

FIELD EXPERIENCE AND THE LONG-TERM DURABILITY OF REINFORCED CONCRETE STRUCTURES

Robert E. Melchers

Centre for Infrastructure Performance and Reliability, Faculty of Engineering and the Built Environment,
University of Newcastle, Newcastle, Australia, 2308. *Email: rob.melchers@newcastle.edu.au

ABSTRACT

For reinforced concrete structures the conventional wisdom is that after some years of exposure to marine conditions reinforcement corrosion is inevitable. Much attention is paid in the literature to the rate of ingress of chlorides through the concrete cover to the reinforcing bars and to ensuring highly impermeable cover and/or deeper cover, to try to prevent chloride-induced or carbonation-induced corrosion initiation. Actual field experience shows that there are many reinforced concrete structures that have survived remarkably well for many decades despite having very high chloride concentrations next to the reinforcing bars. Even with very modest concrete cover by modern standards, exhumation often finds bars free from corrosion. Detailed investigations of a number of such cases showed no corrosion if the concrete pH levels are above about 9. On the other hand, very severe reinforcement corrosion was observed in the few cases where the concrete had cracked right through the cover to the bars. Often there was no external evidence or signs of interior corrosion, including longitudinal cracking. The implications of these findings for practice are discussed.

KEYWORDS

Reinforced concrete, reinforcement, corrosion, alkalinity, field experience, evidence.

INTRODUCTION

The corrosion resistance of reinforcement in reinforced concrete structures exposed to marine environments is a matter of continuing concern for structural engineers and asset managers. According to most texts (Richardson 2002; Hunkeler 2005; Gjørsv 2009) the build-up of aggressive ions such as chlorides adjacent to the reinforcement will cause it to corrode once a sufficient concentration has been reached. Attention is therefore focused sharply on reducing the diffusion of chlorides from the external environment, and for this thick concrete cover, high density concrete, permeability-reducing additives, and cathodic protection are often specified in an attempt to ensure a long life of the asset. High quality workmanship also has been seen as beneficial. As will be shown, these aspects, while desirable, are peripheral to attaining long-term durability.

The other main mechanism implicated in causing reinforcement corrosion is 'carbonation', the process by which carbon dioxide from the atmosphere diffuses into the concrete and, on reaching the reinforcement, is claimed to lower the local pH such that corrosion commences. Interestingly, it is well-known in the industry that good quality concretes permit only some few millimetres of carbonation from the outside surface even over extended periods of exposure (Parrott 1987). Nevertheless, carbonation receives considerable discussion in reinforcement corrosion texts.

One of the difficulties associated with durability studies is that they cannot be replicated in laboratory trials. Accelerated testing can be done for example using salt sprays, higher temperatures, impressed current on the reinforcement, but the relationship of the results obtained to actual in-service behaviour remains tenuous (Hansson 2000). This is not a problem unique to reinforcement corrosion (Lee et al. 2010). An alternative approach is to try to learn something from actual operational experience with real structures. The draw-back for such an approach usually is that there are few structures available for investigation, they tend to be one-off so that investigation of causative parameters is difficult, and typically they are not well-documented (or the documentation no longer exists or cannot be found). Despite these difficulties, the approach does have merits, and can be considered an archaeological one, such that with care useful observations can be made. Several investigations along these lines have been described for reinforced concrete structures (Melchers et al. 2009) as well as for materials of potential use in nuclear waste storage facilities (Chitty et al. 2005).

In the following the corrosion performance of a number of reinforced concrete structures exposed to marine environments is described, admittedly briefly. The observations are then interpreted in terms of research findings, mainly in the materials research literature, and not always well-known to structural engineers dealing with durability issues.

PRACTICAL EXAMPLES

Hornibrook Bridge, Brisbane

In 2010 the 2.7km long, timber superstructure, reinforced concrete substructure, bridge at Bramble Bay, Brisbane was demolished, with considerable difficulty, after some 80 years service immediately adjacent to the Pacific Ocean. Although the vehicular capacity of the bridge was no longer adequate, its substructure was largely in excellent condition. It consisted of 879 reinforced concrete driven piles, each 400 x 400mm in cross-section with (in most cases) only 4 reinforcing bars of 32 mm (1-1/4") diam. with 40 mm cover. The crossheads over the piles were in less good condition. The piles were removed from the seabed with considerable difficulty, in some cases having to be cut just above the seabed because they could not be withdrawn from the soil. With few exceptions, there was no visible evidence of reinforcement corrosion for any of the piles. Figure 1 shows a number of piles in the demolition yard. Several samples of the piles were taken to the Civil Engineering Laboratory, The University of Newcastle for detailed investigation. An early report on this is available (Pape and Melchers 2013) and a detailed paper is in preparation.



Figure 1 Sample piles after demolition showing no exterior evidence of internal corrosion.

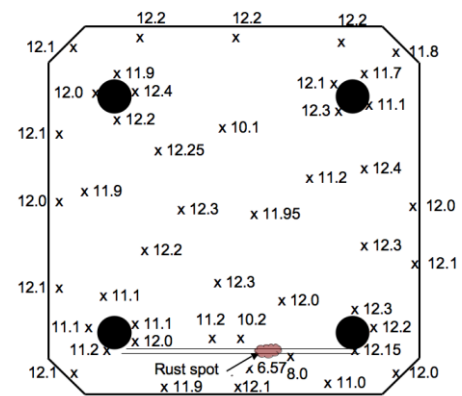


Figure 2 pH map of typical pile cross-section. The pH at the rust spot is about 7.

Schmidt hammer readings were high and compressive tests on cores showed concrete strength of 65-75MPa. This was confirmed empirically by the difficulty laboratory staff experienced in breaking open the samples for examination of the reinforcement. None of the samples showed signs of corrosion although some showed some surface discoloration. Some samples were cut across with a concrete saw and the pH sampled over the cross-sections. Figure 3 gives one example. It shows, as did all others so far examined, that even after some 80 years almost all the concrete still has a pH of at least 9 and mostly around 12. Mostly the cross-sections show no sign of reinforcement corrosion. Petrographic examination of the concrete indicated very minor evidence of alkali-silicate reactions and none of alkali-aggregate reactions. The chloride levels were very high, some 0.6% to 3% by weight of cement – much higher than any permitted by conventional design requirements.

Some of the people associated with the bridge during its construction and subsequently, and with knowledge of the construction industry in the decades after its construction, related that Sir John Hornibrook, the bridge designer and constructor, demanded high quality workmanship and always erred on the side of adding more rather than less cement. The likely sources of cement, sand and aggregate also were identified, although it has not yet been possible to draw conclusions about their possible influence.

During demolition the contractor noted that one pile, on being pulled out of the soil, was obviously cracked about half-way up. Investigation of the cracked area showed the cross-section in Figure 3. It has half the concrete cross-section cracked and showing signs of watery-looking rust stains – the other half was broken during recovery and the reinforcing bars flame-cut. There are no reinforcement bars visible in the area of the rust-stained crack. Evidently, these bars have corroded away almost completely some distance into the concrete (Figure 4). There were no rust stains visible on the exterior concrete surfaces. This means that a routine visual inspection is unlikely to have signalled there were problems with the reinforcement inside.



Figure 3 Cross-section of cracked pile showing rust-stained cracking (left) and flame cut bars and freshly broken concrete (right). (Photo courtesy of Clayton Smith).



Figure 4 Close-up of reinforcing bar at top left of Figure 3 showing extensive inwards corrosion. (Photo courtesy of Clayton Smith).

Handrails at Arbroath, Scotland

Immediately next to the North Sea at Arbroath on the East coast of Scotland there is a 1.6 km long reinforced concrete balustrade constructed during 1943. It consists of some 1000 precast concrete handrail elements each about 2m long and 130 x 150mm in cross-section, with four 6 mm diam. steel reinforcing bars. Some 90% of the 1943 elements remain. The other 10% were replaced in 1968 and in 1993. Remarkably, all replacements have been badly damaged by longitudinal cracking from reinforcement corrosion (Melchers et al. 2009). Samples of the 1943 elements were selected at random by the local Council for detailed examination. This showed the presence of seashells in the concrete, indicating use of beach material and seawater for making the concrete. They also showed very high levels of chlorides in the concrete, much higher than the accepted thresholds for corrosion initiation. There also is wide variations in concrete cover and in aggregate size. There is almost no evidence of external rust staining, perhaps because of the high rainfall in the area washing away any ferrous chlorides (Melchers & Li 2009a). Almost all the cross-sections of the 1943 concrete elements examined showed pH of 9-10 or more, with slight evidence of corrosion initiation only for local pH at reinforcement less than 9.

A number of lengths of 1943 concrete handrails were broken open to reveal almost ‘as-new’ reinforcement. However, one section revealed extremely severe corrosion with almost complete loss of the reinforcing bars, even though there was no longitudinal cracking along the bars. The scenario was generally similar to that in Figs. 3 and 4. Close examination revealed a transverse crack across where the reinforcement had been, with light watery rust staining evident on the adjacent concrete surfaces – again similar to Figs. 3 and 4.

Second Progreso Pier, Yucatan, Mexico

The town of Progreso on the north Yucatan coast of Mexico is perhaps best known as the site of the (first) Progreso pier, completed in 1941 and very lightly reinforced with some stainless steel (grade 304) bars, mostly well inside the otherwise mass concrete structure. It has been used repeatedly to claim (Rostam 2003) the superiority of stainless steel as reinforcement, even though there is clear evidence (Ramboll 1999) of reinforcement corrosion near the ends where the bars protrude from the concrete and despite the bars being well inside the concrete elsewhere and thus well protected by concrete (there are only transverse bars though the bulk concrete). A second Progreso pier was built in about 1969 some 200m west, but was partly demolished some 17 years later because of severe corrosion of its conventional reinforcement in the flat slab deck and in the tops of the reinforced concrete piles. However, the lower parts of the piles, including the parts of the piles in the tidal zone, remain. They protrude above seawater at low tide and, from visual examination, appear not severely affected by reinforcement corrosion and spalling. This can be observed in the field and also in the report by consultants Ramboll (1999). In 2008 the present author was provided with a (random) sample of the concrete from one of the immersed piles. A fresh saw cut through that sample, when examined by optical microscope, showed a dense, highly calcareous structure. The pH of the concrete was 9.5-10.

In interpreting these observations it is noted that the quality of construction along the Yucatan coast is characterized by many examples of severe corrosion damage of reinforced concrete structures (Solis-Carcano et al. 2008). This has been attributed in part to the aggregates and fines used for all concrete construction being the natural limestones that are the only source of rock for much of the Yucatan peninsula (Castro et al. 2000). The resulting concretes typically are relatively porous and sometimes also of poor quality, blamed for domestic construction at least on poor 'construction practices' (Solis-Carcano et al. 2008) including the use of high water-cement ratios (Moreno et al. 2004, Sosa et al. 2007). Although field observations show spalling and delamination of concrete, the reinforcement corrosion rates are not considered to be high. It is unlikely that the second Progreso pier shared the poor quality workmanship but it is likely that with the use of the local limestones it consisted of relatively porous concrete. Despite the deck and the upper parts of the supporting piers not lasting very long, its piers continue to survive, both in the seawater immersion zone and through the tidal zone. This is despite the latter usually being considered the most aggressive of marine exposure zones, with a combination of high salinity, high moisture and high oxygen availability.

Other Cases

A number of older papers describe cases of good quality concrete being made with seawater and in some cases with alkaline materials such as coral (Wig and Ferguson 1917; Narver 1954; Wakeman et al. 1958; Dewar 1963, Mather 1964; Boqi et al. 1983; Burnside and Pomeroy 1984) In addition several more recent cases with features similar to those above have been described. They include:

1. Maria Island cement works silos (1922) (Melchers et al. 2014),
2. Newcastle harbour fortifications (1941) (Melchers 2010a)
3. Thames estuary forts (British Navy, Airforce) (1943) (Melchers 2011),
4. U-boat bunkers along the east Atlantic coast (1940s) (Melchers 2011; Melchers and Pape 2012),
5. Mulberry harbour Phoenix caissons (1944) (Melchers 2010a)
6. Concrete lighters (Severn estuary, Sydney Harbour) (Melchers 2010b; Melchers & Papé 2011)
7. German highway bridges (Lukas 1985)
8. Cylindrical bridge piers in the Gulf of Mexico (Lau et al. 2007).

There also is a review of some 30 reports, extracted from the literature, covering around 300 individual reinforced concrete structures (Melchers and Li 2009b). For these the times to corrosion initiation and to active corrosion were correlated with chloride content and with type of aggregates (both fine and coarse). Within the bounds of the available data, both times were greater for structures likely to have been made with alkaline aggregates (limestones, non-reactive dolomites and blast furnace slags) compared with concretes made with igneous aggregates. Neither times could be correlated with chloride concentration at the reinforcement, concrete cover, concrete quality or cement-making practices (Melchers 2011). The results did not change substantially when cases suspected of alkali-aggregate reactions (AAR) or alkali-silicate reactions (ASR) were removed.

An important observation is that these examples largely are for older reinforced concrete structures made without any of the modern additives claimed to reduce the probability of reinforcement corrosion such as through decreasing concrete permeability. They also were made largely with very modest concrete cover, often much less than increasingly being mandated in modern design codes. It has been proposed that the concretes for the older structures were made with cements that were clinkered at lower temperatures and not as finely ground but close examination shows that there is only a minor difference in active ingredients between the 'older' and 'new' cements (Nixon and Spooner 1993). Further, there certainly were problems with reinforcement corrosion even for the older structures (Wakeman et al. 1958).

ANALYSIS

Several questions arise immediately from the above observations:

1. why very high chloride concentrations do not cause reinforcement corrosion in some concrete structures,
2. how to reconcile the corrosion threshold of pH 11 stated in older texts with field observations showing a much lower threshold (of around pH 9),
3. the reason for pH >9 in some concrete structures even after many years in-service in aggressive environments,
4. why carbonaceous aggregates appear to inhibit corrosion initiation when 'carbonation' is considered to cause corrosion, and
5. how to reconcile severe reinforcement corrosion inside some concrete structures with the lack of exterior signs such as rust staining.

Answers to these questions largely are available in the existing corrosion literature but appear not well-known. It is useful to begin with the fundamentals of corrosion of ferrous materials such as steel. The key recognition is that the structures that behave very well are those for which reinforcement corrosion has not yet become active. Earlier this was idealized as a bi-linear function attributed to Tuuti (1982) but more properly it should consider the possibility that some minor corrosion may occur when small reservoirs of oxygen and water are available immediately around the bars, left over from the casting process and perhaps inadequate compaction (Melchers and Li 2006). Typically the early corrosion will be minor, unless the concrete is of poor quality. For the following, let this possibility be ignored and attention focussed on good quality concretes. Figure 5 shows the modified behaviour. The important time is thus t_{ac} at which active corrosion commences.

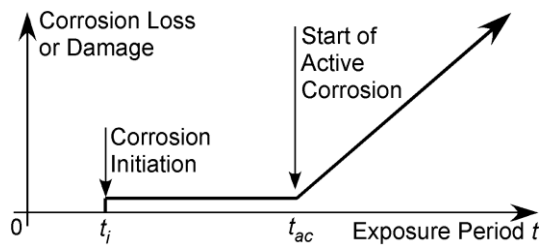


Figure 5 Model for corrosion initiation at time t_i and active corrosion at t_{ac} .

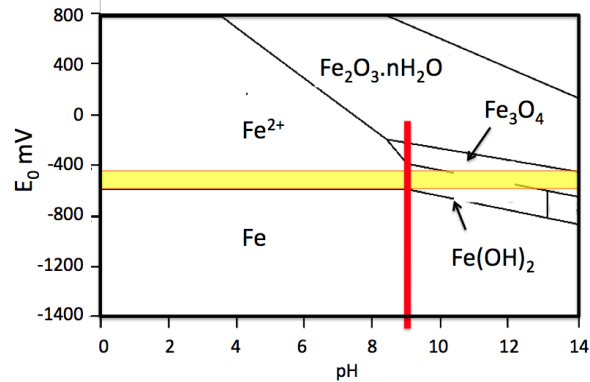


Figure 6 Schematic Pourbaix diagram showing main rust products and pH for initiation.

Corrosion initiation of reinforcing steel (essentially iron, Fe) must follow corrosion science principles. It can occur only when the reaction(s) involved becomes feasible, and this is when the net free (Gibbs) energy ΔG becomes negative (Brown and LeMay 1981). In the corrosion literature this is usually summarized in a Pourbaix diagram for Fe (Figure 6). It shows the various relationships for different reaction outcomes in terms of electrochemical potential E and pH. For Fe in water the relevant potential E_0 at which corrosion products are formed is around -440 mV (SHE) and the pH for corrosion initiation occurs is about 9-9.5 (the exact value depending on the energy level taken as 'zero' corrosion). These values are not changed very much by the presence of chlorides (Garrels and Christ 1965; Jones 1996; Huet et al. 2005). Note that this value corresponds with the observations for actual structures with very high chloride levels for which reinforcement corrosion has not yet occurred (e.g. Figure 2). The important point is that corrosion initiation cannot occur as long as the pH of the concrete (or pore space fluid) in the immediate vicinity of the reinforcement bar is maintained above 9-9.5. Obviously this condition can be violated by cracking of the concrete along, or across, the bar if this results in a mechanism that allows the local pH to reduce below 9-9.5 in value. This possibility is discussed further below.

Not all texts now make the claim that the criterion for reinforcement initiation is pH of around 11 but that was the situation for many years (e.g. Gjorv 2009). The reason is as follows. It arises from laboratory experiments in which $\text{Ca}(\text{OH})_2$ (calcium hydroxide) added to water, or a similar alkali solution, was used to mimic (approximately) concrete alkalinity achieving a pH of about 12.5-13. A steel bar was then added to the solution and the pH of the solution lowered chemically until corrosion initiation of the bar was observed (visually or electrochemically). In such experiments the solution is agitated by stirring or air bubbling to reduce boundary effects (concentration control effects) and so speed-up the reaction. Unfortunately this does not mimic the real condition for a reinforcement bar inside concrete. There, no water velocity conditions are involved and the initiation reaction must occur, if it is to occur at all, under stagnant conditions. Already in 1908 it was demonstrated that salts (including NaCl and CaCl_2) have almost no effect on corrosion in stagnant conditions (Brauns and Schwenk 1908) and this was confirmed by Brasher (1967) who showed that chlorides only become important for corrosion initiation in non-stagnant solutions. It was confirmed independently also by Mercer & Lumbard (1995). Experiments with agitated solutions will cause corrosion to initiate at a higher pH when chlorides are involved.

The above remarks clearly indicate the important of pH in relation to corrosion initiation. New concretes have a pH around 13.5 and it is well-known that the alkalis primarily responsible are KOH, NaOH and $\text{Ca}(\text{OH})_2$. Of these, KOH and NaOH are highly soluble and leach out of concrete relatively easily. In the process the pH reduces to about 12 because of the remaining $\text{Ca}(\text{OH})_2$. It is not very soluble and takes a long time to leach out under the action of freshwater. Thus the concrete will tend to retain a pH around 12. Two mechanisms may lower it. One is well-known as 'carbonation', in which carbon dioxide from the atmosphere diffuses into the

concrete and then eventually reacts with the $\text{Ca}(\text{OH})_2$ to form CaCO_3 (and possibly carbonic acid) which is claimed to reduce the pH sufficiently for corrosion to initiate. However, for good quality concretes this mechanism may be ignored since field experience shows that carbonation penetration seldom exceeds a few millimetres into the concrete (St John et al. 1998; Moreno et al. 2004). The other possibility is that chlorides play a role in lowering concrete pH.

It has been shown that the presence of NaCl increases the solubility of dilute $\text{Ca}(\text{OH})_2$ solutions (Johnston and Grove 1931), thereby permitting a faster rate of leaching out of the concrete matrix. This mechanism has been proposed also for solutions with higher concentrations of $\text{Ca}(\text{OH})_2$ (Hewlett 1988). It is also possible that the magnesium sulfates and chlorides (MgSO_4 , MgCl_2) present in seawater react with $\text{Ca}(\text{OH})_2$ and so reduce its presence and hence the alkalinity of the concrete (Hewlett 1988). These mechanisms are presently again under investigation (Melchers 2014a). However, irrespective of the precise mechanisms involved, the fact remains that seawater is somehow implicated in loss of alkalinity, that is, the loss of *buffering capacity* for maintaining pH, and this is the central factor in maintaining pH high enough for initiation not to occur. This point was made already many years ago in a slightly different context (Glass and Buenfeld 1997; Moreno et al. 2004). Of course, the rate at which $\text{Ca}(\text{OH})_2$ (and KOH and NaOH) leaching can occur depends on the permeability of the concrete matrix and this is consistent with the notion that high quality, high density concretes are less prone to reinforcement corrosion. It follows that it is not the rate of inward diffusion of chlorides, but the rate of outward leaching of alkalis that is the determining factor for the time to corrosion initiation.

For concretes immersed in seawater it often is claimed that the low oxygen concentration in seawater is responsible for the very low rates of reinforcement corrosion under water, that is, after corrosion initiation has already occurred. Unfortunately, the idea that the dissolved oxygen level in waters are so low that corrosion is inhibited is not supported by the considerable corrosion of bare steels, which corrode severely in seawater as well as in fresh water. Examples are shown in Figure 7 for general corrosion and for corrosion pit depth in sea, brackish and fresh waters of similar pH (Forgeson et al. 1960). This shows also that salinity *per se* is not a major issue. The factor actually responsible for reducing the *rate* of corrosion of reinforcement in concrete immersed in seawater is the surface pH of the concrete and, for long-term durability, its alkalinity. It is well-known in the literature that the alkaline surfaces of good concrete attracts deposition of CaCO_3 in the form of aragonite as well as brucite (MgCO_3). This build-up reduces the rate at which oxygen can diffuse to the reinforcement (Buenfeld and Newman 1984). The build-up also tends to increase with time, further reducing the rate of corrosion.

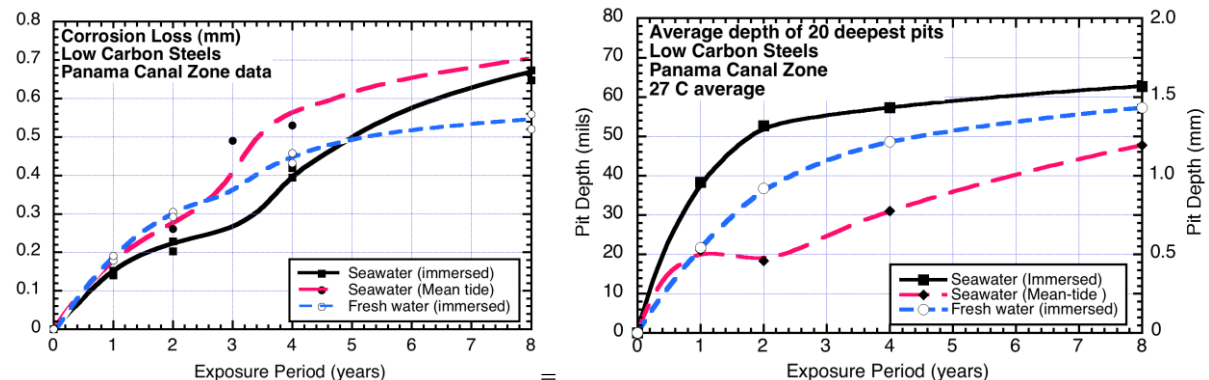


Figure 7 Corrosion trends for seawater and fresh water immersed conditions: (a) corrosion loss and (b) pit depths. (Data from Forgeson et al. 1960 for average of 3 steels with replicate samples).

As noted for the examples given above, the reinforced concrete structures containing calcium carbonates (CaCO_3) (such as limestone aggregates, blast furnace slag or seashells) generally showed longer times to corrosion initiation than other reinforced concrete structures. At first sight this conflicts with the well-known concept of carbonation, for which, as noted, carbon dioxide CO_2 reacts with $\text{Ca}(\text{OH})_2$ to form CaCO_3 which is generally considered, theoretically at least, to be a harmful in terms of corrosion initiation. The contradiction with practical experience that has concretes made with limestones, for example, is sometimes sidestepped by noting that the initiation of corrosion is 'induced' by carbonation, without being specific about the mechanism actually involved. However, the most likely mechanism can be seen from the explanation of the processes involved. To diffuse into the concrete matrix CO_2 must combine with moisture (water). This may be thought of as forming 'carbonic acid' through the 'reaction' $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$ (Brown and Lemay 1981). This

proceeds into the concrete and in so doing reacts with $\text{Ca}(\text{OH})_2$ to form CaCO_3 along the way. Evidently, as the $\text{Ca}(\text{OH})_2$ is consumed more CaCO_3 is formed but eventually the $\text{Ca}(\text{OH})_2$ reachable by the carbonic acid will be exhausted along the carbonation path. Excess H_2CO_3 can then attack the steel (Hamada 1969). Hence it is not the CaCO_3 that lowers the concrete pH under ‘carbonation’ but the (eventual) excess carbonic acid. Particularly under anoxic conditions carbonic acid is very corrosive to steels. Such a condition also is likely to exist inside well-made concretes. All this assumes, of course, that the ‘carbonation’ front reaches the steel. As noted, this is very unlikely for good quality concretes.

Consider now the severe corrosion such as seen in Figure 4. As noted above, for the cases in which this occurred, the concrete showed cracking, usually transverse to the reinforcement but little or no trace of corrosion products, despite the significant loss of steel reinforcement. The immediate question is where did the steel go, and how? The watery rust stains are a direct indicator that the chlorides present in waters reacted with Fe to form highly soluble, almost clear coloured, FeCl_2 that, in wet conditions, such as in the tidal zone (Hornibrook), or under frequent periodic rain (Arbroath, Yucatan), can easily diffuse away. In so doing it leaves little trace, and what is there is oxidized to conventional insoluble rusts. These are the visible watery-looking stains on the cross-section.

The only mechanism consistent with the dissolution of Fe by chlorides is that of highly aggressive pitting or crevice corrosion under anoxic conditions within pits (Wranglen 1974). The fine crack in the concrete adjacent to and interacting with the steel reinforcing bar permits such anoxic conditions. It can be seen as a pitting or crevice corrosion initiator, noting that MnS inclusions, always present in steels, are involved also (Wranglen 1974). No other mechanism is known to cause such aggressive localized corrosion, although it may be aggravated by microbiologically influenced corrosion particularly in nutrient-polluted marine conditions (Melchers 2014b).

DISCUSSION

It should be clear from the above that the most important factor for long term durability of reinforcement in concrete structures is the alkalinity of the concrete, that is, its capacity to buffer the pH of the concrete to a value above that which would allow corrosion initiation. The evidence is that such buffering is provided by high cement content, and addition of high alkalinity aggregates and sands. As shown above, there is strong field experience in support. There also is evidence from controlled corrosion science experiments (Davies and Burstein 1980).

Many of the observations in the analyses given above are already known within various niches in corrosion science and to a lesser extent in the reinforcement corrosion literature. Nevertheless, the notions persist that chlorides (and carbonation) are responsible primarily, sooner or later, for causing the initiation of reinforcement corrosion. This is despite much practical evidence that very high concentrations of chlorides can exist without reinforcement corrosion. In science, one valid piece of evidence that does not fit accepted theory tenders the theory invalid - and the scientists ‘go back to the drawing board’. The same should apply in engineering science.

Unfortunately, there appears also to be a lack of ‘memory’ or, worse, failure to do homework. Prior to about the 1960s in most countries the possibility of using seawater as mixing water for making concretes was not prohibited. There is a rich history of using seawater in concretes (Narver 1954; Wakeman et al. 1958). Although not considered in detail here, all the evidence that is available indicates that sea sands and seawater from the North Sea were used in the construction of the U-boat bunkers along the French coast (Neitzel 1991; Showell 2002) and which even today are in remarkably good condition. Similarly, seawaters and beach sands appear to have been used for many of the Phoenix caissons constructed for the Normandy invasion (1944) and a considerable number of those not destroyed by storm conditions remain in still reasonable condition (Melchers 2010b, 2011).

In practice, to achieve long-term durability of concrete structures and in particular their reinforcement in exposed environments, much more attention needs to be given to producing concretes with high pH buffering capability (i.e. with high alkalinity). The obvious way of doing this is to add more cement, as indeed Hornibrook is reputed to have recommended for his bridge. However, cement is expensive and its production increasingly being seen as environmentally unfriendly, as a result of which there are strong moves to reduce usage of cement. If this causes earlier deterioration of reinforced concrete structures, cement reduction may be counter-productive overall, since structures may need to be repaired pre-maturely, or replaced with consequent direct and indirect costs and environmental implications and consequences.

The present review, and earlier examinations of the available data (Melchers & Li 2009), indicates that an alternative approach is to make greater use of limestones and similar alkaline materials as part of the concrete mix. The evidence shows that concretes made with such aggregates can delay reinforcement corrosion initiation considerably in time, provided the concretes also are of high quality including low permeability. In marine environments the concrete also must be of sufficient tensile strength to reduce as much as possible the occurrence of cracking since, as noted above, this may permit the occurrence of aggressive localized corrosion under chloride conditions. The possible effect of the use of other additives, for example fly-ash, if they reduce concrete tensile strength.

It follows from the above observations that potential causes of concrete cracking must be considered in design for durability. Cracking may result from applied loading during service, but also from early loading when the concrete is still developing strength. For example, it is likely that the cracking seen in Figure 3 was caused during pile handling or driving since after installation the pile would have been in compression. It follows that much more attention needs to be given to the stresses imposed by any of the loadings possible during the whole lifetime, focussing on the possibility of cracking deep enough to allow, eventually, the development of the severe corrosion seen in Figure 4. Also, the current codified design rules for concrete cracking need revisiting. They are based largely on early research that did not consider *long-term* marine exposure conditions (Beeby 1978).

Finally, the observations given above make clear that particularly in marine environments visual inspection may not be sufficient to detect evidence of reinforcement corrosion.

CONCLUSIONS

1. The conventional notion that a high concentration of chlorides is the prime reason for initiation of reinforcement corrosion is not supported by evidence from actual concrete structures. It also is not consistent with fundamental corrosion science. Corrosion initiation largely is the result of the loss of sufficient alkalinity immediately adjacent to the reinforcement bars. This loss can be accelerated by the presence of chlorides.
2. Long-term durability of steel reinforcement in concrete structures requires the concrete matrix to retain high alkalinity, that is, sufficient buffering capacity to maintain the pH of the concrete matrix around the reinforcement to greater than 9 for the desired time to corrosion initiation,
3. The highly alkaline concrete matrix must be in intimate contact with the reinforcement to ensure the pH at the bars is maintained. This requires well-compacted concretes of high density.
4. A high quality, low permeability concrete matrix is required to slow the outward diffusion of the alkalis in the concrete, particularly in chloride environments.
5. Lowering of the pH around reinforcement bars can result also from carbonic acid not neutralized in the carbonation process during inward diffusion of carbon dioxide. Practical experience shows that, except for poor quality concretes, such diffusion extends only a few millimetres into the concrete.
6. The tensile strength of the concrete, including in the initial period, should be high to reduce the probability of concrete cracking severe enough to reach the reinforcement. Field experience shows that particularly in chloride environments such cracking can initiate very severe localized reinforcement corrosion.
7. To assist in developing new criteria for long-term durability, improved understanding is required of the quantitative relationships between concrete permeability, concrete density and the outward diffusion of alkalis as well as the effect of concrete additives on concrete tensile strength and concrete permeability.

ACKNOWLEDGMENT

The author acknowledges the continued financial support of the Australian Research Council, currently through a DORA Fellowship. The author is indebted also to (the late) Dr. Eric Moreno of the Autonomous University of Yucatan, Mexico for stimulating discussions and for the provision (in 2008) of a 200mm sized sample of one of the piles from the second pier at Progreso, Mexico, as well as the support of Prof. C.Q. Li (now at RMIT University, Melbourne Australia), Dr. Torill Pape (now with ARRB, Brisbane), Dr. Robert Heywood (Consultant, Brisbane) and Dr Igor Chaves (The University of Newcastle) for their support during various parts of the investigations reported herein.

REFERENCES

- Beeby, A.W. (1978). "Corrosion of reinforcing steel in concrete and its relation to cracking", *The Structural Engineer*, 56A(3): 77-81.
- Boqi, C., Dinghai, H., Hengquan, G. and Yinghao, Z. (1983). "Ten-year field exposure tests on the endurance of reinforced concrete in harbor works", *Cement and Concrete Research*, 13: 603-610.
- Brasher, D.M. (1967). "Stability of the oxide film on metals in relation to inhibition of corrosion. I. Mild steel in the presence of aggressive ions", *Brit. Corr. J.*, 2: 95-103.
- Brauns, E. and Schwenk, W. (1908). "Korrosion unlegierter Stahle in Seewasser", *Stahl u. Eisen*, 87(12), 713-718.
- Brown, T.L. and Lemay, H.E. (1981). "Chemistry: The Central Science", 2nd Edn., Prentice-Hall, Englewood Cliffs.
- Buenfeld, N.R. and Newman, J.B. (1984). "The permeability of concrete in a marine environment", *Magazine of Concrete Research*, 36(127): 67-80.
- Burnside, O.H. and Pomeroy, D.J. (1984). "Survey of experience using reinforced concrete in floating marine structures", *Report SSC-321*, Ships Structures Committee, US Coast Guard Headquarters, Washington DC.
- Castro, P., Sanjuan, M.A. and Genesca, J. (2000). "Carbonation of concretes in the Mexican Gulf", *Building and Environment* 35: 145-149.
- Chitty, W.-J., Dillmann, P., L'Hostis, V. and Lombard, C. (2005). "Long-term corrosion resistance of metallic reinforcements in concrete - a study of corrosion mechanisms based on archaeological artifacts", *Corrosion Science*, 47: 1555-1581.
- Davies, D.H. and Burstein, G.T. (1980). "The effects of bicarbonate on the corrosion and passivation of iron", *Corrosion*, 36(8): 416-422.
- Dewar, J.D. (1963). "The workability and compressive strength of concrete made with seawater", *Tech Rep, TRA/374*, C&CA, London.
- Forgeson, B.W., Southwell, C.R. and Alexander, A.L. (1960). "Corrosion of metals in tropical environments - Part 3 - Underwater corrosion of ten structural steels", *Corrosion*, 16(3)105t-114t.
- Garrels, R.M. and Christ, C.L. (1965). *Solutions, minerals, and equilibria*, New York: Harper & Row.
- Gjorv, O.E. (2009). *Durability design of concrete structures in severe environments*, London, Taylor & Francis.
- Glass, G.K. & Buenfeld, N.R. (1997). "The presentation of the chloride threshold level for corrosion of steel in concrete", *Corrosion Science* 39(5): 1001-1013.
- Hamada, M. (1969). "Neutralization (carbonation) of concrete and corrosion of reinforcing steel", *Proceedings, International Symposium on Chemistry of Concrete*, Vol. 3 Part 3 Carbonation of Concrete, 343-369.
- Hansson, C.M. (2000). Discussion of "Corrosion effects on bond strength in reinforced concrete", Paper by Stanish, K., Hooton, R.D. and Pantazopoulou, S.J., *ACI Structural Journal*, 97(5): 789-790.
- Hewlett P.C. (Ed) (1988). *Lea's Chemistry of Cement and Concrete*, 4th Edn, Butterworth, Oxford, p. 319.
- Huet, B., L'Hostis V.L., Miserque, F. and Idrissi, H. (2005). "Electrochemical behavior of mild steel in concrete: Influence of pH and carbonate content of concrete pore solution", *Electrochim. Acta* 51: 172-180.
- Hunkeler, F. (2005). "Corrosion in reinforced concrete: processes and mechanisms", (In) *Corrosion in reinforced concrete structures*, (Ed) H. Bohni, Woodhead Publishing Limited, Cambridge, 1-45.
- Johnston, J. and Grove, C. (1931). "The solubility of calcium hydroxide in aqueous salt solutions," *J. of the Am. Chem. Soc.* 53(11) 3976-3991.
- Jones, D. (1996). *Principles and Prevention of Corrosion*. Second Ed. Upper Saddle River: Prentice-Hall.
- Lau, K., Sagues, A.A., Yao, L. and Powers, R.G. (2007). "Corrosion performance of concrete cylinder piles", *Corrosion*, 63(4) 366-378.
- Lee, J.S., Ray, R.I. and Little, B.J. (2010). "The influence of experimental conditions on the outcome of laboratory investigations using natural coastal seawaters", *Corrosion* 66(1) 105001-1 - 6.
- Lukas, W. (1985). "Relationship between chloride content in concrete and corrosion in un-tensioned reinforcement on Austrian bridges and concrete road surfacings", *Betonwerk und Fertigteil-Technik*, 51(11) 730-734.
- Mather, B. (1964). "The effects of sea water on concrete", *Misc Paper 6-690*, US Army Eng Waterw. Exp. Stn, Vicksburg, MI.
- Melchers, R.E. (2010a). "Carbonates, carbonation and the durability of reinforced concrete marine structures", *Aust. J. Struct. Engrg*, 10(3) 215-226.
- Melchers, R.E. (2010b). "Observations about the time to commencement of reinforcement corrosion for concrete structures in marine environments", *Consec'10, Concrete under severe conditions*, (Ed.) P. Castro-Borges, E. Moreno, K. Sakai, O.E. Gjorv and N. Banthia, CRC Press, Boca Raton, 617-624.
- Melchers, R.E. (2011). "Observations about the corrosion of reinforcement in marine environments", *Proc. XII DBMC, Int. Conf. on Durability of Building Materials and Components*, Porto, Portugal, April 12-15, Paper 6.59.

- Melchers, R.E. (2014a). "Fundamentals, mechanisms and reactions in marine reinforcement corrosion", Proc., 23rd Australasian Conf. Mech. Structs. (ACMSM23), Byron Bay, 9-12 Dec., Paper 087.
- Melchers, R.E. (2014b). "Microbiological and abiotic processes in modelling longer-term marine corrosion of steel", *Bioelectrochem*, 97: 89-96.
- Melchers, R.E. and Li, C.Q. (2006). "Phenomenological modelling of corrosion loss of steel reinforcement in marine environments", *ACI Materials Journal*, 103(1): 25-32.
- Melchers, R.E. and Li, C.Q. (2009a). Reinforcement corrosion in concrete exposed to the North Sea for over 60 years, *Corrosion* 65(8): 554-566.
- Melchers, R.E. and Li, C.Q. (2009b). "Reinforcement corrosion initiation and activation times in concrete structures exposed to severe marine environments", *Cement and Concrete Research*, 39: 1068-1076.
- Melchers, R.E. and Papé T.M. (2011). "Aspects of long-term durability of reinforced concrete structures in marine environments", *European Journal of Environmental and Civil Engineering*, 15(7) 969-980.
- Melchers, R.E. and Pape, T.M. (2012). "The durability of reinforced concrete structures in marine environments", *Proc. Australasian Structural Engineering Conf.*, Sydney, July 11-13, 2012. Paper 094.
- Melchers, R.E., Li, C.Q. and Davison, M.A. (2009). "Observations and analysis of a 63-year old reinforced concrete promenade railing exposed to the North Sea", *Magazine of Concrete Research* 61(4): 233-243.
- Melchers, R.E., Papé T.M. and Chaves, I.A. (2014). "The long-term durability of reinforced concrete structures exposed to aggressive marine environments", *Proc. 1st Int. Conf. on Infrastructure Failures and Consequences*, 16-20 July, Melbourne, Paper No. SFC 103.
- Mercer, A.D. and Lombard, E.A. (1995). "Corrosion of mild steel in water", *Brit. Corros. J.*, 30(1) 43 - 55.
- Moreno, E.I., Cob-Sarabia E. and Borges, P.C. (2004). "Carbonation rates from blended cement concretes", *Corrosion 2004*, 28 March – 1 April, New Orleans, NACE International, Houston.
- Moreno, M., Morris, W., Alvarez, M. G. and Duffó, G. S. (2004). "Corrosion of reinforcing steel in simulated concrete pore solutions: Effect of carbonation and chloride content", *Corrosion Sci.* 46(11): 2681-2699.
- Narver, D.L. (1954). "Good concrete made with coral and seawater", *Civil Engineering*, 24(11) 49-52.
- Neitzel, S. (1991). "Die deutschen Ubootbunker und Bunkerwerften", Bernard & Graefe Verlag, Koblenz.
- Nixon, P.J. and Spooner, D.C. (1993). "Concrete proof for British cement", *Concrete* 27(5): 41-44.
- Pape T.M. and Melchers R.E. (2013). "A Study Of Reinforced Concrete Piles From The Hornibrook Highway Bridge (1935-2011)", *Proc. ACA Conf. Corrosion & Prevention 2013*, 10-13 Nov., Brisbane, Paper 086.
- Parrott, L.J. (1987). *A review of carbonation in reinforced concrete*, Building Research Establishment, Department of the Environment, UK.
- Ramboll (1999). "Pier in Progreso, Mexico", *Inspection Report, Evaluation of stainless steel reinforcement*, RAMBOLL Consulting Engineers and Planners, Job no. 990022, March 1999 (Document: P:\bredesager\bro_ved\udvikling.99\990022R_002.doc) (see also: Arminox_Progreso_Pier_Report_web.pdf)
- Richardson, M.G. (2002). *Fundamentals of durable reinforced concrete*. London: SponPress.
- Rostam, S. (2003). "Reinforced concrete structures - shall concrete remain the dominating means of corrosion prevention?", *Materials and Construction* 54: 369-378.
- Showell, JPM (2002). *Hitler's U-boat Bases*, Sutton, Stroud, UK.
- Solis-Carcano, R.G., Moreno, E.I., Castro-Borges, P., Jimenez-Torres, F. and Marquez-Novelo, R. (2008). "Behavior of coastal concrete housings against environmental loading in the Caribbean", *Corrosion 2008*, Paper 08318, Houston: National Association of Corrosion Engineers.
- Sosa, M., Camacho, R., Perez, T. and Gonzalez-Sanchez, J. (2007). "Cathodic protection of concrete structures containing calcareous aggregates in tropical-humid marine environments", *Anti-corrosion Methods and Materials* 54(2): 103-110.
- St. John, D.A., Poole, A.W. and Sims, I. (1998). *Concrete Petrography*, Arnold, London.
- Tuuti, K. (1982). "Corrosion of steel in concrete", *Research Report No 4*, Stockholm: Swedish Cement and Concrete Research Institute, 17-21.
- Wakeman, C.M., Dockweiler, E.V., Stover, H.E. and Whiteneck, L.L. (1958). "Use of concrete in marine environments", *Proc ACI*, 54(4) 841-856.
- Wig, R.J. and Ferguson, L.R. (1917). "Reinforced concrete in seawater fails from corroded steel", *Engineering News-Record*, 79(15) 689-693.
- Wranglen, G. (1974). "Pitting and sulphide inclusions in steel", *Corrosion Science*, 14: 331-349.