

A Review On Effects of Using Electrochemical Extraction Technique In Corrosion Treatment of Reinforced Concrete

Mohammad Ismail, Ph.D

Nordin Yahaya, Ph.D

Department of Structures and Materials
Faculty of Civil Engineering
Universiti Teknologi Malaysia

ABSTRACT

Traditional patch repair of concrete suffers from corrosion of the reinforcements due to the presence of chloride which has penetrated beyond the reinforcement. Methods based on electrochemical technique either in the form of cathodic protection or electrochemical chloride extraction have been used to alleviate this problem. Since electrochemical chloride extraction is a new technique that adopts higher current density with short duration of treatment, this paper reviews the possible side effects that might be caused in using this technique. The review covers possible physical and chemical effects such as steel/concrete bond strength and alkali-aggregate reaction.

INTRODUCTION

Electrochemical chloride extraction (ECE) is also sometimes called Electrochemical chloride removal (ECR) or desalination. This system is similar to CP except that a higher current density is used for a limited time period. ECE is a short term process, whereby a direct current (dc) electric field is applied between the reinforcing steel and a temporary anode/electrolyte system attached to the exterior surface of the concrete. Under the action of the electric field, the negatively charged chloride ions move along the current flow lines from the reinforcement, representing the cathode, towards the external anode system where they can be removed.

So far ECE has been used successfully in many parts of the world with applications such as quays, office buildings, road bridges, parking garages, housing and industrial plants [Miller, 1994]. As with any new technique,

questions regarding possible deleterious effects have been raised in many instances. The important points are: (a) Factors affecting the efficiency of the chloride removal process and possible reinitiation of corrosion. (b) The effect of current on bonding between steel and concrete. (c) Alkali-silica reaction.

REMOVAL EFFICIENCY AND CORROSION RE-INITIATION

The cost factor has always been the main criterion for choosing the repair technique. A rapid and less destructive technique with reasonable cost will of course be popular. With ECE the easiest way to expedite the rehabilitation process is by increasing the current density induced. The highest limit of current that caused no defect to the structure so far is $5A/m^2$ [Polder et. al. 1992]. Furthermore, Bennett & Schue [1990] in their conclusion said that the current efficiency for chloride removal is independent of current density, but varies with chloride concentration and is higher at $80^\circ C$ than at lower temperatures. Practical conditions will however limit the allowable temperature increase.

The fraction of the total current carried by a specific ion is defined as its transference number, t which is

$$t_{Cl^-} = \frac{\text{amount of current by chloride } (Cl^-)}{\text{total current } (tot)} \quad (1)$$

Electrolytes in which the concentration of other mobile ions is high will reduce the current carried out by the chloride ion hence the efficiency is reduced.

The degree and effect of remigration of chloride after treatment is still unclear up to now. Chloride ions can only be removed if an electric field exists between them and the temporary surface anode. Therefore, chlorides in concrete beyond the reinforcement depth or between widely spaced bars, will not be moved during the ECE process. These chloride ions can then back-diffuse into areas where chloride has been extracted whereby increasing the risk of re-initiation of corrosion (Green, 1991). Elsener et al. [1992] discussed the possible existence of a free to bound chloride equilibrium which could have serious long term effects on the durability of the treated concrete and on the efficiency of this system to remove chloride which penetrate beyond the reinforcement. It was suggested that the treatment may need to be run twice. The applied current can be stopped after some period of treatment to allow bound chloride to be released into the matrix which can then be removed by the second treatment. Green [1991], further suggested that the current can be induced intermittently. The rest period is still not clearly indicated. Other factors such as initial chloride distribution,

cement type and water cement ratio could also contribute to the efficiency of the system [Tritthart a&b, 1989).

THE EFFECT OF CURRENT ON BOND STRENGTH

Application of a high current in ECE treatment can lead to loss of bond between steel and concrete. This problem has been the subject of research by many researchers. Locke et al. [1983] studied the effect of an impressed cathodic current of approximately 0.03A/m^2 of steel surface area on the bond strength for a period of 5 years. After 2 years a significant loss in bond was found as compared to the control specimens. After 4 years 20% in bond reduction was found where the sample was treated with approximately 1200Ah/m^2 . Rasheeduzzafar et al. [1993] found up to a 33% decrease in bond strength for a charge of 5426Ah/m^2 of steel surface in studies involving deformed steel bars.

The bond strength decrease is due to changes in the composition in the hardened cement matrix such as accumulation of alkali hydroxide around the cathode which may soften the binder matrix.

Studies by Nustad & Miller [1993] on smooth steel bars showed a loss in bond strength of 60-70% at charge levels of up to 5000Ah/m^2 but the bond strength increased again after the charge level increased to about 12000Ah/m^2 . Ueda et al. [1995] found quite a significant loss in bond strength when the total current density was less than 10000Ah/m^2 . However, the bond strength of some specimens was observed to be restored after 10080Ah/m^2 of total charge was applied. This phenomenon was due to the secondary cathodic reactions,



which occur at the cathode due to the lack of oxygen around the steel bar. When the total current density becomes large, the cement paste hardens again owing to the consumption of moisture in the softened cement paste. Buenfeld & Broomfield, [1994] carried out studies on uncorroded plain round bars embedded in normal and contaminated concrete. Prior to ECE, the bond strength of the specimens containing chloride was around 75% higher than for specimens not containing chloride, as a result of corrosion. The enhanced bond strength of the chloride specimens was largely eliminated by 2 weeks of ECE although results were not clear beyond 2 weeks. This initial drop in bond is attributed to the removal of corrosion product which was supported by visual evidence.

Page [1992], cited that the data recorded by Locke et al. [1983], on bond strength measurements show large scatter. In their work, Sergi and Page [1992] found a

small but significant reduction in micro hardness was seen when small current densities were applied. Based on this observation, Page [1992] concluded that moderate levels of cathodic protection are unlikely to cause any significant degradation of bond strength. On the other hand, the use of high currents in ECE is likely to cause quite a significant reduction in bond strength.

Reduction in bond strength may be attributed to the factors such as, Hydrogen gas evolution, thermal cracking, iron and corrosion product dissolution, paste softening and reduction of frictional forces. [Page, 1992]

HYDROGEN GAS EVOLUTION

The dissolved oxygen in the electrolyte is reduced to hydroxyl ions. Due to the high current densities used and the limited diffusivity of oxygen through hardened cement paste, the reaction is very quickly stifled by the lack of oxygen. The majority of the current is therefore passed by a second reaction; the evolution of hydrogen by the reduction of the water, presented by



The hydrogen gas which is formed at the cathode will try to diffuse through the pores to the surface of the concrete. Bursting forces will be induced in concrete around the steel if the rate of hydrogen evolution is greater than the rate at which it can disperse. If this bursting pressure exceeds the tensile strength of the concrete, cracking will occur and the steel/concrete bond will be reduced [Ali & Rasheeduzzafar, 1991 and Polder, 1994]. Unfortunately, not many publications discuss on the aspect of reduction in bond strength due to hydrogen evolution.

THERMAL CRACKING

Due to the high resistivity of concrete, the high current applied will convert to heat energy which can subsequently cause expansion in concrete. Tensile stresses induced by the expansion of concrete may result in micro cracking. Miller [1994] cited the work by Taywood Engineering that no significant increase in micro cracking was found after the concrete had undergone ECE with a current density of 1A/m^2 of concrete surface for 40 days. However Miller [1994] cited Karlsson [1990] who found an increase in micro cracking after concrete with a high salt content was treated with higher charges for a duration of treatment of 8 weeks.

PASTE SOFTENING

When the current is induced in the ECE process the positive ions Na^+ and K^+ accumulate gradually around the steel bar. These ions combine with OH^- to form NaOH and KOH which are believed to be detrimentally incorporated into the CSH gel and cause soluble silicates to be formed [Locke et al., 1983]. It has been proposed by Page et al. [1994], who observed an increase in sulphate around the cathode, that the stability of the sulphate and chloro-aluminate compound could be weakened by high concentration of alkalis.

Microhardness profiles have been determined by Sergi & Page [1992] for cement paste specimens containing steel cathodes polarised at 5mA/m^2 and 20mA/m^2 for 100 days. They have observed a small reduction in hardness in a zone extending less than 1 mm from the steel for the sample treated using 20mA/m^2 . Ueda et al., [1995] found a reduction in hardness up to 6 mm from the cathode by using 5A/m^2 of current density with total current density 6720Ah/m^2 . However, Bertolini [1993] and Page et al. [1994] found that it was not possible to establish statistically significant changes in hardness for a distance 0.1 mm from the steel after polarising specimens up to 12 weeks at current densities in a range 5mA/m^2 to 5A/m^2 . They concluded that may not be typical behaviour of cement matrices in general and further work is needed to clarify the possible influences of differences in mineralogy and pore structure [Page et al. 1994].

An additional effect that also warrants detailed study is the fate of the sulphate ions that enter the pore solution paste in the vicinity of the steel cathode (Bertolini et al., 1996). When they migrate towards the bulk material of lower pH, it may cause them eventually to be deposited as secondary ettringite. This expansive reaction might cause a local disruption of the matrix.

REDUCTION OF FRICTIONAL FORCES

Sodium hydroxide and potassium hydroxide are formed at the reinforcement steel cathode. These low-density alkali hydroxides may precipitate around the steel at the cathodes and locally disrupt the interfacial bond [Ali & Rasheeduzzafar, 1991]. Nustad [1992], suggests a “soapy film” theory where sodium and potassium hydroxide are hydrophilic and form a wet soapy film on the surface of the steel to reduce frictional force. Such a soapy film was observed after specimens were broken up after treatment.

ALKALI AGGREGATE REACTION (ASR)

The electromigration of the positive ions Na^+ and K^+ towards the cathode which combine with the OH^- ions modify the local composition of the cement paste and can result in an increase in the risk of expansive alkali aggregate reaction. Certain siliceous aggregates are unstable in alkaline conditions. These unstable aggregates exhibit slightly acidic characteristics which react with the hydroxyl ion, attacking some silicon-oxygen bonds and forming a hydrous silicate gel (Hobbs, 1988). The gel will expand by imbibition of water and induce forces which may lead to cracking of the concrete and, in severe cases, to structural damage. This type of reaction can take place at the steel surface region, and have a deleterious effect on the strength of the concrete at the concrete interface (Sergi et al., 1991 and Locke, 1983).

Miller [1994] suggested that ASR would not necessarily occur by the application of ECE and cited the work carried out by Bennett & Schue [1990] and Natesaiyer [1990] but Page & Yu [1995] found that ECE did promote ASR in their study on concrete containing Thames valley flint aggregate and calcined flint aggregate. Sergi et al. [1991] found some significant expansion in similar calcined flint aggregate concrete but by using cathodic protection-type current densities.

The effect of cover thickness, quality of concrete and spacing of the reinforcement on the process of ECE needs to be assessed. These conditions, if studied further in the field, will clarify the capability of ECE as a rehabilitation option for heavily chloride-contaminated reinforced concrete.

Removing chloride which was initially present in the form of CaCl_2 by ECE may be more difficult than NaCl because cements bind more CaCl_2 compared to NaCl . Since CaCl_2 has been used in some of the old structures as an accelerator, it would be of interest to look at the capability of the ECE system in removing this type of chloride and whether a similar equilibrium between free and bound chloride is maintained during treatment.

Preliminary work carried out by Mohammad (1998) to look at the capability of ECE in removing chloride in blended cements was not very comprehensive. It is, therefore, suggested to look into this area in more detail by studying the efficiency of removal as well as side effects that might have occurred as a result of application of ECE to the structures made from these cements and possible remigration of chloride around the steel cathode.

Further work is also needed to define the nature and the stability of the passive film which is formed around the reinforcement after the ECE treatment and also after storage of the specimens for a period of time. It would be useful to know the thickness and quality of the passive film as a result of the ECE treatment, for example, so that a better understanding of its passivating properties could be achieved.

Computer modeling is another promising technique which can be applied for the better understanding of ionic migration in concrete under the influence of current. Several models have been developed so far by Bennett & Turk, [1994], Andrade et al., [1995], Yu & Page, [1996] and Li & Page, [1998] which were moderately successful in modeling ionic redistribution and the removal of chloride. Among the problems encountered, however, in the work at Aston was that the concentration of OH⁻ ions was found in the main to be higher than concentrations determined experimentally. Modeling the remigration of chloride for the ECE process has so far only been carried out in a over-simplified manner by Stoop & Polder [1996]. However, this model needs to be refined by taking OH⁻ ions and alkali cations into consideration. Apart from the requirement of the charge balance in the pore solution, OH⁻ ions also play a major role in the ECE process by enhancing the pH around the steel cathode.

Long term studies on the durability of concrete structures after undergoing ECE treatment are also needed particularly with respect to the ability of surface coatings which may be applied after the treatment, to prevent further chloride ingress.

Monitoring the Cl⁻/OH⁻ ratio around the reinforcement as well as the potential of the steel will enable its corrosion activity to be better predicted thus leading to improved understanding of the long term effectiveness of the treatment.

CONCLUSIONS

Despite many side effects that might result in using electrochemical chloride extraction technique, more chances are being given to this method in treating corrosion of reinforcement problem. This probably due to increased corrosion phenomenon occur around the globe today and also traditional patch repair were found to be ineffective in arresting this problem. However, there are many good progress researches being carried out in Europe and America in order for the electrochemical treatment can be carried out without serious risks from adverse side effects. The future of this technique looks promising.

REFERENCES

- ALI, M.G. and RASHEEDUZZAFAR, [1991], 'Bonding Problems with the Cathodic Protection of Steel in Reinforced Concrete Structures-Part 2', Corrosion Prevention & Control, 38, 6, pp 155-157.
- ANDRADE, C. DIEZ, J.M., ALAMAN, A. And ALONSO, C. [1995], 'Mathematical Modelling of Electrochemical Chloride Extraction from Concrete', Cement and Concrete Research, Vol 25, No. 4, pp 727-740.
- BENNETT, J.E. & SCHUE, T.J. [1990], 'Electrochemical Chloride Removal from Concrete : A SHRP Contract Status Report', paper 316, Corrosion 90, NACE, USA.
- BENNETT, J., TURK, T. and SARINELL, R.F. [1994], 'Mathematical Modeling of the Effect of Current Flow through Concrete', paper no 285, corrosion 94. The Annual Conference and Corrosion Show Sponsored by NACE International.
- BERTOLINI, L. [1993], 'Effect of Electrochemical Chloride Removal on Structure and Mechanical Properties of Hardened Cement Paste', Report submitted to Aston University.
- BERTOLINI, L., YU, S.W., and PAGE, C.L. [1996], 'Effect of Electrochemical Chloride Extraction on Chemical and Mechanical Properties of Hydrated Cement Paste', Advanced Cement Research, Vol. 8, pp 93-100.
- BUENFELD, N.R. & BROOMFIELD, J.P. [1994], 'Effect of Chloride Removal on Rebar Bond Strength & Concrete Properties', Corrosion and Corrosion Protection of Steel in Concrete, ed. R.N. Swamy, Academic Press, Sheffield, ISBN 1 85075 723 2.
- ELSENER, B., MOLINA, M. & BOHNI, H. [1992], 'Electrochemical Removal of Chlorides from Reinforced Concrete', Int. Conf. Advances in Corrosion and Protection, UMIST, Manchester, 28 June-3 July 1992.
- GREEN, W.K. [1991], 'Electrochemical and Chemical Changes in Chloride Contaminated Reinforced Concrete Following Cathodic Polarisation', (unpublished) MSc Dissertation, UMIST, Nov. 1991.
- HOOBS, D.W. [1988], 'Alkali-Silica Reaction in Concrete, Thomas Telford Ltd., London.
- KARLSSON, F. [1990], 'Kloridutdrivning ur betong.' Nordisk Betong 4.
- LI, L.Y., and PAGE, C.L. [1998]. 'Modelling of Electrochemical Chloride Extraction from Concrete: Influence of Ionic Activity Coefficients,' Journals of Computational Materials Science, Vol. 9, pp303-308.
- LOCKE, C.E., DEGHANIAN, C. and GIBBS, I. [1983], 'Effect of Impressed Current on Bond Strength between Steel Bar and Concrete', Corrosion 83, paper no 178, NACE, USA.
- MILLER, J.B. [1994], 'Structural Aspect of High Powered Electro-chemical Treatment of Reinforced Concrete'. Corrosion and Corrosion Protection of Steel in Concrete, ed. By Prof. R.N. Swamy, Academic Press, Sheffield, ISBN 1 85075 723 2.

- MOHAMMAD ISMAIL, [1998], 'Electrochemical Chloride Extraction to Halt Corrosion of Reinforcement', (unpublished) Ph.D Thesis Aston University, May.
- NATESAIYER, K.C. [1990], 'The Effect of Electric Current on Alkali Silica reactivity in Concrete', PhD Dissertation, Cornell University, Ithaca, New York, January.
- NUSTAD, G.E. [1992], 'Laboratory Investigation of the Effects of Electrochemical Treatment of Reinforced Concrete on Bond Strength', Norwegian Concrete Technologies, Oslo, Norway (Unpublished).
- NUSTAD, G.E. and MILLER, J.B. [1993], 'Effect of Electrochemical Treatment on Steel to Concrete Bond Strength,' Paper no. 49, Engineering Solutions to Industrial Corrosion Problems, NAC, Sandefjord, Norway, June.
- PAGE, C.L. AND YU, S.W. [1995], 'Potential Effects of Electrochemical Desalination of Concrete on Alkali Silica Reaction', Magazine of Concrete Research, 47, 170, Mar, p23-31.
- PAGE, C.L. [1992], 'Interfacial Effects of Electrochemical Protection Methods Applied to Steel in Chloride-containing Concrete', in Rehabilitation of Concrete Structures, Proc. RILEM Int. Conf. On Rehabilitation of Concrete Structures, ed. D.W.S Ho & Frank Collins.
- PAGE, C.L. [1995(b)], Personal Communication.
- PAGE, C.L. [1997(a)], 'Cathodic Protection of Reinforced Concrete-Principles and Applications', Proceeding International Conference Repair of Concrete Structures, Ed. Blankvoll A Norwegian Public Road Administration, Oslo, pp 123-131.
- PAGE, C.L. [1998], 'Corrosion and its Control in Reinforced Concrete', The 6th. Sir Frederick Lea memorial Lecture, Paper presented at 26th. Annual convention of the Institute of Concrete Technology, 6-8 April, Bosworth Hall, Market Bosworth, UK.
- PAGE, C.L. and TREADAWAY, K.W.J. [1982], 'Aspect of the Electrochemistry of Steel in Concrete', Nature, 297, May 13.
- PAGE, C.L., and VENNESLAND, O [1983], 'Pore Solution Composition and Chloride Binding Capacity of Silica Fume Cement paste', Materials Et. Construction, Part 16, pp19-25.
- PAGE, C.L., SHORT, N.R. and ELTARRAS, A. [1981], 'Diffusion of Chloride Ions in Hardened Cement Paste', Cement and Concrete Research, Vol 11, No. 3, pp 395-406.
- PAGE, C.K., YU, S.W. and BERTOLINI, L. [1994], 'Some Potential Side Effects of Electrochemical Chloride Removal from Reinforced Concrete', Proc. UK Corrosion and Eurocorr 94, Vol 3, The Institute of Materials London, pp 228-238.
- PARKER, D. And HAYWARD, D. [1995], 'Ioning out Problems', New Civil Engineer, January.

- POLDER, R.B. [1994], 'Electrochemical Chloride Removal from Reinforced Concrete Prisms Containing Chloride from Sea Water Exposure. UK Corrosion and Eurocorr 94, 31 Oct. – 3 Nov., Bournemouth, pp 239-248. The Cameleon Press Ltd. London.
- POLDER, R.B. and HONDEL, A.J. VAN DEN. [1992], 'Electrochemical Realkalisation and Chloride Removal of Concrete-State of the Art, Laboratory and Field Experience', in Rehabilitation of Concrete Structures, eds. D.W.S. Ho & F. Collins, Melbourne, Australia, 31 August - 2 September 1992, p135-148.
- RASHEEDUZAAFAR, ALI, M.G. and SULAIMANI, G.J. [1993] 'Degradation of Bond between Reinforcing Steel and Concrete due to Cathodic Protection Current', ACI Material Journal, 90,1.
- SERGI, G, PAGE, C.L. and THOMSON, D.M. [1991], 'Electrochemical Induction of Alkali Silica Reaction in Concrete', Materials and Structures, 24, pp359-361.
- SERGI, G, and PAGE, C.L. [1992], 'The Effect of Cathodic Protection on Alkali Silica Reaction in Reinforced Concrete', Contractor Report 310, Transport and Road Research Laboratory, Crowthorne, Berkshire, UK, ISSN 0266-7045.
- STOOP, Ben T.J., and POLDER, R.B. [1996], 'Redistribution of Chloride after ECR from Reinforced Concrete Prism', 4th. International Symposium, Corrosion of Reinforcement in Concrete Construction Eds Page, Bamforth and Figg, SCI, Cambridge, ISBN 0-85404-731-X.
- TRITHART, J. [1989(a)], 'Chloride Binding in Cement, I : Investigations to Determine the Composition of Pore Water in hardened Cement', Cement and Concrete Research, Vol. 19, pp 586-594.
- TRITHART, J. [1989(b)], 'Chloride Binding in Cement, 2 : The Influence of the Hydroxide concentration in the pore Solution of hardened Cement Paste on Chloride Binding', Cement and Concrete Research, Vol. 19, pp 683-691.
- UEDA, T et al. [1995], 'Influence of Desalination on Bond Behaviour between Concrete and Reinforcing Steel', CONSEC 95 : International Conference on Concrete under Severe Conditions.
- YU, S.W. and PAGE, C.L. [1996], 'Computer Simulation of Ionic Migration During Electrochemical Chloride Extraction from Hardened Concrete', British Corrosion Journal, Vol 31, No. 1, pp 73-75.