



Iron in carbonate containing AFm phases

B.Z. Dilnesa^{a,*}, B. Lothenbach^a, G. Le Saout^a, G. Renaudin^{b,c}, A. Mesbah^{b,c}, Y. Filinchuk^{d,1}, A. Wichser^a, E. Wieland^e

^a Empa, Laboratory for Concrete & Construction Chemistry, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

^b Clermont Université, ENSCCF, Laboratoire des Matériaux Inorganiques, BP 10448, F-63000 Clermont-Ferrand, France

^c CNRS, UMR 6002, LMI, F-63177 Aubière, France

^d Swiss-Norwegian Beam Lines at ESRF, 6 rue Jules Horowitz, BP 220, 38043 Grenoble, France

^e Paul Scherrer Institute, Nuclear Energy and Safety Research Department, Laboratory for Waste Management, 5232 Villigen PSI, Switzerland

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 $\text{Ca}_3(\text{Al}_x\text{Fe}_{2-x})\text{O}_6\cdot\text{CaCO}_3\cdot n\text{H}_2\text{O}$. It is based on hexagonal and platy 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 Al-monocarbonate (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 $\bar{R}3c$ 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 standard condition the solubility products and other thermodynamic parameters were estimated using temperature-solubility product extrapolation and found to be $\log K_{\text{S}0}(\text{Fe-Mc}) = -34.59 \pm 0.50$, $\log K_{\text{S}0}(\text{Fe-Hc}) = -30.83 \pm 0.50$ and $\log K_{\text{S}0}(\text{Al-Mc}) = -31.32 \pm 0.50$.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

The main hydration products of Portland cements include C–S–H (calcium silicate hydrate), portlandite, ettringite and AFm (Al_2O_3 – Fe_2O_3 –mono) phases. AFm phases are formed from C_3A ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$) and C_4AF ($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$) phases in the presence of carbonates, sulphates, chlorides and hydroxide during the hydration of Portland cement. The general formula is $\text{Ca}_2(\text{Al,Fe})(\text{OH})_6\text{X}\cdot n\text{H}_2\text{O}$, where X denotes a single charged or half of a double charged anion which occupies the interlayer sites. Among possible anions are OH^- , SO_4^{2-} , CO_3^{2-} and Cl^- . AFm phases have a layered structure composed of two layers, a positively charged main layer $[\text{Ca}_2(\text{Al,Fe})(\text{OH})_6]^+$ and a negatively charged $[\text{X}\cdot n\text{H}_2\text{O}]^-$ interlayer. The main layer consists of sheets of $\text{Ca}(\text{OH})_6$ octahedral ions, as in portlandite, in which every third Ca^{2+} is substituted by Al^{3+} and/or Fe^{3+} .

Cements are sensitive to carbonation which can lead to the formation of hemicarbonate $3\text{CaO}\cdot(\text{Al}_x\text{Fe}_{1-x})_2\text{O}_3\cdot(\text{CaCO}_3)_{0.5}\cdot(\text{Ca}(\text{OH})_2)_{0.5}\cdot n\text{H}_2\text{O}$ and/or monocarbonate $3\text{CaO}\cdot(\text{Al}_x\text{Fe}_{1-x})_2\text{O}_3\cdot(\text{CaCO}_3)\cdot m\text{H}_2\text{O}$, $x = 0$ to 1. Al-monocarbonate (Al-Mc) has a triclinic pseudohexagonal symmetry

[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% Fe_2O_3 . 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 Fe-containing 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

* Corresponding author. Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Concrete and Construction Chemistry, Überlandstrasse 129, 8600 Dübendorf, Switzerland. Tel.: +41 44 823 4947; fax: +41 44 823 4035.

E-mail address: belay.dilnesa@empa.ch (B.Z. Dilnesa).

¹ Present address: Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Place L. Pasteur, B-1348, Louvain-la-Neuve, Belgium.