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Alkali sorption by C-S-H and C-A-S-H gels
Part II. Role of alumina

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Abstract

In Part I, it was shown that alkali partition between C-S-H gel and an aqueous phase can be represented by a partition function, R_d, the numerical value of which, at constant temperature, is defined by the Ca/Si ratio. This R_d value is constant or nearly so over wide ranges of NaOH and KOH concentrations up to ~ 0.3 M. In the present paper, Al has been introduced to form C-A-S-H gels, and the influence of Al on alkali sorption properties was determined: Approximately 6–7% replacement of Si by Al was used. Microprobe evidence is presented to show that the Al is actually in solid solution. Introduction of Al into C-S-H markedly increases R_d, indicating enhancement of alkali binding. The results underpin and quantify the beneficial effects of alkali binding arising from the introduction of aluminous supplementary cementing materials, such as fly ash, into cement pastes.

Keywords: Pore solution; Alkali sorption; C-A-S-H gel; Sodium; Potassium

1. Introduction

Sodium and potassium oxides comprise on the order of 1% of the total mass of substance of Portland cement. While this may seem to justify their treatment as minor elements, the alkalis remain partially soluble during cement hydration. As they concentrate in a diminishing amount of pore fluid, effectively as sodium and potassium hydroxides, they moderate the course of hydration and mediate reaction with added materials such as fly ash, slag and, possibly, with mineral aggregates. For example, the strongly basic nature of Na and K hydroxides reduces the solubility of calcium and thereby suppress reactions, which require transport of calcium through the aqueous phase. In hardened concrete, the high pH environment conditioned by soluble alkali may initiate reaction with susceptible aggregates. This phenomena, known as alkali–aggregate reaction, or AAR, can adversely affect the performance of concrete. These factors suggest that the presence of alkalis is more crucial to cement and concrete performance than what might be suggested from their low concentrations in clinker and in hydrated paste.

Pore fluid expression provides a direct measure of alkali concentration in the aqueous phase. These analyses can be coupled with mass balance calculations, using the known bulk composition of the cement clinker, to determine the partition of alkali between the aqueous phase and cement solids. Of course, certain assumptions have to be made in mass balance calculations: For example, regarding the amount of clinker hydrated and the amounts of 'bound' and 'free' water—which are difficult to determine experimentally. Various experimental methods provide sufficient data input so that empirical equations have been developed to predict the distribution of alkali between solid paste constituents and the permeating aqueous phase. These equations [1] enable us to conclude that (i) sodium is rather better bound into paste than is potassium and (ii) that the partition between aqueous and solid phases is not, in general, very favourable for the removal of alkali from pore fluids of normal OPC pastes.

The studies do not reveal which solid phase or phases are responsible for binding alkalis. $Ca(OH)_2$ is known to be inactive in this respect, so suspicion falls on C-S-H; it is quantitatively the most abundant phase in paste, and,

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moreover, alkali binding appears to be sensitive to the Ca/Si ratio of the gel, decreasing as this ratio increases, thereby establishing a link between C-S-H composition and sorption of alkali. In practice, the Ca/Si ratio of pastes may be altered by adding reactive, silica-rich pozzolanic materials such as silica fume, fly ash and metakaolin, although the latter two materials also introduce much alumina in potentially reactive form.

Despite these empirical advances, fundamental data on alkali distributions between C-S-H and its coexisting aqueous phase are scarce. Part I of this paper describes a procedure for determining alkali distributions and formulating the results as a distribution coefficient [2]. It is shown that (i) this distribution coefficient, R_d, can be numerically evaluated by experiment, (ii) a C-S-H of fixed Ca/Si ratio has a characteristic, fixed value of R_d, which, at constant temperature, is essentially independent of alkali concentrations in the range 1–300 mM, (iii) the R_d value, and, hence, the strength of alkali binding into the solid, increases as the Ca/Si ratio of the C-S-H decreases and (iv) that sorption–desorption equilibria are attained rapidly and are approximately reversible.

A mechanistic explanation of sorption was also presented. Alkalis, it was suggested, were being bound into C-S-H mainly at acidic silanol, Si–OH, sites. It was suggested that if this explanation were correct, the acidity and, hence, the strength of binding of alkali into C-S-H, could be affected by changing the number as well as the acidity of silanol sites. Substitution of tetrahedral Al and Fe (III) into C-S-H, it was further suggested, could enhance site acidities and increase the extent of alkali binding. It was therefore proposed that a full explanation of binding should await a study of alkali sorption in Al-substituted C-S-H. The present paper describes relevant work and presents discussion and conclusions.

2. Experimental

The experimental plan and methods are essentially those used in the first part of this study [2]. Three Ca/Si molar ratios, at 1.5, 1.2 and 0.85, were prepared from mixtures of $Ca(OH)_2$ and Degussa "Aerosil 300" silica. The C-S-H gel was homogenised in a previous step. Alumina was introduced as an initially amorphous alumina gel. This was freshly prepared by ammonia precipitation of aluminium nitrate hydrate, with washing of the product to ensure complete removal of ammonium and nitrate irons. The calculated alumina loading was kept constant at ~0.5 mM/g of gel product. The resulting slurries, made from two solid gel phases, were dispersed by high-shear mixing and subsequently allowed to mature, but with regular agitation, for up to 1 year at ~20 °C prior to use. Tests for the homogeneity of the product will be described subsequently.

After ageing, aliquots of the liquid were removed and analysed for Ca (by flame emission) and for Al and Si (by atomic absorption) using certified reagent-grade standards for calibration. The solid product was filtered under N_2 and characterised by X-ray diffraction and by bulk chemical analysis. To establish a base weight for subsequent determination of R_d, the resulting solid products, shown to be amorphous or nearly so by X-ray diffraction, were "soft-dried" over solid $CaCl_2$ at ~20 °C. This generally required ~7 days. Total water was determined by destructive ignition at 1000 °C of soft-dried gels. The weight loss thus determined was slightly less than the loss determined on an oven-dried (105 °C) material. X-ray diffraction disclosed that only traces of $CaCO_3$ were present in the soft-dried gels.

Each alkali partition experiment used ~0.6 g of soft-dried gel, which was weighed and handled under N_2. A previously standardised NaOH or KOH solution, ranging in concentration between 15 and 300 mM, was added in known volume to achieve a w/s ratio of ~1.5. The samples were sealed and allowed to equilibrate with gentle but continuous agitation at 20 °C. The aqueous phase was sampled periodically and filtered through a 0.45-μm "Millipore" filter (Millipore, Bedford, Ireland). Sodium and potassium were determined by flame emission spectroscopy, calibrated with certified reference standards.

In this way, a grid of 12 points for sodium and a further 12 for potassium were obtained by systematically varying the Ca/Si ratio of the gel and initial alkali concentration. Additionally, two reaction times, 2 and 12 months, were allowed for sorption giving a total of 48 data sets.

The uptake of alkali, in moles, can be calculated from the known solution volume (V) and the decrease in aqueous alkali concentration, $V\Delta C$. That is, the number of moles taken up by the solid is $V\Delta C$. Where cation analyses to determine C could not be done immediately, the alkaline filtrates were acidified with a known volume of standard HNO_3 and appropriate correction was subsequently applied for dilution. This avoided carbonation and precipitation of solids, with possible impact on alkali sorption data.

Data are treated using the same method described in Part 1 and are expressed as a distribution ratio, R_d (ml/g), such that:

$$R_d = \frac{\text{Alkali in solid C} - \text{S} - \text{H (mM/g)}}{\text{Alkali in concentration in solution (mM/ml)}}$$

where the mass of solid C-S-H refers to its soft-dried mass.

3. Results

3.1. Al incorporation in C-S-H

The maximum extent of spontaneous solid solution of Al in C-S-H at 20 °C is somewhat uncertain. Analyses and microanalyses of commercial cement pastes disclose rather variable amounts of Al, as well as of sulfur [3], in C-S-H. However, the ratio of measured Al and S suggests that the observed gel chemistry may arise in part from an occluded secondary phase or phases on a scale which cannot be resolved by conventional electron-optical methods, e.g., electron microprobe: For example, AFm or AFt, or mixtures thereof, may be occluded within the C-S-H. On the other hand, studies made on S-free systems suggest that Al can be incorporated in C-S-H and, moreover, ^{27}Al NMR suggests that Al resides on tetrahedral sites where it substitutes for silicon. The atomic populations of C-S-H are not subjected to the same crystallochemical limitations as are those of a well-ordered crystalline phase, so it is difficult to devise additional checks on the state of Al. Considerable preliminary effect was therefore devoted to developing and proving a satisfactory method for synthesis of homogeneous, Al-containing C-S-H. The most direct route, and that which was first considered, was to coprecipitate gel from initially homogeneous solutions containing the desired Ca/Al/Si ratios. However, we were unable to prove conclusively that precipitation was truly homogeneous and that a CAHx [8] phase did not also form during precipitation and ageing. Therefore, it was decided to start with a deliberately inhomogeneous mixture but allow time for it to homogenise and monitor the homogenisation process. By also selecting a conservative target for the maximum extent of Al substitution, it was hoped that sufficient driving force for homogenisation would exist to drive reaction to completion within reasonable time.

In the method selected, a C-S-H gel was prepared by the method described in Ref. [2]. After several weeks, standing to allow homogenisation of the Ca and Si components, this product was physically blended with freshly precipitated alumina gel, using a high-shear mixer. The target ratio of the blended gels was set uniformly at 0.5 mM Al/g weight of soft-dried C-S-H: This proportioning corresponds to approximately 6–7% replacement of Si by Al, i.e., Si/Al ~ 13–16; the exact ratios achieved for each preparation, as determined by batch analyses, are given in Tables 1–3. The alumina gel precursor was shown by X-ray powder diffraction to be virtually amorphous and by TG, to have a composition close to Al $(OH)_3$. The resulting two-phase mixture, of C-S-H and alumina gel, was allowed to age prior to microanalysis.

Table 1
Statistical treatment of measured data and estimated error interval (95% confidence intervals based on Student's *t* test)

Sample	No. of analysis	Average[a]	STD	95% Confidence
(a) Cure duration, 2 months				
C-A-S-H: Ca/Si = 0.85	10	0.478	0.312	± 0.228
C-A-S-H: Ca/Si = 1.2	10	0.481	0.259	± 0.185
C-A-S-H: Ca/Si = 1.5	10	0.469	0.191	± 0.139
(b) Cure duration, 12 months				
C-A-S-H: Ca/Si 0.85	10	0.467	0.071	± 0.051
C-A-S-H: Ca/Si 1.2	10	0.491	0.099	± 0.071
C-A-S-H: Ca/Si 1.5	10	0.467	0.080	± 0.057

[a] Expressed as mmol Al/g C-A-S-H gel.

Bulk chemical analyses of the gel products demonstrated that the target Al concentration was consistently achieved. Against a target concentration of 0.5 mM/g of C-A-S-H product, actual concentrations determined by analysis were 0.47 mM (C/S = 0.85), 0.49 mM (C/S = 1.2) and 0.47 mM (C/S = 1.5). However, proving a homogeneous distribution of Al was more difficult. At the high Si/Al ratios used, NMR was too insensitive for accurate determinations of the coordination state of Al, but analytical electron microscopy was used to determine spatial distributions. Fig. 1 shows the analytical electron microscopic data for Al distributions; a supporting statistical treatment is given in Table 1. The analyses were made at the three C/S ratios and after two cure treatments: 2 and 12 months at 25 °C. Thin, clean foil or flake-like samples were selected and the electron microscope/analytical system was used in transmission mode for analyses. Calibrations against known Ca/Al/Si standards were made before and after each set of analyses. The vertical scale within each panel of Fig. 1 has no physical significance but is used to spread the data for graphical clarity. Open circles were obtained from a product cured for 2 months and closed squares from a product cured for 12 months. The much greater spread of values at 2 months, relative to 12 months, is readily apparent and is attributed to inhomogeneity of product cured for 2 months. The homogeneity of the 12-month cure was determined by application of Student's *t* test to the data. Table 1 shows the relevant parameters; the triangle at the top of each panel in Fig. 1 indicates the disposition of 95% confidence limit. The triangle positions are centred on the chemically determined bulk composition, as measured for a product cured for 12 months. The disposition of this envelope, relative to the data points, suggests that the longer cure gives products, which have achieved a satisfactory degree of homogenisation on a scale of the analysis. This is estimated to have an approximate projected diameter of 100 nm. Further data treatment will be deferred to the discussion, but it is worth noting that for each gel composition, we deliberately used one specimen with an inhomogeneous Al distribution, typical of immature pastes, and another homogeneous gel believed to be typical of mature pastes.

3.2. Sorption data

In subsequent presentations of the sorption data, we also include data on control samples of alumina-free C-S-H. These data are intended as a benchmark to show how Al modifies the intrinsic sorptive properties.

Data on Al-substituted gels and data treatments are shown in Table 2. Three ratios, Ca/Si = 0.85, 1.2 and 1.5, were used together with four initial Na and K concentrations, 15, 50, 100 and 300 mM/l, following gel homogenisation times of 2 and 12 months. The Al contents were determined by actual bulk analysis of the preparation and are relative to the soft-

Table 2
Relationship between Al and sorbed alkali in C-A-S-H gels at 20 °C

(1) Na_2O

1	2	3	4			5	
			Na concentration in solid (mM/g)			Increase of sorbed Na	
Ca/Si	Initial Na (mM/1)	Al in solid (mM/g)	Al free	Al containing		Al in solid (mM/g)	
			C-S-H	2 Months[a]	12 Months[a]	2 Months[a]	12 Months[a]
0.85	15	0.47	0.0540	0.1415	0.1777	0.19	0.26
	50	0.47	0.2040	0.4500	0.5475	0.52	0.74
	100	0.47	0.3015	0.5013	1.0320	0.42	1.58
	300	0.47	0.8880	0.9783	2.1270	0.20	2.66
1.2	15	0.49	0.0255	0.0270	0.0645	0	0.08
	50	0.49	0.0975	0.1110	0.1815	0.02	0.18
	100	0.49	0.1815	0.2190	0.3585	0.08	0.36
	300	0.49	0.4365	0.4635	0.7950	0.06	0.74
1.5	15	0.47	0.0105	0.0240	0.0330	0.02	0.04
	50	0.47	0.0345	0.0435	0.0915	0.02	0.12
	100	0.47	0.0570	0.0765	0.1230	0.04	0.14
	300	0.47	0.1980	0.2745	0.3630	0.16	0.36

(2) K_2O

1	2	3	4			5	
			K concentration in solid (mM/g)			Increase of sorbed K	
Ca/Si	Initial K (mM/l)	Al in solid (mM/g)	Al free	Al containing		Al in solid (mM/g)	
			C-S-H	2 Months[a]	12 Months[a]	2 Months[a]	12 Months[a]
0.85	15	0.47	0.0585	0.1640	0.1715	0.22	0.24
	50	0.47	0.1635	0.5145	0.5400	0.76	0.80
	100	0.47	0.3390	0.8970	1.0800	1.20	1.60
	300	0.47	0.8580	1.7310	1.8945	1.88	2.22
1.2	15	0.49	0.0195	0.0270	0.0615	0.02	0.08
	50	0.49	0.0705	0.1065	0.1815	0.08	0.22
	100	0.49	0.1695	0.2145	0.2655	0.10	0.20
	300	0.49	0.4215	0.5910	0.7740	0.34	0.72
1.5	15	0.47	0.0165	0.0195	0.0240	0	0.02
	50	0.47	0.0465	0.0495	0.0645	0	0.04
	100	0.47	0.1020	0.0825	0.1965	− 0.04	0.20
	300	0.47	0.2055	0.2955	0.4650	0.20	0.56

The contact time for sorption was uniformly 2 days.
The increase is calculated by the subtraction of the benchmark value for Al-free C-S-H (Column 4) from the observed uptake.
C-S-H 12 months: C-S-H cured for 12 months at 20 °C (no Al addition); C-A-S-H 2 months: $Al(OH)_3$ was added to C-S-H and allowed to react for 2 months at 20 °C; C-A-S-H 12 months: $Al(OH)_3$ was added to C-S-H and allowed to react for 12 months at 20 °C.

[a] Time refers to cure duration prior to commencing sorption experiment.

dried weight. Alkali concentrations in the solids are shown for Al-free C-S-H, used as a control, and for C-A-S-H gels, cured for 2 and 12 months. Steady-state alkali concentrations were achieved rapidly, within 2–3 days, of commencing the experiments; subsequent storage for up to 12 months prior to reanalysis did not significantly affect the numerical values shown. The final column records the calculated increase of alkali sorption arising from Al incorporation in gel: These totals are calculated by rounding off and subtraction of data in Column 4. Note that data obtained from material cured for 2 months scatter, but that the scatter envelope is much reduced using a product that has previously been cured for 12 months, and that all results on a product cured for 12 months record an increase in alkali sorbed relative to data on a product cured for only 2 months. The extent of the increase is broadly similar for Na and K but is least for high-ratio gel, increasing as the Ca/Si ratio decreases. With changing Ca/Si ratio, the stepwise increase in alkali sorption is greatest when comparing ratio 1.2 with 0.85.

Table 3 shows the corresponding values of R_d, the distribution coefficient, calculated from the analytical data of Table 2. These data are also shown graphically in Fig. 2. Note that the aqueous solution alkali content is the initial concentration; aqueous alkali decreases in the course of the experiment and will, in general, be slightly lower than the initial concentration given in Table 2. Benchmark values for Al-free C-S-H are also given.

Several trends are evident. The R_d values of Al-free C-S-H are only slightly affected by Na or K aqueous concentrations; the deviation from ideality is most apparent at low

Table 3
Effect of ageing time of C-A-S-H gels on alkali binding and comparison of R_d values

(1) Na_2O

Ca/Si	Initial Na (mM/l)	R_d (ml/g) C-S-H[a]	2 Months	12 Months
0.85	15	4.82	24.1	62.1
	50	5.70	22.3	44.8
	100	3.82	11.2	33.9
	300	3.76	5.11	12.9
1.2	15	1.94	2.00	6.39
	50	2.26	2.21	4.85
	100	2.08	2.56	4.77
	300	1.64	1.72	3.21
1.5	15	0.74	1.75	2.56
	50	0.73	0.92	1.98
	100	0.60	0.80	1.35
	300	0.70	0.97	1.30

(2) K_2O

Ca/Si	Initial K (mM/l)	R_d (ml/g) C-S-H[a]	2 Months	12 Months
0.85	15	5.32	39.3	54.1
	50	4.16	33.2	47.4
	100	4.33	22.5	38.1
	300	3.47	9.39	10.8
1.2	15	1.43	2.03	5.69
	50	1.55	2.14	4.88
	100	1.89	2.51	3.28
	300	1.53	2.27	3.16
1.5	15	1.20	1.41	1.80
	50	0.99	0.96	1.44
	100	1.09	0.98	2.44
	300	0.71	1.34	1.76

2 months: $Al(OH)_3$ was added to C-S-H and reacted for 2 months at 20 °C.
12 months: $Al(OH)_3$ was added to C-S-H and reacted for 12 months at 20 °C.

[a] C-S-H: C-S-H phase, which was cured for 12 months at 20 °C. This C-S-H was used as precursor for preparing C-A-S-H gels.

Ca/Si ratios and at high alkali concentrations, ~0.1 M. When Al-substituted C-S-H gels are cured for 2 months, the gel remains inhomogeneous and a range of Al substitution values is obtained. Nevertheless, R_d values increase, relative to Al-free product having the same Ca/Si ratio, the increase being greatest for those solids having low Ca/Si ratios. For C-A-S-H gels cured for 12 months, the spread of R_d values, from minimum to maximum, is much greater than for the equivalent benchmark C-S-H. For example, at Ca/Si ratio ~0.85, with K as the sorbed species, numerical R_d values range from 0.71 to 5.32, whereas for the alumina-substituted solid, numerical values varied in the same order, but increased from 1.76 to 54.1.

In order to determine a sorption mechanism, it is useful to have the data in a form that shows the excess of alkali absorbed arising from inclusion of Al. Fig. 3 shows the data recalculated in this way. The calculation has been done only for sorption on a product cured for 12 months. The dashed line of Fig. 3 shows the contribution to sorptivity, which would be predicted if one alkali ion, Na or K, were incorporated for each Al replacing silicon, i.e.

$$(\mathrm{Na^+}, \mathrm{K^+}) + \mathrm{Al^{3+}} = \mathrm{Si^{4+}}$$

It is apparent that in four cases, the limit set by this substitution has not been attained, but in two cases (Ca/Si = 0.85), this mechanistic limit is exceeded.

The analytical data show that alumina, physically dispersed into C-S-H, reacts slowly to form C-A-S-H gel. As it disperses in solid solution, the potential of the bulk gel for alkali sorption increases, the extent of the increase being greatest at low Ca/Si ratios. Only one nearly constant and rather low Al substitution was used, equivalent to Si/Al ratios in the range 13–16. Nevertheless, even this level of substitution is markedly sufficient to enhance the alkali sorption capacity. The increase in alkali binding does depend on the chemical nature of the alkali, sodium or potassium, but the dependence on alkali type is confined to a few selected data sets, as will be explained. The improvement in sorptive properties, comparing C-A-S-H gel with C-S-H of the same, or essentially the same, C/S ratio is least for high Ca/Si ratios but increases as the numerical value of the Ca/Si ratio decreases. This comparison is depicted graphically in Fig. 4, showing data for sodium (Fig. 4a) and potassium (Fig. 4b). In each case, data for C-S-H are shown by a solid line, and for the corresponding C-A-S-H, by a dashed line. A dashed horizontal line shows the limit,

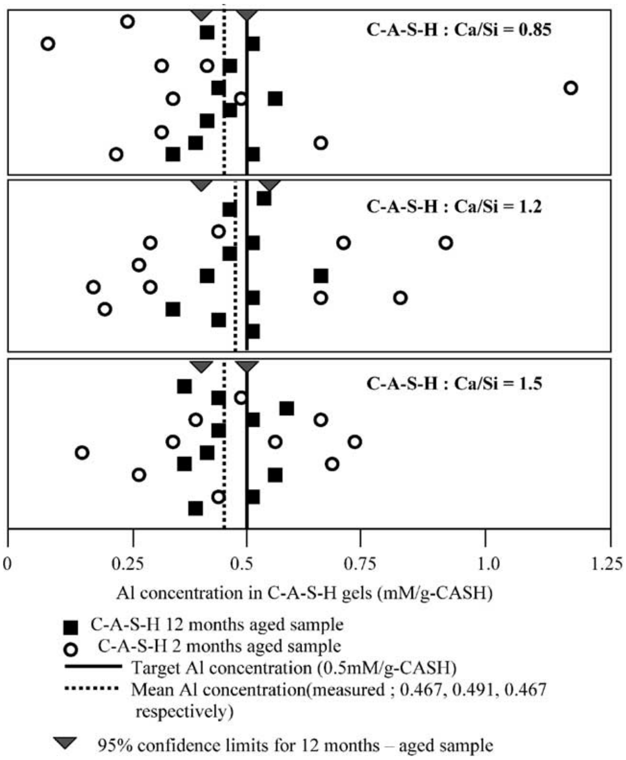

Fig. 1. Effect of ageing time on the distribution of Al in C-A-S-H gel.

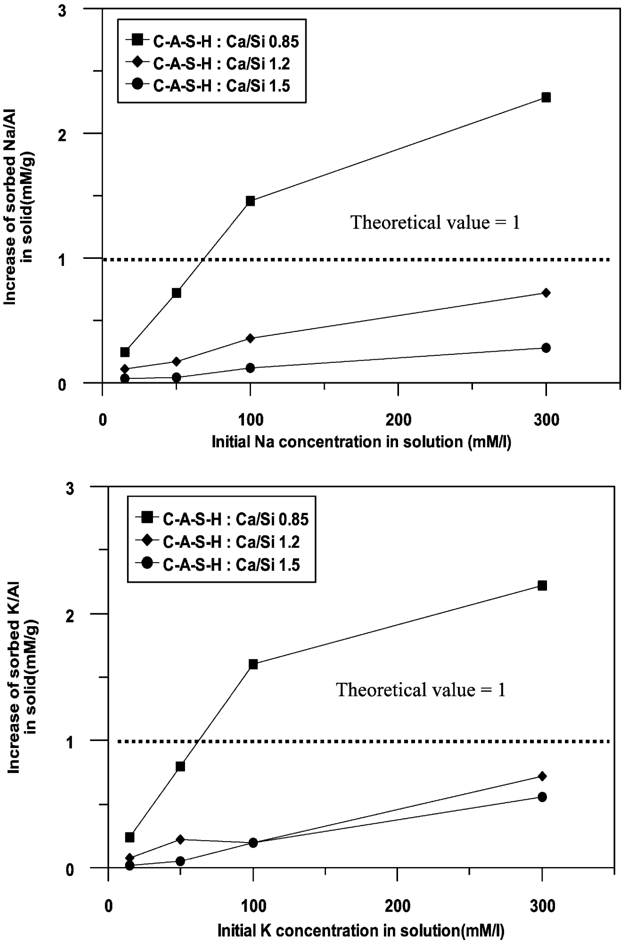

Fig. 2. Relationship between increase of sorbed alkali and Al concentration in solid.

which would be attained if one alkali ion were to be sorbed per Al, i.e., (Na, K) + Al^{3+} = Si^{4+}. Several features deserve comment. Firstly, the sorption curves most nearly approach ideality, shown by having a slope that is concentration independent, by K-loaded C-A-S-H with Ca/Si = 1.5. In this case, experimental differences between gel with and without Al are not statistically significant. Moreover, all numerical values for the alkali uptakes of the C-A-S-H gel lie well below the horizontal line. If these values are compared with the same Ca/Si ratio but with Na as the alkali, the slope of the sorption curve is markedly steeper for K-containing C-A-S-H gel with Ca/Si = 1.5 and, moreover, the horizontal line is more nearly approached at higher aqueous concentrations. Comparing the two other ratios, Ca/Si = 1.2 and 0.85, it is noteworthy that for all remaining data sets, (i) the gel sorption potential is much enhanced by the presence of Al, (ii) departures from constant slopes are more marked for C-A-S-H gels than for C-S-H gels and (iii) the initial slopes of some of the C-A-S-H sorption curves are very steep, with an ill-defined inflection occurring at a point that is approximately coincident with the horizontal line.

3.3. Desorption data

Sorption and desorption are often complimentary processes. However, it is often difficult to prove strict reversibility by experiment. In the work on C-S-H [2], we tentatively claimed reversibility although the experimental grid was not well laid out to prove if reversibility occurred. However, this defect in the experimental plan only became apparent after the experiments had been concluded. In experiments on C-A-S-H gels, similar problems arose but were in part anticipated at the outset. Table 4 lists data obtained on the gel at 0.85 Ca/Si ratios. One data set, shown in bold, is used in the calculation of *desorption* R_d values. The calculation proceeds as follows:

1. 0.600 g of solid C-A-S-H gel was taken as "soft dried" material. It was dispersed and equilibrated in a known volume of NaOH, of initial concentration 0.100 M, i.e., 10^3 mol/ml.
2. After equilibration, the wet solid was found by analysis to contain 0.5475 mM Na/g soft dried weight: The aqueous phase concentration had decreased to 0.0122 mM/ml.
3. The amount of water in the gel had much increased. After centrifugation with subsequent ignition, it was

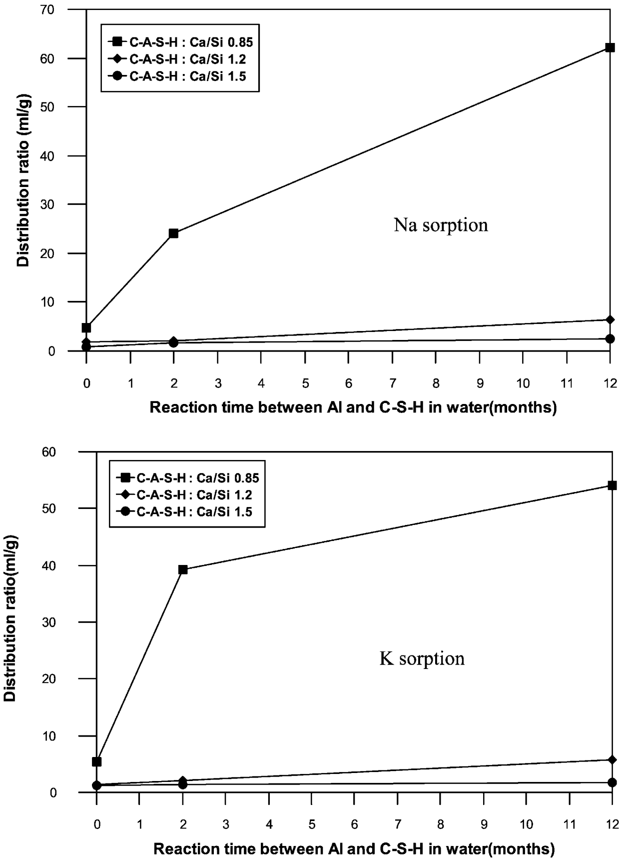

Fig. 3. Effects of ageing time of C-A-S-H gel on alkali binding (initial alkali concentration of water: 15 mM/l).

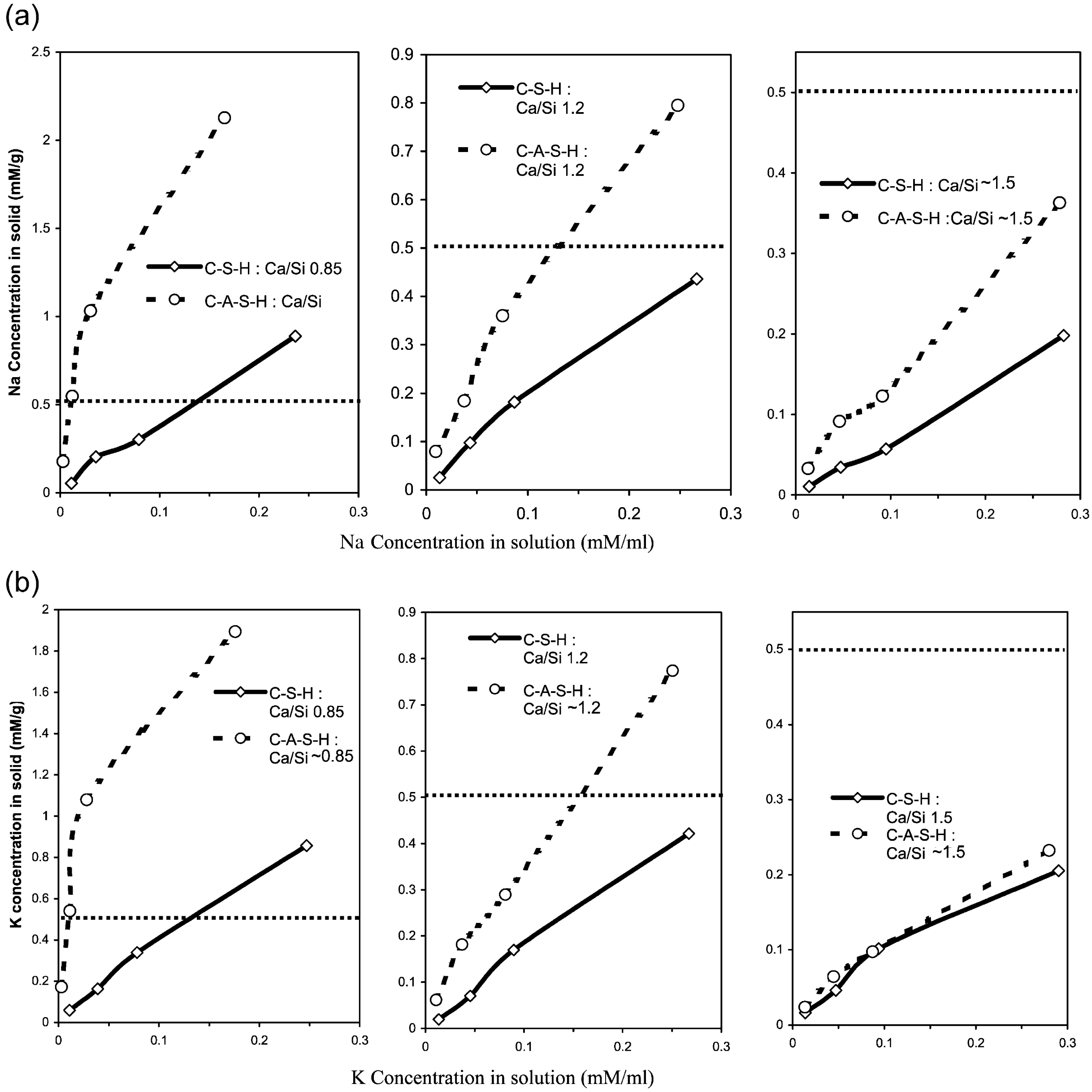

Fig. 4. (a) Comparison of alkali binding between C-S-H and C-A-S-H gels. Solid lines and dashed lines indicate C-S-H and C-A-S-H gel, respectively. (In C-A-S-H gels, Si/Al = 16.2 (Ca/Si = 0.85), 14.1 (Ca/Si = 1.2) and 13.3 (Ca/Si = 1.5)). (· · · · · · · ·) Na concentration in C-A-S-H gel (1 Na = 1 Al). (b) Comparison of alkali binding between C-S-H and C-A-S-H gels. Solid lines and dashed lines indicate C-S-H and C-A-S-H gel, respectively. (In C-A-S-H gels, Si/Al = 16.2 (Ca/Si = 0.85), 14.1 (Ca/Si = 1.2) and 13.3 (Ca/Si = 1.5)). (· · · · · · · ·) K concentration in C-A-S-H gel (1 K = 1 Al).

estimated to contain 5.125 g H_2O, i.e., it has a very water-rich composition.

4. The total mass of Na in the aqueous phase in the gel is 0.0625 mmol.
5. To induce desorption, an additional 3.875 ml of water was added, making a total of 9 ml (the same volume as was used for the sorption). In the absence of desorption, this would dilute the aqueous alkali to 0.0069 mM/ml (0.0625/9 mM/ml), i.e., 9 mmol/10^{-3} l.
6. After desorption equilibration, the sodium concentration of the aqueous phase was found by analysis to be 0.0130 mM/ml.
7. The final sodium concentration in solution was 0.0061 mM/ml. Thus, the sodium removed from C-A-S-H gel is equivalent to 0.0915 mM/g solid.
8. The final sodium concentration in solid after desorption was 0.4560 mM/g solid (0.5475 − 0.0915).
9. The R_d value is therefore 0.4560/0.0061 = 74.8 ml/g.

It should be noted that R_d values thus obtained are subject to numerous error sources, notably in accurately estimating the hydrous state of the gel and the amount of solution occluded by the gel. However, the apparent paradox emerges that R_d values are generally significantly

Table 4
Quantification of sorbed and desorbed alkali in the $Na_2O(K_2O)-Al_2O_3-CaO-SiO_2-H_2O$ system at 20 °C

	Alkali partition between C-A-S-H and aqueous phase after sorption		Alkali partition between C-A-S-H and aqueous phase after desorption		Distribution ratio (R_d)	
C/S ratio (M^+)	C-A-S-H (mM/g)	solution (mM/ml)	C-A-S-H (mM/g)	Solution (mM/ml)	Sorption (ml/g)	Desorption (ml/g)
0.85 (Na)	0.1777	0.0029	0.1146	0.0014	62.1	81.9
	0.5475	0.0122	0.4560	0.0061	44.8	74.8
	1.0320	0.0304	0.8205	0.0141	33.9	58.2
	0.1715	0.0032	0.1340	0.0025	54.1	53.6
0.85 (K)	0.5400	0.0114	0.4335	0.0071	47.4	73.9
	1.0800	0.0283	0.8505	0.0153	38.1	55.6

higher for desorption than for sorption. Reasons for the above are discussed.

4. Discussion

In Part I of this paper [2], it was suggested that alkalis were sorbed into C-S-H at silanol, Si–OH, sites. This sorption, in mass of alkali per mass of solid, was explained as arising from (i) the density, or number per unit volume, of silanol bonds and (ii) the mean acidity of the sites. Both the number and acidity of the sites, it was suggested, increase as the Ca/Si ratio of C-S-H decreased. Thus, at least two complimentary effects were responsible for the observed trends in R_d values. Since the electronegativities of Na and K did not differ greatly, a given C-S-H would be expected to have the same, or nearly the same, R_d values for both sodium and potassium. It was further suggested that over most of the concentration range used (1–300 mM alkali) and Ca/Si ratios (0.85–1.8); 1.5 for C-A-S-H gels, saturation of silanol sites had not been generally achieved. However, additional data in the literature [10] were conflated with those in Ref. [2] to show that saturation for low ratio C-S-H is probably achieved, or nearly achieved at concentrations ~1 to 1.5 M for potassium. Typical concrete pore fluids exhibit moderate (0.1–1.0 M) alkali concentrations. Therefore, C-S-H in Portland cement is unlikely to achieve alkali saturation because of (i) its high Ca/Si ratio gel, (ii) low R_d values and (iii) low to moderate pore fluid alkali contents. To understand the behaviour of real concretes, it is therefore important to consider the response to changing alkali concentrations of the gel phase mainly in the undersaturated region and, if possible, determine the role of Al.

Amorphous aluminosilicates and silicas are much used as catalysts and the acidity concept, invoked in order to explain trends in R_d values, was borrowed from catalytic theory. In this respect, amorphous phases behave differently than crystalline materials. Amorphous aluminosilicate materials resemble C-S-H inasmuch as they lack the structure-specific sorption and bonding characteristics of a well-ordered solid. It is therefore appropriate to describe sorption in terms of acid–base theory. In its application to solids, acids are considered to be electron donors and bases to be electron acceptors. Thus, in the present case, alkalis are the base and silanol the acid. In this view, the silanol groups do not have a specific acidity but instead a range of values depending on the chemical nature of the other linkages to silanol silicons.

In the present context, the introduction of acidic ions, specifically Al, into the tetrahedral sites of a C-S-H gel appears to have two effects. Firstly, it introduces a mechanism for alkali substitution in which charge compensation is maintained by a double substitution for silicon:

$$M^+ + \mathrm{Al}^{3+} = \mathrm{Si}^{4+}$$

where M^+ is (Na, K). Fe^{3+} may also replace Al^{3+} but we treat only Al. These substitutional mechanisms are well documented from crystal chemistry: Al, and to a lesser extent Fe, occupy tetrahedral sites directly replacing Si, while the alkali ion is stuffed into otherwise empty sites. NMR [5–8], in part, corroborates this scheme inasmuch as Al in C-A-S-H gels is found to occupy tetrahedral sites: The overall chemistry of C-A-S-H gels also supports the contention that sites formerly occupied by Si are substituted by Al. Thus, the equilibrium sorption capacity for alkali of an alumina-free C-S-H gel mainly measures silanol-binding capacity. However, for C-A-S-H gels, the observed binding arises from two sources: the valence compensation mechanism, described above, as well as a silanol binding capacity, which is enhanced as a consequence of its linkages to a skeleton modified by inclusion of tetrahedral Al.

We have had only partial success in deconvoluting these two factors by a chemical approach. Firstly, we note that in representations of the type used in Figs. 2 and 3, the slope of the data curve is related to R_d and vice versa: Steep curves correspond to high numerical R_d values. This being so, the introduction of Al into gel, even in the low quantities used here, may have a significant impact on increasing the initial slope of the sorption plot and hence the numerical value of R_d. The slope is also affected by the Ca/Si ratio: Comparing C-S-H and C-A-S-H of similar Ca/Si ratios, introduction of Al into high Ca/Si ratio gels has little or no influence on the slope (compare, for example, data for Ca/Si ratio 1.5 with those from lower ratios). However, as the gel Ca/Si ratio decreases, the introduction of Al has a progressively greater influence on sorption. We attribute this behaviour at low Al concentrations to increases in the number of silanol sites, as well as their increasing acidity as Al is substituted for Si. The density of silanol bonds is lowest for high Ca/Si ratio gels and is believed to change little in the range between the maximum possible ratio, probably ~1.72, and 1.5. Thus the Ca/Si = 1.5 gels used here are probably good models for the performance of C-S-H and C-A-S-H in ordinary cement pastes. However, as the ratio decreases below ~1.5, the density of silanol sites, as well as their mean acidities, increase. For a nearly constant Al content, the increase is slow at first over the range of ratios between 1.5 and 1.2, but thereafter accelerates rapidly as ratios decrease below 1.2.

At all except very low alkali concentrations, binding of alkali occurs by a valence compensation mechanism, in which the potential charge imbalance created by substitution of Al into tetrahedral sites for Si is balanced by inclusion of alkali. This substitution, $M^{+} + \mathrm{Al}^{3+} = \mathrm{Si}^{4+}$, is stoichiometric in many crystalline substances. However, given the disordered nature of the gel, an exact stoichiometry need not be obtained; hydroxyls and calcium can serve to some extent as charge balancing ions. Indeed, given the extent of observed substitution of (Na, K) into alumina free C-S-H, we would, in general, expect alkali substitution to exceed one alkali per aluminium. However, it is noteworthy that where sorption does exceed the maximum predicted from the valence compensation model, a change in the slope of R_d occurs close to the theoretical threshold for valence compensation. The composition intervals of our experiments are too coarse precisely to define an inflection point, but, in general, the most rapid change in slope occurs close to, perhaps somewhat above, the theoretical valence compensation limit, as would be expected if both silanol saturation and valence compensation mechanisms were contributing in a concentration-dependent manner to the observed results. Thus, theory and experiment are broadly reconciled.

The above treatment is semiquantitative: We have not found a quantitative way of deconvoluting silanol densities and acidities, but it is possible that a combination of infrared spectroscopy and solid-state NMR, the latter using Al, Si and proton spectroscopy, could be additionally applied to the task. NMR is potentially very useful as it can also quantify the state of Si polymerisation, a function that is likely to correlate with acidity. However, more accurate mapping of the R_d function and its relationships to composition and properties may of itself be a valuable tool with which to explore C-A-S-H gel structures.

The desorption data are, as explained previously, complicated by the need first to saturate prior to desaturation, and also by the need to handle the solids in such a way as not to interfere with their structure and chemistry during manipulations. Nevertheless, it appears paradoxical that the R_d value for desorption is systematically *higher* than for sorption. This apparent paradox can be resolved by noting the nonlinear shape of the sorption curve of C-A-S-H gels, especially those with low Ca/Si ratios. Fig. 5 has been constructed to explain the situation. The example is hypothetical but relates closely to the shape of experimentally determined values for Ca/Si = 0.85. In the example, an initially sodium-free C-A-S-H gel is dispersed in an alkali hydroxide solution, the composition of which is initially at *M*. After a steady state has been achieved, the composition of the aqueous phase shifts to point *a*. In the course of achieving a steady state, sodium "dissolves" in the solid, giving a solid composition, which lies at point *b*. Thus, the line *a–b* comprises a tie line, connecting the steady-state compositions of a coexisting solid and aqueous phase. It will be recalled that the experiments were so proportioned that the drop in solution concentration, while not large, had to be sufficient to determine with good analytical precision. Next, the solid is separated from the aqueous phase (but not very efficiently separated, even with centrifugation) and the solid is redispersed with an increment of alkali-free water. The solid quickly reestablishes an equilibrium with aqueous phase as a result of which its composition shifts to *c*, giving a coexisting aqueous phase composition at *d*. Thus, *c–d* defines another tie line characteristic of a desorption equilibrium. The respective R_d values are defined by the slope of lines drawn from the origin through points *b* and *c*. The slopes therefore change such that the R_d value for desorption is characteristically greater than for sorption. If, however, the curve had an ideal shape, i.e., it had a constant slope and was a linear function of composition, R_d values for sorption and desorption should have been equal. We are therefore

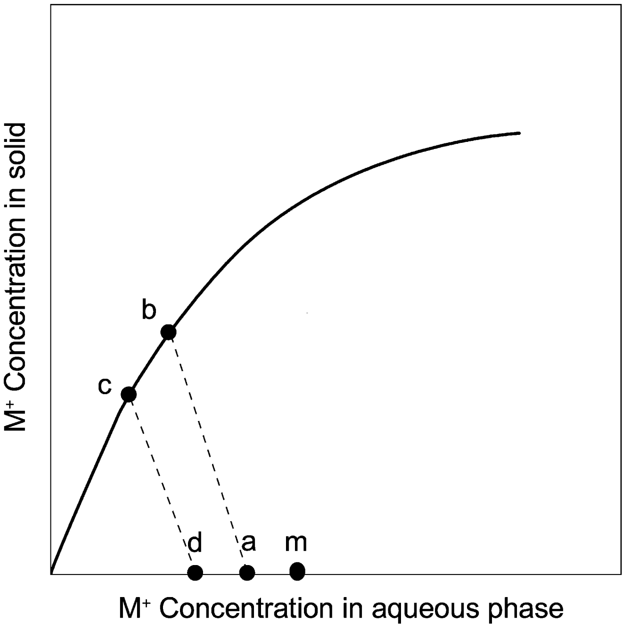

Fig. 5. Schematic, illustration characteristic differences in R_d values from sorption–desorption measurements arising as a result of the methodology. See text for explanation of the symbols.

satisfied that reversibility was achieved, albeit in a nonideal system, and that the apparently higher R_d values on desorption find a systematic explanation.

The number of sites favourable for sorption is indicated by the shape of the saturation isotherms, as constructed from the data or derived from R_d values. While the experiments were insufficient to saturate C-S-H at Ca/Si ratios 1.5 and 1.2, the sharp negative deviations at high concentrations for Ca/Si = 0.85 indicate that saturation is nearly achieved: Data at only four concentrations are insufficient to be certain. However, if saturation has been attained, the number of sites for alkali binding exceeds somewhat the number of Al replacing Si. Thus, saturation is achieved at (Na, K) levels somewhat in excess of the Al population. On this basis, the higher ratio gels, at Ca/Si = 1.2 and 1.5, are only likely to become fully saturated in the range 1–2 M NaOH or KOH.

The measure of the acidity of the intrinsic alkali sorption sites, i.e., those not dependent on the introduction of Al, is given by the initial slope of the R_d plots. We conclude that the silanol acidities are little affected by the introduction of Al at high Ca/Si ratios, but the impact when a constant (or nearly constant) mole fraction of Al is substituted for Si increases rapidly as the Ca/Si ratio decreases.

The question may also be asked: Given the low extent of Al substituted, what would happen if more Al had been introduced into the C-S-H phase, perhaps up to the limit of alumina saturation? The answer to this has to be given in parts. Firstly, in “real” C-S-H, we probably have to include some Fe (III) with Al in tetrahedral sites. However, in the absence of data for Fe, which, however, is likely to be more acidic than Al, we must confine the discussion to Al. We also note that reliable quantitative data on the maximum extent of substitution in real pastes are scarce. However, the amount used in the present study is almost certainly too low to fully saturate C-S-H. The saturation limits appear to be composition dependent, with more Al substitution being possible in low Ca/Si ratio gels than high. However, amongst gels with high ratios, in the range 1.5–1.7, the limit of substitution is probably close to that achieved here. However, the low ratio gels used here are probably undersaturated in Al. Thus, both sorption capacities and R_d values of low ratio gels would be predicted to increase beyond those shown here. In practice, low ratios are most likely to occur if slag, fly ash, metakaolin or silica fume are added to cement. Not only do these materials—especially the last three—convert $Ca(OH)_2$ to C-S-H, thereby increasing the amount present, but they also introduce sufficient alumina (and presumably Fe_2O_3) to saturate the gel. We do not at present know these saturation limits but they are substantially higher than the rather conservative values used in this study. Considering coal-combustion ASTM Type F fly ash, from stoichiometric considerations it is unlikely that sufficient fly ash could be added to lower the mean Ca/Si ratio of an engineering concrete to below, say, 1.2. Fly ash, however, may react inhomogeneously with cement, so that clusters of low ratio gel develop at or close to the site of former fly ash particles, or clusters of particles, such that although the mean Ca/Si ratio might remain high, ca. 1.5 or more, preferential sorption could occur at local inhomogeneities with low Ca/Si ratios and high Al contents. Even using submicron alumina, our C-A-S-H gels took ~1 year to homogenise: Coarser materials—and in this context, fly ash counts as a coarse material—might take much longer to homogenise and thus achieve a steady-state sorption potential. In this connection, it is noteworthy that, contrary to expectation, the R_d values of Na and K doped inhomogeneous gels did not much increase upon subsequent ageing even through their capacity should in theory be enhanced. We speculate that in the presence of alkali, homogenisation is impeded, perhaps as a consequence of decreasing Ca solubility and its contribution to mobility. Thus, caution should be exercised in applying R_d values obtained in the course of this study to “real” materials, the sorption properties of which may depend on the development and persistence of inhomogeneities. Nevertheless, the results obtained here are useful to explain the observed trends. They confirm that positive benefits in reducing pore fluid alkali contents will be achieved by adding aluminosilicate-rich pozzolans to Portland cements in sufficient quantity to lower the mean Ca/Si ratio of the gel significantly below its “normal” value, ca. 1.7.

Some tests of homogeneity are possible, using R_d values, for example, to calculate the alkali sorptivity of blended cements. For example, the data presented here enable an evaluation to be made of silica fume, which, in well-homogenised pastes, reacts rapidly. However, silica fume is difficult to disperse uniformly in pastes. While in theory silica fume up to ~15–20% cement replacement should simply react with and reduce the $Ca(OH)_2$ content, in practise the inhomogeneous nature of the reaction between cement and silica fume leaves regions in which $Ca(OH)_2$ persists while, in adjacent regions, consuming $Ca(OH)_2$ and drastically lowering the Ca/Si ratio of C-S-H. At the same time Al, contributed mainly from Portland cement, may enable low Ca/Si regions to achieve substantial Al contents. Thus, alkali sorption is probably mainly associated with these clusters of low Ca/Si ratio C-A-S-H, although we are unable to assess the volume fraction, composition and persistence of such regions. Probably, all we can conclude that if silica fume were to be added at < 20% cement replacement, and if it were to react in a perfectly homogeneous manner, forming a $Ca(OH)_2$-free paste consisting mainly of C-A-S-H with a Ca/Si ratio of ~1.7, its impact on alkali sorption would be slight. However, pore fluid data discloses significant impact of silica fume on alkali solubility, and we therefore conclude that the experimentally observed impact arises from an inhomogeneous reaction mechanism. Probably, small clusters consisting of low Ca/Si ratio C-A-S-H, or of partially hydrolysed silica, or mixtures thereof, are responsible for most of the observed sorption. In this view, it is not practical to quantify the alkali uptake without also having a method of quantifying the nature, extent and permanence of inhomogeneities within silica fume–cement matrices.

The impact of other cement blending components is more complex to assess. In general, slags and fly ash react like silica fume but are especially likely to contribute sufficient alumina to saturate the gel phase. This excess of alumina also results in the development of other phases, e.g., strätlingite, C_2ASH_8 [4]. These additional phases may also contribute to the sorption so we cannot form a complete picture of the role of supplementary cementing materials until the binding capacity for alkali of the other hydrate product phases has been assessed. These data and assessments will be presented in the concluding section of this paper.

Finally, another factor that requires investigation is the impact of temperature. Temperature has three effects. Two are theoretical: (i) It may directly affect the element partition of Al amongst phases, and (ii) it may indirectly affect partition, as by influencing the substitution of other ions, e.g., sulfate, into tetrahedral positions. The third effect concerns the extent of the solid solution Sharp [10] has recently presented data showing that the maximum extent of Al substitution in C-A-S-H tends to *decrease* with increasing temperature. Nevertheless, we envisage that the principal practical effect of rising temperatures on alkali sorption is to enhance reaction and diffusion rates. The formation and persistence of inhomogeneities in blended cement depend on thermal history, as well as time and, as hypothesised, affect the extent to which cement solids sorb alkalis.

In summary, data obtained in this study provide broad support for experimental observations showing that supplementary cement materials can be quite effective in promoting alkali sorption into the solid hydrate phases with concomitant reduction of pore fluid alkalinity. However, concern is expressed that the alkali sorptivity observed in short-term experiments of 1–2-year duration may be due, in part, to local composition fluctuations, the lifetime of which in a real paste may be finite.

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