NEW RESULTS FOR THE CORROSION OF REINFORCEMENT IN MARINE ENVIRONMENTS

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SUMMARY: The apparently premature corrosion of steel reinforcement in reinforced concrete structures exposed to marine environments continues to be a matter of concern in practice despite decades of research effort and much research funding expenditure and despite much practical experience. Herein results are reported of a long-term (10 year) study of the influence of alkalis on the corrosion initiation and progression of 6mm diam. reinforcing bars centrally embedded in 40x40x160mm concrete specimens. These were made with seawater as mixing water and with a variety of mix proportions including some with added alkalis. All were equally well compacted by vibration. After 10 years continuous exposure in a fog-room only a limited amount of corrosion initiation was observed. These results are in stark contrast with those reported in the famous paper by Shalon & Raphael (1959) who found serious corrosion of reinforcement after only 1-2 years exposure for all mixes. It is shown herein that the corrosion loss trends in those tests are similar to those of steel exposed directly to seawater. This indicates that in the 1959 tests the concrete provided little protection against reinforcement corrosion. The reasons for this are considered herein and the practical implications discussed.

Keywords: Corrosion, reinforcement, seawater, long-term, alkalinity.

1. INTRODUCTION

The prevention of the earlier than expected corrosion of steel reinforcement in reinforced concrete (RC) structures exposed to marine environments continues to be a matter of considerable interest. Despite many decades of research effort and much research funding expenditure, practical experience shows that corrosion damage occurs in some structures even with the best current practice, and sometimes after only some 20 years of exposure to marine conditions. The standard explanation for reinforcement corrosion is that it results from the chlorides present in seawater. Usually the early corrosion of reinforcement is attributed to the diffusion of chloride ions from the seawater or saline atmosphere through the concrete cover and the assumption that when the chloride ions arrive at the reinforcing steel, corrosion commences and that subsequently corrosion damage starts (e.g. Richardson, 2002, Hunkeler, 2005, Gjorv, 2009). This is the well-known, so-called Tutti model. In this scenario the rate of diffusion of chloride ions through concrete governs the period of time before corrosion damage begins. The conventional wisdom is that a high chloride concentration adjacent to the reinforcement indicates a high risk of reinforcement corrosion. To reduce that risk, design recommendations advise the use of sufficiently high concrete cover to the reinforcement, the use of additives to reduce chloride diffusivity of the concrete and improved workmanship to achieve higher quality concretes. Based on this thinking, modern practice also prohibits the use of seawater or saline waters in the concrete mix. In addition, it has led to much effort to find alternatives to steel as reinforcement material and to find suitable protective or sacrificial coatings (such as polymers and galvanizing respectively) for the steel.

The current conventional wisdom is that reinforcement corrosion commences when one or more of the following criteria is reached in the concrete immediately adjacent to the reinforcement (e.g. Richardson, 2002, Hunkeler, 2005, Gjorv, 2009):

- (1) total chloride ion concentration $[\text{Cl}^-] > 0.4-0.6 \%$ mass of cement
- (2) chloride ion concentration / hydroxide ion concentration ratio $[\text{Cl}^-]/[\text{OH}^-] > 0.6 – 0.7$
- (3) $\text{pH} < 11.$

Most texts note that there can be wide variations in the limiting values. Some texts (e.g. Bertolini et al. 2004) prefer to define electrochemical potentials as corrosion initiation criteria but since in practice these cannot be measured with any degree of accuracy this approach is not particularly useful for practical design or for prediction.
The notion that corrosion will commence once the chlorides reach the steel reinforcement has led to increasing demands to make diffusion of chlorides to the reinforcement more difficult, such as through increasing the concrete cover to the reinforcement and through using additives to help block diffusion pathways. It also has led to efforts to find suitable protective coatings for the reinforcing steel and to obviate steel reinforcement altogether by using alternative materials. It also has led to the conclusion that higher chloride levels indicate a higher risk of steel reinforcement corrosion.

In contrast to this conventional wisdom, there are also many examples of actual RC structures that have performed remarkably well for many decades in aggressive marine environments without the benefit of additives, high concrete cover or cathodic protection. The question that appears to have been lost, in time, is why it is that there are many examples of reinforced concrete structures that have survived for long periods of time, with little or only moderate corrosion damage even when exposed to quite aggressive high chloride environments and without the apparent benefit of admixtures now commonly advocated. The reasons for the success of these structures, as distinct from the failures of others, should hold the key to improving understanding of the processes involved in reinforcement corrosion in marine environments. In turn this should then lead the development of tools for the more accurate prediction of the initiation and the likely severity of reinforcement corrosion.

The next section of this paper provides a very brief review of some of that positive experience. This is followed by an outline of an on-going long-term study of steel reinforcement durability in marine environments based on an attempt to replicate the results of the well-known paper by Shalon & Raphael (1959) that has been referred to extensively in the reinforcement corrosion literature.

2. BRIEF REVIEW OF PRACTICAL EXPERIENCE

The conventional wisdom does not compare well with the practical experience of satisfactory long-term performance of many reinforced concrete structures exposed to quite aggressive marine environments. A number of authors have reported such experience (e.g. Lewis & Copenhagen 1957, Wakeman et al. 1958, Griffin & Henry 1964, Mather 1964, Boqi et al. 1983, Burnside & Pomerening 1984, Anderson & Black 1985, Lukas 1985, Lau et al. 2007, Melchers & Li 2009a, Pape & Melchers 2013). In many of these cases the chloride content of the concrete was found to be very high, much higher than the limits (1-3). In others there is strong evidence that seawater was used to make the concrete. There also is field and laboratory experience that shows that reinforcement corrosion is not a significant issue when concrete is made from coral (a form of calcite, CaCO3) including with the use of seawater (Narver 1954, Dewar 1963). Further, a survey of some 300 cases reported in the literature and correlated with information or inferences about chloride concentrations and also with materials used for construction concluded that concretes with additional alkalinity provided by calcium carbonate aggregates (limestone or seashells or non-reactive dolomites) are slower to develop corrosion initiation and serious corrosion damage, irrespective of chloride concentration at the reinforcement (Melchers & Li 2009b). More difficult to measure than salinity at the bars or the ratio [Cl-]/[OH-] (Hausmann 1998), alkalinity imparted by the materials used in the concrete mix as distinct from the alkalinity derived from the cement reactions largely has been ignored in research and in practice. Fig. 1 shows results for the duration to corrosion initiation after cases suspected to have been caused primarily by damage to concrete cover caused by alkali-aggregate (AAR) or alkali-silicate reactions (ASR) have been removed. Such damage should not, of course, be considered within the cohort of experiences dealing primarily with initiation and progression of reinforcement corrosion.

![Figure 1. Duration of time to corrosion initiation and the chloride content of concrete.](image1.png)

Despite the scatter in the data, it is clear from Fig. 1 that there is a clear difference in the time to corrosion initiation for concretes made with limestones and/or (non-reactive) dolomites and those made using other aggregates. There is also little effect of chloride concentration beyond the range usually considered the safe threshold (0.4-0.6% by weight of cement). This latter aspect is of particular interest since the use of seawater as mixing water was prohibited largely as a result of laboratory tests reported in the famous paper by Shalon & Raphael (1959) (cf. Richardson, 2002, Hunkeler, 2005, Gjorv, 2009). They
found serious corrosion losses after only 1-2 years for reinforced concrete samples made with seawater and exposed in a laboratory fog room. Yet prior to that time the use of seawater was quite widespread in practice, including, as already noted above, for many reinforced concrete structures that have survived for long periods of time (Melchers 2010).

3. NEW LABORATORY TESTS

3.1 Replication of concrete samples made with seawater

Because of the apparent conflict between practical experience and the results from the Shalon & Raphael (1959) tests, the decision was made in 2004 to attempt to replicate their study as closely as possible.

The original samples made by Shalon & Raphael (1959) included a wide range of water/cement and aggregate/cement ratios. Local limestone for coarse and fine aggregates (the predominant rock available in Israel) was used, together with standard (Portland) cement. A 5 mm diameter steel reinforcing bar was placed along the central axis. The mixing water for the concrete was Mediterranean seawater collected off the Israeli coast. The concrete samples were exposed in a laboratory fog room and the reinforcing bars were examined after 3, 6, 12, 24 and 48 months by breaking open the concrete.

For the replicate experiment limestone aggregates were not available and instead igneous aggregates were used. In view of Fig. 1 this would, if anything, be detrimental to corrosion initiation. Commercially available conventional standard cement was used. As in the original experiments no additives were used. Pacific Ocean seawater collected along the coast near Newcastle was used as mixing water. Its chemical composition is similar to open sea seaways elsewhere (Svedrup et al. 1942). The concrete mixes were weight-batched with allowance for moisture content of the aggregate and the sand and carefully mixed in the laboratory concrete mixer. Each mix was sufficient to make 20 samples in 2 moulds of 10 samples each. The moulds were steel, of high dimensional accuracy and of the same size as used in the original experiments (Fig. 2). Each sample was 40 x 40 x 160 mm in size, with the ends of the moulds having a central hole for holding the 5 mm diam. carbon steel reinforcing bar exactly along the centreline of the concrete sample.

In the replicate experiment the concrete in the moulds was vibrated for at least 10 seconds or until water reached the top surface. This was to try to ensure adequate compaction and exclusion of voids adjacent to the reinforcement bars. After 5 days the samples were carefully de-moulded and then placed in large open web plastic storage trays in the laboratory fog room at 25˚C average temperature. The samples were made sequentially, by aggregate/cement ratio and then by water/cement ratio. The samples in the main test program (Series B, Table 1) were made over a period of one month (May 2004–June 2004). All samples were labelled with date of construction and coded according to mix design. Attempts to make concretes with aggregate/cement ratios greater than 6 (as was done in the Shalom & Raphael tests) were abandoned as the mixes were unreasonably stiff for the lower water/cement ratios, and are in any case less than practical.

<table>
<thead>
<tr>
<th>Aggregate/cement ratio</th>
<th>2:1</th>
<th>4:1</th>
<th>6:1</th>
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<tbody>
<tr>
<td>Water/cement ratio</td>
<td>0.5</td>
<td>B1</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.65</td>
<td>B2</td>
<td>B4</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>B3</td>
<td>B5</td>
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<tr>
<td></td>
<td>0.95</td>
<td>-</td>
<td>B6</td>
</tr>
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</table>

3.2 Effect of cement type, higher salt concentration and limestone aggregates

In parallel to the Series B tests, concrete samples of exactly the same size and components including the use of seawater were made but with (i) low heat cement instead of normal cement, (ii) with 50% additional NaCl in the mixing water or with (iii) aggregates substituted by crushed limestone, of approximately similar size grading to that in the other series. The test schedule is shown in Table 2.

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<td>6:1</td>
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<tr>
<td>Water/cement ratio</td>
<td>0.5</td>
<td>C1</td>
<td>-</td>
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<td></td>
<td>0.65</td>
<td>C2</td>
<td>C4</td>
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<td></td>
<td>0.8</td>
<td>C3</td>
<td>C5</td>
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<tr>
<td></td>
<td>0.95</td>
<td>-</td>
<td>C6</td>
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3.3 Test program
The intent was to replicate, as closely as possible, given the available information, the original test program as described by Shalon & Raphael (1959). This required assessing the severity and extent of reinforcement corrosion at 3, 6, 12, 24 and 48 months exposures, at each time by lengthwise splitting 3 concrete samples from each concrete mix. However, unlike in the original tests, in the case of the present test program at 6 months none of the samples showed signs of corrosion. As this contrasted significantly with the findings reported by Shalon & Raphael (1959), the decision was made to thenceforth to examine only one sample and to do so at yearly intervals until such time as corrosion became less than nominal. This pattern has been followed and the remaining samples were examined one per year since that time. The observations reported below are for the samples examined late 2013 at approximately 10 years since commencement of the test program. At this time (2014) there are sufficient remaining samples to continue the test program for series B and C for another 15 years and for another 5 years for series D and E, at the rate of one sample examined per year.

4. TEST OBSERVATIONS AT 10 YEARS EXPOSURE

4.1 Replicates of Shalon & Raphael (Series B)
As in the previous years, in late 2013 one sample from each test series was broken open lengthwise to reveal the reinforcing bar. All samples were undamaged and uncracked, without any external signs of reinforcement corrosion (Fig. 3).

The opened section was photographed to show both the visual appearance of the reinforcing bar and any rusts as well as the texture of the fractured concrete. Figs. 3 and 4 show typical examples, respectively for a concrete with low water/cement ratio and low aggregate/cement ratio and with high water/cement ratio and high aggregate/cement ratio. It is clear that the former shows a visually dense and compact, tight concrete that was harder and found more difficult to break open than the latter which shows a relatively weak and permeable (porous) structure. It is clear also that the corrosion for sample B1 (Fig. 4) is negligible and that it is only very light, but somewhat uneven and patchy for sample B8 (Fig. 5).

The concrete, freshly revealed by breaking-open the samples, was immediately spot-sampled for pH using a pH meter and deionized water droplets to allow the readings to be taken. Figs. 6 and 7 show examples of the pH spot readings for the concretes in Figs. 4 and 5 respectively. Of most interest are the pH readings along the location of the reinforcing bars, as it is the pH at these locations that influence the initiation of corrosion of the steel reinforcement. Fig. 6 shows that the pH along the reinforcement bar for sample B1 (Fig. 4) is
around pH = 12, similar to the pH of the surrounding concrete. The pH is much lower (approximately = 10) in Fig. 7 along the location of the reinforcing bar in sample B8 (Fig. 5) - these pH readings, again, are similar to those measured on the rest of the concrete. In both cases there is considerable variability in the spot readings for pH. The important observation is that the average of the pH readings for the more permeable, lower quality concrete (sample B8) are, after 10 years exposure, considerably lower than that of the dense, strong concrete of sample B1. This may be related directly to the difference in aggregate/cement ratio, and possible the water/cement ratio.

Figure 6. Spot values of pH on the concrete adjacent to and away from the reinforcing bars, taken immediately after breaking open a sample from set B1.

Figure 7. Spot values of pH on the concrete adjacent to and away from the reinforcing bars, taken immediately after breaking open a sample from set B8.

Photographs of all the reinforcing bars recovered from the samples of the B series at 10 years exposure are shown in Fig. 8. The samples with the lowest aggregate/cement ratio (2:1) are shown at the top and those with the greatest aggregate/cement ratio tested (6:1) are at the bottom. In each group the water/cement ratio increases down from the top of the group. It is immediately obvious that the amount of corrosion increases primarily with increased aggregate/cement ratio and also somewhat with water/cement ratio. This reflects the changes in the porosity or permeability of the concretes.

Figure 8. Exteriors of reinforcing bars B1-B9 within 60 minutes of recovery from samples with (a) B1-B3: aggregate/cement ratio (a/c) = 2, water/cement (w/c) ratios from top = 0.5, 0.65, 0.8 (b) B4-B6: a/c = 4, w/c = 0.65, 0.8, 0.95, (c) B7-B9: a/c = 6, w/c = 0.65, 0.8, 0.95. Note that the extremities of the bars should be ignored as these extended beyond the concrete.
4.2 Samples with Low Heat Cement (Series C)
The examination of the randomly selected samples from the C series followed the same process, and was conducted in parallel with that of the B series. This included examination of the concretes, pH spot readings and visual examination of the reinforcing bars. Fig. 9 shows a summary of the visual appearance of the reinforcing bars and the extent and (lack of) severity of corrosion.

Figure 9. Exterior surfaces of reinforcing bars C1-C9 within 10 minutes of breaking-open the concrete samples. Aggregate/cement and water/cement ratios are as shown.

4.3 Samples made with added NaCl (Series D)
For the D series the seawater used for making the concrete was supplemented with added common salt (NaCl) by mixing 16 g of salt (NaCl) per litre of seawater prior to adding the water to the cement and aggregates in the concrete mixer. Otherwise everything else was as for the B series. Fig. 10 shows the exterior surface condition of the reinforcing bars as they were exposed during the process of breaking-open the concrete samples. These surface conditions can be compared directly with samples B4-B9 in the B series (Fig. 8).

4.4 Samples made with Limestone Aggregate (Series E)
Because of the role limestone and dolomite aggregates appear to play in longer-term corrosion, both for initiation and for longer term durability (Fig. 1), Series E concretes were made with crushed graded limestone as aggregate instead of the aggregate used in all the other test series. Fig. 11 shows the exterior of the reinforcing bars as they were revealed when the concrete samples were broken-open. These may be compared directly with samples B1-B6 in the B series.
4.5 Corrosion observations

All reinforcing bars recovered from the samples were, after photography and examination, labelled and then cleaned of any rusts using conventional ASTM G1-03 (2011) standard techniques. Each bar then had its end removed to leave as accurately as could be cut, a length of 100mm. Both the actual length and the mass of these trimmed lengths of reinforcing bar were determined and the mass per 100mm length determined. This was compared with the average mass of unexposed 100mm lengths of similar reinforcing bar to obtain an estimate of the remaining mass of each bar. Table 3 summarizes the results. As is evident, apart from the remnant mass values shown in bold, the mass losses in many cases were very small. This would make any estimate of actual corrosion loss likely of low accuracy given the very small amount of corrosion and the errors inherent in mass loss determination. For comparison with the values in Table 3, the mass of 100 mm long uncorroded samples of reinforcing bar has a mean of 21.49 g and a standard deviation of 0.058 g.

Figure 10. Exterior surfaces of reinforcing bars D1-D6 within 10 minutes of breaking-open the concrete samples with (from top) aggregate/cement ratio (a/c) = 4 and water/cement (w/c) ratios = 0.65, 0.8, 0.95 and a/c = 6 and w/c = 0.65, 0.8, 0.95.

Figure 11. Exteriors of reinforcing bars E1-E6 within 10 minutes of breaking-open samples with (a) aggregate/cement ratio (a/c) = 2 and (b) water/cement (w/c) ratios = 0.5, 0.65, 0.8 and a/c = 4 and w/c = 0.65, 0.8, 0.95.
Table 3. Mass of 100mm lengths of 5 mm diameter reinforcing bars after exposure

<table>
<thead>
<tr>
<th>Test Series</th>
<th>B</th>
<th>C – low heat cement</th>
<th>D – higher salinity</th>
<th>E – limestone aggr.</th>
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<tbody>
<tr>
<td>Water/cement ratio</td>
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<td></td>
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<tr>
<td>0.5</td>
<td></td>
<td></td>
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<tr>
<td>0.95</td>
<td></td>
<td>B6=20.98</td>
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4.6 Schmidt hammer results

Because the samples were too small for conventional concrete compressive tests estimates of their compressive strengths, and hence their approximate permeability (inversely proportional to the compressive strength) Schmidt hammer tests were conducted on samples drawn from each sample set in the series. Each sample was tested near both ends and near the centre on the surface adjacent to the surface that was at the top during casting. The results are shown in Table 4. Most readings are the average of 3-5 tests.

Table 4. Schmidt hammer observations

<table>
<thead>
<tr>
<th>Test Series</th>
<th>B</th>
<th>C – low heat cement</th>
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<td>Water/cement ratio</td>
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<tr>
<td>0.5</td>
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<tr>
<td>0.65</td>
<td>B1=39.0</td>
<td>-</td>
<td>-</td>
<td>C1=40.1</td>
</tr>
<tr>
<td>0.8</td>
<td>B2=35.2</td>
<td>B4=31.6</td>
<td>B7=26.8</td>
<td>C2=33.5</td>
</tr>
<tr>
<td>0.95</td>
<td>-</td>
<td>B6=22.5</td>
<td>B9=20.3</td>
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5. ANALYSIS OF RESULTS

Figure 12. Corrosion losses as a function of time for concretes with an aggregate/cement ratio of 2:1. For the Shalon & Raphael test results the trends shown have been extrapolated to 6 years.

The present results, particularly for the directly comparable B series, are in stark contrast to the results reported by Shalon & Raphael (1959). Their results are shown in Figs. 12 and 13 and compared with two extreme cases in the B series (Table 1) – B1 with aggregate/cement ratio of 2:1 and B7 with aggregate/cement ratio of 6:1. Figs. 12 and 13 show that while the Shalon
& Raphael test program produced considerable corrosion losses (reported as % mass loss) already after 6 months and certainly after 1 year, there is almost no corrosion mass loss in the replicate test Series B even after 10 years exposure. This is also the case for test Series C, with a different cement type, Series D with additional NaCl and Series E with limestone aggregates (as in the Shalon & Raphael tests).

It is noted again that the concretes in the Shalon & Raphael (1959) experiments as well as those in the present series B, C, D and E were made with seawater. The difference in results cannot, therefore, be attributed to differences in the rate of inward diffusion of chlorides from the surrounding environment even though it is visually obvious from the quality of the concretes (compare Figs. 4 and 5) and from the Schmidt hammer results (Table 4) that there are considerable differences in diffusion properties of the concretes.

The remaining masses for 100 mm lengths of the 5 mm diam. reinforcing bars shown in Table 3 are plotted in Fig. 14 as a function of the aggregate/cement ratio, the latter as a surrogate for concrete density. Also shown is the mean and standard deviations for uncorroded bars. Fig. 14 confirms, as was visually evident from Figs. 7-11, that relative to the mean of uncorroded bars, there is very little corrosion for the majority of reinforcing bars - about 2 microns on average all round each bar. Fig. 14 also shows that the aggregate/cement ratio has little effect on these small corrosion losses (as estimated by remaining mass). As confirmed by optical microscope examination, the bars all show uniform corrosion. However, bars in samples B6, C7 and D4 show lower remaining masses than the average. This was investigated by optical microscope examination. This showed small areas of localized corrosion, relatively much more aggressive than the uniform corrosion elsewhere on the bars (Fig. 15).

![Figure 14. Remaining mass of 100 mm long lengths of reinforcement compared with original mass, showing also estimated mass loss in microns for each of the 4 test series (B-E).](image1)

![Figure 15. Close up of bars B6, C7 and D4 showing localized corrosion contributing to the larger mass losses in Fig. 14. (Scale rule increments 1 mm, bar diam. = 5 mm).](image2)
Figure 16. Subjective corrosion as a function of Schmidt hammer observation as a surrogate for the reciprocal of the concrete diffusivity.

As an alternative to attempting to measure mass loss, the corrosion shown for each of the bars in Figs. 7-11 was rated subjectively for severity using the following scale: 0 = zero corrosion, 1 = light corrosion around bar, 2 = medium corrosion around bar, 3 = heavy corrosion around bar, with fractional increments for partial corrosion. The results of the ratings for the bars in each sample are plotted in Fig. 16 as a function of the corresponding Schmidt hammer observations for that sample (Table 4). As noted, the Schmidt hammer results are primarily estimates of concrete compressive strength but also can be interpreted as reciprocals of the diffusivity of the concrete. Although there is a lot of scatter, either as a result of the subjective assessment, or because of experimental variability or both, the overall trends in Fig. 16 are consistent. They show that the early, very low level of corrosion is inversely proportional to the Schmidt hammer results or, equivalently, directly proportional to the diffusivity of the concrete. Again, this cannot be related to diffusion of chlorides through the concrete since all concretes were made with seawater and therefore had very high concentrations of chlorides. It is noted that the trend for Series D, the group of samples made with additional NaCl, is generally similar to the other trends.

6. DISCUSSION

The most important observation from Figs. 12 and 13 is that the corrosion results obtained in the present (replicate) test program (particularly in Series B) are very considerably lower than those reported by Shalon & Raphael (1959). In attempting to reconcile this large difference, it is noted again that the replicate tests were identical to the original test series in sample size, used similar aggregate/cement and water/cement ratios, used seawater for making the concretes and had high moisture fog-room exposures. Thus the differences cannot be attributed to differences in chloride diffusion to the bars or to moisture differences. Small differences in composition of steels have only a small influence on their seawater corrosion (Evans 1960) and could not be responsible for the large differences between the present results. Further, for the present tests of 10 years duration, the use of calcareous aggregates appears to have no noticeable effect compared with non-calcareous aggregates (Figs. 11 and 14) even though for long-term corrosion the former appear to be advantageous (Melchers & Li 2009b). Considering all possibilities, the most likely cause of the difference is the degree of compaction between the Shalon & Raphael tests and the present replicates. According to Shalon & Raphael (1959), the bars were “inserted in the … specimens” and an earlier paper (Friedland 1950) using the same experimental techniques noted: ‘Each bar was …. weighed to the nearest 0.1 mg and immediately embedded in the specimens.” There are no further details and no mention of compaction or vibration. In contrast, for the replicate tests the experimental protocol included vibration to attempt to ensure adequate compaction of the concrete.

Support for the proposition that compaction is the most likely reason for the early and high level of corrosion observed by Shalon & Raphael is provided by their reported corrosion losses. They plotted just one corrosion loss trend, but it was for a bare steel bar exposed to the fog room. They did not plot the trends for the data they reported for the reinforcing bars taken from the seawater-saturated concretes. Examples of several such trends are shown in Figs. 12 and 13. All their data, when plotted, show similar corrosion loss trends. These are very similar in characteristics to the corrosion loss trends for bare steel immersed in non-stagnant seawater. Fig. 17 shows two examples of their trends. It also shows the corrosion loss trend for bare steel in seawater (at Taylors Beach, at similar average temperatures (Melchers & Jeffrey 2008)).

The comparison in Fig. 17 showing the generally similar trends for corrosion loss for unprotected steel and the bars in the concretes used by Shalon & Raphael (1959) demonstrate that their test results can be interpreted as valid only for concretes of very poor quality. They are not applicable to well-made concretes, as the results in Figs. 12 and 13 show. This means that the
ban on the use of seawater in concrete is based on a set of experimental results that is, essentially, flawed. The experimental results of Shalon & Raphael (1959) apply only to very poor quality concretes resulting from poor compaction. Most likely this produced permeable concretes that allowed easy access of oxygenated seawater and also did not produce the close contact between high pH concrete and steel required to inhibit corrosion. Support for this can be seen in Fig. 5 showing the mottled corrosion of the reinforcement in concrete with a high aggregate/cement ratio compared to a concrete with a much lower aggregate/cement ratio (Fig. 4). These observations are not new – similar observations were made, for example by Hausmann (1998) already many years ago and are implicit in much sound advice for achieving durability for reinforcement. However, there is one very important difference, namely in the interpretation of the observations.

All the concretes used in the replicate experiments reported herein were made with seawater, just as in the experiments by Shalon & Raphael (1959). It follows it is not the action of chlorides that is responsible for the stark differences in corrosion behaviour between the two sets of experiments. Neither experiment relied on chloride diffusion. Similarly, the issue of bound versus unbound chlorides (Glass & Buenfeld, 1997) would be similar for both and thus is also irrelevant. It follows that the differences in corrosion behaviour must lie not in the role of chlorides and of chloride diffusion but elsewhere. It has already been proposed that the primary mechanism causing corrosion initiation is the loss of alkalis (Melchers & Li 2006, Melchers 2010). Indirectly this proposition is supported by the field data for concretes with very high chloride concentrations that show no corrosion of reinforcement (Melchers & Li 2009b, Papè & Melchers 2012, 2013) for pH > 9. This proposition also is supported by the results of the replicate experiments that show that corrosion initiates at pH less than about 9 (Figs. 4-7).

Importantly, these empirical and experimental observations are consistent with the thermodynamics of the oxidation reactions involved, as usually shown in corrosion science texts by the Pourbaix diagram. The thermodynamics (and hence the Pourbaix diagram) are only slightly influenced by the presence of chlorides (Jones 1996). They were obtained under essentially stagnant conditions (Brauns & Schwenk 1908) and as has been shown by Brasher (1967) chlorides only become of importance under non-stagnant conditions (i.e. conditions involving some degree of fluid flow). This is not the case for the corrosion process under rusts and this allowed the development of corrosion under increasing layers of corrosion products to be modelled by oxygen diffusion considerations, even in seawater (Melchers 2003). Similarly, the corrosion of steel inside protective concrete can be only under essentially stagnant conditions and therefore is dominated by oxygen. Chlorides play only a minor role. It might be noted also that even for modelling the development of pitting corrosion in steel the presence of chlorides is unnecessary except to provide charge equilibrium (Sharland & Tasker 1988).

In summary, the conventional notion that the chloride content must be restricted to a low concentration to ensure reinforcement corrosion does not initiate, is not founded on reliable evidence. Similarly, the Hausmann criterion that the ratio of the concentration of chlorides to hydroxides must not exceed a given amount also cannot be supported. It is based on the notion that there is competition between chlorides and hydroxides, implying that the reactions are about to progress. The progression of corrosion is governed by the availability of oxygen (e.g. Escalante & Ito 1990) although this is seldom made clear in texts. The third criterion, that reinforcement corrosion commences once the concrete pH drops below about 11 also is not supported by experimental and by field evidence. The experimental evidence that has been cited for that criterion (Shalon & Raphael 1959, Escalante & Ito 1990) was obtained under non-stagnant conditions (air bubbled into the experimental containers) and thus is not applicable to the initiation of corrosion inside actual reinforced concrete elements.

Finally, both field experiments and data collected from many cases (e.g. Narver 1954, Dewar 1936, Melchers & Li 2009b) indicates that the use of carbonate aggregates such as limestone, non-reactive dolomites and blast furnace slag can be beneficial for delaying initiation of reinforcement corrosion. This is supported by independent laboratory experiments (Davis & Burstein 1980, Huet et al. 2005) but in the present experiments it was still too early to distinguish initiation between series B and series E (with limestone aggregates). Whether a difference exists may be come evident in due course - there are still enough samples left in the present experiment for another 5-10 years of comparative observations.

7. CONCLUSION

Herein results are given of a long-term (10 year) study of the influence of alkalis on the corrosion initiation and progression of small diameter reinforcing bars embedded in concrete specimens, made with seawater and with a variety of mix proportions and well compacted by vibration. After 10 years continuous exposure in a fog-room for the concretes made with high cement content or added alkalinities there was no evidence of reinforcement corrosion. Others with lower cement contents, high water/cement ratios and/ or high aggregate/cement ratios showed reinforcement with irregular, patchy and localized corrosion initiation on the bars but no serious corrosion losses.

In contrast, very similar tests reported in the famous paper by Shalon & Raphael (1959) showed serious corrosion after only 1-2 years exposure for all mixes. Using the data reported in the original paper, it is shown herein that the corrosion loss trends in the 1959 tests are similar to those of steel exposed directly to seawater. This indicates that in the 1959 experiments the concrete provided little protection against corrosion and that this most likely are the result of inadequate protection by alkaline materials in the concrete. The observations indicate that chlorides are of limited influence in reinforcement corrosion and that leaching or loss of alkalis from the concrete matrix largely is responsible for initiation and progression of reinforcement corrosion.

Taken together, the new observations and the interpretation of earlier work, supports previous notions that reinforcement corrosion can be very much delayed by ensuring concretes (i) have adequate pH buffering capacity (i.e. alkalinities) such as obtained by high cement contents or high content of alkaline aggregates and (ii) are very well compacted to ensure intimate
contact between alkaline material and the reinforcement. Lack of adequate compaction will permit oxygen diffusion to the bars, thus ensuring that subsequent corrosion is generally similar to that of bare steel in seawater. (The highly aggressive, very localized reinforcement corrosion that sometimes occurs without exterior evidence after long-term exposures is recognized but not discussed in the present paper).

8. ACKNOWLEDGMENTS

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