EFFECT OF BaCO₃ ON C₃A HYDRATION

S. Gismera-Diez, B. Manchobas- Pantoja, 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

Ba ions are known to immobilise sulfates by forming BaSO₄. The use of witherite (BaCO₃) as a full or partial substitute for gypsum to regulate C₃A (3CaO•Al₂O₃) hydration was consequently studied with a view to establishing its correct dosage in sulfate-resistant cements presently under development.

The hydration rate of synthetic C₃A was determined in the presence of varying percentages of gypsum, witherite, and gypsum+witherite by running conduction calorimetry analyses on early age (20-h) samples. The hydration products were subsequently identified with XRD, FTIR and DTA/TG.

The addition of (20-42wt%) witherite to C₃A neither regulated the speedy reaction of the latter with water nor reacted with the aluminate. Gypsum+witherite blends proved able to regulate C₃A hydration. The heat flow curves for all the samples studied exhibited an induction period, an indication that gypsum acted as a C₃A hydration regulator while at the same time reacting with witherite to form barite.

Keywords: (A) Hydration; (A) Calorimetry; (D) Ca₃Al₂O₆; BaCO₃

---

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

1. Introduction

Recent studies have shown that, like conventional SR cements, new sulfate-resistant (SR) cements containing witherite (BaCO_3) are able to inhibit the precipitation of expansive ettringite [1,2]. Unlike the former, however, witherite-bearing cements can also prevent thaumasite formation [3] in CEM I cements exposed to external sulfate attack. They owe that capacity to the presence of Ba^{2+} ions in solution, which remove the sulfates from the medium by precipitating as highly stable, insoluble barite (BaSO_4). The present study aimed to determine whether this addition could partially or fully replace gypsum as a setting regulator, thereby limiting or avoiding the inclusion of an additional source of sulfates in cement. To that end, the experiments were conducted on the clinker phase that reacts most intensely with water, C_3A ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$).

C_3A reacts with water so speedily and exothermally that in the absence of a regulator cement setting and hardening is too rapid to yield a workable end product. The hydration products initially formed, metastable hexagonal hydrates (C_2AH_8 , C_4AH_{13}), evolve into stable cubic katoite (C_3AH_6) [4]. To retard C_3A hydration, then, gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$) has traditionally been added to clinker, for it reduces the hydration rate and induces ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$) precipitation. Ettringite is a stable cement hydration product, but only if a sufficient amount of sulfate is available. In solutions with a low SO_4^{2-} concentration, ettringite tends to evolve into calcium monosulfoaluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$), which is metastable at ambient temperature.

In the absence of gypsum, CaCO_3 expedited C_3A hydration. The hexagonal hydrates (C_2AH_8 , C_4AH_{13}) formed first reacted with CaCO_3 to yield calcium

monocarboaluminate hydrate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$), preventing the generation of cubic hydrates (C_3AH_6) that precipitated only after all the CaCO_3 was consumed [4].

Studies exploring the total or partial replacement of gypsum with limestone in cement have found that at replacement rates of up to 25 %, neither setting behaviour nor compressive strength were adversely affected [5]. The calcium monocarbonate hydrate that forms in the presence of limestone has been observed to be more stable than calcium monosulfate hydrate, raising ettringite stability [6]. Moreover, these conditions hasten the initial hydration reaction [6,7] and reduce setting times [7].

Zhang and Zhang [8] reported that C_3A setting time could be controlled not only by gypsum but also by a combination of gypsum and CaCO_3 in suitable proportions (partial substitution of CaCO_3 for $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ at a rate of 20–60 %). In the presence of CaCO_3 , mixes induced ettringite and calcium monocarboaluminate hydrate but not katoite precipitation.

A few studies also have addressed the partial or total replacement of gypsum with BaCO_3 in cement [9,10]. Dumitru et al. [9] attributed the longer setting times observed to the high water content used to prepare the pastes and to the retarding effect of BaCO_3 . The gypsum in the OPC reacted with the BaCO_3 , inducing the formation of monocarboaluminates and large quantities of BaSO_4 . Ettringite formation was suppressed [9,10]. The effect of barium nitrate on inhibiting OPC hydration by forming insoluble compounds has been also studied [11,12].

XRD studies on 7-day samples showed that in the absence of gypsum, BaCO_3 retarded C_3A hydration [13]. In its presence, BaCO_3 accelerated C_3A hydration, inhibited ettringite formation and induced substantial BaSO_4 precipitation [13].

The present study aimed to know the role played by BaCO_3 in the C_3A hydration, in the presence and absence of gypsum. The ultimate objective is to contribute to establishing the grounds for the appropriate use of BaCO_3 in the development of a new type of sulfate-resistant cements. To that end, C_3A -witherite and C_3A -witherite-gypsum reactions as well as the competitive reactions between gypsum and witherite were analysed using calorimetric, XRD, DTA/TG and FTIR methods

2. Experimental

Laboratory reagents $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Merck) and BaCO_3 (Sigma Aldrich) together with synthetic C_3A were the materials used in this study.

C_3A was synthesised by heating a stoichiometric ratio of 3:1 of (Merck) calcium carbonate and (Scharlau) aluminium oxide at 1450 °C for 14 hours. The C_3A synthesised was characterised with X-ray diffraction (XRD) and Fourier transform infrared spectroscopic techniques. Its XRD pattern shows the reflections of cubic C_3A (JCPDS 38-1429) and traces of free lime (JCPDS 037-1497). Its FTIR spectrum shows the absorption bands of cubic C_3A and a very weak signal at 3644 cm^{-1} due to O-H stretching vibration of portlandite revealing a slight weathering of the sample.

The XRD trials were conducted on a Bruker D8 Advance X-ray diffractometer fitted with a high voltage, 3-kW generator and a (1.54-Å CuK) copper anode X-ray tube normally operating at 40 kV and 50 mA. FTIR scans were performed on a Thermo

Scientific Nicolet 600 spectrometer at frequencies of from 4000 to 400 cm^{-1} and a spectral resolution of 4 cm^{-1} . The samples were prepared as potassium bromide pellets with 1 mg of sample per 300 mg of KBr.

The mean diameter (Table 1) and particle size distribution (Figure 1) were found for the C_3A , witherite (W) and gypsum (G) on a Sympatec Helos 12 KA laser ray diffraction spectrometer with a 5-mW He/Ne laser lamp. The samples were dispersed in isopropyl alcohol by stirring for 30 seconds and ultrasound for 60. The BET specific surface was determined on a Micrometrics ASAP 2010 analyser using N_2 as the adsorption gas.

Gypsum and witherite were mixed at a molar ratio of 1:1 (1 gram) in 5 ml of Milli-Q water at 25 $^{\circ}\text{C}$ to find their reaction rate. The samples were subsequently stored at that temperature for 0.5, 1, 1.5, 2, 4, 24, 120 and 720 hours, after which the reaction was detained with acetone. These samples were characterised with XRD, FTIR and DTA/TG. Differential thermal analysis (DTA) was conducted on a TA Instruments SATQ600 analyser able to simultaneously record DTA and TG data. The samples were heated from ambient temperature to 1200 $^{\circ}\text{C}$ in air at a rate of 10 $^{\circ}\text{C}/\text{min}$.

PHREEQC (version 2.7.1.1) speciation software (USGS) was used to determine the saturation index and phases speciation in the $\text{CaCO}_3\text{-BaSO}_4\text{-H}_2\text{O}$ closed system at 25 $^{\circ}\text{C}$ [14]. The solubility product data for the compounds were taken from Stronach [15], with the exception of barium hydroxide [16] and barytocalcite [17].

Analyses of hydration in blends of synthetic C_3A with different percentages of gypsum (control samples with 10, 15, 20 and 30 wt%; Panreac), witherite (20, 30 and 42 wt%;

Sigma Aldrich) and gypsum plus witherite combined (5:5 wt%; 5:15 wt%; 10:10 wt%; 10:20 wt%; 15:5 wt%; 15:15 wt% and 20:10 wt%) were run on a Thermometric TAM isothermal conduction calorimeter. The same solid-liquid ratio (0.7) was used in all the mixes, which were stirred manually for 3 minutes before placement in the calorimeter, where they were kept for 20 hours at 25 °C. The samples were subsequently immersed in acetone to detain hydration and the products were characterised using the aforementioned XRD, FTIR and DTA/TG analysers.

3. Results and discussion

3.1. Gypsum-witherite reaction

It is very well known that gypsum added to cement regulates the rate of C₃A hydration and by that avoids flash setting. However when witherite (BaCO₃) is added to cement, two competitive hydration reactions may take place: gypsum with the barium salt and gypsum with C₃A. Figure 2 shows the association of solid phases in equilibrium with a solution, at the invariant points (only Ba concentration is shown) in the CaO-BaO-CaCO₃-CaSO₄-H₂O system at 25 °C. The figure displays that gypsum is incompatible with witherite, so that they react to yield barite and CaCO₃ (Equation 1). Table 2 shows the dissociation equations and the corresponding solubility constants of the phases in the mentioned system and gives the composition of the calcite-barite equilibrium solution. Sulfur concentration of a gypsum saturated solution is 15.17 mmol/kg [15] and after the reaction of gypsum and witherite, decreases about three orders of magnitude. If the reaction rate of gypsum - BaCO₃ is very quick, many sulfate ions will be removed from the solution at early ages and the C₃A hydration rate could proceed out of control.

149

151

152 XRD characterisation (not shown here) of the gypsum plus witherite reaction products
153 at the selected ages showed that the gypsum-witherite reaction began within the first 30
154 minutes, giving rise to barite and calcite. According to [10], that means that despite
155 witherite's very low solubility (0.0014 g/100 cc), the solution contained more Ba^{2+} ions
156 than required to yield the BaSO_4 solubility product after only 30 minutes. All the
157 gypsum and nearly all the witherite were consumed in the first month, although the
158 reaction reached near completion (minimum presence of gypsum) after just 5 days.

159

160 The infrared spectra (not shown here) corroborated the XRD findings. The bending
161 bands generated at 610 and 635 cm^{-1} by the SO_4 groups in the barite [19] intensified
162 with reaction time, along with the CO_3 group bending vibrations in calcite, which
163 appeared at 876 cm^{-1} within the first 30 minutes. Moreover, the intensity of the signal
164 characteristic of the CO_3 groups in witherite, at 856 cm^{-1} declined, while the OH
165 stretching bands at 3545 cm^{-1} , indicative of gypsum, nearly disappeared.

166

167 Lastly, the TG curves (Figure 3) used to quantify the degree of gypsum and witherite
168 reaction exhibited essentially three mass loss episodes except in the oldest sample,
169 where only the second was clearly visible. In the first stage, gypsum dehydration took
170 place at around 130 °C. Calcite decarbonation occurred in a second stage, between 600
171 and 900 °C. Lastly, witherite decomposed in the third stage, i.e., at upward of 900 °C.

172 The DSC curves exhibited endothermal peaks associated with the polymorphic

transformation of barite (between 1129 and 1158 °C) and the phase decomposition mentioned previously.

Further to the thermogravimetric findings (Figures 3 (right) and 4), the gypsum - witherite reaction proceeded rapidly in the first 4 hours. One-quarter of the initial gypsum was consumed within the first 30 minutes, and nearly half after one hour [20]. The reaction took place essentially within the first 4 hours (degree of gypsum reaction, 84 %) and was complete in the sample analysed after 1 month (720 hours).

Consequently, in cements containing witherite and gypsum both, gypsum effectiveness as a setting regulator would be lessened, given the existence of two competing reactions: gypsum with C₃A on the one hand and with witherite on the other. Nonetheless, since the gypsum-witherite reaction lasted several hours, the gypsum could continue to regulate C₃A hydration during that time frame.

3.2 Hydration of C₃A with gypsum

While the role of gypsum in retarding C₃A hydration is well known, the present study yielded reference calorimetric curves for mixes of synthetic C₃A and different percentages of gypsum in the first 20 hours of hydration (Figure 5). These curves exhibited two peak heat flow rates. It is in general believed [21,22] that the first one is the result of species dissolution and ettringite precipitation (Equation 2) and the second one of the reaction described in Equation 3, which took place after gypsum consumption. This second signal was delayed and widened with rising gypsum content.

201 Gypsum retarded hydration so effectively that in the 20-hour duration of the trial, the
202 peak for the Equation 3 reaction was not observed in the sample with the highest
203 gypsum content (Figure 5, left). Nonetheless, the maximum gypsum dosage added to
204 this system was not high if compared to the proportion in portland cement, which
205 normally contains around 11 % C₃A [23] and 5 % gypsum [24].

206

207 Quennoz et al. [21] and Minard et al. [25] attributed this decline in the reaction rate to a
208 decrease in the reactive surface area of C₃A, as a result of its surface contamination by
209 calcium or sulfate ions that would block dissolution sites. That would explain why on
210 the total heat curves (Figure 5, right) the heat released rose visibly after the gypsum was
211 consumed, for with no sulfate ions in the medium, the C₃A would re-dissolve and react
212 with ettringite (Equation 3).

213 The heat released by C₃A after 20 hours of hydration in the absence of gypsum was
214 lower than in the samples with gypsum (except for the sample containing 39 %
215 gypsum), in all likelihood because the unreacted C₃A content was greater.

216

217 The diffractograms for C₃A hydrated in the absence of gypsum (Figure 6), show the
218 Katoite reflections as hydration product but also lines characteristics of anhydrous C₃A,
219 which would explain the low total heat of hydration observed (Figure 5, right).

220 Unreacted C₃A was also detected in all the gypsum-containing mixes.

221

Where the gypsum content was 20 % or less, monosulfoaluminate precipitated with hemicarboaluminate, an indication of slight sample carbonation. Katoite only precipitated in the presence of ≤ 15 % gypsum. Monosulfoaluminate with 11 water molecules also formed in the samples containing 15 and 20 % gypsum (Figure 6).

The diffractogram for the sample with the highest gypsum content (39 %) exhibited gypsum, ettringite and C_3A (Figure 6). The excess gypsum would have inhibited the reaction described in Equation 3, which would explain the absence of the respective reaction peak from the heat flow curve for this sample.

FTIR analyses of the samples confirm XRD results and yielded further data. The infrared spectra for the C_3A hydrated in the presence of 10 and 15 % gypsum (Figure 7) were similar. In addition to the vibration signals characteristic of aluminates, whose presence was detected by XRD, other weak signals (shoulders at 604 and 3513 cm^{-1}) attributed to a small fraction of gypsum not found with that technique were also identified. The band at 3677 cm^{-1} was attributed to O-H group stretching vibrations in monosulfoaluminate or (sample weathering-induced) carboaluminate. Further evidence of the presence of monosulfoaluminate was the existence of ν_2 (at 422 cm^{-1}) and ν_3 (1100-1170 cm^{-1}) vibration bands attributed to SO_4 groups, while carboaluminate was detected primarily on the grounds of asymmetric C-O stretching bands at around 1400 cm^{-1} [26,27]. When the replacement ratio was 20 %, the SO_4 groups stretching signal at around 1100 cm^{-1} was observed to intensify.

The spectrum for C_3A hydrated with 39 % gypsum (Figure 7) differed from the spectra for the preceding samples, with: significant overlapping between the gypsum and

ettringite SO_4 group vibrations at 1116 and 604 cm^{-1} ; the disappearance of the signals attributed to monosulfoaluminate and monocarboaluminate (3677, ≈ 1400 , 1163 cm^{-1}); and the appearance of other new signals at 3630 cm^{-1} (O-H stretching, ettringite) and 1681 cm^{-1} (O-H deformation, gypsum and ettringite).

3.3 Hydration of C_3A with BaCO_3

Figure 8 (left) shows the heat flow curves for C_3A in the presence of BaCO_3 , which exhibited essentially a single peak produced during the very early age of hydration. Nonetheless, in the first 10 hours, a slight inflection was observed in the total heat curves for the samples with 30 and 42 % witherite, denoting some minor activity on the part of that carbonate. The total heat from C_3A hydration rose when witherite was added, an indication that the salt raised the degree of C_3A hydration, at least in the first 20 hours.

The XRD findings for the C_3A -witherite mixes (Figure 9) showed that barium carbonate barely reacted with C_3A in the first 20 hours, during which katoite was the primary precipitate. The appearance of a second, low intensity heat flow rate peak and a minor inflection on the total heat curve at approximately 10 hours (Figure 8) may have been related to the episodic presence of calcium monocarboaluminate hydrate (Figure 9).

A comparison of the relative areas of the katoite/ C_3A diffraction lines in the 20 hour C_3A and $\text{C}_3\text{A}+\text{BaCO}_3$ samples showed that the ratio was much higher in the samples with the barium salt, confirming that witherite accelerated C_3A hydration, as suggested by the calorimetric data. The degree of reaction of C_3A in the 20-hour samples

calculated from thermogravimetric (TG) observations (Table 3) rose steeply with the addition of BaCO₃.

According to the literature, C₃A hydration is expedited with the addition of CaCO₃, which reacts with hexagonal hydrates to yield calcium monocarboaluminate hydrate, retarding katoite formation [4]. While witherite fails to react with C₃A hydrates, it hastens both their hydration and katoite formation. Several authors [8,28] have reported that the addition of very fine materials to cements accelerates early age hydration and some [29] have suggested that filler particles act as heterogeneous nucleation sites to precipitate more or less crystallised hydrates, thereby expediting hydration.

Witherite might, then, be regarded as inert filler that would expedite C₃A hydration because its specific surface, double the surface in C₃A, would afford numerous nucleation sites.

The spectra for C₃A hydrated with varying percentages of witherite (Figure 10) exhibited vibrations generated by the following phases: witherite (at 1444, 1059, 857, 845 and 693 cm⁻¹) [1]; C₃A, C₃AH₆, and monocarboaluminate (3544 cm⁻¹), barely detectable with XRD, and most certainly due to sample weathering.

3.4 Hydration of C₃A with gypsum and BaCO₃

All the heat flow curves recorded for mixes containing C₃A and gypsum+witherite exhibited an intense initial dissolution peak, followed by a period of low thermal activity and subsequent acceleration and deceleration.

297

298 The inclusion of 10, 20 and 30 % gypsum+withelite yielded heat flow curves in which
299 the hydrate precipitation peak appeared earlier than on the curve for C₃A and gypsum
300 only. This effect was more intense with declining gypsum content (Figures 11 and 12).
301 For instance, the peak appeared at 245 minutes in sample C₃A+15 %G+5 %W, at
302 130 minutes in sample C₃A+10 %G+10 %W and at 52 minutes in the mix containing
303 C₃A+5 %G+15 %W (Figure 11). Moreover, when the gypsum content was the same and
304 the proportion of withelite varied, the peak appeared at practically the same time
305 (approximately 50 minutes in samples C₃A+5 %G+5 %W and C₃A+5 %G+15 %W;
306 Figure 11).

307

308 Therefore, while C₃A hydration was expedited by withelite, it could be controlled by
309 adding gypsum to the mix as well.

310

311 The XRD findings for the C₃A-withelite- gypsum mixes (Figure 13), showed that
312 barite precipitated along with a significant amount of calcium monocarboaluminate
313 hydrate, the result of the reaction between the C₃A and the calcium carbonate released
314 in barite formation (Equation 1 and 4). Katoite continued to precipitate in the samples
315 (albeit only as traces in the C₃A+15 %G+5 %W mix), however, and anhydrous C₃A was
316 detected in all cases.

317

319

321

An excess of carbonate (non-decomposed witherite, gypsum/witherite<1) inhibited calcium hemicarboaluminate hydrate formation. Moreover, the only samples where (low intensity) reflections for calcium monosulfoaluminate, ettringite and barite were recorded were the ones with a higher gypsum/witherite ratio. Utton et al. [10] noted that ettringite and BaSO₄ formation took place simultaneously, competing for the sulfate ions present in the solution, despite the differences in their solubility. They suggested that ettringite decomposes into monocarboaluminate and barite, in addition to calcite (CaCO₃) (Equation 5).

Since ettringite forms in the first few minutes of hydration and, further to the present findings, substantial amounts of gypsum were present for up to 4 hours, ettringite (Equation 2), barite (Equation 1), and calcium monocarboaluminate hydrate (Equation 4) may have formed simultaneously, whereas the reaction described by Utton et al. (Equation 5) may have taken place after all the gypsum was consumed. As none of the samples studied here contained calcite (CaCO₃), the reaction described in Equation 5 may be assumed to have concurred with calcium monocarboaluminate hydrate formation (Equation 4).

The spectra for C₃A hydrated in the presence of gypsum+witherite (Figure 14) confirmed the XRD findings. All the spectra exhibited more or less intense bands due to calcium monocarboaluminate hydrate or the calcium monosulfoaluminate hydrate, as well as bands indicative of the presence of anhydrous C₃A, C₃AH₆. The signals

characteristic of the SO_4 group ν_3 vibrations in barite ($1075\text{--}1180\text{ cm}^{-1}$) [19] were very well defined when the gypsum or witherite content was over 5 %, and more diffuse otherwise.

Witherite was detected only on the spectra for samples containing $\text{C}_3\text{A}+5\text{ \%G}+15\text{ \%W}$ and $\text{C}_3\text{A}+10\text{ \%G}+20\text{ \%W}$. The higher is witherite amount the greater is katoite content.

4. Conclusions

The present findings contribute to a fuller understanding of the role of BaCO_3 in C_3A hydration, with a view to the development of future sulfate-resistant cement.

- In an aqueous medium at $25\text{ }^\circ\text{C}$, the reaction between witherite and gypsum to yield barite and CaCO_3 is relatively quick, for after 4 hours 20 % gypsum remained in the sample.

- The addition of (20-42 wt%) witherite to C_3A neither regulated the speedy reaction of the latter with water nor reacted with the aluminate. The presence of witherite expedited C_3A hydration to C_3AH_6 , while the degree of reaction rose with the witherite content.

- A combination of gypsum and witherite can regulate C_3A hydration. The heat flow curves recorded here exhibited a period of low thermal activity, indicating that gypsum regulates the C_3A hydration rate while simultaneously reacting with witherite to form barite.

- In the $\text{C}_3\text{A}\text{--}\text{BaCO}_3\text{--}\text{CaSO}_4\cdot 2\text{H}_2\text{O}\text{--}\text{H}_2\text{O}$ system, the hydration products depend on the dosage and the gypsum/witherite ratio. With the dosages used in this study, the majority hydrate was C_3AH_6 , while barite and calcium carboaluminate hydrate appeared in all the samples. When the gypsum/witherite molar fraction was greater than 1, calcium sulfoaluminate hydrate also precipitated.

Acknowledgements

Funding from the Spanish Ministry of Education and Science (Project CONSOLIDER CSD2007-00058) and the Regional Government of Madrid (Geomaterials Programme2 S2013/MIT-2914) is gratefully acknowledged

References:

- [1] P.M. Carmona-Quiroga, M.T. Blanco-Varela. Ettringite decomposition in the presence of barium carbonate, *Cem. Concr. Res.* 52 (2013) 140–148.
- [2] P.M. Carmona-Quiroga, M.T. Blanco-Varela. Use of barium carbonate to inhibit sulfate attack in cements. *Enviado a Cem. Concr. Res.*
- [3] P.M. Carmona-Quiroga, M.T. Blanco-Varela, Prevention of sulfate-induced thaumasite attack: thermodynamic modeling in BaCO₃-blended cement, *International Congress on Materials & Structural Stability*, Rabat (Morocco) 27-30 November 2013.
- [4] B. El Elaoui, M. Benkaddour, Hydration of C₃A in the presence of CaCO₃, *J. Therm. Anal.* 48 (1997) 893-901.
- [5] J. Bensted, Some hydration investigations involving Portland cement –effect of calcium carbonate substitution of gypsum, *World Cement.* 10 (8) (1980) 395–406.
- [6] B. Lothenbach, G. Le Saout, E. Gallucci, K. Scrivener, Influence of limestone on the hydration of Portland cements, *Cem. Concr. Res.* 38 (2008) 848–860.
- [7] V.S. Ramachandran, Cement with calcium carbonate additions, *Proceedings of the 8th Internat. Congr. Chem Cem.*, Rio de Janeiro, 5, 1986, pp. 178–182.
- [8] Y. Zhang, X. Zhang, Research on effect of limestone and gypsum on C₃A, C₃S and PC clinker system, *Constr. Build. Mater.* 22 (2008) 1634–1642.
- [9] G. Dumitru, T. Vázquez, F. Puertas, M^a. T. Blanco Varela, Influencia de la adición del BaCO₃ sobre la hidratación del cemento portland, *Mater. Constr.* 49 (1999) 43-48.
- [10] C.A. Utton, E. Gallucci, N.B. Milestone, Interaction between BaCO₃ and OPC/BFS composite cements at 20°C and 60°C, *Cem. Concr. Res.* 41 (2011) 236-243.
- [11] H.G. McWhinney, M.W. Rowe, D.L. Cocke, J.D. Ortego, Gu-Sheng Yu, X-ray photoelectron and FTIR spectroscopy investigation of cement doped with barium nitrate, *J. Environ. Sci. Health A25* (5) (1990) 463–477.

- [12] S.K. Ouki, C.D. Hills, Microstructure of Portland cement pastes containing metal nitrate salts, *Waste Manage.* 22 (2) (2002) 147–151.
- [13] G. Dumitru, T. Vázquez, F. Puertas, M. T. Blanco Varela, Influence of BaCO₃ on the hydration of C₃A, 10th Intern. Congr. Of the Chem. Of Cem. (Gothenburg). 3 (1997) 5pp.
- [14] D.L. Parkhurst, C.A.J. Appelo, User's guide to PHREEQC (Version 2), U.S. Geological Survey, 1999.
- [15] S.A. Stronach, Thermodynamic Modelling and Phase Relations of Cementitious Systems, Thesis (PhD), University of Aberdeen, 1996.
- [16] E. Generalic, M. Bralic, S. Brinic, Faculty of chemistry and Technology, Split (Croatia). <http://www.ktf-split.hr/periodni/en/abc/kpt.html>
- [17] F. Mackenzie, A. Lerman, Mineralogy, chemistry and reactions kinetics of the major carbonate phases. *Carbon in geobiosphere* Vol 25, 89-121, 2006
- [18] P.M. Carmona-Quiroga, S. Martínez- Ramírez, M.T. Blanco-Varela, Thermodynamic stability of hydrated Portland cement phases in the presence of Barium Carbonates, Ed. A. Palomo, A. Zaragoza, J.C. López Agüí. XIII ICCI International congress on the chemistry of cement. Madrid, 3-8 de Julio de 2011
- [19] V.C. Farmer, The infra-red spectra of minerals, Mineralogical Society. Monograph 447 4, Adlard & Son Ltd, London, 1974.
- [20] Instrucción para la recepción de cementos RC-08
- [21] A. Quennoz, K. L. Scrivener, Hydration of C₃A–gypsum Systems, *Cem. Concr. Res.* 42 (2012) 1032–1041.
- [22] S. Pourchet, L. Regnaud, J.P. Perez , A. Nonat, Early C₃A hydration in the presence of different kinds of calcium sulphate, *Cem. Concr. Res.* 39 (2009) 989–996.
- [23] H.F. W. Taylor. *Cement Chemistry*. Thomas Telford, London, 2004.
- [24] EN 197-1: 2011. Cement - Part 1: Composition, specifications and conformity criteria for common cements
- [25] H. Minard, S. Garrault, L. Regnaud, A. Nonat, Mechanisms and parameters controlling the tricalcium aluminate reactivity in the presence of gypsum, *Cem. Concr. Res.* 37 (2007) 1418–1426.
- [26] T. Vázquez- Moreno, Contribución al estudio de las reacciones de hidratación del cemento portland por espectroscopía infrarroja, tesis doctoral, 1975
- [27] L. Fernández-Carrasco, T. Vázquez, Aplicación de la espectroscopía infrarroja al estudio de cemento aluminoso, *Mater. Constr.* 46 (1996) 53–65.
- [28] G. Kakali, S. Tsivilis, E. Aggeli, M. Bati, Hydration products of C₃A, C₃S and Portland cement in the presence of CaCO₃, *Cem. Concr. Res.* 30 (7) (2000) 1073-1077.
- [29] E.H. Kadri, S. Aggoun, R. Duval, Influence of grading and diameter size of admixture on the mechanical properties of cement mortars, in: V. Bilek, Z. Kersner (Eds.) *Proceedings of the International Symposium on Non-Traditional Cement and Concrete*, Brno, 2002, pp. 306– 313.

Table 1. Mean particle size and specific surface of C₃A, witherite (W) and gypsum (G)

	C₃A	W	G
Mean particle size (μm)	13.54	3.29	13.69
BET specific surface (m ² /g)	0.708±0.012	1.6316±0.01	0.675±0.013

Table 2. Model-predicted composition of the calcite-barite equilibrium solution at 25 °C (mmol/kg) and the logarithms of the thermodynamic solubility products (Log K).

Mineral	Dissolution reaction				Log K
Barite	$\text{BaSO}_4 = \text{Ba}^{2+} + \text{SO}_4^{2-}$				-9.970
Witherite	$\text{BaCO}_3 = \text{Ba}^{2+} + \text{CO}_3^{2-}$				-8.562
Barium Hydroxide	$\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O} = \text{Ba}^{2+} + 2 \text{OH}^- + 8 \text{H}_2\text{O}$				-3.593
Gypsum	$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O} = \text{Ca}^{2+} + \text{SO}_4^{2-} + 2 \text{H}_2\text{O}$				-4.60
Calcite	$\text{CaCO}_3 = \text{CO}_3^{2-} + \text{Ca}^{2+}$				-8.41
Barytocalcite	$\text{BaCa}(\text{CO}_3)_2 = \text{Ba}^{2+} + \text{Ca}^{2+} + 2 \text{CO}_3^{2-}$				-17.68
Portlandite	$\text{Ca}(\text{OH})_2 + 2 \text{H}^+ = \text{Ca}^{2+} + 2 \text{H}_2\text{O}$				22.815
mmol/kg	Ba	Ca	C	S	pH
Calcite+barite	1.161e ⁻⁰⁰²	1.214e ⁻⁰⁰¹	1.214e ⁻⁰⁰¹	1.161e ⁻⁰⁰²	9.914

Table 3. Aluminate content and degree of C₃A hydration in samples hydrated for 20 hours at 25 °C (calculated with TG data)

	C₃A (wt%)	C₃AH₆ (wt%)	Witherite (wt%)	α
Hydrated C ₃ A	50.3	49.7	-	0.41
C ₃ A + 20% W	29.4	52.9	17.4	0.56
C ₃ A+ 42% W	12.9	49.9	36.6	0.73

Figure 1. Particle size distribution curves of C₃A, witherite (W) and gypsum (G).

Figure 2. Each circular ring represents the association of stable phases (the coloured ones) at invariant points in system Ca-Ba-SO₄-CO₃-H₂O. The association of phases has been ordered according to the Ba content of the dissolutions in equilibrium with the phases (in ascending order from the inner circle, shown in mmol/kg)

Figure 3. DSC (left) and TG (right) curves for a gypsum/witherite blend (1:1) at several reaction times

Figure 4. Witherite and gypsum consumption and calcite formation during the gypsum-witherite (1:1) reaction at 25 °C (data from TG).

Figure 5. Heat flow (left) and heat of hydration (right) for C_3A with 0, 10, 15, 20 and 39 wt% $CaSO_4 \cdot 2H_2O$.

Figure 6. XRD patterns for C_3A with 0, 10, 15, 20 and 39 % gypsum; AF_t =Ettringite, AF_m =calcium monosulfoaluminate hydrate ($C_4A\check{S}H_{12}$), S_t = $C_4A\check{S}H_{11}$, G =gypsum, C = C_3A , K =katoite, O = C_2AH_8 , H_c = hemicarboaluminate.

Figure 7. FTIR spectra for C_3A with 0, 10, 15, 20 and 39 % gypsum; C=carbonation, *=contamination.

Figure 8. Heat flow (left) and heat of hydration (right) for C_3A with 20, 30 and 42 % witherite (W).

575

576

577

578

579

580

Figure 9. XRD patterns for C_3A with 20, 30 and 42 % witherite; Mc=calcium monocarboaluminate hydrate, W=witherite, C= C_3A , K=katoite.

581

582

583

Figure 10. FTIR patterns for C_3A with 20, 30 and 42 % witherite; *=contamination.

Figure 11. Heat flow (left) and heat of hydration (right) for C_3A with 20 % gypsum, 20 % witherite, and mixes with a total of 10 or 20 % of gypsum and witherite.

Figure 12. Heat flow (left) and heat of hydration (right) for C_3A with 30 % witherite, and various ratios of 30 % gypsum-witherite.

Figure 13. XRD patterns for hydrated C_3A containing gypsum and witherite. Left: total replacement rates of 10 and 20 wt%.; right: total replacement rates of 30% wt.; Mc=monocarboaluminates, W=witherite, C= C_3A , K=katoite, H_c =hemicarboaluminate, AF_m =monosulfoaluminate, AF_t =ettringite, B=barite, O= C_2AH_8 .

Figure 14. FTIR for C_3A with varying percentages of witherite+gypsum
*=contamination.