Prevention of sulfate-induced thaumasite attack: thermodynamic modeling in $BaCO_3$-blended cement

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Abstract. Thaumasite, an expansive salt, remains stable over a wide range of compositions in the CaO-SiO_2-Al_2O_3-$CaCO_3$-$CaSO_4$-H_2O system. Despite its slow formation, it constitutes a risk for the integrity of underground structures such as foundations and tunnels that are in contact with sulfate-containing soil or groundwater. Sulfate-resistant Portland cements, which pursuant to the existing legislation are manufactured with clinker containing 0-5% of C_3A, prevent ettringite- but not thaumasite-mediated concrete deterioration. The present study used thermodynamic modeling to explore the viability of a new type of $BaCO_3$-blended Portland cement able to resist thaumasite formation. The results of sulfate attack (44 wt% Na_2SO_4 solution), simulated with the GEMS geochemical code in cements with 5 or 20% $BaCO_3$, or 2.5, 5, 10 or 20% $CaCO_3$ at 8 ºC, showed that less thaumasite precipitated and at higher sulfate/cement ratios in the presence than in the absence of Ba. Particularly at the higher replacement ratio, Ba proved to be able to immobilise sulfates in the medium via the precipitation of $BaSO_4$, a highly insoluble salt, and hamper the precipitation of thaumasite. The study also showed that a higher $BaCO_3$ content in the system hindered thaumasite formation even in the presence of greater amounts of carbonates. At 5% $BaCO_3$, thaumasite started to precipitate after 53 g of Na_2SO_4 were added per 100 g of cement, while at 20%, the sulfate content threshold was higher, at 70 g per 100 g of cement, and smaller quantities of the salt formed.

1 Introduction

Attack by sulfate-containing soil or underground water is one of the most common causes of the precipitation of destructive salts such as ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$) or thaumasite ($CaCO_3 \cdot CaSO_4 \cdot CaO \cdot SiO_2 \cdot 15H_2O$) [1]. Sulfate-resistant cements with a C_3A content of up to 5% [2] prevent the precipitation of the first phase [3], but not gypsum or thaumasite crystallisation [3, 4], in which silicates rather than aluminates are the phases attacked in the presence of carbonates (limestone, cement additions, aggregate, underground water or soil).

Thaumasite is a complex calcium salt characterised by the presence of octahedrally coordinated Si [5]. Although it was first identified in deteriorated cement in the US in 1965 [6], many more cases of thaumasite sulfate attack (TSA) have been reported in the UK than elsewhere [3]. While formed more readily in moist, cold (8 ºC [7]) conditions, it has also been found at higher temperatures (≥ 20 °C) in southern California [8], Italy [9] and Spain [10]. According to thermodynamic studies [7], thaumasite is known to precipitate when the sulfate content is high (SO_3/Al_2O_3 molar ratio in the system of over 3). Its formation is also favoured by pH≥12.5 [11] and some organic admixtures, including lignosulfonates, sodium aluminate, etc.[12].

Some strategies for preventing its precipitation entail the use of mineral additions that have a beneficial effect on concrete porosity and permeability [13] or ensure portlandite consumption, inducing the formation of more thaumasite-resistant, low Ca/Si ratio C-S-H gels [4].

This paper discusses the use of thermodynamic modeling to explore an alternative method for preventing thaumasite-induced sulfate attack (TSA). The procedure studied entails adding Ba to the cement to capitalise on its capacity to immobilise dissolved sulfates in the form of a very stable and insoluble salt, barite ($BaSO_4$). Prior research has found that compounds such as $Ba(NO_3)_2$, $Ba(OH)_2 \cdot 8H_2O$ [14], $BaCO_3$ and BaO [15-17] are able to either decompose ettringite or obstruct its precipitation.

Since the presence of carbonates in cementitious systems exposed to sulfate attack is requisite to thaumasite formation, Ba was included in the thermodynamic model in the form of $BaCO_3$ (5 or 20 wt%). Its effect was studied by comparing the behaviour of analogous OPC blends with no Ba but the same percentage of carbonates or the same cement replacement ratio by adding $CaCO_3$ instead of $BaCO_3$.

2 Experimental

Thermodynamic modeling was used to assess thaumasite resistance in OPC blends (OPC chemical composition prior to blending given in Table 1) containing 5 or 20 wt% $BaCO_3$ (1.5 and 6% CO_3, respectively). The modeling temperature was 8 ºC (which favours thaumasite formation [7]) in a closed system and in the absence of CO_2, (1 g of CO_2-free air was added). Up to 200 mL of a very aggressive Na_2SO_4 solution (44 wt%) were added to 100 g of each blend and 50 g of water (w/c ratio=0.5). (The ASTM C1012 accelerating test calls for only a 5 per cent Na_2SO_4 solution).

The results were compared to the findings for cements with no Ba but an identical CO_3 content (OPC mixes with 2.5 and 10 wt% $CaCO_3$) or the same replacement ratio (5 or 20% $CaCO_3$).

Table 1. Chemical composition of OPC before blending.

Component	wt%
CaO	65
SiO_2	20
Al_2O_3	4.5
Fe_2O_3	2.8
MgO	2
SO_3	2.5
CO_2	2
Na_2O	0.4
K_2O	0.8

The thermodynamic modeling software used, GEMS [18], which includes built-in general and cement-specific [19] thermodynamic databases, uses the Gibbs free energy minimisation procedure (GEM) to compute system equilibrium phase assemblage and speciation.

3 Results and discussion

3.1 Effect of 5 wt% $BaCO_3$ on TSA resistance in OPC

Figure 1 shows the volume of hydration products in OPC blends containing 1.5% carbonate in the presence and absence of Ba (5 wt% $BaCO_3$ and 2.5 wt% $CaCO_3$, respectively) gradually exposed to up to 200 mL per 100 g of cement of a highly concentrated Na_2SO_4 solution.

The 2.5 wt% SO_3 in the cement (Table 1) reacted with the Ba to yield barite. Since the addition of 5% $BaCO_3$ was stoichiometrically insufficient to fix that proportion of sulfate, a small amount (approximately 1 cm^3, figure 1a) of ettringite precipitated. At least 5.8% $BaCO_3$ would have had to be added to the cement to immobilise the sulfate, as per the following reaction:

$$BaCO_3 + CaCO_3 \xrightarrow{H_2O, SO_4^{2-}} BaSO_4 + CaCO_3 + 2OH^- \quad (1)$$

When the attack began, the addition of a small amount of Ba led to the precipitation and immobilisation of a very small proportion of sulfate as barite: only 1.3 cm^3 of this phase formed, compared to substantially greater volumes of the two expansive salts, ettringite (peaking at 29 cm^3 per 100 g of cement) and thaumasite (up to 18 cm^3). The formation of these two last phases was attendant upon portlandite (and in thaumasite, also calcite) consumption and the destabilisation, respectively, of monocarboaluminate ($3CaO·Al_2O_3·CaCO_3·11H_2O$) and C-S-H gel. Thaumasite, unlike ettringite, only forms in media with a high sulfate content: at least 44 g of Na_2SO_4 per 100 g of cement in the absence of Ba and around 53 g in its presence. Thaumasite resistance improved, then, even at such a minor percentage of $BaCO_3$, although not to any material extent.

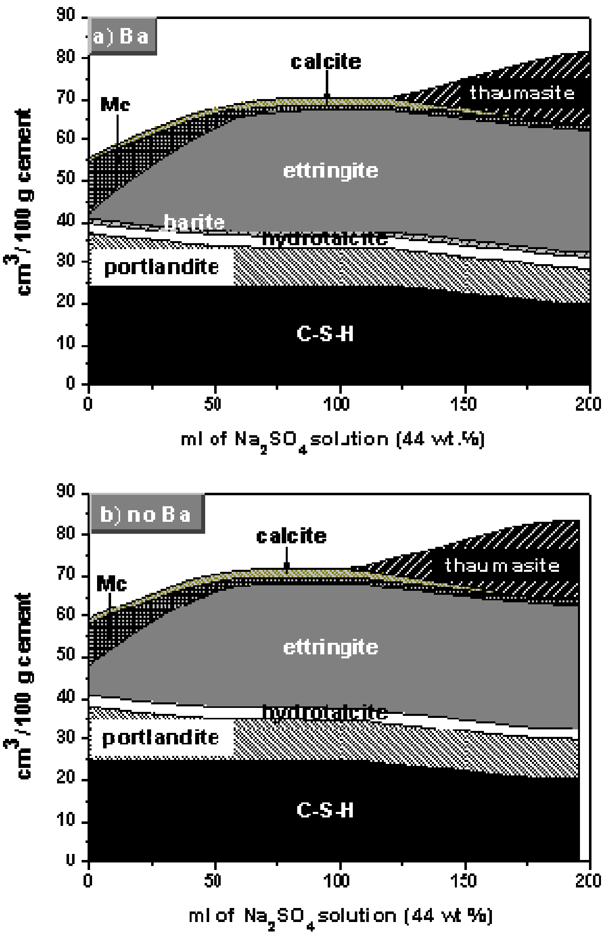

Fig. 1. Volume of hydration products forming in OPC blends with 1.5% CO_3, a) in the presence of barium (5 wt% $BaCO_3$); and b) in its absence (2.5 wt% $CaCO_3$) when interacting with 200 mL of a 44 wt% Na_2SO_4 solution.

3.2 Effect of 20 wt% $BaCO_3$ on TSA resistance in OPC

The inclusion of 20 wt% $BaCO_3$ (6% CO_3) not only confirmed the protection afforded by barium against ettringite precipitation reported in prior research [16], but also revealed the role of this element in preventing thaumasite formation. As figure 2 shows, its presence obstructed ettringite precipitation until over 9 g of Na_2SO_4 per 100 g of cement were added to the mix. For thaumasite to form, the sulfate content in the medium also had to be raised: in the absence of Ba and the presence of 6% carbonates (10 wt% $CaCO_3$), its formation required 40 g of Na_2SO_4, whereas in the presence of the compound (20 wt% de $BaCO_3$), around 70 g were needed.

This beneficial effect of Ba was the more significant bearing in mind that a larger proportion of carbonates, which favor thaumasite precipitation, had been also added to the system. So, thaumasite precipitated later and in smaller concentrations in the OPC blend containing 20% than in the mix with 5% $BaCO_3$. The reason is that sulfate immobilisation was more effective due to the formation of greater amounts of barite (around 5 cm^3 with 20 wt% of $BaCO_3$ compared to 1.3 cm^3 with 5% $BaCO_3$).

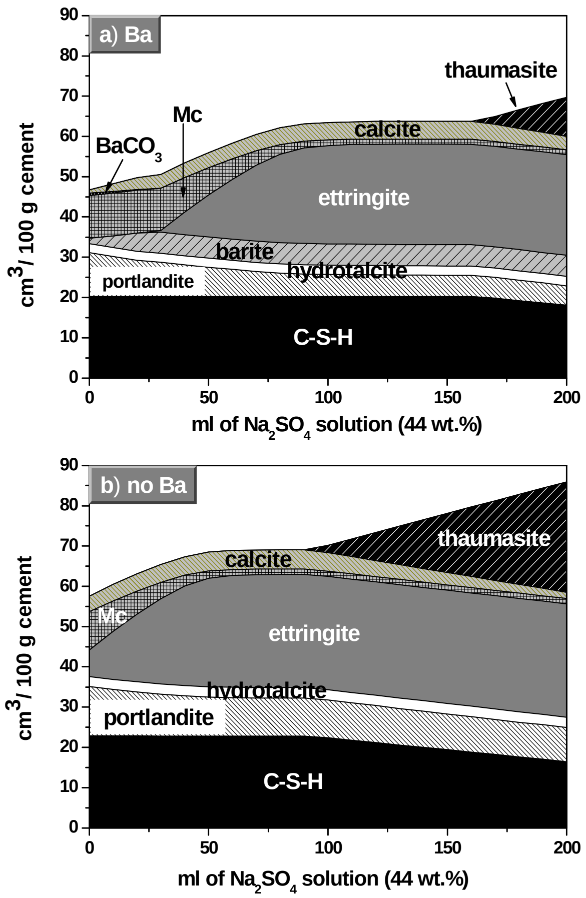

Fig. 2. Volume of hydration products forming in OPC blends with 6% CO_3, a) in the presence of barium (20 wt% $BaCO_3$); and b) in its absence (10 wt% $CaCO_3$) when interacting with 200 mL of a 44 wt% Na_2SO_4 solution.

The beneficial effect of the obstruction of thaumasite precipitation in Portland cement by $BaCO_3$ is summarised in figure 3. The figure shows that the volume of thaumasite forming in the various OPC blends containing $BaCO_3$ and $CaCO_3$ and exposed to rising amounts of Na_2SO_4 was clearly smaller in the former. Moreover, salt formation was retarded in the barium carbonate with respect to the calcium carbonate blends (same carbonate content or identical replacement ratio as in the $BaCO_3$ blends). Lastly, the higher the $BaCO_3$ content, the lower the volume of thaumasite precipitating despite the inclusion of more carbonates in the system, in contrast to what was observed in the $CaCO_3$ blends.

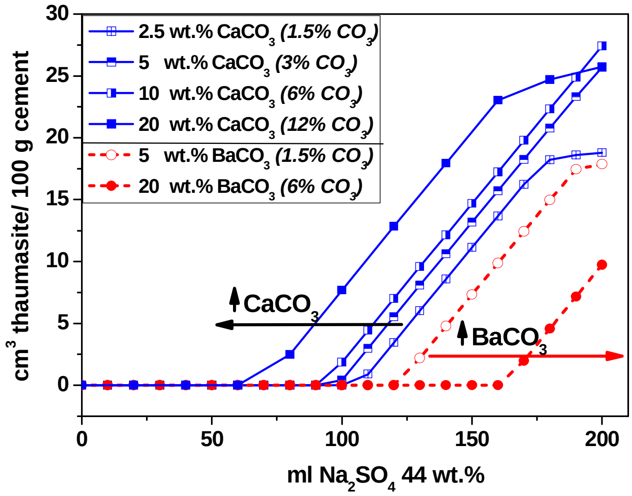

Fig. 3. Volume of thaumasite forming in OPC blends containing 2.5, 5, 10 or 20 wt% $BaCO_3$ when interacting with up to 200 mL of a 44 wt% Na_2SO_4 solution.

4 Conclusions

Thermodynamic modeling showed that the addition of (5 or 20 wt%) $BaCO_3$ to Portland cement raises its thaumasite resistance. Less thaumasite precipitated and at higher sulfate/cement ratios in the presence than in the absence of Ba, particularly at the higher replacement ratio (20 wt% $BaCO_3$), even though at that ratio the carbonate content was greater. These effects can be attributed to the formation of $BaSO_4$, a highly insoluble phase that immobilises part of the external sulfates.

At the most favourable replacement ratio, 20 wt% $BaCO_3$, thaumasite formation was obstructed up to the addition of 70 g of Na_2SO_4 per 100 g of cement, whereas in the absence of Ba and an equivalent carbonate content (10 wt% $CaCO_3$), thaumasite precipitated with slightly over half that amount of Na_2SO_4 (over 40 g).

If $BaCO_3$ were used as a set retarder, the resulting blends would be more thaumasite-resistant because the active ingredient, Ba, would not be consumed in the immobilisation of the sulfates present in the cement itself.

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