USE OF BARIUM CARBONATE TO INHIBIT SULFATE ATTACK IN CEMENTS

P.M. Carmona-Quiroga, M.T. Blanco-Varela*

Instituto de Ciencias de la Construcción Eduardo Torroja (IETcc-CSIC), C/ Serrano
Galvache 4, 28033 Madrid, Spain

Abstract

The present study aims to explore a new approach to producing sulfate-resistant cements by the addition of BaCO_3 to clinker, capitalising on the capacity of Ba to immobilise sulfates in the form of highly insoluble barite (BaSO_4).

The study conducted on white clinker pastes and mortars with 10 and 15 wt% BaCO_3 , analysed the effect of the addition on the durability of materials exposed to external sulfate attack (4 wt% Na_2SO_4 for 5 months at 21 °C), as well as on their mineralogy and microstructure.

The promising findings show that the presence of BaCO_3 improves sulfate resistance by inhibiting ettringite growth. The mortars prepared with high C_3A clinker, sand with no fines (to favour the attack) and 15 % BaCO_3 remained practically unaltered after 5 months in contact with the aggressive solution, whereas the control mortars (clinker + 5 % gypsum) underwent severe deterioration after only 5 weeks.

* Corresponding author: Tel.: +34 913020440; Fax: + 34 913026047
E-mail address: blancomt@ietcc.csic.es

Keywords: (C) Sulfate attack; (D) Sulfate Resistant cements; BaCO₃; (D) Ettringite; (B) X-Ray Diffraction

1. Introduction

BaCO₃ (witherite), whether quarried directly or synthesised from barite [1], has a number of industrial applications, including the immobilisation of sulfates in mining waste water [2] or brick manufacture [3]. In its presence sulfate precipitates as a highly insoluble salt, barium sulfate.

Barium carbonate is no unknown to the cement industry, for it may form part of the composition of portland cement or additions such as paper sludge [4] or encapsulated radioactive waste [5]. It may also be used in clinkerisation trials to significantly shorten the time and lower the temperature needed for C₃S formation [6] or to synthesise barium aluminate cements [7]. Nonetheless, very few studies have been conducted on the de-sulfurising action of witherite, although its effect on the performance of raw cement clinkerised using sulfur-rich coal has been researched [8].

Preliminary experimental and thermodynamic studies for the development of sulfate-resistant cements revealed that BaCO₃ inhibits primary ettringite formation [9,10] or destabilises this salt [11]. It may also immobilise external sulfates [12] by forming barium sulfate, along with CaCO₃. Thermodynamic modelling of the CaO-BaO-Al₂O₃-CaSO₄-CaCO₃-H₂O closed system at 25 °C showed that ettringite is unstable in solutions containing [Ba²⁺] > 0.1176 mmol/kg [12]. According to experimental studies, ettringite decomposition advances more swiftly at higher temperatures [11].

Other authors [5,9,13] have reported that the presence of BaCO_3 reduces the cement hydration rate and, like CaCO_3 , retards C_3A hydration, favouring the precipitation of calcium monocarboaluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$). Those authors likewise found that the greater amounts of mixing water required by such blends had no adverse effect on the resistance due to the formation of Ca monocarboaluminate [9].

Sulfate attack, one of the causes of deterioration in portland cement mortar and concrete, induces the precipitation of salts such as ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$), thaumasite ($\text{CaCO}_3\cdot\text{CaSO}_4\cdot\text{CaO}\cdot\text{SiO}_2\cdot 15\text{H}_2\text{O}$) or gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$) [14]. The measures presently in place to counter these attacks include the use of what is defined in standards and codes as sulfate-resistant (SR) cement [15], processed from clinker with a low C_3A content (from 0 to 5 % in OPC). While these cements prevent expansive ettringite precipitation, they do not curb gypsum or thaumasite precipitation [16]. Other methods include reducing mortar or concrete permeability (low water/cement ratio, high cement content, intense compacting and careful curing) [14] and lowering the $\text{Ca}(\text{OH})_2$ content in cements by adding supplementary cementitious materials (SCMs) that consume $\text{Ca}(\text{OH})_2$ in the pozzolanic reaction and dilute the C_3A content in the system [17]. The combination of SCMs and low permeability mortars and concretes is presently one of the most effective methods for enhancing sulfate resistance in mortars and concretes [17].

The presence of a certain amount of CaCO_3 also raises cement resistance to sulfate attack by favouring the formation of hydration products and therefore physically reducing material porosity, which hinders the ingress of aggressive solutions [18, 19].

This denser microstructure is the result of the formation of calcium monocarboaluminate instead of calcium monosulfoaluminate. An excess of CaCO_3 , by contrast, may make these materials more vulnerable to sulfates by reducing the proportion of clinker and consequently the volume of hydration products, which increases porosity [19]. The presence of this compound may even favour thaumasite precipitation (subsequent to ettringite and gypsum formation) [19, 20]. The beneficial effects on porosity and permeability of certain mineral additions (fly ash, blast furnace slag) also improve sulfate resistance in limestone cements [21].

The present study explores a new approach to developing sulfate-resistant cements: the inclusion of BaCO_3 , capitalising on the capacity of Ba to fix dissolved sulfates as barite (BaSO_4).

2. Experimental

The chemical composition of the white clinker (CK; Cemex, Buñol, Spain) was found with X-ray fluorescence (XRF) conducted on pressed powder with a Bruker S8 TIGER spectrometer. The free lime content [22], HCl-insoluble residue [23] and loss on ignition at 1000 °C were likewise found. The Bogue equations [24] were used to establish the potential mineralogical composition of the clinker and Rietveld quantitative analysis [25] was conducted on the XRD findings using GSAS software [26]. The clinker diffraction pattern was recorded with a 2.2-kW Bruker D8 Advance diffractometer (CuK α 1 radiation: 1.5406 Å; CuK α 2 radiation: 1.5444 Å; operating parameters, 40 kV and 30 mA; 2 θ recording range: 5-70°; step size, 0.02°). The parameters refined included background coefficients, cell parameters, zero shift error,

peak shape and phase fractions (atomic parameters, position, thermal displacement and site occupation were not refined).

Two cements were prepared by blending white clinker with 10 and 15 wt% BaCO₃ (W: Probus laboratory reagent) and labelled CK90W10 and CK85W15, respectively. The surface areas of these cements, the witherite and the clinker were found with a N₂-77K gas Micromeritics ASAP 2010 analyser. Their particle size distribution was analysed with a SYMPATEC Helos diffractometer operating at a He-Ne wavelength of 632 nm and fitted with a detector for 31 channels. The samples were suspended in isopropyl alcohol, continuously stirred and pumped through a closed loop cell (SUCELL dispersion unit). The suspensions were ultrasonically dispersed and subsequently stabilised for 60 and 30 s, respectively, prior to 15-s laser diffraction analysis.

Paste and mortar specimens measuring 1x1x6 cm were prepared with the two cements, using w/c ratios of 0.32 and 0.5, respectively and a cement/sand ratio of 1/3 in the mortar. Coarse sand (1-1.6-mm fraction) was used to increase mortar porosity and consequently its vulnerability to sulfate attack. A 95 % clinker / 5 % gypsum control cement was also prepared and used to make mortar specimens with the same water-cement-sand ratio as above. The paste and mortar specimens were cured under water for 28 days at 21 °C. After curing, some of the specimens were immersed in a concentrated (40-g/l) Na₂SO₄ solution to hasten any possible chemical or physical changes, while the others were stored in water for up to 5 months, likewise at 21 °C. Specimens were removed monthly from the water and the aggressive solution (which was refreshed monthly) and characterised as described below.

Cement and paste mineralogical composition was found with the XRD analyser under the conditions listed above for the clinker. Certain pastes were selected for Rietveld quantitative phase analysis. Thermogravimetric and differential scanning calorimetry (DSC) trials were conducted on the clinker, witherite and pastes with a TA SDT Q600 simultaneous TGA/DSC analyser. The samples, set on a platinum crucible, were heated in air to 1200 °C at a flow speed of 4 °C/minute. Paste infrared spectra were recorded using 1/300-mg KBr pellets analysed on a Nicolet 7600 infrared spectrophotometer, with the following settings: range, 4000-400 cm^{-1} ; scans, 10; spectral resolution, 4 cm^{-1} .

The compressive strength of pastes and mortars was also found. Mortar porosity and particle size distribution were determined with mercury intrusion porosimetry on a Micromeritics Autopore IV 9500 V1.05 and their microstructure was studied under a Hitachi S-4800 field emission scanning electron microscope (FESEM) equipped with a 20-kV Bruker energy-dispersive X-Ray spectrometer (XFlash Detector 5030).

3. Results

3.1 Characterisation of white clinker and witherite

The chemical and mineralogical compositions of the white clinker are given in Table 1. According to the Rietveld refinement of the XRD findings, the majority phase was C_3S (86.83%). The clinker also contained C_3A and C_2S , neither with a proportion of over 10 %. The Bogue method underestimated the C_3S content and doubled the amounts of C_3A and C_2S (Table 1), corroborating Taylor's [27] observations on the limitations of this prediction method, which may lead to substantial quantification errors [28].

Figure 1 shows the DTG curves for witherite, white clinker and the clinker/witherite blends (85/15 and 90/10 wt%), as well as the DSC curve for witherite. The respective thermogravimetric findings are given in Table 2.

Witherite, which decomposed partially (87 %) during the trial, generated four endothermal signals at 816, 976, 1030 and 1113 °C (Fig. 1). The first two were attributed to polymorphic transformations (first from the rhomboid to the hexagonal and then from the hexagonal to the cubic systems) [29, 30], although according to the TG data, decomposition had begun by the second signal and continued through the end of the trial. The peak weight loss was recorded at 1098 °C.

The DTG curves for the clinker denoted slight weathering (weak signals for portlandite dehydroxylation at 347 °C and calcite decomposition at 554 °C) (Fig. 1). In addition to these signals, the curves for cements CK85W15 and CK90W10 (Fig. 1) showed witherite thermal decomposition at temperatures around 100 °C lower than in the pure compound (994, 1013°C in blends vs. 1098 in pure sample) and a new weight loss stage with a maximum around 763-793 °C, attributed to the decomposition of finer BaCO₃ particles [30] produced by the mechanical mixing of the two components. These differences in particle size explain why the peak weight loss of witherite was reached at lower temperatures in the blends than in the pure sample. Barium carbonate decomposition was, then, a two-stage process in the cements (650-850 and >850 °C), whereas in the pure compound decomposition was continuous (>850 °C).

Further to the witherite weight loss data (Table 2), cements CK90W10 and CK85W15 contained 9.4 and 15.8 % of this phase, respectively, i.e., the findings practically concurred with the initial dosage.

The BET area and particle size distribution values for the white clinker and witherite are given in Table 3 and Figure 2. Witherite was observed to be much finer than the clinker, with a BET specific surface three times greater (1.6316 vs. 0.5215 m²/g, Table 3). Its mean particle size was 3.78 µm (while these particles clustered readily, they could be dispersed by stirring) compared to the 12.64 µm in the clinker. The cements obtained by blending clinker and BaCO₃ therefore had a larger specific surface and smaller mean particle size than the clinker (Table 3 and Fig. 2).

3.2 Mineralogical characterisation of the pastes

The diffractograms for all the BaCO₃-containing cement pastes that were stored in water for 5 months exhibited reflections (Fig. 3) characteristic of unreacted alite, belite and witherite, as well as portlandite, and less intense lines for calcite, hydrotalcite, barite and calcium monocarboaluminate. No ettringite reflections were observed in any of the XRD patterns. The variations in the crystalline phases over time were determined with Rietveld quantitative analysis (Table 4). Although this procedure omits the amorphous phase (C-S-H gel) and is not strictly quantitative for the crystalline phases due to the difference in the absorption coefficients between the two Ba-containing phases and all the others, it may nonetheless afford a reasonably good idea of the variations over time.

In the samples stored in water for up to 5 months (Fig. 3 and Table 4), the BaCO₃ fixed the sulfates present in the clinker in the form of barite (Eq. 1), while the CaCO₃, likewise formed, reacted with the aluminates to yield calcium monocarboaluminate hydrate and hydrotalcite. The presence of calcium carbonate phases in the 5-month specimens denoted paste weathering.

Most of the sulfates entering the pore network of the blended paste specimens stored in the Na₂SO₄ solution (Fig. 3 and Table 4) were fixed in the form of barite by the BaCO₃ present (Equation 1). Nonetheless, the diffractograms for the pastes with 10 and 15 % BaCO₃ (Fig. 3) exhibited a very weak reflection at 2θ 9.08° (9.72 Å) attributable to ettringite, which precipitated essentially at the expense of calcium monocarboaluminate hydrate. The diffractograms for the 2-month specimens immersed in the aggressive solution also contained a weak, wide signal at approximately 10.97° (8.06 Å) attributed to a calcium aluminate hydrate (C₄AH₁₃). After 5 months, the reaction described in Equation 1 had not reached completion and ettringite formation continued to be retarded.

219

220 The most prominent feature on the infrared spectra for the pastes (Fig. 4) was the
221 change in the relative intensity of the bending bands generated by the O-C-O in calcite
222 (877 cm^{-1}) and witherite (857 cm^{-1}) with reaction time (Equation 1), denoting the slow
223 consumption of the latter phase. The other signals observed on the spectra for all the
224 samples were: stretching vibration band generated by the OH groups in portlandite at
225 3642 ; stretching and bending vibration bands attributed to water at 3435 and 1634 cm^{-1} ;
226 bands associated with silicates at 974 and 1048 cm^{-1} (Si-O stretching vibration in C-S-H
227 gel); the C-O stretching vibration band at 1441 cm^{-1} ; and the out-of-plane bending
228 vibration at 694 cm^{-1} generated by the CO_3^{2-} groups in witherite. Because the material
229 was so tightly compacted, hindering aggressive ion diffusion and the reaction described
230 in Equation 1, the amount of sulfates (barite and ettringite) precipitating when the pastes
231 came into contact with the aggressive solution was too small to be detected
232 spectroscopically. The characteristic stretching bands at 1120 (ettringite) and 1170 cm^{-1}
233 (barite) were clearly missing.

234

235 The DTG curves for the samples with 15 % BaCO_3 , in water or a sulfate solution
236 reproduced in Figure 5 show three main weight loss stages. The first, up to $375\text{ }^\circ\text{C}$, was
237 related primarily to the dehydration of C-S-H gel, calcium monocarboaluminate and
238 hydrotalcite; the second, from 375 to $485\text{ }^\circ\text{C}$, was due to portlandite dehydroxylation;
239 and in the third, which began at around $500\text{ }^\circ\text{C}$, calcite, witherite and calcium
240 monocarboaluminate were decarbonated (Table 5). The inflections in the DTG curves at
241 $760\text{ }^\circ\text{C}$ (Fig. 5) revealed the overlapping of CO_2 loss in calcite and witherite. Further to
242 the preliminary analysis (Fig. 1), barium carbonate decomposition would continue
243 through the end of the trial, to $1200\text{ }^\circ\text{C}$.

Weight loss due to C-S-H gel dehydration (single stage, signal at 143 °C on the DTG curve, or tiered, with two sub-peaks at 77 and 133 °C [31]) or to portlandite dehydroxylation was not observed to vary materially in pastes with different BaCO₃ contents or immersed in different types of solution (Table 5). Over time, hydration was obviously intensified, as shown by the rise in the weight loss during the first stage.

The differences in the CO₂ losses in the two types of blends could be attributed primarily to the different initial proportions of witherite (Table 5).

3.3 Mortar microstructure: porosity and BSEM

Replacing gypsum with BaCO₃ raised mortar porosity after initial curing by 7 % in the 10-per cent blends and 34 % in the 15-per cent blends (Table 6). The lower clinker content in the mortars with witherite and the difference in the specific surface and consequently in the plasticity of the three cements when mixed with the same w/c ratio contributed to these differences. Over time, the differences in porosity between mortars with different proportions of BaCO₃ declined: from 25 % in the 28-day specimens to around 12 % in the 5-month materials. Total mortar porosity declined with time in all the materials, whether stored in water (expected result) or in the aggressive solution.

As a rule, at a given BaCO₃ content, the porosity of mortars immersed in water was greater than in the materials immersed in sulfates (Table 6); these differences might be associated with the approximate 11-per cent increase in volume attendant upon barite

and calcite formation in the latter, as per Equation 1. As noted in the introduction, the larger volume of reaction products would fill voids, lowering porosity.

Mortar microstructure was examined under an electron microscope (Fig. 6). The backscattering electron images for all the samples (regardless of BaCO_3 content, reaction time or type of soaking solution) exhibited a substantial number of unreacted clinker particles in the hydration product matrix. The thin (white) witherite crystals blanketing the matrix and occasionally clustered were observed to be much smaller than the anhydrous particles (Fig. 6a,b). The presence of Ba inside the C-S-H gel was unclear, for while it was detected in the EDX microanalyses (Fig. 6c1,c2), it was consistently found associated with a sufficient amount of S to suggest that it was in the form of BaSO_4 . In OPC containing 30 % BaCO_3 cured at 20 °C, Utton et al. [5] detected barium inside the C-S-H gel, but not at 60 °C because the denser structure of the latter prevented the diffusion of the large Ba ions. Those same authors [5] did not observe evidence of Ba replacement in calcium monocarboaluminate, verified here via TEM-EDX analysis of this phase when synthesised in the laboratory from C_3A and BaCO_3 .

In mortars in contact with the Na_2SO_4 solution, barite crystals, likewise white but smaller than the witherite crystals, were found scattered throughout the matrix and attached to the large BaCO_3 particles (Fig. 6d,e). Ettringite crystals were observed in samples exposed to the aggressive solution for 5 months, more clearly in the mortars with a lower BaCO_3 content, where they filled a number of voids (Fig. 6f,f1).

3.4 Paste and mortar durability and strength

Compressive strength in the barium-containing paste specimens was similar, regardless of the soaking medium (water or an aggressive solution). Specimen appearance and strength remained unaltered after being immersed for 5 months in the aggressive solution (Fig. 7), corroborating the formation of only minimal amounts of ettringite.

Compared to the initial curing values, mechanical strength underwent no substantial change in mortars immersed for 5 months in water, although the contrary was observed in the specimens immersed in the aggressive solution.

The control mortar specimens (clinker + gypsum) were bent after only 5 weeks in sulfates and the effects were even more visible after 6 (Fig. 8a). After 2 months, these specimens had practically disintegrated altogether. Such findings were not unexpected, for the clinker contained a high proportion of C_3A and the mortars were designed to be highly porous: the sand used contained no fines (Φ sand ≥ 1 mm) with a view to generating less compact materials to favour the ingress of the sulfate solution.

The performance of the Ba-containing mortars exposed to sulfates was much better, although the specimens with only 10 % $BaCO_3$ showed outer signs of deterioration with loss of material around the corners after 4 months. The precipitation of a growing amount of expansive ettringite ultimately generated inner pressure that after 5 months led to the breakage of some of the samples (Fig. 8b), with a concomitant and substantial loss of mechanical strength (Fig. 7).

The specimens made with blends containing 15 % $BaCO_3$, by contrast, remained dimensionally intact through the end of the trial (the only alteration was the greater

visibility of the aggregate). Nonetheless, some ettringite precipitated into their pores, according to the electron microscopic images and EDX microanalysis findings (Fig. 8c).

The role of BaCO_3 in improving mortar durability when exposed to sulfates is not primarily physical, as in other mineral additions (limestone cements [21]), for paradoxically, while a higher BaCO_3 content raises porosity, it also raises sulfate resistance. The mechanism involved is a chemical process in which barite precipitation plays an essential role in stabilising external sulfates, inhibiting ettringite formation: the higher the percentage of BaCO_3 , the more effective is the inhibition.

As a rule, the mortar specimens immersed in the sodium sulfate solution exhibited higher strength than the samples with the same BaCO_3 content immersed in water for the same length of time (Fig. 7). As noted earlier, these differences in strength depending on whether the specimens were stored in water or sulfates, also identified in the porosimetric findings (Table 6), were attributed to an initial rise in the volume of reaction products in the latter [32]. This was less clearly visible in pastes whose more compact matrix hindered ingress of the aggressive solution.

4. CONCLUSIONS

This paper reports on a hydration study of white cements (high C_3A content) containing (10 or 15 wt%) BaCO_3 as a gypsum substituent. It also explores the durability of porous mortars made with those cements and fines-free sand, i.e., mortars designed to favour the ingress of the aggressive 4-per cent Na_2SO_4 solution to which they were exposed. The findings may be summarised as follows.

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344 1. BaCO_3 reacted with the sulfates in the clinker, favouring BaSO_4 and calcium
345 monocarboaluminate over primary ettringite precipitation.

346

347 2. Similarly, the addition of BaCO_3 , which raised mortar porosity, improved resistance
348 to sulfate attack by immobilising the external SO_4^{2-} ions in the form of barite (BaSO_4),
349 likewise hindering expansive ettringite precipitation. When in contact with the
350 aggressive solution, the control specimens, which contained 5 % gypsum as a setting
351 regulator, deteriorated in less than 2 months, while the specimens bearing 10 % BaCO_3
352 remained intact for 4 months and the samples with 15 % BaCO_3 were unaltered after
353 5 months of exposure.

354

355 3. The reaction between the sulfates in the medium and BaCO_3 and portlandite yields
356 barite and calcite, whose volume is 11 % greater than the volume of the reagents,
357 contributing to reduce mortar porosity and thereby hindering aggressive agent access.

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359 4. Despite their deliberately adverse design, the mortars were successfully protected
360 from sulfates.

361

362 5. These preliminary findings support the use of BaCO_3 to produce a new type of
363 sulfate-resistant cements. Nonetheless, a balance must be struck among reaction (sulfate
364 immobilisation in the form of barite, which entails a rise in volume and a concomitant
365 decline in porosity), dilution (lower clinker content) and specific surface (higher values
366 reduce workability) to ensure that inclusion of the compound is not counter-productive.

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Acknowledgements

Funding from the Spanish Ministry of Education and Science (Project CONSOLIDER CSD2007-00058) and the Regional Government of Madrid (Geomaterials Programme) is gratefully acknowledged.

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Table 1. Chemical (XRF), potential (Bogue) and mineralogical (Rietveld) composition

483 of white clinker (wt%) (L.O.I = loss on ignition; I.R. =insoluble residue)

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[illegible]

Table 2. TG curve weight loss (%) in witherite (W), white clinker (CK) and the 90/10
and 85/15 clinker/witherite blends

Weight loss %	W	CK	CK90W10	CK85W15
free water	0.76	0.47	0.35	0.38
H₂O (Ca(OH)₂)	-	0.24	0.19	0.17
CO₂ (CaCO₃)	-	0.33	0.34	0.37
CO₂ (BaCO₃) (*in two stages)	18.72	-	2.10*	3.02*
Residual loss	-	0.22	-	0.19
Total	19.48	1.27	2.99	4.14

Table 3. BET surface area (m²/g) and particle size distribution of witherite, clinker and the 90/10 and 85/15 blends of clinker and witherite

	CK	CK90W10	CK85W15	W
BET surface area (m ² /g)	0.5215	0.7898	0.8335	1.6316
Mean particle size (μm)	12.64	11.24	9.88	3.78

511
512
513 Table 4. Rietveld quantification (%) of the crystalline phases present in 10- and 15-per
514 cent BaCO₃ blended cement pastes immersed in water or a 4 % Na₂SO₄ solution for
515 5 months after initial curing (R_{WP}= weighted profile for the R-factor) (C₃S= alite, C₂S=
516 belite; Ettr.= ettringite, Hydr. = hydrotalcite and MC= calcium monocarboaluminate)

BaCO ₃	exposure	C ₃ S	C ₂ S	BaCO ₃	Ca(OH) ₂	Ettr.	BaSO ₄	Hydr.	CaCO ₃	MC	R _{WP} %
15 wt%	initial curing	33.59	3.16	25.97	30.86	0.00	1.42	0.34	1.55	3.11	8.87
	5 m H ₂ O	27.71	3.43	21.96	29.63	0.00	1.34	1.83	1.58	12.52	8.15
	5 m SO ₄	33.60	4.31	16.54	26.60	0.69	8.30	1.04	1.78	7.13	7.88
10 wt%	initial curing	38.12	3.23	13.63	29.41	0.00	1.16	0.97	1.04	12.45	9.27
	5 m H ₂ O	31.56	2.34	12.81	34.37	0.00	1.89	2.81	0.33	13.90	7.95
	5 m SO ₄	36.14	3.63	11.81	33.31	0.55	4.08	1.84	1.63	7.01	7.54

517

Table 5. Weight loss (in per cent) at approximate temperature intervals in pastes

containing 10 and 15 % BaCO₃, soaked for up to 5 months in water or a 4 wt% Na₂SO₄ solution

		% weight loss		
		up to 375°C	375-485°C	485-965°C
		dehydration (C-S-H gel, MC)	dehydroxylation (Ca(OH) ₂)	decarbonation (CaCO ₃ , BaCO ₃ , MC)
time				
15 wt. %	initial curing	8.54	3.7	5.8
	1 m	12.09	3.92	5.47
	H ₂ O 2 m	11.86	3.88	5.88
	5 m	14.16	4.17	5.12
	1 m	12.49	3.77	4.97
	Na ₂ SO ₄ 2 m	12.51	3.83	5.24
	5 m	13.24	4.07	4.28
	initial curing	10.7	3.76	4.57
	1 m	12.75	3.9	4.65
	H ₂ O 2 m	12.77	4.01	4.83
10 wt. %	5 m	14.64	4.42	3.66
	1 m	12.63	3.82	4.59
	Na ₂ SO ₄ 2 m	13.32	4.02	4.37
	5 m	13.79	4.24	3.59

Table 6. Porosity in mortars prepared with white clinker and 10 or 15 % barium carbonate soaked for up to 5 months (after 28-day curing) in water or a 4 wt% Na₂SO₄ solution, and in a cement mortar (white clinker) with 5 % gypsum, after curing (in parentheses, standard deviation)

	Initial curing 28 d	H₂O 1 m	2 m	5 m	Na₂SO₄		
					1 m	2 m	5 m*
5 wt% gypsum	10.64 (0.11)						
	11.39	11.94	11.74	11.42	12.07	11.28	10.32
10 wt% BaCO ₃	(0.75)	(0.73)	(0.46)	(0.42)	(0.89)	(0.49)	(1.08)
	14.23	12.99	12.89	12.78	11.32	12.07	11.25
15 wt% BaCO ₃	(1.21)	(0.52)	(0.13)	(0.06)	(0.81)	(0.89)	(0.63)

*porosity determined in fragments of naturally fractured specimens (Fig. 8)

Figure 1. From top down: DSC curve for witherite and DTG curves for witherite, the 85/15 clinker/witherite blend (CK85W15), the 90/10 clinker/witherite blend (CK90W10) and white clinker (CK)

Figure 2. Particle size distribution in witherite (W), clinker (CK) and the 90/10 and 85/15 blends of clinker and witherite (CK90W10 and CK85W15)

Figure 3. Diffractograms for cement pastes with 10 and 15 wt% BaCO₃ (left and right, respectively) soaked in water or a sodium sulfate solution for 1, 2 or 5 months (E= ettringite, D= calcium aluminate hydrate, H= hydrotalcite, MC= calcium monocarboaluminate, A=C₃S, B= C₂S, P= portlandite, W=witherite, Br= barite, C= calcite)

Figure 4. Infrared spectra for cement pastes with 10 and 15 wt% BaCO₃ (left and right, respectively) soaked in water or a sodium sulfate solution for 1, 2 or 5 months

Figure 5. DTG curves for cement pastes with 15 wt% BaCO_3 soaked in water or a sodium sulfate solution, after initial 28-day curing, for 1, 2 and 5 months

Figure 6. Back-scattering images and mapping for Ba, Ca and S in mortars containing 15 wt% Ba: a) and b) overview after 1 month in H₂O and 5 months in sulfates, respectively; c) EDX analysis of the anhydrous material (c₁) and the hydration halo (c₂) (2 months in water); d) BaSO₄ distribution (1 month in sulfates); e) BaSO₄ and BaCO₃ crystals in specimens soaked for 2 months in sulfates. f) and f₁) voids filled with ettringite in mortars containing 10 % BaCO₃ after 5 months in sulfates

Figure 7. Compressive strength in cement pastes and mortars containing 10 or 15 wt% witherite or 5 wt% gypsum, after initial curing (28 d) and immersion in a) water or b) 4 wt% Na_2SO_4 solution for up to 5 months

Figure 8. Mortar specimens soaked in 4 wt% Na₂SO₄ (S) containing: a) 5 wt% gypsum (after 6 weeks); b) 10 wt% BaCO₃ (after 5 months); and c) 15 wt% BaCO₃ (after 5 months). On the right (S₂), electron microscopic images of ettringite crystals in the specimens soaked in sulfates (S₁)