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Dissolution kinetics of C–S–H gel: Flow-through experiments

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ABSTRACT

C–S–H gel dissolution kinetics was studied by means of flow-through experiments under CO_2-free atmosphere at room temperature (23 ± 2 °C). The starting C–S–H gel was obtained by hydration of commercial C_3S ($3CaO{\cdot}SiO_2$) and consisted of 67 wt% C–S–H with a Ca/Si ratio of 1.7 ± 0.1 and 33 wt% portlandite. Based on the changes in aqueous chemistry and in the C–S–H solid, it was observed that the C–S–H gel dissolves incongruently when the Ca/Si ratio is high and congruently as the Ca/Si ratio decreases to the tobermorite stoichiometric Ca/Si ratio of 0.83. First, a dissolution rate law for C–S–H gel with Ca/Si ratio equal to 0.83 is proposed based on the dissolution rates normalized to the final BET surface area. Additionally, reactive transport modeling of the changes in aqueous chemistry allowed the fitting of the rate constants for C–S–H with Ca/Si ratio ranging from 1.7 to 0.83. Solid examination by SEM-EDX and EPMA before and after the experiments showed some variability of the Ca/Si ratios of the analyzed particles, suggesting the existence of compositional domains with variable Ca/Si ratios. ^{29}Si MAS NMR spectra showed an increase in polymerization of the reacted C–S–H, and also the formation of Si-rich domains in some cases, mainly under slow flow conditions. Inhibition of the rates in these cases will have to be further investigated.

1. Introduction

The use of concrete for storing low- and intermediate-level nuclear waste requires that the durability of this material is optimal for the lifetime of these repositories. This lifetime is directly proportional to the time the radioactive waste needs to reach natural levels of radioactivity. Durability means the capacity to bear the chemical and physical conditions to which a construction is exposed during its lifetime. One of the most important processes that puts such durability at risk is the attack of concrete by water of low mineral content and neutral pH (Adenot and Buil, 1992; Revertegat et al., 1992). This effect may cause alterations in the microstructure of the concrete, such as decalcification and dissolution of the cement phases, increased porosity and loss of barrier properties. Therefore, it is necessary to know the reactivity of cement and concrete to be able to assess the durability of these materials.

Calcium silicate hydrate (C–S–H) is the main binding phase in all Portland cement-based systems. High resolution (micrometric or nanometric) techniques, such as Transmission Electron Microscopy (TEM) or Electron Probe Microanalysis (EPMA), showed that the C–S–H present in hardened pastes of C_3S or fresh Portland cements generally has a mean Ca/Si ratio of about 1.75, with values ranging from 1.2 to 2.1 (Richardson, 1999). Higher values of the Ca/Si ratio in the literature could be explained by mixtures of C–S–H with portlandite ($Ca(OH)_2$, or CH in cement notation; Chen et al., 2004). Taylor (1997) stated that for aged pastes the range of Ca/Si ratio is approximately 1.6–1.85 with a mean value of 1.78.

C–S–H gel is often described as a poorly crystalline or nearly X-ray amorphous phase. The X-ray (XRD) patterns show that no long-range order exists in the structure. Nowadays it is generally accepted that C–S–H has a disordered layer structure formed by silicate chains of varying lengths held together by layers of calcium (Cong and Kirkpatrick, 1996; Richardson, 2004; Allen et al., 2007; Gaitero et al., 2008; Kulik, 2011). Experimentally, it is observed that these silicate chains are composed of both dimeric silicate units and polymeric units. The most accepted structure considers that C–S–H is similar to the crystalline calcium silicate hydrates 1.4-nm-tobermorite and jennite. Taylor (1986) proposed a model that considers that C–S–H exists as C–S–H(I), structurally similar to 1.4-nm-tobermorite, and C–S–H(II), similar to jennite. These phases are composed of structural units derived from imperfect tobermorite and jennite, respectively. The Ca/Si ratio of C–S–H(I) varies from 0.67 to 1.5 by omission of part of the bridging tetrahedra or variations in the contents of interlayer Ca and of protons attached to Si–O units. C–S–H(II) has Ca/Si ratios between 1.5 and 2.2.

C–S–H is usually synthesized by hydration of C_3S ($3CaO{\cdot}SiO_2$). Hydrated C_3S pastes are prepared with deionized water at a mass water-to-solid ratio of about 0.5 at room temperature and under CO_2-free atmosphere (Chen et al., 2004). Using the stoichiometry

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of C–S–H proposed by Kulik and Kersten (2001), the hydration of C_3S can be written as

$$\underset{C_3S}{Ca_3SiO_5} + 4H_2O \rightarrow \underset{67\,wt\%\ C\text{–}S\text{–}H}{SiO_2 \cdot 1.67Ca(OH)_2 \cdot H_2O} + \underset{33\,wt\%\ CH}{1.33Ca(OH)_2}$$

After C_3S hydration, a hardened paste containing two products (C–S–H gel and portlandite) is produced. Measurements by Chen et al. (2004) indicated that the structure of the obtained C–S–H gel is a mixture of tobermorite and jennite-like structures where that of jennite is dominant.

To predict the long-term behavior of cement-based systems in contact with an aqueous phase it is essential to know the solubility of the C–S–H gel. The thermodynamic modeling of C–S–H solubility initially considered empirical or semi-empirical models and evolved to the application of solid-solution models. Different models for the solubility of C–S–H gel, including its incongruent dissolution, have been proposed. They are mostly based on solubility data of the $CaO–SiO_2–H_2O$ system (e.g. Jennings, 1986; Gartner and Jennings, 1987; Reardon, 1990, 1992; Berner, 1988, 1990, 1992; Atkinson et al., 1989; Börjesson et al., 1997; Rahman et al., 1999; Kersten, 1996; Carey and Lichtner, 2006, 2007; Sugiyama and Fujita, 2006; Walker et al., 2007; Sugiyama, 2008). Kulik and Kersten (2001) described the solubility of C–S–H with two ideal solid solutions: C–S–H(I) (SiO_2-tobermorite) and C–S–H(II) (tobermorite-jennite). Equilibrium with respect to portlandite is also added for Ca/Si ratio >1.7–1.8. The experimental data from Greenberg and Chang (1965) was used to calibrate the model, which is applicable to a wide range of Ca/Si ratios of the C–S–H.

Recently, using a multi-site (sublattice) concept, Kulik (2011) revised the previous ideal solid solution model of C–S–H (Kulik and Kersten, 2001) to make it consistent with the structural model from Richardson and Groves (1992) and with the modern interpretation of spectroscopic (^{29}Si Magic-Angle Spinning-Nuclear Magnetic Resonances (MAS NMR)) and solubility data. According to the author, consideration of two site substitutions, (1) coupled H_2OCa^{2+} for $SiO_2H_2^{2+}$ replacement in bridging tetrahedral and adjacent interlayer sites, and (2) substitution of interstitial $Ca(OH)_2$ for a vacancy, leads to a new C–S–H solid solution model based on two tobermorite-like and two jennite-like end members. However, for the purpose of this experimental study, the model by Kulik and Kersten (2001) was adopted. It is easier to implement and describes well the solubility data.

In this study, flow-through experiments have been carried out to study the dissolution kinetics of C–S–H gel. The flow of demineralized water causes the dissolution of C–S–H and changes in the composition of the solutions. The changes in Ca and Si concentrations and pH have been monitored during the reaction, allowing the measurement of the variation in the atomic Ca/Si ratio of the solution, the calculation of dissolution rates, the assessment of the effect of the solution saturation state on the rates and the derivation of a C–S–H dissolution rate law. Additionally, C–S–H compositional and microstructural changes during dissolution have been analyzed using several techniques (XRD, SEM, EPMA and ^{29}Si NMR).

2. Materials and methods

2.1. C–S–H gel

C–S–H gel was prepared by C_3S hydration. Commercial C_3S was purchased from Mineral Research Processing (France). According to the specifications it was synthesized by burning $CaCO_3$ and silica gel at high temperature. Purity of the final product was determined by XRD using Cu Kα radiation over a 2θ range from 0° to 60° and quantified by Rietveld analysis (Young, 1995). XRD patterns of the sample showed that the C_3S presents triclinic T1 polymorphism. Rietveld analysis showed that the purchased C_3S consisted of 97 wt% C_3S, 1 wt% SiO_2, 1 wt% calcite and 1 wt% portlandite.

C_3S was ground in a ball agate mortar to a particle size smaller than 10 µm. Grinding was controlled by continuous performance of laser granulometry analyses using a LS 13320 laser diffraction-size analyzer (Beckman Coulter) after ultrasonic disaggregation in ethanol for 5 min to prevent particle hydration. Grinding was stopped when the particle size distribution did not change significantly. In the C_3S sample 90% of the particles were smaller than 8 µm with only one main size (~1.9 µm). The morphology of the particles was examined by Scanning Electron Microscopy (SEM) using a JEOL JMS-840 electron microscope. Particles showed rounded shapes and formed clusters (Fig. 1). The particle size ranged from 2 to 15 µm. C_3S hydration was carried out using Milli-Q water (18.2 MΩ cm at 25 °C) and a water/solid ratio of 0.5 in a CO_2-free glove box (N_2 atmosphere) to avoid carbonation of the hydration products.

In the CO_2-free glove box, the Milli-Q water used to hydrate the C_3S was gently purged with a low flux of N_2 for 5 min to further avoid carbonation. C_3S samples were manually mixed. When mixtures were considered to be homogeneous, mixing was stopped. Thereafter, the containers with the mixtures were covered with caps to prevent water evaporation and stored. The samples were stored for 120 d in the glove box at room temperature. C_3S hydration was monitored by examining the samples after 45, 62, 83, 99 and 120 d by XRD and Rietveld analysis to quantify the amount of formed C–S–H and remaining C_3S. After 120 days, the reaction was stopped since XRD (with a detection limit below 1 wt%) could not detect the presence of C_3S. 1.5 wt% quartz was also detected. The sample was then ground inside the glove box in a N_2 atmosphere. Laser granulometry was performed after ultrasonic disaggregation in ethanol for 5 min to prevent particle hydration and agglomeration. 97% of the particles were smaller than 100 µm, presenting a main size population with a peak around 20 µm and another small population around 5 µm (less than 25% of the sample).

Semi-quantitative analysis of the Ca/Si ratio of the C–S–H gel was performed by Scanning Electron Microscope in combination with Energy Dispersive X-ray spectroscopy (SEM-EDX) using a FEI NovaNanoSEM 230 Scanning Electron Microscope employing an acceleration voltage of 15–20 kV. The sample was not polished and was coated with a thin layer of graphite. Quantitative analysis was made with EPMA using a CAMECA SX-50 Electron Microprobe (4 wavelength-dispersive (WD) spectrometers + 1 Energy Dispersive X-ray Spectroscopy system (EDS)) under a 20 kV accelerating potential and 20 nA beam current. The sample for EPMA was embedded into epoxy resin, dried and cured in vacuum to extract

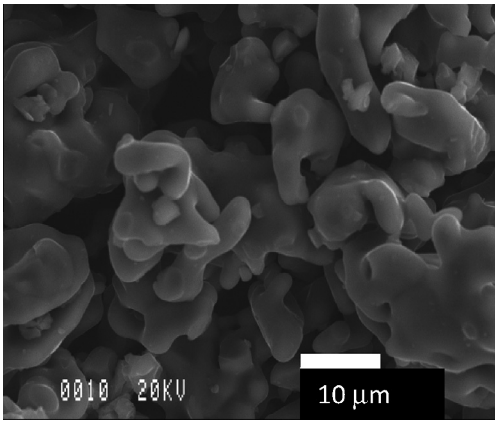

Fig. 1. SEM image of the initial C_3S.