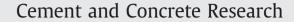
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Iron in carbonate containing AFm phases

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ARTICLE INFO

Article history: Received 6 September 2010 Accepted 23 November 2010

Keywords: Crystal structure (B) AFm phases (D) Solubility product (B) Solid solution (B) Monocarbonate (D)

ABSTRACT

One of the AFm phases in hydrated Portland cement is $Ca_3(Al_xFe_{2-x})O_6.CaCO_3.nH_2O$. It is based on hexagonal and platey structural elements and the interlayer structure incorporates CO_3^{2-} . The solid phases were experimentally synthesized and characterized by different techniques including X-ray techniques (XRD and EXAFS) and vibrational spectroscopy techniques (IR, Raman). Fe-monocarbonate (Fe-Mc) and Almonocarbonate (Al-Mc) were found to be stable up to 50 °C, while Fe-hemicarbonate (Fe-Hc) was unstable with respect to Fe-Mc in the presence of calcite. Fe-Mc has a rhombohedral R3c symmetry which is different from the triclinic of the Al analogue. Both XRD and thermodynamic modelling of the liquid compositions indicated that Al-Mc and the Fe-Mc phases do not form solid solution. The solubility products were calculated experimentally at 20 °C and 50 °C. Under standards condition the solubility products and other thermodynamic parameters were estimated using temperature-solubility product extrapolation and found to be $logK_{50}$ (Fe-Mc) = -34.59 ± 0.50 , $logK_{50}$ (Fe-Hc) = -30.83 ± 0.50 and $logK_{50}(Al-Mc) = -31.32 \pm 0.50$.

1. Introduction

The main hydration products of Portland cements include C–S–H (calcium silicate hydrate), portlandite, ettringite and AFm (Al₂O₃–Fe₂O₃-mono) phases. AFm phases are formed from C₃A (3CaO·Al₂O₃) and C₄AF (4CaO·Al₂O₃·Fe₂O₃) phases in the presence of carbonates, sulphates, chlorides and hydroxide during the hydration of Portland cement. The general formula is Ca₂(Al,Fe)(OH)₆X·nH₂O, where X denotes a single charged or half of a double charged anion which occupies the interlayer sites. Among possible anions are OH⁻, SO²₄⁻, CO²₃⁻ and Cl⁻. AFm phases have a layered structure composed of two layers, a positively charged main layer [Ca₂(Al,Fe)(OH)₆]⁺ and a negatively charged [X·nH₂O]⁻ interlayer. The main layer consists of sheets of Ca(OH)₆ octahedral ions, as in portlandite, in which every third Ca²⁺ is substituted by Al³⁺ and/or Fe³⁺.

Cements are sensitive to carbonation which can lead to the formation of hemicarbonate $3CaO \cdot (Al_xFe_{1-x})_2O_3 \cdot (CaCO_3)_{0.5} \cdot (Ca(OH)_2)_{0.5} \cdot nH_2O$ and/or monocarbonate $3CaO \cdot (Al_xFe_{1-x})_2O_3 \cdot (CaCO_3) \cdot mH_2O$, x = 0 to 1. Al-monocarbonate (Al-Mc) has a triclinic pseudohexagonal symmetry

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[1]. The solubility products of Al-monocarbonate and hemicarbonate have been determined experimentally in the range of 5 to 85 °C [2]. The stability of these phases has an impact on the bulk chemistry of cements as the formation of hemi- and/or monocarbonate indirectly stabilizes ettringite. This results in a higher volume of hydrated phases which can contribute to the improvement in mechanical properties of cement pastes [3,4]. It has been shown that Al-hemicarbonate (Al-Hc) and hydroxy-AFm are unstable with respect to Al-monocarbonate in the presence of calcite [3,5].

OPC contains around 3-4% Fe₂O₃. During hydration, Fe-containing AFm and/or Fe-AFt phases may form. The extent to which Fe is present in AFm and AFt-phases will strongly influence the amount of AFt and AFm phases present and thus the volume of the hydrates and the properties of the hydrated cement. Understanding the characteristic of the hydrates in complex cement matrices is important since the material properties of cement-based materials are related to the chemical environment and the thermodynamic properties of the hydrated phases.

Until recently only rough estimates of the solubility products of Fecontaining monocarbonate and hemicarbonate have been available [6], where the solubility was estimated based on the solubility of the Al-containing phases. The first experimental data on the solubility of Fe-monocarbonate were estimated from Fe-ettringite experiments where contamination with CO_2 led to the formation of Fe-Mc [7].

The formation of solid solutions can play an important role in stabilizing these solids. Solid solutions between anions in the

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^{0008-8846/\$ -} see front matter © 2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.cemconres.2010.11.017