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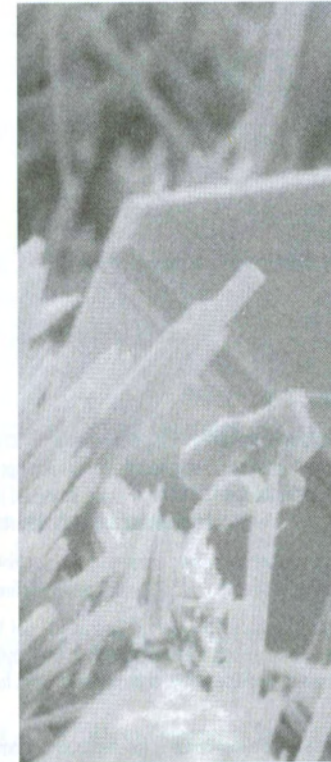
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# Calcium Hydroxide in Concrete

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Magdalena and Jan Skalny with Hal Taylor

## CHLORIDE BINDING TO CEMENT PHASES: EXCHANGE ISOTHERM, $^{35}\text{Cl}$ NMR AND MOLECULAR DYNAMICS MODELING STUDIES

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### ABSTRACT

*Exchange isotherms,  $^{35}\text{Cl}$  NMR spectroscopy, and molecular dynamics modeling probe different time and distance scales relevant to understanding the binding of chloride in cement systems. This paper describes an integrated study of chloride binding to single-phase cement materials using these techniques. Calcium hydroxide shows significant chloride exchange and provides a useful reference point for understanding the chloride exchange behavior of C-S-H and AFm phases.*

### INTRODUCTION

Binding of chloride to the hydration products in cement paste is thought to substantially decrease the rate of chloride penetration into concrete and to increase the time needed for it to participate in depassivation of the protective oxide layer of the reinforcing steel. Previous workers have distinguished three types of chloride in cement pastes: free (solution), sorbed (bound), and lattice (structural) [1-6]. Sorption is thought to both retard the net rate of transport in concrete and to provide a reservoir of chloride for potential detrimental damage [3,7]. The mechanisms of chloride binding and even the binding capacities of the relevant phases are not well understood. This paper presents a brief summary of a combined exchange (sorption) isotherm,  $^{35}\text{Cl}$  NMR and molecular dynamics

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(MD) modeling study of chloride binding to individual hydrated cement phases designed to better understand the structural-chemical factors that control the chloride exchange capacities of the phases present in hydrated cement paste. Sorption isotherm data provide a macroscopic picture of the total binding capacity of a given phase, and modeling of the data with multi-layer theory can provide insight into the sorption mechanisms [8]. The  $^{35}\text{Cl}$  NMR techniques provide a measure of the total binding capacity and insight into the structural environments of the sorbed chloride and its molecular scale dynamical behavior, significantly improving understanding of the sorption isotherm data [9,10]. MD models provide a more specific molecular-scale picture of the surface sorption sites and the dynamics of the motion of chloride at and near the surface and thus further basis for interpreting the isotherms and NMR data [11,12]. Somewhat surprisingly, calcium hydroxide (portlandite) exhibits significant chloride exchange capacity. It provides a useful starting point to understand the chloride exchange behavior of C-S-H and AFm phases.

## EXPERIMENTAL AND COMPUTATIONAL METHODS

The experimental and computational methods used are described in references 8 – 12. Briefly, the exchange isotherm studies were done at room temperature by equilibrating portlandite, the carboaluminate AFm phase ( $\text{C}_4\text{A}\bar{\text{C}}\text{H}_{11}$ ), ettringite, jennite, C-S-H samples with analyzed C/S ratios of 1.5 and 0.9, and aluminous C-S-H samples with C/(S+A) ratios of 0.8 and 1.36 with lime saturated sodium chloride solutions. Solid/solution ratios were 0.2g/25ml, the chloride concentrations varied from 0.005 to 0.1 M, and the pH was about 12.4. Exchange isotherms were calculated using the standard technique of monitoring the change in solution concentration before and after exchange. The  $^{35}\text{Cl}$  NMR experiments were conducted at  $H_0 = 11.7$  T using suspensions of the individual phases in NaCl or KCl solutions and were monitored for chemical shift and  $T_1$  and  $T_2$  relaxation rates. Solid/solution ratios varied to provide stable suspensions. Comparison with the results for neat solutions and suspensions under variable composition and temperature conditions allow investigation of the behavior of the bound chloride. Experiments using variable NaCl solution concentration were conducted at room temperature for portlandite,  $\text{C}_4\text{A}\bar{\text{C}}\text{H}_{11}$ , and jennite. Variable temperature experiments (temperature between 0 and 60 °C) were conducted in 1 M KCl solutions for all the phases listed above.

Molecular dynamics modeling was undertaken for neat 0.25 M NaCl solution, portlandite, the chloroaluminate AFm phase (Friedel's salt), ettringite and tobermorite (model C-S-H) using systems consisting of several unit cells of the

crystal and a layer of 0.25 M NaCl solution 2 to 3 nm thick. This thickness for the solution layer is large enough to effectively exclude direct influence of one interface on another under the periodic boundary conditions used, and the number of water molecules in the layer was chosen to reproduce the density of bulk liquid water under ambient conditions ( $\sim 1 \text{ g/cm}^3$ ). The interaction parameters were modified from the augmented ionic consistent valence force field (CVFF) within the Cerius<sup>2</sup> molecular modeling package (Molecular Simulations Inc., 1998) [13]. Water molecules were modeled using a flexible version of the simple point charge (SPC) interaction potential. Power spectra of atomic motions in the translational, librational, and vibrational frequency ranges and diffusion coefficients for bulk and surface bound chlorides were calculated from the Fourier transforms of the velocity autocorrelation functions.

## CHLORIDE BINDING TO PORTLANDITE

The results of the exchange isotherm experiments show that portlandite has the largest specific exchange capacity ( $\text{Cl atoms/nm}^2$ ) of all the phases investigated, exceeding that of even  $\text{C}_4\text{A}\bar{\text{C}}\text{H}_{11}$  at high solution concentrations (Figure 1). The extent of exchange increases with increasing solution concentration, never reaches a plateau, and is thus well fit with the Freundlich-type isotherm shown. All  $^{35}\text{Cl}$  NMR signals observed for the suspensions are quite narrow, symmetrical peaks ( $\text{FWHM} < 200$  Hz). Their widths decrease with increasing solution concentration. Thus, all the observed chloride is in rapid exchange ( $\nu_{\text{ex}} > 2$  kHz) between the solution and sorbed states. The chemical shifts are within a ppm of the 1 M NaCl solution standard set at 0 ppm, indicating a predominantly hydrated, solution-like local structural environment. In all cases the observed  $T_1$  and  $T_2$  are identical, as expected for rapid exchange conditions. The observed  $T_1$  relaxation rates ( $R_1 = 1/T_1$ ) decrease with increasing solution concentration at constant solid/solution ratio (0.70 g/g for portlandite) and approach the value of the neat solution at high concentrations (Figure 2).  $T_1$  relaxation rates are well known to increase for species near water-solid interfaces due to decreased rates of molecular reorientation [14], and these observations are readily interpreted to indicate that a progressively decreasing fraction of the chloride in each sample is associated with the surface as solution concentration increases. The data can be interpreted quantitatively from the relationship  $R_{\text{obs}} = (1-\square)R_{\text{F}} + \square R_{\text{B}}$ , where  $R_{\text{obs}}$ ,  $R_{\text{F}}$  and  $R_{\text{B}}$  are the relaxation rates of the suspension, neat solution and sorbed species; and  $\square$  is the fraction of the total chloride that is sorbed [9,15].  $R_{\text{obs}}$ , and  $R_{\text{F}}$  are experimentally determined (Figure 2), and  $R_{\text{B}}$  can be determined by extrapolation to extreme dilution (here 98.4 Hz for portlandite, about three times the value for the neat solution). For portlandite the calculated  $\square$ -values decrease with

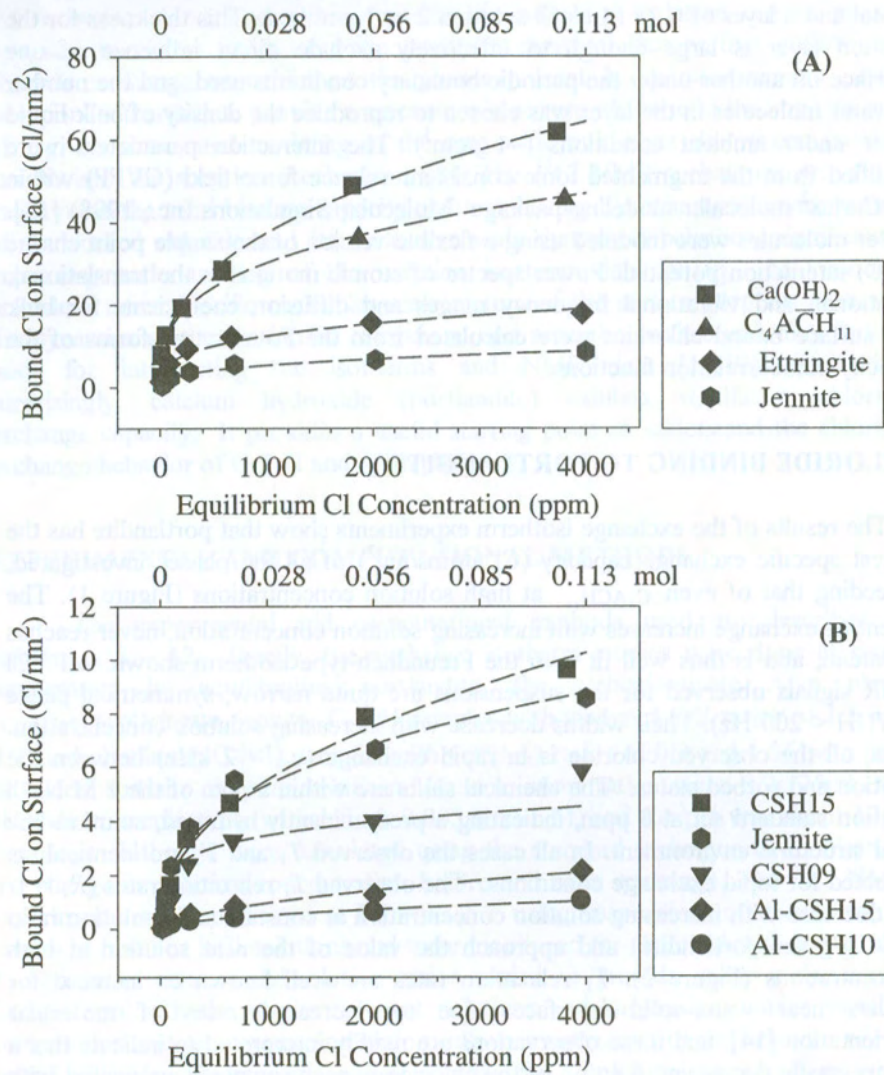


Figure 1. Chloride sorption isotherms for cement hydrate phases in Ca hydroxide saturated 0.25 M NaCl solutions. Fits are to a Freundlich-type isotherm with the relationship  $\theta = A \cdot C^{1/n}$ , where  $\theta$  is the sorption density (Cl atoms/nm<sup>2</sup> of solid surface),  $A$  is a fitting constant,  $C$  is the equilibrium solution concentration, and  $n$  is a fitting constant. [After Reference 8]

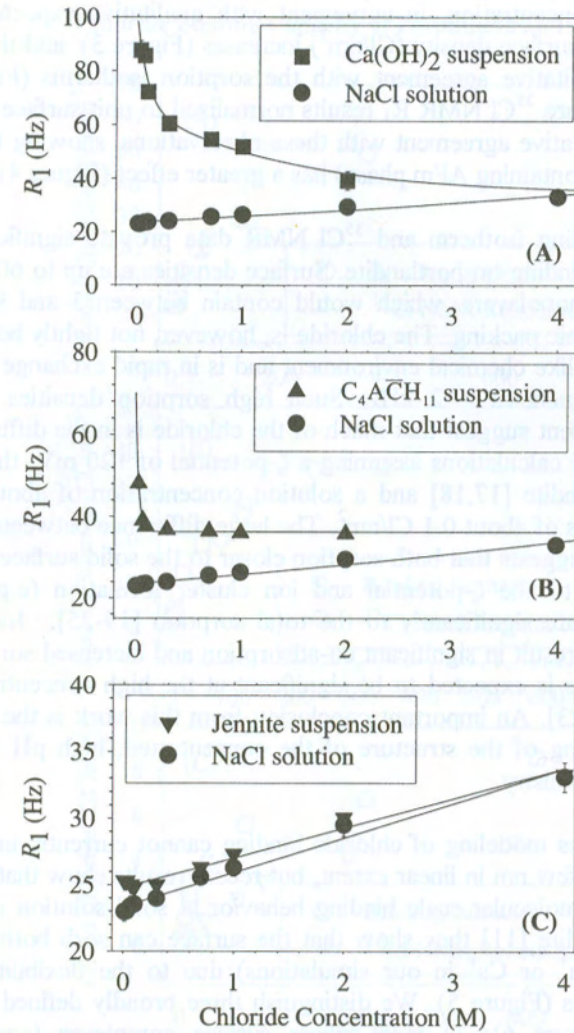


Figure 2. Observed relationships between the <sup>35</sup>Cl NMR T<sub>1</sub> relaxation rate ( $R_1 = 1/T_1$ ) and solution concentration for suspensions of portlandite, C<sub>4</sub>ĀCH<sub>11</sub>, and jennite in Ca hydroxide saturated NaCl solutions, along with data for the neat Ca-hydroxide saturated NaCl solutions. The differences between the two data sets is related to the extent of chloride sorption and is modeled by the relationship described in the text. [After Reference 9]

increasing chloride concentration, in agreement with qualitative expectation. In contrast, the chloride surface density ( $\text{Cl}/\text{nm}^2$ ) increases (Figure 3), and the values are in excellent quantitative agreement with the sorption isotherms (Figure 1). The variable temperature  $^{35}\text{Cl}$  NMR  $R_1$  results normalized to unit surface area are also in excellent qualitative agreement with these observations, showing that only Friedel's salt (the Cl-containing AFm phase) has a greater effect (Figure 4).

Together, the binding isotherm and  $^{35}\text{Cl}$  NMR data provide significant new insight into chloride binding on portlandite. Surface densities are up to  $60 \text{ Cl}/\text{nm}^2$ , equivalent to many monolayers, which would contain between 3 and  $9 \text{ Cl}/\text{nm}^2$  depending on the atomic packing. The chloride is, however, not tightly bound, but rather is in a solution-like chemical environment and is in rapid exchange with the bulk solution at frequencies  $> 2 \text{ kHz}$ . Such high sorption densities and the solution-like environment suggest that much of the chloride is in the diffuse layer. Electrical double layer calculations assuming a  $\zeta$ -potential of  $+20 \text{ mV}$ , the largest ever found for portlandite [17,18] and a solution concentration of about  $0.1 \text{ M}$  yield sorption densities of about  $0.1 \text{ Cl}/\text{nm}^2$ . The large difference between this and the observed values suggests that both sorption closer to the solid surface than the shear plane relevant to the  $\zeta$ -potential and ion cluster formation (e.g., Ca-Cl clusters) may contribute significantly to the total sorption [19-25]. Ion cluster formation, which can result in significant co-adsorption and increased sorption for a given surface charge is expected to be significant at the high concentrations in the diffuse layer [19-23]. An important conclusion from this work is the need for increased understanding of the structure of the concentrated, high pH solutions relevant to cement chemistry.

Molecular dynamics modeling of chloride binding cannot currently investigate systems larger than a few nm in linear extent, but recent results show that they are effective in studying molecular scale binding behavior at solid-solution interfaces [11,12]. For portlandite [11] they show that the surface can sorb both chloride and counter ions ( $\text{Na}^+$  or  $\text{Cs}^+$  in our simulations) due to the flexibility of the surface Ca-OH groups (Figure 5). We distinguish three broadly defined types of aqueous species (Figure 6): 1) inner-sphere surface complexes (coordinated directly to atoms on the solid surface), 2) outer-sphere surface complexes (separated from the surface by one molecular layer of water), and 3) ions in the solution (which in our models feel the presence of the surface but are separated from it by more than one molecular layer of water). In the case of surface-bound  $\text{Cl}^-$ , surface hydroxyl groups are oriented towards the anion, thus forming a nearly solution-like local environment for the surface-adsorbed  $\text{Cl}^-$ . On the other hand, in the case of surface-bound  $\text{Na}^+$  and  $\text{Cs}^+$ , the surface OH groups tend to point

Chloride Binding Capacity of Portlandite and AFm-C

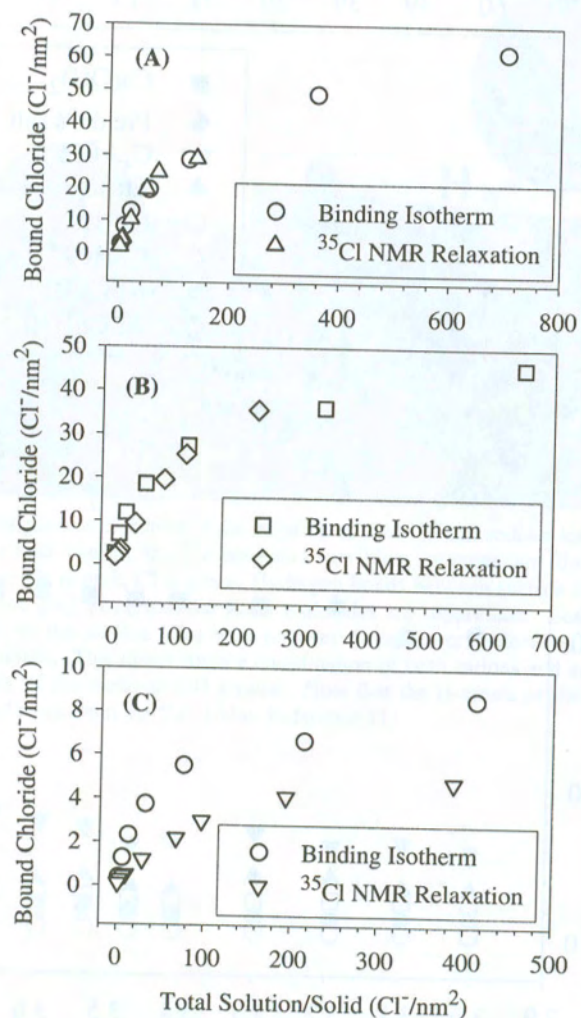


Figure 3. Fraction of sorbed chloride and chloride surface densities for suspensions of A) portlandite, B)  $\text{C}_4\text{A}\bar{\text{C}}\text{H}_{11}$ , and C) jennite determined from the  $^{35}\text{Cl}$  NMR relaxation data presented in Figure 2. For portlandite and  $\text{C}_4\text{A}\bar{\text{C}}\text{H}_{11}$ , the sorption densities are in excellent quantitative agreement with the sorption isotherm results in Figure 1. The results for jennite from NMR are about 40% lower, but the densities are so low, that the results are probably within analytical error. [After Reference 9]

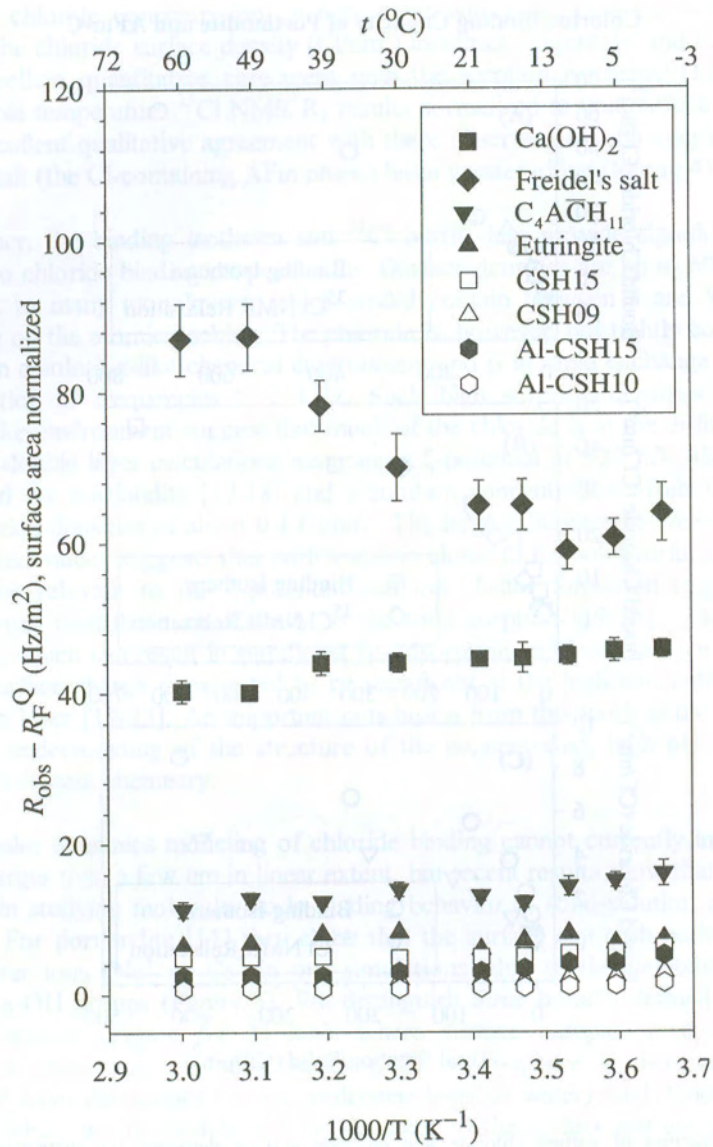


Figure 4. Variable temperature  $^{35}\text{Cl}$  NMR  $T_1$  relaxation rates for suspensions of the indicated cement hydrate phases. The relaxation rates presented are  $(R_{1,\text{obs}} - R_{1,\text{solution}})/\text{surface area}$ , where  $R_{1,\text{obs}}$  is  $1/T_1$  for the suspension,  $R_{1,\text{solution}}$  is  $1/T_1$  for the neat Ca hydroxide saturated 1 M KCl solutions. [After Reference 16]

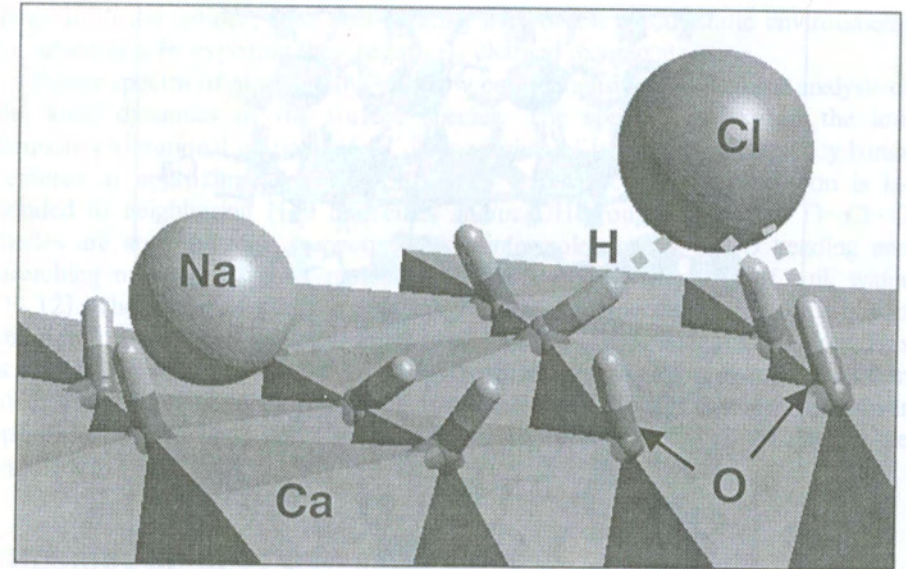


Figure 5. Computer generated picture of the sorption of chloride and sodium ion on the surface of portlandite. For visual clarity, the Ca-octahedra are blue, oxygens are the small red lines, hydrogens are gray, Na is pink, Cl is green. Hydrogen bonds between surface OH-groups and  $\text{Cl}^-$  are shown as dashed gray lines, and the water molecules are suppressed. Both the  $\text{Na}^+$  and  $\text{Cl}^-$  coordinate directly to the surface sites with no intervening water molecules, forming so-called inner sphere complexes. This direct surface coordination of both cations and anions is facilitated by the flexibility of the surfaced OH groups. Note that the H-atoms of the OH groups point towards the  $\text{Cl}^-$  and away from the  $\text{Na}^+$ . [After Reference 11]

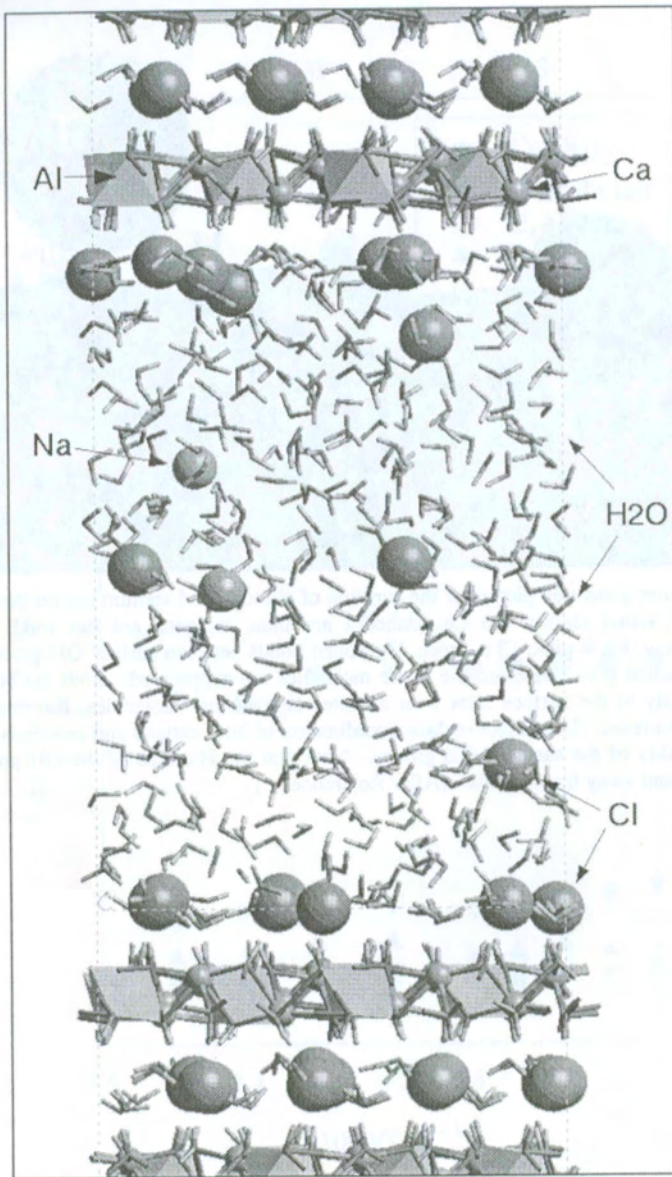


Figure 6. MD-simulation snapshot of the interface between Friedel's salt  $[\text{Ca}_2\text{Al}(\text{OH})_6]\text{Cl} \cdot 2\text{H}_2\text{O}$  and a  $\sim 30 \text{ \AA}$ -thick layer of 0.25 m aqueous NaCl solution. The crystal structure is represented by the shaded octahedral sheets. Water molecules are the arrowhead shaped symbols. Chlorides and water molecules are ordered in the interlayer, and most surface chlorides occur as inner sphere complexes. [After Reference 11]

away from the cations, thus also creating a favorable electrostatic environments for adsorption by exposing their negatively charged oxygen atoms.

Power spectra of atomic motions allow comprehensive and detailed analysis of the ionic dynamics of the surface species. The spectral density of the low frequency vibrational motions of  $\text{Cl}^-$  ions consists of two distinct frequency bands centered at approximately  $50$  and  $150 \text{ cm}^{-1}$ . Because each chloride ion is H-bonded to neighboring  $\text{H}_2\text{O}$  molecules and/or OH-groups, these two  $\text{O}\cdots\text{Cl}\cdots\text{O}$  modes are analogous to, respectively, the intermolecular  $\text{O}\cdots\text{O}\cdots\text{O}$  bending and stretching motions of water molecules in the H-bonded network of bulk water [11,12]. The shape of the low frequency vibrational spectrum of surface-bound chloride, thus, closely resembles that of chloride in a bulk aqueous solution. This is in good agreement with the  $^{35}\text{Cl}$  NMR results. The situation is quite similar in the case of the dynamics of surface-adsorbed heavy  $\text{Cs}^+$  ions, whereas the power spectra of inner-sphere, outer sphere, and bulk solution  $\text{Na}^+$  are all different in the simulations [11].

### CHLORIDE BINDING TO C-S-H

The extent of chloride sorption on C-S-H is much less than for portlandite, with a maximum of about  $10 \text{ Cl/nm}^2$  (Figure 1). It is lowest for the aluminous samples (maximum of about  $2 \text{ Cl/nm}^2$ ), is larger for the sample with  $\text{C/S} = 0.9$  and is largest for the sample with  $\text{C/S} = 1.5$  and for crystalline jennite. These observations are consistent with previous reports (1,2,26-28).  $^{35}\text{Cl}$  NMR results for jennite give sorption densities about 40% lower than those from the isotherms, but the values are probably within experimental error (Figures 2 and 3). As for portlandite, all the observed chloride is in rapid exchange with the bulk solution at greater than kHz frequencies and the chemical shifts are indicative of a solution-like structural environment. The variable temperature  $^{35}\text{Cl}$  NMR  $R_1$  data confirm that sorption on C-S-H phases has a relatively small effect on the relaxation (Figure 4).

These observations can be readily interpreted by reference to the chloride exchange results for portlandite and the structure of synthetic, precipitated C-S-H, which is based on that of tobermorite [24-31]. At low  $\text{C/S}$  ratios near 0.8, the C-S-H structure is comparable to that of tobermorite, with composite layers consisting of a central sheet of Ca-polyhedral sheet sandwiched between dreiketten chains of silicate tetrahedra. Increasing  $\text{C/S}$  ratios are accommodated first by omission of some of the so-called bridging tetrahedra in the chains and then, at  $\text{C/S}$  ratios  $> 1.3$ , by omission of chain segments and replacement of them by OH groups on the Ca-sheet. C-S-H is most commonly observed to have

negative  $\zeta$ -potentials [17,18], as expected at the high pH of cement solutions, and suggesting weak chloride sorption. MD modeling of chloride interaction with tobermorite shows that chloride is not attracted to the surface [11], in agreement with this idea. Al is thought to substitute for Si on primarily the bridging tetrahedra [32,33], increasing the negative surface charge due to this +3 for +4 charge substitution. Thus, low chloride exchange capacities are expected at low C/S ratios, and especially for aluminous samples, as observed. The jennite structure is thought to be broadly similar to that of tobermorite, but with every other chain missing and replaced by OH groups, along with significant rearrangement of the Ca-sheet [34]. Thus, it probably exposes surface sites comparable to those of portlandite, consistent with its increased chloride exchange capacity. Based on the structural model for synthetic C-S-H described above, the C-S-H sample with C/S = 1.5 is likewise expected to expose significant numbers of Ca-OH sites, accounting for its comparatively large chloride exchange capacity.

Although the chloride exchange capacities for all the C-S-H samples are lower than for portlandite, they are still significant, and for the jennite and the C/S = 1.5 sample probably more than a statistical monolayer. Here also, co-adsorption due to ion cluster formation may contribute to the total exchange capacity. In addition,  $^{17}\text{O}$  MAS NMR results for synthetic C-S-H samples suggest the presence of Ca-OH sites in the structure even at low C/S ratios [30], possibly on the broken layer edges. Such sites may also contribute to the observed chloride exchange capacity.

### CHLORIDE BINDING TO AFm AND AFt PHASES

The AFm phases have layer structures with positive charges compensated by interlayer anions and correspondingly positive  $\zeta$ -potentials [17,18,35]. They are expected to have significant chloride exchange capacities, as observed for  $\text{C}_4\text{A}\bar{\text{C}}\text{H}_{11}$  (Figure 1). The  $^{35}\text{Cl}$  NMR results for  $\text{C}_4\text{A}\bar{\text{C}}\text{H}_{11}$  yield exchange capacities essentially identical to the exchange isotherm studies (Figure 3), and as for portlandite and the C-S-H phases all the signals are quite narrow, symmetrical peaks near 0 ppm. Thus, the Cl is in solution-like environments and is in rapid exchange with the bulk solution. The variable temperature  $^{35}\text{Cl}$  NMR results for  $\text{C}_4\text{A}\bar{\text{C}}\text{H}_{11}$  show a much smaller effect than for portlandite, but a larger effect than for the C-S-H phases (Figure 4). The effect for Friedel's salt, the chloride-containing AFm phase, is the largest for all the phases investigated (Figure 4). The temperature dependence is different (negative slope) than for the other phases, suggesting that its relaxation rates are controlled by large fluctuations in the electric field gradient due to rapid exchange of chloride between inner sphere

complexes and solution-like sites [16]. MD models for chloride binding on Friedel's salt [12] show formation of such inner sphere sites and exchange of chloride between them and the solution at frequencies of about  $2 \times 10^{-10}$  Hz, orders of magnitude faster than required to cause the observed single, narrow peak.

Structurally, the AFm phases are related to portlandite by ordered substitution of Al for Ca on 1/3 of the hexagonal sites, resulting in the permanent positive layer charge. The large effect of Friedel's salt on the  $T_1$  relaxation rates is, thus, expected due to its strong affinity for chloride and the MD results suggesting exchange between the surface and solution sites [10,12]. The comparatively low chloride exchange capacity of  $\text{C}_4\text{A}\bar{\text{C}}\text{H}_{11}$ , which is equal to or less than that of portlandite, depending on the solution concentration, is probably due to strong attachment of carbonate on the surface sites, which would reduce the positive surface charge and prevent binding. Carbonate has a charge of -2, compared to -1 for chloride, and is thus expected to bind much more strongly to the surface.

Ettringite (AFt) has a columnar structure with a permanent positive charge that is compensated by intercolumnar sulfate and has positive  $\zeta$ -potentials [17,18,36]. Its chloride sorption density, however, is less than for  $\text{C}_4\text{A}\bar{\text{C}}\text{H}_{11}$ , and the variable temperature  $^{35}\text{Cl}$  NMR  $T_1$  results confirm that it has a significantly lower affinity for chloride than portlandite and the AFm phases. MD models show that if the sulfate ions are in their normal structural positions on the ettringite surface, chloride is not attracted to it and does not exchange with the sulfate. As for carbonate, sulfate has a charge of -2, and is expected to be more strongly attracted to the surface than chloride. In addition, the chloride AFt phase is stable only at low temperatures,  $<0^\circ\text{C}$ , [35] suggesting that the structural conformation of ettringite is more favorable for sulfate than for chloride.

### ACKNOWLEDGEMENTS

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## ROLE OF ALKALINE RESERVE IN THE ACIDIC RESISTANCE OF CEMENT PASTES

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### ABSTRACT

*In realistic conditions, relevant to high-level radioactive waste repositories, concrete durability is limited by its interaction with clays and granitic groundwater. Groundwater is a very weakly mineralised solution containing diluted acids. In contact with the concrete it will leach the ions in the pore solution and will react with the solid phases that contain calcium (CH, CSH and ettringite) producing a progressive neutralisation of the alkaline nature cement paste. The resistance of hardened cement pastes to chemical attack and physical degradation is a combination of chemical composition (in particular the so-called alkaline reserve of the cement pastes) and microstructural factors. At present, a wide variety of experimental procedures are used to characterise the leaching properties of materials used in waste management (Van der Sloot, 1990). In most of the cases, kinetic studies in material test-tubes have been made, in order to know the chemical and microstructural degradation in function of the time (Van der Sloot, 1990; Adenot et al. 1992; Faucon et al. 1998; Unsworth et al. 1997). In this work two types of test methods have been used, an acid neutralisation test method and a permeability test method. The dissolution-precipitation phenomena of cement pastes have been studied by acid attack in powders with a controlled particle sizes; this accelerated test does not fully reproduce reality, but it enables the different variables to be compared. In order to evaluate cements for use as a component in sealing materials in a disposal for nuclear wastes, the water permeability characteristics of cement mortars have been studied. Thus different types of cement and blending agents are compared, and the role of the alkaline reserve has been analysed. The selection of the most resistant cement paste will be the main step in the definition of the most suitable concrete type to be used in high level radioactive waste repositories.*

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