The long-term effectiveness of electrochemical chloride extraction as remediation for corroding steel in reinforced concrete

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The long-term effectiveness of electrochemical chloride extraction as remediation for corroding steel in reinforced concrete

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Abstract

Steel reinforced concrete blocks were subjected to electrochemical chloride extraction after they were dosed with chlorides. Following treatment, the blocks were exposed to the elements at the BRE exposure site for a period of up to 6 years. A selection of blocks were cut into smaller steel-containing prisms after 4 ½ years of exposure and were exposed to controlled laboratory conditions for 6 months while determining the level of corrosion by linear polarisation. At termination, each steel bar was removed and examined visually. The level of corrosion of each bar was also assessed gravimetrically. The final chloride concentration profile of each prism to a depth beyond the steel bars was also determined.

Results suggested that corrosion was reduced significantly following chloride extraction but that the primary controlling factor, both for the desalinated and control specimens, was the level of chloride present at the depth of the steel reinforcement.

Coating the concrete after treatment resulted in an overall increase in corrosion level, possibly because the coatings were not coherent and allowed moisture to penetrate the concrete through cracks and defects which could not subsequently escape owing to the coating.

Key Words
Concrete, Steel Reinforcement Corrosion, Corrosion Control, Electrochemical Chloride Extraction, Chlorides

Introduction
As one of the methods to inhibit corrosion in reinforced concrete or repair damage caused by reinforcement corrosion, electrochemical chloride extraction (desalination) has been claimed to be a permanent solution. Independent justification was sought to ascertain these claims and place the technique in the context of other remedial methods. This paper reports on the procedure employed and on the main findings of the resulting six year research project undertaken by BRE.

The primary objective of the project was to monitor the long term performance of lab produced desalinated concrete to quantify and give definitive advice on the efficacy of the treatment.

Electrochemical chloride extraction is a technique used in cases where reinforcement corrosion was caused by chloride contamination of the concrete. It involves the positioning and fixing of a tank onto the surface of the concrete element to be treated, through which water or a saturated solution of calcium hydroxide is circulated by pump. A conductive anode material, such as steel or titanium based mesh, is contained within the tank stretching over the

whole area of concrete and is connected to the positive terminal of a transducer / rectifier. The negative terminal is connected to the steel reinforcement after it is checked for electrical continuity. The power source maintains a constant direct current of the order of 1-5 A/m^2 of steel reinforcement between the external anode and the steel cathode for a period of a few weeks. The resultant electrical field enables the anionic species (calcium, sodium and potassium ions present in the concrete pore-solution) to migrate along the current lines towards the steel reinforcement. At the steel cathode, cathodic reactions produce hydroxyl ions which both balance the positive charge of the arriving anions and, along with other cations such as chlorides, migrate towards the external anode. Hydroxyl ions are consumed at the anode by anodic reactions while chlorides are washed away by the circulating electrolyte.

The efficiency of chloride removal is dependant on the relative concentration of the chlorides to the total ionic concentration contained in the concrete pore-solution. As chlorides diminish, a smaller proportion of the current is used to transport the chloride ions to the external electrolyte and the process becomes uneconomical [1,2]. As a consequence, a proportion of chloride always remains in the concrete. Furthermore, chlorides that may have been present beyond the influence of the current lines, i.e. a little behind the steel reinforcement and possibly between adjacent bars, are likely to remain there after the treatment. These chlorides then become available to re-migrate towards the steel. Although this re-migration was seen experimentally [3], its effect on the subsequent level of corrosion of the steel reinforcement has not yet been adequately documented.

Experimental

Exposure site blocks

A total of fifty concrete blocks (360 x 360 x 150 mm) were cast around the end of 1995 and the beginning of 1996. Two layers of 8 mm diameter steel reinforcement made into 80 mm square grids were cast in the blocks with a minimum cover of 30 mm. The concrete mix used is shown in Table 1. The fresh concrete slump was between 40 and 80 mm, its fresh density was 2330 kg/m^3 and the average compressive strength obtained was about 32 N/mm^2. A number of the specimens were cast with a silver chloride reference electrode in the centre of the specimen.

Table 1. Concrete mix details

Material	Kg/m^3 of concrete
OPC	238
20-10mm agg	755
15-10mm agg	343
5-0mm agg	794
water	200
Free water to cement ratio	0.70

The blocks, apart from some kept as controls, were either exposed to cyclic chloride ponding (5% NaCl solution) or had chlorides cast into them (1% chloride as calcium chloride by weight of cement). All the chloride-contaminated specimens were desalinated by one of the industrial partners, according to normal procedures applied in-situ, in early 1997 (current density = 4.5 A/m^2 of steel, time = 10 days). The desalination process was repeated two months later at a reduced current density and increased time (current density = 1.6 A/m^2 of steel, time = 24 days) to determine if further chloride removal could be achieved with a prolonged period of polarisation. In order to determine the level of chloride that was removed

from the concrete following the desalination treatment, dust samples were drilled down to the level of the steel mesh. These were analysed by acid extraction and compared to those obtained from the control untreated samples. From the mean initial concentration at the level of the steel of around 2.35% by weight of cement for the blocks exposed to NaCl before treatment the concentration directly over intersecting steel bars (location A in Fig. 3) was reduced to a mean of 1.05% (a reduction of around 55%) following the second treatment. The reduction was less away from the steel (i.e. 46% to 1.27% at locations 25-50mm from the steel, denoted as C in Fig. 1). In the case of the cast-in chlorides, the mean reduction from an initial concentration of 0.89% by weight of cement was 52% above the intersecting steel bars compared to only 18% at location C. The proportion of reduction from the second treatment was only of the order of 3-5%. This, as well as the lower overall reduction in the case of the cast-in chlorides, shows clearly that as the total chloride concentration diminishes, the process of removing chlorides becomes less efficient. The proportion of chloride removed is consistent with that predicted by modelling [4]. The reductions obtained were deemed to be acceptable according to normally accepted criteria.

About half the blocks were coated on all faces with a commercial elastomeric coating of the type normally applied on concrete in practice following ECE. All the blocks were then placed with the long faces vertical at the BRE outdoor exposure site. Each block had one of the larger faces exposed in a northerly and the other in a southerly direction. The corrosion potential of the steel reinforcement was monitored against the embedded reference electrode.

Laboratory experiments

A total of seven reinforced concrete blocks (see Table 2) were selected for more detailed analysis after about 4½ years of exposure.

Table 2. Details of the reinforced concrete blocks selected for detailed analysis

Code	Description	Condition
C 1	Control	Rough surface
C 3	Control	Smooth surface
DC 13	Cast-in chlorides, desalinated	Rough surface
DF 8 C	Control, ingressed chlorides	Rust stains, cracks
DF 15 C	Control, ingressed chlorides	Rust stains, cracks
DF 5	Ingressed chlorides, desalinated	Some rust stains, some cracks
DF 12	Ingressed chlorides, desalinated	Few small cracks

Each of the chosen blocks was cut in such a way as to obtain three ~100 x 60 x 150mm smaller concrete prisms (Figure 1) each containing two separate and isolated sections of embedded steel bar for corrosion monitoring. Electrical connections were made to the steel bars by drilling, tapping and fixing a length of electric wire with stainless steel screws. After weighing cut surfaces of the steel were then masked with a duplex layer of styrene butadiene rubber (SBR) modified white cement slurry and a layer of epoxy resin in order to minimise crevice corrosion. After weighing, the specimens were immersed in water up to a depth of 5 mm for a total of 48 hours, on each of the two opposite originally exposed faces, turning the prisms through 180º after the first 24 hours.
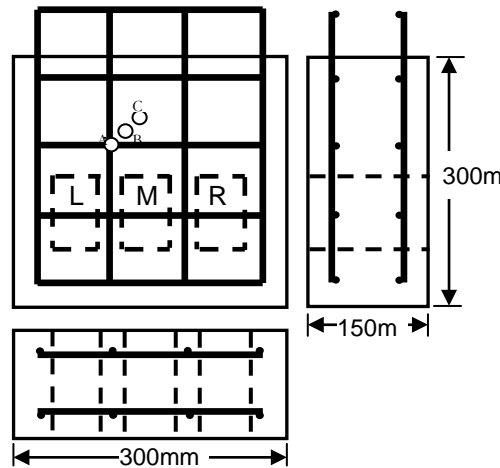
Figure 1. Details of large concrete block showing cutting to obtain three prisms (L, M & R) for corrosion monitoring

Corrosion Monitoring

The corrosion current (i_{corr}) and potential (E_{corr}) of each steel bar were determined, both after the initial exposure to water and subsequently at regular time intervals until steady state conditions were established. Following each set of measurements the prisms were stored in a high humidity constant temperature (>98% RH, 20 ± 2°C) environmental cabinet. Corrosion potentials of the two steel bars were measured with a high impedance voltmeter, versus a saturated calomel reference electrode (SCE) positioned on a pre-determined marked spot in the centre of the concrete surface parallel to the bars, half-way between the bars. The corrosion current of the bars was determined by a linear polarisation technique [5]. This involved shifting the potential of the steel by ΔE (~20 mV) from its rest potential using a potentiostat (Amel 550) fitted with a positive feedback iR compensation facility and measuring the resultant current density (Δi) passing between the first steel bar, acting as the working electrode, and the second steel bar, acting as a counter-electrode, after 60 seconds. Sufficient time was allowed for depolarisation to occur before the two bars were reversed and the procedure repeated to measure the current through the second bar. The polarisation resistance (Rp) was taken to be the measured ratio $\Delta E/\Delta i$. The corrosion current, i_{corr}, was then calculated assuming B=26mV in the Stern and Geary equation [6,7].

$$i_{corr} = B/Rp$$

where
$$B = \frac{\beta a \times \beta c}{2.3 (\beta a + \beta c)}$$

and, βa and βc are the anodic and cathodic Tafel constants respectively.

At the end of the corrosion monitoring, concrete powder samples were obtained by drilling at increasing depths in 15mm increments from the exposed surface down to the depth of the steel reinforcement and beyond. The collected powder samples were analysed for chloride content using a standard analytical technique.

Gravimetric weight loss measurements

The prisms were split along the length of the steel bars perpendicular to the longest dimension. The bars were carefully removed revealing the concrete substrate and the surface of each bar. The corrosion products were removed by pickling in a solution of 25% HCl containing a proprietary corrosion inhibitor. The weight of each bar was recorded at 10 minute intervals until a constant decrease with time was achieved. Extrapolation back to the origin gave the weight of the uncorroded metal allowing the determination of the weight loss due to corrosion.

Results & Discussion

Exposure site blocks

The mean corrosion potential per condition determined from measurements on the blocks using the embedded silver/silver chloride standard reference electrodes over a three year period are summarised in Figure 2. If a simple criterion is used whereby a corrosion potential more negative than -200 mV is considered to signify at least some risk of corrosion to the reinforcement, it appears that the control chloride-free blocks and the desalinated blocks containing cast-in chlorides are in the main showing no evidence of corrosion. The cast-in chloride-containing control blocks appear to suffer from significant corrosion during some periods (i.e. towards the end). Overall, the potential of the chloride-containing controls is more negative throughout.

Assuming the same criterion, the steel bars of the blocks containing ingressed chlorides, judging by their corrosion potentials, are expected to have suffered from significant corrosion over the whole period of exposure. Those subjected to desalination, however, tended to approach the -200 mV level signifying perhaps a degree of success in lowering the level of corrosion. It is known that the potential of the steel, following polarisation to very negative potentials during the desalination process, requires a period of several months, possibly a year, to achieve de-polarisation owing to large enforced chemical, and possibly, physical changes. Some of the physical changes such as reduced porosity by the possible precipitation of certain phases, are likely to be permanent. The simple assumed absolute potential criterion, therefore, is unlikely to always apply, particularly during the early months following treatment. Nonetheless, an indication of trends is possible so at least a reduction in the corrosion activity of the steel could be confidently assumed after desalination.
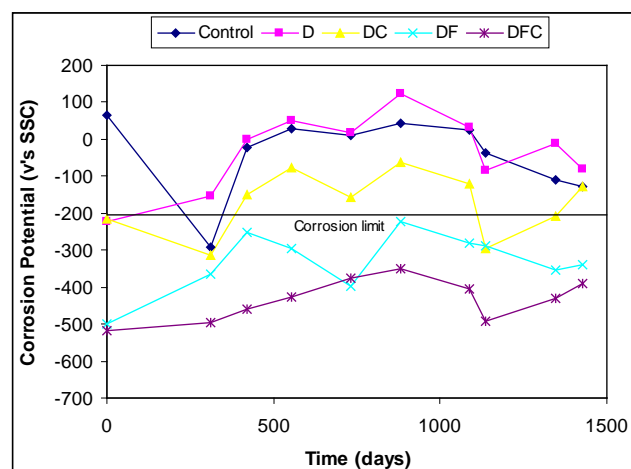

Figure 2. Mean corrosion potential of steel grids in blocks
Control = chloride-free controls, D = desalinated, cast-in chlorides, DC = Cast-in chlorides, control,
DF = desalinated, ingressed chlorides and DFC = ingressed chlorides. controls

Laboratory

A much more accurate assessment was achieved from the laboratory investigations as temperature, humidity and size of steel bars were all controlled parameters. The corrosion potentials confirmed the in-situ findings to a large extend and the corrosion current of the single bars gave a more quantitative indicator. Figures 3 and 4 summarise the results with the mean values from each condition. The corrosion current (Fig. 4) is lowest for the bars in the control chloride-free prisms and highest for the bars in the control 'ingressed-chloride' prisms, as would be expected, the latter being an order of magnitude higher. The order of conditions in an increasing trend of corrosion is then desalinated cast-in chlorides and desalinated ingressed chlorides, these being in-between the two extreme conditions.
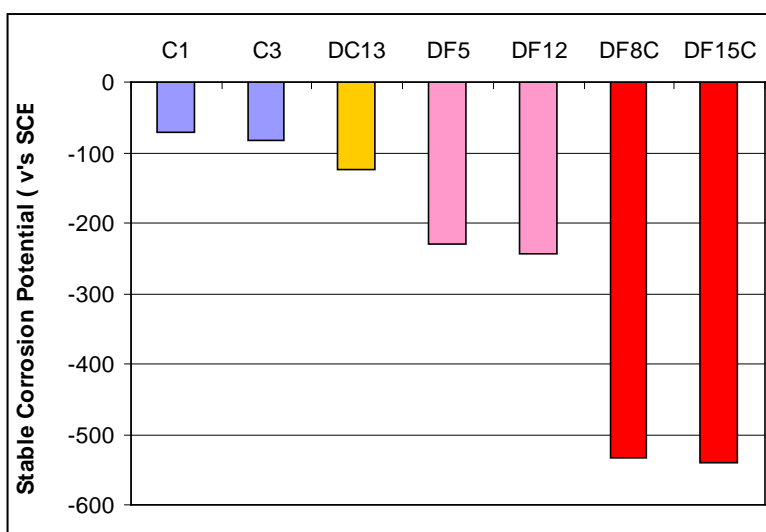

Figure 3. Stable mean corrosion potential of steel bars in the cut 'corrosion-monitoring' prisms
C = chloride-free controls, DC = desalinated, cast-in chlorides, DF = desalinated, ingressed chlorides and DFC = ingressed chlorides, controls
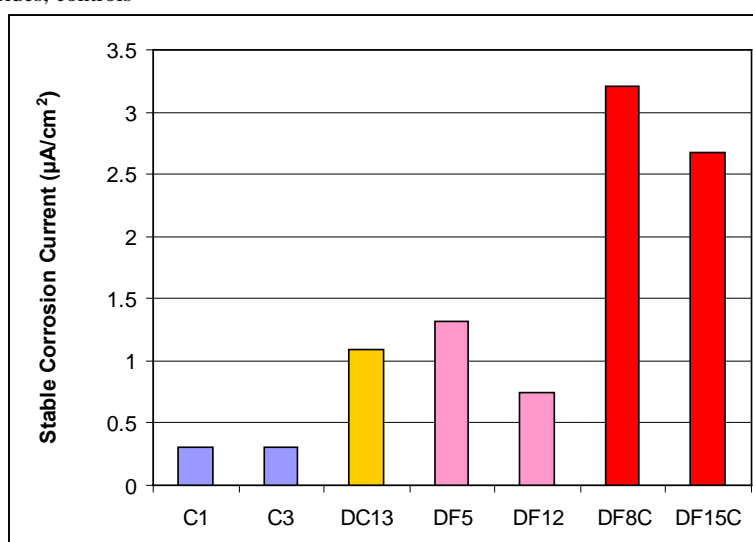

Figure 4. Stable mean corrosion current of steel bars in the cut 'corrosion-monitoring' prisms
C = chloride-free controls, DC = desalinated, cast-in chlorides, DF = desalinated, ingressed chlorides and DFC = ingressed chlorides, controls

The individual results are summarised as a plot of corrosion potential versus corrosion current (Fig. 5). Such plots can both indicate differences between conditions and reveal the possible corrosion mechanisms involved. Points lying in the top left hand corner of the plots show a low incidence of corrosion. Those lying in the bottom right corner suggest a high level of corrosion. If all the points lie in a straight line between the two extremes the likelihood is that corrosion is controlled by polarisation/depolarisation of the anodic half of the corrosion process, that of the dissolution of iron [8]. Figure 5 suggests that anodic control is the predominant mechanism for the chloride-free controls and the desalinated samples with a pseudo-cathodic Tafel slope of about 150 mV/decade. The same figure also clearly shows that the different conditions have resulted in separate populations of points. A somewhat higher corrosion level had resulted in the desalinated ingressed chloride condition compared to the chloride-free control but was significantly lower than the equivalent chloride-containing controls.
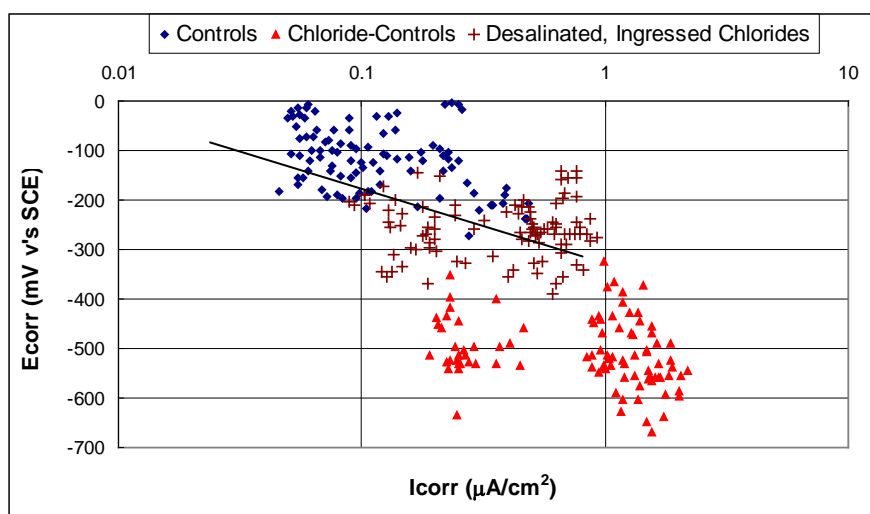

Figure 5. Corrosion current versus potential of all measurements taken for the chloride-free control, ingressed chloride control and desalinated ingressed chloride conditions

The chloride controls appeared to exhibit cathodic control behaviour. This is signified by a potential that is reducing in value but a corrosion current that is essentially unchanging. In view of the low level of potentials (~600mV) the controlling parameter seems to be the low availability of oxygen. This is supported by the formation of magnetite (black low-oxygen corrosion product) seen on steel in the chloride control prisms.

The results suggest, therefore, that the process of desalination in concretes containing relatively high levels of chloride reduces the level of corrosion but not to a level that may be considered insignificant. Cracking and some rust staining appearing on a number of blocks along the steel bars, particularly on those containing ingressed chlorides, confirm that the desalination process as currently applied has a limited success in arresting steel reinforcement corrosion particularly if corrosion of the steel had been occurring prior to the treatment. This is likely to be related to the fact that not all chlorides can be successfully removed. As explained earlier, the process becomes less efficient as the chloride concentration diminishes in relation to the total current carrying ionic concentration.

Figure 6 indicates this. A significant level of chloride had been removed by desalination but the concentration remained significantly higher than the chloride-free control Even though

there is no evidence in the results to suggest that re-migration of chlorides towards the steel after more that 4 years following the desalination process had occurred, the relatively high remaining chloride concentration, in the region of 0.6-0.8% by weight of cement, had allowed significant corrosion of the steel bars to continue [9]. The possibility of chlorides re-migrating to the steel with time must be real as chlorides are unlikely to be removed efficiently if they exist behind the steel reinforcement and in regions between the steel bars.
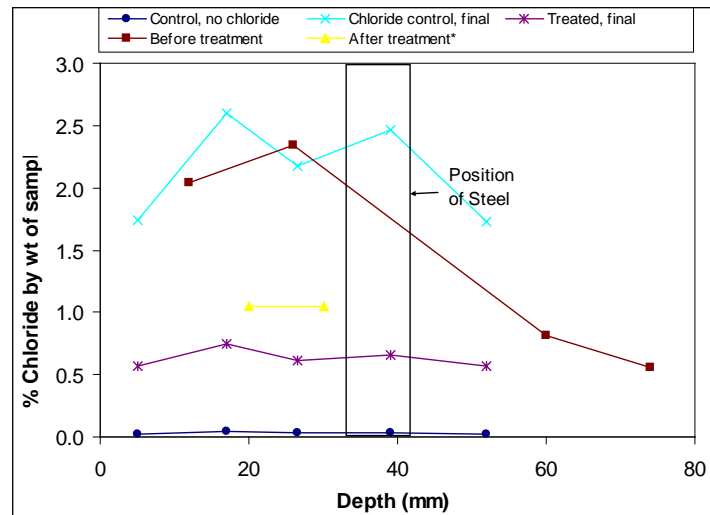

Figure 6. Ingressed chloride concentration profiles before and after desalination treatment
* Concentration determined by industrial partner after carrying out treatment

The corrosion rate as cross sectional loss/year determined electrochemically is compared to the corrosion rate as the total cross sectional loss determined gravimetrically in Figure 7. The figure, as well as showing the good correlation between two methods of corrosion measurement, also confirms that the level of corrosion of the steel is reduced considerably in the chloride-contaminated blocks subjected to ECE but that significant corrosion is still possible.
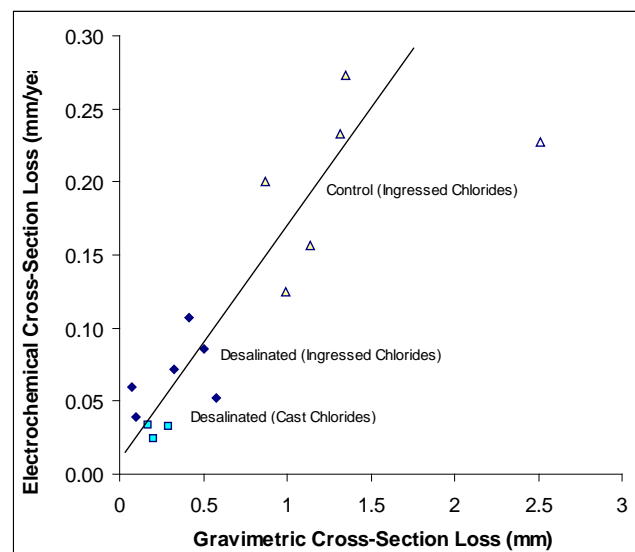

Figure 7. Comparison of cross sectional loss of steel bars in concrete prisms determined either electrochemically or gravimetrically
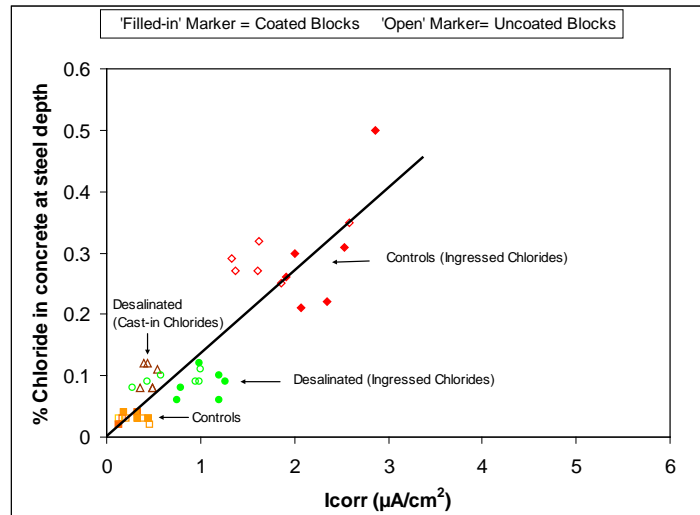
Figure 8. Effect of chloride concentration in the vicinity of the steel on the corrosion current of the bars

In fact, it was found that the level of corrosion was primarily dependant on the amount of chloride in the vicinity of the steel at the time of testing (Fig. 8) suggesting that, as not more than about 50% of the chloride can be effectively removed during desalination, corrosion is not likely to be eliminated totally if the level of chlorides is originally high, particularly as any un-removed chlorides outside the field of current may be able to re-migrate to the steel. Other complementary protection methods may then need to be applied. Contrary to this observation, other short-term research has revealed that short periods of high polarisation currents can lead to a higher tolerance to chloride-induced corrosion believed to be caused, at least in part, by deposition of solid phases at the steel concrete interface [10]. This could be a very important mechanism of enhancing the ECE rehabilitation process if it can be adequately evaluated and assessed. Any long term benefit from such a mechanism would also need to be accurately determined.

A further interesting observation is revealed in Figure 8. Coating the blocks with the type of coatings currently used post-treatment does not, as may have been expected, lower the rate of corrosion of the embedded steel but increases it slightly. This is consistent with results found elsewhere [11] in which local defects developed in the coatings had allowed moisture to penetrate the concrete but was then not allowed to dry out adequately owing to the coating.

Conclusions

The efficiency of chloride removal by the process of desalination appears to be reduced sharply with time of treatment. Following the initial treatment a total reduction of chloride in the region of 50% was achieved but a second identical treatment a few weeks later achieved no more than a further 3-5% reduction. This was not unexpected since, as the concentration of chloride diminishes, less proportion of the current is used to transport the chloride ions to the external electrolyte as opposed to that carried by the other more numerous ions.

Under the specific conditions of these trials, corrosion of the steel reinforcement was reduced after desalination of chloride-contaminated concrete slabs but remained at a significant level, particularly in the case where chlorides were ingressed from an external source as opposed to a lower concentration of chlorides cast-in.

The level of corrosion appeared to be related primarily to the chloride concentration remaining adjacent to the steel. As a significant level of chloride remains or may re-migrate to the area of the steel from the bulk, corrosion may not be totally eliminated in the long term.

Coating the concrete after treatment resulted in an overall increase in corrosion level, possibly because the coatings were not coherent and allowed moisture to penetrate the concrete through cracks and defects which could not subsequently escape owing to the coating.

Acknowledgments

References

1. B Elsener and H Bohni, *Proc. Corrosion and Corrosion Protection of Steel in Concrete,* R.N. Swamy (Ed.), Academic Press, 1994

2. M Ismail, G Sergi and CL Page, The Efficiency of Electrochemical Chloride Extraction in Controlling Corrosion of Reinforcement, *In Preperation*

3. M Ismail, G Sergi and CL Page, Ionic Remigration after Electrochemical Chloride Extraction and its Effect on Steel Passivation, *In preparation*

4. AM Hassanein, GK Glass and NR Buenfeld, *Corrosion,* **54**, 4, 323 (1998)

5. KR Gowers and SG Millard, *Proc. Instn. Civ. Engrs. Structs & Bldgs.,* **134**, 129 (1999)

6. M Stern and AL Geary, *Journal of the Electrochemical Society,* **104**, 56 (1957)

7. JA Gonzalez, A Molina, ML Escudero and C Andrade, *Corrosion Science*, **25**, 917 (1985)

8. GK Glass, N.R Short and CL Page, *Corrosion Science*, **32**, 12, 1283 (1991)

9. BRE Digest 444, Parts 1-3, Corrosion of Steel in Concrete, 2000

10. GKGlass and B Reddy, *COST 521 Workshop*, Luxembourg, 18-20 February 2002

11. G Sergi, A M G Seneviratne, M T Maleki, M Sadegzadeh & C L Page, *Proc. ICE, Structures & Buildings*, 140, 85 (2000)