Cement and Concrete Research 41 (2011) 123–128

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

A new approach in quantitative in-situ XRD of cement pastes: Correlation of heat flow curves with early hydration reactions

Christoph Hesse [1], Friedlinde Goetz-Neunhoeffer, Jürgen Neubauer *

Mineralogy, GeoZentrum Nordbayern, University of Erlangen-Nuremberg, D-91054 Erlangen, Germany

ARTICLE INFO

Article history:
Received 24 June 2010
Accepted 29 September 2010

Keywords:
Calorimetry A
Hydration A
Kinetics A
X-Ray Diffraction B
Thermodynamic Calculations B

ABSTRACT

XRD measurements of the hydration of synthetical cement (SyCem) were used to calculate the resulting heat flow from changes in the phase content. Calculations were performed by application of thermodynamic data. The comparison with data recorded from heat flow calorimetry was in good agreement with the calculated heat flow.

The initial maximum of heat flow mainly is caused by the aluminate reaction. During the entire main period the silicate reaction dominates hydration with a high and long first maximum of heat flow. The second but less intense heat flow maximum – only visible as a shoulder in most of the technical cements – can be attributed to an acceleration of the aluminate reaction with the enhanced dissolution of C_3A and the final formation of ettringite. Moreover, the investigation showed that the dissolution process of C_3A is directly controlled by the availability of the calcium sulfate phases.

1. Introduction

Hydration of ordinary Portland cement (OPC) is a rather complex process which normally results in the hardening of a cement paste. During hydration the cement reacts with water resulting in the formation of the different hydrates. Ettringite ($C_3A\cdot 3Cs\cdot H_{32}$) is formed from calcium sulfate, mainly tricalcium aluminate (C_3A), and water during the aluminate reaction [1]. The major calcium sulfate phases are gypsum (Cs·2H), bassanite (Cs·0.5H), and anhydrite (Cs) depending on the raw material and milling process of the cement. The silicate reaction describes the formation of portlandite (CH) and a C-S-H gel from the hydration of tricalcium silicate (C_3S). The composition of the C-S-H gel formed, in particular the Ca/Si ratio, is known to depend on the water to cement ratio (w/c-ratio), the temperature, and also the composition of the cement [2–4]. According to Allen et al. [5], the Ca/Si ratio is 1.7 after 28 d for a C-S-H gel from hydrated OPC at 20 °C and with w/c = 0.4.

The progress of hydration of OPC can be observed by heat flow calorimetry and X-ray diffraction (XRD) analysis. While heat flow calorimetry gives an insight into the development of the heat evolution of hydration, XRD analysis offers the possibility of time resolved determination of the phase composition in the hardening paste. By Rietveld refinement of in-situ XRD data the phase composition of the cement paste can be determined quantitatively without influencing the sample by further preparation [6]. But up to now a detailed interpretation of heat flow curves regarding the ongoing hydration reactions was not published. Thus the intension of this study was to bridge this gap by calculation of the heat flow curves from the time-dependent phase composition of the cement paste.

2. Materials and methods

2.1. Materials

Synthetic cement (SyCem) with a mineralogical composition given in Table 1 was used for the following experiments. The SyCem was produced from a synthetic clinker composed of 95 wt.-% alite and 5 wt.-% C_3A co-sintered at 1400 °C for totally 9 h in a laboratory furnace. The ground clinker was mixed with a sulfate carrier composed of 52.3 wt.-% α-bassanite and 47.7 wt.-% anhydrite II, with a total SO_3 content of 3.1 ma.-% with respect to the cement. Sulfates were synthesized at defined temperatures and characterized as described in [7]. The determined specific surface of the cement was 3700 cm^2/g (Blaine). At early times (first 22 h) the synthetic cement exhibits a hydration behavior, which is comparable to the technical white cement [8].

2.2. In-situ XRD and Rietveld analysis

Cement and water were weighted out to result in a water to cement (w/c) ratio of 0.5. For the in-situ XRD analysis a custom-made sample holder was used which controls the temperature during the measurement [8]. Two measurement temperatures were used: 23 ± 0.1 °C and

* Corresponding author. Tel.: +49 9131 85 23 986; fax: +49 9131 85 23 734.
E-mail address: neubauer@geol.uni-erlangen.de (J. Neubauer).
[1] Present address: BASF Construction Chemicals GmbH, D-83308 Trostberg, Germany.

0008-8846/$ – see front matter
doi:10.1016/j.cemconres.2010.09.014