



Research review of cement clinker chemistry



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ABSTRACT

This paper aims to review the progress in cement clinker chemistry since the last International Conference on the Chemistry of Cement in 2011. Although Portland cement clinker is still, by far, the most important compound of modern cements we show that there is a strong development of alternatives. This is mainly due to the emission of carbon dioxide during the calcination of calcium carbonate as raw material whose reduction is the goal of international activity due to anthropologically caused climate change. Furthermore, it is an objective to use both more raw materials that are located close to the concrete plants and alternative fuels. Developments in the field of cement clinker chemistry show a potential for alternatives. Thereby we discuss both old and new ideas. But it has been shown that the substitution of Portland cement clinker has to consider not only reduction in CO₂ emission during fabrication: For practical solutions the performance in both in terms of strength development and durability has to be adequate compared to the ordinary Portland cement clinker.

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1. Introduction

Since the first Portland cement with the present definition was produced in 1843 by William Aspdin there has been a continuous process of evolution in cement process technology and cement itself. Compared with other industries the speed of development has been moderate, which can certainly be explained by the huge efforts needed to achieve safe and standardized concrete construction. However, since some years there has been a significant increase in the development rate of new cementitious binders. The main impulse for this development is given by the international agreement linked to the United Nations Framework Convention on Climate Change to reduce global CO₂ emission (i.e. Kyoto Protocol). Due to the fact that cement production is responsible for 5% of the global CO₂ emission (i.e. 0.95 tons of CO₂ per ton of Portland cement) and also the introduction of the European Union Emission Trading System the cement industry is facing the challenge to reduce CO₂ emission. Furthermore concrete production has joined the debate on sustainability of the material and production processes.

To date the most effective way to reduce CO₂ emission of cement production is to reduce the clinker content by blending cements with Supplementary Cementitious Materials (SCMs). These SCMs typically are ground granulated blast furnace slag, fly ash, silica fume and limestone. In several countries and for several applications these Portland-composite cements (CEM II according to EN 197-1 and type IS, IP and IT according to ASTM C595/C595M) have already partly replaced the

classical Portland cement. The main component of Portland-composite cements remains the Portland cement clinker that is burnt in a rotary kiln.

In the light of these facts, the fundamental understanding of clinker chemistry remains an important issue and will become even more important if, as often desired, the SCM percentage further increases. The main drawback of cements containing a high percentage of SCM is the low early strength. Additionally, the durability of concretes is affected by SCMs. Optimisation of SCM characteristics can only partly improve these issues. A more effective option could be to target an increase in performance of the clinker fraction in blended cements. Thus, either the search for SCM specific accelerators or improved clinker reactivity is needed. To improve clinker reactivity a detailed characterization of clinker phases starting from chemical composition of clinker phases including minor components, crystallographic and microstructural characterization is a fundamental prerequisite.

Aside from the development of cement composition also the production conditions of Portland cement clinker have changed significantly. Following the rising social demand for CO₂ reduction and sustainability an increasing amount of secondary fuels and raw materials are used in the cement production process. Who would have thought two decades ago that today some cement plants use up to 100% secondary fuels for production and in some countries (e.g. Germany, Switzerland, Austria) the mean proportion of secondary fuels reaches 70%. These developments have induced important changes not only to process technology but also to product composition (chemical and mineralogical composition of clinkers). To ensure the quality of the product the potential changes with respect to reactivity have to be understood. In this way it may also be possible to identify

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advantages of secondary raw and fuel materials (e.g. increased reactivity to due incorporation of minor components introduced by secondary materials).

In addition to reduction of cement clinker content by blending cements with SCMs a couple of other alternative ideas to reduce the CO₂ footprint of cements exist. There are binary or ternary cementitious materials composed of SCMs and activators (geopolymers, sulfate containing slag cements etc., which is the subject of another paper in this volume) or cements based on complete different materials. Intensive research and development is currently carried out on Calcium Sulfoaluminate and binders based on reactive C₂S polymorphs (Ca-Si-Bi) or hydraulic calcium hydro silicates (Celitement).

Our review starts with the main compounds of OPC clinker alite and belite. Then we focus on the alternative fuels and raw materials (AFR) for the cement production. Finally we report on alternative binders.

2. Research on tricalcium silicate (alite)

2.1. Polymorphism, crystal structure and stabilization of alite

2.1.1. Polymorphism and crystal structure of alite

Tricalcium silicate (C₃S) has a nesosilicate structure with isolated [SiO₄] tetrahedra which are connected by Ca–O polyhedra. Because of the importance of alite, much research work has been done on the crystal structure of C₃S in the past 80 years. C₃S exhibits a complex polymorphism depending on temperature or impurities [1]. Due to the complicated structure and the difficulty in preparing single crystal of C₃S, it is difficult to obtain crystal structure information of individual polymorphs. The analysis of the crystal structure of C₃S has been mainly based on powder XRD, DTA and optical microscopy. Only three polymorphic structures (R, M3 and T1) of C₃S have been determined by synthesizing single crystals [2–5]. In order to perform accurate Rietveld quantitative phase analysis (QXRD), several studies in the last decade have focused on the crystal structure of alite [6–10]. Various models are available for T1, T2, T3, M1, M3 and R polymorphs, however, there is still no structural model for the M2 polymorph. Since various models are available for the polymorphs normally found in clinker, few studies have been done on the crystal structure of alite in the past five years.

The XRD pattern permits the determination of the dimensions and symmetries of the various lattices, but little information can be derived about precise atomic positions in the structure. To resolve these problems and to learn more details about the structure of C₃S we recently synthesized single crystals of suitable size (4 mm) using the high temperature optical floating zone furnace [11]. The single crystal of pure C₃S was tested using a CCD single crystal diffraction. 736 atomic parameters were refined. The final crystallographic R factor is 3.58%, which is much smaller than that reported by Golovastikov (R = 9.7%) [12]. This is by far the most exact determination for the structure of C₃S. Space group: P-1(No.2), Lattice parameters: a = 13.719(2) Å, b = 14.291(3) Å, c = 11.745(2) Å, α = 90.235(3)°, β = 94.395(3)°, γ = 104.306(4)°, V = 2224.1(7) Å³, Z = 18. The structure is shown in Fig. 1. It can be seen from Fig. 2 that the structure of C₃S can be considered as a three-dimensional assemblage of [O₃Ca₁₂] trimers. Three [OCa₆] octahedra are connected to form a [O₃Ca₁₂] trimer, the trimer extends along the [112] direction and has a zigzag conformation. It can be seen in Fig. 3 that oxygen atoms are present in two different coordination environments. Among the 45 atomic sites, nine are present in special coordination environment such as O(5), O(6) and O(9). They are octahedrally coordinated by 6 calcium ions. It is believed that these special oxygen atoms account for the high reactivity of C₃S. The ordinary O in SiO₄ is subject to sp³ hybridization, which is a covalent bond, whereas, the special O in [OCa₆] is not connected with small radius Si, and the Ca–O–Ca is an ionic bond. The latter O would be likely to have higher activity.

Based on the known structure, the different polymorphs differ by the silicate tetrahedral orientations. It is known that a higher symmetry of [SiO₄] tetrahedron is attained as the structural symmetry of alite increases [13]. In any case, the accurate structure (atomic position) of different polymorphs (especially for T2, T3, M1 and M2) is still not fully understood.

2.1.2. Stabilization of high temperature polymorphs of alite

Pure C₃S exhibits polymorphism when heated and can be triclinic (T1, T2, or T3), monoclinic (M1, M2, or M3), or trigonal (R). While at room temperature pure C₃S only exists in the T1 (triclinic) form, the higher temperature forms (T2, T3, M1, M2, M3 and R) are not stable even if C₃S is quenched [1]. A practical way to stabilize high temperature polymorphs is doping with foreign ions. Because the hydraulic reactivity of C₃S polymorphs can be enhanced by doping with foreign ions, this subject has gained great attention in recent studies.

2.1.2.1. Individual ions. The influence of individual ions on the structure of C₃S has been extensively studied in the past decades [8]. It was found that the higher the crystal symmetry of C₃S, the less stabilizing ions can be incorporated. Based on the chemical structure of the ions, the basic patterns of substitution are summarized in Table 1. By defining a quantity called structure difference factor *D* [8], in which the structural parameters, such as radius, electrovalence and electronegativity of the substituent ion were taken into account with respect to Ca²⁺, the relationships between the chemical structure parameters of substituent ions and their substitution patterns and abilities to stabilize the higher-temperature forms of C₃S have been established and quantified. As is shown in Table 1, the substitution position changes gradually from Ca to Si as the value of *D* increases, and at *D* ≥ 0.676 (*D* value for Ti⁴⁺) foreign ions start to replace silicon.

The presence of MgO has a stabilizing effect on C₃S formation (decrease in temperature of formation, acceleration of the process, smaller crystals, M3 alite modification). Also an increase in C₄AF content was observed in the presence of MgO [14–16]. A small amount of Al₂O₃ was shown to be effective in stabilizing the M3-type polymorph of alite [17]. Alite with a high P⁵⁺ concentration (P₂O₅ ≥ 0.5 m.-%) can be stabilized as R-type alite [18]. The phase transformations of alite during reheating are mainly correlated with the polymorphic form of alite and the kind and amount of foreign ions incorporated. For example, for alite stabilized as M3 type and with high Mg²⁺ concentration (2% MgO), the reversion to triclinic at 600 °C on the reheating was blocked. The presence of Fe³⁺ has a reverse effect, i.e. the presence of Fe³⁺ promotes the transformation from M3 to T type [13]. In addition, it was also shown that the lattice parameters of alite vary linearly with the amount of foreign ions up to their limits. A

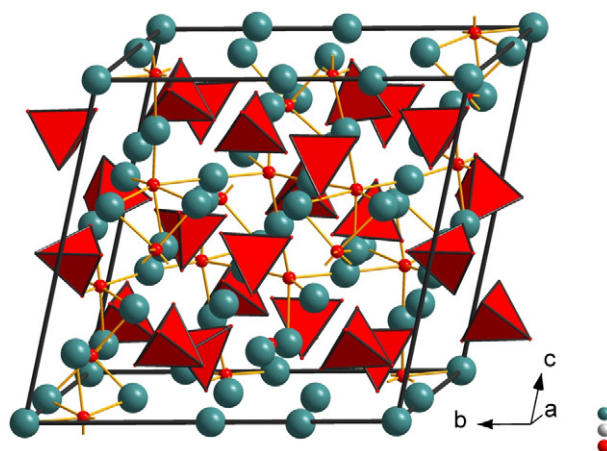


Fig. 1. T1 structure of pure C₃S.

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