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Effect of Alternative De-icers on the Corrosion Resistance of Reinforced Concrete Bridges and Highway Structures

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Additional information is available at the end of the chapter

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1. Introduction

Prolonged periods of snowfall in countries with advanced infrastructure and transport systems have rendered the use of de-icing agents to a common occurrence on roads and highway structures. They are necessary in order to maintain a good level of service with respect to the transport systems, thus avoiding traffic jams and disruptions, but also to provide a high level of road safety. Today, chloride-based products, such as rock salt, are the most commonly encountered de-icers as they are easy to apply and store but mostly because they efficiently melt ice at an affordable price [1]. However, their widespread use over a long period has left the construction industry and the engineering community with a grave problem regarding the durability of highway reinforced concrete bridges and multi-storey parking structures [2], due mainly to the fact that they cause corrosion of the reinforcement and steel components [2, 3].

For reinforced concrete bridges, in particular, the chlorides reach the reinforcement through leaking joints and spray from passing traffic. The corrosion product is known to occupy 2 to 6 times the volume of the metal from which it originates and this results to spalling of the concrete cover [2]. This process has a multitude of implications for the durability of concrete structures as it may imply section loss of the reinforcement and compromise of their load bearing capacity. Loss of the protection provided by the concrete cover further promotes and accelerates corrosion, thus leading to structural deficiencies and reduction of the life cycle of the structure. In the US alone, there are 20-25 year-old bridges, which are already facing this type of problems due to heavy de-icer applications and inadequate maintenance [1]. Furthermore, chloride de-icers have also been reported to have a negative impact on the natural environment [4, 1], and accelerate the corrosion of vehicle parts and roadside objects [5, 1]. These factors have inevitably raised concerns regarding the sustainability of current de-icing practices.

2. Cost of corrosion in general

The annual cost of corrosion consists of both direct costs and indirect costs. The direct costs related to corrosion are made up of two main components:

a. The costs of design, manufacturing, and construction such as; use of new materials such as stainless steel to replace carbon steel; use of novel technologies to achieve increased wall thickness for corrosion allowance; innovations in the mitigation and/or prevention of corrosion, such as coatings, sealants, corrosion inhibitors, cathodic protection, and cost of labour and equipment.

b. The direct and indirect cost of management relating to the inspection, repair, maintenance, replacement of corroded parts, rehabilitation, and loss of productive time in corrosion-damaged structures.

Using highway bridges as an example, the optimized contribution of each of the contributing components is calculated through life cycle cost analysis and characterized by the annualized value. Relevant surveys carried out worldwide has highlighted the heavy cost of maintaining, repairing, and replacing concrete structures due to corrosion. In the United states a Corrosion Costs Study carried out by the National Association of Corrosion Engineers (NACE), revealed the direct cost of corrosion in the U.S. was $276 Billion in 1998, approximately 3.1 % of GDP. The indirect cost of corrosion was also estimated to be at least equal to the direct cost giving a total cost of 552 Billion. The direct and indirect costs increased to $468 Billion in 2011, giving a total cost due to corrosion of $936 Billion in that year. In fact, a significant milestone in the effect of corrosion on the U.S. economy was reached this year (2013), when **the total cost of corrosion in the US exceeded $1 trillion annually** for the first time (based on estimates of GDP from http://forecasts.org/gdp.htm). This represents 6.2% of the GDP.

	Year of Study		
	1998	2011	2013
Direct corrosion cost	$276 Billion	$468 Billion	>$500 Billion
Indirect corrosion cost	$275 Billion	$468 Billion	>$500 Billion
Total Cost	$552 Billion	$936 Billion	>$1 Trillion

Table 1. Result from (NACE Corrosion Costs Study)

An earlier study by Koch, et al [6], established the cost of corrosion to the Government sector, the Production and Manufacturing sector, Utilities sector, Infrastructure and Transportation sector. Of these, the cost of corrosion in the infrastructure category was estimated at $22.6 billion, which was 16.4 % of the total cost of the sector categories examined in the study (see Figure 1).

The infrastructure category is divided into the following industry sectors: (a) highway bridges, (b) gas and liquid transmission pipelines, (c) waterways and ports, (e) hazardous materials storage, (f) airports, and (g) railroads.
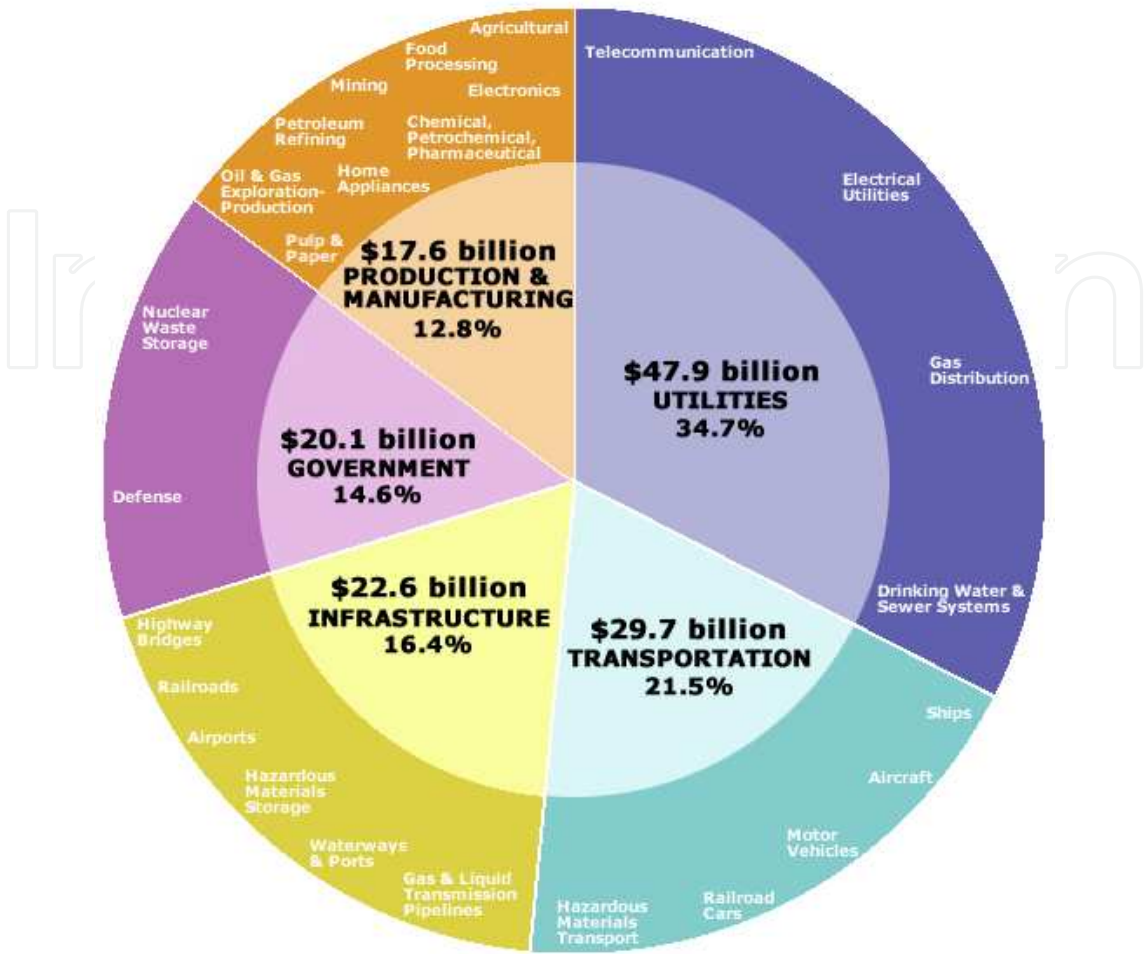
Figure 1. NACE Corrosion Costs Study [6]

2.1. Facts about reinforced concrete bridge corrosion

There are about three quarters of a million conventional reinforced concrete bridges in the USA. According to the latest Federal Highway Administration's National Bridge Inventory, at least 59% of these are reinforced concrete structures [6] and over 30% of the bridges are structurally deficient or functionally obsolete. The annual direct cost of corrosion for highway bridges is estimated to be $13.6 billion. 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 [7, 8], or 0.095% of the 1998 GDP of that country [9]. A similar survey conducted in Japan [10], estimated the corresponding expenditure to be ¥177.4 billion, or 0.059% of the 1999 GDP of that country [11]. In Britain the total estimated cost for the rehabilitation and repair of deficient concrete bridges was found to be £616.5 million spread over a period of ten years after 1989 when the report was published [12]. This would amount to about 0.013% of the 1989 GDP of the UK according to the Office for National Statistics and the figures does not include costs relating to 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 [1]. It is also estimated that indirect costs, such as traffic delays and subsequent lost productivity, can amount to ten times the value of direct costs [1].

Cost of corrosion studies have been undertaken by several other countries, not cited above, including, Australia, Kuwait, Germany, Finland, Sweden, India, and China. The studies have ranged from formal and extensive efforts to informal and modest efforts. The common finding of these studies was that the annual corrosion costs ranged from approximately 1 to 5 percent of the Gross National Product (GNP) of each nation [5]. Furthermore, the cases cited above are mainly before the millennium, however an important point to note is that the cost of remediation of corrosion-damaged structures is ever increasing, even in this decade and millennium, with many developed countries spending an ever greater proportions of their GDP for maintenance and repair of corrosion-damaged infrastructure (see Table 1 below).

3. Facts about de-icers

3.1. Chloride-based de-icers

Due to extensive research on ice-melting chemicals in recent years and their many different applications, there is currently a multitude of solid and liquid road de-icing and anti-icing products on the market. The most common type of de-icers used today is the chloride-based de-icers and in particular rock salt, composed primarily by sodium chloride (NaCl). A figure typical of the extensiveness of its use is the 10 million tons of salt used in the US every year [13, 14]. It is used so widely because of its low price, ease of application, and documented effectiveness. Although chloride-based de-icers perform well with respect to ice melting, their aforementioned impact on the environment and infrastructure has led the industry to pursue different methods of winter operations, which could limit or eliminate their use [1]. In this context, the emerging, acetate-based de-icing chemicals have been chosen for investigation both on-site and in the laboratory by many transportation departments and research establishments especially in the US ([1], as there is evidence that they could provide a more sustainable solution towards winter operations, despite their, currently, high cost. In what follows, this chapter will explore in greater depth the properties of the two common Acetate-based de-icers: CMA (calcium magnesium acetate), and NAAC (sodium acetate)

3.2. Acetate-based de-icers

3.2.1. Calcium Magnesium Acetate (CMA)

Recognition of the negative effects of chloride-based de-icers has generated research into alternative de-icers, especially in the United States. Calcium magnesium acetate (CMA) is one of the chemicals considered for this purpose. CMA has been investigated for its ice-melting characteristics [15], its effects on concrete [16,17,18,19,20] and various metals including reinforcing steel [21,7,8], its environmental impact as well as other aspects. Almost all of these studies have found CMA to be effective and benign. The drawback however, is that its price currently ranges between 20 to 30 times the cost of rock salt [22, 1]. A report carried out

Country/Project	GDP	Annual Cost of Corrosion	Source of information
USA(1998)	$276 Billion	3.15% of GDP	Corrosion Costs and Preventive Strategies in the United States', Report FHWA-RD-01-156 - http://www.nace.org
USA(2007)	$429 Billion	$13,840 billion	NACE figures: http://events.nace.org/publicaffairs/cocorrindex.asp
USA(2013)	$16.535 Trillion	>1 trillion [6.2% GDP]	Bureau of Economic Analysis, Department of Commerce. July 31, 2013 Income and Product Accounts Gross Domestic Product, second quarter 2013 (advance estimate); http://www.bea.gov/newsreleases/national/gdp/2013/ . Retrieved August 1, 2013.
Canada(2005) **Roads, Sidewalks, Bridges Toronto (Canada)**	$992 Billion	$110 million spent in 2005 ... with a backlog of $235 million deferred due to budget constraints	K. McGran's article "On the road to ruin?", Toronto Star, February 5, 2005, pB4-B5.
Canada(2012)	$1.819 Trillion	2-4% of GDP	Bureau of Economic Analysis, Department of Commerce. July 31, 2013
Japan (1997)	$ 4.324 Trillion	0.8-1.0 % of GNP (1997 estimate of direct corrosion costs)	National Institute for Materials Science (Japan).
Japan(2012)	$5.964 Trillion	2-4% of GDP	Bureau of Economic Analysis, Department of Commerce. July 31, 2013
Australia(2008)		A$1-5 billion Australian dollars [~ 2% of GDP]	CSIRO-Re: Holistic Approach to Corrosion control, January 2008 web page.
Australia(2009)	$920 Billion	$70.6 billion	
Australia (2012)		$1,542 Trillion 2-4% of GDP	Bureau of Economic Analysis, Department of Commerce. July 31, 2013
United Kingdom (2007), Corrosion assessment, mitigation and repair of the old Severn Bridge.		£23 million	BBC News, March 7, 2007. (On-line Edition)
United Kingdom (2008)	$2.279 Trillion	$70.6 billion	GDP figures: http://www.economywatch.com/
United Kingdom (2012)	$2,441 Trillion	3-4% GDP	Structure and Infrastructure Engineering Maintenance, Management, Life-Cycle Design and Performance, Taylor & francis Volume 9, Issue 12, 2013, ISBN 1573-2479.

Table 2. Cost of Corrosion

following a request by the US congress [1], identified many benefits which could arise from the replacement of rock salt by CMA. Nevertheless, it highlighted the fact that it was doubtful whether a complete substitution would provide the expected financial benefits; a problem compounded by the fact that much of the data were not easy to quantify. Subsequent studies, by Katsanos and Nwaubani [23], along with data resulting from field experience [24, 25, 26, 27, 28] have all reinforced the view that the use of CMA is a safe and sustainable option.

3.2.2. Sodium Acetate (NAAC)

Another acetate de-icer, sodium acetate (NAAC), which has a similar cost to CMA, is currently used principally as an airport runway de-icer. It has been used been used for road de-icing in the towns of Aspen and Snowmass in the USA and has reportedly performed exceptionally well at very low temperatures [22]. NAAC is exothermic and this property makes it more effective in ice-melting as it stays active at lower temperatures than CMA [22]. Its potential use as a highway de-icer has not been fully researched, little or no few field experience has been documented regarding the effects of NAAC on corrosion behaviour of embedded steel reinforcement although it is commonly regarded as a non-corrosive de-icer [29, 30]. This is possibly due to concerns regarding its potential effects on surface waters. There are fears that, if used, it could increase the BOD of surface waters, more than other acetate de-icers, but less than urea [22]. If NAAC proves to be efficient in minimising reinforcement corrosion, and can be demonstrated to have an acceptable environmental impact, then it could provide a viable solution for use on corrosion prone structures in areas where temperatures fall below the active range of CMA.

De-icing chemicals are incapable of melting snow and ice in their dry (solid) state. They must first attract or encounter moisture to form brine (a chemical/water solution). The brine then penetrates down through the ice and snow until it reaches the pavement, then spreads outwards melting and undercutting the ice and snow for mechanical removal. Although the same chemicals behaviour are involved, there are remarkable differences in how de-icers work. A basic reason for these differences in de-icing is that some chemicals take longer to go into solution before they can begin penetrating ice and snow. Another reason for de-icing action is heat liberation. As they dissolve, some chemicals liberate heat due to exothermic reaction. In addition, pellet de-icers have been found to be more efficient than flake de-icers [24]. Generally, the performance of a de-icer is determined by its ability to melt, penetrate, undercut, and break the bond between the ice and snow. Two of the factors that determine the ability of a de-icer to perform these functions are the eutectic and effective temperatures of the de-icer. From basic physics, it is known that the eutectic temperature is the theoretical lowest temperature to which the de-icer can suppress the freezing point of water. However, this temperature can only be reached at the ideal percent concentration of the de-icer in water. All other concentrations will have higher freezing points [13]. Because de-icers become increasingly diluted as they melt ice, they remain at their ideal concentration only briefly. Consequently, the eutectic temperature has little bearing on real-life de-icing conditions. The effective temperature, which is the lowest temperature at which each de-icer remains effective, is a much more realistic measure of the de-icing capability of these chemicals [22]. Site experience gained by the use of acetate

de-icers over recent years, has provided a clearer picture with respect to the way that acetate de-icers work and their effectiveness in comparison to chloride de-icers. Table 3 displays the eutectic and effective temperatures of the de-icers under consideration. It becomes obvious that the effective temperature of sodium acetate is much lower due to the fact that it possesses exothermic properties.

DE-ICER	EUTECTIC CONCENTRATION (%)	EUTECTIC TEMPERATURE (C°)	EFFECTIVE TEMPERATURE (C°)
CMA (anhydrous calcium magnesium acetate)	32.60	-27.78	-6.67
NAAC (anhydrous sodium acetate)	27.00	-21.67	-15.00
Sodium Chloride	23.00	-21.12	-9.44

Table 3. Eutectic and Effective Temperatures of selected de-icers [13,14]

In another study Shenk [31], observed that the slower rate of ice melting arising from the use of CMA was due primarily, to the tendency of the CMA crystals to be buoyed up in their solution. However, the study revealed that CMA, is in many ways superior to rock salt as a road de-icer, due to its ability to melt ice at lower temperatures, and a marked heat of solution of the anhydrous CMA.

3.3. Site experience on the effectiveness of CMA and sodium acetate deicers

Field evaluation of the performance of CMA was studied in two similar articles from the late 1980's [24, 25]. They discussed experience from CMA applications at different locations. A common finding from those field studies is that CMA works differently from Sodium chloride. CMA prevents snow pack when applied early in a storm, forming a fluffier, drier snow-pack easy to remove by ploughing or by passing traffic, while Sodium chloride produces a wetter and heavier snow-pack. Therefore, timing was crucial in the case of CMA application MI92 MI93.The downside to early application is that, if done before a snow storm, it runs the risk of being blown away by traffic due to its low density. If applied late it may be slower acting, taking around 20 minutes longer to act compared to rock salt [25].

CMA also seems to work at lower temperatures than rock salt, as tendencies to re-freeze after temperature drops seem less, according to the observations made at the Zilwaukee Bridge [27, 28]. It also lasts longer and it sometimes has to be applied once during a 12-hour period compared to two or three for rock salt. This could also be due to the residual effect that CMA seems to have on the road surface as liquefied CMA and pellets stick on the road surface minimising re-freezing and early morning deck icing [27]. Clearly, CMA acts in a different manner and this explains the initial tendency of early users and researchers to believe that a

larger amount of CMA than rock salt would be required to achieve equal de-icing performance. A study conducted in 1993 [26] attributes the CMA-snow-pack interaction to the ability of the calcium acetate and the magnesium acetate to dissociate from the CMA compound and form independent hydrates. Similar studies have not, however been conducted for sodium acetate, and as a result we know little about its corrosiveness with respect to concrete reinforcement. Nonetheless, Sodium Acetate complies with SAE standard AMS 1431 regarding its suitability for use on runways, and is deemed non-corrosive to metal parts of aeroplanes.

3.4. Effects of acetate de-icers on corrosion of steel reinforcement

As the cost of maintaining, repairing and replacing concrete structures such as highway bridges or multi-storey parking buildings soared, academics and the industry were urged to investigate the corrosiveness of non-chloride-based de-icers. The chemical identified as the most likely substitute, as mentioned above, was CMA, and numerous projects have so far been undertaken in order to assess its effects on concrete and on steel reinforcement.

With respect to the corrosiveness of CMA, a study conducted by the Michigan transportation commission [7,8] deduced that prestressing steel strands immersed in NaCl solutions experienced 4 to 15 times more corrosion than identical specimens immersed in CMA solutions designed to have the same freezing point. The study also concluded that mixtures of the two materials produced results comparable to the ones produced by the CMA solutions down to at least a 0.46 CMA/NaCl weight ratio. However, this last claim is dismissed by a study which measured corrosion rates of steel wire embedded in mortar cylinders [32] by observing that corrosion can be inhibited by mixing CMA and NaCl, only for concentrations of about 0.05 M to 0.1 M NaCl, while CMA admixture does not prevent corrosion when the concentration of NaCl is more than 0.2 M. Similar results were obtained for sodium acetate additions. Another study conducted in Oklahoma, US [21], indicated that although CMA solutions ponded on chloride-contaminated reinforced concrete slabs were not able to passivate the reinforcement, the same solutions did not cause any corrosion on reinforcement embedded in uncontaminated concrete slabs. This result is supported by a 4-year long study by Chollar, B. H. & Virmani, Y. P[24], which reported that after four years of ponding on reinforced concrete slabs with NaCl and CMA solutions, no corrosion was produced by the CMA solutions in contrast to the heavy corrosion and subsequent cracking of the concrete produced by the NaCl solutions. Similar conclusions were drawn by two studies that compared the electrochemical behaviour of metals immersed in solutions of various concentrations of CMA and NaCl [33, 34]. In general, it can be said that CMA solutions do not induce corrosion of metals in almost any condition and in some cases even act as inhibitors.

3.5. Effects of acetate-based de-icers on concrete

Several studies have been carried out over the past two decades focussed on the effects of CMA deicers on the properties of concrete in contact with the applied deicer. In some cases, contradictory results have been recorded for similar kinds of tests by different researchers. This is mainly due to the diversity of conditions under which those experiments were undertaken. The effect of CMA can act very differently when in contact with concrete depending on

factors such as ambient temperature, Ca/Mg molar ratio of the CMA, concentration of the CMA solution, concrete mix design, cement composition, possible admixtures, type of aggregates etc. Consequently, the results from various studies cannot be directly compared. Nonetheless, they do offer an indication of the mechanism that governs the changes, which take place in concrete microstructure as well as in the composition of the CMA solution when these come in contact. Santagata & Collepardi [20] record severe deterioration of concrete after long-term, continuous immersion in concentrated CMA solutions (25% wt) at a temperature of 20°C. Another study by Lee et al [35]), involved tests at 58°C and found CMA to be particularly destructive due to the formation of expansive brucite and non-cementitious MSH. They also noted that the greater the Mg/Ca molar ratio, the greater the damage. This latter observation is also supported by a paper published in 1995 [18] which also documents that CMA solutions are more destructive in higher temperatures. However, this last study concluded that dilute solutions of CMA have a greater effect on compressive and flexural strength than concentrated solutions. The author went on to speculate that, this could be due to the fact that most of the magnesium in the solution is being consumed in the formation of $Mg(OH)_2$, and thus, most of the solution ends up comprising mostly calcium acetate, which he considers especially deleterious to concrete, although this is not supported by the tests involving this substance, conducted by Lee in his aforementioned study. However, most of the existing literature on the subject, support the concept of the formation of brucite and potentially the subsequent replacement of CSH in concrete with non-cementitious MSH as a result of the contact of concrete and CMA. Higher temperatures seem to have a detrimental effect on the cementitious matrix, and higher Mg/Ca molar ratios of the CMA appear to make it more destructive towards concrete. Higher concentrations of CMA solutions have a detrimental effect as documented in the literature, although some conflict exists on this matter, as one study has found dilute solutions to be more destructive.

3.6. Environmental effects of acetate de-icers

Modern concepts of sustainability and whole-life costing of structures cannot be complete without consideration for the environmental effect on the construction materials or how the use of structure during the period in service affects the environment. For highway structures, some of the basic environmental considerations, in the case of de-icers applied during the winter months, is whether they can alter the physicochemical properties of soil; their effect on water and air quality or on vegetation. Several studies have been conducted to this end and they have found CMA and NAAC to be environmentally low-risk de-icers in comparison with the chloride-based ones. More specifically, CMA has been found to be beneficial to soil [36, 37, 38] and harmless to vegetation [39, 4]. Certain concerns have been expressed, mainly regarding the possible future effects of the acetate-based de-icers on surface waters and treatment ponds[14, 38]. However, practical application of both CMA and NAAC has indicated no such effect [29]. A summary of the conclusions of some notable studies carried out are presented in Table 4 below.

DE-ICING AGENT	EFFECTS ON SOIL	EFFECTS ON VEGETATION	EFFECTS ON WATER QUALITY
NaCl	Potentially damaging. Exchangeable Sodium Percentage (ESP) more than 13 (toxic) [39].	Salt spray causes leaf burn. ESP higher than 4 kills some species. 0.5% concentration of chloride in plant tissue will result to plant death [39]. Browning, falling leaves, stem dieback, stunted or abnormal growth, premature death. Effect more apparent on grass rather than trees [14]..	Sodium and chloride concentrations in water supplies often higher than the standards set by health organisations [39].
CMA	Beneficial by increasing the pH and decreases solubility of trace metals. No upper limit defined [36, 37, 38]	No apparent adverse effect by spraying. Plants can withstand root exposure of up to 2500mg/l. [39, 4].	Biodegradable. No effects to water biota. It is better if the dilution rate is more than 100:1 [38]. It could cause eutrofication due to high BOD when re-aeration of waterways is limited by ice cover or in poorly flushed ponds [14]. It could significantly increase organic loading in treatment works when used in urban environments [40]. Despite concerns about BOD and DO levels of receiving waters practical experience has recorded no adverse effects.[29].
NAAC	No reports	No reports	Despite concerns about BOD and DO levels of receiving waters practical experience has recorded no adverse effects [29].

Table 4. Environmental effects of de-icers

4. Case study

4.1. Objectives

The main objectives of the laboratory study are:

- To monitor the corrosion rates, if any, of steel reinforcement in concrete exposed to CMA and Sodium Acetate solutions and to compare them with the corresponding effects on steel reinforcement in concrete exposed to NaCl solutions and water.

- To monitor the effects of varying the concentration of the solution of acetate-based de-icers in relation to their ability to prolong the time to corrosion initiation and to suppress corrosion rates.

- To investigate whether and how the addition of microsilica, varying the w/c ratio of concrete and the depth of cover can influence the time to corrosion initiation and corrosion rates if samples undergo the same testing regime.

- To determine whether the exposure of concrete to the de-icers under investigation could compromise the passivity of the rebars in the future, by causing carbonation of the concrete cover and thus alter the pH of the pore solution.

- To develop an understanding of the parameters controlling the behaviour of acetate-based de-icing agents in relation to the corrosion of steel reinforcement in concrete and their interaction with Portland cement and microsilica-containing paste by means of a micro-structural investigation.

4.2. Methods

4.2.1. Corrosion monitoring

The specimens used for this particular part of the study, had to be manufactured in such a way as to cover the needs of the proposed investigation. Thus, small-scale slab specimens (210mm x 330mm 100mm) were manufactured with three sets of three reinforcing bars each. The three sets of bars were placed at three different depths from the bottom of the ponding basin. Specifically, the depths chosen were 10mm, 25mm and 40mm, as shown in Figure 2.1(a) and 2b. 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 may, in turn, reveal information regarding the interaction between the de-icer and the concrete cover.

Steel electrodes were made from 8mm diameter mild steel bars. The bars were initially cut to a 310mm 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. Next, protective coating was applied on both ends of each bar, which served the purpose of ensuring that an equal area of steel was exposed in every bar, a detail essential as the anodic area has to be known for the calculation of the corrosion current. It also ensures that the protruding ends of the bars are protected from aggressive ions and are, 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 binder paste with the same binder and the same water/binder ratio as the specimen in which the bars were to be imbedded in each case. Two coats of marine varnish were applied, also by dipping, to complete the coating process. The bars were then placed in the moulds as described above and the depth of cover checked.

(a)

(b)
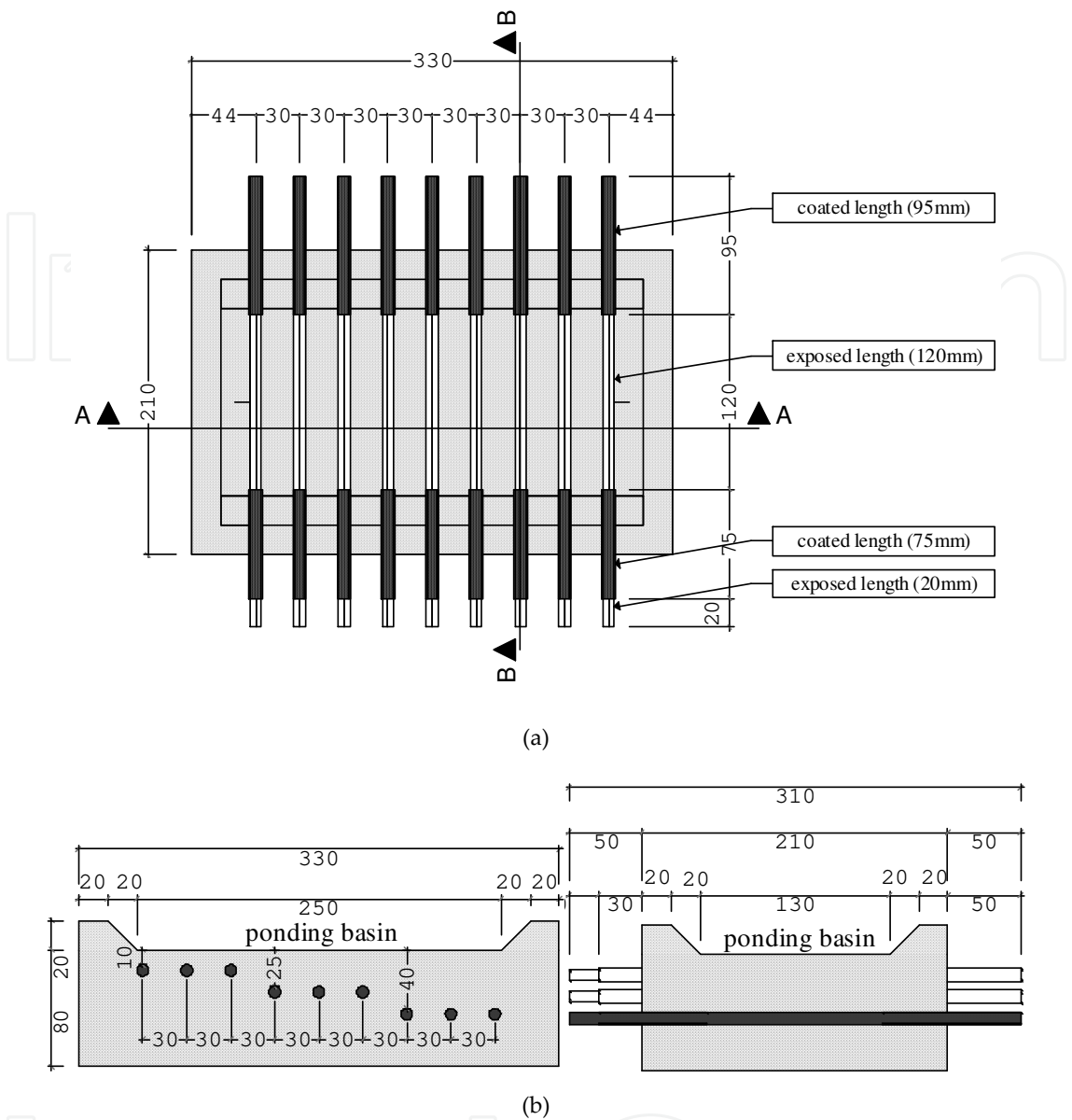
Figure 2. Constructional details of corrosion monitoring specimens, (a) Plan view, (b) Section A/A (c) Section B/B.

Standard batching and mixing techniques were adopted, and the same procedure was adopted for each mix. The mixer used for the preparation of all mixes was a Zyklos ZZ30. When filled and vibrated, the moulds were placed in the curing room (20 oC, 100% R.H.) where they were left to hydrate for 24 hours. Following that period, they were de-moulded and returned to the curing room for a further 27 days before testing. On the 27th and 28th days of curing two coats of anti-slip floor coating were applied on all sides of the specimens, including the protruding ends of the steel bars, except the ponding basin. After curing, the specimens were transferred to a room with constant temperature and relative humidity (20 oC and 70% R.H.), where they remained for the rest of the experimental process. Immediately after their removal from the curing room they were 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 (seven days dry, seven days wet) were followed whereby, the wet period of each cycle involved ponding with 300g of the corresponding solution for each specimen and sealing to prevent evaporation. Measurements were taken at the end of every wet half-cycle in order to ensure conductivity between the surface of the ponding basin and the steel bars.

Table 5., below outlines the specimens manufactured.

TYPE OF BINDER	W/B RATIO	NUMBER OF SLAB SAMPLES	NUMBER OF REINFORCEMENT BARS
OPC	0,40	6	54
	0,65	6	54
90%OPC / 10% Silica fume	0,40	6	54
	0,65	6	54
Total		24	216

Table 5. Slab specimens for corrosion measurements

It becomes obvious, therefore, that six samples were manufactured for each one of the four mixes designed for the project. This was done for comparison purposes as there were six different aqueous solutions chosen for ponding on the samples. The chosen solutions were as follows: i) Water, ii) 3.5% wt. NaCl solution, arbitrarily chosen to correspond to the average concentration of NaCl in sea water, ii)3.5% wt. CMA solution, chosen due to the indications from practical experience in the literature that equal amounts of CMA and NaCl produce equal de-icing performance, iv)6.181% wt. CMA solution, chosen to produce the same freezing point as 3.5% wt. NaCl, v)3.5% wt. NAAC solution, chosen due to the indications from practical experience in the literature that equal amounts of NAAC and NaCl produce equal de-icing performance, and vi)4.367% wt. NAAC solution, chosen to produce the same freezing point as 3.5% wt. NaCl.

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 corrosion rate is at any given time. The two techniques used were the half-cell potential measurement and Linear Polarisation Resistance 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 for most of the samples with the exception of eight samples. Namely, the two samples with pure OPC binder and a w/c ratio of 0.65 that were ponded with CMA solutions and all the six samples with a w/c ratio of 0.65 and a 10% silica fume admixture were tested using the Gamry PCI4-750 potentiostat after the completion of the 19th ponding cycle. A saturated KCl calomel electrode was used as a reference electrode. In both techniques, three measurements were taken at every depth for each sample. This provided an indication of the consistency of the results obtained.

4.2.2. pH shift measurements

A pH meter was used to measure the pH of the 300g of every ponding solution right before ponding and then right before the solutions were removed at the end of the wet cycles throughout the duration of the corrosion monitoring experiments. The negative and positive pH shifts were recorded and plotted over time. This was done to provide some means of observing the interaction between the solution and the specimen and to offer an indication of the exchange of ionic species and compounds between them.

4.2.3. Scanning electron microscope imaging

Small cement paste prisms (10 mm x 10 mm x 110 mm), were cast with a water/cement ratio of 0.4 and were immediately placed in the curing room at 100% RH. The following day they were de-moulded and placed back in the curing room for a further period of 27 days. After curing, the samples were transferred to a room maintained at constant temperature and relative humidity (20°C and 70% RH), where they remained for the rest of the experimental process. They were then coated with resin and left to dry overnight. The coating process was repeated the following day and they were, again, left to dry overnight. The following day the hardened resin along with the as-cast surface was removed from one of the two smaller faces of the sample, with a diamond saw. This way, it was ensured that the penetration of the de-icer solution from that contact face would be unidirectional so that the depth of penetration could be estimated with higher precision. Moreover, the removal of the as-cast surface of that particular face ensured that misinterpretations due to contamination would be avoided. The immersion regime, which the samples underwent, involved two-weekly cycles (one week immersed in solution and one week dry). Although wet-dry cycles may bear no particular significance in this case, the experiment was designed to correlate with the ponding regime performed on miniature slab samples designed for reinforcement corrosion testing, which forms the main core of this general project.

The effect of the immersion process was microscopically examined at predetermined times for a duration of 1 year after the end of the curing process, namely at 28 days, 90 days, 6 months and 1 year. The examination was performed with the help of a HITACHI 3200 scanning electron microscope. Specifically, the samples were cut in the middle with a diamond saw along their longitudinal axis, which, contrary to thin slicing, allows for visualisation of the effects of the solutions on the same sample, simply by moving the cut profile under the microscope. Samples were carbon coated before taken to the SEM for imaging. Images were taken at various locations, at different depths from the surface of the exposed face and at different magnifications, which varied from x300 to x9000. Element mapping was performed with the help of the microscope in order to help identify the elements and compound formations at locations of interest.

5. Results and discussion

In what follows, only selected parts of the results obtained from the different sets of experiments, which forms the key part of the data are presented.

5.1. Corrosion monitoring

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 [41]. 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 [42]. Figures 3. and 4., illustrate the results produced so far by the measurement of the rest potential of the steel bars in OPC and 90% OPC / 10% Silica Fume specimens with a water/cement ratio of 0.65.

The results presented in figures 3. and 4.; concern only the half-cell potential measurements taken from the OPC and OPC/Silica Fume samples respectively, with a w/c ratio of 0.65. Clearly, no corrosion seems to be occurring in any of the corresponding samples with a w/c ratio of 0.4 after 25 wet-dry cycles.

In the OPC samples the only bars which seem to be exhibiting signs of a high probability of corrosion are the bars situated at 10mm depth in the OPC sample ponded with a 3.5% aqueous solution of NaCl (figure 3.a and 3.b). 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 value considered characteristic of a 90% probability of corrosion according to the aforementioned criteria. At the end of the 25th cycle these middle bars have been measured to have a potential of -187mV which is a sign of uncertain corrosion activity. 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. The difference in potential 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 can disturb the passive film on the surface of the steel bars an therefore act as catalysts towards the initiation of corrosion. In addition, the dissociation of iron chlorides can produce locally high levels of acidity at the surface of the steel leading to pit formation (Pullar-Strecker 2002). A careful observation of Figure 3. shows that, with the exception of the sample ponded with the NaCl solution, each one of the rest of the samples exhibits comparable values of rest potential over time at all three depths. The significance of this observation lies in the fact that it indicates the absence of diffusing aggressive ions, which could, directly cause corrosion after reaching a certain threshold, in the same way that chloride ions do. However, the absence of chlorides in a solution does not render it incapable of inducing rebar corrosion as its contact with concrete over a longer period of time could have other undesirable effects such as lowering of the pH of the concrete cover which would, in turn, render the reinforcement susceptible to corrosion.

It is also obvious in Figures 3.a and 3.b that, although the acetate solutions and the water do not seem to corrode the reinforcing bars after 25 ponding cycles, each one of those solutions produces a distinct pattern of potential values over time. The trend evident in the case of the sample ponded with the CMA solution closely resembles the trend produced by the potential

of the bars in the sample ponded with water. This could mean that CMA does not contribute any ions more than water does, to the pore solution. Otherwise, this behaviour could indicate that CMA produces impervious deposits on the surface of the concrete, which block the capillary system of the cement paste and hinder the ingress of ions in the pore solution. In contrast, sodium acetate, at all three depths seems to produce the same behaviour as the graph that corresponds to the potentials measured at the lower bars, located at the 40mm depth, in the samples ponded with the NaCl solution. The chloride ions around these bars have not reached a threshold concentration, which could initiate depassivation and corrosion after 25 cycles of testing. In both cases of the samples ponded with NaCl and the ones ponded with NAAC, the pore solution has been influenced as indicated by the lower rest potentials of these bars compared to the rest potentials of the samples ponded with water. This similarity in patterns could be due to the ingress of sodium ions that are present both in NaCl and in NAAC, on the pore solution of the concrete.

The same patterns are evident in Figure 4., which illustrates the corresponding results for the samples containing Silica Fume. However, in these samples none of the bars has had the time to corrode within the 25 cycles of testing and the only bars which produce lower rest potentials and probably a tendency to initiate corrosion are the bars situated at a depth of 10mm from the surface in the sample ponded with NaCl solution. This is due to the documented effect of silica fume to alter the pore size distribution of the cement paste, reducing the size of the capillary pores, thus, making the concrete more impermeable and more resistant to attacks by chlorides and other aggressive ions [40]. However, in all the samples containing silica fume that were ponded with NAAC solutions the rest potential values tend to dwell consistently around 100 mV more positive than they do in the OPC samples. This could mean that the effects of NAAC on the pore solution are more evident in the samples with larger capillary pores, namely the OPC samples.

Finally, it should be noted that all samples were sectioned and sprayed with a phenolphthalein and alizarin pH colour indicators which showed no sign of reduced pH near the surface and therefore no carbonation taking place in any of them. The bars were extracted from all samples and were visually inspected; they all supported the results of the non-destructive corrosion monitoring, as corrosion was encountered only at the bars closest to the surface in the OPC samples with a w/c ratio of 0.65.

5.2. pH shift

Figures 5. and 6. illustrate the results for the pH shift monitoring described in section 3.2 above throughout the duration of the corrosion monitoring experiments. Although such a technique does not provide solid proof of any microstructural process, the results can be used as supporting evidence for the data derived from the widely used microstructural investigation techniques employed throughout this project. A simple observation of the information on figures 5. and 6. reveals a number of things worth noting.

The general trend observed is that all the plots tend to gradually decrease over time from more positive to more negative values and to eventually stabilise or at least decrease at a lower rate. This is possibly due to leaching of $Ca(OH)_2$ from the concrete and the subsequent dissociation
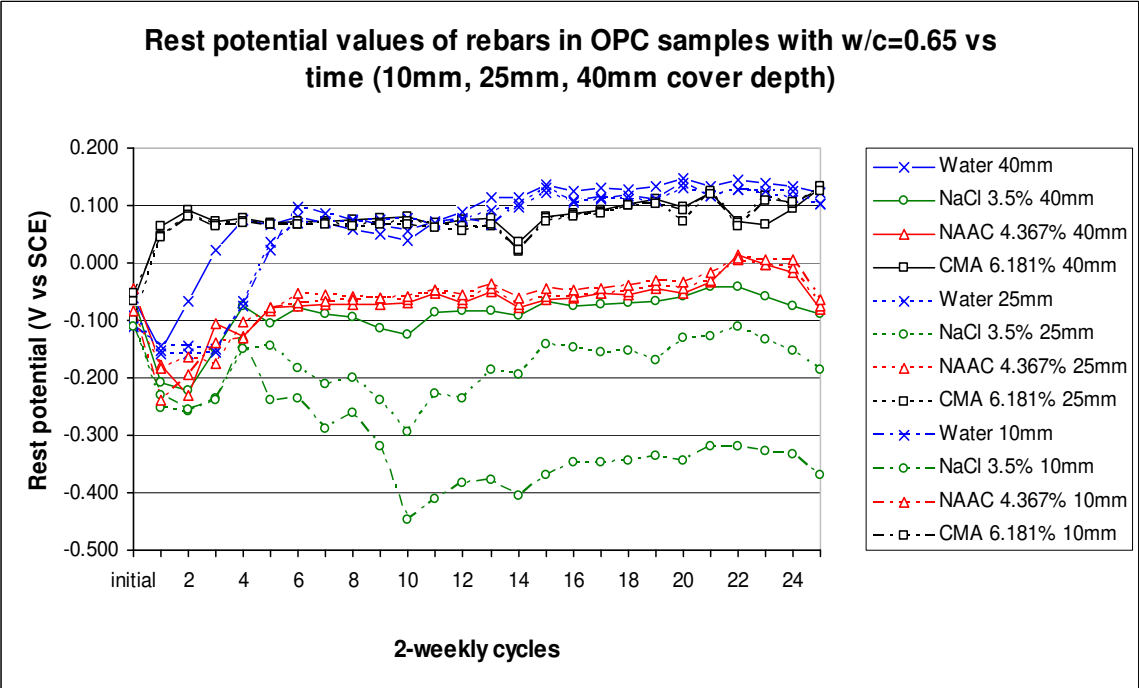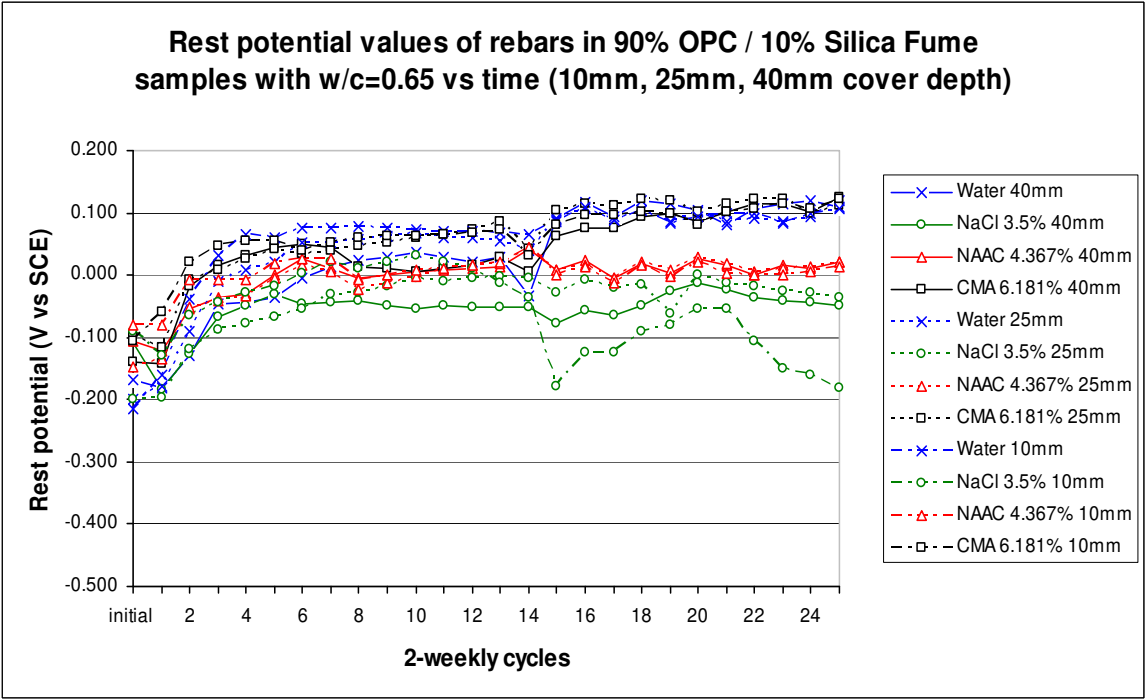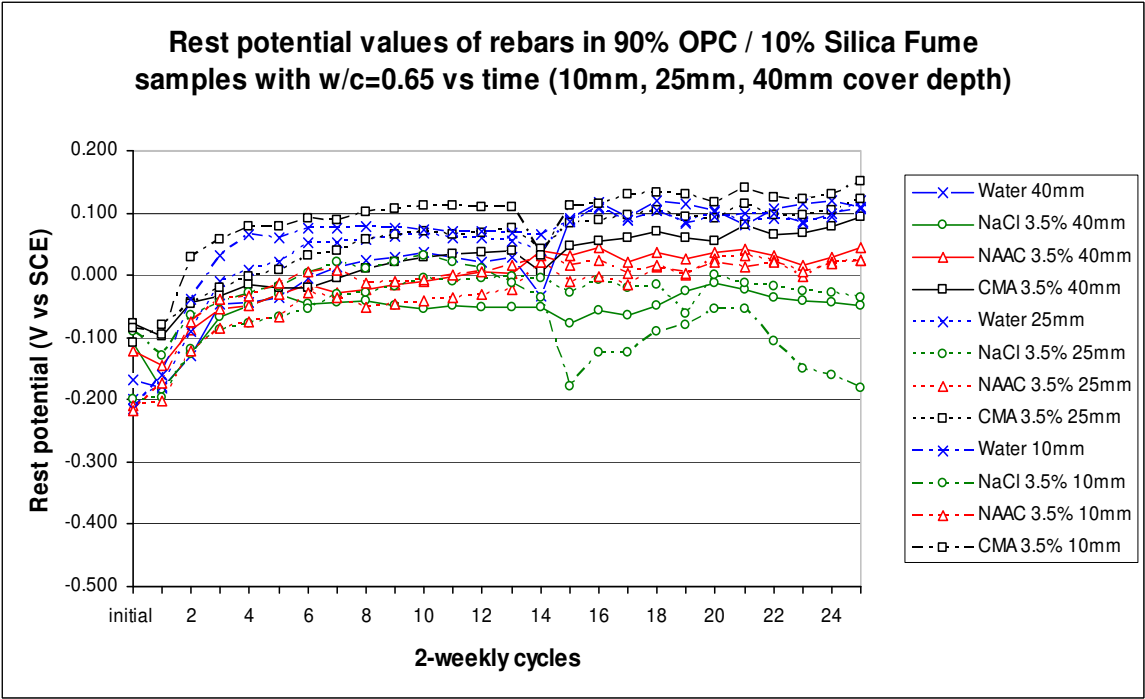
(a)
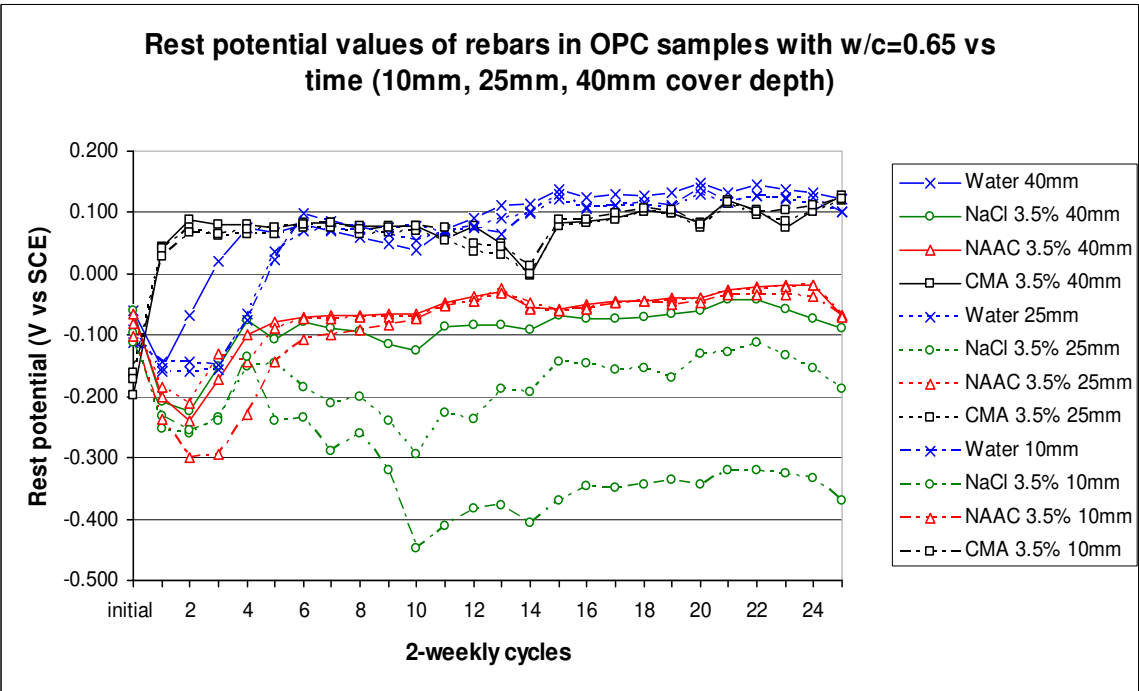
(b)

Figure 3. Half-cell potential values of rebars in OPC samples w/c=0.65 vs. time (10mm, 25mm, 40mm cover depth), a) Samples ponded with solutions with a freezing point equal to that of a 3.5% wt NaCl, b) Samples ponded with solutions of 3.5% wt

(a)

(b)

Figure 4. Half-cell potential values of rebars in 90% OPC/10% Silica Fume samples w/c=0.65 vs. time (10mm, 25mm, 40mm cover depth), a) Samples ponded with solutions with a freezing point equal to that of a 3.5% wt NaCl, b) Samples ponded with solutions of 3.5% wt.

of the calcium and hydroxyl ions, with the latter raising the pH value of the solution. The calcium hydroxide, however, becomes less available as the hydration process progresses and consumes it and the pores diminish in size. It also becomes less available due to the fact that much of it, previously located on and very close to the surface of the ponding basin of the samples has leached out during the initial stages of ponding. This latter phenomenon is probably what causes the abrupt drop of the pH shift graphs towards less positive (or more negative) values, within the first two to four cycles in most samples.
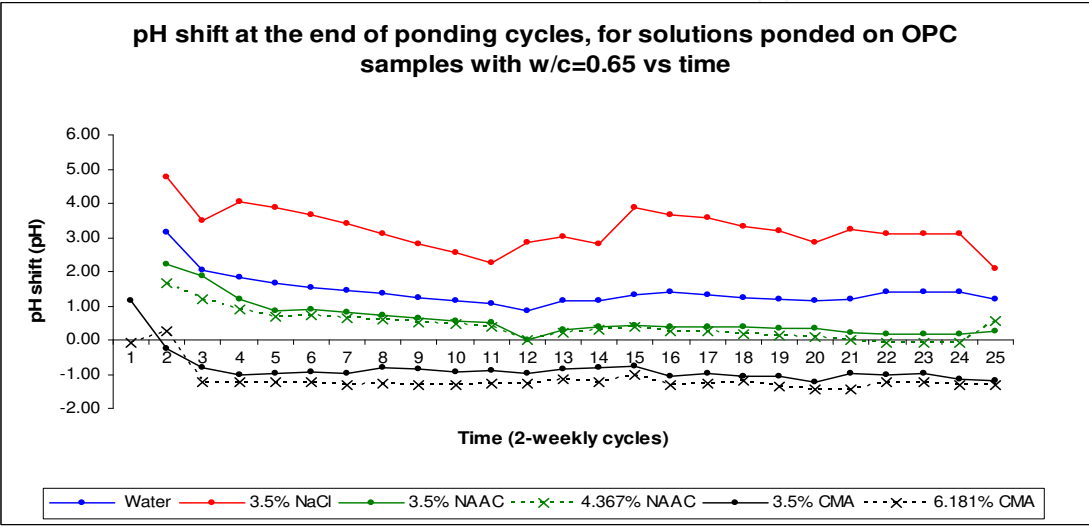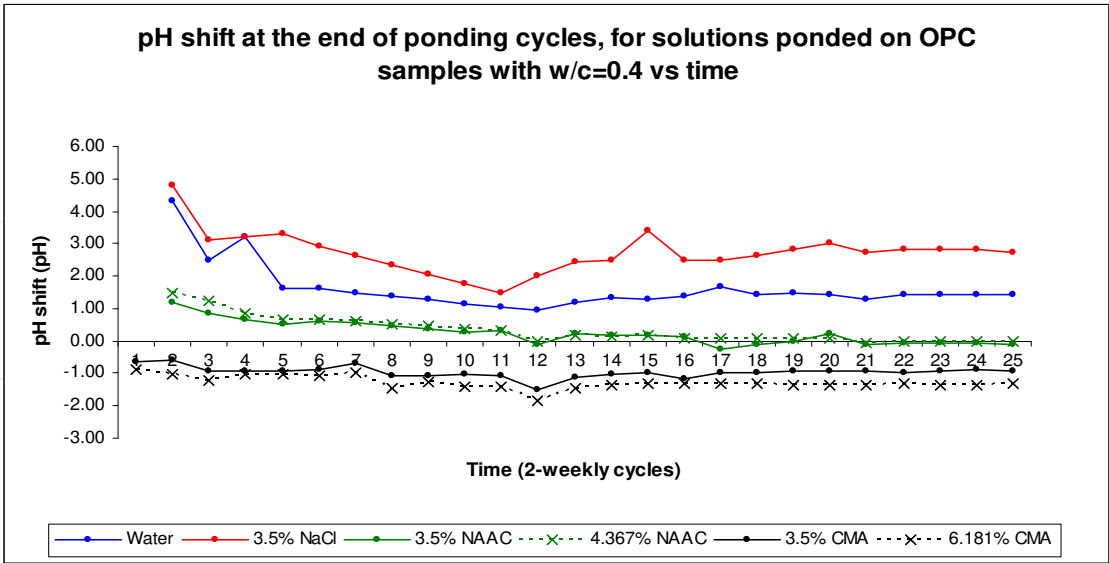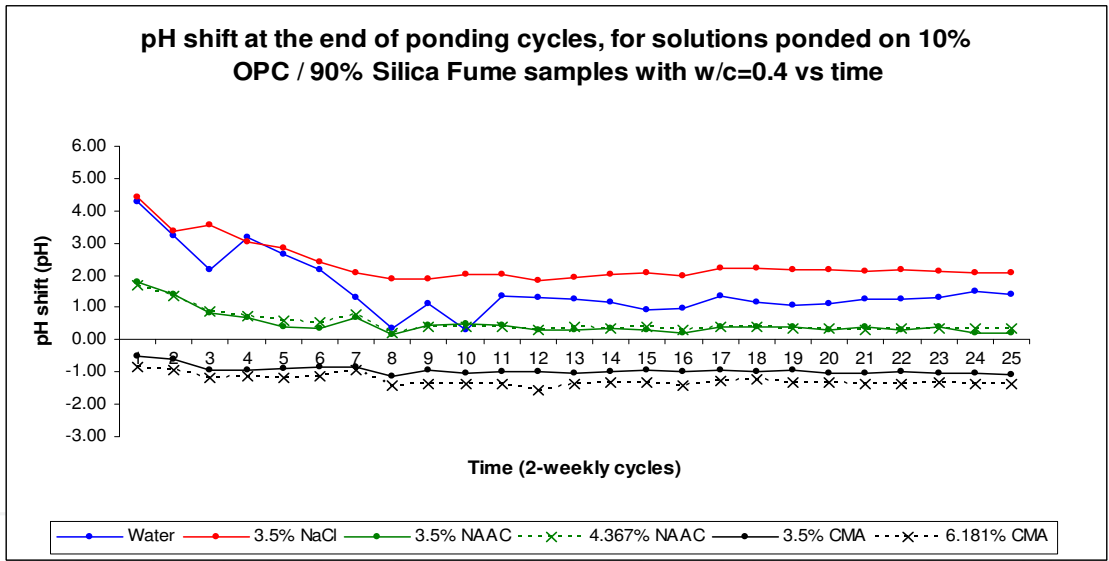

(a)
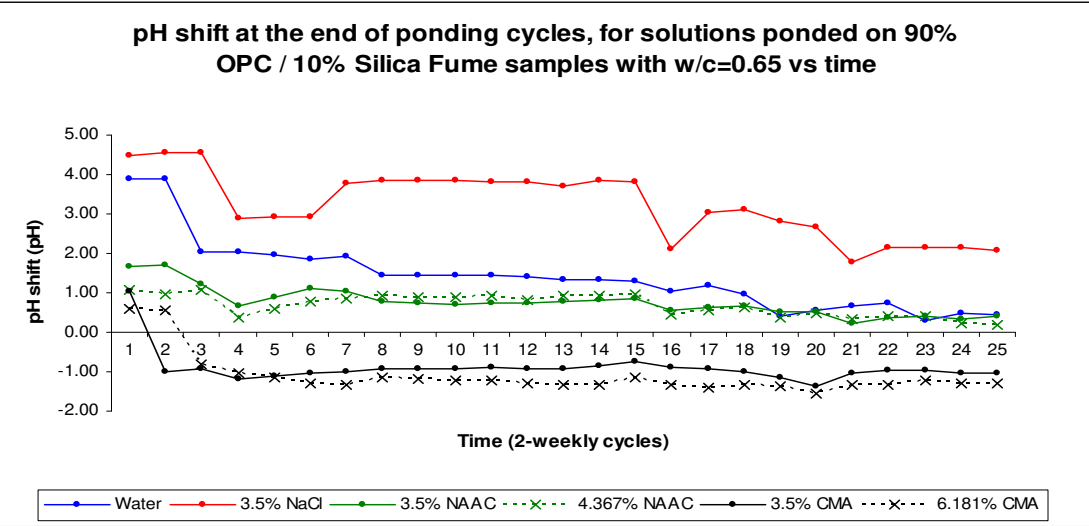
(b)

Figure 5. pH shift in ponding solutions at the end of ponding cycles for samples for samples with w/c=0.65, (a) OPC samples, (b)90% OPC / 10% Silica Fume samples

(a)

(b)

Figure 6. pH shift in ponding solutions at the end of ponding cycles for samples for samples with w/c=0.4, (a) OPC samples, (b)90% OPC / 10% Silica Fume samples

Varying the water cement ratio does not seem to have a major effect on the pH shift, as one might expect. This could be partly due to the fact that the samples with a 0.65 w/c ratio have larger pores while in the 0.4 w/c ratio samples, more calcium hydroxide is available. Therefore, leaching of calcium hydroxide could be facilitated in these two different ways, thus, producing seemingly comparable results. One, however, has to note that in the case of the CMA solutions on the 0.65 w/c ratio samples in figure 5., the graph decreases more abruptly producing positive pH shift initially within the first few cycles, than it does in the case of the corresponding

solutions on samples with 0.4 w/c ratio as illustrated in figure 6. where the shift is negative from the onset of the measurements.

The 10% replacement by silica fume does not seem to have a significant effect on the pH shift for any of the solutions. Moreover, the variations in concentration of the acetate-based de-icer solutions seem to play no significant role either. This is possibly accounted for by the fact that the variations in concentration of the acetate de-icer solutions chosen for this project are relatively small.

It is interesting to note that the resulting pH shift for the CMA solutions is predominantly negative while for the NAAC solutions it is positive or in some cases marginally positive, throughout the graphs. Thus, despite the fact that NAAC and CMA solutions are both acetate solutions, equal or comparable concentrations of the two in this experiment, consistently produce a difference in pH shift at the end of ponding. This effect could be due to the strong presence of magnesium in the CMA. It is worth noting that the Ca/Mg molar ratio in the CMA used is 3/7. Therefore, when soluble lime leaches from the concrete into the CMA solution, and calcium and hydroxyl ions are released, dissociated magnesium is bound to form magnesium hydroxide otherwise known as brucite, a very insoluble and relatively impermeable compound. This possibly led to the decreased values of the pH at the end of the ponding cycles in CMA solutions.

6. Conclusions

This case study suggests that:

1. Acetate based de-icers, unlike NaCl, do not contain deleterious ions which cause the corrosion of the steel reinforcement bars.

2. Presence of Acetate de-icers neutralised the probability of corrosion.

3. The trend for corrosion probability evident in the case of the sample ponded with the CMA solution closely resembles the trend produced by the bars in the sample ponded with water. This could mean that CMA does not contribute any ions more than water does, to the pore solution.

4. NAAC and CMA solutions of equal or comparable concentrations, consistently produce a difference in pH shift at the end of ponding.

5. Varying the water cement ratio does not seem to have a significant effect on the pH shift, as one might expect but no corrosion seems to be occurring in any of the samples with a w/c ratio of 0.4 even after 25 wet-dry cycles.

6. The use of Acetate-based de-icers on reinforced concrete would lead to low maintenance and repair cost for concrete bridges.

7. Recommendation

For better **corrosion** prevention in highway structures, the following preventive strategies need to be considered :

1. The high cost of Acetate based de-icers could be solved by making a change in the de-icing tradition and protocols and on highways..

2. Reinforced concrete bridges may need to locally de-iced with the more expensive but non-corrosive Acetate-based de-icers.

3. There is need to increase the general awareness of the very high corrosion costs and potential savings.

4. There is need to change the misconception that nothing can be done about corrosion rather efforts should not be spared in the quest to reduce cost by effecting adequate change in existing policies, regulations, standards, and management practices to increase corrosion savings through sound corrosion management.

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