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# Assessing the physical suitability of different immobilisation grouts for LLW and ILW encapsulation.

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## ABSTRACT

The issue of legacy wastes from early civil nuclear operations is vast, complex and multifaceted. Variations in composition, radioactivity and state (liquid, solid or a combination) mean that a ‘toolbox’ of different systems is required<sup>1</sup> to provide appropriate conditioning prior to final disposal. For Low level waste (LLW) and Intermediate level waste (ILW), the preferred method in the UK is encapsulation in a cementitious matrix. This study has been performed to assess the physical performance of one such grout in comparison to potential replacements in order to determine their potential suitability. This work aims to define a set of physical tests which may be applied as a precursor to more rigorous assessment of future grouting systems. Samples were prepared at varying cement:replacement and water:binder ratios, as shown in Table 1, in accordance with current practice in industry and to ensure suitable workability and setting time. Following curing at 20°C ±1°C and 98% RH for 28 days, UCS, permeability, sorptivity and Acid neutralising capacity (ANC) were measured with further characterisation via SEM-BSE and simultaneous thermal analysis (STA).

## 1. INTRODUCTION

Civil nuclear operations in the UK date back to 1956 and Calder Hall, the world first civil nuclear reactor. The operation of Calder Hall ceased in 2003 but there continues to be a moderate nuclear industry in the UK, with 19% of our total energy production coming from the nuclear fleet<sup>2</sup>. One drawback of this extensive history of nuclear power is the large volumes of waste that have been produced, with most recent estimates placing the total at 5,000,000 tonnes<sup>3</sup>.

Of the total waste volume, around 0.02% is classed as high level waste (HLW) and accounts for 95% of the overall activity of the total waste volume. Owing to its high radioactivity, this waste is vitrified in a borosilicate glass prior to interim storage (of at least 50 years, and possibly in excess of 150 years<sup>4</sup>) and final disposal.

Of the remainder, roughly 11% is classed as ILW and 89% is LLW or very low level waste (VLLW). The preferred treatment method for these waste streams is encapsulation within a cementitious grout. This method provides a good balance of efficiency and economics, resulting in a solidified and stabilized product which is then suitable for disposal. The relatively high pH, low permeability, ease of manipulation and suitability for remote operation all contribute to the suitability of grouting to this application.

This solidification/stabilization (S/S) process is defined as ‘...mixing waste with a binder to reduce contaminant leachability by both physical and chemical means...[creating] an environmentally acceptable waste form for land disposal’<sup>5</sup>. The three mechanisms of S/S are<sup>6</sup>: Physical adsorption, chemical fixation and physical encapsulation.

Whilst the process and methods used for nuclear waste encapsulation are relatively well defined, the supply of grouting materials is volatile and unpredictable. Susceptibility to variations in the chemical composition of the grouting matrix are not well understood; the result is a potential risk in continuity of supply as the composition of cements, ground granulated blastfurnace slag (GGBS) and pulverized fuel ash (PFA) rapidly evolve due to changes in production and to meet the demands of the construction industry.

## 2. METHOD

This study was carried out using Sellafield Grade OPC, free of grinding aids and minor additional constituents (MACs), Sellafield specification blastfurnace slag (BFS), two different slags (A & B), Drax PFA and silica fume (SF). 9 mixes were prepared, their mix ratios are shown in Table 1. It should be noted that mortar pastes were used, as is the practice in the nuclear waste industry.

Table 1: Mix designs

Mix	w/b	SL OPC	SLAG A	SLAG B	SL BFS	Drax PFA	SF
OPC:BFS	0.35	0.22			0.77		
OPC:A	0.35	0.22	0.77				
OPC:B	0.42	0.22		0.77			
OPC:PFA	0.35	0.25				0.75	
OPC:A:PFA	0.35	0.22	0.385			0.385	
OPC:B:PFA	0.42	0.22		0.385		0.385	
OPC:A:SF	0.42	0.22	0.67				0.11
OPC:B:SF	0.44	0.22		0.67			0.11
OPC:PFA:SF	0.42	0.25				0.56	0.19

50mm cubes were cast in triplicate for UCS<sup>7</sup> testing, with cylindrical samples prepared at a diameter of 50mm for permeability<sup>8</sup> and sorptivity<sup>9</sup> testing; additional samples were prepared in polypots for

ANC<sup>10</sup>, SEM-BSE and STA testing. All samples were cured for 28 days at 20°C ±1°C and 98% RH.

UCS testing was carried out at 28 days, samples prepared for ANC, SEM-BSE and STA were quenched in acetone to arrest hydration. Larger samples for permeability and sorptivity testing were oven dried at 60°C until constant weight; this was felt to be the most suitable method of hydration stopping given the size of the samples and the manner of subsequent testing.

### 3. RESULTS

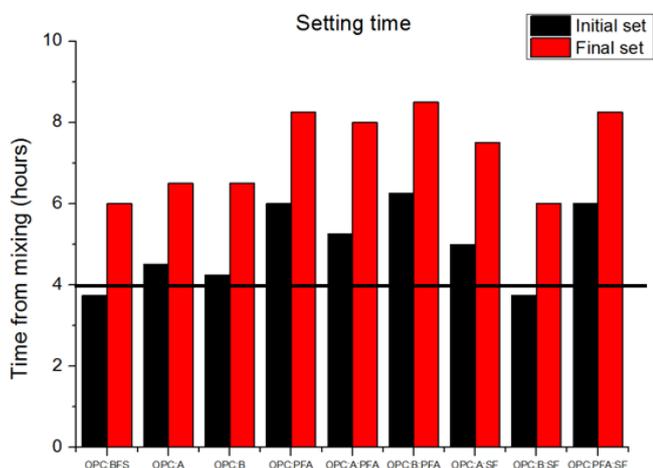
XRF data for the BFS and two slags showed that all conformed to BS EN 15167 and allowed for two commonly used basicity ratios<sup>11</sup> [Table 2 Error! Reference source not found.] to be calculated. As the table shows, the Sellafield specification BFS is deemed to be more reactive than the two slags used in this study.

**Table 2:** Basicity ratios of SL BFS, Slag A and slag B

Ratio	Comments	SL BFS	Slag A	Slag B
$P_1 = \text{CaO}/\text{SiO}_2$	Reactivity will increase with $P_1$ . acid < 1 < basic	1.22	1.06	1.20
$P_2 = (\text{CaO} + \text{MgO})/\text{SiO}_2$	Used in EN197-1. $P_2$ must be $\geq 1$ .	1.43	1.27	1.37

**Table 3:** Fineness and density of materials

	Ribblesdale OPC	SL BFS	Slag A	Slag B	PFA	SF
Blaine (cm <sup>2</sup> /g)	4400	3280	3770	4540		
Density (g/cm <sup>3</sup> )	3.15	2.92	2.84	2.93		

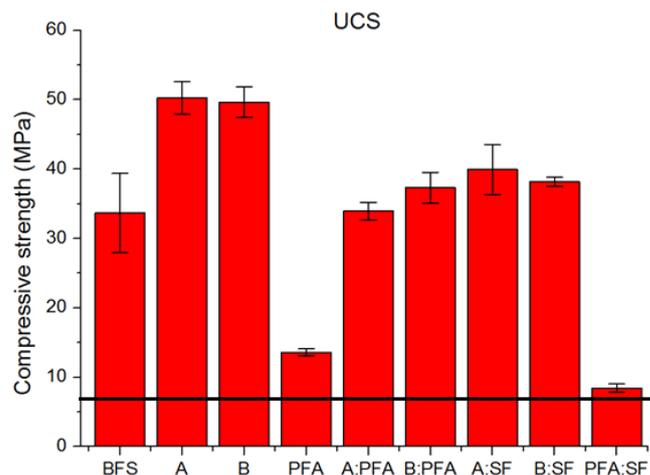


**Figure 1:** Time of initial and final set for all mixes

Table 3 shows the Blaine fineness and density of all six of the materials included in this study. SL BFS was much coarser than the two slags, with slag B having a fineness almost 40% higher. This disparity in fineness and hence specific surface area (SSA) meant that a higher w/b was required in the case of the OPC:B and OPC:B:SF mixes in order to ensure a similar and therefore suitable workability and setting time (see Figure 1).

At initial setting time of no less than 4 hours and a final set of no more than 24 hours are required for practicality<sup>12</sup>. Figure 1 shows that all mixes tested, with

the exception of the reference OPC:SL BFS and OPC:slag B:SF samples, set in the required time frame. This slight discrepancy on the part of the original mix may be a result of slightly accelerated hydration due to relatively higher ambient temperatures<sup>13</sup> of the testing environment in comparison to those experienced in practice. It should also be noted that whilst w/b was increased for some of the mixes (see Table 1) to maintain workability, this had no adverse affect on setting time.



**Figure 2:** UCS of all mixes at 28 days

Following curing for 28 days samples were tested in triplicate for UCS. A minimum value of 7 MPa is suggested to ensure that the waste package is able to be self-supporting; minimizing the risk of cracking during transport, storage and final disposal.

Whilst all samples showed a compressive strength greater than 7 MPa, those containing PFA and a PFA:SF mix performed considerably worse than those which contained BFS or GGBS within either a binary or ternary system. It is postulated that this low strength development is indicative of overall hydration; likely caused by a low CH content which is required to ensure a pozzolanic reaction and hence continued hydration.

The inclusion of SF (effectively pure Si<sub>2</sub>) can be seen to compound this retardation of strength development, suggesting that some CH may have been consumed to form secondary C-S-H before beneficial conditions to allow a pozzolanic reaction had been achieved.

Although the BFS was found to be more reactive (Table 2) than both slag A and slag B; its strength development after 28 days was considerably lower. Even with a considerably higher w/b ratio the OPC:B mix showed a mean strength 47% higher than the reference sample.

In this instance it is clear that fineness has a strong part to play. In ensuring a coarser product is used it is possible to reduce heat of hydration (both peak and cumulative see Figure 3 & Figure 4) and water demand to meet a set workability; however the compromise is a reduction in total degree of BFS/GGBS hydration.

it is not possible to predict the parameters of permeability or sorptivity from UCS data.

There almost seems to be an inverse correlation between UCS and permeability (see Figure 2 & Figure 5) whereby the samples which have developed the greatest strength seem to show the highest permeability. What can be seen is that the samples prepared with PFA show the lowest permeability by a considerable margin, more than 3 times lower than the OPC:BFS mix and more than an order of magnitude lower than those prepared with the other slags. This would suggest why it is the preferred grout for use as a capping layer during encapsulation.

What is interesting and rather counter-intuitive is the fact that the addition of silica fume had increased permeability in all instances. The OPC:PFA:SF sample is still the second lowest in this regard, but intrinsic permeability is more than doubled as a result of replacement. One explanation for this could be the increase in w/b that was required in order to maintain fluidity and workability, which would lead to an increase in capillary porosity<sup>14</sup>.

The reference OPC:BFS sample showed the lowest sorptivity coefficient of all samples, however the disparity was less than a factor of two for all of the BFS/GGBS containing mixes. Replacement by SF increased sorptivity by at least 20% in all instances, with pastes prepared with PFA having the highest sorptivity overall.

Table 4: Sorptivity coefficients at 28 days

Mix	Sorptivity coefficient [x10 <sup>-3</sup> ] (cm/s <sup>1/2</sup> )	Relative to BFS
BFS	7.7	100.00
A	9	116.88
B	10	129.87
PFA	32.5	422.08
A:PFA	9.5	123.38
B:PFA	12.7	164.94
A:SF	12	155.84
B:SF	12	155.84
PFA:SF	44.8	581.82

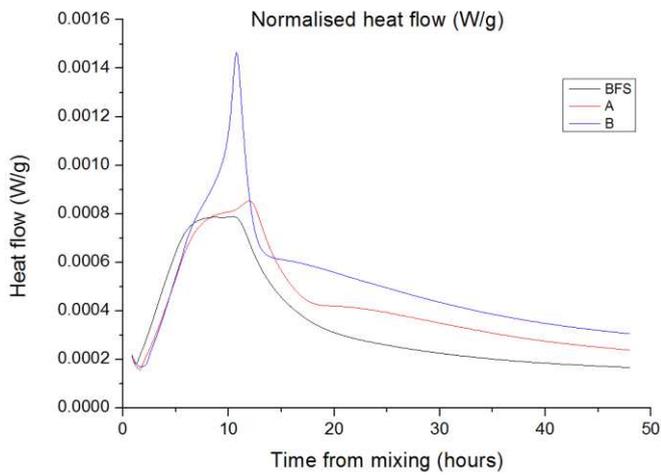
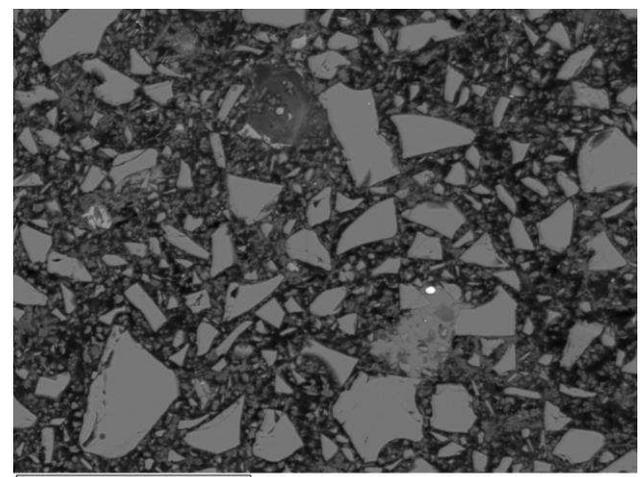


Figure 3: Normalised heat flow of BFS/GGBS samples at 28 days

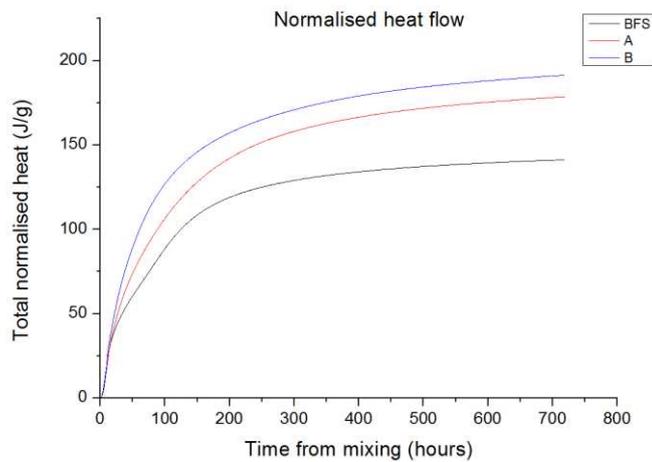


Figure 4: Normalised heat of BFS/GGBS samples at 28 days

In the ternary systems containing both slag and PFA the UCS is considerably higher than binary systems containing only OPC:PFA, however it is still significantly lower than both the OPC:A and OPC:B systems. In these cases there is evidently a more complex interaction occurring within the systems, with insufficient quantities of CH to allow for significant hydration of either slag or PFA.

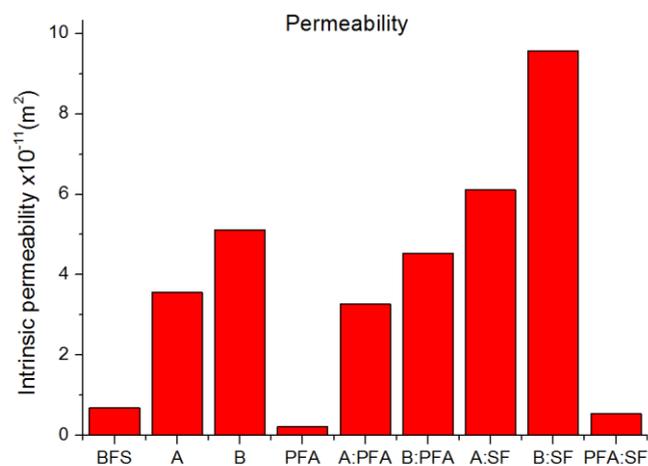
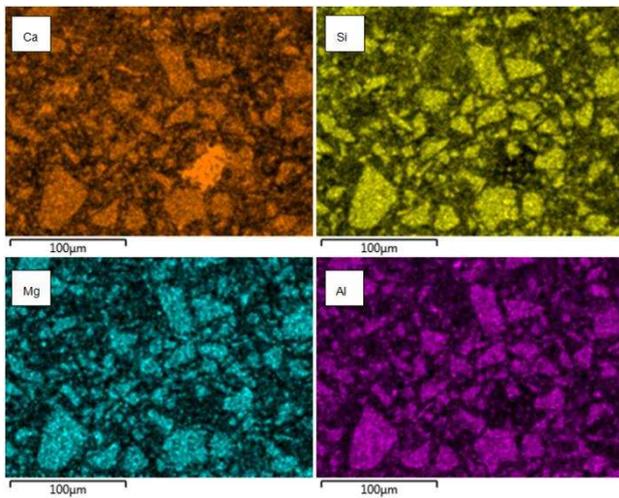


Figure 5: Intrinsic permeability at 28 days

Owing to the large variability in the chemical and physical composition of the materials used in this study



**Figure 6:** SEM-BSE image of OPC:BFS mortar [x500] at 28 days with elemental mapping

SEM-BSE was carried out on all samples using a Jeol 5800LV Scanning Electron Microscope and backscattered electron detector. Images were taken at 500x and 1000x magnification with elemental mapping.

Figure 6 is a micrograph of the OPC:BFS grout at 500x magnification; largely unreacted slag grains are clearly visible, their locations confirmed by Mg and Al mapping, both of which could be used to isolate and segment the images to determine degree of slag hydration<sup>15</sup>.

A small amount of CH can clearly be seen toward the bottom right of the micrograph; this is corroborated by elemental mapping which shows high levels of Ca and a relatively low localised concentration of Si. Although there is expected to be a large degree of CH consumption through secondary C-S-H formation, the heterogeneous nature of the encapsulation systems means that there will always remain small areas of CH within the system.

SEM-BSE for the other systems showed similar results. The overall volume of CH in the OPC:A system seemed lower than the reference sample, however this has not been quantified. It could be that the relatively higher SSA of the slag has allowed for continued hydration and CH consumption, this is supported by relatively higher strength gains at 28 days. Quantitatively, this effect seems more pronounced in the OPC:B system, where slag fineness and hence SSA are considerably higher again.

The consumption of CH to form secondary C-S-H is beneficial for nuclear waste encapsulation in a number of ways. The chemical stability of C-S-H is higher, solubility is decreased and hence leaching will be reduced; the surface area of C-S-H is very high, providing sites onto which radionuclides can sorb<sup>16</sup>.

## CONCLUSIONS

Following this preliminary investigation it is possible to draw the following conclusions-

- Common basicity ratios<sup>11</sup> give an indication toward potential performance; however physical factors such

as SSA and temperature play a strong role and may, in some cases, prove to be dominating factors.

- Fineness may be manipulated to control water demand, setting time and heat of hydration. This will undoubtedly reduce total degree of hydration, in which case it becomes a trade off to optimise efficiency.
- Early age testing provides a good starting point for comparing and predicting performance; it should be noted, however, that complex systems such as these continue to hydrate and evolve indefinitely<sup>17</sup>, and later age testing should be carried out accordingly.
- Although it is often possible in construction to predict or roughly estimate other parameters based on UCS this is not possible in this instance. The variability in materials coupled with the complexity of the systems mean that correlations cannot be drawn.

Whilst the parameters of key importance for this application are well known, there is a lack of a definitive 'envelope of performance'. Defining minimum or maximum levels of w/b ratio, bleeding and segregation, setting time, heat of hydration, pH, Eh, UCS, permeability and leaching would allow for more rigorous testing regimen to be defined. This would in turn allow for a greater number of potential systems to be assessed at pilot scale and create a much more robust encapsulation process through ensuring a continuity of supply despite changes in materials and processes.

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