Relationship between Chloride/hydroxide Ratio and Corrosion Rate of Steel in Concrete

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Abstract

Just as water/cement ratio is an important parameter controlling the strength of concrete, alkali/chloride relationship is an important aspect influencing the performance of steel embedded in concrete. In the past, several studies have been carried out to determine the threshold limit for chloride and it has been established that the tolerable limit for chloride increases with alkalinity. However, in practice, the chloride level is invariably in excess of the tolerable limit and thus is bound to accelerate corrosion. No clear relationship between chloride/hydroxide ratio and corrosion rate of steel has been established so far. This paper addresses this important aspect by carrying out some systematic long term evaluation studies. Two different concrete mixes (lean/rich) and two different exposure conditions (immersion/atmosphere) were used in this investigation. Initial sodium chloride content in the concrete was varied in the range 0, 0.01, 0.05, 0.1, 0.5, 1 and 3.5% N by weight of cement. Corrosion rate was evaluated by conventional gravimetric method. The investigation revealed that even with adequate oxygen availability, the corrosion rate of steel embedded in concrete increases steeply with the Cl/OH ratio, and no such relationship is found to exist when the exposure conditions restricts the availability of oxygen. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The tendency of steel rebar to corrode or not depends on the potential developed by it in its environment. In an acid medium, steel rebars tend to corrode freely whereas in an alkaline medium, corrosion is found to be almost negligible. This is due to the formation of a stable corrosion product (Fe_2O_3) on the surface, termed passivity. However, this stable passive layer can be locally broken and corrosion can be initiated whenever there is a decrease in pH and an increase in salt contamination in the surrounding concrete medium.

The major individual constituent of cement is CaO (free lime) and during setting and hardening of concrete CaO reacts with H_2O (the mixing water) to form Ca $(OH)_2$, that is, calcium hydroxide. The steel rebar is actually reported to be surrounded by such a layer[1]. The pH of a saturated solution of $Ca(OH)_2$ is 12.5.

The passivation strength depends on the alkalinity of the concrete environment and when the chloride contamination in concrete reaches a set level, then breakdown of passivity occurs. Chloride can be introduced into concrete both by the use of chloride contaminated materials and water at the time of laying concrete and by subsequent diffusion through concrete cover. All the chloride present in cement and concrete may not cause corrosion, since aluminate in the cement combines with the chloride to form chloro aluminate. Thus only the free soluble chloride ions are responsible for rebar corrosion.

Mechanism of reinforcement corrosion

Since the concrete is heterogeneous in nature, the concrete environment is also non-uniform and is liable for variation along the steel rebar. Consequently the steel potential varies from place to place. Depending on the potential at a particular place, the steel becomes very active or passive.

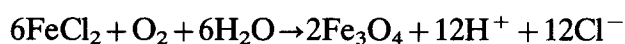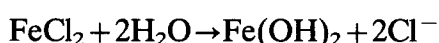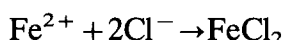Wherever it is active, the solid steel dissolves and goes into solution as ferrous ions.

$$Fe(solid) \rightarrow Fe^{2+}(ions) + 2e$$
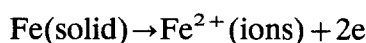
Since the reaction releases electrons (2e), these electrons are simultaneously accepted where oxygen reduction occurs.

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-$$
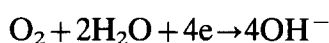
Thus one can see that oxygen (O_2) and water (H_2O) are required to sustain the cathodic reaction of the overall corrosion process. When concrete is dry, the oxygen diffuses and reaches the steel and when concrete is wet, moisture (H_2O) is able to reach the steel. Thus the exposure conditions are an important aspect influencing reinforcement corrosion.

The role of chloride is unique. It can be reused again and again and hence even a small amount of chloride can sustain the corrosion process.

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

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2Cl^-$$

$$6FeCl_2 + O_2 + 6H_2O \rightarrow 2Fe_3O_4 + 12H^+ + 12Cl^-$$

Thus the iron–chloride reaction is self-perpetuating and the free chloride acts as a reaction catalyst.[2]

Chloride–hydroxide relationship

Knowing the importance of both chloride and hydroxide ions in the reinforcement corrosion process, several workers have attempted to assess the threshold limit for chloride in concrete. In 1962, Lawis determined the critical concentration of sodium chloride in saturated calcium hydroxide solution required to initiate corrosion of steel through polarization studies and reported a value of 0.05% by weight.[3] Further studies in cement extracts showed that the critical addition of sodium chloride to cement before the corrosion of steel can start is 0.54%

which corresponds to an effective concentration of soluble sodium chloride of 0.26%. Rajagopalan *et al.* in 1966 used an elegant anodic polarization technique to find out the tolerable limit for chloride in sodium hydroxide solutions of different normality and showed that the tolerable limit for chloride increases exponentially with alkalinity.[4] Hausmann in 1967 showed through simulation studies that the initiation of corrosion requires free oxygen as well as a ratio of chloride to hydroxyl ion activity of at least 0.6.[5] In saturated $Ca(OH)_2$ solution, the threshold of steel corrosion is reached at a chloride concentration of 700 ppm and at pH 13.2, it is <8000 ppm. Gouda reported in 1970 that a linear relationship holds between the pH and the highest concentration of sodium chloride that can be tolerated.[6] In 1975, Page established the existence of a two component protective system composed of a discontinuous layer of portlandite $Ca(OH)_2$ with inclusions of calcium–silicate–hydroxide gel and a thin layer of iron oxide/hydroxide stabilized by the alkaline environment (pH 11–13).[7] Studies by Leek and Pools have shown that the breakdown of passivity by chloride ions is achieved by dissolution of the portlandite layer and destabilization of the substrate bond.[8] Thomas *et al.* have made extensive studies in marine exposed concretes containing pulverized fuel ash (PFA) and showed that concrete mixes containing PFA offers a greater resistance to the penetration of chloride ions compared with plain OPC concrete of similar grade and workability.[9] The weight loss of embedded steel was reliably correlated with the total chloride concentration at the location of the steel. A chloride content of 0.5% by weight of cement was found to be sufficient to initiate corrosion. Even though a linear regression analysis was performed to show a correlation coefficient of 0.888 there was wide scatter in the weight loss data. Further their studies did not include the alkalinity–chloride relationship. On the other hand, a report by Vasanthi *et al.* has indicated that in chloride environments, concrete containing fly ash offers lesser protection to steel reinforcement compared to OPC concrete.[10]

Thus it can be seen that most of the earlier work on the 'chloride–alkalinity relationship' was limited to the assessment of threshold values or critical concentration of chloride required to initiate corrosion. No in-depth study appears to have been made on the role of the

chloride–alkalinity relationship on the rate of corrosion of steel embedded in concrete under different exposure conditions.

In the present work, performance data collected under a long term exposure programme over 3 years have been analysed.

EXPERIMENTAL

Details of the concrete mixes used in this investigation are given in Table 1. A lean mix with a high W/C ratio and low cement content was used to study the influence of carbonation and rapid chloride diffusion. For comparison a rich mix with a lower W/C ratio and higher cement content was also studied.

Ordinary Portland cement (OPC) with a soluble chloride content of 0.002% by weight and an alkalinity of 12.7 was used (90% of the cement passes through a 90 μm sieve). Clean

Table 1. Mix design (in kg m^{-3})

	Lean mix concrete	Rich mix concrete
Cement	138	274
Fine aggregate	414	469
Coarse aggregate	828	573
Water/cement ratio	0.68	0.50

river sand (fineness modules of medium sand = 2.6) was used as fine aggregate. It had no soluble chloride. Clean and graded granite stone in the range 4.75–10.00 mm was used as coarse aggregate. It had no soluble chloride.

Preparation of concrete samples

Figure 1 depicts the specimen details. The mild steel specimen 10 mm in diameter and 25 mm long was mechanically polished to a mirror-like finish, degreased with trichloroethylene and then centrally embedded in a 50 mm diameter 50 mm high concrete mix using appropriate split mould. After 24 h, the specimens were demoulded and cured in distilled water for 7 days.

To simulate initial chloride contamination that may occur through mixing water and raw materials, sodium chloride of specific concentration was dissolved in deionized water and used for mixing concrete. The concentration ranges studied were 0, 0.01, 0.05, 0.1, 0.5, 1 and 3.5% by weight of cement.

Exposure programme

After 7 days curing, the specimens were removed from deionized water and subjected to various exposure conditions as follows:
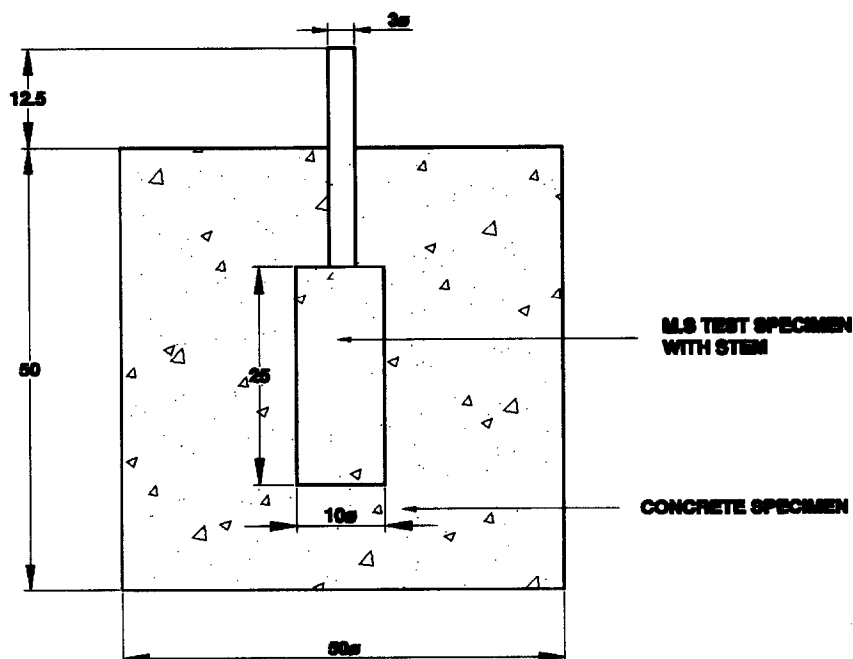

Fig. 1. Cylindrical reinforced concrete specimen.

1. continuous immersion in synthetic seawater to promote chloride diffusion by concentration gradient effect;
2. continuous immersion in potable water to promote moisture diffusion primarily;
3. atmospheric exposure under sheltered condition – this will simulate a benign atmosphere devoid of rain and sunshine; and
4. atmospheric exposure under open condition – this will simulate natural alternate wetting and drying condition.

The total period of exposure was 2 years in respect of lean mix concrete and 3 years in respect of rich mix concrete obviously because of slower corrosion in the rich mix.

Data collection

At the end of the specified test period, the test specimens were with drawn and the following data were collected:

1. alkalinity of concrete extract;
2. soluble chloride content in the concrete;
3. visual observation of steel; and
4. corrosion rate of steel.

Concrete extract preparation

After the test period was over each specimen was crushed mechanically and powder samples were collected. Then 100 g of powdered concrete (which includes cement and aggregates) was shaken with 200 ml of distilled water in a conical flask using a microiod flask shaker for 1 h. The extract was then filtered through a Whatman filter paper No. 42. The extract prepared from the powdered concrete samples was then analysed for alkalinity and free chloride contents.

Determination of alkalinity

A 50 cm³ of filtered solution was taken in a 100 ml beaker and the pH was measured using a pH meter (supplied by Elico Instruments, Hyderbad, India).

Analysis of soluble chloride

A 20 cm³ of filtered solution was taken and the free chloride was estimated by titrating against standard silver nitrate using potassium chro-mate as indicator. The amount of chloride present was expressed in terms of ppm.

Visual observation

After the test period was over, the steel specimens embedded in the concrete were taken out. Visual observation data of corrosion in terms of percentage of area rusted were recorded.

Corrosion rate determination

The steel specimens embedded in the concrete were removed. All the rust products were cleaned with Clark's solution. (A concentrated hydrochloric acid containing $50\,g\,l^{-1}$ of stannous chloride and $20\,g\,l^{-1}$ of antimony oxide). The weight loss of the steel specimens were calculated. The weight loss was then converted into corrosion rate as mills penetration per year (mpy) using the equation

$$\text{Corrosion rate (mpy)} = \frac{534W}{DAT}$$

where W is the weight loss (in g), D is the density (in $g\,cm^{-3}$), A is the area (in sq.inches) and T is the time of exposure (in h).

Calculation of Cl⁻/OH⁻ ratio

The alkalinity measured in terms of pH were converted into corresponding (H^{+}). Then (OH^{-}) were calculated using the formula (H^{+}) $(OH^{-}) = 10^{-14}$ in normality and then converted into ppm. The free chloride contents estimated in terms of ppm were then divided by the corresponding (OH^{-}) in ppm to get the Cl⁻/OH⁻ ratio.

RESULTS OBTAINED

Data obtained on alkalinity, free chloride, visual observation on corrosion and weight loss in mpy at the end of the specified exposure period is presented in Tables 2–5. Since the total period of exposure was 2 years in the case of lean mix concrete and 3 years in the case of rich mix concrete, data are presented separately for lean mix concrete and rich mix concrete.

Table 2. Change of alkalinity estimated for different exposure conditions

Environment	Seawater	Fresh water	Indoor exposure	Outdoor exposure
Added Chloride equivalent by wt of cement (ppm)		Alkalinity (pH)		
(A) **Lean mix concrete**				
0	12.56	12.46	10.77	10.54
56	12.30	12.58	10.56	10.50
560	12.25	12.55	10.47	10.48
1960	12.20	12.50	10.20	10.35
(B) **Rich mix concrete**				
0	12.56	12.72	12.65	12.68
110	12.50	12.68	12.60	12.62
1100	12.38	12.64	12.56	12.58
3850	12.35	12.62	12.40	12.56

Table 3. Change of free chloride estimated for different exposure conditions

Environment	Seawater	Freshwater	Indoor exposure	Outdoor exposure
Added chloride equivalent by weight of cement (ppm)		Free chloride by weight of concrete (ppm)		
(A) **Lean mix concrete**				
0	1700 (3400)	700 (1400)	200 (400)	80 (160)
56	3620 (7240)	740 (1480)	780 (1560)	140 (280)
560	5300 (10600)	1000 (2000)	880 (1760)	160 (320)
1960	5840 (11680)	1400 (2800)	1100 (2200)	200 (400)
(B) **Rich mix concrete**				
0	2973 (8920)	533 (1600)	186 (560)	126 (380)
110	3466 (10400)	1506 (4700)	786 (2360)	186 (560)
1100	4253 (12760)	1933 (5800)	1226 (3680)	466 (1400)
3850	4400 (13200)	2066 (6200)	1373 (4120)	1173 (3520)

Values in parentheses indicate the amount of chloride estimate for the total period of exposure, that is, 2 years for lean mix concrete and 3 years for rich mix concrete.

Table 4. Visual observation data of corrosion (qualitative) and weight loss data of corrosion (quantitative) for mild steel embedded in lean mix concrete and exposed to various environmental conditions

Environment	Visual observation data of corrosion in terms of percentage of area rusted				Weight loss data of CORROSION in terms of $mpy \times 10^{-6}$			
Added chloride equivalent by weight of cement (ppm)	Seawater (%)	Freshwater (%)	Indoor exposure (%)	Outdoor exposure (%)	Seawater	Freshwater	Indoor exposure	Outdoor exposure
0	100	5	75	100	1.330	1.005	0.575	0.665
5.6	100	10	80	100	1.362	1.094	0.587	0.692
28	100	15	85	100	1.395	1.125	0.623	0.768
56	100	20	90	100	1.463	1.168	0.656	0.845
280	100	25	95	100	2.712	1.254	0.982	1.081
560	100	50	100	100	3.245	1.558	1.285	1.305
1960	100	80	100	100	3.897	1.854	1.324	1.432

Table 5. Visual observation data of corrosion (qualitative) and weight loss data of corrosion (quantitative) for mild steel embedded in rich mix concrete and exposed to various environmental conditions

Environment	Visual observation data of corrosion in terms of percentage of area rusted				Weight loss data of CORROSION in terms of $mpy \times 10^{-6}$			
Added chloride equivalent by weight of cement (ppm)	Seawater (%)	Freshwater (%)	Indoor exposure (%)	Outdoor exposure (%)	Seawater	Freshwater	Indoor exposure	Outdoor exposure
0	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
11	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
55	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
110	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
550	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
1 100	Nil	Nil	50	70	Nil	Nil	0.668	0.746
3 850	Nil	Nil	80	95	Nil	Nil	1.1	1.25

Alkalinity

Lean mix concrete

Table 2A gives the pH value data for the lean mix concrete under different exposure conditions. It can be seen that under immersion conditions whether in seawater or freshwater, the alkalinity is preserved. In the case of freshwater, the pH value lies in the range 12.46–12.58. In the case of seawater, the pH value is in the range of 12.20–12.45. Only an insignificant reduction in alkalinity has resulted even when exposed to seawater immersion.

On the other hand under atmospheric exposure condition, whether indoor or outdoor significant reduction in alkalinity has been observed. In the case of indoor exposure, pH values range between 10.20 and 10.77 while in the case of outdoor exposure the values lie in the range of 10.35–10.54. On an average, compared to immersion condition, pH value has been reduced by 2 due to atmospheric exposure. Though insignificant, chloride added at the time of mixing concrete appears to have some influence in reducing the pH value.

Rich mix concrete

Table 2B shows the data for rich mix concrete. It can be seen that under all exposure conditions whether subjected to immersion or atmospheric exposure, alkalinity has been preserved. The overall range lies in between 12.35 and 12.72. Here again, chloride added at the time of mixing concrete appears to have some insignificant influence in reducing the pH

slightly (by 0.10–0.20). It is worth noting that even after 3 years of atmospheric exposure, rich mix concrete has been able to preserve the alkalinity.

Free chloride content

The total free chloride content as analysed at the end of the exposure period as well as the free chloride per year as estimated from the years of exposure is considered in Table 3. On the basis of the mix design, the added NaCl percentage by weight of cement has been converted into chloride in ppm by weight of concrete and included. This is to facilitate easier comparison of data.

Lean mix concrete

It can be seen from Table 3A that chloride added at the time of mixing concrete as well as different exposure conditions have significant influence on the free chloride content. Free chloride (ppm/year) is maximized under seawater immersion and minimized under outdoor exposure. Free chloride content is also found to increase with an increase in added chloride at the time of mixing concrete. Interestingly at 0% added chloride, the outdoor exposure has shown 80 ppm free chloride per year whereas it is 200 ppm per year under indoor exposure. Obviously the concentration gradient is the lowest under outdoor exposure. Considerable chloride diffusion has occurred under immersion condition. Compared to the freshwater chloride diffusion rate this is accelerated by four to five times under seawater immersion,

clearly establishing the role of the chloride concentration gradient.

Rich mix concrete

It can be seen from Table 3B that in the case of rich mix concrete also, exposure conditions as well as initially added chloride have significant influence on free chloride content (ppm year^{-1}). It is the highest in the case of seawater immersion and the lowest in the case of outdoor exposure. However compared to lean mix concrete, the (ppm year^{-1}) values are generally on the higher side excepting for seawater immersion. It is to be pointed out here that because of the higher cement content initially added chloride in rich mix concrete is nearly twice that added in the corresponding lean mix concrete. Compared to outdoor exposure, indoor exposure has shown significant increase in chloride diffusion rate. Similar trend has also been observed in the case of the lean mix.

Visual observation data

Lean mix concrete

Table 4 shows that under seawater immersion and outdoor exposure condition 100% of area has shown rusting. Under indoor exposure, percent area rusted is 75% at 0% added chloride and the same becomes 100% at 1% added chloride and above. The most interesting data is with regard to potable water immersion. At 0% added chloride, only 5% of area is affected where as at 3.5% NaCl, it is 80%. There is a gradual increase in the percentage area of rusting as the initially added chloride is gradually increased.

Rich mix concrete

It can be seen from Table 5, that under immersion either in seawater or freshwater no rusting was observed. Even under indoor and outdoor exposure conditions no rusting was observed up to 0.5% added NaCl. At 1% added chloride, 50–70% of the area rusted and at 3.5% added chloride, 80–95% of the area rusted. Therefore 0.5% added chloride corresponding to 550 ppm by weight of concrete can be considered as the threshold limit.

Weight loss data

Lean mix concrete

From Table 4, it can be seen that the corrosion rate is at a maximum when immersed in seawater. Equally high corrosion rates were obtained in freshwater. When compared to immersion conditions, corrosion rates are lower under atmospheric exposure. In all of the cases, the corrosion rates are found to increase with an increase in initially added chloride content. At higher added chloride contents, the corrosion rate in seawater is more than twice that obtained in potable water.

Rich mix concrete

Table 5 clearly indicates that in rich mix concrete, corrosion occurs only under atmospheric exposure condition that too only when the initially added chloride is 1% and above. Compared to the lean mix, the corrosion rate is lower.

Cl/OH ratio and corrosion

Table 6 compares the behaviour of lean mix and rich mix concretes. In the case of lean mix concrete, corrosion has been observed under a wide range of ratios, that is, from a very low ratio of 0.15 to a very high ratio of 8.18. On the other hand in a rich mix concrete, corrosion has not been observed even at a Cl/OH ratio as high as 9.24 when immersed in seawater. However, a similar rich mix concrete rusted under atmospheric exposure conditions, at Cl/OH ratios ranging from 0.98 to 2.89.

Cl/OH ratio and corrosion rate

Corrosion rate of steel embedded in lean mix concrete has been plotted against the Cl^{-}/OH^{-} ratio in Fig. 2. Excepting for immersion in seawater, under all other conditions, a linear relationship is observed. Outdoor exposure shows the steepest gradient followed by freshwater and indoor exposure. In the case of seawater, the corrosion rate increases steeply, when the Cl/OH ratio exceeds 5.

DISCUSSION

In the present investigation many interesting observations have been recorded. A lean mix

Table 6. Estimated (Cl^-/OH^-) ratio for lean mix and rich mix concretes

Environment	Added chloride equivalent by weight of cement (ppm)	Lean mix concrete		Added chloride equivalent by weight of cement (ppm)	Rich mix concrete	
		(Cl^-/OH^-) ratio	Corrosion yes/no		(Cl^-/OH^-) ratio	Corrosion yes/no
Seawater	0	2.38	Yes	0	6.24	No
	56	5.07	Yes	110	7.28	No
	560	7.42	Yes	1100	8.93	No
	1960	8.18	Yes	3850	9.24	No
Freshwater	0	0.98	Yes	0	1.12	No
	56	1.04	Yes	110	3.29	No
	560	1.40	Yes	1100	4.06	No
	1960	1.96	Yes	3850	4.34	No
Indoor exposure	0	0.37	Yes	0	0.39	No
	56	0.52	Yes	110	0.55	No
	560	1.64	Yes	1100	2.58	No
	1960	2.05	Yes	3850	2.89	No
Outdoor exposure	0	0.15	Yes	0	0.27	No
	56	0.26	Yes	110	0.39	No
	560	0.30	Yes	1100	0.98	No
	1960	0.37	Yes	3850	2.46	No

concrete with a cement content of $138 \, kg \, m^{-3}$ and an aggregate cement ratio of 9 has been studied along with a rich mix concrete with a cement content of $274 \, kg \, m^{-3}$ and aggregate cement ratio of 3.80. By design, the lean mix would be more permeable. It is known that under immersion conditions the solubility and diffusivity of gases such as O_2, CO_2 etc become limited. On the other hand open atmospheric

Fig. 2. Cl^-/OH^- ratio vs corrosion rate of steel embedded in lean mix concrete and exposed to various environments.

exposure facilities diffusion. In the light of thus the results are to be discussed.

Alkalinity

Alkalinity plays an important role in ensuring the passivity of embedded reinforcing steel. A pH value of 12.5–12.6 is normally expected in concrete and this is equivalent to the pH value of the saturated calcium hydroxide solution. The results obtained in this work have shown that under immersion condition, a pH value of > 12 was preserved in both lean and rich mix concretes. This indicates that under moisture saturated conditions calcium oxide from cement reacts with water to form calcium hydroxide and under equilibrium, saturated conditions are maintained. The data pertaining to immersion in seawater also indicates that even a high concentration of chloride is not able to reduce the alkalinity. Even if a leaching action is considered possible in a lean mix concrete then normal alkalinity could still be maintained by the continuous release of calcium hydroxide. Obviously the carbonation effect is negligible.

Even under atmospheric exposure conditions, a rich mix concrete was able to preserve alkalinity. This is attributed to the barrier effect. On the other hand a lean mix concrete has undergone carbonation effect leading to a reduction in pH value. The cement content has its own
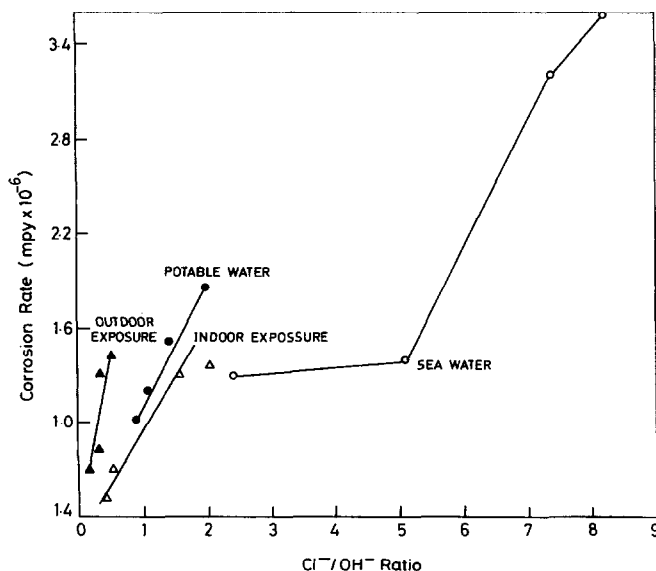
role in this aspect. A lower cement content is not able to provide the continuous reservoir of free lime. Thus a high hydroxyl ion concentration (0.165N–0.128N corresponding to the pH 12.72–12.35) is always maintained in a rich mix concrete. Even a cement content of 274 kg m^{-3} is able to achieve this condition.

Free chloride

Chloride added at the time of mixing of concrete plays an important role. It reacts with calcium aluminate to form calcium chloroaluminate. As more chloride is added initially, more chloro aluminiate is formed. Compared to a lean mix concrete, a rich mix concrete is able to form more chloroaluminate because of the higher cement content. Because of this chloroaluminate formation, initial free chloride content is reduced and in turn helps set up a chloride concentration gradient across the concrete cover.

In view of this, at low added chloride content, chloroaluminate formation is incomplete and a part of the diffusing chloride is involved in chloroaluminate formation. At higher percentages of added chloride, chloroaluminate formation moves towards completion and hence the major part of the diffusing chloride remains as free chloride. According to a modified version of Fick's second law

$$C(x, t) = Co\left(1 - er_f \frac{It}{2Df}\right)$$

where C is the chloride content to the weight of concrete (wt%), t is the time in service (s), x is the distance from the concrete surface (cm), D is the apparent diffusion coefficient (cm^2 s^{-1}), Co is the surface chloride content and er_f is the error function.

The data presented in Table 3, clearly shows that the surface chloride content determines the diffusion rate in addition to the diffusion coefficient which is influenced by the barrier effect of concrete. This is why maximum free chloride contents have been observed under seawater exposure conditions. The minimum free chloride contents observed under outdoor exposure are to be understood in terms of the low surface chloride content.

Combining both the alkalinity and free chloride it can be inferred that under immersion condition, there is a limiting value for alkalinity (pH 12.6) whereas there is no such limitation for free chloride. Hence the Cl/OH ratio can be expected to be very high. Under atmospheric exposure condition, alkalinity may be reduced due to carbonation while the free chloride content may also be on the lower side due to low surface chloride content. Hence Cl/OH ratio can be either low or moderate.

Cl/OH ratio and corrosion rate

In the case of rich mix concrete, corrosion was not observed even at very high Cl/OH ratios. This indicates that something other than the Cl/OH ratio is influencing corrosion. In the case of lean mix concrete, the corrosion rate is found to have a linear relationship with the Cl/OH ratio. This shows that oxygen diffusion is the rate controlling step. In the absence of oxygen or in the case of limited supply of oxygen, cathodic reaction

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-$$
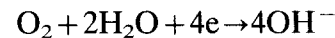
is suppressed. Hence there is no corrosion or low corrosion.

In the presence of oxygen, the cathodic reaction is not suppressed. In this case the Cl/OH ratio controls the corrosion rate. It has already been reported that the threshold limit for chloride depends on the alkalinity and as pH value decreases, the threshold limit drastically decreases. Once the threshold limit is exceeded, chloride ions act as a catalyst for the corrosion reaction as mentioned earlier.

$$Fe + 2Cl^- \rightarrow FeCl_2$$

$$6FeCl_2 + O_2 + 6H_2O \rightarrow 2Fe_3O_4 + 12H^+ + 12Cl^-$$
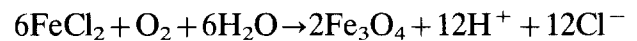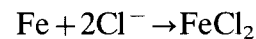
The released chloride ions are again available for FeCl$_2$ conversion. Thus the reaction is self perpetuating.

CONCLUSIONS

1. The Cl$^-$/OH$^-$ ratio alone is not the appropriate index for rebar corrosion under all exposure conditions. Other parameters such as initial chloride content and oxygen diffusion play significant roles.

2. In a rich mix concrete with a cement content of $274 \, kg \, m^{-3}$ and an aggregate/cement ratio of 3.8 corrosion is possible only under atmospheric exposure conditions when the initial chloride content is of the order of 1000 ppm by weight of the concrete.

3. In a lean mix concrete with a cement content of $138 \, kg \, m^{-3}$ and aggregate cement ratio of 9, the corrosion rate is found to have a linear relationship with the Cl^-/OH^- ratio.

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