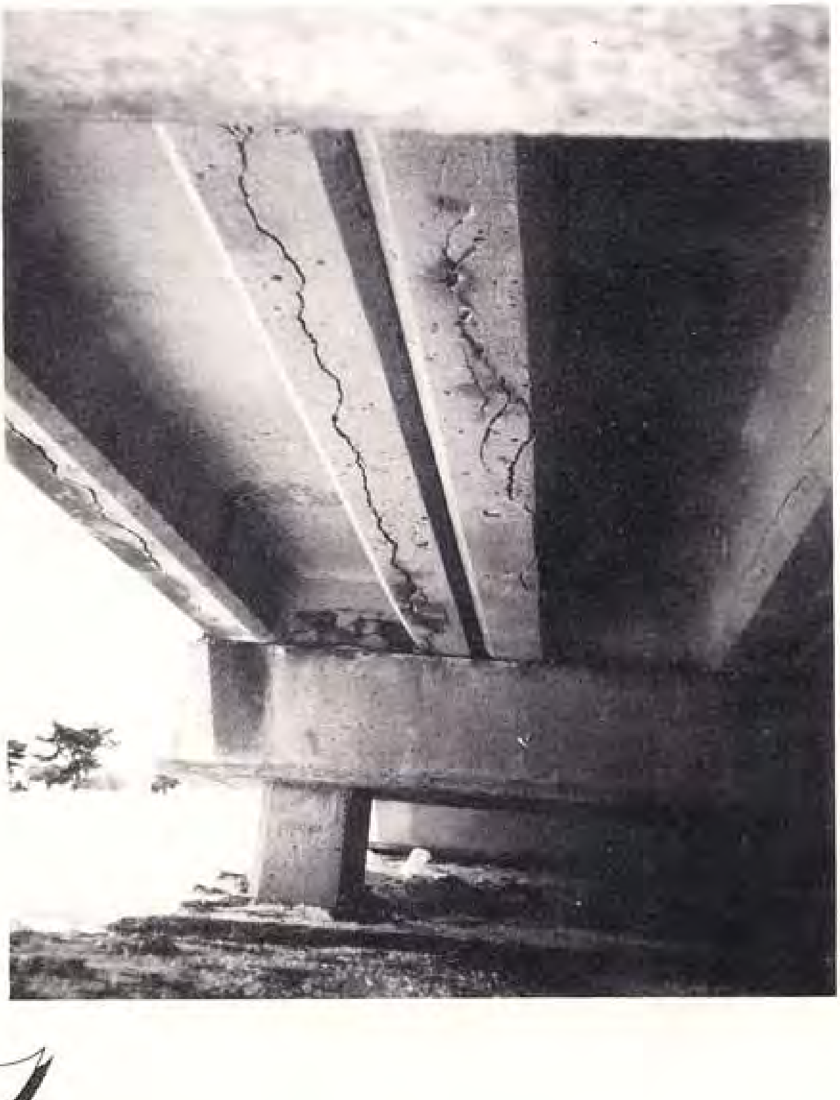
Corrosion of steel in concrete: causes, detection and prediction

State-of-the-art Review

Guangling Song
Ahmad Shayan



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ABSTRACT: Corrosion of steel in concrete is a world wide problem. It is causing billions of dollars of loss through repair and maintenance needed to keep the facilities functional. The potential risks of corrosion in a structure are quite unpredictable. How to monitor, predict, prevent, and rehabilitate the corrosion damage of steel in concrete structures has become a vast area of research interest. A great deal of research work has been done on these aspects, and particularly in the past decade, much progress has been made in the field of monitoring and prevention.

This document is the first of two reports prepared by ARRB Transport Research, dealing with important aspects of corrosion of steel in concrete structures. In this report, achievements in the area of measurement and prediction of corrosion of steel in concrete, as well as the factors affecting the corrosion behaviour of steel reinforcement are summarised. Based on the state of the art review, some suggestions for further work are also presented.

It is hoped that this document will be of help to asset owners and engineers in understanding the underlying causes of corrosion, techniques of assessment and monitoring, and methods of rehabilitation of the damaged structures.

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Main areas of interest:

- Corrosion of metals in various environments
- Corrosion protection engineering
- Electrochemical measurement/ monitoring and corrosion survey

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Review Report 4

Corrosion of steel in concrete: causes, detection and prediction:
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Executive Summary

Corrosion of steel in concrete is a world wide problem. It is causing billions of dollars of loss through repair and maintenance needed to keep the facilities functional. The potential risks of corrosion in a structure are quite unpredictable. How to monitor, predict, prevent, and rehabilitate the corrosion damage of steel in concrete structures has become a vast area of research interest. A great deal of research work has been done on these aspects, and particularly in the past decade, much progress has been made in the field of monitoring and prevention.

This document is the first of two reports by ARRB Transport Research, dealing with important aspects of corrosion of steel in concrete structures. In this report, achievements in the area of measurement and prediction of corrosion of steel in concrete, as well as the factors affecting the corrosion behaviour of steel reinforcement are summarised. Based on the state of the art review, some suggestions for further work are also presented.

The second report (subject to funding) will deal with prevention and rehabilitation of corrosion damage in reinforced concrete structures. It is hoped that these two documents will provide the most up to date collection of information in the field, and will be of help to asset owners and engineers in understanding the underlying causes of corrosion, techniques of assessment and monitoring, and methods of rehabilitation of the damaged structures.

1. Introduction

Corrosion is a thermodynamically spontaneous and unavoidable reaction of metals which is adverse to the metallurgical process of the production of metals from raw ores. Most metals, especially steels which are iron based, are very likely to suffer from corrosion. Depending on the environmental medium and steel properties, the corrosion rate of steel can change widely. The corrosion of steels can only be delayed or slowed down by special measures (i.e. preventive/protective methods). It can never be "stopped" in a natural environment without any protection.

For reinforced concrete structures, because of the high alkalinity of the pore solution in the concrete, and the barrier provided by the cover concrete against the aggressive species from outside environment, the reinforcement has been believed to be "non-corrodable", i.e. the corrosion rate of the steel reinforcement has been believed to be too slow to be of concern. However, with passage of time, some cover concretes would not be able to provide good protection to the reinforcement due to the degradation of concrete and the ingress of corrosive species from environment. Thousands of prematurely damaged concrete structures have been found to be associated with the corrosion of reinforcement. It has been recognised that the concrete can not always be a non-corrosive medium to protect steel from corroding.

Concrete is a very versatile material with its own special properties. It provides a specific environment for the steel inside. Corrosion of steel in such a medium would certainly involve particular processes different from those in other natural environments, such as, sea water, soil, and atmosphere, etc. Many issues pertaining to the corrosion of steel in such a medium are unsolved or still unfamiliar to corrosion scientists and engineers, and need to be investigated. Also because concrete is quite different from the traditional aqueous corrosion media, some theories and techniques used in the traditional corrosion field may not be directly applicable in the corrosion of reinforced concrete.

Reinforced concrete structures are usually very large. Different parts of a structure could be exposed to different environments, so the same steel rebar in a structure may be subjected to different types of corrosion attacks and various extents of corrosion damage.

Even worse, the corrosion processes are closely related to concrete and environment factors. Sometimes the interaction among these factors are very strong, and any change in a factor might cause the changes of all the other factors, and consequently changing the corrosion behaviour of steel in concrete structure. For example, the moisture content in the concrete depends not only on the relative humidity of the atmosphere but also upon the temperature cycling during day and night [*Andrade (1997)*]. Also variation of temperature has multiple simultaneous effects on different parameters which may counter-balance each other. The oxygen content and the pH value of pore solution decrease and the concentration of chloride ion increases when temperature rises. These indicate that in practice the influences from the environment are complicated. Particular caution should be taken when we are considering the factors that can affect corrosion of steel in concrete. Particularly, the interaction among those factors needs to be extensively investigated and carefully analysed.

Certainly, the lack of appropriate techniques to study and monitor the corrosion processes of the steel in such a complicated concrete medium also makes this research area more difficult.

However the need for understanding corrosion of reinforcement in existing, projected, and under construction concrete structures, have accelerated the studies in the field of corrosion of reinforced concrete. The knowledge developed in the past decades has led to improvements in the protection of reinforcement and rehabilitation of damaged structures.

The purpose of this state-of-the-art review is to collect and summarise the latest knowledge on various aspects of corrosion of steel reinforcement, and to provide a guidance for research in the fundamental and applied aspects of corrosion in concrete structures. This is particularly necessary to an authority or an organisation who is responsible for state-wide assets of reinforced concrete structures.

The current review consists of two parts in which we will try to cover the most important issues in the field of corrosion of steel in concrete. The emphasis in this part will be mainly put on the measurement and the prediction of corrosion damage of steel in concrete. A subsequent review (subject to funding) will cover the prevention of corrosion and the rehabilitation of corroded concrete structures. We hope the review will lead to wide application of some well-developed knowledge and to better solutions of some practical problems.

2. Damage Caused By Corrosion Of Steel in Concrete Structures

Corrosion of steel in concrete is a serious problem in the world today. According to the conservative estimates, in the developed countries one-half of highway bridges are deteriorating due to the corrosion of reinforcement, and billions of dollars are required to repair or rehabilitate the damaged structures. Table 1 lists some cases of damage associated with corrosion of steel in concrete as well as the economic loss caused by the damage.

Table 1. Damage and economic loss associated with corrosion of steel in concrete

Event	Damage	Economic Loss	Reference
Estimate in USA	corrosion damage of highway bridges	\$90~150 billion	*Federal Highway Administraton*[(1991)]
Estimate in USA	annual cost of repairs of bridge deck, substructures and car parks	\$200~\$450 million	*Transportation Research Board (1991)*
Estimate in UK	corrosion damage of motorway and trunk road bridges in England and Wales	GBP616.5 million	*Wallband (1989)*
estimate in UK	annual cost of repairs to concrete structures	GBP500 million	*Rosenberg (1989)*
Collapse of the Berlin Congress hall	Collapse		*Isecke (1982)*
Collapse of multistory parking structure in Minnesota	Collapse		*Heidersbach (1986)*
Collapse of post-tensioned concrete bridge in Wales	collapse		*Woodward (1988)*
Slab spalled off a bridge in New York	one man killed		*Broomfield (1997)*

In Australia, the road network includes in excess of 8000 concrete bridges and in excess of 16000 culverts managed by the State Road Authorities (SRAs). The value of the bridges alone is in excess of \$8.5 billion. Many of these structures are exposed to aggressive environments, and a significant number of these bridges are in the coastal areas and potentially subjected to corrosion attack. The cost of repairs is a considerable part of the annual budget of the SRAs.

In addition to the direct economic losses, the consequence of corrosion, for example, in the bridges, channels, gas/oil pipelines, or high rise buildings, could be far beyond the economic loss.

If corrosion of reinforcement could be understood, detected and monitored, and suitable measures could be taken to prevent, or even only to delay the corrosion damage, then greater amounts of labour and money could be saved in repair and rehabilitation, and potentially serious accidents could be avoided. This is of great significance for authorities or organisations who are responsible for managing reinforced concrete structures.

3. Corrosion Processes of Steel in Concrete

It was previously believed that the cover concrete could protect the embedded steel reinforcement from corrosion, and as a consequence, reinforced concrete structures were considered to be highly resistant to corrosion. However, practically, reinforced concrete structures usually do not perform so well, and their service lives are sometimes much shorter than what they were designed for. The steel in concrete is always prone to corrosion attack, and a reasonable explanation for the premature damage to the reinforced concrete structure is that the cover concrete is not free of defects.

3.1 Microstructural Defects in Concrete

Concrete acts as a special medium for corrosion reactions, and plays an important role in the corrosion processes of the steel in concrete. Particularly, some defects in concrete provide the essential causes for the initiation of corrosion of steel in concrete. Even though a full discussion of such defects is beyond the scope of the review, a brief account of some types of the defects related to corrosion processes is necessary to the understanding of corrosion of steel in concrete.

Firstly, micro-cracking is one of the most important defects in concrete that would be responsible for serious corrosion attack of steel in concrete, greatly shortening the service life of reinforced concrete structures. The cracking in concrete usually provides a short-cut for the ingress of corrosive species from environment into the concrete. The aggressive species could change the chemical properties of concrete seating a more aggressive environment in the vicinity of the reinforcement. Cracks in concrete could be formed by various mechanisms. They could be produced due to bleeding effects, rapid drying of exposed surface of wet concrete, temperature difference in the core and surface of a freshly cast concrete element, shrinkage of hardened concrete, freeze/thaw cycles and external seasonal temperature variation, etc.

Secondly, the porous nature of conventional concrete means that the corrosion of steel is unavoidable in concrete. To some extent, the pores in concrete have a similar effect as the cracks. Through the pores, detrimental species can penetrate into the cover concrete, making the concrete pore solution more corrosive to the reinforcement, and finally initiating the corrosion of the reinforcement. The penetration of detrimental species through the pores is relatively slow compared with those via cracks, but sooner or later, this will lead to the corrosion of steel rebars and damage to the reinforced concrete structure. Normally, a hardened concrete contains different sizes of pores. The pores can exist in and between the hydrated, gel-like phase (largely calcium silicate hydrate, CSH). The pore space includes gel pores and capillaries as well as at the interface between the cement paste and aggregates. Some pores are connected, while some are not. Some are relatively large which would allow the flow of solutions, and some are so fine that only a very small amount of moisture could be absorbed on their surface. All these pores could play important roles in the corrosion of reinforcement.

Lastly, the heterogeneity of concrete further accelerates the corrosion of steel in concrete. It can directly lead to different electrochemical activities of steel in different sections in a concrete structure, resulting in non-uniform corrosion, an even worse corrosion damage of steel than the uniform corrosion. Unfortunately, the heterogeneity is unavoidable in field structures. At a micro-scale, the non-uniform distribution of pores, aggregates and micro-cracks in concrete can give rise to the differences in electrochemistry, and consequently generate micro galvanic corrosion cells on steel reinforcement. At a macro scale, spallings and delaminations in structures, repairs at damaged sites, and exposures of different parts of a large concrete element to different environments, can initiate macro galvanic corrosion cells and lead to serious corrosion damage in concrete structures.

If a reinforced concrete structure was free of the defects, then corrosion of reinforcement would not be a problem today. Unfortunately, concrete structures always contain defects which would directly or indirectly initiate or accelerate corrosion of the steel rebars. Because of the defects present in concrete, the occurrence of corrosion of steel in concrete is only a matter of time.

3.2 Basic Corrosion Processes of Steel in Concrete

Generally, corrosion of metal in any environment consists of the following basic processes:

1) Depolarisation reagent arrives at the surface of metal through the medium surrounding it. Commonly the depolarisation reagent is oxygen dissolved in the medium or proton (H^+) naturally existing in the aqueous medium.
2) Electrochemical (anodic and cathodic) reactions occur at the interface between the metal and the surrounding medium, i.e. most probably, the oxidisation of metal and the reduction of O_2 or H^+.
3) Reaction products (corrosion products) are accumulated at the surface of metal or removed away from the surface into the medium. For example, passive film or iron rust is formed at the surface of metal; or generated hydrogen gas, OH^- and Fe^{2+} during the corrosion process move away from the surface of metal into solution.

It should be borne in mind that these three basic processes are essential for any corrosion of metal. The absence or stopping of any one of the processes will end the progress of corrosion.

For steel in concrete, the above basic processes are illustrated in Figure 1 [*Broomfield (1997), Blankvoll (1997)*]. Due to the porosity of concrete, O_2 can easily diffuse into concrete, becoming dissolved in the pore solution and finally reaching the surface of steel. At the surface (cathodic area C), oxygen is reduced into hydroxide ion via an electrochemical cathodic reaction:

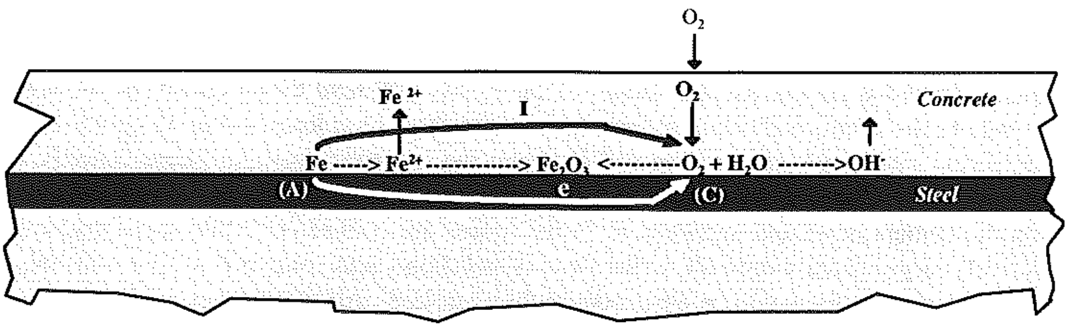

Figure 1. Schematic representation of basic processes of corrosion of steel in concrete

$$O_2 + 2H_2O + 4e = 4OH^- \tag{1}$$

This is a very common cathodic reaction associated with most corrosion of steel in concrete.

However, in some special cases, the cathodic reaction may be in the form of hydrogen evolution:

$$2H_2O + 2e = H_2 + 2OH \tag{2}$$

Equation (2) might occur in two cases:

1) at a very negative potential or a very high cathodic current density;
2) in a carbonated concrete in which the pH value of the pore solution has become very low.

Even in these two cases, reaction (1) still has some contribution to the corrosion of steel, but the effect of reaction (2) prevails over reaction (1). No matter which process is taking place, the cathodic reactions always produce hydroxide ion and increase the pH value of pore solution in the vicinity of cathode.

The anodic reaction occurring at the anodic area (A) on the steel surface can be basically described as a reaction:

$$Fe = Fe^{2+} + 2e \tag{3}$$

With this anodic reaction proceeding, the cross section of steel bar is reduced and finally the rebar could break down. So reaction (3) is a very important process responsible for the corrosion damage of reinforcement.

The intermediate corrosion product, Fe^{2+}, could be further transformed into Fe^{3+} under oxidising conditions, and be accumulated at the surface of steel rebar; or be dissolved into the pore solution and move away from the steel reinforcement, under reducing conditions [*Broomfield (1997), Macdonald (1991)*].

Normally, the pore solution is rich in oxygen with a high pH value. So Fe^{2+} can stay in the form of $Fe(OH)_2$ or $Fe(OH)_3$ due to hydrolysis or oxidation of Fe^{2+}, forming a thin passive film on the steel surface, which consequently retards reaction (3). In this case, the steel can be well protected in concrete, and there will be no detectable corrosion damage. However, at the initial stage after concrete is cast and subjected to moist-curing, the passive film can not be formed so quickly if the concrete is completely immersed in water [*Khan (1991)*]. It was suggested that the formation of passive film on reinforcement might take a significantly long time even when the concrete is not completely immersed in water after casting [*Khan (1991)*]. This is understandable, because in a very basic solution, steel can not be passivated as easily as stainless steel; also the supply of oxygen which is necessary for the passivation of steel in concrete is usually a few orders of magnitude lower than that in a normal aqueous solution.

However, under some conditions the protective film may not be formed or the formed passive film would break down. This applies, for example, to concrete that has been carbonated to a great extent so that the pH value of its pore solution is lower than 9; or when a certain amount of chloride ion has penetrated into a concrete saturated with water and has reached the vicinity of steel. In these cases, passive film is unlikely to be formed, or the formed passive film will be likely dissolved and the dissolved Fe^{2+} in pore solution tends to move away from the steel surface. Hence, the cross section of reinforcement will keep reducing and finally the breakdown of reinforcement will result. Such a damaging process can be facilitated when the concrete is saturated with water, as sufficient water can facilitate reaction (3) and the removal of Fe^{2+} away from steel surface. In this way, Fe^{2+} could move out of the concrete and form rust stain on the surface of concrete structure, but such a corrosion damage of steel has no significant impact on the surrounding cover concrete.

In the first case when passive film can be formed on reinforcement in concrete, corrosion is not a concern. In the second case when corrosion products can move out of the cover concrete, only reinforcement is attacked and the attack can easily be found by the visible rust stain on structure surface. This is not a very dangerous case. The most adverse case is that the corrosion of steel is proceeding at a high rate, and the corrosion products can not move out of the corrosion site, but accumulate on the steel surface as a rust layer. This mostly occurs when the pore solution is rich in oxygen and aggressive species and the cover concrete is not very wet. In this case, some of the dissolved Fe^{2+} could be oxidised but transformed into hydrated ferric oxide ($Fe_2O_3.H_2O$) which is known as rust, and then deposited together with some ferrous oxide or hydroxide at the interface between steel and the surrounding concrete. The volume of the corrosion rust is usually 2~6 times greater than the volume of the metal consumed by corrosion reaction [*Broomfield (1997*[1]]. This means that an expansion stress will be induced by corrosion of steel at the interface between steel and the surrounding concrete. The more the cross section of the steel is corroded, the higher the resulting expansion stress. When the expansion stress exceeds the tensile strength of the cover concrete, cracks in the concrete will be formed. The cracks in cover concrete will in turn act as shortcuts for the ingress of detrimental species, so corrosion process will be further accelerated by the cracking of cover concrete. Therefore a self-catalytic deterioration process is triggered: corrosion → expansion → cracks in concrete → ingress of detrimental species → more serious corrosion → more expansion → more cracks → more detrimental species → .... Finally spalling of the cover concrete takes place, further exposing the interior of the concrete to corrosion. This is the main course of damage of reinforced concrete associated with most damaged structures.

In addition to the three basic processes, there are two electricity charge flows involved in the corrosion of steel. The first one is an electronic charge flow from anodic area (A) to cathodic area (C) through the steel rebar in concrete. As steel is a very good conductor, this process is very easy and does not have significant influence on the corrosion process. The other electricity charge flow is an ionic flow through the concrete (the ionic conductor) surrounding the steel rebar. This flow has an important influence on corrosion of steel, especially for the corroding steel whose anodic and cathodic areas are separated far away from each other. The distance between anodic and cathodic areas in this case also plays a significant role in the corrosion of steel in concrete. Larger distances between anodic and cathodic areas mean higher resistance against the ionic flow, if a constant resistivity of concrete is assumed. Correspondingly, the corrosion of steel driven by the anodic and cathodic reactions at the separated anodic and cathodic areas is reduced.

Under a natural and relatively steady state condition, when no external current is imposed onto the steel/concrete system, the rates of anodic and cathodic reactions should be equal to each other. They should also be equal to the rates of the arrival of depolarisation reagents and the production or departure of corrosion products. They are further equivalent to the current of electronic charge flow within steel bar and the ionic flow in the concrete. In other words, all these processes are "forced" to proceed at the same rate when the system is at a natural steady state. Furthermore, all the processes involved in the corrosion of steel can also be "forced" to slow down or to stop by slowing down or stopping any one of these processes. This is a basic principle on which the corrosion protection techniques were established. For instance, protective coatings are actually to slow down the access of depolarisation reagents to the steel surface; the re-alkalisation technique which restores the alkalinity at the vicinity of reinforcement, is to accelerate the formation of a passive film on the steel reinforcement to retard the anodic reaction (3).

3.3 Types of Corrosion of Steel in Concrete Structures

The basic processes of corrosion are closely related to the medium surrounding the steel, and different basic processes would lead to different forms of corrosion damage to steel. For corrosion of steel in concrete, the above basic processes are mainly governed by the special medium---concrete. Differences in concrete parameters and the environmental factors which can result in changes of the concrete properties would be directly and indirectly responsible for the different forms of corrosion damage to reinforced concrete structures. The corrosion types can be classified according to different criteria. It can be according to the mechanisms of corrosion, final damage appearances, environments that induce corrosion, etc. In this section, the corrosion of steel in concrete would be classified into the following types, mainly according to the corrosion mechanisms as well as partly to the damage forms:

- Uniform corrosion
- Galvanic corrosion
- Localised corrosion
- External current imposed corrosion
- Stress corrosion cracking and hydrogen induced embrittlement

It should be stressed that the classification of corrosion types is not absolute. The definition of each type of corrosion can only be applicable under certain conditions. For example, corrosion can not be absolutely uniform. A corroded surface of steel might look uniform on a large scale, but might have a localised corrosion morphology on a small scale; pitting can be classified into localised corrosion if attention is paid to the pitting site, but it may be termed as galvanic corrosion if the area surrounding the pitting is taken into account.

3.3.1 Uniform Corrosion

In some cases, the distance between anodic and cathodic areas is too small to be separated from each other, i.e, the areas (A) and (C) (Figure 1) are nearly merged together along the steel bar in concrete. So anodic and cathodic processes would nearly uniformly occur along the steel surface, and as a result, the dissolution of steel uniformly occurs on the steel rebar. This is uniform corrosion. The anodic and cathodic sites, (A) and (C), are sometimes at small distances and randomly distributed, and can change from time to time along the steel rebar. Therefore, uniform corrosion can also be regarded as a damage caused by many random galvanic cells whose sizes are very small.

Uniform corrosion is usually observed in carbonated concrete structures. Carbonation of concrete normally proceeds in all the exposed areas of a concrete structure, so the decrease of pH value of pore solution would be expected over a relatively large area. Meanwhile the oxygen is also available over all the exposed area of the structure. In this case, it is quite possible that anodic and cathodic reactions are uniformly and equally distributed along the reinforcement over a relative large area.

Strictly speaking, there is no absolute uniform corrosion in concrete structures. The "uniform" is only a relative concept as mentioned above. In most published materials on corrosion of reinforced concrete, the uniform corrosion has not been specifically mentioned. However, most of the fundamental research studies were carried out in the laboratory, assuming that the studied specimens were uniformly corroded. Also, the famous "guard ring"[*Feliu (1990)*], developed for the field survey of structures, was originally designed assuming uniform corrosion under the sensor, even though now it is used to detect the non-uniform distribution of corrosion [*Filis (1992)*].

3.3.2 Galvanic Corrosion

Due to the heterogeneity of concrete structures and their micro-environment, it is relatively rare for the anodic and cathodic processes to be uniformly distributed along the steel surface. More commonly, at some sites the cathodic process is stronger than the anodic process while at other places the anodic reaction is much faster than the cathodic reaction [*Broomfield (1997)*].

The rate of galvanic corrosion or galvanic current density (Ig) is approximately determined by the following equation [*Gulikers (1996)*]:

$$Ig = (E^{c}_{corr} - E^{a}_{corr})/(Pa + Pc + Rc) \tag{4}$$

where E^{c}_{corr} and E^{a}_{corr} are corrosion potentials at cathodic and anodic areas, respectively when $Ig=0$; Pa and Pc are the polarisities associated with the anodic and cathodic processes at anodic and cathodic areas, respectively; Rc is the concrete resistance between anodic and cathodic areas.

In the case of galvanic corrosion, the resistivity of concrete is usually high, and the distance between anodic and cathodic areas is significant, so Rc in this case has a great contribution to equation (4). To some extent, the galvanic corrosion is mainly governed by the concrete resistivity. The higher the concrete resistivity, the lower the galvanic corrosion rate. In an extreme case, the Rc is so high that Pa and Pc can be neglected compared with it, then galvanic corrosion rate Ig would only depend on Rc, so the value of Rc would reflect the galvanic corrosion rate. This is actually the basic electrochemical foundation for the concrete resistivity to be widely used as a corrosivity indicator to assess the corrosion rate of steel in concrete.

According to equation (4), the ratio of cathodic to anodic areas is also important to the galvanic corrosion process [*Arya (1996)*]. Higher ratios will produce faster and more concentrated corrosion damage to reinforcement. This is very easy to understand from an electrochemical point of view.

Galvanic corrosion is more likely to play an important role in a large dimensioned concrete structure. It generally arises from the differences in aeration (oxygen), alkalinity (carbonation) or salt concentration (chlorides), particularly uneven passivation of reinforcement [*Gulikers (1996)*]. Recently, the galvanic corrosion was found to be induced by the patching effect [*Gulikers (1992)*]; the patching can lead to galvanic corrosion between the patched zone and its surrounding concrete matrix. Because the patching material can not be exactly the same in aeration, alkalinity, or salt content, etc, as the original concrete, new galvanic corrosion cells will be generated after patching at the zone between the patched and intact areas.

Galvanic corrosion has been estimated to contribute about 50-80% of the total corrosion on some US bridge decks, but in European structures, the estimate is about 5~20% [*Gowers (1994)*]. The difference in the estimate between America and Europe might be mainly due to the different use of deicer salt. In north America, the chloride containing deicer is a well-known catalytic reagent for localised corrosion, so the corrosion of reinforcement in concrete structures is more likely to be non-uniform. In Australia, many concrete structures are standing in the coastal marine environments. Even though there is no statistics about the galvanic corrosion damage, we have sufficient reasons to believe that the percentage of the structures suffering from galvanic corrosion in such environments could not be low.

The systematic studies of galvanic corrosion cells in concrete are still relatively few [*Okada (1980), Wheat (1987), Wheat (1990)*]. Some laboratory investigations mainly demonstrated the contribution of galvanic cell to the damage of steel in concrete [*Oberle (1990), Gulikers (1992)*]. Andrade [*Andrade (1992)*] investigated the effects of galvanic cells on the corrosion rates of steel reinforcements in concrete beams and slabs; when passive and active reinforcements were placed opposite each other, the distribution of current lines between the electrodes were uniform, and the anodic current density was a function of the polarisation resistance, the difference between the potentials of these two electrodes, and the concrete resistance; however, a coplanar location of anode and cathode resulted in a non-uniform distribution of the current; linear transmission circuit could successfully model these galvanic cells. It was also found [*Bertolini (1996)*] that galvanic corrosion could take place in a structure with distributed cathodic protection (CP) anodes even when the CP system was not energised (or was switched off), and localised corrosion could also be enhanced slightly by the presence of the distributed anode.

3.3.3 Localised Corrosion

Localised corrosion mainly refers to the corrosion damage morphology. It is the most dangerous attack on steel, and therefore, the most noticeable in the corrosion field. It has many various forms, but for reinforced concrete in this paper the localised corrosion is only referred to pitting and crevice corrosion.

For localised corrosion, the anodic area is much smaller than the cathodic area, but the corrosion penetration rate at the anodic area (A) is usually extremely high [*Broomfield (1997)*]. In this sense, localised corrosion is one of the very special cases of galvanic corrosion, because the corrosion cell consists of a small rapidly corroding anodic area and a large cathodic area surrounding the anodic area. The feature of extremely high ratio of cathodic to anodic areas makes localised corrosion very dangerous to steel in concrete. For example, a corrosion rate of $0.5\mu A/cm^2$ might be acceptable for a reinforcement suffering from uniform corrosion; but such a rate might cause very fast corrosion penetration if the reinforcement has a highly localised pitting corrosion.

The second feature of localised corrosion (i.e. pitting and crevice corrosion) is its self-catalysis. That is, the anodic dissolution process of steel could generate a more aggressive environment (lower pH value of solution and higher content of chloride ions) in the pit or crevice which, in turn, facilitates the corrosion dissolution in the pit or crevice. This feature actually distinguishes the localised corrosion from galvanic corrosion. The corrosion would be automatically accelerated in the pit or crevice after it is triggered. For example, the uniform corrosion might slow down with time because of some barrier effect of the corrosion products formed on the steel surface. However, the corrosion situation might be further worsened if the barrier effect occurs in the case of pitting corrosion or crevice corrosion: The barrier effect increases the occlusion degree of the pitting or crevice cell which tends to keep the inner aggressive environment in the pit or crevice from being neutralised by the pore solution outside the pit or crevice. This further promotes the self-catalytic effect, hence corrosion rate might be greatly increased with time in this case. The self-catalytic feature not only makes localised corrosion very dangerous to steel in concrete, but it also makes the corrosion process very complicated and unpredictable.

Pitting corrosion is the result of attack of chloride on some particular sites of the passive film on the reinforcing steel, which results in the breakdown of the passive film, and leads to rapid anodic dissolution of the steel at those sites. Therefore localised corrosion of rebar in concrete is closely associated with the ingress of chloride. Actually most chloride induced corrosion tends to be localised [*Sagues (1992)*]. The mechanism for pitting corrosion in concrete might be similar to that in aqueous solution [*Broomfield (1997)*]. That is, during the pitting corrosion, the chloride ions tend to be accumulated in the pits and the pH of the solutions in the pits decreases, so the environments inside the pits is getting aggressive; this in turn further accelerates the anodic dissolution of steel in the pits. For pitting corrosion, the loss of cross sectional area or strength of reinforcement at the corrosion sites becomes the main concern. A small amount of corrosion products might mean a significant damage to the reinforcement.

In some cases, the chloride level may not be high enough to cause pitting corrosion of reinforcement in concrete, but it might be sufficient to initiate crevice corrosion at the interface between rebar and concrete [*Gratten-Bellew (1994)*]. The mechanism for the crevice corrosion might be still due to the dissolution, the local acidification by ferrous ion hydrolysis and the chloride accumulation processes [*Vrable (1980), J.A.Gonzalez (1993a)*]. It was proposed by Enos et al [*Enos (1997)*] that the local environment at the steel/concrete interface was variable and different from the highly alkaline pore solution in the bulk of the concrete. For pilings, the pH value of the local pore solution at the interface of steel/concrete could be quite different from the pH value of the bulk pore solution, being ≤6.5 within the atmospheric zone, 4.8 within the splash zone, and 11.8 within the submerged zone [*Enos (1997)*].

3.3.4 External Current Induced Corrosion

If an external current is imposed onto a reinforced concrete system, extra corrosion loss of steel will occur. As the conductivity of steel is much higher than that of concrete, almost all the induced current will be conducted by the reinforcement in concrete. Mainly cathodic reactions occur at the sites where external current flows into the reinforcement through the surrounding concrete, and no severe corrosion is likely. However, the steel is forced to act as anode at the sites where the induced current comes out of the reinforcement and goes back to the external environment through the concrete. Consequently, iron dissolution takes place in such locations, reducing the cross-sectional area of the steel.

The most typical external current induced corrosion is the stray current corrosion, which was once blamed for all the corrosion of steel in concrete in the 1950s [*Broomfield (1997)*]. Most cases of stray current corrosion in concrete structures occur where electric trams, trains or buses run through the structure, or where cathodic protection is applied. Screening off the sources of stray current might be the most effective measure to prevent this kind of corrosion damage. The monitoring of stray current corrosion is important. Recently a drainage method has been tried for the stray currents generated by a metro system [*Bajenaru (1996)*].

3.3.5 Stress Corrosion Cracking and Hydrogen Induced Embrittlement

Stress corrosion cracking (SCC) and hydrogen induced embrittlement (HIE) are caused by the combination of particular corrosion media and stresses for some types of steels. The initiation and development of SCC and HIE are imperceptible, but failures caused by them are a sudden breakdown of reinforcement which could give rise to the collapse of reinforced structures. Even though SCC or HIE of reinforcement is fairly rare in practice compared with other types of corrosion, their possible damage and social impact can never be neglected.

High strength steel is one of the materials that are sensitive to SCC and HIE. Unfortunately, the pre-stressed concrete structures are using high strength steel, so the susceptibility to SCC and HIE should always be considered in prestressed concrete elements.

Extensive problems have been found with post-tensioned reinforced concrete structures due to poor grouting of ducts which can lead to leakage of water into the steel cables. A failed prestressed concrete element had led to the collapse of the roof of a production hall [*Isecke (1982), Mietz (1996)*]. The failure of prestressing wires in the drainage points of a prestressed concrete tube was found to be associated with hydrogen embrittlement in the cathodic zones [*Arpaia (1987)*]. The severe corrosion of steel in other similar cases, can sometimes result in the collapse of bridges [*Woodward (1988)*].

Some research work has been conducted to assess the possibility of SCC in reinforced concrete, but the results were inconclusive. Parkins et al [*Parkins (1982)*] carried out stress corrosion tests on notched and pre-cracked prestressing steel strands in calcium hydroxide solutions; they found that enhanced cracking occurred at potentials lower than -900mV/SCE. Treadaway [*Treadaway (1971)*] conducted tests on cold-drawn prestressing steel wires in concrete. He did not find any evidence of stress corrosion cracking. This might be due to the fact that no polarisation potential was used and the exposure time was not long enough [*Slater (1983)*]. Mietz et al [*Mietz (1996)*] concluded that the crack could propagate even in fully grouted ducts; however the general risk to older, prestressed concrete structures is as yet not proven. Some researchers [*Phillips (1975), Schultz (1990)*] have stated that the premature failure of prestressed concrete structures could have been avoided with proper attention to design, manufacture and installation. Ohta et al [*Ohta (1992)*] in an investigation on a 13 year old bridge concluded that the major cause of deterioration in the bridge might be attributed to the cracks which occurred along the sheaths because of water freezing inside the sheaths; the prestressing wire could partly break in the beam. Even though the

SCC was not specified in their work, the severe corrosion inside the sheaths under such a condition might indicate the existence of a risk of SCC.

The greatest concern about HIE of reinforced concrete structures is the susceptibility of prestressed tendon especially when cathodically over protected. Theoretically, this is the most dangerous case. Even though the applied cathodic protection (CP) current density is not overall high enough to induce HIE, some regions may still be over-protected and there exists the HIE risk because of the non-uniform distribution of CP current density in concrete. A universal CP criterion was proposed to be roughly -900mV/SCE [*Hartt (1993)*]; when the applied CP potential was less negative than the threshold, hydrogen embrittlement could be avoided, and such a threshold was found to be independent of solution pH value. It was also observed that the susceptibility to hydrogen embrittlement tended to increase at more negative potentials (≤ -1000mV/SCE) [*Ishii (1992)*]. Enos et al [*Enos (1997)*] believed that even modest levels of CP ($1\sim2\mu A/cm^2$) could make the hydrogen evolution reaction thermodynamically favorable at the surface of rebar. Scannell et al [*Scannell (1987)*] simulated such a condition for tendons, but no HIE was observed. However, more recently and under similar conditions, Wagner et al [*Wagner*] found that the cathodically generated hydrogen could reduce the ductility of steel if a very negative cathodic protection potentials were applied. Nagi and Whiting [*Nagi (1994)*] carried out a state-of-the-art review on the corrosion of prestressed reinforcing steel in concrete bridges. According to the review, the consequences of corrosion of prestressing steel in concrete were much more critical than that of ordinary steel used in plain reinforced concrete; cold drawn and stress relieved prestressing wire was less susceptible to hydrogen embrittlement than quenched and tempered steel; good quality concrete and sufficient cover concrete would provide corrosion protection to the embedded prestressing steel; the main environmental condition that can lead to corrosion of prestressing steel was the presence of chlorides. However, it was also found [*Lillard (1996)*] that chloride had no direct effect on the hydrogen absorption rate, but other factors had more influence on HIE; Lillard et al [*Lillard (1996)*] found that adsorption of hydrogen in saturated $Ca(OH)_2$ was less than that in the mortar cover; corrosion products and oxides could retard the hydrogen adsorption.

Besides the SCC and HIE, there is still another possible attack on the steel in reinforced concrete subjected to alternate loading and unloading. That is corrosion fatigue. Materials in corrosive media usually fracture much earlier if they are subjected to alternating stresses. Unfortunately, most reinforced concrete structures usually are standing in such an adverse environment. The alternating stresses can be caused by wind, traffic flow, change of temperature, and wave action, etc. So far, there has been no report on the failure of concrete structures due to corrosion fatigue of the reinforcement. However, there is no theoretical reason that this kind of damage could be excluded. Perhaps such corrosion damage exists but has been overlooked in the field surveys of structures.

4. Factors Affecting Corrosion of Steel in Concrete

The corrosion behaviour of reinforcement steel in concrete is a function of parameters of steel and concrete as well as the properties of their interfacial zone. That is, it is determined by the composition of the pore solution of the concrete and chemical properties of the steel. The other parameters of concrete would affect corrosion of steel through their influences on the pore solution. Environmental factors can not affect the corrosion processes directly, but they cause the deterioration of the cover concrete and accelerate the ingress of aggressive species, making the pore solution in contact with the steel more corrosive. Among all the environmental factors, chloride ions and carbon dioxide have been responsible for most corrosion of steel in concrete structures [*Broomfield (1997)*]. In addition to these two factors, temperature and moisture, as well as some other factors that cause deterioration in concrete, also play important roles in corrosion of steel in concrete. What makes the influences of those factors so complicated is that the corrosion of steel in concrete is not determined by a single factor. The interaction among these factors plays an important role in the corrosion process of the steel reinforcement. Thompson et al [*Thompson (1995)*] gave a very complicated regression equation for predicting the corrosion rate, which involved temperature, chloride content, and relative humidity. Liu et al [*Liu (1997)*] also proposed a non-linear regression model, which demonstrated that the corrosion of steel in concrete in service exposure conditions was a function of the concrete chloride content, temperature, ohmic resistance, and active corrosion time; corrosion rate increased with the increases of temperature and amount of chloride ions, and decreased as the ohmic resistance of concrete increased; the corrosion rate decreased rapidly at an early stage after corrosion initiation, and then it tended to reach a certain value after about 1 year.

4.1 Steel

Different types of steels have different microstructures and compositions, so different types of steel usually have different corrosion behaviours in concrete.

Stainless steel and stainless steel clad have been used in Europe for many years as corrosion resistant reinforcement in concrete. Laboratory examinations and field tests carried out in the world showed that many kinds of stainless steels were much more resistant against corrosion than plain steel [*McDonald (1995)*]. The corrosion rate of stainless steel is a few orders of magnitude less than that of steel, and chloride tolerance of stainless steel is several times higher than that of black steel rebar in concrete [*Sorensen (1990), Rasheeduzzafar (1992)*]. Austenitic steel has the highest performance, with almost no corrosion even in relatively high chloride environments [*Guirguis (1994)*]. Bar type, e.g. plain or deformed, has no significant influence on corrosion [*Treadaway (1980)*].

Stainless steel bars are capable of maintaining excellent corrosion resistance in severe chloride environments, but the cost of the use of stainless steel is much higher than plain steel. In most concrete structures, plain steel can last long enough to satisfy the designed service life, so it is not worth using the expensive stainless steel. Only in some very important reinforced elements, for which no corrosion is permitted, would stainless steel be considered. In this case, the increase of the overall cost is not too high considering fewer repairs and less maintenance costs.

The steel surface can directly affect the bond between the reinforcement and the concrete, and further influence the failure of structures. It was found that the rust which was well adhered to the underlying steel helped the bond between steel and concrete [*Maslehuddin (1990)*]. The surface of steel treated with water to form a coating before incorporation of the steel in concrete could increase the bond strength [*Fu (1996)*]. Slight corrosion could increase the bond strength, whereas severe corrosion decreased it [*Fu (1997)*].

4.2 Pore Solution of Concrete

The pore solution in concrete is an electrolyte which is physically absorbed in the pores of the concrete, due to the capillary force produced by menisci and the adsorption resulting from molecular force. It reacts with the steel reinforcement, and under certain conditions can lead to the corrosion damage at the steel surface.

The pore solution contains various ions, such as sodium, potassium, calcium, hydroxyl, sulphate, and sulfite, etc. The composition of the pore solution varies with the cement used and the age of concrete. An example of its composition is 0.6M KOH +0.2M NaOH +0.001M $Ca(OH)_2$ [*Barneyback (1981)*]. Page [*Page (1983)*] reported that the pore solution in a mortar with standard portland cement without additives has a pH value ~ 13.5 with K^+, Na^+ and Ca^{2+} as the main cations. Besides the main components, other species could be introduced by supplementary cementitious additives, aggregates, chemical additives and outside environment. Recently, Burchler et al [*Burchler (1996)*] analysed the pore solutions of hardened cement paste and mortar, and found that the water/cement (w/c) ratio could affect the composition of pore solution, and that the hydration would not significantly affect the chemical composition of pore solution of hardened cement paste after 30 days curing. Other researchers [*Diamond (1975), Longuet (1973), Byfors (1986)*] also found that different cements led to different pore solution compositions, and that the compositions became constant after a certain period of hydration.

The chemical composition of the pore solution influences the conductivity of the concrete and the corrosion process.

If a certain amount of chloride is present in the pore solution, it will become corrosive, even though its pH value may still be high. The chloride can attack the passive film and accelerate the dissolution of steel. It is generally accepted that there is a critical chloride concentration, above which the breakdown of the passive film will be initiated and serious corrosion of steel will be triggered.

As the pH value of the pore solution in a well-cured new concrete is about 13.5, any steel in contact with such a pore solution should be in a passive state, so there is no corrosion problem with a young reinforced concrete structure if there is no chloride. Unfortunately, the pH value can not always be kept so high. Atmospheric CO_2 dissolved in the pore solution, will react with the alkali hydroxide and the $Ca(OH)_2$ and reduce the pH value. When the pH value is lower than 9, the passive film on the steel reinforcement in contact with the pore solution would no longer be stable, and rapid corrosion would occur on the surface of the "active steel" (without passive film protection).

As discussed above, corrosion of the reinforcement steel in concrete is associated with the pore solution "polluted" by chloride or "de-alkalised" by carbon dioxide. Therefore, the chloride "pollution" and CO_2 "de-alkalisation" are two main aspects of the pore solution from a corrosion point of view. They are both directly responsible for the deterioration of reinforced concrete structures. Besides the direct detrimental influences of the chloride "pollution" and the CO_2 "de-alkalisation" on the corrosion of reinforcement steel, they still have other effects on the pore solution, which would also affect the corrosion process of the steel.

It was found [*Haque (1995)*] that the OH^- level in the pore solution was dependent on the concentration of the added NaCl in the concrete; initially, with the increase in the added chloride ions, the OH^- concentration in the pore solution also increased, but after a certain amount of chloride was added, the hydroxyl concentration decreased with the increase of added chloride. This phenomenon has also been observed by other researchers [*Bebei (1986), C.L.Page (1986a), Hansson (1985), Kawamura (1988)*], and is due to the interaction of the chloride with aluminate phases. On the other hand, the CO_2 "de-alkalisation" has also influence on the chloride concentration in the pore solution. More chloride ions would be released from cement and aggregate into the pore solution with lower pH value [*Tuutti (1982), Tritthart (1989a).Byfors (1990), Page (1991)*], resulting in more serious chloride "pollution".

The ingress of chlorides into concrete has also a significant effect on the chemical equilibrium of calcium in pore solution. The concentration of calcium ions in a chloride free pore solution is less than 0.01M [*Taylor (1990)*]. However, 1 to 2 orders of magnitude higher free calcium concentrations have frequently been measured [*Yonezawa (1988), Sandberg (1995)*] in chloride contaminated concrete. A number of theories have been proposed to explain the high concentration of calcium ions in the pore solution when chlorides are introduced into the concrete. It was proposed [*Theissing (1993)*] that a calcium hydroxide-calcium chloride hydrated complex might be formed in the presence of chloride. Moragues et al [*Moragues (1989)*] proposed that calcium and chloride formed molecular species dissolved in the pore solution. Some others [*Chatterji (1992), Chatterji (1994)*] proposed a model in which calcium ions co-diffuse within the electrical double layer with chlorides. However, no direct evidence in support of these mechanisms is available. The influence of the chloride on the chemical equilibrium of calcium in the pore solution could at least lead to change in conductivity of the cover concrete. Therefore, the ingress of chloride may facilitate the galvanic corrosion through increasing the conductivity.

4.3 Permeability of Concrete

Higher porosity and larger pore sizes lead to more severe corrosion damage in the steel. The pores can facilitate the ingress of Cl^-, CO_2, O_2, H_2O, and some other detrimental species from the environment. They also greatly affect the removal of corrosion products from the steel surface. Therefore, the permeability directly affects two of the basic corrosion processes: the supply of depolarisation reagents and the removal or accumulation of corrosion products, and has significant influence on the corrosion of reinforcement. For a normal concrete structure, it is believed that oxygen is very easily able to access the reinforcement [*Funahashi (1994)*], but it is quite difficult for corrosion products to move from the reinforcement surface [*Broomfield (1995)*]. In effect, resistivity of concrete can be partially ascribed to the permeability as well, so the permeability of concrete also exerts an influence on the galvanic corrosion rate through its influence on the ion flowing process in the cover concrete.

If the concrete has low permeability, then the aggressive species would be difficult to access the reinforcement, and the possibility of corrosion of the reinforcement would be low.

The permeability of concrete is mainly determined by the porosity of concrete and its pore size distribution, which are dependent on the ratio of water/cement (w/c) in the concrete. Therefore, the permeability of concrete increases with the increase in w/c ratio, especially when w/c>0.55 [*Guirguis (1994)*]. Sometimes, the permeability of concrete could vary by as much as two orders of magnitude as w/c increases from 0.4 to more than 0.7 [*Cook (1951)*].

Other factors can also significantly affect the permeability of concrete. For example, hydration process of cement also influences porosity and permeability. It was found [*Burchler (1996)*] that the porosity for hardened cement paste changed from 29% at age 40 days to 25.8% at age 296 days. The use of mineral admixture (fly ash) also had a significant effect on the chloride diffusion than on the oxygen diffusion in concrete.

The transport properties of concrete is different for different species passing through it. Diffusion of chloride ions in the pores in concrete is more easily retarded by the surface charge of the hydrated cement gel pastes with a low-capillary porosity [*Ngala (1995)*]. However, the hydrated cement gel is much more permeable to the neutral oxygen molecules [*Thompson (1997)*]. Several researchers [*Alekseev (1993), Sergi (1992)*] have reported that the hydroxide permeability of concrete was in the same order as the chloride permeability. For a typical concrete element, the concentration of OH^- increases with the depth of concrete whereas the chloride level decreases with the depth [*Sergi (1992), Sandberg (1995)*]. This is mainly due to the ingress of chloride and carbonation process initiating from the surface of concrete.

Low w/c, better compaction, and use of mineral admixtures, etc, could lower the permeability of the cover concrete, therefore they are the options to improve the corrosion resistance of reinforced concrete.

4.4 Moisture

The influence of concrete moisture content on the rate of corrosion of steel in concrete is well known [*Gonzalez (1980)*]. If there is no water in concrete, there should be no corrosion problem with the reinforcement. Since electrochemical reactions are mainly responsible for the reinforcement corrosion, moisture should be an essential substance in the corrosion of steel in concrete.

The moisture of concrete has a complicated influence on the corrosion of steel in the concrete. The resistivity of concrete is first affected by the moisture, which can influence the galvanic corrosion rate. However, an increasing moisture has contrary effects on anodic and cathodic reactions. The anodic reaction rate increases and the cathodic reaction rate decreases with the increasing humidity. This is due to the fact that the increase in moisture makes the departure of rust or corrosion products easier, but it decreases the diffusion coefficient of oxygen and makes the supply of oxygen more difficult [*Houst (1994)*].

Tuutti [*Tuutti (1982)*] found that, for chloride-induced corrosion, the maximum corrosion rate appeared at a relative humidity (RH) of about 95%; while for carbonation-induced corrosion. a rise of an order of magnitude in corrosion rate was observed at 85% RH, then the corrosion rate peaked at about 95% HR. High humidity leads to a high corrosion current for steel in concrete, but the effect is usually small as the depth of steel in concrete increases [*Hawkins (1996)*]. Based on experimental results, Clemena et al [*Clemena, Clemena (1992)*] established a relationship between the corrosion rate, and the concrete moisture and environmental temperature. However, it is doubtful whether such an equation is applicable to other systems.

In recent years, research interest has been increasing in the rate of water absorption into cover concrete. The water absorption into concrete from outside environment can rapidly increase the rate of corrosion of depassivated reinforcing steel to the levels that will cause cracking and spalling [*Tuutti (1982), Mullu (1984)*]. The absorption is also an important transport mechanism for the ingress of chlorides into concrete. It was found [*Andrade(1996a)*] that the internal relative humidity (RH) of concrete behaved differently to the external RH; but no direct relationship was found between corrosion rate and internal RH or temperature.

4.5 Chloride

Chloride in concrete is a main cause of corrosion of reinforcement. Most of the damage in concrete structures are caused by chloride-induced corrosion.

The main characteristics of chloride-induced corrosion are as follows [*Blankvoll (1997)*]:

1) Anodes and cathodes are separated, and corrosion rate is very high and localised.
2) Once the corrosion is initiated, it is far more difficult to remedy than carbonation.

Chloride comes from different sources [*Broomfield (1997)*]. It can be cast into concrete in the following ways:

1) deliberate addition of chloride as accelerators;
2) use of water containing Cl^-;
3) contaminated aggregates.

Chloride can also diffuse into concrete as a result of:

1) sea salt spray and direct sea water wetting;
2) deicing salts;
3) use of chemicals.

The chloride cast into concrete might initiate corrosion of steel differently to the chloride coming from environment. Cao et al [*Cao (1994)*] found that in the presence of chloride ion in mixing water, the passive range of steel could still be observed at a concentration of 0.08 M NaCl; in the case of penetrating chloride, passive range of steel was either severely limited or not observed after 6 months of immersion in water containing 0.02M NaCl.

Normally, the chloride exists in concrete in two forms:

- dissolved in pore solution as free chloride; and
- assorbed on cement gel or combined with hydrated cement and aggregates as bound chloride.

Only the free chloride can accelerate corrosion of steel in concrete. The bound chloride is inert to steel before it is dissolved into solution and becomes free chloride. Typically about 40~50% of the total chloride in concrete is bound [*Gaynor (1985)*]. Dhir's estimation [*Dhir (1990)*] of the ratio between the soluble and insoluble chloride in concrete was roughly 3 to 1. Stoltzner [*Stoltzner (1997)*] found that the ratio of free to total chloride contents in concrete with low-alkali, sulfate-resistant cement was about 50~70%, and for portland concrete 35~60%.

It is believed that there is an equilibrium between the adsorption of free chloride from pore solution, and the desorption of bound chloride from cement gel and aggregate. Some researchers [*Tuutti (1982), Arya (1990a), Fishcher (1984)*] have assumed that the equilibrium relationship was only a simple linear adsorption isotherm. However, it was also suggested that [*Dhir (1990)*] the relationship between bound chloride and free chloride was much more complicated, and could be non-linear [*Blunk (1986), Byfors (1990), Sandberg (1993a), Akita (1995)*]. Pereira [*Pereira (1984)*] suggested a Langmuir isotherm to describe the chloride binding behaviour. However, the Langmuir isotherm equation could only give a good expression for the chloride binding behaviour at low concentration. In order to fit the experimental data at intermediate concentration range, Freundlich isotherm adsorption [*Tang (1993)*] and a modified BET [*Xu (1990)*] model were proposed.

The relationship between free chloride and bound chloride is affected by binder type, degree of hydration, amount of pore solution, and other ions in the pore solution. Many researchers [*Arya (1990), Tritthart (1989), Tritthart (1989a), Page (1986a)*] have proposed a correlation between the tricalcium aluminate (C_3A) content and the capability of binding chlorides through the formation of insoluble calcium chloroaluminates. Higher C_3A contents bind more chlorides, resulting in lower chloride ion level in the pore solution. Tang et al [*Tang (1992)*] reported that the total amount of alumia and iron oxide in cement determined the chemical binding capacity; fly ash cement contained higher amounts of alumina and iron oxide, so had a higher chemical binding capacity; slag cement formed finer hydrated products, so had higher physical binding capacity too. This is in addition to their beneficial effects on concrete microstructure and permeability.

Hydroxide concentration in pore solution has a significant influence on chloride binding [*Tuutti (1982), Tritthart (1989a), Byfors (1990), Page (1991)*]. The higher the hydroxide concentration, the less chloride will be found in the pore solution.

Temperature can alter the chloride binding capacity too. The amount of bound chloride decreased as temperature increased [*Larsson (1995)*]. Both physical desorption and chemical reaction tend to increase at higher temperature, decreasing the chloride binding capacity.

Some other factors such as curing temperature, curing age, original alkalinity also affect the chloride binding capacity of concrete [*Arya (1995), Byfors (1986)*]. It has been suggested that the presence of superplasticiser in concrete could lower the chloride binding capacity [*Haque (1995)*]. Larsen [*Larsen (1997)*] found that the chloride uptake and the pore solution composition in concrete were affected by drying/wetting and temperature, but the effects were influenced by chloride concentration; carbonation strongly decreased the chloride uptake and reduced the chloride concentration of concrete. Page et al [*Page (1991)*] pointed out that cement hydrates could bind a substantial portion of chloride in an insoluble form below a total chloride content of

1%, and that beyond this point the binding capacity is largely exhausted. The concentration of sulfate ions has also been reported to significantly influence the chloride binding capacity of a given binder [*Yonezawa (1988), Tritthart (1989a), Byfors (1990), Sandberg (1993)*]. Xu [*Xu (1997)*] reported that calcium sulphate and sodium sulphate had different effects on chloride binding and pore solution chemistry; at the same sulphate content, cement pastes containing calcium sulphate had a higher chloride binding capacity than those containing sodium sulphate; this might be due to their different effects on OH^- ion concentration in the pore solution; sodium sulphate increased the alkalinity of pore solution whereas calcium sulphate decreased it; so sodium sulphate had little effect on the ratio of Cl^-/OH^- while calcium sulphate significantly increased the ratio.

A low concentration of chloride ion in the pore solution will not break down the passive film of steel [*Broomfield (1997)*]. There is a "chloride threshold" in terms of the chloride concentration or chloride/hydroxide ratio above which severe corrosion of steel in concrete will be induced. Table 2 lists some of the "chloride thresholds" reported in the literature. The typical threshold value is assumed to be in the range of 0.2~0.4% chloride ion by mass of cement.

Table 2. Chloride thresholds reported in literature

chloride concentration	**reference**
0.06~1% total chloride by mass of cement	*ACI 318-89*
0.1% total chloride by mass of dry concrete	*Stoltzner (1997)*
0.15% water soluble chloride ion by mass of cement	*Holden (1983), Popovics (1983)*
0.17~2.5% of chloride by mass of cement	*Glass (1995)*
0.2% acid-soluble chloride by weight of cement	*Clear (1973)*
0.2% mass of cement for reinforced concrete; 0.08% mass of cement for prestressed concrete	*ACI 222R-89*
0.4% total chloride by weight of cement	*Broomfield (1997),* *Building Research Establishment (1982)*
0.4~0.8% total chloride by weight of cement	*E.locke (1980)*
Cl^-/OH^- ratio	**reference**
0.29~0.3	*Diamond (1986)*
0.6	*Hausmann (1967)*

All the above "chloride thresholds" are not absolutely fixed, because the pH value, binding capacity of cement, moisture and oxygen, etc. can affect the thresholds [*Broomfield (1997), Tritthart (1989b), Blankvoll (1997), Pettersson (1993), Dhir (1994)*]. The laboratory determined "threshold" values do not bear much relationship with what are found in practice. Tritthart [*Tritthart (1989b)*] believed that there was no definite critical amount of chloride that could be applied to all the cases in practice, and found that the Cl/OH^- threshold could be higher when water/cement ratio was lower, implying that at low w/c ratio, a higher Cl^-/OH^- could be tolerated.

NaCl is a hygroscopic salt [*Haque (1995)*], and concretes with higher chloride contents retain more moisture at a given RH. Laboratory measurements [*Elkey (1995)*] have shown that the resistivity of concrete was reduced by 50% for a saturated concrete containing about 0.15% chloride by weight of dry concrete, compared to a chloride free concrete. Furthermore, it is interesting that the presence of chlorides in the concrete can cause a considerable reduction in the oxygen flux [*Hansson (1993)*].

4.6 Carbon Dioxide

Carbonation of concrete is another main cause of corrosion of steel reinforcement. Carbonation is a result of the reaction of carbon dioxide in the atmosphere with the hydroxides in the concrete

[*Broomfield (1997), Blankvoll (1997)*]. The carbonation process can be generally described as follows:

$$CO_2 + H_2O\ (pore\ solution) \rightarrow H_2CO_3 \qquad (5)$$

$$H_2CO3 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O \qquad (6)$$

This lowers the pH value of the pore solution. The corrosion reaction of steel in concrete is dramatically enhanced when the pH of the pore solution falls below 9.

Carbonation can affect the diffusion of chloride in concrete through changing the pore structure of concrete [*Patel (1985)*]. Ngala et al [*Ngala (1997)*] found a reduction of total porosity and a redistribution of pore sizes as a result of carbonation; the proportion of large pores increased; this trend was more significant for blended cements than OPC. In addition, the chloride binding capacity is decreased with carbonation due to the change of the cement gel into relatively coarse crystalline products and the decrease in the pH of pore solution.

4.7 Components of Concrete

Any factor that affects the pore solution and the porosity of concrete would affect the corrosion of steel in concrete. The types and quantities of binder, aggregate and w/c ratio can determine the performance of concrete to some extent. Workmanship and curing are other important factors that influence the corrosion process of steel in concrete. If these factors could be well controlled, the corrosion performance of reinforced structures would be much improved. Concrete formulation of the main components of concrete can be one of the effective approaches to enhance corrosion resistance of reinforced concrete [*Sennour (1994)*].

The ratio of water/cement (w/c) has a very significant influence on the porosity of concrete. A higher water/cement ratio can produce a higher porosity concrete which is easily penetrated by aggressive species. Steel in such a concrete is more easily corroded. The water/cement ratio in concrete has been founded to significantly influence the corrosion rate of steel in concrete; this influence was even more significant than the binder type [*Baweja*]. Most researchers [*Chang, Hawkins (1996)*] have reported greater corrosion current densities at higher water-cement ratios.

In addition, aggregates are usually inert to corrosion of reinforcement in most cases. However, it was found that the introduction of aggregates (sand particles) into cement paste could result in a higher transport coefficient of chloride ions [*Halamickova (1995)*]. This is because the porous transition zones formed at the aggregate-cement paste interfaces affect the pore size distribution. The alkali concentrations of pore solutions are normally not affected by the presence of aggregates [*Duchesne (1994)*], unless the aggregates are very reactive to alkali.

Blended cements have received considerable attention due to their improved durability performance in severe conditions. Appropriate cementitious material is a critical factor ensuring the durability of concrete construction in severe exposure conditions. In a potential monitoring experiment, blended cement concrete, compared with portland cement concrete of equal strength, took longer to reach the critical corrosion potential criterion for severe corrosion [*Baweja (1994), Baweja (1995)*]. Usually the influence of binder type is more significant in the medium-strength concrete in terms of initiation and propagation stages [*Guirguis (1994)*].

Researchers [*Polder (1996), Bijen (1993), Bamforth (1994a), Sagues (1997), Berke (1994), Chang (1997)*] found that blended cements containing blast furnace slag or fly ash and silica fume had improved durability in marine environment; their service life were estimated to be several times longer than the service life of plain portland cement concrete. Incorporation of silica fume in concrete reduces water absorption and permeability, thus water penetration, chloride and carbon dioxide diffusion become more difficult [*Loland (1981)*], which is beneficial to the corrosion resistance of steel in such concrete mixtures.

Fly ash blended cement is also one of the cements with improved durability performance. It was reported [*Hussain (1994)*] that corrosion initiation time for steel reinforcement in blended cement concrete containing 30% fly ash was about twice longer than that in the corresponding plain cement concrete; the OH^- concentration in pore solution of the fly ash blended cement was lower than that in the corresponding plain cement; unbound chlorides in pore solution could decrease with the partial replacement of cement by fly ash; 30% fly ash blending refined the distribution of pore size; the average pore radius was reduced from 240 to 166 Å; so fly ash blending reduced the permeability of concrete, and the chloride diffusivity was also reduced by about five fold. The electrical resistivity of concrete was increased nearly 2.2 times with the fly ash addition. Similar effects of fly ash on the binding capacity of chloride ions was also reported by Kayyali et al [*Kayyali (1992)*].

Oxygen diffusion in a silica fume concrete is about the same as in an ordinary portland cement based concrete, but the chloride diffusion will be greatly reduced when silica is added.

Some other studies [*Dhir (1993), Dhir (1992), Dhir (1994)*] revealed that the inclusion of pulverised fuel ash in concrete could also reduce the chloride diffusion rate. This might also be due to the change of concrete microstructure and pore solution chemistry. Dehghanian et al [*Dehghanian (1997)*] studied the influence of slag blended cement concrete on chloride diffusion rate; they concluded that blended cement concrete containing up to 30% slag and with a water-cement ratio of 0.45 did not affect the chloride diffusion rate at early age. However, the diffusion rate could be reduced with concrete age.

Ground granulated blastfurnace slag (GGBS) has a high chloride binding capacity, and is used to improve the resistance of concrete against chloride ingress. Its high chloride binding capacity is a result of the high aluminate level in GGBS which reduces the quantities of Friedel's salt [*Dhir (1996)*].

Some chemical additives in concrete have a detrimental effect on corrosion of steel in concrete. In particular, the additives containing chloride can act as catalysts and accelerate the localised corrosion. For example, the accelerator $CaCl_2$ has been well known for its potential adverse side effect on corrosion of steel.

Recently, latex modified concrete (LMC) has been widely used in the construction industry due to its superior performance and suitability for various special applications. Its corrosion resistance has also been examined [*Okba (1997)*] to be much better than the conventional concrete of almost the same strength level.

4.8 Concrete Resistivity

The electrical resistivities of hardened cement paste [*Gu (1992), McCarter (1988)*], mortar [*Page (1986), Hope (1985)*] and concrete [*Millard (1993), Gonzalez (1993)*] have been widely reported as significantly affecting the corrosion of reinforcement in concrete. Normally the electrical resistivity of concrete ranges form 10^0 to 10^7 Ωcm depending on the concrete composition and moisture content [*Fliz (1992), Gjorv (1977)*].

The resistivity of concrete is determined by the pore solution concentration, the microstructure of the concrete (pore size and its distribution), the moisture and salt content as well as the temperature. Variations of resistivity with temperature, pore solution and humidity have been investigated [*Hope (1985), Niklasson (1991)*]. Resistivity decreases as temperature increases; and the effect of temperature is approximately a 3% change in resistivity per 1°C [*Sellevold (1997)*].

Resistivity of concrete directly affects the ionic current flow, and consequently influences the galvanic corrosion activity. A concrete, which contains a high concentration of chloride and a relatively high level of moisture, usually corresponds to a low resistivity. Therefore, there is a relationship between the corrosivity and resistivity of concrete [*Hope (1985), Hope (1986), Alonso (1988)*]. Spellman [*Spellman (1973)*] was the first to suggest a relationship between resistivity of concrete and risk of corrosion. Later, some researchers [*Polder, Fliz (1992), Alonso (1988), Glass (1991), Lopez (1993)*] found an inverse linear relationship between resistivity and corrosion rate. In practice, some criteria have been established to correlate the measured resistivity of concrete with the possibility of corrosion of reinforcement in concrete (Table 3 and Table 4).

Table 3. Concrete resistivity criteria [*Vassie (1980)*]

Concrete resistivity (kΩcm)	Probability of corrosion
<5	corrosion almost certain
5~12	corrosion probably
>12	corrosion unlikely

Table 4. Relationship between resistivity and corrosivity of concrete

Corrosivity	Resistivity of concrete (kΩ.cm)	
	[*Broomfield (1993)*]	[*Langford (1987)*]
low corrosion rate	>100	>20
low to moderate corrosion rate	50-100	10-20
high corrosion rate	10-50	5-10
very high corrosion rate	<10	<5

However, in practice, galvanic corrosion is not the one and only process occurring in reinforced concrete structures. Resistivity of concrete has no direct relationship with the corrosion attacks other than the galvanic. Even for the galvanic corrosion, the contribution of resistivity of concrete is complicated [*Polder (1992)*]. Sometimes the decrease in resistivity is accompanied with the saturation of water in concrete which makes the transport of oxygen in concrete difficult. This may compensate the detrimental effect of the decrease of resistivity on the corrosion rate. Thus the above criteria can be misleading in some cases.

4.9 Thickness and Defects of Cover Concrete

The thickness of cover concrete determines the time for aggressive species to reach the steel rebar in concrete. Sometimes the service life of reinforced concrete structures can be extended greatly simply by increasing the thickness of the cover concrete [*British Standard Institute*]. The normal thickness for most structures is around 50 mm. However, not all parts of structures can strictly follow the designed cover thickness. Field studies [*Morgan (1982), Marosszeky (1987)*] showed that encroachments on specified cover did occur and were widespread; 62% of the buildings surveyed had cover thickness less than specified.

Compact and defect-free concrete tends to be resistant against corrosion of steel reinforcement [*Aarup (1996)*]. Unfortunately, there are no defect-free materials, and almost all the international codes of reinforced concrete designs are related with permissible crack widths. The detrimental effect of cracks in concrete on corrosion of the embedded reinforcement is obvious. Numerous studies were carried out to describe the reinforcement corrosion in the cracked zones. Some of them dealt with the chloride-induced corrosion of steel in the crack zone [*Okada (1980)*]. Cracks in concrete make the corrosion of reinforcement occur more readily than in uncracked concrete [*Ohno (1996)*]; anodic dissolution of steel can be facilitated in cracked concrete. It was believed

[*Raupach (1996)*] that two different corrosion mechanisms were theoretically possible for the corrosion of steel in the cracked regions:

1) the micro-cell corrosion; and
2) macro-cell corrosion (cracked zone as anodic area).

In the simulation studies [*Raupach (1996)*], it was shown that chloride induced corrosion in the cracked zone was related to the formation of macro-galvanic cells; steel in the cracked zone acted as an anode and steel between the cracks acted as a cathode; the thickness of cover concrete could affect the corrosion rate. Overall, the most important factor influencing the degree of macro cell corrosion in cracked concrete might be the water/cement ratio [*Ohno (1996)*]. However, Beeby [*Beeby (1978)*] found that there was no relationship between the width of crack and the corrosion rate. If there are passive and active cracks in multi-crack specimens, then the largest crack of the multi-crack beam tends to initiate corrosion first [*Suzuki (1990)*].

4.10 Temperature

Temperature can influence corrosion rate of reinforcement in concrete. All the processes involved in corrosion (i.e., anodic and cathodic electrochemical reactions, transport of aggressive species to steel surface, accumulation of corrosion products on the steel surface or departure from the interface of steel/concrete, and ionic flow through concrete) can be influenced by temperature. Increases in temperature will lead to increasing rates of all these processes, consequently an increase in corrosion rate. It was reported that two folds higher corrosion rate could be reached by only 10°C increase in temperature [*Shiessl (1990)*]. Tuutti [*Tuutti (1982)*] found that carbonated specimens had a logarithmic rise in corrosion rate with temperature from -20°C to around 30°C. The diffusion processes of species also strongly depend on temperature. A 10°C increase in temperature approximately doubles the diffusion coefficient [*Berke (1994)*]. At the lowest end of the temperature scale, below the freezing point of pore solution, ions can not move in the frozen pore solution, so corrosion of steel stops completely.

The accelerating effect of temperature on chemical reactions is well known, but its effect on concrete chemistry, which can affect corrosion of reinforcement corrosion, is not widely reported. Maslehuddin et al [*Maslehuddin (1996)*] investigated such an effect, and concluded that temperature significantly influenced the chloride binding capacity of cements; an appreciable increase in the chloride concentration in pore solution in chloride contaminated concrete was noticed when temperature was increased above 55°C. However, hydroxide concentration was found to decrease above this temperature [*Hussain (1993)*].

In field structures, the temperatures are not the same at different depths of cover concrete. The inner concrete or the reinforcement has a delayed response to the variation of environmental temperature. Liu et al [*Liu (1997)*] found a couple of hours delay in the temperature rise at the depth of 76 mm in cover concrete responding to an increase of the temperature of the surrounding environment; the difference between the ambient temperature and the concrete interior could be over 10°C.

5. Techniques for Laboratory and Field Studies

Many techniques have been used in laboratory studies and field surveys of corrosion of reinforcement in concrete. Generally, these techniques can be divided into two groups: electrochemical and non-electrochemical. Besides those, there are still conventional techniques for some special purposes.

5.1 Electrochemical Techniques

As corrosion of steel in concrete is basically an electrochemical process, electrochemical methods have been always regarded as the most powerful and reliable non-destructive techniques in laboratory and field measurements.

5.1.1 Half-cell Potential

Potential measurement is one of the simplest electrochemical techniques. Its principle is based on the assumption that the passive film breaks down on the steel surface where serious corrosion occurs, so the potential is much lower than that of the other non-corroded areas where the steel is protected by passive film.

An ASTM standard [*ASTM C867*] has been established to indicate corrosion probability in concrete structures based on the measured potential. The measurement of half-cell potential only requires a potential meter and a reference electrode. According to the measured potentials, the corrosion possibility can be estimated by the established criteria (Table 5).

Table 5. ASTM criterion for corrosion of steel in concrete [ASTM C867]

Measured Potential (mV/CSE)	Corrosion condition
>-200	low (10% risk of corrosion)
-200~-350	intermediate corrosion risk (uncertain)
<-350	high (90% risk of corrosion)

It must be understood that the above critera can only be used as a guide. Under certain situations, some criteria different from the ASTM might also be used to determine the corrosion possibility [*Carse (1990)*].

Normally, half-cell potential values can be obtained from readings made on the concrete surface, using a surface contacting reference electrode. Potential readings are usually recorded one by one on points on the concrete surface. However, for more rapid surveying, a wheel electrode measuring technique is also sometimes used [*Broomfield (1990)*].

Besides using the surface contacting reference electrode, half-cell potentials can also be measured by embedded reference electrodes. A comparison between the results gained by these two methods was provided by Videm [*Videm (1997)*]; the surface potentials obtained using the surface contact electrode were more positive than those monitored with the embedded reference electrodes. This might be mainly attributed to the "junction potential" [*Myrdal (1996)*] and galvanic corrosion current [*Videm (1997)*].

The half-cell potential mapping has been widely used [*Videm (1997)*] in the world, especially in USA. Some users who have used this technique both in the laboratory and in the field [*Fliz (1992), John (1987), Stratful (1975), Langford (1987)*] agree that this technique does indicate the existence of active corrosion sites in concrete.

In those investigations related to potential survey, most of the studied objects were conventionally reinforced concrete structures. However, Novokshchenov [*Novokshchenov (1997)*] extended the application of half-cell potential technique to prestressed bridge members; his study demonstrated good correlation between the half-cell potential and the results of other tests, particularly the visual examination on the prestressed concrete members.

The most attractive advantage of the half-cell potential technique is its simplicity. However, its readings can sometimes be misleading. There have been instances that an area has been deemed passive according to half-cell potential, but in fact active corrosion was occurring there [*Bebei (1986)*]. There are a number of reasons for such misleading results. First, from an electrochemical point of view, the relationship between corrosion rate and half-cell potential is not very strong, or in some sense there is no fixed relationship between them because of too many factors influencing the potential-current density relationship. Second, many factors can cause a misleading potential value. Very negative potential can be found in a water saturated concrete where there is no oxygen to initiate the corrosion or to keep the corrosion of steel reinforcement developing. Third, carbonation of the cover concrete can also induce a misleading potential value. At the carbonation front, the pH value changes from about 13 down to about 8. This leads to a great difference in the concentrations of most ions in the pore solutions in the carbonated and non carbonated layers. Therefore, a "junction potential" would be developed between these two layers which could give rise to a misleading result [*Bennett (1992)*]. Even wetting of the surface with tap water specified in the ASTM standard [*ASTM C867*] could cause a potential drift due to the development of the "junction potential" between the wet outer layer and the dry inner layer in cover concrete. The wetting of concrete surface during potential measurement could also bring about another problem, i.e. the wetting increases the electrical conductivity of the surface layer of concrete. The overall effect is a slight shifting of measured potential toward more positive at anodic sites and more negative at cathodic sites [*Bazzoni (1994)*]. Such an effect reduces the accuracy of potential measurement as an indicator for active corrosion. Fourth, "Membrane potential" may also have an influence on the half-cell potential measurement, especially when the half-cell potential is measured by a reference electrode on the surface of the concrete. The different concentrations of ions at the surface of the cover concrete and the interface between concrete and reinforcement might produce a significant membrane potential. It was reported that the "membrane potential" could be in the range of 20~45mV, if chloride ions were diffusing through this membrane [*Zhang (1997)*]. Fifth, stray currents also influence the measured half-cell potential readings [*Broomfield (1997)*]. This is a serious problem in the measurement of half-cell potential, as it results in instability. In addition to the above reasons, the measurement of half cell potential is sensitive to temperature variations. Different readings could be obtained at the same site due to changes of environmental temperature, whereas such changes do not reflect the actual shift of corrosion potential of steel reinforcement. The dependence of the potential of reference electrode, the junction potential, the membrane potential, the stray current, and the conductivity of concrete, on the temperature contributes to the shift.

Due to this multi-factor influence, it has been reported that there was no real correlation between half-cell potential and corrosion current density [*Broomfield (1994), Escalante (1990)*], corrosion states [*Cigna (1993)*] or polarisation resistance [*Oshiro (1992)*]. In fact, it has been specified in the ASTM standard [*ASTM C867*] that the standard is not applicable in some environments which include too dry or coated concrete surfaces, carbonated concrete, and steel rebar with metallic coating, etc.

In addition to the possible misleading results given by half-cell potential, the non-quantitative characteristic is another disadvantage of the half-cell potential technique. Half-cell potential only indicates the possibility of active corrosion, and the corresponding potential mapping can only indicate the possible site of active corrosion along reinforcement in a concrete structure. It can not provide more important information like corrosion rate of the reinforcement.

Efforts have been made to solve some of the problems in the half-cell potential measurement. It was claimed [*Grimaldi (1996)*] that corrosion state of steel embedded in a concrete saturated with water could be correctly assessed by measuring its half-cell potential using a reference electrode in a confined area where gas was induced. In order to overcome the problem arising from the current flowing in concrete, a method based on the lateral ohmic drop technique which was used in stray current corrosion and soil corrosion was introduced into the concrete corrosion system by Bertolini et al [*Bertolini (1997), Bazzoni (1997)*]. Another attempt to help provide more accurate locations of active corrosion sites was to combine potential mapping and resistivity distribution together [*Figg (1985), Gowers (1993)*]. Carse et al [*Carse (1990)*] empirically estimated the corrosion current by dividing the potential gradient by measured resistivity; calculated corrosion currents in excess of one μA was considered to indicate active corrosion. Also potential gradient (iso-potential contour map) was suggested as a better indicator for corrosion sites [*Clemena (1992)*]; in that technique, modification on the measurement space specified in the ASTM C867 also standard was suggested [*Clemena (1992)*]. It is certainly of significance to correlate corrosion rate with potential gradient or the ratio of potential gradient over concrete resistivity. However, more careful analysis should be applied to these results, and correlation with active corrosion ascertained.

5.1.2 Polarisation Resistance

Polarisation resistance technique is a very widely used electrochemical method. The attractive feature of the technique lies in the relationship between measured polarisation resistance and the corrosion rate of steel in concrete.

The relationship between polarisation resistance (Rp) and corrosion rate (Icorr) was first given by Stern-Gary equation, which is expressed as:

$$Icorr = B/Rp \qquad (7)$$

where B is a constant with a voltage unit.

Theoretically, B is determined by cathodic and anodic Tafel slopes bc and ba (the slopes of cathodic and anodic polarisation curves in Tafel linear regions) :

$$B = ba*bc/(ba+bc) \qquad (8)$$

So long as Rp is measured, Icorr can be estimated according to equation (7).

In concrete, the value of B is generally regarded within the range between 25mV to 52mV [*Aarup (1996),Alonso (1988), Gu (1996), Electrochemical Techniques for Corrosion*]. Even though values of B within this range have been widely used in both laboratory studies and field monitoring, it is better to know an actual constant B for an individual system to be studied.

Table 6. Relationship between Icorr and corrosion situation of steel in concrete

corrosion situation of steel	Icorr (μA/cm^2)	
	[*Broomfield (1993, 1994)*]	[*Clear (1989)*]
passive	<0.1	<0.2
low to moderate corrosion	0.1~0.5	0.2~1
moderate to high corrosion	0.5~1	1~10
high corrosion	>1	>10

Some criteria have been proposed [*Broomfield (1993), Broomfield (1994), Clear (1989)*] to relate a calculated Icorr with corrosion situation of steel in concrete (Table 6).

Rp can be measured by several methods including AC impedance spectroscopy (EIS), transient techniques, or potentiostatic/galvanostatic measurements [*Videm (1997)*]. However, linear polarisation technique is the most widely used in the field to determine Rp. This is because linear polarisation is less complicated and easier to operate than the others.

For linear polarisation technique, Rp can easily be obtained by the relationship:

$$Rp = \Delta E/\Delta I \qquad (9)$$

where ΔE is the amplitude of a linearly scanning potential and ΔI is the change of current responding to the linearly scanning potential. The polarisation potential range should be narrow enough to hold the assumption of linear system. In practice, a range of around ±10 mV is normally used.

Linear polarisation resistance techniques have been widely used in laboratory studies and field surveys. Gowers et al [*Gowers (1994)*] developed a programmable linear polarisation meter for on-site measurement. This made the linear polarisation resistance technique more widely applicable to the corrosion of steel reinforcement in concrete.

The main advantages of linear polarisation technique are:

1) Operation is relatively simple. Rp can easily be obtained by dividing the values of input and output signals (equation (9)).
2) As long as the parameter B would not change too much, which is true in many cases, the measured Rp could correctly reflect the change of corrosion rate of steel in the concrete system.
3) For a reinforced concrete system, if the parameter B is known, then corrosion rate of the system can be quantitatively determined.

However, linear polarisation measurement also has some limitations:

1) Theoretically, the measured Rp is the polarisation resistance against uniform corrosion. However in concrete, localised corrosion is also one of the main corrosion forms. So, in many cases, significant errors could be induced when we are calculating corrosion rate from the Rp, measured from a non-uniformly corroded structure. For example, pit initiation can significantly affect the result [*Provebio (1996)*], leading a variation of the measured Rp with time and underestimating the residual service life of structures [*Provebio (1995)*].
2) Stern-Gary equation (7) is valid for an uniformly corroding system at corrosion potential. Unfortunately, galvanic corrosion is unavoidable in a large reinforced concrete structure. So, during polarisation measurement, the measured section of rebar might be polarised by other sections of the rebar due to a galvanic effect. In this case, the Stern-Gary equation would not be applicable and significant errors might result if it is still used in the calculation of corrosion rate.
3) The estimate of B might introduce a theoretical error in the calculation of corrosion rate [*Andrade (1995)*]. In some cases, B can vary beyond the range of 25mV~52mV. For example, if steel reinforcement is in passive state, then the anodic Tafel slope (ba) for the passivated steel could be regarded as infinite. Meanwhile, if cover concrete is saturated with water, then the cathodic Tafel slope (bc) should also be close to infinity, because the cathodic process is under the control of oxygen diffusion through the water saturated cover concrete. Hence, in this case the value of B could be close to infinity, according to equation (8).
4) Polarisation degree can be affected when linear polarisation is carried out on a steel whose corrosion potential keeps changing with time. Unstable corrosion potential results in unstable linear polarisation and gives rise to an unstable Rp reading with a significant error.
5) When concrete is dry, the IR drop across cover concrete would be very high. The concrete resistance Rc will be combined into the measured result and induce a significant error in the measured Rp [*Escalante (1990)*], if the measurement equipment has not been specially designed to eliminate the IR drop effect.

6) Since a long time is needed for reinforced concrete to respond to an applied signal, Rp will be dependent on the scanning rate of the applied polarisation signal. The plot of current versus potential can exhibit very large variations with different scanning rates [*Videm (1997)*]. A slower scanning rate may give a higher measured Rp, while a faster scanning rate could result in a misleading Rp. It has been reported that the interfacial capacitance of steel in concrete can be up to 1000μF/cm^2, and a steady state could not be observed even for a measurement period of 11 hours [*Videm (1997)*]. So, Gonzalez et al [*Gonzalez (1985)*], based on their laboratory results recommend a compromised scanning rate of 10mV/min.

7) For field concrete structures, the true measured area of the reinforcement bars in concrete is unknown. An estimate of the measured area could result in a significant error in Rp calculation [*Fliz (1992)*].

Most of these limitations are shared by most of the other electrochemical techniques including EIS, transient techniques, polarisation curve, galvanic probe, etc. Attempts are being made to solve these problems.

In the linear polarisation method, the polarised surface area is related to the distribution of polarisation current density along the reinforcement in concrete. A few approaches have been tried to estimate the polarised surface area in the laboratory and in the field [*Andrade (1997)*]. One of the methods is to measure the attenuation of potential with the distance away from the measured site [*Feliu (1996)*]. However this method is not very accurate, and too many factors can affect the results. The heterogeneity of concrete and the interference of stray current could seriously distort the attenuation of potential. Also, from the measured potential to the estimated distribution of current density is not a step free of theoretical error. It requires necessary simplifications and assumptions in theoretical modelling which would introduce errors to the estimated result.

In addition to the measurement of attenuation of potential, the polarised area might be estimated through some mathematical treatment. By modelling the steel-concrete system using a transmission-line equivalent circuit, the dispersion of electric signals can be mathematically treated, and Rp calculated [*Feliu (1988a)*, *Feliu (1989)*]. Matsuoka et al [*Matsuoka (1990)*], using a finite element method, estimated the distribution of equi-potential lines around a reinforcement in a concrete beam. They concluded that the distribution of current density changed very little while the ratio of Rp/ρ (where ρ is concrete resistivity) changed over a wide range. Based on a similar finite-element-analysis, Shehgal et al [*Sehgal (1992)*] found that only half of the surface of the rebar, facing the counter electrode was polarised. Feliu et al [*Feliu (1988)*] found that the critical length that could be reached by an applied signal was dependent on the ratio of concrete resistance to polarisation resistance of reinforcing steel. They [*Feliu (1995)*] developed a theoretical expression for the ratio of maximum to minimum current densities at the opposite points on the surface of a cylindrical steel rebar. The ratio was found to be dependent on the cylinder radius of reinforcing bar and the distance between reinforcing bar and counter plane electrode. Increases in the ratio of Rp/ρ could promote the uniform distribution of current density over the rebar in concrete. A more detailed analysis of the distribution of current density along rebar was carried out by Flis et al [*Fliz (1992)*] whose interest was in the confinement effect of the "guard ring". After all, the results of those studies using the transmission-line model strongly depend on some basic assumptions. A uniform and continuous concrete matrix is always assumed in all the models. Unfortunately, the field concrete structures are not really continuous and uniform media.

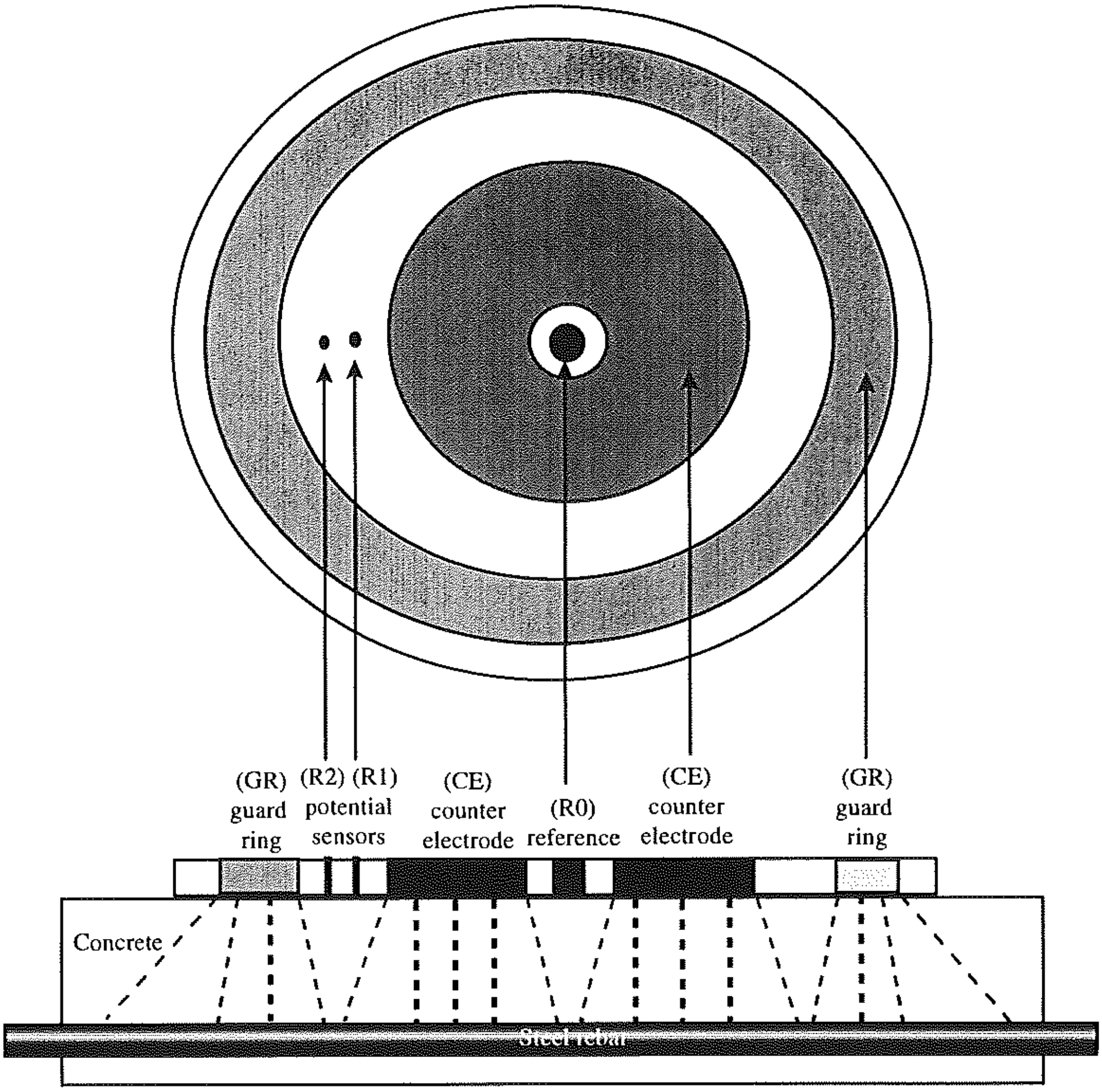

Figure 2. Schematic diagram for guard ring sensor

Instead of the estimate or measurement of non-uniform distribution of current density along rebar in concrete, the best idea might be to control the distribution of current density and make it uniform along the rebar. There are two techniques that can provide a more uniform distribution of current density along the steel rebar in concrete. The first one is the use of large sized counter electrodes. By using different sizes of counter electrodes to obtain different Rps, the value of Rp of an appropriate size of counter electrode can be extrapolated [*Gonzalez (1991)*]. However, in practical operation, the use of large counter electrodes is not very feasible. The second technique, which is more popular, is the use of a "guard ring" to confine the distribution of current density [*Feliu (1990), Feliu (1990a), Goto (1992), Feliu (1993)*]. The principle of the "guard ring" is schematically demonstrated in Figure 2. It was found [*Fliz (1992)*] that decreasing the spacing between the central counter electrode and the "guard ring" or increasing the width of the "guard ring" could improve the confinement effect; resistivity of concrete could significantly affect the confinement. Currently, a commercial "guard ring" has been developed and is being used. So far, the "guard ring" seems to be the most successful technique regarding the estimate of polarised area of rebar in concrete.

However, recently unsatisfactory application of the "guard ring" has been reported by Videm et al [*Videm (1997b)*]. They found that the corrosion rates determined by the "guard ring" instrument were not in good agreement with visual inspection; the results were even worse than galvanostatic charging technique withont "guard ring" confinement. Liu et al [*Liu (1997)*] also demonstrated that the average of annual corrosion rate was better estimated by an unguarded linear polarisation method rather than the "guarded ring" method; the "guard ring" underestimated the real corrosion rate (weight loss) of reinforcement by almost one order of magnitude.

5.1.3 Polarisation Curves

Compared with linear polarisation resistance, polarisation curve technique provides more information over a wide potential range. The extra information provided by polarisation curve is quite useful in the determination of corrosion rate, explanation of corrosion mechanism, and prediction of corrosion behaviour when corrosion potential changes. For example, by extrapolation of Tafel regions or by fitting of the polarisation curve, corrosion rate and corrosion kinetic parameters (ba and bc) can be obtained; from the anodic branch of the polarisation curve, passivation, transpassivation, pitting corrosion and active dissolution of steel can be shown, which can tell us what kind of dissolution process would occur if corrosion potential is shifted positively due to the change of environment; and from the cathodic branch of the polarisation curve, the diffusion rate of oxygen through concrete can be estimated.

Currently, the polarisation curve method is mainly used in laboratory studies. Vogelsang et al [*Vogelsang (1996)*], using galvanodynamic and potentiodynamic polarisation cycling techniques, investigated the effects of some accelerators on corrosion of steel in mortar; the measured results were strongly dependent on the scanning rates. Potentiodynamic scans were also carried out by Bertocci [*Bertocci (1997)*] to supplement the information obtained from electrochemical impedance spectroscopy (EIS); in his measurements, the scanning rates varied from 1 to 0.1 mV/s and the potential range was from +100 mV to -700 mV vs SCE. Based on the polarisation curve, the Tafel slopes ba and bc, the constant B, and corrosion current density (Icorr) were estimated. Gonzalez et al [*Gonzalez (1995)*] measured the polarisation curves of steel in chloride-free and 2% chloride containing concrete specimens; their results showed that there was no difference in the cathodic branches of the polarisation curves, but the anodic branches of the polarisation curve for the specimen with 2% chloride was much higher than that in the concrete specimen free of chloride. Polarisation curves were also employed to investigate the effect of binder type on corrosion of steel embedded in a cement paste [*Cao (1994)*]; in the experiment, a standard scanning rate, 0.17 mV/s as used in most aqueous solution systems, was used, scanning from -1250 mV/SCE to +800 mV/SCE.

The effect of salt penetration into concrete on corrosion process was investigated using polarisation curve [*Dehghanian (1982)*]; the potential of steel was initially kept at -1300 mV (-1600mV/CSE) in comparison with a Mo/MoO_3 electrode for 10 min, then was scanned forward to 2000mV at 0.28mV/s; in the measured polarisation curves, no clear diffusion limited current density was observed at the cathodic region for the specimen even after 300 days of immersion in NaCl solutions. With an IR compensation technique, Wheat et al [*Wheat (1985)*] potentiodynamically scanned a steel bar in concrete from 250mV below corrosion potential up to 1200mV at 0.28 mV/s; the measured polarisation curves had similar shapes as what Dehghanian [*Dehghanian (1982)*] obtained; the curves and corrosion potentials both were found to be shifting with time.

The most obvious advantage of polarisation curve measurement is its informative results, particularly the corrosion rate, obtained either by Tafel extrapolation or curve fitting. In the calculation of corrosion rate, parameter B is no longer required.

However, the polarisation curve technique is not as widely used as the polarisation resistance method in the corrosion study of field concrete structures. The reasons for the limited application of the polarisation curve technique in the field are:

1) In polarisation curve measurement, IR drop is even higher than that in the linear polarisation measurement due to a wider potential range and a higher polarisation current density at anodic or cathodic region. A high IR drop could seriously distort a real polarisation curve and submerge the Tafel regions. In this case, determination of corrosion rate and kinetic parameters is difficult. In an attempt to estimate the error caused by the IR drop effect, a finite-difference computer model was used to predict the shape of polarisation curves for a reinforced concrete system by Sagues et al [*Sagues (1992)*]; they found that the apparent Tafel slopes were several times greater than the actual values. The IR compensation techniques of some modern equipment are not advanced enough to solve such a high IR drop in a concrete system.

2) A high polarisation current density could disturb the surface state of steel and the concrete condition in the vicinity of steel surface, and make them quite different from their natural states. Therefore, corrosion situation of steel during and after measurement might not be the same as what it was be before the polarisation. In this case false information might be obtained.

3) Strong polarisation can result in re-distributions of charge, reaction reagents and corrosion products at the interface of steel and concrete. However, in concrete the redistribution processes are very slow. To obtain a steady polarisation curve, a very slow scanning rate should be used, which might take a few days to complete a curve in some cases. For example, a scanning rate of 0.005mV/s might be desirable for a measurement on a passive rebar [*Videm (1997b)*]. This is impossible for use in the field.

How to overcome these limitations of polarisation curve measurement seems to be a prerequisite for the application of this technique in the field. The first limitation mentioned above might be easily overcome with the rapid development of potentiostat techniques. However, the second and third shortcomings seem to be more obstinate. To develop a rapid and less disturbance polarisation curve method should be an attractive direction in the field of corrosion of reinforcement in concrete.

5.1.4 Electrochemical Impedance Spectroscopy (EIS)

AC electrochemical impedance spectroscopy (EIS) is one of the most powerful electrochemical techniques that can provide sufficient information on corrosion process of steel in concrete.

The principle of AC impedance is based on the following fact. Corrosion of steel in concrete usually consists of several different individual processes. The different processes have different rates at a given electrode potential. Their responses to a changing potential are also different. A process can generate a significant current responding to the changing potential only if the rate of the process matches the changing rate of the applied potential. Therefore, if a series of small AC potentials with different frequencies, from 0 to ∞, are applied to a reinforced concrete structure, then the responses of all the individual processes involved in corrosion of steel in concrete would be strongly reflected in different frequency ranges. By analysing these responses in frequency domain, the individual processes may be deduced and studied.

For simplicity of analysis, some equivalent circuits are often used to simulate the electrochemical corrosion processes of steel in concrete. The most widely used equivalent circuit is a parallel connection of an interface (double layer) capacitance (Cdl) and a polarisation resistance Rp [*Bertocci (1997)*].

Beside the simplest circuit, more complicated equivalent circuits have also been proposed and used which contain at least 2 or 3 time constants [*Electricity Research Institute, Hachani (1994), Sagoe-Crentsil (1992), Bertocci (1997), John (1981), Keddam (1994), Keddam (1997), Feliu (1985), Gu (1996)*]. Concrete resistance, interface capacitance of concrete matrix/pore solution, resistance and capacitance of surface film on rebar, are usually reflected in those equivalent circuits with 2 or 3 time constants.

Models based on transmission line system were also developed to simulate corrosion processes of steel in concrete structures. The typical circuit for the transmission-line mode is illustrated in Figure 3. The element Zi in the figure represents the impedance of concrete in a unit volume; Yj is the electrochemical impedance of the interface between concrete and steel reinforcement per unit length. In these models, the uneven distribution of current density in concrete was specifically considered [*Macdonald (1987), Macdonald (1991a), Macdonald (1991), Feliu (1988), Feliu (1989)*].

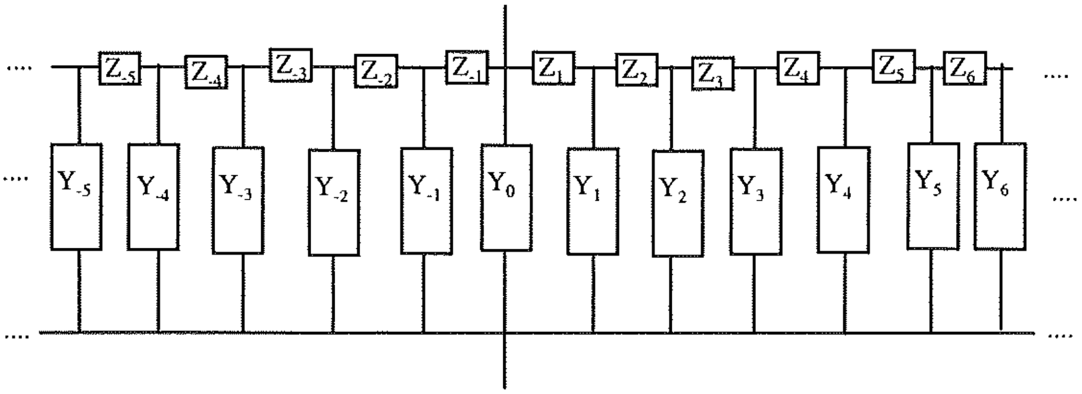

Figure 3. Typical equivalent circuit of transmission line model for steel in concrete

The typical electrochemical impedance spectroscopy in Nyquist plot for a reinforced concrete can be divided into 3 ranges [*Keddam (1997)*]. Figure 4 schematically presents the Nyquist plot of electrochemical impedance spectroscopy (EIS) of steel in concrete. This is not a real EIS. It combines some possible different spectroscopies in one diagram. Sometimes the high frequency or low frequency range may be missed in an experimental EIS due to the frequency limitation of equipment. Also either none or more than one capacitive loops may be obtained in the experiment, depending on the corrosion processes of reinforcement.

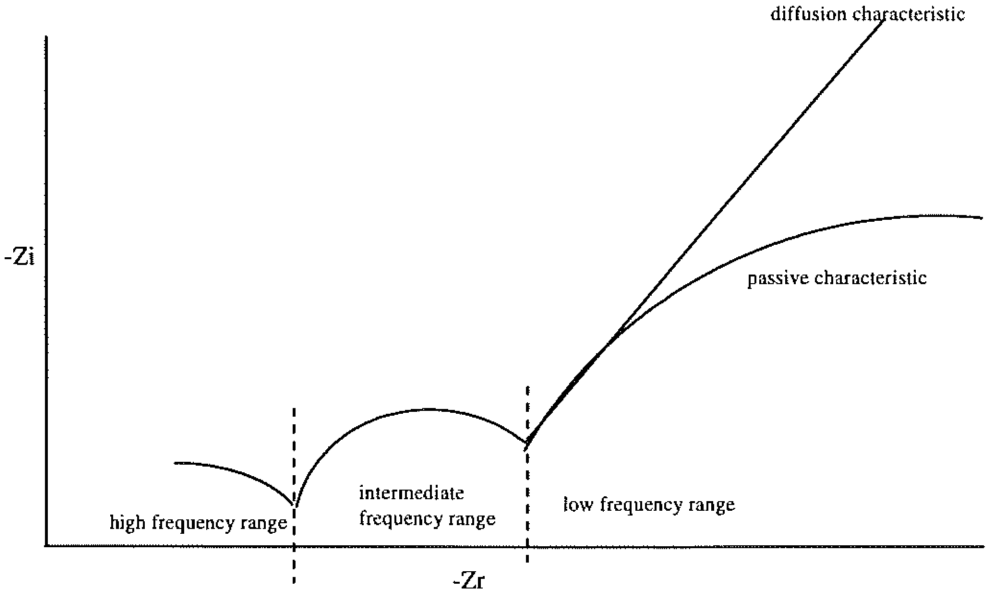

Figure 4. Typical Nyquist plot of electrochemical impedance spectroscopy (EIS) of steel in concrete

At high frequency, there is a capacitive loop which is generally believed to be associated with the resistance of concrete and distributive capacitance of concrete pore walls [*Monenor (1993), Niklasson (1991) Gu (1996)*]. However, some researchers [*John (1981), Newton (1987)*] have attributed this high frequency loop to the interfacial layer between steel and concrete which is either a passive film or corrosion products. In recent years, the studies of the high frequency region have been carried out mainly with an interest in the physical characteristics of microstructure. It was found [*Christensen (1994)*] that the experimentally obtained dielectric constant of concrete was much higher than the theoretically expected value; so a dielectric amplification factor was employed to explain the abnormal phenomenon. However, Keddam et al [*Keddam (1997)*] believed that the deviation was due to a combination of two different time constants, one corresponding to the paste bulk and the other one to the paste/electrode interface.

At low frequency range, there are two kinds of spectroscopic behaviour: diffusion controlled characteristic and passivation characteristic. It was found that if steel was suffering from corrosion attack, the diffusion characteristic with a linear region whose slope was about 1 would appear at the low frequency range in the Nyquist plot [*Sagoe-Crentsil (1992)*]; in contrast, when spectroscopy showed a very large capacitive loop at the low frequency as that exhibited by a passive electrode system, the steel was usually free from corrosion attack. Macdonald et al [*Macdonald (1991)*] particularly paid attention to the ultra-low frequency EIS. By using the EIS information from the low frequency region, they detected, located and characterised the corroding steel rebar in concrete before damage became evident. Thompson et al [*Thompson (1988), Thompson (1991)*] also found that, when corrosion was developing, EIS spectrum was dominated by Warburg impedance behaviour; when there was no corrosion if steel rebar was cathodically protected, then EIS was represented by a single capacitive loop. The diffusion characteristic in EIS at low frequency region was usually ascribed to the diffusion of oxygen in concrete [*Sagoe-Crentsil (1992), Thompson (1991)*].

At intermediate frequency range, different spectroscopies were reported. One capacitive loop in this frequency range was usually measured, but sometimes two capacitive loops were also observed. The EIS spectroscopy at this frequency range was generally related to the processes within the surface film or corrosion product layer on rebar [*Sagoe-Crentsil (1992), Hachani (1992), Hachani (1994a), Wenger (1990)*]. Hachani et al [*Hachani (1994)*] found that the EIS had two parts; they corresponded to the dispersion arising from the concrete inhomogeneity and the dispersion of the corrosion location at the metal surface.

Many researchers have used EIS to investigate corrosion processes or to estimate corrosion rates of steel in cement paste, mortar or concrete [*Feliu (1988), Wenger (1990), John (1981), Lay (1985), Wenger (1990), Monenor (1993), Sagoe-Crentsil (1992), Andrade (1984), Hope (1986), Lay (1985)*]. It was found in laboratory tests [*Sagoe-Crentsil (1992)*] that at stages, the corrosion impedance spectra were dominated by charge transfer controlled kinetics, but gradually after prolonged ageing, EIS was governed by a diffusion controlled process. Bertocci [*Bertocci (1997)*] used EIS to evaluate corrosion inhibitors in highway deicers; it was found that EIS, especially at low frequency range, was sensitive to the presence of corrosion on reinforcing rebar in concrete structures. D.D.Macdonald et al [*Macdonald (1991)*] detected corrosion areas of rebar in concrete by scanning a reference electrode on the concrete surface; based on the different characteristics shown by EIS; they assessed the corrosion situation of steel in the specimen, and found that the most sensitive parameter for detecting and locating corrosion on reinforcing bars in a concrete specimen was the maximum value of the phase angle and the corresponding frequency at which the maximum phase angle appeared. Mansfeld et al [*Mansfeld (1991)*] also reported that EIS was a very sensitive indicator for the initiation of corrosion of reinforced concrete; and it could provide details of corrosion behaviour of the electrodes undergoing localised corrosion in concrete. In addition, Roberge et al [*Roberge (1994)*] used EIS to monitor on-line general and localised corrosion in the field test. Keddam et al[*Keddam (1994)*] used an equivalent circuit with two randle circuits in parallel to model macro-cell corrosion behaviour of rebars placed in parallel in concrete.

In summary, the most successful aspect of EIS lies in its strong ability to reveal individual corrosion processes and its limited disturbance to the reinforced concrete system being measured. As only very small amplitude of signals are input to reinforced concrete specimen, there is no need to consider the change of surface state of steel and the redistribution of reaction reagents and corrosion products during measurement. As spectroscopy in high, intermediate and low frequency regions is closely related to interface charging, growth and breakdown of passive film, and diffusion processes in a reinforced concrete, the EIS would be very informative in the study of corrosion mechanisms.

However, it must be pointed that at present, the application of EIS is still mainly limited to laboratory studies, because of following shortcomings:

1) The equipment used for the EIS measurement is too complicated. It basically consists of a signal generator, a potentiostat, and a frequency analyser. So currently it is hard to compact all these units into a very small and light weight box for field use.

2) Similar to polarisation curve, EIS is also a time-consuming technique, especially at the low frequency range. Sometimes, it takes one day to obtain a data point at a low frequency. This is obviously inpractical in the field test. Furthermore, during a long period of measurement, the drifting of corrosion potential and changes of environmental factors can induce a significant error in the EIS measured results.

3) In EIS measurement, the polarised surface area of steel in concrete is frequency dependent [*Macdonald (1991)*]. This means that the estimate of corrosion rate of steel in concrete will be difficult for the uncertain polarised area. Also, the interpretation of EIS spectroscopy would also become more difficult for the uncertain studied area. So far, all the developed EIS theories are based on a constant polarised electrode area. It is still unknown what contribution a frequency dependent area will have to the measured EIS. Thus there is less confidence to relate the measured EIS with corrosion process without considering the influence of a changing polarised surface area.

4) Even though EIS can provide much information about corrosion state of steel in concrete, it fails to directly provide a corrosion rate. In the estimation of corrosion rate, the Stern-Gary equation (7) still needs to be used. EIS measurement can provide much information like polarisation resistance and interface capacitance, but it can not provide the parameter B, which has to be estimated. The estimate of B can certainly introduce theoretical errors in the calculation of the corrosion rate.

In a reinforced concrete system, EIS is actually a result converted from linear responses of steel in concrete stimulated by a series of special potential signals. If the stimulating signal is too strong, non-linear responses of the steel could be provoked. In this case some other information about corrosion of steel in concrete could be involved in the harmonic responses. The most significant harmony is the second harmonic response. It was reported that Tafel slopes could be obtained from the second harmonic analysis [*Dawson (1990)*]. Even though the harmonic analysis has been promising, there is still no successful application reported in the field.

5.1.5 Transient Techniques

Transient techniques are generally performed as described below: a small amplitude of potential, current density or a certain amount of charge is suddenly applied to the steel in concrete, and immediately the response of current density or potential of the steel is recorded as a function of time. According to different forms of input signals, transient techniques can be classified into potential step (potentiostatic pulse) [*Rodriguez (1994), Feliu (1986), Barnett (1984)*], current step (galvanostatic pulse) [*Rodriguez (1994), Ijsseling (1986), Elsener (1983), Videm (1997), Videm (1997a)*] and coulostatic pulse [*Rodriguez (1994a), Rodriguez (1994)*]. Even though galvanostatic polarisation requires a longer time due to a much larger time constant involved in its response decay than potentiostatic [*Gonzalez (1985)*], it is still most widely used today [*Elsener (1993),* *Elsener (1994), Rodriguez (1994), Mietz (1993)*], and has shown some promise in determining the corrosion risk of steel in concrete [*Newton (1987), Elsener (1990)*].

Theoretically, transient techniques are almost equivalent to EIS. The only difference between them is that the electrochemical response of steel in concrete is analysed in time domain for transient techniques but in the frequency domain for EIS. The response signals in time domain and frequency domain actually can be transformed to each other through Laplace transformation. Newton et al [*Newton (1987)*] used the galvanostatic pulse technique to investigate corrosion of steel in concrete; in their analysis, the transient results were transformed into EIS information.

Equivalent circuits are also frequently employed to analyse the measured transient results. The most widely used equivalent circuit is parallel-connected CR with only one time-constant [*Gonzalez (1985), Elsener (1997), Millard (1995)*]. However, sometimes the measured transient signal decays could be better analysed based on multi-time-constant circuits [*Rodriguez (1994a), Millard (1995), Gowers (1996), Videm (1997)*]. Newton et al [*Newton (1987)*] compared the results obtained from alkaline chloride gel and solution with that obtained from mortar. They found two time constants for the corroding steel in the gel and solution while three time constants in the mortar; the extra time constant being ascribed to the dielectric characteristics of the mortar.

A transient response to a step or a pulse input can be expressed in exponent terms if the system studied is under electrochemical control [*Song (1996), Song (1994)*]. However, a transient current decay responding to a potentiostatic input was reported to be a square root function of time [*Newton (1987), Videm (1997)*]. This might be due to the diffusion process in concrete which controlled the corrosion process in that case. Glass et al [*Glass (1993)*] came up with an empirical function which was claimed to be able to more accurately fit a galvanostatic transient process. From their curve fitting, the time constants were found to be inversely proportional to the corrosion rate of steel.

The most outstanding feature of transient techniques is that their transient results are as informative as EIS but obtained in a much shorter time than EIS. It was claimed [*Rodriguez (1994a), Millard (1995)*] that a transient technique gave a better resolution of time constants, but the measurement time required was much shorter. However, all the transient techniques have shortcomings too:

1) The equipment used for transient measurement is relatively complicated compared with a polarisation resistance instrument. It basically consists of a signal generator, a potentiostat, and an accurate recorder. The recorder should have very high recording speed and sufficient memory storage.

2) Compared with EIS, transient techniques are much faster. However, if a concrete corrosion system is controlled by a diffusion process, then the response which mainly involves the diffusion is a very slow process. So a considerable lengthy time might be required to obtain a complete transient result.

3) Generally, transient techniques are very sensitive to noise interference. In field tests, the noise sources can be stray current, temperature fluctuation, traffic disturbance and magnetic waves, etc. Some of these noises may overwhelm the true transient signal, especially in the late stage of a transient decay process when the transient signal has become relatively weak.

4) Similar to EIS, during a transient measurement the polarised area on the surface of steel in concrete can vary with time. At the later stage of a transient process, the response signal comes from a relatively larger surface area of steel in the concrete; while at the beginning, perhaps only a limited surface area of steel, close to the counter electrode, has contribution to the transient response.

5) Transient techniques can not directly measure the corrosion rate of steel in concrete. The direct results of these techniques are transient decay curves based on which some electrochemical parameters like polarisation resistance and interface capacitance can be calculated. The corrosion rate also needs to be calculated, using the Stern-Gary equation, based on the calculated polarisation resistance, and an estimated value of parameter B.

Among the above disadvantages, the feature of being sensitive to noise is very problematic, and the time dependence of the polarised area of the steel surface seems impossible to overcome.

Transient techniques are currently mainly used in laboratory studies. Only a few applications in the field have been reported [*Klinghoffer (1995), Mietz (1993), Millard (1995)*].

5.1.6 Electrochemical Noise (EN)

Pitting corrosion of passivated metal is a sudden collapse process of the passive film after an incubation period. The pit at its initial stage is not stable, and may disappear due to repassivation of steel. The collapse of the passive film and the repassivation of steel can lead to shift in the corrosion potential, or fluctuation of current density at a given potential. The fluctuation of potential or current density in relation to the corresponding electrochemical corrosion process is defined as "Electrochemical Noise" (EN). By recording and analysing the EN, the corrosion process which generates the EN can be monitored and investigated.

Experiments carried out by Tsukada et al [*Tsukada (1997)*] indicated that EN could be used as a monitoring method to study crevice corrosion of the steels coated by repair materials, and chloride-induced pitting corrosion of steel in concrete. Hardon et al [*Hardon (1988)*] monitored the fluctuation of corrosion potential of steels embedded in a number of different forms of reinforced concrete specimens; after analysing the EN generated from these reinforced concrete specimens, they found that the standard deviation of the potential noise was related to the corrosion rate obtained independently by linear polarisation. Under well controlled conditions it was possible to demonstrate a reproducible correlation between the standard deviation of the potential noise and the measured corrosion rate. This provided a basis for the estimation of local corrosion rate of steel in a large concrete slab.

The most attractive feature of EN is its non-disturbance to reinforced concrete system during measurement. The measurement is carried out at the natural state of the specimen.

However, EN is very sensitive to environmental interference. All the environmental factors that cause interference noise to the transient measurement mentioned earlier can also interfere with the EN results. This makes the application of EN in the field very difficult as true corrosion noise can easily be overwhelmed by false noise. It was found that [*Videm (1997)*] the field structure usually acted as a large antenna, and picked up potential noises caused by environments other than the corrosion process of steel in the structure. The false noise "picked up" in this manner could overshadow the signals generated by corrosion. Another factor which impedes the development of EN might be the difficulty in establishment of a theoretical model to correlate the measured EN with the corrosion process of steel in concrete that generates it. Different electrochemical mechanisms may produce a similar EN spectrum. So from the EN spectrum, it is hard to deduce back to the true kinetics of corrosion of reinforced concrete.

5.1.7 Galvanic Probe

The galvanic probe was originally developed to simulate and measure galvanic corrosion of steel in concrete. Its principle has been discussed in section 3.3.2. It usually consists of a galvanic couple of different types of metallic materials [*Gonzalez (1995), Beeby (1985), Hawkins (1996), Elsener (1996)*], or a galvanic couple of the same kind of steels but in different concrete environments [*Keddam (1994), ASTM G109, Shiessl (1993), Gulikers (1996a), Andrade (1992),* *Hunkeler (1992)*]. These galvanic couples are usually embedded in concrete structures for long term monitoring.

The galvanic probe consisting of the same kind of steel is more reasonable as it directly simulates the galvanic corrosion of steel in concrete, but it might be less sensitive than the type consisting of different kinds of metallic materials. The galvanic couple which consists of different kinds of materials actually measures the galvanic current between the different materials in concrete. If the anode material of the galvanic probe is the same as the reinforcement, then the measured galvanic current is in effect an anodic polarisation current of reinforcement at an unknown and variable potential. So it is relatively easy to have a significant output reading when such a probe is used in reinforced concrete structures. However, the measured result is likely to be misleading, because corrosion reaction on the couple could be different from that of the steel reinforcement.

Compared with linear polarisation, galvanic probe is much easier to operate and the required equipment is also very simple, so it has been widely used in laboratory studies, and long term monitoring in the field. It was reported [*Elsener (1996)*] that the measured galvanic current (Ig) agreed well with the polarisation resistance results, which theoretically is only responsible for uniform corrosion.

The galvanic probe does not actually measure corrosion rate of steel at its natural corrosion potential. Only when the galvanic effect is strong, the galvanic corrosion rate (Ig) is roughly equal to the dissolution rate of anode. However, if corrosion of reinforcement in concrete is not mainly due to galvanic corrosion, then the corrosion rate of the reinforcement might be underestimated by using this technique [*Berke (1990), Berke (1990a)*].

According to equation (4), concrete resistance can considerably affect the value of Ig. Therefore, an appropriate and representative arrangement of anode and cathode and, a reasonable distance between them, in relation to a real corrosion situation, would be extremely important in the installation of a galvanic probe.

Recently, two galvanic probes named "anode ladder" and "multiring electrode" were developed by Schiessl et al; the former has been installed in a newly built bridge in Denmark [*Schiessl (1992), Shiessl (1993)*]. These probes can be used to monitor the progress of carbonation front or the ingress of chloride.

As one of the simplest electrochemical techniques, galvanic probe can provide important information on galvanic corrosion rate of reinforcement. However, the probe needs to be embedded in concrete before measurement. This means that this technique might only be suitable for use in concrete structures under construction. For an existing structure, the installation of the probe would be destructive; the material used for embedding the probe would not be the same as the original concrete, so the results obtained by the probe in such an environment could be misleading.

5.2 Physical Techniques

Besides the above electrochemical techniques, physical, non-electrochemical techniques have been widely used for determination of defects in reinforced concrete structures. The physical techniques include visual inspection, stress wave techniques, magnetic methods, radiopgraphy, thermography, and radar, etc.

Visual inspection is to give a first indication of damage. It can be carried out with human eye and brain, aided with camera. The exact nature of some defects can not be determined by visual inspection. Normally, corrosion of reinforcement could be detected if associated cover spalling or rust staining are visible. Visual inspection is usually followed up by other tests to confirm the source and cause of the deterioration [*Broomfield (1997)*]. One of the most commonly used stress wave techniques is the sounding method which can determine the existence and extent of delaminations [*Manning (1988)*]. ASTM [*ASTM D4580*] provides an industry standard method for measuring delamination by sounding. However, stress wave is not sensitive to corrosion of steel in concrete. The magnetic method is commonly used to locate the size and depth of reinforcement in concrete [*Tomsett (1987)*]. It is expected that section loss of reinforcement due to corrosion can also be measured. Radiographical methods include X-ray and gamma-ray radiation [*Manning (1988)*]. The gamma-ray has been made portable and used in the field. The X-ray currently was mainly used in the laboratory, but recently portable equipment of X-ray has also beeu developed and used in the field. They are good at detecting large defects in concrete, but whether they can also detect the corrosion state of steel in concrete has not been established. Infrared thermography (IRT) can be used to determine the size and location of delaminations which affect the temperature patterns of the concrete surface. Experiments have shown IRT to be a fast and reliable method [*Hagen (1984), Holt (1980)*]. However, IRT could not provide direct information on corrosion of steel. It is doubtful where the radar method can successfully detect the corrosion of steel.

All these techniques were originally designed to determine defects in concrete structures, rather than to detect corrosion of reinforcement. A nationwide survey about the application of these techniques was carried out in USA [*Gannon (1992)*]; from that survey, it seemed that no single technique has been very successful so far.

5.3 Measurement of Some Conventional Parameters

Some factors, such as moisture, oxygen and chloride contents, as well as resistivity and carbonation of concrete are crucial to the corrosion of steel in concrete. In laboratory studies or field surveys, these parameters are usually measured at the time of corrosion measurement.

5.3.1 Moisture

Moisture in concrete is a prerequisite for the occurrence of corrosion of steel, so that corrosion of reinforcement can not occur in a very dry concrete. Moisture provides the electrolyte essential for the electrochemical corrosion of steel in concrete. So, monitoring and measuring the moisture content in concrete is of great significance.

The moisture content in concrete can be described in several ways [*Nilsson (1997)*]: moisture content per volume, moisture content in percentage by mass of dry material, and degree of capillary saturation.

Several methods have been developed to determine the moisture content of concrete. Nilsson [*Nilsson (1997)*] summarised some moisture monitoring probes. Currently, electrical methods through resistivity measurements [*McCarter (1995), Hunkeler (1996)*] are widely used to detect the moisture in concrete both in the laboratory and in the field [*Bungey (1989)*]. Such techniques can measure absolute moisture content through measuring dielectric constant and dissipation factor with two conductive plates placed in parallel across a concrete member. The accuracy has been reported to be ± 0.5% [*Bungey (1989)*]. Also, the relative humidity (RH) can be measured by sealing a probe in a hole in concrete. In this way, RH ranging between 10 to 100% could be measured. In addition, a technique, based on neutron emission and used in measuring the moisture of soil, was also employed in concrete. This method measures the moisture through the determination of hydrogen in water, and is believed to be a good technique for the determination of moisture in surface layers of concrete [*Bungey (1989)*].

5.3.2 Oxygen

The existence of oxygen in the pore solution provides the main driving force for the corrosion of steel in concrete. Without oxygen, the corrosion rate would be too low to be of concern for an uncarbonated concrete.

The measurement of oxygen transport is based on an electrochemical method [*Vennesland (1997), Gjorv (1986), Videm (1997)*] that involves the application of a constant negative potential to an embedded electrode; the oxygen transport through the concrete being recorded as an electrical current which is equal to the rate of oxygen reduction at the electrode.

5.3.3 Chloride Analysis

The chloride ion is a major factor responsible for the corrosion of steel in reinforced concrete structures. The determination of chloride level of the concrete is essential to the diagnosis and prediction of corrosion of steel in concrete.

Most of the chloride measurement techniques are destructive, involving sampling and dissolution of concrete powder in acid. The measured result is termed as the acid-soluble or total chloride in concrete.

The following methods have been used to measure the total chloride content in concrete [*Hearld (1993), Grantham (1993), AASHTO T260-84, Larsen (1997)*]: neutron-gamma ray [*Rhodes (1977), Livingston (1986) Rhodes (1980)*]; X-ray fluorescence [*Provebio (1997)*]; quantab chloride titrator strips, and Argentometric digital titration [*Building Research Station (1977)*]; specific ion probes [*James Instruments, Inc.*], etc. Potentiaometric titration (AASHTO T260-84) is now a standard method to determine chloride content in concrete, but it is time consuming and expensive, and is mainly used in the laboratory. Quantab strip and specific ion electrodes can be easily used in the field. The specific ion electrode technique was reported to have a high accuracy [*Hearld (1993)*], and offers the convenience of chloride measurement in the field. The widely used field test kits for chloride measurement are provided by James instruments Inc and Germann Instruments Inc. However, it was found [*Jackson (1997)*] that even though these kits were very convenient, the test results should be treated with caution; a correction factor of 1.67 was suggested to be applied to the measured results.

For the measurement of free chloride, techniques which are termed as "expression" and "extraction" have been used [*Arya (1990a), Byfors (1986), Duchesne (1994), AASHTO T260-84, ASTM D1411, Larsen (1997), Xu (1997), Hussain (1994)*].

The "expression" is actually such a process that a very high compressive pressure is applied to the concrete sample to "squeeze" or "express" out the pore solution from the concrete sample. It is difficult to use on a very dry and very dense (w/c<0.4) concrete sample. The "expression" is also a method to prepare the pore solution samples for analysis [*Burchler (1996)*]. However, the chloride concentrations in the expressed pore fluids from concretes submerged in sea water were occasionally found to be higher than that of the surrounding sea water [*Nagataki (1993)*]. This might be due to the complexity of the various forms of chloride in the pore solution rather than due to the lack of reliability of the "expression" method.

Leaching (or water extraction) was also used for the analysis of free chloride [*Arya (1990a)*]. The chloride was extracted from concrete into a chloride free water through the leaching effect. However, leaching is a very slow process and the concrete sample needs to be crushed. Dhir et al [*Dhir (1994)*] used a similar technique to analyse water soluble chlorides; the concrete powder sample was boiled for 5 minutes in deionised water and cooled down, then analysed with ion-selective electrode. Unfortunately, the crushing may release some fresh unhydrated cement and introduce some error. Furthermore, the chloride binding capacity of cement paste depends on the concentration of solution, so the concentration of chloride in the greatly diluted solution obtained by the extraction method could not reflect the real chloride concentration in the original pore solution.

Kemp et al [*Kemp (1992)*] came up with a method based on electro-extraction of chlorides from concrete cores or from the powdered concrete obtained at various depths of concrete. This method appeared to be able to provide good chloride profiles. Recently, another method similar to the carbonation spraying technique was used by Otsuki et al [*Otsuki*] to determine the penetration of chloride in concrete; by spraying a freshly broken concrete surface with 0.1 N $AgNO_3$ solution, a color change could indicate the soluble chloride concentration higher than 0.15% by weight of cement.

An in-situ method to measure chloride concentration would be of great value for research and for on site monitoring. Zimmermann et al [*Zimmermann (1997)*] constructed a sensor that could measure the free chloride concentration in the pore solution of mortar in the laboratory and in the field; in their design, Ag/AgCl electrode was cast into mortar blocks in the laboratory, and into concrete cores taken from concrete structures; the electrodes were arranged at different depths. Climent-Llorca et al [*Climent-Llorca (1996)*] also investigated the possibility of using Ag/AgCl electrode as in-situ sensors of chloride concentration in concrete; their results showed that the electrodes could sensitively respond to a change of Cl^- concentration; the stability of potential reading of the electrode depended on the chloride concentration and was good enough to allow the electrode to be used as chloride content sensor in short-term tests. However, this method is only suitable for use in a structure under construction. For an already built structure, it is a destructive method.

5.3.4 Carbonation Analysis

Carbonation is usually measured by spraying a phenolphthalein indicator solution on a freshly exposed concrete surface [*Parrott (1987)*]. The best indicator solution for maximum contrast of the pink colouration is phenolphthalein (1g) in a solution (100ml) with alcohol:water ≥ 1:1 [*Building Research Establishment (1981)*]. This is a practical, accurate and reliable technique. However, it is a destructive method as it needs freshly cut cores.

5.3.5 Resistivity of Concrete

Resistivity of concrete reflects the difficulty for the current to flow in the ionic path of a galvanic corrosion cell. So resistivity of concrete can affect the activity of galvanic corrosion, and it is usually measured as an indicator of corrosivity of concrete [*Hunkeler (1997)*].

The most commonly used technique in practice is a four-probe meter based on the Wenner principle. Sometimes, a less accurate two-probe technique is also used.

The four probe system requires a probe spacing larger than the maximum aggregate size to minimise the error caused by the aggregates in concrete. The "short circuit" effect caused by reinforcement can also give rise to a misleading result. In addition, the heterogeneity of concrete, which is inconsistent with the homogeneity assumption for the resistivity measurement, is another error source [*Millard (1991)*]. Millard [*Millard (1991)*] systematically discussed the advantages and drawbacks of different measurements of concrete resistivity as well as the influences of environmental conditions and specimen configuration; he concluded that the measurement of concrete resistivity promised to be a valuable tool when used in conjunction with potential mapping. The four point resistivity method enabled the concrete resistivity measurement to be taken quickly, accurately and without causing damage to the in-situ reinforced concrete structures. If the electrode spacing and location were properly selected, specimen geometry had less influence on resistivity measurement.

More recently, a disc probe was developed [*Newman (1966), Feliu (1988), Broomfield (1997)*] which was based on Newman's work[*Newman (1966)*]. The disk-like electrode is used on the concrete surface as a probe, and the reinforcement network in concrete acts as a counter electrode. It mainly measures the resistivity of the cover concrete. A commercial polarisation resistance instrument [*Gecor 06*] has used this technique in its sensor.

6. Acceleration and Simulation

Corrosion of steel in concrete usually takes several years to be initiated, which is too long for laboratory studies. Thus laboratory acceleration of corrosion processes is necessary. Moreover, in the field, due to the simultaneous change of the environmental factors, it is impossible to investigate in detail the influences of these individual factors on the corrosion of reinforcement. Laboratory simulation is an essential approach that enables us to distinguish the roles of the individual factors.

6.1 Specimens Preparation

In the laboratory, reinforced concrete specimens used for experimentation are usually small. So, some factors may not be possible to study in the small specimens, such as the macro cell effect, stress effect, uneven distribution of moisture and temperature, and those that might be important to corrosion of steel in a large concrete structure. For example, in a field concrete structure, there is always a certain level of stress in concrete elements because of internal restraint to deformation. The stress can cause micro cracks in the concrete which in turn increase its permeability. This factor was taken into account by Taheri et al [*Taheri (1997)*]; their results confirmed the contribution of stress to the rate of chloride penetration.

Usually, in the laboratory testing for simplicity, only one steel rebar is embedded as working electrode in concrete, but sometimes, more than one are cast into a concrete specimen, and they act as working electrodes, or serve as reference electrode, counter electrode, or galvanic probe.

The basic constituents used in the manufacture of test specimens are ordinary portland cement, sand, coarse aggregate, water and sometimes some special additives, are mixed at a certain ratio, and cast and cured according to some standard methods. Sometimes, in order to investigate the effects of some particular constituents or manufacturing parameters, specially controlled ratios of those constituents or parameters are used. For some fundamental investigations, cement paste or mortar was often used to simplify the system studied.

6.2 Probe Installation

In some studies, specially designed probes are usually installed in the concrete specimens, such as temperature, humidity, or conductivity sensors, galvanic corrosion couple, and reference electrode [*Macdonald (1991)*], etc.

Probes consisting of working electrode, reference electrode and counter electrode have often been embedded into concrete specimens to monitor corrosion of steel rebar [*Tamura (1996)*]. Fisher et al [*Fishcher (1984)*] used some electrode probes, which were embedded at different depths in concrete, to study the effects of added silica on the corrosion behavior of steel; the probe consisted of a central reference electrode, a middle ring of working electrode and an outer ring of counter electrode. Probes embedded at different depths or different sites in concrete with different levels of chloride contamination have also been employed in the laboratory to monitor corrosion behaviour [*Gulikers (1996), Raupach (1996), Thompson (1991)*]. Recently, a new specimen configuration was used by Thompson et al [*Thompson (1997)*], where the working electrode, a metal disk, was cast at the bottom of the cylindrical mortar specimen, which was then ponded.

The reference electrodes used in concrete should be of long durability, stable and alkaline-proof. Some electrodes have been tried in the laboratory and the field, including manganese dioxide, molybdenum oxide, graphite, lead, Zn, silver/silver chloride, copper/copper sulphate, and mercury/mercury oxide, calomel chloride electrodes [*Videm (1997), Gonzalez (1992), Dehghanian (1981), Locke (1978), Dehghanian (1982), Myrdal (1995)*]. The potential of manganese dioxide is independent of the environment in the concrete, but it can be affected by pH due to the liquid junction potentials in its porous plug. The potential of lead is determined by the corrosion of lead, so it is sensitive to the surrounding environment. Graphite electrodes are sensitive to oxygen level, because the oxygen redoxidisation is the main reaction on it. The Ag/AgCl has good prospects for use in concrete as an embeddable reference electrode [*Locke (1979)*]. It has a stable potential in concrete, which is a function of chloride ion concentration in the concrete. The reversibility of mercury/mercury oxide electrode is comparable to that of the Ag/AgCl electrode in simulating or pore solutions, but it is not as sensitive to chloride ions as the latter. It is not sensitive to temperature changes either [*Gonzalez (1992)*]. Molybdenum/molybdenum oxide electrode has also been reported to be good for use in concrete [*Locke (1979)*].

6.3 Simulation and Acceleration

In the study of corrosion mechanisms, steel is simply immersed in simulated pore solutions or specially designed solutions, and various electrochemical measurements are carried out.

Various solutions have been used for laboratory tests [*Bertocci (1997)*]. The most widely used media are simulated pore solutions ($0.6MKOH+0.2MNaOH+0.001MCa(OH)_2$) [*Romirez (1990)*], saturated $Ca(OH)_2$ solution [*Hausmann (1967), Andrade (1997), Baweja*], and NaCl solutions [*Wheat (1985), Dehghanian (1982), Sagoe-Crentsil (1992)*]. Some tests were also carried out in a flowing sea water according to the ASTM standard D1141-52 [*Cigna (1993)*].

However, the difference in the corrosion behaviour of steel in simulated solution and in concrete may be significant [*Raharinaivo (1992), Romirez (1990)*]. In the simulated solution, the transport of oxygen to steel surface through the solution is relatively difficult but the departure of corrosion products in the solution is relatively easy; whereas in concrete the situation is reversed, i.e. relatively easy transport of oxygen but relatively difficult removal of corrosion products. Therefore, conclusions reached based on the results from simulated solutions may be misleading with respect to real concrete.

A recent approach to achieve a better simulation result was the use of a "sand box" [*Bennett (1993)*], which could, to some extent, simulate the difference in the transport processes of oxygen and corrosion products in concrete. Another attempt to better simulate the corrosion environment in concrete was made by Raharinaivo [*Raharinaivo (1992)*], in which steel wire specimens were wrapped in porous polyvinyldience fluoride sheets and placed in solutions equivalent to the cement pore waters of various ages polluted with chlorides. They found that the size of the pores of the sheets influenced polarisation curves.

For a more realistic simulation and acceleration, concrete, mortar or cement paste specimens with embedded steel rebars are often used in the laboratory. The reinforced specimens could be completely submerged, half immersed, or only placed in a controlled atmosphere.

To simulate the ingress of chloride into concrete, a diffusion cell test is usually employed [*Ushiyama (1974), Page (1981), Dehghanian (1997)*]; a thin slice of cement, mortar or concrete is used to separate two cell compartments, one of which contains chloride solution and the other only a blank solution, initially without any chloride ions at all. The increase in the chloride concentration in the cell initially free from it is monitored. When a steady state of the chloride ion flow is reached through the thin slice of cement or concrete sample, the diffusion coefficient of chloride can be calculated according to Fick's first law:

$$J = -D\,(C_1 - C_2)\,/\,x \qquad (10)$$

where J is the flow of chloride through the thin slice, D is the diffusion coefficient of chloride, C_1 and C_2 are the concentrations of chloride in each side of the slice after the steady diffusion has been reached, and x is the thickness of the slice.

Besides the acceleration of chloride induced-corrosion in the laboratory, chambers with controlled carbon dioxide atmosphere were also used to accelerate corrosion through accelerated carbonation process [*Sagoe-Crentsil (1992)*].

In all the above studies, the acceleration effects can only be exerted through increasing the levels of aggressive factors in the simulating media, such as temperature, humidity, chloride concentration, and carbon dioxide pressure. For example, in a European standard [*prEN (1995)*], the immersion test is set at 40°C so that the test duration can be shortened to a few months; In Denmark, a chloride concentration of 165g/L is recommended to greatly shorten testing duration [*Nordtest (1995)*].

It has been found that alternate application of two different aggressive environmental conditions to a reinforced concrete specimen could lead to more severe corrosion of steel than when individual conditions are applied separately. In practice, the corrosion damage in marine substructure tends to be the most severe in a region typically up to 0.5m to 2m above the high-tide mark [*Sagues (1991)*] where the structure is experiencing wetting and drying cycles, i.e. the splash zone. This finding has now been employed as a laboratory acceleration technique to assess corrosion performance of reinforced concrete. The widely used accelerated cycling tests include drying/wetting [*Mangat (1994), Gulikers (1992), Tomosawa (1992)*], low/high temperatures [*Hawkins (1996)*] and drying/wetting/temperature changes [*Bazant (1979a)*].

Electric fields can accelerate the migration of chloride in concrete. In some laboratory tests [*Whiting (1981), Whiting (1991)*], an electric field has been applied across a concrete slice to speed up the ingress of chloride. Typically, the concrete specimen, separates two electrolyte compartments, with a strong electric field applied by anodic and cathodic electrodes in the electrolytes [*Detwiler (1991), Hussain (1994), Page (1981), ASTM C1202-97, Andrade 1996)*]. In this case, the different permeabilities of different concrete specimens to chloride ions can be compared by measuring the flow of electrical charge through the concrete slice. Based on this principle, standard tests [*AASHTO T277-83, ASTM C1202-97*] have been developed to assess the resistance of concrete against chloride penetration. Problems associated with the accelerated chloride diffusion cell caused by IR drop and polarisation of anode and cathode in solution have been addressed by some authors [*Andrade (1994), Streicher (1995), McGrath (1996)*]. They suggested that extra reference electrodes be inserted in the electrolyte compartments to monitor the IR drop and the polarisation of anode and cathode, so that the true potential across the concrete sample could be determined.

The *ASTM C1202-97* test method has received extensive criticism because the current indicator (charge passed through the samples) does not really reflect the chloride flow in concrete [*Whiting*]. It is the sum of the charge flows carried by all the ions, including chloride ion, in concrete. The measured current flow is dependent on the pore solution chemistry and is influenced by temperature [*Feldman, Cao (1996)*]. It was found [*Chang*] that the ASTM C1202-97 exaggerated the impact of secondary cementitious materials; the correlation coefficient (R^2) between the test results measured by cyclic chloride ponding and ASTM C1202 was only 0.59. This appears to be due to the fact that the pore solution of concretes containing SCMs has a much lower ionic concentration compared to that of plain concrete, and thereby are less conductive to electric currents.

To correct the unfavourable aspects of the ASTM C1202, Dhir et al [*Dhir (1990a)*] monitored the flow rate of chloride ions through a diffusion cell until a steady state flow was reached, based on which they calculated the diffusion coefficient of chloride according to Fick's first law. Obviously, the calculated result is not a true diffusion coefficient, but only an index related to the applied electrical field. An improvement was later made by Gautefall et al [*Gautefall (1995)*], in whose analysis the flow of chloride in the accelerated test was completely ascribed to the driving force of the electrical field applied to the system. Recently, an alternating current was employed instead of a DC current in a test method [*Zhao (1998)*] which is otherwise quite similar to ASTM C1202; it was claimed that the new method saved testing time compared with the ASTM C1202 standard; they set up specifications for concrete permeability as measured by alternating current. However, the test principle has not really been improved in this measurement. Resistance (or conductance) is also used as the indicator of permeability.

Theoretically, for a chloride flow simultaneously driven by concentration gradient and electrical field, the chloride diffusion coefficients can be calculated through the electrical field accelerating test [*Sergi (1992)*]. The diffusion coefficient of chloride can be obtained either from the steady state chloride flux [*Dhir (1990), Detwiler (1991), Andrade (1993), Zhang (1994)*], or from the initial non-steady state penetration [*Detwiler (1991), Halamickova (1995)*]. Andrade et al [*Andrade (1993), Andrade (1994)*], using Nerst-Pank and Nerst-Einstein equations, developed a theory for the calculation of diffusion coefficient under electric field and presented solutions for the diffusion coefficient and chloride profile in concrete. They found [*Andrade (1996)*] that the diffusion coefficient of chloride increased with the decrease of the chloride content in tested specimens.

Similar to the electric field accelerating tests, anodic polarisation was also employed as an acceleration method for corrosion of steel in concrete. Sometimes [*Okba (1997), Al-Tayyib (1990), Detwiler (1991)*], concrete cylinders with embedded steel rebars are immersed to half height in a 15% NaCl solution at room temperature, and an anodic DC potential is applied to the steel bar through a cathode steel plate in the NaCl solution. The current flowing through the rebar is recorded as a function of time, and the specimen is monitored periodically by visual inspection to see how long it takes to crack due to the corrosion of the reinforcing bar. Similar accelerated tests have also been conducted by several authors [*Andrade (1990), Heidersbach (1991)*] who applied a constant anodic current to the reinforcements in concrete and measured the time lapse until the appearance of the first crack. Gonzalez et al [*Gonzalez (1997)*] prepared some mortar slabs with a counter electrode in the middle and one steel anode on each side of the counter electrode. A current density of $10\mu A/cm^2$ was applied to the two anodic electrodes while the specimens were exposed to a relative humidity of 100% or immersed completely in water. They found that a few tens of micrometers of corrosion penetration could give rise to cracking in the specimens. The accelerated corrosion tests seem to be successful in laboratory studies, and standards have been established based on potentiostatic and galvanostatic polarisation [*prEN 480 Part XXX, prEN 480 Part YYY*]. It was found [*Jarratt-Knock (1996)*] that the galvanostatic method was the more sensitive of the two methods.

7. Prediction of Service Life of Reinforced Concrete Structures

Prediction of service life is always complicated and difficult in most research and engineering fields. For reinforced concrete, it is even more difficult, because the corrosion mechanisms of the steel in concrete and the influences of environmental factors are not well known. Even though great efforts have been made in this regard in the past few decades, so far successful predictions are rarely reported or still need to be confirmed by long term tests.

7.1 General Model for the Deterioration of Reinforced Concrete Structure

Generally speaking, the deterioration of reinforced concrete with time can be illustrated as in Figure 5.

The deterioration of reinforced concrete structures can be generally defined as a two-phase process [*Schiessl (1987), Broomfield (1995), Blankvoll (1997)*]: initiation and propagation. In the first stage, the diffusion of CO_2 and carbonation of concrete, or the ingress of chloride and transport of chlorides to the surface of steel reinforcement through the cover concrete are the main processes. In the second stage the corrosion of steel in concrete is activated, and from then on the corrosion will develop further with time, which may finally lead to cracking and spalling of the cover concrete if corrosion products are built up on the surface of the steel. In practice, the transition from stage 1 to stage 2 is hard to distinguish during the deterioration of reinforced concrete structure.

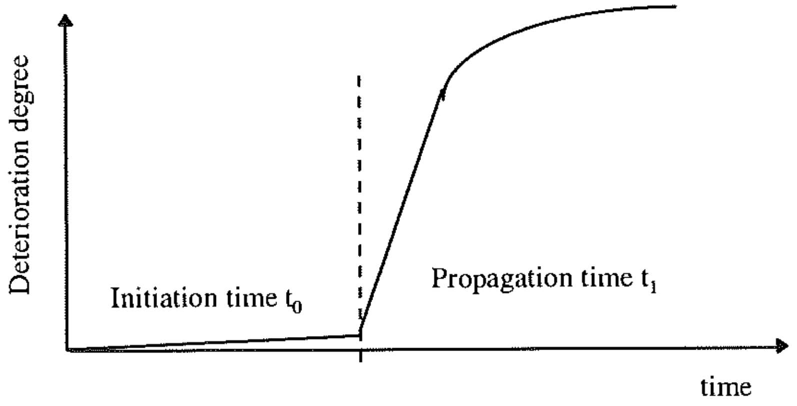

Figure 5. Deterioration curve of reinforced concrete due to corrosion of reinforcement

In the first stage, the carbonation of concrete or the ingress of chloride is generally regarded as a diffusion phenomenon, but the initiation time (t_0) for the carbonation-induced corrosion or the chloride-induced corrosion is different. The ingress of chloride is faster than the carbonation process. That is why most studies are more concerned about the chloride-induced corrosion of reinforced concrete structures.

7.2 Corrosion Development

After the corrosion of reinforcement is triggered, ie, at the second stage, the corrosion rate normally decreases gradually if concrete and environmental factors do not change dramatically. This is due to the formation of corrosion products on the surface of the reinforcement. It was found that corrosion rate decreased rapidly in the first year after the initiation of corrosion and then tended to reach a near constant value [*Liu (1997)*]. However, the corrosion of reinforcement can change the concrete parameters. In some cases the cover concrete might spall off due to the accumulated corrosion products at the interface between the steel and the concrete. This could dramatically accelerate the corrosion rate. In practical cases, it is quite difficult to tell whether the corrosion rate is slowing down or increasing with time.

Compared with the first stage, relatively little research associated with the second stage has been done to deal with the service life of concrete structures. The possible reason might be that, once a reinforced concrete structure gets into the second stage, the corrosion of steel is expected to proceed at a high rate. This means that the damage risk of structure in this case is much higher than that in the first stage. Therefore, repairing the damage and eliminating the potential risk have become more important and urgent than the prediction of service life. Another reason might be the uncertainty of the development of the second stage. In most cases, it is hard to tell whether the corrosion rate of reinforcement in concrete would always increase, decrease or keep constant with time, as it depends on many factors. So, the prediction of the second stage is even more difficult than that of the first stage.

In the second stage of deterioration of reinforced concrete structures, it is also difficult to predict cracking and spalling rates from an instantaneous corrosion rate measured. Due to the dynamic nature of concrete and environmental exposure conditions, the corrosion of steel in concrete is highly dependent on many factors which are changing with time. Simple extrapolation based on the assumption that the measured corrosion rate at a certain time is the average rate throughout the service life of a structure is obviously inaccurate [*Broomfield (1993)*].

As corrosion of reinforcement could eventually cause spalling or cracking of the cover concrete, which is easily visualised and identified, the relationship between the spalling or cracking of concrete and the corrosion states of the reinforcement is of interest and significance for the prediction of the second stage of the deterioration of reinforced concrete. Various efforts have been made to estimate the amount of corroded rebar that can cause spalling of the cover concrete. It was found that cracking can be induced by less than 0.1 mm of steel section loss [*Broomfield (1997)*]. Certainly, the distribution pattern of corrosion products, the ability of concrete to accommodate stress, the geometry of rebar distribution in concrete and rebar diameter can affect the above result. It is obvious that the risks of damage to rebars affected by uniform and localised corrosion are quite different, even if their final mass losses might be the same. So, different observations were often obtained by different researchers on the relationship between the spalling of concrete and the amount of corroded steel. Clemena et al [*Clemena, Clemena (1992)*] found that the corrosion rate of rebar had a reasonable correlation with the metal loss of rebar, and that the threshold of metal loss of rebar that initiated delamination in concrete was about 3~6% by mass of metal. Rodriguez and Gonzalez et al [*Rodriguez (1994), Gonzalez (1997)*] found in laboratory tests that the critical section loss of metal to cause cracking and spalling was 15~40 μm. A higher corrosion penetration depth of around 100μm had previously been proposed to initiate cracking [*Grimes (1979), Andrade (1993)*]. Liu [*Liu (1996)*] even suggested the following function to predict the time (t_{corr}) to the initiation of cracking of concrete:

$$t_{corr} = W^2/(2k) \tag{11}$$

where

$$k = 9.11\ (1/\alpha)\ Icorr \tag{12}$$

where W is the mass of rust products and α is a constant. This expression for the time to start cracking is actually closely related to the corrosion rate of reinforcement in concrete.

In addition, Clear [*Clear (1989)*] found a very simple and broad relationship between corrosion rate and time required for corrosion development (Table 7).

Table 7. Measured corrosion rate and time for corrosion developing[*Clear (1989)*]

corrosion rate (μA/cm^2)	time for corrosion developing (year)
0.2~1	10~15
1~10	2~10
>10	<2

It clearly shows that the larger the corrosion rate, the shorter the period for corrosion development. Researcher [*Weyers (1994)*] tried to relate the observed spalling, cracking and delamination to the remaining service life of existing bridges. It was found that about 4% of cracking, spalling and delamination of a concrete element corresponded to an end of functional service life of the element. A condition index S was given by Purvis et al [*Purvis (1994)*] which was determined by several parameters like chloride concentration above the "threshold", percentage of surface with hidden delaminations, and percentage of surface with visible spalling. It was suggested that the condition index should not exceed 45%; otherwise the safety of a structure should be questioned. Bazant [*Bazant (1979), Bazant (1979a)*] developed a physical-mathematical model to determine the time required for the initiation of cracking in concrete due to chloride-induced corrosion, based on a steady state of corrosion rate. He also found that the time to the start of cracking was a function of corrosion rate, cover depth, and mechanical properties of concrete. Among these, corrosion rate was the most significant parameter in determining the incubation time of cracking of cover concrete.

For field concrete structures, it is sometimes hard to determine which stage they are at when they are inspected. In some cases, an estimate based on experience might be very useful. Despite classifying the initiation and activation stages, empirical determination of the time when distress of reinforced concrete will occur has been proposed. For example, Clear [*Clear (1976)*] found that the time, T (year), for the first cracking to be detected could be expressed as:

$$T=[(0.052\, d^{1.22}\, t^{0.21})/(Z^{0.24}\, P)]^{0.83} \qquad (13)$$

where Z was the surface chloride concentration in percentage by mass of concrete; d was the depth of cover in millimeter; t was the age in years when Z was measured; and P was the water/cement ratio. Other similar expressions have also been proposed [*Purvis (1992)*]. However, there is lack of comparison and evidence as to which model is more appropriate and whether the empirically based models can be applied to all structures.

7.3 Chloride Penetration Profile

A great deal of research work has been carried out on the first stage of the deterioration of reinforced concrete in order to predict the corrosion behaviour before the reinforcement starts to corrode. The ingress of chloride or the carbonation of the cover concrete in the first stage is the key step leading to the observed damage of most affected structures. Browne [*Browne (1982)*] assumed that the corrosion-free life of a structure was the time for chlorides to reach a critical concentration at the surface of reinforcement. Chloride ingress is more complicated than the carbonation process. It is less uniform across the cover concrete, and there is no such clear chloride "front" as in the case of the carbonation "front".

Chloride can penetrate into concrete and reach the surface of steel through diffusion, suction, capillary movement or electrical migration, etc. The chloride transport in concrete can be greatly affected by the mechanisms other than diffusion. Mechanisms such as hydroxide leaching, osmotic pressure, hydraulic flow suction and filtering [*Volkwein (1993)*], and other membrane effects may all affect the chloride transport through the concrete pores. The penetration of chloride into a few centimeters of the outer cover concrete is initially dependent upon capillary suction, but the ingress of chloride ion into a greater depth would mainly be governed by long term diffusion [*Bamforth (1990), Bamforth (1994)*]. On a dry surface the uptake of chloride ion is mainly due to absorption; the chloride containing solution is absorbed into empty micro-cracks and pore spaces, and then penetrates further by capillary suction [*Goto (1981a)*]. If the surface is wet, the initial entry is likely to be by permeation or diffusion.

In a concrete structure the ingress of chloride is very complicated and might be governed by a combination of several mechanisms. Figure 6 is a schematic illustration of some possible transport processes in a sea wall. Because of the combined contribution of different transport mechanisms, in the sea wall [*Concrete Society Discussion Document (1996)*], the deepest penetration of Cl^- was found at about 1~2 metres above sea level, and the highest Cl^- concentration was detected at the surface layer in the wall about 8 metres above the sea level.

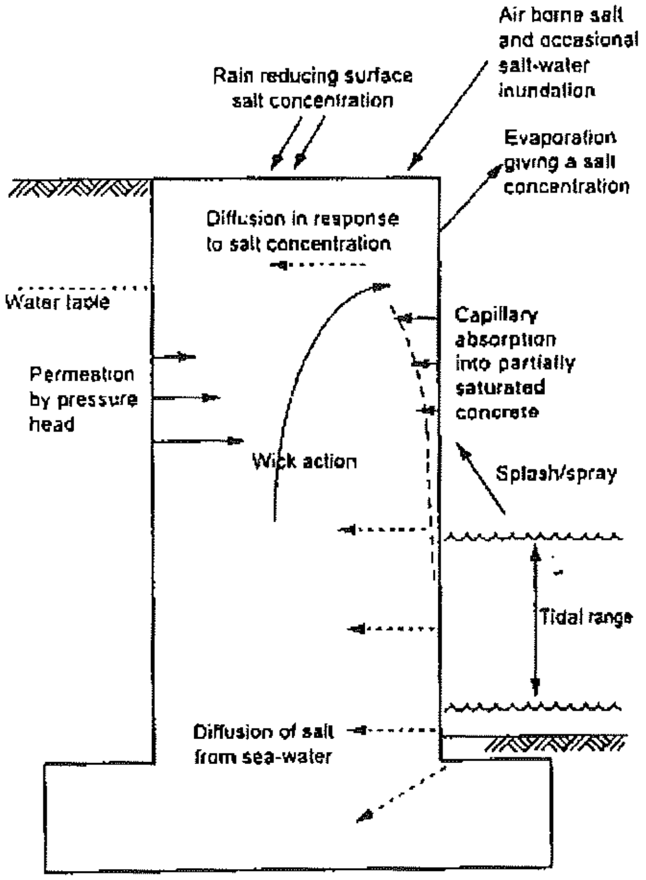

Figure 6. Schematic diagram of the transport process of chloride in a sea wall [Concrete Society Discussion Document (1996)]

Even though, a number of models have been put forward to describe the ingress of chloride [*Helffereich (1970), Frantz (1976), Crank (1979)*], the basis for those models is still the diffusion equation. The general expression for the diffusion of Chloride in concrete is:

$$dC/dt = D\, d^2C/dx^2 \qquad (14)$$

where C is chloride concentration in concrete, and D is the diffusion coefficient. So the concentration ($C_{x,t}$) of chloride at depth x and at time t can be obtained from:

$$C_{x,t} = C_s - (C_s - C_\infty)\, erf[x/(4Dt)^{1/2}] \qquad (15)$$

where C_s is the concentration of chloride in the surface layer of cover concrete; C_∞ is the background concentration of chloride (which is equal to the chloride concentration in the interior concrete, unaffected by the surface concentration of chloride). The typical chloride diffusion coefficient D for a concrete is about 2~3 x 10^{-8} cm^2/s [*Berke (1997), Berke (1994)*], and the typical surface chloride concentration C_s is about 18 kg/m^3 in the splash/tidal zone in a severe marine environment [*Browne (1982), Bamforth (1996), Berke (1994), Hartt (1990)*]. In fact, various diffusion coefficients and surface concentrations have been widely reported and summarised [*Bamforth (1996), Stoltzner (1997), Sagues (1997)*]. These values vary by more than one order of magnitude, mainly due to varying conditions.

Equations (14) and (15) only describe the one dimensional diffusion process of chloride in concrete. The diffusion equation and solution for the two-dimension model are relatively complicated [*Berke (1997)*].

In addition to the analytical solution of the diffusion equation, a numerical model has been developed by Bentz [*Bentz (1996)*] to determine chloride diffusion coefficient using a direct finite difference implementation of Fick's second law.

Theoretically, the above equations can only describe the diffusion of free chloride in concrete as only the free chloride, rather than the bound chloride, is able to move through the concrete [*Sagues (1996)*]. However, equation (14) is sometimes used to describe the total chloride profile in concrete. It is interesting that the diffusion equation could also be theoretically obeyed by total chloride in concrete, provided that linear equilibrium is established between bonded and free chloride ions [*Sagues (1996), Fishcher (1984)*]. Actually, the diffusion coefficient of acid-soluble chloride ions in concrete has a strong relationship with the diffusion coefficient of free chloride in pore fluid [*Mangat (1994)*].

The simplest method [*Broomfield (1997)*] to calculate the initiation time for chloride attack is based on the chloride profile which is simply regarded as a parabolic curve. By fitting the data to a parabolic curve, the depth where "chloride threshold" has been reached can be determined, then the time (t_i) for the concentration of chloride to increase up to its threshold level at the surface of steel reinforcement, and finally lead the corrosion of steel, can be estimated by:

$$t_i = h^{1/2}/A \tag{16}$$

where A is a constant; h is the distance from steel reinforcement to the point where currently the chloride concentration is at the "threshold" level. Similarly, the depth of the ingress of chloride can also be determined in another form proposed by Cady [*Cady (1983)*]:

$$d = K_1 t^{1/2} + K_2 \tag{17}$$

where K_1 and K_2 are constants. Besides these diffusion based expressions, various empirical formulae have also been proposed to estimate the remaining life of reinforced concrete structures [*Beaton (1963), Clear (1976), Cady (1983)*].

The diffusion coefficient of chloride ions is an important parameter essential for service life prediction. The estimate of this parameter is normally conducted [*West (1985)*] as follows: first calculate a concentration ratio u from a chloride profile:

$$u = (C_s - C_{x,t})/(C_s - C_\infty) = erf\,[x(4Dt)^{-1/2}] \tag{18}$$

then look up the error function table, from which x $(4Dt)^{-1/2}$ can be determined, hence D calculated; finally based on the calculated D and measured chloride profile, the rate of advance of the chloride profile can be predicted, i.e. time taken before the chloride concentration at the rebar surface exceeds the threshold value can be determined.

In the laboratory, the above diffusion model (14) for the ingress of chloride may be considered valid, as diffusion, permeability, and absorption of chloride can be measured under controlled conditions. However, even under a strictly controlled condition, the measured data could still deviate significantly from the theoretical prediction due to some unexpected factors. For example [*Tang (1996)*], pore distribution in concrete, chloride binding capacity of cement, and some ions like OH^-, Na^+, K^+ and Ca^{2+}, etc. in pore solution, can all affect the ingress of chloride, resulting in a different chloride profile and diffusion coefficients from those theoretically predicted.

Moreover, the accurate measurements in the laboratory can rarely be equated to field conditions. In the field, transport mechanisms other than diffusion, such as suction, capillary movement, etc. operate and these can cause theoretical errors in the application of equation (14). Furthermore, there are still two barriers to the use of this equation:

1) the surface concentration of chloride is not constant and varies with season and environmental factors (temperature and wetness, etc)
2) the diffusion coefficient is not coustant and varies with age and thickness of concrete.

The variable surface concentration of chloride is the first main source of error in the prediction model. The change of environmental temperature and the wetting/drying of cover concrete can accelerate chloride uptake or wash away the accumulated chloride on the structure surface, making the surface concentration change with time. Sometimes due to some reported condensation effects, the surface concentration of chloride in a saturated concrete can reach a level which is two to four times higher than that of the surrounding saline solution, even though diffusion is still the principal transport process in this case [*Nagataki (1993)*]. Because of the influences of environmental factors, in most practical cases, the chloride concentration profiles are anormalous in the surface layer [*West (1985a)*].

The most common practice to deal with the variation of surface concentration is to discard the first few millimeters of chloride profile and take the concentration of chloride at about 10 mm depth as a constant pseudo surface concentration [*Broomfield (1997)*]. It is expected that the concentration of chloride at this depth would be constant.

Besides the above treatment, ie, discarding the surface layer of the concrete, establishment of a relationship between the surface concentration of chloride and time is another attempt to cope with the difficulty arising from the non constant surface concentration. It was reported [*Uji (1990)*] that the surface concentration of chloride was a function of square root of time. Such an expression was regarded as the best estimate in practical application [*Uji (1990), Purvis (1994), Amey (1996)*]. Lin [*Lin (1990)*] proposed another expression for the surface concentration of chloride:

$$C_s = a[1-exp(-bt)] \tag{19}$$

where a and b are constants. With this exponential equation to describe the time dependent surface concentration of chloride, the diffusion equation can be resolved and analytical solution obtained.

It should be borne in mind that, the change of surface concentration of chloride can not follow one given function of time [*Swamy (1994)*]. Even through the above mathematical treatments can result in a better correlation between measured and analysed curves, particular caution should still be taken to draw conclusions based on such analyses, because the physical meaning of the time dependent function, describing the change of surface concentration of chloride with time, is not clear.

The second source of error in the use of the diffusion equation is the variable diffusiou coefficient. The diffusion coefficient D actually changes with temperature, time, the depth of concrete and from site to site. The reason for the variability of diffusion coefficient of chloride with time and depth in concrete structures might be that the degree of hydation and microstructural development of concrete are affected by these factors. Moreover, the ingress of chloride can be strongly influenced by many factors like environmental conditions, the microstructure and defects of concrete, reaction of concrete constituents with chloride, inhomogeneity of concrete, and surface charge on the hydrated cement phases; all of which depend on time, temperature, and thickness of concrete. It was reported that coarse aggregate could effectively block chloride diffusion [*Castro (1993)*]; and the reaction of chloride with the concrete constituents could delay the penetration of chloride into deep concrete [*Collepardi (1972), Goto (1981), McCarter (1992)*]. Therefore, it was found [*Bentz (1996)*] that the solution (15) to the diffusion equation (14) could result in significant error in the calculation of diffusion coefficient.

In order to deal with the difficulty caused by the variable diffusion coefficient, various attempts have been made by many researchers to improve the prediction of chloride transport in concrete. It was reported that the diffusion coefficient apparently decreased with time [*Mangat (1994), Johansen (1995)*]. Maage et al [*Maage (1993)*] developed a time-dependent diffusion coefficient D(t):

$$D(t) = D_i\,(t_i/t)^{\alpha} \qquad (20)$$

where D_i is the achieved chloride diffusion coefficient at the maturity age t_i of concrete; α represents the decrease in the achieved diffusion coefficient with age due to the combined effect of hydration and all other mechanisms. Lin [*Lin (1990)*] also proposed a time dependent diffusion coefficient which was a function of cement type and w/c ratio. Page [*Page (1981)*] used a temperature dependent diffusion coefficient to describe the influence of temperature on the ingress of chloride by considering the contribution of activation energy to chloride transport. In effect, the dependence of diffusion coefficient on temperature is related to the effects of temperature on the viscosity of the pore solution. In addition, some other mathematical expressions have also been used [*Tang (1996)*] to describe the decrease of diffusivity with age of concrete. In terms of the dependence of diffusion of chloride on chloride concentration, different effects of concentration of chloride ions were reported [*Tang (1996)*].

Because of the complexity of the transport of chloride in concrete, some empirical models have been used to predict service life, based on laboratory and field experience [*Maage (1997), Steen (1997)*]. In recent work [*Takewake (1988), Maage (1993), Maage (1995), Uji (1990), Swamy (1994), Poulsen (1996), Frederiksen (1997), Mejlbro (1996)*] concerning models of chloride transport in concrete, besides particular attention being paid to the time-dependent surface concentration and diffusion coefficient, more and more variables have also been introduced into the models to make them more flexible [*Poulsen (1997), Steen (1997)*].

Computer simulation of diffusion process in concrete appears to be a new trend [*Hoffman (1994)*]. A finite difference model was used by Kranc et al [*Kranc (1994)*] to compute the distribution of electrical potential and oxygen concentration in a reinforced concrete sample. Relatively small changes in oxygen diffusivity were found to have a great impact on corrosion activity. Such attempts could quite likely be extended to the computation of the transport of chloride in concrete.

7.4 Carbonation Depth Estimation

Carbonation is another main cause of corrosion of reinforcement in the atmospheric zones of concrete structures The carbonation of the cover concrete is a key step in the deterioration, and is a common phenomenon in old or badly built structures. In a concrete structure exposed to the atmosphere containing carbon dioxide, a carbonation front would gradually advance inward from the surface of the concrete structure. In the carbonated concrete, the pH of the pore solution drops from 13.5 to approximately 8, which is low enough for the passive film on steel rebars to break down and the corrosion of the steel to be initiated. The carbonation rate is dependent on porosity, pore size and cement content and w/c ratio of the concrete. The time to the initiation of corrosion induced by carbonation is a function of cover thickness and quality of the concrete.

The chemical reaction of carbon dioxide with calcium hydroxide in the pore solution is relatively rapid whereas the diffusion of carbon dioxide from the concrete surface to the carbonation front is relatively slow [*Klopfer (1978)*]. Therefore the rate at which the carbonation front advances and the depth that the carbonation front reaches are governed by the diffusion of carbon dioxide in the concrete, and can be given by equations (21) and (22), respectively, based on a simple diffusion law:

$$dx/dt = A/x \tag{21}$$

$$x = At^n + A_o \tag{22}$$

where x is the carbonation depth, t is the carbonation time, A and n are constants associated with diffusion coefficient of carbon dioxide and permeability of concrete as well as the surrounding environmental parameters, and Ao reflects any initial maltreatment of concrete which can lead to an initial carbonation; it could be as high as 10 mm [*Broomfield (1997)*].

The above equations phenomenally describe the progress of carbonation in a uniform and continuous concrete matrix. They do not hold very well in concrete structures. In some cases, the influence of heterogeneity of concrete is very significant in the carbonation process, porosity, and pore size and other concrete parameters can be modified by the deposit of carbonation product, $CaCO_3$, [*Broomfield (1997)*]. Thus the deviation from equation (21) would be very significant in field concrete structures.

Besides the above ideal equations (21) and (22), various more complicated equations have been proposed [*Broomfield (1997) (source: Parrott (1987)), Parrott (1991), Parrott (1994)*] to estimate the carbonation depth.

It was reported [*Klopfer (1978)*] that the greatest carbonation rate occurs when concrete is exposed to relative humidities of between 50% and 70%; an atmosphere with 100% relative humidity can prevent carbonation of concrete, as the water in the pores close to the surface of the concrete impedes the penetration of carbon dioxide; if the relative humidity is lower than 30%, the carbonation of concrete would not be significant, since the carbonation reaction requires water. The higher the strength class of the concrete, and the cement content, the more slowly the concrete is carbonated. A higher content of carbonatable calcium hydroxide in the concrete could also lead to smaller depth of carbonation in the concrete. Anti-carbonation coatings are recommended to prevent carbonation in existing structures. Mix formulations to reduce the porosity and permeability of concrete are applied to slow down the rate of carbonation for new structures.

8. Conclusions

Corrosion of steel in concrete continues to be a major issue for asset managers in the world. Hundreds of papers are being published in this area every year regarding corrosion behaviour, influences of factors, techniques for monitoring, laboratory simulation and acceleration, and service life prediction. A great deal of progress has been made on the above aspects through decades of efforts and contributions made by corrosion engineers and material scientists. However, there are many unresolved issues which need to be further studied.

8.1 General Comments on Current State of the Art

The economic loss caused by corrosion damage of reinforced concrete structures and the risks associated with the corrosion of steel in concrete have been recognised worldwide. However, the importance of cost effective monitoring and survey of corrosion damage to reinforced concrete structures is sometimes overlooked.

The corrosion mechanisms of steel and related processes in concrete have been investigated to a wide and deep extent. However, there is still a lack of detailed information and convincing evidence on how chloride ions attack the passive film on the reinforcement steel in concrete; what relationship exists between free chloride and bonded chloride; how corrosion products affect the corrosion processes including the electrochemical reactions, transport of oxygen, chloride, hydroxyl and ferrous ions; and the possibility and mechanism of stress corrosion cracking or hydrogen induced embrittlement in prestressed concrete elements, etc.

The factors that can cause or affect corrosion of steel in concrete have been intensively studied, and the understanding of the effects of some factors on corrosion of steel has been employed to improve the durability of structures. For instance, some additives incorporated to reduce the porosity of concrete; the cover concrete and the strength of concrete have been increased and the w/c ratio decreased for the protection of reinforced concrete elements in corrosive environments. However, there are still not many direct and sound pieces of evidence supporting the explanation of the effects of those factors. For example, the complete mechanisms of some mineral and chemical additives influencing corrosion of reinforcement are not very clear. Even though extensive studies on the influences of concrete properties and environmental factors on corrosion of reinforcement have been carried out, the understanding of the interaction among these factors is still superficial and limited. Particularly, no sufficient research work has been done on the interaction and synthetic effects of different factors, such as environmental temperature, wetness of concrete, permeability of the cover concrete, and the tolerance of the amount of reinforcement corroded before cracking in cover concrete takes place. The investigation on this aspect is of more significance from a practical point of view, because in the field, it can not be expected that there is only one factor operating.

Much progress has been made in the past decade in the development of electrochemical techniques for monitoring and measurement of corrosion of steel in concrete. The use of linear polarisation resistance in the field has not only improved the accuracy of locating the sites of active corrosion on the reinforcement, but has also made a quantitative comparison of corrosion rates of reinforcement at different sites possible. Also the application of EIS, transient techniques and EN has extended and improved our knowledge about the corrosion of steel in concrete; all these methods have potential for application in the field. However, electrochemical techniques have the common shortcoming that they can only obtain the instantaneous information at the moment when the measurements are carried out. Unfortunately, the deterioration of reinforced concrete is a gradual process, and the final damage of reinforced concrete structures usually results from an accumulation of long term corrosion. Therefore, continuous monitoring and measurement of corrosion rate by electrochemical methods would be essential in the prediction of service life.

Developments in the laboratory simulation and acceleration of corrosion of steel in concrete have also been significant. Electric field accelerated testing such as two-compartment cell with high electric field might be the most important achievement. An ASTM standard [*ASTM C1202-97*] has been established to rapidly assess the permeability of chloride ion in concrete, although the mechanisms involved in the test and its applicability are questioned. Considerable attention has been paid to the simultaneous measurement of different parameters and factors in the simulation and accelerated tests in order to obtain more information on the acceleration effect and to find out the key factors that could really affect the corrosion of reinforcement during the accelerated test. However, the correlation between the accelerated results and the field measured data is not very satisfactory.

The prediction of service life of reinforced concrete structures has become an issue of widespread concern in recent years. A number of models have been proposed to predict the ingress of chloride and carbonation in concrete, which are essential in the prediction of service life. However, these models are still too simple to describe the complicated processes in field environments, and they have not yet been verified or validated by long term tests in the field.

8.2 Trend and Recommendations for Future Work

There is no doubt that new developments in materials science and engineering will have a great impact on the methodology of dealing with corrosion of reinforcement. More effective and corrosion resistant materials might be introduced into reinforced concrete structures, and more successful and effective corrosion prevention measures might be possibly to take in future structures. Nevertheless, as long as metallic materials are used in concrete, and as long as the concrete is not free of defects, corrosion problems will not be avoided. Furthermore, any newly introduced materials would introduce new corrosion problems which would need to be understood and solved in the future.

To date, research has not fully solved all the corrosion problems encountered in reinforced concrete structures. In order to increase the corrosion resistance of these structures, the accuracy of detection and monitoring corrosion, and the prediction of service life of reinforced concrete structures, further research work should be carried out on the following aspects:

1) Fundamental mechanisms would need to be intensively studied. Only after some basic processes are comprehensively understood, can we know what reactions are taking place in the reinforced concrete, and what measures can most effectively retard these processes and slow down the corrosion of steel in concrete.

2) Interaction of different factors and their synergistic effects on corrosion of steel in concrete would be of increasing interest. This interaction is of practical significance and is an unavoidable problem in assessing a field reinforced concrete structure.

3) More accurate, more rapid and more easily operated measurement and monitoring techniques will always be pursued by researchers and engineers. Meanwhile, more and more techniques which are currently being used in electrochemistry will be introduced into the field of corrosion of steel in concrete. With the development of appropriate equipment, some techniques which are now only successful in the laboratory studies will become applicable in the field. We also expect to be able to know how to use the instantaneous corrosion rate to predict long term corrosion rates and total corrosion damage.

4) Laboratory simulation and acceleration of corrosion of steel in concrete would continue to be a research direction. Increasing effort would need to be made on the improvement of the rationality of simulation and acceleration tests. Particular attention would also need to be paid to the accelerating factors and their correlation with field test results.

5) More data from real structures would need to be collected to verify currently proposed models for service life prediction. At the same time, fundamental studies associated with the transport of chloride and the carbonation processes in concrete, and the relationship between corrosion products and cracking of the cover concrete would need to be greatly strengthened. New models would probably be developed in the future, based on computer simulation which would take more environmental influences into account, and would enable a more precise prediction of the corrosion behaviour of reinforced concrete structures.

9. References

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