Mott MacDonald

Sika Ltd.

Sika Ferrogard® 901 and 903 Corrosion Inhibitors: Evaluation of Test Programme

August 1996

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EVALUATION OF TEST PROGRAMME

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CONTENTS

SIKA FERROGARD® 901 & 903 CORROSION INHIBITORS: EVALUATION OF TEST PROGRAMME

ABSTRACT

This report relates to the use of amino alcohol based corrosion inhibitors (AACI's) to protect against the corrosion of reinforcing bars and other steel components located within concrete structures. SIKA FERROGARD® 901 and 903 have been developed using AACI technology to counter the damaging effects of reinforcement corrosion due to both carbonation and chloride contamination of the concrete. The report covers current research, test data, properties and applications.

1.0 BACKGROUND

Mott MacDonald were commissioned by SIKA Ltd. to evaluate SIKA FERROGARD® 901 (a corrosion inhibitor which is added to concrete and concrete repair materials) and 903 (a corrosion inhibitor which can be applied to the external surfaces of a structure) based on the following documents supplied by SIKA Ltd.:

a. Laboratory report: Investigation on concrete admixtures using electrochemical methods.

   Part 1: Electrochemistry of corrosion and electrochemical test methods, Dr. Jorg Vogelsang, Sika Chemie.

   Part 2: Laboratory report: Investigations on concrete admixtures using electrochemical methods. Inhibitor testing experimental details and results, Dr. Jorg Vogelsang, Sika Chemie.

b. Test of the effectiveness of Sika Armatec corrosion inhibitors on chloride-contaminated reinforced concrete test samples. Interim report, Leopold Franzens University, Institute for Building Materials Science and Materials Testing, Professor Walter Lukas.

c. Test programme Ferrogard 901 summary, Swedish Cement and Concrete Research Institute, Durability Group.

d. Report number 16.743-I, preliminary study of the effectiveness of the corrosion inhibitor, „Sika Ferrogard 901-VP“ for reinforced concrete, Institute de Ciencias de la Construccion, Eduardo Torroja, Dr. M. C. Andrada.

e. Ferrogard 901 Report, J. D Izquierdom, Sika SA, Spain.

f. Corrosion protection of steel in concrete by means of inhibitors, Armatec Study - Part 1, Dr B Etsener, Institute for Construction Materials Chemistry and Corrosion, Zurich.

g. Study of corrosion inhibitors at Au and Fe surfaces, final report, 29 November 1994, C R Brundle.

h. Report on XPS and SIMS measurements on steel surfaces made from a cement matrix, Professor M Grunze, University of Heidelberg.

i. Detection and characterisation of dimethylethanolamine based corrosion inhibitors at steel surfaces, (I) the use of XPS and TOF-SIMS, C R Brundle and Associates, San Jose, USA.

j. First interim report on XPS/SIMS studies of Aminoalcohol exposed to gold and steel surfaces, C R Brundle and M Grunze.

k. Final report: Investigations on the transport of Amino Alcohol based corrosion inhibitors through concrete, J Goschnick, Institut fur Radiochemie Forschungszentrum Karlsruhe.

1. Short report: Investigations on the depth distribution of Ferrogard and Armatec within concrete after different conditions of application, J W G Beritz and J Goschnick, Institut fur Radiochemie Forschungszentrum Karlsruhe.

m. Short report: Investigations on the distribution of Armatec 2000 and Ferrogard 903 within concrete after application in different positions, M Sommer and J Goschnick, Institut fur Radiochemie Forschungszentrum Karlsruhe.

n. Short report: Investigation of the depth distribution of DMEA in concrete after different application conditions, J W G Bentz and J Goschnick, Institut fur Radiochemie Forschungszentrum Karisruhe.

o. Diffusion of the MCI 2020 and 2000 corrosion inhibitors into concrete, D Bjegovic, L Sipos, V Ukrainczyk, B Miksic, Materials Department, Civil Engineering Faculty, University of Zagreb.

p. Final Report: Cracked beam corrosion test of concrete treated with MCI 2000 and MCI 2020 corrosion inhibitor for Cortec Corporation, M Sherman, P Kraus, Wiss, Janney, Eisner Associates Inc.

q. Final Report: Cracked beam corrosion tests of concrete treated with different corrosion inhibitors, B Marrazzani, Sika AG.

r. FA 93.402.090, FG 901 VP and FG 903 VP: deterioration of any possible chloride threshold concentration, G. Meyer, Germany.

s. Report on tests carried out on concrete specimens with current inputs, Sika UK.

1.1 <u>Introduction</u>

Steel reinforcement in good quality concrete is normally protected by a ‘passive film’ produced by the alkaline conditions generated by the hydrated cement. The two principle mechanisms by which passivity is destroyed leading to corrosion of the reinforcement are carbonation and chloride attack.

Carbonation is the result of acidic atmospheric gases, principally carbon dioxide, neutralising the protective alkalinity leading to general corrosion of the reinforcement in the presence of moisture.

Chloride salts, from mix constituents, marine environments and deicing salts, can break down the passive film leading to localised pitting corrosion.

Corrosion of reinforcing steel may occur in concrete structures which are:

- treated with deicing salts,
- subject to normal atmospheric exposure,
- located in a marine environment,
- located in a saline environment,
- manufactured with chloride-based admixtures,
- manufactured with salt contaminated water, sand or aggregate,
- located in industrial areas.

Certain specific chemicals can retard or delay the corrosion process. These chemicals are usually added to the concrete in the form of admixtures during production and are intended to prolong the durability of concrete structures. Such admixtures are already used, principally in the U.S.A. and Japan. Historically, their main or sole content has been calcium nitrite.

1.2 Inhibitors

The use of inhibitors in controlling the corrosion of metals is a well established technology. Most individuals own and maintain several inhibitor-based protection systems, of which cars (both cooling systems and body work) and domestic central heating systems are good examples.

Inhibitors are in effect any materials that are able to reduce corrosion rates when present at relatively small concentrations at or near the steel surface. Corrosion inhibitors generally work either by forming a protective film on the substrate to be protected or by tying up the corrosive species and preventing them from reaching the steel.

By far the largest group of inhibitors are the adsorption type which are typically organic compounds, which suppress both the anodic and cathodic reactions on the steel surface. When correctly specified and applied by experienced professionals inhibitors can be effective for use in both the repair of deteriorating concrete structures and enhancing the durability of new structures. Inhibitors can also provide solutions to areas of high corrosion risk with limited or difficult access, where other forms of repair are difficult or undesirable.

1.3 SIKA FERROGARD® 901 AND 903

The Ferrogard 901 and 903 inhibitors developed by SIKA are based on organic film forming amino compound that can also exist in the vapour phase. This allows the inhibitor to diffuse through pores in the concrete.

Amino film forming inhibitors have a proven track record in the protection of oil and gas pipelines and the protection of packaged and stored machinery to prevent the deterioration of machined surfaces. SIKA FERROGARD® is a modified amino alcohol corrosion inhibitor (AACI) that has been developed with the addition of further corrosion retarding radicals known to prevent the corrosion of steel.

SIKA FERROGARD® 901 and 903, when used in accordance with the manufacturers recommendations, afford no greater risks to health and safety than conventional repair methods and show no detrimental effects to the concrete[1,2].

The diffusion of inhibitors through concrete has been verified by laboratory testing and monitoring of actual repairs undertaken in the USA as part of the Strategic Highways Research Program (SHRP)[3]. The amino alcohol based inhibitor was found to penetrate to the layer of steel reinforcement beneath the repaired area. The encouraging test results from SHRP report lead to the focused development of SIKA corrosion inhibitors for use in admixtures and concrete repairs.

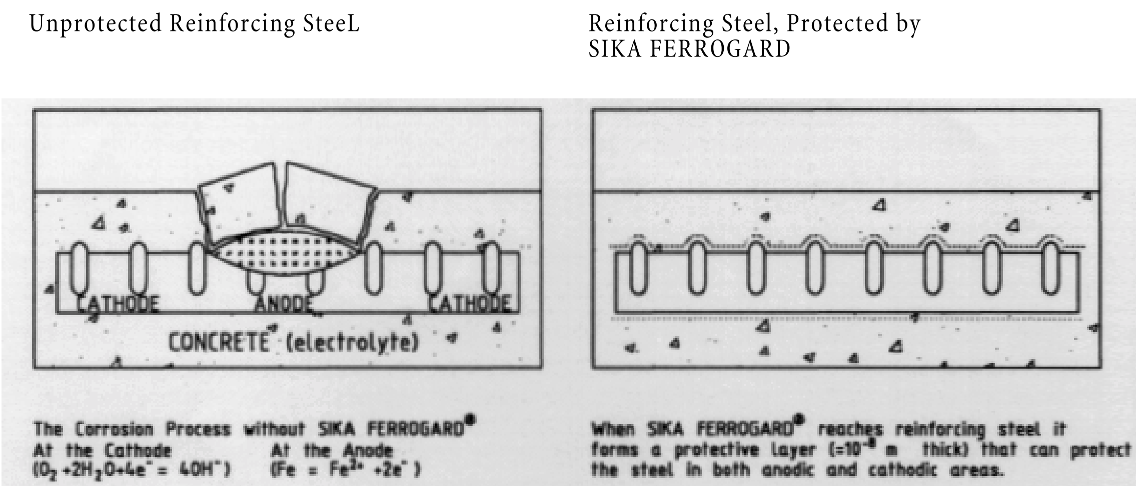


Figure 1: Corrosion Processes with and without SIKA FERROGARD®

The protective film is adsorbed onto the surface of the steel and suppresses the corrosion reactions described in the Figure 1.

Analysis by Secondary Ion Mass Spectrometry (SIMS) (see Section 2.2) has identified the surface layer to be composed of the parent amino alcohol and the associated radicals, which covers the anodic and cathodic sites with a continuous film. The layer is typically 10^8m thick and masks any trace of iron on the spectrograph which is indicative of a high integrity film providing a barrier layer to any aggressive ions.

As additional data becomes available from both laboratory testing and site trials the performance of SIKA FERROGARD® will be further assessed.

2.0 PROPERTIES OF SIKA FERROGARD®

2.1 Penetration

Laboratory tests to evaluate inhibitor penetration rates were undertaken by Goschnick and Bentz, using Secondary Neutron Mass Spectrometry (SNMS), at the Institute for Radiochemistry in Karlsruhe[(4)]. The spatial distribution of corrosion inhibitors in concrete and mortar samples was carried out to establish the transport behaviour and rate of penetration of the amino alcohol inhibitors. Mortar and concrete blocks were subjected to different wetting times at a range of relative humidities. The depth of penetration and distribution of the amino alcohols was determined by breaking open the blocks and taking dust samples for analysis in the SNMS.

The full laboratory testing has shown that when applied to the surface, SIKA FERROGARD® 903 can penetrate through concrete at a rate of between 2.5 to 20mm per day and to a depth of 80mm in 28 days, depending on the quality of the concrete. Tests carried out as part of SHRP showed that AACI's penetrated from the repair material through to the subsequent layer of steel reinforcement[(3)].

The results as graphically presented (Figure 2) show the atomic concentration ratio of nitrogen to silicon versus depth of penetration. Because no other nitrogen component should be present, the ratio is used to express the amount of amino alcohol in the samples. Calibration results were used to correct the intensity ratios into absolute mass concentrations. The carbon to silicon ratio was also used as an additional indicator for the presence of an organic additive.

Atomic Concentration Ratio of N/Si

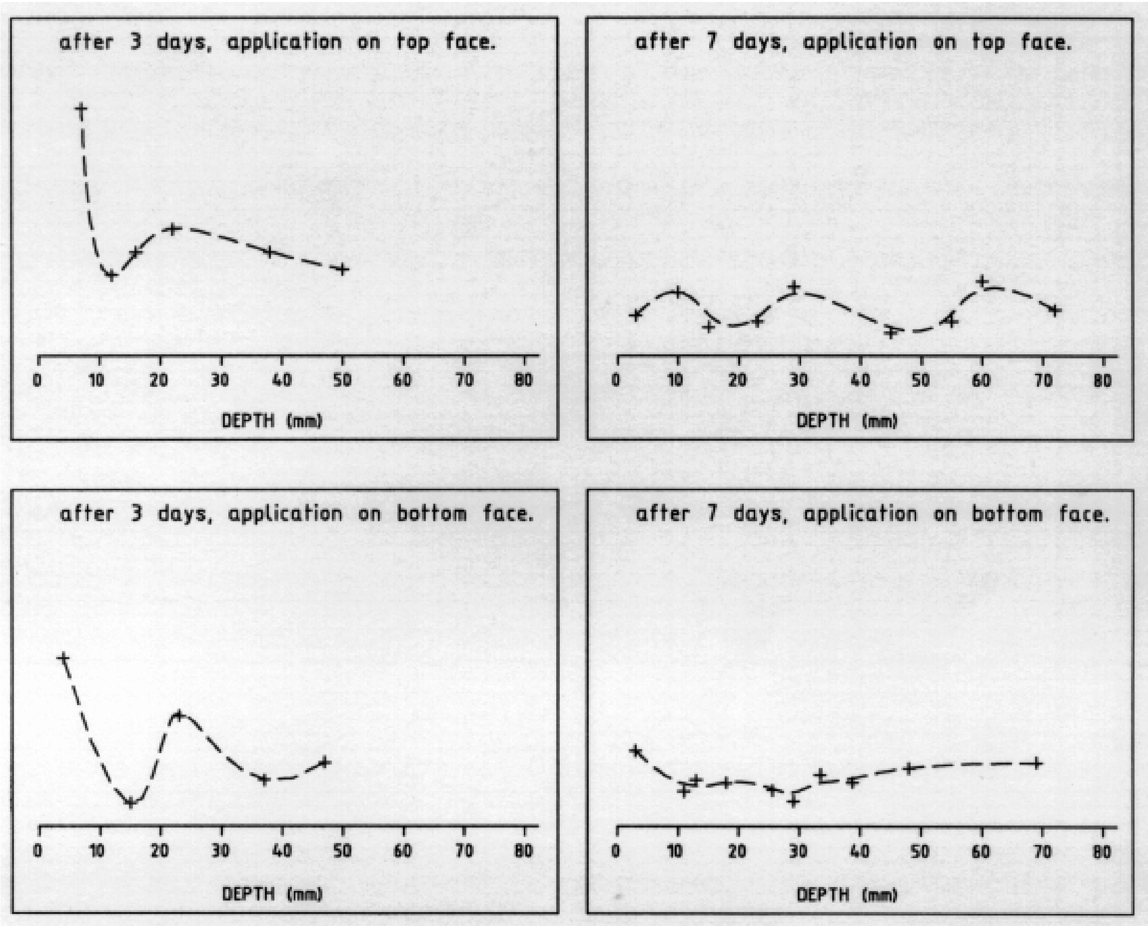


Figure 2: Transport Studies of SIKA FERROGARD® in Concrete Blocks

The above depth profiles show that a concentrated band of SIKA FERROGARD® 903 passes through the cover concrete over a period of days, allowing the penetration of inhibitor to embedded steel surfaces irrespective of the orientation of the application.

SIKA FERROGARD® 903 reached a transport rate of 7mm/day, averaging around 2.5mm/day with the rate of transportation declining as the depth of penetration increased.

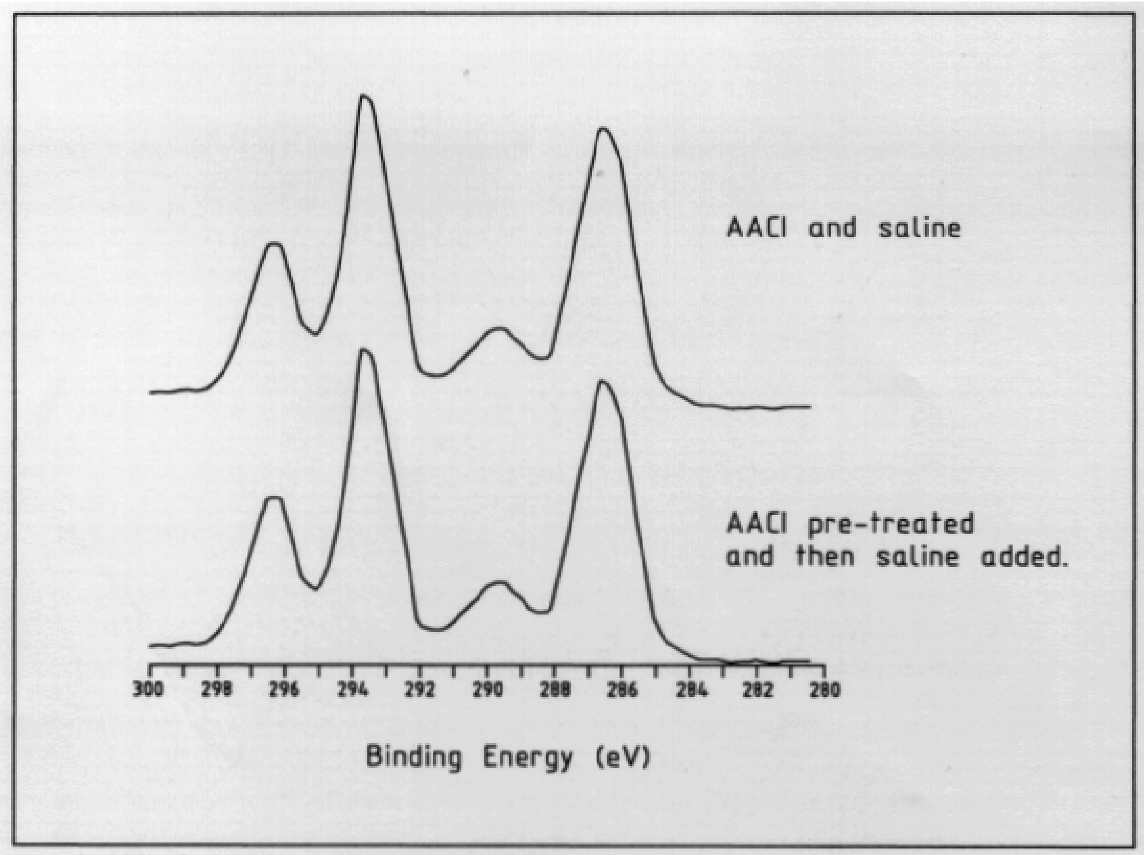
2.2 Film Forming and Chloride Displacement Characteristics

Laboratory tests using X-Ray Photon Spectrometry (XPS) and Secondary Ion Mass Spectrometry (SIMS) surface analysing techniques were carried out by Brundle of

Brundle Associates, San José, California, USA and Grunze of the Heidelberg University[5]. Having established the accuracy and usefulness of using XPS and SIMS to detect the presence of amino alcohols[5], these techniques were then used to provide semi-quantitative information on the coverage and thickness of AACI's on steel samples exposed to solutions of high pH and varying concentration of saline solution. This was used to prove the effectiveness of the inhibitors in forming continuous protective films in chloride contaminated environments.

Experimental test results have shown that amino alcohol corrosion inhibitors (AACI's), when applied to simulated concrete pore water solutions containing chlorides, form a continuous inhibitive film (≈ 10^{-8}m thick), and displace chloride ions from the surface of the steel, even when immersed in a dilute saline solution.

When the steel is dipped in dilute AACI, prior to exposure to saline solution, the AACI film remains intact and the thickness is similar to that when the untreated steel is dipped in a mixed solution (saline and AACI), as shown in Figure 3.



Without the saline solution, the film was found to be thicker.

Figure 3: XPS Results[5]

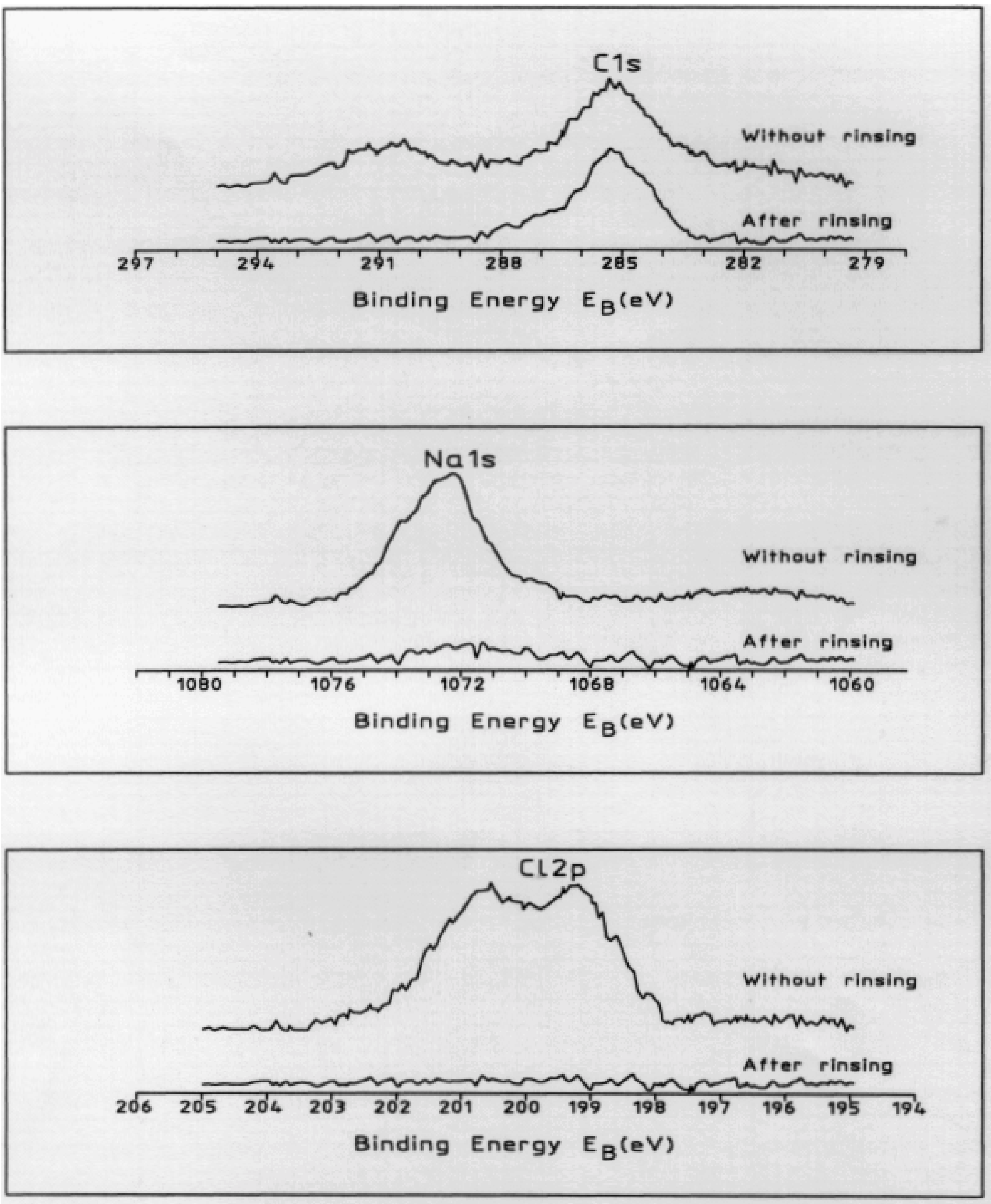


Figure 4: Effect of Rinsing

Figure 4 shows that rinsing the AACI treated steel surface with water does not remove the protective film (peak C1S). Chloride and sodium ions, however, are removed by rinsing as indicated by the reduction in the associated peaks (Na1S and C12P) in Figure 4. Figure 5 shows that AACI's can displace chloride and other ions from a mild steel surface immersed in a saline solution.

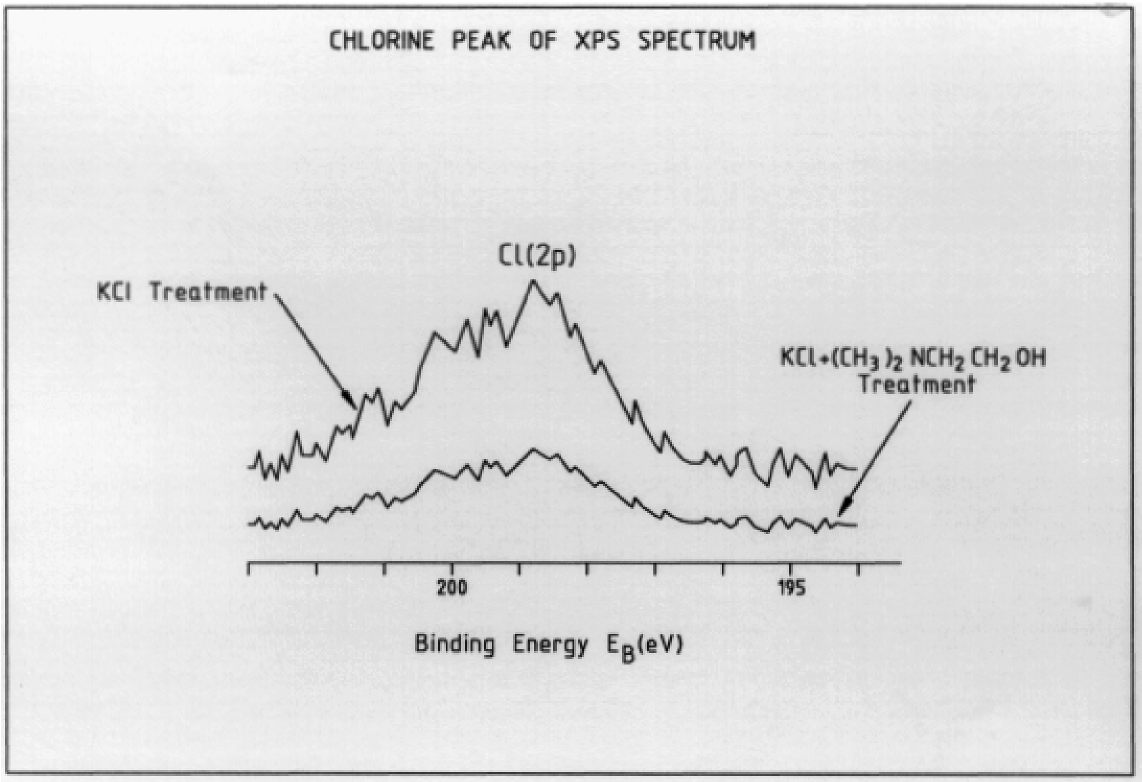


Figure 5: Displacement of Chloride Ions by AACI's

2.3 Corrosion Inhibition

The first tests carried out to prove the effectiveness of AACI's in reinforced concrete were undertaken in aqueous solutions containing various concentrations of chloride ions. Following these initial experiments, further work was carried out to prove the effectiveness of AACI's in carbonated and chloride contaminated mortar and concrete samples.

2.3.1 Tests in Simulated Pore Solutions

The initial studies were carried out at the Instituto De Ciencias De La Construccion Eduardo Toroja by Andrade and Alonso[6]. Electro-chemical techniques were used to determine the effectiveness of the AACI's in reducing pitting corrosion in chloride environments and general corrosion under neutral conditions[7].

Tests were carried out in simulated aqueous pore solutions containing varying concentrations of chloride ions and inhibitor.

They reported that SIKA FERROGARD® 901 responded well as an organic inhibitor by preventing the aggressive ions from associating with the steel interface by forming an adsorbed layer on the steel surface[(6)]. SIKA FERROGARD® 901 was shown to significantly enhance resistance to the initiation of pitting corrosion in alkaline, chloride-rich environments when added prior to the introduction of aggressive ions. SIKA FERROGARD® 901 was also shown to be effective in reducing general corrosion under near neutral test conditions (ie. 98% inhibitor efficiency at 3% inhibitor concentration).

Further experimental tests were carried out at SIKA Chemie, Stuttgart, to evaluate the effectiveness of AACI's by monitoring the electrochemical changes at the steel reinforcement. Vogelsang carried out electrochemical pitting studies using a potentiostatic polarisation technique[(9)]. The results confirmed the benefits of AACI's in improving resistance to pitting corrosion in alkaline solutions containing chloride ions.

2.3.2 Tests in Mortar and Concrete

Tests on cracked concrete beams, using an adapted ASTM Standard test method for evaluation of inhibitors, have shown that AACI's retard the onset of corrosion and subsequently reduce the overall magnitude of corrosion when added as an admixture to the concrete.

Site surveys from SHRP have shown that AACI's have successfully inhibited corrosion of reinforcement in concrete bridge decks. Further examination of the overlay and repair areas revealed that the amino alcohol inhibitors had penetrated to the subsequent layer of reinforcement below the repaired area.

Cracked beam corrosion testing of concrete treated with a range of different corrosion inhibitors was undertaken by Wiss, Janney, Elstner Associates Inc[(10)] as part of SHRP, and by SIKA in-house researchers[(11)].

The cracked beam corrosion test is a laboratory 'time-to-corrosion' test for concrete treated with inhibitors. It evaluates the ability of corrosion inhibitors to protect reinforcing steel embedded in cracked concrete subjected to cyclic wetting and drying in the presence of salt solutions. The free corrosion potential and corrosion current are measured and the time to the onset of corrosion recorded.

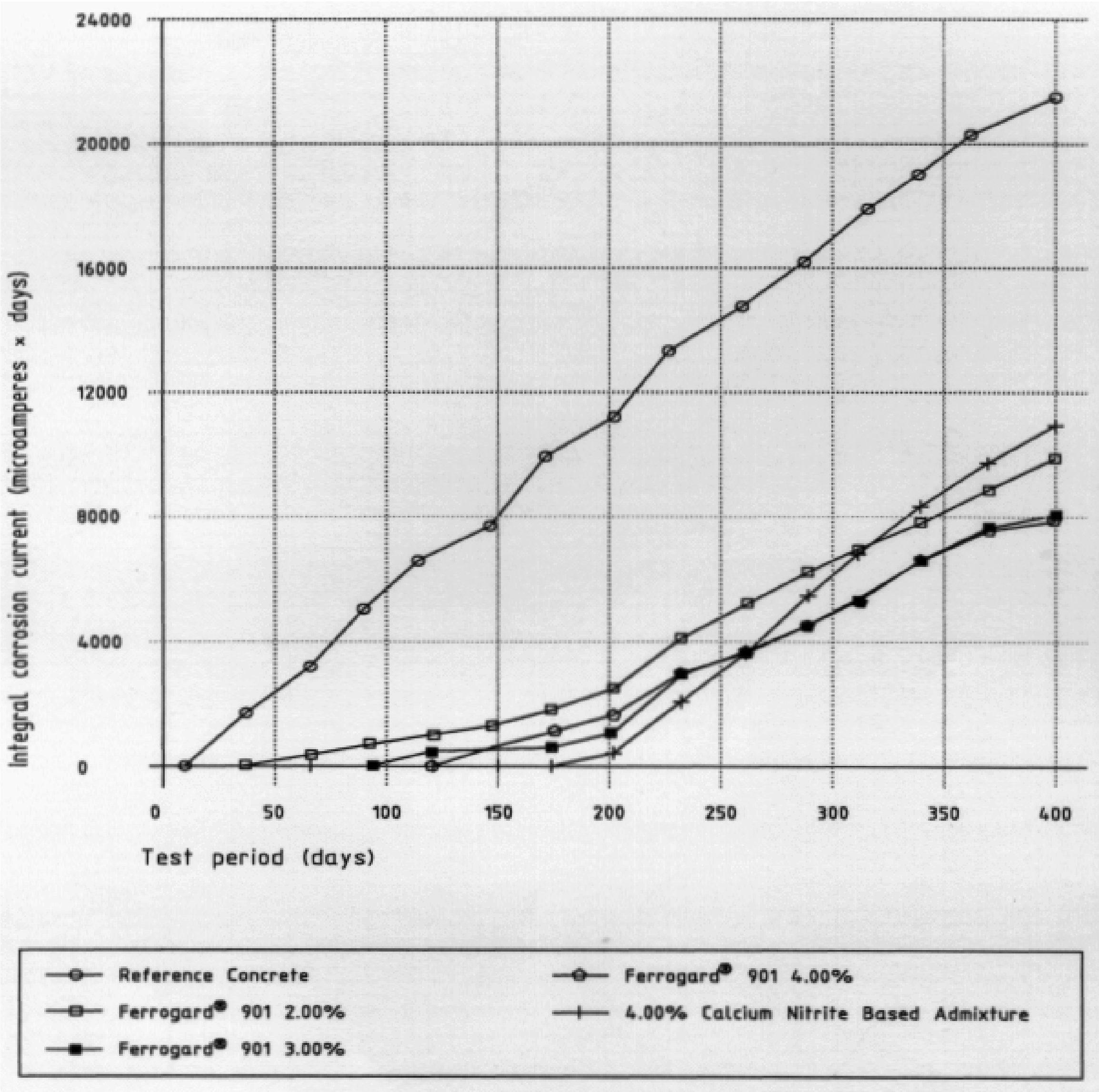


Figure 6: Cracked Concrete Beam Test (series 2): Ag/AgCl Potentials
(Ag/AgC1 potentials: average value of cracked concrete beam specimens)

As can be seen from Figure 6, SIKA FERROGARD® 901 was effective in delaying the onset of corrosion and subsequently reducing the overall magnitude. The results confirmed other work previously carried out by Wiss, Janney, Elstner Associates Inc., and SHRP.

Ongoing tests, commissioned by SIKA, are being carried out by Petterson, at the Swedish Cement and Concrete Research Institute in Stockholm, on mortar and concrete samples exposed to a marine environment, salt spray, and artificial sea water.

The initial results show that FERROGARD® is successfully retarding the onset of corrosion, most notably for the concrete samples [(12)] Further research on repaired reinforced concrete slabs is being undertaken at Institutes in Italy and France.

2.4 Effects on Concrete Properties

A test programme into the effects of SIKA FERROGARD® 901 on the properties of fresh and hardened concrete was started in October 1995(2). The results to-date show that at recommended levels of addition, SIKA FERROGARD® 901 does not significantly influence the following factors:

Fresh Concrete: Water consumption (slight plasticising effect)
Air entrainment
Setting time (slight retarding effect)

Hardened Concrete: Compressive strength (currently up to 91 days)
Pull-out strength
Porosity
Permeability
Freeze/thaw resistance
Shrinkage (currently up to 28 days).

Further results, particularly with regard to compressive strength and shrinkage, are expected to become available within the next year.

3.0 APPLICATION

3.1 Preventative Use Including New Construction

The addition of SIKA FERROGARD® 901 as an admixture in fresh concrete or application of SIKA FERROGARD® 903 as a surface impregnation can lead to enhanced durability and extended service. SIKA FERROGARD® can be employed in the protection of a wide range of reinforced concrete structures. It can be applied in the concrete mix and is compatible with a range of other SIKA products[(2)]. By monitoring the level of inhibitor at the steel it is possible to maintain the required level of corrosion protection over extended periods.

SIKA FERROGARD® protects both anodic and cathodic areas of the steel, and provides a degree of protection even at dosage rates below the recommended minimum and has been shown to be effective in concentrations of chloride ions up to 2.0% by weight of cement at the depth of the reinforcement[(8)].

SIKA FERROGARD® when used at dosage rates recommended by SIKA, does not constitute a higher health and safety risk than conventional repair materials[(1)] and has no reported adverse affects on the durability and integrity of reinforced concrete or properties of wet concrete[(2)].

3.2 Use In Repairs and Restoration.

SIKA FERROGARD® can:

- penetrate through the structure to protect remote areas of reinforcement[(4)], and is not 'washed-off' under normal exposure conditions[(5,6)],

- be applied to concrete that contains up to 2.0% chloride ions by weight of cement at the depth of the reinforcement[(8)]. This accounts for the vast majority of repairable structures,

- be monitored, and if required the level of inhibitor can be replenished thus ensuring the integrity of the protective film is maintained,

SIKA FERROGARD® 901 can:

- be added to repair materials and fresh concrete to retard the onset of corrosion on suitably prepared steel substrates[(6)],

SIKA FERROGARD® 903 can:

- be applied to the surface of existing repairs and the surrounding area to prevent the setting up of incipient anodes,

- be applied to any surface orientation and to areas with limited access where other repair options could not be used,

- be applied to the surface of structurally sensitive areas where break out of existing concrete is not permissible.

- be brush or spray applied, or ponded onto the external surface of a structure and allowed to penetrate to the steel interface without the need to break out the concrete,

- be applied in relatively small quantities, typically 0.3 - 0.5 litres per m^2, depending on the service conditions and quality of the concrete. This may require replenishment at some future time, dependant upon concrete quality and exposure conditions,

- be applied as a post-treatment following other remediation techniques.

4.0 SUMMARY

Based on our evaluation of the results obtained from the test programme, SIKA FERROGARD® 901 and 903 can:

- improve resistance to the initiation of pitting corrosion in chloride contaminated concrete and reduce the risk of general corrosion in carbonated concrete,

- retard the onset of corrosion in new structures that might be subject to exposure to chlorides,

- reduce the risk of incipient anode corrosion occurring in areas adjacent to repairs,

- achieve a rate and penetration depth of up to 20mm per day and 80mm in 28 days respectively.

Development and research work is continuing to further monitor the properties and performance of SIKA FERROGARD® and the results from this work will be reported when data becomes available.

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Proof Statements
Mott MacDonald

General

Key Conclusions

- ▲ **Penetrates 80 mm**
- ▲ **Protective film cannot be washed off**
- ▲ **Reduces risk of incipient anodes**
- ▲ **Reduces risk of corrosion in carbonated and chloride contaminated concrete**