CORROSION INHIBITORS IN CONCRETE - AMA (ALKANOLAMINES) -BASED INHIBITORS - STATE OF ART REPORT

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ABSTRACT

Corrosion inhibitors based on alkanolamines show a promising effect on protecting steel in concrete from corrosion. Based on successful results from the United States an extensive test program was started by SIKA in 1993 with objective to basically investigate and understand the effect of alkanolamine based inhibitors for both carbonation- and chloride induced corrosion. Tests are running in own laboratories and also at Universities and Research institutes and supervised by experts with a long experience in the electrochemistry processes involved in the corrosion process. The test results are very promising showing that alkanolamine based inhibitors have a reducing effect on the corrosion initiation process, and do not seem to have any negative effects on neither fresh/hardened concrete properties nor environment.

1. INTRODUCTION

Steel corrosion in concrete structures is an electrochemical phenomena that consists of two partial reactions: On the anode, the metal is broken down to ions ($Fe \rightarrow Fe^{2+} + 2e^-$) and these react further with the hydroxyl ions ($Fe^{2+} + 2OH \rightarrow Fe(OH)_2$). The electrons released at the anode have to be adsorbed to the cathode due to electroneutrality. The corresponding cathodic reaction is oxygen reduction ($1/2\ O_2 + H_2O + 2e^- \rightarrow 2OH$).

The model shown in Figure 1 illustrates the steel corrosion sequence in concrete /1/

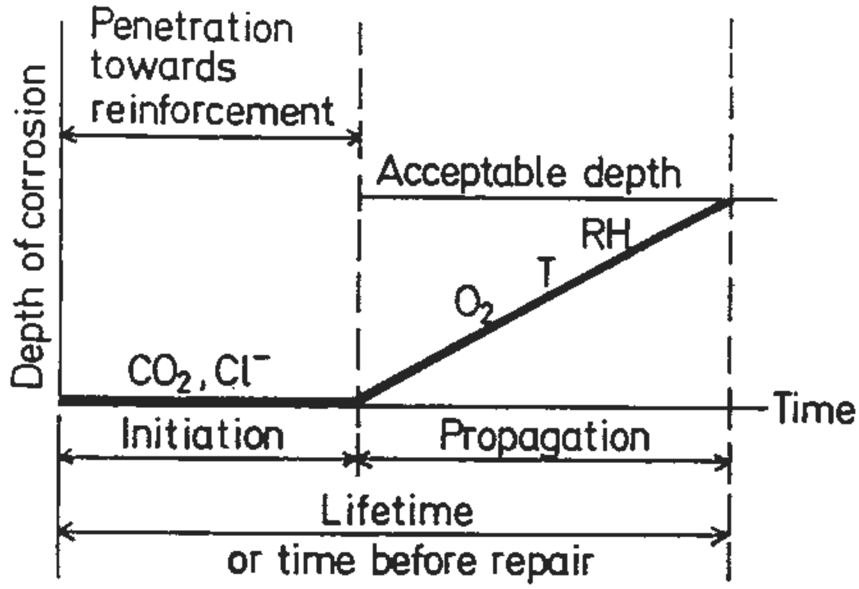

Figure 1. Illustration of steel corrosion in concrete /1/

The two main causes of corrosion are carbonation of concrete and chlorides in the concrete. The aim of this report is not to discuss neither the corrosion mechanisms nor causes, but to concentrate on corrosion inhibitors, mainly alkanolamine (AMA)-based inhibitors that show a promising effect according to the recent research work.

Corrosion inhibitors have been successfully used for several years in the United States. This report enlightens the later development mainly in Europe and contains results from some Nordic tests. The following figure 2 shows the intended function of the corrosion inhibitors.

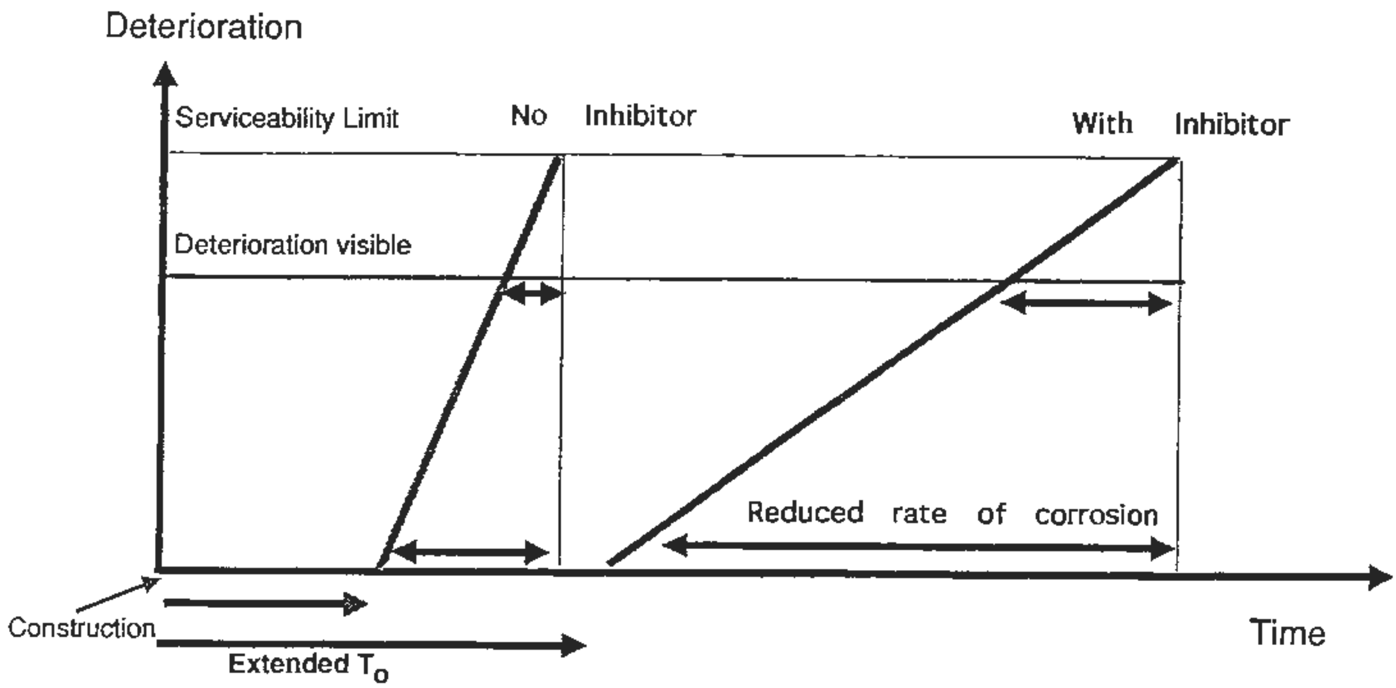

Figure 2. Extention of the service life of a concrete structure with corrosion inhibitor /5/

The types of corrosion inhibitors used in concrete can be classified into three different groups: Anodic, cathodic and mixed, depending on their type of interference with the corrosion process. Anodic inhibitors accept electrons. The reaction takes place on the anode. The cathodic inhibitors increase the pH of the of the medium and thereby decrease the solubility of ferrous ion.

Mixed inhibitors contain molecules in which electron density distribution causes the inhibitor to be attracted to both anodic and cathodic sites /2/.

There exist several classification models. One of them divides the corrosion inhibitors in two categories: Adsorptive and film forming. Most of the inhibitors have a double effect.

The main application methods for corrosion inhibitors are:

- added to fresh concrete as an admixture
- applied on the hardened concrete surface, so called penetrating corrosion inhibitor.

The inhibitors can also be added to repair mortars or used as a surface treatment on the reinforcement bars before concreting.

The most widely used anodic corrosion inhibitor has been calcium nitrite. (Also sodium nitrite, sodium benzoate and sodium chromate have been used). The nitrite ions in this inhibitor are thought to compete with the chloride ions for the ferrous ions at the anode. The reaction forms a stable passive layer on the reinforcement steel. The main drawback of anodic inhibitors can be severe pitting when insufficient quantity of inhibitor is used compared to the level of chloride in the concrete /2/.

The main cathodic inhibitors used are based on sodium hydroxide and sodium carbonate that increase the pH of the medium. These inhibitors reduce the oxygen transport to the steel surface. The inhibiting chemical mechanism can be complex depending on the type of inhibitor.

AMA-based inhibitors are typically dual effect inhibitors (or mixed inhibitors): They give both cathodic and anodic protection. They are film forming and can be classified as adsorptive. The following results are based on AMA: DMEA (dimethylethanolamine) and EA (ethanolamine) or mixed Ferrogard® (AMA-based with other organic and inorganic inhibitors).

2. TESTING OF THE CORROSION INHIBITORS

2.1 General

Testing and documentation of the effect of the inhibitors and their ability to extend the life time of a reinforced concrete construction is a difficult task. The field testing can take a life time!

The testing of AMA-based inhibitors was done in following six different phases:

1. Testing of the effects on the fresh and hardened concrete properties
2. Testing of AMA-inhibitor in different solutions and on reinforcement
3. Testing in mortars
4. Testing in concrete, simulations in laboratories
5. Field tests

2.2 Testing of the effects on the fresh and hardened concrete properties

First of all the corrosion inhibitor should not have any negative effects on neither fresh nor hardened concrete properties. This was the reason for SIKA-internal testing of the AMA based inhibitor with all European cement types. These tests were conducted in 1994 in 9 European countries and included 14 type I and 2 type V cements together with 20 different HRWR (High Range Water Reducing) and WR (Water Reducing) from the different producers in respective countries. Some of the tests include combinations with air entrainers, inhibitor and HRWA as well as freeze-thaw resistance testing. These tests indicate no significant effect on concrete properties.

2.3 Anticorrosive effect, electrochemical measurements in solutions

The electrochemical measurements were carried out at ICCET (Instituto de Ciencaias de la Construccion, Eduardo Torroja) in Madrid /3/ and Sika Chemie, Stuttgard by Dr. Vogelsang /4/.
ICCET tests were done by galvanostatic-, galvanodynamic polarisation and polarisation methods.

The test results show that AMA-inhibitor is an effective inhibitor in neutral and alkaline solution. The increased concentration correlates with an increased effect. This indicates a thicker film formation. The protective film is effective when it is built up. It was uncertain if the film formation takes place when the chlorides are present in the solution at the beginning /3/. Further work has shown that the film is formed even at high chloride levels /6/.

The non treated specimens show corrosion, and the specimens with 3% neutralised AMA-inhibitor were intact. The concentration of used chloride solution was 1.6 NaCl (1 % Cl^- on mass of cement).

The electrochemical changes at the steel reinforcement were monitored to evaluate the effectiveness of the inhibitor. Extensive electrochemical testing was carried out using potentiodynamic polarisation techniques in solutions of varying pH with different levels of chloride contamination. The results showed that inhibitor prolonged the start of the corrosion and reduced the rate of corrosion after initiation. See figure 3.

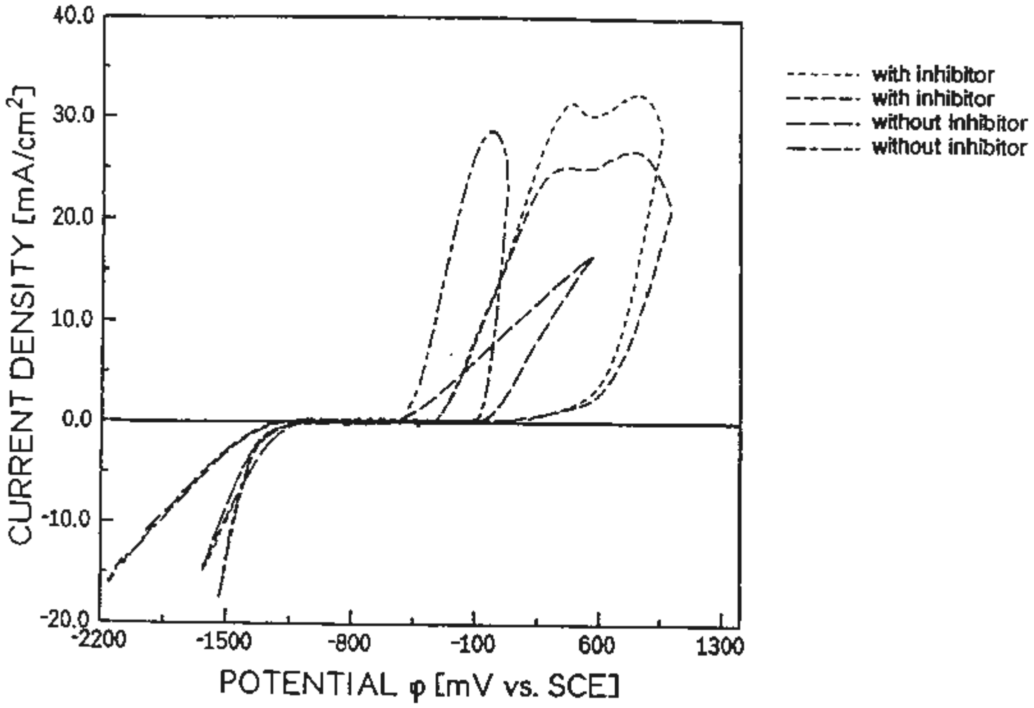

Figure 3. Potentiodynamic polarisation of mild steel /4/

2.4 Adsorption of aminoalcohols on steel and the protective film formation on the steel surface

These tests were carried out by Prof. Grunze, Angewandte Physikalishe Chemie, Uni Heidelberg in Germany /5/ and C.R. Brundle and Ass., San Jose, CA /6/ using X-ray photoelectron spectroscopy and the contact angel measurements.
The results show that AMA-inhibitors can adsorb on the mild steel in a layer of about 20 Å. This may indicate a replacement of hydroxides, chloride and other ions on the steel surface by AMA. According to these results, it seems to be impossible to remove the protective film layer by water rinsing./5/

Mixed inhibitors seem to adsorb in thicker layers i.e. about 100 Å . This may suggest that the high concentration of AMA leads to multilayers. The adsorption time needed was less than one hour /6/.

The results indicate a high affinity of AMA-inhibitor on the steel surface as a displacement of chlorides and a formation of a protective film /5/. On the other hand the results indicate that ionic species as well as carbon residues can be displaced on the mild steel /6/. The contact angle measurements show increased hydrophilic behaviour of the surface with AMA-layer when the steel was exposed to AMA-solution.

Results from the studies containing 50 mmol AMA and NaCl indicate that aminoalcohols can displace chloride ions from mild steel in chloride solutions. Also in concrete specimens AMA-layers seem to withstand water, while Na- and Cl-ions are washed off /6/.

2.5 Cracked Beam Corrosion Tests (adapted ASTM G 109)

The cracked beam corrosion tests show that the specimens containing different corrosion inhibitors perform better than the reference concrete, see table 1 and figure 4.

The investigation of the anodic steel removed from the concrete resulted in following observations:

- The pitting in reference specimens was larger and slightly deeper than the beams with corrosion inhibitor.
- The correlation between the visual examination of the reinforcement and the electrochemical measurements (integral corrosion currents) of the individual beams and the cracked beam, was good, at the end of the testing period.

Table 1. Cracked beam corrosion test results /7/

		Cracked concrete beam corrsion test: Average integral corrosion current (3 specs) after 15 ponding cycles (399 days)	
Admixture	Dosage of cement (%)	Average integral corrosion current (mA x days	Relative average integral corrosion current, based on control (%)
reference concrete	0.00	21378	100
neutralized AMA inhibitor	2.00	9418	44
neutralized AMA inhibitor	3.00	8026	38
neutralized AMA inhibitor	4.00	7796	36
calcium nitrite inhibitor	4.00	10544	49

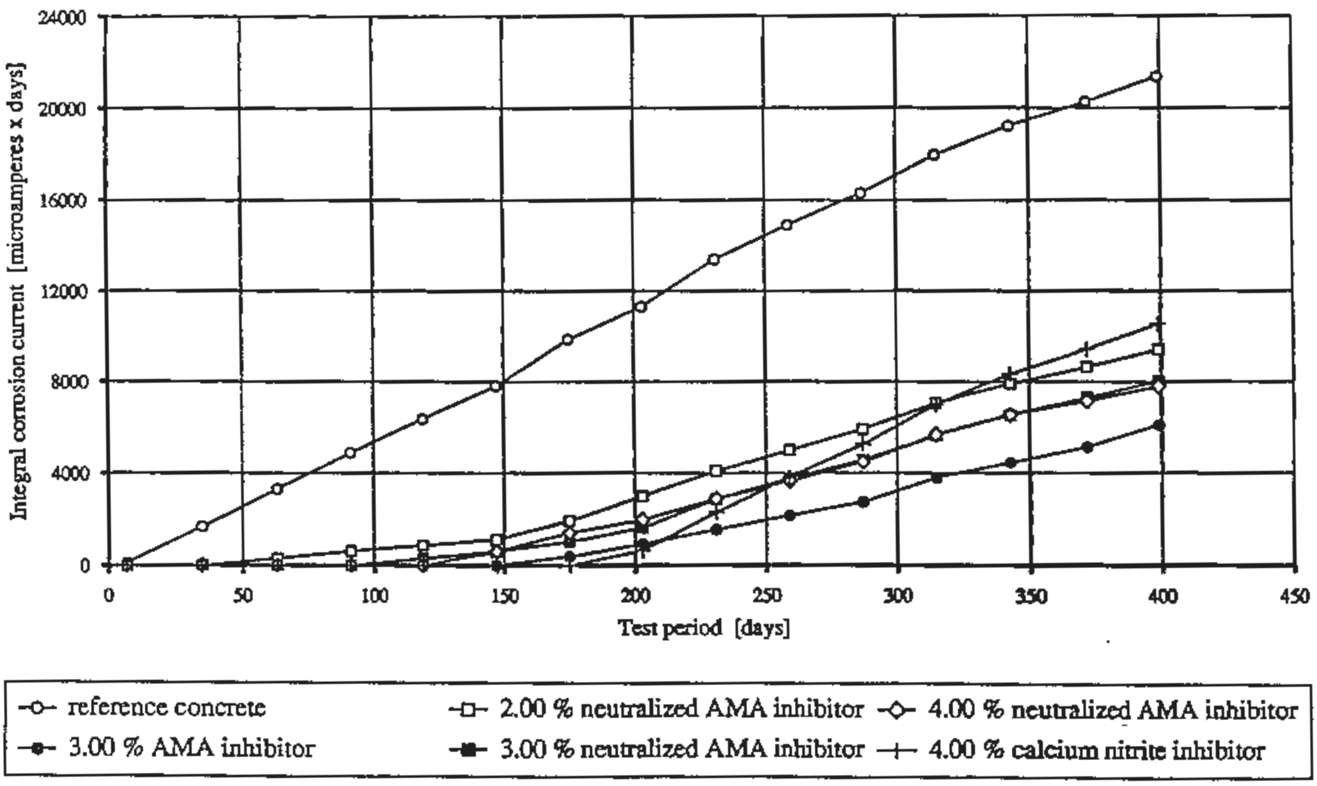

Figure 4. Integral corrosion currents /7/

2.6 Penetration tests of migrating AMA-inhibitors

Theoretically this enables AMA-based inhibitors to diffuse a considerable distance in concrete.

Figure 5 shows the capacity of AMA to penetrate into concrete. The test was conducted by Karlsruhe Research Centre, Institute of Radiochemistry using secondary neutron particle mass spectrometry (SNMS). The ratio of N/Si and C/Si was analysed as a function of concentration of AMA. These result are valid for AMA's and neutrialised AMA's.

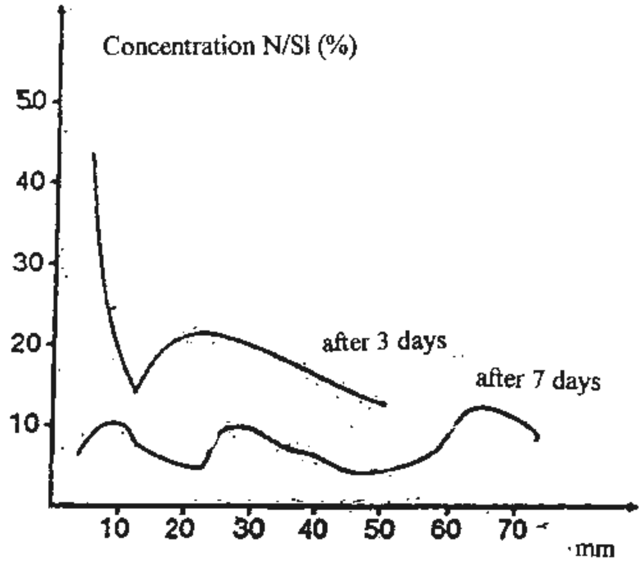

Figure 5. Transport studies of inhibitor in concrete blocks (application face at top)

The penetration rate occurs to be about 2 - 20 mm per day. The transport rate was found not to be depending on neither the humidity level nor transport direction. The transport distance of 70 mm was detected (maximum testing distance).

The penetration results may also indicate a possible «disappearance» of the inhibitor: The inhibitor penetrates out from the concrete. The use of a corrosion inhibitor can not exclude the surface treatment (the sealing of the inhibitor in concrete) /5/. Partly therefor, the concrete surface should be treated f.ex. painted to ensure adequite protection.

3. CORROSION TESTS ON AMA-INHIBITORS RUNNING IN CBI[1], SWEDEN

3.1 Test Program

A test program initiated by Sika Sweden, Norway and Denmark has been running since 1994. Cements from all three Nordic countries are included. The program was designed on the basis of different «practise and acceptance criteria» in these Nordic countries. Parallel to the corrosion tests the influence on the other important concrete properties f. ex. frost resistance, has been running in Sika laboratories in Sweden and many other countries in Europe. The corrosion test program at CBI[1] is supervised by Karin Petterson.

The tests are carried out as lab tests on mortar and concrete specimens and field tests in sea water at Träslövsläge at the Swedish west coast. In both cases polarisation resistance

[1] Swedish Cement and Concrete Research Institute

The tests are carried out as lab tests on mortar and concrete specimens and field tests in sea water at Träslövsläge at the Swedish west coast. In both cases polarisation resistance techniques is used to evaluate the effect of the inhibitor on the corrosion process including the process before (initiation) and after (propagation) onset of corrosion. These techniques takes time, but on the other hand it has shown to be «harmless» in the aspect of not disturbing the electrochemical process at the steel surface ant the correlation to gravimetric tests has been found to be very good. The tests are accelerated only by using thin covers (5-7 mm for mortar specimens and 10-15 mm for concrete specimens). Detailed information on the test methods is given by Karin Petterson /9/ and /10/.

In the laboratory tests, concrete and mortar specimens are exposed to chlorides in two different ways: immersed in artificial sea water and sprayed by chloride solution. The corrosion behaviour of concrete and mortar specimens containing 3 % AMA-based inhibitor (Ferrogard 901) are compared to the reference specimens with exactly the same composition, water cement ratio and cover, but without inhibitor. The corrosion rate of the embedded steel bars were measured weekly since the start in August 1994.

3.2 Mortar specimens - laboratory tests

After one year of testing, the first results on salt sprayed specimens could be seen, see table 2. For the specimens with w/c=0,60, corrosion had started and the chloride threshold values are in all cases higher (4-6 % Cl^-/ cement) for specimens containing 3 % Ferrogard 901 compared to references (1-3 % Cl^-/ cement).

Some of the salt sprayed reference mortar specimens, w/c = 0,45 started to corrode at a chloride threshold value 2-3 % Cl^-/ cement. The specimens containing 3% Ferrogard 901 has not yet (after 15 months) started to corrode.

This means that the corrosion inhibitor shows a clear positive effect on increasing the chloride threshold values and delaying the chloride initiated corrosion for mortars exposed to salt spray.

Table 2. Chloride threshold values for salt sprayed mortar specimens after 1 year exposure /11 /

Cement	**w/c**	**Chloride threshold value (% Cl^-/ cement)**	
		Reference	**3% Ferrogard 901**
Std P Degerhamn	0.45	2-3	no corrosion
Aalborg low alkali	0.45	2-3	no corrosion
Std P Degerhamn	0.60	1-1.5	4-6
Aalborg low alkali	0.60	2-3	4-6

The specimens submerged in artificial sea water started to corrode after approximately one year. In this case the difference between references and test specimens containing inhibitor is not clear. The tests are continued to find out more information about this matter.

3.3 Concrete specimens - laboratory tests

The concrete specimens containing Norwegian HS 65 cement, w/c=0.50 are submerged in artificial sea water. After 15 months, all the three reference specimens started to corrode at the same time, see figure 5. When the corrosion was initiated, the specimens were broken up and chloride content was determined, see figure 6. The chloride threshold value was calculated to be 2.4% ± 0.4 % Cl⁻/cement. None of the specimens containing Ferrogard 901 has started to corrode. Based on this we can make the conclusion that Ferrogard has a positive effect even when concrete is submerged in salt water. The continuing test program will tell us more about the magnitude of the parameters and give us further data and figures for comparable life time assesments for concrete containing AMA based inhibitors.

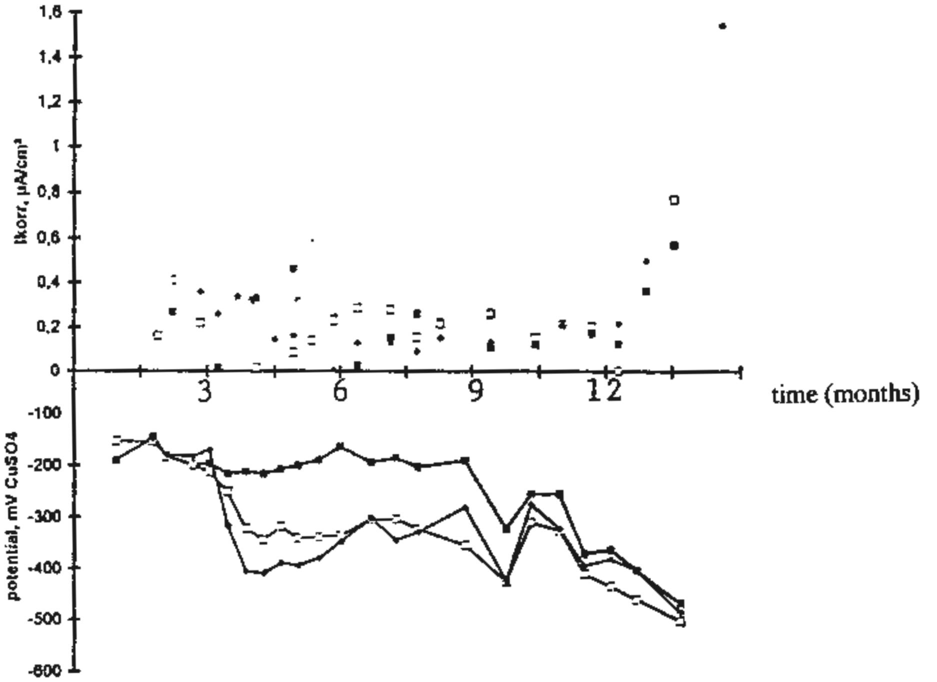

Figure 6.
Corrosion rate and potential for concrete specimens (references) tested in laboratory /11/.

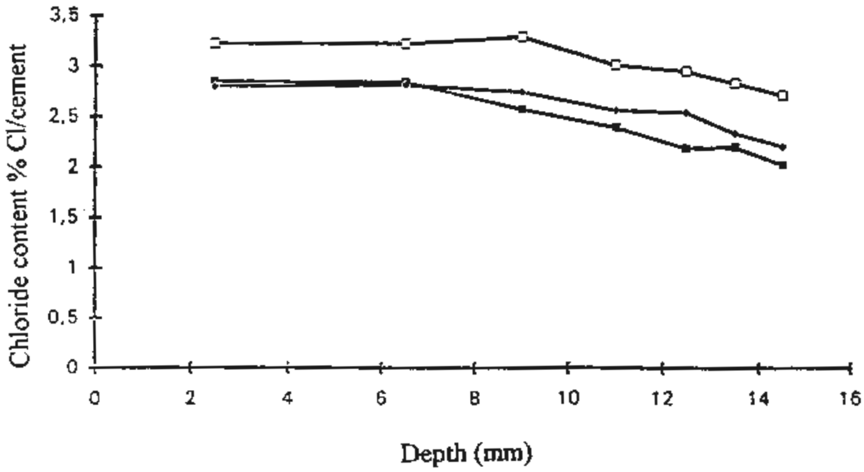

Figure 7. Chloride content in concrete cover /11/.

4. OTHER TEST PROGRAMS

AMA based inhibitor is also included in the Norwegian Road Authorities long term testing program for «Concrete with High Resistence to Chloride Induced Corrosion». This test program includes also some waterproofing admixtures and polymer concretes. The concrete specimens are exposed both for the deicing salts and marine environment (tidal zone) /12/.

The corrosion rate measurements are not yet executed.

5. ENVIRONMENTAL ASPECTS

Alkanolamine is a clear liquid with pH of 10 and a ammonia type of odour. It is not carcinogenic and the oral LD 50 is high 2340 mg/kg rat. It is classified as a moderate sensitiser in the Guinea Pig Sensitisation Test.

The tested inhibitor, Ferrogard 901, is classified as an irritating product in Sweden and Norway as many of the concrete admixtures because of their high alkalinity. The biodegradability rate is relatively good. Based on this, the inhibitor can be described as a environmentally sound product.

6. DISCUSSION

Based on this research work and testing, there are still some open questions to be answered. The following aspects will remain for a construction/building owner to be considered:

- The correlation between the «small scale tests» and the full scale concrete structures can not be established at this stage. The only extended life time estimates are found in the SHRP-report /8/. At the same time the development work and modifications of mixed inhibitors have been carried out, and the achievement of the latest data will take time.

- The leaching properties (« when the inhibitor penetrates out») are not fully known. This means that a possible necessity of surface treatment like impregnation and painting can not be left out by using a corrosion inhibitor. On the other hand there exists no data for need of the application frequency for the surface applied inhibitor.

The further research work will include f. ex. studies of stability of the inhibitor in alkaline solutions, testing of the cores from existing concrete structures and combining the inhibitor with a sealing compound. The results of these studies are expected to be available in 1998/99.

7. CONCLUSIONS

Based on these results the following conclusions can be made:

1. The AMA-based corrosion inhibitors have a reducing effect on the corrosion initiation process.

2. The penetrating AMA-inhibitor can diffuse through concrete and provide both cathodic and anodic protection.

3. The tested AMA-based inhibitors do not seem to have any negative effect on neither fresh nor hardened concrete properties.

4. Based on the environmental impact assessment Ferrogard 901 may be described as an environmentally sound product.

8. REFERENCES

/1/ K. Tuutti., Corrosion of Steel in Concrete. Swedish Cement and Concrete Research Institute CBI report Fo 4:82.

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/12/ Statens Vegvesen, Bruavdeling, Utvikling av kloridbestandig betong, Report 94-13, 1994, in Norwegian.

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