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Cementitious grouts for intermediate level nuclear waste (ILW) encapsulation - effect of compositional changes upon hydration

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Summary

Grouts containing high levels of replacement by BFS are the preferred route to disposal for a large majority of ILW in the UK (NDA 2013). A number of techniques, SEM image analysis, chemical shrinkage, ICC, TGA and XRD, have been applied to assess the rate and degree of hydration of such cementitious grouts. This study forms a base for quantifying the effects of modifications to the physical and chemical composition of both the OPC and the BFS components of the matrix in order to identify the sensitivity or otherwise of the technique to ensure that a continuity of supply is maintained.

Keywords

Hydration, Image analysis, BFS, Blended cement, Degree of reaction.

Introduction

Encapsulation within a cementitious grout is the preferred route to disposal for ILW within the UK (Glasser 1992, Wilson 1996, Glasser 2011) owing to the rheological properties of the encapsulant prior to setting and the chemical and physical barrier to release of contaminants that the hardened product provides (Collier, Milestone et al. 2006, Shi and Fernandez-Jimenez 2006). The anhydrous materials which are used to form the grouting matrices must conform to strict physical and chemical compositional limits. As a result of these tight parameters on composition there is the potential for possible difficulties to be encountered in ensuring a continuity of supply. Quantification of the effects of compositional changes is essential in determining the resilience of the technique to current and future changes in supply. Furthermore, a clear and thorough understanding of the rate and degree of hydration of these materials is not well established. It has been shown that at high levels of replacement, hydration of BFS is diminished significantly (Gruyaert 2011) but until recently there have been difficulties in accurately determining degree of hydration of SCMs in blended systems (Scrivener, Lothenbach et al. 2015).

Materials and methods

2 OPCs and 3 BFS powders were used throughout this project. Mixes were prepared with 75% replacement by BFS at a w/b of 0.35. 6 mixes in total were prepared (C1S1, C2S1, C1S2c, C2S2c, C1s2F and C1S3c, where the numbers indicate the two slags and cements, while subscripts 'c' and 'f' indicate coarse and fine (defined by the upper and lower fineness limits for grouting materials). S1 is a blend of 65% fine slag and 35% extra coarse slag (S3 prior to grinding).

Heat evolution was followed for 28 days using a TamAir 8 isothermal calorimeter. Chemical shrinkage was measured in triplicate via dilatometry, as described by (Geiker 1983) and further developed by (Whittaker 2014). SEM image analysis was performed after hydration for 2, 7 & 28 days, acquiring 50 images per sample at 800x magnification at a working distance of 8mm and 15keV accelerating voltage. Mg maps at a nominal count rate of 30k cps for 2-3 minutes per image were used to determine the degree of slag hydration. Subsequent segmentation and analysis was carried out using ImageJ.

Table 1: Surface area and density For anhydrous materials

Material	SSA (m^2/Kg)	Density (g/cm^3)
C1	325	2.91
C2	384	2.90
S1 fine (65%)	526	2.91
S1 extra coarse (35%)	[redacted]	2.80
S2c	242	3.15
S3c	294	3.18
S2f	419	2.92

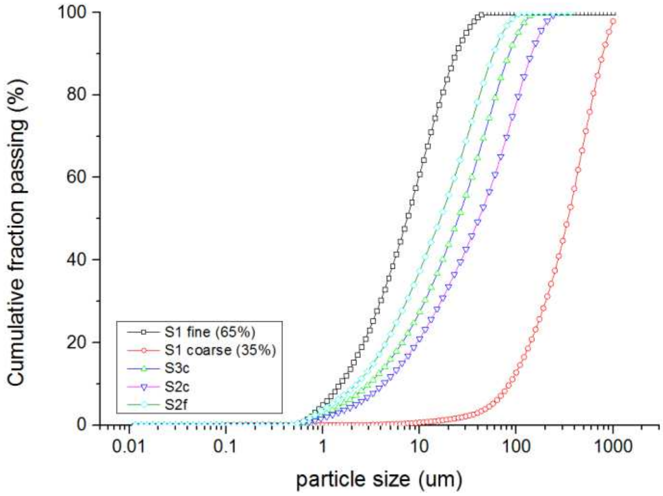

Figure 1: Particle size distribution for anhydrous materials

Results

Reaction of OPC was accelerated at early age due to the filler effect; w/c ratio was significantly increased causing dilution, thus promoting hydration of the BFS within all systems. Even at high levels of replacement the correlation between heat evolution and dilatometry is very strong (Figure 2a) as shown previously (Kocaba, Gallucci et al. 2012, Whittaker 2014) it is also possible to correlate these results to SEM image analysis whereby the heat release or chemical shrinkage due to hydration of the BFS component is isolated to an accuracy of 5% (Scrivener, Lothenbach et al. 2015).

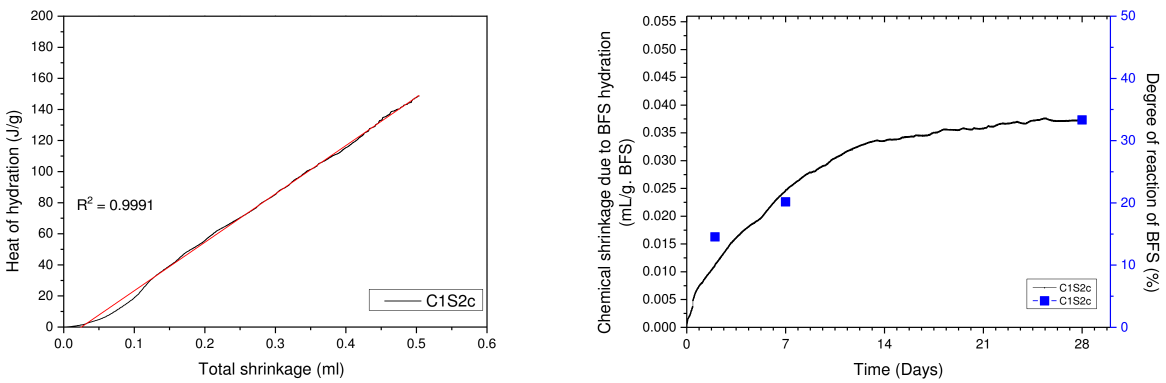

Figure 2: a). Calorimetry vs. chemical shrinkage, and b). Chemical shrinkage vs. SEM image analysis for system C1S2c.

Figure 2a illustrates that both calorimetry and chemical shrinkage may be used to accurately estimate degree of BFS hydration within a composite cement, especially when corroborated with a more quantitative technique such as image analysis. Another advantage of these techniques over that of image analysis (as well as being less time and labour intensive) is their improved accuracy at early age, where results from SEM have been shown to overestimate early age hydration (Kocaba 2010, Whittaker 2014).

Table 2 shows that BFS fineness is a significant factor in early age hydration, whilst BFS composition has negligible influence. This is believed to be in part due to the accelerated hydration of the OPC within the system due to enhanced filler effect (nucleation in addition to dilution) but also due to the increased surface area of the BFS grains. The impact of OPC composition upon rate and degree of hydration was negligible (results not shown); however, the OPC powders used within this study had SSA measurements within 20% difference.

Table 2: Degree of hydration of BFS as calculated via SEM image analysis

Mix	DoH of BFS (%)		
	2 days	7 days	28 days
C1S1	7.72	12.96	28.64
C1S2c	14.53	20.16	33.34
C1S2f	28.38	37.53	48.64
C1S3c	11.76	19.25	32.03

Conclusions

Quantification of hydration within blended cements containing BFS is a complex task. However the application of a number of direct and indirect techniques appears to allow for relatively accurate and promising results to be obtained.

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