Effect of Mechanism of Chloride Ion Attack on Portland Cement Concrete and the Structural Steel Reinforcement

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Abstract: The effect and mechanism of chloride ion concentration of portland cement concrete and the structural steel reinforcement was investigated. At low concentrations, chloride ion has little or no effect on the physical stability of concrete structure but it causes the corrosion of the re-enforcing steel in the concrete but at high concentration and especially at low temperature, it causes expansion and cracking in the concrete. The degradation is usually accompanied by formation of calcium oxychloride salts. The mechanism for this destruction was discovered in this work as a result of the thermal transformations of the calcium oxychloride salts: $3CaO.CaCl_2.15H_2O$ to $CaO.CaCl_2. 2H_2O$.

Key words: Chloride, port land, concret structure, steel, oxychloride salt

INTRODUCTION

At low and moderate concentration chloride has relatively little disruptive effect on the volume stability of the concrete. However it destabilizes the passivating layers on steel reinforcement, Ramachandran[1,2].
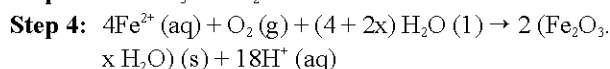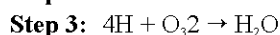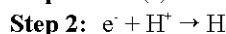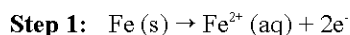
At high concentration, chloride affects the stability of concrete due to formation of basic chloride salts-calcium oxychloride,[3,4] Chloride ions may be introduced into cement paste via internal and external sources. Internal sources include mixing water, clinker, chloride-bearing aggregate or when calcium chloride is used as accelerating admixture. External sources maybe through the use of sodium chloride as de-icing salt, by absorption chloride from underground or sea water.

The chloride ions do not form compounds with the calcium silicate hydrate even though they accelerate the hydration of the calcium silicate phases[5]. Chloride reacts with calcium aluminate hydrate phases to form some complex chloride salts.
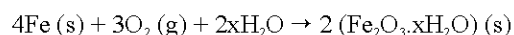
Corrosion of reinforcing steel: The reinforcing steel in concrete has a tightly adhering thin γ-Fe_2O_3 film at the steel/concrete interface which renders the steel passive to corrosion process. This protective thin layer is stable in the alkaline environment of hydrated cement (pH 13).

The passivity may be destroyed by drops in the alkalinity of the environment in the vicinity of the steel surface to a level less than pH 11. such drop in pH is usually caused by carbonation or the presence of chloride ions.

Chloride concentration of the order of 300 to 1200 g dm^{-3} (8.0-34.0M) in the pore fluid are reported to be sufficient to cause dissolution of the passive film. When a sport on the steel is depassivated the area becomes anodic with respect to another area of steel that remains passive. Therefore, the passive area acts as cathode while the pose fluid act as electrolyte. The following steps have been proposed as the mechanism by which rusting occurs: The initial anode reaction is the change from metallic ion to ferrous ions.

Step 1: $Fe (s) \rightarrow Fe^{2+} (aq) + 2e^-$

Step 2: $e^- + H^+ \rightarrow H$

Step 3: $4H + O_32 \rightarrow H_2O$

Step 4: $4Fe^{2+} (aq) + O_2 (g) + (4 + 2x) H_2O (1) \rightarrow 2 (Fe_2O_3. x H_2O) (s) + 18H^+ (aq)$

In step (1) ferrous ions are produced by loss of electrons from neutral Fe. This process cannot go very far unless there is some way to get rid of the electrons which accumulate on the residual Fe. One way to do this is by step (2), in which H^+ ions either from water or from acid substances in the water (e.g. $H_2O (1) + CO_2 (g) HCO_3^- (aq) + H^+ (aq)$, pick up electrons to form neutral H atoms. In the meantime, the ferrous ion from step (1) reacts with O_2 gas by step (4) to form the rust and restore H^+. The net reaction, obtained by adding all four steps is:

$$4Fe (s) + 3O_2 (g) + 2xH_2O \rightarrow 2 (Fe_2O_3.xH_2O) (s)$$

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Thus in the presence of oxygen and water the ferrous ions released in the corrosion process first form ferrous hydroxide:

$$Fe^{2+} \, 2OH^- \, Fe(OH)_2$$
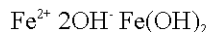
In the presence of chloride ions, chlorocomplexes of iron may form:

$$4Fe(OH)_2 + 2Cl^- \, 3Fe(OH)_2.FeCl_2 + 2OH^-.$$
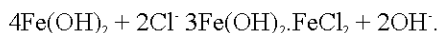
The chloro-iron complex is believed to be the intermediate product in the formation of β–FeO.OH (akagamite) and other rust gelatinous products such as $Fe_2O_3.xH_2O$ e.t.c[6].

Goni and Andrade[7] are of the opinion that the pitting process of steel in chloride environment is as result of intense localized attack so that the steel bars become deeply notched. The authors noted that for stable pit growth to be sustained, the local chloride concentration must rise and the local hydroxyl concentration must fall, otherwise repassivation is said to occur. Hence depassivation is now agreed to occur when the Cl/OH ratio is equal to or more than 1/3.

Destabilisation of concrete: At high chloride levels and particularly at low temperatures, Portland is strongly attacked. Lawrence and Vivian[8] reported that a strong Calcium chloride solution caused a severe damage to cement mortar when continuously stored in a 30% Calcium chloride solution. They noted that the damage was because of expansion caused by formation of complex salts that they did not identify.

Similarly Chatterji and Jenson[9] observed that a 30% calcium chloride solution at temperatures below $20°C$, cause degradation, swelling and cracking of Portland cement concrete. Subsequently Chatterji[10], demonstrated that a chemical reaction occurs between the hydrate cement and calcium chloride solution. He noted that when the cement paste was kept in 5-30% calcium chloride solution at 4-50°C, calcium aluminate mono chloride hydrate $(3CaO.Al_2O_3.CaCl_2.xH_2O)$ are formed. He also noted that with calcium chloride solution, stronger than 15% and at temperatures lower than $20°C$, a complex salt containing $C\,aCl_2.Ca(OH)_2$ and/or $CaCO_3$ could form. He finally concluded that the crystalisation of this complex salt was responsible for the concrete damage. Monosi et al.[11] studied the action of 30% calcium chloride solution on Portland cement by X-ray diffraction on moist samples Monosi and Collepardi[12] studied the action of mixtures of $Ca(OH)_2$ and $CaCl_2$ on Portland cement paste. They found the peaks for $3CaO.CaCl_2$.

$15H_2O$ (3.1.15) only in the moist paste and the peaks disappeared when the paste was ground or when it was dried at relative humidity of less than 1% or when washed in alcohol or water. According to literature, the solid phases in the system $CaO-CaCl_2-H_2O$ depending on the temperature, are $Ca(OH)_2$, $3CaO.CaCl_2.15H_2O$, $CaO.CaCl_2.H_2O$ and $CaCl_2.6H_2O$.

The data in the literature on the stability of these compounds are incomplete. For example, they overlook the importance of the pH of the solutions with which the salts co-existed. The pH values are essential to extend the data to predict the stability and solubility of compounds in those chemically more complex systems relevant to cements.

Synthesis of reagents and sampling: The reagents used included chemically pure grades of $CaCl_2$. $2H_2O$ and $CaCO_3$. The latter was calcined at 1200^0C and the resultant fresh lime was used. Then the CaO was added to the calcium chloride solution. Before adding CaO to the calcium chloride solutions, the containing plastic plastic bottle was first immersed into a cool water bath to avoid melting the containers because of the large hydration heat of CaO. A series of samples were prepared in the ratio $CaO:CaCl_2 = 1:9$ to $9:1$. The paste or slurry so produced was kept in sealed plastic bottles at $20 + 5°C$.

After four weeks each sample was vacuum filtered. The solid was characterized by power X-ray diffraction. The filtrate was refiltered with fine filtration discs and analysed for calcium, chloride and pH.

RESULTS AND DISCUSSION

Table 1 below shows the hydration products of the various sample mixtures and the analyses of the aqueous phase in which they were in equilibrium.

Table 1 shows that at 20^0C, the solid phases in the system $CaO-CaCl_2 \; H_2O$ are $Ca(OH)_2$, $3CaO.CaCl_2.15H_2O$ and $CaO.CaCl_2.2H_2O$. These results agree with those of Schreinemakers and Figee who studied the system at $25°C$. It can be seen that of the various hydrates of calcium chloride (i.e. $CaCl_2.H_2O$, $CaCl_2.2H_2O$ $CaCl_2.4H_2O$ and $CaCl_2.6H_2O$) Table 1 indicates that only $CaCl_2.6H_2O$ exists at $20°C$.

The system $CaO-CaCl_2-H_2O$ was studied by O'Connor[13] at $O°C$. The results indicate that there are only three solid phases in the system at that temperature. These phases are $Ca(OH)_2$, $3CaO.CaCl_2.15H_2O$ and $CaCl_2.6H_2O$. Milikan [14] studied the same system at 40, 45 and $50°C$. Milikan's results show that $CaCl_2.6H_2O$ and $3CaO.CaCl_2.15H_2O$ were not stable at temperatures above 40^0C and 50^0C respectively. That is to say that $CaCl_2.6H_2O$ is no longer stable above $40°C$.

Table 1: The System CaO-$CaCl_2$-H_2O at 20°C

Sample CaO:$CaCl_2$	Solid phase	Aqueous phase analysis $(mol.dm^{-3})$			
		Ca	Cl	OH x 10^{-3}	pH
1:9	$CaCl_2.6H_2O$	4.034	8.068	-	5.77
2:8	1.1.2 + 3.1.15	3.084	6.076	3.70	11.57
3:7	1.1.2 + 3.1.15	3.036	5.985	4.50	11.65
4:6	3.1.15	2.694	5.232	6.70	11.83
5:5	3.1.15	2.218	4.384	7.20	11.86
6:4	3.1.15	2.170	4.289	27.90	11.90
7:3	3.1.15 + $Ca(OH)_2$	1.662	3.271	28.20	12.45
8:2	$Ca(OH)_2$	1.389	2.728	35.50	12.55
9:1	$Ca(OH)_2$	0.922	1.802	39.80	12.60

Key:- 1.1.2 = $CaO.CaCl_2.2H_2O$ and 3.1.15 = $3CaO.CaCl_2.15H_2O$

Table 2: Solid phases formed with variation of [Cl] in the solution at 20°C

[C] (mol dm^3)	Solid phase
0.00-3.00	$Ca(OH)_2$
3.00-6.00	$3CaO.CaCl_2.15H_2O$
6.00-8.00	$CaO.CaCl_2.2H_2O$
8.00-9.00	$CaCl_2.6H_2O$

Table 3: Composition of invariant points

Invariant point	Aqueous phase $(mol.dm^{-3})$			
	Ca	Cl	OH x 10^{-3}	pH
$CaCl_2.6HO$ + 1.12	4.027	8.053	0.0046	8.66
1.12 + 3.1.15	3.084	6.076	2.00	11.30
3.1.15 + $Ca(OH)_2$	1.635	3.271	22.40	12.35

It is apparent that the range of existence of $3CaO.CaCl_2.15H_2O$ increases as the temperature falls. The amount of water of crystallization of calcium chloride hydrate decreases with increasing temperature as indicated in the equations below [15]:

$CaCl_2 + H_2O \rightarrow CaCl_2.6H_2O$ at 30°C and [Cl] = 9.00M
$CaCl_2.6H_2O \rightarrow CaCl_2.4H_2O$ at 30-45°C and [Cl] = 9.00-10.00M
$CaCl_2.4H_2O \rightarrow CaCl_2.2H_2O$ at 40-180°C and [Cl] = 10.00-13.00M
$CaCl_2.2H_2O \rightarrow CaCl_2.H_2O$ at 180-260°C and [Cl] = 13.00-14.00M.
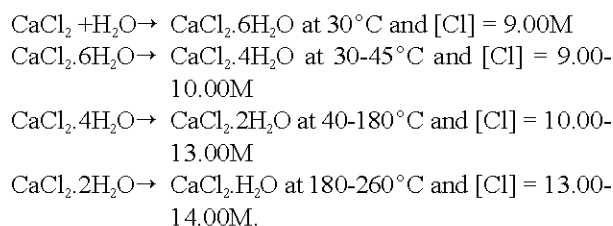
These equations show that the amount of water of crystallization of calcium chloride hydrate depends both on the temperature and the chloride concentration of the aqueous phase.

Monosi and Collepardi [11] reported the transformation of $3CaO.CaCl_2.15H_2O$ into $CaO.CaCl_2.2H_2O$ with increase in temperature and the reverse with fall in temperature. This is affirmed by noting the absence of $CaO.CaCl_2.2H_2O$ in the system at O°C. Similarly $3CaO.CaCl_2.15H_2O$ no longer exists at 40°C or above. Therefore, when in contact with solution the transformation of the solids can be represented as:

$3CaO.CaCl_2.15H_2O$ (s) $\rightarrow CaO.CaCl_2.2H_2O$ (s) + $2Ca(OH)_2$ (s) + $11H_2O$ (1)
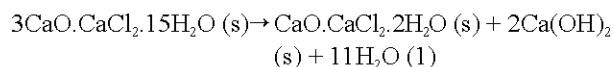
So, the formation of $3CaO.CaCl_2.15H_2O$ is favoured by decrease in the chloride content necessary to form $3CaO.CaCl_2.15H_2O$. Hence its formation in weaker chloride solutions becomes more feasible. Thus for a similar chloride attack more $3Ca.CaCl_2.15H_2O$ is formed at lower temperatures than 40⁰C. This justifies the observation of severer chloride attack on cement paste at temperature lower than 5⁰C. At 20⁰C, the nature of the solid phases in the system changes with the change of the chloride concentration in the solution. The sequence of occurrence of the solids with increasing chloride is as shown in Table 2 below:

Table 2 indicates that Ca $(OH)_2$ which is a major hydrate in cement paste is not stable at chloride concentration higher than 3 moles per litre.

At 20°C, the system $CaO.CaCl_2$-H_2O consists of three isothermal invariant points at which two solid phases co exists with solution Table 3. These are:

- $CaCl_2.6H_2O$ + $CaO.CaCl_2.2H_2O$
- $CaO.CaCl_2.2H_2O$ + $3CaO.CaCl_2.15H_2O$
- $3CaO.CaCl_2.15H_2O$ + Ca $(OH)_2$

A saturated aqueous solution of $Ca(OH)_2$ at 20°C was found to contain 0.019M Ca and had a pH value of 12.58 similarly an aqueous solution in which $CaCl_2.6H_2O$ was stable contained 4.034M and 8.068M Cl with a pH value of 4.77.

CONCLUSION

In this study it is interestingly discovered that in the system CaO-$CaCl_2$-H_2O at temperature greater than 40°C, the predominant solid is $CaO.CaCl_2.2H_2O$ with a density of 2.40 g dm^{-3}. As the temperature falls to less than 20°C, this solid is converted to another solid $3CaO.CaCl_2.15H_2O$ with a density of 1.805 g dm^{-3}. This transformation is therefore accompanied by 25% increase in volume (i.e., decreases in density) and hence the reason for the expansion observed in concrete especially at low temperatures. The loss of eleven molecules of water as shown in the conversion equation, indicates increase in porosity of the concrete which in turn weakens the structure.

Conversion of $CaO.CaCl_2.2H_2O$ to $3CaO.CaCl_2.15H_2O$ can be represented by the equation:

$CaO.CaCl_2.2H_2O + 2Ca(OH)_2 + 11H_2O \rightarrow 3CaO.Cl_2.15H_2O$.
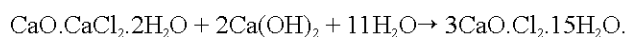
In isochemical conditions, this transformation deplete $Ca(OH)_2$ from the system and hence the pH is reduced. Such fall in pH may cause the destabilization of the hydration products like ettringite and monosulphate [16] and even $3CaO.Al_2O_3.CaCl_2.10H_2O$ (Friedel's salt) [17] The increase in density during the conversion means decrease in volume i.e., contraction.

In dry desert areas, the temperature difference between day and night could be up to $40°C$. Such temperature fluctuations would cause formation of $3CaO.CaCl_2.15H_2O$ at night and its transformation to $CaO.CaCl_2.2H_2O$ by the day. The expansions-contraction cycle could cause cracking and degradation of the concrete.

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