

ROLE OF TERNESITE ON THE HYDRATION OF C₃A IN THE PRESENCE AND ABSENCE OF GYPSUM

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ABSTRACT

In the search for new eco-cements it has been found that ternesite ($2C_2S \cdot CaSO_4$), which has traditionally been regarded as a hydraulically inactive phase, can be activated by aluminum hydroxides (AH₃) and some calcium aluminates. This research, in particular, studies the role of ternesite on C₃A hydration, with and without gypsum. After laboratory synthesis, C₃A was blended with ternesite, gypsum and ternesite+gypsum. The early hydration of those blends was monitored with isothermal conduction calorimetry at 25 °C for 7 days. The resulting pastes were analysed with XRD, FTIR and DTA/TG. Additionally, mixtures of C₃AH₆ and ternesite in water were prepared in order to study their compatibility. The calorimetric results showed a higher total heat per gram of aluminate in the sample containing gypsum and ternesite than in the sample C₃A+ternesite. XRD diffractograms and DTG-TG analysis revealed the presence of AFm in all the samples with gypsum but not in C₃A+ternesite which shows no evidence of ternesite activation by C₃A.

1. INTRODUCTION

It was not until 2013 when it was proven that ternesite ($C_5S_2\bar{5}$), a mineral found as crusts in areas of the kiln where temperature reaches less than 1250°C (Ben Haha et al. 2015) or in belite containing CSA cements with and excess of anhydrite and in which temperatures reach $\leq 1200^\circ\text{C}$ (Bullerjahn et al. 2015), has hydraulic activity in the presence of amorphous AH₃ as reported by Bullerjahn et al. (2014) yielding ettringite, strätlingite and C-S-H as hydration products.

Synthetic calcium aluminates such as $C_{12}A_7$, CA and $C_4A_3\bar{5}$ (ye'elimite), which are among the variable phases of CSA clinkers, activate ternesite with varying degrees of effectiveness as shown by Montes et al. (2018). $C_{12}A_7$ and CA activate ternesite more intensively than ye'elimite, yielding the former two the same hydration products, AFm ($C_3A \cdot C\bar{5} \cdot H_{12}$) and strätlingite ($C_2A_5H_8$) and the latter AH₃ and AFm.

Recent studies (Montes et al., unpubl.) on the influence of gypsum in the reactivity of blends of ternesite with $C_{12}A_7$ or CA revealed that ternesite is still activated by both aluminates but the presence of other source of sulfates reduces its reactivity. On the hydration of CSA clinkers containing ternesite, the phase is active (Bullerjahn et al. 2015). However, it also was reported that the oversaturation of $Al(OH)_4^-$ in the pore solution and the presence of sulfates, different from gypsum and anhydrite, can hinder ternesite dissolution (Bullerjahn et al. 2014).

Given the increasing interest of CSA binders as reduced-carbon footprint cements, studies on the reactivity of ternesite are of special relevance as shown by recent developments of "belite-(ferrite)-ye'elimite-ternesite" cements (Dienemann et al. 2013; Gartner & Hirao, 2015). However, there is still insufficient knowledge on the reactivity of ternesite as the hydration kinetics varies notably depending on the amount of sulfates in the systems. To gain more knowledge, in this study was explored the role of gypsum on the reactivity of ternesite in the ternary system, ternesite+C₃A+gypsum.

2. EXPERIMENTAL

C₃A and ternesite were synthesised from stoichiometric blends of laboratory-grade CaCO₃, SiO₂, Al₂O₃ and gypsum (CaSO₄·2H₂O) and their phase purity, verified by the Rietveld refinement method: ternesite (94.0 % C_5S_2 + 6.0 % C_2S) and C₃A (100%). Particle size distribution of ternesite, C₃A and gypsum was determined on a Malvern Mastersizer S particle size analyser fitted with 632.8 nm He-Ne laser optics (Figure 1) being their respective mean diameter (D[4,3]) 35.13; 21.17 and 107.14 μm.

Blends of C_3A +gypsum, C_3A +ternesite and C_3A +ternesite+gypsum were prepared to the following ratios by weight: C_3A /gypsum=2.5/0.5; C_3A /ternesite=1/2; and C_3A /gypsum/ternesite = 1/0.2/1.8 and mixed with water in a liquid/solid ratio = 0.7. The hydration of the samples (3 grams of solid and 2.1 g of water) at 25°C was monitored on a Thermometric TAM Air isothermal conduction calorimeter for 7 d.

To stop hydration, crushed samples were submerged in acetone for 10 min followed by gentle vacuum for 1 h to eliminate the solvent and then characterized on a Bruker D8 Advance X-ray diffractometer (2θ range=5-60°; step size=0.019746°; step time= 0.5 s); a Thermo Scientific Nicolet 600 FTIR spectrometer (spectral resolution=4 cm^{-1}); and a TA Instruments Q600 TGA-DSC-DTA differential gravimetric analyser (T range=ambient to 1000°C; ramp rate=10°C/min; nitrogen flow rate=100 mL/min).

A supplementary study on the compatibility of C_3AH_6 with ternesite was carried out through FTIR spectroscopy. First, C_3AH_6 was obtained by hydrating the synthesized C_3A (5g C_3A in 200ml water) at 80 °C with magnetic stirring for 10 days. Most of the XRD reflections of the synthetic phase were attributed to C_3AH_6 with small peaks assigned to C_3A and calcium monocarboaluminate hydrate. Through TG-DTG analysis, which shows a main inflection in its DTG curve at 286°C, its purity was quantified: 86% C_3AH_6 , 7.9% C_3A and 6% calcium monocarboaluminate hydrate. Ternesite and C_3AH_6 were mixed on a stoichiometric ratio of 1:1 with excess of water and stirred for another 10 days at room temperature when the reaction was stopped as previously described.

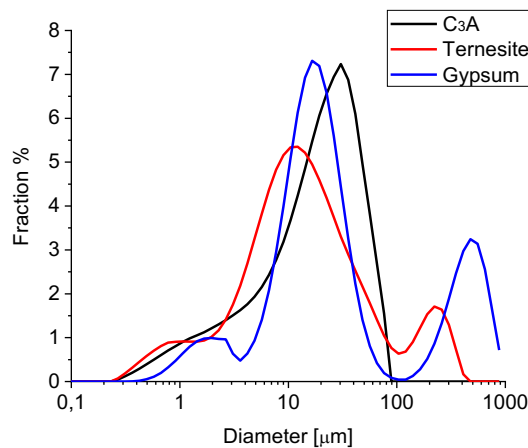


Figure 1. Particle size distribution of synthetic C_3A and ternesite and of commercial gypsum (From Montes et al. 2018)

3. RESULTS

3.1 Isothermal conduction calorimetry

Figure 2 shows the heat flow and heat of hydration curves for C_3A with ternesite and gypsum+ternesite per gram of aluminate at $25^\circ C$. For sample of C_3A mixed with ternesite there is only an exothermal peak due to the species dissolution after which heat flow slowly declines to zero at 7.5 hours. On C_3A +gypsum+ternesite blend, the decrease of the heat flow after dissolution was more abrupt reaching 0.002 W/g at 4 hours, however as it happens in C_3A +gypsum systems (Pommersheim & Chang, 1988) after the induction period, that lasted 6 hours, a second exothermal peak was recorded as a result of gypsum consumption. Until the appearance of that second peak at 10 hours, total heat released by C_3A +ter blend was higher than that of C_3A +ter+gyp mix. After that, more heat was emitted by C_3A +ter+gyp than C_3A +ter and after 7 days, the total heat released per gram of aluminate by the former blend was 1.8 times higher than that of the latter.

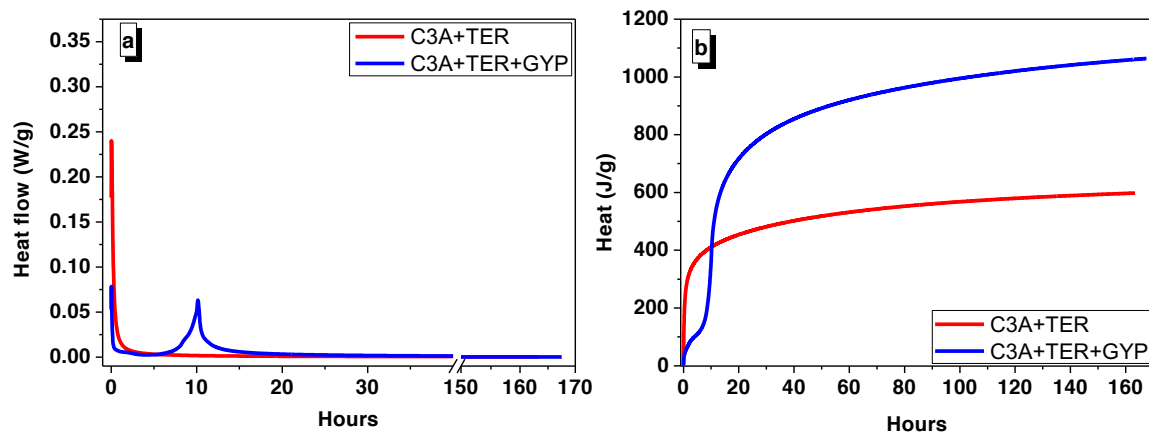


Figure 2. Heat flow (a) and heat of hydration (b) curves of C_3A +ternesite and C_3A +ternesite+gypsum at $25^\circ C$ per gram of aluminate

3.2 XRD

The XRD patterns for the 7-day pastes, C_3A +ternesite, C_3A +ter+gyp and C_3A +gypsum as a reference are shown in Figure 3 with the one of synthetic ternesite.

The main hydration product for 7-day C_3A +gypsum mix was AFm-12 ($C_3A.C\bar{5}.H_{12}$) accompanied by C_4AH_{19} and calcium hemicarboaluminate ($C_3A.C\bar{C}_{0.5}.H_{12}$) as reported in literature (Black et al. 2006) and unreacted C_3A .

The diffractogram for the C_3A +ternesite paste mainly exhibited reflections attributed to the anhydrous phases. The presence of poorly crystallized hemicarboaluminate and C_3AH_6 as it points the broadness of their respective strongest peaks $2\theta\ 10.8^\circ$ and 17.3° was also recorded.

On the XRD pattern of the C_3A +ter+gyp paste were identified peaks associated with AFm-12, poorly crystallized hemicarboaluminate, ternesite and C_3A .

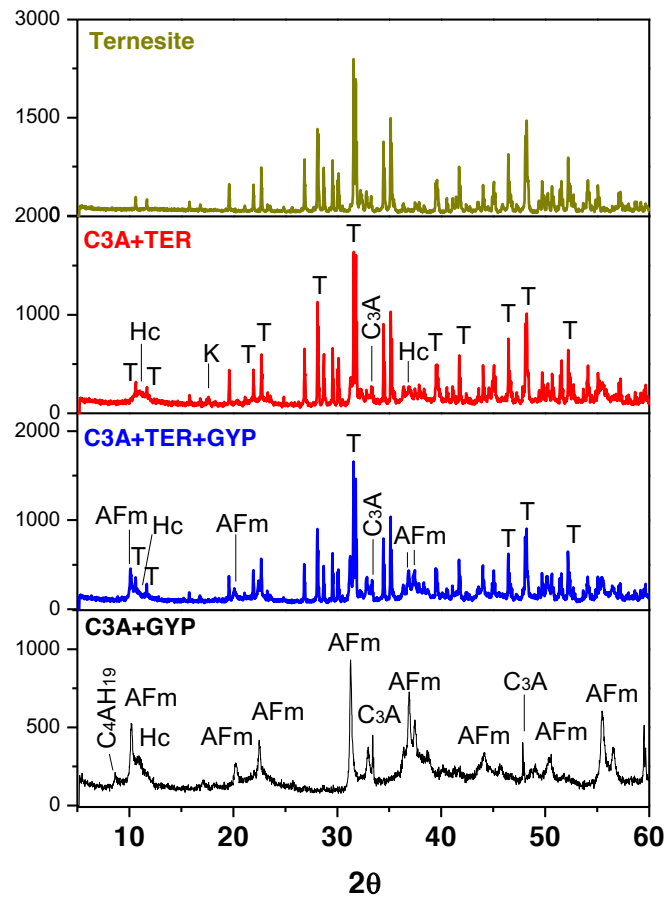


Figure 3. XRD patterns for ternesite and 7-day hydrated pastes: C₃A+ternesite C₃A+gypsum+ternesite, C₃A+gypsum. T=ternesite; AFm = calcium monosulfoaluminate hydrate; Hc = calcium hemicarboaluminate hydrate; K= C₃AH₆

To further identify the presence of poorly crystalline hydrates, FTIR spectra of the aforementioned 7-day pastes were also recorded (Figure 4).

The three spectra exhibited O-H stretching bands in the 4000-3000 cm⁻¹ range and a band at 1650 cm⁻¹ from H-O-H bending generated by hemicarboaluminate and monosulfoaluminate hydrates. Bands in the region of 1450-1300 cm⁻¹ are attributed to the vibration of CO₃²⁻ groups, specifically signal at 1368 cm⁻¹ is characteristic of hemicarboaluminate (Horgnies et al. 2013).

In C₃A+ter and C₃A+ter+gyp were identified some of the characteristics band of ternesite at 1153, 1121 and between 947-837 cm⁻¹ (Chukanov 2014). Regarding C₃A, its presence was only observed in samples containing ternesite (band at 894 cm⁻¹; Fernández-Carrasco et al. 2012).

At 1100 cm^{-1} in $\text{C}_3\text{A}+\text{gyp}$ and $\text{C}_3\text{A}+\text{ter}+\text{gyp}$ was identified the characteristic S-O stretching band of SO_4^{2-} groups in calcium monosulfoaluminate hydrate and below 900 cm^{-1} , they were recorded Al-O vibrations generated by calcium aluminate hydrates.

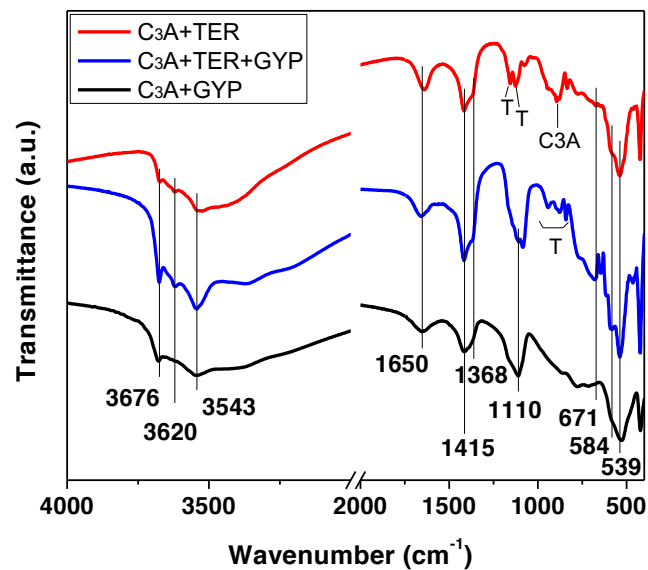


Figure 4. FTIR spectra for 7-day hydrated pastes: $\text{C}_3\text{A}+\text{ternesite}$ $\text{C}_3\text{A}+\text{gypsum}+\text{ternesite}$, $\text{C}_3\text{A}+\text{gypsum}$

To explore the hydraulic activity of ternesite in the presence of C_3AH_6 , FTIR spectrum of $\text{C}_3\text{AH}_6+\text{ter}$ paste hydrated for 10 days was also recorded (Figure 5). No products of hydration were identified, only bands attributed to the individual species blended together (C_3AH_6 main distinctive signal at 3664 cm^{-1} ; Horgnies et al. 2013); ternesite characteristic bands at $1155, 1123, 945, 876$ and 517 cm^{-1} (Chukanov 2014)) which indicated that bot phases are compatible.

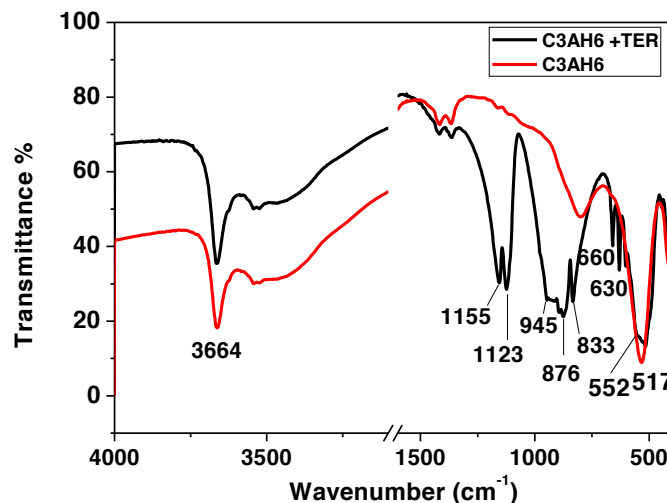


Figure 5. FTIR spectrum of synthetic C_3AH_6 and of $\text{C}_3\text{AH}_6+\text{ternesite}$ paste hydrated for 10 days

3.3 TG-DTG

Finally, TG-DTG analyses were carried out on 7-day hydrated pastes (Figure 6). Results are consistent with previous findings. Only on the samples containing gypsum, $\text{C}_3\text{A}+\text{gyp}$ and $\text{C}_3\text{A}+\text{ter}+\text{gyp}$, were

identified the main peaks of loss of interlayer water of AFm (81, 111 and 171°C; (Lothenbach et al. 2017)).

On the three pastes, main dehydration peak of hemicarboaluminate was recorded at 149°C and its CO₂ loss above 800°C (Huang et al. 2014). Dehydroxylation weight loss of aluminium hydroxide mainly from AFm and hemicarboaluminate was identified between 200-300°C also in all the samples (Lothenbach et al. 2017).

In C₃A+ter, the presence of C₃AH₆ was inferred from the inflection in DTG curve at 276°C. AH₃ could also be present as an amorphous phase (Zhang et al. 2018)

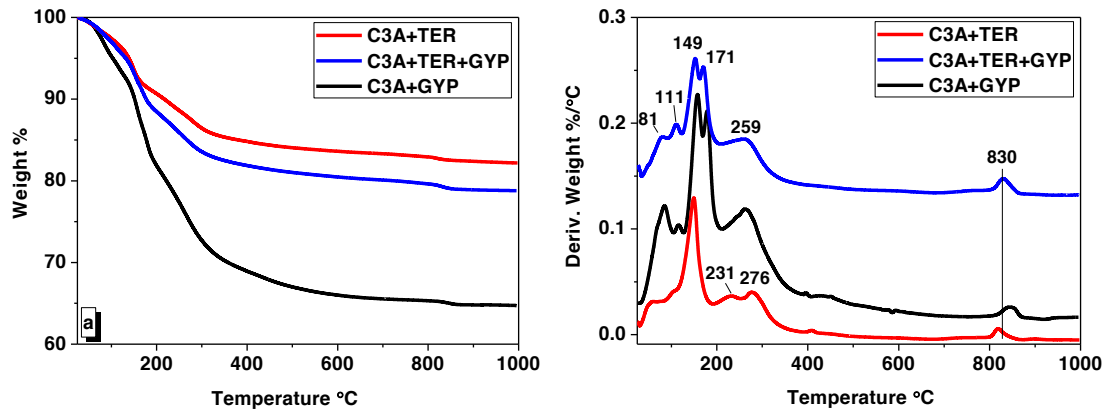


Figure 6. TG (a) and DTG (b) analysis of C₃A+gypsum; C₃A+ternesite and C₃A+ternesite+gypsum (DTG curves vertical displaced for better visualization)

4. DISCUSSION

Heat flow curves of samples containing C₃A+ ternesite exhibited a single exothermal dissolution peak, unlike analogous samples with C₃A+ternesite+gypsum and C₃A+gypsum systems that shows a second one after gypsum consumption as described in the literature (Quennoz & Scrivener 2012). After 7 days of hydration in samples with gypsum and with and without ternesite, AFm-12 is the main hydration product as found through XRD, FTIR and TG analysis whereas for C₃A+ternesite they were C₃AH₆ and calcium hemicarboaluminate (C₃A.C \bar{C} _{0.5}.H₁₂). Unreactive ternesite and C₃A were also found after 7 days in their respective blends. From these results, no evidence of ternesite activation can be reported in the presence of C₃A, regardless of the gypsum content unlike CA and C₁₂A7 that recently were found to be ternesite activators, specially in the absence of gypsum. Ternesite hydration in the presence of those aluminates yielded AFm and strätlingite with the amount of undissolved ternesite being 59-75% at 7 days (Montes et al. unpubl.). In the presence of another ternesite activator, AH₃, ettringite precipitation was reported (Ben Haha et al. 2015).

Neither can C₃AH₆ activate ternesite after 10 days of hydration as also found with infrared spectroscopy since no reaction products were formed.

5. CONCLUSIONS

Further to XRD, FTIR, TG-DTG and calorimetric analyses, C₃A cannot be regarded to activate ternesite at 25°C for 7 days in its own and therefore neither in the presence of gypsum. Neither C₃AH₆ in the absence of gypsum after 10 days of hydration is a ternesite activator.

Ternesite hydration in the presence of C₃A produces C₃AH₆ and calcium hemicarboaluminate (C₃A.C \bar{C} _{0.5}.H₁₂) whereas in the presence of C₃AH₆.no hydration products apart from the hydrated aluminate precipitated. The reaction of ternesite with C₃A and gypsum yields also calcium hemicarboaluminate hydrate, due to the contact of the paste with atmospheric CO₂, and calcium

monosulfoaluminate hydrate ($C_3A.C\bar{S}.H_{12}$) as a result of C_3A and gypsum reaction that raises the heat of hydration per unit of aluminate in C_3A paste with ternesite at 25°C.

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