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BINDING
OF CHLORIDE BY CALCIUM ALUMINATE**

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ABSTRACT

The risk of pitting corrosion attack of the embedded steel reinforcement is determined by the amount of the free chloride present in the cement pore environment. Some of the chloride anion is bound as the Friedel salt i.e., $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$ or it is adsorbed in the cement matrix by CSH gel or other cement phases and is thus rendered harmless. Even the effectively bound chloride may be conditionally released due to a change in the equilibrium parameters and may cause serious damage to the exposed steel. The present investigations focus upon studies conducted on synthesized calcium chloroaluminate (SCCA) as the function of temperature and pH of the solution. The effect of temperature upon the chloride release was also monitored upon small mortar balls. It is observed that the pH of the medium is more important i.e., more chloride is released from the SCCA in at pH 14 solution as compared to the SCCA at a solution pH of 10. However, the SCCA is stable between the temperature range of 20 °C till 60 °C. In case of the real mortar balls physical adsorption of the chloride ion is more important and it shows temperature dependence across the temperature range of 20 °C - 60 °C. It is deduced that these parameters play a decisive role in the overall solution chemistry regarding bound/free chloride ratio in the cement pore environment. The effect of pH is also reflected for OPC, OPC/fly ash and OPC/slag cement blended mortars of the composition 1:1 and 4:1 cement/sand ratio. Polarisation resistance measurements have shown that higher the cement content higher is the protection offered to the embedded steel during the hydration period.

INTRODUCTION

The chloride anion (Cl^-) may be bound in cement in two ways: a) by a chemical bond through reaction with the hydration products or b) by the physical adsorption on to the surface of the hydration products. However, when the Cl^- levels are very high a part may be bound and thus harmless¹⁻², and a portion of Cl^- may be free to cause damage to the embedded steel i.e., the ratio of the free Cl^- /bound Cl^- is an important controlling factor in determining whether the steel will pit or not.

The C_3A i.e., tricalcium aluminate ($3\text{CaO}.\text{Al}_2\text{O}_3$) and tetra alumino ferrite (C_4AF) in cement binds Cl^- anion to form an insoluble product, called the Friedel salt, with the composition $3\text{CaO}.\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3.\text{CaCl}_2.10\text{H}_2\text{O}$ and reduces the levels of free Cl^- in the pore solution³⁻⁴. Rasheeduzzaffar and coworkers⁵ have shown that the concentration of water soluble chloride, extracted with hot water, falls from 86 % for 2% C_3A content in OPC mortars to 33 % for OPC mortars containing 14 % C_3A . A higher chloride complex of the composition, $3\text{CaO}.\text{Al}_2\text{O}_3.3\text{CaCl}_2.30\text{H}_2\text{O}$ ⁶, has also been also reported which is formed with a 21-23 % CaCl_2 solution at -10°C : a condition which is not normally encountered in hydrating cements. Thus, the corrosion resistance of steel in cements can be elucidated on the basis of the C_3A content of the cement⁷. e.g., the poor performance of sulphate resisting cement is generally attributed to low C_3A content i.e., low binding capacity resulting in higher corrosion rates⁸.

Several researchers have also reported the physical adsorption of the Cl^- anion: Ramchandran suggested that a high proportion of Cl^- ions form an interlayer chemisorbed complex within C-S-H gel⁹. Midgley and Illston¹⁰ have reported a reduction in the pore size of the hardened cement pastes in presence of Cl^- ion, by the mercury intrusion porosimetry technique. Lambert¹¹, however, did not find any detectable capacity to bind Cl^- in C_3S (Jeffery's alite) from analysis of the pore solution expressed from C_3S hardened pastes.

Benjamin and Sykes observed that a steel mortar specimen containing 3 % NaCl (by weight of OPC) showed pitting at 40°C ¹². The same pitted specimen did not show pitting at 0°C . This raised an important question that whether the stability of Friedel salt was temperature dependent.

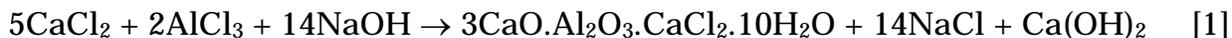
The present investigations specifically deal with two important parameters i.e., the stability of synthesised calcium chloroaluminate (SCCA) as the function of temperature and the pH to understand the role this component of cement in binding chloride. The studies are further extended to simple experiments with mortar spheres to correlate the binding mechanism operative in the real cement environment.

The studies have been extended to the performance of blended cements i.e., ordinary Portland Cement (OPC) mixed with blast furnace slag (BFS) cement and fly ash (FA). Earlier works on blended cements have been conducted on hardened cement pastes¹³⁻¹⁴. However, the chemistry changes in the hydrating cement with

inherently present Cl^- ion may start to effect the passivation of steel embedded in concrete at a very early stage. The results are amalgamated to reach a reasonable conclusion regarding the role of C_3A in cements.

EXPERIMENTAL

Calcium chloroaluminate was synthesised by the titration of NaOH solution against a mixed solution of aluminum chloride and calcium chloride in the correct stoichiometric ratio, till pH 11.99 was achieved. The reaction can be presented as follows:



The detailed procedure is described elsewhere¹⁵. The titration was performed in deaerated atmosphere. The precipitates were filtered in deaerated conditions and dried to constant weight in a desiccator over fused CaCl_2 . The SCCA precipitates were identified by XRD on Phillips PW 1050 and compared against standard tables¹⁶. The chloride content of SCCA was also determined by chemical analysis by Mohr's method¹⁷. Finally, the SCCA was analyzed by electron probe microanalyses (EPMA) on Cameca Cambex, to confirm the calcium/aluminum and calcium/chloride ratio in the compound.

An accurately weighed amount of dried SCCA was added to solutions of pH-10, pH-12.6 and pH-14. The compound was allowed to equilibrate in the solutions for two weeks before analyzing for the chloride content by the spectrophotometric technique on a Perkin Elmer 552. This standard method involves addition of 0.25 M ammonium iron (III) sulphate in 9 M nitric acid, followed by the addition of a saturated solution of mercury(II) thiocyanate in alcohol. The absorbency was measured at 460 nm. The same samples were held at different temperatures i.e., 22°, 40°, 50° and 60 °C for two hours and the Cl^- released was checked. After tests the suspensions were cooled for one day and fresh aliquots were again checked for chloride levels to observe whether the reaction was reversible or not. Lastly, XRD patterns of SCCA in the test solutions were taken again to confirm the compound.

To monitor the chloride binding mechanism in mortars, small spherical mortar specimens were cast in 1 cm diameter, with 1:1 cement/sand ration and a water/cement ratio of 0.5. NaCl was added to the mix water to ensure even distribution of salt in the cement matrix. The mortar slurry was shaped into balls in plastic molds. The samples were de-molded after 24 hours, sealed inside polythene bags and cured for 40 days at 25 °C.

Six mortar spheres of each mix were immersed in 50 ml of distilled water which was just enough to cover the samples. Mortar spheres were allowed to equilibrate with the surrounding solution for two weeks at room temperature i.e., 22 ± 2 °C, sealed inside polythene bottle. Periodically, chloride determination tests of the immersion water were carried out by the same method as for SCCA. After 14 days tests were started when the Cl^- concentration changed very little especially for 1 % NaCl mortar spheres. Tests were conducted at 22 °, 40° and 60 °C. The solutions with mortar samples were cooled and kept at the specific temperature for

ten days and again checked for the chloride levels to understand the binding mechanism in mortars.

Studies on blended cements were performed on commercial grade Pakistani steel. Its nominal composition was determined through SEM analysis on Philips XL 30, Holland and given in table I.

Table-I

Element	Fe	Si	P	S	Ti	Mn
% composition	98.79	0.27	0.04	0.03	0.10	0.62

Nominal composition of the steel

Samples of steel having dimensions 1cm x 1cm were prepared. A steel wire was wrapped around the steel specimen and these were cold mounted leaving an exposed area of 78.5 mm². The specimen were lightly mechanically polished and washed and dried with alcohol.

The mounted samples were mechanically embedded in mortars prepared from OPC, OPC/BFS, OPC/FA mixtures. The OPC/BFS and OPC/FA ratios were kept at 1 : 0.54. The composition of OPC, BFS and FA is given in table II.

Table II

Chemical composition %	Type of Cement		
	OPC	BFS	FA
L.O.I	1.05	1.1	3.5
SiO ₂	21.12	24.85	59.7
Al ₂ O ₃	6.08	8.08	4.94
Fe ₂ O ₃	3.78	3.12	26.71
CaO	63.86	57.6	1.63
MgO	1.15	2.5	0.5
SO ₃	2.37	2.33	traces
Na ₂ O	0.97	-	0.28
K ₂ O	0.35	-	0.80
I.R	0.14	0.30	0.28
LSF	0.90	0.69	0.89

Chemical composition of OPC, slag cement and Fly ash

Ordinary silica sand after washing and drying was used for the preparation of mortar specimen.

Two mix proportions were studied i.e., OPC/blending cement, in the ratio of 1:1 and 1:3. The behavior was monitored against plain OPC cement mortars. The water/cement ratio was kept at 0.5 for both the mix proportions. The specimens were embedded in the mortar in a way that the exposed face was held in a vertical fashion having a cover of 0.75 inches on all sides.

The mortars were allowed to set for 2 days before these were remolded and placed in the immersion solution. The measurements were started after 2 days of immersion in water containing 3 % sodium chloride (NaCl) solution. Linear potentiostatic polarization resistance (LPR) measurements were continuously conducted for 30 days on a home made low noise potentiostat. The changes in the potential were recorded against standard Calomel reference electrode and a platinum wire was used as a counter electrode. A potential of ± 10 mV was applied around the free corrosion potential (E_{corr}), and the corresponding changes in the current were noted on a voltmeter in series with the potentiostat, after a time span of 60 seconds. This method was adopted for quick assessment and nondestructive effects.

RESULTS AND DISCUSSION

The XRD pattern for SCCA is presented in Fig. 1. The major peak appearing at 2θ of 7.8° identified the compound as β -calcium chloroaluminate.

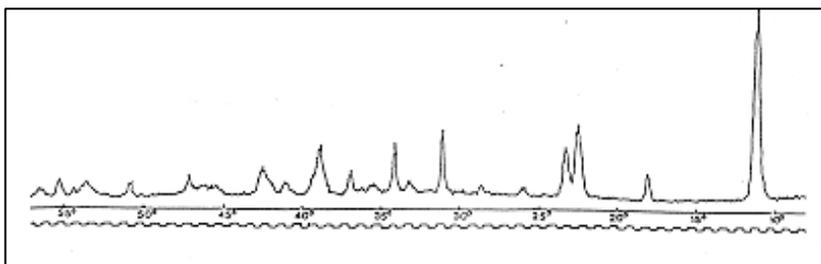


Fig. 1: X-Ray diffraction pattern of the synthesized calcium chloroaluminate.

Also, the ratios of the intensities of the characteristic peaks were similar. The chemical analysis showed that 0.148 gm Cl^- /gm of the sample. Theoretically $\text{Cl}^- = 0.123\text{g}$ for the Friedel salt. The EPMA results showed that the SCCA, on average, contained $\text{Al}=0.42$, $\text{Cl}=0.53$ and $\text{Ca}=1.04$. The ratio is satisfied in terms of $\text{Ca}/\text{Cl}=1.96$ but the $\text{Al}/\text{Cl}=1.26$, and $\text{Ca}/\text{Al}=2.3$ was higher than the Friedel salt. The data as weight percent however, confirms that this compound is β -calcium chloroaluminate in the anhydrous form. Complexes with different composition are expected to form in a situation when OH^- ions are competing with Cl^- ions to combine with the aluminate species¹⁸. Lea⁶ has reported that the phase i.e., β -calcium chloroaluminate is only stable at temperatures above 28°C . Therefore, it is expected that this phase exists in hot climates. Kuzel¹⁶ found, through precise optical measurements that the rhombohedral β -phase crystals that are high symmetry and uniaxial, can change to monoclinic α -phase, double axial and lower symmetry upon cooling through twinning.



This change that occurs at an equilibrium temperature of $28\pm 2^\circ\text{C}$ was reversible and spontaneous without changing the crystal morphology and the water content. Pöllman and Kuzel¹⁹ have also reported that all monoclinic phases in the

system can be converted into rhombohedral by heating or light rubbing. Thus, any of these factors can change α -phase into β -phase and vice versa.

Test in SCCA: The results obtained for SCCA in different pH solutions, presented in Fig. 2, show that as the pH of the medium is increased the concentration of Cl^- released into the solution is also increased.

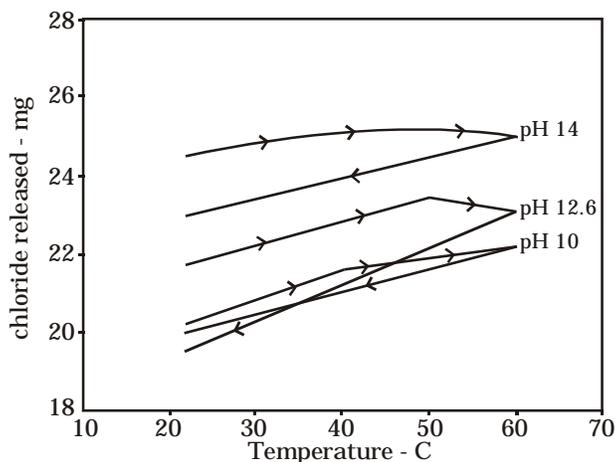


Fig. 2: Effect of temperature on the stability of the synthesized calcium chloroaluminate in different pH solutions.

It seems that the SCCA formation took place according to the reaction described in Fig. 3. So reasonably it may be assumed that as the OH^- concentration of the medium increases, the complex would take up OH^- ion and Cl^- would be released:



Though pH has its influence showing that OH^- ion takes the place of Cl^- in this complex, the interchange cannot be explained in terms of simple thermodynamics. It is obvious that some Cl^- will be released in aqueous environments, from systems like the one under study unless sufficient Cl^- is already present²⁰.

Page²¹ suggested that poor performance of silica fume-OPC blend (30%) was due to solubility of Friedel salt at low pH-11.6. Our studies show contrary results i.e., SCCA is stable at this pH and higher alkalinity does not appreciably favors Cl^- binding by this compound. Al-Amoudi²² and co-workers have supported the use of silica fume-OPC blend as compared to plain OPC as it showed the least corrosion rates for steel reinforcement in sulphate environments in presence of chloride ions. It is plausible that Page only presented a speculation and did not actually investigated the Friedel salt's stability.

The amount of Cl^- that stayed bound, calculated from Fig. 2, at $\text{pH}_{10} = 0.72$, $\text{pH}_{12.6} = 0.6$ and $\text{pH}_{14} = 0.5$, which indicates the stability of mono chloride complex.

It is expected that the hydrate formation i.e., C_4AH_{13} is favored if the Cl^- content of the compound falls to 0.3^{23} .

Temperature affected the Cl^- release from $20\text{ }^{\circ}C$ to $40\text{ }^{\circ}C$, but after this temperature, the Cl^- ion concentration in the solution did increased markedly. This shows that Cl^- release takes place when the equilibrium conditions are disturbed. Low Cl^- release from $40\text{ }^{\circ}C$ to $60\text{ }^{\circ}C$ indicates that some stability of the compound is maintained. The Cl^- concentration decreased upon cooling in all the pH solutions, falling even below the starting equilibrium values suggesting that Cl^- binding is favored at low temperatures and a reversible process is operating. Roberts²⁴ observed similar release of Cl^- with temperature in solutions of $NaOH$ and $Ca(OH)_2$. He however, described it in terms of an irreversible process due to the formation of stable C_4AH_{13} complex.

We observed a reversible behavior i.e., cooling leads to the re-absorption of Cl^- ion. Results do not seem to fit a simple thermodynamic treatment of ion exchange either, but this will be influenced by the thermodynamics of the solid phase. Re-absorption can, however, be explained in terms of the structural consideration of the complex. Butler and Taylor²⁵, established the structure of C_4AH_{13} as parallel layers stacked in a complex manner with six OH^- groups in octahedral layer and seventh OH^- group outside it where it is closely associated with water molecules. Complete replacement of OH^- groups outside the octahedral layers occurs in the synthetic compound as $CaO.Al_2O_3.CaX_2$ aq. where X is an anion. Thus, water and extra interchangeable ions can sit at interfaces between layers and can interchange reversibly with species from solution whenever, equilibrium is disturbed. This was confirmed by the XRD patterns after the tests which showed that the compound was still mono chloride complex as shown in Fig. 3.

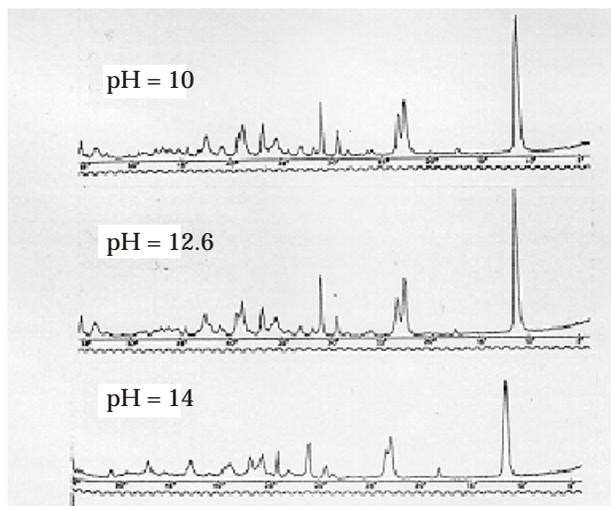


Fig. 3: X-Ray diffraction patterns of the synthesized calcium chloroaluminate after tests in solutions of pH 10, 12.6 and 14 at different temperatures.

UTests in 1% NaCl OPC mortar spheres: The chloride concentration in solution increased slightly with an increase in temperature from $22-40\text{ }^{\circ}C$ and

markedly at 60 °C, Fig. 4. Upon cooling the temperature falls to level below the start level. In these experiments, it is assumed that the outer layer of mortar spheres achieved equilibrium with the solution. Only the outside layer released Cl^- , more can come into the solution but slowly with time from the interior. Raising the temperature also accelerated the transport outward from the inner core but the Cl^- determined was mainly from the outside layer as the steady state conditions will take much longer to achieve.

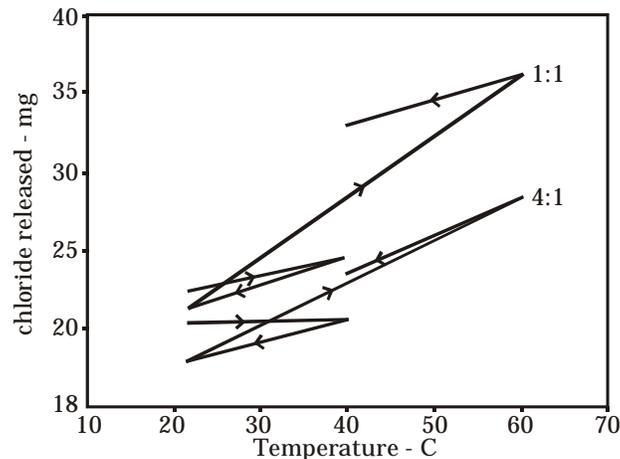


Fig. 4: Concentration of free Cl^- in solution from the mortar spheres containing 1% NaCl (by wt of OPC) as the function of temperature having aggregate/cement ratio 1:1 and 4:1.

It seems at first that the increase in the Cl^- concentration is due to the higher diffusion rate of Cl^- into the surrounding water. Page and coworkers²⁵ observed 9 times increase in the value of effective diffusivities of chloride ion into hardened cement pastes for temperature change from 7° – 44 °C. If solely the diffusion of free chloride into the surrounding water was responsible then even upon lowering the temperature the Cl^- concentration in the solution should remain constant or continue to increase till equilibrium is established. This shows that some absorption into the mortar spheres has taken place, and that there is reversible chloride release with a strong effect of temperature. The results are similar to the work reported by Luping and Nelson²⁰ with their work on OPC pastes and mortars. They showed that the relationship between the bound Cl^- and the free Cl^- can be well described by Cl^- binding isotherm which obeys Freundlich equation at high free Cl^- concentrations of >0.01 mol/l, and Langmuir equation at low concentrations. The absorption is mainly the function of the amount of CSH gel regardless of the W/C and the A/C content. They also emphasized that some percentage of Cl^- is always retained as C_3A -complex. The behavior of these mortar spherical balls have also shown that adsorption of Cl^- by the mortar matrix is the key operative mechanism involved when the temperature is varied. The results disagree with Robert's²⁴ postulation that the Cl^- is released from the Friedel salt at similar temperatures and the process is irreversible.

Chatterje²⁷, Ludwig and Darr²⁸ in separate studies have shown that Friedel salt with different chloride content are stable and can form at 5 °C, 20 °C and 60 °C. Maslehuddin and coworkers²⁹ also observed an increase in the Cl^- ion levels in the

pore solution with both OPC and blended cements at higher exposure temperatures and also when sulphate ions were present. However, the results also showed that the OH^- levels decreased above 70°C , which was considered to be due to the instability of calcium chloroaluminate at this temperature. Chloride compounds formed with SCCA were stable up to 60°C in this study. Differential thermogravimetric analysis³⁰ have also shown that the mono chloride peak appears at 350°C and this again attests to the stability of Friedel salt. It is only the adsorbed chloride in the matrix which is affected by the changes in the equilibrium state.

The mortar ball experiments are also consistent with potentiodynamic tests for iron embedded in mortars of A/C ratio 1:1 and w/c ratio of 0.5 containing 3 % NaCl as an admixture, given in our earlier papers¹². The specimen showed pitting at 40°C , but the same specimen when cooled quickly to 0°C did not pit at all. This also agrees with the postulation that absorption in the matrix plays an important role after stable binding with tri-calcium aluminate. Parkinson³¹ also found a lot of temperature dependence of free Cl^-/OH^- ratio with SRPC cements, though lower ratio was obtained with OPC. Lambert and Page¹¹ however, did not find any role of calcium silicates in binding Cl^- . This discrepancy could be due the difference in the method adopted. These investigations with the synthesized calcium chloroaluminate and simple mortar ball experiments, both attest that, adsorption of chloride in the cement matrix plays a key role in the corrosion of steel reinforcement embedded in concrete.

UTESTS ON OPC, OPC/FA and OPC/SLAG BLENDED CEMENTS The results for mortars with cement/sand ratio 1:1 are presented in Fig. 5-6.

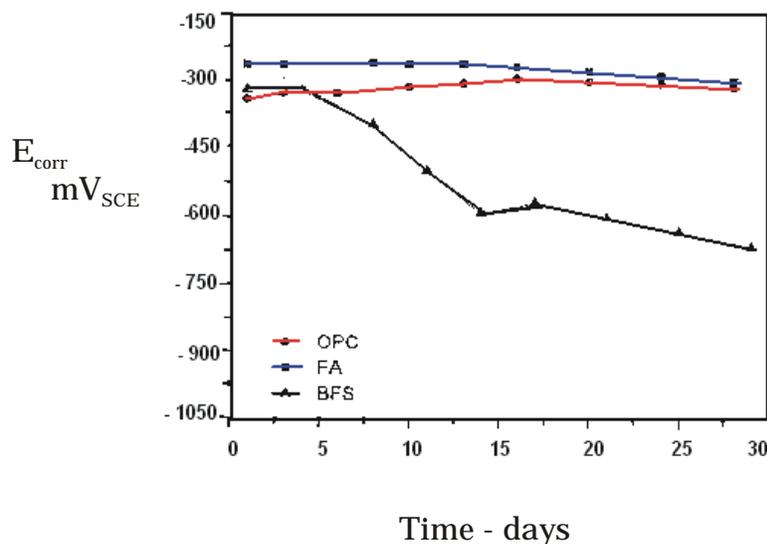


Fig. 5: Changes in Free Corrosion Potential (E_{Corr}) of the specimen with time embedded in different types of cements (W/C ratio 1:1)

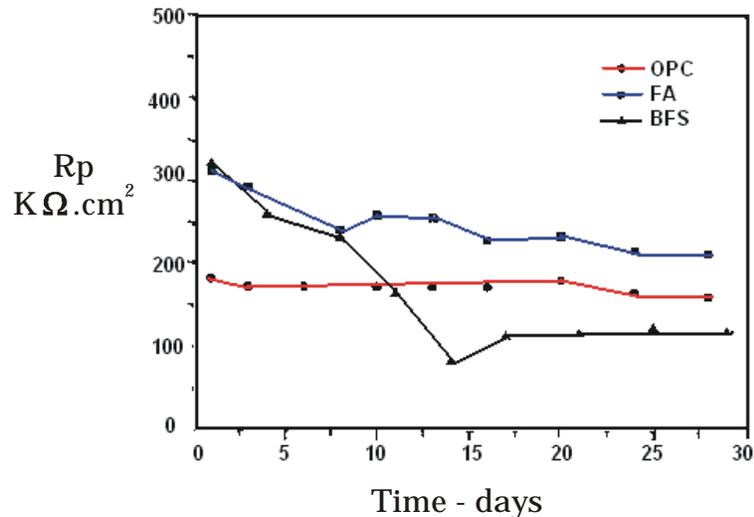


Fig. 6: Changes in Polarisation Resistance (R_p) of the specimen with time embedded in different types of cements (W/C ratio 1:1)

The OPC and OPC/PFA mortars showed higher E_{corr} at around -300 mV and the R_p declined from 300 $Kohm.cm^2$ to 210 $Kohm.cm^2$ at later stages. The R_p for the plain OPC mortars stayed around 175 $Kohm.cm^2$. The OPC/BFS mortars (cement/sand ratio 1:1) failed only after 4 days of immersion in the saline media. The E_{corr} values settled to low values of -600 mV in 13 days with the R_p values also declining to 90 $Kohm.cm^2$. Such R_p values indicate that still the steel is maintaining some passivity. Plausibly a crevice developed at the steel mortar joint which is expected in case of low oxygen availability.

The E_{corr} for all types of mortars with cement/sand ratio of 3:1 was low i.e., between -450 to -600 mV with OPC/PFA slightly higher than the OPC plain and OPC/BFS blended cements, Fig. 7-8.

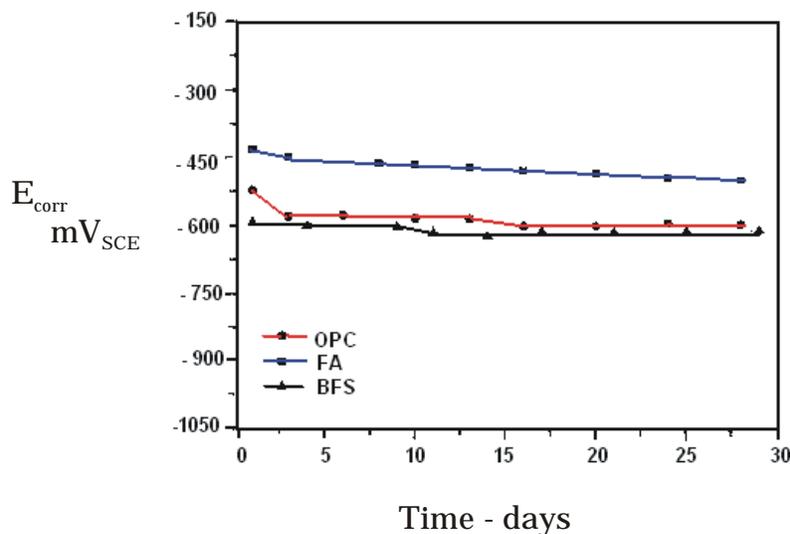


Fig. 7: Changes in Free Corrosion Potential (E_{corr}) of the specimen with time embedded in different types of cements (W/C ratio 3:1)

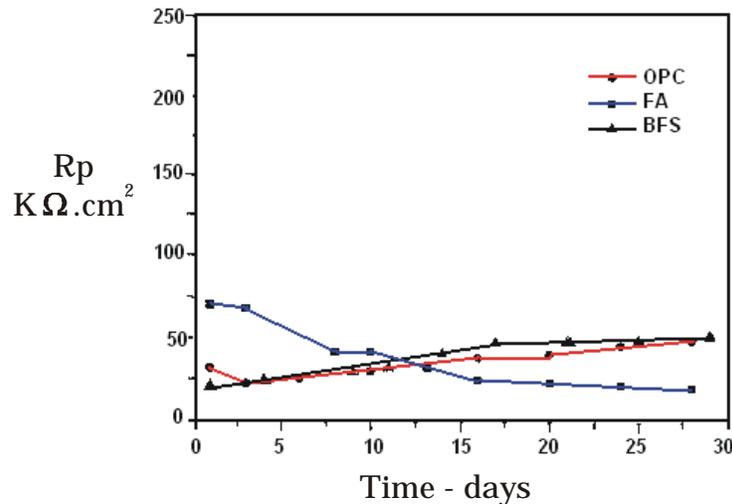


Fig. 8: Changes in Polarisation Resistance (R_p) of the specimen with time embedded in different types of cements (W/C ratio 3:1)

It is interesting to note that slowly the R_p values started to recover especially for OPC plain and OPC/BFS. The main reason could be the increase in the alkalinity of the pore solution of slag and OPC as the hydration reaction proceeded, see table II. Also, some chloride binding proceeded with time. More alkalinity is required to trigger the hydration reactions in PFA and it is expected that PFA will recover with time.

These results show that if the cement content is high, then the cement mortars even if blended, can provide a good protection to the embedded steel immediately after the setting of cement.

CONCLUSIONS

1. The stability of SCCA is affected by the changes in temperature but more markedly by the changes in pH.
2. Synthesized calcium chloroaluminate (SCCA) always releases some chloride in different alkaline solutions. The highest amount of Cl^- ion is released for the synthesized compound at pH- 14 and the least is observed for the pH-10 solution. The amount of Cl^- that stayed bound, calculated from Fig. 2, amounts to 0.72 at pH_{10} , 0.6 at $\text{pH}_{12.6}$ and 0.5 at pH_{14} . This Cl^- content slightly increases with an increase in temperature and decreases when the solution is cooled. The XRD patterns of the compound Fig. 3, after the Cl^- ion release, in all pH solutions, and subjected to different temperatures, indicates the stability of mono chloride complex.
3. Reversible mechanisms such as exchange of anions $\text{OH}^- \leftrightarrow \text{Cl}^-$ or adsorption is involved.
4. Adsorbed Cl^- is most affected by the changes in temperature. In mortars, besides C_3A , Cl^- binding can be associated with adsorption by other cement constituents as CSH gel, which is affected by the changes in the equilibrium

state, e.g., temperature. Fig. 4. The trend is the same for both 1:1 and 4:1 cement/sand mix proportions. The Cl^- ion concentration marked increases with an increase in temperature and re-adsorption of Cl^- anion takes place when the temperature is lowered down.

5. The blended cements, especially FA/OPC, offer good protection to the embedded steel even during the hydration period, provided the OPC content of the blend is high.

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