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THE BINDING OF CHLORIDE IONS BY SULPHATE RESISTANT PORTLAND CEMENT

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ABSTRACT

The relative tendency of different portland cements to remove chloride ions from the mix water by forming chloro-complexes is an important factor in the study of the corrosion of the embedded steel. The tri-calcium aluminate(C_3A) phase of the ordinary portland cement(OPC) plays a dominant role in binding the chloride ions, but little quantitative information is available in the literature concerning the relative influence of the tetra-calcium aluminoferrite(C_4AF) phase of the cement. The present investigation is an attempt to elucidate the role of C_4AF in the sulphate resistant portland cement with respect to chloride binding. It is concluded that the chlorides in SRPC are bound in the form of the chloro-complex $C_3F.CaCl_2.10H_2O$ which is derived from the C_4AF phase of the cement.

Introduction

In hydrated cements chlorides are bound in a variety of ways. Smolczyk(1) showed the formation of a complex salt from $Ca(OH)_2$ and $CaCl_2$ by X-ray diffraction. According to Chatterji(2), this complex salt forms at temperatures below 20 °C if the $CaCl_2$ concentration in the solution is 15% or higher. Ramachandran(3) has suggested that a high proportion of the chloride ions contributed by $CaCl_2$ are rapidly removed from the solution phase, as an interlayer chemisorbed complex within the C-S-H gel. Lambert et al(4) in their investigation with synthetic alite found an insignificant quantity of chlorides incorporated into the hydration product of C_3S. The tri-calcium aluminate(C_3A) forms the high chloro-aluminate hydrate $C_3A.3CaCl_2$.aqueous in 23% $CaCl_2$ solution at -10 °C(5). However this would not be formed under practical conditions in hydrated cements. A low chloro-aluminate $C_3A.CaCl_2.10H_2O$ called "Friedel's salt" forms in the hydrated ordinary portland cements(OPC) by the C_3A phase at room temperature even at low chloride concentrations under practical conditions(6,7).

Apart from the C_3A content of the cement, Roberts(8) in the early 60's showed the existence of the analar grade chloro-ferrite phase $C_3F.CaCl_2.10H_2O$ at room temperature. Roberts in the investigation with the sulphate resistant portland cement(SRPC) paste(with low C_3A and high C_4AF) when admixed with $CaCl_2$ found a moderate reduction in free chlorides in the pore solution. But with the SRPC paste there is no evidence to believe the formation of the $C_3(AF).CaCl_2.10H_2O$ in the hydrated cement paste admixed with $CaCl_2$.

In the present study an attempt has been made to elucidate the role of C_4AF in chloride binding, if any, in SRPC mortars hydrated with different levels NaCl added at the time of mixing. For comparison OPC mortars are also included.

Experimental Work

The binding of chlorides

The first part of the experimental work deals with the pore solution study. In order to confirm the binding of chlorides by the SRPC cement, a pore solution study was carried out. For this, the SRPC confirming to BS 4027(9) was used in the investigation. For comparison OPC conforming to BS 12(10) was included in the investigation. Table 1 gives the oxide and the compound composition of both the cements and the composition of the four main crystalline phases, that is, C_3S, C_2S, C_3A and C_4AF are calculated by using the formulas recommended by ASTM C 150-92(11).

TABLE.1.
Oxide and Compound Composition of OPC and SRPC.

COMPOSITION	OPC. % BY WEIGHT	SRPC. % BT WEIGHT
SiO_2	20.3	19.98
Al_2O_3	5.7	3.62
Fe_2O_3	2.3	4.86
CaO	65.1	64.25
SO_3	3.1	2.07
K_2O	0.6	0.11
Na_2O	0.2	0.11
C_3S	47.6	63.9
C_2S	22.29	9.06
C_3A	11.2	1.41
C_4AF	7.0	14.79

To investigate the binding of chlorides by both the above cements a series of cylindrical mortar specimens were cast in plastic bottles and were sealed after compacting the mortar. The sealed specimens were then cured under laboratory conditions until pore solution extraction by using a pore press. The procedures followed for the pore press operation and the sample collection are similar to those recommended by Barneyback and Diamond(12).

Three levels of chlorides that is, 1%, 1.75% and 3.5% were added to the mix by weight of cement as NaCl by dissolving in the mix water. The mortar used in the present investigation has a cement content of 400 Kg/m^3 and a water-cement ratio of 0.7. The mortar was compacted by rodding.

Identification of chloro-complexes

In order to identify the chloro-complexes, X-ray diffraction and differential scanning calorimetry(DSC) were carried out on hydrated cement. For this, mortar specimens of size 6.8 cm X 2.8 cm X 6.9 cm were cast in a perspex mould and were cured for 70 days in a humidity chamber maintained at 100% relative humidity. The mortar mix proportions, mode of compaction, the levels of chlorides added and the source of chlorides added were similar to that of the cylindrical specimens prepared for the pore solution studies.

At the end of the curing period, the mortar specimens were dried in air and then were crushed to powder to pass through the 100 micron sieve as these particle sizes are believed to be enriched in cement hydration products. The powder method of X-ray diffraction was used in the present study to identify the crystalline phases. The diffracted X-ray was detected on a Phillips diffractometer. The Cu kα radiation of wavelength 1.54 Å was used as the X-ray source. The DSC studies were also carried out on the powdered hydrated cement samples on a Perkin Elmer DSC(model DSC-2). The powdered sample weight was around 10 mg which was deliberately selected to avoid the thermal gradients within the sample during the analysis. The scanning rate was 10 degrees per minute. To make sure the proper functioning of the instrument, material of known endothermal response was checked prior to the actual experiment.

Preparation of chloro-complexes

The two chloro-complexes reported in the literature $C_3A.CaCl_2.10H_2O$ and $C_3F.CaCl_2.10H_2O$ were prepared by following the method suggested by Roberts(8). The chemical reactions leading to the formation of the above chloro-complexes were carried out at room temperature. The final products were washed with methanol and then filtered using a vacuum pump.

Results

The binding of chlorides

Table 2 gives the free chlorides and bound chlorides for both the cements at the three levels of chlorides added by weight of cement as NaCl. The values given in the brackets in the first column indicate the concentration of chlorides in the mix water, while those in brackets under the 3rd and 5th column indicate the percentage of bound chlorides. All the values in the table correspond to the equilibrium condition after 33 days of curing, after which no further significant chloride binding was noticed.

All the values given in the table have been corrected for the hydration effects and hence the values represent the concentrations corresponding to the original mix water content. For this the evaporable water was determined by heating the duplicate mortar specimens to 105 °C to a constant weight.

TABLE.2.
Free and Bound Cl^- for OPC and SRPC.

% OF Cl^- ADDED BY WEIGHT OF CEMENT	OPC		SRPC	
	Free Cl^- in M	Bound Cl^- in M	Free Cl^- in M	Bound Cl^- in M
1% Cl^- as NaCl (0.403 M)	0.105	0.298 (74%)	0.219	0.184 (46%)
1.75% Cl^- as NaCl (0.705 M)	0.240	0.465 (66%)	0.488	0.217 (31%)
3.5% Cl^- as NaCl (1.41 M)	0.945	0.465 (33%)	1.246	0.164 (12%)

From Table 2 it is clear that the SRPC also binds a significant amount of chloride, however the amount of chlorides bound are consistently lower than that of the OPC at all the levels of chloride addition. In a separate publication by the present authors(13), more details on the characterization of the pore solutions of the OPC and SRPC mortar contaminated and admixed with chlorides are provided.

Chloro-complex in hydrated OPC

Figure 1 shows the X-ray diffractograms for the hydrated OPC containing 1%, 1.75% and 3.5% Cl^- added by weight of cement as NaCl. For the purpose of comparison the X-ray diffractogram for 0% Cl^- is also included in Figure 1.

In Figure 1 a maximum intensity(100%) peak corresponding to the $C_3A.CaCl_2.10H_2O$(Friedel's salt) appears at 7.88 Å, which is in good agreement with the values reported in the literature for the analar grade Friedel's salt(14,15). The peaks corresponding to the next lower intensities of 50% and 30% also appear at 2.85 Å and 2.2 Å respectively. It is clear from the Figure 1 that the 100% and the 50% intensity peaks appear distinctively in all the diffractograms except for the 0% Cl^- addition. Apart from the Friedel's salt, portlandite($Ca(OH)_2$), α-quartz(SiO_2), ettringite($C_3A.3CaSO_4.32H_2O$) and calcite($CaCO_3$) also appear in the X-ray diffractograms. The α-quartz is believed to be from the sand used for compounding the mortar while the calcite might be as a result of the carbonation of portlandite during curing in the humidity chamber. Ettringite is one of the hydration products of C_3A in presence of sulphate. The ettringite superimposes the 50% intensity peak corresponding to Friedel's salt at 3.85 Å.

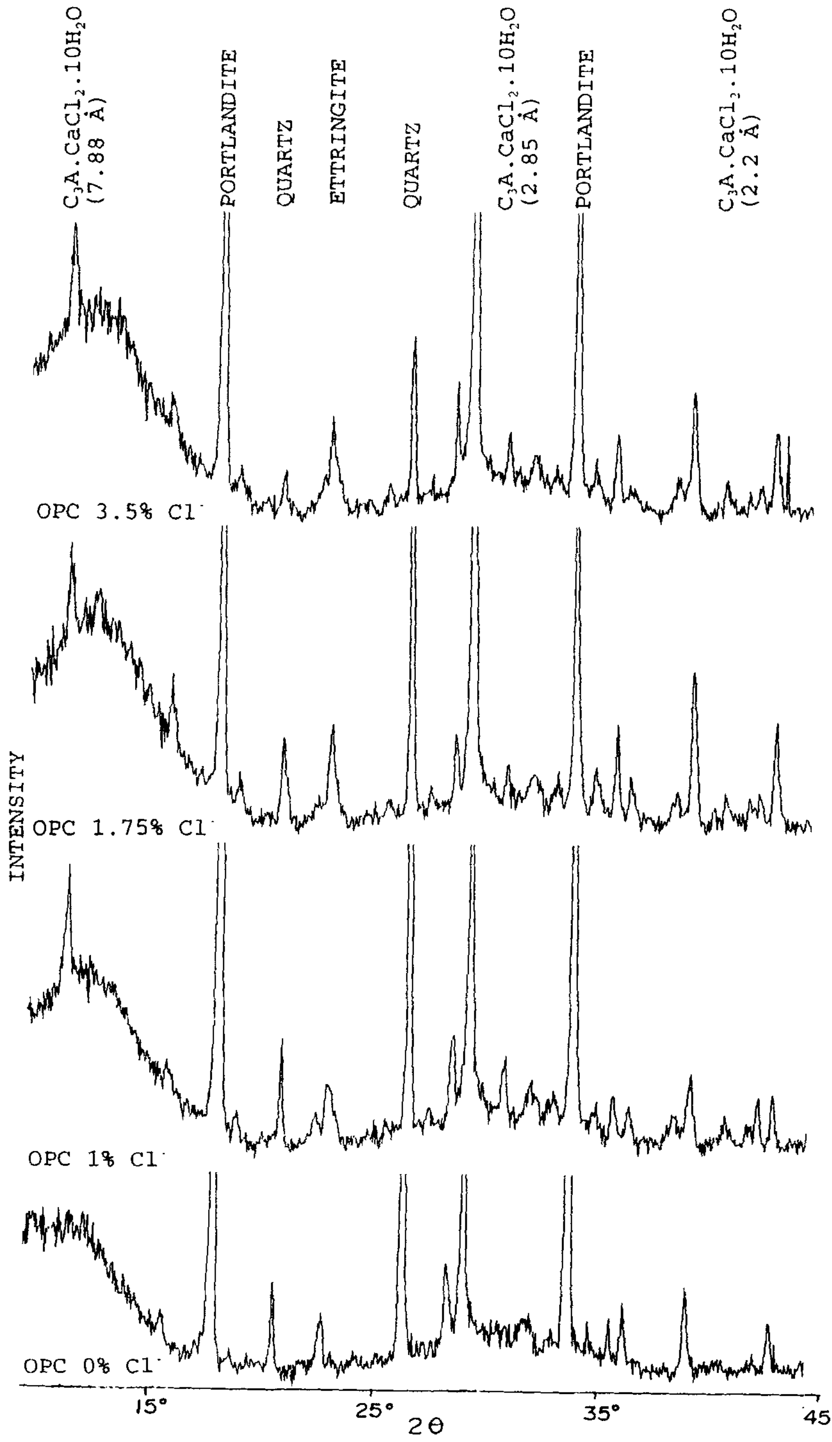

FIG.1.
X-ray diffractograms for hydrated OPC contaminated with different levels of chlorides.

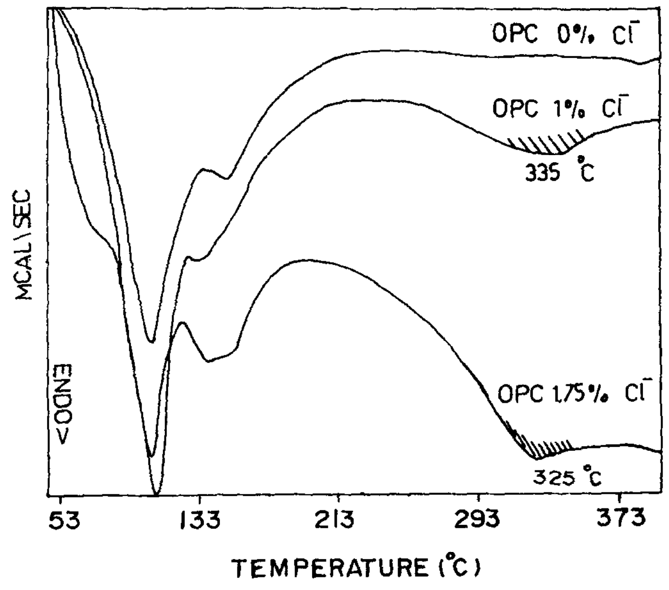

FIG.2.
DSC thermograms for the hydrated OPC contaminated with different levels of chlorides.

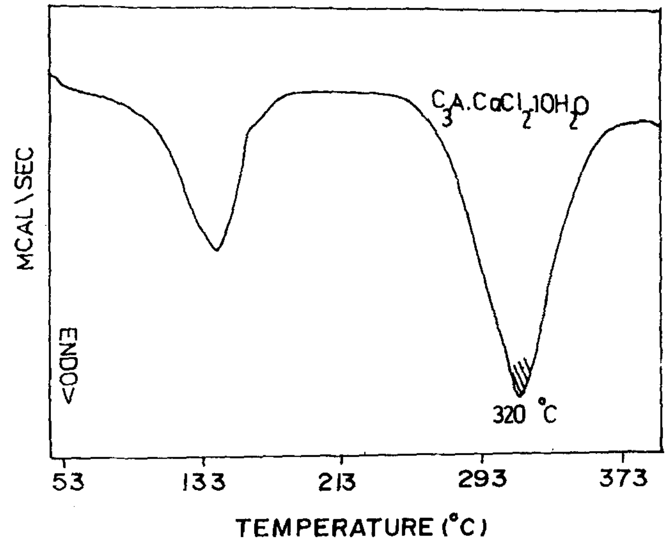

FIG.3.
DSC thermogram for the Friedel's salt.

Unfortunately, C_4AH_{13}, a meta-stable hydrate of C_3A, also has the maximum intensity peak at 7.9 Å(15). This makes the identification of Friedel's salt more complicated. Differential thermal analysis (DTA) was recommended by Page et al[16] as a more sensitive tool for making distinction between the Friedel's salt and C_4AH_{13}.

According to Ramachandran(17), the Friedel's salt if present yields an endothermal effect at around 350 °C. The presence of C_4AH_{13} is indicated on the DTA thermograms by a series of endotherms below 300 °C at 280, 190, 125, 90 and at 75 °C(18). These endotherms indicate the gradual loss of crystalline water from the C_4AH_{13} phase with rise in temperature.

In the present study DSC was used instead of DTA. Figure 2 shows the DSC thermograms for the hydrated OPC powder samples containing 0%, 1% and 1.75% Cl^- by weight of cement. All the chloride bearing hydrated OPC showed a fairly definite endothermic response(hatched portion) with its peaks in the region of 325-335 °C, while the thermogram for 0% Cl^- clearly did not show any endothermic response in the above temperature region. Figure 3 shows the thermogram for the Friedel's salt. The DSC thermogram for the Friedel's salt also showed a clear endothermic response(hatched portion) with a peak in the region of 320 °C which confirms that those responses observed in hydrated OPC powder samples containing 1% and 1.75% Cl^- are also due to Friedel's salt, even though a small difference exists in the peak temperatures. Diamond(19) in his investigation with OPC admixed with $CaCl_2$ based on DTA thermograms reported the endothermic peak for Friedel's salt in the region of 320 °C but Page et al(16) and Ramachandran(17) also using DTA thermograms, reported the same at a slightly higher temperature around 350 °C. Thus the present observations are well correlated to the earlier findings.

Chloro-complex in hydrated SRPC

In Figure 4 similar to that in Figure 1, a distinct peak appears at 7.87 Å in diffractograms corresponding to those containing 1%, 1.75% and 3.5% Cl^- by weight of cement. The lower intensity peaks corresponding to 2.87 Å and 2.12 Å are not distinctive in all cases. The 0% Cl^- sample did not show any of the above intensity peaks. It is clear from Figures 1 and 4 that the hydrated SRPC, similar to that of hydrated OPC, also showed peaks exactly at the d-spacings corresponding to that of Friedel's salt. This means that Friedel's salt, a crystalline phase iso-structural to the Friedel's salt, or a solid solution of both would have formed in hydrated SRPC containing chlorides.

Figure 5 shows the X-ray diffractogram for $C_3F.CaCl_2.10H_2O$. The diffractogram also shows a maximum intensity peak at 7.8 Å and the low intensity peaks corresponding to 3.89 Å and 2.2 Å. The other low intensity peak at 2.87 Å is superimposed by the strong peak corresponding to NaCl, one of the products of the chemical reaction which could not be eliminated completely after washing with methanol. From this observation it appears that the crystalline phase under discussion in the hydrated SRPC may be $C_3F.CaCl_2.10H_2O$, which is the crystalline phase iso-structural to the Friedel's salt.

Similar to the hydrated OPC, the C_4AF of the SRPC on hydration forms a meta stable hydrate C_4FH_{13}, which also has a maximum intensity peak at 7.8 Å(15). The C_4FH_{13} is iso-structural with its aluminate phase C_4AH_{13} and hence shows an endothermic response similar to that of C_4AH_{13} on the DTA thermogram. Thus the X-ray

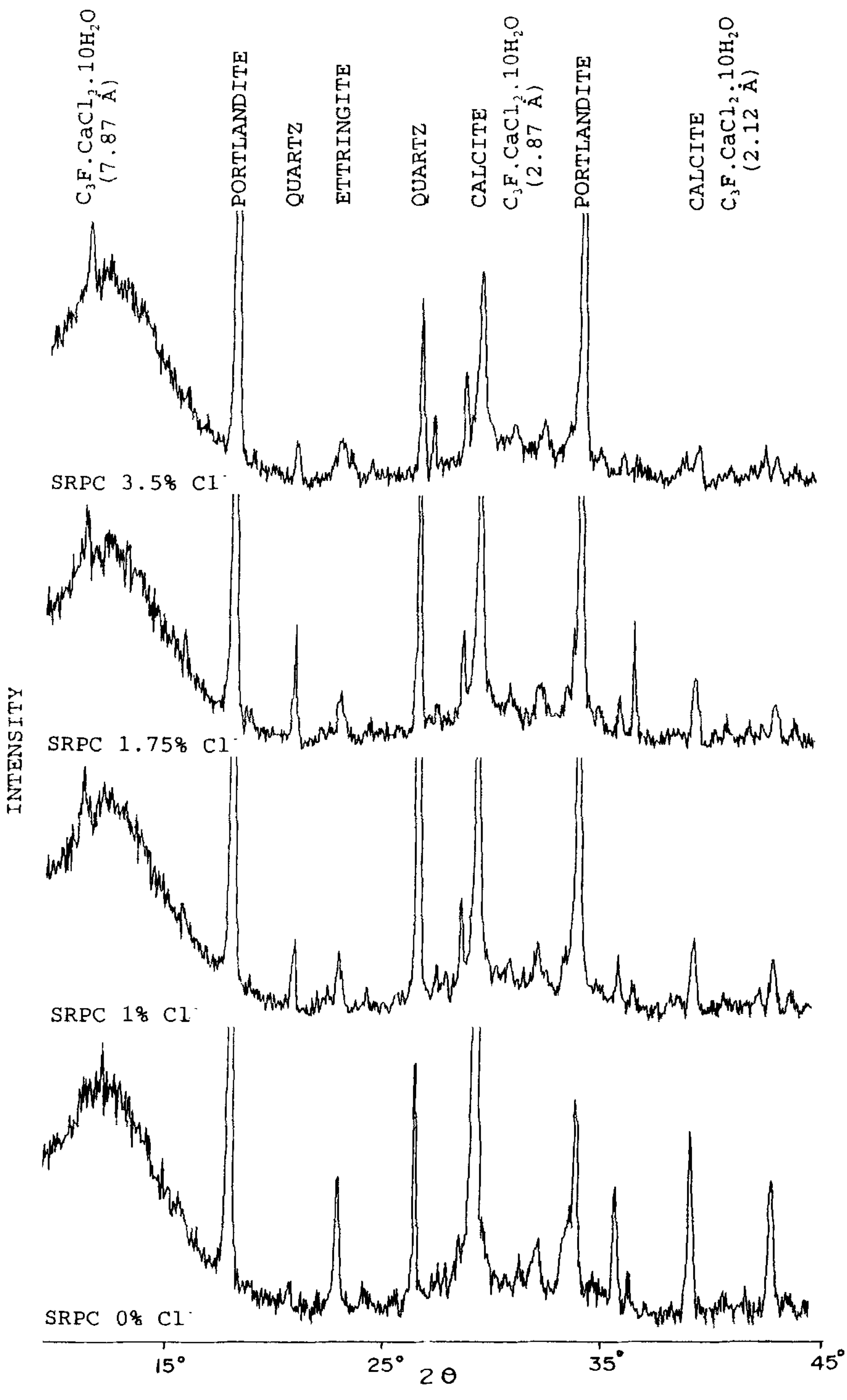

FIG.4.
X-ray diffractograms for the hydrated SRPC contaminated with different levels of chlorides.

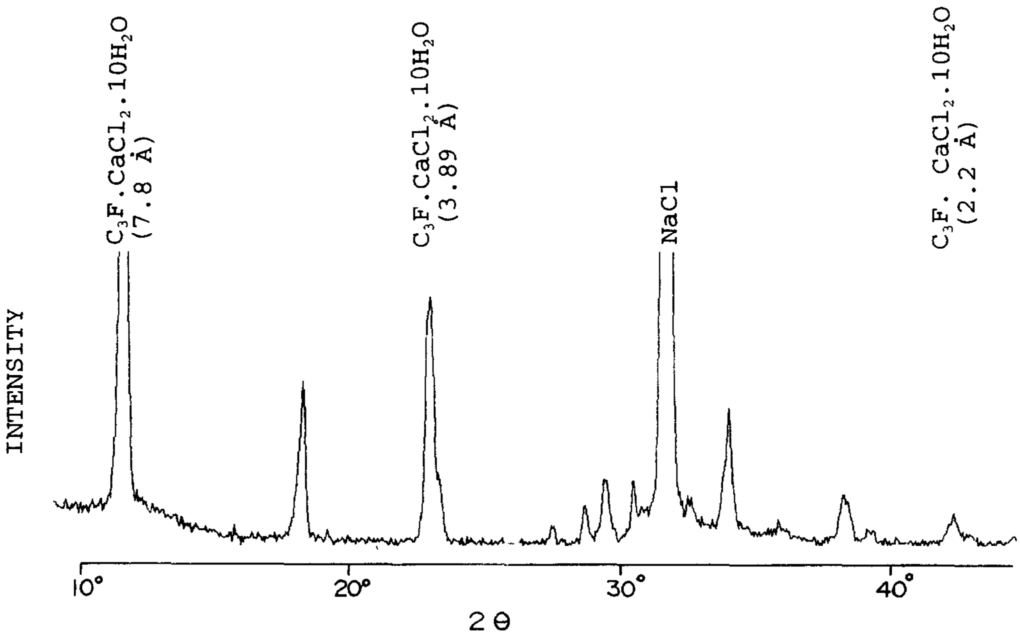

FIG.5.
X-ray diffractogram for the $C_3F.CaCl_2.10H_2O$.

diffraction results are inconclusive and hence DSC was done in order to obtain the conclusive evidence.

Figure 6 shows the DSC thermograms for the hydrated SRPC containing 1%, 1.75%, 3.5% and 0% Cl⁻ added by weight of cement. The chloride

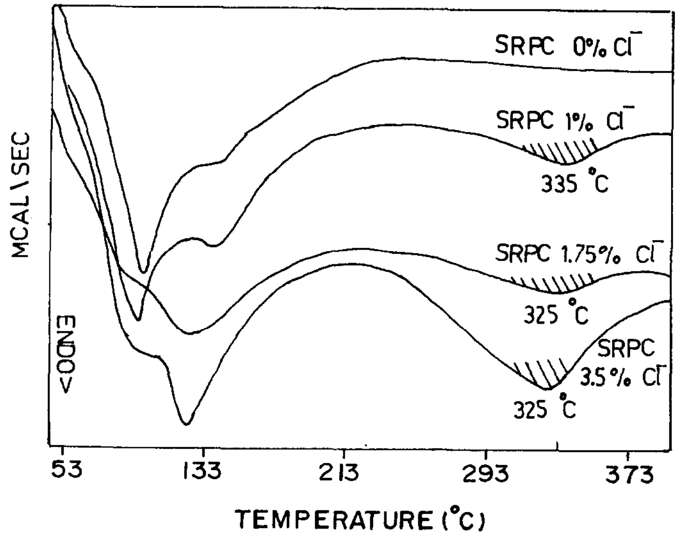

FIG.6.
DSC thermograms for the hydrated SRPC contaminated with different levels of chlorides.

contaminated samples showed a definite endothermic response(hatched portion) similar to that of hydrated OPC with peaks in the range of 325 to 335 °C. The sample containing 0% Cl⁻ did not show a similar response. Figure 7 shows the DSC thermogram for $C_3F.CaCl_2.10H_2O$. The $C_3F.CaCl_2.10H_2O$ also shows a fairly broad endothermic response(hatched portion) with a peak around 310 °C, which is almost approaching those of the hydrated SRPC contaminated with chlorides. Thus the crystalline phase under discussion in the hydrated SRPC may still be either the Friedel's salt, the $C_3F.CaCl_2.10H_2O$, or a solid solution of both the phases. The above results eliminate the presence of C_4FH_{13} in the hydrated SRPC.

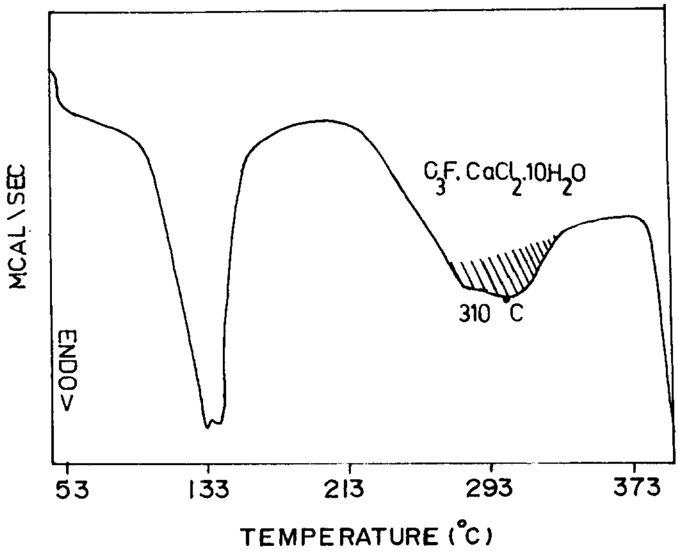

FIG.7
DSC thermogram for $C_3F.CaCl_2.10H_2O$.

Discussion

In case of the hydrated OPC the evidence indicate unambiguously the formation of the Friedel's salt. The other reports in the literature also confirm the above conclusion(6,7,16,19).

In case of the hydrated SRPC the results point to either the formation of the Friedel's salt or the $C_3F.CaCl_2.10H_2O$ or a solid solution of both. The SRPC cement used in the present investigation consists of 1.41% C_3A, 14.79% C_4AF and 2.07% SO_3(or 4.45% gypsum) by weight. It is well known that in the presence of both the sulphate and the chlorides the C_3A preferentially reacts with the sulphates to form ettringite(20,21). On stoichiometric considerations, the 1.41% C_3A present in the cement would be transformed into ettringite by the consumption of about 2.7% gypsum out of the total 4.45% present. Hence the possibility of unreacted C_3A remaining to react with the chlorides is ruled out. Thus the possibility of C_3A taking part in the chloride binding to form Friedel's salt is too remote a possibility. This indirectly proves that the chloro-complex formed in the hydrated SRPC is

$C_3F.CaCl_2.10H_2O$. This phase is formed by the reaction between C_4AF and the chlorides after the C_4AF preferentially reacts with the sulphates as in the case of C_3A. There is no evidence in the literature that suggests the formation of Friedel's salt may take place by the reaction between C_4AF and the chlorides.

The $C_3F.CaCl_2.10H_2O$ phase and the Friedel's salt have an identical crystalline structure. The Friedel's salt and its ferrite analogue $C_3F.CaCl_2.10H_2O$ belong to the family of aluminate-ferrite mono(AFm) phases(18). The AFm phases have layer structure in which one Ca^{2+} ion in three present in the lattice is replaced by a Al^{3+} or Fe^{3+} ion. To balance the charge a Cl^- ion enters the lattice due to the attraction by the Ca^{2+} and the Al^{3+} ions. When a Al^{3+} ion replaces a Ca^{2+} ion the resultant AFm phase is the Friedel's salt and similarly when a Fe^{3+} ion replaces a Ca^{2+} ion the resultant phase is $C_3F.CaCl_2.10H_2O$. The reason for the preferential entry of Fe^{3+} into the lattice in case of SRPC is due to its low iron modulus or alumina ratio(Al_2O_3/Fe_2O_3). Each principlal layer of the AFm phase has the composition $[Ca_2(Al,Fe)(OH^-)_6.2H_2O]^+$.

In a recent investigation(22), the DTA thermograms showed the formation of Friedel's salt even at low C_3A levels in the cement. The cement used in the investigation was containing 2.43% C_3A, 14.61% C_4AF and 1.71% SO_3. It appears that the phase formed may be $C_3F.CaCl_2.10H_2O$ which also shows the endothermic response around the same temperature as the Friedel's salt. The formation of Friedel's salt appears to be doubtful based on the stoichiometric considerations as discussed above.

The OPC used in the present investigation apart from 11.2% C_3A consists of 7.0% C_4AF. Hence it may be possible that the chloro-complex formed may be a solid solution of the Friedel's salt and the $C_3F.CaCl_2.10H_2O$. Under comparable conditions, the C_4AF normally appears to react more slowly than the C_3A during the early stages of the cement hydration(18). Based on the above, it is believed that the chloro-complex formed in the hydrated OPC is mostly composed of the Friedel's salt.

Conclusions

1. The present investigation confirms chloride binding in hydrated OPC is by the formation of Friedel's salt.
2. The SRPC also binds moderate amounts of chloride and the binding is by the formation of the chloro-complex $C_3F.CaCl_2.10H_2O$.
3. The C_4AF content of the cement is responsible for the formation of the chloro-complex $C_3F.CaCl_2.10H_2O$ in SRPC.

Acknowledgement

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