Study on the activation of ternesite in $\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ blends with gypsum for the development of low- CO_2 binders

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ARTICLE INFO

Article history:

Received 22 April 2020

Received in revised form

8 December 2020

Accepted 26 December 2020

Available online 30 December 2020

Handling editor: Prof. Jiri Jaromir Klemes

Keywords:

Ternesite

C_{12}A_7

CA

Hydration

Gypsum

Calcium aluminate cements

ABSTRACT

This study aimed primarily to broaden the limited knowledge presently at hand about ternesite, $5\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{SO}_3$ (shorthand $\text{C}_5\text{S}_2\bar{\text{S}}$, ter), reactivity in calcium sulfoaluminate-calcium aluminate (CSA-CAC) blended cements by exploring the hydration of the constituents of simplified $\text{CaO} \cdot \text{Al}_2\text{O}_3$ (CA) + $5\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{SO}_3$ (ter) + $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum, gyp) or $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ (C_{12}A_7) + $5\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{SO}_3$ (ter) + $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gyp) systems.

According to earlier research, ternesite, a mineral constituent in some eco-efficient calcium sulfoaluminate cements, may be activated during the hydration of $\text{Al}(\text{OH})_3$ or other calcium aluminates. The extent to which such activation may be affected by the presence of calcium sulfate (gypsum) in CSA cements is not currently known, however.

The present findings showed that ternesite is activated by both C_{12}A_7 and CA in the presence and absence of gypsum, although less intensely in its presence. Calorimetric analysis revealed that ternesite favours calcium aluminates reactivity with water in the presence and absence of gypsum because its surface serves as a nucleation site where aluminate hydrates cluster just minutes after the reaction begins. The mineralogical characterisation of the aluminate pastes bearing gypsum and ternesite was consistent with thermodynamic modelling, which predicted the same hydration products in both, although with different stability ranges.

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1. Introduction

Ordinary portland cement (OPC) manufacture is an energy and raw material-intensive process that contributes to air pollution, accounting for 7% of anthropogenic CO_2 (Nidheesh and Suresh Kumar, 2019), (0.87t CO_2 /t clinker) (Hanein et al., 2018). One of the industry's alternative approaches to contribute to sustainable development is to manufacture a lower energy consumption binder such as calcium sulfoaluminate (CSA) cement, which requires temperatures of 1250 °C, 200 °C lower than OPC clinker that also involves the reduction of the needed limestone content for the clinker production between 15 and 45% (Bullerjahn et al., 2015).

CSA clinkers are positioned in lower calcium and silicon oxide and higher alumina and sulfate areas of the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{Fe}_2\text{O}_3-\text{CaSO}_4$ system than Portland cement clinkers. Hanein et al. (2018) calculated the CO_2 footprint of the production of various CSA and standard PC clinkers in a cradle-to-

gate approach through a simplified life cycle assessment and found that CSA formulations can reduce net emissions by 25–35% relative to OPC, these values largely vary as a function of the composition of the clinkers. Given the resultant abatement in greenhouse gas emissions, CSA cements can be deemed to be an eco-efficient material (Ben Haha et al., 2019; Hanein et al., 2018).

CSA clinkers can be used to make blended cements with fly ash or blast furnace slag allowing for further CO_2 reductions while improving their dimensional stability (Gao et al., 2019; Shen et al., 2018). Furthermore CSA cements are combined with OPC for special field applications that allow achieving a fast setting and rapid hardening or not shrinkage (Chaunsali and Mondal, 2015; Le Saoût et al., 2013).

Special purpose cements include binary blends such as OPC and calcium aluminium cement (CAC) used to manufacture shotcrete (Gu et al., 1997; Lemay et al., 2014) and CSA and CAC, designed for application as self-levelling mortars (Li et al., 2018; Nehring et al., 2018). Ternary binders bearing portland cement, calcium aluminate and calcium sulfate (gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), used as adhesives for tile flooring adhesives and self-levelling screeds, exhibit

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properties that distinguish them from products made with OPC or CAC only (Lamberet et al., 2008; Xu et al., 2017). Such systems, in which the prevalent phase is ettringite, are characterised by rapid setting and strength development, prevention of CAC hydrate conversion (and concomitant decline in mechanical strength), water solubility and dimensional soundness (offsetting drying shrinkage) (Xu et al., 2017; Li et al., 2016). Variations in ternary cement hydration and durability with OPC/CAC and CAC/CaSO₄ ratios have likewise been studied (Moffatt and Thomas 2018; Torrns-Martin et al., 2013; Martinez-Ramirez and Fernandez-Carrasco 2012; Lamberet 2005).

In line with research that pursues lower-carbon binders, the present study forms part of a project aiming to develop new, alternative (to OPC) special purpose cements containing CAC, gypsum and low-energy CSA as raw materials. Possible advances in the understanding of new cement blends in which CAC could be used to activate ternesite-containing CSA clinkers are contingent upon understanding the activating effect of aluminate phases and the impact of adding more calcium sulfate for subsequent CSA-CAC blend optimisation. Whilst both CAC and CSA are more costly than OPC to manufacture, the former are more competitive in terms of CO₂ emission costs (Gartner, 2004). If such alternative systems are to have a perceptible impact on global CO₂ emissions, however, they will have to exhibit the same or better mechanical performance and durability than OPC, given the (at least initial) higher cost to the consumer (Gartner, 2004). That, in turn, will entail intensive research.

The minerals contained in CSA cements normally include C₄A₃ $\bar{S}$ (ye'elimite), C₂S, C $\bar{S}$, C₄AF, and as minor phases some calcium aluminates (such as CA, the prominent hydraulic phase in CAC, C₁₂A₇ and C₃A) (Bullerjahn et al., 2015; El Khessaimi et al., 2019; Winnefeld and Lothenbach, 2016). Ternesite (C₅S₂ $\bar{S}$; ter) is also found as a constituent in some sulfo-belite and CSA cements (Blanco-Varela and Carmona-Quiroga 2018; Al Horr et al., 2017; Marroccoli et al., 2010; Sherman et al., 1995) as well as in cement kiln crusts in the areas where the temperature is under 1250 °C. Note that standard cement phase notation abbreviations (C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃, $\bar{S}$ = SO₃, $\bar{C}$ = CO₂, H = H₂O) are used throughout this paper.

Specifically, ternesite forms in the reaction between anhydrite and belite at temperatures under 1290 °C, whilst new (one- (Hanein et al., 2017) or two-phase (Bullerjahn et al., 2014, 2015)) procedures have recently been described to obtain clinkers containing this phase at temperatures of under 1250 °C. Its development during firing has been also recently explored (Dvořk et al., 2020). Ternesite releases less CO₂ (0.79 t of CO₂ per tonne of phase, 0.42 t attributable to decarbonation + 0.28 t to combustion) than ordinary calcium silicate cements (such as C₃S, with 0.92 t CO₂/t phase = 0.58 t + 0.34 t), although more than some calcium aluminates (e.g. CA: 0.26 t + 0.34 t = 0.60 t CO₂/t phase) (Gartner, 2004; Ludwig and Zhang, 2015). Factors that affect its formation apart from the cooling rate are the content of SO₃ and the presence of mineralisers (phosphates or fluorides) (Bullerjahn et al., 2014).

Although some authors deem ternesite to be non-hydraulic in studies on the hydration of calcium sulfoaluminate binders (Sherman et al., 1995), recent researches have shown that it can play a relevant role in determining the hydration kinetics of these cements (Bastos da Costa et al., 2016), since its reactivity is strongly affected by the presence of Al(OH)₃ and sulfates in dissolution (Dienemann et al., 2013). So lately, ternesite activation by aluminium hydroxides or certain calcium aluminates has been reliably proven (Ben Haha et al., 2015; Bullerjahn et al., 2014; Montes et al., 2018). Bullerjahn et al. (2014) and Ben Haha et al. (2015) showed that the presence of amorphous aluminium

hydroxide (AH₃) activates ternesite, yielding strtlingite (C₂ASH₈), C–S–H gel and AFm (calcium monosulfoaluminate hydrate; C₄A $\bar{S}$ H₁₂) or ettringite (C₆A $\bar{S}$ ₃H₃₂) depending on the sulfate content in the medium, all phases with cementitious properties. Montes et al. (2018) showed that calcium aluminates such as C₁₂A₇, CA and C₄A₃ $\bar{S}$ also activate ternesite to varying degrees of effectiveness. Both C₁₂A₇ and CA activate ternesite intensively in the absence of other sources of sulfates, yielding C₂ASH₈ and AFm as hydration products. C₄A₃ $\bar{S}$, in contrast, appears to activate ternesite less effectively, although its hydration gives rise to AH₃. Additionally, Shen et al. (2019, 2018, 2015) reported the cementitious properties of ternesite. So, in the presence of aluminium contained in fly ash, ternesite improved the mechanical strengths of CSA-fly ash blended cements (Shen et al., 2018). In belite calcium sulfoaluminate ferrite clinkers, large amount of this phase (from 32 to 44 % wt), which was more reactive than belite, increased the mechanical strength after 56 days of hardening (Shen et al., 2015). Also, the addition of lower percentage of ternesite to CSA cements (5%) significantly increased their compressive strength (Shen et al., 2019). In summary, in spite of its low hydration rate and the decrease in mechanical strength that promotes at early ages in calcium sulfoaluminate cements (Shen et al., 2015, 2019), ternesite contributes to the mechanical strength of cement at later ages.

Since both ternesite and anhydrite can be constituents of CSA blended cements and the presence of the common sulfate ion could alter the solubility of ternesite and therefore its activation process, this study explored ternary samples containing ternesite, gypsum and two calcium aluminates, C₁₂A₇, CA, main constituents of CAC cement, to determine the role of sulfate, e.g. provided by gypsum.

The study described here consequently aimed to broaden the current limited knowledge on ternesite reactivity in CSA-CAC blended cements by exploring two simplified systems, CA + ter + gyp and C₁₂A₇ + ter + gyp.

2. Material and methods

Ternesite (C₅S₂ $\bar{S}$), C₁₂A₇ and CA were synthesised from laboratory reagents as described in Montes et al. (2018). Phase purity, verified by refining the respective diffractograms with the Rietveld method, was as follows: ternesite (94.0% C₅S₂ $\bar{S}$ + 6.0% C₂S), C₁₂A₇ (99.8% C₁₂A₇ + 0.2% CaO) and CA (97.5% CA + 2.5% C₁₂A₇).

Particle size distribution of the aforementioned phases and gypsum was determined on a Malvern Mastersizer S particle size analyser fitted with 632.8 nm He–Ne laser optics. Prior to analysis, the samples were suspended in ethanol with 5 drops of DOLAPIX CE64 1/100 dispersant and ultrasonicated for 5 min. Based on the span values (a measure of the width of the particle size distribution; span (D₉₀ - D₁₀)/D₅₀), the most uniform samples were CA (3.17) and gypsum (2.39). The largest particle sizes were observed for gypsum (107.14 µm) and C₁₂A₇ (D[4,3]; 59 µm) and the smallest for CA (11.52 µm) and ternesite (35.13 µm) (Appendix, Table SM1).

Blends of C₁₂A₇ or CA with gypsum (gyp; Merck chemical reagent), ternesite or gypsum + ternesite were prepared to the following ratios by weight: aluminate/gypsum = 2.5/0.5; aluminate/ternesite = 1/2; and aluminate/gypsum/ternesite = 1/0.2/1.8.

Paste hydration at 25 °C for 7 days was monitored with isothermal conduction calorimetry on a Thermometric TAM Air calorimeter. Three grams of sample were stirred manually with the help of a rod in 2.1 g of water (liquid/solid ratio = 0.7) for 3 min (complete homogenisation). Calorimetric readings were recorded immediately, after which paste hydration was halted by immersing the crushed samples in acetone for 3 min followed by vacuum drying (Venturi pump) for 1 h to eliminate the solvent. The powdered pastes were characterised on a Bruker D8 Advance X-ray

diffractometer (Cu K α radiation, 2 θ 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).

Just for the CA series, CA + gyp and CA + ter + gyp, hydration was stopped at different times before and after the thermal signals on the heat release curve as described earlier, after which XRD and SEM analyses were conducted. SEM/EDX study was carried out with a JEOL5400 microscope coupled to a X-ray energy dispersion spectrometer (OXFORD LINK–ISIS–EDX). The samples were vacuum-dried and carbon-coated.

²⁷Al and ²⁹Si MAS (magic angle spinning) and CP-MAS (cross polarization) spectra were recorded respectively at 104.26 MHz and 79.48 MHz on a Bruker AVANCE-400 NMR spectrometer with a 9.4 T external magnetic field for C₁₂A₇ + gyp; C₁₂A₇ + ter + gyp; CA + gyp and CA + ter + gyp. All measurements were made at 20 °C and the samples were spun around the magic angle (54°44' relative to the magnetic field) at 10 kHz. The 400 scans yielding the ²⁷Al spectra were acquired at a $\pi/2$ pulse length of 2 μ s and a relaxation delay of 2 s; 180 scans were acquired at a $\pi/2$ pulse length of 4.5 μ s and a relaxation delay of 20 s to record the ²⁹Si MAS spectra. ¹H/²⁷Al and ¹H/²⁹Si CP-MAS NMR spectra were collected at contact times of 1 ms from 400 ²⁷Al scans and of 5 ms from 800 ²⁹Si scans, with TPPM15 proton decoupling. The ²⁷Al chemical shift values are given relative to an aqueous AlCl₃ external standard and the ²⁹Si values to a (CH₃)₄Si external standard.

The GEMS 3 geochemical code was used to analyse the theoretical hydration of C₁₂A₇ and CA blends with ternesite or ternesite + gypsum. This modelling software with built-in thermodynamic databases applies Gibbs free energy minimisation (GEM) to quantify equilibrium phase assemblage and mix speciation. The bulk chemical compositions simulated consisted in a mix of 1 g of CA or C₁₂A₇ with 2.1 mL of water at 25 °C in the presence of ternesite (0–1.8 g) with (0.2 g) and without gypsum assuming a CO₂-free atmosphere.

3. Results

3.1. Role of ternesite in initial aluminate hydration

The heat flow curves for the four samples containing ternesite were less intense than the ones containing gypsum only, due to the lower aluminate content in the former (Fig. 1a and b and Table 1). Nonetheless, the total heat of hydration per gram of aluminate was consistently higher in the ternesite-bearing samples (Fig. 1c and d).

CA and C₁₂A₇ hydration in the presence of gypsum alone has been widely studied and is generally divided into three periods (Bayoux et al., 1990; Damidot and Rettel, 2003). In the first, when gypsum dissolves quickly and the aluminates moderately, small amounts of ettringite and AH₃ form. The induction period is characterised by further AH₃ and ettringite formation, whilst during the acceleration period hydrates (sulfoaluminate phases (AFm, ettringite) and AH₃) precipitate massively. Nonetheless, hydration kinetics in those systems varies notably depending on the amount of gypsum added.

The heat flow curves for the C₁₂A₇ and CA blends with gypsum (Fig. 1a and b) contained a very intense initial peak followed by a low activity (induction) period and subsequently two overlapping exothermal peaks. The low activity period on the heat flow curve finalised and the two subsequent signals peaked earlier in CA + gyp than in C₁₂A₇ + gyp.

The two samples containing C₁₂A₇ and ternesite (Fig. 1a) exhibited a more intense initial exothermal peak (peak 1) and much

greater (4.5- to 5-fold) activity in the induction period, suggesting that the second peak described for the C₁₂A₇ + gyp paste occurs during that apparent induction period. Heat flow was observed to rise thereafter, with a 5 h peak at 10 mW/g in C₁₂A₇ + ter and a 4.3 h peak at 11.5 mW/g in C₁₂A₇ + ter + gyp. These pastes exhibited yet another wide, low intensity exothermal signal (C₁₂A₇ + ter: 13.5 h, 1.8 mW/g; C₁₂A₇ + ter + gyp: 11.9 h, 1.1 mW/g) (Table 1).

The CA + ter curve (Fig. 1b) exhibited a longer induction period than the CA + gyp curve and a single asymmetric reaction peak. The induction period was much shorter on the CA + ter + gyp curve than the CA + gyp curve and a single asymmetric reaction peak, on which peaks 2 (0.9 h and 18.9 mW/g) and 3 (1.2 h and 35 mW/g) overlapped and were followed by a wide, low intensity signal at 9.2 h (1.2 mW/g) (Table 1).

In decreasing order, total heat released per gram of aluminate (normalized) in the 7 d (25 °C) samples studied (Fig. 1c and d) was: CA + ter > C₁₂A₇ + ter > CA + ter + gyp > C₁₂A₇ + ter + gyp > C₁₂A₇ + gyp > CA + gyp. Therefore, all the samples with ternesite had more heat per unit of aluminate than those with gypsum alone and adding gypsum lowered the heat released in the samples with ternesite. Despite its larger mean particle size, paste C₁₂A₇ + gyp released more heat than CA + gyp.

Since the calorimetric curve for CA + ter + gyp (Fig. 1b) differed substantially from the heat flow curve for CA + gyp during early hydration, the role of ternesite in that process was studied by halting the reaction at different time intervals during the first 6 h (after 30 min: minimum induction period; 1 h: shoulder on reaction peak; 1.15 h: reaction peak time; 6 h: end of reaction peak) for subsequent XRD analysis of the hydration products.

In the gypsum-CA blend hydration reaction, ettringite began to form (Equation (1)) in the induction period and proceeded while dissolved sulfate and Ca ions were both present. When all the gypsum was consumed or its concentration sank locally while CA continued to hydrate, ettringite became unstable and calcium monosulfoaluminate hydrate (AFm) precipitated (Equation (2)), as attested to by the appearance of the third exothermal peak.

The 30 min (minimum induction period) diffractogram for CA + ter + gyp contained reflections for the anhydrous phases but none for crystalline hydrates. Ettringite signals appeared in the 1.15 h (peak reaction time) sample. Ternesite appeared to favour ettringite formation and stability, for precipitation did not decline even in the 6 h samples. In contrast, no AFm was identified in the reflections on the 6 h XRD pattern. The intensity of the diffraction lines for CA and gypsum, and to a much lesser extent for ternesite, declined abruptly between 1.15 h and 6 h, concurring with the rise in ettringite. Crystalline gibbsite (AH₃) was not detected on any of these traces.

The microstructural development of the CA + ter + gyp samples in the first hours of hydration was also monitored by SEM analyses. The gypsum particles were elongated prisms and ternesite ones were globular, whereas the CA crystals adopted irregular polyhedral shapes and sizes (Fig. 2).

The hydration products, which must be XRD-amorphous, were sparsely deposited on the CA and ternesite particles after just 30 min (Fig. 3a). After 1.15 h CA morphology was variable, irregular and pitted and the amount of hydration product grew on the surfaces of both CA and ternesite (Fig. 3b). The explanation for the accelerated CA hydration observed in the calorimetric findings for

Fig. 1. Heat flow and heat of hydration curves: a) $C_{12}A_7$ with gypsum, ternesite and gypsum and ternesite; b) CA + gypsum, ternesite and gypsum and ternesite; c) and d) 7 d heat of hydration curves (25 °C) for hydrated aluminates with gypsum, ternesite and gypsum and ternesite (normalized per g of aluminate).

Table 1

Data for the heat flow curves shown in Fig. 1.

	Initial peak (peak 1)		Induction period (end)		Peak 2 maximum		Peak 3 maximum		Exothermal signal	
	Heat flow (mW/g)		Heat flow (mW/g)	Time (h)	Heat flow (mW/g)	Time (h)	Heat flow (mW/g)	Time (h)	Heat flow (mW/g)	Time (h)
$C_{12}A_7$ +gyp	60		1.25	2.7	17.7	4.4	54	5.9		
$C_{12}A_7$ +ter ^a	134		6.3	3	—	—	10	5	1.8	13.5
$C_{12}A_7$ +ter + gyp	111		6.7	2.7	—	—	11.5	4.3	1.1	11.9
CA + gyp	121		0.4	1.8	16	3.1	54	5.1	1.8	7.8
CA + ter ^a	121		1.3	2	—	—	24	4.5	0.8	13
CA + ter + gyp	77		3.4	0.5	18.9	0.9	35	1.2	1.2	9.2

^a reference data shown in Montes et al. (2018).

the sample bearing ternesite would lie in the dense hydration product deposits on both the CA and ternesite grain surfaces, which acted as nucleation sites. After 6 h the entire surface of CA and ternesite particles (Fig. 3c) was covered with fibrous and shapeless hydration products. According to the EDX analyses, these deposits appeared to comprise mixed hydrates, for the findings included no analyses characteristic of ettringite, gibbsite or strätlingite.

3.2. Characterization of samples after 7 days of hydration

The XRD patterns for the aluminate + gyp, aluminate + ter or aluminate + ter + gyp pastes for the 7 d are reproduced in Fig. 4.

The reflections found on the diffractogram for the $C_{12}A_7$ + gyp paste (Fig. 4) were attributed to calcium monosulfoaluminate hydrate, hemicarboaluminate ($C_4A\bar{C}_{0.5}H_{11.5}$), gibbsite, C_4AH_{19} ,

ettringite and anhydrous $C_{12}A_7$. Where $C_{12}A_7$ hydrated in the presence of enough gypsum, the reaction ran its full course, generating ettringite and aluminium hydroxide (Equation (3)). Where insufficient amounts of gypsum were present the ettringite became unstable and reacted with the dissolved $C_{12}A_7$ ions. The result was calcium monosulfoaluminate hydrate and hexagonal hydrate (such as C_2AH_8 , and CAH_{10}) precipitation (Equation (4)). As all the gypsum was depleted in the 7 d $C_{12}A_7$ + gyp sample, the reaction described in Equation (3) was followed by the one represented in Equation (4), although the latter was incomplete and anhydrous aluminate remained in the paste.

Fig. 2. SEM micrographs of anhydrous CA + ter + gypsum sample; a) CA, gypsum and b) ternesite.

The hydration products found in the C_{12}A_7 +ternesite paste included strätlingite and calcium monosulfoaluminate; ternesite reflections were also recorded but no C_{12}A_7 , gibbsite or ettringite was found (Montes et al., 2018). Given the higher C_{12}A_7 than ternesite solubility, the former hydrated first to form gibbsite and katoite (C_3AH_6) (Equation (5)). Gibbsite activated ternesite, releasing sulfates that generated ettringite or calcium monosulfate hydrate in the reaction with katoite (Equations (6) and (7)). Silicates from the ternesite solution, in turn, reacted with gibbsite, prompting strätlingite precipitation (Equation (8)).

The absence of anhydrous aluminate and gibbsite was an indication that all the aluminate had dissolved (Equation (5)) and the reaction products were consumed via the pathways described in Equations (7) and (8).

The diffractogram for the C_{12}A_7 + ter + gyp paste (Fig. 4) contained signals attributed to ternesite, strätlingite, calcium monosulfoaluminate hydrate and ettringite. Here the reactions would proceed as in Equation (3), followed by those set out in Equations (4) to (8). The ettringite remained partially stable after all the gypsum was consumed thanks to the sulfate sourced from ternesite dissolution.

The XRD pattern for the 7 d CA + gyp (Fig. 4) paste contained reflections induced by calcium monosulfoaluminate hydrate, calcium hemicarboaluminate hydrate, ettringite (very low intensity), gibbsite and anhydrous CA, Eqs. (1) and (2).

CA + ter diffractogram (Fig. 4) exhibited signals attributed to strätlingite and calcium monosulfoaluminate hydrate, same hydration products as found in C_{12}A_7 +ter paste, and ternesite (Montes et al., 2018). No reflections of the anhydrous aluminate were observed either when compared with the analogous blend with

C_{12}A_7 .

Peaks associated with strätlingite, calcium monosulfoaluminate hydrate, ternesite and even ettringite (higher intensity than in the absence of ternesite, which favours stabilisation) were identified on the diffractogram for CA + ter + gyp. No signals for anhydrous CA or gibbsite were observed.

FTIR studies of pastes hydrated for 7 day confirmed results given by XRD. The only difference that arose from the FTIR spectrum of CA + ter + gyp paste (Fig. 5) was the identification of the presence of gibbsite in this system.

It shows a signal at 3676 cm^{-1} attributed to AFm, the one at 3620 cm^{-1} to strätlingite (Chukanov and Chervonnyi, 2014) as well as bands at 3526 and 3475 cm^{-1} characteristic of gibbsite. To enhance hydration product band visibility, particularly in the 1300 to 400 cm^{-1} range, the spectrum for ternesite was subtracted conveniently from CA + ter + gyp, however the 1300 to 400 cm^{-1} zone furnished scant information: AFm ($780, 582, 539\text{ cm}^{-1}$) and strätlingite ($1013, 969, 710\text{ cm}^{-1}$) bands were identified, whilst gibbsite overlapped with ternesite residual bands.

In the DTA curve for the C_{12}A_7 + (ter) + gyp pastes (Fig. 6a), the peak observed at 76°C was mainly attributable to the loss of water from ettringite. The very pronounced endothermal peak at 180°C , and the signals at 120 and 290°C on the curves for C_{12}A_7 + gyp, C_{12}A_7 + ter and C_{12}A_7 + ter + gyp samples (Fig. 6a) were principally related to water loss from calcium monosulfoaluminate and calcium hemicarboaluminate hydrates. On the DTA curves for the C_{12}A_7 pastes containing ternesite were identified other signals at 152°C and 213°C that were assigned mainly to strätlingite dehydration (Lothenbach et al., 2016; Winnefeld and Lothenbach, 2010). A very intense endothermal signal was observed at around 256°C on the curve for C_{12}A_7 + gyp, and it was not perceptible in the presence of ternesite. Pure gibbsite, katoite, and AFm and Aft phases are characterized from having a weight loss in this temperature range (260 – 320°C) (Lothenbach et al., 2016). However, this peak could be assigned to gibbsite dehydroxylation since the sample contains this phase and the disappearance of this signal in the presence of ternesite is related with the precipitation of strätlingite (reaction of silicates and AH_3).

On the DTA curves for the CA pastes (Fig. 6b) a small endothermal signal was observed again at around 80°C . Water loss was identified at 120 – 180°C on the curves for all the samples related mainly to dehydration of monosulfoaluminate phases. The pastes containing ternesite also exhibited the aforementioned signals at 152°C and 213°C , mainly attributable to strätlingite dehydration. The signal at around 250 – 270°C , assigned to water loss from

Fig. 3. SEM micrographs of CA + ter + gyp pastes: distribution of hydration products after a) 30 min; b) 1.15 h and c) 6 h on the surface of 1) CA and 2) T = ternesite.

gibbsite, was very intense in the sample with gypsum and has very low intensity in the one with gypsum + ternesite.

The signal at around 290 °C that exhibited all the curves, apart from that of CA + gyp (Fig. 6b), may have been generated not only by AFm but a scanty crystalline katoite (C_3AH_6), as it was not identified with XRD.

Further to TG analysis (weight loss at 700 °C), the amount of bound water in the 7 d pastes in decreasing order, was as follows: CA + ter (24.4%) > CA + ter + gyp (23.4%) > $C_{12}A_7$ + ter (21.7%) ~ $C_{12}A_7$ + ter + gyp (21.8%) > $C_{12}A_7$ + gyp (normalized) (11.8%) ~ CA + gyp (normalized) (11.6%) (Fig. 6c). This order was established by considering the same aluminate content in all the samples. For that reason, the curve for CA + gyp and $C_{12}A_7$ +gyp

samples that were mixed with 2.5 g aluminate and 0.5 g gypsum, were recalculated (normalized) to 1 g of aluminate.

The ^{27}Al MAS NMR spectra for the 7 d pastes with ternesite ($C_{12}A_7$ + ter, $C_{12}A_7$ + ter + gyp; CA + ter, and CA + ter + gyp) (Fig. 7) were very similar, with bands in the same position albeit with different relative intensities. On all the spectra (MAS and CP-MAS), a signal for octahedral Al was observed at 10 ppm and another at 61 ppm in the tetrahedral Al region, with a shoulder at 68 ppm on the spectra for CA pastes.

Further to the literature (Santacruz et al., 2016), the Al in strätlingite is located in both tetrahedral and octahedral positions and its ^{27}Al MAS spectrum has two bands, at 61 ppm (Al^{IV}) and a more intense signal at 9.9 ppm (Al^{VI}). The Al in AFm, in turn, is

Fig. 4. Diffractograms for 7-day hydrated pastes. AFm = hydrated calcium mono-sulfaluminate; E = ettringite; Hc = hemicarboaluminate; S = strätlingite, G = gibbsite and CA, $C_{12}A_7$, C_4AH_{19} calcium aluminates. $C_{12}A_7$ + ter and CA + ter diffractograms from Montes et al. (2018).

octahedrally coordinated, with a band at 10.2 ppm (Gastaldi et al., 2016). The 2.8 ppm mid-height width of the $Al^{(VI)}$ band would attest to an overlap between the octahedral signals generated by AFm and strätlingite.

In addition to the band at 10 ppm, in the $Al^{(VI)}$ zone the ^{27}Al CP-MAS spectra (Fig. 7) exhibited in CA + ter + gypsum and $C_{12}A_7$ + ter + gypsum pastes, a low intensity signal at ~13 ppm assigned to ettringite (Gastaldi et al., 2016; Skibsted et al., 2017). The intensity of the band at 61 ppm ($Al^{(IV)}$ band) recorded with cross polarization (CP-MAS) was much lower relative to the $Al^{(VI)}$ band than observed on the ^{27}Al MAS spectrum. Santacruz et al. (2016) described the same pattern for spectra recorded for strätlingite samples.

Two bands were observed on the ^{29}Si MAS NMR spectra (Fig. 8) for the pastes analysed, assigned to Q^0 tetrahedral Si units: an

Fig. 5. FTIR spectrum for 7 d CA + ter + gyp paste hydrated at 25 °C (ternesite spectrum subtracted).

intense signal at -73 ppm generated by ternesite in all the four samples and a weaker signal at -71 ppm, attributed to larnite (Bastos da Costa et al., 2016) and only observed on gypsum contained samples. Neither of the spectra contained the Si signals associated with the strätlingite structure (Kwan et al., 1995) identified by the other techniques or with the possible presence of C-S-H (Sáez del Bosque et al., 2013). ^{29}Si MAS NMR C-S-H spectrum is characterized by exhibiting very wide, overlapping bands from -79 ppm to -85 ppm, assigned to end-of-chain (Q^1) or mid-chain bridging $Q^2(OH)$ or paired ($Q^2(1Al)$) and (Q^2) Si atoms (Sáez del Bosque et al., 2013).

Nonetheless, the ^{29}Si CP-MAS NMR spectra for all samples contained a signal at -86 ppm, with a mid-height width of 1.4 ppm–1.7 ppm. Kwan et al. (1995) assigned that signal to the Q^2 Si in strätlingite. According to their findings, that peak overlapped with the C-S-H peak on ^{29}Si MAS NMR spectra but could be distinguished in the ^{29}Si CP-MAS NMR spectra. Santacruz et al. (2016) also assigned the signal at -86 ppm to strätlingite, attributing the low condensation of Si in the double tetrahedral layer $[Si_2Al_2O_4(OH)_8]^{2-}$ to the existence of large amount of vacancies.

In the samples without gypsum a weak band at -82 ppm was also recorded in the ^{29}Si CP-MAS NMR and in the pastes containing CA another band at -90 ppm, also with very low intensity, was observed. The former was assigned to $Q^2(2Al)$ and the latter to $Q^3(2Al)$, both associated with strätlingite in the literature (Santacruz et al., 2016; Kwan et al., 1995).

3.3. Thermodynamic modelling

Thermodynamic modelling was conducted by completely dissolving 1 g of aluminate and increasing quantities (0 g–1.8 g) of dissolved ternesite in 2.1 g of water in the absence or presence (0.2 g) of gypsum respectively for the samples aluminate + ternesite and aluminate + ternesite + gypsum.

For $C_{12}A_7$ + ter and $C_{12}A_7$ + ter + gyp blends (Fig. 9 a,b), AFm, strätlingite, gibbsite and C_3AH_6 were predicted from the outset. The precipitation of the former phase was initially more intense in the presence of gypsum and its amount increases with the amount of dissolved ternesite as it also happens in the absence of gypsum. The stability range of gibbsite is not altered by the gypsum addition and remains stable until 0.5–0.6 g of dissolved ternesite. Gypsum

Fig. 6. a and b) DSC curves for the $C_{12}A_7$ and CA series; c) TG curves for the two series including the normalized curves (per gram of aluminate) of $C_{12}A_7$ + gyp and CA + gyp. CA + ter, and $C_{12}A_7$ + ter data from Montes et al. (2018).

decreases the stability range of katoite from 1.1 g to 0.5 g of dissolved ternesite. In the $C_{12}A_7$ + ter + gyp blend, when the amount of dissolved ternesite reached 0.9 g, ettringite began to precipitate, in contrast, no ettringite was formed in the absence of gypsum. The initiation of C–S–H gel precipitation concurred with the maximum

proportion of strätlingite in both blends. As the amount of dissolved ternesite is higher than 0.6 g, the strätlingite started to dissolve while the C–S–H and AFm contents rose.

For CA + ter and CA + ter + gyp (Fig. 9 c,d), the phases precipitating earliest were the same as in the aforementioned $C_{12}A_7$ systems: AFm, strätlingite, gibbsite and C_3AH_6 . The latter two also disappeared with the increasing amount of dissolved ternesite: gibbsite with more than 1 g of ternesite, both in the absence and presence of gypsum, and C_3AH_6 with more than 0.3 g or 0.8 g of ternesite, in the system with or without gypsum, respectively. The disappearing of C_3AH_6 concurs with the beginning of ettringite precipitation which increases with further dissolved ternesite. The addition of gypsum clearly increases the stability range of ettringite. The amount of strätlingite increased while gibbsite is stable, then its proportion began to slide and C–S–H gel started to precipitate. With the increasing amount of dissolved ternesite, more C–S–H was formed.

As the amount of dissolved ternesite rose, AFm content increases until the precipitation of ettringite. Then it started to decline and rose again after the strätlingite content began to slide for both types of blends.

Thermodynamic modelling yielded a potential weight loss due to dehydration of the associated hydrates (30–37%), slightly higher on the mixes with CA. On the other hand, weight losses determined with TG (700 °C) in the 7 d pastes were lower, in the 22%–24% range, but still higher in the CA blends (Fig. 6). Those differences on weight loss between thermodynamic modelling data and TG analysis would arise for the presence of unreacted ternesite in 7 d pastes.

4. Discussion

The heat flow curves for $C_{12}A_7$ and CA with gypsum, ternesite or gypsum and ternesite contained an initial dissolution peak and an induction period followed by an intense reaction peak. The addition of ternesite shortened the induction period of the hydration of CA + gypsum and $C_{12}A_7$ + gypsum bringing forward the main reaction signal.

During the first 6 h of hydration the total heat released by $C_{12}A_7$ + ter and $C_{12}A_7$ + ter + gyp was similar, then, the heat released by the former was superior. Total heat recorded along the first 7.5 h of the hydration of CA + ter + gyp paste was higher than that of CA + ter blend, from that moment tendency changed and more heat was emitted by the latter. Thus, the 7 d pastes containing $C_{12}A_7$ or CA plus gypsum and ternesite exhibited 51–76% higher heat per unit of aluminate than the analogous pastes containing gypsum only and 28% lower heat than the pastes with ternesite only.

The SEM studies carried out in the sample in which the speedier hydration reaction was observed on the calorimetric curves, CA + ter + gyp mix, denoted the presence of aluminate hydrates on the surface of ternesite as well as CA in the induction period. Ternesite grains acted as nucleation sites for the hydration products in the early ages which would explain the acceleration of the reactions rate.

The presence of this amorphous or poorly crystallised $Al(OH)_3$ ($Al(OH)_3$ gel) on CA particles during early hydration has been described by a number of authors in the literature (Amer et al., 2020; Klaus et al., 2013; Rettel et al., 1985). Further to the XRD results, in these first hours of hydration AFm and ettringite were the main crystalline 6 h hydration products for CA systems with gypsum (CA + gyp and CA + ter + gyp) while no crystalline AFm or strätlingite was detected in CA + ter blend. In any case, the SEM identification of these phases was complex due to the presence of hydration products with poorly defined morphologies and very high Al contents. Ben Haha et al. (2015) also did not observe by SEM

Fig. 7. 7 d NMR spectra for a) $\text{C}_{12}\text{A}_7 + \text{ter} + \text{gyp}$ (^{27}Al MAS/CP); b) $\text{C}_{12}\text{A}_7 + \text{ter}$ (^{27}Al MAS/CP); c) $\text{CA} + \text{ter} + \text{gyp}$ (^{27}Al MAS/CP); d) $\text{CA} + \text{ter}$ (^{27}Al MAS/CP).

typical cement hydrates on ternesite-alumina pastes at early age, even if they were detected through XRD. The conclusion drawn from these findings is that gypsum dissolution released additional sulfates into the medium with ternesite to stabilise ettringite, favouring its growth, along with AFm during the third reaction peak in the heat flow rate trace of $\text{CA} + \text{ter} + \text{gyp}$. In contrast, no crystalline ettringite or AFm was able to precipitate in the absence of gypsum during these first hours of hydration for $\text{CA} + \text{ter}$. Crystalline gibbsite, clearly identifiable on the XRD patterns for the ternesite-free paste, was absent in these samples.

On the 7 d diffractograms for all the ternesite-bearing pastes (aluminate + ter and aluminate + ter + gyp), reflections attributable to AFm, strätlingite, ternesite were recorded and also very low intensity lines for ettringite only in the mixes with ternesite + gypsum. In turn, no reflections attributable to anhydrous aluminates were observed, an indication that they had completely reacted by that age, unlike in the aluminate + gyp samples, and that activated ternesite released silicate ions into the solution and favoured strätlingite formation. Nor were there lines for C_3AH_6 , AH_3 or C_4AH_{19} . As expected, the products of $\text{CA} + \text{gyp}$

Fig. 8. 7 d NMR spectra for a) $\text{C}_{12}\text{A}_7 + \text{ter} + \text{gypsum}$ (^{29}Si MAS/CP); b) $\text{C}_{12}\text{A}_7 + \text{ter}$ (^{29}Si MAS/CP); c) $\text{CA} + \text{ter} + \text{gypsum}$ (^{29}Si MAS/CP); d) $\text{CA} + \text{ter}$ (^{29}Si MAS/CP).

and $\text{C}_{12}\text{A}_7 + \text{gyp}$ hydration were AFm and AH_3 , plus respectively a very small or small amount of ettringite and low amount of C_4AH_{19} in paste C_{12}A_7 .

^{27}Al MAS spectra for the 7 d pastes confirmed the full dissolution of C_{12}A_7 and CA and their absence in the pastes, since no signal whatsoever was observed in the tetrahedral region between 80 ppm and 86 ppm (chemical shifts at which several researchers describe Al(IV)) bands (Skibsted 2016; Pena et al., 2008; Skibsted et al., 1993). The sole signals detected corroborated the XRD findings: the ettringite signal at 13 ppm and the lines typical of strätlingite at 10 ppm and 61 ppm, overlapping with the AFm signal on the ternesite and gypsum spectra.

Through DTA and FTIR, it was possible to detect the presence of AH_3 in $\text{CA} + \text{ter} + \text{gyp}$ mix, not observed with XRD. Furthermore via

DTA, traces of katoite, not detected with the other techniques, could be inferred in all the blends, apart from $\text{CA} + \text{gyp}$ and $\text{CA} + \text{ter} + \text{gyp}$. Those findings are consistent with the thermodynamic modelling results. The absence of the reflections for AH_3 may be due its scant crystallinity, frequently observed in calcium aluminate hydration (Winnefeld and Lothenbach, 2016; Gessner et al., 1985; Rettel et al., 1985), and for katoite to the small proportion present.

The amount of ternesite activated in these lab samples could be estimated by combining thermodynamic modelling and TG. For this, modelling data had to be adjusted by factoring in the effect of the dilution due to the unreacted ternesite in the lab samples. This adjustment was done by adding to the total hydrates calculated by modelling the initial amount of ternesite in lab samples (2 g or

Fig. 9. Results of thermodynamic modelling for a) C₁₂A₇ + ternesite, b) C₁₂A₇ + ternesite + gypsum, c) CA + ternesite and d) CA + ternesite + gypsum blends. Vertical line in each graph represents the estimated amount of ternesite activated in the lab samples inferred from Table 2.

1.8 g) minus the amount of dissolved ternesite in each point of the calculated system, and then recalculating the percentages of the hydrates and anhydrous phases (Appendix, Table SM2-1,2,3 and Fig. SM2-1). The re-calculated percentage of hydrates allows us to compare their theoretical amount of water with TG experimental

mass loss at 700 °C (Table 2) and determine the amount of reactive ternesite in lab samples when both theoretical and experimental values of water content coincide. Further to those findings, 35% of ternesite in C₁₂A₇ + ter, 24% in C₁₂A₇ + ter + gyp, 42% in CA + ter and 29% in CA + ter + gyp reacted.

Table 2

Amount of ternesite dissolved (absolute values) and per cent of bound water in pastes calculated from thermodynamic modelling data (TG-delivered percentage underlined).

	Amount of ternesite dissolved (g) C ₁₂ A ₇ +ter (1:2) (by weight)	C ₁₂ A ₇ +ter + gyp (1:1.8:0.2) (by weight)	CA + ter (1:2) (by weight)	CA + ter + gyp (1:1.8:0.2) (by weight)
	bound water (%)	bound water (%)	bound water (%)	bound water (%)
0	13.26	15.93	13.18	14.84
0.1	14.02	17.35	14.69	18.00
0.2	15.50	18.75	16.15	19.37
0.3	16.93	20.07	17.55	20.65
0.4	18.31	<u>21.38</u>	18.91	21.81
0.5	19.65	<u>22.60</u>	20.23	23.12
0.6	20.94	23.76	21.50	<u>24.58</u>
0.7	<u>21.80</u>	24.36	22.73	26.03
0.8	22.63	24.99	<u>23.93</u>	27.39
0.9	23.45	25.51	25.08	28.66
1	24.24	26.41	26.04	29.91
1.1	25.02	27.21	27.13	30.88
1.2	25.72	27.99	27.92	31.63
1.3	26.27	28.73	28.69	32.26
1.4	26.81	29.54	29.45	32.94
1.5	27.35	30.24	30.18	33.60
1.6	27.88	31.01	30.90	34.32
1.7	28.40	31.67	31.60	34.92
1.8	28.92	32.40	32.28	35.60

Thermodynamic modelling did not predict the presence of C–S–H gel for such degrees of ternesite reaction in the lab samples (Fig. 9), a result consistent with the ^{29}Si MAS/CP NMR data, which only detected the presence of strätlingite at -86 ppm (CP-MAS) and unreacted ternesite at -73 ppm (MAS). In turn, it did predict the presence of small amounts of ettringite ($\sim 4\%$) in CA + ter + gyp, whereas XRD and ^{27}Al MAS/CP NMR also identified that phase in paste C_{12}A_7 + ter + gyp.

Whilst both CA and C_{12}A_7 activated ternesite in both the absence and presence of gypsum, the former did so more effectively in the absence of gypsum. In accordance with Bullerjahn et al. (2015), ternesite is able to react in spite of the presence of another source of sulfates, however its reactivity is being reduced. Based on the amount of bound water (TG), more hydration product per unit of aluminate was obtained in CA pastes containing ternesite (CA + ter; CA + ter + gyp) than in C_{12}A_7 systems (C_{12}A_7 + ter, C_{12}A_7 + ter + gyp).

5. Conclusions

Eco-efficient CSA cements contain variable proportions of ternesite, whose slow activation during hydration could be hastened by adding CAC. This study aimed to improve the current limited knowledge on ternesite reactivity in CSA-CAC blended cements by studying the CA + ter + gyp and C_{12}A_7 + ter + gyp simplified systems. CA and C_{12}A_7 blend hydration in the presence of gypsum, ternesite or both was consequently monitored with isothermal conduction calorimetry and the reaction products were characterised to determine whether ternesite is activated in the presence or absence of gypsum. The conclusions drawn are set out below.

- Thermodynamic modelling of CA + ter + gyp and C_{12}A_7 + ter + gyp paste hydration predicts the same hydration products for both, although with different ranges of stability. The phase assemblages predicted are highly consistent with the experimental findings found with XRD, FTIR, DTA-TG and ^{27}Al and ^{29}Si NMR.
- Ternesite is activated by both aluminates, but more intensely by CA, with and without gypsum although the presence of gypsum reduces its reactivity.
- Ternesite acts as a nucleation site for the formation of hydration products in aluminate + gyp pastes, which explains the acceleration of the reactions reflected in the calorimetric findings and the raise of heat of hydration per unit of aluminate in C_{12}A_7 and CA pastes hydrated at 25°C for 7 d, in both the presence and absence of gypsum.

The present findings constitute a first contribution to the development of sustainable CSA-CAC binders bearing ternesite, one of the hydraulic phases most recently identified in cements. Further advances in the understanding of these sustainable binders will call for the study of complex systems (industrial cements), for whose optimisation the results on ternesite reactivity described in this article will prove particularly useful.

CRedit authorship contribution statement

P.M. Carmona-Quiroga: Formal analysis, Investigation, Writing - original draft, Writing - review & editing. **M. Montes:** Formal analysis, Investigation, Writing - original draft. **E. Pato:** Formal analysis, Investigation, Writing - original draft. **A. Fernández-Jiménez:** Conceptualization, Writing - original draft, Funding acquisition. **M.T. Blanco-Varela:** Conceptualization, Writing - original draft, Writing - review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This study was funded by the Spanish Ministry of Economy and Competitiveness (BIA2016-76466-R project), the Regional Government of Madrid and the European Social Fund (Top Heritage-CM S2018/NMT_4372). Dr Paula Carmona's participation was financed by the Ministry of Economy and Competitiveness and the European Regional Development Fund under project BIA2015-73237-JIN (MINECO/ERDF; EU), whilst author Myriam Montes collaborated as beneficiary of a young researcher internship (PEJ-2014-A-75310).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2020.125726>.

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