TECHNICAL NOTE

CEMENT CONCRETE & AGGREGATES AUSTRALIA

Amorphous Silica properties, characterisation and uses

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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 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[1]. Similar materials were used much later by Smeaton when he built the Eddystone Lighthouse[2] 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[3].

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[4]. 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[5].

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[6]. This initial use was in Norway[7] particularly, while in Australia silica fume use began in about 1977[8]. Silica fume sourced from operations in Tasmania and Western Australia has been 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 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 document, and differentiated 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.

AMORPHOUS SILICA STANDARDS

In 1986 Canada prepared a Standard for "Supplementary Cementing Materials" that included silica fume – making it the first country to include these products in concrete-related Standards[9]. In 1995 the USA followed with ASTM preparing a Standard (ASTM C 1240) for the American marketplace.

The Australian Standard AS 3582.3[10] provides coverage for all 'amorphous silica' materials – whether naturally occurring or synthetic. Updated in 2016, this Standard superseded a 2002 version[11] which also covered 'amorphous silica' materials. These contrast with the first version of AS 3582.3 in 1994[12] which provided specifications for silica fume only.

AS 3852.3[10] 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 ≤400kg.m^{-3}), densified (bulk density ≥400kg.m^{-3}) or slurried (typically 40-60% silica fume by weight).

AS 3582.3[10] nominates 8 compositional and performance properties but only provides limits for four of them. The four limits define 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[10] is shown in Table 1.

While the Standard[10] 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 3 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.

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In contrast with the single Australia Standard, the American ASTM Standards covering amorphous silica include (a) ASTM C 618[13] (Standard specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete), and (b) ASTM C 1240[14] (Standard Specification for Silica Fume Used in Cementitious Mixtures).

The amorphous silica products covered by ASTM C 618 include diatomaceous earths; opaline cherts and shales; tuffs and volcanic ashes or pumicites (calcined or uncalcined); and various materials requiring calcination to induce satisfactory properties, such as some clays and shales. These amorphous silica products have the same performance requirements as

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 2350.2
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.

Table 1. Properties nominated in AS 3582.3 (2016)[8]

Property	Australia	USA	Europe	Japan	China
	AS 3582.3	ASTM C 1240	EN 13263-1	JIS A 6207	GB/T 18736
SiO2 %	>85	>85.0	>85	>85	>85
SO3 %	≤3.0	-	<2.0	<3.0	-
Free CaO %	-	-	<1.0	<1.0	-
Chloride %	-	-	<0.3	<0.1	<0.2
Moisture %	≤3.0#	<3.0	-	<3.0	<3.0
Spec Surface m2/g	-	>15	15 - 35	>15	>15
LOI %	≤6.0	<6.0	<4.0	<5.0	<6.0
Activity Index %	-	>105 @ 7d*	>100 @ 28d**	>95 @ 7d**	>85 @ 28d**

Notes: * uses accelerated curing process; ** uses standard curing process; # - refer to Notes – Table 1.

Table 2. Comparative silica fume requirements – some International Standards

the Class F and Class C fly ashes covered by the Standard[13], except for Loss on Ignition and Water Requirement for which higher limits are nominated for the amorphous silica materials.

For silica fume, ASTM C 1240[14] requires, for densified or slurried products, that testing be carried out on the raw silica fume used to make these products. The Standard[14] focuses on, and provides limits for, chemical characteristics [SiO_2 content, moisture content and Loss on Ignition (LOI)] and physical requirements (sieve sizing to limit agglomeration, Strength Activity Index and specific surface area).

In Europe, EN 13263-1[15] nominates chemical (SiO_2 content, free Si, free CaO, sulfate, chloride and LOI) and physical (specific surface area and activity index) requirements for 'silica fume for concrete'. This Standard includes a conformity assessment process to ensure the ongoing quality and consistency of the silica fume.

A comparison of several international Standards requirements for silica fume shown in Table 2 (page 2).

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 Standards or specification requirements, and (b) providing a product of consistent quality.

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 2000°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 to 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[16].

Silica fume as produced is an extremely fine material and is comprised primarily of high purity (typically >95%) amorphous silicon dioxide (SiO_2). A small proportion of crystalline SiO_2 is produced. This varies dependent on the manufacturer, with reported levels of from <0.05% to <0.5%. The physical characteristics of the product are:

Particle Sizing:	95% <1µm
SG:	about 2.2
Specific Surface Area:	15 – 30m^2/g
Bulk Density:	130 – 430kg.m^{-3} (as produced)
	480 – 720kg.m^{-3} (densified)

Silica fume as produced is very light, and to improve its handling characteristics and transportability, it needs to be densified by agglomerating the fine particles into larger masses. This then introduces 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 has also been supplied in a slurried form - these slurries sometime 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 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[17]. The product is mined, ground and blended to achieve a product of high quality with consistent physical and chemical properties. The product has a SiO_2 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 500-600kg.m^{-3} and an average particle size of about 2µm[17].

Metakaolin

Metakaolin is a fine, amorphous, alumino-silicate 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 700-900m^2/kg[18] resulting in an average particle size of about 3µm. 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 SiO_2 content of about 80%, and contains both amorphous and crystalline silica particles. The average particle size can be quite high (about 50µm), but because of the highly porous structure of the product it can have an extremely high surface area (up to 50-60,000m^2/kg), which makes it highly reactive[5]. 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[19]. 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 work has been done on glassy

pitchstone material found in North Queensland[20,21].

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 their diverse 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 3 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[22], and the results give values very much higher than those for Portland 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 45µm screen is also used as a measure of the degree of agglomeration. For silica fume, ASTM C 1240[14] sets a maximum of 10% retained on the 45µm screen to limit the degree of agglomeration, as well as a minimum SSA of 15m^2/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 high porisity.

Relative Density or Specific Gravity (SG) – this is not a specified property in either the Australian Standard[10] or the ASTM[14] or EN[15] Standards. It is a reportable property in ASTM C 1240[14] and the method of determination is described in the Standard. The SG is a function of the chemistry and mineralogy of the material and is used in mix designs to convert weight to volume.

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[23] and ASTM C 311[24]. These tests involve 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.

Property	Silica Fume		Microsilica	Metakaolin	Rice Husk Ash	Natural Pozzolans
	Un-Densified	Densified				
Specific surface area (m2/g)	15-30	15-30	-	8-15	50	variable
Average Particle size (µm)	0.2	0.2	2.0	8-15	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	1000 - 1400
Water Requirement	increased	increased	increased	increased	increased	increased
Activity Index (%)	120	120	108	120	120	variable

Table 3. Typical Physical properties of amorphous silica products

Chemical Composition (general) – determined using AS 2350.2[21], this information is primarily used to assess the SiO_2 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[25] or AS 2350.2[26], 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[8] 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[26] or AS 3583.12[27] respectively. The total alkali content may provide useful information if needed to assess likely susceptibility to ASR if reactive aggregates are being used in a concrete mix.

Chloride – limits for chloride are set in AS 3582.3[10] and EN 13263-1[15]. Able to be determined using either AS 3583.13[28] or AS 2350.2[26], 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[29], this test measures the amount of moisture adsorbed on the surface 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[30], 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).

AMORPHOUS SILICA USE

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 15,000tpa[31]. 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[32]. 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 Portland cement – dependent in part on the overall cementitious content and the proportion of silica fume[32]. 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.

Silica fume reacts strongly and relatively quickly with lime present in the concrete paste, and this has led to concerns about a reduction in 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[35].

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[33]. Arguably, silica fume dose rates of ≤5% are far less effective at improving strength and durability because there is insufficient material to properly enhance the paste-aggregate interface[33].

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. While some laboratory studies have suggested that the early-age high strengths can demonstrate some strength regression at later ages, this has not been borne out in field studies[34].

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

Microsilica, although not as fine as silica fume, performs in 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 4 years[17]. 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 curent Microsilica deposits. MIcrosilica is not as fine as silica fume and appears to have less detrimental effects on concrete workability[35]. It can give a slight reduction in setting time despite the usual presence of a super-plasticiser.

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 in mining situations).

In the USA, in addition to the availability of the ASTM C 1240 standard specification already described, two other documents providing guidance in the use of silica fume are available, namely:

- AASHTO Designation M307-04; Standard Specification for Use of Silica Fume as an Admixture in Hydraulic Cement Concrete, Mortar and Grout[36], and
- ACI 234-R; Guide for the Use of Silica Fume in Concrete[37]

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 cohesivity found with silica fume mixes, concrete slump targets 25mm to 50mm higher than those used for Portland cement mixes are necessary in order to achieve similar levels of compaction[38].

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 350kg of cementitious material were 15% higher than a cement-only control (43MPa 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[32]. 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 56MPa at 28-days[34]. For Microsilica, trials demonstrated increases in 28-day strength of 15-30% against a cement-only control with Microsilica additions of 7% and 10%[35]. 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[39].

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[40], while elsewhere lower and slower drying shrinkage has been noted[36]. 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 1 year against a cement-only control[41].

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[32]. Other testing confirms the reduction in concrete permeability, at least at up to a 10% cement replacement level[42], with dramatic reductions in permeability being noted with both silica fume alone or when used in combination with other SCM's[43].

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[44]. 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[45]. When using Microsilica, concrete containing 10% Microsilica was found to have significantly lower electrical conductance[35] when assessed using the ASTM C1202 Rapid Chloride Permeability Test[46].

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[47]. The improved resistance is likely due to (a) the refined pore structure, and (b) the lower lime content. Testing with Microsilica using ASTM C 1012[48] showed very significant improvements in sulfate resistance against a cement-only control[35].

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[49]. 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[49]. 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[50,51]. 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[52]. A substantial Australian review of ASR and its control suggests that 8-10% silica fume is sufficient to mitigate ASR[53].

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[39].

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[54] 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[21] 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 Portland 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[55].

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[56] such as those comprehensively described in the American Concrete Institute "Guide to Shotcrete"[57].

Special Amorphous Silica Applications

One of the main benefits of silica fume is the ability to make very high strength concrete, typically 80-100MPa and above. With these very high strengths comes a high modulus which can be used to advantage in high rise structures in particular[58]. 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 – like Scandinavian bridge structures and tall Middle Eastern tower buildings[52].

Metakaolin is a suitable raw material for the manufacture of geopolymer concrete[59]. With its high reactivity it has the potential to impart good strength and durability performance characteristics to this alternative to Portland cement concrete.

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), increasing its bulk density from <400 $kg.m^{-3}$ 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 4 years, no agglomeration of the product is observed[17].

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 measure should be put in place to manage exposure to silica fume dust.

ENVIRONMENT

Prior to the installation of effective filter systems that are now used to collect silica fume, the extremely fine material was generally exhausted to the atmosphere[60]. The use of silica fume in concrete provides a beneficial use for this material – a material that would otherwise be considered a 'waste' and also a contributor to atmospheric pollution.

While other typical amorphous silica products may need to be mined and processed, their environmental credentials derive from their use as a replacement for Portland cement in concrete – by reducing the carbon dioxide and embodied energy levels in concrete, and through improving the durability of concrete. The ability to use some of the amorphous silica materials in the manufacture of alternative binders and further reduce the reliance on Portland cement provides an additional environmental benefit.

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