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Beaudoin, J. J.; Ramachandran, V. S.; Feldman, R. F.

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Interaction of Chloride and C-S-H

by J.J. Beaudoin, V.S. Ramachandran and R.F. Feldman

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Résumé

On examine ici la capacité de fixer le chlorure que possèdent des préparations de C-S-H synthétique ayant un large éventail de rapports C/S et H/S. Le chlorure fixé est séparé en deux genres : insoluble dans l'alcool et lié solidement. On observe une dépendance du chlorure dit «chimisorbé» à l'égard du rapport C/S, du rapport H/S et de la surface réelle. Les auteurs avancent l'hypothèse d'un mécanisme d'interaction du chlorure compatible avec les modèles Feldman et Taylor de C-S-H. Il examinent aussi les conséquences au niveau de la corrosion des armatures d'acier dans le béton.

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INTERACTION OF CHLORIDE AND C-S-H

J.J. Beaudoin, V.S. Ramachandran and R.F. Feldman
National Research Council Canada, Institute for Research in Construction
Ottawa, Ontario K1A 0R6 CANADA

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ABSTRACT

The chloride binding properties of synthetic C-S-H preparations having a wide range of C/S and H/S ratios are examined. Bound chloride is separated into two types, alcohol-insoluble and tightly held. Dependence of so-called chemisorbed chloride on C/S ratio, H/S ratio and surface area is observed. A mechanism for chloride interaction compatible with the Feldman and Taylor models for C-S-H is suggested. Implications with respect to corrosion of steel in concrete are also discussed.

Introduction

Models for durability prediction of concrete generally consider the effects of chloride and other potentially deleterious ions on matrix stability [1]. Chloride ion is known to significantly increase the corrosion rate of steel in reinforced concrete. Multiple states of chloride in the hydration of tricalcium silicate have been suggested [2]. These include: free, adsorbed, and interlayer chloride. The concentration of active or free chloride in the pore solution of concrete is relevant to establishing durability failure criteria where the rate determining parameters are dependent on the diffusivity of ionic species to steel-concrete interfaces. Silica fume addition to concrete has been shown to significantly reduce diffusivity of chloride ion [3]. It has been observed however, that chloride ion concentrations in pore water of cement pastes, (w/c = 0.50) containing up to 30% silica fume are much higher than for control pastes with no silica fume addition [4,5]. In cement pastes initially containing 0.4% chloride by weight of solids, Cl^- concentration in the pore water increased from 146 to 256 $m.mole \cdot l^{-1}$ with silica fume addition up to 30%. This has been attributed to the increased solubility of the chloroaluminate phase (Friedel's salt) at the reduced pH levels. It is possible that differences in pore-water chloride concentration are due in part to a variable chloride binding capacity of the C-S-H phase itself. Binding capacity becomes dependent on the C/S and H/S ratio of the hydrated silicate phase. In the C_3S paste C/S ratios for C-S-H may vary between 0.8 and 2.0 [6-10]. Average values for hydrated C_3S, C_3S-silica blends, portland cement paste, portland cement fly ash and slag blends are typically 1.70 [6], 0.80-1.47 [7], 1.53-1.69 [8], 1.39 and 1.60 [9]. Higher values of C/S eg. C/S = 2.0 for α C_2SH are typical of C-S-H formed under hydrothermal conditions.

To test the dependence of chloride intake on C/S ratios in C-S-H, several chloride adsorption experiments were performed with six synthetic C-S-H preparations (C/S = 0.68-1.49; H/S = 1.91-6.69). Results of these studies are reported and implications for concrete durability discussed.

Experimental

Material

Six calcium silicate hydrate (C-S-H) preparations with a wide range of C/S and H/S ratios were supplied by Lafarge Coppee Recherche, France [11]. Specimens were prepared at room temperature by reaction of calcium hydroxide with sodium silicate solutions. Different C/S ratios were obtained by varying the C/S ratio of the solution from 0.1 to 1.75. After reaction the precipitate was washed and dried with acetone and ether, flushed with nitrogen (for 4 days) and further dried at 40°C for 24 hours. X-ray diffraction and IR spectra were typical of C-S-H. X-ray d-spacings were observed at 3.03, 2.80 and 1.83Å. A large absorption band around 970 cm^{-1} was observed in the IR spectra. No carbonate peaks were observed. All specimens contained less than 0.6% Na_2O as determined by flame photometry. The C/S ratio was determined by flame spectrophotometry and x-ray microanalysis. The H/S ratio was determined from the ignition loss at 1000°C attributing the whole loss to water. Surface areas were measured by nitrogen adsorption method. Density values were determined using helium pycnometric technique. Characteristics of the samples are given in Table I.

TABLE I Characteristics of C-S-H Preparations

Samples	H/S	C/S	Surface Area (m^2/g)	Density (g/cc)
C-S-H A	1.91	0.68	111.9	2.00
C-S-H B	2.01	0.87	56.6	2.05
C-S-H C	2.58	1.17	68.2	2.07
C-S-H D	2.49	0.99	110.7	2.05
C-S-H E	5.53	1.49	30.7	2.03
C-S-H F	6.69	1.26	40.2	2.02

Chloride Adsorption

Chloride adsorption was determined by titration and energy dispersive x-ray analysis (EDXA). Procedures for determination of the extent of chloride adsorption on the C-S-H samples by titration method are as follows: C-S-H samples, 0.5 or 1.0 g were placed in 30 mL centrifuge tubes and aqueous solutions containing 3.8% calcium chloride were added to give a 1:20 solid to solution ratio. The tubes were rotated at 20 rpm for 2 days. Samples were centrifuged using an ultra-speed centrifuge for 7 to 10 min. Then 5 mL aliquots were taken for chloride determination by potentiometric titration using 0.1 N silver nitrate and glass-calomel electrodes. After decanting the remaining solution, solid samples were washed with ethanol at a ratio of 1:30 solid to solution, rotated for 3 hours and centrifuged to separate the ethanol and C-S-H. Samples were rewashed with ethanol and the estimation procedure repeated.

EDXA was performed on the 0.5 g samples which were removed from the centrifuged tubes and dried under vacuum at 100°C for 3 hours. Calibrations were performed with chloride bearing minerals of known composition. The C-S-H material was compacted at 100 MPa to form discs 1.27 cm in diameter and 1 mm thick. Chloride estimation was determined using the SQ software package with the Tracor-Northern X-ray Analyzer attached to a Cambridge stereoscan SEM.

The 1 g samples (treated with chloride) were washed with water using a solid-liquid ratio of 1:30, rotated 1 day and centrifuged. Then 10 mL aliquots of solution were used for chloride determination by potentiometric titration. Samples were rewashed with water twice.

EDXA was also performed on the 1 g samples which were vacuum dried for 3 hours at 100°C and compacted at 100 MPa to form discs used for examination.

Thermal Analysis

Differential Thermal Analysis (DTA) curves were obtained on the reference C-S-H samples and those treated in aqueous solutions containing 3.8% calcium chloride and subsequently washed with ethanol and water. A Dupont Thermal Analyzer was used for the measurements. Ten mg of sample was heated in air using a heating rate of 20°C per min.

Results and Discussion

Evidence for the argument that anions associated with large organic molecules can penetrate interlayer spaces in hydrated C_3S and C_3A phases is germane to the discussion of chloride interaction with C-S-H.

In previous work observations on the adsorption-desorption isotherms of calcium lignosulfonate (CLS) on hydrated C_3S in aqueous and non aqueous media indicate that at all equilibrium concentrations of CLS, adsorption is completely irreversible [13]. This is illustrated by the flat scanning loops in figure 1. CLS not only adsorbs as a surface complex on the hydrated C_3S phase, it enters the interlayers of the C-S-H. Intercalation of CLS into the hexagonal calcium aluminate phase is accompanied by an increase in the c-axis spacing. It would thus appear that penetration of chloride ion into interlayer spaces in C-S-H is likely.

In this present investigation chloride determination by EDXA is plotted against values obtained by titration method in figure 2. The correlation coefficient obtained from linear regression analysis is 0.96. Although the correspondence is not 1:1 (possibly from errors due to non-uniformity of spatial distribution of chloride, accuracy of end point determination, etc.) the correlation is excellent and the dependences established essentially independent of the technique.

In earlier work several possible states of chloride in the hydration of tricalcium silicate in the presence of calcium chloride have been suggested [2]. These include a chemisorbed chloride layer on the surface of C-S-H, chloride in the interlayer space and incorporated Cl^- in the lattice of C-S-H. Free chloride resident in the pore system

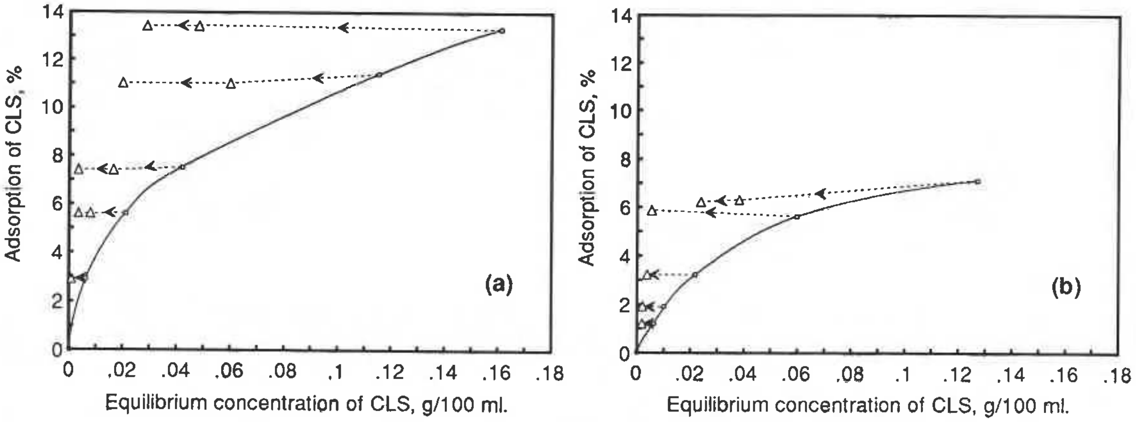

FIG. 1
Adsorption-desorption isotherms of CLS on hydrated C_3S:
(a) in aqueous medium; (b) in non-aqueous medium (ref 13)

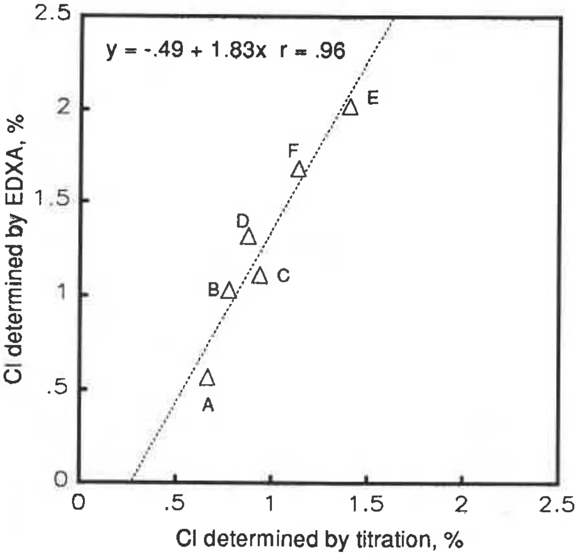

FIG. 2
Correlation of chemisorbed chloride determined
by EDXA and by titration.

of C-S-H is soluble in water and ethanol. It is suggested that chemisorbed and interlayer species are removed by water. Lattice substituted chloride is that which cannot be removed with water leaching. It has been suggested that most of the chloride ions are chemisorbed on the surface of hydrated C_3S [2]. In this work the difference in bound chloride between ethanol washed C-S-H and C-S-H washed first in ethanol and then in water is referred to as 'alcohol-insoluble' chloride. Chloride remaining after washing with water is tentatively referred to as 'tightly held' chloride. Results of alcohol-insoluble chloride determined by titration and EDXA are plotted versus H/S ratio, C/S ratio and surface area in figure 3. There is a linear dependence

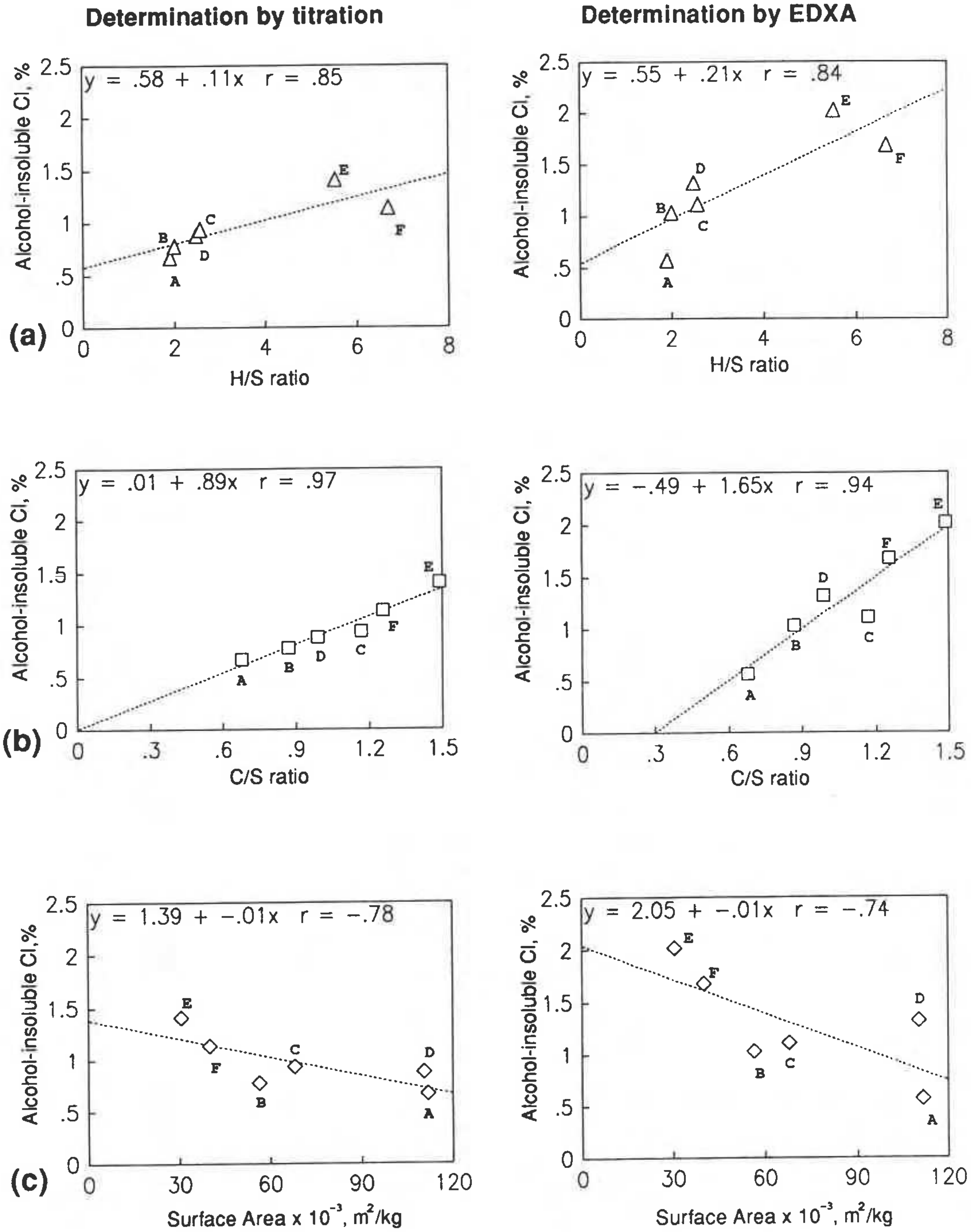

FIG. 3

Correlation of alcohol-insoluble chloride with H/S, C/S and surface area.

between alcohol-insoluble chloride and these three variables. Alcohol-insoluble chloride increases with H/S and C/S ratio and decreases with surface area. The results confirm that the chloride estimation values are reliable. Correlation coefficients are 0.85, 0.97 and 0.78 respectively for determination by titration methods and 0.84, 0.94 and 0.74 by EDXA. The results confirm that the chloride estimation values are reliable. Correlation with both H/S and C/S would be expected as H/S generally increases with C/S for these C-S-H preparations. It has also been reported that the surface area of tobermorite gel was found to decrease with increase in C/S ratio [12]. The alcohol-insoluble chloride can be considered to be less available for removal if it is associated in locations between the layers of C-S-H. The degree of layering of the C-S-H decreases with an increase in surface area. This is a possible explanation of the inverse dependence of alcohol-insoluble chloride and surface area.

The observation that alcohol-insoluble chloride is directly dependent on C/S and H/S ratio can be used to explain the determination by other workers that chloride concentration of pore water in silica fume cement paste is significantly higher than reference pastes with no silica fume addition because low C/S ratio C-S-H present in silica fume pastes imbibes lower amounts of chloride ions [4, 5]. The water soluble chloride is in equilibrium with that taken up by the solid. Pore solutions are expressed from specimens and then analyzed for chloride which would not include the alcohol-insoluble state. This may not be the case for solutions obtained by leaching the specimens. The C-S-H formed in silica fume pastes has a lower C/S ratio than C-S-H in normal paste and hence binds less chloride making more available for the pore solution. The mechanism controlling the amount of alcohol-insoluble chloride is not clear. It is suggested that alcohol-insoluble chloride resides both in the interlayer positions and on the surface of the C-S-H sheets. Chloride may interact with Ca^{++} ions and OH^- groups to form oxychloride complexes which can be leached by water but not alcohol. Interactions which take place in the interlayer region may be relatively inaccessible to water requiring extended leaching periods before chloride can disassociate and desorb. The Feldman and Taylor models for C-S-H feature missing tetrahedra in the silicate chain which are replaced by hydroxyl groups [14, 15]. These are potential sites for oxychloride complex formation. At low C/S ratio values there would be fewer OH^- sites for chloride complexing to occur as the degree of polymerization is higher.

The relative ability of C-S-H to bind chloride has important implications for durability assessment. A number of investigators have identified the Cl^-/OH^- ratio as an important indicator for determining the onset of depassivation of the steel in concrete [4, 16, 17]. It was concluded that pores of dense matrices in contact with chloride solutions of similar concentrations to that of sea water could contain solutions with very high values of Cl^-/OH^- in terms of corrosion risk.

It was also suggested that reduction in the pore size resulting from exposure of cement paste to chloride solution is due to the formation of calcium chloride complexes on the surface of the C-S-H [17]. It can be inferred from this that flow through paste aggregate interfaces might be affected by chloride interactions.

It was observed by other workers that flow of solution through paste does become restricted after long immersion in chloride solution [18]. This supports the above view.

The amount of tightly held chloride is an order of magnitude lower than alcohol-insoluble chloride. The relative amount of 'alcohol-insoluble' and 'tightly held' chloride is of practical significance as alcohol-insoluble chloride is more easily dissociated and potentially active with respect to corrosion processes. The percentage of tightly held chloride is plotted against H/S ratio, C/S ratio and surface area (figure 4). Correlation of tightly held chloride with these terms is generally poor. Examination of the plots does indicate some tendency however for tightly held chloride to decrease with H/S and C/S ratio. The reason is not clear.

Additional evidence provided by DTA indicates that the C-S-H samples have been modified after chloride treatment.

The exothermic peak beyond 800°C was attributed to the formation of β-wollastonite.

Significant changes were observed in the transition temperature at which β-wollastonite forms for the high C/S ratio C-S-H preparations (see Table II). The transition temperature for C-S-H (F) containing both alcohol-insoluble and tightly held chloride is about 45°C lower than the reference. The corresponding temperature difference for C-S-H (E) is about 30°C. These two C-S-H samples contain the highest amount of alcohol-insoluble chloride. Differences are also evident in the samples containing only tightly held chloride. Such differences in the temperature of crystallization are expected when lattice substitutes occur.

TABLE II Temperature for Formation of β-Wollastonite in C-S-H Samples (°C)

			C-S-H			
Treatment	A	B	C	D	E	F
Reference C-S-H	845	820	845	820	895	860
C-S-H + Alcohol-Insoluble Chloride and Tightly Held Chloride	845	820	820	820	865	815
C-S-H + Tightly Held Chloride	845	840	840	840	865	830

Conclusions

1. The C-S-H preparations containing various C/S ratios bind chloride. 'Alcohol-Insoluble chloride' defined as water leachable but not alcohol leachable and 'tightly held chloride' which cannot be removed by water leaching have been distinguished.
2. The amount of chloride held by C-S-H in the so-called chemisorbed state is dependent on H/S ratio, C/S ratio and nitrogen surface area.
3. There appears to be no dependence of tightly held chloride on H/S ratio, C/S ratio and nitrogen surface area.

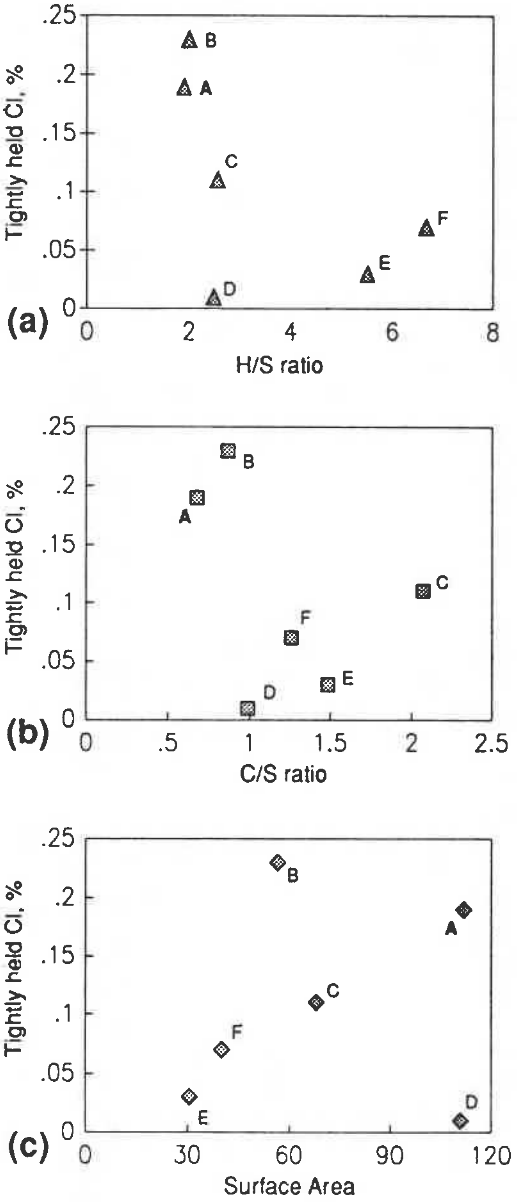

FIG. 4
Tightly held chloride determined by EDXA.

4. Higher concentrations of chloride in the pore water of silica fume cement pastes observed by Page and co-workers can be partially explained by the lower C/S ratio of C-S-H in these systems compared to C-S-H in portland cement pastes without silica fume.
5. The C-S-H transition temperature at which β-wollastonite forms can decrease for C-S-H preparations containing alcohol-insoluble chloride. The effect is largest for C-S-H having highest C/S ratio.

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