

Laboratory investigation of electrochemical chloride extraction from concrete with penetrated chloride

Rob B. Polder, TNO Building and Construction Research, The Netherlands

Anthony W.M. van den Hondel, NEBEST B.V., The Netherlands

Chloride extraction of concrete is a short-term electrochemical treatment against corrosion of reinforcing steel. The aim is to remove chloride ions from the concrete cover in order to reinstate passive behaviour. Physically sound concrete is left in place. To make this method more predictable and reliable, a laboratory study was carried out. Concrete specimens with penetrated chloride were subjected to electrochemical chloride extraction. The influence on chloride extraction was studied of: cement type (Portland, blast furnace slag), water-cement-ratio, cover to the reinforcement, steel geometry, amount of charge passed and type of electrolyte. Additionally, some potential 'killing' factors and the effect of the treatment on corrosion pits were studied. Chloride profiles before and after treatment were measured. The durability of the final situation is predicted from calculation of the redistribution by diffusion of the remaining chloride ions. For various cement types and cover depths, the minimum amount of electrical charge was determined to obtain corrosion protection for at least 10 years. The presence of bending cracks in the specimens or tie wires close to the concrete surface did not have a significant effect on the extraction result. The test results suggest that active corrosion pits are extinguished by the treatment.

Key words: concrete, reinforcement corrosion, chloride extraction, desalination, durability

1 Introduction

Corrosion protection of steel reinforcement in concrete can be lost due to ingress of chloride ions or carbonation of concrete. Conventional methods for concrete repair aim at removing all chloride contaminated concrete, cleaning the steel and reprofiling the surface with new, chloride-free, cementitious concrete or mortar. In general this is a cumbersome procedure, that requires heavy labour and produces large amounts of noise, dust and waste material. Unless all chloride is removed in particular from the steel surface, corrosion may re-initiate after a short time. To overcome these disadvantages of conventional repair, electrochemical methods have been introduced during the last decades [COST 521, 2002]. One such electrochemical method is cathodic protection (CP), which requires a permanently installed electrode material and a permanent current flow of low density [Polder, 1998]. CP reduces the corrosion rate by depressing the steel potential, which neutralises the corrosive effect of chloride ions. Consequently, chloride containing concrete can be left in place.

Another method is electrochemical chloride extraction (abbreviated CE, also called chloride removal or desalination), which removes chloride from contaminated concrete by passing a direct current of a relatively high density for a limited period of time. The aim of CE is to suppress corrosion of reinforcement by reducing the chloride content of the concrete to below corrosive values. A temporary anode is fixed to the external concrete surface, surrounded by an aqueous electrolyte; a direct current of about 1 A/m^2 of concrete surface is passed between the anode and the reinforcement from a transformer/rectifier for several weeks to months. Subsequently, the anode and the electrolyte are removed and the surface and the site are cleaned. No permanent installation is necessary, except monitoring devices if desired. This non-destructive maintenance method has been applied to many structures over the past ten years with in general positive experience. In the mid 1990's, the experience with chloride extraction was limited to a small group of companies. From independent sources, a few case studies [Tritthart, 1996, Elsener et al., 1997] and limited laboratory experiments have been described [Bennett & Schue, 1990, Polder, 1996, Vennesland et al., 1996]. General guidelines for application [COST 509, 1997] and a state-of-the-art report [Mietz, 1998] were published. By the year 2002, chloride extraction has become current practice with good success using impressed current (as described above). The use of sacrificial anodes, where a base metal provides the electrical energy and no external power is needed, seems to be a promising development. Improvement is considered possible with regard to the economic side and non-destructive testing methods and criteria for effectiveness [COST 521, 2002].

In the mid 1990's it was felt that some questions regarding CE needed to be answered. It is difficult to predict how long CE should be carried on for an acceptable result; in some cases the treatment had to be repeated at least once [Elsener et al., 1997]. It is not clear whether cracks and local differences in electrical concrete resistance or variation of reinforcement cover depth reduce the effectiveness. These issues are potentially killing factors for effective and economic application of CE. It is unclear if active corrosion pits are effectively extinguished. The durability of the achieved protection is not well-defined. On the short term, hydroxide production at the steel and displacement of chloride from the steel certainly suppress corrosion [Polder et al., 1995]. However, after stopping the polarisation the hydroxide that is accumulated at the steel will diffuse away relatively quickly. Because some chloride inevitably remains in the concrete, this will redistribute and may come back at the steel in corrosion inducing levels after some time [Stoop & Polder, 1999]. Obviously, this depends on the spatial distribution of chloride remaining after CE, its transport rate and the critical chloride content.

Because of the risk associated with high **local** current densities at the steel surface (high gas pressures, loss of bond between steel and concrete), **average** current densities significantly higher than 1 A/m^2 should not be applied (designed). Higher current densities would reduce the process time, but negative side-effects should be avoided [COST 509, 1997]. A recent paper provides some insight in the effect of current flow on bond between concrete and steel bars [Chang, 2002]. Experiments were carried out where steel/concrete bond was determined by pulling out ribbed bars from cylindrical concrete specimens after polarisation. Water-to-cement ratios (w/c) investigated were 0.48, 0.58 and 0.66. Polarisation duration was 1, 3 and 5 months, at current densities of 4

and 12 A/m² of cathode (steel) surface. It was found that bond strength was reduced by 7 to 55%, increasing with longer polarisation time, higher current density and higher w/c of the concrete. The author concludes that the product of time and current (which is equivalent to the total electrical charge passed during treatment) determines the loss of bond, in combination with the w/c of the concrete. Microhardness and analysis of Na and K near the steel supported the hypothesis that softening of the cement paste around the steel after polarisation caused the reduction of bond strength. The aim of Chang's paper was to investigate bond reduction due to cathodic protection. In our view the current densities in his experiments are not representative for CP, where typically 0.01 A/m² of steel surface is applied. However, they are representative for the high end of the usual current density range for CE application. One month at 4 A/m² is equivalent to 2880 A·h/m², which was found to cause 7 to 15% loss of bond strength. The results support the view expressed above that current densities significantly higher than 1 A/m² of steel surface should be avoided in order to avoid loss of bond between reinforcement and concrete. Similar results in term of bond strength reduction and accumulation of Na and K in CE tests were found by others [Vennesland et al. 1996].

2 Experimental details

In order to systematically investigate the effectiveness of CE and some of the other issues mentioned above, a large number of concrete specimens was made. They measured 0.5 × 0.4 × 0.14 m³ and were cast with variation of the concrete composition and the amount of reinforcement as described in Table 1. The part first to be exposed to chloride ingress and subsequently treated by CE was a mould surface measuring 0.4 × 0.3 m², with a surrounding wall to form a pond, as shown in Figure 1. Specimens were demoulded at an age of five days and the cement skin was removed by water blasting. Chloride penetration was stimulated by repeatedly filling the ponds with saturated NaCl solution for 1 day, removing the solution and then leaving the specimens in dry air for 6 days. Specimens were subjected to these weekly cycles for 20 to 77 weeks. Periodically chloride profiles were taken; the aim was to obtain about 0.15% chloride by concrete mass at 15 or 30 mm depth. Such chloride levels were thought to be representative for moderate to strong chloride penetration, supposedly making up the majority of cases to be treated.

For the chloride extraction treatment, specimens were provided with an activated titanium mesh anode and electrolyte liquid in the pond. Anode and steel were connected to stabilised rectifiers and a total of 144 specimens were polarised for 3 or 6 weeks at 1 or 4 A/m² (steel surface), with saturated calcium hydroxide or tap water as the liquid electrolyte. The total charge passed varied from 504 to 4032 A·h/m² of steel surface. Current and voltage were monitored. After the treatment, 50 mm diameter cores were taken, both from around the rebars and in the mesh between the bars as indicated in Figure 1, and sawn in 0-15, 15-30 and 30-45 mm slices. Chloride was analysed by dissolving crushed slices in acid and potentiometric chloride determination using the RCT method.

Table 1: Variables included in concrete and specimens ($D_{max} = 16 \text{ mm}$)

Variable	PC, CEM I (Portland cement)		BF, CEM III/B LH HS (blast furnace slag cement, about 70% slag)
water-cement ratio & cement content (kg/m ³)	0.45 380	0.55 345	0.65 310
cover depth (mm)	15		30
rebar diameter & spacing (mm)	$\phi 8$ #100	$\phi 8$ #200	$\phi 16$ #100

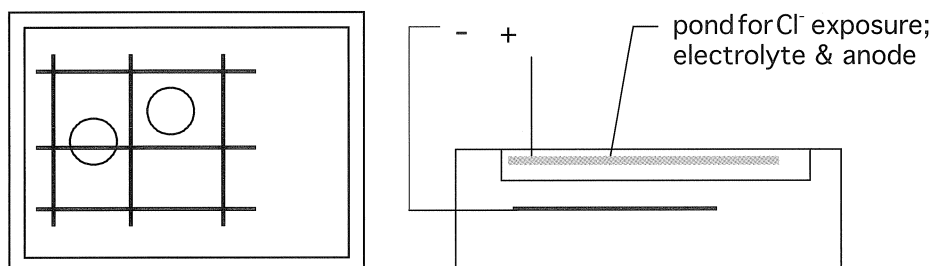


Figure 1: Layout of specimens for chloride extraction (outer dimensions $0.5 \times 0.4 \times 0.14 \text{ m}^3$); circles indicate location of sampling for chloride after extraction

To investigate potentially “killing” factors, additional (“special”) specimens were made and tested, which:

- were cracked by bending, with crack widths at the surface to be treated of 0.1 to 0.6 mm;
- contained two separate (half) steel nets, one at 15 and one at 30 mm cover depth;
- contained tie wires protruding from the steel net until close to the treated surface;
- were made with a low Portland cement content (250 kg/m^3) and w/c 0.65, representing very poor concrete;
- had pitting corrosion caused by locally mixing in a high chloride content.

All “special” specimens were subjected first to chloride exposure and then to chloride extraction tests, similar to the other specimens.

3 Results

Compressive strengths of concrete ranged from about 60 MPa (both cement types, w/c 0.45) to 40-50 MPa (w/c 0.55) and 40 MPa (w/c 0.65). The average chloride content after exposure (“initial”) in the outer 45 mm ranged from 0.06 to 0.27% chloride by mass of concrete (0.3 to 1.6% by mass of cement). Most of the chloride was present in the outer 15 mm (average 2.5% by mass of cement). It

was assumed that there was a uniform chloride penetration. CE was carried out as planned. Chloride profiles after CE treatment (“final”) showed a decrease of the chloride content at all depths, which was stronger around the rebars and less in between bars (“mesh”). Examples of profiles before and after extraction are given in Figure 2. From the profiles and the charge passed Q (in A·h/m² concrete surface), the removed fraction of the initial chloride Fr , the removed amount of chloride dM (in gram chloride ion per m² of treated concrete surface), and the efficiency factor E (mole chloride removed per mole electrons passed) were calculated. Table 2 gives the average initial and final chloride contents, treatment details and results of the two examples shown in Figure 2.

Table 2: Initial and final chloride contents, treatment and results of two example specimens (chloride average over 0 - 45 mm, by mass of concrete); cover depth #185: 30 mm, #252: 15 mm

cement type	w/c (-)	exposure (weeks)	Cl initial (%)	Cl final (%)	Q (A·h/m ²)	Fr (-)	dM (g/m ²)	E (-)
BF (#185)	0.55	32	0.16	0.09	340	0.44	77	0.17
PC (#252)	0.65	20	0.16	0.04	2300	0.74	128	0.04

In the results of the investigated 144 specimens, the following trends were observed:

- the data contain a considerable amount of scatter, which is mainly due to the scatter in the initial chloride content and the inaccuracy of chloride analyses
- the removed amount of chloride increases steadily with increasing amount of charge passed, up to 200 g chloride per m² concrete surface, however with a decreasing rate
- the removed fraction Fr steadily increases with charge; for a charge Q of more than 2000 A·h/m², Fr is between 0.69 and 0.93 (average); in the mesh Fr is 0.05 lower than near the rebars
- the efficiency factor E is relatively low, and for $Q > 2000$ A·h/m² it is lower than 0.1
- the average remaining chloride at the rebars over a depth of 0 - 45 mm is below 0.4% by mass of cement for $Q > 2000$ A·h/m²; more chloride remains in the mesh, however
- other factors do not seem to be important (cement type, w/c, electrolyte, bar geometry).

With a few exceptions, all “special” specimens had extraction results which were in line with the normal specimens. No influence was found of the presence of bending cracks, tie wires between the steel and the surface, or a low cement content. The presence of active pits in specimens with locally admixed chloride was confirmed by strongly negative local potentials before CE tests (ranging from -365 to -600 mV versus CSE). Corrosion products were taken from pits (typical size 30 x 5 x 1 mm³) in two specimens (without extraction) and dissolved in acid. They contained 3.5 to 7% chloride by mass of sample. After extraction of eight similar specimens with about 1500 A·h/m², it took between 15 and 100 days for potentials to relax. Once relaxed, they had all become more positive than -310 mV CSE, with an average shift of +250 mV compared to the condition before CE testing. Corrosion products after CE treatment showed low chloride contents: five samples contained less than 0.1% chloride, three samples between 0.3 and 1.3% chloride by mass of sample.

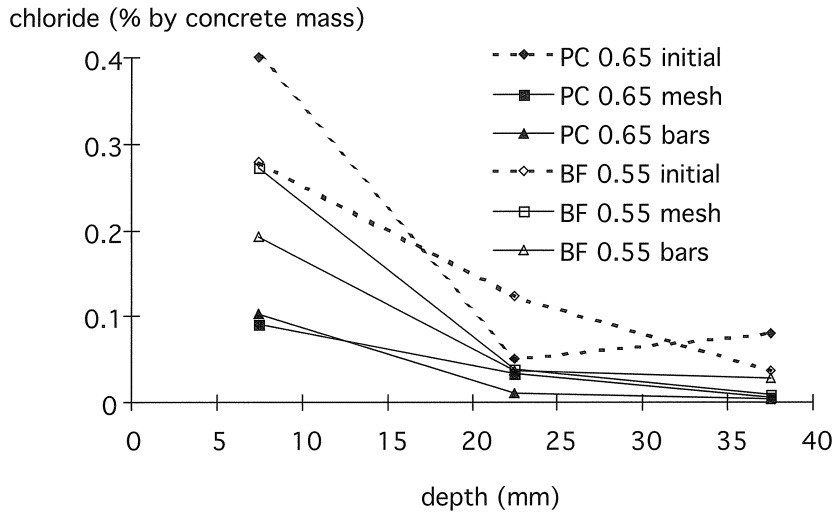


Figure 2: Chloride profiles before (“initial”) and after extraction (“mesh” in between bars, “bars” around the rebars) for two example specimens; PC 0.65 (#252) cover depth 15 mm, charge 2300 A.h/m², BF 0.55 (#185) cover depth 30 mm, charge 340 A.h/m²

4 Discussion

The results of the CE treatment tests carried out agree with other published data. There is no question that large amounts of chloride can be removed from concrete in this way and that the steel can be repassivated. The main question is how long the reinforcement will remain protected, in particular because significant amounts of chloride remain in the concrete, even after long treatment. It appears to be difficult to obtain a final situation in which the average chloride content over the relevant cross section is below 0.4% by mass of cement (considered a safe value for long term absence of corrosion). Because of the (in part inevitable) scatter in the results, the amount of charge needed to obtain such a safe situation is impractically high (more than a few months at high current densities). Situations with a higher **average** chloride content than 0.4% may be tolerated however, if it can be shown that during a reasonable period of time, the chloride content **at the rebar** will not become higher than 0.4%.

A procedure was developed to evaluate the durability of the reinforcement after CE, taking into account the chloride remaining in the concrete. The remaining chloride is assumed to develop from the profile present after CE is stopped, to a uniform distribution by diffusion, as observed in previous work [Stoop & Polder, 1999]. Diffusion coefficients are taken from a study of 16 years submersion of concrete in sea water [Polder & Larbi, 1995]: for PC (w/c 0.45) $D_{Cl} = 2 \times 10^{-12} \text{ m}^2/\text{s}$, for PC (0.65) $6 \times 10^{-12} \text{ m}^2/\text{s}$ (assumed); for BF $0.3 \times 10^{-12} \text{ m}^2/\text{s}$. Furthermore, it is assumed that no additional chloride penetrates. This can be achieved by applying a coating or hydrophobic treatment using silanes to the concrete surface after CE [Polder 2001]. However, the effective working life of such

surface treatments should be considered; their effectiveness may be lost over periods of about 10 years [Polder & Hug, 2000].

If the remaining chloride in the mesh is not significantly higher than at the rebars, it is safe to use only chloride profiles taken at the rebars, so the calculation model may be one-dimensional. It was assumed that 0% chloride was present at depths over 30 mm. A finite difference method was used to calculate at what minimum depth the chloride content will not exceed 0.4% by mass of cement in 10 years (using 150 slices of 1 mm and 105 steps of 10^{-4} year). This depth is termed the “durable cover depth”: steel at this depth will not develop corrosion in 10 years time. In many cases, the chloride content at this depth does not exceed 0.4% for much longer times (due to diffusion of chloride to deeper parts). If the calculated “durable cover depth” is rounded up to the nearest higher 5 mm, the difference between the two D_{Cl} values for PC concrete (with w/c 0.45 or 0.65) disappears. If significantly more chloride remains in the mesh than at the rebar, two-dimensional calculations are necessary, e.g. with a finite element programme like DIANA [Stoop & Polder, 1999].

From the profiles of remaining chloride in all specimens subjected to chloride extraction, the “durable cover depth” is calculated. It depends on the chloride content in the slices 0 - 15 and 15 - 30 mm and the (assumed) rate of transport. The calculations result in strongly varying “durable cover depths”, depending on the profile after CE, as shown in Table 3.

Table 3: Durable cover depth in mm for a period of at least 10 years, as a function of cement type and chloride remaining after CE in 0 - 15 mm (**bold**) and 15 - 30 mm (*italic*)

cement type	remaining chloride profile after extraction at depths of 0-15/15-30 mm (in % by mass of cement)									
	0.5/0.3	1/0.1	1/0.2	1/0.3	2/0.1	2/0.2	2/0.3	3/0.1	3/0.2	3/0.3
BF (#185)	15	20	25	30				35		
PC (#252)	15	20	25		40	45		60		

Using this procedure, the extraction results of all specimens were analysed. For example: PC specimen #252 (Table 2) received 2300 A.h/m²; the chloride content at 0-15 mm is 0.6% (by mass of cement), the chloride content at 15-30 mm is 0.06% and the durable cover depth is 20 mm (Table 3). BF specimen #185: 340 A.h/m², chloride at 0-15 mm is 1.2 %, chloride at 15-30 mm is 0.22%, so the durable cover depth is 25 mm. Please note that #185 is a relatively favourable exception in its group.

The chemical analysis of corrosion products from specimens with active pits shows that the chloride content inside the pits is significantly reduced, in some cases down to almost zero. Potential measurements show that the corrosion activity is strongly suppressed; however, it may take several months for potential values to relax.

5 Conclusions

The following conclusions can be drawn.

- Substantial amounts of penetrated chloride can be extracted from concrete by passing a direct current between the reinforcement and an external anode in a liquid electrolyte.
- The extracted amount of chloride increases with the amount of electrical charge passed per unit of concrete surface area during the treatment (which equals the treatment time multiplied by the integrated current density), however with decreasing rate, generally independent of concrete composition, geometrical and process variables, such as current density or time (as long as their product is constant) and type of electrolyte (water or saturated lime).
- Significant amounts of chloride remain in the concrete, even after large amounts of charge have passed.
- On the short term, reinforcement corrosion is suppressed by the strong polarisation and the associated chemical effects involved with CE. The chloride remaining in the concrete will redistribute, however, and the durability of the treated structure should be evaluated, for instance for a period of at least 10 years. The approach outlined in this paper for the durability prediction of the result of CE considers the final chloride profile, the cover depth to the first layer of rebars and the cement type, while assuming no new chlorides penetrate.
- For the concrete investigated, with about 2.5% chloride by mass of cement in the outermost 15 mm and about 0.6% from 15 to 30 mm, and taking into account that it should take at least 10 years after treatment before the chloride content at the rebar surface exceeds 0.4% chloride by mass of cement, it appears that:
 - for Portland cement concrete, at least 2400 A.h/m² (concrete surface) is required to obtain a sufficiently low remaining chloride profile, provided the minimum cover depth is 15 mm; this is equivalent to 100 days at 1 A/m²
 - for Blast Furnace slag cement concrete, the required charge depends on cover depth; for cover depths of 15 to 20 mm, 2230 A.h/m² is required; for cover depths 20 - 25 mm, 1130 A.h/m² is needed; for cover depths over 25 mm, about 1000 A.h/m² is required (equivalent to 42 days at 1 A/m²).
- To avoid damage to the concrete or the structure, average current densities higher than 1 to 2 A/m² of concrete surface should be avoided. Currents in excess of 4 A/m² have been found to negatively influence steel/concrete bond.
- Chloride profiles after extraction can be evaluated for satisfactory “after treatment” durability using diffusion calculations; such models may be one-dimensional in general, but two-dimensional calculations are necessary when Portland cement concrete is treated with high chloride amounts remaining in between the rebars.
- The above guidelines are somewhat conservative, because for good concrete quality, 0.4% chloride by mass of cement is on the safe side; furthermore, if the concrete is sealed after CE, drying out will slow down transport of remaining chloride and the diffusion calculation will be too pessimistic.
- It seems advisable to prevent new chloride ingress after CE, for example by applying a coating

or a hydrophobic treatment to the concrete.

- It appears that the following “defects” that may be present in the concrete do not significantly reduce the effectiveness of CE:
 - bending cracks with widths at the surface up to 0.6 mm (for other reasons, cracks wider than 0.2 mm are usually sealed);
 - the presence of rebars with varying minimum cover depths between 15 and 30 mm;
 - the presence of tie wires protruding from the rebars until a few mm from the treated surface (obviously, short circuits between the anode and the reinforcement should be avoided);
 - a low cement content (250 kg/m³).
- Potential measurements and chemical analysis of corrosion products from specimens with active pits strongly suggest that chloride is removed from inside the pits and that corrosion activity is reduced strongly.

References

- Bennett, J.E., Schue, T.J., 1990, Electrochemical chloride removal from concrete; a SHRP contract status report, Corrosion '90, NACE, paper 316
- Chang, J.J., 2002, A study of bond degradation of rebar due to cathodic protection current, Cement and Concrete Research, Vol. 32, 657-663
- COST 521, 2002, Corrosion of steel in reinforced concrete structures, Final Report, Chapter 3 Maintenance, ed. R. Weydert, to be published by the European Commission
- COST 509, 1997, Corrosion and protection of metals in contact with concrete, Final report, eds. R.N. Cox, R. Cigna, Ø. Vennesland, T. Valente, European Commission, Directorate General Science, Research and Development, Brussels, EUR 17608 EN, ISBN 92-828-0252-3, 148 pp.
- Elsener, B., Zimmermann L., Büchler, D. and Böhni, H., 1998, Repair of Reinforced Concrete Structures by Electrochemical Techniques - Field Experience, in Corrosion of Steel in Concrete, EFC Publication No. 25, The Institute of Materials, London, 125 - 140
- Mietz, J., 1998, Electrochemical rehabilitation methods for reinforced concrete structures, a state of the art report, European Federation of Corrosion Publications No. 24, The Institute of Materials, London, 57 pp.
- Polder, R.B., Borsje, H., Vries, J. de, 2001, Prevention of reinforcement corrosion by hydrophobic treatment of concrete, HERON, Vol. 46, no.4, 227-238
- Polder, R.B., Hug, A., 2000, Penetration of chloride from de-icing salt into concrete from a 30 year old bridge, HERON, Vol. 45, no.2, 109-124
- Polder, R.B., 1998, Cathodic Protection of Reinforced Concrete Structures in The Netherlands - experience and developments, HERON, Vol. 43, no. 1, 3-14
- Polder, R.B., 1996, Electrochemical chloride removal from reinforced concrete prisms containing chloride penetrated from sea water, Construction and Building Materials, Vol. 10, no.1, 83-88
- Polder, R.B., Larbi, J.A., 1995, Investigation of Concrete Exposed to North Sea Water submersion for 16 Years, HERON, Vol. 40, no.1, 31-56
- Polder, R.B., Walker, R., Page, C.L., 1995, Electrochemical Desalination of Cores from a Reinforced Concrete Coastal Structure, Magazine of Concrete Research, Vol. 47, no. 173, 321-327

- Stoop, B.T.J., Polder, R.B., 1999, Redistribution of chloride after electrochemical chloride removal from concrete, *HERON*, Vol. 44, no.1, 31-44
- Tritthart, J., 1996, Electrochemical chloride removal - a case study and laboratory tests, Proc. Fourth Int. Symp. on Corrosion of Reinforcement in Concrete Construction, eds. C.L. Page, P.B. Bamforth, J.W. Figg, Society of Chemical Industry, Cambridge, 433-447
- Vennesland, Ø., Humstad, E.P., Gautefall, O., Nustad, G., 1996, Electrochemical removal of chlorides from concrete - effect on bond strength and removal efficiency, Proc. Fourth Int. Symp. on Corrosion of Reinforcement in Concrete Construction, eds. C.L. Page, P.B. Bamforth, J.W. Figg, Society of Chemical Industry, Cambridge, UK, 1-4 July, 448-455