The coupled substitution of F⁻ and Al³⁺ guest-ions in the tricalcium silicate phase of Portland Cement

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Portland cement clinker is made by heating a mixture of limestone, sand, and clay, or other materials with a similar bulk composition, up to approx. 1450°C. At this temperature the main hydratable phase, tricalcium silicate 3CaO•SiO₂, is formed. In modern Portland cement production, addition of small amounts of calcium fluoride, CaF₂, to the raw mix of starting materials is increasingly used to facilitate the formation of 3CaO•SiO₂. This process, denoted fluoride mineralization, allows a significant reduction of the upper kiln temperature and hereby reduces the associated energy consumption and CO₂ emission. Furthermore, double-resonance NMR techniques such as CP and REDOR have been employed to study the isolated ²⁹Si – ¹⁹F spin-pairs in the crystal lattice of tricalcium silicate.

Introduction

The coupled substitution mechanism Si⁴⁺ + (O interstitial)²⁻ ↔ Si⁴⁺ + (Oi)²⁻ (int) demonstrated that an increased incorporation of fluoride anions in tricalcium silicate requires a similar increase in the quantity of Al³⁺ guest-ions in this phase. Thus, the F⁻ and Al³⁺ ions may be incorporated in tricalcium silicate by the coupled substitution mechanism, which results in the general formula of Ca₂₇Si₉₋ₓAlₓ(Ob)₃₆(Oi)₉₋ₓ(Fi)x for tricalcium silicate. The result reveals that coupled substitution of F⁻ and Al³⁺ ions is necessary to maintain charge balance in the tricalcium silicate structure. The spectra show a decrease in the amount of tricalcium aluminate when the fluoride content is increased. Thus, the phase is partially consumed by the incorporation of Al³⁺ ions in tricalcium silicate.

EXPERIMENTAL DETAILS

Samples with different fluoride contents (adding 0 – 1.0 wt.% F to the raw mix of starting materials) were synthesized from a white Portland cement clinker including a relatively high amount of Al₂O₃ (5 wt.%). The ²⁹Si – ¹⁹F coupled substitution mechanism is supported by ²⁹Si MAS NMR experiments. Following reactions 1 – 3 (cf. Figure 3) for fixed bulk contents of CaO and Al₂O₃, the increased incorporation of fluoride anions in tricalcium silicate tends to increase the quantity of dicalcium silicate as a result of the release of Si from the substitution by Al³⁺ guest-ions in the tetrahedral site for this phase. Thus, the decrease in molar 3CaO/2Ca₂SiO₄ ratio may account for the Si⁴⁺ ↔ Al³⁺ substitution in tricalcium silicate as well as an increase in the quantity of dicalcium silicate formed from the released Si atoms.

CONCLUSION

Al low F-contents (0 – 1.0 wt.% F), the fluoride anions are exclusively incorporated in the interstitial oxygen sites of the crystal lattice for tricalcium silicate, in accordance with the coupled substitution mechanism Si⁴⁺ + (Oi)²⁻ ↔ Al³⁺ + (F⁻)²⁻ and the composition Ca₂₇Si₉₋ₓAlₓ(Ob)₃₆(Oi)₉₋ₓ(Fi)x for tricalcium silicate. The result reveals that fluoride anions depart from the general trend that impurity ions are preferentially incorporated in dicalcium silicate, since interstitial oxygen sites are only present in the crystal lattice of dicalcium silicate.