Cement and Concrete Research 77 (2015) 60–68

Contents lists available at ScienceDirect

Cement and Concrete Research

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

Magnesium and calcium silicate hydrates

B. Lothenbach [a,*], D. Nied [b], E. L'Hôpital [a], G. Achiedo [c], A. Dauzères [c]

[a] Empa, Laboratory for Concrete & Construction Chemistry, 8600 Duebendorf, Switzerland
[b] HeidelbergCement Technology Center GmbH, 69181 Leimen, Germany
[c] IRSN, French Institute of Radiation Protection and Nuclear Safety, BP 17, 92262 Fontenay aux Roses, France

ARTICLE INFO

Article history:
Received 13 March 2015
Accepted 17 June 2015
Available online 17 July 2015

Keywords:
M-S-H
C-S-H (B)
Solubility
^{29}Si NMR
Raman

ABSTRACT

The structure and chemistry of magnesium silicate hydrates (M-S-H) is significantly different from calcium silicate hydrates (C-S-H), although both phases are poorly crystalline and have a variable chemical composition. The molar Ca/Si ratio in synthetic C-S-H varies from approximately 0.7 to 1.5 and the Mg/Si ratio in M-S-H from 0.7 to 1.3. In M-S-H silica sheets are present, while the silica in C-S-H is organized in single chains. In addition, M-S-H contains more chemically bound water than C-S-H. Analyses of synthetic samples containing both magnesium and calcium with a total (Mg + Ca)/Si of 0.8 indicate the formation of separate M-S-H and C-S-H gels with no or very little uptake of magnesium in C-S-H or calcium in M-S-H. The clear difference in the silica structure and the difference in ionic radius of Ca^{2+} and Mg^{2+} make the formation of an extended solid solution between M-S-H and C-S-H gel improbable.

1. Introduction

Long-lived intermediate- and high-level radioactive wastes are planned to be discarded in deep geological disposal facilities. Clay host rock formations are favoured in the design of the geological disposal facility, which act to limit the ingress of groundwater and reduce the mobility of radionuclides. However, in the pore solution of Portland cements (PC), pH values of 13.5 or even higher are often encountered [1,2], which can lead to a local degradation of the clay-based barriers [3,4]. Cements with lower pH values help to improve the compatibility with the clay barrier and prevent the formation of an extended alkaline plume [5]. Nevertheless, in the interaction zone between these low-pH cements and the clay, the formation of alteration products has been observed due to the interaction with the clay pore water. In the case of PC calcium is weakly leached and sulfate concentration is increased in the cement due to the interaction with the clay solution, which has a near neutral pH and can contain up to 30 mMol/L of sulfate [6,7]. In low-pH cements in contact with clays however, strong calcium leaching and magnesium enrichment is observed near the interaction zone [7–9]. The pH change near the cement–clay interface leads to significant calcium leaching in the cement, and the diffusion of magnesium from the clay pore solution towards the cement leads to a magnesium enriched layer in the cement up to 2 mm of the interface [7,8]. TEM and SEM investigations showed that these magnesium enrichment zones contain mainly magnesium and silica, while very little or no aluminium and calcium seems to be present [7,8], indicating the presence of magnesium silicate hydrates (M-S-H).

Investigations of synthetic M-S-H samples have shown that M-S-H has a variable composition within the range of 0.6–0.7 ≤ Mg/Si ≤ 1.0–1.4 [10–13], where Mg/Si is the molar Mg/Si ratio. For Mg/Si ratios ≤ 0.5–0.7 excess silica is present as amorphous silica (SiO_2(am)) and for Mg/Si ≥ 1.0–1.5 excess Mg is present as brucite (MH) [10–13]. ^{29}Si NMR, Raman and infrared (IR) spectroscopic investigations show a high polymerisation degree of the Si-network in M-S-H. Mainly Q^3 silica tetrahedrons (Q^3: silicate tetrahedron connected to three silicate tetrahedra) are observed by ^{29}Si NMR consistent with a sheet like silica structure or with strongly interconnected silica chains [11,12,14]. Observations by SEM/EDS indicate the formation of a homogeneous M-S-H gel [15,16] and X-ray diffraction (XRD) shows the presence of a few very broad, diffuse peaks [10–12,16]. Thermogravimetric analyses (TGA) reveal a multistep weight loss for synthetic M-S-H gel: the loss of interlayer water between 50 and ~300 °C, followed at higher temperature by a stepwise dehydroxylation [11,16] related to hydroxyl groups bound to Mg and as silanol groups in the M-S-H [11]. Although the structure of M-S-H is unknown, the position of the Raman bands and XRD peaks suggest that for 0.8 < Mg/Si < 1 the M-S-H structure is related to a disordered talc ($3MgO \cdot 4SiO_2 \cdot H_2O$) precursor as discussed in detail in [11,17]. At higher Mg/Si ratio M-S-H has been reported to correspond to a serpentine precursor similar to lizardite [18] or antigorite [11,19], both with a chemical composition corresponding to $3MgO \cdot 2SiO_2 \cdot 2H_2O$.

The findings of the different methods indicate that the sheet-like structure of M-S-H is significantly different from C-S-H, which has a structure based on single silica chains [20]. It is unclear whether and

---

* Corresponding author. Tel.: +41 58 765 47 88; fax: +41 58 765 69 35.
E-mail address: Barbara.lothenbach@empa.ch (B. Lothenbach).

http://dx.doi.org/10.1016/j.cemconres.2015.06.007
0008-8846/

to what extent magnesium is able to substitute for calcium ions in C-S-H, which is crucial for understanding the M-S-H formation in the contact zone between low pH cements and clayey rock. Based on ^{29}Si NMR, TGA and differential thermal analysis (DTA) data and the decrease of aqueous magnesium concentrations in the presence of C-S-H, the formation of mixed M-C-S-H phases has been suggested by different authors [21–23]. However, recent investigations indicate rather the co-existence of separate M-S-H and C-S-H phases [15,24].

The current paper reports the solid and the liquid phase characterization of synthetic C-S-H and M-S-H gels with (Ca + Mg)/Si ratio = 0.8 to investigate the structural features of M-S-H gel and the possible formation of a solid solution between C-S-H and M-S-H gels. Thermodynamic modelling is used to describe the composition of liquid phase.

2. Materials and methods

Magnesium–calcium silicate hydrate gels were synthesised by mixing appropriate quantities of magnesium oxide (MgO, Merck, pro analysis), calcium oxide (CaO) and silica fume (SiO_2, Aerosil 200). CaO was obtained by burning calcium carbonate ($CaCO_3$, Merck, pro analysis) at 1000 °C for 12 h.

For the synthesis, different Ca/Si molar ratios (0, 0.2, 0.3, 0.4, 0.5 and 0.8) were prepared with a total (Mg + Ca)/Si = 0.8. The samples were labelled according to their Mg/Si and Ca/Si ratio as 0.8M-S-H, 0.6M–0.2C-S-H, 0.5M–0.3C-S-H, 0.4M–0.4C-S-H, 0.3M–0.5C-S-H, and 0.8C-S-H. All samples were prepared in PE containers with a water/solid ratio of 45 in a N_2 filled glove box to minimize CO_2 contamination. A high water/solid ratio was used ensure the presence of sufficient water. The samples were placed on a horizontal shaker for 1 year and then filtered with 0.45 μm Nylon filter, rinsed first with approximately 50 mL of 1:1 water–ethanol solution and then with 50 mL 94% ethanol solution in the N_2 filled glove box (as in [11,25]). The solids were freeze dried for seven days, ground in an agate mortar and then stored in N_2 filled desiccators over saturated $CaCl_2$ solution at ~30% relative humidity (rh) using sodium hydroxide pellets to act as a CO_2 trap until analysis.

2.1. Analytical methods

TGA/DTA was done with a Mettler Toledo TGA/SDTA 8513 on 30 to 40 mg samples using a heating rate of 20 °C/min from 30 to 980 °C. The amount of brucite was quantified from the weight loss between 330 and 480 °C using the tangential method.

XRD patterns were collected using a PANalytical X'Pert Pro MPD diffractometer in a θ–2θ configuration using CuK$_\alpha$ radiation ($\lambda = 1.54$ Å) with a fixed divergence slit size of 0.5° and a rotating sample stage. The samples were scanned between 5° and 75° 2θ with the X'Celerator detector.

The ^{29}Si NMR measurements were performed at room temperature using a Bruker Avance 400 NMR spectrometer with a 7 mm CP/MAS probe. The ^{29}Si MAS NMR single pulse experiments were recorded at 79.49 MHz using the following parameters: 4500 Hz spinning speed, 9216 scans, $\frac{\pi}{3}$ pulses of 2.5 μs, 20 s relaxation delays, 90° pulses of 7.5 μs and RF field strengths of 33.3 kHz during TPPM decoupling sequence. The chemical shifts of the ^{29}Si MAS NMR spectra were referenced to an external sample of tetramethylsilane (TMS). The observed ^{29}Si resonances were analysed using the Q^n classification, where a Si tetrahedron is connected to n Si tetrahedral with n varying from 0 to 4. The relative distribution of silica species was obtained by non-linear least-square fits of the regions of interest using the software “DMFIT” developed by Massiot et al. [26]. The peak shapes were constrained with a Lorentzian/Gaussian ratio = 0.5, full width at half height ≤ 3 ppm for C-S-H, ≤6 ppm for M-S-H and with constant chemical shifts between the different peaks of C-S-H as described in [27]. The dreierketten structure of the C-S-H was respected by keeping the ratio $Q^2{}_p$/($Q^2{}_b$ + $Q^2{}_u$) equal to 2, as for each bridging tetrahedra two pairing tetrahedra are present. $Q^2{}_b$: bridging tetrahedra neighbouring Ca in the interlayer, $Q^2{}_u$: bridging tetrahedra neighbouring H^+ in the interlayer, $Q^2{}_p$: pairing tetrahedra. The main chain length (MCL) was calculated as $\mathrm{MCL} = \frac{2(\mathbf{Q}^1+\mathbf{Q}^2_\mathbf{p}+\mathbf{Q}^2_\mathbf{b}+\mathbf{Q}^2_\mathbf{u})}{\mathbf{Q}^1}$.

IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer using the ATR technique (attenuated total reflection) on bulk material. The investigated frequency range was from 600 to 4000 cm^{-1} with a step size of 1.9 cm^{-1}. The data are reported in wavenumbers (cm^{-1}).

The Raman spectra were measured with Bruker Senterra instrument of 5 cm^{-1} spectral resolution using a 532 nm laser (20 mW) at room temperature and ×50 objective lens. Spectra acquisition time was 10 s with 5 cumulative spectra collected for each sample in the frequency ranges of 110–1560 and 2700–3800 cm^{-1}.

SEM investigations were carried out with a HITACHI SEM at 15 KeV and a working distance of 16 mm. Observations were done on powder samples placed on a carbon disc, and covered by a carbon layer of 40 nm. Transmission electron microscope (TEM) investigation was done with a JEOL 2100 F microscope equipped with a field effect gun (FEG) and associated to a JEOL EDS detector. Powders of M-S-H or M-C-S-H samples were prepared by a dilution in ethanol with an ultrasonic bath, and placed on a copper grid (diameter: 3.05 mm with pores of 38 μm) and covered by a carbon layer. Chemical analyses were performed by energy dispersive spectrometry (EDS) with two BRUCKER SDD detectors, which allowed minimizing the acquisition time.

The pH measurements were carried out immediately after filtration on small aliquots of the pore solution using a Knick pH meter (pH-Meter 766) equipped with a Knick SE100 electrode at 20 °C. The pH electrode was calibrated with CertiPUR® buffer solutions from Merck (pH 4.01 with potassium hydrogen phthalate, pH 7 with KH_2PO_4/Na_2HPO_4 and pH 12.00 with NaOH/Na_2HPO_4). A second part of the solution was diluted 1:10, 1:100 and 1:1000 with Milli-Q H_2O and used for ionic chromatography (IC) analysis. The dissolved concentrations of calcium, magnesium and silicon were quantified using a Dionex DP series ICS-3000 ionic chromatography. Each sample was diluted by a factor 1, 5, 10, 100 and/or 1000 depending on the ion concentration and measured in duplicate. Standards from 0.1 to 50 mg/L were used. The measurements are associated with a measurement error of ≤10%.

2.2. Thermodynamic modelling

Thermodynamic modelling was carried out using the Gibbs free energy minimization programme GEMS (v3.2) [28]. GEMS is a multipurpose geochemical modelling code which computes equilibrium phase assemblage and speciation in a complex chemical system from its total bulk elemental composition. The thermodynamic data for aqueous species as well as for SiO_2, brucite and portlandite were taken from the PSI-GEMS thermodynamic database [29], the data for C-S-H solid solution (CSHQ model) from [30] and the data for M-S-H solid solution were taken from Nied et al. [11]. Ideal solid solution models have been used to model both C-S-H and M-S-H to be able to reproduce their variable composition. Instead of using an apparent solubility product for each of the solid phase compositions, solubility constants for end-member solids (i.e., for high and low Ca/Si or Mg/Si ratio) are defined and the variability of the solid phase compositions and the aqueous concentrations are modelled using a solid solution approach (for details on solid solutions and its applications for C-S-H phases see Refs. [30–32]). A summary of the thermodynamic data of the solid phases is given in Table 1. The measured composition of the solution was used to calculate saturation indices with respect to amorphous SiO_2, brucite, and C-S-H to assess which solid phases should be stable.