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Alkali binding in cement pastes
Part I. The C-S-H phase

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Abstract

The binding of sodium and potassium into cement paste influences the performance of concrete: for example, alkali balances between solid and paste constituents and pore fluid affect the potential for reaction with alkali-susceptible aggregates. However, quantification of the binding potential into paste solids has proven to be difficult, although much empirical data are available from pore fluid analyses. In this study, single-phase homogeneous C-S-H phases have been prepared at Ca:Si molar ratios of 1.8, 1.5, 1.2, and 0.85 and reacted with six alkali hydroxide concentrations, both NaOH and KOH, between 1 and 300 mM, giving a grid of 48 alkali concentrations and Ca:Si ratios. A steady-state alkali partition is attained in less than 48 h. A distribution coefficient, R_d, was calculated to express the partition of alkali between solid and aqueous phases at 20°C. The numerical value of R_d is independent of alkali hydroxide concentration and depends only on Ca:Si ratio. Approximate reversibility is demonstrated, so the R_d values are constants of a C-S-H over wide ranges of alkali concentration. The trend of R_d values indicates that alkali binding into the solid improves as its Ca:Si ratio decreases. © 2000 Elsevier Science Ltd. All rights reserved.

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

1. Introduction

Hydration of Portland cement normally occurs in the presence of a limited amount of water. This fluid tends to dissolve sodium and potassium from the clinker and as a result of ongoing hydration, alkalis become concentrated in the remaining water, which is termed "pore fluid." This effect was first demonstrated by Longuet et al. [1], who expressed pore fluid from mature pastes and observed alkali concentrations ranging between 0.1 and 1.0 M. The results (with obvious implications for hydration mechanisms and the potential for interaction of soluble alkali with aggregates in concrete) have stimulated numerous other studies that corroborate and extend pore fluid studies. These studies show that not all the alkalis are in pore fluid: some sodium and potassium must be bound into cement paste constituents.

Many investigators have attempted to measure the alkali content of cement paste constituents directly, using electron microscopy coupled with an analytical system. Such efforts are bound to yield artificially high alkali contents because specimen preparation for microscopy involves rigorous drying of wet pastes, resulting in soluble alkalis precipitating in or on solids as water evaporates. Nor can solids be washed to remove alkali-containing pore water prior to microscopy: weakly held alkalis in the solid are also redissolved and washed out.

Pore fluid expression data have been collected [2] and the impact of soluble alkalis on the chemical balances examined [3,4]. Taylor [5] has compiled pore fluid expression data from the literature and used these data to derive empirical expressions for alkali partition between solid and aqueous phases. By making certain reasonable assumptions, he was able to derive empirical relationships between clinker alkali concentration and subsequent alkali partition between pore fluid and paste. A "b coefficient" was defined, which is effectively a partition coefficient. However, it was not possible to determine which of the solid phases present in paste was sorbing alkali, although it was suspected that C-S-H (quantitatively the most abundant solid phase) contributed most of the apparent sorption.

It was found that the sorptivity of the paste correlated with its Ca:Si ratio; decreasing the Ca:Si ratio appeared to increase the overall strength of sorption, although the results exhibited considerable scatter.

Stade [6] prepared C-S-H gels at 80 to 150°C for subsequent sorption studies of potassium at ambient tempera-

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tures. It is not known if the high temperature preparation induced crystallinity in the C-S-H phase: other "warm" preparations, studied by high resolution microscopy, have been shown to contain nanocrystalline regions [7] and may differ in sorption characteristics from ordinary C-S-H.

The present study draws upon lessons learned from the previous literature showing the need to determine sorption using homogenous, well-characterised single phases and use of experimental techniques that avoid problems of phase purity and partial crystallisation of C-S-H, as well as circumventing alkali precipitation or dissolution during analysis.

2. Methods

Several preparation methods were assessed for the preparation of alkali-free, homogeneous C-S-H materials. Since it was also desirable to conduct the synthesis at temperatures not exceeding ~25°C, trials showed that the so-called direct reaction method gave the most homogeneous product. Four compositions, at Ca:Si molar ratios of 1.8, 1.5, 1.2, and 0.85, were made from $Ca(OH)_2$ and a very reactive, high surface area silica gel (Degussa, Frankfurt, Germany) "Aerosil" 300 grade. The carefully homogenised dry mix was slurried in double-distilled, CO_2-free water, sealed into thick-walled polyproylene bottles with good closures to prevent carbonation, and allowed to react for 12 months at 20 ± 2°C with regular agitation. Chemical analysis of the product disclosed that the target was achieved.

After 12 months an aliquot of the liquid was filtered and analised by flame emission spectroscopy; it had $Na \leqslant 0.02$ mM/L and $K \leqslant 0.03$ mM/L. The solids were analised by X-ray diffraction, thermogravimetric analysis, and electron microscopy. The C-S-H preparations were nearly amorphous to X-ray. Thermogravimetric analysis (TGA) disclosed the presence of traces of $Ca(OH)_2$, estimated to be 0.2 wt.% in the preparation with Ca:Si = 1.8; the others were $Ca(OH)_2$-free. Analytical electron microscopy revealed that the gels were essentially uniform in composition on the nanometer scale. The homogeneous phase formation achieved using these procedures has also been corroborated by other investigators [8–10].

The gels were moist-dried over solid $CaCl_2$ at 20°C prior to weighing. This "soft" drying at the vapour pressure conditioned by the equilibrium between $CaCl_2$ and its dihydrate was deemed essential: it was necessary to establish a consistent and stable basis for weighing the gel but without alteration of its nanostructure by desiccation. The water contents of the "soft-dried" gels were subsequently determined on subportions by destructive ignition, first at 100°C then at 1000°C.

In a typical sorption experiment, about 0.6 g of soft-dried C-S-H was weighed out in CO_2-free conditions, using a N_2-filled "Atmos"(Aldrich Chemical, WI, USA). A previously standardised NaOH or KOH solution, ranging in concentration from 0.1 to 300 mM, was added in known volume to achieve a water:solid (w:s) ratio ~15. A few samples were prepared at higher w:s ratios (approximately 30), but as this had no influence on the results, work at other w:s ratios was not pursued. The samples were tightly sealed to prevent CO_2 access and kept at ~20°C with continuous agitation. After a few days agitation was stopped momentarily to permit an aliquot of the aqueous phase to be sampled through a 0.45-mm "Millipore"(Bedford, Ireland) filter. Sampling of representative batches was continued for ~1 year, but it is apparent that the alkali distribution achieved within the first few days has remained unchanged.

The uptake of alkali can be calculated in moles from the known solution volume and the decrease in aqueous alkali concentration, ΔC. That is, the number of moles taken up by the solid is $V\Delta C$. The blank error was checked: the vessels did not sorb sodium or potassium. Sodium and potassium were determined (as earlier) by flame emission spectroscopy; Ca was determined by atomic absorption spectroscopy (AAS). The hydroxyl ion concentration was determined in two ways: by using a pH meter in conjunction with an electrode suitable for high pH and by titration, using certified standard HCl with phenolphthalein indicator. Where cation analyses could not be done immediately the alkaline filtrates were acidified with a known volume of standard HNO_3 and an appropriate correction applied for dilution. All calibration curves for flame emission, AAS, and pH determinations were constructed using certified standard solutions.

Data are presented in the tables. The plan of the experiments enabled the data to be calculated to a distribution ratio, R_d, such that [see Eq. (1)]:

$$R_d = \frac{\text{alkali in solid C-S-H (mM/g)}}{\text{alkali concentration in solution (mM/mL)}} \tag{1}$$

The units of R_d are volume per mass; in this paper its units are mL/g.

3. Results

3.1. Sorption

Table 1 records steady-state, aqueous-solid phase balances. The first column of Table 1 gives the actual solution analyses and data used to calculate electrostatic balances while the last columns record pH, measured with an alkali-insensitive electrode as well as by titration.

The calcium solubility is greatest at the high Ca:Si ratio. However, at the w:s ratio used (~15), its maximum solubility is not sufficient to affect significantly the Ca:Si ratio of the remaining solid, especially as Ca solubility is, in general, greatly reduced by increasing alkali concentrations. The impact of alkali is greatest for low Ca:Si ratio gel, which, in the absence of alkali, is less able to condition a high aqueous pH. Silicon solubilities were not measured but are known to increase with increasing alkali concentration [12,13]. But even at the highest alkali concentration used

Table 1
Analytical results for the aqueous phase

Conditions		Concentration of ion species in solution (mM/L)				
Aq mM/L (Na or K)	Solid C/S	Na^+ or K^+ cation	Ca^{2+} cation	Σ + charge (Na or K+ 2Ca)	Anion (OH^-)	pH
		Na_2O-CaO-SiO_2-H_2O system at 20°C				
1	0.85	0.76	0.65	2.06	0.92	10.96
5	0.85	3.65	0.40	4.45	2.87	11.46
15	0.85	11.2	0.27	11.7	10.4	12.02
50	0.85	36.0	0.24	36.5	34.0	12.53
100	0.85	79.0	0.10	79.2	72.0	12.85
300	0.85	236.4	0.09	236.6	247.4	13.39
1	1.2	0.84	6.10	13.0	11.9	12.08
5	1.2	4.38	4.34	13.1	12.5	12.10
15	1.2	13.1	3.26	19.6	20.6	12.31
50	1.2	43.1	1.20	45.5	45.8	12.66
100	1.2	87.0	0.63	88.3	91.4	12.96
300	1.2	266.5	0.56	267.6	275.4	13.44
1	1.5	0.94	17.5	35.9	21.2	12.33
5	1.5	4.63	14.1	32.8	28.2	12.45
15	1.5	14.1	12.1	38.3	39.6	12.60
50	1.5	47.3	7.26	61.8	56.9	12.76
100	1.5	95.3	5.20	105.7	102.1	13.01
300	1.5	282.4	1.73	285.9	281.0	13.45
1	1.8	0.96	19.5	40.0	38.4	12.58
5	1.8	4.78	16.0	36.8	39.3	12.59
15	1.8	14.4	12.7	39.8	44.0	12.64
50	1.8	48.2	8.01	64.2	54.8	12.74
100	1.8	96.9	4.88	106.7	101.4	13.00
300	1.8	288.1	2.06	292.2	288.6	13.46
		K_2O-CaO-SiO_2-H_2O system at 20°C				
1	0.85	0.80	0.57	1.94	1.66	11.22
5	0.85	3.72	0.38	4.48	3.53	11.55
15	0.85	11.0	0.23	11.5	10.4	12.02
50	0.85	39.3	0.17	39.6	34.7	12.54
100	0.85	78.2	0.10	78.4	74.7	12.87
300	0.85	247.1	0.06	247.2	233.2	13.37
1	1.2	0.86	5.60	12.1	12.7	12.10
5	1.2	4.36	4.54	13.4	12.8	12.11
15	1.2	13.6	2.92	19.4	21.4	12.33
50	1.2	45.5	1.71	48.9	51.3	12.71
100	1.2	89.5	1.02	91.5	95.2	12.98
300	1.2	276.2	0.74	277.7	267.8	13.43
1	1.5	0.93	19.5	39.9	32.2	12.51
5	1.5	4.60	18.0	40.6	38.6	12.59
15	1.5	13.8	14.5	42.8	39.0	12.59
50	1.5	47.1	8.60	64.3	59.6	12.78
100	1.5	94.0	4.80	103.6	100.7	13.00
300	1.5	290.6	2.03	294.7	294.1	13.47
1	1.8	0.98	20.0	41.0	34.9	12.54
5	1.8	4.82	19.0	42.8	39.1	12.59
15	1.8	14.6	15.5	45.0	43.8	12.64
50	1.8	48.9	9.40	67.7	65.2	12.81
100	1.8	98.2	3.90	106.0	109.0	13.04
300	1.8	296.7	2.37	301.4	300.3	13.48

Abbreviations: Aq = aqueous; C/S = molar Ca/Si ratio.

(300 mM), silicon solubility is not believed to be significant with respect to having an impact on the bulk Ca:Si ratio of the solid [14]. The electrostatic balances are generally satisfactory (±5%) for solutions with high ionic strengths but are somewhat less satisfactory for dilute solutions (i.e., those having low ionic strengths). This is attributed to a culmination of analytical errors that tend to affect the dilute solutions. The reconciliation of data by charge balance, however, does serve as a useful internal check on the accuracy of the analytical procedures and calculations.

Graphical treatments of the experimental data, shown in Table 2, are also plotted in Figs. 1 to 3. Fig. 1 shows that the alkali concentrations of a solid, plotted against aqueous alkali concentrations, defines a series of essentially straight line relationships, the slopes of which increase with decreasing Ca:Si ratio. For a given Ca:Si ratio, the slope is essentially identical for both sodium and potassium.

The data, expressed as R_d values, are shown in Fig. 2. Each Ca:Si ratio is characterised by having a fixed R_d value that is essentially independent of alkali concentration over the range 1 to 300 mM alkali: the greater data scatter at low concentrations is attributed to the greater analytical uncertainties toward the low end of the concentration scale. The R_d values are lowest for high Ca:Si ratios, 1.8 and 1.5, and

Table 2
The alkali-binding potential of C-S-H

C/S ratio	Target Na or K (mM/L)	Initial Na or K (mM/L)	Final Na or K (mM/L)	Solution volume (mL)	No. of moles in solid (mM)	Solid weight (g)	Na or K concentration in solid phase (mM/g)	R_d (mL/g)
				Na_2O-CaO-SiO_2-H_2O system at 20°C				
0.85	1	1.00	0.76	9	0.0022	0.6	0.0037	4.87
	5	4.91	3.65	9	0.0113	0.6	0.0188	5.15
	15	14.8	11.2	9	0.0324	0.6	0.0540	4.82
	50	49.6	36.0	9	0.1224	0.6	0.2040	5.70
	100	99.1	79.0	9	0.1809	0.6	0.3015	3.82
	300	295.6	236.4	9	0.5328	0.6	0.8880	3.76
1.2	1	1.00	0.84	9	0.0014	0.6	0.0023	2.73
	5	4.91	4.38	9	0.0048	0.6	0.0080	1.83
	15	14.8	13.1	9	0.0153	0.6	0.0255	1.94
	50	49.6	43.1	9	0.0585	0.6	0.0975	2.26
	100	99.1	87.0	9	0.1089	0.6	0.1815	2.08
	300	295.6	266.5	9	0.2619	0.6	0.4365	1.64
1.5	1	1.00	0.94	9	0.0005	0.6	0.0009	0.96
	5	4.91	4.63	9	0.0025	0.6	0.0042	0.91
	15	14.8	14.1	9	0.0063	0.6	0.0105	0.74
	50	49.6	47.3	9	0.0207	0.6	0.0345	0.73
	100	99.1	95.3	9	0.0342	0.6	0.0570	0.60
	300	295.6	282.4	9	0.1188	0.6	0.1980	0.70
1.8	1	1.00	0.96	9	0.0004	0.6	0.0006	0.63
	5	4.91	4.78	9	0.0012	0.6	0.0020	0.42
	15	14.8	14.4	9	0.0036	0.6	0.0060	0.42
	50	49.6	48.2	9	0.0126	0.6	0.0210	0.44
	100	99.1	96.9	9	0.0198	0.6	0.0330	0.34
	300	295.6	288.1	9	0.0675	0.6	0.1125	0.39
				K_2O-CaO-SiO_2-H_2O system at 20°C				
0.85	1	1.01	0.80	9	0.0019	0.6	0.0032	3.94
	5	4.95	3.72	9	0.0111	0.6	0.0185	4.96
	15	14.9	11.0	9	0.0351	0.6	0.0585	5.32
	50	50.2	39.3	9	0.0981	0.6	0.1635	4.16
	100	100.8	78.2	9	0.2034	0.6	0.3390	4.33
	300	304.3	247.1	9	0.5148	0.6	0.8580	3.47
1.2	1	1.01	0.86	9	0.0014	0.6	0.0023	2.67
	5	4.95	4.36	9	0.0053	0.6	0.0088	1.78
	15	14.9	13.6	9	0.0117	0.6	0.0195	1.43
	50	50.2	45.5	9	0.0423	0.6	0.0705	1.55
	100	100.8	89.5	9	0.1017	0.6	0.1695	1.89
	300	304.3	276.2	9	0.2529	0.6	0.4215	1.53
1.5	1	1.01	0.93	9	0.0007	0.6	0.0012	1.29
	5	4.95	4.60	9	0.0032	0.6	0.0053	1.14
	15	14.9	13.8	9	0.0099	0.6	0.0165	1.20
	50	50.2	47.1	9	0.0279	0.6	0.0465	0.99
	100	100.8	94.0	9	0.0612	0.6	0.1020	1.09
	300	304.3	290.6	9	0.1233	0.6	0.2055	0.71
1.8	1	1.01	0.98	9	0.0003	0.6	0.0005	0.51
	5	4.95	4.82	9	0.0012	0.6	0.0020	0.40
	15	14.9	14.6	9	0.0027	0.6	0.0045	0.30
	50	50.2	48.9	9	0.0117	0.6	0.0195	0.40
	100	100.8	98.2	9	0.0234	0.6	0.0390	0.40
	300	304.3	296.7	9	0.0684	0.6	0.1140	0.38

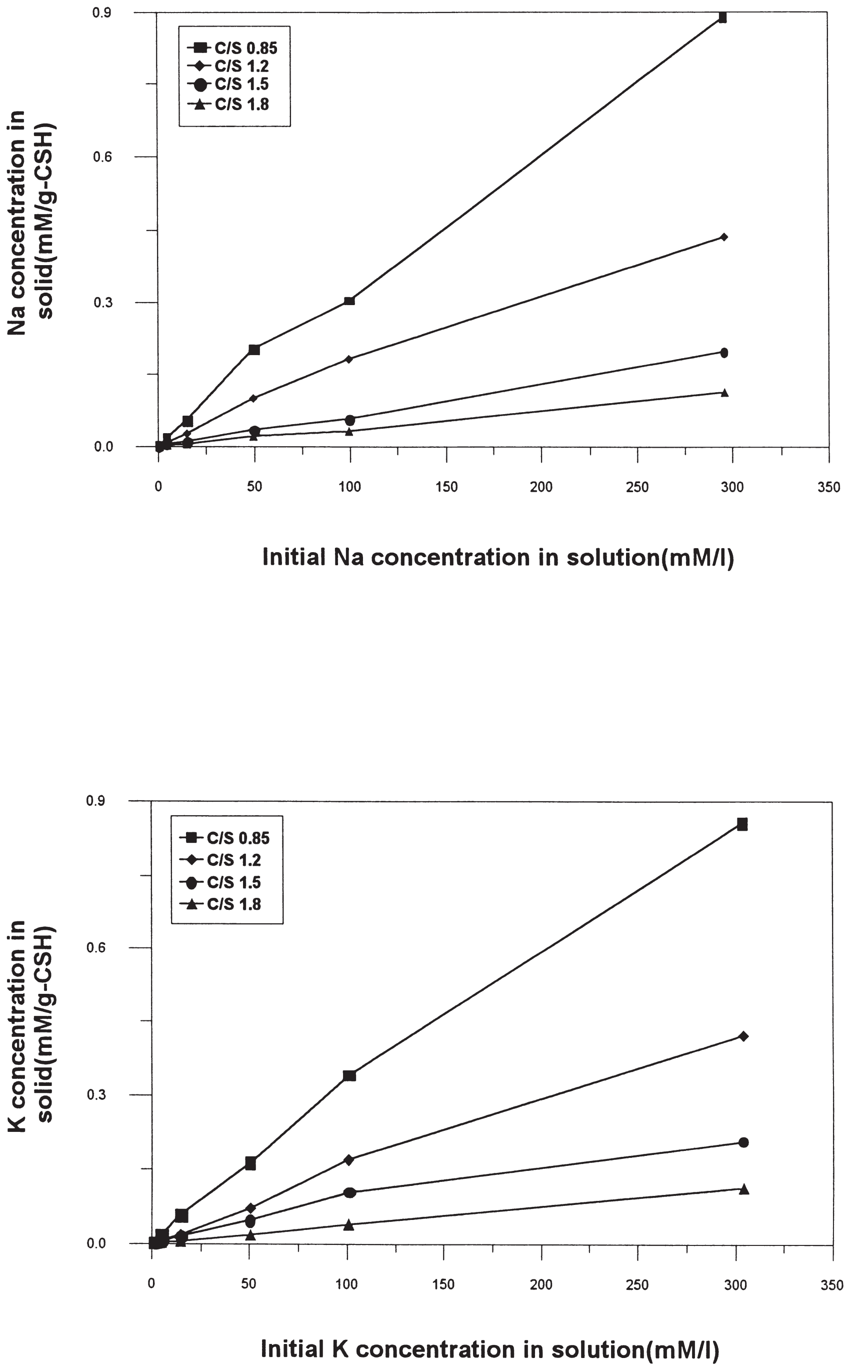
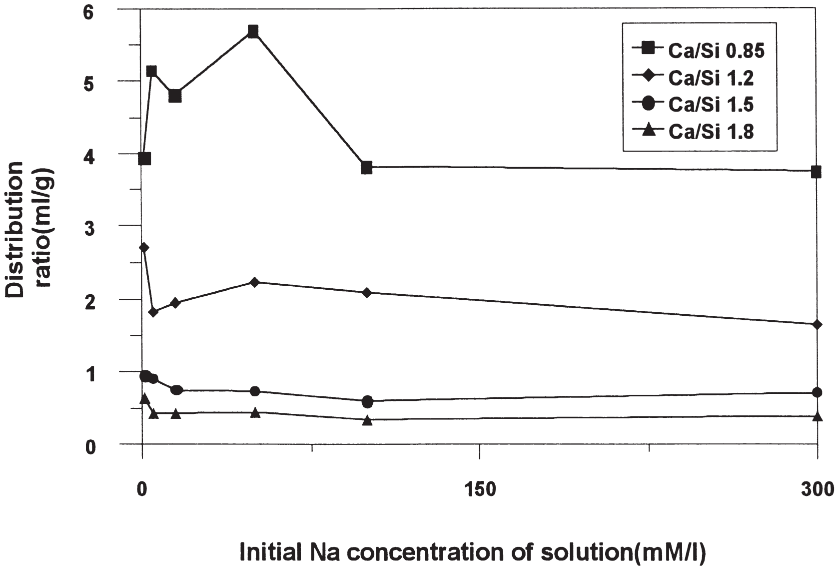


Fig. 1. Sodium and potassium steady-state concentrations in solid C-S-H of varying Ca:Si ratios as a function of aqueous alkali concentration. Temperature = 20°C.

are typically in the range of $\sim$0.4 to 0.5 and 0.8 to 1.0 for Na and K, respectively. Such numerically low values indicate weak binding. However, decreasing the Ca:Si ratio to 1.2 results in an increase in the values of R_d into the range of 1.5 to 2.0, while a further decrease in Ca:Si ratio to 0.85 increases the R_d value to between 4 and 5, indicating progressively stronger binding. Fig. 3, which plots R_d values as a function of Ca:Si ratio, shows that all the data fall within a narrow envelope with the exception of a few outlier points. The slope of the R_d curve tends to steepen as Ca:Si ratio of the C-S-H decreases, especially below 1.2.

3.2. Desorption

C-S-H preparations were first loaded with alkali then subjected to desorption by redispersion into initially pure water. We have not found a completely satisfactory way of implementing the necessary experimental steps. The initial



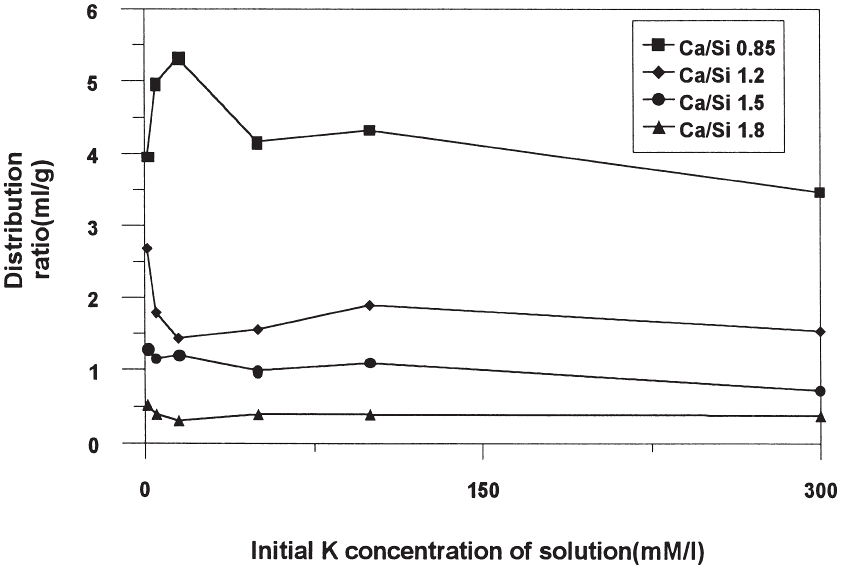
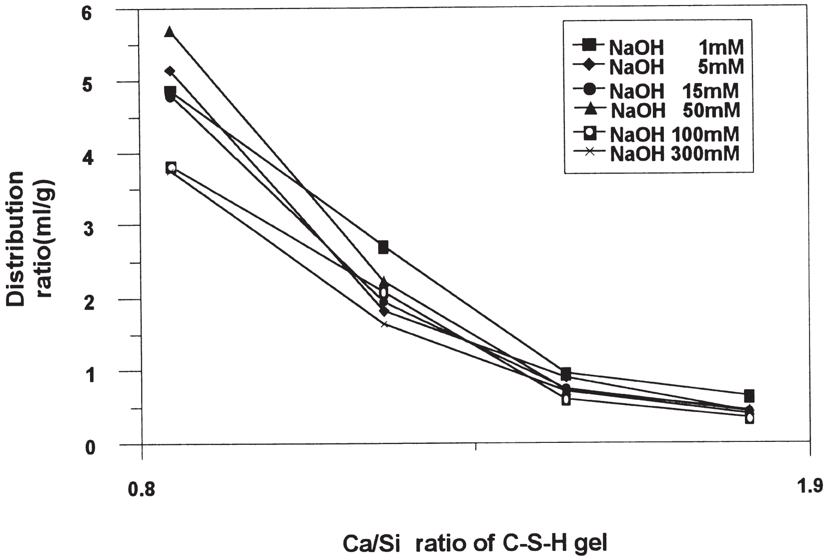


Fig. 2. Sodium and potassium steady-state distribution ratios between solid C-S-H and aqueous phase as a function of aqueous alkali concentration. Temperature = 20°C. The distribution ratio is essentially constant for a fixed solid Ca:Si ratio and is numerically almost identical for sodium and potassium at comparable solid Ca:Si ratio.

loading, accomplished by the methods described, is satisfactory but upon completion of loading, the solid must be prepared for desorption by separating it from aqueous phase prior to its redispersion in a known volume of initially alkali-free water. The solid should preferably not be washed or dried, so the most practical scheme was to remove as much as possible of the aqueous phase by centrifugation and apply a correction based on the analytically determined mass of remaining water, estimated from drying an aliquot, and the known alkali concentrations of solid and aqueous phases. The corrections enable the true mass of solid and the number of moles of alkali carried over in the solution to be estimated. The accuracy of this procedure generally decreases as the alkali content of the solution increases but, on



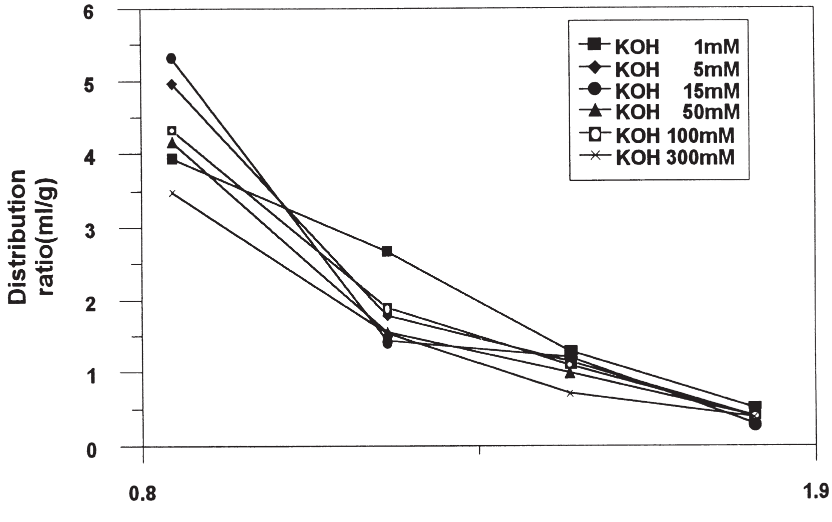


Fig. 3. Solid-aqueous distribution ratios for sodium and potassium as a function of Ca:Si ratio of the solid. Data for 20°C. The R_d values define a narrow envelope essentially independent of alkali concentration in the range 1 to 300 mM.

the other hand, increases as the ratio of Na:Ca in the solid increases. The set of data reproduced here, and in which we have most confidence, is that obtained from the C-S-H at Ca:Si = 0.85: Table 3 records the results for Na and K. The sorption values are comparable with those obtained in other experiments while desorption R_d values are similar, within ±50% at the two lower concentrations and increasing to ±100% at the highest concentration. Nevertheless, it is our interpretation that broad reversibility is established, although much greater refinement of technique would be required to establish the extent of hysteresis (if any).

4. Discussion

The introduction of sodium or potassium in place of calcium in a crystalline structure is generally governed by crystallochemical restraints that limit the number of possi-

Table 3
Quantification of sorbed and desorbed alkali in the $Na_2O(K_2O)$-CaO-SiO_2-H_2O system at 20°C

C/S ratio and (M^+)	Alkali partition between CSH and aqueous phase after sorption		Alkali partition between CSH and aqueous phase after desorption		Distribution ratio (R_d)	
	CSH (mM/g)	solution (mM/mL)	CSH (mM/g)	solution (mM/mL)	Sorption (mL/g)	Desorption (mL/g)
0.85 (Na)	0.0188	0.0037	0.0061	0.0012	5.15	4.90
	0.2040	0.0358	0.0691	0.0126	5.70	5.48
	0.8880	0.2362	0.3826	0.0485	3.76	7.89
0.85 (K)	0.0185	0.0037	0.0063	0.0011	4.96	5.73
	0.1635	0.0393	0.0580	0.0086	4.16	6.74
	0.8580	0.2473	0.3948	0.0445	3.47	8.87

Note: 0.6 g of C-S-H was used for this experiment. After sorption, the specimen was centrifuged to remove the aqueous phase, and the C-S-H was redispersed into degassed, deionised water for desorption. A correction was made for residual alkali in solution after centrifugation.

ble replacement mechanisms and their stoichiometry. The structure of C-S-H cannot, however, be assumed to require such restraints, except of course that the solid is subject to the condition of overall electroneutrality. To illustrate the general impact of substitution on C-S-H composition, it is useful to calculate the extent of replacement in terms of the atomic ratios of cations: this can be unambiguously calculated from the analyses, provided the water content of C-S-H is known.

For high ratio gels, Ca:Si = 1.5 and 1.8, we use the water content given by Taylor as 18% [11]. This is in reasonable accord with our measurements, although we find a water content of 14% for C-S-H, with ratios of 1.2 and 0.85. If these values are introduced into the calculation, the results shown in Table 4 are obtained. Table 4 gives the data necessary for the calculation and shows the results, expressed to one or two significant figures depending on the accuracy of the data, as ratios of Na:Ca and Na:Si in the C-S-H solid. If ~2% substitution, expressed as a ratio of Ca ions to alkali (Na, K) atoms, is taken as the boundary for significant substitution, it can be seen that this limit is most readily exceeded at high Na or K aqueous concentrations and at low Ca:Si ratios. Of course the data shown here extend only to a maximum aqueous concentration of ~300 mM; at still higher alkali concentrations, an increasing range of C-S-H gels would be expected to attain significant substitution.

Table 2 shows data necessary for the calculation of the alkali-binding potential, expressed as a distribution coefficient. The results reflect the differences between nominal and actual alkali concentrations, the latter having been determined by analysis. Data are obtained after interfacing the solution with C-S-H solid and are identical to those in Table 1. The method of experiment and data treatment developed and described in this paper provide a measure of the capacity of C-S-H gels to bind sodium and potassium at high pH. The characterisation parameter, R_d, is shown to be a fundamental property of the solid and because it is not an artefact of the experimental design, it can be applied generally. The trend of R_d values supports the generally held view that the low Ca:Si ratio C-S-H, characteristic of blended cements, binds alkali better than high ratio C-S-H typically present in ordinary Portland cement pastes. However, it is unlikely that sufficient slag or fly ash will be present in normal practice to lower the Ca:Si ratio of C-S-H below 1.5 so the gain in alkali absorptivity achieved by the introduction of these supplementary materials, expressed as absorptivity per unit volume of C-S-H, must be modest. A full assessment, of course, would also have to take into account the increase in the amount of C-S-H per unit volume of paste as well as the possible presence of inhomogenities in the C-S-H of “real” pastes, in which case local regions having low Ca:Si ratios could contribute significantly to the overall observed sorption.

The data presented here do not provide a unique proof of the sorption mechanism. Both surface and bulk sorption, or some combination of the two, could be operative. We know that (1) a steady-state distribution is achieved rapidly, within a few days; (2) R_d increases only slowly as the Ca:Si ratio of C-S-H decreases from 1.8 to 1.5 but thereafter increases more rapidly as its ratio decreases to 1.2 and is especially rapid between 1.2 and 0.85; (3) the R_d values are not alkali-sensitive: within limits of experimental error, sodium and potassium give the same R_d; and (4) the binding of sodium and potassium into C-S-H is weak, as evidenced by rapid sorption and desorption, coupled with generally low R_d values.

Of the hypotheses presented in the literature [5,6] to explain alkali binding, the most attractive is that binding occurs at relatively acidic silanol (Si-OH) sites. In this hypothesis binding occurs because the acidic sites are neutralised by reaction with strong base, either NaOH or KOH. Since both hydroxides have approximately equal basic strengths, this would explain the equal or nearly equal R_d values. The concentration and acidity of silanol groups should increase rapidly as the Ca:Si ratio of C-S-H decreases, especially below 1.5, thus accounting for the trend of R_d values. However, the data can also be subject to other treatments, possibly broadening the interpretation and scope of applicability.

Stade [6] reports data on K sorption using C-S-H of two Ca:Si ratios, 1.0 and 1.5. We previously expressed reservations about the extent to which these preparations may have been affected by thermal treatment, and for this reason we have deferred comparison of the two data sets to the discus-

Table 4
Alkali content of C-S-H as a function of C/S ratio

C/S ratio	Initial Na or K concentration (mM/L)	Final Na or K concentration (mM/L)	Na or K concentration in C-S-H (mM/g)	Ca concentration in C-S-H (mM/g)	Si concentration in C-S-H (mM/g)	Na/Ca	Na/Si
			20°C data for sodium				
0.85	1.00	0.76	0.0037	6.78	7.99	0.0005	0.0005
	4.91	3.65	0.0188	6.78	7.99	0.0028	0.0024
	14.8	11.2	0.0540	6.78	7.99	0.0080	0.0068
	49.6	36.0	0.2040	6.78	7.99	0.0300	0.0255
	99.1	79.0	0.3015	6.78	7.99	0.0445	0.0377
	295.6	236.4	0.8880	6.78	7.99	0.1310	0.1111
1.2	1.00	0.84	0.0023	8.20	6.66	0.0003	0.0003
	4.91	4.38	0.0080	8.20	6.66	0.0010	0.0012
	14.8	13.1	0.0255	8.20	6.66	0.0031	0.0038
	49.6	43.1	0.0975	8.20	6.66	0.0119	0.0146
	99.1	87.0	0.1815	8.20	6.66	0.0221	0.0273
	295.6	266.5	0.4365	8.20	6.66	0.0532	0.0655
1.5	1.00	0.94	0.0009	8.53	5.69	0.0001	0.0002
	4.91	4.63	0.0042	8.53	5.69	0.0005	0.0007
	14.8	14.1	0.0105	8.53	5.69	0.0012	0.0018
	49.6	47.3	0.0345	8.53	5.69	0.0040	0.0061
	99.1	95.3	0.0570	8.53	5.69	0.0067	0.0100
	295.6	282.4	0.1980	8.53	5.69	0.0232	0.0348
1.8	1.00	0.96	0.0006	9.17	5.09	0.0001	0.0001
	4.91	4.78	0.0020	9.17	5.09	0.0002	0.0004
	14.8	14.4	0.0060	9.17	5.09	0.0007	0.0012
	49.6	48.2	0.0210	9.17	5.09	0.0023	0.0041
	99.1	96.9	0.0330	9.17	5.09	0.0036	0.0065
	295.6	288.1	0.1125	9.17	5.09	0.0123	0.0221
			20°C data for potassium				
0.85	1.01	0.80	0.0032	6.78	7.99	0.0005	0.0004
	4.95	3.72	0.0185	6.78	7.99	0.0027	0.0023
	14.9	11.0	0.0585	6.78	7.99	0.0086	0.0073
	50.2	39.3	0.1635	6.78	7.99	0.0241	0.0205
	100.8	78.2	0.3390	6.78	7.99	0.0500	0.0424
	304.3	247.1	0.8580	6.78	7.99	0.1265	0.1074
1.2	1.01	0.86	0.0023	8.20	6.66	0.0003	0.0003
	4.95	4.36	0.0088	8.20	6.66	0.0011	0.0013
	14.9	13.6	0.0195	8.20	6.66	0.0024	0.0029
	50.2	45.5	0.0705	8.20	6.66	0.0086	0.0106
	100.8	89.5	0.1698	8.20	6.66	0.0207	0.0255
	304.3	276.2	0.4215	8.20	6.66	0.0514	0.0633
1.5	1.01	0.93	0.0012	8.53	5.69	0.0001	0.0002
	4.95	4.60	0.0053	8.53	5.69	0.0006	0.0009
	14.9	13.8	0.0165	8.53	5.69	0.0019	0.0029
	50.2	47.1	0.0465	8.53	5.69	0.0055	0.0082
	100.8	94.0	0.1020	8.53	5.69	0.0120	0.0179
	304.3	290.6	0.2055	8.53	5.69	0.0241	0.0361
1.8	1.01	0.98	0.0005	9.17	5.09	0.0001	0.0001
	4.95	4.82	0.0020	9.17	5.09	0.0002	0.0004
	14.9	14.6	0.0045	9.17	5.09	0.0005	0.0009
	50.2	48.9	0.0195	9.17	5.09	0.0021	0.0034
	100.8	98.2	0.0390	9.17	5.09	0.0043	0.0077
	304.3	296.7	0.1140	9.17	5.09	0.0124	0.0224

Water content in C-S-H: Ca:Si 0.85, 1.2 → 14% (from experimental results); Ca:Si 1.5, 1.8 → 18% (from [5]).

sion. Results are shown in Fig. 4. Stade presents his data in the form of analyses showing K:Si ratios of the solid. Direct comparison of data sets at Ca:Si = 1.5 is shown in Fig. 4 (bottom). However, we have had to equate data for his preparation with a Ca:Si ratio = 1.0 with data for the 0.85 ratio, measured in this study: Fig. 4 (top) depicts the results of our recalculation. Stade mostly used higher potassium concentrations than we did, but despite differences, the two data sets appear to form a good fit. The linear trend of K:Si ratios, characteristic of lower (≤ 0.3 M) potassium concentra-

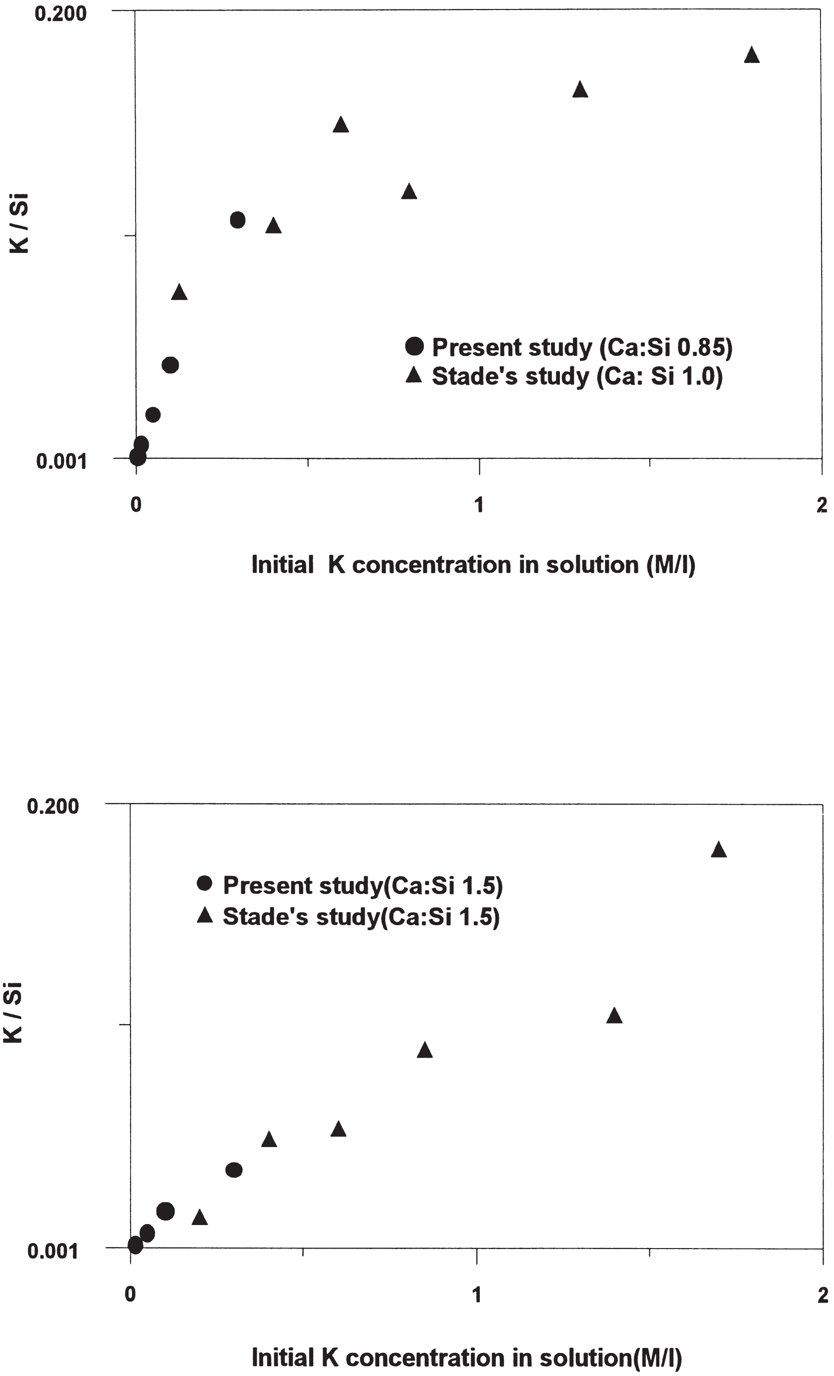


Fig. 4. Potassium:silicon ratio of the solid as a function of potassium concentration. The diagrams are obtained by combining results from Stade [6] with those obtained in this study; the two data sets appear to form a good fit. The linear trend at lower concentrations (≤300 mM) gradually develops a negative deviation at higher concentrations. This deviation is most apparent for low Ca:Si ratios, but see text for some cautionary notes that should be applied.

tions, gradually develops a negative deviation at higher concentrations. We explain this on the basis that increasing potassium substitution lessens the mean acidity of the silanol sites not yet neutralised by potassium, with the result that R_d values tend to decrease at high potassium hydroxide loadings. The increasing departures from ideality suggested by data from Stade [6] imply that (1) R_d values given here should not be extended to high alkali concentrations (>0.3 M), and (2) reversibility of sorption-desorption, approximately demonstrated at < 0.3 M alkali, cannot necessarily be assumed at higher concentrations.

Taylor [5] concluded from his analysis of pore fluid data that sodium was significantly better bonded into hydrated cement paste than potassium. However, our study does not reveal significant differences between R_d values for Na and K on synthetic C-S-H. Of course, Taylor used data derived from mixtures of phases and had to assume that C-S-H made the main contribution to sorption. However, several additional factors must be considered in any comparison of data sets between synthetic C-S-H and C-S-H in "real" pastes. Real cement pastes (i.e., those resulting from hydration of a commercial Portland cement) contain C-S-H, in which some of the silicon may be substituted by Al. It could be argued by analogy with zeolites that this will increase the acidity of Si-O and Si-OH bonds and hence the strength of alkali binding. It is less likely, however, that Al substitution in C-S-H could alter its selectivity for Na and K unless other factors were also operative. A fuller understanding of the role of Al is necessary, preferably by experiments made on synthetic Al-substituted C-S-H. Those experiments are in progress and will be reported in the second part of this work.

Another consideration is that blended cements may develop substantial amounts of phases whose alkali-binding capacity has not yet been assessed [15,16] or that alkali may affect the crystallinity of C-S-H [17]. The binding potential of several of these contender phases will also be assessed in a subsequent paper and the results integrated into an overall alkali sorption model appropriate to a range of Portland and blended Portland cements.

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