Optimising Blends of Blast Furnace Slag for the Immobilisation of Nuclear Waste – 16245

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ABSTRACT

The legacy of nuclear waste at the Sellafield site in the UK is an ongoing issue, and the current preferred route for the disposal of low and intermediate level waste is encapsulation in a cementitious matrix, formulated by blending Portland cement with blast furnace slag (BFS). Due to demands and economic challenges faced by the cement and steel industries, the supply of BFS to the UK nuclear industry has been inconsistent. These changes have caused the industry to move from a unique BFS powder supply with a certain specification to a combination of standard commercially available cementitious powders. The material currently used at the Sellafield site is a blend of ground granulated blast furnace slag (GGBS) and a coarser fraction of the same composition called Calumite, combined with Portland cement.

This work involves future-proofing the supply of BFS for the UK nuclear industry by optimising the blend of the two fractions of BFS in order to replicate the unique specification required by Sellafield Ltd. The main emphasis is on the particle size distribution (PSD) and how this impacts the properties of the final wasteform. The study investigates the performance properties of the blended grouts such as workability, particle packing and heat evolution. Results show that the PSD of the cement powders affect both the physical and chemical properties of the cementitious matrix produced.

INTRODUCTION

In the UK, the current preferred route for the disposal of low and intermediate level waste (LLW/ILW) is encapsulation in a cementitious matrix grout. A high volume fraction of blast furnace slag (BFS) is used in the cementitious material used for encapsulation. The cement and iron industries have been affected by economic challenges, causing an inconsistent supply of BFS to the UK nuclear sector.

The cementitious grout used is a blend of Portland cement (PC) with BFS and must conform to a set of tightly controlled performance requirements in the fresh and hardened states. The composition of the cement powder has a significant impact on the performance of the grout system, and therefore, it is necessary to control the powder properties within a tight specification. The nuclear industry has previously used a unique cement powder specification for the BFS component, but unfortunately the original powder supply meeting this specification has become unavailable. The surface area required by the specification is much lower than that of the products which are now widely used by the construction industry and which are thus available in large quantities. The alternative material now being used is a blend of industry grade ground granulated blastfurnace slag (GGBS) and a coarser fraction of slag called Calumite (Cann, Carruthers et al. 2011). The compositions of both materials are very similar and shown in Table I. The reason for blending the two fractions is that the finer powder has increased reactivity and yields poor paste fluidity due to its higher surface area increasing water demand. Therefore, the coarse Calumite fraction is essential to help control the fluidity and heat evolution rate of the cement grout for the successful infill of complex shaped solids often found in nuclear waste streams.

BFS particle size significantly influences the fluidity of a cement grout because finer slag particles increase water demand due to their higher surface area (Farris, Miller et al. 2004). This means that at a fixed water/solids ratio, a higher content of the finer slag is expected to lead to lower grout fluidity, in addition to generating a higher rate of heat output. Therefore, the coarser BFS fraction is required to reduce water demand and reduce the heat evolution rate during hydration. In this work, tests were carried out to further understand the rheology of the cement systems in order to produce safe and durable wasteforms. The fluidity of the cement grout is crucial due to plant conditions and the need to remotely fill and set around irregularly shaped waste components in stainless steel drums. Calorimetry was conducted to further understand the effect of blending the two different powders on the heat evolution of the system. A low heat of hydration is essential to reduce the risk of cracking within the wasteform once it has been set due to thermal stresses. This study therefore focuses on the physical and chemical properties of cement grouts produced from slag blends with a range of PSDs at various water contents. This was achieved by changing the ratio of GGBS:Calumite within the BFS fraction of the system whilst maintaining a constant wt% of PC to activate the latently hydraulic slag.

METHODOLOGY

The GGBS and Calumite material used during this study were sourced from the Scunthorpe steelworks, Scunthorpe, UK (Hanson Cement). The Portland cement is a Sellafield Ltd. grade and is also supplied by Hanson Cement from their Ribblesdale works.

Composition

The composition of the GGBS and Calumite materials was analysed by X-ray fluorescence (XRF). The main components of the materials are shown in Table I.

Table I. Main components of GGBS and Calumite in wt% measured by XRF.

Element/Oxide	GGBS (wt%)	Calumite (wt%)
CaO	39.0	38.9
SiO_2	36.31	38.3
Al_2O_3	11.56	11.3
MgO	8.13	7.9

Particle Size Distribution

The particle size distributions of the two BFS fractions were analysed using laser diffraction. The PSDs of both the GGBS and Calumite are shown in Figure 1. From this data, it is clear that a blend of the two materials would create a bi-modal distribution which suggests that the BFS produced would be a gap graded powder.

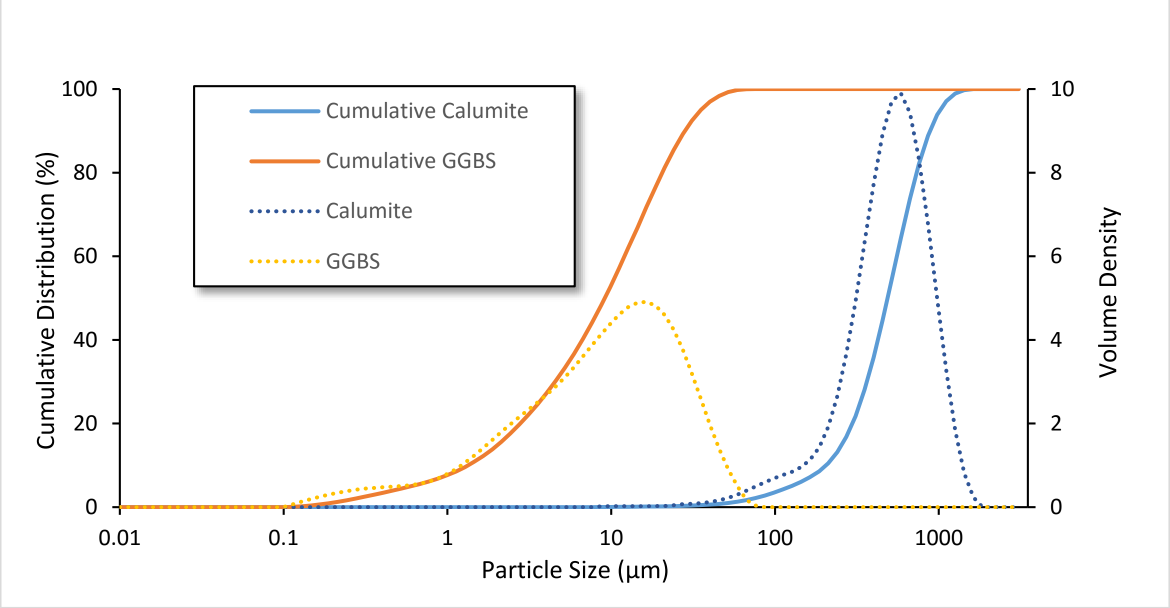

Figure 1. Particle size distribution data for the GGBS and Calumite materials.

Mix Design

The baseline grout formulation used is 3:1 BFS:PC by mass, at a 0.35 water/solids (w/s) ratio, where the BFS component comprises of a fine and coarse (Calumite) fraction. The fine fraction was a blend of the fine GGBS with Calumite at a 65:35 ratio, and is named here as GGBFS. Additional w/s ratios (0.33 and 0.37) were used to analyse the effect of water on the different grout formulations. The ratios of the

GGBFS:Calumite blends used to formulate the BFS fraction within the mix design are shown in Table II.

TABLE II. Blend ratios of GGBFS:Calumite comprising the BFS fraction of the binder.

GGBFS:Calumite Wt. ratio
100:0
65:35
50:50
35:65
0:100

Slump Tests

Mini slump tests were used to measure the workability of the cement grouts. The test apparatus is a scaled down version of the standard Abrams slump cone widely used in the construction industry (Clayton, Grice et al. 2003). The slump test consists of filling an up-turned cone which has a height of 57 mm, a 19 mm top and a 38 mm base, with a grout sample. The cone is then lifted vertically from a base-plate and the grout is allowed to flow; the slump flow measurement is defined as the distance the sample travels under gravity, which is measured as the area covered by the grout using a grid marked on the base-plate.

Particle Packing

Centrifugation of the grout formulations was used to measure the particle packing density of the different mixes. Each cement mix was subject to 30 minutes of centrifugation at 4000 rpm. The voidage of the centrifuged bed of solids within each sample was calculated, and thus the maximum particle packing density obtained. The test was conducted in triplicate.

Calorimetry

Isothermal calorimetry was carried out using a TAM air calorimeter at 25 °C to measure the heat evolution from the samples over an 80 hour time period. Alongside this, semi-adiabatic calorimetry was carried out using a home-built instrument on each of the mixes in order to obtain a temperature profile of the hardening of the cement. In both instances, fresh paste was mixed, weighed into an ampoule and immediately placed into the calorimetry apparatus. Sample masses of 20 g were used for the isothermal calorimeter. The semi-adiabatic calorimeter used 1 L vacuum flasks as sample vessels, with the temperature monitored at the centre-line of each flask using a thermocouple and data-logger.

RESULTS AND DISCUSSION

Slump Tests

The fluidity of the cement grout used during immobilisation and encapsulation is a crucial performance property required when producing wasteforms. Due to the nature of the encapsulation plants on the Sellafield site, the cement grout produced has to have a high fluidity and a long enough working time to allow the grout to flow in and around irregularly shaped solid wastes. The water content also needs to be minimised as some ILW metals have enhanced corrosion rates in high water grout.

The slump test provides a simple but effective method of measuring the workability of the cement formulations. This in turn produces comparable results that can be used to explain the effect of water within the different blends.

The results in Figure 2 show that the 35:65 GGBFS:Calumite blend yields the highest fluidity across all three w/s ratios. This can be attributed to a balance between large and small particles. The 100:0 blend has the lowest fluidity because the GGBFS material contains more finer particles which therefore have a higher surface area and greater water demand.

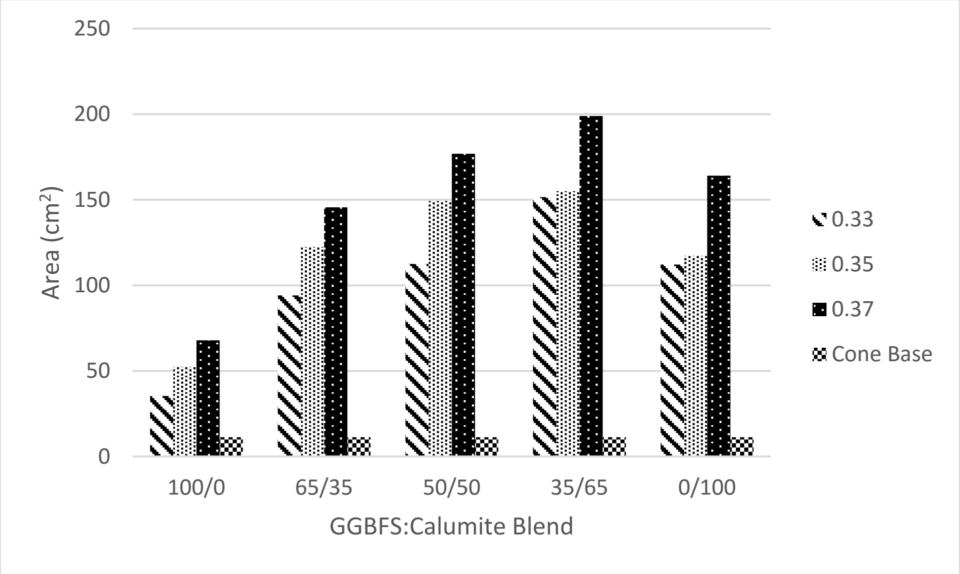

Figure 2. Slump areas for the 5 blends at a 3:1 BFS:PC ratio and at a 0.33, 0.35 and 0.37 w/s content.

As expected, the higher w/s content grouts have the highest fluidity across all of the blends. However, increased w/s content causes the formation of a bleed water layer on the top of the hardened cement paste. This settlement of water on the hardened cement is undesirable as it then becomes a secondary waste that requires disposal or the encapsulation process must be halted to allow bleed water to evaporate, as the UK waste acceptance criteria do not permit the presence of a liquid component in a cemented waste drum.

Calorimetry

Semi-adiabatic calorimetry shows that there is almost a 20 °C difference in the peak temperatures produced by the 5 different blends of GGBFS:Calumite as shown in Figure 3.

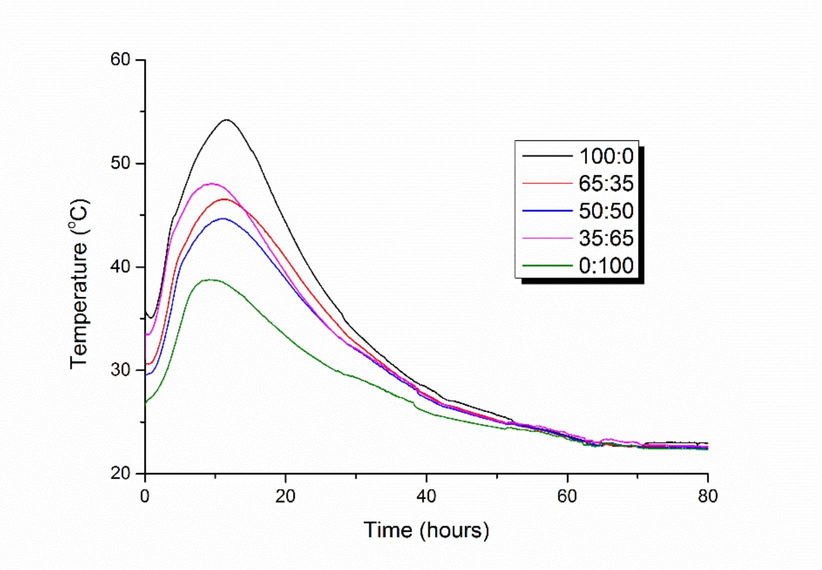

Figure 3. Semi-adiabatic calorimetry curves for the 5 blend ratios measured at RT for 80 hours at w/s = 0.35.

Similar results were seen at the 3 w/s ratios (0.33, 0.35 and 0.37) whereby there is not a monotonic trend between the blends. However, the 0:100 blend containing the highest amount of large particles is approximately 20 °C lower in peak temperature than the 100:0 mix. These results show a representative temperature profile of the cement grouts produced, and provide an idea of what could occur within the full-scale wasteform.

Isothermal calorimetry was carried out to understand the heat production rate of the samples, which is considered to be proportional to the rate of reaction of the cement and to obtain the total heat evolution for each grout formulation. Again, three w/s ratios (0.33, 0.35 and 0.37) were considered, producing very similar results; the 0.35 w/s data are shown in Figure 4.

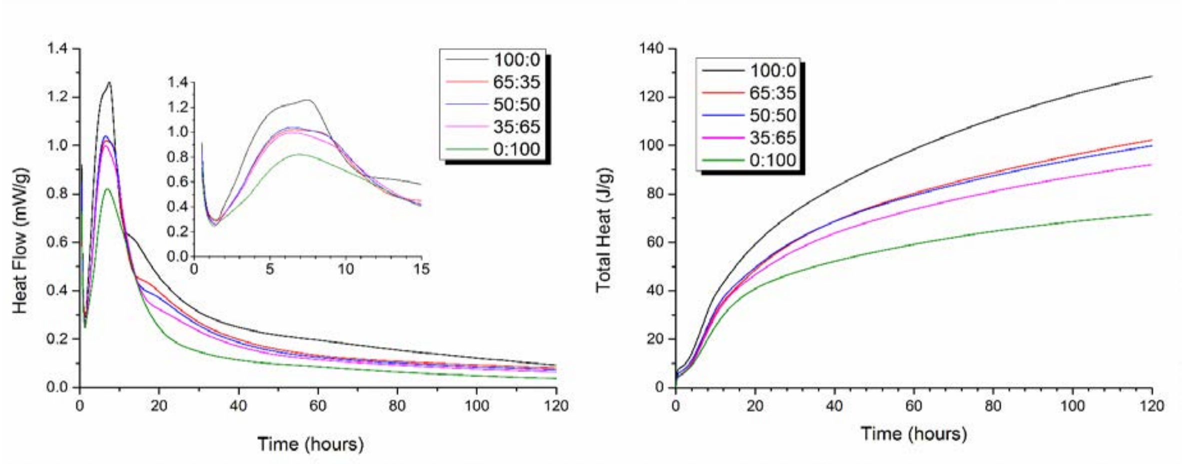

Figure 4. Isothermal calorimetry (left) and total heat evolution (right) curves for the 5 blend ratios measured at 25°C for 120 hours at w/s = 0.35.

The data show that as the Calumite fraction increases, the peak heat of reaction reduces, which can be attributed to reduced reactivity of the larger particles. The formation of an initial peak was observed in all five blends between 3-9 hours (inset on Figure 4), which was assigned to alite hydration (Bullard, Jennings et al. 2011). However, additional peaks are formed and become more prominent as the GGBFS content increases, including the peak which is related to sulphate depletion which takes place immediately after the main alite peak (Bullard, Jennings et al. 2011). This suggests that the change in PSD has an effect on both the physical and chemical properties of the cement produced.

The total heat evolution during hydration is one of the main criteria required by Sellafield Ltd. in their specification when considering alternative grout formulations. Figure 3 illustrates that, as the GGBFS content increases, the total heat evolution also increases. However, all of the blends here can be considered as very low heat cements under European standard classifications (British Standards Institution, 2011).

CONCLUSIONS

It has been established that the PSD of the cement powder used for the encapsulation of nuclear waste affects the performance properties of the resultant hardened material. It is clear from the slump tests carried out that by blending the finer and coarser fractions of BFS the fluidity of the grout is significantly affected. The 35:65 GGBFS:Calumite showed the highest workability across the 3 w/s ratios investigated, and as expected the mixes containing a 0.37 w/s content achieved the largest slump across all 5 blends. However, fluidity cannot be improved by increasing the water content due to bleeding and the risk of increasing corrosion of reactive metals.

Calorimetry experiments showed that all the cements used during this work are all low heat cements and can therefore be considered for this application. The blend containing the finer material produces the highest temperature profile due to increased reactivity of the particles. These effects should be taken into consideration when deciding on the material used during this process.

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