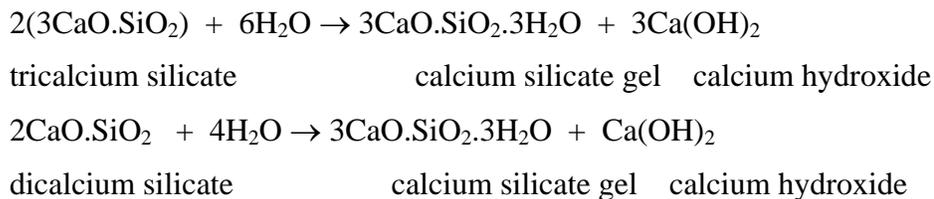


## FACTORS AFFECTING THE PERFORMANCE OF STEEL IN CONCRETE

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### CONDITION OF STEEL IN CONCRETE ENVIRONMENT

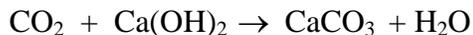
Steel in concrete is generally passive in the concrete environment due to the formation of  $\gamma$ - $\text{Fe}_2\text{O}_3$  formed on its surface. This passive condition is achieved by the high alkalinity in the cement pore solution that is generated due to the hydration of reactions of cement particles according to the following reactions:



Calcium hydroxide imparts a buffered pH value of 12.6 that rises to values of  $\sim 13.2$  due to the sodium and potassium alkalis present in cement. The hydroxide ion has an inhibitive action and steel can stay in a good condition for several decades. The concrete around the steel reinforcement also acts as a physical barrier against the ingress of deleterious substances. Further, the tri-calcium aluminate present in cement binds the chloride ion ( $\text{Cl}^-$ ) to form Friedel salt ( $3\text{CaO} \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ ).

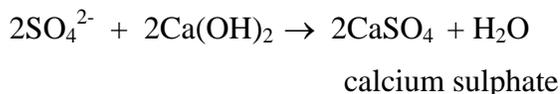
### THE DEGRATION PROCESSES

The passive state of steel is destroyed due to several degrading processes caused by different substances. Carbon dioxide of the atmosphere combines with  $\text{Ca}(\text{OH})_2$  in the cement to form calcium carbonate and the alkalinity of the pore solution is reduced:



The alkalinity may be lowered to value of 7<sup>1</sup> and general form of corrosion of steel reinforcement occurs.

Sulphates from the soil/water etc., may also cause deterioration of concrete structures by consuming  $\text{Ca}(\text{OH})_2$  by the following reaction:



Sulphate ion also combines with the alumina phase in the cement to form mono sulpho aluminate ( $\text{CaO} \cdot \text{CaSO}_4 \cdot 10\text{H}_2\text{O}$ ) after the formation of ettringite ( $\text{CaO} \cdot 3\text{CaSO}_4 \cdot 24\text{H}_2\text{O}$ ), which has an expansive volume, and cause the cracking of the concrete. Alkali-silica reactions may also cause cracking of the concrete by dissolution occurring at the particle interface<sup>2,3</sup>. It should be noted that the corrosion processes at the steel/mortar interface, due to the expansive volume of the rust product, create stresses in concrete and spalling of concrete cover takes place, Fig.1.

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Fig. 1. Fall of concrete cover due to corrosion of the steel reinforcement

Carbonation and the sulphate attack though harmful cannot be regarded as dangerous as the pitting corrosion due to the  $\text{Cl}^-$  anion that causes intense localized pitting corrosion of the steel reinforcement. The pits may through the entire diameter of the embedded reinforcement bar in a short period of time due to coupling of a small anodic area with a large cathode and drastic failure may occur without any visual symptoms<sup>4,5</sup>, Fig. 2.



Fig. 2. Corrosion of the Steel in Concrete

In certain cases, the pits coalesce and appear like general form of corrosion, Fig. 3.



Fig. 3. Pitting appearing as general form of corrosion of steel

#### **MECHANISM OF CHLORIDE ATTACK**

The exact mechanism of the chloride attack is not known, but the theories put forward so far

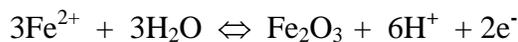
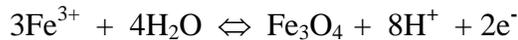
take penetration of the chloride ion through the passive film<sup>6</sup>, adsorption of Cl<sup>-</sup> ions<sup>7,5</sup> on the metal surface, the metal ion vacancy model and the film breakdown concepts<sup>9</sup> into consideration. In any case, when the concentration of the aggressive species exceeds a certain critical value, pitting occurs. Pitting corrosion may continue and a catastrophic failure of the concrete structure may occur without any warning symptoms. The common sources of chloride ions are as follows:

- 1) Deliberate addition of salt to accelerate cement setting
- 2) Use of contaminated water or aggregates
- 3) Use of de-icing salts in cold regions

The corrosion of the passive steel progresses inside the concrete due to following electrochemical reactions:



Other electro-chemical reactions controlling the corrosion processes are as follows:



Thus, the pit environment is rich in hydrogen ions (H<sup>+</sup>) with current flow from the anodic to the cathodic sites. The pit propagation is auto catalytic due to the generation of acidity that neutralizes the effect of inhibitive hydroxyl ions (OH<sup>-</sup>) in the cement pore solution. Thus, the passive state of steel is ruined. Pit re-passivation i.e., where the pit propagation is stopped, is only possible when the OH<sup>-</sup> ions are in sufficient quantities to inhibit the aggressive action of the chloride ion.

The amounts of permissible chloride ion in concrete in the international codes of practice vary widely. ACI 318 allows a maximum water-soluble chloride ion content of 0.06% in prestressed concrete, 0.15% for the reinforced concrete that will be dry or protected from moisture in service and 0.3% for all other reinforced concrete construction. The British code, CP110 allows an acid soluble chloride content of 0.35% for 95% of the test results with no result greater than 0.50%. It is considered that at 0.4% chloride content there is a risk of corrosion but in actual, corrosion has occurred at values lower than that, particularly, where the chloride content was not uniform. The Norwegian code, NS 3474, allows an acid soluble chloride content of 0.6% for the reinforced concrete made with ordinary Portland cement (OPC) but only 0.002% chloride ion for the prestressed concrete. Thus, the highways, the parking areas, marine environments and industrial plants where chloride ion is present, additional protection against corrosion of embedded steel is necessary.

The civil engineers place their concerted efforts around the building design driven by the economics of the project but the corrosion scientists regard it extremely important to elucidate the environmental factors, before construction is started. Critical review of such factors can only guarantee a durable safe life of the structure.

### CRITICAL CL/OH<sup>-</sup> RATIO

Hausman<sup>10</sup> was the first to put forward the concept of critical Cl<sup>-</sup>/OH<sup>-</sup> ratio from free corrosion experiments of steel in alkaline solutions inferring that ratios of <0.6% cannot possibly produce corrosion in aerated alkaline solutions. Diamond<sup>11</sup> found that 1% Calcium chloride (CaCl<sub>2</sub>)

by weight of cement or its equivalent of NaCl (~0.48% Cl<sup>-</sup>) resulted in a Cl<sup>-</sup>/OH<sup>-</sup> ratio of 0.77 in CaCl<sub>2</sub> cement pastes and 0.64 in NaCl in cement pastes, analyzed through pore solution squeeze technique, and concluded that CaCl<sub>2</sub> was more aggressive due to the common ion effect, which leads to a reduction in pH. Goni and Andrade<sup>12</sup> have found that ratios of 0.25 to 0.8 can cause depassivation of steel in concrete mortars. Page<sup>13</sup> has reported a value of 3, obtained through polarization resistance measurements (Rp), above which serious corrosion rates can be expected.

The critical Cl<sup>-</sup>/OH<sup>-</sup> ratio in the pore solution is also influenced by temperature to a large extent. Parkinson<sup>14</sup> observed a higher Cl<sup>-</sup>/OH<sup>-</sup> ratio for solution extracted in pore press at 50 °C for both OPC and sulphate resisting Portland cement (SRPC) cement pastes. Benjamin and Sykes<sup>15, 16</sup> also investigated the effect of temperature on the critical Cl<sup>-</sup>/OH<sup>-</sup> ratio in simulated solutions of pH 13.2. Pitting was observed at a ratio of 0.15 at 40 °C, 0.25 at 20 °C and 0.35 at 0 °C. They also showed that steel embedded in cement mortar of 1:1 aggregate/cement ratio (A/C) and water/cement ratio (W/C) of 0.5 containing 3% by weight of OPC, showed pitting at 40 °C and the same already pitting specimen re-passivated and became safe, when tested at 20 °C, Fig. 4.

#### Potential mV vs SCE

Fig. 4. Effect of temperature on the pitting corrosion of Swedish Iron in Concrete with 3% NaCl as an admixture. A/C ratio 1:1, W/C ratio 0.5

Benjamin<sup>17</sup> developed zones of passivation and corrosion for different chloride levels as the function of temperature, Fig. 5. The BRE<sup>18</sup> standards, which specify 0.4% NaCl (by weight of OPC) as safe limits with onset of serious corrosion problem at about 1% have thus become very doubtful for applications world wide, as these are set at temperatures around 20 °C, only.

Temperature °C

Fig.5. Domain of Pitting of Swedish Iron in OPC mortars as the function of chloride and temperature A/C ratio 1:1, W/C ratio 0.5 P– pitting (figures in parentheses show the pitting potentials) S – safe

### FACTORS CONTROLLING PERFORMANCE OF STEEL IN CONCRETE

Several important parameters affect the performance of concrete structures:

FACTOR	IMPACT
i. Cement content	Alkalinity of the pore environment
ii. Compaction	Strength and porosity
iii. Curing	Strength, porosity and alkalinity
iv. Cement/aggregate ratio	Porosity and alkalinity
v. Water/cement ratio	Porosity and alkalinity
vi. Depth of cover	Time for initiation of pitting

ACI 201.2R recommends a minimum of 50mm (2 inches) for bridge decks if the water cement ratio is 0.40 and 65 mm (2.5 inches) if the water/cement ratio is 0.45. Even greater cover, or the provision of additional corrosion protection treatments may be required in some environments.

Chloride attack is further aggravated by the changes in temperature especially when the structure is subjected to freezing and thawing. Internal friction between the crystals of ice and salt in the capillary pores of hardened cement pastes<sup>19-20</sup>, expansion together with cracking and loss of

strength due to hydraulic pressure in presence of chloride<sup>21</sup>, all add to the destruction of the concrete. Fly ash and silica fume are finding special applications in recent years. Usually the blast furnace slag cement concretes have proved successful to freeze thaw attack but failure is encountered in freeze de-icer situation<sup>22</sup>. Differences in the types of cements are a result of variation in composition or fineness or both, and not all types of cement have the same ability to provide protection to steel.

### **EFFECT OF TEMPERATURE ON THE DIFFUSION PROCESSES.**

Processes occurring at the interface and in the bulk through diffusion of species importantly account for the condition of steel in concrete. Flux of species towards the steel is dependent on the concentration gradient existing between steel and the surface of concrete following Fick's second law of diffusion<sup>23</sup>. The passive state of steel in concrete is maintained in the presence of oxygen (O<sub>2</sub>). The O<sub>2</sub> diffusion coefficient in water saturated concrete is of the order of 10<sup>-4</sup> to 10<sup>-6</sup> cm<sup>2</sup>/s<sup>24</sup> compared with values of the order of 10<sup>-2</sup> to 10<sup>-4</sup> cm<sup>2</sup>/s<sup>25</sup> in dry concrete. Thus, in submerged conditions, the concrete pores are completely filled with water and therefore, the O<sub>2</sub> content in the concrete is limited by its solubility in water which is affected by temperature. Therefore, at higher temperatures the diffusion rate of O<sub>2</sub> will increase but the decrease in solubility may result in the depassivation of steel, which especially controls the de polarization process of cathodically protected reinforced concrete structures<sup>26</sup>.

The chloride ion (Cl<sup>-</sup>) diffusion towards the steel/mortar interface plays a critical role in the de-passivation of steel i.e., at a critical threshold of Cl<sup>-</sup> at the interface, pitting occurs. Page et al<sup>27</sup> have reported that the effective diffusivities of Cl<sup>-</sup> in OPC pastes of water/cement (W/C) ratio of 0.4 increase from 11.03 x 10<sup>-9</sup> cm<sup>2</sup> s<sup>-1</sup> at 7 °C to 84 x 10<sup>-9</sup> cm<sup>2</sup> s<sup>-1</sup> at 44 °C. Similar increase has been shown for other W/C ratios. At higher temperatures the diffusion imparts to the pitting propensity<sup>28</sup> by directly affecting the Cl<sup>-</sup>/OH<sup>-</sup> ratio.

### **THE EFFECT OF TEMPERATURE ON CHLORIDE BINDING**

The Cl<sup>-</sup> anion is bound in the cement matrix by tricalcium aluminate (C<sub>3</sub>A) forming Friedel salt (3CaO.Al<sub>2</sub>O<sub>3</sub>.CaCl<sub>2</sub>.10H<sub>2</sub>O)<sup>29</sup> and thus reduces the amount of free Cl<sup>-</sup> in the pore solution. Rasheeduzzafar and coworkers<sup>30</sup> have shown that the concentration of water soluble chloride, extracted with hot water, falls from 86% for 2% C<sub>3</sub>A content in OPC mortars to 33 % for OPC mortars containing 14% C<sub>3</sub>A. Others observed that this binding of Cl<sup>-</sup> can be significantly reduced by carbonation, high levels of SO<sub>4</sub><sup>2-</sup> and high ambient temperatures<sup>31</sup>.

Roberts<sup>32</sup> worked with synthesised Friedel salt and postulated that this complex releases Cl<sup>-</sup> at higher temperatures and that the process is irreversible. However, the results given in Fig. 4 do not conform to Robert's postulation. Benjamin and Sykes<sup>33</sup> developed the understanding of the mechanism by work on the stability of synthesised calcium chloroaluminate (SCCA) as the function of pH and temperature. The results showed that the stability of SCCA is affected by the changes in temperature but more markedly by the changes in pH. Some Cl<sup>-</sup> was re-absorbed by the complex when the temperature was lowered. They construed that it is not the tri calcium aluminate breaking at high temperatures but it is actually adsorption and de-sorption from the cement matrix that is markedly influenced by the changes in temperature.

The pitting of steel depends upon several interactive parameters that need more elaborate discussions as the problem diversifies. The foregoing context has merely taken the root causes that must be taken into account to safe guard the durability of the concrete structures. It is extremely important that the civil engineers utilize such information when outlining a construction plan, with a

particular emphasis on temperature in conjunction with the other conditions of exposure.

## CONCLUSIONS

1. Chloride/hydroxide ratio is an important parameter that effects the corrosion of steel in concrete. The ratio is markedly influenced by the changes in temperature i.e., it decreases with an increase in temperature.
2. The threshold chloride concentration to cause the pitting of steel embedded in concrete decreases with an increase in temperature from 6% at 0 °C to 2% at 40 °C.
3. Synthesised tricalcium chloro aluminate is stable in the temperature range of 0 – 60 °C but is markedly influenced by the changes in pH.
4. Desorption of chloride from the cement matrix at higher temperatures contributes to the corrosion of steel in concrete.
5. The international codes of practice defined for chloride threshold in concrete must be revised for the tropical and the high temperature regions.

## REFERENCES

1. Alonso, M.C., Toraja Institute, Madrid, Spain. Private communication
2. A. Traetteberg & P.E Gratten-below., J. of Am. Cer. Soc., 1975, 58, No. 5-6.
3. L. Heller & M. Ben Yair, Nature, 1961, p.191.
4. J.A. Gonzalez' & C. Andrade', Brit. Corr. J., 1980, 15, No.3.
5. J.A. Gonzalez', M.C. Alonso, & C. Andrade', "Corrosion of reinforcement in concrete construction", ed. By A.P. Crane, Ellis Horwood Ltd., 1983, pp.159.
6. T.P. Hoar, D.C. Mears, &, G.P. Rothwell, Corr. Sci., 1965, p.5.
7. W. Schwenk, Corrosion, 1964, p.20.
8. H.H., Strehblow, B. Titze, B. & B.P. Lochel, Corr. Sci., 1979, p.19.
9. N. Sato, Electrochimica Acta, 1971, p.16.
10. D.A. Hausman, Materials Protection, 1967, 6, p.19.
11. S. Diamond, Cem. Conc. & Aggregate, 1986, No.2.
12. S. Goni, and C. Andrade, Toraja Inst., Madrid, Spain. Private communication.
13. C. L. Page, Proc. 2nd. Int. Conf. on, "Deterioration of concrete in Arabian Gulf", Bahrain, 1987, p.161.
14. D.T. Parkinson, 2<sup>nd</sup> year Research Report, Aston Univ., 1989.
15. S. E. Benjamin and J.M. Sykes, "Corrosion of Steel reinforcement in concrete construction", eds. C.L. Page, K.W.J. Treadaway, and P.B. Bamforth, SCI: Elsevier App. Sc. publishers, ISBN 1-85166-487-4, 1990. pp. 59.

16. S. E. Benjamin and J.M. Sykes, 3rd Int. Conf. on deterioration of concrete in Arabian Gulf, 1989, 1, p.573.
17. S.E. Benjamin, F.A. Khalid & J.M. Sykes, EUROCORR 98, The European Corrosion Congress on, "Solution of corrosion problems", Event No. 221, Netherlands, 28 Sept. – 1<sup>st</sup> Oct. 1998.
18. L.H. Everett, & K.W.J. Treadaway, Building Res. Establishment, Info Paper, IP 12/80, 1980.
19. Xu; and M.J. Setzer, RILEM Proc. 1997, 34, p.269.
20. Q.B. Yang, X.L. Wu, and S.Y. Huang, Int. Congr. Chem. Cem., 9<sup>th</sup>, 1992, 5, p. 282.
21. U. Balters, and U. Ludwig, RILEM Proc. 1997, 34, p. 111.
22. J. Stark, H-M. Ludwig, ACI Mater. J., 1997, 94 (1), p. 47.
23. N.S. Berke and M.C. Hicks, Corr., 50 (3), 1994, p.234.
24. C.L. Page and P. Lambert, J. Material Sci., 22, 1987, p.942.
25. A. A., Sagues and S.C. Kranc, Corr., 8, 1992, p.624.
26. M. Z. Lourenco and B.W.Cherry, "Factors which Control the Depolarisation process of Cathodically Protected Reinforced concrete Structures", presentation at Conf. on Understanding Corrosion Mechanisms in Concrete, Cambridge,USA,July 25-29, 1997.
27. C.L. Page, N.R. Short and A. El Tarras, Cem. Conc. Res., 11, 1981, p.395.
28. A.V. Saetta, R.V Scotta., and R.V. Vitaliani, ACI Materials J., 90(5), 1993, p.441.
29. L. Heller, and M. Ben-Yair, Nature, 191, 1961, p. 488.
30. S.S. Rasheeduzaffar, F.H. Saadoun, Dakhil, & A.S. Al-Ghatani, Corrosion of steel reinforcement in concrete construction", ed. C.L. Page, K.W.J. Treadaway and P.B. Bamforth, SCI: Elsevier Applied Science, London, ISBN1-85166-487-4, 1990, p.213.
31. M. Masslehuddin, C.L. Page, Rasheeduzaffar and Al-Mana, "Corrosion of steel reinforcement in concrete construction", ed. C.L. Page, P.B. Bamforth, and J.W. Figg, Roy. Soc. Chem., Cambridge, 1996, p.67.
32. M. H. Roberts, Mag. of Concrete Res., 1962, 14, p. 143.
33. S. E. Benjamin, J.M. Sykes, & F.A. Khalid, "The Effect of Temperature and pH on the Binding of chloride by calcium aluminate", paper presented at Conf. on Understanding Corrosion Mechanisms in Concrete", July 27-31, Massachusetts Inst. of Tech., Cambridge, USA, 1997.