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Original Article

Solid-state synthesis of pure ye'elimite

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ABSTRACT

Ye'elimite is formed during the production of sulfoaluminate cement. In this article, the orthorhombic ye'elimite formation, the optimal synthesis conditions and the microstructural evolution during synthesis, by solid-state reaction from pure oxide raw materials, is investigated. The phase assemblage was substantially affected by temperature and duration of sintering. Making reference to Rietveld quantitative analysis results, optimal solid-state synthesis conditions of ye'elimite was 1300 °C for 3 h. During ye'elimite synthesis, significant gas releases were observed at different stages of firing using TGA coupled with mass-spectrometer. The gases are the product of carbonate decomposition, gypsum dehydration and sulfate decomposition from the unreacted anhydrite and the formed ye'elimite. Based on the present work, it emerges that a key strategy for forming ye'elimite with a high purity is to compensate sulfate decomposition by the addition of a slight excess of $CaSO_4$ before repeating the firing cycle at optimal conditions. Finally, the porosity was investigated using Archimedes principle measurements compared to BSE-image analysis. It shows the difficulty to achieve dense sintered ye'elimite because of the high decomposition gas releases during the firing process.

1. Introduction

Calcium sulfoaluminate (CSA) cements belong to a family of cements which present some advantages compared to Ordinary Portland Cement (OPC): lowered sintering temperature, reduction of CO_2 emissions, rapid hardening, and shrinkage compensation [1]. The main constituent of CSA cements are ye'elimite ($C_4A_3\overline{S}$ in cementitous notation where C = CaO, A = Al_2O_3, S = SiO_2, $\overline{S}$ = SO_3, C = CO_2, H = H_2O, F = Fe_2O_3), belite (C_2S) and some other phases containing two, three or more of the individual oxides C, A, F, S. According to recent surveys about the different CSA compositions (Fig. 1), it is clear there are several types of CSA cements [1–20]. Because of the chemical and mineralogical nature of the CSA clinkers, it is not possible to standardize under EN 197-1 which only covers Portland compositions. This standardization, which is a necessary condition for the use of these cements in the building sector, will need the development of a completely new standard different from EN 197-1. In this respect, the composition of a cement has to be described precisely and thoroughly, together with its chemical and physical characteristics. At the present time, to our knowledge, CSA cements have not been normalized according to European standardization procedure because neither the composition nor the characteristics have been described precisely. Therefore, there is a need to identify the composition of each phase together with its chemical and physical behaviors.

To examine the hydration behaviour of calcium sulfoaluminate cements, individual and pure components should be prepared, one being ye'elimite. As commercially available CSA cements are a mix of several phases, it is impossible to separate ye'elimite from the other phases. Therefore, a need exists to synthesize $C_4A_3\overline{S}$ phase in a pure state at the lab scale. Table 1 summarizes various protocols described in the literature for the synthesis of ye'elimite by solid-state reaction [21–33]. It can be prepared from a mixture of different raw materials such as limestone ($C\overline{C}$), gypsum ($C\overline{S}H_2$) and bauxite (A) blended with water (or ethanol) in agate mortars. Some authors also pre-fired the raw materials in order to convert gypsum into anhydrite ($C\overline{S}$) whereas limestone is decarbonated inducing the formation of lime (C) and carbon dioxide ($\overline{C}$). Nevertheless, none of the protocols describe completely the experimental conditions, there is always one piece of information missing, especially the quantity of material prepared. The tricky point with the synthesis is the instability at high temperature of ye'elimite [34] and anhydrite [29] leading to their decomposition. 10–20 wt% of calcium sulfate can be decomposed during the thermal treatment [29,35]. Peixing et al. [36] mentioned the used of non-stoichiometric blends to compensate sulfur evaporation. Therefore, it's difficult to produce pure ye'elimite and the synthesis induces the formation of minor phases (C, $C_{12}A_7$, CA, CA_2).

The aim of this paper is to describe thoroughly the protocol to prepare ye'elimite. It is important to know each step and experimental

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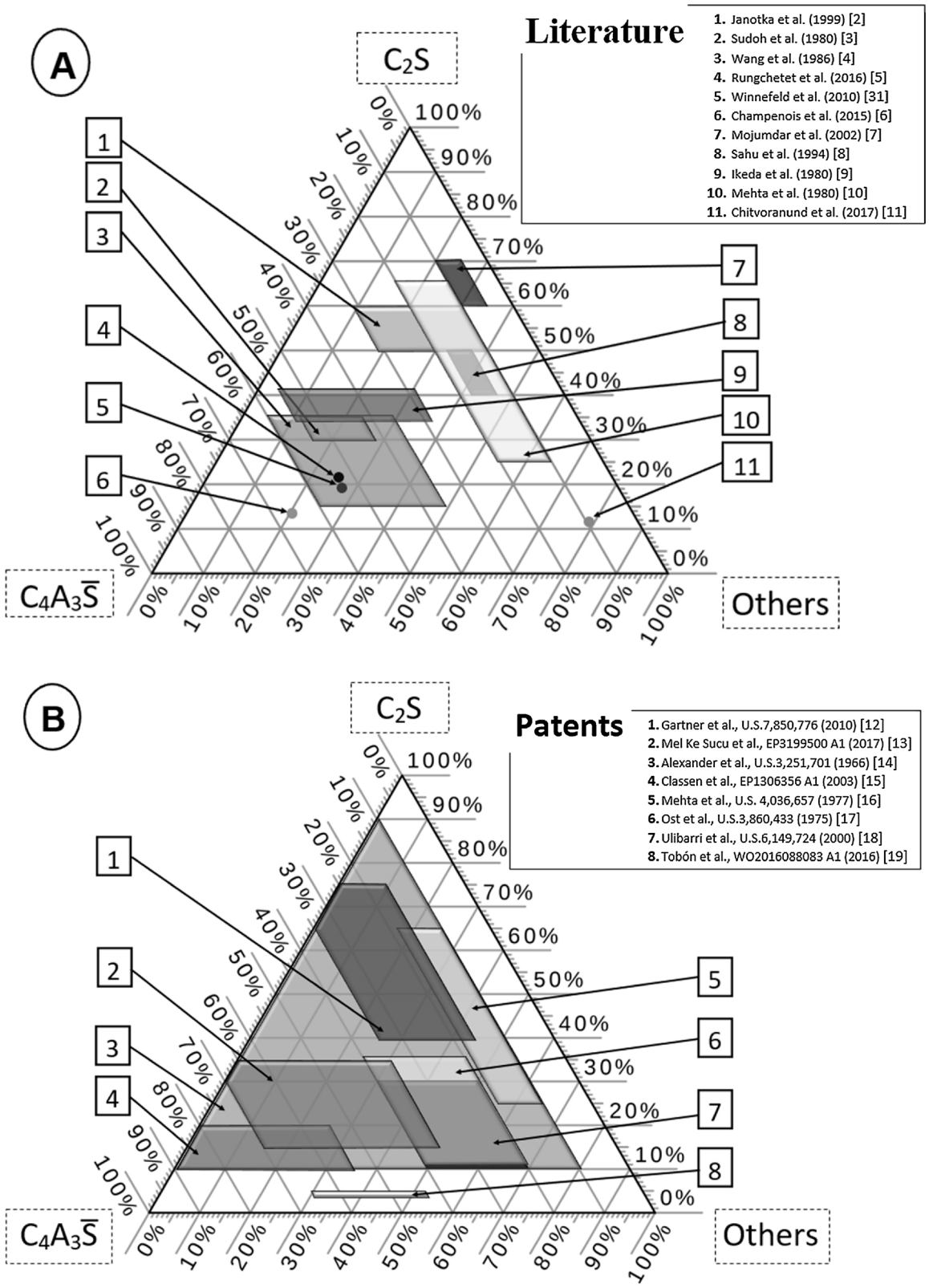

Fig. 1. State of the art about CSA composition collected from literature (A) and patents (B) in the $C_4A_3S^{-}$-C_2S-others ternary system.

procedure because these pieces of information are often missing in the literature, which lead to results that cannot always be understood. It also presents the influence of sintering duration and temperature on the ye'elimite proportion and the minor phases formed. It describes the phase assemblage at various temperatures and proposes a protocol to form pure ye'elimite. It also details a protocol to compensate the sulfate decomposition. During ye'elimite synthesis, the microstructure evolution and phase assemblage determination are investigated in order to