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Incorporation of aluminium in calcium-silicate-hydrates

E. L'Hôpital [a], B. Lothenbach [a,*], G. Le Saout [a], D. Kulik [b], K. Scrivener [c]

[a] Empa, Laboratory for Concrete & Construction Chemistry, CH-8600 Dübendorf, Switzerland
[b] Paul Scherrer Institute, Laboratory for Waste Management, 5232 Villigen PSI, Switzerland
[c] EPFL, Laboratory of Construction materials, CH-1015 Lausanne, Switzerland

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ABSTRACT

Calcium silicate hydrate (C-S-H) was synthetized at 20 °C to investigate the effect of aluminium uptake (Al/Si = 0–0.33) in the presence and absence of alkalis on the composition and the solubility of a C-S-H with a Ca/Si equal to 1.0.

C-S-H incorporates aluminium readily resulting in the formation of C-A-S-H at Al/Si ≤0.1. At higher Al/Si ratios, in addition to C-A-S-H, katoite and/or stratlingite are present. Aluminium is mainly taken up in the bridging position of the silica dreierketten structure, which increases the chain length. The aluminium uptake in C-S-H increases with the aqueous aluminium concentrations.

The presence of potassium hydroxide leads to higher pH values, to the destabilisation of stratlingite and to higher dissolved aluminium concentrations, which favours the aluminium uptake in C-S-H. Potassium replaces partially the calcium ions on the surface and interlayer, thus leading to more negative surface charge and to shortening of chain length.

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* Corresponding author.
E-mail address: Barbara.Lothenbach@empa.ch (B. Lothenbach).

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1. Introduction

Partial substitution of Portland cement by supplementary cementitious materials (SCM), such as fly ash, slag or calcined clays, offers the potential to reduce CO_2 emissions. However such systems inevitably have different chemistry, form different hydrates than Portland cements and will therefore perform and behave differently in concrete. In the presence of silica-rich SCM, the Ca/Si ratio of the C-S-H drops from $\approx$1.5–1.9 in Portland cements [1] to 1.5 or lower in cements blended with slag, fly ash or metakaolin [2–4] while the Al/Si ratio may increase up to about 0.25 [3]. These changes in chemistry modify the structure and can affect the performance, mechanical properties and durability of the system. The composition and properties of low Ca/Si C-S-H phases are significantly different from those of C-S-H formed in Portland cement systems [5,6] with different capacity for the incorporation of alkalis or other ions.

Calcium silicate hydrate (C-S-H) is the main hydration product in cement and it contributes significantly to the physical, chemical and mechanical properties. The C-S-H present in Portland cements is poorly crystalline with a variable composition and can contain other ions such as aluminium or alkalis within its structure [5,6]. C-S-H can be described as calcium (hydr)oxide layers with silica chains attached on both sides organized in a dreierketten structure, a repeating chain of three silica tetrahedra (see Fig. 1). Two of these silica tetrahedra are linked to the calcium oxide layer (pairing tetrahedra), while the third one, the bridging tetrahedron, is linked to two pairing tetrahedra. In a C-S-H particule, a few sheets are connected by an interlayer containing water, calcium, alkalis and other ions. The solubility of C-S-H as a function of the Ca/Si ratio can be described by a family of solubility curves depending on the synthesis method, the equilibration time and the temperature history as shown in Chen et al. [7], which indicates, at least after shorter equilibration times, the existence of several metastable C-S-H phases.

Several NMR studies have investigated the incorporation of aluminium in C-S-H. The substitution of aluminium occurs primarily as tetrahedrally coordinated Al(IV) in the bridging position ($Q^2{}_b$) [9–12], as indicated in Fig. 1. In tobermorite, Al(IV) is reported to be present also in Q^3 sites which link two dreierketten chains together [9,11].

At higher Ca/Si ratios, the relative amount of Al(IV) in C-S-H decreases, instead more octahedrally coordinated Al(VI) is observed [10, 11,13,14]. The octrahedrally coordinated Al(VI) has been suggested to represent either an amorphous aluminium hydroxide or a calcium aluminate hydrate at the C-S-H surface: third aluminium hydrate (TAH) [15] or in the interlayer within the C-S-H [13]. In addition to Al(IV) and Al(VI), approximately 10% of the aluminium associated with C-S-H is present as pentacoordinated Al(V) regardless the Ca/Si ratio of the C-S-H [10,13,14]. Sun et al. [11] suggested that Al(V) and Al(VI) could compensate the negative charge introduced by the replacement of Si(+IV) by Al(+III) in the silica chain. However, the amount of Al(V) and Al(VI) does not correlate with the amount of Al(IV) in the silica chains [10,13].

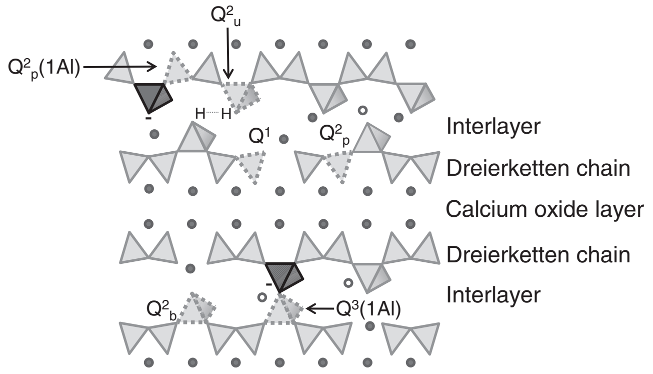

Fig. 1. Schematic structure of C-A-S-H. Grey circle: calcium ion; empty circle: species in the interlayer (water or alkali); light grey tetrahedra: SiO_4^-, dark grey tetrahedra: AlO_4; −: negative charge (compensated by proton, calcium or other cations). $Q^n{}_{(mAl)}$: n indicates the numbers of Si neighbours and m the number of aluminium neighbours, b: bridging position, p: pairing position. Adapted from [8].

NMR studies indicate that the presence of alkali hydroxides increases the uptake of aluminium in synthetic C-S-H [14] and white Portland cement [16].

While there is a number of studies focused on the effects of aluminium uptake on the C-S-H structure [10,11,13–15], very little data is available on the relations between the dissolved aluminium, calcium, silicon and hydroxide concentrations in the aqueous (pore) solution and the aluminium uptake in C-S-H, with the exception of a recent paper of Pardal et al. [17], where relatively high aluminium concentrations (1 mmol/L) and short reaction times (1 day) have been used. The lack of systematic experimental data at equilibrium conditions hinders the development of adequate thermodynamic models which would allow prediction of the aluminium uptake in C-S-H.

In this paper, C-S-H with a constant Si/Ca = 1.0 is investigated. The effect of aluminium at Al/Si ratios from 0 to 0.33 is studied in the first part and the effect of alkalis (potassium hydroxide) on C-S-H and C-A-S-H are considered in the second part. The solubility, the structure and the chemical composition of the resulting C(-A)-S-H gel are investigated after equilibration times of 6 months or longer.

2. Material and methods

2.1. Synthesis

Calcium oxide (CaO), silica fume (SiO_2) and monocalcium aluminate (CA: $CaO.Al_2O_3$) were used to synthesize C(−A)-S-H. CaO was obtained by burning calcium carbonate ($CaCO_3$, Merck, pro analysis) at 1000 °C for twelve hours. SiO_2, provided by Aerosil 200, Evonik, was chosen for its high specific surface area of 200 m^2/g. CA ($CaO·Al_2O_3$) was used due to high reactivity [18]. CA was synthesized from $CaCO_3$ and Al_2O_3 (Sigma Aldrich).The homogenized powder mixture was heated for 1 hour at 800 °C, 4 hours at 1000 °C and 8 hours at 1400 °C and cooled with a rate of 600 °C/h. The resulting solid was ground to a Blaine surface area of 3790 cm^2/g. The CA contained 99.1% CA and 0.9 % $C_{12}A_7$ as determined by X-ray diffraction and Rietveld refinement analysis using X'Pert HighScore Plus.

C(−A)-S-H samples were prepared by adding a total of 2 g of CaO, SiO_2 and CA to 90 ml of Milli-Q water (water/solid = 45). The proportions of CaO, SiO_2 and CA were varied to obtain C-A-S-H with a Ca/Si ratio of 1.0 and Al/Si ratios from 0 to 0.33 as indicated in Appendix A. The C-S-H was equilibrated in 0.5 M KOH solutions to mimic alkali concentrations relevant for Portland cements [19,20] and to study the effect of alkali on aluminium uptake.

Synthesis and all sample handling were carried out in a N_2 filled glovebox to minimize CO_2 contamination. The samples were stored in 100 mL PE-HD containers placed on a horizontal shaker moving at 100 rpm and equilibrated at 20 °C. For each equilibration time a separate sample was prepared. After different equilibration times, the solid and the liquid phase were separated by filtration using 0.45 μm nylon filter, and subsequently analysed.

2.2. Solid phase analyses

After filtration, the solid was washed with approximately 30 mL of a 50–50% water-ethanol solution, afterwards with approximately 30 mL of pure ethanol, dried for seven days by freeze drying and then stored until analysis in N_2 filled desiccators in the presence of saturated $CaCl_2$ solutions ($\approx$30% RH) and NaOH pellets as CO_2 trap. The solid