Concentration monitoring and performance of a migratory corrosion inhibitor in steel-reinforced concrete

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Abstract

Inhibitor concentration depth profiles for concrete samples treated with a proprietary migratory corrosion inhibitor (of the Cortec MCI range) are presented. The treated concrete was cored and these cores were then sectioned and crushed before being immersed in distilled water to extract the available inhibitor. The amine concentrations were quantified using an ammonium-sensing electrode and were then related to the inhibitor concentration present. The inhibitor examined, reported to contain a combination of volatile amines and amino carboxylate compounds, was found to readily diffuse through concrete. The inhibitor was subjected to a 5-year trial and found to be effective in suppressing corrosion of steel reinforcement in the presence of high chloride concentrations. The concentration profiles indicate that only relatively low concentrations of inhibitor were required to achieve inhibition in this case.
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1. Introduction

Since its inception in the mid-19th century, reinforced concrete has become the most widely used construction material in the world. Today, the degradation and rehabilitation of concrete due to corrosion of the reinforcing steel (rebar) holds considerable economical significance [1]. Rebar corrosion can result in the cracking and spalling of the concrete cover, thus leading to an overall loss in structural integrity. The prevention and treatment of this problem can be addressed by several methods including concrete sealers, realkalisation, cathodic protection and corrosion inhibitors [2]. In recent years, many investigations and review articles have been published on organic migratory corrosion inhibitors (MCIs) for concrete [3–13]. For most commercial MCIs, the primary inhibiting component is suggested to be an amino carboxylate or amino alcohol [3,11,14]. The inhibitors are either admixtures or directly applied to the concrete surface. These inhibitors are said to be able to diffuse through concrete to the underlying rebar where they act to suppress both the anodic and cathodic corrosion reactions by forming a monolayer film at the steel–concrete interface [4]. This film acts as a barrier to the passage of aggressive ions (Cl⁻) and other species required for corrosion reactions.

MCI diffusion characteristics have been the focus of several studies performed over the past decade [8,14–17]. From a review of this work and laboratory trials [18], a method for determining the concentration profiles of amine-based inhibitors in concrete was developed. The studies of MCI diffusion properties have shown that the amine component of these inhibitors can diffuse through concrete relatively rapidly. One investigation into the diffusion of volatile amine-based inhibitors through concrete membranes revealed that loss of this volatile group from the concrete surface was significant [8]. Elsener suggests that losses to the atmosphere may affect the long-term effectiveness of the inhibitor.

Research has indicated that the performance of these inhibitors may be governed by the concentration of inhibitor, relative to chloride concentration, at the rebar and its ability to sustain these concentrations [7,12,19]. Elsener et al. [7] found in simulated pore water solution testing that a certain concentration of inhibitor was necessary for protection against chloride-induced corrosion. Another investigation, involving reinforced concrete samples contaminated

with varying amounts of Cl^-, found that corrosion was only moderately retarded at low Cl^- concentrations [12]. A recent study conducted in our laboratories reported the inhibition efficiency of MCI2005 when supplied as an admixture, a topical treatment and a combination of surface application and electromigration [19].

A more detailed appreciation of inhibitor concentration in concrete and its relationship to corrosion mitigation will promote the responsible application of inhibitors for reinforced concrete structures. In this work, the ability to monitor concentration profiles using an amine-sensitive electrode is applied to reinforced concrete samples that had undergone various treatments of MCI2005. A correlation between concentration profiles and their long-term effectiveness for mitigating chloride-induced corrosion is discussed.

2. Experimental

2.1. Sample design and preparation

Reinforced concrete samples were sourced from a previous investigation [19]. These samples were designed to be of poor quality with a w/c of 0.6 and a sand-to-cement ratio of 3:1. Chlorides were initially introduced to the concrete by admixing NaCl at the rate of 14 kg/m³ concrete, this is considerably higher than chloride contamination thresholds determined to induce corrosion of reinforced concrete [20], but desired to imitate a severely degraded marine structure. The samples (Fig. 1) were formed in wooden moulds with a centrally mounted reinforcement bar (surface area 100 cm², diameter 12.5 mm), and a mixed metal oxide rod counterelectrode running parallel to the rebar. After 24 h, they were removed and placed in a fog room to cure for a further 28 days. To allow access of a luggin probe, a hole was drilled into the concrete stopping approximately 2 mm from the rebar. This was done in an attempt to minimize the effect of concrete resistance on the electrochemical measurements.

2.2. Sample treatment

As part of the original investigation, three different inhibitor applications methods were trialed, admixed (AD), surface applied (SA) and a combination of surface applied and subsequent electromigration (SA + EM). Each test was carried out in duplicate. In the case of the AD sample, the inhibitor (MCI2005) was added to the mix water

Fig. 1. Reinforced concrete sample dimensions and orientation.

according to the manufacturer's recommended dosage rate of 0.84 kg/m³.

Inhibitor application for the SA and SA + EM samples began after they were removed from the fog room. For the SA samples, a neat solution of MCI2005 was painted on the top of the sample every 3 weeks for 300 days; in addition, a sponge containing a MCI2005/Ca(OH)$_2$ solution was maintained on top of the sample to avoid inhibitor loss due to evaporation.

Inhibitor was painted on the top surface of the SA + EM samples and a sponge containing the MCI2005/Ca(OH)$_2$ solution was placed on top. A titanium wire mesh was then placed on the sponge to act as a counterelectrode for the electromigration process. To promote the migration of positively charged inhibitor species (specifically quaternary ammonium, e.g., R_3NH^+) towards the reinforcement, the reinforcement was negatively polarised by applying constant current density of 7370 mA/cm² to the samples for 2 weeks. At this point, it is important to note that the absolute dosage rates for the SA and SA + EM samples is unknown; however, it can be said that the SA sample was exposed to considerably more inhibitor than the SA + EM due to the repeated applications.

All samples were also exposed to external chlorides during the 300 days of monitoring. The samples were placed on sponges saturated with a 3.5 wt.% NaCl solution, only the very bottom surface of the samples being in contact with the solution.

2.3. Extraction and measurement

Core samples were taken from the concrete blocks using a diamond-tipped coring bit, lubricated with a steady flow of water. The core samples were then cut into approximately 1-cm-thick sections using a bench-mounted rock saw, also lubricated with water. Around 25 g of each section was then crushed, weighed and put in a sealable glass jar with 25 ml of distilled water. The samples were agitated and then allowed to stand for 7 days to allow extraction of the available amines from the concrete.

The particulates were filtered off and the solution was analysed for amine content. The amine concentrations of the solutions were measured using an Orion model 95-12 ammonia-sensing electrode, connected to a millivolt meter. This electrode has been previously proven as an effective means for measuring amine concentration in Ca(OH)$_2$ solutions as part of 'diffusion cell' experiments [8,14,17]. The solutions were magnetically stirred during measurement; care was taken to insulate the solution from the stirrer plate and maintain the temperature around 22 °C as temperature has a significant effect on the electrode response. Typical time for stabilization of the electrode voltage was 3–10 min, with more dilute solutions requiring longer times. A calibration curve was used to relate the electrode voltage to the amine concentration, which was subsequently used to calculate the volume of MCI2005 per gram of original concrete sample.
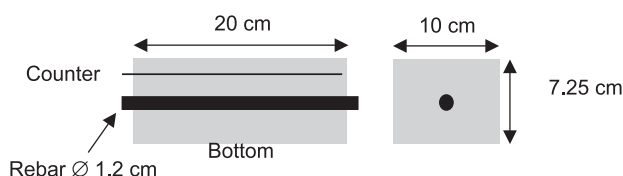
To determine the efficiency of the extraction method, samples with 'known' additions of MCI2005 were prepared. To simulate the exposure to water during coring and cutting, they were rinsed with water and dried prior to being crushed. Following the extraction process previously described, with 25 ml of distilled water and around 25 g of known sample, the extract concentrations were determined and related to the expected concentrations.

The reliable detection of low-level amine-based inhibitor concentrations (in excess of 0.0001 vol.%) in solution using the Orion ammonia-sensing electrode and the technique used here has also been shown by us previously [18].

2.4. Calibration

Previous investigations using the Orion model 95-12 ammonia-sensing electrode have reported a linear relationship for concentration and electrode response for concentrations of a similar MCI product above 0.001 vol.% MCI in water [14]. For concentrations below this value, the electrode response flattens off significantly and a linear fit is no longer suitable. An example of a calibration curve is presented in Fig. 2, and clearly shows this shape. Calibrations are made regularly, as the electrode response may vary causing the calibration curve to shift. In order to quantify low-level concentrations (i.e., below 0.001 vol.% MCI), care was taken to fit the curved region of the calibration data, as shown in Fig. 2. The error associated with these data falls within or just outside the data points shown.

2.5. Electrochemical monitoring

It is acknowledged that there are limitations and assumptions associated with the use of linear polarization resistance (LPR) for quantifying the rate of corrosion of steel rein-

forcement in concrete. Therefore, in this case, the polarization resistance (R_p) has been used as a qualitative measure to compare inhibition relative to a control and not a direct correlation to corrosion rate. A comparative expression (%Inhibition) for the inhibition achieved by the inhibitor treatments was calculated (Eq. (1)).

$$\%\text{Inhibition} = \frac{(R_{p,sample} - R_{p,control})}{R_{p,sample}} \times 100 \tag{1}$$

The LPR measurements were carried out on a Solartron 1208B, using Corrware control software. A saturated calomel electrode (SCE) was connected to the sample via the lugging capillary. The potential of the reinforcement was scanned ± 20 mV from the open-circuit potential (OCP) of the sample, at a scan rate of 0.1667 mV/s. The R_p of the sample was taken as the slope of the potential versus current density plot, assuming linearity over range between + 15 and − 15 mV relative to the OCP.

2.6. Breakout and visual inspection

The rebar segments were contained within the fourth centimetre section of the core samples taken from the MCI2005-treated concrete. The concrete attached to the rebar segments was knocked away carefully using a small hammer; no attempt was made to remove the tightly bonded concrete in order to preserve the rebar surface. The visual images were recorded using a stereomicroscope.

3. Results and discussion

3.1. Effectiveness of the extraction process

The efficiency of the extraction technique was tested using mortar samples with known additions of MCI2005 added to the mix water. Fig. 3 shows the measured concentrations as a percentage of the expected concentrations for various extraction times. A maximum extraction efficiency of 7% is observed after 7 days immersion. This level of extraction efficiency may be due to either loss of the amine during the extraction process or the amine-based compounds chemically reacting or 'binding' with the concrete, and hence, being unavailable for extraction. This extraction effectiveness is less than that previously reported for another proprietary inhibitor MCI2020 [18]; this may be due to the MCI2005 product containing amine-based compounds that are slightly more volatile or alternatively less soluble. Additionally, pore-blocking components, such as microsilicates, may cause extraction from the cement to be hindered.

The process of extraction of the amines from the concrete has been shown to be time dependent. Samples were tested 1, 2, 4 and 7 days after being immersed and Fig. 3 shows the resulting percentages of the admixed MCI detected. The results show that in the case of MCI2005 extraction,
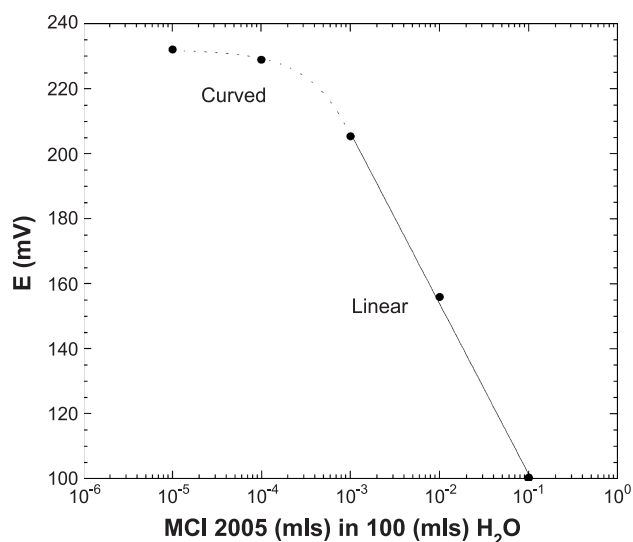

Fig. 2. Typical calibration curve obtained in this case for MCI2005. Each point was accurate to within or just outside the size of the data point.
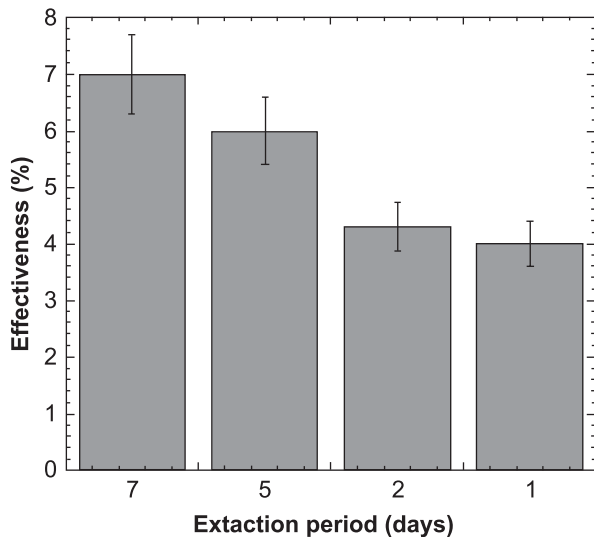
Fig. 3. Change in extraction effectiveness in relation to immersion period for samples prepared with known additions of MCI2005.

effectiveness increases with immersion time. This is to be expected because an equilibrium will be reached between the chemical adsorbed onto the powdered concrete sample, the inhibitor in the pores and the testing solution. This equilibrium will be affected by the solubility product of the amine in the solution tested. The cloudiness of the solution upon addition of neat inhibitor to a high-pH environment suggests that at least some components of MCI2005 are not highly soluble and this is likely to affect the extraction rate.

3.2. Long-term effectiveness of MCI2005

The concentration profiles after 7-day extractions for all the MCI2005-treated samples are presented in Fig. 4. The concentrations through the bulk of the samples are all relatively similar. Considerably higher concentrations were detected in the 0- to 1-cm sections of the SA and SA + EM
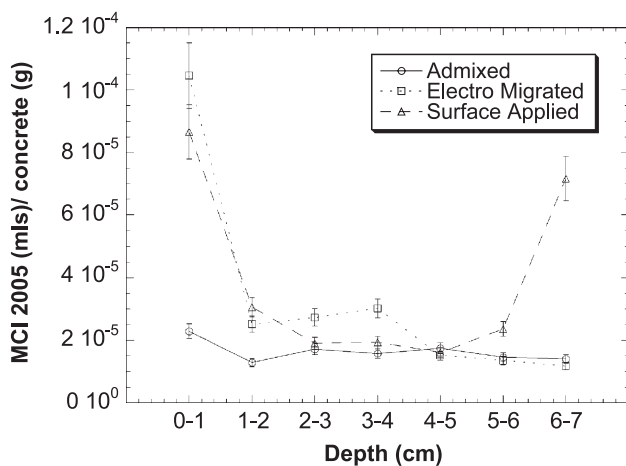

Fig. 4. Concentration profiles for three reinforced concrete samples (w/c 0.6) that have undergone various treatments of MCI2005 including SA, AD and SA + EM.

samples; interestingly, the 6- to 7-cm section of the SA sample also contained a much larger concentration than the bulk. The higher concentration in the 0- to 1-cm sections of the surface-treated samples can be related to the initial application of inhibitor; however, the concentration of the 6–7 cm in the SA sample is not as easily understood. In all cases, in the 3- to 4-cm region surrounding the rebar, inhibitor concentrations between 2×10^{-5} and 3×10^{-5} MCI (ml)/concrete (g) were detected with the highest levels being measured for samples which underwent a combined surface application and electromigration treatment (SA + EM). It is interesting to note that the concentrations of inhibitor achieved with the surface-applied treatments coincides with that remaining in the admixed samples, indicating that at least internally, all the samples have reached the same equilibrium inhibitor concentration for the given environment. The true concentrations are of course likely to be at least 10 times the values reported here given the extraction efficiency noted above. On the other hand, this level of inhibitor detection may also reflect that either (i) some inhibitor has volatilised during the extraction/measurement procedure or (ii) some inhibitor is bound in the concrete and is not readily extractable, and (iii) only a small fraction of the inhibitor is in fact a volatile amine and hence, the remaining inhibitor cannot be detected. The slightly higher inhibitor concentrations detected for SA + EM may be a result of the high electric current driving the positively charged quaternary amine towards the rebar.

Continuous LPR monitoring of the samples over 300 days was used to determine R_p values of the samples. Although R_p is often used to calculate the corrosion rate via the Stern–Geary equation, this involves several assumptions and hence, quantification is ambiguous. Therefore, the data are presented as the %Inhibition achieved by the various treatment regimes as compared to a control in Table 1. E_{corr} values are also presented here for the three specimen types. After 1 year of exposure and remediation, the SA + EM sample is still showing a less negative potential with respect to the control and other treated samples. The R_p value of this sample is also the highest. It is possible that these readings are still somewhat influenced by depolarisation behaviour, although this is less likely given the 12-month 'off' period. It is likely that an anodic component is present which is itself positively charged and hence rapidly finds its way to the steel rebar upon application of a large cathodic current. An anodic inhibition mechanism would shift the rest potential to more positive values [21].

In the case of the admixed treatment, inhibition was observed from the outset [19]. The SA sample, however, did not show equivalent inhibition until 100 days posttreatment, suggesting that this amount of time is required for inhibitor concentration at the rebar to reach protection levels.

Following the 300-day period of LPR monitoring, these samples were exposed to a laboratory environment for 4 years without further interference before being investigated

Table 1
Electrochemical data obtained for various MCI2005-treated reinforced concrete samples, at 1 and 4 years postcasting

Sample	1 year			4 years		
	E_{corr} (mV) vs. SCE	R_p (kΩ cm^2)	%Inhibition	E_{corr} (mV) vs. SCE	R_p (kΩ cm^2)	%Inhibition
AD	− 433	28.9	50	− 609	4.8	50
SA	− 485	26.7	47	− 487	13.7	83
SA + EM	− 227	32.6	55	− 431	15.1	84
Control	− 488	14.2	NA	− 545	2.4	NA

further via profiling and visual inspection of the reinforcement. This allowed the correlation of the original LPR results to inhibitor concentration and inhibitor longevity in the concrete specimens. Table 1 indicates that the AD sample maintains its inhibition at about 50% although the potential is now quite negative. It is possible that a slower cathodic component (i.e., the cathodic inhibition mechanism will result in a reduction of the rest potential [21]) has diffused over this longer period and so the potentials climb to more negative values as the oxygen reduction reaction is progressively suppressed. The specimens treated with surface-applied 2005, or SA and EM, show a significant improvement relative to the control (although the absolute values are almost half those observed after 300 days).

The visual inspection of the rebar was also a more direct affirmation of the inhibitor's effectiveness under these conditions. Fig. 5 presents the images recorded of rebar sections taken from each sample, the 'top' and 'bottom' labels refer to the orientation of the rebar relative to Fig. 1. The control sample shows severe corrosion covering the whole rebar segment including large pits of millimetre scale. When this segment was broken out of the concrete large fragments of the oxide also came away revealing a significant loss in section. In contrast, all the other samples show little to no evidence of corrosion on the top side of the rebar. The SA rebar segment broke free of the concrete easily and there was no evidence of staining or pitting on the top side. In the case of the AD sample, a little concrete did remain attached and there was some red oxide buildup on the top. The SA + EM showed signs of rust staining, but this was difficult to truly quantify due to the amount of attached concrete remaining on the SA + EM sample. The bottom side of the samples all showed considerably more evidence of corrosion with millimetre scale pitting. The difference between the two sides of the rebar is attributed to the exposure to addition chlorides during the electrochemical testing from the bottom of the sample. Overall, it is difficult to distinctly quantify the differences in the amount of inhibition achieved in the three samples; however, all three performed markedly better than the control. These results confirm that corrosion inhibition can be achieved by MCI2005 applied in poor-quality, chloride-polluted concrete. Additionally, the required concentrations of MCI2005 to allow inhibition, although relatively low, can still be confidently measured using the procedure described above.

In comparing the visual inspection results with LPR, we see that a correlation is not obvious. The SA + EM sample, which LPR suggested was the better performing treatment, does not show considerably improved corrosion mitigation visually. This apparent inconsistency may be due to difficulties in using LPR to monitor reinforced concrete corrosion. It has previously been shown that the value of B (proportionality factor from the Stern–Geary equation) will vary depending on the state of the reinforcement [22]. LPR is also been shown to be influenced by mass transport issues [23]. Nevertheless, it is important to note that all the treatments
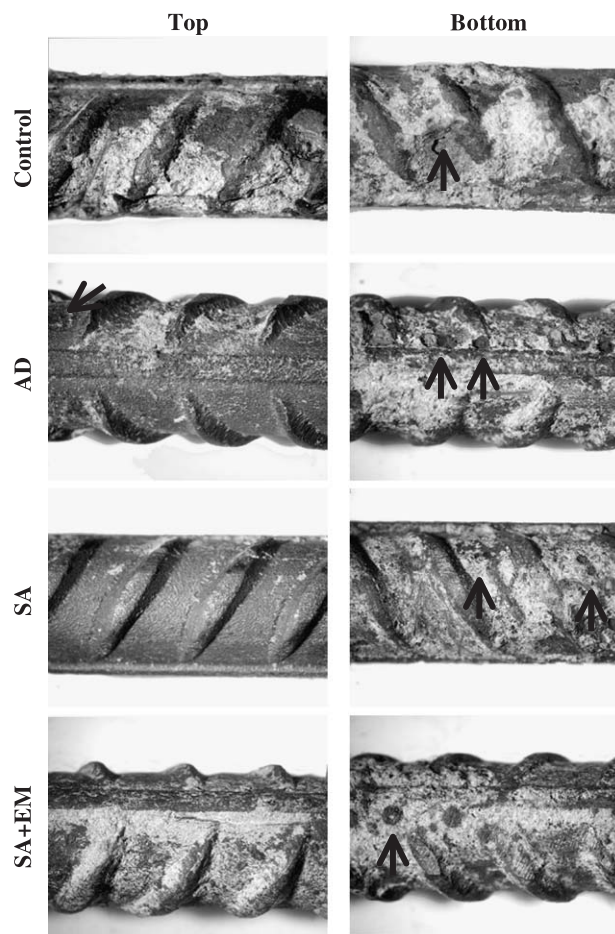

Fig. 5. Visual inspection images of the surfaces of rebar segments taken from three reinforced concrete samples (w/c 0.6) that have undergone MCI2005 treatments as presented in Fig. 4. The arrows indicate examples of pits.

have resulted in significantly reduced corrosion of the steel reinforcement despite the low levels of inhibitor measured.

4. Conclusions

The process described for extracting and measuring the concentration of amine-based MCIs in concrete has been shown to be an informative approach for monitoring the diffusion of the amine component. The extraction method is time dependent and yields a maximum effectiveness of less than 10% for an immersion period of 7 days in contrast to the 40% effectiveness achieved for a related inhibitor MCI2020 [18] previously reported by us.

Concentration profiles, taken from samples 5 years after being treated with MCI2005, revealed that the inhibitor was still present in the concrete. Repeated surface applications of MCI2005 over a period of 1 year yielded concentrations similar to those achieved by admixing, while the combination of a single-surface application and electromigration resulted in slightly higher concentrations through the bulk of the sample. Visual inspection of rebar segments taken from these samples confirmed the effectiveness of MCI2005 for mitigation of chloride-induced corrosion. The inhibitor concentrations measured at the level of the rebar necessary to achieve this inhibition were in the order of $2-3 \times 10^{-5}$ MCI2005 (ml)/concrete (g), noting the effectiveness of the amine extraction technique the actual concentration at the rebar are approximately 10 times greater than those detected.

Acknowledgements

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