

An alternative to Portland Cement for waste encapsulation—The calcium sulfoaluminate cement system

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Abstract

Currently, Portland Cement (PC) is used extensively in the solidification/stabilisation of a wide variety of wastes. In the nuclear industry, low and intermediate level radioactive wastes are encapsulated or immobilised within composite PC cement systems based on high replacement with blast furnace slag or fly ash. However, the high alkalinity of these PC-based systems will corrode reactive metals found in some wastes releasing hydrogen and forming expansive corrosion products. Alternative cement systems could provide a different hydration chemistry, which would allow wastes containing these metals to be encapsulated with lower reactivity. Calcium sulfoaluminate (C \bar{S} A) cement is one such cement. It combines economy of cost and low emission of CO₂ with rapid strength gain and compatibility with other construction materials. Hydration provides an internal pore solution where the pH is considerably lower than that of PC. The main hydration product, ettringite, can incorporate a number of ions into its crystal structure, making it an ideal candidate for waste immobilisation.

This paper details some results from a commercial C \bar{S} A system that examines aspects of mixing, hydration of different formulations and aluminium corrosion behaviour. The fluidity of mixes can be adjusted by changing the formulations. All designed mixes were set within 24 h with little bleeding and the pH values were in the range of 10–11.5. In addition, a significant reduction in Al corrosion was observed compared to a composite OPC system. Although these results provide encouragement for the idea that C \bar{S} A cement can provide a possible alternative to PC in the immobilisation of difficult and reactive wastes, further investigation is needed.

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1. Introduction

In the field of inorganic waste management, cement-based processes are widely used for both immobilisation and encapsulation as well as for stabilisation. Cementitious systems have many attributes which make them suitable for waste encapsulation and immobilisation [1], including:

- Readily acting as a barrier to the migration of ions.
- Incorporation of many ions into solid solution within hydrated calcium silicates.
- Low liquid and gas permeabilities in the hardened state.
- Relatively easy processing suitable for a remotely operated plant.
- Low price and ready availability.

While Portland Cement (PC) is widely used, composite cement systems where PC is combined with supplementary cementing materials (SCMs) are becoming increasingly popular. These include materials such as blast furnace slag (BFS) or pulverised fuel ash (PFA), which are also waste materials. These composite systems offer several advantages over PC alone, providing a lower heat of hydration and lower permeability as well as economic benefits.

In the nuclear industry, significant quantities of radioactive wastes are produced, both from fuel reprocessing and from the decommissioning of old nuclear stations. To ensure that these wastes are contained for storage and ultimate disposal, they are encapsulated or immobilised in monolithic waste forms. High-level waste (HLW), which is highly radioactive and self-heating, is vitrified. Waste with intermediate radioactivity and without heat generation (ILW) as well as low-level activity waste (LLW) are cemented, either in 500 l drums or larger steel containers for ease of handling. As these wastes are cast in large volume, very high levels of SCM replacements are used to avoid the problems associated with high heat output as the temperature rise

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can lead to thermal stresses and cracking. Cement formulations for cementing nuclear waste are subject to extremely tight standards which are very demanding as the cementation process is handled remotely. The cement grout, a slurry of cement powder and water, should have the following properties:

- High fluidity and a long working life before stiffening.
- Low free water content when hardened and bleed free.
- Controlled low heat of hydration to avoid excessive temperature rises.
- Known properties, such as thermal, mechanical and physical properties.
- Radiation stability.
- Acceptable chemical/physical compatibility with waste form.

While most current operational waste is now immobilised by vitrification or cementation, large amounts of historic wastes arising from older work associated with weapons research and early power generation remain stored in large silos or ponds. The challenge for the nuclear industry is to demonstrate that this waste can be treated for ultimate disposal.

Despite the widespread use of PC-based formulations for current nuclear waste operations, they are not suitable, or may produce inferior wasteforms, for all waste types. Many of the historic wastes contain reactive metals such as Mg and Al, formerly part of the fuel cladding. The high pH of the PC systems will corrode these metals, which generates hydrogen gas and can cause cracking as a result of the expansion of corrosion products. Some alternative cementing systems have different hydration chemistries that may be more suitable for encapsulating particular wastes. One of these is calcium sulfoaluminate (C \bar{S} A) cement.

C \bar{S} A cement was developed in the 1970s by calcining natural materials such as limestone, bauxite and clay together with gypsum or anhydrite at 1250–1350 °C, in a composition that produces calcium sulfoaluminate or yeelimite (3CaO·3Al₂O₃·CaSO₄). Depending on the raw materials, dicalcium silicate (belite) or an aluminate or ferrite phase may also be present. The yeelimite is used or activated with an addition of calcium sulfate, either as gypsum or anhydrite. C \bar{S} A cement has been extensively investigated and developed as a construction material in China for about 30 years [2] and is currently attracting a great deal of interest worldwide [3,4]. Its advantages include:

- *Reduced energy consumption during manufacturing.* The clinker is fired at temperatures that are up to 200 °C lower than those for PC and the resultant clinker is relatively soft, friable and easy to grind. Consequently, the whole manufacturing process results in considerable energy savings.
- *Low CO₂ emission during manufacturing.* According to calculations performed by Sharp et al. [5], up to 40% less carbon dioxide emission than in the production of PC is achievable due to a reduction in limestone utilisation.
- *Low alkalinity.* The pH of the pore solution lies between 10 and 11.5 due to the different hydration chemistry of C \bar{S} A as Ca(OH)₂ is not formed, unlike in PC systems. This property has provided an

advantage for making glass-fibre reinforced concrete (GRC) products [2]. The hydration products are mainly ettringite 3CaO·Al₂O₃·3CaSO₄·32H₂O, and alumina gel, Al₂O₃·nH₂O, but monosulfate, 3CaO·Al₂O₃·CaSO₄·12H₂O, can co-exist depending on the level of sulfate addition.

- *High-early strength development.* Under controlled conditions, which include the addition of gypsum/anhydrite, C \bar{S} A cement can achieve acceptable setting times and good strength development in a shorter time frame than PC systems [2].
- Very good durability under normal service conditions; particularly in marine construction [6].

Ettringite, the main hydration phase of C \bar{S} A cement, normally crystallizes as prismatic needles, laths or prisms. The crystal structure of ettringite consists of columns and channels running parallel to the hexagonal prisms (*c*-axis) with SO₄²⁻ groups and H₂O molecules lying in the channels [7,8]. Several studies [9,10] have shown that ettringite can act as a host to a number of ions in both the columnar and channel sections of the crystal structure with substitution at the calcium, aluminium, hydroxide and sulfate sites. These results along with its low pH and moderate rate of hydration, means that C \bar{S} A cement offers a potential alternative to PC for applications where waste immobilisation is required, such as for nuclear wastes.

There is still a limited understanding of how the C \bar{S} A cement system functions compared to that of PC. Aspects of the chemistry, microstructure and physical properties of the hydration products, as well as the mechanism by which the waste ions can be incorporated in the structure, and the durability of the phases produced have yet to be determined. This paper reports some of the preliminary results from a study being carried out at the Immobilisation Science Laboratory (ISL), Sheffield, UK. This study aims to examine the potential of this system for waste immobilisation as well as the mixing properties, hydration products and corrosion of aluminium metal within a commercial C \bar{S} A cementing system.

2. Experimental

2.1. Materials

A commercial C \bar{S} A product, Rockfast 450, was provided by Lafarge Cement UK. The chemical analysis and compound composition supplied for the clinker are shown in Table 1. The specific surface area was 450 m²/kg with a specific gravity of 2.7 g/cm³. Unlike OPC, the product is C₃S and C₂S free but it does contain 15% monocalcium aluminate.

The ground clinker was activated by mixing with different proportions of anhydrite (CaSO₄), supplied by Chance & Hunt Limited UK.

2.2. Mix formulations and curing

Based on theoretical calculations, 31.2 wt.% anhydrite is needed at a w/s ratio of 0.67 in order to ensure the complete hydration and reaction of the Rockfast clinker. Various ratios of

Table 1
Chemical and compound composition of Rockfast clinker (wt.%)

	Chemical composition (wt.%)
SiO ₂	3.6
Al ₂ O ₃	47.4
Fe ₂ O ₃	1.4
CaO	38.0
MgO	0.3
SO ₃	7.5
TiO ₂	2.2
K ₂ O	0.16
LOI	0.3
Free lime	0.3
	Compound composition (wt.%)
3CaO·3Al ₂ O ₃ ·CaSO ₄	57
CaO·Al ₂ O ₃	15
12CaO·7Al ₂ O ₇	1
CaSO ₄	0.5
2CaO·Al ₂ O ₃ ·SiO ₂	16
4CaO ₄ ·Al ₂ O ₃ ·Fe ₂ O ₃	4
CaO·TiO ₂	4
Free CaO	0.3
2CaO·SiO ₂	0
3CaO·SiO ₂	0

anhydrite and Rockfast were mixed at different water/solid (w/s) ratios around this theoretical value. The range of formulations is given in Table 2.

Weighed amounts of Rockfast and anhydrite were added to water at room temperature and blended. After mixing for 20 min, the fluidity was measured using a Colflow apparatus. This piece of equipment measures the distance that 1 l of slurry will flow in a confined channel under gravity.

pH and temperature rise during mixing were measured using close range pH paper and a thermometer. These measurements were repeated at 60, 90 and 120 min and then every 30 min until the cement fluidity reading was zero. Eighty to 100 g portions of grout were transferred to 50 ml sealed centrifuge tubes and stored in environmental chambers at 20 and 60 °C, 95% relative humidity (RH) for 1, 3, 7 and 28 days to determine the phases formed. At appropriate ages, samples were removed, crushed and dried in a vacuum to inhibit further hydration prior to further analysis.

Bleed volumes were measured by sealing the grout in a 100 ml measuring cylinder and measuring the amount of water that collected on the surface of the hardened material after 24 h. This is

Table 2
Mix design of Rockfast with anhydrite system

Rockfast/anhydrite (wt.%)	Water/solid ratio	Number of samples
65/35	0.75, 0.67, 0.60	3
70/30	0.75, 0.67, 0.60	3
75/25	0.75, 0.67, 0.60	3
80/20	0.75, 0.67, 0.60	3
Total		12

an important parameter because bleed liquid, if not reabsorbed, forms a secondary waste that must be treated.

2.3. X-ray diffraction (XRD) analysis

To avoid destroying the ettringite structure, the dried samples were lightly ground to pass a 63 μm sieve using an agate mortar and pestle. This is not fine enough to avoid possible problems due to preferred orientation of platy crystals but was used as a compromise in order to avoid degrading the ettringite. A Philips X-ray diffractometer with monochromatic Cu Kα radiation was operated at a voltage of 50 kV and a current of 30 mA. A scanning speed of 2° 2θ/min with a step size of 0.02° were used to examine the samples over the range of 5–65° 2θ.

2.4. Thermogravimetric analysis

Thermogravimetric analysis was conducted on selected samples using a Perkin Elmer Pyris 1 thermogravimetric analyser under flowing N₂ atmosphere, at a heating rate of 10 °C/min from room temperature to 1000 °C. The weight loss with increasing temperature was analysed using the Pyris Manager software.

2.5. Scanning electron microscopy (SEM)

Selected samples were mounted in a cold setting epoxy resin and evacuated for 10 min to reduce bubbles in the resin. Once set, the samples were removed and ground using SiC wheels of 120, 240, 400, 600 and 1200 grit progressively, and then polished using 6, 3 and 1.25 μm diamond pastes. The samples were carbon coated prior to examination in a CCCU1 carbon coater and examined in a JEOL JSM 6400 SEM using backscattered imaging modes. The high water content of the ettringite created problems because under the high vacuum and electron beam energy of the SEM, dehydration occurred as the samples took a long time to achieve the required vacuum degree. This is likely to degrade the quality of images recorded. All analysis was conducted using a Be window in the microscope which restricted analysis of the lighter elements. Link ISIS software was used to evaluate the data from the energy dispersive spectroscopy EDX detector.

2.6. Aluminium corrosion trials

Al metal rods (~4 cm long, Grade 1050, 99.5% Al) were embedded in C₃A (Rockfast/anhydrite = 75/25, w/s = 0.67) and PC/BFS (BFS/PC = 9/1, w/s = 0.33) systems. The C₃A formulation was selected due to its high initial fluidity, low temperature rise during mixing and similarity to the theoretical formulation for complete reaction. The PC/BFS system that was used is one of the commonly used formulations for nuclear waste immobilisation. Both sets of samples were placed in sealed containers inside sealed plastic bags to avoid water/moisture escape during the curing process at 60 °C and 95% RH. Samples were examined after curing for 1, 3, 7, 28 and will be at 365 days. Results up to 28 days are shown in this paper but the samples are still being monitored.

3. Results

3.1. Mixing properties

The fluidities of the different formulations are shown in Fig. 1. Thousand millimetres was the maximum readable fluidity, all data greater than that are reported as 1000 mm in Fig. 1. At $w/s = 0.75$ (Fig. 1a), the fluidity increased with the decreasing content of anhydrite. At $w/s = 0.67$ (Fig. 1b), the same trend was generally observed, but the fluidity decreased more rapidly at early stages compared with that at $w/s = 0.75$ while at $w/s = 0.60$, the decrease was even more rapid (Fig. 1c). All mixes set within 24 h with little bleeding and it is anticipated that zero bleed would be observed at full process scale. These results show that the initial fluidity and stiffening time of the Rockfast/anhydrite system can be adjusted by changing the w/s ratio and amount of anhydrite added.

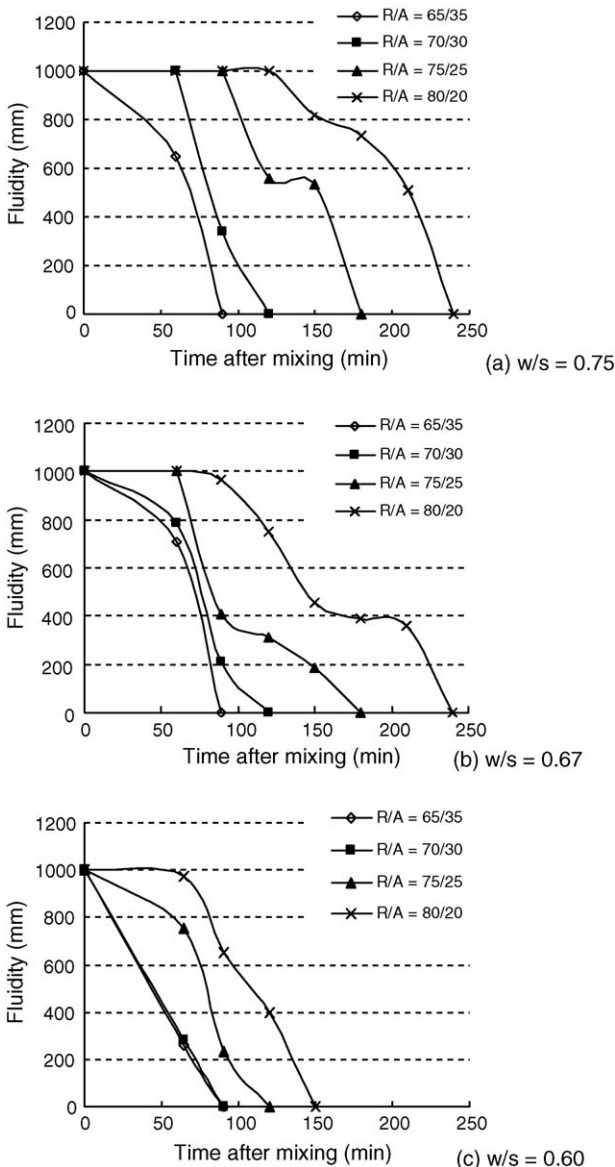


Fig. 1. Fluidity of different formulations: (a) at $w/s = 0.75$, (b) at $w/s = 0.67$, (c) at $w/s = 0.60$.

Table 3

Temperature increase at the end of mix periods and bleeding at 24 h for different mixes at $w/s = 0.67$

Rockfast/anhydrite (wt.%)	ΔT ($^{\circ}C$)	Bleeding (ml/100 ml grout)
63/35	4.0	0.2
70/30	7.4	0.1
75/25	3.4	0.2
80/20	4.4	0.0

For all three w/s ratios, the recorded temperature rise increased with time after initial mixing. Temperature increases and bleed results are summarised in Table 3.

The pH values measured for all mixes over time were around 11, which is about 2 units lower than that of a pure PC system.

3.2. X-ray diffraction (XRD) analysis

XRD was used to identify the hydration phases for the various formulations. Based on the theoretical calculation and mixing performance results, a formulation of $R/A = 75/25$, $w/s = 0.67$ at $20^{\circ}C$ was selected for presentation. Fig. 2 shows the XRD traces at various ages for this sample with the results for the other formulations tabulated in Table 4. Phases are marked as uncertain if less than three major phase peaks could be identified. This uncertainty is due to low peak intensity or overlapping peaks. Due to preferred orientation, the intensity of the ettringite peaks can vary between samples, which makes quantitative analysis difficult. Backpacking of sample with a smaller particle size might reduce the preferred orientation, but an internal standard would be needed for a semi-quantitative analysis.

Ettringite was well formed after 1 day and the amount increased with hydration time. After 1 day, some unreacted yeelimite remained but this was consumed within 7 days. Gehlenite, $2CaO \cdot Al_2O_3 \cdot SiO_2$, from the clinker was present and appears to remain inert during hydration up to 28 days. Unreacted anhydrite remained after 28 days. Formulations which contained higher amounts of anhydrite than the theoretical value ($R/A = 65/35$)

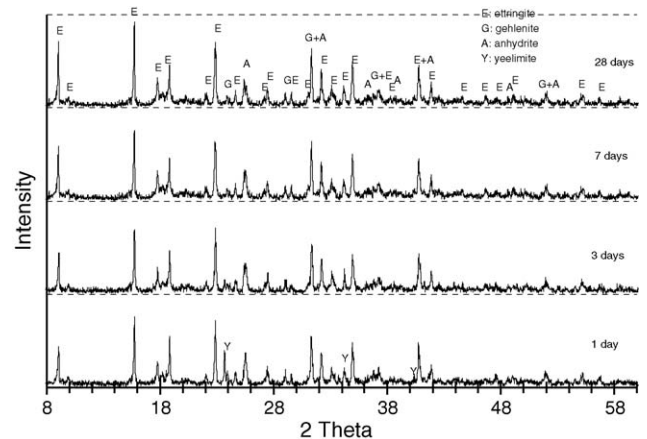


Fig. 2. XRD traces of phases after 1, 3, 7 and 28 days hydration: $R/A = 75/25$, $w/s = 0.67$ at $20^{\circ}C$.

Table 4
Phases identified by XRD in the hydrated Rockfast at $w/s=0.67$

	Ettringite	Anhydrite	Yeelimite	Gibbsite	Monosulfate
R/A = 65/35					
1 d 20 °C	✓	✓			
1 d 60 °C	✓	✓			
3 d 20 °C	✓	✓			
3 d 60 °C	✓	✓			
7 d 20 °C	✓	✓			
7 d 60 °C	✓	✓			
28 d 20 °C	✓	✓			
28 d 60 °C	✓	✓		✓	
R/A = 70/30					
1 d 20 °C	✓	✓	?		
1 d 60 °C	✓	✓			
3 d 20 °C	✓	✓	?		
3 d 60 °C	✓	✓			
7 d 20 °C	✓	✓	?		
7 d 60 °C	✓	✓			
28 d 20 °C	✓	✓			
28 d 60 °C	✓	✓			
R/A = 75/25					
1 d 20 °C	✓	✓	✓		
1 d 60 °C	✓	✓	?	?	
3 d 20 °C	✓	✓	?		
3 d 60 °C	✓	✓	?		
7 d 20 °C	✓	✓			
7 d 60 °C	✓	✓			
28 d 20 °C	✓	✓			
28 d 60 °C	✓	✓		?	
R/A=80/20					
1 d 20 °C	✓	✓	✓		
1 d 60 °C	✓	✓		?	
3 d 20 °C	✓	✓	✓		
3 d 60 °C	✓	✓	?		
7 d 20 °C	✓	✓	✓		
7 d 60 °C	✓	✓			
28 d 20 °C	✓	✓		?	✓
28 d 60 °C	✓	✓		?	✓

Note: ✓ means phase identified, ? means phase uncertain, blank means phase not identified.

showed similar results but with an increased amount of anhydrite remaining, even at later ages.

When a high ratio of Rockfast ($R/A = 80/20$) was used, unreacted yeelimite along with monosulfate were identified because insufficient anhydrite was available to react with the yeelimite to form ettringite. Monosulfate was only observed after 28 days of curing. This is because ettringite formation occurs within hours, much faster than that of monosulfate formation, which can take days or even months [11]. As the hydration progresses, the concentration of available sulfate is reduced, which leads to the formation of monosulfate. While amorphous $Al(OH)_3$ forms below 40 °C, curing at 60 °C gives rise to gibbsite.

3.3. Thermogravimetric analysis

Since XRD can only identify crystalline phases and not poorly crystalline or amorphous phases, TGA-DTG was used to detect any other phases present. Again, the formulation $R/A = 75/25$, $w/s=0.67$ hydrated at 20 °C was used and the

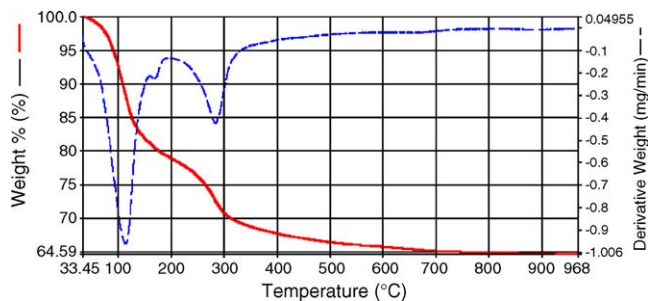


Fig. 3. TGA-DTA curves of Rockfast/anhydrite = 75/25, $w/s=0.67$ cured at 20 °C for 7 days, with a heating rate of 10 °C/min under N_2 atmosphere.

TGA-DTG curves for 7 days hydration are presented in Fig. 3. By this time, the reaction is mostly complete. There were three distinct stages of weight loss corresponding to the three peaks in the DTG curve at 113, 169 and 283 °C. The first weight loss of 18.8% of the initial mass corresponds to the decomposition of ettringite [12]. The second, with 2.1% weight loss at 169 °C, corresponds to the water loss from gypsum [13], which was confirmed by running a reference sample of gypsum under the same conditions. Crystalline gypsum was not detected by XRD suggesting it may be poorly ordered or below the level at which it can be detected. The third, with 10.0% loss at a peak temperature of 283 °C, corresponds to water loss from the alumina gel [14].

3.4. Scanning electronic microscopy (SEM)

Fig. 4 shows a typical backscattered electron image and EDX analysis of the formulation Rockfast/anhydrite = 75/25, $w/s=0.67$, hydrated for 7 days at 20 °C. Unhydrated clinker grains (spot 1, which contains a small peak of Ti from clinker) are surrounded by a layer of gel-like hydration products (spot 2). This product probably consists of partially crystallised ettringite and aluminium hydroxide as well as anhydrite as there is slightly higher S present. There is a clearly defined zone of crystalline hydration products outside this layer. Prismatic-shaped ettringite crystals are visible (spot 3) with lengths around 10 μm forming an interlocking network, which grows around the cement particles. This zone contains a high proportion of Al suggesting that as ettringite crystallised, the alumina gel formed around it.

Fig. 5 shows the same formulation cured at 60 °C for 7 days. The smaller size of unreacted clinker indicates that more rapid hydration has occurred at 60 °C. No clear gel-like hydration zone is present but larger ettringite crystals (with length around 15–20 μm) have formed suggesting rapid growth.

3.5. Aluminium corrosion trials

The corrosion behaviour of BFS/PC and Rockfast C \bar{S} A cements was compared by running parallel experiments of the two systems with embedded aluminium rods. After 1 day, significant corrosion had occurred in the BFS/PC sample. A hole, marked with a circle in Fig. 6, formed at the top of the BFS/PC sample due to the release of hydrogen from aluminium corrosion (the cracks were caused by breaking the sample to observe corrosion). Fig. 7 compares the two systems at 1, 7, and 28 days.

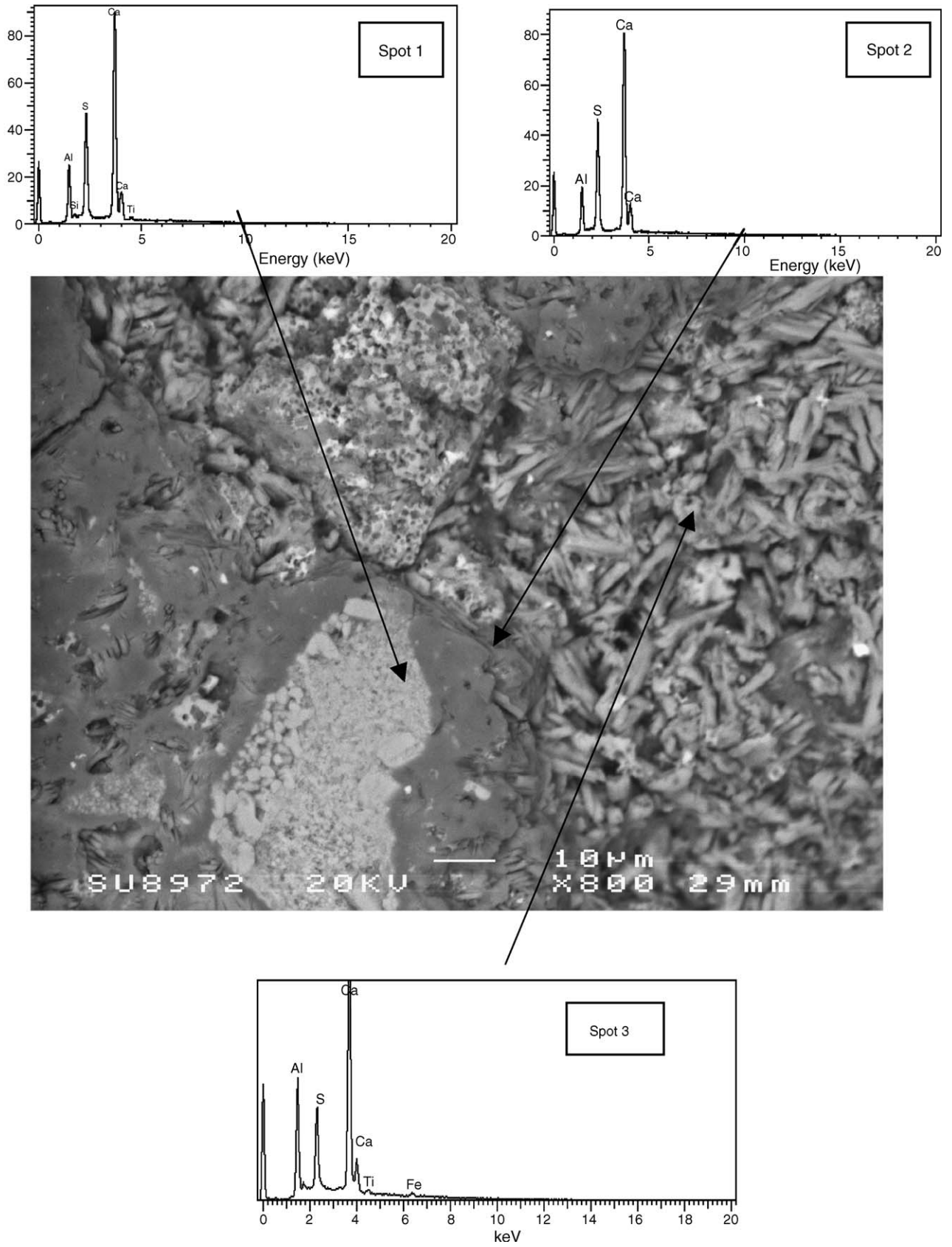


Fig. 4. BSE image and EDX analysis of Rockfast/anhydrite = 75/25, w/s=0.67 curing at 20°C for 7 days.

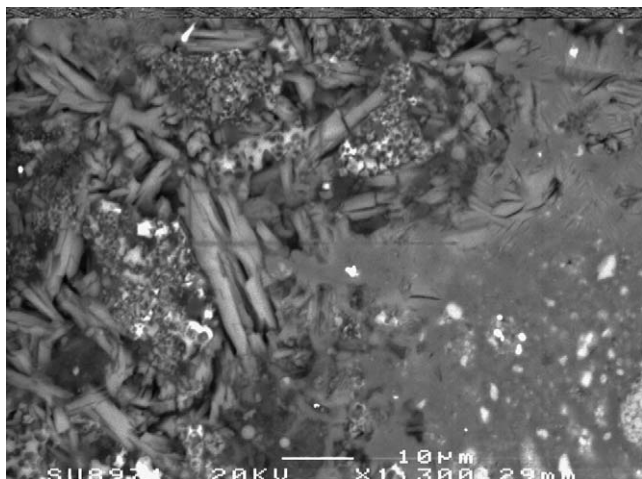


Fig. 5. BSE image of Rockfast/anhydrite = 75/25, w/s = 0.67 curing at 60 °C for 7 days.

A layer of yellow/pink corrosion products formed on the surface of the aluminium in the BFS/PC system. Microvoidage around the aluminium rod was observed as well as a pathway for gas release to the surface. The top surface of the paste was also covered with a yellow/pink layer (~2 mm), which is possibly consists of the same corrosion products drawn to the top by the escaping hydrogen. After 7 days, the corrosion process had continued with more corrosion products formed, but the colour of the corrosion products changed from yellow/pink to grey while the colour of the paste had changed from dark grey to light grey. The reasons for these colour changes are not clear, but are probably due to oxidation of the reduced sulfur species present in the slag and carbonation after the sample was crushed and exposed to the atmosphere. Little change was observed after 28 days. An ongoing investigation [15] has shown that during the corrosion of aluminium within the BFS/PC system, the hydroxy aluminium species migrate and participate in the calcium silicate hydration forming strätlingite $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot 8\text{H}_2\text{O}$, i.e. soluble aluminium becomes incorporated in the cement binder.



Fig. 6. Hole formed on the top surface of BFS/PC system after 1 day (the cracks were caused by breaking the sample to observe corrosion).

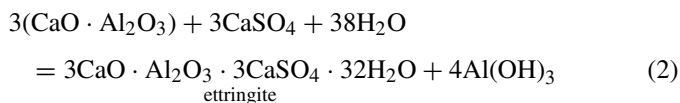
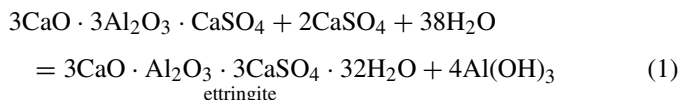
In comparison, aluminium corrosion in the Rockfast/anhydrite system up to 28 days was highly limited. There was a slight initial change on the surface of the aluminium rod: as it was not as shiny as it was initially after 1 day but little further visual change was observed with time. The colour of the paste also changed from light yellow to grey, which was probably due to changes in the coordination of the iron phases and/or carbonation. The reduced pH in the C \bar{S} A system may mean that the aluminium becomes protected with a layer of aluminium hydroxide but further studies are needed to confirm this. Work is being conducted using the Synchrotron Radiation Source at Daresbury Laboratory to elucidate the nature of the corrosion layer.

4. Discussion

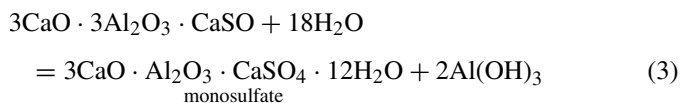
4.1. Hydration

The hydration of a commercial C \bar{S} A/anhydrite mix leads to the rapid formation of ettringite in the set cement. Depending on the amount of anhydrite added and whether or not $\text{Ca}(\text{OH})_2$ is present, the possible reactions can be summarised as follows [16].

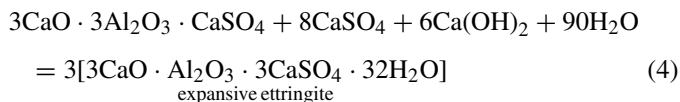
If there is sufficient CaSO_4 present, reactions (1) and (2), which do not result in expansion [17–19], occur:



If there is insufficient CaSO_4 present, then a third reaction (3) can occur where monosulfate is formed directly from yeelimite but this reaction is slow:



Previous studies [20,21] have indicated that if excess calcium hydroxide was present along with excess sulfate, yet a fourth reaction (4) could occur giving a higher yield of ettringite. It is this reaction that occurs with PC and normally causes expansion, so it is used for shrinkage compensation:



Under the current experimental conditions, which have been conducted at close to optimum, ettringite is the main hydration phase from all formulations. Monosulfate was only observed at longer curing time with a low anhydrite ratio (R/A = 80/20, 28 days) where it formed according to Eq. (3) and co-existed

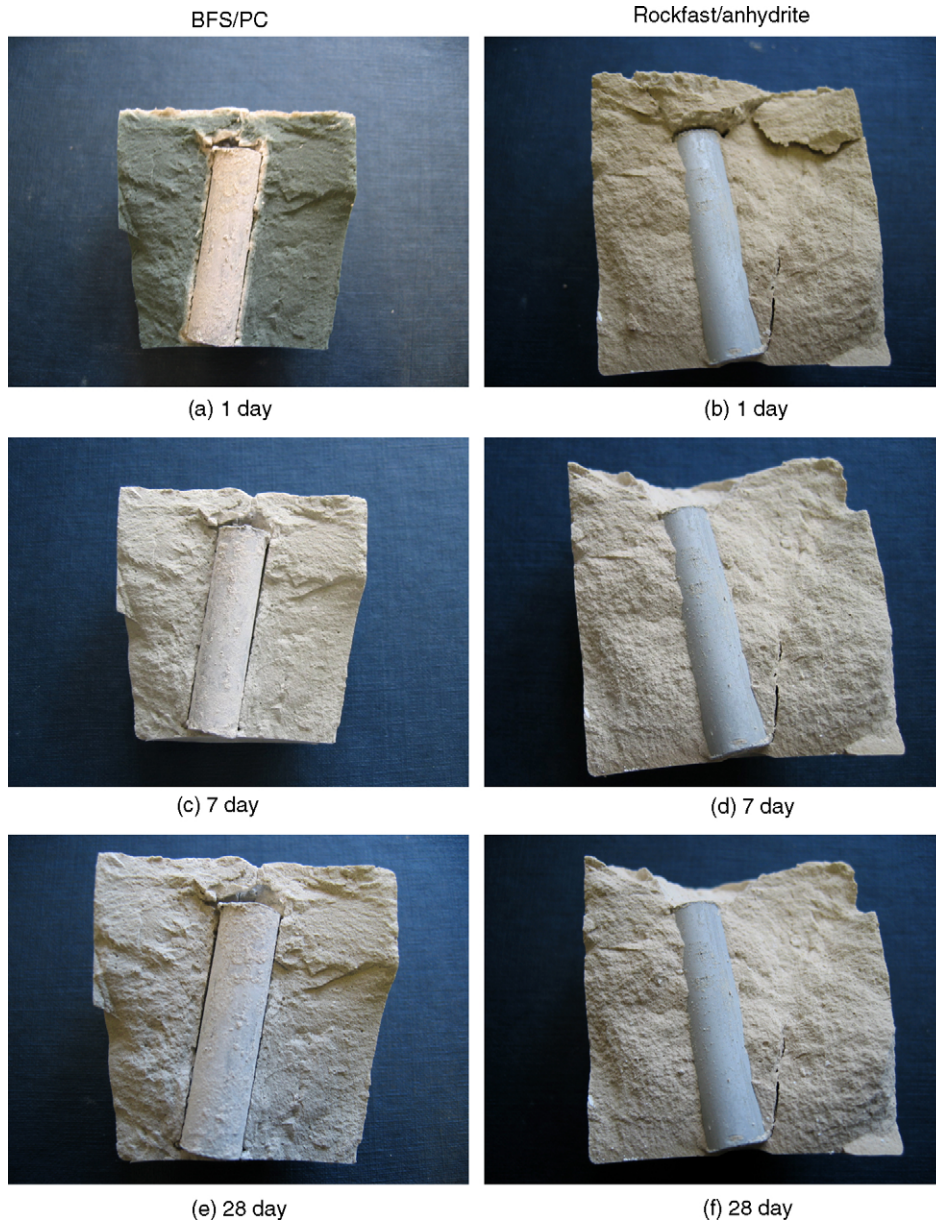


Fig. 7. Visual observation of Al corrosion: BFS/PC and Rockfast/anhydrite systems at 1, 7 and 28 days. (For interpretation of the references to colour, the reader is referred to the web version of the article.)

with ettringite. This is in line with calculations and hydration phase compositions of a commercial C₃A blended with varying amounts of gypsum [6].

The aluminium hydroxide formed is amorphous in most cases [22], but crystallises to gibbsite after extended curing and/or at elevated temperatures. Unreacted yeelimite was observed at low temperatures and early ages if the Rockfast/anhydrite ratio was high. DTG confirms that a small amount of gypsum, not identified by XRD, formed when excess anhydrite was present.

SEM images show that hydrated phases grow from the clinker grain surfaces forming an initial layer of gel-like hydration products. Well-formed prismatic-shaped ettringite crystals grow outside this layer and generate a network which engulfs the cement particles. Curing at higher temperature (60 °C) not only

increases the rate of hydration but produces bigger ettringite crystals and crystalline aluminium hydroxide.

4.2. Mixing performance

By controlling the amount of sulfate added as well as the w/s ratio, fluidities greater than those found for PC systems can be achieved for up to 150 min. However, once hydration starts, the fluidity drops off rapidly. In general, the more sulfate is added, the quicker the grout sets and the fluidity decreases.

The temperature rises observed during hydration for the formulations used in this study are greater during the early hydration stage than that for PC, but the rate of heat evolution depends on clinker components. The Rockfast clinker contains a significant amount of monocalcium aluminate, which hydrates rapidly

resulting in this temperature rise. In the large volumes of cement grout used in routine cementing operations of nuclear wastes, this rapid heat output will give rise to a high temperature in the centre of the grout. Introduction of BFS or PFA, which provide silicates, may be a potential way to lower the hydration temperature but this assumption needs to be tested.

Ettringite is generally regarded as thermally unstable so its thermal stability under high temperature is of concern. While detailed studies [23,24] can predict its thermal performance under service conditions, confirmatory studies on the thermal properties of C \bar{S} A cement will be required to understand the long-term phase durability.

The crystal structure of ettringite contains 32 molecules of water. This large amount of ‘bound’ water has several advantages. High fluidity grouts are needed for immobilisation of the complex shapes which arise from cut up metal in the historic nuclear wastes. This can be obtained by using the C \bar{S} A system with high w/s ratios but the water becomes quickly bound and does not lead to bleeding where unreacted water seeps to the surface.

4.3. Corrosion

The binding of a large amount of water into the ettringite structure is likely to lead to self-desiccation, lowering the internal humidity and reducing ongoing corrosion problems [6]. In addition, unlike PC systems, calcium hydroxide is not a hydration product of C \bar{S} A cement, so the pH of the system remains low. The C \bar{S} A cement system studied here clearly shows a significant improvement in reducing aluminium corrosion up to 28 days compared to the PC system even at an elevated curing temperature of 60 °C. Whether it is the low internal RH or the lowered pH (or a combination of both) that leads to reduced corrosion is unclear at this stage. However, this observation is very encouraging and warrants further work.

5. Conclusions and future work

Calcium sulfoaluminate cement is a new cement system which combines economy of cost, low CO₂ emission with rapid strength gain and compatibility with other construction materials and it offers a different hydration chemistry. The internal pore solution pH is low and the main hydration product, ettringite, binds large amounts of water. These unique properties make it a potential candidate for the immobilisation of wastes that contain reactive metals.

The preliminary results from this ongoing study show that:

- High fluidity grout can be prepared from the C \bar{S} A/anhydrite system which can be adjusted by changing the w/s ratio and the amount of anhydrite added.
- Despite the high w/s ratios used, bleeding is normally low as ettringite formation rapidly binds the water.
- Ettringite and aluminium hydroxide are the main hydration products and lead to a moderate internal pH ~ 11.
- The corrosion of aluminium metal within the C \bar{S} A/anhydrite system is markedly reduced compared with that of the

BFS/PC system, even at an elevated curing temperature and high humidity.

An optimised formulation (R/A = 75/25, w/s = 0.67) based on the theoretical calculation and mixing performance has been used to illustrate the results presented in this paper, which are encouraging for use in waste immobilisation. However, in order to define the formulation envelope required for nuclear waste immobilisation, more research must be conducted to obtain the letter of compliance needed for its acceptance. These studies should include:

- Long-term aluminium corrosion behaviour monitoring to provide a corrosion mechanism, which may also explain the corrosion behaviour of other metals.
- Developing methods to reduce or control the temperature rise during hydration.
- Better understanding of hydration chemistry, phase formation and equilibrium between the different phases.
- Understanding the incorporation mechanism of wastes.
- Long term stability of C \bar{S} A cementing system with waste ions immobilised.
- Field trials to test practical applications on a large scale.

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