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# MECHANISM OF FRIEDEL'S SALT FORMATION IN CEMENTS RICH IN TRI-CALCIUM ALUMINATE

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## ABSTRACT

In the present investigation, based on pore solution analyses, the mechanisms of Friedel's salt formation and the related chemical processes taking place in mortar due to chloride binding are dealt with. Pore solutions from mortars containing NaCl and $CaCl_2$ added during mixing were analyzed. Based on the results it is proposed that in the presence of NaCl the Friedel's salt forms by two separate mechanisms; an adsorption mechanism, and an anion-exchange mechanism. In the adsorption mechanism, Friedel's salt forms due to the adsorption of the bulk $Cl^-$ ions present in the pore solution into the interlayers of the principal layers, $[Ca_2Al(OH^-)_6.2H_2O]^+$, of the AFm (Aluminate Ferrite mono) structure to balance the charge. In the anion-exchange mechanism, a fraction of the free-chloride ions bind with the AFm hydrates ($C_4AH_{13}$ and its derivatives) to form Friedel's salt by an anion-exchange with the $OH^-$ ions present in the interlayers of the principal layer, $[Ca_2Al(OH^-)_6.nH_2O]^+$. As a result of Friedel's salt formation by the adsorption mechanism, an amount of $Na^+$ ions equivalent to the adsorbed chloride ions (in moles) are removed from the pore solution to maintain the ionic charge neutrality. The $Na^+$ ions thus removed from the pore solution, bind with the calcium silicate hydrate (C-S-H) gel lattice to balance the charge arising due to the replacement of $Si^{4+}$ ions by $Al^{3+}$ and $Fe^{3+}$ ions. In contrast, the Friedel's salt formation by the anion-exchange mechanism involves the release of $OH^-$ ions from the AFm hydrates into the pore solution, thereby increasing the pH of the pore solution. The above mechanisms are also valid for $CaCl_2$ salt introduced in a similar way. Although the addition of $CaCl_2$ salt to the mortar lowers the net pH of the pore solution, the total bound chlorides were significantly higher in comparison with the equivalent $Cl^-$ added as NaCl salt. The higher chloride binding with equivalent $CaCl_2$ addition is explained by the lower degree of competition offered by the $OH^-$ ions during the bulk free-chloride adsorption into the interlayers of the principal layers.

## Introduction

Many investigators have reported the chloride binding ability of cements and its dependence on various parameters such as the associated cation type ($Ca^{2+}$, $Na^+$), cement type and content, mineral admixtures, water-cement ratio, curing period and sulphate additions (1–13).

As early as in 1962, the chloride binding capacity of ordinary portland cement (OPC) and sulphate resistant portland cement (SRPC) in the presence of admixed $CaCl_2$ salt, was demonstrated (1). A few researchers during the 1980's showed the process of chloride binding at room temperature in the form of a chloro-complex called "Friedel's salt", $3CaO.Al_2O_3.CaCl_2.10H_2O$, in cements rich in $C_3A$ by applying techniques such as differential thermal analysis (DTA) and X-ray diffraction (XRD) (3,14). An experimental study by the present authors, using XRD and differential scanning calorimetry (DSC), has demonstrated at room temperature, the formation of a ferrite based chloro-complex, $3CaO.Fe_2O_3.CaCl_2.10H_2O$, analogous to Friedel's salt in cements rich in $C_4AF$ and poor in $C_3A$ like in SRPC (15). However, the stability of Friedel's salt is pH dependent, that is, if the pH falls, for example due to carbonation, the dissolution of Friedel's salt will increase and free-chloride ions are released into the pore solution (4). Apart from Friedel's salt, the chlorides can also bind in the form of a high chloro-complex, $3CaO.3CaCl_2.Al_2O_3$.aqueous, by the hydration of $C_3A$ in 23% $CaCl_2$ solution at -10°C (16). A chloro-complex salt containing $CaCl_2$, $Ca(OH)_2$ and/or $CaCO_3$ is also known to crystallise from portland cement at temperatures below 20°C, if the $CaCl_2$ concentration of the solution is 15% or higher (17). However, both the last two chloro-complexes are not expected to form in hydrated cements under field conditions.

Contrary to the reports above, it is also reported that as high as 40% of added chlorides, when mixed with $C_3S$ paste, bind with the C-S-H gel as an interlayer chemisorbed complex (18), though the extent of chloride binding appears to be considerably lower than had previously been reported (19). However, recent studies carried out with synthetic grade $C_3S$ showed that the amount of free-chloride ions that became incorporated into the hydrated products of $C_3S$ was insignificant (20).

Limited knowledge exists on the mechanisms leading to the formation of Friedel's salt and the associated chemical processes that takes place as a result of chloride binding. According to Ben-Yair (21), the formation of Friedel's salt in aqueous solution is due to a direct chemical reaction between the $C_3A$ of the cement and the admixed $CaCl_2$ salt. According to Yonezawa (22), the formation of Friedel's salt involves an ion-exchange between the $OH^-$ ions present in the interlayers of the $C_3A$ hydrates and the free-chloride ions derived from the NaCl salt added during the mixing. Thus, this mechanism does not disturb the ionic charge neutrality in the pore solution.

According to Lambert et. al.(20), the removal of free-chloride ions from the aqueous phase to form Friedel's salt would necessitate either the removal of an equivalent quantity of cations from the aqueous phase or the entry of other anions to the aqueous phase to maintain the ionic charge neutrality in the pore solution. The $OH^-$ ions from the $Ca(OH)_2$ crystals are the main source of anions to balance the charge. Thus the binding of the free-chloride ions derived from NaCl salt to form Friedel's salt involves an increase in pore solution $OH^-$ ion concentration.

In the present investigation, an attempt is made to explain the mechanisms leading to the formation of Friedel's salt in $C_3A$ rich cements in the presence of NaCl and $CaCl_2$ salts added during mixing. Attempts are also made to understand the related chemical processes that take place in the mortar as a result of chloride binding.

## Experimental

The experimental work consisted of examining the pore solutions for $Cl^-$, $OH^-$, $K^+$, and $Na^+$ ions with different levels of chlorides added as NaCl and $CaCl_2$ salts during mixing.

For this, cylindrical mortar specimens (4 cm diameter × 5 cm height) were cast in plastic bottles. After placing and compacting the mortar, the plastic bottles were sealed by wrapping with plastic sheet to avoid interaction of the mortar with the environment. The sealed specimens were then cured under laboratory conditions until the day of pore solution extraction.

Chlorides were added to the mix by dissolution of NaCl or $CaCl_2$ salt in the mix water. When NaCl was introduced into the mix, three chloride levels were investigated, that is, 1%, 1.75% and 3.5% by weight of cement which give mix water chloride concentrations as 0.403 M, 0.704 M, and 1.41 M respectively. When $CaCl_2$ was introduced into the mix investigations were carried out for 1% and 1.75% $Cl^-$ by weight of cement. Addition of 1% chloride by weight of cement as anhydrous $CaCl_2$, is approximately equivalent to 1.4% anhydrous $CaCl_2$ by weight of cement as recommended for the set acceleration of concrete. While the addition of 1.75% chloride by weight of cement as NaCl to the mix water approximately simulates the condition of using sea water as mix water. The free-chloride concentration was also examined for 0.5% chloride by weight of cement as NaCl only for the 33rd day of hydration.

OPC conforming to BS:12 (23) containing 11.25% $C_3A$ was used in the present investigation. The cement content of the mix was 400 kg $m^{-3}$ and the aggregate/cement ratio by weight was 4. Water-cement ratio of the mix was 0.7.

The mortar specimens were demoulded from the plastic bottles at the end of the 3rd, 30th and 70th day of curing and were subjected to pore solution extraction using a pore press of 375 MPa capacity. The procedure adopted for pore press operation and the sample collection are similar to those recommended by Barneyback and Diamond (24). The chloride concentration of the diluted pore solution was measured on a chloride analyser (Corning model 926), and the pH was measured on a laboratory pH meter (Rapide instruments AGB-2001) with a Lithium glass pH probe. The pH was measured immediately after the extraction to avoid errors due to carbonation. The measured pH values were then converted to the corresponding $OH^-$ ion concentrations by using the classical definition of pH, and assuming an activity coefficient of unity for $OH^-$. The $Na^+$ and $K^+$ ion concentrations in the diluted pore solutions were measured on a flame photometer (Corning model 400).

The measured $Cl^-$, $OH^-$, $K^+$ and $Na^+$ ion concentrations were corrected for hydration effects. This essentially consists of converting the measured concentrations to the original mix water content by compensating for the bound water. For this, the evaporable water contents were determined by heating the parallel mortar specimens to 105°C to constant weight.

## Results

Table 1 presents the $Cl^-$ (bound and free), $OH^-$, $Na^+$, and $K^+$ ion concentrations in the pore solution in the presence of NaCl and $CaCl_2$ additions respectively. All the ionic concentrations presented in Table 1 are corrected for hydration effects, and hence the values represent the concentrations in the original mix water.

$Cl^-$ and $Oh^-$ Ion Concentrations. It is evident from Table 1 that for both NaCl and $CaCl_2$ additions the chloride concentration in the pore solution drops rapidly during the initial period of hydration, that is, there is an appreciable reduction by the 3rd day. However, by the 33rd day of hydration an quasi-equilibrium is established, and there after no further significant reduction in chloride concentration in the pore solution is observed. The small variations observed in the bound chloride concentrations by the 70th day are insignificant compared to the mix water

TABLE 1

Ionic Concentrations in the Pore Solutions Obtained from OPC Mortar Mixed with NaCl and $CaCl_2$ Salt

| $Cl^-$ levels by wt of cement | Age days | Average free chloride conc mM | | Average bound $Cl^-$ conc. mM | | Average$OH^-$ conc. mM | | Average$Na^+$ conc. mM | | Average $K^+$ conc. mM | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | NaCl | $CaCl_2$ | NaCl | $CaCl_2$ | NaCl | $CaCl_2$ | NaCl | $CaCl_2$ | NaCl | $CaCl_2$ |
| No $Cl^-$ addition | 3 | --- | --- | --- | --- | 79 | 79 | 65 | 65 | 136 | 136 |
| | 33 | --- | --- | --- | --- | 77 | 77 | 74 | 74 | 142 | 142 |
| | 70 | --- | --- | --- | --- | 102 | 102 | 66 | 66 | 151 | 151 |
| 0.5%(0.201 M) | 33 | 70 | --- | 131 | --- | --- | --- | --- | --- | --- | --- |
| 1%(0.403 M)** | 3 | 238 | 148 | 165 | 255 | 95 | 52 | 273 | 72 | 134 | 158 |
| | 33 | 105 | 63 | 298 | 340 | 104 | 78 | 329 | 73 | 124 | 137 |
| | 70 | 120 | 68 | 283 | 335 | 120 | 89 | 281 | 82 | 138 | 133 |
| 1.75%(0.705 M) | 3/8 | 722 | --- | 17 | --- | 72 | -- | --- | --- | --- | --- |
| | 3 | 434 | 260 | 271 | 445 | 102 | 29 | 619 | 91 | 143 | 160 |
| | 33 | 240 | 113 | 465 | 592 | 140 | 62 | 548 | 89 | 128 | 136 |
| | 70 | 260 | 121 | 445 | 584 | 156 | 78 | 437 | 91 | 139 | 156 |
| 3.5%(1.41 M) | 3 | 1058 | --- | 352 | --- | 99 | --- | 1268 | --- | 160 | --- |
| | 33 | 945 | --- | 465 | --- | 133 | --- | 1111 | --- | 160 | --- |
| | 70 | 920 | --- | 489 | --- | 158 | --- | 1056 | --- | 164 | --- |

** Value in the bracket indicates the chloride concentration in the mix water.

chloride concentrations for NaCl additions. Although, the bound chloride increases initially with the mix water chloride concentration, at 0.705 M mix water chloride concentration as NaCl the cement reaches its maximum chloride binding capacity (stable equilibrium). No more significant increase in the bound chloride concentration was evident with further increase in mix water chloride concentration to 1.41 M. It is also evident that there was no chloride binding by the 9th hour day after mixing (for 1.75% $Cl^-$). Thus, significant chloride binding starts between this time and the 3rd day of hydration.

From Table 1 it is clear that the bound chloride concentrations are consistently higher at all the measured hydration periods with equivalent chloride ions added to the mix as $CaCl_2$ instead of NaCl.

From Table 1 it is also seen that NaCl addition to the mix water results in a general rise in the $OH^-$ ion concentration from the 3rd day onwards. However, the $OH^-$ ion concentration increases only when there is a corresponding increase in the bound chlorides. For example, at 33rd day the $OH^-$ ion concentration increases from 0.077 M for chloride-free mortar to 0.104 M and 0.140 M when the added chloride was 1% and 1.75% $Cl^-$ by weight of cement respectively. At the above two levels of chloride addition to the mix water a significant amount of chloride ions were found to be bound. No more $Cl^-$ ions were bound with further increase in added chloride to 3.5% by weight of cement. The $OH^-$ ion concentration was 0.133 M at 33rd day for 3.5% $Cl^-$ mortar, which is nearly equal to the $OH^-$ ion concentration with 1.75% $Cl^-$ by weight of cement. Thus, the $OH^-$ ion concentration increases only when bound chloride concentration increases, which means that the chloride fixing involves an associated release of $OH^-$ ions into the pore solution.

Contrary to NaCl, the $CaCl_2$ addition to the mortar lowered the $OH^-$ ion concentration for the 3rd day of hydration compared with the chloride-free mortar. However, the $OH^-$ ion concentration showed an increasing trend from the 3rd day onwards with the significant rise from 3rd day to 33rd day. Nevertheless, the $OH^-$ ion concentration at the 70th day of hydration was still lower than that for the chloride-free mortar at the corresponding period.

$K^+$ and $Na^+$ Ion Concentrations. For the chloride-free mortar, the $K^+$ ion concentration showed an increasing trend from the 3rd (136 mM) to the 70th day (151 mM) of hydration. However, considering the experimental errors involved the $K^+$ion concentration is believed to be nearly stable over the period of hydration. Similarly, in the presence of both NaCl and $CaCl_2$ the $K^+$ ion concentration is taken to be stable as they did not show a clear trend.

The $Na^+$ ion concentration was almost stable for the chloride-free mortar over the period of hydration which is also true for the $CaCl_2$ admixed mortar. The addition of 1%, 1.75% and 3.5% $Cl^-$ by weight of cement as NaCl to the mix water results in $Na^+$ ion concentrations of 0.403 M, 0.705 M and 1.41 M respectively. However, the measured $Na^+$ ion concentrations for all the corresponding levels were less than the above from the 3rd day onwards, which implies that a significant amount of $Na^+$ ions were bound by the cement hydration products.

## Discussion

Chloro-complex in $C_3a$ Rich Cement. It is evident from the results that the free-chloride concentration decreases with the hydration and eventually reaches a quasi-equilibrium (33rd day). This means that, the missing $Cl^-$ ions have been bound in some form during hydration. The XRD and DSC studies carried by the authors indicated the formation of chloro-complexes, although with the above techniques it was not possible to distinguish between the Friedel's salt and its ferrite analogue, $C_3F.CaCl_2.10H_2O$, derived from $C_4AF$ (15). The cement used in the present investigation has 7% $C_4AF$ in addition to 11.2% $C_3A$. Thus it may be possible that the chloro-complex formed is a solid solution of Friedel's salt and its ferrite analogue, $C_3F.CaCl_2.10H_2O$. However, the latter has limited miscibility with Friedel's salt (25). Also under comparable conditions, $C_4AF$ normally appears to react slowly compared to $C_3A$ during cement hydration (25). Hence it is believed that the majority of chlorides bind in $C_3A$-rich cements in the form of Friedel's salt. The structure and composition of Friedel's salt is presented below for a better understanding of the mechanisms of free-chloride ion binding.

The Friedel's' salt and various aluminate and ferrite bearing hydrates formed in the cements belong to the family of AFm hydrates. These are formed at room temperature when the constituents they contain are brought together in appropriate concentrations in aqueous systems (25).

The AFm hydrates have a stacked layered structure which resembles the crystalline structure of portlandite (25). As shown in Figure 1 portlandite crystallises in a stacked layered structure with each $Ca^{2+}$ surrounded by six hexagonally close packed $OH^-$ ions (26). Each one of these $OH^-$ ions are co-ordinated to the two adjacent $Ca^{2+}$ ions in addition to the central $Ca^{2+}$ ion (not shown in the Figure 1). The formation of Friedel's salt can be imagined by an ordered replacement of one $Ca^{2+}$ ion out of the three in a layer $Ca(OH)_2$ by a $Al^{3+}$ ion as shown in the simplified Figure 2A. The reason for the replacement is not clear however, since the Al atoms are smaller in size compared to Ca atoms and hence stabilise the crystal structure. As the result of the above replacement an ionic charge imbalance is caused in each "principal layer," $[Ca_2Al(OH^-)_6.2H_2O]^+$. To balance the unit positive charge a $Cl^-$ ion (in hatched line) occupies

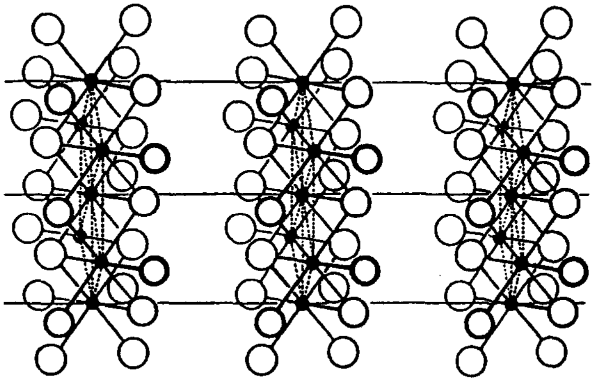

FIG. 1.
Crystal structure of $Ca(OH)_2$ (25). Key: large circles: $OH^-$ ions, small black circles: $Ca^{2+}$ ions.

the site above $Al^{3+}$ in the gap between the $OH^-$ ions as shown in Figure 2B. Thus, the composition of the principal layer becomes $[Ca_2Al(OH^-)_6.2H_2O]Cl$. The unit cell of Friedel's salt consists of two such principal layers of the above composition, each with a $Cl^-$ ion in the interlayer to balance the charge. The other abundantly available monovalent anion in the pore solution, that is, $OH^-$ may also compete with the $Cl^-$ ions during the adsorption process. In that event the structure formed would be $C_4AH_{13}$. In comparison to Friedel's salt, this phase has an additional $H_2O$ molecule associated with the principal layer, $[Ca_2Al(OH^-)_6.3H_2O]OH$. Similar

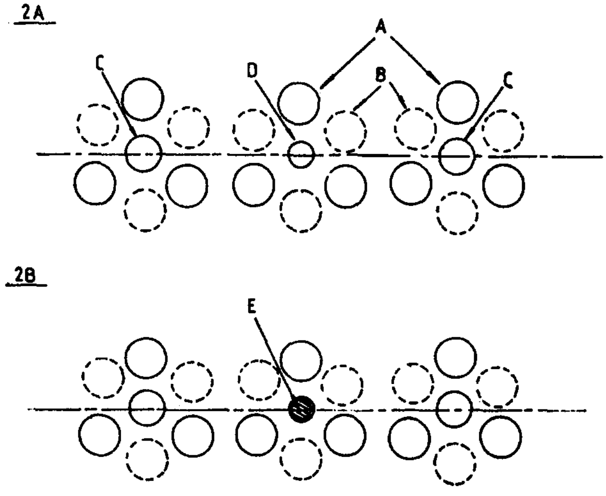

FIG. 2.
2A: A shematic view of the AFm principal layer: The co-ordination of $Ca^{2+}$ and the $Al^{3+}$ with the $OH^-$ ions. 2B: Adsorption of a $Cl^-$ ion above the $Al^{3+}$ in the gap between the $OH^-$ ions. Key: A: $OH^-$ ions in upper layer, B: $OH^-$ ions in lower layer, C: $Ca^{2+}$ ion, D: $Al^{3+}$ ion, and E: $Cl^-$ ion.

to Friedel's salt the unit cell of $C_4AH_{13}$ has two such principal layers of the above composition, each with a $OH^-$ ion in the interlayer to balance the unit positive charge. The phases $C_4AH_{19}$, $C_4AH_{11}$, and $C_4AH_{11}$ are structurally derived from $C_4AH_{13}$ by the addition/subtraction of $H_2O$ molecules in the principal layer.

Mechanisms of Chloride Binding. From the results it is evident that binding of $Cl^-$ occurs with an increase in $OH^-$ ion concentration in the pore solution. However, the quantity of $OH^-$ ions released into the pore solution was not equal to the quantity of chlorides bound during hydration. This result is contrary to an earlier investigation (22), in which the bound chlorides and the released $OH^-$ ions were approximately equal on a molar concentration basis over a period of hydration. Based on the above discussion it is suggested that the free-chloride ions bind simultaneously with the cements in two different ways. A fraction of the free-chloride ions bind by releasing equivalent amount of $OH^-$ ions in moles into the pore solution. Whereas, the bulk of the free-chloride ions bind without releasing $OH^-$ ions into the pore solution. These are discussed individually below.

Mechanism for $Cl^-$ Ion Binding with $OH^-$ Ion Release. The rise in $OH^-$ ion concentration associated with free-chloride binding in the presence of NaCl addition to the mix was explained by Ben-Yair by the following equations (21).

$$Ca(OH)_2 + 2NaCl \leftrightarrow CaCl_2 + 2Na^+ + 2OH^- \qquad [1]$$

$$C_3A + CaCl_2 + 10H_2O \rightarrow C_3A.CaCl_2.10H_2O \qquad [2]$$

The consumption of $CaCl_2$ by the reaction [2] displaces the equilibrium of the equation [1] to the right and causes the dissolution of the portlandite to generate hydroxyl ions in the pore solution. Thus, the release of $OH^-$ ions is dependent on equation [2]. However, the formation of Friedel's salt by equation [2] is open to debate as $CaCl_2$ is highly soluble even in strong alkaline solution. Also, the formation of Friedel's salt by the equation [2] is difficult to explain based on its structure. In addition to the above drawbacks, the Ben-Yair's suggestions fail to explain the significant rise in $OH^-$ ion concentrations from 3rd to 33rd day in presence of $CaCl_2$ addition to the mortar as presented in Table 1.

Alternatively, the rise in $OH^-$ ion concentrations associated with chloride binding in the presence of both NaCl and $CaCl_2$ can be explained by an ordered replacement of $OH^-$ ions present in the interlayers of AFm hydrates ($C_4AH_{13}$ and its derivatives) by the $Cl^-$ ions from the pore solution. The unreacted $C_3A$, remaining after preferentially reacting with sulphates reacts in the presence of excess of $Ca(OH)_2$ at room temperature to form $C_4AH_{13}$ as shown below (27).

$$3CaO.Al_2O_3 + Ca(OH)_2 + 12H_2O \rightarrow 4CaO.Al_2O_3.13H_2O \qquad [3]$$

The phase $C_4AH_{13}$ is meta-stable and readily undergoes changes in water contents to form other AFm hydrates with a higher/lower water molecule content in the principal layer as already explained. The $OH^-$ ions in the interlayers are particularly prone to ion exchange (28,29). Thus, the anion-exchange reaction occurring between the $OH^-$ in the interlayers of AFm hydrates and the free-chloride ions of the pore solution to form Friedel's salt is expressed as follows.

$$R\text{-}OH^- + Na^+ + Cl^- \rightarrow R\text{-}Cl^- + Na^+ + OH^- \qquad [4]$$

Where, "R" is the principal layer of the AFm hydrates of composition, $[Ca_2Al(OH^-)_6.nH_2O]^+$, the value of "n" depends on the type of AFm hydrate participating in the reaction. Thus, the increase in $OH^-$ in moles occurring during chloride binding is equal to the amount of chloride ions bound in moles. Hence, the question of ionic charge imbalance in the pore solution does not arise.

The amount of $OH^-$ ions that will exchange with the $Cl^-$ ions depends on the number of sites available for ion exchange, or indirectly the quantity of AFm hydrates present at any instant in the hydrated cement. Thus under this explanation, the maximum limit of ion exchange can be interpreted as the ion-exchange capacity of the AFm hydrates.

Mechanism for $Cl^-$ Binding Without $Oh^-$ Release. From the above discussion it is clear that out of the total free-chloride ions present in the pore solution a fraction of it binds by an anion-exchange mechanism. However, the data imply that this accounts only for a minority of the $Cl^-$ binding. While the bulk of the free-chloride ions due to NaCl and $CaCl_2$ bind by direct adsorpion in the interlayers of the principal layer, $[Ca_2Al(OH^-)_6.2H_2O]^+$, of the AFm structure to balance the charge arising due to the replacement of a $Ca^{2+}$ ion by a $Al^{3+}$ ion. The adsorption of $Cl^-$ ions leads to the formation of Friedel's salt as already explained and disturbs the ionic charge balance in the pore solution. To maintain charge neutrality an equivalent amount of $Na^+$ ions leave the pore solution and enter the C-S-H gel lattice, as explained below.

Cations like $Al^{3+}$ and $Fe^{3+}$ ions can replace the $Si^{4+}$ of the C-S-H gel lattice and, as a result of this to balance the charge, monovalent alkali cations, $K^+$ and $Na^+$ ions enter the C-S-H gel lattice along with $Ca^{2+}$ ions (30,31). The upper limit of such replacement is one atom of Al or Fe for six atoms of Si. The replaced $Si^{4+}$ forms silicate hydrates with appreciable crystalline water (hydrogarnets). Table 2 presents the chlorides bound by the cement in mM by adsorption alone and the bound $Na^+$ ions in mM from the NaCl that enter the C-S-H gel lattice to balance the charge. It is quite evident that the bound $Na^+$ ions nearly balance the bound $Cl^-$ ions by the 70th day of hydration for all the levels of $Cl^-$ additions. Thus, the $Na^+$ ions require time to bind with the C-S-H gel in order to maintain the ionic charge neutrality in the pore solution. An example for the above calculation is given in appendix 1. In the present case however, the $Na^+$ ion concentration showed a decreasing trend while, the $K^+$ ion concentration remained approximately stable over the period of hydration.

TABLE 2

The Adsorbed $Cl^-$ & The Bound $Na^+$ Ion Concentrations

| $Cl^-$ levels by wt of cement | Age of the specimens days | Total bound $Cl^-$ mM | $Cl^-$ bound by adsorption mechanism. mM | Bound $Na^+$ mM |
|---|---|---|---|---|
| 1% | 33 | 298 | 266 | 144 |
| | 70 | 283 | 235 | 188 |
| 1.75% | 33 | 465 | 404 | 373 |
| | 70 | 445 | 361 | 334 |
| 3.5% | 33 | 465 | 404 | 373 |
| | 70 | 489 | 403 | 420 |

When $CaCl_2$ is admixed, the increased concentration of $Ca^{2+}$ ions in the pore solution raises the solubility product of $Ca(OH)_2$ and the latter precipitates in conformity with its solubility product. This causes a general decrease in pH of the pore solution at 3rd day compared to that with equivalent $Cl^-$ added as NaCl. Thus the removal of the $Ca^{2+}$ ions from the pore solution indirectly facilitates maintenance of charge neutrality as a result of $Cl^-$ adsorption. Apart from this some of the $Ca^{2+}$ ions also enter the C-S-H gel as already explained above.

Relationship between the Mix Water and the Bound Chloride Concentrations. Figure 3 shows the relationship between the mix water chloride concentration and the maximum bound chloride (at quasi-equilibrium-33rd day) with NaCl salt addition to the mix. It is evident that with increase in mix water chloride concentration to 0.705 M, the amount of bound chloride does not increase indicating a stable equilibrium between the free and the bound chlorides. Since the bulk of the chloride ions are bound by an adsorption process the above relationship shown in Figure 3 is approximately described by a Langmuir adsorption isotherm, which represents the equilibrium between the adsorbed and the free-species. The present observation is in accordance with an earlier report (32).

The maximum chloride binding limit in Figure 3 is interpreted as the chloride adsorption capacity of the cement. The chloride adsorption capacity of the cement depends on the number of sites available for $Cl^-$ ion adsorption and also the competition offered by the monovalent anions other than $Cl^-$ during adsorption. The latter explains the higher chloride binding observed with $CaCl_2$ addition which is discussed below.

From Table 1 it is seen that for the similar mix water chloride concentrations the amount of chlorides bound with $CaCl_2$ salt were higher than with equivalent chloride added as NaCl to the mix water. Also the pH of the pore solutions with $CaCl_2$ addition are significantly lower from the 3rd day onwards compared to that with NaCl additions. Hence it appears that the $OH^-$ ion concentration influences the chloride adsorption process. Since with $CaCl_2$ addition the bulk of the chlorides are bound by adsorption in the interlayers, hence it is possible that the competition offered by the $OH^-$ ions during the $Cl^-$ ion adsorption is to a limited extent. Thus,

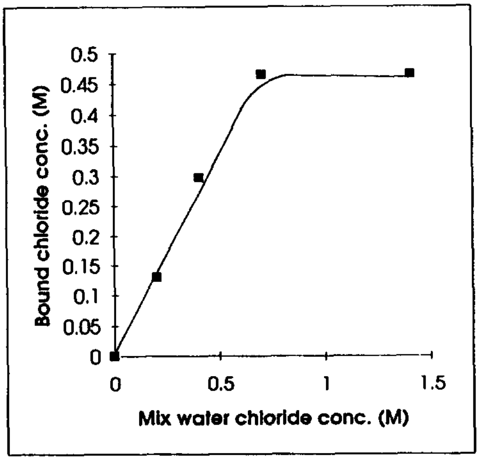

FIG. 3.

Relationship between the chloride concentrations in the presence of NaCl.

the relatively less alkaline pH of the pore solution with $CaCl_2$ addition facilitates the higher adsorption of $Cl^-$ ions to form the Friedel's salt. In the event of the preferential $OH^-$ adsorption $C_4AH_{13}$ or its derivative hydrates are formed as already discussed.

## Conclusions

The following conclusions are drawn from the present investigation.

1. A fraction of $Cl^-$ ions in presence of both NaCl and $CaCl_2$ bind by releasing an equivalent amount of $OH^-$ ions in moles into the pore solution. The rise in $OH^-$ ion concentration is explained by an ordered replacement of the $OH^-$ ions present in the interlayers of AFm hydrates (viz. $C_4AH_{13}$ and its derivatives) by the $Cl^-$ ions from the pore solution by an anion-exchange mechanism.
2. The bulk of the $Cl^-$ ions in presence of both NaCl and $CaCl_2$ are bound by adsorption in the interlayers of the principal layer, $[Ca_2Al(OH^-)_6.2H_2O]^+$, of the AFm structure to balance the charge. Due to the adsorption of $Cl^-$ ions from NaCl an equivalent amount of $Na^+$ ions (in moles) are removed from the pore solution to maintain ionic charge neutrality in the pore solution. The $Na^+$ ions enter the C-S-H gel lattice to balance the charge.
3. The higher chloride binding in presence of equivalent $Cl^-$ as $CaCl_2$ compared to NaCl is due to the lower degree of competition offered by the $OH^-$ ions during the bulk $Cl^-$ ion adsorption in the interlayers of the principal layer, $[Ca_2Al(OH^-)_6.2H_2O]^+$.

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## Appendix 1

For 1.75% $Cl^-$ Added as NaCl. For the mortar containing 1.75% $Cl^-$ the corrected free $Na^+$ ion concentration by the 33rd and 70th day were 548 and 437 mM respectively. This includes the $Na^+$ ions derived from the NaCl addition as well as the $Na^+$ ions released from the cement itself. The chloride-free mortar released 74 mM and 66 mM of $Na^+$ in the pore solution at 33rd and 70th days of hydration. It is reasonable to assume that the cement also releases the same amount of $Na^+$ ions into the pore solution in the presence of added NaCl. Thus, the $Na^+$ ion concentration due to NaCl addition alone by the 33rd day would be 474 mM (548 mM–74 mM). In a similar way, the $Na^+$ ion concentration by the 70th day of hydration due to NaCl alone would be 371 mM (437 mM–66 mM). The bound $Na^+$ ion concentration is the difference between the initial $Na^+$ ion concentration in the mix water (705 mM) and the free $Na^+$ ion concentration due to NaCl addition. Thus, the bound $Na^+$ ion concentration works out to be equal to 231 and 334 mM by the 33rd and 70th day of hydration respectively.

The bound chloride concentration by the 33rd and 70th days were 465 and 489 mM respectively. Out of this total bound chlorides a fraction of the chloride ions are bound by the anion-exchange mechanism. From the Table 1 it is clear that no chloride ions were bound by the 3/8th day after mixing. The total rise in $OH^-$ ion concentration from the 3/8th day of hydration to the 33rd and 70th day of hydration are equal to 68 mM and 84 mM respectively, which also equals the amount of $Cl^-$ ions bound by anion-exchange mechanism. The balance chlorides bound by adsorption in the interlayer is 397 mM (465 mM–68 mM) and 361 mM (445 mM–84 mM) by the 33rd and 70th day respectively.

The $OH^-$ ion concentration at 3/8th day is assumed to be equal to 0.072 M for the purpose of calculation for 1% and 3.5% $Cl^-$ additions.