

## **Corrosion Resistance of Reinforced Concrete Exposed to Calcium-Magnesium Acetate De-Icing Salt**

**S. O. Nwaubani<sup>1</sup>, A.Katsanos<sup>2</sup>, and M. Mulheron<sup>2</sup>**

<sup>1</sup>*Department of the Built Environment, Faculty of Science & Technology, Anglia Ruskin University - Bishop Hall Lane, Chelmsford Campus, Essex, CM1 1SQ.1, UK, E-mail: <s.nwaubani@anglia.ac.uk>.*

<sup>2</sup>*Faculty of Engineering and Physical Sciences, University of Surrey - Stag hill, Guildford, Surrey, GU2 1BJ, UK, E-mail: <a.katsanos@surrey.ac.uk>, <m.mulheron@surrey.ac.uk>.*

### **ABSTRACT**

This paper reports the result of a study aimed at assessing the impact of Calcium-Magnesium Acetate (CMA) solutions on the corrosion of reinforcing steel embedded in concrete. It is part of a larger research to evaluate the efficacy of adopting alternative de-icing chemicals and methods in winter de-icing operations. This part of the study involves the use of half-cell potential and Linear Polarisation Resistance (LPR) techniques to compare the corrosion risk in small-scale reinforced concrete slabs subjected to a ponding regime with distilled water, salt water or CMA solutions over a period of one year. The influence of different de-icers on the corrosion behaviour of the reinforcement are compared. Further work concerning longer term effects is in progress to ascertain the significance of the observed changes on the mechanism of the interaction between CMA solutions and cement paste.

### **INTRODUCTION**

The use of de-icing and anti-icing products is widespread in countries experiencing prolonged periods of snowfall during the winter. Currently, rock salt and other chloride-based products, are dominating this market due to their effectiveness with respect to ice melting, their low cost, ease of application and storage [Hart, P., 2009]. However, their adverse effects on the life cycle of reinforced and prestressed highway bridges and parking structures, due to the corrosion of the steel reinforcement and steel components [Pullar-Strecker, P 2002, Richardson, M.G, 2002] which they cause, have inevitably raised concerns regarding the sustainability of current de-icing practices. The problem is compounded by the negative impact they have on the natural environment and the fact that they accelerate corrosion of vehicle parts and roadside objects [Dore, S. and Laursen A., 2009].

Structural surveys carried out in many countries reveal the high cost of maintaining, repairing, and replacing concrete structures. In the United States, the direct annual cost of repair and replacement of deficient concrete bridges has been estimated to be around US\$ 8.3 billion [Kosh, et al, 2001]. Similar surveys conducted in Japan [Shibata, T., 2000] and in the UK estimated the corresponding expenditures to be ¥177.4 billion and £600 million respectively. The aforementioned figures do not include costs inflicted by damage on

roadside objects, vehicles, the loss of floral and faunal species and surface water quality, the adverse effects on soil structure and the migration of sodium and chloride ions into water supplies [Brenner, R. and Moshman, J., 1976]. Furthermore, they established that the indirect costs to the user, such as traffic delays and lost productivity, are estimated to reach ten times the value of direct costs.

Recognition of the negative effects of chloride-based de-icers has triggered extensive investigation of alternative approaches such as the use of environment-friendly de-icing chemicals. Much of the data reported to date relate to pilot projects commissioned by the US Federal Highways Administration. Calcium magnesium acetate (CMA) is one of the most widely examined de-icers and it has been demonstrated to be no more corrosive than water to embedded reinforcing steel and roadside objects [McCrum, R.L., 1989, & Kennelley, K.J., 1990].

CMA has been investigated for its ice-melting characteristics, its effects on concrete and various metals including reinforcing steel, its environmental impact and other aspects. It is manufactured by reacting dolomitic lime with acetic acid. Alternative methods of production from waste products have also been researched and identified. The most significant drawback of CMA is its high cost, which can be between 20 to 30 times the cost of rock salt. A report carried out following a request by the US congress, identified many benefits which could arise from the replacement of salt by CMA [TRB 1991]. Nevertheless it highlighted the fact that it was doubtful whether a complete substitution would provide the expected financial benefits due to insufficient data; a problem compounded by the fact that they were not easy to quantify. Subsequent studies, which have been carried out since, along with data resulting from field experience, have all reinforced the view that the use of CMA is a safe, and sustainable, option [Miller, W. L., 1992].

## **MAIN OBJECTIVES**

The work presented in this paper aims to investigate the presence of corrosion, and subsequent corrosion rates, of steel reinforcement in concrete exposed CMA and to compare them with the corresponding properties of steel reinforcement in concrete exposed to NaCl solutions and water. The influence of varying the w/c ratio of concrete is also examined. A further objective of this paper is to compare and interpret the effects of varying the concentration of the solution of acetate-based de-icers in relation to their ability to influence the aforementioned tendencies.

## **EXPERIMENTAL DETAILS**

Small-scale slab specimens (210mm x 330mm x 100mm) were manufactured with three sets of three reinforcing bars each. The three sets of bars were located at three different depths from the bottom of the ponding basin. Specifically, the depths chosen were 10mm, 25mm and 40mm, as shown in Figure 1. The purpose of employing different cover depths was, i) to establish the time to corrosion initiation induced by the different solutions at different depths, and, ii) to investigate the effect of the cover depth on the corrosion rates of the reinforcement which might reveal any interaction between the de-icer and the concrete cover.

The steel electrodes were made from 8mm diameter mild steel bars. The bars were initially cut to a 130mm length each, and a 4mm hole was drilled on one side, at a distance of 10mm from the edge of the bars. They were then turned to a bright steel finish and degreased with

acetone in order to remove any manufacturing grease. Subsequently, the bars were placed in a desiccator awaiting the application of protective coating, which was applied on both ends of each bar. The coating of the ends served the purpose of ensuring that an equal area of steel was exposed on every bar. This was required for the calculation of the corrosion current density. It also ensured that the protruding ends of the bars were protected from moisture and aggressive ions and therefore not corroding.

The protective coating was applied by dipping 95mm of either end of the bar thus, ensuring an exposed length of 120mm in the middle. The coating comprised initially two coats of cement paste with the same binder and the same water/binder ratio as the specimen in which the bars were to be embedded. The bars were dipped to the aforementioned length and then left to dry overnight. This process was repeated the following day, and the bars were, again, left to dry overnight. Two coats of marine varnish were then applied, also by dipping, to complete the coating process. Each one of these two varnish coats, after being applied was left to dry overnight. A lathe was then used to remove the excessive paste and varnish from the middle 120mm of the steel ensuring that all the bars had an equal area of exposed surface. The bars were then placed in the moulds and the concrete was cast the following day.

A total of twelve specimens with PC were cast. Half of them had a w/c ratio of 0.65 while the rest had a w/c ratio of 0.4. Figure 1 specifies the constructional details of the samples.

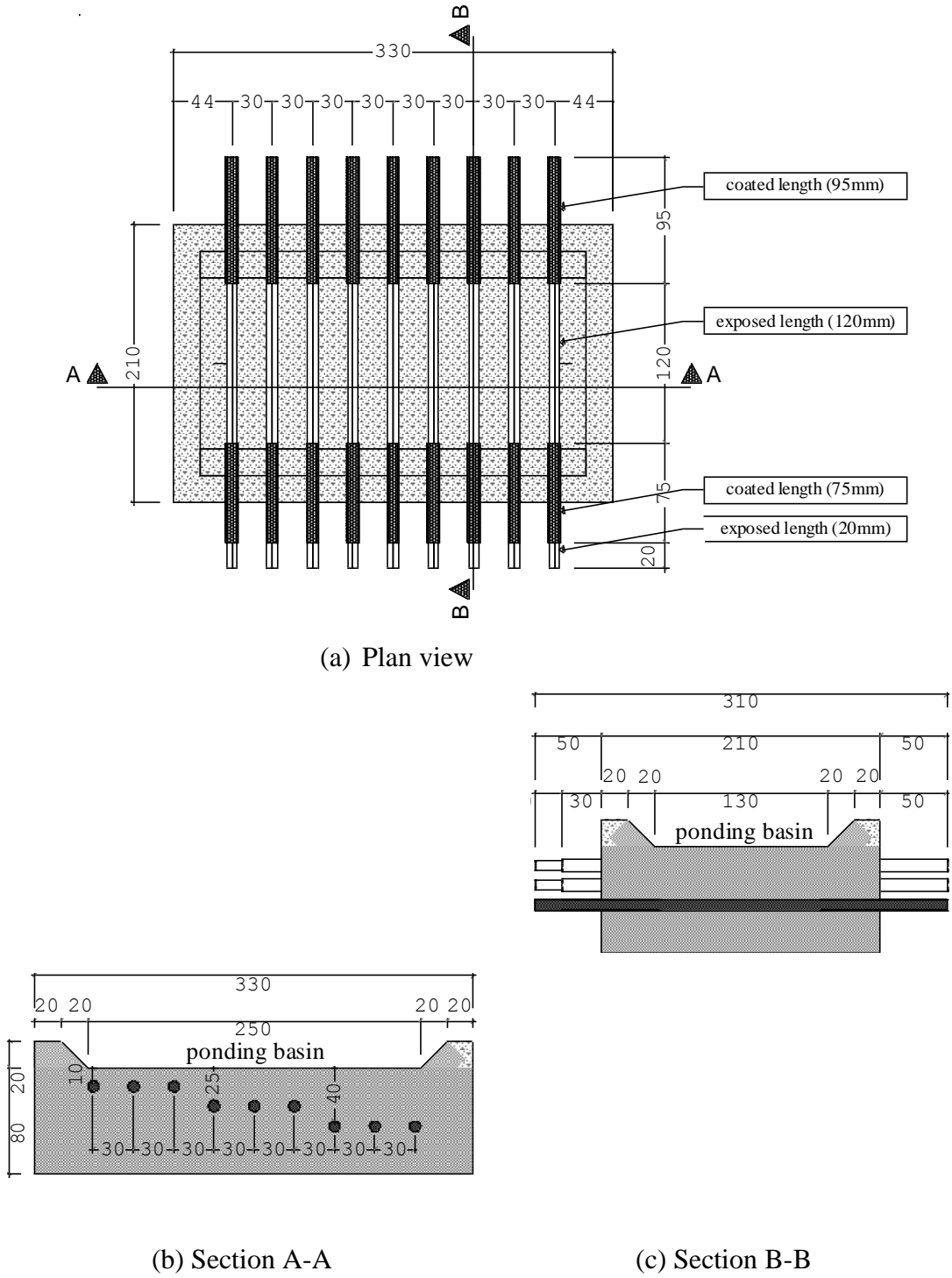
**Table 1. Slab specimens for corrosion measurements**

<b>Type of Binder</b>	<b>W/C Ratio</b>	<b>Number of Slab Samples</b>	<b>Number of Reinforcement Bars</b>
<b>PC</b>	0.40	6	54
	0.65	6	54
<b>Total</b>		12	108

After curing for 28 days at 100% RH, the specimens were transferred to a room with constant temperature and relative humidity (20 C° and 70% R.H.), where they remained for the rest of the experimental process. A 20mm length of the edge of each bar was exposed for the connections to the electrodes that were necessary for corrosion monitoring. The specimens were immediately ponded with 300g of water saturated with calcium hydroxide. Forty eight hours later the initial base-line measurements were taken as described below. Thereafter, two-weekly dry-wet cycles were followed, whereby the wet period of each cycle involved ponding with 300g of the corresponding solution for each specimen. During the ponding period the top of the ponding surfaces would be carefully sealed with polythene sheets in order to prevent evaporation of the solution and the consequent alteration of their concentrations.

Measurements were taken every two weeks at the end of the wet cycle in order to ensure wet conditions and therefore adequate conductivity between the surface of the ponding basin and the steel bars. Two well established types of corrosion measurement techniques were used so that their combined results could provide an insight into whether corrosion is taking place and what the rate is at any given time. The two techniques used were the half-cell potential measurement and Linear Polarisation Technique. The corrosion measurements were conducted by the use of a Sycopel Scientific Superstat potentiostat that was operated manually throughout the duration of the experiments. A calomel electrode was used as a

reference electrode, and, for both techniques, three measurements were taken at every depth for each sample.



**Fig. 1. Constructional details of the corrosion monitoring specimens**

**RESULTS AND DISCUSSION**

The “Van Daveer” criteria for the interpretation of half-cell potential measurements taken with a copper/copper sulphate reference electrode specify that a potential more positive than -200mV indicate less than 10% probability of corrosion and a potential more negative than -350mV indicates more than 90% probability of corrosion [Pullar-Strecker, P. 2002]. The electrode used for the half-cell potential measurements was a saturated calomel electrode whose potential is 72mV more positive than the potential of a copper/copper sulphate electrode. Thus, a half-cell potential more negative than -278mV, indicates a 90% probability of corrosion. Similarly, potentials more positive than -128mV represent an indication of a less than 10% probability of corrosion. Values in between, represent an uncertain corrosion activity. Table 2 offers the criteria for the interpretation of the Linear Polarisation Technique results. Figures 2 and 3, illustrate the half-cell potential and LPR results of the steel bars in PC specimens with water/cement ratios of 0.40 and 0.65.

**Table 2 Interpretation of  $i_{corr}$  values**

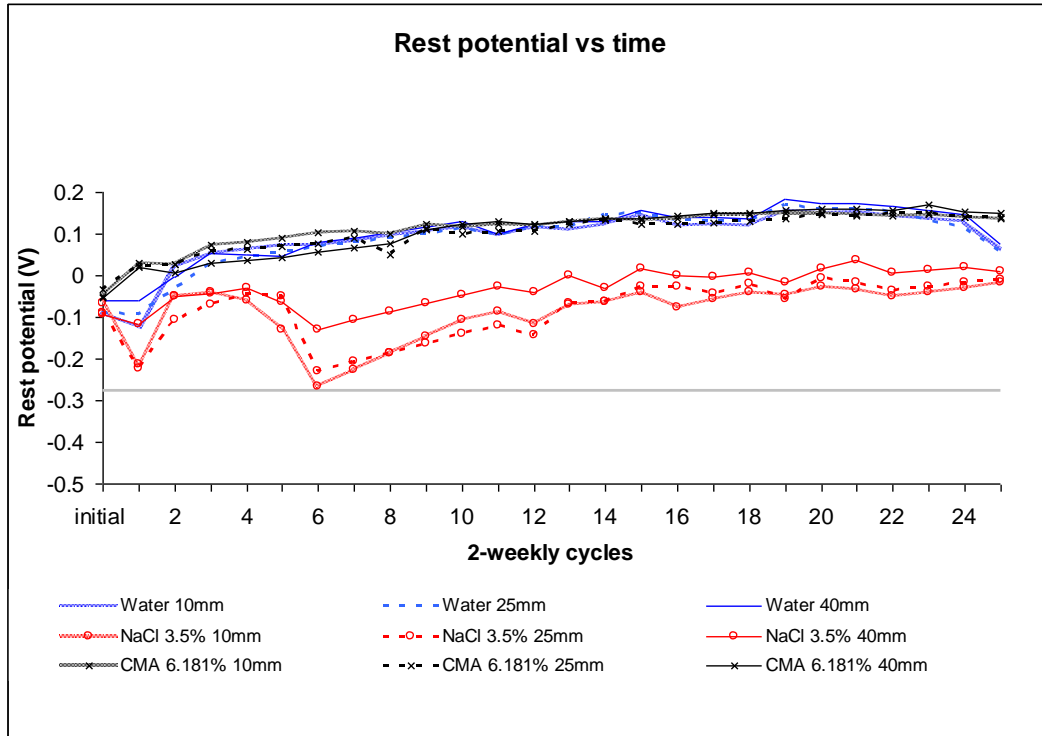
$i_{corr}$	Interpretation
$<0.2\mu\text{A}/\text{cm}^2$	Reinforcement in the passive condition
$0.2 - 0.5\mu\text{A}/\text{cm}^2$	Low to moderate corrosion rates
$0.5 - 1\mu\text{A}/\text{cm}^2$	Moderate to high Corrosion rates
$> 1\mu\text{A}/\text{cm}^2$	High Corrosion rates

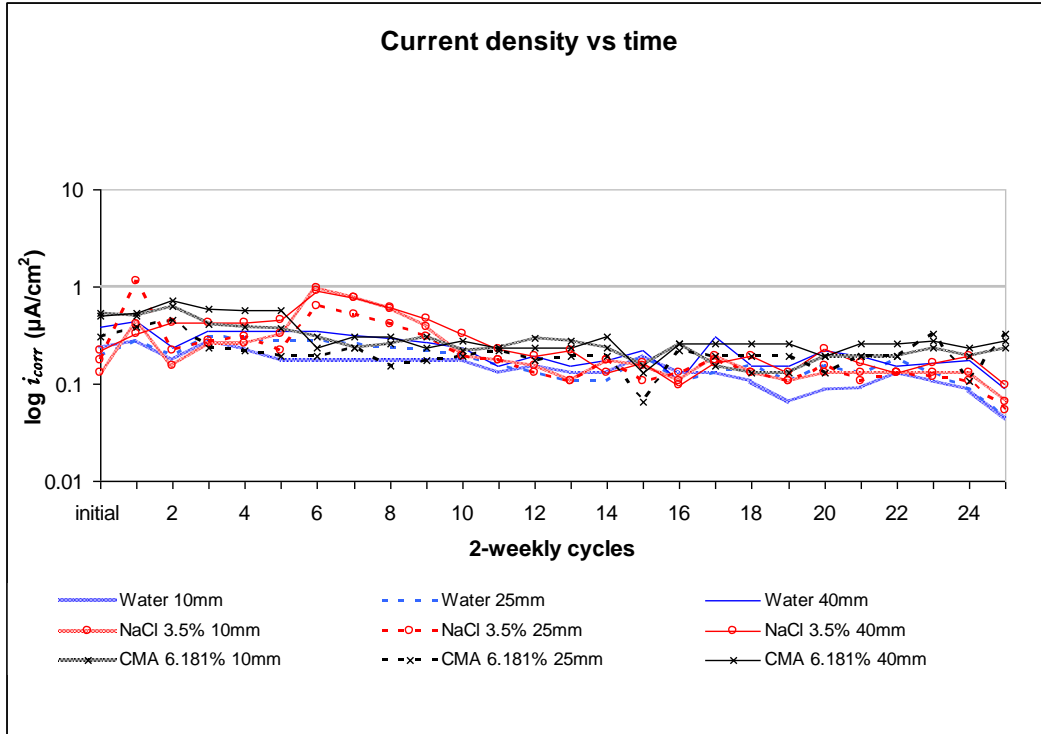
The only bars which seem to be demonstrating signs of corrosion are the bars situated at 10mm depth in the PC sample with a w/c=0.65, and ponded with a 3.5% aqueous solution of NaCl. The bars at 25mm depth in the same specimen show a tendency to corrode but the half-cell potential values obtained are more positive than the ones characteristic of a 90% probability of corrosion according to the aforementioned criteria. This is corroborated by the LPR results which indicate low corrosion rates. The half-cell potential values of the bars at 40mm depth dwell at around -100mV, which is a value characteristic of a very low probability of corrosion, while the  $i_{corr}$  values of these bars are below  $0.2\mu\text{A}/\text{cm}^2$ , which shows that the steel is in the passive condition. The difference in corrosion between bars situated at these three different depths probably results from differences in the concentration of free chloride ions around each bar. The free chloride ions act to disturb the passive film on the surface of the steel bars. In addition, the dissociation of iron chlorides can produce locally high levels of acidity at the surface of the steel leading to pit formation [Richardson, M.G., 2002].

A similar pattern is evident in the corrosion measurements of the bars in the PC sample with a w/c=0.4, ponded with a 3.5% aqueous solution of NaCl. The thicker the concrete cover, the more positive the half-cell potential. However, in this specimen, none of the bars demonstrate high probability of corrosion after 24 cycles as they all produce half-cell potential readings below and around -100mV and the  $i_{corr}$  values indicate passive conditions. This is probably due to the lower permeability of concrete in this specimen which delays the ingress of chlorides and limits the oxygen levels which assist the corrosion process [Richardson, M.G., 2002]. This specimen produced the most negative half-cell potential values at the end of the 6<sup>th</sup> cycle, and the  $i_{corr}$  values indicated moderate to high corrosion, when the bars at 10mm depth seemed to be reaching the threshold values for corrosion, but in the following months the values measured at all depths shifted to more positive values. At the end of the 24<sup>th</sup> cycle, the results obtained from the bars at all three depths seem to indicate passive conditions. This indicates that lowering the water/cement ratio provides inherent resistance to chloride

contamination with respect to the length of the period before the corrosion initiation, which is critical in determining the service life of a structure.

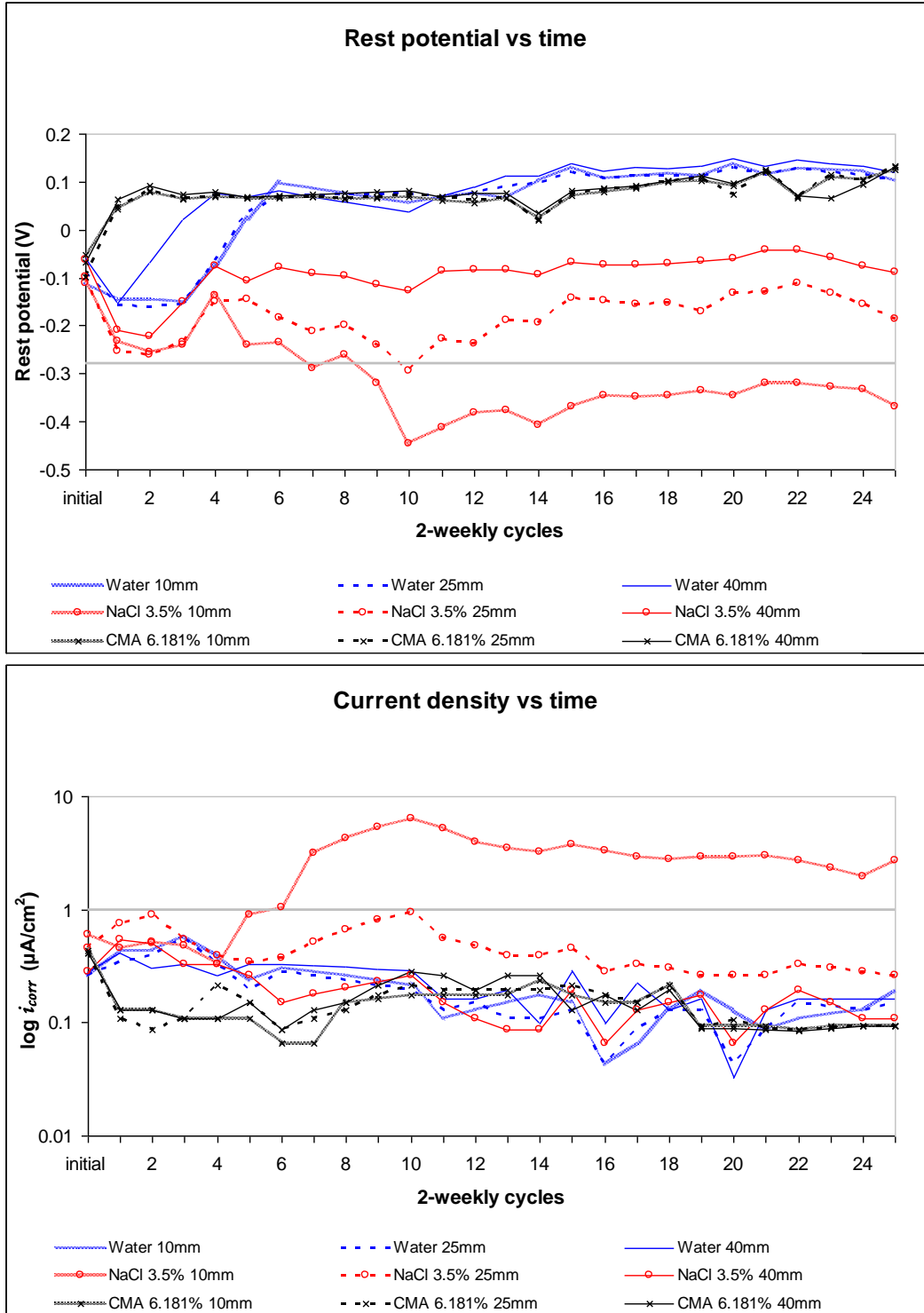
With respect to the specimens ponded with water and CMA, there seems to be no difference in behaviour between the steel bars embedded at different depths. The “half-cell potential vs. time” curves recorded for each separate de-icer almost coincide for all three depths. This occurs in samples of both qualities of concrete used. This is an indication that CMA, unlike NaCl, does not contain migrating ions which can potentially facilitate the corrosion of the rebar, at least within the first 14 cycles of testing.





**Fig. 2 Half-cell potential and LPR results for specimens with w/c=0.40 vs. time (10mm, 25mm, 40mm cover depth)**

The rest potential of the bars in PC samples with w/c=0.4 seems to be following the trend of the corresponding measurements taken from the control sample ponded with water. Specifically, these readings appear to be constantly shifting positively and at the end of the 24<sup>th</sup> cycle they are higher than +100mV, which is indicative of a passive state on the surface of the steel. The readings for the lower quality concrete sample exhibit an almost identical behaviour. The half-cell potential measurements are corroborated by the LPR results which for specimens of both concrete qualities and for all cover depths, indicate that the steel bars are likely to be in the passive condition.



**Fig. 3 Half-cell potential and LPR results for specimens with w/c=0.65 vs. time (10mm, 25mm, 40mm cover depth)**



## CONCLUSIONS AND RECOMMENDATIONS

Certain conclusions can be drawn from this on-going study with reference to the corrosiveness of CMA and its implication about the life cycle of concrete bridges. These can be summarised as follows:

- i. CMA has produced no corrosion of the rebar within the first year of testing, while NaCl has produced corrosion, in the top bars of the low quality specimens ( $w/c=0.65$ ).
- ii. The water/cement ratio of concrete and the depth of cover do not seem to play a significant part in the half-cell potential readings taken from samples ponded with water and CMA. This implies that CMA, unlike NaCl, does not contain deleterious ions which can facilitate the corrosion of the rebar.
- iii. The fact that CMA does not seem to facilitate rebar corrosion implies that all maintenance and repair work on concrete bridges could be avoided.

However, it needs to be established whether or not the CMA can compromise the quality of concrete in a different manner. A possible formation of expansive or non-cementitious products due to this agent could create cracks, which could, in turn, facilitate carbonation or the ingress of other aggressive ions. The need, therefore, for a microstructural investigation that could identify such adverse effects, becomes evident. This realisation has triggered a relevant microstructural investigation in the University of Surrey as part of the aforementioned, larger project currently.

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