

# The Effect of Simulated Barium Carbonate Waste Stream on the Hydration of Composite Cement Systems

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## **Introduction**

Composite cements, comprised of ordinary Portland cement (OPC) and blast furnace slag (BFS), are used to encapsulate a range of intermediate level wastes (ILW) produced by the nuclear industry. ILW is radioactive but non heat generating, containing over 4GBq/tonne alpha or 12GBq/tonne beta/gamma and requires sophisticated handling and disposal [1].

The safe disposal of these wastes is an important issue. A fundamental knowledge of the microstructural evolution and physical properties of cementitious systems will therefore aid in understanding the long term behaviour of the encapsulated waste.

In the nuclear waste encapsulation industry it is not uncommon for up to 90% of the OPC to be replaced by BFS, which will have significant effects on the chemical and physical properties and resulting microstructure of the package. The most obvious effect is the reduction in the heat evolved during hydration, which decreases as OPC content decreases. Other positive effects of replacing OPC by BFS include the formation of a less permeable product and a reducing environment.

In this study the effect of simulated barium carbonate waste slurry on the microstructural evolution and physical properties of both cement and composite cement systems was investigated.

In the Thermal Oxide Reprocessing Plant (THORP) at BNFL, Sellafield, CO<sub>2</sub> is released during the dissolution of spent uranium oxide fuel and passed through a caustic scrubber producing a sodium carbonate waste form. Radioactive C-14 from this waste form is precipitated out as BaCO<sub>3</sub> by the addition of barium nitrate. The precipitate is allowed to settle forming a barium carbonate waste slurry. The final waste stream contains 20 – 30wt% BaCO<sub>3</sub> precipitate in a solution of 10wt% soluble salts and is classed as an intermediate level waste [2]. The influence of BaCO<sub>3</sub> on the microstructural evolution of the composite cements is likely to be a significant factor in the long term behaviour and durability of the encapsulating medium and hence it becomes an objective of the work to understand the processes and their consequences.

## **Experimental**

Three systems were studied; 100% OPC, 9:1 BFS:OPC and 100% BFS with water to solid ratios of 0.35 – 0.5. Barium carbonate loadings of 20% and 30% weight replacement were used. The

samples were hand mixed in small batches (<250g). The systems were cured either at 40°C or ambient temperatures for 3-7 days. Hydration was stopped by quenching in acetone. Isothermal Conduction Calorimetry (ICC) was used to investigate early hydration properties. The phases produced were examined by XRD. SEM/EDS was used to observe changes in microstructure.

## Results

A number of peaks in the Isothermal Conduction Calorimetry curve correspond to various reactions occurring within the system. The following figure illustrates an idealised rate of heat output curve.

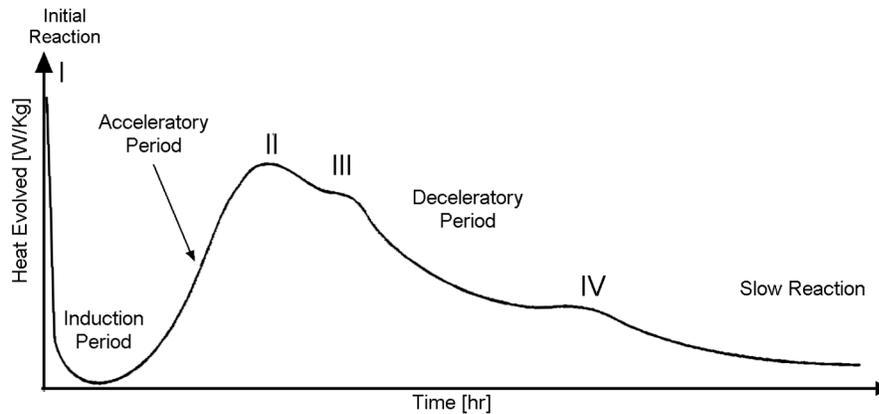


Figure 1: Idealised Rate of heat output curve [3]

- Peak I is associated with the initial reaction of the cement with water and other early stage reactions. This peak is observed only with internal mixing experiments, where water is added to cement within the apparatus.
- After the initial peak, a dormant period occurs where heat output significantly decreases and stiffness of the paste increases.
- Setting is accompanied by a sudden acceleration in the heat evolved resulting in Peak II, generally believed to be the result of alite hydration and the production of calcium hydroxide (CH) and calcium silicate hydrate gel (C-S-H).
- Two further peaks may be observed, the causes of which are not well established but are often associated with ettringite formation and  $\text{Ca}_3\text{Al}_2\text{O}_6$  ( $\text{C}_3\text{A}$ ) hydration.
- With composite cements, a further peak is observed called peak S, which appears after Peak II as either a shoulder or a more well defined peak. Peak S is attributed to the hydration of the slag fraction of the composite cement [4].

ICC results indicate that  $\text{BaCO}_3$  has pronounced effects on the early hydration properties of cementitious systems.

*100% OPC system containing 30% by weight of  $\text{BaCO}_3$  w/s 0.35 40°C*

- Peak II is reduced in height however the overall peak is broader indicating a greater total heat output (the integral of the rate of heat output)
- Normalising the total heat output curve (i.e. adjusting to take into account 30% less OPC) indicates an increase in the overall heat evolved with the presence of  $\text{BaCO}_3$ .

*9:1 BFS:OPC system containing 30% by weight of  $\text{BaCO}_3$  w/s 0.35 40°C*

- Peak II is almost completely reduced and is not easily identifiable.
- Peak S is less affected and reaches a maximum at similar times and magnitudes for samples both with and without BaCO<sub>3</sub>.

#### *100% BFS 40°C*

- One weak peak is observed.
- By increasing the water to slag ratio from 0.35 to 0.5, the rate of heat output increases by ~15%. The total heat output curve is almost to the output of the BFS sample containing BaCO<sub>3</sub>.

#### *100% BFS system containing 30% by weight of BaCO<sub>3</sub> w/s 0.35 40°C*

- Two peaks are observed, in contrast to the one peak seen in a 100% BFS sample. The second peak is stronger than the first.
- Normalising the total heat output curve shows a 100% increase in the amount of heat evolved, implying reactions are accelerated (i.e. BaCO<sub>3</sub> is activating the BFS grains in some manner).
- Comparing the 100% BFS sample with the sample containing BaCO<sub>3</sub> it is noticeable that the curves cross at approximately 20 hours, indicating reactions are suppressed initially by the presence of the BaCO<sub>3</sub> but at later times accelerated.

#### *Phase formation upon hydration*

On the addition of BaCO<sub>3</sub> to both the 9:1 BFS:OPC and 100% OPC systems, two new phases form; insoluble BaSO<sub>4</sub> and a mono calcium carboaluminate phase. No ettringite (AFt) or monosulfate (AFm) were found in the BaCO<sub>3</sub> containing samples at 7 days.

EDS analysis of a 100% OPC sample containing BaCO<sub>3</sub> suggests that the Ba ions are substituting into hydration products, such as C-S-H gel or calcium carboaluminate phases.

### **Discussion**

From the results presented the addition of barium carbonate has significant effects on the chemical and microstructural evolution of both neat and composite cements. Due to the insolubility of BaSO<sub>4</sub>, it precipitates out thereby encouraging further reactants to enter solution. Ca in solution appears to be left with only the carbonate and aluminate ions with which to combine, as identified by XRD analysis.



The presence of mono carboaluminate rather than AFt phases indicates that there is a lack of sulfate ions in the pore solution, implying the Ba<sup>2+</sup> ions effectively remove all the sulfate ions, either before they are able to react to form AFt or by causing AFt which initially forms, to decompose. In an OPC sample loaded with 30% by weight of BaCO<sub>3</sub> there is approximately 9 times the required amount of Ba<sup>2+</sup> ions to completely react with all available SO<sub>4</sub><sup>2-</sup>.

Possible explanations for greater total heat output in the OPC/Ba systems are that OPC hydration may be accelerated by the greater effective water to cement ratio (w/c) or the presence of fine BaSO<sub>4</sub> particles.

The increased total heat output from the BFS:OPC/Ba samples is unexpected, as it was hypothesised that since the OPC reaction is shown to be suppressed, less CH would be formed,

thereby inhibiting activation of the BFS. The lack of change in the reaction may be the result of increased water/slag and w/c ratios or some as yet un-established reactions between the barium and cementitious components.

From this study the possibility that Ba may be substituting into other hydration products is also indicated, through both SEM/EDS and XRD analysis. From XRD and the literature [5] it is expected that the Ba ions will combine to form BaSO<sub>4</sub> or calcium carboaluminate type phases perhaps with some Ba ion substitution onto Ca sites. Incorporation of Ba into the C-S-H is not established by this study and as indicated by the literature [6] may not occur. Any substitution of Ca ions will affect the microstructure significantly, resulting in changes in durability and permeability of the cement. Further hydration products may also be involved, for example, Ba may substitute into AFt or AFm phases forming a barium analogue, again changing the properties of the material. This is to be investigated further.

### Conclusions

From this study on the effect of barium carbonate on composite cement systems, the following conclusions can be made.

- BaCO<sub>3</sub> is not inert within the composite cement matrix
- BaCO<sub>3</sub> interacts with the cement systems forming BaSO<sub>4</sub> and calcium carboaluminate type phases
- Hydration of BFS is accelerated by the presence of BaCO<sub>3</sub>, whilst OPC is initially suppressed then later accelerated
- Ba ions appear to be incorporated into cement hydration products

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