

PART II. CONSTITUENTS OF CONCRETE

**SUPPLEMENTARY
CEMENTITIOUS
MATERIALS**



**CEMENT CONCRETE
& AGGREGATES AUSTRALIA**

This section discusses and describes the nature and effect of Supplementary Cementitious Materials (SCM's) when used in concrete as replacement materials for a proportion of Type GP cement. Each of the SCM's is different to the other – in terms of their sourcing and their effectiveness as cement replacement materials. The similarities and differences will be discussed.

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1 INTRODUCTION

Supplementary cementitious materials (SCM's) have been used in building construction for decades. In Australia the use of these materials began seriously in the 1960's and they are now firmly established as mainstream cementitious materials with coverage by the AS 3582 series of Australian Standards.

The original term used to describe these materials was 'pozzolan'. Roman masons used a volcanic ash from the Italian village of Pozzouli which, when mixed with aggregate, lime and water made a water resistant and durable mortar. These 'pozzolans' were glassy materials rich in silica and/or alumina which reacted readily with lime in the presence of water to form compounds that are virtually identical to the products found in hydrated cement.

Modern day SCM's used elsewhere in the world include naturally occurring materials, but in Australia, at this time, SCM's are sourced solely from waste materials from large manufacturing processes.

The three types of SCM's used in Australia are:

- **Fly ash** – A fine powder removed from collection devices (electrostatic precipitators or fabric filters) used to

clean the flue gases in black-coal burning power stations;

- **Ground Granulated Blast Furnace Slag (GGBFS)** – Waste material removed during the operation of blast furnaces used for the smelting of iron ore;
- **Amorphous Silica (Silica Fume)** – A very fine particulate matter collected during the production of silicon metal or ferro-silicon alloys in arc furnaces.

(NOTE: Silica fume is often provided in a densified form or as a slurry to make it easier to handle in a concrete plant.)

A naturally occurring amorphous silica product is also obtained from geothermal deposits in New Zealand.

The 'waste' products are processed after collection and converted into 'concrete grade' products.

All of the SCM's may be used in the manufacture of blended cements that meet the requirements for Type GB cements in AS 3972. Generally, silica fume is blended with Type GP cement at a maximum level of 10%, while 'slag' and fly ash may be either inter-ground with cement clinker to make Type GB cement, or the fly ash or 'slag' may be (post) blended with Type GP cement to form the Type GB product.

Blends of SCM's and Type GP cement may also be used to meet the requirements for the Type SR, SL and LH Special Purpose cements. Blended cements are generally much more effective for these 'Special' purposes than modified 'Portland' cements.

At most concrete plants, separate silos of Type GP cement and one or more SCM are present. This allows the concrete producer to provide concrete mixes with a wide range of Type GP / SCM combinations for either Normal Class or Special Class concrete applications. While the concrete produced using these on-site blends will perform in the same way as if a Type GB cement was used, the site-blended concrete mixes cannot claim to have been made using Type GB cement that conforms with AS 3972 requirements.

2 HOW SCM's WORK

The effects of all three SCM's on concrete are attributable to two primary mechanisms, namely:

- **Filler Effect** – Physical effect of void filling to produce a more-dense concrete; and
- **Chemical Reaction** – Reaction of the SCM's, in the presence of water, with lime (the by-product of the hydration of cement) to form calcium silicate hydrates (CSH) and calcium aluminate hydrates (CAH).

Fly ash and silica fume exhibit only pozzolanic activity, while GGBFS exhibits some limited hydraulic activity (reaction with water) and is activated by lime, alkalis and sulfates present in the paste. Sulfates can also act as the primary activator for GGBFS – these promoting the hydration of GGBFS resulting in a rapid gain of compressive strength. This type of cementitious material is known as a 'super-sulfated cement'.

The dependence of the pozzolanic reaction on the presence of the lime produced as a by-product of cement hydration means that the overall rate of reaction and strength gain with mixes containing SCM's lags that of mixes containing cement only. However, the ongoing reaction of the SCM's results in (generally) higher later-age strengths (after 28 days) than cement-only mixes.

The reactions and relative reaction rates of cement and cement, GGBFS and cement + fly ash are shown in **Figures 2.1 to 2.4** below.

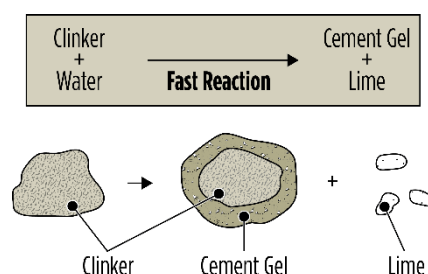


Figure 2.1 – Reaction of Portland Cement and Water

Slag has some hydraulic properties similar to Portland cement but to a very minor degree.

This reaction (**Figure 2.2**) is very slow and hence slag is not a useful cementitious material on its own. It requires an activator to speed up the pozzolanic reaction. Activators include alkalis, lime and sulfates.

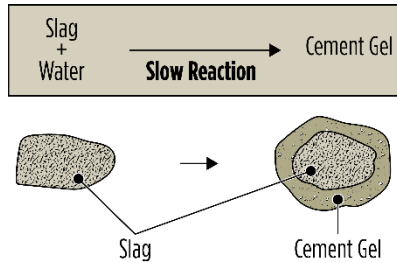


Figure 2.2 – Reaction of Slag with Water

Fly ash does not react at all with water (**Figure 2.3**).

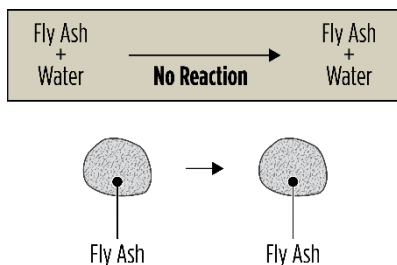


Figure 2.3 – ‘Reaction’ of Fly Ash with Water

Fly ash requires lime from the cement hydration reaction (in the presence of water) to react and form calcium silicate hydrate gel (**Figure 2.4**).

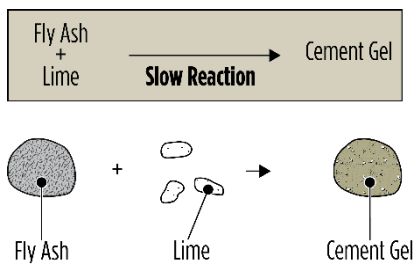


Figure 2.4 – Reaction of Fly Ash with Lime

Amorphous Silica(s) are similar to fly ash in that they rely on the lime from the hydration of cement to react with them to form cementitious products. Silica fume, due largely to its very high fineness, is the most reactive of the SCM's.

3 WHY USE SCM's?

There are environmental, technical and commercial advantages to using SCM's. Availability and product cost and performance generally dictate which SCM is used in a given situation or market area. All SCM types are not necessarily available in all regions of Australia, so 'local' availability will often dictate the SCM(s) used or specified.

Commercial Advantages

SCM's are wastes or by-products from other industries and are generally available at lower cost than General Purpose cement. The actual cost varies considerably around Australia depending on material availability and transport distance. The increasing use of imported SCM's in Australia means that source countries and exchange rates also influence pricing in any particular region.

Environmental Aspects

The SCM's are generally 'wastes' and it can be difficult for industry to find practical, economic and environmentally sensitive ways to dispose of them. Unused fly ash has been placed in waste dams or lakes. Slag tends to accumulate in large stockpiles. Silica fume disposal is problematic. There are advantages to the industries producing the 'wastes' to have the materials used profitably in concrete.

Current concerns about the CO₂ intensity of cement (and hence concrete) mean that the substitution of cement by SCM's has become a strong environmental focus. SCM's can also be used in the production of alternative binder materials with low-CO₂ intensities – binders like geopolymers and super-sulfated cements – which are gaining some credibility and utility.

Technical Considerations

SCM's generally have a positive influence on both the plastic and hardened properties of concrete. Disadvantages are minimal and any can readily be offset by other means.

As with the use of any new materials, consideration of the use of a new SCM requires that trials should be carried out to ensure that the expected and required concrete properties are achieved.

4 AUSTRALIAN STANDARDS FOR SCM's

The quality requirements for the three SCM's are described in Australian Standards (**Table 2.1**).

Table 2.1 – Australian Standards for SCM's

Material	Source	Australian Standard
Fly Ash	Black coal combustion facilities, usually power stations	AS 3582.1
GGBFS	Blast Furnaces for smelting of iron ore	AS 3582.2
Amorphous Silica	Naturally occurring deposits or Silica Fume – fine particulate matter collected from the refining of silicon metal / ferro-silicon alloys	AS 3582.3

5 COMPARISONS – SCM's AND TYPE GP CEMENT

Chemical Composition

The indicative chemical compositions of Type GP cement and the three SCM's types are shown below in **Table 2.2**.

The following broad comparisons between the four material types can be made:

- **Type GP Cement** – High in calcium and silica;
- **Fly Ash** – High in silica and alumina and low in calcium;
- **GGBFS** – High in calcium and silica with moderate alumina;
- **Amorphous silica** – High in silica, low in calcium and other elements.

Mineral Composition

The other significant contrast is in terms of the mineralogy of these materials. Type GP cement is comprised of crystalline, mineral materials (C₃S; C₂S; C₃A; C₄AF), while all three of the

SCM's gain their reactivity through being glassy (non-crystalline) materials. The glassy nature of these materials comes about through the rapid cooling of (essentially) molten materials which are produced as by-products in each of their respective industrial processes.

Particle Shapes

By virtue of their initial production and/or processing, Type GP cement and the three SCM's have different particle shapes and sizes.

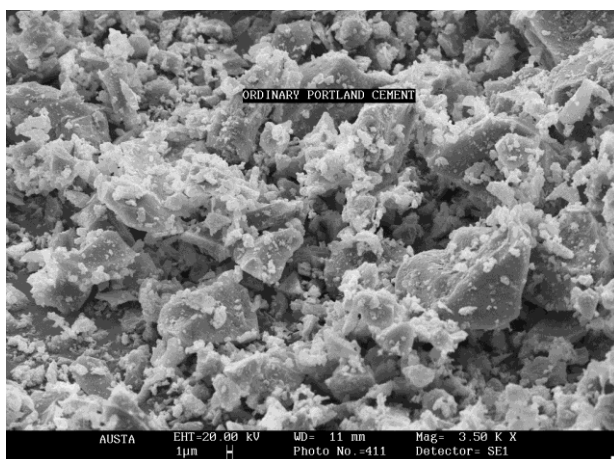
Type GP cement and GGBFS are both produced by grinding an interim product (clinker and GBFS respectively) in a 'cement mill' to achieve the final cementitious product – yielding an angular, glassy looking product. Fly ash and silica fume are not usually milled (or ground) and their particle shape is more spherical reflecting the conditions (very high temperatures; molten particles transported in a gas stream) in the processes they derive from. The indicative shapes are shown in **Figure 2.5** below.

Effects of SCM's on Concrete Performance

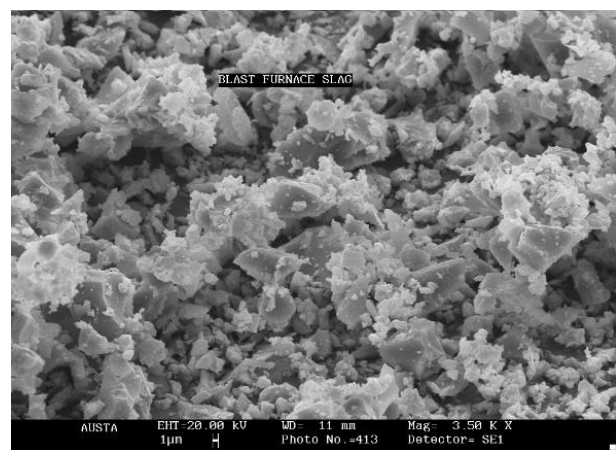
SCM's affect both the plastic and hardened properties of concrete – these effects being briefly compared in **Tables 2.3** and **2.4** below. These properties will be elaborated upon in the following sub-sections of this section.

Table 2.2 – Comparison of Chemical Compositions

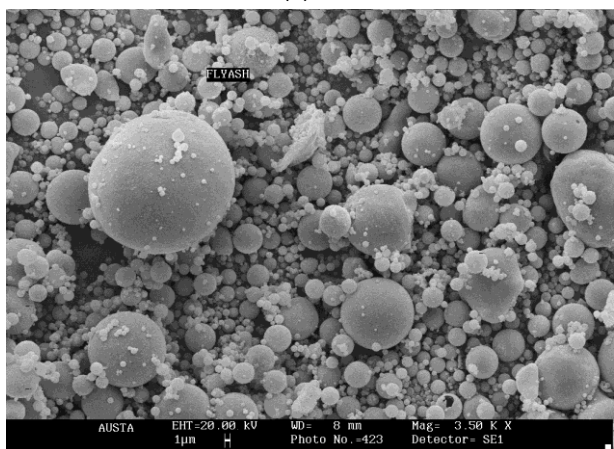
Component (%)	Type GP Cement	Fly Ash	GGBFS	Amorphous Silica (Silica Fume)
SiO ₂	19-26	50-70	32-35	85-95
Al ₂ O ₃	4.5-5.5	20-30	11-16	0.1-2
Fe ₂ O ₃	2-5	2-15	0.5-1.5	0.1-4
TiO ₂	-	1-2	1-2	-
Mn ₃ O ₄	-	0-0.5	0.5-1	-
CaO	62-65	0-5	32-42	0.1-0.5
MgO	1-3	0-2	7-13	0.1-1
Na ₂ O	0.2-0.7	0.2-2.5	0-0.5	0.1- 1
K ₂ O	0.5-2.5	0.2-2.5	0.5-1	0.1-1
P ₂ O ₅	0.1-0.2	0-2	-	-
SO ₃	2-3.5	0-2	1-2.5	0.1-0.5
LOI	0.5-3.5	0.1-4	0.5	1-6



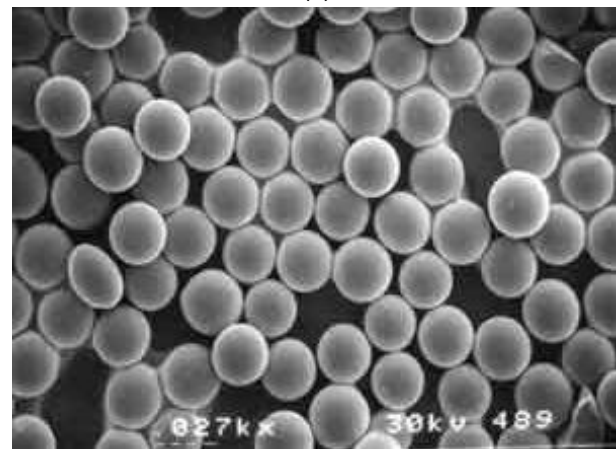
(a)



(b)



(c)



(d)

Figure 2.5 – Comparative Particle Shapes of Type GP Cement and SCM's: (a) Type GP Cement; (b) GGBFS; (c) Fly Ash; (d) Silica Fume

Table 2.3 – Comparisons of Effects on Plastic Concrete Properties

PLASTIC PROPERTIES – SCM CONCRETE VERSUS CEMENT-ONLY CONCRETE			
Property/Effect	Fly Ash	GGBFS	Silica Fume
Water Demand	Reduced	Reduced	Increased
Workability	Improved	Improved	Reduced
Segregation	Reduced	Reduced	Reduced
Cohesiveness	Improved	Same	Increased
Air Entrainment	Limitations	Same	Limitations
Pumpability	Improved	Improved	Reduced
Bleeding	Reduced	Reduced (65%)/ Improved (30%)	Greatly reduced
Finishing	Improved	Improved	Reduced
Set Times	Delayed	Delayed	Similar

Table 2.4 – Comparisons of Effects on Hardened Concrete Properties

HARDENED PROPERTIES – SCM CONCRETE VERSUS CEMENT-ONLY CONCRETE			
Property/Effect	Fly Ash	GGBFS	Amorphous Silica
Compressive Strength	Lower early, higher later	Lower early, higher later	Higher
Tensile/Flexural Strength	Slightly higher	Slightly higher	Slightly higher
Drying Shrinkage	Lower	Variable	Lower
Creep	Similar	Similar	Lower
Permeability	Much lower	Much lower	Very much lower
Sulfate Resistance	Higher (at >25-30%)	Higher (at >60%)	Higher
Chloride Resistance	Higher	Higher	Higher
Heat of Hydration	Lower	Lower	Higher/Lower
Carbonation	More at surface	Similar	Similar
AAR/ASR Resistance	Higher (at >20%)	Higher (at >50%)	Higher (at 7-10%)

6 FLY ASH

6.1 INTRODUCTION

Fly ash, a by-product or 'waste' product from the combustion of coal, has become an important material in a variety of construction industry applications. Most particularly it has been found to provide significant benefits when used as a partial cement replacement in concrete and related products, and it is this function that will be the primary subject of this

section. The fly ash in question derives from pulverised fuel-fired coal combustion where the coal is ground into a fine powder before being injected into a high temperature combustion chamber where temperatures reach about 1,800°C. The nature of the fly ash is determined in part by the nature of the coal it derives from and this in turn can determine its applicability in concrete applications. Schematic representations of a coal-fired power station and the fly ash production process are shown in **Figures 2.6 and 2.7.**

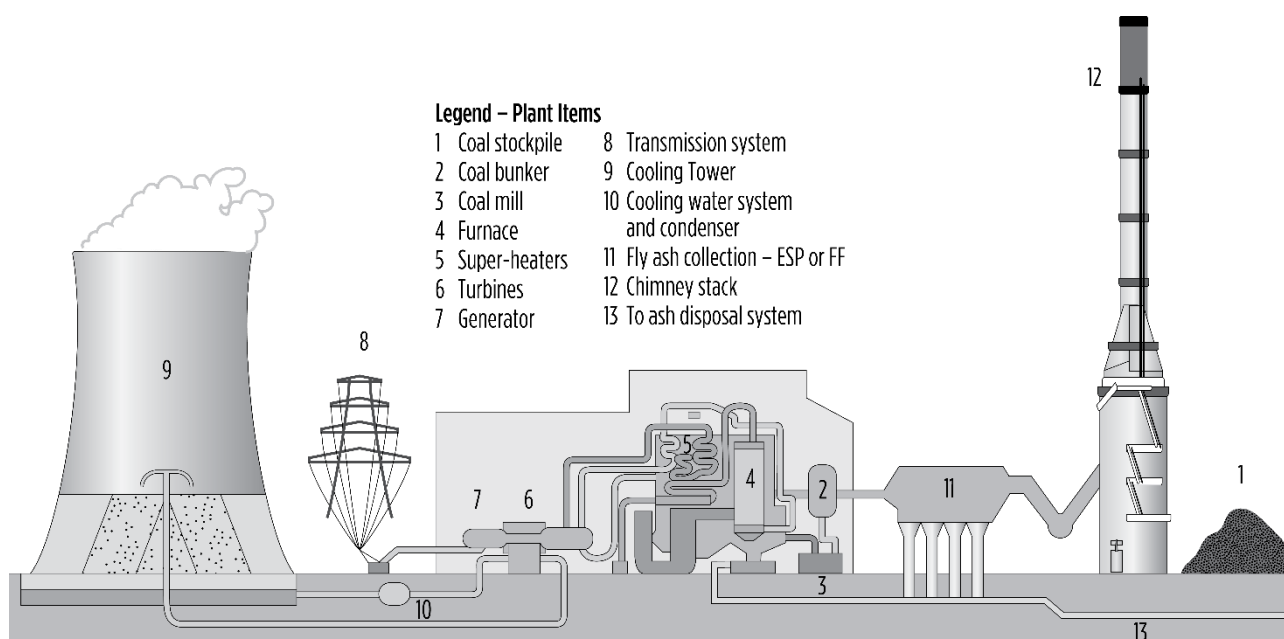


Figure 2.6 – Schematic Representation of Coal Fired Power Station

Fly ash use in concrete began in the USA in the 1930's, though its first use in Australia was not until 1949 when fly ash imported from the USA was used in grouts in the Snowy Mountains Hydro-Electric scheme in NSW. Subsequently, and certainly since the 1960's, fly ash has become a standard component in concrete mixes in regions in Australia where fly ash is available. This ready availability has been along the eastern seaboard of mainland Australia and in South Australia, though this is now changing as coal-fired power stations close.

As a material, fly ash is not unlike the volcanic ashes used by the Romans some two-thousand years ago. Their similarity derives from their chemical composition – both being rich in silica and alumina – and from their crystallinity (or lack of it), both being glassy materials.

Fly ash has as an advantage of being lower in cost than cement and hence makes concrete more cost effective. It allows a reduction in the Type GP cement content of concrete and improves concrete's environmental credentials.

Unlike Type GP cement which has a quite consistent chemical composition and mineralogy wherever it is made in the world, almost all fly ashes are chemically different. The chemistry of a given fly ash depends on the nature and proportions of the minerals (typically clays and silicate minerals) associated with the coal source. Variable mineralogy leads to variable chemistry in the fly ash which means that there is no 'typical' fly ash.

This likely variability in chemical composition for different fly ashes results in the use of their

physical characteristics as the key control parameters when producing commercial products for the concrete industry.

MANUFACTURE OF FLY ASH

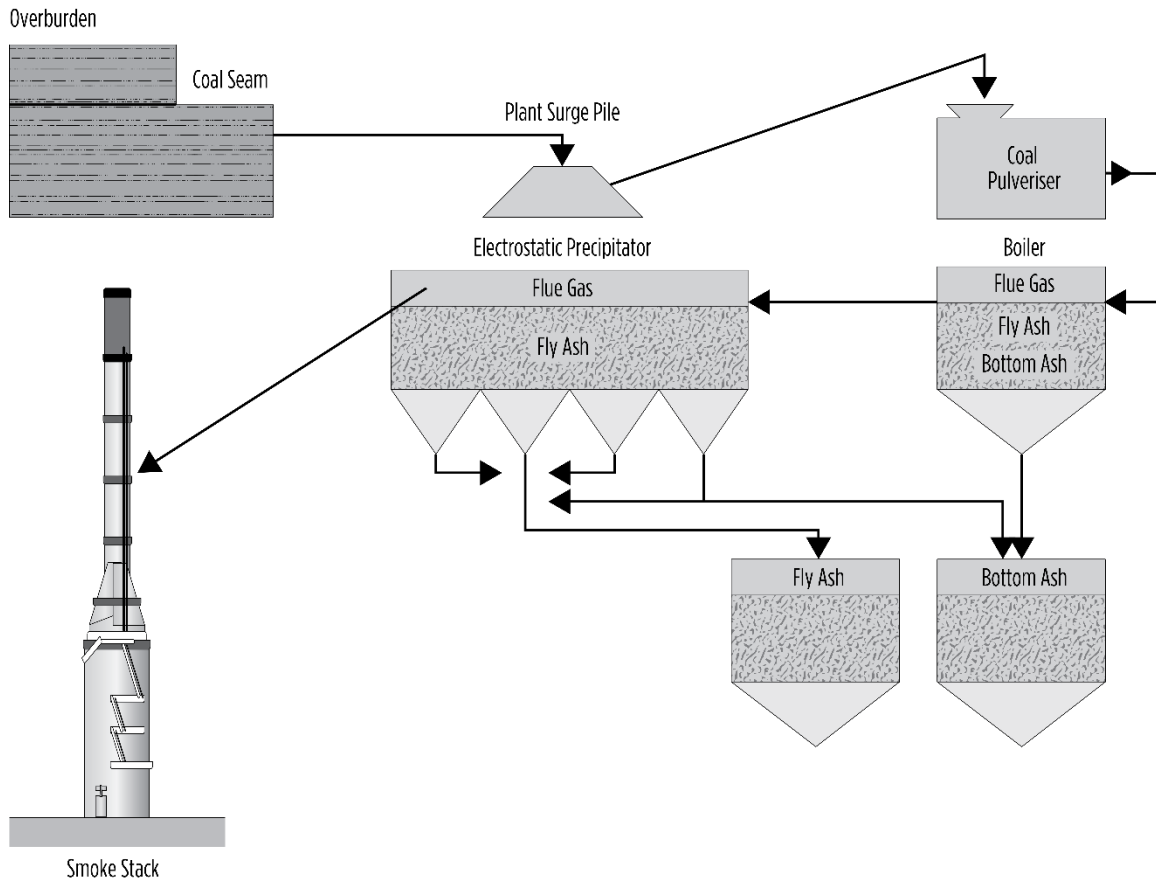


Figure 2.7 – Process for Manufacture of Fly Ash

6.2 AS 3582.1

The first Australian Standards for fly ash were published in 1971 as AS 1129 and AS 1130. The current Standard is AS 3582.1, the latest version of which was published in 2016. AS 3582.1 (2016) has the following features and inclusions:

- It defines three grades of fly ash – Grade 1 and Grade 2 for general concrete use and Special Grade, which is described as a ‘highly reactive’ material;
- It aligns with ASTM and EN requirements for the chemistry of conforming fly ashes in requiring the sum of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ to be $\geq 70\%$ (for Australian fly ashes);
- It introduces a Strength Index minimum requirement for Grade 1 fly ash;
- It introduces a chloride ion maximum limit for all products – the value being consistent with that for cement;
- It aligns testing approaches and testing frequencies with the cement Standard; and
- It introduces the concept of Proven and Unproven Sources – with increased testing frequencies for Unproven Sources.

The key requirements for the three grades are shown in **Table 2.5**.

Table 2.5 – Specified Requirements from AS 3582.1

Property	Special Grade	Grade 1	Grade 2	Test Method
Fineness (% passing 45 µm, minimum)	85	75	55	AS 3583.1
Loss on Ignition (% maximum)	3.0	4.0	6.0	AS 3583.3
Moisture Content (% maximum)	0.5	0.5	0.5	AS 3583.2
Sulfate (as SO ₃) (% maximum)	3.0	3.0	3.0	AS 3583.8
Chloride Ion (% maximum)	0.1	0.1	0.1	AS 2350.2
Strength Index (% minimum)	100	75	-	AS 3583.6

6.3 FLY ASH PRODUCTION AND PROCESSING

Fly ash is produced when pulverised coal is burned in the combustion chambers of coal-fired power stations and derives from mineral matter present in the coal – with mineral matter comprising from 10% to 50% of the ‘coal’ that is burned. Typical mineral matter includes clays, sand and a variety of other minerals that may be found within or between coal seams. The ‘coal’ is pulverised to a fine powder in either vertical roller mills or hammer mills – with pulverised coal typically having 75% of the particles <75 µm. The pulverising frees the mineral particles from the coal particles and coal and mineral particles are exposed separately in the combustion zone. On entering the combustion zone, the temperature of the particles increases at a rate of about 2,000°C per second, and a peak temperature in the order of 1,800°C is reached. Residence time in the combustion zone is about 2-3 seconds. The coal material degasses and combusts while most mineral particles melt and are then entrained in the flue gases.

Upon leaving the combustion zone the mineral particles cool quickly and become, in the main, spherical glassy particles of fly ash. Small quantities of char – unburned coal material – are also entrained in the flue gases. The flue gases pass through particulate collection devices to clean the flue gas before the ‘clean’ gas exits the power station through the chimney.

The particulate collection devices used may be of two types – either Electrostatic Precipitators (ESP) or fabric filters (FF). ESP’s create a charge on the surface of the fly ash particles, and the charged particles are then attracted to earthed plates from which the ash is removed periodically. Fly ash removal efficiencies of 99+% are achievable. The alternative and more modern collection device are the FF which acts much like a vacuum cleaner bag. The flue gas passes through filter bags and the solid fly ash is filtered out. The fly ash is then removed periodically from the filter bags. Fly ash removal efficiencies of 99.8+% are achievable with this process.

To obtain a fly ash product suitable for use as a cementitious material in concrete, some processing of the fly ash is generally required. Initially, the fly ash needs to be assessed for its unburned carbon content (known as its LOI level = Loss on Ignition). Fly ash with suitably low levels of LOI may then also be beneficiated to produce a product of the required Fineness (where Fineness means the % passing a 45-micron sieve using wet sieving). Processing to increase Fineness levels usually involves passing the fly ash through a centrifugal separator (known as a classifier) where coarser fly ash particles are removed leaving the final, finer cementitious product. Fly ash may also be milled (in a ball mill) to increase Fineness levels. ‘Fineness’ as measured using a 45-micron sieve provides a very coarse measure of the particle size distribution of ‘concrete grade’ fly ash which typically has a median particle size in the range of 10-20 microns.

However, the Fineness measure is suitable for use as a production tool.

Routine testing used to control production usually involves testing for moisture content, Fineness and LOI. In situations where high LOI levels are encountered or where problematic LOI material is found, a 'Foam Index test' may also be used for additional screening.

Fly ash processing primarily involves (a) controlling the Fineness of the fly ash product (the actual Fineness level and its consistency) and (b) ensuring that LOI levels meet Standards requirements. This processing does not alter the fly ash chemistry or otherwise alter the inherent reactivity of the fly ash.

6.4 FLY ASH CHARACTERISATION

Bearing in mind that the major use of fly ash as a cementitious material is as a partial cement replacement in Normal Class concrete mixes, fly ash characterisation, at its simplest level, involves ensuring that (a) Standards requirements are met and (b) the product is of consistent quality – which in a practical sense means managing Fineness and LOI levels. Most other fly ash properties are intrinsic and are not able to be easily modified. However, knowledge of other fly ash chemical components and how effective the fly ash is likely to be as a cement replacement are key requirements for understanding the likely performance of fly ashes intended for commercial use.

Physical Characterisation

Understanding physical fly ash properties is important if it is to be produced and used optimally.

Fineness – The Fineness is determined, in accordance with AS 3583.1, by wet sieving through a 45-micron sieve. In the Australian Standard the Fineness represents the weight % of fly ash **passing** through the sieve. (In other Standards the weight % **retained** on the sieve is used.) Fineness provides a coarse measure of fly ash particle sizing. It is of value as a control measure for fly ash processing in terms of (a) ensuring the Fineness value meets the requirement of the Standard, and (b) as a

measure of the consistency of the product. For any high performance/high reactivity fly ash (e.g. Special Grade), where the improved performance is obtained primarily by increasing the Fineness, the test at 45 microns serves little purpose as generally, 100% of the product would pass 45 microns. A more accurate estimate of likely reactivity for a fly ash is obtained from a full particle size distribution (PSD) using, for example, a laser diffractometer device. Typically, the mass median diameter (MMD) for a Grade 1 fly ash would be in the range 10-20 microns, while a high performance/high reactivity fly ash would have an MMD of about 3-4 microns. Increasing the Fineness of a given Fly ash results in a decrease in the Relative Water Requirement and an increase in the Strength Index value. To produce a fly ash conforming with the Special Grade requirements of AS 3582.1 it is usually necessary to increase the Fineness of the ash – either by additional centrifugal separation (i.e. classifying) or by milling the ash.

Relative Density – The Relative Density (RD), determined using AS 3583.5, is dependent on (a) the chemical composition of the fly ash, (b) the proportion of hollow fly ash particles or particles containing voids, and (c) the Fineness. The typical range of Relative Density for fly ashes is 2.0-2.5. For a given fly ash at a particular Fineness value the RD is generally quite consistent. As Fineness increases, so too does the RD – in part through removal of coarser particles that are more likely to contain voids. The RD value is used in concrete mix design to convert the weight of fly ash added into volume.

Relative Water Requirement and Strength Index – Relative Water Requirement (RWR) and Strength Index (SI) determinations are carried out using a mortar mix containing cement and fly ash, a standard sand and water and according to the methods described in AS 3583.6. The Relative Water Requirement and Strength Index values of the cement+fly ash mortar are determined relative to a cement-only mortar. The fly ash replacement level used is about 25%. The RWR is improved where the fly ash has a finer PSD and where the particles are more spherical. The same properties also improve the Strength

performance of the fly ash mortar. The RWR and SI values cannot be used to determine the likely efficiency of a fly ash when used in concrete, though a performance trend can be assumed. (**NOTE:** It is *incorrect* to believe that a fly ash with a SI of 90% would provide 90% of the strength performance of the test cement used. Because the proportion of fly ash in the cement/fly ash mix is only 25%, a 90% SI means that the fly ash has only 60% of the strength performance of the cement – as determined by this particular test.)

Microscopy – Microscopy generally, and scanning electron microscopy (SEM) in particular, are useful in assessing the shape of fly ash particles and the proportion of other components like hollow fly ash particles (called cenospheres) and hollow fly ash particles containing smaller particles (called perlospheres).

Mineral and Chemical Characterisation

As previously mentioned, fly ash forms when the fine mineral particles present in pulverised coal (mostly) melt at the high temperatures in the combustion zone and then quite rapidly cool. As a result of the rapid cooling a high proportion of fly ash is glassy material – that is, it has no crystalline structure. A few minerals, in low proportions, may be found in fly ash. The two predominant minerals are quartz (SiO_2) and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). Magnetite (Fe_3O_4) may also be present where iron-based minerals (e.g. siderite) are part of the coal mineral assemblage. The ‘glass’ content of fly ashes is typically about 60%. The presence of quartz in the fine fly ash presents OH&S concerns as noted in the Handling and Storage sub-section to follow.

Key chemical parameters used to characterise fly ash are those that potentially impact end-use performance. These include the overall chemical composition and some critical individual components, as discussed below.

Chemical Composition (General) – Determined using AS 2350.2, the overall chemical composition, and particularly the combined proportions of silica, alumina and iron provide a primary performance criterion that is necessary to meet AS 3582.1 requirements. This criterion is also used in the ASTM and EN Standards, where the proportion of ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) must exceed 70% for siliceous

fly ashes and 50% for calcareous fly ashes. Having sufficiently high levels of silica and alumina-based materials is important to ensure that a pozzolanic reaction will occur so that the products of the pozzolanic reaction (calcium silicate hydrates and calcium aluminate hydrates) are in sufficient quantity to contribute to concrete strength and durability performance.

Sulfate – Determined using either AS 3583.8 or AS 2350.2, the sulfate content is important when using fly ash in concrete as excess sulfates may contribute to expansive reactions in concrete and these may result in concrete cracking. In siliceous fly ashes particularly, sulfate levels are usually quite low (<0.5%).

Alkalis – Determined using AS 2350.2 the alkali content of fly ash is of importance most particularly when the total alkali content, expressed as % Na_2O Equivalent, exceeds 5%. (Total alkalis, as % Na_2O Equivalent = % Na_2O + 0.658% K_2O .) The importance of the alkalis will be discussed in the ‘Uses’ sub-section following.

Chloride – Determined using either AS 3583.13 or AS 2350.2, the chloride ion content is useful in helping determine the overall amount of chlorides in a concrete mix, which includes the chloride ion content of cement, admixtures and aggregate materials. Chloride ions may migrate through the concrete over time and, if and when they reach any embedded reinforcing steel, may initiate and/or accelerate corrosion of the steel.

Moisture Content – Determined using AS 3583.2, this test measures the amount of moisture adsorbed on the surface of the fly ash particles. The moisture content, if too high, may affect the free-flowing nature of fly ash and in more severe circumstances may result in the formation of lumps which will affect the flow of fly ash through a silo.

Loss on Ignition (LOI) – Determined using AS 3583.3, the LOI test measures the amount of unburned char remaining in the fly ash. High levels of LOI may (a) create dark (and variable) colouration of the ash, (b) appear on the surface of concrete – on the bleed water or on the finished surface, and (c) adsorb air entraining

agent added to concrete and limit the ability to entrain air which may be required for slip-formed concrete or to manage Freeze-Thaw durability issues.

Magnesium Oxide (MgO) – Determined using AS 2350.2, the determination of MgO content is meant to ensure that the mineral periclase (MgO) is not present in detrimental amounts. If present, periclase may cause expansive reactions in hardened concrete leading to cracking. While periclase may be present in fly ashes derived from brown coals it is not likely to be present in black coal ashes. The limit for MgO has been removed from AS 3582.1 but persists in some international fly ash Standards, primarily because these Standards include coverage of brown coal fly ashes.

6.5 FLY ASH USES

In Australia, fly ash has been a standard cementitious additive in concrete since the mid-1960's, almost always as a partial cement replacement. Australia's historic dependence on coal-fired electricity meant that in most States, fly ash was readily available. The use of high-quality coals in modern power stations meant that fly ash quality was generally high and consistent and consequently fly ash became the most common SCM in use in Australia. Previously, the only mainland State where fly ash was not available locally was Victoria. The ready uptake of fly ash was due to it (a) being of lower cost than cement, (b) having a similar cementitious efficiency to cement (at 20-25% replacement rates) and (c) improving concrete durability, particularly in relation to mitigation of Alkali Silicate Reaction (ASR) which had been demonstrated by Australian research. Using fly ash to limit the risk of ASR was effectively mandated by some authorities (e.g. in Queensland) which meant nearly all concrete plants in those regions had a silo of fly ash.

While fly ash is used to improve concrete durability performance, its general use is driven by economic factors. Its lower cost and the improvement in concrete plastic properties, particularly increased cohesiveness that improves the 'pumpability' of fly ash mixes, are

the major drivers for fly ash in 20-32 MPa concrete for general applications.

Fly ash use as a cementitious material is effective because of its pozzolanic behaviour.

Fly ash considerably improves the workability and pumpability of plastic concrete. This is often attributed to the 'ball bearing effect' – this being a consequence of the sphericity of the fly ash particles. It is more likely however, to be due to the increased paste content in fly ash mixes – a result of the difference in density between fly ash and Type GP cement. If 100 kg of Type GP cement (SG = 3.15) is substituted with 100 kg of fly ash (SG of 2.1), there is an increase in paste volume of about 15 Litres/cubic metre.

Typical Fly Ash Use in Concrete

For the 'typical' 20-32 MPa concrete mix, fly ash is used as cement replacement at a level of 20-30%. This may be adjusted seasonally, particularly in the southern-Australian States, where replacement levels may be lower in winter. In North Queensland, replacement is typically at 30% all year around. At these replacement levels, lower early-age strengths (3-days and 7-days) can be expected relative to cement-only mixes, and depending on the fly ash being used, a slightly higher cementitious content may also be required to achieve 28-day strengths equivalent to cement-only mixes.

It is not uncommon now, with the wider availability of ground granulated blast furnace slag (GGBFS), for ternary mixes to be used in Normal Class concretes – again most often for improved economy. Usually, the cement content is kept at about 50% and two SCM's make up the remainder of the cementitious content – typically with fly ash at 20% and GGBFS at 30%. The increased proportion of SCM's in these ternary mixes also means lower early-age strengths. The high reactivity of the GGBFS component usually provides good 28-day strength performance.

Relative to cement-only mixes, binary or ternary concrete mixes show elongated setting times (typically 30-45 minutes at 'normal' ambient temperatures, and potentially longer at temperatures <10°C), good workability and pumpability, lower bleed and are typically

easier to finish. The combination of lower bleed rates, slightly longer setting times and lower early-age strengths can mean an increased risk of plastic shrinkage cracking, though experienced concrete placers are readily able to cope with this potential issue.

High Volume Fly Ash (HVFA) Concrete (usually with cement replacement levels of at least 40%) – HVFA is used in some applications, most typically in mass concrete where lower concrete temperatures are required. HVFA concrete has also been proposed for general concrete applications though uptake has been low. With HVFA concrete, the plastic concrete can be quite ‘sticky’, and early-age and 28-day strengths are affected by the high fly ash content. A somewhat higher cementitious content (at least 40 kg/cubic metre more) is required to be able to achieve the same 28-day strengths as a mix with a 25% fly ash replacement level. Alternatively, a much lower water/binder (W/B) ratio can be used to improve strength performance. Australian research (*‘Guidelines for the use of High-Volume Fly Ash Concretes’*, CSIRO, 1995) has developed mix designs and carried out a comprehensive testing program involving HVFA concrete. While recognising some of its limitations the study shows that HVFA concrete gives excellent durability performance. The research work also notes several prominent uses of HVFA concrete in a range of construction projects.

6.6 DURABILITY OF FLY ASH CONCRETE

The use of fly ash as a partial cement replacement material in concrete results in significantly improved durability performance of the concrete – relative to cement-only concrete. The reasons for the improved performance and the actual effects are quite similar for each of the SCM’s. Rather than describe the durability-related performance for each SCM separately, a sub-section is dedicated to durability performance (sub-section 9).

7 GGBFS

7.1 INTRODUCTION

In the Australian concrete industry context, the term ‘slag’ generally refers to ground, granulated, (iron) blast furnace slag – with the descriptors to be explained and developed in this section.

(NOTE: In a general sense, the term ‘slag’ refers to a waste material separated from metals during the smelting or refining of an ore in a blast furnace. ‘Slags’ are formed during the smelting or refining of many ore types, and consequently there are (for example) copper slags, lead slags, and of particular interest to the Australian concrete industry, iron slags.)

To be of value as a cementitious material, (iron) blast furnace slag needs to be appropriately processed to create a product with the necessary performance and consistency. Specifically, the (iron) slag must first be quenched to form slag granulate (GBFS) – a glassy mineral product – and then the granulate is milled to cement-like fineness in a ‘cement’ mill – creating Ground Granulated Blast Furnace Slag (GGBFS).

GGBFS has a long history of use as a cementitious material in many countries, but in Australia its use began in about 1966 as a cement replacement in concrete used in the expansion of the steel works at Port Kembla. This use continued over the next 20 years with the placement of over 1 million cubic metres of concrete at that location. The initial use of GGBFS in the Port Kembla, Sydney and Newcastle areas was often as a separate cementitious material, though subsequent price increases saw it fall out of favour. In NSW in particular, the use of slag then developed as a component of blended cements from about 1969 – as a 30% GGBFS blend for general concrete use and as a 65% GGBFS blend for Low Heat and Marine Concrete uses. Where slag was readily available it was also being used in ternary mixes with cement and fly ash – these mixes then known as ‘triplex’ mixes. Typically, these ‘triplex’ mixes comprised 40% Portland cement/ 40% GGBFS/ 20% fly ash. In addition to Port Kembla, slag was also produced and used in the regions surrounding the steel works in Newcastle (NSW) and

Kwinana (WA). Today only the Port Kembla steel works remains in operation. This has not limited the use of slag however, with slag granulate being imported from Japan into most Australian States.

While GGBFS use as a cement replacement was quite well understood through the initial experiences, its role in enhancing the durability characteristics of concrete became more prominent as a result of the use of a blended cement containing 60% GGBFS/ 40% ACSE (Shrinkage Limited) cement in the manufacture of concrete immersed tube units for the Sydney Harbour Tunnel which was constructed in about 1990. Concrete made with the slag blend cement met the demanding requirements for this project – these included high compressive strength, high durability, low heat, able to be easily placed and able to be made with a high degree of consistency.

In addition to its being an effective cementitious material, GGBFS improves the environmental credentials of concrete through its use as an efficient cement replacement – lowering the embodied CO₂ and embodied energy levels attributable to concrete. GGBFS does this in a more effective way than other Supplementary Cementitious Materials (SCM's) through being able to be used at higher replacement levels – typically up to 65%. This contrasts with the usual replacement levels for fly ash and silica fume of about 30% and 10% respectively.

7.2 AS 3582.2

Slags derive from processes that are well managed and highly controlled. While the chemistry of slags may vary from blast furnace to blast furnace, from any single source they are generally quite consistent. The chemistry of slag is determined by (a) minerals associated with the iron ore, and (b) the limestone added to the melt to control the melting point of the slag. The chemistry of slag is consequently

dominated by calcium from the limestone and silica from the ore minerals. Critical to GGBFS performance is the proportion of glass content, this being a result of the 'granulation' process – the rapid cooling of the molten slag that forms the slag granulate precursor to GGBFS. The glass content is a significant contributor to GGBFS reactivity and is a function of the efficiency of the granulation process.

The first Australian Standard for GGBFS was published in 1991. The current version is AS 3582.2 (2016).

AS 3582.2 nominates 14 important compositional and performance properties but only provides limits for four of them. These four limits are for key chemical components. The Standard does not set any limits for physical (e.g. Fineness) or performance (e.g. Relative water requirement or Strength Index) characteristics. The nominated suite of compositional and performance properties is shown in **Table 2.6**.

While the Standard does not require that the product be tested in concrete to ensure that it is suitable, it does differentiate between 'Proven' and 'Unproven' slag sources. 'Unproven' sources need to be tested at a higher frequency (for a period of six months) until there is confidence in the quality and consistency of the material. While not all nominated properties have limits defined in the Standard, purchasers may request test data for any or all nominated properties.

Like the fly ash Standard, AS 3582.2 uses the % passing a 45-micron sieve as a measure of Fineness and as an indicator of relative reactivity for a given slag source. While Blaine surface area measurement (as used for cement) can be carried out on GGBFS, it does not provide as good an indication of likely reactivity/performance as the Fineness measured using the 45-micron sieve.

Table 2.6 – Properties Nominated in AS 3582.2 (2016)

Property	Limit	Reference Test Method
Fineness, by mass, % passing 45-micron sieve	-	AS 3583.1 or AS 2350.9
Insoluble Residue (%)	-	AS 3583.14
Loss on Ignition (%)	-	AS 3583.3
Sulfate, as SO ₃ (%)	-	AS 3583.8 or AS 2350.2
Sulfide Sulfur, as S (% maximum)	1.5%	AS 3583.7
Magnesia (MgO) (% maximum)	15.0%	AS 3583.9 or AS 2350.2
Alumina (Al ₂ O ₃) (% maximum)	18.0%	AS 3583.10 or AS 2350.2
Total Iron (FeO) (%)	-	AS 3583.10 or AS 2350.2
Manganese (MnO) (%)	-	AS 3583.11 or AS 2350.2
Chloride Ion Content (% maximum)	0.1%	AS 3583.13 or AS 2350.2
Total Alkali (%)	See note	AS 2350.2
Relative Density	-	AS 3583.5
Relative Water Requirement (%)	-	AS 3583.6
Strength Index (%)	-	AS 3583.6

NOTE: If alkali aggregate reaction is considered likely, the Available Alkali test to AS 3583.12 may be required. See HB 79 for further information.

7.3 GGBFS PRODUCTION AND PROCESSING

Iron blast furnace slag is a by-product of the iron-making process – a process that involves the production of iron metal from iron ore. Iron ore, fluxing agents (typically limestone or dolomite), fuels (typically coal or natural gas) and oxygen are fed into a blast furnace where the mixture is heated until the ore and flux are molten. The mineral materials associated with the iron ore combine with the fluxing agents allowing the molten materials (iron and ‘slag’) of very different densities to be separately ‘tapped off’ from the blast furnace and subsequently separately processed. The process is shown diagrammatically in **Figure 2.8**, and the molten iron and slag materials in **Figure 2.9**.

The slag that has been ‘tapped off’ can be treated in either of two ways – it can be air cooled or it can be quenched. Quenching involves the rapid cooling of the slag using (typically) water sprays. This rapid cooling

BLAST FURNACE

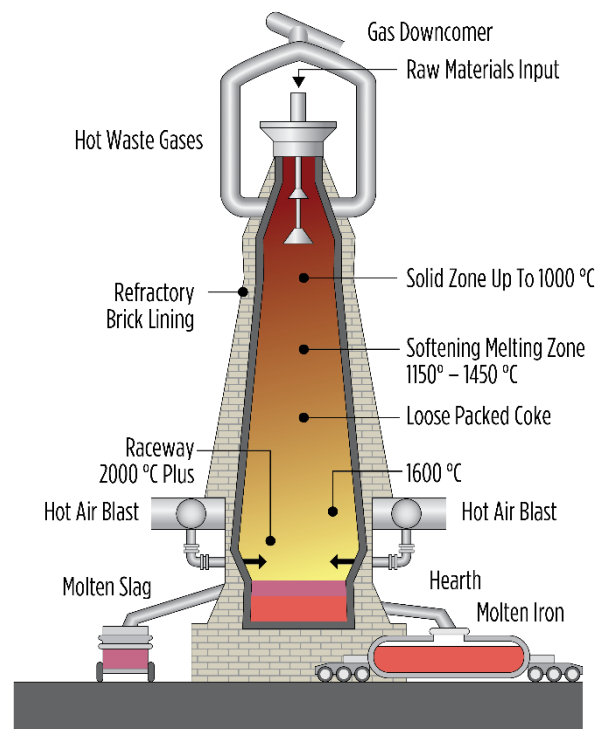


Figure 2.8 – Blast Furnace Process

results in the formation of a glassy product known as slag granulate (GBFS) which has a sand-like consistency – typically 1-3 mm in size, with a maximum particle size of about 8 mm. This material contrasts with the air-cooled slag which is a more massive material and which, after crushing and screening using conventional quarry processes, is commonly used as an aggregate material in road-making and in a variety of other end uses (see **Figures 2.10 (a) and (b)**).

Slag granulate contains a high proportion of glassy material (often >90%) with a chemical composition like that shown in **Table 2.7**.



Figure 2.9 – Molten Iron and Slag

Table 2.7 – Typical Slag Granulate Composition

Component	Proportion (%)
CaO	40
SiO ₂	35
Al ₂ O ₃	15
MgO	5
Total Alkali (as Na ₂ O Equivalent)	0.5
Fe ₂ O ₃	0.5

Slag granulate is a relatively fine and partly reactive material that can be stored in exposed stockpiles for some time before milling to form GGBFS. In some ambient conditions, particularly with higher temperatures and moisture levels, slag granulate can undergo 'weathering' that reduces the cementitious efficiency of the final GGBFS product. Weathered granulate shows higher moisture and Loss on Ignition (LOI) levels than fresh

product and the performance of the GGBFS product, as indicated by strength testing of mortar or concrete samples using the product, is reduced.



(a)



(b)

Figure 2.10 – (a) GBFS and (b) Slag Aggregate

Milling Slag Granulate

Slag granulate is milled to form GGBFS in 'cement' mills – either ball mills or Vertical Roller Mills (VRM's) – and this milling can be carried out by alternating manufacturing runs of cement and GGBFS if required. Granulate may be milled alone to form GGBFS or by inter-grinding with cement clinker to form Slag Cements.

(NOTE: Slag (Type GB) cements may also be manufactured by (post) blending Type GP cement and GGBFS.)

Granulate is harder to grind than cement clinker, and when inter-grinding clinker and granulate the cement may dominate the finer fractions of the resultant Slag Cement due to the relative grindabilities of the two components. Grinding agents are invariably used to improve milling efficiencies and to

provide a free-flowing cementitious product – for both GGBFS and Slag cement.

Some manufacturers add gypsum when milling slag granulate – at levels of up to about 5% gypsum, but typically at 2-3% gypsum.

(NOTE: Gypsum is always used when manufacturing inter-ground Slag Cements.)

There is some conjecture about the value of using gypsum in GGBFS manufacture as it (a) requires an additional material in the process, and (b) requires another property (SO₃ content) to be monitored and tested. There is some theoretical and empirical evidence that milling granulate and gypsum, with resultant SO₃ levels in the GGBFS of up to 3.0%, can improve concrete performance by way of (a) improved early-age strength development, (b) lower levels of concrete drying shrinkage, and (c) improved durability performance, particularly resistance to sulfate attack.

The 'Fineness' of the GGBFS product can be measured in two ways – using air permeability, with the result expressed as a surface area value with the unit m²/kg; or as the %-retained on (or passing) a 45-micron sieve. In Australia, GGBFS surface area levels are usually at least 450 m²/kg, while the proportion retained or passing a 45-micron sieve is dependent on the effectiveness of the separator on the mill – with typical values of '%-retained' in the range 1-5%. For a given GGBFS product, the proportion of product retained on or passing the 45-micron sieve provides a higher correlation with Strength Index performance results than does the surface area measurement using air permeability.

7.4 GGBFS CHARACTERISATION

Like any material used in concrete manufacture, GGBFS must meet the requirements of the Australian Standard and any relevant specification and should be of consistent quality. As a cementitious material, and particularly when used in high proportions, GGBFS is an important determinant of concrete compressive strength consistency. Where granulate is imported this creates a risk of potential variability that must be understood

and addressed (tested for) when manufacturing GGBFS.

Physical Characterisation

Fineness – The Fineness is determined, according to either AS 3583.1 or AS 2350.9, by sieving through a 45-micron sieve, and determining the percentage of the sample, by mass, that passes through the sieve. This provides a coarse measure of the particle size distribution but is adequate to manage the consistency of the product during manufacture. Alternatively, the air permeability method used for cement (AS 2350.8) can be used and Fineness Index /surface area expressed as m²/kg determined. In practice, variability in strength performance of GGBFS appears to be more closely related to the Fineness determined by sieving than that expressed as a surface area.

Relative Density – The Relative Density (RD) of GGBFS is determined using AS 3583.5, and typically has a value of about 2.9 and is generally quite consistent for a given granulate source. The RD value is used in concrete mix design to convert the weight of GGBFS added into volume.

Relative Water Requirement and Strength Index

– Relative Water Requirement (RWR) and Strength Index (SI) determinations are carried out using a mortar mix containing cement and GGBFS, a standard sand and water and according to the methods described in AS 3583.6. The Relative Water Requirement and Strength values of the cement + GGBFS mortar are determined relative to the water requirement and strength obtained with a cement-only mortar. The slag replacement level used in the tests is about 50%. The RWR is improved where the GGBFS has a higher Fineness, as is the Strength Index. The RWR and SI values cannot be used to determine the likely efficiency of GGBFS when used in concrete, though a performance trend can be assumed.

Microscopy – Whether using a light microscope or Scanning Electron Microscopy (SEM) there is little value that can be obtained by observing the GGBFS product. It is instructive that the appearance of GGBFS and Portland cement particles are very similar –

both being fractured 'glassy' particles ranging from coarse to relatively fine – though this is not surprising since both are produced by crushing larger particles in a mechanical comminution (see image **Figure 2.5**).

Mineral and Chemical Characterisation

As previously noted, GGBFS is a reactive cementitious material because of its high glass content, this being a consequence of the rapid cooling/quenching that occurs during the granulation process, forming what has been described as 'supercooled liquid silicates'. Comparing blast furnace slags from various sources it is apparent that the calcium and silica contents are quite consistent (about 40% as CaO and 33-37% as SiO₂ respectively), but that there are quite variable alumina and magnesia contents (8-18% as Al₂O₃ and 5-14% as MgO respectively). Iron, manganese and sulfur contents are reasonably variable, but these components are found at much lower levels, each typically at 0.5-2%. In general terms, GGBFS is described as being comprised of glass silicates and alumino-silicates of calcium and magnesium plus compounds of iron, sulfur, manganese and other minor and trace elements. GGBFS chemistry and its importance will be discussed in greater detail below.

Generally, national Standards do not nominate a minimum glass content for GGBFS for cementitious use – they usually rely on performance requirements rather than prescribing properties like minimum glass content. GGBFS products used commercially would be expected to have a glass content (determined microscopically or by X-Ray Diffraction) of >90%.

Chemical Composition (General)

Determined using AS 2350.2, this testing measures the proportions of the major and minor elements, expressed as the relevant oxide, and allows chemical moduli such as those described in international Standards like EN 15167-1, to be determined. The chemistry of slag from a single source is generally quite consistent as the iron making process is carried out with a high degree of chemical control. There may, however, be some variation in chemistry between slag sources because of raw material variations.

Sulfide Sulfur – Determined using AS 3583.7 and expressed as %S. The AS 3582.2 limit of 1.5% controls the proportion of this reduced sulfur species that can potentially have some detrimental effects in concrete in its original form, or when ultimately oxidised to sulfate. Testing of concrete has shown that sulfides have oxidised and are no longer present after about one year – generally without causing any expansion or instability.

Sulfate Sulfur – Determined using AS 3583.8 or AS 2350.2 and expressed as %SO₃. Sulfates derive directly from the slag or by oxidation of slag sulfides, or from the intended addition of gypsum during GGBFS milling. Maximum allowable levels of sulfate are set in all cementitious materials because of concerns about the formation of expansive reaction products in concrete – this leading to an increased risk of concrete cracking.

Magnesium Oxide – Determined using AS 3583.9 or AS 2350.2 and expressed as %MgO. The AS 3582.2 limit of 15.0% provides some confidence that the mineral periclase will not be present. Periclase can react to form expansive products, and if present in sufficient proportion, can cause concrete cracking.

Alumina – Determined using AS 3583.10 or AS 2350.2 and expressed as %Al₂O₃. Despite the increased resistance of concrete to sulfate attack when using (for example) 65% slag cement, there is evidence that slags with higher alumina contents (about 18%) may have less resistance to sulfate attack than slags with lower alumina contents (about 11%). Limiting the alumina content to a maximum of 18.0% (AS 3582.2) helps ensure that slag concrete provides good durability performance.

Iron Oxide – Determined using AS 3583.10 or AS 2350.2 and expressed as %FeO. This measure reflects, in part, the effectiveness of the separation of the slag from the molten metal. Typical levels are 0.5-2.0%.

Manganese Oxide – Determined using AS 3583.11 or AS 2350.2 and expressed as %MnO. Manganese is a mineral associated with iron. The levels of MnO in GGBFS are typically 0.5-1.0%.

Chloride – Determined using AS 3583.13 or AS 2350.2 and expressed as %Cl – the chloride ion content is useful in helping determine the overall amount of chloride in a concrete mix, along with the chloride ion content of cement, admixture and aggregate materials. Chloride ions may migrate through the concrete over time and, if and when they reach any embedded reinforcing steel, may initiate and/or accelerate corrosion of the steel.

Total Alkalis – Determined using AS 2350.2 and expressed as %Na₂O Equivalent (%Na₂O + 0.658%K₂O). The alkali content of GGBFS is of importance most particularly if the GGBFS is to be used in any concrete mix using potentially reactive aggregates. AS 3582.2 requires that reference be made to the HB 79 document if any risk of alkali aggregate reaction exists. The importance of the alkalis will be further discussed in the 'Uses' sub-section below.

Loss on Ignition (LOI) – Determined using AS 3583.3, the LOI test measures the amount of combustible material in the GGBFS. The test result should be corrected to account for any oxygen uptake by the sample during testing due to the oxidation of reduced sulfur or iron species.

7.5 GGBFS USES

While early GGBFS use in Australia was confined to regions where steel mills were operating – around Port Kembla and Newcastle in NSW from the mid-1960's, and around Kwinana in WA from the early 1970's – it has now become the most widely-used SCM in Australia. While the availability of 'local' slag granulate (GBFS) is now confined to the Port Kembla (NSW) region, slag granulate is being imported into all mainland Australian States, with GGBFS being produced locally for supply in those regions. Little if any GGBFS is imported.

In part, the growing volumes of GGBFS use are attributable to (a) the ready acceptance of SCM's as fundamental cementitious materials in this country, and (b) the decline in fly ash availability in many areas. Slag is a particularly versatile SCM and is able to be used as a low-

level cement replacement (nominal 30%) in Normal Class concrete and also as a high-level cement replacement (nominal 65-70%) for special end uses. While early-age concrete strengths with slag use (at all proportions) are lower than those obtained with 100% cement mixes, later age strengths are equivalent to, or better than, 100% cement mixes. There are several added advantages to using GGBFS including (a) lower cost, (b) lower concrete embodied CO₂ and embodied energy levels and (c) improved durability performance. One of the first uses of GGBFS was in ternary blends with cement and fly ash, and this is not an uncommon approach today.

Use of GGBFS as a cementitious material in Australia has grown to almost 2 Mt in 2016, with about 60% of this being imported material.

GGBFS use as a cementitious material is effective primarily because of its activation by lime, alkalis and sulfates in the cementitious paste. Unlike fly ash, GGBFS does have some slight reactivity with water alone – a property known as latent hydraulic behaviour.

In a concrete paste, lime is formed as a product of cement hydration and this lime is available to react with SCM's used as partial cement replacements. GGBFS hydration is also activated by alkalis and sulfates dissolved from the cement, however the initial rate of hydration is slow as the lime needs to initially break down the glassy GGBFS material. Silica and alumina compounds in the GGBFS react with lime to form calcium silicate hydrate and calcium aluminate hydrate – products similar to the primary cementitious materials produced by the cement hydration reaction. The calcium silicate and calcium aluminate hydrates formed in these reactions add to concrete strength and to the refinement of the pore structure of the concrete paste which improves concrete durability performance.

Typical Uses of Slag in Concrete

For Normal Class 20-32 MPa concrete, GGBFS is often used as a 30% replacement for cement. In this situation the slag provides optimal performance in relation to (a) cost, (b) early and later-age strength performance and (c) setting time performance. GGBFS can be used as a 1:1 replacement for cement in these mixes and

later-age strength performance is generally excellent. Workability of the concrete is not greatly affected one way or the other at this replacement level and the increase in setting time is manageable. There can be some increased bleed when GGBFS is used and this can be advantageous in hot weather.

It is not uncommon now, with the wider availability of GGBFS, for ternary mixes to be used in Normal Class concretes – most often for improved economy. Usually, the cement content is kept at about 50% and two SCM's make up the remainder of the cementitious content – typically with fly ash at 20% and GGBFS at 30%. The increased proportion of SCM's in these ternary mixes also means lower early-age strengths. The high reactivity of the GGBFS component usually provides good 28-day strength performance.

For high durability mixes and low heat mixes, cement replacement at levels of 65% and 70% is not uncommon. There has been a large amount of research work carried out in Australia to assess the durability performance of concretes containing high slag replacement levels – in relation to their improved resistance to sulfate attack, chloride ingress and alkali aggregate reaction. A particularly common use of concrete with high slag replacement levels is in low heat/mass concrete applications that are becoming much more prevalent.

One unusual experience with (conventional and geopolymer) concrete containing GGBFS as a cementitious material is the formation of blue or green surface colouring which is evident soon after removal of forms. This colouration is related to the presence of sulfides in the GGBFS and most likely, their interaction with traces of copper, manganese or vanadium from the GGBFS. The colouration typically disappears after a few weeks when surface oxidation due to air exposure occurs, without any detriment to the concrete.

High GGBFS substitution levels also occur with 'paste fill' mixes used in mining operations. These low strength mixes are used to fill mine voids and allow more effective mineral extraction. Where sulfur-bearing ores are involved, the sulfates strongly activate the GGBFS which allows very high early and later-

age strengths to be obtained even with low binder contents.

GGBFS is also a primary material used in a new concrete product known as Envisia™. The binder used in this product includes GGBFS activated by sulfates – a binder type known as super-sulfated cement. The resultant concrete is claimed to provide good plastic and hardened properties and to have a low level of embodied CO₂.

7.6 DURABILITY OF GGBFS CONCRETE

The use of GGBFS as a partial cement replacement material in concrete results in significantly improved durability performance of the concrete – relative to cement-only concrete. The reasons for the improved performance and the actual effects are quite similar for each of the SCM's. Rather than describe the durability-related performance for each SCM separately, a sub-section is dedicated to durability performance (sub-section 9).

8 AMORPHOUS SILICA

8.1 INTRODUCTION

The amorphous silica materials are a class of Supplementary Cementitious Materials (SCM's) more diverse than the other SCM's commonly used in concrete. Their origins are similarly diverse – including naturally occurring minerals associated with volcanic activity and geothermal deposits; waste material resulting from the processing of a common grain (e.g. rice husk ash); and a synthetic product derived from the processing of silicon metal or ferro-silicon alloys (silica fume). The first of the natural occurring minerals were the pozzolanas – harvested from volcanic sources around Pozzuoli (in southern Italy) and used by the Romans in structures that created a paradigm shift in concrete construction. Similar materials were used much later by Smeaton when he built the Eddystone Lighthouse in the UK in about 1759 – a structure that still stands today (albeit in a new location). The success of the

cementitious mix used in this structure led to further experimentation with binder materials and ultimately to the discovery and development of Portland cement in 1824.

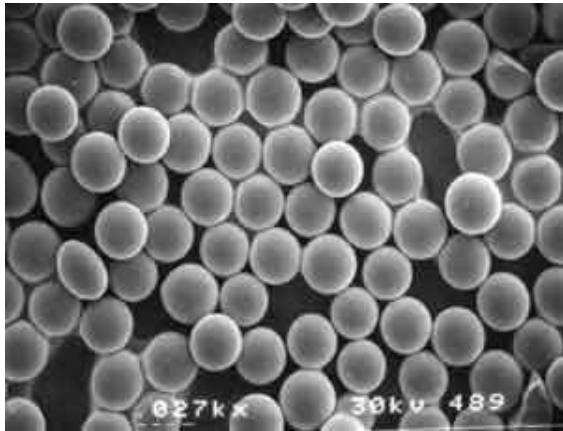


Figure 2.11 – Silica Fume Particles



Figure 2.12 – 'Microsilica' Deposit

The original pozzolanas were of pyroclastic origin – resulting from very fine magma particles being blasted into the air during volcanic activity and then quenched in the relatively cool atmosphere. Known now as pozzolanic materials, the glassy particles contain reactive silica and alumina compounds – which, while possessing little inherent cementitious value alone, can react with calcium hydroxide (lime) in the presence of water to form products with cementitious properties.

Silica fume was first identified as a potential SCM in the 1940's but it wasn't until large scale collection devices came on-line in silicon and ferro-silicon alloy plants in the early 1970's that commercial use was possible. This initial use was in Norway particularly, while in Australia silica fume use began in about 1977. Silica fume sourced from operations in Tasmania and

Western Australia was used in concrete in Australia, but now, most silica fume is imported. The nature and use of silica fume will be discussed in detail below.

In New Zealand, product mined from geothermal deposits near Rotorua (North Island) has been commercialised. These natural materials have been found to improve concrete performance – particularly concrete strength and durability, and to also provide a means of mitigating Alkali Silica Reaction (ASR). This material will also be described in some detail in this sub-section and differentiated from other amorphous silica materials by using the name Microsilica – which is the commercial name used for the New Zealand geothermal product, but which is also sometimes used as a generic name for fine amorphous silica products more generally.

There is a wide variety of amorphous silica materials used throughout the world that have not gained acceptance in Australian or New Zealand concrete markets. These materials include metakaolin, rice husk ash and a variety of glassy materials of geological origin, including (calcined) diatomaceous earth and pitchstone. These materials will not be examined in detail but may be referred to by way of comparison with other amorphous silica products.

8.2 AS 3582.3

The Australian Standard AS 3582.3 provides coverage for all 'amorphous silica' materials – whether naturally occurring or synthetic. While the first version of AS 3582.3 published in 1994 provided specifications for silica fume only, the latest (2016) version covers 'amorphous silica' materials generally.

AS 3582.3 (2016) defines the various amorphous silica SCM's as follows:

Amorphous Silica – very fine pozzolanic material comprised mostly of non-crystalline silica.

Naturally Occurring Amorphous Silica – Refined pozzolanic material – composed mostly of amorphous silica – derived either from hydrothermal alteration of ignimbrite or pumice

breccia or from the extraction of precipitated silica from geothermal water – and supplied as either powdered, slurried or pre-wetted compressed filter cake – these varying in solids and moisture contents.

Silica Fume – Very fine pozzolanic material comprised mostly of amorphous silica produced by electric arc furnaces – a by-product of elemental silicon or ferro silica alloy production – and supplied in several forms including undensified (bulk density $\leq 400 \text{ kg.m}^{-3}$), densified (bulk density $\geq 400 \text{ kg.m}^{-3}$) or slurried (typically 40-60% silica fume by weight).

AS 3582.3 nominates eight compositional and performance properties but only provides limits for four of them. The four limits describe chemical compositional requirements. The Standard does not set any limits for physical (e.g. Fineness) or performance (e.g. Relative water requirement or Strength Index) characteristics. The nominated suite of compositional and performance properties from AS 3582.3 is shown in **Table 2.8**.

While the Standard does not require that a product be tested in concrete to ensure that it is suitable, it does differentiate between ‘Proven’ and ‘Unproven’ amorphous silica sources. ‘Unproven’ sources need to be tested at a higher frequency (for a period of three months) until there is confidence in the quality and consistency of the material. While not all nominated properties have limits defined in the Standard, purchasers may request test data for any (or all) of the nominated properties.

8.3 AMORPHOUS SILICA PRODUCTION AND PROCESSING

The wide variety of materials in the ‘amorphous silica’ class necessitates separate consideration of the nature and extent of processing required for each material type. As with all raw materials for use in concrete, the key processing considerations are (a) meeting Standard or specification requirements, and (b) providing a product of consistent quality.

Table 2.8 – Properties Nominated in AS 3582.3 (2016)

Property	Limit	Reference Test Method
Total Silica Content (SiO ₂) (%)	>85	AS 2350.2
Loss on Ignition (% maximum)	6.0*	AS 3583.3
Moisture Content (% maximum)	3.0**	AS 3583.2
Sulfate (as SO ₃) (% maximum)	3.0	AS 3583.8
Bulk Density	-	***
Surface Area	-	****
Chloride Ion Content (% maximum)	-	AS 3583.13
Strength Index (% minimum)	-	AS 3583.6

NOTES:

- * may exceed 6.0% if Strength Index is acceptable;
- ** limit does not apply to slurried products;
- *** method defined in Standard;
- **** to be carried out in accordance with ASTM C1069.

Silica Fume

Silica fume is a by-product of the production of silicon metal or ferro-silicon alloys in electric blast furnaces. In these processes, silica sand (quartz) is fed into the blast furnace with coke, coal and wood chips. These materials are reacted at temperatures of about 2,000°C to produce the silicon product, with very fine silica fume being produced as a by-product of the reactions. Decades ago, the smoke-like silica fume fines were released into the atmosphere. In the 1970’s more substantial environmental regulations required that the fines be collected in fabric filters which allowed the silica fume to be recovered and made available for use in the concrete industry.

Silica fume as produced is an extremely fine material and is comprised primarily of high purity (typically >95%) amorphous silicon dioxide (SiO₂). A small proportion of crystalline SiO₂ is also produced. The level of crystalline silica varies dependent on the manufacturer, with reported levels of from <0.05% to <0.5%. The physical characteristics of the silica fume product are:

- Particle Sizing: 95% <1 µm;
- SG: about 2.2;
- Specific Surface Area: 15-30 m²/g;
- Bulk Density:
 - 130-430 kg.m⁻³ (as produced);
 - 480-720 kg.m⁻³ (densified).

Silica fume as produced is very light, and to improve its handling characteristics and transportability, it needs to be densified. i.e. agglomerating the fine particles into larger 'lumps'. This then creates a need to ensure that, when using the densified product in concrete, the material is de-agglomerated to ensure full value is achieved. To improve its ease of handling, silica fume can also be supplied in a slurried form – these slurries sometimes containing a super-plasticiser. They are not now widely used. Undensified silica fume may be used in bagged cement-based products or in applications where mix designs require little or no coarse aggregate – a situation where de-agglomerating densified silica fume is more difficult.

Microsilica

In New Zealand, natural amorphous silica deposits in the Rotorua district have been commercialised. These deposits are hosted in hydrothermally altered rhyolitic rocks – Mamuka Ignimbrites and Rotoiti Breccia – estimated to be 60,000 to 200,000 years old. The deposits have been extensively altered geologically, with widespread silification. The product is mined, ground and blended to achieve a product of high quality with consistent physical and chemical properties. The product has a SiO₂ content of 85-90%, being mainly amorphous silica but containing a small proportion of crystalline quartz and cristobalite. It has a bulk density of about 500-600 kg.m⁻³ and an average particle size of about 2 µm.

Metakaolin

Metakaolin is a fine, amorphous, aluminosilicate SCM that is made by calcining pure or refined kaolinitic clay at a temperature of 650-800°C, and then grinding it to a specific surface area of about 700-900 m²/kg resulting in an average particle size of about 3 µm. The product is a highly reactive SCM.

Rice Husk Ash

A reactive pozzolanic material is produced when rice husks are burned under controlled conditions – typically at 500-700°C. The resultant material has a SiO₂ content of about 80% and contains both amorphous and crystalline silica particles. The average particle size can be quite high (about 50 µm), but because of the highly porous structure of the product it can have an extremely high surface area (up to 50-60,000 m²/kg), which makes it highly reactive. The need to closely control the burning conditions limits the practicality of producing the product in many regions, and particularly in under-developed countries.

Natural Pozzolans

There is a wide variety of natural pozzolan materials used throughout the world, with a variety of origins. Many are of volcanic origin and the glassy deposits may be 'incoherent' layers of glassy material or compacted materials (known as tuffs) that may have been chemically altered by later geological activity. Some sedimentary materials (clays and diatomaceous earths) also demonstrate strong pozzolanic behaviour. In the main these materials are glassy, silico-aluminate compounds and often with significant porosity. They can contain small proportions of crystalline silica as well as quite high alkali contents. The materials can be mined and milled into fine powders for use in concrete and related applications. There has been little interest in this class of pozzolans in Australia, although some research work has been done to assess the potential for use in concrete of a glassy pitchstone material found in North Queensland.

8.4 AMORPHOUS SILICA CHARACTERISATION

The variety of natural and synthetic sources of amorphous silica materials results in a wide range of material properties and reactivities. While synthetic materials derive from highly controlled manufacturing processes and are expected to be quite consistent, the properties of the natural materials reflect the diversity of their sourcing. Many of the key physical

properties result from processing activities that have been described above. The significance of the physical properties is discussed below, and a comparison of key properties is given in **Table 2.9** to allow a comparison of these materials to be made.

Physical Characterisation

Surface Area – The specific surface area (SSA) of amorphous silica materials is a function of the processes from which they are derived and is fundamental to their performance in concrete. The SSA is typically measured using the BET method, and the results give values very much higher than those for Type GP cement or more conventional SCM's. High levels of pozzolanic reactivity and increased (relative) water requirement are a consequence of the very high surface areas. For some of these fine materials, where agglomeration is a problem, conventional 'fineness' testing using a 45-micron screen is also used as a measure of the degree of agglomeration. For silica fume, the American ASTM C 1240 Standard sets a maximum of 10% retained on the 45-micron screen to limit the degree of agglomeration, as well as a minimum SSA of 15 m²/kg to ensure adequate reactivity.

Average Particle Size – In general this value is related to the SSA, but for some of the amorphous silica materials, high SSA values come about because of the porous structure of the material. Rice Husk Ash (RHA) is an example of a relatively coarse material having a high SSA because of its highly porous structure. For silica fume, the MMD is about 0.1-0.2 µm.

Relative Density or Specific Gravity (SG) – This is not a specified property in either the Australian Standard or most international Standards. The SG is a function of the chemistry and mineralogy of the material and is used in mix designs to convert mass to volume. For silica fume the SG is about 2.1-2.2.

Bulk Density – This property is important from handling, transport and packaging perspectives. The very low bulk density of silica fume as produced creates difficulties in handling and transporting the product. Densification of the product, effectively an

agglomeration process, assists with handling but creates potential problems when using the material in concrete. Unless the product is effectively de-agglomerated during concrete mixing its full pozzolanic activity potential will not be realised.

Water Requirement and Strength Index

These complementary properties affect the strength able to be achieved when using the product in concrete. A high SSA generally means an increased water demand in concrete and this needs to be mitigated using admixtures. The high SSA also means high reactivity and concrete strength performance is generally much higher than with conventional SCM's. Typical of the test methods used to assess these properties are those described in AS 3583.6. This test involves the preparation of mortars containing (a) cement only – the control mortar, and (b) cement plus a proportion of the test material – the test mortar. The amount of water required to achieve a similar flow to the control mortar allows calculation of the (relative) Water Requirement, while the strength of the test mortar (at either 7 days under accelerated curing, or 28 days under standard curing) allows calculation of the (Strength) Activity Index.

Mineral and Chemical Characterisation

The amorphous silica materials are either silica-rich or silico-aluminate rich materials derived primarily from geological sources. To ensure adequate levels of pozzolanic activity these materials must be mainly amorphous. Given their geological origin, many amorphous silica products contain small proportions of crystalline silica minerals (quartz and cristobalite) which must be given proper consideration when handling and using the products (see 'Handling and Storage' below). Key chemical parameters used to characterise the amorphous silica materials are those that potentially impact end-use performance. These include overall chemical composition and some individual components, as described below.

Chemical Composition (General)

– Determined using AS 2350.2, this information is primarily used to assess the SiO₂ content – for which a minimum value (85%) is set in almost all national Standards. For a product like silica fume that derives from a well-controlled

industrial process, variations in chemistry would be expected to be small. For potentially more variable materials of geological origin, chemical content provides a simple measure of product consistency.

Sulfate – Determined using either AS 3583.8 or AS 2350.2, the sulfate content is an important property when using SCM's in concrete as high levels of sulfate may contribute to expansive reactions in concrete and these may result in concrete cracking.

Alkalis – While AS 3582.3 does not set any limits for alkali content, it requires that any determination of total alkali or available alkali content be carried out using methods AS 2350.2 or AS 3583.12 respectively. The total alkali content may provide useful information if needed to assess likely susceptibility of a concrete mix to ASR if reactive aggregates are being used in the mix.

Chloride – Limits for chloride are set in AS 3582.3. Able to be determined using either AS 3583.13 or AS 2350.2, the chloride ion content is useful in helping determine the overall amount of chloride in a concrete mix, along with the chloride ion content of cement, admixtures and aggregate materials. Chloride ions may migrate through the concrete over time and, if and when they reach any embedded steel, may initiate and/or accelerate corrosion of the steel.

Moisture Content – Determined using AS 3583.2, this test measures the amount of moisture adsorbed on the surface or in the pores of the material. The moisture content, if too high, may affect the free-flowing nature of a material and in more severe circumstances may result in the formation of lumps.

Loss on Ignition (LOI) – Determined using AS 3583.3, the LOI test measures the amount of unburned carbon remaining in the product. This test provides useful information about

silica fume (where carbon electrodes are used in the silicon / ferro-silicon manufacturing process) and for Rice Husk Ash (which is produced in a combustion process).

8.5 AMORPHOUS SILICA USES

Australian experience with amorphous silica products is limited to local and imported silica fume, while in New Zealand the locally produced Microsilica product and imported silica fume have been used. In Australia, recent data suggests that silica fume use is about 15,000 tpa. Silica fume and Microsilica are used for two primary reasons, namely (a) to reduce Portland cement content for economic reasons, and (b) to produce high strength / high durability concrete. Most of the current use of silica fume is for the latter reason.

Silica fume is highly reactive pozzolan with a cementitious efficiency nominally between 2 and 5 times that of Type GP cement – dependent in part on the overall cementitious content of the mix and the proportion of silica fume. Silica fume is not often used at a cement replacement rate of greater than 8-10% as concrete mixes can become very sticky and difficult to place and finish at higher replacement levels. Almost invariably, silica fume mixes require a super-plasticiser to provide reasonable workability, however care needs to be taken to ensure that total water is not reduced to a point where it might affect strength development. Highly cohesive silica fume mixes generally have a lower susceptibility to segregation. Another noticeable property of concrete containing silica fume is the very low bleed level and rate. This needs to be understood and managed for any flat-work applications.

Table 2.9 – Physical Properties of Amorphous Silica Products

Property	Silica Fume		Microsilica	Metakaolin	Rice Husk Ash	Natural Pozzolans
	Un-Densified	Densified				
Specific Surface Area (m ² /g)	15-30	15-30	-	8-15	50	variable
Average Particle Size (µm)	0.2	0.2	2.0	1.0	11-30	variable
S.G.	2.2	2.2	2.15-2.3	2.4-2.6	2.1	2.3-2.6
Bulk Density (kg.m ⁻³)	130-430	480-720	500-600	600	500	1,000-1,400
Water Requirement	increased	increased	increased	increased	increased	increased
Activity Index (%)	120	120	108	120	120	variable

Silica fume reacts strongly and relatively quickly with lime present in the concrete paste, and this has led to concerns about a reduction in concrete paste pH sufficient to compromise the passivation of any embedded steel in the concrete. Testing on mature cement pastes has shown that 10% silica fume can reduce the paste pH by 0.5 pH units, while 20% silica fume can reduce the pH by 1.0. Even with the higher proportion of silica fume the paste pH remained above 12.5 and steel passivation is not compromised at this level.

Silica fume imparts high durability performance in part because of the high concrete strengths that are able to be achieved, and in part because of the ability of the very fine particles to alter the nature of the cement paste-aggregate interface – a known source of weakness in concrete. Arguably, silica fume dose rates of ≤5% are far less effective at improving strength and durability because there is insufficient material to properly enhance performance at the paste-aggregate interface.

Early-age concrete strengths with silica fume mixes are high because of its rapid hydration and because of the physical filler effect. The reaction can be so rapid that it can use up available mix water leading to 'self-desiccation'. The dense early-age microstructure also makes it difficult for external water to enter the concrete to assist with curing. While some laboratory studies have suggested that the early-age high strengths can lead to

some strength regression at later ages, this has not been borne out in field studies.

From a commercial perspective, silica fume is quite expensive relative to Type GP cement and other SCM's.

Microsilica, although not as fine as silica fume, performs in a very similar manner. One advantage of Microsilica over silica fume is that it does not have issues with agglomeration that are common with silica fume. Microsilica has a shelf life, without suffering agglomeration, of at least four years. Despite this, care still needs to be taken to ensure adequate dispersion of the Microsilica through the concrete mix. Appropriate replacement rates are also considered to be 8-10% and the primary use of Microsilica is in high strength and high durability concrete applications. Amorphous silica materials were first used in the 1950's and 1960's in a series of dam constructions in the North Island of New Zealand, prior to the development of the current Microsilica deposits. Microsilica is not as fine as silica fume and appears to have less detrimental effects on concrete workability. It can give a slight reduction in setting time despite the usual presence of a super-plasticiser.

Microsilica also attracts premium pricing.

Typical Uses of Silica Fume / Microsilica in Concrete

Typically, silica fume / Microsilica are used for the primary purposes of obtaining high strength

and superior durability performance in concrete. Some special applications of note are (a) those requiring low heat, where the ability to reduce cement content and still obtain high early-age strengths is critical, and (b) where high strength and highly cohesive mixes are required (e.g. sprayed concrete/shotcrete used in mining situations).

The wide-spread use of silica fume in the USA has led to the preparation of several guidance documents in addition to their Standard (ASTM C 1240), including:

- AASHTO Designation M307-04 – *Standard Specification for Use of Silica Fume as an Admixture in Hydraulic Cement Concrete, Mortar and Grout*; and
- ACI 234-R – *Guide for the Use of Silica Fume in Concrete*.

The use of Silica fume and Microsilica results in improvements to a range of concrete properties as described below. It has been noted that, because of the high degree of cohesiveness found with silica fume mixes, concrete slump targets of 25 mm to 50 mm higher than those used for cement-only mixes are necessary in order to achieve similar levels of compaction.

Compressive Strength – Test work carried out on Australian silica fume involving comparisons with silica fume sourced from Europe showed that (a) the performance of the materials was similar, regardless of source, and (b) 28-day concrete strengths for silica fume mixes containing 350 kg of cementitious material were 15% higher than a cement-only control (43 MPa at 28 days) at 5% replacement level; 35% higher than the control at 10% replacement level; and 40% higher than the control at 15% replacement level. At higher cementitious contents the proportional improvement is expected to be lower. In a separate study with higher cementitious contents and higher strengths, improvement of 25% and 35% were noted against a control that yielded 56 MPa at 28 days. For Microsilica, trials demonstrated increases in 28-day strength of 15-30% against a cement-only control with Microsilica additions of 7% and 10%. It has also been noted that the modulus of elasticity of concrete containing silica fume is higher than concrete of similar strength containing cement only.

Drying Shrinkage – Differing views appear in the literature regarding the drying shrinkage of concrete containing silica fume. An increase in drying shrinkage of about 15% has been reported in one study, while elsewhere lower and slower drying shrinkage has been noted. This suggests the need for trials to be carried out if specific drying shrinkage performance is required as the outcome will be dependent on a variety of factors. Testing of Microsilica showed that slightly higher drying shrinkage was observed at one year against a cement-only control.

Pore Structure – The durability performance of concrete is determined to a large extent by the pore structure and the consequent permeability of the concrete. Mercury porosimetry testing carried out on concrete containing Australian silica fume showed reduced levels of total porosity and a reduction in the number of larger pores – both indicative of reduced permeability. Other testing confirms the reduction in concrete permeability, at least at up to a 10% cement replacement level, with dramatic reductions in permeability being noted with both silica fume alone or when used in combination with other SCM's.

Chloride Ion Permeability – With silica fume there are several factors at play in relation to chloride ion penetration, most particularly the much lower permeability of concrete containing silica fume and the consequent slower diffusion rate of chloride ions. This lower diffusion rate counters concerns about increased corrosion risk due to the slight lowering of paste pH as a result of the silica fume / lime reaction in the paste. The increased resistivity of concrete containing silica fume also assists in reducing corrosion rates if corrosion is initiated. When using Microsilica, concrete containing 10% Microsilica was found to have significantly lower electrical conductance when assessed using the ASTM C1202 Rapid Chloride Permeability Test.

Sulfate Resistance – The use of silica fume concrete has been found to be as effective as using Type SR cements to prevent sulfate attack, and if used in combination with fly ash or GGBFS, is even more effective than Type SR cements. The improved resistance is likely due to (a) the refined pore structure, and (b) the

lower lime content. Testing with Microsilica using the ASTM C 1012 method has shown very significant improvements in sulfate resistance against a cement-only control.

Alkali Silica Reaction (ASR) – One of the first commercial uses of silica fume was for the control of ASR in Iceland, where since 1979, all concrete has included about 7% replacement of cement with silica fume. This has proved to be a very effective solution. Silica fume acts in several ways to mitigate ASR – by (a) reacting with, and binding, available alkalis and (b) reducing water ingress because of lower concrete permeability. It has been reported that agglomerated silica fume may act as an initiator of ASR, so care must be taken to ensure efficient mixing and complete distribution of the silica fume. In New Zealand where ASR has been problematic, natural mineral materials like diatomite and pumicite were used in the 1950's and 1960's to mitigate ASR until, in the 1990's, both Microsilica and meta-kaolin were introduced for ASR mitigation. A substantial Australian review of ASR and its control suggests that 8-10% silica fume is sufficient to mitigate ASR.

Carbonation – Carbonation does not appear to be a significant issue with high strength concretes containing silica fume, but with lower strength concrete it may be problematic, particularly if there has been inadequate concrete curing.

Applications of Other Amorphous Silica Materials

Where silica fume, fly ash and GGBFS are not readily available, natural pozzolans are used as cement replacement materials and for concrete durability improvement where required. Some of these materials increase concrete water demand. Some materials are used after simply mining and milling them to an appropriate fineness, while others are subjected to 'calcination' – heating (to 500-800°C) to activate certain (clay) minerals. Activated products like meta-kaolin are highly reactive and are used in both conventional concrete and in the manufacture of 'geopolymer concrete'. In Australia, some research has been carried out on the cementitious efficiency of pitchstone – a glassy mineral found in large outcrops. There are an estimated 100 million tonnes of

pitchstone available in North Queensland. This mineral can be mined and milled to a fine powder and behaves as a moderately cementitious material and has been shown to improve concrete durability.

Low Heat Applications – While silica fume has almost the same contribution to concrete heat of hydration as Type GP cement on a unit weight basis, the higher strengths able to be achieved and the consequent lower cementitious content requirements mean silica fume has a role in low heat applications, often in combination with other SCM's like fly ash.

Sprayed Concrete Applications – Silica fume is a key ingredient in sprayed concrete (or Shotcrete) which is used particularly for tunnel linings and in mines. Silica fume concrete, alone or with steel fibres included, provides cohesive, high early strength concrete that is particularly suitable for sprayed concrete applications such as those comprehensively described in the American Concrete Institute 'Guide to Shotcrete'.

Special Amorphous Silica Applications – One of the main benefits of silica fume is the ability to make very high strength concrete, typically 80-100 MPa and above. With these very high strengths comes a high modulus which can be used to advantage in high rise structures in particular. These performance characteristics allow thinner columns to be used and create additional savings in materials through the need for less concrete and reinforcing steel.

High durability performance also makes silica fume concrete the material of choice in projects requiring a long (e.g. 100 year) design life – and was the SCM of choice for some Scandinavian bridge structures and tall Middle Eastern tower buildings.

Metakaolin is a suitable raw material for the manufacture of 'geopolymer concrete'. With its high reactivity it has the potential to impart good strength and durability performance characteristics to this alternative to conventional concrete.

8.6 HANDLING AND STORAGE

Like other SCM's, powdered amorphous silica products should be kept dry to facilitate effective handling, batching and transport.

Silica fume as produced is a very fine powder of very low bulk density – so low that it compromises effective handling and batching. This necessitates that silica fume be densified (by agglomerating particles), to increase its bulk density from $<400 \text{ kg.m}^{-3}$ to values in the order of 700 kg.m^{-3} . In the past, slurries of silica fume have also been used to improve its handling characteristics though these are not common now. Densified silica fume must be de-agglomerated once batched into a concrete mix to (a) ensure its efficiency is maximised, and (b) prevent the possibility of agglomerations acting as a nucleus for ASR.

Microsilica, while very fine, has been 'designed' to ensure that agglomeration does not occur. It is claimed that even after four years, no agglomeration of the product is observed.

As is the case for the other fine SCM products, care must be taken in the workplace to ensure that dust levels are properly managed. All amorphous silica products contain significant proportions of respirable material. For most of the products, particularly Microsilica and many of the natural amorphous silica products, they contain (generally) low levels of crystalline silica and need to be treated with considerable caution in terms of workplace exposure to dust. In potentially high exposure areas involving the use of 'amorphous silica', engineering systems should be used to manage ambient dust levels, and as a last resort, PPE should be worn to limit personal exposure levels.

While silica fume is often described as an amorphous product, effectively all Safety Data Sheets for silica fume note some (small) proportion of crystalline silica. With the current levels of concern about crystalline silica and recognising the extremely high fineness of the product, proper control measures should be put in place to manage exposure to silica fume and amorphous silica dust.

8.7 DURABILITY OF AMORPHOUS SILICA CONCRETE

The use of amorphous silica products as partial cement replacement material in concrete results in significantly improved durability performance of the concrete – relative to cement-only concrete. The reasons for the improved performance and the actual effects are quite similar for each of the SCM's. Rather than describe the durability-related performance for each SCM separately, a sub-section is dedicated to durability performance (sub- Section 9).

9 THE EFFECTS OF SCM'S ON CONCRETE DURABILITY

9.1 INTRODUCTION

Concrete that is able to provide high durability performance is generally characterised by having high strength – which in turn generally means a relatively high cement (plus SCM) content and a low water/cementitious ratio. These characteristics impart properties of low porosity and low permeability which are conducive to preventing aggressive fluids from entering the concrete and reacting, in one way or another, with components of the cement paste and/or embedded steel. The effectiveness of water/cementitious ratio on porosity and permeability are shown in **Figures 2.13** and **2.14**.

It is readily able to be shown that the use of SCM's as partial cement replacements – the levels of replacement varying with SCM type – is able to improve durability performance through several mechanisms, including:

- By reacting with lime, in the presence of water, to form additional hydration products that lower both porosity and permeability;
- By, in some cases, significantly increasing the volume of paste in the mix because of the (relatively) low density of the SCM creating a higher paste volume (fly ash and silica fume particularly);
- By way of fine SCM particulates blocking

- pores in the paste; and
- By increasing the reactive silica content in the paste beyond the 'pessimism level' resulting in reduced (ASR) gel expansion.

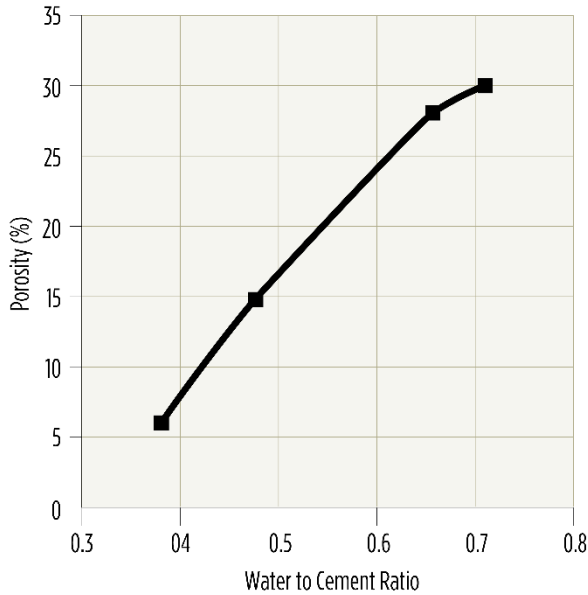


Figure 2.13 – Effect of W/C Ratio on Concrete Porosity

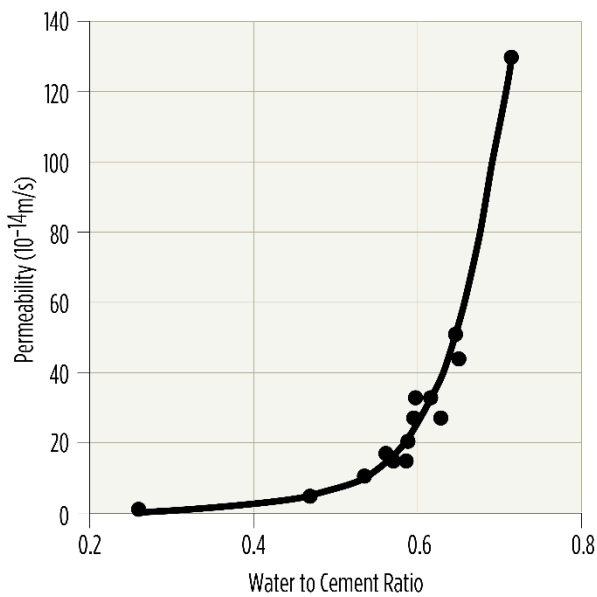


Figure 2.14 – Effect of W/C Ratio on Concrete Permeability

The extent of this improved performance and the effect of SCM proportion will be demonstrated with selective examples for each of the important concrete durability performance characteristics in the following sub-sections.

9.2 DURABILITY PERFORMANCE IMPROVEMENT EXAMPLES

Chloride Ion Permeability – Chloride ions may be found within the paste – their source being the materials used in concrete manufacture, **or** the chloride may derive from external sources as exemplified by the concrete (a) being submerged in sea water or (b) having airborne salts deposited on the surface in locations adjacent to the ocean. Regardless of the source, chloride ions will slowly but surely penetrate into the body of the concrete and ultimately destroy the passivated layer on any embedded steel and initiate corrosion. The rate of penetration of the chloride ions will be determined, in part, by the permeability of the concrete. Assuming that the fundamental concrete performance is adequate (sufficiently high strength, sufficiently low water/cementitious ratio), the use of SCM's will provide high durability performance through creating additional resistance to chloride ion penetration. The effectiveness of the SCM is determined in part by its substitution rate. Typically, fly ash is used at 25% replacement; GGBFS at 65% replacement; and silica fume at 8-10% replacement in high durability concrete mixes. Examples of the effectiveness are shown in **Figures 2.15** and **2.16** for fly ash and GGBFS respectively.

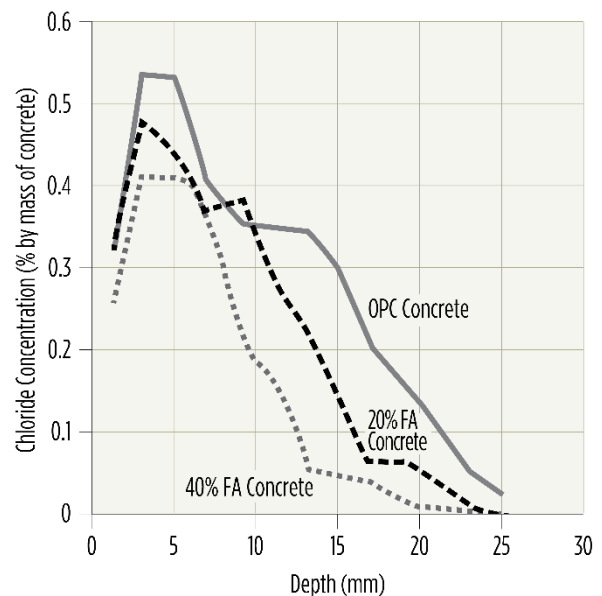


Figure 2.15 – Fly Ash Proportion and Chloride Ingress

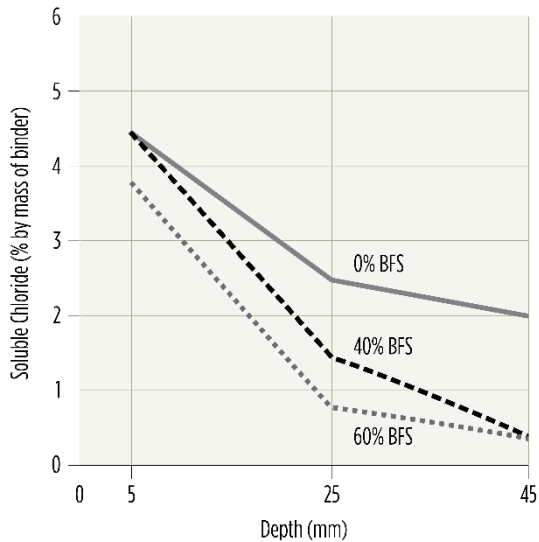


Figure 2.16 - GGBFS Proportion and Chloride Ingress

Sulfate Resistance – Sulfates may attack concrete paste in several ways, including reacting with lime or other constituents to form expansive compounds that then cause cracking, or by attacking the calcium silicate hydrate component and causing it to disintegrate and the concrete to crumble. In each case, decreasing concrete permeability is a key element to increasing concrete sulfate resistance. Examples of the effect are shown in **Figures 2.17** and **2.18**.

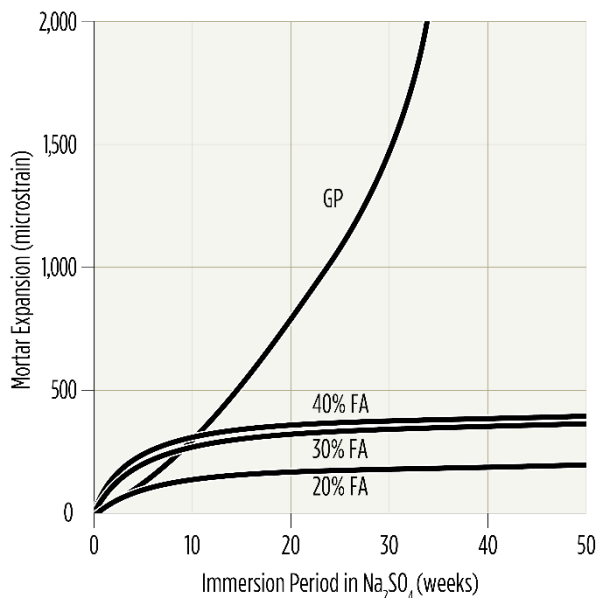


Figure 2.17 – Fly Ash Proportion and Sulfate Resistance

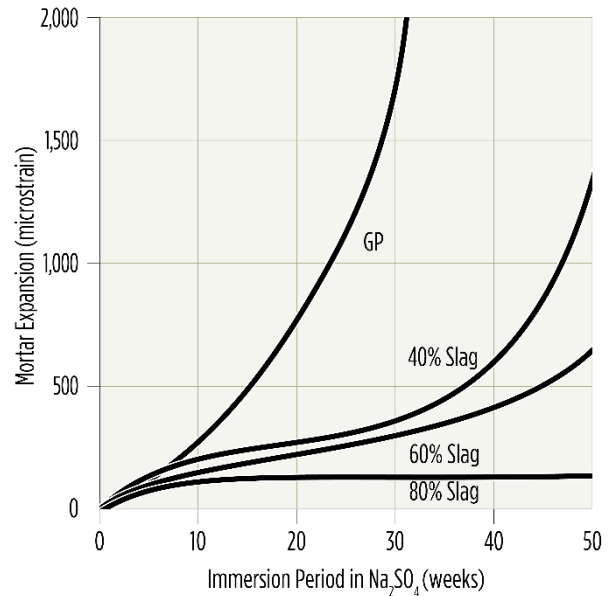


Figure 2.18 – GGBFS Proportion and Sulfate Resistance

Drying Shrinkage – Drying shrinkage results from the long-term loss of moisture from the concrete paste due to atmospheric drying conditions. Levels of drying shrinkage are not determined by any single factor, and the nature of the cementitious material has little influence – other than in the test used to measure drying shrinkage performance for cements when conformance with Type SL requirements in AS 3972 are considered. Fly ash in particular has a significant effect on drying shrinkage of the mortar used in the test described in AS 2350.13. GGBFS also generally results in lower drying shrinkage based on this test. Typically, a Type GP cement will lead to a mortar drying shrinkage of about 600 microstrain, while Type GB cements containing either fly ash or GGBFS lead to a drying shrinkage value of about 250-300 microstrain with the AS 2350.13 test.

As noted in Table 1 of AS 3972, there are multiple factors involved in determining concrete drying shrinkage, and all need to be considered.

Heat of Hydration – The hydration of cement produces heat as a by-product and for mass concrete structures, this can be problematic. Low heat (Type LH) cements are useful in dealing with high concrete temperatures (and temperature differentials) and are routinely employed. SCM's are used to effectively dilute

Type GP cement in a conforming Type LH cement – the effectiveness of the SCM dependent largely on the replacement proportion, as shown for GGBFS in **Figure 2.19**. In commercial type LH cements, either 40% fly ash or 65% GGBFS replacement rates are used. Silica fume is not generally used for Type LH cement manufacture.

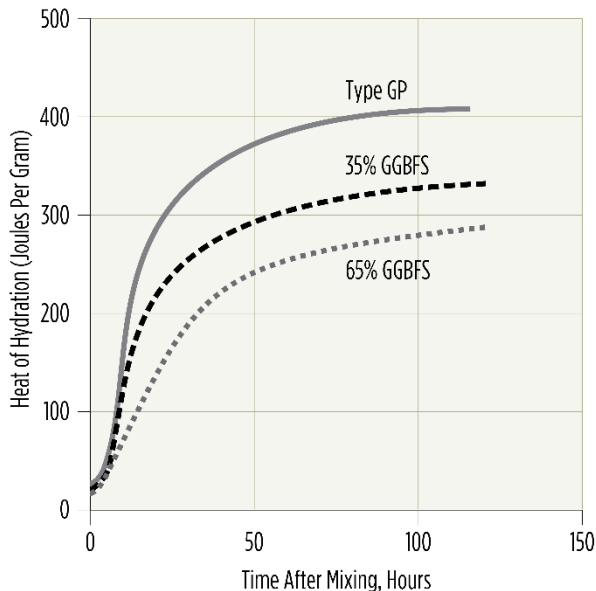


Figure 2.19 – The Effect of Increasing Proportions of an SCM on Heat of Hydration

ASR / AAR – Alkali aggregate or alkali silicate reaction is a significant issue for concrete durability for various reasons, including (a) it often occurs in significant infrastructure, and (b) it does not generally appear for 20 or more years and is practically impossible to remediate.

ASR/AAR requires there to be (a) reactive aggregate, (b) sufficient alkali to initiate ASR/AAR, and (c) sufficient water ingress to cause the ASR/AAR gel to expand and cause concrete cracking. SCM's are able to mitigate the likelihood of ASR/AAR by two primary means, namely (1) providing fine reactive silica evenly dispersed through the concrete paste to (effectively) react with the available alkali, and (2) reduce concrete permeability to prevent sufficient water entering the structure to allow any ASR/AAR gel to expand.

All of the common SCM's are effective in mitigating ASR/AAR, but at different replacement levels. Fly ash is typically used at

25%; GGBFS is used at 50+%; while silica fume is used at 8-10%. For silica fume, the replacement proportion and the percentage of silica in the product are both determinants of its effectiveness in mitigating ASR/AAR (see **Figure 2.20**). **Figure 2.21** shows the reduction in expansion obtained from increasing the reactive silica level beyond the 'pessimism level'.

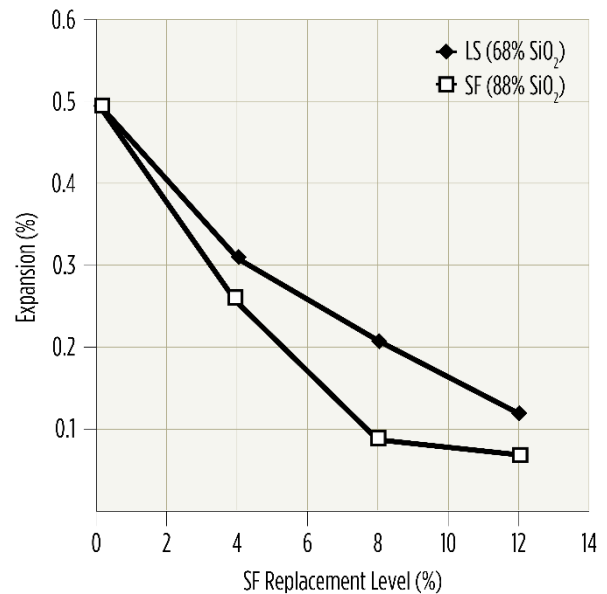


Figure 2.20 – Effect of Silica Fume Proportion and SiO₂ Content on Expansion Due to ASR

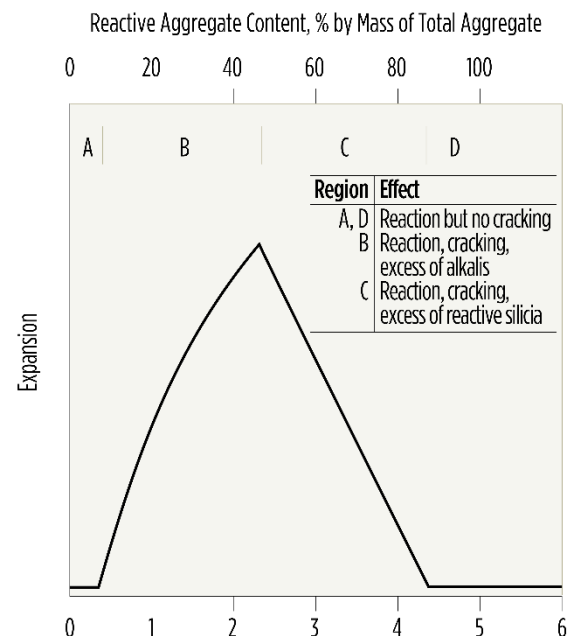


Figure 2.21 – Effect of Reactive Silica Content on Expansion Due to ASR

It should be noted that research has established that if silica fume is present in an agglomerated form it may initiate ASR/AAR. This emphasises the need to ensure that silica fume is fully dispersed through a concrete mix.

10 SUMMARY

SCM's, and most particularly fly ash and GGBFS, are now commonly used and fully accepted cementitious materials for use in concrete manufacture in Australia. Silica fume is less widely used as it is quite expensive – however, in specific end-uses it is particularly effective (e.g. high strength and high durability applications, shotcrete).

Although these SCM's derive from materials which are nominally 'wastes' from large scale industrial processes, once processed they become reliable and consistent cementitious materials. There are Australian Standards (the AS 3582 series) specific to each of these material types.

SCM's give improved performance in almost all aspects of concrete performance. Generally, they improve workability and pumpability of plastic concrete as well as strength and durability performance improvement in hardened concrete. A huge amount of research has been carried out to substantiate these improvements and to understand the mechanisms that drive them.

A key element of SCM use in modern concrete is the positive benefit of reducing the embodied CO₂ and embodied energy levels in concrete which is a critical requirement for modern construction materials. Fly ash and GGBFS can also be used in 'alternative binder' materials which can substitute for Type GP cement in certain applications.

In a variety of different ways, SCM's will continue to be important concrete materials and to make an ongoing positive contribution to all aspects of concrete technology.

11 RELEVANT AUSTRALIAN STANDARDS

- 1) AS 1379 – *The specification and supply of concrete*
- 2) AS 2758 – *Aggregates and rock for engineering purposes*
- 3) AS 2758.1 – *Concrete aggregates*
- 4) AS 3600 – *Concrete structures*
- 5) AS 3972 – *General purpose and blended cements*
- 6) AS 2350 – *Test methods for general purpose and blended cements (series of Standards)*
- 7) AS 3582 – *Supplementary cementitious materials (series of Standards)*
- 8) AS 3582.1 – *Fly ash*
- 9) AS 3582.2 – *Ground granulated blast furnace slag*
- 10) AS 3583.3 – *Amorphous silica*
- 11) AS 3583 – *Test methods for supplementary cementitious materials (series of Standards)*

12 FURTHER READING

- 1) Neville, A.M. '*Properties of Concrete*' (4th Edition) (1995), Longman Group Limited, ISBN 0 582 23070 5
- 2) CCAA Technical Notes – TN 77 (Fly Ash); TN 78 (GGBFS); TN 79 (Amorphous Silica); TN 59 (Cements)
- 3) CSIRO, '*Guidelines for the use of High-Volume Fly Ash Concrete*' (1995), ISBN 0 643 05822 2
- 4) Standards Australia, '*Alkali Aggregate Reaction – Guidelines on minimising damage to concrete structures in Australia*' (2015), SA HB 79-2015, ISBN 9 781 76035 060 4
- 5) Ash Development Association of Australia, '*Coal Combustion Products Handbook*' (2nd Edition) (2014), ISBN 9 780 992514 006

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