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## FUNDAMENTALS, MECHANISMS AND REACTIONS IN MARINE REINFORCEMENT CORROSION

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### ABSTRACT

According to conventional wisdom reinforcement corrosion commences when the inward diffusion of chlorides causes a critical concentration at the steel or when the pH of the concrete falls below about 11. These criteria are inconsistent with basic corrosion science and with field observations. A 10 year study showed only negligible corrosion for concretes made with seawater. Compaction was high. It influences contact between reinforcement and concrete. Loss of alkalis is the main cause for corrosion initiation. This is consistent with classical observations that in stagnant conditions, as inside well-made concretes, oxygen rather than chloride is the governing electron acceptor. Mechanisms for alkali loss are described. Although these mechanisms depart from the conventional wisdom, the requirements for durable reinforced concrete structures do, however, agree.

### KEYWORDS

Reinforcement, corrosion, marine, chlorides, alkalinity, thermodynamics.

### INTRODUCTION

The corrosion of steel reinforcement in reinforced concrete structures exposed to marine environments continues to be a matter of considerable interest for structures that are expected to have a long lifetime. Despite much research effort, the mechanisms involved remain elusive and theory does not always relate to practical experience (Li & Melchers 2009a, 2009b, Melchers 2010, Pape et al. 2013, 2014).

An outstanding example is the Hornibrook bridge, recently demolished because of inadequate traffic capacity. Few of nearly 900 reinforced concrete driven piles, exposed to tidal Pacific ocean seawater for more than 80 years at Bramble Bay, Brisbane, showed signs of reinforcement corrosion (Pape et al. 2013). Random samples of complete cross-sections showed very high chloride concentrations (>4% by weight of cement). Current design guidelines for reinforcement in marine exposures would predict these piles to show considerable distress. Nearly all of the concrete cross-sections showed pH readings above 12, except for isolated small spots with pH below 9, where there was minor (tie-bar) corrosion.

A second example is the 65 year old reinforced concrete balustrade at Arbroath, Scotland, where detailed investigations of some 1000 identical elements showed chloride concentrations above 2%, well above the usually accepted limits, pH of the concrete cross-sections mainly around 10 or more and only very mild reinforcement corrosion and almost no longitudinal cracking. The concrete contained many seashells, suggesting it had been made with seawater. This practice was not disallowed in the UK (and Australia) until the 1960s (Melchers & Li 2009a).

These and other observations conflict with current conventional wisdom that attributes the initiation of reinforcement corrosion entirely to the arrival of a sufficient high concentration of chlorides at the reinforcing bars. Specifically, the conventional wisdom is that corrosion starts when:



- (1) total chloride ion concentration  $[Cl^-] > 0.4-0.6$  % mass of cement, or
- (2) chloride ion concentration / hydroxide ion concentration ratio  $[Cl^-] / [OH^-] > 0.6 - 0.7$

Usually there is recognition that concrete alkalinity (acid neutralizing capacity) may have a role to play, stated in some (but not all) texts as:

- (3) corrosion initiates once the concrete  $pH < 11$ .

The two examples given above clearly violate one or more of these 'criteria'. In science even one (proper) example that does not fit an accepted theory is considered to disprove it. For reinforcement corrosion there are many practical cases inconsistent with the conventional wisdom, including the models accepted for the initiation and progression of reinforcement corrosion. The question that arises, therefore, is whether the conventional wisdom is correct. To throw light on this it is useful to re-examine some early experiments, particularly those that led to the notion that chlorides are directly responsible for reinforcement corrosion. This is described in the following section, followed by a brief review of fundamental principles of steel corrosion in marine conditions. Although the argument is presented in terms of corrosion mechanics, ultimately it is about untangling various and possibly conflicting pieces of information and developing new theory supported by scientific principles. It is an issue not only for corrosion mechanics.

## EXPERIMENTAL OBSERVATIONS

The notion that the chlorides present in seawater are responsible for reinforcement corrosion usually is attributed to the laboratory studies of Shalon & Raphael (1959) who reported serious corrosion already after 1-2 years exposure for steel bars in small concrete samples made with seawater. Because this seemed inconsistent with field observations, a replicate test program was commenced in 2003. Samples of the same size (40 x 40 x 160 mm) each with one 5 mm diam. central longitudinal reinforcing bar were constructed with (mainly) standard cement and well-graded igneous aggregates. As in the 1959 tests, the samples were made with seawater. After casting and careful stripping they were exposed, as in the 1959 tests, to warm humid air in the laboratory fog room. Every year one sample was examined for corrosion loss (Melchers & Chaves 2014). Unlike the 1959 samples, the new samples showed negligible corrosion, after 10 years exposure, irrespective of aggregate/cement (a/c) and water/cement (w/c) ratios. Fig. 1 shows example corrosion loss trends plotted from data reported by Shalon & Raphael (1959) and the corresponding new test results.

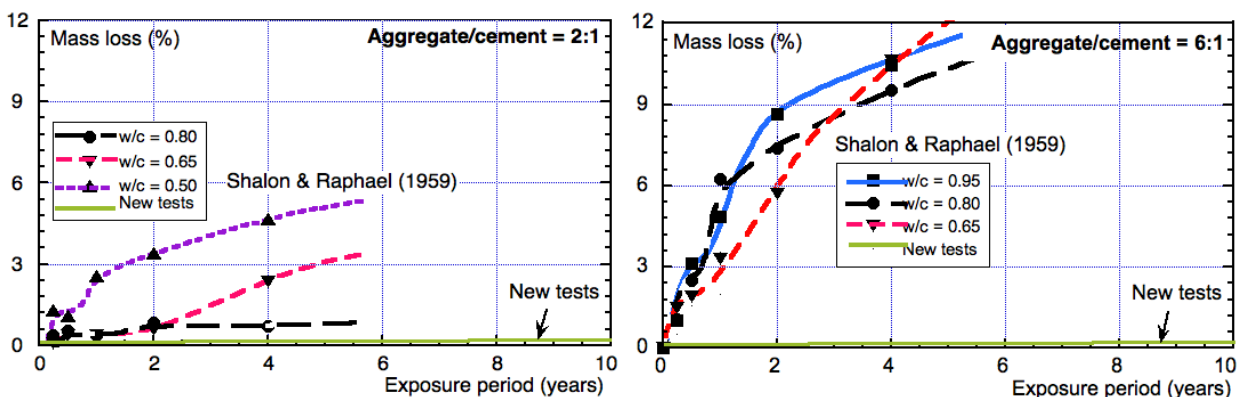


Figure 1. Corrosion loss as a function of time, and concrete mix properties (© RE Melchers).

The trends for corrosion shown Fig. 1 for the 1959 experiments have a pattern that is remarkably similar to the bi-modal pattern for the corrosion of bare steels in water, including in seawater (Melchers 2003a). Of course, that pattern would not have been recognized at the time even if Shalon & Raphael had plotted their data. It is now clear that the reinforcement in the 1959 tests corroded in a manner similar to bare steel in seawater. It follows that the 1959 concrete provided little protection against corrosion. In short, the 1959 tests are unrepresentative of good quality concrete.

For the new tests, the most obvious difference between the concretes in Fig. 1 is the quality of the concrete, evident from visual inspection (Fig. 2). This is indicative also of concrete strength, hardness, and inversely of diffusion capability. The higher quality concretes (e.g. Fig. 2 left) show higher pH readings (around 12) than do the weak, porous concretes (e.g. Fig. 2 right) that showed pH around 10. pH readings were not reported for the 1959 tests.

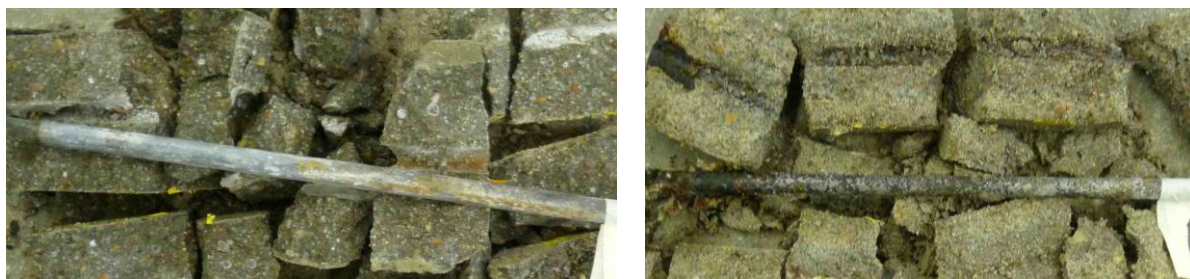


Figure 2. Concretes and the reinforcing bars immediately after breaking open samples, from (left) B1 ( $a/c = 2:1$ ,  $w/c = 0.5$ ) showing dense, strong concrete (pH about 12) and negligible reinforcement corrosion, and (right) B7 ( $a/c = 6:1$ ,  $w/c = 0.65$ ) showing relatively weak and porous (permeable) concrete (with pH about 10) and evidence of reinforcement corrosion. (© RE Melchers)

The new and the 1959 programs both used specimens of identical sizes and similar aggregate/cement and water/cement ratios. Both used seawater as mixing water. Changes in cement-making are known not to have changed significantly the concrete calcium hydroxide (alkali) content (St John et al. 1998). Small differences in reinforcement steel composition have negligible effect on corrosion (Evans 1960). The non-calcareous aggregates in the new tests should, if anything, have had a deleterious effect compared with the limestone aggregate used in the 1959 tests (Melchers & Li 2009b). Most likely the difference in corrosion results lies in the degree of compaction of the concrete. In the new tests the specimens were well vibrated. This was not the case for the 1959 tests - the bars were “inserted in the ... specimens” (Shalon & Raphael 1959). There is no mention of vibration or similar. Taken together, these points indicate the 1959 test program was flawed. Inadequate compaction left the 1959 concretes with high permeability and with poor contact between alkaline concrete and the steel bars. In contrast, the new test results show that irrespective of aggregate/cement and water/cement ratios, the presence of high levels of chlorides, even immediately adjacent to the reinforcement, does not necessarily cause reinforcement corrosion or its initiation. These observations and conclusions are consistent with field observations. The question remains how it compares with corrosion fundamentals.

## INITIATION OF CORROSION IN WATER

The corrosion of reinforcing steel, which is mainly iron (Fe), must follow well-established principles. Corrosion initiates when the reaction(s) involved becomes feasible, i.e. when the net free energy  $\Delta G$  becomes negative (Brown & LeMay 1981). This says nothing about the *rate* of the ensuing reaction. The various possible reactions (and the relevant corrosion products) usually are summarized in the Pourbaix diagram for Fe (Fig. 3). It shows a summary for the relationships between electrochemical potential and pH. For steel (or Fe) in water the relevant potential  $E_0$  is around -440 mV (SHE). This is not changed very much by the presence of chlorides (Jones 1996). Also, the pH below which thermodynamics permits a corrosion reaction is about 9-9.5 (the exact value depending on the energy level taken as ‘zero’ corrosion). This fits in with the field observations mentioned earlier. The obvious question is why this does not fit the criterion (3) stated in many reinforcement corrosion texts.

To understand origin of the criterion  $pH < 11$  the original experiments must be re-visited. Usually the typical test arrangement uses  $Ca(OH)_2$  (calcium hydroxide) as the alkali to mimic concrete, added to water (Shalon & Raphael 1959, Escalante & Ito 1990). This leaves a liquid with pH around 12.5-13 into which a steel sample is immersed and sufficient salt added to mimic seawater. The pH of the solution is then lowered artificially until corrosion is observed. Invariably the solution is either stirred mechanically while exposed to the open air or air is bubbled through it. This last step is the fatal flaw in the experiment – the solution is not stagnant as would be the case inside real concrete. Brauns and

Schwenk (1908) showed that salts (e.g. NaCl, CaCl<sub>2</sub>) have almost no effect on corrosion in stagnant conditions, and Brasher (1967) showed that chlorides only become important for initiation in non-stagnant solutions. Support for this idea is apparent in the corrosion loss trends for steel in seawater, in brackish water and in soft fresh water (Fig. 4). Chloride concentration is important only while there is no significant rust protecting the steel surface where the corrosion process occurs (Mercer & Lumbard 1995). Thus criteria (1) and (2), which rely on chloride concentrations, also cannot be supported.

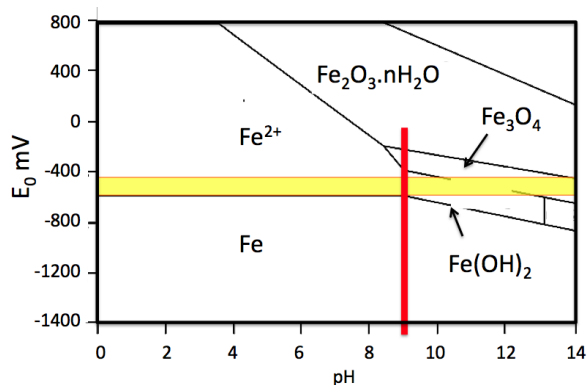


Figure 3. Schematic Pourbaix diagram showing main rust products and pH for initiation.

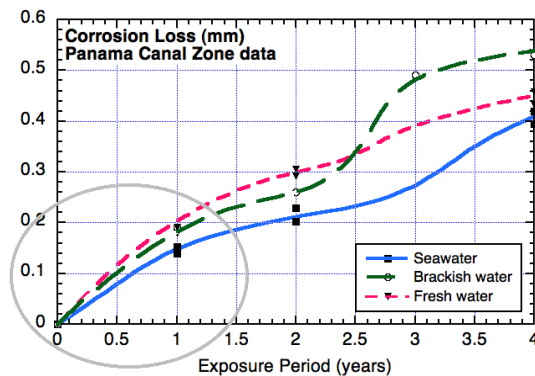


Figure 4. Schematic corrosion loss trends. Based on data from Southwell & Alexander (1970).

If high concentration of chlorides at the reinforcing bars is not the direct cause of corrosion initiation, there must be at least one other mechanism. One possibility is the reduction of concrete pH sufficient for corrosion to initiate (Sagues et al. 1997, Melchers & Li 2006). This notion is consistent with good quality concrete structures (see above) that show corrosion only when the pH immediately adjacent to reinforcing steel is less than about 9-9.5. It requires the concrete pH to move to the left in Fig. 3.

Reduction in pH implies loss of alkalinity. The alkalis in concrete are KOH, NaOH and Ca(OH)<sub>2</sub>. Both KOH and NaOH are highly soluble and can easily leach out of the concrete matrix. This reduces the pH to about 12. Ca(OH)<sub>2</sub> is only very slightly soluble in water and leaching in freshwater takes a long time. One well-known mechanism for reduction in Ca(OH)<sub>2</sub> is ‘carbonation’ caused by CO<sub>2</sub> ingress. This depends on environmental factors (e.g. St John et al. 1998) and is very low in wet or seawater environments. Another possibility is that presence of NaCl increases the solubility of dilute Ca(OH)<sub>2</sub> solutions (Johnston & Grove 1931), permitting a faster rate of leaching, and this is considered also the case of solutions with higher concentrations (Hewlett 1988).

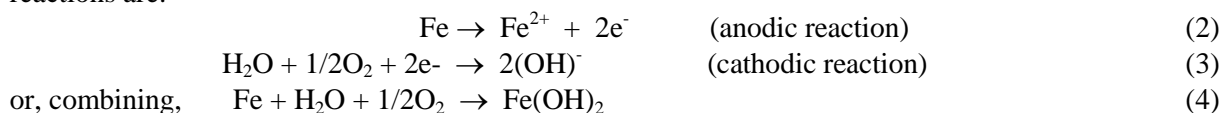
Reduction of alkalinity by chemical reaction also is possible. The magnesium sulfates and chlorides (MgSO<sub>4</sub>, MgCl<sub>2</sub>) present in seawater react with Ca(OH)<sub>2</sub> in the concrete (Hewlett 1988), for example:



Thus highly alkaline Ca(OH)<sub>2</sub> is lost and replaced by magnesium hydroxide Mg(OH)<sub>2</sub>. This is almost insoluble, precipitates and makes negligible contribution to concrete alkalinity. MgSO<sub>4</sub> and CaCl<sub>2</sub> are highly soluble, make no contribution to alkalinity and being of relatively large molecular size are likely to be slow in leaching out. For concretes in seawater environments reaction (1) should be *rate* controlled by the rate of inward diffusion of MgCl<sub>2</sub>. In this case it can be pictured as a ‘reaction front’, leaving behind a field of concrete with lowered pH. When that field reaches the reinforcement, corrosion can initiate. If concretes are made with seawater the MgCl<sub>2</sub> will be present from the start and its leaching rate will not be critical. For MgSO<sub>4</sub>, which is more commonly recognized as involved in concrete deterioration, similar comments apply. Using XRD measurements, recent experiments show small amounts of Mg(OH)<sub>2</sub> content in concretes surrounding bars with corrosion initiation and with local pH below about 9-9.5. No Mg(OH)<sub>2</sub> content was found for concretes with higher pH and without corrosion initiation. The concretes were high quality and well compacted.

## CHLORIDES AND ACTIVE REINFORCEMENT CORROSION

The possible involvement of chlorides in active corrosion (i.e. once corrosion has initiated) also is of interest. Fig. 4 shows that chlorides have a clear effect in the early stages of corrosion (although not as might be expected conventionally). This is consistent with the argument that once the rusts become sufficiently protective, further corrosion occurs (under and within the rusts) in essentially stagnant conditions. Thus oxygen is the critical electron acceptor for long-term corrosion and which is then influenced by other factors. This is also the basis for mathematical modelling of corrosion trends (Evans 1960, Melchers 2003b). Similar considerations would apply for steels inside concretes. The reactions are:



Here  $\text{Fe}(\text{OH})_2$  is the precursor to all other ferrous and ferric hydroxides that are the commonly observed rusts (Jones 1996). Reactions (2-4) do not involve chlorides (Pape & Melchers 2014).

It follows from (2-4) that the *rate* of the corrosion process once initiated is controlled by the rate at which oxygen can reach the corroding surface. Initially this will depend on the rate at which oxygen can diffuse out of the adjacent water (*concentration control*), and later by the rate of diffusion through the surrounding concrete and the gradually increasing thickness of the rusts (*diffusion control*).

## DISCUSSION

The mechanisms for reinforcement corrosion described above are consistent with field observations than are the mechanisms usually accepted in the conventional wisdom. They are consistent also with various aspects of currently accepted good practice, including the desirability of high quality, dense, impervious concretes, with sufficient cement to have high alkalinity reserve, and adequate cover.

In practice, active corrosion is undesirable since the expansive rusts it creates will tend to cause cracking of concrete along the reinforcing bars. A much safer strategy is to inhibit corrosion from initiating, and to do so as long as possible. As implied in the above observations, this can be achieved best by a concrete with high alkalinity (high pH buffering capacity) and high density. This usually will ensure the concrete has low permeability. As shown above, this is not only to reduce the inward diffusion of  $\text{NaCl}$  and  $\text{CO}_2$  as commonly assumed but possibly also the (slower) inward diffusion of  $\text{MgCl}_2$  to the reinforcement, and, once corrosion has initiated, the diffusion of oxygen.

Finally, the precise mechanism by which ‘carbonation’ causes corrosion remains unclear (St John et al. 1998, Melchers 2010). In the conventional wisdom the calcium carbonate it produces is claimed to lower concrete pH sufficiently for corrosion initiation to occur. However, the carbonated zone in concretes does not always reach corroding reinforcement. Further, carbonates as aggregates have been shown in real structures to be beneficial in delaying corrosion initiation (Melchers & Li 2009b). Both aspects conflict with the conventional wisdom. Carbonation thus remains a matter for further research.

## CONCLUSION

Mechanisms for the initiation and the progression of reinforcement corrosion must be consistent with corrosion science fundamentals and with field observations for actual reinforced concrete structures that have survived for many decades in aggressive marine environments and show very high chloride concentrations. It is proposed that apart from some early effects, the role of chlorides in longer term exposures is not direct initiation of corrosion but is confined to reduction of concrete alkalinity that then causes initiation of corrosion. Mechanisms by which this is possible include carbonation, accelerated calcium hydroxide leaching caused by seawater and the chemical reaction of calcium hydroxide with the magnesium chloride and sulphate present in seawater.

## ACKNOWLEDGEMENT

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