

Interaction between Salts (NaCl, CsCl) and Calcium Silicate Hydrates (C–S–H)

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High resolution ^{29}Si , ^{23}Na , and ^{133}Cs solid-state NMR spectroscopy was used to study the interaction of sodium and cesium chloride salts with calcium silicate hydrates (C–S–H), the main components of hydrated Portland cement. Spectra were collected at different levels of moisture and suggested that Cs^+ and Na^+ in contact with C–S–H behaved differently, mainly because of their different hydration energy, which is smaller for Cs^+ than for Na^+ . An interpretation of the results is given, using a conceptual model based on an analogy between C–S–H and smectites, which present analogous structural features. The results suggest that cesium and sodium have an affinity for the C–S–H surface. In hydrated C–S–H, the cations may be located in a diffuse ion swarm. In dry C–S–H, sodium cations would form outer-sphere complexes, i.e., they would be adsorbed with their hydration sphere, whereas cesium cations would be adsorbed as inner-sphere complexes with two distinct environments, one without chloride and the other with chloride anions in their coordination sphere. At low Ca/Si ratios, the mechanism involved for cationic adsorption is probably a compensation of the negative surface charge of C–S–H.

1. Introduction

Calcium silicate hydrates (C–S–H) are natural minerals (e.g., tobermorite, plombierite) which have been found, in more or less large amounts, in a variety of geological settings.¹ Processes such as the high-temperature low-pressure contact metamorphism and metasomatism of siliceous limestones and calcareous rocks or the zeolitization of basaltic lavas are favorable to their formation. These phases can be well crystallized but are frequently poorly crystalline. The recent renewed interest in C–S–H compounds stems from the fact that about forty of them can be considered as good natural analogues of cement compounds and can therefore give invaluable hints about the long-term durability of these materials in the natural environment.² This is a key issue for the safety of nuclear waste disposal, notably for an underground cement-conditioned repository.³ Thus, it is of great interest to study the interaction between C–S–H and salts, especially sodium and cesium salts, since these very soluble cations are important components of nuclear waste and could migrate easily in natural environments. Preliminary works concerning the retention of cesium by C–S–H^{4,5} have been made. The insertion of aluminum and iron in the layer structure of C–S–H^{6–8} has also been studied.

Unfortunately, the detailed structure of C–S–H is incompletely understood, which considerably limits our capability to decipher the mechanisms of cation retention in this material. A conceptual model of C–S–H is thus necessary to interpret experimental data and to deduce testable predictions for retention mechanisms and to relate these properties to structural characteristics. Smectites, which are swelling clays known for their high capacity of cation retention,^{9–14} can be used to build such a conceptual model because they exhibit a number of structural analogies with C–S–H. Of course, smectites also present notable differences with C–S–H, e.g., the occurrence of a structural charge defect induced by isomorphous substitutions in the silicate layers. Therefore, the concept of analogy is not used here as a mere comparison between the two types of

materials, but rather as a heuristic tool¹⁵ to help us understand the basic properties of C–S–H with respect to cation retention.

2. Background

2.1. The C–S–H Structure. Calcium silicate hydrates are nanocrystalline and porous materials. They form, for example, in aqueous solution from silica and calcium hydroxide. In that case, C–S–H precipitates in the mixture and the higher the molar Ca/Si ratio of the initial mix of solids, the higher the calcium concentration of the equilibrium solution and the Ca/Si ratio of C–S–H. In these conditions, the stoichiometry of pure C–S–H is between Ca/Si = 0.66, and Ca/Si = 1.5. Both limits are invariant points; at Ca/Si = 0.66 silica gel and C–S–H with Ca/Si = 0.66 coexist. At Ca/Si = 1.5, portlandite is in excess and cannot dissolve in the mixture because of its solubility limit.¹⁶ Higher Ca/Si ratios (1.5–2) may be reached in calcium hydroxide supersaturated solutions by hydrating tricalcium or dicalcium silicate for example. C–S–H might be aggregated in platy particles of about 50 nm diameter and 5 nm thickness.^{17–19} However, the nano- and mesostructures have not been resolved definitively. Inside the particles the structure is organized in layers along the thinner direction. The external surface of C–S–H is the particles' surfaces; the internal surface is constituted of the interlayer spaces.

Solid-state NMR studies (^{29}Si MAS NMR) have revealed the presence of silicate tetrahedral linear chains of variable length.^{20–24} In NMR spectroscopy, the silicate tetrahedra are usually designated Q_n , where Q represents a silicon atom and n is the number of siloxane bonds attached to silicon. Thus Q_1 represents an end group of a chain, Q_2 a middle group, Q_3 a chain branching site, and Q_4 a fully cross-linked group. Valuable information concerning the organization of Si–O–Si links can be obtained from the shifts of the ^{29}Si nuclei.^{25–27} In C–S–H at Ca/Si = 0.66, the structure of C–S–H is similar to that of tobermorite^{28–31} in which the chain length is infinite. A layer is composed of two silicate tetrahedral chains running along a

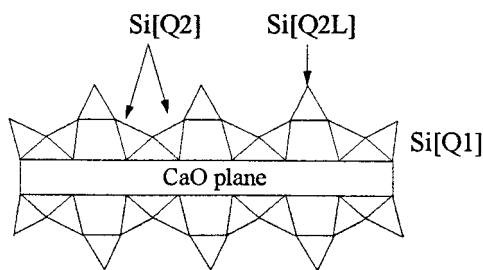


Figure 1. Dreierketten structure of C-S-H.

sheet of calcium where the Ca^{2+} cations are 7-fold coordinated and form a plane. The silicate tetrahedral chains consist of dimers connected by a bridging tetrahedron (dreierketten structure, analogous to that of wollastonite). Using classical NMR nomenclature throughout this manuscript, we shall designate Si[Q2] the nonbridging tetrahedra, Si[Q2L] the bridging tetrahedra, and Si[Q1] the end-chain tetrahedra (Figure 1).

Each Si[Q2] shares all of its oxygen atoms with the calcium of the plane or with the Si[Q2L], whereas the Si[Q2L] tetrahedron has two of its four oxygen atoms unshared. At $\text{Ca}/\text{Si} = 0.66$, these oxygen atoms are protonated to form silanol groups. Water molecules occupy well-defined crystallographic sites in the structure. An increase of Ca/Si from 0.66 to 1 can be obtained by substituting the protons by calcium ions³² (Figure 2). Molecular dynamics simulations revealed that such substitutions make the silicate chains unstable,³³ leading to rupture of the chains. NMR studies^{22,24} showed the presence of Si[Q1] tetrahedra (end-chain tetrahedra) in the C-S-H structure and a decrease of Si[Q2L] and Si[Q2] percentages. At higher Ca/Si ratios, from 1 to 1.5, elimination of the bridging tetrahedra occurs.³² At $\text{Ca}/\text{Si} = 1.5$, the silicate structure is mainly composed of dimers. For ratios of Ca/Si higher than 1.5, $\text{Ca}(\text{OH})_2$ may be in the interlayer space.²²

The structure of C-S-H presents different analogies with that of smectites: both have "Te-Oc-Te" units in their layer structure. However, in C-S-H, the tetrahedral sheets are formed by SiO_2 linear chains, whereas in smectites they are silicate sheets. The calcium sheet in C-S-H, even if calcium atoms do not have an octahedral coordination,³¹ may be analogous to the octahedral plane of smectites. In both cases, the study of the interaction with cationic species will rely on an adsorption phenomenon onto a charged surface.

2.2. Structure and Cationic Retention of Smectites.^{34,35} The capacity of a smectite for cationic retention is due to isomor-

phous substitutions that take place in the tetrahedral sheet, where Si^{4+} can be substituted by Al^{3+} or Fe^{3+} , and in the octahedral sheet, where Al^{3+} can be replaced by Fe^{2+} or Mg^{2+} (aluminum smectites) or Mg^{2+} by Li^+ (magnesium smectites). These substitutions lead to a deficit of positive charges in the smectite layers, i.e., they carry a negative charge, which is compensated by insertion of cations in the interlayer space. These cations are mobile in the structure, i.e., they jump fast from one crystallographic site to another, as shown by NMR studies.^{38,42}

The retention of cations in the structure of smectites greatly depends on the hydration state of the sample and on the hydration energy of the cation. Studies have been made on the cationic retention power of smectites as a function of hydration to characterize the structural environment of the cation.³⁸⁻⁴² Here, a similar work has been made on C-S-H to compare the behavior of each mineral toward the interaction with cations.

2.3. Objectives of the Study. Considering the analogy between C-S-H and smectites, the interesting question that could be raised concerns the actual possibility of whether C-S-H retains cations or not. If some insertion occurs, it would be worthwhile to investigate the possible interaction mechanisms in comparison to those occurring in smectites.

High-resolution solid-state NMR techniques have proven useful to characterize the structural sites occupied by cations adsorbed on smectites, especially sodium and cesium.³⁸⁻⁴² Indeed, ^{133}Cs and ^{23}Na both have 100% natural abundance and good NMR sensitivities. Moreover, these nuclei have small electric quadrupolar moments (narrow line widths). Thus, information about the cationic environment can be directly deduced from chemical shifts.

This paper presents results obtained on the interaction of C-S-H with two alkali salts: NaCl and CsCl. Cs^+ is one of the most problematic cations in the context of radioactive waste disposal, first because two of its radioactive isotopes have long or very long half-lives (^{137}Cs , 30.2 years; ^{135}Cs , 2.3×10^6 years) and second because it is an extremely mobile element in geological environments, very poorly sorbed by mineral surfaces. Na^+ is one of the species retained in the interlayer space of smectites studied in the literature and is responsible for their swelling. Multinuclear high-resolution solid-state NMR (^{29}Si , ^{23}Na , and ^{133}Cs) was used as the main characterization technique. The influence of the C-S-H initial composition and the water content of the C-S-H samples was studied. A possible interpretation of the results obtained will consider the hydration sphere and hydration energy of the cations.

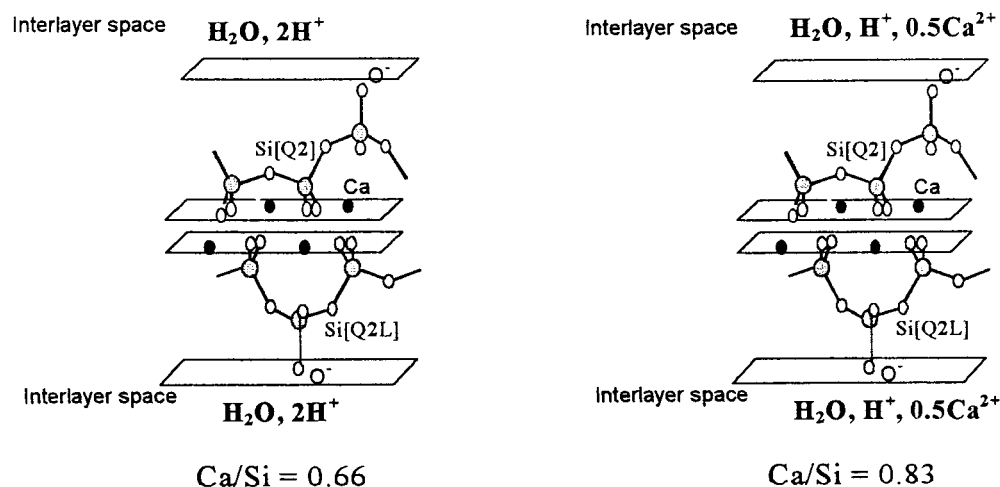


Figure 2. Proposed structure of C-S-H for $\text{Ca}/\text{Si} = 0.66$ and $\text{Ca}/\text{Si} = 0.83$.

TABLE 1: Parameters Used for NMR Experiments

nucleus	freq (MHz)	ZrO ₂ MAS probe (mm)	spinning rate (MAS) (kHz)	acq time (h)	rep time (s)	ref used
²⁹ Si (I=1/2)	59.63	7	4	8	30	TMS
²³ Na (I=3/2)	79.38	4	7	2	1	NaCl 0.1 M
¹³³ Cs (I=7/2)	39.36	4	≈7	6	10	CsCl 0.1 M

3. Experimental Section

3.1. Materials. All of the samples were synthesized at room temperature from calcium hydroxide that had been freshly dehydrated and decarbonated at 1000 °C for 12 h and silica ("Aerosil 200", Degussa). Freshly demineralized and decarbonated water was added so that the water/solid ratio equalled 50 (1.8 g of dry solid for 90 mL of water). Three series of samples were prepared: A, B, and C series. For each series, four compositions were prepared (Ca/Si of the initial mixture: 0.66, 0.83, 1.2, and 1.7). In the A series, no salt was added. In the B and C series, CsCl and NaCl were added, respectively, after three weeks so as to have a salt concentration of 0.5 M. The mixtures were kept under nitrogen atmosphere without stirring.

In such conditions, after about three days,⁵ the ionic concentrations in the solution do not evolve anymore. After three more weeks, all of the samples were filtered. One part of each sample was kept at 100% moisture, the other part was freeze-dried for 10 days (−20 °C, under vacuum). These samples were then analyzed by several techniques: X-ray diffraction, elemental analyses, and multinuclear NMR (²³Na, ¹³³Cs, ²⁹Si). In what follows, the samples with added CsCl will be denoted: Cs-C-S-H, and the samples with added NaCl: Na-C-S-H.

3.2. Methods. X-ray diffraction data were recorded using a Siemens D-500 powder diffractometer with CuKα radiation. The goniometer speed was 0.02°/s. Solid-state NMR spectra were acquired on a Bruker DMX-300 (7.1T) spectrometer. The different parameters of the experiments are given in Table 1. The spectra were recorded in static or magic angle spinning (MAS) conditions.

The ²⁹Si NMR spectra were accumulated using single- $\pi/2$ -pulse excitation and high-power ¹H decoupling with a 60 kHz-rf-field. For quadrupolar nuclei, such as ²³Na and ¹³³Cs, such $\pi/2$ pulses are not quantitative. For the present study, the proportions of the lines had to be determined. $\pi/12$ Pulses were then used for ²³Na and ¹³³Cs MAS NMR, which allowed quantification of the occupation of the sites.⁴³ The spectra were treated using the WINNMR program and were simulated using a modified version of the Winit Bruker program.⁴⁴

4. Results

4.1. Chemical Analyses. Chemical analyses of the freeze-dried C-S-H are given in Table 2 and reveal high Cs/Si and Na/Si ratios in the solids. The Cs/Cl and Na/Cl ratios reveal an excess of cations relative to chloride anions, especially at low Ca/Si ratios (<1), which may indicate an interaction between cesium or sodium cations and the silicate C-S-H surface. However, because of the uncertainty on the weight percentages, caution must be taken on the Cs/Cl and Na/Cl evaluation.

4.2. X-ray Diffraction Results. The phase composition of the solid was controlled by X-ray diffraction analyses. Addition of a salt to the C-S-H leads to the precipitation of CsCl and NaCl in the B and C series, respectively, during freeze-drying of the sample. Figure 3 presents the X-ray diffractograms of freeze-dried samples A1, B1, and C1 (Ca/Si = 0.6). Observation

TABLE 2: Chemical Analyses of the Freeze-Dried Samples (10 Days of Freeze-Drying)^a

A Series								
sample	introduced Ca/Si	% Ca	% Si	solid Ca/Si				
A1	0.66	19.5	23.5	0.6				
A2	0.83	23	22	0.7				
A3	1.2	27	18.5	1.0				
A4	1.7	28.5	15	1.3				

B Series								
sample	introduced Ca/Si	% Ca	% Si	% Cs	% Cl	solid Ca/Si	solid Cs/Si	solid Cs/Cl
B1	0.66	10.5	12	36.5	8.5	0.6	0.6	1.1
B2	0.83	11	10	40	10	0.8	0.8	1.05
B3	1.2	13.5	9	35.5	10	1.0	0.8	0.95
B4	1.7	18	9	28.5	8.5	1.4	0.7	0.9

C Series								
sample	introduced Ca/Si	% Ca	% Si	% Na	% Cl	solid Ca/Si	solid Na/Si	solid Na/Cl
C1	0.66	15	16	10	12.5	0.6	0.8	1.25
C2	0.83	16	15.5	11	15	0.7	0.9	1.1
C3	1.2	20	13	10	15	1.1	0.9	1.0
C4	1.7	25	12	8	12.5	1.5	0.8	1.0

^a The introduced Ca/Si is the initial molar ratio between CaO and SiO₂ in the synthesized suspension. The % are determined by elemental analyses of the solid C-S-H, and they are given as weight percentages (precision ± 3%). The solid ratios are molar ratios and are calculated from the elemental analyses results.

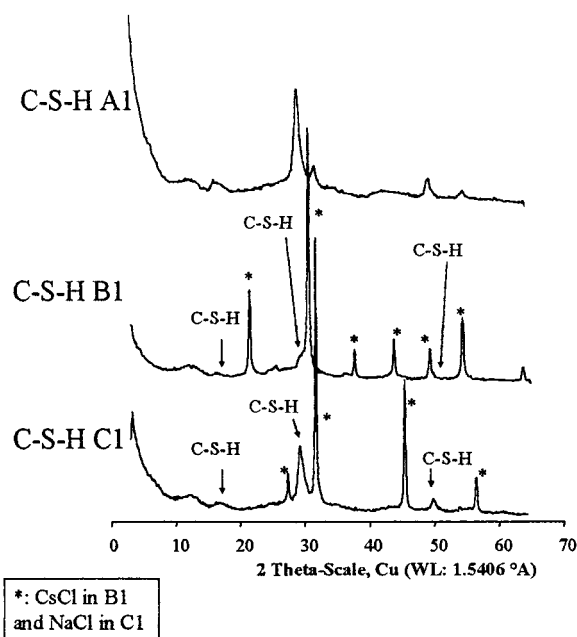


Figure 3. X-ray diffractograms of A1, B1, and C1 freeze-dried C-S-H sample (C-S-H with Ca/Si = 0.6, pure, with added CsCl, and with added NaCl, respectively).

of these diagrams leads to the conclusion that in Cs-C-S-H, there is a loss of crystallinity as a result of adjunction of CsCl.

4.3. ²⁹Si MAS NMR results. *Salt-free C-S-H.* Figure 4 presents the ²⁹Si NMR spectra of synthesized pure C-S-H (A series) as a function of the Ca/Si ratio in the solid. The resonances are assigned according to works carried out at Saclay.²² At low Ca/Si, the resonance at −85 ppm is attributed to Q2 silicon tetrahedra connected to two other silicon atoms. A second resonance is present at −82.5 ppm, the intensity of which is about half that of the Q2 resonance and which is assigned to Q2L (bridging tetrahedra). At Ca/Si = 0.7, a new

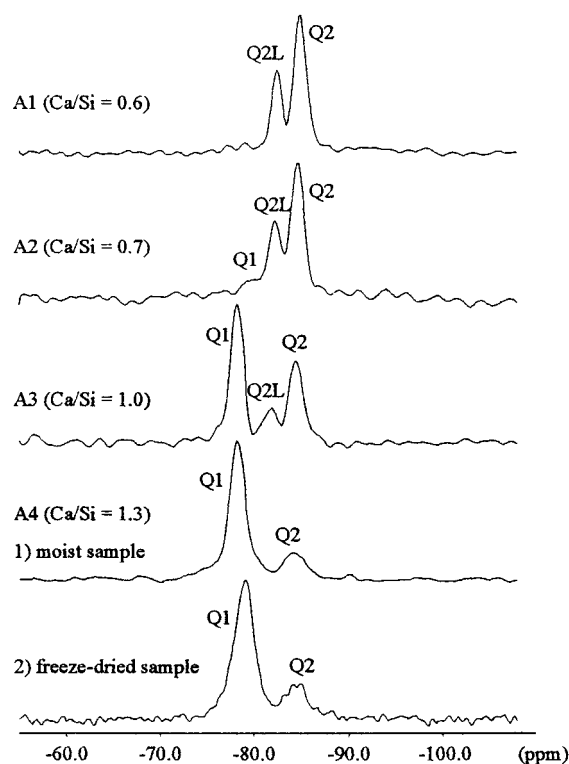


Figure 4. ^{29}Si MAS NMR spectra (4 kHz) of the A series (pure C-S-H).

TABLE 3: Results of ^{29}Si MAS NMR Experiments (4 kHz) on Moist Samples of A, B, and C Series and on A4 Freeze-Dried Sample^a

sample	δ Q1 (ppm)	δ Q2L (ppm)	δ Q2 (ppm)	% Q1	% Q2L	% Q2
A series pure C-S-H						
A1 (Ca/Si = 0.6)		-82.5	-85.0	0	30	70
A2 (Ca/Si = 0.7)	-79.5	-82.5	-84.7	5	30	65
A3 (Ca/Si = 1.0)	-78.3	-81.8	-84.5	60		40
A4 (Ca/Si = 1.3)	-78.2		-84.4	80	20	
Freeze-dried A4	-79.0		-84.6	85	15	
B series Cs-C-S-H						
B1 (Ca/Si = 0.6)		-82.1	-84.7	0	30	70
B2 (Ca/Si = 0.8)	-79.1	-81.9	-84.6	10	20	70
B3 (Ca/Si = 1.0)	-78.1	-81.7	-84.3	60		40
B4 (Ca/Si = 1.4)	-77.8		-83.7	90	10	
C series Na-C-S-H						
C1 (Ca/Si = 0.6)		-82.1	-84.7	0	25	75
C2 (Ca/Si = 0.7)	-78.8	-82.1	-84.7	10	25	65
C3 (Ca/Si = 1.1)	-78.2	-81.6	-84.3	60		40
C4 (Ca/Si = 1.5)	-77.8		-83.4	85	15	

^a The percentages are given with $\pm 5\%$ uncertainty.

resonance appears at -79.5 ppm. It is assigned to Q1 tetrahedra, i.e., silicon at the end of the chains. The intensity of the Q1 resonance increases with the Ca/Si ratio, indicating that rupture of the chains occurs. This is confirmed by the parallel decrease of the Q2 contribution. These spectra agree with the dreierketten structure of the silicon chains in the C-S-H, with one bridging tetrahedra for two nonbridging ones (Figure 1). As Ca/Si increases, fitting the Q2 and Q2L resonances becomes difficult, owing to the uncertainty in defining the correct baseline. Thus, the proportions of Q2L and Q2 tetrahedra have not been determined for $\text{Ca/Si} \geq 1$ (Table 3).

The spectra were performed on 100% moist samples. A comparison between a ^{29}Si NMR spectrum of a moist C-S-H at high Ca/Si (short silicate chains) and the same freeze-dried C-S-H showed that no polymerization of the chains occurs

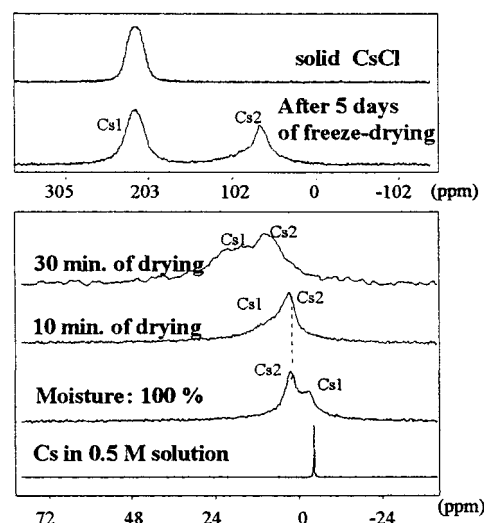


Figure 5. Static ^{133}Cs NMR spectra of C-S-H B2 (Ca/Si = 0.8) with different moisture. The reference used is CsCl 1 M.

upon freeze-drying (Figure 4 and Table 3). However, ^{29}Si NMR measurements on moist samples allow better resolution of the spectra. Indeed, in the presence of water, the hydrogen atoms of the C-S-H structure are easily exchanged with the protons of water adsorbed at the C-S-H surface, since protons are mobile in the structure and they are thus better decoupled from silicon. The heteronuclear interactions between Si and H, a source of peak broadening, are then partially averaged. Thus, all of the ^{29}Si NMR spectra of C-S-H with added salts were performed on moist samples.

With Alkaline Cations. Table 3 is a summary of the NMR results where the chemical shifts and the proportions of each resonance are indicated for the three series. The tetrahedral chains do not seem to be modified when C-S-H are in contact with salts, whatever the Ca/Si ratio. However, the chemical shifts are moved to higher values by the salts relative to pure C-S-H.

4.4. ^{133}Cs NMR Results (B series). Effect of Moisture. First, we observed the effect of moisture on a C-S-H with a final Ca/Si ratio of 0.8 (B2 sample). Two cesium resonances were observed in the ^{133}Cs static spectra of this C-S-H sample (Figure 5). The chemical shifts of both resonances are greatly modified by drying, in that they are less and less shielded (more positive chemical shifts). At 100% moisture, the Cs₁ resonance has a chemical shift analogous to Cs⁺ in solution; its chemical shift moves toward low field more rapidly than the Cs₂ resonance. After 5 days of drying, the Cs₁ resonance, which has spinning sidebands on the MAS spectrum (Figure 6), has the same chemical shift as solid CsCl. X-ray diffraction data show that CsCl is indeed present in the freeze-dried sample. The measured chemical shift for CsCl salt (227 ppm) is in agreement with the NMR data in the literature.⁴⁵ It can therefore be concluded that some cesium precipitates as CsCl as the sample dries, which is considered an artifact of freeze-drying. The proportion of both resonances Cs₁ and Cs₂ changes during drying: Cs₂ dominates at the beginning of drying, whereas Cs₁ presents the major contribution to the spectrum after several days of drying. Figure 6 also shows the ^{133}Cs MAS NMR spectrum of B2 C-S-H sample (Ca/Si = 0.8) freeze-dried for 10 days. This spectrum provides evidence for different Cs environments than in the moist C-S-H or the C-S-H freeze-dried for 5 days. The decrease in water content between five and 10 days of freeze-drying is about 20% relative to the weight of dry solid. CsCl salt (Cs₁ site) has a cubic structure, so its

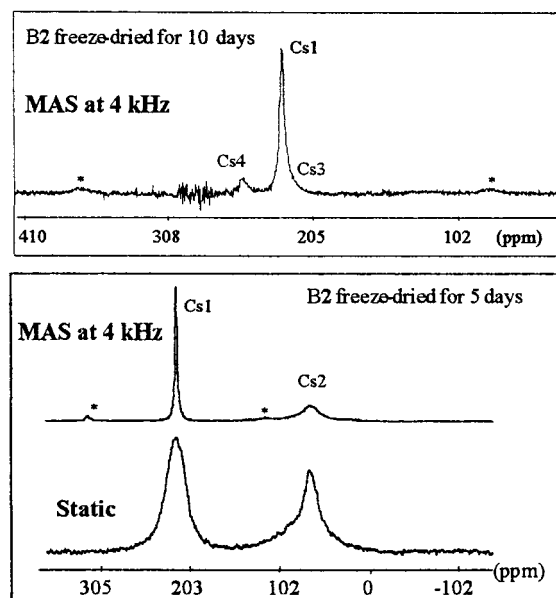


Figure 6. ^{133}Cs static and MAS (4 kHz) NMR spectra of C-S-H B2 (Ca/Si = 0.8) after 5 days of freeze-drying, comparison with ^{133}Cs MAS (4 kHz) NMR spectrum of C-S-H B2 after 10 days of freeze-drying. Asterisk (*): rotational bands.

NMR spectra in static or MAS conditions have no quadrupolar shape.⁴⁶ Thus, there are actually two contributions to the major resonance. The so-called Cs_3 resonance has almost the same chemical shift as solid CsCl. Another cesium site, designated Cs_4 (250 ppm), is present in the C-S-H.

Mobility of Cesium in the Cs_2 Site. In the ^{133}Cs MAS spectrum of the B2 C-S-H sample freeze-dried for 5 days (Figure 6), the Cs_2 resonance does not seem to have spinning sidebands, unlike the Cs_1 site. Moreover, although magic angle spinning allows the averaging of the dipolar and quadrupolar interactions, which are responsible for resonance broadening,^{47–49} the Cs_2 contribution remains broad on the MAS spectrum. The resonance width is, in fact, the same in the static and the MAS spectra. So the second contribution seems to be unaffected by spinning, and this can be interpreted as the occurrence of rapid cesium movements between different sites having different chemical shifts. Thus, it can be concluded that cesium cations in the Cs_2 site move rapidly inside a population of equivalent sites. Cesium in the Cs_2 site is hence mobile.

Ca/Si Effect on the Sites for Freeze-Dried Samples. Figure 7 gives the evolution of the ^{133}Cs NMR spectra of the C-S-H samples freeze-dried for 10 days, with increasing Ca/Si ratios. As Ca/Si increases, the proportion of Cs_3 and Cs_4 sites greatly decreases until disappearance, whereas their chemical shifts are not really modified by changing the Ca/Si ratio (Table 4).

4.5. ^{23}Na NMR Results (C series). Ca/Si Effect on the Sites for 10 Day Freeze-Dried Samples. A ^{23}Na MAS NMR spectrum of a C-S-H with Ca/Si = 1.1 (C3 sample) shows that two contributions can be observed (Figure 8). The major resonance (Na_1) presents spinning sidebands. This site may be assigned to NaCl salt which has precipitated during freeze-drying (comparing the present results with those obtained with the samples containing added CsCl). This is further confirmed by both the observation that Na_1 has the same chemical shift as solid NaCl (Figure 8) and the X-ray diffraction data. The chemical shift obtained for NaCl salt (7.7 ppm) is in agreement with the NMR data found in the literature.⁴⁵ Another site, designated Na_2 , is also observed. This second resonance does

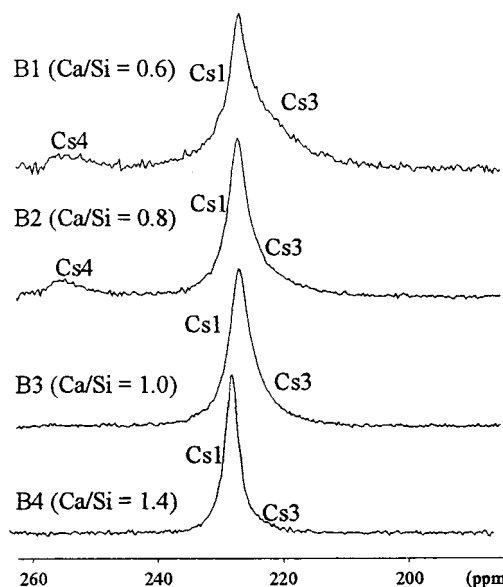


Figure 7. ^{133}Cs MAS NMR spectra of freeze-dried C-S-H (10 days) with different Ca/Si.

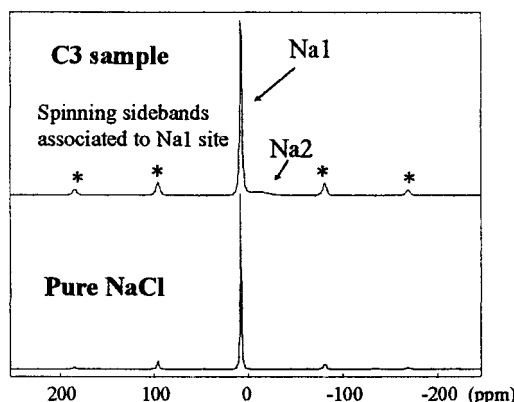


Figure 8. ^{23}Na MAS NMR spectrum at 7 kHz of a freeze-dried C-S-H sample with NaCl at Ca/Si = 1.1 (C3 sample). Comparison with ^{23}Na MAS NMR spectrum of pure NaCl.

TABLE 4: Results of ^{133}Cs MAS NMR Experiments on Freeze-Dried Samples (10 Days) of the B Series: Chemical Shift Values of the Different Sites

sample	NMR method	δCs_1 (ppm)	δCs_3 (ppm)	δCs_4 (ppm)
B1 (Ca/Si = 0.6)	MAS (8.2 kHz)	227	225	254
B2 (Ca/Si = 0.8)	MAS (5.7 kHz)	227	223	255
B3 (Ca/Si = 1.0)	MAS (7 kHz)	227	224	
B4 (Ca/Si = 1.4)	MAS (8.6 kHz)	227	222	

not present sidebands. By comparison with cesium, sodium in the Na_2 site seems to be mobile. Figure 9 gives the evolution of the ^{23}Na NMR spectra of the Na-C-S-H freeze-dried samples for increasing Ca/Si ratios. The results suggest that the second site, Na_2 , has approximately always the same chemical shift (Table 5) and also has the same contribution compared to the Na_1 site, whatever the Ca/Si ratio. The variation of the proportions of Na_1 and Na_2 sites, as a function of Ca/Si, seems then to be less apparent than in samples with added CsCl.

Influence of Moisture. As in the case of cesium, the proportions of Na_1 and Na_2 sites vary greatly during drying. At high moisture the Na_2 site is predominant, and at low moisture it becomes minor (Figure 10). For sample C1 (Ca/Si = 0.6), the shift of the Na_2 site is -1.5 ppm at 100% moisture, and it becomes -14 ppm after 10 days of freeze-drying. The Na_1 site

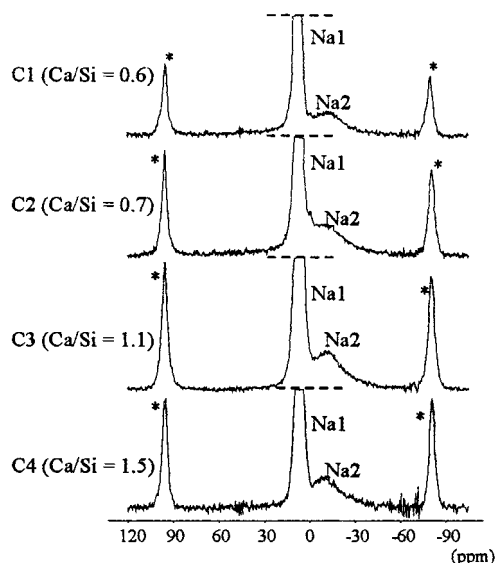


Figure 9. ^{23}Na MAS NMR spectra of freeze-dried C-S-H (10 days) with different Ca/Si.

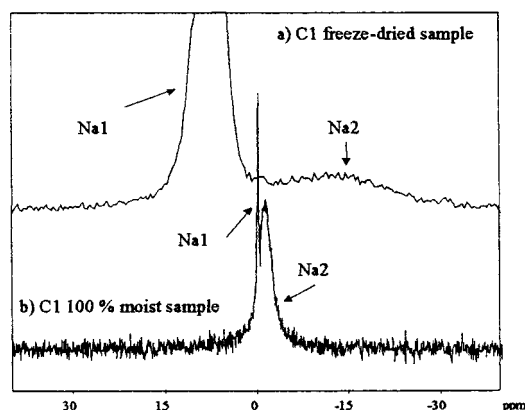


Figure 10. Comparison between ^{23}Na MAS NMR spectra (7 kHz) of C1 sample (C-S-H with NaCl, Ca/Si = 0.6). (a) Freeze-dried sample (10 days). (b) 100% moist sample.

TABLE 5: Results of ^{23}Na MAS NMR Experiments on Freeze-Dried Samples (10 Days) of the C Series: Chemical Shift Values of the Different Sites

sample	NMR method	δNa1 (ppm)	δNa2 (ppm)
C1 (Ca/Si = 0.6)	MAS (7 kHz)	7.7	-14
C2 (Ca/Si = 0.7)	MAS (7 kHz)	7.7	-12
C3 (Ca/Si = 1.1)	MAS (7 kHz)	7.7	-13
C4 (Ca/Si = 1.5)	MAS (7 kHz)	7.7	-13

is at -0.3 ppm at 100% moisture (Na^+ in aqueous solution) and shifts toward 7.7 ppm in the freeze-dried samples (solid NaCl).

5. Discussion

5.1. The C-S-H Dreierketten Structure. The ^{29}Si NMR results on pure C-S-H, where $\text{Q2L}/\text{Q2} \approx 0.5$, are in agreement with the dreierketten model of C-S-H previously proposed in the literature^{20-24,28-30} (Figure 4 and Table 3). The following interpretations will therefore be based on this model. From ^{29}Si NMR results (Table 3), the structure of the silicate chains in the C-S-H does not seem to be affected by the presence of salts. So, the dreierketten structure of C-S-H is maintained. However, the chemical shifts are a little higher (less negative) when C-S-H is in contact with a concentrated electrolytic solution. This tendency may be related to an effect of magnetic

susceptibility of the interstitial solution of the C-S-H, which increases with its ionic concentration. An additional constant magnetic field would be created in the C-S-H sample, which slightly shifts the resonances.⁵⁰

5.2. Behavior of Alkaline Cations in Smectites. Sposito defined cation fixation at mineral surfaces.⁵¹ The following definitions are now well-known and classical in mineral studies. In general, cations in contact with a mineral surface may form two types of complexes: inner-sphere complexes or outer-sphere ones. Inner-sphere complexes are in direct contact with the oxygen atoms of the mineral surface, with an incomplete hydration sphere, i.e., no water molecule between the cation and the surface. Outer-sphere complexes are fully hydrated and have only a weak interaction with the surface. Which type of complex forms depends on cationic hydration considerations. Concerning adsorption of sodium and cesium in the interlayer space of smectites, Na^+ usually forms outer-sphere complexes, whereas Cs^+ can form outer- or inner-sphere complexes.^{38,40,42} Indeed, Cs^+ has a lower hydration energy (-227 kJ mol^{-1}) than Na^+ (-405 kJ mol^{-1})^{42,52-54}. The water content of the analyzed sample then has a great influence on the behavior of each cation retained in the smectite. NMR chemical shifts are good indicators of the hydration state of the studied cation.^{41,55,56} Thus, NMR studies have allowed a description of how these cations are fixed in the structure of smectites.³⁸⁻⁴² Cation fixation and selectivity are determined by the interaction of two forces, namely, the force of attraction of the cation for a hydration shell of water (described by the cation hydration energy) and the electrostatic attraction between the cation and the smectite layer.⁵⁷ Large monovalent cations (of which cesium is the largest) have small hydration energies, so the electrostatic attraction between the cation and the clay can be large, and therefore they are preferentially adsorbed.³⁸ Weiss observed a loss of hydration of cesium cations and a bonding of cesium directly to the basal oxygen atoms when decreasing the level of hydration of the clay minerals.⁴¹ Indeed, unlike strongly hydrated cations (such as sodium), weakly hydrated cations (cesium) are expected to come into direct contact with the surface, pushing aside the water molecules separating the cation from the surface.^{41,58} Moreover, it has been observed that when the water content of smectites increases, the sodium cations with their hydration spheres are progressively detached from the surface and form a diffuse ion swarm.⁵⁹

In the present study, the electrostatic interaction between the alkaline cations and the C-S-H surface samples is analyzed by analogy with smectites, introducing three site categories: diffuse ion swarm, inner-sphere, and outer-sphere complexes.

5.3. Existence of a Diffuse Ion Swarm. The proportions of Cs_1 and Cs_2 sites vary greatly when drying the sample, as seen in Figure 5. In moist samples, the Cs_1 resonance may be assigned to alkaline cations in aqueous solution in the pores of C-S-H. As seen in Figure 5 the chemical shift of the Cs_1 site increases when the sample moisture decreases. This tendency is in agreement with the NMR data on cesium solutions, which show that the chemical shift of Cs^+ increases with the concentration of salt in solution.^{46,60,61} The Cs_2 site gives the main contribution in moist samples, and its intensity decreases upon freeze-drying. Moreover, the chemical shift of the Cs_2 site increases upon freeze-drying, paralleling that of the Cs_1 site. A possible interpretation would rely on the existence of a diffuse ion swarm at the C-S-H surface. When the C-S-H structure is fully hydrated (100% moisture), cesium cations interacting with the C-S-H surface (Cs_2) are surrounded by water molecules and behave like cations in solution (the chemical shift of Cs_2 is very

close to that of Cs^+ in dilute solution). At intermediate moisture contents (5 days of freeze-drying), the Cs_2 site may be assigned to cesium cations adsorbed in a diffuse ion swarm, as defined by Sposito.⁵¹ The increasing chemical shift may be related to the increasing concentration of cesium cations at the C–S–H surface, because of freeze-drying. The decrease of the line intensity upon drying is due to precipitation as CsCl salt of the more poorly bound cations.

5.4. Highly Freeze-Dried C–S–H. After 10 days of freeze-drying, the environment of cesium at the C–S–H surface seems to be different. In a 500 °C-dried hectorite, a magnesium smectite, two environments of cesium are observed, which are both dehydrated or nearly dehydrated. One is cesium in a probably 12-coordinated site, which chemical shift is about –120 ppm, the second is cesium in a possibly 9-coordinated site, at about 30 ppm.³⁸ Indeed, in this structure, the ^{133}Cs chemical shifts would decrease with increasing coordination number. Thus, in C–S–H freeze-dried for 10 days, cesium chemical shifts of 200 or 250 ppm may also be assigned to dehydrated cesium cations which would form inner-sphere complexes at the C–S–H surface and which would have a coordination number < 9. However, the exact interpretation of their high chemical shifts remains incompletely understood. Sodium cations have negative chemical shifts in freeze-dried C–S–H samples, which suggests that they would have a higher coordination number than cesium cations. Indeed, the variation of ^{23}Na chemical shifts with the coordination number may be the same as that of ^{133}Cs chemical shifts. Therefore, sodium cations may remain hydrated after drying, as already observed in clays,⁴² and they may form outer-sphere complexes at the C–S–H surface. The number of water molecules per cesium or sodium atom in the freeze-dried C–S–H was not estimated. Indeed, an ignition loss value of C–S–H with added salts would also take into account other kinds of water, such as, for example, water associated with the precipitated salts, since NaCl and especially CsCl are both hygroscopic. Thus, further studies are needed to estimate this parameter.

5.5. Influence of the Ca/Si Ratio. The influence of the Ca/Si ratio is studied on C–S–H freeze-dried for 10 days. The chemical analyses (Table 2) seem to indicate that at low Ca/Si ratios (< 1) there is an excess of cesium or sodium cations relative to chloride anions. It is possible to calculate this excess of cations: about 0.3 cesium or sodium cation for one bridging tetrahedron in the structure at Ca/Si = 0.6, where there is one bridging tetrahedron for three silicon atoms (Figure 1). However, caution must be taken for the chemical analyses which are given with 3% uncertainty, and this value of 0.3 cation is only indicative. Estimating the proportion of the Cs_4 site in freeze-dried B1 sample at about 10% (Figure 7), and the proportion of the Na_2 site in freeze-dried C1 sample at about 15% (Figures 8 and 9), the number of cations is also about 0.3 for one bridging tetrahedron in these sites. Thus, these sites are likely to contain cations which are not compensated by chloride anions in their coordination sphere. They would compensate the negative charge of the C–S–H surface at low Ca/Si ratios because of the two oxygen atoms carried by each bridging tetrahedron. The cations would be able to substitute a part of the protons at the C–S–H surface. The Cs_3 resonance may be assigned to cesium cations adsorbed at the C–S–H surface which would be compensated by a chloride anion in their coordination sphere. This would explain the chemical shift of this site, which is very close to that of CsCl salt. For Na–C–S–H, NMR results (Figure 9) seem to show that no sodium cations adsorbed at the C–S–H surface after freeze-drying are compensated by a

chloride anion in their coordination sphere, which is in agreement with chemical analyses (Table 2).

At high Ca/Si ratios (> 1), specific adsorption of calcium at the C–S–H surface⁶² leads to a competition between alkaline cations and calcium ones, which are doubly charged. There seems to be less and less adsorption of cesium cations with or without chloride anions in their coordination sphere (Figure 7). However, ^{23}Na NMR spectra seem to indicate that sodium cations are still adsorbed at the surface of C–S–H, even at high Ca/Si ratios (Figure 9). Further studies are needed to clarify the behavior of alkaline cations toward adsorption at the C–S–H surface at high Ca/Si ratios.

6. Conclusions

This work characterizes an interaction between alkaline cations and the C–S–H surface. A possible interpretation of the results relies on the structural analogy between C–S–H and smectites and is based on cationic hydration notions. When the C–S–H sample is hydrated, cesium or sodium cations would be in the diffuse ion swarm. In dry samples, cesium cations may be adsorbed as inner-sphere complexes, directly in interaction with the oxygen atoms carried by the bridging silicon without water molecules between them, whereas sodium cations may be adsorbed as outer-sphere complexes with their complete hydration sphere. At low Ca/Si ratios, cesium and sodium cations would compensate the negative charge of the C–S–H surface. Some cesium cations would also be adsorbed with chloride anions in their coordination sphere. At high Ca/Si ratios, the mechanisms of cationic adsorption are not well-understood yet, and further studies are underway. Theoretical models are probably needed for the interaction with salts at high Ca/Si ratios.

It would be of great interest to study the effect of decreasing temperature on the C–S–H samples with added cations, to limit motions in the structure, and then to obtain further information on the different sites involved in the adsorption mechanisms. NMR studies on the interaction of chloride anions with C–S–H will contribute to improve the models proposed for the interaction of C–S–H with salts and allow a better understanding of the mechanisms of charge compensation at the C–S–H surface.

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References and Notes

- (1) McConnell, J. D. C. *Mineral. Mag.* **1954**, *30*, 293.
- (2) Miller, W.; Alexander, R.; Chapman, N.; McKinley, I.; Smellie, J. *Natural analogue studies in the geological disposal of radioactive wastes; Studies in Environmental Sciences 57*; Elsevier: Amsterdam, 1994.
- (3) Petit, J.-C. *Nucl. Technol.* **1996**, *115*, 125.
- (4) Faucon, P.; Charpentier, T.; Henocq, P.; Petit, J.-C.; Virlet, J.; Adenot, F.; *Proceedings of the Scientific Basis for Nuclear Waste Management XXI Symposium*; Materials Research Society; Davos, 1997; 551.
- (5) Faucon, P.; Richet, C.; Lefebvre, C.; Adenot, F.; Jacquinot, J.-F.; Petit, J.-C. *Key Eng. Mater.* **1997**, *132–136*, 2204.
- (6) Faucon, P.; Charpentier, T.; Bertrandie, D.; Nonat, A.; Virlet, J.; Petit J.-C. *Inorg. Chem.* **1998**, *37* (15), 3726.

- (7) (a) Faucon, P.; Charpentier, T.; Nonat, A.; Petit, J.-C. *J. Am. Chem. Soc.* **1998**, *120*, 12075. (b) Faucon, P.; Petit, J.-C.; Charpentier, T.; Jacquinot, J.-F.; Adenot, F. *J. Am. Ceram. Soc.*, in press.
- (8) Faucon, P.; Hammida, R.; Bonville, P.; Petit, J.-C. *J. Mater. Res.*, submitted.
- (9) Swartzen-Allen, S. L.; Matijevic, E. *Chemical Reviews* **1974**, *74* (3), 385.
- (10) Sposito, G.; Prost, R. *Chem. Rev.* **1982**, *82* (6), 553.
- (11) Lubetkin, S. D.; Middleton, S. R.; Ottewill, R. H. 1984 *Philos. Trans. R. Soc. London* **1984**, A 311, 353.
- (12) Odom, I. E. *Philos. Trans. R. Soc. London* **1984**, A 311, 391.
- (13) Fripiat, J. J.; Letellier, M.; Levitz, P. *Philos. Trans. R. Soc. London* **1984**, A 311, 287.
- (14) Laszlo, P. *La Recherche* **1990**, *21* (219), 314.
- (15) Petit J.-C. *Appl. Geochem. Suppl. No. 1* **1992**, 9.
- (16) Greenberg, S. A.; Chang, T. N. *J. of Phys. Chem.* **1965**, *69*, 1151.
- (17) Gauffinet, S.; Finot, E.; Nonat, A. *Experimental study and simulation of C-S-H nucleation and growth*; Proceedings of the Second RILEM Workshop on Hydration and Setting, Dijon France; Nonat A., Mutin J. C., Eds.; RILEM Editions, 1997.
- (18) Gauffinet, S.; Finot, E.; Lesniewska, E.; Nonat, A. *C. R. Acad. Sci. Paris, Earth Planetary Sciences* **1998**, *327*, 231.
- (19) Gauffinet, S.; Finot, E.; Lesniewska, E.; Collin, S.; Nonat, A. *Proceedings of 20th International Conference on Cement Microscopy*, Guadalajara, Mexico; International Cement Microscopy Association: Duncanville, Texas, 1998; 337.
- (20) Grutzeck, M.; Benesi, A.; Fanning, B. *J. Am. Ceram. Soc.* **1989**, *72* (4), 665.
- (21) Bell, G. M. M.; Bensted, J.; Glasser, F. P.; Lachowski, E. E.; Roberts, D. R.; Taylor, M. J. *Adv. Cement Res.* **1990**, *3* (9), 23.
- (22) Klur, I.; Pollet, B.; Virlet, J.; Nonat, A. *Nuclear Magnetic Resonance Spectroscopy of Cement-Based Materials*; Colombet, P., Grimmer, A.-R., Zanni, H., Sozzani, P., Eds.; Springer-Verlag: Berlin, 1998.
- (23) Cong, X.; Kirkpatrick, R. J. *Cem. Conc. Res.* **1993**, *23*, 1065.
- (24) Cong, X.; Kirkpatrick, R. J. *Adv. Cem. Res.* **1995**, *7* (27), 103.
- (25) Engelhardt, G.; Michel, D. *High-resolution solid-state NMR of silicates and zeolites*. Wiley: New York, 1987.
- (26) Magi, M.; Lippmaa, E.; Samoson, A.; Engelhardt, G.; Grimmer, A. R. *J. Phys. Chem.* **1984**, *88*, 1518.
- (27) Colombet, P.; Grimmer, A. R. *Application of NMR spectroscopy to cement science*; Gordon and Breach Science Publishers: Amsterdam, 1994.
- (28) Taylor, H. F. W. *J. Am. Ceram. Soc.* **1986**, *69* (6), 464.
- (29) Taylor, H. F. W. *Adv. Cem. Based Mater.* **1993**, *1*, 38.
- (30) Taylor, H. F. W. *Cement Chemistry*; 2nd ed.; Thomas Telford Edition: London, 1997.
- (31) Hamid, S. A. *Zeitschrift für Kristallographie* **1981**, *154*, 189.
- (32) Nonat, A.; Lecoq, X. *Nuclear Magnetic Resonance Spectroscopy of Cement-Based Materials*; Colombet, P., Grimmer, A.-R., Zanni, H., Sozzani, P., Eds.; Springer-Verlag: Berlin, 1998; p 197.
- (33) Faucon, P.; Delaye, J. M.; Virlet, J. *J. Solid State Chem.* **1996**, *127*, 92.
- (34) Grim, R. E. *Clay Mineralogy*; McGraw-Hill in Geology: London, 1953.
- (35) Guven, N. *Rev. Mineral.* **1988**, *19*, 497.
- (36) Tokuhito, T.; Mattingly, M.; Iton, L. E.; Ahn, M. K. *J. Phys. Chem.* **1989**, *93*, 5584.
- (37) Bank, S.; Bank, J. F.; Ellis, P. D. *J. Phys. Chem.* **1989**, *93*, 4847.
- (38) Weiss, C. A.; Kirkpatrick, R. J.; Altaner, S. P. *Geochim. Cosmochim. Acta* **1990**, *54*, 1655.
- (39) Weiss, C. A.; Kirkpatrick, R. J.; Altaner, S. P. *Am. Mineral.* **1990**, *75*, 970.
- (40) Kim, Y.; Cygan, R. T.; Kirkpatrick, R. J. *Geochim. Cosmochim. Acta* **1996**, *60* (6), 1041.
- (41) Kim, Y.; Kirkpatrick, R. J.; Cygan, R. T. *Geochim. Cosmochim. Acta* **1996**, *60* (21), 4059.
- (42) Kim, Y.; Kirkpatrick, R. J. *Geochim. Cosmochim. Acta* **1997**, *61* (24), 5159.
- (43) Massiot, D.; Bessada, C.; Coutures, J. P.; Taulelle, F. *J. Magn. Reson.* **1990**, *90*, 231.
- (44) Massiot, D.; Thiele, H.; Germanus, A. *Bruker Report* **1994**, *140*, 43.
- (45) Haase, A. R.; Kerber, M. A.; Kessler, D.; Kronenbitter, J.; Kruger, H.; Lutz, O.; Muller, M.; Nolle, A. *Z. Naturforsch.* **1977**, *32a*, 952.
- (46) Hayashi, S.; Hayamizu, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 913.
- (47) Andrew, E. R.; Bradbury, A.; Eades, R. G. *Nature (London)* **1958**, *182*, 1659.
- (48) Andrew, E. R.; Bradbury, A.; Eades, R. G. *Nature (London)* **1959**, *183*, 1802.
- (49) Lowe, I. *Phys. Rev. Lett.* **1959**, *2*, 285.
- (50) VanderHart, D. L. *Encyclopedia of Nuclear Magnetic Resonance*; Grant, D. M., Harris, R. K.; Wiley: Chichester, England, 1996; Volume 5, p 2938.
- (51) Sposito, G. *Chimia* **1989**, *43*, 169.
- (52) Conway, B. E. *Ionic Hydration in Chemistry and Biophysics*; Studies in Physical and Theoretical Chemistry 12; Elsevier: Amsterdam, 1981.
- (53) Ohtaki, H.; Radnai, T. *Chem. Rev.* **1993**, *93*, 1157.
- (54) Hummer, G.; Pratt, L. R.; Garcia, A. E. *J. Phys. Chem.* **1996**, *100*, 1206.
- (55) Laperche, V.; Lambert, J. F.; Prost, R.; Fripiat, J. J. *J. Phys. Chem.* **1990**, *94*, 8821.
- (56) Cases, J. M.; Berend, I.; Besson, G.; François, M.; Uriot, J. P.; Thomas, F.; Poirier, J. E. *Langmuir* **1992**, *8*, 2730.
- (57) Eberl, D. D. *Clay Miner.* **1980**, *28*, 161.
- (58) McBride, M. B. *Environmental Chemistry of Soils*; Oxford University Press: Oxford, 1994.
- (59) Boek, E. S.; Coveney, P. V.; Skipper, N. T. *J. Am. Chem. Soc.* **1995**, *117*, 12608.
- (60) Deverell, C.; Richards, R. E. *Mol. Phys.* **1966**, *10*, 551.
- (61) Halliday, J. D.; Richards, R. E.; Sharp, R. R.; Sharp, F. R. S. *Proc. R. Soc. London* **1969**, A313, 45.
- (62) Nachbaur L.; Nkinamubanzi P.-C.; Mutin J.-C.; Nonat A. *J. Colloid Interface Sci.* **1998**, *202*, 261.