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Testing of models of the dissolution of cements—leaching of synthetic CSH gels

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Abstract

The exhaustive leaching of a range of synthetic calcium silicate hydrate (CSH) gels in demineralised water has been studied. This has tested the applicability of experimental data and models based on the static dissolution of synthetic CSH gels in pure water (dissolution of a set of CSH gels with a range of compositions, each at effectively constant composition) to the description of the slow leaching of cementitious materials by flowing waters. This provides additional confidence in the modelling of the long-term evolution of conditions in a repository backfilled with cementitious materials and thereby helps underpin the assessment of the performance of such a repository. The results demonstrate that the initial stages of the dissolution of a range of CSH gels in demineralised water are apparently incongruent, followed by an approach to congruent behaviour. This behaviour is broadly similar to that predicted from the static dissolution of CSH gels. The congruently dissolving composition is found at a Ca/Si ratio of approximately 0.8 to 0.9. This is comparable to the ratio of about 0.8 suggested by static dissolution. However, sequential leaching of CSH gels apparently results in a lower solubility for the congruently dissolving composition than is predicted from static dissolution. The experimental results are compared with data obtained from static dissolution measurements for synthetic CSH gels and with the predictions of a computer model based on the Berner model of cement dissolution. The need to revise the model of dissolution to take account of the behaviour of CSH gels during sequential leaching is examined.

Keywords: pH; Calcium silicate hydrate; Thermodynamic calculations; Degradation; Radioactive waste

1. Introduction

Cementitious materials based on Portland cement are expected to be used extensively in the construction and backfilling of a repository if deep geological disposal of intermediate-level and certain low-level radioactive wastes is adopted in the United Kingdom. These materials provide the benefits of an alkaline environment, limiting the solubility of many radionuclides, and a high surface area for sorption. These properties, together with a reducing chemical environment, result in a 'chemical barrier' to the migration of many significant radionuclides.

The provision of appropriately alkaline conditions for an extended time is primarily a result of the slow dissolution of cement minerals in groundwater flowing into and through such a repository. Hence, the chemical barrier performance of a cementitious material is determined by solubilities of the individual minerals that comprise the material.

The chemistry within a repository backfilled with materials based on ordinary Portland cement is expected to be dominated by the dissolution of portlandite (calcium hydroxide) and calcium silicate hydrate (CSH) gel [1–4]. CSH gels are nonstoichiometric colloidal gels that are essentially amorphous. In practice, the description CSH gel applies to material with a range of possible compositions. In Portland cements, this range may encompass gels with average Ca/Si molar ratios in the range 0.8 to 1.8, although spatial variations are commonly observed on a very fine scale [5]. Furthermore, it has been speculated that materials with Ca/Si ratios below 0.8 may be formed in systems where a large excess of silica is added [6].

Although CSH gels are believed to be metastable with respect to crystalline CSH minerals such as tobermorite and

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afwillite, they are known to persist for extremely long times under geological conditions [7,8]. Consequently, predictions of the evolution of the equilibrium chemistry in a repository have concentrated on defining the contribution from the dissolution of CSH gels [1–4,9].

There have been numerous previous studies in which synthetic CSH gels have been equilibrated with water and the solution chemistry characterised. These are typified by the work of Greenberg and Chang [10,11] and of Fuji and Kondo [12]. In many cases, such work has considered the solution chemistry of anhydrous cement minerals in an effort to elucidate the mechanisms of CSH gel formation during cement hydration [13,14]. However, as noted above, it also has been recognised that CSH gel dissolution represents a basis for engineering the conditions within a repository for radioactive waste to provide the 'chemical barrier' discussed above. The application of CSH gel dissolution models to represent this situation was pioneered by Berner, who has presented a comprehensive compilation of relevant experimental data [15].

The description of the behaviour of CSH gel is complicated by the observation that the dissolution is apparently incongruent, with calcium being preferentially dissolved from CSH gels with a higher Ca/Si ratio. This behaviour has been demonstrated in the numerous experimental studies and in the compilation by Berner [15]. Although the application of the term 'incongruent dissolution' to an apparently metastable phase may not be strictly correct, the terminology is widely used in this context and, for convenience, will be adopted herein.

A model of the dissolution of CSH gel was proposed by Berner [15], drawing upon the concept of a non-ideal mixture of congruently soluble components originally developed by Greenberg and Chang [10,15]. Subsequently, numerous authors have sought to develop refined versions of this original model, based on differing or more rigorous descriptions of the thermodynamics of non-ideal solid solutions [6,16–20]. A detailed review of the relative merits of these various models is outside the scope of the current report. However, it may be observed that all such models are parameterised using the same or a similar set of experimental data for synthetic CSH gels.

The significance of the apparently incongruent dissolution of hydrated CSH gels for the long-term maintenance of alkaline conditions in a radioactive waste repository is readily illustrated [3,9,21]. The maintenance of the desired conditions is an important requirement for a demonstration of the overall performance of such a repository.

The solubility data upon which the existing models of CSH gel dissolution are based have been derived from either the dissolution or precipitation of synthetic CSH gels manufactured at a range of compositions [6,11–13,15]. Such methods are termed 'static dissolution' in this paper. In such experiments, care is exercised to avoid extensive redispersion of the CSH gel to maintain an approximately constant composition and thereby provide data for a range of well-defined compositions. In contrast, during the slow dissolution of cement under repository conditions, the composition of CSH gel will change continuously as calcium is preferentially leached [2].

The validity of applying models based on static dissolution data to the description of the evolution of the chemistry in a repository is therefore dependent on two related assumptions:

- that the process of continuous leaching of the cementitious materials is adequately described by analogy with the static dissolution of synthetic CSH gel;
- that the properties of the CSH gel in Portland cement are sufficiently similar to those of synthetic CSH gels of similar compositions.

This paper presents an investigation of the validity of models and experimental data based on static dissolution data to the description of the leaching of the principal components of hydrated Portland cements. This is intended to provide additional confidence in the modelling of the long-term evolution of conditions in a repository backfilled with cementitious materials and thereby underpin the assessment of the performance of such a repository.

Table 1
Compositions of synthetic CSH gels

Target Ca/Si	Mass of CaO (g)	Mass of silica suspension (g)	Estimated H_2O content (g)	Ca/Si in gel[a]
3.0	1.88	1.34	1.2	2.7
1.8	1.68	1.99	1.0	1.6
1.5	1.59	2.27	0.97	1.4
1.2	1.48	2.64	0.90	1.1
1.0	1.38	2.96	0.84	0.90
0.90	1.33	3.15	0.81	0.81
0.85	1.29	3.25	0.79	0.76
0.80	1.26	3.36	0.77	0.72

Quantity of water is based on a H_2O/CaO ratio of 2.

Compositions were designed to produce 3.75 g of gel.

[a] Assumes that calcium oxide is 95% CaO and silica suspension is 53% silica.

The work comprises studies of the exhaustive leaching of synthetic CSH gels in demineralised water. Where appropriate, modifications to existing models have been suggested to provide a closer description of the leaching of cements. Although predictions of the long-term chemical conditioning by cements have been published, validation of such predictions through comparison with the results of the leaching of cements is limited [2,22]. Published exhaustive leaching data may differ from the predictions, possibly due to disequilibrium [2], and some datasets are limited to the relatively early stages of leaching [17,23]. Most other published data relate to the kinetics of the leaching or dissolution of cement monoliths and are dominated by the kinetics of transport and the structure of the specimens [24,25].

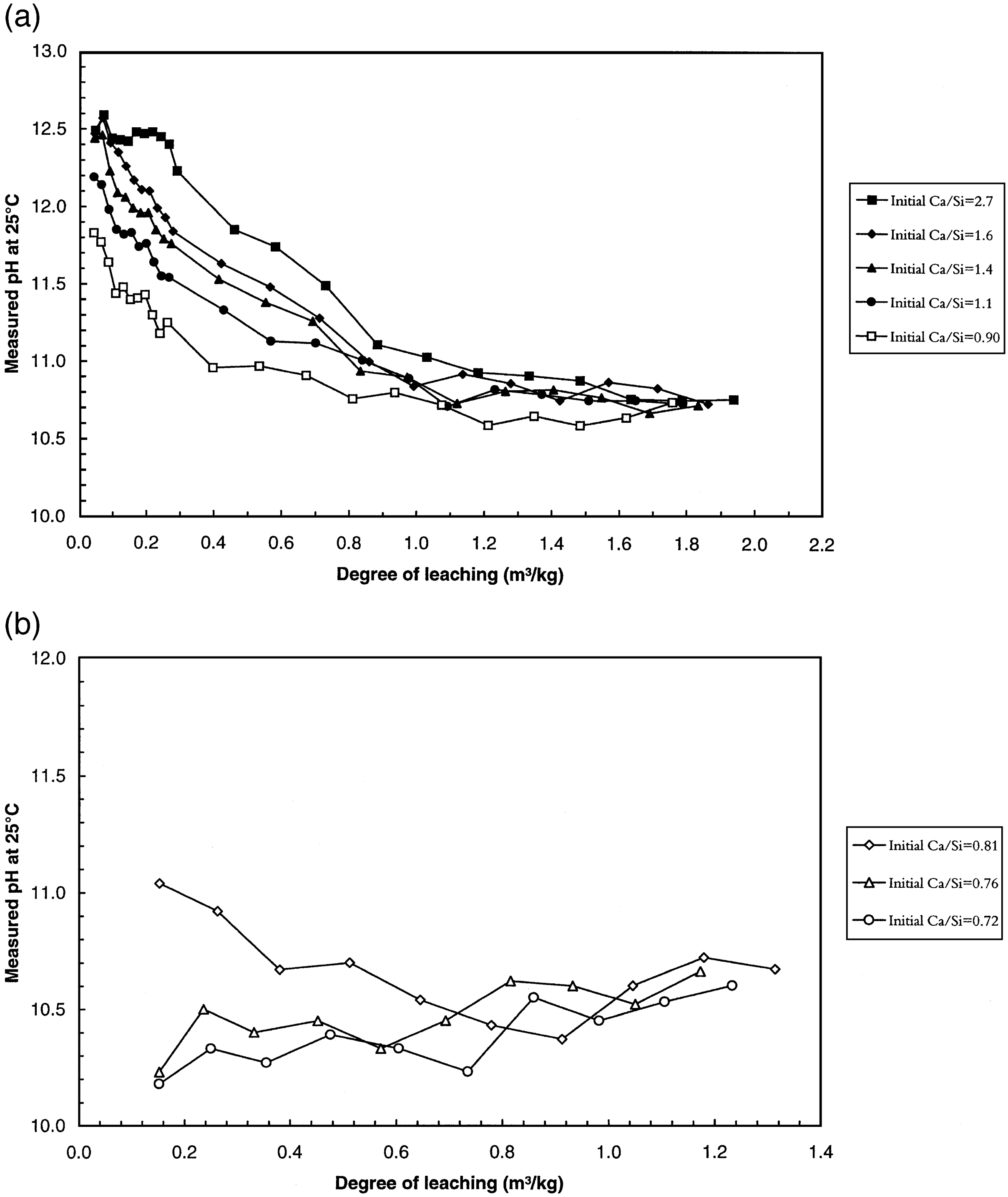

Fig. 1. (a) Variation in pH during leaching of higher Ca/Si ratio synthetic CSH gels in demineralised water. (b) Variation in pH during leaching of lower Ca/Si ratio synthetic CSH gels in demineralised water.

2. Experimental procedures

2.1. Manufacture of synthetic CSH gels

Synthetic CSH gels were prepared by reacting calcium oxide and silica in the aqueous phase under a nitrogen atmosphere [6,26]. The calcium oxide was either reagent-grade material supplied by Fisher Scientific or high-purity material supplied by Aldrich (minimum calcium oxide content 95%). Calcium oxide was handled and stored under a carbon dioxide-free atmosphere and used within 1 month of the stated month of manufacture. The silica was a suspension of colloidal silica in water with a nominal silica content of 50%, as supplied by Aldrich Chemicals (Syton HT-50). The silica content of the suspension was measured as 53% by weight, based on weight loss on drying at 105 °C.

The colloidal silica suspension was added to fresh, finely divided calcium oxide powder to give the correct calcium–silicon (Ca/Si) ratio. A prior dilution of the silica suspension with demineralised water was necessary to prevent solidification of the mixture. The mixture was agitated for a short time, re-suspended in a known quantity of demineralised water (allowing for the prior dilution of the silica suspension), and agitated again.

The water content of each gel was required to be known to allow the mass of material to be determined. For simplicity, a uniform water–calcium ratio of 2 was assumed. This value is comparable with values suggested in the literature. For example, Taylor gives a ratio of 2.5 for saturated CSH gel [27]. Elsewhere, a ratio of 2.35 has been reported [28]. Furthermore, any small differences from the actual ratios are judged unlikely to be significant in these studies.

The synthetic CSH gels were prepared in two separate sets. The first set of five CSH gels was prepared with nominal Ca/Si ratios of 3.0, 1.8, 1.5, 1.2 and 1.0 (referred to as higher Ca/Si ratio gels). The second set of three CSH gels was prepared with nominal Ca/Si ratios of 0.9, 0.85 and 0.8 (referred to as lower Ca/Si ratio gels). This range of Ca/Si ratios was selected to cover the expected composition of CSH gel in materials based upon Portland cement [21,27].

The preparations of the gels are summarised in Table 1. This includes the estimated actual Ca/Si ratios, based on an assumption of 95% CaO in the starting material and a 53% silica content in the slurry. Hereafter, these Ca/Si ratios will be used to identify the various CSH gels in this report.

2.2. Exhaustive leaching experiments

2.2.1. Equilibration of solutions

The exhaustive leaching experiments required the equilibration of the synthetic CSH gels with known volumes of demineralised (AnalaR) water. The leachant was previously sparged with nitrogen to minimise the quantity of dissolved carbon dioxide. The resulting leachates were periodically decanted and replaced with fresh leachant. The leachates subsequently were analysed.

The experiments were carried out in polythene containers and set up under a nitrogen atmosphere. All experiments were stored in a nitrogen glove box during equilibration and periodically agitated. The temperature within the glove box was not independently controlled and the ambient temperature was typically 20–25 °C. The temperature was monitored and recorded prior to the solutions being decanted.

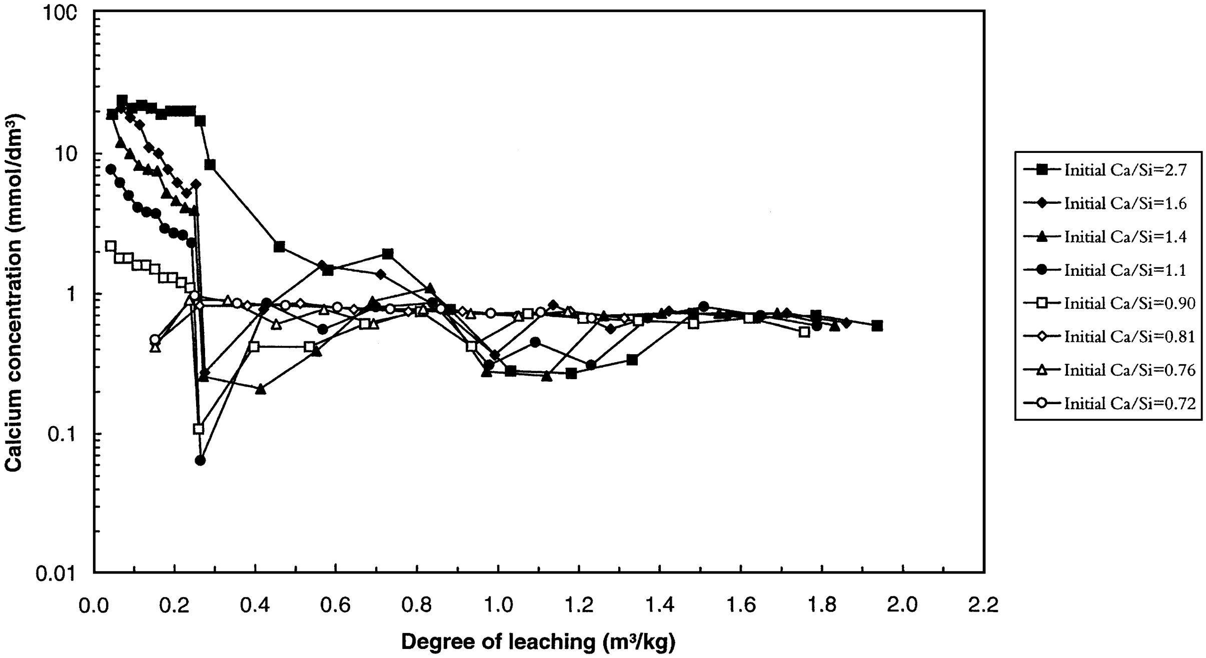

Fig. 2. Variation in calcium concentration during leaching of synthetic CSH gels in demineralised water.

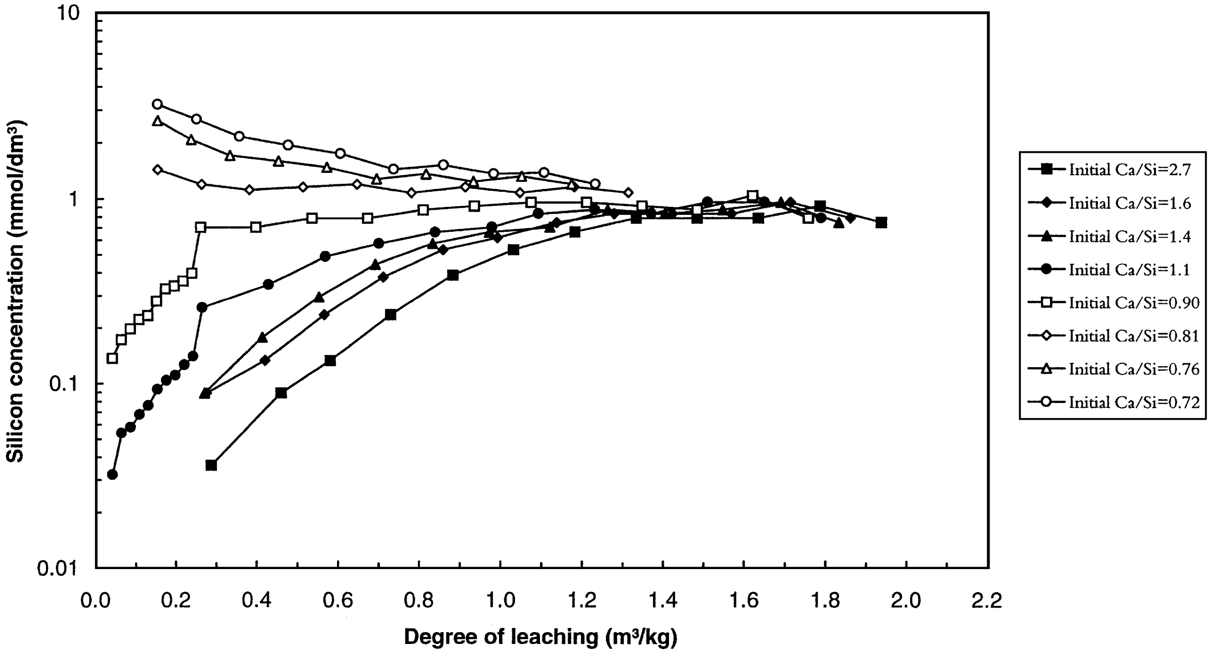

Fig. 3. Variation in silicon concentration during leaching of synthetic CSH gels in demineralised water.

Decanting of the leachate was delayed if the temperature fell to below 20 °C.

The appropriate equilibration times were determined during the course of the experiments by monitoring the pH measurement regularly. The initial equilibration was prolonged to allow the completion of the reaction between calcium oxide and silica. A constant pH value was achieved after about 30 days and the leachate was then decanted.

Subsequently it was demonstrated that an equilibration time of 10 to 20 days was sufficient to achieve a constant pH. Ten days was therefore adopted as a minimum equilibration time.

2.2.2. Higher Ca/Si ratio CSH gels

An initial solid–liquid ratio of 3.75 g of CSH gel to 150 cm^3 of leachant was adopted to give a leaching ratio

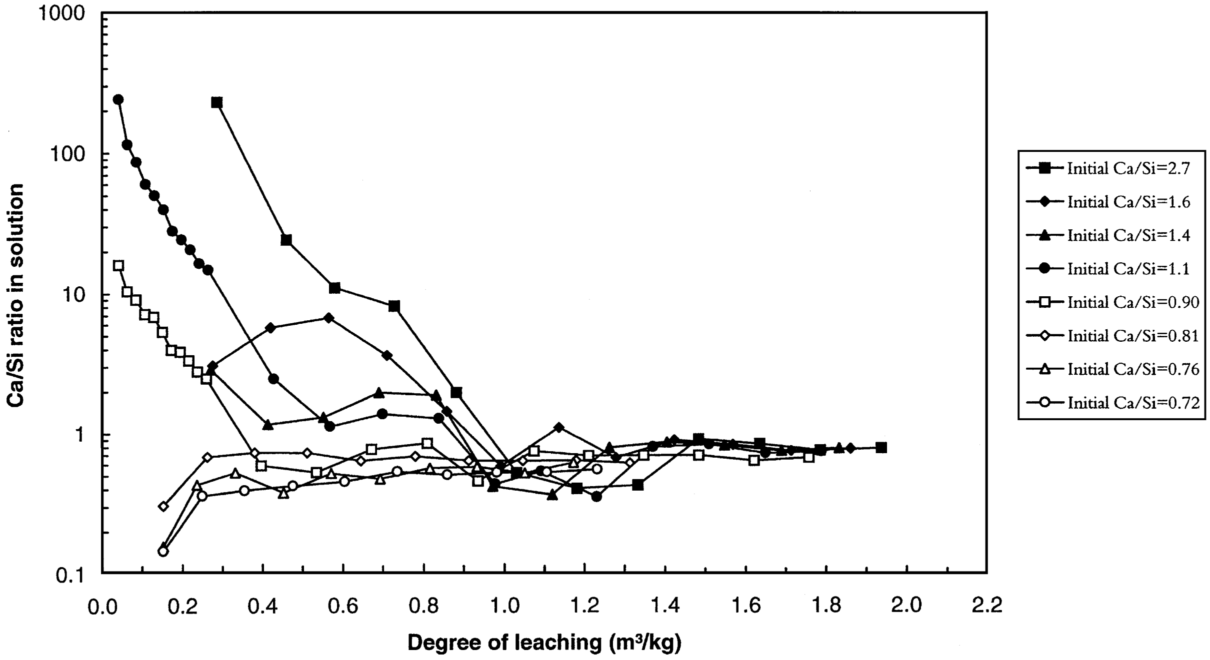

Fig. 4. Variation in Ca/Si in solution during leaching of synthetic CSH gels in demineralised water.

of 0.04 m^3 kg^{-1}. This ratio was adopted as an appropriate compromise between the need to provide detail of the initial leaching behaviour and achieving a reasonable experimental timescale. Approximately 80 cm^3 of leachate could be decanted without disturbing the settled gel and the leachate was changed 10 times. The total volume of leachant was 950 cm^3 per experiment under these conditions, giving a cumulative degree of leaching of 0.25 m^3 kg^{-1}.

After 10 equilibrations, the 80 cm^3 of decanted leachate was replaced with 500 cm^3 of water, increasing the leaching ratio to 0.15 m^3 kg^{-1}. It was found that the 500 cm^3 of additional leachate could be decanted without disturbing the settled gel. A further 12 equilibrations were then per-

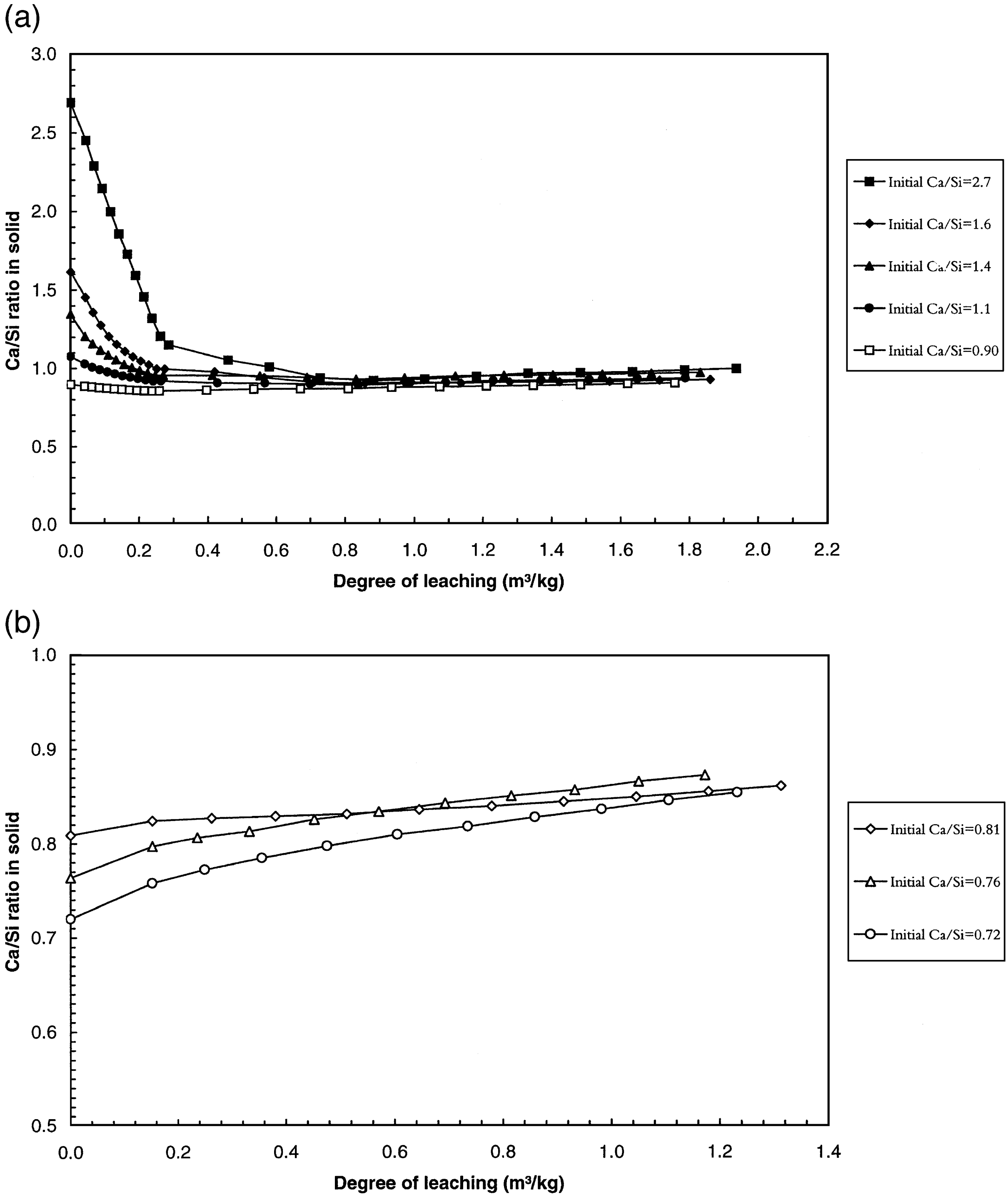

Fig. 5. (a) Variation in Ca/Si in the solid phase during leaching of higher Ca/Si ratio synthetic CSH gels in demineralised water. (b) Variation in Ca/Si in the solid phase during leaching of lower Ca/Si ratio synthetic CSH gels in demineralised water.

formed at this increased solid–liquid ratio to accelerate the leaching process. The total duration of the experiments was 2 years. This gave a cumulative degree of leaching of about 1.9 $m^3 kg^{-1}$ for the experiment.

2.2.3. Lower Ca/Si ratio CSH gels

A solid–liquid ratio of 3.75 g of CSH gel to 570 cm^3 of leachant was adopted, a leaching ratio of 0.15 $m^3 kg^{-1}$, and 500 cm^3 of leachate could be decanted without disturbing the settled gel. The leachate was changed a total of 10 times and the total volume of leachant was approximately 5000 cm^3 per experiment. This gave a cumulative degree of leaching of about 1.3 $m^3 kg^{-1}$ for the experiment.

2.3. Solution analysis

During the course of each equilibration, the pH was measured periodically using a simple instrument (Sentron pocketFET 501pH). The probe was calibrated using the supplied buffers. The accuracy of these measurements was estimated as ±0.1 pH units.

The compositions of the decanted leachates were determined after filtration through a 30,000 NMWCO filter to remove any residual particles of CSH gel.

Upon completion of each equilibration, the pH of the decanted leachate was determined more accurately using an Alpha 200 pH and conductivity meter and an Orion combination electrode. The pH electrode was calibrated before each measurement using standard buffers. Initially, pH 7 and 13 buffers were used for calibration. However, when the measured pH had fallen significantly, the pH 13 buffer was replaced by a pH 10 buffer to provide an upper calibration point closer to the measured pH. The leachate samples and buffers were temperature-conditioned at 25 °C in a water bath for not less than 1 h, prior to the measurement of pH. The accuracy of these measurements was estimated as ±0.01 pH units.

The higher calcium concentrations, those for the first 10 equilibrations of the higher Ca/Si ratio gels, were determined using ultraviolet (UV) spectrophotometry, based on a WTW MPM-2010 spectrophotometer and a commercial analytical reagent (calcospectral) [29]. The limit of detection of the analysis was 2.5×10^{-4} mol dm^{-3}. The accuracy of the analysis was estimated as about ±5%, based on a series of measurements using a standard solution containing 100 mg dm^{-3} (2.5×10^{-3} mol dm^{-3}) of calcium.

The more dilute calcium concentrations in the leachates from the later equilibrations (those produced after the increase in leachant volume to 500 cm^3) were determined using inductively coupled plasma optical emission spectrometry (ICP-OES) analysis. The limit of detection for this analysis was 70 ppb (1.8×10^{-6} mol dm^{-3}) with a precision of ±20%.

Silicon concentrations were determined using ICP-OES analysis. The limit of detection for this analysis was 300 ppb (1.1×10^{-5} mol dm^{-3}) with a precision of ±20%. This analysis was not performed for the first 10 equilibrations of the CSH gels with Ca/Si ratios of 2.7, 1.6 and 1.4.

3. Results

The variation in pH with the degree of leaching by demineralised water is shown in Fig. 1a) and (b) for the

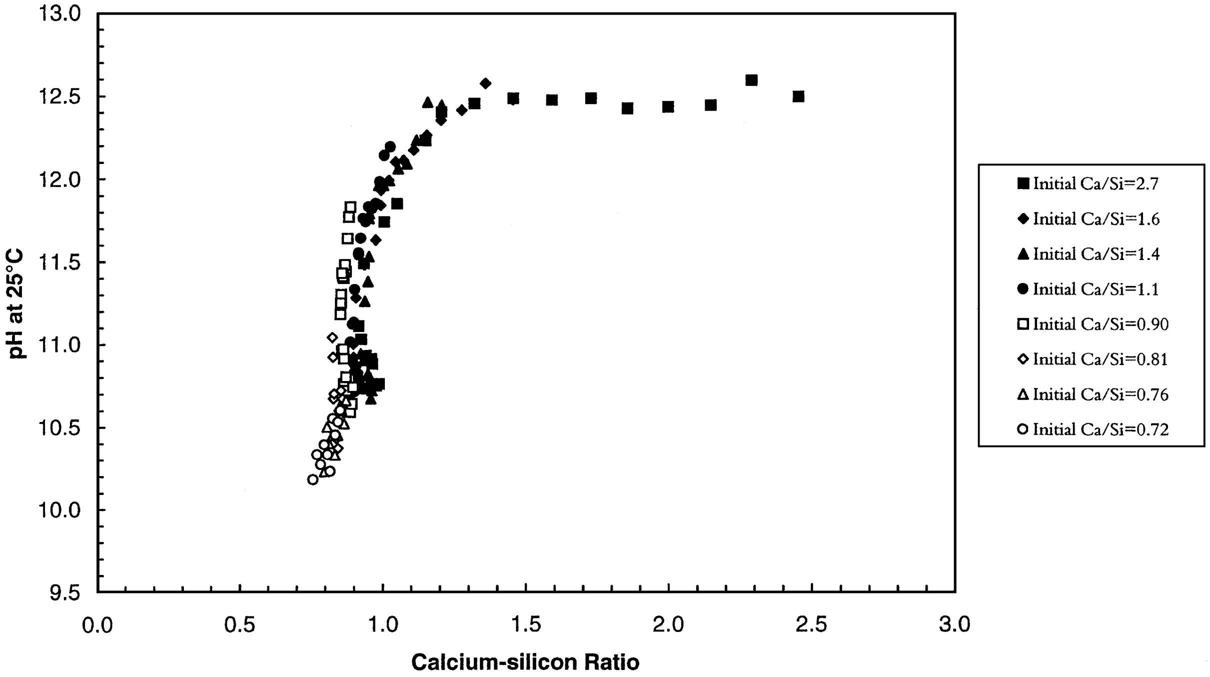

Fig. 6. Variation in pH with Ca/Si in the solid phase during leaching of synthetic CSH gels in demineralised water.

higher and lower Ca/Si ratio gels, respectively. Figs. 2 and 3 show the equivalent variations in the total aqueous calcium and total aqueous silicon concentrations, respectively. The variation in the Ca/Si ratio in the aqueous phase is shown in Fig. 4. Fig. 4 suggests that the leaching of the various gels ultimately results in solutions of apparently similar, constant compositions.

The degree of leaching has been expressed as the cumulative volume of leachate per unit mass of CSH gel. These masses include the assumed water contents of the gels.

The variation in the Ca/Si ratio of the CSH gel as leaching proceeds may be calculated by sequentially subtracting the quantities dissolved into solution from the initial solid compositions. The results of these analyses are shown in Fig. 5(a) and (b) for the higher and lower Ca/Si ratio gels, respectively. These figures demonstrate that approximately constant solid compositions are achieved for CSH gels with initial Ca/Si ratios of 0.81 and above. For the gels with initial Ca/Si ratios of 0.76 and 0.72, a constant composition may not have been achieved for the degree of leaching obtained at the termination of the experiments.

The leaching behaviour of all eight gel compositions is summarised in Fig. 6, which shows the variation in pH as the gel composition changes during leaching.

4. Discussion

4.1. General comments on the leaching of CSH gels

The initial leaching of the CSH gels generally exhibits the incongruent dissolution behaviour seen in static dissolution experiments. Fig. 4 demonstrates that, for the higher Ca/Si ratio gels, the initial Ca/Si ratios in solution are very much greater than those in the solids. Consequently, the calculated Ca/Si ratios in the solids initially decrease during leaching, as shown in Fig. 5(a).

The lower Ca/Si ratio CSH gels exhibit the opposite behaviour. The initial Ca/Si ratio in solution is less than that in the solid and the calculated Ca/Si ratios in the solids increase slowly as leaching proceeds, as shown in Fig. 5(b).

In all cases, the Ca/Si ratios in the solid and aqueous phases tend to a constant value as leaching proceeds. This suggests that the dissolutions are approaching congruency. Where continued leaching does not change the composition of the solid, the solid and aqueous compositions would be expected to have become equal. This is illustrated by the ratio of the Ca/Si ratio in the solid to that in aqueous phase (the ‘composition ratio’), given by Eq. (1):

$$R = \frac{([\mathrm{Ca}]/[\mathrm{Si}])_{\mathrm{solid}}}{([\mathrm{Ca}]/[\mathrm{Si}])_{\mathrm{aqueous}}} \qquad (1)$$

The variation in this composition ratio as leaching proceeds is shown in Fig. 7(a) and (b) for the higher and lower Ca/Si ratio gels, respectively. Clearly, a composition ratio of unity would indicate congruent dissolution.

For the higher Ca/Si ratio gels the composition ratio is initially small and less than unity. As leaching proceeds, the data exhibit considerable scatter and, in some cases, individual values exceed unity. Furthermore, the ultimate value of the composition ratio seems to be slightly greater than unity (about 1.2–1.4). However, it is not possible for the composition ratio to be maintained above unity in this manner, provided that equilibrium is maintained. It is therefore speculated that the greater than unity final value reflects unrecognised systematic errors in some of the data.

The lower Ca/Si ratio gels initially exhibit a composition ratio greater than unity, as shown in Fig. 7(b). This decreases towards unity (or a value close to unity) as leaching proceeds, indicating an approach to congruency through the preferential leaching of silica from the gel. This may be contrasted with the expected behaviour of CSH gels in cements, where the preferential leaching of calcium is commonly observed. A relatively high silica solubility is reported by those authors that have studied CSH gels of lower Ca/Si ratio [6,11].

The composition ratio for the gel with an initial Ca/Si ratio of 0.81 apparently does not vary greatly during leaching. It is therefore concluded that the composition of this gel is close to the congruently dissolving composition.

The gels with Ca/Si ratios of 0.76 and 0.72 apparently have compositions further from the congruently dissolving composition. The composition ratios therefore decrease towards unity during leaching, and congruent dissolution may not have been reached during the experiments. This observation reflects the low and similar solubilities of calcium and silicon for these gels and the consequent slow change in composition during leaching.

The failure of the gels to achieve a final composition ratio of unity may be attributed to systematic errors in the data. A number of sources of systematic errors are possible and these are discussed below.

The actual composition of the calcium oxide has been corrected for a less than 100% calcium oxide content in the derivation of the variations of the solid compositions. The exact magnitude of the necessary correction has not been determined and instead the typical composition has been assumed to apply. Some residual systematic error therefore may remain.

The solution analyses may be subject to both random and systematic errors. A precision of ±20% applies to the ICP-OES analyses for concentrations well in excess of the detection limit (as is the case with these current data). In addition, a systematic under-reporting of concentration by 10–20% was suggested by measurements on 90- and 10-μg cm^{-3} standards for calcium and silicon. This inaccuracy has not been fully quantified and may be concentration and batch dependent. However, the effect of applying an appropriate systematic correction to the data tends to move the final composition ratio towards unity.

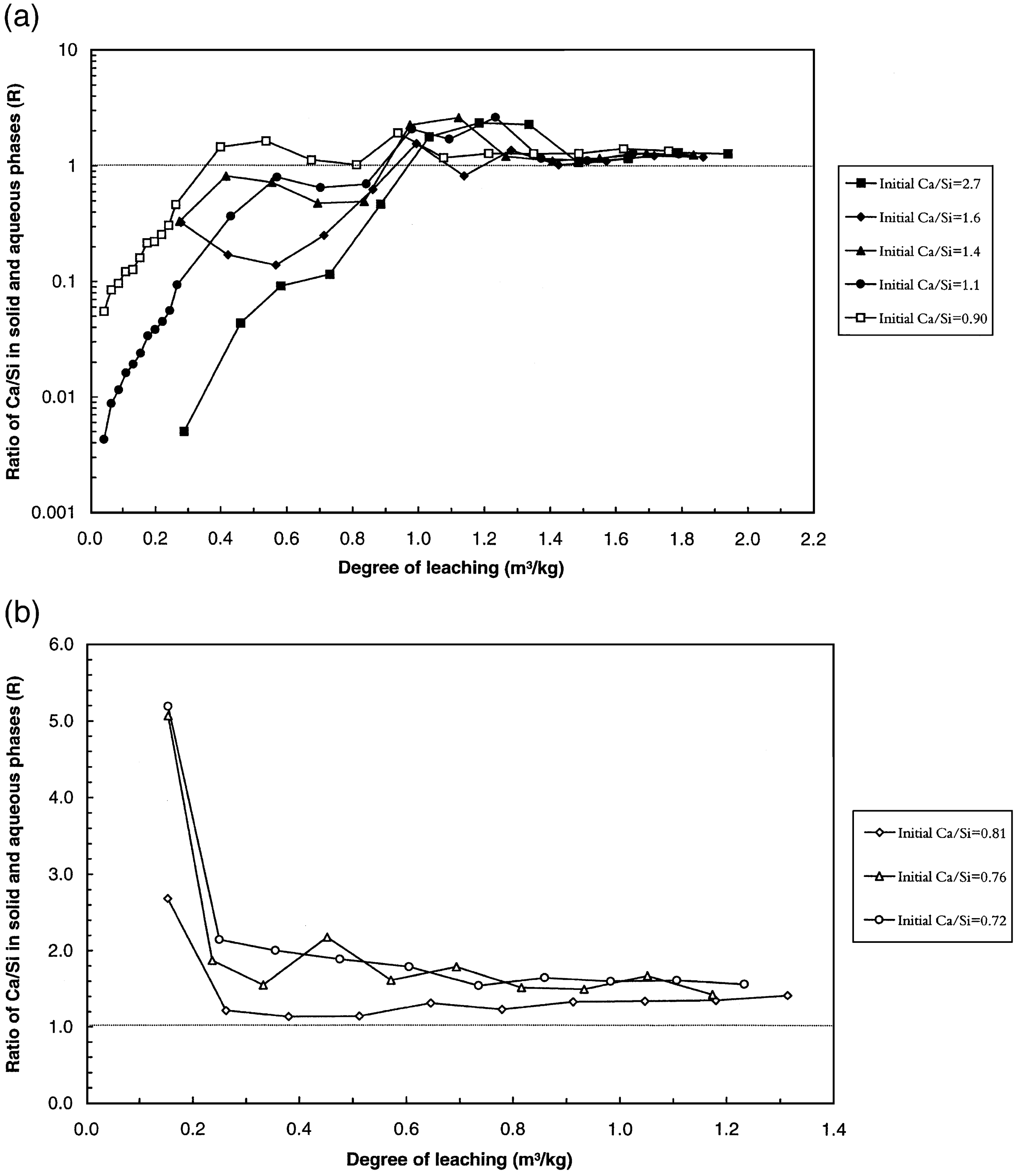

Fig. 7. (a) Variation in the relative compositions of the solid and aqueous phases during leaching of higher Ca/Si ratio synthetic CSH gels in demineralised water. (b) Variation in the relative compositions of the solid and aqueous phases during leaching of lower Ca/Si ratio synthetic CSH gels in demineralised water.

4.2. pH Conditioning at higher Ca/Si ratios

The hydration of Portland cements results in the formation of both portlandite and CSH gel. Typically the composition of the CSH gel so formed, and assumed to be in equilibrium with portlandite, is quoted as Ca/Si ratio in the range 1.5 to 1.8 [3,27]. Similarly, the analysis of synthetic CSH gels with Ca/Si ratios greater than perhaps 1.5 to 2.0 commonly indicates that portlandite is present [26]. However, reported analyses of CSH gel in hydrated cements present a more confused picture, as indicated by Reardon [30]. Measurements may be affected by inhomogeneity in composition and by ageing effects. Lower Ca/Si ratios, perhaps less than 1.5, also may be consistent with some experimental data.

The leaching of the CSH gel with an initial Ca/Si ratio of 2.7 results in no significant change in pH or calcium concentration in solution until it has been extensively leached. Initially the leachate has a constant pH of 12.4 ± 0.1 and a calcium concentration of 21 ± 2 mmol dm^{-3} (based on the first nine equilibrations). The CSH gel with a Ca/Si ratio of 1.6 produces a similar leachate, although for the first three equilibrations only. The first equilibration for the gel with a Ca/Si ratio of 1.4 may also be consistent with these observations. These initial leachate compositions are consistent with the equilibrium dissolution of calcium hydroxide from the gel.

These observations indicate that the synthetic gels with Ca/Si ratios of 2.7, 1.6 and possibly 1.4 comprise a mixture of portlandite and a CSH gel. The gel in equilibrium with the portlandite therefore has a Ca/Si ratio less than 2.7, probably in the range 1.3–1.5. These data are consistent with the noted formation of portlandite during the hydration of Portland cements. However, an accurate comparison with the composition of hydrated cement is difficult, for the reasons outlined above.

4.3. Chemistry of congruent dissolution

The congruently dissolving composition may be determined from Fig. 5(a) and (b). The data suggest that the congruently dissolving composition lies in the range 0.8 to 0.9. The decreasing Ca/Si ratios during leaching shown in Fig. 5(a) demonstrate that an initial Ca/Si ratio of 0.9 is greater than the congruently dissolving ratio. Conversely, Fig. 5(b) shows that the congruently dissolving composition lies at Ca/Si ratio of greater than 0.76 as this gel shows an increase in calcium concentration during leaching.

Fig. 5(b) indicates that the gel with a ratio of 0.81 shows only a slight increase in calcium concentration during leaching, and may be close to the congruent composition. However, the Ca/Si ratio in solution for this gel is apparently lower than is ultimately achieved for gels with lower initial Ca/Si ratios. This may be due to accumulated errors, or may indicate that gels of differing initial compositions, when leached, achieve slightly different congruently dissolving compositions. The available data do not allow these possibilities to be distinguished.

The solution chemistry as the system approaches congruency is summarised in Fig. 8. This figure compares the behaviour of the gels during leaching with the aqueous phase chemistry established by Jennings [14] for static dissolution, the experimental static dissolution data of Greenberg and Chang [11], and the data fit at low Ca/Si ratio provided by Berner [15].

The initial CSH gel leaching results, those giving higher calcium concentrations, are similar to the behaviour established by Jennings for 'stable' CSH gel. However, as the leaching proceeds and the calcium concentration falls, Fig. 8 shows that the measured silicon concentrations due to leaching fall below the values determined for static dissolution (and reflected in the Berner model).

The comparison provided in Fig. 8 shows that the concentration of silicon is apparently lower during leaching than is predicted from most static dissolution measurements. The leaching data indicate a silicon concentration of less than 10^{-3} mol dm^{-3} during congruent dissolution of high Ca/Si ratio gels. The data for static dissolution suggest higher silicon concentrations at low Ca/Si ratios, particularly

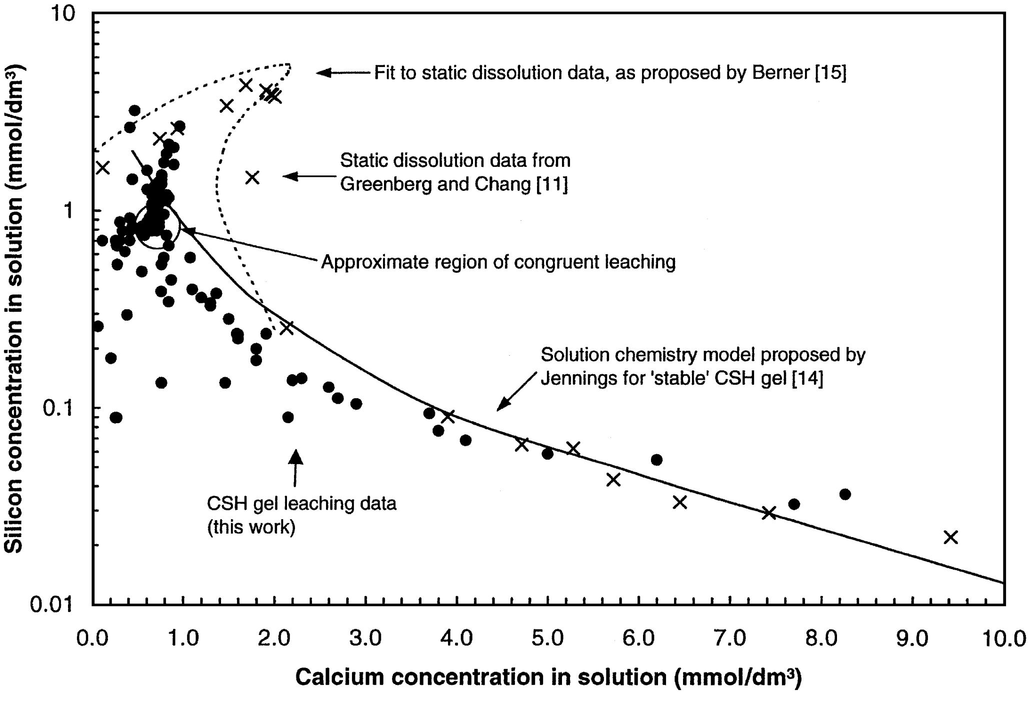

Fig. 8. Comparison of solution chemistry during leaching of synthetic CSH gels in demineralised water with results and models based on static dissolution.

if the Greenberg and Chang [11] data or the Berner model are considered [15].

In summary, the data, although scattered, apparently cluster around congruently dissolving compositions equivalent to Ca/Si ratios of 0.8 to 0.9. At this point, the calcium concentration in solution is apparently $(0.6 \pm 0.2) \times 10^{-3}$ mol dm^{-3}. As noted above, the corresponding silicon concentration is lower than generally found in static dissolution.

Berner suggests that the static dissolution data indicate that the congruently dissolving composition lies at a Ca/Si ratio of approximately 0.8 [15]. Atkinson et al. similarly suggest a value of 0.8–0.9 [6]. The congruently dissolving composition from static leaching is apparently comparable with that of the crystalline CSH mineral tobermorite, typically assumed to be $C_5S_6H_{5-9}$ [21,27,31]. The results from CSH gel leaching may be interpreted as being consistent with these assertions.

Some authors have proposed compositions closer to a Ca/Si ratio of unity, commonly as the basis for modelling. For example, Berner adopted a composition of CaH_2SiO_4 (CSH) as the notional end member for the description of the portlandite–CSH gel system as a solid solution [21,32]. Kersten has suggested a similar composition, CaH_4SiO_5 [33]. It may be observed that the congruently dissolving composition indicated by the CSH gel leaching results is not entirely consistent with these end member compositions.

4.4. Comparison with leaching of cements

The leaching of synthetic CSH gels also may be compared with the leaching of real materials based on Portland cement. This would provide further validation of the suitability of synthetic CSH gels as an analogue of the CSH gel formed during the hydration of cement.

However, despite the prevalence of predictions of the long-term behaviour of cements, experimental studies of the extensive leaching of such materials, and the possible achievement of congruent dissolution of the CSH gel component, are not widely available. In several cases, the experiments were apparently terminated well before congruency was achieved [22].

Fig. 9 provides a comparison between the leaching of CSH gel and two previously published sets of data obtained by the exhaustive leaching of sulphate-resistant Portland cement (SRPC) [2]. To allow the comparison to be made, the degree of leaching has been adjusted to the mass of unhydrated material in each case. To compensate for the differing initial Ca/Si ratios, the data have also been shifted so that the points at which the dissolution of calcium hydroxide is completed in each case coincide.

The comparison suggests that the leaching of synthetic CSH gels provides a reasonable model of the leaching of real materials such as SRPC. Some difference in pH is observed, but this may in part be due to the contribution of the additional minerals present in the SRPC. It is noted that the silicon concentration observed in the later stages of the SRPC was found to be lower than predicted from models based on CSH gel dissolution. This was attributed to a failure to achieve equilibrium [2]. However, a similar observation was made during the present study and it is possible that leaching

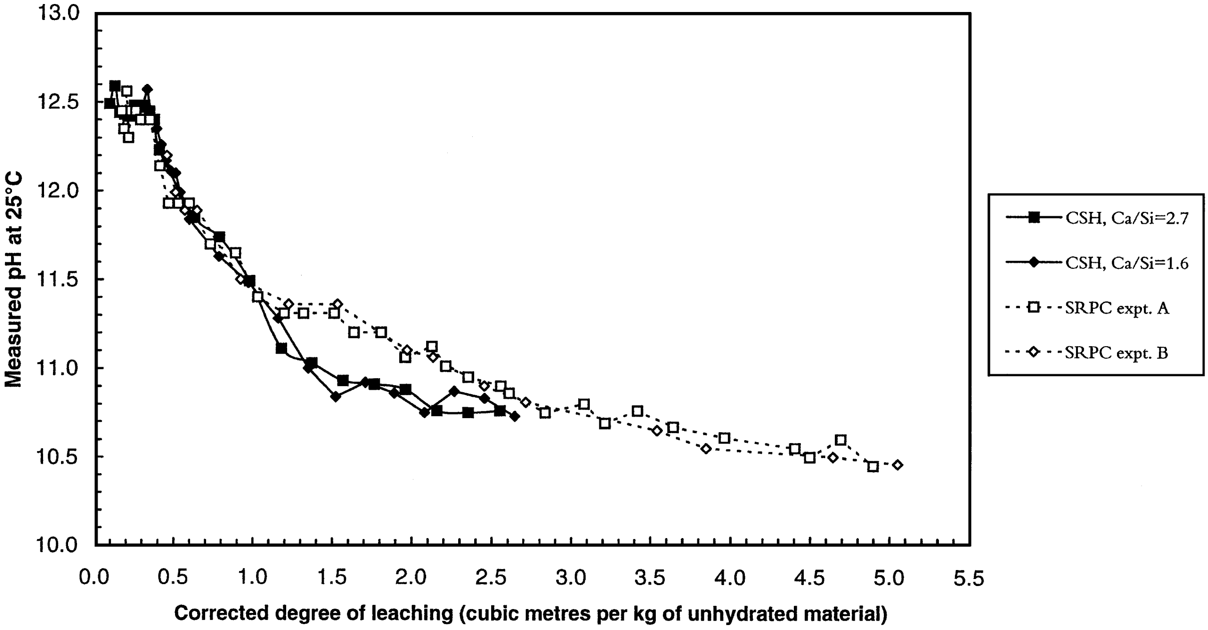

Fig. 9. Comparison of SRPC and CSH gel leaching (degree of leaching corrected to unhydrated mass, data shifted to allow for differing calcium hydroxide contents).

Table 2
Summary of the adjusted Berner model as derived from static solubility measurements on synthetic CSH gels [32]

Region	Ca/Si ratio	End member	log K_{sp} value
IV	> 2.5	$Ca(OH)_2$	− 5.25
III	1.5 − 2.5	$Ca(OH)_2$	− 5.25
		CaH_2SiO_4	− 7.12
II	1.0 − 1.5	$Ca(OH)_2$	$-11.11+3.91\mathrm{casi}$
		CaH_2SiO_4	− 7.12
I	<1.0	SiO_2	$-1.994+\frac{0.861}{\mathrm{casi}-1.2}$
		CaH_2SiO_4	$-7.12-(1-\mathrm{casi})\left(0.79+\frac{0.861}{\mathrm{casi}-1.2}\right)$

gives rise to lower concentrations than obtained in static dissolution experiments.

5. Modelling of leaching behaviour

5.1. Models of CSH gel dissolution

The incongruent dissolution of CSH gel may be described as [15]:

$$[x\mathrm{CaO}\cdot\mathrm{SiO_2}\cdot y\mathrm{H_2O}]_{(\mathrm{solid})}$$
$$\rightarrow [(x-a)\mathrm{CaO}\cdot(1-b)\mathrm{SiO_2}\cdot(y-a)\mathrm{H_2O}]_{(\mathrm{solid})}$$
$$+\,a\mathrm{Ca(OH)}_{2(\mathrm{aq})}+b\mathrm{SiO}_{2(\mathrm{aq})}$$

where $Ca(OH)_{2(aq)}$ and $SiO_{2(aq)}$ in fact represent a range of possible dissolved species. Incongruent dissolution means that the ratio a/b initially is not equal to x. As the value of x is decreased (or is reduced by continuous leaching), the ratio a/b decreases until, if congruent dissolution is achieved, it becomes equal to x.

The original model proposed by Berner has been adopted as a basis for comparison in the current work. It is recognised that other authors have suggested different approaches, for example using free energies rather than solubility constants or a more correct description of the thermodynamics of non-ideal solutions [6,22]. However, the Berner approach has the merit of simplicity and, for the purposes of predicting long-term chemical conditioning, is believed to provide an equally good representation of the behaviour of CSH gel.

The model of CSH gel dissolution represents the observed incongruent behaviour as a non-ideal solid solution between two congruently soluble components [15,16,21,32]. These components may have compositions that are observed as discrete minerals in nature or may be convenient end members with little basis in reality.

The solubility constants of the end member components of CSH gel are assumed to depend on the Ca/Si ratio of the material and are parameterised by fitting to the experimental solubility data [15]. It is important to note that, although alternative models may be based on a more complete thermodynamic description, the necessary fitting means that they remain empirical models. Consequently, any modifications to the solution chemistry to be modelled require a re-parameterisation of the description of CSH gel dissolution.

The original Berner model was divided into three main regions, defined by the Ca/Si ratio, each of which utilised different expressions for the solubility constants [15]. This

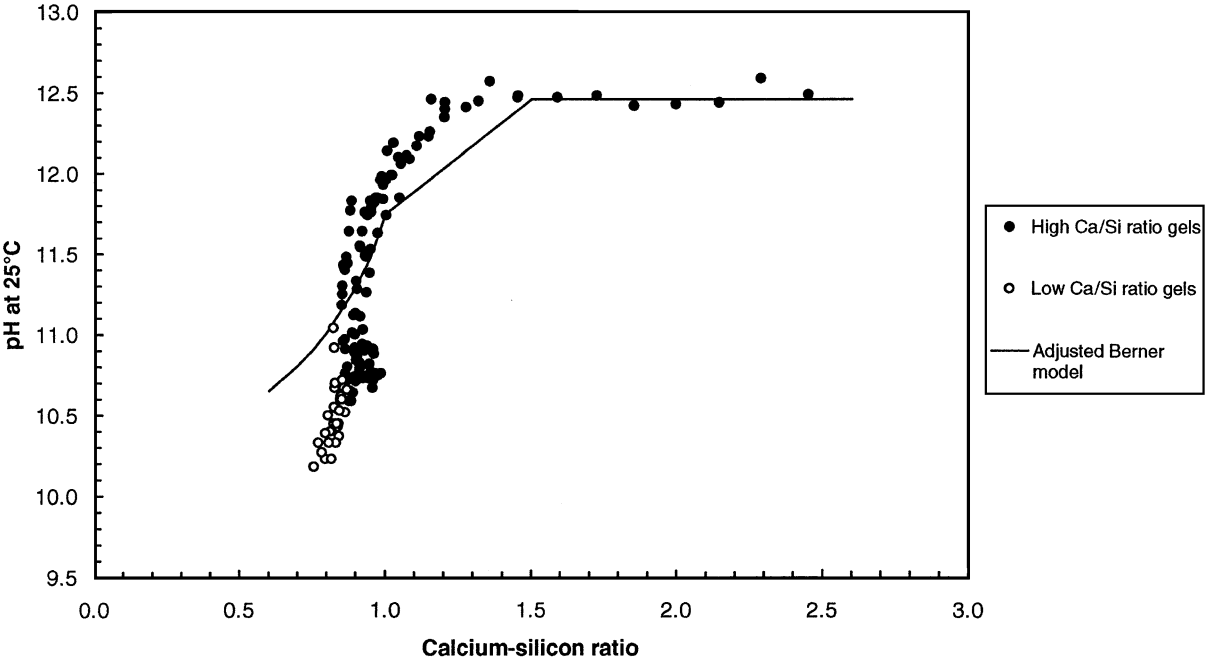

Fig. 10. pH of solution during leaching of CSH gels — comparison of the adjusted Berner model with experimental data.

Table 3
Summary of the leaching model, derived from experimental data for the leaching of synthetic CSH gels by demineralised water

Region	Ca/Si ratio	End member	log K_{sp} value
IV	> 2.5	$Ca(OH)_2$	-5.19
III	1.5–2.5	$Ca(OH)_2$	-5.19
		CaH_2SiO_4	-8.64
II	1.0–1.5	$Ca(OH)_2$	$-4.783-\left(\frac{0.261}{\text{casi}-0.861}\right)$
		CaH_2SiO_4	-8.64
I	0.7–1.0	SiO_2	$-0.471+\frac{1.301}{\text{casi}-1.024}$
		CaH_2SiO_4	$-9.59-\left(\frac{0.024}{\text{casi}-1.025}\right)$

casi = molar Ca/Si ratio in the material.

model subsequently has been adjusted by re-defining the boundaries and including an additional region to make it more consistent with an observed point of inflexion in the data [32]. This adjusted model is summarised in Table 2.

5.2. Modelling of CSH gel leaching

5.2.1. Modelling using the adjusted Berner model

The adjusted Berner model has been used in conjunction with the computer program HARPHRQ to simulate the leaching of the CSH gels by demineralised water [34].

The variation in pH during the leaching of the CSH gels by demineralised water is compared with the predictions of the adjusted Berner model in Figs. 8 and 10. The adjusted Berner model predicts the general trend of the experimental observations. However, the fit is best for the region where Ca/Si exceeds 1.5. This region is assumed to be dominated by the dissolution of calcium hydroxide. Between Ca/Si ratios of 1.5 and 1.0, the model tends to predict a lower pH than observed. In contrast, for Ca/Si ratios of less than 1.0, the adjusted Berner model may predict a higher pH than observed and does not predict congruency at the same point.

5.2.2. Development of a model based on leaching results

The results of the modelling described above show that the adjusted Berner model does not necessarily provide a good prediction of the variation in pH with degree of leaching. To take account of potential differences in the behaviour of unleached and leached CSH gels, a revised model has been developed based on the results of the CSH gel leaching experiments to improve the fit to experimental data. The formulae describing the two regions of the Berner model where discrepancies were observed between prediction and experimental results were refitted using the results of the CSH gel leaching experiments. Major changes to the model were not justified by these data, so the revision was limited to a change in the expression for the equilibrium constants and updating for consistency with recent information on calcium hydroxide and silica aqueous species in the HATCHES database [35].

The experimental data cover the range of Ca/Si ratios down to approximately 0.7. Consequently, the modifications to model for the region including Ca/Si ratios of less than 1.0 are limited. The model parameters are given in Table 3. A comparison of the experimentally measured pH with that obtained from the leaching model is shown in Fig. 11. Comparison with Fig. 10 shows that the fit with experimental data has improved.

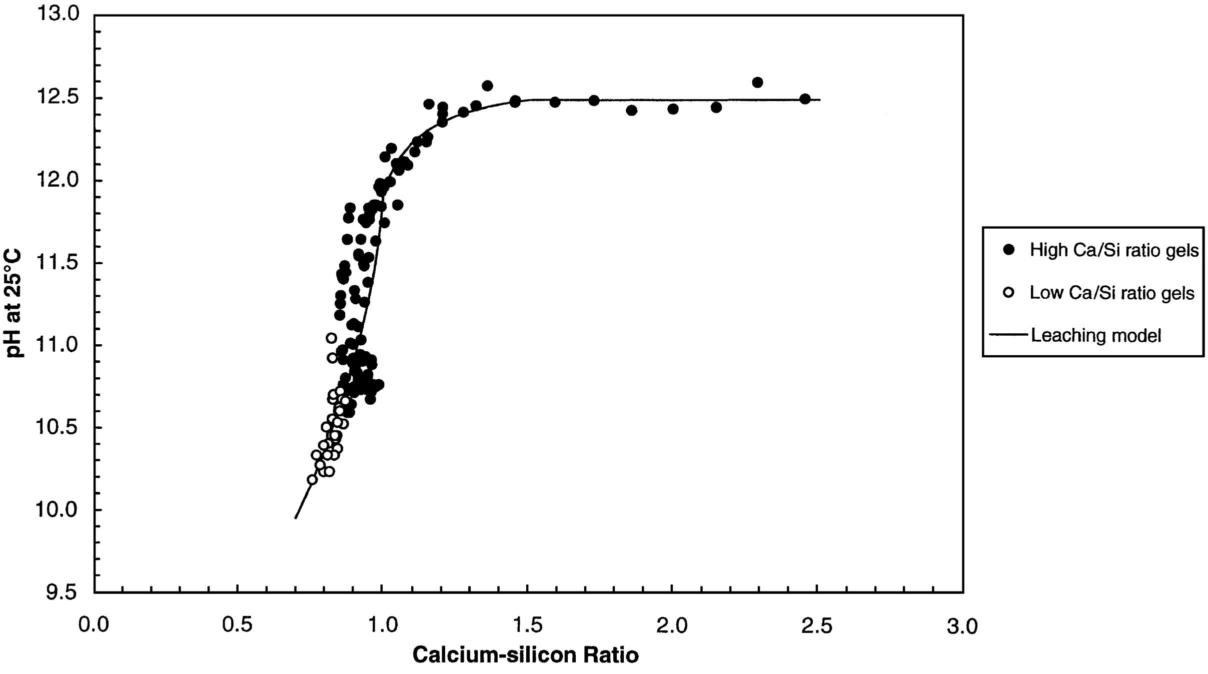

Fig. 11. pH of solution during leaching of CSH gels—comparison of the leaching model with experimental data.

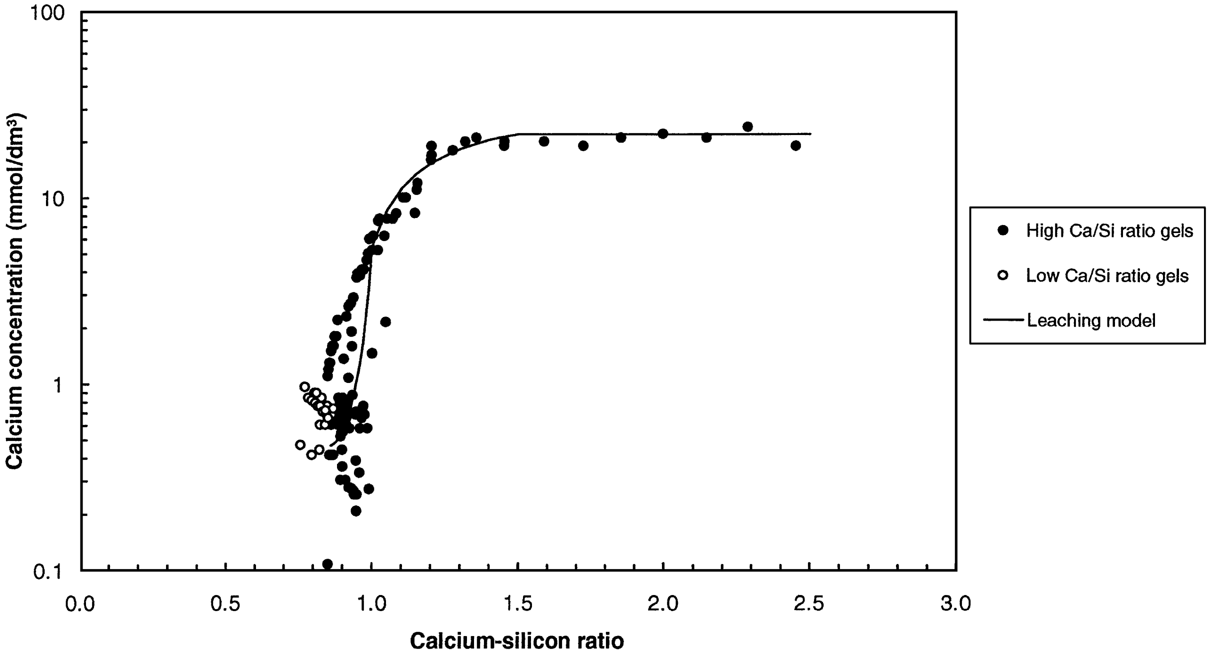

Fig. 12. Evolution of calcium concentration during the leaching of CSH gels — comparison of the leaching model with experimental results.

Fig. 12 illustrates the modelled variation in calcium concentration and compares this with the observed behaviour. Since, in practice, it is not possible to reach the lower Ca/Si ratios by leaching of CSH gels, the fit is terminated at the congruent point.

A limited number of experimental measurements of the concentration of silicon in the leachate are reported above. These have been used in the revision of the model. Fig. 13 shows that the revised model may slightly underestimate the silicon concentration when the Ca/Si ratio is lower, although this discrepancy is not large. It is noted that the silicon concentrations for the higher Ca/Si ratio gels are always less than 10^{-3} mol dm^{-3} and are therefore lower than are generally predicted by static dissolution measurements.

It can be seen that the fit is generally improved and, given the experimental uncertainties, is adequate to describe the leaching of CSH gels in demineralised water.

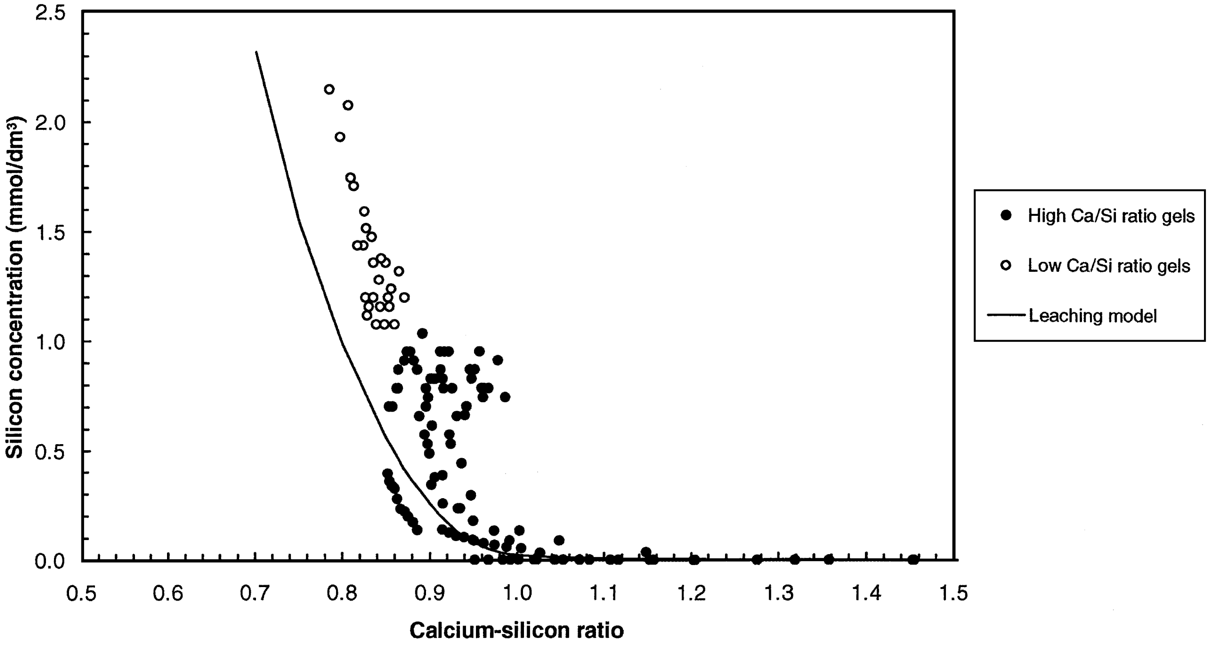

Fig. 13. Evolution of silicon concentration during the leaching of CSH gels — comparison of the leaching model with experimental results.

6. Conclusions

The behaviour of synthetic CSH gels during extended leaching in demineralised water has been studied. The results have been compared with previously existing models based on the dissolution of gels at constant composition to test the validity of some of the assumptions underlying existing models of cement leaching.

The results confirm that the leaching of CSH gels in demineralised water initially may be described as incongruent dissolution, followed by an approach to congruent dissolution. This behaviour is broadly similar to that predicted from the static dissolution of CSH gels. The congruently dissolving composition is found at a Ca/Si ratio of approximately 0.8 to 0.9. This is comparable to the ratio of about 0.8 suggested by static dissolution. However, leaching of CSH gels apparently results in a lower solubility for the congruently dissolving composition.

The observed behaviour is apparently similar to that obtained by leaching of cements. This broadly confirms that synthetic CSH gels are indeed a suitable analogue for the CSH gels formed through the hydration of Portland cement. Some of the observed discrepancies are believed to be due to the presence and leaching of calcium aluminate hydrate minerals in actual cements. The work reported herein therefore helps validate the modelling of the long-term evolution of conditions in a repository backfilled with cementitious materials.

The results of the experiments have been compared with calculations based on an adjusted version of the Berner model of CSH gel dissolution. In demineralised water, the experiments and model are in good agreement for lower degrees of leaching (higher Ca/Si ratios), but some divergence is observed for higher degrees of leaching. A revised model of CSH gel leaching has been proposed, based on direct measurements of the behaviour of CSH gels. This leaching model provides an improved fit to the experimental results compared with the adjusted Berner model.

Acknowledgments

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