



# Hydration of water- and alkali-activated white Portland cement pastes and blends with low-calcium pulverized fuel ash



I.G. Richardson<sup>\*</sup>, A.V. Girão<sup>1</sup>, R. Taylor<sup>2</sup>, S. Jia

School of Civil Engineering, University of Leeds, Leeds LS2 9JT, United Kingdom

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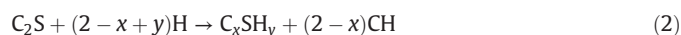
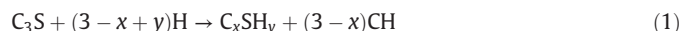
## ABSTRACT

Pastes of white Portland cement (wPc) and wPc-pulverized fuel ash (pfa) blends were studied up to 13 years. The reaction of wPc with water was initially retarded in the presence of pfa particles but accelerated at intermediate ages. Reaction with KOH solution was rapid with or without pfa. A universal compositional relationship exists for the C-A-S-H in blends of Pc with aluminosilicate-rich SCMs. The average length of aluminosilicate anions increased with age and increasing Al/Ca and Si/Ca; greater lengthening in the blends was due to additional Al<sup>3+</sup> at bridging sites. The morphology of outer product C-A-S-H was always foil-like with KOH solution, regardless of chemical composition, but with water it had fibrillar morphology at high Ca/(Si + Al) ratios and foil-like morphology started to appear at Ca/(Si + Al) ≈ 1.2–1.3, which from the literature appears to coincide with changes in the pore solution. Foil-like morphology cannot be associated with entirely T-based structure.

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## 1. Introduction

The main silicate phases that are present in Portland cement are a chemically impure tricalcium silicate (C<sub>3</sub>S<sup>3</sup>) that is called alite, and an impure β-dicalcium silicate (β-C<sub>2</sub>S) that is called belite [1]. The products of the hydration of these two phases are the same: a calcium silicate hydrate of variable composition and calcium hydroxide (CH), as shown in Eqs. (1) and (2) [2].



The values of  $x$  and  $y$  in Eqs (1) and (2) can vary and so the calcium silicate hydrate is commonly referred to as C-S-H, the dashes denoting non-stoichiometry. In neat C<sub>3</sub>S pastes, the value of  $x$  – i.e. the molar Ca/Si ratio of the C-S-H – ranges between 1.3 and 2.1 [3] with a mean value of about 1.75 [4]. Substitution of this value for  $x$  into Eq. (1) and a value of 4.0 for  $y$  (which corresponds to a relative humidity (RH) of 90% [2]) shows that the mass % of calcium hydroxide in a fully reacted paste at 90% RH is 28.7%, or 40.6% when referred to the mass of the original C<sub>3</sub>S (i.e. when expressed on the basis of the ‘ignited weight’). The equivalent values for β-C<sub>2</sub>S are 7.4 and 10.8%.

In addition to alite and belite, Portland cement also contains tricalcium aluminate (C<sub>3</sub>A) and a calcium aluminoferrite phase, which is often represented as C<sub>4</sub>AF although in a clinker it typically includes about 10% substituent oxides [5]. Whilst hydration of these phases results in the formation of calcium aluminate hydrates (Aft, AFm, hydrogarnet), some Al is also accommodated in the C-S-H; the Al/Si ratio is typically about 0.08 [3,6]. In concrete, Portland cement is often partially replaced by material that is either latently hydraulic (ground granulated blast-furnace slag (ggbs)) or pozzolanic (e.g. silica fume (sf), pulverized fuel ash (pfa), or metakaolin (mk)). Such materials are referred to as mineral admixtures, cementitious replacement materials (CRMs) or supplementary cementitious materials (SCMs). SCMs are a source of Al (except for sf) and Si during hydration but have either little or no Ca (the pozzolans) or a much-reduced amount (ggbs) when compared with Portland cement. The use of SCMs therefore results in C-S-H that has a lower Ca/Si ratio than occurs with neat Portland cement and – with the obvious exception of silica fume – in higher Al/Si ratio; Al-substituted C-S-H is often called C-A-S-H. The extent of the change in composition depends on the amount of SCM in the cement and on its degree of reaction. The most extensive set of compositional data for C-A-S-H in cement pastes that is demonstrably free of intermixture with other phases is for neat ordinary Portland cement (oPc) pastes or blends of oPc with ggbs: Richardson & Groves [6] collated TEM-EDX data from a number of studies on such systems [3,7,8] and showed that there is a good linear relationship between the Si/Ca and Al/Ca ratios, Eq. (3).

$$\frac{Si}{Ca} = 0.428 + 2.366 \left( \frac{Al}{Ca} \right) r^2 = 0.98 \quad (3)$$

<sup>\*</sup> Corresponding author. Tel.: +44 113 3432331.

E-mail address: [i.g.richardson@leeds.ac.uk](mailto:i.g.richardson@leeds.ac.uk) (I.G. Richardson).

<sup>1</sup> Current address: Universidade de Aveiro, CICECO, 3810–193 Aveiro, Portugal.

<sup>2</sup> Current address: Department of Civil and Environmental Engineering, 760 Davis Hall, University of California, Berkeley 94720–1710, USA.

<sup>3</sup> C = CaO; S = SiO<sub>2</sub>; A = Al<sub>2</sub>O<sub>3</sub>; H = H<sub>2</sub>O.

This linear relationship was confirmed by later work on older samples [9]. The change in the composition of the C-A-S-H is accompanied by a decrease in the quantity of calcium hydroxide [6,9,10] and a change in morphology of the C-A-S-H from fibrillar at low Si/Ca and Al/Ca ratios to foil-like at higher values [4,7,9].

Studies using trimethylsilylation-gel permeation chromatography (TMS-GPC; [11–14]) have indicated that the silicate anions that are present in the C-S-H that is formed in water-activated cements follow a 2, 5, 8, ... (3n–1) sequence, where *n* is integer [15,16] and there is strong evidence that when Al<sup>3+</sup> substitutes for Si<sup>4+</sup>, the substitution only occurs in the central tetrahedron of pentameric linear chains, or in every third tetrahedron of longer chains [14,17–20]. These data support the view that the aluminosilicate anions that are present in C-A-S-H are linear chains that have the *Dreiereinfachketten* conformation [21] that is present in a number of natural calcium silicates, including 14 Å tobermorite [22], clinotobermorite 9 Å [23], pectolite [24–29], wollastonite [25,26,30–32], bustamite [30], hillebrandite [33], foshagite [34], and jennite [35]. The *Dreiereinfachketten* conformation involves infinite chains of tetrahedra that have a kinked pattern that has a 3-tetrahedron repeat sequence. In the tobermorite phases, pairs of silicate tetrahedra are clasped to a central Ca-O sheet (and so are called paired tetrahedra, abbreviated PT), and the gap between adjacent pairs is bridged by a single tetrahedron (which is called a bridging tetrahedron, BT). Removal of BT (i.e. the presence of vacant tetrahedral bridging sites) leads to the 2, 5, 8, ... (3n–1) sequence of chain lengths that is observed in C-S-H. The two shortest chain segments are dimers and pentamers, which are shown schematically in Fig. 1 (reproduced from [36]); the unfilled triangles represent Si–O tetrahedra and the shaded triangle represents an Al–O tetrahedron. Whilst these are followed in the sequence by octamers, undecamers, etc., there is evidence that for semi-crystalline synthetic C-S-H preparations that have Ca/Si less than about 1.4, the anions are either dimeric or long-chain [37–44]. Richardson [36] has shown recently how this evidence can be accommodated through the interstratification of dimeric (T<sub>2</sub>) and infinite-chain (T<sub>∞</sub>) layers that were derived from the structure of a staggered-chain clinotobermorite. It is possible that a similar arrangement is also present in C-A-S-H that is less well-ordered, albeit with a greater fraction of vacant tetrahedral bridging sites in the T<sub>∞</sub> layers and more stacking faults.

The mean length of the (alumino)silicate anions (called the mean chain length, MCL) can be calculated using Eq. (4) [45].

$$\text{MCL} = \frac{2}{\left( \frac{Q^1}{Q^1 + Q^2(0Al) + \frac{3}{2}Q^2(1Al)} \right)} \quad (4)$$

In this equation – and those that follow –  $Q^n(mAl)$  represents the relative intensity of a peak determined from the deconvolution of a <sup>29</sup>Si single-pulse MAS NMR spectrum (assuming that the spectrum was collected using quantitative conditions); there are 15 possible  $Q^n(mAl)$  structural units where the silicate tetrahedron, Q, is connected via oxygen bridges to *m* Al and *n–m* other Si atoms, with *n* = 0 to 4 and *m* = 0 to *n* [46]. Andersen et al. [47] introduced a modified version of

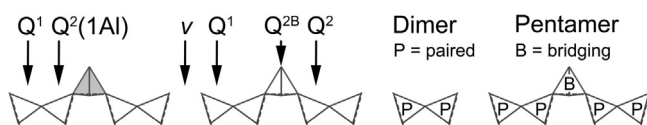


Fig. 1. Schematic diagram that illustrates the nature of the linear aluminosilicate chains that are present in C-S-H (reproduced from [36]). The  $Q^n(mAl)$  notation is explained in the text following Eq. (4).

Eq. (4) that gives the mean length of just the silicate part of the chains, which can be written as Eq. (5):

$$\text{MCL}_{\text{Si}} = \frac{2}{\left( \frac{Q^1 + Q^2(1Al)}{Q^1 + Q^2(0Al) + Q^2(1Al)} \right)} \quad (5)$$

The most extensive sets of MCL-composition data for C-A-S-H in hardened cements that incorporate SCMs are reported by Taylor et al. [8,48] for 20-year-old ggbs/oPc blends with full range of slag replacement (i.e. from 0 to 100%) reacted at normal temperature, and by Girão and co-workers [49,50] for 70% white Portland cement (wPc)–30% pfa pastes hydrated at elevated temperatures (55 and 85 °C) and aged up to 1 year. Those data show that the MCL lengthens with an increase in Si/Ca and Al/Ca ratios, with higher curing temperature, and with the age of the paste. The purpose of this paper is to supplement those data with additional data for blended cements that incorporate 30% pfa but reacted at 20–25 °C and aged for up to 13 years; for comparison, data are also included for pastes that contain 50% pfa aged for 9 and 13 years.

## 2. Experimental

Pastes of wPc and wPc blended with 30% low-calcium pfa were hand mixed with distilled water or with a 5 M KOH solution for 5 min in a plastic beaker. For the blended cement, the anhydrous wPc and pfa powders were first stirred together dry for 5 min and sieved to improve dispersion. All four systems were mixed at a liquid to solid ratio of 0.4 or 0.5 (mL g<sup>-1</sup>) and were cast into 5 mL polystyrene specimen tubes, which were capped and heat sealed individually in polythene tubing; those at 0.4 were cured in a fog room at 20 ± 2 °C for 6, 10 and 15 h, 1, 3, 7, 14, 28 and 56 days; those at 0.5 were cured in a continuously stirred water bath at 25 ± 1 °C for 1 and 28 days, 1 and 4 years, and, in the case of the blended pastes, also for 9 and 13 years. Samples cured for 1 and 28 days were thus prepared using both liquid to solid ratios and curing conditions; the quantities of calcium hydroxide in the pastes at those ages were very similar (%CH<sub>L/S=0.5</sub> = 1.03 × %CH<sub>L/S=0.4</sub>; *n* = 8; *r*<sup>2</sup> = 0.97) and so the data for the two liquid to solid ratios are as a consequence treated together and the CH data that are presented for these ages in §3 are average values. A water-activated blend with liquid to solid ratio of 0.5 was also made that contained 50% pfa, samples of which were examined after 9 and 13 years. Three batches of wPc and pfa were used in the work but they had very similar characteristics; the oxide composition for one of each obtained by X-ray fluorescence spectroscopy is given in Table 1. A small number of the blended samples were made with pfa from which magnetic particles had been removed using the following procedure: (i) the pfa was passed through a 75 μm sieve; (ii) the material was placed in a sealed plastic bag and a hand magnet (SEPOR Automagnet) used to isolate magnetic particles; (iii) the process was repeated until no more particles could be removed. The process had no impact on

Table 1

Bulk oxide composition for the anhydrous wPc and pfa determined by XRF. The pfa included some mullite and quartz.

Oxide (mass %)	wPc	pfa
SiO <sub>2</sub>	24.8	52.9
Al <sub>2</sub> O <sub>3</sub>	2.4	26.9
Fe <sub>2</sub> O <sub>3</sub>	0.5	8.6
MgO	0.8	1.7
CaO	68.6	4.5
SO <sub>3</sub>	2.0	0.4
Na <sub>2</sub> O	0.2	1.2
K <sub>2</sub> O	0.1	3.3

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