Use of barium carbonate to inhibit sulfate attack in cements

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A B S T R A C T

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 wt.% $BaCO_3$ remained practically unaltered after 5 months in contact with the aggressive solution, whereas the control mortars (clinker + 15 wt.% gypsum) underwent severe deterioration after only 5 weeks.

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1. Introduction

$BaCO_3$ (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 C_3S 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 $BaCO_3$ inhibits primary ettringite formation [9,10] or destabilises this salt [11]. It may also immobilise external sulfates [12] by forming barium sulfate, along with $CaCO_3$. 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 [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 ($3CaO·Al_2O_3·CaCO_3·11H_2O$). 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 ($3CaO·Al_2O_3·3CaSO_4·32H_2O$), thaumasite ($CaCO_3·CaSO_4·CaO·SiO_2·15H_2O$) or gypsum ($CaSO_4·2H_2O$) [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 wt.% 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 $Ca(OH)_2$ content in cements by adding supplementary cementitious materials (SCMs) that consume $Ca(OH)_2$ 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

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Table 1
Chemical (XRF), potential (Bogue) and mineralogical (Rietveld) composition of white clinker (wt%) (L.O.I. = loss on ignition; I.R. = insoluble residue).

L.O.I.	I.R.	SiO$_2$	CaO	MgO	Fe$_2$O$_3$	Al$_2$O$_3$	SO$_3$	CaO Free	Na$_2$O	K$_2$O	Cl$^-$
0.06	0.03	22.36	69.42	0.85	0.34	5.66	0.51	1.32	0.23	0.29	0.01

% phase	Rietveld (ICSD code)	Bogue
	Rwp = 10.57	
C$_3$S	66.61 (94742)	68.79
C$_2$S	4.82 (81096)	12.22
C$_3$A	5.28 (1841)	14.44
C$_4$AF	–	1.02
Amorphous content	23.29	

Table 2
TG 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 (100 °C)	0.76	0.47	0.35	0.38
H$_2$O (Ca(OH)$_2$)	–	0.24	0.19	0.17
CO$_2$ (CaCO$_3$)	–	0.33	0.34	0.37
CO$_2$ (BaCO$_3$) (*in 2 stages)	18.72	–	2.10*	3.02*
Residual loss	–	0.22	–	0.19
Total	19.48	1.27	2.99	4.14

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$_4$). New industrial uses of BaCO$_3$ would require further research to analyse any potential health and environmental impacts [22].

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 [23], HCl-insoluble residue [24] and loss on ignition at 1000 °C were likewise found. The Bogue equations [25] were used to establish the potential mineralogical composition of the clinker and Rietveld quantitative analysis [26] was conducted on the XRD findings using GSAS
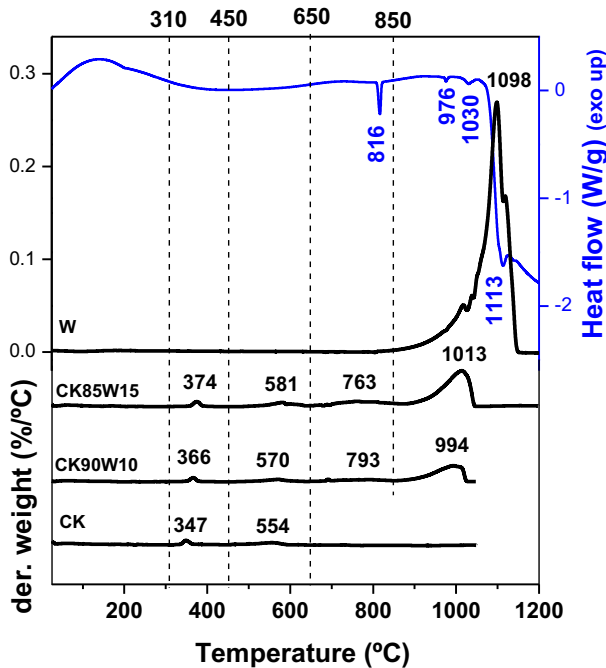
software [27] with an internal standard (corundum). The clinker diffraction pattern was recorded with a 2.2-kW Bruker D8 Advance diffractometer (CuKα1 radiation: 1.5406 Å; CuKα2 radiation: 1.5444 Å; operating parameters, 40 kV and 30 mA; 2θ recording range: 5–70°; step size, 0.02°). The parameters refined 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.% BaCO$_3$ (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 N$_2$-77 K 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 1 × 1 × 6 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 wt.% clinker/5 wt.% 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) Na$_2$SO$_4$ 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 with or without internal standard. 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/min. 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; and 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

Fig. 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).

Table 3
BET surface area (m^2/g) and particle mean size 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