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Selection and Validation of Alternate Slag Sources for Saltstone Production – 16145

Steven Simner,* Victoria Kmiec,* and Ian L. Pegg**

* Savannah River Remediation LLC

** Vitreous State Laboratory, The Catholic University of America

ABSTRACT

To stabilize low activity salt solution produced at the Savannah River Site (SRS) the salt waste is mixed with a combination of fly ash (FA), ground granulated blast furnace slag (GGBFS), and ordinary Portland cement (OPC) to form a grout termed saltstone. Upon curing, the low activity waste is encapsulated within the hardened cementitious matrix. While the sources of the dry feed components have remained unchanged for several years, SRS was recently notified that its domestic source of GGBFS would no longer be available due to the shutdown of the steel making plant that produced the ferrous slag as a by-product. This shut-down follows a trend in the reduction of domestic ferrous slag sources. Alternate GGBFS sources were sought and a program developed to validate the alternate materials for use in saltstone. GGBFS is primarily utilized in the construction industry as a replacement for OPC and the requirements of a GGBFS source, based on an ASTM standard, are predominantly limited to demonstrating that the GGBFS replacement will provide equivalent strength in comparison to the baseline OPC-based concrete. This affords the construction industry significant flexibility with respect to the GGBFS source that can be used. In contrast, GGBFS has a role of significantly more import when utilized in saltstone. In particular, the reducing blast furnace environment under which GGBFS is produced yields reducing species, such as sulfide (S^{2-}) and ferrous iron (Fe^{2+}), which are believed to facilitate the long-term immobilization of redox sensitive contaminants (e.g. technetium-99 (^{99}Tc)). In addition, a change in GGBFS source has the potential to impact the rheological properties and the reactive heat generation of the grout, which may adversely affect the ability to pump the grout to a Saltstone Disposal Unit (SDU) and the temperatures attained within an SDU, respectively. As such, alternate GGBFS sources for the processing of saltstone require significantly more scrutiny than is prescribed by the ASTM standard. Four alternate source GGBFS materials were evaluated. All four sources met the ASTM requirements, only one source was considered viable for use in saltstone based on preliminary evaluation. The other three sources will require a more intensive assessment to determine their potential applicability.

INTRODUCTION

Saltstone is a cementitious wasteform utilized for stabilizing low activity, caustic salt solution produced at the Savannah River Site (SRS). In processing saltstone, salt solution is combined with a 45/45/10 weight percent mixture of Grade 100 Ground Granulated Blast Furnace Slag (GGBFS), Thermally Beneficiated Class F Fly Ash (FA), and Type II Ordinary Portland Cement (OPC), respectively. GGBFS is perhaps the most critical component of the dry feeds mixture since:

- (1) It is readily activated by the alkaline salt solution (≈ 1.5 M $[OH^-]$) to produce a calcium silicate hydrate (CSH) gel similar to that formed during the hydration of cement, and
- (2) It contains reduced chemical species (S^{2-} and Fe^{2+}) that are capable of reducing redox sensitive contaminants, such as ^{99}Tc .

The Grade 100 GGBFS utilized at SRS has historically been sourced from a single steel production plant in the United States (U.S.), though recently SRS was notified that this material will no longer be available

due to permanent shut down of the plant. As such alternate GGBFS sources have been sought. Initial vendor inquiries indicated that:

- (1) Alternate GGBFS would potentially be sourced from non-domestic iron and steel production plants due to a trend in the shut down and decreased operation of steel production plants utilizing blast furnaces in the U.S., and
- (2) Grade 120 slag is becoming more ubiquitously available than its Grade 100 counterpart.

Any alternate GGBFS selected for use at SRS would thus be expected to have a different chemical composition and a different grade in comparison to the Grade 100 GGBFS previously utilized. The GGBFS grades are defined in ASTM C 989, *Standard Specification for Slag Cement for Use in Concrete and Mortars*, which provides a comparison of the cured strength of 100% OPC with 50-50% OPC-slag mixtures. Substituting with Grade 120 slag will result in a higher compressive strength OPC-slag sample than substituting with a Grade 100 material. The strength differential between the 100 and 120 slag grades is provided by the smaller particle size and/or increased reactivity associated with changes in chemistry and glass content.

Changes in GGBFS source and grade have the potential to impact the processing and/or long-term performance of saltstone. For example, a more reactive Grade 120 GGBFS may exhibit faster gelation thereby adversely affecting grout pumping and flow, as well as resulting in higher heats of hydration and higher emplaced grout temperatures. Equally a change in GGBFS source may result in compositional variations that yield undesirable changes in the capacity of saltstone to immobilize redox sensitive contaminants, such as ⁹⁹Tc. Hence, prior to initiating a change in the GGBFS material utilized in the production of saltstone, confirmatory analysis must be conducted to ensure that the material modification will not adversely affect the key fresh and cured properties of the grout wasteform.

This paper describes the process associated with GGBFS selection and ultimate validation for its future use in the production of saltstone. It is also important to note that when the proposed Salt Waste Processing Facility (SWPF) becomes operational the intent is to process approximately 34 million liters (9 million U.S. gallons) of salt solution per year through the Saltstone Production Facility (SPF), which equates to a required GGBFS supply of approximately 25,000 MT. As such it is considered prudent to validate multiple GGBFS sources such that process interruptions (e. g. plant outages, shut-downs, source shortages due to competing demands etc.) do not disrupt the predicted higher volume production of saltstone.

GGBFS BACKGROUND

Production

Blast furnace slag (BFS) is a by-product obtained in the manufacture of iron or steel in a blast furnace and is formed by the combination of iron ore and coke (or coal) with a limestone flux. When molten, the slag floats on the liquid iron, and is periodically tapped and rapidly quenched to form a fine, granular, and predominantly non-crystalline, glassy material (in the form of sand-sized particles) termed granulated blast furnace slag (GBFS). It is this glassy material that is the main source of the cementitious properties of the granulated slag. More gradual cooling in air allows crystallization, and the formation of a product with limited hydraulic properties.

In an effort to produce a more reactive slag material, the GBFS is further processed into GGBFS using conventional cement clinker grinding technology to reduce particle size (e.g. ball milling). Grinding GBFS consumes significant energy, and thus grinding aids are added in order to reduce particle agglomeration

and improve process efficiency. Typical grinding aids are based on triethanolamine (TEA) as well as glycols, such as ethylene glycol and propylene glycol, and are usually added at $\leq 0.1\%$ with respect to the mass of GBFS.

Chemical and Physical Properties

GGBFS is a white powder with a specific gravity of approximately 2.90 and a bulk density in the range of 1200–1300 kg/m³ [1]. The fineness (and hence surface area) of the GGBFS is a determining factor in its reactivity, though the fineness of the material is limited by the economic constraints of the size reduction process. The mean particle size for GGBFS is typically in the range of 10-20 μm . In addition to fineness both mineral composition and glass content are key factors that influence the reactivity of GGBFS. The primary mineral components in GGBFS are silica, alumina, calcium oxide, and magnesium oxide, with other minor elements like manganese, iron, and sulfur. The exact concentrations of elements vary slightly depending on the chemical composition of each component utilized in the iron or steel production process. Typical compositional ranges for BFS produced in the U.S. are shown in Table 1 [2]. It is the glass content of GGBFS that is considered to be the most significant variable with respect to its hydraulic properties. More rapid quenching yields higher glassy phase contents.

Table 1: Constituent range in US-sourced BFS [2]

Chemical Component	Guideline (wt%)
Calcium Oxide (CaO)	32 – 45
Silicon Dioxide (SiO ₂)	32 – 42
Aluminum Oxide (Al ₂ O ₃)	7 – 16
Magnesium Oxide (MgO)	5 – 15
Sulfide Sulfur (S)	1 – 2
Iron(III) Oxide (Fe ₂ O ₃)	0.1 – 1.5
Manganese(II) Oxide (MnO)	0.2 – 1.0

GGBFS Use in Concrete

GGBFS is often utilized as a partial replacement for OPC in construction concrete. Blended cement concretes have a number of advantages in comparison to OPC-based concretes such as lower heat generation during curing, reduced permeability, and improved durability with enhanced resistance to chemical attack. In addition, blended cements, by incorporating GGBFS, utilize an industrial by-product that would otherwise require disposition, and also reduce cement manufacturing which is associated with the use of virgin raw materials and the production of significant quantities of carbon dioxide (CO₂). When replacing OPC with GGBFS in commercially used concrete, perhaps the most significant parameter to assess the effectiveness of the GGBFS addition is strength gain. Using GGBFS as a replacement material for OPC changes the rate of strength gain since the hydration characteristics of GGBFS are different from OPC. GGBFS is considered to be a latent hydraulic material that relies on the formation of OPC hydration products to enhance its own reactivity. During the hydration of OPC, calcium hydroxide is produced in addition to the calcium silicate hydrate (CSH) gel, and the hydroxyl ions serve to enhance the dissolution of the glassy GGBFS structure. Hence, due to the dependence of the GGBFS reactivity on OPC hydration, concretes incorporating GGBFS generally develop strength more slowly than OPC-based concretes though the long-term strength of the concretes with blended cements can actually be

superior.

Slag Cement Standard

Based on the importance of ensuring that concretes incorporating GGBFS (termed slag cement in upcoming discussion) demonstrate similar or superior compressive strength to their OPC-based counterparts, an American Society for Testing and Materials (ASTM) standard was developed as a means of comparing the strengths of blended and OPC mortars. ASTM C989, “*Standard Specification for Slag Cement for Use in Concrete and Mortars*”, is the principal specification for slag cement, and identifies a slag activity index (SAI). The SAI is defined as the percentage ratio of the average compressive strength of a blended cement mortar cube (50% OPC – 50% slag cement) to the average compressive strength of reference OPC mortar cubes (100% OPC) after a curing duration of 28 days. SAI is calculated by:

$$\text{SAI (\%)} = (\text{SP/P}) \times 100$$

where:

SP = average compressive strength of blended cement mortar cubes

P = average compressive strength of reference cement mortar cubes

Based on this relationship, slag cement (or GGBFS) can be classified into three grades – Grade 80, Grade 100, and Grade 120. Per ASTM C989 the average SAIs for 28-day cured samples are as follows:

Grade 80 GGBFS – 75%

Grade 100 GGBFS – 95%

Grade 120 GGBFS – 115%

Therefore, for a Grade 120 designation a 50% OPC – 50% slag cement sample would require an average compressive strength of 115% of the reference OPC sample.

Other than SAI, ASTM C989 does not provide many requirements for slag cements. Physical requirements in addition to SAI are limited to fineness (20% maximum amount retained when wet screened on a 45- μm (No. 325) sieve), and an air content of the mortar no greater than 12%. The only chemical requirement is that the sulfide content cannot exceed 2.5%.

EVALUATING ALTERNATE GGBFS SOURCES FOR SALTSTONE PRODUCTION

Since the function of GGBFS in saltstone differs significantly with respect to that in construction concrete, compliance with ASTM C989 does not provide sufficient bases for selecting alternate GGBFS materials for the production of saltstone. Changes in GGBFS source, and hence the chemical and physical attributes of the material, have the potential to impact the desirable properties that GGBFS imparts on saltstone, such as alkali-activated reactivity and reducing capacity. Changes to the reactivity can influence the fresh grout properties and the ability to transfer the grout to the SDUs. In addition, changes in reactivity, and the heat evolved during saltstone curing may result in higher grout temperatures that can affect cured grout quality and the volatility of organic species contained within salt solution that contribute to vapor space flammability in an SDU. Changes to reduction capacity may adversely affect the ability for long-term immobilization of saltstone contaminants. As such a validation program was needed in which key attributes of alternate GGBFS materials were directly compared to the traditionally utilized material. EnergySolutions and their partner the Vitreous State Laboratory at the Catholic University of America were contracted to conduct a feasibility study with respect to impacts on the processing and long-term performance of alternate GGBFS saltstone formulations. The viability of

each GGBFS material was determined by evaluating the following key properties and comparing them to saltstone produced with the traditionally utilized GGBFS.

- *Gelation Time* – this is the time at which the CSH gel structure begins to form in saltstone and may impact the ability to pump the material. For saltstone the onset of gelation should ideally occur after the material has been emplaced into the Saltstone Disposal Unit (SDU).
- *Yield Stress* – freshly prepared saltstone behaves like a Bingham plastic and requires a finite yield stress to initiate fluid flow. Higher yield stresses may be impactful with respect to transfer pump operation.
- *Plastic Viscosity* – plastic viscosity is a measure of the resistance to fluid flow once the yield stress has been exceeded. Higher viscosity fluids may be impactful with respect to transfer pump operation and the flow of saltstone once inside the SDU.
- *Heat of Hydration* – hydration reactions are exothermic and generate heat within the emplaced saltstone. Higher hydration heats result in higher grout temperatures that may impact the grout quality, the volatilization of flammable components in the material, and the feasible range of grout pouring schedules.
- *Reduction Capacity* – reduction capacity is a measure of the ability of a material to supply electrons for reducing redox sensitive components, such as ⁹⁹Tc. Reductants, or reducing agents, are the ingredients that donate electrons to redox sensitive radionuclides. The reduction capacity of the GGBFS materials was determined using the method of Angus and Glasser [3], as adapted by the Savannah River National Laboratory (SRNL) [4]. In this method, the reduction capacity, reported in units of microequivalents per gram of solid, refers to the ability of the sample material to reduce a given mass of Ce(IV). It is acknowledged that reduction capacity measured via this method may not be directly analogous to the ability of saltstone to reduce, for example, soluble Tc(VII) to the significantly less soluble Tc(IV) oxidation state. It does, however, provide a fairly straightforward means for quantitative comparison of the total reducing capabilities of various materials.

Through the procurement process four vendors expressed interest in supplying GGBFS for the production of saltstone; hereafter the GGBFS from these vendors will be referred to as Alternates 1 through 4. Tables 2 and 3 provide vendor supplied data. Note that Alternate 4 was the only GGBFS sold as a Grade 100 GGBFS; Alternates 1 through 3 were sold as Grade 120 GGBFS. Table 2 emphasizes the chemical differences between alternate sources of GGBFS noting that all sources were nonetheless compliant with the ASTM C989 requirements.

Table 2: Vendor supplied GGBFS compositions (wt%)

Component	Historical	Alternate 1	Alternate 2	Alternate 3	Alternate 4
Aluminum Oxide (Al ₂ O ₃)	11.1	14.1 – 15.1	10.0	12.6 – 13.4	16.5
Calcium Oxide (CaO)	40.4	41.0 – 42.6	40.9	42.5	35.4
Iron(III) Oxide (Fe ₂ O ₃)	0.4	0.6 – 0.9	0.5	0.8	0.4
Magnesium Oxide (MgO)	7.8	5.0 – 5.8	8.3	5.5	10.5
Silicon Dioxide (SiO ₂)	36.0	32.8 – 36.5	37.3	33.2	31.3
Sulfur Trioxide (SO ₃)	0.0 – 2.3	1.5 – 3.2	0.3 – 1.1	3.2 – 3.3	1.6 – 1.77
Other	2.0 – 4.3	0 – 5.0	1.9 – 2.7	1.1 – 2.1	4.3 – 4.4

Table 3 indicates vendor supplied physical property data. It is interesting to note that based on SAI (as defined in ASTM C989) all five of the GGBFS materials, including the traditionally utilized Grade 100 GGBFS, meet the Grade 120 requirements (i.e., SAI% ≥ 115).

Table 3: Vendor-supplied physical data for alternate GGBFS materials

GGBFS	Grade	Vendor Supplied Data			
		SAI	Sulfide (wt%)	Blaine Fineness (m ² /kg)	% > 45 μm Retained
Historical	100	116	1.0	643	0.6
Alternate 1	120	124	0.9	511	3.1
Alternate 2	120	129	0.8	642	1
Alternate 3	120	125	0.9	539	0.8
Alternate 4	100	124	0.8	439	2.2

Table 4 indicates the measured property data for each of the alternate GGBFS materials. The data is discussed in the latter text. The data in red signifies those properties that are considered substantially disparate with respect to the baseline (historical) saltstone material.

Table 4: Measured property data for saltstone processed with alternate GGBFS materials

GGBFS	Grade	Yield Stress (Pa)	Plastic Viscosity (cP)	Gel time (min)	Heat Release 12 day (J/g)	Reduction Capacity* (μeq/g)
Historical	100	7.1	67.8	50	60.6	722
Alternate 1	120	5.5	55.6	45	68.9	537
Alternate 2	120	7.1	71.7	50	79.7	740
Alternate 3	120	7.7	57.7	55	65.2	812
Alternate 4	100	3.2	50.7	40	86.7	831

* **Note:** Reduction capacity was measured on the GGBFS components as opposed to the saltstone prepared with the alternate GGBFS.

Rheological Properties and Gel Times

All saltstone samples processed with the alternate GGBFS materials indicated similar viscosities, yield stress values, and gel times. The measured differences in these properties in comparison to the baseline with historical GGBFS are not anticipated to adversely impact the ability to process saltstone.

Heat of Hydration

If the 12-day heat release for saltstone samples processed from the alternate GGBFS are normalized to the value for the historical sample the relative reactivity can be expressed as:

Alternate 1: 11% > Historical

Alternate 2: 32% > Historical

Alternate 3: 8% > Historical

Alternate 4: 43% > Historical

As formentioned, the heat generated by saltstone in the SDUs can affect vapor space flammability and limit the allowable pour schedules. To meet SDU safety requirements the bulk of the grout poured into an SDU should not exceed a temperature of 95 °C. A qualitative impact assessment (based on recorded temperature data in an SDU and assuming that the heat capacity and thermal conductivity of each alternate saltstone composition are equivalent) indicates that only Alternates 1 and 3 would satisfy the 95 °C temperature limitation with reasonable margin. It is important to reiterate, however, that this assessment is qualitative, and a quantitative evaluation in the form of a 2D thermal (finite element) model is planned in the future to more accurately determine heat generation associated when utilizing the alternate GGBFS materials.

Reduction Capacity

All but one of the alternate GGBFS materials (Alternate 1) indicated a higher reduction capacity in comparison to the baseline GGBFS. In Performance Assessment (PA) modeling of long-term contaminant transport, the model assumes a starting reduction capacity that is linearly consumed over time. The point at which the reduction capacity is totally consumed signifies the point at which, for example, reduced Tc(IV) can be oxidized to the more mobile Tc(VII) species. Thus, a lower initial reduction

capacity in saltstone decreases the duration that redox sensitive contaminants will remain immobile. It is not known precisely how the lower reduction capacity measured for Alternate 1 will influence the PA model, since it is only one of many inputs that influence contaminant transport. However, in order to validate the use of the Alternate 1 GGBFS the contaminant transport would require simulation utilizing the lower reduction capacity.

SUMMARY

Following notification that the GGBFS historically utilized in the production of saltstone would no longer be available due to the permanent closure of the source steel production plant, alternate GGBFS suppliers were sought. However, in contrast to the standardized requirements for using GGBFS as a replacement for OPC in the construction industry, the role of GGBFS in saltstone is such that changes in the source material may impact key properties such as rheology, heat generation, and reduction capacity. Hence, alternate GGBFS materials were subjected to preliminary evaluation to provide a comparison to the baseline material. Four alternate GGBFS materials were evaluated but only one material (Alternate 3) is currently considered viable as a replacement for the historically utilized material. However, identifying a single alternative is not satisfactory since the supply of the alternate material may also be compromised in the future. The U.S Geological Survey (USGS) notes that [5]:

“The availability of blast furnace slag is becoming problematic in the United States because of the closure and (or) continued idling of a number of active U.S. blast furnaces in recent years, the lack of construction of new furnaces, and the depletion of old slag piles. At yearend 2014, granulation cooling was available at only three active U.S. blast furnaces and was unlikely to be installed at any other sites.”

“Long-term demand for GGBFS likely will increase because its use in concrete yields a superior product in many applications and reduces the unit carbon dioxide (CO₂) emissions footprint of the concrete related to the portland cement content. Recent draft regulations to restrict emissions of CO₂ and mercury by coal-fired power plants, together with the plant closures or switchover at many such plants to low-cost natural gas, have led to a reduction in the supply of fly ash in some areas, including that of material for use as cementitious additive for concrete. This has the potential to increase future demand for GGBFS.”

“Long-term growth in the supply of GGBFS will mainly depend on imports, either of ground or unground material. Imports may be constrained by increasing international demand for the same material and because not all granulated slag produced overseas is of high quality.”

As such near term production of saltstone will proceed with the use of GGBFS Alternate 3, but future efforts will be directed at validating other sources to negate the potential impacts associated in the reduced supply of a given single source.

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