Can calcium aluminates activate ternesite hydration?

M. Montes, E. Pato, P.M. Carmona-Quiroga, M.T. Blanco-Varela*

Instituto de ciencias de la construcción Eduardo Torroja (IETcc) (CSIC), Serrano Galvache 4, 28033 Madrid, Spain

ARTICLE INFO

ABSTRACT

Aluminum hydroxide (AH_3) has recently been shown to be able to activate hydration in ternesite, a phase found in some calcium sulfoaluminate (CSA) cements.

This study explored the capacity of a number of calcium aluminates (C_3A, $C_{12}A_7$, CA and $C_4A_3\overline{S}$) to activate ternesite hydraulic reactivity. After laboratory synthesis, the aluminates were blended with ternesite at a ratio of 1:2 and their hydration was monitored with isothermal conduction calorimetry for 7 days at 25 °C. The resulting pastes were analysed with XRD, FTIR and DTA. The presence of ternesite in the pastes altered the aluminate heat flow curves, shortening the induction period and bringing the reaction peak forward, an indication of hastened hydration. Ternesite also altered the reaction products, which included calcium monosulfoaluminate hydrate and strätlingite.

1. Introduction

The mass production of portland cement (OPC) entails the consumption of vast amounts of raw materials and accounts for 4% to 6% of worldwide anthropogenic CO_2 emissions (0.8–0.9 t CO_2/t clinker) [1].

The cement industry is currently seeking to develop less energy-intensive, lower greenhouse gases (GHG) emission cements. Calcium sulfoaluminate (CSA) cements, one of the most promising alternatives, are characterised by lower energy costs (at 1250 °C, the clinkering temperature is 200 °C lower than in OPC clinker) and GHG. These products emit from 25% to 40% less CO_2 during manufacture than OPC, depending on the composition [2]. While not presently used for structural purposes due to the lack of the necessary regulation, they are commercialised as components for special mortars and concretes (such as repair or self-levelling concrete, sealing mortar or shotcrete).

The composition of the clinker in these cements may differ, although all lie in the $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}Fe_2O_3\text{-}CaSO_4$ system and have lower calcium and silicon and higher aluminate and sulfate phase contents than portland cements. The minerals present in the clinker include $C_4A_3\overline{S}$, C_2S, $C_{12}A_7$, CA, Cs and C_4AF*, although the aluminates predominate [3,4].

Ternesite, $C_5S_2\overline{S}$, which also lies within this system, is a phase compatible with ye'elemite ($C_4A_3\overline{S}$) and C_2S. It is found primarily in the crust covering the areas of portland cement kilns where the temperature is no higher than 1250 °C and as a minority component in some CSA cements [5,6,10]. A calcium sulfosilicate, ternesite is formed in the reaction between anhydrite and belite. Bullerjahn et al. [6,7] proposed a two-stage method for ternesite formation, in which clinker is synthesised at a temperature of 1250 °C and then cooled by gradually ramping the temperature down to 800 °C. Further to recent thermodynamic predictions and empirical observation, if atmosphere (partial pressure of SO_2 and O_2) and temperature are controlled, belite- and ternesite-high sulfoaluminate clinkers can be readily produced in a single-stage process at temperatures of over 1200 °C [8].

Although ternesite has traditionally been regarded as hydraulically inactive and of no technological interest [9], recent studies have shown that it is activated by amorphous AH_3. It hydrates, then, in their presence, yielding ettringite and C-S-H respectively the main hydration products in CSA and portland cements and the phases to which they owe their mechanical strength and durability. Strätlingite may also form with or instead of C-S-H [11].

Solubility of amorphous aluminum hydroxide in water at 25 °C is very low ($[Al] \approx 1{,}607 \times 10^{-7}$ M/L and pH 6789; database used: concrete_3T_V07_02 and calculated with Phreeqc), it depends on the pH of medium and it rises both when pH increases or decreases from neutrality, being $Al(OH)_4^-$ the only ionic specie present at pH higher than $\approx 8{,}5$ [11]. Solubility of ternesite is not known, but it seems that its dissolution produces hydrolysis and a pH near to 12 [12].

The solution in contact with ternesite and AH_3, contains $Al(OH)_4^-$, Ca^{2+}, SO_4^{2-}, SiO_3H^-, OH^- ions that will react when the solubility products of ettringite or strätlingite or calcium monosulfoaluminate hydrate or C-S-H etc., are achieved; the precipitation of the said phases will consume ions in solution stimulating then new ternesite

---

solubilisations.

Given the low water solubility of AH_3, other, more soluble aluminates might be thought to act as activators and stimulate ternesite hydration more efficiently.

Such aluminates and ternesite might be the main phases in a future CSA cement with a composition lying within the $CaO-Al_2O_3-SiO_2-Fe_2O_3-CaSO_4$ system.

The purpose of this study is to explore the capacity of a series of calcium aluminates (C_3A, $C_{12}A_7$, $C_4A_3\bar{S}$ and CA) to activate ternesite hydration, establishing the reactions involved and identifying the reaction products.

2. Experimental

Ternesite ($C_5S_2\bar{S}$), ye'elemite ($C_4A_3\bar{S}$), C_3A, $C_{12}A_7$ and CA were synthesised from stoichiometric blends of laboratory-grade $CaCO_3$, SiO_2, Al_2O_3 and gypsum ($CaSO_4 \cdot 2H_2O$). The samples were weighed, ground in a ceramic mortar, homogenised in an ethanol medium and dried at 100 °C. A pressure of 300 kp/cm^2 was applied to the powder obtained to prepare 2 cm diameter cylindrical pellets weighing approximately 4 g. The pellets were calcined at 1200 °C ($C_5S_2\bar{S}$), 1250 °C ($C_4A_3\bar{S}$), 1350 °C ($C_{12}A_7$ and CA) or 1400 °C (C_3A) for 2 h. They were subsequently ground, homogenised, dried and new pellets were prepared and calcined at the same temperatures, ternesite and ye'elemite for 6 h and the other calcium aluminates for 5 h. This process was repeated through conclusion of the synthetic reactions.

Particle size distribution in the synthesised phases was determined and recorded on a Malvern Mastersizer S particle size analyser with 632.8 nm He-Ne laser optics after subjecting samples suspended in ethanol with 5 drops of dispersant (DOLAPIX CE64 1/100) to ultrasonic dispersion for 5 min. The findings are given in Fig. 1 and Table 1.

Phase purity was determined by applying Rietveld refinement to the X-ray diffraction (XRD) patterns (Table 2).

Aluminates and ternesite blend hydration (aluminate:ternesite = 1:2 by mass) were monitored for 7 d at 25 °C on a Thermometric TAM Air isothermal conduction calorimeter. Three grams of sample was stirred manually with 2.1 g of water (liquid/solid ratio = 0.7) for 3 min prior to insertion in the calorimeter. Upon finalisation of the calorimetric tests, the samples were submerged in acetone to detain hydration and vacuum drying was used to remove water. The products were characterised with X-ray diffraction (XRD), IR spectroscopy (FTIR) and differential thermal analysis-thermogravimetry (DTA-TG).

The mineralogy of the synthetic phases and hydrated samples was determined on a Bruker D8 Advance X-ray diffractometer, fitted with a high voltage, 3 kW generator and a 1.54 Å CuKa anode X-ray tube operating at 40 kV and 50 mA. This instrument was coupled to a Lynxeye detector with a 3 mm anti-scatter slit and a 0.5% Ni K-beta filter, with no monochromator.

XRD patterns of synthesised aluminates and ternesite were recorded at 5°–70° 2θ angles, with a step size of 0.01973°, and a 2 s step time.

Table 1
Particle size distribution parameters determined by laser diffraction.

µm/%	C_3A	CA	$C_{12}A_7$	$C_4A_3\bar{S}$	$C_5S_2\bar{S}$
d_{90}	100	100	76.5	78	89.5
d_{50}	93.5	99.3	66.4	46	85
d_{10}	31	57	34	14	43.5
$D_{4.3}$	21.17	11.52	59	59.14	35.13
Span	2.41	3.17	8.25	1.99	8.29
RRSB	0.74	0.97	2.36	0.62	2.48

Rietveld quantitative analysis [13] was conducted on the XRD findings using GSAS software [14].

XRD patterns were recorded for the ternesite-bearing hydrated aluminates, likewise at 5°–70° 2θ angles with a step size of 0.01973°, while varying the step time to 6 s–10 s. Corundum (Al_2O_3) was added to these samples at a rate of 25% to quantify the amorphous phase [15].

XRD scans were taken of the aluminate hydrated samples 5°–60° 2θ at a step size of 0.019746° and a 0.5 s step time.

$C_{12}A_7$ + ternesite hydration was also XRD-monitored for 20 h: 5°–30° 2θ angles, step size 0.019746° and step time 0.5 s. Scans were recorded every 10 min during the first 10 h, and every 30 min from the 11th through the 20th hours. The paste was introduced in an air-tight sample holder to prevent carbonation and drying.

For FTIR analysis of the 7 d pastes, vacuum pressure of 10 atm was applied for 3 min to pellets prepared with approximately 1 mg of sample in 300 mg of KBr. FTIR scans were performed at frequencies of 4000 cm^{-1}–400 cm^{-1} on a Thermo Scientific Nicolet 600 FTIR spectrometer with a spectral resolution of 4 cm^{-1}. The CA and $C_{12}A_7$ pastes were also scanned after heating to 188 °C at 10 °C/min in an N_2 atmosphere.

Thermogravimetric (TG) and differential thermal (DTA) analyses were conducted on a TA Instruments Q600 TGA-DCS-DTA analyser. The samples were heated from ambient temperature to 1000 °C in a nitrogen atmosphere (100 mL/min) at a rate of 10 °C/min.

3. Results

3.1. Isothermal conduction calorimetry

The heat flow curve for ternesite alone contained only the first exothermal peak, which after 1 h had declined to 31 µW/g, given its scarce reactivity with water [6], the total heat of this reaction was very low (Fig. 2 and Table 3). During hydration at 25 °C, the heat flow curves for both the synthesised aluminates (C_3A, $C_{12}A_7$, CA, $C_4A_3\bar{S}$) and their blends with ternesite (Fig. 3 and Table 3) showed an early exothermal reaction after mixing followed by a decline in the heat production rate and, in the $C_{12}A_7$, CA and $C_4A_3\bar{S}$ samples, a second exothermal reaction that appeared earlier in the presence of ternesite.

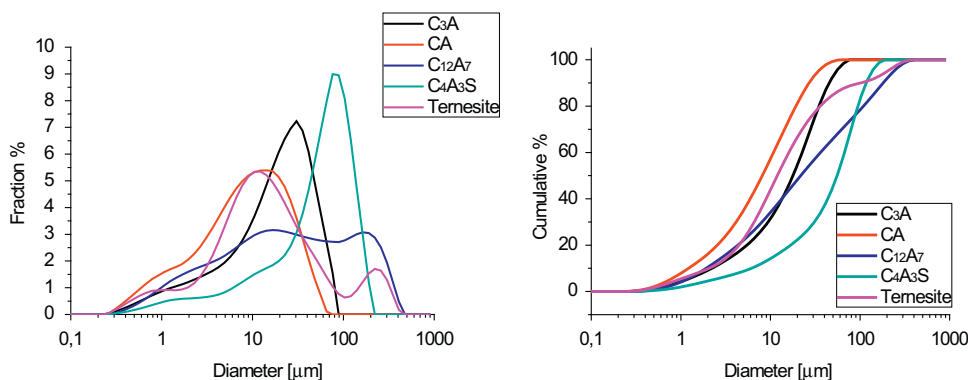The intensity of the initial exothermal signal in the C_3A heat flow

Fig. 1. Particle size distribution (PSD) and the derivative of the PSD of samples C_3A, CA, $C_{12}A_7$, $C_4A_3\bar{S}$, and ternesite.