



Effect of raw mix design and of clinkering process on the formation and mineralogical composition of (ternesite) belite calcium sulphoaluminate ferrite clinker



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(Fe_2O_3)_{1-x}) \cdot CaSO_4 polymorphs
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ABSTRACT

The effect of the clinkering process on mineral formation in calcium sulphoaluminate clinker and its reactivity has been investigated using a multi-method approach. Industrial by-products were used as main raw materials for clinker production. Under the given conditions, clinker burning processes lead to variable clinker reactivity and sometimes to an uncontrollable early hydration. The rapid early age hydration seems to result from a simultaneous incorporation of iron in ye'elimite, which stabilises its cubic polymorph at the expense of the orthorhombic one. Ye'elimite has demonstrated as well a high capacity to substitute aluminium with iron. This study proves the possibility to adjust the performance of calcium sulphoaluminate ferrite based systems by applying specific clinkering and cooling processes, and by optimizing the raw mix design accordingly. Additionally, ternesite is formed. Ternesite, which is usually assumed to be inert, has shown reactivity potential when it is a part of belite calcium sulphoaluminate ferrite clinker.

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1. Introduction

Clinkers based on (belite) calcium sulphoaluminate clinkers are promising low CO₂-emitting alternatives to ordinary Portland cement (OPC). Such clinkers are produced by burning raw materials like limestone, clay and bauxite in addition to calcium sulphate within a temperature range of 1250 to 1350 °C. This is 100 up to 200 °C lower compared to OPC, which is typically produced at around 1450 °C. The raw meal composition of (belite) calcium sulphoaluminate clinkers contains less limestone, which results in a clear reduction of the raw material related CO₂ emissions [1]. Additionally, the clinker is more friable and therefore easier to grind due to the lower temperatures involved. The overall production related CO₂ emissions could be reduced by more than 25% [1]. As a result, the production of so called ternesite belite calcium sulphoaluminate ferrite clinkers offers further potential for the beneficiation and the optimisation of clinkers and cements based on calcium sulphoaluminate. These clinker types could be produced using a comparable process to (belite) calcium sulphoaluminate clinkers, but within a temperature range of 900 to 1300 °C. Ternesite, C₅S₂ \bar{S} (cement notation used throughout the document: A = Al₂O₃, C = CaO, F = Fe₂O₃, H = H₂O, K = K₂O, M = MgO, S = SiO₂, T = TiO₂, \bar{S} = SO₃), is a calcium sulphosilicate, known also as sulphospurrite (within this paper, for

simplification purposes further referred to as ternesite). When ternesite is formed or stabilised at temperatures above 1200 °C, the use of a mineralizer such as phosphates or fluorides is required. Another possibility to form ternesite is a methodology developed by the authors which is based upon a two-step clinkering procedure. In a first step, the clinker is sintered at a temperature of at least 1250 °C. In a second step, a slow cooling or so called "second clinkering" is applied by decreasing the temperature from 1200 to 800 °C. Apart from the advantage brought by lowering the energy consumption, this procedure is necessary when low quality raw materials are used for the clinker production. These materials contain high quantities of crystalline phases, e.g. components from the melilite- or mullite-group. Generally, these phases are stable around 1200 °C. A temperature rise to 1250 and even up to 1350 °C is required to decompose them.

Many parameters and factors influencing the performance of (belite) calcium sulphoaluminate based cements such as the clinker formation and composition, the kinetics of the hydration reactions and the microstructure development, are not yet fully understood and still a topic of intense research.

Several authors investigated the formation and the performance of various (belite) calcium sulphoaluminate clinkers [2–12] using a wide range of raw materials, raw mix designs, clinkering processes, cement compositions and different cement quality. Therefore, the resulting performance data of such clinkers and cements are difficult to compare and interpret.

Various research groups investigated the effect of iron on the formation of pure ye'elimite and of ye'elimite in (belite) calcium

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sulphoaluminate clinkers [6,13–26]. Unfortunately, the available data is inconsistent and the results are often contradictory. Previous investigations [19,21] reported the formation of $C_4F_3\bar{S}$ ($Ca_4Fe_6O_{12}[SO_4]$) in a narrow temperature range of 1100 to 1150 °C and 950 to 1205 °C, respectively. On the contrary, other groups never observed the phase $C_4F_3\bar{S}$ and reported a maximum isomorphous substitution within a solid solution of $C_4A_{3-x}F_x\bar{S}$ of A by F of 2 up to 10% [11,12,14,23,25,27–29] (x between 0.08 and 0.40) or even up to 25% [15,17,20,26] ($x \sim 1.05$). Similarly, the effect on the reactivity, by means of kinetics of reactions, of iron-doped and iron-rich ye'elimite is contradictory [15,21,26]. Andac and Glasser [30] investigated the polymorphism of ye'elimite and its solid solutions in the presence of Na^+ and Fe^{3+} . They initially assumed a linkage between the polymorphism and the hydraulic reactivity. Finally, several studies reported that Fe_2O_3 promotes the formation of ye'elimite [12,17,18].

A recent study [27] coupled the X-ray diffraction and Rietveld approach to investigate calcium sulphoaluminate (belite) cement compositions. Besides a complex mineralogical composition of the industrially available clinkers and cements, two different polymorph forms of ye'elimite (cubic and orthorhombic) were observed to occur. In most of the samples, a significant amount of orthorhombic variety forms. However, all commercial calcium sulphoaluminate clinkers contain the cubic form as well. Authors inferred that ye'elimite of an ideal stoichiometry ($Ca_4Al_6O_{12}(SO_4)$) crystallizes in a tectosilicate sodalite type structure e.g. cubic – $Na_4Al_3Si_3O_{12}Cl$ (sodalite) or $Na_3CaCl_3Si_3O_{12}(SO_4)$ (hauyne). However, some aluminates with sodalite-like structure are known to be present in an orthorhombic form as well [29,32]. Others [27] speculate that the simultaneous presence of Na^+ , Fe^{3+} and Si^{4+} leads to the stabilisation of the cubic variety. It would be interesting to investigate (i) the extent of foreign ions incorporation into the crystal structure of ye'elimite, (ii) its influence on the hydraulic reactivity of this phase and (iii) the effect of ye'elimite polymorphism on its own reactivity.

Finally, ternesite is frequently reported as a component in (belite) calcium sulphoaluminate clinkers [2–5,7,11,33]. A previously mentioned comparative study [33] describes that cements containing ternesite show rapid setting and stiffening in contact with water. Nevertheless, various research groups reported that this phase is only slightly reactive at later ages of hydration or even inert [2,8,19,33,34].

The purpose of the actual investigations is to determine the parameters which influence the formation of calcium sulphoaluminate type clinkers and with that the composition and reactivity of ye'elimite. Additionally, a lab scale clinker burning procedure was developed to enhance the formation of ternesite as well as of ye'elimite and to facilitate the use of industrial by-products as raw materials. Therefore, the effect of (i) the substitution of aluminium by iron, (ii) the SO_3 to $(Al_2O_3 + Fe_2O_3)$ ratio ($R_{S/(A+F)}$) and (iii) the clinkering process in correlation with (i) and (ii) was investigated in detail.

2. Materials and methods

The materials used in this study are: high-purity calcite powder (Cc) and high-purity gibbsite powder (AH_3) delivered by Merck, a class F siliceous fly ash (FA) and a natural anhydrite ($C\bar{S}$). The chemical compositions determined by XRF and the physical properties of the investigated raw materials are given in Table 1. The respective mineralogical compositions, determined by coupled X-ray diffraction and Rietveld analysis, are given in Table 2. In order to prepare a big batch of the basic raw mix, all raw materials were used as received and homogenized in a first step for 60 min in a multi-axle rotating mixer. The batch has been split to obtain smaller samples of approximately 50 g each. These were either used directly in the subsequent experimental programme or homogenized further with additions of anhydrite. In a second step, the final mixes were homogenized manually using a ceramic mortar, a pestle and ethanol as dispersive media to improve the sample homogeneity. The raw meal samples were further dried

Table 1
Chemical raw materials composition.

| | | Cc | FA | $C\bar{S}$ |
|--------------------------------|--------------------|-------|-------|------------|
| GV 1050 °C | g/100 g | 43.97 | 0.10 | 4.64 |
| SiO ₂ | | – | 45.60 | 4.17 |
| Al ₂ O ₃ | | – | 20.60 | 1.36 |
| TiO ₂ | | – | 0.68 | 0.04 |
| MnO | | – | 0.05 | – |
| Fe ₂ O ₃ | | – | 8.17 | 0.37 |
| CaO | | 56.03 | 19.30 | 37.40 |
| MgO | | – | 2.17 | 1.82 |
| K ₂ O | | – | 1.63 | 0.28 |
| Na ₂ O | | – | 0.30 | 0.06 |
| SO ₃ | | – | 1.13 | 49.80 |
| P ₂ O ₅ | | – | 0.22 | – |
| Density | g/cm ³ | – | 2.66 | 2.86 |
| Blaine | cm ² /g | – | 3350 | 4380 |

for 24 h at 60 °C in the oven and ground to powder in a ceramic disc mill.

The intended mineralogical clinker composition of the basic mix was 60% C_2S (belite), 25% $C_4A_3\bar{S}$ (ye'elimite), 10% C_4AF (ferrite) and 5% $C\bar{S}$ (anhydrite). The raw mix design was chosen according to a reverse Bogue calculation [10,35] and is presented in Table 3.

Three raw mix designs and two clinker burning and cooling procedures were investigated to evaluate the effects of (i) the clinkering procedure, (ii) the sulphate and (iii) the iron content on the mineral clinker formation. For clinkering, the raw mixes were compacted in a corundum crucible. The clinkering procedures were as follows:

- Clinkering for 1 h at 1250 °C and rapid cooling in air.
- Clinkering for 1 h at 1250 °C, cooling within the furnace to 1100 °C (30 min), second clinkering for 1 h at 1100 °C followed by rapid cooling in air.

According to the literature [2,9,34,36] and to our own investigations $C_5S_2\bar{S}$ (ternesite) does not form but rather decompose above 1200 °C and in special cases, e.g. when mineralizers are used, above 1250 °C. As a result, the two mixes with higher amounts of sulphate would contain high quantities of dead-burned anhydrite. To avoid side effects, arising from the presence and the delayed reaction of dead-burned $C\bar{S}$ e.g. during the calorimetric measurements, only mixes which were submitted the second clinkering step were investigated in detail.

The nomenclature of the six samples is given in Table 4 together with the specific applied clinkering procedure.

The synthesized clinkers were ground using a vibration disc mill to a Blaine fineness of 5000 (± 100) cm²/g. After blending of 90% clinker with 10% $C\bar{S}$, the resulting cement powders were homogenized for 60 min in a multi-axle rotating mixer. The quantitative X-ray diffraction (QXRD) investigations of clinkers and cements were performed using

Table 2
Mineralogical raw materials composition determined by Rietveld analysis.

| | Cc | FA | $C\bar{S}$ |
|-----------------|---------|------|------------|
| | g/100 g | | |
| Amorphous | – | 88.0 | – |
| Calcite | 100.0 | – | 3.2 |
| Dolomite | – | – | 7.1 |
| Quartz | – | 1.3 | 3.5 |
| Mullite | – | 1.9 | – |
| Free lime | – | 2.8 | – |
| Anhydrite | – | 1.3 | 84.1 |
| Gypsum | – | – | 2.1 |
| Gehlenite | – | 1.0 | – |
| βC_2S | – | 1.4 | – |
| Σ Belite | – | 1.4 | – |
| Ferrite | – | 0.7 | – |

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