

Ternesite as a component of sulfobelite cements

M.T. Blanco-Varela and P.M. Carmona-Quiroga

Instituto de Ciencias de la Construcción Eduardo Torroja, Cements and Recycling Materials Department, Madrid, Spain

Abstract. The cement industry is presently devoting substantial effort to the development of less energy intensive, lower emission cements. Calcium sulfoaluminate (CSA) cements, one of the most promising alternatives, are known as ‘eco-cements’ in light of their lower energy costs and GHG emissions. Whilst their clinker composition may vary, all these cements lie in the $\text{CaO-A}_{12}\text{O}_3\text{-SiO}_2\text{-Fe}_2\text{O}_3\text{-CaSO}_4$ system, with constituent minerals that include C_2A , C_2S , C_{12}A_7 , CA , $\text{C}\hat{\text{S}}$, and C_4AF . Ternesite ($\text{C}_5\text{S}_2\hat{\text{S}}$), a phase compatible with ye’elemite ($\text{C}_4\text{A}_3\hat{\text{S}}$) and C_2S , can also be found in that system. Recent studies show that it is activated and hydrated in the presence of AH_3 and gypsum, yielding ettringite and C-S-H gel, the main hydration products of CSA and OPC, respectively, as well as C_2ASH_8 . This study analyses ternesite reactivity in different aluminate blends.

1 Introduction

The environmental impact of Portland cement manufacture has prompted the industry to implement a number of strategies geared to lowering energy and natural raw material consumption while reducing greenhouse gas, particularly CO_2 , emissions. The use of secondary cementitious materials (SCMs, often industrial by-products), alternative fuels, grinding additives, along with improvements in combustion, heat exchange and grinding technologies have diminished both consumption and emissions with no detriment to binder properties [1].

Another strategy consists in developing calcium sulfoaluminate cements (CSA) based on ye’elemite ($\text{C}_4\text{A}_3\hat{\text{S}}$), a phase initially used to produce expansive cement and subsequently stable high-performance binders. CSA cement manufacture is less energy-intensive (at 1250°C , the clinkering temperature is 200°C lower than in OPC) and, depending on the composition, emits 25 % to 40 % less CO_2 than OPC production [2,3]. Whilst not presently used for structural purposes for want of the necessary regulation, these cements are commercialised as components in 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 $\text{CaO-A}_{12}\text{O}_3\text{-SiO}_2\text{-Fe}_2\text{O}_3\text{-CaSO}_4$ system and have lower calcium and silicon and higher aluminate and sulfate phase contents than portland cements. The minerals present in the clinker include $\text{C}_4\text{A}_3\hat{\text{S}}$, C_2S , C_{12}A_7 , CA , $\text{C}\hat{\text{S}}$ and C_4AF , with a predominance of aluminates [4,5].

Ternesite, $\text{C}_5\text{S}_2\hat{\text{S}}$, a phase formed in the reaction between anhydrite and belite and compatible with ye’elemite ($\text{C}_4\text{A}_3\hat{\text{S}}$) and C_2S , also lies within this system.

Ternesite was found as a natural mineral at Ettringer Bellerberg, near Mayen, Eifel, Germany, in the nineteen nineties. Its synthetic form had been identified earlier, however, as a component of cement [6] or lime [7] kiln crust, the sulphur for which was sourced from the fuel, as well as a minority component in some CSA cements [8,9,10].

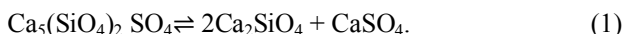
Ternesite was chemically, physically, structurally and petrologically characterised between 1960 and 2000 [6, 7, 11-13]. Regarded as a non-hydraulic material [14-15] until it was recently proven to be activated by aluminium hydroxide [16], it has since become a target for research. This paper describes some of the characteristics of ternesite and its hydraulic activation by other mineral compounds.

2 Physical and structural characteristics

Natural [11] and synthetic ternesite, which are identical, are isostructural with silicocarnotite, $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$ [12,13]. The unit-cell parameters of this orthorhombic mineral, Pnma space group crystal are $a=6.863(1)\text{ \AA}$, $b=15.387(2)\text{ \AA}$, $c=10.181(1)\text{ \AA}$, $Z=4$. Its structure consists in isolated SiO_4 and SO_4 tetrahedral units connected by octa- or heptahedrally coordinated Ca ions. Both S and Si tetrahedrally coordinated with oxygen occupy different tetrahedral positions in the structure, in which double layers of silicate tetrahedral alternate with a layer of sulphate tetrahedral. Natural ternesite is optically biaxial and negative, with refractive index $n_x = 1.630$, $n_y = 1.637$ and $n_z = 1.640$ and an optical angle, $2V_x = 63.5^\circ$.

3 Thermal stability of ternesite

$C_5S_2\hat{S}$ thermal stability has been studied by several authors, some of whom position it in a narrow range of temperatures (1100 °C to 1180 °C [16] or 1200 °C to 1298 °C [15]), above which it would decompose further to the equation:



The decomposition temperature depends on whether it is determined in an open (≈ 1180 °C) or closed (1289 °C) system at a total pressure of 1 atm. [17,18]. Similar findings (≈ 1290 °C at 1 atm.) were reported by Hanein et al. [19], who determined the thermodynamic constants of ternesite to lie between 1000 °C and 1400°C, based on previously published vapour pressure measurements of several sulphates obtained between those temperatures [22]. Those studies showed that the vapour pressure of ternesite, like that of anhydrite, rises with temperature, while ternesite exhibits a pressure lower than anhydrite at 1000 to 1290 °C and higher above that range.

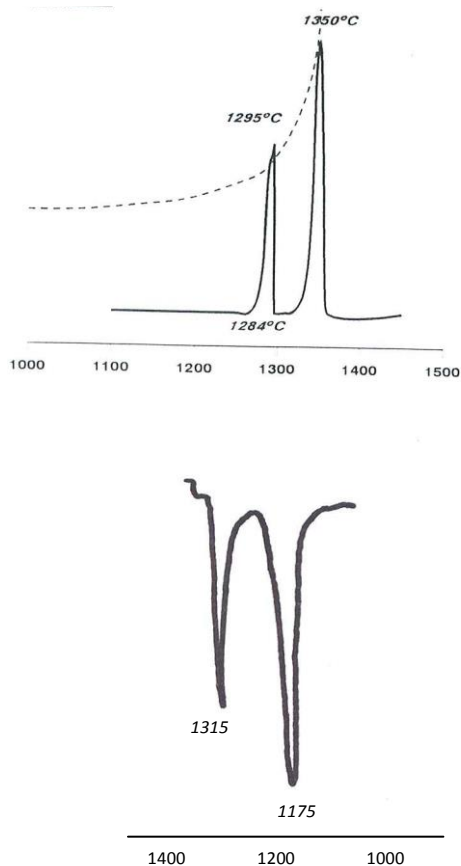
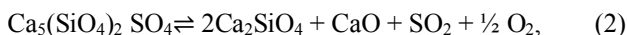


Fig. 1. DTA/TG curves for ternesite, heating (top) and cooling (bottom)

The decomposition reaction of ternesite would also depend, then, on the rate of SO_2 loss and for high temperatures could be described by the equation:



in which ternesite thermal decomposition would be a function of temperature and the partial pressure of SO_2 and O_2 .

For a given temperature and partial pressure of O_2 (which must always be higher than in SO_2 for SO_3 to form), there is a maximum SO_2 pressure above which ternesite does not form [19].

On the DTA curve (10 °C/min in CO_2 -free air), ternesite thermal decomposition induces an endothermic peak at around 1290 °C. As the temperature rises, a second endothermic peak appears due to the fusion of the C_2S - $CaSO_4$ eutectic, which accounts for 10 %-20 % of the composition of $CaSO_4$ [18]. Mass loss intensifies on the TG curve at temperatures of over 1200 °C. During cooling, the DTA curve exhibits two exothermic peaks, respectively denoting the solidification of the C_2S - $CaSO_4$ eutectic (1310 °C) and the α to β polymorphic transformation of $CaSO_4$ (1175 °C). No signal whatsoever is detected that would indicate new ternesite formation along cooling. FTIR and XRD identify $\alpha' C_2S$ and anhydrite (traces of CaO on the XRD pattern), but no ternesite, an indication that at the cooling rate applied (10 °C/min) the decomposition reaction is not reversible.

Table 1. Minerals forming after ternesite thermal treatment

T (°C)	Time	Phases
1315	20 min	$\alpha_L' C_2S$; $CaSO_4$; CaO
1400	20 min	$\alpha_L' C_2S$; $CaSO_4$; CaO
1315 and 1000	20 min and 24 h	$\alpha_L' C_2S$; $Ca_5S_2\hat{S}$; CaO
1400 and 1000	20 min and 24 h	$\alpha_L' C_2S$; $CaSO_4$; CaO

The XRD findings for ternesite exposed to different thermal treatments (Table 1) suggest that once it decomposes, its recrystallization depends on the cooling rate and the temperature reached. Recrystallization is possible after reheating to 1000 °C when the temperature reached does not exceed the melting point of the eutectic; otherwise, recrystallization does not appear to occur.

According to the literature, ye'elemite, ternesite and anhydrite clinkers at a ratio (by weight) of 1:1:0.5 can be obtained from traditional raw materials or industrial by-products at temperatures of around 1200 °C [14]. Two-stage clinkering has also been successfully applied to produce such cements, clinkering the raw meal at 1250 °C for 1 h, followed by gradual cooling to 1100 °C and quick cooling below that temperature [10,20,21]. Single-stage belite and ternesite-rich calcium sulphoaluminate (BY(F)T) have been obtained at a maximum temperature of 1260 °C in a pilot plant where the partial pressure of O_2 and SO_2 was controlled in the kiln [19].

4 Compatibility between ternesite and CaO - SiO_2 - Al_2O_3 - $CaSO_4$ system phases

The following is a discussion of some of the features of the equilibrium phases of the three subsystems most

closely related to the chemistry of cement, namely: $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$; $\text{CaO-SiO}_2\text{-CaSO}_4$ and $\text{CaO-Al}_2\text{O}_3\text{-CaSO}_4$.

The equilibrium phases of the system $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ have long been known in the fields of cement chemistry and ceramics [23]. In addition to mullite, the calcium silicates (C_3S , C_2S , C_3S_2 , CS) and calcium aluminates (C_3A , C_{12}A_7 , CA , CA_2 , CA_6), the system includes two ternary phases: gehlenite and akermanite. C_2S is compatible with C_3A , C_{12}A_7 , CA and gehlenite, as well as with C_3S and C_3S_2 .

In system $\text{CaO-SiO}_2\text{-CaSO}_4$, CaSO_4 is incompatible at 1100°C with C_2S , with which it reacts to form ternesite. Consequently, the equilibrium phases in the CaO -rich zone would be: i) $\text{CaO-CaSO}_4\text{-Ca}_5\text{S}_2\hat{\text{S}}$; ii) $\text{CaO-C}_2\text{S-Ca}_5\text{S}_2\hat{\text{S}}$; iii) $\text{C}_2\text{S-Ca}_5\text{S}_2\hat{\text{S-C}}_3\text{S}_2$; iv) $\text{CaSO}_4\text{-Ca}_5\text{S}_2\hat{\text{S-C}}_3\text{S}_2$ [18].

A ternary phase, $\text{C}_4\text{A}_3\hat{\text{S}}$, present in system $\text{CaO-Al}_2\text{O}_3\text{-CaSO}_4$, is positioned in between the CaSO_4 and the C_3A , C_{12}A_7 and CA . The phases in the Ca -rich zone of the system that are compatible at temperatures under 1350°C are: i) $\text{CaO-C}\hat{\text{S-C}}_4\text{A}_3\hat{\text{S}}$; ii) $\text{CaO-C}_3\text{A-C}_4\text{A}_3\hat{\text{S}}$; iii) $\text{C}_3\text{A-C}_{12}\text{A}_7\text{-C}_4\text{A}_3\hat{\text{S}}$; iv) $\text{C}_{12}\text{A}_7\text{-CA-C}_4\text{A}_3\hat{\text{S}}$ [24].

Studying system $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-CaSO}_4$ at temperatures between 950°C and 1150°C , Pliego-Cuervo [9] found ternesite to be incompatible with C_{12}A_7 and CA , and both C_2S and C_3A to be compatible with ternesite, ye'elemite or both. The compatible phases in the CaO -rich zones of the system were identified as: i) $\text{CaO-C}\hat{\text{S-C}}_4\text{A}_3\hat{\text{S-C}}_5\text{S}_2\hat{\text{S}}$; ii) $\text{CaO-C}_3\text{A-C}_4\text{A}_3\hat{\text{S-C}}_5\text{S}_2\hat{\text{S}}$; iii) $\text{CaO-C}_2\text{S-C}_3\text{A-C}_5\text{S}_2\hat{\text{S}}$; iv) $\text{C}_3\text{A-C}_2\text{S-C}_5\text{S}_2\hat{\text{S-C}}_4\text{A}_3\hat{\text{S}}$; v) $\text{C}_2\text{S-C}_{12}\text{A}_7\text{-C}_3\text{A-C}_4\text{A}_3\hat{\text{S}}$; vi) $\text{C}_2\text{S-C}_{12}\text{A}_7\text{-CA-C}_4\text{A}_3\hat{\text{S}}$.

Strigac [23] broadened the field of study, identifying two new sets of compatible phases in which ye'elemite and ternesite would co-exist: vii) $\text{C}_2\text{S-C}_3\text{S}_2\text{-C}_4\text{A}_3\hat{\text{S-C}}_5\text{S}_2\hat{\text{S}}$; viii) $\text{C}_2\text{AS-C}_3\text{S}_2\text{-C}_4\text{A}_3\hat{\text{S-C}}_5\text{S}_2\hat{\text{S}}$.

Ye'elemite and ternesite can co-exist, then, not only in calcium-rich zones of the system but also in areas with less CaO and more CaSO_4 and SiO_2 , although obviously at temperatures below the ternesite decomposition threshold.

5 Ternesite activation

Although a number of authors have concluded that ternesite is a non-hydraulic phase [14-15], as early as 1992 Berteka et al. [25] synthesised clinkers consisting primarily in ye'elemite and ternesite, with anhydrite as a residual phase. Produced at 1200°C , they exhibited very high strength after hydration. Later studies [16] showed that ternesite hydration would be moderate and very slow.

According to Ben Haha et al. [26], ternesite can be activated with aluminate hydroxide to yield ettringite, stratlingite and C-S-H , the proportions of which depend on the proportion among reactives and their degree of reaction. Bullerjahn et al. [27] reported that ternesite contributed more to early age cement properties than C_2S in the CSA cements they synthesised.

Montes et al. [28] showed that ternesite can also be activated by other aluminates, such as C_3A , C_{12}A_7 , CA

and $\text{C}_4\text{A}_3\hat{\text{S}}$, and established the order of activating effectiveness as: $\text{C}_{12}\text{A}_7 > \text{CA} > \text{C}_3\text{A} > > > \text{C}_4\text{A}_3\hat{\text{S}}$.

The calorimetric curves for hydrated aluminate pastes contain a first dissolution peak, followed by an induction period and an intense reaction peak in pastes CA , C_{12}A_7 and $\text{C}_4\text{A}_3\hat{\text{S}}$ [29-31]. In 2:1 ternesite: aluminate blends hydrated at 25°C for 7 d, the presence of ternesite in the pastes was reported to alter the calorimetric curves of four aluminates, shortening the induction period and bringing the reaction peak forward [28].

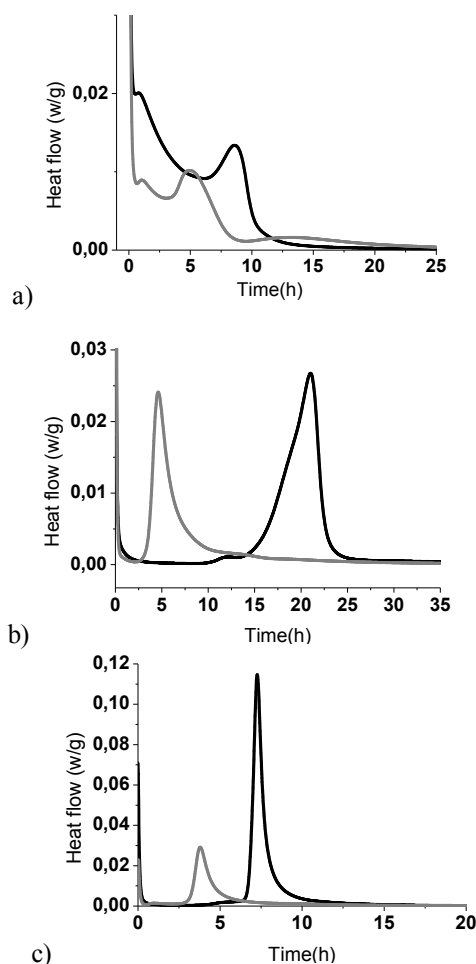


Figure 2. Heat flow curves for: a) C_{12}A_7 (black), C_{12}A_7 +ternesite (grey); b) CA (black), CA +ternesite (grey); c) $\text{C}_4\text{A}_3\hat{\text{S}}$ (black), $\text{C}_4\text{A}_3\hat{\text{S}}$ +ternesite (grey)

The presence of ternesite alters the hydration products of the aluminates. Pastes obtained after calorimetric studies of the ternesite/aluminate blends contain $\text{C}_4\text{A}\hat{\text{S}}\text{H}_{12}$ as a hydration product. C_2ASH_8 is also found in pastes containing C_{12}A_7 or CA . Stratlingite forms neither in ternesite + C_3A pastes nor in the pastes with $\text{C}_4\text{A}_3\hat{\text{S}}$, in which amorphous AH_3 is present [29].

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