



Stability of ternesite and the production at scale of ternesite-based clinkers



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ABSTRACT

A method to synthesize high-purity ternesite is presented and the importance of reaction volume is highlighted; a brief description of the product morphology is also presented. Thermodynamic data for ternesite are derived and the limits of ternesite stability are then explored. An upper temperature stability limit of ≈ 1290 °C at 1 atm is determined; however, this temperature is dependent on the fugacity of the volatile components in the atmosphere. Thermodynamic predictions confirm that belite and ternesite rich calcium sulfoaluminate clinkers can be readily produced in a single stage process at temperatures above 1200 °C provided the atmosphere and temperature are controlled. To demonstrate this control at larger scales, a conventional 7.4-meter rotary kiln has been used to produce ≈ 20 kg of ternesite-containing clinkers. This demonstrates the usefulness of thermodynamic modelling as it has enabled ternesite-based clinkers to be readily produced at scale in a single-stage process using existing equipment without major modifications.

1. Introduction

Ternesite has recently been observed to have cementitious properties [1–4] and its formation and hydration properties have become a major area of research in the cement industry. Belite and ternesite rich calcium sulfoaluminate (BY(F)T; belite-ye'elimite-(ferrite)-ternesite) cement is a relatively new cement system which is a potentially promising alternative to Portland cement (PC) in general use around the world. BY(F)T cement offers a reduced carbon footprint compared to PC due to its lower clinkering temperatures [1] and reduced lime factor [5]. Production of ternesite can also be targeted to help combine unwanted sulfur oxides arising from the combustion of cheaper “sour” fuels and/or sulfur by-product, thus offering an economic advantage over processes paying a premium to use low-sulfur fuels.

In order to estimate the production costs and stability boundaries of ternesite containing clinkers, it is necessary to understand its composition and phase relations in the CaO–Al₂O₃–SiO₂–SO₃ system (see Ref. [6]). Recent work [2–4,7,8] has focused on a two-stage batch production process for synthesising ternesite-based clinkers; however, the differences between this process and the traditional PC process may hinder its acceptance into the conservative cement industry. This work demonstrates that single-stage production of BY(F)T clinker at temperatures above 1200 °C is not only feasible but can also be carried out in a standard cement rotary kiln with only minor modifications. The

key to this is in understanding the stability of ternesite and its coexistence with ye'elimite under various atmospheric conditions.

Ternesite is a naturally-occurring mineral and its crystal structure was first reported by Pryce in 1972 [9]. The synthetic isomorphous calcium sulphosilicate phase has long been known from its occurrence in lime kilns and a more refined crystal structure was reported by Brotherton et al. [10]. The composition of synthetic ternesite is usually close to the stoichiometric formula, Ca₅(SiO₄)₂SO₄. Ternesite has the space group *Pnma* [11] where silicon and sulfur are four coordinated in regular tetrahedral arrangements to oxygen. Two non-equivalent sets of tetrahedral sites occur and, in the synthetic, silicon and sulfur are ordered between these sites. The arrangement is layered, with double layers of silicate tetrahedra alternating with single layers of sulfate tetrahedrons and calcium is in an irregular seven coordination to oxygens.

Ternesite has the same structure as silicocarnotite (Ca₅(PO₄)₂SiO₄) [12]; however, in silicocarnotite, silicate and phosphate groups are distributed randomly amongst both types of tetrahedral sites. Other chemical representatives include cadmium substituted for calcium and GeO₄ for SiO₄ and, with appropriate valence compensation, sodium has also been observed to partially substitute for calcium. Thus the structure of ternesite may be stable under a wide range of thermal conditions and disordering amongst tetrahedral sites in some chemical representatives enables the range of compositions to vary considerably

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from the ideal stoichiometry; with anion disorder enabling entropy stabilization of some compositions.

In the naturally-occurring mineral form of ternesite found in thermally metamorphosed “hornstone”, the formation temperatures are estimated to be in the range 1000–1300 °C [11,13,14]. This stability range is consistent with its appearance in cement kilns where it has been observed to form as rings in the cooler zones of PC kilns. Notably, the raw solid feed to kilns in some reported occurrences did not contain sulfur: the sulfur was instead introduced from “sour” (i.e., sulfur-containing) fuels (e.g., see Ref. [9]). Thus, oxidation of sulfur dioxide to sulfur trioxide SO_3 , and the transfer of SO_3 from the kiln atmosphere to the solid phase are necessary in these cases to supply the sulfur essential for ternesite formation. This method of production of ternesite at scale via sulfur combustion for belite rich calcium sulfoaluminate cements was recently reported by the authors where ternesite appeared as a minor phase in some trial points [15].

The quantitative characterisation of the raw materials and produced clinkers is an essential part of this work; the techniques used for characterisation are therefore described in the following section. A laboratory technique for the synthesis of ternesite and a brief depiction of its morphology is then provided. Existing vapour pressure data are then used to derive thermodynamic data for ternesite which are then combined with thermodynamic modelling to study the limits of ternesite stability including the dependence of phase coexistence on the kiln atmosphere. Theoretical predictions are verified by experiments in controlled atmospheres. A single stage production process for the production of BY(F)T clinkers, predicted via thermodynamic modelling, is then implemented at kg scale in a 7.4 m rotary kiln originally designed for conventional cement manufacture.

2. Characterisation techniques

Material phase assemblages were determined and quantified using Rietveld refinement of X-ray Diffraction (XRD) patterns which were collected with a Philips Epyrean diffractometer in the Bragg-Brentano geometry. The diffractometer was operated at 45 kV and 40 mA and is equipped with a Cu K- α X-ray source, a Ge monochromator, and a PIXcel1D detector. For analysis, each clinker was ground to a fine powder (Blaine fineness $\approx 4000 \text{ cm}^2/\text{g}$) and back loaded into the sample holders and measured from 5° to 65° 2-theta with a step size of 0.026° . The stage was rotated at a revolution time of 4 s to improve counting statistics. The Rietveld refinements were carried out using the GSAS software [16] and the crystal structures of the phases encountered were taken from various sources as follows: orthorhombic ye'elimite [17], cubic ye'elimite [18], belite [19], ferrite [20], gehlenite [21], anhydrite [22], ternesite [11], rankinite [23], and perovskite [24]. The peaks were fitted using a Pseudo-Voigt profile function [25] with an asymmetry correction [26] included. The backgrounds were automatically fit using a linear interpolation function. A March-Dollase ellipsoidal preferred orientation correction algorithm [27] was used when the preferred orientation parameter needed refinement.

The quantification of the oxide composition is determined by X-ray Fluorescence (XRF) analysis; two XRF instruments were used: a PANalytical PW2402 wavelength dispersive sequential spectrometer and the other is an energy dispersive Rigaku NEX QC⁺ bench-top instrument. All XRF oxide composition measurements reported were carried out using the PANalytical instrument except for the analysis of the clay raw material (discussed in the Pilot Kiln Trial section of this paper) which was carried out on the Rigaku instrument. Oxides were measured on both instruments using fused discs of sample material dissolved in a borate flux matrix. The sulfur content of the clinker was not measured by XRF analysis but was determined by chemical analysis using the procedure described in EN 196-2 (Section 4.4.2). In order to analyse the properties of ternesite, it is essential to have a single-phase stock of the material and a technique for its synthesis is now presented.

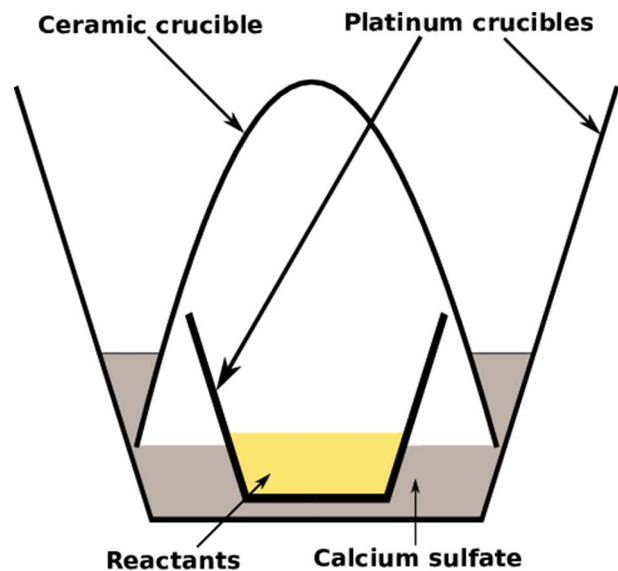


Fig. 1. A schematic of the experimental set-up used for the synthesis of ternesite. The volumes of the large platinum cup, ceramic crucible, and small platinum cup are 360 cm^3 , 100 cm^3 , and 30 cm^3 respectively.

3. Ternesite synthesis and morphology

Choi and Glasser [28] reported that complete reaction of oxide constituents to form ternesite can be achieved after ten days using stoichiometric amounts of belite and calcium sulfate at 1075°C in a “closed system”. Their closed system approach consisted of a platinum crucible covered with platinum foil and physically surrounded with sacrificial calcium sulfate to prevent sulfur vapour losses. Due to difficulties with this method and the danger of contaminating the sample when removing the platinum foil, a variant of this method is reported here. A closed system was formed as shown in Fig. 1 by covering a small platinum cup ($V \approx 30 \text{ cm}^3$) with an inverted ceramic crucible ($V \approx 100 \text{ cm}^3$) to create a dome inside a larger platinum cup ($V \approx 360 \text{ cm}^3$). The underside and the extremities of the ceramic crucible were surrounded with sacrificial CaSO_4 (approx. 50 g) in order to buffer the local atmosphere and minimise sulfur vapour losses.

For the synthesis of ternesite, stoichiometric amounts of SiO_2 (83340-Sigma-Aldrich) and CaCO_3 (C6763-Sigma-Aldrich) sufficient to form 100 g of belite were mixed and ground in a mortar for 5 min with sufficient ethanol to enhance mixing. The mix was placed in a drying oven at 105°C for 2 h. The mixed sample was then placed in a furnace at 1300°C for a total of three days during which the sample was removed daily and characterised then mixed again in a mortar to enhance the reaction. A 100% belite (62% γ and 38% β) powder was obtained after three days. Stoichiometric amounts of the produced belite and CaSO_4 (C/2440/60-Fisher-Scientific) sufficient to form $\approx 20 \text{ g}$ of ternesite were ground, mixed, and dried following the same procedure as for the belite sample. Using the design shown in Fig. 1, the sample was then reacted at 1175°C for three days and a 98% pure ternesite sample was produced. In order to further increase the purity of the ternesite, the sample was again placed in the furnace at the same temperature (1175°C) for another 24 h resulting in a 99% pure ternesite sample. In both Rietveld analyses, the impurities were β -belite and CaSO_4 . It is explained later how the crucible volumes and solid masses chosen led to favourable conditions ($\approx 1\% \text{ v/v}$ partial pressure SO_2) for the formation of ternesite.

The morphology of the synthetic ternesite was analysed using a Hitachi S-520 Scanning Electron Microscope (SEM) with an acceleration voltage of 20 kV. The loose powder was deposited on a sticky tape and gold coated. As shown in Fig. 2, equant crystals up to several microns developed. The texture of crystals and pores is typical of a

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