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:

J.L. Provis (✉)
Department of Materials Science and Engineering,
University of Sheffield, Sheffield S1 3JD, UK

Department of Chemical and Biomolecular Engineering,
University of Melbourne, Melbourne, VIC 3010, Australia
e-mail: j.provis@sheffield.ac.uk

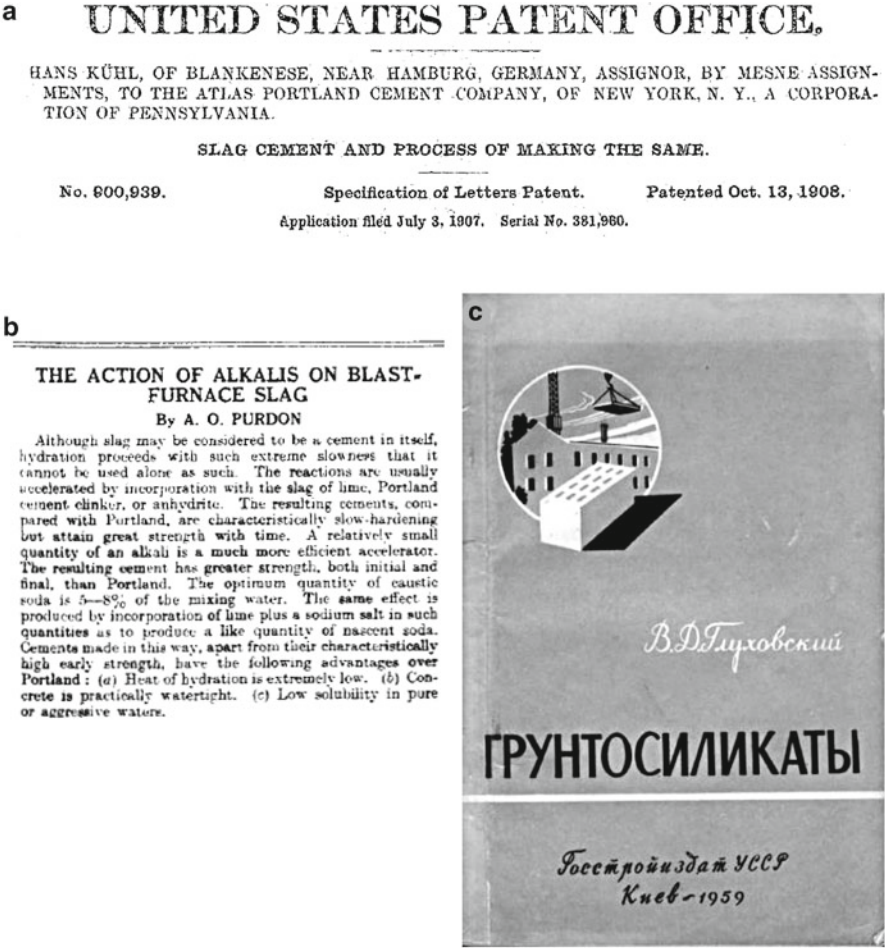
J.L. Provis and J.S.J. van Deventer (eds.), *Alkali Activated Materials: State-of-the-Art Report, RILEM TC 224-AAM*, RILEM State-of-the-Art Reports 13,
DOI 10.1007/978-94-007-7672-2_1,

  - 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.



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. 900,939. Specification of Letters Patent. Patented Oct. 13, 1908.

Application filed July 3, 1907. Serial No. 381,960.

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.

В.Д.Глуховский

ГРУНТОСИЛИКАТЫ

Госстройиздат УССР
Киев–1959

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	$M_2O{\cdot}rSiO_2$	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	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 $M_2O \cdot r\ SiO_2$ 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 $CaO-Al_2O_3-SiO_2-M_2O-Fe_2O_3-SO_3-H_2O$ (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.

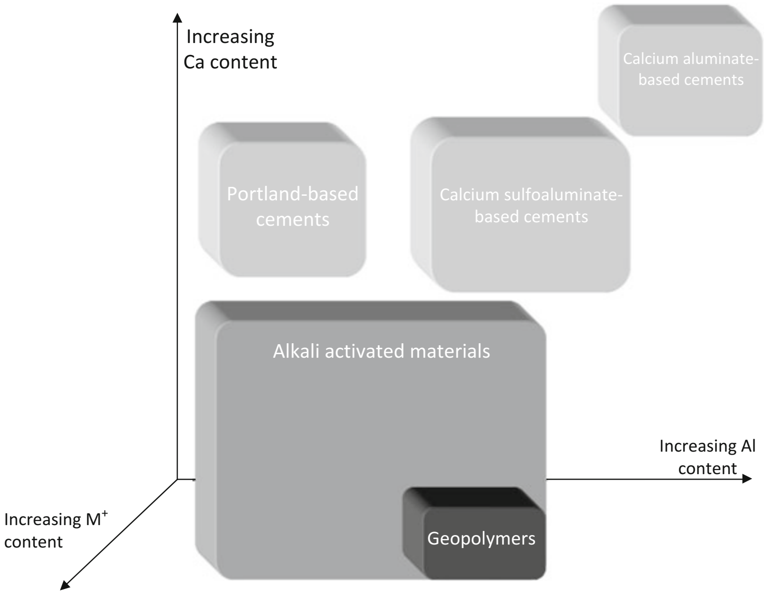


Fig. 1.2 Classification of AAMs, with comparisons to OPC and calcium sulfoaluminate binder chemistry. *Shading* indicates approximate alkali content; *darker shading* corresponds to higher concentrations of Na and/or K (Diagram courtesy of I. Beleña)

References

1. Kühl, H.: Slag cement and process of making the same. US Patent 900,939 (1908)
2. Purdon, A.O.: The action of alkalis on blast-furnace slag. J. Soc. Chem. Ind. Trans. Commun. **59**, 191–202 (1940)
3. Purdon, A.O.: Improvements in processes of manufacturing cement, mortars and concretes. British Patent GB427,227 (1935)
4. Wang, S.-D., Pu, X.-C., Scrivener, K.L., Pratt, P.L.: Alkali-activated slag cement and concrete: a review of properties and problems. Adv. Cem. Res. **7**(27), 93–102 (1995)
5. Glukhovsky, V.D.: Gruntosilikaty (Soil Silicates). Gosstroyizdat, Kiev (1959)
6. Roy, D.: Alkali-activated cements – opportunities and challenges. Cem. Concr. Res. **29**(2), 249–254 (1999)
7. Davidovits, J.: Mineral polymers and methods of making them. US Patent 4,349,386 (1982)
8. Davidovits, J.: Geopolymer Chemistry and Applications. Institut Géopolymère, Saint-Quentin (2008)
9. Malone, P.G., Randall, C.J., Kirkpatrick, T.: Potential applications of alkali-activated aluminosilicate binders in military operations. Geotechnical Laboratory, Department of the Army, GL-85-15 (1985)
10. van Deventer, J.S.J., Provis, J.L., Duxson, P., Brice, D.G.: Chemical research and climate change as drivers in the commercial adoption of alkali activated materials. Waste Biomass Valoriz **1**(1), 145–155 (2010)
11. Buchwald, A., Kaps, C., Hohmann, M.: Alkali-activated binders and pozzolan cement binders – complete binder reaction or two sides of the same story? In: Proceedings of the 11th International Conference on the Chemistry of Cement, Durban, South Africa, pp. 1238–1246 (2003)

12. Shi, C., Krivenko, P.V., Roy, D.M.: Alkali-Activated Cements and Concretes. Taylor & Francis, Abingdon (2006)
13. Wagh, A.S.: Chemically Bonded Phosphate Ceramics. Elsevier, Oxford (2004)
14. Wagh, A.S.: Chemically bonded phosphate ceramics – a novel class of geopolymers. Ceram. Trans. **165**, 107–118 (2005)
15. Cross, D., Stephens, J., Vollmer, J.: Structural applications of 100 percent fly ash concrete. In: World of Coal Ash 2005, Lexington, KY. Paper 131 (2005)
16. Taylor, R., Richardson, I.G., Brydson, R.M.D.: Composition and microstructure of 20-year-old ordinary Portland cement-ground granulated blast-furnace slag blends containing 0 to 100 % slag. Cem. Concr. Res. **40**(7), 971–983 (2010)
17. Davidovits, J.: Geopolymers – inorganic polymeric new materials. J. Therm. Anal. **37**(8), 1633–1656 (1991)
18. Duxson, P., Provis, J.L., Lukey, G.C., Separovic, F., van Deventer, J.S.J.: ^{29}Si NMR study of structural ordering in aluminosilicate geopolymer gels. Langmuir **21**(7), 3028–3036 (2005)
19. Rahier, H., Simons, W., Van Mele, B., Biesemans, M.: Low-temperature synthesized aluminosilicate glasses. 3. Influence of the composition of the silicate solution on production, structure and properties. J. Mater. Sci. **32**(9), 2237–2247 (1997)
20. Provis, J.L., Lukey, G.C., van Deventer, J.S.J.: Do geopolymers actually contain nanocrystalline zeolites? – A reexamination of existing results. Chem. Mater. **17**(12), 3075–3085 (2005)
21. Provis, J.L.: Activating solution chemistry for geopolymers. In: Provis, J.L., van Deventer, J.S.J. (eds.) Geopolymers: Structure, Processing, Properties and Industrial Applications, pp. 50–71. Woodhead, Cambridge (2009)
22. Duxson, P., Fernández-Jiménez, A., Provis, J.L., Lukey, G.C., Palomo, A., van Deventer, J.S.J.: Geopolymer technology: the current state of the art. J. Mater. Sci. **42**(9), 2917–2933 (2007)