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Electrochemical Extraction of Chlorides from OPC and Fly Ash Concrete

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ABSTRACT:

Electrochemical extraction of chlorides from concrete has been recommended as a feasible repair technique for structures with chloride-induced corrosion damage. The technique employs an external anode and impressed direct current to effect the removal of chloride ions from concrete and restore passivating conditions around the reinforcement.

A series of OPC and fly ash concrete blocks, reinforced with high tensile steel, were initially exposed to wet/dry cycles with a salt solution. Thereafter, an electrochemical extraction process was used in an attempt to desalinate the concrete. Results indicated that chloride ions were readily extracted from OPC and fly ash concrete, except when chlorides had already penetrated well past the reinforcement before application of the electrochemical treatment.

Findings also indicated that currently accepted current densities may cause harmful side-effects and regular monitoring is essential during the extraction process. The study was limited to laboratory concrete and the validity of the results for site concrete was not fully assessed.

ELECTROCHEMICAL EXTRACTION OF CHLORIDES FROM OPC AND FLY ASH CONCRETE

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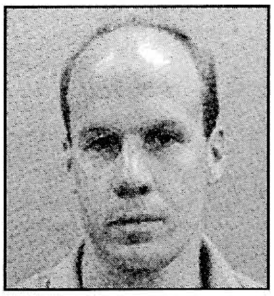
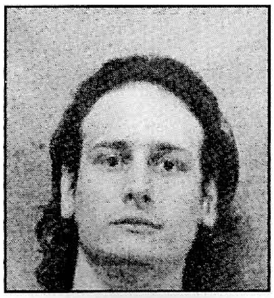


James R Mackechnie

Dr James Mackechnie is presently employed as a Research Officer in the Department of Civil Engineering at UCT. He is currently researching in the area of marine concrete structures, reinforcement corrosion and durability issues. His doctoral thesis, completed in 1996 was entitled 'Prediction of reinforced concrete durability in the marine environment'. Before being involved in research Dr Mackeshnie worked as a structural engineer in Zimbabwe and South Africa.



HRA Le Maire

Mr Arnu Le Maire was a BSc thesis student at the time of this research and graduated in December 1995. Mr Le Maire was tragically killed in a motor accident in 1996.

SYNOPSIS

Electrochemical extraction of chlorides from concrete has been recommended as a feasible repair technique for structures with chloride-induced corrosion damage. The technique employs an external anode and impressed direct current to effect removal of chloride ions from concrete and restore passivating conditions around the reinforcement. A series of OPC and fly ash concrete blocks reinforced with high tensile steel were initially exposed to wet/dry cycles with a salt solution. Thereafter an electrochemical extraction process was used in an attempt to desalinate the concrete. Results indicated that chloride ions were readily extracted from OPC and fly ash concrete except when chlorides had already penetrated well past the reinforcement before application of the electrochemical treatment. Findings also indicated that currently accepted current densities may cause harmful side-effects and regular monitoring is essential during the extraction process. The study was limited to laboratory concrete and the validity of the results for site concrete was not fully assessed.

INTRODUCTION

The feasibility of using electrochemical techniques to remove chloride ions from concrete has been investigated in the past but the high current densities employed raised concerns about negative side-effects such as cracking from high temperatures, increasing permeability and debonding of reinforcement as a result of hydrogen evolution (1). Renewed interest in the process using lower current densities has produced promising results which may help solve the growing number of cases of chloride-induced reinforcement corrosion. The technique has the advantage of requiring only temporary application unlike other electrochemical methods such as cathodic protection which have to be installed permanently. The time required to extract chlorides from concrete is reported to range from a few weeks to several months depending on impressed current densities, initial chloride levels, concrete quality and reinforcement distribution (2).

The electrochemical extraction process uses an impressed direct current between the external anode and the reinforcement which acts as the cathode. The impressed current creates an electric field in the concrete which induces negatively charged ions (Cl^- and OH^-) to migrate from the reinforcement to the external anode. The effect of the electric field promotes "easy desorption of adsorbed chloride" which effectively allows bound chlorides to dissolve into solution and be extracted with the free chlorides from the concrete (3). Hydroxyl ions are formed at the reinforcement by the cathode reaction between water

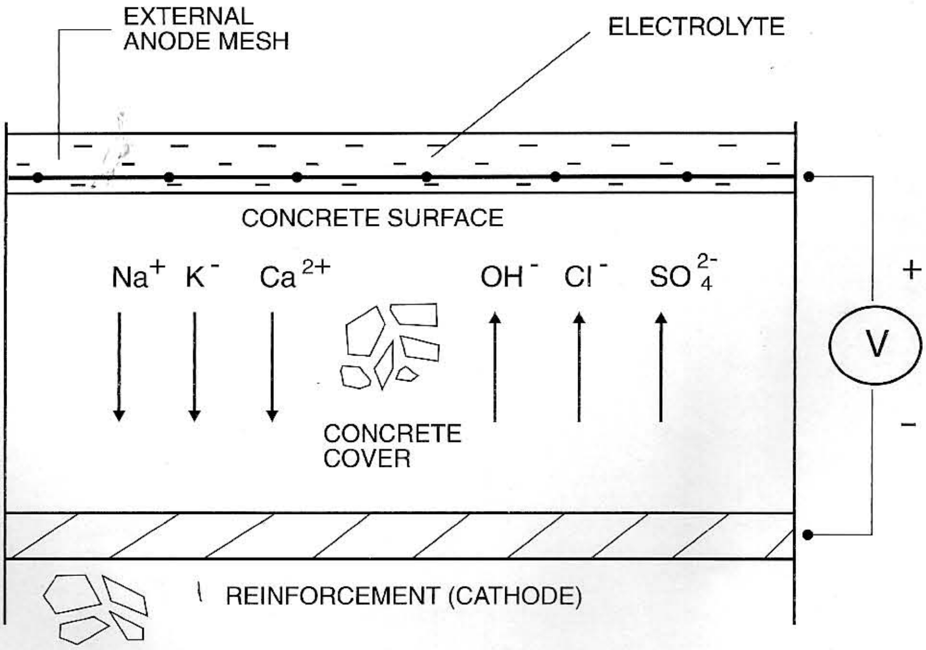


Figure 1: Schematic of Electrochemical Extraction Process

and oxygen while oxygen and chlorine gas are formed at the anode. The technique is generally believed to decrease the potential of the reinforcement, increase the hydroxyl ion concentration and decrease the chloride concentration around the steel thereby restoring passivating conditions for the reinforcement. A schematic representation of the extraction process is shown in Figure 1.

During the extraction process regular monitoring (by chemical and electrochemical means) is essential to ensure suitable progress of chloride removal and safe rebar potentials to prevent alkali aggregate reaction, hydrogen embrittlement of the steel and acid generation at the concrete surface. Alkali aggregate reaction may be caused by an increase in the alkali content of concrete from hydroxyl ion production, hydrogen embrittlement and debonding of reinforcement may be caused at high current densities when gaseous hydrogen is evolved at the steel surface and acid generation may occur when excessive chloride levels accumulate in the external electrolyte. Assessing the risk of hydrogen embrittlement and debonding of reinforcement is difficult to monitor on site and it is therefore necessary that driving voltages are kept sufficiently low to prevent any possibility of hydrogen evolution at the reinforcement. This is particularly important for complex shaped structures where the current density may concentrate in localized areas (2). Concern has been expressed about the effectiveness of the technique in removing chlorides which have diffused beyond the reinforcement, particularly for structures containing multiple reinforcement mats (4). Chlorides which are not removed from the concrete may diffuse back towards the reinforcement, after the impressed current has been disconnected, and activate corrosion.

EXPERIMENTAL PROCEDURE

A series of concrete blocks of size 300 x 450 x 180mm were cast using grade 20, 40 and 60 OPC and fly ash concrete with greywacke stone and dune sand aggregate but without any admixtures. Details of the cementitious materials and aggregates are given in Tables 1 and 2. A grid of 16mm high tensile ribbed bars was placed with a minimum cover of 30mm from the bottom of each block. External connections were made to the reinforcement for monitoring and completing the impressed current circuit. The concrete blocks were cast in wooden moulds, compacted with an internal vibrator, stripped after 24 hours and thereafter stored at 23°C and 60% R.H. in an environmentally controlled room until 28 days. The sides of the blocks (180mm high) were coated with two layers of coal tar epoxy paint to ensure uniaxial water penetration from the test surface (the bottom surface as cast) during later testing.

Table 1

COMPOUND / PROPERTY	Ordinary Portland Cement	Classified Fly Ash (Lethabo)
SiO_2	21.5%	54.1%
Al_2O_3	3.8%	32.9%
Fe_2O_3	3.3%	3.3%
TiO_2	0.2%	1.7%
SO_3	2.3%	0.4%
MnO	0.1%	0.0%
MgO	0.8%	1.3%
CaO	65.1%	4.7%
Na_2O	0.3%	0.6%
K_2O	0.5%	0.6%
P_2O_5	0.1%	-
Loss of Ignition	2.3%	0.5%
Blaine Fineness	2835 cm^2/g	4300 cm^2/g

Table 2

Material Property	Cape Flats Dune Sand	Greywacke Stone (19mm)
Loose Bulk Density	1492 kg/m^3	1341 kg/m^3
Compacted Bulk Density	1689 kg/m^3	1515 kg/m^3
Relative Density	2.63	2.68
Fineness Modulus	1.92	7.15

After 28 days the blocks were placed outdoors in an inverted position, exposed to summer conditions in the Cape Peninsula, and wet daily with a 5% $NaCl$ solution. Wetting was done by pouring 200ml of salt solution over the horizontal test surface of each block which caused minor ponding. A total of 200 wet/dry cycles were carried out to ensure significant chloride penetration into the concrete. During this period, the concrete blocks were tested at regular intervals using half-cell potential mapping and chloride content in order to assess the likelihood of reinforcement corrosion. Half-cell potentials were measured using a copper/copper sulphate electrode in accordance with ASTM C876-91 (5). Chloride contents were determined from drilled samples extracted from two 20mm diameter holes at 15mm depth increments and analysed in accordance with BS 1881 Part 124 but using a potentiometric titration (6).

The concrete blocks were left outdoors for three months exposed to wet winter conditions at the end of the wet/dry cycles before being subjected to electrochemical chloride extraction under controlled conditions in the laboratory (23°C and 60% R.H.). Chloride extraction was effected using a stainless steel mesh as the external anode submerged in an electrolyte of 0.5M NaOH solution with an impressed current density of 1 A/m^2 of concrete surface (representing current accepted practice). The external electrolyte was contained using a perspex frame attached to the edges of the concrete blocks such that a constant depth of 20mm could be maintained. The impressed current was applied for 56 days and measurement of chloride levels and rebar potentials was done at fourteen day intervals. The test setup for three concrete blocks connected in series is shown in Figure 2. Two identical systems of this configuration were used for OPC and fly ash concrete respectively.

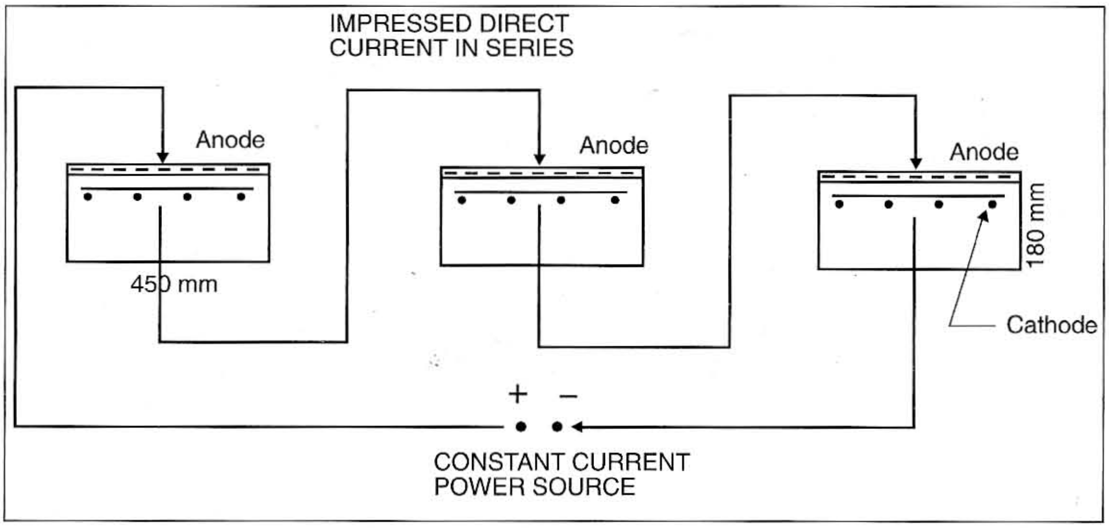


Figure 2: Electrochemical Extraction Apparatus.

The impressed current was disconnected after 56 days of electrochemical extraction and the blocks were placed outdoors to allow the reinforcement to depolarize and return to resting potentials (achieved within three months). No assessment was made of the risk of alkali aggregate reaction from the increased alkalinity around the reinforcement from the electrochemical process but the risk of hydrogen evolution was estimated from rebar potentials. A nominal figure of -1100mV (Cu/CuSO$_4$) was selected as the water stability line from the Pourbaix diagram.

RESULTS AND DISCUSSION

During the initial wet/dry cycling, rebar potentials of grade 20 and 40 concrete decreased rapidly (ie. became more negative) and within 20 days reached levels indicative of corrosion activation. Grade 60 concrete exhibited moderate rebar potentials throughout the wet/dry cycling indicating low chloride levels at the reinforcement. Rebar potentials of OPC and fly ash concrete are shown in Figure 3.

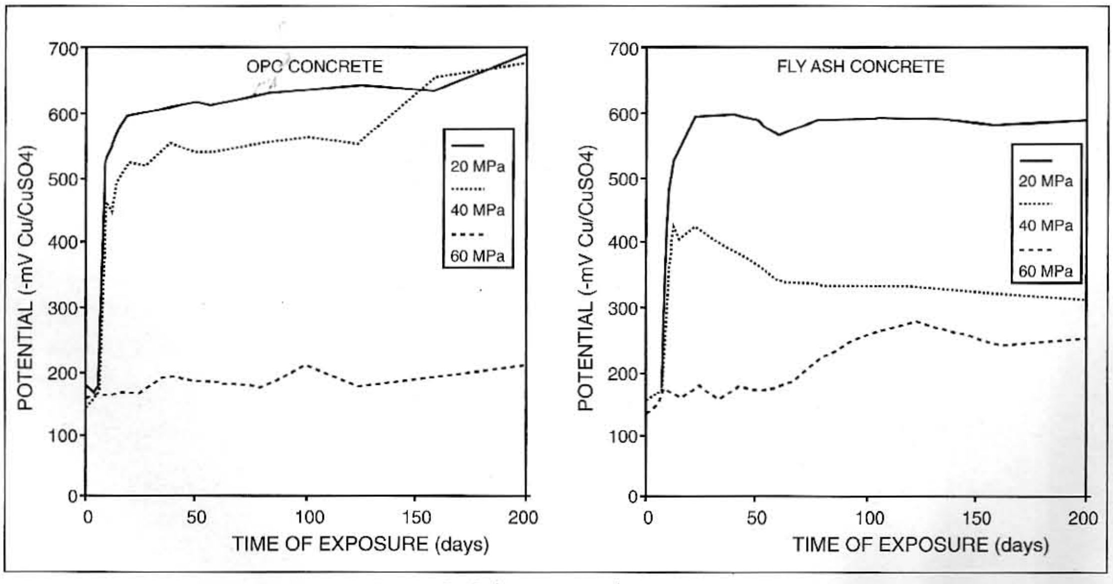


Figure 3: Rebar potentials versus time

Chloride levels at the reinforcement were found to increase consistently with time and after 200 wet/dry cycles were over 2.0% for grade 20 concrete, substantially higher than the corrosion threshold level of 0.4%. Fly ash concrete had significantly lower chloride levels than similar OPC concrete particularly when internal concentrations were compared, as was expected given the finer pore structure and superior chloride binding characteristics of the material (7). A comparison of rebar potentials and chloride levels at the reinforcement (shown in Figure 4) revealed a trend of low negative potentials (>-350mV) for chloride contents below 0.5% and highly negative potentials (<-350mV) for chloride contents above 0.5%. This finding corresponds with the generally accepted corrosion threshold level of 0.4 – 0.5% total chloride at the steel surface (8).

During the electrochemical extraction process chloride levels were found to reduce consistently with time but 56 days was not long enough to reduce chloride levels sufficiently for concretes which had high initial chloride levels (grade 20 concrete). Chloride located in the cover concrete appeared to be easily extracted but internal chloride that had diffused beyond the reinforcement before electrochemical treatment was only partly removed after 56 days extraction and further extraction would be needed to reduce chloride levels to safe values. Grade 60 OPC concrete and grade 40 and 60 fly ash concrete had low internal chloride levels at the start of the extraction process and these concretes responded well to electrochemical extraction with chloride levels being well below the threshold level after 56 days. The poor degree of success in extracting chloride from beyond the reinforcement was partly due to the relatively low cover of the reinforcement and close spacing of the bars (100mm) which restricted the electric flux paths bringing internal chlorides to the external anode. Site concrete with higher covers and larger bar spacing should provide more suitable conditions for extraction of internal chlorides. Chloride contents and rebar potentials recorded during the extraction process are shown in Table 3 while chloride profiles recorded at fourteen day intervals for grade 20 OPC concrete are shown in Figure 5.

Table 3 – ELECTROCHEMICAL DESALINATION RESULTS

SAMPLE NAME	TIME (days)	CHLORIDE (%) AT DEPTH INTO CONCRETE (mm)						REBAR POT. (-mV Cu/CuSo4)	
		0 - 15	15 - 30	30 - 45	45 - 60	60 - 75	75 - 90		
GRADE 20 OPC	0	2.48	3.76	3.46	3.66	3.91	3.45	BEFORE	692
	14	1.07	2.07	2.23	3.25	3.93	3.60		
	28	0.84	2.02	2.36	2.99	2.77	3.80	DURING	1145
	42	0.69	0.85	1.44	1.86	2.19	3.24		
	56	0.45	0.74	0.93	1.48	2.49	3.53	AFTER	382
GRADE 40 OPC	0	1.55	2.15	1.71	1.04	0.60	0.38	BEFORE	677
	14	2.06	1.29	1.72	1.31	0.96	0.55		
	28	1.04	0.90	0.91	0.78	0.36	0.17	DURING	1136
	42	0.51	0.76	0.75	0.85	0.99	0.59		
	56	1.15	1.06	0.81	0.92	0.60	0.53	AFTER	212
GRADE 60 OPC	0	1.59	0.99	0.23	0.05	0.03	0.03	BEFORE	206
	14	1.36	0.48	0.13	0.03	0.03	0.03		
	28	0.70	0.31	0.10	0.02	0.03	0.03	DURING	1123
	42	0.48	0.22	0.12	0.08	0.03	0.03		
	56	0.23	0.12	0.08	0.05	0.03	0.03	AFTER	283
GRADE 20 FLY ASH	0	2.28	3.58	2.44	0.83	0.42	0.28	BEFORE	576
	14	1.98	4.00	2.32	1.19	0.47	0.44		
	28	2.77	3.51	2.15	0.88	0.26	0.13	DURING	1171
	42	1.58	0.86	0.69	0.53	0.50	0.29		
	56	0.96	0.87	0.97	0.55	0.18	0.20	AFTER	435
GRADE 40 FLY ASH	0	2.47	1.16	0.29	0.09	0.06	0.04	BEFORE	298
	14	0.85	0.48	0.07	0.05	0.05	0.03		
	28	1.54	0.49	0.06	0.04	0.05	0.06	DURING	1082
	42	0.86	0.54	0.19	0.05	0.04	0.04		
	56	0.58	0.31	0.16	0.14	0.04	0.03	AFTER	264
GRADE 60 FLY ASH	0	1.27	0.34	0.08	0.03	0.03	0.03	BEFORE	236
	14	0.90	0.20	0.07	0.05	0.03	0.03		
	28	0.84	0.12	0.03	0.02	0.03	0.03	DURING	1122
	42	0.59	0.10	0.04	0.03	0.03	0.02		
	56	0.27	0.08	0.04	0.04	0.03	0.03	AFTER	243

Fly ash concrete responded well to electrochemical extraction with virtually all interior chloride being removed after 56 days despite the high chloride binding potential of this type of concrete. Higher driving voltages were needed for fly ash concrete compared with OPC concrete to maintain a current density of 1 A/m^2 due to the higher resistivity of fly ash concrete. Grade 20 and 40 OPC concrete and grade 20 fly ash concrete still had dangerous chloride levels near the steel after 56 days, this was due to the higher initial chloride levels of these concretes. Typical chloride profiles for OPC and fly ash concrete before and after the extraction process are shown in Figure 6.

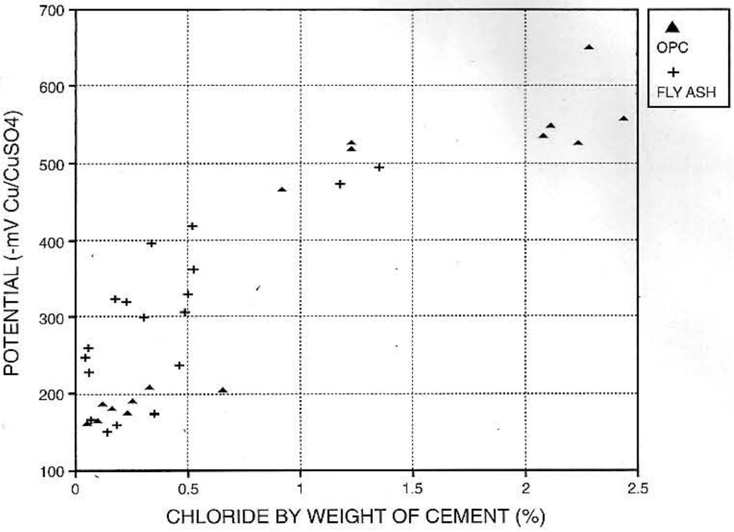


Figure 4 Rebar potentials versus chloride content at bar.

Several concrete blocks showed evidence of hydrogen evolution at the reinforcement (in the form of bubbles on the concrete surface immediately above the location of embedded bars) and rebar potentials (<-1100mV) indicated that the current density was too high for the reinforcement configuration. A more rational approach towards selecting the applied current density in terms of steel surface area rather than concrete surface area needs to be adopted. Using lower current densities for heavily chloride contaminated concrete would require an extraction period of several months to achieve sufficiently low chloride levels and so increase the cost of repairs. The increased cost of using lower current densities should be more than compensated by the reduced risk of negative side-effects in the longer-term.

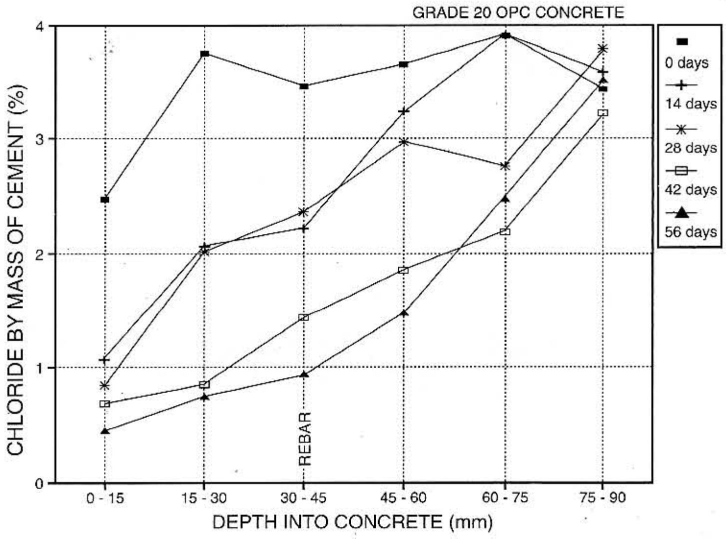


Figure 5 Chloride profiles for grade 20 OPC concrete

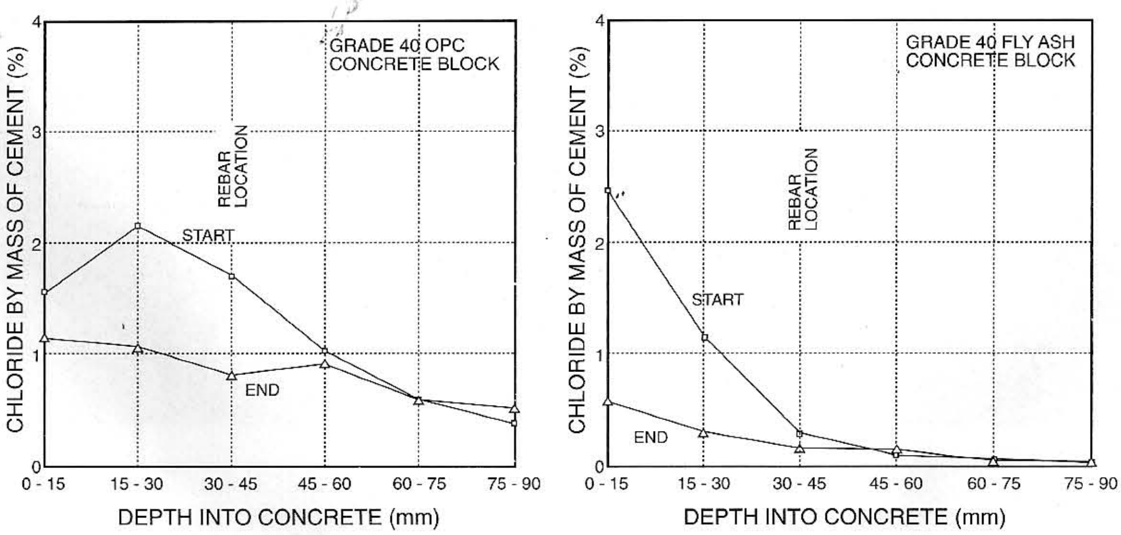


Figure 6 Chloride profiles before and after extraction

CONCLUSIONS

Electrochemical chloride extraction from laboratory concrete was found to be a feasible remedial technique which should reduce the risk of corrosion of reinforced concrete structures by lowering the chloride concentration around the reinforcement. The process should however be applied before chlorides have diffused past the reinforcement in significant quantities and major corrosion damage has occurred. Chloride ions were successfully removed from OPC and fly ash concrete but extraction periods of greater than two months may be required for some concretes. The current density of 1 A/m^2 of concrete surface area appeared to be excessive for the test specimens and a more rational means of specifying the current density in terms of steel surface area should be used.

Careful monitoring of driving voltages and rebar potentials is essential to prevent potentially harmful side-effects such as hydrogen evolution at the reinforcement. A better fundamental understanding of the effect of electric fields on the ionic migration of chlorides through concrete would provide useful information particularly as the time needed to decrease chloride levels below a certain threshold could then be estimated theoretically (9). Modelling of the physical and chemical effects caused by the application of an impressed current would also assist in optimizing parameters such as current density, anode mesh and electrolyte. Further development and refinement of the technique is possible and should be undertaken to improve the effectiveness and reliability of this concrete repair technique.

REFERENCES

(1) Elsener, B., Molina, M. and Bohni, H., 'The electrochemical removal of chlorides from reinforced concrete', *Corrosion Science*, 35(6), 1993, 1563-1570.

(2) Schiessl, P., 'Recommendations for repair strategies of concrete structures damaged by reinforcement corrosion', *Materials and Structures*, 27(171), 1994, 415-436.

(3) Tritthart, J., Pettersson, K. and Sorenson, B., 'Electrochemical removal of chlorides from hardened cement paste', *Cement and Concrete Research*, 23(5), 1993, 1095-1104.

(4) Hansson, I.L.H. and Hansson, C.M., 'Electrochemical extraction of chlorides from concrete. Part 1 – A quantitative model for the process', *Cement and Concrete Research*, 23(5), 1993, 1141-1152.

(5) American Society for Testing and Materials, 'Test method for half-cell potentials of uncoated reinforcing steel in concrete', *ASTM C876-91*, Philadelphia, 1991.

(6) British Standards Institute, 'Chloride content determination for concrete', *BS 1881 Part 124*, 1988.

(7) Arya, C., Buenfeld, N.R. and Newman, J.B., 'Factors influencing chloride binding in concrete', *Cement and Concrete Research*, 20(2), 1990, 291-300.

(8) Browne, R.D., 'Marine durability survey of the Tongue Sands Tower, Concrete-in-the-Oceans, P4 Final Report', *Cement and Concrete Association*', London, 1980.

(9) Andrade, C., 'Calculation of chloride diffusion coefficients in concrete from ionic migration measurements', *Cement and Concrete Research*, 23(3), 1993, 724-742.