

SPECIMEN MONITORING PROJECT

ASSESSMENT OF “CAST-IN” CORROSION INHIBITORS IN PREVENTING/SUPPRESSING REINFORCEMENT CORROSION

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1 INTRODUCTION

A laboratory investigation has been undertaken to assess the effectiveness of "cast-in" corrosion inhibitors in preventing the onset of corrosion. Two types of inhibitor were investigated:

- calcium nitrite (Inhibitor A); and
- amino alcohol (Inhibitor B).

They were cast into reinforced concrete specimens with water/cement ratios of 0.50 and 0.65. For comparison, control slabs without inhibitors were also cast.

Table 1 gives details of the number of specimens cast.

Table 1: Number of specimens cast for corrosion inhibitor trials

Water / cement ratio	Corrosion Inhibitor		Control specimens
	Inhibitor A	Inhibitor B	
0.50	2	2	2
0.65	2	2	2

All the slabs were ponded fortnightly with 5% sodium chloride solution and the corrosion activity monitored using electrochemical techniques.

Chloride profiles were obtained from one of each pair of specimens and one of the controls in September 2001. These specimens were subsequently broken up and the reinforcing bars examined. It was found that no protection was being given by either of the inhibitors to concrete with a water/cement ratio of 0.65 and the monitoring of these specimens was stopped in 2001.

Electrochemical monitoring of the remaining three specimens (i.e. water / cement ratio 0.5) continued until January 2006 and ponding continued until September 2009. Further chloride profiles were obtained in October 2010 and the reinforcing bars were removed and examined.

This report gives the results of the electrochemical monitoring and the chloride profile measurements and describes the condition of the reinforcement in the remaining three specimens after they were broken up in October 2010.

2 EXPERIMENTAL DETAILS OF “CAST-IN” INHIBITOR SPECIMENS

2.1 Introduction

The design of the specimens is shown in Figure 1. The corrosion inhibitors were added to the mix at the dose recommended by the manufacturer to provide protection at a chloride concentration of 2% by weight of cement.

2.2 Ponding and electrochemical monitoring

Ponding started in November 1997 (after the specimens had fully cured) and was repeated every fourteen days with 500ml of 5% sodium chloride solution. This regime resulted in the specimens being wet for 3-4 days on average and dry for 10-11 days during each cycle.

The corrosion activity of the reinforcing bars was monitored periodically during ponding. The outer pairs of bars (T1 and B1, and T4 and B3) were electrically connected together so that galvanic currents flowed between the bottom stainless steel bars and the top reinforcing bars (Figure 1). The galvanic currents between each of these pairs of bars were monitored periodically using a zero resistance ammeter (ZRA). The electrode potential of each pair of outer bars and the inner top reinforcing bars (T2 and T3) were measured relative to an embedded silver/silver chloride (Ag/AgCl) reference electrode.

Linear polarisation resistance (LPR) measurements were carried out on bars T2 and T3. Two devices were used: the ACM field machine and a portable device. The ACM field machine used a continuous ramp of 20mV whereas the portable device applied a positive 20mV step.

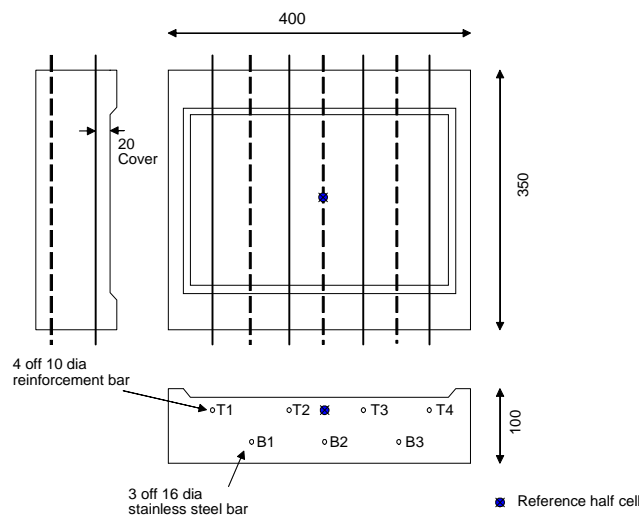


Figure 1: Design of test specimen

The electrochemical monitoring described above was carried out periodically until January 2006.

2.3 Determination of Chloride Profiles

Chloride profiles were determined from 50mm diameter cores. One core was removed from each specimen from an area between the top reinforcing bars T1 and T2, along the centre line of the specimen. The cores extended down to the top surface of the bottom stainless steel bar B1 and were approximately 80mm in length. Each core was profile ground to produce four slices: 0-5mm, 5-15mm, 15-25mm and 25-35mm. The chloride concentrations of each slice were measured using automatic potentiometric titration and the results expressed as the percentage chloride ion by mass of sample.

2.4 Destructive Examination

In October 2010, the samples were broken up and the reinforcing bars extracted for visual examination.

Before being broken up, the ponded area of each specimen was photographed to record any rust staining and cracking on the surface. The photographs were compared with similar photographs taken in December 2004 and January 2006.

The specimens were then cut into slices by sawing them transversely approximately 20mm each side of each of the top (T1-4) high yield bars. It was then relatively easy to remove each of these bars for examination.

The bars from each specimen were photographed to record any corrosion along their length. The severity of the corrosion was assessed visually and assigned to the following groups:

- 0: no loss in section
- 1: some pitting or loss in section
- 2: significant loss in section such as loss of ribbing
- 3: extensive loss in section extending into the main body of the bar

The results were compared with those from the destructive examination in 2001.

3 RESULTS

3.1 Electrochemical monitoring

The criteria for classifying the half-cell potential and LPR corrosion current measurements are given in Table 2.

The results from each specimen are shown in Figures 2-4, respectively. The top graphs show the variation of galvanic current and half-cell potential (HCP) with time for each pair of outside bars (left and right). The bottom graphs show the variation of corrosion current (as measured using the ACM field and portable linear polarisation resistance devices) and half-cell potential of the inner bars (T2 and T3) with time.

Table 2: Classification of half-cell potential and LPR corrosion currents

Half cell potential	
Silver/silver chloride reference electrode	Classification
Potential range (mV)	
> -100	< 10% probability of corrosion
-100 to -250	Probability of corrosion is uncertain
< -250	> 90% probability of corrosion
LPR Corrosion Currents	
Corrosion current ($\mu\text{A}/\text{cm}^2$)	Corrosion rate category
< 0.1 to 0.2	Passive
0.2 to 0.5	Low to moderate
0.5 to 1.0	Moderate to high
> 1.0	High

For specimens containing inhibitors, the galvanic currents measured between the outer pairs of bars were close to zero for the duration of the monitoring, indicating passivity. The half cell potentials indicated that the probability of corrosion was uncertain. By contrast, the galvanic currents in the control specimen which were zero prior to the start of ponding, increased to significant levels after about 20 weeks. On the last two occasions that the specimens were monitored, the measured galvanic currents in the outer pairs of bars in the control specimen had increased significantly. This corresponded with a reduction in half-cell potential.

The corrosion currents measured on the inner bars of the specimens including inhibitors using both the linear polarisation devices were between 0.1 and 0.2 $\mu\text{A}/\text{cm}^2$ which also indicated that the reinforcement was in the passive state. This compared with values mostly between about 0.8 and 1.0 $\mu\text{A}/\text{cm}^2$ for the control specimens suggesting moderate to high corrosion rates. The specimens including inhibitors exhibited half-cell potential values generally between -200mV and -300mV compared with values of between -400 and -600mV for the control specimen.

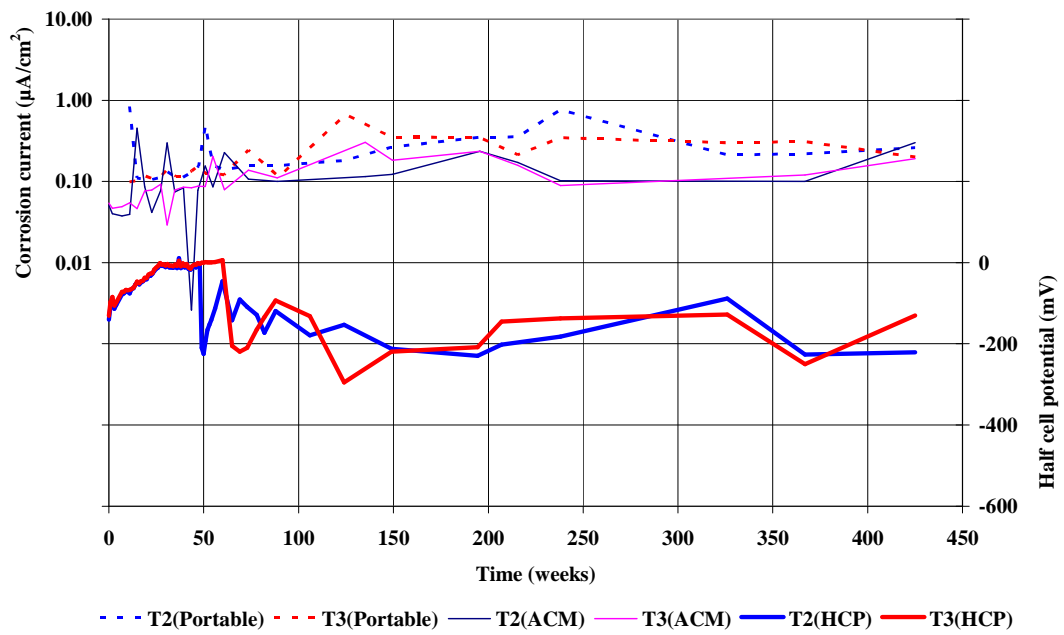
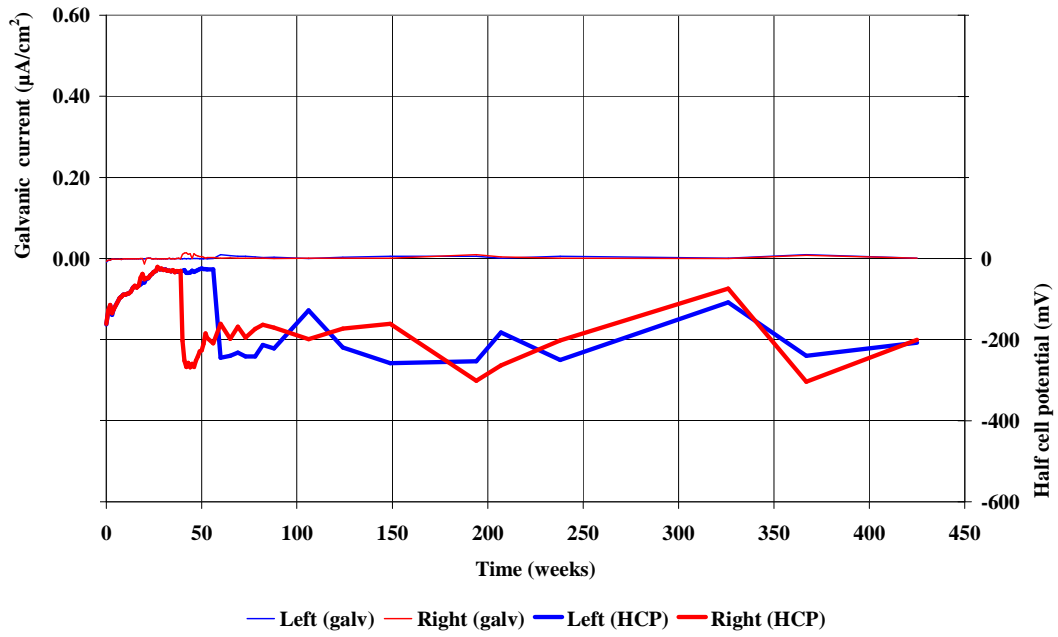


Figure 2: Results of electrochemical monitoring of specimen containing Inhibitor A

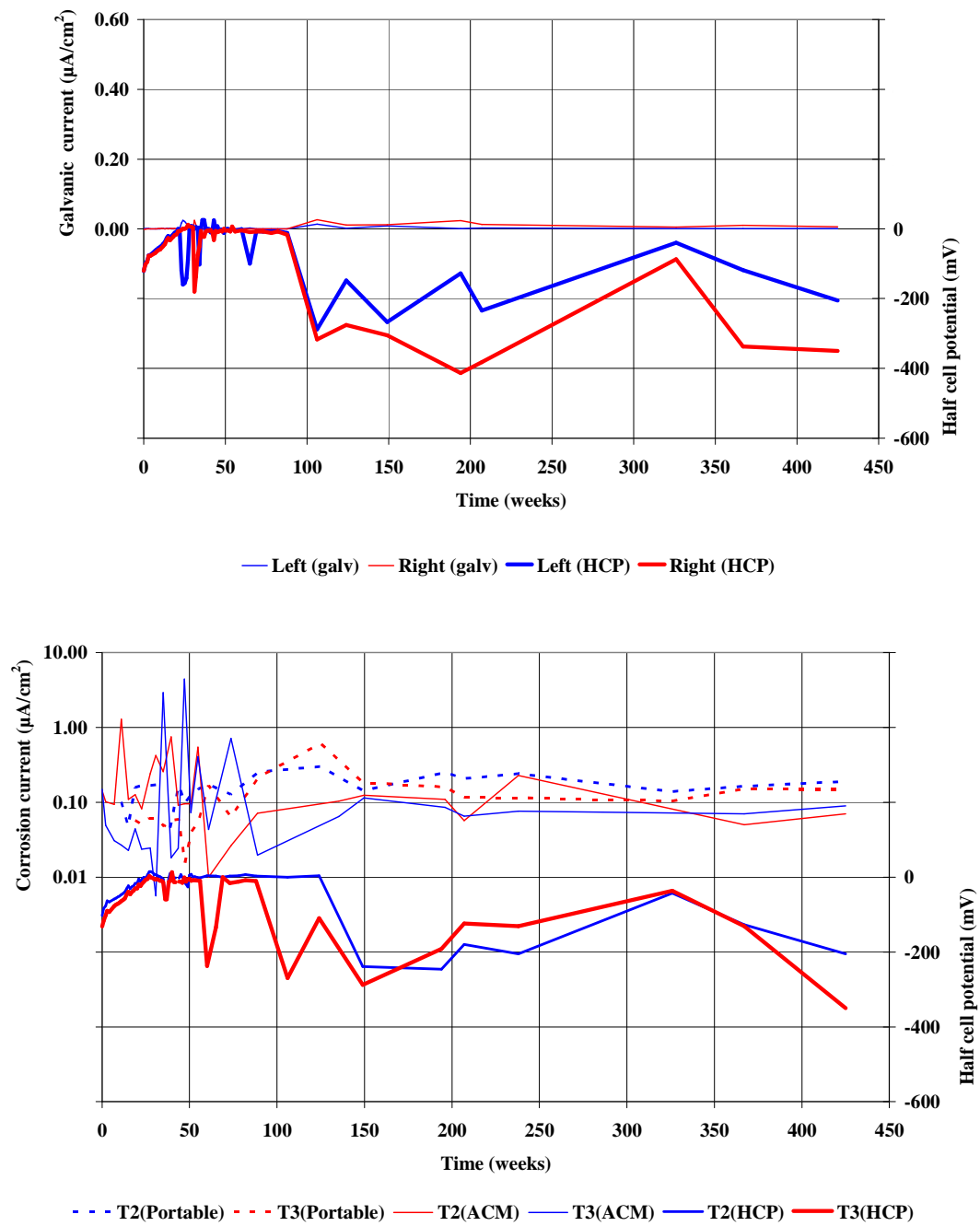


Figure 3: Results of electrochemical monitoring of specimen containing Inhibitor B

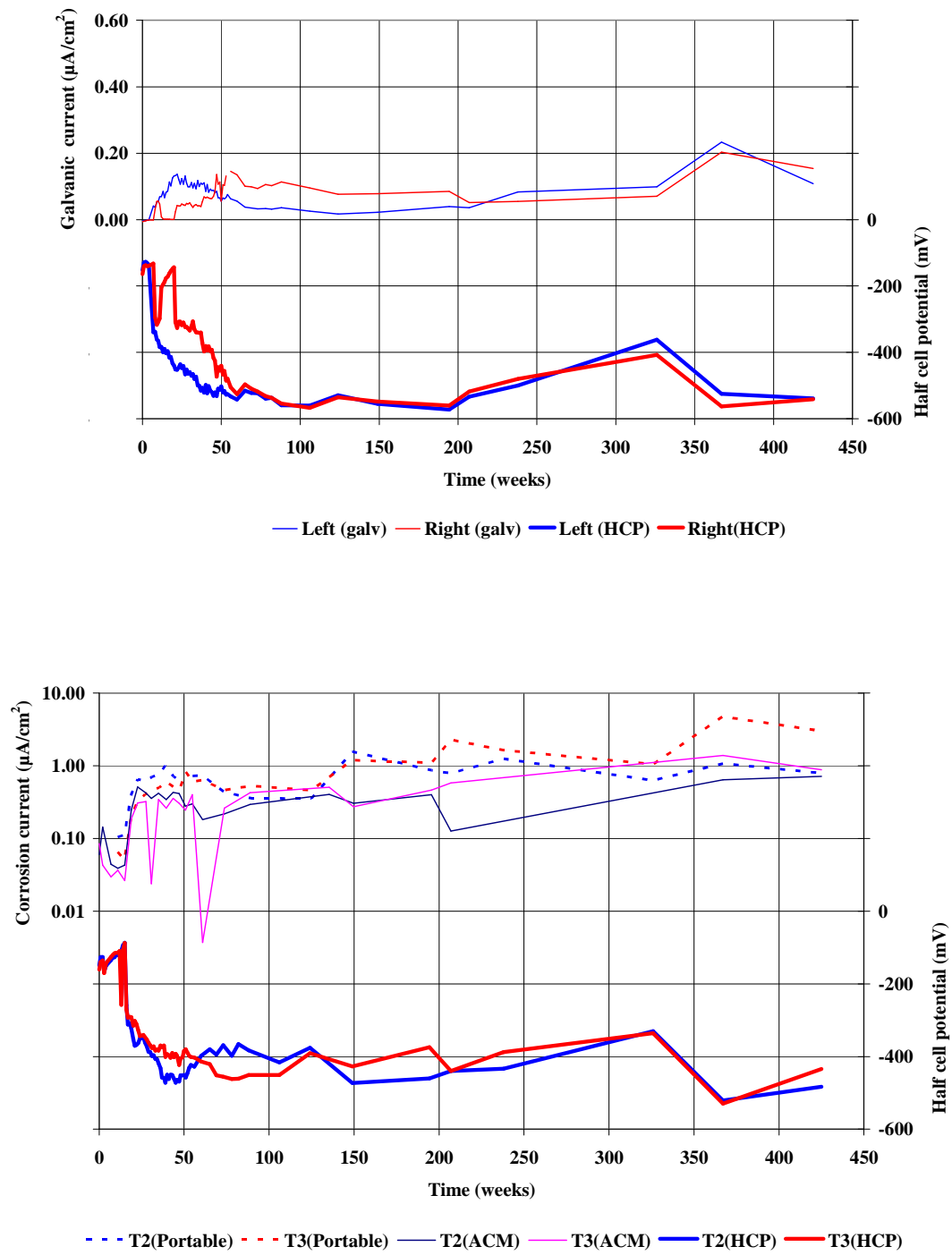


Figure 4: Results of electrochemical monitoring of control specimen

3.2 Photographs of ponded areas

Figures 5 to 7 show the ponded surface of each of the specimens in December 2004, January 2006 and October 2010. The photographs show that, for specimens which contained inhibitors, there was no evidence of corrosion products on the surface or cracking of the concrete. The only indication of deterioration was a small amount of corrosion staining on one small area of the lip of the specimen containing Inhibitor B which was observed in October 2010. This is in marked contrast to the surface of the control specimen. In December 2004, there were cracks which ran along the surface over each of the bars and there was significant corrosion product on the surface of the concrete close to the cracks. The pattern and width of the cracks had not increased significantly in January 2006 and October 2010.

These observations are consistent with the electrochemical measurements which indicated high corrosion rates on the bars in the control specimen while the bars in the specimens containing inhibitors remained passive.



December 2004



January 2006



October 2010

Figure 5: Photographs of ponded area of specimen containing Inhibitor A



December 2004



January 2006



October 2010

Figure 6: Photographs of ponded area of specimen containing Inhibitor B



December 2004



January 2006



October 2010

Figure 7: Photographs of ponded area of control specimen

3.3 Chloride concentration profiles

The chloride profiles for the three specimens measured in 2001 and 2010 (i.e. after about 4 and 12 years of ponding with salt solution) are given in Figure 8. Generally, the 2010 values were higher than those from 2001. In 2001, the chloride concentration reduced as the depth from the surface increased for all the specimens and the values for the specimens containing corrosion inhibitors were similar and lower than for the control specimens. By contrast, the profiles from 2010 did not decrease with increasing depth; the highest values being at a mean sample of depth of 20mm, corresponding to level of the reinforcing bar. This was somewhat surprising, as normally the concentration is highest at the surface reducing with depth. However, higher values away from the surface may have been as result of the surface drying out during the year that the specimens were not ponded before the cores were extracted. The concentrations in the control specimen were higher than in the specimens containing inhibitors.

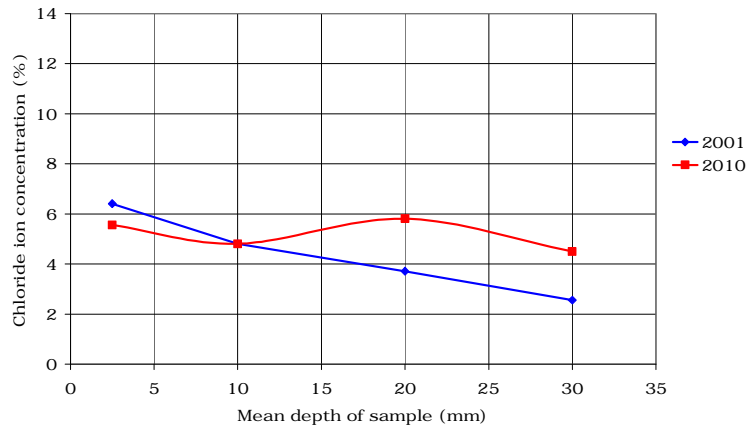
The chloride concentrations (by weight of cement) measured at the level of the reinforcement (i.e. 20mm from the surface) in 2001 and 2010 are given in Table 3. Both the mixes with cast-in inhibitors were designed to provide protection against reinforcement corrosion with up to 2% chloride ion by weight of cement. The chloride ion concentrations measured in 2001 were almost twice the design value and the level in 2010 had increased to nearly three and four times the design value for specimens including both Inhibitor A and Inhibitor B, respectively. The electrochemical monitoring indicated that all the reinforcing bars were in a passive state up until 2006 when the monitoring was terminated. This is a good indication the inclusion of inhibitors had suppressed corrosion activity.

The lower concentrations at the level of the reinforcement for the specimens containing corrosion inhibitors compared with the control specimens suggests that the inhibitors may also have the additional benefit of reducing the rate of ingress of salt solution into concrete.

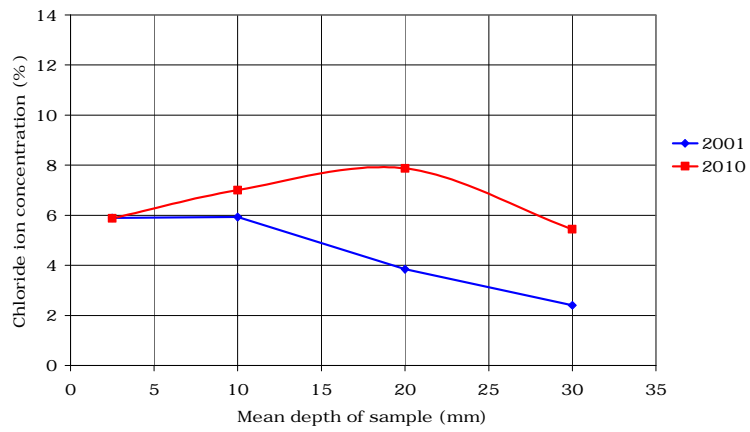
Table 3: Chloride concentration at the level of the reinforcement

Inhibitor	2001	2010
	Chloride ion concentration (by weight of cement) (%)	
Inhibitor A	3.7	5.8
Inhibitor B	3.8	7.9
Control	5.2	11.2

Inhibitor A



Inhibitor B



Control

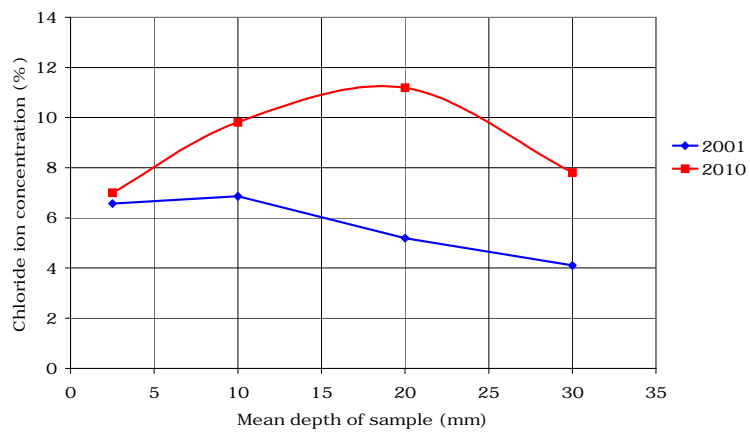


Figure 8: Chloride profiles measured in specimens in 2001 and 2010

3.4 Examination of bars removed from specimens

The extent and severity of the corrosion on the bars removed from the specimens in October 2010 was compared with that of bars removed from the specimens in September 2001 (Table 4). Figure 9 shows the variability in the length of corrosion on individual bars within each specimen.

The bars from specimens containing corrosion inhibitors had corroded lengths of between 15 and 60mm in 2001 compared with 20 to 120mm in 2010. The corroded lengths of the bars from the control specimen varied between 85 and 250mm in 2001, and 190 to 250mm in 2010. For the bars examined in 2001, corrosion was limited to their top surface whereas it extended all around the surface of the bars examined in 2010.

Figures 10-12 show the top surface of the bars removed from the specimens in 2001 and the top and bottom surfaces of the bars removed from the specimens in 2010. There was light surface corrosion on the bars from specimens containing inhibitors, with some loss of section and loss of ribs. Corrosion was more severe on the bars removed from specimens in 2010 than on the bars removed in 2001. The corrosion on the bars from the control specimens was much more severe with extensive loss of section extending into the main body of the bars.

These results show that the extent and severity of the corrosion was significantly less on the bars from specimens with inhibitor than on the bars from the control specimens. There was somewhat more corrosion on the bars from specimens removed in 2010 than those removed in 2001.

The difference between the severity of the corrosion on bars from specimens containing corrosion inhibitors and the control specimens is illustrated in Figures 13-15. These photographs show the most corroded areas on each of the bars from the 2010 specimens. For the bars from specimens containing Inhibitor A and Inhibitor B, the corrosion resulted in some slight loss of section. By contrast, the corrosion on all the bars from the control specimen was much more severe with up to about half of the section lost in the worst case.

These results are consistent with the electrochemical monitoring and chloride profile data and demonstrate that the two cast-in corrosion inhibitors tested provide a very effective method of controlling corrosion in reinforced concrete.

Table 4: Length and severity of corrosion on bars removed from specimens in 2001 and 2010

Bar Number	Length of bar affected (mm)		Severity of corrosion ^a	
	2001	2010	2001	2010
Inhibitor A				
1	60	85	0	2
2	35	30	0	0
3	50	65	1	1
4	40	20	1	1
Mean	43	50		
Inhibitor B				
1	35	20	0	1
2	30	65	0	2
3	15	70	0	2
4	40	120	0	2
Mean	30	69		
Control				
1	85	280	2	3
2	250	280	2	3
3	145	230	2	3
4	160	190	2	3
Mean	160	245		

Note a: See classification in Section 2.4.

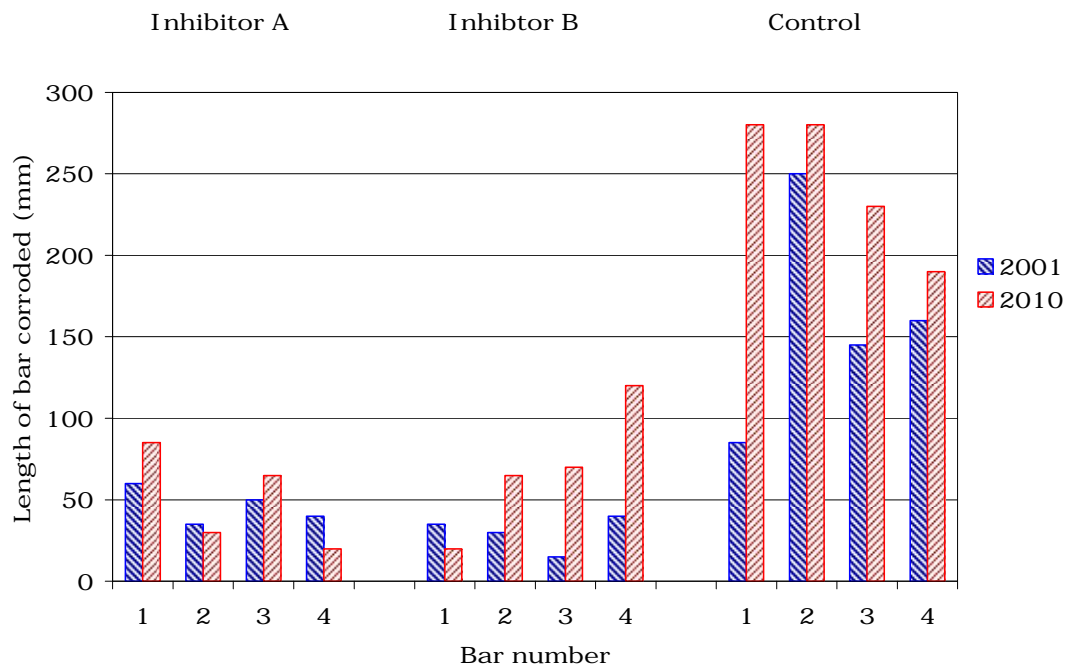


Figure: 9: Length of corrosion on bars removed from specimens

2001 - Top surface



2010 - Top surface



2010 - Bottom surface



Figure 10: Photographs of bars from removed specimens containing Inhibitor A

2001 - Top surface



2010 - Top surface

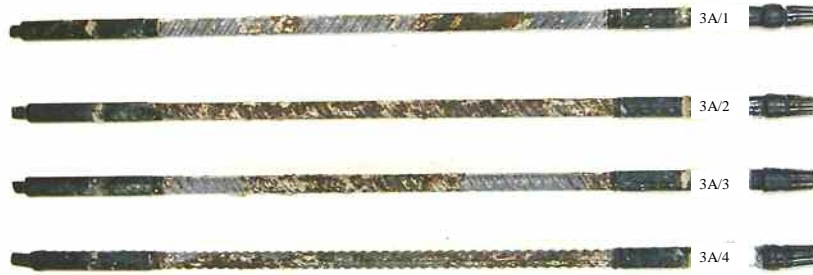


2010 - Bottom surface



Figure 11: Photographs of bars removed from specimens containing Inhibitor B

2001 - Top surface



2010 - Top surface



2010 - Bottom surface



Figure 12: Photographs of bars removed from the control specimens



Figure 13: Close up photograph of bars removed from specimen containing Inhibitor A



Figure 14: Close up photograph of bars removed from specimen containing Inhibitor B



Figure 15: Close up photograph of bars removed from the control specimen

4 CONCLUSIONS

The results have confirmed that “cast-in” corrosion inhibitors are an effective method for controlling chloride induced corrosion in reinforced concrete. The main conclusions are summarised below:

- The corrosion rates in the specimens containing “cast-in” inhibitors, as measured by electrochemical monitoring, remained low during the nine years up to 2006 that the corrosion activity was monitored. By contrast, the corrosion rates in the control specimen were moderate to high.
- After 12 years of ponding, the chloride ion concentration at the level of the reinforcement in the specimens containing Inhibitor A and Inhibitor B were 5.8% and 7.9% by weight of cement, respectively. The chloride ion concentration at the level of the reinforcement in the control specimens was 11.2%. Thus the inhibitors may have provided an added benefit of reducing the rate of ingress of salt solution into concrete.
- There was significantly less corrosion on the bars removed from specimens containing inhibitors than on the bars removed from the control specimens.
- The chloride ion concentrations at the level of the reinforcement in the specimens containing inhibitors were significantly greater than the 2% by weight of cement for which the inhibitors were designed.