Developing new sulfate-resistant cements: a $BaCO_3$ approach

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Abstract

OPC mortar and concretes can be attacked by sulphate solutions giving rise to different decaying processes, related with the formation of ettringite, gypsum, thaumasite etc. At present deterioration due to ettringite formation is avoided by limiting aluminate phase in clinker Portland, however it does not prevent other forms of sulphate attack. Barium carbonate has been used in several fields to eliminate sulphate ion from solutions due to it reacts with them and produces a very insoluble salt, $BaSO_4$*. There are in the literature studies demonstrating that ettringite as well as gypsum decompose in the presence of barium carbonate. Studies on the hydration rate of synthetic* C_3A *in the presence of varying percentages of gypsum,* $BaCO_3$ *or gypsum+*$BaCO_3$ *revealed that* $BaCO_3$ *neither regulated the speedy reaction of* C_3A *with water nor reacted with the aluminate. Blends of gypsum plus* $BaCO_3$ *proved able to regulate* C_3A *hydration.*

The objective of this paper was to know the behavior of mortars elaborated with optimized mixes of clinker-gypsum-$BaCO_3$ *in 4.4 wt%* Na_2SO_4 *solution. For this four cements were elaborated by mix of: a) clinker M with 5% of gypsum; b) Clinker M with 3% of gypsum and 15% of* $BaCO_3$*; c) clinker V and 7 wt% of gypsum; d) clinker V plus 3wt% of gypsum and 15% of* $BaCO_3$*. Studies on durability were performed on mortar prisms of 10x10x60 mm size, with cement/sand ratio = 1/3 and water/cement ratio = 0.5. Cement Mortar prisms remained submerged under water and under sodium sulfate solution for one year. Samples were extracted from solution after 1,3,5,7 and 12 months and then mechanically tested. XRD and SEM/EDX were performed on the said samples.*

The compressive but mainly flexural strengths of mortars a), decreased from 5 months in contact with sulphate solution while in the mortars b) strengths remain unaltered after 12 months. Mechanical strengths of mortars c), decreased from 3 months in contact with sulphate solution and were completely destroyed after 12 months of exposition. $BaCO_3$ *fails as protector from sulphate attack in d) mortars which were cracked after one year of sulphate exposition.*

Correlations between mineralogical composition and microstructural changes in mortars along time of test were established.

Originality

The present study explores a new approach to developing sulfate-resistant cements: the inclusion of BaCO3, capitalizing on the capacity of Ba to fix dissolved sulfates as barite (BaSO4)

Keywords: *$BaCO_3$; Portland cement; durability; sulfate attack.*

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1.-Introduction

$BaCO_3$ (witherite) has a number of industrial applications, including the immobilization of sulfates (Hlabela *et al*, 2007; Schriener *et al, 1997*). In its presence sulfate precipitates as a highly insoluble salt, barium sulfate ($BaSO_4$, barite). In the cement industry barium carbonate has been used in clinkerization trials to significantly shorten the time and lower the temperature needed for C_3S formation (Katyal *et al.* 1999) or to synthesize barium aluminate cements (Rezaie *et al.* 2009). Its effect on the performance of raw meal cement clinkerized using sulfur-rich coal has been also researched (Xie *et al.* 2005) but literature published on the hydration of cement in the presence of $BaCO_3$ is limited (Dumitru *et al.*, 1999; Utton *et al.* 2011) unlike $CaCO_3$ (Lothenbach *et al.*, 2008; Matschei *et al.*, 2007; Kakali *et al.* 2000).

Since the use of what is currently defined in standards and codes as sulfate-resistant (SR) cements (UNE-EN 197-1) elaborated from clinker with a low C3A content (from 0 to 5 wt.%), just prevents the formation of expansive ettringite (3CaO·Al2O3·3CaSO4·32H2O), but it does not curb the formation of other common mineral phases derived from sulfate attack (Mehta, 1992) on the cement paste such as gypsum (CaSO4·2H2O) or thaumasite (CaCO3·CaSO4·CaO·SiO2·15H2O) (Bellmann et al., 2007), recently a new approach to produce new sulfate-resistant cements by the addition of $BaCO_3$ to clinker (Carmona-Quiroga *et al.* 2015), capitalizing on the capacity of Ba compounds to immobilize sulfates in the form of barite (Ciliberto *et al*. 2008), has been explored.

Preliminary experimental and thermodynamic studies on the hydration of cement based systems revealed that $BaCO_3$ inhibits primary ettringite formation (Dumitru *et al.*, 1999; Carmona-Quiroga *et al.* 2011) or destabilizes this salt (Carmona-Quiroga *et al.,* 2013a) and that the decomposition advances more swiftly at higher temperatures (Carmona-Quiroga *et al.*, 2013 a). Thermodynamic modelling of the $CaO–BaO–Al_2O_3–CaSO_4–CaCO_3–H_2O$ closed system at 25 °C showed that ettringite is unstable in solutions containing $[Ba^{2+}] > 0.1176$mmol/kg (Carmona-Quiroga 2011).

$BaCO_3$ may also immobilize external sulfates by forming barium sulfate, along with $CaCO_3$ and preventing expansive ettringite and thaumasite precipitation according to thermodynamic modelling (Carmona-Quiroga *et al.* 2013 b). Mortars elaborated with white clinker and 15% of $BaCO_3$ showed a good sulfate resistance in spite of the clinker containing 14 wt% of C_3A (Bogue calculation) (Carmona-Quiroga 2015).

Addition of $BaCO_3$ to Portland cement interferes with the hydration reactions of clinker aluminates because of the two competitive reactions that take place: gypsum with the barium salt and gypsum with C_3A. Whereas $BaCO_3$ neither regulates the speedy reaction of C_3A with water nor reacts with the aluminate, gypsum + $BaCO_3$ blends are able to regulate C_3A hydration giving rise to barite, and calcium carboaluminate hydrates precipitation from the earliest ages of hydration (Gismera Díez *et al.*, 2015).

The aim of this work is to study the mechanical behavior and mineralogical evolution along one year of two cements with different C_3A content, plus gypsum and $BaCO_3$ when they are submitted to sulfate attack.

2. Experimental

2.1. Raw Materials

The commercial clinkers used were provided by Molins (clinker M) and Valderribas (clinker V). Table 1 gives the data on the chemical composition determined by X-Ray fluorescence (Bruker S8 TIGER XRD) and its potential composition based in Bogue equations, as described in Spanish standard [UNE 80304:2006]

Tab. 1 Chemical (XRF) and mineralogical composition (Bogue calculations) of both clinker /%

	Compositions	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	K_2O	SO_3	Na_2O	C_3S	C_2S	C_3A	C_4AF
M	Content	21.2	3.1	5.0	65.7	1.7	1.0	1.2	0.15	60	16	8	9.4
V	Content	20.2	3.1	6.2	63.1	3.46	1.08	1.15	0.12	57.2	14.8	11.2	9.4

The optimal amount of gypsum to produce cements from these clinkers was determined. The industrial Clinkers (M and V) were mixed with 5% (wt) and 7% (wt) of gypsum respectively giving laboratory cements called MG and VG.

In order to establish the effect of the barium in the sulphate attack, previously both M and V clinker were mixed with 15% (wt) of $BaCO_3$. After that it was necessary to determine the minimum amount of gypsum to regulate the setting time of the new cements. Different proportions of gypsum, 1, 2, 3, 4, 5 or 6% (by weight) were added to the 85% clinker + 15% $BaCO_3$ and setting time and consistency water were determined [UNE EN 197-1] concluding that 3% (wt) is the minimum amount of gypsum to setting regulation.

For the previous laboratory cements (MG and VG) and new laboratory cements (MGW and VGW), water demand, setting time and consistency were determined (Table 2).

Tab. 2 Composition and physical characteristics of cements

Cement name	Clinker	Clinker (wt%)	Gypsum (wt%)	$BaCO_3$ (wt%)	Water demand (l/s)	Consistencia	Fraguado	
							Inicio	Final
MG	M	95	5	0	0.27	36 mm	2h 22’	3h 42’
MGW	M	82.45	3	14.55	0.245	32 mm	4h 31’	6h 41
VG	V	93	7	0	0.3	30mm	2h 20’	3h 25’
VGW	V	82.45	3	14.55	0.28	34 mm	2h 10’	4h 20’

Gypsum substitution (5 or 7wt%) by 3% (wt) gypsum + 14.55% (wt) $BaCO_3$, decreases the amount of water necessary to get normal consistency and increases final setting time.

Calcium sulfate ($CaSO_4 \cdot 2H_2O$), sodium sulfate (Na_2SO_4) and barium carbonate ($BaCO_3$) were laboratory reagents.

2.2. Experimental Process

Prismatic mortars using aggregate/sand ratio 1/3 and water/cement ratio 0.5 were prepared with the four laboratory cement (MG, MGW, VG, VGW) and added into 10x10x60 mm size moulds. Samples were cured at 25°C and 99% R.H. for 21 days, and subsequently they were submerged in water (control) or a 4.4% Na_2SO_4 solution. Specimens were removed and tested for flexural strength after 1, 3, 5, 7 and 12 months. Mineralogical composition of the samples was determined by XRD (2.2-kW Bruker D8 Advance diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) (CuKα1 radiation: 1.5406 Å and CuKα2 radiation: 1.5444 Å; operating parameters, 40 kV and 30 mA; 2h recording range 5°–70°; step size, 0.02. Morphological analysis after 7 months of exposure in the aggressive solution was analysed by SEM/EDX (Hitachi S-4800 field-emission scanning electron microscope (FESEM; Hitachi High-Technologies Corporation, Tokyo, Japan) equipped with a Bruker nano energy-dispersive X-Ray spectrometer (XFlash Detector 5030; Bruker Nano GmbH, Berlin, Germany), operating at a voltage of 20 kV.

3. Results and Discussion

3.1. Mechanical Properties

Flexural mechanical strength values of the samples after 21 days of curing were 11.09 ± 0.73 and 10.06 ± 0.4 MPa for the samples with the clinker M without and with witherite MG and MGW respectively. For the cement prepared with clinker V the flexural strength values were 10.06 ± 0.48 and 8.32 ± 0.48 MPa, for the samples VG and VGW respectively. Then it is clear that mechanical strength values of cements prepared with clinker M are higher than for cements with clinker V.

After immersion in the aggressive solution the flexural strength of the samples MGS and MGWS increases until 210 days and afterwards a decrease is observed until 1 year in contact with the aggressive solution. This behavior is related to the gypsum an ettringite formation in MGS and Gypsum in MGWS, according to results from XRD patterns (not showed). Sample MGWS shows better mechanical behavior than MGS, due to the protective effect of witherite to sulfate attack.

It should be noted that after 12-months the flexural strength decreases in the sample MGWH, that is, the sample with the pair gypsum + witherite but submerged in water, not in the aggressive solution, while the sample without witherite, MGH, does not shows strength decreases

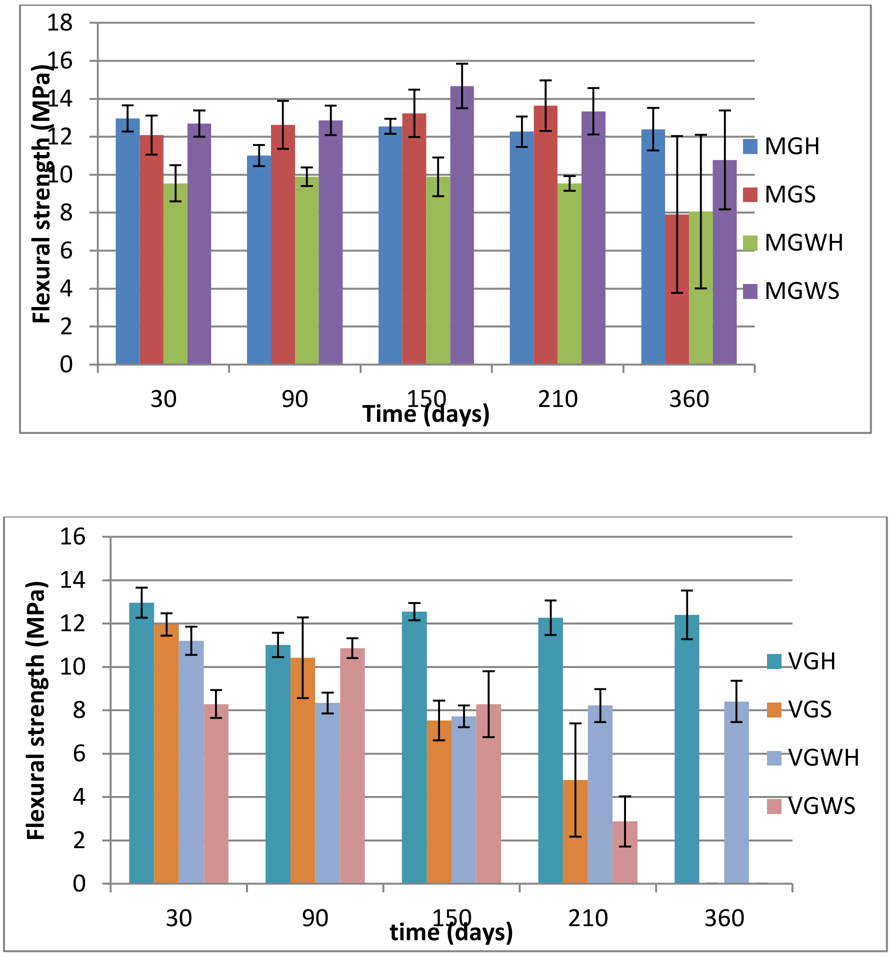


Figure 1 Flexural strength of the mortar samples

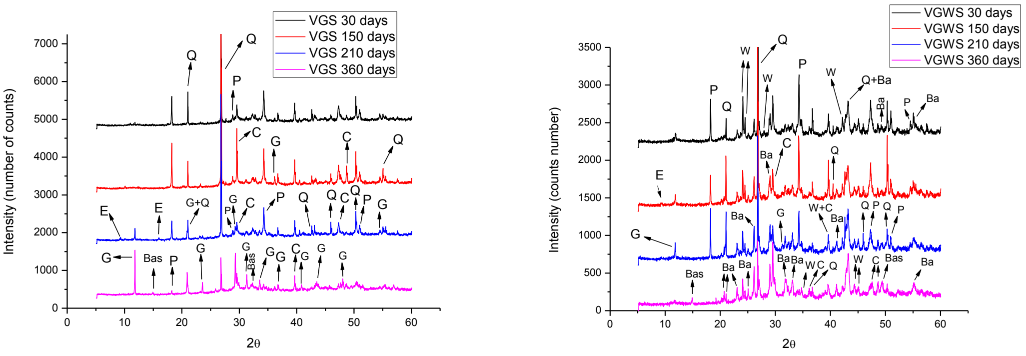
Nevertheless, for the cement prepared with clinker V (VGS and VGWS), a gradual strength decreases is noticed in all the samples, excepted for the references (without witherite and submerged in water), what is more, samples breaking after 360 days in sulfate solution (Figure 1).

3.2. Mineralogical composition

To found out about the cause of the breaking of the samples V immersed in the aggressive solution of sodium sulfate (VGS and VGWS) (Figures 2), a mineralogical study of the testes specimen were done. For the samples without witherite (VGS) it can be observed that gypsum diffraction lines increase from 1 to 12 months while those of portlandite decrease. Figure 3 presents enlargement of the diffractogram in the interval 2θ = 6º-20º and it can be 1-month hemicarboaluminate precipitation that evolve to ettringite and monosulfoaluminate formation with time; however after 360 days none of previous phases is present in the samples but gypsum is formed in a very high proportion. In turn, portlandite consumption with time is observed.

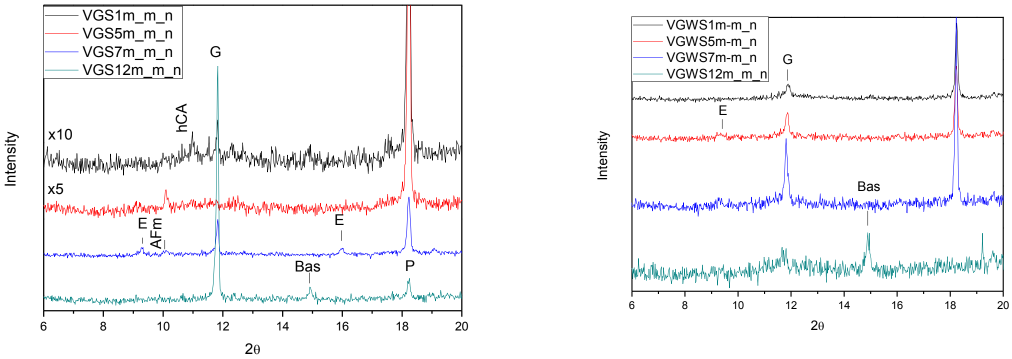
For the samples with witherite, carboaluminate phases have not been formed, but traces of ettringite and small amounts of gypsum are present from, almost, the first month in the sulfate solution immersion. XRD pattern of MGWS sample after 360 days of immersion presents intense reflections assigned to $BaSO_4$ together to those due to $BaCO_3$, while no reflections from portlandite are observed. This indicates that, $BaCO_3$ have reacted with sulfate from aggressive medium according to reaction [1], while it has neither avoided the precipitation of bassanite nor the mechanical deterioration of the mortar prisms. From the thermodynamic point of view (Carmona-Quiroga *et al.*, 2011) witherite is incompatible with ettringite and gypsum or bassanite however small diffraction lines from gypsum or bassanite or ettringite are present in XRD pattern of samples. This can be evidence that, for some reason, witherite fail in the complete protection to sulfate attack, therefore a SEM study of the samples before breaking, 210 days, was proposed.

$$BaCO_3 + Ca(OH)_2 + SO_4^{=} \rightarrow BaSO_4 + CaCO_3 + 2OH^- \quad [1]$$



(a) VGS (b) VGWS

Figure 2 XRD patterns evolution with immersion time in Na_2SO_4 solution. Q = quartz; P = portlandite; C = calcite; G = $CaSO_4 \cdot 2H_2O$; E = ettringite; Bas = $CaSO_4 \cdot 0.5H_2O$; W = $BaCO_3$; Ba = $BaSO_4$.



(a) VGS (b) VGWS

Figure 3 XRD patterns evolution with immersion time in Na_2SO_4 solution in the interval 2θ = 6º-20º. hCA = monocarboaluminato; E = ettringite; G = $CaSO_4 \cdot 2H_2O$; P = portlandite; Bas = $CaSO_4 \cdot 0.5H_2O$; AFm = monosulfoaluminato

3.3 SEM/EDX

Scanning electron microscopy with elemental analysis was used to do the microstructural study of the mortars. Samples of mortar prisms prepared with clinker V (VGS) and submerged in sulfate aggressive solution for 210 days shows some fissure with gypsum and ettringite inside that can explain flexural strength decreases and the following breaking of the specimens after 12 months (Figure 4).

For the specimens with Ba in its composition and immersed in the sulfate solution for 12 months the only small amounts of gypsum could be identified, but some agglomeration of ettringite could be observed in the sand-paste interface (Figure 5).

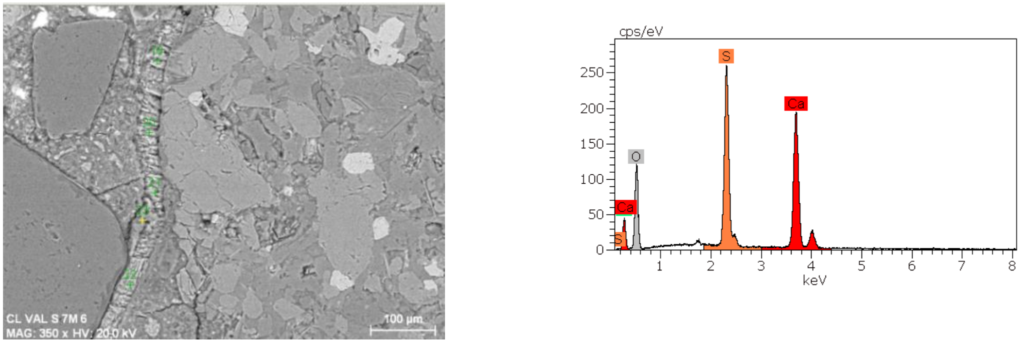


Figure 4 SEM of the VGS specimes after 12 months immersion in sulphate solution. EDX analysis of deposits on the crack.

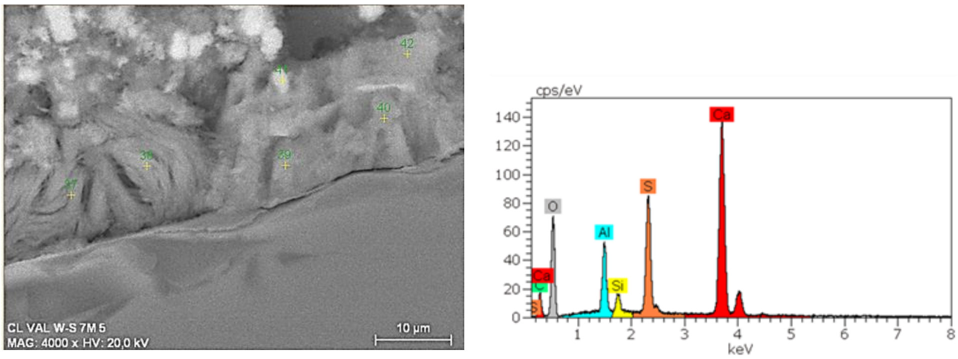


Figure 5 SEM of the VGWS specimen after 12 months immersion in sulphate solution. EDX analysis of ettringite on the interface .

On the other hand a lot of witherite agglomerations have been observed (Figure 6) that can be an indication that salt distribution it is not randomly, and it is not homogeneous spread out. Then the specimens are not properly protected against sulfate attack as expected. This inhomogeneous distribution of the $BaCO_3$ can justify gypsum and ettringite presence in spite of their thermodinamic incompatibility with witherite.

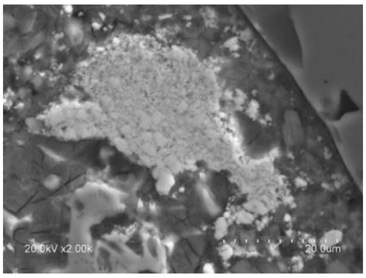


Figure 6 SEM images of whiterite agglomerations in the sample VGWS 210-days immersed in sulphate solution.

4. Conclusions

Behavior against sulfate of several cements prepared with two different clinkers containing 8 or 11% of C_3A and gypsum or gypsum + witherite used as setting regulators, were studied. The main conclusions that can be draw from the results are the following:

Cement setting can be regulated with 3 wt % of gypsum and 14.55 wt % of $BaCO_3$ mixture.

None of the cements elaborated with clinker with 8 wt% of C_3A break after 12 months immersed in 4.4 wt% Na_2SO_4 solution although flexural strength decreases, to a greater extent in the specimens prepared without $BaCO_3$. At this age laboratory cement specimens manufactured with the clinker having the highest amount of C_3A (11 wt%), with and without $BaCO_3$, have been broken.

Main deterioration products in the broken samples were gypsum or bassanite. $BaCO_3$ presence prevent ettringite formation and reduce calcium sulphate (as gypsum or bassanite) formation.

The $BaCO_3$ inhomogeneous distribution can be the reason of the fault in specimen protection against sulfate attack. Researches about a proper system to get the homogenous distribution of $BaCO_3$ in the cement have to be carried out.

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