THE THRESHOLD LIMIT FOR CHLORIDE CORROSION OF REINFORCED CONCRETE

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ABSTRACT:

Of the annual production of steel rebars, a substantial portion of 2 million tons of steel rods are used as reinforcements in RCC structures. Due to rebar corrosion, often more than the cost of construction is being spent on the repair of bridge structures in ports and industrial areas. Especially some RCC structures have to be repaired within 2 or 3 years of construction. In the years to come, if rebar corrosion problems continue, nearly 10 to 15% of the cost of annual construction will be spent on repairs and renovations.

In India, the cost due to rebar corrosion problems was estimated at Rs.100 crores being spent annually by the building and construction industry and the likely potential saving by application of proper corrosion control methods may be estimated at Rs.20 crores.

Chloride-induced corrosion of reinforcing steel is recognized as a primary factor contributing to the deterioration of concrete structural elements. Moisture, oxygen dissolved in moisture and aggressive ions (particularly chlorides) are the three important factors necessary to induce corrosion of rebars. If oxygen and water are eliminated completely then corrosion will be arrested completely. However, it is normally impossible to eliminate oxygen or moisture from the structural elements because these species are inherently present in the structure. But it is possible to remove the aggressive ions (particularly chlorides) from the existing structures by a desalination process or by adding suitable chloride scavengers. In National Highway Bridges and Concrete Structures, if the chloride content exceeds the threshold value, suitable preventive measures may be implemented to enhance the service life of bridges and structures.

The objective of this review article is to analyze the critical chloride content in concrete structures exposed to various environmental conditions

and to correlate with corrosion conditions of embedded steel. From the correlation an attempt has been made to predict a universal threshold limit of chloride to initiate rebar corrosion.

From this critical analysis of the threshold limit of chloride, it is concluded that the Cl^-/OH^- ratio is not the appropriate index to predict rebar corrosion under all conditions. Other environmental parameters like alkalinity, oxygen availability and impermeability do play a significant role besides the Cl^-/OH^- ratio. Hence it is impossible to predict a universal threshold limit of chloride to initiate rebar corrosion in National Highway Bridges and Concrete Structures. Depending upon the environment the threshold limit will vary.

INTRODUCTION

In reinforced concrete structures, the pore solution surrounding the reinforcements attains a pH of 12.6 after completion of the hydration reaction. The high alkalinity is buffered at this pH by calcium hydroxide in a lime-rich layer in intimate contact with the surface of the reinforcements. So far, the alkalinity remains at a high pH and the rebars also remain free from corrosion /1/ (Figure 1).

Of the various anions encountered in concrete structures the chloride ion has acquired a significant reputation as the most aggressive ion /2/. Earlier study revealed that chloride ions possess a very high penetrating power in the passive oxide films on metals. This effect is considered to be associated with its smaller size in comparison to other ions /3/.

The most common cause of the rebar corrosion problem stems from introduction of chloride ions. The existence of chloride in concrete structures is due to (i) its use as an accelerator in the concrete mix, (ii) the presence of a marine atmosphere and (iii) the use of deicing salts. Chloride occurs in concrete in three forms: (i) chemically bound, (ii) physically adsorbed and (iii) free chloride /4/.

The free chlorides are mainly responsible for rebar corrosion. If the free chloride to hydoxide ratio exceeds 0.6, loss of passivity occurs and pitting progresses. The presence of free chloride not only alters the Pourbaix equilibrium diagram (it reduces the area of the passive region as shown in Figure 2, but also transfer the rebar from the passive to the active region) /5/. The corrosion reactions occurring can be represented as follows /6,7/.
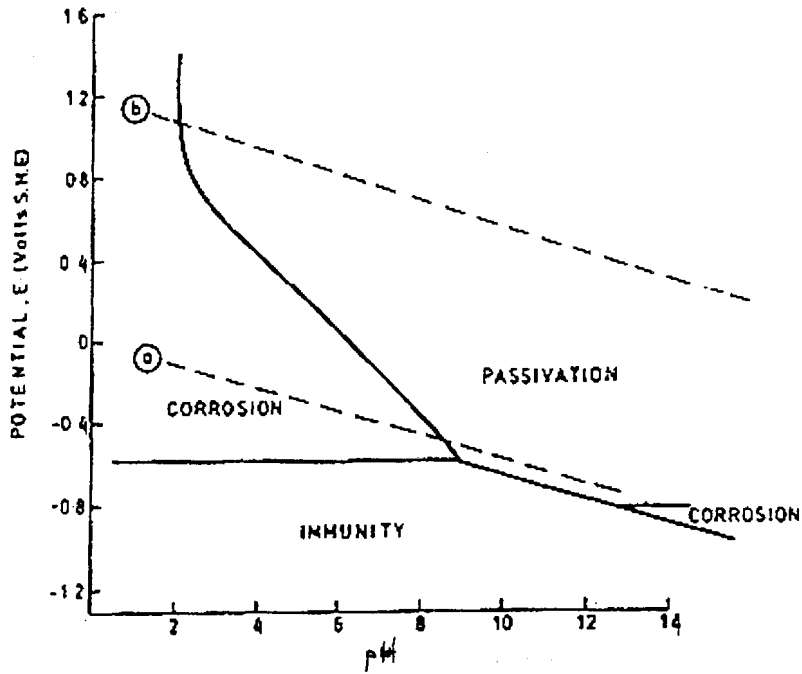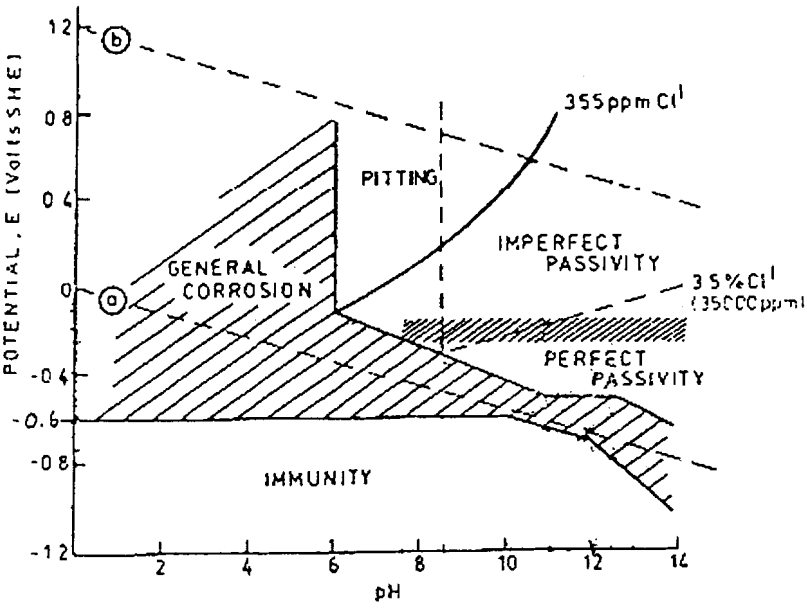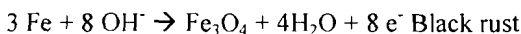
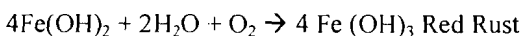**Fig. 1:**   The iron Pourbaix diagram.

Fig. 2:   Theoretical conditions for corrosion and passivation of iron.

$Fe \rightarrow Fe^{2+} + 2 e^-$

$O_2 + 2 H_2O + 4 e^- \rightarrow 4 OH^-$

$Fe^{2+} + 2 OH^- \rightarrow Fe(OH)_2$ white corrosion product

$4Fe(OH)_2 + 2H_2O + O_2 \rightarrow 4 Fe(OH)_3$ Red Rust

$3 Fe + 8 OH^- \rightarrow Fe_3O_4 + 4H_2O + 8 e^-$ Black rust
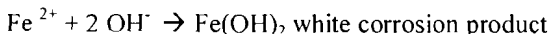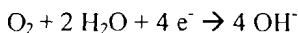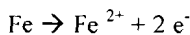
At high chloride concentrations

$Fe + 2 Cl^- \rightarrow FeCl_2 \rightarrow Fe^{++} + 2 Cl^- + 2 e^-$ Yellowish green

$O_2 + 2H_2O + 4 e^- \rightarrow 4 OH^-$

$6 FeCl_2 + O_2 + 6H_2O \rightarrow 2 Fe_3 O_4 + 12H^+ + 12 Cl^-$
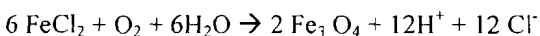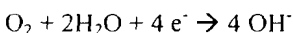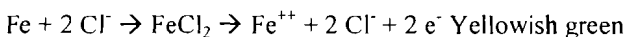
The reaction between iron and free chloride is self-perpetuating in that the free chloride originally responsible for the reaction is released for re-use when iron hydroxide is formed. In fact, the free chloride acts as a reaction catalyst /2/.

Even though a high level of alkalinity remains around the steel embedded in concrete, the chloride ions can locally depassivate the steel and promote rebar corrosion.

Threshold value:

Corrosion first begins when a certain chloride concentration has been reached around the steel This concentration is called the threshold value.

Expression of "Threshold value"

Normally, in concrete core sample analysis in the laboratory, chloride content is expressed as a percentage on the basis of the weight of cement because cement constituents like calcium oxide and aluminium oxide play a major role in converting chloride from the free state to the complexing state.

In contrast, in the case of core samples collected from bridges and structures chloride content is expressed as a percentage on the basis of the weight of concrete as it is very difficult to find the cement content in existing structures. But from a corrosion point of view, only the free chloride content, not the total chloride content, is responsible for inducing rebar corrosion. In estimating the chloride content in concrete core samples, only the chloride content at the steel/concrete interface plays a major role in inducing passivity. But it is also very difficult to estimate the chloride content at the steel/ concrete interface. Microelectrodes should be developed on the basis of ion-selective electrodes to estimate the chloride content at the steel/concrete interface, because the steel/concrete interface plays a major role in identifying the active/passive condition of steel rebars. A literature survey carried out on the threshold limit of chloride to induce rebar corrosion in bridges and concrete structures revealed that various factors in the design stage itself as well as during prolonged exposure influence the quantity of chloride required to destroy passivity and induce rebar corrosion. The objective of this review article is to study the factors influencing the threshold limit of chloride and to clarify the question: "Is it possible to predict a universal threshold limit of chloride to initiate rebar corrosion in National Highway Bridges and Concrete Structures?".

FACTORS INFLUENCING THE THRESHOLD LIMIT OF CHLORIDE

The following are the main factors influencing the threshold value of chloride in the design stage itself:

a. Proper mix design
b. Type of cement
c. Curing period
d. Concrete cover thickness
e. Porosity / voids in the concrete

a. Proper Mix Design

Poor concreting practice produces micro and macro cracks in the concrete. The aggregate - cement ratio, water cement ratio, the maximum size

of aggregate and its grading, the methods of compaction of concrete, its curing etc. are the parameters to be considered in the design stage itself. Low cement content and high water cement ratio produce a readily permeable concrete /8,9,10/. As a result, concrete allows oxygen, water and salts to pass through it, facilitating corrosion of the rebar. Proper mix design can tolerate a higher threshold value of chloride, whereas improper mix design decreases the threshold value of chloride.

Experiments carried out in the laboratory by exposing two grades of concrete (lean mix concrete, rich mix concrete) to immersed conditions (seawater, potable water) and exposure conditions (indoor and outdoor weathering) revealed that in the case of lean mix concrete even though the Cl^-/OH ratio is found to be less than 0.6, severe corrosion occurred. On the other hand, in the case of rich mix concrete even though the Cl^-/OH^- ratio is found to be greater than 0.6, a negligible amount of corrosion was observed /35/.

In the case of the lean mix concrete, apart from the Cl^-/OH^- ratio, porosity and low alkalinity also induced corrosion. On the other hand, in the case of the rich mix concrete, apart from the Cl^-/OH^- ratio the denser mix reduced the permeability of aggressive ions. The availability of oxygen at the steel surface is severely restricted by the low permeability of the rich mix concrete. Thus lean mix concrete decreases the threshold level of chloride, whereas rich mix concrete increases the threshold level of chloride to induce rebar corrosion.

b. Type of Cement

Pozzolana cement, which contains sulfides, initiates rebar corrosion and concrete deterioration /11/. It was reported that the corrosion rate with ordinary portland cement was about five times lower than that with pozzolana cements like fly ash and slag cements /12/. It is found that the concrete with portland cement (OPC) has a higher pH value than that with pozzolana cement. Hence, the former has a better passivating capacity. Thus ordinary portland cement increases the threshold level of chloride due to high alkalinity, whereas pozzolana cements decrease the threshold level of chloride due to low alkalinity.

c. Curing Period

During the curing period, the hydration which is mainly responsible for the strength of the concrete proceeds /13/. A longer duration of curing favors complete gel formation and decreases the permeability of the concrete cover. The curing period should not be less than 72 hours /9,14/. As the curing time increases, the strength of the concrete also increases. Inadequate curing causes shrinkage cracking and earlier spalling of concrete structures /15/. The curing period is found to be directly proportional to the threshold value of chloride.

d. Concrete Cover Thickness

Provision of adequate concrete cover is essential. A minimum cover of 40mm is necessary for marine exposure and a 50mm cover will be the optimum /16/. However, cover thicknesses of 70mm and 100mm have also been recommended for structures exposed to marine environments /17,18,19/. Cover thickness is found to be directly proportional to the threshold value of chloride.

e. Porosity of Concrete

Concrete is naturally a porous material. The porosity, in other words the permeability of the concrete to liquids, is a strong function of water / cement ratio /9,20/. As the water / cement ratio increases, the porosity will also increase. Concrete capillaries vary from approximately 15-1000 A^o in diameter. Chloride ions are less than 2 A^o in diameter /21/. As a result, faster penetration of aggressive ions occurs, causing reinforcement corrosion. Thus porosity is directly proportional to the threshold value of chloride.

The factors mainly responsible for influencing the threshold value of chloride during prolonged exposure are:
a. Alkalinity of concrete
b. Carbonation of concrete
c. Sulfate attack on concrete
d. Leaching action in concrete
e. Environmental action on concrete

a. Alkalinity of concrete

Normal concrete has a pH value of 12.6. At this high pH value concrete can tolerate a higher quantity of chlorides. If pH decreases due to carbonation, the threshold value of chloride also decreases. The threshold value of chloride is directly proportional to the alkalinity of concrete.

b. Carbonation of concrete

Fresh concrete has a pH value of 12.6. The moist carbon dioxide present in the atmosphere reacts with the alkaline material present in concrete as follows:

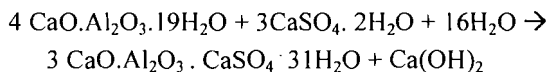$$Ca(OH)_2 + CO_2 \rightarrow Ca\ CO_3 + H_2O\ (pH = 7)$$
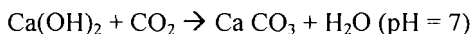
This neutralization is a continuous process /22/. Hence the pH value near the rebar drops to 7-9 which leads to corrosion of rebars with the formation of different complex iron oxides. Moreover, the carbonated concrete does not have the same capacity for binding of chlorides as does non-carbonated concrete. This increases the amount of free chloride in the concrete. As a result, carbonation decreases the threshold value of chloride.

c. Sulfate attack on concrete

This is caused by the following chemical reactions between concrete and sulfates present in the underground soil and seawater.

i. Formation of gypsum
ii. Formation of ettringite

$$Ca(OH)_2 + Na_2SO_4.10\ H_2O \rightarrow CaSO_4 - 2H_2O + 2\ NaOH + 8\ H_2O$$

$$4\ CaO.Al_2O_3.19H_2O + 3CaSO_4.\ 2H_2O + 16H_2O \rightarrow$$
$$3\ CaO.Al_2O_3 . CaSO_4\ 31H_2O + Ca(OH)_2$$

$$3\ CaO.\ 2SiO_2 + 3\ MgSO_4 . 7\ H_2O \rightarrow CaSO_4.\ 2H_2O + 3\ Mg\ (OH)_2 + 2\ SiO_2.$$

Thus the conversion of $Ca(OH)_2$ and calcium aluminate to gypsum and ettringite more than doubles the solid volume. These reactions account for the expansion and cracking of concrete structures. As a result, sulfate attack on concrete decreases the threshold value of chloride /23/.

d. Leaching action in concrete

For structures completely submerged in water, the leaching of lime is a major weakening factor /22,24/, During the leaching process, hydroxide ion is always diffused outwards. If extensive leaching of lime takes place, it will increase the porosity and decrease the strength and durability of concrete structures. The presence of chemicals like ammonium chloride, ammonium sulfate, acids like hydrochloric acid, sulfuric acid, phosphoric acid, etc., in the environment brings about accelerated deterioration of the concrete. As a result, leaching action in the concrete decreases the threshold value of chloride.

e. Environmental action on concrete

Normally, concrete structures are exposed to seawater, potable water, and indoor and outdoor weathering conditions. Experiments carried out in the laboratory revealed that under immersed conditions the alkalinity of concrete was maintained irrespective of the mix design studied. Under immersed conditions, continuous hydration preserved the alkalinity during prolonged exposure. As a result, concrete under immersed conditions can tolerate greater quantity of chloride. On the other hand, in indoor and outdoor weathering conditions the normal alkalinity was maintained only in rich mix concrete. The alkalinity was found to be considerably reduced in the case of lean mix concrete. As a result, concrete in exposure conditions, particularly lean mix concrete, can tolerate only a lower quantity of chloride.

TOLERABLE LIMIT OF CHLORIDE

Experiments were carried out in simulated concrete environments as well as core samples collected from bridge sites. The data collected are reported in Table 1. From this table, it was inferred that the threshold level of chloride showed a fluctuating trend depending upon the concrete conditions and the methods of testing /29/.

It was reported that if the Cl^-/OH^- ratio exceeds 0.6, depassivity occurs and corrosion proceeds. This criterion cannot be considered as universal because there are environments where even though the Cl^-/OH^- ratio exceeds 0.6 no corrosion was observed (Table 2). Perfect passivity was maintained. Under such conditions, alkalinity and impermeability of concrete play a major role in controlling the rate of corrosion of steel in concrete /35/.

Table 1

Reported tolerable limit of chloride

System studied	Tolerable limit reported	Reference
Depassivation of steel by chloride occurs beyond the limit	$Cl^- / OH^- \sim 0.6$	25
The threshold Cl^-/OH^- ratio seemed to depend on the pore solution pH	Threshold Cl^-/OH^- ratios ranged from 1.28 to 2.0 for a pore solution pH of 13.26 to 13.36	26
Reduced oxygen availability is predicated to increase the Cl^- /OH^- ratio	Threshold Cl^-/OH^- ratios ranged from 0.66 to 1.4 for most reinforced concretes	27
The threshold concentration of sodium chloride causing pitting corrosion of mild steel with free oxygen present	0.02M (moles per liter) or 700 ppm of chloride	28
Threshold limit determined by galtomostatic polarization in simulated concrete (NaOH-NaCl system)	500 ppm of chloride	29
Threshold limit determined by anodic polarization technique in NaOH - NaCl system	1000 ppm of chloride	30
Threshold level determined by polarization resistance method	0.1 - 0.2% by weight of cement	31
Threshold level estimated by polarization resistance method	1.0 - 2.5% of sodium chloride	32
Threshold level determined in terms of water soluble chloride	0 - 15% water soluble chloride by wt. of cement	33
Threshold level determined by anodic polarization measurements	0.6% by wt of cement	34
Steel embedded in concrete and exposed to immersion and weather conditions	Threshold value depends on various factors, like oxygen availability, alkalinity, mix design, etc.	35

Table 1 (continued)
Reported tolerable limit of chloride

System studied	Tolerable limit reported	Reference
Steel distress has been noted when chloride levels exceed the threshold value	330 ppm by wt. of concrete (1.3lb / yd ^{3})	36-39
	383 ppm (1.5lb/ yd^3)	40
	255 ppm (1.5lb/ yd^3)	41
	357 ppm (1.5lb/ yd^3)	42
	510 ppm (1.5lb/ yd^3)	43
Inspection of reinforced structure exposed to wet environments	0.1%	
Reinforced structure exposed to wet (absence of chloride) environments	0.15%	44
Reinforced structures exposed to dry above ground levels	No limit for corrosion purposes	
Inspection of bridge decks showed the level of chloride at which activation of rebar occurred.	US 0-4% (a) UK >1% wt of cement, rust of corrosion - high < 0.4% wt of cement, rust of corrosion - small (b) Sweden > 1.5% by wt. of cement (c)	45 46
When sufficient moisture, O_2 and other necessary factors are present, the threshold limit was found	0.2% by wt of cement This corresponds to 330 ppm	47
Field survey carried out on 473 bridge decks.	Minimum quantity of chloride required to initiate rebar corrosion was found to be 0.4%	48,49

Table 2

Estimated free chloride content (ppm) for lean mix and rich mix concrete
concrete exposed to various environmental conditions

Mix Design	Sea Water	Potable Water	Indoor Exposure	Outdoor Exposure
Lean mix concrete	3400	1400	400	160
Rich mix concrete	8920	1600	560	380
Visual observation data (%) & weight loss data on corrosion (mpy x 10^{-6})				
Lean mix concrete	100% (1.330)	5% (1.005)	75% (0.575)	100% (0.665)
Rich mix concrete	---	---	---	---
Relationship between chloride hydroxide ratio and corrosion				
Lean mix concrete	2.38 (Yes)	0.98 (Yes)	0.37 (Yes)	0.15 (Yes)
Rich mix concrete	6.24 (No)	1.12 (No)	0.39 (No)	0.27 (No)

Particularly in structures immersed in deep sea, even though greater amounts of aggressive ions are present, there to induce corrosion, negligible corrosion was reported due to limited oxygen availability at the steel / concrete interface. Moreover, the solubility of oxygen was also reduced at a high concentration of chloride. In such environments oxygen availability plays a major role in controlling rate of corrosion of steel in concrete.

Experiments carried out in simulated concrete environments revealed that the threshold limit of chloride was found to be in the range 500 ppm – 1000 ppm of chloride (0.05% to 0.1%). On the other hand, data reported for core samples collected from a bridge site showed a threshold limit of chloride in the range of 0.1% to 2.5%. This deviation in the threshold limit of chloride was due to the environmental conditions to which the concrete structures were exposed.

Chloride-induced corrosion of reinforcing steel is recognized as a primary factor contributing to the deterioration of concrete structural elements. Moisture, dissolved oxygen in moisture and aggressive ions (particularly

chlorides) are the three important factors necessary to induce corrosion of rebars. If oxygen and water are fully eliminated then corrosion will be arrested completely . But it is normally impossible to eliminate oxygen or moisture from the structural elements because both these species are inherently present in the structure. It is, however, possible to remove the aggressive ions (particularly chlorides) from the existing structures by a desalination process or by adding suitable chloride scavengers. In National Highway Bridge and Concrete Structures, if the chloride content exceeds the threshold value suitable preventive measures may be implemented to prolong the service life of bridges and structures.

CONCLUSION

From this critical analysis of the threshold limit of chloride it is concluded that the Cl^-/OH^- ratio is not the appropriate index to predict rebar corrosion under all conditions. Other environmental parameters, like alkalinity, oxygen availability and impermeability, do play a significant role besides the Cl^-/OH^- ratio. Hence it is impossible to predict a universal threshold limit of chloride to initiate rebar corrosion in National Highway Bridges and Concrete Structures. Depending upon the environment the threshold limit will vary.

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