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Interaction between $BaCO_3$ and OPC/BFS composite cements at 20 °C and 60 °C

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ABSTRACT

A $BaCO_3$ slurry, containing radioactive ^{14}C, is produced during the reprocessing of spent nuclear fuel. This slurry is encapsulated in a Portland-blastfurnace slag composite cement. The effect of $BaCO_3$ on the hydration of OPC and Portland-blastfurnace slag cements has been studied in this work. Samples containing a simulant $BaCO_3$ slurry were cured for up to 720 days at 20 and 60 °C and analysed by XRD, SEM(EDX) and ICC. $BaCO_3$ reacted with OPC to precipitate $BaSO_4$ from a reaction between soluble sulfate and $BaCO_3$. Calcium monocarboaluminate subsequently formed from the carbonate released. The monocarboaluminate precipitated as crystals in voids formed during hydration. At 60 °C in OPC, it was not identified by XRD, suggesting the phase is unstable in this system around this temperature. In the Portland-blastfurnace slag cements containing $BaCO_3$, less monocarboaluminate and $BaSO_4$ were formed, but the hydration of BFS was promoted and monocarboaluminate was stable up to 60 °C.

1. Introduction

A radioactive ^{14}C containing slurry of $BaCO_3$, is produced from nuclear fuel reprocessing at the Thermal Oxide Reprocessing Plant (THORP) at Sellafield, UK. This slurry is classified as an intermediate level waste (ILW), and is typically encapsulated in a 9:1 blast furnace slag: Ordinary Portland cement (BFS:OPC) blended system. To fully understand the interactions within this ternary composite cement, the interactions between this system, neat OPC and $BaCO_3$ were studied.

^{14}C is an important radioactive element to consider in a waste stream, as it has a long half life (5730 years) and will actively combine with other elements within its environment replacing stable $^{12,13}C$ [1], making the species mobile, and a challenge to immobilise. Gases released during the THORP process, where spent uranium oxide fuel is dissolved in nitric acid, include $^{14}CO_2$ and ^{14}CO. These gases are passed through a caustic scrubber to remove any $^{14}CO_2$ and ^{14}CO forming sodium carbonate. The resulting solution is treated with $Ba(NO_3)_2$, precipitating $Ba^{14}CO_3$, which is allowed to settle, forming a waste slurry which is dewatered to give a final waste stream containing 20–30 wt.% $Ba^{14}CO_3$ precipitate in a solution of 10 wt.% soluble salts [2].

Literature published on the interactions between OPC based systems and $BaCO_3$ is limited, but there is extensive literature on the reactions between calcium carbonate ($CaCO_3$) and OPC, where $CaCO_3$ is used as a filler material [3–9]. Filler materials are inert or mildly reactive materials which replace a proportion of the cement to reduce costs and improve physical properties [10]. $CaCO_3$ is often used in the construction industry with up to 5% limestone filler incorporated in Portland cement without formally declaring its presence [11]. Limestone is often used as an aggregate in concrete, but normally only the very fine material reacts. Studies of $CaCO_3$ additions are useful when comparing the addition of $BaCO_3$.

Barium is in Group II of the periodic table, below calcium and strontium and is the largest and most electropositive, which influences its substitution reactions. The difference in solubility between the carbonates, hydroxides and sulfates of the Group II elements (Table 1) will affect reactions. It is interesting to note that barium sulfate is less soluble than barium carbonate, whereas all forms of calcium sulfate are more soluble than calcium carbonate. Both calcium and strontium readily form or substitute into AFt/AFm type phases. However barium, being a much larger cation, is reported to not form a fully substituted AFt phase [12]. Dumitru et al. [13,14] also reported only partial substitution of barium into an AFm calcium monocarboaluminate phase, using EDX analysis. The CO_3^{2-} ion once released into the solution is expected to react in the same manner, within the cement environment, regardless of its source.

The addition of $CaCO_3$ to OPC changes both the hydration products formed and the rate of the hydration reactions. In OPC hydrated with $CaCO_3$, an AFm phase, calcium monocarboaluminate, $Ca_4Al_2(CO_3)(OH)_{12}\cdot 5H_2O$ (Mc), forms through a reaction between $Ca_3Al_2O_6$ (C_3A) and $CaCO_3$ [3,10]. Monocarboaluminate forms instead of monosulfate, which has the effect of stabilising ettringite (Al/S ratio stays high). It is also reported that a hemicarboaluminate phase, $(Ca_4Al_2(CO_3)_{0.5}(OH)_{13}\cdot 5.5H_2O)$, precedes the formation of Mc, where the activity of the carbonate is low [7,9,16].

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Table 1
Solubility of selected calcium, strontium and barium compounds at 20–25 °C [15].

Chemical	Solubility$^{(temp.\ °C)}$ g/100 cc H_2O
$Ca(OH)_2$	0.160^{20}
$CaCO_3$	0.00066^{20}
$CaSO_4.2H_2O$	0.205^{20}
$Sr(OH)_2$	2.25^{25}
$SrCO_3$	0.00034^{20}
$SrSO_4$	0.0135^{25}
$Ba(OH)_2.8H_2O$	4.91^{25}
$BaCO_3$	0.0014^{20}
$BaSO_4$	0.00031^{20}

Table 2
Chemical analysis (XRF) of OPC and BFS.

Chemical analysis	OPC, wt.%	BFS, wt.%
CaO	64.58	42.1
SiO_2	20.96	34.5
Al_2O_3	5.24	13.74
Fe_2O_3	2.61	0.97
MgO	2.09	7.29
SO_3	2.46	–
K_2O	0.59	0.49
Na_2O	0.28	0.22
Chloride	0.048	0.022
Insolubles	0.27	–
Loss on ignition	0.73	−1.05

Mc is an AFm phase, analogous to monosulfate, where SO_4^{2-} ions are replaced by CO_3^{2-} ions [10]. Although there is an equivalent carbonate phase to ettringite with the general formula $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$, known as calcium tricarboaluminate, this phase does not form in cements with carbonate additions as, of the two carbonate AFt/AFm phases, Mc is the more stable phase with a greater insolubility at ambient temperatures [3,17].

Typically only a maximum of 2–3 wt.% $CaCO_3$ reacts with OPC at ambient temperatures [10]. Additions of less than 5 wt.% $CaCO_3$ have been found to accelerate initial hydration and decrease porosity [7] as well as increasing early strength [18,19]. Higher additions of greater than 10–15 wt.% were found to increase porosity and decrease the compressive strength [8].

Limited studies on the addition of barium carbonate, or soluble barium salts to OPC have been reported. The reaction of $BaCO_3$ with C_3A and OPC is similar to that of $CaCO_3$. Dumitru et al. [13,14] reported that $BaCO_3$ delays the hydration of C_3A, forming a hemicarboaluminate phase containing 6 wt.% of barium (determined by EDX). Reacting OPC and $BaCO_3$ resulted in the formation of monocarboaluminate and large quantities of $BaSO_4$, from the reaction between gypsum and $BaCO_3$. Ettringite formation was also suppressed, with setting times prolonged, in proportion to the amount of $BaCO_3$ added. The addition of barium as a soluble salt, such as barium nitrate, also resulted in the precipitation of $BaSO_4$ and $BaCO_3$ [20]. It was suggested that the presence of large quantities of insoluble compounds hinders OPC hydration resulting in lower non-evaporable water contents and a greater proportion of anhydrous OPC [21].

In practice, the radioactive waste $Ba^{14}CO_3$ slurry is mixed with a BFS:OPC composite cement, forming a complex ternary system. Mendéndez et al. [22] reported the strength development of a ternary blended cement system containing OPC, between 0% and 35% BFS and between 0% and 15% $CaCO_3$. $CaCO_3$ improved the early strength while BFS improved later strength and refined the pore system. The ternary systems therefore offered an improvement in strength properties over binary cements of either combination. But, a limit exists as adding vast quantities of filler material will negate these effects, decreasing the overall strength due to cement dilution [2].

In this paper the effect of a simulated ^{14}C containing waste slurry, in the form of $BaCO_3$ dispersed in distilled water, on the hydration of OPC and a 9:1 BFS:OPC composite cement, is presented, alongside a simplified system containing C_3A, $CaSO_4.2H_2O$ and $BaCO_3$.

2. Materials and experimental procedure

2.1. Raw materials

OPC (Castle Cements) used had a fineness of 352 m^2/kg Blaine. The BFS (Redcar steel works) was a coarsely ground granulated blast furnace slag, with a fineness of 286 m^2/kg Blaine. Oxide compositions of these materials are presented in Table 2. A coarse ground BFS is used for waste encapsulation to minimise heat of hydration, which may result in thermal cracking. A simulated waste slurry was prepared by mixing analytical grade $BaCO_3$ (Sigma Aldrich) with distilled water, in a high shear mixer. Although the actual waste produced at THORP also contains soluble salts in the solution, these compounds were omitted to simplify the system and purely assess the effect of $BaCO_3$ alone on hydration. It is understood that the presence of soluble salts could effect hydration, with likely acceleration of reactions.

2.2. Sample preparation

Neat OPC and 9:1 BFS:OPC systems were mixed in a Hobart mixer with a water to solid ratio (w/s) of 0.37 and cured at 20 °C and 60 °C at 95% RH for up to 720 days. 30 wt.% $BaCO_3$ by solid replacement was added to these systems. Hydration was stopped at specific times by quenching the samples in acetone for 3 days followed by drying under vacuum. Microstructure and phases formed were studied using scanning electron microscopy (SEM/EDX), X-ray diffraction (XRD) and early hydration (up to 72 h) using isothermal conduction calorimetry (ICC).

Laboratory synthesised C_3A, $CaSO_4.2H_2O$ and $BaCO_3$ were mixed by hand with a molar ratio of 1:1:1 in an excess of distilled water (approximately 10:1 w/s) to form a slurry under a nitrogen blanket, to minimise carbonation. The slurry was mixed continuously for up to 24 h. A sample was taken at 2 and 24 h, and then vacuum filtered, washed and dried over silica gel, for analysis of the precipitates.

Powdered samples (passing 63 μm) for XRD were scanned either between 5 and 65° 2θ at 2 ° 2θ/min, or between 5 and 25° 2θ at 0.5° 2θ/min, using a Siemens D500 diffractometer with CuKα radiation set at 30 kV/40 mA. SEM(EDX) was performed at the Laboratory of Construction Materials at the Ecole Polytechnique Fédérale de Lausanne (EPFL) using a FEI quanta 200 ESEM, with a SiLi EDS detector from PGT . Samples were prepared by mounting in a cold set resin and polished to ¼ μm in a diamond spray and carbon coated. Quantitative analyses were performed using external standard mineral calibration. All micrographs presented were taken using the backscattered electron imaging (BSEI) mode.

Isothermal conduction calorimetry (ICC) was performed at 25 °C, 40 °C and 60 °C using a Wexham Developments JAF Calorimeter. 15 g of powder was mixed with the required volume of distilled water and placed in a sealed plastic bag in the ICC cells, and the rate of heat evolution measured for up to 72 h.

3. Results

3.1. Phase analysis

3.1.1. OPC with $BaCO_3$

On addition of $BaCO_3$ to OPC, the hydration products identified at 20 °C were calcium hydroxide, ettringite and calcium monocarboaluminate (Mc) (Fig. 1). $CaCO_3$ may form, however was not identified using XRD. This may be a consequence of overlapping peaks from $BaCO_3$ and $BaSO_4$. $BaSO_4$ was formed from a reaction between $BaCO_3$ and SO_4^{2-} ions from

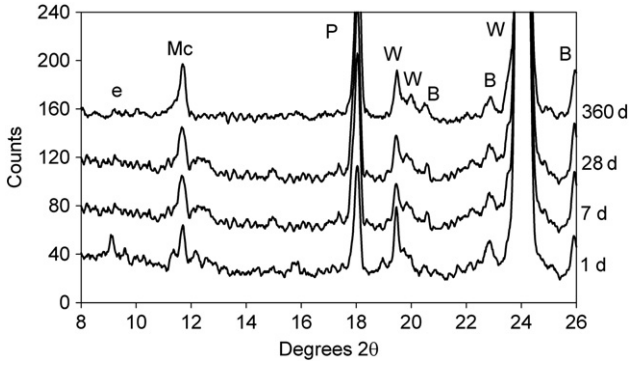

Fig. 1. OPC with 30 wt.% $BaCO_3$ w/s 0.37 cured at 20 °C between 24 h and 360 days. Mc — calcium monocarboaluminate, P — $Ca(OH)_2$, W — $BaCO_3$, B — $BaSO_4$, and e — ettringite.

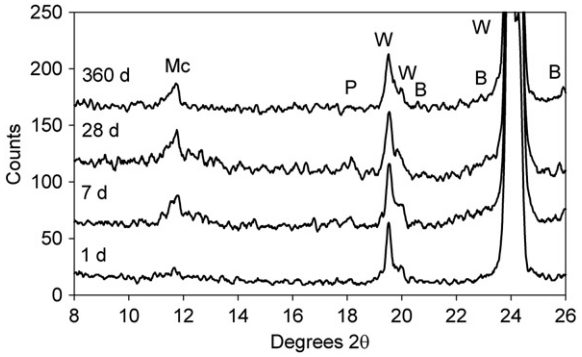

Fig. 3. 9:1 BFS:OPC 30 wt.% $BaCO_3$ cured at 20 °C between 24 h and 360 days. Mc — calcium monocarboaluminate, W — $BaCO_3$, and B — $BaSO_4$.

the hydrating OPC. A large amount of $BaCO_3$ did not react. Ettringite was observed after curing at 24 h alongside calcium monocarboaluminate, but after 7 days peaks were significantly weaker. The calcium monocarboaluminate phase persisted, in this case, up to 360 days.

Curing at 60 °C gave similar results and a comparison between XRD at 20 and 60 °C after 360 days is shown in Fig. 2. At 60 °C $BaSO_4$ was again observed, but Mc was not. Weak peaks for a hydrogarnet-type phase were identified. Hydrogarnet formation is considered to be kinetically inhibited, and hence is more often observed at higher curing temperatures. While the presence of $BaSO_4$ suggests that decomposition of $BaCO_3$ has occurred, calcite, the most likely phase to form in the absence of Mc, could not be positively identified using XRD. But in view of the level of portlandite present this is likely to be the sink for the released CO_3^{2-} ions. Aluminate from the decomposition of Mc may be incorporated into the hydrogarnet phase.

3.1.2. 9:1 BFS:OPC with $BaCO_3$

The hydration products formed from the reaction between $BaCO_3$ and 9:1 BFS:OPC are shown in Fig. 3. Again calcium monocarboaluminate (Mc) and weak $BaSO_4$ peaks were observed, but they were smaller than for the neat OPC system as there is less sulfate available. Ettringite and portlandite peaks were not observed, however, this is not unusual in a high replacement level BFS composite cement [23]. Initially, after 1 day hydration, Mc was not detected, but after 7 days, sufficient reaction had occurred for Mc to form. At this point, weak peaks for $BaSO_4$ were detected. As in previous samples calcite was not identified.

Fig. 4 shows a comparison between a 9:1 BFS:OPC sample with 30 wt.% $BaCO_3$ cured at 20 and 60 °C. In contrast to that shown in Fig. 2, Mc is stable at both temperatures. At 20 °C the peak assigned to Mc is highly asymmetric but at 60 °C has split into a doublet, suggesting the presence of a hydrotalcite-type phase often found in BFS/OPC composite cements [10,23]. Hydrotalcite is a Mg-Al layered double hydroxide similar to the natural mineral $Mg_6Al_2(OH)_{16}CO_3.4H_2O$ [24]. Hydrotalcite-type phases may contain carbonate ions. Equally non-carbonate containing hydrotalcite may be formed. It is difficult to distinguish between carbonate and non-carbonate containing hydrotalcite from qualitative XRD, and therefore substitution of CO_3^{-2} into this phase cannot be concluded. Hydrotalcite is however more stable than Mc, particularly at higher temperatures, so retention of ^{14}C carbonate in this phase would be more desirable.

At 60 °C the hydration of the BFS is accelerated, providing sufficient quantities of aluminium and magnesium ions, which encourage hydrotalcite to form. This reaction also proceeds at 20 °C, but at a slower rate and the product is not as crystalline. Curing at 60 °C also causes hydrogarnet to form, although there is still some Mc present. The stability of Mc at 60 °C in the BFS:OPC system may be due to increased $[Al^{3+}]$ although with Mg^{2+} present it usually reacts to form the hydrotalcite. The stability of Mc is not well defined and is influenced by pH, $[Al^{3+}]$, temperature, etc.

3.1.3. C_3A, $BaCO_3$ and $CaSO_4.2H_2O$

The reaction between C_3A, $BaCO_3$ and $CaSO_4.2H_2O$ was studied as a simplified reaction between components, in particular to analyse the initial formation of hydration products, such as ettringite in the presence of $BaCO_3$. Fig. 5 shows XRD of the system after 2 and 24 h of hydration in an excess of distilled–decarbonated water.

After reacting for 2 h, C_3A peaks were not observed. Strong $BaCO_3$ peaks were detected along with weaker gypsum peaks. Both ettringite and $BaSO_4$ formed showing that although $BaSO_4$ is the most insoluble species in this system, other sulphate containing phases initially form. Mc was not observed.

After 24 h of reaction, the intensity of the $BaCO_3$ peaks had decreased significantly, while the intensity of the $BaSO_4$ peaks had increased. Ettringite was also still observed, however, the intensity of its peaks had decreased, suggesting the phase was decomposing. Due to the reaction

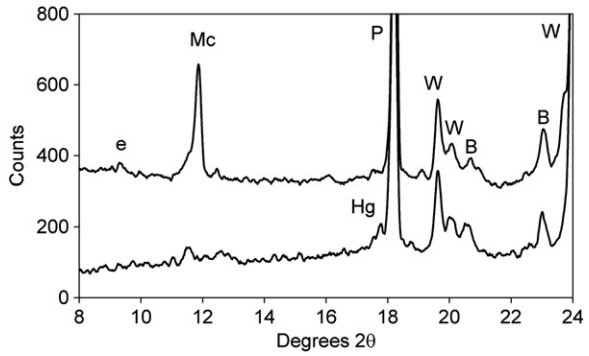

Fig. 2. OPC with 30 wt.% $BaCO_3$ w/s 0.37 cured at 20 and 60 °C for 360 days. Mc — calcium monocarboaluminate, P — $Ca(OH)_2$, W — $BaCO_3$, B — $BaSO_4$, e — ettringite, and Hg — hydrogarnet-type phase.

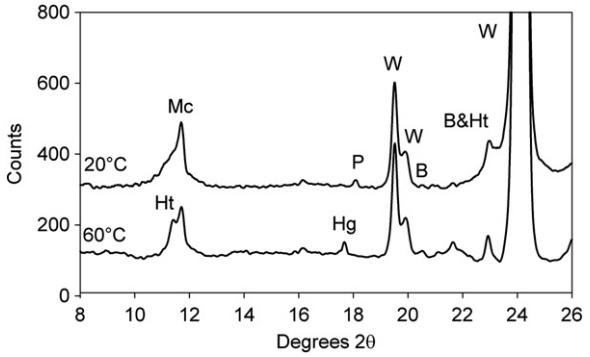

Fig. 4. 9:1 BFS:OPC 30 wt.% $BaCO_3$ cured at 20 °C and 60 °C for 360 days. Mc — calcium monocarboaluminate, W — $BaCO_3$, B — $BaSO_4$, P — $Ca(OH)_2$, Ht — hydrotalcite, and Hg — hydrogarnet.

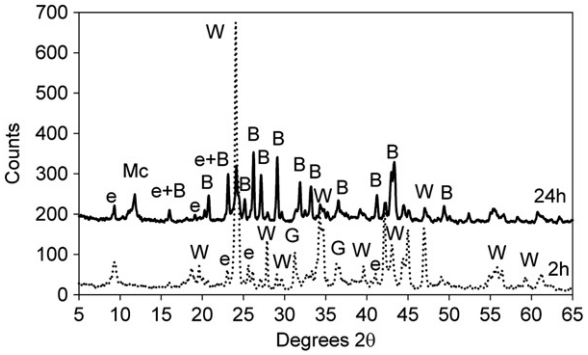

Fig. 5. 1:1:1 C_3A:$BaCO_3$:$CaSO_4.2H_2O$ cured at room temperature for 2 h and 24 h. Mc — calcium monocarboaluminate, P — $Ca(OH)_2$, W — $BaCO_3$, B — $BaSO_4$, G — gypsum, and e — ettringite.

of $BaCO_3$ with gypsum to form $BaSO_4$, sufficient carbonate was released into the solution to form Mc, suggesting that the formation of $BaSO_4$ drives the release of carbonate ions into the solution and the formation of Mc.

3.2. Microstructural analysis

3.2.1. OPC with $BaCO_3$

Backscattered electron images (BSEI) of polished cement samples were taken to examine the microstructure. Fig. 6 shows an OPC clinker particle with a hydration rim within a matrix of $BaCO_3$ particles and other outer hydration products after 720 days hydration at 20 °C. The particles containing barium (e.g. $BaCO_3$ or $BaSO_4$) are the brightest spots observed in the image, due to the high atomic number of barium (197) compared to other elements present. EDX analysis of the C–S–H gel formed around the hydrating particle suggests the presence of trace amounts of barium within the C–S–H gel but this barium rich zone of C–S–H gel has a low sulfur content, indicating that the barium is not present within this region as $BaSO_4$. No EDX evidence was found either to suggest the substitution of barium into Mc or other AFt/AFm phases, as reported by Dumitri et al. [13,14]. Fig. 7 shows a comparable feature in a sample cured at 60 °C, where there is little anhydrous material present with the exception of C_4AF which was visibly hydrating, indicating hydration has been accelerated at 60 °C. In contrast to the sample cured at 20 °C, barium was not detected to any significant level within the C–S–H gel in the hydration rim analysed suggesting that whereas barium is incorporated into C–S–H at 20 °C, at 60 °C this does not occur. The hydration products formed at elevated temperatures are typically denser than those formed at

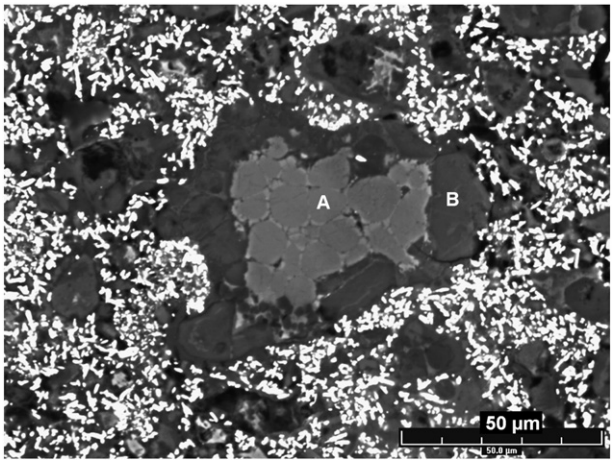

Fig. 6. OPC with 30 wt.% $BaCO_3$ cured for 720 days at 20 °C, A — anhydrous OPC, and B — hydration rim containing traces of barium.

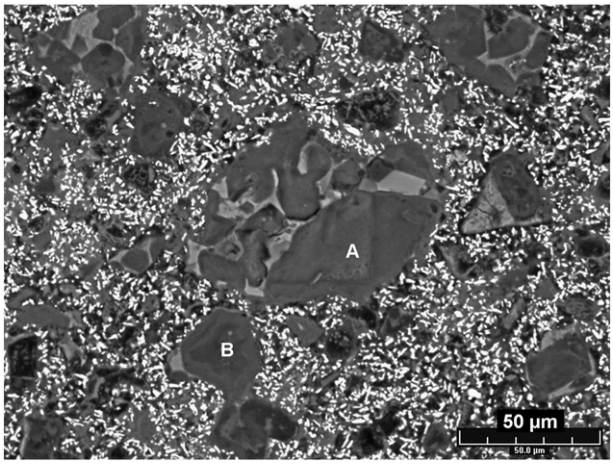

Fig. 7. OPC with 30 wt.% $BaCO_3$ cured for 720 days at 60 °C.A — Completely reacted particle, which shows no traces of barium, and B — completely reacted particle showing paler rim.

ambient temperatures [25], so diffusion of the large barium ions into the structure may not be permitted. Consideration was given to the fact that the barium signal may originate from $BaCO_3$ particles below the plane of the image, but given the difference observed between the 20 °C and 60 °C samples, it suggests the result is real.

Another unique feature in the $BaCO_3$ doped OPC samples is the presence of voids, as shown in Fig. 8. Both the shape of the voids and the presence of hydration rims indicate that the origin of the majority

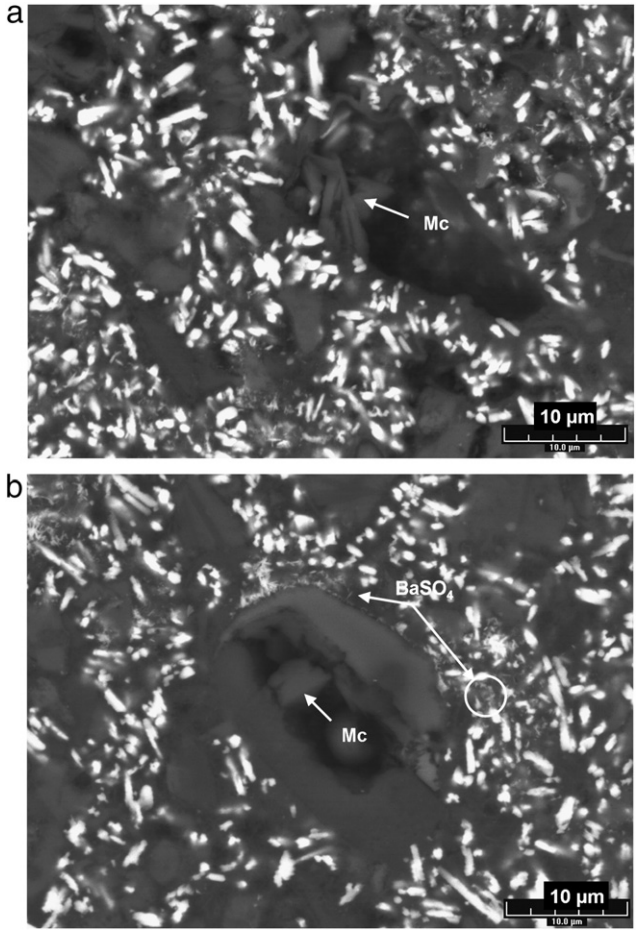

Fig. 8. a and b: OPC with 30 wt.% $BaCO_3$ cured for 720 days at 20 °C showing voids containing precipitated hydration product identified as Mc using EDX and fine particulates of $BaSO_4$.

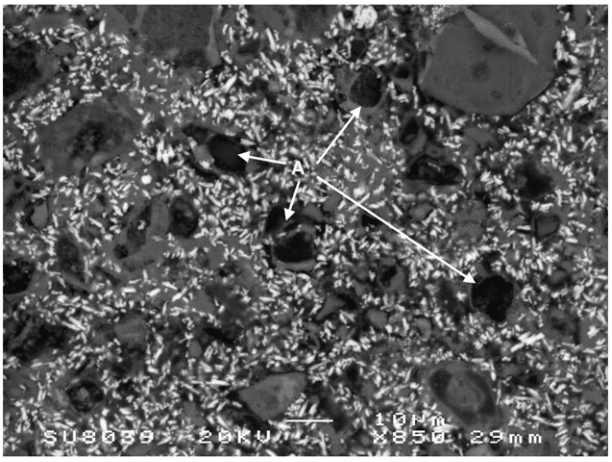

Fig. 9. OPC with $BaCO_3$ cured for 90 days at 60 °C showing empty voids (A).

of these hollow shells is the complete hydration of OPC particles, driven by the high relative water to cement ratio and the presence of many fine particulates. Platelet-like hydration products were observed within the voids, and identified by EDX as Mc. Fig. 8a and b shows typical shells observed in the microstructure and within them small platelet-like crystals. Similar voids have also been observed in OPC systems hydrated with large amounts of silica fume (up to 50%), with AFm phases precipitated in these hollow shells after 90 days of hydration [26] mirroring the precipitation of Mc in voids in this study. Fine $BaSO_4$ particles were also identified by EDX, dispersed throughout the microstructure, as indicated in Fig. 8b.

At 60 °C the voids were also observed (Fig. 9), however, a significant number were empty, corroborating the XRD results, which suggests that Mc is unstable in this system at 60 °C.

3.2.2. 9:1 BFS:OPC containing $BaCO_3$

In the 9:1 BFS:OPC system, $BaCO_3$ dominates the microstructure, as shown in Fig. 10. Anhydrous OPC was not observed, and the larger BFS particles appeared not to have reacted significantly. The voids observed in neat OPC samples were not present, so any Mc formed may be assumed to be dispersed throughout the microstructure. The samples cured at 60 °C showed few microstructural differences, aside from thin hydration rims surrounding some of the larger BFS particles, which follows with the greater amount of hydrotalcite observed at 60 °C.

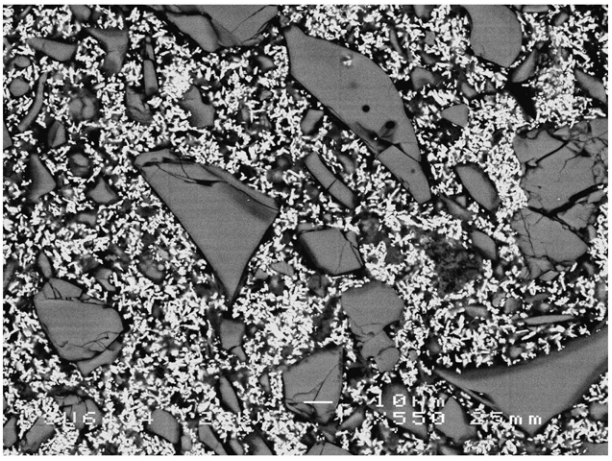

Fig. 10. 9:1 BFS:OPC 30 wt.% $BaCO_3$ 20 °C 720 days.

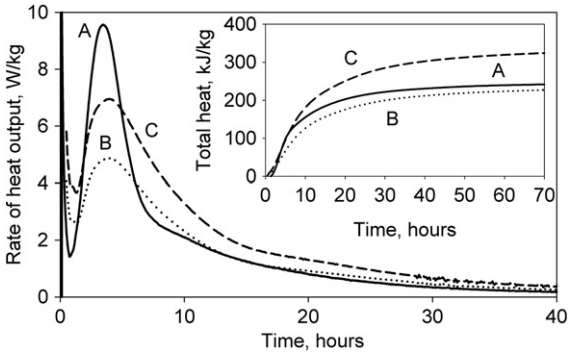

Fig. 11. Rate and total heat output for A — neat OPC, B — OPC with 30 wt.% $BaCO_3$, and C — normalised OPC with 30 wt.% $BaCO_3$ cured at 40 °C.

3.2.3. Isothermal conduction calorimetry

3.2.3.1. Addition of $BaCO_3$. The addition of $BaCO_3$ to OPC, 9:1 BFS:OPC and BFS systems has a significant effect on the heat of hydration. Fig. 11 shows the heat output of OPC both with and without $BaCO_3$ hydrated at 40 °C. ICC was also performed at 20 and 60 °C, presented later, on OPC and 9:1 BFS:OPC with $BaCO_3$ systems.

On the addition of $BaCO_3$, the maximum rate of heat output, q_{max}, decreased from 9.6 Wkg^{-1} to 4.5 Wkg^{-1}, whereas t_{max}, the time at which q_{max} occurs, was similar for both samples. The integral of the rate curve gives the total heat output overtime, Q. After 72 h, the normalised Q_{72} was similar for both doped and undoped samples. Normalising the curves to take into account the dilution effect of replacing 30 wt.% of OPC with $BaCO_3$, showed that the maximum rate of heat output (6.5 Wkg^{-1}) was still less than for neat OPC. The normalised total heat output curves, in contrast, showed a greater value for the doped system after 72 h, than for neat OPC, suggesting $BaCO_3$ is reacting and not acting as a dilutant alone.

Fig. 12 shows data for 9:1 BFS:OPC system, neat and with 30 wt.% $BaCO_3$ hydrated at 40 °C. Typically in neat 9:1 BFS:OPC, two peaks are observed, Peak II (attributed to the hydration of OPC) and Peak S (attributed to the hydration of the slag) [25]. These features can be clearly observed for neat 9:1 BFS:OPC in Fig. 12. However with 9:1 BFS:OPC containing $BaCO_3$, Peak II was completely suppressed and Peak S for both doped and undoped samples had similar t_{max} and q_{max} (1.2 Wkg^{-1}). When the data was normalised, the total heat output curve was greater after 72 h than for the neat 9:1 BFS:OPC sample.

To observe the effect of $BaCO_3$ on BFS alone, ICC was performed on a BFS system containing 30 wt.% $BaCO_3$. The tests were performed at 40 °C instead of at room temperature, due to the high signal to noise ratio at 25 °C. To assess the effect of the water to BFS ratio, as a

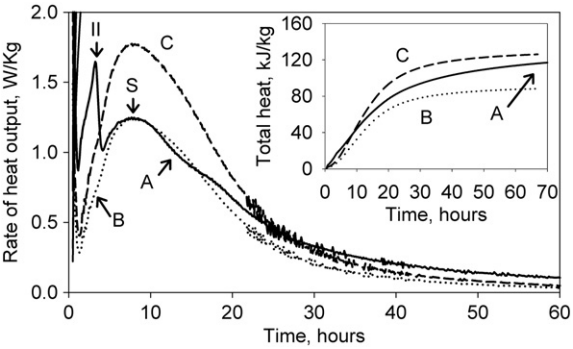

Fig. 12. Rate and total heat output for A — neat 9:1 BFS:OPC, B — 9:1 BFS:OPC with 30 wt.% $BaCO_3$, and C — normalised 9:1 BFS:OPC with 30 wt.% $BaCO_3$ cured at 40 °C.

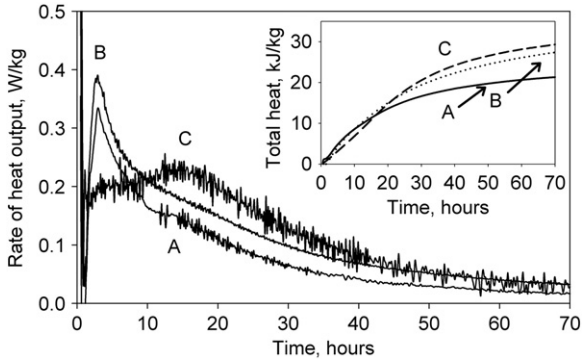

Fig. 13. Rate and total heat output for BFS with and without $BaCO_3$ cured at 40 °C. A — BFS w/s 0.35, B — BFS w/s 0.5, and C — BFS 30 wt.% $BaCO_3$ w/s 0.35.

consequence of adding $BaCO_3$, a neat BFS system was tested at a high (0.5) and low (0.35) water to solid ratio at 40 °C. The results (Fig. 13) have a high signal to noise ratio because of the low slag reactivity and small heat outputs measured. Only one small peak was observed for the 100% BFS samples, attributed to activation and hydration of the BFS. When the water to solid ratio was increased, q_{max} increased slightly.

In contrast, two peaks were observed for the $BaCO_3$ containing sample and a greater total heat of hydration curve obtained. Normalised, the total heat evolved was approximately 100% greater for the BFS/$BaCO_3$ sample, implying that the $BaCO_3$ activates the BFS. This could be due to a combination of factors. The pH of the $BaCO_3$ slurry was measured and shown to be slightly alkaline, which may aid in activating the BFS. The higher water to cementitious solid ratio, the presence of fine $BaCO_3$ particles providing nucleation sites and also the extraction of sulfur species from the slag and precipitation of $BaSO_4$, may also contribute.

3.2.3.2. Increase in temperature. Fig. 14 shows the rate of heat output in kW/kg and total heat output in kJ/kg over time for OPC containing 30 wt.% $BaCO_3$ cured at 25 °C, 40 °C and 60 °C for the first 72 h of hydration. Increasing the temperature from 25 °C to 60 °C, increased q_{max} from 1.7 W/kg to 11.1 W/Kg, whereas t_{max}, decreased from 10.3 to 3.7 h. This shows that hydration is accelerated with increasing temperature [25]. The shape of the curve at 25 °C differed to the curves of the samples at 40 °C and 60 °C The total heat outputs for 40 and 60 °C samples were similar, flattening off to approximately the same total heat output of 225 kJ/kg after 50 h suggesting that the presence of $BaCO_3$ is offset by the increase in temperature. At 25 °C the heat output was significantly retarded between 0 and 10 h, which is likely due to dilution.

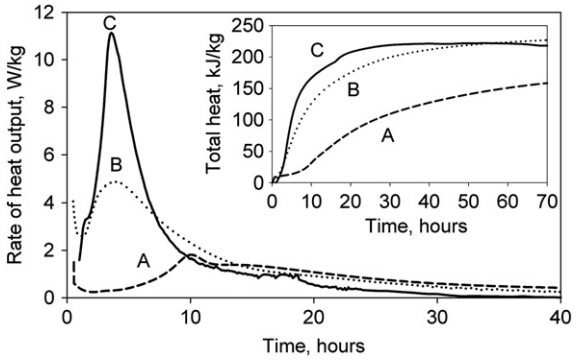

Fig. 14. Rate of heat output and total heat output for OPC with 30 wt.% $BaCO_3$ hydrated at 25, 40 and 60 °C w/s 0.37. A — 20 °C, B — 40 °C, and C — 60 °C.

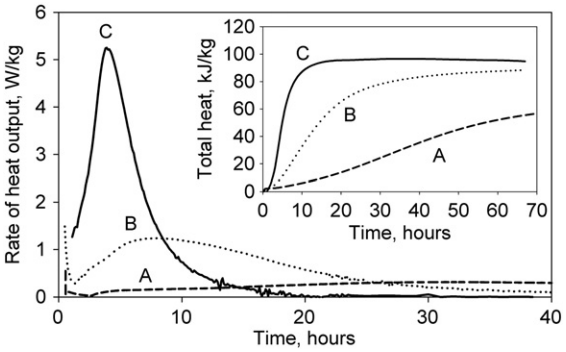

Fig. 15. Rate of heat output and total heat output for 9:1 BFS:OPC with 30 wt.% $BaCO_3$ hydrated at 25, 40 and 60 °C w/s 0.37. A — 20 °C, B — 40 °C, and C — 60 °C.

Fig. 15 shows the rate of heat output and total heat for 9:1 BFS:OPC with 30 wt.% $BaCO_3$ with increasing temperature from 25 °C to 60 °C. Increasing the temperature from 25 °C to 60 °C, increased q_{max} from 0.31 to 5.2 W/kg, and decreased t_{max} significantly from approximately 32 h to 4 h, indicating that the hydration of BFS is strongly thermally activated [25]. As with the OPC/$BaCO_3$ samples, at 25 °C the total heat output was significantly lower than for the samples cured at 40 °C and 60 °C.

4. Discussion

4.1. Interaction of $BaCO_3$ with OPC

In an undoped OPC system, C_3A reacts with any soluble sulfate species to form ettringite within the first 24 h. In a doped system, $BaCO_3$ interferes in this process through a reaction between $BaCO_3$ and soluble sulfate to form $BaSO_4$. Despite the very low solubility of $BaCO_3$ (Table 1), sufficient Ba^{2+} ions enter the solution so that the solubility product of $BaSO_4$ is exceeded. In an OPC sample containing 30 wt.% $BaCO_3$, there is approximately 9 times the amount of Ba^{2+} ions present to completely react with all available SO_4^{2-}. On formation of $BaSO_4$, carbonate is released. XRD showed this to react with aluminates to form calcium monocarboaluminate phase, $Ca_4Al_2(CO_3)(OH)_{12}\cdot 5H_2O$ (Mc). $CaCO_3$ was not identified, however may form as an intermediate phase e.g.

$$BaCO_3 + CaSO_4 + Ca_3A1_2O_6 + 11H_2O \rightarrow BaSO_4 + Ca_4Al_2(CO_3)(OH)_{12}\cdot 5H_2O$$

or

$$BaCO_3 + CaSO_4 \rightarrow BaSO_4 + CaCO_3$$

$$CaCO_3 + Ca_3A1_2O_6 \rightarrow Ca_4Al_2(CO_3)(OH)_{12}\cdot 5H_2O$$

While hemicarboaluminate, $(Ca_4Al_2(CO_3)_{0.5}(OH)_{13}\cdot 5.5H_2O)$, has been reported to form first in an OPC/$CaCO_3$ system, followed by the slow formation of Mc [7,16], no trace of hemicarboaluminate was detected using XRD in the OPC/$BaCO_3$ system. Hemicarboaluminate is unstable at high carbonate activities [9]. The excess of carbonate in this system appears to be sufficient to suppress its formation.

Although $BaSO_4$ is the most insoluble sulfate containing phase in this system, ettringite was initially observed by XRD. The two reactions, ettringite formation and $BaSO_4$ precipitation, therefore occur simultaneously, competing for the sulfate ions in the solution. While ettringite is initially present, XRD suggests that it decomposes to form Mc and $BaSO_4$, for example by the reaction below, where $CaCO_3$ may be formed.

$$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O + 3BaCO_3 \rightarrow 3BaSO_4 + Ca_4Al_2(CO_3)(OH)_{12}\cdot 5H_2O + 2CaCO_3 + 21H_2O$$

The presence of large quantities of $BaCO_3$ maintains a sufficiently high concentration of Ba^{2+} ions in the solution to ensure all sulfate

eventually precipitates as $BaSO_4$. The decomposition of ettringite is likely to occur after all calcium sulfate has been consumed in forming $BaSO_4$.

ICC showed the hydration of OPC, 9:1 BFS:OPC and BFS were altered by the presence of $BaCO_3$. Normalised q_{max} was lower for OPC with $BaCO_3$ than for the neat OPC sample. Typically, when small additions of $CaCO_3$ are added to OPC, the rate of hydration, q_{max}, increases due to the accelerated dissolution of C_3S and precipitation of $Ca(OH)_2$, which contrasts with the decrease in q_{max} observed in this study. Other authors have reported the inhibition of OPC hydration with $BaCO_3$ additions, due to the formation and presence of insoluble compounds [20,21].

In contrast, the normalised Q_{72} for OPC containing $BaCO_3$ was greater than Q_{72} for neat OPC. This indicates that $BaCO_3$ is not just acting as a dilutant. A higher Q_{72} could suggest greater hydration. However additional reactions occur in the $BaCO_3$ containing samples (e.g. see previous equations) which may contribute to the total heat recorded. Experiments showed that additional aluminate reactions occur between 2 and 24 h. The presence of fine particulates can also accelerate hydration of cement by providing nucleation sites for hydration products to form [18,19]. This and a higher effective water to cement ratio may also contribute to the greater Q_{72} observed.

The primary difference between the reaction of $CaCO_3$ and $BaCO_3$ in cements is due to the difference in solubility of the corresponding sulfate phases. At 20–25 °C $BaCO_3$ is more soluble than $BaSO_4$, whereas the opposite is true for the calcium compounds. Any Ca^{2+} ions released may therefore contribute to the hydration reactions, forming hydration products. In contrast, Ba^{2+} released into the solution reacts preferentially with sulfate ions producing an even more insoluble phase than $BaCO_3$, which may inhibit further reactions.

4.2. Interaction of $BaCO_3$ with BFS

In a 9:1 BFS:OPC system with added $BaCO_3$, similar phases were formed (Mc, $BaSO_4$), however to a lesser extent due to the lower sulfate content, as a consequence of reduced OPC content, which reacts most significantly with $BaCO_3$. The additional phase, hydrotalcite was positively identified, and was encouraged to form with increasing hydration temperature.

ICC suggests that $BaCO_3$ has a positive effect on the hydration of BFS, increasing its rate of hydration over a period of days. The activation of BFS by $BaCO_3$ in the presence of OPC is thought to be similar to the mechanism observed for supersulfated cements, where setting and hardening are associated with the formation of AFt/AFm phases from ions released from BFS, OPC and calcium sulfate [10]. In a similar manner, the release of CO_3^{2-} from $BaCO_3$ as $BaSO_4$ forms allows the formation of Mc, with constituents released from the slag and hydrating OPC, albeit forming fewer hydration products. $BaCO_3$ in the solution is mildly alkaline. This and the fine particulates of $BaCO_3$, which act as nucleation and growth sites, accelerate the dissolution of the slag. The formation of phases, such as hydrotalcite, which may also contain carbonate ions, may be encouraged to form by the excess of carbonate ions in the solution.

4.3. Encapsulation of ^{14}C

Although ^{14}C may be released by the reaction of $BaCO_3$ with soluble sulfate, Mc forms, thereby removing ^{14}C from the pore solution reducing its mobility. The stability of Mc formed in both cement systems was good at ambient temperatures, under high humidity conditions. However, in the OPC matrix the phase was thermally unstable and decomposed after prolonged hydration at 60 °C. A similar decomposition temperature was reported by Fentiman [27] for Mc formed in calcium aluminate cements reacted with $CaCO_3$. It is suggested that Mc decomposes at 60 °C in OPC to form hydrogarnet, and the CO_3^{2-} forms $CaCO_3$. In contrast, in the 9:1 BFS:OPC system, the phase was stable at 60 °C along with the hydrotalcite formed, possibly due to the higher $[Al^{3+}]$.

While Mc is observed in OPC/$CaCO_3$ systems it is not stable in sulfate or chloride containing environments, where it forms ettringite and chloroaluminate respectively. An OPC/$BaCO_3$ system is less likely to be susceptible to sulfate attack, because of the presence of an excess of $BaCO_3$, which can react with sulfate forming $BaSO_4$ instead of ettringite, meaning the Mc phase is likely to persist, containing any ^{14}C.

5. Conclusion

- $BaCO_3$ reacts significantly with OPC, scavenging all available SO_4^{2-} ions forming $BaSO_4$ with the released CO_3^{2-} ions forming monocarboaluminate. The reactivity of the $BaCO_3$ waste is determined by the sulfate content in the cement system.
- When a 9:1 BFS:OPC system is used to encapsulate $BaCO_3$, this reaction is minimised due to lower $CaSO_4$ content, and hydrotalcite is formed, which may also accommodate $^{14}CO_3^{2-}$.
- Although small amounts of monocarboaluminate and hydrotalcite form, the predominant carbonate phase is, and is likely to remain, $BaCO_3$.
- The presence of $BaCO_3$ enhances the hydration of the BFS. Mc is stabilised at 60 °C in the BFS system. Therefore, the ^{14}C in $BaCO_3$ may be effectively encapsulated in high replacement level BFS composites.

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