



Alkali uptake in calcium alumina silicate hydrate (C-A-S-H)



E. L'Hôpital^a, B. Lothenbach^a, K. Scrivener^c, D.A. Kulik^b

^a Laboratory for Concrete and Construction Chemistry, Empa, Dübendorf, CH 8600, Switzerland

^b Laboratory for Waste Management, Paul Scherrer Institute, Villigen 5232, Switzerland

^c Laboratory of Construction Materials, EPFL, Lausanne, CH 1015, Switzerland

ARTICLE INFO

Article history:

Received 4 June 2015

Accepted 4 March 2016

Available online xxxx

Keywords:

C-S-H

C-A-S-H

Aluminium

Alkali

Characterization

ABSTRACT

Uptake of the alkalis K and Na by calcium silicate hydrate (C-S-H) and calcium alumina silicate hydrate (C-A-S-H) of molar Ca/Si ratios = 0.6 to 1.6 and molar Al/Si ratio = 0 or 0.05 has been studied at 20 °C. Alkalis are thought to be bound in the interlayer space of C-A-S-H and show preferred uptake by lower Ca/Si ratios and by higher alkali concentrations. A consequence of alkali uptake into C-A-S-H is a rearrangement of the C-A-S-H structure. Less calcium is present in the interlayer and shorter silica chains are observed for the same molar Ca/Si ratio. No significant difference was observed between sodium and potassium uptake. Equilibration times of 91 days to 1 year or the solid phase being either C-S-H or C-A-S-H had seemingly no effect on alkali uptake.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The alkalis potassium and sodium are common to all portland cement (PC)-based materials, but no solid phase buffers their concentration in the pore solution. A direct result of high alkali contents is therefore a high pH pore solution, which affects the dissolution of all other minerals in the PC system and therefore the concentrations of other elements in the pore solution [1–4]. In addition, alkali and hydroxide concentrations in the pore solution determine whether and to what extent alkali silica reaction (ASR) can occur in concrete [5,6]. The risk of ASR can be lowered by the addition of supplementary cementitious materials such as fly ash or silica fume, which act to decrease the Ca/Si ratio of C-S-H, leading to higher alkali uptake in its structure. Alkalis in PC-based materials are mainly taken up by C-S-H, with only negligible amounts being taken up by other mineral hydrates such as portlandite, ettringite, hydrogarnet, or hydrotalcite [7,8]. Rather than being phase pure, however, C-S-H in PC-based materials is a C-A-S-H, which becomes increasingly significant if a high aluminium content supplementary cementitious material is added [9,10]. A detailed knowledge of the alkali uptake in C-A-S-H is therefore important.

Experiments with synthetic C-S-H [3,11] and low pH cements [1,12,13] indicate that more alkalis are taken up into low-Ca/Si C-S-H than into high-Ca/Si C-S-H. A strong correlation between dissolved alkali concentrations and alkali uptake by C-S-H in the concentration range up to 300 mmol/L [1,3,14] was observed. At higher alkali concentrations of 500–1500 mmol/L, the alkali uptake by C-S-H increases less strongly with concentration, and maximum molar ratios of Na/Si and K/Si = 0.3–0.5 in C-S-H have been reported [11,14].

Alkali sorption studies have identified either preferred or equivalent sodium or potassium sorption [1,3,11,15–18]. Preferred sodium sorption was used to interpret pore solution analysis of PC by Taylor [19] and has also been measured for synthetic C-S-H [15]. Preferred potassium sorption, however, has also been measured on synthetic C-S-H [1]. Sodium as Na⁺ has a larger solvated ionic radius than K⁺ and so sodium uptake might be physically inhibited, which is consistent with observations of [1], but contradicts preferential sodium sorption [11,15,19].

Hong and Glasser [20] reported a strong increase of alkali sorption in the presence of C-A-S-H as opposed to C-S-H alone and suggested that the replacement of SiO₂ by AlO₂⁻ would further increase alkali uptake to maintain charge balance. By contrast, Stade [11] observed less alkali uptake in C-A-S-H than in C-S-H, while Chappex and Scrivener [8] and Bach et al. [1] observed no significant difference in the alkali uptake whether aluminium was present or not. It also has been suggested that alkalis may charge-balance the silanol group by the substitution of protons (SiOH + K⁺ + OH⁻ → SiO⁻ ... K⁺ + H₂O) or of calcium ions (SiOH + Ca²⁺ + OH⁻ → SiOCa⁺ + H₂O/SiOCa⁺ + K⁺ → SiO⁻ ... K⁺ + Ca²⁺) [3,11,21], or occupy empty sites in the interlayer [21].

The scatter of results reported in the literature indicates either that a large experimental error is associated with the measurement of alkali uptake, that the synthesis protocol has an important influence, and/or that a number of different mechanisms are responsible for the alkali uptake in C-S-H and C-A-S-H, such that the results may vary depending on the alkali concentration, the C-S-H composition, and the presence of other ions or solids. Moreover, ²³Na NMR data indicate the presence of two different sites for sodium binding in C-S-H [22,23].

In order to elucidate these seeming contradictions, the focus of the present paper was on the uptake of the alkalis by synthetic C-A-S-H. Solid phases were characterized by thermal gravimetric analysis (TGA), X-ray diffraction (XRD), and ^{29}Si nuclear magnetic resonance (NMR) and the liquid phase by pH measurement and composition by ionic chromatography (IC).

2. Materials and methods

Both C-S-H and C-A-S-H were synthesized by a one-step protocol at 20 °C as described in detail previously [4,24] and summarized below.

2.1. Synthesis

Calcium oxide (CaO), silica fume (SiO_2), and monocalcium aluminate (CA: CaOAl_2O_3) were used in different proportions to synthesize C-A-S-H. Ca/Si ratios = 0.6, 0.8, 1.0, 1.2, 1.4, and 1.6 and Al/Si = 0.05 were targeted as detailed in Appendix A. For comparison, the alkali uptake on some C-S-H samples without aluminium was also studied. In addition, samples with Ca/Si = 1.0 and Al/Si = 0.1 were synthesized and studied by ^{29}Si NMR as described previously [4]. Water-to-solid mass ratio equal to 45 was used to ensure the homogeneity of the samples. C-S-H and C-A-S-H were equilibrated in Milli-Q water or in potassium or sodium hydroxide solutions with a concentration between 0.01 and 0.5 mol/L. Synthesis and all sample handling were made in a N_2 -filled glove box to minimize CO_2 contamination. For each equilibration time, a separate sample was prepared, which was stored in a 100 mL PE-HD container placed on a horizontal shaker moving at 100 rpm, and equilibrated at 20 °C. After different equilibration times, the solid and liquid phase were separated by filtration using 0.45 μm nylon filters and subsequently analyzed.

2.2. Solid phase analysis

After filtration, the solid was washed with 30 mL of a 50%–50% water–ethanol solution, then with 30 mL pure ethanol, dried for 7 days by freeze drying, and then stored until analysis in a N_2 -filled desiccator in the presence of saturated CaCl_2 solutions ($\approx 30\%$ RH) and of NaOH pellets to act as a CO_2 trap. The solid phases were analyzed by TGA, XRD, and ^{29}Si NMR.

TGA data were measured with a TGA/SDTA851^e Mettler Toledo device using approximately 30 mg of sample. The weight loss of the samples was recorded from 30 °C up to 980 °C with a heating rate of 20 °C/min under N_2 atmosphere. The amount of portlandite was quantified from the weight loss around 450 °C using the tangential method and the total water bound in the sample from the total water loss between 30 and 550 °C. The water bound in C-S-H and C-A-S-H was the difference between the total water loss and the weight loss due to portlandite.

X-ray powder diffraction patterns were recorded on a PANalytical X'Pert Pro MDF diffractometer equipped with an X'Celerator detector. Diffraction patterns were collected in increments of 5° from 70° 2 θ at a conventional step size of 0.017° 2 θ and a step measurement time of 460 s.

The phases present were determined with X'Pert HighScore Plus. The quantification of the amounts of the phases was carried out with calcium fluoride as external standard. This method allows the amount of amorphous phases such as C-S-H to be quantified indirectly [4]. To determine the exact peak positions, anatase was added to some samples as internal standard.

The ^{29}Si NMR measurements were performed at room temperature using a Bruker Avance 400 MHz 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; the 90° pulse at the decoupling power level of 8 dB is 7.5 μs . The RF field is calculated by $1 / (4 \times 7.5 \mu\text{s}) = 33.3$ kHz. 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 analyzed using the $Q^n(\text{mAl})$ classification, where a Si tetrahedron is connected to n Si tetrahedral with n varying from 0 to 4 and m is the number of neighbouring AlO_4 tetrahedra.

The deconvolution of the Si-NMR data was carried out using the dmfit software [25]. Peak shapes were constrained as pseudo-voigt using a Lorentzian/Gaussian ratio = 0.5, full width at half height ≤ 3 ppm and constant chemical shifts between the different peaks as described in [4]. The dreierketten structure of the C-S-H was respected by defining the ratio $Q_p^2 / (Q_b^2 + Q_u^2)$ equal to 2, as for each bridging tetrahedra two pairing tetrahedra are present, as shown in Fig. 1. Q_b^2 denotes the number of bridging tetrahedra neighbouring Ca in the interlayer, $Q_{b\text{OH}}^2$ stands for bridging tetrahedra neighbouring H^+ in the interlayer, and Q_p^2 is the pairing tetrahedra. The mean dreierketten chain length (MCL) was calculated using Eq. 1, and the Al/Si ratio with Eq. 2.

$$\text{MCL} = \frac{2 \left(Q^1 + Q_p^2 + Q_b^2 + Q_u^2 + \frac{3}{2} Q^2(1\text{Al}) \right)}{Q^1} \quad (1)$$

$$\frac{\text{Al}}{\text{Si}} = \frac{\frac{1}{2} Q^2(1\text{Al})}{Q^1 + Q_p^2 + Q_b^2 + Q_u^2 + Q^2(1\text{Al})} \quad (2)$$

2.3. Solution analysis

The elemental concentrations of calcium, silicon, sodium, potassium, and aluminium in the filtrates were determined with a Dionex DP ICS-3000 ion chromatograph. Each sample was diluted by a factor of 1, 5, 10, 100, and/or 1000 so that the standard solutions used of 0.1, 0.5, 1.0, 5.0, 10.0, 25.0, and 50.0 mg/L correctly bracketed all concentrations up to 50,000 mg/L. Samples were measured in duplicate. The relative error of the measurements was $\leq 10\%$ of the measured value. Silicon was analyzed using sodium carbonate/bicarbonate eluent and sodium molybdate, and sodium lauryl sulfate in metasilicic acid as a post-column reagent using an ion pack AS22 column.

To quantify the hydroxide concentration, pH measurements were performed at room temperature with a Knick pH meter (pH-Meter 766) equipped with a Knick SE100 electrode. The pH electrode was calibrated against KOH solutions of known concentrations in order to

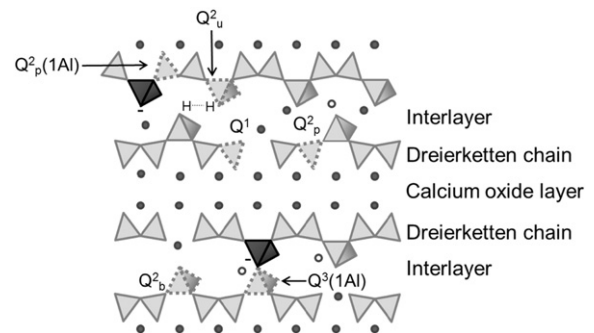


Fig. 1. Schematic structure of C-A-S-H. Grey circle: calcium ion; empty circle: ion in the interlayer (water or alkali); light grey tetrahedra: protonated silicate; dark grey tetrahedra: aluminium; —: negative charge (compensated by proton, calcium, or other cations). $Q^n(\text{mAl})$: n indicates the numbers of Si neighbours and m the number of aluminium neighbours; b, bridging position; p, pairing position [4].

Download English Version:

<https://daneshyari.com/en/article/7885099>

Download Persian Version:

<https://daneshyari.com/article/7885099>

[Daneshyari.com](https://daneshyari.com)