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MECHANICAL PROPERTIES OF ANODIC AND CATHODIC REGIONS OF ECE TREATED CONCRETE

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ABSTRACT

This paper describes a laboratory program undertaken to examine the macrostructural implications of applying electrochemical chloride ion extraction (ECE), to concrete structures. An examination is made of the effect of ECE and, thus ionic redistribution on the anodic and cathodic regions of treated concrete. Test cylinders were cast from two concrete batches containing, respectively, 1.7% and 3.0% chloride ion (as NaCl) by weight of cement. The electrochemical treatments were based on two applied current densities of 1.0 A/m^2 and 3.0 A/m^2 of concrete end surface, and thereafter all cylinders were sectioned into their anodic and cathodic halves for testing. Post-ECE chloride ion contents, and the alkali metal ions of sodium and potassium were mainly concentrated in the anodic and cathodic halves of the concrete cylinders, respectively. Although the softening effect of ECE was small, it was found to be greater for the cathode than anode region, and also the concrete density and compressive strength were consistently higher in the cathode halves. In spite of the decrease in concrete compressive strength as the total applied current density increased, it is predicted that any effect on the structural integrity of a candidate structure will be small.

Introduction

Electrochemical chloride extraction (ECE), from steel reinforced concrete structures is being considered by the concrete industry, especially transportation authorities, parking garage owners, and marine facility operators, among others, as a viable alternative rehabilitation method to cathodic protection (CP). Though the principles of ECE and impressed current CP are very much the same, the choice is simply a matter of cost and simplicity of application. The basic (electrochemical) difference, however, is that ECE employs a very high current density for a few weeks or days whilst CP requires a relatively smaller current density for the remaining service life of the structure. The main features of ECE application to steel reinforced concrete are well known and have been extensively detailed elsewhere (1-9).

The mechanism governing ionic transport during ECE is mainly electro-diffusion although other physico-chemical processes such as ionic diffusion, bulk electrolyte flow by electro-osmosis and direct absorption contribute to both ionic redistribution and electrolyte penetration. Ionic migration during ECE involves transport of Cl^- ions and other anions (e.g. OH^-, CO_3^{2-}, SO_4^{2-}) away from cathode region and towards the anode, while cations (mainly Ca^{2+}, K^+, and Na^+) migrate to the cathode region. The ions migrate in relative proportion to their transference (or, transport) numbers, which is indicative of the amount of total polarizing current carried by a migrating ion. Hence the level of ionic redistribution achievable under ECE is a function of each ion's mobility as well as the concrete's resistive characteristics.

Current research efforts focus mainly on durability aspects of the ECE process. As with any new technique, many aspects of ECE application including the post-treatment effect on the concrete structural integrity remain unclear. In this study, the effect of ECE on the macrostructural and mechanical features of treated concrete is examined. The paper presents the results of a laboratory investigation on the ECE effect on the compressibility of the anodic and cathodic regions of the bulk concrete in relation to its impact on concrete durability. Desalination of concrete pore structure usually will have some effect on the structure of the cement matrix, hence the effect of redistribution and dissolution of electro-migrating ions on cement paste softening, concrete permeability, and variations in concrete strength are examined. Also a correlation of experimental results with other research findings is carried out to determine possible durability problems that can be associated with ECE application.

Method

Plain concrete cylinders 200 mm long and 100 mm diameter, were cast using readymix concrete as shown in Table 1. Two premixed Cl^- ion contents of 1.7% and 3% by weight of cement (as NaCl) were used, and these are designated as batches #1 and #2, respectively. Three sets of five concrete cylinders were cast from the two concrete batches for electrochemical treatment. The ECE system was in form of two stainless steel plates (as electrodes) wrapped with cellulose

TABLE 1

Concrete Mix

OPC Type 10 Cement	432 kg/m^3
Sand	600 kg/m^3
Pea stones, 10mm max	1150 kg/m^3
Water	130 kg/m^3
ProAir AEA	6 %
Protard water reducer	1.0 ml/kg cem.
Superplasticizer	2.8 ml/kg cem.
Chloride ions	1.7% & 3.0% (cem. wgt.)

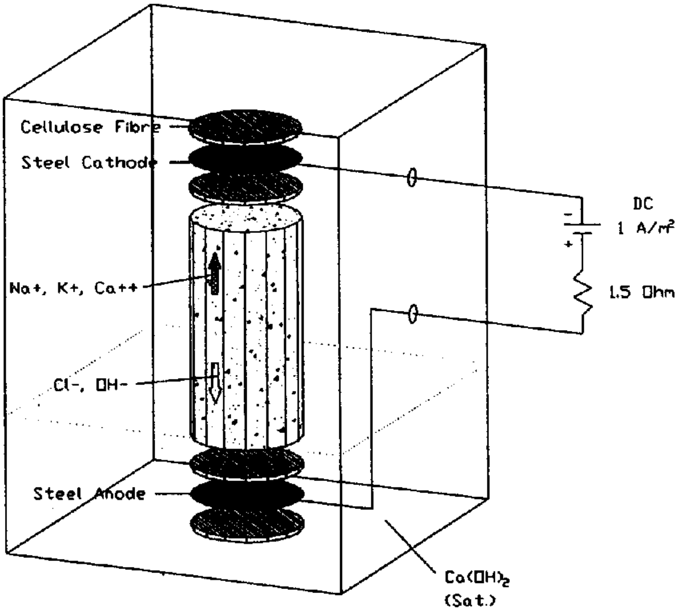

FIG. 1.
ECE setup and ionic transport direction in concrete.

fibre and placed at each end of the concrete cylinder as shown in Figure 1.The electrolyte was saturated calcium hydroxide solution prepared from laboratory grade $Ca(OH)_2$, and deionized water. The anode was electrically coupled to the positive terminal of a rectified (and filtered) DC power source, and the circuit completed by connecting to the cathode plate with wires incorporating 1.5Ω shunts for monitoring applied current. Two sets of each concrete batch, consisting of five cylinder specimens having similar Cl^- ion content, were electrochemically treated by cathodic polarization using two direct current densities of about 1.0 A/m^2 and 3 A/m^2 of concrete surface covered by anode plate. The remaining set of specimens of each concrete batch were stored in plastic bags and served as control. ECE application was continuously operated without interruption for eight weeks. It is recognized, that there are bound to be variations between different batches of concrete both from the point of view of ECE performance and mechanical properties although such variations between concreting batches are observed under real conditions.

After ECE application, all concrete cylinders were cut into their anodic and cathodic halves for both ionic profiling and mechanical testing. Compressive strength tests as per ASTM C39-86 were carried out with loading discontinued when the maximum load was reached and after the first few cracks. This was to allow 20 mm thick concrete slices to be obtained at mid-depth of each sample for ionic profiling. The Cl^- ion profiles were determined by potentiometric titration with silver nitrate using protocol outlined in AASHTO T-260. The free chlorides were digested in hot water while laboratory grade concentrated nitric acid (HNO_3) was used for the total chlorides. Atomic absorption spectrophotometry was used in analysing the cations of interest, i.e., sodium (Na^+) and potassium (K^+) ions. Compressive strength and density determinations were carried out for all concrete batches, and the average result of each set of test is reported. The concrete compression test results were corrected for size effect (due to reduced length/diameter ratio) as per ASTM C42-87.

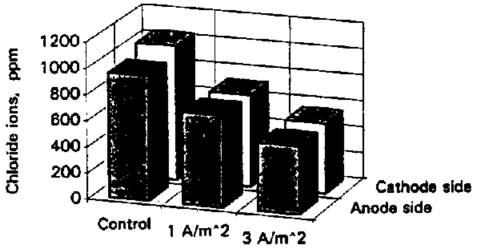

FIG. 2.
Total Cl- ions in concrete batch #1.

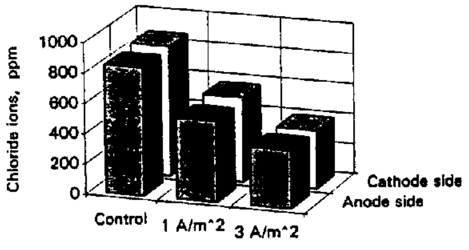

FIG. 3.
Free Cl- ions in concrete batch #1.

Results

Concrete is an ionic conductor and applied current flows as a result of the movement of dissolved ions in the cement paste pore solution. During ECE application, the applied electric field gradient initiates ionic transport causing substantial redistribution of both anions (i.e., Cl^-, OH^- and SO_4^{2-} ions, etc) and cations (i.e., Na^+, K^+ and Ca^{2+} ions, etc) from the cast-in levels. In concrete structures subjected to ECE application, Cl^- ion migration effect is usually most pronounced in the concrete cover nearest the anode system and in the vicinity of cathodic reinforcing steel. Also substantial accumulations of cations occur mainly in the cathode steel regions. In uncarbonated concrete that has undergone sufficient hydration such as the specimens, complex formation of chloroaluminate compounds from the reaction of free Cl^- ions and cement aluminate hydrates, C_3A and C_4AF, tend to break down under ECE application thereby replenishing the free Cl^- ion levels in the cement pore solution (6,10). Hence the need in this study to test the treated concrete within the first 24 hours of terminating the ECE process when any resulting harmful effect is expected to be most severe.

Figures 2 and 3 show the chloride ion contents of the ECE treated specimens for concrete batch #1 premixed with 1.7%Cl^- ion (by cement weight). There was a smaller absolute reduction in Cl^- ion content at the sampled points in specimens treated at a current density of 1.0 A/m^2 compared with those treated at 3 A/m^2 of concrete surface. The reduction in total

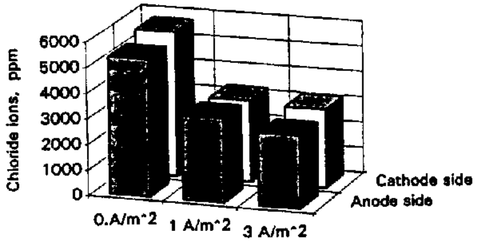

FIG. 4.
Total Cl- ions in concrete batch #2.

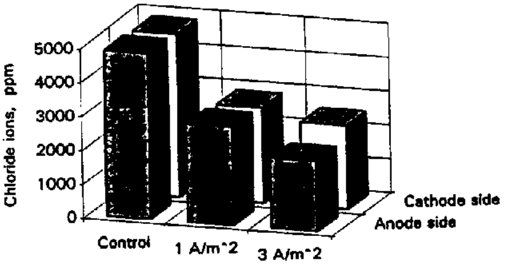

FIG. 5.
Free Cl- ions in concrete batch #2.

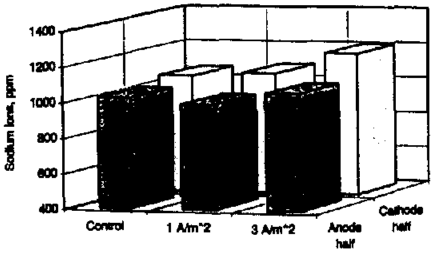

FIG. 6.
Sodium ions in concrete batch #1.

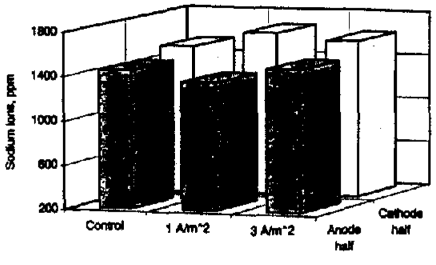

FIG. 7.
Potassium ions in concrete batch #1.

(acid-soluble) Cl$^-$ ion content (Figure 2) for the anode half was about 26% at current density of 1 A/m^2, and 45% at 3 A/m^2, compared with about 32% at 1 A/m^2, and 48% at 3 A/m^2 for the cathode half. Similarly in concrete batch #2 (Figures 4 and 5) premixed with 3.0% Cl$^-$ ion (by cement weight), the residual Cl$^-$ ions in the anode section reduced by about 41% at 1.0 A/m^2 of applied current density and about 47% at 3 A/m^2, which approximates the ionic levels in the cathode section with about 44% reduction at 1.0 A/m^2 and 46% at three times the applied current density. The reduction trend in ionic percentages were approximately the same as for the free Cl$^-$ ions although the differences were in general smaller.

In Figures 6 - 9, the accompanied redistribution of alkali ions during the ECE process shows somewhat greater accumulations in the cathode half than the anode half. In the specimens of concrete batch #1 (Figures 6 & 7), the 'total alkali' (i.e., Na$^+$ + K$^+$) ions for the anode half showed a 5% decrease from the initial (control) levels based on a current density of 1 A/m^2, although an increase of about 3% at 3 A/m^2 was observed. Compared with the cathode half, the alkali ion content showed an increase of 6% at the current density of 1.0 A/m^2, and 8% at three times this current density. For concrete batch #2, the 'total alkali' ions increased by about 9% at 1.0 A/m^2 and 19% at 3.0 A/m^2 current densities in the anode half, compared with about 24% increase at 1.0 A/m^2 and 22% at 3.0 A/m^2 for the cathode half. As expected, the significantly greater accumulations of alkali ions as found in the cathode halves when considered with the moist conditions associated with the electro-diffusion, can provoke the onset or exacerbate on-

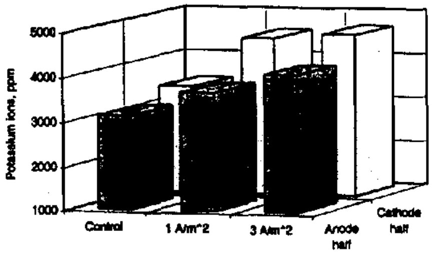

FIG. 8.
Sodium ions in concrete batch #2.

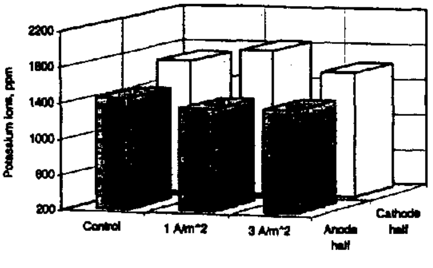

FIG. 9.
Potassium ions in concrete batch #2.

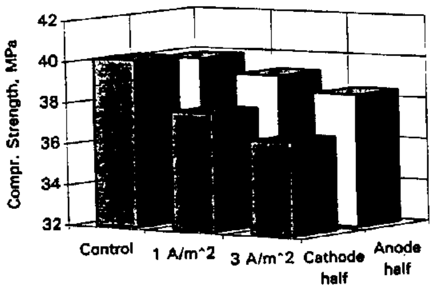

FIG. 10.
Concrete compr. strength for batch #1.

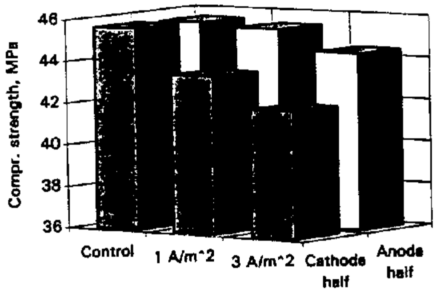

FIG. 11.
Concrete compr. strength for batch #2.

going alkali-aggregate reactions (AAR). Rock types that are prone to AAR such as chert, shales and limestone are often found in sufficient quantities in both fine and coarse aggregate components of concrete. In a previous ECE study, concrete paste degradation was observed although such effect was attributed to chemical attack (4).

In Figures 10 - 13, the influence of applied current density on the compressive strengths for both concrete batches illustrate varying features. The average compressive strength of the concrete specimens is reported with the standard deviation of the set of five specimens tested to determine each strength value (Table 3). Concrete batch #1 showed comparatively lower compressive strength than batch #2 at all applied current densities and admixed chloride ion contents. The ECE effect was somewhat more pronounced in the cathode half of the concrete specimens. The specimens of both concrete batches which were treated at an applied current density of 1.0 A/m^2 showed larger variabilities as indicated by their standard deviations than specimens treated at the higher current density. Since chlorides act as accelerating admixtures in concrete, the different values may be the result of this increased Cl$^-$ ion content in the concrete batches in addition to normal variabilities. Moreover, concrete batch #2 showed a higher strength than batch #1 even at the same w/c ratio and cement content.

In Figures 12 and 13, the concrete densities of the anode and cathode halves of specimens of all concrete batches show the effect of electro-diffusion in terms of accumulation of species

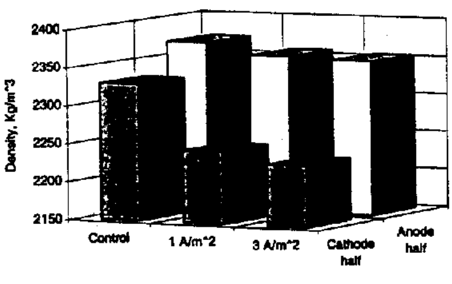

FIG. 12.
Concrete density for batch #1.

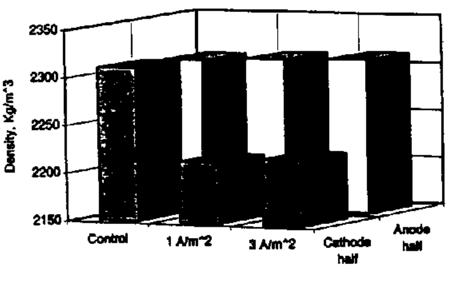

FIG. 13.
Concrete density for batch #2.

in the anode half of all ECE specimens than in the cathode half concrete. This is the case irrespective ofthe applied current density used in the electrochemical treatment. These concrete density values indicate small comparative changes (Figures 12 & 13) for the anode and cathode sections of the test specimens, averaging about 1% of the control specimen values. However at each current density and admixed Cl^- ion content, the cathode half of each specimen was less dense than the anode half by as much as 100 Kg/m^3 of concrete. This is a difference of about 5% at each applied current density between the concrete densities of the respective halves of the ECE specimens (Table 5). In both concrete batches the concrete densities of the anode section was more or less the same, although it was about 50 Kg/m^3 of concrete higher in concrete batch #1 than in #2.

Discussion

The basic fact that the effect of applied current density on ionic transport can be influenced by the concentration and mobilities of the dissolved ions of the concrete's pore solution is clearly indicated in the Cl^- ion extraction regime although not as strongly as it influenced the 'total alkali' ions. This is evident at the level of applied current density used in this study, especially as the large quantity of charge required in systems operated at 3.0 A/m^2 show a pronounced effect but the difference with those treated at a current density of 1.0 A/m^2 is not significant. A possible cause of this is the comparatively small proportion of the total electric charge passed that is actually available for extracting Cl^- ions from concrete in relation to that portion of charge used by other migrating anions because of their higher transport numbers. It follows then that ECE performance of a candidate structure with respect to chloride removal may not necessarily depend on the level of applied current density but rather on the total charge passed (i.e., applied current density spread over the treatment duration).

The greater reduction in Cl^- ion contents observed in specimens containing higher initial chloride contents and/or treated with high applied current density may have structural implications. The concrete compressive strengths indicated greater changes for specimens treated at 3.0 A/m^2, a trend that is more pronounced in the cathode side of such specimens and increases with chloride contamination. It is believed that a consequence of cation migration to the cathode region is that because of the small ionic radius of Na^+ and K^+ ions, they tend to electro-diffuse heavily solvated with a sheath of water molecules (11,12). A possible structural implication is that since cationic electro-diffusion during ECE can cause wetness in the cathode regions, differential softening effect between the cathode and anode regions can easily occur. Another explanation for the variabilities in such specimens may well be the effect of water hydrolysis drying up parts of cathode regions as water molecules are electrolytically reduced during ECE according to the following equation:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (1)$$

It is also possible for OH^- ions produced at the cathode region to electro-diffuse away from such regions due to prevailing electric field gradient. From electrochemical considerations, hydroxyl ions can be fully repelled from the cathode region since an OH^- ion has a transport number that is far greater than that of Cl^- ion. Typical ionic mobilities in concrete at 25°C for anions and cations usually encountered in ECE studies are shown in Table 2, and are three orders of magnitude lower than in aqueous medium (11,12). The ion mobilities indicate the pattern of

TABLE 2

Ion Mobilities (x $10^{-4} cm^2V^{-1}s^{-1}$)

Ion	OH^-	Cl^-	Na^+	K^+	Ca^{2+}	H^+
λ_o	20.5	7.91	5.19	7.62	5.95	34.9

possible amperage distribution during electrochemical treatment of chloride contaminated concrete. The ionic mobilities of H^+ and OH^- are much higher than that of other species because of their structural affinity with water molecules.

It then follows that the cathode regions of concrete specimens subjected to ECE can either be wet or dry depending on the prevailing electrochemical process. In addition to introducing variabilities in the mechanical properties of the anode and cathode regions of such concrete structures, rebar corrosion can similarly be influenced. Despite a high concentration of cations around the rebar, a wet concrete with sufficient residual Cl^- ions can indicate probable corrosive conditions around the rebar. Conversely, dry concrete conditions around the rebar even with an inefficient ECE application can indicate false passive conditions. Though, these structural and electrochemical problems can easily dissipate within a few days or months after ECE application, the effects are perceived to be important within the first twenty-four hours after terminating the treatment.

Concrete cylinder compressive strengths show different effects of ECE depending on the concrete location with respect to the polarizing electrodes. In absolute terms, the cathode half of each concrete test specimen consistently showed both lower strength and density values (~ 5%) relative to the anode half. These changes in concrete properties as shown by the compressive strength (Figures 6 & 7) and density (Figures 8 & 9) were more pronounced in specimens treated with higher applied current density and/or premixed with higher Cl^- ion concentration. It is remarkable, though, that electrochemically treating concrete with an applied current density of about 1.0 A/m^2 has little effect on cement paste macrostructure. When higher applied current densities are used, ECE application is found to affect, to some degree, the concrete's mechanical

TABLE 3

Concrete Compressive Strength (MPa)

Applied Current	Concrete batch #1		Concrete batch #2	
	Anode	Cathode	Anode	Cathode
Control	39.9±1.7	40.2±2.3	45.6±0.3	45.6±0.6
1.0 A/m^2	39.2±2.3	37.7±6.1	44.7±5.8	43.5±3.6
3.0 A/m^2	38.4±1.8	36.5±2.6	44.2±3.3	41.9±2.0

TABLE 4

Concrete Density (kg/m^3)

Applied Current	Concrete batch #1		Concrete batch #2	
	Anode	Cathode	Anode	Cathode
Control	2357±29	22294±29	2307±42	2210±4
1.0 A/m^2	2353±34	2229±19	2310±15	2213±52
3.0 A/m^2	2372±16	2230±9	2312±52	2218±4

properties as tested. Although in relation to the structural integrity, the reductions in concrete compressive strength and density are small even by factoring in the standard deviation of individual strength test result from the mean value (Table 3). However, in practice the contributory effect of the concrete's inhomogeneity, and the associated variabilities inherent in concreting from different batches are recognised. The practical significance of the test results, however, is that since conventional repairs of chloride contaminated concrete will often involve removal of sound concrete sections of relatively high compressive strength, application of ECE can thus be conveniently used as an alternative rehabilitation technique for such structures without initiating excessive damage.

In general, the ionic reductions in all specimens of both acid- and water-soluble chlorides, and the high concentration of alkali metals in the cathode region may be advantageous, in certain situations, for the restoration of passive conditions of any embedded reinforcing steel. Moreover, a correlation of measurements of concrete properties such as freeze-thaw resistance, porosity, water absorption, oxygen diffusivity/permeability, and accelerated chloride ion diffusion, as investigated by other workers, show varying effects of ECE application on concrete cover (which is the anode region). Freeze-thaw resistance tests indicate that ECE treated concrete has lower water absorption than non-treated control specimens (13), although mercury porosimetric studies indicate increase in porosity mainly in the lower pore size range of 1 μm (14). Despite observed variabilities, the non-treated concrete shows increased trend of oxygen permeability or diffusivity than ECE treated concrete mainly because of its susceptibility to freeze/ thaw damage. Also since electro-diffusion of cations (mainly Na^+ and K^+ ions) during ECE reduces the solubility of $Ca(OH)_2$ in the cement matrix, scanning electron microscopy (SEM) studies show a preferential precipitation and redistribution of $Ca(OH)_2$ in ECE concrete, which may have caused its increased resistance to molecular transport (13).

Summary

1. The effect of ECE application on the mechanical properties of concrete are found to be small. In absolute terms, concrete density and compressive strength were found to be consistently higher (~ 5%) in the anode region than in the cathode region, although the differences appear to be real they are not far from the range of standard deviation permitted for concrete tests.

2. Application of ECE to chloride contaminated concrete with relatively high compressive strength appear to be a better option than conventional repair techniques that utilize concrete replacement. Concrete mechanical properties and microstructure are not significantly harmed by such electrochemical treatment.
3. ECE performance is found to be less destructive for concrete electrochemically treated with applied current densities of about 1.0 A/m^2 of concrete surface. Higher applied current densities (about 3.0 A/m^2) appear not beneficial to concrete durability in view of greater reductions in the mechanical properties tested. Also, the concrete in the cathode regions are prone to softening resulting in reduced density, and the accumulations of substantial cations can provoke harmful reactions that can alter the composite nature of the reinforced concrete.
4. Higher reductions in chloride ion contamination and more alkali metal ion accumulations (both in the range of about 10% to 50%), are observed in specimens treated with higher applied current densities. It is predicted that the observed changes implies that concrete durability will not be adversely affected by electrochemical treatments that are based on applied current densities in the range of 1.0 A/m^2 of concrete surface.

Acknowledgement

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