



Dissolution rates during the early hydration of tricalcium silicate

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ABSTRACT

The hydration of triclinic tricalcium silicate containing foreign oxides was investigated in this study. Two water/solid-ratios of 50 and 0.50 were applied. The kinetics of the reaction was analyzed by a combination of methods including thermal analysis, pore solution analysis, and calorimetry. From these data, the evolution of the rate of reaction during hydration was calculated. The results were compared to the free, unconstrained dissolution of tricalcium silicate in undersaturated solutions. Such dissolution rates were analyzed in a dissolution cell connected to an ICP-OES instrument. A comparison of the free dissolution rate in the absence of precipitation of hydrates to the rate of reaction showed that the dissolution of tricalcium silicate is much faster than the rate of reaction of the global process.

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1. Introduction

Tricalcium silicate (Ca_3SiO_5 or C_3S in cement chemistry shorthand notation) is the main component of Portland cement clinker. Its reaction with water is directly responsible for setting and hardening of cement. The early stage of hydration of tricalcium silicate is discussed for a long time and different theories were introduced to explain the kinetics of this reaction [1]. Apparently, there is still no consensus about the slow reaction during the induction or dormant period which is followed by a much faster reaction during the main hydration period [2].

The reaction of tricalcium silicate with water to C–S–H and calcium hydroxide is a dissolution–precipitation reaction that proceeds in several steps. These individual steps are: dissolution of the educt, nucleation of meta-stable and stable reaction products, and finally growth of these reaction products. It can be expected that the rate of the slowest step dictates the kinetics of the global process. The critical kinetic step can be different for the individual stages during reaction. An identification of the rate-limiting step requires a separate analysis of the rates of the individual steps, their mutual dependence and a comparison of the results to the true rates that are observed for the global process.

In this study, the dissolution rates of tricalcium silicate in the absence of hydration products on its surface are compared to rates of reaction during hydration. The rates of reaction can be analyzed by a number of experimental techniques that are used for a long time in cement chemistry. These include direct observation methods such as heat conduction calorimetry and electrical conductivity as well as the analysis of the educt/product-ratio after stopping the hydration after

distinct time intervals. A number of experimental methods can be used for the analysis of this ratio including X-ray diffraction (XRD), ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR), thermogravimetry (TG) and also other methods [1].

In contrast to the rates of the global process, rates of individual kinetic steps such as dissolution rates, nucleation time lag, and precipitation rates are not frequently reported. Dissolution rates are traditionally measured by analyzing the evolution of the ionic concentrations over time or by measuring the volume of the dissolved educt after discrete time intervals. Both approaches depend critically on the ability to prevent the precipitation of hydration products during the analysis because this would shift the experiment from a pure dissolution process to a dissolution–precipitation process. Dissolution rates of tricalcium silicate in undersaturated condition were reported by Nicoleau [3], Nicoleau et al. [4], Bisschop and Kurlov [5], and Bellmann et al. [6] using different techniques. This data is summarized in Table 1.

The dissolution rate in undersaturated condition is affected by specific surface area, composition of the solution, temperature, and potentially by the presence of dislocations in the crystal lattice [7]. Pure dissolution rates measured in the absence of precipitation should be equal to the global rate of the reaction if dissolution is the critical kinetic step of the reaction. In contrast to this, dissolution is not the rate-limiting step if the dissolution rate is significantly higher than the rate of reaction. Such a comparison between individual and global rates requires the determination of dissolution rates in undersaturated solutions at exactly the same conditions (specific surface area, ionic concentrations in solution, temperature) that are observed during hydration experiments representing the complete dissolution–precipitation process.

In this study, the hydration of tricalcium silicate was investigated by pore solution analysis, calorimetry, and thermogravimetry. The pore

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Table 1

Summary of dissolution rates of tricalcium silicate at 20–25 °C in undersaturated condition reported in the literature.

Study	Material	Specific surface area	Method to analyze dissolution rate	Solution	Dissolution rate [$\mu\text{mol}/(\text{s}\cdot\text{m}^2)$]				
Nicoleau [3]	Triclinic Ca_3SiO_5	0.36 m^2/g (Blaine)	Analysis of Si-concentration in the aqueous phase during dissolution	Water	–61.0				
				Ca = 5.5 mmol/l	–11.4				
				Ca = 11 mmol/l	–4.97				
				Ca = 22 mmol/l	–0.20				
				Ca = 22 mmol/l	–0.25				
Nicoleau et al. [4]	Monoclinic Ca_3SiO_5 (sample m)	0.40 m^2/g (calculated from particle size distribution)	Analysis of Si-concentration in the aqueous phase during dissolution	Ca = 0.24 mmol/l, Si = 81 $\mu\text{mol}/\text{l}$	–74.0				
				Ca = 1.09 mmol/l, Si = 31 $\mu\text{mol}/\text{l}$	–51.6				
				Ca = 2.10 mmol/l, Si = 22 $\mu\text{mol}/\text{l}$	–36.0				
				Ca = 1.77 mmol/l, Si = 590 $\mu\text{mol}/\text{l}$	–20.2				
				Ca = 3.31 mmol/l, Si = 101 $\mu\text{mol}/\text{l}$	–14.4				
				Ca = 3.36 mmol/l, Si = 1120 $\mu\text{mol}/\text{l}$	–10.4				
				Ca = 6.12 mmol/l, Si = 75 $\mu\text{mol}/\text{l}$	–8.39				
				Ca = 10.1 mmol/l, Si = 55 $\mu\text{mol}/\text{l}$	–3.18				
				Ca = 19.81 mmol/l, Si = 24 $\mu\text{mol}/\text{l}$	–0.68				
				Ca = 0.06 mmol/l, Si = 20 $\mu\text{mol}/\text{l}$	–128				
Nicoleau et al. [4]	Triclinic Ca_3SiO_5 (sample t1)	0.22 m^2/g (calculated from particle size distribution)	Analysis of Si-concentration in the aqueous phase during dissolution	Ca = 0.21 mmol/l, Si = 69 $\mu\text{mol}/\text{l}$	–119				
				Ca = 0.30 mmol/l, Si = 110 $\mu\text{mol}/\text{l}$	–123				
				Ca = 0.89 mmol/l, Si = 3 $\mu\text{mol}/\text{l}$	–114				
				Ca = 0.70 mmol/l, Si = 79 $\mu\text{mol}/\text{l}$	–114				
				Ca = 1.10 mmol/l, Si = 41 $\mu\text{mol}/\text{l}$	–67.1				
				Ca = 2.60 mmol/l, Si = 10 $\mu\text{mol}/\text{l}$	–36.5				
				Ca = 2.69 mmol/l, Si = 12 $\mu\text{mol}/\text{l}$	–27.4				
				Ca = 2.70 mmol/l, Si = 23 $\mu\text{mol}/\text{l}$	–45.7				
				Ca = 2.69 mmol/l, Si = 27 $\mu\text{mol}/\text{l}$	–45.7				
				Ca = 2.64 mmol/l, Si = 38 $\mu\text{mol}/\text{l}$	–46.7				
				Ca = 5.00 mmol/l, Si = 2 $\mu\text{mol}/\text{l}$	–20.6				
				Ca = 5.54 mmol/l, Si = 5 $\mu\text{mol}/\text{l}$	–10.5				
				Ca = 5.50 mmol/l, Si = 6 $\mu\text{mol}/\text{l}$	–17.8				
				Ca = 5.52 mmol/l, Si = 8 $\mu\text{mol}/\text{l}$	–8.68				
				Ca = 5.50 mmol/l, Si = 9 $\mu\text{mol}/\text{l}$	–8.18				
				Ca = 5.48 mmol/l, Si = 10 $\mu\text{mol}/\text{l}$	–8.21				
				Ca = 8.50 mmol/l, Si = 1 $\mu\text{mol}/\text{l}$	–6.84				
				Ca = 8.43 mmol/l, Si = 7 $\mu\text{mol}/\text{l}$	–8.68				
				Ca = 8.40 mmol/l, Si = 10 $\mu\text{mol}/\text{l}$	–8.68				
				Ca = 10.6 mmol/l, Si = 5 $\mu\text{mol}/\text{l}$	–5.47				
Nicoleau et al. [4]	Triclinic Ca_3SiO_5 (sample t2)	0.37 m^2/g (calculated from particle size distribution)	Analysis of Si-concentration in the aqueous phase during dissolution	Ca = 0.25 mmol/l, Si = 82 $\mu\text{mol}/\text{l}$	–103				
				Ca = 0.29 mmol/l, Si = 10 $\mu\text{mol}/\text{l}$	–95.2				
				Ca = 0.38 mmol/l, Si = 126 $\mu\text{mol}/\text{l}$	–96.5				
				Ca = 1.36 mmol/l, Si = 438 $\mu\text{mol}/\text{l}$	–69.2				
				Ca = 1.74 mmol/l, Si = 548 $\mu\text{mol}/\text{l}$	–65.4				
				Ca = 11 mmol/l, Si = 3 $\mu\text{mol}/\text{l}$	–2.94				
				Ca = 15 mmol/l, Si = 2.4 $\mu\text{mol}/\text{l}$	–1.08				
				Ca = 21 mmol/l, Si = 7.5 $\mu\text{mol}/\text{l}$	–0.24				
				Ca = 21 mmol/l, Si = 8.6 $\mu\text{mol}/\text{l}$	–0.33				
				Ca = 20 mmol/l, Si = 13 $\mu\text{mol}/\text{l}$	–0.06				
				Ca = 25 mmol/l, Si = 15 $\mu\text{mol}/\text{l}$	–0.02				
				Bisschop and Kurlov [5] Bellmann et al. [6]	Synthetic alite Triclinic Ca_3SiO_5	3.7 mm^2 (SEM image analysis) 0.27–0.44 m^2/g (Blaine) 0.55–1.12 m^2/g (BET)	Analysis of dissolved volume Analysis of Si-concentration in the aqueous phase during dissolution	Water	–93
								Ca = 20.4 \pm 0.5 mmol/l, Si = 5 \pm 4 $\mu\text{mol}/\text{l}$	–0.55 \pm 0.25 (BET)

solution composition data is used to estimate the free, unconstrained dissolution rate of tricalcium silicate under identical condition in the absence of any hydrates that are precipitated directly after contact with water. These rates are compared to the rates of the global process in order to derive information if dissolution is the rate-controlling step in the early stage of hydration.

2. Materials and methods

Tricalcium silicate was produced by high temperature solid state reaction at 1550 °C in a platinum crucible. The synthesis was terminated by rapid quenching in air. In order to obtain a fine powder with a particle size smaller than 63 μm , the material was ground in a disk mill for 3 min. The chemical and mineralogical composition of this sample of tricalcium silicate was analyzed by classical wet chemistry methods and XRD, respectively.

Information about the specific surface area was obtained by the Blaine-method and laser light scattering.

The sample of tricalcium silicate used in this study was composed of 90.7 wt.% triclinic tricalcium silicate and 9.3 wt.% dicalcium silicate

in the form of the β -polymorph. Other crystalline phases were not detected by XRD. The following chemical composition was obtained: 26.5 wt.% SiO_2 , 71.0 wt.% CaO, 1.0 wt.% Al_2O_3 , 0.6 wt.% ZnO, 0.4 wt.% MgO, 0.1 wt.% Fe_2O_3 , and 0.1 wt.% SO_3 . Selective dissolution gave a free lime content of 0.1 wt.%. These data indicate that the sample used in this study was a mix of triclinic alite and belite containing a rather high concentration of foreign elements.

The specific surface area was analyzed by the Blaine-method (0.283 m^2/g), and calculated from the particle size distribution (1.33 m^2/g). The dissolution rates reported in this paper refer to the specific surface area measured by the Blaine method.

The hydration of tricalcium silicate was investigated in suspension at a water/solid-ratio of 50 and in form of a paste at a water/solid-ratio of 0.50. For the suspension experiment, a saturated calcium hydroxide solution was produced by mixing twice deionized water with freshly decarbonated CaO. Undissolved remains of the solid were removed from the solution by filtration (Millipore, 0.45 μm) and the Si and Ca concentrations in the solution were analyzed by ICP-OES. For the hydration experiment, 200.0 g of this solution were mixed in a glass beaker with anhydrous tricalcium silicate (4.00 g) to obtain a water/

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