



Interaction between BaCO₃ and OPC/BFS composite cements at 20 °C and 60 °C

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ARTICLE INFO

Article history:

Received 5 November 2010

Accepted 11 November 2010

Keywords:

Radioactive waste
Waste management
Blended cement
BaCO₃

ABSTRACT

A BaCO₃ slurry, containing radioactive ¹⁴C, is produced during the reprocessing of spent nuclear fuel. This slurry is encapsulated in a Portland-blastfurnace slag composite cement. The effect of BaCO₃ on the hydration of OPC and Portland-blastfurnace slag cements has been studied in this work. Samples containing a simulant BaCO₃ slurry were cured for up to 720 days at 20 and 60 °C and analysed by XRD, SEM(EDX) and ICC. BaCO₃ reacted with OPC to precipitate BaSO₄ from a reaction between soluble sulfate and BaCO₃. 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 BaCO₃, less monocarboaluminate and BaSO₄ were formed, but the hydration of BFS was promoted and monocarboaluminate was stable up to 60 °C.

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1. Introduction

A radioactive ¹⁴C containing slurry of BaCO₃, 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 BaCO₃ were studied.

¹⁴C 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 ¹⁴CO₂ and ¹⁴CO. These gases are passed through a caustic scrubber to remove any ¹⁴CO₂ and ¹⁴CO forming sodium carbonate. The resulting solution is treated with Ba(NO₃)₂, precipitating Ba¹⁴CO₃, which is allowed to settle, forming a waste slurry which is dewatered to give a final waste stream containing 20–30 wt.% Ba¹⁴CO₃ precipitate in a solution of 10 wt.% soluble salts [2].

Literature published on the interactions between OPC based systems and BaCO₃ is limited, but there is extensive literature on the reactions between calcium carbonate (CaCO₃) and OPC, where CaCO₃ 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]. CaCO₃ 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 CaCO₃ additions are useful when comparing the addition of BaCO₃.

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 CO₃²⁻ 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 CaCO₃ to OPC changes both the hydration products formed and the rate of the hydration reactions. In OPC hydrated with CaCO₃, an AFm phase, calcium monocarboaluminate, Ca₄Al₂(CO₃)(OH)₁₂·5H₂O (Mc), forms through a reaction between Ca₃Al₂O₆ (C₃A) and CaCO₃ [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, (Ca₄Al₂(CO₃)_{0.5}(OH)₁₃·5.5H₂O), precedes the formation of Mc, where the activity of the carbonate is low [7,9,16].

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