Cement and Concrete Research xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: www.elsevier.com/locate/cemconres

The synthesis and hydration of ternesite, $Ca_5(SiO_4)_2SO_4$

Solon Skalamprinos[a,*], Gabriel Jen[b], Isabel Galan[a], Mark Whittaker[b], Ammar Elhoweris[a], Fredrik Glasser[a]

[a] Department of Chemistry, University of Aberdeen, Aberdeen AB24 3UE, UK
[b] School of Engineering, University of Aberdeen, Aberdeen AB24 3UE, UK

ARTICLE INFO

Keywords:
Ternesite
Synthesis
Hydration
Calcium sulfosilicate

ABSTRACT

The hydration and strength evolution of two multi-phase ternesite-based cements with 15 and 29 wt% ternesite are reported. The synthesis and hydration properties of single phase ternesite, nominally $Ca_5(SiO_4)_2SO_4$, are also reported including both chemically-pure ternesite and preparations doped with sodium, potassium, phosphorous, magnesium, manganese, strontium, zinc and titanium oxides. Hydration of the samples at 25 °C was studied by calorimetry and quantitative X-ray diffraction. Unconfined compressive strength development was determined for up to 1 year. Single-phase chemically activated ternesite hydrated rapidly at 25 °C achieved compressive strengths of ≈30 and ≈65 MPa at 28 and 90 days respectively, with C-S-H and gypsum as hydration products. The multi-phase ternesite-based cements reached 7 day strengths of ≈30 MPa. It is concluded that ternesite reacts with water, exhibiting strength gain. The future of calcium sulfoaluminate and sulfosilicate cements is discussed and it is suggested that a considerable, and as yet unrealised scope exists for simultaneously optimising cementing properties while lowering production costs and reducing CO_2 emissions.

1. Introduction

Following its discovery in cement kilns and shortly afterwards as a natural mineral, ternesite (calcium sulfosilicate or sulfospurrite) was studied by several authors. Pryce [1] presented data on ternesite occurring as a wall coating near the flame area of a lime kiln, where temperatures were ≈1100 °C. In addition to its main components, CaO, SiO_2 and SO_3; ternesite incorporated many substituents: Li_2O, SrO, MgO, P_2O_5, Na_2O, K_2O, Al_2O_3, Fe_2O_3; and at ppm level, FeO, Cr_2O_3, TiO_2, NiO, PbO, MnO, CuO and ZnO [1]. More recently, Nievoll et al. [2] also studied the ring formation 3 suspension preheater kilns concluding the rings were also made of ternesite. Pryce [1] and Nievoll et al. [2] described ternesite crystals as granular nodules composed of radiating needles and blades with deeply etched surfaces or as needle shaped crystals, respectively, similar to the naturally-occurring ternesite described by Galuskin et al. [3].

Irran et al. [4] investigated ternesite found as a bright blue mineral in Ca-rich xenoliths in the Ettringer Bellerberg volcano in Eastern Eifel, Germany. Thin section analyses of the assemblage revealed naturally occurring ternesite, ellestadite and a solid solution of ettringite and thaumasite. The morphology of ternesite was described as consisting of radially arranged prismatic crystals that included trace amounts of iron and titanium. The strongest reflections observed by powder X-ray diffraction occurred between 31°–32° 2θ (CuK radiation), but with reflection intensities differing from previously analysed samples of synthetic ternesite. The differences were attributed to preferred orientation caused by elongation of crystals parallel to [100].

Tadzhiev et al. [5] synthesised ternesite using beta belite and anhydrite as starting materials, and measured the strength evolution of the single-phase ternesite during hydration for up to 2 years at ambient temperature, and for 8 h in autoclaves at 8 and 15 atm. Reportedly, the reactivity of single-phase ternesite increased with increasing pressure, being more rapid than beta belite and continuing to increase in strength over the 2 year period of analysis, eventually reaching ≈39 MPa.

Choi and Glasser [6] reported a more detailed procedure for the synthesis of phase pure ternesite, used to measure its vapour pressure and thermal stability. Stoichiometric amounts of belite and calcium sulfate were placed in a “closed system” (consisting of a sealed crucible surrounded by sacrificial calcium sulfate) to protect the reactants against sulfur vapour losses and sintered at 1075 °C for ≈10 days.

Australia's Commonwealth Scientific and Industrial Research Organisation (CSIRO) conducted investigations on calcium sulfoaluminate (CSA) ternesite containing and ternesite-based clinkers synthesised from natural raw materials and industrial waste products; the latter including fly ash and blast furnace slag [7–9]. A three-stage sintering process consisting of initial heating at 1200 °C for up to eight hours with subsequent one-hour holds, first at 850 °C and then at 1000 °C, was used to produce clinkers containing ye'elimite, ternesite

---

* Corresponding author.
E-mail address: s.skalamprinos@outlook.com (S. Skalamprinos).

https://doi.org/10.1016/j.cemconres.2018.06.012
Received 24 July 2017; Received in revised form 19 May 2018; Accepted 13 June 2018

and calcium sulfate. The reported strength of the resulting clinker, formulated to a water to solids weight ratio (w/s) equal to 0.4, reached ≈50 MPa at one day and ≈75 MPa at 1 year [7]. Single-phase pure ternesite was synthesised at 1200 °C for 2 h using as reactants previously synthesised beta belite and calcium sulfate. The resulting phase-pure ternesite was hydrated for up to 2 years at 55 °C and 100% relative humidity and characterised using thermogravimetric analysis (TGA), where ternesite hydration was categorised as very slow [7]. Ternary blends of ye'elimite-ternesite-calcium sulfate were sintered at 1200 °C in a single firing step, at weight ratios of 1:5:0.5, 1:3:0.5 and 1:2:0.5 were hydrated with w/s = 0.20, 0.29 and 0.37, respectively. These mixtures developed strengths of ≈36 MPa, ≈55 MPa and ≈36 MPa after 1 day and 79 MPa, ≈93 MPa, ≈81 MPa after 1 year, respectively [8]. For ternesite-rich (up to ≈60 wt%) CSA clinkers produced in a 1200 °C single firing, the strength of paste samples (hydrated at w/s = 0.4 and 23 °C) after 1 and 28 days were ≈40 MPa and ≈60 MPa, respectively [9]. Despite the apparent success of these clinkers, as evidenced by strength development, the contribution made by ternesite was characterised as being minimal. The authors specifically noted that ternesite hydrates but concluded that its hydration reaction was very slow.

Subsequent to these studies, the Heidelberg Cement Technology Centre, focused on several production methods of clinkers containing ternesite and their resulting reactivity during hydration, reported an activation mechanism for ternesite based on the presence of soluble aluminium hydroxide [10–13]. Ternesite was not however formed in clinkers sintered at 1280 and 1300 °C without the use of mineralizers [14] and it was instead blended as a supplemental additive. The replacement of 11 wt% clinker with ternesite corresponded to ≈16 MPa higher strength relative to a clinker without ternesite following 28 days of hydration [11]. By using a two-stage sintering process, consisting of sintering the batch at 1250 °C for 1 h followed by 1100 °C for 1 h and with subsequent air quenching, ternesite was formed directly and was stabilised as a clinker component. The resulting clinker, with ≈50 wt% ternesite content, was reported to show ≈30 wt% ternesite hydration after 28 days when mixed with water at w/s = 0.6 [12]. Clinkers containing 5 and 12 wt% ternesite were achieved by reducing the temperature and time of the second heating stage to 850 °C and 45 min, respectively. For these compositions (with 0.7 w/c ratio) the ternesite component reportedly achieved 28 and 69 wt% reactivity after 48 h at 20 °C, respectively [13]. Separate investigations of synthesised, single phase ternesite reactivity exhibited higher heat release and enhanced ternesite dissolution in the presence of an aluminium hydroxide additive (typically 30 wt%) [10, 15, 16]. Across the various studies, several explanations, some proven, some not, were reported whereby the reactivity of ternesite could be enhanced: the availability of aluminium hydroxide in the pore solution, the presence of other easily soluble sulfate sources (e.g., gypsum), the particle size distribution, and distortion of the precursor ternesite crystal lattice due to the presence of foreign ions were advanced to explain variations in ternesite reactivity. However, enhancing the reactivity/dissolution of ternesite was noted to inhibit the hydration of beta belite, the retardation was tentatively attributed to oversaturation of Si ions in the pore solution [13].

Similarly to CSIRO and the Heidelberg Cement Technology Centre, Shen et al. [17] produced laboratory belite-sulfoaluminate-ternesite clinkers using phosphogypsum, bauxite and limestone as raw materials as well as pure ternesite using laboratory grade materials, in order to test their hydration behaviour. Two clinkering procedures were investigated, a single stage sintering at 1270 °C for 30 min and a two stage sintering first at 1270 °C for 30 min following by air quenching and reheating for another hour between 1100 and 1200 °C. Shen et al. [17] reported similar results to Heidelberg group [11], whereby ternesite was absent from the clinkers when a single stage sintering was applied. When present, it was concluded that: a) ternesite decreased the early strength evolution of a belite-sulfoaluminate-ternesite clinker but increased after 56 days of hydration (between ≈30 and 38 MPa after 90 days of hydration) and b) pure ternesite had a slow rate of hydration but could be promoted via the addition of 20 wt% ye'elimite (based on the intensity of ternesite XRD peaks).

In the search for new generations of sustainable, reduced carbon emission cements, the Aberdeen group has taken a new approach. Principle to this study has been the partial replacement of hydrocarbon fuels by combustion of chemically-reduced forms of sulfur e.g., as sulfide in reactants or as elemental sulfur, incorporating mineralogical changes to the clinker and giving various cement combinations including e.g. a belite-ye'elimite-ternesite (BYT) formulation [18–20]. The combustion and oxidation of chemically-reduced sulfur species supplies process heat, lessening the use of hydrocarbon fuel and lowering CO_2 emissions [21]. The chemically reduced sulfur, oxidised to "SO_3" in the kiln and preheater, becomes chemically combined into the solid clinker in phases such as ternesite, ye'elimite and anhydrite. An updated version of the phase compatibility in the C-S-A-$\bar{S}$-F[1] system published by Suha and Majling [22] was published by Galan et al. [23]: ternesite was shown to be compatible with both ye'elimite and belite; it was also demonstrated that single stage production of a ternesite-based clinker could be achieved under specific SO_2 (and O_2) partial pressures and temperature but that choice of conditions was crucial to ternesite formation. In many clinkering processes, the vapour phase can be neglected but this is not so for ternesite; its stability limits are sensitive to temperature as well as partial pressures (strictly, fugacities) of both SO_2 and O_2 [24]. Although these pressures are independently variable, the controls necessary to stabilise ternesite are not difficult to achieve in the rotary kiln: a single stage, and pilot-plant production of a BYT clinker was described by Hanein et al. [24]. The conditional upper limit of thermal stability of ternesite without having to pressurise the kiln, was found to be ≈1290 °C.

In the title paper, to further understand the properties of ternesite, a BYT and a ternesite-rich CSA cement (CSA-t) were investigated with regard to hydration kinetics and strength evolution. The impact of dopants and other variables on the synthesis and hydration of single phase[2] ternesite are also presented.

2. Materials preparation and evaluation methods

2.1. Materials preparation methods

2.1.1. Ternesite-based cements

The technology of the pilot scale (10–100 kg) production of BYT and a description of the controlled atmosphere have been given by Hanein et al. [24]. CSA-t was formed as a heat-treated derivative of an experimental BCSA (belite calcium sulfoaluminate) clinker made in a rotary kiln from a pilot plant trial and containing ≈15 wt% alpha prime belite [25]. A 200 g sub-portion of this ground clinker (≈400 m^2/g) was reheated to 1250 °C for 1 h in a box furnace and cooled to 700 °C at 1 °C per minute deliberately to test the stabilisation of alpha prime belite. The isothermal hold and slow cooling destabilised alpha prime belite, transforming it into beta belite and ternesite, the latter forming by reaction of belite with clinker anhydrite.

The phase composition of the two cements, as determined by Rietveld analysis is given in Table 1. The raw mill oxide compositions of the two cements are given subsequently in Table 6. Both cements contain < 50 wt% total ye'elimite ($C_4A_3\bar{S}$), present as both the cubic and orthorhombic polymorphs. The other two principal phases of both cements are ternesite ($C_5S_2\bar{S}$) and beta belite (β-C_2S). For cement BYT, a significant amount of calcium sulfate ($C\bar{S}$) remained from the clinkerisation process while for CSA-t, anhydrite was almost negligible. Minor

---

[1] Cement notations used throughout the text: C: CaO; A: Al_2O_3; $\bar{S}$: SO_3; H: H_2O; S: SiO_2; T: TiO_2, F: Fe_2O_3

[2] Designed and synthesised to be a single phase ternesite but impurities like belite and anhydrite are present (typically no > 7 wt% in total).