

MECHANISM OF CORROSION AND PROTECTION IN REINFORCED CONCRETE STRUCTURES AND SERVICE LIFE - A REVIEW

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ABSTRACT. Reinforced concrete structures show good durability as they are capable of withstanding different environmental exposures. The major limitation of concrete, however is penetration of air, moisture and chloride causing corrosion. Corrosion of reinforcement is the greatest cause of durability failure. Corrosion is an electrochemical process whereby a metal undergoes a reaction with chemical species in the environment. Sometimes due to inadequate design, poor quality of construction and due to adverse environment conditions, the concrete structures do not remain durable. Consequently, many structures in the built environment suffer from corrosion induced damage. This paper explains the factors behind the mechanism of corrosion of steel embedded in concrete. This results in the deformation due to corrosion which leads to initiation of damage and further results in cracks during propagation phase. This paper also explains the changes by corrosion induced deterioration of concrete structures. We have also made efforts to explain the preventive measures for minimizing the cracks and explaining the corrosion management techniques. Corrosion of concrete can be reduced by proper monetary efforts at proper time intervals leading to safer structures with more service life.

Keywords: Corrosion, concrete, reinforcement bars, chloride, carbonation.

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INTRODUCTION

Reinforcement concrete is one of the most durable, versatile and widely used construction material. It can be molded into variety of shape and finishes. It is used more than any other man-made material. Sometimes due to inadequate specifications, poor quality construction and sometimes due to adverse environment conditions, the concrete doesn't remain durable and strong. Consequently, many structures in the built environment suffer from corrosion induced damage.

Corrosion of reinforcement is the greatest cause of durability failure. Corrosion is an electro chemical process whereby a metal undergoes a reaction with chemical species in the environment to form a compound. Steel reinforcement in a natural tendency to corrode if access to oxygen is possible in a moist environment. Depending upon the environmental conditions and metal properties, the rate of corrosion can vary. Corrosion can occur when the passive level protecting steel is lost. With the passage of time, old concrete structures show sign of deterioration due to environment condition which lead to physical and chemical deterioration of concrete. Determination process may include physical or chemical process or a combination of both. The corrosion would result in the reduction in effective cross section area of rebars and this may lead to significant decrease in load carrying capacity. Consequently, rebar corrosion causes a significant threat to serviceability and operation of structures.

Two main reasons are associated with this integration of the oxide layer.

1. A process called as carbonation due to ingress of CO₂ from atmosphere into concrete leads to reduction in pH of the pore solution. At low pH (less than 9), the oxide layer becomes unstable and then disintegrate.
2. Chloride ions from external source or internal source reach the steel and react with hydrogen ions forming sufficient quantity of acid. To neutralize the alkalinity of concrete and thus promote breaking down of protective layer.

The damage to the structure is manifested by reduced cross section area of reinforcement and the load carrying is reduced and due to corrosion, there would be volume expansion and the structure may exhibit cracking and spalling.

Factors influencing the rate of corrosion

- The moisture content of the concrete exposed by means of Relative Humidity in the pore system.
- The temperature around the corrosion area.
- The porosity of the concrete.
- The thickness of the concrete cover.
- The average loss of strength, load capacity due to deterioration of concrete.

Mechanism of corrosion of steel embedded in concrete

The corrosion of steel in concrete is an electro chemical process. The electro chemical potential to form the corrosion cells may be generated due to formation of composition cells. When the similar metals are embedded in concrete in the vicinity of reinforcing steel consultation of dissolved ions. Corrosion of steel in concrete is a 3-step process.

Corrosion of steel in concrete is a three-step process:

- Depolarization reagent arrives at the surface of metal through the mediums surrounding it.
- Electrochemical reactions occur at the interface between the metal and the surrounding medium.
- Corrosion products are accumulated at the surface of the metal.

It is observed that a durable concrete with rebar the metal remains passivated owing to the higher pH (over 12.5) of the pore solution in concrete. It is, known that ingress of carbonation and chloride ingress destroys the corrosion inhibitive properties and will de-passivate steel in lime water at pH (=12.5). The penetration by the chloride ions to the reinforcing bar in concrete bars takes place within a small fraction of service life.



Deterioration due to corrosion

Figure 1 Deterioration resulting from corrosion.

Initiation Phase

During the initiation phase aggressive substances that can de-passivate the steel penetrate the steel from the surface into the bulk of the concrete. The duration of the initiation phase depends on the cover depth and the penetration rate of the aggressive agents depends on the quality of the concrete cover and on the microclimatic conditions at the concrete surface.

Propagation phase



Cracks formation

Figure 2 Cracks Formation

Table 1 Several recent corrosion studies

REFERENCE	STUDY PERFORMED	SIGNIFICANT OBSERVATIONS	COMMENTS
Pour-Ghaz et al., 2009 [7]	Presented a tool for the interpretation of the results of half-cell potential measurement. It relates half-cell potential values to the probability of corrosion through concrete resistivity, cover thickness, temperature and anode to cathode ratio. A model is developed by solving Laplace's equation, relating corrosion current with average potential on the surface, potential difference on the concrete surface, temperature, resistivity, and concrete cover.	In concrete with low resistivity potential distribution on surface represents potential at steel concrete interface. For better results interpretation of potential readings can be done in accordance with resistivity. With the increase in concrete cover difference between surface and interface potential increases.	More realistic results can be obtained by considering availability of oxygen and increasing the test points. More experimental validation of the model is required to increase the confidence.
Song and Saraswathy 2007 [6]	Reviewed several electrochemical and nondestructive testing methods for the assessment of corrosion in concrete structures.	Combining several techniques can provide more information about corrosion state of steel bars. An integrated monitoring system for new and existing concrete structures can reduce inspection cost.	Presented methods are useful to monitor corrosion in concrete structures and all these reviewed methods can be used to develop more accurate and better techniques for monitoring corrosion.
Ahmad, 2003[3]	Reviewed mechanism of corrosion, corrosion monitoring techniques, and methodologies to predict the remaining service life of structures. Observed that corrosion rate is affected by pH of electrolyte, availability of oxygen, capillary water, and concentration of Fe^{2+} in the concrete near the reinforcement.	Information regarding corrosion state required three parameters half-cell potential, concrete resistivity, and corrosion current density.	Presented all the aspects of corrosion, and may be useful for understanding the corrosion theory, progress of corrosion, factors affecting corrosion, monitoring techniques and for predicting service life of structures.
Bjegovic et al., 2000 [2]	Described different corrosion monitoring techniques such as half-cell potential measurement, macrocell current	Nondestructive methods for measuring corrosion are advantageous as measurements can be done over entire	Presented overview of several nondestructive methods with their relative advantages and disadvantages

	measurement, linear polarization method, Geocor 6, electrochemical impedance spectroscopy, Galvanostatic pulse method, and scanning reference electrode method.	structure, provide fast results, and are inexpensive.	based on experiences and interpretation of results. It is a useful study covering almost all the present corrosion measuring techniques.
Carino, 1999 [4]	Presented an overview of corrosion process and nondestructive evaluation techniques such as half-cell potential method, concrete resistivity test, and the linear polarization method.	Corrosion rate in a concrete structure is governed by several parameters such as moisture content, availability of oxygen, and temperature. So, for better results it is necessary to repeat corrosion rate measurement in regular time interval.	A useful review has been presented by considering the behavior of electrolytic cells.
So and Millard, 2007 [8]	Presented Galvanostatic pulse transient technique for evaluating the corrosion rate in reinforced concrete structures and also presented the advantages of this technique over linear polarization (LPR) method.	Corrosion rates calculated from Galvanostatic pulse transient technique are generally higher than those evaluated from LPR technique.	It is a useful study presenting a relatively more reliable technique for measuring corrosion rate in RC structures.
Pradhan and Bhattacharjee, 2009 [9]	Discussed results of a study conducted on concrete specimens with different cement, steel, and varying water/cement ratios. Specimens are subjected to 3% Sodium chloride solution and half-cell potential measurements were carried out to evaluate corrosion activity.	Critical chloride content causing corrosion initiation is influenced by steel type, cement type, and w/c ratio. Found half-cell potential as a parameter indicating rebar corrosion initiation in chloride contaminated concrete.	It has been observed from this study that corrosion initiation time is influenced by the rate of ingress of chloride ions and depassivation of protective passive film.
Hussain and Ishida, 2012 [1]	Performed multivariable laboratory experiments to evaluate effect on oxygen on reinforcement corrosion under different environmental conditions and also explained half-cell potential measurement in different conditions such as submerged exposure condition and under cyclic	It was observed that oxygen is an influencing factor for corrosion only for concretes placed completely under water.	Results of this analysis can be used for calibrating half-cell potential measurements performed under water.

	wetting-drying exposure.		
Cairns and Melville, 2003 [10]	Performed nondestructive electrochemical measurements of corrosion to evaluate effect of protecting coatings on the reliability of these tests.	It has been observed from results that half-cell potential measurements were not affected significantly by coating.	Useful study to evaluate reliability of corrosion monitoring techniques.
Elsener, 2001[11]	Discussed about application and limitations of half-cell potential mapping for assessing reinforced concrete structures to evaluate repair work. Repairs include replacement of chloride contaminated concrete, electrochemical chloride removal, electrochemical realkalization and application of corrosion inhibitors.	For interpretation of half-cell potential readings, it requires precise understanding of corrosion protection mechanisms and good knowledge and experience in half cell potential mapping.	A useful study explaining half-cell potential mapping and effect of corrosion repairing over the results provided by half-cell potential method.
Pratibhan et al. 2006 [12]	Carried out simultaneous potential measurements on different points on concrete slab, using computer based I/O cards and also development software based on ASTM C-876 for interpretation of measured values.	Among the various electrochemical methods potential measurement has been the mostly used field technique for detecting corrosion activity in steel. Manually measuring half-cell potential values is a tedious job on a large structure, so an automatic system to evaluate the half-cell potential values is present.	An automated useful method to evaluate half-cell potential at different points on a large structure simultaneously is present. This method can reduce time required to evaluate potential values at different points for monitoring the corrosion.
Moon and Shin , 2006 [13]	Studied corrosion evaluation of the steel bars embedded in underwater concrete. Performed accelerated corrosion tests on three series of reinforced underwater concrete with different admixtures in different conditions.	It has been observed that specimens casted in seawater develop early corrosion of steel bars. Among all the specimens, in OPC manufactured concrete corrosion rate is fastest and exceeds threshold value earlier than other specimens. Mineral admixtures are more effective in delaying the development of corrosion in	A careful study on antiwashout underwater concrete to evaluate effect of different admixture on corrosion of steel bars.

		underwater concrete.	
Poursae and Hanson, 2009 [14]	Described pitfalls in assessment of chloride induced corrosion through electrochemical methods. Factors influencing the results of electrochemical process are found to make more measurements in short period to reduce the costs, choosing appropriate electrochemical method, and laboratory tests are usually conducted on young and immature concrete.	Results of electrochemical assessment may not represent actual condition of rebars.	Explained the pitfalls in electrochemical assessment of chloride induced corrosion of steel, which can be utilized to regulate the results of measurements.
Soleymani and Ismail, 2004	Performed a study to estimate the corrosion activity of steel bars embedded in two types of concrete specimens, ordinary and high performance, applying different corrosion measurements methods. Methods applied are half-cell potential, linear polarization method, Tafel plot, and other chloride content methods.	Results indicated that all these methods would assess the same level of corrosion in only 24% of specimens.	Presented a useful comparison between different corrosion measurements methods. This study can be used by researchers to select better corrosion monitoring technique.
Ahn and Reddy, 2001 [16]	Performed accelerated corrosion test to evaluate durability of marine concrete structures subjected to fatigue loading with different water cement ratios. Ultimate strength testing followed by half-cell potential measurement and crack investigations has been performed.	Deterioration is faster under fatigue loading than static loading. Durability decreased with increase in water cement ratio.	Presents significant findings about the effect of fatigue loading and water cement ratio over the durability and life of the structures.
Elsener, 2002 [17]	Studied effect of conductivity and cover depth on potential and macrocell current distribution. Also, discussed consequences of monitoring corrosion through half-cell potential mapping and	Low electrolyte conductivity and cover make it possible to locate anode of the macrocell by potential measurements.	Discussed about influence of macrocell corrosion on corrosion monitoring.

	polarization measurement technique on locally corroded bars.		
Alhozaimy et al., 2012 [18]	Performed laboratory experiments to evaluate half-cell potential, corrosion current, and concrete resistivity over chloride contaminated concrete specimens, to investigate the phenomenon of high corrosion at intersection of steel rebars in the wall footing.	Observed that experimental measurements are higher at intersection of steel bars in comparison with the areas between them. This high corrosion rate is found to be due to coupled effects of corrosive binding wire materials, electrical connectivity, reduction in center to center spacing of steel rebars, and poor concrete micro mixtures.	Phenomenon reported in this paper is new and interesting. More and extensive research is required to understand the effect of all factors influencing the corrosion at intersection of steel rebars.
Duong et al., 2013 [19]	Performed half cell potential and corrosion current density test on concrete specimens to monitor corrosion activity. This corrosion activity had been monitored to evaluate the effect of leaching on carbonation and corrosion initiation of steel bars.	Observed that with the increase in leaching exposure carbonation depth also increases. Replacing cement partially with fly ash reduces the resistance against carbonation and leaching.	Presents the performance of half-cell potential measurement and corrosion current density to detect corrosion due to leaching activity. It has been observed that suitable test methods are required.
Sadowski, 2010 [20]	Describes linear polarization and four point Wenner resistivity methods to evaluate corrosion rate without making a direct connection to the reinforcement.	Observed that short circuit influence of embedded steel can be used to evaluate the rate of corrosion on the surface of the bars.	More validation of methods is required on concrete with wider range of resistivity.
Jung et al., 2003 [21]	Half-cell potential and linear polarization measurements have been performed for one year to evaluate the parameters affecting the corrosion rate. Measurements have been made to predict the remaining service life of land concrete affected from steel corrosion.	Quantitative polarization method provides more precise results than those of half-cell potential method in evaluating the corrosion activity.	Comparison between methods helps researchers to select better techniques for evaluating residual service life of structures.
Lai et al., 2013 [22]	Presented a new technique to investigate corrosion of	Results show that both GPR and modified HCP	More researches are required to relate

	steel bars in concrete using ground penetrating radar (GPR) and modified half-cell potential method. Attempted to measure potential difference with two moving probes and making no connection with steel bars.	methods can measure electrochemical corrosion process.	laboratory results with real time structures.
Leelalerkiet et al., 2004 [23]	Performed half-cell potential measurements to estimate corrosion of reinforcing steel bars embedded in concrete slabs under cyclic wet and dry exposures. Influence of void over potential distribution and current distribution has also been investigated.	Observed from results that half-cell potential is marginal successful. In the void specimens half-cell potential values required compensation for more reliable results.	Useful study to demonstrate corrosion estimation in both intact and void specimens.
Faber and Sorensen, 2002 [24]	Discussed the application of half-cell potential measurements to evaluate the probability of corrosion and repair after 50 years. This is explained on a corroded concrete structure.	It has been observed that half-cell potential measurements may be utilized to update the probability of corrosion.	Provided a study on the utilization of half-cell potential method.
Hussain, 2011 [25]	Investigated underwater half-cell corrosion potential in submerged RC structures and compares with various other relative humidity conditions.	Half-cell potential values for submerged underwater RC structures are not representing actual corrosion rate and these values are required to be calibrated using the experimental results of this research.	This study enables researches to perform underwater corrosion measurement for evaluating condition of submerged RC structures.

Once the layer is passive destroyed, corrosion will occur in presence of oxygen and water on the surface of the reinforcement. Carbonation of concrete leads to complete dissolution of the protective layer on the whole surface of steel in contact with carbonated concrete. Corrosion induced by chloride in localized, with penetrating attack of limited area surrounded by non-corroded areas. This results in pitting corrosion. Only when high levels of chlorides are present the passive film may get destroyed over wide areas of reinforcement and the corrosion will be of a general nature.

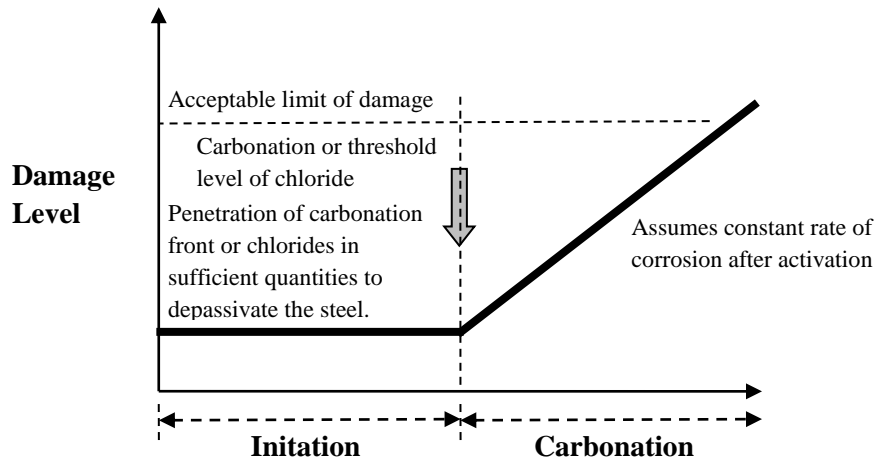


Figure 3 Stages of corrosion induced deterioration of a concrete structure (Mathew 2014)

ELECTROCHEMICAL PROCESS

Due to porous nature of concrete, oxygen diffuse into concrete, becoming dissolved in the pore solution and finally reaching surface of the steel. In presence of moisture and oxygen, anodic and cathodic regions are formed due to the difference in electrochemical potential on the surface, connected by electrolyte in the form of the salt solution in the hydrated cement. The positively charged ferrous ions Fe^{2+} at the anode pass into solution while the negatively charged free electrons pass along the steel into the cathode where they are absorbed by the constituents of the electrolyte and combine with water and oxygen to form hydroxyl ions.

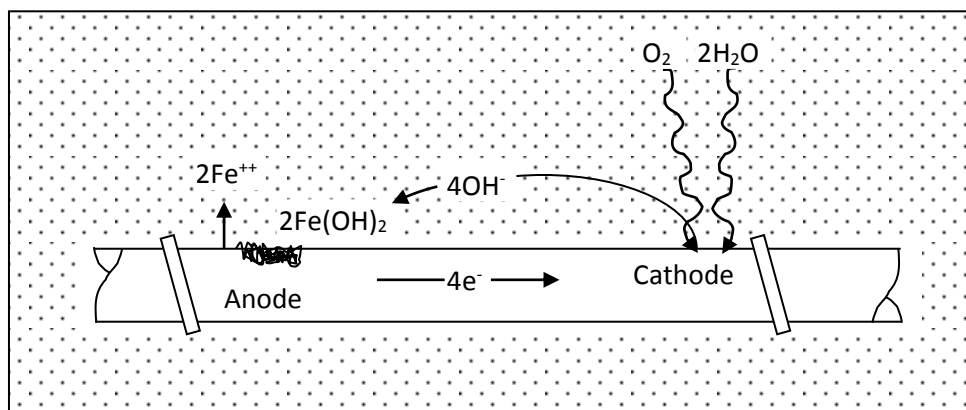
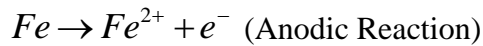
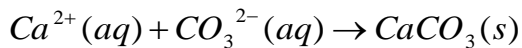
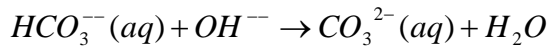
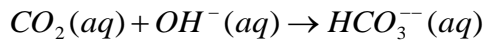
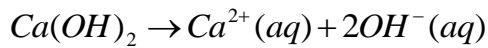
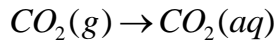


Figure 4 Mixed electrode in reinforced concrete

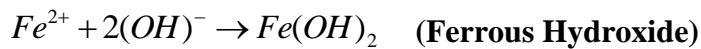
CORROSION MECHANISM IN CARBONATED CONCRETE

The carbonation of concrete is a complex physiochemical process. The carbon dioxide diffuses from atmosphere into capillary pores of concrete. The hardened concrete always has water present in pores in larger or smaller quantities which plays a key role in process of

carbonation. Carbon dioxide dissolves in pore water forming carbonic acid which reacts with alkali solutes available in pore solution from dissolution of solid matrix. The dissolved CO₂ reacts with cement. The reaction of carbon dioxide with calcium hydroxide predominates as concentration of it is usually higher as compared to other hydration products. The carbonation reaction can be described by following chemical reactions:



Apart from hydroxide the other hydration products which are present in concrete also gets eventually carbonated. Because of carbonation the pH of concrete reduces, at such low pH the passive film protecting reinforcement gets destroyed. The exposed reinforced surface gets oxidized and form ferrous ions. The ferrous ions pass into solution. The electrons flow through the reinforcement to the cathodic region and produces hydroxyl ions. The hydroxyl ions move from the cathodic site through the moist concrete, towards the anodic site where ferrous hydroxide is formed.



The ferrous hydroxide formed is unstable in the presence of oxygen and gets oxidized to ferric hydroxide.

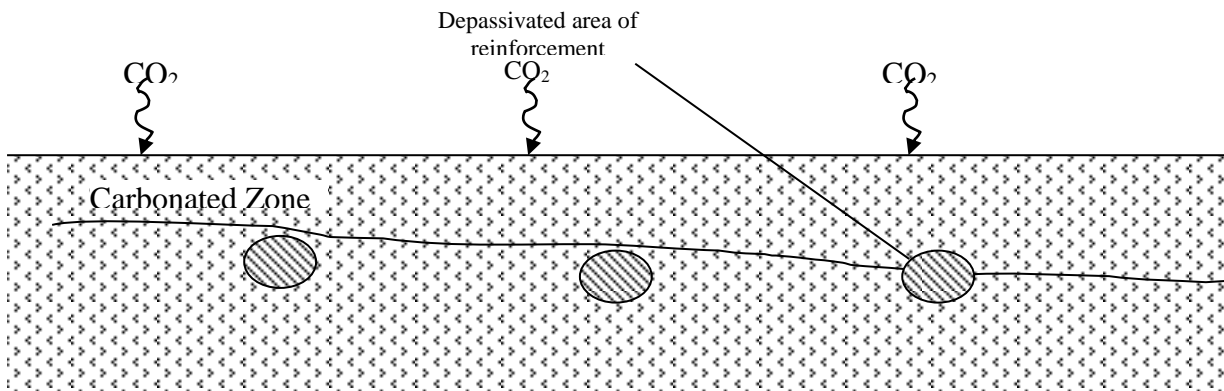
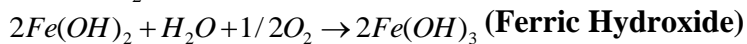
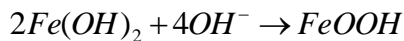


Figure 5 Ingress of the carbonated zone to the reinforcement (Richardson 2002)

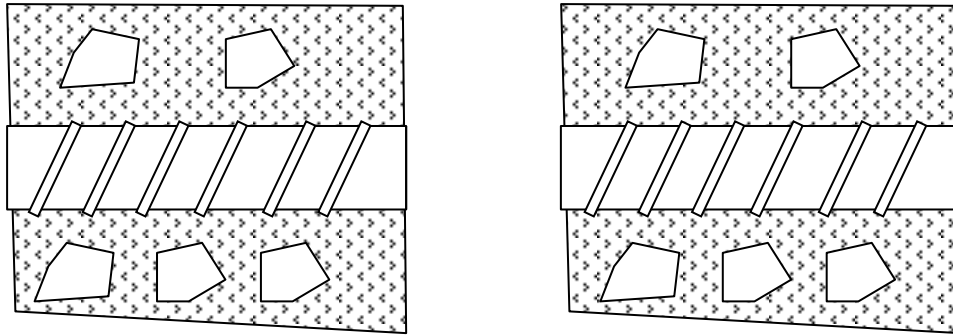


Figure 6 Diagrammatic view of steel carbonated from carbonation induced in partially carbonated concrete and view of steel corroding in carbonated concrete

Further advances of the carbonation front will increase the de-passivated area. Widespread corrosion may then follow with the development of cracking along the lines of the reinforcement.

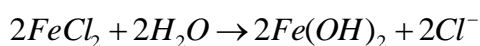
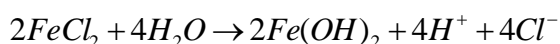
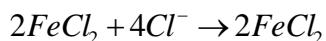
The ability of concrete to carbonate is strongly dependent on the porosity, the amount of carbon table material present in the concrete and relative humidity.

CORROSION MECHANISM IN CHLORIDE-RICH CONCRETE

The presence of oxygen and sufficient quantities of free chloride ions in the pore water of concrete can produce reinforcement corrosion even in highly alkaline environment. Chlorides may be present in the components used to make the concrete at the time of casting or enter the concrete from the environment after placing. Chloride ingress is due to either diffusion, taking place in totally or partially water filled pores, or capillary suction of water containing chloride. The passive film is rendered ineffective in circumstances where the chloride level in the surrounding concrete exceeds a critical level. A low level of chloride can be present and tolerated in concrete. Chloride induced corrosion is focused on a small area, which forms a pit surrounded by uncorroded concrete. This can lead loss of cross section and critically reduce the load bearing capacity of the reinforced concrete member. The anodic reaction is of particular interest in the case of concrete subject to high chloride levels. During the corrosion cycle ferrous ions become available to combine with the chloride ions to form compounds such as ferrous chloride.



The process then becomes self-propagating due to acidic conditions created. Hydrolysis of these products over time releases chloride ions with a consequent reduction in the anode pH. The increase acidity also encourages further oxidation of the iron.



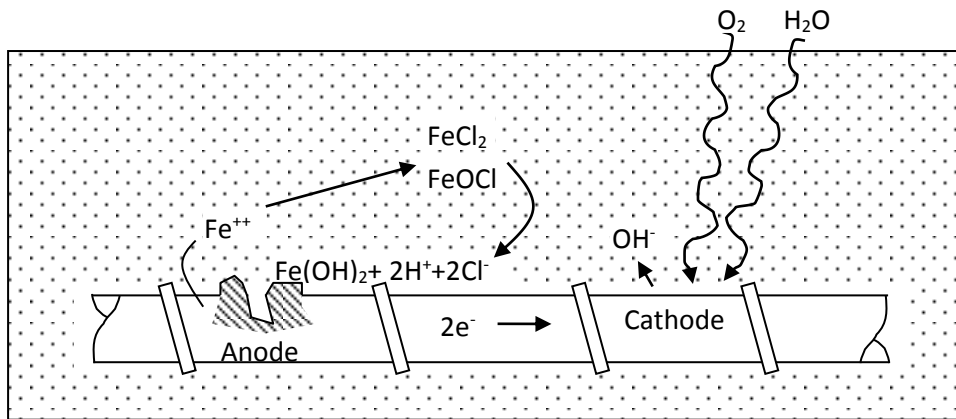


Figure 7 Process of pitting corrosion in a chloride rich environment (Mathews 2014)

An influencing parameter is the chloride and hydroxyl ion ratio at the reinforcement. If the chloride ions predominate the loss of ferrous ions is accelerated. If the hydroxyl ions predominate precipitation of Fe(OH)_2 ions help to repair the reinforcement's passive oxide film [Richardson].

Chlorides may be present in the three states: free chloride ions in the pore solution, chlorides strongly bound, and chlorides loosely bound. The free chlorides are the most significant contributors to the corrosion risk. The aluminates are able to combine with internally or externally introduced up to a certain concentration of chloride and prevent them remaining as dangerous free chlorides. However, the lowering of pH by carbonation releases some of these bound chloride's ions into the pore solution.

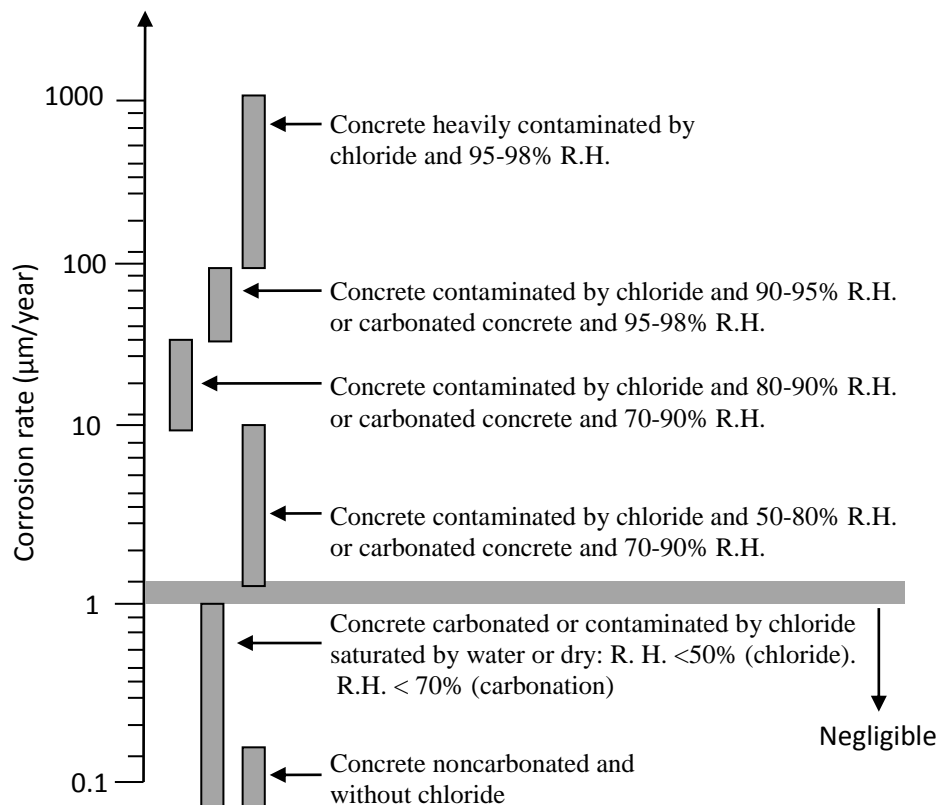


Figure 8 Schematic representation of corrosion rate of steel in different concrete and exposure condition (Bertolini et al. 2013)

The Fe^{2+} formed in the pore solution tends to move away from the steel surface, resulting in reduction of cross section of reinforcement. Such attack can be easily found by the visible rust stain on concrete surface. At times, corrosion of steel proceeds at a very high rate giving less time for the corrosion products to move out of the corrosion site, but accumulate on the steel surface as a rust layer. The volume of the corrosion rust is usually 2-6 times greater than the volume of the metal consumed by corrosion reaction. This will reduce expansive stress at the interface between steel and surrounding concrete. When the expansion stress exceeds the tensile strength of the cover concrete, eventually leading to spalling of concrete. This is the main course of damage of reinforced concrete associated with most damaged structures.

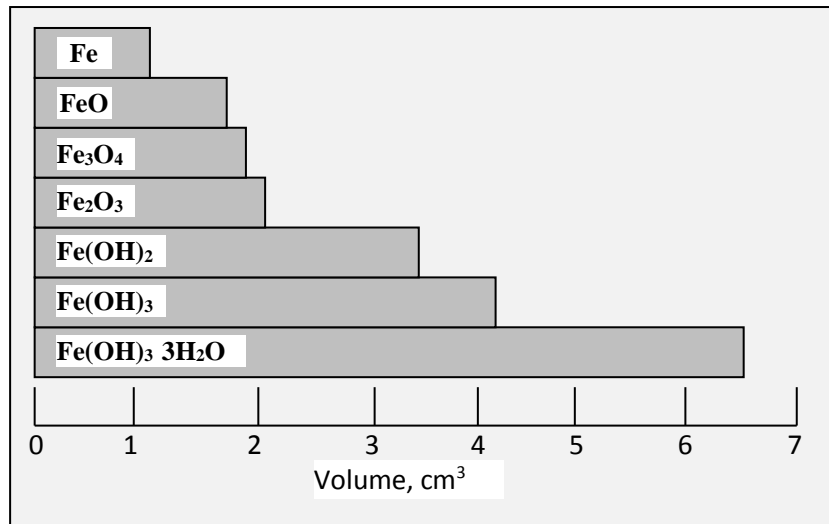


Figure 9 Volume of different compounds in cement produced during corrosion (Metha 2006)

FACTORS AFFECTING CORROSION OF STEEL IN CONCRETE

The corrosion behavior of reinforcement steel in concrete is a function of parameters of steel and concrete as well as the properties of their interfacial zone, i.e., it is determined by the composition of the pore solution of the concrete and chemical properties of the steel. Environmental factors cannot affect corrosion process directly, but they cause the deterioration of the cover concrete and accelerate the ingress of aggressive species, making the pore solution in contact with steel more corrosive. Different factors affecting corrosion rate of steel in concrete is described below:

- Components of Concrete
- Moisture
- Electrode Potential
- Influence of oxygen supply
- Temperature

Prevention

- Keep concrete dry, so that there is no moisture to form rust. If concretes wet, there would be no oxygen to form rust.

- Epoxy coating to rebar to protect from moisture and aggressive agents. The embedded epoxy coating on steel bars provide a certain degree of protection to steel rebars and thereby, delay the initiation of corrosion. The coatings prevent movement of moisture to the steel surface but would resist oxygen penetration.
- Stainless steel could be used in lieu of conventional reinforcement.
- Use of fly ash concrete with low permeability would delay the arrival of carbonation and chlorides at the level of rebar. They would form Calcium Silica Hydrates (CSH) compound that over time effectively reduce concrete diffusivity to Oxygen, Carbon Dioxide, Water and Chloride ions.
- Electro chemical injection of organic base corrosion inhibitors into Carbonated Concrete
- Physical properties of Durable Concrete would improve the extent of Carbonation decline
- Installation of physical barrier system such as coatings, sealers, membrane, etc.
- The Zinc surface layer applied either hot dipped or electro deposits would result on low corrosion rate for Zinc, thereby providing Galvanic Cathode Protection
- Concrete mix design modification involves such as reduced water-cement ratio including use of water reducing admixtures of super plasticizers, type of cement, permeability reducing admixtures such as silica fume, corrosion inhibiting admixtures

CONCLUSION

With the use of modeling software evaluation reports, it would be possible to select from the best of several alternative protection, repair and rehabilitation techniques. Cathodic protection would prevent corrosion of steel reinforcement by either deployed sacrificial corrosion nodes or sending a current through rebars. Sealers, membranes, organic inhibitors and admixtures from either internal or external barriers that prevent chlorides from coming into contact with steel. Patching and overlay methods can be used to repair damage and increase the cover depth, thereby reducing the time to corrosion initiation. Chloride extraction is an electro chemical process that would provide short term protection against corrosion. By corrosion management techniques and timely decision could be efficient and effective in the use of public resources, leading to safer structure inventory throughout the country.

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