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Analysis of aluminum concentrations in the pore solution during hydration of tricalcium silicate

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ABSTRACT

The hydration of two batches of tricalcium silicate was followed by isothermal heat conduction calorimetry and analysis of pore solution composition. These two samples were different in Al_2O_3-content and free lime concentration. It was observed that the material containing aluminum reacts slower than the pure one. The reactivity was also analyzed in the presence of ettringite, gypsum and tricalcium aluminate, respectively.

The aluminum concentration in the pore solution was always below the limit of detection during hydration of the samples independent of the presence of aluminum in tricalcium silicate or the addition of most supplementary phases. Elevated aluminum concentrations were only observed in the presence of tricalcium aluminate.

The experimental investigations confirm earlier results that aluminum can reduce the reactivity of tricalcium silicate. It is shown in this study that this mechanism is not based on elevated aluminum concentrations in the pore solution.

1. Introduction

Tricalcium silicate (Ca_3SiO_5, abbreviated as C_3S) containing different foreign ions is the major phase of Portland cement clinker and responsible for strength gain during hydration of cement. The most important foreign ions present in tricalcium silicate produced under industrial conditions are aluminum, magnesium and iron, whereas other ions such as sulfur and potassium appear in much lower concentrations [1].

Hydration of tricalcium silicate is still a strongly discussed issue [1,2] and the kinetics of this reaction is affected by a number of parameters including fineness, temperature, presence of foreign ions, addition of admixtures, pore solution composition, thermal history of the starting material and others. Most of the information regarding the impact of these parameters on the kinetics were derived from phenomenological studies whereas understanding of the basic mechanisms governing these interactions is still poorly developed. This applies also to the impact of aluminum on the hydration of tricalcium silicate.

Previous studies have shown that the hydration of tricalcium silicate is affected by aluminum. Odler and Schüppstühl [3] analyzed the reactivity of tricalcium silicate samples with 0.0, 0.5 and 1.0 wt% Al_2O_3, respectively by calorimetry. The maximum of the main hydration period was delayed by the incorporation of aluminum in the crystal lattice of tricalcium silicate.

Samples of tricalcium silicate containing different concentrations of Al_2O_3 (0.0, 0.5 and 1.0 wt%) were prepared by a sol-gel method followed by burning at 1500 °C in a study by Stephan et al. [4]. The incorporation of 1.0 wt% Al_2O_3 led to shortening of the induction period and broadening of the main hydration period that was compensated by a reduction in intensity. The total heat dissipated after 7 days was slightly increased by the addition of aluminum [5].

Data related to the composition of the pore solution was obtained in a study by Minard [6]. It was shown that the evolution of the silicon concentration during the first 30 min of tricalcium silicate hydration is hardly affected by the presence of aluminum ions in the starting solution (20 μmol/L). This experiment was conducted in a saturated calcium hydroxide solution at a water/solid-ratio of 50. It was observed in a related experiment that the reactivity of tricalcium silicate is slightly reduced when aluminum is present in the starting solution (20 μmol/L) indicated by a slower increase of conductivity during hydration at water/solid-ratios of 50 and 100, respectively. Much higher aluminum concentrations (5 mmol/L) at lower calcium concentrations (8 mmol/L) in the starting solution extended the length of the induction period when the hydration was monitored at water/solid-ratio = 50. This effect was strongly reduced at a much lower water/solid-ratio (0.45).

The role of aluminum during hydration of tricalcium silicate was also studied by Begarin et al. in dilute suspensions at a water/solid-ratio of 250 starting in water [7]. A sample of pure tricalcium silicate showed an induction period (indicated by a plateau in the electrical conductivity curve) of approximately 20 min that was extended to approximately 60 min when a sample of tricalcium silicate containing 0.1 wt% Al was used, i.e. the hydration was delayed under these conditions. The ion concentrations were monitored during the first 30 min of hydration

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Table 1
Properties of both tricalcium silicate samples used in this study. The chemical composition was analyzed by classical wet methods in combination with ICP-OES. The concentration of the crystalline phases was obtained by X-ray diffraction in combination with the Rietveld method. Limits of detection (LOD): Al_2O_3 = 0.2 wt%, free CaO = 0.2 wt%, dicalcium silicate = 3.0 wt%, free lime (QXRD) = 0.2 wt%.

	Pure C_3S	Al-doped C_3S
CaO [wt%]	73.3	73.2
SiO_2 [wt%]	26.4	25.6
Al_2O_3 [wt%]	<LOD	0.5
Free CaO [wt%]	<LOD	1.0
Other foreign elements	<LOD	<LOD
BET [m^2/g]	0.41	0.53
Blaine [m^2/g]	0.29	0.22
Tricalcium silicate (triclinic) [wt%]	100.0	99.2
Dicalcium silicate [wt%]	<LOD	<LOD
Free lime (QXRD) [wt%]	<LOD	0.8

indicating almost constant calcium concentrations of approximately 4 mmol/L and silicon concentrations of approximately 1500 μmol/L. Slightly higher calcium and silicon concentrations were observed during hydration of the undoped sample compared to the sample containing Al as a foreign ion. The aluminum concentration rose to approximately 20 μmol/L in the first minutes and fell back to approximately 8 μmol/L after 30 min in the sample containing aluminum.

Nicoleau et al. [8] studied the impact of aluminum ions in the pore solution on the dissolution of tricalcium silicate at a water/solid-ratio of 10 000. It was shown that the presence of $AlCl_3$ in a concentration up to 2000 μmol/L resulted only in minor modifications of the dissolution rate when the pH value was relatively high (NaOH = 50 mmol/L). In contrast to this, the addition of $AlCl_3$ had a much stronger effect on the dissolution of tricalcium silicate in less basic solutions (NaOH = 5–10 mmol/L). In this case, the addition of $AlCl_3$ in a concentration of 100 μmol/L resulted in a decrease of the dissolution rate by up to 20% compared to the absence of $AlCl_3$.

The impact of aluminum on the hydration also depends on the simultaneous presence of sulfate ions. Early research on the interaction of tricalcium silicate with tricalcium aluminate and gypsum has focused on systems with a high content of tricalcium aluminate [9] and it was difficult to extract information how the kinetics of tricalcium silicate are affected. More relevant were compositions used by Minard [6] and also by Quennoz and Scrivener [10]. It was observed in the latter study that the reaction of alite containing 1% alumina is strongly accelerated by the addition of gypsum, whereas the reaction of pure tricalcium silicate was slightly delayed by an extension of the induction period in the presence of gypsum. The retarding effect of aluminum in systems containing insufficient amounts of gypsum was attributed to an increase of the aluminum concentration in the pore solution [10].

The aforementioned studies indicate that the reaction of tricalcium silicate can be affected by the availability of aluminum but a reduction of reactivity was not reported in all studies. The interaction of tricalcium silicate with aluminum seems to be independent from its source. Aluminum incorporated as a foreign element in tricalcium silicate and

Table 2
Chemical and mineralogical composition of the materials used as addition to tricalcium silicate.

	Ettringite	Gypsum	Tricalcium aluminate
Source	This sample was prepared by continuous stirring of 2.5 g tricalcium aluminate, 4.8 g gypsum and 100 g water for 14 days at 22 °C.	Riedel-de-Haen	Tricalcium aluminate was produced by high temperature solid state reaction of $CaCO_3$ and Al_2O_3 at 1300 °C.
Purity according to QXRD [wt%]	100 (no other phases detected)	100 (no other phases detected	100 (no other phases detected
LOI 1000 °C [wt%]	46.6	20.6	0.1
CaO [wt%]	27.1	32.2	61.2
Al_2O_3 [wt%]	8.6	0.1	37.8
SO_3 [wt%]	19.6	46.8	0.1
Sum other oxides [wt%]	0.3	0.1	0.8

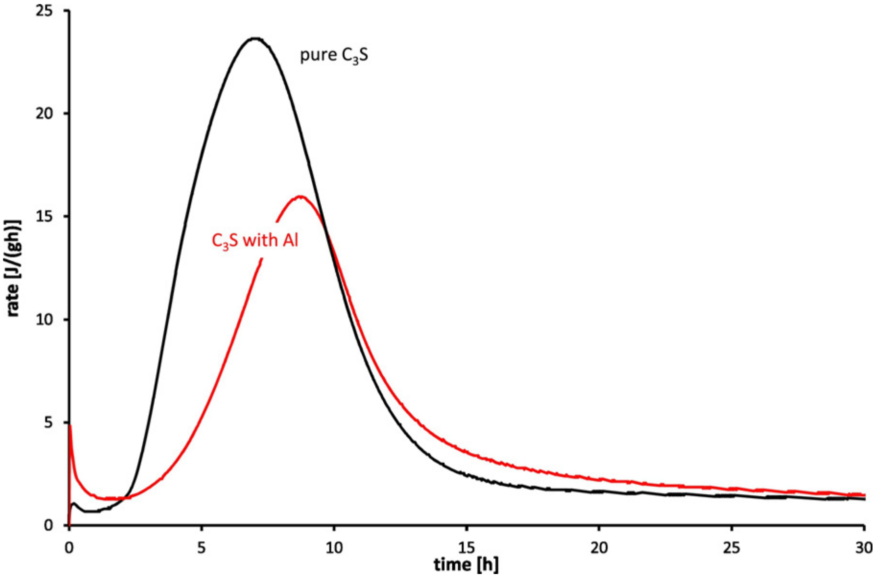

Fig. 1. Isothermal heat conduction calorimetry data for two samples of tricalcium silicate (w/s = 0.50).