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The magnesia–silica gel phase in slag cements: alkali (K, Cs) sorption potential of synthetic gels

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Abstract

Blends of Portland cement with blast furnace slag hydrate to yield two gel phases, one essentially a calcium silicate hydrate (C-S-H) composition, the other a magnesium silicate hydrate (M-S-H) composition: the two gel phases are essentially immiscible. Together, the gel phases comprise an important source of sorption potential for the alkalis present in ordinary cement and blending agents. M-S-H gels have been synthesised and their sorption potential measured for postassium (K) and cesium (Cs) at 25 °C by using fresh gels as well as gels previously aged at 85 °C for 6 months. The ability of slag–cement blends to lower pore fluid alkalinity generally, and in nuclear waste technology to incorporate Cs, is interpreted in terms of the sorption data.

Keywords: M-S-H gel; Alkali sorption; Pore fluids; Cs; Cement paste

1. Introduction

The use of supplementary cement materials such as iron blast furnace slag is well established in civil engineering and has important applications to immobilisation technology [1,2]. Cement matrices used to contain toxic, hazardous and radioactive species afford physical containment for particulates and, additionally, have an insolubilising effect on many potentially soluble species. The high internal pH of cement matrices precipitates many metallic cationic species as insoluble hydroxides, whereas anionic species may be incorporated into the crystal structures of hydrated cement products [3–5]. However, addition of blast furnace slags also creates chemically reducing conditions within the matrix without at the same time much decreasing the internal pH. This chemical reduction potential arises from the content of sulfide (S^{2-}) species in slag and affords additional possibilities for insolubilisation, e.g, precipitation of more covalent species such as Ni and Pt-group metals as their sulfides: also, by reducing higher valent soluble species to lower oxidation states, e.g., Cr(VI) to Cr(III) [6]. However, the solubilities of elements such as sodium (Na), potassium (K) and cesium (Cs), which do not form insoluble sulfides at high pH and which are not subject to chemical reduction in aqueous solution, are also known to be lowered in the presence of slag: although slag cements were found to be beneficial in this application several decades ago, reasons for their ability to lower pore fluid alkali contents remain unclear. By analogy with the benefits associated with reduction of Na and K in pore fluids in the presence of slag, it has been supposed that an additional sorption potential for Cs is created by the presence of slag, although the source of the potential remains unknown [7].

Recent studies of slag hydration have shed new light on the source of this immobilisation potential, which is shown to be due in part to formation of magnesium silicate hydrate (M-S-H) gels in certain compositions. The purpose of this paper is to demonstrate the role of M-S-H gels, explain their coexistence with calcium silicate hydrate (C-S-H) and, through synthesis of M-S-H gels, explore their sorption potential for K and Cs.

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2. Formation, role and constitution of M-S-H gels

Analogous with C-S-H, precipitation at or near ambient temperature of soluble Mg- and Si-containing precursors yields a low-crystallinity, gel-like product containing variable Mg:Si ratios and water contents. The resulting M-S-H products give extremely diffuse X-ray diffraction patterns, which, it is suggested, resemble—albeit in degraded form—those of M-S-H minerals, e.g., sepiolite. Methods of producing these gels, characterisation data for the products and a review of the relevant literature are given in [8]. The Mg:Si ratio of the gels is shown to range between ~ 0.67 and 1.0. The crystallinity of gels, determined by X-ray diffraction, was not significantly improved by wet annealing at either 25 or 85 °C for 6 months although changes to the NMR spectra for ^{29}Si and Fourier transform infrared (FTIR) patterns suggested that changes did occur in the internal constitution of the gels, especially after prolonged treatment at 85 °C. The range of persistent gel compositions also seemed to contract somewhat, to Mg:Si ratios ranging between ~ 0.75 to 1.0, upon annealing at 85 °C.

Slags introduce much Mg into the composition of blended cements. The literature is unclear with respect to the favoured Mg product; brucite, hydrotalcite and M-S-H gel have all been recorded (the latter is sometimes described as sepiolite or sepiolite-like gel). Fig. 1, derived from experiment as well as examination of analysed slag–cement blends cured up to 10 years at 25–85 °C, is presented to show the relationships between $CaO-MgO-SiO_2-H_2O$ phases in this temperature range. Brucite is the favoured Mg-containing product at low silica activities. However, slag additions raise the activity of silica and, in proportion to the amount of slag added, its fractional reactivity and silica content, mixtures of portlandite, $Ca(OH)_2$, and brucite occur together with C-S-H in these blends. At still higher silica activities, portlandite-containing assemblages give way to C-S-H–brucite assemblages from which portlandite is absent; the Ca/Si ratio of C-S-H decreases to ~ 1.5 after portlandite is consumed. Eventually, at higher slag replacements, M-S-H coexists with C-S-H and brucite; the C-S-H in this assemblage has a fixed Ca/Si ratio in the range 1.4 to 1.5. Fig. 1 also shows diagrammatically projected averaged compositions of Portland cement and modern blast furnace slag; the dashed line connecting the two compositions defines the reaction pathway of the two solids and results in sequential formation of the assemblages enumerated above. The diagram needs to be applied to real systems with caution. Diffusion of ions through the paste may be slow and reaction may be inhomogeneous: former slag grains give relict structures that locally have much higher Mg and silica contents than the bulk composition. Thus, outer hydrated product may still contain free portlandite and lack M-S-H, whereas the silicate phases of inner product, formed mainly by direct hydration of slag, tends to consist mainly of coexisting C-S-H and M-S-H. Secondly, because Fig. 1 fails to include other important components, especially Aℓ and sulfate, it is

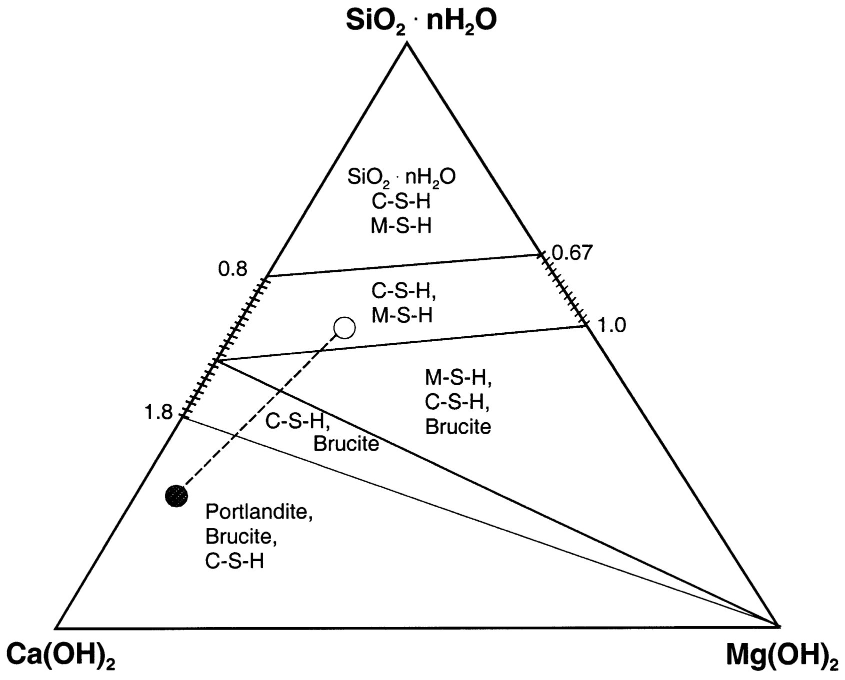

Fig. 1. Solid phase relations in the $MgO-SiO_2-H_2O$ system, 25–85 °C, relevant to the mineralogical composition of blended Portland cement with significant magnesia contents. The dark circle suggests the composition of a Portland cement and the open circle, the composition of an iron blast furnace slag. The composition of blends of the two components projects onto the dashed tie line connecting the circles. Crosshatch lines show solid solutions. The composition of C-S-H in the three-phase assemblage of M-S-H, C-S-H and brucite has a Ca/Si mol ratio of ~ 1.5.

an incomplete guide to the overall paste mineralogy because Mg also reacts with the alumina component forming a hydrotalcite-like phase, M_4AH_{10}. The figure does, however, establish that (i) C-S-H and M-S-H are essentially immiscible, forming two physically and chemically distinct gels and (ii) other factors being equal, the importance of M-S-H increases with the extent of slag replacement, slag Mg content and its fractional reactivity. These conclusions, taken together, provide justification for study of M-S-H gels and their properties because many of the slag–cement blends favoured for nuclear waste containment are formulated with high slag contents.

3. Synthesis, characterisation and sorption

3.1. M-S-H preparation

The M-S-H phase is readily prepared in gel form by the "double decomposition" route: by mixing in stoichiometric proportions a soluble silicate, e.g., sodium silicate, and magnesium nitrate. It is important to exclude CO_2 from the mixing and reaction steps. The resulting precipitate can be collected by filtration and washed under nitrogen or CO_2-free air until the solid is free from sodium. The wet solid has been analysed for phase purity by FTIR, by solid state NMR and chemically, for Mg/Si ratio, by atomic absorption; Refs. [8,9] give additional details and results of the characterisation studies. Defining the high Mg/Si ratio of homogeneous M-S-H preparations proved to be relatively easy; above ratio 1.0, free $Mg(OH)_2$ persists and is readily detected by X-ray powder diffraction. However, the lower ratio proved more difficult to define. Best estimates of this lower ratio for the product obtained at 25 °C are Mg/Si ~ 0.67 increasing to 0.75 following prolonged cure at 85 °C. It is noteworthy that comparing ranges of persistent gel formation in systems of the type $MO–SiO_2–H_2O$ (M = Ca, Mg), the molar ratio of gel formation is greatest amongst the C-S-H gels and, moreover, the range of persistent homogeneous, single-phase chemistries extends to higher MO/SiO_2 ratios.

3.2. Alkali sorption

To measure alkali sorption, about 1.5 g of gel was accurately weighed under CO_2-free conditions into a screw-top plastic tube found by experience not to leak CO_2 in the course of prolonged storage. Sufficient aqueous solution, prepared by diluting certified analytical standard KOH or CsOH, was added to maintain a water:solid (w/s) ratio approximately equal to 15. The sealed tubes were gently agitated for up to 28 days. Aliquots of solution were removed for analysis commencing at 2 days; the resulting solutions were filtered through sealed 0.45-μm filters and immediately thereafter acidified with a known volume of certified standard HNO_3 to prevent carbonation. K and Cs were subsequently determined by flame photometry calibrated against certified commercial standards. Data are shown in Tables 1 (for K) and 2 (for Cs); access to the raw data is important because a variety of interpretations can be made.

One interpretation of the data, using the R_d approach, is shown. R_d is defined by the equation:

$$R_d = \frac{\text{alkali in solid (mol/g)}}{\text{alkali concentration in solution (mol/ml)}}$$

It is necessary to determine cation concentration in the solids, which was generally weighed moist to avoid structural damage by drying. The sample therefore contained both free and bound water. These were arbitrarily determined first by drying to constant weight at 105 °C and, subsequently, at 1000 °C: loss to 1000 °C gives total water, whereas bound

Table 1
Sorption data: potassium at 25 °C on fresh M-S-H gels

Initial $[K^+_{(aq)}]$ (mM)	Final $[K^+_{(aq)}]$ (mM)	% K removal	Mass of K in solid (μmol/g)	Mass of K in solid (μmol/ml)	R_d (ml/g)
Mg/Si = 0.80					
0.13	0.02	83	1.58	0.02	72
0.25	0.06	76	2.90	0.06	49
0.76	0.19	76	8.65	1/19	46
1.27	0.32	75	14.03	0.32	44
2.52	0.35	86	31.69	0.35	92
7.78	2.75	65	79.50	2.75	29
Mg/Si = 0.90					
0.15	0.06	58	1.31	0.06	21
0.25	0.11	59	2.25	0.11	22
0.76	0.25	68	7.73	0.25	31
1.27	0.38	70	13.44	0.38	36
2.55	0.62	76	28.92	0.62	47
7.68	4.32	43	49.29	3.32‘	15
Mg/Si = 0.96					
0.13	0.03	73	1.35	0.03	39
0.25	0.06	77	3.03	0.06	52
0.77	0.22	72	8.06	0.22	37
1.28	0.30	76	14.47	0.30	48
2.57	0.58	78	30.16	0.58	52
7.63	4.25	44	50.40	4.24	12
Mg/Si = 0.66					
0.14	0.04	69	0.58	0.02	34
0.27	0.09	65	1.11	0.04	29
0.78	0.31	60	2.96	0.13	23
1.30	0.38	71	5.35	0.16	34
2.61	0.58	78	12.56	0.24	53
7.82	3.77	50	24.65	1.63	156
Mg/Si = 0.75					
0.13	0.08	37	0.30	0.04	8
0.26	0.07	73	1.26	0.03	44
0.78	0.15	81	4.05	0.06	64
1.32	0.28	79	6.87	0.12	59
2.56	0.34	86	13.88	0.14	98
7.83	3.89	50	25.46	1.61	16

Table 2
Sorption data: potassium at 25 °C on M-S-H gels previously aged 6 months at 85 °C

Target $[K^+_{(aq)}]$ (mM)	Initial $[K^+_{(aq)}]$ (mM)	Final $[K^+_{(aq)}]$ (mM)	% K removal	Mass of K in solid (μmol/g)	Mass of K in solid (μmol/ml)	R_d (ml/g)
Mg/Si = 0.82						
0.13	0.13	< 0.002	99	0.89	< 0.0007	1395
0.26	0.27	0.01	95	1.74	0.06	294
0.77	0.79	0.12	86	4.34	0.05	91
1.28	1.33	0.22	83	7.67	0.09	82
2.56	2.63	1.40	47	7.91	0.58	14
7.69	8.08	7.18	11	7.14	2.91	2
Mg/Si = 0.86						
0.13	0.13	< 0.002	99	0.78	< 0.007	1109
0.26	0.26	0.008	97	1.63	< 0.004	510
0.77	0.79	0.09	89	4.48	0.04	121
1.28	1.31	0.16	88	7.38	0.07	111
2.56	2.63	1.21	54	9.10	0.58	18
7.69	7.85	6.28	20	9.88	2.21	4
Mg/Si = 0.89						
0.13	0.13	< 0.002	99	0.86	< 0.007	1349
0.26	0.27	0.03	90	1.52	0.01	143
0.77	0.79	0.12	85	3.99	0.05	84
1.28	1.31	0.27	79	6.32	0.11	56
2.56	2.63	1.52	42	6.92	0.63	11
7.69	7.93	6.04	11	5.64	2.93	2
Mg/Si = 0.94						
0.13	0.13	0.02	84	0.72	< 0.0009	86
0.26	0.26	0.04	85	1.41	0.02	87
0.77	0.77	0.14	82	3.77	0.06	65
1.28	1.30	0.22	83	7.14	0.19	77
2.56	2.58	1.46	43	6.79	0.06	112
7.69	7.88	7.18	9	4.96	2.98	2

water is taken as the difference between mass at 1000 and 105 °C. Values in tables that are sensitive to this parameter are corrected to 105 °C weight, i.e., including structural water according to this definition. The history of the gel before commencing the sorption experiments is indicated: "fresh" gels were prepared at 5 °C and stored for ~ 24 h at 25 °C before their use. "Aged" gels were prepared at 5 °C but cured at 85 °C for ~ 180 days before sorption experiments, which were also uniformly done at 25 °C.

3.2.1. Results and interpretations

Figs. 2 and 3 compare the mass of potassium sorbed into solid as a function of Mg/Si ratio and initial potassium aqueous concentration for fresh (Fig. 2) and aged (Fig. 3) gels. Fig. 2 shows a nearly linear relationship between the K sorbed that is essentially independent of Mg/Si ratio up to ~ 2.5 mM concentrations; at higher concentrations these values decrease somewhat, indicating gradual saturation of sites available for sorption.

These trends are reflected in the R_d values shown in Fig. 3. Note that to include the wide range of R_d values, these have been plotted on a square root scale. The high numerical values of R_d, in the range 16–100, confirm the high specific removal of K by M-S-H gels, especially at low concentrations in the range 0–3 mM.

Corresponding values for Cs, Figs. 4 and 5, show trends similar to K. Cs sorbed onto M-S-H gel is broadly unaffected by Mg/Si ratio or by ageing and is linear in the range of initial Cs concentrations up to ~ 1.5 mM. Very high R_d values are obtained at the lowest concentration used. As these values tend to be the least accurate, it is suggested that the R_d values obtained, ranging to over 400, should be confirmed perhaps using radiotracers that are reliable at very low concentrations. Nevertheless, over a wide range of initial Cs concentrations, up to 1.6 mM, R_d values lie in the range 10–40 and possibly higher, up to 400.

4. Discussion

Circumstances governing the formation of M-S-H gel in Portland cement or blended Portland cements have been outlined. Two sets of circumstances favour M-S-H gel formation in slag cement blends: one is conditioned by local reaction of slag grains with the internal hydroxyl- and water-rich environment of cement, such that slag grains hydrate independently, or nearly so. Under these conditions, little or no cation exchange occurs with cement and the slag grains hydrate to mixtures of C-S-H, M-S-H and a hydrotalcite-like phase. The M-S-H-rich regions thus formed are physically about the size of the precursor slag grains. Experimentally we have observed inner hydrate persisting

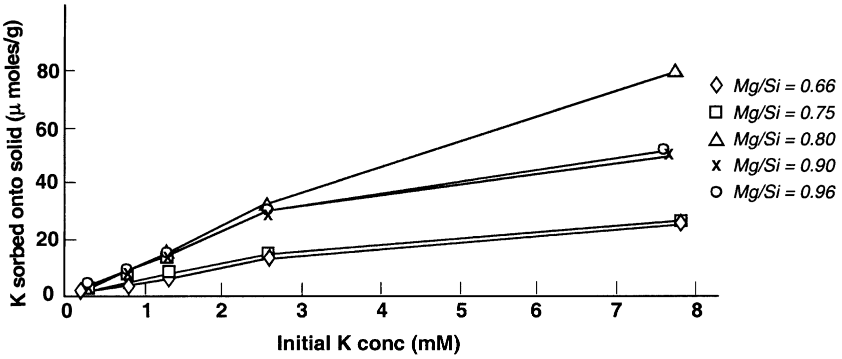

Fig. 2. Mass of K sorbed onto solid M-S-H as a function of initial $[K^+_{(aq)}]$. Data for fresh M-S-H gels.

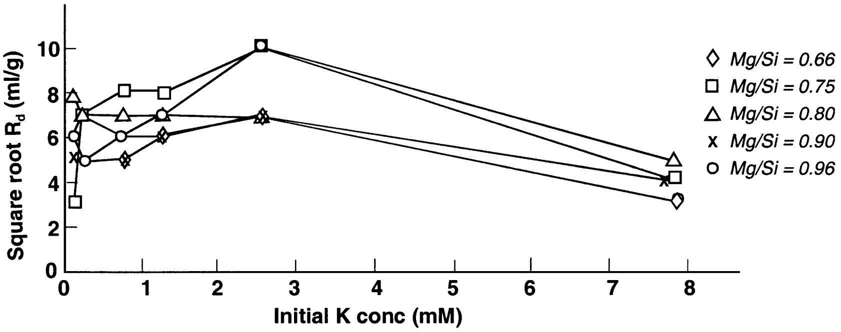

Fig. 3. Solid–aqueous R_d for potassium as a function of initial [$K^+_{(aq)}$] at 25 °C. Data for fresh M-S-H gels. See text for definitions.

in samples cured at 85 °C for 8.4 years. However, the mineralogy of the regions thus formed may not be stable; as reaction occurs between inner and outer product, increasingly equilibrium is approached and the persistence and amount of M-S-H depends on the blend proportioning and exact compositions of cement and slag. Nevertheless, it is apparent from Fig. 1 that M-S-H is likely to be a persistent constituent matrix mineral of most high slag formulations. This second set of circumstances leads to persistent M-S-H formation: like C-S-H, the M-S-H is thermodynamically metastable, but persistent at ≤85 °C.

Data reported here were derived from synthetic M-S-H gels. Synthetics have advantages in determining sorptive properties. The composition and homogeneity of the bulk gels can be controlled and monitored. However, it is possible that the synthetic gels differ in structure from those developed in "real" slag cements. Similar questions arise concerning relationships between "synthetic" C-S-H and "real" C-S-H formed in the course of hydrating cements and blended cements. It is impossible conclusively to resolve the question without having adequate operative definitions of "structure" in poorly ordered materials and the means of quantifying structural parameters. However, no present evidence exists to show that significant differences occur. Moreover, as will be shown, the sorptive properties of synthetic M-S-H gels broadly account for the bulk sorptive properties of slag cement pastes containing, amongst other phases, M-S-H gel.

R_d values for K and Cs may be compared with those in the literature. In systems without Mg, Crawford et al. [10] hydrated cement clinker minerals including C_3S, C_4AF, C_2S (β and γ polymorphs); gypsum and ettringite, prepared in a previous operation, were also included in the sorption studies [10]. Using radiotracer methods, Cs concentrations in mix water were found to decrease by sorption in the course of reactions lasting up to 40 days. However, the benefits of adding microsilica, fly ash and slag to cements in respect of reducing pore fluid alkali contents are well recognised from the literature on alkali–aggregate reaction and were confirmed by experiment. Despite the rather high alkali contents of fly ash and slag, pore fluid expression measurements confirm that the presence of these supplementary cementitious materials actually lower pore fluid alkali contents [11,12] relative to those obtained from plain cement. Subsequent work showed that whereas lime-rich C-S-H had poor sorption potential for Cs, low Cs/Si ratio C-S-Hs showed enhanced sorption potential [12–15]. However, a practical difficulty arises in achieving low ratio C-S-Hs in engineering formulations. Silica fume is arguably the most efficient additive with which to condition formation of low Ca/Si C-S-H in a cement matrix on account of its high bulk silica content, often >90%. But the amounts of silica fume required to react with $Ca(OH)_2$ and significantly lower the Ca:Si ratio of C-S-H, ca. 20% or more replacement of cement, are difficult to blend; moreover, mix rheology

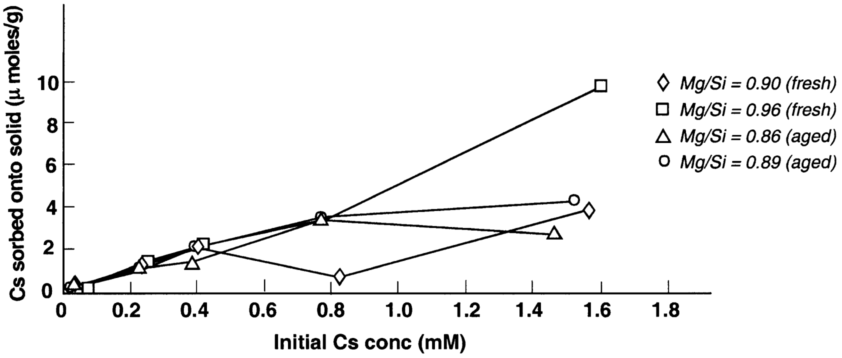

Fig. 4. Mass of Cs sorbed onto solid M-S-H as a function of initial [$Cs^+_{(aq)}$].

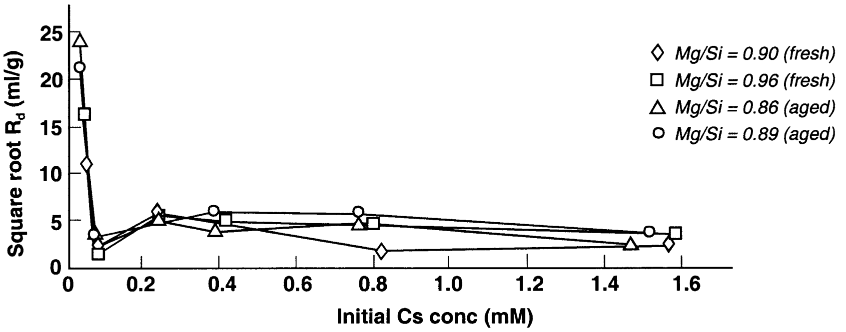

Fig. 5. Solid: aqueous R_d for Cs as a function of initial [Cs$^+_{(aq)}$] at 25 °C. See text for definitions.

requires to be controlled by increasingly large doses of organic superplasticisers to achieve low w/s ratios. Thus, it is uncommon to find blends rich in silica fume being used in practical applications. Slags are much less effective in reducing the C/S ratio of C-S-H because of their relatively high chemical CaO content (typically 35–39 wt.%), and because some silica is fractionated into other phases, e.g., M-S-H, yet are very effective in lowering alkalies, especially K, in pore fluid. Thus, in practice, low-ratio C-S-H does not occur in slag cements, but C-S-H makes a significant contribution to potassium sorption, although less effective for Na.

Slag blends are an effective way of immobilising Cs partly because of their potential to develop an M-S-H gel. Thus, M-S-H is seen as a principal sorber of large ionic radii alkali ions, K and, if present, Cs. Basic Mg-containing eruptive rocks that develop an M-S-H gel in the course of subsea reaction are also known selectively to sorb potassium and are responsible for the low K/Na ratio of seawater. We identify M-S-H gel as an effective sorbant but accept that other phases characteristically present in high slag cement blends, such as hydrotalcite and strätlingite, have not been assessed and may also contribute to the sorption potential.

5. Conclusions

- Cement pastes derived from blends formulated with magnesium-containing substances, such as glassy blast furnace slags, develop two gel-like phases, one designated C-S-H, the other M-S-H, a hydrated magnesium silicate.
- The M-S-H gel has a characteristic Mg/Si ratio in the range 0.67 to 1.0 at ~ 25 °C, but which at 85 °C contracts to the range 0.75 to 1.0.
- The M-S-H gel coexists with lower ratio C-S-H (Ca/Si 1.4 to 1.5 approximately), brucite and an aqueous phase.
- Synthetic M-S-H gel has significant sorptive potential for K and Cs. This sorption is quantified by calculating distribution ratios between aqueous and solid phases. It is believed that the synthetic M-S-H gels closely reflect the behaviour of M-S-H gel formed in blended cement pastes. The reported lowering of pure fluid alkali contents in slag–cement blends is, in part, attributed to sorption into M-S-H.

Acknowledgements

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