TECHNICAL NOTE

CEMENT CONCRETE & AGGREGATES AUSTRALIA

# Ground Slag Properties, Characterisation and uses

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## 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 technical 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 – 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 a number of 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[1]. 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[2]. 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[2]. 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[2]. 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 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[3].

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 including high compressive strength, high durability, low heat, able to be easily placed and able to be made with a high degree of consistency[4]. Technical aspects of the use of concrete containing GGBFS, while well understood through many decades of use in other countries, were researched and further developed by various influential Australian researchers from both industry and Government bodies like CSIRO[5,6,7,8].

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 greenhouse gas (GHG) 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 amorphous silica of about 30% and 10% respectively.

## SLAG STANDARDS

Portland cement has quite consistent chemistry and mineralogy no matter where it is made in the world. This contrasts with fly ash, where the chemistry is essentially wholly dependent on the nature and relative proportions of minerals associated with the coal matter being burned. Slag lies between these two extremes, with its chemistry being 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 significant contributor to GGBFS reactivity and a function of the efficiency of the granulation process.

GGBFS Standards generally seek to (a) measure and control the chemical composition of the slag with respect to certain components that can cause performance issues, (b) set physical requirements that ensure adequate reactivity, and (c) define minimum performance requirements.

The first attempt at an Australian Standard for slag was published in 1991 reflecting the relatively recent use of this material. The current Australian Standard is AS 3582.2 (2016)[9] – "Supplementary Cementitious Materials – Part 2: Slag – Ground granulated blast furnace" which is an update of an earlier (2001) version.

AS 3582.2[9] nominates 14 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 of Strength Index) characteristics. The nominated suite of compositional and performance properties is shown in Table 1.

| Property | Limit | Reference Test Method |
|---|---|---|
| Fineness (% min. passing 45 µm) | - | AS 3483.1 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 (% max.) | 1.5% | AS 3583.7 |
| Magnesia (MgO) (% max.) | 15.0% | AS 3583.9 or AS 2350.2 |
| Alumina ($Al_2O_3$) (% max.) | 18.0% | AS 353.10 or AS 2350.2 |
| Total iron (FeO) (%) | - | AS 353.10 or AS 2350.2 |
| Manganese (MnO) (%) | - | AS 353.11 or AS 2350.2 |
| Chloride ion content (% max.) | 0.1% | AS 353.13 or AS 2350.2 |
| Total alkali (%) | See note | AS 2350.2 |
| Relative density | - | AS 3583.5 |
| Relative water requirement (%) | - | AS 3583.6 |
| Strength Index (% min.) | - | 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[10] for further information.

Table 1. Properties nominated in AS 3582.2 (2016)[9].

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 6 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[11], AS 3582.2 uses the % passing a 45µm 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 ground slag, it does not provide as good an indication of likely reactivity as the Fineness measure using the 45µm sieve.

There are ASTM and EN Standards for GGBFS. The ASTM Standard C 989-99[12] was the "Standard Specification for Ground Granulated Blast Furnace Slag for use in Concrete and Mortars", though this has now been superceded by ASTM C 989 – C 989M-16[13] which is the "Standard Specification for Slag Cement for use in Concrete and Mortars". The ASTM Standard[12] describes three grades of GGBFS – Grades 80, 100 and 120. This grading relates to the performance of the product in the Slag Activity Index (SAI) test. In this test, 50:50 mixes of GGBFS and Portland cement are used to make mortar samples which are then subjected to compressive strength testing and the results compared to those from a mortar containing 100% Portland cement. For a Grade 80 GGBFS, the mortar containing the 50% GGBFS blend has a 28-day compressive strength of 80% of the Portland cement control. In addition to the SAI requirements, the Standard[12] also sets a maximum Fineness requirement of 20% of material retained on a 45µm sieve and chemical limits for sulfide (2.5% maximum, as S) and sulfate (4% maximum as $SO_3$).

The relevant EN Standard is EN 15167-1, "Ground granulated blast furnace slag for use in mortar and grout – Part 1: Definitions, specifications and conformity criteria"[14]. This Standard defines both (a) the constituent materials for a conforming GGBFS product, and (b) limits for several chemical constituents – as noted in Table 2. The main component material is required to be granulated blast furnace slag which is defined as 'vitrified slag material made by rapid cooling of slag melt of suitable composition, obtained by smelting iron ore in a blast furnace, consisting of at least two-thirds by mass of glassy slag, and possessing hydraulic properties when suitably activated', and where its chemical composition consists of at least two-thirds by mass of CaO + MgO + $SiO_2$, while the remainder is required to be $Al_2O_3$ with small amounts of other compounds. In addition, the ratio (CaO + MgO) / ($SiO_2$) must exceed 1.0.

The chemical components must conform with the limits noted in Table 2.

| Property | Limit | Reference Test Method |
|---|---|---|
| Magnesium oxide | ≤18% | EN 196-2 |
| Sulfide | ≤2.0% | EN 196-2 |
| Sulfate | ≤2.5% | EN 196-2 |
| LOI (corrected for sulphide oxidation) | ≤3.0% | EN 196-2 |
| Chloride[Note] | ≤0.10% | EN 196-2 |
| Moisture content | ≤1.0% | Annex A of Standard |

Note: May contain >0.10% chloride but if so the maximum must be noted on documentation.

Table 2. Chemical limits for slag – EN 15167-1

Importantly, and in contrast with the manufacture and use of GGBFS in many parts of the world, EN 15167-1 requires that GGBFS contains no added materials except grinding aids, and that these should not exceed 1%. This then excludes the addition of gypsum during the milling process – a practice common in many parts of the world - one which (arguably) improves GGBFS performance[15,16] and milling throughput. This Standard also sets a minimum Fineness requirement of ≥275m$^2$/kg (using an air permeability method as used for the assessment of Fineness Index for cement.)

## SLAG PRODUCTION AND PROCESSING

Iron blast furnace slag is a by-product of the iron-making process – a process that involves the separation 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 processed.

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 results in the formation of a glassy product known as slag granulate which has a sand-like consistency, typically 1-3mm in size, with a maximum particle size of about 8mm. 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 end uses.

Slag granulate contains a high proportion of glassy material (at least two-thirds by mass as required by EN 15167-1[14], but often >90%) with a chemical composition like that shown in Table 3.

| Typical Slag Granulate Composition | |
|---|---|
| **Component** | **Proportion (%)** |
| CaO | 40 |
| $SiO_2$ | 35 |
| $Ai_2O_3$ | 15 |
| MgO | 5 |
| Total Alkali (as $Na_2O$ Equivalent) | 0.5 |
| $Fe_2O_3$ | 0.5 |

Table 3. Typical Slag Granulate Composition

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.

### Milling Slag Granulate

Slag granulate is milled to form GGBFS in same (type of) mills used for Portland cement manufacture – 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 cements may also be manufactured by blending separately milled Portland 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 – whether GGBFS or 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 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 ($SO_3$ content) to be monitored and tested. There is some theoretical and empirical evidence that milling granulate and gypsum, with resultant $SO_3$ 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[15,16].

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 $m^2/kg$; or as the %-retained on (or passing) a 45µm sieve. In Australia, GGBFS surface area levels are usually at least 400 $m^2/kg$, while the proportion retained or passing a 45µm 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 45µm sieve provides a higher correlation with Strength Index performance results than does the surface area measurement using air permeability.

## CHARACTERISATION OF SLAG

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 when manufacturing GGBFS.

### Physical Characterisation

Fineness – the Fineness is determined, according to either AS 3583.1[17] or AS 2350.9[18], by sieving through a 45µm 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[19]) can be used and Fineness Index /surface area expressed as $m^2/kg$ 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[20], 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[21]. 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 process (see Figures 1 and 2).

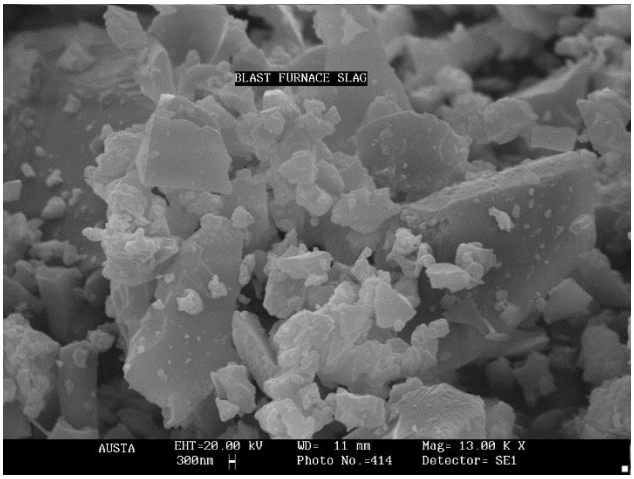


Figure 1. GGBFS (x13.5k magnification)

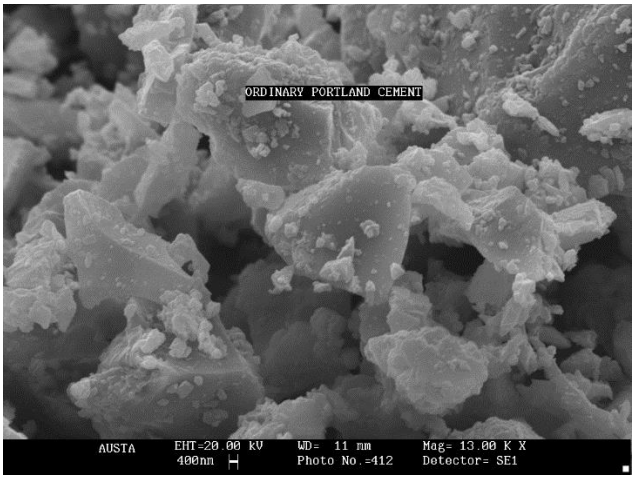


Figure 2. Cement (x13.5k magnification)

### 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’[22]. 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

$SiO_2$ respectively), but that there are quite variable alumina and magnesia contents (8-18% as $Al_2O_3$ 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%[22]. In general terms, GGBFS can be described as being comprised of glass silicates and alumino-silicates of calcium and magnesium plus other compounds of iron, sulfur, manganese and other minor and trace elements[23]. The 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 – and usually rely on performance requirements rather than prescribing the 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[24] 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 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 variations in raw materials.

Sulfide sulfur – determined using AS 3583.7[25] and expressed as %S. The limit of 1.5%[9] 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 1 year - generally without causing any expansion or instability[26].

Sulfate sulfur – determined using AS 3583.8[27] or AS 2350.2[24] and expressed as $\%SO_3$. 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[28] or AS 2350.2[24] and expressed as %MgO. The limit of 15.0%[9] 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[29] or AS 2350.2[24] and expressed as $\%Al_2O_3$. 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%)[30]. Limiting the alumina content to a maximum of 18.0%[9] helps ensure that slag concrete provides good durability performance.

Iron oxide – determined using AS 3583.10[29] or AS 2350.2[24] 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[31] or AS 2350.2[24] 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[29] or AS 2350.2[24] 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[24] and expressed as $\%Na_2O$ Equivalent ($\%Na_2O + 0.658\ \%K_2O$). 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[9] requires that reference be made to the HB 79[10] document if any risk of alkali aggregate reaction exists. The importance of the alkalis will be further discussed in the "Uses" section below.

Loss on Ignition – determined using AS 3583.3[33], 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.

## SLAG USE

While early use of 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 the country. While the availability of 'local' slag granulate is confined to the Port Kembla (NSW) region, slag granulate is being imported into all mainland Australian States, with GGBFS being produced 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 cementititous materials in this country, and (b) the decline in fly ash availability in many areas[3]. Slag is a particularly versatile SCM and is able to be used as a low-level cement replacement (nominal 30%) and also as a high-level cement replacement

(nominal 65-70%) for special end uses. While early-age concrete strengths 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 lower cost, lower concrete GHG and embodied energy levels and 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 1.9Mt in 2016[34], with 1.1Mt of this being imported material.

GGBFS use as a cementitious material is effective primarily because of its pozzolanic behaviour. Unlike fly ash, GGBFS does have some slight reactivity with water – a property known a latent hydraulic behavior.

By definition, a pozzolan is a material that has little or no cementitious value, but which can react with lime (calcium hydroxide), in the presence of water, to form cementitious products[35]. In a concrete paste, lime is formed as a product of cement hydration and this lime is available to react with pozzolanic materials used as partial cement replacements. GGBFS hydration is 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 and calcium aluminate hydrates – products similar to the primary cementitious materials produced by the cement hydration reaction. The calcium silicate and calcium aluminate hydrates formed in the pozzolanic reaction add to concrete strength and to the refinement of the pore structure of the concrete paste.

### Typical Uses of Slag in Concrete

For Normal Class 20-32MPa 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. Typical strength performance, relative to 100% cement mixes, is shown in Table 4.

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 – 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. The strength / age comparisons for typical ternary mixes are shown in Table 4.

| Time (days) | Compressive Strength (% of 28-day strength) | | |
|---|---|---|---|
| | Cement Only | Binary Blend 70% cement 30% GGBFS | Ternary Blend 50% cement 30% GGBFS 20% fly ash |
| 3 | 65 | 45 | 40 |
| 7 | 80 | 60 | 55 |
| 28 | 100 | 100 | 100 |
| 56 | 110 | 115 | 120 |

Table 4. Compressive strength versus time – cement only versus binary and ternary blends

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[5,6,7,8]. 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[36,37] which is evident soon after removal of forms. This colouration is related to the presence of sulphides 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.

### Durability Performance of Slag Concrete

It is generally accepted that concrete containing GGBFS, and particularly at cement replacement levels of at least 50% (and typically 65%) provides more durable concrete than when using cement alone. Concrete durability is not dependent solely on the cementitious material however, and it is important that concrete for use in high durability applications has adequate strength and a relatively low water : binder (w:b) ratio. High durability concrete should be 40+MPa and have a w:b ratio at or below 0.4.

Specific areas of durability improvement expected with concrete containing GGBFS include increased resistance to (a) chloride ion penetration, (b) sulfate attack and (c) alkali silica reaction (ASR). With the first two issues, improved concrete performance comes about primarily because of lower (improved) concrete permeability, while improved resistance to ASR is more complex. While some improvement in

durability performance is expected at lower replacement levels, high durability performance generally requires a cement replacement level of about 60-65%. Two other concrete performance areas of interest are (a) drying shrinkage of concrete containing GGBFS (which has been the subject of considerable research), and (b) thermal performance. These aspects of concrete durability are discussed below.

Chloride ion penetration – Concrete containing reinforcing steel and exposed to marine environments, de-icing salts or other high salinity environments has a high risk of cracking and/or spalling if chloride ions are able to penetrate the concrete and corrode the reinforcing steel. To prevent or delay chloride-ion induced corrosion it is necessary for there to be adequate cover between the steel and the external environment and for the concrete cover to be a high quality, low permeability concrete. It is possible to estimate the service life of a concrete in a chloride environment by understanding the Diffusion Rate[38,39] of chloride ions through the concrete in question – a function that is improved in slag concrete because of the denser microstructure[36] and varies directly with concrete strength / grade and as shown in Figure 3 below.

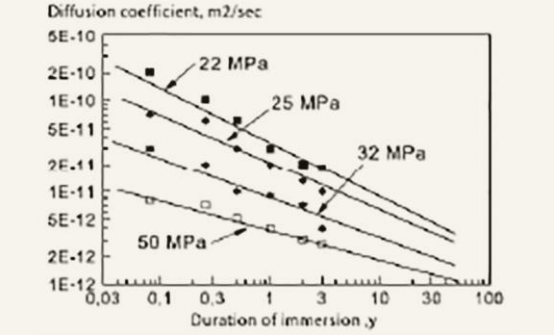


Figure 3. Diffusion coefficient and concrete grade (after Cao et al[38])

It has been noted[36] that, with a GGBFS content of at least 60% and a w:b ratio of 0.5, the diffusion coefficient of concrete exposed to chloride ions is at least 10 times lower than that obtained with a cement-only mix.

Sulfate attack – Concrete may be exposed to sulfates from a variety of sources – marine environments, sewerage treatment plants, industrial wastes and sulfate-containing soils. Sulfate compounds may attack concrete either directly or indirectly and may result in expansion and cracking and/or loss of compressive strength. Magnesium sulfate can attack the CSH glue that holds concrete together causing the concrete to disintegrate. Sodium sulfate attacks concrete by reacting with aluminates to form expansive compounds that cause cracking initially, followed then by more substantial failure and finally disintegration. Sulfate attack on concrete can be reduced by both physical and chemical means. GGBFS, through improvements to concrete microstructure[36], reduces the ability of sulfate ions to penetrate the concrete. Reduction in sulfate attack can also be brought about by altering the nature of the cementitious materials – for example by using a Type SR (Sulfate Resisting) cement[40]. Type SR cement may be obtained by altering the mineral composition – specifically by reducing the aluminate ($C_3A$) content – as is required for an ASTM Type V (sulfate resisting) cement[41]. The Australian Standard[40] does not nominate how SR performance is to be achieved – it relies on performance of a mortar tested in accordance with AS 2350.14[42]. This test sets a maximum expansion limit of 750 microstrain for the mortar bar after 16 weeks exposure to a 5% sodium sulfate solution. Generally, either 30% GGBFS and 65% GGBFS blends will meet Type SR requirements as determined by the mortar test, though as noted in AS 3972[40] (Table 2), there are many contributors that determine the resistance of concrete to sulfate attack. There is evidence that the chemistry of GGBFS can also impact the sulfate resistance of concrete. It has been noted[16] that where high (>70%) GGBFS blends are used, or where moderate blends with GGBFS that has an alumina content greater than about 11% is used, GGBFS manufacture should involve gypsum being inter-ground with the granulate to achieve an $SO_3$ content in the GGBFS of about 3%.

Alkali-silica reaction (ASR) – Concrete made with 'reactive aggregates' can, often 10-20 years after placing, demonstrate severe 'map cracking' as a result of a reaction between silicate minerals in the aggregate and alkalis (primarily) from the cement. This alkali-silica reaction forms a gel product that can absorb large proportions of water. The gel expands within the concrete pores causing the 'map cracking'. The problem, encountered in many part of Australia, is seen in large infrastructure like dams, bridges and power station cooling towers and rectification of these structures would usually be very expensive. Recently, two improved tests[43,44] have been developed to allow the potential reactivity of aggregate materials to be assessed. Additionally, an ASR handbook[10], a joint publication between CCAA and Standards Australia has recently been updated. This comprehensive ASR handbook provides a broad range of information including methods by which the risk of ASR can be mitigated. One of the simplest ways is the inclusion of GGBFS at a level of at least 50% of the cementitious material in the concrete[10]. The GGBFS acts in several ways to reduce or prevent ASR, including by (a) reacting with some of the alkali limiting its availability for other reactions, (b) providing reactive silica to react with free alkali and (c) limiting water movement through the concrete. To be effective, it is required that the alkali content of the GGBFS be less than 1.0% (as $Na_2O$ equivalent)[10].

Concrete drying shrinkage – When water is lost from hardened concrete in unsaturated air it causes drying shrinkage which leads to increased tensile stress in the concrete surface and (unless managed or controlled), cracking of the concrete. The shrinkage is (a) caused by loss of water from the paste, and (b) limited to some

degree by restraint by the aggregate. Many modern concrete specifications have tight limits on concrete drying shrinkage. It has been suggested that using GGBFS as a cement replacement may result in increased concrete drying shrinkage, though this has been disputed. In the test work carried out for design of the immersed tube units for the Sydney Harbour Tunnel, it was noted[4] that higher drying shrinkage results were obtained for the slag blend concretes – relative to the cement-only mixes - using the laboratory-based test method. These results did not necessarily accord with other observations and it was noted that, with slag blend mixes, expansion of the concrete occurs in the early stages of the hydration process, and this, coupled with the initial length measurement after 7-days curing as required by the test, tended to exaggerate the 56-day drying shrinkage results for the slag blend concretes. Other findings in relation to drying shrinkage include (a) the view that, with the slow strength and microstructure development of (high) slag mixes there is a greater likelihood of water loss from the surface of slag concrete - this emphasising the need for moist curing[15,45], and (b) optimisation of the gypsum content of GGBFS and slag cements is important to minimise drying shrinkage[15], particularly with slags with higher $Al_2O_3$ contents.

Thermal performance - The exothermic hydration reactions of cementitious materials can cause major issues in certain concrete structures. With an increased demand for high strength concrete and for structures considered to be mass concrete applications (e.g. footings, pile caps), the thermal performance of concrete has become an important durability issue. One of the simplest and most effective methods of reducing the rate and extent of temperature rise in concrete is to replace significant proportions of the Portland cement with one or more SCM's – ideally with the least effect on rate of strength gain. GGBFS has the significant advantage of being able to be used at high substitution rates (up to 80%) – providing a balance between significant concrete temperature reductions and manageable strength performance. Typical 'low heat' GGBFS blends contain 60% or 65% GGBFS[46]. This combination of thermal and strength performance, combined with a significant improvement in concrete durability performance, was the key determinant of the use of high slag blends in the Sydney Harbour Tunnel Project[4].

## OTHER CONCRETE-RELATED USES OF GGBFS

GGBFS is a very versatile material, of quite consistent quality and able to be activated in several ways to form stable, effective binders.

Alkali-activated slags and Geopolymers – The development and use of alkali-activated slag cements occurred in Europe in the 1960's and 1970's – particularly in Russia and Poland[47]. Granulated slag can be activated by sodium or potassium hydroxide, by sodium carbonate or by sodium silicate – sometimes in combination – to form a cheaper binder than Portland cement, and one which has been demonstrated to be quite effective, provided it is properly used. The 'cement' is very reactive giving short working and setting times and is sensitive to ambient temperature conditions[47]. The resultant concrete gives good strength performance and reasonable durability performance but is reported to be vulnerable to carbonation and drying and may have an increased tendency to suffer from ASR. An extension of the alkali-activated concept is geopolymer concretes which are now the subject of considerable research. Typically, geopolymer binders contain a mixture of GGBFS and fly ash, and these are activated by strong alkalis like sodium hydroxide. Geopolymer concretes generally show good strength and durability performance, and have the added advantage of having lower embodied energy and lower associated GHG emissions than Portland cement[48]. The use of GGBFS in these mixes allows curing at ambient temperatures which is important for any alternative to Portland cement.

Super-sulfated cements – These cements are formed by milling together granulated slag, anhydrite (calcium sulfate) and a small proportion of Portland cement clinker to a surface area of >400$m^2$/kg (similar to Type HE cement) and require a minimum SO3 content of 4.5%[49]. Upon hydration, these cements form ettringite and calcium silicate hydrate. They provide good strength and durability performance in sea water and some sulfate environments, but are less resistant in the presence of magnesium sulfate[49]. A low-carbon concrete technology using this cement type has been developed and commercialized in Australia[50].

Mine backfill – An important material used in underground mines is Cemented Paste Backfill (CPB). CPB is used to fill stopes (previously mined voids) which allows more complete extraction of ore from the mine. CPB is a low strength fill material (up to 2MPa compressive strength) which uses mine tailings and often mine water in the manufacture of the CPB. The binder, typically used at about 5% by weight in CPB, represents about 75% of CPB cost, so binder efficiency is a critical issue[51]. While Portland cement is often used, GGBFS may also be used as a cement replacement. Where the tailings derive from sulfur-rich ores, it is observed that with slag blends, CPB strength and particularly early-age strength, is far superior to CPB made using Portland cement alone. The activation of the slag by sulfates is highly effective, and provides a means of reducing cement content and cost, and producing a more resistant CPB. While CPB sounds like a simple material it forms several key functions in mines including (a) providing ground support, (b) mitigating the risk of surface subsidence, and (c) providing a disposal option for waste rocks and mill tailings[52]. It is also subject to severe conditions due to high temperature development in the wholly insulated environment and through contact with sulfate-rich mine waters[52]. The use of a GGBFS-containing binder also assists in the management of these environmental issues.

## HANDLING AND STORAGE

While GGBFS does not react strongly with water like (for example) cement it still must be kept dry to ensure that it is able to be easily transported and transferred as a bulk material. GGBFS as produced has a low moisture content. If the moisture content increases to about 0.5% it may result in reduced flowability and/or cause lump formation. While these lumps are not as hard as those formed when cement that has been exposed to water, they may cause difficulties in pneumatic conveying of GGBFS or restrict flow in a silo.

GGBFS is generally a very fine product and may contain up to 50% of respirable material. It is important in the handling and transport of GGBFS that (a) engineering systems be used to reduce the presence of dust in the workplace, and (b) where workers are exposed to GGBFS in the atmosphere that they wear appropriate respiratory protection. GGBFS safety data sheets (SDS) should be referred to for guidance.

GGBFS is harmful to the eyes and mucous membranes and may cause alkali burns. It is also irritating to the skin and prolonged exposure may cause sensitization and potentially, dermatitis. Any GGBFS spill must be cleaned up and the material disposed of in an appropriate manner. The SDS should be referred to in the event of a spill.

## ENVIRONMENT

From a concrete industry perspective, the use of GGBFS is a positive contributor to 'the environment'. When used as a cement replacement, GGBFS contributes to a reduction in greenhouse gas (GHG) and embodied energy levels in concrete. Its use has been a significant contributor to the about 30% reduction[53] in GHG per tonne of cementitious materials achieved in Australia in the period 1990 to present.

The ability to use GGBFS in non-Portland cement binders (geopolymers and activated slags) provides further opportunities for it to contribute to CO2 reduction in the construction industry.

By using slag products (GGBFS and slag aggregates), materials that would otherwise potentially be landfilled are used beneficially. In addition, the contribution GGBFS makes to improved concrete durability adds significantly to the sustainability credentials of concrete as a construction material.

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