS activated with Na₂CO₃ than with NaOH, but lower than silicate-activated BFS binders, along with extended setting times. Małolepszy [105] identified that Na₂CO₃ activation is more effective for BFS containing åkermanite, while activation with NaOH is more suitable when using BFS containing gehlenite. Wang et al. [53] reported similar mechanical strengths in Na₂CO₃-activated BFS concretes when the activator is ground together with the BFS or added in solution, and Collins and Sanjayan [106, 107] also observed that NaOH/Na₂CO₃-activated BFS binders developed early-age mechanical properties at a similar rate to that expected for conventional Portland cement with similar contents of binder. In that study, improved workability was observed with a higher ratio of Na₂CO₃ to NaOH in the binder formulation.

In the early stages of reaction, Na₂CO₃ activation of BFS leads to formation of calcium carbonates and mixed sodium/calcium carbonate double salts, as a consequence of the interaction of the CO₃²⁻ from the activator with the Ca²⁺ from the dissolving BFS. At more advanced times of curing, an Al-substituted C-S-H type gel forms, which promotes the hardening of the paste [102]. The C-A-S-H formed in Na₂CO₃-activated BFS has a highly crosslinked structure including Q³ sites, and forms in parallel with carbonate salts including gaylussite, Na₂Ca(CO₃)₂·5H₂O [24]. Xu et al. [100], assessing aged BFS concretes activated with Na₂CO₃ and Na₂CO₃/NaOH blends which had continued to gain strength over a period of years to decades, identified the main reaction product in these materials as a highly crosslinked C-S-H type phase with a relatively low Ca/Si ratio as the outer product, and an inner product involving carbonate anions. It has been proposed [100] that in Na₂CO₃ activated BFS binders, the long-term activation reaction takes place through a cyclic hydration process where the Na₂CO₃ supplies a buffered alkaline environment, with the level of CO₃²⁻ available in the system maintained by the gradual

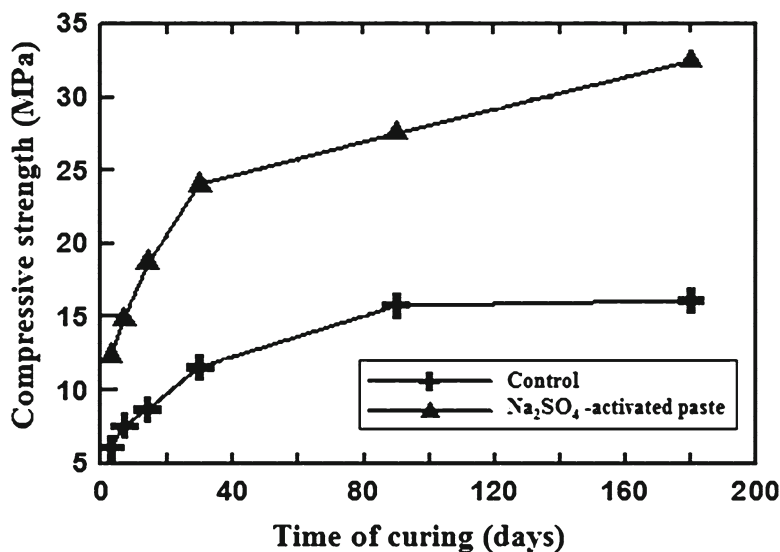


Fig. 3.10 Strength development of sodium sulfate activated lime-BFS cement, cured at 50 °C, compared to a control without Na₂SO₄ (Adapted from [46])

dissolution of CaCO₃ releasing Ca to react with the dissolved silicate from the BFS. However, there is not yet detailed evidence of how this mechanism might proceed over the first months of reaction in Na₂CO₃-activated binders.

3.3.4 Binder Structure – Sulfate Activation

Lime-BFS cement was the earliest cementitious material made from BFS, first produced in Germany and subsequently spreading to many other countries, but lost popularity because of its long setting times, low early strength and fast deterioration in storage compared with modern Portland cement [108]. However, this type of cement has excellent resistance to sulfate-rich ground water, and some of the disadvantages associated with its strength development have been overcome with the use of alkaline activators, such as sodium sulfate, as shown in Fig. 3.10 [46]. Compressive strengths as high as 60 MPa after 56 days have also been achieved through the use of a composite Na₂SO₄-Na silicate-Ca(OH)₂ activator [109].

Structural characterisation of these binders indicates the formation of foil-like C-A-S-H along with C₄AH₁₃ as the main reaction products in lime-BFS cements without sodium sulfate, while the inclusion of Na₂SO₄ in the binder promotes the formation of ettringite at the expense of C₄AH₁₃ and AFm type phases [46]. In lime-BFS systems without Na₂SO₄, the formation of hydrated calcium (alumino) silicates is favoured at early times of curing, and these hydration products cover

the surfaces of the BFS particles. The addition of Na_2SO_4 to lime-BFS binders accelerates the dissolution of BFS, but appears to retard the dissolution of $\text{Ca}(\text{OH})_2$ [46]. The presence of Na_2SO_4 accelerates early hydration, controlled by the initial dissolution of BFS, forming more extensive C-S-H product rims around the BFS particles as well as AFt needles. These factors contribute to the early strength of Na_2SO_4 -lime-BFS pastes. However, the formation of more C-S-H products around the BFS particles in Na_2SO_4 -containing pastes inhibits later hydration, which is controlled by the diffusion of water through the hydrated layer to the unreacted cores of BFS particles [46].

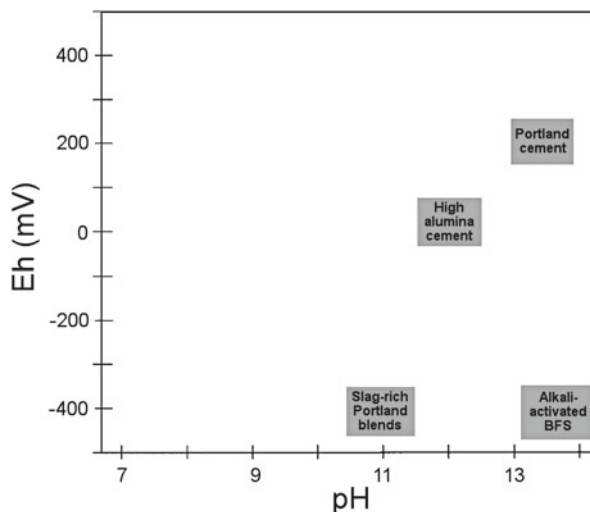
Sulfate activation has also been shown to provide promising results in production of binders using a small quantity of lime or Portland cement clinker, with a larger quantity of an aluminosilicate source such as calcined clay or a natural pozzolan [66, 110–113]; such materials will be addressed in more detail in Chap. 5 in the discussion of blended binder systems.

3.4 Pore Solution Chemistry

In any binder to be used in the production of reinforced concrete, it is important that the pore solution pH is maintained at a sufficiently high level to passivate the embedded steel reinforcing bars. Given the initially high pH of almost all alkali-activated binder systems, it would superficially appear that this should be a fairly straightforward consideration. However, the absence of a pH-buffering phase such as portlandite in the hardened binder, as is the case for Portland cement, means that the retention of high alkalinity will depend on the ability of the material to prevent either ingress of acidic external components, or leaching of pore solution alkalis [114]. This means that the pore structure of an alkali-activated binder is the key factor determining its durability – and so this point will be revisited in detail in Chaps. 8, 9 and 10 of this report in the context of durability testing.

The pore solution chemistry of alkali-activated BFS binders is dominated by alkali hydroxides, with pH generally between 13 and 14, and the concentration of dissolved silicates falling to <10 mM levels in a mature binder [88, 114–117]. Puertas et al. [117] extracted pore solution under high pressure during the first 7 days of reaction, and observed a decrease in both dissolved Na^+ and SiO_2 concentrations as curing progressed. Lloyd et al. [114] studied samples with a higher activator dose after 28 days of curing, and found a lower SiO_2 concentration than Puertas et al. [117]. The Al concentration observed in [114] was <1 mM, compared to ~5 mM in most of the samples in [117], which suggests that the use of a higher activator concentration enhances the incorporation of Al into the gel structure. Similar trends were also observed for pure C-S-H samples by Faucon et al. [118]. The Al concentrations have also been observed to decrease over time in the pore solutions of alkali silicate-activated and NaOH-activated BFS [88, 116]; Gruskovnjak et al. [88] observed concentrations as high as 7 mM at 1 day, but decreasing to 3 mM after 180 days.

Fig. 3.11 Pore solution pH-Eh conditions of various types of binders for use in cement (Adapted from [119])



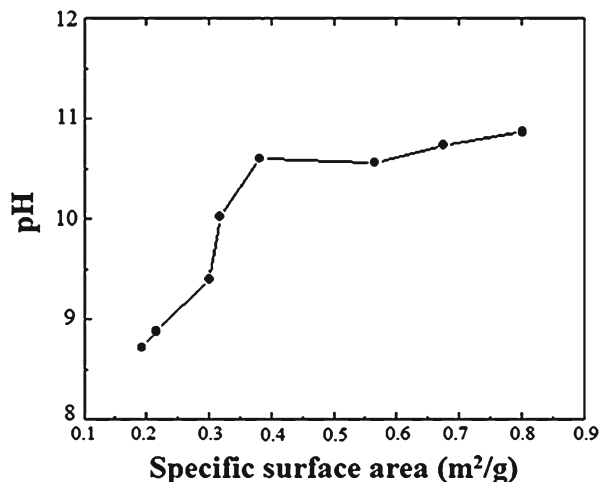
The other important aspect of the pore solution chemistry of BFS-based binders relates to the redox environment within the material, where the sulfide content of BFS leads to the generation of strongly reducing conditions, with Eh (redox potential) values as negative as -400 mV (Fig. 3.11) [119]. The balance between sulfide and sulfate depends on the degree of weathering of the BFS and also the extent of oxidation which takes place while the material is in service. Gruskovnjak et al. [88] found that the concentration of sulfate in Na silicate-activated BFS cured under sealed conditions was roughly constant at ~ 40 mM over the first 180 days, while the sulfide concentration reached almost a factor of 10 higher (350 mM) after 7 days, demonstrating a strongly reducing environment in the pore solution. X-ray absorption spectroscopy [120] also shows that the presence of a more alkaline environment stabilises the sulfur in reduced form in BFS-alkali systems. This is likely to be important in defining the relationship between the pore solution and any embedded steel reinforcing elements in an AAM, but is undoubtedly an area requiring further detailed analysis.

3.5 Effects of BFS Characteristics

3.5.1 Fineness

It has been identified in various studies, and is logical from consideration of particle-fluid reaction processes [121], that the fineness of the BFS is a key factor influencing the reaction, setting, strength development and final microstructure of AAMs. Wang et al. [53] and Puertas [18] have indicated that the optimal fineness range of BFS for the production of AAM is between 400 and 550 m^2/kg . Brough

Fig. 3.12 Variation of pH in supernatant solution (100 g of mechanically treated BFS immersed in glass tubes with water) above water-hydrated finely ground BFS, after 14 days of reaction, as a function of the specific surface area (Adapted from [125])



and Atkinson [25] identified that using BFS with an increased fineness promotes the development of higher compressive strengths, which is consistent with the increased reactivity of the material at smaller particle size.

However, the setting rate can be strongly affected by the fineness of the BFS. Talling and Brandstetr [122] reported that the use of finely ground BFS beyond 450 m²/kg gave setting times between 1 and 3 min, meaning that the material was impossible to pour. Conversely, Collins and Sanjayan [123] identified that the partial (10 %) replacement of regular BFS by ultra-fine BFS (1,500 m²/kg) gave only a slight reduction in the workability of AAS concretes, but a significantly increased mechanical strength development, so that 1-day cured concretes exhibited compressive strengths as high as 20 MPa. Lim et al. [124] used 1,500 m²/kg “nanoslag” as the sole silicate precursor for NaOH-activated concretes, obtaining similar setting rate, strength development and semi-adiabatic temperature profiles compared to a control Portland cement concrete, and calculated a significantly reduced CO₂ emissions profile for the BFS-based material, although this was also significantly more expensive due to the energy cost of ultra-fine grinding of the BFS.

Kumar et al. [125] report that the reactivity of BFS can be improved through mechanical activation using an attrition mill, so that mechanically treated BFS can completely react with water after a few days, in the absence of an alkaline activator, compared to the measured 22 % extent of reaction in BFS of a coarser slag after 20 years of hydration in water as reported by Taylor et al. [41]. The main reaction products formed upon hydration of this very finely ground BFS in water were calcium silicate hydrate type products, and even though the starting BFS contained 8.8 wt.% MgO, formation of hydrotalcite was not observed. The porosity of the binding phase forming in the hydrated BFS was strongly dependent on the specific surface area of the material, and the zeta potential achieved after the milling process. The BFS hydration did in itself generate a significant increase in pH over time, Fig. 3.12, favouring the dissolution of the material and the consequent formation of reaction products.

Shi and Day [55] assessed the applicability of the standard testing method ASTM C 1073 [126] (BFS + NaOH, cured for 24 h at 50 °C) as a quality control method to determine the feasibility of using different types of BFS as precursors for the production of alkali-activated binders. Considering that this method is restricted to the use of solutions of NaOH, it is not universally suitable for the evaluation of a BFS as AAM precursor, as improved performance can be obtained when the material is tailored using other alkaline activators. Therefore, it is suggested that to improve the applicability of this quality control test, the alkali should be selected based on an activator-optimisation testing rather than specifying NaOH as the sole activator.

3.5.2 BFS Chemistry

Although it is possible to activate slags from different metallurgical processes (and some results based on the use of such slags will be discussed in the following sections), ground granulated blast furnace slag (BFS) is the most widely used for the production of alkali-activated materials [18, 46, 53, 122], because its chemical composition and highly amorphous nature favour the formation of reaction products that develop high mechanical strengths within a moderate curing duration [50], and with a relatively low water demand. The chemical composition of BFS can generally be described in the quaternary system CaO-MgO-Al₂O₃-SiO₂, with additional components including manganese, sulfur and titanium, depending on the chemical composition of the iron ore used. Slow-cooled BFS tends to be crystalline and unreactive, but many rapidly-cooled (granulated or pelletised) slags can also contain crystalline inclusions. The nature and content of these inclusions in the BFS are influenced by the relationship between the slag composition (and thus liquidus temperature) and processing conditions. This is particularly influenced by the CaO and MgO contents in the systems at moderate Al₂O₃ contents (10–15 % Al₂O₃) [127].

The hydraulic activity of BFS is measured through parameters such as the basicity coefficient $(\text{CaO} + \text{MgO}/\text{SiO}_2 + \text{Al}_2\text{O}_3)$ and the quality coefficient $(\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3)/(\text{SiO}_2 + \text{TiO}_2)$ [53, 122], in addition to a variety of alternative descriptors which have been developed and applied under specific circumstances [6, 46]. However, there is not always a good correlation between the mechanical strength of AAMs and these parameters. In general, glassy BFS with CaO/SiO₂ ratios between 0.50 and 2.0, and Al₂O₃/SiO₂ ratios between 0.1 and 0.6, will be considered suitable for alkali-activation [122]. The chemical and mineralogical differences among BFS materials from different sources lead to some of the main limitations facing the complete understanding of the mechanism of development of AAM binder structure.

Douglas et al. [109] reported the 28-day compressive strengths of silicate-activated BFS with different contents of MgO (9, 12 and 18 wt.%), where the BFS containing 18 wt.% MgO reported a compressive strength three times higher than was obtained by activating BFS with 9 wt% MgO. This is consistent with the results of a more recent study conducted by Ben Haha et al. [32], activating BFS with MgO contents

between 8 and 13 wt.%, where it was identified that an increased content of MgO led to faster reaction and higher compressive strengths as a consequence of the formation of higher amounts of hydrotalcite type products. This reduced the degree of Al incorporation in the C-S-H type gels formed when sodium silicate was used as the activator. However, this was not the case for NaOH-activated BFS binders, where only slight variations in strength were observed as a function of MgO content.

In blast furnace slags with different Al_2O_3 contents (between 7 and 17 wt.%), it has been observed [47] that increased Al_2O_3 content in the BFS reduces the extent of reaction at early times of curing, and consequently decreases the compressive strength of activated BFS binders. This was associated with a reduction in the Mg/Al ratio in the hydrotalcite formed in activated BFS binders with higher contents of Al_2O_3 , along with an increased Al incorporation in the C-(A)-S-H type product, leading to the formation of strätlingite. However, after 28 days of curing there were not significant structural or mechanical differences between activated BFS binders based on slags with different Al_2O_3 contents [47].

3.6 Alkalis in C-S-H (Including Alkali-Activated Portland Cements)

Alkalis play a crucial role in the properties and structure of the products formed during the alkali activation of BFS and aluminosilicate precursors [46]. The effect of alkaline oxides (particularly Na_2O) on the composition and microstructure of calcium silicate hydrate gels has been studied by many authors in both synthetic gels and in 'real' binding systems. This section will provide a very brief discussion of the results available in this area; an excellent review covering the literature up to approximately 1990 is available in [128]. In the 1940s, Kalousek [129] identified that the maximum content of Na that can be incorporated into C-S-H type gels is an $\text{Na}_2\text{O}/\text{SiO}_2$ ratio of 0.25, so that a structure of the type $\text{Na}_2\text{O}\cdot\text{CaO}\cdot\text{SiO}_2\cdot x\text{H}_2\text{O}$ (N-C-S-H) was formed. The presence of small amounts of Na (even on the order of 0.6 wt% Na_2O by total gel mass) has been observed to affect the stability of silicates and hydrosilicates, as well as their hydration rate [130].

There is a general agreement that the extent of alkali incorporation into C-S-H gel increases with lower Ca/Si ratios in the gel. Taylor [131] reported Na/Ca ratios around 0.01 in hydrated Portland cement pastes whose Ca/Si ratios ranged between 1.3 and 2.3, while Hong and Glasser [132] identified a negative linear relationship between Na/Si and Ca/Si ratios in C-S-H gels within the range $0.85 < \text{Ca}/\text{Si} < 1.8$.

The mechanism of incorporation of alkalis into C-S-H type gels, as described by Stade [133], is governed by three main steps:

- neutralisation of the Si-OH acid groups (favoured in C-S-H type gels with low Ca/Si ratios),
- exchange of M^+ and Ca^+ cations (particularly in gels with high Ca/Si ratios),
- final dissociation of the Si-O-Si bonds due to the presence of alkalis (dependent on the surface area of the gel).

As a consequence of the complexity of the system, it is likely that multiple mechanisms at any time may be operating to influence uptake of alkali ions.

Atkins et al. [134] determined by ^{29}Si MAS NMR spectroscopy that the Q^2/Q^1 ratio in a C-S-H type gel declines at increased contents of Na in the systems, indicating that the presence of alkalis reduces the chain length in the C-S-H gels formed, consistent with the third step as noted above. Chen and Brouwers [135] evaluated a large set of literature data for alkali binding capacity in C-S-H, finding that the binding of Na^+ is linearly proportional to the alkali concentrations in the solution. Data for K^+ were found to be much more scattered, and were proposed to be approximated by a Freundlich-type (power-law) isotherm, although with a low correlation coefficient [135].

The incorporation of Al into the C-S-H type gel, leading to the formation of C-A-S-H type products, has been observed to enhance the uptake of alkalis in the system compared with binders solely based on pure C-S-H type products, consistent with the reduced $\text{Ca}/(\text{Si} + \text{Al})$ ratio in C-A-S-H gels [136]. Alkali binding occurs through a valence compensation mechanism, in which the charge imbalance created by substitution of trivalent tetrahedral Al into tetrahedral Si sites is balanced by the inclusion of alkalis. The possibility of enhanced silanol binding capacity (as described for C-S-H type products), due to the enhanced linkages to a skeleton modified by inclusion of tetrahedral Al, was also proposed [136]. Skibsted and Andersen [137] identified that the amount of Al incorporated in the C-S-H is also partly associated with the availability of alkali ions in the system, as the alkalis act as a charge balancer (adsorbed/bonded) in the interlayer of the C-S-H phase in the vicinity of bridging AlO_4 sites substituted into the silicate chains.

Recent studies conducted using synthetic gel systems [138, 139] reveal that high concentrations of alkalis cause the deterioration of fresh C-S-H gels at short reaction times (72 h) due to the formation of depolymerised C-N-S-H type gels. The inclusion of alkalis is also influenced by the degree of crystallinity of the gel formed; in highly crystalline gels the number of possible alkali sites is limited, while in disordered systems, the incorporation of alkalis will instead be mainly constrained by electroneutrality.

The temperature also has an important effect on alkali incorporation in C-S-H type gel structure. For a given Ca/Si ratio, gels forming at high temperatures are more crystalline and have less surface area; therefore, they can capture less alkalis than gels forming at lower temperatures. In gels synthesised under hydrothermal conditions, the formation of pectolite has been observed [140, 141]. This phase is a stable calcium-sodium silicate that may co-exist with other calcium silicates formed in Portland cement hydration, such as tobermorite and (at higher temperature) xonotlite. A comparative study assessing the effects of different alkali cations reported that sodium was bonded significantly more strongly than potassium in hydrated cement pastes [131]; it is noted that this is the reverse of the effects noted in alkali aluminosilicate 'geopolymer' gels, where K is preferentially bound over Na [142].

Thus, it is evident that in Ca-rich AAMs, the alkalis can be present in several forms [50]:

1. incorporated into C-S-H;
2. physically adsorbed on the surface of hydration products, and
3. free in the pore solution.

In these systems, it is expected that the incorporation of alkalis in the C-S-H type gel begins to occur at the initial stage of reaction, when the effective Ca/Si ratios in the fluid phase available for reaction are very low, and the Na/Ca ratio in the reacting regions is therefore very high. However, this mechanism will be dependent on the type of activator used, considering that both the Ca/Si ratios and the crystallinity of the gels will vary with time and system composition. Although it is likely that NaOH-activated BFS will form a C-S-H type gel with higher Ca/Si ratios than when using silicate-based activators [37], it is expected that the uptake of alkalis in those gels will still be much higher than in the C-S-H gels formed in conventional Portland cement systems.

3.7 Non-blast Furnace Slag Precursors

3.7.1 Steel Slags

In addition to BFS, which is produced during extraction of iron from its ores, there are also various types of slags produced in the process of converting this iron to steel. With compositions depending on the exact process route, and also the degree to which recycled materials are incorporated into the steelmaking process, these slags are much more variable in chemical composition, which changes from plant to plant, as well as from batch to batch even within the same plant. The main types of steel slag include electric arc furnace (EAF) slag, basic oxygen furnace (BOF) slag, ladle slags and converter slags. The slags generated from the production of alloys or stainless steel are quite different in composition, presenting lower FeO and higher Cr contents when compared with most other slags. This the main reason why these slags are classified as hazardous wastes in some jurisdictions.

The main mineral phases in steel slags can include olivine, merwinite, C_3S , $\beta-C_2S$, $\gamma-C_2S$, C_4AF , C_2F , the “RO” phase (a CaO-FeO-MnO-MgO solid solution), free CaO and free MgO [143, 144]. A particularly interesting phase in these slags is $\gamma-C_2S$, which is obtained from $\beta-C_2S$ during cooling. The conversion of $\beta-C_2S$ to $\gamma-C_2S$ is accompanied by an increase in volume of nearly 10 % and results in the shattering of the crystals into dust, making the material effectively self-pulverising and thus potentially providing significant cost savings in terms of grinding processes. However, $\gamma-C_2S$ is not hydraulic, and so does not contribute significantly to the reaction processes leading to formation of a cement-like binder. The presence of

C_3S , C_2S , C_4AF and C_2F does provide some weak cementitious properties to these slags, increasing with the basicity of the slag [46].

Cements based on blends of steel and iron slag, mainly composed of steel furnace slag, BFS, cement clinker and gypsum, with or without an added alkaline activator, have been marketed in China for more than 20 years [145]. Some applications of these alkali-activated materials are described in Chap. 11. The strength of steel slag-based cement depends on the basicity of the steel slag, and these materials have been approved for general construction applications under a variety of prescriptive national standards in force in China [46].

Steel slag itself can display very good binding properties under the action of a proper alkaline activator; several studies have confirmed that the use of an alkaline activator can increase the early strength and other properties of a steel slag cement [146–148]. Usually, some other materials such as BFS or fly ash are used together with steel slag in order to eliminate problems related to dimensional stability. Alkali-activated steel slag-BFS cement can show very high strength and corrosion resistance [46, 146, 149–152], and a combination of BFS and high-basic steel slags has been found to give a good balance of dimensional stability and controlled heat evolution, which can both be influenced in undesirable ways by some of the crystalline calcium-bearing phases present in steel slag [153]. Strengths as high as 120 MPa with steam curing, or 62 MPa after 3 days and 96 MPa after 28 days under standard ambient conditions, have been measured for such binders [153]. Alkali-activated blends of metakaolin and steel slag have also shown good properties as a material for bonding mortar sandwich specimens [144], and AAMs based on ladle slag and metakaolin have also shown promising strength development, microstructural properties and high temperature resistance [154, 155].

3.7.2 Phosphorus Slag

The production of elemental phosphorus from phosphate ores also results in the generation of a calcium silicate-rich slag, referred to as phosphorus slag, which is generated worldwide in quantities exceeding five million tonnes p.a. In North America, much of the phosphorus slag which has been produced in the past decades (and some of which has been reused as an aggregate in construction) contains high levels of naturally occurring radioactive material, and so emits radiation at a level higher than the regulatory limits, which places restrictions on its re-use. However, phosphorus slags in China and Russia have a lower radiation level and are widely used as a cement admixture, which has led to the development of standards for the use of granulated phosphorus slag as supplementary cementitious material and for the production of Portland-granulated phosphorus slag cement [14].

Shi [156, 157] started the earliest academic study on the preparation of alkali-activated phosphorus slag binders in the 1980s. It was reported that the increase of modulus or dosage of a sodium silicate activator solution led to the shortening of the setting time, and that the soluble phosphorus contained in the slag did not have any significant influence on the setting of the binder. The optimal solution modulus of

the sodium silicate activator, leading to higher strength development with acceptable workability, is in the range 1.2–1.5. Using these activation conditions, it was possible to achieve 28-day compressive strengths of 120 MPa in mortar samples [156, 157], although the sensitivity to temperature in the curing process was high. In activated-phosphorous slag systems, the use of NaOH as activator promotes the development of higher early strengths, while silicate-based activators yield higher strength development at advanced times of curing [14]. Fang et al. [158] also developed AAM binders based on phosphorus slag-fly ash blends using silicate activators, reaching 28-day compressive strength in mortars up to 98 MPa, and higher chemical and freeze-thaw resistance when compared with Portland cement, although at the cost of higher drying shrinkage.

3.7.3 *Other Metallurgical Slags*

There are numerous other pyrometallurgical processes operated worldwide producing non-ferrous metals (particularly Pb, Zn, Ni and Cu) which result in the production of various volumes of silicate-based slags. Around half of the total non-ferrous slag production is nickel slag, and around a third is copper slag [46]. These slags are generally rich in SiO₂ and Fe oxides, usually with around 5–15 % each of Al₂O₃ and CaO, plus minor sulfur, MgO, Cr₂O₃ and other oxides depending on the details of the ore and the process [46, 159, 160]. These slags are also generally mostly vitreous, with minor crystalline components sometimes enriched in Fe, and tend to display pozzolanic character. This means that they are potentially amenable, at least to some extent, to use in alkali activation. Various studies of the alkaline activation of non-ferrous slags have been published, but the focus of much of this work has been on parametric mix design using a particular slag available in a specific region. Such work has been published for, among others:

- Copper slag [14, 161]
- Nickel slag [162]
- Magnesia-iron slags [163]
- Phosphatic slag and ferrochrome alloy slag [164]
- Titaniferous slag – [165]
- Cu-Ni slag [166]

An extensive research program led by Komnitsas has developed a range of workable and high-strength AAM formulations based on low-Ca ferronickel slag [167–170], which are described in more detail in Sect. 4.6 of this report. Pontikes et al. [171] have also recently published a systematic study of (Fe,Al)-rich synthetic slags from a pilot scale plasma reactor, with a view towards developing the science base required for utilisation of these materials as precursors for AAMs. The key finding from that study was that for a given slag composition, water-quenching provided a product which was much more reactive in an alkaline-activation context when compared with air-cooling or combined air-water cooling in layers [171].

It has also been proposed that the hydraulic activity of the granulated non-ferrous slags can be evaluated using a quality coefficient (Eq. 3.1) which considers the distribution of oxidation states of the iron which is usually present in these slags [46], and where a higher K value corresponds to a greater amenability to alkaline activation:

$$K = \frac{CaO + MgO + Al_2O_3 + Fe_2O_3 + \frac{1}{2}FeO}{SiO_2 + \frac{1}{2}FeO} \quad (3.1)$$

This concept has been utilised in the development of a classification system for non-ferrous slags according to their likely reactivity, and thus in the development of a set of prescriptive standards for AAM concretes based on these binders, in Ukraine and Russia [46].

3.7.4 Bottom Ash and Municipal Solid Waste Incineration Ash

The bottom ashes obtained from coal-fired boilers are also able to be used in alkaline activation; these tend to be much coarser than fly ash, and so require grinding before use in alkaline activation [172, 173]. Heavy metal accumulation in bottom ashes has also been identified as being potentially problematic in terms of the use of this material in construction applications [172]. Bottom ash from fluidised bed coal combustion is similar in chemistry and mineralogical nature, and also requires grinding from an initially quite large particle size (up to several millimetres) before use in alkaline activation. Its thermal history differs from most coal ashes in that the combustion temperature is only around 800–900 °C, rather than >1,300 °C in a standard boiler, meaning that mullite formation is less prevalent. However, once milled, its high Si and Al content mean that it can perform quite acceptably as a source material for AAMs [174–176], although its potentially high heavy metals content does need to be taken into consideration in construction applications [175].

Municipal solid waste incineration (MSWI) ash is slightly pozzolanic and able to react during alkaline activation, but also requires careful consideration of its high content of both toxic metals and chloride. Its use in AAMs is therefore more commonly a stabilisation/solidification process for waste treatment and prevention of leaching, rather than use as a true aluminosilicate AAM precursor [177–179].

3.8 Concluding Remarks

This chapter has summarised the basic chemistry of Ca-rich alkali-activated binder systems, in the context of activator selection, precursor chemistry, and availability of a diverse range of Ca-aluminosilicate precursors beyond the most widely applied

BFS-based binder systems. This is an area with much scope for further development and optimisation, as the broadening of the range of natural and industrial by-product materials which are utilised in AAM production will certainly require the identification and optimisation of the most desirable activator chemistry for each precursor (or blend of precursors). Much of the work which has been published in this area to date has been focused on a single precursor per study, with limited scope for broader applicability of the results to other precursor sources. Even the effect of variability in BFS chemistry between sources is not yet particularly well understood, providing strong impetus for research in this area. The calcium-rich AAM systems are the most mature commercially-applied AAM material systems in most parts of the world, as the role of calcium in enhancing the durability-related properties of AAM concretes is beginning to be well understood. However, continuing interaction between commercial development and advanced research appears essential in enabling these materials to reach true technological maturity as required for national and international standardisation.

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Chapter 4

Binder Chemistry – Low-Calcium Alkali-Activated Materials

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4.1 Low-Calcium Alkali-Activated Binders

4.1.1 *Development and Basic Chemistry of Low-Calcium Binders*

Early developments in the developments of low-calcium (including calcium-free) alkali-activated binders were led by the work of Davidovits in France, as noted in Chap. 2. These materials were initially envisaged as a fire-resistant replacement for organic polymeric materials, with identification of potential applications as a possible binder for concrete production following relatively soon afterwards [1]. However, developments in the area of concrete production soon led back to more calcium-rich systems, including the hybrid Pyrament binders, leaving work based on the use of low-calcium systems predominantly aimed at high-temperature applications and other scenarios where the ceramic-like nature of clay-derived alkali-activated pastes was beneficial. Early work in this area was conducted with an almost solely commercial focus, meaning that little scientific information was made

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available with the exception of a conference proceedings volume [2], several scattered publications in other conferences, and an initial journal publication [3]. Academic research into the alkaline activation of metakaolin to form a binder material led to initial publications in the early 1990s [4, 5], and the first description of the formation of a strong and durable binder by alkaline activation of fly ash was published by Wastiels et al. [6–8]. With ongoing developments in fly ash activation, which offers more favourable rheology than is observed in clay-based binders, interest in low-calcium AAM concrete production was reignited, and work since that time in industry and academia has led to the development of a number of different approaches to this problem. A review of the binder chemistry of low-calcium AAM binder systems published in 2007 [9] has since received more than 350 citations in the scientific literature, indicating the high current level of interest in understanding and utilisation of these types of gels.

The fundamental binder structure in low-calcium alkali-activated systems is known to be a highly disordered, highly cross-linked aluminosilicate gel. Both Si and Al are present in tetrahedral coordination, with the charges associated with tetrahedral Al sites balanced through the association of alkali cations with the gel framework. Similarities between this gel structure and the structure of zeolites have been noted in numerous publications, including through the early work of Glukhovskiy and colleagues [10], who used zeolitic structures to draw an analogy between alkali-activated binders and ancient Roman concretes, and of Davidovits [3], who sketched molecular structure fragments based on the zeolitic or similar structures (analcime, sodalite, phillipsite, leucite, kalsilite). Some time later, it was proposed in more detail [11] that the similarity between hydrothermal zeolite synthesis and the synthesis of alkali aluminosilicate binders leads to the generation of nanosized zeolite-like structural units throughout the AAM gel, in addition to the crystalline zeolites which are widely observed embedded within the disordered gel, particularly at higher curing temperatures [12]. Such structural units were later identified directly by the use of X-ray and neutron pair distribution function analysis [13–16], where the local structures of metakaolin-derived aluminosilicate binders were shown to be very similar, on length scales of up to 5–8 Å, to the local structures of the crystalline structures formed by heating of the same gels beyond 1,000 °C.

This information then provides a useful structural model by which the chemistry (and other properties, such as thermodynamics) of these materials can be understood, approximately analogous to the use of tobermorite and jennite as model structures for the understanding of the calcium silicate hydrate gels formed by Portland cement hydration [17]. The analogies are, at this point in time, much less developed for the case of these ‘pseudo-zeolitic’ binders than is the case for the much more widely-studied tobermorite-like C-S-H structures, including the Al-substituted gels generated through the alkaline activation of BFS [18], as discussed in Chap. 3 of this Report.

4.1.2 *‘Geopolymers’ as a Subclass of Alkali-Activated Materials*

The term ‘geopolymer’ was first applied to the products of alkaline activation of calcined clays (particularly metakaolin) by Davidovits in the 1970s [1]. This term, along with the associated ‘poly-sialate’ nomenclature [19], gained some degree of acceptance among the scientific community as a result of the extensive and successful advertising work conducted through the Geopolymer Institute over a period of more than 30 years. The term ‘geopolymer’, as noted in Chap. 1, has been applied to a wide range of alkali-activated binders, but most commonly to low-calcium or calcium-free systems derived from fly ashes or clays. There is ongoing debate whether the term ‘geopolymer’ can (or should) be applied to Ca-rich systems such as alkali-activated BFS; the resolution to this question appears to be primarily based in marketing (as opposed to scientific) fields, and will not be the subject of further discussion here.

The applications for low-Ca AAM technology, which will be outlined in detail in Chaps. 12 and 13, fall into two distinct fields – these materials can be used as a cement-like binder, or as a low-cost alternative to fired ceramics [20]. While mix designs and precursor blends can be tailored to one or the other of these fields of application, it is important to make a clear distinction between the specific formulations that are best suited to each application. For example, it has been stated that it is possible to form ‘geopolymer’ products across the compositional range from $0.5 < \text{Si}/\text{Al} < 300$ [21]. Some of the compounds formed at the extremes of this compositional range may indeed have interesting properties in given applications, and in particular where resistance to aggressive environments is not important. However, the products formed at the Si-poor ($\text{Si}/\text{Al} < 1$) or Si-rich ($\text{Si}/\text{Al} > 5$) ends of this compositional range will not be suited to general construction applications due to their low strength, low thermal stability, generally low chemical resistance, and tendency to dissolve in water. So, while such materials may be useful in applications where these characteristics are not problematic (or are even desirable), they fall in general beyond the scope of this report. Such materials may be described as ‘geopolymers’, but the question of whether they should also be classified as ‘alkali-activated binders’ in the context of construction materials design is a different matter. Similar comments may also apply to other systems, where for example the very high water demand of some metakaolins may lead to an excessively high porosity in binders where this is used as the sole raw material. Care must be taken when defining and analysing AAMs in a laboratory environment, as negative durability results obtained from poorly-formulated and/or poorly-characterised systems will have a negative impact on perceptions of alkali-activated materials as a viable alternative to traditional cement technologies.

4.2 Binder Structure – Characterisation and Influence of the Activator

4.2.1 Binder Structure – Hydroxide Activation

Alkali hydroxides are usually combined with an aluminosilicate source in the form of an aqueous solution, due largely to the high degree of heat release associated with the dissolution of solid alkali hydroxides into water [22]; this would be problematic if it occurred within a developing binder due to the generation of thermal stresses within the evolving gel. It is also possible to calcine solid aluminosilicates together with alkali hydroxides to form a precursor for ‘just add water’ binder synthesis [23, 24], but this process has not yet been developed on such a large scale as has been achieved with the two-part (activating solution plus solid precursor) systems which are the main focus of the discussion here. A form of this technology was initially developed almost 200 years ago, as the ‘aqua-fortis cement’ discussed by Vicat [25] and others [26], where a source of alkalis (KNO_3 or K_2CO_3) was calcined with clays to generate a pozzolanic material which was then mixed with lime to form a successful cement. However, developments since that time have been relatively limited in scope and scale.

The binder structures formed by alkali-hydroxide activation of low-calcium precursors (fly ashes, metakaolins and other materials) are known to be dominated by an alkali aluminosilicate gel, with tetrahedral aluminium and silicon atoms forming a highly cross-linked structure and alkali metal cations charge-balancing the tetrahedral Al(III) sites [27, 28]. These alkali cations are directly associated with the (negatively charged) oxygen ions of the framework, rather than being located immediately adjacent to the (positively charged) tetrahedral species, and are to some extent exchangeable in ion exchange processes, although the extent to which this is possible will depend on the nature of the alkali cations and the permeability (both macroscopic and in terms of ring sizes in the gel) of the binder [29]. The gel binder structure is known [11] to be closely related to the precursor gels observed as intermediates during the hydrothermal synthesis of zeolites from the same aluminosilicate solids [30–32]. Crystalline zeolites and related materials are also developed over time, with higher temperatures and higher water contents favouring higher crystallinity. Thermal or steam curing is usually applied to alkali hydroxide-activated fly ash binders, as strength development is slow at room temperature [33, 34].

The discussion of crystalline phase formation here is based mainly around the use of Na as the alkali source; KOH-activated aluminosilicate binders have been much less extensively studied, and tend to show a lower tendency towards crystallisation than their Na-containing counterparts [35]. The crystallites formed in NaOH-activated metakaolins (with overall Si/Al ratios close to 1.0) are predominantly feldspathoids in the hydrosodalite-hydroxysodalite family, although some zeolitic phases (usually zeolite Na-A and/or low-silica faujasites) are observed as either transient or later-developing reaction products [27, 36, 37], as is the case when

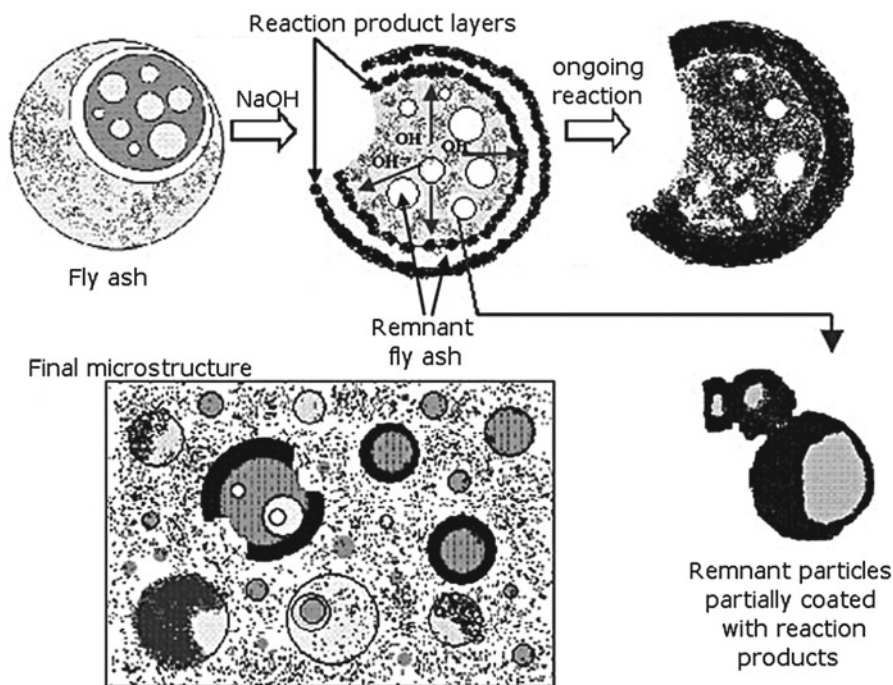


Fig. 4.1 Microstructural description of the formation of an alkali-activated binder from fly ash (Adapted from Fernández-Jiménez et al. [49])

metakaolin is reacted hydrothermally with the same solutions at higher liquid/solid ratios [38–40]. NaOH-activated fly ashes generally have a higher overall Si/Al ratio in the binder gel, and tend to form chabazite-Na (also known as herschelite) and/or faujasite (although this is preferred at higher Si content) as well as the more Al-rich sodalite-group and cancrinite-group phases [41–43].

The characterisation of hydroxide-activated aluminosilicate binders by nuclear magnetic resonance has shown the predominance of $Q^4(nAl)$ sites, with n distributed between 1 and 4 but usually at the higher end of this range for hydroxide-activated systems [34, 44, 45]. The concentration of bound hydroxyl groups (i.e. Q^3 silicate sites) has been observed to be low in well-cured binders with hydroxide or low/moderate-modulus silicate activators [46]; a higher silicate concentration is required before these sites are notable in well-cured materials, although they are certainly present at early age at all Si/Al ratios. In mixed-alkali systems, larger cations are preferentially bound by the gel, with the Na/K ratio of the pore solution in a 1:1 blended binder exceeding the Na/K ratio of the gel by a significant degree [47]. NaOH also favours a higher extent of reaction of a fly ash precursor than does KOH [48].

A conceptual and microstructural model for the alkali hydroxide activation of fly ash was presented by Fernández-Jiménez et al. [49], and is summarised in Fig. 4.1. The process of attack on the glassy shell of a partially hollow spherical fly ash

particle by the hydroxide activator leads to the formation of reaction products both outside and inside the particle, leading to a final microstructure which contains embedded fly ash particles with varying degrees of reaction. Other workers have since [43, 50–52] expanded on the conceptual aspects of that reaction model, in particular discussing the role of gel nucleation on (or away from) the particle surfaces in determining the final extent of reaction which is achieved; this is able to be manipulated by the addition of soluble silica to the activator [51, 52], or by seeding with high surface-area nanoparticles [53].

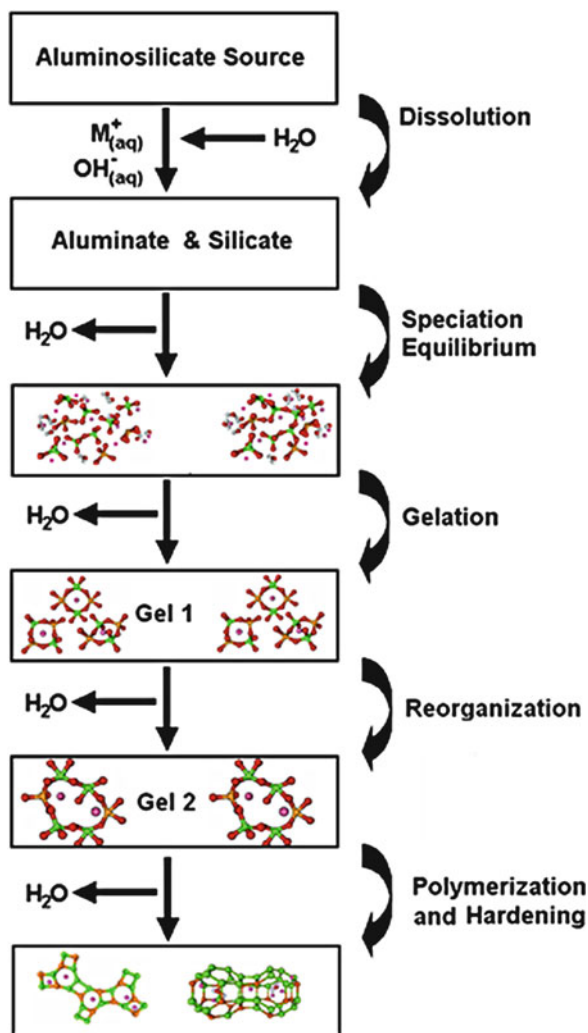
Given the highly heterogeneous nature of fly ash-containing alkali-activated binders, and the difficulties associated with accurate NMR characterisation of iron-containing materials, the development of a fuller understanding of the binder structure and chemistry of alkali hydroxide-activated fly ash systems has benefited greatly from the application of infrared (FTIR) spectroscopy. Lee and van Deventer [54] studied the interactions between hydroxide or low-modulus silicate solutions and fly ash particles, providing useful insight into the structural evolution of the gel products forming on the surfaces of fly ash particles. Fernández-Jiménez and Palomo [55] used FTIR to characterise NaOH-activated binder systems, and identified two stages of gel evolution: ‘Gel 1’, which is identified as being relatively richer in Si-O-Al bonding, and ‘Gel 2’, which forms as the extent of Si crosslinking within the gel increases at longer reaction times (Fig. 4.2). This identification was supported by later work which combined in situ (ATR-FTIR) and ex situ analysis to demonstrate the chemical mechanisms involved in the evolution from the initial to final gel structures [43, 50], as well as synchrotron-based infrared microscopy [56] combined with in-situ ATR-FTIR analysis to provide spatially-resolved information. Energy-dispersive X-ray diffraction [57] and neutron pair distribution function analysis [16] of metakaolin-based samples have also provided nanostructural information regarding the nature of the Gel 1/Gel 2 transition, although in situ analysis of this process is obviously hindered by the longer timescales (days/weeks) on which it takes place.

There are also some potentially important effects induced by the presence of small amounts of calcium in ‘low-Ca’ precursors such as fly ash. In the presence of hydroxide activators, the initial rapid release of Ca into the solution environment can lead to supersaturation with respect to $\text{Ca}(\text{OH})_2$, and thus precipitation of nanosized particulates of this phase [58]. This is not observed in systems with silicate activators, as the higher levels of Si present initially in the solution will lead to silicate complexation of the calcium rather than reaching supersaturation with respect to a hydroxide phase. The presence of even a relatively small amount of calcium is also known to retard crystallisation of zeolites [59], which is likely to contribute to the known lower tendency of fly ash-based binders to crystallise, compared to their metakaolin-based counterparts.

4.2.2 Binder Structure – Silicate Activation

The binder gel structure formed through the application of a silicate activator to a low-Ca aluminosilicate raw material is seen (through the application of NMR,

Fig. 4.2 Conceptual model for the synthesis of an alkali-activated binder by hydroxide activation of an aluminosilicate source, including multi-step gel evolution reactions (From Duxson et al. [9], copyright Springer)



FTIR, and other spectroscopic techniques) to be rather similar to the structures formed through hydroxide activation of the same precursors. The main differences observed at an atomic length scale are in the Si/Al ratios of the respective gel products, and also in the generally lower tendency towards zeolite/feldspathoid crystallisation at higher Si content. Microstructurally, silicate-activated binder systems tend to be more homogeneous on a length scale of microns or more [49, 60], which is believed to be related to the tendency of the lower-silica gels to densify into distinct particulates over time, rather than remaining as a percolating gel network [61]. Silicate activation of fly ash or metakaolin tends to give more robust chemistry (i.e. the systems develop acceptable strength across a wider range of mix designs and curing conditions than for hydroxide activation), and so these have been the

systems which have attracted the most attention in the academic literature to date. The earliest publications on alkaline activation of metakaolins [5, 19, 62, 63] and fly ashes [6] made use of silicate activators, and much work since that time has been focused on analysing and understanding these materials.

Silicate activation of low-calcium binders is usually achieved most effectively by the addition of dissolved alkali silicates to the solid precursor; solid silicate sources have been trialled in fly ash-based binders [64, 65], but tend to give slow strength development. There are various ways of manipulating the composition of a sodium silicate solution, and each has a somewhat different effect on the binder structure. Moving from a hydroxide to a silicate solution tends to lead to a higher-strength, lower-porosity binder [42, 60, 66–69], up to a modulus (molar ratio $\text{SiO}_2/\text{M}_2\text{O}$, where M is an alkali cation) of between 1 and 2, where the exact value of this optimum depends on the nature of the aluminosilicate precursor. An optimum in strength also seems to be observed at a ratio Na/Al in the binder (i.e., not including Al in unreacted precursor) of around 1, although this depends to some extent on the Si/Al ratio also [11, 36]. The use of a highly concentrated activating solution can also bring advantages in terms of reducing the water/binder ratio necessary to supply a given alkali content to the binder, while dilution of the activator reduces its alkalinity and thus effectiveness [70]. The influence of the nature of the alkali cation is similar to the case of hydroxide activation as discussed above, although it has been noted [71] that there are different blends of Na and K which give optimal performance when combined with different fly ashes, depending on the composition, glass content and structure, and particle size of the fly ash.

Given the complexity of the gel structure which is formed through silicate activation of fly ash or metakaolin, and in particular its dependence on a large number of compositional and processing parameters, various approaches to the analysis of the gel binder have been developed and implemented in the past years. Calorimetry and rheology [72–77], for example, provide immediately valuable information regarding setting and hardening processes, although the interpretation of some features of the data sets obtained by these techniques is still open to discussion. However, some of the techniques which have been applied to AAM binder systems move beyond the traditional laboratory analytical techniques which are widely applied in the study of cements, and the study of AAM binders has been at the forefront of technique development in several areas. The pair distribution function method, using both X-rays [13, 14] and neutrons [15] as probes of local structure, was applied to silicate-activated metakaolin binders some time prior to its first application to the study of Portland cement chemistry [78]; the application of this technique to construction materials chemistry (including alkali-activated binders) has recently been reviewed by Meral et al. [79]. The first ever in situ neutron pair distribution function study characterising a reacting system in real-time [16] was also based around the analysis of alkaline activation of metakaolin. Similarly, synchrotron X-ray fluorescence microscopy [58], hard X-ray nanotomography [80] and synchrotron infrared microscopy [56, 81, 82] have been applied to alkali-activated binders in advance of their use in more traditional cement systems.

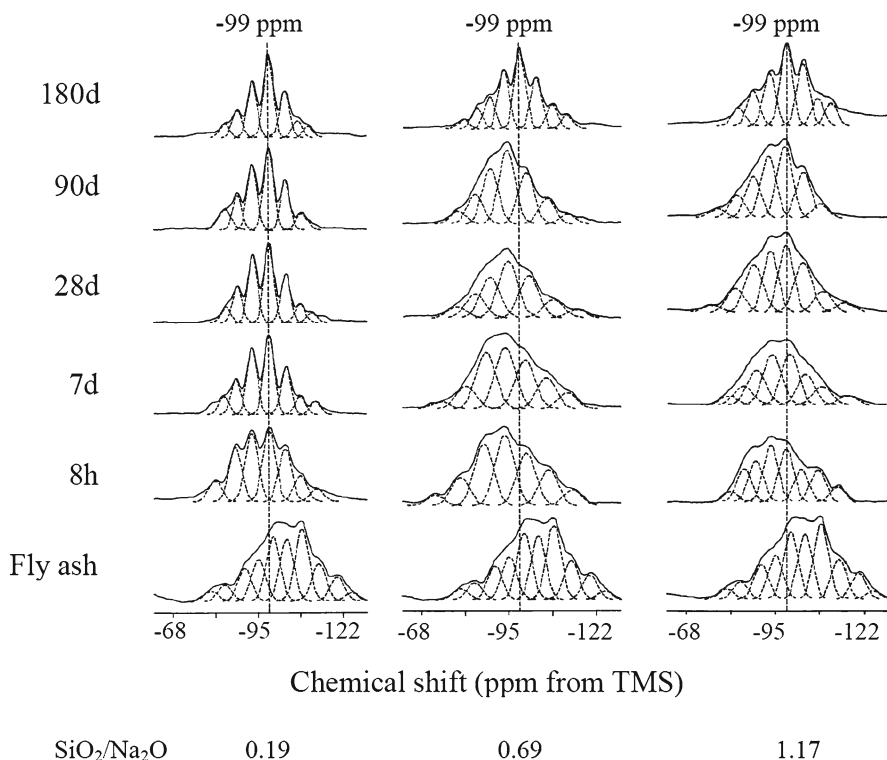


Fig. 4.3 ^{29}Si MAS NMR-MAS spectra of AAFA pastes activated with solution $\text{SiO}_2/\text{Na}_2\text{O}$ ratios and curing durations (sealed in an oven at 85°C) as marked (Data from Criado et al. [85])

Nuclear magnetic resonance (NMR) spectroscopy has proven to be a key tool in the analysis of alkali silicate-activated binder structures, due to its ability to directly probe the bonding environments of atoms in non-crystalline phases [3, 44, 83–86]. Most studies have focused on the analysis of the bonding environments of Si and Al, although other nuclei such as ^{23}Na [46, 83, 84, 87], ^1H [83, 87], ^2H [46], ^{17}O [88, 89], ^{43}Ca [87, 90] and ^{39}K [47, 91] have also been studied in alkali-activated systems. Deconvolution of NMR spectra has also proven valuable in generating quantitative data for analysis and comparison with thermodynamic models [45], but careful application of this procedure is imperative if chemically sensible results are to be obtained [92]. Figure 4.3 shows an example of the value of ^{29}Si MAS NMR spectroscopy in characterising alkali silicate-activated fly ash binders as a function of solution modulus and curing duration; the differences in crystallinity (prominence of component peaks) and connectivity (a more negative chemical shift is related to higher connectivity and lower Al content) are clearly visible between the three samples shown.

Infrared spectroscopy, as discussed above for the case of hydroxide-activated binders, has also been applied to silicate-activated systems, and in conjunction with the results of NMR analysis can be taken to indicate that the general reaction mechanism proposed in Fig. 4.2 is also valid for silicate-activated binders. Electrical

resistivity [93, 94] has also been used as a probe of reaction kinetics, and some of these data, along with those obtained by in-situ high-energy X-ray diffraction [57, 95] have been coupled with computational modelling [94, 96] to provide a more chemically-detailed mechanistic interpretation of the reaction process through the description of individual reaction steps. Alternative simulation approaches which have been applied to this problem – primarily for the more conceptually accessible case of metakaolin rather than fly ash – include the use of semi-empirical molecular orbital computations [97], or density functional theory coupled via a multi-scale coarse-graining approach with Monte Carlo simulation [98, 99].

In the characterisation of binder structures in the hardened state, thermal conductivity measurements [100] have been shown to be particularly sensitive to the water content of the gel (including the relative humidity under which the test was conducted). The water in a low-calcium binder gel is seen to be predominantly free and mobile within open pores, in good agreement with the results of NMR spectroscopy [46] and the analysis of superficially-dried samples by gas sorption and positron annihilation lifetime spectroscopy [101]. Dilatometry [102, 103] has also provided useful information about the gel structures present within alkali-activated binders, specifically related to the role of a phase identified as a low-connectivity silica-rich gel, which is able to generate expansive behaviour at elevated temperatures. The onset temperature and extent of this expansion have been used to characterise the presence of this type of phase at early age; it appears that the presence of a small amount of an expansive phase after 3–7 days correlates well with high mechanical strength, possibly due to its role in mediating ongoing reactions, but too much of this low-connectivity gel indicates a poorly-formed and immature binder structure [102, 103].

The key outcomes of the published literature in the area of silicate-activated low-Ca binders up to this point in time relate to the ability to apply both standard and advanced experimental techniques, in carefully selected combinations, to fit together the pieces of a complex puzzle regarding gel chemistry and structure. No single analytical technique can provide all of the necessary details, and each must be applied (as in all areas of materials characterisation) with a keen understanding of its limitations in application to complex materials which may be heterogeneous on every length scale from nanometres to centimetres. There are many details of the gel chemistry in these systems which require further elucidation, from top-down and bottom-up approaches, and there exists much scope for significant scientific advancement in the field in coming years.

4.2.3 Binder Structure – Other Activators

There have been a small number of published attempts to generate low-Ca binders using activators other than alkali silicates and hydroxides. Of these possible alternatives, as discussed briefly in Chap. 1, probably the most promising is a concentrated sodium aluminate solution. These solutions are available as by-products from the

aluminium processing industry [104], and have shown the potential for the generation of binders with strengths exceeding 40 MPa [105, 106], and an alumina-rich aluminosilicate gel structure. Alkali carbonate activators tend to give extremely slow strength development in low-Ca systems due to their lower alkalinity, meaning that the addition of NaOH is needed to provide strength development, leading to products which resemble partially carbonated NaOH-activated gel binders [107]. Sulfate activation is also slow in these systems; the addition of a calcium source such as CaO [108] or cement clinker [109] appears necessary for satisfactory strength development, and so these binders will be discussed in more detail in Chap. 5 of this report. The addition of alkali sulfate salts to alkali-activated low-Ca binders with predominantly hydroxide [110] or silicate [94, 110] activators seems to have a generally negative influence on setting rates and strength development, with the sulfate not participating to any notable extent in the gel formation processes.

4.3 Fly Ash and Its Interaction with Alkaline Solutions

The use of fly ash as a component of cementitious binders is not new; fly ashes have been blended with Portland cement since the 1930s [111], including almost ubiquitous use in current practice in some parts of the world (although in a much more limited way in some others, depending on jurisdictional preferences and local ash availability). High-volume fly ash concretes, where Portland cement is blended with more than 50 % fly ash, are finding more widespread application as their specific workability and curing requirements are beginning to be better understood [112], but the specific case of alkaline activation, in the absence of clinker, necessitates a much fuller understanding of fly ash glass chemistry, as this is the only source of reactive components for binder formation.

In understanding the formation and structure of an alkali-activated binder, it is thus essential to understand the reaction mechanism by which the solid precursor is converted to the final binder structure. In the case of fly ash, the reaction mechanisms involved in its conversion to a monolithic alkali-activated gel are complex and not yet well understood. This issue is complicated further by the fact that fly ashes vary dramatically between sources, and as a function of time even when sourced from the same power station. A brief discussion of fly ash chemistry, and its relationship to the mechanical and durability performance of the alkali-activated products, is thus important here.

It has been identified that the amount of aluminium available in the reacting system is crucial in properly formulating alkali-activated fly ash binders, as it is this component which leads to the crosslinked, chemically-stable nature of the aluminosilicate gel. In the absence of sufficiently reactive Al, the gels which form may show acceptable mechanical strength development, but are unstable when exposed to moisture, and thus will show limited applicability in large-scale construction applications.

Fernández-Jiménez and colleagues [55, 113–115] interpreted FTIR and NMR results for fly ash with similar reactive silica contents but different availability of

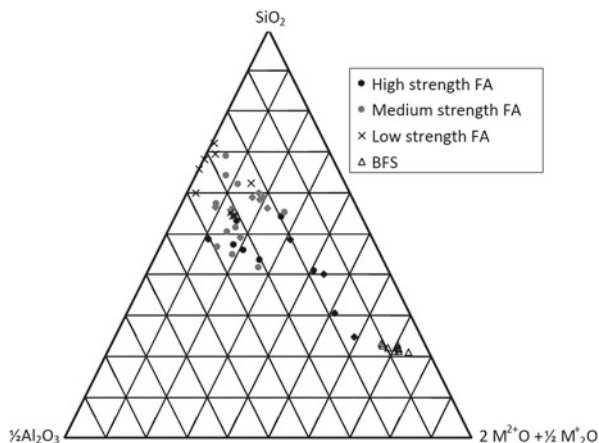


Fig. 4.4 Pseudo-ternary plot relating fly ash oxide composition to the compressive strength of alkali-activated binders obtained from that ash, based on the diagram presented by Duxson and Provis [120] summarising data from the literature for pastes and mortars, with the addition of the data set of Diaz and Allouche [121] for concretes synthesised from 16 different fly ashes

alumina, and demonstrated the importance of reactive aluminium in gel formation and mechanical performance. If an ash has an initially high reactive alumina content, large amounts of aluminium are released into the solution. Conversely, an ash with a low percentage of reactive alumina, and/or where all of the available alumina is consumed in the early phases of the reaction, will exhibit generally poor performance.

The role and importance of Ca in fly ash has also been discussed at some length [41, 69, 116–123], and it is becoming increasingly clear that simply comparing the Ca contents of fly ashes as a means of predicting which is likely to give better outcomes in terms of binder strength is an oversimplification of the system; some of the literature reports high-Ca ashes as showing higher strength development, while other papers report the opposite.

To address these issues jointly, Duxson and Provis [120] developed a pseudo-ternary classification for fly ashes based on the content of silica, alumina, and a scaled sum of alkali and alkaline earth metal (i.e. glass network modifier) content, as depicted in Fig. 4.4. The concept underlying this diagram is that the presence of alkali and alkaline earth metal cations leads Al to be present in a charge-balanced, and relatively reactive, aluminosilicate glass, rather than forming less-reactive (crystalline or cryptocrystalline) mullite regions embedded in silica-rich glassy particles, as would be the case otherwise. The strength classifications depicted in Fig. 4.4 are approximate, and take into account the activator, curing conditions and sample age, rather than being strictly correlated to numerical strength values. The compositions of several BFS sources, taken from [124], are also presented for comparison. The bulk of the ash sources depicted are Class F according to ASTM C618; those few which are approaching the BFS region are Class C.

In general, Fig. 4.4 shows that the presence of a sufficient content of Al and of network-modifying species is a necessary, but not a sufficient, condition for high strength development. Additional, potentially complicating factors which are not considered in this analysis include particle size, iron content, the presence of unburnt carbon, and also sulfate or chloride contamination. Nonetheless, as a method for pre-screening based solely on bulk compositional data, this approach does present some potential benefits in its simplicity. It has been noted that formal network connectivity analysis of fly ashes based on bulk composition does not appear to give a good correlation with reactivity [125]; this semi-empirical approach may provide a possible alternative. It was predicted by Van Jaarsveld et al. [126] in 2003 that “*a chemical dissolution test, XRF analysis, and infrared absorption spectrum will provide almost all the necessary information to predict how a specific fly ash will behave when used as a starting material in geopolymer synthesis.*” This prediction does not appear to have been fully substantiated at this point in time, and the concept of the use of the maximum in the broad X-ray diffraction feature due to the glassy phases as a measure of reactivity [127] may also add further insight in this area, but it is likely that the major advances in future fly ash characterisation for alkali-activation purposes will require more detailed (but currently highly labour-intensive) work related to individual glass phase analysis [117, 118, 128–133].

It is also not yet fully clear what the differences or similarities are between the behaviour of fly ashes in Portland cement blends and under alkaline activation conditions, or whether the detailed reaction models which have been developed for fly ash within cement pore solutions [134–136] are able to be directly applied to the specific case of alkali activation. Specific mathematical models which have been developed to describe the alkali activation of fly ash [96, 137, 138] have worked from a distinctly alkali-focused perspective, and have not considered calcium chemistry in detail, which has led to outcomes which differ in some significant regard from the environments present in cement (or even alkali-activated BFS) pore solutions. This is an important point in the development and application of such models, which are likely to become increasingly important in predicting properties of alkali-activated fly ash binders for mix design purposes as their use in concretes becomes more widespread. Possibly even more fundamentally, the ability to characterise (or even to define) the degree of reaction of fly ash [139] is essential in this endeavour.

There have also been important discussions recently, particularly in the USA, surrounding the regulation of fly ash as a hazardous waste material [140], and this issue necessitates careful consideration, to understand and mitigate any potential leachability of toxic components which are contained in many ashes. Work on chromium speciation and localisation within fly ashes [58] has shown that the use of silicate activators is less likely to cause problematic release of Cr than if hydroxide activation is used, and the importance of redox conditions in controlling Cr mobility has also been identified [141]. This issue becomes particularly important where co-combustion ashes or municipal solid waste incineration ashes are used [142], as these are more likely to contain dangerous levels of problematic elements. It should be noted that this is not solely an issue to be faced by the alkaline-activation research

community; the use of high volumes of these ashes in Portland cement concretes raises similar questions, and these issues are of broad importance across the industry and in the community at large.

The fineness of fly ash has also been identified as a key parameter in determining its value in alkaline activation processes [123, 143], and mechanochemical activation [144–146] has been demonstrated to be an effective means of enhancing the performance of some fly ashes. The surface chemistry of fly ashes is known to be essential in determining reactivity in the early stages of the alkali activation process [147], and although the influence of mechanochemical processing on chemistry (as opposed to particle size and shape modification) has been discussed for various other silicate materials, its influence in fly ash chemistry is not well known and remains a point in need of detailed analysis.

Finally, it should also be noted that the ashes which show value in alkali activation processes are not only those resulting from traditional combustion of black coal. Ash sources including some low-Ca brown coal fly ashes [148], fluidised bed coal combustion ash [149, 150], as well as the silica-rich ash resulting from the combustion of rice husk and bark [151], have all shown potential value in this area.

4.4 Natural Mineral Resources

4.4.1 *Metakaolin*

Metakaolin is the name which is applied to the dehydroxylated product of calcination of kaolinite clays at temperatures of around 500–800 °C; sufficiently high to remove the majority of the bound water from the clay structure, but not so high as to lead to the formation of mullite [152–160]. The kaolin can be mined directly from natural deposits, or sourced as a component of mine tailings or paper industry wastes; these different source routes will lead to difference in particle size, purity and crystallinity, which are known to influence reactivity under alkaline activation conditions [161–163], but whether or not the kaolin is sourced as a waste product does not inherently control its value in alkali-activated binder synthesis.

The usage of metakaolin in production of alkali-activated binders has predominantly been focused on more ‘ceramic-like’ applications and small-scale laboratory testwork, as the high water demand caused by its plate-like particle shape tends to cause difficulties in the workability of concretes [164]. Nonetheless, the production of concretes from alkali-activated metakaolin has been achieved successfully, and with relatively low water-binder ratios [165]. Alternative approaches, such as flash calcination of metakaolin to achieve a more spherical particle morphology [166], or the use of mechanical compaction [167], provide pathways around this obstacle, and may prove to be valuable in future developments in this field.

It should also be noted that the structure of metakaolin itself is the subject of ongoing discussion and debate. While derived from a crystalline layered clay structure, metakaolin does not show X-ray crystallinity, which renders its structural

analysis challenging. However, the presence of a residual modulated/layered structure is directly observable [168], which provides some useful information and potential for further insight. The calcination temperature of metakaolin has been identified as being important in determining its reactivity under alkaline activation conditions [169–172], which indicates that it is also important to understand and optimise this process. Direct molecular simulation of the calcination process [160] has shown little nanostructural difference among products heated between 500 and 750 °C, which indicates that some degree of kinetic control during calcination is important in determining the differences in reactivity of metakaolins processed across this temperature range. Chemical modification of kaolinite prior to calcination, particularly through the intercalation of small organic species, enables further control of the extent of chemical disorder in the metakaolin, which is also likely to influence reactivity [173].

The reactivity of metakaolin is determined by the presence of geometrically-strained Al sites within the formerly octahedral layer of kaolinite [99], which have been reduced in connectivity by the dehydroxylation process. While the exact connectivity of these sites is the subject of ongoing debate [159, 160, 174, 175], particularly with regard to the possible presence of highly strained III-coordinated sites in addition to the more dominant IV- and V-coordinated Al atoms, the fact that these sites are undoubtedly linked, as a layer, by energetic Al-O-Al bonds means that the Al is very readily available for reaction under alkaline conditions. This does not, however, mean that the extent of reaction of metakaolin during alkaline activation is likely to reach 100 % [92], as the silicate layers are less disrupted by calcination [174] and thus less reactive than the aluminate layers, and these remain within the microstructure of the binder as remnant particles visible under SEM, with chemical structures also identifiable by NMR [44, 45, 60].

Metakaolin has also been identified as a key component of several useful precursor blends, including combinations with fly ashes and various slags, as a means of supplying additional Al to the reaction process [93, 176, 177], tailoring reaction rates and thermal properties [178, 179] and/or to control alkali-aggregate interactions [180]. This avenue of utilisation may also provide an alternative pathway around the workability issues discussed above, and provides a good deal of scope for future developments in the area.

4.4.2 *Other Clays*

Kaolinite is not the only clay source material which has been successfully utilised in alkaline activation; a variety of other 1:1 and 2:1 clay sources have also been valorised in this manner. A productive research program in Portugal has focused on the utilisation of thermally-treated clay-rich (mainly muscovite) waste obtained from a tungsten mine [181–185] in the production of binders, concretes, and specialised systems for concrete repair applications. Illite-smectite clays have also shown strong potential for utilisation in alkaline activation applications, and the

high Si content of the clays favours the use of a low-silica alkaline activating solution in these systems [186]. The thermal treatment of pyrophyllite did not lead to a suitable source material for alkaline activation, possibly due to the insufficient degree of chemical disruption to the mineral structure which was achieved through this process, although mechanochemical processing was able to generate the necessary reactivity [187]. Conversely, successful pre-treatment of halloysite for use in alkaline activation is possible through either thermal or mechanical means [188, 189]. Hwangtoh, which is a mixture of kaolinite and halloysite [190], has been used in the production of concretes with acceptable workability and strength performance for structural applications, although the activator details were not described beyond the fact that alkalis and $\text{Ca}(\text{OH})_2$ were used in a composite activator. In some instances, the Fe content of the clay has also been identified as being important in determining reactivity during alkaline activation and the nature of the reaction products formed [191, 192].

4.4.3 Feldspars and Other Framework Aluminosilicates

Given that feldspars and natural zeolites are major components of the Earth's crust, and contain alkali metals, aluminium and silicon in appropriate proportions for use in alkaline activation, it is not surprising that these minerals have also been the subject of investigations in this area. The crystalline, chemically stable nature of these minerals is, however, a hindrance in these efforts, meaning that blending or chemical modification is in general necessary. Alkali-activated binders generated from combinations of albite, kaolinite (calcined or uncalcined) and sodium silicate, with or without the addition of fly ash [193–196], have shown acceptable (but rarely outstanding) mechanical strength development for general applications as binder materials. Xu and Van Deventer [197] conducted tests on a set of 15 aluminosilicate minerals in combination with kaolinite and mixed Na/K silicate solutions of low modulus, and proposed that the 5-membered ring structure of stilbite was responsible for its higher reactivity among those minerals studied [198, 199]. Studying minerals across several different mineral structure families, there was a strong positive correlation between the observed extent of dissolution of the minerals into alkali hydroxide solutions and the compressive strength of the binders formed [197].

More recently, the concept of alkali-thermal pretreatment of minerals has been developed and discussed as a means of valorising high-volume mineral wastes. Pacheco-Torgal and Jalali [200] attempted calcination of their clay-rich tungsten mining waste together with Na_2CO_3 , and then combined this material to obtain a product which suffered problematic efflorescence due to its excessive alkali content. More recently, Feng et al. [24] developed a method whereby albite and alkali sources (NaOH or Na_2CO_3) were jointly calcined, and the resulting glass was milled and combined directly with water as a one-part mix alkali-activated cement. The mechanical strengths of paste cubes synthesised from this binder reached 15 MPa at 1 day and exceeded 40 MPa at 28 days, and the processing temperature of 1,000 °C

is likely to provide the possibility for Greenhouse emissions savings compared to Portland cement production which will be approximately comparable in magnitude to those achieved through the use of a sodium-silicate activated slag or fly ash binder. Processes such as this may therefore provide a pathway to the uptake of alkali-activated materials in regions where the supply of suitable fly ash or BFS is problematic, or if the world market for sodium silicate becomes more constrained due to higher demand in future, as NaOH or Na₂CO₃ are more readily and inexpensively produced than sodium silicates.

4.5 Volcanic Ashes and Other Natural Pozzolans

As mentioned in Chap. 2, volcanic ash was the original pozzolanic material used in ancient Roman binders and concretes, and consists of small tephra, which are small particles of pulverized rock and glass created by volcanic eruptions. The rapid cooling of the ash upon ejection from a volcano leads to a relatively high degree of chemical reactivity, particularly in the glassy phases present, and the reactive silica and alumina content of many natural pozzolanic materials also renders them of interest in alkaline activation. Ash particles can also become geologically cemented together over time to form a solid rock called tuff, which may also be ground and utilised, and retains much of the reactivity of the fresh ash. Natural pozzolanic materials sourced from locations in Europe, Iran and Africa [201–211] have shown good performance in alkaline activation in studies to date.

The bulk chemical composition of volcanic ash is characterised by high amounts of SiO₂, Al₂O₃, Fe₂O₃ and CaO, associated with minor quantities of MgO, Na₂O, K₂O and TiO₂, and trace quantities of many other elements. Crystallographically, minerals such as plagioclase, olivine and pyroxene are embedded in a glassy matrix; pyroxene is a mineral characteristic of volcanic materials, giving the ash a black colour. Amphiboles, micas and natural zeolites are also commonly identified in volcanic ash, the latter two groups often as alteration products due to reaction with water on geological timescales.

Ghukhovsky [10, 212] proposed that, since the geological transformation of some volcanic rocks into zeolites takes place during the formation of sedimentary rocks at low temperatures and pressures, it might be possible to transfer this process to cementitious systems by the use of the same precursors with alkaline activators. Direct synthesis of alkaline aluminosilicate minerals in the phase composition of such cementitious systems was thus projected to ensure strength and durability in the artificial stones formed. The amorphous nature of the glass present in volcanic ash, particularly its high non-crystalline silica content, accounts for the dissolution of this material in alkaline solution, leading to reaction processes similar to those observed for metakaolin or fly ash. For natural pozzolans with low CaO content, and for pozzolans containing sodium-rich zeolites and high soluble silicate content, the optimum water glass modulus (SiO₂/Na₂O ratio) is lower, but this increases for natural pozzolans with high CaO or which have been calcined [210]. Curing at

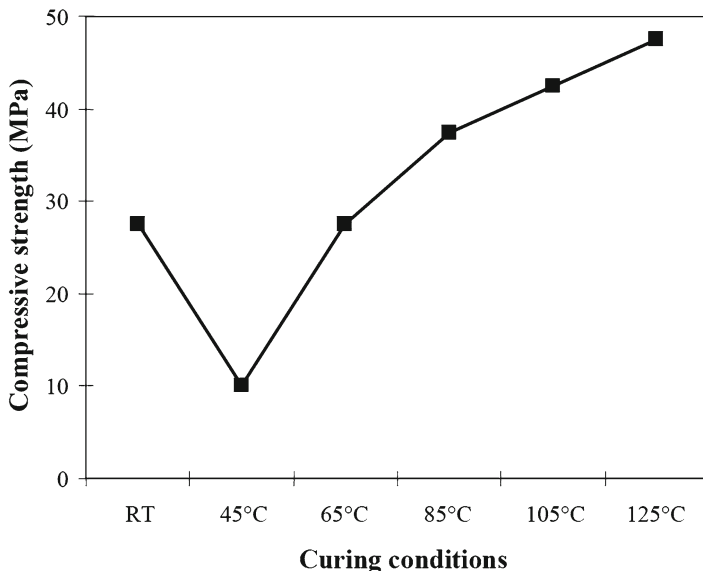


Fig. 4.5 Influence of curing conditions on compressive strength of alkali-activated natural pozzolans (pumice type, sourced from Taftan, Iran). Sample RT was sealed at 25 °C for 28 days; others were pre-cured under sealed conditions at 25 °C for 7 days then exposed to saturated water vapour/steam at the temperatures shown for 20 h (Data from Najafi Kani et al. [209])

elevated temperature has been observed to give improved compressive strength (Fig. 4.5) [207, 209, 213] and reduced tendency towards efflorescence [209]; the addition of supplementary Al sources such as metakaolin or calcium aluminate cements has also been shown to be beneficial in this regard [204, 209].

The alkaline activation of volcanic ash leads to the formation of an aluminosilicate gel which encapsulates the less-reactive crystalline phases present. However, because these phases are not as inert as the crystalline mullite or quartz phases present in fly ash, as discussed above, the alkaline solution not only dissolves alumina and silica precursors but also hydrolyses the surfaces of particles, allowing reactions to occur between dissolved silicate and aluminate species and the particle surface. Thus, in many cases, a surface reaction is responsible for bonding the undissolved particles into the final geopolymer structure. The thermal and geological history of volcanic ash, which is different from that of metakaolin or fly ash and involves many years of exposure to environments inducing chemical reaction (and thus reduction in intrinsic reactivity), can explain the low dissolution rate. This low dissolution rate and slow hardening behaviour still require investigation in relation to the dissolution behaviour of calcium, iron and magnesium ions during the alkaline activation of volcanic ash; the extent to which these ions influence the process, and also the role of Al and its availability, will be determined by the specific chemistry of the material being studied. These ions might participate to strengthen

the structure of the alkali-activated binders developed from the natural pozzolanic material, but if they instead precipitate as hydroxides, they may instead be detrimental to strength and long term binder stability.

Alkaline activation of volcanic ash thus provides an opportunity whereby a valuable product may be derived from this currently under-utilised material. The good densification behaviour, good mechanical properties and acceptably low porosity of volcanic ash-based alkali-activated binder materials indicate that these materials seem to be suitable for building applications. The strength of volcanic ash-based binders is believed to originate from the strong chemical bonding in the aluminosilicate gel formed, as well as the physical and chemical interactions occurring between the gel, unreactive or partially reacted phases, and particulate aggregates. Given that many of the precursor particles are porous, this may also contribute to strength development through mechanical interlocking with the gel, although the high water demand of the porous particles will sometimes be problematic. Most of the work that has been conducted in this area has been focused on the production of small specimens (pastes or mortars) rather than concretes, although the work on concretes which has been published [211, 213] appears to show good strength development and workability at acceptably low w/b ratios (0.42–0.45) based on two different sources of raw materials.

4.6 Low-Ca Metallurgical Slags

Other than the blast furnace slags which are commonly used in both Portland cement-based and alkali-activated binder and concrete production, there are a variety of alternative metallurgical slags which show notable reactivity under alkali-activation conditions. Among these, there are some which may be classified as ‘low-Ca’, and others containing intermediate levels of Ca will also be discussed in Chap. 5 of this Report. Magnesite-iron slags containing as little as 2–3 % CaO (and more than 30 % FeO) have been alkali-activated in Russia for waste immobilisation and structural purposes, with strengths of up to 80 MPa reported [214]. A Greek ferronickel slag has also been subjected to a detailed research and development program [215–218], both as a sole raw material activated by alkali silicates [215, 216], and also blended with kaolinite, metakaolin, fly ash, red mud and/or waste glass as supplementary sources of reactive Si and Al [217, 218]. The non-trivial levels of available chromium in these systems have been noted as being potentially problematic [218], and this point, along with a high and relatively unreactive Fe content in the slag, may prove to be an issue common to the use of many slags derived from processing of non-ferrous metals in general applications. However, given that these slags are currently treated as hazardous waste, and often disposed in environmentally unsound ways such as dumping into the ocean, any beneficial form of utilisation is likely to provide a positive step forward, even if general construction applications are not feasible at present.

4.7 Synthetic Systems

Direct synthetic approaches to alkali-activated binders based on reagent chemicals (usually derived from a combination of aluminium nitrate or sodium aluminate with silicon alkoxides or colloidal silica) have been used mainly for the development of ceramic-type alkali-activated products, and also as model systems for the study of alkali-activated binder chemistry without the complications induced by the use of waste or natural materials. The precursors can be converted to a synthetic glass prior to combination with an alkaline solution [219], chemically combined in solution and then calcined and crushed to provide a pure aluminosilicate precursor powder for later reaction with alkaline solutions [220–222], chemically combined in solution directly with dissolved alkalis [223–226] (although the gels resulting from this method are generally high in water content), or combined directly as separate solid alumina and silica sources. In this two-powder method, the alkalis may be directly incorporated into one of the solid precursors to give a ‘just-add-water’ mix design [81, 82, 227, 228], or added in the form of an alkali hydroxide or silicate solution to give a solid monolithic binder [229, 230]. The likelihood of immediate use of a pathway such as this in large-scale concrete production may appear low, due mainly to the cost of the reagent chemicals utilised in most of these studies and also the complexity of the chemical processes required. However, valuable scientific insight may be gained through the study and analysis of these types of materials. This processing route also provides a means of generating relatively pure, low-cost ceramic-like structures – either directly by use of alkali-activated monolithic products, or through the crushing and use of these amorphous materials as precursors to ceramics by thermal processing [231, 232].

4.8 Concluding Remarks

The development of low-calcium alkali-activated binders, including those which have been described as ‘geopolymers’, has most commonly been based on the utilisation of metakaolin or fly ash, although other solid precursors have also been used in more limited ways. The use of alkali metal hydroxide or silicate solutions with these precursors has in general provided the products with the highest mechanical performance, while carbonate or sulfate activating solutions are in general less effective in the absence of high levels of calcium. The gels formed in low-calcium alkali-activated binder systems resemble zeolites on a nanostructural level, and are generally highly-crosslinked, leading to good mechanical performance and chemical durability. The low content of bound water in these gels does lead to some complications in the design of durable concretes, but the low-calcium range of alkali-activated binders does appear to provide a good deal of versatility across a range of applications, providing scope for valorisation of a number of currently under-utilised resources in the production of construction materials on a worldwide basis.

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Chapter 5

Binder Chemistry – Blended Systems and Intermediate Ca Content

John L. Provis and Susan A. Bernal

5.1 Introduction

Following the discussion in the two preceding chapters, which addressed high-calcium and low-calcium alkali-activated binder systems respectively, this chapter will provide a brief discussion of the progress which has been made in the development and characterisation of hybrid binders derived from intermediate-Ca precursors and mixtures of precursors. The need for durable, high-performance, low-CO₂ alternative binder systems, along with the good existing understanding of the chemical mechanisms of mechanical strength development and durability of high-calcium and low-calcium alkali-activated materials (AAMs) as outlined in Chaps. 3 and 4, has given motivation for an increasing focus on hybrid systems over the past years. These binders are expected to provide a good synergy between mechanical strength and durability, making use of the stable coexistence of the hydration-reaction products characteristic of hydration of Portland clinker or alkali-activated BFS (mainly C-S-H gels) and alkali-activated aluminosilicates (geopolymeric gel) [1–3]. Blending of aluminosilicate-rich materials with more reactive calcium sources (including Portland cement clinker) and with the use of a source of alkalis also opens the possibility for the use of aluminosilicate wastes or by-products which may be insufficiently reactive to provide good strength development when activated alone, providing a pathway to valorisation for these materials.

This chapter will provide a very brief discussion of gel phase chemistry in the intermediate-calcium region of the AAM composition space, and also an overview

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of the developments which have been made in the application of different combinations of precursor materials to the development of alkali-activated binder systems. The focus here will be on scientific rather than purely engineering developments; there have been a very large number of technical papers published in this field which simply report the strength development and basic microstructural properties (mainly determined by microscopy, diffractometry and infrared spectroscopy) achieved when blending a 'new' type of waste material at low volume percentages into an otherwise well-understood AAM system. Such publications serve an important role in building wider confidence in the robustness of alkali-activation chemistry, but provide limited new scientific insight and so will not be listed in detail as part of the literature survey presented here.

5.2 Gel Coexistence in Blended Binders

Chapters 3 and 4 have discussed the chemistry of binder phase formation in alkali-activated materials derived from high-Ca systems (leading to 'tobermorite-like' C-S-H type gels) and low-Ca systems (with 'zeolite-like' N-A-S-H type gels), respectively. The various desirable properties of each of these two types of gel have been identified, and so it seems logical to seek methods by which their coexistence can be used to provide synergies in optimisation of the performance of the material as a whole [4]. The coexistence of C-S-H and N-A-S-H type gels is the main structural characteristic of systems involving the presence of reactive aluminosilicate and calcium sources when hydrated in alkaline media, as long as the pH is not so high as to cause precipitation of all of the reactive calcium as portlandite [4–9].

Studies of synthetic mixes designed to produce pure phases of both types of gel, and their mixtures, have been carried out [10–13], and the pH of formation of the synthetic phases is seen to play an important role in determining their stability, in agreement with the observations for waste-derived AAM systems. At $\text{pH} > 11$, a C-S-H type gel, enriched in SiO_2 and with higher polymerisation degree than the reaction product of a conventional Portland cement, can be identified. At $\text{pH} > 12.5$, the microstructural features of the N-A-S-H gels formed are to some extent similar to those exhibited by the reaction products of alkali-activated binders [10].

Formulation of gels with a high Ca/Si ratio in the absence of Al leads to the formation of portlandite as secondary reaction product [11]. Alkali-induced modification of the original C-S-H gel favours the formation of a Ca-containing N-S-H gel [11], which has also been observed by Bernal et al. [14, 15] in alkali silicate-activated BFS/MK blends and by Ben Haha et al. [16] in NaOH-activated and silicate-activated BFS binders. On the other hand, the simultaneous incorporation of aluminium and alkalis in these gels leads to an increased degree of cross-linking in the C-S-H phase and the crystallisation of strätlingite-like phases at high pH [12]. In analysis of co-precipitation of gels in the system $\text{Na}_2\text{O-CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$, it was claimed that a high pH led to ion exchange of Ca for Na within the solid phases, favouring the formation of C-A-S-H phases at high concentrations of both Ca and Na, and

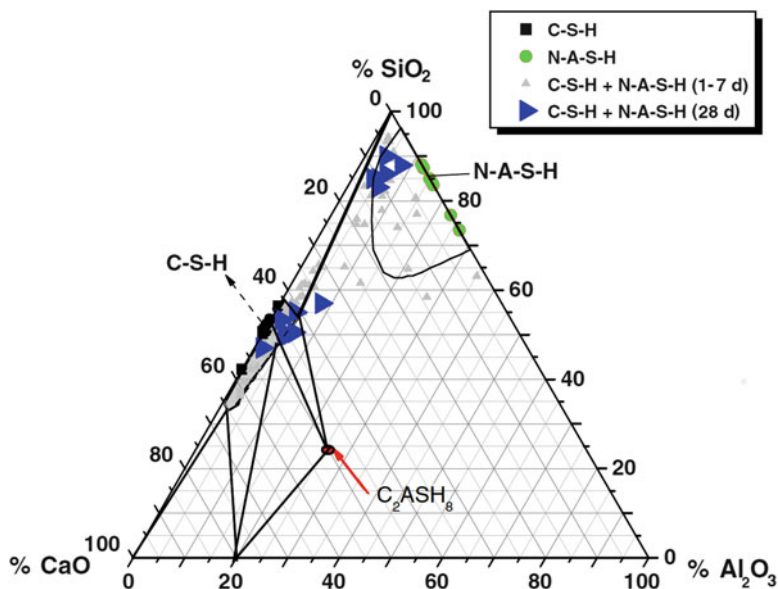


Fig. 5.1 Pseudo-ternary phase diagram developed from TEM-EDX data for the precipitates formed upon mixing of previously-synthesised C-S-H and N-A-S-H gels in ultrapure water for 1–7 days (*small grey triangles*) and 28 days (*large blue triangles*). Regions corresponding to specific phases are marked. Segregation into two chemically distinct regions is evident at later ages (Adapted from [13])

destabilising N-A-S-H gel structures [13]. When synthetic C-S-H and N-A-S-H gels were mixed in water (Fig. 5.1), the chemistry of the later-age products as measured by TEM-EDX segregated into regions characteristic of each of the two types of gel, rather than showing a chemistry intermediate between the two, indicating that these compositional regions are in fact representing genuine thermodynamic phases which can coexist under favourable conditions.

5.3 Activators for Intermediate-Ca Systems

The optimal selection of activators for an intermediate-calcium AAM binder depends very strongly on the nature of the precursor(s) to be used. As discussed in Chaps. 3 and 4, hydroxide activation can give very good results for low-calcium binder systems, carbonate and sulfate activation can be desirable for high-calcium binders, and silicate activation is the most generally applicable across the widest range of binder compositions. These trends also hold for intermediate-Ca binder systems, where the use of reactions involving calcium to generate a high pH from an activator supplied as an alkali sulfate or carbonate can also be beneficial in providing the conditions required for the reaction of an aluminosilicate component.

When the availability of calcium in a blended binder system is high, it is sometimes possible to achieve satisfactory setting and strength development by simply adding water to a solid precursor powder; examples of this are the 100 % class C fly ash-based concretes which have been produced in the Rocky Mountains region of the USA [17, 18], although these technically fall outside the classification of ‘alkali-activated’ because of the absence of alkalis. Clinker-containing materials such as the Pyrament blended cement system [19] can also be activated with water alone, with the alkali content supplied by the solid phase. However, in the context of AAMs, these systems are the exception rather than the rule. In general, the discussion presented in Chaps. 3 and 4 regarding activator selection holds true also in the intermediate-Ca region, and the reader is referred to those chapters for details rather than repeating the analysis in detail here.

In this context, the sections to follow will provide some brief discussion of the specific precursors or blends of precursors which can be used to produce intermediate-Ca AAMs, and also the activators which are suited to use with each particular type of precursor.

5.4 Single Source Materials

5.4.1 High-Calcium Fly Ash

The fly ashes classified as Class C according to ASTM C618 [20], and analogous ‘calcareous’ ashes in the European standards environment, generally contain more than 20 wt.% CaO (as much as 40 wt.% in some cases) and are less widely studied for AAM synthesis than are the lower-calcium (Class F) ashes which were discussed in Chap. 4. These ashes are usually produced from lignite or sub-bituminous coals, and are widely available in some parts of the world where these coals are widespread, particularly in the western region of the USA and many parts of Europe and Asia.

The earliest discussion of AAMs derived from Class C fly ashes is in the patent literature rather than in the open scientific literature, where a blend comprising Class C ash with citric acid and an alkali hydroxide or carbonate was patented by Lone Star in 1991 [21], and a composition without citric acid was patented by Louisiana State University in 1996 [22]. A Class C fly ash sourced from Huntly, New Zealand, has also been shown to give very good strength development properties [23–26], with creep and shrinkage also measured to be comparable to those of a control Portland cement concrete of comparable strength [27].

A key advantage which can be achieved through the use of well-formulated AAM binders based on Class C fly ashes is the development of a very dense binder gel with pores predominantly on the order of a few nanometres. Figure 5.2 shows examples of this, via a comparison of specimens with similar mix designs formulated using a Class F fly ash (Fig. 5.2a) and a Class C fly ash (Fig. 5.2b), where the pore space in both binders has been filled with a high-elemental number

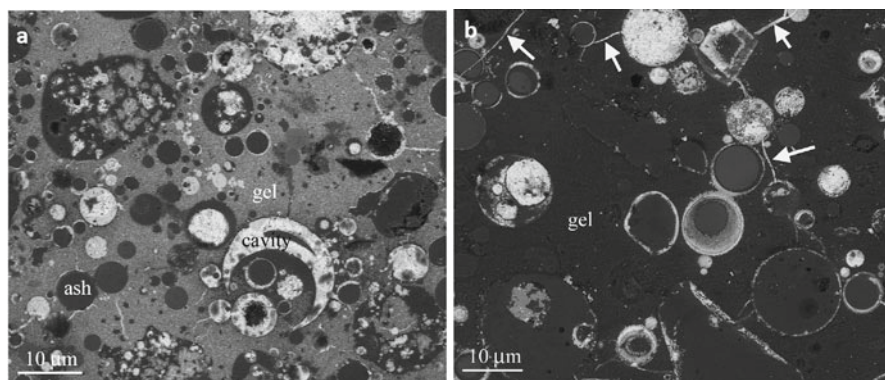


Fig. 5.2 Back-scattered electron images of AAM samples produced by the reaction of fly ashes (a: Class F fly ash; b: Class C fly ash) with a sodium metasilicate activator. The pore space has been intruded with Wood's metal, so pores connected to the outside of the sample through pores larger than ~ 11 nm show as bright regions in both images. The gel in (a) is notably brighter than in (b), indicating a much higher extent of gel porosity. Arrows in (b) indicate cracks linking voids due to pore volume within unreacted fly ash particles, where the gel appears to have fractured during intrusion to enable the liquid metal to fill these spaces (Adapted from [28])

alloy (Wood's metal) which was able to intrude pores larger than ~ 11 nm under the experimental conditions used [28], and therefore shows these pores as bright regions in the SEM images. The gel of the Class F fly ash-based material shows extensive permeation by the Wood's metal, while there is very little filling of pores by Wood's metal within the Class C fly ash-based AAM, indicating a very low extent of permeable porosity in this material [28].

In the extensive study of Diaz-Loya et al. [29], analysing concretes made by alkali-activation of 25 fly ashes from different North American coal-fired power stations, the highest strengths achieved were from Class C ash sources. However, it is not universally true that high-Ca fly ashes produce better AAM binders than their low-Ca counterparts; both Winnefeld et al. [30] and Oh et al. [31] found that various high-Ca ashes tested gave relatively less desirable performance in terms of strength development and binder phase evolution than the Class F ashes tested in parallel. In the case of the study of Winnefeld et al. [30], all of the German high-calcium fly ashes tested were very high in SO_3 (up to 14 % on an oxide basis, which exceeds the 5 % maximum allowed in an ASTM C618 Class C ash) and low in Al_2O_3 ; two of the four ashes were in fact too low in network-forming components ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) to meet the 50 % minimum sum of these components which is required for classification as Class C according to ASTM C618 [20], so the strength development of the AAM binders was low, and the authors recommended the use of a lower-calcium (Class F) fly ash in preference to the higher-calcium materials to provide better strength development in AAMs. Similarly, in the study of Oh et al. [31], acceptable strength (35 MPa at 14 days) could be achieved from a Class C ash within a limited range of activator compositions, but the system was not robust to changes in activator modulus, with very low strengths observed at either high or low activator modulus.

A similar lack of robustness was observed by Guo et al. [32], who observed a sharp optimum in strength as a function of activator modulus using a different source of North American Class C ash.

This discussion highlights one of the main drawbacks associated with the use of high-calcium fly ashes: the variability between the different ashes available within this classification (whether or not complying with the Class C requirements of ASTM C618) is much greater than in the case of lower-calcium ashes, and so much more careful mix design work is required for each source of ash, leading to a system which is less robust than is the case for low-Ca fly ash-based AAMs. In the work of Díaz-Loya et al. [29], some of the Class C ashes tested had inconveniently high water demand and/or rapid setting (less than 5 min), which again indicates that there may be challenges related to quality control of concretes made from these materials in large-scale production.

5.4.2 Other Single Source Materials

There are few reports in the literature of the development of AAMs from single source materials at intermediate Ca content. An exception is the work of Fares and Tagnit-Hamou [33], who activated a spent pot liner waste obtained from the aluminium refinement industry (14.6 wt.% CaO) with NaOH to form alkali-activated binders, achieving 28-day strengths of more than 60 MPa with steam curing, although showing some strength regression from 1 day to 28 days in samples with high activator doses. Tashima et al. [34] also achieved mortar strengths in excess of 80 MPa through alkali-activation of a waste calcium aluminosilicate glass, indicating good potential for future developments in alkali-activation to produce high-strength materials, through the identification of suitable niche waste materials in specific locations.

5.5 Mixed Source Materials

5.5.1 Aluminosilicate + $\text{Ca}(\text{OH})_2$ + Alkali Source

Binder systems containing an aluminosilicate source with little or no calcium, blended with calcium hydroxide and an alkali source, are sometimes used as a model system for the analysis of pozzolanic reactions; this will not be the focus of discussion here, as the main point of interest is the analysis of the alkali-induced reactivity in such systems when higher alkali doses are used. Alonso et al. [7, 8] found that in a highly alkaline environment, the activation of metakaolin in the presence of $\text{Ca}(\text{OH})_2$ leads to the formation of an amorphous sodium aluminosilicate gel, similar to the gel obtained when metakaolin is activated in the absence of $\text{Ca}(\text{OH})_2$. This is possibly

due to the low solubility of $\text{Ca}(\text{OH})_2$ at high pH, meaning that it remains largely unaffected by the reaction process. C-S-H type gel is also reported as a secondary reaction product in blends of MK and $\text{Ca}(\text{OH})_2$ activated with lower concentrations of NaOH [7, 8, 35]. Dombrowski et al. [9] assessed the effect of FA/ $\text{Ca}(\text{OH})_2$ ratio in alkali-activated binders under constant activation conditions; an increased content of $\text{Ca}(\text{OH})_2$ in the binder was found to promote the formation of higher amounts of C-S-H type gels in the samples, favouring the evolution of higher mechanical strengths and a more dense binder structure over time.

Shi showed that Na_2SO_4 activation of a lime-fly ash blend resulted in the formation of C-S-H and AFt phases as hydration products [36], while Williams et al. [37] activated fly ash with $\text{Ca}(\text{OH})_2$ and NaOH to form a binder based on C-S-H and partially ordered katoite. Activation of a natural pozzolan by addition of $\text{Ca}(\text{OH})_2$ and Na_2SO_4 was also found to give a combination of AFm and AFt phases in addition to C-S-H products [38–40], and chemical activation was found to be a more effective means of generating binders from a 4:1 blend of natural pozzolan and $\text{Ca}(\text{OH})_2$, compared to either mechanical or thermal processing [41].

5.5.2 *Calcined Clay + BFS + Alkali Source*

Similar findings to those discussed in the preceding section have been also identified when BFS and metakaolin are blended to form the basis for alkali-activated binders. Yip and van Deventer [5] proposed that the alkali activation of metakaolin in the presence of BFS is highly dependent on the alkalinity of the alkali activator and the ratio of blending of solid precursors. Under high alkalinity conditions, the activation of BFS is hindered by the fast formation of reaction products on the surface of GBFS particles and the low solubility of Ca^{2+} ions, which leads to the reduced dissolution of Ca and tends toward forming $\text{Ca}(\text{OH})_2$ instead of C-S-H type gels. Such systems are characterised by formation of an aluminosilicate gel through the activation of metakaolin, while calcium often precipitates as $\text{Ca}(\text{OH})_2$.

On the other hand, under lower alkalinity conditions (either more dilute activator solutions or with activator modulus exceeding 2.0), the dissolution of calcium species from GBFS is promoted by the formation of C-S-H type gels from early in the reaction process, where the aluminosilicate component reacts later to form a higher-Al gel, leading to the coexistence of N-A-S-H and C-S-H type gels. A relationship between the nature of the reaction products formed in these systems and the mechanical strength developed over time has been also reported [4, 6]. The N-A-S-H component formed at high alkalinity conditions is the main contributor to the mechanical strength, while at lower alkalinity, the presence of C-S-H gel formed from the activation of the BFS significantly contributes to the binder performance, which is highest in the case where the coexistence of C-S-H and N-A-S-H gels is reached [6]. These results are in good agreement with those observed by Buchwald et al. [42] in blended binders, indicating that when gel coexistence takes place, the geopolymeric gel formed presents a lower degree of crosslinking and, as a result of

the interaction between both systems, additional Al is incorporated into the C-S-H type gel, leading to increased average chain lengths in this product.

The kinetics of reaction are also modified through blending of BFS and metakaolin [43–45], so that the condensation reaction can be accelerated at increased activator alkalinity [43, 44]. This raises the aluminium concentration in the pore solution, promoting the condensation of C-S-H gels by incorporation of aluminium tetrahedra [43]. However, this relationship is not straightforward, and depends on the metakaolin content of the precursor blend, and on the solution modulus. Bernal et al. [14, 44, 46] activated BFS/metakaolin blends under the same conditions which are usually applied to binders solely based on BFS (high modulus and relatively low activator Na_2O concentration), and identified an increase in setting time and reduced development of reaction products at higher metakaolin content. In this case, because dissolution-condensation processes involving BFS and metakaolin take place simultaneously, the relatively low level of alkalis available was rapidly consumed through formation of aluminosilicate gels, inhibiting the subsequent dissolution of MK.

A reduced reaction degree in BFS/metakaolin binders with higher contents of metakaolin has also been reported when using KOH as an activator [47]. In this case, higher $\text{SiO}_2/\text{K}_2\text{O}$ ratios were necessary to extend the setting times, but reduced mechanical strength. Lecomte et al. [48] identified the fine BFS particles in blends with calcined clays as the main source of nutrients for initial hardening and development of early strength. They also identified both highly-coordinated ($\text{Q}^4(n\text{Al})$) and under-coordinated (Q^1 and Q^2) Si sites in binders with a 2:1 ratio of BFS and calcined clay, activated by a mixture of KOH and high-modulus sodium silicate. The mixing procedure used by those authors was to first combine the clay and activator, and then 30 min later add the BFS. This enabled the development of a high degree of dissolution of the clay, but raises questions regarding whether the gel phase assemblage was kinetically stabilised rather than approaching a thermodynamically stable condition in the longer term. Zhang et al. [49] identified an optimum in strength, and good behaviour in immobilisation of heavy metal wastes at a 1:1 ratio of BFS to metakaolin, while Bernal et al. [14, 15, 46, 50, 51] found that a higher metakaolin content necessitated the use of a higher activator modulus, with the optimum BFS/metakaolin ratio for compressive strength development increasing directly as a function of activator modulus. The work of Burciaga-Díaz et al. [52] was also in agreement with these results.

The residual strength of blended BFS-metakaolin samples after exposure to 1,000 °C was also found to be better than that of the BFS-based materials in the absence of metakaolin [53], as the thermally-induced shrinkage and cracking processes were better controlled and less damaging in the blended systems.

5.5.3 Fly Ash + BFS + Alkali Source

The combination of fly ash, BFS and an alkali source has long been considered to be a promising AAM binder formulation, with the first journal publication in this area dating as far back as 1977 [54], where the binder system was investigated as a

part of a study which was focused on making comparisons with the Trief process for manufacture of alternative binders with a lower calcium content than Portland cement. Those authors experienced difficulty related to efflorescence at the high alkali contents tested, and obtained low strengths due to inappropriate curing regimes as the specimens were stored either underwater (leading to alkali leaching) or in relatively dry conditions (20 °C and 65 % relative humidity, leading to loss of water and halting of the reaction process), which limited the longer-term strengths to around 20 MPa [54]. Since that time, it has been shown that sealed curing of fly ash-BFS binders can give excellent results in terms of final strength, with values around 100 MPa at 28 days, and increasing to 120 MPa at 180 days, have been reported for 1:1 blends of BFS and fly ash [25]. Bijen and Waltje [55] also noted difficulties with efflorescence and water demand in their NaOH-activated binders, and found an almost total insensitivity to NaOH dose beyond 4 wt.% by mass of dry binder; they did not report the curing conditions used, but these results are also consistent with the difficulties observed when curing AAMs underwater due to alkali leaching.

In many studies, a small amount of BFS is added to otherwise fly ash-based binder systems to accelerate setting and give higher strength development; for example, Li and Liu [56] found that as little as 4 % BFS was sufficient to improve the strength of a 90 % fly ash/10 % metakaolin blend by more than 40 % after 14 days of curing. Kumar et al. [57] found that the BFS was more influential in the chemistry of the system when cured at lower temperature, while fly ash contributed a greater fraction of the total extent of reaction under elevated-temperature curing. This may be compared to the well-known differences in apparent activation energy between fly ash and BFS when blended with Portland cement [58, 59].

An alkali-activated BFS-fly ash binder, containing a small amount of Portland clinker in addition to the sodium metasilicate activator, was also patented in the 1990s in the Netherlands, and marketed under the name Diabind as an acid-resistant material for pipe production [60]. More recently, BFS-fly ash blends have been highlighted as a key commercial AAM system (marketed in Australia by Zeobond as “E-Crete”) in a review of technical, commercial and regulatory developments in this field [2], again demonstrating the strong commercial interest in this particular combination of precursors for use in AAM systems.

There have also been significant developments in this area in China, a nation with abundant resources of both fly ash and BFS, and these have been reviewed in detail by Shi and Qian [61] and more recently by Pan and Yang [62]. A lot of this work has been focused on mix design optimisation for strength and durability through the use of blended activators, where activation with NaOH in combination with additional alkali sources such as carbonates has been found to be of particular interest [62].

Puertas et al. [63] assessed the effect of activator dose, BFS/fly ash blending ratio and curing temperature, and identified that the blending ratio was the factor that most strongly influences mechanical strength development. The main reaction product was identified as a C-S-H type gel with a high concentration of tetrahedrally coordinated Al and interlayer Na ions incorporated into its structure [63]. In a later

study [64], hydrated alkali-aluminosilicate gel phases similar to those which are characteristic of alkali-activated fly ash were also identified. This can also be attributed to an improved dissolution of the fly ash in an alkaline medium in presence of calcium, with a corresponding increase in the extent of participation of the fly ash in the alkali-activation reaction process [65]. Recent NMR results obtained as a part of a study of carbonation [66] are also consistent with the gel coexistence argument here; accelerated carbonation was found to alter the structure of the C-S-H type gel, but not the N-A-S-H type gel, within a blended fly ash/BFS binder. The addition of more BFS to a blended binder tends also to increase the Na^+ concentration of the pore solution, showing that this ion is less strongly bound into C-S-H type gels than N-A-S-H type gels, consistent with the chemical details of the chain-based and framework-based structures respectively [67].

Escalante García et al. [68] also conducted a parametric study of activation conditions and blending ratios in BFS-fly ash AAM binders, and found (similar to the case for BFS-calcined clay blends as discussed in the preceding section, and due to the same chemical mechanisms) that a lower activator modulus and higher activator dose were required for good strength development in the presence of higher contents of fly ash.

The work of Lloyd et al. related to the microstructure and chemistry of 1:1 blends of fly ash and BFS has also provided notable advances in the understanding of these systems [28, 69, 70]. By combining elemental composition mapping and backscattered electron imaging in a scanning electron microscope, reaction rims were identified around some of the partially-reacted BFS particles with morphological and chemical features that differ from those observed in systems without fly ash, in particular Si-depleted regions in the BFS reaction rims [69, 70]. This indicates that not only does the calcium from the BFS influence the reaction of the fly ash as noted above, but also that the aluminium and silicon supplied by the fly ash cause differences in the reaction pathway of the BFS particles. The exact mechanisms controlling this process remain slightly elusive, and this is an area of ongoing and important research.

It is also important, in the context of durability, to understand the role of each of the precursors in determining the porosity and pore structure of the blended binder systems. While gravimetric determination of porosity did not provide a clear trend as a function of BFS content [28] – possibly due to C-S-H type gels suffering dehydration effects induced by drying at elevated temperature during these measurements [71] – data obtained from X-ray tomography does show a clear trend of decreasing porosity with increasing BFS content (Fig. 5.3) [3]. It is particularly interesting to note that the tomography data show a clear distinction between the samples with 50 % or more BFS, which show a reduction in porosity over time, compared to those with less than 50 % BFS, which do not. Although this precise cut-off value is likely to differ as a function of the reactivity (and particularly the calcium content) of the fly ash and BFS sources used, the general concept that it is possible to achieve AAM binder structures similar to alkali-activated BFS but with a greatly reduced BFS content is particularly important in parts of the world where BFS supply is constrained, or where the addition of another aluminosilicate

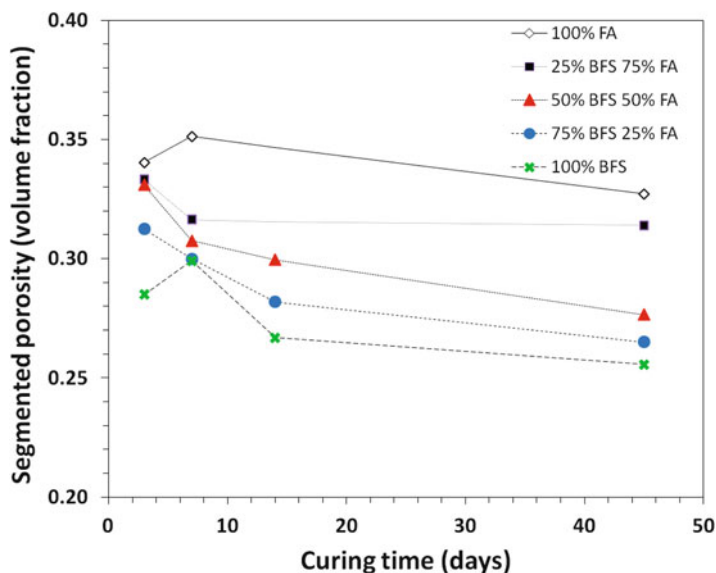


Fig. 5.3 Porosity of blended BFS-fly ash binders as a function of composition and curing duration, as determined using x-ray microtomography (Adapted from [3])

component is desirable in for control of rheology or setting time. The direct relevance of this can be shown by comparison of these results with the H_2SO_4 resistance data of Lloyd et al. [72], who found that acid penetration depth increased with BFS content from 0 to 100 %, but the 1:1 blend gave similar performance to the 100 % BFS sample, in very good agreement with the tomography data, although the sources of BFS and fly ash tested in those two studies were different.

5.5.4 Red Mud-Blended Binders

Red mud is an alkaline by-product of the Bayer process for alumina extraction, where bauxite ore is digested in NaOH solutions. After the majority of the Al has been recovered, the solid residue of the ore, usually containing a significant quantity of entrained NaOH, is dewatered and sent to large tailings dams. The material is red due to its content of Fe oxides, but is also usually relatively rich in Si from impurities in the bauxite, as well as containing some residual Al if the process is operating below 100 % efficiency (which is usually the case). This material is generated in quantities of an estimated 35 million tonnes p.a. [73], is highly underutilised, and provides some properties which are obviously desirable for AAM production, specifically the presence of potentially-reactive alkalis, Ca, Al and Si within a single inexpensive material. The relatively low Al availability from many red muds is the greatest challenge facing utilisation in AAMs; as the purpose of the Bayer process

is to extract Al, it is undesirable if this element remains in the waste rejected from the process. Thus, the use of red mud as a sole binder component has generally been unsuccessful, with the exception of some work using quite Al-rich red mud sources which can be activated directly by sodium silicate [74].

Supplementary Al sources such as metakaolin [73], calcined oil shale [75] and fly ash [76] have all successfully been used in red mud-containing AAM mixes. However, in the context of this discussion of high-Ca binder systems, the most relevant work relates to the use of red mud in combination with BFS to produce high-performance binders at a lower cost than can be achieved through the use of BFS alone, and with potentially desirable changes in the properties of the binders. Pan et al. [77, 78] investigated the use of solid sodium silicate to activate a blend of BFS and red mud, and found that red mud itself did not produce satisfactory strength development, while activation of BFS and red mud together gave high strength. BFS-red mud mixtures activated by a combination of solid sodium silicate and sodium aluminate showed compressive strengths exceeding 55 MPa at 28 days, with freeze-thaw damage, carbonation rate, and strength loss following accelerated carbonation lower than for a control Portland cement [79, 80]. Calcination of relatively Al-rich red muds has also been shown to give improvements in geopolymerisation performance, via enhancement of the availability of alumina [81].

5.5.5 Portland Cement + Aluminosilicate + Alkali: Hybrid Binders

To design hybrid binders based on Portland clinker/cement and alkali-activated aluminosilicate sources, the differences in the mechanisms of structural development in both types of systems should be taken into account, to enable the generation of reaction conditions and mix designs which promote each of the components of these complex binder systems to contribute to strength and durability properties. Studies related to the hydration of Portland cement under different alkalinity conditions, assessed through the incorporation of substances such as NaOH, NaCO₃, Na₂SiO₃ and Na₂SO₄, have been widely published over the past decades, and are largely beyond the scope of this report. Rather, the focus here will specifically be on the analysis of systems where the interaction of the alkali with an additional aluminosilicate source provides the major contribution to strength development, with Portland clinker or cement playing a secondary role. The potential of such 'hybrid cement' systems, particularly using fly ash as the aluminosilicate source, in production of high performance, low-CO₂ concretes has been highlighted recently [1, 82–85], and these materials are increasingly of interest in the international community, both in research and in application.

The hydration products resulting from the OPC component of hybrid AAM binder systems differ notably from standard OPC hydration products in terms of the formation of AFt and AFm phases. High concentrations of Na⁺ supplied as a hydroxide or sulfate solution tend to favour the AFm-structured, alkali-substituted

“U – phase” over ettringite [86–91], although this can be reversed by the addition of larger contents of sulfate [92]. The reaction process is also influenced by the decreased solubility of $\text{Ca}(\text{OH})_2$ in highly alkaline environments. The incorporation of sodium silicates has a strong accelerating effect in the hydration of Portland clinkers [93–95]. Blazhis and Rostovskaya [96] also analysed the effect of incorporating sodium silicate/potassium fluoride blends in Portland clinkers to produce binders with very high early strength (up to 86 MPa compressive strength after 1 day of curing). In this case the potassium fluoride controlled setting time, and the mixed activator enhanced mechanical strength development and formation of both crystalline and disordered silicate and aluminosilicate binder phase products.

Within the scope of hybrid AAM-Portland cement systems, studies related to the production of hybrid binders based on the combination of aluminosilicate sources with the constituent minerals of Portland clinker [97], or Portland clinker itself [4, 83, 92, 98–100], have shown promising results in terms of binder durability and mechanical performance. Krivenko et al. [101] also found that sodium silicate-activated fly ash-Portland cement hybrid binder systems showed performance in hazardous waste (Pb) immobilisation which was significantly superior to the performance of Portland cement alone, and noted that steam curing of such binder systems was particularly beneficial for mechanical strength development.

Gelevera and Munzer [102] assessed alkali silicate-activated Portland clinker/BFS blends, and found that increased BFS content in conjunction with an alkali silicate solution led to higher compressive strength. Frost resistance was also enhanced with the use of an alkaline activator in Portland clinker/GBFS blends [102]. Fundi [103] studied binders composed of 50–70 % natural pozzolan (volcanic ash) and 30–50 % Portland cements, activated by various sodium and potassium compounds. In samples formulated with 50 % OPC, K_2CO_3 seemed to be a relatively ineffective, while sodium silicate and (particularly) sodium sulfate were identified as the most effective chemical activators, giving an increase in mechanical properties by as much as 100 % when added at doses as low as 3 wt.%. High performance (74 MPa compressive strength after 12 months) was achieved at 70 % substitution of Portland cement by natural pozzolans through incorporation of sodium sulfate. Under these conditions the formation of low-basic calcium silicate hydrate and gradual crystallisation of alkaline aluminosilicate phases was promoted, with portlandite, calcite and sulfoaluminate phases absent from the hardened binders.

Sanitskii [98, 99] found that alkali metal carbonates and sulfates were effective in activating blends of clinker and clay-derived aluminosilicates or fly ash. The assessment of the complex systems of Portland clinker – fly ash – sodium sulfate was approached through the study of the interactions $\text{Ca}(\text{OH})_2\text{-Na}_2\text{SO}_4$ and $\text{Ca}(\text{OH})_2\text{-Na}_2\text{SO}_4\text{-fly ash}$, suspended in water. Importantly, an increase in pH over time was observed in the suspension of the model system $\text{Ca}(\text{OH})_2\text{-Na}_2\text{SO}_4\text{-fly ash}$. In the presence of the aluminosilicate source, the reaction between $\text{Ca}(\text{OH})_2$ and Na_2SO_4 was driven towards the formation of NaOH through consumption of gypsum by ettringite formation (Fig. 5.4), involving Al_2O_3 supplied by the fly ash. Related mechanisms have also been observed in Portland clinker-calcined clay- Na_2SO_4 binders [100], where the importance of ettringite formation in the generation of

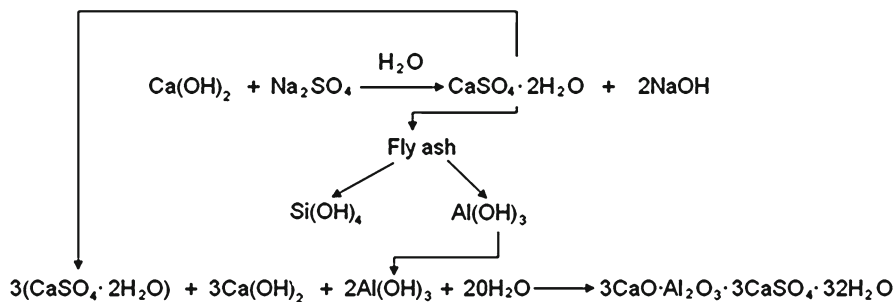


Fig. 5.4 Interaction reaction of the model system portlandite – sodium sulfate – fly ash (Adapted from [98])

alkalinity was particularly noted, and also in Portland cement-fly ash- Na_2CO_3 binders [92], where CaCO_3 precipitation drives the generation of a high pH. In both of these systems, an aluminosilicate type gel is observed as a secondary binder phase, enhancing the performance compared to systems where C-S-H is the only binder gel formed.

5.5.6 Aluminosilicate + Other Ca Sources + Alkali Source

Various other calcium sources, including calcium silicate [4] and carbonate [104–107] minerals, have also been used in combination with aluminosilicate sources to modify the properties of alkali-activated binder systems. In general, the effectiveness of the calcium source depends on the balance between Ca availability from the source, and the alkalinity of the activating solution. Under moderate alkalinity activation conditions, calcium is dissolved from silicate minerals to a lower extent compared with Portland cement or BFS, leading to little or no formation of C-S-H type gels. The unreacted mineral particles can then disrupt the aluminosilicate gel network, resulting in lower overall strengths. Carbonates appear to provide more Ca availability and more contribution to the strength of the binder, although dolomite is less effective than calcite in altering the properties of the binder systems, because magnesium does not play the same role as calcium in formation of strength-giving gels [104]. Binders based on the combination of BFS, limestone and sodium silicate or carbonate have been shown to give good strength development and mechanical performance [105–107], with diatomaceous earth also useful as a supplementary silica source [108]. The focus of much of this particular program of work was on low-cost construction materials for developing nations, so sodium carbonate activation was preferred for cost, safety and environmental reasons; compressive strengths up to 40 MPa at 3 days were able to be achieved, while giving CO_2 and energy reductions quoted at 97 % compared with Portland cement, with a cost reduction also calculated to be greater than 50 % [107].

The other major component which has been used as a secondary calcium source in alkali-activated hybrid binder systems is calcium aluminate cement. The reactions of this material with various alkaline solutions have been widely discussed in the context of avoidance of conversion reactions, but it is also a useful component of hybrid AAM binders. Calcium aluminate cement can be blended with natural zeolites [109], calcined clays [110] or natural pozzolans [111], to enhance the strength development of the binder systems and/or for secondary purposes such as efflorescence control. When added in concentrations of less than ~20 %, the calcium aluminate cement appears to act as a source of nutrients for the growth of Al-substituted silicate phases rather than forming its more usual crystalline hydration products [110, 111], although systematic studies of phase evolution in such binder systems are to date relatively scarce.

5.6 Conclusions

The combination of a calcium-rich precursor with a predominantly aluminosilicate precursor to form a hybrid alkali-activated binder system is an area with enormous scope for variations in mix design and precursor selection, providing opportunities to tailor the performance, cost and environmental footprint of a binder system in a myriad of ways. The formation of separate and distinct high-calcium (“C-A-S-H type”) and low-calcium (“N-A-S-H type”) gels in these systems is able to be observed in many systems, with potentially interesting implications for the thermodynamics and long-term stability of the binder system. The properties of the materials formed in this region of intermediate calcium content are not always immediately predictable simply from consideration of the properties of endmember systems formed from one precursor or the other, as there are notable synergistic effects achievable through the selection of a calcium source-activator combination which controls the availability of calcium in such a way as to optimise the properties of the binder product formed. This is an area in which there is a wealth of empirical information available, but only a much smaller number of detailed scientific studies, and certainly provides a good deal of scope for future developments, both scientific and technical.

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Chapter 6

Admixtures

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6.1 What is an Admixture in an Alkali-Activated System?

To commence the discussion of admixtures in alkali-activated binders, it is necessary to first give a brief discussion on the definition of the word ‘admixture’. Many of the components which are essential to the formulation of alkali-activated binders are sometimes described as admixtures (mineral or chemical) in Portland cement systems. In the context of alkali activation chemistry, neither the alkaline activator nor the solid (aluminio)silicates should be considered to be an admixture; these are binder components. Similarly, the addition of clinker compounds, or related materials such as cement kiln dust, is beyond the scope of this review. The discussion to follow will predominantly address organic admixtures, although a brief discussion of inorganic components used as accelerators or retarders will also be presented.

The effect of organic and inorganic admixtures (commonly used in Portland cement concrete technology) on alkaline cement concrete, mortar and paste behaviour and properties has not been very widely addressed in the literature. Moreover, the results reported by different authors are often contradictory, perhaps due to variations in conditions such as the nature of the material to be activated (slag, fly ash, metakaolin), the nature and concentration of the alkali activator, and the type

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and dosage of the admixture. What these studies have unanimously revealed, however, is that organic and inorganic admixtures behave very differently in Portland and alkaline cement systems. A number of explanations have been put forward for this difference, although further research in this regard is still needed. The patent literature does contain reference to a large number of admixtures in various contexts within the realm of alkaline activation technology; however, given both the limited scientific background which is provided in most patent disclosures and the tendency towards defensive strategies in the drafting of patent claims, it is very difficult to obtain detailed scientific information from these sources.

There are some points which are worthy of comment at this point in the general context of the usage of admixtures in AAM concretes:

- In the addition of a liquid admixture to an AAM concrete mix, the water content of the admixture should be taken into consideration in the mix design, due to the high sensitivity of most such mix designs to water/binder ratios.
- The unburnt carbon component of fly ashes is often problematic in determining desired admixture doses; a slightly increased carbon content can lead to significant increases in the required admixture doses due to selective sorption of the organic components.
- The results of admixture addition, both desired effects and side-effects (positive and negative) must be understood in the context of what an admixture is supposed to do, as the results discussed can only be judged when it is clear what must be achieved with an admixture. This is common knowledge in concrete science, but still important to put in context. For example, the more hydrophobic a polymer chain is, the more air-entraining it is. This may be either a positive or a negative point in terms of the desired properties of the final material. Hydrophobicity may help in making surfaces water resistant, and some controlled air entrainment is required for freeze-thaw resistance, but too much air is detrimental for durability and permeability. Also, some plasticisers in AAMs may appear to be effective in increasing slump, but this is not necessarily desirable if only achieved through air entrainment rather than through a fundamentally effective plasticising action.
- The use of curing compounds (internal or external) with alkali-activated concretes is potentially of interest, and organic internal curing compounds would certainly be considered to act as admixtures, but there does not appear to be any publicly available literature in this area at present.

Working from this basis, the following is a review of the state of knowledge about the effect of admixtures on alkali-activated concrete, mortar and paste behaviour and properties. The review is organised essentially around the nature of the admixture.

6.2 Air-Entraining Admixtures

Douglas et al. [1] found that the addition of a sulfonated hydrocarbon-type air entraining admixture was reasonably effective in achieving an air content of up to 6 % in sodium silicate/lime slurry-activated BFS concretes; there was a high degree

of variability in their results, but they commented that the dosages required to achieve the desired air content were in general similar to those used in Portland cement concretes. However, Rostami and Brendley [2] found that the use of an (unspecified) air-entraining agent did not enhance the freeze-thaw resistance of their sodium silicate-activated fly ash concretes. Freeze-thaw resistance, as will be discussed in Chap. 10 of this Report, relates not only to the content of entrained air but also to its distribution, and so it may be that an admixture which can entrain an equivalent amount of air into AAM or OPC concretes has very different effects in terms of distribution of air voids, and thus influences freeze-thaw performance differently. This remains to be addressed in detail in the open literature at this time.

Bakharev et al. [3] studied the effect of an alkyl aryl sulfonate air-entraining admixture on the workability, shrinkage and mechanical strength of BFS concrete alkali-activated with waterglass or a mix of NaOH and Na_2CO_3 . These authors concluded that the admixtures increased workability, had no effect on mechanical strength, and reduced shrinkage.

Other studies showed that the air content can be modified in alkaline mortars and concretes with inorganic admixtures, although this is strictly not air entrainment but foam formation, as the pores will be much larger and are formed due to gases generated by the chemistry of the binder. For example, Arellano Aguilar et al. [4] obtained lightweight concretes (with densities of up to 600 kg/m^3) by adding Al powder to metakaolin mortars and concretes and to a 25/75 % blend of fly ash/metakaolin mortars and concretes. In both cases the activator used was sodium silicate ($\text{SiO}_2/\text{Na}_2\text{O} = 1.29$) with an Na_2O concentration of 15.2 %. These authors observed that the addition of Al powder in a highly alkaline environment generated hydrogen bubbles which, when trapped in the paste, enlarged the volume and reduced density. A good thermal conductivity-strength balance was obtained in the resulting aerated concretes. Further discussion of lightweight and foamed alkali-activated systems will be presented in Chap. 12 of this Report.

6.3 Accelerating and Retarding Admixtures

A broad range of admixtures are used to accelerate or retard setting in alkali-activated cements, although their activity varies widely and has yet to be fully explained.

Chang [5] added H_3PO_4 as a retarder in sodium silicate-activated BFS systems, and found a very strong concentration sensitivity, with little effect below 0.78 M H_3PO_4 concentration, and a slight influence between 0.8 and 0.84 M, but an extremely strong retarding effect (6 h increase in setting time) at 0.87 M. The inclusion of 0.87 M phosphoric acid also reduced early age compressive strength and raised drying shrinkage. The combined use of phosphoric acid and gypsum blocked phosphoric acid-mediated retardation, affected compressive strength development in much the same way as phosphoric acid alone, and unlike gypsum alone, failed to reduce drying shrinkage. The chemical mechanisms underlying this behaviour are probably related to those identified by Gong and Yang [6], who observed that the

strong retarding effect of a relatively high concentration of sodium phosphate in alkali silicate-activated BFS-red mud blends was attributable to the precipitation of $\text{Ca}_3(\text{PO}_4)_2$, which withdrew calcium from the reacting system and thus retarded setting. Lee and van Deventer [7] identified K_2HPO_4 as a very effective retarder for alkali-silicate activated fly ashes, with no loss of 28-day strength. However, Shi and Li [8] found no notable retardation effect when incorporating Na_3PO_4 in the alkali activation of phosphorus slags. It has also been reported that borates and phosphates can be used as accelerators in medium strength alkali-activated BFS cements [9].

Recently, Bilim et al. [10] have shown that the use of an (unspecified) retarder has a much lower impact on the setting time of alkali silicate-activated BFS than on OPC mortars. The retarding effect of this polymer decreased with the increase of the silicate modulus of the activator, and at the same time the polymer showed a positive effect on the workability during the initial 60 min. These authors concluded that this admixture retarded early strength development, but had no impact on the later mechanical strength of the mortars.

The use of borates as retarders for Portland cements is well known [11]; attempts have also been made at incorporating borates into alkali-activated Class C fly ash systems which would otherwise show inconveniently rapid setting behaviour [12], although concentrations exceeding 7 wt.% by binder mass were shown to be required for a significant effect on setting time, and the strength of the binders was affected detrimentally at these concentrations. Tailby and Mackenzie [13] developed an innovative use for the borate retardation of aluminosilicate gel formation in the reaction of a blend of sodium silicate, calcined clay and clinker minerals; borate retardation of aluminosilicate gel formation provided advantages in enabling the clinker components to hydrate, and thus enhanced strength development of the hybrid binder formed.

As in Portland cement systems, the inclusion of 4 % NaCl accelerates the activation reaction in alkali silicate-activated BFS using a 1.5 M $\text{Na}_2\text{Si}_2\text{O}_5$ solution as activator [9]. However, in the same system, the addition of 8 % of the salt was observed to retard and nearly halt the reaction, as well as the development of mechanical strength. Brough et al. [14] observed acceleration due to NaCl at levels up to 4 %, but retardation above this, in silicate-activated BFS pastes, while malic acid was shown to be a much more efficient retarder. In another silicate-activated BFS system [15], little effect of NaCl on setting time was observed up to a 20 % addition, beyond which point the setting was significantly retarded; there was limited influence of NaCl on the final strength development. However, the influence of the addition of such large quantities of chloride in the context of reinforced concretes must be considered potentially troublesome in the long term [16]; these mixes should be considered mainly suitable for use in unreinforced applications, or where steel is not the reinforcing material (e.g. with synthetic fibre reinforcing).

Lee and van Deventer [7, 17] tested a range of salts in alkali-silicate activated fly ash systems. Their results for Mg and Ca salts are summarised in Fig. 6.1; the calcium salts generally showed an accelerating effect, while magnesium salts showed little effect. They also observed that KCl and KNO_3 both retarded setting. Provis et al. [18] studied the influence of caesium and strontium salts on the kinetics of

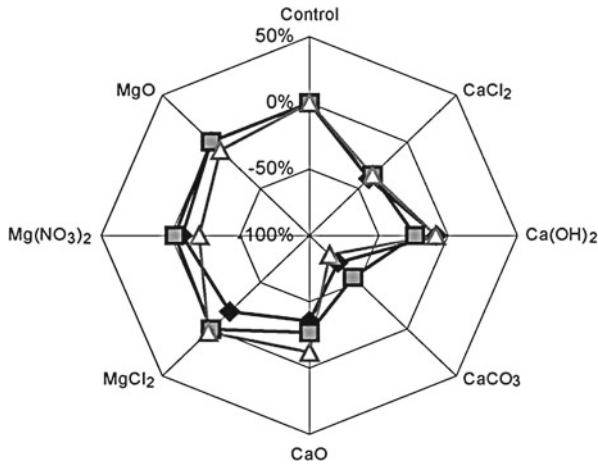


Fig. 6.1 Effects of addition of 0.09 M calcium and magnesium salts on the Vicat final setting time of three different fly ash/kaolinite blends (each set of symbols reflect a different ash/kaolinite ratio), activated by a mixed Na-K silicate solution (Adapted from Lee and van Deventer [17])

metakaolin-sodium silicate systems, and found that nitrates and sulfates showed a retarding effect initially, but then interfered with the later stages of gel formation and gel structure, leading to a more porous and permeable gel than was obtained in their absence. These effects were much stronger for nitrates than for sulfates. Conversely, and related to the discussion of sulphate activation in Chaps. 3, 4 and 5, many authors including Douglas and Brandstetr [19] have shown a significant accelerating influence of Na_2SO_4 in their alkali silicate-activated BFS binders, which again highlights the differences between high-Ca and low-Ca binder systems in terms of strength development and the influences of different components. The potential formation of AFm and AFt-type phases in the presence of calcium, aluminium and sulfates is particularly important in the discussion of the role of sulfates in AAM binders [20]; the formation of such phases is much less prevalent in the absence of elevated calcium concentrations.

Alternative setting regulators which have been shown also to have some influence in AAM systems include tartaric acid and various nitrite salts [21, 22], although there is often also some influence on final strength. Pu et al. [23] also developed a proprietary inorganic setting regulator named YP-3 specifically for alkali activated BFS binder, which was reported to prolong the setting time from 70 to 120 min without significant loss of strength. Rattanasak et al. [24] used various organic and inorganic admixtures, including sucrose, to achieve enhancement of the strength of high-calcium fly ash activated by sodium silicates. Sucrose showed no effect on initial setting time, but delayed the Vicat final set and enhanced the compressive strength of the materials. Finally, C_{12}A_7 showed a significant reduction in the setting time of fly-ash activated binders although it decreased 28-day mechanical strength [25].

6.4 Water-Reducing and Superplasticising Admixtures

The “F-Concrete” developed and patented in Finland [26, 27] was perhaps the first alkaline binder in which the use of a water-reducing admixture, in this case a ligno-sulfonate, was attempted. However, the studies conducted in this regard did not explain the behaviour of these admixtures in activated systems. Douglas and Brandstetr [19] also reported that neither lignosulfate nor naphthalene sulfonate type superplasticisers were effective in their alkali-silicate activated BFS paste systems. Wang et al. [28] also observed that lignosulfonate-based admixtures reduced compressive strength without improving workability.

However, Bakharev et al. [3] reported that lignosulfonate-based admixtures behaved similarly in Portland cement concrete and waterglass- or NaOH and Na_2CO_3 -activated BFS systems, i.e., raising concrete workability while retarding setting and mechanical strength development. These admixtures also reduced drying shrinkage slightly. In the same study, naphthalene-based admixtures raised the workability of waterglass- or NaOH and Na_2CO_3 -activated BFS concrete in the first few minutes, but subsequently induced rapid setting. Moreover, these admixtures reduced later age mechanical strength and intensified shrinkage, leading several authors to conclude that their use in alkali-activated BFS concrete is detrimental.

As a part of the same research program, Collins and Sanjayan [29] studied the effect of a calcium and sodium gluconate water-reducing admixture on blast furnace BFS mortars and concretes activated with a mix of NaOH and Na_2CO_3 . In this case, mortar workability was improved, and was observed to be better than in 120-min cement. The admixture lowered 1-day strength, however, and the higher its content, the steeper was the decline. Additionally, the retarder was expressed from the samples along with the bleed water, which led to significant softening of the surface concrete.

Puertas et al. [30] studied the effect of vinyl copolymer- and polycarboxylate-based superplasticisers on BFS and fly ash mortars and pastes activated with waterglass. These authors concluded that the inclusion of 2 % of a vinyl copolymer-based admixture reduced mechanical strength in 2- and 28-day activated BFS mortars (Fig. 6.2), failed to improve paste flowability, and retarded the activation process. By contrast, a polycarboxylate-based admixture had no effect on mortar mechanical strength behaviour or the activation mechanism, although it did improve paste flowability. Their study also showed that the nature of the superplasticiser had a visible effect on the activation process and behaviour of alkali-activated BFS cements, while those effects were much less intense in alkali-activated fly ash systems. Similar conclusions were drawn in the study conducted by Criado et al. [31] on the impact of a superplasticiser on activated fly ash paste rheology.

Recently, Kashani et al. [32] have developed comb-structured polycarboxylate admixtures which provide a reduction in yield stress of up to 40 % in sodium silicate-activated BFS binders, but these molecules were tailor-designed in the laboratory and are not yet commercially available. Molecules of relatively similar chemistry were seen to give either a decrease or increase in yield stress depending on the

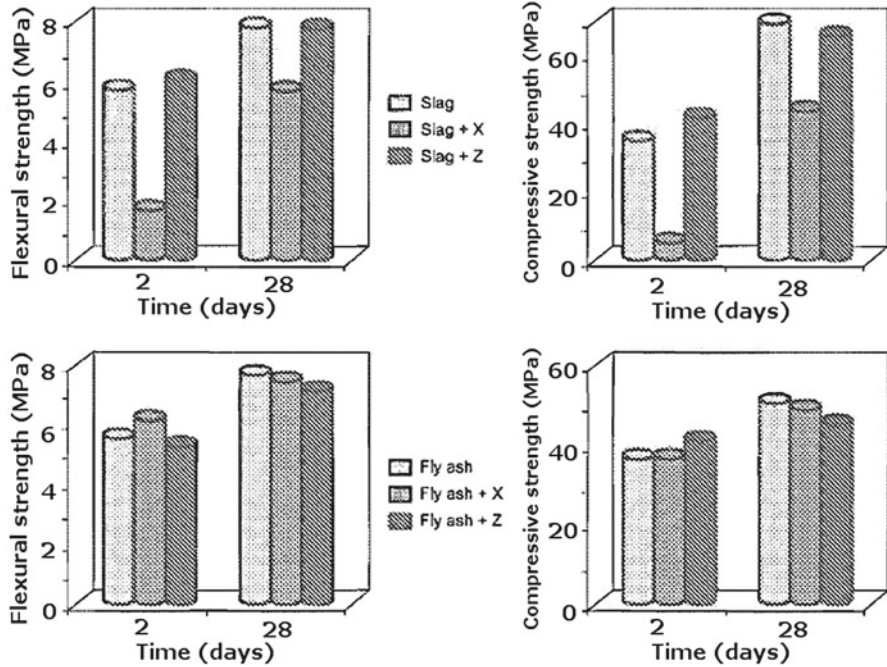


Fig. 6.2 Mechanical strengths of alkali silicate-activated fly ash and slag mortars at 2 and 28 days, with addition of vinyl copolymer (“X”) and polyacrylate copolymer (“Z”) superplasticisers (Adapted from Puertas et al. [30])

details of the molecular architecture, while molecules with both anionic and cationic backbone charges were able to show an effective plasticising effect.

Sathonsaowaphak et al. [33] reported that the use of naphthalene admixtures at a naphthalene/ash ratio of 0.01–0.03 raised workability slightly while maintaining mechanical strength in alkali-activated bottom ash mortars, but had an adverse effect on mechanical strength when the ratio was increased to 0.03–0.09. Studying metakaolin-activated paste, mortar and concrete workability in the presence of polycarboxylate and sulfonate-based superplasticisers, Kong and Sanjayan [34] found that mix workability was scantily improved and concrete fire resistance declined. However, Hardjito and Rangan [35] found that up to 2% addition of a naphthalene sulfonate superplasticiser gave an improvement in slump in their (initially relatively low-slump) fly ash/sodium silicate AAM concretes without a decrease in 3- or 7-day compressive strength.

Palacios et al. [36] studied the interaction of several superplasticisers with alkali-activated BFS cements, and showed that melamine-based, naphthalene-based and vinyl copolymer admixture adsorption on alkali-activated BFS pastes was 3–10 times lower than on OPC pastes and independent of the pH of the admixture solution used. The slightly more negative zeta potential of the pH 11.7 NaOH-activated BFS

suspensions studied (approximately -2 mV) than the zeta potential of OPC suspensions (approximately $+0.5$ mV) was put forward as a partial explanation of the differences in the adsorption behaviour of the two cements.

These authors also found the effect of the admixtures on the rheological parameters of alkali-activated BFS to depend directly on the type and dosage of the superplasticiser, as well as on the pH of the alkaline activator solution. The only admixture observed to decrease the rheological parameters in pH 13.6 NaOH-activated BFS was naphthalene-based. Dosages as low as 1.26 mg naphthalene/g BFS were observed to induce a 98 % reduction in yield stress. However, none of the superplasticisers enhanced flowability when a waterglass solution was used the activator [36–38].

An explanation for such singular behaviour in superplasticiser admixtures in alkaline cement systems was proposed by Palacios and Puertas [39]. These authors studied the chemical stability of different types of superplasticiser admixtures (melamines, naphthalenes, vinyl copolymers and polycarboxylates) in highly alkaline media and concluded that all except the naphthalene admixture in an NaOH environment were chemically unstable at $\text{pH} > 13$. At such high values, vinyl copolymers and polycarboxylate-based admixtures underwent alkaline hydrolysis that altered their structure and consequently their dispersing and fluidising properties.

Given the results reported in the literature, therefore, it is clear that new superplasticiser admixtures, chemically stable at the high pH levels prevailing in AAM systems, must be developed to enhance AAM cement, mortar and concrete flowability. Some of the retarding effects which are often observed when adding commonly-used Portland cement superplasticisers to AAM concretes should also be addressed in the development of these admixtures; sometimes this retardation is desirable in terms of reducing slump loss, but sometimes it can cause excessive delays before setting.

6.5 Shrinkage Reducing Admixtures

One of the most important technological problems posed by many alkali silicate-activated BFS mortars and concretes is the high chemical and (especially) drying shrinkage rate often observed, as will be discussed in detail in Chap. 10 of this report. These rates may be up to four times higher than in Portland cement concretes prepared, cured and stored under the same environmental conditions [40]. Although not falling strictly within the category of admixtures, a number of methods based on the use of different types of fibre (acrylic, polypropylene, carbon or glass, including some specially designed for this purpose) have been used as a physical approach to mitigating this problem [41–44]. The development of fibre-reinforced AAM products is addressed in detail in Chap. 12 of this report.

Scarcely any studies have been published on the effect of shrinkage reducing admixtures on activated BFS systems. Bakharev et al. [3] reported that some standard (but chemically unspecified) shrinkage-reducing admixtures, along

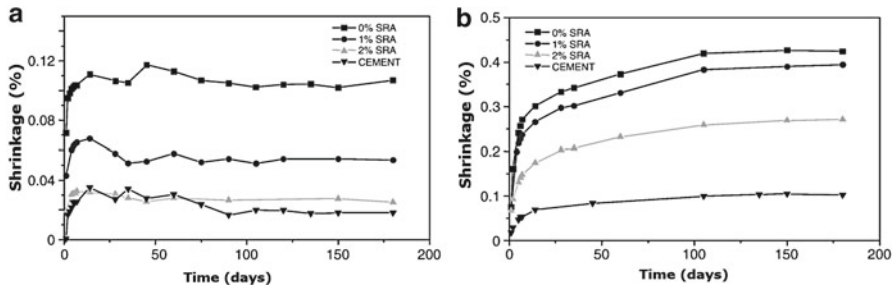


Fig. 6.3 Shrinkage in waterglass-activated BFS mortars, with and without SRA addition, under different curing conditions: (a) RH=99 %, and (b) RH=50 % (Adapted from Puertas et al. [43])

with air-entraining admixtures, could reduce drying shrinkage to less than that of a standard OPC mix (with no admixtures). These authors also stated that the reduction of drying shrinkage in BFS concrete with the addition of gypsum was attributable to the expansion induced by ettringite and monosulfoaluminate formation, which offset such shrinkage, but which is not a mechanism that is available in most AAM systems.

Palacios and Puertas [37, 45] found that shrinkage-reducing admixtures (SRAs) based on polypropylene glycol reduced autogenous shrinkage by 85 % and drying shrinkage by 50 % in waterglass-activated BFS mortars (Fig. 6.3). The beneficial effect of SRAs on shrinkage was observed to be due primarily to the decline in the surface tension of the pore water and the change induced in the pore structure by the admixture. Specifically, the presence of the admixture induced the formation of larger pores, raising the percentage of pores with diameters in the 0.1–1.0 μm range, where capillary stress is much lower than in the smaller capillaries prevailing in mortars without the admixture. The SRA was observed to retard the alkali activation of BFS, with longer delays at higher dosages of the admixture, but its addition did not modify the mineralogical composition of the pastes.

6.6 Conclusions

In conclusion, it can be seen from a survey of the available literature that the majority of the commonly-available admixtures which are used in Portland cement-based materials, and which have been developed over several decades to provide detailed control of the rheological properties as well as hydration process of Portland cement systems, are either ineffective or detrimental when added to alkali-activated binder systems. This is predominantly due to the very different chemistry of the alkali-activation process when compared with the hydration of Portland cement, and in particular the high pH conditions prevailing during the synthesis of most alkali-activated binders. The depth and breadth of scientific information available in this

literature are not high, although some high-quality scientific studies have become available within the past decade, and there are many key areas which require further detailed analysis from a fundamental standpoint. It is likely that the development of specific organic additives designed for the particular chemical conditions of alkali-activation will be necessary for future developments in this area to enable the full potential of chemical admixtures in alkali-activated binders to be unlocked.

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Chapter 7

AAM Concretes: Standards for Mix Design/ Formulation and Early-Age Properties

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7.1 Introduction (Standardisation Philosophies)

RILEM TC AAM was initiated in 2007 to bring together leading alkali activation practitioners from academia, government laboratories and industry in an international forum, to develop recommendations for the future drafting of standards that are specifically applicable to alkali activated materials.

It has been recognised that innovative and non-conventional technology is difficult to transfer to practice, as existing standards do not allow for new technology, and new standards do not yet exist [1]. In the case of alkali activated material (AAM), it does not conform to most national and international cement standards, as they are mainly inherently based on the composition, chemistry and hydration products of Ordinary Portland Cement (OPC) or OPC-blended cement. Existing cement standards are mostly prescriptive regarding cement compositions, and therefore tend to

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rule out non-traditional binders in favour of OPC and OPC-based products. These standards, though, were developed after OPC had gained significant uptake in the construction market.

In general, standards help to regulate products that are already accepted in the marketplace, ensuring that consumers purchasing a generic product class can be confident that the product has generic qualities, which in turn aids with procurement and in meeting regulatory requirements. They also provide product manufacturers with a market-wide minimum specification that drives competition, efficiency and facilitates innovation around those minimum performance criteria [2] – but in general without providing strong incentives for *maximum* performance. Cement and concrete standards, including specifications, methods of testing, recommended practices, terminology, uniformity, and so on, are living documents which normally are reviewed and amended every number of years (e.g. 5 years in the Canadian CSA system). Their content is derived from the properties of materials manufactured and utilised as recommended, not from a priori technical requirements. Therefore, to change an existing standard which has been born out of the historical performance of a necessarily commonplace product, or to initiate the drafting of a new standard, can be (and usually for good reasons is) a very long process. Although there are many performance tests for Portland cement and concrete, as most properties are in many ways physically or chemically linked to cement content and hence ‘strength’, with the standardisation and categorisation of the chemistry of cement over time, there are only a limited number of performance tests (e.g. setting time, strength, and soundness) which cannot be at least implied by strength grade and class. Directly, the need for a very narrow range of cement tests and standards is now widely accepted, to describe with confidence to the market the performance of cement and concrete. Unless there is a fundamental change in the current understanding of relationships between numerous properties of cement and concrete and generic strength grades and classes, cement standards will likely stay largely prescriptive and leverage assumed properties from a few key pieces of test information.

If producers would like to commercialise AAM and introduce it to the market, it is essential that over time new standards are generated that are able to provide the market with confidence in the quality of the product based on cheap, rapid and easily generated information. At this stage, as has been clearly demonstrated by numerous groups working in AAM development, and by their publications (including those summarised throughout this Report), there are various ways to produce and utilise AAM. For example, it is possible to use different raw materials (e.g. slag, fly ash, pozzolans), alkali activators (e.g. alkali-silicate, alkali-hydroxide, alkali-carbonate and alkali-sulfate), production by grinding, blending, or directly mixing in concrete, and application to repair mortars, ready-mix concrete or precast concrete. The large variety of approaches makes it seem almost impossible to prescribe this class of new materials in the same narrow compositional and procedural way that has been adopted by the OPC market over the last 150 years.

It is implicit in maintaining a high degree of flexibility in manufacturing methods and compositions that it becomes complex to provide simple and rigid standards. It would be easy to provide standards for a single method and composition

for AAM, but this would then remove the inherent flexibility and potential for innovation of the technology. Over time track-record and other factors may well see a prescriptive path become favoured for the development of standards for AAM, as has been the case in the Ukrainian market as will be discussed in detail below. However, at this early stage in the broader market-based utilisation of the technology, the opinion of the TC is that a more flexible and open approach should be followed where possible.

Among the existing EN and ASTM standards, there is only one performance based cement standard, ASTM C 1157 [3], which has no restrictions on the composition of the cement or its constituents. An AAM concrete may thus be able to be qualified as an ASTM C 1157 cement based on its specific performance, e.g. general use (GU), high early strength (HE), etc. However, the general acceptance of ASTM C 1157 by the market or authorities is still limited; there is regulatory acceptance in only a handful out of 50 states in the USA. Beside these two main streams of cement standards, there are other national standards which may be applicable to the use of AAM, e.g. Canadian standards (CSA A3004-E1, with highly significant performance-based provisions [4]) and former USSR and Ukrainian standards (an extensive prescriptive framework including [5–13]).

As is stated in the Australian Standard AS 3972 Appendix A [14]: *although prescription-based specifications are convenient, this convenience is achieved at the expense of innovation and being able to easily incorporate new or advanced knowledge. The three most essential elements for the development of performance-based standards are:*

- (a) *performance parameters: usually the properties that best relate to the desired performance*
- (b) *criteria quality levels of the required property that yield the desired performance*
- (c) *test methods: clear, reliable, easy-to-use, inexpensive methods of testing which determine compliance with the criteria*

7.2 The Proposal of TC 224-AAM – A Performance Based Approach

Based on the assessment of current existing and relevant standards for AAM, as detailed throughout this Report, the TC agreed to develop recommendations for standards using a predominantly **performance based approach**. To avoid the challenging and time consuming processes involved in creating entirely new testing standards, future AAM standards should be derived largely from existing standards (particularly testing methods) wherever possible.

As has been shown by the leading researchers and practitioners, there are two possible pathways to the production of alkali activated concrete – either to first produce an alkali activated binder then mixing with water, sand and aggregate to form a concrete, or to directly produce alkali activated concrete by mixing all of the binder

components with water, sand and aggregate without first producing a distinct binder. Therefore, **two lines of recommendations** have been drafted: standardisation for **alkali activated “cement”** and standardisation for **alkali activated “concrete”**.

The recommendations for alkali activated cement will include the following important topics:

- the definition of alkali activated cement,
- examples of suitable mineral components and activators,
- classification based on the properties before and after hardening,
- requirements on the information which should be provided to the customers, and
- testing methods

In order to incorporate scope for future developments into the AAM standards, it is suggested not to prescribe the materials to be used, but rather to define the basic performance requirements which must be met by the materials. With regard to the various aspects of durability, it is not necessary to regulate these in the alkali activated binder standard, but these will rather be discussed directly in a performance based standard for alkali activated concrete.

Similarly, the recommendation for alkali activated concrete addresses these essential subjects:

- definition of alkali activated concrete,
- effective constituents (e.g. alkali activated cement, and/or mineral components, activators, water, fine and coarse aggregate, and/or chemical admixtures) and mix proportioning,
- fresh and hardened concrete properties which satisfy performance requirements,
- durability tests (including applicable existing testing methods) and the performance requirements which must be achieved for each, and
- health and safety issues

7.3 Standardisation of Alkali Activated Binders

7.3.1 *Scope*

This document deals with the standardisation of alkali activated binders to be used in mortars or concretes. It is not in any way meant to become a standard itself, but should instead be regarded as a recommendation on how to create a standard for this class of materials.

As the general class of alkali activated binders covers a very broad range of materials, and the range of suitable materials is far from fully explored, the development of a performance based standards regime (e.g. similar to ASTM C 1157 [3] or CSA A3004-E1 [4]) instead of a set of prescriptive standards (such as EN 197 [15] or ASTM C 150 [16]) is essential. This will mean that future developments can more easily be incorporated into standardisation.

7.3.2 Definition – Alkali Activated Binder

An alkali activated binder is composed of one or more mineral components containing aluminium and silicon oxides, and generally one or more activators. The activators will contain alkali metal ions and will generate an elevated pH environment (e.g. alkali silicates, hydroxides, sulfates or carbonates).

Mineral component(s) and activator(s) can be premixed as a dry binder. This premixed binder can then be mixed with water, sand, aggregates and other components to obtain a mortar or concrete. Alternatively, the activator can be added separately to the mineral component(s) as an aqueous solution. This two-component binder can then be mixed with additional water (in the case that the alkaline activator is a concentrate), sand, aggregates and other components to obtain a mortar or concrete. Other integrated, self-activating processes have also been proposed, and over time novel methods not contemplated here may become popular. Ultimately, though, all process routes result in an alkali activated binder, which may be sold separately, e.g. to a mortar or concrete producer, and thus should be standardised.

There is also the possibility of producing alkali-activated concrete by directly mixing mineral binder component(s), activator(s), water, sand, aggregates and other additions such as admixtures or fillers without first producing a separate alkali-activated binder. This kind of material is not within the scope of this section of the Report, but is covered in Sect. 7.4 to follow.

7.3.3 Examples of Suitable Mineral Components and Activators

The nature of the materials to be used should not be specified, as a performance based standard is targeted. A certain minimum content of reactive silica and alumina might be recommended for good reactivity (although agreement on a definition and test for ‘reactive’ would be required here), as well as a maximum level of free lime to avoid flash setting. However, it must be ensured that no harmful materials can be used; a disclaimer similar to that which is included in ASTM C 1157 ([3], section 1.5) could be sufficient. One could also refer to respective national laws and guidelines. The standard should provide a list of suitable materials.

Suitable mineral components are, for example

- ground granulated blast furnace slags (e.g. according to EN 15167-1 [17] or ASTM C989 [18]),
- silica-containing fly ashes (e.g. according to EN 450 [19], or type C or F ashes according to ASTM C618 [20]),
- calcined clays,
- non-granulated blast furnace slags, granulated slags of other processes (non-ferrous metallurgy, manganese ferroalloys, man-made and natural aluminosilicate glasses),
- other aluminosilicate-containing materials including natural pozzolans, bottom ashes, fluidised bed combustion ashes, and others.

Suitable activators are, for example:

- alkali silicates,
- alkali hydroxides,
- alkali sulfates, or
- alkali carbonates.

The use of other alternative activators is certainly technically possible, but is too technically immature to warrant discussion in the context of standardisation at this point. The suitability of different solid-activator combinations is summarised in Chap. 1 of this report, and discussed in more detail in Chaps. 2, 3, 4 and 5; the discussion will not be recapitulated here. For other possible material combinations, national standards on alkali activated binders (particularly those from the former USSR, including [5–13]) can be consulted.

7.3.4 Classification and Requirements

Alkali activated binders should be classified according to their performance, as this makes it easier for the concrete producer to design a product, and for the general market to specify and understand what they are purchasing. Also, the customer should not be asked to buy a “black box” material system. It should also be stated that the material should be of a sufficient soundness, although we prefer to define this term according to the results of performance testing according to specific degradation mechanisms rather than in a general sense.

The following data and information should be provided to the customer (some of these to be provided only upon request, where noted):

Raw materials (upon request)

- Origin of material(s)
- Elemental composition, loss on ignition
- Mineral composition, X-ray diffraction analysis
- Density, specific surface, sieve residue (e.g. 45 μm)

Properties before hardening (classification)

- Workability, rheological properties (e.g. flow curve, spread diameter), upon request
- Setting time at a given temperature (some materials set very slowly and need heat treatment), e.g. penetration test
- Heat of hydration

Properties after hardening (classification)

- Mechanical properties (early, late), definition of mix composition and curing conditions needed
- Compressive strength (early, late)
- Flexural strength, upon request

- Tensile strength, upon request
- (potentially) Shrinkage and/or creep under specified conditions

It could be convenient for the customer to introduce strength classes, e.g. similar to ASTM C 1157 [3]. However, if strength classes or other prescriptive limits are defined, regulations concerning conformity are needed in the standard. Strength classes should also include the curing temperature, as some slow reacting AAMs such as those based on some fly ashes will often need heat treatment for acceptable strength development rates to be achieved. If strength classes are used in the standard, there should also be a strength class “not classified” in order not to exclude some low strength materials or those with somewhat higher variations in performance which could still be used for certain applications (hydraulic road binders, non-classified concrete, etc.). However, in general a minimum requirement should be given in order to ensure the quality of the final concrete product, together with a limit on variation of performance.

Durability of alkali activated binders should not necessarily be regulated in the binder standard, but rather directly in a performance based standard for alkali activated concrete; more work is required in the area of test method development and validation before this can be achieved with full confidence, and this falls within the remit of RILEM TC 247-DTA, established 2012.

7.3.5 Testing

The designation of suitable testing methods is within the scope of RILEM TC 224-AAM, and will be presented in detail in Chaps. 8, 9, 10 and 11 of this Report. However, we do note here that when a standard for AAMs is created, it is necessary to decide whether to establish separate standards for materials and testing methods, or to create a standard containing both; the preferences here may differ between jurisdictions. It is also recommended that testing of mortars, e.g. for strength, should refer to volume based mix compositions at a fixed consistency (although the definition of this term as it applies to AAMs is another issue requiring careful attention), instead of mass-based mix designs with fixed water/cement ratio as used in EN 196-1 [21] and other standards.

7.4 Standardisation of Alkali Activated Concrete

7.4.1 Scope

This section deals with the standardisation of alkali activated concretes (AACs). It presents guidelines along with some recommendations to create standards for the new and future generations of AACs. Alkali activated concretes are not widely

investigated as traditional concretes; thus, a performance based standard should be adopted to provide scope for future developments, and also to protect end-users against poorly-understood material systems which may fall within the bounds of a prescriptive standard based on compositions alone.

7.4.2 Definition – Alkali Activated Concrete

An alkali activated concrete is composed of one or combined mineral components based on aluminosilicates or calcium aluminosilicates, one or combined alkaline activators (e.g. alkali silicates, hydroxides, sulfates or carbonates), water, fine and coarse aggregates, and with or without chemical admixtures that may be added according to the intended utilisation of the material and with regard to their compatibility with the activators. According to this definition, each constituent should be selected based either on the general performance of the concrete, or a given effect of this constituent on the overall performance of the concrete.

7.4.3 Effective Binder Formulation

The efficient triple combination of mineral component(s), activator(s) and water to form a binder should be formulated according to the conditions of activation (at ambient temperature or with external heat input), and also with consideration of the performance of this binder in paste and mortar mixtures.

7.4.4 Binder to Fine Aggregate Ratio

The optimum sand-to-binder ratio should be determined based on the ultimate strength (determined according to a selected standard test method, e.g. ASTM C109/C109M [22]) at a given age (possibly defined as equivalent maturity according to some scale based on reaction progress, rather than strictly by chronological age), of different mixtures with different sand-to-binder ratios. This optimum ratio can be used in the calculation of raw mixture composition. It is important to designate a flow value for all tested mixtures, instead of being based on the water-to-binder ratio, although this value may in the end not be identical to the desirable values for Portland cement due to fundamental differences in rheology. Workability should be defined based on a flow table test, and a reference flow value can be selected (e.g. ASTM C230/C230M and C1437 [23, 24], or EN 12350-5 [25]). Any ratio satisfying the target performance could be chosen, but a systematic optimisation of fine and coarse aggregates should be proposed.

7.4.5 Calculation of Raw Mixture Composition

The ACI method for absolute volume concrete mix design (ACI Recommended Practice 211.1 [26]) is considered applicable, and is widely used in North America. Densities of solid activator(s), as well as their water contents, should be determined. The solubility of solid activator(s) in water and the density of the final mixing solution should be measured to calculate the volume.

7.4.6 Effect of Quality of Mixing Water

The quality of mixing water is important if it has a remarkable effect on the solubility of activator(s) (ASTM C1602/C1602M and D1193 [27, 28], and EN 1008:2002 [29]). Generally, mixing water quality has an important effect on the overall quality of concrete, and should be ensured in AAMs.

7.4.7 Effect of Mixing Procedure on Slump and Compressive Strength

Mixing protocol has a remarkable effect on the slump and its retention, as well as the final compressive strength [30, 31]. The mixing method that is shown in test work to result in the most efficient activation of the mineral component(s) should be adopted. Two methods can accordingly be suggested:

In the first method, the activator(s) is/are added into mixing water. In the beginning, fine and coarse aggregates are premixed with a small amount of the activator solution for time t_1 . The mineral component(s) is/are then added into the mix and the remaining activator solution is gradually introduced; these constituents are mixed for time t_2 . After a rest period of time t_3 , mixing is resumed and continued for time t_4 . A predefinition of time values of $t_1 - t_4$ has to be established according to the solubility (overall and rate) of the activator(s) in the mixing water, as well as issues related to the initial setting time. This method is widely used in North America.

In the second method, the only difference is that the mineral component(s) is/are added into mixing water solution (water with well-dissolved activator(s)) and are mixed for a given time to initiate the activity of the mineral component(s). Then, the same sequence mentioned in the first method is followed.

In specifying (or recommending while deciding not to strictly specify) mixing protocols for laboratory testing methods for AAM concretes, it is important to simulate, as far as possible, the typical process of concrete production. This means that the solid binder including activator(s), aggregates and potable water are used in a similar way as in commercial concrete production. Most liquid activators are caustic and hazardous, and thus it may be desirable to recommend that their use should be avoided or minimised if

possible in a large-scale production context. Moreover, the heat of dissolution released from some solid activators can be helpful in accelerating the reactivity of some mineral components – but this may or may not be desirable, depending on the mix design, specimen geometry, and intended application. In the case of some activators with low solubility which require some heat input to achieve dissolution within a reasonable time-frame, warm water or any other practical means can be suggested.

7.4.8 Chemical Admixtures and Their Stability in a Fresh Alkali Activated Concrete Mixture

To adjust the workability of alkali activated concrete mixture, a variety of chemical admixtures can be used to improve concrete workability and performance (ASTM C494/ C494M and C260 [32, 33] as well as EN 934 and 480 [34, 35]). However, the stability of some of the chemical admixtures is not yet widely investigated, as the case with traditional concrete, and as was discussed in detail in Chap. 6. The effect of the type and nature of activator, amount of heat input (if required), the type and nature of chemical admixture and the type and nature of activated mineral components should be assessed.

7.4.9 Nature of Aggregates and Sensitivity to ASR

Inertness of the aggregates plays an important role in the quality of concrete. Therefore, sensitivity of aggregates towards alkali-silica reaction (ASR) expansion should be evaluated (e.g. similar to ASTM C1260 and 1293 [36, 37], CSA A23.2-14A and 25A [38, 39], CR 1901:1995 [40] and/or AFNOR P18-588 [41]). Existing concrete performance tests such as AFNOR P18-454 [42] should be evaluated to determine whether they are suitable for AAM concretes; further discussion of this issue will be presented in Chap. 8 of this report. Some precautions should be taken as most of mineral components are sensitive to heat input during activation. The accelerating effect of heat input (according to ASTM and CSA specifications) may lead to misguidance and misinterpretation of the real effectiveness of the mineral components against ASR under the actual activation conditions and curing. Binary and ternary combinations of different mineral components (such as silica fume, Class F fly ash, metakaolin) are also proposed to be used to counteract the expansion due to reactive aggregates.

7.4.10 Concrete Fresh Properties

Requirements for fresh concrete properties that satisfy performance based standards should be adopted. As in ordinary Portland concrete, specific gravity, air content,

slump, temperature and time of setting (e.g., ASTM C143/143M, C231, C403 [43–45], and the EN 12350 series [46]) are used. Curing of concrete test specimens in the laboratory can be carried out according to ASTM C192/C192M [47] or EN 12390 [48], among other procedures, although the issue of the curing environment (sealed, open, immersed or steam) requires attention, and some of the curing methods which are highly desirable for Portland cement products may prove to be inappropriate for AAM specimens due to issues including alkali leaching/washout. The required curing time of alkali activated concrete may vary according to the temperature, setting time and activation conditions. Therefore, curing time should be defined according to the nature and activation conditions of alkali activated concrete mixture. Further research and development work in this area is necessary to determine whether it should be mandatory to fix the curing time to 24 h, or whether it is preferable to instead specify the use of a given time where an acceptable compressive strength is obtained. Heat of hydration is another important property which requires measurement; the validity of the assumptions inherent in testing methods such as ASTM C186 [49] should be considered for the specific case of AAMs. In this case, the use of pre-dissolved (liquid) or solid activators would be expected to give significantly different outcomes, and thus the issue of mixing protocol raised in Sect. 7.4.7 again becomes important.

7.4.11 Concrete Hardened Properties

Hardened properties are usually measured at different curing ages. Different specifications used for ordinary concrete can be used in alkali activated concretes for the measurement of compressive strength, drying shrinkage, flexural and splitting tensile strengths, and other parameters (e.g. similar to ASTM C39/C39M, C426, C78, C496 [50–53], respectively, and also various sections of EN 12390 [48]). Chloride ion permeability, efflorescence, leaching and other durability tests should also be carried out; these are addressed in detail in Chaps. 8, 9 and 10 of this report.

7.4.12 Health Precautions

Effort needs to be taken to ensure awareness of any potential health risks due to contact with AAC, and the required precautions should be precisely verified before starting any contact with alkali activated concrete. Alkali activated cement can be potentially harmful, as in the case of ordinary Portland cement and its blends, as it can contain:

- alkaline compounds (alkali hydroxides and silicates)
- trace amounts of leachable elements that may be dangerous (this should be assessed using leaching tests, and is particularly important for mixes containing fly ash)

The issue of radiation emission, particularly in the form of radon, is an ongoing area of discussion with regard to the use of industrial byproducts (especially fly ash) in concretes [54], and this may also become important in some jurisdictions and in specific applications, but there are many open scientific questions remaining in this area, and so it would seem premature to make specific recommendations related to alkali-activated materials at present.

7.4.12.1 Skin Contact

Any direct skin contact with fresh alkali activated paste or concrete should be avoided; first aid procedures should be described in the Materials Safety Data Sheet supplied with the product.

7.4.12.2 Allergic Skin Reaction, Eye Contact, Inhalation

These three issues should be described separately by specialists according to the nature of the majority of the activators, and also according to the nature of interaction of mineral component with activators (synergistic or antagonistic reaction).

7.5 Survey of Existing Standards Related to AAM

RILEM TC 224-AAM has surveyed the existing cement and concrete standards which are relevant to Alkali Activated Materials (AAM). The following sections summarise the relevance and drawbacks of these standards with regard to AAM.

7.5.1 *Ukrainian and Former USSR Standards for AAM*

Over 60 standards of different status have been developed and implemented in the former USSR and Ukraine between 1961 and 2007. These standards cover various areas, such as constituent raw materials, cement compositions, concrete mix design, manufacturing processes, structures and designs, and recommendations on use in special field. Most of these standards are technical specifications to prescribe the materials which are suitable to be used in the AAM applications, to regulate various types of concrete made with AAM or to guide manufacturing and application processes. Whenever a new type of raw materials became available, they were submitted to the standardisation committee to be investigated and to be further specified for their use in AAM. The wide acceptance of these specifications and regulations helped the industry to successfully drive AAM development and utilisation. One of the important elements of the successful implementation of AAM developed in the former USSR,

which should not be ignored, is the urgent need for alternative construction materials during that period of time when limited OPC was available for the building industry.

These documents have high relevance to the future of AAM standard development, but they are prescriptive and therefore are not aligned with the outline presented in Sect. 7.1 for the initial development of AAM standards. Initial standards will not and should not be targeted to cover all the possibilities of prescribing the materials, formulations, and the methods for how to produce and utilise AAM. The Ukrainian standards provide an excellent showcase of long-term objectives in refinement of specific AAM products and should certainly be utilised as references and examples for choosing suitable raw materials, and in guiding the selection of process parameters.

It is well known that in various jurisdiction areas, drafting and finalising new cement or concrete standards is a time-consuming process as most of the stakeholders, e.g. consumers, manufacturers, government officials, etc., in the standardisation committee must achieve a majority agreement for acceptance. The interests of various stakeholders often focus not only on product quality, health and safety issues but also on commercial and technical (know-how) advantages. This differs from the Ukrainian situation, where a delegated organisation with authority was able to issue the specifications and guidelines; such an approach is not globally scalable. Future national and international standards in the area of AAM must be based on performance criteria and open the potential to integrate or incorporate new technologies.

7.5.2 Australian Standards

Within the current Australian standards framework (AS 3972 [14] and AS 1379 [55]), there is not a primary interest in moving away from OPC-reliant standards, but some optimisation may be possible. Appendix A of AS 3972, as mentioned in Sect. 7.2 above, provides philosophical support for the implementation of a performance-based standards framework in the future. The restriction on the use of non-specified materials (e.g. a broader range of feedstocks such as non-blast furnace slags, bottom ash, and alkali activators) may be able to be opened up by demonstrating practical experience on performance. The scope for the use of hybrid Portland/AAM binders with the Australian standards regime also appears relatively broad; the type GB (general blended) cements have a requirement to contain at least some Portland cement, but a minimum content is not specified. There is a maximum allowable sulfate content of 3.5 % SO₃ specified, which would appear to restrict the use of sulfate activation, but other than this, the degree of prescription in the Standard which would restrict the use of AAMs appears low.

7.5.3 ASTM C1157 – A Performance-Based Cement Standard

ASTM C 1157 covers hydraulic cements for both general and special applications. This is a specification giving performance requirements and it classifies cements by

six types: General Use (GU), High Early-Strength (HE), Moderate Sulfate Resistance (MS), High Sulfate Resistance (HS), Moderate Heat of Hydration (MH), Low Heat of hydration (LH).

This standard gives no restrictions on the composition of the cement or its constituents. Fundamentally, AAM may conform to one of the classified cement types, as long as the performance requirement is met. However, ASTM C 1157 acceptance is currently very limited (only in 5 states, out of 50) in the US.

7.5.4 Canadian Standard CSA A3004-E: Alternative SCMs

CSA A3004-E [4] covers materials other than common SCMs (FA, slag, silica fume) which may be suitable for use in concretes, but which do not completely meet the requirements of clause 5 of CSA A3001 [56]. It specifies the determination of the hydraulic or pozzolanic properties of ASCMs (alternative supplementary cementing materials) as well as the requirements for concrete testing with regard to strength and durability. The evaluation of the materials includes four stages:

1. Characterisation of the Materials – a complete chemical and mineralogical analysis of the material, including environmental assessment. No hazardous waste is allowed to be classified as an ASCM.
2. Determination of Optimum Fineness – when production of ASCMs includes crushing and grinding, optimum fineness can be obtained from compressive strength tests on mortars.
3. Concrete Performance Tests – the performance of ASCMs in fresh and hardened concrete should be evaluated in a broad range of concrete mixtures to reflect the scope of the intended use of the material. A pre-qualification concrete mix should be conducted in combination with local materials prior to use in a concrete project.
4. Field Trials and Long-Term Performance and Durability (3 years) – the performance of ASCMs in fresh and hardened concrete should be evaluated in a broad range of concrete mixtures to reflect the scope of the intended use of the material.

This standard practice may open the door to the new class of materials (ASCMs), potentially including materials which provide alkali-activated cementing properties, to be used in concrete.

7.5.5 EN 206-1: Concrete – Part 1: Specification, Performance, Production and Conformity

Due to the definitions and wording in EN 206-1 [57], it could be possible to use AAM binders in concretes which comply with this standard; it appears that there is not an explicit and strict requirement for cements to comply with EN 197-1 [15], as

the words “general suitability” and “should” are used. However, this lack of an explicit requirement has not been legally tested. In addition, European Technical Approvals (for products which do not conform to any other existing standard) and National Standards/Regulations are allowed to extend the range of binder materials, as is the case in the Swiss National Appendices to these standards, which offer scope for a broader range of binders including alkali-activated materials.

7.6 Analysing Raw Materials

In selecting raw materials for use in AAM binders and concretes, it is important to analyse the likely reactivity (and reaction products) of the raw materials; this reactivity under alkali-activation conditions will likely differ from the reactivity observed when the same materials are added to Portland cements as SCMs. There are many existing standards describing and specifying SCMs as cement components, but it remains to be determined which of these tests are valid under alkali-activation conditions. The analysis of SCMs, including methods for their characterisation, falls within the scope of RILEM TC 238-SCM (initiated in 2011) [58], and is thus beyond the scope of TC 224-AAM. However, some points of interest and importance which have been raised through the work program of TC 224-AAM, and which require attention as a component of future standards development, include the following:

- Which physicochemical parameters of the precursor are actually important?
- Is it possible to give a definition of ‘reactive’ alumina and silica concentrations, or even ‘glass content’, in a fly ash which is relevant to AAM synthesis using the range of available activators – and if so, how can this be achieved in such a way that there is not confusion by comparison to the (undoubtedly different) definitions which are useful in Portland cement blends? Work in this area has utilised HF attack to selectively dissolve glassy phases [59], but for reasons of health and safety, the use of HF as a leaching agent is increasingly being discouraged; it is regulated as a poison in some jurisdictions and so is not able to be widely used. So, is there an alternative test (preferably involving alkalis, to replicate reactivity in alkali-activation) which provides reliable results?
- For the case of slags, is it possible to choose a definition of the slag ‘quality coefficient’ (or a related oxide ratio) which gives reliable predictions of reactivity? There are many formulae which are used at present [60], and they do not agree well with each other, or with material performance in general.
- Should the content of unburnt carbon in fly ash be restricted, or simply commented upon as a potential complicating factor?
- How can (or should) the release of potentially hazardous elements from fly ashes be monitored? This is known to depend on the selection of activator and the redox environment under which leaching takes place [61, 62]; these are not well replicated in most standard leaching tests (see Sect. 8.2).

- What is an appropriate technique for measuring the particle size of different precursors? Blaine fineness [63, 64] is widely used, and the Wagner turbidimeter is also standardised by ASTM [65] – but these methods rarely agree. An additional question which arises is: are these methods sensible for particles with high aspect ratios, such as metakaolin? Sieve residues are also used in some standards. Advanced instrumentation can give reliable particle size distribution information across a very broad range of particle sizes (with appropriate instrumentation used in each size regime), but it is difficult, if not impossible, to incorporate a specific instrument into a standards regime, and different instruments or measurement techniques do not always give exactly corresponding results for complex particle shapes or broad size distributions. Agglomeration during measurement is also potentially problematic. This area is currently under discussion in TC 238-SCM in the context of blended Portland cements, and the outcomes of that TC will be of great value in the application of AAMs also.

7.7 The Importance of Curing

There is widespread debate in the scientific community regarding the most appropriate form of curing to be applied to alkali-activated binders for optimal strength development and durability. There are many scientific publications in this area, including [66–77]; the consensus seems to be that the optimal curing temperature depends on the specific details of the mix design, but it is almost universally agreed that an extended period of sealed curing is important in the development of a dense and durable matrix. As is well known for the case of Portland cement blends with SCMs [78, 79], reactions of these non-clinker materials is slower than the reaction of Portland cements, and the binding of water is generally weaker and/or slower in these lower-calcium systems than in the Ca-rich C-S-H phases and/or calcium sulfoaluminate hydrate phases (AFm or AFt) which are formed through Portland cement hydration. This means that it is even more imperative to control the curing conditions and environments applied to alkali-activated concretes; otherwise, severe carbonation, cracking and/or surface dusting are observed to result. This can be prevented by the provision of adequate curing environments; the definition of ‘adequate’ depends strongly on the mix design and other parameters (both solid precursor and activator nature, as well as water/binder ratio and temperature).

Such behaviour provides challenges in standardisation; curing conditions which are ideal for one product may be entirely unsuitable for another. This is another area in which performance-based specifications have been proposed as an alternative to prescriptive; it may be that the selection of curing conditions prior to testing may need to become more flexible, rather than being explicitly defined in the testing methods, although it may also be that allowing this variability in curing regimes would cause more problems than it solves. This remains an open area of discussion within the TC, as well as in TC 247-DTA, and more broadly in the scientific community.

7.8 Conclusions

The recommendation of RILEM TC 224-AAM is that a performance-based standards regime should be implemented to provide description and regulation of alkali-activated binders and concretes. The standards for binders and for concretes are proposed to be drafted separately, to allow for production of a distinct binder in isolation (e.g. as a dry-mix cement) or for the binder ingredients to be combined directly with the aggregates to form a concrete without first producing a distinct alkali-activated ‘cement’. Some of the existing standards regimes are more amenable than others to making provision for alkali-activated binders within existing standards frameworks; ASTM C1157 in particular is a purely performance-based standard which provides particularly evident opportunities for uptake of AAM concretes if the standard gains more widespread acceptance. Areas in which developments in standardisation are required have been highlighted through the discussion presented in this chapter; there are a number of areas in which a large amount of work is required prior to standardisation, particularly with regard to curing.

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Chapter 8

Durability and Testing – Chemical Matrix Degradation Processes

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8.1 Introduction

This chapter, and the two that follow, are structured to provide an overview of the available test methods for assessment of the performance of construction materials under a wide variety of modes of attack. These are divided, broadly, into ‘chemical’ (Chap. 8), ‘transport’ (Chap. 9) and ‘physical’ (Chap. 10) – and it is noted that this classification is to some extent arbitrary, with a significant degree of crossover between the three categories which is difficult to take explicitly into consideration in a format such as this. Some areas are discussed in far more detail than others, either because they are critical points related to certain areas of alkali-activation technology, or sometimes simply because limited information is available regarding

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some forms of attack on alkali-activated materials (AAMs); biologically-induced corrosion is one such case, where very little information is available in the open literature. These chapters will in general raise questions for future consideration rather than providing detailed answers, due to the limited state of understanding of AAM degradation mechanisms at present, although recommendations will be drawn wherever possible.

8.2 Sulfate Resistance Tests

8.2.1 Introduction

There is a very large amount of information in the literature and existing standards related to test procedures, test results and decay mechanisms regarding sulfate resistance of mineral binders, mortars and concretes. However, as is common throughout most testing methodologies for construction materials, the test procedures are in general inherently designed for systems based on ordinary Portland cement (OPC) and blended OPC binders. In contrast, there is not much information provided on sulfate resistance of alkali activated materials with respect to possible modifications of testing protocols, case studies or deterioration mechanisms. The mechanism of sulfate attack on OPC is reasonably well understood [1, 2], although work in this area is certainly ongoing with respect to the chemical and thermodynamic details of the process, and in development of meaningful accelerated test protocols, as many jurisdictions (including the European Union) still rely on prescriptive regulations rather than performance-based tests in this area. Key aspects to consider, in the context of differences between OPC and AAM degradation under sulfate attack, are related to the role of decalcification of the C-S-H type binder phases and formation of (usually expansive) calcium sulfate-containing degradation products in OPC. The lower levels of calcium present in most AAMs than in OPC are likely to induce differences in the details of this mechanism, and may mean that the test parameters used to measure the performance of OPC under sulfate attack would need to be modified to give a good representation of the likely in-service behaviour of alkali-activated binders.

One of the tasks of RILEM TC 224-AAM has been to specify possible test methods for AAM. These should ideally be as similar as possible to those used for OPC systems, but probably need to be modified to meet the special requirements of AAM (e.g. sample preparation, curing, and other AAM-specific issues). This section presents: (i) a short literature overview on sulfate resistance tests for OPC systems in general, (ii) some case studies on sulfate resistance of AAM, and (iii) some general considerations concerning possible ways to test sulfate resistance of AAM. Attack by sulfuric acid (mineral or biogenic) is not considered in this section, and will be discussed later in this chapter.

The RILEM technical committee TC 211-PAE (Performance of cement-based materials in aggressive aqueous environments) has recently dealt in detail with durability testing including sulfate resistance, and a state-of-the-art report on sulfate resistance of (mainly) OPC based systems has been created. A preliminary version of this report [3] was consulted during creation of this document; the discussion presented here will by no means be an exhaustive summary, and the reader is referred to that document for more detailed discussion. Other key information sources used in the preparation of this section are the CEN report [4] and the Swiss state-of-the-art report [5].

8.2.2 Sulfate Resistance Tests for OPC Systems

In general, testing methods for sulfate resistance can be classified as follows:

1. **External sulfate attack:** This is simulated either by immersion of a specimen in a test solution, or by performing wetting and drying cycles. In both cases, a sulfate-containing aqueous solution (most commonly Na_2SO_4 or MgSO_4) is used. In some testing protocols the solution is renewed during the measurements. External attack tests the “chemical” potential of the binder itself to show expansion due to the formation of expansive sulfate-containing phases, but also the performance of the entire system (paste, mortar, concrete) under this mode of attack, as the porosity of the system influences its behavior under external sulfate attack.
2. **Internal sulfate attack:** In this case the binder is mixed with additional gypsum to make it “oversulfated”. This type of procedure tests the sulfate resistance of the binder only, as the effects of water and ionic transport are excluded by the direct addition of gypsum to the paste or mortar.

The different methods which have been implemented by various researchers worldwide each apply specific testing protocols, which will certainly influence the results obtained. Some of the testing protocols use realistic exposure conditions, whereas others use accelerated conditions such as very high sulfate concentrations or elevated temperatures. Also, various evaluation methods (e.g. expansion, flexural strength) and evaluation criteria are used. The validity of some of the highly accelerated test methods may be called into question by considering the phase chemistry of the sulfate solutions themselves (and the crystalline products of their interaction with cementitious binders) as a function of concentration and temperature. This is a point which is valid across many modes of chemical attack on binder structures, not only sulfate attack, and will be raised throughout various sections of the discussion in this and the following chapters.

Some common testing methods, together with their characteristic features, are listed below.

8.2.2.1 Internal Attack

ASTM C 452 [6]

<i>Designed for:</i>	only OPC (not for blended cements)
<i>Samples:</i>	mortars, with gypsum added up to 7 wt.% SO ₃ in OPC, w/c 0.485 (0.460 for air-entrained mortars), (cement + added gypsum)/sand=2.75
<i>Sample dimensions:</i>	25 mm × 25 mm × 285 mm
<i>Curing:</i>	1 day at 23 °C in mould, then under water at 23 °C, with water exchanged from time to time
<i>Evaluation:</i>	expansion between 1 day and 14 days

Duggan test [7]

<i>Designed for:</i>	OPC concrete
<i>Samples:</i>	Concrete, water/cement=0.40
<i>Sample dimensions:</i>	76 mm × 76 mm × 356 mm
<i>Curing:</i>	thermal cycles (max. temperature 85 °C), then in water, no sulfate addition (testing of delayed ettringite formation)
<i>Evaluation:</i>	expansion after 90 days

Le Chatelier-Anstett test (see [8, 9])

<i>Designed for:</i>	OPC
<i>Samples:</i>	Hydrated cement paste mixed with 50 % gypsum, and 6 % additional water added
<i>Sample dimensions:</i>	Cylinder 80 mm diameter, 30 mm height, moulded by pressing with a force of 20 kg/cm ² (1.96 MPa)
<i>Curing:</i>	water
<i>Evaluation:</i>	expansion after up to 90 days

8.2.2.2 External Attack

ASTM C 1012 [10]

<i>Designed for:</i>	OPC, OPC blended with pozzolans or BFS, blended hydraulic cements
<i>Samples:</i>	Mortars of OPC, w/c 0.485 (0.460 for air entrained mortars, or adjusted to flow for blended/hydraulic cements), cement/sand=2.75
<i>Sample dimensions:</i>	50 mm cubes for controlling strengths, bars 25 mm × 25 mm × 285 mm for expansion testing
<i>Curing and exposure:</i>	1 day at 35 °C in mould, then in lime water at 23 °C until compressive strength >20 MPa, then in Na ₂ SO ₄ solution (50 g/L) at 23 °C. Other solutions possible (e.g. MgSO ₄).
<i>Evaluation:</i>	Expansion in sulfate solution after 12–18 months

CEN Test (see [11])

<i>Designed for:</i>	OPC, blended OPC
<i>Samples:</i>	mortars with $w/c=0.50$, cement/sand = 1:3
<i>Sample dimensions:</i>	20 mm × 20 mm × 160 mm
<i>Curing and exposure:</i>	1 day at 20 °C and >90 % R.H., then under water at 20 °C for 27 days, then storage in Na ₂ SO ₄ solution (16 g/L SO ₄ =24 g/L Na ₂ SO ₄), which is renewed monthly; reference sample in water
<i>Evaluation:</i>	length change up to 1 year

Koch and Steinegger [12]

<i>Designed for:</i>	OPC, BFS-blended OPC
<i>Samples:</i>	mortars with $w/c=0.60$, cement/sand = 1:3
<i>Sample dimensions:</i>	10 mm × 10 mm × 60 mm
<i>Curing and exposure:</i>	1 day in the mould, then 20 days in demineralised water, then in 10 % Na ₂ SO ₄ ·10H ₂ O solution (44 g/L Na ₂ SO ₄); reference samples stay in demineralised water
<i>Evaluation:</i>	sulfate uptake by titration with sulfuric acid against phenolphthalein, flexural strength, visual observation, duration 77 days

Mehta and Gjrrv [13]

<i>Designed for:</i>	OPC, blended OPC (BFS, pozzolan)
<i>Samples:</i>	cement paste, $w/c=0.50$
<i>Sample dimensions:</i>	12.5 mm cubes
<i>Curing and exposure:</i>	50 °C moist curing for 7 days, then in (i) CaSO ₄ solution (0.12 % SO ₃ =2 g/L CaSO ₄) or in (ii) Na ₂ SO ₄ solution (2.1 % SO ₃ =37 g/L Na ₂ SO ₄), renewal of sulfate by titrating with H ₂ SO ₄ against bromothymol blue
<i>Evaluation:</i>	Compressive strength after 28 days

NMS Test (see [11])

<i>Designed for:</i>	mortar and concrete, also concrete removed from service
<i>Samples:</i>	mortar or concrete with $w/c=0.50$, or samples removed from service
<i>Sample dimensions:</i>	40 mm × 40 mm × 160 mm (mortar/concrete), cores of diameter 50 mm and length 150 mm (concrete)
<i>Curing and exposure:</i>	2 days in the mould at 20 °C and >90 % R.H., then 5 days under water, then 21 days at 20 °C and 65 % R.H. Afterwards, saturation in 5 % Na ₂ SO ₄ solution (50 g/L Na ₂ SO ₄) at 150 mbar underpressure, then storage at 8 °C in solution with 50 g/L Na ₂ SO ₄ . Reference sample in water.
<i>Evaluation:</i>	tensile strength after 56–180 days, depending on test setup.

SVA Test (see [14])

<i>Designed for:</i>	Mortar and concrete, also concrete removed from service mortars with $w/c=0.50$, cement/sand=1:3
<i>Samples:</i>	10 mm × 40 mm × 160 mm (mortar), cores of diameter 50 mm and length 150 mm
<i>Sample dimensions:</i>	2 days in the mould at 20 °C and >90 % R.H., then 12 days in saturated lime solution, then at 20 and 6 °C, respectively, in saturated sodium sulfate solution (44 g/L Na ₂ SO ₄). Reference samples in saturated lime solutions at 20 and 6 °C. Replacement of solutions every 14 days. The original procedure only considers testing at 20 °C.
<i>Curing and exposure:</i>	Length change up to 91 days
<i>Evaluation:</i>	

Swiss Standard SIA 262/1 Appendix D [15]

<i>Designed for:</i>	concrete
<i>Samples:</i>	concrete samples in general
<i>Sample dimensions:</i>	cores of diameter 28 mm and length 150 mm
<i>Curing and exposure:</i>	28 days wet curing according to EN 12390-2, then 4 cycles of sulfate loading applied as follows: Drying 48 h at 50 °C, cooling 1 h to 20 °C, 120 h in 50 g/L Na ₂ SO ₄ solution
<i>Evaluation:</i>	length change, weight gain

(Note: This standard is currently under revision, and some details will differ slightly in the revised version)

Wittekindt [8]

<i>Designed for:</i>	OPC, BFS-blended OPC
<i>Samples:</i>	mortars, $w/c=0.60$, cement/sand=1:3
<i>Sample dimensions:</i>	10 mm × 40 mm × 160 mm
<i>Curing and exposure:</i>	2 days in the mould, 5 days under water, then in 0.15 M Na ₂ SO ₄ solution (21 g/L), solution is exchanged at different intervals
<i>Evaluation:</i>	expansion (duration variable, months – years)

8.2.3 Sulfate Resistance of AAM

There are not very many investigations reported in the literature concerning the sulfate resistance of AAM. In general, external sulfate attack using mortar or concrete samples is applied as the test method. Some of the findings are briefly highlighted below.

Early work in Finland [16], and in Canada [17], showed little change in the properties of alkali silicate-activated BFS concretes during 4–6 months of sulfate exposure (in MgSO₄ and Na₂SO₄ solutions), as measured by resonance frequency

analysis, compressive or tensile strength, dimensional stability, ultrasonic pulse velocity, and elastic modulus. However, Kukko and Mannonen [16] showed that test durations of 12 months or more, in 10 wt.% MgSO_4 , did cause disintegration of all test specimens (alkali-activated BFS, OPC and a high-volume BFS-OPC blend). However, with 1 wt.% MgSO_4 , or 1 or 10 % Na_2SO_4 , the samples remained intact and retained (or improved) their compressive strength after exposure periods as long as 25 months.

In the book of Shi et al. [18], a literature review on sulfate resistance of AAM is given, however the test methods are not treated separately. In general AAMs are reported to perform equivalently to or better than OPC, but the performance of the AAM depends strongly on the chemistry of the source material (BFS, fly ash, or others), on the type of the activator, and on the composition and concentration of the sulfate solutions used for testing.

Bakharev et al. [19] developed a sulfate resistance test for AAM on the basis of ASTM C 1012, which was applied to an alkali activated BFS concrete. They used concrete cylinders of 100 mm diameter and 200 mm length, which were cast and cured in a fog room for 28 days. Afterwards, the specimens were immersed either in a 50 g/L Na_2SO_4 or in a 50 g/L MgSO_4 solution, which were periodically replaced. After different exposure times up to 12 months the compressive strength was tested and compared to reference samples stored in potable water. The AAM concretes performed better than OPC in Na_2SO_4 solution, and similarly to OPC in MgSO_4 solution. With sodium sulfate, no visual signs of degradation were found, while magnesium sulfate attack caused gypsum formation and decomposition of the C-S-H. In a second paper from the same researchers [20], the sulfate resistance of alkali activated fly ash was tested by a similar approach. In this case, heat cured pastes were used and immersed in the same solution environments as described above, using compressive strength as the evaluation criterion. It was found that the durability of these AAMs varies notably with the activator type (NaOH activation + heat curing performed best) and with the nature of the exposure conditions.

In the study of Puertas et al. [21], the sulfate resistance of alkali activated BFS and fly ash mortars was investigated using variants of the Koch-Steinegger and ASTM C 1012 methods. Instead of curing under water, curing in a humidity chamber was applied. In general the samples showed sulfate resistance described as ‘good’, with the NaOH-activated BFS being the most sensitive to sulfate attack. Gypsum and ettringite formation was proven in those samples. However, Ismail et al. [22] have shown that the response of alkali-activated BFS-fly ash blends to sulfate attack is strongly dependent on the nature of the cation accompanying the sulfate; Na_2SO_4 immersion caused little damage to the paste specimens, while MgSO_4 caused severe decalcification of the binder, gypsum formation, and loss of structural and dimensional integrity.

Four fly-ash based AAM concretes proved to be sulfate resistant when tested according to Swiss Standard SIA 262/1 Appendix D [23], however a specific non-standard curing regime was applied for the AAM (heat curing at 80 °C, afterwards storage in air). Škvára [24] observed no deterioration of alkali activated fly ash mortars cured for 28 days in a laboratory environment then immersed in solutions

containing 44 g/L Na_2SO_4 or 5 g/L MgSO_4 . Other papers using similar test protocols mainly also report good resistance of AAM to sulfate solutions, e.g. [17, 24–29].

8.2.4 Remarks Concerning Testing Methods for AAM

In general, the testing methods to be used should be close to those applied for OPC and blended OPC systems, as this will help to create acceptance for the durability properties of AAM. Thus, it is proposed that the existing standard tests should only be modified slightly, where necessary, in a way that means that they are applicable for AAM. The modifications should mainly be restricted to the sample preparation and curing, and not to the testing method itself.

8.2.4.1 Testing of External or Internal Sulfate Attack?

The external attack of sulfate containing aqueous solutions on mortar or concrete is the most realistic setup which should be tested. In such tests, the whole system is tested, taking into account also the porosity and permeability properties.

8.2.4.2 Testing the Binder or the Concrete?

The test should be on the concrete, not on the binder, as an AAM concrete can be produced directly from the raw materials without having a distinct ‘binder’ in the sense of an OPC supplied from a silo or in bags. The durability of the final product should be the decisive parameter, where porosity and permeability properties play a role. There is scope for important outcomes to be obtained from laboratory testing of pastes and mortars, but standardisation of concrete tests is preferred.

8.2.4.3 Defined Mix Composition or Concrete “As Is”?

AAM based concretes can have a wide range of composition concerning water/binder ratio, sand/binder ratio and use of admixtures. Thus, the “real” concrete to be applied on the construction site should be tested, not a mortar or concrete of a special mix composition as is defined in some existing testing methods.

8.2.4.4 Curing Before Interaction with Sulfates

Depending on the composition of the AAM, special curing regimes are often applied, including heat curing. Curing under water or in lime water is not always suitable for AAMs, as alkali leaching may result. Moist curing can be used instead.

In general, the curing regime should not be specified in the testing method (other than possibly the sample age, which could be 28 days), but one should use a curing regime suitable for the specific AAM.

8.2.4.5 Testing Sulfate Interaction

Other than this, it is recommended that the test protocols should not be modified, as one needs to measure the performance in comparison to OPC, which means that the same exposure conditions should be applied.

8.2.4.6 Which Test Method Should Be Used?

There are several test methods which appear suitable after slight modification concerning sample preparation and curing, including the ASTM C 1012, CEN, NMS and SVA tests. The sulfate dosages in these tests, and the evaluation method and criteria, however, vary widely, and there are important chemical and physical implications which flow from these differences. It is not possible at present to come to a final conclusion regarding which is the most suitable method (and it is noted that this has not even been achieved for OPC).

8.3 Alkali-Aggregate Reactions

The alkali content of the binder is very critical in relation to alkali-aggregate reactions (AAR) in Portland cement concrete [30]. This reaction can be divided into two categories: alkali-silica reaction (ASR) and alkali-carbonate reaction (ACR). The former takes place between potentially reactive aggregates and the alkalis present in cements, Na_2O , K_2O , and $\text{Ca}(\text{OH})_2$. The reaction product is an alkali silicate gel that swells after absorbing moisture and causes expansion and cracking of concrete [31]. The alkali-carbonate reaction is an expansive de-dolomitisation process resulting from the reaction between dolomite in carbonate aggregates and alkalis in the concrete. It is much less common than ASR.

In OPC concrete, the danger of a damaging ASR reaction is usually minimised by limiting the alkali content of the concrete. A typical restriction when OPC is used is that the alkali content should not exceed 0.6 wt.% $\text{Na}_2\text{O}_{\text{eq}}$ (where the K_2O content is included on a molar equivalency basis) by weight of cement, but it has been noted that the addition of BFS can enable the relaxation of this restriction, and alkali contents exceeding 1 % have been stated to be acceptable when using 50 % or more BFS in a blend with OPC [32, 33]. However, in AAMs, the alkali content is much higher than in PC due to the use of significant amounts of alkali for activation of the BFS or fly ash in manufacturing the AAM. For example, for alkali-activated BFS cement (AAS), the amount of alkali reaches 2–5 % [34]. Therefore, research on

ASR in alkali activated materials (AAMs) has attracted a lot of attention and there is concern that AAMs may be susceptible to ASR.

On the other hand, because of the low calcium content of the initial component materials such as BFS or Class F fly ash, alkali activated binders based on these materials might be expected to exhibit different behaviour to PC with respect to the alkali–aggregate reaction, as the role of calcium in the ASR processes is known to be important in determining the rate and extent of potentially deleterious processes [35].

The following sections review the evidence for ASR in AAM binders, and discuss the existing measurement tests or standards used to predict the potential for harmful expansion.

8.3.1 Test Methods

There is a need to consider the suitability of the commonly used test methods for evaluating the ASR expansion in AAM systems, as well as more broadly for OPC systems, as identified in a recent review paper [36] and through the work of RILEM TC 219-ACS. Many AAM researchers have used the ASTM or Canadian Standard (CSA) methods developed for PC systems. In North America, a number of tests are available for evaluation of the potential alkali reactivity of aggregates, and the reactivity of a particular cement–aggregate combination, such as the mortar bar method (ASTM C227) and the concrete prism test method (ASTM C1293, CSA A 23.2-14). Chemical analysis and petrographic (optical microscopy) methods (ASTM C289 and C295) are also available.

The concrete prism test is regarded as a more suitable and accurate indicator of the performance of the material in actual concrete, since the same mix can be used in laboratory specimens as in a proposed pre-cast concrete product or structure [37]. However, these two concrete testing methods take at least 1 year to complete.

The chemical analysis method (ASTM C289) is a more rapid test method, but it does not give an estimate of the expansion potential of the aggregate. The petrographic method (ASTM C295) for evaluation of aggregates can identify the potentially reactive materials in aggregates, but it cannot provide information on the expansiveness of a particular cement–aggregate combination.

The accelerated mortar bar test (ASTM C1260) is a rapid test method and the results are conservative. It is the most commonly used test applied in evaluating ASR in alkali-activated binders [38–42]. However, this test method, which entails immersing mortar bars in 1N NaOH at 80 °C, is designed for the evaluation of aggregates, not aggregate/cement systems, and its use for an inherently high alkali system such as AAMs seems suspect. Xie et al. [42] considered that this method often gives an overestimated result, even when evaluating aggregates; i.e. an aggregate with satisfactory field performance might be classified as deleteriously expansive when tested by this method.

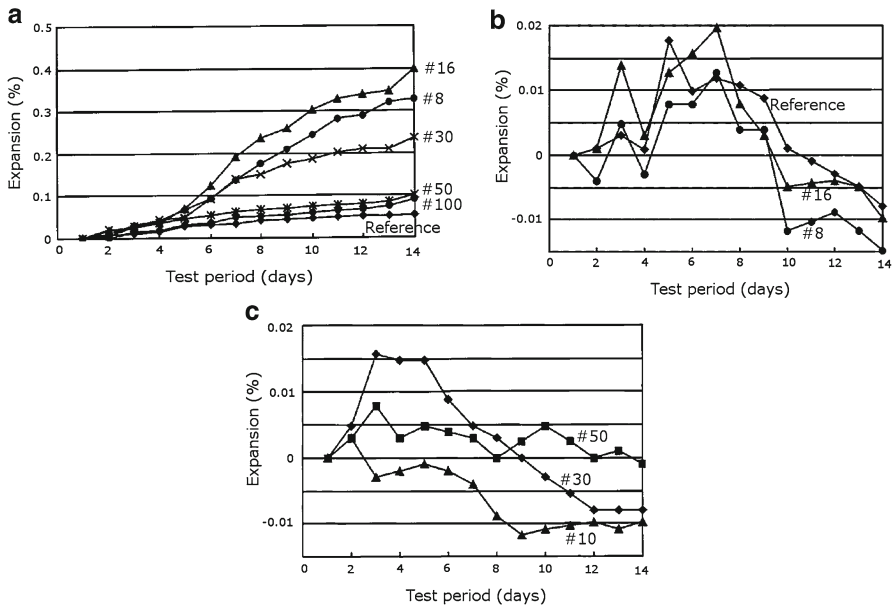


Fig. 8.1 Expansion observed during the ASTM C 1260 test for ASR, with 10 % glass substituted for quartz sand in the aggregate: (a) OPC, and (b, c) sodium-silicate activated fly ash. Aggregates in the mortar samples were graded according to the ASTM C 1260 recommendations, and then the aggregate in a specified sieve size (as marked) was partially (or entirely, for the #8 size) replaced by reactive glass (Plots adapted from Xie et al. [42])

When cements are exposed in a normal environment, the timescales for the autogenous shrinkage and ASR expansion are quite different – autogenous shrinkage occurs during the main hardening period, whereas ASR is a slower and later process, causing long-term expansion. The acceleration provided by the accelerated mortar bar test (ASTM C1260) makes these two mechanisms partially overlap, which apparently affects the estimation of ASR expansion [42]. This is a factor that should be considered when testing for the ASR potential of AAM, as well as for PC mortar. Figure 8.1 shows the lower ASR expansion in alkali activated fly ash in comparison with PC, due to the compensating effect of early-age autogenous shrinkage (seen in particular later in the test period in Fig. 8.1b, c).

In addition, when following the ASTM C1260 protocol, the ASR reaction may occur before the activation of the aluminosilicate precursors has reached a truly representative (or satisfactory) extent. Yang [43] indicated that ASR expansion mainly develops during first 30–60 days, and reaches a plateau thereafter. Some authors [44] have also noted that the initially slow rate of expansion in mortars containing BFS means that the accelerated test method of ASTM C1260 may not be the most suitable test to determine the possible expansion over a more extended service

life due to ASR in these mortars. This test method is designed to permit detection, within 16 days, of the potential for deleterious ASR with use of a particular aggregate in PC mortar bars. However, in AAS mortars, this time is insufficient; if the test is limited to 16 days, deleterious ASR may not be observed, giving a misleading “safe” result for AAS mortars. It has been recommended that the test should continue for at least 6 months in AAS mortars [38], although the interpretation of the results of longer-term testing may also require further validation against OPC and blended OPC samples with the same test duration.

In addition to the ASTM and CSA methods, Ding [45] used a RILEM accelerated concrete prism test (RILEM TC-106; [46]) with a curing temperature of 60 °C, and Al-Otaibi [47] followed the method specified in the 1995 draft of BSI DD218 (note that this standard has been replaced by BS 812-123:1999 [48]), with a test duration of 12 months.

When testing for ASR in Portland cement (PC) based systems, it is common to add extra alkalis to accelerate the reaction. In the ASTM mortar bar test (C227), for example, the alkali content of the test cement is adjusted to 1.25 % $\text{Na}_2\text{O}_{\text{eq}}$. However, in AAMs, since a high alkali content is already present in the initial mix composition, researchers have generally considered that no extra alkali should be added during the test. Generally, sodium silicate, sodium carbonate, sodium hydroxide and/or sodium sulfate are selected as the chemical activators in AAMs, leading to an alkali content of 3.5–6 % $\text{Na}_2\text{O}_{\text{eq}}$ [34, 37, 38, 41, 47, 49].

8.3.2 Results of Tests Using Mortar Bars

Because of its relative speed, the ASTM mortar bar test (C227) (or variants of this procedure) is a popular choice with researchers. The earliest studies of ASR in AAMs [16] used this test method, with a reactive opal aggregate replacing part of the quartz sand, and found less expansion in their “F-concrete” samples than in control Portland cement specimens. Yang and co-workers have assessed the reactivity of alkali activated BFS cements using mortar bars with reactive glass aggregates [43, 50]. Among the sodium silicate ($\text{Na}_2\text{O}\cdot n\text{SiO}_2$), Na_2CO_3 and NaOH-activated BFS cements, $\text{Na}_2\text{O}\cdot n\text{SiO}_2$ -activated BFS cement was found to exhibit the highest expansion, and NaOH-activated BFS cement the lowest expansion for given Na_2O dosages and testing conditions (Fig. 8.2). Regardless of the selection of activator, Yang claimed that the expansion increases with increase of alkali dosage and the basicity of BFS.

Chen et al. [34] used a alkali content of 3.5 % Na_2O to activate BFS in mortar bars containing quartz glass aggregate and confirmed that sodium silicate activated BFS developed most expansion due to ASR. They also agreed that using a more basic BFS led to greater expansion (Fig. 8.3).

The modulus ($\text{SiO}_2/\text{Na}_2\text{O}$ ratio; Ms) of sodium silicate also has a notable effect on the ASR expansion of silicate-activated BFS cement, with a sodium

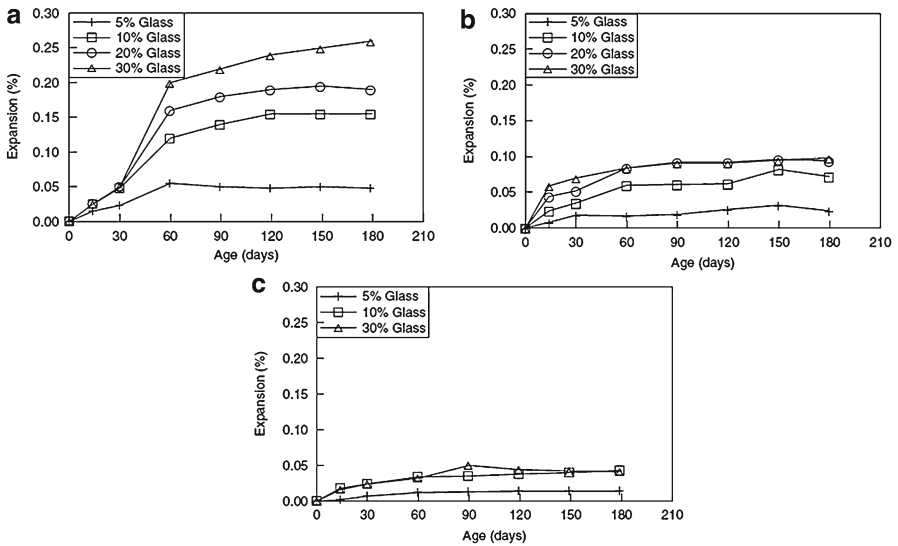
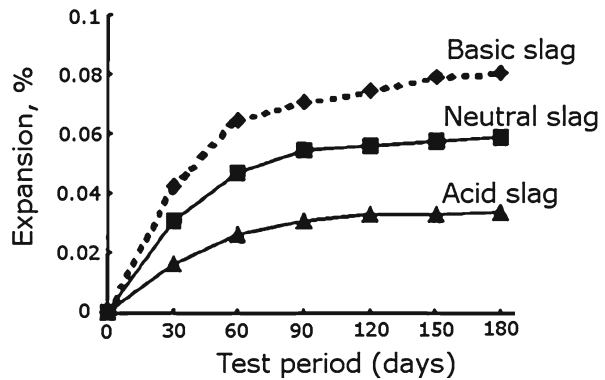


Fig. 8.2 Effect of the nature of activator and silica glass content on mortar bar expansion: (a) Na₂O·nSiO₂-activated, (b) Na₂CO₃-activated and (c) NaOH-activated BFS cements (Data from Yang [43])

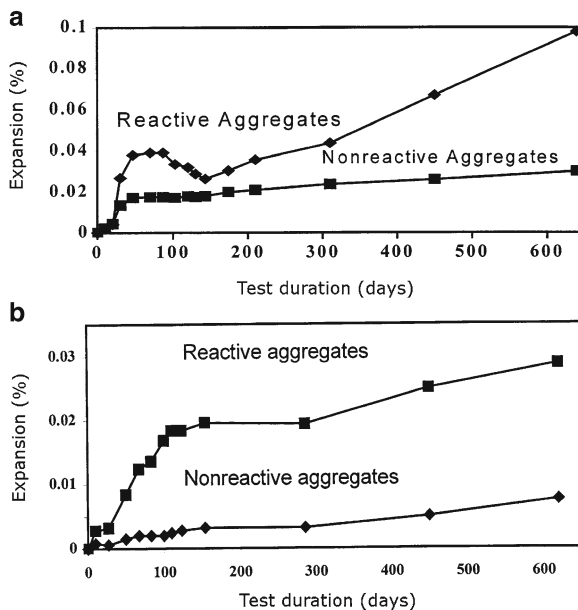
Fig. 8.3 Influence of the type of slag on mortar bar expansion (Adapted from Chen et al. [34])



silicate activator modulus of 1.8 leading to the greatest observed expansion [50]. Al-Otaibi [47] explained that when Ms is higher, the decrease in the expansion may be due to the binding of alkalis to the silicate of the activator in forming part of the hydration products.

In the case of alkali-activated fly ash, the activators which have been used in tests for measuring ASR have been 8 M NaOH [39], or sodium silicate with Ms = 1.64–3.3 [40, 42]. García-Lodeiro et al. [39] used the ASTM C1260 accelerated mortar bar test, in which the bars are immersed in 1 M NaOH at 80 °C, with both opal and

Fig. 8.4 Expansion measured in (a) OPC and (b) sodium silicate activated BFS concrete in the concrete prism test for ASR (ASTM C 1293-95) (Adapted from Bakharev et al. [37])



silica aggregates, and compared the behaviour of a low-alkali (0.46 % Na_2O) PC and a fly ash activated by 8 M NaOH. They found that although there was a small expansion in the fly ash system with this test, it was much less than in the PC system where the expansion and cracking were extreme. Using the same test method, Fernández-Jiménez et al. [40] found that fly ash activated with a sodium silicate solution produced greater expansion than when the activator was NaOH, but still less than the low-alkali OPC. Xie et al. [42] also used the ASTM C1260 mortar test, with container glass aggregate. They found very little expansion in mortars made with fly ash activated by sodium silicate, whereas the PC mortars exhibited considerable expansion.

8.3.3 Results of Tests Using Concrete Specimens

Bakharev [37] used the ASTM concrete prism test (ASTM C1293) to assess the reactivity of concrete made with BFS activated with sodium silicate of modulus 0.75 (Fig. 8.4), and reported that the AAS concrete was more susceptible to deterioration from ASR than a PC concrete of similar grade. Those experiments showed that ASR expansion in AAS concrete may be mitigated by rapid strength development; thus, observation of BFS concrete specimens over at least a 2-year period is essential.

Al-Otaibi [47] used a British greywacke aggregate known to be reactive in PC systems, under the conditions of the accelerated concrete prism test BS 812-123,

where concrete prisms are stored at 38 °C and 100 % RH. He tested a series of mixes made with BFS, activated with sodium silicate, and found that the activated BFS systems produced very low expansions, much less than would be considered deleterious by the test criteria. The observed expansion increased with increasing Na₂O content of the mix, but decreased with increasing silicate activator modulus.

8.3.4 Effect of Aggregate on ASR Expansion in AAM Systems

Several researchers have investigated the effect of dosage, size and nature of reactive aggregate in the role of ASR in determining the performance of AAMs. It is well known that an important factor influencing the amount of ASR expansion of regular PC mortar is the size of the reactive aggregate; the aggregate size causing the highest ASR expansion depends on the nature and composition of the aggregate. This is due to competing effects between the formation of a greater quantity of potentially expansive gel as the aggregate particles are reduced in size, and the participation of very reactive and/or very fine aggregates in pozzolanic reactions instead of ASR processes, which reduces the likelihood of expansion [51]. For example, in one specific study of OPC systems, the particle size resulting in the highest expansion for opal was 20–50 mm, for flint, the particle size was 1–3 mm, and for waste glass aggregate, 300–600 μm [42]. However, the amount of ASR expansion in sodium silicate-activated fly ash mortar was found in the same study to depend less on the size of the reactive aggregate than on its total content; the ASR expansion of activated fly ash mortar generally increased in proportion to the content of the glass aggregate up to 100 % replacement of inert aggregate by glass aggregate [42].

Yang [43] indicated that when the reactive glass aggregate content is less than 5 wt.%, the expansion of alkali-activated BFS cement systems was within the expansion limit, regardless of alkali dosage and the nature of activators. Conversely, Metso [52] measured the ASR expansion of alkali activated BFS cement using mortar bars containing opal as reactive aggregate. He noted that the expansion of alkali-activated BFS cement depended on the nature of the BFS used and the opal content, and observed a maximum expansion when the opal content was about 5 %.

Pu and Yang [53] examined the expansion and microstructure of ASR in alkali activated BFS cement. They found that ASR took place when the aggregate contained a reactive component, but noted that the expansion differed from activator to activator. In their systems, no destructive expansion took place when NaOH was used as an activator and the reactive aggregate content was less than 15 %, while the maximum allowable reactive aggregate content can be as much as 50 % when Na₂CO₃ or Na₂O·*n*SiO₂ is used as an activator.

The results of Chen et al. [34] showed that ASR classified as ‘dangerous’ only occurred in an AAS system when the amount of active aggregate was above 15 % in a 180-day test, even for the 80–150 μm aggregate size grading which led to the highest ASR expansion in their tests, and the degree of expansion increased with the content of active aggregate up to 50 %.

These results demonstrate a lack of clarity or consistency in the outcomes across the investigations which have been published to date, demonstrating a definite need for further scientific work and test method validation in this area.

8.3.5 The Comparison of ASR in PC and in AAM Binders

Although alkali-activated BFS (AAS) cements are lower in calcium than OPC, and characterised by the absence of Ca(OH)_2 (which is considered beneficial), the concentration of alkalis in these binders is high; usually over 3 %, while OPC usually contains less than 0.8 % $\text{Na}_2\text{O}_{\text{eq}}$. This leads to concern in the minds of users and/or specifiers that the high alkali content may promote ASR when reactive aggregates are used. However, when the alkalis are chemically combined in the reaction products rather than remaining entirely free in the pore solutions [38, 54], or when high levels of reactive alumina are available (either directly from aluminosilicate precursors or through the addition of Al-rich components such as metakaolin) [55, 56], this danger is proposed to be reduced.

As discussed in the preceding sections, some studies have reported that using the method of ASTM C1260 (accelerated mortar bar test), the AAM system developed less ASR expansion than a PC. Puertas et al. [41] used three types of aggregate (siliceous, non-reactive calcareous, and reactive (dolomitic) calcareous), and compared the expansion of PC and sodium silicate-activated BFS (AAS) mortars. For a test duration of 4 months, the PC sample with siliceous aggregate revealed an expansion four times greater than that of the corresponding AAS when both were exposed to the ASTM C1260 test conditions. The expansions of all AAS-calcareous aggregate samples were slightly higher than the corresponding OPC mortars, but the worst expansion of any of these samples after 4 months in 1N NaOH at 80 °C was around 0.05 % [41], and so the fact that it was higher than for the OPC mortars is not considered particularly problematic.

Conversely, as noted in 8.3.2, Bakharev et al. [37] reported that the AAS concrete was more susceptible to deterioration from ASR than PC concrete of similar grade when using the concrete prism test (ASTM C 1293). They suggested that the early-age ASR expansion in alkali-activated BFS concrete may be mitigated by rapid strength development; thus, observation of BFS samples over extended periods is important.

8.3.6 Discussion of Alkali-Aggregate Reaction Test Outcomes

As detailed above, there have been a number of investigations of the possibility that AAM systems can generate damaging ASR. Most have used small scale accelerated test methods using mortar bars, with artificial or unusually reactive aggregates. From these tests, it can be concluded that there is the potential for damaging

alkali–aggregate reaction in an alkali-activated cement system when the aggregate is alkali-reactive. In these tests, the expansion has been shown to be dependent on the aggregate type and the composition of the binder, as well as the nature of each component such as activator, BFS or fly ash. In general, however, these results suggest that the potential for a damaging alkali reaction in AAM systems is less than in PC systems. The limited numbers of accelerated tests conducted using concrete specimens have given opposing indications of whether AAMs are more or less susceptible to ASR than PC concretes.

Some authors have pointed out that the test methods have a significant influence on predicting ASR expansion. The high temperatures and high humidity (or immersion) used to accelerate the ASR reactions are particularly suited to promoting the hardening reactions of AAM systems. Instead of relying on such tests, which may or may not provide valid outcomes, long-term observation of expansion under more normal service conditions, along with the development of a detailed scientific understanding of the mechanisms which control ASR in AAM systems, is recommended. This is important due to the lower early reaction rate and sometimes high shrinkage of AAM in ambient conditions, which may lead to misunderstanding of the ASR performance.

There have been, however, almost no specific studies of ASR in AAM concrete specimens with naturally occurring aggregates exposed to natural environments; the best information available is the work summarised in Chaps. 2 and 11 of this report, where no evidence of deleterious expansive reactions has been noted on the samples which have been analysed. The situation is very similar to that which pertained 20 years so ago with supplementary cementing materials such as fly ash and BFS in PC blended systems. There had been many studies using rapid tests and artificially reactive aggregates which gave contradictory results and led to confusion in the industry. It was only when there was a concerted study focusing on concrete specimens containing a range of naturally occurring aggregates, exposed both in the laboratory and in natural environments, that a consensus view was formed that these materials can be a valuable aid to mitigating ASR if used in accordance with strict standards [57].

8.3.7 Summary of Test Methods Reported in the Literature

Some of the test methods applied by different researchers to assess the potential for ASR in AAM systems are summarised in Table 8.1.

8.3.8 Remarks Concerning Test Methods for AAMs

There have been a number of investigations of the possibility that AAM systems can generate damaging ASR. Many of these have been conducted using

Table 8.1 Summary of the test methods applied for the analysis of alkali-aggregate reactions in alkali-activated materials

Source	Area	Test method	Sample composition	Aggregate	Sample dimensions	Alkali content	Curing and exposure
Kukko and Mannonen [16]	Finland	ASTM C 227-71	“F-concrete” (BFS with proprietary activator) w/b=0.27	Standard sand + reactive opal replacing finest part, 3–15 %		OPC: 1.54 % F-concrete: 1.89 % in BFS, up to 2 % from activator	Demoulded after 24 h, then 40±2 °C, 98 % R.H., 75 day test duration
Gifford and Gillott 1996 [49]	Canada	CSA A23.2-14A-94	Binder: 420 kg/m ³ w/b=0.43 Coarse agg./sand=1.5	Dolomitic limestone (ACR), reactive siliceous limestone	75×75×305 mm	OPC: 1.25 % Na ₂ O _{eq} (by mass of cement) A.A.S: 6 % Na ₂ O by mass of BFS	Heat curing for 6 h at 70 °C or normal moist curing, stored in a common sealed, insulated and heated cabinet maintained at 38 °C and 100 % RH
Bakharev et al. 2001 [37]	Australia	ASTM C 1293	Sodium silicate-activated BFS, Ms=0.75 w/b=0.5	Nonreactive sand + reactive coarse aggregate	75×75×285 mm	4 % Na by mass of BFS	After 24 h, demoulded and stored in moist conditions at 38±2 °C. Expansion
Chen et al. 2002 [34]	China	“Mortar bar method”	Na ₂ CO ₃ /NaOH/ Na ₂ SO ₄ /water glass activated AAS Agg./binder=2.25 w/b=0.4	Size-fractionated quartz glass	10×10×60 mm		Demoulded after 1 day, cured at 38±2 °C, RH>95 %
Fernández-Jiménez and Puertas 2002 [38]	Spain	ASTM C1260-94	NaOH-activated BFS Solution/BFS=0.57 Agg./BFS=2.25	Reactive opal aggregate (21 % activate silica)	25×25×230 mm	4 % Na ₂ O by mass of BFS	25 °C, 99 % RH curing for 24h, demoulded, immersed in 1 M NaOH solution at 80 °C

Xie et al. 2003 [42]	USA	ASTM C 1260	Sodium silicate-activated fly ash; Ms = 1.64 w/b = 0.47	Waste glass aggregate 10 % replacing normal river sand	OPC: 24 °C, 100 % RH for 24 h AAFA: 60 °C for 24 h
Li et al. 2005, 2006 [58, 59]	China	ASTM C 441-97	w/b = 0.35, sand/binder = 2.25	Sieve residues 2.375 mm 10 % 1.18 mm 25 % 600 µm 25 % 300 µm 25 % 150 µm 15 % Reactive quartz glass fine agg., 20 % in each grading: 2.5–5 mm 1.25–2.5 mm, 0.63–1.25 mm 0.315–0.63 mm 0.16–0.315 mm	After demoulding (24 h), submerged in water bath 80 °C, 24 h; measure the length as the initial length, then placed in 1N NaOH at Cured at 20 °C for 24 h, demoulded, measure initial length, then exposed to 38 °C For geopolymer: 12.1 % Other mixes: 0.94, 0.57, 0.47 %

(continued)

Table 8.1 (continued)

Source	Area	Test method	Sample composition	Aggregate	Sample dimensions	Alkali content	Curing and exposure
García-Lodeiro et al. 2007 [39]	Spain	ASTM C 1260	OPC w/b=0.47 AAFA, 8 M NaOH, solution/FA=0.47 Agg./binder=2.25	Reactive opal aggregate: 2–4 mm, 10 % 1–2 mm, 25 % 0.5–1 mm, 25 % 0.25–0.5 mm, 25 % 0.125–0.25 mm, 15 %	25 × 25 × 285 mm		OPC: After mixing, curing at 21 °C and 99 % RH for 1 day, demoulded, immersed in water at 85 °C for 1d AAFA: after mixing, placed at 85 °C and high RH for 20 h, demoulded For both OPC and AAFA mortar bars: exposed in 1 M NaOH in 85 °C, length measured up to 90 days
Fernandez-Jimenez et al. 2007 [40]	Spain	ASTM C1260-94	8 M NaOH (NH), and 85 % 12.5 M NH + 15 % Ms 3.3 sodium silicate (SS) Agg./FA = 2.25 solution/FA = 0.47 (NH) or 0.64 (SS) OPC, w/cm = 0.47	Non-reactive agg.	25 × 25 × 285 mm		Initially cured 20 h at 85 °C with RH 99 %, demoulded, submerged in 1 M NaOH at 85 °C

Al-Otaibi 2008 [47]	Kuwait	BS DD218:1995	Solid or liquid sodium silicate, Ms=1 or 1.65	Reactive fine aggregate	75×75 ×280 mm	4 or 6 % Na ₂ O by mass of BFS for OPC, 1 % Na ₂ O
Puertas et al. 2009 [41]	Spain	ASTM C1260-94 Mortar prepared by EN-UNE 196-1	w/b=0.48 Waterglass-AAS Ms=1.08 Solution/binder=0.52	Siliceous/calcareous aggregates 2.36–4.75 mm, 10 % 1.18–2.36 mm, 25 % 0.6–1.18 mm, 25 % 0.3–0.6 mm, 25 % 0.15–0.6 mm, 15 %	Mortar bar, 25×25 ×287 mm	In water: 99 % R.H., T 21 ±2 °C (1st day), demould, submerged in water at 80 °C for 1 day, measure first shrinkage, then immerse in 1 M NaOH, at 80 °C for 4 months
Kupwade-Patil and Allouche 2011 [60]	USA	ASTM C 1260	Control(OPC), w/b=0.47 Agg./binder=2.25 Class F or Class C FA, with 14 M NaOH + sodium silicate	Reactive aggregate: quartz, sandstone and limestone	51×51 ×254 mm	Specimens immersed in 1 M NaOH and placed in oven at 80 °C

combinations of accelerated tests, unusual aggregates and test methods based on the study of mortar bars. From these tests, it can be concluded that there is the potential for damaging alkali–aggregate reaction in an AAM system when the aggregate is alkali-reactive and where there is less binding of the alkalis during the hydration process. The effects of early age shrinkage and the influence of temperature on the strength development of AAM systems mean that tests should ideally be conducted at lower temperatures and over longer periods than is appropriate for PC based concretes.

In these tests, the expansion has been shown to be dependent on the aggregate type and its proportion, the composition of the binder and/or activator. There is some evidence that expansions increase with the Na_2O content of the mix and decreases with increasing silicate modulus ($\text{SiO}_2/\text{Na}_2\text{O}$). In general, published results suggest that the potential for a damaging alkali reaction in AAM systems is less than in PC systems when using comparable aggregates.

The limited numbers of accelerated tests conducted using concrete specimens have given opposing indications of whether AAMs are more or less susceptible to ASR, and thus it will be more appropriate to go back to basic principles and study the effect of naturally occurring and reactive aggregates in concrete specimens exposed to natural environments.

8.4 Leaching Tests

8.4.1 *Introduction to Leaching Testing*

It is generally recognised that one of the most important environmental risks associated with the use of by-product materials in construction is the potential for release, and subsequent migration, of contaminants from the material into the environment. Release may occur during initial material placement, in service, in re-use after recycling, and after final disposal. Any contaminants which are released upon contact with water may pose a risk to the quality of groundwater, surface water and soil.

The starting materials usually employed in AAM binders and concretes are by-products or wastes from industrial processes which contain not only desirable or inert components, but also in many cases toxic elements (heavy metals, organic elements as aromatic polycyclic hydrocarbons, naturally occurring radioactive species, and others). When these materials are applied in areas exposed to interactions with the environment, rain water, surface water or groundwater can be responsible for leaching processes. If the concentration of one of the toxic elements is very high, this can pose a risk for the environment and human health. This is the key reason why leaching tests are of vital importance: to assure harmlessness to the environment and human health, and to improve confidence of end users in these materials.

Due to the importance of leaching determination, in some countries construction materials are regulated from an environmental point of view based on leaching tests.

A network on Harmonization of Leaching/Extraction Tests was created in 1995 in the EU, with the aim of unifying different existing leaching and extraction tests and evaluation criteria. From this time onwards, several documents and European standards addressing this issue have been published and established. Useful reviews and discussions of some of these test methods include [61–65].

In this section, a brief review of different leaching test procedures and standards suitable for building and waste materials will be presented. Analysis of their application in AAM based on previous work and experience will be made, and some recommendations or modifications will be provided.

8.4.2 Leaching Tests for Waste Disposal and Material Usage

By definition, leaching is the process by which inorganic, organic contaminants or radionuclides are released from a solid phase into surrounding water under the influence of mineral dissolution, sorption/desorption equilibria, complexation, pH, redox environment, dissolved organic matter and/or biological activity. The process itself is universally observed, as any material exposed to contact with water will leach components from its surface or its interior depending on the porosity of the material considered, and has been considered in a great deal of depth in contexts ranging from geochemistry to extractive metallurgy to cultural heritage preservation to processing of nuclear wastes.

In any of these contexts, including in the development and use of construction materials, the ‘total availability’ of an element is the total amount of this element which can be leached in a long time under extreme conditions. However, it is important in designing test protocols to reproduce the real environmental conditions to get a real value of this parameter, because it is not necessarily the case that the total availability of an element is equal to its total concentration of this element. On the contrary, usually the availability is lower than the total concentration, depending on the external scenario and conditions.

Some of the intrinsic and extrinsic parameters which can affect leaching rates include (Fig. 8.5):

- Solid-liquid equilibrium as a function of pH: solubility, adsorption, release, redox potential, acid buffering capacity
- Solid-liquid equilibrium as a function of solid/liquid ratio: pore water composition, ionic strength, soluble salt concentrations.
- Mass transfer and release mechanisms: diffusion, dissolution, diffusion-dissolution, surface phenomena, wash-off (linked to the flowrate of the water in the external environment), wet/dry cycling, and combinations of two or more of these processes
- Physical properties: shape (powder, granular, monolithic), humidity, porosity, density, permeability. It is important to note that granular and monolithic specimens will often have quite different leaching behaviour, due to differences in mass transport rates.

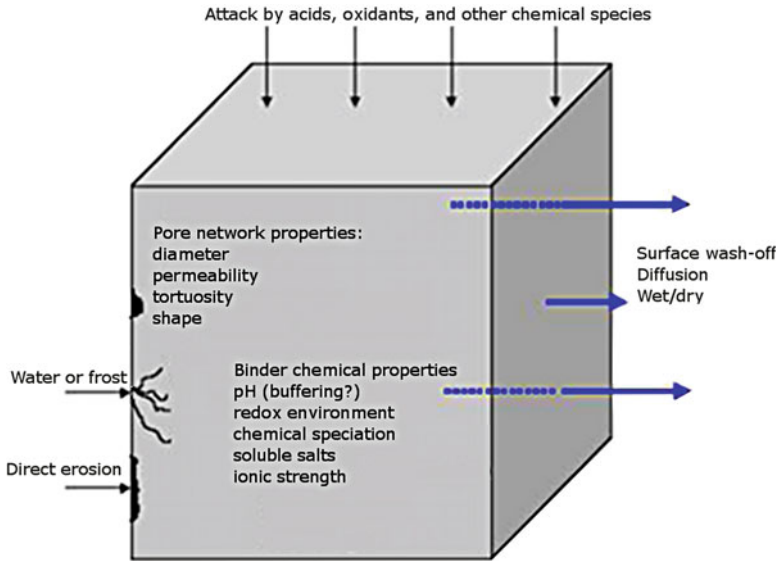


Fig. 8.5 Factors which can affect release of toxic elements in monolithic materials (Adapted from Van der Sloot and Dijkstra [62])

A methodology must therefore be recommended for the leaching evaluation of an alkali-activated material, as follows:

1. Definition of potential release scenarios and leaching parameters needed as a function of the material application. To evaluate scenarios different parameters should be known, such as:
 - Geotechnical specifications
 - Origin of raw materials and processing method
 - Hydrology associated with the proposed application
 - Intrinsic properties of the material.
2. Selection of the test methods to measure the most relevant leaching parameters
3. Material testing to determine leaching parameters
4. Verification of the laboratory test under actual exposure scenarios
 - Calculation of toxic element release based on real scenarios and field conditions (default scenarios, site-specific conditions, prior knowledge database)
5. Evaluation of environmental impact based on default criteria, site-specific impact, and prior experience.

Due to the difficulty and complexity associated with the prediction of leaching behaviour, occurring under service conditions which are (almost by definition)

relatively uncontrolled, a large number of different tests have been proposed, which are broadly divided into three categories:

1. Basic characterisation: tests based on determination of specific properties related to leaching behaviour of materials. Different factors can vary, including liquid/solid (L/S) ratios, leaching media composition, pH, redox potential, complexation capacity, material ageing, physical parameters of the material, and many others.
2. Compliance tests: used to compare leaching parameters of material (previously determined in basic tests) with reference values describing 'acceptable' leaching behaviour.
3. Verification or quality control tests: rapid tests to verify that material behaves as per compliance tests.

8.4.3 Screening Tests: Availability or Leaching Potential

These tests are intended to measure maximum potential leaching, often under rather extreme conditions, so high liquid/solid ratios are used (~100 mL/g), and pH selected to maximise release: pH <4 to release cations, pH 7 to release oxyanions. A chelating agent such as EDTA is sometimes used, and agitation is often applied. The test outcome is reported as the availability of the species of interest, either as a concentration in the leaching solution (although this information is not transferable between test protocols, and so is only useful for comparing different materials by a single test), or as the total quantity of the species released during the test duration, or as the percentage of the initial content of each element which was released (if the total concentrations in the solid material are known). Some of the tests implemented in this category are very briefly summarised in Table 8.2, with information on standard particle size distribution classifications used in many of the tests here and in other sections of the chapter presented in Table 8.3.

These tests are not necessarily only applied to cements or binders, but are rather general leaching methodologies, so there should not be any major difficulties associated with their application to AAMs, once the issue of alkali release from the material into the leaching solution is considered; this may necessitate the addition of acids to maintain a low pH environment during the test. Conversely, if the tests are applied to the raw materials (particularly fly ash and metallurgical slags, which are generated as by-products), some materials will release acidic components which necessitate the addition of alkalis to maintain a constant testing pH. Redox environments are not generally specified in the testing methodologies, but control of redox conditions is particularly important in determining the rate and extent of release of transition metal species such as chromium, so this may be an important issue to consider in the application of the tests. The TCLP test is an older method, and several of the other tests listed in Table 8.2 have been developed in large part to address some of its shortcomings [67], but it remains a relatively widely accepted test. The EDTA test (AV002.1) is also noted to be more aggressive than the direct leaching test (AV001.1) [70].

Table 8.2 Summary of standard screening tests

Test method	Testing restrictions	Test conditions
US EPA TCLP Method 1311 leaching test [66]	Particle size <9.5 mm, or surface area between 1 and 3.1 cm ² /g	Extraction time 18 h Liquid to solid ratio (L/S) ratio 20 L/kg Agitation by rotation of sample vessels at 30 rpm pH 2.9 in acetic acid Leachates acidified to pH <2 using HNO ₃ for preservation until analysis (intended to prevent precipitation)
AV001.1 – Availability at pH 4 and pH 8 [67]	Contact time based on particle size (Table 8.3)	Two parallel extractions L/S ratio 100 mL/g HNO ₃ or NaOH solution to provide final pH values of 4 and 8
EA NEN 7371:2004 [68] – Leaching characteristics of moulded or monolithic building and waste materials. Determination of the availability of inorganic components for leaching. “The maximum availability leaching test”	Size-reduced material (<125 µm)	Two subsequent extractions Cumulative L/S ratio 50 mL/g dry material HNO ₃ solution to provide pH values of 7 and 4 Leaching time 3 h at each pH An earlier version of the test [69] also used a higher L/S ratio (100 mL/g cumulative)
AV002.1 – Availability at pH 7.5 with EDTA [70]	Contact time based on particle size, specified as in RU-AV001.1 (Table 8.3)	Single extraction L/S ratio 100 mL/g 50 mM EDTA solution Addition of HNO ₃ or NaOH solution to provide a final pH 7.5

Table 8.3 Contact times used for different particle sizes in several of the leaching tests described

Particle size (mm)	Contact time (h)
<0.3	18
<2	48
<5	168

The generality of application of the tests also means that parameters such as sample preparation, curing and conditioning are rarely (if ever) specified. These parameters are very important in determining the performance of AAM binders, or cements in general in waste immobilisation, and so should be reported in full detail along with any presentation of test outcomes.

Table 8.4 Summary of some equilibrium-based leaching tests

Test method	Testing restrictions	Test conditions	Test results
SR002.1 – Solubility and release as a function of pH [70]	Size reduced material; contact time based on size (Table 8.3)	11 parallel solubility extractions, $3 \leq \text{pH} \leq 12$ Deionised water, with HNO ₃ or KOH addition L/S ratio: 10 mL/g dry material Agitation by rotating at 28 ± 2 rpm	Results reported as titration curve and constituent solubility or release curve
PrEN 14429 – pH-stat test [71]		Batch test (initial HNO ₃ or NaOH addition) Final pH values 4–12 pH control by automated acid/base addition L/S ratio: 10 mL/g	Results reported as concentrations in mg/L or availabilities in mg/kg
SR003.1 – Batch extraction at different L/S ratios – Solubility and release as a function of L/S ratio [67]	Size reduced material; contact time based on particle size (Table 8.3)	5 parallel extractions Deionised water LS ratios: 0.5, 1, 2, 5 and 10 mL/g dry material	Claimed to provide an estimate of the concentrations of the elements of interest in the pore water

8.4.4 Equilibrium-Based Leaching Tests

These tests, as listed in Table 8.4, are carried out on size reduced material, and aim to measure contaminant release related to specific chemical conditions (usually pH and L/S ratio), either under static or agitated conditions.

8.4.5 Mass Transfer-Based Leaching Tests

These tests (Table 8.5) are carried out either on monolithic material or compacted granular material, and aim to determine contaminant release rates by accounting for both chemical and physical (permeability) properties of the material.

Table 8.5 Summary of some mass transfer-based leaching tests

Test method	Applicability	Test conditions	Results report
Tank leaching test (MT00x.1) [67]	Can be applied in one of two formats: monolithic (MT001.1) or compact granular (MT002.1)	Initially deionised water (i.e. autogenous pH conditions) Liquid to surface area ratio 10 cm ³ /m ² Refresh intervals: 2, 3, 16 h, 1, 2, 3 days	Cumulative release as a function of time – results reported as mg released per m ² of sample surface area
Tank leaching tests (NEN 7347, NEN 7375) [72, 73]	Either monolithic (NEN 7375) or compact granular (NEN 7347) samples	Deionised water (autogenous pH), or pH control (pH 4 or 7–8) Liquid to sample volume ratio 2–5 Water replaced at 8 intervals from 6 h to 64 days	Cumulative release as a function of time – results reported as mg released per m ² of sample surface area
CEN/TS 14405 -Percolation (column) leaching test [71]	Either equilibrium or mass transfer rate. The L/S ratio is related to the time scale determined by the infiltration rate, density, and height of application	Pre-equilibration after saturation for more than 24 h Up-flow through the column L/S ratio between 0.1 and 10 L/kg	Cumulative release as a function of the L/S ratio, reported in mg/L or mg/kg
ANSI/ANS 16.1 [74]	Monolithic samples, designed for nuclear waste glasses	Static immersion test Either 5- or 90-day test durations Demineralised water, replaced at designated intervals Liquid to surface area 10 cm ³ /cm ²	Leachability index calculated from dissolution rates of network-forming elements

8.4.6 Conditions Which Can Affect Leaching in OPC and AAM Systems

8.4.6.1 Leaching pH

Acidic pH accelerates leaching by dissolving calcium species. Dolomite and limestone aggregates also are degraded by acids, forming soluble salts which leach in water. Depending on the acid type, the deterioration mechanism will be

different: some acids (oxalic, phosphoric) form insoluble salts which precipitate on the surfaces of materials. Acids with soluble calcium salts tend to be more damaging, and a weak acid is more aggressive at the same pH than a strong acid, due to buffering effects. Sulfuric acid is particularly aggressive to calcium-rich binders because the sulfate anion will react to form ettringite or gypsum, as discussed in Sect. 8.2.

Alkaline pH can be protective if there is also a high carbonate content, and does not lead to decalcification, but tends instead to cause solubilisation of silica and alumina.

8.4.6.2 Water Composition (Cation or Anion Concentration and Nature)

Low ionic strength, e.g. distilled or deionised water, can lead to an enhancement of leaching due to the higher concentration gradient induced when ‘soft’ water is in contact with the binder. Sulfates react with the calcium and aluminates present in cement pastes, as discussed in the previous section. Magnesium or ammonium salts dissolve high-Ca binder products and form soluble salts such as brucite, or expansive compounds such as thaumasite, leading to decalcification. Chlorides can cause formation of Friedel’s salt in Portland cements, but are considered most damaging through their effects on embedded steel rather than on the chemistry of the binder itself.

8.4.6.3 Water Flow Regime

This is critical in determining leaching rate. Static water will be less aggressive than running water because diffusion is the sole mechanism of mass transport, whereas flowing water brings the possibility of enhancement of mass transport. Physical erosion caused by flow, or particle breakage caused by agitation, will also accelerate the degradation of the material under these conditions.

8.4.6.4 Curing and Ageing

It is essential to provide adequate curing time for a waste-form material to develop its stable chemical nature and microstructure before testing, or otherwise misleading results can be obtained. However, excessive ageing or weathering of the product will affect the rate of leaching of some toxic elements because of degradation of the specimen (loss of strength, changes in porosity, cracking, salt formation, alteration of hydration products, changes of oxidation form of leachable elements), caused by factors including drying, carbonation and other gradual forms of attack leading to binder degradation.

8.4.7 Leaching Tests in AAMs

There have been numerous studies of alkali-activated binders in applications related to waste immobilisation and minimisation of heavy metals leaching, beginning with the early work of Comrie, Davidovits and others [75, 76]. The performance (and thus value) of AAM binders in such applications will be discussed in detail in Chap. 12 of this Report; at this point, it is sufficient to note that the performance of these binders has been reported to range from excellent to unacceptable, depending on the binder formulation and curing conditions, the elements of interest, and the specific test applied.

Tests which have been applied to the analysis of alkali-activated binders include those standard tests listed above, and also a wide range of non-standard test protocols. The TCLP test has been widely used, both unmodified and in slightly adapted forms, and the ANSI/ANS 16.1 test is also popular in testing of alkali-activated nuclear waste-forms. However, most leaching tests applied to alkali-activated binders in the literature have not specifically followed a standardised testing protocol, which raises difficulties in comparing performance between investigations. However, in general, it appears that cationic species are immobilised more effectively than anionic species, and large cations more so than small cations.

Detailed discussions of waste immobilisation in alkali-activated binders, which is intrinsically related to leaching resistance, are provided in Chap. 13 and in references [77–79], and so will not be repeated here. However, one important issue related to leaching which is distinct from applications in waste immobilisation is the question of alkali leaching; this has been shown to be most strongly related to binder microstructure, and so any compositional parameters which restrict diffusion through the pore network will also hinder alkali leaching [80]. For Portland and blended cements, the acid neutralisation capacity of the matrix itself is known to be important in determining resistance to leaching [81], and it is also likely that this is the case for AAMs, although this remains to be tested in detail.

8.4.8 Remarks Concerning Testing Methods for AAM

The literature related to AAMs shows the use of many different methodologies for leaching studies. Some authors employ some of the standards or methods described, but others have applied non-standard or modified protocols. It seems clear that depending on the purpose of the study, leaching tests should be selected or adapted from standards as far as possible, with the selection of the test determined by whether the test program aims to assess quality control, harmlessness of a specific product or application, study of migration mechanisms, or another parameter.

The first question asked should be to specify what kind of information is sought, and only then is it possible to select the most appropriate test, or (when necessary)

adapt a test to the specific needs or scenarios in place. This approach should be the same for all materials, both traditional and non-traditional. In particular, samples to be tested also should be in concordance with the purpose of the study, and thus composition, curing conditions and the selection of paste, mortar or concrete as test specimens should be selected in an appropriate way. This advice may sound obvious, but it is surprising how many published scientific studies do not appear to follow this methodology.

If the idea is to assure compliance with environmental and health specifications of a specific product based on AAM, analysis should be based around the extent to which different scenarios and parameters can affect product leachability under extended environmental exposure, and considering ageing of the product. In this regard, it should be noted that ageing of AAMs has different chemical and microstructural effects to its role in traditional OPC systems, and this is even more important for N-A-S-H systems without significant concentrations of Ca in their binder composition [82].

The standards discussed above have been developed for a wide range of solid materials or wastes; some (but by no means all) of them are specific for construction materials (usually OPC systems). Some of the fixed conditions in these methods, such as L/S ratio, pH and particle size are a function of specific scenarios and leachable elements, and thus are considered independent of the materials analysed. However, factors such as sample size or duration of extraction are directly related to the nature of the sample. Thus, sample size should always be enough to be representative of the whole material. So in this case, it is not the same to analyse a paste, a mortar or a concrete, when discussing either ground or monolithic specimens.

In the case of extraction time, as mentioned above, it is very important to keep in mind that aging conditions do not affect AAMs in the same way as OPC systems; even between different AAM systems (C-A-S-H or N-A-S-H) there are significant (and important) differences. In AAM specimens, pH influences the extent of leaching of elements, but in some cases quite differently from the behaviour observed in Portland cement. In particular, acidic media do not appear to affect AAM binders in the same way as in OPC-based systems, as will be discussed in Sect. 8.5 below. Exposure to alkaline media may also be of benefit in AAM systems in some instances, by enabling further curing of specimens, although the benefits (or lack thereof) are determined to a significant extent by the AAM mix design [83].

It may be said that leachability of materials is directly related to durability, and thus this is the key parameter (either via matrix breakdown or via pore network diffusion properties) which will determine the relevant extraction time which can be used in different scenarios and leaching methods. There is a risk that, if the selected extraction time for a certain material or scenario is shorter than is required to obtain useful results, the results obtained could lead to the wrong conclusions being reached. Key factors which could be important here include matrix heterogeneity (i.e. when the species of interest are located primarily in the centre of a specimen rather than close to the surface), or if the leaching rate is likely to be influenced by redox equilibria which may cause sudden release of an immobilised species as the Eh passes a specific value.

Finally, it can be concluded (in a very broad sense) that:

- It is important to select methods or design scenarios depending on the aims of the study; few of the methods summarised are going to be universally ‘better’ than others.
- More work is needed, related to durability (ageing conditions) and the extraction time needed to obtain reliable results, to assure that a material is harmless (or not) in a specific exposure scenario during a specific time.

8.5 Acid Resistance

8.5.1 Introduction

Although most concrete is not subjected to highly acidic conditions, there are some applications where this does become an issue, and in these circumstances the lifetime of concretes can be severely curtailed. Acid rain [84], acid sulfate soils [85, 86], animal husbandry [87, 88] and industrial processes [89] can all produce acids which could potentially degrade concrete. However, the most industrially and economically important cause of acid induced damage to infrastructure elements is biogenic sulfuric acid corrosion, which often takes place in sewer pipes [90–93], and is a major research focus in a number of long-running research programs worldwide, with various technical solutions (either related to manipulation of the concrete of the pipe itself, or by the use of coatings) developed and implemented [94–96].

Many of the procedures used in acid attack testing of concretes are similar, in a general sense, to the leaching tests described in Sect. 8.4, several of which specifically involve exposure to acidic conditions. Under attack by strong acids, there are some additional mechanisms which can be important, and these will be discussed briefly in this section. It is noted that the recent State of the Art Report of RILEM TC 211-PAE [3] addresses these issues in more detail for the case of Portland cement-based systems, and the reader is referred to that document for a full analysis of different acid attack processes, effects and tests.

The most important mode of acid attack on a binder, whether based on OPC or AAM, takes place via degradation of concrete by ion exchange reactions. This leads to a breakdown of the matrix nano- and microstructure, and weakening of the material. In some cases this can be extremely rapid and serious, and the acidic conditions may be induced by either industrial or biogenic processes.

In a laboratory test, different parameters are adjusted in order to mimic the real-life situation as closely as possible, or to accelerate the degradation and thus obtain results more rapidly, and the extent and manner to which this acceleration is applied will influence the test results. These parameters include the pH and concentration of the acidic solution, the physical state of the sample (monolith or

powder; paste mortar or concrete), temperature, rate of acid replenishment, presence or absence of mechanical action/flow, alternate wetting and drying, alternate heating and cooling, and pressure. These parameters should be carefully selected, and should always be reported together with test results. Also, the choice of the selected measure of degradation (strength loss, mass loss, penetration depth) may lead to differing conclusions regarding relative performance of concrete types, in particular when the binder chemistry is quite different between samples [97]. Often, a combination of multiple relevant indicators will be necessary. Additionally, sample preparation and conditioning procedures, and the maturity at the time of testing, are of utmost importance.

8.5.2 Classification of Test Methods

Because of the very wide range of acid exposure conditions which are of interest in practice, and the range of performance parameters which are important in determining success or failure of a material under these conditions, the vast majority of acid exposure testing is conducted using non-standardised test protocols. The existing test methods can be classified in different ways, as listed below:

8.5.2.1 Type of Aggressive Species

There is a difference between chemical and microbiological degradation mechanisms. Chemical degradation processes include attack by organic acids such as lactic and acetic acids, and inorganic/mineral acids such as H_2SO_4 or HCl . The test methods applied in the analysis of these mechanisms of degradation are generally based fairly straightforwardly around immersion of paste or binder specimens into solutions of the selected acid at one or more concentrations.

Microbiological degradation mechanisms feature aggressive substances produced by micro-organisms; these may in fact be the same acids that are present in simple chemical degradation processes, but the physicochemical environment prevailing under microbiologically-induced attack conditions is likely to be more complex, which can lead to additional degradation effects. A particularly important example is the redox cycle in sewer pipes which leads to oxidation of sulfides, and causes biogenic sulfuric acid attack on the concrete pipes [90, 91]. This may therefore demand the use of special test methods. Monteny et al. [92] provide a review of chemical, microbiological and in situ test methods for biogenic sulphuric acid corrosion of concrete, and describe a test procedure whereby the oxidation of H_2S to H_2SO_4 was achieved during the test by the provision of *Thiobacillus* species in a suitable nutrient environment, with the rate of loss of binder material from the sample surface used as the key measure of performance.

8.5.2.2 Scale of the Test Method

The scale of the test method can have a significant effect on the test results, since it may affect factors such as the specimen surface area/liquid ratio, the presence or absence of replenishment of aggressive substances, presence of an interfacial transition zone (concrete versus mortar specimens), use of industrially-generated or simulated aggressive liquids, and the degree of acceleration compared to in-service conditions. Research carried out on mortar or cement paste specimens cannot always be extrapolated to concrete because of differences in microstructure and permeability induced by the interfacial transition zone. Differences in the selection of the aggregate (siliceous or carbonaceous) may also be important.

It is also important to highlight that tests carried out at low liquid/solid ratios and without replenishment of the acid can be subject to major changes in pH due to the high alkalinity associated with the AAM binder. In some cases, the leaching solution may in fact become alkaline, which is a possible explanation for the number of reports in the literature of ‘acid exposure’ tests causing additional zeolite formation in AAM binders; this would not be expected if the test conditions had actually remained acidic.

8.5.2.3 Presence or Absence of Mechanical Action

When only chemical action is present, a slowly growing layer of degraded material is formed, and this can slow down further reactions. When mechanical action is combined with the acid exposure, abrasion will remove the degrade layer and leave a new surface to be subject to chemical attack without hindered transport by diffusion through the product layer; this may thus accelerate the degradation process. Common ways of exerting an abrasive action are manual or automated brushing (the use of the Los Angeles Apparatus has proven effective in the study of AAMs [98]), or immersion in water that is shaken or stirred.

In some cases, the ingress of acids can also be accelerated by the application of wetting and drying cycles, allowing uptake of aggressive agents through convective processes, which are much faster than pure diffusion.

8.5.2.4 Parameters to Accelerate Degradation in Simulation Tests

Acceleration of the process can be achieved in different ways. The concentration or temperature of the aggressive solution can be increased – although, as was the case for sulfate attack as discussed in Sect. 8.2, there are potential thermodynamic/phase equilibrium complications which may become evident if too high a concentration or temperature is selected [92]. The reactive surface area can also be increased through the use of specimens with a large surface area-to-volume ratio, although there is again a risk of reaching unrepresentative conditions if the concentration of dissolved silica is allowed to increase too far [82].

8.5.2.5 Nature of the Acid Used

The strength of the acid in the attacking solution can also be important in determining the rate and extent of acid attack; strong acids are normally assumed to be very aggressive (for a given concentration), because they generate a low-pH environment. Nevertheless, some weak acids may also be highly aggressive due to buffering effects, and the presence of weak acids with highly soluble calcium salts is likely to be more damaging to a BFS-based binder than the presence of strong acids with less-soluble calcium salts [99]. Sulfuric acid is also more aggressive than nitric acid under equivalent pH conditions [100–102], as the diprotic nature of sulfuric acid can also provide low-pH buffering effects and additional degradation [97].

Dry, non-hygroscopic solid acids do not attack dry concrete, but some will attack moist concrete. Dry gases, if aggressive, may come into contact with sufficient moisture within the concrete to make attack possible. CO₂ attack, leading to carbonation of the binder, is a special case of this and will be addressed in detail in Chap. 9.

8.5.3 Methods of Measuring the Degradation of Specimens

The parameters utilised in degradation measurements may include change in the dimensions (expansion due to deposition of salts such as gypsum, or loss of cross-section due to dissolution of the binder) or mass of the specimen, loss of strength or elastic modulus of monolithic specimens, depth of acid penetration/binder alteration, pH change of the leaching liquid or of the binder pore solution, the concentrations of calcium or network-forming elements released into the liquid, and others. These direct measurements may be supplemented by SEM, XRD or spectroscopic analysis to examine the microstructure and nanostructure of the altered binder regions.

The choice of the degradation measure may lead to different conclusions regarding the relative performance of concrete types [97]. Therefore, one simple measure may not suffice to characterise the degradation sufficiently. It is recommended to use multiple relevant indicators, carefully selected according to the test conditions, the nature of the binder, and the information which is sought. For example, changes in mass have been shown to correlate poorly with the extent of degradation of AAMs in H₂SO₄ due to the competing effects of partial binder dissolution (causing mass loss) and gypsum deposition, while samples exposed in HNO₃ showed quite different effects and trends [97].

8.5.4 Application of Acid Resistance Testing to AAMs

AAMs have often been advertised as being highly acid resistant; this has in fact proven to be a major driver for academic and commercial developments in this area for many years [103–107]. However, many of the claims that have been made have not been tested in sufficient detail to enable utilisation of AAMs in acid-exposure applications where long-term performance is critical. Additionally, the tests that

have been applied were in general designed for Portland cement binders, and have not yet been validated for AAMs, and so may or may not be providing the expected information regarding ‘real-world’ performance [108, 109].

Due to the use of different raw materials, curing durations, mix designs, sample formats, acid exposure conditions and performance parameters in each published study of the acid resistance of AAMs, it is difficult to make an immediately meaningful comparison between the results obtained. Many of the test methods used vary drastically from the conditions expected in service; for example, 70 % nitric acid [104] at room temperature, or 70 % H₂SO₄ at 100 °C [110]. Testing at conditions close to those expected in service is expected to provide more representative results, but at the cost of potentially longer test durations; this is more or less universal in the development of accelerated testing methods, as discussed throughout this chapter.

The majority of published work in this area has used mass loss as a measure of acid induced degradation of cements and concretes, while there are fewer reports of strength loss or corroded layer depth. Loss of compressive strength is possibly the most immediately meaningful measure of performance under many circumstances, but its use as a measure of degradation during an accelerated test with a duration of weeks or months can be complicated by the increase in strength of the undamaged binder regions during the test, which can to some extent counteract the strength losses in the degraded binder. Variability between replicate samples in compressive strength testing is also potentially problematic when samples are damaged or degraded, as the sample geometry may change (where flattening of sample ends can be difficult when the samples are partially degraded), and the non-uniformity of the samples (with a strong core and a weaker outer region) can cause undesirable effects related to fracture modes under compressive load. However, the greatest drawback of residual strength as a measure of acid-induced degradation is that the percentage mass loss experienced at a given corrosion depth is determined to a significant extent by the sample geometry; a larger sample will lose less strength at the same corrosion depth as a smaller sample, leading to severe difficulties in comparing results between investigations.

Conversely, corroded depth [97, 99–102] is seen to provide a more direct measurement of the resistance to acid-induced degradation, and may be less likely to develop systematic or random error than the other methods discussed, particularly when comparing groups of materials with greatly differing compositions or strength development profile. Corroded depth can be measured to a high precision and, assuming dimensional stability of the intact portion of the sample throughout the test, is relatively independent of sample geometry and thus theoretically more reproducible and comparable between laboratories.

8.6 Alkali Resistance

The resistance of AAMs to extended alkali immersion has only been tested in a limited number of test environments. Generally good performance was observed for alkali silicate-activated and hydroxide-activated fly ashes in concentrated alkali



Fig. 8.6 Application of an alkali-activated binder coating to marine concrete elements in China (Photograph courtesy of Z. Zhang, University of Southern Queensland)

hydroxides and carbonates [111, 112], but BFS-based binders did not show such good performance when exposed to carbon capture solvents [83], possibly due to ion exchange effects involving Ca. Moderate-temperature calcination has also been seen to enhance the resistance of alkali-activated low-Ca aluminosilicate binders to alkaline leaching [112], although this approach may not be as relevant when the binder products are based on calcium (alumino)silicate hydrates. There are not existing standardised testing methodologies describing exposure tests under such environments, and the scenarios in which concretes may be exposed to alkaline aqueous environments are likely to be rather specialised, meaning that the design of specific test conditions selected for each application is likely to be needed.

8.7 Seawater Attack

The immersion of alkali-activated BFS binders in simulated seawater has long been known to give good performance outcomes [16], with an increase in compressive strength and no corrosion of embedded steel (with 16 mm cover depth) observed during 12 months of exposure [16]. Puertas et al. [21] showed that the degree of alteration of the binder pore structure during seawater immersion was lower for alkali silicate-activated BFS than when an NaOH activator was used, although all samples proved resistant to degradation during 180 days of exposure. Zhang et al. [113–115] developed alkali silicate-activated fibre-reinforced BFS/metakaolin pastes for application as a coating for marine concrete structures (Fig. 8.6), with

results to date showing good resistance and durability under the intermittent exposure conditions which are well known to be damaging to Portland cement binders (minor surface cracking but a very strong bond to the underlying concrete).

8.8 Soft Water Attack

Flowing soft water is known to be aggressive towards Portland cement through leaching-related mechanisms [116, 117], but there do not appear to be any studies in the literature specifically aimed at determining the performance of AAMs under soft water attack conditions. There have been numerous studies where AAM samples were immersed in distilled water under static conditions, usually as a control sample for an exposure test where the main focus is on resistance to acids or other aggressive solutions. However, the ionic strength of the initially distilled water environments in such tests will rapidly increase due to elution of pore solution components, and will soon reach a point where leaching of components from the binder will be slow. This therefore remains an area in need of investigation.

8.9 Biologically-Induced Corrosion

As was mentioned in Sect. 8.5 in the discussion of acid attack on AAM binders, there are important scenarios in which biological effects lead to the generation of conditions which are corrosive to construction materials. There have not yet been any published studies where biologically induced corrosion of AAMs has been studied under laboratory testing conditions. However, the analysis of alkali-activated BFS concretes after extended periods of service in lining silage trenches (where the decay of plant matter leads to the generation of organic acids) has shown a very low extent of degradation in service [118]; this will be discussed as a case study in Chap. 11 of this report.

8.10 Conclusions

There are a number of important scenarios in which chemically-induced binder degradation is important for alkali-activated binders, probably the most important of which are related to attack by sulfates, alkali-aggregate reaction processes, and leaching of matrix components or immobilised species into neutral or acidic conditions. In each of these areas, there are a significant number of existing test methods and procedures, and several of these have been applied to the analysis of AAMs in the past. In each case, there are test methods which are preferred over others for the analysis of AAMs, either because they more closely replicate the expected conditions of exposure (and thus the in-service degradation mechanisms) to which the materials are likely to be exposed. However, it has not been possible in any of these

scenarios to recommend a single particular test as being the most preferred option for analysis of AAMs, because there are a range of service conditions which must be simulated in the laboratory, and so different tests are required to simulate different service conditions and the corresponding degradation processes. Key recommendations are made regarding some existing test methods:

- The resistance of AAMs to sulfate attack appears to be rather good, although more work is necessary in validating the results of laboratory tests against in-service data. This is potentially problematic when little change is observed in the specimens as a result of exposure, meaning that it is not easy to determine whether the test methods are representing the real chemical processes taking place in service.
- The analysis of alkali-aggregate reaction by immersion in hot NaOH is deemed unlikely to give representative outcomes due to evolution of the binder structure itself under such conditions. Longer-term testing is necessary to analyse the issue of ASR in AAMs. Even the question of whether or not the reaction mechanisms leading to expansive reactions are the same in AAMs as in Portland cement remains open.
- Corroded depth is likely to be a more useful and reproducible measure of acid resistance of AAMs than loss of mass or compressive strength, due to the formation of partially-intact corroded layers
- Leaching tests must be tailored to match specific exposure conditions, otherwise the results will almost certainly be misleading
- More work is required before recommendations can be proposed related to tests for degradation by immersion in alkalis, soft water, biologically-induced aggressive environments, or marine conditions.

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Chapter 9

Durability and Testing – Degradation via Mass Transport

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9.1 Introduction

In most applications of reinforced concrete, the predominant modes of structural failure of the material are actually related more to degradation of the embedded steel reinforcing rather than of the binder itself. Thus, a key role played by any

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structural concrete is the provision of sufficient cover depth, and alkalinity, to hold the steel in a passive state for an extended period of time. The loss of passivation usually takes place due to the ingress of aggressive species such as chloride, and/or the loss of alkalinity by processes such as carbonation. This means that the mass transport properties of the hardened binder material are essential in determining the durability of concrete, and thus the analysis and testing of the transport-related properties of alkali-activated materials will be the focus of this chapter. Sections dedicated to steel corrosion chemistry within alkali-activated binders, and to efflorescence (which is a phenomenon observed in the case of excessive alkali mobility), are also incorporated into the discussion due to their close connections to transport properties.

9.2 Permeability and Porosity

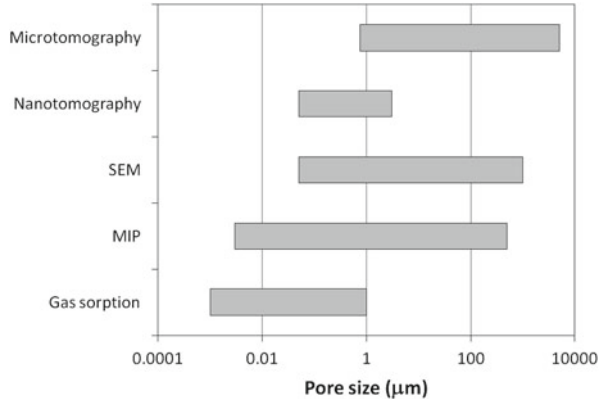
There have been numerous studies of the relationships between microstructure and permeability of Portland cement-based concretes, including those presented and reviewed in detail in [1–4]. Many different porosimetric techniques are available, some of which have been formally standardised in different jurisdictions, but the majority of which rely on either commercially-available or home-built laboratory apparatus for the analysis of samples. The discussion in this section will therefore present results and information obtained in both standardised and non-standardised analytical protocols, and the reader is referred to the original publications for full experimental details in each instance. The State of the Art Reports prepared by RILEM TCs 116-PCD [5] and 189-NEC [6] also contain descriptions and analysis of many of the available techniques for in situ permeability analysis of concretes.

9.2.1 Porosimetry in the Laboratory

Porosimetric analysis of complex materials is most commonly conducted with the use of a fluid which is forced into the sample under pressure, with measurement either of the volume of fluid which has passed into the pore space of the solid material, and/or of the rate or extent of passage of a fluid through a monolithic sample. Gas permeability testing is usually conducted using compressed air or oxygen, providing direct information regarding the passage of the gas through a sample, although test methods which work purely on diffusion of a gas driven by a concentration gradient rather than a pressure differential are also available [7–9].

The approximate pore size ranges which can be probed through the use of some selected pore size distribution characterisation methods are given in Fig. 9.1. It is evident that no single technique spans the full pore size range of interest in the study of AAMs (or concretes based on OPC), which necessitates the application – and thus the discussion here – of a range of different techniques in the characterisation of these materials.

Fig. 9.1 Approximate pore size ranges which are able to be probed through the use of several available analytical techniques



Gas sorption analysis (usually using nitrogen, argon or helium) can also be used to calculate pore size distributions and surface areas via various algorithms such as the popular Brunauer-Emmett-Teller (BET) [10] and Barrett-Joyner-Halenda (BJH) [11] methods, and mercury intrusion porosimetry (MIP) is also widely used in the study of hardened binder phases. Some controversy surrounds the applicability of MIP to complex pore geometries such as those observed in construction materials [12], but these complications can also offer opportunities for more advanced analytical procedures such as multi-cycle MIP and Wood’s metal intrusion to provide more understanding of the pore geometries present within the material [13–15]. Water permeability analysis also provides useful information when applied to hardened concrete – either where the water is forced into the sample under pressure, or where capillary suction is used to draw water into the sample. Each of these classes of test is able to provide information which is essential in understanding the structure and durability of AAM concretes, and in predicting their in-service performance. There is no universally applicable technique which can provide a full multiscale characterisation of a complex material such as an AAM binder or concrete; a fuller toolkit of techniques is required to obtain detail across the length scales of interest.

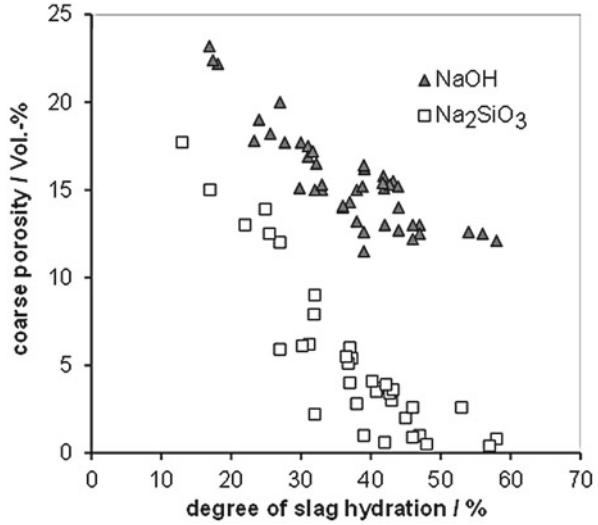
The BJH method for pore size distribution calculations [11] has been standardised in various jurisdictions [16, 17], but for porous materials in general rather than with specific application to cements or construction materials. Although this method has in recent years been compared unfavourably to more advanced methods of converting gas sorption data into pore size distribution information [18, 19], this remains the method which has been applied most widely to the extraction of pore size distribution information from gas sorption data for alkali-activated binders. Lloyd et al. [15] and Zheng et al. [20] have each used the BJH technique to observe pore refinement in fly ash-derived AAMs with increasing activator concentration, which is consistent with the conceptual understanding of the formation of these materials as described in Chap. 4. The study of alkali hydroxide/silicate-activated metakaolin materials by BJH analysis showed a reduction in pore radius with

increasing activator modulus; the data of Sindhunata et al. [21] for comparable fly ash-based materials are in general consistent with this observation. However, in both cases, the fact that important pore volume appeared to be present both above the largest measurable pore diameter (just over 100 nm) and below the smallest measurable pore diameter (between 2 and 3 nm) provided significant complications in the analysis of the data. This is particularly important in terms of the functional properties of the very largest pores present, which are likely to dominate mass transport, and thus the fact that these are not represented in the BJH data is likely to be important; this technique can also underestimate total porosity by a factor of 6–8 when compared with gravimetric determinations of pore volume [15]. There are also disagreements between BJH and MIP determinations of pore size distributions in alkali-activated fly ash binders, which are attributed to the fact that complexities in the pore network geometry cause difficulties in the computation of pore size distributions using the standard models for both techniques, which assume cylindrical pore shapes [22]. The analysis of pores in the size range below 2–3 nm is also standardised in DIN and ISO documents [23, 24], but does not appear to have been applied to the analysis of AAMs up to this time, beyond a brief discussion of results from the “t-plot” method for metakaolin-derived materials synthesised for catalyst applications [25].

The limitations and inaccuracies of MIP in application to cements are also well known [12], but it is widely used due to its apparent simplicity and the ready availability of instrumentation. MIP largely fails in the case of samples with complex pore geometries (the “ink-bottle” effect), as the full volume of a complex-shaped pore is registered as having an effective pore size equivalent to that of the narrowest part of its entry. This results in an underestimation of mean pore size. The high pressures used to intrude mercury into the smallest pores in a sample are also problematic, as the applied pressure will often exceed the strength (compressive or tensile) of the material to which it is being applied, which can result in significant crushing effects. The application of MIP to the analysis of soil and rocks [26] and porous catalysts [27] has been standardised by ASTM, and its application to porous materials in general is described in various standards [28–31].

MIP analysis of alkali silicate-activated BFS [32] shows the presence of a bimodal pore size distribution, with significant porosity in the >1 and <20 nm ranges, but very little porosity between these size ranges, whereas the Portland cement analysed in the same study showed a unimodal pore size distribution with most of the pore volume in the pore diameter range between 10 and 100 nm. These capillary pores are important in mass transport, and the fact that MIP shows that they are largely absent in alkali-activated BFS may lead to some important differences in the mechanisms by which species such as chloride, sulfate and carbonate are transported through the structures of these materials, but detailed scientific work in this area remains to be undertaken. Additional observations which have been obtained through MIP analysis of AAMs include the fact that the substitution of Na by K leads to a notable reduction in the median pore diameter of alkali silicate-activated metakaolin binders [33–35], as does the incorporation of BFS into a predominantly metakaolin-based binder [36].

Fig. 9.2 Coarse (capillary) porosity 0.05–5 μm (±0.5 %) vs. degree of hydration (±3 %) of alkali activated slag pastes obtained by SEM image analysis using polished sections. Eight slags of different chemical composition activated either with NaOH or with Na₂SiO₃ at an Na₂O dosage of 3 %, water/slag=0.40 (Data from Ben Haha et al. [39–41])



Analysis of the pore structure of AAMs in two dimensions is predominantly conducted using microscopic methods, in particular scanning electron microscopy (SEM). The primary challenge associated with the observation of porosity by SEM is that the aim of the measurement is to detect the regions which contain no solid matter, and this provides challenges in pore identification. Some of these problems can be overcome for calcium-rich systems, such as Portland cement or alkali-activated BFS, by the use of image analysis algorithms [37–42].

Figure 9.2 shows the development of coarse (capillary) porosity (0.05–5 μm) of various blast furnace slags activated either by sodium hydroxide or by sodium water glass with increasing hydration degree [39–41]. With increasing hydration progress, coarse (capillary) porosity is decreasing as expected, making the paste more impermeable. It is also evident from Fig. 9.2 that the nature of the activator plays a much greater role concerning the development of porosity than the chemical composition of the slag.

For aluminosilicate AAM systems with lower electron density contrast between the solid and pore regions, techniques such as Wood’s metal intrusion prior have proven to be of value [15]. In this technique, a high elemental-number, low melting point alloy is intruded in liquid form into the pore space of the sample under moderate pressure (lower than the pressures used in MIP, to prevent damage to delicate parts of the microstructure) and temperatures below 100 °C. The sample is then cooled, and the alloy solidifies within the pore network, to provide elemental contrast against the low-elemental number binder regions [43, 44]. In the recent application of this technique to alkali-activated fly ash and BFS binders [15], it was calculated that pores as small as 11 nm are able to be filled with the molten alloy, while using an intrusion pressure lower than the compressive strength of the binder material to minimise microstructural damage.

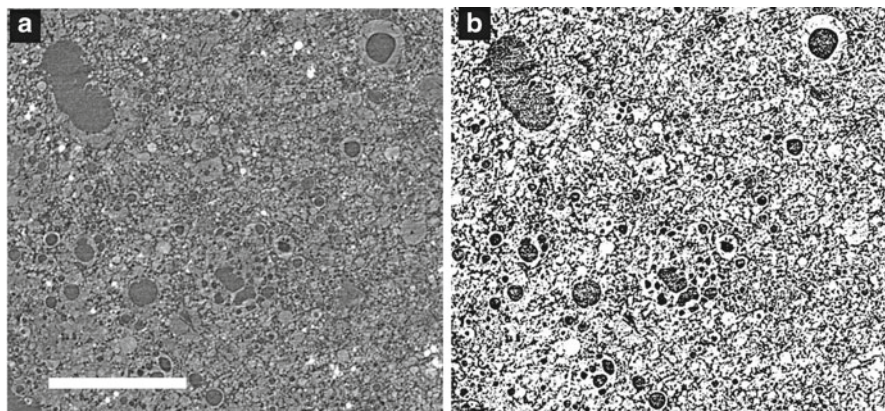


Fig. 9.3 Binary thresholding of a microtomographic image of a fly ash-derived AAM: (a) original greyscale image, (b) binary segmented image. Scalebar represents 200 μm

The primary three-dimensional characterisation technique which is able to be applied to the analysis of cements (alkali-activated and traditional) is X-ray microtomography. There have been a number of studies of Portland cement-based materials by this technique over the past decade or more [45–49]; the systematic analysis of alkali-activated binders by X-ray microtomography has recently been presented for the first time [50–52], at 750 nm voxel resolution. An example showing the greyscale and segmented images for a given region of a fly ash-Na silicate AAM binder is given in Fig. 9.3. Data at a 30 nm voxel resolution have also been collected for a limited number of AAM samples [53], but this ‘nanotomography’ technique is experimentally challenging and not yet widely available.

Figure 9.3 also demonstrates some of the challenges associated with microtomographic characterisation of fly ash-derived AAM samples [51, 52]. The large dark regions in the images represent the interior of hollow or partially hollow (cenosphere or plerosphere) fly ash particles, which are not connected to the pore volume within the gel, and so will not contribute to the transport properties of the material. However, the calculation of total porosity from the tomographic data sets will include these regions, and so they must be excluded via the use of algorithms which considers ‘connected porosity’ only. This is less problematic for samples based on BFS (or Portland cement) because the precursor particles do not contain significant inaccessible pore volumes.

Segmentation and diffusion simulations conducted in the reconstructed tomography data of [51], as shown in Fig. 9.4, demonstrate that the porosity of the alkali-activated binders containing 50 % or more BFS decreases as a function of curing duration, indicating that there is some chemical binding of water taking place in this system, consistent with the known formation and coexistence of sodium aluminosilicate hydrate (“N-A-S-(H)”) and calcium (alumino)silicate hydrate (“C-(A)-S-H”) gels in mixed fly ash/BFS AAM binders, as discussed in Chap. 5 of this Report. The substitution of BFS for fly ash is seen in Fig. 9.4 to

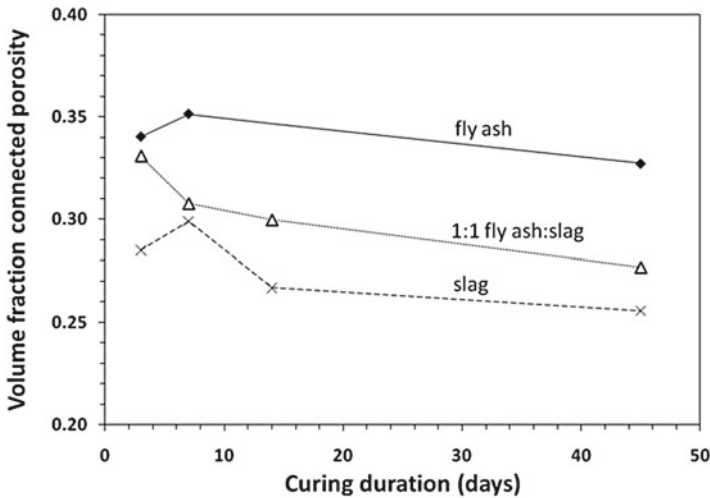


Fig. 9.4 Relationship between segmented porosity and curing duration for a range of sodium silicate-activated fly ash/BFS systems (Data selected from Provis et al. [51])

lead to higher porosity. This is consistent with the results of nitrogen sorption analysis of a set of similar binders [15], and the porosities obtained from tomography are within 2 vol.% of the values obtained in that study for samples of similar mix design and curing duration.

As the gel evolves, and its porosity decreases over time, the tortuosity of the pore network also increases [51]. An increase in this parameter by almost a factor of 2 between early age (<7 days) and 45 days of age indicates that the rate of diffusion through a well-cured BFS-rich AAM binder would be halved when compared to a poorly-cured binder. This further highlights the importance of adequate curing in achieving high performance and durability in alkali-activated concretes. However, it is clear from the tomography results that, regardless of the rate of early strength development, an extended period of sealed curing will provide marked advantages in service life and overall durability performance once the binder is placed in service and exposed to aggressive environments.

The discussion presented here therefore highlights the importance of understanding and controlling the porosity of AAM binders, particularly in the case of fly ash-rich systems. If the higher porosity of the sodium aluminosilicate gel when compared with calcium silicate gels such as those produced by Portland cement hydration were to lead to high diffusivity (and thus rapid mass transport) of aggressive ions through the binder to reach the embedded steel reinforcing, this would mean that the durability of these materials would in all likelihood be unacceptably poor. Evidence from the in-service performance of geopolymer and other alkali-activated binders [54–56], as discussed in Chaps. 2 and 11, as well as from laboratory chloride penetration testing as discussed in Sect. 9.4 below, shows that the observed performance is significantly better than would be expected from raw permeability data

[54, 57–60]. This suggests that there are additional effects which compound with, or mitigate, the direct influence of porosity on permeability (particularly ionic permeability, which also relates to gel chemistry-specific effects and interactions) and durability in these materials. However, these effects are not yet well understood.

9.2.2 *Gas Permeability*

There are a wide variety of testing protocols which have been applied to the analysis of gas permeability of cement-based binders and concretes, most of which are fundamentally based around the use of Darcy's Law for the permeability of porous materials. These tests measure either the rate of ingress of a gas into an initially evacuated chamber via passage through the material, or the quantity of gas flowing from a pressurised chamber, through the material and into a chamber held under a lower (ambient or reduced) pressure. The same general principle is applied in tests using a concentration rather than pressure gradient, which are sometimes used in the analysis of diffusion of gases such as radon, O₂ or CO₂. Various different geometries, apparatus and applied pressures have been applied, and rather a wide range of results obtained depending on the specific details of the test, the nature of the binder, and (particularly) the degree of saturation and process of preconditioning of the test specimens [61–65]. A RILEM round-robin test [66] showed reasonably good correlation and agreement between the outcomes of the commercially-available Autoclam, Hong-Parrot and Torrent air permeability apparatus, with the Torrent instrument providing slightly better agreement with the 'known' trends in permeability as a function of concrete mix design than the other two methods assessed [66]. However, there are known to be difficulties in the application and comparability of these types of tests when samples are subject to differences in cracking and/or moisture condition, which necessitates extreme caution in the preparation of samples and in comparisons between samples with different water-binding tendencies (i.e. maturity, pore structure and/or gel chemistry).

Most laboratory tests are conducted using home-built or customised commercial systems, often based around variants of the CEMBUREAU oxygen permeability method [67], which specifies a variety of possible cell geometries, two acceptable pre-conditioning methods (which are noted to give substantially different results), and is stated to be applicable both to either cast or cored concrete specimens. This range of variability within a single test method leads to inevitable difficulties in direct comparison of the permeability values obtained by different laboratories, and renders the process of compilation of data for different materials as tested in different laboratories in general rather unfruitful. In particular, it has been shown that differences in sample size and geometry can lead intrinsically to differences in the permeability results obtained [68], which highlights the need for careful and detailed reporting of all experimental parameters in any presentation of permeability data.

Field testing of air permeability is largely conducted by the Torrent method [69], which is standardised as part of SIA 262/1 [70, 71]; a detailed bibliography related

to the development, validation and application of this test is available online [72]. This method utilises a concentric two-chamber setup, designed to reduce leakage due to lateral air flow, and is able to be applied to concretes in the field through the commercial availability of portable test apparatus. The moisture condition of the concrete is known to be significant in determining the test outcomes, and corrections based on resistivity testing are available for field application where moisture is less controllable than in the laboratory. The evaporation of water from the sample into the evacuated test chamber is known to be an issue for fresh concretes [73], although this is likely to be an issue which is consistent across all tests involving the use of a vacuum chamber into which gas flows and is measured, and issues related to the application of the Autoclam test method [74] to moist concretes have also been noted and discussed in previous RILEM TC publications [75]. This then necessitates careful monitoring (or, if possible, control) of temperature during testing of fresh concrete, to ensure that the results are accurately interpreted.

Reports of testing of gas permeability of alkali-activated binders and concretes are relatively sparse in the published academic literature to date. The early work of Häkkinen [76] showed that the alkali-activated BFS “F-concretes” had an N_2 permeability approximately ten times higher than Portland cement concretes of comparable mechanical strength and total pore volume when tested at 70 % relative humidity. The higher extent of cracking of the F-concrete after drying (as discussed in more detail in Chap. 10 of this Report) then resulted in a much higher gas permeability in dried samples, and also influenced the water permeability as discussed in Sect. 9.2.3. However, the data set available is small, and there do not appear to have been published studies of gas permeability of alkali-activated BFS using any of the widely-available commercial apparatus discussed in the preceding paragraphs to enable direct comparisons with Portland cement concretes tested using the same apparatus.

Similarly, it appears that there has been only a single published study each of the gas permeabilities of fly ash-based AAMs; Sagoe-Crentsil et al. [77] found that the gas permeability of a steam-cured fly ash-derived AAM concrete was equivalent to that of a Portland cement concrete with similar compressive strength (40 MPa), although did not provide details of the testing methodology or sample age at testing.

9.2.3 *Water Permeability*

It is necessary to consider gas and water permeability of AAMs separately, as it is believed that the relationship between these parameters for concretes in general is at best indirect [78]. A disadvantage of most water permeability tests is that the duration of the preconditioning and/or test period is long (weeks or months), and although accelerated procedures for preconditioning of samples have been developed and published [79], these methods are not universally in use. Differences in sample maturity induced by long preconditioning periods are likely to be significant in the analysis of alkali-activated binders and concretes.

The simplest water penetration tests that are standardised in various jurisdictions involve the measurement of total pore volumes by boiling of the samples, and measuring dry and saturated mass to calculate water uptake (and thus pore volume) by difference. Standards describing variants of this test method include ASTM C642 [80] and AS 1012.21 [81]. This test is used as the primary predictor of concrete durability in some jurisdictions [82], and is able to measure the volume within a Portland cement-based product which is filled by hydrate or other solid phases with good repeatability and precision, although it has been noted that the connection to actual permeability (and thus to chloride penetration and carbonation) is somewhat weak [83]. In application of this type of test to AAMs, questions must be asked regarding the role of the weakly-bound water within the aluminosilicate gel phases present, and specifically whether this water is removed in the pre-drying step prior to the boiling test [84]. This remains unclear at present, and although interesting and potentially instructive data have been obtained by the use of this test for BFS-based AAM concretes [85, 86], full interpretation of the outcomes of this test will require more detailed examination of the chemical and microstructural processes taking place within AAM binders during drying, re-wetting and boiling. Similar tests which involve immersion without boiling, such as BS 1881-122 [87] which uses immersion at 20 °C, may prove to be more applicable to AAMs, but the issue of sample preconditioning (including the use of pressure or vacuum saturation) remains a point of discussion nonetheless. It has also been noted that the available variants of the water absorption testing protocol, although apparently similar in nature and implementation, can give very different results depending on the test methodology [78].

Direct measurement of water penetration into concretes is usually achieved in similar geometries to the air permeability tests discussed in Sect. 9.2.2, and some of the same apparatus (e.g. the Autoclam system) can be used for both water and gas permeability testing, although this is generally limited to systems where high pressure (rather than vacuum) is used to drive the test fluid into the sample. Because the penetration of water through the specimens tends to be slower than that of gases, the depth of water penetration is generally measured by splitting a specimen after a specified duration (as codified, for example, in EN 12390-8 [88]), rather than waiting for a steady-state flow situation. A notable exception is the CRD-C 163-92 method [89], which is a steady-state flow test using a sample which is initially vacuum saturated, and with a relatively small (diameter 3× maximum aggregate size) cylindrical sample. Methods such as the Figg test [90], where a hole is drilled into a concrete sample and filled with water, and the rate of flow of water out of the hole into the concrete is recorded, can be used for in-situ testing of concrete in the field, although the likelihood of cracking during drilling of the holes and the uncertainty regarding the moisture state of the surrounding concrete (e.g. due to heating during drilling) provide challenges in the repeatability of this test. The Figg test is also used for gas permeation analysis, but regardless of the fluid used in the test, has the disadvantage that it is not in general possible to use this method to directly calculate permeability coefficients.

The EN 12390-8 [88], ISO 7031 [91] and DIN 1048-5 [92] standards each involve the application of pressure to force water into a previously-dried concrete

sample, and the measurement of the penetration depth after splitting of the concrete; the applied pressures in these tests vary from 150 to 700 kPa, with the ISO 7031 test using a pressure which increases with each day of the test. Each test also has a specified set of drying and sample pre-conditioning conditions and a specified duration, and the combination of these differences and the differences in applied pressure mean that the results of the tests are not directly comparable with each other. The CRD-C 48 method also uses applied pressure to force water into a large specimen, but the extent of penetration is calculated from the change in volume of the water reservoir rather than by post-test analysis of the specimen itself.

Direct water and air permeability measurements of alkali-activated binders and concretes have shown a range of performance, depending mainly on the mix designs tested; AAMs with well-cured binders and low water/binder ratios perform acceptably in these tests [77, 93, 94], but generally do not provide results which could be considered particularly outstanding, most likely due to the low levels of space-filling bound water associated with the key binder gels. Comparisons between AAMs and Portland cements show a very wide range of results; Shi [94] obtained a water permeability approximately 1,000 times lower for sodium silicate-activated BFS concretes than for Portland cement, while Wongpa et al. [95] found that their alkali silicate-activated fly ash concretes were between 100 and 10,000 times more permeable than Portland cement concretes of similar strength grade; each of these investigations used Darcy's law to calculate water permeability in pressurised apparatus. However, the majority of data fall approximately within the centre of this range, showing similar (to within an order of magnitude) water permeability values for alkali-activated fly ash [77, 93], BFS [96], or blended ash/BFS binders [97] when compared with Portland cement concretes. Zhang et al. [98] also studied alkali-activated metakaolin/BFS binders, and found that the water permeability was able to be reduced by either addition of more BFS, or a reduction in w/b ratio, as expected from the discussion of gel chemistry presented in Chap. 5 of this Report.

9.2.4 Capillarity

The other primary method of testing of water penetration into concretes is via capillary suction tests, in which a dried (or partially-dried) specimen is placed in contact with a source of water at one end, and the water is drawn into the interior of the specimen through capillarity effects. Measurement during the test is usually achieved by weighing of the sample at regular intervals, and the data obtained are then used as an indirect measure of the pore network geometry and connectivity. This test was analysed in detail by Fagerlund [99], and has been standardised in various forms including ASTM C1585 [100], EN 1015-18 [101], SIA 262/1 Appendix A [102], as well as a detailed description in the recommendations of RILEM TC 116-PCD [103]. The RILEM methodology involves very specific control of temperature and pore pressure, but only recommends weighing of the sample at four different times, and so does not provide scope for fitting to a diffusion

equation ($t^{1/2}$ dependence), which is achieved in the other protocols through more regular weighing and the use of an extended test duration (up to 15 days according to the standard methods; longer durations than this are sometimes required to achieve full saturation of the capillary system of alkali-activated BFS concretes [60, 86]). However, the main drawback of an extended test duration is that, as with other long-duration tests, the maturity of the sample is increasing during the test.

Capillary sorptivity tests have shown that the pore networks of alkali-activated BFS concretes are sufficiently refined and tortuous to lead to quite a low extent of capillary sorptivity in these materials [32, 58–60, 104–106], although the total porosity was in most cases similar to or higher than that of comparable Portland cements. The use of a higher-modulus activator [107] or a lower water content [108] in alkali-activated BFS systems reduces the rate of water uptake, and the sorptivity decreases with increasing time of curing under moist conditions [108]. Attempts have also been made to model the rate of flow through the pore networks of alkali-activated BFS concretes by describing the capillary pores with an elliptical pore shape model [109, 110], which was to some extent successful, although it is known that the actual pore network geometry of alkali-activated binders involves significant ‘ink-bottle’ effects, where pore volumes with larger radius are only accessible through narrow necks [15, 51].

The very high capillary suction of highly porous alkali-activated metakaolin or natural pozzolan-based binders is potentially problematic in many applications, and may lead to efflorescence if the movement of alkalis is not properly controlled [111], but also provides possible applications in thermal control by providing a water source for evaporative cooling [112].

Another standardised testing method is the Initial Surface Absorption Test (ISAT), as described in BS 1881-208 [113], which uses a narrow capillary brought into contact with the surface of a dried (or in-service) concrete specimen, and calculates the sorptivity of the concrete from the rate of movement of the water from the capillary into the material. This test has the advantage of being relatively rapid (approx. 1 h per sample), but does not appear to have been applied to alkali-activated concretes in the open literature at present. Similar methods include the EN 772-11 [114] test, which is specified for mortars and also measures the flow of water from an external tube into the pore structure of the material.

9.2.5 *Wet/Dry Cycling*

Alternating wet-dry cycling conditions have been known for around 200 years to be potentially damaging to construction materials [115], but it does not appear that there are any specific standardised test methods to describe and analyse the performance of concretes specifically under wet/dry cycling. There are methods which involve wet/dry cycling in the analysis of phenomena such as chloride or sulfate penetration, or freeze-thaw processes, but not specifically for wetting and drying in fresh water. This is probably because the deleterious effects of wet-dry

cycling of Portland cement-based materials are mainly related to acceleration of mass transport rather than a direct influence of the wet/dry cycling process itself; it was noted in a major ASTM publication related to Portland cement concretes that “*the writers are not aware of cases where alternate wetting and drying per se have caused deterioration*” [116], although some damage due to leaching of Ca and alkalis (including efflorescence) has also been noted to be possible [117]. Nonetheless, in the introduction of a new class of materials such as AAMs, it is important to consider the possibility that mechanisms which are relatively innocuous to widely-used materials can have a detrimental effect on materials with very different chemistry but serving in similar applications.

With this concept in mind, there have been several published studies investigating wet/dry cycling of alkali-activated binders, mortars and concretes. Puertas et al. [118] studied sodium silicate-activated BFS and NaOH-activated fly ash and 1:1 fly ash:BFS mortars, with and without polypropylene fibres, under alternating conditions of 6 h in an oven at 70 °C and 18 h immersed at 21 °C for 50 cycles, where the samples were analysed by an impact test method. The data show that the wet-dry cycling process did not have a significantly detrimental impact on the performance of the material as measured by this test; the number of impacts to first cracking was generally increased, but the number required for full fracture of the specimens was reduced. This may indicate that the cyclic treatment enhanced the surface hardness of the material, by effectively providing extra curing duration, but that there was probably some microcracking introduced by the changes in temperature and/or moisture conditions. The issue of microcracking will be explored in more detail in Chap. 10. Slavik et al. [119] and Zhang et al. [98] also noted that there was not a significant difference in strength introduced by wet-dry cycling throughout the first few months of age of the samples, for metakaolin-fluidised bed coal combustion ash and metakaolin-BFS binder systems, respectively.

Häkkinen [120] also studied alkali-activated BFS concretes under alternating high/low relative humidity (40 %/95 %) conditions, with 1 week in each environment per cycle and ten test cycles conducted; this did not show a significant influence on either compressive or flexural strength compared to maintaining the samples continuously at 95 % relative humidity.

9.3 The Interfacial Transition Zone

The interfacial transition zone (ITZ) between aggregate and paste has long been a focus of study in concrete technology in general. In the area where the binder contacts the aggregate, there are often microstructural differences when compared with ‘bulk’ binder regions, meaning that these interfacial regions can exert a disproportionately high (and usually unfavourable) influence on the mass transport, tensile and flexural properties of the geopolymer concrete. The key differences in structure are believed to be due to the fact that the presence of aggregates introduces a higher heterogeneity, and the relative movement of paste and

aggregate during the mixing of concrete can also induce a large variation in the microstructure of the ITZ. This zone is known to measure 15–20 μm in width [3, 121] and generally has a deficit of cement grains, which means that there is effectively a higher water to cement ratio than in the bulk cement paste; consequently, the ITZ has a different chemistry and porosity. When compared to the bulk, the ITZ typically has a higher concentration of portlandite crystals as well as a lower concentration of calcium silicate hydrate (C-S-H) [121–123]. As portlandite crystals are larger than C-S-H grains, and do not pack closely, the porosity of the ITZ is significantly higher than that of the bulk cement paste [124, 125], and as a result the ITZ is generally the weakest area within a concrete. The higher porosity of the ITZ can also lead to pore percolation, allowing easier penetration of harmful species such as chloride into the concrete [126, 127].

There is no standardised test which is designed specifically to quantify the presence and structure of the interfacial transition zone, as this is generally analysed in detail in academic studies rather than as a practical test parameter for concrete producers. Backscattered electron imaging in a scanning electron microscope, applied in parallel with compositional analysis, is considered to be the best two-dimensional technique to distinguish between porosity, reacted and unreacted particles [37–42]. The main drawback of this technique is that it provides information regarding the porosity, but not the connectivity or permeability around this zone, which is also necessary in understanding durability phenomena.

Little detailed attention has been paid to the interactions between aggregates and alkali-activated binders, and there is not yet consensus regarding the nature of this zone. This is also certainly related to the question of alkali-aggregate reactions as discussed in Chap. 8, and further detailed work in distinguishing between ‘desirable’ and ‘deleterious’ processes taking place in this region will certainly be necessary. Some authors, including Brough and Atkinson [128], have reported that there is an interfacial transition zone as in OPC concrete, but that it is less different from the bulk paste than is the case for OPC systems. Other authors [57, 129–136], did not observe any distinct interfacial transition zone in alkali activated fly ash, metakaolin or BFS mortars. However, there is in general a consensus that this zone is not notably weaker than the bulk binder, as is the case for OPC systems. Krivenko et al. [137] particularly noted that the addition of metakaolin to a BFS-based binder aided in further densification of the ITZ in these materials, with the chemical interactions between the binder and the aggregates, and involving Al, believed to increase the microhardness of the material in this zone.

This may thus be an area in which AAM binders could provide significant advantages over traditional Portland cements. The chemistry of Portland cement tends to lead to the formation of a porous zone containing large, mechanically weak crystals surrounding aggregate particles [3, 125], and the percolation of these regions is a key pathway for both mechanical failure and mass transport in concretes. The alkali activators of an alkali-activated concrete interact not only with the aluminosilicate precursor, but also with the aggregate surface, and this interaction tends to lead

to an increase in the degree of homogeneity of the hydration products over the width of the contact zone. This may be beneficial in the final properties of the concrete, but further investigation is required to validate the basis for these remarks before full confidence can be gained.

9.4 Chloride

9.4.1 *The Importance of Chloride Penetration Resistance*

Chloride ions have the ability to destroy the passive oxide film of steel, even at high alkalinities, although it is known that there are threshold effects related to the Cl^-/OH^- ratio which play some role in determining the onset of corrosion [138, 139]. The penetration of chlorides in sufficient amounts through the binder matrix and/or the interfacial transition zone to reach the surface of the reinforcing steel will thus cause corrosion of the reinforcing and damage to reinforced concrete structures. Chloride-induced corrosion is a very common cause of concrete deterioration along sea coasts and in cold areas where de-icing salts are used, and the repair of damaged concrete structure caused by chloride-induced corrosion is very expensive. Thus, the use of a quality concrete material with low chloride permeability is very important in construction of durable reinforced concrete structures. It is therefore essential to determine and understand the relationships between permeability, chloride penetration rate and steel corrosion for the specific chemistry and microstructure of the alkali-activated binder systems. This section will focus on the measurement of chloride penetration, and the following section (Sect. 9.5) will be dedicated to the analysis of steel corrosion within the pore solution environment of alkali-activated materials.

9.4.2 *Chloride Penetration Testing*

It is noted that it is impossible, within the scope of a report such as this, to provide a full description of every chloride penetration test which has been developed for the analysis of concretes; there are a multitude of tests available, and detailed reviews have been provided in recent years by Stanish et al. [140] and by Tang [141], among others. RILEM TCs have also been active in this area, including 178-TMC and 235-CTC, and the reader is referred to their important outputs, including [142, 143], for a broader analysis of chloride testing in general. Table 9.1 shows some of the more common chloride testing methodologies, categorised approximately according to the degree of acceleration which is applied to the migration of chloride through the samples.

Table 9.1 Summary of different widely-used chloride tests, listed approximately from low to high degree of acceleration of chloride migration

Standard test method	Time	Measurement	Comments on application
EN 13396 – 04 [144]	6 months	Immersion in 3 wt.% NaCl, measuring chloride content at three depths	6 replicate specimens; no calculation of transport parameters
ASTM C1543 – 10a [145] (based on AASHTO T259)	90 days	Ponding with 3 % NaCl, sampling of chloride content at specified depths by drilling	2002 preliminary version specified 40 °C, 2004 approved version 23 °C Spatial resolution of extracted samples very coarse (12.5 mm spacing); use of partially dried samples can accelerate initial chloride ingress [146]
Nordtest NT Build 443 [147] (& related, e.g. ASTM C1556 – 11 [148])	35–40 days	Immersion in 16.5 wt.% NaCl (or 15 % for ASTM test), measuring chloride penetration depth profile by profile grinding, unsteady state diffusion coefficient calculated from Fick's second law	Triplicate specimens Very high NaCl concentration Analysis of sample after test can be time-consuming
Accelerated Chloride Migration Test [149, 150]	5–15 days	Variant of RCPT protocol, with larger solution volumes and longer duration to reduce heating effects Measurement is mainly through determination of chloride passed, but correlations exist between steady-state current, charge passed, and chloride passed for OPC materials [151]	High voltage (60 V) used Relatively long duration for an electrically accelerated test

Nordtest NT Build 355 [152]	At least 7 days	Steady state migration under 12 V DC, measuring chloride concentration in downstream cell	Limitations in application to low-permeability concrete
Nordtest NT Build 492 [153] (based on CTH test [154])	Usually 24 h (range 6–96 h)	Chloride migration coefficient from non-steady-state migration under DC current between 10 and 60 V; penetration depth from coulometric analysis	Gaining significant popularity in recent years as a rapid test; reported to have the best precision among the Nordtest methods [155]
Rapid Chloride Permeability Test (ASTM C1202 [156]) – based on AASHTO T277 [157])	6 h	Current passed under application of 60 V DC during test duration; low charge passed is correlated with low chloride permeability	High variability and poor reproducibility [158] Controlled by movement of hydroxide and cations rather than chloride [159] Heating during the test is problematic; shorter test durations have been suggested as a solution to this [146] Poor correlation with 90-day ponding results for OPC [160], and particularly for blended cements [161, 162]

9.4.3 Chloride Penetration Testing of AAMs

The rapid chloride ion permeability test method (ASTM C1202 or AASHTO 227) is widely used to predict the chloride permeability of concretes, although it is essentially a measurement of electrical conductivity, which depends on both the pore structure and the chemistry of the pore solution, rather than measuring chloride movement directly. Also, the test conditions are quite severe, with a voltage of 60 V applied across the sample, leading to heating effects and other changes in the sample structure during the test. The test has been widely criticised (and also applied in modified forms) for this and other reasons. When comparing concrete mixtures with different binder chemistry, the electrical conductivity can be significantly affected by changes in pore solution composition. Analyses and calculations based on electrochemistry indicate that the replacement of Portland cement with supplementary cementing materials may reduce the charge passed by as much as a factor of 10 due to the change in pore solution composition, while the actual change in the transport of chloride ions is much less than this [162, 163]. Nonetheless, this is the test which has been most widely used (and is most widely requested and accepted by specifiers and regulators worldwide) to predict chloride penetration rates, both in Portland cement-based materials and AAMs, and so the results obtained by various workers through the use of this test will be discussed here.

Douglas et al. [164] used the rapid chloride permeability test to measure the charge passed by six batches of sodium silicate-activated BFS concrete, obtaining values between 1,300 and 2,600 C at 28 days and 650–1,850 C for concretes tested at 91 days of age. Values below 2,000 are classified by the standard as being ‘low’, and below 1,000 ‘very low’, which would provide positive indications regarding the likely durability of these materials. However, the charge passed did increase with increasing activator/BFS ratio, which indicates that the measurement may be related to the alkali concentration in the concrete pore solution, as the use of a higher activator content is well known to provide a denser, less porous structure for silicate-activated BFS materials, whereas these test results would indicate the opposite.

The replacement of Portland cement by blast furnace slag is known to reduce chloride diffusion in hardened cement pastes, mortars and concretes [165], and Roy et al. [166] found that the addition of alkalis to blended Portland-BFS cement reduced the rate of chloride diffusion, as measured by the flux of chloride through discs of hardened paste via natural diffusion.

In a comparative study between BFS mortars activated by Na_2SiO_3 , Na_2CO_3 or NaOH, and ASTM Type III Portland cement mortars [94], the alkali silicate-activated materials exhibited higher compressive strength, much lower porosity and finer pore structure than the other specimens when analysed by mercury porosimetry, but the samples activated by Na_2CO_3 and NaOH showed much lower charge passed in the rapid chloride permeability test at each age tested, from 3 to 90 days. This also agrees with the results of water permeability testing in the same study. Wimpenny et al. [85] have also shown that synthetic fibre-reinforced AAMs show

similar overall porosity, but much lower chloride penetration as measured in a ponding test, when compared with a Portland cement control with a similar volume of synthetic fibres as reinforcement.

As with almost all testing of transport-related properties in alkali-activated materials, the issue of sample maturity at the time of the test is essential to the correct interpretation of the test outcomes. For Portland cement systems, most of the tests listed in Table 9.1 are commonly conducted on samples at 28 or 56 days of age, although the testing of cores obtained from field structures is also often undertaken. For an alkali-activated binder, which gains significant maturity via microstructural and physicochemical evolution beyond 28 days of age, the evolution of the sample during a test duration of 30 days or more (and considering that pre-conditioning periods of several weeks are often applied between the end of ‘curing’ and the start of the test period) will be likely to lead to discrepancies between the results obtained from short-duration and longer-duration tests. There have been a number of comparative inter-laboratory studies between different testing protocols for Portland cement-based materials, but no such study of alkali-activated materials has yet been published. An investigation of alkali silicate-activated BFS concretes using the ASTM C1202 RCPT method in parallel with a steady-state migration test (method as described by Mejía et al. [167] and similar to the Nordtest NT Build 355 protocol) [86] showed that pore solution chemistry dominates the outcomes of the RCPT, while the direct measurement of chloride passage through the sample under steady-state electrically accelerated conditions appears to provide more sensitivity to the pore geometry of the binder. Consistent with this, Bernal et al. [60] also showed that the effect of paste content in AAM concretes on the charge passed during the RCPT test was minimal, although other permeability properties of the concretes differed significantly across the range from 300 to 500 kg/m³ of paste volume.

The studies of Shi [94] and of Bernal et al. [86] did not in most cases show strong variation in RCPT results as a function of curing time in alkali-activated BFS, and Husbands et al. [168] showed similar trends in the charge passed by the commercial alkali-activated Pyrament AAM product at 7 or 28 days, but then observed a notable reduction (into the charge passed range classified as ‘negligible’) with 1 year of curing. The results of the ponding tests which were carried out in parallel also showed excellent resistance to chloride penetration in the Pyrament samples, although it is noted that the water/binder ration of 0.23 used in these concretes was extremely low. Zia et al. [169] found that the RCPT results for Pyrament were significantly impacted by the selection of aggregate, where the material with a marl aggregate (predominantly carbonates) showed higher charge passed than with a siliceous aggregate, which indicates further that the pore solution chemistry (and thus its interactions with the aggregate) dominates the test results.

Adam [58] studied alkali silicate-activated fly ash and BFS-based concretes using the RCPT method and shorter-term variants of that protocol, where heating effects were identified to be particularly problematic in the analysis of the alkali-activated samples. In the shorter-duration tests, the alkali silicate-activated BFS

concretes showed a much lower charge passed than the corresponding fly ash-based AAMs, and the use of a higher activator modulus also reduced the charge passed, but there was very little difference between samples tested at 56 or 90 days. However, while the RCPT protocol predicted notably higher chloride diffusion in the alkali-activated fly ash sample than in the control Portland cement, the cement/BFS blends or the alkali-activated BFS, the ponding test showed much less ingress of chloride into the alkali-activated fly ash samples than any of the other samples tested. This was proposed to be due to a combination of the alkali-rich pore solution chemistry of the alkali-activated fly ash causing an excessively high charge passed, and the microcracking close to the surface of the alkali-activated BFS due to issues with shrinkage in the mixes developed in that study. Al-Otaibi [170] also found that the charge passed decreased with increasing activator modulus, although this effect was much more notable at longer ages (182 days) than at 7 or 14 days.

9.4.4 Mechanistic Details Related to Chloride Penetration in AAMs

The rate of progress of chloride through the pore network of Portland cement-based binders is reduced by the formation of Friedel's salt, a calcium chloroaluminate phase which results mainly from the interaction of chlorides with the calcium sulfoaluminates present as hydration products in that binder system. Friedel's salt has not been observed in alkali-activated binder systems (and nor would it be expected in low-calcium systems), and neither have other crystalline chloride compounds, which indicates that this route for specific chemical binding of chlorides is not available during ingress into AAMs. Any differences in the sorption of chloride onto the gels present in AAMs compared to Portland cement remain to be understood, as these effects are convoluted with the effects of differences in pore geometry in chloride migration tests conducted on hardened binders, and it has not yet proven possible to separate the two sets of factors in a laboratory test. On the other hand, the absence of chemical conversion of the binder components to Friedel's salt has been proposed to be responsible for the higher stability of alkali-activated binders than Portland cement during exposure to concentrated CaCl_2 solution [171], and so may prove advantageous in some circumstances.

The discussion presented in this section highlights the importance of conducting multiple parallel tests of as many properties as possible in determination of durability properties of alkali-activated materials, rather than selecting or discarding a material or formulation on the basis of poor results in a specific test. In many cases, the chloride penetration resistance of alkali-activated binders as predicted by the RCPT test protocol appears to be either extremely good or extremely poor, while other permeability parameters (as discussed in Sect. 9.2) do not show the same extreme variability in predicted performance. It is highly desirable to conduct alternative chloride penetration tests in future studies of AAM binders and concretes, to obtain a more realistic understanding of the likelihood of

chloride penetration becoming problematic while the materials are in service; it must be concluded that this phenomenon is currently not well understood in this class of materials.

9.5 Rebar Corrosion Direct Analysis

Steel rebars embedded in concrete are protected from corrosion by a thin oxide layer that is formed and maintained on their surfaces because of the highly alkaline environment of the surrounding concrete, with a pH usually exceeding 12.5 for Portland cement [172], and potentially higher than this for an undamaged alkali-activated binder [173]. The high pH results in the formation of a passive layer on the surface of steel reinforcement in the concrete, which is a very dense, impermeable film preventing any further corrosion of the steel. However, with time, severe corrosion may occur in reinforced concrete structures, as the passive layer can be destabilised by a reduction in pH (induced by processes including carbonation, as discussed in Sect. 9.6, or through the leaching of alkalis), and/or due to the transport of chlorides to the surface of the steel, as discussed in Sect. 9.4. Once the passive layer is destroyed, the steel can be corroded very rapidly. The threshold chloride concentration which induces the onset of corrosion is often reported in terms of the Cl^-/OH^- ratio [138, 139], as high alkalinity can reduce the damaging effects of chloride.

ASTM C876 [174] describes a method for testing the likelihood of corrosion of a rebar, by comparison of its electrochemical potential against that of a Cu/CuSO_4 reference electrode. A potential difference higher (less negative) than -200 mV is stated to indicate a 90 % probability of no corrosion, while a potential difference lower (more negative) than -350 mV corresponds to a 90 % probability of corrosion. These criteria are believed to provide a good indication of the likelihood of corrosion in systems containing chlorides [175], but the onset of corrosion is also influenced by O_2 concentration (which is dependent on permeability), carbonation (which can give large changes in corrosion for small shifts in redox potential (Eh) [175]), and other parameters. Corrosion inhibitors such as calcium nitrite are used in Portland cement systems to stabilise the passive layer by controlling the Eh [176], and either a strong oxidant or a reductant can be effective if applied correctly. Methods such as ASTM G109 [177] or EN 480-14 [178] are used in parallel with the recommendations of documents such as ASTM C876 to test the efficacy of such additives. However, such work does not appear to have been undertaken in detail for alkali-activated binders in the open literature. The time taken to conduct some of these tests (ASTM G109 couples chloride ponding with electrochemical testing, for example) has led to the recommendation of adoption of more accelerated protocols such as a ‘rapid macrocell test’ [179], and this may provide a good opportunity to move forward in the analysis of AAMs.

Gu and Beaudoin [175] also summarised some of the factors which can influence the measured corrosion potential of a concrete; some of the information presented

Table 9.2 Some of the parameters that can influence measurements of corrosion potential in Portland cement concretes, after [175]

Parameter	Shift in half-cell potential	Change in steel corrosion rate
O ₂ concentration	More O ₂ → more positive	In some circumstances
Carbonation	More negative	Increase
Chloride	Often much more negative	Increase
Oxidant (anodic corrosion inhibitor)	Positive	Should decrease
Reductant (cathodic corrosion inhibitor)	Negative	Should decrease
Epoxy coated rebar	Makes cell difficult to establish	Should decrease, if coating is not damaged
Galvanised rebar	Negative	Can be effective, but less so in high-alkali cements [181]
Coatings, patches and stray currents	Measurement can be unreliable	Various effects

by those authors is shown in Table 9.2. Many of these points are likely also to be relevant to AAMs, but this in most cases remains to be verified in detail through scientific analysis. Poursae and Hansson [180], in a paper discussing the applicability (or lack thereof) of various accelerated techniques for assessment of rebar corrosion in concretes, describe the subject in general as a “minefield”, and state that “*any technique designed to accelerate the corrosion process should be considered with scepticism*”. From this basis, it is unlikely that laboratory testing will ever provide a full representation of the in-service performance of AAM concretes with regard to steel corrosion, but it is also probable that carefully-designed tests will be able to provide at least some useful information for the prediction of the durability of different binder types.

It has often been assumed that, with an alkalinity comparable to the levels found in conventional concrete, alkali-activated concrete would be capable of holding steel rebar in the passivity region of the Pourbaix diagram, thereby providing low corrosion levels in reinforced concrete structures. Wheat [182] reported excellent performance of Pyrament alkali-activated concretes in holding steel rebar in a passive state during 3 years of immersion in 3.5 wt.% NaCl solution, and in cyclic wetting/drying with the same solution, which was attributed to the high impermeability of the binder. However, both the passivation capacity and the duration of the passive state depend on the nature and dosage of the binder, the type of activator and the conditions prevailing in the medium [183–185]. It is also interesting to note that although the pore solution Eh of alkali-activated BFS concretes and high-volume BFS-OPC blends is known to be reduced by several hundred mV by the presence of sulfide in almost all blast furnace slags [186], this does not appear to lead directly to steel corrosion problems in these materials. In fact, high-volume BFS-OPC blends such as EN 197 CEM III or CEM V are used specifically in many applications where high durability is essential, which indicates that the standard electrochemical arguments are not able to capture the full details of the pore solution chemistry of these materials with regard to protection of embedded steel.

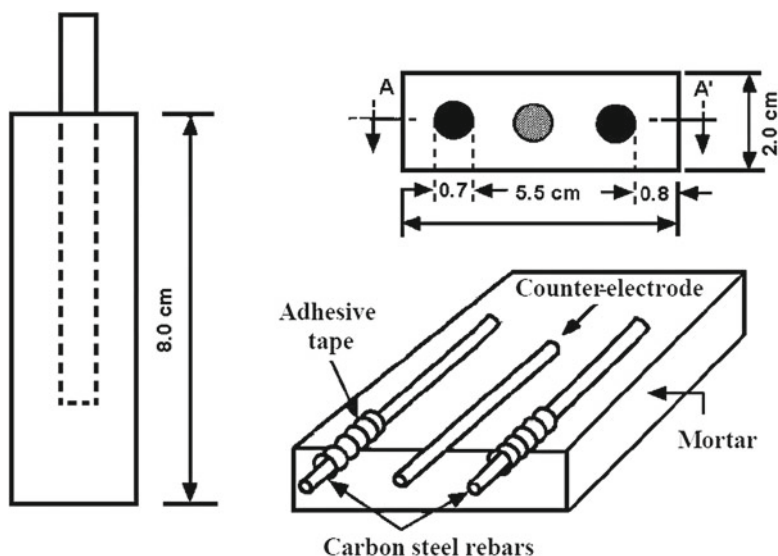


Fig. 9.5 Prismatic specimens used for the corrosion tests of Bastidas et al. [184] and Fernández-Jiménez et al. [187]

9.5.1 Steel in Alkali-Activated Fly Ash

Bastidas et al. [184] and Fernández-Jiménez et al. [187] reported studies of the corrosion rates of steel rebars embedded in fly ash mortars with and without Portland cement, activated by sodium silicate or sodium carbonate, and with chloride addition (up to 2 wt.% CaCl_2 in the binder) using mainly electrochemical techniques. Ordinary Portland cement (OPC) mortars were prepared as reference samples. Prismatic specimens measuring $80 \times 55 \times 20$ mm were used for the corrosion measurements, as shown in Fig. 9.5, with two 6 mm diameter carbon steel reinforcing bars used as test electrodes during the measurements. The auxiliary electrode was an external 50 mm diameter stainless steel disc with a hole in the centre to house a saturated calomel electrode (SCE) used as the reference. The contact between the electrolyte (concrete matrix) and the auxiliary electrode (stainless steel disk) was enhanced with a moist sponge to facilitate the electrical measurements, and the surface area of the test electrodes (10 cm^2) was controlled with adhesive tape (Fig. 9.5).

Samples were demoulded after curing and stored at ambient temperature, and the test commenced with exposure at 95 % relative humidity (RH) for 90 days, then 30 % RH for 180 days, and then returned to 95 % RH until the end of the experiment after 760 days [187]. Under these conditions, alkali-activated fly ash mortars passivated steel reinforcement successfully at high relative humidity (Fig. 9.6). Drying of all samples increased the potential, and thus decreased the likelihood of corrosion, and the presence of chloride was harmful in all cases.

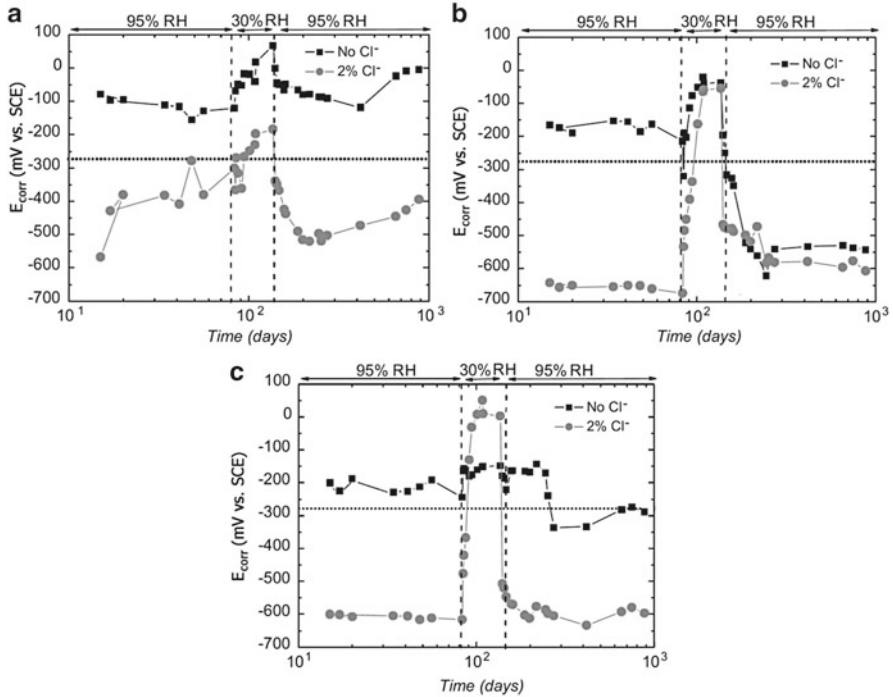


Fig. 9.6 Corrosion potential E_{corr} , reported as half-cell potentials against saturated calomel electrode (SCE; add 75 mV for potentials vs. Cu/CuSO₄ electrode): **a** Portland cement CEM I mortar, **b** fly ash + 8 M NaOH mortar, **c** fly ash + sodium silicate mortar. Grey lines and points are samples with 2 % Cl⁻ added as CaCl₂, black lines and points contain no added chloride (Data from Fernández-Jiménez et al. [187]). Dashed horizontal lines show the ASTM C876 specification for 90 % probability of corrosion; values more negative than this indicate a high likelihood of corrosion according to the standard test method

Passivation in the NaOH-activated fly ash samples was seen to fail (according to the classification of the test method) after the drying period, possibly due to carbonation of the very alkali-rich and rather porous matrix under intermediate relative humidity, while the silicate-activated fly ash and the Portland cement did not show this effect. The trends in corrosion current (i_{corr}), and observations of corrosion products in the specimens, were consistent with the corrosion potential data [187].

Stainless steel (SS) reinforcing elements were first used in Portland cement concretes many decades ago, and have proven the ability to resist corrosion in very aggressive environments [188]. However, application has been limited due to the high cost of SS compared to carbon steel. For this reason, new stainless steels, in which the nickel content has been lowered by replacement with other elements, are being evaluated as possible alternatives to conventional carbon steel [189]. When embedded in alkali-activated fly ash mortars with up to 2 wt.% chloride added to the binder, the corrosion behaviour over 180 days at 95 % RH was similar to those of

regular (AISI 304) stainless steel in AAM mortars with and without chloride addition, with E_{corr} values around -100 to -200 mV relative to the saturated calomel electrode, suggesting good durability performance of low-nickel SS embedded in fly ash mortars.

9.5.2 Steel in Alkali-Activated BFS and Other Binders Based on Slags

Kukko and Mannonen [190] observed that their alkali-activated BFS “F-concrete” materials provided good protection for embedded reinforcing steel during 1 year of immersion of the specimens in simulated sea water, with no visual evidence of corrosion products formed on the samples, but did not provide electrochemical measurements. Deja et al. [191] and Malolepszy et al. [192] investigated the corrosion of steel in alkali-activated slag mortars cured in water and in 5 % MgSO_4 solution by measuring polarisation curves, corrosion current and mass loss of the reinforcement. MgSO_4 immersion was seen to slightly impact the passivation of the rebar, while immersion in fresh water had little effect. The corrosion current data indicated that the steel in the alkali-activated slag mortar had a higher corrosion rate than in the Portland cement mortar, but the current decreases with time in both mortars.

Holloway and Sykes [193] applied detailed electrochemical characterisation to the analysis of mild steel rebars in sodium silicate-activated BFS mortars, with malic acid added as a retarder, and NaCl added into the mix water to accelerate corrosion processes. In this study, the addition of higher levels of NaCl appeared to reduce the initial corrosion current, a trend which was not able to be clearly explained from a fundamental chemical perspective. However, a similarly counter-intuitive result was obtained by Bernal [194] with regard to the effects of binder carbonation on corrosion rates, where a partially carbonated binder showed a higher resistance to corrosion during 12 months immersed in water, compared to an uncarbonated material. These, and other results which are not able to be straightforwardly explained by standard theories, indicate that there is a strong need for further detailed scientific and analytical work in determining the mechanisms involved in controlling steel corrosion within alkali-activated BFS binders. Holloway and Sykes [193] proposed, using arguments based on pore solution chemistry and electrochemical testing, that the sulfide in the slag was responsible for some of the complications in the electrochemistry of their specimens, influencing both the kinetics of corrosion and the measurement of the corrosion currents. Those authors also noted that all of the corrosion rates measured in their study were ‘low’ by comparison with expectations for such high chloride doses in the mix water.

Bernal [194] and Aperador et al. [195] also noted that the corrosion potentials of all samples studied in that investigation fell in the region where ASTM C876 indicates that there is a high likelihood of corrosion. Montoya et al. [196] also proposed, on the basis of finite element simulations, that alkali-activated BFS mortars appear to be quite amenable to durability enhancement through cathodic protection.

Table 9.3 Mass loss of rebar in alkali-activated slag cement concrete made from different slags and alkaline activators under wetting and drying cycles [198]

Slag type	Activating solution density, kg/m ³	Mass loss of reinforcement (g/m ²), during time (months; bottom row of column titles)							
		90 % Na ₂ CO ₃ +10 % NaOH				45 % Na ₂ CO ₃ +40 % Na ₂ SO ₄ +15 % NaCl			
		6	9	12	18	6	9	12	18
Basic	1,100	0.52	0.53	0.52	0.52	0	0	0	0
	1,150	0.70	0.73	0.71	0.72	0.89	0.91	0.90	0.91
	1,200	0.98	0.96	0.98	0.97	1.07	1.09	1.07	1.06
Acid	1,100	0	0	0	0	0	0	0	0
	1,150	0.41	0.43	0.40	0.42	0.63	0.61	0.62	0.62
	1,200	0.71	0.70	0.72	0.71	0.58	0.60	0.59	0.59
Neutral (electro-thermo-phosphorus)	1,100	0	0	0	0	0	0	0.36	0.36
	1,150	0.71	0.76	0.73	0.72	46.91	74.73	78.54	84.10
	1,200	1.12	1.14	1.11	1.13	59.12	85.73	86.04	87.40

Table 9.4 Effect of additives on the mass loss of reinforcement in alkali-activated phosphorous slag concrete activated by 45 % Na₂CO₃+40 % Na₂SO₄+15 % NaCl, under wet-dry cycling [198]

Additive	Mass loss of reinforcement (g/m ²)		
	6 months	12 months	18 months
Reference concrete (without additive)	46.9	78.5	84.1
Sodium hydroxide (5 wt.%)	18.0	31.1	42.1
OPC clinker (5 wt.%)	0.41	0.38	0.39
Ferroniobium slag (10 wt.%) + CaF ₂ (5 wt.%)	8.81	0.52	0.51

Alkaline by-products can also be used as activators for BFS and other metallurgical slags, and this has been an area of particular interest in the former Soviet Union [54, 197]. However, some by-products contain chlorides and sulfates, which may initiate corrosion of steel in concrete. Krivenko and Pushkaryeva [198] investigated the corrosion of steel in alkali-activated concretes using two mixed activators, one consisting of 90 % Na₂CO₃+10 % NaOH and the other 45 % Na₂CO₃+40 % Na₂SO₄+15 % NaCl. The results in Table 9.3 indicate that the corrosion of steel depends on the nature of the slag, the nature and dosage of alkaline activator, and carbonation of the concrete. When the carbonate-hydroxide activator was used, the mass loss increased with the activator concentration. The carbonate-sulfate-chloride activator showed similar corrosion performance, except for the two batches of specimens made with phosphorus slag and the highest activator concentrations; these were rapidly carbonated and had a high concentration of chloride, which led to much more severe corrosion than was observed in any other specimens.

The addition of additives can densify the structure of hardened concrete and change the pore solution chemistry. Table 9.4 shows the effects of additives on the rate and extent of mass loss of the reinforcement in alkali-activated concretes made with granulated phosphorous slag and an activator containing 45 % Na₂CO₃+40 %

$\text{Na}_2\text{SO}_4 + 15\% \text{ NaCl}$ under wet-dry cycling. The addition of 5 wt.% Portland cement clinker was effective in reducing the corrosion rate (by a factor of as much as 100), as was the combination of 10 wt.% ferroniobium slag (which is rich in Al) and 5 wt.% CaF_2 . However, this route to corrosion reduction may be less widely applicable due to the low availability (and often also the radioactive character [199]) of ferroniobium slags, and also the fact that fluorides can greatly accelerate the corrosion of steel if present at low concentrations, only providing corrosion inhibition at higher concentrations (~100 ppm or more) [200].

9.5.3 Remarks on Test Methods for AAMs

At present, the understanding of the corrosion chemistry of steel within AAM binders is probably insufficient to enable development of test methods specific to the chemistry of AAMs. This is particularly the case for AAMs based on BFS or other metallurgical slags containing sulfide, which generates a reducing environment within the binder and causes complexities in electrochemistry which are not yet well understood. It will certainly be necessary to learn from the analysis of high-volume BFS blends with OPC (which has reached a more advanced stage than the analysis of AAMs due to the greater maturity of that research topic) to gain a basic understanding of the sulfide chemistry which influences steel corrosion rates in complex ways. The effects of the presence of high concentrations of alkalis, and in particular the interaction between carbonation, chloride, and alkalis, and the relationship between transport properties and steel corrosion chemistry at the rebar-paste interface, will provide fruitful ground for researchers in the coming decades, as much remains to be understood in this area. Thus, it appears important to recommend that whichever test methods are selected for the analysis of AAMs, a full reporting of experimental conditions and details in each published study is essential in providing the reader with the ability to understand and utilise the outcomes of the work. This is universally important in the implementation of durability tests, but is particularly critical in areas such as corrosion testing where there are so many incompletely-understood parameters which could potentially influence the results obtained from every test undertaken.

9.6 Carbonation

9.6.1 Introduction

Carbon dioxide (CO_2) is known to drastically affect the durability of cement-based materials in the long-term, through a degradation process referred to as carbonation [201–203]. This phenomenon is controlled by both gas diffusion and

chemical reaction mechanisms [204], and is mainly determined by the structural characteristics of the matrices, and the permeability of the material. The usual effects of carbonation are the reduction of the alkalinity of the material, decalcification of the main reaction products (portlandite, C-S-H gel and ettringite in the case of OPC-based materials), along with decreased mechanical strength and increased permeability, which favours the ingress of chlorides or sulfates and consequently increases the susceptibility to corrosion of the steel reinforcement [201, 204–206]. This is why carbonation is considered one of the main causes of degradation of cement-based structures.

Carbonation of mortars and concretes produced with ordinary Portland cement has been widely studied, and can be considered a relatively well-understood phenomenon. In these systems, the CO_2 from the atmosphere diffuses through the pores of the material, and dissolves in the pore solution, forming HCO_3^- . This ion reacts with the calcium-rich hydration products present in the matrix [202, 204, 207]. On the other hand, for concretes based on AAMs there is relatively little existing knowledge about the carbonation mechanism and the variables affecting its progress.

9.6.2 Carbonation of Ordinary Portland Cement-Based Materials

For conventional Portland cement-based systems, it is well known that the progress of carbonation is dependent on the reaction products composing the binder with which the CO_2 is going to react, as well as the factors conditioning the CO_2 diffusivity such as pore network and exposure environment (mainly the relative humidity and the temperature). It has been reported that the main parameters conditioning the carbonation progress are those controlling the CO_2 diffusivity and the reactivity of CO_2 with the binding paste [204, 208], as summarised in Fig. 9.7.

The effect of the type of binder is associated with the amount and type of phases formed during the hydration process, with those containing alkali metal or alkali-earth metal cations being the most susceptible to react with the CO_2 present in the environment [209]. It has also been identified that carbonation can be aggravated by the presence of organic substances and anions reacting with the hydration products in hardened pastes, increasing the CO_2 diffusivity [204]. On the other hand, the higher CO_2 concentration in an accelerated carbonation process, which initially promotes an increase in the density of the solid, leads to superficial porosity of the pastes, and also increases the capillary sorptivity in the material [210]. There may also be changes in the CaCO_3 phase formation at higher CO_2 concentration, with metastable phases forming, also altering the pore size distribution.

It has been reported [206, 211] that carbonation is more rapid at intermediate (50–70 %) relative humidity (RH), and decreases at higher and lower relative humidities. High humidity increases the fraction of pores filled with water, hindering the diffusion of CO_2 , and low humidity means that there is not sufficient water to promote the solvation and hydration of the carbon dioxide. Under intermediate

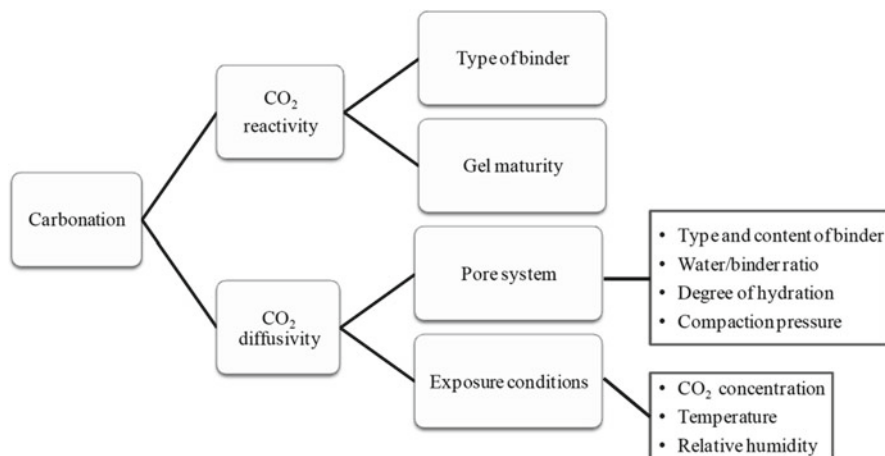


Fig. 9.7 Factors conditioning the carbonation of cementitious materials, according to the classification of Fernández-Bertos et al. [204]

moisture conditions, both reaction kinetics and diffusion of CO_2 are favoured, which leads to optimum conditions for carbonation [204].

The use of supplementary cementitious materials (SCMs) in concretes has increased dramatically over the past decade, so that most of the cements currently available in the market are now blended binders. However, less attention has been addressed towards the understanding of carbonation in these materials, whose pozzolanic reaction reduces the content of the $\text{Ca}(\text{OH})_2$ in the binder. These usually present higher susceptibility to carbonation than cements without any mineral admixture, when tested using the phenolphthalein indicator method [212–215].

The question must therefore be asked: does this mean that the metallic reinforcing component of a structure is more likely to develop a corrosive process when embedded in a concrete based on blended or other alternative cements in the absence of $\text{Ca}(\text{OH})_2$, than if it were embedded in a concrete produced with Portland cement alone? In fact, the use of blended cements has a remarkable positive effect on concrete durability, and the corrosion rate of the steel reinforcement is known to be substantially reduced in concretes including slags [216, 217] or other pozzolans [218, 219]. This may suggest that the use of the phenolphthalein indicator test as the sole measure of carbonation progress is somehow overly simplistic for assessing the carbonation performance of ‘modern’ cements, whose chemistry and microstructure are different to those of the cements in common use 20 years ago, when these test methods were formally proposed.

This is critical for the understanding of carbonation in AAMs, considering that $\text{Ca}(\text{OH})_2$ is not identified as a reaction product in AAM binders, and where the chemistry differs significantly from that of Portland cement, as indicated in Chaps. 3, 4, and 5.

9.6.3 Test Methods for the Determination of Carbonation

The carbonation process of a cement or concrete under ambient conditions is generally slow, as a consequence of the relatively low concentration of CO₂ in the atmosphere (0.03–0.04 %), and the low gas permeability of hardened binders (concretes and mortars). This is why the experimental methods implemented for assessing carbonation in cementitious materials are fundamentally based on induced-accelerated carbonation of the specimens under controlled conditions, through exposure to high CO₂ concentrations.

One approach has been the exposure of specimens under a gas environment of 100 % CO₂ while controlling the relative humidity as described in the standard procedure ASTM E 104-02 [220], by using saturated salt solutions [208, 210, 214, 221, 222]. This approach is relatively popular, but the scientific foundations for the use of such a high CO₂ concentration are far from certain. In recent years the use of climatic chambers for inducing accelerated carbonation has increased, as the exposure conditions can be fully controlled (CO₂ concentrations, relative humidity and temperature) [223–225]. This has promoted the development of three international standards for the assessment of carbonation in cementitious materials:

- **EN 13295:2004:** *Products and systems for the protection and repair of concrete structures – test methods – Determination of resistance to carbonation* [226]

This accelerated test method measures the resistance of a building product or system against carbonation when assessed under accelerated testing conditions. In this case the specimens are exposed to a gas environment of 1 % CO₂, temperature of 21 ± 2 °C and relative humidity (RH) 60 ± 10 %. One of the fundamental assumptions made in this standard is that under these carbonation conditions, the same reaction products that are identified in Portland cement when exposed to atmospheric carbonation are formed. This is essential in the application of an accelerated carbonation test, but has only been validated for the case of Portland cement.

Specimens are prepared in accordance to the European standard EN 196-1, covered with a plastic film for 24 h, then demoulded and sealed again with a plastic film for 48 h. After this, the samples are aged and preconditioned for 25 days under the same temperature and humidity conditions specified for the carbonation testing. The specimens need to be preconditioned in order to assure uniform moisture content. The carbonation depths are measured after the preconditioning period and after 56 days of storage in this environment. Considerations related to geometry effects and the incorporation of large aggregates are also included.

- **Draft BS ISO/CD 1920-12:** *Determination of the potential carbonation resistance of concrete – Accelerated carbonation method* [227]

This standard is currently under development, and has not yet been formally published. The 2012 draft specifies 4 % CO₂, 20 °C and 55 % RH as a basic

testing method, with the option of 27 °C and 65 % RH for hot climate locations. Specimens are specified to be 100 mm cubes or 100 × 100 × 400 mm rectangular prisms, cured for 28 days at a temperature matching the selected test temperature, dried (conditioned) at 18–29 °C and 50–70 % RH for 14 days (or a different condition can be used and reported if preferred), then exposed to elevated CO₂ conditions for 56–70 days. Carbonation depth is revealed on split (not sawn) specimens by application of phenolphthalein (1 % in a 70/30 ethanol-water mixed solvent).

- **EN 14630:2006:** *Products and systems for the protection and repair of concrete structures – test methods – Determination of the carbonation depth in a hardened concrete through the phenolphthalein method* [228]

This method is used to analyse specimens after exposure to CO₂, and explains the process of application of 1 g of phenolphthalein indicator dissolved in 70 mL of ethanol, diluted to 100 mL with distilled or deionised water. Considerations for the measurements of carbonation depths and the report description are also included.

Other methods for assessing accelerated carbonation of concretes are the following:

- **RILEM CPC-18.** *Measurement of hardened concrete carbonation depth* [229]

This method of testing consists of determining the depth of the carbonated layer on the surface of hardened concrete by means of an indicator composed of a solution of 1 % phenolphthalein in 70 % ethanol. For accelerated carbonation this method does not suggest any particular exposure conditions, but climatic conditions of storage need to be precisely indicated when testing. For natural carbonation studies of specimens stored indoors, temperature and relative humidity are defined (20 °C and 65 % RH). When samples are stored outdoors they need to be protected against rain. The air must be able to reach the test surfaces unhindered at all times, with a free space of at least 20 mm around the specimens.

- **NORDTEST METHOD: NT Build 357.** *Concrete, repairing materials and protective coating: Carbonation resistance* [230]

This method specifies an accelerated test procedure monitoring the rate of carbonation (using the phenolphthalein indicator) of specimens exposed to an atmosphere of 3 % CO₂ and 55–65 % relative humidity. Sample preparation is strictly specified: concretes should be produced with a water:binder ratio of 0.60 ± 0.01, slump 120 ± 20 mm, and with an aggregate with maximum diameter of 16 mm. In cases where the mix requires a plasticiser, a melamine type can be used. No provision is made for binder types where the specified mix parameters cannot be reached, or where melamine-type plasticisers are not compatible with the binder. The specimens are stripped 1 day after casting, and cured in water at 20 ± 2 °C until 14 days of age, then cured in air at 50 ± 5 % RH, 20 ± 2 °C until 28 days of age before they are subjected to the test. It is important to note that in this case the phenolphthalein solution is prepared by mixing 1 g phenolphthalein in a solution of 500 mL distilled/ion-exchanged water and 500 mL ethanol, which is a much more dilute solution than is used in EN14630:2006.

- **Portuguese Standard LNEC E391.** *Betões. Determinação da resistência à carbonatação. Estacionário* [231]

This method recommends accelerated carbonation of specimens exposed to a CO₂ concentration of 5 ± 0.1 %, with RH between 55 and 65 % and a temperature of 23 ± 3 °C. Samples need to be cured submerged in water for 14 days at 20 ± 2 °C, and then stored in an enclosed environment at 50 ± 5 % RH and 20 ± 2 °C until reaching an age of 28 days. The measurements of carbonation depth are conducted in accordance with the method recommended in RILEM CPC-18 as previously described. The phenolphthalein indicator is a 0.1 % alcoholic solution.

- **French test method AFPC-AFREM.** *Durabilité des bétons, méthodes recommandées pour la mesure des grandeurs associées à la durabilité, Mode opératoire recommandé, essai de carbonatation accéléré, mesure de l'épaisseur de béton carbonaté* [232].

This accelerated carbonation method uses a carbonation chamber at 20 °C and 65 % relative humidity with 50 % CO₂. Carbonation depth is measured after different times of exposure using a 0.1 % alcoholic solution of phenolphthalein indicator. For natural carbonation assessment, the specimens after 28 days of conventional curing (immersed in water) are storage in controlled climatic conditions of 50 % RH and 20 °C until testing.

In general, in each of these test methods, the ingress of the carbonation front (which is assumed to be sharp rather than diffuse) is measured as a function of the time of exposure under specific environmental conditions. Variations in weight, mechanical strength and permeability are sometimes also monitored, but these measurements are not specified as a part of the carbonation test method itself. In this report, detailed attention is addressed to the phenolphthalein method and the issue of carbonation shrinkage, considering that the particular properties of AAMs might affect the measurements obtained in these tests.

9.6.4 Carbonation Depth – The Phenolphthalein Method

The carbonation front in an initially alkaline building material is usually measured by observing the colour change of a pH indicator as a result of CO₂ exposure. The colour transition of phenolphthalein, the most commonly applied indicator, begins to occur at a pH of 10 (fading from purple/pink to colourless; the transition is completed at pH 8.3), which roughly corresponds with the pH below which the passive film on steel in Portland cement systems becomes unstable and stops protecting the steel from corrosion. It is therefore broadly assumed that a carbonation depth greater than the cover depth over the steel will lead to a corrosive process at the steel surface. The main problem associated with this approach is that the carbonation depths of different parts of a particular structure can be different, although a uniform CO₂ exposure concentration is present. This is a consequence of

the differences in relative humidity, wet/dry conditions and sunlight exposure in different parts of the structure, which will lead to changes in permeability of the concrete. The details of the pore solution of the concrete should also be taken into consideration, and there are known (but poorly understood) complicating effects when chlorides and carbonates are present simultaneously in a reinforced concrete element [233]. In practice, the cover depth may also differ from place to place in a structure. Another disadvantage of this method is that it is destructive, which means that it is impossible to repeat a measurement in the same specimens to identify variations as a function of time, and that concretes in key structural applications cannot be analysed while in service. This makes the phenolphthalein indicator a poorly reliable method for assessing carbonation of building materials at a scientifically satisfactory level of detail [234]; however, it is extensively used and generally accepted. Also, as identified in the discussion of the different testing methods above, the phenolphthalein indicator can be prepared at different concentrations and in different solution environments, which will quite possibly modify the results obtained for carbonation depths in AAMs.

9.6.5 Carbonation Shrinkage

Less attention has been paid to the assessment of carbonation shrinkage in building materials in general, which is associated with the stresses induced in cement pastes as a consequence of the formation of carbonation products, initially in the pore network and then, at advanced carbonation conditions, in the gel binder [235]. There is no specific standard method for measuring carbonation shrinkage, but in some of the few studies conducted assessing this behaviour [236], similar procedures to those described in ASTM C596-09 [237] or ASTM C1090-10 [238] are adopted. In this case, the shrinkage is measured at different times of CO₂ exposure to correlate carbonation depth with any dimensional changes shown by the specimens. The extent of carbonation shrinkage in AAMs is, in terms of the available literature, completely unknown. However, Shi [171] identified that during 75 days of exposure of an alkali-activated BFS paste to 15 % CO₂ at 53 % RH, cracks appear a few days after starting the carbonation testing as a combined effect of drying shrinkage and carbonation shrinkage.

9.6.6 Carbonation of AAMs

9.6.6.1 Effect of Exposure Conditions

There is limited existing knowledge regarding the carbonation of AAMs. Byfors et al. [239] identified higher rates of carbonation in F-concretes (plasticised alkali silicate-activated BFS) when compared, in accelerated testing, with ordinary

Portland cement reference specimens of similar compressive strengths. These results are in good agreement with the observations of Bakharev et al. [222], who also reported higher susceptibility to carbonation in AAM concretes prepared with sodium silicate and BFS than in reference concretes based on ordinary Portland cement, when evaluated under accelerated carbonation conditions.

Conversely, Deja [55] identified that alkali-activated BFS mortars and concretes showed carbonation depths comparable to those obtained for reference samples of Portland cement, along with increased compressive strengths at increased times of exposure to CO_2 . This was associated with a refinement of the pore structure, as carbonates precipitated during the carbonation reaction. This was more remarkable in samples activated with silicate-based activators than in specimens activated with sodium carbonates. It is important to note that the accelerated carbonation of the specimens in that study was induced using a carbonation chamber at a relative humidity of 90 %, and fully saturated with CO_2 . These results must be carefully interpreted because, at such high relative humidity, the saturation of the pores in these specimens is such that even when exposing AAMs to extremely severe concentrations of CO_2 , the carbonation reaction is not taking place in the same way as it would at lower RH. This is coherent with the trends identified by Byfors et al. [239], who identified that carbonation of AAMs is faster when the materials are exposed to reduced relative humidities.

The relative humidity conditions at which carbonation of AAMs is assessed is critical, as shrinkage due to drying and subsequent carbonation can be favoured in low humidity conditions which can induce microcracks in the material, increasing the carbonation progress. Studies conducted by Bernal [194] in alkali-activated BFS/metakaolin blended concretes show that the progress of carbonation and the consequent increase in the total porosity are slightly higher when samples are carbonated at 65 % RH, compared with specimens carbonated at RH values of 50 or 80 %; however, after longer periods of carbonation exposure, the effect of the RH becomes less relevant, and slightly increased carbonated depths are identified with increasing RH.

For carbonation tests of alkali silicate-activated BFS and BFS/metakaolin concretes, where the specimens were not dried prior to testing, a separate measurement of the water absorption of the uncarbonated samples was seen to provide a good indication of whether drying effects during the test duration were likely to retard the initial stages of carbonation [240]. Testing of samples with low water absorption (i.e. when the pore network is initially highly saturated and refined) at high relative humidity gives a very low carbonation rate in the early stages of the test, as the carbonation rate of the saturated binder is relatively slow, and later there is an acceleration of the carbonation process as the drying front enters the sample and enables carbonation to proceed.

9.6.6.2 Effect of Sample Composition

Studies of pastes and mortars of alkali-activated BFS, and BFS/metakaolin blends, have shown potentially higher susceptibility to carbonation in these materials when

compared with conventional Portland cements, as a consequence of the differences in the mechanism of degradation and its effects on microstructure, especially due to the absence of portlandite as a reaction product in these binders [60, 107, 241, 242]. However, this susceptibility is strongly influenced by the type and concentration of the alkaline activator.

Puertas et al. [241] identified that specimens of alkali-activated BFS prepared using silicate-based activators present high carbonation depths, associated with a reduced matrix density, along with a significant increment in the porosity and a reduced mechanical strength, when exposed to a fully saturated CO₂ atmosphere. On the other hand, when BFS was activated with NaOH solutions, the carbonation enhanced mortar compaction and consequently mechanical strength. It was suggested [243] that a possible cause for this behaviour was the difference in the composition and structure of the C-S-H gel, which in the case of the silica-based activators presented lower Ca/Si ratios (~0.8) than those formed when NaOH was used (Ca/Si ratio ~1.2); however, other factors such as pore solution chemistry, and the differences in gel porosity and stability, are likely to affect the behaviour of AAMs when exposed to saturated CO₂ environments.

Palacios and Puertas [242] analysed sodium silicate-activated BFS pastes exposed to a fully saturated CO₂ atmosphere, where precipitation of natron and CaCO₃ in its different polymorphs was identified, as a consequence of severe carbonation of the C-A-S-H products, which is higher than was identified for comparable Portland cement specimens. A similar effect of CO₂ exposure in the structure of the C-A-S-H formed in sodium silicate-activated BFS was also observed by Bernal et al. [107]. In that case, calcite was identified as the sole calcium-containing carbonation product, along with trona as the sodium-containing carbonation product. Thermodynamic modelling of AAM pore solution chemistry [244] predicts sodium bicarbonate formation at lower pCO₂, hydrous sodium carbonate at higher pCO₂, and trona increasing in prevalence at higher temperature at intermediate pCO₂, and these trends are also consistent with the results of 7-year natural carbonation exposure tests of alkali-activated BFS concretes [245].

Studies of concretes based on silicate-activated BFS [60] also revealed that higher paste content in the concrete mix design can lead to substantial increments in the resistance to carbonation, so that the carbonation depths reached are comparable to those obtained in Portland cement concretes produced with similar mix designs (Fig. 9.8). This highlights that manipulation of design parameters of the concretes is possible, and necessary, to achieve desired performance in AAMs.

Specific studies of natural carbonation in alkali-activated binders are limited; some data obtained from in-service structures in the former USSR and in Poland are presented in Chaps. 2, 11 and 12, where it is possible to identify generally moderate to low carbonation rates (<0.5 mm/year) under service conditions in continental climates [54–56]. Particularly, Shi et al. [54] report the natural carbonation rates of concrete structures with ages between 12 and 40 years, located in Russia, Ukraine and Poland; the in-service carbonation rates measured using the phenolphthalein method did not exceed 1 mm/year in any of the cases described (Table 9.5).

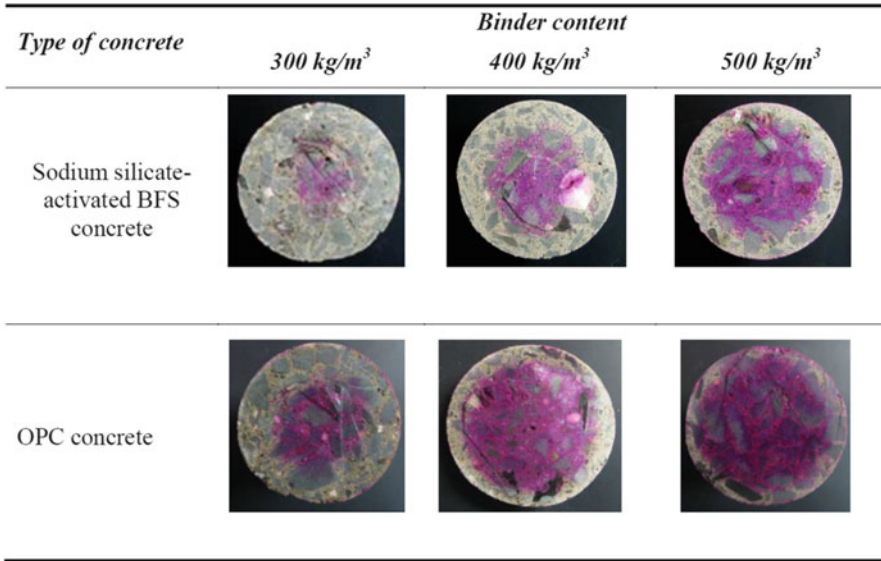


Fig. 9.8 Transverse sections of carbonated concretes after 1,000 h of exposure to a 1 % CO₂ environment, with the extent of carbonation revealed by a phenolphthalein indicator (*purple* is uncarbonated, *colourless* is carbonated). Samples are 76.2 mm in diameter (Adapted from Bernal et al. [60])

Table 9.5 Summary of in-service carbonation rates of alkali-activated concretes, from [54]

Application	Location	Date	Compressive strength (MPa)	Average carbonation rate (mm/year)
Drainage collector ^a	Odessa, Ukraine	1966	62 (34 year)	<0.1
Precast floor slabs and wall panels	Krakow, Poland	1974	43 (27 year)	0.4
Silage trenches ^a	Zaporozhye Oblast, Ukraine	1982	39 (18 year)	0.2–0.4
Heavy duty road	Magnitogorsk, Russia	1984	86 (15 year)	1
High-rise residential buildings	Lipetsk, Russia	1986	35 (14 year)	0.4
Prestressed railway sleepers	Tchudovo Russia	1988	82 (12 year)	0.7–1

^aMaterials serving in covered or underground applications, where carbonation would be expected to be slow

Bernal and co-workers [224, 244, 245] identified that the carbonation of AAMs is more severe when assessed under accelerated induced carbonation than under natural carbonation conditions, to a greater extent than is the case for Portland cement materials. It seems that there is not the same correlation between the natural and accelerated carbonation results for AAM and OPC materials (Fig. 9.9), which indicates that accelerated testing as applied to Portland cement specimens is not as

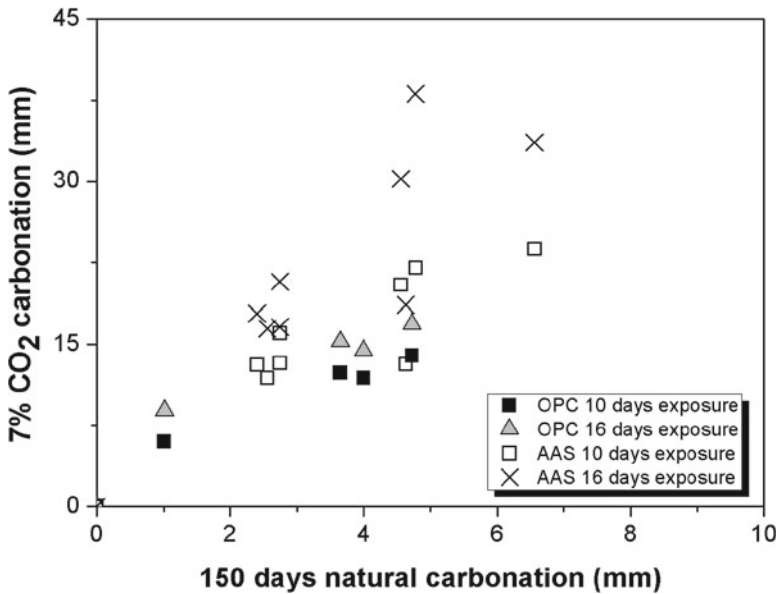


Fig. 9.9 Relationship between natural and accelerated (different exposure times) carbonation depths of AAM concretes (Data from Bernal and Rodríguez [224])

accurate in replicating the carbonation process that might be taking place in these AAM systems. This is related at least in part to differences in pore solution chemistry induced at higher CO₂ concentrations, and particularly differences in the carbonate/bicarbonate ratio [244], although further research work in this area is certainly required to provide a full understanding of the interacting and/or competing mechanisms taking place during carbonation of AAMs.

As discussed in Chapter 2, Xu et al. [56] assessed the natural carbonation of mature concretes (more than 35 years old, developed and utilised in the former Soviet Union), where the binders were based on alkali carbonate-activated BFS. A carbonation depth lower than 8 mm was identified in most cases, demonstrating the good durability of these materials against natural carbonation. In accelerated carbonation testing of alkali-activated BFS concretes, it was also identified that for carbonation depths of up to approximately 8 mm, the carbonation process appeared to be predominantly chemical reaction controlled, and the rate-controlling step was close to first order with respect to CO₂ [60]. Beyond this point of the carbonation process, diffusion control appeared to be more significant. This could be an indication that over the time of the carbonation reaction, the refinement of the pore structure of AAMs is such that diffusion of CO₂ is limited by the carbonation reactions that can take place.

There are also disagreements in the literature regarding the effect of carbonation on the mechanical properties of alkali silicate-activated BFS concretes. Bernal et al. [86] found that these materials decrease notably in compressive strength with

accelerated carbonation, but Hakkinen [104] observed 40 % higher compressive strength after 22 months of accelerated carbonation compared to the same materials after 28 days of curing.

Carbonation of AAMs based on low-Ca aluminosilicate precursors has only been assessed in detail in a single published study to date. Criado et al. [246], in assessing the effect of different curing conditions of alkali-activated fly ash, identified the formation of nahcolite (sodium bicarbonate) in samples cured under atmospheric conditions, which was associated with the carbonation of the alkalis in the pore solution. These specimens also revealed a lower extent of reaction and lower mechanical strengths compared with those cured at moderately elevated temperatures (85 °C), which is likely to be in part associated with the consumption of the alkalis during the carbonation reaction, inducing a reduction in the solution pH and consequently a decreased extent of dissolution of the unreacted fly ash.

9.6.7 Remarks Regarding Test Methods for Alkali-Activated Materials

The standardisation of test methods for the evaluation of the carbonation performance of conventional cements is very recent. The main consideration for the acceptance of these protocols is that when exposing materials under the conditions suggested by the standards, similar reaction products are formed when compared with those identified in naturally carbonated specimens. This is assumed to provide sufficient evidence that the test and the conditions suggested by these protocols are accurately replicating what could be happening in a natural carbonation situation.

There is no standard or proposed methodology to assess carbonation performance specifically for AAMs, and in some cases, poorly controlled testing conditions have been used to carbonate the specimens evaluated. That is why the results of the few reports examining the carbonation of AAMs should be understood as indicators of the performance of those materials under specific carbonation exposure conditions, which differ from natural carbonation conditions, and cannot be accepted as a general statement of the performance of all AAMs when exposed to ambient CO₂. The control and scientific interpretation of simultaneous drying and carbonation processes – where aggressive drying conditions may lead to cracking of the material – is also essential, but not yet fully mature in terms of incorporation into testing methods.

The good stability of aged structures in the former USSR and Poland over a period of decades is the best available evidence that AAMs can resist the passage of time without revealing carbonation problems, which is in general contrary to the outcomes of accelerated carbonation tests reported in the literature. Changes in the carbonation reaction equilibria taking place under natural conditions are likely to occur when the specimens are analysed under accelerated carbonation conditions, which leads to poor performance results, despite the low permeability and good mechanical strength identified in the specimens before accelerated carbonation

testing. This highlights that further research in this area needs to be targeted not just to understand how the degradation process might proceed in these systems, but also how the testing conditions are affecting the outcomes of the test conducted, in order to generate a methodology that can give 'real' proof of the durability of AAMs when exposed to CO₂.

This state of the art summary thus reveals that little attention has been given in the literature to main factors that can be strongly affecting the performance of these materials when assessed by accelerated carbonation tests, such as carbonation shrinkage and the chemistry of the pore solution, which can strongly influence how the phenolphthalein indicator might work when prepared in different solutions, modifying the outcomes of tests. This suggests that further research in developing methods for measuring the progress of the carbonation front in AAMs needs to be conducted, and that the interpretation of the results in AAMs obtained using the phenolphthalein indicator can be questioned.

The progress of carbonation in alkali-activated concretes is also very strongly dependent on the CO₂ concentration used during the accelerated testing, as differences in the pore structure are induced at higher CO₂ concentrations [240]. The rates of pore solution carbonation (as revealed by phenolphthalein) and gel degradation due to carbonation (as evident in the pore structure) are particularly distinct from each other at higher CO₂ concentration [240] and the carbonate/bicarbonate ratio in the pore solution is also strongly influenced by elevated CO₂ concentrations [244]. It is therefore not recommended to carry out accelerated carbonation testing of alkali-activated binders at CO₂ concentrations higher than 1 % CO₂, and further work is required to determine accurate recommendations regarding other aspects of the testing procedure.

9.7 Efflorescence

9.7.1 Testing Methods

Efflorescence is a phenomenon whereby the motion of water through a porous material results in the deposition of a white deposit on the surface of the material as the water evaporates. This is unsightly, and so it is desirable to avoid it, but it is rarely harmful to the performance of the material. One example of a situation in which efflorescence may occur is when a concrete member is in contact with damp soil, with water moving upwards through the concrete by capillary action and evaporating from its surface. This leaves the surface enriched in the soluble cations which were present in the pore solution. The deposited cations (alkali or alkali earth metals) can then react with atmospheric carbon dioxide, and/or sulfate present in the pore solution or groundwater, resulting in the formation of white surface deposits.

There are several standards in effect internationally which describe efflorescence testing of building products, although many of these are designed specifically to relate to bricks and masonry products rather than concretes in general. Among these

methods are ASTM C67 [247], AS/NZS 4456.6:2003 [248], ČSN 73 1358 [249]. The ČSN (Czech) standard also includes discussion of autoclaved aerated concretes. The provisions related to efflorescence testing have recently been withdrawn from the British standard (BS 3921) for masonry. Non-standardised testing protocols are also used in the laboratory, including the use of alkali leachability as a proxy to describe the potential for efflorescence [111]. In most standardised efflorescence tests, the testing specimens (cubes, beams or cylinders) are partially immersed in a specified quantity of water. Water is drawn into the concrete through capillary suction, rising up through the material and carrying salts from the pore solution as it migrates. After soaking and drying, the mobilised salts stay on the surface of concrete, and are evaluated visually or removed for weighing.

Efflorescence depends on both the microstructure of concrete and its composition, as efflorescence products are normally alkali or alkaline earth carbonates and/or sulfates, which must be supplied by the binder or pore solution, or by atmospheric carbonation [250, 251]. To enable the formation of these products, sufficient mobility of the dissolved pore solution components is required for these products to reach the surface of the material to become visible, and this therefore means that efflorescence testing is essentially a combination of microstructural and pore solution chemistry analysis. The pore pressure induced by the expansive nature of some salts, particularly hydrous sodium sulfates, may also be important here.

9.7.2 Efflorescence of AAMs

AAMs with a low calcium content and high alkali content – which is common in materials synthesised in the laboratory from fly ash or metakaolin – tend to have a porous and open microstructure as discussed in the preceding sections of this chapter and in Chap. 4. Sodium aluminosilicate binders, particularly those synthesised with a high $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio [111, 252–257], can particularly suffer from efflorescence caused by excess sodium oxide remaining unreacted in the material. The unreacted sodium oxide is mobile within the pore network, and is prone to formation of white crystals (i.e. efflorescence) when in contact with atmospheric CO_2 . It should be noted that this is distinct from the process of atmospheric carbonation of the binder as discussed in Sect. 9.6. Carbonation usually results in binder degradation, pH reduction and the deposition of carbonate reaction products in the bulk of the sample, which may or may not be visible to the naked eye, whereas efflorescence causes the formation of visible surface deposits.

The tendency towards efflorescence in AAMs is due partly to the very open microstructure of low-Ca materials, partly due to the high alkali concentration in the pore solution [173] and also partly due to the relatively weak binding (and exchangeability) of Na in the aluminosilicate gel structure [258–260]. Some attempts have been made to reduce efflorescence by using potassium instead of sodium as the source of alkalis in the activator [258, 259], because potassium binds more strongly to the aluminosilicate gel framework [261], and also because potassium carbonate

crystals are usually less visually evident than their sodium counterparts. The addition of supplementary Al sources such as calcium aluminate cement to binders which would otherwise show a low extent of reaction has also proven to be valuable in reducing alkali mobility [111], by providing additional reactive Al to which the alkalis can be bound. However, it appears that the most important factor in reducing alkali mobility is a reduction in overall permeability, in common with most of the other parameters discussed throughout this chapter, which means that a well-formulated AAM which is resistant to modes of attack such as chloride penetration and carbonation will also be resistant to efflorescence.

9.8 Concluding Remarks

The transport-related durability properties of alkali-activated binders depend very strongly on pore structure, which is determined both by binder chemistry (the presence of reactive calcium tends to reduce permeability) and maturity (the provision of adequate curing is essential in developing an impermeable and durable AAM binder). It does not appear that there are specific regions of high permeability close to the edge of an aggregate particle to form a distinct ‘interfacial transition zone’, as is the case for Portland cement-based materials, which may provide performance advantages but which remains to be explored in detail.

Chloride permeability testing of alkali-activated mortars and concretes has shown a wide range of performance, with the outcomes depending strongly on the details of the testing methodology selected. The widely-used ASTM C1202 test methodology is dominated by pore solution chemistry, and so it sometimes registers alkali-activated binders as showing very good resistance to mass transport, and sometimes as performing rather poorly. Alternative methodologies which provide a more direct measurement of the progress of chloride migration into the binder – for example ponding tests, or the NordTest NT Build 492 accelerated test, will provide a more valid comparison which is relatively independent of the pore solution chemistry of the binder.

The issues of steel corrosion and carbonation in AAM concretes are both believed to be highly important in determining in-service performance and durability. Both are strongly influenced by pore solution chemistry, and careful interpretation of the results obtained through widely-used testing protocols is required in both areas. Steel corrosion chemistry is believed to be strongly influenced by the presence of sulfide in BFS-based binders, and the predictions obtained through the application of guidelines designed for Portland cement concretes may therefore not be reliable. Testing of AAMs at elevated CO₂ concentrations alters the sodium carbonate-bicarbonate phase equilibria in the pore solution, leading to effects in the binder chemistry and related to the rate of ingress of the carbonation front which may not represent in-service performance. From a limited data set available for long-term (>20 years) aged materials, AAM concretes have been shown to provide relatively good resistance to carbonation in service, which is contrary to the results obtained from accelerated testing.

In general, and in common with the chemical durability processes discussed in Chap. 8, it appears necessary to validate accelerated testing methods in detail for AAMs by comparison with in-service performance. The details of the chemistry (particularly pore solution chemistry) and microstructure of alkali-activated binders appear to lead to significant differences in the mechanisms which control transport-related durability of these materials, and it is likely that several of the widely-used and standardised testing protocols provide results for these materials which are not fully reliable in predicting long-term performance.

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Chapter 10

Durability and Testing – Physical Processes

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10.1 Introductory Remarks

Concrete is well known to be strong in compression but weak in flexion and tension. However, by the use of steel reinforcing, often in combination with techniques such as pretensioning, and through appropriate structural engineering design methodologies, it is possible to compensate for this weakness by ensuring that the binder and aggregate of the concrete are subjected to minimal tensile load. This means that the relationship between compressive strength, flexural strength and other mechanical properties of concrete is used as an essential basis for civil and structural engineering design purposes. In practice, and with the current almost-universal use of Portland cement-based concretes in civil infrastructure applications, many of these relationships are codified in standards as empirical power-law relationships involving the 28-day compressive strength of the material,

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sometimes as the sole property used in the predictive equations or sometimes along with a small number of additional physical parameters. For example, the American Concrete Institute [1] specifies the prediction of elastic modulus as a function of compressive strength and concrete density, but an equation solely based on compressive strength is also provided, and is probably more widely used in practice. More sophisticated and more detailed theoretical models, or empirical correlations involving larger numbers of parameters, are often published in the academic literature, but are not in widespread application. An excellent discussion of phenomena and models for Portland cement concrete is presented by Neville [2], and the reader is referred to that text for further information.

These standardised and commonly-used correlations are based on large volumes of data which have been generated for many thousands of Portland cement concrete samples over a number of decades. However, the use of correlations based on concretes derived from Portland cement and its blends in predicting the performance of alkali-activated concretes is prone to error, as the physicochemical properties of the alkali-activated binder and its interactions with aggregate particles are notably different from those of Portland cement, as discussed in the preceding chapters of this report. The volume of data which have been generated and correlated for alkali-activated concretes is much smaller, which means that there are not yet specific well-validated correlations available for the relationships between the various mechanical properties of alkali-activated concretes. The availability of such relationships for AAMs (and/or the validation of the currently standardised relationships for these materials, if appropriate) appears to be imperative for the uptake of AAM concretes in large-scale construction applications, meaning that it is important to develop a full understanding of the appropriate methods of testing and predicting the mechanical properties of these materials.

10.2 Mechanical Testing

10.2.1 Testing Methodologies

There are a number of testing protocols and geometries which are commonly used for the testing of the mechanical strength of Portland cement-based materials, which have been described in detail in a recent ASTM publication [3]. Given that the mechanical and elastic properties of alkali-activated binders, mortars and concretes generally fall within a similar range, there does not appear to be any *prima facie* reason why these methods should not also be applicable to AAMs, subject to practitioners being able to mix and mould good-quality specimens without large flaws, bleeding or segregation. The standard test method ASTM C39 [4], which also has equivalents in many national and international standards regimes, is widely used for analysis of concrete cylinder samples. Although sample dimensions are not strictly specified in the standard itself, most samples to which this test is applied are

prepared according to ASTM C31 [5], and are thus either 100 or 150 mm in diameter (or the almost-equivalent 4-in. and 6-in. sizes in the USA), with an aspect ratio of 2, and with no coarse aggregate particle larger than one third of the diameter of the cylinder. Testing of cylinders with aspect ratios lower than 1.75 is stated [4] to result in erroneously high strength measurements, and correction factors are provided within the standard to account for this known discrepancy. This standard was first introduced in 1921, highlighting the fundamental nature of the compressive strength testing procedure in determination and standardisation of the properties of concrete, and has been refined numerous times since its introduction. Cylinder ends are capped with either sulfur mortar, gypsum plaster or a re-useable neoprene pad (with the use of neoprene generally restricted to lower-strength specimens), and tested at a loading rate which should be controlled between 0.20 and 0.30 MPa/s [4].

Testing of smaller samples and the application of higher strain rates generally leads to higher measured strengths for the same material, and smaller samples also have notably higher fracture toughness [6], which means that it is important to maintain consistency in these parameters as far as possible in a testing program. The dependence of mechanical properties on strain rate has also recently been shown [7, 8] to follow similar trends in AAMs to those observed in Portland cement concretes, which indicates that most of the large body of existing knowledge in this area for traditional concretes can be applied relatively directly in understanding the behaviour of AAMs during mechanical testing. Alkali-activated BFS concretes have been reported to show a stronger specimen size effect than OPC concrete [9], which was attributed to the greater inhomogeneity in the AAM samples in that study due to difficulties in mixing.

The European standard EN 12390-3 [10] also specifies testing procedures for hardened concrete, but using cubic (100 or 150 mm) specimens in addition to cylinders [11], with a wider range of allowable capping compounds, and with a range of acceptable loading rates spanning 0.20–1.0 MPa/s. The higher reproducibilities and repeatabilities of the tests conducted on cylinders compared with cubes of corresponding size are noted in this standard document, but either type of sample is considered acceptable. Due to differences in aspect ratio, a cube will be expected to give a measured strength ~10–15 % higher than an ASTM-equivalent standard cylinder [6], which should be considered when comparing data obtained from the different test methods.

Compressive strength testing of mortars is similarly regulated by a number of similar standards in force internationally, including ASTM C109 [12], which specifies the use of 50 mm cubes containing a standard sand as the test specimens. This is very widely used as a laboratory test in the materials development process, where mixing and casting of large numbers of concrete specimens may be logistically difficult in a small-scale testing facility. ASTM C109 specifies the cube formulations according to either water/cement ratio (for Portland cement) or flow (for other binders), which may be an issue if AAMs with paste rheology notably different from that of Portland cement are used. Additionally, the curing regimes specified in this standard (stripping moulds after 20–72 h then immersing samples in lime water until testing) may not be appropriate for alkali-activated binder systems. It is well

known that careful control of testing conditions and sample preparation protocols (parameters such as air content, aggregate moisture, curing, and sample maturity at testing) are required when correlating mortar strength data with concrete strengths [13, 14], but it is likely that reasonably close correlations should be achievable with well-designed tests. The correlation is also known to be better for compressive than tensile/flexural strength data [15].

Documents such as EN 196-1 [16] or ASTM C349 [17] specify the use of $40 \times 40 \times 160$ mm prismatic moulds for mortar testing, where the prism is broken in flexion (or by '*suitable means which do not subject the prism halves to harmful stresses*'), and then the end sections are used for compressive strength determination. These methods bring the advantage of providing both flexural and compressive strength data from a single specimen, but at the cost of difficulties in controlling specimen geometry for the compressive strength testing on two fractured ends of a prism, and also possible microstructural damage to the ends due to the application of the flexural load in the first part of the test. The assumption inherent in this test method is that the flexural failure is induced in such a way as to induce minimal damage in the end sections of the specimens – but the ASTM standard specifically states that this method is for reference purposes, not as a substitute for the direct cube test (ASTM C109), indicating a potentially lower level of reliability of the data.

A similar assumption is utilised in laboratory test programs where small (often 10 mm or less in the shorter dimension) prismatic specimens of hardened binder, or small cylinders, are used in the absence of aggregate, following testing methodologies designed for technical ceramics [18]. It has been noted that this type of test is rarely used in practical situations for the prediction of concrete strengths due to the large differences in water/binder ratios used in pastes compared to concretes [15], but it does still show some value as a screening tool for binder designs. Also, the ASTM C773 standard for testing of whiteware porcelains in compression, which is a similar test to the methods often used for small paste cylinders, specifies the use of a minimum of ten replicate specimens per test [18], to account for the variability inherent in the brittle failure of these types of materials, compared to two to three replicate mortar specimens in ASTM C109 [12], or two concrete cylinders in ASTM C39 [4]. Laboratory tests of paste specimens rarely follow this guideline regarding the number of samples required, and are thus subject to significant uncertainty and/or error, so are mainly useful as a screening method rather than in prediction of concrete performance.

The elastic properties of concrete can either be measured directly during mechanical loading, or using any of a wide range of techniques based on the degree and rate of transmission of vibrations through the material, including ultrasonic techniques and various forms of resonant frequency analysis [19]. Tests may be applied to either fresh or hardened materials, and the results obtained are then of great value in structural design calculations and in condition assessment of concrete in service. The use of ultrasonic and resonant frequency techniques to estimate the compressive strength of concrete elements in service is both widespread and somewhat scientifically controversial [19], and results in this area are starting to be published for

AAMs, as described in Sect. 10.2.4 below. It is well known that the measurement of both the static and the dynamic modulus of elasticity can be strongly influenced by the testing method applied [20], and that the correlation between measurements of these properties can often be poor. Additionally, there are numerous different testing protocols and standards in place worldwide governing the application of ultrasonic testing (20 are reported in [21]), and the main outcome of a review across these testing protocols [21] was that “*the inherent uncertainty... is so high that the assessments are not suitable for many practical purposes.*” The ASTM testing method C597 [22] specifically warns against its use as a method for measurement of strength or elastic modulus, but notes that it is possible to generate calibration data from a particular concrete for further assessment of that concrete. It is therefore imperative that data from this type of tests are compared and used only as far as is scientifically justifiable when looking across different sample sets and testing protocols.

The sample conditioning procedure will also be expected to have a marked influence in the measurement of mechanical properties of alkali-activated materials. It is known that testing concrete samples while wet leads to lower compressive strength than if the sample has been dried, and although there are various explanations available for this phenomenon, it is a point which should be particularly carefully considered in the testing of AAMs given the known susceptibility of these materials to drying and consequent cracking and/or carbonation, as discussed in Chap. 9 and below.

10.2.2 Mechanical Strength of Alkali-Activated Materials

Almost every academic publication related to engineering properties of AAMs includes some degree of mechanical characterisation of pastes, mortars or concretes, with the published mechanical strength data spanning the full range from very low performance to very high performance in mortars and concretes. Reported mortar cube strengths in compression have exceeded 95 MPa for alkali silicate-activated BFS and 70 MPa for alkali silicate-activated fly ashes cured for 28 days at no more than 25 °C [23–26], and a compressive strength of 120 MPa was achieved by 30 mm paste cubes of alkali silicate-activated phosphorus slag cured for 28 days at 20 °C [27]. Strengths of more than 90 MPa have also been reported for alkali silicate-activated metakaolin specimens (paste cylinders, 25 mm diameter × 50 mm height), cured for 20 h at 40 °C then held at ambient temperature (20 ± 5 °C) up to 28 days of age [28]. These data contradict the often-repeated statement that alkali-activated materials require extended periods of heat curing for satisfactory mechanical strength development. Rather, an adequately controlled and designed AAM formulation can certainly harden and develop excellent mechanical properties under ambient or near-ambient conditions.

Concrete strengths higher than 50 MPa have been relatively widely reported for laboratory samples derived from BFS and/or fly ash [9, 29–34], and strength grades of up to 110 MPa have been standardised in Ukraine [34]. The consistent

achievement of such strengths in large-scale production is much more complex, but the commercial-scale production of “high-performance” concretes by alkaline activation of suitably chosen precursor blends is certainly possible, as discussed and demonstrated in Chaps. 2 and 11 of this Report.

There are well-known relationships between strength and porosity in Portland cement-based materials, and more generally across the entire field of brittle materials, where a characteristic power-law is observed for a set of materials ranging from stainless steel to sintered alumina [2, 6]. In the case of concretes, this relationship is influenced to some extent by the very wide range of pore sizes present in the material, and there is little to indicate that the situation would be different for AAM concretes. Some alkali-activated binders, particularly those based on metakaolin, have a tendency to be relatively porous due to the high water demand of the fresh mix. A micromechanical model describing the influence of porosity and other binder parameters on strength has been developed by Šmilauer et al. [35], and may prove to be of value in future analysis of these materials. The use of high-pressure compaction at low water/binder ratio to reduce porosity has also been shown to produce very high paste compressive strengths in alkali-activated materials; more than 250 MPa for alkali-activated BFS compacted at 500 MPa [36].

Steam-curing of AAM concretes has also been shown to give good results in terms of compressive strength development for precast members [34, 37–40]. The mechanical performance of heat-cured slender columns of alkali silicate-activated fly ash (175 mm² cross-section, 1,500 mm length), with longitudinal and lateral reinforcement, showed good agreement with the standard specifications AS 3600 [41] and ACI 318 [42] for structural concretes [43]. Recently, Yost et al. [44, 45] also demonstrated good agreement between the performance of alkali-activated fly ash concretes designed to be over-reinforced, under-reinforced, and shear-critical, and the respective ACI specifications for service and limit states of each of these types of reinforced element.

10.2.3 *Flexural-Compressive Strength Relationships*

There is an increasing body of evidence indicating that AAMs demonstrate flexural and tensile strengths significantly higher than would be predicted from the standard relationships for Portland cement concretes of similar compressive strength [30, 32, 43, 46–48]. These standard relationships vary slightly between different national standards globally, but generally involve a power law relationship (exponent 0.5–0.7) between compressive and flexural strength; the American Concrete Institute specifies the relationship $\sigma_f = 0.6 \sigma_c^{0.5}$, where σ_f is the flexural strength (modulus of rupture) in MPa, and σ_c is the compressive strength of the concrete (also in MPa) [42]. This relationship is shown in Fig. 10.1 for data obtained from a variety of literature sources [9, 30, 32, 48–54], where almost all of the data for AAM concretes show higher flexural strengths than are given by the specified relationships for Portland cement concretes. It is noted that some authors consider the ACI equation to be a lower bound on the modulus of rupture of Portland

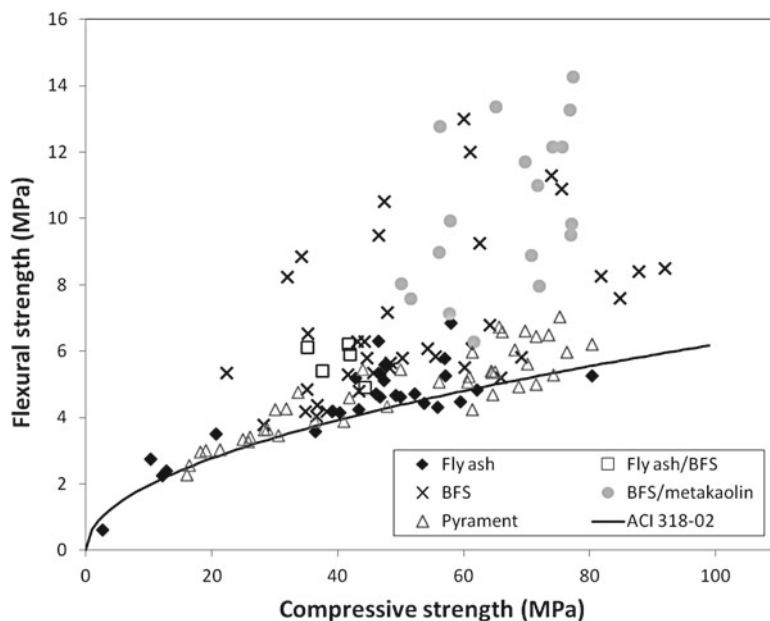


Fig. 10.1 Relationship between flexural and compressive strength of alkali-activated concretes synthesised from various precursors as marked, at ages between 4 h and 1 year, with the relationship for OPC concretes as specified in ACI 318-02 shown for comparison (Data for AAM concretes are taken from [9, 30, 32, 48–54])

cement-based materials [55], and the data presented here for alkali-activated concretes are also consistent with such a suggestion.

Sumajouw and Rangan [39, 47] and Dattatreya et al. [56] tested steel-reinforced alkali-activated fly ash concrete beams and columns under various applied loads, and found that the failure modes and deflections observed were similar to those expected for Portland cement concretes, and that the provisions of the Australian Standard AS 3600 [41], the Indian Standard IS 456:2000 [57] and ACI 318-02 [42] appear appropriate for application to the prediction of this aspect of the mechanical performance of AAM concretes. Similar trends also appear to hold for splitting tensile strengths of alkali-activated natural pozzolan concretes [58] and alkali-activated fly ash concretes [37] when compared to the relationships commonly used for OPC concretes.

10.2.4 Modulus of Elasticity and Poisson's Ratio

Two additional pieces of information which are essential in structural design are the Poisson's ratio and the elastic modulus. Better knowledge of these properties is important when it comes to the mechanical modelling of structures manufactured with AAM concretes. These can either be determined directly – elastic modulus

from stress-strain curves and Poisson's ratio from strain gauges installed in orthogonal directions – or by ultrasonic techniques. For alkali-activated metakaolin pastes, Lawson [59] showed using an ultrasonic technique that the elastic modulus decreases with increasing Si/Al ratio, with values between 5.5 and 9.1 GPa measured at Si/Al ratios between 1.5 and 5.0. However, Duxson et al. [60] observed (using measurements taken directly from stress-strain curves) an increase in elastic modulus, from 2.3 to 5.2 GPa, when increasing the Si/Al ratio of alkali-activated metakaolin pastes from 1.15 to 1.90; in those data, a decrease in modulus with Si addition was only observed beyond Si/Al=2.0. For alkali-activated fly ash concretes, Wongpa et al. [61] found that the elastic modulus decreases with increasing curing time, and Talling and Krivenko also found that the modulus of elasticity is reduced by initial steam curing of high-strength AAS [34]. However, Douglas et al. [62] found a slight increase in the elastic modulus of alkali-activated BFS concretes from 28 to 91 days, and obtained elastic moduli of around 30–35 GPa for their samples, which agree very well with the ACI 318 model, as do the available data for alkali-activated BFS 'F-concrete' [33, 46].

It is clear that more work is needed in this area to determine the interrelationships between binder structure evolution and elastic properties, and recent work using micromechanical modelling and nanoindentation [35, 63] may be providing some useful initial steps in this direction, but the complete links between this work and macroscopic concrete performance remain to be drawn. Němeček et al. [64] have proposed, based on nanoindentation analysis of alkali-activated fly ash and alkali-activated metakaolin binders, that the "N-A-S-H" type gel has an intrinsic elastic modulus of around 17–18 GPa (compared to around 43 GPa for crystalline hydrosodalite, a related model zeolite structure [65]), while Puertas et al. [63] found modulus values between 28 and 50 GPa for the C-A-S-H gel binder in alkali silicate-activated BFS specimens, and 12–42 GPa in alkali hydroxide-activated BFS. Oh et al. [66] also showed that Al substitution in C-S-H has little influence on its basic mechanical properties, including elastic modulus.

Diaz-Loya et al. [30] found that the elastic moduli of their alkali-activated fly ash concretes, as well as data from the work of Fernández-Jiménez et al. [50] and of Sofi et al. [48], generally fell below the predictions obtained from the ACI 318 models (0.5 power law functional form) for Portland cement of a given compressive strength. Diaz-Loya et al. [30] proposed a linear relationship between compressive strength and elastic modulus of AAM concretes, but also proposed that a 0.5 power law relationship that included a factor correcting for the density of the concrete could also give a good correlation with their data set.

The compressive stress-strain curve for alkali-activated fly ash concrete has also been compared against curves predicted by an equation developed for OPC concretes [67], and the measured and predicted curves show excellent agreement up to the point of compressive failure [43]. Sarker [68] developed a slight modification of the equations for high-performance OPC to provide better description of the post-failure part of the stress-strain curve, but the fit to the standard forms of the equations was also reasonably satisfactory in that data set.

There are relatively fewer experimental data available in the literature for Poisson's ratio of AAMs. For alkali silicate-activated metakaolin pastes, Lawson

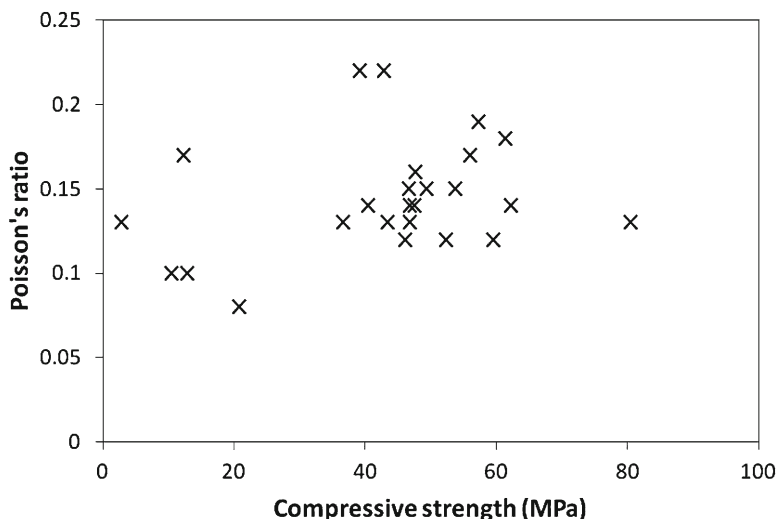


Fig. 10.2 Poisson's ratio of alkali-activated fly ash concretes as a function of compressive strength (Data from [30])

[59] also used an ultrasonic technique to determine Poisson's ratio, which showed a decrease with increasing Si/Al ratio, from 0.221 at Si/Al 1.5 to 0.111 at Si/Al=3. Diaz-Loya et al. [30] measured values between 0.07 and 0.23 for alkali silicate-activated fly ash concretes, tending to increase at higher compressive strength (Fig. 10.2), although the data appear rather scattered.

In general, the fundamental mechanical properties of AAM concretes show a relatively good agreement with the standard relationships developed for Portland cement concretes. However, it is necessary to develop a theoretical and mechanistic understanding of the likely deviations from the 'expected' (i.e. Portland cement) behaviour in an engineering context, and also potentially in terms of parameters such as creep and shrinkage (see Sects. 10.3 and 10.4 below). It may, in time, also be necessary to explore the rationale behind the derivation of the equations provided in the standards for OPC, and to explore any possible modifications which could better reflect the fundamental chemomechanical nature of AAM concretes, but it is likely at this point that a good deal of further research work will be necessary before such steps can confidently be taken.

10.3 Shrinkage and Cracking

10.3.1 Shrinkage Testing

There are a multitude of testing protocols used in the assessment of dimensional stability of hardened and fresh cement pastes, mortars and concretes, including ten

testing methods in the ASTM regime alone [69]. Tests are sometimes intended to be specific to one mechanism of shrinkage (drying or autogenous shrinkage are often isolated in this way), or sometimes measure the convolution of a number of effects leading to dimensional change in different ways and at different rates. It has been suggested, from relatively fundamental chemical and thermodynamic viewpoints, that the C-A-S-H phases present in alkali-activated BFS binders should be more prone to shrinkage than are the lower-Al C-S-H phases formed through hydration of OPC [70, 71]. However, the shrinkage of alkali-activated mortars and concretes formulated with moderate w/b ratios and well-graded aggregates has often been reported to be lower than that of comparable OPC-based binders, suggesting that there are additional effects which are significant in determining the performance of the materials in service. It is thus important to understand the specific details of some of the testing protocols which are used in making these assessments, to determine whether the tests are in fact giving an accurate representation of the likely performance of the materials in service.

The basic ASTM testing method describing the measurement of dimensional stability of hardened materials is ASTM C157 [72], which makes use of prismatic specimens 285 mm in length, and either 25 × 25 mm (mortars), 75 × 75 mm (concretes with no aggregate >25 mm), or 100 × 100 mm (concretes with some aggregate >25 mm) in cross-section, with gauge studs embedded in the ends for measurement purposes. The specimens are moist-cured for 24 h, measured to determine the ‘initial’ length, and then stored under lime-water until reaching 28 days of age and measured again. At this point, samples to be tested under drying conditions are removed from the lime-water bath, and either exposed to 50 % relative humidity (RH) at 23 °C, while samples to be tested for dimensional stability under moist conditions are replaced in the lime-water bath, and regular length measurements are taken up to 64 weeks. The main issue related to the application of this test to alkali-activated binders is the fact that lime-water immersion is designed to provide an environment saturated in Ca²⁺ to prevent decalcification of OPC binders through soft water attack, whereas alkali-activated binders would be expected to lose alkalis from the pore solution, particularly with immersion at such an early age when the alkalis are only weakly bound into a relatively undeveloped gel.

The mortar drying shrinkage test ASTM C596 [73] is essentially similar to C157, except that the samples are exposed to 50 % RH from the age of 3 days rather than 28 days, meaning that the test is probing the properties of a much more immature sample than C157. The standard does include comments indicating that the shrinkage of a concrete would be expected to correlate with that of a corresponding mortar, but the validity of these statements has also been called into question [69]. Standards such as the Australian standard AS1012.13 [74], which involve a longer (e.g. 7-day in AS 1012.13) moist curing period prior to the first measurement of length, have been noted to be less than ideal for binders containing high contents of slag, as these materials tend to expand somewhat (and reversibly) during this period, and the extent of expansion is therefore effectively added to the actual shrinkage when measured at 56 days [75].

Early-age dimensional stability can be assessed under restrained shrinkage conditions via a ring specimen test according to ASTM C1581 [76], where the ring is monitored for cracking, or according to tests of the dimensional changes within a mould of a specific geometry (conical or cylindrical) during and after setting (e.g. ASTM C 827 [77] or ASTM C1090 [78]). In applying these tests to AAMs, which tend to be somewhat stickier than OPC-based materials, it may be important to take the effect of adhesion between the test specimen and the mould. These tests are also commonly applied for the study of crack resistance, and will be discussed in more detail in Sect. 10.3.4 in that context.

10.3.2 *Shrinkage of Alkali-Activated Materials*

There is a significant dichotomy in the published literature regarding the shrinkage performance of alkali-activated materials, as the published studies of alkali-activated binders report a range from very low to very high shrinkage. In particular, shrinkage in alkali-activated BFS binders is known to be problematic in some circumstances, and particularly when inadequate curing is provided prior to exposure to drying conditions. Alkali-activated metakaolin binders are known to shrink very significantly, and alkali-activated fly ash materials can either shrink very little or very significantly, depending on the mix design. In general, the addition of excess water to an AAM formulation, or exposure to drying conditions at early age, can almost be guaranteed to lead to problems in terms of drying shrinkage (and/or cracking), because the degree of chemical binding of water in these gel structures is much less than in Portland cement-based materials.

The early report of Kukko and Mannonen [46] shows that the drying shrinkage (at 40 % RH) of alkali-activated BFS “F-concrete” is slightly (~10 %) lower than that of Portland cement concrete of comparable mix design, workability and strength grade over a 2-year period, and that the drying shrinkage increases with increasing w/b ratio. Conversely, Häkkinen [79, 80] found that the initial (<2 months) shrinkage at ~70 % RH (over saturated sodium nitrite solution) was lower in F-concrete than in OPC concrete, but that the shrinkage of the AAM concrete continued for a more extended period of time and overtook the total extent of shrinkage of the OPC samples at around 4 months of age. This may be related to the expansive effects of the BFS in the mix at early age, as mentioned in Sect. 10.3.1 above, as a similar trend (lower initial shrinkage but longer-duration shrinkage when compared with rapid-hardening Portland cement) was also observed in [79, 80] for a 70 % BFS/30 % rapid hardening Portland cement blend. Exposure to an accelerated carbonation environment (5 % CO₂) also gave a slight reduction in the observed extent of shrinkage [79].

The difference in the behaviour at 40 and 65 % RH also indicates that the combined autogenous/drying shrinkage taking place at the higher RH was proceeding at a different rate to the purely drying-based processes at 40 % RH in the work of Kukko and Mannonen [46]. Melo Neto et al. [81] used parallel drying/autogenous

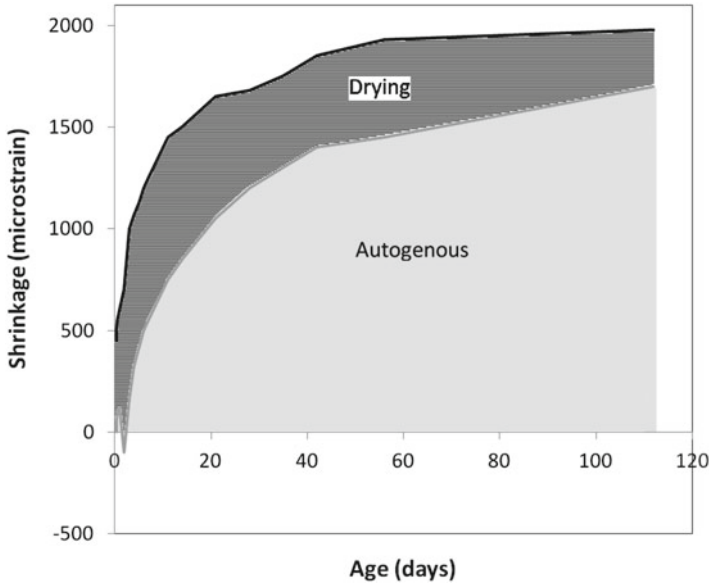


Fig. 10.3 Drying and autogenous shrinkage in an alkali silicate-activated BFS mortar at 24 °C, with drying tests conducted at 50 % RH (Data from Melo Neto et al. [81])

shrinkage testing to determine the influence of each mode of shrinkage (Fig. 10.3), and showed that the ongoing shrinkage of alkali-activated BFS was related to autogenous rather than drying processes, and they related this to a higher extent of self-desiccation in these materials than in OPC, consistent with the modelling work of Chen and Brouwers [70]. However, immersion of alkali-activated BFS mortar specimens in water for up to 28 days at early age was observed to not lead to observable shrinkage – instead, a slight expansion was observed [80], compared to a slight shrinkage in Portland cement-based materials. Douglas et al. [62] also observed this expansion, and found that it continues for more than 9 months in alkali-activated BFS mortars stored in water. Sakulich and Bentz [82] successfully used internal curing via incorporation of pre-saturated expanded clay particles to mitigate shrinkage of alkali-activated BFS concretes, influencing both the autogenous and drying-related shrinkage mechanisms.

Wang et al. [83] and Duran Atiş et al. [84] noted that activation of BFS by either NaOH or Na₂CO₃ gave similar shrinkage properties to OPC, while waterglass-activated BFS binders shrank more than OPC under drying conditions. Collins and Sanjayan [85] attributed this shrinkage to the presence of more mesopores within the AAM binder, while Krizan and Zivanovic [86] proposed a mechanism based on gel syneresis, derived conceptually from the earlier work of Glukhovskiy. Douglas et al. [62] and Cincotto et al. [87] found that the extent of drying shrinkage increased with increasing activator content in BFS-based binders, and Krizan and Zivanovic [86] observed an increase in the extent of shrinkage with increasing activator

modulus. In each of those studies, the extent of shrinkage observed was relatively high compared with the expected shrinkage of OPC-based mortars.

Collins and Sanjayan studied and modelled restrained shrinkage and cracking of alkali-activated BFS concretes [88, 89], and found that when AAM and OPC-based specimens were cured for 24 h then subjected to restrained shrinkage, the AAM concretes had a much higher extent of shrinkage and a stronger tendency towards cracking. However, curing the AAM concretes in a bath for 3 days brought their performance to be approximately equivalent to that of OPC concretes cured for the same duration (the difference between 1 and 3 days of curing of OPC concrete was negligible). The inclusion of a porous and slightly reactive blast furnace slag coarse aggregate, in place of the natural rock aggregate, was also found to reduce shrinkage due to internal curing effects [90].

In alkali-activated fly ash and blended fly ash-BFS mortars, the effects of a wide range of mix design parameters and processing conditions were studied by Yong [91]. Both autogenous and drying shrinkage were observed in these materials, and the presence of as much as 40 % BFS in a fly ash-based binder was not sufficient to cause early-age expansion, while tending to give a higher extent of shrinkage. Water content was important in determining early-age drying shrinkage, but due to the relatively porous nature of the gels formed, the main parameters determining later-age expansion were related to the nature of the activator (and thus the extent of gel formation, and the composition of the aluminosilicate gel) [91]. Activation of a 60 % fly ash/40 % BFS blend with a low-modulus sodium silicate solution ($\text{SiO}_2/\text{Na}_2\text{O}=0.5$) gave shrinkage results of around 500 microstrain after 7 months, compared to 6,000 microstrain with a metasilicate solution ($\text{SiO}_2/\text{Na}_2\text{O}=1.0$) [91]. It has been reported that an access path poured from alkali-activated fly ash concrete did not show significant shrinkage cracking, even when placed in 12 m lengths with no shrinkage cuts [92].

Yong [91] also investigated the influence of the sealed curing duration on the drying shrinkage of alkali-activated mortars, as shown in Fig. 10.4. Curing the specimens for a longer period of time prior to the commencement of the test provides a more mature binder which is more resistant to dimensional change. Rangan [37] also noted that heat curing of fly ash-based AAMs tended to bring a reduction in drying shrinkage compared to ambient-temperature curing of the same mixes, and this is also likely to be related to binder gel maturity. However, for systems which developed strength and microstructure effectively closer to room temperature, the use of an excessively high curing temperature or an overly extended period of high-temperature curing can lead to more, rather than less, shrinkage [93].

Calcined clay-based AAMs tend to have a high water demand, as discussed in Chap. 4, and so are very prone to shrinkage. It has been proposed that this is intrinsic to the microstructural and chemical nature of these N-A-S-H type gels [25, 94], because the lack of bound water and the low skeletal density of the gels tends to lead to gradual microstructural collapse and zeolite crystallisation. The substitution of 20 % of the clay-derived aluminosilicate precursor by calcite or dolomite has been shown to make the shrinkage more severe [95], as does the use of a limestone aggregate [96]. Elimbi et al. [97] also showed a relatively close

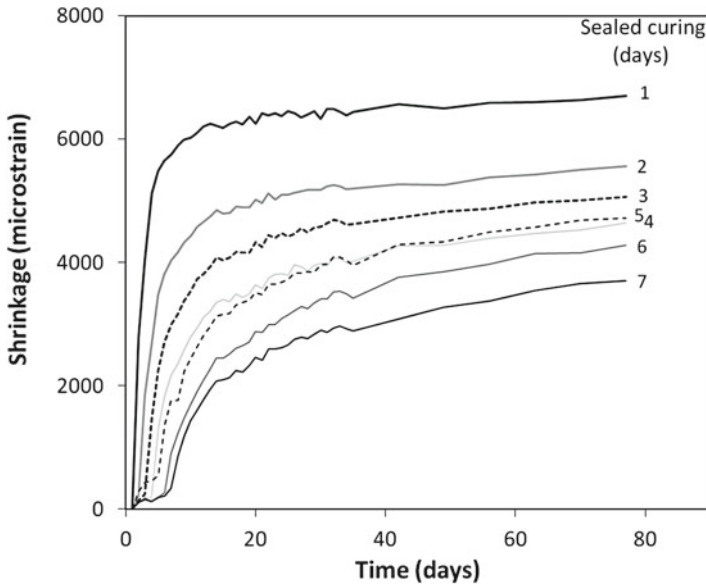


Fig. 10.4 Shrinkage of 60 % fly ash/40 % BFS mortars activated with sodium silicate solution, modulus 1.5, cured sealed in bags for different periods as marked (Data from [91])

correlation between compressive strength and dimensional stability for a set of samples synthesised from clays calcined at different temperatures, indicating that a more reactive precursor leads to the formation of a more microstructurally evolved and thus dimensionally stable gel.

Given the potential sensitivity of AAMs to drying processes and resulting shrinkage and cracking, various methods have been proposed and developed to minimise this issue. Other than the provision of effective curing regimes, which is essential in developing a high-quality material, there is also the possibility to use shrinkage-reducing chemical admixtures (as discussed in Chap. 6). The use of fibre-reinforcement to control crack growth in AAMs will be covered in detail in Chap. 12, and has been demonstrated to be effective in controlling cracking due to dimensional changes as well as due to applied mechanical load.

10.3.3 Analysis of Cracking

Cracking of a construction material is more or less universally undesirable, as it leads to a reduction in mechanical properties and accelerates the ingress of potentially damaging ionic species into the core of a structural element. Cracking of concretes can be caused by chemomechanical (dimensional change of binder or aggregate due to crystallographic changes, chemical reactions or heat evolution) or

physicomechanical (applied load or external temperature cycling) processes. The fundamental cause of much of the microcracking observed in concretes is the partially restrained chemical shrinkage of binder phases after hardening, which has been proposed from a thermodynamic basis to be intrinsic to the chemistry of alkali-activated binders and related (pozzolanic) systems [70, 98]. Almost all of the binders which are used in construction materials show either shrinkage or expansion during or after hardening as a result of the phase evolution which results in strength generation and development [99]. Thus, the control of dimensional stability is a key challenge across the field of cement and concrete technology.

Probably the most commonly used type of test applied for the evaluation of cracking of concretes is a restrained ring test such as ASTM 1581 [76], where the onset of cracking due to restrained shrinkage is monitored over an extended duration. There are various variants on this type of test available, including a dual concentric ring method capable of detecting expansive processes as well as shrinkage [100], but these methods have not yet been standardised. A drawback of these methods is that specimens with lower shrinkage or higher tensile strength may take many months to crack, meaning that specimen geometries such as an oval ring (as standardised in China [101]), a restrained beam with embedded stress magnifier plates [89], or a partially restrained slab [102] may provide advantages. Cracking can be observed visually, or through acoustic, electrical or ultrasonic methods, and these latter methods tend to be more sensitive in detecting very fine cracking.

In smaller (thin-section concrete, mortar or paste) specimens, it is also possible to analyse microcracking by optical microscopy using fluorescent dyes, or by scanning electron microscopy [103], although no results obtained through this technique for AAMs have yet been published in the open literature. Impregnation of cracks with a molten metal such as Wood's metal, which then solidifies at room temperature, can also be beneficial in preserving crack patterns for later observation [104, 105], but also does not appear to have been applied in this way to the study of crack patterns in AAMs.

10.3.4 Microcracking of Alkali-Activated Materials

Significant microcracking tendencies were observed in samples of F-concrete activated by NaOH/Na₂CO₃ [46, 106] or NaOH [9, 80]. Hakkinen [79, 107] also observed a corresponding increase in the rate of carbonation and a reduction in strength, and found that a high activator content tended to correlate with a high extent of microcracking. Collins and Sanjayan [89, 108] conducted a detailed investigation in this area, applying both restrained ring and restrained beam test protocols, in parallel with capillary suction, microscopy and mercury intrusion testing, and concluded that drying effects during curing were a primary cause of cracking of alkali-activated BFS, but that the use of a porous coarse BFS aggregate led to crack resistance performance which was even higher than that of OPC concretes. Shen et al. [109] used the Chinese standard JC/T 603-2004 restrained oval ring test [101]

to show that the addition of either fly ash or reactive MgO could reduce the cracking tendency of alkali-activated BFS.

Bernal et al. [31] also showed via capillary suction measurements that the extent of microcracking in silicate-activated BFS-based concretes depends significantly on the paste content of the concrete mix design; excessive binder content leads to heat generation during curing of concrete specimens, which causes thermally induced microcracking of the concrete at early ages. However, in this case, microcracking was not observed to have any significant influence on the rate of carbonation of the concretes, indicating that the higher binder content was able to provide sufficient densification of the matrix to compensate for additional carbonation taking place via transport along cracks.

The observed trends in microcracking intensity in alkali-activated concretes as a function of paste content and curing regime thus highlight the value of understanding interactions between the binder and aggregate, and effects related to heat generation and heat and moisture transport during curing, in mitigating the effects of microcracking on concrete performance and durability.

10.4 Creep

Creep is the gradual dimensional change of a concrete under long-term application of a mechanical load. In practice, the load is usually applied in compression, as in ASTM C512 [110] or ISO 1920-9 [111], although tensile creep testing methods have also been developed and applied [112, 113]. Creep is both a valuable mechanism for relief of stresses within a concrete material, and a potential cause of damage to structures if not considered carefully in design procedures. So, it is important that the correct degree of creep is present in any concrete material to compensate for its shrinkage, but not so much as to cause cracking of other structural or non-structural elements within a building.

However, because creep tests require timeframes on the order of several months or longer, but it is generally not possible to wait for such a long time before deciding whether a given concrete mix is suitable for use in a desired application, it is more usual to describe creep by one of a selection of standard models. The prediction of creep is a field with particularly rich literature, and there are a very large number of models available, which usually derive their predictions from a set of empirical relationships and which take the 28-day compressive strength as the main (often the sole) input parameter to be determined from laboratory testing. From this strength value, plus information regarding the mix design, type of aggregate and age of loading, it is considered that the available models provide a sufficiently accurate prediction of the creep of Portland cement to enable their use in structural engineering worldwide. Given the number of available models, it is obvious that there are many controversies regarding which is the most accurate and appropriate for concretes of a particular type and strength grade, and the details and outcomes (if any) of these debates are far beyond the scope of this report. The

most important point, with respect to the analysis of AAMs, is that all of the models have been derived based on the physicochemical properties (particularly the relationship between 28-day compressive strength and elastic modulus) of Portland cement and closely related materials.

As was discussed in Sect. 10.2, the relationship between 28-day compressive strength and elastic modulus in AAMs is not the same as in Portland cement concretes, meaning that this aspect of the standard creep models may not be immediately transferrable to AAMs. Additionally, the differences in microstructure, gel structure, and strength development mechanisms between AAMs and Portland cement-based concretes may lead to differences in the time-dependent responses of the materials to applied compressive load, and the differences in strength development profiles during curing of AAMs compared to Portland cement may also lead to a need to reconsider the use of the 28-day compressive strength as the primary measure of concrete quality.

It appears, from the data available in the literature, that the main difference between the creep of Portland cement concrete and AAM concrete is apparent in the longer term rather than in the first 90 days. This was observed by Kukko and Mannonen for alkali-activated BFS F-concrete [46], where the degree to which the creep of the AAM concrete exceeded that of the OPC concrete became greater with age, as the creep of the OPC concrete decreased. Shorter-term creep testing, with data collected for around 100 days [52], does not make this trend evident, and therefore may be unable to display key behaviours of importance in long-term service. Loading the AAM concrete at earlier age also led to a higher creep coefficient, as was the case in Portland cement concretes. There are few data available regarding the influence of mix design parameters on the creep of alkali-activated BFS concretes, although there appears to be a trend where silicate-activated concretes show lower creep than hydroxide-activated mixes, and carbonate-activated binders creep the most [34].

There have also been only a small number of published studies of the creep of fly ash-based AAM concretes; Gourley and Johnson [114] reported that the creep was ‘low’ when fly ash-based materials were used in precast applications. Wallah and Rangan [115] studied the creep of two different heat-cured fly ash-based AAM concretes according to the Australian standard AS 1012.16 [116], with cylindrical specimens loaded at 40 % of compressive strength after 7 days, and monitored for 12 months. Total creep strains at this time were around 1,400 microstrain in all specimens, with almost no influence from the curing regime or mix design. The specific creep (ratio of creep to compressive strength) was lower than that of OPC concretes of similar strength [115], but because the total creep was similar across all samples tested, the lower-strength samples showed the highest specific creep. Australian Standard AS 3600 [41] contains an empirical model which is stated to be applicable to prediction of creep in Portland cement concretes, based on the work of Gilbert [117, 118], and Fig. 10.5 shows a comparison between this model and the experimental data for the alkali-activated fly ash concrete over a 12-month period, showing a much lower degree of creep than is predicted by the standard.

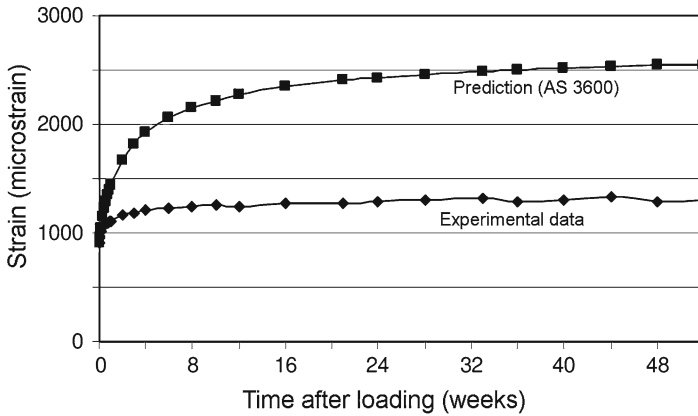


Fig. 10.5 Comparison of experimental creep data for an alkali-activated fly ash concrete with the model described in AS 3600 (Adapted from [115])

Lee [92] also observed lower creep rates in ambient-cured blended fly ash/BFS-based AAM concretes than in OPC concrete when testing according to AS 1012.16 [116], and similar specific creep across a range of strength grades of AAM concrete, but a factor of up to four difference between the creep of exposed and sealed AAM concrete specimens, with exposed samples creeping much more.

The drying shrinkage and creep of the Pyrament blended AAM concrete were also tested, according to the ASTM C512 procedure [49], and it was noted that the calculation procedures described in that standard for linearisation of the creep rate data were not applicable to the AAM material, but no comments on the direction or extent of the deviation were provided.

Based on this discussion, it is clear that distinct models will be needed to describe the creep of AAMs – if the existing empirical models for Portland cement concrete happen to fit the trends in AAM concrete data, it will be through coincidence rather than based on sound mechanistic or micromechanical reasoning – and these models will need to be developed from a body of experimental data for well-characterised AAM concrete mixes under well-controlled conditions. The data which are available in the literature to date, as will be outlined below, have been collected for a broad range of mix designs under various testing conditions, and are far from sufficient to enable the development of a detailed model for AAM creep. This is therefore identified as a key area in which future research work is required in the AAMs community. It will also be important to determine the influence of the loading stress on the creep performance of AAM concretes, as standardised tests and other laboratory investigations have been conducted at a variety of loadings, usually between 25 and 40 % of unconfined compressive strength, and the influence of this testing parameter is likely to be different between AAM and Portland cement concretes due to the microstructural and nanostructural differences between the materials.

10.5 Freeze-Thaw and Frost-Salt Resistance

10.5.1 Testing Methodologies

Frost resistance evaluation of concrete is mainly important where the material is exposed to freeze-thaw cycling, and can be analysed in accordance with test methods such as ASTM C 666 [119], CSA 231 [120, 121], ASTM C1645 [122], or related methods such as ASTM C 1026 [123] or ISO/NP 15045-12 [124] which are both designed for the testing of tiles. The freeze-thaw test described in ASTM C67 [125] is also sometimes applied to the testing of concrete specimens, particularly for precast pavers, but was designed for clay brick wall units, and has been noted to be insufficiently stringent as a test to predict performance under North American exposure conditions due to the slow cooling rate and relatively moderate freezing temperature [126]. Exposure classes, and requirements for concretes to be used in each class of exposure conditions, are also defined in EN 206-1 [127].

In these tests, concrete specimens (often prisms) are exposed to freezing and thawing cycles, where the temperatures of freezing and thawing, cycle count and duration differ in accordance to different norms. The ASTM C666 test includes provisions for freezing either in air or in water, but also notes that “*no relationship has been established between the resistance to cycles of freezing and thawing of specimens cut from hardened concrete and specimens prepared in the laboratory*” [119]. The RILEM TC 176-IDC recommendation [128] specifically distinguishes freeze-thaw damage incurred during cycling in contact with demineralised water, and scaling damage which results from the presence of salts (NaCl in the test method recommended by that TC). An earlier RILEM recommendation was published by TC 117-FDC [129], presenting the “CDF” test method; the later work of TC 176-IDC further developed this test to give recommendations for the “CIF” test method, as well as the Slab test [128]. Scaling resistance is measured by various national methods; these are usually similar to CEN/TS 12390-9 [130] or the now-withdrawn ASTM C672 [131] for scaling during exposure to deicing chemicals. NaCl is most commonly used as the salt solution in these tests.

In each test, after a specific number of freeze-thaw cycles, the visual appearance, mass loss per unit area, and/or mechanical properties of the cycled specimens are compared with those of the concrete before cycling, or with those of corresponding specimens which were stored in standard conditions. A convenient characteristic measured in these tests is the dynamic modulus of elasticity, derived from ultrasonic testing conducted on pristine and cycled specimens. Some norms and standards also measure bending and compressive strengths of beams, as well as their dimensional stability, or change in mass (particularly in tests designed to analyse scaling, or related to moisture uptake into the damaged specimens). Most of the major international standards do not specify acceptance or failure criteria; they are generally used for comparative purposes, although some national regimes do provide detailed scaling limits.

A point which is of particular importance in the freeze-thaw testing of AAMs is the issue of curing of the sample prior to the start of the test. Boos et al. [132] provide an analysis of several blended cement concretes which have been shown to provide adequate freeze-thaw resistance in service in northern Europe, but which show poor performance when analysed according to the three methods described in CEN 12390-9. Those authors recommend that blended cements should be tested for freeze-thaw resistance after 56 (rather than 28) days, and that the use of this curing duration provides test results which rank the blended and pure Portland cement concretes more comparably to their observed field performance. Given the relatively slow gains in maturity observed in some AAMs, particularly those derived from BFS, this recommendation is also likely to be directly relevant to the analysis of these materials.

10.5.2 Performance of Alkali-Activated Materials

Both freeze-thaw and scaling tests are widely used for Portland cement concretes, and it appears that they should also be able to be applied similarly for alkali activated materials. A detailed review of the freeze-thaw resistance of Portland cement concrete was provided by Janssen and Snyder [133], and the mechanism of salt scaling has been elucidated by Valenza and Scherer [134]. Based on the available information, it seems that the mechanisms and parameters which control frost resistance of Portland cement concrete (including pore structure, pore saturation, mechanical properties, and entrained air voids) are largely physicommechanical rather than chemical in nature, and thus likely to be the controlling parameters also in AAM concretes. However, the freezing temperature of the pore solution is also very important [135], and this is likely to differ between AAMs and OPC concretes, due to differences in ionic strength and also differences in the critical pore radius confining the pore fluids. This may be an important issue in comparing the performance of the two classes of materials; Krivenko [136] noted that the frost-related destruction of BFS-based AAM occurs during the freezing of the microcapillary moisture at a temperature below $-50\text{ }^{\circ}\text{C}$, and that this freezing point is depressed strongly by the high ionic strength of the pore solution.

There are a variety of reported degrees of performance of AAMs under freeze-thaw or frost-salt attack; alkali activated materials have, in some circumstances in service, shown better frost resistance than comparable ordinary Portland cement concretes exposed under the same conditions [33, 137]. Many examples of good frost resistance of alkali activated concretes in practice are presented by Rostovskaya et al. [138]. It is interesting that the concretes discussed by those authors generally showed a low strength when placed into service, but their frost resistance was good. Kukko and Mannonen [46] and Bin and Pu [139] have also noted very good frost resistance in BFS-based AAMs, and explained this observation via the reported low total porosity and small pore radius in AAM paste. In the test program of Kukko and Mannonen, the exposure of an AAM concrete to 100 freeze-thaw cycles ($+20/-20\text{ }^{\circ}\text{C}$)

led to an increase in the flexural strength compared to a reference sample, although Hakkinen [140] showed that exposure to 700 freeze-thaw cycles did lead to a slight decrease in strength in their similar specimens; residual compressive strengths of 87–97 %, and flexural strengths of 66–87 %, were reported.

Douglas et al. [62] found a similar extent of flexural strength loss (~60 % residual strength) after 500 freeze-thaw cycles in most mixes tested, except a concrete with very low activator content which was more susceptible to damage. However, almost no change in dynamic modulus of elasticity (no more than ± 7 %) was observed in any specimens except the low-activator mix. The fact that the flexural strength changed by around 40 % with effectively no change in elastic modulus indicates that there is the need to further investigate the relationship between these parameters in AAM concretes, both within and beyond the context of freeze-thaw testing. Gifford and Gillott [141] found that the freeze-thaw durability of alkali silicate-activated BFS concretes was mainly dependent on air content and air bubble distribution, and the poor performance of some of their specimens was attributed to difficulties in achieving the desired air void distribution. However, they concluded that when similar air void system characteristics were achieved in concretes made with AAM or OPC binders, the freeze-thaw durability of the AAM concretes was “*at least as good*” as that of the OPC concretes.

Talling and Krivenko [34] also noted that the use of Na silicate as an activator for BFS gave much better freeze-thaw resistance than NaOH activation, with the silicate-activated specimens resisting 1,000 freeze-thaw cycles (+20/–15 °C), and the NaOH-activated specimens failing between 200 and 700 cycles and showing lower performance than OPC concretes of similar strength. Byfors et al. [106] found that the frost-salt resistance of alkali-activated BFS concretes appears to be independent of air content (although this was difficult to control, even with large quantities of air-entraining agents added to the mix), and depends mainly on water/binder ratio. They also found that freezing of the material at early age (to –20 °C) was only notably detrimental when it took place before the strength reached 5 MPa, and that early freezing and re-thawing was less damaging to AAM concretes than OPC concretes [106].

The freeze-thaw resistance of fly ash-based AAM concretes has also been shown to be acceptable, with around 70 % compressive strength retention during 150 freeze-thaw cycles [142]. Husbands et al. [49] also found high resistance to freeze-thaw degradation (according to the ASTM C666 and C672 procedures) for Pyrament hybrid AAM concretes.

In a detailed investigation entailing mix design according to life-cycle analysis principles, concretes made with alkali-activated materials were compared with those based on Portland cement on technical, economic and ecological levels [143–147]. Several binders based primarily on fly ash, and others based primarily on BFS, were designed and tested to provide a comparison between the freeze-thaw performance of the two classes of materials. Sodium silicate was used as the activator, and mixes were designed to give approximately comparable mechanical performance across the sample set. A reference Portland cement concrete (320 kg/m³ cement, w/b 0.5, no admixtures) that was resistant to freezing-thawing and frost/de-icing

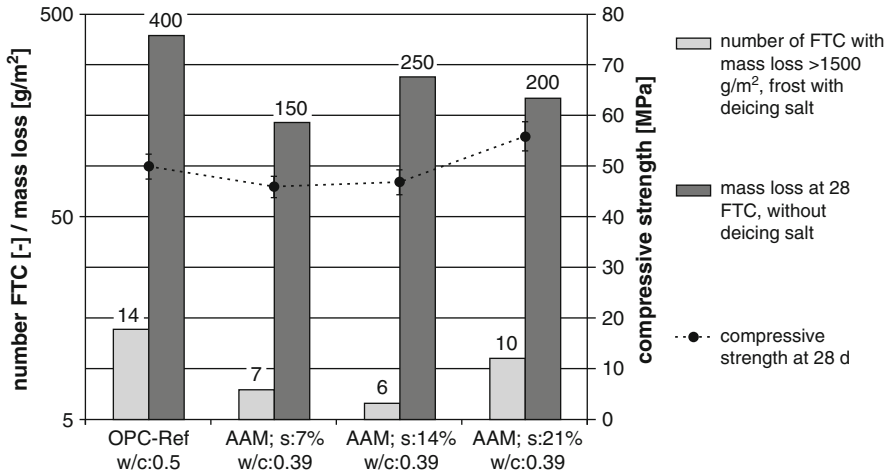


Fig. 10.6 Results of the CDF frost-thaw test for the concretes with fly ash-rich binders – s: content of silicate addition; w/c: water/cement ratio; c: fly ash + BFS

salt attack (exposure classes XF2 and XF4 according to EN 206-1/DIN 1045-2 [127, 148]) was also tested for comparative purposes. AAM samples were cured in the moulds for 24 h at 40 °C and 100 % relative humidity, then stored above water at 20 °C until testing. This was a departure from the procedure specified in DIN EN 206 (which specifies storage under water), but prevented the activator from leaching out of the immature samples.

The resistance to freezing and thawing with and without de-icing salt was determined by the CF and CDF tests [149]. At 28 days the 110×150×75 mm concrete beam samples were immersed in test solution for the 7-day capillary suction exposure, before 28 freeze-thaw cycles were carried out. From the beginning of the capillary suction to the end of the 28 freeze-thaw cycles some of the samples were immersed with the test surface in de-ionised water as the test solution (for the freeze-thaw test) and the rest were immersed in 3 % sodium chloride solution (for the frost/de-icing salt attack). The results of the freeze-thaw tests with the fly ash-dominated binders are shown in Fig. 10.6, whereas the results of the freeze-thaw tests with the BFS-dominated binders are shown in Fig. 10.7.

The alkali-activated fly ash dominated binders (Fig. 10.6) have a frost resistance slightly better (less loss of mass) than that of the reference Portland cement concrete frost resistance if no de-icing salts are used. However, if de-icing solution is present, the alkali-activated concretes (fly ash dominated) fail earlier than the reference concrete. To fulfil the criteria for XF4 classification, 28 freeze-thaw cycles (FTC) must be reached without crossing the 1,500 g/m² limit. The reference concrete crosses the 1,500 g/m² mass loss criteria after 14 frost cycles (FTC), while the concretes made from alkali-activated material (fly ash dominated) cross that limit earlier (at 6–10 FTC).

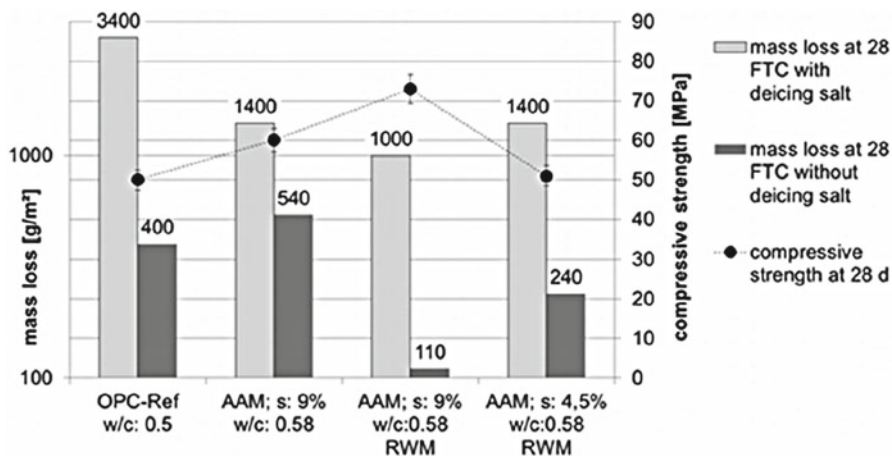


Fig. 10.7 Results of the CDF frost-thaw test for the concretes with BFS-rich binders – s: content of silicate addition; w/c: water/cement ratio; c: fly ash + slag; RWM: addition of 16 % secondary alkaline material

The alkali-activated BFS dominated binders (Fig. 10.7) show better frost resistance in both tests, both with and without de-icing salt loading. All of the AAM compositions fulfil the criteria of the XF4 exposure class.

Some other authors have also noted worse frost resistance in AAMs than in OPC [150], which was attributed to the presence of a higher amount of free water available for freezing in the structure of alkali activated concrete. Much of the water present within hardened Portland cement paste is chemically bound within crystal phases (portlandite, ettringite, monosulfate and/or related phases). As these compounds do not occur in alkali activated materials, these binders can thus contain more water within the pore network and associated with the gel, which is able to freeze, if the tests are carried out with the concrete close to water saturation.

The frost resistance and the scaling resistance of alkali activated materials can also be significantly affected by carbonation (as discussed in Chap. 9) and by the occurrence of microcracks which arise as a consequence of higher shrinkage (as discussed in Sect. 10.3) [151]. Carbonation is one of the most important parameters affecting scaling resistance, as it can impact the mechanical properties of the surface layer of concrete, making the material more brittle and particularly reducing tensile strength, which is known to be important in salt scaling resistance [134]. The shrinkage of alkali activated materials, as discussed in Sect. 10.3, can be higher than in the case of Portland cement concrete. Microcracks arising from shrinkage-related processes can strongly affect scaling resistance.

Finally, it is noted that alkali activated materials represent a very wide group of materials with various properties (porosity and composition). It is impossible to formulate fully general conclusions regarding their frost resistance – but this is not possible even in the case of concretes made with Portland cement. However, with

the possible exception of the need to modify some of the curing regimes used for Portland cement concrete specimens, the widely used testing methods appear to be generally applicable for alkali activated materials.

10.6 Conclusions

In general, it appears that most of the testing methods related to mechanical properties of concretes are more or less directly applicable to the analysis of AAM concretes. The most important differences are identified as being related to the curing and sample conditioning regimes which are applied prior to testing; this is an area in which detailed comparative studies are certainly necessary before recommendations can confidently be presented. Some types of alkali-activated concrete are intrinsically more prone to shrinkage and cracking than Portland cement concrete, but this appears in most cases to be controllable through appropriate curing and/or mix design. Excessive water content is particularly problematic in this regard for AAMs. Freeze-thaw testing of AAMs seems to give quite good results for well-cured, low-porosity mixes, although the standard curing regimes applied to Portland cement concrete test specimens prior to laboratory analysis are probably inappropriate for AAMs.

The most notable difference between AAMs and Portland cement concretes noted in this chapter is in the area of creep. The creep behaviour of AAM concretes is poorly understood, but does not appear to follow the standard empirical models which are used to predict the long-term behaviour of Portland cement concretes under applied load. This is an area in which further experimental work, validation and model development will certainly be highly necessary to give confidence in the use of AAMs in structural applications.

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Chapter 11

Demonstration Projects and Applications in Building and Civil Infrastructure

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11.1 Introduction

In the context of a Report such as this, it is of immense value to be able to provide tangible examples of structures and applications in which alkali-activated concretes have been utilised throughout the past decades. A detailed outline of the utilisation of AAM concretes in the former Soviet Union and in China is given in Chap. 12 of the book by Shi, Krivenko and Roy [1], and this chapter will briefly describe some of the applications mentioned in that (more extensive) document, along with applications elsewhere in the world where AAMs have been utilised on a significant scale in the construction of buildings and other civil infrastructure components.

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An overview of developments and applications in the former USSR has also been presented by Brodtko [2] and by Krivenko [3]. Each project reported in this chapter involves at least pilot-scale, and in some cases full commercial-scale, production of alkali-activated concretes utilising largely standard concrete mixing and placement equipment and labour, indicating that these materials are both accessible and useful on this length scale, given sufficient expertise in mix design based on locally available precursors. In the former USSR in particular, slags obtained from local iron production facilities were used in each of the different locations in which the concretes were produced, and activators were sourced in large part from locally available alkaline industrial waste streams.

In the limited number of scientific studies which have been able to access AAM concretes taken from service, the in-service performance of AAM components and structures has been analysed up to several decades after placement, and the analysis in each case showed dense binder structures with generally well-protected steel reinforcing and high strength retention (in most cases, significantly higher than the design strength) [4–7]. There have not yet been a large number of studies of a sufficiently wide range of AAMs exposed under different environmental conditions for decades or more to provide definitive proof of durability performance in service. However, it should be noted that a similar situation holds for modern Portland cement concretes, which differ (often dramatically) in clinker phase content, mix design and the use of admixtures when compared with those concretes which were used in the seminal long-term exposure and durability studies conducted since the 1930s. The cements available 70 years ago are not the same as modern Portland cements, with a much higher alite content and lower belite content used in modern cements [8], and also with the introduction of a full suite of organic additives to control rheology, water/binder ratio and other parameters during the past decades. Yet, the results of these test programs are used, in conjunction with laboratory tests and physicochemical understanding, to justify and predict the performance of today's concretes. An equivalent methodology must be applied to modern alkali-activated binders if the results obtained from these older materials are to be utilised in predicting durability; the chemical information presented in Chaps. 3, 4, 5, and 6 of this report, and the details of the degradation mechanisms discussed in Chaps. 8, 9, and 10, should be used in conjunction with the information presented in this chapter to provide an overarching view of the value and applicability of durability information from field-exposed older samples in the analysis of modern AAMs.

11.2 Structural Alkali-Activated BFS Concretes

11.2.1 High-Rise Residential Buildings in Lipetsk, Russia

Several high-rise residential buildings (exceeding 20 storeys) were built using alkali-activated BFS concrete by the industrial enterprise Tsentrmetsmetallurgremont between

Fig. 11.1 24-storey building built with alkali-activated slag cement concrete, Lipetsk, Russia, 1994 [3]



1986 and 1994, including the 24-storey building depicted in Fig. 11.1. The exterior walls of the three buildings were cast in situ, and the floor slabs, stairways and other structural components were pre-cast, all using alkali carbonate activated BFS concrete with w/b 0.35; full mix design information is given in [1]. The concrete for in situ casting was transported from the mixing station to the construction site using regular concrete trucks, and cured with electrical heating elements. The precast elements were cast and steam-cured in a precast plant, to a design strength after steam curing of 25 MPa. Quartz sand was the fine aggregate, and dolomitic limestone was the coarse aggregate; good compatibility between the alkali-activated binder and the aggregates was observed, with no signs of alkali-aggregate reaction evident.

11.2.2 *Masonry Blocks, Mariupol, Ukraine*

The commercial production of alkali hydroxide-activated BFS concretes in Mariupol was started in the Stroydetal mill of the association Azovshelezobeton, in 1960 [1].

Fig. 11.2 Residential building in Mariupol, Ukraine, constructed from alkali hydroxide-activated BFS precast blocks (exterior clad in plaster) [3]



These concretes, in the form of precast blocks, have been used for the construction of houses, garages, and other structures including two-storey and 15-storey apartment buildings (Fig. 11.2) [1]. The AAM blocks were also used for construction of a long wall on the bank of the Kalmius River. The block manufacture plant was closed down in about 1980, but the Ilyich Iron and Steel Integrated Works re-started the production of ready-mixed alkali-activated BFS concrete and concrete products in 1999 [9]. Its pre-mixed alkali-activated BFS concrete is mainly used for its own needs, including cast-in-situ or precast slab driveways for heavy vehicles, as well as commercial production for load-bearing structures [9]. Self-levelling concretes have also been developed and applied in road construction. More than 20,000 m³ of concrete has been produced by this facility since 2002, in various strength grades, and economic calculations show very significant cost savings (up to 50 %) for sodium carbonate-activated BFS concretes compared to OPC concretes of equivalent strength grade [9].

11.2.3 Office and Retail Building, and Precast Beams and Columns for Workshop, Yinshan County, Hubei Province, China

Na_2SO_4 -activated Portland-BFS-steel slag cement has been commercially manufactured and applied in China since 1988 [1]; this product was first manufactured and marketed by Anyang Steel Slag Cement Plant, Anyang City, Henan Province. Several months of monitoring of the cement quality indicated that this hybrid AAM cement showed more consistent performance than Portland-blast furnace slag-steel slag cement in the absence of an alkaline activator. Since Na_2SO_4 in solid form is interground with the other components, rather than being added as a separate liquid activator, the cement can be used in concretes in the same manner as conventional cements, from both materials handling and mix design viewpoints. The concretes made with Na_2SO_4 -activated Portland-BFS-steel slag cement exhibited excellent workability, relatively short setting time, high early strength and a smooth surface finish, and were found to be suitable for a wide range of construction purposes. These cements were produced by a number of plants in China and widely used through the 1980s.

A 6-storey office and retail building ($8.6 \text{ m} \times 31.5 \text{ m}$) was built in Yinshan County, Hubei Province in 1988, using this Na_2SO_4 -activated Portland-BFS-steel slag cement concrete, with crushed limestone as coarse aggregate and w/b 0.44 (Fig. 11.3). The design compressive strength was 20 MPa, and the average actual strength at 28 days was 24.1 MPa. The concrete was mixed on site using a small concrete mixer for in situ casting, and had a slump of 30–50 mm. The side forms were removed 1 day after casting, and bottom forms were removed 7 days after casting. The concrete surface was very smooth with no indication of cracking upon demoulding, and performance in service since this time has been very good.

Also in the same County, a workshop with an area of $3,500 \text{ m}^2$ was built in 1988, using Grade 425 (design strength 30 MPa, actual 28-day strength 35.9 MPa) Na_2SO_4 -activated Portland-BFS-steel slag cement concretes with w/b 0.50, again produced by Anyang Steel Slag Cement Plant (Fig. 11.4). The cross section of the columns was $400 \times 400 \text{ mm}$, while the beams had a cross sectional area of $350 \times 450 \text{ mm}$ and a span of 12.6 m. Concrete beams were precast on site and then assembled; forms were removed 1 day after casting. Performance in service has been very good, with no durability problems noted.

11.2.4 Storehouse in Kraków, Poland

In 1974 a storehouse was built in Kraków using precast steel-reinforced alkali-carbonate activated BFS concrete for the floor slabs and wall panels [5, 10]. The concrete compositions included ground granulated blast furnace slag (300 kg/m^3),



Fig. 11.3 6-storey office and retail building built with Na_2SO_4 -activated Portland-BFS-steel slag cement concrete [1]



Fig. 11.4 Workshop built with Na_2SO_4 -activated Portland-BFS-steel slag cement concrete beams and columns [1]

Table 11.1 Compressive strength and carbonated depth of concrete cores [5]

Sample	Compressive strength (MPa)		Carbonated depth (mm) (27 years)
	28 days	27 years	
1	22.1	43.4	10.1
2	21.7	41.9	10.3
3	21.2	46.2	9.4
4	22.3	41.1	11.8
5	23.1	45.1	12.9
6	22.8	41.6	11.7
Average	22.6	43.2	11.0

mixed aggregates (1,841 kg/m³), Na₂CO₃ (18 kg/m³) and water (140 kg/m³). The products were cast and cured in air at 70 °C for 6 h, in a heating tunnel, and then later installed into service.

This building has been monitored for many years. More than 25 years after its construction, cylindrical core samples of 100 mm diameter were taken from the outside wall panels, tested for compressive strength, carbonation depth and microstructure. The compressive strength and carbonation depths of the concrete cores are summarised in Table 11.1; there is a very significant increase in strength from 28 days to 27 years in all cases, as well as an average rate of carbonation of less than 0.5 mm/year in all samples. Electron microscopy [5] showed a dense C-S-H phase as the main binder. There was no observable evidence of micro-cracking, alkali-silica reaction problems, or steel corrosion after this extended period of time in service.

11.3 Concrete Pavements

11.3.1 Heavy Duty Road to a Quarry, Magnitogorsk, Russia

Two alkali-activated concrete roads built in the City of Magnitogorsk, Russia, in 1984 were inspected in 1999. The first was about 6 km long, a heavy-duty road to the Magnitnaya Mountain Quarry, with a typical vehicle load of 60–80 tons on the section where the loaded trucks returned from the quarry. The side of the road on which the loaded vehicles travel has a concrete bed depth of 45–50 cm, and the side of the road for unloaded vehicles has a concrete bed depth of 25–30 cm. The second road section is about 5 km long, near the vehicle refuelling station Shuravi, and had a concrete bed depth of 25–30 cm.

The concrete used contained 500 kg/m³ of ground granulated BFS (400 m²/g Blaine), 25 kg/m³ of Portland cement, 28 kg/m³ of Na₂CO₃ (dissolved in the mix water) as activator, and had a w/b ratio of 0.35. The fresh concrete mixtures for the road construction had a slump of 9–12 cm, steel reinforcing mesh was used, and



Fig. 11.5 Comparison of cast-in-situ alkali-activated slag concrete (*left side*) and ordinary Portland cement concrete road (*right*), Ternopol, Ukraine

the design strength of the concrete was 30 MPa. The concrete mixtures were delivered to the site by mixer trucks and compacted by use of a vibration strip.

During inspection in 1999, after 15 years in service, a large piece of concrete was taken by pick-hammer and sawn into 70 mm cubes for investigation. The compressive strength of these cubes averaged 86.1 MPa (almost three times the design strength), with a water absorption of 8 %, and the carbonation depth from the exposed surface was 10–15 mm (i.e. averaging less than 1 mm/year). There was no evidence of reinforcement corrosion or freeze-thaw scaling, in spite of exposure to several months per year of freeze-thaw load.

11.3.2 Concrete Road and Fountain Basin, Ternopol, Ukraine

A 330 m section of cast-in-situ alkali-activated BFS concrete road and a cast-in-situ alkali-activated BFS concrete fountain basin were built by the Industrial Enterprise of Trust Ternopol-promstroy, City of Ternopol, Ukraine, between 1984 and 1990. In 1999, the road and fountain basin were inspected, as were equivalent structures built side-by-side using Portland cement concrete. The road and basin built using alkali-activated BFS cement concrete were in very good working condition, while those built using Portland cement concrete deteriorated seriously, as exemplified by Fig. 11.5 [3].

11.4 Underground and Trench Structures

11.4.1 *Drainage Collector, 1966, Odessa, Ukraine*

To prevent soil erosion, a 33 km long underground drainage collector (denoted No. 5) was built along the sea bank in the City of Odessa in 1965. The design and construction of the collector were similar to those used for underground railway tunnels, meaning that the technical requirements for the construction materials were high; the design strength was 40 MPa. Around 40 alkali-carbonate activated BFS concrete pipes were fabricated by the Kievmetrostroy Integrated Plant and used to construct part of collector No. 5. The concrete was formulated with 500 kg/m³ BFS, a mixed sodium-potassium carbonate activator (30 kg/m³ activator solids), a w/b ratio of 0.37 to give 8–9 cm of slump, and river sand as aggregate.

The results of an examination in 2000 (after 34 years in service) confirmed that the alkali-activated slag cement concrete pipes exhibited good durability; the compressive strength of the material had increased to 62 MPa, the pH remained above 11.5, water absorption was less than 5 %, and there was no visual indication of corrosion of embedded steel reinforcing, although the cover depth was only 3 mm [1].

11.4.2 *Silage Trenches, Orlyanka, Zaporozhye Oblast, Ukraine, 1982*

The enterprise Zaporozhoblagozdorstroy, located in Zaporozhye Oblast, Ukraine, produced commercial alkali-activated BFS concretes and concrete products for use in the local region for more than 20 years starting in 1972 [1]. In 1982, silage trenches were built to serve dairy farms in the village of Orlyanka, Vasilyevka region; access roads, and the bottoms and walls of the silage trenches were constructed using 2×3×0.2 m precast, steam-cured reinforced alkali-carbonate activated BFS concrete panels. The total area was about 20×60 m, which required the use of about 2,000 tonnes of alkali-activated concrete. The activator used was a mixed sodium-potassium carbonate solution, obtained as an industrial waste.

The fermentation of silage is known to result in the formation of aggressive organic acids [11, 12], and so the silage effluent is highly corrosive towards concrete, although the blending of BFS into Portland cement concretes is known to be beneficial in partially resisting this mode of attack [12]. Silage trenches are also subjected to reasonably heavy mechanical loads due to the work carried out in and around the trenches by heavy machinery. Field inspection after 18 years in service indicated that the part of the silage trench constructed from alkali-activated BFS concrete panels did not show any indication of deterioration, while the Portland cement concrete panels installed and inspected at the same times and serving under the same conditions showed evidently deteriorated concrete and exposed, rusting reinforcement.

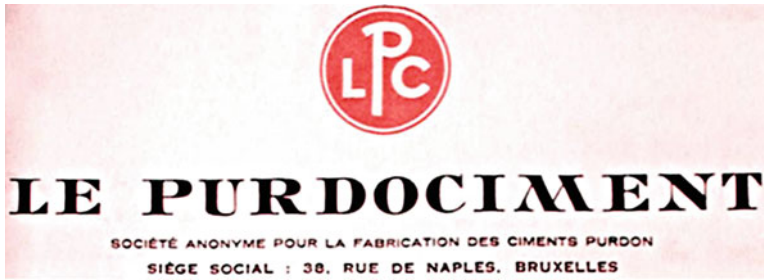


Fig. 11.6 Letterhead of the company “Le Purdociment”

11.5 Le Purdociment, Brussels, Belgium

Based on the pioneering scientific work of Purdon [13] in Belgium (and patents filed in Belgium, Luxemburg, France, the UK, Poland, and elsewhere [13]), alkali-activated cement and concrete production was implemented on a commercial scale in Brussels in the 1950s under the trade name “Le Purdociment” (Fig. 11.6). This company operated a production facility in Brussels from 1952 to 1958, supported by a number of commercial partners, but did not prove to be profitable, either because of the relatively small scale of its production capabilities, or from low interest in the market (the available archive documentation does not provide clear information). Production of Purdociment ceased at the end of 1958. In the building shown in Fig. 11.7, parts of the first six levels were constructed from Purdociment; these parts have been identified through the archives of the SOFINA company (by whom A.O. Purdon was employed), and inspection in 2010-1 showed them to be serviceable and in relatively good condition, although with some damage due to erosion and/or carbonation [14].

11.6 Pyrament and Related Products (Cordi-Géopolymère, France/Lone Star, USA)

The company Cordi-Géopolymère, founded by Davidovits in the early 1970s, has been active in the development and promotion of alkali-activated binders and related materials since this time, including the founding of the Geopolymer Institute to promote the technology related to alkali-activation of aluminosilicates. The first commercial products from this research and development program were mainly fire-retardant inorganic replacements for organic polymer resins, hence the basis of the name ‘geopolymer’ [15, 16], but developments related to construction materials applications commenced in the early 1980s through a joint venture involving the US company Lone Star Industries [17, 18]. This material, as originally patented [19], involved the combination

Fig. 11.7 The “Parking 58” structure, Brussels, Belgium. Parts of the first six levels were constructed from Purdociment



of BFS as a calcium source into a mix based on alkali-activated clay; the addition of cement clinker was also found to be useful in enhancing setting and strength development to form a product which was commercialised as Pyrament Blended Cement [18]. The Pyrament cement was advertised as a high early strength, high performance cement, offering compressive strengths of up to 80 MPa, with 20 MPa achieved within 4–6 h of pouring even at low ambient temperatures, and with setting and strength development consistently achievable at temperatures below -5°C [20]. The clinker content of Pyrament products varied, but was around 60 % in the “PBC-XT” mix which was marketed commercially; this was blended with fly ash and potassium carbonate, with admixtures including citric acid and high-range water reducers used to control setting and strength development [21]. This material is therefore best classified as a hybrid AAM system rather than a pure alkali-activated binder; nonetheless, its track record in service speaks in favour of the wide applicability durability of high-alkali binding systems.

The Pyrament product range was met with strong interest, and found application in test projects and full-scale application via the U.S. Army Corps of Engineers [20, 22], state and federal transportation agencies in several jurisdictions in the USA and Canada [7, 23–26], particularly as a material for bridge deck overlays or as a repair material for damaged pavements, and with performance that has generally been

qualified as ‘acceptable’ or better after several years in service. Even now, some years after its production ceased, Pyrament is still listed on the ‘Approved Materials’ listings of a number of state roads agencies in the USA. The performance of Pyrament sections used in airport runways has also been classified as very good after 25 years in service [27].

Detailed technical and engineering reports on Pyrament cement and concrete performance have been released by government agencies with views towards military [20, 22] and civilian (highways) [28] applications. These have generally displayed that the performance of the Pyrament concrete was proven to be equivalent to or better than that of standard Portland cements according to most performance criteria, although a tendency towards some alkali-aggregate reaction processes was identified. Long-term exposure of Pyrament samples at the U.S. Army Corps of Engineers test site, Treat Island, Maine (100 freeze-thaw cycles per annum, with daily immersion in sea water according to tidal variations) showed no visible degradation, and less than 10 % variation in physical parameters as measured by ultrasonic pulse testing, during 8 years of exposure [20, 29]. Laboratory testing also showed good protection of embedded steel reinforcing [30, 31]. However, the sensitivity of Pyrament to slight variations in water content, as well as limited ‘margin for error’ in various applications, were also noted in some studies [32]. It should be noted that such criticisms are encountered with some regularity in the application of AAM concretes beyond the laboratory environment, but have only been put into writing in a limited number of instances. The issue of water/binder sensitivity is one which is general to AAMs, not restricted to Pyrament, but the number of technical reports written about Pyrament by general concrete practitioners (who are the workers most likely to raise these issues) is much greater than the number which have been written by non-AAM specialists about any other AAM product.

11.7 F-Concrete and Other Materials Developed in Finland

Research in Finland into the F-cement binder [33] through the 1980s led to the development of a number of precast concrete items, including road paving slabs, pipes and sleepers [34]. Strengths exceeding 50 MPa at 7 days, and increasing to more than 100 MPa after 1–2 years for certain mix designs, were reported for both air-cured and water-cured mortar samples [34]. Exposure to atmospheric carbonation for 15 months, and to salt solutions for 4 years (in conditions replicating service), showed good durability performance from the hardened F-concrete products.

During the years 1980 to 1994 a very comprehensive study on alkali activated BFS concrete took place at Partek, at that time the largest construction materials company in Finland. Various mix designs were tested in production of both stiff and pumpable concrete at laboratory scale. After this evaluation, full scale pilot production of pre-stressed hollow core slabs, low height high strength beams, waste water system products, pressurised pipes, railway sleepers and pavement stones was

undertaken in several factories. Extensive testing of products was performed regarding strength development, modulus of elasticity, shrinkage and creep, strain and deformation, adhesion to reinforcement, freeze-thaw, frost-salt, sulfate resistance, porosity and gas adsorption, permeability, thermogravimetry and fire resistance.

A variety of alkali combinations and many types of accelerators and additives were tested, as well various substitute materials including fly ashes, other finely ground slags, natural minerals, flotation residues, and calcined minerals, both under normal conditions and at elevated temperatures and/or pressure. Official concrete testing was performed at the State Research Center (VTT), Helsinki Technical University.

Generally, the properties were similar or better than reference OPC concretes. The adhesion to steel reinforcement was much higher, often resulting in breakage of the steel when testing pipes, hollow core slabs and railway sleepers. Fire behaviour testing at Braunschweig Institute in Germany showed that there was no risk of explosion of the concrete due to spalling, and that residual strength was higher than for OPC concrete. Starting from 1994 some alkali activated systems have successfully been applied as fireproofing adhesives in composites, and as fire and gas-tight layers in insulating composites on board large cruise ships built in Finland [35].

An alkali activated binder system based on ground granulated blast furnace slag (GGBFS), coal fly ash, silica fume and sodium silicate and sand rich in fines was developed for encapsulation of hazardous waste. The strength development of the material was 5 MPa at 14 days, 20 MPa at 182 days and 35 MPa at 364 days. The hydraulic permeability was extremely low, measured at a factor of 10,000 lower than natural rock; in practice, the material was considered impermeable.

11.7.1 Roofing Tiles

At the end of 1988, the first test run to produce roofing tiles was undertaken at full scale. As cementing material, GGBFS containing 4 % of inter-ground slaked lime was activated by sodium metasilicate made by mixing liquid $\text{Na}_2\text{O}\cdot 2.6\text{SiO}_2$ and liquid NaOH in advance in the factory. Fourteen different recipes were used, containing from 240 kg to 440 kg BFS per m^3 of concrete with some variation in activator content (Na_2O dose 2.5–4 % based on BFS content). Small corrections in sand grading were made to guarantee proper compaction properties. The tiles were pigmented with black iron pigment and painted with a black acrylic paint. One batch was left without pigment and only painted. The tiles were installed on a private house (Fig. 11.8), and samples were taken annually for 15 years and replaced with spare tiles.

Some general observations and conclusions regarding these tiles are as follows: The green strength and de-moulding strengths were higher than with a comparable OPC mix design, while water permeability was lower and tensile strength higher with all AAM combinations. The highest tensile strength of an AAM mix was double the average strength of the OPC mixes produced. During the observation time



Fig. 11.8 House close to Helsinki, Finland, roofed with alkali-activated BFS tiles in 1988 (Image courtesy of B. Talling)

(24 years), an average increase in tensile strength of about 25 % was observed. In 2012 the roof was repainted. No cracked tiles were found and the painted surface was intact. The non-pigmented batch was in no way visible. No moss was found, and only minor yellow algae appeared in some places. After re-painting, the service life expectation for the roof is very long.

11.7.2 Outcomes of the R&D Program in Finland

Alkali activation of BFS is considered to be very suitable for the production of stiff concrete compacted by vibration. The cohesion and green strength are much better than OPC concrete, and small amounts of lime can be used to increase the early strength development. Sodium silicate based activators (modulus less than 2.8) give the highest early and final strength. The binder is less sensitive to stone dust, clay residues, fines and impurities than OPC. With proper mix design the durability is equal and in many cases superior to OPC concrete. After 24 years in service, roofing tiles have continuously developed increased tensile strength and

reduced water permeability. The future in mix design and applications is to identify combinations of BFS with other slags and other by-products such as ashes from burning of coal, lignite, oil schist, biofuels, mining residues and chemicals including alkali-rich wastes from the pulp/paper and chemical industries as well as natural alkaline materials. In this way it is possible to tailor individual solutions for many new applications.

11.8 ASCEM Cement (Netherlands)

The ASCEM® cement, which has been commercialised in the Netherlands [36], combines two main ideas, the alkaline activation of aluminosilicate materials and the reuse of secondary raw materials such as fly ashes with varying compositions. This challenge is solved by transforming a desired mix of secondary raw materials into a constant-quality technically high-performing material via a smelting process. Advantages of this strategy are the flexibility on the raw material side (with variable composition and properties) on one hand, and the delivery of a constant product quality on the other hand.

ASCEM® cement is a type of alkali-activated cement consisting of multiple components:

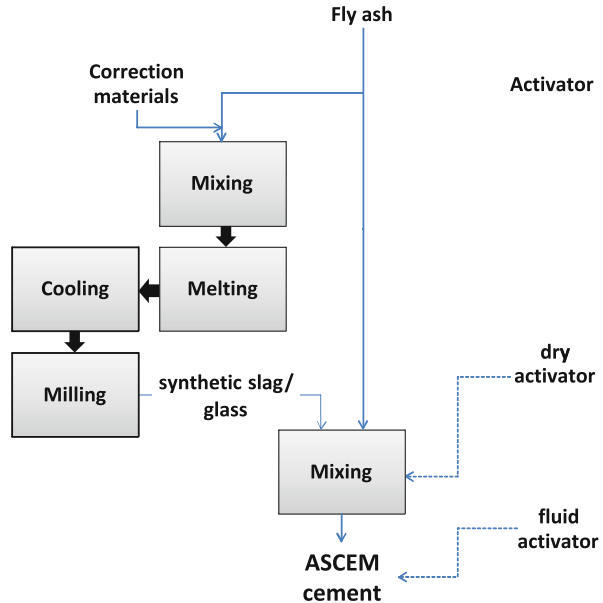
1. A reactive glass in the CaO-Al₂O₃-SiO₂ glass system made from a mix of (preferably secondary) raw materials
2. A filler component
3. An alkaline activator

Although it is derived from a high temperature process, operated at about 1,450 °C, this material embodies less CO₂ than ordinary Portland cement and can compete in terms of technical properties. The idea is based on re-use strategies of different waste materials such as fly ashes and municipal wastes [37]. The technology was already successfully tested in the late 1980s, but not commercialised at that time. Nowadays, other drivers such as CO₂-reduced cements led to a reanimation of that research direction within ASCEM B.V. as a successor to the original development company.

The heart of the ASCEM® cement technology is the melting process of the secondary resource mix. This mix (for instance fly ash + correction materials) is melted to meet a certain composition in the CaO-Al₂O₃-SiO₂ ternary system, to obtain a reactive glass. After rapid cooling of the melt, the cooled glass is milled and mixed with filler. For this, fly ash can also be utilised, along with other fine filler materials. A usual glass/filler ratio is about 1. A flow chart of the technological steps of ASCEM® cement production is given in Fig. 11.9.

Depending on the application, either a dry activator or a fluid activator can be used. The advantage of the dry activator is the production of a one-compound system; the user only has to add water for the production of binder/concrete. The advantage of the fluid activator – added in-situ during the concrete production – is

Fig. 11.9 Technological steps of ASCEM cement production



that it enables a flexible activator dosage, but it does require more knowledge about dosage areas from the operating staff.

11.8.1 Upscaling I: Cement Production

The process was proven on a larger scale in the past, but this needs to be reproduced in the modern implementation of the technology. Therefore, an up-scaling project was started in 2009, pursuing the goal to upscale both the cement production and the concrete production on an industrial scale. It has to be noted that these actions were made without the availability of a dedicated production location for ASCEM cement. The cement production took place in different places using production facilities either from similar processes or available toll production services (the mixing and milling, for instance). Figure 11.10 shows the end of the melting step of the furnace used, with the outflow of fluid glass melt into the cooling unit. The production was carried out using a furnace temperature of 1,450 °C and a continuous melting process. Cooling took place in a large volume water tank. The cooled glass granulate was batch-wise extracted from this tank.

Milling of the glass took place in a vertical roller mill. Different fineness grades were realised; 5,000 and 6,000 Blaine were targeted for later use in cement mixing and concrete production. As filler, a common hard coal fly ash was used. Activator was only added within the concrete production, not dependent on fluid or dry state, in order to enable flexible dosing over the whole test period.

Fig. 11.10 Outflow of the glass melt into the cooling unit



11.8.2 Upscaling II: Concrete Production

Two different products were chosen to test the cement performance:

1. Stelcon® slabs for industrial terrain (produced 2011 by B.V. De Meteor in Rheden, NL), 2×2 m plates with a thickness of 14 cm. These elements are normally produced using a Portland cement, CEM I 52.5 R.
2. Pipes for (waste) water treatment (produced 2011 by B.V. De Hamer in Alphen, NL), unreinforced concrete pipes with diameter 800 mm.

11.8.2.1 Production of Stelcon® Slabs

Concrete pavement units of 2×2 m were produced under the trade-name Stelcon®. The concrete production technology requires a stiff concrete with a low cement paste volume, about 230–250 L/m³. A consistency class of C1 according to EN 206 (compaction value of 1.4–1.5) is required for the filling and compaction step

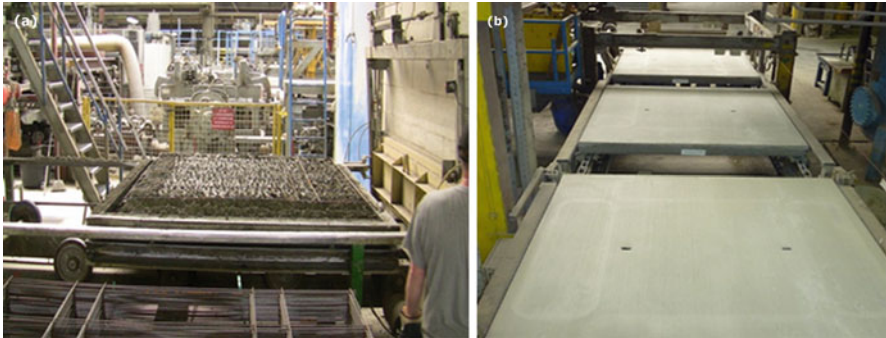


Fig. 11.11 (a) Filled mould for the entry into the vibration chamber; (b) Demoulded

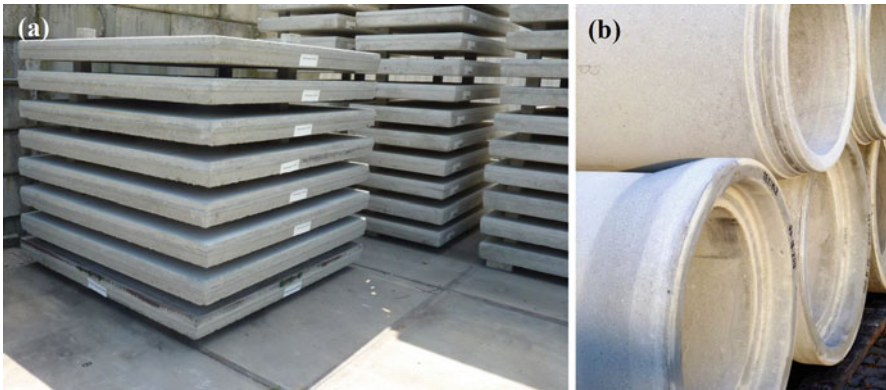


Fig. 11.12 Products in outdoor storage: (a) slabs; (b) pipes

(Fig. 11.11a). The compaction is achieved by combined vibration and pressing. After compaction, the green concrete unit is reversed and stored for about 16 h in a closed chamber. Therein, due to the exothermic reaction of the cement hardening, the temperature rises by up to 30 °C. After the initial storage the concrete elements are demoulded (Fig. 11.11a) and stored in an outside climate (Fig. 11.12a).

11.8.2.2 Production of Sewer Pipes

This production was done using a machine that produces concrete pipes by compacting the earth-moist concrete. In the production of pipes, the consistency and the green body strength are crucial for the production process. The green pipe is immediately demoulded, transported to and stored in a climate chamber. The pictures in Fig. 11.13 show the successfully produced pipes. On the following day, the pipes are transported for outside storage (Fig. 11.12b).



Fig. 11.13 Production of pipes

11.8.3 Concrete Design and Composition

The starting point was to design highly comparable concretes with the same binder/aggregate ratio by volume. The concretes should have a comparable workability. Therefore the w/c ratio was different compared to the reference concrete due to the different water demand of the different binder types. Two different ASCEM cement compositions were used:

- (A) a fluid activator based on NaOH solution (50 %) and potassium silicate solution (13.8 % K_2O , 26 % SiO_2) in mass ratio 4:3. In this case the premixing of reactive glass and fly ash (ASCEM cement) is shown separately from the fluid activator.
- (B) a dry activator. In this case the whole mix is given as *ASCEM cement plus*.

The concrete compositions are given in Table 11.2.

11.8.4 Properties of Concrete and Concrete Elements

Figure 11.14 shows the strength development of the pipe concrete, as measured on concrete cubes (stored under water), compared to the reference concrete. Figure 11.15 provides the results of the breaking test measured directly on the pipe. The required strength is achieved. As was seen for the cubes, the reference concrete performed higher. Improvement of the strength is possible by increasing the fineness of the reactive glass that was not reached within the test production.

Table 11.2 Concrete compositions formulated using ASCEM cement

	unit	Plate			Pipe		
		Ref	MIX IA	MIX IB	Ref	MIX IIA	MIX IIB
Reference cement	kg/m ³	320 ^a			390 ^b		
ASCCEM cement plus (incl. dry activator)	kg/m ³		–	326			389
ASCCEM cement	kg/m ³		310	–		365	–
ASCCEM activator (mix of NaOH and potassium silicate)	kg/m ³		43.4	–		51.26	–
Aggregates 0/32 (natural round grains)	kg/m ³	1967	1967	1967	–	–	–
Aggregates 0/16 (partly broken)	kg/m ³	–	–	–	1823	1800	1807
Water (incl. water in fluid activator)	kg/m ³	134.4	115.4		144.2	143.8	163.4
w/c (exclusive of activator)	–		0.37	0.46		0.39	0.42
Activator content (mass dry content activator/ mass cement)	%		6	11.6		6	11.6
Na ₂ O content in the cement (Na ₂ O equivalent)	%		3.4	2.2		3.4	2.2

^aCEM I; additional use of a plasticiser 2.08 kg/m³

^bCEM III/B; no additives used

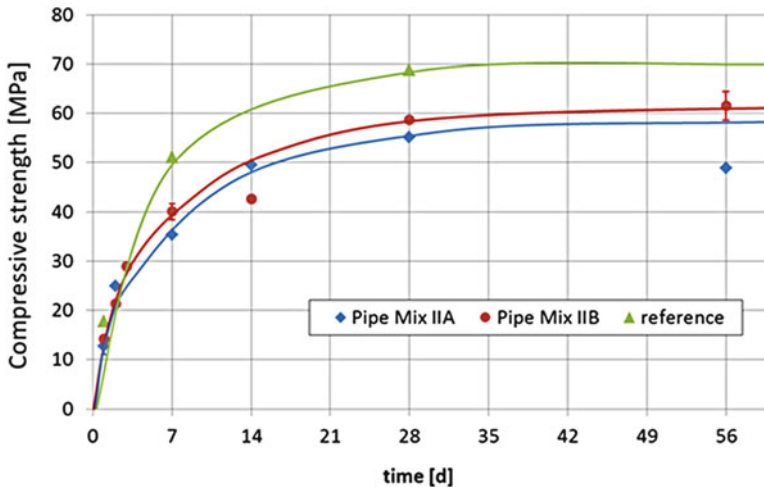


Fig. 11.14 Strength development of the concrete for pipe production (measured on cubes stored at standard conditions)

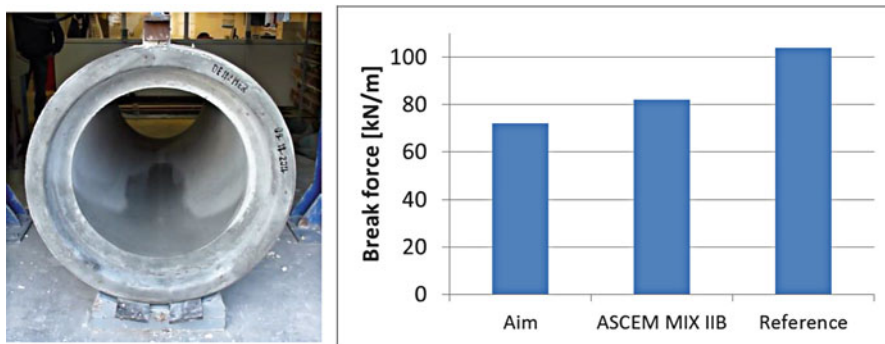


Fig. 11.15 Results of the breaking test on real pipes (see left side for measurement set-up) compared to the aims and the reference concrete

11.9 E-Crete (Zeobond, Australia)

11.9.1 Features of E-Crete™ Technology

The main reasons for the lack of industrial application of alkali-activated materials, to date, have been identified as [38, 39]: (a) Vested interests and established practices in the construction materials industry; (b) The huge technological gap between laboratory and industrial scale concrete in terms of the handling of powders and wet concrete, and the engineering behaviour of wet and hardened concrete; (c) A lack of industrial and commercial experience of many researchers; (d) A lack of understanding of supply chain dynamics and control; (e) Limited experience of a small selection of source materials, instead of extensive experience of a wide variety of source materials used under different operating conditions in different climates and countries.

Since 2006, the Zeobond Group (www.zeobond.com) in Melbourne, Australia, has built a team in collaboration with commercial partners to overcome these obstacles towards commercial adoption of alkali-activated concrete. Zeobond has also developed the E-Crete™ cement binder which is generally produced from blends of fly ash, slag and alkaline activators. This is mixed with sand and aggregate in similar proportions to traditional cement binders to form concrete. E-Crete may use standard alkali activators and whatever source materials, such as fly ash and slag, are available. However, proprietary technology is used to combine such starting materials with a range of admixtures, including proprietary admixtures. E-Crete uses patented methods and proprietary methods to pre-treat and process source materials in order to modify their properties and tailor their reactivity to suit certain applications. Zeobond received INNOVIC's national "The Next Big Thing Award" in 2008 for E-Crete.

E-Crete technology uses a database of extensive test results on source materials from around the world, which enables the rapid development of new mix designs. Zeobond has been able to train several industrial teams to produce E-Crete on a large scale without direct supervision by Zeobond staff, which has substantially enhanced the scalability of the technology. This demonstrates that the technology is robust under the demanding conditions of industrial concrete application. E-Crete has the same performance outcomes as traditional cement, is cost competitive in most markets, and utilises low cost source waste materials, which offers a competitive advantage in markets where waste beneficiation is a market driver.

A commercial life cycle analysis was conducted on E-Crete by the NetBalance Foundation, Australia, as commissioned by the Victorian Government. This life cycle analysis compared the geopolymer binder to the standard OPC blends available in Australia in 2007 on the basis of both binder-to-binder comparison and concrete-to-concrete comparison. The binder-to-binder comparison showed an 80 % reduction in CO₂ emissions, whereas the comparison on a concrete-to-concrete basis showed slightly greater than 60 % savings, as the energy cost of aggregate production and transport was identical for the two materials.

11.9.2 Industrial Application of E-Crete

Substantial progress has been made in the industrial application of E-Crete technology, including:

- (a) Extensive and commercial application of structural and non-structural E-Crete continues in Victoria and Queensland in Australia.
- (b) E-Crete has been demonstrated at industrial scale in the USA, United Arab Emirates and China.
- (c) Extensive application of pre-mixed E-Crete has taken place in new residential developments by property companies in Melbourne.
- (d) Zeobond has collaborated with consulting engineers, architects, city councils, government departments and key specifying agencies to build understanding and comfort with the use of a new cement binder technology.
- (e) Existing plants for manufacturing concrete pipe have been modified to produce E-Crete pipes.
- (f) The production of fire-resistant, fibre-reinforced E-Crete tunnel segments has been demonstrated successfully [40].
- (g) VicRoads, the state roads authority in Victoria, Australia, recognised geopolymer concrete as being equivalent to OPC for non-structural applications in a 2010 update to their design specification Section 703 [41].
- (h) E-Crete is already used in VicRoads structural projects, and by local councils and housing developers in sub-divisional works and slabs. These large scale



Fig. 11.16 E-Crete pre-cast footpath panel segments across the Salmon Street bridge in Port Melbourne, Australia

applications are pivotal to the process of gradually convincing standards authorities to accept geopolymer concrete.

- (i) Zeobond is working with VicRoads to also recognise geopolymer concrete for structural applications in their Section 620 for precast concrete units [42], based on successful demonstration projects.

11.9.3 Precast Footpath Panels Across Bridge

E-Crete pre-cast footpath panel segments (Fig. 11.16) across the Salmon Street bridge in Port Melbourne were specified by VicRoads to the highest quality concrete under their specification for 55 MPa structural grade concrete (Section 620 [42]), such as that used for bridge structures. The product required high early strength for lifting, low shrinkage and long term durability. This project was completed in 2009 and is being used for long term monitoring and as a demonstration trial prior to use in structural applications.



Fig. 11.17 E-Crete retaining wall at the Swan Street bridge in Melbourne, Australia

11.9.4 Bridge Retaining Walls

This project involved the reinstatement of the retaining walls (Fig. 11.17) at the Swan Street bridge in Melbourne and was completed in 2009. E-Crete was selected by VicRoads for this project due to the high profile location and demanding requirements. 40 MPa grade structural concrete [42] was specified for this application with requirements of extended slump retention and the ability to be pumped. Equipment was installed into the wall for long-term monitoring of the steel reinforcement.

11.9.5 Footpaths

The Westgate Freeway Alliance used E-Crete for 25 MPa footpaths on Brady St, Port Melbourne (Fig. 11.18). This was the first of many pavement projects that led to Vicroads' approval of E-Crete grades 20, 25 and 32 MPa in the specification for general concrete paving and non-structural use in footpaths and kerb and guttering in 2010 [41]. This project involved the engagement and collaboration of many parties, including VicRoads, Melbourne City Council, Port Melbourne City Council and the Alliance partners.



Fig. 11.18 E-Crete footpaths at Brady St in Port Melbourne, Australia

11.9.6 Pavement and Ground Works

The Thomastown Recreation and Aquatic Centre works (Fig. 11.19) were completed in 2010 and show the culmination of a long term relationship with the City Council, architects, engineers and builders. This represents the first example of E-Crete being specified from the initial stages of design right through to construction. Extensive footpaths and driveways were completed in 25 MPa grade E-Crete in a range of colours and decorative finishes.

11.9.7 Pre-cast Panels

The Melton Library in Melbourne consists of 3,500 m² of floor space over two levels and has a focus on sustainable design and energy efficiency. 35 E-Crete pre-cast panels make up the exterior of the building (Fig. 11.20) and were installed in 2012. Each panel is 9 m long and is manufactured from 40 MPa E-Crete designed for high early strength. The aggregate is a natural river pebble that has been exposed for a decorative finish.



Fig. 11.19 E-Crete pavement and in situ works for Thomastown Recreation and Aquatic Centre, Melbourne, Australia

11.10 Railway Sleepers in Various Locations

Another obvious civil infrastructure-related application for AAMs, with their known desirability in precast applications and high achievable strength, is in the production of railway sleepers. Prestressed sleepers meeting the national standards of Japan have been produced on a laboratory scale by alkali-silicate activation of fly ash [43]. Alkali-activated BFS sleepers were also developed in Poland in the 1980s, reaching the required 70 MPa strength through the use of finely ground slag [44], and providing performance reported as being equivalent to that of Portland cement sleepers during a 5-year service period [45]. A pilot-scale research and development program in Spain [46, 47] led to the development of pre-stressed steam-cured sleepers based on alkali hydroxide-activated fly ash which were able to meet the requirements of Spanish and European specifications for such products.

In 1988, prestressed reinforced alkali silicate-activated BFS concrete sleepers were installed on the railway between St Petersburg and Moscow, Russia, near the Tchudovo station, in a section of track approximately 20 m long. The design



Fig. 11.20 E-Crete pre-cast panels for Melton Library, Melbourne, Australia

strength of the sleepers was 45 MPa, which was achieved using a w/b ratio of 0.35 and 500 kg/m^3 BFS. In 2000, a field inspection of these sleepers indicated that they remained in good working condition. One sleeper was removed and subjected to detailed investigation, and the outcomes of that work are detailed in [48]. The observed carbonation rate was less than 1 mm/year, the strength of the concrete had increased to 82 MPa during its time in service, and there was no visual evidence of corrosion, cracking, spalling or other defects [1, 48]. The embedded steel reinforcing was fully protected and passivated, and the micro-structure of the material was reported to be stable during this extended service period [48], which took place under challenging freeze-thaw and impact load environments.

11.11 Conclusions

This chapter has described the observed in-service performance of alkali-activated concretes in Europe, Asia, North America and Australia. Commercial-scale production has taken place in various formats (although not necessarily continuously in all cases) since the 1950s in Western Europe, the 1960s in the former USSR, since the 1980s in Finland, China and the USA, and the products which have been placed into use through these production activities provide the opportunity to examine the durability of AAM concretes exposed to a relatively wide range of climatic and service conditions. The case studies presented display that, in general, the alkali-activated concretes which have been placed into service have been able to serve the purposes for which they were designed, without evident problems related to carbonation, freeze-thaw resistance, mechanical or chemical stability, acid resistance, protection of reinforcing steel, alkali-silica reaction, or any other forms of degradation. In general, the measured strengths of products taken from service after a period of a decade or more have been significantly above the initial design strength requirements. It is noted that not every commercial endeavour related to AAMs has been with market success, and there are known complications related to water sensitivity, curing conditions and workability which are more challenging in the application of AAM concretes than for Portland cement concretes. However, there is a growing body of evidence which speaks in favour of the usability, durability and marketability of alkali-activated concretes under service conditions in civil infrastructure applications.

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Chapter 12

Other Potential Applications for Alkali-Activated Materials

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12.1 Introduction

The focus of this chapter is the discussion of a variety of niche applications (other than as a large-scale civil infrastructure material) in which alkali-activated binders and concretes have shown potential for commercial-scale development. The majority of these applications have not yet seen large-scale AAM utilisation, except as noted in the various sections of the chapter. However, there have been at least pilot-scale or demonstration projects in each of the areas listed, and each provides scope for future development and potentially profitable advances in science and technology. In addition to the applications specifically discussed in this chapter, there are also commercial and academic developments in alkali-activation for specific applications including a commercial product which is being marketed as a domestic tiling grout showing some self-cleaning properties [1], as well as

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alkali-activated metakaolin binders as a vehicle for controlled-release drug delivery [2, 3]. Although undoubtedly promising and of commercial interest, these are rather specialised applications, and so the focus of this chapter is instead on broader categories of research and development rather than in providing detailed analysis of specific products. The areas to be discussed will include lightweight materials, well cements, fire-resistant materials, and fibre-reinforced composites.

12.2 Lightweight Alkali-Activated Materials

12.2.1 Foamed Binders and Autoclaved Aerated Concrete

There are various routes by which lightweight alkali-activated binders can be generated. One of the pathways which is widely used in the production of lightweight Portland cement concretes is the hydrothermal method which leads to autoclaved aeroclated concretes; this method has been adapted to alkali-activated systems with some success in the USA, Europe and the former Soviet Union [4–9]. The majority of methods which have been applied to the production of foamed alkali-activated binders have been based around the generation of hydrogen or oxygen to form bubbles while the binder is in slurry form, and this can be achieved through the oxidation of any one of a number of binder components. Finely divided metallic aluminium [10–13], metallic silicon, either added directly [13] or as a component of silica fume [14–17], hydrogen peroxide [4, 18, 19], sodium peroxide [20], and sodium perborate [4, 19] have been used as foaming agents. Chlorine gas generation through the decomposition of calcium hypochlorite has also been proposed [21], although it is unclear what would be the effect of the generated chlorine on the durability of the material in the long term. It is also possible to achieve foaming through the use of suitable surfactants [22, 23], and this method has been applied in practice to the production of lightweight alkali-activated BFS panels containing fibrous additions for use as acoustic insulation [24].

Pilot-scale production of autoclaved foamed alkali-activated BFS concrete was initiated in 1978 in Berezovo, Russia, using a waste mixed-alkali hydroxide solution as an activator, and continued for a number of years [8]. Later work in Kiev involved the development of autoclaved aerated concretes by alkaline activation of metakaolins and fly ashes [6, 7], and Fig. 12.1 shows examples of one of the products which have been developed and placed into service as a result of this research program.

A number of authors have also made use of the foaming tendencies of partially-polymerised (alumino)silicate gels at elevated temperature to develop alkali-activated materials which expand into a foam at elevated temperature [25–28]. This property has been noted to be of value in passive fire prevention applications [19, 29], as it is endothermic and also leads to the generation of a space-filling incombustible foam material. The high-temperature behaviour of AAMs will be addressed in more detail in Sect. 12.3 of this report.

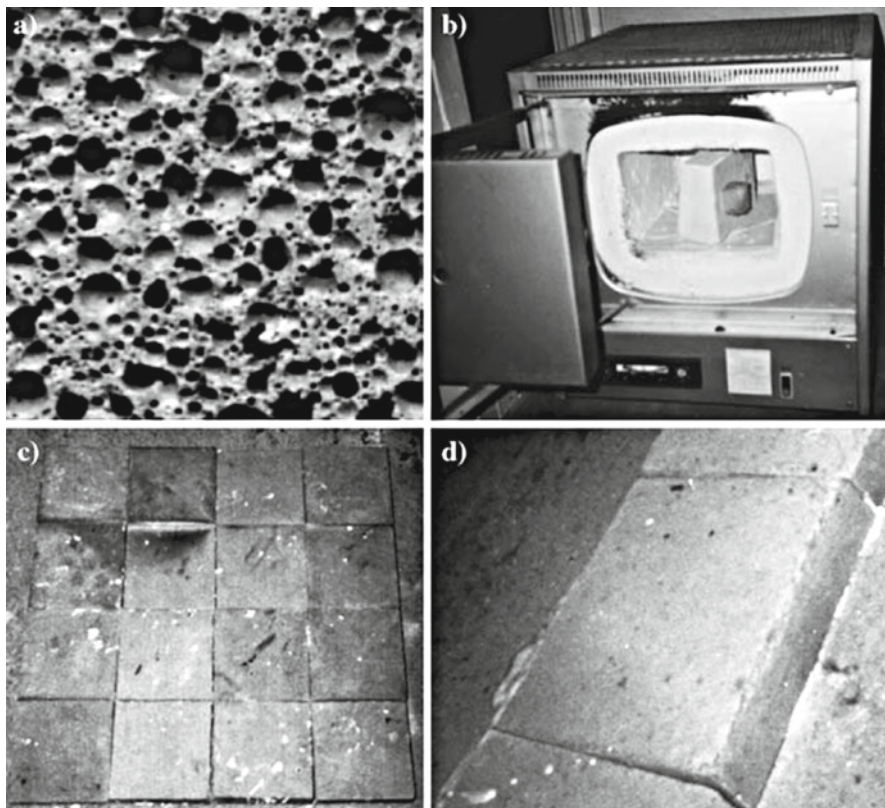


Fig. 12.1 Heat-resistant aerated alkali-activated fly ash foamed using aluminium metal powder, used as furnace lining: (a) structure of the binder (visible pores are tens to hundreds of microns in size, material density 600 kg/m^3); (b) material being tested in a laboratory furnace; (c and d) tiles of size $40 \times 40 \times 4 \text{ cm}$ made from this material after 6 months in service in a furnace operating at up to $700 \text{ }^\circ\text{C}$ (Images from reference [7], copyright Springer)

12.2.2 Alkali-Activated Concretes with Lightweight Aggregates

Lightweight aggregates have also been shown to be compatible with alkali-activated binders in the production of concretes, with both liquid [5, 30] and solid [31, 32] alkali sources used as activators. Strengths of up to 90 MPa have been achieved for alkali-silicate activated BFS concretes with lightweight aggregates [33]; the strength of the aggregate itself was far below this level, but the binder was able to gain sufficient strength to account for this. Frost resistance of alkali-activated concretes was also noted to improve with the incorporation of lightweight aggregates [8]. Alternative aggregates (or, more accurately in some cases, fillers in porous ceramic-type applications) which have been used include fly ash cenospheres [34] and expanded polystyrene [35, 36]. Pre-saturated lightweight (expanded clay) aggregates have also been

used successfully in alkali-activated BFS binders as internal curing agents, to mitigate the effects of autogenous and drying shrinkage [37].

Alkaline activation has also been used to produce binders in conjunction with waste fines from the production of aluminosilicate lightweight aggregates (from clays or perlite) as a source of reactive alumina and silica [18, 38, 39]. The fact that these reactions take place under such conditions provides an indication that there is likely to be a chemical interaction involving the binder when coarser size fractions of the same materials are used as aggregates, and this may be an area in need of further investigation in the development of lightweight alkali-activated materials by this method.

It is also of note that alkali-activation of fly ash has itself been used as a method for the production of AAFA as both lightweight aggregate and paste in concretes [40]. It is not clear how useful such aggregates would be in a realistic concrete system, due to the hygroscopic nature of alkali-activated fly ashes, which would be likely to cause difficulties related to water demand of the concretes, as is commonly observed when recycled aggregates are used. The potential alkali reactivity of such aggregates, both in terms of the presence of glassy components, and acting as an additional alkali source within a Portland cement-derived concrete, should also be considered.

12.3 Well Cements

Sodium carbonate-activated BFS cements were developed for use as oil-well cements in several of the former Soviet republics in central Asia, applied at depths of up to 3,500 m, temperatures up to 80 °C, and pressures exceeding 60 MPa [8]. The use of alkali-activated slag cements for underground cementing applications including borehole sealing has also been reported in several other contexts, in particular in salt and sulfur mines and for hydrotechnical sealing in Europe [41–43]. AAMs have also been developed for down-well cementing in CO₂ storage and sequestration [44]. Drilling fluid and mud can also be mixed with alkali-activated BFS to form a cementitious slurry for cementing operations [45, 46], and there has also been work based around the use of alkali silicate-activated fly ash/BFS blends for similar purposes [47]. Alkali-activated BFS formulations for this application were initially developed by Shell Oil Co. in 1991 for use in the Gulf of Mexico, and similar mixes have also been successfully used in China [48] and Brazil [49]. The Shell product, named ‘Slag-Mix’, was used as a complete replacement for Portland cement-based well cements on several projects in the Gulf of Mexico in the 1990s [45], and was reported to show technical, environmental and economic benefits compared to Portland cement in this application [46], including application as a ‘universal fluid’ to provide both drilling fluid and cementing behaviour [50]. Work reported from the laboratories of some other oil companies [51] did show that under some circumstances, alkali-activated BFS slurries were prone to cracking and variability between mixes, which has to some extent limited their more widespread use

throughout the industry. However, there has continued to be ongoing interest in this area, as evidenced by the filing of patents by Schlumberger related to the use of alkali-activated cements in oil wells [52] and CO₂ sequestration wells [53].

A collaboration involving Brookhaven National Laboratory and Halliburton [54, 55] has also developed sodium silicate-activated BFS and BFS/fly ash cements for use in geothermal wells containing concentrated H₂SO₄ and dissolved CO₂ at elevated temperatures. They were able to generate compressive strengths of more than 80 MPa and low water permeabilities, and the inclusion of fly ash in the mixes was also seen to aid acid resistance [55]. The binding phases formed under autoclave curing conditions were dominated by partially-crystallised C-S-H phases including tobermorite, although excessive crystallisation of the BFS-only mixes at higher temperatures (300 °C) led to a preference for increasing fly ash content with increasing temperature [55].

This is certainly an area which provides opportunities – in a niche but nonetheless relatively high-volume application – for the uptake of non-traditional cementing materials. Recent events related to the Deepwater Horizon well cement failure in the Gulf of Mexico in 2010 may be predicted to signal a return to more conservative attitudes in the selection of well cements in oilfield applications, but at the same time, the push towards carbon capture and storage technology and geothermal energy will enhance interest in the development of specialised cements capable of resisting extremely challenging chemical and physical environments.

12.4 High-Temperature Properties and Performance

This section presents an overview of the thermal properties of alkali-activated materials. These materials, and in particular the low-calcium systems described as ‘geopolymers’, have been shown in many instances to have superior high temperature properties when compared to Portland cement-based materials, which provides strong interest in this aspect of the technology from an industrial perspective; this was in fact the predominant driver for the development and commercialisation of the Geopolymer trademark and range of products in France since the 1970s, and the focus of a large number of patents awarded to Davidovits and various collaborators since that time [19, 56]. The bulk of the discussion in this section will be based around the discussion of such geopolymer-based systems, given the limited volume of data available regarding the performance of alkali-activated BFS binders at high temperature. Low-calcium AAM systems including geopolymers can also be tailored as a precursor material for the production of specialist ceramics by thermal treatment [57–59].

The inorganic framework of alkali-activated aluminosilicate binders leads to excellent thermal stability [60]. This characteristic enables these materials, and composites containing AAM binders, to be used in high temperature applications such as furnace linings, fire resistant coatings, thermal insulation and wall panels. A particular application of note is the use of alkali-activated binders in the production

of fireproof panels and interior fittings for cruise ships, which has been ongoing in Finland for more than a decade through the work of Renotech Oy [61].

The following physical characteristics are critically important when considering a material for high temperature, insulating applications: low thermal expansion or compatible thermal dilation when used as a coating on a substrate, low thermal conductivity, minimal spalling and a high melting point. In addition, thermally resistant materials must exhibit phase stability and a low degree of morphological change.

Discussion of the thermal performance of OPC under after high temperature exposure in this chapter will be limited to a brief comparative analysis; readers are directed to the work of Mendes [62, 63] and of Hertz [64] for a more detailed overview of this topic.

12.4.1 Thermal Expansion

The thermal expansion or shrinkage of any binder is of particular interest when assessing its potential for high temperature applications. Shrinkage or expansion during heating introduces stresses which can weaken or damage the structure. For coatings, dimensional changes lead to cracking and spalling of the coating from the substrate. The rate of thermal expansion/shrinkage of AAMs can be measured *in situ* with a dilatometer [65–67], which can include dimensional data being measured directly with a ‘push rod’ system or remotely using a laser measurement system.

Thermal expansion of geopolymers is generally isotropic due to their amorphous gel structure, but non-uniform expansion can occur due to local variations in composition and temperature elevating thermal stresses and leading to cracking and spalling. Thermal expansion characteristics common to most geopolymer materials are listed in Table 12.1. A breakdown by temperature region, first proposed by Duxson et al. [68] and expanded by Rickard et al. [69], is detailed in Table 12.1 and depicted in Fig. 12.2. The precise temperature range corresponding to each region is somewhat variable, depending on sample composition and testing conditions. It should also be noted that not all geopolymers will exhibit all the regions defined in Table 12.1 and Fig. 12.2, depending on microstructural and nanostructural details.

Low-Ca AAMs, like most solid materials, expand upon heating (Region I). However, they typically contain a high proportion of water either adsorbed in the pores or chemically bound in the structure. Upon heating there is a loss of water resulting in overall shrinkage. At temperatures up to 100 °C the dehydration of water is slow and the dominant dilation change is the expansion of the solid gel. As the temperature increases, the dehydration rate also increases, and as such the measured dilation is a convolution of the expansion of the binder and the shrinkage of the water containing pores (Region II). In most low-Ca AAM samples the dominant dilation event in this region is shrinkage, the amplitude of which is proportional to the water content of the sample. However, in very low water content samples and

Table 12.1 Thermal expansion characteristics of geopolymers – see Fig. 12.2 for depiction of the different regions [69]

Region	Temperature range (°C)	Description	Effect	Factors
I	0–150	Resistive dehydration	Slight expansion	Young’s modulus of sample; heating rate
II	100–300	Loss of free water	Significant shrinkage	Water content; heating rate
III	250–600	Dehydroxylation	Slight shrinkage	Abundance of hydroxyl groups (chemically bound water)
IV	550–900	Densification by viscous sintering	Significant shrinkage	Residual water content; Si:Al ratio
V	Above densification temperature	Gel bloating and/or crystallisation; expansion due to cracking	Usually moderate expansion	Gel composition and microstructure; concentration and type of impurities
VI	Above densification temperature	Further densification	Large shrinkage	Gel composition

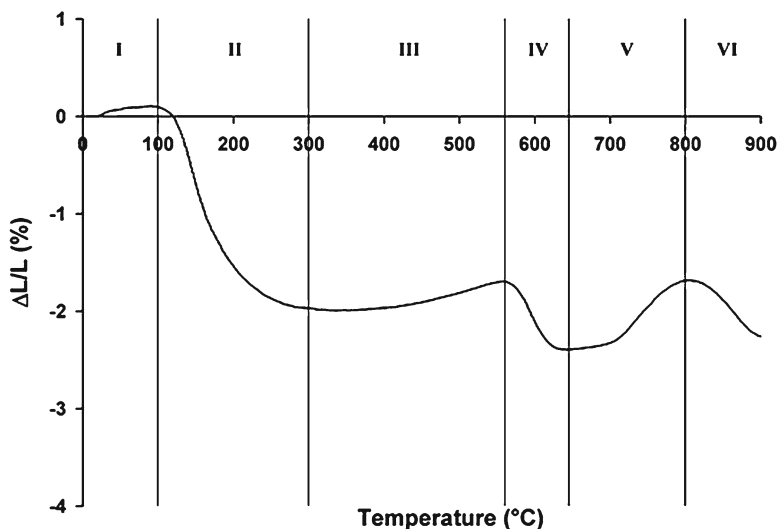


Fig. 12.2 Thermal expansion of an alkali-silicate activated fly ash, showing breakdown into temperature regions (Table 12.1). Si/Al=2.3, w/c=0.2 [69]

samples containing additives, such as vermiculite, there can be a net expansion in this region [70]. Other reactions such as crystallisation (of the gel and secondary phases), oxidation (secondary phases only), sintering and melting, can affect the thermal expansion at high temperatures. Secondary phases are defined as phases

other than the aluminosilicate gel, usually unreacted precursor material such as metakaolin, or the quartz, mullite and iron oxides present in fly ash.

The extent of the dehydration shrinkage is dependent on the water content of the material. For example, Rickard et al. [69] found that alkali silicate-activated fly ash pastes with a pre-curing water content of 15.2 wt.% ($w/c=0.2$) experienced 2 % dehydration shrinkage between 100 and 300 °C (Fig. 12.2). The nature of the dehydration shrinkage, such as onset temperature and duration, is dependent on the structure of the geopolymer and the heating rate during measurement. Duxson et al. [68] proposed that the resistance to dehydration shrinkage of alkali-activated metakaolin is proportional to the Young's modulus of the sample. Binders with a higher Young's modulus can withstand greater capillary strain forces developed during dehydration, and as such the onset temperature of the initial shrinkage is increased. The rate of dehydration is controlled by the rate of diffusion of the water from the structure. Thus the pore structure also has a strong influence on the dehydration rate. Duxson et al. [68] found that increasing the heating rate increased the onset temperature and duration of the dehydration shrinkage event in alkali-activated metakaolin geopolymers.

Dehydroxylation occurs between 250 and 400 °C and is accompanied by a small mass loss. The thermal shrinkage that occurs in region III, (generally occurring between 300 and 600 °C) is due to the physical contraction of the gel as the hydroxyl groups are released [68]. However, the small amount of shrinkage in this region can be masked by the expansion of solid phases (gel and secondary phases) as shown in Fig. 12.2. This is often the case in alkali-activated fly ashes due to the relatively high concentration of secondary phases such as quartz, mullite and hematite.

The second major shrinkage event occurs between 550 and 900 °C (region IV) due to the densification of the sample as the gel sinters and viscous flow fills the voids in the material. Rahier et al. [71] proposed that the shrinkage in this region is an indication of the glass transition temperature (T_g) of the gel. Duxson et al. [68] found that the onset temperature of the densification reduced with increasing Si/Al ratio.

Beyond the densification region (region V), no consistent trend in thermal expansion has been reported in the literature. Rickard et al. [69] and Rahier et al. [71] measured a thermal expansion, Duxson et al. [68] and Dombrowski et al. [72] measured a sharp thermal shrinkage and Barbosa and MacKenzie [60] observed their samples to be dimensionally stable. These different observations regarding thermal expansion in this region are believed to be due to differences in composition and the presence of secondary phases. Provis et al. [65] found the thermal expansion in this region to be proportional to the liquids to solids ratio in alkali-activated fly ash systems, and described this feature (onset temperature and total expansion) in terms of the extent of reactivity of the solid and liquid precursors as a function of the mix design [65, 73]. It was suggested the expansion was due to the presence of partially depolymerised silicate gels, which increased in concentration with increasing liquids to solids ratio.

Crystallisation has also been observed to contribute to the thermal expansion in region V. Feldspar-based phases such as kaliophilite (K-activated), leucite (K-activated) and nepheline (Na-activated) crystallise from amorphous geopolymer at high temperatures [60, 74–76]. Bell et al. [58, 59] demonstrated that Cs- and

K-based geopolymers could be used as precursors to form the ceramic phases pollucite and leucite, respectively. Barbosa and MacKenzie [60] observed that off-stoichiometric geopolymers exhibited increased feldspar growth due to the presence of unbound alkali cations.

Other factors which are believed to influence thermal expansion in region V are crack formation and an increase in porosity. Rickard et al. [69] also found that thermal expansion in this region is dependent on sample size, with larger samples exhibiting greater thermal expansion. It was suggested that this was due to increased cracking due to a larger temperature differential between the centre of the sample and the surface in samples of greater diameter.

The final characteristic region of thermal expansion is region VI, which is identified by large and usually rapid shrinkage. This is often the failure point of the material. Subaer [77] reported a sharp shrinkage leading to the failure of the material, whereas Duxson et al. [74] observed a slower shrinkage, though the magnitude in both cases was similar. The cause of the shrinkage in this region is due to one or more of the following: continued densification (similar to region IV), destruction or further transformation of crystalline phases formed in region V, collapse of the pore structure, or melting of the sample.

12.4.2 High Temperature Applications

The intrinsic thermal resistance of some alkali-activated materials has led them to be considered for a range of high temperature applications, and in particular fire-proofing. AAMs have been observed to offer an advantage over OPC of significantly reduced spalling and superior mechanical strength retention after exposure to fire [78]. Applications for fire-resistant products include tunnel linings, high rise buildings, lift doors and marine structures/coatings [79]. Structures can be protected by a fire-resistant coating, which may be sprayed (as shotcrete) or precast during the construction phase, with particular value in protecting metal beams from deformation during a fire. Structures built entirely from fire-resistant concrete may prove to provide the highest degree of fire protection by removing the possibility of delamination effects caused by differential thermal expansion between the coating and the structure. Tunnels built from fire-resistant concrete will be significantly safer in the event of a fire than those constructed using traditional materials, and this is the motivation for a good deal of research into a variety of concrete mix and non-conventional reinforcement types at present, following several catastrophic tunnel fires in the past decades.

Geopolymer composites have been trialled for use in aircraft due to their fire resistance and comparatively low density [80]. This technology is still in its infancy, however it has shown the potential for wider utilisation. Geopolymer composites have also been used as thermal insulation on the exhaust pipes of Formula 1 race cars [56]. Specialised geopolymer formulations are also suitable for refractory applications, where their low cost and acceptable performance at moderately high

temperatures can provide advantages over other available materials [81–83]. Low water content and high-purity geopolymers suit industrial refractory applications where the material may be subjected to temperatures in excess of 1,200 °C.

For fire resistant applications there are two distinct product types: those that are to be used as structural components (tunnels, walls, etc.), and those that will be used as coatings to insulate structural steel beams or other items. The first type requires high compressive strength over a wide temperature range so the structure is not compromised, while the second type needs high adhesion to a substrate and must be lightweight. Wear resistance rather than mechanical strength is important in coating applications.

12.4.3 Coatings

A useful and comprehensive review of fire protection of structural steel in high rise buildings is provided by Goode [84]. Figure 12.2 shows that for typical geopolymer compositions, heating will result in shrinkage. Geopolymer coatings have been previously shown to be robust on exposure to elevated temperatures, but there is a tendency to delaminate due to incompatible thermal expansion with the substrate (which usually has a positive thermal expansion coefficient, for example in the case of steel). The challenge is thus to modify the aluminosilicate structure so that it has a thermal coefficient of expansion similar to that of steel, leading to a composite that will respond more favourably when heated and thus not delaminate. Temuujin et al. [85] prepared metakaolin-based geopolymers with a range of Si/Al and water/binder solids (w/b) ratios, and demonstrated that for Si/Al=2.5 and w/b=0.74, the thermal expansion was positive, providing the capacity to adjust this property to match the expansion of steel (Fig. 12.3). In addition, this composition exhibited strong adhesion to steel substrates, before and after exposure to elevated temperature. Calcination of this geopolymer to 1,000 °C resulted in the formation of crystalline sodium aluminosilicate phases, which did not appear to have a deleterious effect on the efficacy of the coating when returned to room temperature. It was noted that after 72 h in water there was a mass loss of approximately 8 wt.%, suggesting that there was residual soluble sodium silicate present. Nevertheless, the overall performance of these coatings shows that they are well suited to applications as fire resistant coatings.

Temuujin et al. [29] also made fire resistant alkali-activated aluminosilicate coatings using class F fly ash. Considerably less water is needed to manufacture such coatings from fly ash than from metakaolin, and successful coatings were made with Si/Al=3.5 and w/b=0.25 (Fig. 12.4).

12.4.4 Fire Resistant Structural Components

A large portion of the research into fire resistant alkali-activated materials is currently focused on bulk applications such as structural components which take advantage of the superior engineering properties of AAMs, as well as their intrinsic

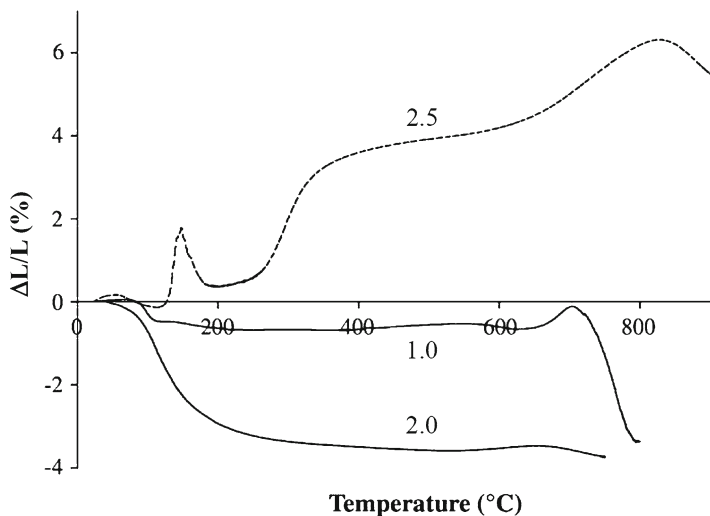


Fig. 12.3 Thermal expansion characteristics of metakaolin-based AAM samples with Si/Al ratios as marked, and w/b=0.74 (Data from [85])

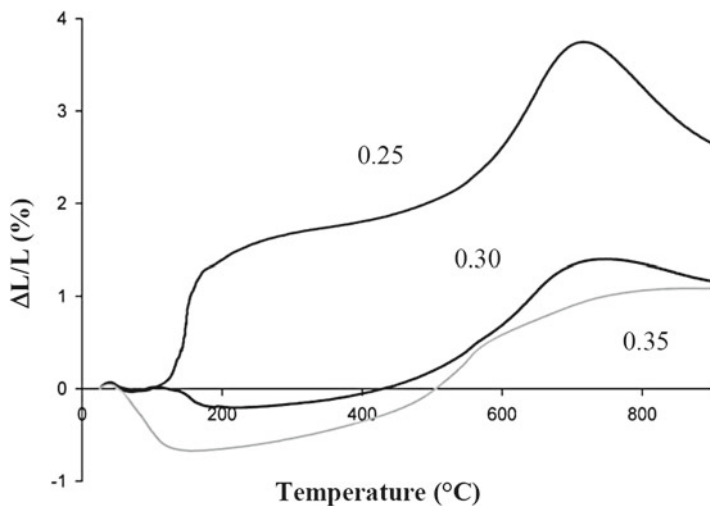


Fig. 12.4 Thermal expansion characteristics of fly ash-based geopolymers with Si/Al=3.5, and w/b ratios as marked (Data from [29])

fire resistance. Rickard et al. [86] used three different Australian fly ashes of varying chemical composition to manufacture a range of alkali-silicate activated binders, and was able to achieve notable strength increases after exposing the samples to 1,000 °C (Table 12.2). Not all mixes exhibited a strength increase after firing, and this was attributed to the relatively high iron oxide content of some sources of

Table 12.2 Compressive strength of alkali-silicate activated pastes made from each of three Australian fly ashes

Fly ash	Iron oxide (wt.%)	Si/Al	Compressive strength @ 28 days (MPa)	Compressive strength after 1,000 °C (MPa)	Percentage of room temperature strength
Collie	13.2	2.0	128(9)	24(9)	19
		2.5	53(10)	15(4)	29
		3.0	29(3)	–	–
Eraring	4.03	2.0	31(2)	78(11)	249
		2.5	33(8)	132(19)	396
		3.0	28(5)	126(20)	457
Tarong	0.64	2.0	26(2)	13(8)	49
		2.5	26(4)	73(17)	277
		3.0	25(2)	99(24)	396

The sample listed as ‘–’ was too weak to be tested [86]. Values in brackets are the uncertainty in the final digit

fly ash. The morphology of the samples changed significantly after firing to 1,000 °C. Sintering of the unreacted fly ash particles and the aluminosilicate gel resulted in a more homogenous and better connected microstructure in all samples. This, however, does not explain the strength loss in the Collie fly ash samples. It was proposed that sintering caused localised strength increases, although bulk cracking caused by crystallisation of the iron oxides resulted in the general strength loss.

Aside from the iron oxide content, other fly ash characteristics have also been identified as important influences on thermal performance. Fly ash particle size, morphology and the presence of crystalline phases will greatly influence the characteristic of the resulting binder. Finer fly ash particle size is preferable for increased as-cured compressive strength. A spherical morphology is preferable for low water content mixes (due to higher workability) which is beneficial for reduced shrinkage at elevated temperatures. The presence of free quartz particles in the fly ashes may also reduce workability, and have the potential to induce expansion cracking at elevated temperatures.

Kong et al. [87–89] compared alkali-activated binders made with metakaolin and fly ash after exposure to elevated temperatures, and found that strength decreased after heating in the metakaolin-based samples, while fly ash-based samples increased in strength. Mercury porosimetry revealed that the metakaolin-derived AAM had predominantly mesopores (2–50 nm), while the fly ash-derived AAM had a higher proportion of micropores (<2 nm). This difference in pore size and inferred pore distribution was reported to be responsible for retention of strength in the fly ash-based binders due to differences in the ability of water to escape during heating without damaging the structure. Bakharev [90] conducted similar experiments on alkali silicate-activated and NaOH-activated fly ash, and also concluded that changes in porosity due to high temperature exposure directly influenced compressive strength of post fired samples. Bernal et al. [91] studied alkali-silicate activated metakaolin and metakaolin/BFS blends, and found that the addition of 20 % BFS gave higher residual strengths after firing at temperatures up to 800 °C, although the BFS-blended sample did not show the increase in post-firing strength after 1,000 °C

exposure which was observed in the metakaolin-only binder as a result of gel densification in that system.

Provis et al. [65, 66] developed correlations between mechanical and thermal properties of sodium silicate-fly ash pastes. The binders which displayed the best strength also showed a small expansion in the 700–800 °C temperature range, which was identified as corresponding to swelling of a high-silica phase present as pockets within the gel structure. Samples in which this phase was either absent or excessive exhibited low strength. XRD conducted on this suite of samples showed the presence of zeolitic and related phases such as faujasite, hydrosodalite and chabazite-Na. These phases play a role in the thermal response of these geopolymer samples, as each has specific thermal characteristics such as dehydration temperature, thermal expansion and melting point.

Kovalchuk and Krivenko [79] manipulated the Si content in fly ash-based systems ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios from 2 to 8) to design binders containing zeolites. When these were exposed to high temperatures, crystallisation resulted in creation of nepheline, cristobalite and albite. Their conclusion was that these materials form an excellent base for application as fire resistant materials. Dombrowski et al. [72] demonstrated that addition of calcium hydroxide to alkali-activated binders improved strength and reduced shrinkage; in samples with 8 wt.% $\text{Ca}(\text{OH})_2$ addition, nepheline formed at 800 °C and at 1,000 °C this converted to feldspar. This is consistent with the data of Bernal et al. [91] for metakaolin/BFS systems at up to 800 °C, as noted above.

Most alkali-activated binders can be considered composites as they may contain quartz, mullite, iron oxide, glassy ash or slag, and/or other remnant precursor particles, as well as the alkali activated gel. It is often this complex microstructure that provides the ability for the material to be forgiving in harsh environmental conditions such as high temperatures. Research has been undertaken to assess the use of additives such as vermiculite to make composite geopolymers with improved the thermal performance. Zuda and colleagues [30, 92] added both vermiculite and electrical porcelain to slag, and alkali-activated this blend to make a lightweight composite with valuable properties. The strength of their composite decreased to 35 % of its room-temperature value when heated to 800 °C, but thereafter the strength increased so that by 1,200 °C it was 30 % higher than that at room temperature. Lin et al. [93] also manufactured geopolymer composites by adding $\alpha\text{-Al}_2\text{O}_3$ to KOH-activated metakaolin. The presence of the $\alpha\text{-Al}_2\text{O}_3$ filler reduced shrinkage as temperature was increased while maintaining porosity, in addition flexural strength increased. As the fraction of $\alpha\text{-Al}_2\text{O}_3$ increased the crystalline onset temperature also increased, though at 1,400 °C the gel binder fully crystallised to leucite. Kong and Sanjayan [89] heated fly ash geopolymers to 800 °C and noted that for paste there was an increase in strength of 53 %, while for aggregate-containing samples the strength decreased by 65 %. The strength decrease for the aggregate-containing samples was attributed to a thermal expansion mismatch: the aggregate expanded by approximately 2 % at 800 °C while the geopolymer matrix contracted by 1.6 %. The thermal expansion mismatch of the different components in concrete remains a challenge yet to be overcome if these materials are to be utilised as construction materials in a fire proofing application. Lyon et al. [94] also exposed fibre-reinforced

geopolymer to high heat flux (50 kWm^{-2}), with 67 % of the original flexural strength retained post-exposure.

In a publication in 2002, Davidovits [56] described his involvement in 30 years of experience and commercialisation work, much of which had been focused on the development of composite geopolymer materials for use at high temperature, including carbon fibre-containing and a large range of other systems. The majority of this work was described in the patent literature, making a large number of claims across binder compositions described by molar ratios; the more important of these patents are summarised in a recent book by the same author [19], and will not be recapitulated in detail here, although it is noted that commercialisation of products based on several of these patents has taken place successfully over a period of decades.

One of the limitations of the majority of the research described in the preceding paragraphs is that strength testing and microstructure evaluation are conducted post-heating, and thus conclusions drawn regarding high-temperature properties are actually based on measurements taken at ambient temperature. To overcome this limitation, Pan and Sanjayan [95] directly measured the stress-strain behaviour of waterglass-activated fly ash pastes *in situ* at elevated temperatures. They observed that the hot strength of the samples increased almost two-fold at $52 \text{ }^\circ\text{C}$ compared with the initial room temperature strength, but beyond $520 \text{ }^\circ\text{C}$ the glass transition process resulted in an abrupt loss of stiffness. Fernández-Jiménez et al. [96] also conducted *in situ* compressive and flexural strength analysis of alkali-activated fly ash paste specimens, and found a marked softening above $800 \text{ }^\circ\text{C}$, although waterglass-activated fly ashes did show an increase in strength between 400 and $600 \text{ }^\circ\text{C}$ before decreasing above this. These observations suggest that more dynamic and in-situ measurements must be made to ensure that strength-temperature characteristics are correctly interpreted.

12.4.5 Fire Resistance

The research described above is a snapshot of current and past efforts to develop, design and characterise AAMs for thermal-resistance applications. However, for these materials to be adopted and incorporated into buildings and engineering infrastructure, testing needs to be undertaken to evaluate their response to standard fire tests. In a fire, the materials are not only exposed to elevated temperatures, but also at a specified rate of temperature increase. The time versus temperature variation of a fire depends on the type of fire and where it occurs.

There are many opinions as to what should constitute a ‘standard’ fire. A typical sequence of a room fire can be expressed in terms of the average air temperature in the room. Figure 12.5 illustrates three stages of such fire:

1. the growth or pre-flashover stage, in which the average temperature is low and the fire is localised in the vicinity of its origin;
2. the fully-developed or post-flashover fire, during which all combustible items in the room are involved and flames appear to fill the entire volume; and
3. decay or cooling period.

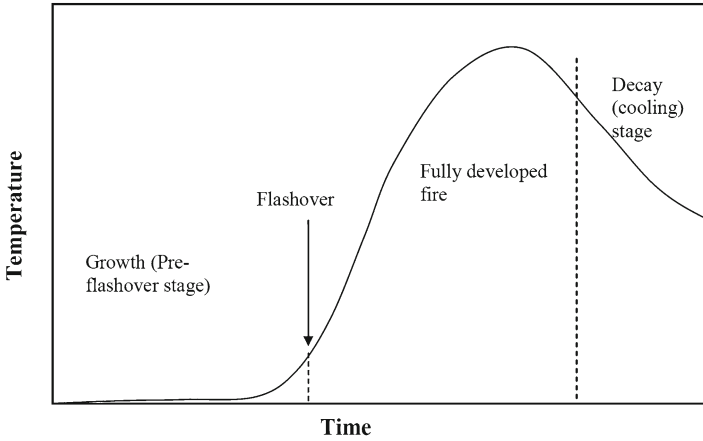
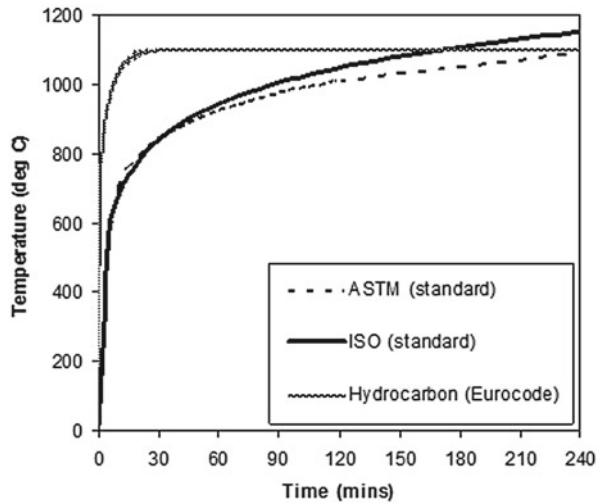


Fig. 12.5 Time versus temperature curve of a typical room fire, based on concepts from [97]

Fig. 12.6 Temperature versus time relationship of standard fires (ASTM E119, ISO 834, Eurocode EN1991-1-2)



Building and structural components are generally required to be shown to withstand an accidental fire. For this purpose, it is necessary to adopt a standard fire curve so that there is a common benchmark test to compare different options for the building components. The most commonly adopted fire curve is described by ISO 834 [98], while the ASTM E119 [99] fire curve is also commonly used and differs slightly from the ISO curve. The ISO 834 curve is based on a cellulose fire, and is also adopted by the Australian (AS 1530.4), Norwegian (Nordtest NT Fire 046) standards and Eurocode (EN 1991-1-2:2002) [100]. The time versus temperature relationship of the standard (cellulose) fire is shown in Fig. 12.6. The standard fire curves aim to simulate the temperature versus time curve of Fig. 12.5, starting from the flashover stage. The pre-flashover stage of the fire is normally ignored, as it has insignificant impact on building

components. For many materials, performance in a fire can be predicted by knowing the maximum temperature to which the material is exposed. However, materials which are relatively brittle, such as concretes, are also affected by the thermal gradients developed in the material during asymmetric heating. One significant parameter that affects the thermal gradient is the rate of temperature rise of the fire during the initial stages. When compared to a standard fire which is modelled based on a cellulose fire, a hydrocarbon fire results in a more rapid initial temperature rise. In situations where the probability of occurrence of a hydrocarbon fire exposure is significant, such as road and railway tunnels, offshore and petrochemical industries, the response of the building component to such a fire should be considered in the design.

Eurocode (EN1991-1-2) provides a curve for this purpose, which is also shown in Fig. 12.6. Hydrocarbon fire is particularly damaging to materials such as concrete, because the rapid temperature rise causes steep thermal gradients, and steam pressure build-up in the pores can lead to explosive spalling. Therefore, unlike materials such as steel where the actual temperature and duration of exposure are the primary factors that influence the fire response, in relatively brittle materials, rate of temperature rise is a critical factor.

Full scale testing of structural components in the same configuration that will be used in service conditions is required to definitively assess a material for fire resistance. There are few facilities that can conduct these tests, and the size and sophistication required means that these tests are very expensive. Scaled down tests, such as the apparatus used by Vilches et al. [101], are available at a number of facilities and can be used as a cheaper and more convenient alternative prior to full-scale testing.

Portland cement concrete, and in particular high strength concrete, is highly susceptible to spalling in a fire [62–64]. High strength concretes are generally defined as concretes with compressive strengths above 50 MPa, and have been widely used in construction since the late 1980s. Spalling of high strength concrete involves the explosive dislodgement of pieces from the surface of concrete in a fire. The elevated risk of spalling of high strength concretes is believed to be due to their reduced permeability and increased brittleness, compared to normal strength concretes [102]. The risk of spalling is further exacerbated when the concretes are exposed to a rapid temperature rise, such as in hydrocarbon fires. A comparative test of alkali silicate-activated fly ash concrete and high strength OPC based concrete demonstrated that the AAM concretes have significant advantages over OPC at high temperature [78, 103]. It was concluded [78] that the more porous nature of the low-calcium AAM binder facilitated the release of steam pressure during heating, which greatly reduced spalling when compared to OPC concretes of similar initial compressive strength.

12.4.6 Summary of Thermal Performance

The preceding discussion shows that considerable effort has been directed towards developing a greater understanding of the thermal performance of both metakaolin and fly ash-based AAMs, although comparatively less work has addressed similar

properties for alkali-activated slags. There have, however, been a number of studies of fibre-reinforced alkali-activated slags exposed to elevated temperatures, which are discussed in section 12.6 below, in the context of the analysis of the effects of fibre reinforcing in AAMs. The published work on the thermal performance of low-Ca AAMs has concentrated on thermal expansion and (mainly) post-heating analysis of strength. There is a deficiency in the literature regarding thermal conductivity measurements at elevated temperatures. Knowing that a binder will survive exposure to high temperature is one thing, but until it is known how the heat is conducted to reinforcing bars or substrates during heating, the full performance of the materials cannot be determined. In addition, there is a need to conduct *in situ* monitoring of phase composition over a range of temperatures to correlate with dilatometry results, although recent advances in this area are showing interesting outcomes [66, 67]. There is also the need to evaluate changes in pore size and melting point during a heating cycle. This will be challenging, but is becoming possible with state-of-the-art synchrotron x-ray imaging techniques. Finally, and probably most critically from a commercial sense, there is a need to conduct large scale fire testing so that standard fire ratings can be ascribed to geopolymer products. Without a standard fire rating it will be difficult to gain acceptance of geopolymer products in fire protection applications.

12.5 Stabilisation/Solidification of Wastes

12.5.1 Introduction

Solidification/stabilisation (S/S) is, in general terms, the mixing of a waste with a binder to convert it into a monolithic solid, to reduce the likelihood of release of hazardous components to the environment. This can involve binding of waste components by physical and/or chemical means, and converts hazardous waste into an environmentally acceptable waste form for disposal or, in some cases, valorisation and use [104–108]. The mechanisms effective in S/S of contaminants by cements and related binders can include chemical fixation by interactions between contaminants and binder phases, physical adsorption of the contaminants onto the surfaces within the pore structure of the solidified binder, and/or physical encapsulation within a low-permeability phase to reduce accessibility during exposure to potentially aggressive environments. The relationships between these mechanisms of immobilisation, and the prevalence of each mechanism in each specific scenario, will fundamentally depend on the chemistry of the binder and the contaminant (and the degree of radioactivity if present), as well as the microstructure of the monolithic product. Thus, while no binder type provides a universally optimal answer to all S/S problems, a low-permeability matrix is generally going to provide better results.

The most commonly-used binder in S/S applications at present is Portland cement, although for cost reasons, and to reduce the temperature rise inside larger

H																				He
Li	Be											B	C	N	O	F				Ne
Na	Mg											Al	Si	P	S	Cl				Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br				Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I				Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At				Rn
Fr	Ra	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus				Uuo
		*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb				Lu
		**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No				Lr

Have been bound in AAMs
 Bound with limited or mixed success
 Alkali-activation seems to increase availability
 Not studied (grey text: short-lived synthetic elements)

Fig. 12.7 Elements which have been bound (and/or treated through S/S) in alkali-activated binders updated from [112] based on a survey of the available literature

monoliths [109], blends of cement with BFS or fly ash are also used. Alkali-activated binders have been tested, and used in practice, for the immobilisation of a wide variety of wastes. Detailed reviews of the use of alkali-activated binders in the treatment of toxic [8, 110–116] and radioactive [8, 111, 113, 117–119] wastes have been published in the past; the discussion presented here will be a summary rather than an exhaustive overview. Because there are some distinct and important considerations which apply only to the treatment of radioactive wastes, these streams will be discussed separately from other general toxic wastes.

In general, it seems that cationic species are far more effectively immobilised in alkali-activated binders than are anions; transition metals which form oxyanionic species in particular tend to be troublesome. A summary of the elements which have been treated through S/S in AAM binders is given in Fig. 12.7; the elements classified as ‘bound’ are those whose total mobility has been reduced by the treatment, including framework-forming species, as well as elements such as N, S and Cl which are usually present as counter-ions to the species of primary interest in immobilisation studies. This is a rather broad definition of this term, but provides a useful starting point for a discussion as presented here.

12.5.2 Stabilisation/Solidification of Hazardous Waste

12.5.2.1 Alkali-Activated BFS Cements

The leachability of Pb, Cr, Cd and Zn species incorporated into alkali-activated BFS pastes (either individually or as components of complex mixed industrial wastes) has been noted to be low [120–122]. Cho et al. [121] used NaOH and Na silicate as activators for BFS, noting similar leaching behaviour of immobilised species for the two activator types, while Deja [120] used Na₂CO₃ and Na silicate, and found that Na₂CO₃ was more effective due to beneficial effects associated with carbonate

precipitation, as well as the potential role of microcracking in their silicate-activated samples. Blending of the BFS with zeolites has also been noted to be beneficial in reducing leaching of Pb and Cr [123].

Chromium is a widespread environmental pollutant, and is prominent in several classes of mineral processing and metallurgical wastes. Hexavalent chromium is particularly toxic, and is also mobile in the environment. Cr(III) is both less toxic and less mobile, being relatively insoluble as $\text{Cr}(\text{OH})_3$ and also as mixed hydroxide phases containing some Ca [124]. The sulfide present in slag has been noted to be particularly helpful in generating a reducing redox environment within the pore solution, which converts Cr(VI) to Cr(III) to reduce its mobility [120, 122]. This change in redox chemistry does oxidise Fe(III) to Fe(II) and render it more mobile [122], but the toxicity of Fe(II) is much lower than that of Cr(VI), so this is less likely to be problematic. Ahmed & Buenfeld [122] also reported that nickel and molybdenum were reported to be relatively insensitive to Eh conditions, but with the possibility of mobilisation due to the higher pH environment within alkali-activated BFS binders. In the same discussion, elements (such as As, Sb and Sn) which form soluble complexes with reduced sulfur species were also predicted to be unsuited to treatment in alkali-activated BFS systems [122]; the literature data summarised in Fig. 12.7 display that this prediction has to date proven to be accurate. Acidic wastes may also need to be neutralised prior to treatment by alkali-activation; this can otherwise lead to consumption of the alkalinity of the activator, meaning that excessive doses (and thus costs) are required [125].

The influence of a low concentration (up to 0.5 wt.%) of Zn on strength development in NaOH-activated BFS binders was noted to be much less notable than its (strongly detrimental) role in retardation of Portland cement hydration via calcium zincate formation [126], although a retarding effect and a notable reduction in final strength are observed at 2 wt.% Zn in these materials [127]. Immobilisation was also found to be relatively ineffective at this high Zn concentration. Similar degradation in performance was observed with the addition of Hg to similar binder systems; low levels had little effect on setting or strength, and were relatively immobile, whereas 2 % was again sufficient to degrade binder setting, strength and immobilisation performance [128].

It has been reported that, in general, heavy metals show less interference with the setting and strength development of alkali-activated BFS cements than with Portland cement [8, 113]. This is potentially due to the enhanced availability of Si in most alkali-activated binder systems (particularly those with waterglass activators), and its dominance of the gel chemistry of alkali-activated binders, whereas Portland cement hydration is more sensitive to factors which reduce silica availability by retarding cement dissolution. This was demonstrated experimentally by Shi et al. [129], who used calorimetry to investigate the early-age reactions involved in S/S of an electrical arc furnace (EAF) dust (containing a mixture of toxic metal species) with OPC and alkali-activated BFS binders, and observed a much more notable effect on setting rate, heat evolution and final strength in the OPC systems (which were entirely prevented from setting at high waste loadings) than in the AAM systems. A field demonstration of the use of this S/S system at a 45 wt.% loading of EAF dust, with

BFS, lime, waterglass and a small amount of silica fume comprising the binder, provided good in-service performance. However, there was a notable difference in performance between laboratory-cured and field-cured specimens, which was attributed to the differences in curing regimes applied under the two conditions [130, 131].

12.5.2.2 Alkali-Activated Metakaolin or Fly Ash Binders

There have been a large number of published studies of the application of alkali-activated fly ash or metakaolin-based binders in S/S applications; the vast majority of these studies have been solely laboratory-based, and have provided sets of leaching data which in general show good performance (although there is a distinct possibility of ‘publication bias’ leading to non-reporting of tests giving negative outcomes, as is well-known in almost every field of medicine and science). However, the published field studies have also in general shown acceptable S/S performance across this class of materials, and it is these studies, along with laboratory studies explicitly aimed at determining immobilisation and leaching mechanisms (as opposed to simply reporting performance of a given binder system under a single set of conditions) which will provide useful information in this area. Utilisation of alkali-activated binders as a capping agent for highly saline mine tailings has also been demonstrated [132], where small amounts of reactive aluminosilicate components were blended with larger quantities of less-reactive tailings to form a controlled low-strength material which, when used as a cap, reduced the tendency towards dust release and metals leaching compared to untreated tailings.

Lead is probably the element that has been most widely studied as a hazardous waste component for immobilisation in AAMs, but the understanding of the immobilisation mechanism is not yet complete. The early work of Van Jaarsveld and co-workers [114, 133, 134] showed that lead seemed to be chemically bound within the aluminosilicate matrix, although its specific chemical form could not be distinguished. Lead modified the binder pore structure, and its release during batch leaching tests was found to be controlled at least partially by diffusion limitations involving the large Pb^{2+} cations moving through confined spaces. Palacios and Palomo [135, 136] attributed the immobilisation of lead in NaOH-activated fly ash binders to the formation of insoluble Pb_3SiO_5 . Their identification of this phase was tentatively supported by the results of Zhang et al. [137], although in both studies this identification was made on the basis of a single XRD peak. Zhang et al. [137] did, however, find that the immobilisation of Pb in a sodium silicate-activated fly ash must be due to chemical entrapment of Pb^{2+} in the matrix, as opposed to simple physical effects. If the lead were only physically bound, addition as sparingly soluble PbCrO_4 would have been expected to give a higher degree of immobilisation than when it was added as the more soluble $\text{Pb}(\text{NO}_3)_2$. The fact that this was not the case, in either H_2SO_4 or Na_2CO_3 leaching environments, shows that there must have been some form of chemical binding taking place.

Several reports available in the literature detail difficulties in the use of low-Ca alkali-activated binders for immobilisation of Cr(VI) [135, 137–139]. The issue of

possible chromium release from fly ash during reaction has been addressed in detail recently [140]; it was observed that the likelihood of problematic chromium mobilisation from fly ash particles is much lower during silicate activation than at the higher pH prevailing during hydroxide activation. The addition of 0.5 wt.% S^{2-} as Na_2S to an alkali silicate-activated fly ash binder enhanced the immobilisation performance [141], due to the generation of a reducing environment similar to those observed in BFS-based systems. The partially-reduced chromium may become microencapsulated throughout the growing aluminosilicate gel phase, possibly as $Cr(OH)_3$ or similar alkaline salts. However, if the Cr is added in the form of a sparingly soluble chromate salt such as $PbCrO_4$, reduction will not be completed prior to setting, and the remnant Cr(VI) will then be available for leaching [141]. This has interesting implications in terms of the use of waste conditioning prior to S/S treatment; it may be that some of the preliminary steps that are sometimes used in an attempt to reduce the solubility of Cr before mixing with the binder are in fact counterproductive in this instance.

Arsenic is a particularly important element in large-scale waste immobilisation, as it is highly toxic, soluble, and commonly present in waste streams from mineral processing operations and several other industries. Its S/S treatment with cements is implemented only on a case-by-case basis due to limited effectiveness [142]. The incorporation of arsenic into alkali-activated aluminosilicate binders has usually been studied in cases when the arsenic is supplied as part of a multicomponent mixed waste [110, 118, 143, 144]. In most of these studies S/S was reported to be relatively effective, although several groups [144–146] have each reported that alkali-activation was quite ineffective in the immobilisation of arsenic supplied as part of a contaminated fly ash. Fernández-Jiménez et al. [147, 148] studied a simulated case where the arsenic was supplied as $NaAsO_2$, enabling more analysis of specific chemical effects. Arsenic was observed by transmission electron microscopy to be associated with iron-rich fly ash particles, although similar behaviour was not observed when Fe_2O_3 particles were added directly to the mixture. This correlates to some extent with the known sorption of arsenic onto iron hydroxide surfaces [149]; this is the most likely mechanism of immobilisation of arsenic in fly ash-derived binders.

Few detailed studies of zinc immobilisation in geopolymers have yet been published; Minaříková & Škvára [150] showed that adding ZnO to alkali silicate-activated fly ashes led to ~50 % reduction in the final compressive strength reached, but the relative rate of strength development was not significantly different. Given that the strength requirements of stabilisation/solidification products are not in general very high, a 50 % reduction is not necessarily severely problematic. In that study, immobilisation performance was generally good but not uniformly outstanding, and the incorporation of less than 5 % gypsum gave a reduction in leaching by a factor of 10. Fernández Pereira et al. [151] also showed relatively good (>90 %) immobilisation in S/S of a zinc-rich electric arc furnace dust in alkali-activated fly ash binders.

Cadmium is extremely toxic and a known human carcinogen, and is found in many mining and metallurgical wastes, as well as being used in many batteries. It is

relatively successfully immobilised in Portland cement matrices, substituting for Ca^{2+} to form mixed Ca/Cd-silicate hydrate gels [152, 153]. However, immobilisation of cadmium in low-calcium alkali-activated binders has not been as successful [150, 154]. This is particularly notable considering the very stringent environmental regulations covering Cd^{2+} leachability, and thus the high binder performance level required. The performance of alkali-activated fly ashes in cadmium immobilisation has been shown to depend critically on the leaching conditions applied [137]. Leaching in sulfuric acid gave very poor immobilisation performance (more than 30 % release in 90 days' exposure), whereas deionised water gave better than 99.95 % immobilisation efficiency during the same period, and leaching at all was detected after 90 days of exposure to saturated Na_2CO_3 solution. These results were attributed to the presence of cadmium as a discrete hydroxide or similarly alkaline salt in the geopolymer system; with little calcium present, the more stable phases which host Cd^{2+} in high-Ca binders cannot form. The solubility of $\text{Cd}(\text{OH})_2$ is lower at elevated pH, and it appears that it is also sufficiently low at near-neutral pH to provide reasonable immobilisation performance. However, upon exposure to a strong and/or concentrated acid, this phase becomes quite soluble. Treatment of cadmium-rich wastes in a high-calcium binder system (Portland cement or alkali-activated BFS) is thus more likely to prove beneficial.

Other waste components which have been treated with some success using alkali-activated fly ash or metakaolin-based binders include copper [114, 115, 133, 134, 155], cobalt [110] and mercury [156]. The combination of municipal solid waste incineration ash (containing some Ca, Si and Al which can participate in matrix formation) with alkali silicates, with or without the addition of extra aluminosilicate sources, can be effective as a means of S/S, although the high levels of chloride and sulfate present can cause challenges in mix design or indicate the use of a pre-washing step [157–160].

12.5.3 Stabilisation/Solidification of Radioactive Wastes

S/S of radioactive wastes is another area in which alkali-activation technology has received significant attention in both research and development fields. The majority of work in the use of cements and similar binders has been focused on low/intermediate level wastes (L/ILW); the use of ceramics or glasses is favoured for high-level waste immobilisation. Key radioactive components of L/ILW include ^{137}Cs and ^{90}Sr ; most laboratory studies are conducted through the use of non-radioactive simulants (stable isotopes of Cs and Sr) to avoid hazard to laboratory workers. These studies are able to replicate the chemistry of the radioisotopes, but cannot capture issues such as radiolytic hydrogen generation or radiation-induced damage to the binder matrix, which are inherently very difficult to study in a research environment. Alkali-activated wasteforms are in some instances dewatered by thermal treatment after hardening to reduce radiolysis [161, 162], although this may not be practical in all cases due to handling issues and the possibility of cracking of larger blocks

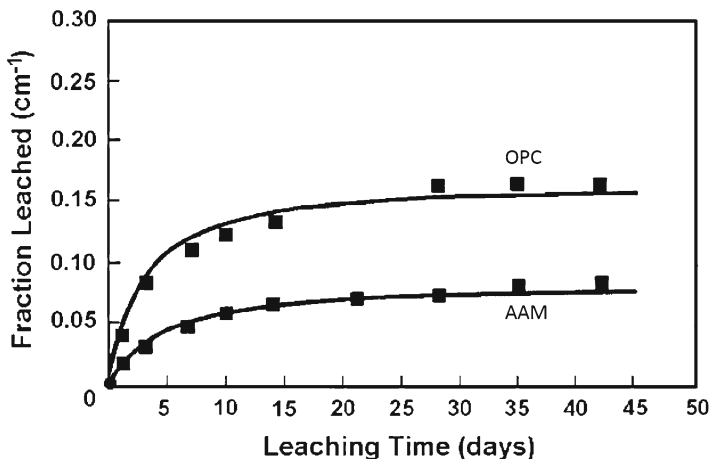


Fig. 12.8 Leaching of Cs^+ from hardened Portland and alkali-activated BFS cement pastes at 25 °C (Data from [171])

during thermal treatment. In some cases, mixed nuclear wastes will include reactive metals (particularly Al used in cladding) which can corrode at the high pH prevailing within AAM (or OPC) binder systems, leading to hydrogen generation and potential cracking of wasteforms; special low-alkalinity binders are desirable in such instances [163]. In designing and constructing an underground waste repository, barriers of swelling clays are often used with the intention of providing additional protection against groundwater ingress, but are also potentially reactive with concentrated alkalis, and so a low-alkalinity binder system would be preferred under such conditions [164].

Caesium is often considered the most difficult radionuclide to stabilise in most L/ILW radioactive wastes, because it is weakly bound and readily eluted from many common cementing systems [165]. However, it does tend to be strongly incorporated into aluminosilicate and other zeolite-like structures [166]. Strontium is less problematic when combined with Portland cements, because it is relatively readily bound into C-S-H phases by substitution onto Ca^{2+} sites [167], but given that the two isotopes ^{137}Cs and ^{90}Sr often occur together as uranium fission products (plutonium fission produces more technetium than strontium), and are the predominant contributors among fission products to radiation emission on a timescale of decades to centuries, they are the components which are of primary interest.

Several laboratory studies have confirmed that the caesium leaching from alkali-activated BFS pastes into deionised water is much lower than from Portland cement pastes [113, 168–170]. Figure 12.8 shows the leaching of Cs^+ from Portland cement and alkali-activated BFS pastes containing 0.5 % CsNO_3 , immersed after 28 days of moist curing at 25 °C, with much higher leaching from OPC than the AAM paste. This result was attributed to differences in pore structure and the lower C/S ratio in the C-S-H present in the AAM binder [171]. As in the case of Pb and Cr

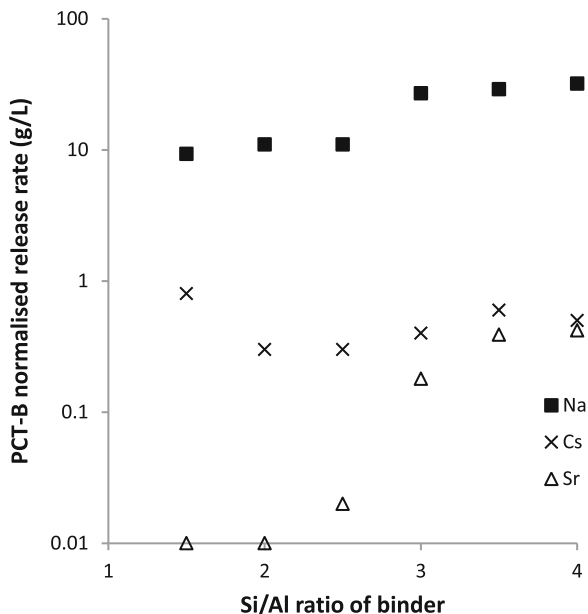
immobilisation, noted in section 12.5.2.1, partial replacement of BFS by zeolite or metakaolin has also been reported to decrease the leaching of Cs^+ and Sr^{2+} from the hardened pastes [170, 172], due to the specific adsorption properties of C-(A)-S-H and zeolite precursor-type phases. Alkali-activated binders derived from magnesia-iron slags have also been developed in Russia for the treatment of wastes bearing radioactive Cs, Co and Ru, with apparent success in terms of physical property development and leaching performance [173].

For reasons related to the binding of Cs^+ in gels with pseudo-zeolitic (or proto-zeolitic) structures, alkali-activated metakaolin and fly ash binders have been studied reasonably extensively for waste immobilisation purposes [117, 161, 162, 174–178]. Chervonnyi and Chervonnaya [179] studied the combination of ^{137}Cs and ^{90}Sr as present in wood ash from the region surrounding the damaged Chernobyl reactor complex, and found that geopolymerisation of the wood ash together with thermally activated bentonite provided a factor of 20 improvement in leaching performance compared to Portland cement. A binder system named EKOR, developed in the Kurchatov Institute, Russia, commercialised by Eurotech and described as a ‘silicon-based geopolymer’, was applied as a sealing and dust-reduction agent as a part of the construction of the sarcophagus protecting the damaged reactor core [180, 181]. Alkali-activated clay-based binders have also been developed and applied in S/S of radioactive wastes in the Czech and Slovak Republics by the company ALLDECO [182], and also in Germany (treating uranium- and radium-bearing streams) as a result of work carried out by mine operators in collaboration with Cordi-Géopolymère in France [118, 183].

The immobilisation of Cs^+ and Sr^{2+} ions in low-Ca alkali-activated binders has been shown to take place by distinct mechanisms determined in part by the different charge states of the two ions. As mentioned above, Sr^{2+} can substitute for calcium in the formation of C-S-H type gels; when these gels are not present (i.e. in the presence of little or no calcium), strontium appears to be present in the pore solution of intact matrices, or very readily precipitated as carbonates if the material is exposed to the atmosphere [162, 184]. SrCO_3 is quite insoluble, and so this does provide a reasonably effective means of immobilisation, as shown in Fig. 12.9. Caesium does not form such precipitates; instead, as an alkali metal cation, it substitutes more or less directly for sodium or potassium in the alkali-aluminosilicate gel, and takes on more or less the same structural roles as these other alkalis within the binder structure [59, 177, 185–187], as discussed in Chap. 4. The leaching of Cs is, however, much slower than the leaching of Na from a binder containing both cations when normalised for total concentrations (Fig. 12.9), consistent with its stronger interaction with silicates as a more polarisable and larger alkali metal cation [188], and also the difficulty associated with the passage of larger cations through constricted pore networks.

The generation of zeolites by hydrothermal (up to 200 °C) treatment of high-volume fly ash/OPC hybrid binders has been shown to lead to effective S/S of highly alkaline low-level radioactive waste solutions, where the alkalinity of the waste stream carried out an activating role [189, 190]. The term ‘hydroceramics’ was applied to a series of hydrous materials developed by alkaline activation of clays

Fig. 12.9 Normalised release rates of Na, Cs and Sr from alkali silicate-activated metakaolin binders into deionised water (PCT-B test) as a function of Si/Al ratio; binders contained 1 wt.% Cs as CsOH and 1 wt.% Sr as Sr(OH)₂ (Data from [161])



under hydrothermal conditions, designed for the treatment of sodium bearing wastes and mainly consisting of zeolites (in particular, cancrinite or sodalite tend to form in the presence of the high levels of oxyanions present in the waste streams) bound in an alkali aluminosilicate gel matrix [191–194]. The raw materials blend also included vermiculite to enhance ¹³⁷Cs fixation, and a small amount of Na₂S as a redox buffer and to precipitate heavy metals. The hydroceramic waste forms were specifically developed to deal with the highly alkaline and sodium-rich reprocessing waste stockpiles present at U.S. Department of Energy sites in Idaho, Washington and Georgia, as an alternative to vitrification in borosilicate glass wastefoms, and developments in this area (related to hydrothermally-treated and low-temperature cured products) within Department of Energy laboratories are still ongoing [195].

Other utilisation of alkali-activation in the area of radioactive or nuclear fuel cycle-related waste treatment has included the solidification of spent ion exchange resins [125], and S/S treatment of radioisotopes including ¹⁵²Eu, ⁶⁰Co and ⁵⁹Fe [196] ⁹⁹Tc [197, 198] and ¹²⁹I [198]. This does appear to be an area in which the versatility of alkali-activation chemistry, in developing matrices based either on calcium-silicate chemistry or alkali-aluminosilicate chemistry, or a mixture of the two gel types, can provide advantages over purely calcium silicate-based systems, particularly if water removal (by moderate-temperature heat treatment) to prevent radiolytic hydrogen generation is desired. The high alkalinity of alkali-activated binder systems may be problematic in some circumstances, and there is a need to carefully control porosity and permeability to ensure long-term immobilisation performance, but alkali-activation chemistry may prove to be an important part of future radioactive waste cleanup efforts and/or as a component of a cleaner nuclear fuel cycle in coming decades.

12.6 Fibre Reinforcing

Fibre reinforcement is used in AAMs for the same reasons that it is used in OPC systems: to improve performance by raising the tensile strength and the fracture toughness, and enhancing the ductility and durability of the final product. The greater ductility attained reduces crack size and propagation during failure, and contributes to the volumetric control of the material, especially when exposed to different loads and high temperatures, reducing the harmful impact of creep and shrinkage.

Studies assessing the mechanical performance of alkali-activated composites reinforced with short fibres of silicon carbide [199], polypropylene [200–202], glass [203], carbon [204–209], basalt [210–212], PVA [213], wollastonite [214] and steel [215–217] have been published. In some cases, increased flexural strength and modulus of elasticity are exhibited by specimens reinforced with fibres, along with reduced autogenous/drying shrinkage and enhanced dimensional stability at room temperature.

The effect on drying shrinkage (at 50 % relative humidity) of adding polypropylene, glass or carbon fibres to alkali silicate-activated BFS mortar is shown in Fig. 12.10. According to these findings, polypropylene and alkali-resistant (AR) glass fibres can control shrinkage, giving a reduction of up to 35 %. This demonstrates that a variety of short fibres can be used to reinforce AAM matrices for dimensional control, as long as they remain stable at high pH. Sakulich [218] suggests that likely applications for this type of composites lie in large-scale infrastructure projects, as they display no anisotropic behaviour and can usually be prepared with standard mixers.

The effect of the type of alkali-activated matrix on the mechanical and durability properties of composite mortars reinforced with polypropylene fibres (between 0

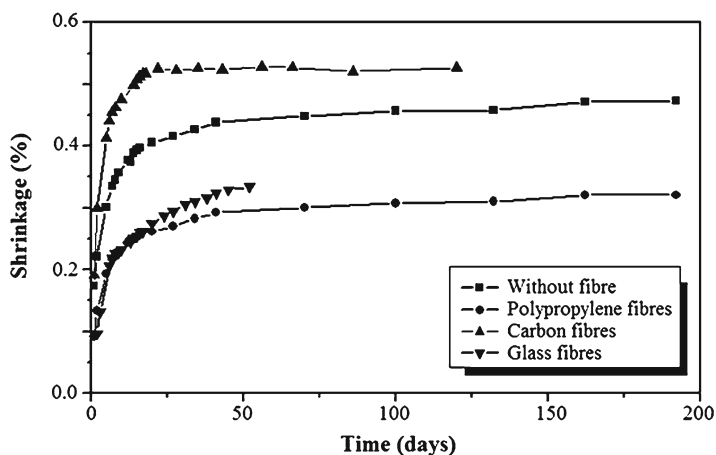


Fig. 12.10 Drying shrinkage of fibre-reinforced alkali-activated BFS mortars as a function of the type of fibre incorporated (Data courtesy of F. Puertas)

Table 12.3 Mechanical parameters of mortars with and without polypropylene fibres (1 % v/v) [200]

Binder	Fibres (%)	Flexural strength (MPa)	Elastic modulus (MPa)	Deflection (mm)
BFS	0	7.36	4,860	0.1277
	1	5.91	3,896	0.1361
Fly ash	0	5.79	4,441	0.1071
	1	4.79	3,660	0.1084
Fly ash/BFS	0	4.80	4,906	0.0852
	1	4.66	3,810	0.1068
OPC	0	7.76	5,679	0.1136
	1	7.61	6,137	0.1051

and 1 % by volume) has been studied by Puertas et al. [200] using three alkaline matrices: BFS activated with waterglass (4 g Na₂O/100 g BFS) cured at room temperature; a class F fly ash activated with 8M NaOH cured at 85 °C for 24 h; and a blend of 50 % fly ash and 50 % BFS activated with 8M NaOH cured at room temperature. Independent of the nature of the alkali-activated matrix, the inclusion and amount of fibre was the most predominant factor in the strength development of these composites. It can be seen (Table 12.3) that the flexural strength and elastic modulus values are slightly lower in fibre-reinforced composites, as a consequence of the reduced mechanical performance exhibited by these fibres when compared with the strength of alkali-activated mortars, and the reduced mortar workability identified with the inclusion of fibres. These results are coherent with those obtained by Zhang et al. [201] in silicate-activated fly ash/metakaolin blends reinforced with polypropylene fibres.

On the other hand, including glass fibres (at a proportion of 0.22 wt.% by binder mass) in alkali-activated BFS mortars enhanced flexural strength without modifying the compressive strength values [203]. While neither toughness nor impact resistance was modified by the fibre incorporation, the glass-fibre reinforced mortars perform well at high temperatures. This was attributed to the melting of anhydrous slag and fibres filling pores, which led to recovery of over 50 % of the initial mechanical strength. It is important to note that deterioration in the surface of the glass fibres is identified in these mortars (Fig. 12.11) due to the high pH environment.

Studies of the behaviour of AAMs reinforced with carbon fibres [204] and nanotubes [219] showed that neither improved the mechanical strength of the specimens tested. However, the inclusion of 1 % carbon fibre improved mortar corrosion resistance. The presence of carbon nanotubes was also observed to raise the geopolymer conductivity more than the presence of graphite. Bernal et al. [205] identified, using pre-treated (by removal of the polymeric coat) carbon fibres, improvements in flexural strength, elastic modulus and fracture toughness of AAS mortars with the incorporation of more fibres. The discrepancies between these results are mainly attributed to the different length and volume of fibre incorporated in each of the studies.

Thaumaturgo and colleagues [210, 214] investigated the fracture toughness of AAMs reinforced with basalt fibres and with wollastonite microfibres. Each study

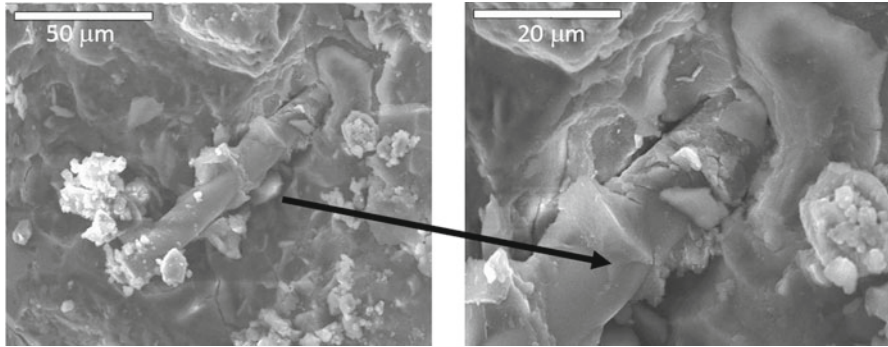


Fig. 12.11 Scanning electron micrographs of glass fibre-reinforced BFS mortars, showing deteriorated fibres [203]

identified a substantial increment in the splitting tensile and flexural strengths, along with an increased fracture toughness of the reinforced material. This is associated with the strong matrix-fibre bond identified in both systems.

The incorporation of high performance steel fibres in alkali-activated BFS concretes has a remarkable effect on the mechanical performance of these materials [215, 216]. Flexural strength and toughness are increased with the incorporation of higher contents of fibres in the concrete (Fig. 12.12). Pull-out results showed that the interfacial interaction between the AAS concretes and the steel fibre exhibited a very marginal slip-hardening response under uniaxial tensile loading. This is associated with a controlling mechanism after post-peak resistance typical of high-friction shear displacement, which is responsible for high toughness generation. These results are coherent with those reported by Penteado Dias and Thaumaturgo [210] and by Silva and Thaumaturgo [214], in reinforcing with basalt and wollastonite fibres. Steel fibre reinforced concretes also present reductions in water absorption, sorptivity and water penetration, which can contribute to the enhancement of the durability of these concretes.

The use of continuous fibre reinforcement in AAM matrices has been also evaluated. Lyon et al. [94] developed composites of a potassium aluminosilicate and potassium silicate-activated metakaolin with carbon fabric, He et al. [207, 208] used carbon fibre sheets, and Zhao et al. [217] used a stainless steel mesh. These studies highlight the importance of the fibre/matrix interface, which has occasionally been observed to be weak, as the factor controlling the composite strength and durability. The AAM systems reinforced with continuous fibres also report an improved bending strength, depending on the preparation method (usually vacuum-bagging in conjunction with heat treatment) and the type and proportion of the fibre used.

A comparative analysis of the perceived ‘green’ value of fibre-reinforced AAM composites, along with a review of the improved ductility reached by the materials, has been presented in detail by Sakulich [218], and Fig. 12.13 is

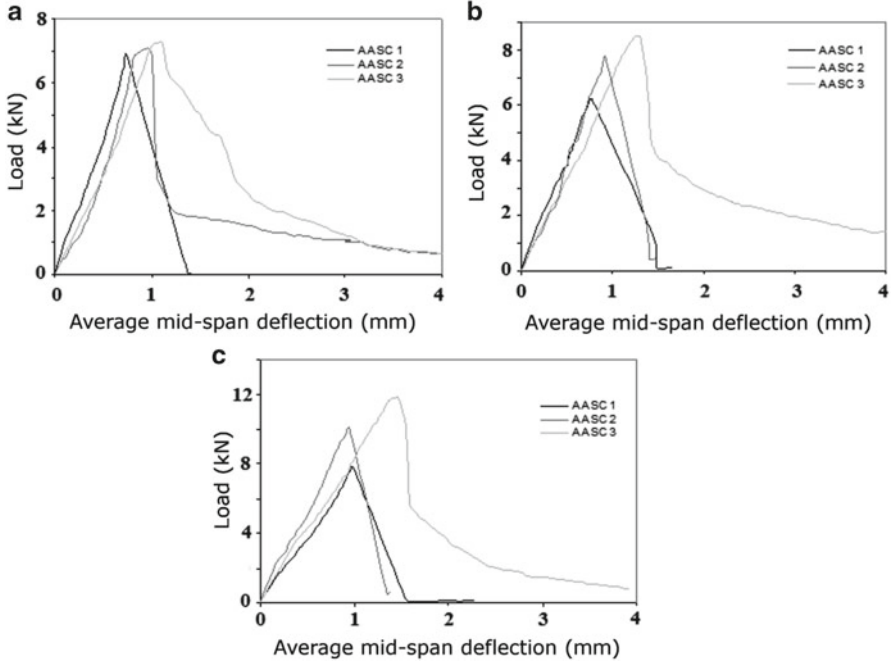


Fig. 12.12 Flexural load-deflection curves of alkali silicate-activated BFS concretes with 0 kg/m³ (AAS1), 400 kg/m³ (AAS2) and 1,200 kg/m³ (AAS3) of steel fibres, after curing for: (a) 7 days, (b) 14 days and (c) 28 days (Data from [215])

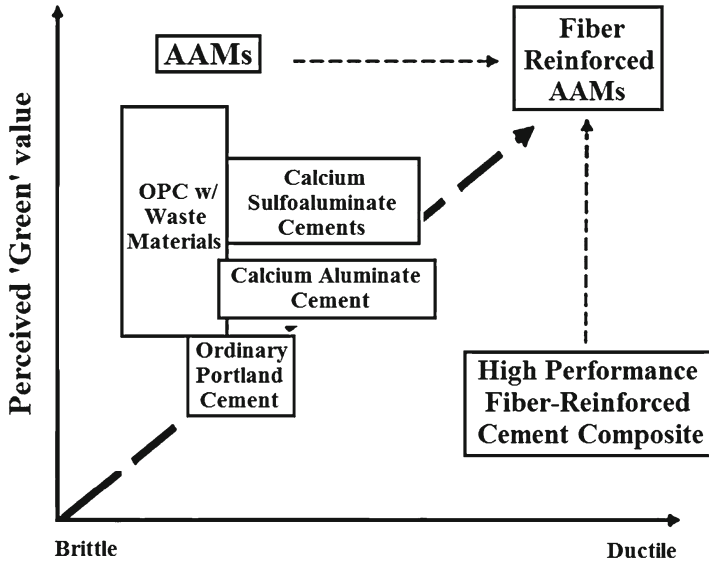


Fig. 12.13 Relationship between perceived 'Green' value and ductility of various binders and products (Adapted from [218])

adapted and somewhat simplified from that source. A 2D fabric-reinforced composite exhibits anisotropic mechanical properties and generally requires more advanced processing techniques, while AAM composites with randomly oriented and discontinuous fibres can be compared with high performance fibre-reinforced cement composites.

It has been identified that the inclusion of fibres makes a remarkable contribution to the performance of AAMs when used for high temperature applications. Composite materials based on AAM matrices have been produced for different applications such as fire resistance [94, 220, 221], refractories for the glass industry [222], thermal insulation [18, 81, 223], and other applications requiring good performance at high temperatures [7, 79]. According to Papakonstantinou et al. [224], several factors make AAM materials ideal matrices in fibre-reinforced systems for fire-proofing: (a) AAMs are stable at temperatures above 1,000 °C, and the incorporation of fibres in suitable proportions increases the volumetric stability, linked to reduced thermal contraction and promoting retention of mechanical strength; and (b) since AAMs are processed at temperatures near to ambient, a great variety of fibres can be used to produce the composites. This, coupled with the fire-resistance properties of the matrix, provides a potentially valuable application for these materials.

The promising mechanical and durability properties identified in fibre- or mesh-reinforced alkaline mortars and concretes make them suitable for a wide range of applications (construction, transport, aeronautics and others) in areas where their use can be introduced or consolidated. Further research efforts need to be addressed toward the use of AAMs as matrices for high performance fibre reinforced composites.

12.7 Conclusions

In addition to the civil infrastructure-related applications discussed in Chap. 11, there are a number of areas in which alkali-activation chemistry has been shown to provide the potential for utilisation in niche applications in various areas of civil and materials engineering. It is unlikely that any specific binder formulation will show all of these properties at once, but it is certainly possible to tailor alkali-activated materials for applications in lightweight materials production, as a well cement for underground utilisation, for high-temperature applications, as a stabilisation/solidification matrix for hazardous or radioactive wastes, and in conjunction with fibre reinforcing to enhance flexural, tensile and/or shrinkage properties. Although the total volume of material used in each of these applications is significantly lower than the volume of concrete applied worldwide as civil infrastructure construction material, the relatively higher value achievable in some of these applications can provide opportunities and avenues for commercial utilisation, or development and application by government or commercial organisations with specific requirements in waste treatment or remediation.

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Chapter 13

Conclusions and the Future of Alkali Activation Technology

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13.1 Summary of Outcomes from This Technical Committee

The key outcome of RILEM TC 224-AAM has been the development of a conceptual framework from which the discussion of standardisation of alkali-activated binders and concretes can proceed. There has been agreement from the members of the TC that a performance-based approach to both materials formulation (as described in Chap. 7 of this report) and testing (as outlined in Chaps. 8, 9, and 10) is essential in enabling the scale-up of alkali-activation as a method of concrete production in the global context. However, it is essential to proceed with a degree of conservatism, to avoid becoming ‘the next high-alumina cement problem’ through use of a material in environments and/or systems where it is not fit for purpose. So, it is critical that standards development is conservative to ensure that due care is taken, and to make sure that poor-quality AAM products, and/or products used in unsuitable applications, do not ruin the global reputation of the technology. A key discussion which occupied much of the time of the TC was the issue of how to achieve this – and the conclusion

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reached was that the use of strict performance criteria (and maybe even criteria which seem excessively strict until a higher degree of certainty regarding performance levels can be reached), and with good scientific foundations, must underpin any testing method applied to these materials.

The increasing focus on global climate change, the public and consumer preferences for “green” products, and the associated markets in carbon credits, have made a strong case for the use of alternative cements in place of pure Portland cement binders, and it is increasingly recognised that there are limits to the industry-wide CO₂ emissions savings which can be obtained through the use of blended Portland cements in isolation from other types of binder chemistry. These alternative binding systems can provide a viable direct opportunity for near term and substantial CO₂ emissions reduction. There are a variety of binder systems available that deliver the potential for high performance and/or environmental savings, and thus also potential profits for market participants, while representing a significant departure from the traditional chemistry of OPC. However, alternative cements have generally been constrained from full scale application by key gaps in one or more of the following areas: (a) validated long term durability data; (b) appropriate regulatory standards (and accompanying awareness from regulatory authorities regarding the state of technological maturity of AAMs); (c) industrial and commercial experience in materials design, production, quality control and placement; (d) raw materials supply chain.

Alkali activated materials do face such hurdles, but have a much longer in-service track record than many of the competing technologies (Chaps. 11 and 12), and are made using predominantly high-volume, widely available industrial wastes. Glassy aluminosilicate wastes such as fly ash and blast furnace slag appear the most promising precursors for large-scale industrial production of AAMs. It is also possible to use volcanic ash, natural pozzolans and calcined clays as source materials, but cost and supply chain constraints present challenges at an industrial scale.

There is a close link between R&D and commercial development in the field of AAMs, where cutting-edge scientific research, in parallel with engineering-focused development, remains critical in both enhancing and validating the performance of AAM concretes. Fundamental understanding of mix design procedures, rheology, reaction mechanisms, gel chemistry and binder microstructure must be used to feed information into the practical advancement of the workability, engineering and durability properties of these materials. However, it is also important to note that it simply conducting the R&D, and publishing the outcomes in scientific journals and conferences, is not sufficient to drive commercial uptake. Pioneering research needs to be supported by pioneering behaviour in driving uptake of new materials, and sometimes this means challenging the accepted practices, norms and protocols in the process of introducing changes which can lead to improved outcomes in terms of global sustainability.

A brief overview of the key outcomes as presented in this report is presented in the following sections.

13.1.1 Reaction Mechanisms of Gel Formation

- Much progress has been made to understand the mechanisms of AAM gel formation from both low-calcium and high-calcium sources. The gel chemistry (and in particular whether the gel is based on a silicate chain or network structure) depends very significantly on the available calcium content of the precursor(s). The use of advanced analytical techniques such as nuclear magnetic resonance spectroscopy, as well as synchrotron-based analysis of gel nanostructures, has led to some very significant recent advances in the understanding of phase chemistry in AAM systems.
- Many different source materials are available for use in AAM production. Although variability of waste sources remains a problem, much progress has been made in linking reactivity to raw material characteristics.
- AAM concrete can be more porous than OPC concrete, and despite progress in understanding the gel nanostructure, more insight is required to understand the role of water in determining both nanostructure and microstructure in these binders. Further detailed microstructural analysis using microscopic and tomographic techniques, in parallel with porosimetry and permeability testing, will be essential in resolving some of these open questions.

13.1.2 Durability

- AAM concretes have been observed to perform well in service in a range of applications, from civil construction and infrastructure to niche applications such as waste immobilisation.
- AAMs can show drying problems if exposed to low humidity at early age as the gel does not strongly bind water of hydration, so curing is an important challenge. In practice, drying conditions during placement and in the early stages of curing may lead to shrinkage and surface micro-cracking.
- Rigorous drying, as required by many durability testing procedures, is known to be challenging with regard to the stability of AAM gels, which may influence the outcomes of the tests.
- AAMs seem to show good chloride resistance, acid resistance, fire resistance, leaching resistance and sulfate resistance; under exposure to MgSO_4 in some 'sulfate exposure' tests, it is the Mg^{2+} rather than the SO_4^{2-} that has been identified as the cause of the lower than anticipated results.
- AAMs show limited carbonation resistance in conventional laboratory tests; this contrasts field performance, which does not seem to show major problems. Some steps towards elucidating the reasons for this discrepancy are beginning to become evident.
- Corrosion of steel in AAM concrete is not understood, so it cannot be predicted just based on alkalinity; this is an important field that requires research.

13.1.3 Practical Technical and Design Considerations

- Although there have been many published (and unpublished) studies of the engineering properties of AAM, there remains a lack of generalisable insight into the behaviour of AAM over the long term, particularly in the area of creep. The sensitivity of creep performance to environmental conditions is not understood, and acts as a barrier to wider structural applications.
- In view of the differences in chemistry between OPC and AAM, standard water-reducing plasticisers, and other organic admixtures, do not in general work effectively in alkali-activated systems. So, new admixtures need to be developed. For this to happen, a detailed new understanding of surface chemical phenomena in AAM systems is required.

13.2 The Future of Alkali Activation

The commercial future of alkali activated materials, similar to the case of many other alternative binders for concretes, depends not only on technical readiness, but also on the economic and social readiness. Standardisation is an important component of commercialisation, but in fact (and contrary to the assumptions of many researchers) represents only a small part of the whole commercialisation process.

Figure 13.1 provides a schematic illustration of some of the key components of the process of commercialising AAM concretes on a full industrial production scale.

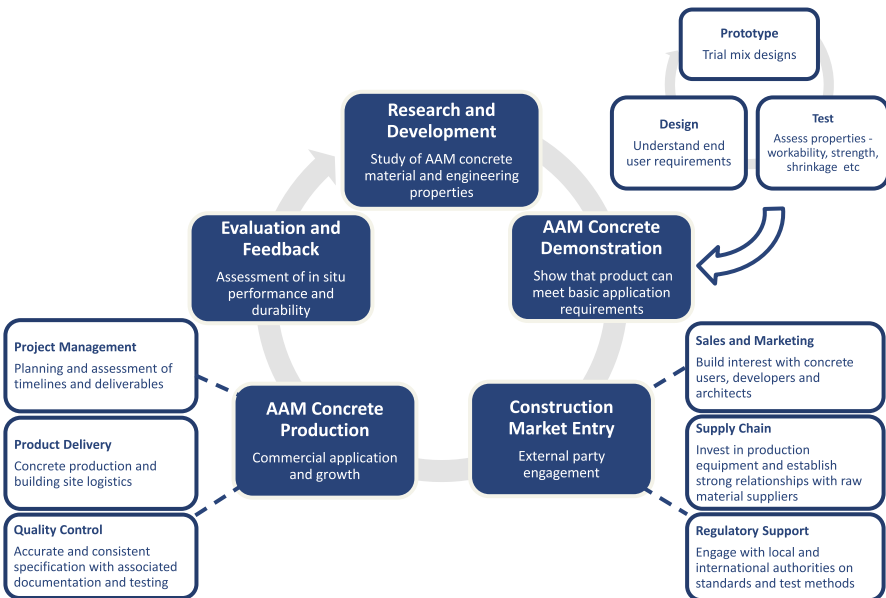


Fig. 13.1 Illustration of the key steps in the commercialisation of AAM concretes

Pre-commercial, independent accredited testing has proven critical in demonstration of product performance to the market. For non-structural concrete, this assessment will typically include analysis of density, air content, slump, setting time, compressive strength (early and ultimate), and shrinkage. Additionally, for higher strength and structural grade concretes, further required tests may include flexural and/or tensile strength, acid or chemical resistance, fire resistance, permeability, carbonation rate, water sorptivity, creep, and protection of embedded reinforcing steel. Knowledge gained from this testing is continuously fed back into the industrial product development cycle, as well as stimulating further research (basic and/or applied).

The preference of many customers is to make their first use of AAM concretes in lower-risk applications; particularly, projects which have flexible timelines, are readily accessible, and where the consequences of a material falling short of defined performance targets are limited. Progression to the use of a new material in higher-risk applications then requires the engagement of regulatory authorities, engineers and specifiers. These parties typically prefer to take a step-wise approach towards the development of standards and commercial adoption.

The main challenges faced in the scale-up and commercialisation of alkali activated materials have been identified as:

- **Sourcing raw materials:** both quantity (e.g. stable volume supplies) and the quality (most critically, consistency of quality). Not only the base aluminosilicate materials, but also the alkali activators, need to be able to be sourced via a stable and dependable supply chain for a relatively long-time span, to provide a return on the investment required to establish a production facility. In OPC production, it is considered necessary to have ca. 50 years of raw material reserves. The question is: how can something similar be achieved for AAM precursors, given the fact that the materials are mainly wastes or by-products? Alternatively, a producer must be technically ready to receive raw materials from various sources and use them accordingly; an approach which has successfully been used in Ukraine for several decades has been instructed and guided by a well-developed set of standard specifications. In some large markets such as India and China, the utilisation of coal combustion wastes and metallurgical slags will actually provide a driver for uptake of alkali activation, although this is less likely in Europe where these wastes are in demand for blending with Portland cement.
- **The costs:** alkali activated materials could become very economically attractive if CO₂ taxation, or other pollution-related financial charges, are implemented in an effective (global and/or regional) manner, and thus become a serious issue for the building materials industry. The raw materials costs, including slag, fly ash, other natural aluminosilicates and alkali activators, may then be lower than those of OPC clinker if CO₂ taxation is imposed on top of the conventional OPC production cost. The change from coal-fired power generation to co-firing or biomass fuels will certainly influence the properties of the ashes that are available, and this needs to be considered in cost assessments. Additionally, the process of producing AAMs should be considered: whether a greenfield facility must be established, or an existing OPC manufacturing site adapted, depends on

the nature of the local market and industry. Potential future limits on limestone quarrying in some jurisdictions could also influence the cost of OPC manufacture, which may lead to an advantage for alternatives to OPC in certain local markets.

- **Quality control (QC) and quality assurance (QA):** these are the most crucial and challenging steps during cement and concrete productions. As most of the operations personnel in a cement or concrete manufacturing facility are accustomed to following certain procedures for QC and QA during OPC production, it will be an important educational step to change mindsets regarding management of the consistent quality and uniformity of incoming raw materials and output products. Although this is not necessarily more complicated than the steps required for Portland cement QC and QA, technical operators must understand the strong dependence of product quality on the entire production processes, as there is no clinkerisation process as the “gate-keeper” of product quality.
- **Long term performance:** acceptance of the accelerated testing methods and data evaluation are key issues when performance based standards are to be established. Most of the accelerated methods to assess durability are mainly designed for OPC based materials, with implicit assumptions regarding binder and pore solution chemistry, and are not always suitable for alternative materials such as AAM. Scientists and researchers need to propose reasonable and meaningful modifications to these accelerated testing methods – and a key recommendation of TC 224-AAM is that there is an urgent need to establish another RILEM TC to work in this area; in response to this need, TC 247-DTA has been established in 2012. Another frequently asked question is the field evidence – structures which are exposed to the real environment and elements produced in large scale – demonstrating material performance during production and service. The discussions given in Chaps. 2 and 11 of this report present the best available evidence for long-term serviceability of alkali-activated binder systems, showing that these materials are in fact capable of long-term durability, but it is also obvious that much more work is needed as part of the process of proving AAM durability under specific local conditions (precursor availability and climatic exposure) to provide a fully satisfactory body of evidence. This can only take place through the process of end-users actually putting the materials into service in different parts of the world. There is often a conflict between the desire to innovate and develop a large scale project built with new materials, and the need for prior certification for new materials to realise a large scale project. In some jurisdictions (e.g. Japan, Austria), governments or authorities can provide special permits enabling practitioners to demonstrate long term behaviour of materials. However, in many other areas, this is a very challenging step.
- **Standardisation:** In many markets, without the existence of specific standards and certification, new cement or concrete products may face great obstacles to market entry, as discussed in Chap. 7. To draft a new cement standard is not an easy process, as final consensus must be reached by the majority of the stakeholders who are participating in the standardisation committee. These stakeholders include industrial manufacturers, trade associations (industry), professional

institutions, government, consumer bodies, academia, education bodies, customers, and certification bodies. These various groups are interested not only in the use of standards to guarantee the quality and performance of their products or services, and to increase the safety of products and foster the protection of environment and health, but also to improve the competitiveness of their business through ensuring that their own systems comply with all legal obligations. As soon as a business advantage can be delivered by the suppliers to the customers, technical barriers to achieving final consensus will be readily removed. Thus, it is essential that the participants in this process are able to see the potential commercial (as well as environmental) benefits of AAM technology.

- **Acceptance from the customers:** To win the acceptance of customers, sufficient convincing facts comparing an alternative material to OPC must be presented. These facts can either be opportunities or threats, such as economic benefits, better performance (e.g. strength, durability), or environmental competitiveness (e.g. green labelling, LEED credits). Education efforts can be focused on local councils, government authorities, corporations, project developers and architects, to highlight CO₂ emissions benefits and alleviate concerns or potential misconceptions held by the market stakeholders. Successful product education builds confidence in product performance, and in turn, creates project and technology advocates who further raise awareness within the specifier/user community. It is increasingly seen in the market that an additional “green advantage” for the end user can be the key element in achieving product differentiation. This is probably the key question that must be asked: is the social readiness in place? Are we putting environmental concerns (e.g. greenhouse gas emissions) over the economical benefit? In this process, ‘greenwashing’ of certain products is currently very prevalent, and the scientific basis upon which many life cycle analysis studies are based is rather sketchy. A more rigorous approach to environmental assessment must be applied if claims of sustainability are to be justified, including careful assessment of the currency and accuracy of the data used as inputs into life-cycle studies.

13.3 Conclusions

Increasing efforts have been committed by leading practitioners from both academia and industry, to demonstrate the suitability of using AAMs in various concrete applications, and to validate the long-term performance of AAM concretes. Customers in different market areas are becoming more and more aware of technical progress in the development of non-Portland binder systems, and AAMs are a class of materials which are ideally positioned to take advantage of this awareness. Although there are still great challenges facing AAM producers, concerted commercialisation efforts in parallel with ground-breaking research will be the only path forward to reach the final goal of large-scale deployment of this technology. Fundamental research should be targeted at improvement of the application and

performance properties of AAM, including development of chemical admixtures and analysis of durability, and remains pivotal to ongoing technical and commercial progress.

Summarising the preceding discussion in a very general sense, to enable large-scale deployment of alkali-activated binders in concrete production, the following are required:

- (a) broad scale, field experience in non-structural applications;
- (b) advanced trial experience in structural applications;
- (c) international engagement on performance standards, and
- (d) quality research focused on analysis and prediction of long term in-service performance.

These issues are by no means limited to the area of AAMs – these points are relevant across many areas of non-traditional cement and concrete development and commercialisation – but they have been identified by this TC as being essential for AAM development in particular, and thus represent the key conclusions of this State of the Art Report.