

RILEM State-of-the-Art Reports

Nele De Belie
Marios Soutsos
Elke Gruyaert *Editors*

Properties of Fresh and Hardened Concrete Containing Supplementary Cementitious Materials

State-of-the-Art Report of the RILEM
Technical Committee 238-SCM, Working Group 4



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RILEM State-of-the-Art Reports

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Preface

Supplementary cementitious materials (SCMs) are commonly used in concrete practice nowadays, either in blended cements or as separate additions into the concrete mixture. The use of hydraulic and pozzolanic by-products allows to reduce the carbon dioxide emissions related to Portland clinker production and hence provides a way to obtain a more sustainable binder for the construction industry. Furthermore, the use of by-products entails benefits related to costs and some durability aspects. In general, the effects of these supplementary cementitious materials on microstructure and durability have been widely studied over the last decades. Nevertheless, several aspects have been denoted to merit further attention:

- The interaction between Portland clinker hydration and SCM reaction is not yet fully understood. Determination of reaction degrees of SCM is difficult; this is even more so if ternary mixes are concerned.
- The interaction between SCM and commonly used admixtures is often not well documented.
- The quality of by-products such as fly ash is changing due to, for instance, co-combustion in the electrical power plants. The effect of changing composition on the clinker and SCM reactions, and on the resulting microstructure, should be elucidated.
- The ongoing move from Portland to blended cements, and the replacement of Portland cement by SCM in the mix design, will affect construction practices. The exact composition of blended cements, which is often unknown, will affect early age strength development. For the construction industry, it is important to know how the variability of SCM affects the properties of their concrete and curing requirements.

Hence, in July 2011, the RILEM technical committee TC 238-SCM was established with the aim to support the increasing utilisation of hydraulic and pozzolanic industrial by-products, natural resources and societal waste (fly ash, blast-furnace slag and other by-products and residues of thermal industrial processes, calcined clays, limestone, natural pozzolans, natural zeolites, ...) to obtain more sustainable, less CO₂-intensive binders for the construction industry. It was decided that

durability issues would not be a main focus of this TC. The TC was meant to serve as a knowledge platform where fundamental science and practical expertise are gathered to create a horizontal overview of the research area and to implement and promote the dissemination of more integrated generic approaches into the scientific community.

In one of their first meetings, TC 238-SCM defined a Supplementary Cementitious Material or SCM as “*an inorganic material that, when used in conjunction with Portland cement, contributes to the properties of the hardened concrete through chemical reaction e.g. hydraulic or pozzolanic activity*”.

The following subtopics were identified and studied in four different working groups with specific scope:

1. *SCM characterisation* (chairs: Maria Juenger, Jan Elsen)
Quantitative characterisation of the physico-chemical properties of a wide range of traditional and potential SCMs. Identifying challenges on an expanding and evolving SCM market.
2. *SCM reaction kinetics* (chairs: Karen Scrivener, Nele De Belie)
SCM reactivity and overall reaction kinetics in blended cements. Determination of reaction degrees of SCM, also in ternary mixes. Interaction between Portland clinker hydration and SCM reaction.
3. *Hydration product assemblage and microstructure of SCM-blended cements* (chairs: Barbara Lothenbach, Ruben Snellings)
Hydrate reaction product assemblages and pore solution composition in SCM-blended cements, binary and ternary mixtures. Optimisation of sulphate additions. Effect of temperature and clinker replacement proportion. Effect of SCM incorporation on the microstructure. Linking microstructure to performance.
4. *Properties of concrete containing SCMs and interaction of SCMs and admixtures in concrete* (chairs: Marios Soutsos, Guang Ye)
Effect of SCMs and mix proportioning on the properties of fresh and hardened concrete (e.g. early strength development, workability, shrinkage) and curing requirements (especially for in situ cast concrete in adverse weather conditions). Post-blending versus pre-blending. Implications of SCM variability. Interaction between SCM and commonly used admixtures (e.g. superplasticizers, air entrainers).

Over the period 2011–2017, the TC 238-SCM has convened 12 times and has published the outcome of their collaborative research and discussions in various articles, which are mentioned below for further reading. This book is the final outcome of working group 4 of the TC and provides an overview of the state of the art regarding the properties of fresh and hardened concrete containing supplementary cementitious materials. Each chapter was a joint effort of different co-authors and was reviewed by at least two other TC members.

Details of TC members are given after this Preface. I wish to acknowledge their contribution to meetings and discussions, their efforts in writing, reading and commenting on the various drafts of this book and of the other publications mentioned further. Special thanks go to the chairs of the working groups, which have given tremendous assistance to organise the activities within their group. Finally, I want to acknowledge my co-editors, Prof. Marios Soutsos and Dr. Elke Gruyaert, for ensuring that this STAR could be realised within the lifetime of the TC.

Ghent, Belgium

Prof. Nele De Belie
Chair of RILEM Technical Committee TC 238-SCM

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- Chapter 2. Fly Ash : Wolfgang Brameshuber, John Provis
- Chapter 3. Silica Fume : Doug Hooton, Harald Justnes
- Chapter 4. Limestone Powder : John Provis, Nele De Belie
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TC 238-SCM Publication List

WG1: Characterisation of SCMs

Juenger, M., Provis, J., Elsen, J., Matthes, W., Hooton, D., Duchesne, J., Courard, L., He, H., Michel, F., Snellings, R., De Belie, N. (2012). Supplementary Cementitious Materials for Concrete: Characterization Needs. International symposium on concrete with smart additives and supplementary cementitious materials, IMRC, 12–17 August 2012, Cancun, Mexico. Abstract on CD of abstracts. Full paper in MRS Online Proceedings Library—January 2012—VOLUME 1488 p imrc12-1488-7b-026.

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WG2: SCM reaction kinetics

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WG3: Hydration product assemblage and microstructure

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WG4: SCMs in concrete

Vollpracht, A., Soutsos, M., Kanavaris, A. Strength development of GGBS and fly ash concretes and applicability of fib model code's maturity function – a critical review. *Construction and Building Materials*, submitted.

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Introduction

Supplementary cementitious materials (SCMs) have become a common ingredient of the concrete mix design nowadays. Many studies have focused on the effects of SCMs on reaction kinetics, microstructure and concrete properties. This state-of-the-art book aims to focus particularly on the properties of concrete containing supplementary cementitious materials, in the fresh and hardened state.

The SCMs identified include the most commonly used ones, like ground granulated blast-furnace slag, fly ash and silica fume, but also others that may not have attracted as much attention but nonetheless show promise for use in concrete. Dedicated chapters for each SCM were considered necessary, and thus, the chapters are as follows:

- Chapter 1. Ground Granulated Blast-furnace Slag
- Chapter 2. Fly Ash
- Chapter 3. Silica Fume
- Chapter 4. Limestone Powder
- Chapter 5. Metakaolin
- Chapter 6. Natural Pozzolans
- Chapter 7. Alternative Supplementary Cementitious Materials
- Chapter 8. Rice Husk Ash
- Chapter 9. Ternary Blends

The following points have been in general addressed:

- Overview/production of SCMs, pre- and post-blending, uses in concrete (historical perspective),
- Relevant standards,
- Health and safety issues,
- Environmental sustainability,
- Fresh properties, workability, water demand, rheology, bleeding, etc.,
- Chemical admixture interaction,
- Setting times, plastic settlement, (chemical) shrinkage, curing,
- Early age strength development,

- Heat of hydration, rate of reaction (influence of temperature and curing, maturity functions),
- Compressive strength,
- Tensile strength,
- Flexural strength,
- Modulus of elasticity,
- Fatigue,
- Transport properties.

We hope this book will contribute to a better understanding of the effects of SCMs on concrete properties, and that it will stimulate appropriate use of these valuable materials.

Nele De Belie
Marios Soutsos
Elke Gruyaert

Chapter 1

Ground Granulated Blast-Furnace Slag

Winnie Matthes, Anya Vollpracht, Yury Villagrán,
Siham Kamali-Bernard, Doug Hooton, Elke Gruyaert,
Marios Soutsos and Nele De Belie

Abstract Since the discovery of the latent hydraulic reactivity of ground granulated blast-furnace slag (ggbfs) by Emil Langen at the end of the 19th century, this material has been used successfully as cement and concrete addition. This chapter includes all relevant information about this valuable material—from production and processing to the effect, which ggbfs additions have on the concrete performance. In this context, light is shed on decisive performance parameters of ggbfs. Of special interest nowadays is certainly also the information given about trace element contents in ggbfs and their leachability. Here and throughout the entire chapter, the latest insights from research and development work are included. Last but not least, the chapter contains very practical information when it comes to the use of ggbfs in concrete, including insights on rheological effects, concrete color and “greening”, and adequate curing. Moreover, an overview about relevant norms and standards on ggbfs as concrete addition is given.

Keywords Carbonation · Chloride ingress · Concrete · Granulated blast-furnace slag · Ggbfs · Permeability · Slag cement · Strength · Workability

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1.1 Blast-Furnace Slag—An Overview

1.1.1 History of Blast-Furnace Slag

The latent hydraulic reactivity of granulated blast-furnace slag (gbfs) was discovered in 1862 by Emil Langen in Germany (Lea 1971; Smolczyk 1978). The first use of slags in cements dates back to 1865, when in Germany a slag-lime cement was commercially produced. By 1901 the manufacture of “Eisenportlandzement” containing maximum 30% of ground granulated blast-furnace slag (ggbfs) became accepted and in 1907, the first “Hochofenzement” with up to 85% ggbfs content was produced (Moranville-Regourd 1998; Smolczyk 1978). Ever since, ggbfs has been successfully used in cementitious applications.

1.1.2 Production and Use of Blast-Furnace Slag

Blast-furnace slag (bfs) is a by-product in the manufacture of pig iron in the blast furnace. It forms by fusion of the gangue, i.e. non-ferrous material of the iron ore, mainly silica and alumina compounds, with calcium and magnesium oxides of the thermally decomposed carbonatic flux and combustion residues of the coke. These reactions take place at temperatures between 1300 and 1600 °C. The slag floats on top of the liquid iron and is tapped at regular intervals. When leaving the blast furnace, the molten bfs has a temperature of around 1450 °C and is cooled down, either slowly in contact with air in open pits or rapidly through pelletization or granulation. The latter is the state-of-the-art solution. It involves the rapid quenching

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and mechanical dissemination of the molten slag with water jets. Also dry slag granulation techniques exist, which however never succeeded at large scale. In the context of energy recovery from molten slag, main granulation equipment suppliers have recently revived the development of dry granulation techniques.

Air cooled slag is essentially crystalline and hardly reactive. After crushing and sieving it is typically used as back-fill material in road construction or as aggregate in concrete manufacture.

Gbfs has a maximum particle size around 5 mm and is predominantly vitreous. This high glass content is the prerequisite for the latent hydraulic reactivity of gbfs, which makes it an excellent supplementary cementitious material (SCM) for the production of composite cements as a clinker substitute and for concrete manufacture as a cement substitute.

In order to produce a suitable SCM the gbfs must be ground to a specific fineness, which influences the hydraulic reactivity of the gbfs.

Per ton of iron produced, between 0.2 and 0.5 t of bfs are obtained. The exact amount depends on the composition of the iron ore and on efficiency and size of the blast furnace. In state-of-the-art blast furnaces, the amount of bfs/ton of iron does not exceed 0.3 t.

The worldwide production of bfs is estimated at ~ 360 million t/a (Reynolds 2009). About half of it is being granulated and used in cementitious applications as SCM, taking advantage of the latent hydraulic reactivity, which allows for maximum replacement levels of clinker in cement production and of cement in concrete manufacture.

1.1.3 Composition and Reactivity of Gbfs

The main constituents of bfs are lime-silica-alumina and magnesia compounds. Figure 1.1 shows the position of bfs in the ternary diagram $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ including the stability fields of the respective minerals. Gbfs typically contains minor amounts of crystals, normally melilite [solid solutions from Gehlenite $\text{Ca}_2\text{Al}(\text{AlSi})\text{O}_7$ to Akermanite $\text{Ca}_2\text{MgSi}_2\text{O}_7$]. In basic slags with a CaO/SiO_2 ratio >1 , also merwinite $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$ occurs.

The chemical composition of bfs depends on quality, type and proportioning of the burden, i.e. iron ore, coke and flux, and the fuels used in the blast furnace. Thus, the composition of slags from different regions varies within certain limits (Table 1.1, Matthes 2012). This is especially important to consider when importing gbfs or ggbfs from other parts of the world. However, bfs originating from the same blast furnace exhibits a rather constant composition, because priority for blast furnace operation is a constant quality of the pig iron.

The hydration of ggbfs in Portland-composite cements was extensively discussed by Taylor (1997). In presence of water ggbfs hydrates to a limited degree. A protecting film deficient in calcium is quickly formed, which slows down further reaction. If the pH is kept sufficiently high in presence of activators, the ggbfs hydration is accelerated and intensified. The most common activator of ggbfs is Portland cement clinker, but

Fig. 1.1 Composition of bfs in the ternary diagram CaO-SiO₂-Al₂O₃ with 10% MgO, redrafted after Satarin (1974)

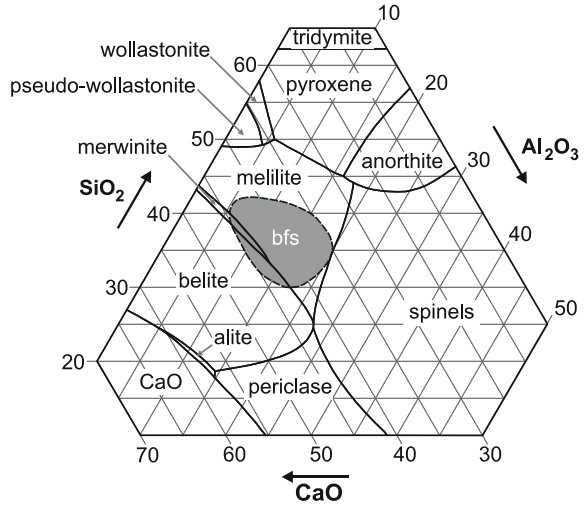


Table 1.1 Typical ranges of selected properties of granulated blast-furnace slags produced worldwide and in specific regions, including chemical composition, glass content, and bulk density (Matthes 2012)

| Parameter | Unit | Min | Max | North America | Central and South America | Western Europe | Eastern Europe | India, Japan, Australia, RSA |
|---------------------------------|------|-----|-----|---------------|---------------------------|----------------|----------------|------------------------------|
| SiO ₂ | % | 32 | 42 | 34.6–39.9 | 33.5–34.8 | 32.0–39.4 | 33.5–41.5 | 32.6–36.9 |
| CaO | % | 35 | 48 | 35.3–42.8 | 39.1–43.8 | 34.9–44.3 | 36.9–47.5 | 33.0–43.0 |
| Al ₂ O ₃ | % | 6 | >19 | 6.6–11.5 | 10.0–13.0 | 9.5–12.5 | 5.5–12.4 | 10.2–19.3 |
| MgO | % | 3 | 14 | 7.0–13.1 | 5.9–9.9 | 5.0–13.4 | 2.5–11.2 | 4.9–13.8 |
| TiO ₂ | % | 0.2 | >2 | 0.3–0.8 | 0.5–0.6 | 0.4–1.3 | 0.2–1.3 | 0.6–2.1 |
| Na ₂ O _{eq} | % | 0.3 | 1.2 | 0.3–0.8 | 0.4–0.8 | 0.3–1.2 | 0.6–1.1 | 0.4–0.8 |
| SO ₃ ^a | % | 1 | 4 | 2.0–3.0 | 1.1–3.7 | 2.0–4.5 | 1.6–3.8 | 1.7–4.0 |
| CaO/SiO ₂ | – | 0.9 | 1.3 | 0.9–1.2 | 1.1–1.3 | 1.0–1.3 | 0.9–1.3 | 0.9–1.3 |
| Glass content | % | 66 | 100 | Not analysed | | | | |
| Bulk density | kg/l | 0.6 | 1.3 | Not analysed | | | | |

^aAlthough expressed as SO₃ in the chemical analysis, essentially all sulfur in gbfs is present in sulfide form due to the reducing conditions in the blast furnace (% SO₃ = 2.5 x% S²⁻)

also other alkaline materials, for example water glass, alkali carbonates, alkali hydroxides, etc. can be used. Calcium sulfates accelerate the hydration of medium to high-alumina gbfs glass (Al₂O₃ > 11%) due to the formation of ettringite, which consumes calcium and alumina released from the ggbfs. Calcium sulfates, combined with alkali compounds are effective activators of ggbfs applied in composite cements and also supersulfated cements. In all cases, calcium silicate hydrate (C-S-H) phases form as hydration products, which are responsible for strength development. Depending on the activator, also other phases form which influence hydration progress and strength development (Matthes et al. 2011; Taylor 1997).

In general, the reactivity of a ggbfs increases with increasing contents of CaO, Na₂O, and Al₂O₃ and with decreasing contents of SiO₂, FeO, TiO₂, MnO, and MnS (Dron and Brivot 1980; Kollo 1991; Kollo and Geiseler 1987; Schröder 1969; Smolczyk 1978; Sopora 1959; Yang 1969). A high CaO/SiO₂ ratio generally indicates a good reactivity. Elevated alumina contents in ggbfs are favorable for strength development of slag cements in presence of sulfate, especially at early ages due to enhanced ettringite formation (Matthes 2012; Olbrich 1999; Smolczyk 1978).

Numerous indices have been developed to predict and specify the reactivity of ggbfs. Some of them are given in Table 1.2. While such indices may be convenient for quality control of ggbfs from one source, they are not satisfactory for a general prediction of strength of various ggbfs in cement, because there is no linear relationship between strength and oxide contents in ggbfs over a large composition range (Hooton and Emery 1983; Schröder 1961; Smolczyk 1978).

Apart from the chemical and mineralogical composition, the degree of pre-hydration of gbfs affects its hydraulic reactivity. Due to its latent hydraulic properties, gbfs starts to hydrate as soon as it gets in contact with water. After granulation the gbfs typically has a moisture content between 8 and 12%, sometimes up to 20%, depending on its pore volume. When gbfs is stockpiled outside, a hard crust of prehydrated gbfs can form on the stockpile over time. When recovering the gbfs, the lumps may require extensive disaggregation before any further processing can be done. The intensity of the prehydration depends on the reactivity of the gbfs, climatic conditions, particle shape, compaction, and storage time. It can

Table 1.2 Summary of the reactivity indices for ggbfs (De Langavant 1949; Ehrenberg et al. 2008a, b; Tetmajer 1886; Tigges 2010; Wang et al. 1994)

| Reactivity index | Year | Definition | Criteria |
|--|----------------------|---|-----------------------------------|
| Basicity according to Tetmajer | 1886 | $\text{CaO} / \text{SiO}_2$ | – |
| German Standard for “Eisenportlandzement” (CEM II-S) | 1909 | $\frac{\text{CaO} + \text{MgO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3}$ | ≥ 1 |
| German Standard for “Hochofenzement” | 1932 | $\frac{\text{CaO} + \text{MgO} + 0.33 \cdot \text{Al}_2\text{O}_3}{\text{SiO}_2 + 0.67 \cdot \text{Al}_2\text{O}_3}$ MnO | ≥ 1 $\leq 5 \text{ wt\%}$ |
| German Standard for special cements | 1942 | $\frac{\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3}{\text{SiO}_2}$ | ≥ 1 |
| F-value according to Keil | 1942 | $\frac{\text{CaO} + \text{CaS} + 0.5 \cdot \text{MgO} + \text{Al}_2\text{O}_3}{\text{SiO}_2 + \text{MnO}}$ | >1.5 |
| Reactivity according to De Langavant | 1949 | $20 + \text{CaO} + \text{Al}_2\text{O}_3 + 0.5 \cdot \text{MgO} - \text{SiO}_2$ | – |
| F-value according to Sopora | 1959 | $\frac{\text{CaO} + \text{CaS} + 0.5 \cdot \text{MgO} + \text{Al}_2\text{O}_3}{\text{SiO}_2 + \text{MnO}_2}$ | >1.5 |
| Basicity according to Schwiete | 1963 | $\frac{\text{CaO} + \text{Al}_2\text{O}_3 - 10}{\text{SiO}_2 + 10}$ | – |
| Reactivity according to Wang | 1994 | $\frac{\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3}{\text{SiO}_2 + \text{TiO}_2}$ | – |
| European Standards for cement and blast-furnace slag | 1994 2001 2006 | $\frac{\text{CaO} + \text{MgO}}{\text{SiO}_2}$ CaO + MgO + SiO ₂ | >1 $>67 \text{ wt\%}$ |

be measured via loss on ignition (LOI), which accounts for chemically bound water, or bound CO_2 . While fresh gbfs has an LOI of 0.2–0.5%, stockpiled gbfs can reach an LOI of 2% and beyond (Matthes 2012).

The prehydration of gbfs is relevant for gbfs processing. As the soft hydration products are very easy to grind, a given target fineness is obtained with a lower grinding energy compared to fresh gbfs. Due to the contribution of the soft hydration products to target fineness, the reactive fresh ggbfs grains will be coarser and thus, the compressive strength obtained from prehydrated gbfs will be lower compared to fresh gbfs of same fineness and composition (Ehrenberg 2012; Matthes 2012). When applying the same grinding energy as to fresh gbfs, the prehydrated gbfs will show a higher overall fineness due to the contribution of the soft hydration products, but the reactivity and strength development will be comparable to fresh gbfs.

Concerning the assessment of gbfs reactivity, strength testing combined with chemical and mineralogical characterization remains a very reliable and simple method. For non-routine analyses, numerous laboratory methods allow assessment of the hydration degree of gbfs. Promising among those are electron microscopy and image analysis (SEM-BSE-IA), isothermal calorimetry and chemical shrinkage (Kocaba et al. 2012).

Apart from the intrinsic reactivity, fineness and particle size distribution of the ground gbfs, in Portland composite systems, the properties of the Portland cement clinker, type and dosage of the calcium sulfate set modifier, the particle size distribution of the cement constituents and the actual concrete mix design determine the ultimate concrete performance (Fig. 1.2, Wolter et al. 2003). In production, the reactivity of ggbfs is mainly controlled by varying fineness and particle size distribution. In the ASTM C 989 there are three strength grades of ggbfs specified, which are largely influenced by gbfs quality, fineness, and also by possible calcium sulfate additions.

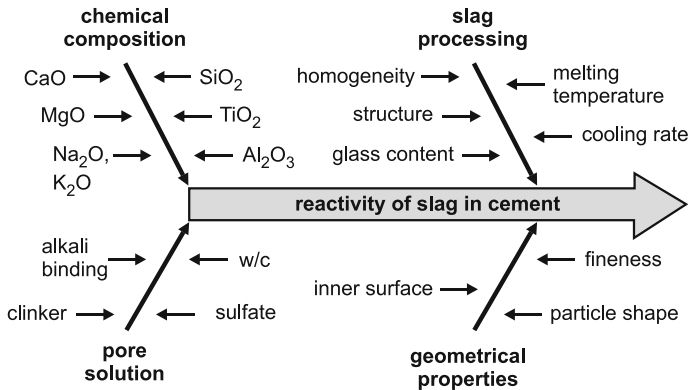


Fig. 1.2 Factors affecting the reactivity of ggbfs, redrafted after Wolter et al. (2003)

1.1.4 Ggbfs as Cement Constituent and as Concrete Addition

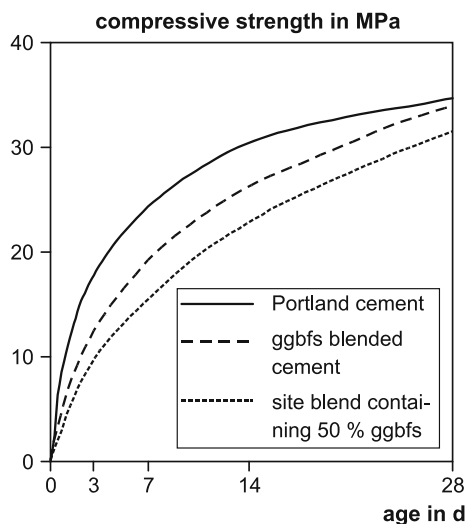
Typical ggbfs contents in concrete range from 20 to ~80% of the total cementitious material. The cement replacement level depends on the requirements on:

- Strength development
- Durability, e.g. resistance to ASR, or attack by sulfates, sea water, or other chemicals or frost and deicing salt
- Heat of hydration
- Setting time.

Ggbfs is either used as a cement constituent replacing Portland clinker and/or as concrete constituent replacing cement. The kind of ggbfs utilization differs locally. North America, the UK and Australia, for example, have a long tradition of using ggbfs as concrete addition, while in Latin America, most of central Europe and India, ggbfs is mainly used as cement constituent.

Both applications have their advantages and disadvantages. The direct use of SCM in concrete gives the concrete producer a maximum flexibility for designing concretes for various applications with a minimum number of silos for cement and SCM. The prerequisite is an adequate knowledge about concrete design and performance. A disadvantage of direct SCM addition to concrete is that the performance of the cementitious part cannot be optimized. In cases where ggbfs and/or cement were of lower reactivity, higher cement contents can be necessary to achieve the same performance as a concrete made with an optimized Portland composite cement with ggbfs (Fig. 1.3, Addis 1986). Intergrinding calcium sulfate

Fig. 1.3 Concrete compressive strength of composite cements with 50% ggbfs versus 50% ggbfs site blends, redrafted from Addis (1986)



with gbfs can help to improve the reactivity of the cementitious system, especially when the gbfs has a medium alumina content >10%.

When using ggbfs as concrete addition it is the responsibility of the ready mix concrete producer to handle changes in the quality of cement and SCMs. This is typically done via adjustments to the concrete design. Composite cements are optimized for performance including quality control of the single cement constituents, optimization of type and dosage of the calcium sulfate phase for optimum setting and hardening and optimum fineness and particle size distribution for best fresh concrete properties and strength. Due to permanent quality control of all cement constituents and of the final product by the cement producer, the concrete producer will obtain cements with a consistent quality.

When proportioning concrete with ggbfs, the lower specific gravity of ggbfs of $\sim 2.9 \text{ g/cm}^3$ versus Portland cement of $\sim 3.14 \text{ g/cm}^3$ has to be considered. Replacing cement by ggbfs on a mass basis leads to higher volume of cementitious phase, which usually improves placeability, finishability, and compaction of the concrete. Moreover, coarser aggregate can be used to increase strength and to reduce water demand without affecting plastic properties (SCA 2002).

Ternary composites including Portland cement and ggbfs plus another SCM such as fly ash, silica fume or limestone are beneficial to further improve concrete properties, e.g. in high performance concrete. Combinations with fly ash can further improve workability due to the ball-bearing effect of spherical fly ash particles and further reduce heat of hydration. Combinations with silica fume will further increase strength and reduce permeability of the concrete at early ages (ACI 2011; Matthes 2012).

1.2 Relevant Standards for Ggbfs as Cement and Concrete Addition

The different options of using ggbfs, either as a cement or concrete constituent, are reflected by the existing standards. Examples of standards for ggbfs as a cement addition are the European EN 197-1 or ASTM C 595. They include different cement classes differentiated according to the amount of Portland clinker and to the type and amount of SCMs. EN 197-1 for example differentiates between Portland composite cements with up to 35% SCMs, be it pure or in combinations. Apart from that, three classes of blast-furnace cements exist, CEM III/A, B, C, which have ggbfs contents from 36 to 95%. So far, apart from 5% minor constituents, no combinations with other SCMs are allowed in these blast-furnace cements, but this is expected to change in the revised version. The CEM V/A and CEM V/B cements are low clinker cements containing a combination of ggbfs and pozzolans or siliceous fly ash, each with minimum contents of 18 and 31%, respectively.

Special cements for exposure to chemical attack are usually covered by national standards. In this respect, slag composite cements are often mentioned. For example, the French NF P 15-317 on sea-water resisting cements allows CEM II/A-S, II/A-M (S-V), CEM III/A with minimum 60% ggbfs and CEM III/B,

CEM III/C and CEM V cements, together with specifications on the composition of the cements and clinker, including C_3A and sulfate contents etc. The same cements plus CEM II/B are allowed by NF-P 15-319, which specifies cements for applications in high sulfate environment, again in connection with chemical specifications. The German DIN 1164 defines CEM III/B and CEM III/C cements according to EN 197-1 as high sulfate resistant.

Examples of standards on ggbfs as addition to concrete, mortar and grouts are the American ASTM C 989 and the European EN 15167-1:2006. ASTM C 989 differentiates three grades of ggbfs, based on their strength development when mixed at 50% with a reference, ordinary Portland cement (OPC). The addition of calcium sulfate is allowed. EN 15167-1 does not include strength classes and does not foresee calcium sulfate additions. Apart from standards for single SCMs such as ggbfs as concrete addition, also combinations are specified, for example by the Austrian öNORM B 3399 or by ASTM C 1697.

Recommendations on how to account for ggbfs in the concrete mix design are given by the European concrete standard EN 206. The EN 206 lists ggbfs conforming to EN 15167-1, along with fly ash and silica fume, as type II concrete additions. The prescriptive k -value concept as well as the Equivalent Concrete Performance Concept (ECPC) and Equivalent Performance of Combinations Concept (EPCC) are included.

The k -value concept is based on the comparison of the 28-day strength performance of a reference concrete with a specified cement versus a test concrete, in which part of this cement is replaced by a type II addition. The concept permits type II additions to be taken into account by replacing the term “water/cement ratio” with “equivalent water/cement ratio” ($w/c_{eq} = \text{water}/(\text{cement} + k \cdot \text{addition})$). The amount of (cement + $k \cdot$ addition) shall not be less than the minimum cement content required for the relevant exposure class. According to EN 206:2013, the k -value for ggbfs and the maximum acknowledgeable amount of ggbfs have to comply with the respective national regulations. In Annex L, the following recommendations are given: The k -value of ggbfs in combination with CEM I or CEM II/A shall be 0.6. The maximum ggbfs useable for calculating the water/binder ratio and the minimum cement content shall comply with the weight ratio $\text{ggbfs}/\text{cement} \leq 1.0$.

As the k -value concept, also the performance concepts ECPC and EPCC are used on a national basis. The ECPC permits amendments to the requirements for minimum cement content and maximum water/cement ratio when one or more specific additions and one or more specific cements are used, for which the manufacturing source and characteristics are clearly defined and documented. Such amendments are in place for example in Belgium and the Netherlands. The concept includes comparative testing of concrete compositions, which deviate from the generally specified and accepted design criteria for defined applications versus the specified reference composition. If the defined properties such as compressive strength, resistance to carbonation, chloride penetration and freeze-thaw deicing salt attack, are comparable, the suitability of the new concrete design can be certified. In Belgium the methodology for the assessment and the validation of the fitness for use of cements or additions for concrete as slag amongst others is described in NBN B15-100.

The EPCC treats a combination of a cement and additions as technically equivalent to a standardized cement of the same composition. This concept may permit a defined range of combinations to count fully towards the requirements for maximum w/c ratio and minimum cement content specified for the standardized cement (EN 206).

In North America, k-values are not used and ggbfs is treated as equivalent to Portland cement. Due to its latent hydraulic properties, ggbfs is referred to as slag cement. For concrete placements in cool weather, ggbfs replacement levels are often reduced, while they are increased in hot weather to provide similar setting times and early-age strength development. The ACI 233R *Guide to the use of Slag Cement in Concrete and Mortar* (ACI 2011) states, that the proportioning techniques for concrete incorporating ggbfs are similar to those used in proportioning concrete made with Portland cement or blended cement. Methods for proportioning are given in the ACI 211.1 *Standard Practice for Selecting Proportions for Normal, Heavyweight, and Mass Concrete*. Adjustments must be made for changes in solid volume due to the difference in specific gravity of slag and Portland cement.

1.3 Selected Environmental Aspects on Gbfs and Ggbfs

It is recognized that supplementary cementitious materials or additions used as secondary main constituents in cement or concrete influence the environmental impact during manufacturing and service life of the material. In this chapter, the CO₂ emissions, the heavy metal contents and leaching and radioactivity are discussed.

1.3.1 CO₂ Footprint

Using ggbfs as secondary main constituent, either in cement or in concrete production reduces the carbon footprint of total cementitious materials. Proceeding from 913 kg CO₂/t CEM I and 67 kg CO₂/t ggbfs as quoted in the UK, the CO₂ footprint of the cementitious materials can be reduced to less than 30% of that of CEM I, due to the high replacement levels of ggbfs (Table 1.3).

When using supplementary cementitious materials, attention has to be paid to the allocated environmental impact. Bfs is a useful by-product, and part of the environmental load of the steel production can be allocated to it. In this context different allocation principles can be adopted (Van den Heede and De Belie 2012). In some countries the environmental load from steel production is completely attributed to the steel and the only environmental load of the ggbfs results from grinding and transport. In the UK, the carbon footprint of ggbfs is 67 kg/t. This excludes any CO₂ allocation from the primary process, i.e. iron production. According to EN 15804, processes contributing of the order of 1% or less to the overall revenue are allowed to be neglected.

Table 1.3 CO₂e (carbon dioxide equivalent) of combinations with ggbs produced at the concrete plant (Technical Datasheet 2014)

| Combination (CEM I + ggbs) | Content of the addition | CO ₂ e ^a (without transport of constituents to the concrete plant) |
|----------------------------|-------------------------|--|
| | wt% | kg CO ₂ e/t (addition content low–high) |
| CIIB-S | 21–35 (ggbs) | 735–617 |
| CIIA | 36–65 (ggbs) | 608–363 |
| CIIB | 66–80 (ggbs) | 354–236 |

^aCO₂e can be interpolated for proportions of addition between the minimum and maximum, noting that the minimum CO₂e is associated with the highest proportion of addition

1.3.2 Heavy Metal Contents

Gbfs may contain small quantities of heavy metals. Table 1.4 compares the contents of these elements with that of OPC. The heavy metal contents of gbfs are usually lower than that of OPC.

Table 1.4 Contents of heavy metals and trace elements of CEM I and blast furnace slag

| Parameter | CEM I (Brameshuber and Vollpracht 2007) | | | Gbfs ^a | |
|-----------------|---|-----------|---------|-------------------|--------|
| | n | Range | Average | n | Median |
| | – | mg/kg | | – | mg/kg |
| Antimony (Sb) | 21 | <1–9.4 | 2.4 | 53 | <5 |
| Arsenic (As) | 14 | <2–12 | 6.1 | 53 | <5 |
| Barium (Ba) | 8 | 104–818 | 346 | – | – |
| Lead (Pb) | 21 | 5–145 | 27 | 53 | <5 |
| Cadmium (Cd) | 18 | <0.1–1.7 | 0.5 | 53 | <0.5 |
| Chromium (Cr) | 21 | 29–129 | 61 | 53 | 21.2 |
| Cobalt (Co) | 15 | 5.6–14 | 8 | – | – |
| Copper (Cu) | 18 | 14–101 | 35 | 53 | <5 |
| Molybdenum (Mo) | 14 | <1–6.9 | 2.9 | 53 | <5 |
| Nickel (Ni) | 18 | 14–84 | 31 | 53 | <5 |
| Mercury (Hg) | 18 | 0.003–0.7 | 0.06 | – | – |
| Selenium (Se) | 5 | <5–10 | 5.9 | – | – |
| Thallium (Tl) | 15 | <0.1–3.9 | 0.6 | – | – |
| Vanadium (V) | 16 | 22–100 | 39 | 53 | 34 |
| Zinc (Zn) | 14 | 30–514 | 146 | 53 | 7.4 |

n: Number of tested samples

^aResults from the database of the FEHS, Duisburg, personal note from Dr. Bialucha

1.3.3 Leaching

The Technical Committee 351 of the European Committee for Standardization (CEN/TC351) is developing harmonised leaching tests for building materials. For monolithic materials like concrete, the following technical specification has been published: CEN/TS 16637-2:2014 (Construction products—Assessment of release of dangerous substances—Part 2: Horizontal dynamic surface leaching test—DSLTL).

The DSLTL is a method to determine the release of substances from a specimen with demineralised water in contact with its surface as a function of time. The specimen is placed in a leaching vessel and completely submerged in the demineralised water, which is changed at defined time steps (0.25, 1, 2.25, 4, 9, 16, 36 and 64 days). The leachates are analysed for the relevant parameters. The cumulative release of these parameters is calculated in relation to its surface (Eq. 1.1)

$$R_n = \sum_{i=1}^n r_i = \sum_{i=1}^n c_i \cdot \frac{L}{A} \quad (1.1)$$

R_n cumulative release of the substance for period n including fraction $i = 1$ to n in mg/m^2

r_i release of the substance in fraction i in mg/m^2

c_i concentration of the substance in leachate i in mg/l

L/A volume of the liquid, divided by the surface area of the sample, $L/A = (80 \pm 10) \text{ l}/\text{m}^2$.

Similar tank tests have been carried out in the Netherlands and in Germany for many years. The leaching steps and the L/A -ratio differ, but the principle of the test is the same. The storage conditions before starting the leaching test are relevant. Even a slight carbonation of the surface changes the pH of the leachates and thus the concentration of heavy metals (Rickert and Vollpracht 2014). Thus, for comparative studies it is necessary to use the same storage conditions.

The release of trace elements from mortars and concretes made of commercial Portland cement and blast furnace slag cements was studied by Rickert et al. (2011), Rickert and Vollpracht (2014), Van der Sloot et al. 2001, and Vollpracht, RTWH Aachen (unpublished data). The trace element contents of the cements used (Table 1.5) indicate, that CEM III cements do not show elevated contents versus CEM I, except for V and Ba in some cases.

After demoulding the samples were wrapped airtight in a polyethylene foil and stored at $20 \pm 3 \text{ }^\circ\text{C}$ until testing. The leaching tests started at 28 or 56 days. The release of Ba, Cr, Co, Cu, Ni, Pb of CEM III cement concrete is comparable to Portland cement concrete, the release of V can be higher (Figs. 1.4, 1.5, 1.6 and 1.7). The concentrations of Sb, As and Se were below $1 \text{ } \mu\text{g}/\text{l}$, the concentrations of

Cd below 0.5 µg/l and of Hg below 0.1 µg/l for all tested mixtures. Due to these low concentrations the release was not calculated.

In the EU the evaluation of leaching results is regulated at national level.

1.3.4 Radioactivity

The radioactivity of gbfs or ggbfs generally does not exceed typical concentrations in other commercial products and building materials (Table 1.6).

According to Bialucha (2000), who tested 30 gbfs, all samples had sums of Ra-226 + Th-232 lower than the German sum index of 500 Bq/kg, above which a material is required to be observed (Table 1.7). For 80% of the slags this sum was below 200 Bq/kg. The content of K-40 was lower than stated in Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit (1993).

1.4 Impact of Ggbfs on Fresh Concrete Properties and Setting Time

1.4.1 Workability and Superplasticizer Demand

Using ggbfs in concrete improves workability. Thus, with increasing content of ggbfs, either the water/binder ratio (w/b), the dosage of superplasticizer or the paste content can be reduced, compared to a mix with Portland cement (Figs. 1.8 and 1.9) (Beushausen et al. 2012; Eren et al. 1995; Megat Johari et al. 2011; Osborne 1989; Wimpenny et al. 1989).

This workability improvement by ggbfs additions is usually perceivable at elevated contents of ggbfs of at least ~50 wt% of total cementitious material. It can be attributed to the smooth, glassy surface of ggbfs, which creates slip planes in the paste (Wood 1981). Moreover, ggbfs has a latent hydraulic reactivity and therefore binds less water than Portland cement during concrete manufacture. At ggbfs contents of 40–65% the mixing water can be reduced by ~5% compared to OPC concrete (Lothia and Joshi 1995; Meusel and Rose 1983). If in presence of major amounts of ggbfs the mixing water volume or superplasticizer dosage would not be adjusted, excessive bleeding may occur, coupled with prolonged setting and strength reduction.

The effectiveness of ggbfs to reduce superplasticizer demand decreases with increasing ggbfs fineness and/or at low water/binder ratios <0.3 (Gesoglu et al. 2009; Lothia and Joshi 1995; Marushima et al. 1993; Nakamura et al. 1991; Peterson Becknell and Hale 2011). Boukendakdji et al. (2012) confirmed in SCC

Table 1.5 Contents of heavy metals and trace elements of the cements used in the mortars/concretes of the tank leaching tests, data from Rickert et al. (2011) [CEM I B1 (2011), CEM III/A (2011)], Rickert and Vollpracht (2014) [CEM I B1 (2014), CEM III/B (2014)], Van der Sloot et al. (2001) [CEM I N1, N2, D1, D2, H1, H3, H6, H7, H9]

| Heavy metal/ trace element | CEM I | | | | | | | | | | CEM III | | | | |
|-------------------------------|----------------|-------|------|-------|-------|-------|-------|-------|-------|------|--------------|--------------|---------------------------------------|---------------------|---------------------|
| | I ^a | N1 | N2 | D1 | D2 | H1 | H3 | H6 | H7 | H9 | B1 (2011) | B1 (2014) | CEM III/A I ^a (2011) | CEM III/A (2011) | CEM III/B (2014) |
| | mg/kg | | | | | | | | | | | | | | |
| Sb | 2 | 2.1 | <1 | 1.2 | 3.6 | 4.8 | <1 | <1 | <1 | 3.9 | 8.6 | 3.8 | 5 | 5.1 | <1 |
| As | 4 | 23 | 4.5 | 8.6 | 6.9 | 7.2 | 2.3 | 5.7 | 10 | 4.9 | 16 | 172 | 2 | 11 | <1 |
| Ba | 331 | - | - | - | - | - | - | - | - | 201 | 47 | 269 | 420 | 72.5 | 515 |
| Pb | 14 | 20 | 30 | 106 | 15 | 64 | 12 | 19 | 5.8 | 57 | 29 | 155 | 14 | 22 | 12 |
| Cd | 0.2 | 0.21 | 0.38 | 0.61 | <0.1 | 0.96 | 0.15 | 0.57 | 0.51 | 0.94 | 1.46 | 4.93 | <0.5 | 0.85 | 0.46 |
| Cr | 59 | 184 | 70 | 76 | 29 | 89 | 92 | 578 | 129 | 33 | 85 | 41 | 46 | 62 | 40 |
| Co | 4 | 12 | 8.9 | 7.3 | 7.5 | 13 | 14 | 22 | 7.6 | 5.9 | 12 | 11 | 4 | 8.6 | 2.1 |
| Cu | 22 | 16 | 14 | 16 | 29 | 54 | 16 | 27 | 16 | 15 | 89 | 158 | 18 | 57 | 61.7 |
| Mo | - | 1.9 | 5 | 6.9 | 1.1 | 3.7 | <1.0 | <1.0 | <1.0 | 4.3 | 2.7 | 39 | - | 2.02 | 3.7 |
| Ni | 36 | 61 | 22 | 45 | 14 | 47 | 25 | 75 | 42 | 14 | 41 | 25 | 23 | 26 | 12.8 |
| Hg | 0.2 | <0.02 | 0.03 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | 0.12 | 0.05 | 0.12 | <0.1 | 0.04 | <0.02 |
| Se | - | - | - | - | - | - | - | - | - | - | <1 | <1 | - | <1 | <1 |
| Tl | 0.2 | <0.5 | <0.5 | <0.5 | <1 | <0.5 | <0.5 | <0.5 | <0.5 | <1 | <0.2 | 3.37 | 0.5 | <0.2 | <0.2 |
| V | - | 44 | 30 | 31 | 22 | 100 | 73 | 36 | 34 | 27 | 67 | 35 | - | 51 | 206 |
| Zn | 281 | 55 | 43 | 104 | 130 | 382 | 33 | 83 | 30 | 223 | 528 | 1178 | 245 | 341 | 93 |

^aUnpublished data Vollpracht, RWTH Aachen; -: Not determined

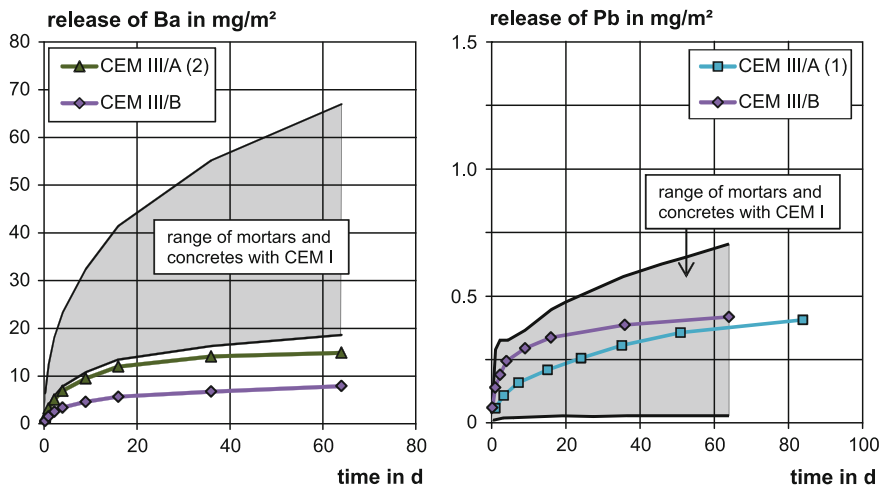


Fig. 1.4 Release of barium and lead from mortars and concretes with different cements (Rickert et al. 2011; Rickert and Vollpracht 2014; Van der Sloot et al. 2001; Vollpracht, unpublished data)

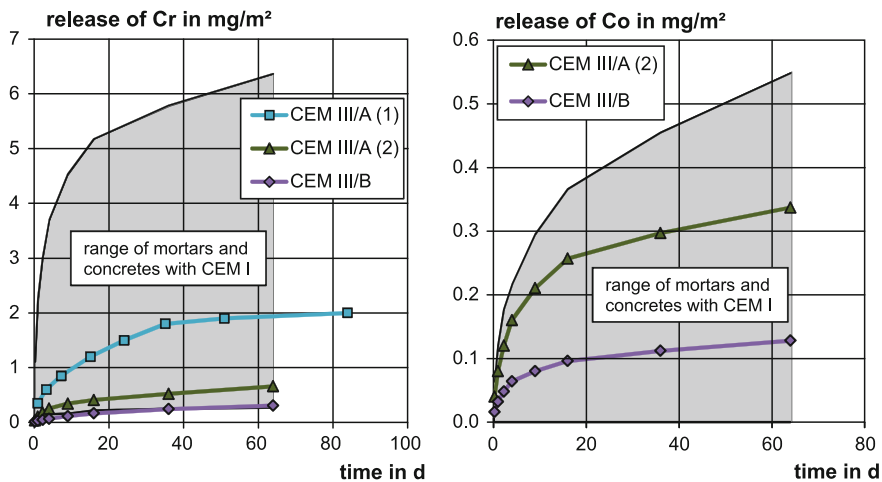


Fig. 1.5 Release of chromium and cobalt from mortars and concretes with different cements (Rickert et al. 2011; Rickert and Vollpracht 2014; Van der Sloot et al. 2001; Vollpracht, unpublished data)

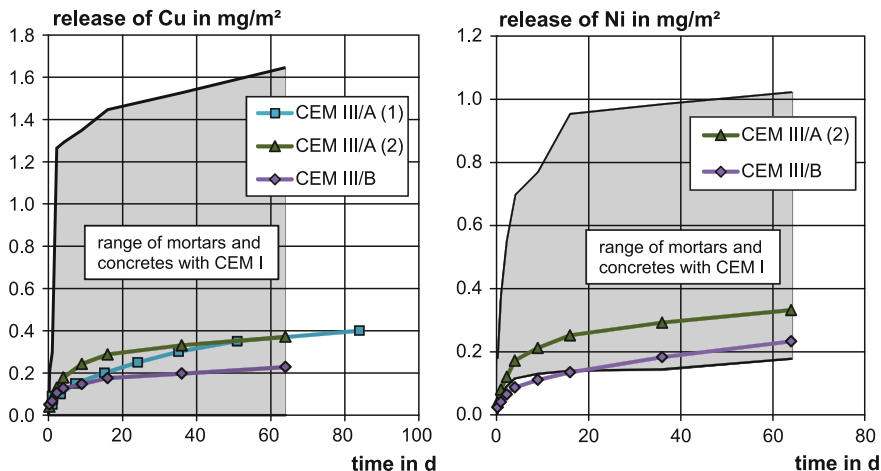
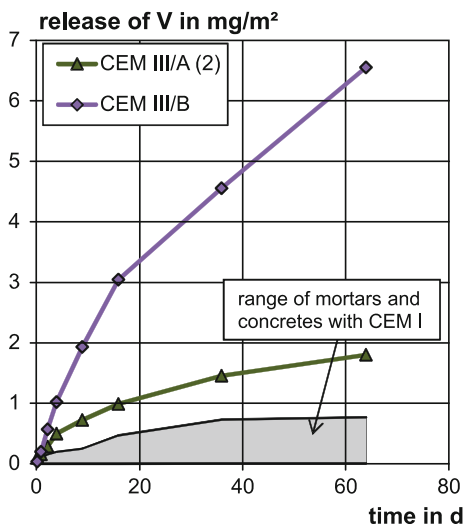


Fig. 1.6 Release of copper and nickel from mortars and concretes with different cements (Rickert et al. 2011; Rickert and Vollpracht 2014; Van der Sloot et al. 2001; Vollpracht, unpublished data)

Fig. 1.7 Release of vanadium from mortars and concretes with different cements (Rickert et al. 2011; Rickert and Vollpracht 2014; Van der Sloot et al. 2001; Vollpracht, unpublished data)



the effectiveness of ggbfs additions of 15% and higher in reducing superplasticizer demand for a targeted workability.

Regarding the response of cements to polycarboxylate-based superplasticizers (SP), CEM III/B with 72% ggbfs showed a higher sensitivity towards SP dosage than OPC (Alonso et al. 2007; Hamada et al. 2000; Puertas et al. 2005). The relation between ggbfs content and SP demand decreases with increasing w/b (Carette and Malhotra 1987). The influence of 0–75% ggbfs additions on the zeta potential and

Table 1.6 Radioactivity of gbfs compared to natural rocks and other building materials

| Material | Ra-226 | | Th-232 | | K-40 | | Reference | |
|--------------------------------|---------|---------|---------|--------|---------|----------|---|-----------------------|
| | Average | Range | Average | Range | Average | Range | | |
| | Bq/kg | | Bq/kg | | Bq/kg | | | |
| Soils (worldwide) | 32 | n. i. | 45 | n. i. | 412 | n. i. | UNSCEAR Report (2010) | |
| Limestone | 24 | 4–41 | 5 | 2–20 | 90 | <40–240 | Bundes-ministerium für Umwelt, Naturschutz und Reaktorsicherheit (1993) | |
| Sand/gravel | 15 | 1–39 | 16 | 1–64 | 380 | 3–1200 | | |
| Basalt | 26 | 6–36 | 29 | 9–37 | 270 | 190–380 | | |
| Sandstone | 20 | 13–70 | 25 | 15–70 | 500 | <40–1100 | | |
| Tuff | 100 | <20–200 | 100 | 30–300 | 1000 | 500–2000 | | |
| Granite | 100 | 30–500 | 120 | 17–311 | 1000 | 600–4000 | | |
| Expanded clay | 40 | <20–70 | 70 | 30–90 | 600 | 70–800 | | |
| Brick | 50 | 100–200 | 52 | 12–200 | 700 | 100–2000 | | |
| Gbfs | 100 | 40–200 | 100 | 30–300 | 500 | 200–1000 | | |
| Fly ash | 200 | 26–1110 | 100 | 14–300 | 700 | 170–1450 | | |
| CEM I | 30 | 10–50 | 20 | 10–40 | 200 | 100–700 | | |
| CEM II | 60 | 20–100 | 80 | 30–200 | 100 | < 40–200 | | |
| Concrete | 30 | 7–92 | 23 | 4–71 | 450 | 50–1300 | | |
| Average for building materials | 50 | – | 50 | – | 500 | – | | UNSCEAR Report (2008) |

n. i.: No information

Table 1.7 Radioactivity of bfs (30 samples), (Bialucha 2000)

| Material | Ra-226 | | Th-232 | | K-40 | |
|----------|---------|--------|---------|--------|---------|--------|
| | Average | Range | Average | Range | Average | Range |
| | Bq/kg | | Bq/kg | | Bq/kg | |
| Bfs | 130 | 66–360 | 62 | 28–129 | 167 | 60–405 |

rheology of cement pastes with and without polycarboxylate-based admixtures was studied by various authors (Palacios et al. 2009a, b).

Fulton (1974) and Swamy (1990) mention the improved cohesiveness of concrete containing major amounts of gbfs. However, this cohesiveness, also called “stickiness”, does not impair the ease of compaction on the construction site. Also high gbfs concrete is easy to compact by conventional mechanical vibration. When comparing the placeability of concrete using the Vebe apparatus, concrete with 50% gbfs was easier to place than the mix without gbfs (Fulton 1974).

Shi et al. (2004) confirmed the workability improvement through gbfs additions in concrete, which resulted in a decrease in plastic viscosity and yield stress. With

Fig. 1.8 Effect of water content on slump of concrete mixtures with and without ggbfs (Meusel and Rose 1983)

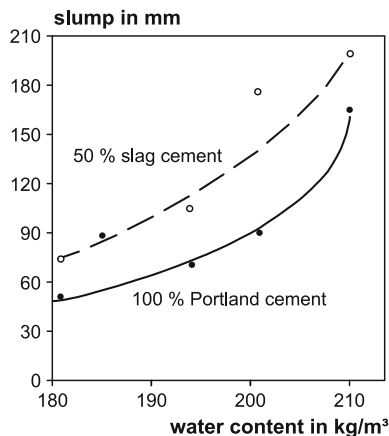
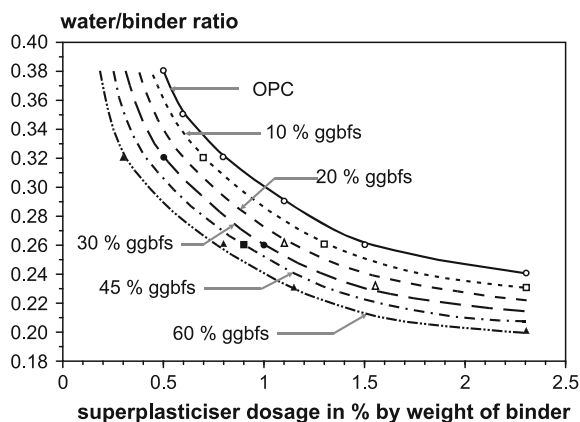


Fig. 1.9 Effect of partial cement replacement by ggbfs on dosage of superplasticizer (naphthalene based) required for concrete with a slump of 150 mm, redrafted after Domone and Soutsos (1995)



decreasing amorphous content of the ggbfs this dispersing effect was reduced. However, also contradictory experiences exist, especially when working at very low w/b ratios as done by Soutsos (1992). Under such conditions the influence of ggbfs on the rheological properties can be rather limited (Fig. 1.10).

Generally, the effects of chemical admixtures on concrete with ggbfs are similar to those for OPC concrete. Retarding admixtures are typically more effective when ggbfs is present, especially if the cement is low in C_3A or alkalis (ACI 2011). At elevated ggbfs contents, the dosage of air entraining agent usually has to be increased to achieve a target air content, especially at low w/b (ACI 2011; Lothia and Joshi 1995; Matthes 2012).

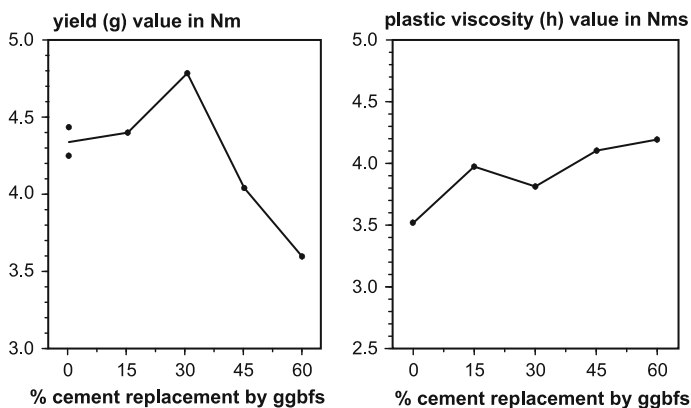


Fig. 1.10 Effect of partial cement replacement by ggbfs on the yield (g) and plastic viscosity (h) values for concrete mixes with water/binder ratio of 0.26 and a slump of approx. 150 mm, data from Soutsos (1992)

1.4.2 Segregation and Bleeding

Coupled with the effect of workability improvement by ggbfs is an increased tendency to bleeding and segregation. To adjust the concrete design the superplasticizer dosages and/or the water added should be reduced to achieve the target workability. Following the national standards and working practices, further adjustments ensure the required concrete performance in terms of strength development and, potentially, durability (Ait-Aider 1988; Cesareni and Frigione 1969; Matthes 2012; Rickett 1990; Swamy 1990; Wainwright and Ait-Aider 1995; Wainwright and Rey 2000).

Generally, the bleeding capacity and bleeding rate of concrete are influenced by the ratio of the surface area of the solid constituents to the volume of water and thus are sensitive to changes in the surface area of the cementitious constituents (ACI 2011). Thus, if a fine ggbfs would replace a coarser cement, bleeding can be reduced and vice versa. Especially effective for reducing bleeding would be very fine ggbfs (Blaine $> 10,000 \text{ cm}^2/\text{g}$, Nakamura et al. 1991).

1.4.3 Slump Loss

The data on slump loss of ggbfs concrete are varying. Frigione (1986) reported a reduced rate of slump loss, while Meusel and Rose (1983) reported a similar slump loss of concrete containing 50% ggbfs versus OPC concrete. Lea (1971) described reduced slump loss, especially when OPC with rapid slump loss is replaced by ggbfs. Boukendakdji et al. (2009) reported an increase of open time of

self-compacting concrete (SCC) from 30 to 60 min when 15% of Portland cement was replaced by ggbfs.

1.4.4 *Setting Time*

When OPC is replaced by ggbfs, usually the time of setting is increased. The degree of this increase depends on various factors, for example on the amount of cement substituted, the initial concrete temperature, the w/b ratio, and the properties of the cement and additives used (Fulton 1974; Swamy 1990). In fact, concrete temperature is a key parameter for the setting time of ggbfs composites. The delay of time of set is especially pronounced at low concrete temperatures and/or at major ggbfs contents >50% (Robeyst et al. 2008; SCA 2002; Yoshida et al. 1986). At 20 °C and above, the reported results are manifold, reaching from no or little impact (Alshamsi 2001; Hooton 2000; Juenger et al. 2008) to even reduced times of set (Eren et al. 1995). Hogan and Meusel (1981) for example reported that at 23 °C initial setting can be prolonged by 30–60 min, while at 29 °C hardly any change is detected. Similar trends are described by SCA (Fig. 1.11, SCA 2002) and numerous other authors. Prolonged setting can be compensated either by using accelerators, by reducing the cement substitution by ggbfs in the concrete mix (ACI 2011), or by adjusting the concrete design, including w/b and superplasticizer dosage.

By continuous monitoring of the evolution of the ultrasonic wave velocity through concrete containing high amounts of ggbfs, valuable information can be extracted about the setting behaviour (Fig. 1.12; Robeyst et al. 2008). During the dormant period, the P-wave velocity is nearly constant. However at that time, the signal attenuation is large and the determination of the signal onset time and thus P-wave velocity is less accurate. After the dormant period, the P-wave velocity increases rapidly as the stiffness of the concrete develops. The P-wave velocity is lower for mixes containing high amounts of ggbfs (>50%), because the stiffness develops slower. For these mixes, the initial increase in P-wave velocity is mainly due to the hydration of OPC. Moreover, at early ages, the presence of ggbfs decelerates the temperature rise and increases the distance between the cement particles (Robeyst 2009). When comparing different CEM III cements, the increase of P-wave velocity depends not only on the ggbfs content, but also on their fineness, clinker reactivity, and content of set modifiers and accelerators (Robeyst et al. 2008; Robeyst 2009). For concrete with high ggbfs contents in the binder [S85 and S (CEM III/C 32.5)], a second increase of P-wave velocity can be noticed, which can be attributed to the hydration of slag particles.

In comparison to the more traditional tests to determine the initial and final setting times (e.g. penetration resistance test), the ultrasonic transmission method is non-destructive. The change of ultrasonic velocity in time is sensitive to the

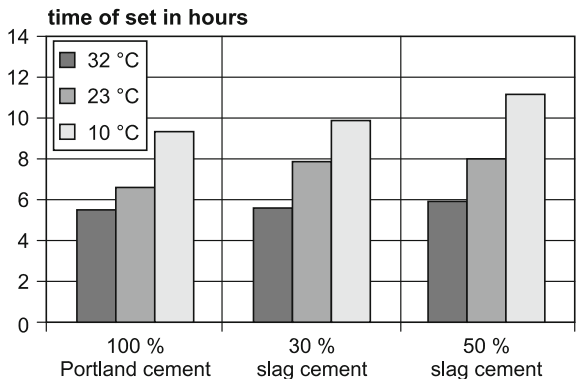


Fig. 1.11 Influence of ggbs and temperature on time of set, redrafted after SCA (2002)

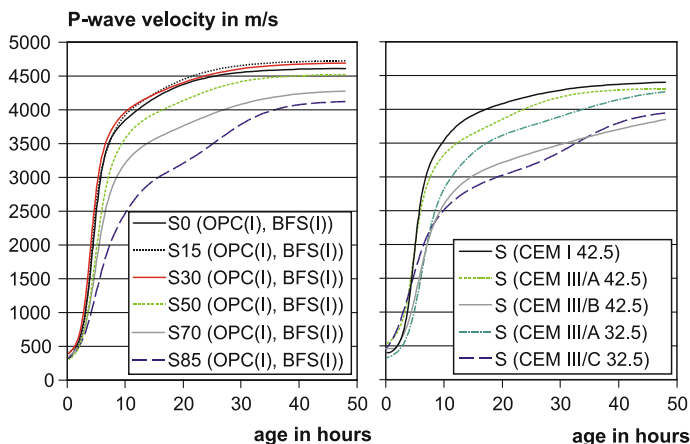


Fig. 1.12 Evolution of the P-wave velocity in function of concrete age (left: slag added as a separate component to the concrete mix at OPC replacement levels ranging from 0 to 85%, right: blended cements) (Robeyst et al. 2008)

differences in setting behaviour of the tested mixtures. The initial setting seems to correspond with the inflection point of the velocity versus time curve and the final setting with the point at which the velocity increase levels off (Robeyst 2009).

1.5 Impact of Ggbfs on Heat of Hydration

The hydration of cement is an exothermal chemical process. Based on the mineralogical composition of the Portland clinker and the total heat produced during complete hydration of these minerals, the total theoretical hydration heat of OPC can be determined (Q_{tot}). For cement composites with ggbfs, the maximum heat released at the end of the reaction can be experimentally determined. Literature results range from 355 to 461 J/g ggbfs (Bensted 1981; De Schutter 1999; Kishi and Maekawa 1995; Schindler and Folliard 2003).

By replacing part of the hydraulic, rapidly hydrating OPC by the latent hydraulic, slower reacting ggbfs, the heat production rate and total heat of hydration is reduced. This is especially beneficial for mass concrete to avoid thermal shrinkage cracking.

The heat production rate of ggbfs containing concrete is also sensitive to curing temperature (Fig. 1.13) and so is its strength development.

Some researchers reported, that the tensile strain capacity of concrete with 70% ggbfs at early age was lower than that of equivalent OPC concrete and it was estimated, that with sections over 2.5 m deep the reduced tensile strain capacity of ggbfs concrete may cancel out the benefit of the reduced temperature rise (Bamforth 1980). Also others indicated, that the use of ggbfs should not be based on its ability to reduce heat of hydration alone (Springenschmid et al. 1994; Thomas and Mukherjee 1994).

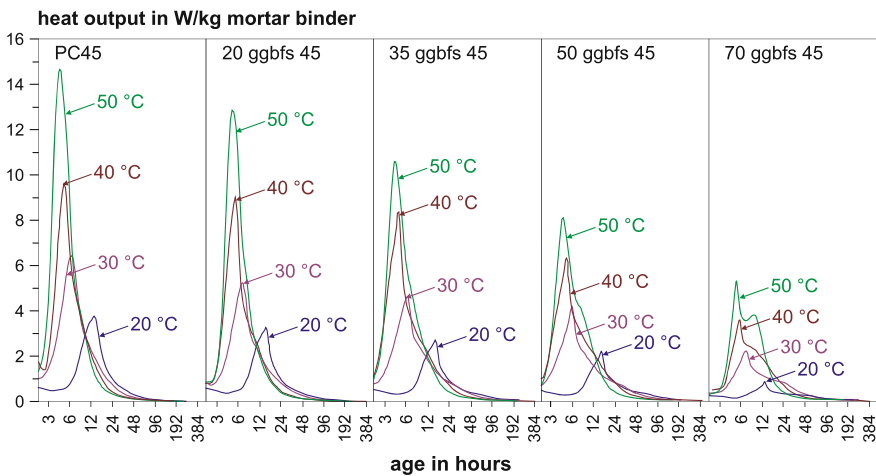


Fig. 1.13 Heat output per kilogram binder of mortar grade C45 cured at 20, 30, 40 and 50 °C at cement replacement rates of 20, 35, 50 and 70% with ggbfs. Redrafted after Turu'allo (2013)

Fig. 1.14 Effect of ggbfs additions on temperature increase versus time in mass concrete, adopted from SCA (2002)

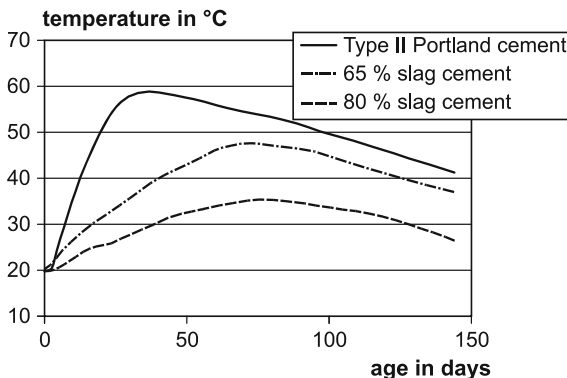
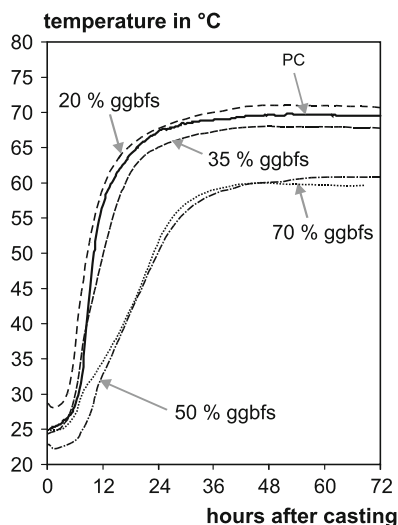


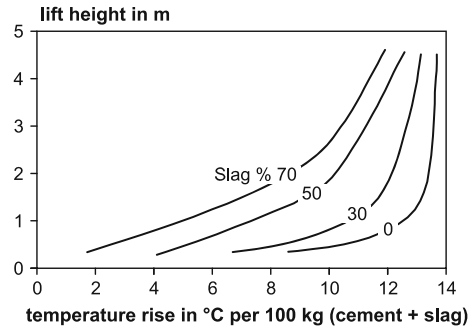
Fig. 1.15 Adiabatic temperature histories for concretes with target mean strengths 94–105 MPa, redrafted after Soutsos et al. (2005)



Apart from reducing the total cementitious content, the partial replacement of OPC by ggbfs or other SCMs is an effective and common means to reduce peak temperatures in mass concrete (Fig. 1.14). Generally, OPC replacement rates between 65 and 80% are considered effective, whereas for smaller mass pours 50–65% ggbfs were successfully used (SCA 2002).

For mass concrete projects the performance of the concrete designs should be tested using the local materials to ensure their performance regarding temperature and strength development. Adiabatic tests may be used for this purpose. The adiabatic temperature histories of concretes with different ggbfs contents are shown in Fig. 1.15 (Soutsos et al. 2005). The Portland cement concrete had a temperature rise of 45 °C from the casting temperature of 25 °C. Low levels of cement replacement with ggbfs, i.e. 20 and 35%, do not appear to be effective in reducing the peak

Fig. 1.16 Effect of ggbfs and lift height on temperature increase of massive concrete foundations redrafted after Bamforth (1980)



temperature. Higher levels of 50 and 70% are required to reduce the peak temperature by 10 °C. It must be noted that the high levels of cement replacement also, in addition to reducing the peak temperature, reduce the rate of temperature rise at early ages.

Bamforth 1980 showed that, although the temperature development in mass concrete decreases with increasing replacement of OPC by ggbfs, this effect becomes less pronounced with increasing volume poured, i.e. higher lift heights (Fig. 1.16, Bamforth 1980). Nevertheless, temperature data from the center of three 4.5 m deep foundations containing 144–212 m³ of concrete respectively, revealed the following temperature increases:

- Plus 54.5 °C from placing temperature of 20.5 °C for OPC concrete
- Plus 47.5 °C from placing temperature of 21.5 °C for concrete with 30% low calcium FA
- Plus 46.0 °C from placing temperature of 18.0 °C for concrete with 75% ggbfs (Bamforth 1980).

The temperature development in concrete blocks is not only affected by their size but also by the ambient temperature at the time of casting. Strength grade and level of replacement by ggbfs both affect the temperature increase in the concrete. Figure 1.17 shows concrete blocks that were cast to determine the ratio of in situ strength, determined from cores, to companion cubes cast and cured alongside the blocks. The different temperature histories of the same mix during winter and summer make such ratios impossible to determine. Winter temperatures allow more heat dissipation from the concrete blocks and the lower reaction of ggbfs assists in obtaining lower peak temperatures. The differences in peak temperatures between the OPC and ggbfs mixes increased with winter conditions.

In the laboratory, the core temperature of insulated, very massive concrete blocks can be estimated based on adiabatic calorimetric measurements (De Schutter 1999; De Schutter and Taerwe 1995; Soutsos et al. 2005). As shown in Fig. 1.18,

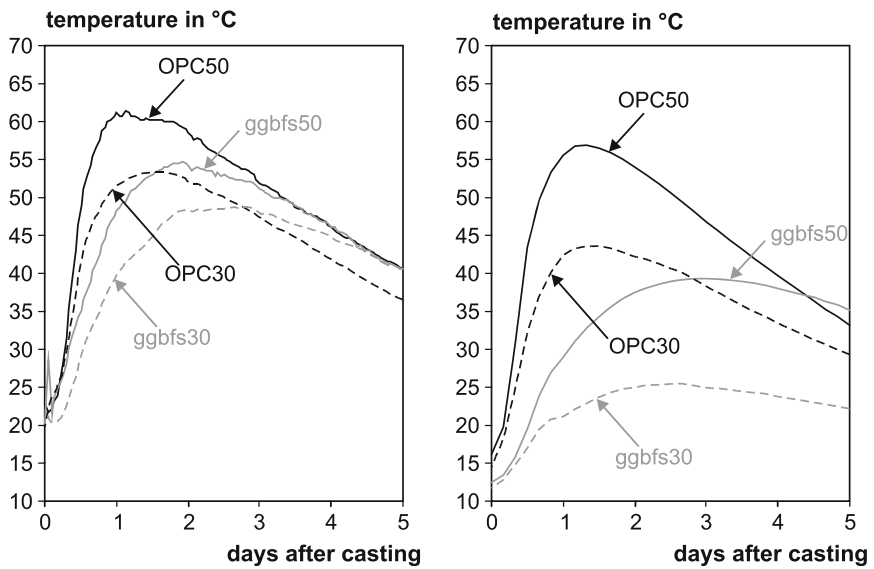


Fig. 1.17 Temperature rise in concrete blocks made of OPC and a mix of 50% OPC and 50% ggbfs, both with 30 and 50 MPa compressive strength. Left: summer, right: winter (Soutsos et al. 2016)

the temperature in OPC concrete can reach over 65 °C, while these values are significantly decreased as soon as the ggbfs content of the cementitious phase is 50% and higher.

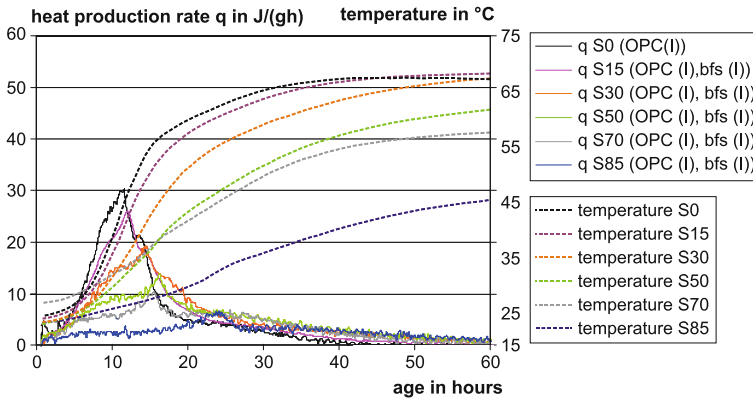


Fig. 1.18 Heat production rate and temperature evolution in function of concrete age under adiabatic conditions for concrete mixes containing different amounts of ggbfs (ggbfs/(ggbfs + OPC) ranging from 0 to 85%), redrafted after Gruyaert (2011)

1.6 Impact of Ggbfs on Strength Development

1.6.1 Compressive Strength

1.6.1.1 Hardening at Standard Conditions

Due to its latent hydraulic properties, ggbfs starts to hydrate when in contact with water. However, this reaction diminishes with time. Only in presence of an activator the ggbfs hydration continues. The nature and dosage of activators play an important role for strength development of ggbfs concrete. The most common activator of ggbfs in concrete is Portland cement. Here the ggbfs activation is alkaline due to the liberation of calcium hydroxide and alkalis during Portland clinker hydration and sulfatic due to the presence of calcium sulfate in the cement. Apart from that, ggbfs can also be activated by other compounds such as alkali and alkali earth hydroxides, sulfates, chlorides, nitrates, carbonates, and silicates (Andersson and Gram 1988; Daugherty et al. 1983; Douglas and Brandstetr 1990; Hooton 1987; Malolepszy 1986; Roy and Idorn 1982; Shi and Day 1996; Song and Jennings 1999; Teoreanu and Georgescu 1974). The activation potential depends significantly on the properties of the ggbfs.

Compared to OPC the hydration rate of ggbfs is slower. This is reflected by a later initial setting time and lower early strength with increasing ggbfs content (Fig. 1.19). However, late strength development of concrete with ggbfs composites mostly exceeds that of OPC concrete. Depending on the reactivity and fineness of the ggbfs and its content in the mix, the strength of slag concrete typically reaches the strength of OPC concrete between ~ 10 and 35 days for a given concrete design (Demirboga 2003; Hewlett 1998; Hogan and Meusel 1981; Neville 1995; Oner and Akyuz 2007; Wang et al. 2007).

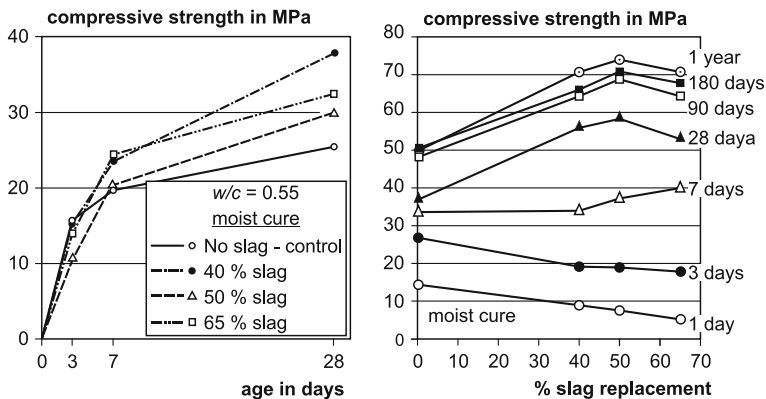


Fig. 1.19 Effect of ggbfs on compressive strength, adopted from Hogan and Meusel (1981)

At very high replacement levels, a persistent strength reduction compared to a reference OPC concrete was noticed by several researchers (Duran Atis and Bilim 2007; Khatib and Hibbert 2005). An optimum cement replacement level regarding fresh concrete properties and late strength development is about 50% (Dubovoy 1986; Hogan and Meusel 1981; Hwang and Lin 1986; Meusel and Rose 1983; Roy and Idorn 1982).

The reactivity of ggbfs itself is significantly influencing the strength development at a given ggbfs content and constant fineness (Fig. 1.20). It is mainly governed by its basicity index, expressed as CaO/SiO_2 , or also $(\text{CaO} + \text{MgO})/\text{SiO}_2$ ratio (Matthes 2014). The example given in Fig. 1.20 shows the strength development of 50:50 composites of ggbfs and OPC. Both ggbfs materials were ground to the same fineness. The more reactive ggbfs had a CaO/SiO_2 ratio of ~ 1.2 and created a far higher strength gain than the ggbfs of low reactivity, which had a CaO/SiO_2 of ~ 0.9 (Matthes 2014). Furthermore, an elevated alumina content in ggbfs tends to increase early strength development, often on cost of late strength (Matthes 2014; Taylor 1997). Also the presence of minor components can have a significant influence. Especially critical is TiO_2 , which significantly reduces ggbfs reactivity and thus strength development at all ages (Matthes 2014).

As far as the content of crystalline materials is concerned, ggbfs from state-of-the-art granulation facilities usually have a glass or amorphous content of $>95\%$. Typical crystalline phases are merwinite or melilite. Significantly lower amorphous contents will affect strength development, as the latent hydraulic behaviour originates from the glassy phase (Matthes 2014).

Also the fineness of the ggbfs has a major impact on its hydration degree and its strength development, but also on transport properties of the concrete (Chen 2006; Feldrappe et al. 2016; Matthes 2012). Finer grinding mainly improves medium and late strength. The influence on early strength is limited due to the lower hydration rate of ggbfs (Fig. 1.21, Matthes 2014). This is valid for minor and major additions of ggbfs of a fineness ranging from ~ 3500 to $\sim 6000 \text{ cm}^2/\text{g}$ Blaine.

Fig. 1.20 Influence of ggbfs reactivity on development of compressive strength in standard ASTM mortars (50% OPC, 50% ggbfs), Fineness of ggbfs 4500 cm²/g Blaine (Matthes 2014)

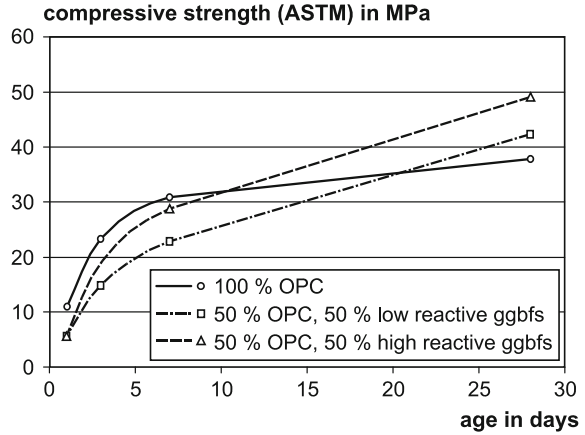
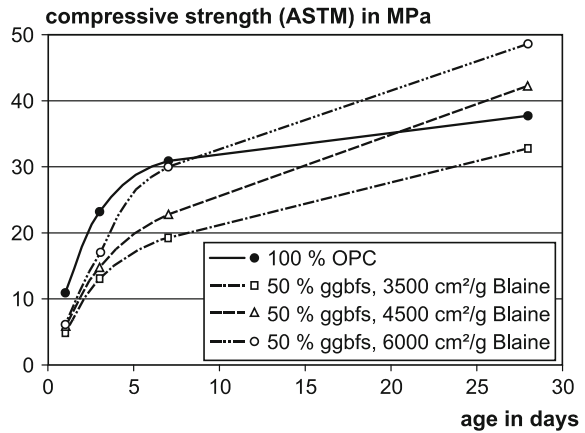


Fig. 1.21 Influence of ggbfs fineness on development of compressive strength in standard ASTM mortars (50% OPC, 50% ggbfs), redrafted after Matthes (2014)



Also concrete design parameters such as w/b, temperature and curing conditions strongly influence the strength gain achievable through ggbfs additions. With increasing w/b, the compressive strength decreases at all ages. The late strength increase due to ggbfs additions tends to be greater for concretes with higher w/b than for concrete with lower w/b (Fulton 1974; Malhotra 1980; Meusel and Rose 1983; Soutsos 1992).

1.6.1.2 Importance of Curing and Curing Temperature

At early ages, all concrete has to be kept in proper moisture and temperature conditions in order to fully develop the required strength and durability properties. As ggbfs has a lower hydration rate than OPC, less hydration products are formed at early stage and

less water is bound. Therefore, concrete with ggbfs is more sensitive to poor curing than OPC concrete, especially if the ggbfs content exceeds 30% of cementitious materials (Fulton 1974). Therefore prolonged curing times have to be applied when using ggbfs in concrete as described in procedures such as ACI 308R (2001).

When proportioning concrete mixtures and matching them with construction schedules, which also depend on early strength development, it needs to be taken into account, that the rate of hydration of ggbfs is more sensitive to concrete temperature than that of OPC. This results at low temperatures, i.e. 10 °C and below, in a lower early strength development of ggbfs concrete compared to OPC concrete, which however, is compensated by a higher late strength development (Fig. 1.22). According to Hewlett (1998) this is especially true for concrete with w/b ratios above 0.5 and s/b ratios above 0.7. Generally, it is not recommended to use ggbfs at temperatures below 10 °C (Neville 1995).

At high temperatures of 30 °C and above, as found in hot climates or during steam curing, for example, a higher early strength is achieved in concrete with ggbfs, however often at the cost of late strength development (Fig. 1.23). The magnitude of this effect depends on the cement and ggbfs fineness and reactivity and on the proportion of ggbfs in the concrete mix (Barnett et al. 2006; Neville 1995; Sato and Masuda 2005). In this context Barnett et al. (2006) recorded, that at elevated curing temperatures the ultimate strength is lower compared to OPC concrete and concluded, that further hydration was prevented due to the formation of dense hydration products around the unhydrated particles. Since the hydration products were not uniformly distributed, a coarser pore structure was obtained. While Barnett et al. (2006) did not observe a clear trend with the cement replacement level, Neville (1995) mentioned, that the harmful effects of high curing

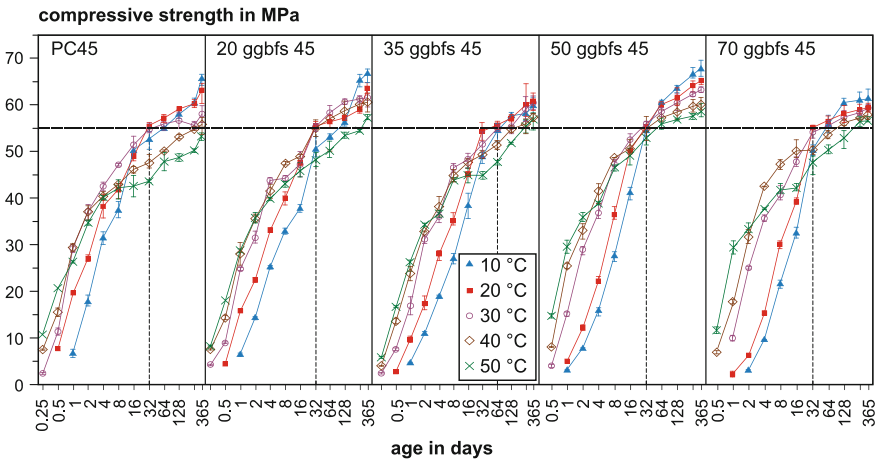
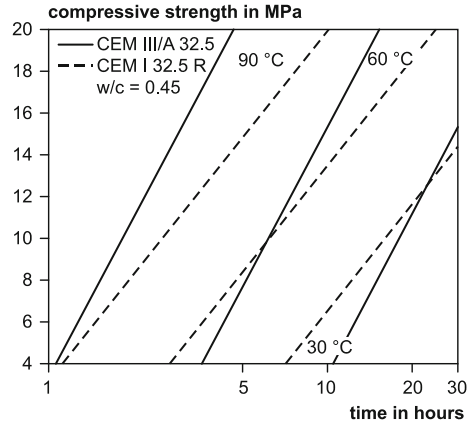


Fig. 1.22 Effect of curing temperature in the range of 10–50 °C on strength development of concrete containing varying amounts of ggbfs, redrafted after Soutsos and Turu’allo (2016)

Fig. 1.23 Influence of temperature on strength development of concretes with OPC (CEM I) and ggbfs composite cement (CEM III/A, 36–65% ggbfs), redrafted after Brand et al. (1982)



temperatures on the long-term strength are not that pronounced in ggbfs concrete, in comparison to OPC concrete.

Also the relative humidity has an influence on the strength development of ggbfs concrete. In Neville (1995), the importance of moist curing in case of ggbfs concrete is emphasized. Poor curing in combination with the initial slow hydration process of ggbfs can lead to evaporation of the capillary pore water which prevents further hydration. This was confirmed by Duran Atis and Bilim (2007), who cured ggbfs and OPC concrete at 22 °C and a relative humidity RH of 65 and 100%. Concrete with ggbfs, especially at elevated amounts, showed a reduction of compressive strength at 65% RH versus 100% RH of 15%. The compressive strength of OPC concrete was reduced by only 6%.

1.6.1.3 Adiabatic Curing Experiments for Simulation of Field Conditions

In order to get an insight how strength data of ggbfs concrete obtained under laboratory conditions at 20–22 °C and close to 100% RH compare to concrete hydrated under field conditions with the influence of the climate and of the dimensions of the concrete elements as described above, Soutsos et al. (2005) compared the strength development of laboratory cured concrete samples with different amounts of ggbfs (Figs. 1.24 and 1.25, left sides) with samples of the same concrete mixes cured under adiabatic conditions (Figs. 1.24 and 1.25, right), which should reflect possible conditions in the field. The authors confirm for the laboratory cured samples the adverse effect of increasing ggbfs contents on early strength, which is set off at later age. Curing under adiabatic conditions revealed and confirmed the higher sensitivity of ggbfs versus OPC to curing temperature. Laboratory cured concrete with 20 and 35% ggbfs achieved at 1 day 90 and 70% of the OPC concrete strength, respectively. Adiabatic curing resulted in 100% OPC strength at 1 day. Concrete with 50 and 70% ggbfs which had developed under laboratory

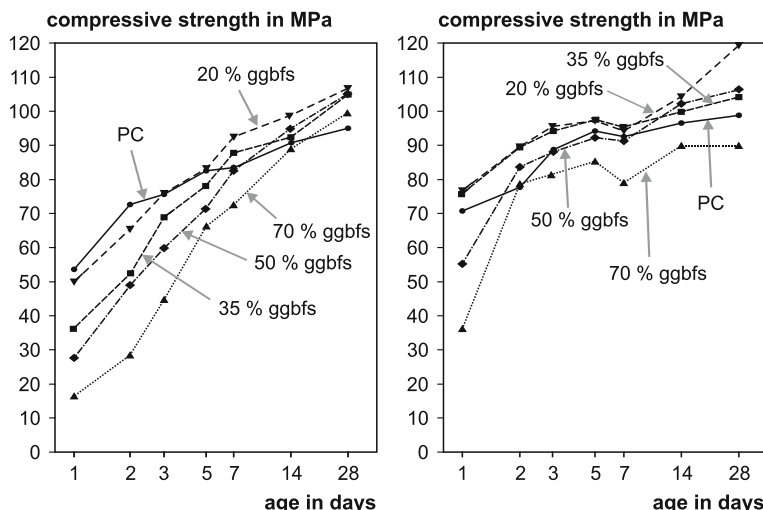


Fig. 1.24 Strength development of concretes with varying ggbfs content at standard 20 °C curing (left) and at adiabatic curing (right), redrafted after Soutsos et al. (2005)

curing 45 and 25% of OPC strength at 2 days achieved essentially 100% of OPC strength during adiabatic curing (Fig. 1.25).

While in mass concrete high temperatures can be achieved, which accelerate hardening, under cold conditions and within thin concrete structural elements the concrete temperatures can be lower than during laboratory curing, which can delay strength development. Similar to Soutsos et al. (2005), Bamforth (1980) compared the strength development of laboratory concrete with OPC, 30% FA or 75% ggbfs cement with concrete cured according to temperature profiles measured in mass concrete foundations (Fig. 1.26). During temperature matched curing, all concretes showed a more rapid early strength development, but reduced late strength development, compared to the laboratory cured samples. Interestingly and in contrast to the results by Soutsos et al. (2005), the 90d strength of the OPC concrete was significantly reduced during temperature matched curing. As found by Soutsos et al. (2005), the late strength of the concretes with SCM was essentially comparable under both curing regimes.

1.6.2 Flexural and Tensile Strength

Ggbfs in concrete does not only improve compressive strength over the service life, but improves also flexural strength, which is a key parameter for concrete pavements (Fig. 1.27, Hogan and Meusel 1981). This has to be attributed to the denser

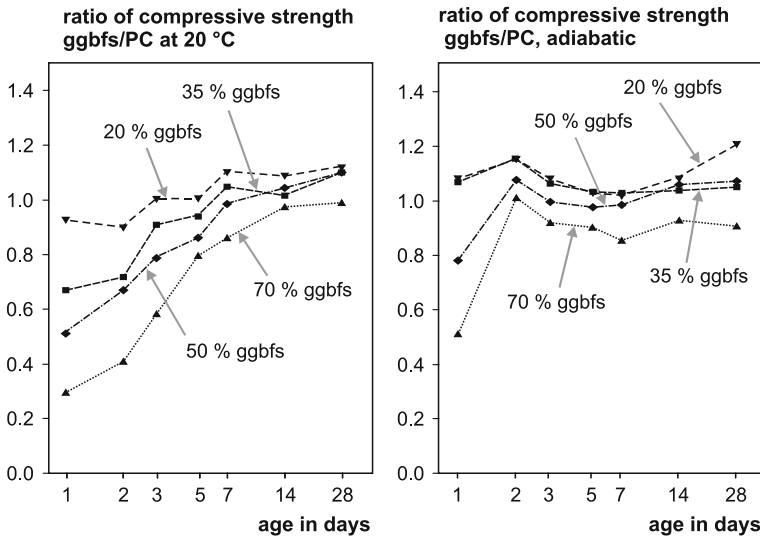


Fig. 1.25 Ratio of compressive strengths of ggbfs concretes to Portland cement concretes under standard (left) and adiabatic (right) curing regimes, redrafted after Soutsos et al. (2005)

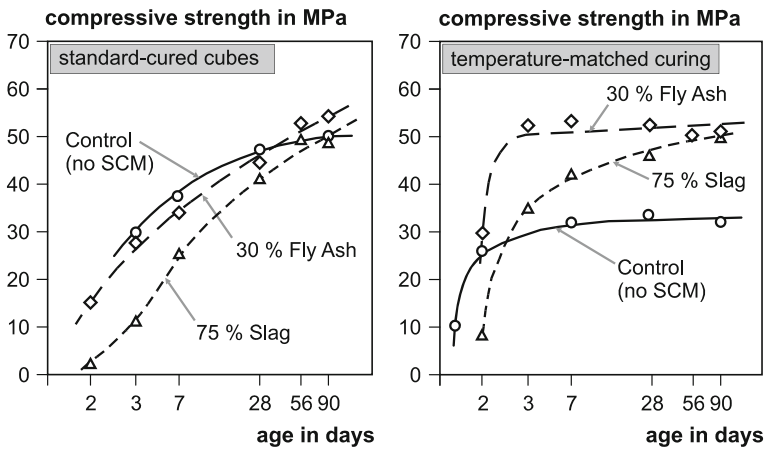
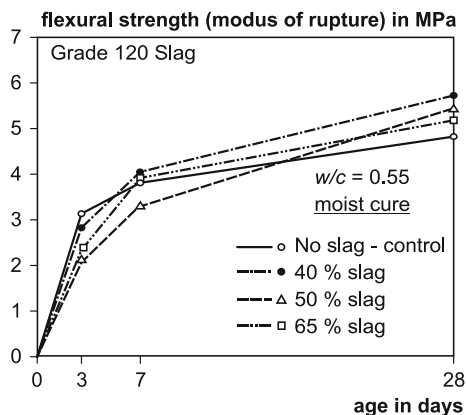


Fig. 1.26 Effect of partial OPC replacement by fly ash or ggbfs on the strength development of 100 mm concrete cubes exposed to standard laboratory curing and temperature matched curing reflecting conditions in mass concrete, redrafted after Bamforth (1980)

microstructure achieved through pore refinement, which also results in an improved bonding between paste and aggregates.

Results obtained from three-point bending tests of water cured mortar prisms, showed at ages below 28 days a decreasing flexural strength with increasing ggbfs content. However at later ages, the concretes with 30–85% ggbfs reached or

Fig. 1.27 Effect of ggbfs on flexural strength, adopted from Hogan and Meusel (1981)



exceeded the flexural strength of OPC concrete. This was confirmed with mortars containing commercial CEM III/A 42.5 and CEM III/C (Fig. 1.28, Gruyaert 2011).

The relation between the flexural strength and compressive strength for mortar prisms containing different amounts of ggbfs from 1 day to 1 year is essentially constant (Fig. 1.29, Gruyaert 2011). The replacement of cement by ggbfs has no significant effect on this relation. In Neville (1995) different empirical formulae, based on a power law function (Eq. 1.2), are quoted to connect the compressive strength (f_c) with the flexural strength (f_{fl}). The values of the parameters for the best fitted curves are given with 1.106 for k and 0.512 for n .

$$f_{fl} = k \cdot (f_c)^n \quad (1.2)$$

For all concretes, an increase of compressive strength results in an increase of flexural strength, but at a decreasing rate. Consequently, the ratio of the compressive strength to the flexural strength increases as time proceeds.

Regarding tensile strength development, Darquennes (2009) shows a more important increase of tensile strength with time for cements with slag compared to Portland cement. At late ages, tensile strength of concrete with ggbfs cements exceeds the one of OPC concrete (Fig. 1.30).

1.7 Impact of Ggbfs on Modulus of Elasticity

The relationship between modulus of elasticity and compressive strength of concrete is essentially unaffected by the presence of SCMs. Existing predictive equations can be used for concrete with and without SCM (Thomas 2013). Thus, the modulus of elasticity of concrete with moderate amounts of ggbfs can be expected to be lower at early age and higher at late ages (Fig. 1.31, Thomas 2013).

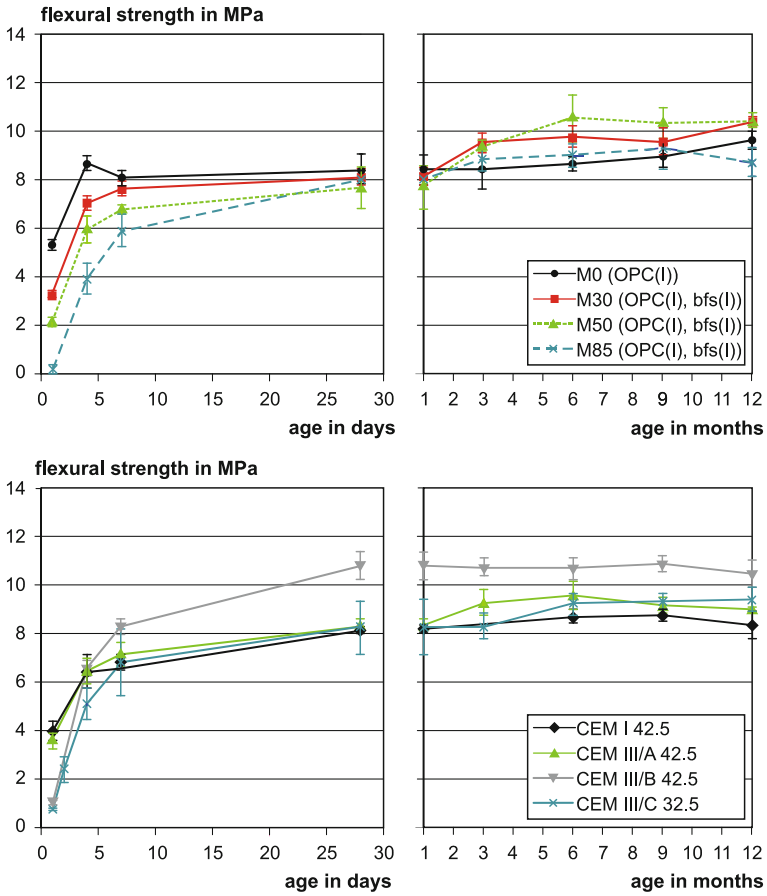


Fig. 1.28 Evolution of the flexural strength of mortar prisms containing different amounts of ggbfs in function of age (top: ggbfs added as a separate component to the mix at OPC replacement levels ranging from 0 to 85%, bottom: blended cements). Redrafted after Gruyaert (2011)

Darquennes (2009) illustrated similarities in the evolution of elastic modulus versus tensile strength for Portland and ggbfs composite cements with high and moderate ggbfs contents (Fig. 1.32, Darquennes 2009).

1.8 Impact of Ggbfs on Concrete Color

Usually concrete containing ggbfs has a lighter color than Portland cement concrete. At elevated ggbfs contents >60% the color could be described as off-white.

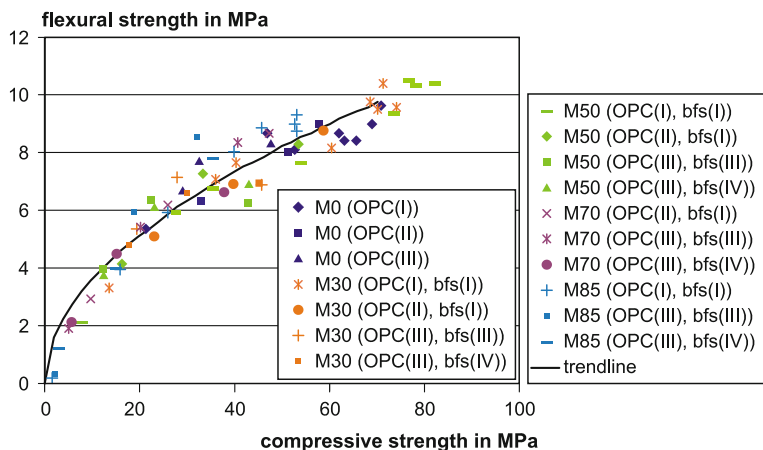


Fig. 1.29 Relation between the flexural strength (three-point bending test) and compressive strength (mean values) of mortar prisms containing different amounts of ggbs, indicated by the numbering in the legend. Redrafted after Gruyaert (2011)

Fig. 1.30 Evolution of tensile strength with time for Portland and ggbs composite cements CEM III/A and CEM III/B, redrafted after Darquennes (2009)

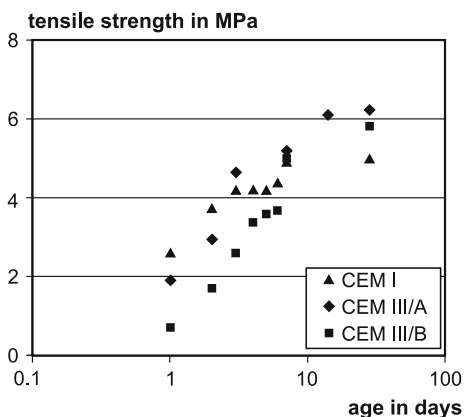


Fig. 1.31 Effect of ggbs on modulus of elasticity, redrafted from Thomas (2013); data from Wainwright and Tolloczko (1986)

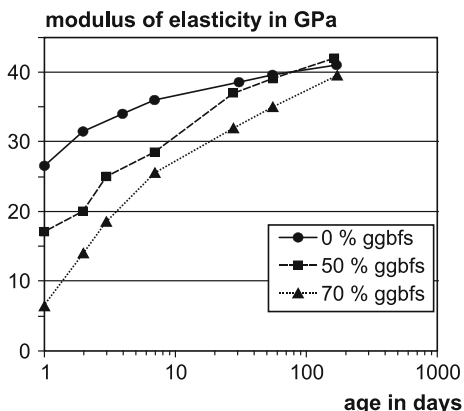
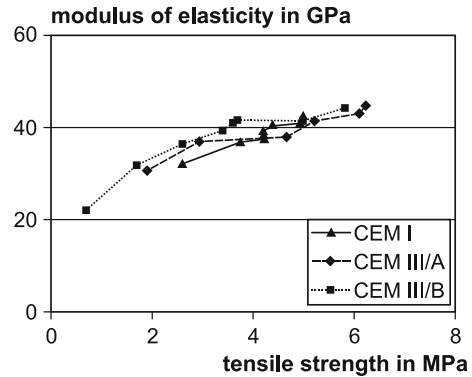


Fig. 1.32 Elastic modulus E versus tensile strength of Portland cement, CEM III/A and CEM III/B, redrafted after Darquennes (2009)



After demoulding, concrete with ggbfs can exhibit greening at the surface—these are stains of dark bluish-green to black color. Also inside, the concrete displays an intense dark coloration.

These dark stains are caused by sulfide minerals, which form during the hydration of the cement. When finely dispersed in the concrete, these compounds cause shades from green/blue to black, according to their composition. The phases are sulfides of mainly iron and manganese in low oxidation states, which are supplied by the ggbfs. The higher the content of ggbfs in the concrete, the higher the fineness of the binder constituents and the lower the water/cement ratio, the higher is the probability of greening.

Generally, greening at the surface of the concrete is a passing effect. In contact with air, the blue/green color vanishes after a few days due to oxidation of the sulfides to sulfates. Exposure to sunshine accelerates this process.

After the greening has vanished, the concrete containing ggbfs usually is lighter than concrete made from OPC.

If the oxygen in the atmosphere cannot reach the concrete, greening will persist. This can be the case if the concrete surface is sealed, e.g. by traces of oil/fat from the formwork or by a glaze applied on bricks, etc. In the case of excess form oil, the surface greening may persist for several weeks until form oil/fat wears off. In applications where concrete would be permanently sealed and greening would be aesthetically disturbing, e.g. glazed concrete bricks, swimming pools etc., the use of ggbfs should be avoided (Slag Cement Association 2002, Matthes 2012, Le Cornec et al. 2017).

In rare cases where surface greening does not vanish after several days of exposure to the atmosphere and the stains are optically disturbing, they can be removed by chemical treatment of the surface of the hardened concrete, e.g. with diluted solutions of hydrogen peroxide, sodium hypochlorite, or diammonium citrate (Problem Clinic 2011).

Inside the concrete, greening will persist as long as oxygen is not entering the system. The denser the structure of the concrete, the longer greening will persist. Thus, greening within the concrete can be regarded as an indicator of the low

permeability and thus, high quality of a concrete. The core of concrete of good quality can maintain its dark color during the whole service life.

1.9 Impact of Ggbfs on Shrinkage and Creep

Regarding the influence of ggbfs on shrinkage, conflicting observations exist. Apparently, drying shrinkage of concrete with ggbfs is similar to OPC concrete (ACI 2011). A review by Hooton et al (2009) found that with low-alumina ggbfs, drying shrinkage of concretes over a range of replacement levels was similar to that of OPC concrete. When ggbfs with alumina content in excess of 12% was used, shrinkage was increased due to alumina reacting with some of the calcium sulfate from the OPC, but this could be corrected by intergrinding calcium sulfate with the ggbfs. There did not appear to be a difference in relative drying shrinkage between concretes made with blended cement and those made with ggbfs added separately at the time of mixing.

Autogenous shrinkage generally increases with decreasing w/b. For concrete with ggbfs it was shown, that with increasing ggbfs content autogenous shrinkage increased (Fig. 1.33, Fulton 1974; Lee et al. 2006). Other authors reported small differences in shrinkage or even reduced shrinkage when ggbfs was used in concrete. Obviously, the amount of ggbfs has an influence on the results as well as the amount of calcium sulfate added (ACI 2011).

The amount of creep of a concrete mainly depends on the concrete design and nature of loading. The most important parameters to reduce creep are a high aggregate content, a low water content, a low w/b, and sufficient maturity prior to loading, because creep depends on the loading stress/concrete strength ratio (Thomas 2013). The conflicting results in literature on the influence of ggbfs on creep are probably due to different concrete designs and testing regimes. Generally,

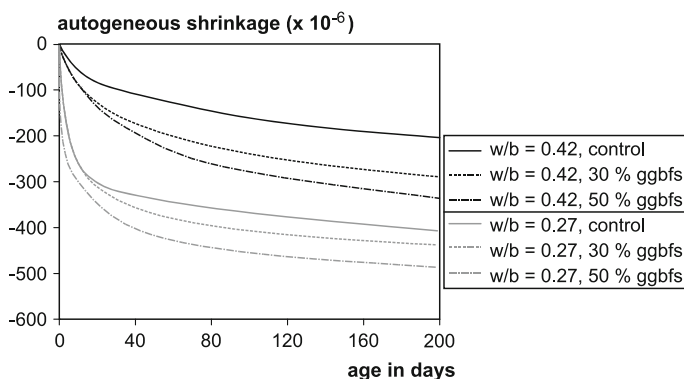
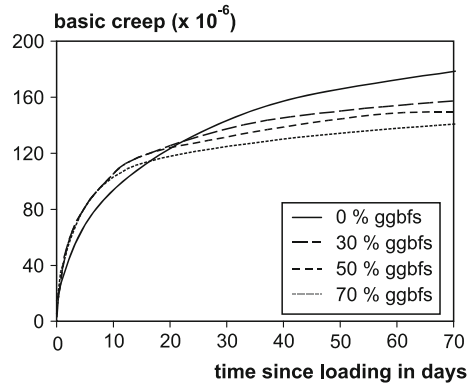


Fig. 1.33 Effect of ggbfs on autogenous shrinkage of concrete redrafted after Lee et al. (2006)

Fig. 1.34 Effect of ggbfs on basic creep of sealed concrete specimens (Brooks et al. 1992)



concrete with major amounts of ggbfs, if loaded at early age, will probably creep more than OPC concrete because of its lower early strength. At late age, this relation is inverse (Fig. 1.34, Brooks et al. 1992).

1.10 Impact of Ggbfs on Transport Properties

1.10.1 Pore Refinement and Permeability

The movement of fluids through the concrete can occur by flow, diffusion, and sorption. Strictly speaking, permeability refers to the flow, and penetrability is a more general term including all processes. However, for concrete research, ‘permeability’ is commonly used instead of ‘penetrability’ (Neville 1995).

The permeability of concrete is not simply related to the total volume of pores, but depends on the size, distribution, shape, tortuosity and continuity of mainly the capillary pores. Since the formation of gel gradually fills the pore space, the pore structure continuously changes and the permeability of pastes decreases with progressing hydration (Neville 1995). The partial replacement of cement by ggbfs lowers the permeability, provided that enough time has elapsed for sufficient slag hydration (Taylor 1997). Pores in concrete are partly and progressively filled with C-S-H resulting from the hydration of ggbfs. Compared to an OPC paste of same w/b and comparable maturity, the total pore volume of a slag cement paste would be comparable, even slightly higher. However, the pore structure is strongly refined (Figs. 1.35 and 1.36, Romberg 1978; Roy and Parker 1983). The volume of fine capillary and gel pores is increased at the cost of the volume of large capillary pores. The capillary pores include macropores and mesopores (Fig. 1.35, Roy and Parker 1983). Macropores, 10,000–50 nm in size, and large mesopores of 50–10 nm enable mass transport processes. The mesopores, 50–2.5 nm, are also responsible for shrinkage at 50–80% RH. Thus, a lower volume of capillary pores reduces pore connectivity and thus reduces mass transport processes.

Fig. 1.35 Effect of ggbfs on the pore size distribution of hardened cement pastes, redrafted after Roy and Parker (1983)

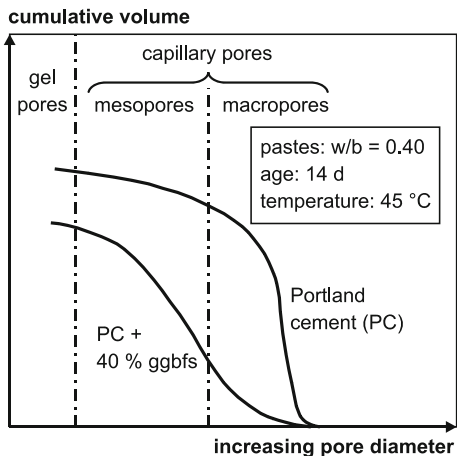
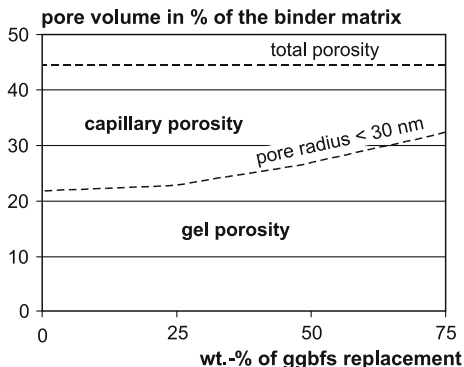


Fig. 1.36 Pore refinement by replacing cement clinker by ggbfs, redrafted after Romberg (1978)



The gel pores, including micropores 2.5–0.5 nm and the interlayer spaces of C-S-H ≤ 0.5 nm influence both, shrinkage and creep.

Due to this pore refinement the strength of the ggbfs concrete is increased. The reduced permeability on the other hand increases the durability of the concrete against chemical attack, such as chloride, sea water or sulfate ingress. A prerequisite, however, is an adequate curing of the concrete.

The pore refinement by ggbfs additions was reported by numerous other researchers (Gruyaert et al. 2013; Hadj-Sadok et al. 2011; Megat Johari et al. 2011; Panesar and Chidiac 2009). In Megat Johari et al. (2011), for example, results of mercury intrusion porosimetry of mortars show that with increasing ggbfs contents between 20 and 60% the relative volume of pores in the size range <30 nm is progressively increased at the expense of the relative volume of pores between 30

and 50 nm. Bouikni et al. (2009) showed on the basis of pore refinement, that a high OPC replacement of 50 and 65% by ggbfs with a Blaine of only 350 m²/kg showed an enhanced performance regarding transport properties, even though total porosity of concrete increased with increasing ggbfs replacement.

De Belie et al. (2010) compared pore size distributions of OPC paste and 50 and 85% ggbfs pastes obtained from data of water vapor sorption isotherms. They found similar pore size distributions in the size range 2–10 nm, but a high reduction of pores in the size range of 1–2 nm when ggbfs was included.

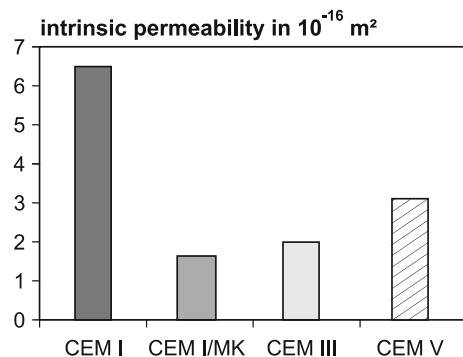
Besides porosity measurements, results of permeability tests can also be found in the literature. The capability of ggbfs to reduce concrete permeability is widely accepted however the extent of its impact varies in literature.

Berndt (2009) performed permeability tests according to ASTM D 5084 on concrete specimens with s/b ratios of 0, 50 and 70%, which were wet cured for 84 days and found similar permeability coefficients for all mixes, ranging from 1.0 to 1.4 × 10⁻¹² m/s. Contrarily, Cheng et al. (2005) obtained permeability coefficients at 91 days, which decreased with increasing ggbfs content. For concrete containing 0, 40 and 60% ggbfs the permeability coefficients obtained by their permeability test setup amounted to 2.56, 1.52 and 1.32 × 10⁻¹³ m/s respectively.

Shi et al. (2009) investigated the influence of ggbfs on nitrogen gas permeability of high strength concrete. They found that replacement percentages between 15 and 60% of cement by ggbfs produce no significant further improvement in gas permeability measured as recommended by RILEM TC116-PCD (RILEM 1999). Niknezhad and Kamali-Bernard (2015) measured the intrinsic permeability of different SCCs based on different cements containing various mineral admixtures. Figure 1.37 shows the significant effect of a CEM III with 62% of ggbfs and CEM V with 25% of ggbfs on the decrease of this intrinsic property.

Nokken and Hooton (2004) found that 35% ggbfs replacement of cement in concrete with w/b = 0.40 resulted in reduced water permeability by a factor of 7, and reduced chloride bulk diffusion by a factor of 3 at an age of 28 d.

Fig. 1.37 Intrinsic permeability of different SCCs based on different binders (Niknezhad and Kamali-Bernard 2015)



1.10.2 Sorptivity

Ggbfs influences the transport properties and sorptivity (Güneyisi and Gesoğlu 2008; Hadj-Sadok et al. 2011; Villagrán Zaccardi et al. 2012), even without significant reduction in the volume of accessible pores. This is connected with an increase in tortuosity and pore refinement.

An informative study on the on-site performance of ggbfs concrete is presented in (Lane 2012), where comparisons are made between the properties of ggbfs concretes and OPC concretes used in the construction of bridge decks, all of them with a w/b of 0.45, which were 12–16 years old at the time of testing. Concrete properties were evaluated on extracted cores from the structure. Ggbfs cement concretes generally showed lower transport properties than OPC concrete. Two thirds of samples of ggbfs concrete showed lower capillary suction rates than the targeted maximum sorptivity values, whereas only one third of OPC concrete met this limit. The absorption rates of ggbfs concretes were about half of those of OPC concrete. Similar results were found for concrete conductivity, where the values for OPC concrete were double those of ggbfs concrete.

Gruyaert (2011) determined the sorptivity coefficients for specimens containing different amounts of ggbfs at different ages from 1 to 12 months, which were oven-dried at 105 °C until constant mass. These sorptivity coefficients decreased with increasing ggbfs contents and decreased as a function of time.

1.10.3 Carbonation

The carbonation resistance of concrete depends mainly on the concrete design parameters, the cement type, especially Portland clinker content, w/c and total water added, and on the applied curing. These parameters determine the long term porosity and permeability of the concrete. Of high importance are furthermore the humidity conditions of the concrete. High carbonation rates are obtained, when the concrete faces conditions between 50 and 70% relative humidity (Hunkeler and Lammar 2012).

Especially the Portland clinker content is decisive for the carbonation rate, because it determines the amount of calcium hydroxide, which is available for carbonation (Fig. 1.38). Consequently, when tested at constant w/b, the carbonation coefficient of concrete increases with the ggbfs content (Brameshuber et al. 2008, 2009; Scholz and Wierig 1988).

Moreover, it is likely that CO₂ also affects the other phases in ggbfs concrete, especially CSH phases, which also can react with CO₂. The reaction mechanism is that CSH decomposes and a porous silica gel is formed. Since the formation of silica gel results from a condensation of Si-OH groups to Si-O-Si linkages and thus polymerisation of the silicate chains in CSH, this reaction is accompanied by carbonation shrinkage. For ggbfs concrete, the resulting effect of carbonation is thus

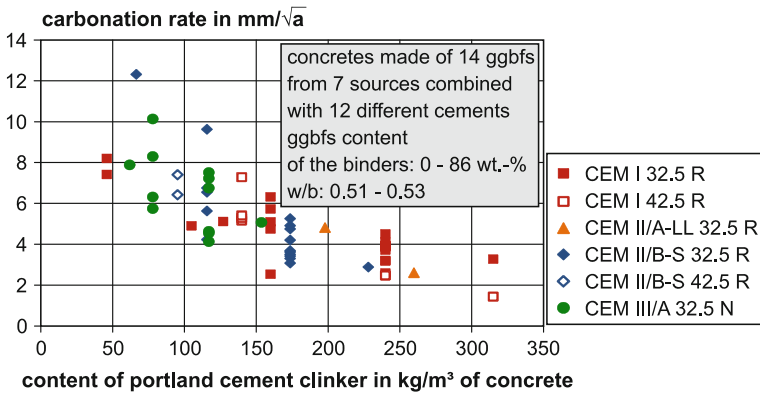


Fig. 1.38 Influence of the Portland cement content on the carbonation rate, results from Brameshuber et al. (2008, 2009), Feldrappe et al. (2016)

a coarsening of the pore structure (Sisomphon et al. 2010; Valenza and Scherer 2007a, b). Borges et al. (2010) mention a reduced overall porosity due to pore filling by carbonates, but an increased permeability due to carbonation shrinkage and cracking for ggbfs pastes after carbonation. In contrast, the carbonation of OPC concrete yields a denser microstructure because of the formation of voluminous calcite, which overcompensates the shrinkage induced by CSH decomposition (Sisomphon et al. 2010).

Decisive is also the w/c or w/b ratio. The data of Osborne (1989) show, that concrete with 40% ggbfs and a w/b of 0.45 would have a comparable carbonation coefficient as concrete with OPC with a w/b of 0.55 (Fig. 1.39, Hunkeler and Lammar 2012).

In practice, the concrete is designed to achieve a certain strength at 28 days and a target workability. In presence of major amounts of ggbfs, the water addition can often be reduced, which would lead to a lower concrete permeability and thus to a lower carbonation depth—provided, that the concrete is properly cured. Most importantly, increasing additions of ggbfs slow down hardening and strength development at early age, so that concrete with major amounts of ggbfs requires adequate curing, more than OPC concrete.

1.10.4 Chloride Ingress

Chloride ingress into concrete can be notably diminished by the addition of ggbfs, with a very significant improvement at replacement levels >50% (Bijen 1996; Tuutti 1982; Bleszynski et al. 2002). This is due to the reduced capillary porosity and the increased chloride binding capacity of ggbfs concrete. Figure 1.40 presents results of free, bound and total chloride content of SCC samples subjected to an

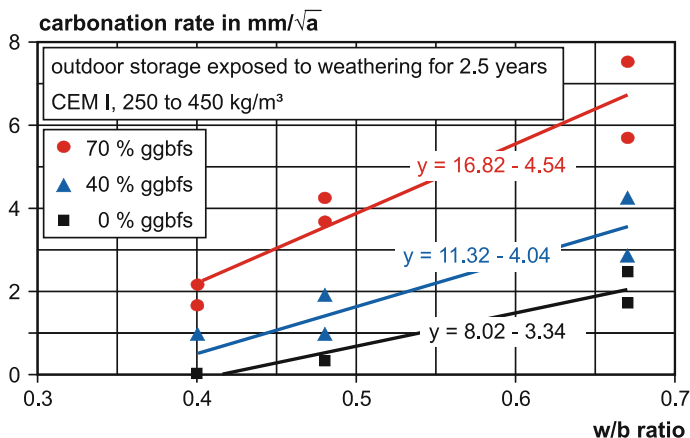
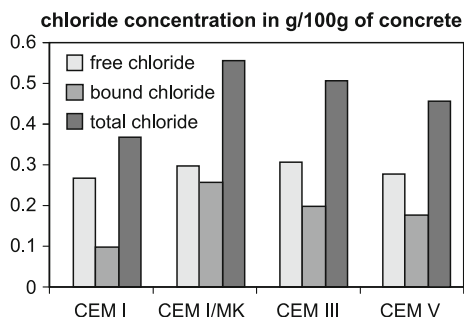


Fig. 1.39 Influence of ggbfs content and w/b on carbonation coefficient (Hunkeler and Lammar 2012), data Osborne (1989)

Fig. 1.40 Total, free and bound chloride contents of different SCC samples (Niknezhad and Kamali-Bernard 2015)



electrical steady-state migration test. SCC based on CEM III containing 62% ggbfs or CEM V with 25% ggbfs exhibit a significantly higher bound chloride content than SCC based on OPC (Niknezhad and Kamali-Bernard 2015).

Other authors confirm, that the replacement of cement by ggbfs, fly ash or silica fume has a positive influence on the binding capacity (Angst et al. 2009; Izquierdo et al. 2004; Tang 1996; Thomas et al. 2012). The use of ggbfs increases the chemical (Dhir et al. 1996; Luo et al. 2003) as well as the physical binding of chlorides (Arya et al. 1990). The calcium aluminate hydrates, which are formed during the hydration of ggbfs, can transform to Friedel’s salt (Dhir et al. 1996; Luo et al. 2003) and the large amount of CSH gel provides a high surface area for adsorption of chloride ions. According to Xu (1997), the higher binding capacity of cement with ggbfs can be attributed to the dilution effect of sulfate ions. He found that the higher binding capacity disappears when the sulfate level in slag cement paste is increased up to that of OPC paste. Luo et al. (2003) also mention that sulfates greatly reduce the binding capability of ggbfs. They concluded that the

lower content of sulfate of ggbfs is one of the reasons for the better performance of ggbfs concrete towards chloride-induced corrosion. Contrarily to these findings, the experiments of Yuan (2008) did not show a higher binding capacity for ggbfs concrete in comparison to OPC concrete.

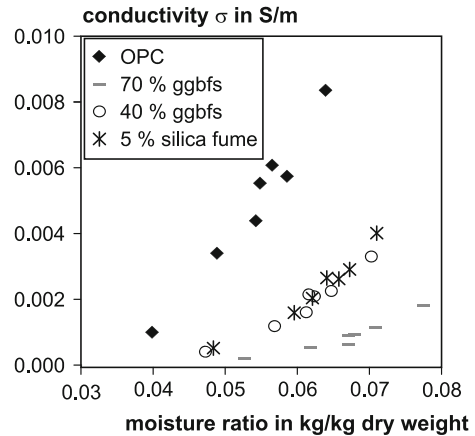
Over time, the chloride diffusion coefficient of ggbfs concrete decreases significantly - more than in conventional concrete. At early ages the chloride diffusion may be higher for ggbfs concrete in comparison with conventional concrete, but at later ages this relationship is inverted (Thomas and Bamforth 1999). Using ultrafine ggbfs (Blaine = 870 m²/kg, BET = 4968 m²/kg), Teng et al. (2013) achieved a 25 and 88% reduction of the chloride migration coefficient according to NT Build 492 (1999) after 28 d of curing with only 30% of cement replacement by ggbfs in concrete with w/b = 0.35 and 0.28 respectively. The ultrafine ggbfs refined the particle size distribution of the cement. Gruyaert (2011) also showed the better performance of ggbfs concrete with regard to chloride ingress with non-steady state migration and diffusion tests. The level of replacement of cement by ggbfs, being 50, 70 or 85%, did not significantly alter the chloride resistance of the concrete. However, the on-going hydration in ggbfs mixes caused still a significant decrease of the migration coefficients with time, while this was not the case for OPC concrete. Chloride bulk diffusion measurements of cores taken from 14 year old concrete slabs showed that 25 and 50% ggbfs replacement of cement reduced values by factors of 2 and 4 respectively, compared to a reference OPC concrete (Hooton et al. 2013).

Studies on samples exposed in marine environment for 25 years have confirmed significant reduction in the chloride ingress rate of concrete when 45–65% replacement levels of cement by ggbfs are employed (Thomas et al. 2008). The obtained penetration depth of the control concrete with w/c of 0.40 and 0.60 was higher than 100 mm, more than twice of the penetration depth of the 45 and 65% ggbfs concretes. On the basis of these results, a modified model for chloride ingress considering the effect of ggbfs has been established and validated (Riding et al. 2013).

1.10.5 Resistivity

Resistivity is affected by the addition of SCMs and the degree of hydration, as they affect the concrete microstructure and the chemistry of pore solution (Osterminsky et al. 2006). The refinement of pores increases resistivity as it reduces the volume of conductive phase (Basheer et al. 2002). Moreover, resistivity is very sensitive towards changes of the chemical composition and pH of the pore solution. Teng et al. (2013) obtained increases of 81 and 462% of concrete resistivity when replacing 30% of OPC with ultrafine ggbfs in w/c = 0.35 and 0.28 concrete, respectively. This variation was much higher than that of other transport properties. The variation of resistivity with time was more pronounced in ggbfs concrete than in OPC concrete. Ggbfs was observed, among SCMs, as the one, which increases

Fig. 1.41 Results of conductivity measurements on mortars with $w/b = 0.38$, as a function of moisture ratio (Olsson et al. 2013)



concrete resistivity the most (Basheer et al. 2002; Polder and Peelen 2002). A similar trend was found for reduction of conductivity, the inverse of resistivity, of ggbfs concretes with time (Nokken and Hooton 2006). Concrete with 35% ggbfs was found to increase resistivity by 230% while 50% ggbfs increased resistivity by 400–500%, depending on the Portland cement and the water/binder ratio of the concrete mixtures (Hooton and Charmchi 2015).

Olsson et al. (2013) studied the relationship between desorption isotherms and conductivities of mortars with different binders. Plotting conductivity versus moisture content of mixes prepared with the same w/c ratio, they found different correlations, depending on the ggbfs content (Fig. 1.41, Olsson et al. 2013). Ggbfs has a strong impact on the conductivity of the pore solution. This is confirmed by Lübeck et al. (2012), who obtained a decreased electrical conductivity of pore liquid due to ggbfs replacement of both, OPC and white cement.

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Chapter 2

Fly Ash

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Abstract Fly ash is an industrial by-product deriving from electricity generating plants. It is the by-product of burning coal or lignite. Fly ash is one of the first artificial admixtures used for the production of concrete since the first decades of the 20th century. Its chemical and mineralogical composition mainly depends on the relevant properties of the raw material used as well as on the type of furnace and the way it is collected. Fly ash may have beneficial effects on both the fresh and hardened properties of concrete mixtures. This chapter provides an extensive report on the use of fly ash in concrete. Reference is made to the regulatory framework governing the application of fly ash, mainly in Europe and America, to factors affecting the quality of the product and to the effects of different fly ashes on fresh and hardened characteristics of concrete.

Keywords Fly ash · Pozzolans · Supplementary cementitious materials
Sustainability · Transport properties

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2.1 Overview, Production of Fly Ash, Pre- and Post-blending, Uses in Concrete

Fly ash, also known as pulverized fuel ash, is produced from burning pulverized coal in electricity generating plants. During combustion, mineral impurities in the coal (clay, feldspar, quartz, and shale) fuse in suspension and float out of the combustion chamber along with exhaust gases. As the fused material rises with the gas flow, it cools and solidifies into spherical glassy particles called fly ash. It is a fine grained, powdery particulate material that is collected from the exhaust gases by electrostatic precipitators or bag filters.

Depending upon the collection system, varying from mechanical to electrical precipitators or bag houses and fabric filters, more than 90% of the ash from the flue gases is retrieved in the form of fly ash. Fly ash accounts for 75–85% of the total coal ash, and the remainder is collected as bottom ash or boiler slag (Fly Ash and Coal Conversion By-Products 1988).

Fly ash produced from thermal power plants is a variable material because of several factors. These factors include (Siddique and Khan 2011):

- (i) type and mineralogical composition of the coal;
- (ii) degree of coal pulverization;
- (iii) type of furnace and oxidation conditions; and
- (iv) the manner in which fly ash is collected, handled and stored before use.

Since no two utilities or plants may have all these factors in common, fly ash from various power plants is likely to be different. Fly ash properties may also vary within the same plant because of load conditions over a 24-hour period. Fly ash particle size primarily depends upon the type of dust collection equipment. It is generally finer than Portland cement. Diameter of fly ash particles usually ranges between 1–150 μm . The chemical composition of fly ash is determined by the types and relative amounts of incombustible material in the coal used. Depending upon the source and makeup of the coal being burned, the components of fly ash vary considerably, but all fly ash includes substantial amounts of silicon dioxide (SiO_2) (both amorphous and crystalline), aluminium oxide (Al_2O_3) calcium oxide (CaO) and ferric oxide (Fe_2O_3), both being endemic components in many coal bearing rock strata. Use of fly ash in concrete was first reported by Davis et al. (1937).

2.2 List of Relevant Standards

ASTM C618 (2015) categorizes fly ashes into the two categories as shown in Table 2.1. Class F fly ashes are usually of lower CaO content. They are normally produced from burning anthracite or bituminous coal. This class of fly ash exhibits

Table 2.1 Requirements for fly ash for use as a mineral admixture in Portland cement concrete (Data taken from ASTM C618-2015)

| Requirements | Fly ash classification | |
|--|------------------------|------|
| | F | C |
| Chemical requirements $\text{SiO}_2 + \text{AlO}_3 + \text{Fe}_2\text{O}_3$, min (%) | 70.0 | 50.0 |
| SO_3 , max (%) | 5.0 | 5.0 |
| Moisture content, max (%) | 3.0 | 3.0 |
| Loss of ignition, max (%) | 6.0 | 6.0 |
| Physical requirements. Amount retained when wet sieved on 45- μm sieve, max (%) | 34 | 34 |
| Pozzolanic activity index, with Portland cement at 28 days, min (%) of control | 75 | 75 |
| Pozzolanic activity index with lime at 7 days, min (MPa) | 5.5 | – |
| Water requirements, max (%) of control | 105 | 105 |
| Autoclave expansion or contraction, max (%) | 0.8 | 0.8 |
| Specific gravity, max variation from average | 5 | 5 |
| Percentage retained on 45 μm sieve, max variation, percentage points from average | 5 | 5 |

pozzolanic property but rarely, if any, self-hardening property. They are predominantly (70%) non-crystalline silica, which is the determining factor for pozzolanic activity. Their crystalline minerals are generally composed of quartz, mullite, and spinels magnetite (Gomes et al. 1999). Class C fly ashes are generally produced from lignite or sub-bituminous coal. This class of fly ash has both pozzolanic and varying degree of self-cementitious properties. Most Class C fly ashes contain more than 15% CaO, but some Class C fly ashes may contain as little as 10% CaO. Class C fly ashes contain predominantly calcium aluminosilica glass which is highly reactive. Crystalline phases in Class C ash include: quartz, lime, mullite, gehlenite, anhydrite, and cement materials such as C_3A , C_2S and $\text{C}_4\text{A}_3\text{S}$.

In Europe, the use of high-calcium fly ashes HCFA(s) blended directly into concrete is not defined by a specific regulative frame as in the case of siliceous fly ashes where there is the standard EN 450-1:2005, but there are definitions in European standards for cement (www.ecoba.com 2007, EUROGYPSUM-ECOBA-VGB 2005). Therefore, the only way of utilizing HCFA as an acceptable mineral admixture is to follow limits according to standard EN 197-1 (2013), where HCFA(s) are symbolized by (W)—calcareous fly ashes. Logically, the main limits in the quality of HCFA(s) are related to the quality of produced cement with a specified replacement level of clinker with HCFA.

In Greece, after long term working period of a relevant Scientific Committee, the Hellenic Specification for the Use of HCFA in Unreinforced Concrete or Cement

Products was approved by the State and put in force in October 2007 (Hellenic technical specifications 2007). Two categories of HCFA are specified in this standard: the EIT1 with $R_{45} \leq 45\%$ and $SO_3 \leq 7\%$ and EIT2 with $R_{45} \leq 30\%$ and $SO_3 \leq 5\%$ and CaO free $\leq 3\%$. EIT refers to unprocessed while EIT refers to processed high calcium fly ash. In Poland, national certifications for the use of HCFA in concrete and road construction have also been issued. In addition, different processing methods of HCFA have been used for improving their quality, such as: sieving for reducing grain size and unburnt carbon content, slaking for reducing hot lime undesirable effect, milling and slaking for increasing fineness, reduction of free lime content and homogenization of HCFA (Papayianni 2010a, b).

2.3 Environmental Sustainability

While the production of energy from coal does produce about 25% of the CO₂ released by the humans globally (World coal Institute 2003), the impact of this can be reduced if beneficial use is made of its by-product, fly ash. Hence, increasing the use of fly ash in construction works can yield significant technical, environmental and economic benefits and such use would contribute considerably to sustainable development. Fly ash has been widely used for numerous applications and no environmental problem resulting from its use has ever been reported (Camoses et al. 2003).

For conventional structural applications, fly ash as a cement constituent in concrete is well accepted. This is due to several factors, including: better consistency during the fresh stage, and superior durability with respect to chloride resistance; coupled with lower material cost. Fly ash concrete also decreases environmental impact by reducing the amount of cement used, thus consuming less energy and releasing fewer greenhouse-gas emissions than conventional Portland cement concrete (Manmohan and Mehta 1981). Utilization of fly ash in cement and concrete has significant environmental benefits such as (Siddique and Khan 2011):

- Increasing the service life of concrete roads and structures by improving concrete durability,
- Reduction in energy use and greenhouse gas and other adverse air emissions when fly ash is used to replace or displace manufactured cement,
- Reduction in amount of coal combustion products that must be disposed in landfills, and
- Conservation of other natural resources and materials.

Making blended cements with fly ash also makes the cement plant utilize their limestone source longer and postpone building new cement plants.

2.4 Fresh Properties of Fly Ash

2.4.1 Size, Shape and Colour

Fly ash particle size is finer than ordinary Portland cement. Fly ash consists of silt sized particles, which are generally spherical in nature and their size typically ranges between 1 and 100 μm . These small glass spheres improve the fluidity and workability of fresh concrete. Fineness is one of the important properties contributing to the pozzolanic reactivity of fly ash. Fly ash colour depends upon its chemical and mineral constituents. It can be tan to dark gray. Tan and light colours are generally associated with higher lime content, and brownish colour with the iron content. A dark gray to black colour is attributed to elevated unburned carbon (LOI) content. Fly ash colour is usually very consistent for each power plant and coal source (Siddique and Khan 2011).

2.4.2 Fineness

Fineness of fly ash is most closely related to the operating condition of the coal crushers and the grindability of the coal itself. Fineness of fly ash is related to its pozzolanic activity. For fly ash use in concrete applications, fineness is defined as the percent by weight of the material retained on the 45 μm (#325) sieve. ASTM C618 (2015) limits the maximum amount of fly ash retained on the 45 μm (#325) mesh sieve on wet sieving as 34%. Generally, a large fraction of ash particles is smaller than 3 μm in size. In bituminous ashes, the particle sizes range from less than 1 to over 100 μm . A coarser gradation can result in a less reactive ash and could contain higher carbon content.

2.4.3 Specific Gravity

The specific gravity is related to shape, color and chemical composition of fly ash particles. In general, specific gravity of fly ash may vary from 1.3 to 2.8. Canadian fly ashes have specific gravity ranging between 1.94 and 2.94, whereas American ashes have specific gravity ranging between 2.14 and 2.69 (Siddique and Khan 2011).

2.4.4 Pozzolanic Activity

The property of low calcium fly ashes possessing little or no cementing value by themselves, to react with calcium hydroxide (usually from cement hydration) in the

presence of water and produce highly cementitious water insoluble products, is called pozzolanic reactivity. The meta-stable silicates present in self-cementitious high calcium fly ash react with calcium ions in the presence of moisture to form water insoluble calcium-alumino-silicate hydrates.

The pozzolanic activity of a fly ash depends on its: (1) fineness; (2) calcium content; (3) structure; (4) specific surface; (5) particle size distribution; and (6) LOI content (Joshi 1979). Several investigators have reported that when fly ash is pulverized to increase fineness, its pozzolanic activity increases significantly. However, the effect of increase in specific surface area beyond 600 m²/kg is reported to be insignificant (Joshi 1979).

2.4.5 Particle Morphology

Fly ash particles consist of clear glassy spheres and a spongy aggregate. Several morphological investigations have been carried out on particle shape and surface characteristics of various types of fly ashes using scanning electron microscope (SEM) and energy dispersive x-ray analysis (EDXA) (Diamond 1985; Mehta 1988). Scanning electron micrographs of different fly ashes show the typical spherical shape of fly ash particles, some of which are hollow. The hollow spherical particles are known as cenospheres or floaters as they are very light and tend to float on water surface. Cenospheres are unique free flowing powders composed of hard shelled, hollow, minute spheres. Cenospheres are made up of silica, iron and alumina. Cenospheres have a size range from 1 to 500 µm. Colours range from white to dark gray.

Sometimes fly ashes may also contain many small spherical particles within a large glassy sphere, called pherospheres. The exterior surfaces of the solid and hollow spherical particles of low-calcium oxide fly ashes are generally smooth and better defined than those of high-calcium oxide fly ashes which may have surface coatings of material rich in calcium (Mehta 1988).

2.4.6 Moisture

Any amount of moisture in Class C fly ash may cause hardening from hydration of its cementitious compounds. Even surface spraying may cause caking. To prevent caking and packing of the fly ash during shipping and storage and to control uniformity of fly ash shipments, a 3.0% limit on moisture content is specified in ASTM C618 (2015). Therefore, it is important that such ashes are kept dry before being mixed with cement.

2.4.7 Chemical Composition

Chemical composition of fly ashes include silica (SiO_2), alumina (Al_2O_3), and oxides of calcium (CaO), iron (Fe_2O_3), magnesium (MgO), titanium (TiO_2), sulphur (SO_3), sodium (Na_2O), and potassium (K_2O), and Loss of ignition (LOI). Amongst these, SiO_2 and Al_2O_3 together make up about 45–80% of the total ash. The sub-bituminous and lignite coal ashes have relatively higher proportion of CaO and MgO and lesser proportions of SiO_2 , Al_2O_3 and Fe_2O_3 as compared to the bituminous coal ashes. Table 2.2 presents the chemical analysis of different American fly ashes (ACI 226 1987).

2.4.8 Mineralogical Characteristics (References)

Mineralogical characterization determines the crystalline phases that contain the major constituents of fly ash. Fly ashes usually have 15–45% crystalline matter. The high-calcium ashes contain larger amounts of crystalline matter ranging between 25 and 45% (McCarthy et al. 1988).

Although high-calcium Class C ashes may have less glassy or amorphous material, they do contain certain crystalline phases such as anhydrite (CaSO_4), tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$), calcium sulpho-aluminate ($\text{C}_4\text{A}_3\text{S}$) and very small amounts of free lime (CaO) that participate in producing cementitious compounds (Siddique and Khan 2011). Also, glassy phase in Class C ashes is usually more reactive. The glassy particles in Class C fly ashes contain large amounts of calcium, which possibly makes the surface of such particles highly strained, and probably, this is the reason for the highly reactive nature of Class-C fly ashes (Papayianni-Papadopoulou 1981; Papayianni 2010a, b).

Anhydrite (CaSO_4) is formed from the reaction of CaO , SO_2 and O_2 in the furnace or flue. Quantity of anhydrite increases with the increase in SO_3 and CaO contents. It has a significant role in hydration behavior of fly ash because it participates along with tricalcium aluminate and other soluble aluminates to produce ettringite and calcium sulphoaluminate hydrate (Papayianni-Papadopoulou 1981;

Table 2.2 Composition of Class F and Class C fly ashes (data taken from ACI 226 1987)

| Parameter (%) | Class F fly ash | Class C fly ash |
|------------------|-----------------|-----------------|
| Silicon dioxide | 45–64.4 | 23.1–50.5 |
| Calcium oxide | 0.7–7.5 | 11.6–29.0 |
| Aluminum oxide | 19.6–30.1 | 13.3–21.3 |
| Iron oxide | 3.8–23.9 | 3.7–22.5 |
| Sodium oxide | 0.3–2.8 | 0.5–7.3 |
| Magnesium oxide | 0.7–1.7 | 1.5–7.5 |
| Potassium oxide | 0.7–2.9 | 0.4–1.9 |
| Loss on ignition | 0.4–7.2 | 0.3–1.9 |

Table 2.3 Concentration range of minerals in bituminous fly ashes (data taken from Alonso and Wesche 1992)

| Minerals | Concentration (%) |
|-----------|-------------------|
| Mulite | 6.5–9.0 |
| Hematite | 1.1–2.7 |
| Magnetite | 0.8–6.5 |
| Quartz | 2.2–8.5 |
| Free CaO | Up to 3.5 |

Papayianni 1996; Papayianni 2010a, b; Mehta 1986a, b). Tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$) is one of the most important crystalline phases to identify and quantify the fly ash because it contributes to ettringite formation, and also in self-hardening reactions as well as disruptive sulfate reactions in hardened concrete.

Periclase is the crystalline form of magnesium oxide (MgO). Presence of this form of MgO in fly ash affects the soundness of the resulting concrete through its expansive hydration to brucite, $\text{Mg}(\text{OH})_2$ (Papayianni-Papadopoulou 1981; Mehta Mehta 1986a, b). Crystalline iron oxide, ferrite spinel and/or hematite are generally found in all fly ashes. In most of the fly ashes, about 0.33–0.50% of iron is present as crystalline oxide. The reactivity of fly ash is, however, dependent on the Fe_2O_3 content in the glassy phase (Siddique and Khan 2011). The concentrations of important minerals found in bituminous coal fly ashes, as reported by Alonso and Wesche (1992) are given in Table 2.3.

2.5 Effect of Fly Ash on the Fresh Properties of Cement and Concrete

Fresh concrete is a concentrated suspension of particulate materials of different densities, particle sizes and chemical composition in a solution of lime and other compounds. Fresh concrete properties include workability, air-entrainment, bleeding and segregation, pump ability, compactability, and finishability. In fresh concrete, fly ash plays an important role in the fluidity of concrete.

2.5.1 Workability

The spherical shape and glassy surface of most fly ash particles, usually finer than cement, permit greater workability or slump for equal water–cement ratios.

Lane and Best (1982) concluded that the use of fly ash as partial replacement of cement usually reduces the water content for a given consistency. With proper proportioning of the concrete, cohesion and plasticity are adequate, and bleeding is reduced. Helmuth (1987) has reported that if the water reduction were due to the

spherical shape of the fly ash particles or the lack of chemical reactivity, the water reduction would progressively increase with increase in fly ash content.

Brown (1982) conducted several studies with fly ash replacing cement and fine aggregate at levels of 10–40% by volume. He concluded that for each 10% of ash substituted for cement, the compacting factor or workability changed to the same order as it would by increasing the water content of the mix by 3–4%. When fly ash was substituted for sand or total aggregate, workability increased to reach a maximum value at about 8% ash by volume of aggregate. Further substitution caused rapid decrease in workability.

Yuan et al. (1982) showed that the water demand decreased by adding 15 and 20% fly ash and increased when fly ash content was higher than 20%. This was attributed to the increase in water demand from the introduction of additional specific surface and porous grains, and the decreased deflocculation resulting from the adsorption of fine grains of fly ash on cement clusters. Owens (1979) reported that with the use of fly ash containing large fraction of particles coarser than 45 μm or a fly ash with high amount of unburnt carbon, exhibiting loss on ignition more than 1%, higher water demand was observed. Water demand was noticeably increased to maintain the desired level of fluidity. The effect of coarse fly ash particles on the water demand of concrete mixtures is clearly shown in Fig. 2.1.

At a given content of cementitious materials in concrete the addition of fly ash generally reduces water demand and improves workability. However, some fly ashes may increase the water demand by up to 5% (Gebler and Klieger 1986). Jiang and Malhotra (2000) have studied the effect of 8 different fly ashes on the water demand, and the experimental results are given in Table 2.4. At a given fly ash content of 55% by mass of cementitious materials, 8.8–19.4% reduction in the water demand was achieved depending on the quality of the fly ashes. The

Fig. 2.1 Influence of coarse particles of fly ash on the water required for equal workability in concrete (data taken from Owens 1979)

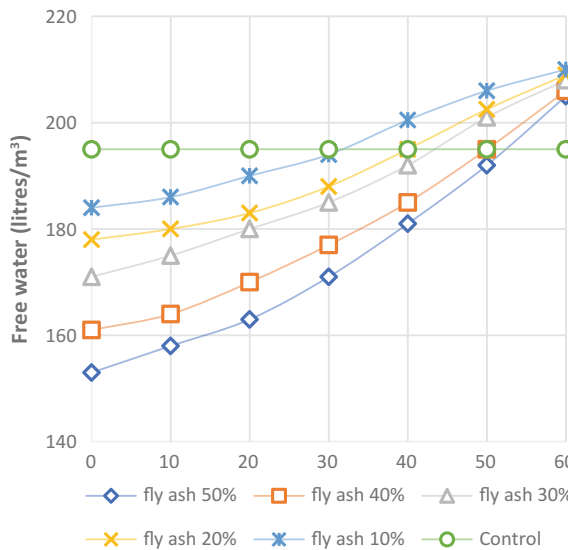


Table 2.4 Reduction in the water demand due to the addition of different fly ashes (data taken from Jiang and Malhotra 2000)

| Fly ash | Fly ash-to-cementitious material ratio | Water-to-cementitious material ratio | Reduction in water demand, % |
|---------|--|--------------------------------------|------------------------------|
| – | 0 | 0.43 | – |
| F1 | 55 | 0.38 | 11.2 |
| F2 | 55 | 0.39 | 8.8 |
| F3 | 55 | 0.37 | 14.1 |
| F4 | 55 | 0.35 | 17.6 |
| F5 | 55 | 0.34 | 18.8 |
| F6 | 55 | 0.38 | 9.4 |
| F7 | 55 | 0.38 | 10.6 |
| F8 | 55 | 0.34 | 19.4 |

reduction of the water demand is often attributed to the spherical shape and plain surface of fly ash particles, called “ball-bearing effect” and also to the improved grain size composition, called “filling effect”. Due to the electrical charges of fly ash, the finer fly ash particles are adsorbed on the surface of cement particles. If enough fine fly ash particles are present to cover the surface of cement particles, the cement particles will become deflocculated and the water demand for a given workability will be reduced (Roy 1987). In this manner, fly ash has similar action on the water demand as plasticizers (Helmuth 1987).

The effect of fly ash on the water demand is determined mainly by its fineness, grain size composition, shape and carbon content. The increase in fineness generally results in a reduction of the water demand, which is attributed to the improved grain composition of the cement and fly ash mixture (Efes 1980). The spherical particle of fly ash contributes to the “ball bearing effect” and therefore has a positive effect on reducing the water demand (Braun and Gebauer 1983). High carbon content in fly ash has a negative effect on the workability due to the water absorption by porous carbon particles (Neville 1995).

The effect that fly ash has on the fresh properties of concrete mixtures strongly depends on its chemical composition (Low calcium or high calcium ash) and the fineness of the ash. According to Papayianni (2010a, b) the role of high calcium fly ash (HCFA) in the rheology of fresh concrete is governed by the fact that these fly ashes more or less take part in the hydration reaction of cementitious systems as soon as they are mixed with water. Regarding the water demand of HCFA concrete mixtures, it could be said that the issue of Abdun Nur (1961) about HCFA improving the workability is not verified in all cases. Moderately cementitious HCFAs (with relatively low CaO and SO₃ content) usually do not greatly affect the water required for a given workability, while the highly cementitious fly ashes (high content in CaO, Al₂O₃ and SO₃) increase the water demand. This extra water does not have so close relation to HCFA carbon content nor to the coarse fragment of grains >45 μm, but rather to the presence of free lime, calcium aluminates and

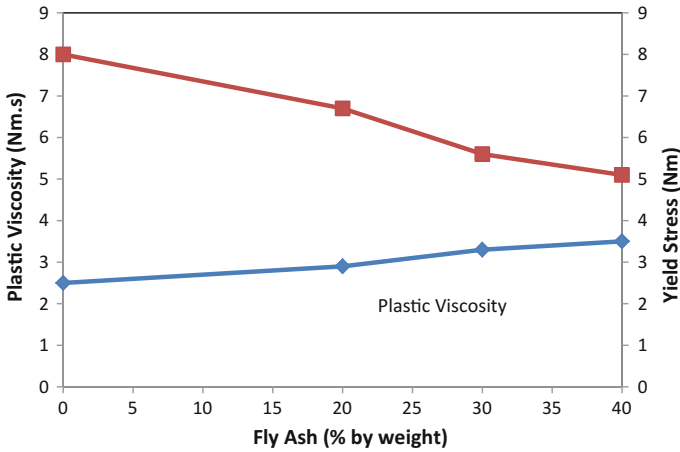


Fig. 2.2 Influence of fly ash content on plastic viscosity and yield stress of concrete (data taken from Khan 2010)

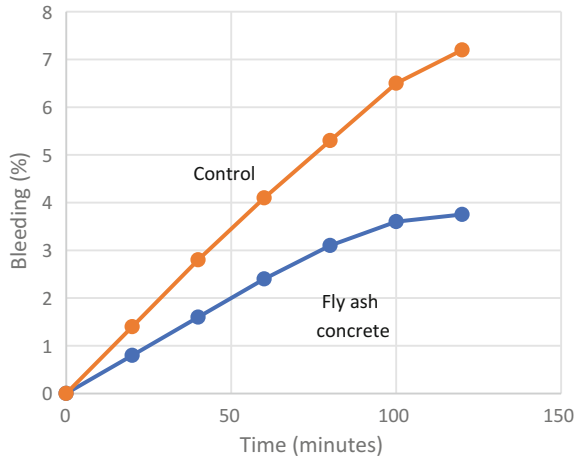
calcium sulfoaluminates (concentrated in fine particles) which are rapidly hydrated by binding a great number of H_2O molecules in their phase.

In order to develop a theoretical concept and understanding of the rheology of fresh fly ash concrete, Tattersall and Banfill (1983) suggested mathematical expressions relating the yield value (τ) and the plastic viscosity (μ) to the volumetric proportions of concrete mix constituents, in terms of Bingham model. Yield stress and plastic viscosity varied with volumetric proportions of concrete mix constituents, water-to-cement ratio, replacement levels of cement/aggregate with fly ash, and fineness of fly ash. An increase in the volume of the paste at a constant ratio of ash to total cementitious material resulted in an increase in plastic viscosity. Apparently because of fine particle size and smooth glassy texture as well as spherical shape, fly ash acts to plasticize concrete at a given water content when used as partial replacement of cement or fine aggregate. Khan (2010) reported that the incorporation of 20, 30 and 40% fly ash increased the plastic viscosity of concrete whilst the yield stress of concrete reduced with increase in fly ash content, see Fig. 2.2.

2.5.2 Bleeding and Segregation

Incorporation of fly ash in mortar or concrete significantly reduces the bleeding and segregation. This is due to the lubrication effect of the glassy spherical fly ash particles and the increased ratio of solids to liquid which make the concrete less prone to segregation and improve concrete pumpability. Figure 2.3 shows the bleeding rate of fly ash concrete compared to that of control concrete (CEGB 1967).

Fig. 2.3 Relative bleeding of control and fly ash concretes (data taken from CEGB 1967)



Joshi and Lohtia (1993) used Alberta fly ashes in making high-volume fly ash concrete mixes, and concluded that fly ash concrete mixes were more cohesive than control mixes. During the slump test, the fly ash concrete mixes subsided more slowly and gradually than the control mixes which exhibited abrupt fall or subsidence.

In general, concrete containing fly ash is cohesive and has reduced bleeding and segregation. The addition of fly ash can, therefore, solve the excessive bleeding problem particularly in concretes which are deficient in fine aggregates. Figure 2.3 shows a comparison of the bleeding of concretes with and without fly ash. The reduced bleeding is due to the reduced water demand by the addition of fly ash. Gebler and Klieger (1986) have reported the correlation between the reduced bleed water and the reduced water demand. Another reason is that finer fly ash provides a greater surface area of solid particles for a given workability (Idorn and Henriksen 1984).

2.5.3 *Setting Time*

With the addition of water to concrete, hydration reaction starts and the cement paste begins to stiffen accompanied by heat release. The rate of stiffening of cement paste is expressed in terms of setting time. Generally, the effect of fly ash on the setting time depends upon the characteristics and amount of fly ash used.

The interacting effects of fly ash with other chemical and mineral admixtures may also influence the setting of concrete. Investigations have revealed that the addition of low-calcium Class F fly ashes result in retarding the cement setting. High-calcium fly ashes, generally low in carbon and high in reactive and/or cementitious components sometimes exhibit the opposite behavior, i.e. reduced

Table 2.5 Properties of some Canadian fly ashes (data from Carette and Malhotra 1984)

| Fly ash source | Type of coal | Major chemical compounds (% by weight) | | | | | |
|----------------|----------------|--|--------------------------------|--------------------------------|------|------|------|
| | | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | LOI |
| 1 | Bituminous | 47.1 | 23.0 | 20.4 | 1.21 | 1.17 | 2.88 |
| 2 | Bituminous | 44.1 | 21.4 | 26.8 | 1.95 | 0.99 | 0.70 |
| 3 | Bituminous | 35.5 | 12.5 | 44.7 | 1.89 | 0.63 | 0.75 |
| 4 | Bituminous | 38.3 | 12.8 | 39.7 | 4.49 | 0.43 | 0.88 |
| 5 | Bituminous | 45.1 | 22.2 | 15.7 | 3.77 | 0.91 | 9.72 |
| 6 | Bituminous | 48.0 | 21.5 | 10.6 | 6.72 | 0.96 | 6.89 |
| 7 | Sub-bituminous | 55.7 | 20.4 | 4.61 | 10.7 | 1.53 | 0.44 |
| 8 | Sub-bituminous | 55.6 | 23.1 | 3.48 | 12.3 | 1.21 | 0.29 |
| 9 | Sub-bituminous | 62.1 | 21.4 | 2.99 | 11.0 | 1.76 | 0.70 |
| 10 | Lignite | 46.3 | 22.1 | 3.10 | 13.3 | 3.11 | 0.65 |
| 11 | Lignite | 44.5 | 21.1 | 3.38 | 12.9 | 3.10 | 0.82 |

setting time. Not all Class C fly ashes cause rapid setting. Ramakrishan et al. (1981) reported an increase in setting time with the use of high-calcium fly ash in concrete. Lane and Best (1982) concluded that the influence of fly ash on setting time is less than the influence due to cement fineness, water content, and ambient temperature. Carette and Malhotra (1984) studied the effect of Canadian fly ashes on the fresh concrete properties. Fly ashes were collected from 11 different sources. Cement was replaced with 20% fly ash in all the mixes. The w/b ratio was equal to 0.40 for all mixtures. Chemical properties of fly ashes are given in Table 2.5 and fresh concrete properties in Table 2.6.

Table 2.6 Properties of concrete with Canadian fly ashes (data from Carette and Malhotra 1984)

| Mix No | Cement (kg/m ³) | Slump (mm) | Air (%) | Bleeding (%) | Setting time (h:min) | |
|---------|-----------------------------|------------|---------|--------------|----------------------|-------|
| | | | | | Initial | Final |
| Control | 295 | 70 | 6.4 | 2.9 | 4:10 | 6:00 |
| F1 | 236 | 100 | 6.2 | 3.1 | 4:50 | 8:00 |
| F2 | 237 | 102 | 6.2 | 4.6 | 7:15 | 10:15 |
| F3 | 237 | 100 | 6.2 | 5.1 | 5:20 | 8:10 |
| F4 | 238 | 110 | 6.3 | 4.3 | 6:20 | 8:25 |
| F5 | 237 | 65 | 6.4 | 2.7 | 5:15 | 8:55 |
| F6 | 238 | 75 | 6.5 | 2.6 | 4:30 | 6:50 |
| F7 | 239 | 100 | 6.1 | 2.9 | 4:15 | 6:20 |
| F8 | 236 | 115 | 6.2 | 5.6 | 5:10 | 7:30 |
| F9 | 236 | 100 | 6.4 | 4.4 | 5:25 | 9:00 |
| F10 | 237 | 130 | 6.5 | 2.5 | 4:45 | 7:00 |
| F11 | 237 | 140 | 6.6 | 0.6 | 4:00 | 6:05 |

Rodway and Fedirko (1989) studied the setting times of concretes made with varying percentages (0, 56, 68 and 76%) of fly ash of the total cementitious material. High fly ash concrete mixes exhibited increasingly greater initial setting times of 22–42.5 h with increasing fly ash content from 56 to 76% compared to 7.6 h for the control mix without fly ash. They observed that delays appeared to be related to the problem of compatibility between cementitious materials and superplasticizer used to maintain workability. Sivasundram et al. (1990) investigated the setting time of high-volume fly ash (HVFA) concrete mixes, and concluded that the initial setting time of 7.50 h was comparable to that of the control concrete, whereas the final setting time was extended by about 3 h as compared to that of the control concrete. Joshi et al. (1993) examined three different sub-bituminous Alberta coal ashes at replacement levels of 40–60% by cement weight to produce superplasticized and air entrained concretes. They observed that fly ash concrete achieved an initial setting time of 5–11 h as compared to about 5 h for neat Portland cement concretes. The final setting time varied from 10 to 13 h compared to 7 h for control mixes without fly ash.

2.5.4 Chemical Admixture Interaction

Ng and Justnes (2016) studied the influence of 5 different plasticizers on cementitious paste in which the OPC was replaced by siliceous (Class F) fly ash (FA) in increments of 20–60% by mass and with a constant water-to-powder ratio of 0.36. The plasticizers were lignosulfonate (LS), naphthalene sulfonate-formaldehyde condensate (NSF) and 3 different polycarboxylate ethers (PCEs). The flow resistance (FR) of the pastes decreased steadily with increasing replacement of OPC by FA in spite of increased total volume of solids resulting from the density of FA being lower than OPC. The decrease in FR is due to the spherical nature of FA and

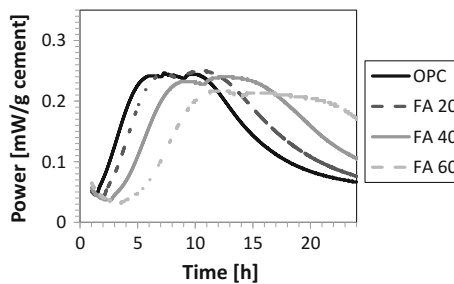


Fig. 2.4 Heat of hydration (Power) evolution for cementitious pastes with 0 (OPC), 20 (FA20), 40 (FA40) and 60% (FA60) replacement of OPC with FA. All pastes are plasticized by 0.2% dry NSF of powder mass (data taken from Ng and Justnes 2016)

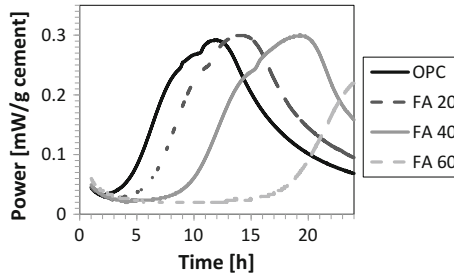


Fig. 2.5 Heat of hydration (Power) evolution for cementitious pastes with 0 (OPC), 20 (FA20), 40 (FA40) and 60% (FA60) replacement of OPC with FA. All pastes are plasticized by 0.2% dry PCE of powder mass (data taken from Ng and Justnes 2016)

the low reactivity of the glass phase at this early stage. Furthermore, there is much lower interaction of the plasticizers with FA than with cement, so the effective plasticizer-to-cement ratio is increasing and thereby also increasing the retardation of the cement as illustrated in Figs. 2.4 and 2.5 for NSF and one PCE, respectively. Hence, the required plasticizer dosage for equal flow and/or acceptable setting time has to be reduced when cement is replaced by Class F FA. The situation may be different for Class C FA depending on its C_3A content etc.

2.6 Early Age Strength Development

Figure 2.6 shows the effect of temperature on the strength development of fly ash concrete grade 40. At an early age, in all mixes, the strength development of PC and FA concretes at higher curing temperatures is faster than at lower curing temperatures. This is attributed to an increase in the hydration rate. However, at a later age, the strength achieved at higher curing temperatures was reduced. The later age strength of Portland cement was much more detrimentally affected by higher curing temperatures than that of fly ash concretes, the so-called “crossover” effect. Furthermore, this effect appeared earlier for Portland cement concretes than FA concretes. The crossover effect is significantly delayed with increasing cement replacement by fly ash (Elsageer 2011; Hatzitheodorou 2007; Soutsos et al. 2016). The later age strengths of the 30 and 45% fly ash concrete samples cured at 30 and 40 °C, i.e. other than those cured at 50 °C, did not significantly get affected by the high early age curing.

The strength development under all curing temperatures relative to achieved standard 20 °C cured specimens for 32-day strength is shown in Fig. 2.7. The ratio of the strength development at all curing temperatures of fly ash concretes was slightly below the equivalent PC concrete up to the age of 4 days, except from the

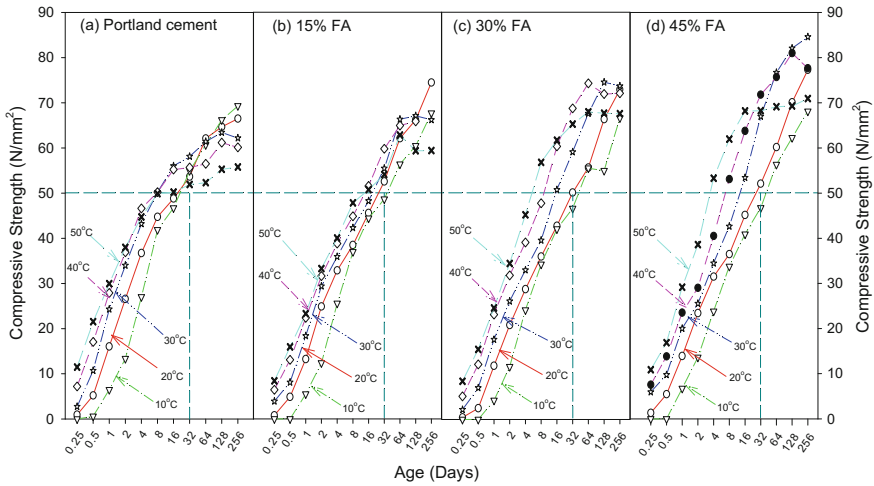


Fig. 2.6 Strength development of PC and FA concrete under 10, 20, 30, 40 and 50 °C curing temperatures (grade 40) (data from Elsageer 2011)

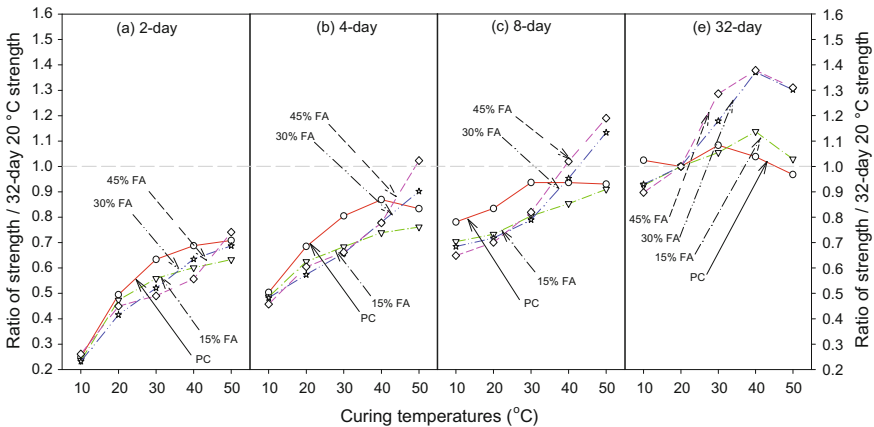


Fig. 2.7 Relative strength of all concrete mixes (grade 40) (data taken from Elsageer 2011)

45% FA concrete that reached more than 100% of its 32-day strength at 20 °C at the age of 4 days. It can be also seen that the 45% FA concrete cured at 40 °C is capable of reaching the 32 days standard 20 °C cured strength within just 8 days. On the other hand, 30% FA concrete reached more that 100% of the 32 days standard cured strength within 8 days, only when cured at 50 °C.

The strength development of all the concretes under adiabatic conditions is shown in Fig. 2.8 (Elsageer 2011). Higher early age strength was achieved for all

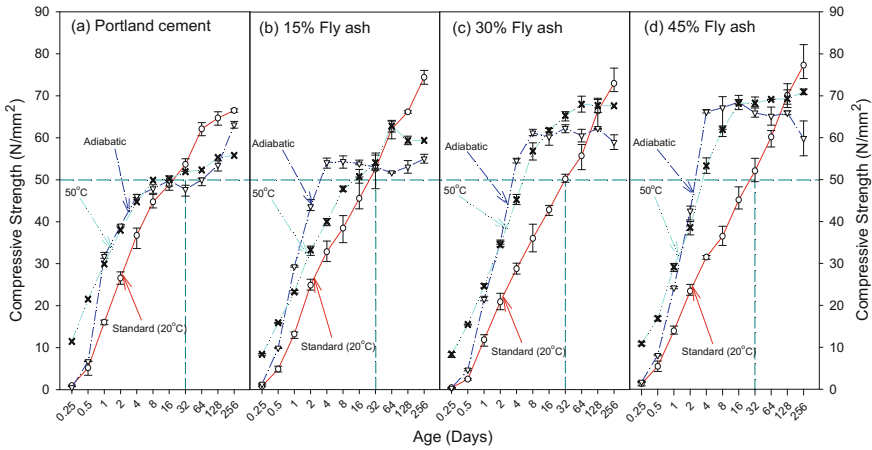


Fig. 2.8 Adiabatic, standard and 50 °C strength development of PC and PFA concrete (grade 40) (data taken from Elsageer 2011)

concretes, compared to the standard cured strength; however, at later age the strength development was detrimentally affected by the high adiabatic curing temperature, i.e. the strength development was lower in comparison with the samples cured under standard curing condition. It can be observed that the fly ash concretes benefited from the adiabatic temperatures more than Portland cement concrete. The greatest strength benefit appears to take place within the first 4 days. At this age, i.e. 4 days, all fly ash concrete had achieved more than 100% of their 32-day standard strength, but the strengths levelled off from this age onwards. The peak temperatures of these concretes are reached after 3 days and therefore, a more pronounced improvement in strength at 4 days is observed.

A comparison of the strength development of FA concretes to PC concrete at standard and adiabatic curing conditions is shown in Fig. 2.9. The early age strengths at standard curing are slightly lower as levels of cement replacement with FA increased, for example, the strength of 30% FA at 1-day was 73% of the strength of the Portland cement concrete. Nevertheless, from the age of 64-days onwards, the strength is higher as the levels of cement replacement with fly ash increase. The strength development of FA concretes benefits considerably more from the adiabatic temperature rise than the PC concrete. However, at later age, the adiabatic temperature rise is responsible for a levelling off of strength gain for all the concretes. For example, as shown in Fig. 2.9b, at 2 days, 15 and 45% fly ash concretes had greater strength than PC concrete and the greater improvement was observed at the age of 4 days. From the age of 4 days onwards, the strength ratios drop continuously with age and the ratios are higher as the percentage of fly ash increases.

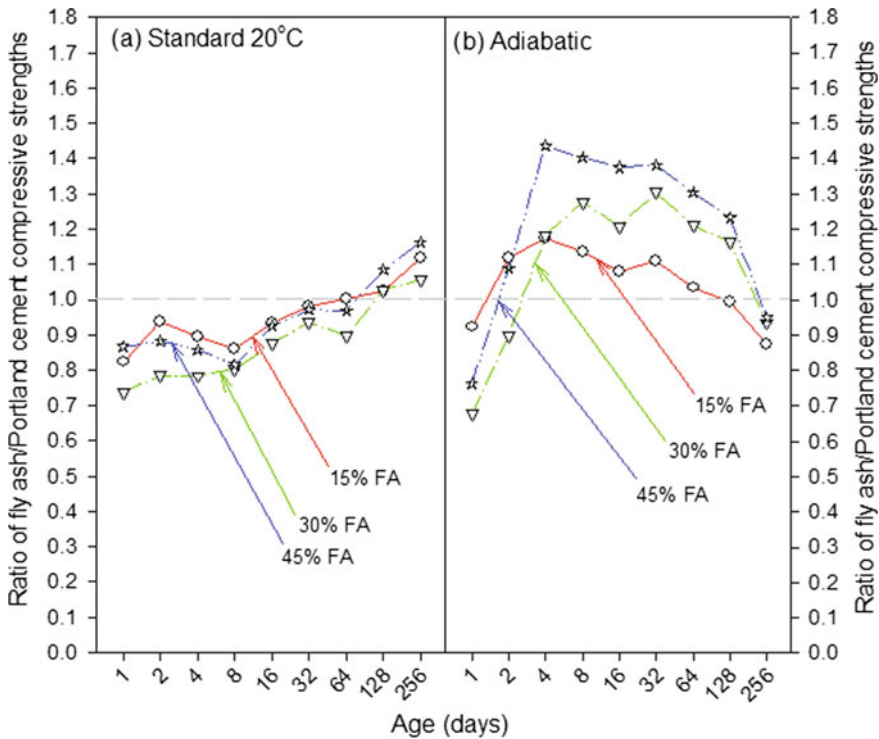


Fig. 2.9 Ratio of fly ash/Portland cement compressive strength development and standard and adiabatic curing regimes (grade 40) (data taken from Elsageer 2011)

2.7 Heat of Hydration, Rate of Reaction (Influence of Temperature and Curing, Maturity Functions)

The rate of heat output generation is highly dependent on temperature and time, i.e. it increases at higher temperatures for Portland cement and Portland cement/fly ash mixes. The use of fly ash reduces the amount of heat generated when compared to that of Portland cement (Papayianni-Papadopoulou 1981; Elsageer 2011; Hatzitheodorou 2007; Poole et al. 2010), thus potentially reducing the risk of thermal cracking in concrete and this can be the main reason for its use in concrete.

The binder mortars' isothermal heat output results in W/kg are plotted on log scale to highlight the differences at early ages. Figure 2.10 indicates that the higher the temperature, the earlier and sharper the heat of hydration peak appears. In all mortars and under all curing regimes, the peak of PC was higher than all levels of FA and the heat decreased gradually with the increase of the level of FA.

Higher temperature accelerates the reactions of fly ash to a greater extent than in the case of Portland cement alone. As a consequence, the behaviour of concrete

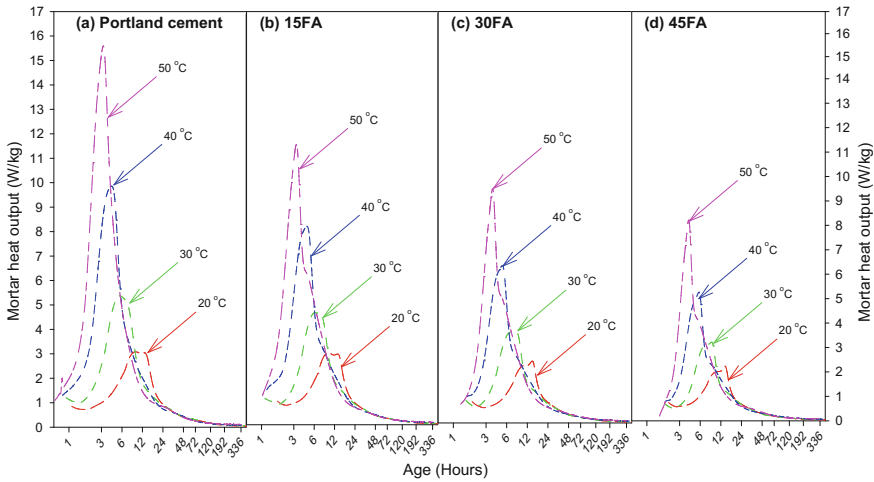


Fig. 2.10 Heat output per kg of binder of mortar (grade 40) (data taken from Elsageer 2011)

containing fly ash may be different in massive concrete elements from the behaviour in small concrete elements. This is relevant to the strength development of fly ash concrete.

For mass concrete projects the performance of the concrete designs should be tested using the local materials to ensure their performance regarding temperature and strength development. Adiabatic tests may be used for this purpose. The adiabatic temperature histories are shown in Fig. 2.11 for Grade 40 concretes (Elsageer 2011). The maximum temperature rise was highest for the PC concrete, which is 49 °C from the casting temperature of 16.7 °C and slightly lower for concrete with 15% fly ash. The maximum temperature rise was reduced in the concretes with 30% and 45% fly ash. The rate of temperature was higher and the maximum temperature was reached in a longer time as the level of fly ash increased. The temperature development in concrete blocks is not only affected by their size but also by the ambient temperature at the time of casting. Strength grade and level of replacement by fly ash both affect the temperature increase in the concrete. Figure 2.12 shows the DETR project blocks (Soutsos et al. 2016) that were cast to determine the ratio of in situ strength (determined from cores) to companion cubes cast and cured alongside the blocks. A unique ratio does not exist as the strengths will be affected by the different temperature histories depending whether it is winter or summer. Winter temperatures allow more heat dissipation from the concrete blocks and the lower reaction rate of fly ash assists in obtaining lower peak temperatures. The differences in peak temperatures between the PC and fly ash mixes increase with winter conditions (Fig. 2.13).

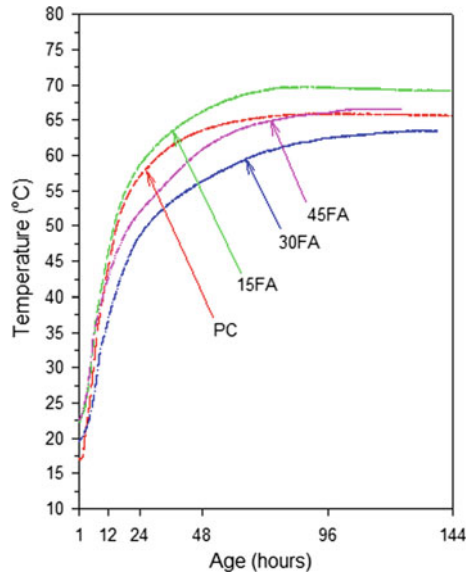


Fig. 2.11 Adiabatic temperature rise of grade 40 concretes (data from Elsageer 2011)

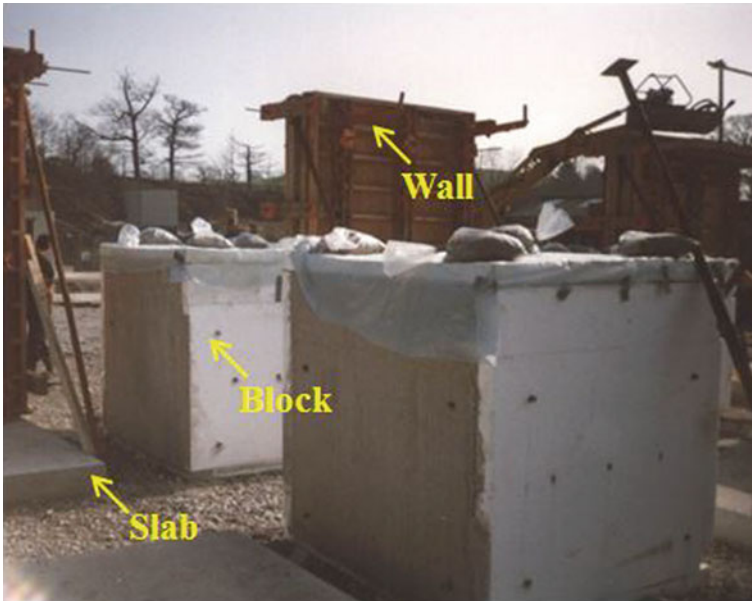


Fig. 2.12 The DTI Concrete Core project (photo from Soutsos et al. 2016)

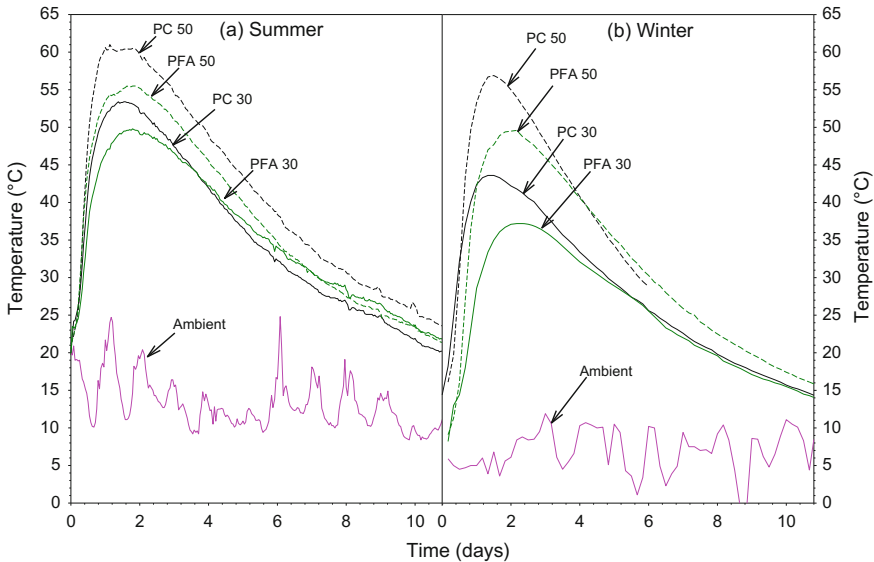


Fig. 2.13 Temperature development in concrete blocks containing 30% fly ash during summer and winter (30 and 50 MPa concretes) (data from Soutsos et al. 2016)

2.8 Compressive Strength

The pozzolanic reaction of fly ash affect the compressive strength of concrete mixtures by different ways. Mehta (1986a, b) has identified these as:

- the reaction is slow, so that the rates of both heat liberation and strength development are correspondingly slow
- the reaction consumes lime rather than producing it
- the reaction products are efficient in filling up space and subdividing pores.

The rate of strength development depends upon the following factors (Siddique and Khan 2011):

- fly ash characteristics such as its chemical and mineralogical composition, fineness, and pozzolanic reactivity
- type of cement (in particular alkali content, but also fineness)
- replacement level of cement with fly ash
- mixture proportions
- ambient temperature
- curing environment reference.

When aggregates or cement are replaced by low-calcium fly ash (up to a certain level, P_{max}) higher strengths are observed. In the former case the strength enhancement is significantly higher and obvious 2–3 weeks after the mixing,

whereas in the latter case the enhancement is much lower and obvious after 3 months. The final strength gain is roughly proportional to the content of active silica in the concrete volume. (Papadakis 1999).

High calcium fly ashes start their contribution to strength development almost from the onset of Portland cement hydration (Siddique and Khan 2011). Some high-calcium fly ashes, with calcium oxide content more than 15%, result to compressive strength increase as early as 3 days after mixing because of their self hardening and pozzolanic properties (Siddique and Khan 2011; Papayianni 2010a, b).

Because of its fineness as well as pozzolanic reactivity, fly ash in concrete significantly improves the density of cement paste and the micro-structure of the transition zone between the binder matrix and the aggregate (Siddique and Khan 2011; Papadakis 2000a, b). As a result of the continual process of pore refinement, due to the inclusion of fly ash hydration products in concrete, a gain in strength development with curing age is achieved. When high-calcium fly ashes are used, the strength development with time is usually different from the one observed when using low calcium fly ashes. The self-hardening reactions in the high calcium fly ashes are likely to occur within the same time frame as the normal Portland cement hydration reactions, giving equal or sometimes greater strengths at early ages (Papayianni-Papadopoulou 1981; Mehta 1986a, b; Sideris 1996; Papadakis 2000a, b; Siddique and Khan 2011). The pozzolanic activity of such cementitious fly ashes further enhances strength at later ages (Sideris 1996; Papadakis 2000a, b; Papayianni 2010a, b).

Lane and Best (1982) observed that proportioning fly ash concrete on strength basis requires a replacement ratio greater than one-to-one by mass so that the fly ash in effect replaces some of the fine aggregate. When fly ash replaces cement on a one-to-one basis, the rates of hardening and strength gain at early ages are reduced. In order to take into consideration the reactivity of fly ash on the compressive strength of concrete mixtures the concept of fly ash efficiency factor was introduced by EN 206-13 (EN206 2013). The efficiency factor (or k-value) is defined as the part of the fly ash in a pozzolanic concrete, which can be considered as equivalent to Portland cement, having the same properties as the concrete without SCM (obviously $k = 1$ for Portland cement). The quantity of the fly ash in the mixture can be multiplied by the k-value to estimate the equivalent cement content, which can be added to the cement content for the determination of the water/cement (W/C) ratio, minimum required cement content etc. (Papadakis and Tsimas 2002). According to EN 206 (2013), when a fly ash conforming to EN 450 is used a k-value of 0.4 is permitted for concrete containing cements CEM I and CEM II-A conforming to EN 197-11. Papadakis and Tsimas (2002) reported that the pulverized high calcium fly ash used in their research performed k-values ranging from 0.9 to 1.4.

Carette and Malhotra (1984) studied the effect of Canadian fly ashes on the compressive strength of concrete mixes. Cement was replaced with 20% fly ash in all the mixes. Compressive strength was measured up to the age of 365 days, and results are given in Table 2.7. It can be seen from this table that compressive strength of all tested mixtures continued to increase with age, indicating pozzolanic reaction of fly ashes.

Table 2.7 Compressive strength of hardened concrete (data taken from Carrette and Malhotra (1984))

| Mix No | Compressive strength (MPa) | | | |
|---------|----------------------------|---------|---------|----------|
| | 7 days | 28 days | 91 days | 365 days |
| Control | 23.4 | 30.6 | 34.9 | 39.2 |
| F1 | 18.4 | 25.7 | 31.4 | 38.3 |
| F2 | 16.9 | 25.2 | 34.8 | 37.0 |
| F3 | 14.4 | 21.0 | 27.6 | 34.4 |
| F4 | 17.8 | 23.3 | 32.3 | 36.9 |
| F5 | 20.1 | 28.0 | 33.9 | 44.3 |
| F6 | 18.4 | 24.8 | 31.8 | 39.2 |
| F7 | 16.7 | 24.1 | 29.1 | 35.7 |
| F8 | 17.9 | 27.7 | 29.0 | 40.4 |
| F9 | 16.7 | 24.9 | 31.1 | 35.6 |
| F10 | 19.2 | 28.5 | 33.7 | 39.7 |
| F11 | 21.1 | 29.4 | 35.3 | 40.1 |

Mehta (1994) reported that no significant contribution to strength development was noticed up to 7 days with the use of low-calcium fly ash in concrete. At 28 days and beyond, most fly ashes at the replacement levels of up to 30% by cement weight exhibited strength gain in concrete and the strength generally equalled that of control concrete.

Haque et al. (1988) concluded that for concrete mixes with 40–75% bituminous fly ash replacing cement, the increase in flexural strength was slightly less than the increase in compressive strength between 28 and 91 days of curing. Klieger and Perenchio (1972) found that concrete made with Type-I cement [EN 197-1(2013)] partially replaced with fly ash had lower strength than the control (neat Type_I cement) at all ages up to 3 years. Lower casting and initial-curing temperatures resulted in higher strengths at later ages for both types of concretes. Korac and Ukraincik (1983) found that the early-age strengths of 50% fly ash concrete were lower than the controls; after 90 days strengths were comparable.

Erdoğdu and Türker (1998) studied the effect of particle size of high and low calcium fly ash on the compressive strength of mortar. Fly ashes were sieved from the 125, 90, 63, and 45- μm sieve by a sieve-shaker. Six different size groups, including the all-in ash, were investigated by combining the materials retained on each sieve. They were; material retained on 125 μm sieve, material having 125–90, 90–63, and 63–45, and material passing 45- μm sieve. For strength tests, mixtures composed of 25% fly ash and 75% Portland cement, by weight, were prepared. Tests were conducted up to the age of 90 days, and results are given in Table 2.8. It is evident from these results that (1) mortars with high-calcium ash exhibited higher strengths than mortars with low-calcium ash at all ages; (2) the finer the size of a fraction then the higher was the compressive strength.

Table 2.8 Compressive strength results of the mortars (data taken from Erdoğan and Türker 1998)

| | | Compressive strength (N/mm ²) | | | |
|-------------------|--------------|---|--------|---------|---------|
| | | 2 days | 7 days | 28 days | 90 days |
| 25% High + 75% PC | All-in ash | 27.6 | 36.7 | 46.7 | 55.7 |
| | Above 125 μm | 19.2 | 26.6 | 31.2 | 33.2 |
| | 125–90 μm | 22.6 | 27.6 | 35.0 | 38.4 |
| | 90–63 μm | 24.8 | 31.3 | 35.4 | 42.6 |
| | 63–45 μm | 26.6 | 35.1 | 41.4 | 47.5 |
| | Under 45 μm | 32.0 | 43.0 | 55.8 | 64.6 |
| 25% Low + 75% PC | All-in ash | 23.5 | 33.2 | 39.6 | 47.4 |
| | Above 125 μm | 17.9 | 24.4 | 26.7 | 29.9 |
| | 125–90 μm | 21.6 | 29.2 | 32.0 | 37.1 |
| | 90–63 μm | 22.6 | 29.6 | 34.9 | 40.6 |
| | 63–45 μm | 23.8 | 33.5 | 37.4 | 46.8 |
| | Under 45 μm | 26.6 | 37.3 | 43.4 | 57.2 |
| 100% PC 32.5 | | 38.0 | 44.4 | 51.6 | 58.2 |

Siddique (2003) studied the effect of partial replacement of fine aggregate (sand) with varying percentages of Class F fly ash on the compressive strength of concrete up to the age of 365 days. Fine aggregate (sand) was replaced with five percentage levels (10, 20, 30, 40, and 50%) of Class F fly ash by weight. Control mix (without fly ash) was proportioned to have a 28-day cube compressive strength of 26.4 MPa. Compressive strength results are shown in Fig. 2.14.

Based on the results shown in Fig. 2.14, it was concluded that (1) compressive strength of fine aggregate (sand) replaced fly ash concrete specimens was higher

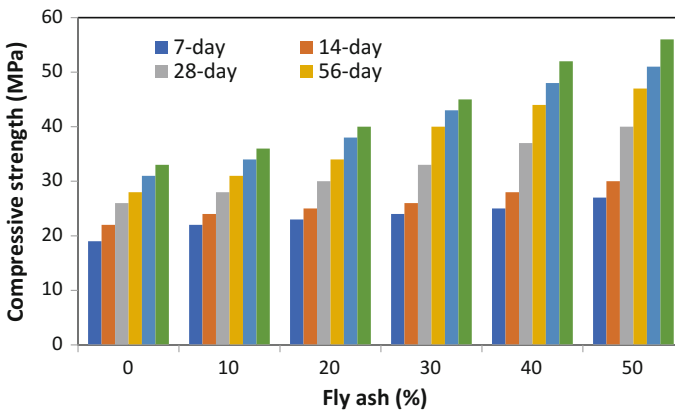


Fig. 2.14 Compressive strength versus fly ash percentage (data taken from Siddique 2003)

than the plain concrete (control mix) specimens at all the ages. The strength difference between the fly ash concrete specimens and plain concrete specimens became more distinct after 28-days; (2) compressive strength continued to increase with age for all fly ash replacement levels; and (3) The maximum compressive strength occurs with 50% fly ash content at all ages. It was 40 MPa at 28-day, 51 MPa at 91-day, and 55 MPa at 365-day.

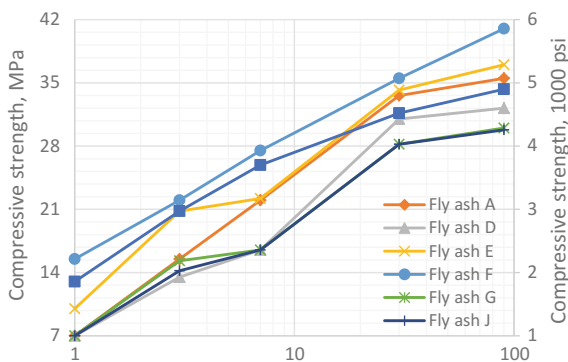
Demirboğa et al. (2007) investigated the role of high-volumes of Class C fly ash on the compressive strength of concrete. Cement was replaced with 0, 50, 60, and 70% fly ash. Compressive strength of concrete mixtures was determined at the ages of 3, 7, 28 and 120 days. The researchers reported that:

- (i) fly ash reduced the compressive strength of tested mixtures at all tested ages and at all replacement levels
- (ii) strength reductions were very high at the early ages of hydration, but the percent of strength reduction decreased as the hydration age increased
- (iii) cement paste containing fly ash showed a steady reduction in strength at 3, 7, 28 and 120 days as a function of replacement percentage.

Chindaprasirt et al. (2007) studied the effect of fly ash fineness on the compressive strength of concrete. Three fly ash finenesses: coarse, medium and fine were used. The coarse fly ash was 100% original fly ash (100FA). The medium fly ash was the 45% fine portion of the original fly ash (45FA). The fine fly ash was the 10% fine portion of the original fly ash (10FA). Three concrete mix series viz. a low, a normal/medium and a high strength concrete mix series were made. For the low- and normal-strength concrete, the water-to-cement ratios of 0.54 and 0.48, respectively, were used for Portland cement mixes. For the high strength concrete, the water-to-cement ratio was kept low with the use of a superplasticizer. The fly ash dosage of 30% by weight of binder was used for all fly ash concrete mixes. The strengths of fly ash concrete were higher than those of the Portland cement concrete in the same group. For the normal-strength concrete, the 28-day strength of the PC2 concrete was 49 MPa, whereas those of fly ash concretes were between 44 and 52 MPa. For the high strength concrete, the strength of the PC3 concrete was 80 MPa, whereas those of the fly ash concretes were between 71 and 84 MPa. For the low strength concrete series, the strength of PC1 concrete was lower than the fly ash concrete owing to a very large reduction in the water content of the fly ash concrete. The reduction in the water content, the good dispersing and the filling effect of the fly ash contributed to the relatively good strength development of the fly ash concrete in this series. With the use of finer fly ash, the water content was further reduced and the strength of concrete enhanced further.

In general, the replacement of cement by fly ash has a retarding effect on the early-age strength development of concrete and a positive effect on the later-age strength. However, some highly reactive fly ashes, especially Class C fly ashes, could increase the compressive strength even at early ages. Figure 2.15 shows the strength development of concrete with different fly ashes (Whiting 1989).

Fig. 2.15 Compressive strength of concrete containing 307 kg/m^3 of cementitious materials, where 25% of cement was replaced by fly ash. Fly ashes A, F are class C, and fly ashes D, E and J were class F (data taken from Whiting 1989)



Beside the mix composition of concrete and the properties of aggregates and the curing conditions, the strength of concrete containing fly ash is determined by the pozzolanic reactivity of fly ash. The chemical composition of fly ash strongly affects its pozzolanic reactivity. The major components in fly ash contributing to the reactivity are silicates and aluminates contained in the glass phase (Wesche 1991). In general, Class C fly ash has a higher reactivity than Class F fly ash, and this results in different performance in terms of strength development (Neville 1995). The fineness of fly ash is another important factor affecting the reactivity. Many researchers (Costa and Massazza 1983; Ravina 1980) reported a direct correlation between the fineness of fly ash and its reactivity as well as the strength development of the concrete containing it. Grinding fly ash increases the fineness, which has a positive effect on the reactivity (Jaturapitakkul et al. 2004). However, the grinding destroys the spherical particles of fly ash and results in an increase in the water demand (Monzo et al. 1995), which possibly causes an adverse effect on the strength development.

Papayianni (2010a, b) used two high calcium lignite fly ashes for the production of concrete mixtures in cement replacement levels from 50 to 100%. She reported that plain concrete mixtures with only raw fly ash (100% replacement) developed 7- and 28-days compressive strength of 2.5 and 5.0 MPa, respectively. When processed fly ash was used the mixtures developed comparable strength values with the reference mixture produced with CEM II 32.5N cement from the age of 7 days, see Fig. 2.16.

Sideris et al. (1997) used two high calcium lignite fly ashes at replacement levels of 10 and 30% for the production of concrete mixtures with limestone or silicate aggregates. They concluded that only the 10% fly ash mixtures developed 28 day strength comparable with the one measured in the reference mixture. However at the ages of 60 days and beyond all fly ash mixtures gained significant strength values (Fig. 2.17).

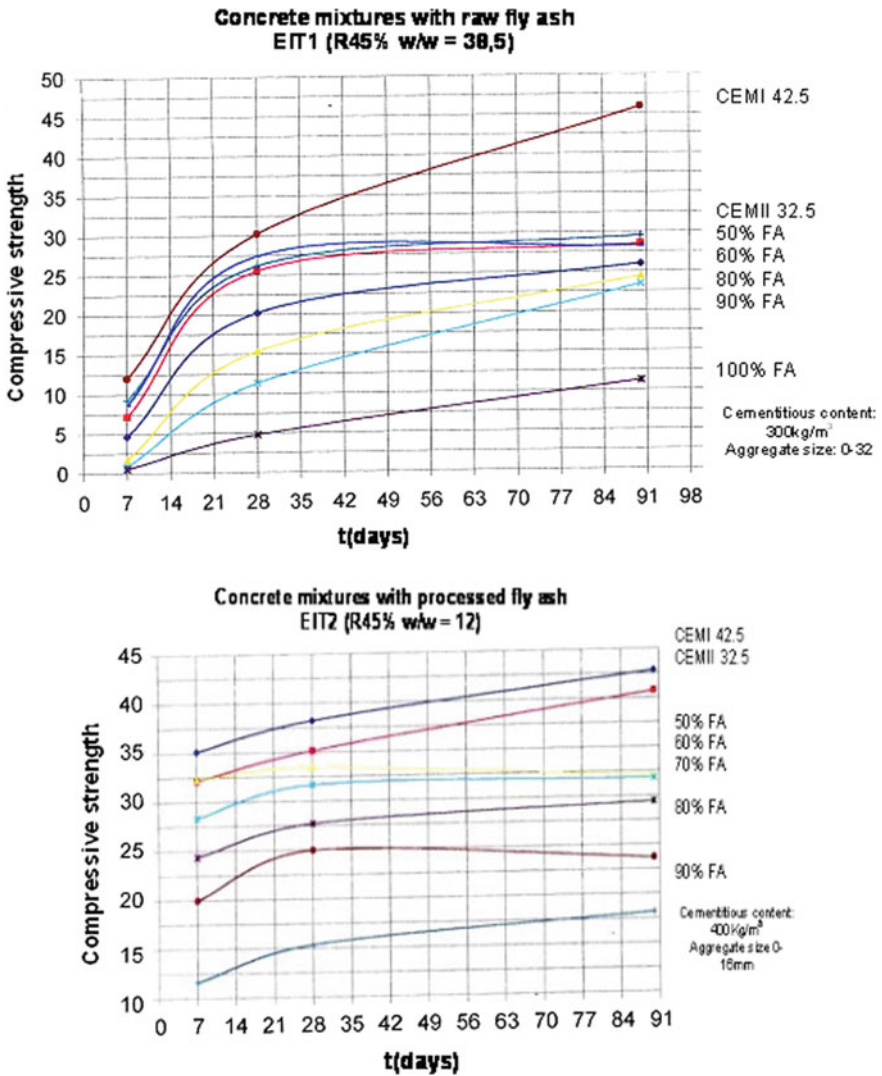


Fig. 2.16 Compressive strength development of concrete mixtures produced with raw (EIT1) and processed (EIT2) high calcium lignite fly ashes (data taken from Papayianni 2010a, b)

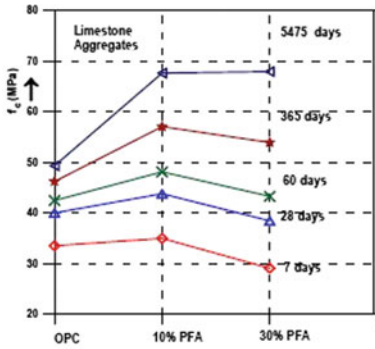


Figure 5: Compressive strength of different PFA concretes for various hydration ages.

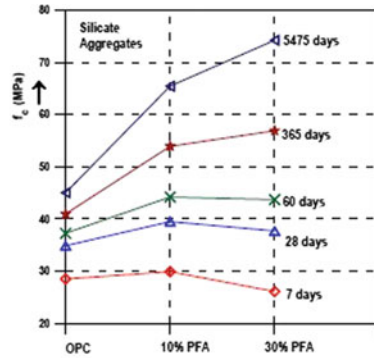


Figure 6: Compressive strength of different PFA concretes for various hydration ages.

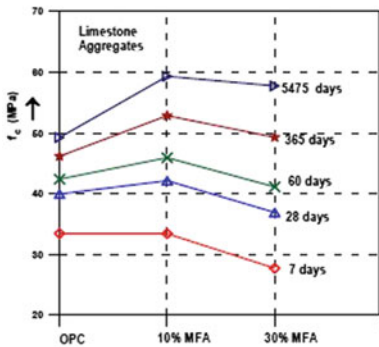


Figure 7: Compressive strength of different MFA concretes for various hydration ages.

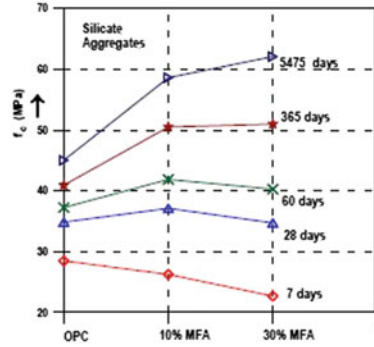


Figure 8: Compressive strength of different MFA concretes for various hydration ages.

Fig. 2.17 Compressive strength development of mixtures produced with high calcium lignite fly ashes at different replacement levels. Total cementitious content: 300 kg/m³, w/c ratio = 0.60 (data taken from Sideris et al. 1997)

2.9 Tensile Strength

Carette and Malhotra (1984) studied the effect of Canadian fly ashes on the flexural strength of concrete mixes up to the age of 91 days. According to the results of this research, flexural strength continued to increase with age. The researchers attributed this trend to pozzolanic action of fly ash.

Siddique (2003) investigated the effect of partial replacement of fine aggregate (sand) with varying percentages of Class F fly ash on the splitting tensile strength and flexural strength of concrete. Fine aggregate was replaced with five levels of percentages (10, 20, 30, 40, and 50%) of Class F fly ash by weight. A reference mix (PC concrete) was designed with a 28-day compressive strength of 26 MPa. Tests were performed up to the age of 1 year (365 days). Siddique (2003) concluded that:

- splitting tensile strength, and flexural strength of fine aggregate (sand) replaced fly ash concrete specimens was higher than OPC concrete (reference mix) specimens at all the ages. However, the strength differential between the fly ash concrete specimens and OPC concrete specimens became more distinct after 28-days
- both splitting and flexural strengths continued to increase with age for all fly ash percentages
- fly ash concrete mix with the higher content of 50% performed best at all tested ages having the maximum measured values.

2.10 Transport Properties

In ordinary Portland cement concrete, calcium hydroxide formed during hydration of Portland cement can be leached out over a period of time (Siddique and Khan 2011). This creates channels available for the ingress of water and deleterious salt solutions. When fly ash is incorporated in the mixture, it reacts with the calcium hydroxide to produce calcium silicate and aluminate hydrates of the same or similar type that are formed in the normal hydration of cement (Papayianni-Papadopoulou 1981; Mehta Mehta 1986a, b; Papadakis and Tsimas 2002; Siddique and Khan 2011). Thus pozzolanic reaction consumes calcium hydroxide and converts it to water insoluble hydration products. The reactions reduce the risk of leaching calcium hydroxide, pozzolanic products fill capillaries and reduce diffusion to aggressive fluids such as chloride or sulfate solutions. It is clear therefore that addition of fly ash results in pore refinement since it transforms bigger pores into smaller ones due to the formation of pozzolanic reaction products concomitant with the progress of cement hydration (Sideris 1996; Siddique and Khan 2011). Since permeability of concrete is related to the volume of pores larger than 100 Å in the hydrated paste, incorporation of fly ash results to more impermeable concrete mixtures.

The effect of low-calcium fly ash on the pore size distribution at the ages of 28 days and 1 year for pastes with $w/cm = 0.50$ is shown in Fig. 2.18 (Manmohan and Mehta 1981). The partial replacement of cement with 30% fly ash results in a higher porosity and a greater volume of macropores measured at the age of 28-days. The total volume of the pores measured at the age of 1 year is reduced in both pastes, but the difference is most significant in the fly ash paste. In this case there is a very significant reduction in the capillary-sized pores between 28 days and 1 year. It is also noticeable that there is a significant shift from the macropores to mesopores for this mixture resulting to a more refined pore structure of the fly ash paste as compared with that of the plain cement paste (100% Portland cement (PC) at the age of 1 year. The improvements in pore structure with time emphasize the importance of curing, especially with slowly reacting pozzolans, if the potential benefits associated with their use are to be realized.

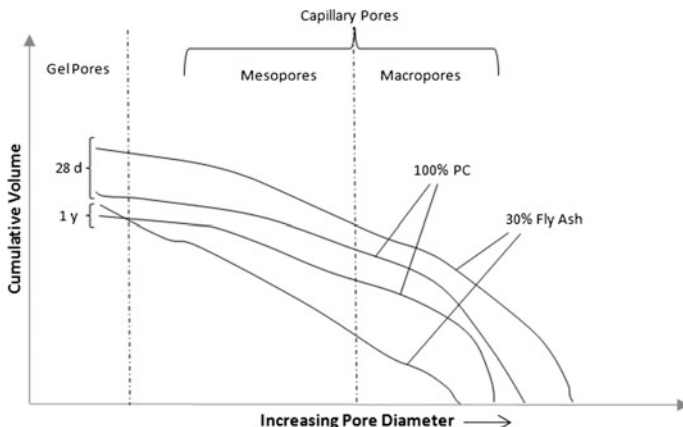


Fig. 2.18 Effect of fly ash on pore size distribution at 28 days and 1 year (data taken from Manmohan and Mehta 1981)

High-CaO lignite fly ashes exhibit both pozzolanic and hydraulic behaviour (Papayianni 1996). When mixed with water some high-calcium fly ashes will harden due to the hydration of crystalline calcium silicate, the reaction between free lime and some of the glass, and the formation of ettringite. According to Taylor (1997) the hydration products in blends of Portland cement and high CaO are essentially the same as those that form in Portland cement mixes with the addition of strätlingite and C_2AH_8 (and increased quantities of calcium aluminate hydrates).

The porosity of mixtures produced with high calcium fly ash (HCFA) at different ages is plotted in Fig. 2.19 (Sideris 1996). HCFA replaced ordinary Portland cement (OPC) at different levels up to 40%. All cement pastes produced were with a water/cement ratio of 0.50. Porosity measurements were taken up to the age of 730 days (two years). The porosity of cement pastes at the age of 5475 days (15 years) was calculated using the cement hydration equation model (Sideris and Sideris 1997, 2003). Total porosity of fly ash cement pastes was slightly increased

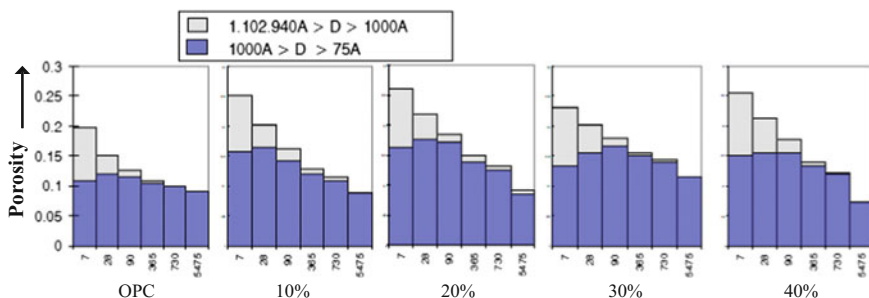


Fig. 2.19 Total ($1.102.940 \text{ \AA} < D < 75 \text{ \AA}$) and water permeable ($1.102.940 \text{ \AA} < D < 1000 \text{ \AA}$) porosity of cement pastes produced with high calcium fly ash (data taken from Sideris 1996)

at all ages as compared with OPC paste. However, the water permeable porosity was decreased or remained the same with the one measured on OPC pastes at ages greater than 90 days for replacement levels of 20–40%.

This pore refinement taking place at later ages is responsible for the impermeability observed in fly ash mixtures. Davis (1954) was among the first researchers who studied the permeability of concrete used for pipes and the effects of replacing 30 or 50% of the cement with Class F fly ash from two different sources. Fly ash concrete was found to be more permeable at the age of 28 days, especially at higher levels of replacement. However, the trend was reversed at the age of 180. At this age fly ash concrete was found to be significantly less permeable.

2.10.1 Carbonation

Kasai et al. (1983) studied the carbonation of mortar specimens produced with different types of cement and fly ash after 7 days of moist curing. The researchers observed that (i) carbonation was found to progress rapidly up to the age of 3 months and after that it slowed down; and (ii) the greater the coefficient of permeability of the specimen, the greater was its susceptibility against carbonation. Specimens prepared with fly ash cement exhibited greater carbonation depth than ordinary Portland cement specimens.

Nagataki and Ohga (1992) found that addition of fly ash increased the carbonation depth of mortars. However, longer curing periods reduced the rate of carbonation, and mortars with greater fly ash contents were found to be more sensitive to extension of the curing period. These results are consistent with the slower hydration and development of a discontinuous pore system in fly ash cement pastes.

Sideris et al. (2006) produced 9 different cement mortars using high calcium lignite fly ashes—HCFA—in replacement levels up to 60%. Different w/cm ratios were used in each case in order to keep the mixtures' fluidity constant. All specimens were water cured for 28 days. After this age they were exposed to indoor conditions. Carbonation measurements were taken for a time period of up to 18 months. The researchers reported that carbonation depths of all fly ash mixtures were greater than the one of the plain cement mixture. This finding was also reported by Papadakis et al. (1992). On the other hand, the carbonation rate, i.e., the increase in carbonation depth at later ages as compared with the one at the initial measurement (6 months), was greater with the plain cement mixture. Carbonation rate generally reduced, as the fly ash content increased. The researchers attributed this finding to the pore refinement phenomenon.

Sideris and Savva (2001) produced five different concrete mixtures using two natural pozzolans and two lignite fly ashes. All SCMs replaced Portland cement at a constant level of 20%. Concretes were produced with a w/cm ratio of 0.65 and the content of cementitious materials was 350 kg/m³. Concrete specimens were fog cured for 28 days. After this age specimens were exposed in two different environments: (a) specimens of the first series were exposed to a coastal environment,

150 m away from the beach and left unprotected to the rain, and (b) specimens of the second series were exposed in indoor conditions. Carbonation measurements were performed at different ages up to 4 years.

Carbonation depth of blended cement mixtures was in both curing environments greater than the one of normal Portland cement mixture. Among all blended cement mixtures tested, specimens with pre-treated high calcium lignite fly ash performed the lowest carbonation rate, mainly due to the high CaO content of the ash.

Papadakis (2000a, b) examined the carbonation resistance of different mortars produced with low calcium fly ash (FL) and high calcium lignite fly ash (FH). Both ashes were used to replace cement or aggregates at percentages of up to 30%. All specimens were kept for 28 days in a laboratory air environment. They were then placed in a carbonation chamber with a controlled 3% concentration of CO₂, at a temperature of 25 °C, and relative humidity of 61% for 100 days. He reported that the carbonation depth decreased as aggregate replacement by fly ash increased (positive replacement on the right of horizontal axis), and increased as cement replacement by fly ash increased (negative replacement on the left of horizontal axis). The lowest carbonation depth was observed for high-Ca fly ash, then for low-Ca fly ash produced concretes (Figs. 2.20 and 2.21).

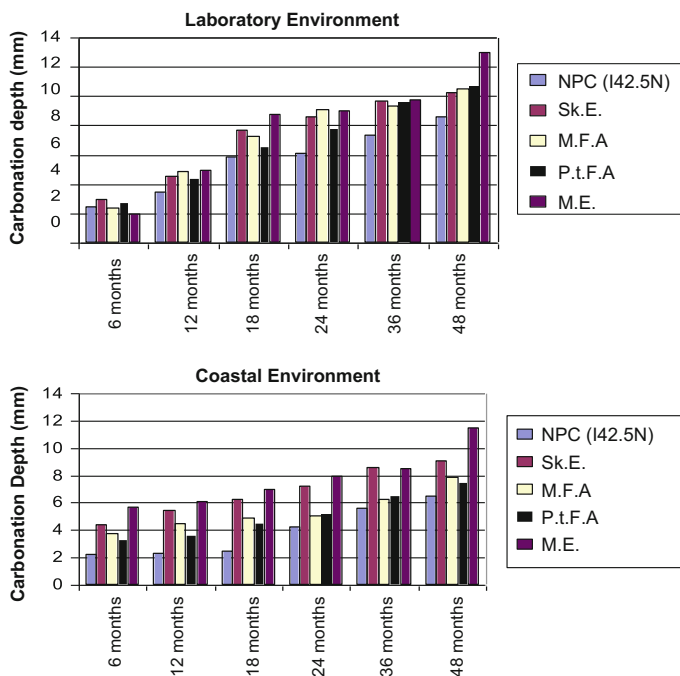
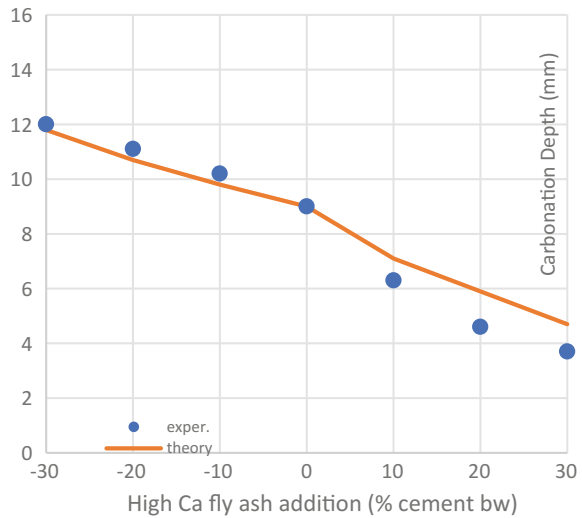
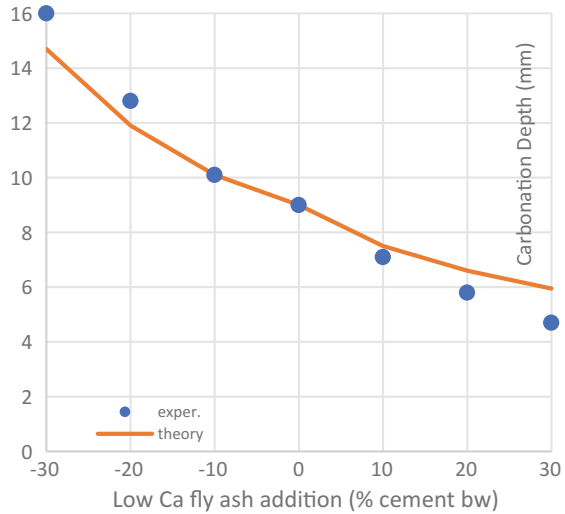


Fig. 2.20 Carbonation depth of concrete mixtures produced with ordinary Portland cement, natural pozzolans (SkE and ME) and lignite fly ashes (PtFA and MFA) (data taken from Sideris and Savva 2001)

Fig. 2.21 Experimental results and model predictions of carbonation depth of mortars incorporating low-calcium fly ash and high-calcium fly ash as cement (left hand) or aggregate (right hand) replacement (data taken from Papadakis 2000a, b)



The influence of fly ash on carbonation depth of concrete mixtures depends on many parameters such as:

- the chemical and mineralogical composition of the ash, the fineness of the ash.
- the water to cementitious materials ratio (c/cm),
- the level of replacement and the type of replacement (replacing cement or aggregates),
- the type of ordinary Portland cement used (chemical composition and fineness), and the curing period of the specimens.

One must be very careful when comparing some of the conflicting data available in the literature due to the parameters mentioned above.

2.10.2 Resistance to Chloride Ingress

There are many research results available in the literature in the majority of which researchers report that fly ash improves the resistance of concrete to chloride ion penetration, however the extent of the improvement depends on the following factors:

- the chemical and mineralogical composition,
- the replacement level and the fineness of the ash,
- the w/c, and to a lesser extent, the composition and fineness of the Portland cement used,
- the maturity of the concrete,
- the exposure conditions (mainly temperature and carbonation of the concrete), and,
- the extension of the initial curing period of the mixtures.

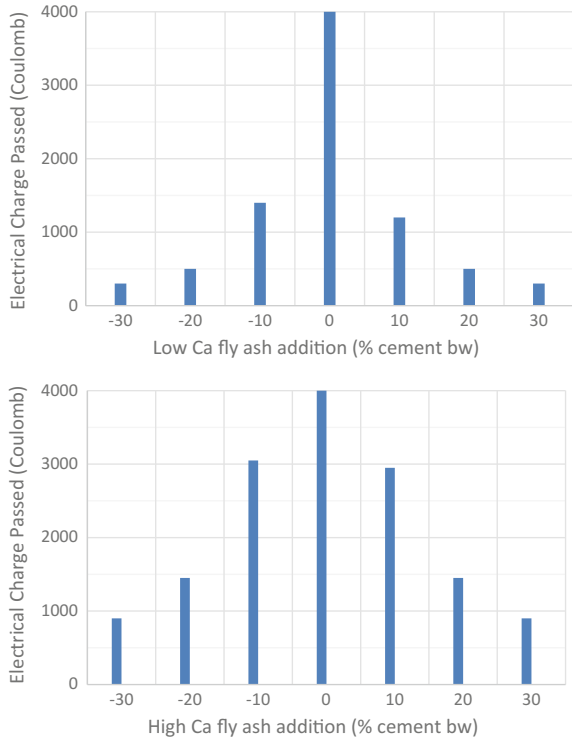
Papadakis (2000a, b) examined the resistance to chloride ingress of different mortars produced with low calcium fly ash (FL) and high calcium lignite fly ash (FH) by using the Rapid Chloride Permeability test (Fig. 2.22). Both ashes were used to replace cement or aggregates at percentages of up to 30%. The electrical charge passed through the control specimen may be higher than 4000 °C. This quite high value was due to high cement paste volume and the absence of coarse aggregate. All specimens incorporating fly ashes, whether it substituted aggregate or cement, exhibited lower electrical charge.

Most researches available in the literature focus on the chloride permeability of fly ash mixtures measured according to the standards at the age of 28 days. However, resistance of concrete to chloride penetration increases as the concrete matures. As mentioned above both total porosity and permeability of concrete containing fly ash is significantly reduced at later ages.

Thomas and Bamforth (1999) measured the chloride diffusion coefficient of different concrete blocks exposed to the south-eastern coast of the United Kingdom. Concrete blocks were produced with three different mixtures containing 100% ordinary Portland cement, 30% fly ash and 70% slag. All mixtures had the same compressive strength at the age of 28 days and were produced with w/cm ratio of 0.66, 0.54 and 0.44 respectively.

Results from this study indicated that at early ages (e.g., 28 days), the diffusivity of concrete containing 30% fly ash may be expected to have a similar chloride ion diffusivity as an equivalent grade Portland cement concrete. However, after approximately 2 years the diffusivity of the fly ash concrete may be one order of magnitude lower than the Portland cement and decrease further at later ages. This

Fig. 2.22 Rapid chloride permeability of mortars incorporating low-calcium fly ash and high-calcium fly ash as cement (left hand) or aggregate (right hand) replacement (data taken from Papadakis 2000a, b)



reduction in the chloride diffusion coefficient of fly ash concrete mixtures has a significant impact on the long-term performance of concrete in chloride environments and on the interpretation of data from tests based on estimating the chloride diffusion coefficient (D28 value). This long term reduction in chloride diffusion coefficient is well known as the *aging factor*. The chloride diffusion coefficient at a particular time t during the service life of a structure is calculated using the following equation:

$$D_{app(t)} = D_{app(t_0)} \left(\frac{t_0}{t} \right)^a$$

where

$D_{app}(t_0)$ is the apparent diffusion coefficient measured at a reference time of t_0 (usually at the age of 28 days)

a is the aging-factor giving the decrease over time of the apparent diffusion coefficient.

According to fib Bulletin 34 (2006) the aging factor a has a value of 0.30 for ordinary Portland cement and a value of 0.60 for fly ash cements with a fly ash replacement higher than 20%.

2.10.3 Sulfate Resistance

The principal method available to limit sulfate attack is the use of a sulphate resistant cement (Type II or Type V Portland cements instead of Type I Portland cement according to ASTM (2015) or sulfate resistant (SR) cements as described in EN197-1 [2013]) and by ensuring that the concrete has a low w/cm. Among the SR cements described in EN197-1, sulfate resistant pozzolanic cements CEM IV/A-SR and CEM IV/B-SR should contain combinations of natural pozzolanas and siliceous fly ash only up to a content of 55% per weight of cement. In this case the C₃A content of the cement should be lower than 9%, almost double the upper limit value of sulfate resistant Portland cement CEM I-SR5. Another alternative is the use of additives – such as natural pozzolanas, fly ashes or silica fume. Pozzolanic materials have an important role in the long-term durability of mixtures exposed in sulfate environments because they contribute chemically and physically to their properties. Their effect is thought to be explained by two primary mechanisms (Tikalsky et al. 1990): The “dilution effect” (decrease of the C₃A content of the binder when they replace a portion of Portland cement) and the “pozzolanic effect” (formation of secondary CSH). The latter results in a less permeable mortar, from which the excess calcium hydroxide has been consumed and rendered unavailable for the expansive formation of ettringite and gypsum compound (Mehta 1981; Al-AMoudi 1999).

Several attempts have been made in order to predict the sulfate resistance of a fly ash based on its chemical composition. Among them the first is that of Dunstan (1980). He introduced the “Resistance value” which was:

$$R = \frac{CaO - 5}{Fe_2O_3}$$

According to Dunstan, a fly ash improves the sulfate resistance of the mixture if $R < 1.5$, whereas this decreases if the R-value of the ash is higher than 3. In a later research Dunstan (1987) reported that the sulfate resistance of mortars tested according to ASTM C-1012 will be improved, if fly ash with $R \leq 3.5$ is used.

In other research (Tikalsky 1990) the ratio CaO/SiO₂ of the fly ash was introduced as an indicator of their contribution to the sulfate resistance of mixtures. According to the researchers, fly ash with CaO/SiO₂ ratio less than 0.25, contained no detectable C₃A and provided a level of resistance to sulfate attack equal or greater than that of cement Type II alone. When fly ash had a CaO/SiO₂ ratio greater than 0.60, it reduced the sulfate resistance of the mixtures. Erdogan et al. (1992) reported that the (Free CaO)/Fe₂O₃ and (C₃A + Free alumina)/(Free CaO) ratios of the cement-high lime fly ash mixtures can be used to determine their sulfate susceptibility. According to the authors, there is a clear relationship between these ratios and the sulfate resistance of the mixtures: sulfate resistance increases when the (Free CaO)/Fe₂O₃ ratio decreases and the (C₃A + Free alumina)/(Free CaO) ratio increases.

Mehta (1986a, b) observed that if a fly ash is high in reactive aluminate phases it will not improve the sulfate resistance of concrete. He found that sulfate resistance depends on the type of aluminate phases at the time of sulfate exposure. Upon immersion in sulfate solution, pastes containing monosulfoaluminate or calcium aluminate hydrate suffered from strength loss due to ettringite formation. In contrast blended cement pastes containing fly ash that promoted the formation of ettringite prior to immersion into sulfate solution showed superior resistance. The free SiO_2 , the free CaO and the fineness of the material are also of great importance (Mehta 1981; Stamatakis et al. 1997).

Fay and Pierce (1989) performed a study on air-entrained fly ash concrete using three fly ashes from the United States, representing a range of CaO contents of 11–28.8% and used 10–100% fly ash by weight of the total cementitious material. The specimens were cured for 14 days in a 100% humidity room and for another 14 days in a 50% humidity room before they were immersed in 10% Na_2SO_4 solution or subjected to cyclic soaking and drying phases in 2.1% Na_2SO_4 solution to generate data by accelerated test. They concluded that both low-calcium Class C and Class F fly ashes can be effective cement replacements in controlling sulfate expansion, however Class F fly ash at replacement level of 30% significantly improved the sulfate durability for the cementitious levels and appeared to be optimum for both test conditions employed in their investigation, while for low-calcium Class C fly ash replacement levels were suggested to be greater than 30% and for high-calcium Class C fly ashes the corresponding suggested levels were greater than 75% to achieve the most improved sulfate durability.

Sideris et al. (2006) investigated the sulfate resistance of 8 different cement mortars prepared using two high calcium lignite fly ashes—MFA and PFA—in replacement levels up to 60%. Different w/cm ratios were used in each case in order to keep the mixture's fluidity constant. All cements used in this research were produced in the laboratory by mixing clinker, pozzolanic material and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The SO_3 content of the pozzolanic material was taken into consideration and the added gypsum was properly adjusted in order to keep the total SO_3 content of the binder (clinker + pozzolan) equal to 3.5%. This was not achieved for the mixtures with a high PFA content. The high SO_3 of PFA increased the total available amount of SO_3 of the mix (clinker + gypsum), although no gypsum was added. The sulfate resistance of binders was evaluated using expansion measurements of mortar prisms immersed in a 5% Na_2SO_4 solution, according to ASTM C1012-95 (2015), up to the age of two years.

They concluded that lignite fly ashes, with high CaO and SO_3 content may have a positive effect on the sulfate resistance of blended cements. Specimens containing PFA fly ash blended cements gave the smallest expansion among all cement mixtures tested in this research and developed high compressive strength from early ages. These specimens also gave the least reduction in compressive and flexural strengths due to sulfate attack. On the other hand specimens containing MFA fly ash blended cements gave the worst performance since they totally deteriorated very fast.

Table 2.9 Compressive and flexural strength loss (%), final expansion (%), deterioration age and first crack observed age (months) for all mixtures (data taken from Sideris et al. 2006)

| Mixture | Compressive strength loss (%) | Flexural strength loss (%) | One year expansion (%) | Final expansion (%) | Deterioration age (months) | First crack (months) |
|-------------|-------------------------------|----------------------------|------------------------|---------------------|----------------------------|----------------------|
| CEM I 42.5N | 30 | 67.5 | 1.10 | 1.10 | 6–8 | 6 |
| 10% FA | (–) | (–) | 0.544 | 0.544 | 3–4 | No cracks |
| 20% MFA | (–) | (–) | 0.428 | 0.428 | 3–4 | 2 |
| 30% MFA | 30 | (–) | 0.408 | 0.408 | 4–6 | No cracks |
| 30% PFA | 19 | 17 | 0.033 | 0.049 | 12–16 | No cracks |
| 40% PFA | 15.3 | 14.7 | 0.033 | 0.055 | 16–20 | 16 |
| 50% PFA | –0.8 ^a | –153 ^a | 0.016 | 0.022 | Not deteriorated | No cracks |
| 60% PFA | –8 ^a | –179 ^a | 0.012 | 0.016 | Not deteriorated | No cracks |

–Totally deteriorated, not measured;

^aStrength increased

The R-value for the two ashes used were RMFA = 1.86 and RPFA = 1.21. Despite the fact that in both cases the R-value is much less than 3.5, their contribution to the sulfate resistance of the mixtures was totally different: MFA had a deleterious effect, whereas PFA had a beneficial one. The two examined lignite fly ashes had similar chemical composition but they had totally different performance regarding the sulfate resistance of the mixtures, indicating that it is the mineralogical composition that really counts and makes the difference (Table 2.9).

2.10.4 Freezing and Thawing Resistance

Addition of fly ash results to changes in pore size distributions due to pozzolanic reactions (Schiepl and Hardtle 1994). The phenomenon of pore refinement as a result of pozzolanic reactions leads to the breaking of continuity of the capillary pore structure. As reported by Malhotra et al. (1982) the pozzolanic reactions alter the pore structure of the cement paste and thus densify the transition zone between the paste and aggregates.

There are many researches in the literature dealing with freeze and thawing resistance of fly ash concretes (Perenchio and Klieger 1976; Majko and Pistilli 1984; Yuan and Cook 1983; Virtanen 1983; Carette and Malhotra 1984; Joshi 1987; Malhotra et al. 1990; Schmidt 1992; Joshi et al. 1993; Thomas 1999; Naik et al. 2003; Knutsson 2010). The majority of them conclude that air content has the greatest influence on the freeze–thaw resistance of concrete and that addition of fly

ash had no influence on the freeze–thaw resistance of concrete if the air content of the mixtures is kept constant. However, if the fly ash contains some residual unburnt carbon, higher dosages of air entrainers may be used to achieve target air content and sometimes unstable air may occur.

2.10.5 Alkali Aggregate Reactions

Replacing cement with SCMs generally reduce expansion due to AAR (Thomas 2011). This has in general been thought to be caused by a reduction in pH (i.e. hydroxyl concentration) of pore water and a lower content of calcium hydroxide. In the author's opinion, the reduction in pH will be the case as long as the alkalis are busy in dissolving SCM in a catalytic way, but the implication is that this may cause only a delay of AAR until the SCM has reacted totally.

According to Thomas (2013) the level of cement replacement required to control AAR expansion increases as (1) SiO₂ content of SCM decreases, (2) CaO of SCM increases, (3) alkali content of SCM increases, (4) alkali availability in the concrete increases, and (5) reactivity of the aggregate increases. Shehata and Thomas (2000) showed that low calcium fly ashes (ASTM Class F) are much more effective in reducing AAR expansion (typical cement replacement level >20%) than high calcium fly ashes (ASTM class C). Shehata and Thomas (2002) demonstrated that the required level of low calcium fly ash could be reduced to 10% when combined with 5% SF as a ternary blend.

Some have suggested that the presence of alumina in SCMs contributes to prevent the release of alkali back to the pore solution by binding in the hydration products. However, Chappex and Scrivener (2012a) showed that this effect is extremely small, and instead it was found that alumina is an inhibitor of silica dissolution Chappex and Scrivener 2012b, 2013 as in their system with metakaoline as SCM.

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Chapter 3

Silica Fume

Robert C. Lewis

Abstract Silica fume concretes have been used since the mid-1970s, in many areas of the world. Such uses have included high strength, high chemical resistance—especially high chloride and sulfate resistance—abrasion and erosion resistance. With the increased focus on sustainability, silica fume—being a by-product—is used to great effect in reducing the Portland cement content of a mix, and allowing the use of higher cement replacement levels of other SCMs such as blastfurnace slag and fly ash. This can reduce both the energy used and the carbon footprint. The higher performance of the silica fume concrete, in terms of strength, can allow for reductions in structural element size, thus reducing the concrete volume needed, saving natural resources. The increased durability can provide greatly extended lifetimes compared to normal Portland concretes, thus also reducing the need for repairs and replacement. Numerous examples are available from the past 40 years of use, and reference should be made to the relevant manufacturers and associations web-sites, for more information.

Keywords Silica fume · Microsilica · Supplementary cementitious materials Ternary blends · High strength · Chloride resistance · ASR · Durability Sustainability

3.1 Introduction

Silica fume is a very fine powder mostly composed of amorphous silicon dioxide. The terms ‘condensed silica fume’ or ‘microsilica’ are also used. However, these terms may also be used for any powder coming out of the smelting industry, so compliance with the accepted standards for ‘Silica Fume’ is essential for a product that has the properties and quality required for use in concrete. The material is a by-product of the silicon and ferrosilicon smelting industries. Silica fume was first tested in concrete in Norway in the early 1950s (Bernhard 1951, 1952). Good

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strength results were obtained and later it was established that sulfate exposure tests, begun in those early days (Fiskaa et al. 1971) documented silica fume concrete to be as durable as concrete made with sulfate-resisting cement. However, at that time industrial production was impossible: no method of retaining the large quantities of the ultrafine particles was available. Thus, these favourable results only ended up as an incident, and might have been forgotten.

In the early 1970s the Norwegian government announced strict environmental requirements for the smelting industry. This made necessary huge improvements in filtering technology. Filtering of the particles from the exhaust gases thus became possible and, within a few years, substantial quantities were being collected. The consequence of regulatory action temporarily turned silica fume into a waste product, a stigma which is still noticeable today.

In order to accommodate and use the large volumes of material, large-scale and intensive research efforts were undertaken by the principal Norwegian smelting companies. These efforts, following on and adding to the earlier work, form a large part of the basis of silica fume technology and are essential to the large and increasing use of the material worldwide.

3.2 Production and Use in Concrete

3.2.1 Production

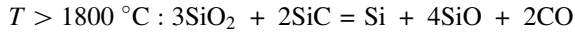
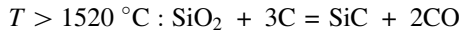
Silica fume is produced during the high-temperature reduction of quartz in electric arc furnaces where the main products are silicon or ferrosilicon alloys. The high-purity quartz is heated to 2000 °C in an electric arc furnace with coal, coke or wood chips added to remove the oxygen. The alloy is collected at the bottom of the furnace. As the quartz is reduced to alloy, it releases silicon monoxide vapour. In the upper parts of the furnace this fume oxidises and condenses into microspheres of amorphous silica (silicon dioxide).

The fumes are drawn from the furnace by powerful fans, often through a pre-collector and cyclone which removes the larger coarse particles of unburned wood or carbon, and are then blown into a series of special filter bags.

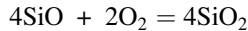
Essentially, this main process has not changed since the development of the arc furnace technology (at the Fiskaa plant in Norway, circa 1908). Production is centred on the alloy quality and the input materials—coal, coke, wood chips and quartz purity. As such, production from plant to plant, depending on the furnace input, can mean different characteristics being found in the silica fume. This can be as simple as a colour variation, or silicon dioxide content, or surface properties. As such, reputable sourcing and quality control is essential for consistency of performance within the concrete.

Some plants have been modified for post-production treatment of the silica fume, such as re-burners to reduce carbon content. Such qualities of product are more often used in very high tech applications due to extra cost, and are not used in concrete production.

The chemistry of the process is composed of temperature-dependent steps. The silicon carbide (SiC) formed initially plays an important intermediate role, as does the unstable silicon monoxide gas (SiO) that eventually forms the silica fume:



The unstable gas travels up into the relatively cooler part of the furnace where it reacts with oxygen to form the silicon dioxide:



As the temperature drops in the smokestack, the SiO₂ condenses into small droplets of silica. These small spherical particles have an average diameter of 0.1–0.2 μm. However, while they are in the molten state, a common occurrence is that some of these primary particles come into contact and fuse into primary agglomerates, typically with a circumscribed diameter of 0.5–0.8 μm.

3.2.2 *Characteristics*

Silica fume, in its basic form, is a grey powder (although shades of nearly white to nearly black, due to variable carbon content, may be seen from different furnace operations). The following properties are typical for a silica fume for use in concrete:

- at least 85% SiO₂ content;
- mean primary particle size of 0.1–0.2 μm;
- specific surface area >15,000 m²/kg;
- spherical particle shape;
- low carbon content.

While silica fume for concrete, according to the main standards, should contain a minimum of 85% silicon dioxide, greater values are often obtained and very high purity products are used in specific applications. If the origin is a ferrosilicon furnace, a small proportion of iron may be present, other elements are only present in small amounts (1% or less).

3.2.3 *Available Forms*

As the particle size of the powder is approximately 100 times finer than ordinary cement, there are certain transportation, storage and dispensing considerations to be taken into account. To accommodate some of these difficulties, silica fume is

available in various forms. The differences between these forms are related to the shape and size of the particles and do not affect the chemical make-up of the material. (These differences have an influence on the areas of use and careful thought should be given to the type of silica fume chosen for a specific application).

The main forms of are as follows.

- **Undensified** (bulk density 200–300 kg/m³) Due to the very low bulk density and subsequent problems in handling, undensified silica fume is often considered impractical for use in normal concrete production. Areas where it is used successfully are in refractory products and formulated bagged materials such as grouts, mortars, concrete repair systems and protective coatings.
- **Densified** (bulk density >500 kg/m³) The densification process causes the ultrafine particles to become loosely agglomerated, making the particulate size larger. This makes the powder easier to handle and cheaper to transport than the undensified form. Areas where this material is successfully used are in those processes that utilise high-shear mixing facilities, such as precast works, concrete roof tile works or ready-mixed concrete plants with central mixing units, and in the refractory industry. If the densification process results in a bulk density that is too high, the user will experience problems with obtaining proper dispersion of the material (Fidjestøl et al. 1989). Additionally, material that has been densified beyond 700 kg/m³, has shown a tendency, given pessimum combinations of silica fume dosage and cement alkalinity, towards deleterious performance, closely resembling ASR, if the large (>100µm) agglomerates are not broken up (Fidjestøl 1991; Lagerblad and Utkin 1993).
- **Pelletised** (bulk density >600 kg/m³) Pelletising involves forming the silica fume into pellets about 0.5–1 mm in diameter on a pelletising table using water and a small amount of cement to bind the pellets. Material in this form is not suitable for use in concrete since it is virtually impossible to disperse properly during mixing. In Canada, recovered pelletised silica fume has been interground with cement clinker in the manufacture of silica fume blended cement. Pelletising is most commonly used at times of excess or out-of-specification production to prepare the material for use in landfill.
- **Slurry** (specific gravity 1400 kg/m³) This material is produced by mixing undensified powder and water, in equal proportions by weight, to produce a stable slurry. The production of stable slurry is a complex process, requiring very efficient, high-shear mixers and special silica fume qualities. In this form the material is easily dispersed into the concrete mix.

3.2.4 Use in Concrete

In terms of the practicalities of using silica fume in concrete, a number of documents are available. The Silica Fume Association has produced technical data and published a “User’s Manual” (FHWA-IF-05-016). A very comprehensive guide is

Table 3.1 Guideline dosages for different applications

| Type of concrete (Application) | Dosage of MS % by cementitious* wt. |
|--------------------------------|-------------------------------------|
| Pumping aid | 2–3 |
| Normal strength (~40–70 MPa) | 5–10 |
| High strength (~80–100 MPa) | 8–15** |
| Underwater | 10–15** |
| High chemical resistance | 12–15^ |
| UHPC | 15–25^^ |

*Total includes Fly Ash or Slag combinations

**Higher dosages may be used with attention to mix proportioning

^Normally a triple blend with Fly Ash or Slag

^^Highly specialised mix designs are required here

available from the American Concrete Institute: ACI 234.06R “Guide to the use of Silica Fume in Concrete” (American Concrete Institute 1996).

The level of addition depends on the application, but the values given in Table 3.1 can serve as guidelines for initial trial mixes. Many project details and research designs are available for reference. However, it should be stressed that even with the precedent of past work contained therein, trial mixes should always be conducted before acceptance of a mixture.

Because of the high surface area of the silica fume, in nearly all ready-mix concrete production a plasticiser or superplasticiser is used to give optimum dispersion while maintaining the water/cement ratio. This can be alleviated—reducing the dosage used—by adjusting the particle packing of the aggregates and powders. Several software programs are available that can review and balance the coarse/fine aggregate ratio, utilising the superfine nature of the silica fume. Such a mix design relies on the silica fume filling the bottom end in the fines percentage and producing a workable mix.

Mixing times will need to be adjusted, depending on dosage and equipment performance, to allow for maximum dispersion of the silica fume. This is most important when using any of the powder forms to prevent any agglomerates within the mix. The slurry form should not need increased mixing times.

Early production often used standard lignosulfonate plasticisers to achieve good dispersion. As workability requirements moved towards more fluid concretes, the use of the lignosulfonate with a pure naphthalene or a sulfonated naphthalene became more widespread—one giving dispersion and the other high workability. Under the drive of major construction in the Middle East, specifically targeted admixtures were designed for use with silica fume, leading to further improvements in durability characteristics. This development continued into the creation of PCEs (polycarboxylate superplasticisers) which are now the most used chemical admixture in silica fume concrete. Like most cementitious materials, the silica fume will function more efficiently with some types of chemical admixtures than with others and here again the need for comprehensive trial mixtures is emphasised. No specific incompatibilities with concrete admixtures are known to the author.

3.2.5 Standards

Various national standards, codes of practice and recommendations relating to silica fume have been in use for a number of years. The two globally accepted standards for the product are the American ASTM and the European EN, as listed. Others may also be seen in local use or within certain project specifications. A number of national and project guidelines/specifications for silica fume also exist.

| | |
|--------------|---|
| USA | ASTM C1240 ‘Silica Fume for use in concrete’ |
| Europe (CEN) | EN 13263—‘Silica Fume for Concrete’ |
| Canada | CSA A3001-13 ‘Cementitious materials for use in concrete’ |
| Japan | JIS A 6207 2000 |
| Australia | AS 3582. Supplementary cementing materials (1992) |
| China | GB/T 18736 |
| India | IS 15388 |

3.2.6 Health and Safety

Silica Fume is classified by CAS (Chemical Abstracts Service) number 69012-64-2. The corresponding EINECS (European Index of Existing Chemical Substances) number is 273-761-1. Other forms of silicon dioxide, including fumed silica, colloidal silica, diatomaceous earth and quartz have other classification numbers. Individual producers should also have REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) classifications for their products.

Papers presented at a symposium entitled the Health Effects of Synthetic Silica Particulates (Dunnom and Wagner 1981) indicated that there is little health hazard potential from the inhalation of amorphous silica due to the non-crystalline structure. Jahr (1980) stated that experience in Norwegian ferrosilicon manufacturing plants indicated that if the limits (TLV) given in ACGIH (The American Conference of Governmental Industrial Hygienists) are not exceeded, then there is only a very small risk of silicosis from exposure to this type of amorphous silica since the silicon dioxide that causes this lung disease appears to be of the crystalline form. ACGIH specifies as Threshold Limit Value (TLV) a time-weighted average (TWA) of 2 mg/m³ for the respirable portion of the dust.

The author is not aware of any reported health-related problems associated with the use of silica fume in concrete. There are no references to the use of microsilica in the concrete industry in the publications of either OSHA (the Occupational Safety and Health Administration of USA) or ACGIH. It is recommended that workers handling silica fume use appropriate protective equipment and procedures which minimise the generation of dust.

Spillages of the powder or slurry should be treated as a ‘common mess’ i.e. non-hazardous and dealt with accordingly (An exception here is when hydrofluoric acid is present because the reaction product would be silicon tetrafluoride, which is toxic). There are no special requirements for the disposal of the waste material.

Flash inflammation of the material is not a hazard since the powder is completely non-flammable and will act as an extinguishing medium. The use of the slurry material will reduce any potential hazards to a minimal level (with the exception of hydrofluoric acid as stated above).

3.2.7 Environmental Sustainability

Due to the nature of its manufacture (a recovered by-product) and use in the concrete industry, silica fume is a material that can significantly contribute towards sustainable concrete construction due to the improvements in the performance of concrete. Because of its properties, silica fume can be used to significantly increase strength, reduce permeability, and provide a general increase in the overall durability of concrete (ACI 234 Guide for the Use of Silica Fume in Concrete, redraft 2017).

The contribution of silica fume can be noted as follows:

1. Cementitious effect—silica fume can be used to replace cement at up to 5 to 1 due to the increased pozzolanic reactivity. This can mean significant reductions in portland cement used for a given strength.
2. Increased strength can be achieved using silica fume as an addition, and if incorporated into the engineering design, savings in concrete volume can be achieved. Increased strength can also extend lifetime use in areas of high physical damage.
3. Using silica fume to augment multiple blends (OPC with high Fly Ash or Slag volumes) can negate the delay effects usually seen—enabling workable strengths and durability factors at earlier ages.
4. The increased durability factors associated with the incorporation of silica fume into a concrete (water resistance, chloride, sulfate and ASR resistance) can mean greatly extended lifetime performance, meaning less repairs or re-builds.

Such methodologies have been used to great effect, reducing concrete volume and utilising SCMs with recycled aggregates, achieving recognised sustainability (LEED) and cost reductions in projects such as 311, South Wacker Drive, Chicago (Orth 1988; Elkem Datasheet C4-12 2001) and the Indianapolis Airport Parking Garage (Vogel 2008).

3.3 Fresh and Early Age Concrete Properties

3.3.1 *Workability*

The large increase in surface area gives a corresponding increase in internal surface forces which means an increase in the cohesiveness of the concrete. This effect is mostly advantageous, but it also means that the concrete seems to be slightly stiffer in placing, which means that an increase in slump is required to maintain ‘apparent’ workability. This is one important reason why silica fume is used with plasticisers or superplasticisers.

The term ‘apparent’ workability refers to the effect of silica fume on the slump cone measurement of a concrete and on how the slump compares with the workability of the mix: a fresh silica fume concrete will have a lower slump than a similar ordinary concrete due to the cohesiveness of the mix. When energy is applied to the mix, as in pumping, vibration or tamping, the silica fume particles, being spherical, will act as ball bearings and lubricate the mix giving it a greater mobility than ordinary concrete of similar slump. The effect is thoroughly described by Wallevik and Gjorv (1988). In the (Tattersall) two-point tester, the addition of silica fume will cause a decrease in the viscosity of the material while slightly increasing the shear strength of the fresh mix.

The effect on workability will vary between silica fumes from different sources (see ‘Production’). In addition, the form of product (undensified or densified powder, liquid slurry—see Available Forms) that is used will influence the water demand of the material (Fidjestøl 1991). The high specific surface area of silica fume (typically 15,000–30,000 m²/kg) means that there will be an increased water demand. This can be partly offset by additional modifications to the mix design, such as reducing the content of other fines. Concrete mixes using silica fume are now frequently designed using particle packing methodology. This incorporates the ultrafine spherical particles into the total grading for the mix and thus enables balance between the fine and coarse materials, reducing the extra water demand, and giving improved rheology to the concrete.

3.3.2 *Rheology*

Since silica fume concrete is more cohesive, it is therefore less susceptible to segregation than regular concrete, even in flowing concretes. The reduced tendency to segregation is also useful for high-fluidity grouts and pumped concrete mixes. The addition of small amounts of silica fume to a mixture designed for pumping will act as a pumping aid, giving very good pumping characteristics (Sandvik et al. 1989; Burnett 1990). The world’s tallest building (2015) The Burj Khalifa in Dubai, achieved a world record, of over 600 m, for vertical pumping—with a single pump—using a high performance ternary blend silica fume concrete.

3.3.3 *Bleeding*

Another consequence of the cohesiveness is that a silica fume concrete will produce virtually no bleed water. Therefore, fresh concrete must be protected from excess evaporation to prevent plastic shrinkage cracking and the hardened concrete must be cured in accordance with good site practice. The lack of bleed water also means that finishing of flatwork, such as power-floating, can start much earlier than with ordinary concretes.

3.3.4 *Chemical Admixture Interaction*

Vikan and Justnes (2007) made cement pastes with a constant total particle volume of 0.442 corresponding to w/c about 0.40 as basis, while the amount of silica fume (SF) was replacing cement in volume increments of 0.01 from 0.00 to 0.06. They concluded that the influence of SF replacement on the flow resistance depended on the plasticizer type: The flow resistance increased with increasing silica fume replacement when naphthalene sulfonate—formaldehyde condensate (NSF) was added as a plasticizer and decreased when a polycarboxylate ether (PCE) was added. Increased flow resistance and gel strength with SF replacement using NSF may be caused by early gel formation due to water binding by SF or the ionization of SF surface due to the high pH and possible bridging with polyvalent cations like calcium. Decreased flow resistance with increasing SF replacement using PCE can be explained by the dispersing power of the plasticizer and its ability to coordinate to calcium adsorbed on the surface of SF (Lesti et al. 2010) coupled with SF particle packing between cement grains displacing water or by a ball-bearing effect of silica spheres.

3.3.5 *Setting Time*

The lack of bleed water, increased shear resistance and a tendency to gelling (stiffening when not agitated) have been taken to indicate that the addition of silica fume means a more rapid set. However, it is a pure pozzolan and requires calcium hydroxide to start the pozzolanic reaction. The necessary calcium hydroxide is produced by the hydration of cement and thus the pozzolanic reaction is only possible after the cement has started reacting. The setting times for silica fume concretes are similar to those of ordinary concretes. The effect on the rate of hardening—for a normal concrete (not specifically designed for rapid high strength)—can usually be seen after 8 h and the reaction is strongest during the first 7 days (Fidjestøl and Frearson 1994).

3.3.6 *Initial Protection and Curing*

Due to the lack of bleed water with a silica fume concrete, all exposed surfaces must be protected from evaporation in the plastic state and then cured properly. This can take many forms.

Misting, wet hessian, membrane forming compounds or evaporation retarders, plastic sheeting or combinations of these. Curing is dependent on the ambient conditions and the nature of the concrete being placed—and should be designated before any concrete work starts.

3.3.7 *Shrinkage*

The shrinkage of silica fume concrete is similar to that of normal concrete. However, due to the reduced rate of drying, shrinkage takes place at a slower rate. In standard tests this means that shrinkage observed at a relatively early age will be less in silica fume concrete than in normal concrete (Burg and Ost 1994; Johansen 1979; Buil and Acker 1985).

3.3.8 *Early Age Strength*

As the concrete hardens, the chemical action of the silica fume takes over from the physical effects (Detwiler and Mehta 1989). Silica Fume reacts with calcium hydroxide to produce calcium silicate hydrates (C–S–H). Thus the amount of binder is increased, which both increases the strength and reduces the permeability by densifying the matrix of the concrete.

Since silica fume has a very high surface area and a high content of reactive silicon dioxide, it is more reactive than other supplementary materials, such as pulverised fuel ash/ fly ash (pfa/fa) and ground granulated blastfurnace slag (ggbs) (Regourd 1983; Glasser and Marr 1984). Some investigators have found that the increased reactivity appears to accelerate the hydration of the C₃S fraction of the cement initially (Andrija 1986; Sellevold et al. 1982), thus creating more calcium hydroxide, and that this settles down to more normal rates beyond 2 days.

As the silica fume reacts and produces the calcium silicate hydrates, voids and pores within the concrete are filled as the hydrates that are formed bridge the gaps between cement grains and aggregate particles. The combination of chemical and physical effects means that a silica fume concrete will be very homogeneous and dense. This gives greatly improved strength and impermeability (Diamond 1986).

It has been found that the relatively porous interface, rich in Portlandite, that surrounds aggregate particles in normal concrete is almost absent in silica fume concrete (Bentur et al. 1987; Bentur and Cohen 1987).

3.3.9 Heat of Hydration

Silica fume will give approximately the same heat of hydration as portland cement on a kilo for kilo basis. When used in concrete to replace an equal mass of cement, the total heat of hydration will be approximately the same. When designed for a given 28-day strength, a silica fume concrete will normally develop less heat than a regular portland cement concrete. This is because the silica fume can be added at one-third of the amount of the cement that can be removed and thus, while contributing as much heat as the cement per kilo, the overall reduction in cement content gives a lower total heat. Cement 'replacement' is normally only used where low heat is specifically required. Silica fume is used mainly for higher performance concrete, to increase strength and reduce permeability, and hence is an addition to the base cementitious content. When used in this way, with a lower water cementitious ratio, the heat of hydration may rise faster in the early stages and this should be taken into consideration in the curing of the concrete.

Silica fume concrete is more sensitive, than a pure portland mix, to temperature variations while hardening. The rate of hydration and the gain in strength, will be reduced with low temperatures, and dramatically accelerated with increased ones (Sandvik 1981).

3.4 Hardened Properties

3.4.1 Summary of Effects on Mechanical Properties

High-strength (80 MPa) and very high-strength (120 + MPa) concretes are produced on a routine basis with the addition of silica fume. This can mean faster turnaround and the potential for reduced section thickness, or the ability to build longer spans or taller structures. Tensile and flexural strengths are as in normal concretes, and increase proportionally with the compressive strength, although the addition of fibres, with the increased bond resulting from the silica fume, can increase these properties.

In fire testing, very high-strength, low water/cementitious ratio concrete, may be susceptible to spalling on exposure to a very rapid temperature rise. With correct design and the use of polypropylene fibres (a now standard procedure) high strength silica fume concretes can give excellent fire resistance performance. The increased strength and bond to the aggregate in the matrix means that high-strength silica fume concrete has excellent potential for abrasion and erosion resistance.

3.4.2 Compressive Strength

Many reports are available (Loland 1983; Loland and Hustad 1981; Sellevold and Radjy 1983) which show that silica fume, when added to a concrete mix, will increase the strength of that mix significantly. The actual amount and percentage of strength increase will depend upon numerous factors, some of which are: the type of mix, type of cement, amount of silica fume, use of water reducing admixtures, aggregate properties and curing regimes.

Concrete with silica fume appears to follow the conventional relationship between strength and water/cement (w/c) ratio.

As with other supplementary cementitious materials, silica fume concretes are somewhat sensitive to early drying; one consequence can be reduced final strength (Johansen 1981). Some combinations of silica fume and fly ash appear more resistant to this effect (Maage and Hammer 1985).

With proper mix design, concretes of very high strengths can be produced using normal ready-mix facilities. In the USA concretes of 100–130 MPa are used in tall buildings. Silica fume concrete of approximately 100 MPa was used in the construction of the Petronas Towers in Kuala Lumpur, the Burj Khalifa in Dubai (Elkem Datasheet C13-02 2013) and the [under construction, 2017] Kingdom Tower in Saudi Arabia, three of the world's tallest buildings. Concrete's averaging 130 MPa have been used in towers in Japan (Elkem Datasheet C4-32 2003).

3.4.2.1 High Strength Concrete

High-strength concrete is used in various applications and, as the achievable strength increases with developing technology, the advantages of concrete as opposed to other building materials become more defined. Typically, 'high strength' refers to concretes of 80 MPa and above, but with the advent of highly efficient superplasticisers and silica fume, strengths can be as high as 130 MPa or more, for casting *in situ*. As an example, UK production concrete has reached values in excess of 155 MPa. Such high strengths allow improvements in design, such as a reduction in the cross-section of a compressive member and increased spans of flexural members. Thus large savings can be made on materials and construction and the rent-generating area of a building can be increased. A Brite Euram study (Project 5480. 1995) into the ready mix production and use of concretes over 100 MPa has been led by Taylor Woodrow. The mechanical properties of the 120 MPa concretes easily met the anticipated performance levels with respect to handling and mechanical properties (Price and Hynes 1996; Price 1996).

3.4.2.2 High Early Strength—High Ultimate Strength

High early strength is utilised in the precast industry for faster turnaround of moulds and increased strength for early age handling. High early strength ready-mixed

silica fume concrete can be delivered, placed, finished, cured and gain strength of more than 40 MPa within 24 h. This allows fast construction with high turnaround on formwork and short downtime for projects which may require suspension of other activities during construction (e.g. motorway work).

Concretes with high ultimate strength have similar mix design parameters, such as a low water/cement ratio. High ultimate strengths can also be obtained with blended cement, pfa or ggbs (Domone and Soutsos 1995) with a small dosage of silica fume. Here the lower heat of hydration and slower pozzolanic action reduces problems in massive sections, while still giving sufficient early age strength values for construction purposes. A major example of such use was the slipform construction of the twin towers of the Tsing Ma bridge in Hong Kong (Elkem Datasheet C4-14 2001). 65% ggbs was used to reduce thermal effects and 5% silica fume was added to give improved rheology to the mix and better strength gain at early ages (in addition to improved durability to seawater).

High-strength lightweight concretes can also be produced using the pozzolanic action of silica fume. In this way, a wide variation of strengths and densities can be achieved, from 100 MPa at 2000 kg/m³ to 5 MPa at 500 kg/m³.

An example of the use of high-strength silica fume concrete is in one of the world's tallest reinforced concrete buildings, 311 South Wacker Drive, Chicago, completed in 1990. This construction used silica fume concrete of varying strengths. This allowed the same formwork to be used on the columns from the first to the top floor. Nearly 84,000 m³ of concrete was used; starting at 83 MPa for the first 14 floors and ranging from 69 MPa through to 52 MPa at the top. By using high-strength concrete, to give a uniform column size, a saving was achieved, in comparison to the conventional design quantities, of 3000 tonnes of reinforcing steel and 7650 m³ of concrete. The saving in concrete volume is directly equivalent to increased space within the building and hence increased return for the client.

3.4.3 Tensile and Flexural Strength

The relationships between tensile, flexural and compressive strengths in silica fume concrete are similar to those of ordinary concrete. Thus an increase in the compressive strength using silica fume will result in a proportional increase in the tensile and flexural strengths, the same as in concrete without it.

The improved tensile and flexural strengths are important to the use of silica fume concretes in flooring, bridging or roadway projects. The increased tensile strength allows for a possible reduction in the slab thickness while maintaining high compressive strengths, thus reducing overall slab weight and cost. Another facet of the very high strength, 100–120 MPa, silica fume concrete is the utilisation of the high modulus, 45–50GPa. Buildings can be designed to resist fatigue effects that can cause structural failure with normal concretes.

3.4.4 Modulus of Elasticity

The modulus of elasticity is not proportional to the compressive strength, so that a high compressive strength does not mean a similar increase in modulus (Larrard et al. 1987). The final strain before failure in uniaxial compression increases with increasing strength, but the stress–strain curve is often close to linear before such failure. The ductility of the whole structure will rely more on reinforcement and detailing than on the ductility of the component material concrete. Use of particle packing technology is helping to reduce this, by balancing the aggregate/cement relationship and improving the integrity of the concrete mix.

3.4.5 Bond

The improved packing contributed by the very small size of the particles of silica fume will improve the contact surface and the bond between the fresh silica fume concrete and the substrate, such as reinforcement, old concrete, fibres and aggregates. Investigation has shown (Carles-Gibergues et al. 1982) that the aggregate cement interface is altered when silica fume is present, and pull out tests (Gjorv et al. 1986; Monteiro et al. 1986) show improved strength. Bonding to fibres is greatly improved (Bache 1981; Krenchel and Shah 1985; Ramakrishnan and Srinivasan 1983) and is particularly beneficial in steel fibre/silica fume-modified shotcrete.

3.4.6 Creep

Most work on the creep of silica fume concrete is related to high-strength concretes. Ost and Burg (PCA/CTL undated) found significant reduction in creep with the addition of silica fume, while Hansen (1987) reports scant effect of silica fume on creep, providing the modulus of elasticity was constant. Persson (1996) and Tomaszewicz (1985) report reduced specific creep for high-strength concrete with silica fume compared to conventional normal-strength concrete.

3.4.7 Fire Resistance

Based on some early tests (Hertz 1981) a concern formed that high-strength silica fume concretes could explode when exposed to fire. However, several tests (Wolsiefer 1982; Maage and Rueslatten 1987; Shirley et al. CI undated) have shown that under normal fire conditions silica fume concrete does not behave any

differently to normal concrete. The mechanism involved is probably one of high resistance to steam movement (Jahren 1989). If soaked concrete is tested in very intensive fire tests, where the low permeability of the silica fume concrete means that steam cannot escape, spalling occurs due to steam pressure. Well-cured and conditioned concretes like those above have not shown spalling; however, there are indications that for all high-strength concretes, regardless of silica fume content, there is a water/binder ratio below which spalling due to fire may be a concern. Some investigators (Oredsson 1997) put this limit at about 0.33. Below this limit, special care should be taken, and plastic fibres are suggested to reduce spalling (the plastic fibres burn out quickly, leaving pathways for steam to escape).

It should be noted that the type of fire is of great importance. The concerns mentioned above are much more valid for fires with very rapid rise, while for the typical ISO fire, (ISO 834. 1975) the concern and associated risks of spalling are much less, perhaps even absent.

3.4.8 Abrasion and Erosion

High-strength silica fume concretes show greatly improved resistance to abrasion and erosion. This has become an important application area for such concrete. One of the first test beds for this, a large repair project on the Kinzua Dam, USA, has been studied (Holland 1983) and subsequent inspections after 30 years (Luther and Halczak 1995) showed good performance of the silica fume concrete. Increased use in such applications has become widespread, with India and Turkey using this performance characteristic of the concrete for major projects.

The Norwegian practice of using studded tyres on cars during winter means extreme wear of the road surface. In recent years high-strength silica fume concrete has become the paving material of choice for high wear resistance. One example is a 95 MPa concrete on a 10 km stretch of highway north of Oslo. It has been found that the use of such paving reduces the wear by a factor of 5–10 compared to high-quality black-top (Helland 1990).

3.4.9 Transport Properties

3.4.9.1 Porosity

The main physical effect of silica fume on the microstructure of hardened concrete is a refinement of the pore structure. The total pore volume is not necessarily changed, but large pores appear to be subdivided into smaller pores (Yogendran and Langan 1987). The improvement in pore structure is reflected in the higher strength, but it is also of great importance in reducing the permeability of the material.

Another important factor is the improvement in quality of the transition zone between aggregate particles and cement paste. Studies have shown significant improvement in structure and composition (Goldman and Bentur 1989; Regourd M.⁵⁹; Monteiro and Mehta 1986). Apart from the improved bond between aggregate particles and paste, the porosity and transport capacity of the interface region is reduced.

3.4.9.2 Permeability

Permeability is a measure of the ease of passage of liquids or gases through the material. Permeability is determined by measuring the depth of penetration of a liquid or gas into, or passing through, the sample. Measurements using pressure heads can be supplemented by capillarity and porosity studies. Similar information can be obtained (for water) by measuring rate of mass loss during drying.

Permeability, or more generally resistance to fluid penetration, is important for two reasons: the parameter describes how rapidly deleterious substances may enter the concrete and how easily material can be leached from the concrete.

Many examples of testing silica fume concrete, in binary or ternary blends, show that addition of silica fume can significantly reduce the permeability of concrete. Results of zero penetration for water and ‘negligible’ results (using the ASTM C1202 index test) for chloride ingress have been recorded in numerous major projects (Burj Khalifa, Elkem 2013).

3.5 Durability

The major influence of the silica fume on the chemical and physicochemical durability of concrete is through the large reduction in the permeability. For water, the reduction in permeability can be by a factor of between 10 and 100 times compared to a control concrete. The reduction in the chloride diffusion value can be as high as 500–1000 times.

The deterioration of silica fume concrete is demonstrably slower than comparable normal concretes for most chemical and physicochemical attacks. The actual increase in resistance depends on the mix design, quality control and curing of the concrete. Neglect in the execution of any of these may result in a weaker and less durable concrete than normal.

3.5.1 Sulfate Resistance

A major study was started in Oslo during the first years of testing silica fume in concrete. This involved submerging specimens, of various mixes, in acidic

sulfate-rich groundwater leached from the alum shale in Oslo. (Alum shale contains high amounts of unstable iron sulfides. On contact with air, the sulfur is oxidised into sulfur dioxide, which will give a low pH dissolved in water.) The 12 and 20-year results are available from this trial (Fiskaa et al. 1971; Fiskaa 1973). The results show that the silica fume concretes (15% MS, w/c = 0.6) performed as well as the mixes with sulfate-resisting cement (w/c = 0.45). This is confirmed in unpublished data from 30 years of reports and by laboratory tests (Mather 1980; Fidjestøl 1990).

When used with ggbs or pfa (Carlsen and Vennesland 1982; Fidjestøl and Frearson 1994) silica fume mixes have been found to be more resistant to sulfate attack than special sulfate-resisting portland cements. This experience has caused silica fume to be required for concrete in the Arabian Gulf to combat the severe deterioration of the concrete due to both sulfate attack and chloride initiated corrosion (Rasheeduzzafar 1992).

The good performance of the silica fume mixes in a sulfate environment can be attributed to several factors (Fidjestøl 1987a, b) of which the most important are likely to be:

- the refined pore structure and thus the reduced passage of harmful ions (Popovic et al. 1984)
- the lower calcium hydroxide content, which leads to reduced formation of gypsum (and consequently of ettringite).

3.5.2 Chloride Resistance

Chloride resistance is normally considered in terms of chloride entering from the surface of the concrete. Occasionally, however, chloride can be introduced into concrete at the time of mixing. A common source used to be chloride-based accelerators and poorly cleaned marine aggregates. Thus the ability of the concrete to bind chlorides chemically is of interest, in addition to the ability to withstand chloride penetration, from sea water or de-icing salts.

A number of studies have been made (Mehta 1981; Page and Havdahl 1985; Monteiro et al. 1985) which consider the combined effects of reduced permeability and the reduction of pH in the pore water and how these factors interact regarding the passivity of embedded steel.

The slight reduction in pH, caused by the uptake of calcium hydroxide by the silica fume, will cause a reduction in the threshold chloride concentration, i.e. the amount of chlorides necessary to destroy the passive layer and initiate corrosion. This effect is counter-balanced by the reduced rate of chloride diffusion due to the addition of the silica fume (Gautefall 1986a, b).

The rapid chloride permeability index test (ASTM C1202 1996) is routinely used to describe the resistance of concrete to chloride ingress. Typically, silica fume concrete will achieve a very low (good) to negligible (excellent) rating in this test.

Silica fume works in several ways to reduce the risk of corrosion. The reduced permeability properties of silica fume concrete mean greatly reduced rates of chloride penetration in marine structures and structures exposed to de-icing salts. These concretes also have very high electrical resistivity, thereby greatly diminishing the rate of corrosion, should it be initiated (Wolsiefer 1991; Petterson 1995; Fidjestøl 1993; Fidjestøl and Frearson 1994; Alonso et al. 1992; Berke et al. 1992; Gautefall 1986a, b; Gautefall and Vennessland 1985; Zhang and Gjörv 1991; Fidjestøl 1987a, b).

3.5.3 Alkali Silica Reaction

This aspect of silica fume concrete was one of the first to be commercially exploited on a large scale. Consideration of the effect of silica fume on this form of chemical attack requires attention to the three main factors that are required for possible ASR to take place:

1. high alkali content in the mix (normally supplied by the cement);
2. reactive aggregates, containing reactive silica;
3. available water.

Well-dispersed silica fume reacts with the available alkalis in the fresh concrete, forming alkali silicates. This binds the alkalis, and should prevent attack on reactive siliceous aggregates. This mechanism reduces the risk of ASR through combating factor 1 above. The reduction in pore solution alkalinity provided by silica fume (the conversion of calcium hydroxide to calcium silicate hydrates) will also help prevent deleterious ASR. Since silica fume contributes to a reduced permeability, the amount of available water is less. These factors combine to reduce the susceptibility of the concrete to ASR.

Between 1979 and 2012 the high-alkali blended cement produced in Iceland was made with an average of 7.5% microsilica, a remedy which, together with other improvements in construction procedures, has put an end to the previously severe ASR problems (Asgeirsson and Gudmundsson 1979; Asgeirsson 1986). Although all cement is now imported, and has a lower alkali content than previously, Iceland still use the addition of silica fume to prevent ASR.

The use of 4% silica fume in combination with 25% ggbfs has been effective for over 20 years in controlling ASR in beam and pavements at a field exposure site in Canada (Thomas et al. 2007). Recent, separate, testing in Turkey and Iceland has shown that even with very reactive aggregates, the addition of silica fume, at levels between 8 and 11%, will control expansion to below 0.1% (Lewis and Bayrak 2015).

3.5.4 Carbonation

The conclusions shown by the available reports (Vennesland and Gjrv 1983; Vennesland 1981) are that, for a given strength below 40 MPa, a microsilica concrete may show increased carbonation rates, corresponding to the increase in water/cementitious ratio. Silica fume concrete above 40 MPa, with a lower water/cementitious ratio, shows little change in carbonation rate. As silica fume concrete will normally be intended for special use and have a low water/cementitious ratio, the concern over the change in carbonation rate is not normally warranted. As always, correct adherence to initial and long term curing are essential for optimum performance of the silica fume concrete.

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Further Reading/Information Sources

- ACI publications—ACI 234.R “Guide for the use of Silica Fume in Concrete”
- Concrete Society (UK)—Technical Report 41 “Microsilica in Concrete”
- CRC Press—“Condensed Silica Fume in Concrete” (1987)
- Elkem Silicon Materials—www.elkem.com/en/Concrete
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- Institute of Concrete Technology (UK) - Advanced Concrete Technology (Constituent Materials) (2003)
- The Silica Fume Association (including Life365)—www.silicafume.org

Chapter 4

Limestone Powder

Luc Courard, Duncan Herfort and Yury Villagrán

Abstract Limestone has been successfully used as a constituent of cement and concrete for decades. Fine limestone is commonly included in Portland cement by intergrinding, resulting in an optimal particle size distribution of the modified cement. In other applications, limestone powder is added separately from cement, for producing more stable and robust mixes, especially self-compacting concrete. This chapter examines the performance of limestone modified Portland cement and concrete. The review comprises the effects on cement hydration in relation with the fineness of the limestone, on the fresh properties of mortar and concrete (including its role in self-compacting concrete), and on the strength development in the hardened state. Complementarily, comments regarding sulphate attack and environmental benefits of the use of limestone modified cement are included. Limestone is an effective constituent of cement and concrete, and comparative analyses should always be made to mixes produced to the same strength. In this way, it has to be regarded as a supplementary cementitious material when included by intergrinding with cement clinker, or as a filler when added separately to concrete.

Keywords Limestone · Filler · Concrete · Cement · Durability
Hydration · SCC

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4.1 Introduction

Fine limestone has been added to Portland cement for decades. This is normally achieved by “intergrinding” it with Portland cement clinker in the cement mill. Under normal operating conditions this will result in a surface area of the limestone fraction of between 800 and 1100 m²/kg (depending on the *grindability* of the limestone) for a surface area of the clinker fraction of in the region of 400 m²/kg. Less often the limestone is ground separately and blended with Portland cement. Separate addition of limestone to concrete as a clinker replacement is not widely practiced in conventional concrete, but is used as filler for modifying the rheology of self-compacting concrete.

In the early literature limestone was generally regarded as “inert filler”. For this reason it has e.g. become the main constituent in most masonry cements where high levels of replacement of the Portland cement are needed to reproduce the properties of traditional lime mortars. However, for its application in concrete, which is the primary focus of this report, the limestone’s contribution to the hydration reactions can be significant when it is co-ground with the clinker, albeit in relatively small amounts. So much so that it can arguably be classified as an SCM alongside GBFS and fly ash.

The first significant use of limestone in general purpose Portland cement took place during WWII when it was used in several European countries to cut costs and increase output (Lea 1998). Its widespread use today can be traced back to the 1973 oil crisis, with France, which had low production of fly ash and blast furnace slag, leading the way. The Portland limestone cements in the European cement standard EN 197-1 (2001), were adopted more or less un-changed from the French standard NF P 15-301 (1981).

A systematic review of all standards and specifications for limestone and Portland limestone cements is beyond the scope of this report. The most recent and comprehensive review of this can be found in Tennis et al. (2011). Many countries allow minor clinker replacement in cement of 5 or 10% limestone, including China (10%), India (5%), Brazil (10%), and the US (5% in ASTM C150). Higher amounts are allowed in the cement standards in Europe (35%), Mexico (35%), Argentina (20%), the US (15% in ASTM C595) and Canada (15%).

Taking Europe as an example (Figs. 4.1 and 4.2), where the volume of limestone used is greatest, in 2010, Portland limestone cements accounted for 27% of all cements produced, or even 46% if the CEM II M composite cements which allows mixtures of limestone and other SCMs is to be considered. This amounts to 4-fold increases in the relative amount of Portland cement containing limestone as a major constituent since 1990 (Hertfort 2008).

As shown in Fig. 4.2 most of the Portland limestone and composite cements conform to the 32.5 and 42.5 strength classes, although “*very high strength*” 52.5 Portland limestone cements are also produced.

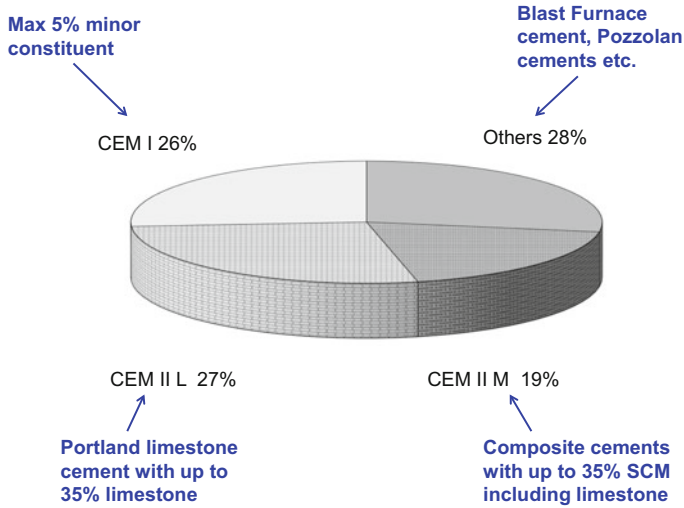
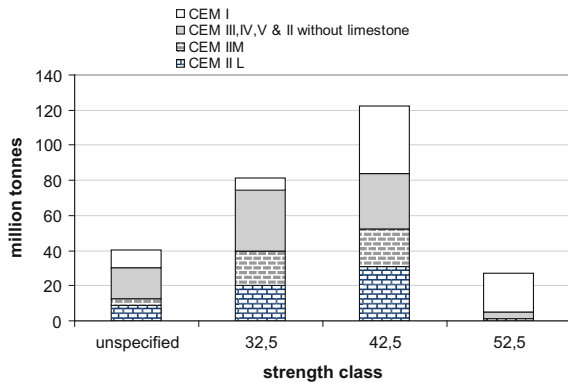


Fig. 4.1 Cement types produced in Europe in 2010 (reproduced from CEMBUREAU 2008). Others include CEM II, IV, V and CEM II not containing limestone as a major constituent (i.e. Portland-slag, silica, pozzolana, fly ash, and burned shale cements containing up to 35% clinker replacement)

Fig. 4.2 Breakdown of cement types into strength classes (reproduced from CEMBUREAU 2008)



Most countries around the world specify similar chemical and physical requirements for the limestone that can be used, including a minimum CaCO_3 content of 70 or 75%, and maximum contents of clay and TOC (total organic carbon).

A comprehensive review of the application standards for Portland limestone in concrete is beyond the scope in this report, and practices differ widely from country to country. In the US for example cement types for a given application are specified at state level. In Europe, although the cement standard EN 197-1 is harmonized, the cement types that can be used in a given exposure class (defined in the European concrete standard, EN 206) are specified in the national application standards. This

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| | | | | | | SEA WATER | | | OTHER | | | | | | | | | | |
| | | | | | | XS1 | XS2 | XS3 | XD1 | XD2 | XD3 | | | | | | | | XF1 |
| Exposure class | X0 | XC1 | XC2 | XC3 | XC4 | XS1 | XS2 | XS3 | XD1 | XD2 | XD3 | XF1 | XF2 | XF3 | XF4 | XA1 | XA2 | XA3 | |
| DK | A | | | | | | | | | | | | | | | | | | |
| | B | | | | | | | | | | | | | | | | | | |
| UK | A | | | | | | | | | | | | | | | | | | |
| | B | | | | | | | | | | | | | | | | | | |
| DE | A | | | | | | | | | | | | LL | LL | LL | | | | |
| | B | | | | | | | | | | | | | | | | | | |
| FR | A | | | | | | | | | | | | | | | | | | |
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| SE | A | | | | | | | | | | | | | | | | | | |
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Fig. 4.3 National application standards allowing Portland limestone cements in selected European countries (Herfort 2008). Red filled square—not allowed, Open square—allowed, Square with upper left to lower right fill—allowed except for highly aggressive sulphate environments, [LL] LL refers to a maximum of 0.20%

is shown for selected countries in Fig. 4.3. Germany and Denmark, for example, allow the CEM II/A L, LL cements, with up to 20% limestone, in all exposure classes except where high sulphate concentrations are involved in classes XA2 and XA3. The CEM II/B cements allowing up to 35% limestone have more limited application, and where they are allowed, are restricted to the exposure classes where carbonation is the sole source of attack.

4.2 Hydration Reactions and Strength of Portland Limestone Cements

Although it has not been widely accepted until fairly recently that limestone additions are not inert, reports in the literature date back at least 30 years (Bensted 1980) showing that calcium carbonate reacts with the AFm phases to form carbo-aluminate analogues, i.e. the so-called hemi- and mono-carbo-aluminate hydrates. Probably the most comprehensive work on these reactions to date has been performed by Nanocem network partners over recent years (Matchei et al. 2007; Lothenbach et al. 2008; De Weerd et al. 2010). The results from this work are adapted in this report to show the compatibility of relevant phase assemblages on the sub-ternary phase diagram shown in Fig. 4.4 (a detailed account of ternary phase diagrams applied to hydrated cement can be found in Herfort and Lothenbach

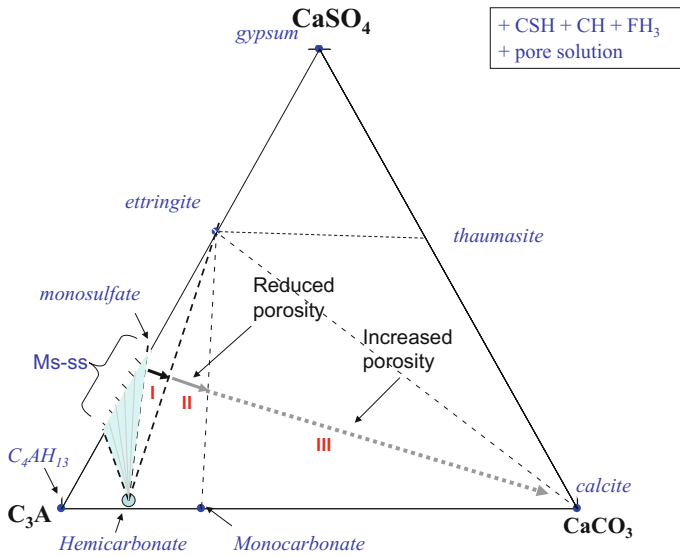


Fig. 4.4 Hydrate phase assemblages in the ternary sub-system for CaSO_4 - C_3A - CaCO_3 within the multicomponent system for Portland limestone cement. Phases in this subsystem are given in italics, and regions of stability are indicated by the 3-phase regions in which the composition of any given system (e.g. CEM II L + additional CaSO_4) plots onto the diagram. Excess phases are shown in the top right inset of the diagram

2015). This makes it clear that the addition of limestone to a typical Portland cement will result in the following sequence of reactions:

1. ettringite forms via consumption of monosulphate,
2. when monosulphate is exhausted, monocarbonate forms via consumption of hemicarbonate,
3. when the hemicarbonate phase is used up additional calcium carbonate does not react but persists as a stable phase.

Reactions 1 and 2 are space filling resulting in a reduction in porosity, whilst the further addition of carbonates in reaction 3 results in increased porosity. This type of diagram shows the relative contents of phases that form within the sub-system. Of course, higher absolute contents of aluminates (or C_3A defined here as a “component”) result in more monocarbonate formation and therefore higher amounts of reacted calcium carbonate before further additions result in an increase in porosity.

By calculating the contents of phases in volume % (by assigning realistic densities to the phases), it is possible to calculate the theoretical porosities and then using an empirical relationship between strength and porosity the theoretical strength can also be predicted. This is illustrated in Fig. 4.5 (from Lothenbach et al. 2008). What is important is the point at which additional calcite ceases to result in increased strength (reduced porosity) and the extent that this correlates with real

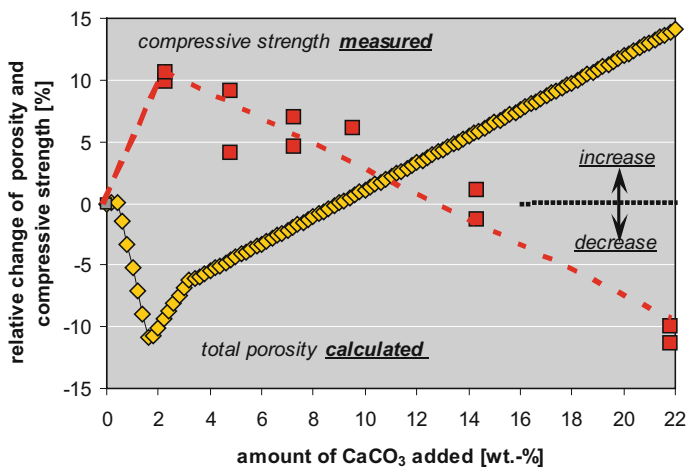


Fig. 4.5 The effect on 28 day cement (EN 196 mortar) strengths with additions of fine limestone (c. 1100 m²/kg) to mineralised cement (c. 400 m²/kg) (from Lothenbach et al. 2008)

strength data (in this case EN 196 strengths). In the example used here there is indeed good agreement with real data for the increased strengths achieved by the addition of limestone to mineralised cement (Borgholm et al. 1995). Several other workers have confirmed the reactions shown in Fig. 4.4, and the associated reduction in porosity (Lothenbach et al. 2008; De Weerd et al. 2010).

The optimum 28 day strength occurs at c. 2% addition corresponding to the point where all of the available alumina from the clinker has reacted with the calcium carbonate and sulphate to form AFm and AFt phases. The theoretical porosity is calculated by the method described e.g. in Bensted (1980).

In addition to the hydration reactions described above, fine limestone has also been shown to result in an accelerated hydration of the C₃S phase in Portland cement without directly taking part in the reactions: this is resulting in early strengths being, either unaffected, or increased with up to 10% fine limestone replacement (Borgholm et al. 1995; Kristensen 2008).

4.3 Effect of Limestone Fillers on Fresh Properties of Mortar and Concrete

4.3.1 Influence on Water Requirement

Usually, the main physical characteristics of limestone powder that are highlighted regarding water requirement are fineness, particle size distribution (PSD), and particle morphology (Arvaniti et al. 2015). From the comparison of different studies in the literature on limestone powder use in concrete, Diederich et al. (2012)

concludes that water demand of concrete is affected by the limestone powder content depending on its physical properties. However, a warning should be made as only focusing on the physical properties of limestone powder may lead to contradictory outcome due to the potential influence of certain minor components of limestone on its water requirement (Diederich et al. 2012).

Michel et al. (2007) studied the relation between the properties of several limestone powders and their water requirements. These limestone powders were different from each other with regard to fineness and clay content. Differences between Blaine and BET specific surface areas (Arvaniti et al. 2015) were pointed out and linked to the clay content of limestone. A clear connection between BET specific surface area and clay content determined by methylene blue adsorption (EN 933-9) can be seen in Fig. 4.6. This is reflected in the water requirement (Fig. 4.7), which did not show a good correlation with the Blaine specific surface area or the

Fig. 4.6 Comparison between Blaine specific surface area, BET specific surface area, and methylene blue adsorption (MBA) of limestone powders (F1–F6) from data in Michel et al. (2007)

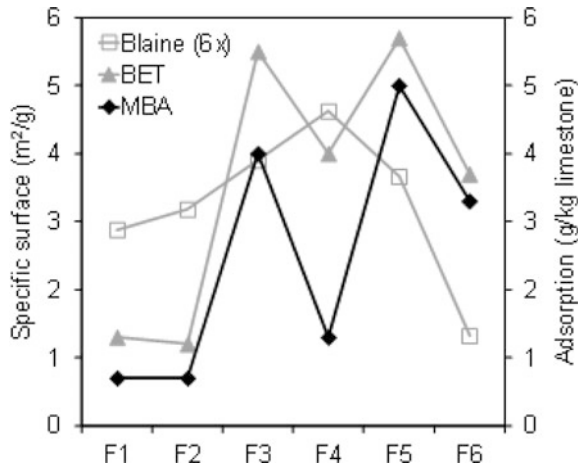


Fig. 4.7 Comparison between Blaine specific surface area, BET specific surface area, and water requirement (β_p) of limestone powders (F1–F6) from data in Michel et al. (2007)

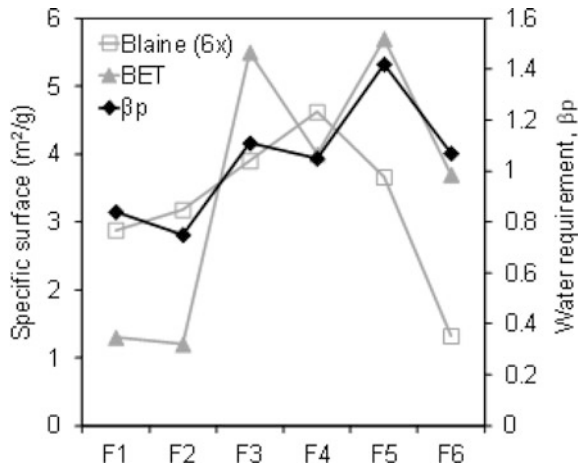
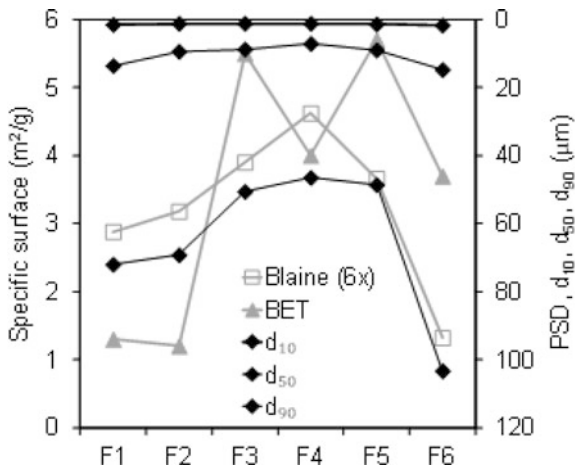


Fig. 4.8 Comparison between Blaine specific surface area, BET specific surface area, and particle size distribution (PSD—laser granulometry) of limestone powders (F1–F6) from data in Michel et al. (2007)



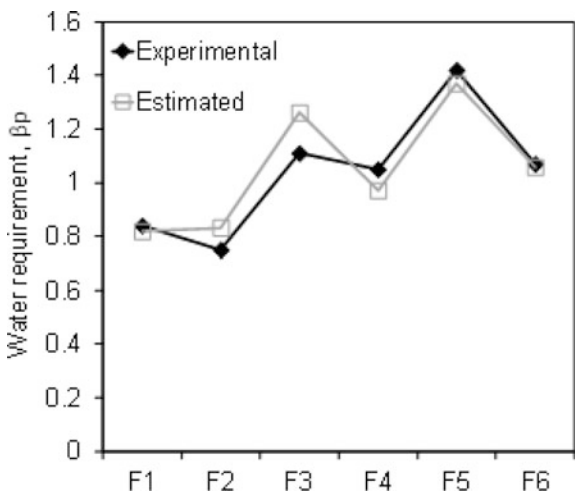
particle size distribution (Figs. 4.7 and 4.8), even if these results are changing for the different methods at the same time (Fig. 4.8).

Clay content and type are changing dramatically the percentage of fine particles in the mix.

Equation 4.1 can be empirically derived (Michel et al. 2007) for estimating the water requirement of limestone powder on the basis of its Blaine specific surface area and clay content, where MBA is the methylene blue adsorption in g/kg of limestone and Blaine is the Blaine specific surface area in m²/g. The coefficients in Eq. 4.1 were obtained by multiple linear regression of data (Michel et al. 2007), with R² = 0.86 (Fig. 4.9).

$$\beta_p = 0.6 + 0.12 \cdot MBA + 0.28 \cdot Blaine \tag{4.1}$$

Fig. 4.9 Correlation between the estimated water requirement with the experimental water requirement of limestone powders (F1–F6) from data in Michel et al. (2007)



The clay content of limestone powder is definitely a key parameter to appreciate its influence on water demand. Good correlations (Michel et al. 2007) have been found between mortar consistence and water requirement of limestone powder, i.e. fineness and clay content. It should be noted that Michel et al. (2007) obtained lower values for β_p than those obtained for the ordinary Portland cement (OPC) when they used in mortar manufacture only limestones F1 and F2. Then, these two limestone powders would have been capable of reducing water requirement, whereas the rest would have increased it. F1 and F2 were characterized by a Blaine specific surface area lower than $0.55 \text{ m}^2/\text{g}$ and a methylene blue adsorption lower than $1 \text{ g}/\text{kg}$ of limestone. This implies that the maximum limit established in EN 197 (EN 197-1: 2011) of $1.2/100 \text{ g}$ is about ten times higher than the value for which water requirement seems to be affected by the inclusion of limestone.

Moreover, Courard et al. (2011) also analyzed differences between bentonite and kaolinite as minor components of limestone powder. They found a remarkable influence of bentonite on water demand, and a very little influence of kaolinite, which is explained by the much higher swelling property of bentonite. Therefore, they refer to the swelling clay content as the key property as regards water demand, instead of the total clay content.

Diederich et al. (2012) found no relationships between the flow properties of mortar including limestone powder and its morphology. They derived that it should not be considered that clay is included as grains, but as phases included in the grains of limestone particles. Therefore, under the effect of the grinding process, these phases would be exposed at the surface of grains and modify the surface properties that affect the flow.

In a comparison with other blended Portland cements (Voglis et al. 2005) and despite a higher fineness of limestone cement (required to achieve a similar strength level than others), water demand of limestone cement was not higher than that of OPC, but it was lower than for pozzolanic and fly ash cements. Similar results are presented in Courard and Michel (2014) where they use limestone powder in partial substitution of cement to produce mortars. All these binary cements were produced by intergrinding of clinker, gypsum and supplementary cementitious materials (replacement percentage of 15%). The main reason given for this lower water demand of limestone cement is that its particles had a wider particle size distribution than the particles of the other blended cements. This may imply a better packing density of particles and a lower requirement of water.

When cement is blended with different limestone percentage replacements, the optimum dry packing density of fines is obtained for a certain powder content dependent on the particle size distribution of both cement and limestone powder. In this regard, Joudi-Bahri et al. (2012) reported optimum limestone powder contents in concrete between $100\text{--}120 \text{ kg}/\text{m}^3$. They argued that intergranular voids are not well filled with lower limestone powder contents, whereas excess of single-sized particles lead to a loose suspension that demands higher mixing water content for a specific consistence level. This is in partial agreement with results from (Jones et al. 2003), where it is shown that the limestone powder content giving the lowest water

demand is less than the powder content required to achieve a minimum voids ratio from theoretical dry packing computations. They argue that the agglomeration of limestone powder particles, which increases its particle size and voids ratio, is responsible for this difference. In concrete with a lower Portland cement content ($<350 \text{ kg/m}^3$), the voids ratio of the concrete decreases with an increase in limestone content up to a certain limit, after which further increases in limestone content only result in small changes in the voids ratio. The decrease of voids ratio with increasing limestone content is reduced with increasing Portland cement contents; for high cement contents, the addition of cement-sized powder will even increase the voids ratio and the water demand. Since the lowest water demand, for a given workability of a binary limestone powder-Portland cement, was obtained for a limestone powder content lower than the one corresponding to the highest packing density, Jones et al. (2003) suggested two criteria to determine the optimum powder content for minimum water demand in plasticized mixes: a voids ratio reduction of 0.02 (equivalent to a reduction of concrete water demand of 15 l/m^3) in comparison with cement paste without limestone powder and a voids ratio reduction rate larger than $0.02\% \text{ m}^3/\text{kg}$ (i.e., the voids ratio reduced by more than 0.02% per m^3 of concrete through the addition of 1 kg of powder).

In a different direction, Wong and Kwan (2008) asserted that the packing density of particles is not directly related to the solid concentration in the mix, which varies with the w/c ratio. Therefore, the water demand could not be deduced from dry packing density of particles. Here, it is noted that the mixing water content at standard consistence of the mix is quite different from the basic water content, which is just sufficient to fill up the voids in the granular skeleton, or the minimum voids ratio. Moreover, entrapped air in the mix causes a positive effect giving more mobility to the mix and indirectly affecting water demand (Wong and Kwan 2008).

Using the method to determine the wet packing density (Wong and Kwan 2008) for limestone and cement blends, Diederich et al. (2012) found that the multiple influences of the different limestone powder and cement characteristics can be accurately represented through the evaluation of the excess water volume ratio defined as the surplus over the minimum void volume ratio of the paste. Accordingly, they found a general relationship between excess water volume ratio and flow parameters (yield stress and viscosity) for several limestone powders and cement types (Diederich et al. 2012).

4.3.2 Influence on Bleeding

Soria and Rahhal (2003) obtained similar bleeding values for 19 cm-slump at 20°C for concrete with or without a limestone powder content near 20%. At higher temperatures, however, they found that limestone concrete reduced bleeding capacity. The main explanation comes from the increase in the hydration rate caused by the filler effect.

On the other hand, Joudi-Bahri et al. (2012) reported decreasing bleeding capacity with higher limestone powder content for 23 cm-slump concrete. The influence reported for 15 and 7 cm-slump concrete mixes analyzed in the same study was much lower. The Blaine specific surface area of limestone was $310 \text{ m}^2/\text{kg}$, and its PSD was $d_{10}/d_{50}/d_{90} = 1.5/18/65 \text{ }\mu\text{m}$, respectively; the same parameters for the OPC were $320 \text{ m}^2/\text{kg}$, and $d_{10}/d_{50}/d_{90} = 0.8/7.5/35 \text{ }\mu\text{m}$, respectively. The decreasing in bleeding is explained by the requirement of a high volume of powder for high-slump concrete in order to stabilize the suspension of particles: when high flow concrete with low powder content, an excess in mixing water content will increase bleeding.

It should be mentioned that, as finer limestone powder tends to give more cohesive mixes and stronger suspensions (Diederich et al. 2012), an impact of the fineness of limestone powder on concrete bleeding may be expected, in accordance with the respective powder content. Three main physical phenomena acting on fresh cement paste are linked to bleeding (Perrot et al. 2012): Brownian motion, colloidal attractive forces and gravity. For pure cement systems, if colloidal attractive forces prevail over gravity, a stable suspension of particles in which particles cannot rearrange their relative positions is obtained. Low bleeding is usually observed in stable mixes. Predominant colloidal attractive forces also result in the ability to withstand an external stress up to a critical value, called yield stress. Though there is no direct correlation between yield stress and bleeding (Perrot et al. 2012), these two properties are strongly linked. On the other hand, gravity will dominate colloidal attractive forces in low viscosity mixes, and particles may settle with high bleeding capacity as a result. The phenomenon is of interest in the case of very fluid mixes such as self-consolidating ones. Several results on the influence of limestone powder on the yield stress and viscosity of cementitious systems can be found in the literature, especially for self-consolidating mixes. Forward, a section dealing with this topic can be found. It could be claimed that in the same way that limestone powder affects yield stress, and viscosity in the case of fluid mixes, it may also affect bleeding.

Joserrand et al. (2006) suggested that the influence of a limestone powder (BET s.s.a. = $6081 \text{ m}^2/\text{kg}$ and PSD $d_{10}/d_{50}/d_{90} = 1.7/10.5/52 \text{ }\mu\text{m}$) on cement hydration and particle flocculation can lead to more prolonged bleeding, and a consequent high bleeding capacity. This is in agreement with (García et al. 2008; Bentz and Garboczi 1991), where initial setting time is reported as an indication of a percolation threshold that affects connectivity between solid particles and voids within the newly hardened cement paste.

4.3.3 Influence on Setting

Fineness of limestone powder is a main characteristic as regards its influence on setting. Soria and Rahhal (2003) investigated the influence of ambient temperature of concrete made with limestone powder on slump, slump loss, setting time and

bleeding. They found that, in hot weather conditions, concrete produced with limestone cement may result in a greater reduction in slump compared to OPC concrete. They also found shorter setting times for limestone concrete in comparison with pure cement concrete at 20, 30, and 40 °C; they suggested that this is due to the increase in the hydration rate caused by nucleation effect. Similar results for the effect of the limestone powder content on setting time are presented in Khaleel and Razak (2014). On the other hand, limestone cement with replacement percentage of 15% showed similar setting times to ordinary, pozzolanic and fly ash cements, even when limestone cement had higher fineness (Voglis et al. 2005). In this sense, Michel et al. (2007) noticed an influence of limestone powder on initial setting time only when it had a Blaine specific surface area of 770 m²/kg, whereas no influence was determined for limestone powder with Blaine fineness between 220 and 650 m²/kg. Courard et al. (2005) present results in agreement when they tested mortars with limestone powder with Blaine s.s.a. = 305 m²/kg in partial replacement of cement. Accordingly, Sato and Beaudoin (2011) proposed the addition of nano-CaCO₃ for accelerating the hydration of OPC when delayed by the presence of high volumes of supplementary cementitious materials, such as fly ash and slag. Based on this work, Bentz et al. (2012) added fine limestone powder to high volume fly ash concrete to compensate for the excessive retardation effect on hydration, delayed setting times, and low strengths at early age. They analyzed a nano-limestone powder and two other limestone powders of increasing median particle size (4.4–16.4 μm) for their propensity to reduce setting times in a Class C fly ash/cement blend. They obtained a measurable acceleration of hydration and compensation of setting times due to the fineness of the limestone, which they attributed to both physical and chemical action mechanisms of limestone particles.

On the other hand, Ezziane et al. (2010) found increasing setting times with limestone powder (Blaine s.s.a. = 340 m²/kg) content when they tested superplasticized mortar. They attributed this delay to the higher effective relationship superplasticizer dosage/cement content. Thus, the increase in setting time should be attributed to the effect of the superplasticizer, in which the relative content to the cement weight is increased by the increase in the limestone powder content.

Courard et al. (2011) reported values for setting times of mortars including different limestone powders and without chemical admixtures. The influence of the mineral additions seems to be linked to their clay content and BET specific surface area. In most cases, however, this effect is very low and the overall effect on setting time is essentially neutral.

The effect of temperature on setting of limestone blended mixes has been also analyzed in Ezziane et al. (2010). They found consistent shortening of setting time with increasing temperature, but no influence of the limestone powder content on these decreases could be found, as the relative differences according to the limestone powder content remained similar for each series.

4.3.4 Influence on Superplasticizer Demand

Studies on interaction between limestone-blended cements and superplasticizers have primarily focused on polycarboxylic-ether (PCE) based admixtures (Magarotto et al. 2003; Şahmaran et al. 2006; Artelt and Garcia 2008; Plank et al. 2010; Banfill 2011), as they are commonly used in self-consolidating concrete.

Differences in superplasticizer demand between limestone-blended cement and ordinary cement would be mainly due to limestone-admixture interaction. According to Alonso et al. (2007), the effect of PCE admixtures on CEM II/B-L (Blaine s.s.a. = 438 m²/kg) cement pastes is similar to the changes induced in cement pastes without mineral additions. The use of 30% limestone in cement pastes (Burgos-Montes et al. 2012) raises the adsorption of both lignosulfonate-(LS) and melamine-(PMS) based superplasticizers, indicating that these admixtures had greater affinity to CEM II/B-L (Blaine s.s.a. = 524 m²/kg, BET s.s.a. = 2110 m²/kg) than to CEM I (Blaine s.s.a. = 502 m²/kg, BET s.s.a. = 1220 m²/kg), while naphthalene—(PNS) and PCE based superplasticizers behaved similarly with limestone blended and non-blended cements. The presence of supplementary cementitious materials changes the physical–chemical properties of the cement and its behavior in terms of superplasticizer adsorption. Results in Burgos-Montes et al. (2012) show that superplasticizer adsorption on limestone—or limestone and clayey material—was similar to its adsorption on limestone-blended cement because, although affinity was much smaller for limestone than for cement particles, the presence of limestone in the blend led to a higher total consumption of admixture as a result of its greater specific surface. Similarly, Mikanovic and Jolicoeur (2008) observed adsorption of PNS was twice as much as that of PCE, and that adsorption of both polymers was twice as high on CEM I cement as on pure CaCO₃ particles, both with the same BET s.s.a. = 1200 m²/kg. Also Petit and Wirquin (2010) found increasing superplasticizer demand with limestone powder (of unknown fineness) content in self-consolidating mortar mixes with PNS admixture, but this increase was in connection with an increase in the content of fines in the mix.

Adsorption of PCE admixture on limestone particles is due to an enthalpic contribution resulting from the electrostatic attraction between the opposite charges of substrate and PCE molecules, and the entropic contribution originated in the release of numerous counter ions and water molecules into pore liquid. These contributions are influenced by the ionic composition of pore liquid. Plank et al. (2010) investigated the adsorption of different PCE admixtures on CaCO₃: whereas the electrostatic attraction between the substrate and the PCE molecules decreases in the presence of Ca²⁺ ions, PCE adsorption is connected with a high gain in entropy due to the same reason. The PCE molecule characteristics (structure, molecular weight, types of anchor groups), and the surface loading of the substrate with PCE are also important features in the adsorption process. These influences of the molecular weight and structure of the PCE have therefore a significant influence on the rheological behavior and water-reduction of the limestone cement

(Magarotto et al. 2003; Banfill 2011). The anionic charge density of PCE molecules (Plank et al. 2010) influences both enthalpy and entropy. With higher anionic charge density, the enthalpic contribution to adsorption increases, whereas the entropic contribution decreases. A higher anionic charge density results from decreasing the side chain length of the PCE macromolecule. In consequence, a gain in entropy is the major force driving PCE adsorption and a decisive parameter of its effectiveness as superplasticizer.

Mikanovic and Jolicoeur (2008) studied the relationship between particle–superplasticizer interactions, rheology and paste stability, and blending, sedimentation and consolidation. Their findings showed that the mechanisms involved in superplasticizer action on limestone and OPC cement varied depending on whether the admixture was PCE or PNS-based. They also observed that even if the dispersion effect of both admixtures was similar in water–limestone pastes, the presence of Ca(OH)₂ improved the effectiveness of PCE admixture. In this sense, Hallal et al. (2010) observed better compatibility of superplasticizers with limestone blended cement than with pozzolana blended cement.

Additionally, the BET is essential to describe the powder/superplasticizer interaction that controls particle dispersion (Diederich et al. 2012). BET specific surface area allows the fineness of particles and their texture to be quantified as well (Arvaniti et al. 2015). It is therefore more descriptive of the surface on which PCE molecules may be adsorbed than Blaine s.s.a., which is connected with particle size only. Therefore, the increase in specific surface area and packing density due to the partial replacement of OPC by limestone powder might affect concrete flowability (Esping 2008), and the dosage of superplasticizer must therefore be modified to maintain it.

In this regard, Diederich et al. (2012) showed that the effectiveness of superplasticizer depends on the composition and surface charge of the limestone powder, specifically the effect of the presence of impurities such as clay. Limestone powder usually exhibits a rather low hydrophilic behavior (Diederich et al. 2012). However, when a PCE admixture is included, different evolutions of the contact angle may be expected depending on the nature of the powders and in connection with their electrostatic charge. In this regard, negatively charged powders show a decrease in the contact angle, i.e. a higher affinity with the aqueous solution, whereas other powders show a lower affinity with the liquid phase (Diederich et al. 2012). These dissimilar interactions between PCE admixture and limestone powder induce a modification of the rheological properties of suspensions: the yield stress (Fig. 4.10) and the apparent viscosity of suspensions with limestone powder are reduced with the use of a PCE admixture to different extents depending on the nature of the limestone powder.

The obtained relative decreases in static yield stress and viscosity were significant only for limestone powders that showed a wettability decrease with the inclusion of PCE admixture. The lower wettability would allow a larger amount of free water available for the fluidification of the mix (Diederich et al. 2012). In this analysis, it is important to note that the lower wettability may be in conjunction with a positive electrostatic charge of the powder, and, if so, limestone powder may

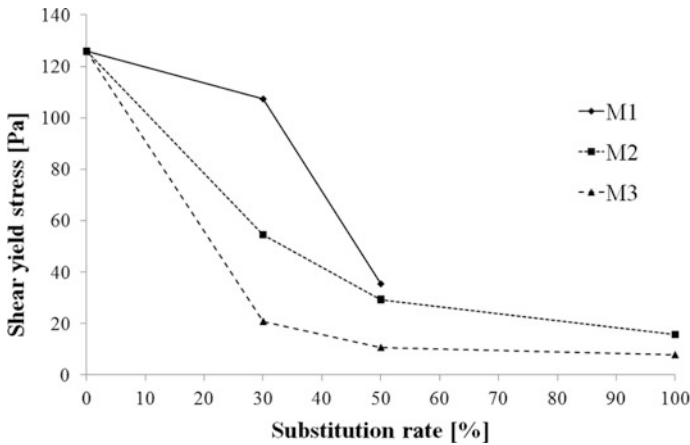


Fig. 4.10 Variation of the shear yield stress of slurries with constant spreading (ASTM C230) and with 0.5% polycarboxylate superplasticizer as a function of the filler amount (3 types of natural limestone fillers) (Rossomme 2010)

be in competition with cement for the adsorption of PCE molecules. Therefore, this may result in a net negative influence on the flow properties of superplasticized mixes with limestone blended cement. On the other hand, Diederich et al. (2012) found no relationships between the flow properties of limestone suspensions incorporating PCE and those of limestone-blended cement-based suspensions. They accordingly conclude that the flow of the *cement + limestone + PCE + water* suspension is influenced by the properties of the individual components and also by their concentration and the interactions existing between them.

Then, it seems very important to take into account the particle size distribution and the complementary effect with that of the cement in order to achieve minimum voids and allow lower superplasticizer demand.

4.4 Effect of Limestone Powder on Fresh Properties of Self-Consolidating Concrete

In a comprehensive study performed by the BRE (Building Research Establishment) and BCA (British Cement Association) in the early 90s (Moir and Kelham 1993), Portland limestone cements were shown to “*have a largely neutral effect on slump, and are mostly beneficial particularly if the limestone is inter-ground with the clinker and the fineness of the clinker fraction is less than c. 380 m²/kg*” (Moir and Kelham 1997). The same study showed clear benefits in reducing the tendency of bleeding for cements that without limestone addition had a narrow size distribution (which are more common nowadays with more efficient closed circuit cement mills), or in self compacting concrete (Moir and Kelham

1997; Livesey 1991). These conclusions were generally confirmed in a recent review of limestone cements by the PCA (Tennis et al. 2011).

Much of the research that has been done on the influence of limestone powder on the fresh state concerns self-consolidating concrete. Self-consolidating Concrete (SCC) is stable highly flowable concrete that can spread readily into place and fill the formwork without any consolidation and without undergoing any significant segregation. The solid fraction of paste phase of concrete must be increased in order to obtain stable and flowable SCC. In this sense, non-pozzolanic powders are frequently used to optimize the particle packing and flow behavior of cementitious paste in SCC mixtures.

By using limestone powder with fineness and grading that can greatly improve the particle packing and deformability of the cementitious paste, the amount of mixing water can be considerably reduced for set values of rheological parameters (Ghezal and Khayat 2002; Bokan Bosiljkov 2003; Yahia et al. 2005b, Courard et al. under revision). Alternatively, limestone powder may enable superplasticizer contents to be reduced in some cases (Nepomuceno et al. 2012); this is conditioned by the fineness of limestone powder. Increased superplasticizer demand of SCC due to the inclusion of limestone powder has also been reported (El Hilali et al. 2006; Gesoğlu et al. 2012) (Fig. 4.11).

Limestone powder may play a significant role in the stability of self-consolidating concrete (Georgiadis et al. 2010) by compensating poor gradation and enhancing mixture consistency. Yahia et al. (2005a, b) investigated the effect of a limestone powder addition in superplasticized cement mortar rheology. Their results show that the physical effect of limestone powder is mainly affected by the W/C and the limestone powder content; for a given W/C, the addition of

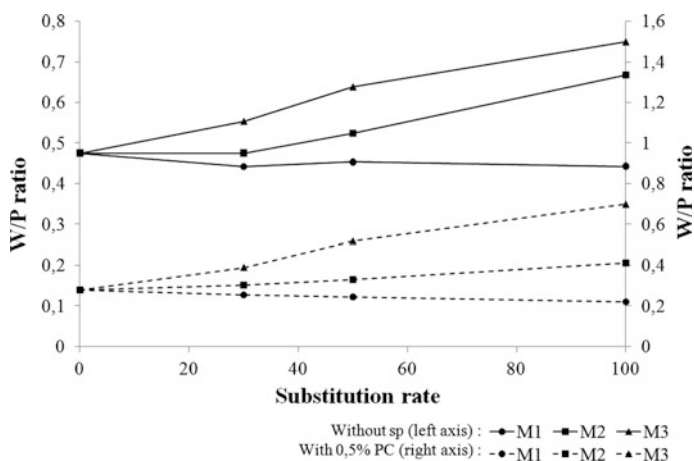


Fig. 4.11 Variation of W/P ratio for constant spread (ASTM C230) of 220 mm, with and without PC superplasticizer (Courard et al. under reviewing)

limestone powder within a certain range did not affect fluidity. However, beyond a critical dosage, the incorporation of some limestone powder resulted in a substantial increase of mortar viscosity. However, it must be taken into account that sand may be a substantial source of fines which may reduce the optimum limestone powder content to obtain a stable and flowable self-consolidating mix (Tobes et al. 2007).

Similarly to conventional concrete, results for setting time of SCC with limestone powder are somewhat variable. Şahmaran et al. (2006) obtained increasing setting times when fly ash was included in SCC that could be reduced by using ternary mixtures including also limestone powder. In contrast, Gesoğlu et al. (2012) reported increased setting times for both binary and ternary self-consolidating mixes with limestone powder and fly ash. Again, the clear influence of limestone powder is a result of opposite effects of hydration stimulation and dilution of clinker. Limestone powder fineness might be the deciding factor on the predominance of one or the other.

Partial replacement of cement by limestone powder may reduce plastic viscosity and yield stress of highly-flowable mortars (Yahia et al. 2005b). On the other hand, Gesoğlu et al. (2012) reported increased values for the viscosity of self-consolidating concrete due to the inclusion of limestone powder, including binary and ternary blended mixes with Portland cement and fly ash. The contradictory results on the effect of limestone powder on flow behavior may be explained by the fact that flow properties of the mix are highly influenced by the surface charges, wettability and fineness of limestone powder, which in turn may differ very much among different sources of raw material (Diederich et al. 2012). In this sense, clay content of limestone powder, which affects its characteristics, is a key factor controlling the flow of limestone blended mixes.

Evidence on the influence of limestone powder on rheological parameters has also been presented by Vieira and Bettencourt (2007), in relation to the modification of particle packing. They reveal a higher influence of limestone powder content on the V-funnel time than the influence of superplasticizer content. In this sense, they explain that the V-funnel test is very dependent on the lubricant effect of particles, whereas the flow spread, which is less affected by the limestone powder content, depends on the characteristics of the paste as a whole. Similarly, slump flow was found to be more affected by the limestone powder content than by the superplasticizer content (Yahia et al. 2005b). Diamantonis et al. (2010) also attributed the decreased values of plastic viscosity with limestone powder content for both binary and ternary pastes to a better packing density of fines provided by the inclusion of limestone powder. They also found lower values of yield shear stress when compared to other binary mixes, but not lower than that of the reference mix. In consequence, they suggest limestone powder as the most convenient mineral addition as regards SCC rheology.

Many authors (Heirman et al. 2007) are suspecting that an excessive limestone powder content can considerably increase water demand of self-consolidating mixes if the specific surface area of the powder is increased (Yahia et al. 2005a, b; Şahmaran et al. 2006; Emdadi et al. 2007; Uysal and Yilmaz 2011; Petit and Wirquin 2010). Though the specific surface area of limestone might not show a

significant effect on slump flow and flow time responses (Yahia et al. 2005b), it has a comparable opposite effect on plastic viscosity than the replacement percentage of limestone powder. Therefore, the use of powder with higher surface specific area increases the water and superplasticizer demands (Esping 2008). Accordingly, Czarnecki et al. (2010) found decreased fluidity in mortar when they used limestone powder in comparison with coarser quartz powder, and Uysal and Yilmaz (2011) obtained increased fluidity in concrete when they used limestone powder in comparison with finer marble and basalt powders. On the contrary, Jones et al. (2003) showed that if limestone powder is included in replacement of sand instead of cement, it can lead to a reduction in the water demand as long as it reduced voids ratio of fines. This is more likely for ultrafine limestone powder than for coarser limestone powder. Diederich (Diederich et al. 2012) contends that, to infer the influence of limestone powder on water demand of SCC, it is very important to characterize the BET specific surface area of limestone powder, as it is descriptive of its fineness, smoothness and particle shape, whereas the Blaine method only describes fineness.

Thixotropic characterization of cement pastes with different limestone powder contents has been pointed out (Rubio-Hernández et al. 2013), where transitory flow was measured. Whereas the non-steady flow curve depends on the initial structural state of the material, flow after a pre-shear has been applied since it requires less work. Results from this study show that the required work per time and volume units necessary to break the microstructure that forms in the material decreases when the limestone powder proportion increases. Limestone powder develops a weaker structure than cement particles and its particles agglomerate without appreciable structural binding (Rubio-Hernández et al. 2013): only cement particles develop a microstructure network, and, thus, the substitution of cement by limestone powder does not have substantial effect on the kinetic of microstructural development related with the thixotropy of cement paste.

The air content in SCC does not seem to depend on the limestone powder content used in the mix, but on its rheological properties (Valcuende et al. 2012). SCC usually shows lower volume of air than conventional concrete, but if its flowability is reduced or viscosity increased the air content increases and can far exceed the values recorded for normally vibrated concrete. In practical terms, air content can be directly linked to the parameters from the slump flow test: final diameter of the concrete mass and the time the mass takes to reach a diameter of 50 cm. Consequently, limestone powder content would affect air content to the extent that it also affects concrete rheology.

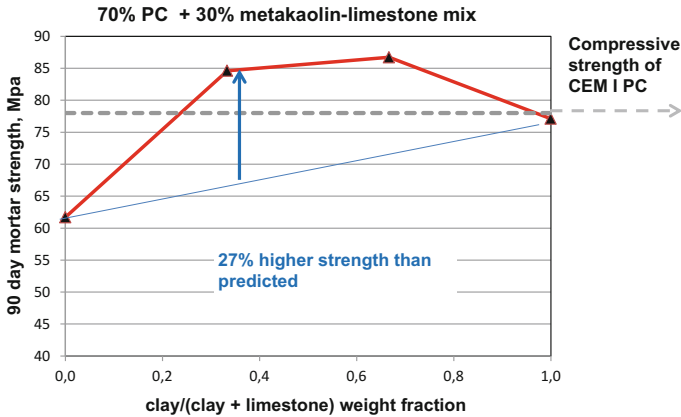


Fig. 4.12 Synergetic effect of metakaolin-limestone reaction on strengths (Steenberg et al. 2011)

4.5 Hydration and Strength of Portland Composite Cements Containing Limestone

As shown in Fig. 4.1, Portland composite cements (CEM II M), the bulk of which consist of combinations of limestone and slag or limestone and fly ash, account for close to 20% of cements produced in Europe. It has been shown that these combinations result in increased performance of the limestone constituent (Borgholm et al. 1995). The same synergetic effect has also been shown for combinations of natural pozzolans and limestone (Torresan et al. 2000; Steenberg et al. 2011). This is illustrated in Fig. 4.12 (from Steenberg et al. 2011) where the synergetic effect of the metakaolin-limestone reaction on strengths was shown to result from the increased formation of carboaluminate hydrates (Fig. 4.5) and the increased reaction of the limestone (Antoni et al. 2012).

The impact of limestone on the hydration reactions described above, and the effect that this has on strength and porosity, is strongly dependent on the fineness of the limestone. In general, when the limestone is ground separately to a fineness comparable to the clinker fraction, e.g. in the region of 400 m²/kg, performance resulting from either of the above reactions (early acceleration of the C₃S reaction, or later formation of carbo-AFm's) is limited. There seems to be a general agreement in the literature that the fineness of the limestone needs to be at least 600 m²/g determined by the Blaine method, or with a median size of less than 5 μm (Pera et al. 1999; Berodier et al. 2013; Khanh 1999; Hawkins et al. 2003), with the best results achieved at a fineness of 1000 m²/kg or more. This degree of fineness is only consistently achieved when the limestone is interground with the clinker, and in the majority of published reports where the limestone is blended with the clinker, the Blaine fineness of the limestone is less than 500 m²/kg. That is not to say that

blending cannot be achieved with a finer limestone, but in practice this is not normally the case.

In addition to the benefits of a high fineness of the limestone on the hydration reactions, the greater the difference between the fineness of the clinker fraction and the limestone fraction, the higher the packing density, resulting in a lower water content for the same concrete consistence. Evidence of this is clearest when the limestone and clinker is interground, or where the surface area of limestone is at least twice as high as the surface area of the clinker (Khanh 1999; Moir and Kelham 1993).

4.6 Evaluation of Industrially Produced Portland Limestone Cements

Even though industrially produced Portland limestone cements are overwhelmingly interground, performance, either regarding strength or durability, is not always in the limestone cement's favor.

The most common reason for this is that, even though a Portland cement and comparable Portland limestone cement may be produced on the same mill from the same clinker with optimum gypsum addition, etc., the correct fineness needed to allow a meaningful comparison is not always targeted. For example, in normal closed circuit cement mill, a constant output and separator speed will achieve a significantly finer finished product for the limestone cement (c. 10 m²/kg for each additional %-point of limestone) at an essentially constant fineness of the clinker fraction (CemCalc 2011–2013). However, in some cases the target fineness of the limestone cement is relaxed, either to increase production output and reduce the specific power consumption, or due to bottlenecks elsewhere in the process such as insufficient capacity in the packing department for a finer product. Whatever the reason, direct comparison of the performance of Portland cement and Portland limestone cement is not possible if they are produced under different operating conditions of the mill because this will result in different finesses of the clinker fraction. Lower fineness of the clinker fraction will of course lead to poorer performance (i.e. slower rates of reaction and, higher porosity) other things equal. Despite this, for a given output and clinker fineness, optimum performance in terms of strength, porosity and workability is ensured when the limestone is interground with the clinker.

4.7 Durability

With the possible exception of thaumasite formation discussed below, to the authors' knowledge even if likely to be contentious, no investigations performed at equal strength have shown significantly inferior performance of Portland limestone cements compared to Portland cements. The conclusion of the BRE/BCA study mentioned above, (Moir and Kelham 1993) was as follows: “*A relationship exists between the strength class of the cement, the cement content and the strength of the concrete. It demonstrates that the strength of the concrete is a better guide to carbonation than the type of cement used (which included a wide range of cements with different contents and sources of limestone); that the degree of air entrainment governs the performance in freeze/thaw conditions, and that the chemical composition of the base cement controls the resistance to sulphates and chlorides (i.e. regardless of the limestone content as long as the concrete is produced to the same strength)*”.

In principle, dilution by limestone addition implies a reduction of chloride binding capacity in connection with lower content of aluminate and ferrite phases in cement. However, some results indicate a contribution of the carbo-AFm phases to the chloride binding capacity owing to a continuous solid solution that forms between the chloride and carbo-AFm phases, Friedel's salt and monocarbonate (Nielsen et al. 2003). This is a different case from carbo-AFm phases formed during carbonation of concrete, where the associated reduction in pH decomposes Friedel's salt.

The increased use of Portland limestone cements is reflected by the national application standards where these cements are permitted in most European countries. Except for the exposure classes involving chemical attack (XA1, 2 and 3 defined in EN 206), most European national application standards permit the use of Portland limestone cements in the majority of exposure classes: this is particularly true for the CEM II/A-L,LL types, not so for the CEM II/B-L,LL (Fig. 4.3). In the UK for example they are permitted in all classes not involving chemical attack (BS 8500-1). In Denmark they are allowed in all classes except XS3 and XA3 (severest sea water and chemical attack) (DS/INF 158). The main reason for excluding Portland limestone cements from conditions involving sulphate attack is probably the perceived risk of thaumasite attack which is discussed in more detail below.

The general consensus after several years of research on the formation of thaumasite (Juel et al. 2003; Schmidt et al. 2008) is that:

1. although thaumasite may be thermodynamically stable at temperatures above 10 °C, reported field cases of thaumasite formation are virtually non-existent in warmer climates, even if not completely true (Torres et al. 2011), and
2. where climatic conditions are conducive to thaumasite formation, an external source of sulphate is required, since there is invariably insufficient sulphate present in Portland cement to thermodynamically stabilise thaumasite regardless of the kinetic conditions.

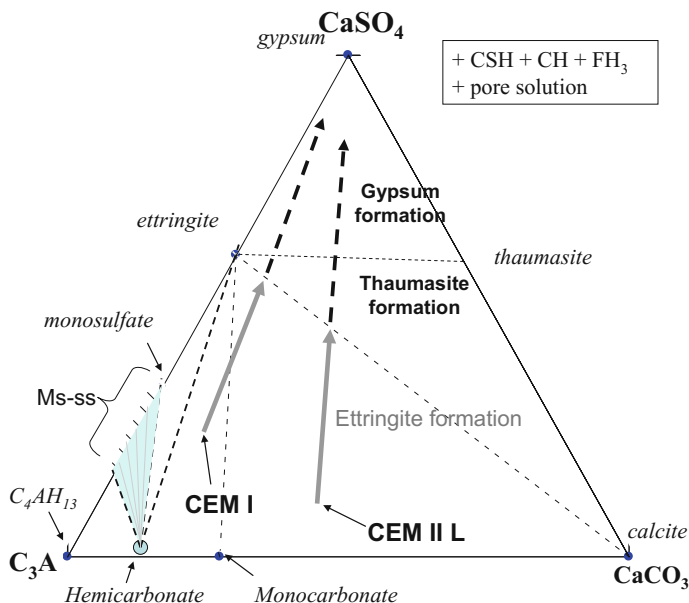


Fig. 4.13 Ternary sub-system for CaSO_4 - C_3A - CaCO_3 from Fig. 4.4 showing the effect on the hydrate mineralogy of external sulphate attack of a typical CEM I and CEM II L

This latter point is illustrated in Fig. 4.13. This diagram shows that thaumasite can only form at much higher sulphate contents than are present in normal Portland cements (between 6 and 8% SO_3 by weight of the anhydrous cement). Thaumasite can therefore only occur where external sulphate attack is involved, and to all extents and purposes, only where ambient temperatures are consistently below 10 to 15 °C. These phase relationships have been extensively tested and verified experimentally (Juel et al. 2003; Schmidt et al. 2008).

Where external sulphate attack is involved, it can be argued that resistance to ettringite related expansion is the main factor affecting performance, since as shown in Fig. 4.13, ettringite precedes thaumasite formation with increasing sulphate contents. In most cases the main cause of failure probably results from expansion due to ettringite formation, rather than thaumasite which is simply the final product to form. Maximum resistance is achieved at low C_3A contents and low porosity. In practice, the most workable means of achieving a low porosity is to target a high strength. For this reason specifying sufficiently high strengths for the concrete, and minimizing the water/cement ratio in the final application should offer the best protection against all types of attack, both chemical and physical. The situation is the same for Portland limestone cements regardless of the limestone content.

The relationships apply equally to attack by MgSO_4 or alkali sulphates which are of course much more soluble than the calcium sulphates and therefore more severe. In the case of MgSO_4 , brucite forms as an excess phase, so that the composition

plotted onto the sub-system follows the same path towards CaSO_4 , and remains valid as long as calcium hydroxide (CH) remains in excess. This is also the case with alkali sulphates, but where the concentration of alkalis and hydroxyl ions (and therefore the pH) increases in the pore solution.

4.8 Environmental Benefits

The 4-fold increase in the use of Portland limestone cement in Europe or as a substitute for cement since the early 1990s is a reflection of the limited supply of traditional supplementary cementitious materials such as fly ash and granulated blast furnace slag and the relative cheapness of limestone fillers (Damtoft et al. 2008). Since further reductions in the clinker content of cement is a key element in reducing CO_2 emissions, this development is likely to continue with even higher contents of limestone. Moreover, limestone is one of the supplementary cementitious materials with the lowest transport-related CO_2 emission for cement production, as the source for the raw material is the same source for clinker production. This will no doubt lead to the increased use of CEM II/B Portland limestone cement and its acceptance in the concrete codes. Of course, this must take place at the same concrete performance in terms of strength and durability, so the synergies outlined above between clinker, limestone and other SCMs must be fully exploited if levels of clinker replacement are to be maximised.

The current average clinker-to-cement ratio over all cement types in the EU27 is 73.7% (<http://lowcarboneconomy.cembureau.eu>). If all of the global production of hard coal fly ash and slag currently not utilized was used as a one to one clinker replacement for the same concrete performance, overall clinker contents in Portland cements could be reduced to current European level of about 0.76 (Herfort 2008). It has been estimated that the theoretical limit for clinker replacement in Portland cement using combinations of limestone and traditional SCMs is about 40% before concrete performance is significantly affected. If this is to be achieved globally the level of replacement by limestone will probably need to be increased by c. 20% on average (Herfort 2008).

4.9 Conclusions

As described above, when the limestone is ground to a Blaine fineness greater than c. $600 \text{ m}^2/\text{kg}$, its impact on the hydration reactions is usually significant. The acceleration of the C_3S reaction is significant within the first 24 h, and formation of carbo-AFm phases is significant within 28 days, the latter having the biggest impact at higher aluminate contents, either from high C_3A contents in the clinker or from alumino-silicate pozzolans. The carbo-aluminate reaction involves the reaction of calcium carbonate with the alumina present in the pozzolan and $\text{Ca}(\text{OH})_2$ supplied

from the cement. To all intents and purposes limestone under these conditions should be regarded as an SCM with surface area being the primary determining factor. If it is sufficiently fine it will contribute to the space filling reactions which reduce porosity and increase strength within a period of around 28 days at normal temperature. If it is too coarse it will primarily function as inert filler. When ground separately to a comparable fineness of the clinker it will contribute to some (albeit limited) extent to the hydration reactions, but have little impact on reducing the water demand. Of course, when the limestone is ground to a lower fineness than the clinker this will improve workability, but it will have essentially no impact on the hydration reactions. In this case it should be solely characterized as filler.

Any attempt to define limestone as an SCM in a prescriptive standard or specification as a stand-alone material (i.e. not an integral constituent in a Portland cement) would require a dedicated systematic research program (<http://www.astm.org/WorkItems/WK36906.htm>), but the current literature does suggest a minimum fineness in the region of $600 \text{ m}^2/\text{kg}$ as a working definition. At present, in order to ensure optimum workability and reactivity, the only effective solution at this stage is that the limestone is interground with the clinker. Intergrinding fulfills the requirements for both SMC reactivity and improved workability. There is no guarantee that similar performance can be achieved with a blended cement or direct concrete addition without specifying both the clinker and limestone fineness for a given application. Also, if a limestone of proven performance with a given source of clinker is used with another source of clinker, e.g. with a lower aluminate content or reactivity, or without optimizing the SO_3 content, its performance may be significantly affected. This is in contrast with other essentially pozzolanic SCMs such as fly ash and GBFS which are less dependent on the source of clinker, and makes it much more difficult to specify performance requirements such as the activity index or k-value for limestone additions to concrete.

Comparison of performance in concrete other than strength should also be made under realistic conditions. For example, ready mixed concrete is usually specified according to range of slump and minimum strength (e.g. S2 and C30 in EN 206). The amount of water needed to achieve the slump target may of course differ between a Portland and Portland limestone cement. In some cases the Portland limestone cement may require more water for the same concrete consistence, but in most cases when it is interground it will require less water (Tennis et al. 2011). After adding the correct amount of water for the desired slump, the cement content is then adjusted to achieve the required w/c ratio for the desired strength. At low limestone contents, the W/C ratio (and cement content) will usually be comparable, or even higher (lower cement content) for the Portland limestone cement resulting in a direct saving and improved environmental performance. At higher limestone contents (e.g. higher than c. 10%), a lower W/C ratio (and higher cement content) will normally be required, but even here the overall clinker content would normally be lower compared to concrete produced from Portland cement for the same concrete strength. i.e. also resulting in a net saving and improved environmental performance; but admixtures will also probably be needed.

Regarding the interaction with water reducers, limestone shows more extensive compatibility with these admixtures than other supplementary cementitious materials. Limestone cement usually exhibits lower superplasticizer demand than ordinary Portland cement due to less adsorption of the admixture on limestone than on clinker particles, but this reduction depends on the difference in the fineness and surface area. In this sense, limestone filler represents a key constituent for stable self-consolidating concrete, with some advantages over other types of filler.

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Standards

- ASTM C150/C150M-15, Standard Specification for Portland Cement, ASTM International, West Conshohocken, PA, 2015, www.astm.org
- ASTM C595/C595M-09, Standard Specification for Blended Hydraulic Cements, ASTM International, West Conshohocken, PA, 2009, www.astm.org
- ASTM C230/C230M-14, Standard Specification for Flow Table for Use in Tests of Hydraulic Cement, ASTM International, West Conshohocken, PA, 2014, www.astm.org BS 8500-1:2015. Concrete. Complementary British Standard to BS EN 206. Method of specifying and guidance for the specifier
- BS 8500-2:2015. Concrete. Complementary British Standard to BS EN 206. Specification for constituent materials and concrete
- DS/INF 158:2004, Concrete technology—Compilation of DS/EN 206-1 and DS 2426 together with DS/EN 206-1/A1 (*in Danish*)
- EN 197-1:2011. Cement—Part 1: Composition, specifications and conformity criteria for common cements.
- EN 206-1:2000. Concrete—Part 1: Specification, performance, production and conformity
- EN 933-9+A1: 2013. Tests for geometrical properties of aggregates. Assessment of fines. Methylene blue test

Chapter 5

Metakaolin

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Abstract Metakaolin (MK) is known to be a highly pozzolanic material that can be used in concrete. MK is usually produced by heating kaolin-containing clays, within the temperature range of about 600–900 °C. This chapter summarizes the utilization of metakaolin in relevant worldwide standards, mainly in Europe and North America. The health, safety and environmental sustainability concerns on using metakaolin as a supplementary cementitious material are also addressed in this chapter. It is reported that MK incorporation has benefits on both early-age and long-term properties. On the other hand, this chapter also reports that the results of heat of hydration and rate of reaction in metakaolin-blended concrete are controversial and need further investigation. Overall, the optimum level of cement replacement by MK is around 10–20%, which provides concrete the maximum strength. Metakaolin appears to have an excellent potential as a supplementary

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cementitious material in structures made of high-performance concrete, because it controls deleterious expansion due to alkali-silica reaction in concrete (depending on the nature of the aggregate), and reduces the ingress of chloride by improving the microstructure and chloride binding behavior.

Keywords Metakaolin · High-performance concrete · Supplementary cementitious material · Properties · Sustainability

5.1 Overview and Background

To reduce the environmental impact of the global cement industry, and to achieve cost and performance benefits in concrete production, metakaolin (MK) and other supplementary cementitious materials are used as partial replacements for cement in concrete. Metakaolin reacts chemically via a pozzolanic process with $\text{Ca}(\text{OH})_2$, as a source of reactive Si and Al, and its degree of structural disorder plays a major role in determining its reactivity (Shvarzman et al. 2003).

Sabir et al. (2001) carried out a review of the utilization of metakaolin as a pozzolanic material for mortar and concrete and reported that the use of metakaolin as a pozzolan will help in the development of early strength and also give some improvement in long term strength. Metakaolin addition alters the pore structure in cement paste, mortar and concrete, and greatly improves its resistance to transport of water and diffusion of harmful ions, which can lead to the degradation of the matrix, as will be discussed in detail later in this chapter. Siddique and Klaus (2009) also reviewed the use of MK as a partial replacement for cement in mortar and concrete, producing results which are in general agreement with those of Sabir et al. (2001): MK was found to be an effective pozzolan in concrete, enhancing both the early age and long-term mechanical performance, reducing the water penetration into concrete by capillary action, reducing permeability, improving the resistance to sulfate attack, increasing chemical resistance, and offering control of deleterious expansion due to alkali-silica reaction. These properties, and others, will be addressed in this chapter.

Kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, (shown in Fig. 5.1) is a clay mineral that provides the basis of the plasticity of traditional ceramics in the unfired (hydrous) state; it can be converted by firing to produce a hard, durable, watertight, water-resistant material, which has for millennia been used in everyday life worldwide. The name of kaolin is derived from the Chinese term ‘Kao-ling’ meaning high ridge, the name of a hill in the city of Jingdezhen, where this material was mined centuries ago for use in ceramic production. Structurally, kaolinite consists of octahedral alumina sheets and tetrahedral silica sheets stacked alternately, and takes on a plate-like morphology as shown in Fig. 5.2.

The typical microstructure observed is shown in Fig. 5.3.

Metakaolin, which has the approximate chemical formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ or AS_2 , is produced by heating kaolin-containing clays within the temperature range of

Fig. 5.1 Kaolin (Rashad 2013)



Fig. 5.2 Kaolin plates and stacks (Murray 2000)



about 600–900 °C. Kaolinite crystals with hexagonal morphology tend to be preserved when heating kaolin at a temperature of 550 °C. Heating kaolin above 550 °C transforms it into MK by the loss of structural OH groups and a rearrangement in Si and Al atoms leading to a decrease in octahedral Al and the appearance of penta- and tetra-coordinated Al (Brown et al. 1985). As the temperature increases (650 and 800 °C), the kaolinite flakes become more deformed and locally condensed into disordered material, although the original layered structure of the kaolinite is at least partially retained (White et al. 2010a, b; Lee et al. 1999, 2001). Above 900–950 °C, MK begins to recrystallize to a siliceous spinel and disordered silica; at higher temperatures, crystalline mullite is generated (Brown et al. 1985). The spinel and mullite phases both have low pozzolanic

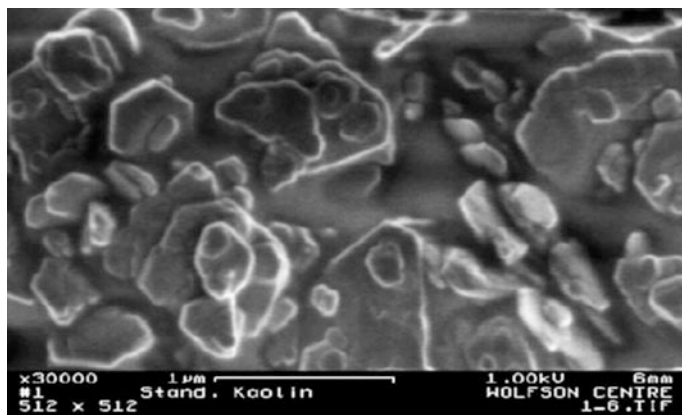


Fig. 5.3 HR-SEM micrograph of pure standard kaolin Shvarzman et al. (2003)

activity, and sintering also takes place, so the over-calcination of MK reduces its reactivity as a supplementary cementitious material.

In the pure form, disordered kaolins tend to yield metakaolin with higher pozzolanic activity (Kakali et al. 2001), and it has also been suggested that chemical treatment to introduce additional stacking faults into a high-crystallinity kaolin may provide a more highly reactive material (White et al. 2011). The calcination conditions need to be selected and optimized for each type of kaolin to provide optimal reactivity (Shvarzman et al. 2003), as the dehydroxylation of kaolinite during calcination is known to be a complex, multi-step, kinetically-controlled process (Bellotto et al. 1995; Lee et al. 1999; MacKenzie et al. 1985; White et al. 2010b). This process is also complicated by impurities in the clays, where the processing conditions may need to be altered to optimize the removal of sulfates (Badogiannis et al. 2005b) or to account for the presence of a larger volume of unreactive components such as quartz (Castillo et al. 2010), or less-reactive non-kaolin type clays (He et al. 1995; Habert et al. 2009).

According to Shvarzman et al. (2003), the dehydroxylation of kaolinite is preceded by a “pre-dehydroxylation” stage in the range 80–150 °C where the evolution of a small amount of water is observed, see Fig. 5.4a. Between 900 and 1100 °C, the exothermic formation of crystalline phases such as spinel and mullite is characterized by an exothermic peak in the DTA curve and insignificant weight loss in the TGA curve, see Fig. 5.4b. It is also noted that the commercial calcination of kaolinite, whether carried out via traditional rotary kiln processes or the increasingly-popular flash calcination process, often does not result in full dehydroxylation of the clay particles, and a non-zero loss on ignition is thus observed (San Nicolas et al. 2013, 2014).

Rashad (2013) presented a comprehensive overview of the previous works carried out on kaolin history, MK sources, production and composition. Based on the comparison of different thermal treatment, which includes calcination

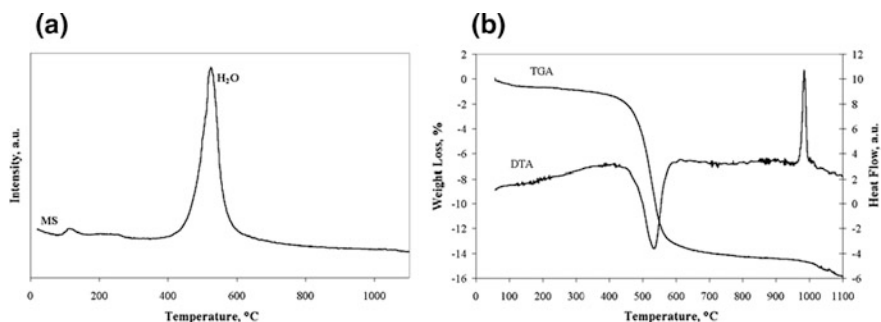


Fig. 5.4 **a** Mass spectroscopy analysis of water released by pure kaolinite during calcination; **b** DTA and TGA curves for pure kaolinite (Shvarzman et al. 2003)

Table 5.1 Typical chemical composition of a metakaolin (Ambroise et al. 1994)

| Component | % by weight |
|--------------------------------|-------------|
| SiO ₂ | 51.5 |
| Al ₂ O ₃ | 40.2 |
| Fe ₂ O ₃ | 1.2 |
| CaO | 2.0 |
| MgO | 0.1 |
| K ₂ O | 0.5 |
| SO ₃ | 0.0 |
| TiO ₂ | 2.3 |
| Na ₂ O | 0.1 |
| L.O.I. | 2.0 |

temperatures and heating periods, he concluded that the optimum temperature for heating kaolin to obtain MK may be in the range from 600 to 850 °C for 1–12 h.

The typical chemical composition of metakaolin as reported by Ambroise et al. (1994) is given in Table 5.1. Commercial sources of kaolin are rarely 100% pure kaolinite, often containing silica (quartz) impurities, as well as some substitution of Fe³⁺ for Al³⁺ in the octahedral layers. The ceramics industry generally demands higher purity (and thus ‘whiteness’) of the clay than is required for use as a pozzolan, but commercial exploitation of clay deposits tends to focus on those of higher purity and thus higher value, as it is currently motivated more by demand from the higher-value-added ceramics industry, with the production of cementitious components a secondary consideration for many producers.

There are also alternative sources of materials which can be used in place of pure calcined kaolinite clay. These include:

- Lower purity kaolin clays containing moderate to high amounts of quartz can be used as pozzolans (Castillo et al. 2010)
- Paper sludge—this is often a mixture of kaolin with cellulose, sometimes also containing calcite, which can be calcined to give an impure metakaolin-like material (Banfill and Frias 2007)

- 2:1 layered clays such as illite and montmorillonite can be used, but tend to show lower pozzolanic activity, and thermal processes for their amorphization are less effective than for kaolinite (Snellings et al. 2012)
- The 1:1 tubular clay halloysite is not yet widely studied in PC blends, but is known to be moderately reactive in alkali-activation (MacKenzie 2009), and so may offer scope for utilisation in place of metakaolin in the parts of the world where it is available.

5.2 List of Relevant Standards

Blends of Portland cement (PC) with up to 30% metakaolin are fairly widely tested, and are incorporated into the European standard for common cements (EN 197-1: 2011) (European Committee for Standardization (CEN) 2011) in two categories: CEM II/A-Q, 6–20% metakaolin, and CEM II/B-Q, 21–35% metakaolin. Metakaolin can also be included in Portland-composite cements (CEM II/A-M and CEM II/B-M), and in potentially higher fractions in the CEM IV and CEM V specifications in parallel with another SCM. The main limitations on the achievable degree of metakaolin inclusion in many concretes are related to the water demand of this material, related to its plate-like particle morphology, as well as its very high specific surface area, which is far higher than that of fly ash, and almost approaching that of silica fume considered as the finest SCM, see Table 5.2.

In Europe (except France) metakaolin is not among the materials whose general suitability as a Type II (at-mixer pozzolanic or latent hydraulic) addition is incorporated into EN 206: 2013 (European Committee for Standardization (CEN) 2013), and so no k -value has been defined in that standard for metakaolin. Since 2012 in France, the national complement of NF EN 206/CN (Association Française de Normalisation (AFNOR) 2014) allows the use of up to 15% MK for all exposure classes of concrete, with a k -value of 1. The requirements for MK are found in the French standard NF P18-513 (Association Française de Normalisation (AFNOR) 2012), entirely dedicated to the specifications of MK. The main requirement is the need of an activity index of 1 at 28 days (based on a substitution level of 15 wt%). Other requirements include chemical characteristics of the metakaolin (e.g., $\text{Al}_2\text{O}_3 + \text{SiO}_2 > 90$ wt%), and calcium hydroxide fixation (Chapelle modified test)

Table 5.2 Specific surface area of kaolin and metakaolin measured by BET (N_2 adsorption-desorption at 77 K, Monosorb, Quantachrome) method (Ambrose et al. 1994), in comparison with that of fly ash and silica fume

| SCM | Specific surface area, m^2/kg |
|-------------|---|
| Metakaolin | 12–15 |
| Kaolin | 16–18 |
| Fly ash | 2.3 |
| Silica fume | 18.0 |

of at least 700 mg $\text{Ca(OH)}_2/\text{g}$ of metakaolin. Moreover, two categories of fineness and water demand are defined to characterize the metakaolin.

In the North American regime, metakaolin is classified by ASTM C 618 (ASTM International 2015b) as a Class N material, acceptable as long as it does not increase the water requirement of the cement by more than 15% (among other stipulated properties), and so ASTM C 595 (ASTM International 2015a) allows its use in blended cements at replacement levels of up to 40%. The American Concrete Institute has also reported on the use and application of metakaolin in concrete via a report (ACI Committee 232 2012), including commentary on the technical rationale underpinning the ASTM standards in this area. Similarly, metakaolin is described in Canadian standard A3001-08 (Canadian Standards Association 2008a) as a Type N material, while requirements of primary properties are aligned with ASTM. A3004-E1 (Canadian Standards Association 2008b) represents a practical evaluation of alternative SCMs which do not meet current definitions of SCMs in A3001-08 (Canadian Standards Association 2008a).

Metakaolin is not included as a possible cement component in Australian Standard AS 3972-2010 (Standards Australia 2010). Indian Standard IS 456: 2000 includes metakaolin as an allowed mineral admixture, with the properties of the metakaolin itself governed by the recently-approved IS 16354 (Bureau of Indian Standards 2015). Brazilian Standard NBR 5736: 1991 (Associação Brasileira de Normas Técnicas 1999) describes pozzolanic cements with replacement levels of Portland cement by pozzolans (including metakaolin) of up to 50% as cements of class CP-IV.

5.3 Health and Safety Issues

Metakaolin appears to be exempt from the REACH legislation (EC Regulation 2006) under Annex V.7, as a mineral that has not been chemically modified (*definition: Not chemically modified substance: means a substance whose chemical structure remains unchanged, even if it has undergone a chemical process or treatment, or a physical mineralogical transformation, for instance to remove impurities*). Little information is available regarding the leaching of any potentially hazardous elements from the metakaolin itself. Cr^{6+} seems to be found only in very small quantities in commercial MK (<1 ppm) (San Nicolas 2011). It would be expected that any leaching would differ very significantly between materials from different clay deposits, and so this absence of hazard will need to be validated on a local level rather than by making general assumptions. Metakaolin is often used in blended cements to decrease the leaching of nuclear or toxic wastes. Pera and Bonnin (1996) showed that the use of 20% of metakaolin led to a reduction in the heavy metals leached into the mixing water from pastes and mortars containing solutions of chromium, lead and cadmium. Metakaolin was used by Cyr et al. (2012) in ternary and quaternary binders using cement (75 wt%), metakaolin (22.5 wt%), and industrial by-products from combustion processes containing

heavy metals. Results showed that the use of metakaolin led to a significant decrease in soluble fractions and heavy metals like Cr, Cd, As, Cu or Pb.

The key concern related to most commercial metakaolins would be associated with respirable crystalline silica, which is a minor component of a high-reactivity metakaolin but is present at much more significant levels in less-pure products, and requires appropriate precautions and personal protective equipment to be employed.

5.4 Environmental Sustainability

Kaolinite clays are widely available worldwide, and have been identified as potentially providing a low-cost, high-volume source of SCMs, if some technical issues related to the physicochemical nature of the metakaolin particles can be overcome. Because metakaolin is not generally sourced as an industrial by-product, its supply is much more future-proof than most commonly used supplementary cementitious materials. Industries such as coal-fired electricity generation and ironmaking are likely to see significant structural and technological changes in coming decades—either led by the industries or imposed by regulators—which means that the supply and characteristics of the by-products derived from these processes are likely to be affected. Conversely, metakaolin is a direct manufactured mineral product, relying only on the availability of (globally widely distributed) kaolin-type clay deposits, moderate-temperature calcination, and grinding facilities.

If cement is to be partially substituted by metakaolin, the following ecological aspects play an important role: the production process itself, and the transport to the site of utilization, see Fig. 5.5.

Specifically:

1. **Transport distance** from the production place of the metakaolin to the place where the concrete is produced needs to be taken into account. The transport distance is sometimes not transparent through the cost price, because the ex-factory prices are highly different. Relevant metakaolin production in Europe takes place in France, Great Britain, Germany, Czech Republic, Ukraine and Bulgaria, among others. There are also commercially known metakaolins

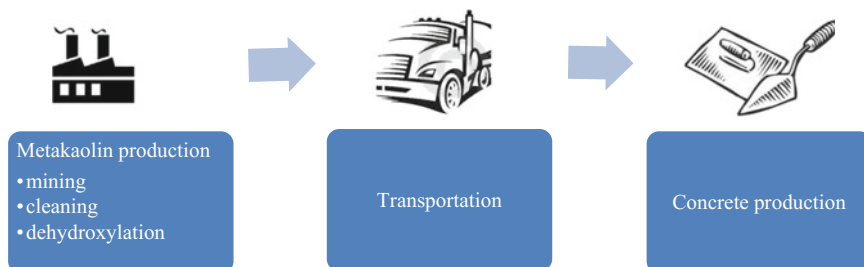


Fig. 5.5 Steps involved in the utilization of metakaolin

produced in the USA, Brazil, Canada, China and India. The transport history cannot be neglected and should be investigated by the supplier. Long transport distances might turn a positive eco-balance into a less favorable situation.

2. The production process itself: how much ecological impact is made during the production process of the metakaolin. The production process can be separated into the activities of mining and cleaning steps to reach a certain kaolinite quality, and as third step the transformation to metakaolin during a heat treatment at about 500–900 °C. Within the mining step several activities might be necessary such as breaking/milling and drying of the raw kaolin source. Extensive cleaning steps might be necessary if the resource contains low amounts of kaolinite and/or a very pure or white material has to be produced. These activities have consequences for the environmental impact, for instance in the energy demand and pollution of the environment due to cleaning chemicals. The dehydroxylation to obtain highly reactive metakaolin takes place either in a rotary kiln, a shaft kiln, fluidized bed furnace, flash calciner or a pulsation furnace. Due to the different efficiencies of these thermal processes and the amount and type of fuels used, the energy demand (CED—cumulative energy demand) as well as the CO₂ emissions [GWP 100—global warming potential (GWP)] might be very different between processes. Reliable and verified data about the environmental impact are difficult to obtain, but Table 5.3 summarizes some of the data which have been collated. The main differences are related to whether the kaolin is originally produced with a high purity or not, see columns 2–4 in comparison to columns 5–7. Further, the furnace and fuel type seem also to play an important role (Table 5.3).

For a plausibility check, two other processes might be considered. The GWP given in the ECOINVENT database (<http://www.ecoinvent.org/>) for comparable processes are:

- The whole process of producing natural anhydrite is specified with 0.085 kg CO₂ eq./kg anhydrite. This natural material is produced by surface mining and further crushing, drying and milling. No further burning process is required.
- Production of expanded clay is specified with 0.3 kg CO₂ eq./kg. For this process also the clay is obtained from a surface mine, and the material is further crushed, dried and milled. The clay powder is afterwards granulated and burned in a rotary kiln at about 900 °C. Usually gas, oil or coal is used as fuel.

With this background, the data given can be evaluated as follows:

- A GWP below 0.1–0.2 kg CO₂ eq./kg metakaolin seems to be very ambitious, and probably only feasible with renewable fuel and usage of a very efficient furnace type such as a flash calciner.
- A GWP between 0.2 and 0.7 kg CO₂ eq./kg metakaolin seems to be a conservative basis for comparison with CEM I.
- Transport distances must be considered, especially if cement from nearby manufacturers is to be substituted by metakaolin purchased far away. For quick evaluation of the breakeven point, a GWP of 0.154–0.185 kg CO₂ eq./t km may be used.

Table 5.3 Environmental assessments of different metakaolins by comparison to CEM I cement

| Source | Weil et al. (2010) | Weil et al. (2010) | Weil et al. (2010) | Habert et al. (2011) | ARGECO (2013) | CEM I |
|---------------------------------|-----------------------|--------------------|---------------------|-----------------------|-----------------------|-----------|
| Product/area | EU | EU | Brazil | France | France | EU mean |
| GWP (kg CO ₂ eq./kg) | 0.67 | 0.52 | 0.57 | 0.09 | 0.09–0.2 | 0.8–1 |
| ARC ^a (kg Sb eq./kg) | 5.32 | 4.03 | 4.54 | 0.00017 | – | 1.5 |
| CED (MJ/kg) | 12.41 | 9.52 | 10.3 | – | 2.1–2.4 | 3.8–4.2 |
| Data source | Producer ^a | Different | Different | Different | Producer ^b | Ecoinvent |
| Mining | Producer ^c | Ecoinvent | Brazil ^d | Ecoinvent | | |
| Cleaning | Producer ^c | Ecoinvent | No | No | No | |
| | Intense ^e | | | | | |
| Burning | Producer ^c | | | Producer ^f | | |
| Furnace | Rotary kiln | | | | Flash calciner | |
| Fuel | Gas/oil | | | Biomass | Oil | |

^aData from a producer in Europe

^bARGECO (<http://www.argeco.fr/>), producer of ARGICEM/F (flash calcined), calculation made by LCPC

^cAbiotic resource consumption

^dSurface mine, transported by ship to Europe for further burning

^eKaolin produced for paper industry

^fAGS Mineraux/Imerys Group

5.5 Fresh Properties

5.5.1 Workability, Slump, Water Demand, Rheology, Bleeding

In terms of the influence of metakaolin on concrete rheology, the results described in the literature are very mixed (Hassan et al. 2010). In general, the workability of concrete containing metakaolin seems to be slightly poorer than plain Portland cement concrete, but less problematic (creamier and less sticky) than when silica fume is included. Processes such as flash calcination seem to produce, in addition to plate-like particles, some spherical particles similar to those obtained for fly ashes (Claverie et al. 2015). San Nicolas et al. (2013) found up to 20% of these spherical particles in MK, which improve the workability of the mixtures when compared to MK produced in rotary kiln (composed of only plate-like particles).

There is also a tendency towards higher thixotropy (Quanji 2010), which is probably related to the particle shape of the platy clay particles. For this, and other reasons, the agglomeration/dispersion state of the metakaolin powder seems to be important in determining the early-age properties of the concrete. Metakaolin addition may also reduce bleed of concrete (Andriolo and Sgarboza 1986).

Moulin et al. (2001) evaluated the rheology of metakaolin-blended pastes using a shear vane rheometer to characterize yield stress, and found that the presence of MK significantly increased both the 5 and 90-min yield stress when compared to reference pastes. This confirmed that MK blending results in a higher water demand and leads to thixotropic behavior, which was explained to be linked to the accelerating effect of MK on PC hydration.

Wild et al. (1996) reported that workability of concrete at 0.45 water cement (w/c) decreased with increase in replacement of cement by metakaolin. It is found that slump loss was in the range of 2–32 mm when replacement level of cement was in the range of 5–35%. Dubey and Banthia (1998) reported that on inclusion of 10% metakaolin, slump loss of 20 mm was observed as compared to control concrete. Qian and Li (2001) reported that for concrete with 1% superplasticizer addition, the slump progressively decreased with increasing metakaolin content. Comparable results showing reductions in slump or fluidity have been observed by other authors (Brooks and Johari 2001; Li and Ding 2003).

Bucher et al. (2015b) assessed the relevance of the use of metakaolin in self-compacting concretes (SCC) by using it as sole supplementary cementing material. Although the water demand of MK was higher, it was shown that this material could be used in SCC with the condition of using a suitable method of design that took into account the specific surface area of MK.

5.5.2 *Chemical Admixture Interaction*

Due to its sometimes-detrimental influence on rheology and its high surface area, the addition of metakaolin to concrete can lead to a higher demand for superplasticizers (San Nicolas et al. 2013). There also appears to be an increase in the demand for air-entraining agents (or a reduction in their efficiency) with metakaolin addition (Christodoulou 2000), but there is little openly available information in this regard. The balance between cement, metakaolin and gypsum is also challenging with regard to early-age behavior, and has been identified as particularly needing attention in ternary systems also containing limestone (Antoni et al. 2012).

5.5.3 *Setting Times, Plastic Settlement, Plastic Shrinkage, Curing*

Previous researchers have found MK incorporation to have varying effects on the setting behavior of mortars and pastes. The comparison of setting times depends significantly on whether mixes are designed to standard consistency (in which case the metakaolin-containing mixes have similar setting times to a PC control), or at constant w/cm—water to cementitious materials ratio (which yields a much shorter setting time in the metakaolin-containing mixes due to the high water demand of

metakaolin) (Justice et al. 2005). Problems in the determination of early-age properties by standard test methods have also been noted due to the dry nature of mixes at lower w/c ratios (Sabir et al. 2001). Brooks et al. (2000) examined the effect of silica fume, MK, FA, and slag on setting time of high strength concrete (HSC) via ASTM C403. For HSC containing MK, there was a progressive increase in the retarding effect up to 10% replacement, but a reduction at higher replacement levels.

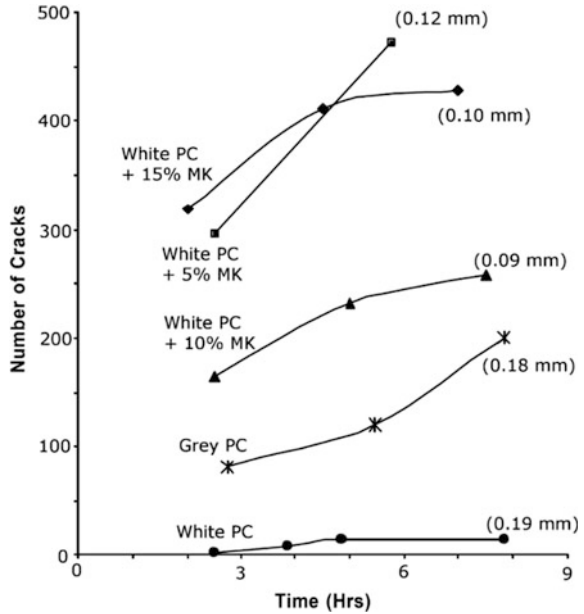
Similar results were reported by Batis et al. (2005) who examined both a commercially available MK product and local Greek kaolin heat-treated in their own lab, and found all MK mixtures to have significantly longer setting times than control pastes at normal consistency. The mixture with 20% MK set slowest, requiring 205 min for initial set compared to 105 min for the control. However, while the control mix required a w/cm of 0.275 to achieve normal consistency, 20% MK mixtures required a w/cm of 0.41. Vu et al. (2001) reported that for the particular Vietnamese kaolin used, setting times of pastes at normal consistency in the lower replacement range (10–20% MK) were not significantly affected by blending. Beyond this range, the initial and final setting times increased by 15 and 10%, respectively, attributed to the lower cement and higher water contents involved.

Badogiannis et al. (2005a) reported the water demand and setting times of cements containing five metakaolins, see Table 5.4. The amorphous contents in metakaolins MK1, MK2, MK3, and MK4 (derived from poor Greek kaolins) were 36, 37, 71, and 49% respectively, but 95% in a commercial metakaolin (denoted MKC) of high purity. The authors concluded that (1) blended cements demanded significantly more water than the unmodified cement; and (2) the initial and final setting time of metakaolin cements were affected by the metakaolin content. Cements with 10% metakaolin generally exhibited similar setting times to that of PC, while for 20% metakaolin content there was a delay in setting. MK4 showed the greatest effect on the setting time, as well as the highest water demand, see Table 5.4.

Table 5.4 Properties of metakaolin blended cements (Badogiannis et al. 2005a)

| Sample | Metakaolin (% mass) | Water demand (% mass) | Setting time | |
|--------|---------------------|-----------------------|--------------|-------|
| | | | Initial | Final |
| PC | – | 27.5 | 105 | 140 |
| MK1-10 | 10 | 29.0 | 75 | 130 |
| MK2-10 | 10 | 29.0 | 85 | 130 |
| MK3-10 | 10 | 32.0 | 105 | 160 |
| MK4-10 | 10 | 32.5 | 155 | 180 |
| MKC-10 | 10 | 31.0 | 95 | 130 |
| MK1-20 | 20 | 32.0 | 105 | 160 |
| MK2-20 | 20 | 31.5 | 110 | 165 |
| MK3-20 | 20 | 38.5 | 120 | 160 |
| MK4-20 | 20 | 41.0 | 205 | 230 |
| MKC-20 | 20 | 37.5 | 140 | 170 |

Fig. 5.6 Count of plastic shrinkage cracks on the surface of 610 × 915 × 19 mm slabs of concretes exposed to moving air conditions at early age, for different percentages of replacement with MK. Values in parentheses are the average crack widths at 8 h for each specimen (Marikunte et al. 2004)



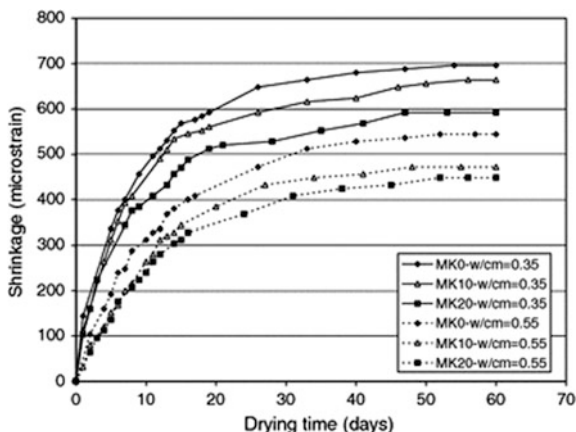
Cracking due to plastic settlement has been observed to be much higher in metakaolin-containing concretes than in control PC mixes (Marikunte et al. 2004), although the widths of the cracks appeared slightly narrower in specimens containing MK than in the unmodified samples, see Fig. 5.6.

5.6 Properties at Early Age

5.6.1 Autogenous Shrinkage

Metakaolin is known to be very effective in reducing autogenous shrinkage at later age (Gleize et al. 2007). Wild et al. (1998) investigated chemical shrinkage and swelling of MK-PC pastes with 5–25% MK, at a water/binder ratio of 0.55, for up to 45 days. Chemical shrinkage was also found to reach a maximum between 10 and 15% MK and then decrease sharply for higher MK contents. At later age in metakaolin-containing concretes, autogenous shrinkage appears to be reduced compared to PC alone (Gleize et al. 2007), and drying shrinkage also tends to be lower than that of PC, see Fig. 5.7, as long as the samples are cured appropriately before testing (Güneyisi et al. 2008, 2012), but seems to be less than PC-silica fume systems.

Fig. 5.7 Drying shrinkage of MK-blended concretes at 10 and 20% replacement levels, and w/c ratios of 0.35 and 0.55, from (Güneyisi et al. 2008)



5.6.2 Early Age Strength Development

The influence of MK on the early-age strength of concretes depends strongly on its particle size (i.e., reactive surface area), and also whether the comparison is conducted at constant w/c or at constant consistency. High fineness metakaolins can enhance early strength, less fine metakaolins sometimes have little influence on early strength and can sometimes reduce it, particularly at higher blending fractions. Sets of samples prepared at constant consistency will generally require more water in the MK-blended materials, as noted above, and this will have a negative influence on mechanical performance.

The reactivity of MK generally takes effect after a few days, so poor short-term performance can sometimes be obtained, which is a disadvantage in cases where the concrete needs to be rapidly stripped of its formwork. The use of chemical activators such as sodium sulfate is an efficient method to increase the short-term strength, but it could lead to a decreased activity at later ages (Saidat et al. 2012). Strength evolution as a function of curing duration will be considered in more detail later in the chapter.

5.6.3 Heat of Hydration, Rate of Reaction (Influence of Temperature and Curing, Maturity Functions)

Results available in the literature related to reaction rates and heat output are very mixed, largely because of the differences between the characteristics of various metakaolins as noted in the previous section. Some reports show a higher overall heat of hydration of blended cements containing metakaolin, others show similar or slightly lower, but few authors account in detail for the filler effect and corresponding acceleration of PC hydration in these discussions. The potential role of

metakaolin in chemically accelerating PC hydration has also been suggested but requires further investigation (Ambroise et al. 1994; Wild and Khatib 1997). There seems to be a tendency towards increased heat release beyond the first few days due to the pozzolanic reaction (Frías et al. 2000), but the point at which the heat evolution exceeds that of plain PC seems to depend mainly on the fineness of the metakaolin, which is both (a) variable, and (b) rarely reported accurately. So, it becomes difficult to draw overall conclusions regarding the influence of metakaolin on early-age heat evolution.

According to Zhang and Malhotra (1995), 10% replacement of PC with MK caused a 7 °C increase in the early-age temperature rise compared to PC concrete. Ambroise et al. (1994) reported temperature rises of 8, 6 and 1 °C over controls, for 10, 20 and 30% replacement, respectively, in mortars. The smaller temperature increases at higher replacement levels are likely to be due to the dilution effect of removing such a large mass of Portland cement from the system. By comparison, replacement with 10% silica fume produced a temperature rise of only 0.5 °C in the same study.

Bai and Wild (2002) looked specifically at the effects of FA and MK on heat evolved from insulated 150 mm cube mortar specimens, see Fig. 5.8. With increasing replacement levels, the temperature rise in FA systems was found to decrease, while the temperature rise in MK systems increased substantially. Ternary blends at total PC replacement levels of up to 40% appeared to have a compensatory effect on temperature rise: the temperature rise for a 10% FA-10% MK blend was the same as that of the control, see Fig. 5.8b.

Figure 5.9 shows the time to peak temperature for the binary and ternary blend mortars. Both FA and MK delay the time taken to reach peak temperature. The time delay imparted by MK, see Fig. 5.9a, is, however, greater than that imparted by FA at the same replacement level and, unlike FA, MK does not produce systematic changes in delay time with an increase in the replacement level. When both FA and MK are blended together with PC, see Fig. 5.9b, the delay time may increase substantially with an increase in the proportion of MK to FA in the blend. At 30 and

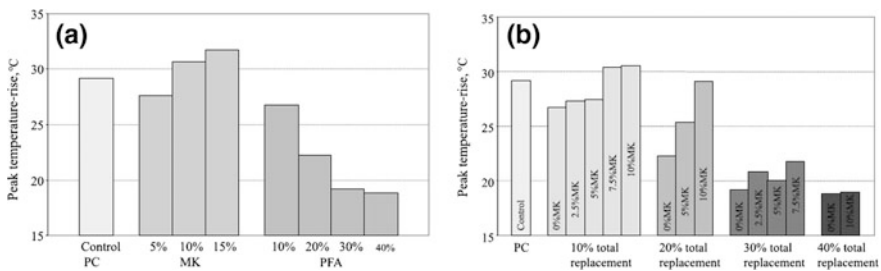


Fig. 5.8 **a** Peak temperature rise for metakaolin and FA blended PC mortars; **b** Peak temperature rise for PC-MK-FA blended mortars, as a function of the total replacement level and the fraction of this that is MK (Bai and Wild 2002)

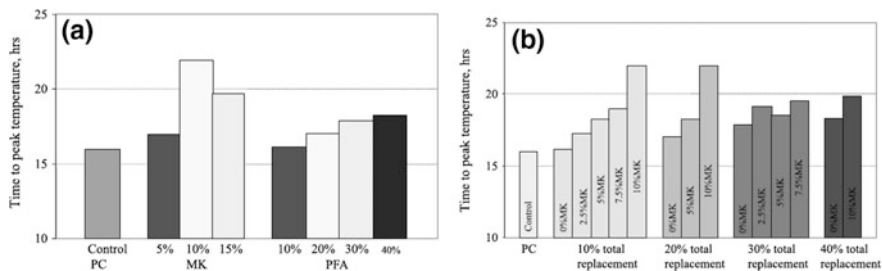


Fig. 5.9 **a** Time to peak temperature for metakaolin and FA blended mortars; **b** Time to peak temperature for MK-FA-PC blended mortars as a function of the total replacement level and the fraction of this that is MK (Bai and Wild 2002)

40% total replacement levels, the observed impact of the MK on the delay time was less pronounced because of the much lower MK to FA ratios employed in these mixtures.

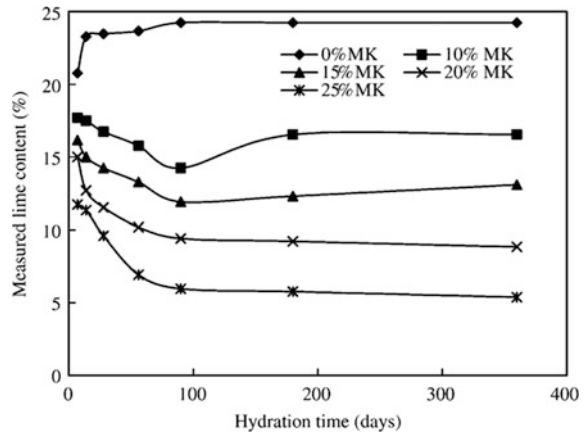
The principal reaction of metakaolin during cement hydration is between the MK (represented here as AS_2) and the CH derived from cement hydration, in the presence of water. This reaction forms additional cementitious C-A-S-H gel, together with crystalline products, which include calcium aluminate hydrates and aluminosilicate hydrates (C_2ASH_8 , C_4AH_{13} and C_3AH_6). The crystalline products depend principally on the AS_2/CH ratio and the reaction temperature.

Kostuch et al. (2000) reported that the CH content of hydrated cement paste was significantly reduced during the time of the reaction for MK replacement levels of 10 and 20%; 20% replacement of cement by MK led to consumption of all of the CH at 28 days. Oriol and Pera (1995) reported that between 30 and 40% MK was required to remove all the CH from an MK-PC paste at a water binder ratio of 0.5 when cured in lime-saturated water for 28 days. Ambroise et al. (1994) showed that during the hydration period, CH was quickly consumed, the microstructure was rich in C-S-H and strätlingite (C_2ASH_8), and the pore size distribution was refined. At up to 30% replacement, MK acted as an accelerating agent, and the CH content was considerably reduced.

Frias and Cabrera (2000) determined the degree of hydration of MK-PC pastes according to the measured CH content at a w/c ratio of 0.55 as a function of blending fraction and age, see Fig. 5.10. Calcium hydroxide contents of MK/PC samples increased with age until 3–7 days as the PC hydrated. Subsequently, the values started decreasing, at a time that depends on the MK content. In the cases of mixtures with 10 and 15% MK, an inflection point at 56 and 90 days, respectively, was observed and corresponded to the consumption of the CH by MK in the pozzolanic reaction, and beyond this point, the calcium hydroxide content progressively increased.

The pozzolanic reaction of metakaolin could be promoted by microwave heating (Oriol and Pera 1995). As heat is generated quickly inside the cementitious material, thermal acceleration of the reaction becomes more efficient, allowing both

Fig. 5.10 Calcium hydroxide content as a function of time in pastes at $w/c = 0.55$ and with different levels of replacement of PC by MK, as marked (Frias and Cabrera 2000)



reduction of the necessary amount of metakaolin (15% instead of 30–40% in normal conditions) and of the w/c ratio (0.4 instead of 0.5). These results are quite interesting for the development of fiber-reinforced cement composites, in which microwave heating allows the reduction of the curing period.

5.7 Compressive Strength

Many researchers have found that compressive strength of concrete produced with metakaolin increased when compared to control mixtures, for instance Wild et al. (1996) reported that a maximum increase of 35% in 28-day strength was identified at a 20% replacement level. Higher surface area metakaolins generally yield a higher strength and the fastest rate of strength gain. Dubey and Banthia (1998) reported that upon inclusion of 10% high reactivity (high purity and fineness) metakaolin, compressive strength increased by 9% at 28 days. Qian and Li (2001) also reported that the compressive strength increases substantially with metakaolin addition; at 3 days, an increase of 51% in concrete strength was achieved at 15% MK relative to concrete without metakaolin. The 3 day strength achieved at 15% MK was higher than the 28 day strength without metakaolin, confirming that metakaolin has a pronounced influence on early strength. Li and Ding (2003) also showed that the ternary combination of MK with PC and ultra-fine slag provided higher strength gains at 28 days than were achieved in the absence of slag.

As with other SCMs, the mechanical efficiency of MK is strongly dependent on the characteristics of the cement used. A statistical analysis done on a set of 11 different PC (Cyr et al. 2014) showed a good correlation of compressive strength of MK mixes with the contents of C_3A , C_4AF and SO_3 of PC. On the other hand, the fineness of cements, and their C_3S , C_2S , and Na_2O_{eq} contents were not correlated.

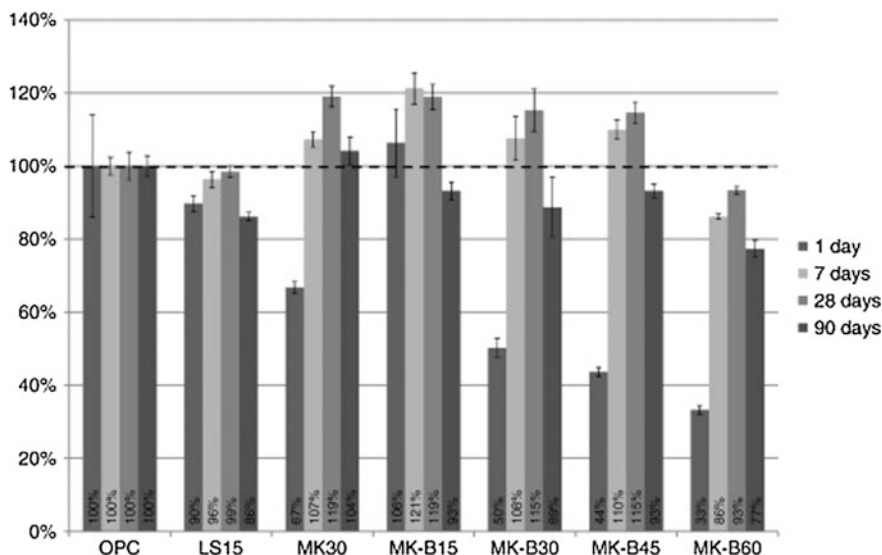


Fig. 5.11 Relative compressive strengths of Portland cement blends with various percentages (as marked) of limestone (LS), metakaolin (MK), and a 2:1 blend of the two (MK-B); data from (Antoni et al. 2012), all values are presented as a percentage of the Portland cement control specimen at the same age

In particular, the pozzolanic reaction was postponed with low- C_3A cements compared to normal Portland cement.

The combination of metakaolin with limestone at high substitution percentages, both with (Bernal et al. 2011) and without (Antoni et al. 2012) an added alkali source, has also recently been noted to give improved binder properties related to the formation of carboaluminates, strätlingite, and other Al-rich binding phases which contribute to the strength, see Fig. 5.11, and impermeability of the material.

5.8 Tensile Strength

The tensile strength of concrete incorporating metakaolin shows similar tendencies to those observed in concretes without metakaolin; there does not appear to be strong evidence for modifying the standard calculation processes whereby tensile strength is predicted from compressive strength by power-law relationships (Lawler et al. 2007). Any metakaolin addition that improves compressive strength, as outlined in section 10, would therefore be expected to correspondingly enhance tensile strength also. For example, Qian and Li (2001) reported that the tensile and compressive strengths of concrete both increase systematically with increasing metakaolin replacement level up to 15%, as shown in Table 5.5.

Table 5.5 Tensile and compressive strengths of concrete with different replacement levels of Portland cement by metakaolin (Qian and Li 2001)

| Metakaolin content (% mass) | | | | |
|-----------------------------|------|------|------|------|
| Strength at 28 d | 0 | 5 | 10 | 15 |
| Direct tensile | 3.35 | 3.58 | 3.88 | 4.29 |
| Compressive | 37.8 | 45.7 | 63.8 | 69.7 |

5.9 Flexural Strength

The comments presented earlier for tensile strength are also relevant for discussion of flexural strength; it is highly likely that the improvements in compressive strength that are achieved by addition of metakaolin will induce corresponding improvements in flexural strength. For example, Dubey and Banthia (1998) reported that on inclusion of 10% metakaolin, flexural strength increased by 9% at 28 days; the flexural toughness factor for concrete containing metakaolin was about 9% greater than for nonpozzolanic control concrete and 21% greater than for the silica fume concrete in the same study. Justice and Kurtis (2007) also reported that flexural strength measured in 4-point loading of concrete specimens was increased by 20–40% at 8% metakaolin addition.

5.10 Modulus of Elasticity

As it has been shown to increase compressive strength and to densify the microstructure, it follows that the addition of MK might also lead to increased modulus of elasticity (MOE), yielding a stiffer or more brittle concrete. From the literature, MOE generally seems to increase with increasing MK content, although the rate of increase is lower than that observed for compressive strength.

Qian and Li (2001) reported that after three days of curing, concrete containing 15% MK had an elastic modulus of 26.2 GPa, compared to 24.1 GPa for the control sample at this age. At 60 days of age, 15% MK and control concretes showed modulus values of 34.7 and 30.4 GPa, respectively. Those authors also commented on the notable increase in the brittle behaviour of the metakaolin concretes during mechanical testing. Khatib and Hibbert (2005) evaluated dynamic modulus of elasticity for $w/c = 0.50$ concretes containing 0, 10, or 20% MK. They found that MK increased the modulus values at all curing times, but that there was little difference observed between 10 and 20% MK replacement. Between 28 and 90 days in the metakaolin, the dynamic modulus of elasticity increased from 38 to 50 GPa, indicating significant ongoing reaction of the MK beyond 28 days. Justice and Kurtis (2007) reported that by inclusion of 8% metakaolin, an increase in elastic modulus by 5–19% compared to control concrete was observed.

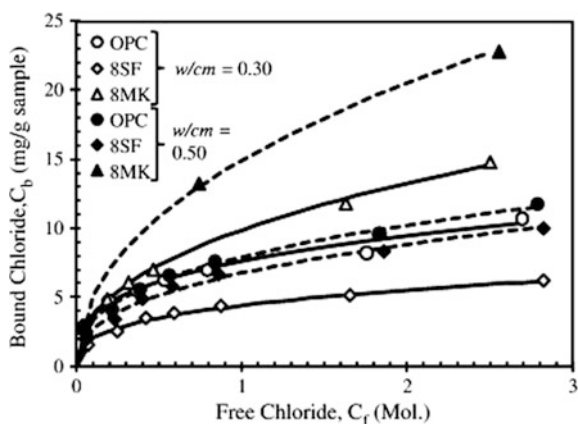
5.11 Fatigue

Based on the results of static and fatigue flexural tests conducted by Kaur et al. (2014), it is revealed that the addition of MK (and also of silica fume and fly ash) enhances the mechanical behaviour of fiber-reinforced concretes, probably through densification of the paste and interfacial transition zone microstructures (as identified in other studies, e.g., (Duan et al. 2013), analysing microhardness). However, metakaolin was only tested under fatigue conditions as a component of ternary blends so it is difficult to isolate its effects from those of the other blending components (fly ash and limestone powder). There are very few data available in the literature regarding the influence of metakaolin on fatigue performance of concrete, so this is an area that would benefit from further study.

5.12 Transport Properties and Related Durability Issues

Metakaolin is well known to contribute to the technical properties of concretes with regard to pore refinement leading to lower permeability (Ambroise et al. 1994; Frías and Cabrera 2000; Poon et al. 2006; Ramezani-pour and Bahrami Jovein 2012). However, this depends to some extent on the testing method adopted for analysis of porosity and permeability, and also in some cases on the curing duration prior to testing (Courard et al. 2003; Frías and Cabrera 2000; Khatib and Clay 2004). The additional aluminate phases formed through the pozzolanic reaction of metakaolin can also aid in resistance to chloride penetration through chemical binding effects, see Fig. 5.12, specifically the conversion of AFm phases to Friedel's salt (Thomas et al. 2012), and can also reduce alkali-silica expansion (Ramlochan et al. 2000). However, the carbonation rates of concretes containing MK may be either better or worse than those of plain PC—there is a trade-off between binder chemistry (where

Fig. 5.12 Chloride binding isotherms of pastes with 8% replacement of PC by either silica fume or metakaolin, at w/c ratios of 0.30 and 0.50 (Thomas et al. 2012)



lower calcium content tends to give higher carbonation rates) and permeability (which is normally reduced by metakaolin addition). The carbonation depths of mixtures of MK and PC (up to 25%) are similar to the ones of commercially blended cements containing fly ash or GGBS (e.g., CEM III/A and CEM V/A) (Bucher et al. 2015a). Combination of MK and limestone filler could be an interesting way to reduce the carbonation of MK blended cements (Bucher et al. 2015a), as the hemicarboaluminates formed in these ternary mixtures (Antoni et al. 2012) tend to be transformed into calcite when the CO₂ concentration increases (Damidot et al. 1994), meaning that these hydrates could play the role (as Portlandite) of CO₂ pump in clinker-limestone filler-MK mixtures (Bucher et al. 2015a).

The influence of MK in improving concrete durability is achieved to a significant degree in the interfacial transition zone (ITZ), which is characterized by a higher local w/c, a higher porosity, and differing mineralogical and chemical composition than the bulk paste. These properties of the ITZ can be detrimental to transport-related durability properties, in particular resistance to chloride and sulfate transport. MK has shown an effect on the chemistry and microstructure of the ITZ, and may thus play a significant role in reducing ion diffusion and improving concrete durability (Asbridge et al. 2001).

PC-MK concretes show significantly lower conductivity values than PC concrete (Zhang and Malhotra 1995), which is often taken as an indication of good resistance to chloride ingress. Courard et al. (2003) examined the chloride diffusion rates of mortars which contained 0, 10, 15, and 20% metakaolin as partial replacement of cement using a non-steady state through-diffusion test. The apparent diffusion coefficient of the mortar rose with 5% MK addition but then decreased with metakaolin content from 5 to 15%, see Table 5.6; however, the mortar with 20% MK did not show breakthrough of chlorides through a 7 mm thick specimen even after 300 days.

Khatib and Wild (1998) evaluated the effect of metakaolin on the sulfate resistance of blended cement mortars. Expansion was found to decrease systematically with an increase in MK content (from 5 to 20%), for two cements having high C₃A and intermediate C₃A levels. Mortars containing high C₃A cement and 0–10% MK showed rapid expansion and deterioration between 40 and 70 days of exposure to a 5% sodium sulfate solution, while those with 15 or 20% MK showed a small but rapid expansion during this time period, but subsequently stabilized and

Table 5.6 Chloride diffusion rates for mortars with CEM I 42.5, metakaolin and kaolin (Courard et al. 2003)

| Material | Breakthrough time (days) | Apparent diffusion coefficient (m ² /s) |
|----------------|--------------------------|--|
| CEM I 42.5 | 13 | 1.29 × 10 ⁻¹² |
| 5% metakaolin | 45 | 4.71 × 10 ⁻¹² |
| 10% metakaolin | 82 | 3.31 × 10 ⁻¹² |
| 15% metakaolin | 203 | 1.23 × 10 ⁻¹² |
| 20% metakaolin | >300 d | – |

contracted slightly. For the intermediate-C₃A cement mortars, the expansion process was delayed significantly. Those containing 10% or more MK exhibited essentially no expansion, while those containing 0 or 5% did not begin expanding until 150 days and did not grow rapidly until approximately 350 days. Al-Akhras (2006) also showed an improvement in resistance to sodium sulfate attack, even at w/c ratios as high as 0.6.

However, Lee et al. (2005) found that metakaolin influences negatively the performance of mortar or paste specimens when exposed to magnesium sulfate solution. This is partially attributed to the formation of gypsum, but not ettringite and thaumasite. Another possible reason may be the decalcification of primary and secondary C-S-H gel following the formation of M-S-H gel.

In terms of alkali-silica reaction (ASR), Ramlochan et al. (2000) reported that incorporation of metakaolin as a partial cement replacement at levels between 10 and 15% may be sufficient to mitigate deleterious expansion from ASR in concrete, depending on the nature of the aggregate. The mechanism by which metakaolin may suppress expansion due to alkali-silica reaction appeared to be entrapment of alkalis by the supplementary hydrates and a consequent decrease in the pH of pore solutions.

Zhang and Malhotra (1995) evaluated the performance of air-entrained concretes incorporating metakaolin in ASTM C 666 (ASTM International 2015c) freeze-thaw tests and in ASTM C 672 (ASTM International, 2012) salt scaling tests. Concrete with 10% metakaolin showed great resistance to freeze-thaw damage, with a residual flexural strength of 89% and a durability factor of 100.3%, after 300 cycles of freezing and thawing. On the other hand, the residual flexural strength and durability factor values for the control Portland cement concrete specimens were 85 and 98.3% respectively. For the salt-scaling test, the concrete incorporating 10% metakaolin underperformed slightly when compared to the control concrete, but had similar results to the concrete with 10% SF.

Badogiannis and Tsvivilis (2009) prepared nine concrete mixtures: a reference PC concrete and eight metakaolin concretes where metakaolin replaced either cement or sand in percentages 10 or 20% by weight of the control cement content. The metakaolin concrete, compared to PC concrete, exhibited significantly lower chloride permeability, gas permeability and sorptivity because of refinement of the pore structure of the metakaolin mixtures.

Batis et al. (2005) prepared eight mortar mixtures: a reference PC concrete and six metakaolin mortars where metakaolin replaced either cement or sand in percentages 10 or 20% by weight of the control cement content. They measured the corrosion resistance of prepared mortars against chloride and carbonation induced corrosion. They concluded that the use of metakaolin, either as a sand replacement up to 20% weight of the control cement content, or as a cement replacement up to 10%, improved the corrosion behavior of mortar specimens. However, higher percentages of metakaolin decreased the corrosion resistance.

San Nicolas et al. (2014) applied the concept of equivalent performance by assessing the durability of concrete using metakaolin as a Portland cement replacement. The study considered large panels of concrete types, with different

workabilities, from immediate release to self-compacting concrete, and different strengths from low to high performance concrete, for either general or structural purpose. Many technical benefits for the concrete user, such as lower permeability, higher strength and decreased chloride ion penetration were found. It seemed from that study that MK met the requirements of the equivalent performance concept.

5.13 Concluding Remarks

Metakaolin can be considered as a highly pozzolanic material and appears to have an excellent potential as a supplementary cementing material for high-performance cementitious materials. However, there are a number of characteristics of metakaolin-blended concrete, which need additional detailed analysis to aid in the deployment of this material as a large-scale supplementary cementitious material:

- Sulfate resistance depends on metakaolin content and the method of measurement (strength or expansion) (Khatib and Wild 1998)
- Shrinkage behaviour seems variable and needs further analysis
- Effect of clay source/mineralogy is complex—this is currently understood mainly on an empirical level, but theoretical developments are now moving rapidly
- Other long-term mechanical properties, e.g., creep of concrete, require additional investigation
- Molecular level details of interactions with organics are not yet well described.

The optimum level of cement replacement seems to be around 10–20%, where maximum strength is observed. Incorporation of high reactivity metakaolin as a partial cement replacement between 10 and 15% may also be sufficient to control deleterious expansion due to alkali-silica reaction in concrete, depending on the nature of the aggregate. The addition of metakaolin reduces the ingress of chloride by improving the microstructure and chloride binding behaviour.

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Chapter 6

Natural Pozzolans

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Abstract This chapter is dedicated to several kinds of natural pozzolans that occur around the globe and describes their specific characteristics, origin and use in concrete. Moreover, the advantages and disadvantages of their use in concrete mixes are highlighted in terms of concrete properties. In particular, the referenced

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properties in this chapter are that of fresh and hardened concrete, its microstructure and chemical durability. The chapter is summarized by mentioning the specifications concerning natural pozzolans according to the relative standards. Overall, the benefits of using natural pozzolans in cement and concrete are evident in terms of higher later age compressive strength, increased concrete durability, lower heat of hydration, reduced bleeding and others.

Keywords Natural pozzolans • Concrete properties • Volcanic ash
Pumice • Zeolite • Scoria • Tuff • Diatomite • Perlite durability
Compressive strength

6.1 Introduction

Natural pozzolans were the first cementing materials used for the production of artificial stones—ancient mortars and concretes—3000 years ago. Ancient Romans used volcanic tuffs, known as pozzolans (also spelled pozzolana) in combination with lime as hydraulic binders for the construction of bridges and other masonry and brickwork. Roman engineers used two parts by weight of pozzolan mixed with one part of lime. During the 3rd century BC, the Romans used pozzolan instead of sand in concrete and mortared rubblework, giving extraordinary strength. Used with an aggregate of broken tuff, travertine, brick, or marble, the material contributed to the evolution of new architectural forms in such monumental constructions as the Pantheon and the Baths of Caracalla in Rome (Encyclopædia Britannica, n.d.).

An even older concrete came to light during the archaeological excavations in the area of the ancient Greek city of Kamiros in the island of Rhodes. Citizens of Kamiros constructed during the 8th century BC a water storage tank with a storage capacity of 600 m³ of water. They used a concrete layer as a water sealing material (Fig. 6.1). This ancient concrete was investigated by Efstathiadis (1978) in the early 1970s.



Fig. 6.1 Water storage tank in the ancient city of Kamiros, Rhodes, Greece. Concrete layers were used as water sealers. The water tank was put out of order during the 3rd century BC due to the construction of a Doric Portico with foundations of 1.60 m × 200 m (Efstathiadis 2004)

Fig. 6.2 Concrete from the water storage tank of ancient city of Camiros (Efstathiadis 2004)



According to Efstathiadis (2004) this sealing material was an ancient concrete produced with limestone and silicate aggregates with maximum aggregate size of 20 mm. The binder consisted of Santorinian Earth (volcanic tuff from the eruption of Santorini’s volcano in 1500 BC) and lime (Fig. 6.2) with a ratio 3:1.

Efstathiadis (2004) reported that this concrete performed at the age of the test a compressive strength of 13 MPa while its water sealing capacity was verified in the laboratory. It is particularly of interest to note that the aggregates consisted of limestone and silicate natural coarse aggregates with a grading curve similar to the Fuller’s curve (Fig. 6.3).

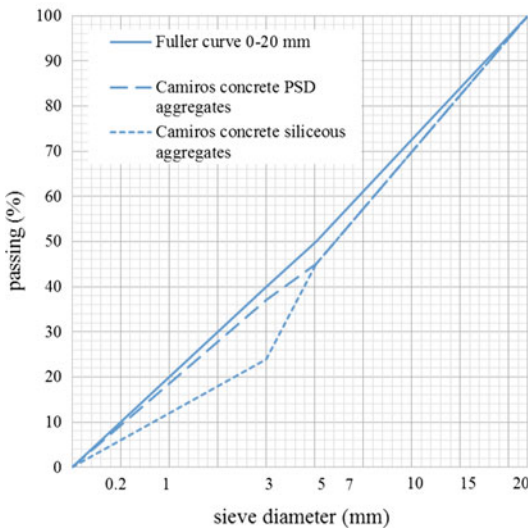


Fig. 6.3 Grading curve (left) (Efstathiadis 1978) of aggregates used in the concrete of ancient Camiros (right) (Efstathiadis 2004)

Efstathiadis (2004) reported that similar concretes were found in other ruins of ancient infrastructure such as in a bridge at the river Ilissos in Athens and a water storage tank in the ancient city of Paleros in western Greece.

During the next centuries volcanic tuffs were used as hydraulic binder by the ancient Romans for the construction of infrastructure works and monuments. Although pioneered by the ancient Greeks, it was the Romans that eventually fully developed and widely used the potential of lime-pozzolan pastes as binder phase in Roman concrete used for buildings and underwater construction. Vitruvius speaks of four types of pozzolan: black, white, grey, and red, all of which can be found in the volcanic areas of Italy, such as Naples. Typically it was very thoroughly mixed two-to-one with lime just prior to mixing with water. The Roman port at Cosa was built of pozzolan-lime concrete that was poured underwater, apparently using a long tube to carefully lay it up without allowing sea water to mix with it. The three piers are still visible today, with the underwater portions in generally excellent condition even after more than 2100 years (McCann 1994). Jackson et al. (2013) have studied the concrete blocks created by the Romans by mixing lime with pumiceous earth and seawater as binder and packed with decimeter-sized chunks of zeolithic tuff as aggregates. The hydrated binder phase was found to be intact after 2 millenia of immersion in seawater. The extraordinary durability of this sea-water concrete was attributed to the formation of Al-tobermorite and hydrocalumite hydrates as binder.

The Byzantines used Santorinian earth to a great extent as the main constituent to produce hydraulic binders for the construction of infrastructure, palaces, churches and monasteries (Manita 1999; Manita and Triantafilloy 2011; Moropoulou and Bakolas 1998; Papayianni 1998; Binda et al. 1999; Moropoulou et al. 2002; Manita 2005). During the last centuries Santorinian earth was used as a main constituent for the production of modern concretes mainly used in marine structures all over the Aegean Sea and the Eastern Mediterranean basin (Corinthos' Canal, Suez Canal in Egypt (Ramachandran 1995), etc.). Santorinian earth was used for the production of the "Greek type Cement Ia", a blended type cement where Santorinian earth replaced Portland clinker at a standard percentage of 10%. The production of this kind of cement stopped by 1980 (cf. infra).

6.1.1 Types of Natural Pozzolans

Pozzolans are (alumino-) silicate materials that can be used as a substitute for cement in mortar mixtures. Some forms of it occur naturally and others are man-made. Pozzolans commonly used in modern Portland cement are coal combustion fly ashes and silica fume by-products from (ferro-) silicon production.

Naturally occurring pozzolan deposits are mainly of volcanic origin. They occur as tuffs, volcanic ash and pumice and are found abundantly in areas with a geological history of volcanic activity. The meaningful use of such volcanic debris can transform them into natural resources, and does not only provide a lower cost of

cement and concrete but can also help to decrease CO₂ emissions related to Portland cement production by replacing clinker.

In general, a good natural pozzolan contains low quantities of unreactive minerals such as clay minerals, alkali feldspar and quartz and high quantities of reactive components such as zeolite minerals and volcanic glass. The dissolution of the silicates in the alkaline cement pore solution enables them to react readily as the cement hydrates. Chemically, natural pozzolans are comprised principally of silicon and aluminium oxides. Table 6.1 gives the chemical and physical composition of some natural pozzolans.

The materials that have been investigated or even commercially applied as natural pozzolans the recent years are classified based on their geological origin as follows:

Volcanic ash (VA) and pumice: Volcanic ash and pumice are non-consolidated materials consisting of a mixture of minerals and glassy phases ejected from vents during a volcanic eruption. Volcanic ash is the fine counterpart, pumice the coarser counterpart. Often they are found mixed or interstratified as during volcanic eruptions first the coarse material is deposited, while later the finer material settles. In areas that experienced past volcanic activity, volcanic ashes and pumices have been widely used with Portland cement and other components to make blended cements. The pozzolanic activity of this material is related to its siliceous components. Comprehensive research has been conducted over the last few years on the use of volcanic ash and pumice in cement and concrete production (Hossain 2005a, b; Hossain and Lachemi 2004; Mechti et al. 2012; Dadu et al. 2012).

Scorias are coarse, porous natural materials of volcanic origin. They resemble pumice but derive from basic—basaltic magmas, thus they contain less silica than the corresponding pumices. They contain glass and mineral phases such as feldspar and biotite. Clay minerals and zeolites occur as alteration products. The high porosity of the natural pozzolan is an advantage for easy and economical crushing (Binici et al. 2007). It has a dark brown/blackish color, porous structure and low crystal water.

Tuffs are lithified volcanic ashes and pumices. These rocks generally contain clay, zeolite and carbonate minerals as filling/binding materials. Zeolitization is the alteration of the volcanic glass to zeolite-group minerals and occurs under alkaline conditions in a range of geological environments. When tuffs rich in zeolite minerals are mixed with slaked lime and water, they form calcium silicate hydrate and calcium aluminate hydrate phases (Mertens et al. 2009). Zeolites of different origin and varying mineralogy and chemistry have been investigated regarding the influence of their addition in concrete. Even though zeolites have a crystalline nature, fine size and higher surface area of this natural sediment make them suitable as a pozzolan in cements. Recent research efforts are focused in evaluating the influence of zeolites and zeolitic tuffs addition in concrete. A review of these efforts is provided by Najimi et al. (2012).

Besides zeolites, tuffs suitable for use as natural pozzolans can also include combinations of various silicate minerals such as quartz, feldspar, mica, hornblende, pyroxene, cristobalite, clay minerals and volcanic glass (Cavdar and Yetgin

Table 6.1 Chemical composition and physical properties of some natural pozzolans

| Chemical analysis (%) | Natural zeolite | | Pumice | | Natural pozzolan (Algeria) | Volcanic ash | Natural pozzolan (Algeria) | Volcanic tuff (Argentina) |
|--|----------------------|---------------------------|----------------------------|---------------------|----------------------------|--------------|----------------------------|---------------------------|
| | Najimi et al. (2012) | Karakurt and Topçu (2011) | Hossain and Lachemi (2006) | Kabay et al. (2015) | | | | |
| CaO | 1.68 | 2.37 | 4.44 | 0.1 | 8.98 | 6.1 | 9.2 | 1.34 |
| SiO ₂ | 67.79 | 62.78 | 60.82 | 77.52 | 45.67 | 59.3 | 46.8 | 62.53 |
| Al ₂ O ₃ | 13.66 | 10.66 | 16.71 | 12.99 | 15.10 | 17.5 | 18.8 | 10.76 |
| Fe ₂ O ₃ | 1.44 | 4.2 | 7.04 | 1.5 | 10.14 | 7.0 | 10.5 | 1.81 |
| MgO | 1.2 | 1.1 | 1.94 | 0.4 | 3.45 | 2.6 | 3.8 | 1.13 |
| K ₂ O | 1.42 | 0.74 | 2.25 | 0.95 | – | 3.8 | 0.5 | 3.67 |
| Na ₂ O | 2.04 | 0.35 | 5.42 | 0.12 | – | 3.8 | 0.8 | 5.66 |
| SO ₃ | 0.52 | – | 0.14 | 0.52 | 0.19 | 0.7 | 0.2 | 0.34 |
| Specific surface blaine (m ² /kg) | – | – | 295 | 440 | 366 | 285 | 300 | 858 ^a |
| Density (kg/m ³) | 2200 | – | – | 2320 | 2610 | – | 2670 | 2410 |

^aLaser diffractometry: dv10 (μm) 1.36, dv50 (μm) 7.05, dv90 (μm) 28.14

2007). Next to zeolites, the volcanic glass phase is usually the major reactive component.

The most widespread siliceous zeolites are clinoptilolite and mordenite. These zeolites are observed to form in the alteration of siliceous glasses, whereas the common more aluminous zeolites, phillipsite, chabazite, analcime and heulandite (alumina-rich polymorph of clinoptilolite) form from the alteration of more basic glasses. Heulandite-clinoptilolite is by far the most frequently (up to 60%) identified zeolite mineral in natural zeolite-rich pozzolans (Snellings et al. 2012).

Diatomite: Diatomite is a pozzolanic material of biogenic origin containing amorphous silica, opal CT (components of the siliceous skeletons of diatoms) and minor amounts of residual minerals. Diatomaceous earth consists of fossilized remains of diatoms, a type of hard-shelled algae.

Hydrothermal siliceous sinters: The supply of natural amorphous silica from hydrothermal deposits is limited. A few years ago, the only quarry evaluated to be economical was in New Zealand in the Tikitere region (Christie et al. 2000). This amorphous silica rock has been used in traditional concretes and high performance concretes. The material from this deposit can be classified as ‘silica fume’ according to the corresponding international standards (Microsilica NZ, n.d.). A new deposit in the Keciöorlu region of Turkey has been evaluated concerning the pozzolanic properties in concrete (Davraz and Gunduz 2005).

Bentonite: Bentonite is an absorbent aluminium phyllosilicate clay consisting mostly of montmorillonite. Recent citations concern the evaluation of dried and milled Pakistani Ca-bentonite without any thermal treatment as partial replacement of cement (up to 21% by weight). Test results showed that all the mixes satisfied the requirement of strength activity indices as laid down by ASTM C618. The workability, fresh concrete density and water absorption decreased as the ordinary Portland cement substitution by bentonite increased, while later age compressive strength (56 days) increased compared to control mix. Mixes containing bentonite performed better than control mix against acid attack. The aggressiveness of sulfuric acid on concrete was more pronounced than hydrochloric acid (Shazim et al. 2012).

Perlite: Perlite is an amorphous volcanic glass that has a relatively high water content, typically formed by the hydration of obsidian. It occurs naturally and has the unusual property of greatly expanding when heated sufficiently. There is no previous investigation so far on the use of natural perlite in concrete. The use of calcined perlite in concrete has been investigated with positive effects on concrete durability (surface resistivity, rapid chloride permeability and chloride migration coefficient) (Ramezaniapour et al. 2014). There is however literature information concerning perlite incorporated in blended cements (Erdem et al. 2007; Erdogan and Saglik 2013; Cobirzan et al. 2015) demonstrating good pozzolanic reactivity but never reaching the compressive strength of the baseline (100% cement) without the addition of activators.

6.1.2 Type of Incorporation

Natural pozzolans, like all other SCMs, can be introduced upstream at the cement facility to produce “blended” or “composite” cement or downstream at the concrete manufacturer to produce concrete products. Composite cements have the advantage of stable quality and less machinery and infrastructure in concrete production. Downstream introduction results in “tailored-made” concrete products with specific properties, especially durability. However this approach results in higher delivered cost due to higher processing cost and more complex logistics.

Recent research results concern various combinations of SCMs, natural and/or manmade (Belaidi et al. 2012; Herbert and Li 2012; Shannag 2000; Ghrici et al. 2007). By systematic adjustment of the proportions, ternary blended cement (see Chap. 9) is produced (Ordinary Portland Cement–Limestone Filler–Natural Pozzolan otherwise abbreviated as OPC–LF–NP) which utilizes the desirable characteristics of one addition while compensating for the undesirable characteristics of the other. For example, the limestone filler contributes to the early strength and the natural pozzolan increases the long-term strength. On the other hand, the best combination of these mineral additions, can lead to an enhanced durability performance. Such combinations are used in special applications, like in high strength concrete where the use of natural pozzolan with silica fume is often met (NP–SF) or in self-compacting concrete (SCC) with the use of natural pozzolan and marble powder (NP–MP).

On the other hand, successful results are not always obtained (Sisman and Gezer 2011). Combination of zeolitic pozzolan with rice husk ash resulted in specimens with lower strength and increased water absorption.

6.2 Geographical Occurrence

Natural pozzolans are either reactive materials with an amorphous structure or materials that are derived from amorphous minerals. It seems then natural that their occurrence is strongly connected with recent volcanic activity (Snellings et al. 2012) (Fig. 6.4).

6.2.1 Occurrence

The following data concern the research efforts since 2000. These efforts are subdivided by the geographical occurrence of the investigated pozzolans.



Fig. 6.4 Global distribution of volcanic rocks (grey areas) and deposits of reported natural pozzolans (black dots) (Snellings et al. 2012)

6.2.1.1 Europe

Greece: The Minoan eruption of Santorini, also referred to as the Thera eruption or Santorini eruption, was a major catastrophic volcanic eruption with a Volcanic Explosivity Index (VEI) of 6 or 7 and a dense-rock equivalent (DRE) of 60 km^3 (14 cu mi), (McLeish 2006), which is estimated to have occurred in the mid-second millennium BC (Hardy 1989). The eruption was one of the largest volcanic events on Earth in recorded history (Oppenheimer 2003; McCoy and Dunn 2002; Sideris 1996). The volcanic tuff produced was a well-known pozzolanic material since the antiquity and was widely used for mortar and concrete production for more than 25 centuries all over the Aegean Sea and the eastern Mediterranean basin. This so-called Santorinian earth (SE) was used till 1980 for the production of Greek type cement, a blended type cement with a 10% replacement of clinker by SE.

In 1981 the Greek government prohibited the mining and exploitation of Santorinian earth for reasons related to the protection of the island of Santorini. Nowadays the natural pozzolans used in Greece for the production of natural pozzolan blended cements are Milos's earth and Skydrian earth.

Milos's earth is a volcanic tuff originated from the nearby island of Milos. It is originated from the same eruption of Santorini's volcano, so actually consists of similar chemical composition; however it consists of lower percentages of volcanic glass and is more altered to clay minerals, therefore Milos's earth is less reactive than Santorinian Earth (Table 6.2).

Skydrian earth is a volcanic zeolite tuff located in the area of Skydra in Northern Greece. Its suitability for the production of blended cements was extensively investigated by Savva (1991).

Italy: The zeolitization of the Neapolitan yellow tuff took place soon after emplacement in a well-insulated thermal system in presence of hot aqueous

Table 6.2 Chemical composition of Greek natural pozzolans (Sideris 1996)

| Oxides (%) | Santorinian earth | Milos's earth | Skydrian earth |
|--------------------------------|-------------------|---------------|----------------|
| SiO ₂ | 66.2 | 65.9 | 61.7 |
| CaO | 4.1 | 4.0 | 4.62 |
| Al ₂ O ₃ | 15.4 | 15.7 | 19.6 |
| Fe ₂ O | 3.9 | 3.95 | 4.1 |
| MgO | 1.3 | 1.4 | 2.6 |
| SO ₃ | – | – | – |
| Alkalis | 3.83 | 5.65 | 3.9 |

solutions of hydromagmatic origin. The distribution and the type of zeolites in the Tufo Lionato have been analyzed by Giampaolo et al. (2006), which is the lower ignimbrite unit of the Villa Senni Eruption Unit, a large mafic ignimbrite eruption from the Colli Albani volcano, a few kilometers south of Roma (central Italy). The Tufo Lionato ignimbrite is radially distributed around the Colli Albani volcano over 1500 km² and occurs as far as 35 km from the vent.

Germany: One of the deposits of natural zeolite is found near the town of Freiburg in the small volcanic region called Kaiserstuhl. The volcanic material with the name phonolite contains 45% zeolite (=natrolite) (Hauri 2006). Another well-known natural pozzolan called “trass” is found in the Eifel region. Trass is quarried at various locations and consists of variable proportions of volcanic glass and the zeolite minerals phillipsite, chabazite and analcime as reactive phases.

Bulgaria: There are six deposits of zeolites in the Eastern Rhodopes. The deposits are associated with the first Oligocene acidic volcanism (Beli Plast, Gorna Krepost, Most, Golobradovo and Ljaskovetz) and to the second Oligocene acidic volcanism (Bilia Bair). The zeolites from the deposits Beli Plast, Gorna Krepost, Most, Golobradovo and Bilia Bair are clinoptilolitic types while those from the Ljaskovetz deposit are mordenitic. The estimated reserves of clinoptilolite rocks total 722 million tones and those of mordenite total 114 thousand tones. The Beli Plast deposit is composed of thick- to moderately thick-layered rocks with a white, red or pink color (Petrov 2006).

Croatia: In spite of the fact that zeolites have been found at several locations, so far only two regions with economically interesting concentrations are known, both situated in the northern part of the country. The first one is located in the Macelj area in north-western part of Hrvatsko zagorje (NW Croatia) in which Lower Miocene (Egerian-Ottngian) volcanoclastic rocks crop out on several localities. They have variable primary composition, and contain various alteration products of volcanic glass. The alteration products comprise zeolites (clinoptilolite as the most abundant zeolite, analcime and mordenite), clay minerals (smectite, authigenic mica), SiO₂ phases and authigenic feldspars. Performed investigations indicate that alteration products are the result of burial diagenesis. In the other deposit, located in the vicinity of village Poljanska in Požega Valley, on the southern slopes of Mt. Papuk (Slavonian Mountains, N Croatia) analcime-bearing rocks can be found.

Analcime was formed within closed hydrological system i.e. shallow saline alkaline lake which existed during early Miocene (Ottangian) time (Tibljaš and Jelavić 2006).

6.2.1.2 Middle East

Turkey: Turkey is rich in natural pozzolans. Almost 155,000 km² of the country is covered by Tertiary- and Quaternary-age volcanic rocks, among which tuffs occupy important volumes. Although there are many geological investigations on these volcanic deposits their potential as natural pozzolans is not well established (Cavdar and Yetgin 2007).

As seen from the study of Cavdar and Yetgin (2007), it is possible to easily find rich natural pozzolan resources in Northeast of Turkey (Trabzon–Bayburt district). The rocks that were taken from this region and investigated were volcanic origin and they showed pozzolanic property. They consisted of tuffs, except one, and they mostly fulfilled the TS 25 standard requirements for both pozzolanic activity and chemical composition.

Other recent studies have been focusing on several natural pozzolans in Turkey such as scoria (Ozvana et al. 2012), diatomite (Ergün 2011), perlite (Erdem et al. 2007) and natural amorphous silica (Davraz and Gunduz 2005).

Syria—S. Arabia—Jordan: Ash-like product of volcanic activity can be found in the Middle East Syria and Saudi Arabia (Al-Chaar et al. 2011), among other regions. Research on these deposits showed that this type of pozzolan is very suitable for use in concrete in wet conditions. Tuff from Jordan (Shannag 2000), incorporated together with silica fume, resulted in high strength concrete.

Iran: The interest in natural pozzolans has been increased in Iran recently. Natural zeolites are abundantly present in Iran and it can be easily quarried and processed while usual pozzolans such as fly ash, silica fume, high-reactivity metakaolin and slag are rarely available and relatively expensive. Additionally, with the focus on increasing the durability of concrete structures especially in aggressive environments such as the Persian Gulf region, finding of an available and economical supplementary cementitious material has gained great importance in Iran. Therefore, Ahmadi and Shekarchi (2010) evaluated the effect of natural zeolite, coming from Semnan in the center of Iran, on properties of concrete using various testing methods. Natural pozzolan from Ghorve, located in the west of Iran, and the influence of their addition for the production of massive high-strength concrete was investigated by Nili and Salehi (2010). Numerous other studies have been focused on Iranian pozzolans such as clinoptilolite (Najimi et al. 2012), volcanic pumice (Ramezani-pour et al. 2012), tuffs (Jamshidi et al. 2009) and other pozzolans from Iranian mines in Rafsanjan, Sirjan and Sharbabak areas (Foroughi et al. 2012).

6.2.1.3 Americas

USA: Natural pozzolans are not as widely used as other SCMs. Commercially available pozzolans in the U.S. include calcined shale or clay and metakaolin, a popular variety of treated natural pozzolan. To date, commercial production of natural pozzolans in the U.S. has been limited to less than ten locations (Keybridge Research LLC 2010).

Mexico: Since natural pozzolans are available in Mexico, the exploitation of pozzolanitic or both pozzolanitic and cementitious properties of mineral admixtures, when used as a partial replacement for cement, can lead to a considerable economic benefit and durability.

Cuba: Cuba has over 500 million tons of prospective resources in several deposits. Presently, a blended cement containing 20% zeolite tuff is produced in the area while other materials located around the island containing altered, vitreous (volcanic glass) and zeolitized tuff are being studied. In addition, the country is in possession of several hundred million tons of forecast vitreous tuff which requires more thorough study to make sure it can be used as pozzolan.

Argentina: There are several regions in the country where suitable natural pozzolans are found and exploited. The most exploited natural pozzolans are located near the Andes Mountains, where significant volcanic activity is still present. Pyroclastic pozzolans are found in Mendoza, San Juan and Neuquén (Batic et al. 2003), which were deposited by airborne transport. In some places they underwent diagenetic processes and turned into tuffs that are found as extensive banks with limited thickness (1–2 m). They generally have a homogeneous appearance and very high porosities. These materials are commonly found as mixes of the original volcanic glass and alteration products. Also significant exploitation of pumice takes place in Argentina [120,000 tons/year (Harben 2006)], including application to the production of blended cement. Pozzolanitic portland cement with up to 50% (admitted) or 40% (in practice) replacement ratio is broadly produced in Argentina. Zeolitic tuffs are also found in the provinces of La Rioja, Catamarca, San Luis and Salta.

Paraguay: In the east of the country there are reserves of sediments of volcanic ashes (MOPC 1993) that are exploited by the cement industry (40,000 tons/year). There are also significant reserves of kaolinitic clays mixed with diatomite on the border with Brazil.

Ecuador: In the inter-Andean region of the country at least a dozen volcanoes can be found, many of them are active. Significant deposits of volcanic ashes can be found mainly around the 4 most active volcanoes of Ecuador, which are Cotopaxi, Tungurahua, Sangay and Reventador. These natural pozzolans are currently exploited for the production of pozzolanitic cements. Pozzolanitic cement including up to 40% content of pozzolan is the most used cement in Ecuador (Delgado-Vallejo and Negrete-Martínez 2012), and it is produced for the five cement plants in the country.

6.2.1.4 China

In China, since the first zeolite mineral deposit on an industrial scale was discovered in Jin-yun County of Zhejiang Province in 1972, there are more than one hundred zeolite mineral deposits found in a great range of twenty one provinces. Three of the largest are: (a) Dushikou Mine at Chi-cheng County of Hebei Province, which contains middle- and high-quality clinoptilolite at a mineral content of 50–70%, and has a deposit of 400 million tons; (b) Jin-yun County Mine in Zhejiang Province, which has a deposit of over 100 million tons, and mostly comprised of clinoptilolite and some mordenite; and (c) Hai-ling County Mine in Heilongjiang Province, which has a deposit of over 100 million tons at a zeolite content of 65%, with the longest history of supplying zeolite as a blended material for cement plants, and the largest production scale (Feng and Peng 2005).

Nowadays, the industry of the largest zeolite consumption in China is cement production. Cement produced in many plants with vertical kilns possesses an inferior volume stability, due to its high content of free lime ($f\text{-CaO}$). Natural zeolite can be used as a blending material in most of these cement plants to solve the volume stability problem of hardened concrete. Zeolite has also been applied as a mineral admixture for concrete production during more than twenty years in China. It can prevent bleeding, segregation and delamination of fresh concrete so as to make pumping process easier, decrease permeability of hardened concrete, enhance durability especially the resistance to alkali-aggregate reaction, increase concrete strength, and minimize cracking caused by self-shrinkage in high performance concrete. As a result, in 2005 the China Concrete Association has put forward a technical recommendation to promote the application of natural zeolite in the construction industry in China. Presently, the annual consumption of natural zeolite in China is over 30 million tons (Feng and Peng 2005; Najimi et al. 2012).

6.2.1.5 Africa

Algeria: In Algeria, most of the cement is being blended with additions such as limestone and natural pozzolan. Natural pozzolan from the Beni-Saf quarry in the west of Algeria that consists mainly of Cordierite, Analcime and Axinite is being used for cement manufacturing by at least six of the twelve Algerian cement plants whereas two cement plants use limestone. These cement plants add usually about 15% of natural pozzolan and 10% of limestone filler as cement replacement by weight (Ghrici et al. 2007).

Nigeria: The pumice tuffs studied by Dadu et al. (2012) were obtained from Kajuru, Kaduna in North East Nigeria. Compressive strengths and the strength activity index of concrete containing the tuffs indicated that the materials met the ASTM C618 (2005) specifications for a natural pozzolan to be used as a mineral admixture in Portland cement concrete.

6.2.1.6 Oceania

Papua New Guinea: Extensive research has been done on a pozzolan deposit of pumice in the East New Britain province of Papua New Guinea (Hossain 2005a, b; Hossain and Lachemi 2004). Hossain (2005a, b) showed that blended concretes with 20% cement-replaced by Volcanic Ash (VA) and pumice showed better performance in terms of Cl-diffusivity and perform better in resisting reinforcing bar corrosion than does the plain concrete. All mixes containing up to 40% Volcanic Pumice (VP) or VA, satisfy the ASTM C 618 requirement of 0.8% maximum autoclave expansion. Strength activity index values for mixes with 10, 20 and 30% VA or VP content are more than 75% as required by ASTM C 618.

6.2.2 Global Consumption of Natural Pozzolans

Globally, about 75 million tons/year are utilized in the cement and concrete industry (Cement Sustainability Initiative GNR, n.d.). Recently, the most important utilization of natural zeolite in cement and concrete industry has been reported in China. As mentioned by Najimi et al. (2012) in 2012, the total quantity of zeolite consumed in this field was as much as 30 million tons per year in China. Zeolitic tuffs are also used as pozzolanic materials in some cement plants of Russia, Germany, Slovenia, Cuba, Serbia and Spain. In general the material has been applied in the production of paving stones, concrete slabs, ready mixed concrete, and high-strength concrete pipes (Najimi et al. 2012; Hossain 2005a, b; Hossain and Lachemi 2006). In addition, the use of natural zeolite as a pozzolanic material is gaining an increasing trend in Iran recently (Najimi et al. 2012).

It has been reported in 2007 that approximately 50,000 tons/year of zeolitic tuff have been used for the production of Portland pozzolan cements in Germany. At the same period Italy consumed yearly about 3 million tons and China about 5 million tons of zeolitic tuffs as a component of blended portland cements (Jana 2007).

6.3 Influence of Natural Pozzolans Addition on Concrete Properties

6.3.1 Properties of Fresh Concrete

6.3.1.1 Consistency and Water Demand

The effect of natural pozzolans on water demand for a certain slump value depends on the type of pozzolan. Some natural pozzolans may notably increase water demand, such as diatomite and zeolite which are usually characterized by a high

water absorption capacity. Others like volcanic ash and pumice have moderate impact only if they are included at high percentages.

In general, some reduction in slump by natural pozzolan addition is because the cement is partially replaced with natural pozzolan by weight and therefore, according to the lower specific gravity of natural pozzolan in comparison with that of cement, the volume of solids in the paste is higher than that of the control mixture. Then more mixing water is necessary for lubricating particles.

The increase in volume may require more mixing water but this is not necessarily a disadvantage. As indicated in Ramezaniyanpour et al. (2013), this increase in volume allows for a more stable mix, and better conditions for the design of fluid mixes such as self-consolidating concrete might be obtained.

Particle size, shape and internal structure are very important characteristics that define the impact of the pozzolan on water demand. In general, pozzolanic cements require higher fineness than ordinary portland cement to achieve similar strength level, due to its slower reaction rate. Therefore, the increase in water demand can initially be linked to this technological aspect that is a consequence of cement design rather than the properties of the natural pozzolan itself. However, Menéndez et al. (2003) reported no increase in water demand when natural pozzolan was finely ground separately (760 m²/kg Blaine fineness), as the extensive grinding destroyed internal pore structure of natural pozzolans it reduced their water absorption capacity. In consequence, the effect of natural pozzolans on the demand of mixing water for same consistency can vary significantly.

For zeolites, characterized by a highly porous internal structure, a main reason for the significant increase in water demand is its high surface area and water absorption capacity (Şahmaran et al. 2006; Ezziane et al. 2007; Feng et al. 1990; Adjoudj et al. 2014; Uzal and Turanli 2012; Perraki et al. 2010). In consequence, a reduction in slump with the inclusion of zeolite as replacement of cement is found in many studies (Jana 2007; Najimi et al. 2012; Adjoudj et al. 2014; Feng et al. 1990).

The inclusion of diatomite also increases water demand significantly (Stamatakis et al. 2003; Kastis et al. 2006). This is as well due to the pore structure of diatomite which allows its very high water capacity. In this sense, Yilmaz (2008) obtained much more water demand with inclusion of diatomite than volcanic tuff.

Also using volcanic tuff, Turanli et al. (2005) reported a 14% increase in water demand when increasing the pozzolan content from 35 to 55%. Çolak (2003) reported similar results for 40% replacement, but for lower replacement ratios (20 and 30%), no significant change in water demand in comparison with control cement was obtained.

Also moderate increase in water demand due to perlite inclusion in cementitious systems is found in the literature (Erdem et al. 2007; Uzal et al. 2007). This lower impact seems to be connected with a coarser particle size distribution, which might cause perlite to show also a lower superplasticizer demand than other natural pozzolans such as natural zeolite or volcanic tuff (Uzal et al. 2007).

Volcanic ash and pumice are also among the natural pozzolans with most moderate effect on water demand. Hossain and Lachemi (2006) found little

influence of volcanic ash and pumice on slump of concrete at up to 20% of cement replacement. Similarly, Hossain (2003) reported that normal consistency decreased by about 4–5% when 25% of volcanic ash or volcanic pumice was included in cement, and about 12–14% when this ratio increased to 50%. Therefore, little influence was noted for low replacing ratios whereas the effect triplicated when the replacing ratio duplicated. Here, the only effect of these natural pozzolans seems to be caused by the reduction of cementitious binder in the fresh mixture with the increasing content of natural pozzolan and the lower density of the natural pozzolans in comparison with clinker phases.

The opposite influence has also been reported by Al-Chaar et al. (2011) in their investigation on the use of volcanic ash from Syria in concrete. They report that the pozzolan addition results in slump increment, and water reduction was required in order to maintain the slump stable.

6.3.1.2 Setting

The influence of natural pozzolans on setting times is governed by the dilution effect of cement in the paste. This causes a delay in setting. However, this effect is compensated by water absorption for the particular cases of zeolite and diatomite. And whereas a balanced net effect is obtained for diatomite, for the case of zeolite the water absorption prevails resulting in a reduction of setting times.

Çolak (2003) investigated the effect of a volcanic tuff with a $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ proportion (which relates to the pozzolanic activity within the material) of 80.6%. The setting times of the pastes increased with increasing content of this natural pozzolan. Here, the increase in setting time is attributed to the increase in the water to Portland cement ratio. However, amounts under 20% of the natural pozzolan had little effect on the setting times, and only for 40% of replacement significant delaying of setting times in comparison with the plain ordinary portland cement paste was obtained. However, Turanli et al. (2005) obtained dissimilar effect of volcanic tuffs on setting time. Whereas reduced setting times were obtained for 55% of replacement, increased times for 35% and similar setting times to those of the reference paste for 45% were obtained. In fact, Uzal and Turanli (2003) obtained different effects of volcanic tuffs from two different origins in Turkey, which decreased and increased setting times according to their origin. Here, the mechanism that governs the effect of pozzolan content on setting time could not be explained by the authors.

As said, the high water absorption of zeolite also plays a significant role in its effect on setting. As a lower proportion of OPC is present in the blended system, a delay in setting times could be expected. But there is also the competing effect of water absorption by the zeolite which increases stiffness of the paste as it progresses. Then, delayed setting times with the inclusion of low amounts of zeolites are reported in Perraki et al. (2010), but earlier setting times are reported by Uzal and Turanli (2012) and Şahmaran et al. (2008) when they applied high replacement ratios. Shorter setting time values recorded for mixtures with natural zeolite are

probably due to reduction in consistency of the mixtures rather than faster hydration of the blended system. However, in practical terms both events affect concrete workability similarly. As the water absorption rate reduces when zeolite particles approach to saturation, the effect of zeolite water absorption is more significant on initial setting time than on final setting time. In consequence, when used in high percentage (50% replacement) and compared with other natural pozzolans, zeolite seems to be the one that might reduce the setting times the most (Uzal et al. 2007), whereas a slight reduction of setting times is also demonstrated by volcanic tuff, and a retardation is showed by perlite. Delayed setting with 30% replacement by perlite and up to 50% by volcanic ash is also reported in Erdem et al. (2007) and Hossain and Lachemi (2010), respectively.

A balanced effect is noticed for diatomite. Stamatakis et al. (2003) found similar setting times to those of the reference paste for the diatomites they studied except for one, which was actually characterised as diatomaceous limestone instead of diatomite. In this case, the increased fineness of the interground pozzolanic cement increased setting time, and intergrinding seems to destroy the structure of the pozzolan, reducing its water absorption capacity. The same material studied in (Kastis et al. 2006) with separate grinding resulted in similar setting times for control and diatomite blended cements. Therefore, competing effects of water absorption and cement dilution will result in an increase or reduction of setting times depending on the fineness of the pozzolan.

6.3.1.3 Bleeding and Segregation

As natural pozzolans tend to have a flocculent structure when blended in cementitious mixes, more cohesive mixes with higher water retention capacity are obtained. Consequently, bleeding and segregation are considerably reduced with the use of pozzolan as a mineral admixture in concrete (Jana 2007) and thus improving the pumpability of concrete (Mehta and Monteiro 2001). In general this is due to (1) the lubricating effect of the glassy particles; (2) increased ratio of solids to liquid make the concrete less prone to segregation and increase concrete pumpability and (3) increased volume of fines as natural pozzolans are less dense than Portland cement.

6.3.1.4 Rheology and Interaction with Chemical Admixtures

The use of a superplasticizer breaks the flocculent structure in pozzolan blended mixes and in some cases the late inclusion of the admixture may cause segregation of water initially absorbed by the pozzolan.

The compatibility between pozzolanic cement and water reducers is connected to the particular characteristics of cement hydration and the dilution effect of the pozzolan in the contents of C_3A , sulfate and soluble alkali, and also its particle size distribution. On its own, several characteristics of the water reducer such as

molecular weight and its distribution, chemical composition, structure and nature of the counter ion, have main impact on the performance of the system cement-water reducer (Alonso et al. 2007; Bonen and Sarkar 1995).

The compatibility between a given cement and a superplasticizer differs depending on whether the admixture is polycarboxylate-based or polysulfonate-based. In general, cements that are more compatible with a polynaphthalene-based admixture are also more incompatible with a polycarboxylate-based admixture, and vice versa (Yamada and Hanehara 2001). In this sense, alkali sulfates play a key role in the efficiency of polycarboxylates, and the optimum sulfate content for polycarboxylates is much lower than for polynaphthalenes (Saric-Coric 2001). In this sense, Sosa et al. (2012) reported results for compatibility that do not correlate with the total alkali content in pozzolanic cements. They explain their results considering that natural pozzolan contains alkalis which are less soluble than those of clinker, and thus, pozzolanic cement can also show extended compatibility to polycarboxylate-based water reducers despite the amount of alkali provided by the pozzolan. Therefore, high alkali contents from some natural pozzolans (e.g. Hossain (2003) reported 5.83 and 7.69% for volcanic ash and volcanic pumice, respectively) might not show proportional effect on the cement-admixture compatibility depending on the solubility of these alkalis.

In connection with its effect on the previously mentioned fresh properties, a potential reduction in the ability of admixtures to reduce the mixing water content with pozzolanic cement than with ordinary portland cement is reported (Erdogdu 2000).

As an increasing proportion of natural pozzolan causes a decrease in the workability of the mixture, the demand of superplasticizer for a certain consistency level is expected to increase as well. The efficiency of the superplasticizer is also connected with the MgO content of the mineral admixture (Moncef 2000), and in this regard the addition of a natural pozzolan with a high MgO content will likely inhibit the dispersing effects of the superplasticizer and cause a loss in fluidity of the mixture. In practical terms this means an increase in the demand of water-reducer.

Results in Hallal et al. (2010) indicate that the fluidity of pastes including natural pozzolan (presumably of volcanic origin) increases with the increase of w/c ratio but does not always increase with the superplasticizer dosage. In this sense, the use of natural pozzolans may lead to an increase in the saturation dosage of superplasticizer. Even more, similar results reported in (Agullo et al. 1999), with lower fluidity for pastes including diatomite in comparison with silica fume admixed pastes, showed that the lower efficiency of water reducers with diatomites may require to be also compensated with an increase in mixing water content to maintain the fluidity level.

On its own, the higher requirement of superplasticizer to maintain the slump of concrete with higher replacement ratio of cement by natural zeolite (Şahmaran et al. 2008; Chan and Ji 1999; Feng et al. 1990; Ahmadi and Shekarchi 2010; Ramezani-pour et al. 2013) is again connected to the large amount of micropores in the zeolite framework structure and the resulting high surface area. Therefore, using higher amounts of natural zeolite leads to an increase of the viscosity of fresh

concrete, and this might mean reduced workability but also an advantage for pumpability of concrete. Similar results for these fresh properties of concrete incorporating natural zeolite are reported by other authors (Feng et al. 1990, 1988), but some reports of unaffected workability of fresh concrete by natural zeolite can also be found (Chan and Ji 1999).

The high specific surface and internal porosity of zeolites is the main reason for the increase in yield stress, plastic viscosity and apparent viscosity (Şahmaran et al. 2008; Chan and Ji 1999; Ahmadi and Shekarchi 2010; Adjoudj et al. 2014; Ramezaniapour et al. 2013), but higher interaction between fine particles can also be claimed as a cause (Şahmaran et al. 2008). In this sense, higher amounts of superplasticizer are necessary for reducing both yield stress and plastic viscosity. Furthermore, the impact of a polycarboxylic-ether type superplasticizer on the rheology of the zeolite admixed grouts in Şahmaran et al. (2008) was higher than that of a viscosity-modifying agent (Welan Gum), and the former admixture is therefore recommended for zeolite admixed grouts. It is also known from the work of Şahmaran et al. (2008) that the addition of a superplasticizer in the grout mixtures including natural zeolite allowed a compensation of the accelerating effect of the pozzolan on setting times.

In contrast, two reports including replacement ratios of up to 50% of volcanic ash (Hossain and Lachemi 2010) and up to 20% of volcanic ash (Triwulan et al. 2011) show no significant influence of this pozzolan on the superplasticizer demand for producing self-consolidating concrete. However plastic viscosity still seems to be slightly increased (longer flow times were obtained with the inclusion of volcanic ash), this is not due to water retention by the natural pozzolan as a slight tendency to increased bleeding is also reported for increasing volcanic ash content. Then, the interaction among fines seems to be the main mechanism in this case.

In connection with this, Diamantonis et al. (2010) obtained intermediate levels of improvement in the rheological properties of pastes with the use of volcanic ash. Here, increased values of plastic viscosity and shear stress were obtained with 20 and 40% replacement ratios by volcanic ash. However these results are not as good as those obtained for limestone (still the use of a pozzolan further contributing in the hardened state is an advantage), they are better than the ones obtained for fly ash. Also, after previous verification of compatibility between superplacizer and pozzolan cement (containing volcanic ash), delayed setting was interpreted as an advantage over limestone when producing stable self-consolidating concrete with extended maintenance of slump over time with consequent reduced redosing requirement (Egüez-Alava and Aguirre-Vera 2009).

Ramezaniapour et al. (2012) studied the fresh and hardened properties of self-consolidating concrete (SCC) containing Volcanic Pumice (VP) as natural pozzolan in comparison with ordinary SCC mixture, SCC containing Silica Fume (SF) and conventionally vibrated concrete mixture. When the properties of fresh SCC such as slump-flow and V-funnel time are considered, they showed that using pumice in binary blends slightly decreased the flow diameter of the mixtures whereas on incorporation of silica fume a gradual fall was observed in the flow diameter. Generally, incorporating pumice increased the cohesion of the SCCs

specimens. In comparison with the ordinary SCC specimens and vibrated specimens, it seems Pumice as a pozzolanic material increased the later age compressive strength of SCC. However, it decreased the early age compressive strength. While silica fume increased both early and late age compressive strength by filling of voids and pozzolanic activity.

6.3.2 Heat of Hydration

The hydration of cement paste is accompanied by liberation of heat that raises the temperature of concrete. Because of the slower pozzolanic reaction, partial replacement of cement by natural pozzolans results in a release of heat over a longer period of time enabling the heat to dissipate and the overall concrete temperature to remain lower. This is of immense importance in mass concrete where cooling, following a large temperature rise, can lead to cracking.

As can be seen in Fig. 6.5, a pozzolan from Syria reduced the heat of hydration (Al-Chaar et al. 2011).

6.3.3 Shrinkage and Cracking

The effects of natural pozzolans on drying shrinkage are highly related to the effects on water demand. When incorporation of a pozzolan involves a demand for additional water in the mixture and, correspondingly a larger volume of paste and C–S–H, increased drying shrinkage occurs (Itim et al. 2011; Seraj et al. 2014).

In fact, drying shrinkage in mortars and concrete with natural pozzolans is directly proportional to water lost during drying (Seraj et al. 2014), and most

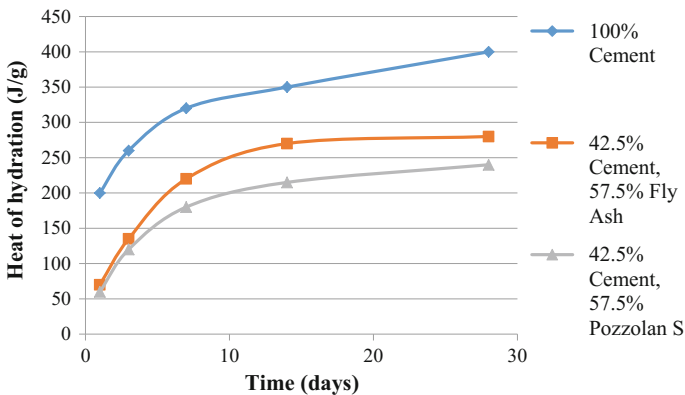


Fig. 6.5 Influence of different SCMs on the heat of hydration of concretes (Al-Chaar et al. 2011)

differences observed in drying shrinkage are related to water or paste content. Many studies have shown natural pozzolans, including Santorinian earth (Mehta 1981; ACI Committee 232 2012), pumice (Hossain et al. 2011), volcanic ash (Hossain et al. 2006), and calcined shale (Khanna and Puri 1957), to have no significant effect on drying shrinkage within the error of the test method (Seraj et al. 2014). It is possible that the impact of pozzolans on drying shrinkage may be time dependent since it has been shown that pozzolans can mostly decrease early drying shrinkage (≤ 7 days) (Itim et al. 2011).

The expansion and shrinkage mentioned above also create microcracks inside the hardened C–S–H paste and in-between the aggregate and the C–S–H paste. These microcracks significantly contribute to concrete permeability as well as to other concrete defects. The natural pozzolan-Portland cement mixture expands these shrinks so moderately that there is significantly limited microcracking inside the C–S–H paste after curing (Asare et al. 2010).

While concrete is hardening, part of the water is consumed and heat is produced. The surface of the hardening mass then begins to shrink as the temperature goes down from outside. This may result in shrinkage and cracks. In general, natural pozzolans help to moderate the expansion and shrinkage of concrete by reducing thermal cracking. They can also help to lower the water content of the fresh concrete. Therefore, the thermal shrinkage and cracks can be significantly reduced without the process of water cooling.

6.3.4 Microstructure

6.3.4.1 Porosity and Pore Size Distribution

The effect of the use of natural pozzolans on the porosity of cementitious materials is quite varied, mainly depending on the overall reactivity of the pozzolan (derived from the amount of glassy phases, specific surface area, particle size distribution, etc.). On the one hand, some pozzolans that have a high water demand (zeolites, diatomite) may affect the hardened state by increasing porosity (especially at early age) when requiring a higher w/b ratio. On the other hand, some have a strong pozzolanic effect, which decreases total porosity. Regarding pore size distribution, a shift into the smaller pore sizes is generally found due to the pozzolanic reaction.

For the case of volcanic tuff and diatomite, microstructural analysis through SEM was performed by Yilmaz (2008). The author found that the structure of pastes at 28 days with 10% diatomite and 10% volcanic tuff contained much less pores and capillary voids in comparison with the paste containing 20% of diatomite. This might be due to the higher water demand of diatomite in comparison with volcanic tuff, but also due to the fact that the pore structure of the ternary blended paste consisted of more complex shapes (increased tortuosity). In consequence, a much denser structure was seen after 365 days for the ternary blend than for the diatomite blend. Also for the case of diatomite, Janotka et al. (2014) studied the

porosity of pastes with natural clayey diatomite (5, 10 and 15% replacement of cement) and found that the total porosity at 365 days was slightly increased with diatomite content in comparison with the control paste.

Clinoptilolite-rich zeolite tuffs from two different origins were studied by Uzal and Turanli (2012). They applied mercury intrusion porosimetry to pastes with 55% replacement after 28 and 91 days of curing and found that the intruded porosities of control pastes were higher than the respective blended pastes for all cases. However, according to the origin of the zeolite, porosity changes over time were different. One of the zeolites noticeably reduced the total intruded porosity of the blended paste at 91 days, while the other did not show any improvement. This difference was due to the different pozzolanic activity that both zeolites had, as indicated by the lower amount of free CH present in the paste with higher porosity reduction.

Regarding volcanic pumice and ash, Hossain and Lachemi (2006) studied the effect of 20% cement replacement on the porosity of pastes. Results at 56 days show a lower porosity than that of the control paste, both for the volcanic ash and volcanic pumice mixes. Also porosity reduction was found by Senhadji et al. (2014) when using natural pozzolans with a strong acidic character. Results of mortars at 365 days made with 20% of replacement indicate a 47% porosity reduction with respect to the value of OPC mortar. Accordingly, compressive strength at early ages of mortars with natural pozzolans were lower than control, however, at 365 days results were similar.

The porosity of mixtures produced with natural pozzolans at different ages is plotted in Figs. 6.6 and 6.7 (Sideris 1996). Milos's earth and Skydrian earth replaced ordinary Portland cement (OPC) at different levels up to 40%. All cement pastes were produced with a water/binder mass ratio of 0.50. Porosity measurements were taken up to the age of 730 days (two years). The porosity of cement pastes at the age of 5475 days (15 years) was calculated using the cement hydration equation model (Sideris and Sideris 1997, 2003). Water permeable porosity (pores

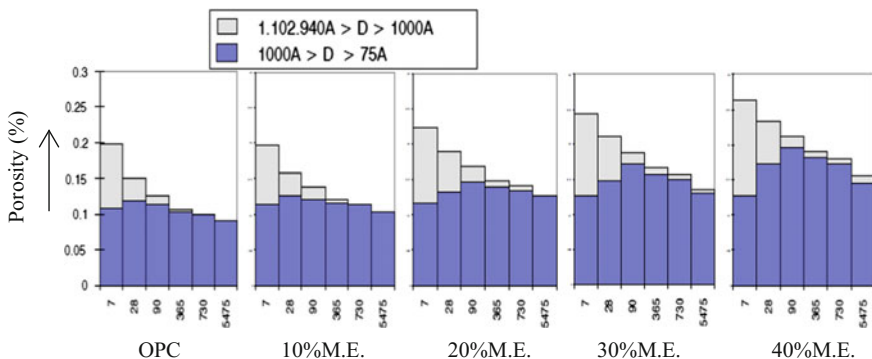


Fig. 6.6 Total ($1.102.940\text{\AA} < D < 75\text{\AA}$) and water permeable ($1.102.940\text{\AA} < D < 1000\text{\AA}$) porosity of cement pastes produced with Milos's earth (M.E.) (Sideris 1996)

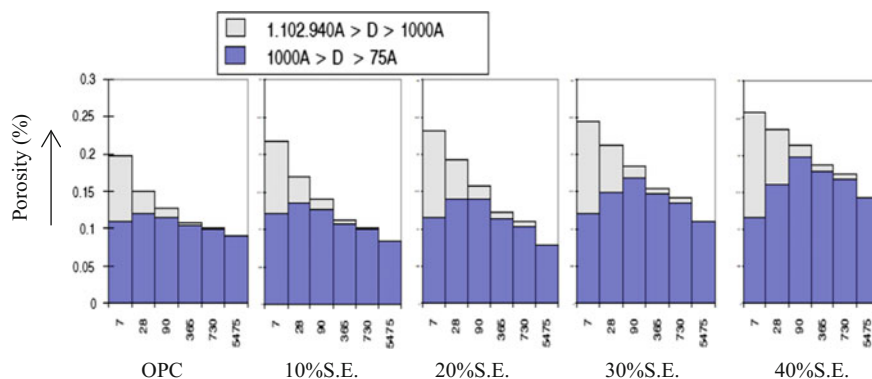


Fig. 6.7 Total ($1.102.940 \text{ \AA} < D < 75 \text{ \AA}$) and water permeable ($1.102.940 \text{ \AA} < D < 1000 \text{ \AA}$) porosity of cement pastes produced with Skydrian earth (S.E.) (Sideris 1996)

with diameter between 1000 and $1.102.940 \text{ \AA}$) is indicated with grey colour while water impermeable porosity (pores with diameter between 75 and 1000 \AA) is indicated with blue colour. Total porosity measured (pores with diameter between 75 and $1.102.940 \text{ \AA}$) is the sum of grey and blue colour. Total porosity of cement pastes produced with natural pozzolans was increased at all ages as the replacement level also increased. However the water permeable porosity was about the same as the one measured on OPC pastes at ages greater than 90 days for replacement levels of 10%.

Regarding pore size distribution, the main result of the use of pozzolans in cementitious materials is the pore refinement. Particularly, there is an increase in small pores ($<50 \text{ nm}$) at later ages as a result of densification due to secondary C–S–H or C–A–S–H. In this sense, Senhadji et al. (2014) found that the volume of the pore size distribution between 2.5 and 125 nm was more noticeable for mortar with 20% of natural pozzolans than for mortar with silica fume or OPC mortars. Moreover, the mean pore size at 365 days was drastically reduced from 60 to 16 nm on mortar samples when incorporating only 20% natural pozzolan. Likewise, mean pore reduction at 365 days was found by Janotka et al. (2014) on pastes with 5, 10 and 15% of clayey diatomite in comparison to control pastes. For the cases of zeolites, Uzal and Turanli (2012) found that at 91 days zeolite blended cement pastes (with 55% of replacement) contained lower volumes of pores with size $>50 \text{ nm}$ than OPC paste, this was indicated as the reason for better impermeability performance of blended cements containing high volume of natural zeolite. Pores size distribution of mortars blended with volcanic ash from Papua New Guinea was studied in Hossain and Lachemi (2004). The authors found a larger amount of pores $>20 \text{ nm}$ in the control mortar than in the ones with 20 and 40% of volcanic ash, as well as a larger amount of pores $<20 \text{ nm}$ in the mortars with volcanic ash. This indicates that the incorporation of volcanic ash leads to appreciable pore refinement. Furthermore, later Hossain and Lachemi (2006) performed differential scanning calorimetry on reference mortar samples and samples

with volcanic ash and volcanic pumice. They correlated this with a lower content of CH in the samples with volcanic ash or volcanic pumice than in the control mix. And then related the consumption of CH due to pozzolanic action with pore refinement due to the resultant C–S–H.

Changes in microstructure due to pozzolanic activity not only affects total porosity and pore size distribution but also have an impact on tortuosity and pore connectivity. Several authors (Stroeven 2000; Wong et al. 2006; Promentilla et al. 2009; Provis et al. 2012; Liu 2012) have studied those features and their effect on transport properties. The complex microstructure due to the pore refinement effect is directly translated in the performance regarding transport properties, given that the pore size distribution and connectivity and not the total pore volume are the main responsible features that govern those properties. Therefore, pozzolanic action from natural pozzolans is generally reported to have a higher impact on transport properties than on total porosity.

6.3.4.2 Transport Properties

Usually, the durability properties of concrete are improved by the partial replacement of Portland cement with natural pozzolans. Particularly, values for transport properties like gas permeability and diffusivity are generally lower in cementitious materials with pozzolans. This is mainly attributed to the pore refinement action mentioned in Sect. 3.4.1. In this sense, Ahmadi and Shekarchi (2010) found that concrete made with 5, 10, 15, and 20% of clinoptilolite type natural zeolite from Iran had lower water absorption than the control concrete. However, only concretes made with 5 and 10% of natural pozzolan showed reduced oxygen permeability in comparison with the control, at 28 days. The authors suggested that the reason for this increase in oxygen permeability with the highest natural zeolite replacements (15 and 20%) is that a partial amount of the zeolite is still unreacted in hardened concrete paste. Still, this should have had a similar impact on the water absorption tests. It should also be mentioned that samples were dried at 105 °C during 7 days before measuring oxygen permeability, which very likely had a strong impact on the microstructure of the mixes. Furthermore, electrical resistivity of the concrete mixtures with natural zeolite was registered at different time intervals until 90 days and it was always higher than the one recorded for control concretes. Since the samples were cured under water during the whole period, the authors attributed this enhancing effect to the finer pore size distribution and decreasing ionic strength. Najimi et al. (2012) also studied concrete mixes with the same natural zeolite from Iran, with 15 and 30% replacement of cement. Here, water penetration depth at 28 and 90 days was lower for higher replacement levels. On the other hand, water absorption of the concrete mixtures containing natural zeolite was higher than that of the control concrete. This was attributed to the fact that natural zeolite has a considerably higher water absorption than the paste at concrete surface.

Positive effects of natural pozzolans on the transport properties of self-compacting concrete (SCC) have also been reported. Siad et al. (2014) showed

that the incorporation of natural pozzolan reduces sorptivity, water porosity, chloride diffusion, and gas permeability. The SCCs with natural pozzolan and with fly ash exhibit quite equivalent coefficients, significantly lower than those obtained with the control SCC containing limestone filler. Likewise, Samimi et al. (2016) also found an improved durability performance of SCC with natural pozzolans.

6.3.5 Properties of Hardened Concrete

6.3.5.1 Compressive Strength

The pozzolanic reaction between natural pozzolans and calcium hydroxide usually occurs after the C_3S in the cement has started hydrating and portlandite is formed as a result.

Usually pozzolanic effects of strength improvement are more pronounced at late ages (i.e., beyond 28 days) than at early age. It was reported by several researchers that the most obvious disadvantage of the natural pozzolan used as substitutes for Portland cement is that early strength is normally decreased (Ozvana et al. 2012; Itim et al. 2011). The strength of the pozzolanic cement is directly affected by the mineralogical features (amorphous/crystalline components) and physical properties (micro-meso porosity, particle size, surface areas) of the pozzolanic material.

In general, at the early stage of curing (up to 7 days), 30% natural pozzolan substituting Portland cement mixture is slightly lower than reference OPC (Ordinary Portland Cement) in regard to compressive strength. As time goes by, natural pozzolan continues to react with the calcium hydroxide produced by cement hydration and increases the compressive strength by producing additional C–S–H. After 21 curing days, the 30% natural pozzolan/70% Portland cement mixture begins to exceed the reference OPC in compressive strength. After 28 days, it exceeds the reference OPC by about 15%. The pozzolanic reaction continues until there is no free calcium hydroxide available in the mass and the compressive strength exceeds the reference OPC by 30–40% (Asare et al. 2010).

There are however references on natural pozzolans (Ozvana et al. 2012), where the addition resulted in improvement of the mechanical strength at early age. Compressive strength of scoria (added up to 30%) concrete mixtures showed higher compressive strengths up to 112% from the first tested curing ages (3 days). Some pozzolans start to chemically react very shortly after contacting with water. The hydration of C_3S was accelerated by the addition of pozzolan caused by the filler effect (Ozvana et al. 2012).

It has been found (Shannag 2000) that certain natural pozzolan-silica fume combinations can improve the strength of mortars more than natural pozzolan or silica fume alone. Considerably, a higher 28-day compressive strength of about 110 MPa was achieved by adding 15% silica fume and 15% natural pozzolan by weight of cement, compared to just 15% silica fume (87 MPa) or just 15% natural pozzolan (69 MPa). The increase in strength can be attributed to the improved

aggregate-matrix bond resulting from the formation of a less porous transition zone in the silica fume concrete.

An important factor that affects the mechanical properties is the particle size distribution of the pozzolan, as many researchers have shown up to now (Mechti et al. 2012). Apart from the impact on the pozzolanic activity, the finer the grain size is more closed the pores are, resulting in denser structures. This results in increased mechanical strength (Mechti et al. 2012).

Imerys micrasil (Imerys Minerals Arabia L.L.C. 2015), a natural pozzolanic material consisting of highly active volcanic glass, has proven a superior behaviour by the combination of highly reactive natural pozzolanic properties and finer grain size. When compared to silica fume, one of the most effective industrial pozzolans used in concrete today, in terms of compressive strength, it showed improved results in basic commercial concrete mixes while in parallel it demonstrated an improvement in workability and chloride permeability (Fig. 6.8).

In particular, compressive strength results of several natural pozzolans mentioned in previous sections are summarized below:

Ergün (2011) investigated the mechanical properties of concrete specimens containing diatomite and waste marble powder (WMP) as partial replacement of cement. Test results indicated that the concrete specimens containing 10% diatomite, 5% WMP and 5% WMP + 10% diatomite replacement by weight for cement had the best compressive and flexural strength. The replacement of cement with diatomite and WMP separately and together using a superplasticizing admixture could be utilized to improve the mechanical properties of the conventional concrete mixtures.

Sideris et al. (1997) used Skydrian earth (SE) at replacement levels of 10 and 30% for the production of concrete mixtures with limestone or silicate aggregates. They concluded that only the 10% SE mixtures developed 28 days strength

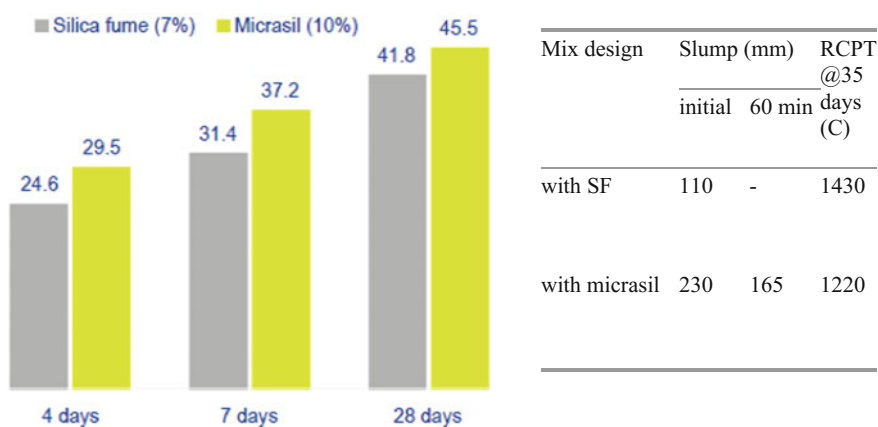
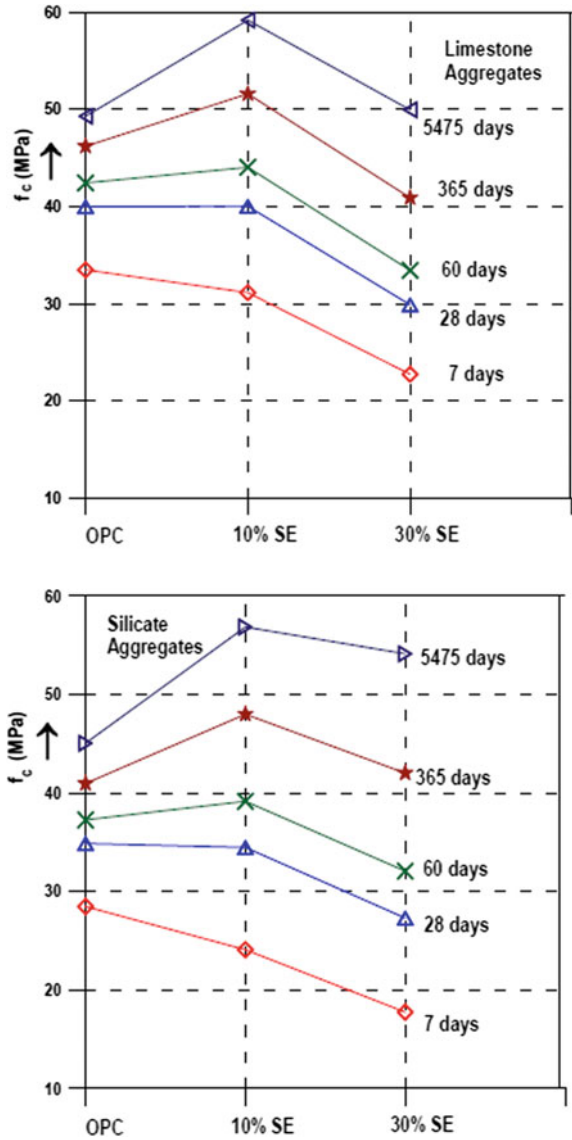


Fig. 6.8 Compressive strength (MPa) of C35 concrete mixes with w/b = 0.39 containing micrasil or silica fume (Imerys Minerals Arabia L.L.C. 2015)

Fig. 6.9 Compressive strength development of mixtures produced with Skydrian earth at replacement levels of 10 and 30%. Total cementitious content: 300 kg/m³, w/cm ratio = 0.60 (Sideris et al. 1997)



comparable with the one measured in the reference mixture. However at the ages of 365 days and beyond all SE mixtures gained significant strength values (Fig. 6.9).

Sideris (1996) used both Milos’s earth and Skydrian earth at replacement levels up to 40% for the production of cement mortars (Figs. 6.10 and 6.11). All mixtures were produced according to EN 196-1 with a w/cm = 0.50. Both natural pozzolans were grinded up to a fineness of 5000 Blaine. The retaining in the 45 μ m sieve was 18.75% and 4.8% for Milos’s earth and Skydrian earth respectively.

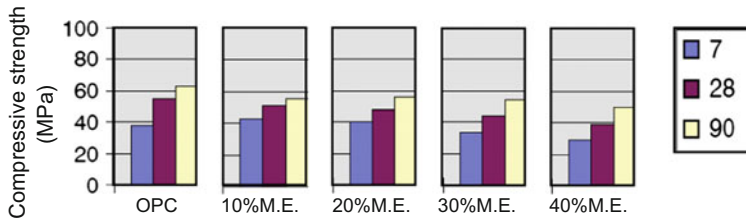


Fig. 6.10 Influence of Milos's earth (M.E.) on the development of compressive strength of cement mortars. Compressive strength values were measured till the age of 90 days (Sideris and Sideris 1997)

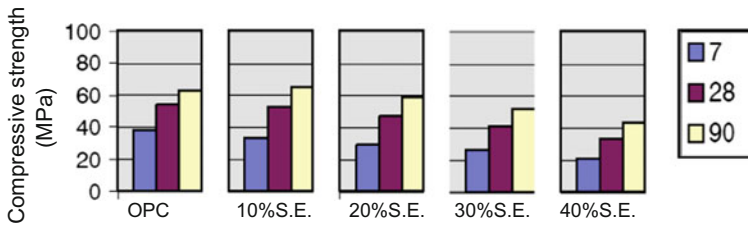


Fig. 6.11 Influence of Skydrian earth (S.E.) on the development of compressive strength of cement mortars. Compressive strength values were measured till the age of 90 days (Sideris and Sideris 1997)

Mortars produced with 10% Skydrian earth had similar compressive strength with the reference OPC mortars at the age of 28 days. At later ages mixtures produced with 20 and 30% M.E and 10 and 20% S.E gained higher strength values than the reference mortar. The better strength development of Skydrian earth mortars at young ages was attributed to the increased fineness of the pozzolan as measured with the retaining in the 45 μ m sieve.

Erdem et al. (2007) studied two different Turkish perlites by intergrinding them with clinker for the production of blended cements in 20 and 30% substitution rates. The blended cements showed slightly lower compressive strengths but significantly lower energy consumption and CO₂ emissions. Another study (Erdogan and Saglik 2013) focused on perlite-cement blends up to 75% substitution and on the use of inorganic activators for managing the strength decrease. Cobirzan et al. (2015) studied by optical methods cement-perlite blends with 25% cement substitution which also demonstrated compressive strength lower than the baseline (100% cement).

A study of untreated Ca-bentonite of Pakistani origin with up to 21% cement substitution demonstrated compressive strength results at 3 days of testing lower than the control mix while at 56 days of testing, the bentonite mixes showed higher strength than the control mix (Shazim et al. 2012).

The effects of diatomite as additive on the properties of concrete have also been studied intensively in recent years (Stamatakis et al. 2003). Some authors (Degirmenci and Yilmaz 2009; Aydin and Gul 2007) have shown that the use of diatomite in place of cement for production of cement mortar and concrete did not improve the mechanical properties. Other authors (Paiva et al. 2016) showed an increase at compressive strength of the mortar with addition of 10% diatomite rocks in cement.

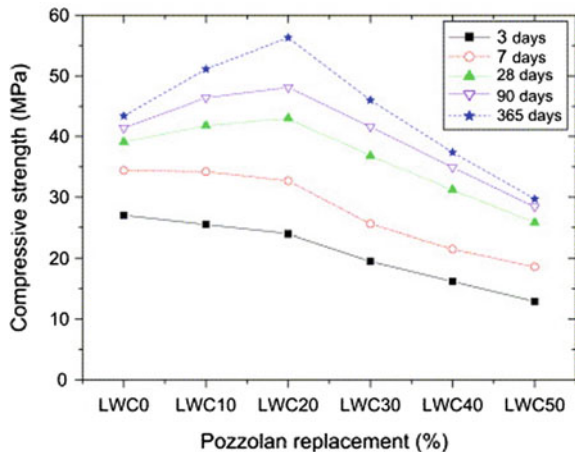
Davraz and Gunduz (2005) studied the behavior of natural amorphous silica from Turkey as an admixture in concrete. The amorphous silica was added as 5, 10 and 15% admixture and blended with cement as a partial replacement at 5, 10 and 15% levels, respectively. The strength of all concrete mixtures is higher than control mixture, with 10% addition giving the best results.

Pozzolan obtained from natural deposits in North-West Algeria (Bouhamidi Source situated at about 100 km from Oran) resulted in concrete strength increment when replacing cement. This research (Senhadji et al. 2012) showed that the concrete incorporating 20% pozzolan had higher compressive, splitting and flexural strengths than the control concrete at all ages after 7 days up to 365 days. The concrete incorporating 30% pozzolan develops higher strengths than the control concrete at 90 days and over. While concrete mixed with 40 and 50% cement replacement by pozzolan gives lower compressive strengths at all ages up to 365 days.

6.3.5.2 Lithification

Once the natural pozzolan-cement mixture is hydrated, the pozzolanic reaction begins immediately and continues for many years. Eventually, the mass will reach complete lithification. The compressive strength as well as the flexural strength will continue to increase for a long time, as it is shown in Fig. 6.12 (Moulia and

Fig. 6.12 Effect of pozzolan content on the compressive strength of lightweight concrete (LWC) (Moulia and Khelafib 2008)



Khelifib 2008). This unique characteristic is one of the main reasons many great ancient structures have lasted for over two thousand years.

6.3.5.3 Abrasion Resistance

Natural pozzolan increases the long term compressive strength of concrete and makes the concrete matrix stronger and denser. It also prevents the formation of pulpy, crispy, or water-soluble materials created by chemical attack. Therefore, it helps the concrete to durably resist abrasion.

6.3.6 Chemical Durability

6.3.6.1 Carbonation

Carbonation of cement/concrete is a multi-factor phenomenon, which despite being abundantly researched, is not yet entirely explained.

According to several literature papers (Bier 1987; Papadakis et al. 1992; Ho and Lewis 1983) concrete with pozzolans are usually less resistant to carbonation. This lower resistance is usually explained by the lower portlandite content in these concretes. In the previous years, Bier (1987) has shown that the depth of carbonation increased as the portlandite content in the cementitious material decreased. However, the portlandite amount is not the only parameter that controls the carbonation mechanisms, permeability and diffusivity are also important parameters to be considered. In concrete with pozzolans, these two parameters have usually low values compared to concrete without pozzolans. Consequently, contradictory results can be found in the literature. Adding natural pozzolans to Portland cement can actually enhance its resistance against carbonation (Ramasamy and Tikalsky 2012).

Kaid et al. (2009) have studied the resistance to carbonation of concrete with and without Algerian natural pozzolans using an accelerated carbonation test. They show that the kinetics of carbonation of the two concretes tested after 60 days of aging are almost equivalent. Bilim (2011) has studied the carbonation of mortars prepared by replacing the Portland cement with 0, 5, 10, 15, 20 and 30% clinoptilolite by weight. He shows that the carbonation depth of mortars containing clinoptilolite was higher than that of the control mortar at early ages. However, this negative effect disappeared at longer term. He concludes on the fact that the resistance to carbonation of the mortar made with clinoptilolite increased with increasing the clinoptilolite replacement level, the best results are obtained with mortar containing 30% clinoptilolite.

Sideris et al. (2006) produced 15 different cement mortars using natural pozzolans—Milos Earth (ME) and Skydrian Earth (SkE)—and high calcium lignite fly ashes—HCFA—from two different geographic locations in Greece—Megalopolis

Table 6.3 Carbonation depth of plain and blended cements

| Mix. no. | Composition | Carbonation depth (mm) | | |
|----------|---------------------------------------|------------------------|-----------|-----------|
| | | 6 months | 12 months | 24 months |
| 1 | Portland cement (ASTM Type I) | 1.0 | 3.0 | 4.5 |
| 2 | II—B-M 32.5 N (commerc. Blended cem.) | 2.0 | 4.0 | 5.5 |
| 3 | 10% ME | 1.5 | 3.0 | 5.0 |
| 4 | 20% ME | 2.2 | 4.0 | 6.5 |
| 5 | 30% ME | 2.6 | 5.5 | 8.5 |
| 6 | 10% SkE | 1.5 | 4.0 | 4.7 |
| 7 | 20% SkE | 1.7 | 4.0 | 6.6 |
| 8 | 30% SkE | 3.5 | 7.5 | 9.0 |
| 9 | 10% MFA | 1.6 | 3.5 | 5.5 |
| 10 | 20% MFA | 2.0 | 4.0 | 6.2 |
| 11 | 30% MFA | 3.0 | 5.0 | 8.3 |
| 12 | 30% PtFA | 2.5 | 4.0 | 6.2 |
| 13 | 40% PtFA | 2.7 | 5.0 | 9.0 |
| 14 | 50% PtFA | 4.0 | 6.0 | 9.5 |
| 15 | 60% PtFA | 4.8 | 8.0 | 13.5 |

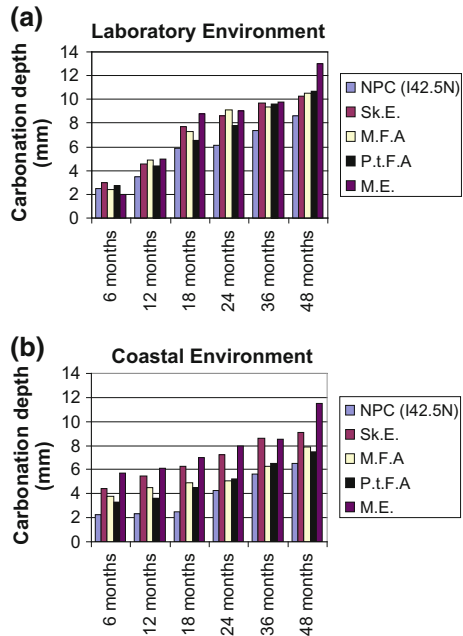
Data taken from Sideris et al. (2006)

Fly Ash (MFA) and Ptolemaida Fly Ash (PtFA)—in replacement levels up to 60%. Different w/cm ratios were used in each case in order to keep the mixture's fluidity constant. All specimens were water cured for 28 days. After this age they were exposed to indoor conditions. Carbonation measurements were taken for a time period up to 24 months. The researchers reported that carbonation depth of all mixtures produced with natural pozzolans was the greatest among all mixtures tested (Table 6.3). This finding was also reported by Papadakis et al. (1992) who reported that the lowest $\text{Ca}(\text{OH})_2$ concentrations were measured on mixtures produced with natural pozzolans.

Sideris and Savva (2001) produced five different concrete mixtures using two natural pozzolans and two lignite fly ashes. All SCMs replaced Portland cement at a constant level of 20%. Concretes were produced with a w/cm ratio of 0.65 and the content of cementitious materials was 350 kg/m^3 . Concrete specimens were fog cured for 28 days. After this age specimens were exposed in two different environments: specimens of the first series were exposed to a coastal environment, 150 m away from the beach and left unprotected to the rain. Specimens of the second series were exposed in indoor conditions. Carbonation measurements were performed at different ages up to 4 years (Fig. 6.13).

Carbonation depth of blended cement mixtures was in both curing environments greater than the one of normal Portland cement mixture. Among all blended cement mixtures tested, specimens produced with natural pozzolans performed the greatest carbonation depth, mainly due to the lower $\text{Ca}(\text{OH})_2$ of these mixtures.

Fig. 6.13 Carbonation depth of concrete mixtures produced with ordinary Portland cement, natural pozzolans (SkE and ME) and lignite fly ashes (PtFA and MFA) in laboratory (a) and coastal (b) environments (Sideris and Savva 2001)



6.3.6.2 Resistance to Chloride Attack

Effects of pozzolanic reactions of natural pozzolans are far more significant in improving concrete durability than in affecting compressive strength. Concrete deterioration caused by the penetration of chloride occurs quickly when chloride ions react with calcium hydroxide. The expansion of hydrated calcium oxy-chloride enlarges the microcracks and increases the permeability that causes quicker chloride penetration and more damage from freezing and thawing action.

One of the most commonly reported effects of natural pozzolans on cementitious materials is the reduction of the chloride ingress. On the one hand, there is the dual action of pore refinement and OH^- reduction due to the pozzolanic activity. As the consumption of CH increases, the content of OH^- decreases and the chloride penetration is slowed down. Moreover, the chloride binding capacity is enhanced in pozzolans with high alumina contents. Several authors have consistently found reductions in the chloride permeability of cementitious materials made with different levels of replacement of volcanic ash (Hossain and Lachemi 2004); natural zeolite (Valipour et al. 2013) volcanic ash (Siad et al. 2014) and clinoptilolite type pozzolans from different origins: USA (Jana 2007), and Iran (Ahmadi and Shekarchi 2010; Najimi et al. 2012).

ASTM C1202 (2017) specifies concrete as highly permeable if the charge that passes through it is more than 4000 Coulombs. According to a recent review on the influence of VA addition in concrete, a significant decrease in porosity and consequently in the measured charge was observed with pozzolanic VA addition as

compared with the control OPC concrete. This influence is even more evident when the corresponding specimens are subjected to elevated temperatures at 600 and 800 °C (Siddique 2012).

The 30% natural pozzolan added into cement can react with almost all the free calcium hydroxide and form a less permeable paste. Thus, the penetration of chloride can be minimized and the few penetrated chloride ions cannot find free calcium hydroxide with which to react even at early age. This early age effect, however, is more pronounced in non-air-entrained mixtures than in air-entrained ones, as it is shown in Fig. 6.14 (Jana 2007).

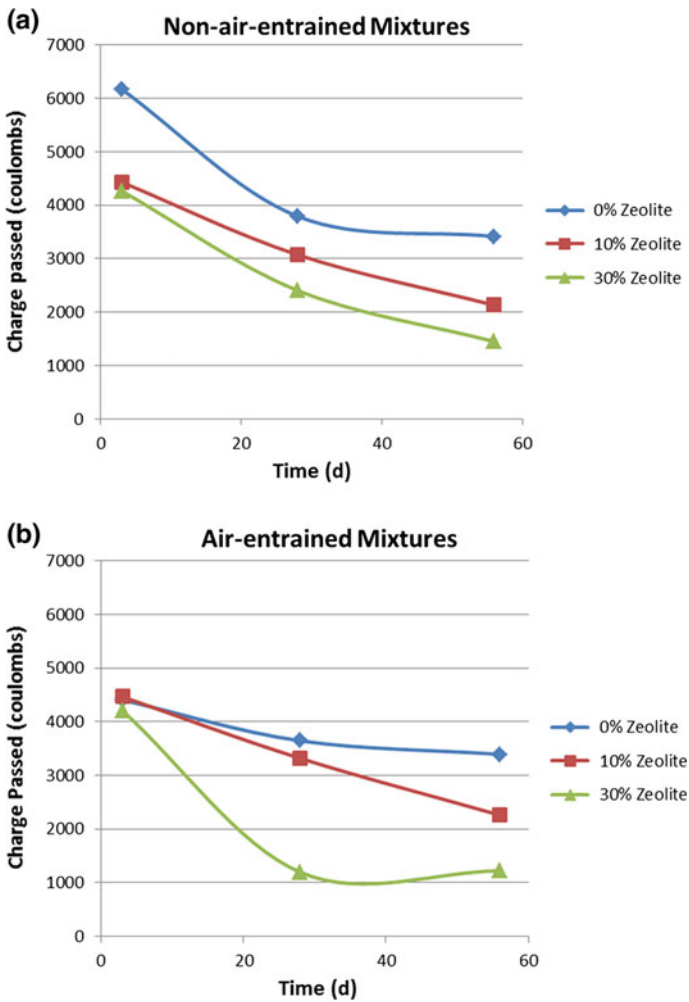


Fig. 6.14 Rapid chloride permeability of various zeolite in non-air-entrained **a** and air-entrained **b** concrete mixtures (Jana 2007)

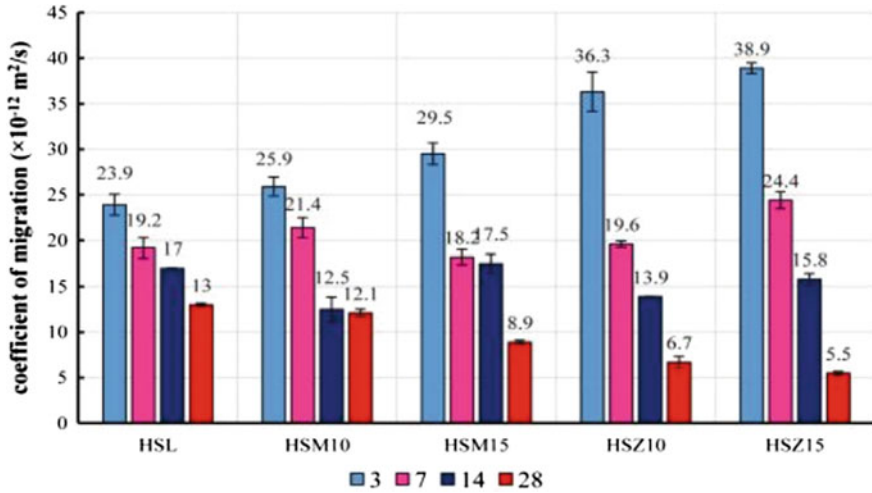


Fig. 6.15 Non-steady-state migration coefficient of chloride ion in different SCC containing metakaolin and zeolite pozzolans

Samimi et al. (2016) have studied the durability properties of SCCs containing metakaolin and zeolite. They found that at the early ages of 3 and 7 days, due to the low pozzolanic activity of the zeolite pozzolan, no improvement in the trend of reducing the chloride migration coefficient occurred. However, at longer ages of 14 and 28 days, natural zeolite at the two different percentages (10 and 15% of OPC replacement) reduced significantly the chloride migration coefficient compared to the control mix (Fig. 6.15).

In addition to the above, a significant decrease of rapid chloride permeability has been noticed with the gradual replacement of cement by the natural pozzolan micrasil (Imerys Minerals Arabia L.L.C. 2015) in standard concrete mixes (Fig. 6.16). Particularly the measured permeability from the ASTM C1202 was reduced by 88% with a 20% cement replacement by micrasil at the age of 28 days, while by just replacing 5% of cement the achieved reduction was 76%.

6.3.6.3 Resistance to Sulfate Attack

There are three chemical reactions involved in sulfate attack on concrete:

- Combination of free calcium hydroxide and sulfate to form gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).
- Combination of gypsum and calcium aluminate hydrate (C–A–H) to form ettringite ($\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$).
- Combination of gypsum and calcium carbonate with C–S–H to form thaumasite ($\text{CaSiO}_3 \cdot \text{CaCO}_3 \cdot \text{CaSO}_4 \cdot 15\text{H}_2\text{O}$).

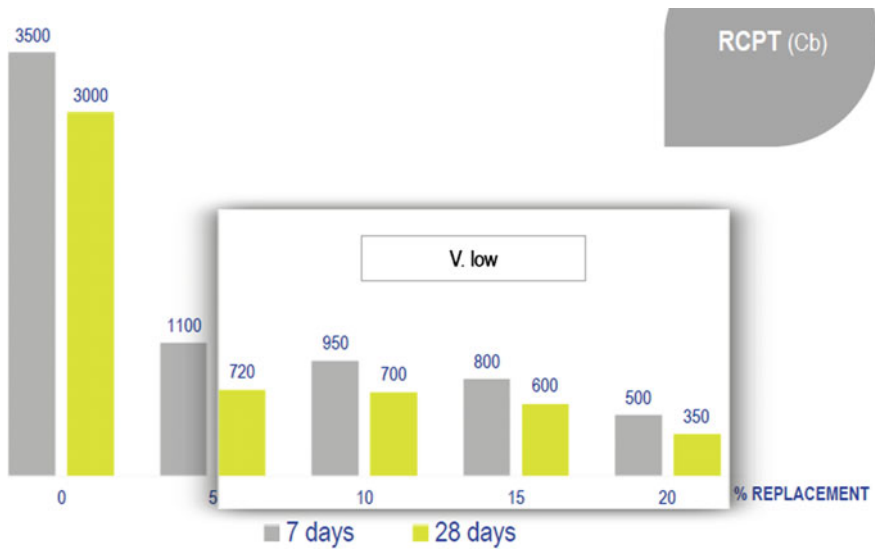


Fig. 6.16 Rapid chloride permeability testing results of concrete mixes with partial replacement of cement by micrasil (Imerys Minerals Arabia L.L.C. 2015)

These volumetric changes cause expansion and internal stresses, which ultimately weaken and destroy the paste bonds, deteriorating the concrete. Thaumascite formation in particular is accompanied by a very severe damaging effect which is able to transform hardened concrete into a pulpy mass.

SCMs induce three phenomena that improve sulfate resistance by:

- consuming the free lime and making it unavailable to react with sulfate;
- reducing permeability by refining the pore size distribution prevents sulfate penetration into the concrete; and
- replacing the cement and reducing the amount of reactive aluminates available.

Karakurt and Topçu (2011) investigated the influence of blended cements produced with different types of pozzolans on sulfate resistance of concrete. Natural zeolite (Z) (clinoptilolite tuff), fly ash (FA), and ground granulated blast furnace slag (GBFS) were used. As observed from the test results, Z-, FA-, and GBFS-blended cements (ZBC, FBC and SBC respectively) protect the composite material against sulfate attack. Ettringite formation in the blended cement specimens is reduced compared to the reference ordinary Portland cement (Fig. 6.17). Under the applied test conditions ettringite formation was found to be the main cause of sulfate deterioration.

Hossain and Lachemi (2006) compared the performance of volcanic ash (VA) and finely ground volcanic pumice (VP) based ASTM Type I and Type V (low C_3A) blended cement concrete mixtures. 20% VA or VP were used in blended cement for preparing concrete mixtures with two (0.35 and 0.45) water-to-binder

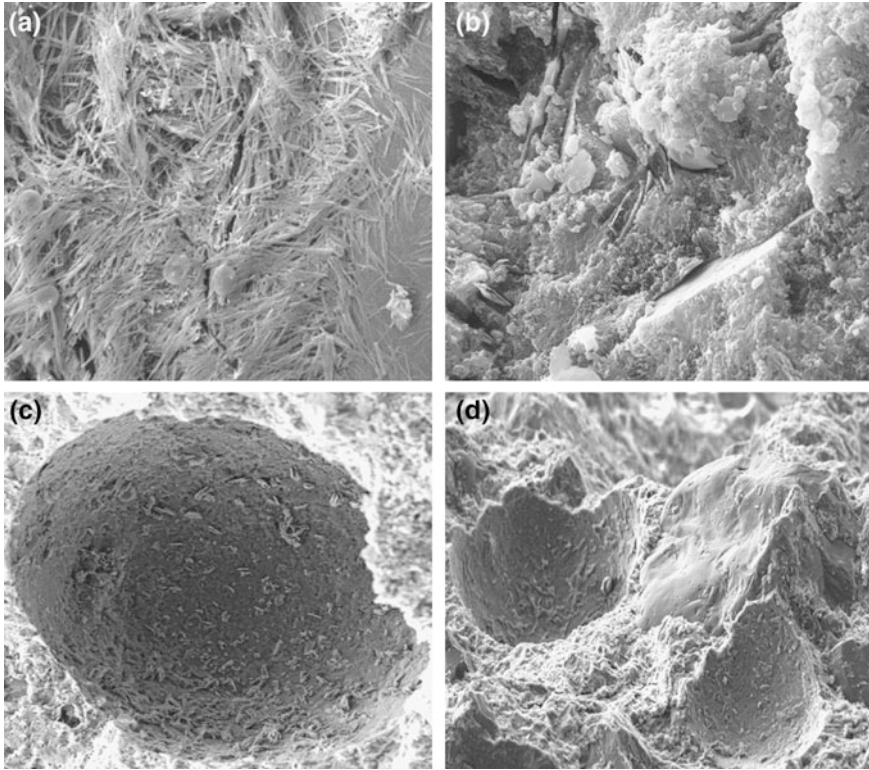


Fig. 6.17 Microstructure of test specimens. **a** CEM I 42.5; **b** ZBC-30; **c** FBC-30; **d** SBC-30 (Karakurt and Topçu 2011)

ratios. Concrete mixtures were immersed in magnesium–sodium sulfate solution for a period up to 48 months. They concluded that type I/V VA/VP based blended cement concrete specimens showed higher and faster rate of deterioration than those of Type I/V plain cement concrete specimens. The higher deterioration in Type I and Type V VA/VP based blended cement concretes in sulfate environment compared to Type I and Type V plain Portland cement concretes can be attributed to the presence of Mg^{2+} cations associated with $MgSO_4$. The consumption of portlandite ($Ca(OH)_2$) by the pozzolanic reaction in VA and VP blended cements causes Mg^{2+} cations to react directly with the calcium silicate hydrate (C–S–H) gel converting it to cohesionless, porous, reticulated magnesium silicate hydrate (M–S–H) gel.

Sideris et al. (2006) investigated the sulfate resistance of 15 different cement mortars prepared using natural pozzolans and two high calcium lignite fly ashes—MFA and PFA—in replacement levels up to 60%. Different w/cm ratios were used in each case in order to keep the mixture’s fluidity constant. The SO_3 content of the pozzolanic material was taken into consideration and the added gypsum was properly adjusted in order to keep the total SO_3 content of the binder (clinker + pozzolan)

equal to 3.5%. This was not achieved for the mixtures with a high PFA content. The high SO_3 of PFA increased the total available amount of SO_3 of the mix (clinker + gypsum), although no gypsum was added. The sulfate resistance of binders was evaluated using expansion measurements of mortar prisms immersed in a 5% Na_2SO_4 solution, according to ASTM C1012, up to the age of two years.

They concluded that the sulfate resistance of blended cements was better than the one of CEM I 42.5 N. All natural pozzolans blended mixtures performed better than the reference I 42.5 N mixture regarding the deterioration age and the final expansion of the specimens. They also observed that sulfate resistance of the mixtures increased as the replacement of cement by the natural pozzolan also increased (Table 6.4). This phenomenon was attributed to the so called ‘dilution effect’ (decrease of the C_3A content of the binder and consumption of $\text{Ca}(\text{OH})_2$ when pozzolans replace a portion of Portland cement) (Tikalsky and Carrasquillo 1992).

Table 6.4 Compressive and flexural strength loss (%), final expansion (%), deterioration age and first crack observed age (months) for all mixtures

| Mixture | Compressive strength loss (%) | Flexural strength loss (%) | One year expansion (%) | Final expansion (%) | Deterioration age (months) | First crack (months) |
|--------------|-------------------------------|----------------------------|------------------------|---------------------|----------------------------|----------------------|
| CEM I 42.5 N | 30 | 67.5 | 1.10 | 1.10 | 6–8 | 6 |
| CEM II32.5 N | 15.4 | –3.5* | 0.026 | 0.035 | Not deteriorated | 16 |
| 10% ME | 26.3 | 79.7 | 0.458 | 0.79 | 16–20 | 8 |
| 20% ME | 31.6 | 84.6 | 0.040 | 0.546 | 22–24 | 12 |
| 30% ME | 0.4 | 44.3 | 0.044 | 0.048 | Not deteriorated | 20 |
| 10% SkE | 13 | 69.3 | 0.650 | 0.650 | 6–8 | No cracks |
| 20% SkE | 17 | 41.7 | 0.042 | 0.220 | 20–22 | 8 |
| 30% SkE | 21 | –216* | 0.036 | 0.824 | 22–24 | 12 |
| 10% MFA | (–) | (–) | 0.544 | 0.544 | 3–4 | No cracks |
| 20% MFA | (–) | (–) | 0.428 | 0.428 | 3–4 | 2 |
| 30% MFA | 30 | (–) | 0.408 | 0.408 | 4–6 | No cracks |
| 30% PFA | 19 | 17 | 0.033 | 0.049 | 12–16 | No cracks |
| 40% PFA | 15.3 | 14.7 | 0.033 | 0.055 | 16–20 | 16 |
| 50% PFA | –0.8* | –153* | 0.016 | 0.022 | Not deteriorated | No cracks |
| 60% PFA | –8* | –179* | 0.012 | 0.016 | Not deteriorated | No cracks |

Data taken from (Sideris et al. 2006). Sulfate resistance test according to ASTM C1012

–: Totally deteriorated, not measured

*: Strength increased

These results are in a good agreement with those of Siad et al. (2015) on SCC with natural pozzolan. In this study, after 4 years of exposure in magnesium sulfate solution, SCCs with natural pozzolan as well as SCCs with fly ash samples have shown severely deteriorated surfaces, while less deterioration was observed on ordinary concrete mixture. However, the same mixtures (with natural pozzolan and fly ash) have shown a better resistance to sodium sulfate solution. The authors concluded on the beneficial effect of the incorporation of natural pozzolan on the resistance of the SCC if sodium sulfate is the medium (Siad et al. 2013).

Jamshidi et al. (2009) investigated the physical/mechanical properties of concretes made by blended cement containing tuff as natural pozzolan. The microstructure of mortars under sulfate attack is studied using SEM analysis and reaction products are characterized using EDS analysis. The results suggest that, contrary to other studies results, mortars containing this pozzolanic tuff show more expansion and unsatisfactory performance in sulfate solution.

6.3.6.4 Alkali-Silica Reaction (ASR)

Because natural pozzolans usually have a high surface area, it can react quickly with calcium hydroxide and can trap the alkali inside the cement paste by formation of alkali-enriched C–S–H phases. Thus, it helps to form a denser paste and concrete less prone to alkali aggregate reaction.

Expansion due to alkali-aggregate reaction can be a serious problem in concrete. This undesirable expansion causes micro cracks between the aggregate and hardened cement paste. The ASTM C 618 requires that, for effectiveness against the alkali-silica reaction, the expansion (the ratio between the length change of the test mix and that of the control mix) at day 14 should have a maximum value of 100%.

A general review on the influence of the supplementary cementing materials (Thomas 2011) shows that they are effective means for controlling expansion due to alkali-silica reaction and most, if not all, SCMs can be used in this role provided they are used at a high enough level of replacement. The level of SCM required generally increases with the following parameters:

- The alkali available from the Portland cement increases (if significant alkalis are available from the aggregates—e.g. feldspars and greywackes—or from external sources, this will likely also increase the level of SCM required)
- The alkali from the SCM increases
- The CaO/SiO₂ of the SCM increases
- The reactivity of the aggregate increases

SCMs control ASR mainly by reducing the amount of alkalis available for reaction with the aggregate and the ability of SCMs to bind alkalis appears to be strongly related to the CaO/SiO₂ ratio of the SCM. SCMs that are low in alkali and calcium, and high in silica tend to be the most effective in reducing pore solution alkalinity and these materials can be used at relatively low replacement rates to eliminate

damaging expansion. SCMs with increased amounts of alkali and calcium have to be used at higher replacement levels. There is evidence that the alumina may play an important role in determining the alkali-binding capacity of SCMs, and can also inhibit the dissolution of silicates.

A number of research studies have confirmed that natural zeolite effectively prevents the deleterious expansion of concrete due to alkali silica reaction (Ahmadi and Shekarchi 2010). The mechanism by which natural zeolite inhibits alkali silica reaction is by decreasing the alkaline ions (Na^+ , K^+) concentration in the pore solution through pozzolanic reaction of natural zeolite.

Experiments show that only substituting 25% PozZ natural pozzolan (a commercial grade of pumice) for OPC can reduce alkali-silica expansion by up to 70%. There are three reasons for this high ASR reduction:

- (A) The alkalies in PozZ are fixed in the glass phase and do not contribute to the ASR.
- (B) During cement hydration, PozZ reacts with the freed calcium hydroxide and maintains the pH level in the paste.
- (C) By binding the alkalies inside the paste in the hydration products the concrete is rendered less prone to alkali aggregate reaction (Ramasamy and Tikalsky 2012).

Research on the ASR mechanism showed that the finer the admixture is the better for the mitigation. Admixtures with low CaO content act as ASR inhibitors, whereas those with more than 10% CaO content act as ASR promoters (Ichikawa 2009). Foroughi et al. (2012) determined that 5% of the total alkalis in the natural pozzolan from Iranian mines of volcanic origin contributed to the expansions of concrete specimens. Furthermore, they concluded that it is inappropriate to use a singular value to estimate the contribution of the alkalis of the pozzolan to the rate of ASR. It is dependent upon the aggregate nature and levels of replacements. Specifications for using pozzolan as an ASR mitigation alternative should take into consideration that highly reactive aggregates require higher amounts of pozzolan in the mixture. As the calcium content of the pozzolan increases, the amounts of the pozzolan used in the concrete should also be increased (Foroughi et al. 2012).

Karakurt and Topçu (2011) investigated the influence of blended cements produced with different types of pozzolans on alkali-silica reaction (ASR) of concrete. For this reason, natural zeolite (clinoptilolite), fly ash (FA), and ground granulated blast furnace slag (GBFS) were used in different types of blended cement production (Karakurt and Topçu 2011). The ASR performance of blended cements is better than ordinary Portland cement. Zeolite (Z-series), FA (F-series), and GBFS (S-series) reduce the ASR gel formation in the microstructure of the composite. As it is shown in Fig. 6.18, GBFS showed best performance against ASR tests, despite the fact that it is usually richer in CaO than zeolite and fly ash.

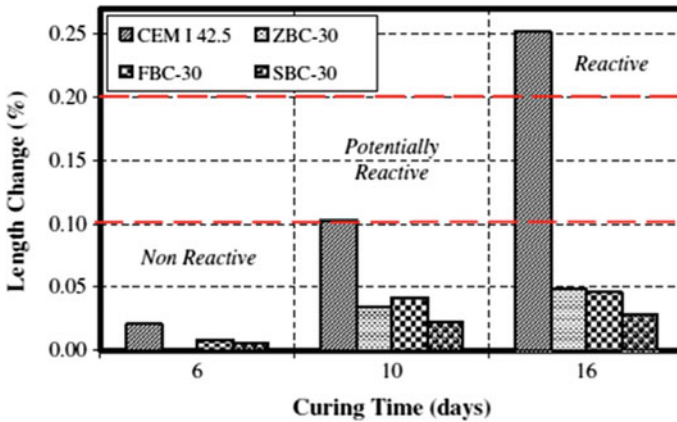


Fig. 6.18 The ASR length change of mortar bar specimens (Karakurt and Topçu 2011)

6.3.7 Protection of Steel Reinforcement from Corrosion

Investigation results (Hossain 2005a, b; Fajardo et al. 2009) show that the addition of natural pozzolans to concrete mixes appears to improve the long-term corrosion resistance of concrete. Their role is related to both the initiation and the progression of corrosion. They are added as fine particles and upon hydration of cement, they increase the tortuosity of the cement paste. This is accompanied by a decrease of pore size and a smaller effective diffusivity for either chloride or other species. This improves the long-term corrosion resistance of concrete structures. The pozzolanic reaction with calcium hydroxide produces a less permeable concrete and thus mitigates the ingress of chloride ions. This takes place at a slower rate.

The use of natural pozzolan from Puebla State of Mexico as a partial 10–20% substitution of Portland cements (Normal Portland Cement NPC and Commercial grade Portland Cement—CPC) had a beneficial effect on the corrosion behavior of steel as seen in Fig. 6.19 (Fajardo et al. 2009). It resulted into a significantly higher mortar resistivity. A 20% replacement of cement by pozzolan led to a significant increase of the induction time and reduces the corrosion rate by one order of magnitude, improved protection for the reinforcement steel as compared to normal and composite Portland cement as it can also be visually seen in Fig. 6.20. Therefore, the use of natural pozzolans influences both the initiation and propagation time of the progress in steel corrosion. The addition of finely ground natural pozzolan and its subsequent reaction with cement hydrates provides an effective pore filling effect.

The preceding discussions make it very clear that concrete made from 20% natural pozzolan/80% Portland cement mixture can better protect steel reinforcement because of a much lower permeability of the concrete.

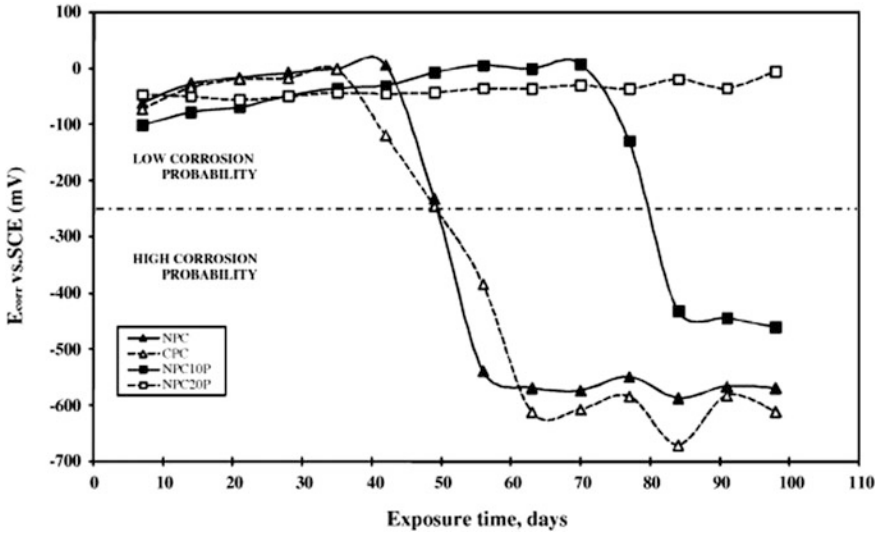
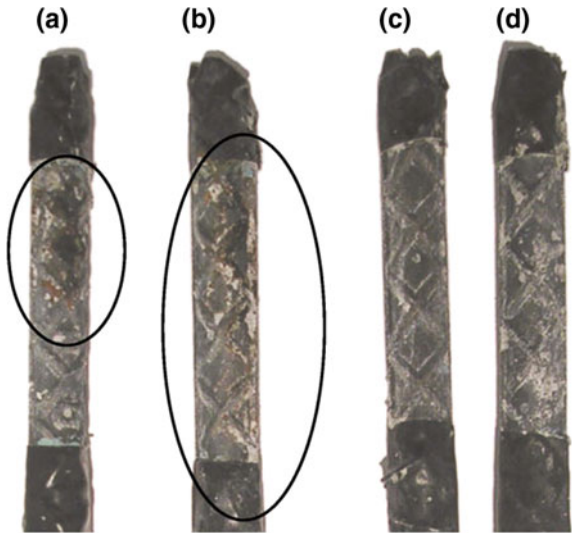


Fig. 6.19 Evolution of the corrosion potential, E_{corr} , of specimens versus time—20% pozzolan substituting cement leads to lower corrosion probability through time (until 100 days) (Fajardo et al. 2009)

Fig. 6.20 Surface state of the steel bars after 77 days of exposure for: **a** NPC, **b** CPC, **c** NPC10P and **d** NPC20P



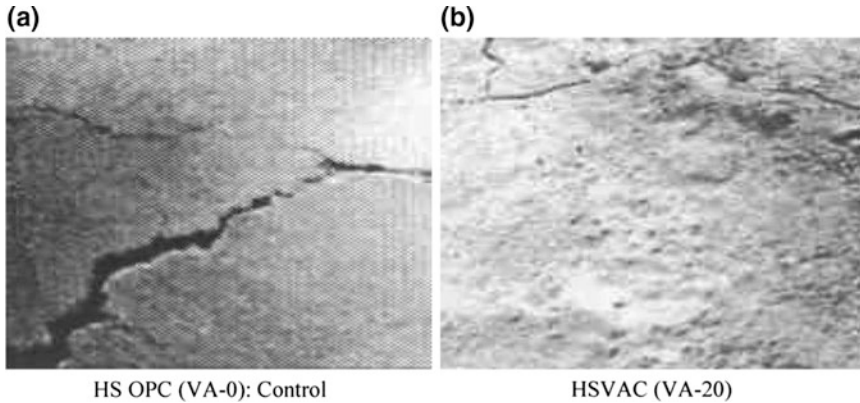


Fig. 6.21 Crack patterns at 800 °C for control mix (a) and mix with 20% VA (b) (Hossain 2006)

6.3.8 Performance at Elevated Temperatures

Although concrete is generally believed to be an excellent fireproofing material, many recent studies have shown extensive damage or even catastrophic failure at high temperatures. Investigation (at macro- and micro-levels) on the strength and durability characteristics of high strength volcanic ash concrete (HSVAC) subjected to elevated temperature showed that HSVACs were found to be able to retain their strength and durability properties better at elevated temperatures. The surface cracks started to appear at around 300 °C and continued to grow till the final rise in temperature up to 800 °C. The crack widths reported in Fig. 6.21 show typical crack patterns observed in different concretes at 800 °C (Hossain 2006).

6.4 Specifications

The specifications that govern the natural pozzolans, raw or calcined are ASTM C 618 “Standard specification for coal fly ash and raw or calcined natural pozzolan for use as a mineral admixture in concrete” (Table 6.5) based on the following classification (only specifications considering natural pozzolans are mentioned): Class N: Raw or calcined natural pozzolans such as some diatomaceous earths, opaline chert and shale, stuffs, volcanic ashes and pumice are included in this category. Calcined kaolin clay and laterite shale also fall in this category of pozzolans.

The minimum amount of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ for Class N pozzolan is 70%. There are also chemical requirements for maximum sulfate, maximum moisture content, and maximum loss on ignition. There is an optional available alkali limit. Mandatory physical requirements include maximum percentage of material retained when wet sieved on a 45 μm (No. 325) sieve, 7- and 28-day minimum percentage

Table 6.5 Standard specifications of class N pozzolans according to ASTM C618

| Test/property | Requirement |
|---|-------------|
| $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$, % | ≥ 70 |
| SO_3 , % | ≤ 4.0 |
| Moisture content, % | ≤ 3.0 |
| Loss on ignition, % | ≤ 5.0 |
| Amt. retained when wet-sieved on 45 μm (No. 325) sieve, % | ≤ 34 |
| Strength activity index, 7-day, % of control | ≥ 75 |
| Strength activity index, 28-day, % of control | ≥ 75 |
| Water requirement, % of control | ≤ 115 |
| Soundness: autoclave expansion or contraction, % | ≤ 0.8 |
| Density, variation from average, % | ≤ 5 |
| Percent retained on 45- μm (No. 325) sieve, variation (percentage points from average) | ≤ 5 |
| Available alkalis, % | ≤ 1.5 |

of control strength (strength activity index), maximum water requirement as a percentage of control, maximum autoclave expansion or contraction (soundness), and uniformity. There are some optional physical requirements, including a maximum increase in drying shrinkage, maximum difference of air entraining agent (AEA) required from a control, effectiveness in controlling ASR, and effectiveness in contributing to sulfate resistance.

Recently the standard ASTM C1697—10 “Standard Specification for Blended Supplementary Cementitious Materials” has been finalized. This specification covers blended supplementary cementitious materials that result from the blending or intergrinding of two or three ASTM compliant supplementary cementitious materials for use in concrete or mortar where hydraulic or pozzolanic action, or both, is desired. The supplementary cementitious materials include slag cement conforming to Specification C989, natural pozzolans and coal fly ash conforming to Specification C618 and silica fume conforming to Specification C1240.

6.5 Conclusions

Natural pozzolans have been used in construction since ancient times in pozzolan-lime concrete providing durable structures that survived over 2000 years. There are many minerals that demonstrate pozzolanic properties such as volcanic ashes and pumices, scorias, tuffs, diatomite, perlite and other. They can be found in several parts of the world with volcanic activity such as Turkey, Greece, Iran, China, Algeria, Middle East, South America and others.

Their use is now extended to modern cement and concrete as supplementary cementitious materials due to the many advantages they offer apart from the obvious environmental benefit of supplementing clinker or cement which require a lot of energy and emit high quantities of CO₂ during their production.

They are responsible for higher compressive strength in later ages of cement hydration which continues to increase for a long period of time, they provide self-healing properties to the concrete and overall significantly improved durability which is the main reason for their use. In particular they demonstrate lower chloride migration and improved sulfate resistance while in most cases their addition leads to mitigation of ASR. Moreover, they reduce bleeding and segregation considerably, lower the heat of hydration which is beneficial in large concrete structures and eliminate micro-cracking. However, their use can lead to reduced workability (especially with zeolites and diatomites) and higher water and superplasticizer demands, and more evident shrinkage.

It is important to acknowledge that each different natural pozzolan has different effects on cement and concrete properties and can be used in different ratios in a concrete mix. In addition, several studies have reported the beneficial effect of using natural pozzolans in combination with several industrial pozzolans (i.e. silica fume, fly ash and slag). Comparative effects of different natural pozzolans to several important properties of concrete are given in Table 6.6.

Overall the benefits of using pozzolans in concrete are well established in most parts of the world leading to extensive research and application in construction worldwide.

Table 6.6 Natural pozzolans effect on concrete properties

| Type of pozzolan | Water demand | Early compressive strength | Late compressive strength | Chloride resistance | Sulfate resistance |
|----------------------------------|--------------|----------------------------|---------------------------|---------------------|--------------------|
| Zeolite | ↑ | ↓ | ↑ | ↑ | ↑ |
| Tuff | → | ↓ | ↑ | | ↑↓ |
| Volcanic Ash/ Volcanic Pumice | ↑↓ | ↓ | ← | ↑ | ↑↓ |
| Diatomite | ↑ | ↑ | ↑ | | |
| Perlite | → | ↓ | ← | | |
| Scoria | | ↑ | ↑ | | |
| Bentonite | | ↓ | ↑ | | |
| Siliceous sinters | ↑ | | ↑ | | |

↑: increase

↓: decrease

←: slight decrease

→: slight increase

↑↓: both effects have been reported

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Chapter 7

Alternative Supplementary Cementitious Materials

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Abstract The use of supplementary cementitious materials (SCM) has become a major trend in concrete technology with effective utilization of industrial by-products (IBP) such as fly ash, ground granulated blast furnace slag and silica fume. Many types of industrial by-products (IBP) such as fly ash, silica fume, rice husk ash and waste glass are becoming the predominant source of mineral components with pozzolanic properties required to improve the performance of portland cement based materials. The availability of decent quality SCM has almost reached its limits and cannot offset the need for higher volumes of concrete required by developing markets. The use of alternative supplementary cementitious materials, including off-spec products and less-investigated by-products can be a viable alternative. However, there are many obstacles and limitations which hinder the utilization of such products. These are related to the lack of long-term results related

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to strength and durability, the potential variability in terms of composition and the presence of undesirable substances including heavy metals. These limitations dictate the need for higher production control and product consistency. This report presents the state of the art experience with utilization of modern technologies and potential SCM such as steel slag, pulverized bottom ash, sugarcane bagasse ash, waste glass and low-grade silica fume. Certainly, the current economic conditions make recycling feasible for only a limited number of by-products. Waste materials can be used only when they can be collected, processed, and reused at a cost the same or less than natural raw materials. To increase the rates of recycling, cement and concrete manufacturers need a uniform supply of quality waste; this would require better sorting and also the development of waste identification technology. On the other hand, it is also evident that innovative technologies capable of tolerating multiple contaminants are needed to boost the recycling of industrial by-products and waste beyond the current limits.

Keywords Cement · Concrete · By-product · Steel slag · Bottom ash
Sugarcane bagasse ash · Waste glass · Silica fume · Waste · Recycling
Supplementary cementitious materials

7.1 Introduction

In the past 15 years, the world production of cement has greatly increased. This trend is the most significant factor affecting technological development and update of manufacturing facilities in the cement industry. In 2015, the demand for cement was at the level of 4.2 billion metric tons. Existing technology for the production of cement clinker is ecologically stressing as it requires the consumption of much energy and natural resources and also results in the emission of pollutants. Indeed, cement production is responsible for about 5% of the total CO₂ emitted and associated with global warming. Since the 2008 G8 summit, the International Energy Agency started to work on the identification of specific industries in order to achieve the sustainable development benchmarks. The cement industry was identified as one having a high improvement potential. Assuming no or little alternative to portland cement clinker chemistry (Ramachandran et al. 1981; Mehta and Polivka 1976; Damtoft et al. 2008; Scrivener and Kirkpatrick 2008) and established limits to utilization of conventional supplementary cementitious materials (SCM), there is only one alternative for reducing the carbon footprint, which is to increase the diversity and utilization rates of SCM in blended cements with new natural materials, industrial by-products, secondary and waste materials. The utilization of industrial by-products and waste (IBPW) as binder components and aggregates comprises a valuable segment of cement and concrete technology. Traditionally, all those mineral components were used in blended cement or concrete individually (Damtoft et al. 2008; Scrivener and Kirkpatrick 2008; Roads and Bridges 1992; Royak and Royak 1983). Nowadays, two or more of these components can be

Table 7.1 Classification and production of waste materials in the USA (after Miller and Collins 1976)

| Group I | Group II | Group III |
|--------------------------------------|-----------------------------------|-------------------------------|
| | ← Steel slag (10–15) ^b | |
| Blast furnace slag (30) ^a | Steel slag (10–15) ^b | Alumina muds (5–6) |
| Fly ash (32) | Bituminous coal refuse (100) | Phosphate slimes (20) |
| Bottom ash (10) | Phosphate slag (4) | Sulphate sludge (5–0) |
| Boiler slag (5) | Slate mining waste | Scrubber sludge |
| Reclaimed concrete | Foundry waste (20) | Copper tailings (200) |
| Anthracite coal refuse (10) | Tailings (150–200) | Dredge spoil (300–400) |
| | Incinerator residue (10) | Feldspar tailings (0.25–0.50) |
| | ← Waste glass (12) | Iron ore tailings |
| | Zinc smelter waste (5–10) | Lead/zinc tailings (20–40) |
| | Building rubble (20) | Nickel tailings |
| ← Silica fume (0.1) | | Rubber tires (3–5) |
| ← Sugarcane bagasse ash | | Battery casings (0.5–1.0) |

^aThe numerals in parentheses refer to the annual production (in 10⁶) in the USA

^bThe transfer of materials from Group II to Group I occurred over the past decade

effectively combined to optimize the properties of concrete and so ternary and quaternary binders are becoming more common (Sobolev 1993; Swamy 1986; Ramachandran 1995; Purdon 1940; Kruger 1990).

There are many examples of successful utilization of industrial by-products, essentially Group I materials in the cement and concrete industry (Table 7.1): burning organic waste including scrap tires as cement kiln fuel and using blast furnace slag and fly ash in cement (Roads and Bridges 1992; Schroeder 1994; Collins and Ciesielski 1993); using blast furnace and steel slag, glass and waste ash as aggregate in hot mix asphalt and sub-base filler material in highway construction (Ramirez 1992; FHWA Final Report 1993; Dewey et al. 1993; Pasetto 1993); using blast furnace slag and fly ash in dam construction (Togawa et al. 1992; Van Jaarsveld et al. 1995; Davidovits 1994; Dole 1989; Comrie and Davidovits 1988a, b); utilization of fly ash and silica fume (Ramachandran et al. 1981; Malhotra 1998; Comrie 1988; Comrie and Davidovits 1988a, b; Glukhovskiy et al. 1980). The following IBP have been successfully used in construction (Davidovits et al. 1990; Saylak et al. 1993; EPA 1992; Clean Washington Center Report 1993; FHWA-RD Report 1977):

- Blast furnace slag;
- Coal fly ash;
- Coal bottom ash;
- Flue gas desulfurization waste;
- Glass;
- Mining tailings;
- Municipal waste combustion ash;

- Reclaimed concrete and asphalt;
- Scrap tires;
- Steel slag;
- Waste rock;
- Carpet fiber waste;
- Waste paper.

Indeed, the use of supplementary cementitious materials has become a major trend since the 1970s with industrial by-products such as fly ash, ground granulated blast furnace slag (also defined as slag cement in the USA) and silica fume. Industrially developed countries such as the USA, the former USSR, China, France, Germany, Japan and the UK are among the largest producers of fly ash, granulated blast furnace slag, and silica fume. In addition to industrial by-products, rice producing countries such as China and India have a promising potential of generating massive quantities of rice husk (or rice hull) ash. Another industrial by-product that can be potentially used as a mineral admixture is calcined red mud, a waste material obtained from the aluminum extraction industry (Ramachandran et al. 1981; Royak and Royak 1983).

Mineral admixtures or SCM refer to finely divided materials that are added to cement or concrete to replace portland cement. Historically, natural pozzolans such as volcanic earth, tuffs, trass, clays, and shale, in raw or calcined form, have been successfully used in concrete for several types of structures such as aqueducts, roads, and water retaining structures (Mehta and Polivka 1976; Sobolev 2003a, b). Natural pozzolans are still used in some parts of the world. In addition to these, many industrial by-products (IBP) such as fly ash, slag, silica fume, red mud, rice husk ash and waste glass are becoming the predominant source of mineral components with pozzolanic properties required for the use in cement and concrete (Table 7.1), Miller and Collins (1976).

As the largest man-made commodity sector, concrete industry demonstrates the increasing demand and interest in new raw materials such as mineral powders and aggregates from non-traditional sources such as industrial by-products and recycled waste (Miller and Collins 1976). There has been considerable interest in realizing the potential of construction materials for the utilization of industrial by-products and waste (IBPW) (Damtoft et al. 2008; Malhotra 1998; Sobolev and Soboleva 1999). Following industrial development, the volume of IBP has significantly increased and will dramatically expand in the future; this is creating several economic and ecological problems (Scrivener and Kirkpatrick 2008; Roads and Bridges 1992; Sobolev 1993; Swamy 1986). Consequently, there is a demand for the development and application of technologies to reduce IBP and transform these into useful products (Ramachandran 1995; Purdon 1940; Kruger 1990; Schroeder 1994).

The availability of decent quality SCM is still limited and cannot offset the need for higher volumes of cement and concrete as required by developing markets (Scrivener and Kirkpatrick 2008; Sobolev 1993). In this regard, one viable alternative can be the use of alternative supplementary cementitious materials, including

off-spec products and less-investigated by-products, Sobolev (2003a, b, 2005), Sobolev and Arikan (2002), Gokmenoglu and Sobolev (2002), Heidrich (2002). Miller and Collins (1976) grouped different waste materials that are commonly used or have a potential application as aggregates (Table 7.1). This classification can be further extended to IBP with potential application as mineral components in blended cement. Some materials of Group I are extensively used in concrete technology. However, materials of Group II and Group III have considerable potential and can be utilized upon further investigation.

Many processes for the recycling of industrial waste and contaminated soil utilize cement, bentonite, zeolite or lime as a binder (Van Jaarsveld et al. 1995; Davidovits 1994; Dole 1989; Comrie and Davidovits 1988a, b; Comrie 1988). The final products were marketed in a form of soil cement, cement treated base (CTB), bentonite mix and roller compacted concrete. Generally, the use of industrial by-products in concrete as cement replacing is strictly defined by existing standards (Royak and Royak 1983; Swamy 1986) and the requirements for by-products or mineral admixtures are summarized in separate standards. According to current standards for use as SCM, the IBP or mineral admixtures must demonstrate some binding or pozzolanic properties as a sign of a synergetic effect and compatibility with portland cement.

Some of the products listed in Group II proved their applicability in different concrete applications. However, despite promising research data, there are many obstacles and limitations which hinder the utilization of products listed as Groups II and III. These are related to lack of long-term results related to strength and durability, the potential variability of IPB in terms of composition, especially for heavy metals. This may dictate the need for higher production control and product consistency. Also, the application of new products usually sparks the resistance of conservative construction industry often driven by the construction schedules and early strength requirements.

7.2 The Need for Innovative Technologies

For many types of industrial by-products, the rate of utilization is limited to less than 30% (Van Jaarsveld et al. 1995; Comrie and Davidovits 1988a, b), mainly because of an incompatible nature of the IBP. In this case, the compatibility of the product and cement system with respect to the simultaneous hydration reactions and structure formation is a most important criterion for the successful utilization of IBP (Comrie 1988; Comrie and Davidovits 1988a, b). Indeed, it is a challenging problem to facilitate the compatibility and, at the same time, increase the performance and utilization rate of IBP (Royak and Royak 1983; Sobolev 1993). The combination of certain mineral and chemical admixtures has been found to be very effective in solving this problem (Swamy 1986; Ramachandran 1995; Van Jaarsveld et al. 1995; Davidovits 1994; Dole 1989). The application of sodium silicate (liquid glass) in combination with granulated blast furnace slag (GBFS) was

recognized as a very effective solution to reduce the permeability and improve the strength of resulting alkali-activated binders, which are essential for the utilization of the IBP at higher volumes (Glukhovskiy et al. 1980; Davidovits et al. 1990).

The mechano-chemical activation approach for improving properties of portland cement has been successfully applied for utilization of alum waste and spent chromium-bauxite catalyzer (Sobolev 2005; Sobolev and Arikan 2002; Gokmenoglu and Sobolev 2002). When the maximal loading of these products in conventional blended cement was limited to 10–15%, an activated cement blended with up to 45% of waste resulted in binders possessing strength levels comparable to normal cement. An innovative approach to improve the performance of IBP in cementitious systems includes the addition of nanoparticles, such as nanosilica Flores et al. (2010).

In the production of activated cement, the amounts of clinker can be considerably reduced. Even at high volumes of IBP, the complex admixture “supersilica” used for mechano-chemical activation (Sobolev 2005) provided a blended cement of improved performance (Fig. 7.1). It was demonstrated that activated cement can be made to order: from super-strong cement with extended durability to low cost binders with up to 70% of IBP. Blended or high-volume mineral additive (HVMA) cement of improved performance and ecological compatibility was reported by Sobolev (2005). The technology is based on intergrinding of portland cement clinker, gypsum, supersilica, mineral additives, and—at the same time—using inexpensive natural mineral additives or industrial by-products. This improvement leads to a reduction of

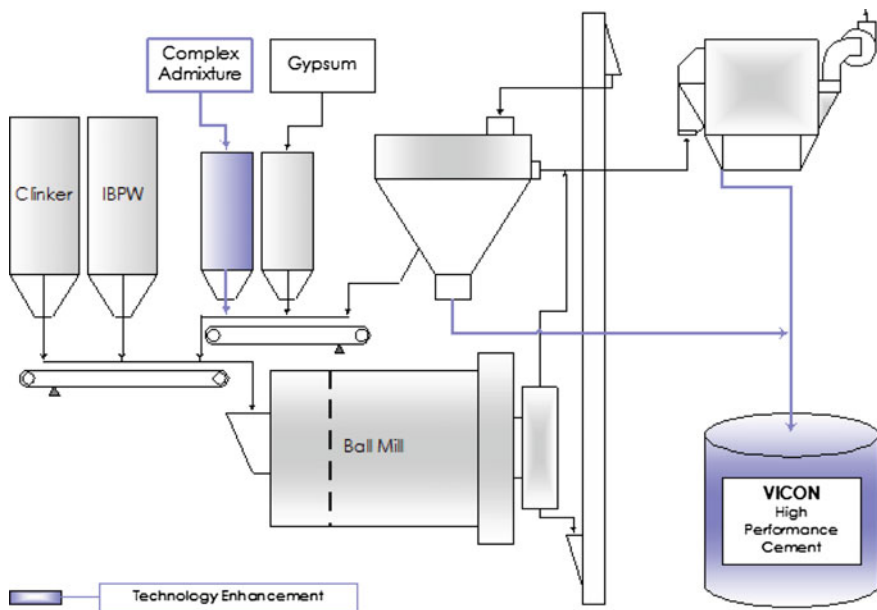


Fig. 7.1 The flow chart of high-performance cement technology (Sobolev 2005)

energy consumption per unit of the cement produced. Higher strength, better durability, reduction of pollution at the clinker production stage, and a decrease of landfill areas occupied by industrial by-products all provide considerable ecological advantages for such cement. Furthermore, the use of higher volumes of mineral additives (limestone, sand or various industrial by-products) can have an important economic and ecological impact. The following mineral additives were used successfully in the composition of HVMA cement (Sobolev and Arikan 2002):

- natural pozzolanic materials;
- pulverized natural sand (used as a part of the binder);
- limestone;
- granulated blast furnace slag (GGBFS);
- ponded fly ash;
- glass or ceramic breakage.

There are two possible approaches to HVMA cement production: the “optimal” approach, which involves keeping the constant dosage of supersilica additive at the level of 5–10% and the “economical” approach when a dosage of supersilica is proportional to the clinker component (and so reduced in low-clinker binders). The technological approach and performance of eco-cements based on inter-milling of portland cement components, supersilica and finely ground mineral additives (FGMA) such as limestone, natural sand, perlite, ponded fly ash, blast furnace slag, waste glass, spent catalyzer, and a waste of alum process was reported by Sobolev and Arikan (2002). In that study, all investigated mineral additives were ground up to the Blaine specific surface area 400–850 m²/kg in the vibrating mill to increase the reaction ability.

The strength characteristics of HVMA cements were determined in accordance with an accelerated test procedure based on ASTM C109 as the strength of mortar

Table 7.2 The effect of various IBPW on compressive strength of blended cement (Sobolev and Arikan 2002)

| Mineral additive/IBPW | Cement type | Compressive strength, MPa @ mineral additive content, % | | | | |
|-----------------------|-------------|---|-------|-------|-------|-------|
| | | 0 | 15 | 30 | 45 | 60 |
| Limestone | Economical | 135.4 | 129.7 | 108.5 | 82.1 | 79.4 |
| | Optimal | | 134.2 | 132.7 | 133.9 | 135.8 |
| Quartz sand | Economical | 135.4 | 121.1 | 112.7 | 89.9 | 81.2 |
| | Optimal | | 133.3 | 131.9 | 136.1 | 140.5 |
| Waste glass | Economical | 135.4 | 136.6 | 131.2 | 89.8 | 43.4 |
| | Optimal | | 157.7 | 165.6 | 149.4 | 80.7 |
| Waste catalyzer | Economical | 135.4 | 130.7 | 104.5 | 50.5 | – |
| | Optimal | | 141.3 | 125.9 | 111.8 | – |
| Alum waste | Economical | 135.4 | 101.5 | 77.1 | 45.9 | – |
| | Optimal | | 115.9 | 87.4 | 62.3 | – |

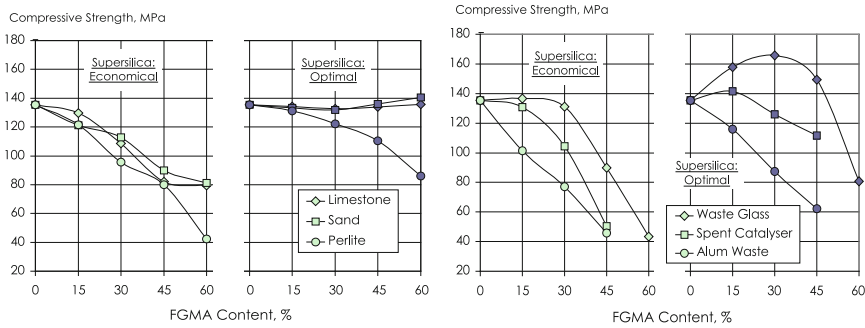


Fig. 7.2 The effect of IBPW on compressive strength of eco-cements (Sobolev and Arikani 2002)

consisting of cement, standard sand and water (in volume required to obtain a flow of 106–115 mm) at a cement to sand ratio of 1:1 using $40 \times 40 \times 160$ mm prismatic samples, cured for 8 h at 80 °C in a steam chamber. The test results outlining the performance of developed cements are reported in Table 7.2 and Fig. 7.2. It was concluded that the HVMA cement with a strength level comparable to that of normal portland cement can be manufactured with up to 45% of FGMA (Sobolev and Arikani 2002).

7.3 The Use of Steel Slag

The steel industry provides valuable raw materials in a form of different slags. Because slag replaces nonrenewable mineral resources and reduces the consumption of natural materials in construction, its use is a sustainable approach. Steelmaking slag includes blast furnace slag (BFS) from cast iron production, electric arc furnace (EAF), basic oxygen furnace (BOF/BOS) and ladle steel slag types (Heidrich 2002). The EAF mills produce steel by remelting scrap steel (Azom 2012) and integrated mills produce steel by combining molten cast iron with scrap steel in the BOF. Steel manufactured in an EAF or BOF is further refined in a ladle furnace and this process further produces different grades of steel ladle slag, LS (Heidrich 2002; Azom 2012).

7.3.1 Composition and Application of Steel Slag

Blast furnace slags have a bulk density similar to natural materials used in cement and concrete technology. Chemical composition and cementing properties make BFS an ideal supplementary cementitious material for application in portland cement concrete. Steel slag has a higher bulk density and results in a cementitious

Table 7.3 Typical constituents of EAF and BOS slags (CCAA 2008)

| Constituents as oxides | BFS (%) | BOS Slag (%) | EAF slag (%) |
|---|---------|--------------|--------------|
| Calcium oxide (CaO) | 41 | 40 | 35 |
| % Free lime | 0 | 0-2 | 0-1 |
| Silicon oxide (SiO ₂) | 35 | 12 | 14 |
| Iron oxide (Fe ₂ O ₃) | 0.7 | 20 | 29 |
| Magnesium oxide (MgO) | 6.5 | 9 | 7.7 |
| Manganese oxide (MnO) | 0.45 | 5 | 5.7 |
| Aluminium oxide (Al ₂ O ₃) | 14 | 3 | 5.5 |
| Titanium oxide (TiO ₂) | 1 | 1 | 0.5 |
| Potassium oxide (K ₂ O) | 0.3 | 0.02 | 0.1 |
| Chromium oxide (Cr ₂ O ₃) | <0.005 | 0.1 | 1 |
| Vanadium oxide (V ₂ O ₅) | <0.05 | 1.4 | 0.3 |
| Sulphur S | 0.6 | 0.07 | 0.1 |

matrix that is prone to expansion due to the presence of dead burned lime (CaO) and magnesium oxide (MgO). EAF slag contains different forms of iron oxides and includes magnesium and manganese compounds. The major compounds in EAF slag are quick lime (CaO), magnesium compounds and calcium silicates. The BOF/BOS slag products consist of calcium silicates and ferrites combined with fused oxides of iron, aluminum, calcium, magnesium and manganese (Heidrich 2002). Typical composition and physical properties of EAF and BOS slags are given in Tables 7.3 and 7.4.

In an extensive study of the utilization of steel slag, Yildirim and Prezzi (2011) reported on the composition of different slag products available from the literature (Table 7.5). The study confirmed that the EAF slag consists of CaO, FeO, SiO₂ and Al₂O₃ with some minor components such as MgO, MnO, SO₃. The mineralogical composition of EAF slag is represented by belite, calcium aluminosilicates and free CaO and MgO along with other minerals based on CaO, FeO, and MgO, Table 7.3 (CCAA 2008). The physical properties such as density, porosity, and particle size of slag are determined by the cooling rate and process used (air-cooling, expanding and granulating). Steel slag is typically stored and “cured” for up to six months allowing dead burned lime and magnesium oxide to hydrate and expand. The slag may then be crushed, sized, and screened for many applications, such as construction aggregate or mineral additive as reported by Wintenborn and Green (1998).

The BOS slag is composed of CaO, FeO and SiO₂ and the iron content can vary between 10 and 40%. The CaO content is very high (CaO > 35%) and SiO₂ (Wintenborn and Green 1998) is relatively low (7–8%). Most of the lime (CaO) or periclase (MgO) exists in bound forms with other constituents with free lime up to 10% and magnesia up to 10%. The dead burnt lime (CaO) and magnesia (MgO) hydrate expansively at later ages when a dense cementitious matrix has already formed and so it can cause the volumetric instability of the cement-based

Table 7.4 Physical properties of slags (CCAA 2008)

| Physical property | Iron slag | Steel slag | EAF | Test method | |
|--|-------------------|------------------------|------------------------|---------------------------|-------------------------|
| | BFS | BOS | | | |
| <i>Concrete applications</i> | | | | | |
| Particle density (kg/m ³) | Dry | 2400–2500 | 3300–3400 | 3300 | AS 1141.5 and AS 1141.6 |
| | SSD | 2500–2600 | 3350–3450 | 3400 | |
| Dry strength (kN) | 85–100 | 275 | 250 | AS 1141.22 | |
| Wet strength (kN) | 65–90 | 230–300 | 240–300 | | |
| Wet/dry strength variation (%) | 10–20 | 5–20 | 5–15 | | |
| Water absorption (%) | 4–7 | 1–2 coarse 2–4 fine | 1–2 coarse 2–4 fine | AS 1141.5 and AS 1141.6 | |
| LA abrasion | 37–43 | 12–18 (B) | 16 (B) | AS 1141.23 | |
| Polished aggregate friction value (PAFV) | NA | 52–58 | 58–63 | AS 1141.41 and AS 1141.42 | |
| Sodium sulphate soundness (%) | – | <4 | <4 | AS 1141.24 | |
| <i>Road-base applications</i> | | | | | |
| Max. dry density (kg/m ³) 20 mm GMB standard compaction | 2050–2150 | 2300–2400 | 2300–2400 | AS 1141.5.1.1 | |
| Optimum moisture content (%) | 8–12 ^a | 8–12 ^a | 8–12 ^a | AS 1289.2.1.1 | |

^aOptimum moisture content depends on the components of the mix

materials with basic-oxygen-furnace slag. BOF slag also contains oxides of other minor elements (such as Al, Mn, Ti, etc.). Dicalcium silicate (C₂S or 2CaOSiO₂), wustite (FeO), ferrites (Fe₃O₄) and solid solutions of iron oxide (FeO) and (MgO) are typically observed in BOF slag (Robinson 2000; Schoenberger 2001; Shi 2004; Manso et al. 2005).

Ladle slag is composed of CaO, Al₂O₃, SiO₂, and MgO (with less FeO and a higher Al₂O₃ content vs. EAF/BOF) with CaO as the main component (>45%) of the slag. The main phase in the ladle slag is C₂S (Ca₂SiO₄). During the cooling of the slag, conversion from the β-C₂S to γ-C₂S results in an increase in volume, stresses in and self-destruction of the crystals. In this way, ladle slag shows volumetric instability mainly due to the presence of free lime and the C₂S (CCAA 2008; Schoenberger 2001; Shi 2004; Manso et al. 2005). The presence of free lime and magnesia in LS can cause some problems due to delayed expansion (Emery 1982), and several methods have been proposed for the control of the long-term expansion of LS, such as rapid cooling of LS (Tossavainen et al. 2007), weathering in outdoor conditions for a period of at least six months (Altun and Yilmaz 2002; Da Silveira

Table 7.5 Mineralogical phases of BOF, EAF and ladle slags (Yildirim and Prezzi 2011)

| Reference | Slag | Mineralogical phases |
|---------------------------|------------------|--|
| Barra et al. (2001) | EAF | CaCO_3 , FeO , MgO , Fe_2O_3 , $\text{Ca}_2\text{Al}(\text{AlSiO}_7)$, Ca_2SiO_4 |
| Geiseler (1996) | – | $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$, FeO , $(\text{Ca}, \text{Fe})\text{O}$ (calciowustite), $(\text{Mg}, \text{Fe})\text{O}$ (magnesiowustite), free MgO , CaO |
| Juckes (2003) | BOF | C_3S , C_2S , C_2F , RO phase (FeO-MgO-CaO-FeO), MgO , CaO |
| Luxán et al. (2000) | EAF | Ca_2SiO_5 , $\text{Ca}_2\text{Al}(\text{AlSiO}_7)$, Fe_2O_3 , $\text{Ca}_{14}\text{Mg}_2(\text{SiO}_4)_8$, MgFe_2O_4 , Mn_3O_4 , MnO_2 |
| Manso et al. (2005) | Ladle | $\text{Al}_2\text{O}_4\text{Mg}$, $\text{Ca}(\text{OH})_2$, $\text{Si}_2\text{O}_6\text{CaMg}$, MgO , Ca_3SiO_5 , $\beta\text{-Ca}_2\text{SiO}_4$, $\gamma\text{-Ca}_2\text{SiO}_4$, SO_4Ca |
| Nicolae et al. (2007) | BOF | $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, Fe_2O_3 , CaO , FeO |
| Nicolae et al. (2007) | EAF | MnO_2 , MnO , Fe_2SiO_4 , $\text{Fe}_7\text{SiO}_{10}$ |
| Nicolae et al. (2007) | Ladle | $\text{CaO} \cdot \text{SiO}_2$, $\text{CaOAl}_2\text{O}_3 \cdot 2\text{SiO}_2$, CaS , Al_2O_3 |
| Qian et al. (2002) | EAF | $\gamma\text{-Ca}_2\text{SiO}_4$, C_3MS_2 , CFMS , FeO-MnO-MgO solid solution |
| Qian et al. (2002) | Ladle | $\gamma\text{-Ca}_2\text{SiO}_4$, C_3MS_2 , MgO |
| Reddy et al. (2006) | BOF | $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$, $2\text{CaO} \cdot \text{P}_2\text{O}_5$, $2\text{CaO} \cdot \text{SiO}_2$, CaO |
| Reddy et al. (2006) | BOF ^a | $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$, $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, Fe_2O_3 |
| Tossavainen et al. (2007) | Ladle | $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, $\text{MgO} \cdot \beta\text{-Ca}_2\text{SiO}_4$, $\gamma\text{-Ca}_2\text{SiO}_4$, $\text{Ca}_2\text{Al}_2\text{SiO}_7$ |
| Tossavainen et al. (2007) | BOF | $\beta\text{-Ca}_2\text{SiO}_4$, FeO-MnO-MgO solid solution, MgO |
| Tossavainen et al. (2007) | EAF | $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$, $\beta\text{-Ca}_2\text{SiO}_4$, Spinel solid solution $(\text{Mg}, \text{Mn})(\text{Cr}, \text{Al})_2\text{O}_4$, wustite-type solid solution $(\text{Fe}, \text{Mg}, \text{Mn})\text{O}$, $\text{Ca}_2(\text{Al}, \text{Fe})_2\text{O}_5$ |
| Tsakiridis et al. (2008) | EAF | Ca_2SiO_4 , $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, $\text{Ca}_2\text{Al}(\text{AlSiO}_7)$, Ca_3SiO_5 , $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, FeO , Fe_3O_4 , MgO , SiO_2 |
| Wachsmuth et al. (1981) | BOF | Ca_2SiO_4 , Ca_3SiO_5 , FeO , $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ |

^aQuenched—type of slag not provided

et al. 2005), the use of ternary systems with siliceous material and cement (Shi and Hu 2003), and mixing with inert material (Deneele et al. 2005).

7.3.2 Utilization of Steel Slag

The EAF/BOS slag from steel mills can be recycled into a range of useful products for building roads and pavements, and to substitute for virgin quarried materials,

mainly aggregates for asphalt and portland cement concrete. Some common applications for EAF/BOS slag are (Heidrich 2002):

- Base course and top course for asphalt roads;
- Sub-base material for rigid pavements;
- Anti-skid surfacing for roads on accident-prone intersections and curves;
- Low strength concrete;
- Controlled low strength material for backfill and trench stabilization;
- Raw material for production of portland cement clinker;
- Control of CO₂ emissions.

Steel slag has been used in construction since at least the mid-19th century. It is used in all industrialized countries. The German steel industry conducted extensive research on the application of BOF, EAF and blast furnace slags. Modern steel slags are well characterized and evaluated for long-term performance. These are commonly used as aggregates for road construction (e.g., asphaltic or unbound layers), as armor stones for hydraulic engineering construction (e.g. shore stabilization), and as a fertilizer for agriculture.

The suitability of steel slags for particular applications is regulated by national and/or international standards. Based on long-term experience, steel and blast furnace slags have been removed from the European Waste Catalogue and the European Shipment of Waste Regulation of the European Community. European Standards for construction raw materials do not discriminate between diverse sources and are for materials of “natural, recycled and manufactured” origin (Motz and Geiseler 2001). The Australian construction industry currently utilizes more than 4 million tons of fly ash and iron/steel slag per year. These materials are mainly used in road construction, blending with cement and can improve the life expectancy of concrete structures (Heidrich 2002). The EAF/BOS slag is primarily used as asphalt aggregate or for road base and subbase. It was reported that BOS slag aggregate should not be used in concrete due to potential durability issues caused by lime expansion and an aesthetic problem associated with the rust stains on concrete surfaces (Leshchinsky 2004).

The use of steel slag as an aggregate is a standard practice in the US, with many applications in granular base, embankments, engineered fill, highway shoulders, and hot mix asphalt (FHWA-RD 2008). Wintenborn and Green (1998) concluded that steelmaking slag is an environmentally safe product with a wide range of valuable uses. Based on risk assessment it was concluded that “these slags pose no meaningful threat to human health or the environment when used in a variety of residential, agricultural, industrial, and construction applications” (Wintenborn and Green 1998).

7.3.3 Blended Cement with Steel Slag

The chemical composition of steel slags makes these by-products an attractive raw material for the production of portland cement clinker and also as a component of blended cement (Yildirim and Prezzi 2011; Robinson 2000; Shi 2004; Manso et al. 2005). Several researchers demonstrated that Ladle Slag (LS) possesses latent hydraulic and pozzolanic properties and can be used as an alternative component of binder (Hewlett 2004; Akinmusuru 1991; Muhmood et al. 2009; Rodriguez et al. 2009; Papayianni and Anastasiou 2010). The chemical and mineralogical composition of steel slags reveals the potential for application as SCM for the production of blended cement (Tables 7.3 and 7.6). It was reported that blending steel slag with fly ash, blast furnace slag or with alkalis reduces or eliminates the expansion due to delayed MgO and CaO reactions (Hewlett 2004).

The reactivity of LS, as an SCM, increases significantly with its fineness. This increase can be achieved by selecting the finer material or by grinding, which can provide a higher final strength as reported by Papayianni and Anastasiou (2006, 2012). This trend was attributed to the increase of the reactivity of the binding materials due to the milling and higher surface area. At 20% cement replacement rate mortar with ground LS has developed 93% of the strength of the reference mortar (Papayianni and Anastasiou 2012). Because of the increased fineness of the material, the possibility to use LS as a filler material in order to increase the total powder content in self-compacting (SCC) concrete (Georgiadis et al. 2007;

Table 7.6 The chemical composition of investigated steel slags, *after* Shi (2004) and Sobolev (2005)

| Components | Chemical composition, % | | | | |
|--------------------------------|-------------------------|----------------------|-------------------------------------|--|------------------|
| | BFS | Basic oxygen furnace | Electric arc furnace (carbon steel) | Electric arc furnace (alloy/stainless) | Ladle |
| SiO ₂ | 40.7 | 8–20 | 9–20 | 24–32 | 2–35 |
| Al ₂ O ₃ | 11.9 | 1–6 | 2–9 | 3.0–7.5 | 5–35 |
| Fe ₂ O ₃ | 0.4 | 10–35 | 15–30 | 1–6 | 0.1–15 |
| CaO | 35.4 | 30–55 | 35–60 | 39–45 | 30–60 |
| MgO | 8.99 | 5–15 | 5–15 | 8–15 | 1–10 |
| MnO | N/A ^a | 2–8 | 3–8 | 0.4–2 | 0–5 |
| TiO ₂ | N/A ^a | 0.4–2 | N/A ^a | N/A ^a | N/A ^a |
| S | N/A ^a | 0.05–0.15 | 0.08–0.2 | 0.1–0.3 | 0.1–1 |
| P | <0.1 | 0.2–2 | 0.01–0.25 | 0.01–0.07 | 0.1–0.4 |
| Cr | N/A ^a | 0.1–0.5 | 0.1–1 | 0.1–20 | 0–0.5 |

^aNot available

Anagnostopoulos et al. 2009; Anastasiou et al. 2014; Sideris 2014) was proposed. It was demonstrated that LS can be used to increase powder content in SCC without compromising self-compacting performance, strength and durability. The use of LS reduced the risk of segregation (at a dosage of superplasticizer adjusted to ensure the adequate fluidity) (Anastasiou et al. 2014) while SCC mixtures prepared with LS had lower superplasticizer demand compared with traditional SCC mixtures prepared with limestone filler (Georgiadis et al. 2007). It was reported that LS had a positive effect on strength development of concrete at the age of 28 and 120 days and increased the durability of concrete (Anastasiou et al. 2014; Sideris 2014). The SCC with ladle furnace slag was found to be more susceptible to spalling effects after fire exposure compared to limestone SCC mixtures because of the pore refinement in the cementitious matrix (Anagnostopoulos et al. 2009).

In China, portland-steel and ground granulated blast furnace slag (GGBFS) blended cements were used for more than 50 years (CABM 1985). For the design of blended cement, several steel slags were tested, and it was found that the basicity was a key factor associated with strength development (Fig. 7.3). The hydraulic reactivity of EAF is due to the presence of C_3S , C_2S , C_4AF , and C_2F and due to the basicity of the material. Free-CaO increases the basicity and reactivity of EAF (Table 7.7), but it lowers the C_3S content (Tang 1973).

The addition of fly ash to portland—steel slag blended cement reduces the detrimental effect of free-CaO. Several combinations of portland cement, steel slag, fly ash and gypsum were investigated by Wu et al. (1999), Bin et al. (1992) as reported in Table 7.8. Lower drying shrinkage and corrosion resistance were demonstrated by the blended cement based on a portland clinker—fly ash—steel slag composition. Due to the replacement of portland cement clinker, the compressive strength of blended cement was reduced in compositions with fly ash and steel slag; however, the addition of 2% of high alumina cement helped to improve the strength of developed cement (Fig. 7.4). The research data reported by Wu et al. (1999) are in a good agreement with CAMB (1985) study.

Fig. 7.3 The compressive strength of steel slag cement as a function of basicity (after CABM 1985)

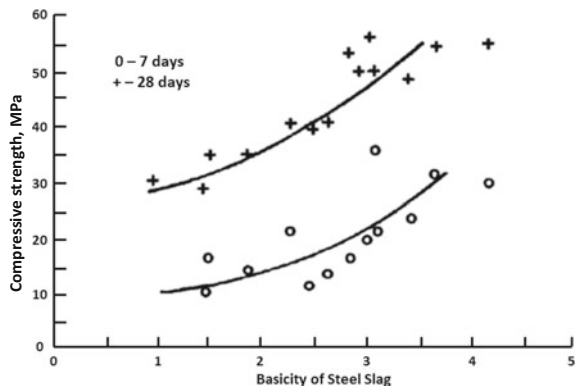


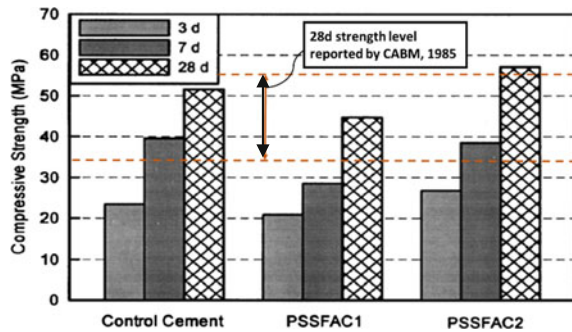
Table 7.7 The basicity, mineral composition and reactivity of steel slags (after Tang 1973)

| Hydraulic reactivity | Types of slag | Basicity as CaO/SiO ₂ | Major mineral phases |
|----------------------|---------------------|----------------------------------|---|
| Low | Olivine | 0.9–1.5 | Olivine, RO phase, and merwinite |
| | Merwinite | 1.5–2.7 | Merwinite, C ₂ S, and RO phase |
| Medium | Dicalcium silicate | 1.6–2.4 | C ₂ S and RO phase |
| High | Tricalcium silicate | >2.7 | C ₃ S, C ₂ S, C ₄ AF, C ₂ F, and RO phase |
| High | BFS | <0.9 | Akermanite, Melilite, Quartz, Merwinite, Monocicellite |

Table 7.8 Composition of portland-steel slag-fly ash cement, after Wu et al. (1999) and CABM (1985)

| Materials | Control | PSSFAC1 | PSSFAC2 | CABM 1985 |
|----------------------------|---------|---------|---------|-----------|
| Portland cement clinker, % | 93 | 45 | 45 | 35 |
| Gypsum, % | 7 | 5 | 3 | 5 |
| EAf, % | – | 30 | 30 | 30 |
| Fly Ash, % | – | 20 | 20 | – |
| Blast furnace slag | – | – | – | 30 |
| High alumina cement, % | – | – | 2 | – |

Fig. 7.4 Strength development of portland-steel slag-fly ash cement, after Wu et al. (1999) and CABM (1985)



7.4 The Use of Pulverized Bottom Ash

The pulverized coal—fired power plants, especially when low-quality carbon source is used, are responsible for substantial amounts of by-product residues called Coal Combustion Products (CCP) Churcill and Amirkhanian (1999), Pera et al. (1997), Ramme et al. (1998), Cheriaf et al. (1999), Bai and Bashaer (2003), NCAB (2005), ACAA (2006), Sanjuan and Menéndez (2010), Sanjuán and Zaragoza (2013), Argiz (2013), Menéndez et al. (2014a), Sanjuan et al. (2016a, b). The CCP

collected from pulverized coal—fired furnaces such as fly ash (FA) and bottom ash (BA) originate from the unburnt impurities (sand, clays, etc.) from the coal deposit. Also, ash can contain some quantities of unburnt carbon (characterized by higher LOI) due to an incomplete combustion of coal. The BA constitutes around 20% of total CCP volume, and it is composed of larger particles, which drop, melt, conglomerate and vitrify in the bottom of the furnace Siddique (2010), Asokan et al. (2005). Ash can contain trace metals that could be leached to water and damage the aquatic ecosystem Izquierdo and Querol (2012). In Europe, 41 million tons of coal ash was generated in 2009, and around half of these were placed into the landfills ECOBA (2003, 2009). The production of fly ash and bottom ash CCP during 2006 was 300 million tons and the cumulative stock available for utilization is more than 2,500 million tons Sanjuán and Zaragoza (2013), Argiz (2013), Menéndez et al. (2014a), Sanjuan et al. (2016a, b). According to the study completed in 2003, 48.2% of bottom ash is used to manufacture concrete blocks and 33.1% for road construction NCAB (2005). Also, the statistics of the American Coal Ash Association (ACAA) demonstrated that more than 45% of bottom ash is used mainly in transportation applications (structural fill, road base materials and snow and ice control products). Bottom ash is commonly used as an aggregate in lightweight concrete masonry units ACAA (2006). Recently, bottom ash has been investigated to be used alone or in combination with fly ash in blended cement as a mineral admixture Cheriaf et al. (1999), Bai and Bashaer (2003), Sanjuan and Menéndez (2010). Traditionally, the coarse-grained, fused, glassy texture of bottom ash is adequate to substitute natural aggregates Ramme et al. (1998), Pera et al. (1997), Churcill and Amirkhanian (1999).

Many research projects have been conducted to investigate the feasibility of using BA as a partial replacement for portland cement. The use of BA and BA-FA mixes has been studied to analyze the potential utilization in blended cement. The proportion 80:20 of FA to BA was a better option because this represents the ratio at which these types are produced by the power plants. It was reported that the use of 25% substitution level in the BA-FA blends helps to achieve the adequate mechanical properties Argiz et al. (2013, 2014).

7.4.1 Chemical and Mineralogical Composition

In general, the FA and the BA from the same power plant have similar compositions, except for the amount of calcium, iron, magnesium and chromium content, which could be slightly higher in BA. Depending on the type of coal used, higher LOI is observed in the fly ash. Actually, the values of LOI in the bottom ash are significantly lower than these in the fly ash, and the influence of the type of coal on LOI content is considerably less Menéndez et al. (2013). Typical major and minor components of FA and BA from two different coal power stations are reported by Fig. 7.5.

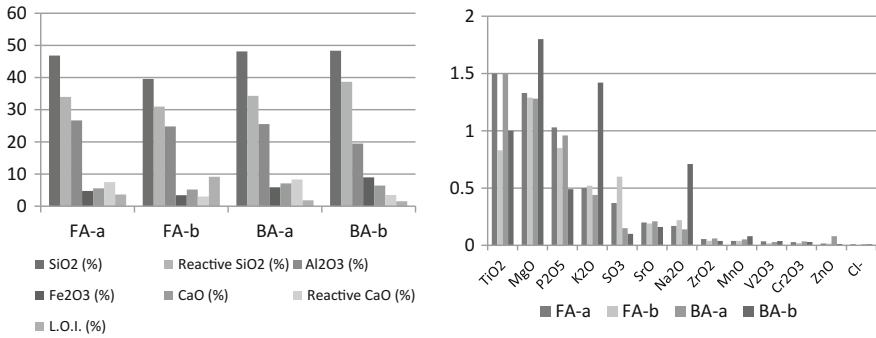


Fig. 7.5 The chemical composition of CCP (Menendez et al. 2013)

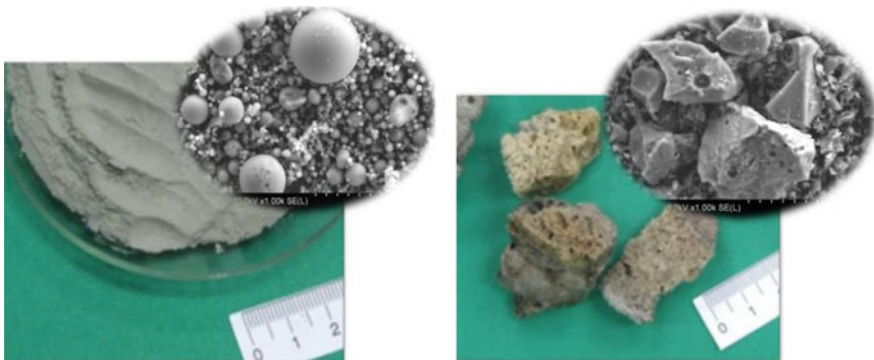


Fig. 7.6 The microstructure of CCP: fly ash (left) and bottom ash (right) (Menendez et al. 2013)

The crystalline composition of FA and BA are very similar. The main crystalline phases are quartz (SiO_2) and mullite ($\text{Al}_4\text{Si}_2\text{O}_{10}$) in fly ash and bottom ash, and small amounts of anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) in BA. In general, the quartz to mullite ratio was higher in BA than FA, which is associated with the presence of anorthite in BA. While FA-b had a greater proportion of mullite than FA-a, BA-b had a lesser proportion of mullite than BA-a, due to the higher content of anorthite in BA Menéndez et al. (2013), Ward and French (2006).

7.4.2 Microstructure and Physical Properties

The microstructure of FA is determined by spherical particles with different particle distributions and typical values from 10 to 100 μm , while the BA has angular particles with very porous surface texture. The BA particles range in size from a fine gravel to a fine sand and require grinding to be used as SCM. The morphology of FA and BA (before and after grinding) is reported in Fig. 7.6 (Menéndez et al.

(2013, 2014b). The difference in particle morphology can be explained by the use of different combustion process, the different quality of coals and the grinding process realized for BA Siddique (2010).

7.4.3 Pozzolanic Activity and Mechanical Properties

When the BA products are tested to analyze the pozzolanic activity, it was reported that both FA and BA had similar pozzolanic characteristics when compared at similar fineness Menéndez et al. (2013, 2014b, 2015a, b). The specific surface area of CCP plays a key role in their pozzolanic properties and hence in the mechanical performance of cementitious materials; commonly, the FA had a greater Blaine surface area than ground BA. The CaO content is decreased similarly to the solution alkalinity when FA was tested. While in the case of BA, the CaO content, and the solution alkalinity had no significant changes over time (Fig. 7.7).

The test results related to the compressive strength of standard mortars according to EN 196-1 (2005) are reported in Fig. 7.7 Argiz et al. (2014), Sanjuan and Menéndez (2010), Menéndez et al. (2009, 2013, 2014a), Menéndez and de Frutos (2011). These mortars have used the substitution rate of 10, 25 and 35% for FA, BA and FA and BA mixes at 80:20, 50:50 and 20:80 ratios. At the age of 28 days, the mechanical properties of mortars made with cement containing individual CCP and their blends were similar for the CCP of similar composition (e.g., from the same power plant), especially when the same replacement levels are being used. The compressive strength of specimens with 10% cement replacement was higher than the minimum 28-day strength required by the standard which is 42.5 MPa according to EN 196-1 (2005). Despite this, mortars with 25% replacement were close to the limit, while mortars with 35% of replacement had values of the compressive strength of less than 40 MPa. However, it was proposed that an

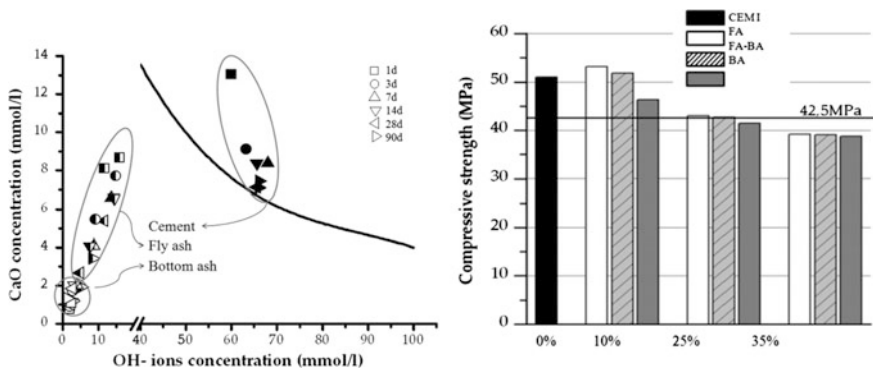


Fig. 7.7 The pozzolanic activity (left) and mechanical properties (right) of mortars with CCPs (Menendez et al. 2013)

additional grinding of BA can enhance the mechanical properties of mortars Cheriaf et al. (1999). This behavior was in accordance with the results confirming that the reaction of FA decreases at higher levels of cement replacement, and a better performance is obtained at lower cement replacement levels Menéndez et al. (2014c), Hanehara et al. (2001), Jaturapitakkul and Cheerarot (2003), Kurama and Kaya (2008).

7.4.4 Durability Performance

According to different studies Sanjuan et al. (2016a, b), Menéndez et al. (2014a, 2015a, b), Argiz (2013), mortars manufactured with partial substitution of BA and FA and BA mixes had a good durability with respect to alkali-silica reaction and external sulfate attack. While mortars with CCP had a lower resistance to carbonation or frost damage, this behavior can be associated with higher porosity of mortars. Due to this, it is recommended to limit the CCP substitution levels to 25%. However, the performance of BA and FA and BA mixtures can be further improved with the effective use of water-reducing admixtures.

In general, BA has higher levels of heavy metals than the FA from the same power plant, and the long-term environmental behavior of such materials must be analyzed. The environmental impact of mortars with CCP has been evaluated by leaching tests performed under different conditions (pH of 5 and 10, and the exposure temperatures of 20 and 60 °C). It was reported that the test temperature is a determinant parameter controlling the leaching process. Greater leaching was produced at an acidic pH, except in the case of strontium, which experienced greater leaching at a higher pH. No significant differences were observed in the behavior of mortars with different CCP and CCP blends at 10% of substitution Menéndez et al. (2014a, b).

7.5 The Use of Sugarcane Bagasse Ash

Sugarcane bagasse ash (SCBA) is obtained from boilers of sugar industries as a combustion by-product. After crushing of sugarcane in sugar mills and extraction of juice from prepared cane by milling, the discarded fibrous residual matter of cane is called bagasse. Bagasse is very commonly used as fuel in boilers in the sugar mills for cogeneration process. After burning in the cogeneration boiler, bagasse ash is collected in a baghouse filter and is disposed locally, which causes severe environmental problems. Because of rapid implementation of cogeneration plants in sugar industries, bagasse ash generation is also increasing significantly in India and other major sugarcane producing countries such as Brazil and Thailand. SCBA is mainly composed of silica and can be used as a supplementary cementitious material in concrete instead of disposal. Several studies have reported that sugarcane bagasse

ash can be used as pozzolanic material (Bahurudeen et al. 2015; Frias et al. 2011; Montakarntiwong et al. 2013; Chusilp et al. 2009; Cordeiro et al. 2009a; Bahurudeen et al. 2016).

7.5.1 Composition and Pozzolanic Activity of SCBA

The SCBA primarily contains SiO₂ along with smaller amounts of other oxides. Silica content depends on the burning temperature of bagasse in the boiler (Cordeiro et al. 2008; Singh et al. 2000). Table 7.9 presents the compositions of SCBA reported in the literature. The as-collected SCBA tends to have a large fraction of unburnt carbon particles that causes it to have a very high loss on ignition. The degree of unburnt carbon depends on the efficiency of burning in the cogeneration boiler. Bahurudeen et al. (2016) have reported on the occurrence of coarse and fine fibrous carbon particles in SCBA, as demonstrated by Fig. 7.8. The unburnt carbon particles also reduce the specific gravity of bagasse ash to the values as low as 1.9–2.1 (Ganesan et al. 2007). Furthermore, the fineness of as-collected bagasse ash is affected by more than 65% of relatively coarse material retained on a 45 µm sieve (Somna et al. 2012).

Cordeiro et al. (2009a) used the Chapelle test to compare the pozzolanic activity of bagasse ash samples that were calcined to different degrees; the results of the study proved that the maximum reactivity of bagasse ash was found in the sample that was burned at around 500 °C. The key factor in obtaining the desired degree of pozzolanic activity is, therefore, the removal of the unburned carbon particles, achieved by separation and fine grinding. The effect of three grinding methods on

Table 7.9 Chemical composition of SCBA and fly ash Class C and F (data collected from Chusilp et al. 2009; Cordeiro et al. 2009a; Bahurudeen et al. 2016; Sobolev et al. 2015)

| Oxide composition (%) | SCBA1 | SCBA2 | SCBA3 | Fly ash | |
|--------------------------------|-------|----------------------------|----------------------|---------|---------|
| | | | | Class C | Class F |
| SiO ₂ | 64.88 | 60.96 | 72.95 | 32.7 | 46.9 |
| Al ₂ O ₃ | 6.40 | 0.09 | 1.68 | 17.6 | 22.9 |
| Fe ₂ O ₃ | 2.63 | 0.09 | 1.89 | 5.9 | 19.2 |
| CaO | 10.69 | 5.97 | 7.77 | 27.3 | 3.8 |
| MgO | 1.55 | 8.65 | 1.98 | 6.6 | 0.8 |
| K ₂ O | N/A | 9.02 | 9.28 | 0.4 | 1.7 |
| Na ₂ O | N/A | 0.70 | 0.02 | 2.2 | 0.6 |
| SO ₃ | 1.56 | N/A | 4.45 | 2.0 | 0.3 |
| LOI | 8.16 | 5.70 (optimal calcination) | 21.00 (as collected) | 0.3 | 2.3 |

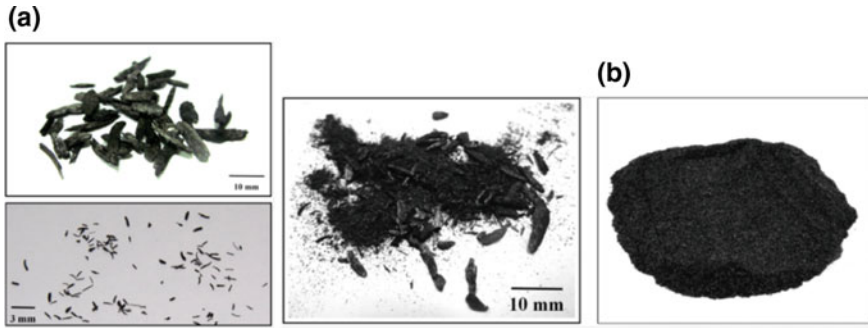


Fig. 7.8 Coarse and fine fibrous particles in SCBA (a), and as-collected and sieved SCBA (b) (Bahurudeen et al. 2016)

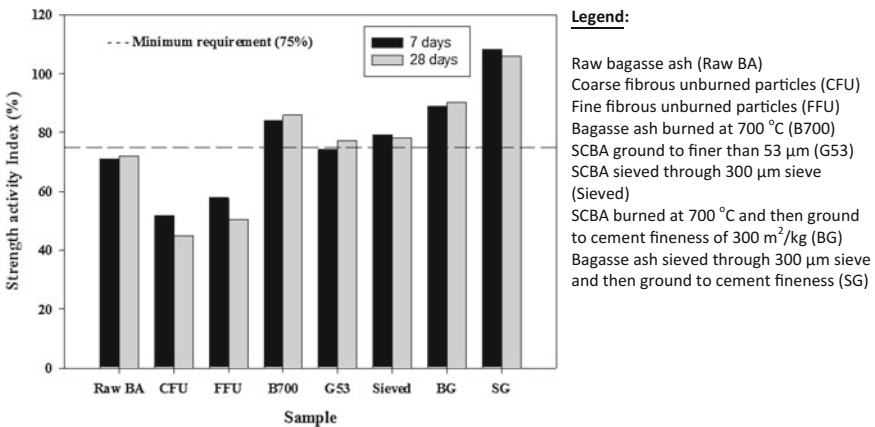


Fig. 7.9 The comparison of performance for different SCBA products (Bahurudeen and Santhanam 2015)

pozzolanic activity of bagasse ash was also investigated in a separate study (Cordeiro et al. 2009b), reporting the increase of pozzolanic activity with fineness, and that grinding to values of D80 (80% passing size) below 60 μm and Blaine fineness above 300 m²/kg resulted in the products classified as pozzolanic. Recently, Bahurudeen and Santhanam (2015) demonstrated that direct calcination or grinding of as-collected material may not be an efficient strategy, both from the point of energy expenditure as well as from the performance perspective. After a thorough assessment, a combination of sieving of as-collected ash (through a 300 μm sieve) and consequent grinding to a fineness of about 300 m²/kg produced an excellent product performance in the pozzolanic activity tests. A comparative evaluation of the pozzolanic activity index as per ASTM C618 (2012) obtained by processing SCBA through different techniques was reported, as shown in Fig. 7.9 (Bahurudeen and Santhanam 2015).

7.5.2 The Effect of SCBA on Fresh Properties of Concrete

The reactive silica particles in SCBA are usually irregular in shape, with a high surface area, as depicted in Fig. 7.10 (Bahurudeen et al. 2014). As a result, a reduction in workability of concrete with SCBA is expected. The influence of sugarcane bagasse ash and fly ash blends on the rheological behavior of cement pastes was studied by Quero et al. (2013), and loss on fluidity was observed with SCBA replacement rate. An increase in viscosity and yield stress was observed with the increase in bagasse ash replacement, but the interaction of different superplasticizers with bagasse ash was not addressed.

Bahurudeen et al. (2014) reported that bagasse ash replacement caused an increase in the optimal dosage of superplasticizer. Further, the relative fluidity of bagasse ash based cement paste was lower than the control for the same water-binder ratio and superplasticizer dosage, due to the combined effect of an increase in powder volume (owing to the lower density of SCBA) and the irregular particle shape of the SCBA. Nevertheless, SCBA and cement blends had demonstrated satisfactory compatibility with polycarboxylic ether (PCE) based superplasticizers.

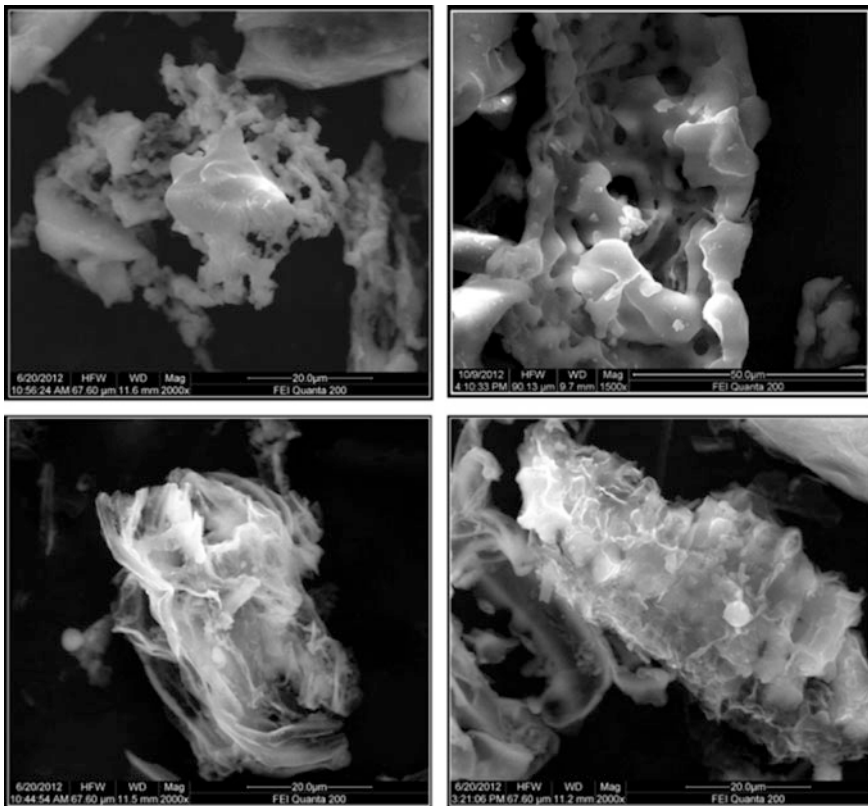


Fig. 7.10 The SEM micrograph of SCBA particles (based on Bahurudeen et al. 2014)

The influence of SCBA on the heat of hydration of concrete using a semi-adiabatic system was reported by Montakarntiwong et al. (2013) and this study demonstrated that SCBA reduced the heat evolution compared to plain cement concrete. Bahurudeen et al. (2015) used an adiabatic calorimeter and detected up to 25% reduction of the total heat evolved for the mixtures with 10–20% SCBA; similar reductions were also reported for the peak heat rates, indicating the positive influence of SCBA for hot weather applications.

7.5.3 The Effect of SCBA on Strength and Durability

The replacement of cement with up to 25–30% SCBA does not cause any major changes in the attainment of the 28 and 90 days compressive strength (Bahurudeen et al. 2015; Montakarntiwong et al. 2013). However, the use of SCBA leads to several advantages in terms of durability. The positive influence of SCBA replacement on water permeability was reported by Bahurudeen et al. (2015) and Chusilp et al. (2009), while Frias et al. (2011) were able to demonstrate the reduction in chloride diffusion when SCBA was used in concrete. In a comprehensive evaluation of the durability characteristics of concrete containing SCBA, Bahurudeen et al. (2015, 2016) used a combination of water, gas, and chloride penetration techniques to compare the durability of concretes with and without SCBA, and they also compared the performance to fly ash concrete with the same level of compressive strength. The charge passed in the Rapid Chloride Permeability Test (RCPT) as per ASTM C1202 (2012) and the Chloride Conductivity Index (CCI) as per the South African Durability Index Manual (2009) is reported in Fig. 7.11, while the SIA 162/1-E (2003) in comparison with fly ash

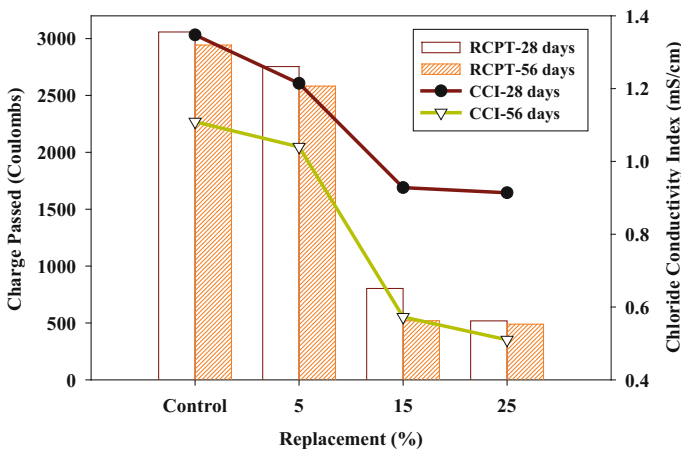


Fig. 7.11 The resistance of SCBA concrete to chloride penetration (based on Bahurudeen et al. 2015, 2016)

Fig. 7.12 The performance of SCBA concrete in the air permeability test (Bahurudeen et al. 2016)

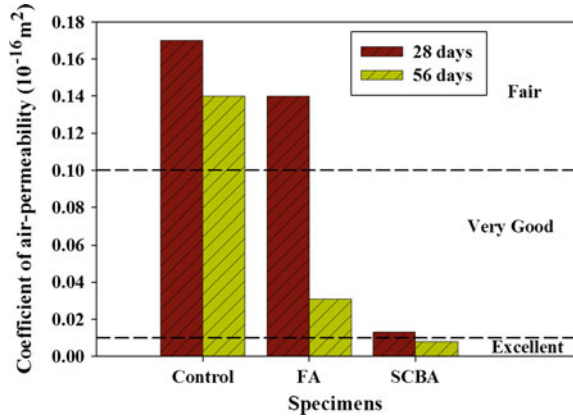


Table 7.10 Water penetration results of SCBA concrete based on DIN 1048 test (based on Bahurudeen et al. 2016)

| Concrete type | Penetration depth, mm | |
|------------------------------|-----------------------|---------|
| | 28 days | 56 days |
| Control concrete | 81.0 | 65.4 |
| Fly ash blended concrete | 54.7 | 28.3 |
| Bagasse ash blended concrete | 48.0 | 19.0 |

blended concrete is demonstrated in Fig. 7.12. Table 7.10 reports on the relative performance of investigated concrete in water penetration test as per DIN 1048—Part 5 (1994).

7.6 The Use of Silica Fume with Reduced SiO₂ Content

It is well-documented that concrete with silica fume (SF) and metakaolin is characterized by reduced pore volume (for a range of pore diameters of 0.1–4.0 μm), high strength, reduced permeability, and improved sulfate resistance (Sobolev 1993, 2004; Sobolev and Yeginobali 2005; Arikan et al. 2009; Aras et al. 2007; Batrakov et al. 1992). The bulk of reported research is related to concrete with silica fume containing at least 85% of SiO₂; however, there are very few papers on the use of off-spec silica fume with lower SiO₂ (Batrakov et al. 1992).

The performance of by-product silica fume (including off-spec material, OSF) from metallic silicon (S), low-grade ferrosilicon (FS), and ferro-silicon-chrome (FSC) production was reported by Batrakov et al. (1992). These products contained 91.7, 70.1, 65.6% of SiO₂ and had a surface area of 25.0, 44.9, and 18.5 m²/g, respectively. The S/SF product was like other SF products (Ref/SF) used by industry and reported in scientific literature (Sobolev and Yeginobali 2005). The main chemical and physical properties of investigated SF/OSF vs. Reference SF are

Table 7.11 The chemical and physical characteristics of various silica fume products, after (Batrakov et al. 1992; Sobolev and Yeginobali 2005)

| Characteristics | Types of silica fume products | | | |
|--|-------------------------------|------|--------|---------|
| | Ref/SF ^a | S/SF | FS/OSF | FSC/OSF |
| Component content, % | | | | |
| SiO ₂ | 90.0 | 91.7 | 70.1 | 65.6 |
| Al ₂ O ₃ | 0.4 | 0.5 | 2.0 | 1.5 |
| Fe ₂ O ₃ | 0.36 | 0.4 | 3.4 | 2.4 |
| CaO | 1.63 | 1.2 | 11.4 | 0.6 |
| MgO | 1.02 | – | 0.1 | 14.6 |
| K ₂ O + Na ₂ O | 2.78 | – | 0.9 | – |
| SO ₃ | 0.44 | – | 0.4 | – |
| SiC | – | 4.2 | – | – |
| Cr ₂ O ₃ | – | – | – | 2.2 |
| LOI | 2.28 | 2.0 | 11.7 | 2.0 |
| Surface area by BET, m ² /g | – | 25.0 | 44.9 | 18.15 |
| Bulk weight, kg/m ³ | – | 160 | 150 | 260 |
| Specific gravity, kg/m ³ | 2.25 | 2.16 | 2.07 | 2.84 |
| Water demand (as normal consistency of SF slurry), % | – | 42 | 137 | 40 |

^aFrom Sobolev and Yeginobali (2005)

Table 7.12 The composition of cement pastes and compressive strength results (Batrakov et al. 1992)

| Mixture No. | Silica fume | Binder, % | | HRWR, % (C + SF) | $\frac{W}{C+SF}$ | Compressive strength, MPa at the age of, days | | | |
|-------------|-------------|-----------|----|------------------|------------------|---|------|------|------|
| | | Cement | SF | | | 3 | 7 | 14 | 28 |
| 1 | – | 100 | 0 | – | 0.28 | 22.1 | 33.5 | 35.7 | 43.6 |
| 2 | FS/OSF | 91 | 9 | 0.6 | 0.28 | 36.0 | 47.1 | 50.0 | 56.2 |
| 3 | FS/OSF | 83 | 17 | 1.3 | 0.28 | 36.6 | 50.9 | 55.5 | 62.5 |
| 4 | FS/OSF | 77 | 23 | 2.7 | 0.28 | 40.0 | 55.1 | 61.8 | 72.2 |
| 5 | FS/OSF | 83 | 17 | 2.0 | 0.28 | 29.9 | 58.8 | 62.6 | 75.1 |
| 6 | S/SF | 83 | 17 | 0.4 | 0.28 | 38.2 | 53.0 | 57.5 | 64.2 |
| 7 | FSC/OSF | 83 | 17 | 0.3 | 0.28 | 30.0 | 44.9 | 50.1 | 60.0 |

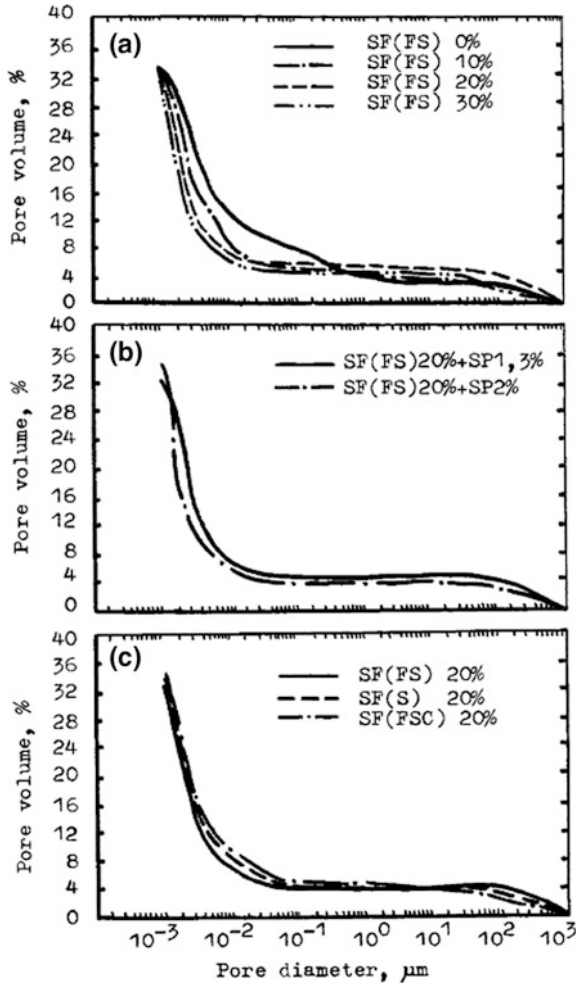
listed in Table 7.11. It was reported that the use of SF/OSF leads to an increase of gel porosity, a decrease of capillary porosity and an increase in strength, Tables 7.12 and 7.13.

The porosity characteristics were investigated by the Proton Magnetic Resonance (PMR) method enabling the determination of pore sizes ranging from 1 to 100 nm. The PMR test procedure involved the complete saturation of hydrated cement paste specimens with water, followed by subsequent freezing and step-wise heating. The porosity characteristics are reported by Table 7.12 and Figs. 7.13, 7.14

Table 7.13 The porosity and pore size distribution (Batrakov et al. 1992)

| Mixture no | Designation of SF samples | Gel pores, % | | | Capillary pores, % | | Technological pores, % | | Total porosity, % |
|------------|---------------------------|---|---|--|---|--|------------------------|------|-------------------|
| | | Supermolecular level | Submicroscopic level | Microscopic level | Submicroscopic level | Microscopic level | Macroscopic level | | |
| 1 | – | $1 \times 10^{-3} < d \leq 5 \times 10^{-3}, \mu\text{m}$ | $5 \times 10^{-3} < d \leq 1 \times 10^{-1}, \mu\text{m}$ | $1 \times 10^{-1} < d \leq 4 \times 10^1, \mu\text{m}$ | $4 \times 10^1 < d \leq 1 \times 10^3, \mu\text{m}$ | $1 \times 10^{-3} < d \leq 1 \times 10^3, \mu\text{m}$ | | | |
| 2 | FS/OSF | 18.1 | 8.2 | 4.7 | 2.5 | | | 33.5 | |
| 3 | FS/OSF | 21.6 | 7.4 | 1.6 | 2.9 | | | 33.5 | |
| 4 | FS/OSF | 23.4 | 5.0 | 1.0 | 4.3 | | | 33.7 | |
| 5 | FS/OSF | 24.5 | 4.2 | 1.8 | 2.9 | | | 33.4 | |
| 6 | S/SF | 26.7 | 3.8 | 1.1 | 3.6 | | | 35.2 | |
| 7 | FSC/OSF | 23.1 | 6.4 | 1.6 | 4.3 | | | 35.4 | |
| | | 22.6 | 7.0 | 1.9 | 3.7 | | | 34.2 | |

Fig. 7.13 The pore size distribution of hydrated cement pastes with different: **a** silica fume content, **b** superplasticizer (HRWR/SP) content, **c** silica fume type (Batrakov et al. 1992)



and 7.15. The total porosity of specimens produced with several types and volumes of SF/OSF at the same $W/(C + SF)$ ratio of 0.28 was virtually at the same level of 33–35%; however, the specimens based on different SF/OSF types were significantly different in terms of pore size distribution (Fig. 7.13). It was reported that the use of silica fume products in portland cement systems resulted in the increase of the volume of gel pores, depending on the dosage and type of SF/OSF. With SF/OSF dosage increased to 10–30%, the gel porosity increased by 3.5–6.4% as compared to the reference specimen (Batrakov et al. 1992).

It was found that the gel porosity was affected by the type of SF/OSF used. For example, the specimen with S type of silica fume and the highest SiO₂ content of 91.7% and the finest specimen FS demonstrated very high gel porosity. The volume of capillary pores of cement pastes with SF/OSF was less than that of the reference

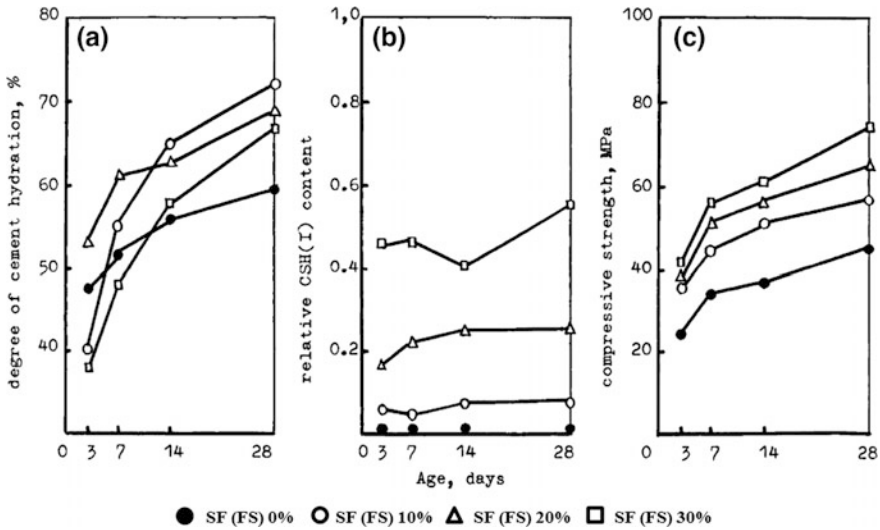


Fig. 7.14 The effect of silica fume content on: **a** degree of cement hydration, **b** relative CSH(I) content, **c** compressive strength (Batrakov et al. 1992)

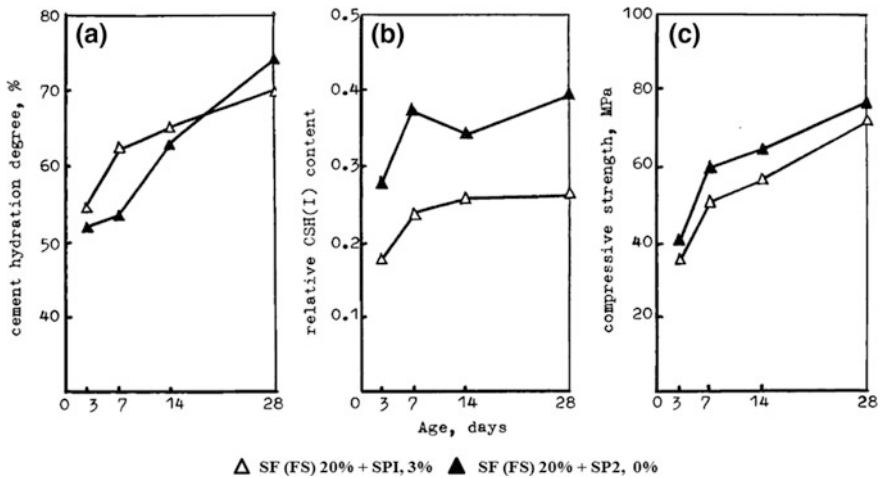


Fig. 7.15 The effect of superplasticizer (HRWR/SP) content on: **a** degree of cement hydration, **b** relative CSH(I) content, **c** compressive strength of cementitious systems with silica fume (FS at 20%) (Batrakov et al. 1992)

specimen. Normally, the porosity decreased with the increase in the SF/OSF content. The lowest value of capillary porosity was reported for the specimens with FS/OSF characterized by higher fineness (e.g., mixtures 3, 4, 5).

The use of higher dosage of SF/OSF had resulted in the acceleration of cement hydration, the increase of CSH(I) content, and improvement of compressive strength. It was concluded that the overall modification of cement paste microstructure was similar for different types of SF/OSF regardless of SiO₂ content, and so all these products had similar improvements of concrete performance. All investigated SF/OSF increased the strength of hardened cement paste and concrete. Permeability to water and gas was lower than that of the reference concrete. This observation was confirmed by low values of permeability to air, CO₂ diffusion coefficient, and water filtration coefficient. Still, the FS type of silica fume with large surface area appeared to be the best.

Overall, the following conclusions regarding the effects of different SF products were made (Batrakov et al. 1992):

- The SiO₂ content of silica fume product did not affect the parameters of gel and capillary porosity;
- An increase of silica fume fineness caused a decrease in the cement paste capillary porosity and hence reduced the permeability;
- An increase of silica fume dosage led to an increase of CSH(I) and the volume of gel pores, and promoted a decrease in cement paste capillary porosity, contributing to an increase of concrete strength.

7.7 The Use of Waste Glass

Glass is one of the earliest man-made materials, having been made for over 9000 years. Because of its wide availability, cost effectiveness and unique mechanical, chemical, thermal, and optical properties, glass is currently found in many applications U.S. Department of Energy (2002), EPA (1992), Sobolev 2003a; Sobolev et al. 2007). For example, in 2014, in the USA alone about 20 million tons of glass products were manufactured with a shipment value of about \$26.2 billion (Statista 2014). Theoretically, glass is a 100% recyclable material, and it can be indefinitely recycled without any loss of quality. According to EPA statistics, the municipal solid waste (MSW) stream contains about 4.6% of waste glass corresponding to 11.6 million metric tons (with some historical volumes reported by Fig. 7.16) EPA (1992), Sobolev et al. (2007), The Statistics Portal (2014). In 2015, only about 25% of this volume of glass was recycled and the remaining 75% was landfilled Sobolev (2003a, b). Therefore, in spite of the apparent simplicity of glass recovery, its recycling rate in the USA is among the lowest (at an average MSW recovery level of 30%), American Recycler News (2015). In contrast, the European countries achieve the recycling rates for waste glass above 95% U.S. EPA (2002), Sobolev et al. (2004).

Waste glass comes from various sources: glass containers (bottles and jars), construction glass (windows), and electrical equipment (lamps, old style monitors, and TVs). Most (89%) of the waste glass comes from various containers (Fig. 7.17)

Fig. 7.16 The generation and recovery of waste glass in the USA (Sobolev et al. 2004)

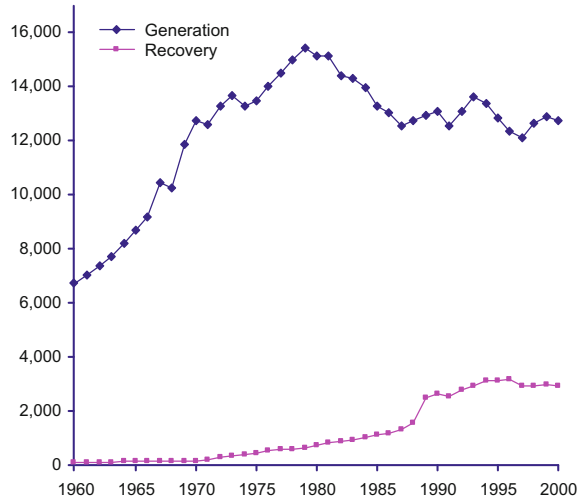
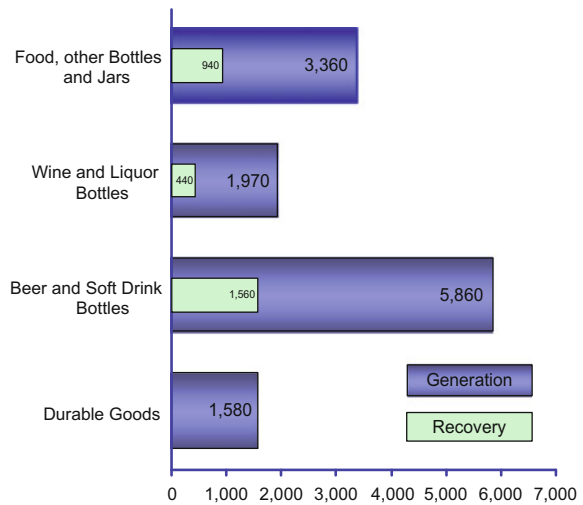


Fig. 7.17 The structure of waste glass stream (Sobolev et al. 2004)



EPA (1992), Sobolev et al. (2004). Generally, recovered glass containers are recycled into new containers, other portions are used in newly emerging sectors such as fiberglass insulation, abrasives, light-weight aggregates, yet some quantities are used for concrete and asphalt as an aggregate Geiger (1994), GPI (1999), Stewart (1986), CWC (2003), Apotheker (1989). Recycling of waste glass is attractive to the glass manufacturers because it reduces the costs associated with raw materials and technological process; it lowers energy consumption; and also eliminates the need to dump waste glass in landfills. However, to recycle waste glass effectively within the glass industry, it must contain glass of similar

composition, which has been separated from contaminants which could reduce the quality of new glass products. The following contaminants affect the recycling of waste glass (Sobolev et al. 2004; Gunalaan and Kanapathy 2013; Stewart 1986; Rodriguez 1995; Mayer 2000):

- Glass of fluctuating composition or color (compared with the mainstream);
- Ceramics (dishware, porcelain, pottery, bricks, concrete);
- Metals (including container lids or seals);
- Organics (paper, plastics, cork, wood, plants, food residue, especially sugar).

The construction industry has demonstrated great potential in recycling industrial by-products and waste, including waste glass (Sobolev 2005; Sobolev and Arikan 2002). There are many examples of successful recycling of waste glass in construction: heat insulation (fiberglass and light-weight aggregates), aggregates for concrete and asphalt, base and sub-base filler materials, and as a constituent of cement (as a pozzolanic additive) (GL-93-3 1994; Day and Schaffer 1975; Science Daily 2003; Nash et al. 1995; Shin and Sonntag 1994; Shao et al. 1998). Usually, considerable volumes of contaminants can be tolerated in such applications (Khmiri et al. 2012; Khatib et al. 2012; Kumarappan 2013). When the waste glass is proposed as a constituent of cement (as a mineral additive) and concrete (as an aggregate), the immediate concerns with strength reduction and potentially deleterious alkali-silica reaction (ASR) are discussed (Shao et al. 1998; Dyer and Dhir 2001; Naik and Kraus 1999; NRC 1993; Xie et al. 2003; CWC 2003; Meyer 2003; Shayan and Xu 2006; Idir et al. 2010). Usual precautions to avoid ASR (such as the application of low alkali cement and pozzolanic additives) were found to be effective when the waste glass was used in concrete as aggregate. The application of waste glass as a finely ground mineral additive (FGMA) in cement is another promising direction for waste glass recycling EPA (1992), Sobolev 2003a; Sobolev et al. 2004, 2005). According to Sobolev et al. (2007), FGMA glass with a high surface area participates in the relatively quick pozzolanic reactions eliminating the danger of a slower alkali-silica reaction at a later stage.

Utilization of glass powder (GLP) from mixed color waste packaging glass comprising soda-lime glass was reported by Shayan and Xu (2006). It was demonstrated that incorporating different proportions (0, 20, and 30%) of GLP (Table 7.14) as a cement replacement in 40 MPa concrete can result in some improvements with respect to drying shrinkage and alkali reactivity. Incorporation of GLP into concrete matrix decreases chloride ion penetration, thereby reducing the risk of chloride corrosion of steel rebars in concrete. The results of reported research proved that up to 30% of GLP can be used as a supplementary cementitious material to replace cement without loss in concrete performance. At the age of 28 days, concrete with up to 20% GLP met the strength requirements set for a 40 MPa concrete. Concrete with 30% of GLP effectively gained the compressive strength between the 28 and 90 days, reaching 34.0 and 50.6 MPa, respectively. It was demonstrated that considerable pozzolanic reaction occurs in GLP concrete after 7 and 28 days of hardening. At the age of over one year, concrete with 10–20% GLP reached the strength of up to 70 MPa (Shayan and Xu 2006). This

Table 7.14 The mix proportions of glass powder concrete (kg/m^3) (Shayan and Xu 2006)

| Mix number | Description | Cement | SF | GLP | Coarse aggregate | Coarse sand | Fine sand | Crushed glass | Water |
|------------|--|--------|----|-----|------------------|-------------|-----------|---------------|-------|
| Mix 1 | Reference mix | 380 | 0 | 0 | 1019 | 576 | 192 | 0 | 185 |
| Mix 2 | 10% SF in binder | 342 | 38 | 0 | 1019 | 566 | 189 | 0 | 185 |
| Mix 3 | 20% GLP in binder | 304 | 0 | 76 | 1019 | 564 | 188 | 0 | 185 |
| Mix 4 | 30% GLP in binder | 266 | 0 | 114 | 1019 | 558 | 186 | 0 | 185 |
| Mix 5 | 10% SF in binder; 50% CGS ^a | 342 | 38 | 0 | 1019 | 283 | 94 | 356 | 185 |
| Mix 6 | 20% GLP in binder; 50% CGS | 304 | 0 | 76 | 1019 | 282 | 94 | 355 | 185 |
| Mix 7 | 30% GLP in binder; 40% CGS | 266 | 0 | 114 | 1019 | 335 | 112 | 281 | 185 |
| Mix 8 | 30% GLP in binder, 75% CGS | 266 | 0 | 114 | 1019 | 141 | 47 | 523 | 185 |
| Mix 9 | No GLP; 50% CGS | 380 | 0 | 0 | 1019 | 288 | 96 | 363 | 185 |
| Mix 10 | 100% cement 50% CGS 30% GLP by mass of cement replaced fine sand | 380 | 0 | 114 | 1019 | 288 | 36 | 306 | 185 |

^aCGS—crushed glass sand

study demonstrated that the use of up to 30% of soda-lime glass did not cause deleterious AAR expansion; moreover, the obtained results and laboratory evidence indicate that GLP was an effective suppressor of AAR in concrete similar to other SCM. Figure 7.18 reports the results of a rapid chloride permeability test on the cores and cylinders. The chloride penetrability of the mixes 3 and 4 with GLP content of 20 and 30% was significantly lower than that of control (mix 1) and comparable to or lower than that of mixes 2 and 5 containing silica fume (SF).

Considerable research effort on utilization of waste glass was undertaken at Sherbrooke University by Idir et al. (2010). Most of the studies used bottle soda-lime-silica glass of mixed colors, composed of 40, 33, 20 and 1% of colorless, brown, green and blue glasses, respectively. The waste glass material also contained around 6% of impurities (Table 7.15).

It was found that the recycled glass powder with particles smaller than 75 μm does not induce alkali-silica reaction (ASR); furthermore, some studies suggested that ASR can be reduced by the addition of reactive glass powders (Shao et al. 1998; Dyer and Dhir 2001; Idir et al. 2010). According to the research results, glass particle

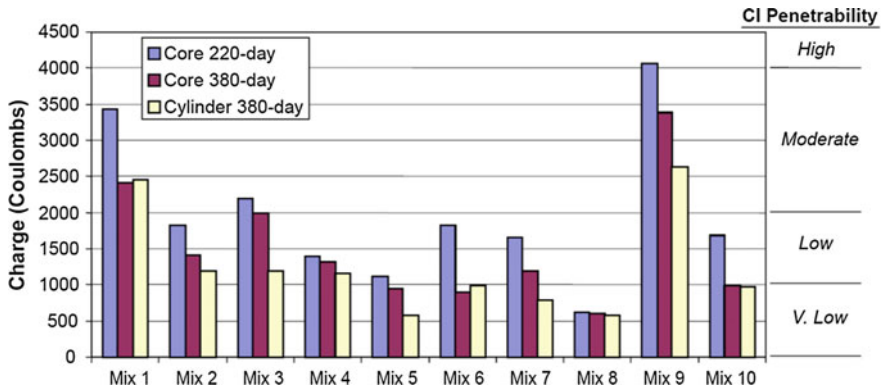


Fig. 7.18 The results of rapid chloride permeability of waste glass concrete (Shayan and Xu 2006)

Table 7.15 The chemical composition and fineness of glass powders (Idir et al. 2010)

| | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | SO ₃ | Na ₂ O | K ₂ O | LOI ^a |
|---|------------------|--------------------------------|--------------------------------|------|-----|-----------------|-------------------|------------------|------------------|
| Glass | 68.6 | 2.0 | 0.3 | 12.3 | 1.0 | 0.2 | 13.5 | 0.6 | 1.0 |
| Cement | 19.8 | 5.6 | 2.5 | 63.6 | 1.8 | 3.1 | 0.1 | 0.7 | 1.7 |
| Glass classes | C0 | C1 | C2 | C3 | C4 | C5 | C6 | C7 | C8 |
| Mean diameters of particles (pm) | 3750 | 1875 | 940 | 473 | 238 | 120 | 11 | 11 | 8 |
| Specific surface area ^b (m ² /kg) | 1 | 2 | 5 | 11 | 18 | 35 | 182 | 389 | 538 |

^aLOI—loss on ignition

^bC1–C5—calculated from the average diameter of particles

sizes less than 1 mm were not deleterious in terms of the ASR. However, it was found that the use of glass powder with particle size of 2.5–5 mm and 1.25–2.5 mm led to significant expansion of mortar specimens (Fig. 7.19).

The compressive strength of mortars containing coarse size classes of glass C0 and C1 (Table 7.15) was up to 10 MPa lower, compared to reference mortar without glass. In contrast, particles of finer classes C3–C8 systematically improved the strength, which increased with the fineness of the glass particles. The best results were obtained with fines of 80 μm or less, which demonstrated strength increase of up to 35 MPa (Idir et al. 2010).

The glass powders exhibit pozzolanic activity enabling the formation of a densified hydrated cement matrix. This material can enhance the properties of concrete with fly ash or silica fume (Khmiri et al. 2012). Some recent studies demonstrated that incorporating soda-lime-silica glass powder can improve the workability of fresh concrete (Gunalaan and Kanapathy 2013; Khatib et al. 2012; Kumarappan 2013). The 28-day compressive and relative strength values of concrete with up to 40% of waste glass powder are reported in Fig. 7.20. At 10% glass

Fig. 7.19 The effect of particle size on expansion and compressive strength of mortars with waste glass (Idir et al. 2010)

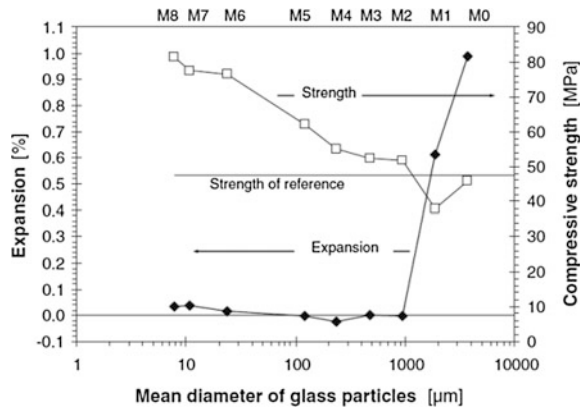
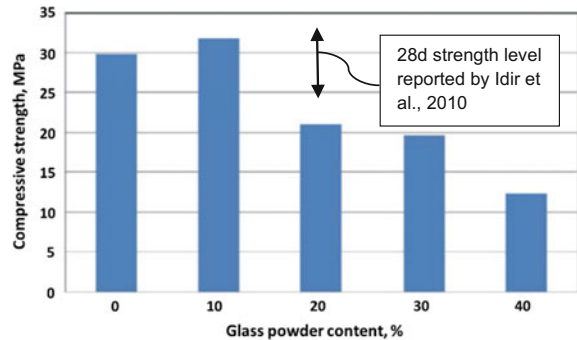


Fig. 7.20 Compressive strength characteristics of concrete with different percentage of GLP (after Khatib et al. 2012)



powder, there was an increase in compressive strength compared to the control. However, the incorporation of glass powder above 30% results in considerable reduction of compressive strength (Khatib et al. 2012).

It was demonstrated that the technology of high performance activated cement can be used for engineering of eco-cement with a high volume of mineral additives. Supersilica, a reactive silica-based complex admixture that is added during the cement grinding process, promotes the mechano-chemical activation of cement and imparts high strength and excellent durability to concrete Sobolev and Arikan (2002), Sobolev et al. (2004, 2007). In eco-cement, relatively substantial amounts (up to 70%) of portland cement clinker can be replaced with inexpensive locally available mineral additives, including waste glass Sobolev (2003a). It was proposed that the complex admixture and finely ground mineral additive (FGMA) glass containing significant amounts of amorphous, highly reactive silicon dioxide will participate in simultaneous pozzolanic reactions. A comparison study using a 2-stage grinding process was reported by Sobolev (2003a, b). The effect of FGMA glass (waste sital glass) on the strength behavior of high strength cement based materials has been reported (Sobolev 2005), and recycling of several types of waste glass was discussed (Sobolev and Arikan 2002; Sobolev et al. 2004).



Fig. 7.21 Waste glass materials used in the research (Sobolev et al. 2004)

Table 7.16 The chemical analysis of cement components (Sobolev et al. 2004)

| Composition | Clinker | Limestone (LS) | Window glass | Monitor glass | Bottle glass | |
|--------------------------------|---------|----------------|--------------|---------------|--------------|-------|
| | | | | | Brown | Green |
| SiO ₂ | 20.84 | – | 71.71 | 83.96 | 71.19 | 71.12 |
| Al ₂ O ₃ | 5.52 | – | 1.26 | 2.03 | 2.38 | 1.71 |
| Fe ₂ O ₃ | 3.61 | – | 0.09 | 0.04 | 0.29 | 0.24 |
| TiO ₂ | 0.29 | – | 0.07 | 0.20 | 0.15 | 0.07 |
| CaO | 65.57 | 52.05 | 8.44 | 0.37 | 10.38 | 10.02 |
| MgO | 2.13 | 3.04 | 4.16 | 0.01 | 1.70 | 3.01 |
| Na ₂ O | 0.82 | – | 13.61 | 7.98 | 13.16 | 13.17 |
| K ₂ O | 0.19 | – | 0.40 | 5.35 | 0.70 | 0.19 |
| SO ₃ | 0.91 | – | 0.25 | 0.05 | 0.04 | 0.25 |
| Cr ₂ O ₃ | 0.03 | – | – | – | – | 0.23 |
| Loss on ignition (LOI) | 0.23 | 42.90 | – | – | – | – |

The evaluation of the effect of four different waste glass materials (in a form of glass cullet, as per Fig. 7.21): window glass (WG), black-and-white monitor glass (MG), brown and green bottle glass (BBG and GBG, respectively) was evaluated. The chemical composition of investigated waste glass products is reported in Table 7.16. All waste glass materials were milled with clinker (ASTM Type I) and

Table 7.17 The flexural and compressive strength of glass cement mortars (Sobolev et al. 2004)

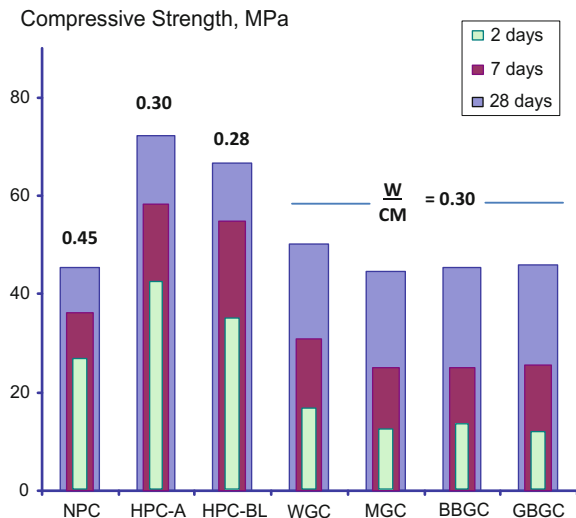
| Type | Composition, % | | | | W (cm) | Flexural strength, MPa | | | Compressive strength, MPa | | |
|--------|----------------|--------|---------------|--------------|--------|------------------------|--------|---------|---------------------------|--------|---------|
| | Clinker | Gypsum | LS W.Glass | super silica | | 2 days | 7 days | 28 days | 2 days | 7 days | 28 days |
| NPC | 95 | 5 | 0 | 0 | 0.45 | 5.5 | 5.8 | 6.7 | 26.5 | 36.1 | 45.4 |
| HPC-A | 85 | 5 | 0 | 10 | 0.30 | 6.0 | 7.3 | 8.5 | 42.1 | 58.4 | 72.3 |
| HPC-BL | 48 | 2 | 40 | 10 | 0.28 | 5.3 | 6.9 | 8.7 | 34.8 | 54.8 | 66.7 |
| WGC | 35 | 5 | 50 | 10 | 0.30 | 3.4 | 4.5 | 7.2 | 16.4 | 31.0 | 50.1 |
| MGC | 35 | 5 | 50 | 10 | 0.30 | 3.0 | 4.3 | 7.0 | 12.1 | 25.0 | 44.5 |
| BBGC | 35 | 5 | 50 | 10 | 0.30 | 3.0 | 4.2 | 6.9 | 13.2 | 25.0 | 45.3 |
| GBGC | 35 | 5 | 50 | 10 | 0.30 | 2.6 | 4.2 | 7.3 | 11.6 | 25.5 | 46.0 |

reactive silica-based complex admixture supersilica. These eco-cements were compared with reference cements such as portland cement CEM-I 42.5 (NPC), high strength cement Type A (HPC-A) and Type B (HPC-BL containing 35% of limestone, LS) Sobolev 2003a; Sobolev et al. 2004).

The 2-day compressive strength of activated cements was almost the same for the group of glass cements, where glass cement based on WG demonstrated the best strength. Similar behavior of cement with waste glass was observed at the age of 7 days (Table 7.17 and Fig. 7.22). Considerable delay with strength development of eco-cement (vs. NPC), at the level of up to 50% at 2 days and 30% at 7 days, was explained by the use of a very low clinker content (35%). The simultaneous pozzolanic reactions, as well as the hydration of cementitious matrix at a low W/C ratio, helped to offset this trend at later stages of hardening. Binders with 50% of waste glass had the 28-day flexural and compressive strength at a level similar to NPC, in the range of 6.9–7.3 and 44.5–66.7 MPa, respectively. The best compressive strength was demonstrated by the cement based on the window and green bottle glass (Sobolev et al. 2004). It was mentioned that the low-water demand property of developed cement results in mixtures with very high workability obtained at a relatively low W/CM. This feature helps to improve the strength of mortars and also to offset the performance of slow-reacting mineral additives.

The selection of an appropriate method to produce blended cement is essential in the manufacture of the final product with the required specifications. It was proposed that the pre-grinding of waste glass to obtain the particles of finer size than those of cement clinker (e.g., in the form of FGMA) can considerably improve the strength characteristics of blended cement with waste glass (Sobolev et al. 2004).

Fig. 7.22 The compressive strength of glass cement mortars (W/C ratio was different among the reference and waste glass cements) (Sobolev et al. 2004)



7.8 Conclusions

There are many examples of successful utilization of industrial by-products in the cement industry, and the largest commodity sector, the concrete industry, demonstrates the increasing demand and interest in the use of new cement replacing materials, including mineral powders and aggregates from non-traditional sources such as industrial by-products (IBP), off-spec pozzolans and recycled waste.

There has been considerable interest in realizing the potential utilization of industrial by-products and waste (IBP) as a component of binders or blended cement. According to wide-scale investigations, the performance of concrete with controlled volumes of SCM can be improved. The combination of well-investigated mineral additives such as granulated blast furnace slag, fly ash, and silica fume not only bring about concrete with improved properties and economical effectiveness, but they also improve the eco-balance of these materials. Such materials, particularly in finely divided form can improve the performance of concrete such as permeability, sulfate resistance, and resistance to alkali-silica reaction and chloride resistance. Depending on the performance, the optimal substitution rate is established for mineral additives to determine (a) whether the material is indeed improving the property, and (b) the correct dosage, as an overdose or under-dose can be detrimental for the performance or not allow for achieving the desired effect.

The availability of decent quality SCM and CCP is still limited and cannot offset the need for higher volumes of cement and concrete as required by developing markets. Following the industrial development, the volumes of IBP have significantly increased and will expand in the future creating several economic and ecological problems. Consequently, there is a demand for the development and application of technologies to reduce the IBP and pivot the associated waste streams to the supply of raw materials. Following this demand, the use of alternative supplementary cementitious materials discussed in this report such as steel slag, bottom ash, sugarcane bagasse ash, including “off-spec” products such as low SiO₂ silica fume and less-investigated by-products such as waste glass can be very promising. It was demonstrated that such materials can be valuable components of blended cements.

The reactivity of LS and EAF slag increases with its fineness achieved by grinding, which can provide an improved performance. This trend was attributed to the increase of the reactivity of the binders due to the milling and higher surface area. Finely ground LS can be effectively used as a filler material in self-compacting concrete providing improved workability, strength, and durability. Up to 30% of EAF slag can be used in the multicomponent binders incorporating fly ash and blast-furnace slag. Due to fine tuning, these binders have demonstrated a better strength vs. reference portland cement systems. Furthermore, the use of ternary fly ash—portland—steel slag blended cement reduces the detrimental effect of free-CaO from steel slag resulting in a cementitious material with lower drying shrinkage and improved corrosion resistance.

Up to 25% of pulverized bottom ash can be used as an effective pozzolanic additive complementing commonly used fly ash. It was proposed that an additional grinding of bottom ash can enhance the mechanical properties of mortars and concrete.

Processed sugarcane bagasse ash (SCBA) can be used as a pozzolanic material in blended cements providing a positive impact on durability. This component presents a viable alternative to fly ash in regions with limited availability of fly ash.

The use of silica fume with reduced SiO_2 content (such as off-spec silica fume with 65-70% of SiO_2) in blended cement and concrete is beneficial enabling the increase of compressive strength. In this regard, the use of ferrosilicon (FS) type of silica fume with a large surface area and SiO_2 content of 70% had the most significant impact on performance of cement based materials. Water and gas permeability of concrete with off-spec silica fume was lower than that of reference concrete.

Glass powders exhibit pozzolanic activity enabling the formation of a densified hydrated cement matrix. This enables to enhance the properties of concrete with fly ash or silica fume. Incorporating of 10% of soda glass powders can improve the workability and strength of concrete.

The use of fine glass powders systematically improves the compressive strength of mortars and concrete, which was increased with the fineness of the glass particles. The best results were reported for glass powders with particle size of less than 80 μm which demonstrated an increase of strength by up to 35 MPa.

The selection of an appropriate method to produce blended cement is essential in the manufacture of the final product to meet the required specifications. It was demonstrated that pre-grinding of waste components to obtain particles of finer size than those of cement can considerably improve the strength characteristics of blended cements. It was demonstrated that the use of mechano-chemical activation can significantly improve the performance of cement-based materials and engineer cements with high volumes of supplementary cementitious materials including alternative components and IPB. The developed eco-cements can be available at a significantly reduced cost, making the application of alternative components feasible. Fine milling and mechano-chemical activation can further extend the limits of IBP utilization in blended cements; however, there is a need for quick and reliable separation of undesirable components from alternative components. As most of the research work was focused on mechanical properties and compatibility of alternative components and portland cement matrix, there is a need to investigate the long-term performance of these components including the durability, corrosion resistance, deformational stability and potential leaching of heavy metals. Often IBP have higher levels of heavy metals than traditional SCM, and, therefore, the long-term environmental behavior of these materials must be analyzed. The challenges must be addressed for successful utilization of IBP in cement and concrete. Upon verification of these parameters, alternative components can fill the void in the raw materials supply for sustainable blended cements and future construction.

Certainly, the current economic conditions make recycling feasible for only a limited number of products. Waste materials can be used only when they can be collected, processed, and reused at a cost the same or less than natural raw materials. The inconsistency of the waste streams sometimes makes it more difficult to separate the required product from other recycled materials and so minimize contamination, especially for fine fractions. To increase the rates of recycling, cement and concrete manufacturers need a uniform supply of quality waste; this would require better sorting and also the development of waste identification technology. On the other hand, it is also evident that new alternative technologies capable of tolerating multiple contaminants are needed to boost the recycling of industrial waste products beyond the current limits.

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Chapter 8

Rice Husk Ash

Guang Ye, Hao Huang and Nguyen Van Tuan

Abstract This chapter reviews the performance of rice husk ash (RHA) as partial cement replace in ordinary Portland cement concrete. After pyroprocessing with controlled combustion, highly pozzolanic RHA can be produced. Due to the high specific surface area and pozzolanic properties, RHA shows very good performance as a supplementary cementitious material in concrete. For early age properties, concrete made of RHA needs more water and high dosages of superplasticizer compared to ordinary Portland cement concrete. The RHA concrete has slightly longer setting times than ordinary Portland cement concrete. When the replacement level of ordinary Portland cement by RHA is about 20% by weight of the total binder material, the compressive strength, tensile strength and flexural strength of concrete made of RHA are enhanced. Due to the special porous structures, RHA shows excellent capacity to keep high relative humidity in the concrete, thus RHA significantly mitigates the autogenous shrinkage of concrete, especially high performance or ultra-high performance concrete made with RHA as addition. From water permeability and chloride diffusivity tests the coefficient of water absorption of RHA concrete is lower and the chloride diffusion coefficient is reduced.

Keywords Rice husk ash · Supplementary cementitious materials
Pozzolanic reaction · Concrete properties

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8.1 Introduction

8.1.1 General

The rice plant is one of the plants that absorbs silica from the soil and assimilates it into its structure during the growth (Smith and Kamwanja 1986). Rice husk is the outer covering of the grain of rice plant with a high concentration of silica, after burning generally more than 80–85% (Siddique 2008). It is responsible for approximately 30% of the gross weight of a rice kernel and normally contains 80% of organic and 20% of inorganic substances. The husk normally contains about 50% cellulose, 25–30% lignin, and 15–20% of silica. Upon burning, cellulose and lignin are removed, leaving behind silica ash. On the average, each ton of rice husks, on completion of combustion, produces 200 kg of ash. In 2010 the world-production of rice paddy is approximately 690 million tonnes; thus about 140 million tonnes of rice husks are available for disposal.

There are several methods to convert rice husks to ash that have been suggested. In 1973, Mehta (1973) investigated the effect of pyroprocessing on the pozzolanic reactivity of RHA. Based on his work, Pitt (1976) developed a fluidized bed furnace for the controlled combustion of rice husk. It was found that when the temperature of burning and the residency time inside the furnace are controlled, highly pozzolanic RHA could be produced. Since then, many attempts have been made to produce and use reactive RHA in several countries including, among others, China, Vietnam, Japan, India, Guyana, Malaysia, Senegal, Taiwan, and the UK (Yu et al. 1999; Yamamoto and Lakho 1982; Boateng and Skeete 1990; Singh et al. 1994; Mahmud et al. 1997; Cisse and Laquerbe 2000; Cook et al. 1976; Hwang and Wu 1989; Zhang and Malhotra 1996; Bouzoubaa and Fournier 2001; Bui et al. 2005).

There are two forms of RHA, i.e. the crystalline and amorphous RHA after thermal treatment. The amorphous RHA is a highly reactive pozzolanic material suitable for use in lime-pozzolana mixes and for Portland cement replacement (Smith and Kamwanja 1986; Zhang and Malhotra 1996; Nicole et al. 2000; Sakr 2006; Sata et al. 2007). The use of RHA in concrete has been associated with the following essential assets: increased compressive and flexural strengths (Zhang and Malhotra 1996; Ismaila and Waliuddin 1996; Rodriguez 2006); reduced permeability (Zhang and Malhotra 1996; Ganesan et al. 2008), increased resistance to chemical attack (Chindaprasirt et al. 2007). RHA could reduce the effects of alkali-silica reactivity (ASR) (Nicole et al. 2000) and reduced shrinkage (Habeeb and Fayyadh 2009; Ye and Nguyen 2012).

8.1.2 Environmental Issue of RHA

To obtain a major reduction in the CO₂ emission associated with cement production, the clinker content of the final product must be lowered as much as possible by

maximizing the proportion of mineral admixtures in cement, and by increasing the use of blended cements in general construction (Mehta 2002, 2009). Among the technically acceptable and economically available mineral admixtures produced every year, such as fly ash (500 million tons), limestone (170 million tons), and blast-furnace slag (75 million tons), RHA with about 28 million tons also offers a potential for reducing a considerable amount of the CO₂ emission attributable to the cementitious materials used in concrete.

During rice cultivation, the bulky nature of rice husk could cause difficulty for storage and transportation. When rice husk is not treated properly, such as dumping into ponds or streams, it seriously pollutes the environment. Using the ash obtained from the husk combustion as a mineral admixture in concrete is one of the useful solutions. As a result, the problems and costs associated with the environmentally safe disposal of this waste can be reduced or sometimes entirely eliminated. The socio-economic benefits, achieved by the utilization of RHA as a mineral admixture in concrete, are now well recognized by all those concerned with the production, disposal, and utilization of this waste.

Like other biomass (e.g. wood), the content of S in rice husk is very low, and the toxic gas generated in the burning of rice husk does not cause a significant damage to human's body.

8.1.3 Reactivity and Pozzolanic Reaction of RHA

The reactivity of RHA associated to lime depends on a combination of two factors: namely the non-crystalline silica content and its specific surface (Dakroury and Gasser 2008). The surface area of the incinerated ash is 60–100 m²/g when determined by nitrogen adsorption. The chemical analyses of the ashes produced by the incineration of rice husks show that the silica content ranges from 90 to 95%, alkalis (K₂O and Na₂O) from 1% to 2%, and unburnt carbon from 3% to 18% (Della et al. 2002). The XRD pattern (He et al. 2013) in Fig. 8.1 shows one sharp peak superimposed on a broad hump at 10–35 2θ. The sharp peak is from cristobalite, a high-temperature polymorph of silica. The very broad hump is from amorphous silica, a major constituent in RHA. A very weak peak from quartz, a crystalline phase of silica, is also present, but its height is masked by the broad hump from the amorphous silica. According to the chemical composition, silica in the RHA is mainly present as amorphous phase with cristobalite and traces crystalline quartz.

As a consequence of the characteristic, RHA is an extremely reactive pozzolanic substance appropriate for use in lime-pozzolana mixes and for Portland cement replacement. The scanning electron microscopic images of typical RHA indicated that RHA particles are angular and still keep the porous structure after grinding as shown in Fig. 8.2 (Nguyen et al. 2011). Experiments have shown that rice husk ash when replacing cement will accelerate the early hydration of C₃S. This is attributed to the high specific surface area of the rice husk ash (Feng et al. 2004).

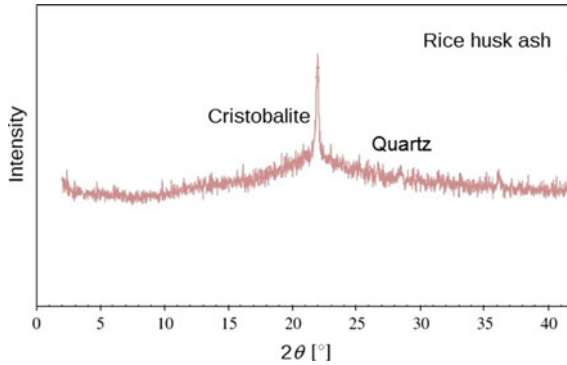


Fig. 8.1 XRD pattern of rice husk ash Reproduced from He et al. (2013)

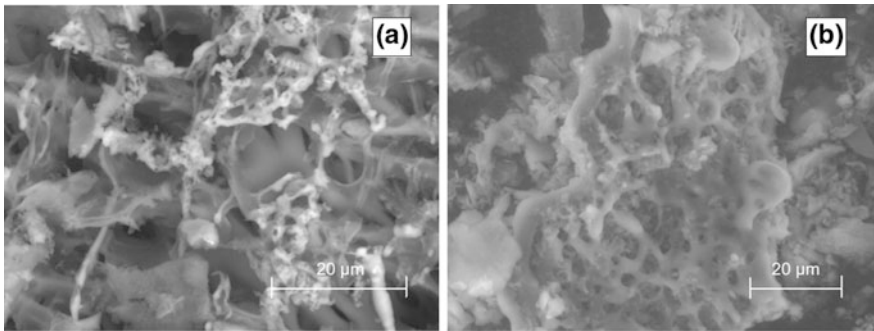


Fig. 8.2 SEM images of RHA before grinding (a) and after grinding (b) (Nguyen et al. 2011)

This phenomenon specially takes place with fine particles of RHA. Although the small particles of pozzolans are less reactive than Portland cements (Mehta 1990), they produce a large number of nucleation sites for the precipitation of the hydration products by dispersing in cement pastes. Consequently, this mechanism creates the more homogenous and denser paste as for the distribution of the finer pores due to the pozzolanic reactions between the amorphous silica of the mineral admixture and the calcium hydroxide (CH) (Isaia et al. 2003). Mehta (1987) reported that the finer particles of RHA speed up the reactions and form smaller CH crystals. Berry et al. (1994) revealed that high volume of not completely reacted pozzolanic particles in the cement paste might fill up the voids and enhance density of the paste.

As mentioned, the addition of RHA in cement paste leads to a reduced CH content caused by the pozzolanic reaction. Nguyen (2011) investigated the reactivity and pozzolanic reaction of RHA by comparison with silica fume (SF). The content of $\text{Ca}(\text{OH})_2$ present from 0.25 to 360 days in cement paste with and without RHA and SF is shown in Fig. 8.3. It can be seen that the addition of RHA decreases strongly the content of $\text{Ca}(\text{OH})_2$ of cement paste beyond 3 days for both w/b ratios

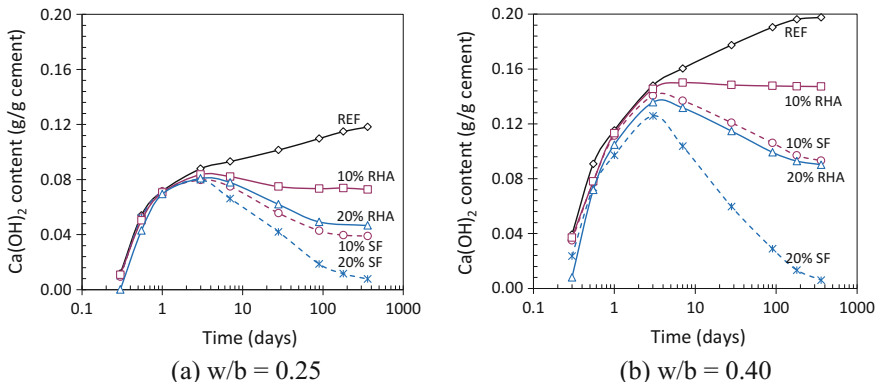


Fig. 8.3 The content of Ca(OH)_2 of cement blended with 0, 10 and 20% RHA or SF at ages from 0.25 to 360 days (Nguyen 2011).

of 0.25 and 0.40. The Ca(OH)_2 content falls to a well-defined minimum, which occurs at about 91 days. Compared with the SF paste, the RHA paste had similar CH content from 0.25 to 3 days, but higher values after 7 days. More added SF strongly decreases the CH content of cement paste. This can be caused by the more significant pozzolanic reaction of SF versus time than that of RHA.

8.2 Effect of RHA on Fresh Concrete Properties

8.2.1 Influence on Workability and Bleeding

Laskar and Talukdar (2008) examined the effects of RHA on the rheological behaviour of high performance concrete. In their study, RHA was used to replace cement on mass basis at rates of 5, 10, 15 and 20%. Based on their test results, plastic viscosity increases tremendously with the increase in cement replacement level of RHA. RHA particles have the highest surface area and fineness and lower reaction ability than cement (Shetty 2004). RHA particles fill into the spaces made by larger cement particle, decrease frictional forces of RHA-ordinary Portland cement (OPC) system and improve packing efficiency thereby reducing the yield stress. The steep increase in plastic viscosity with the replacement levels suggests that fineness and shape of RHA play a critical role. The higher fineness and the higher number of contacts among the particles result in the higher resistance to flow. (Nehdi et al. 1998).

Due to the hydrophilic nature and high specific surface of RHA, the water demand increases (Nehdi et al. 2003; Givi et al. 2010). The concrete incorporating RHA required higher dosages of the superplasticizer and the air-entraining admixture than those of the control Portland cement and silica fume concretes to

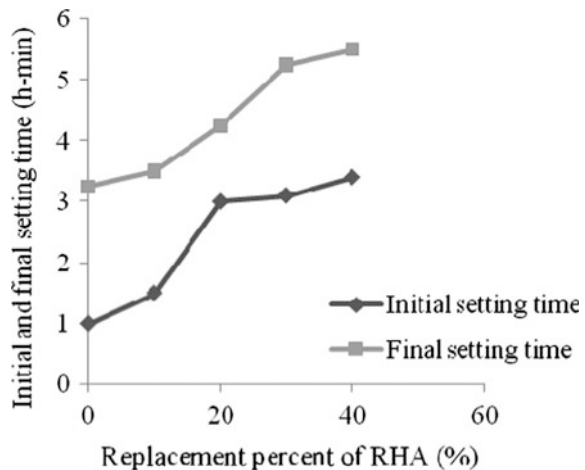
achieve the same slump and air content (Cordeiro et al. 2009; Hwang et al. 2011). However, studies by Owen (1979) and Jiang and Malhotra (2000) show a different behaviour. They found that there is the possibility of water reduction higher than 20% in the presence of RHA compared to ordinary Portland cement concrete. This is because fine particles of rice husk ash get absorbed on the oppositely charged surfaces of cement particles and prevent them from flocculation. The cement particles are thus effectively dispersed and will trap a large amount of water meaning that the system will have a reduced water requirement to achieve a given consistency.

The bleeding of the concrete incorporating RHA was negligible (Zhang and Malhotra 1996).

8.2.2 Influence on Setting Time

Initial and final setting time tests were shown to yield different results on plain cement paste and pastes containing rice husk ash (Dakroury and Gasser 2008). The studies by Ganesan et al. (2008), Cook (1986), and Bhanumathidas and Mehta (2004) showed that addition of RHA increases the setting time of pastes. Just like for hydraulic cement, the reactivity of rice husk ash cement depends significantly upon the specific surface area or particle size. The rice husk ash cement with finer particles exhibits superior setting time behaviour. Research has shown the increase of the initial setting time by increasing the RHA content compared to plain cement paste. Dakroury and Gasser (2008) concluded that this might be due to the slower pace of heat-induced evaporation of water from the cement and RHA mixture (Fig. 8.4).

Fig. 8.4 Initial and final setting times of cement paste containing RHA with different cement replacement percentages (Dakroury and Gasser 2008)

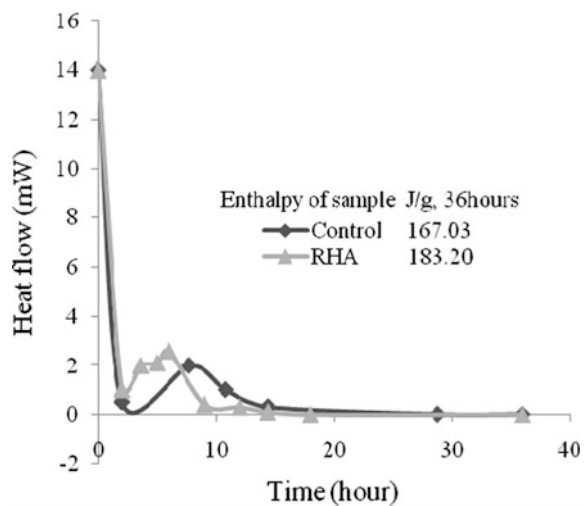


8.2.3 Temperature Effects in Concrete

Exothermic reactions occur during the cement hydration. Hydration heat is an essential aspect that influences the setting and behaviour of Portland cements. This temperature variation, from the initial moment of setting until the hardening of the cement paste, may cause shrinkage, which results in the cracks formation that can be seen in some constructions (Rojas et al. 1993). Cement blended with pozzolanic materials usually has decreased heat of hydration compared to pure cement during the period of C_3S hydration (Mostafa and Brown 2005). The rate of hydration heat release of the cement added with pozzolanic material mainly depends on three factors, calcium silicate (C_3S) hydration, aluminates (C_3A) hydration and pozzolanic reaction (Hewlett 1998). Likewise, RHA showed an increase of hydration heat behaviour (positive values) during the first 12 h. The increase in the hydration heat of cement blended with RHA may be due to (1) the acceleration of the early hydration of C_3S ascribed to the high specific surface area of the RHA (Feng et al. 2004) and (2) pozzolanic reaction. The comparison between the hydration heats of control sample (plain cement) with samples by partial pozzolanic materials replacement of cement is shown in Fig. 8.5. Figure 8.5 demonstrates the cement added with RHA has larger enthalpy compared to the plain cement (within 36 h). These effects can be summarized as the pozzolanic activity and the dilution effect. The pozzolanic effect is expected to increase the heat output due to the reaction of pozzolans with calcium hydroxide. The dilution effect is expected to decrease the heat output due to the dilution in the main cement compounds (C_3S) (Mostafa and Brown 2005).

The replacement of cement by condensed SF and RHA does not lower the temperature rise and their use for this purpose is not recommended (Malhotra 1993).

Fig. 8.5 Calorimetric curves from the hydration of cement with 30% by weight of RHA (Feng et al. 2004)



8.3 Influence of RHA on Mechanical Properties of Concrete

8.3.1 Effect of RHA on Compressive Strength of Concrete

The incorporation of RHA as a partial replacement of cement enhances the compressive strength of concrete. The optimum replacement level of OPC by RHA to give maximum long-term strength enhancement has been reported between 10% up to 30% by weight of the total binder material (see Table 8.1). Ganesan et al. (2008) replaced OPC in concrete by RHA from 5 to 35% by weight of cement and tested the compressive strength from 7 to 90 days. He concluded that 15 to 20% cement replacement by RHA appeared to be an optimal level for achieving maximum strength for all ages. However, Dakroury and Gasser (2008) reported that using 30% RHA as a partial replacement of cement could be considered optimum for all water to cement ratios (w/c) in investigated mortar cubes because of its high value of compressive strength. For 50% cement replacement mixes, there was a significant reduction in the compressive strength of mortar samples at early ages as well as at 60 days (Al-Khalaf et al. 1984).

The increase in compressive strength of concretes with residual RHA may also be justified by the filler (physical) effect. It is concluded that RHA can provide a positive effect on the compressive strength of concrete at early ages. In the long term, the compressive strength of concrete blended with RHA produced by controlled incineration shows better performance. According to Rodriguez (2006), the RHA concrete had higher compressive strength at 91 days in comparison to that of the concrete without RHA. Zhang and Malhotra (1996) reported that achieving higher compressive strength and decrease of permeability in RHA blended concrete are perhaps caused by the reduced porosity, reduced calcium hydroxide content and reduced thickness of the interfacial transition zone between the paste and the aggregate. The development of more C–S–H gel in concrete containing RHA due to the reaction between RHA and calcium hydroxide in hydrating cement may progress the concrete properties (Yu et al. 1999).

8.3.2 Effect of RHA on Tensile and Flexural Strength of Concrete

Habeeb and Fayyadh (2009) investigated the effects of concrete incorporating 20% RHA as a partial replacement of cement at three different particle sizes. In their study the tensile strength of concrete increased slightly with increasing RHA replacement. The results of tensile and flexural strength of concrete containing RHA with different particle sizes are shown in Table 8.2.

The use of RHA also resulted in slight improvement in flexural strength of concrete (Habeeb and Fayyadh 2009; Sensale 2006; Sakr 2006; Hesami et al. 2014).

Table 8.1 Compressive strength of concrete made with RHA as a partial cement replacement

| Mix No | RHA (%) | Quantities (kg/m ³) | | Water (kg/m ³) | Aggregate | | Compressive Strength (MPa) | | | | Citation |
|--------|---------|---------------------------------|------|----------------------------|-----------|--------|----------------------------|---------|---------|------------------------|----------|
| | | Cement | RHA | | Fine | Coarse | 7 days | 28 days | 90 days | | |
| | | | | | | | | | | | |
| 0 | 0 | 383 | 0 | 203 | 1150 | 575 | 27.2 | 37.1 | 38.3 | Ganesan et al. (2008) | |
| 1 | 5 | 364 | 19 | 203 | 1150 | 575 | 27.6 | 40.0 | 43.3 | Ganesan et al. (2008) | |
| 2 | 10 | 345 | 38 | 203 | 1150 | 575 | 28.0 | 41.3 | 44.8 | Ganesan et al. (2008) | |
| 3 | 10 | 279 | 31 | 186 | 1020 | 835 | – | 39 | – | Antiohos et al. (2014) | |
| 4 | 10 | 481 | 53.4 | 172 | 1050 | 690 | 51.1 | 60.4 | 64.3 | Sensale et al. (2006) | |
| 5 | 15 | 326 | 57 | 203 | 1150 | 575 | 29.3 | 41.8 | 45.7 | Ganesan et al. (2008) | |
| 6 | 15 | 360 | 64 | 191 | 767 | 957 | – | 42.9 | – | Chalee et al. (2013) | |
| 7 | 20 | 306 | 77 | 203 | 1150 | 575 | 29.7 | 42.5 | 46.0 | Ganesan et al. (2008) | |
| 8 | 20 | 427 | 107 | 172 | 1050 | 690 | 44.3 | 54.8 | 62.7 | Sensale et al. (2006) | |
| 9 | 20 | 248 | 62 | 186 | 1030 | 840 | – | 37 | – | Antiohos et al. (2014) | |
| 10 | 25 | 287 | 96 | 203 | 1150 | 575 | 28.7 | 38.8 | 43.0 | Ganesan et al. (2008) | |
| 11 | 30 | 268 | 115 | 203 | 1150 | 575 | 27.4 | 37.6 | 38.7 | Ganesan et al. (2008) | |
| 12 | 30 | 400 | 171 | 215 | 557 | 933 | 43 | 54 | 64 | Hwang et al. (2011) | |
| 13 | 35 | 249 | 134 | 203 | 1150 | 575 | 25.7 | 35.1 | 37.2 | Ganesan et al. (2008) | |

Table 8.2 Mechanical properties of concrete (Habeeb and Fayyadh 2009)

| Mix | Flexural strength (MPa) | | | Tensile splitting strength (MPa) | | |
|-------------------|-------------------------|-----|-----|----------------------------------|-----|-----|
| | Age (days) | | | Age (days) | | |
| | 28 | 90 | 180 | 28 | 90 | 180 |
| CM ^a | 4.5 | 4.9 | 5.1 | 2.6 | 2.8 | 2.9 |
| 20F1 ^b | 4.9 | 5.4 | 5.5 | 2.9 | 3.0 | 3.2 |
| 20F2 ^c | 5.0 | 5.4 | 5.7 | 3.2 | 3.3 | 3.5 |
| 20F3 ^d | 5.2 | 5.7 | 6.1 | 3.2 | 3.5 | 3.9 |

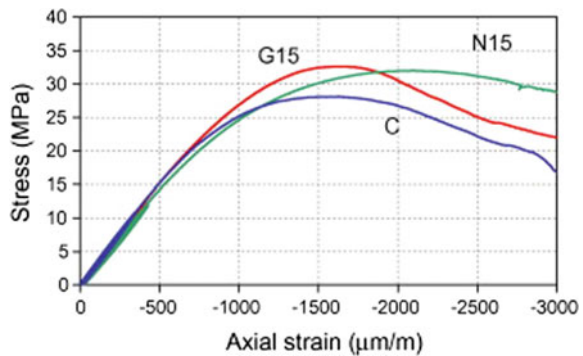
^aControl mix

^bRHA with average particle size of 31.3 μm

^cRHA with average particle size of 18.3 μm

^dRHA with average particle size of 11.5 μm

Fig. 8.6 Stress–axial strain curves in compression, N15—natural RHA, G15—ground RHA, C—reference concrete (Zerbino et al. 2011)



Hesami et al. (2014) stated that the increase in flexural strength could be due to the improvement of the bond between the cement paste and aggregate in the presence of RHA. It is clear from Table 8.2 that the coarser RHA particle mixture showed the least improvement in flexural strength as well in tensile splitting strength. This might be caused by the increased pozzolanic reaction and the packing efficiency of the RHA fine particles.

8.3.3 Effect of RHA on Stress-Strain Relation and Modulus of Elasticity of Concrete

Figure 8.6 compares the stress-axial strain curves of concretes C (reference concrete), N15 (natural RHA, 15% replacement) and G15 (ground RHA, 15% replacement) at 28 days. The modulus of elasticity was 30.8, 28.3 and 31.3 GPa for concretes C, N15 and G15 respectively. As it was indicated, the incorporation of RHA does not cause significant changes in the modulus of elasticity-strength relationship (Zerbino et al. 2011).

Table 8.3 Elastic modulus and flexural strength of concrete mixes at 56 days (Salas et al. 2009)

| Mix* | Modulus of elasticity (GPa) | Flexural strength (MPa) |
|---------|-----------------------------|-------------------------|
| Control | 29.1 | 3.7 |
| TRHA | 30.2 | 4.5 |
| SF | 31.8 | 5.1 |
| ChRHA | 32.1 | 5.4 |

*Control conventional concrete

TRHA concrete made of 10% conventional type RHA as partial replacement of cement

SF concrete made of 10% silica fume as partial replacement of cement

ChRHA concrete made of 10% chemically treated RHA as partial replacement of cement

Salas et al. (2009) examined the mechanical properties of concrete made of 10% of thermal treated RHA (TRHA) and chemical treated RHA (ChRHA) and compared to concrete of 10% silica fume (SF) and ordinary Portland cement concrete (control). The tests results for flexural strength and modulus of elasticity of the concretes are given in Table 8.3. These data also confirmed that flexural strength and modulus of elasticity of the control and TRHA mixes are comparable, while the same properties are comparable for SF and ChRHA (Chemical treated RHA) added mixes (Salas et al. 2009).

Zhang and Malhotra (1996) also found that even if the RHA concrete had lower compressive strengths at ages up to 180 days compared with that of the silica fume concrete, the flexural and splitting tensile strengths, modulus of elasticity, and drying shrinkage were comparable.

8.4 Influence of RHA on Shrinkage and Creep of Concrete

8.4.1 Effect of RHA on Shrinkage of Concrete Mixes

The higher the replacement level of RHA in concrete, the more the volume change characteristics differ from with those of the ordinary Portland cement mixes.

Sensale et al. (2008) claimed that RHA has considerable influence on autogenous deformation and on the autogenous relative humidity change of hardening Portland cement paste with low w/b. RHA markedly decreases the autogenous shrinkage as well as produces an autogenous relative humidity change. Huang and Ye (2016) examined the relative humidity of cement paste with w/b ratio of 0.25, made of 20% RHA addition with different particle sizes and compared to reference sample without RHA (Fig. 8.7). They tested the RH change 20 min after casting. They found that relative humidity started to differ after 2 days curing.

An increase in the RHA content decreases the autogenous deformation. Figure 8.8a shows the development of autogenous shrinkage of ultra-high performance cement paste incorporating different amounts of RHA with average particle size of 5.6 μm (Ye and Nguyen 2012). When a higher amount of RHA is added,

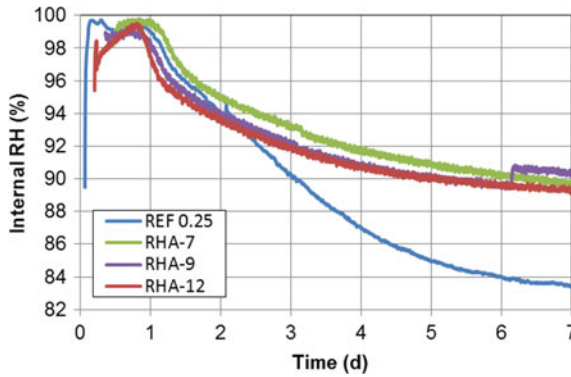


Fig. 8.7 Internal RH change of different cement pastes in 7 days (Huang and Ye 2016)

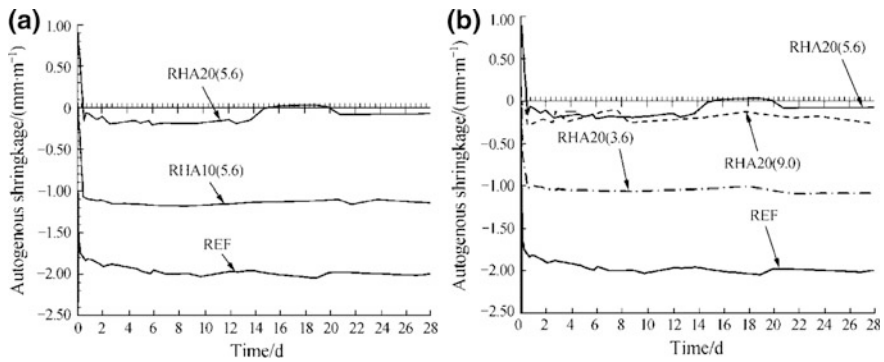


Fig. 8.8 Autogenous shrinkage of UHPC mixtures (water/binder = 0.18) with **a** different amounts of RHA with $d_{(RHA)mean} = 5.6 \mu m$, and **b** with different mean particle sizes, measured from the final setting time (Ye and Nguyen 2012)

i.e. 20%, the autogenous shrinkage of UHPC is significantly reduced compared to the reference sample without RHA. After the first twelve hours from the final set, the RHA modified samples show only a very small increase in autogenous shrinkage. In addition, after reaching the age of 10 days, the autogenous shrinkage of the RHA modified samples was further mitigated. Especially the autogenous shrinkage of the 20% RHA sample was even completely eliminated after 15 day of curing.

The effect of the fineness of RHA on autogenous shrinkage is depicted in Fig. 8.8b (Ye and Nguyen 2012). It is clear that RHA particles are particularly effective in mitigating the autogenous shrinkage of UHPC when the mean size of RHA particles ranges between 5.6 and 9.0 μm . The sample containing the RHA with a smaller particle size, i.e. 3.6 μm , shows a higher autogenous shrinkage. This may be caused by the collapse of the porous structure, which reduces the amount of absorbed water in RHA. The less absorbed water will reduce the positive effect of

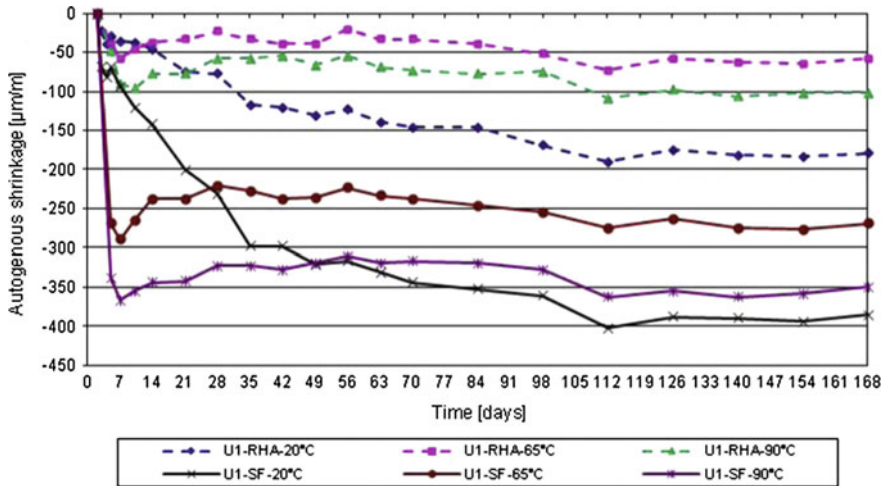


Fig. 8.9 Autogenous shrinkage of UHPC containing RHA or SF at different treatment conditions (Van et al. 2014)

RHA particles to mitigate the autogenous shrinkage of UHPC. This result implies that the benefit of RHA on reducing the autogenous shrinkage can be achieved when the mean particle size is bigger than 5.6 µm.

Similar results were also found by Van et al (2014), they investigated the influence of curing temperature (20, 65 and 90 °C) on the autogenous shrinkage of UHPC incorporating 20% RHA and compared to the UHPC made with the same amount of silica fume. They found that UHPC with 20% RHA has significant lower shrinkage deformation when cured at 65 and 90 °C (Fig. 8.9).

Similarly, Habeeb and Fayyadh (2009) studied the effect of RHA on dry shrinkage of concrete mixtures containing 20% of RHA at three different average particle sizes. They also concluded that the drying shrinkage was significantly affected by RHA fineness. The addition of micro fine particles of RHA to concrete would increase the drying shrinkage. While coarser particles of RHA exhibited lower values than those of the plain cement based concrete. These contributions can be justified by the pozzolanic and the filler effects on the microstructure, especially the pore structure of cement paste.

8.4.2 Effect of RHA on Creep of Concrete

Figure 8.10 shows the evolution of total strains under loading, the differed strains, the free shrinkage strains, and the weight losses corresponding to C (reference concrete), N15 (natural RHA, 15% replacement) and G15 (ground RHA, 15% replacement) (Zerbino et al. 2011). All specimens were stored in a dry room

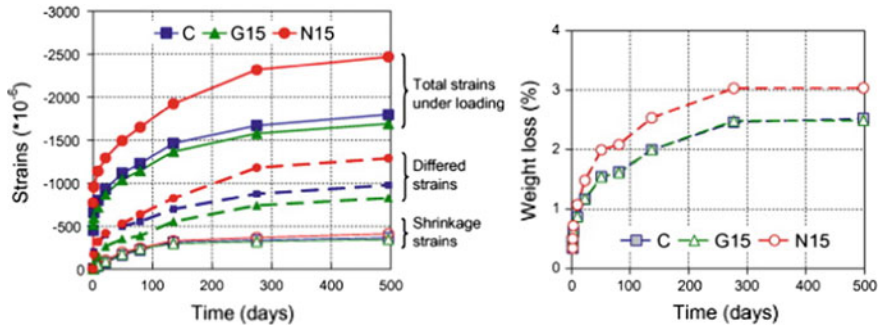


Fig. 8.10 Creep tests: (left) total strains under loading, differed creep strains, and free shrinkage strains; (right) weight losses during exposure in dry room. N—natural RHA, G—ground RHA (Zerbino et al. 2011)

(21 ± 2 °C and $55 \pm 5\%$ moisture humidity). The smallest differed strains correspond to G15; this can be attributed to a reduction in porosity both at the interfaces and into the bulk cement paste. The free shrinkage strains were similar in all concretes, but the weight loss was greater in concrete N15. The same occurs with the elastic strains. Creep and shrinkage were similar in reference concrete and concretes containing ground RHA or natural RHA. However, increases in weight losses and higher elastic and differed strains, that can be associated with differences in the pore size distribution, were observed in natural RHA concrete (Zerbino et al. 2011).

8.5 Influence of RHA on Transport Properties of Concrete

8.5.1 Effect of RHA on Water Permeability of Concrete

Ganesan et al. (2008) tested the coefficients of water absorption of RHA blended concrete specimens, presented in Table 8.4. It can be seen that at 28 days of curing, coefficient of water absorption progressively decreased with increase in RHA content up to 25%. At 30 and 35% RHA there is an increase in coefficient of water absorption and these values are also lower than that of control concrete specimens. At 90 days of curing, the coefficient of water absorption values are lower for all concrete specimens with RHA content up to 35% confirming that with prolonged curing, the presence of RHA leads to a reduction of permeable voids.

The sorptivity values calculated for RHA blended concrete specimens after 28 and 90 days of curing are also presented in Table 8.4. It can be seen that at 28 days of curing, sorptivity progressively decreases with increase in RHA content up to 25%. At 30 and 35% RHA there is an increase in sorptivity and these values are also lower than that of control concrete. At 90 days of curing, the sorptivity values

Table 8.4 Permeability related properties of RHA blended concretes (Ganesan et al. 2008)

| Mix designation | RHA (%) | Saturated water absorption (%) | | Coeff. of water absorption*10 ⁻¹⁰ (m ² /s) | | Sorptivity *10 ⁻⁶ (m/s ^{1/2}) | |
|-----------------|---------|--------------------------------|---------|--|---------|--|---------|
| | | 28 Days | 90 Days | 28 Days | 90 Days | 28 Days | 90 Days |
| R0 (control) | 0 | 4.71 | 3.76 | 1.62 | 0.85 | 11.05 | 9.76 |
| R1 | 5 | 4.83 | 3.21 | 1.42 | 0.71 | 10.6 | 7.09 |
| R2 | 10 | 5.02 | 3.2 | 1.03 | 0.61 | 9.16 | 4.86 |
| R3 | 15 | 5.58 | 3.11 | 0.99 | 0.46 | 7.37 | 4.09 |
| R4 | 20 | 5.81 | 2.2 | 0.92 | 0.31 | 6 | 3.61 |
| R5 | 25 | 6.09 | 2.8 | 0.51 | 0.2 | 5.53 | 2.28 |
| R6 | 30 | 6.35 | 3.05 | 1.06 | 0.43 | 6.08 | 3.38 |
| R7 | 35 | 6.92 | 3.98 | 1.51 | 0.58 | 10.3 | 4.04 |

up to 35% RHA are quite lower than that of control concrete. This again confirms that prolonged curing leads to a reduction in pore space. It is also observed from the sorptivity data that 30% RHA concrete specimens have shown a 45% reduction in sorptivity at 28 days compared to that of control.

8.5.2 Effect of RHA on Chloride-Ion Diffusion of Concrete

Concretes made with blended cements generally have lower permeability and more discontinuous pore structure than ordinary Portland cement concrete. The diffusivity of chloride ions in blended cement concretes tends to be lower (Cook et al. 1989). The ability of RHA mixtures to reduce the potential detrimental effects of chloride intrusion into concrete was reported by several authors (Hettiarachchi et al. 1987; Anwar et al. 2000; Nehdi et al. 2003; Salas et al. 2009 and Anwar et al. 2000). They demonstrated that RHA samples outperform the specimen containing OPC alone and the levels of total and soluble chloride ions had large reductions as the depth of concrete zones surveyed increased. They also determined that for concretes studied, the first 10 mm of concrete cover provides little barrier to chloride ion penetration and underscores the importance of concrete cover to the reinforcement. On the other hand, all the results of zone 20–30 mm show lower values of total chloride ions content than the limits of reinforcement corrosion threshold. Therefore it can be concluded that there are significant reductions in chloride ions permeability due to replacing the OPC with RHA. As the replacement level of the RHA increases from 10 to 20% by weight the results are affected and low chloride ions contents are obtained. Consequently, they concluded that concrete containing RHA might require less depth of cover to protect the reinforcing steel than those concretes using OPC alone. However, using finely ground RHA reduced the rapid chloride penetrability of concrete from a moderate rating to low or very

low ratings depending on the type and addition level of RHA (Nehdi et al. 2003). Salas et al. (2009) reported that the reduction in the average pore diameter of cement paste caused by the incorporation of rice husk ash in the mix will effectively reduce the pore sizes, permeability, and diffusivity of chloride ions in concrete.

Saraswathy and Ha-Won (2007) investigated the corrosion performance of concrete made with 0, 5, 10, 15, 20, 25, and 30% RHA as partial replacements of cement. They have monitored the open circuit potential measurements with reference to saturated calomel electrode (SCE) periodically with time as per ASTM C876. From their study it can be observed that the time of cracking were 42, 72, and 74 h for concretes made with 0, 5, and 10% RHA. However, no cracking was observed for concretes with 15, 20, 25, and 30% RHA ever after 144 h of exposure. In contrast, ordinary Portland cement concrete, the specimen was cracked after only 42 h of exposure in 5% NaCl solution. It can be concluded from their study that the replacement of rice husk ash refined the pores, thereby reducing the permeability. Moreover, the study by Saraswathy and her colleagues (2007) suggests that the incorporation of RHA up to 30% replacement level reduces the chloride penetration, decreases permeability, and improves strength and corrosion resistance properties. Finally, they have recommended the replacement level of up to 25%. In the same vein, Chindaprasirt et al. (2007) studied the effect of RHA and fly ash on corrosion resistance of Portland cement concrete and concluded that both fly ash and RHA are very effective in improving the corrosion resistance of mortars indicating better contribution of RHA to corrosion resistance in comparison to that of fly ash.

Chalee et al. (2013) examined concrete made of RHA during 5 years exposure to a marine environment, they concluded that concrete containing 15 - 35% RHA as a Portland cement replacement had a lower chloride diffusion coefficient and a little steel corrosion. The chloride binding capacity increased as the amount of RHA in the concrete increased, especially in concrete containing 15% and 35% RHA as cement replacement.

8.6 Conclusion

Rice husk ash, a material obtained after burning an agricultural by-product, due to high specific surface and pozzolanic property, has gained growing interest for use as a supplementary cementitious material in concrete. This paper reviews the performance of the rice husk ash as a partial cement replacement in concrete. It shows that:

1. In RHA concrete, due to the hydrophilic nature and high specific surface of the RHA, water demand increases, and higher dosages of the superplasticizer are needed to achieve the same workability as that of ordinary Portland cement concrete. The RHA concrete has slightly longer setting time, the bleeding of RHA concrete can be negligible.

2. The incorporation of RHA as a partial replacement of cement enhances the compressive strength, tensile and flexural strength of concrete. The optimum replacement level of Portland cement by RHA to give maximum long-term strength enhancement is about 20% by weight of the total binder material. The compressive strength of the RHA concrete at 28 days varied from 35 to 60 MPa depending on the w/b ratio and the replacement level. The incorporation of RHA in concrete does not cause significant changes in the modulus of elasticity.
3. The advantage in using RHA in concrete, especially in high performance or ultra-high performance concrete is the possibility to keep high relative humidity in the concrete. This characteristic of RHA significantly mitigates the autogenous shrinkage of UHPC/HPC concrete.
4. From both water permeability tests and chloride diffusivity tests, in the RHA concrete the coefficient of water absorption values are quite lower, the prolonged curing of RHA leads to a reduction of permeable voids. When the replacement level of the RHA increases from 10 to 20% by weight lower chloride diffusion coefficients are obtained.

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Chapter 9

Ternary Blends

R. Doug Hooton, Semion Zhutovsky and Siham Kamali-Bernard

Abstract Ternary binders have become used more frequently for several reasons. In some cases, such as combining a rapidly reactive SCM such as silica fume with a more slowly reactive SCM such as fly ash or slag, the use of ternary binders can provide benefits for both early-age and later-age properties and durability of concrete. In other cases, high-alkali pozzolans have been combined with slag to both accelerate the slag hydration and bind the alkalis from the pozzolan. As well, two SCMs may be combined to improve economy of the concrete mixture. This chapter describes properties of various ternary binders.

Keywords Ternary cements • Synergy • Fly ash • Slag • Silica fume

9.1 Introduction

Ternary binders can be produced by separate addition of two supplementary cementitious materials (SCMs) with cement in the concrete mixer, by pre-blending two SCMs and using the blended SCM at the concrete plant, or by adding an SCM together with a blended hydraulic cement. In some cases, limestone blended cement

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(e.g. EN CEM IIA-L or ASTM C595 Type IL) can be mixed with a single SCM to create a ternary binder. The selection of one of these options depends on factors including number of available silos at a concrete plant, and locally available materials.

Ternary binders are used to optimize the required properties of concrete. The pozzolanic reaction of silica fume or metakaolin is typically more rapid than that when using slag or fly ash. However, there is a synergy when combining fly ash or slag with silica fume so that concrete proportions of 4–5% silica fume (by mass of total cementitious), with 25–35% fly ash or slag, can provide higher resistance to fluid ingress (Thomas et al. 2007).

A factory blend, produced by intergrinding Portland cement clinker, silica fume (3–5%), slag (20–25%) and gypsum, has been available in Canada since 1999 (Thomas et al. 2007). Extensive testing of this product has shown that this cement has equivalent early-age strength and improved later-age strength compared to Portland cement produced from the same clinker.

While most standards for SCMs just deal with individual SCMs, there are provisions in some standards for the combined use of two or more SCMs for partial replacement of Portland cement. The Canadian CSA A3001 standard for hydraulic cements allows use of ternary and quaternary binders, either added separately to concrete or as blended SCMs (CSA A3000-13 2013). Similarly, ASTM C1697 (2010) is the Standard Specification for Blended Supplementary Cementitious Materials. The blended SCM can be produced from any combination of fly ash (high or low calcium), slag, silica fume and natural pozzolan and testing for compliance is based on the predominant SCM in the blend.

The EN 197 standard allows ternary composite cements as CEM II/A-M (6–20% combination of SCM and limestone), CEM IIB-M (21–35% combination of SCM and limestone), CEM V/A (18–30% slag plus 18–30% fly ash or raw or calcined natural pozzolan) and CEM V/B (31–50% slag plus 31–50% fly ash or raw or calcined natural pozzolan).

The health and safety issues for ternary systems would simply reflect those of the individual SCMs incorporated in the ternary binder.

The advantages of ternary binder systems incorporating more than one SCM, are the potential synergistic effects, where one SCM compensates for the weakness of the other SCM, allowing for a higher level of Portland cement replacement in concrete. The lower the clinker-factor in the binder and the lower the total binder content, the lower will be the embodied energy and carbon footprint of the concrete. An example of this is the use of silica fume together with either slag or fly ash: the silica fume provides higher early strengths while the slag or fly ash provides longer term strength development. As another example, slag has been blended with high-calcium fly ash: the fly ash accelerates early strength of the slag and the slag helps by binding up potentially troublesome levels of alkalis and/or sulfates (Thomas et al. 2010).

9.2 Fresh Properties

Some high-surface area SCMs, especially silica fume and metakaolin, require higher doses of high-range water reducers (HRWR) to obtain sufficient workability in the fresh concrete. These high dosages can sometimes cause “stickiness” that negatively impacts finishing operations. The addition of slag or low-calcium fly ash to such mixtures has been found to improve workability and require lower doses of HRWR, thus easing the finishing process (Hooton 2000). In the 13 km long Confederation Bridge project in Eastern-Canada, 10% fly ash was added to the high-strength silica fume concretes to improve pumpability. When the use of chemical admixtures is considered, relative to silica fume alone, lower doses of HRWR are typically required when slag or fly ash is combined with silica fume.

High levels of cement replacement by SCM, such as 40% fly ash, may not only cause problems with low early-age strengths, but also delay setting times (Bentz 2010; Bentz and Ferraris 2010). Creating ternary blends with nano-limestone helps to prevent the retardation in the mixes with high volume SCM (Sato and Beaudoin 2011; De Weerd et al. 2011a, b; Bentz et al. 2012).

Addition of an ultrafine SCM together with a fly ash or slag will often improve cohesiveness and reduce segregation of a workable concrete. As with other SCM concretes, appropriate periods of curing need to be considered to develop the potential of the concrete.

The 423 m tall, 98-storey Trump Tower in Chicago was completed in 2009 using high strength concrete. The concrete design was selected for its high elastic modulus, 68 GPa. A 110 MPa self-consolidating concrete mixture contained slag, fly ash, and silica fume as well as Portland cement and was pumped and placed to an elevation up to 200 m above grade (PCA 2009).

Ternary blends were also successfully used for reduction of heat of hydration in mass concrete. The 1990 m span Akashi Kaikyo bridge used ternary tremie-placed mass concrete (Kashima et al. 1992a, b), and massive inner-core, wall, and foundation mixtures employed blended cements with cementitious slag contents around 50% and fly ash contents around 30% (Kashima et al. 1992b).

The Freedom Tower in New York City used a quaternary binder with silica fume, fly ash and slag, to obtain pumpable mixtures with strengths as high as 100 MPa. Quaternary binder mixtures were also used in the Great Belt Link in Denmark.

9.3 Compressive Strength

In 1985–86, when the 68-storey Scotia Plaza tower in Toronto was planned, there was a need for high-performance concrete which could be pumped and placed at high slump, but which could also develop >20 MPa at 11 h (for rapid column form removal) and attain a design strength of 70 MPa. While slag concretes were initially

proposed, the early strengths were very close to the limit. Then, it was decided to add 7.8% silica fume and reduce the slag to 25%. At a cementing materials content of 470 kg/m³ and w/cm = 0.31, and with superplasticizer (SP) added at the pump, the requirements were exceeded. It was found that the slag made the silica fume concrete easier to pump, place and finish (it also reduced the amount of HRWR needed to obtain and maintain the required workability) and it contributed to continued long-term strength gain (Bickley et al. 1991, 1994). After that initial success, numerous other towers were built and continue to be built in Toronto with either 70 or 85 MPa design strengths using similar mixtures.

Simulating precast operations, using accelerated curing at 65 °C, 18-hour strengths in excess of 40 MPa were obtained using slag in ternary mixtures with silica fume (Titherington and Hooton 2004).

Ternary cementitious blends can offer significant advantages over binary blends and even greater enhancements over pure Portland cement. In fact, ternary blended cements can be optimized to minimize the shortcomings of each component, resulting in synergistic improvements in mechanical and durability properties of the combined cementitious material. Different ternary systems using several components (including OPC, calcium sulfate cement, calcium sulfoaluminate cement, calcium sulfates, silica fume, fly ash, blast-furnace slag, metakaolin, residues) have been investigated in the literature. This section focuses on the compressive strength of ternary blends. Table 9.1 provides some references that are discussed in this section.

Thomas et al. (1999) studied concrete containing ternary blends of OPC-silica fume-fly ash. They reported that the combination of silica fume and low-CaO fly ash is complementary and synergistic. They show that using silica fume increases the strength of concrete at all ages, but it is apparent that much of the increase is realized at early ages and the rate of strength development at later ages is similar for silica fume concrete and plain Portland cement concrete.

Table 9.1 Partial list of literature references dealing with compressive strength of ternary systems

| References | Ternary blend system | Compressive strength obtained on |
|-------------------------------------|--|----------------------------------|
| Nehdi and Sumner (2002) | OPC-SF-class F FA OPC-SF-ground granulated blast furnace slag | Mortar |
| Celik et al. (2014) | OPC-natural pozzolan-LF OPC-FA class F-LF | Self-consolidating concrete |
| Niknezhad and Kamali-Bernard (2015) | OPC-MK-LF | Self-compacting concrete |
| Cyr et al. (2012) | OPC-MK-MSWIFA OPC-MK-SSA | Mortar |
| Raj et al. (2013) | OPC-MK-Redmud waste | Concrete |

LF limestone filler; SF silica fume; MK metakaolin; FA fly ash; MSWIFA municipal solid waste incineration fly ash; SSA sewage sludge ash

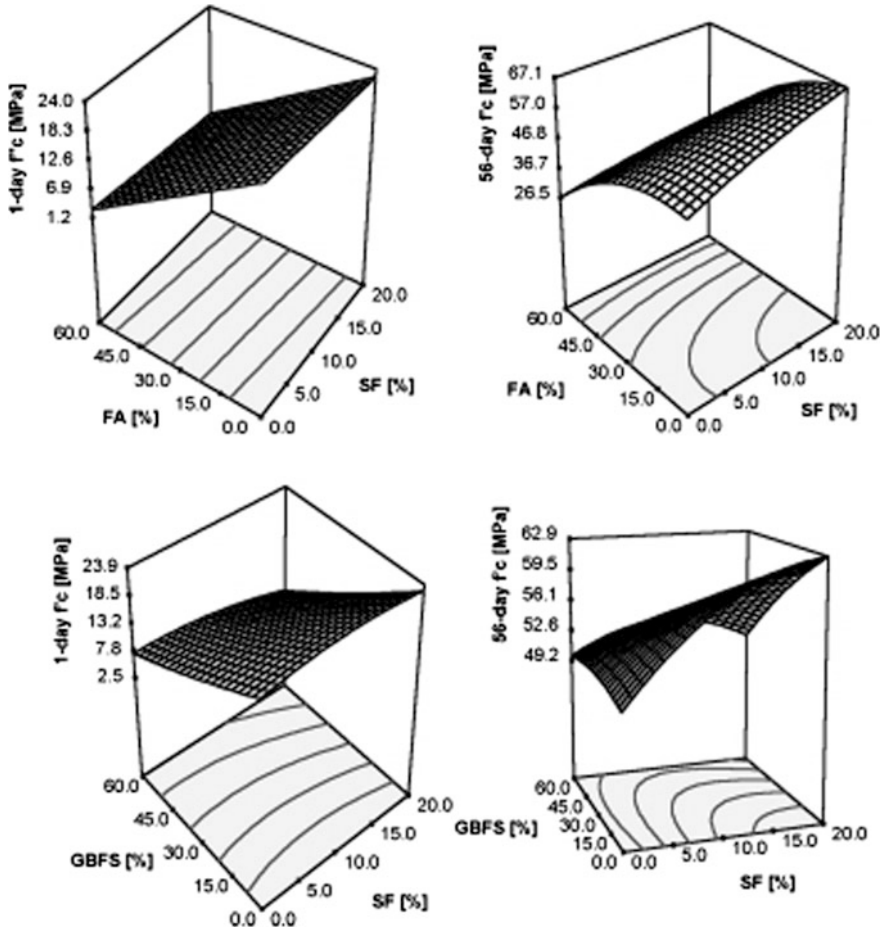


Fig. 9.1 Response surfaces of compressive strength at 1 day and 56 days for OPC-SF-FA and OPC-SF-GBFS ternary cement mortars according to Nehdi and Sumner (2002)

Nehdi and Sumner (2002) used factorial experimental design to investigate the performance of OPC-silica fume–Class F fly ash and OPC-silica fume-ground granulated blast furnace slag (GBFS) ternary cementitious blends. Response surfaces for the compressive strength at 1, 7, 28, and 56 days were obtained for the corresponding ternary cement mortars and results at 1 and 56 days are given in Fig. 9.1. The authors reported that at 1 day the compressive strength of the ternary cement mortars decreased as the content of GBFS or FA increased. For both OPC-SF-GBFS and OPC-SF-FA systems, silica fume did not significantly enhance the 1-day strength whether at low or high GBFS/FA contents. The authors reported that the obtained behaviour is in contrast with Swamy (1997) who argued that to enhance the early age strength of FA and GBFS concrete, highly reactive pozzolans

such as SF could be added in a ternary blend. At 7 days, they found that the effect of SF on increasing the compressive strength of the ternary cement mortars became more significant, particularly for the ternary blend containing GBFS. However, the 7-day compressive strength decreased with increased content of GBFS and FA. The 7-day compressive strength values of OPC-SF-GBFS mortar are generally higher than those obtained for OPC-SF-fly ash. At 28 days, the compressive strength of OPC-SF-GBFS increased with increasing GBFS content up to around 30% for low SF contents and up to 15% for high SF contents and decreased beyond those levels. The effect of SF on increasing the strength of the ternary cement mortars is significant at this age when GBFS levels were below 30%. The authors reported that for OPC-SF-FA ternary cement mortars, higher levels of SF also increased the 28-day compressive strength at low FA contents, but did not have a significant effect at FA levels beyond 15–20%. However, the 28-day strength consistently decreased as the FA level was increased regardless of the SF content. At 56 days, varying the GBFS content from 0 to 60% did not have a significant effect on the compressive strength of the OPC-SF-GBFS cement mortars at low SF levels. The higher the SF content in the ternary blend the more significantly the 56-day compressive strength decreased with higher GBFS dosage.

Celik et al. (2014) studied the effect of Portland cement substitution by class F fly ash or natural pozzolan (NP) on the strength of self-consolidating concretes (SCC). The cement replacement ratio varied from 30 to 50% in mass. The authors show that in the case of ternary blended cement containing 15% of limestone filler (LF), the larger amount of natural pozzolan or fly ash addition led to reduced compressive strength compared to the concrete specimen with only 15% of LF at early ages. However, at late ages, identical compressive strengths to the control specimen were obtained for 30% of natural pozzolan or class F fly ash replacement. Among the ternary mixtures, the 55 OPC-30 NP-15 LF mix had higher strength, while 45 OPC-40 NP-15 LF and 35 OPC-50 NP-15 LF mixes had lower strength when compared to the corresponding mixes with fly ash.

Niknezhad and Kamali-Bernard (2015) investigated self-consolidating concrete containing ternary blends composed of OPC-metakaolin-limestone filler. They found that the replacement of Portland cement by 15% of metakaolin resulted in a decrease of the compressive strength at very early ages. At one day of age, compared to the reference SCC, a decrease in strength of 18% was observed. However, at 7 days, this decrease dropped to 6% and at 28 days of hardening, SCC with MK exhibited higher compressive strength value than the reference SCC.

Cyr et al. (2012) studied ternary blends composed of 75% Portland cement, 22.5% metakaolin and 2.5% of different ash residues. The studied industrial residues are municipal solid waste incineration fly ash (MSWIFA) and sewage sludge ash (SSA). They show that when using such small contents of ash residue, the mechanical strength of mortars was not affected.

Raj et al. (2013) investigated ternary high strength concrete containing OPC, metakaolin (MK) and red mud (RM) as by-product. They tested different percentages of replacement of OPC by metakaolin and red mud blend: 6, 8, 10, 12 and

14%. The authors reported that the optimum percentage of cement replacement by metakaolin and red mud blend for achieving maximum compressive strength is 10%. In 10% replacement ratio, the compressive strength of 50MK-50RM and 80MK-20RM are 6.2 and 6.7% higher than the control concrete.

Following the idea of synergetic effects between less reactive pozzolan and more reactive ones, Isaia et al. (2003) studied ternary blends with equal amount of fly ash and rice husk ash. The replacement levels of 25 and 50% cement were tested on concrete mixtures with w/b ratio of 0.35, 0.50 and 0.65. It was shown that lower w/b ratio ternary blends demonstrated lower 28 day compressive strength than OPC reference mixes. However, for the lowest tested w/b ratio (0.35), the compressive strength of ternary concrete mixes exceeded the compressive strength of reference and binary blends at 91 days. Bhanumathidas and Mehta (2001) also reported that the use of 10% rice husk ash in ternary blends with 40% type F FA improved compressive strength in comparison with binary blends of 50% FA.

Ternary blends with various combinations of slag, fly ash and limestone filler and replacement levels between 35 and 80% were studied by Alonso et al. (2012). All tested blends demonstrated the initial development of strength to be slower than the OPC reference. However, at 91 days, compressive strength of mixes of slag with fly ash and slag with limestone filler at 35% replacement level surpassed the compressive strength of the reference mix. Ternary mixes of fly ash and limestone, as well as mixes with higher replacement levels, didn't reach the same level of compressive strength as the OPC reference mixture.

Ternary blend of 30% class F FA and 5% LS was tested by De Weerd et al. (2011a, b) on mortars with w/b ratio of 0.50. An increase of 15.2% in 90 days compressive strength, as compared to a 100% OPC mix, was observed, while 7.3% and 9.0% increases in the binary blends of 5% LS and 30% FA, respectively, were measured. The compressive strength at early-ages and up to 28 days was significantly reduced in blends with FA, while replacement of 5% of cement by LS resulted in a slight increase of compressive strength at the ages 1–7 days. Flexural strength measured in ternary blends of 30% FA and 5% LS was 23% higher than in reference mortar at 90 days, but significantly lower at earlier ages tested (1–28 days). The authors concluded that the beneficial effect of LS in the binary and ternary blends should be attributed to chemical reaction of carbonates from LS and ettringite, forming carboaluminates. This effect was found to be even more pronounced in FA ternary blends due to the resulting lower SO_3/Al_2O_3 ratio caused by cement replacement by FA (De Weerd et al. 2011a, b).

Elahi et al. (2010) studied HPC with the ternary blends of silica fume with slag and fly ash at w/b ratio of 0.30. The ternary blends of FA (20 and 40% replacement) and SF (7.5%) didn't reach the values of compressive strength of the reference mix event at 91 days. The ternary blend of SF (7.5%) and GGBS (50%) demonstrated compressive strengths higher than the 100% OPC reference mix, at ages of 28 and 91 days, but not earlier. In this case, no strength benefit from combining SF and the other SCM was found, since the binary blend with 7.5% SF demonstrated higher performance than both reference and ternary blends at all ages starting from 3 days,

while the strengths of all binary mixes with GGBS and FA lagged behind the reference mix at all ages.

El-Chabib and Ibrahim (2013) tested ternary and quaternary blends of SF with GGBS, Type C and Type F fly ash at w/b ratios of 0.3 and 0.33 and using 60 and 70% levels of cement replacement. Only the ternary blend of 10% SF and 60% GGBS at w/b ratio of 0.30 exceeded the strength of the reference mix. It is interesting to note that concrete with ternary blend of the same proportions, but at slightly higher w/b ratio of 0.33 didn't surpass the compressive strength of the reference mix with 100% OPC. The compressive strength in all other ternary and quaternary blends was inferior to the reference mix. However, it should be pointed out that at these high levels of cement replacement only the mixes with slag reached compressive strengths close to the reference mix, while blends without GGBS exhibited significant reductions in compressive strength in comparison to the reference.

Compressive strength of ternary blends of SF and FA (type F) with w/b ratio of 0.32 studied by Seshasayi et al. (2001) is shown in Fig. 9.2. The content of SF was varied over the range of 0–16% in 4% steps, and the content of FA was varied between 0 and 40% in 10% steps, so the total replacement in the ternary blend reached the maximum of 56%. Ternary blends with FA up to 30% replacement and SF above 4% demonstrated compressive strength superior to the reference and binary mixes at the tested ages of 28 and 56 days. As can be seen in Fig. 9.2, the highest compressive strength was achieved in the ternary blends of 12% SF and 20% FA (total 32% of cement replacement) at both ages, and 12% SF and 30% FA came second in compressive strength at both ages. The synergy between SF and FA can be noted in this case since the increase in compressive strength in the ternary blends was higher than the sum of the increases observed in the binary mixes with the same replacement levels.

The synergistic effect between FA and SF was also studied by Radlinski and Olek (2012) on ternary blended mortars with 20% class C FA and 5% SF and w/b ratio of 0.41. The synergistic effect on compressive strength was observed starting

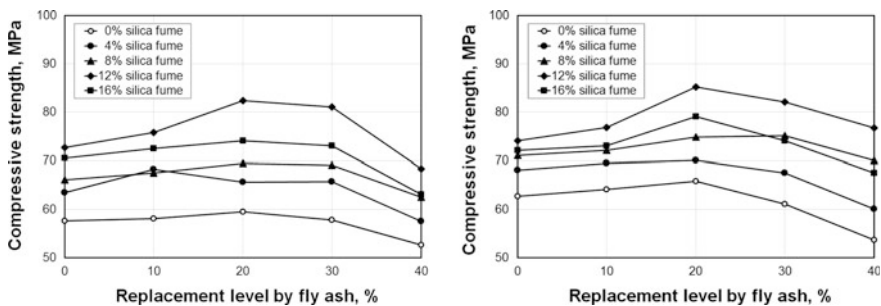


Fig. 9.2 Compressive strength at 28 days (left) and 56 days (right) for OPC-SF-FA ternary blended concretes, adopted from Seshasayi et al. (2001)

from the age of 7 days, while at earlier ages, lower strengths than expected were measured.

Kannan and Ganesan (2014) tested ternary blends of metakaolin and rice husk ash. MK and RHA were blended at the ratio of 1:1 and used in SCC with w/b ratio of 0.55. The total replacement level was varied from 10 to 40% of cement. Compressive strength at 28 days in all ternary blends improved in comparison to the 100% OPC mix, while the optimal replacement level was 30%. Splitting tensile strength at 28 days improved in all ternary blends with the optimal replacement level of 30% (15% MK and 15% RHA). The authors declared there to be a synergetic effect between the MK and RHA. However, from the data there is little support to call the combination of MK and RHA synergetic, because all binary blends of MK in the range of 5–30% cement replacement and all RHA binary blends in the range of 5–25% cement replacement resulted in improvement of mechanical properties of concrete at the same age.

Antiohos et al. (2004) used amorphous silica at the rate of 5–10% in ternary blends with two different Class C fly ashes in order to compensate for early age strength loss in the fly ash binary mixes. The early-age compressive strength was significantly improved, though at later age the strength was lower than with the binary blends.

Bentz et al. (2013) tried to resolve the early-age strength problem of high volume (40–60% cement replacement) Class F and Class C fly ash mixes using ternary blends with limestone filler. In order to achieve the same level of compressive strength as the reference mix with 100% Type I/II cement or exceed it, it was necessary to reduce w/b ratio from 0.40 to 0.37–0.29 and to switch to ASTM Type III (high-early strength) cement.

Summarizing the above, in ternary blends, a good synergy may be expected between SCM that give high early-age strength, such as SF, RHA or fine limestone filler, and an SCM that is able to provide high late-age strength, such as GGBS and fly ash. However, it seems that this synergetic effect depends on w/b ratio, especially at high levels of cement replacement. It is more likely that ternary blends will be more effective, specifically with respect to compressive strength, at lower w/b ratios (0.30 and below), where cement doesn't react fully and by itself partially serves as filler.

A ternary cementitious system that recently generated considerable research interest is the OPC-MK-LS combination. While improved particle packing may have played a role, the synergy between metakaolin and limestone in this ternary blend was attributed to the formation of carboaluminate phases (Antoni et al. 2012; Hernandez and Scrivener 2015). Thus in such ternary blends the optimal ratio between MK and LS is determined by the stoichiometry of formation of monocarboaluminate hydrate from these two materials. Since 1 mol of alumina reacts with one mole of calcium carbonate (in addition to 3 mol of hydrated lime and 1 mol of water) to form 1 mol of monocarboaluminate, the optimal molar ratio of the blend is 1:1, which translates to a 2:1 mass ratio of MK to LS (Antoni et al. 2012). The result is that replacement ratios of up to 60% cement can be achieved without significant reduction of compressive strength. Furthermore, to improve

sustainability and reduce the cost, the use of calcined clays produced from low-grade clay with a kaolinite content of less than 40%, instead of using high-purity MK, in ternary blends with LS was suggested and proved to be efficient (Hernandez and Scrivener 2015).

9.4 Transport Properties

In Ontario, Canada, ternary blends of silica fume with either fly ash or slag have been used extensively in high-performance precast tunnel liners as well as for cast-in-place parking and bridge decks to obtain high resistance to chloride ingress (Hart et al. 1997). Similar ternary cementitious systems have also been found to be excellent for prevention of deleterious expansion due to alkali-silica reaction (ASR), while also having good resistance to de-icer salt scaling when used in highway structures and pavements. The relatively low (25%) slag content is not enough on its own to resist ASR damage, but when 5–6% silica fume is added, ASR resistance is excellent and chloride penetration resistance is increased (Bleszynski et al. 2002; Hooton et al. 2013; Nokken and Hooton 2006; McGrath and Hooton 1997; Hooton 2014) as shown in Table 9.2. These ternary combinations also complied with the Ontario highway authority's limit on slag replacement, due to perceived concerns about de-icer salt scaling resistance. However, ternary blends were found to exhibit good deicer salt scaling resistance (Bouzoubaâ et al. 2011). Fly ash-silica fume ternary mixtures have also been found to suppress deleterious expansion due to ASR (Shehata and Thomas 2002). Similar good performance is indicated for sulfate resistance of ternary blends.

Numerous parking structures in North America have been built using ternary binders for high resistance to penetration of chloride de-icers. An example is the General Mitchell airport garage in Milwaukee Wisconsin, built in 1999 using 335 kg/m³ cement, 60 kg/m³ high-calcium fly ash and 17 kg/m³ silica fume at w/cm = 0.35 (Rocole 1993). Strengths in excess of 14 MPa at 36 h and 28-day ASTM C1202 Coulomb values of less than 1000 were obtained. Cores taken after 12 years had 875 Coulombs and an average bulk diffusion coefficient (ASTM C1556) of $5.1 \times 10^{-12} \text{ m}^2/\text{s}$ (Hooton et al. 2010).

Table 9.2 Transport properties of ternary concrete mixture compared to Portland and binary mixtures using the same materials and mix proportions (Bleszynski et al. 2002; Hooton et al. 2013)

| | Age when cored | 100% Portland cement | 25% slag | 25% slag + 3.8% silica fume |
|--|----------------|----------------------|----------|-----------------------------|
| ASTM C1202 (coulombs) | 4 years | 2080 | 840 | 380 |
| | 8 years | 1660 | 835 | 210 |
| ASTM C1556 ($10^{-12} \text{ m}^2/\text{s}$) | 4 years | 13.1 | 5.2 | 1.7 |
| | 8 years | 6.8 | 6.3 | 1.6 |

9.5 Summary

As stated in the introduction, the advantages of ternary binder systems incorporating more than one SCM, are the potential synergistic effects, where one SCM compensates for the weakness of the other SCM, allowing for a higher level of Portland cement replacement in concrete. Ternary binder systems have been used successfully to produce concretes with high strength at both early and later ages, and for increased durability.

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