

Chloride attack of reinforced concrete: an overview

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The mechanism of chloride-induced corrosion of steel embedded in concrete, the ingress of chlorides into the concrete, and the threshold chloride content for corrosion to occur are discussed. The binding of chloride ions by cement compounds and the associated effect of using different cements, both Portland and blended, as well as other factors influencing corrosion, are considered. Tests for the penetrability of concrete to chlorides are described. Finally, the prevention of corrosion is discussed.

1. INTRODUCTION

In many parts of the world, reinforced concrete structures deteriorate, sometimes seriously, due to chloride attack. Numerous papers continue to be published; for the most part, these describe isolated experiments involving one or two variables. However, in practice, the variables interact so that a broad picture of the phenomena involved is difficult to discern. This paper attempts to provide such an overview.

A particular feature of chloride attack which distinguishes it from other mechanisms of deterioration of reinforced concrete is that the primary action of chlorides is to cause corrosion of steel reinforcement, and it is only as a consequence of this corrosion that the surrounding concrete is damaged. The topic of corrosion of steel is wide ranging, and this paper is limited to a consideration of those properties of concrete which influence corrosion, with emphasis on the transport of chloride ions through the concrete in the cover to the reinforcement. Nevertheless, a brief description of the mechanism of chloride-induced corrosion will be helpful in understanding the processes involved.

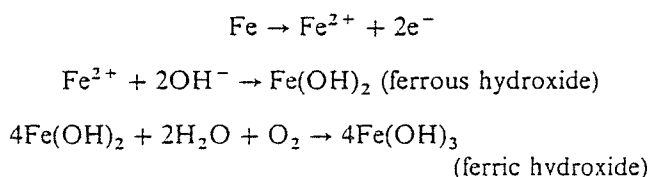
2. MECHANISM OF CHLORIDE-INDUCED CORROSION

Embedded steel develops a protective passivity layer on its surface. This layer, which is self-generated soon after the hydration of cement has started, consists of γ - Fe_2O_3 adhering tightly to the steel. As long as that oxide film is present, the steel remains intact. However, chloride ions destroy the film and, in the presence of water and oxygen, corrosion occurs. Chloride ions were described by Verbeck [1] as "a specific and unique destroyer".

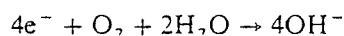
It may be useful to add that, provided the surface of the reinforcing steel is free from loose rust (a condition which is always specified), the presence of rust at the time the steel is embedded in concrete does not influence corrosion [2].

A brief description of the corrosion phenomenon is as follows. When there exists a difference in electrical potential along the steel in concrete, an electrochemical

cell is set up: anodic and cathodic regions occur, connected by the electrolyte in the form of the pore water in the hardened cement paste. The positively charged ferrous ions Fe^{2+} at the anode pass into solution while the negatively charged free electrons e^- pass through the steel into the cathode where they are absorbed by the constituents of the electrolyte and combine with water and oxygen to form hydroxyl ions OH^- . These travel through the electrolyte and combine with the ferrous ions to form ferric hydroxide, which is converted by further oxidation to rust. The reactions involved are as follows:



cathodic reaction

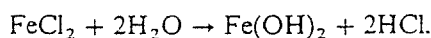
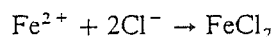


It can be seen that oxygen is consumed and water is regenerated, but it is needed for the process to continue. Thus there is no corrosion in dry concrete, probably below a relative humidity of 60%; nor is there corrosion in concrete immersed fully in water, except when water can entrain air, for example by wave action. The optimum relative humidity for corrosion is 70-80%. At higher relative humidities, the diffusion of oxygen through the concrete is reduced considerably.

The differences in electrochemical potential can arise from differences in the environment of the concrete, for example when a part of it is submerged permanently in sea water and a part is exposed to periodic wetting and drying. A similar situation can arise when there is a substantial difference in the thickness of cover to a steel system which is electrically connected. Electrochemical cells form also due to a variation in salt concentration in the pore water or due to a non-uniform access to oxygen.

For corrosion to be initiated, the passivity layer must be penetrated. Chloride ions activate the surface of the

steel to form an anode, the passivated surface being the cathode. The reactions involved are as follows:



Thus, Cl^{-} is regenerated so that the rust contains no chloride, although iron chloride is formed at the intermediate stage.

Because the electrochemical cell requires a connection between the anode and the cathode by the pore water, as well as by the reinforcing steel itself, the pore system in a hardened cement paste is a major factor influencing corrosion. In electrical terms, it is the resistance of the 'connection' through the concrete that controls the flow of the current. The electrical resistivity of concrete is influenced greatly by its moisture content, by the ionic composition of the pore water, and by the continuity of the pore system in the hardened cement paste.

There are two consequences of the corrosion of steel. First, the products of corrosion occupy a volume several times larger than the original steel so that their formation results in cracking (characteristically parallel to the reinforcement), spalling or delamination of concrete. This makes it easier for aggressive agents to ingress towards the steel, with a consequent increase in the rate of corrosion. Second, the progress of corrosion at the anode reduces the cross-sectional area of the steel, thus reducing its load-carrying capacity. In this connection, it should be pointed out that chloride-induced corrosion is highly localized at a small anode, with pitting of the steel taking place.

3. CHLORIDES IN THE MIX

Chlorides can be present in concrete because they have been incorporated in the mix through the use of contaminated aggregate or of sea water or brackish water, or through admixtures containing chlorides. None of these materials should be permitted, and standards generally prescribe strict limits on the chloride content of the concrete from all sources. For example, British Standard BS 8110: Part 1: 1985 limits the *total* chloride-ion content in reinforced concrete to 0.40% by mass of cement. The same limit is prescribed by European Standard ENV 206: 1992. The approach of American Concrete Institute Building Code ACI 318-89 is to consider water-soluble chloride ions only. On that basis, the chloride-ion content of reinforced concrete is limited to 0.15% by mass of cement. The two values are not substantially different from one another because water-soluble chlorides are only a part of the total chloride content, namely, the free chlorides in pore water. The distinction between *free* and *bound* chlorides is considered in a later section, but, at this stage, it can be noted that the total chloride content is determined as the *acid-soluble* chloride content, using ASTM Standard C 1152-90 or British Standard BS 1881: Part 124: 1988. There exist

several techniques for the determination of the content of water-soluble chlorides.

As a possible source of chlorides in the mix, Portland cement itself contains only a very small amount. However, ground granulated blastfurnace slag may have a significant chloride content if its processing involved quenching with sea water. As far as aggregate is concerned, British Standard BS 882: 1992 gives guidance on the maximum total chloride ion content; compliance with this guidance is likely to satisfy the requirements for concrete of British Standard BS 5328: Part 1: 1991 and of BS 8110: Part 1: 1985. For reinforced concrete, the chloride content of the aggregate should not exceed 0.05% by mass of the total aggregate; this is reduced to 0.03% when sulfate-resisting cement is used. For pre-stressed concrete, the corresponding figure is 0.01%.

The various limits on chlorides referred to in the section are generally conservative, so that compliance with them should ensure no chloride-induced corrosion unless more chlorides ingress into the concrete in service. The view that the limits are conservative is disputed by Pfeifer [3].

4. INGRESS OF CHLORIDES

The problem of chloride attack arises usually when chloride ions ingress from outside. This can be caused by de-icing salts, a topic not considered in this paper. Another, particularly important, source of chloride ions is sea water in contact with concrete. Chlorides can also be deposited on the surface of concrete in the form of airborne very fine droplets of sea water (raised from the sea by turbulence and carried by wind) or of airborne dust which subsequently becomes wetted by dew. It is useful to point out that airborne chlorides can travel substantial distances: 2 km has been reported [4], but travel over even greater distances is possible, depending on wind and topography. The configuration of structures also affects the movement of airborne salts: when eddies occur in the air, salts can reach the landward faces of structures. Brackish ground-water in contact with concrete is also a source of chlorides.

Although it is a rare occurrence, it should be mentioned that chlorides can ingress into concrete from conflagration of organic materials containing chlorides. Hydrochloric acid is formed and deposited on the surface of concrete where it reacts with calcium ions in the pore water. Ingress of chloride ions can follow [5].

Whatever their external origin, chlorides penetrate concrete by transport of water containing the chlorides, as well as by diffusion of the ions in the water, and by absorption. Prolonged or repeated ingress can, with time, result in a high concentration of chloride ions at the surface of the reinforcing steel.

When concrete is permanently submerged, chlorides ingress to a considerable depth but, unless oxygen is present at the cathode, there will be no corrosion. In concrete which is sometimes exposed to sea water and is sometimes dry, the ingress of chlorides is progressive. The

following is a description of a situation often found in structures on the coast in a hot climate.

Dry concrete imbibes salt water by absorption and, under some conditions, may continue to do so until the concrete has become saturated. If the external conditions then change to dry, the direction of movement of water becomes reversed and water evaporates from the ends of capillary pores open to the ambient air. It is, however, only pure water that evaporates, the salts being left behind. Thus, the concentration of salts in the water left behind increases near the surface of the concrete. The concentration gradient thus established drives the salts in the water near the surface of the concrete towards the zones of lower concentration, i.e., inwards; this is transport by diffusion. Depending on the external relative humidity and on the duration of the drying period, it is possible for most of the water in the outer zone of the concrete to evaporate so that the water remaining in the interior will become saturated with salt and the excess salt will precipitate out as crystals.

It can be seen thus that, in effect, the water moves outwards and the salt inwards. The next cycle of wetting with salt water will bring more salt present in solution into the capillary pores. The concentration gradient now decreases outwards from a peak value at a certain depth from the surface, and some salts may diffuse towards the surface of the concrete. If, however, the wetting period is short and drying restarts quickly, the ingress of salt water will carry the salts well into the interior of the concrete; subsequent drying will remove pure water, leaving the salts behind.

The exact extent of the movement of salt depends on the length of the wetting and drying periods. It should be remembered that wetting occurs very rapidly and drying is very much slower; the interior of the concrete never dries out. It should also be noted that the diffusion of ions during the wet periods is fairly slow.

It is apparent that a progressive ingress of salts towards the reinforcing steel takes place under alternating wetting and drying, and a chloride profile of the kind shown in Fig. 1 is established. The profile is determined by chemical analysis of dust samples obtained by drilling to various depths from the surface. Sometimes, there is a lower concentration of chlorides in the outermost 5 mm or so of the concrete where rapid movement of water takes place so that the salts are carried quickly a small distance inwards. The maximum chloride ion content in pore water can be in excess of the concentration in sea water; this was observed after 10 years exposure [6]. The crucial fact is that, with the passage of time, a sufficient quantity of chloride ions will reach the surface of the reinforcing steel. What constitutes a 'sufficient' quantity will be discussed in the next section.

As just mentioned, the ingress of chlorides into concrete is influenced strongly by the exact sequence of wetting and drying. This sequence varies from location to location, depending on the movement of the sea and on the wind, on exposure to the sun, and on the usage of the structure. Thus, even different parts of the same

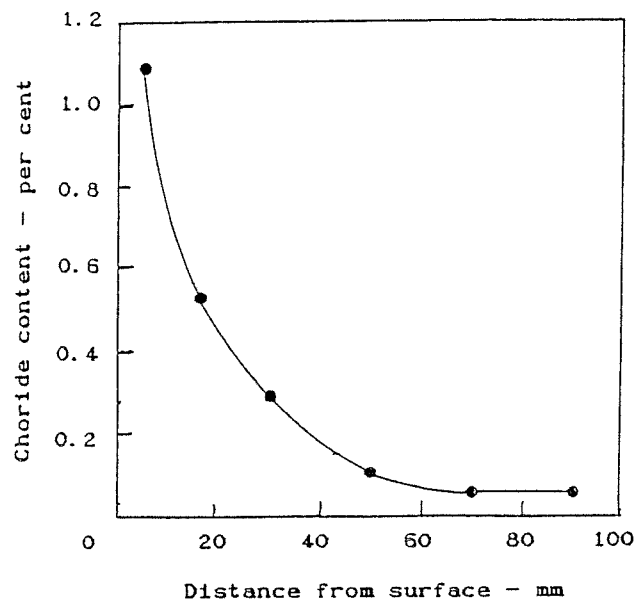


Fig. 1 A typical profile of total chloride ion content by mass of cement.

structure may undergo a different pattern of wetting and drying; this explains why, sometimes, there is a considerable variation in the extent of corrosion damage in a single structure.

It is not only wetting and drying of the surface zone of the concrete that influences the ingress of chlorides: drying to a greater depth allows subsequent wetting to carry the chlorides well into the concrete, thus speeding up the ingress of chloride ions. For this reason, reinforced concrete in the tidal zone (where the period of drying is short) is less vulnerable to corrosion than concrete in the splash zone (where wetting may occur only when the sea is high or the wind is strong). The most vulnerable is the concrete wetted by sea water only occasionally, such as areas around bollards (where wet ropes are coiled) or in the vicinity of fire hydrants (using sea water), or in industrial areas subjected to periodic washdown with sea water, but at other times exposed to the drying effects of the sun and of a high temperature.

5. THRESHOLD CONTENT OF CHLORIDE IONS

It was mentioned earlier that, for corrosion to be initiated, there has to be a certain minimum concentration of chloride ions at the surface of the steel. As far as chlorides incorporated in the original mix are concerned, the threshold concentration was considered earlier. It is useful to add that the presence of a given excessive amount of chlorides in the original mix results in a more aggressive action, and therefore a higher corrosion rate, than when the same amount of chlorides has ingressed into the concrete [7].

As far as chlorides which have ingressed into the concrete are concerned, it is even more difficult to establish a threshold concentration of chloride ions below

which there is no corrosion. This threshold depends on a number of factors, many of which are still imperfectly understood. Moreover, the distribution of chlorides within the hardened cement paste is not uniform, as found in chloride profiles in actual structures. For practical purposes, prevention of corrosion lies in controlling the ingress of chlorides by the thickness of cover and by the penetrability of the concrete in the cover.

While, under any given circumstances, there may be a threshold chloride content for corrosion to be initiated, its progress depends on the resistivity of the hardened cement paste, which varies with humidity, and on the availability of oxygen, which is affected by the immersion of concrete.

In any case, it is not the total chloride content that is relevant to corrosion. Some of the chlorides are chemically bound, being incorporated in the products of hydration of cement. Other chlorides are physically bound, being adsorbed on the surface of the gel pores. It is only the remaining chlorides, namely, free chlorides, that are available for the aggressive reaction with steel. However, the distribution of the chloride ions among the three forms is not permanent, since there is an equilibrium situation such that some free chloride ions are always present in the pore water. It follows that only the chloride ions in excess of those needed for this equilibrium can become bound.

6. BINDING OF CHLORIDE IONS

The main form of binding of the chloride ions is by reaction with C_3A to form calcium chloroaluminate, $3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$, sometimes referred to as Friedel's salt. A similar reaction with C_4AF results in calcium chloroferrite, $3CaO \cdot Fe_2O_3 \cdot CaCl_2 \cdot 10H_2O$. It follows that more chloride ions are bound when the C_3A content of the cement is higher, and also when the cement content of the mix is higher. For this reason, it used to be thought that the use of cements with a high C_3A content is conducive to good resistance to corrosion.

This may be true when chloride ions are present at the time of mixing (a situation which should not be permitted) because they can react rapidly with C_3A . However, when chloride ions ingress into concrete, a smaller amount of chloroaluminates is formed, and, under some future circumstances, they may become dissociated, releasing chloride ions so as to replenish those removed from the pore water by transport to the surface of the steel.

A further factor in deciding on the desirable C_3A content of the cement is the possibility of sulfate attack on some parts of the given structure, other than those subject to the ingress of sea water. As is well known, sulfate resistance requires a low C_3A content in the cement. For these various reasons, it is nowadays thought that a moderately sulfate-resisting cement, ASTM Type II, offers the best compromise.

In the case of cements containing ground granulated blastfurnace slag, it has been suggested that binding of

chlorides takes place also by the aluminates in the slag, but this has not been confirmed fully [8].

Concerning a possible use of cement with a high C_3A content, it should be remembered that a high C_3A content results in a higher early rate of heat evolution, and therefore a temperature rise. This behaviour can be harmful in moderately large concrete masses often associated with structures exposed to the sea [9].

Some standards, for example, British Standard BS 8110:Part 1:1985, severely limit the chloride content when sulfate-resisting cement (Type V) is used, on the assumption that chlorides adversely affect sulfate resistance. This has now been proved not to be the case [10]. What happens is that sulfate attack results in a decomposition of calcium chloroaluminate, thus making some chloride ions available for corrosion; calcium sulfoaluminate is formed [11].

Carbonation of hardened cement paste in which bound chlorides are present has a similar effect of freeing the bound chlorides and thus increasing the risk of corrosion. Ho and Lewis [12] quote Tuutti as having found an increased concentration of chloride ions in pore water to occur 15 mm in advance of the carbonation front. This harmful effect of carbonation is in addition to the lowering of the pH value of the pore water, so that severe corrosion may well follow. It has also been found in laboratory tests [13] that the presence of even a small amount of chloride ions in carbonated concrete enhances the rate of corrosion induced by the low alkalinity of carbonated concrete.

In considering both carbonation and ingress of chloride ions, it is important to remember that the optimum relative humidity for carbonation is between 50% and 70%, whereas corrosion progresses rapidly only at higher humidities. The occurrence of both of these relative humidities, one after another, is possible when concrete is exposed to long periods of alternating wetting and drying. Another occurrence of both chloride ingress and carbonation was observed in thin cladding panels of a building: airborne chlorides ingressed from outside and reached the reinforcing steel; carbonation progressed from the relatively dry inside of the building.

Returning to the topic of the chloride ion concentration present in the pore water in an equilibrium situation, it should be noted that the chloride ion concentration depends on the other ions present in the pore water; for example, at a given total chloride ion content, the higher the hydroxyl (OH^-) concentration the more free chloride ions are present [14]. For this reason, the Cl^-/OH^- ratio is considered to affect the progress of corrosion, but no generally valid statements can be made. It has also been found that, for a given amount of chloride ions in the mix, there are significantly more free chloride ions with NaCl than with $CaCl_2$ [15].

Because of these various factors, the proportion of bound chloride ions varies from 80% to well below 50% of the total chloride ion content. Therefore, there may not exist a fixed and unique value of the total amount of chloride ions below which corrosion will not occur.

Tests [14, 16] have shown that, in consequence of the various equilibrium requirements of the pore water, the mass of bound chlorides in relation to the mass of cement is independent of the water/cement ratio.

7. INFLUENCE OF BLENDED CEMENTS ON CORROSION

While the preceding discussion was concerned with the influence of the type of *Portland* cement on the chemical aspects of chloride ions, it is also important, indeed more so, to consider the influence of the type of *blended* cement on the pore structure of the hardened cement paste and on its penetrability, as well as on resistivity. Those aspects of various cementitious materials which are particularly relevant to the movement of chloride ions will now be discussed. It should be added that the same properties of hardened cement paste which influence the transport of chlorides also influence the supply of oxygen and the availability of moisture, both of which are necessary for corrosion to occur. However, the locations on steel where chlorides are present and where oxygen is needed are different: the former at the anode, and the latter at the cathode.

The cementitious materials of interest are fly ash, blastfurnace slag, and silica fume. All three, when properly proportioned in the mix, significantly reduce the penetrability of concrete and increase its resistivity, thereby reducing the rate of corrosion [17–19]. As far as silica fume is concerned, its positive effect is through improvement of the pore structure of hardened cement paste, which increases resistivity, even though silica fume reduces somewhat the pH value of the pore water as a consequence of its reaction with $\text{Ca}(\text{OH})_2$.

It should be remembered that, because of its effect on workability, the use of silica fume usually involves the inclusion of a superplasticizer. Superplasticizers *per se* do not affect the pore structure and therefore do not alter the process of corrosion.

The beneficial effects of the various cementitious materials are so significant that their use in reinforced concrete liable to corrosion in hot climates is virtually necessary: Portland cement alone should not be used [20]. Tests on chloride ion diffusion through mortar indicate that fillers do not affect the movement of chlorides [21].

Chloride ions in concrete made with high alumina cement lead to a more aggressive situation than with Portland cement [22], the comparison being made at the same chloride ion content. It can be added that the pH value in high alumina cement concrete is lower than with Portland cement so that the passive state of the steel may be less stable [22].

8. FURTHER FACTORS INFLUENCING CORROSION

The preceding discussion of the influence of the composition of concrete upon its resistance to corrosion

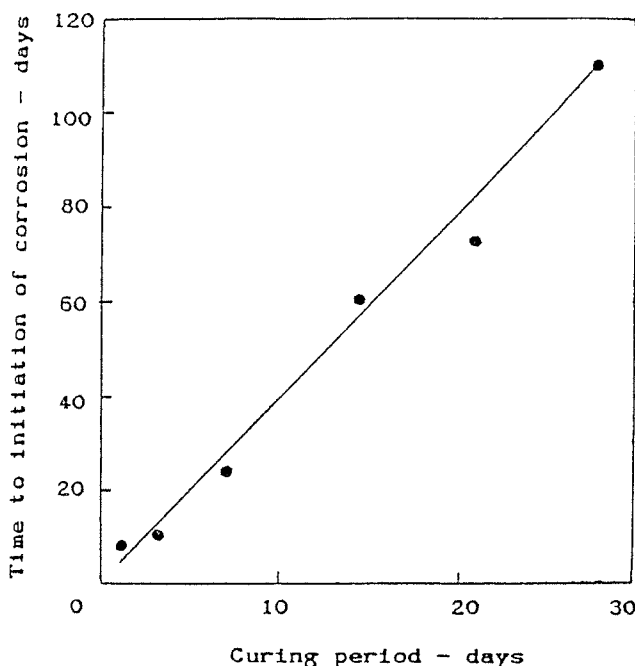


Fig. 2 Influence of the period of wet curing on the time to initiation of corrosion of reinforcing steel in concrete [23].

should be complemented by re-emphasizing the importance of good curing, the effect of which is primarily upon the concrete in the cover zone. The time to *initiation* of corrosion is reduced substantially by prolonged curing, as shown in Fig. 2 for concrete made with sulfate-resisting cement and a water/cement ratio of 0.5, partially immersed in a 5% solution of sodium chloride [23]. However, only fresh water must be used for curing because brackish water greatly increases the ingress of chlorides [23].

Once the corrosion has been initiated, its continuation is not inevitable: the progress of corrosion is influenced by the resistivity of the concrete between the anode and the cathode and by the continuing supply of the oxygen at the cathode. On the one hand, it is very doubtful that the supply of oxygen can be stopped completely and reliably by the application of a membrane, although developments in this field continue. On the other hand, the resistivity of concrete is a function of its moisture condition so that drying out would halt the corrosion which, however, can re-start upon subsequent wetting.

Cracking of concrete in the cover facilitates the ingress of chlorides and therefore enhances corrosion. Although virtually all reinforced concrete in service exhibits some cracks, cracking can be controlled by appropriate structural design, detailing, and construction procedures. Cracks wider than about 0.2–0.4 mm are harmful. It may be worth mentioning that, although prestressed concrete is crack-free, the prestressing steel is more vulnerable to corrosion because of its nature; also, the small cross-sectional area of prestressing tendons means that pitting corrosion greatly reduces their load carrying capacity.

Higher temperatures have several effects on corrosion. First, the content of free chlorides in the pore water

increases; the effect is more pronounced with cements having a high C_3A content and with lower chloride concentrations in the original mix [24]. More importantly, the reactions of corrosion, like many chemical reactions, occur faster at higher temperatures. It is usually assumed that a rise in temperature of 10°C doubles the rate of reaction, but there is some evidence that the increase is only 1.6-fold [25]. Whatever the exact factor, the accelerating effect of temperature explains why there is so much more corrosion-damaged concrete in hot coastal areas than in temperate parts of the world.

It is known that initial hardening of concrete at high temperatures results in a coarser pore structure [26], a consequence of which is a lower resistance to the diffusion of chloride ions [27]. The temperature differential between the surface of the concrete and its interior affects the diffusion; direct exposure to the sun can result in a significant rise in the temperature of the surface concrete above the ambient value.

9. THICKNESS OF COVER

The thickness of cover to reinforcement is an important factor controlling the transport of chloride ions: the greater the cover the longer the time interval before the chloride ion concentration at the surface of the steel reaches the threshold value. Thus, the quality of the concrete (in terms of its low penetrability) and the thickness of cover work together and can, therefore, to some extent, be traded off one against the other. For this reason, standards often specify combinations of cover and strength of concrete such that a lower thickness of cover requires a higher strength, and vice versa.

However, there are limitations to this approach. First of all, thick cover is of no avail if the concrete is highly penetrable. Moreover, the purpose of cover is not only to provide protection of reinforcement, but also to ensure composite structural action of steel and concrete, as well as, in some cases, to provide fire protection or resistance to abrasion. Unduly large thickness of cover would result in the presence of a considerable volume of concrete devoid of reinforcement. And yet, the presence of steel is required to control shrinkage and thermal stresses, and to prevent cracking due to those stresses. Were cracking to occur, the large thickness of cover would be proved to be detrimental. In practical terms, the cover thickness should not exceed 80–100 mm, but the decision on cover forms part of structural design.

Too small a thickness of cover should not be used either because, however low the penetrability of the concrete, cracking, for whatever reason, or local damage or misplaced reinforcement can result in a situation where chloride ions can be transported rapidly to the surface of the steel.

10. TESTS FOR PENETRABILITY TO CHLORIDES

A rapid test for the penetrability of concrete to chloride ions is prescribed by ASTM Standard C 1202 - 91.

which determines the electrical conductance, expressed as the total electrical charge in coulombs (ampere seconds) passed during a certain time interval through a concrete disc between solutions of sodium chloride and sodium hydroxide. The charge is related to the penetrability of the concrete to chloride ions, so that the test can be of help, in a comparative manner, in selecting a suitable concrete mix. A somewhat similar test determines the AC impedance of specimens of various shapes [28].

Tests of the kind just described do not necessarily replicate the transport of chloride ions in a real-life situation, nor do they have a sound scientific basis. Nevertheless, they are useful and certainly preferable to the assumption that resistance to chloride ion ingress is related simply to the strength of the concrete; this assumption has been shown not to be valid [29] except in the most general manner.

11. PREVENTION OF CORROSION

Simplified statements about methods of controlling or remedying corrosion which has been initiated could be unhelpful. All that should be stated here is that the progress of corrosion would be reduced by drying the concrete or by the prevention of oxygen supply using surface barriers. This is a specialized field, and *ad hoc* solutions may, in fact, prove harmful; for instance, applying a barrier at the anode (rather than the cathode) would increase the ratio of the size of the cathode to the anode, which would increase the rate of corrosion.

It is reasonable to raise the question of whether there exist integral corrosion inhibitors, i.e., substances which, while not preventing ingress of chlorides into concrete, inhibit corrosion of steel. Nitrites of sodium [30] and calcium [31] have been found to be effective in laboratory tests. The action of the nitrite is to convert ferrous ions at the anode into a stable passive layer of Fe_2O_3 , the nitrite ion reacting preferentially to the chloride ion. The concentration of nitrites must be sufficient to cope with a continuing ingress of chloride ions. Indeed, it is not certain that corrosion inhibitors are effective indefinitely; they may simply delay corrosion. The accelerating effect of the nitrites can be offset by the use of a retarding admixture, if need be. The search for other corrosion inhibitors continues [32].

Being incorporated in the mix, the inhibitors protect all the embedded steel. Nevertheless, inhibitors are no substitute for concrete of low penetrability: they are merely an additional safeguard. Moreover, sodium nitrite increases the hydroxyl ion concentration in the pore water, and this may increase the risk of alkali-aggregate reaction. Thus, the beneficial effect of an increased hydroxyl ion concentration upon the risk of corrosion of steel is accompanied by a negative effect on the risk of alkali-aggregate reaction. Of course, this is relevant only if the aggregate is susceptible to such a reaction in the first place.

A discussion of the prevention of corrosion of steel in concrete would be incomplete without a mention of the

protection of steel by epoxy coating and by cathodic protection which makes the entire steel surface cathodic. Epoxy coating of steel is a specialized technique which can be helpful *in addition* to an adequate thickness of cover concrete of low permeability. Cathodic protection has been shown to be effective in some applications but its use in a new structure is an admission of defeat in that the particular reinforced concrete structure is manifestly not durable.

A question which has to be faced occasionally is: can chloride ions be removed from the surface of the steel? There has been developed a technique for desalinating concrete, in which chloride is removed by passing a heavy direct current between the corroding reinforcing steel (now acting as a cathode) and an external anode in electrolytic contact with the concrete; chloride ions migrate towards the external anode, thus moving away from the surface of the reinforcement [33]. It seems that only about one-half of the chloride in the concrete can be removed and, with time, corrosion is likely to re-start. Some negative consequences of the process may follow [34].

12. CONCLUDING REMARKS

Understanding the phenomena involved in the corrosion of steel reinforcement in concrete and the factors influencing corrosion should make it possible to design successful reinforced concrete structures which will be exposed to chlorides. Nevertheless, there exist extreme conditions of exposure, in terms of temperature and the pattern of wetting by sea water alternating with drying, which put into question the appropriateness of reinforced concrete under those conditions. It could be postulated that there exist two excellent construction materials: concrete and steel. The combination of the two, one inside the other, may be catastrophic.

REFERENCES

- Verbeck, G. J., 'Mechanisms of corrosion in concrete', in 'Corrosion of Metals in Concrete', SP-49 (American Concrete Institute, 1975) pp. 21-38.
- Al-Tayyib, A. J. *et al.*, 'Corrosion behavior of pre-rusted rebars after placement in concrete', *Cement Concr. Res.* **20** (1990) 955-960.
- Pfeifer, D. W., Perenchio, W. F. and Hime, W. F., 'A critique of the ACI 318 chloride limits', *PCI J.* **37** (1992) 68-71.
- Nireki, T. and Kabeya, H., 'Monitoring and analysis of seawater salt content', in Fourth International Conference on Durability of Building Materials and Structures. Singapore 4-6 November 1987, pp. 531-536.
- Lammke, A., 'Chloride-absorption from concrete surfaces', in 'Evaluation and Repair of Fire Damage to Concrete', SP-92 (American Concrete Institute, Detroit, MI, 1986) pp. 197-209.
- Nagataki, S. *et al.*, 'Condensation of chloride ion in hardened cement matrix materials and on embedded steel bars', *ACI Mater. J.* **90** (1993) 323-332.
- Lambert, P., Page, C. L. and Vassie, P. R. W., 'Investigations of reinforcement corrosion. 2. Electrochemical monitoring of steel in chloride-contaminated concrete', *Mater. Struct.* **24** (1991) 351-358.
- Bakker, R. F. M., 'Initiation period', in 'Corrosion of Steel in Concrete', edited by P. Schiessl, RILEM Report of Technical Committee 60-CSC (Chapman & Hall, London, 1988) pp. 22-55.
- Hoff, G. C., 'Durability of offshore and marine concrete structures', in 'Durability of Concrete', SP-126 (American Concrete Institute, Detroit, MI, 1991) pp. 33-53.
- Harrison, W. H., 'Effect of chloride in mix ingredients on sulphate resistance of concrete', *Mag. Concr. Res.* **42** (1990) 113-126.
- Mather, B., 'Calcium chloride in Type V-cement concrete', in 'Durability of Concrete', SP-131 (American Concrete Institute, Detroit, MI, 1992) pp. 169-176.
- Ho, D. W. S. and Lewis, R. K., 'The specification of concrete for reinforcement protection—performance criteria and compliance by strength', *Cement Concr. Res.* **18** (1988) 584-594.
- Glass, G. K., Page, C. L. and Short, N. R., 'Factors affecting the corrosion rate of steel in carbonated mortars', *Corrosion Sci.* **32** (1991) 1283-1294.
- Tritthart, J., 'Chloride binding in cement. II. The influence of the hydroxide concentration in the pore solution of hardened cement paste on chloride binding', *Cement Concr. Res.* **19** (1989) 683-691.
- Al-Hussaini, M.-J. *et al.*, 'The effect of chloride ion source on the free chloride ion percentages of OPC mortars', *Cement Concr. Res.* **20** (1990) 739-745.
- Tang, L. and Nilsson, L.-O., 'Chloride binding capacity and binding isotherms of OPC pastes and mortars', *Cement Concr. Res.* **23** (1993) 247-253.
- Schiessl, P. and Raupach, N., 'Influence of blending agents on the rate of corrosion of steel in concrete', in 'Durability of Concrete: Aspects of Admixtures and Industrial By-products. 2nd International Seminar', Swedish Council for Building Research, June, 1989, pp. 205-214.
- Ellis, W. E. Jr., Rigg, E. H. and Butler, W. B., 'Comparative results of utilization of fly ash, silica fume and GGBFS in reducing the chloride permeability of concrete', in 'Durability of Concrete', SP-126 (American Concrete Institute, Detroit, MI, 1991) pp. 443-458.
- Al-Amoudi, O. S. B. *et al.*, 'Prediction of long-term corrosion resistance of plain and blended cement concretes', *ACI Mater. J.* **90** (1993) 564-571.
- Stuvo, 'Concrete in Hot Countries', Report (STUVO). Dutch member group of FIP, The Netherlands, 1986.
- Cochet, G. and Jésus, B., 'Diffusion of chloride ions in Portland cement-filler mortars', in 'International Conference on Blended Cements in Construction', edited by R. N. Swamy (Elsevier Applied Science, Barking, 1991) 365-376.
- Goñi, S., Andrade, C., and Page, C. L., 'Corrosion behaviour of steel in high alumina cement mortar samples: effect of chloride', *Cement Concr. Res.* **21** (1991) 635-646.
- Rasheeduzzafar, Al-Gahtani, A. S., and Al-Saadoun, S. S., 'Influence of construction practices on concrete durability', *ACI Mater. J.* **86** (1989) 566-575.

24. Hussain, S. E. and Rasheeduzzafar, 'Effect of temperature on pore solution composition in plain concrete', *Cement Concr. Res.* **23** (1993) 1357-1368.
25. Virmani, Y. P., 'Cost effective rigid concrete construction and rehabilitation in adverse environments', 'Annual Progress Report, Year Ending Sept. 30, 1982' (US Federal Highway Administration, 1982).
26. Neville, A. M., 'Properties of Concrete', 3rd Edn (Longman, London, 1981).
27. Detwiler, R. J., Kjellsen, K. O., and Gjrrv, O. E., 'Resistance to chloride intrusion of concrete cured at different temperatures', *ACI Mater. J.* **88** (1991) 19-24.
28. 'SHRP-C-365, Very high performance concretes', in 'Mechanical Behavior of High Performance Concretes', Volume 5 (Strategic Highway Research Program, National Research Council, Washington, DC, 1993).
29. Samaha, H. R. and Hover, K. C. 'Influence of microcracking on the mass transport properties of concrete', *ACI Mater. J.* **89** (1992) 416-424.
30. Alonso, C. and Andrade, C., 'Effect of nitrite as a corrosion inhibitor in contaminated and chloride-free carbonated mortars', *ACI Mater. J.* **87** (1990) 130-137.
31. Berke, N. S., 'Corrosion inhibitors in concrete', *Concr. Int.* **13** (1991) 24-27.
32. Nmai, C. K., Farrington, S. A. and Bobrowski, S., 'Organic-based corrosion-inhibiting admixture for reinforced concrete', *Concr. Int.* **14** (1992) 45-51.
33. 'SHRP-S-347, Chloride Removal Implementation Guide' (Strategic Highway Research Program, National Research Council, Washington DC, 1993).
34. Tritthart, J., Pettersson, K. and Sorensen, B., 'Electrochemical removal of chloride from hardened cement paste', *Cement Concr. Res.* **23** (1993) 1095-1104.

RESUME

L'attaque du bton arm par les chlorures: une revue gnrale

Cet article discute des divers facteurs qui sont responsables de nombreux cas de dtrioration des structures en bton arm. L'acier dans le bton est protg par une pellicule autogne d'oxyde de fer qui adhre à l'acier. Cette pellicule est dtruite par les ions chlorure. Cependant, les ions chlorure sont rgnrs d'une manire telle que la raction d'oxydation de l'acier continue à l'anode à condition que de l'oxygne et de l'eau soient prsents à la cathode. Les produits de cette raction font clater le bton et causent typiquement des fissures le long des armatures. La teneur en chlorure du bton est rigoureusement limite par les codes nationaux; cependant, la quantit d'ions chlorure est tantt exprime en terme d'ions solubles dans l'eau, tantt en terme d'ions solubles dans l'acide. En pratique, les ions proviennent de l'extrieur du bton: de l'eau de mer, des embruns, si bien que des particules de sel sont dposes sur le bton et mouilles par la rose. Des btons situs jusqu'à 2 km au-delà des ctes peuvent tre affects.

Les ions chlorure pntrent le bton par diffusion ionique dans l'eau et par absorption. Les cycles de schage et de mouillage augmentent leur pntration: elle est plus profonde quand le schage dure longtemps et qu'il est suivi par une humidification rapide par l'eau de mer. C'est le

cas de certaines surfaces horizontales mouilles de temps en temps. Il n'y a pas, à proprement parler, de seuil de nocivit des ions chlorure dans le bton parce que les ions chlorure peuvent tre fixs par le C_3A mais une certaine quantit d'ions reste toujours dans l'eau des pores dans la pte de ciment. La carbonatation de la pte libre les ions fixs et augmente ainsi le progrs de la corrosion. L'humidit optimale pour dvelopper la corrosion des aciers est suprieure à celle qui est ncessaire pour dvelopper la carbonatation de la pte de ciment. Ainsi, les deux phnomnes ne peuvent coexister.

Les matriaux cimentaires tels que les cendres volantes, les laitiers de hauts fourneaux et la fume de silice rduisent tous la pntrabilit du bton par les ions chlorure. Un mrissement humide pendant une priode assez longue rduit les risques de corrosion, mais une hausse de la temprature les augmente. L'paisseur de recouvrement des armatures doit tre adquate, mais pas excessive, afin d'viter qu'une couche de bton ne se retrouve prive d'armature.

L'article traite des essais de pntration d'ions chlorure dans le bton et des possibilits de dsalinisation du bton. Pour limiter la corrosion des armatures, on peut utiliser des inhibiteurs de corrosion, des barres d'armature recouvertes d'poxy; cependant, c'est la prise en compte du problme de corrosion qui permet de construire des structures qui rsistent à la corrosion.