ELECTROCHEMICAL CHLORIDE EXTRACTION ON PRESTRESSED CONCRETE STRUCTURES

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ABSTRACT

Chloride attack is a major cause of deterioration of reinforced and prestressed concrete structures. Chloride contamination can occur through the application of de-icing salts, from cast-in chlorides (accelerating admixtures) or through contact with seawater in marine environments. Traditionally, the repair of chloride contaminated concrete involves the breaking out and removal of all contaminated concrete, even though it may be otherwise perfectly strong. Electrochemical chloride extraction (ECE) is the removal of chlorides from the vicinity of the reinforcement leaving all sound concrete intact. ECE involves the passage of a relatively high current (1-2 A/m^2) for a short period (3 to 5 weeks). The chloride ions migrate away from the reinforcement towards the external anode. The use of ECE on normally reinforced structures is quite common and generally accepted. When considering hydrogen embrittlement of prestressed steels, the critical threshold for hydrogen generation in concrete is - 0.9 V_{SCE}. This threshold is known to be exceeded during ECE and atomic hydrogen is created at the surface of the cathodically polarised reinforcement. Some high strength steels used in prestressed concrete structures are therefore susceptible to the absorption of hydrogen and can suffer brittle fracture. Consequently, the application of electrochemical chloride extraction on prestressed concrete structures is avoided. An experimental study was conducted on small prestressed concrete specimens containing cold drawn and hardened steel strands to investigate the feasibility of using electrochemical chloride extraction on prestressed concrete structures. Hydrogen embrittlement occurred in only one steel sample treated with a K_2CO_3 electrolyte.

INTRODUCTION

Many structures, such as bridges and car parks are affected by chloride induced reinforcement corrosion either through contact with sea water, as in marine environments, or through the application of de-icing salts. It is estimated that £500 million are spent annually on maintenance and repair of structures damaged through the effects of chlorides (Hobbs, 1996).

The main causes of reinforcement corrosion are poor detailing and poor workmanship (Wouters et al, 1999). Poor workmanship in the form of poor compaction and low cover perhaps have the greatest effect on concrete quality since concrete pore size and chloride concentrations determine the speed of the diffusion process. Even in good quality concrete, chlorides will eventually reach the reinforcement and initiate corrosion.

There are two main types of reinforcement corrosion:

- General corrosion i.e. the uniform corrosion of the steel surface in carbonated concrete.

- Pitting corrosion i.e. the breakdown of the passive film in small spots on the steel surface with fast propagation. Chloride induced pitting corrosion can be initiated even when the concrete provides a pH value above 12 i.e. in un-carbonated concrete.

Pitting corrosion is the most dangerous form of corrosion in prestressed and post-tensioned concrete because steel section is reduced very quickly in corrosion pits and the remaining steel surface remains unaltered and shows no sign of corrosion. The propagation of corrosion pits is accelerated when the steel is stressed or in favourable environmental conditions. The reason for pitting corrosion in alkaline concrete lies in the formation of a water soluble iron-chloride salt which liberates hydrogen thereby lowering the pH- value in corrosion pits. The iron-chloride salt subsequently dissolves and is reduced to iron oxide.

Traditionally, chloride-contaminated concrete is broken out from around the reinforcement and replaced by polymer modified repair mortars. However, there is a danger of the formation of macro-cell corrosion if not all chloride contaminated concrete is removed (Page, 2000). Electrochemical chloride extraction (ECE) removes the chlorides from the vicinity of steel and at the same time increases the alkalinity at the reinforcement through the formation of hydroxides and the enrichment of alkali-ions (Hettiarachchi, 1994). Therefore, ECE treatment not only stops the corrosion processes but also creates the conditions where a passive film is reformed on the steel surface.

HYDROGEN EMBRITTLEMENT IN HIGH STRENGTH STEELS

Hydrogen is produced on the surface of reinforcement in concrete during electrochemical processes such as corrosion, cathodic protection or electrochemical chloride extraction. For concrete under atmospheric exposure condition where as much oxygen diffuses through the bulk as is consumed by the electrode process, the reaction at low current densities typical for cathodic protection is:

$$O_2 + 2H_2O + 4e^- = 4OH^-$$
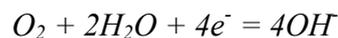
The hydrogen evolution reaction occurs after the oxygen is consumed (Mietz, 1998) and is typical for high current densities as are applied during ECE:

$$2H_2O + 2e^- = H_2 + 2OH^- \text{ (Volmer reaction)}$$

$$H_{ads} + H_3O^+ + e \leftrightarrow H_2 + H_2O \text{ (Heyrovský reaction)}$$

Both reactions produce one mole of hydroxide ions for each Faraday of charge (Bennet et al, 1994). As can be seen from the above equations the presence of oxygen is crucial to the suppression of hydrogen generation on the cathode. This means that even at lower potentials than those given in the Pourbaix-Diagram, hydrogen generation is possible once the oxygen is consumed.

Corrosion is an electrochemical process and during electrochemical processes hydrogen is generated, which may cause hydrogen embrittlement (Funahashi, Young, 1996). It is stated that hydrogen can be generated in the presence of chloride ions. Initially, chlorides break down reinforcement passivity and at damage locations, corrosion pits occur. In the pits the metal (M) dissolves anodically, with the release of valence electrons and the formation of M^{n+} ions which, together with the chlorides, form soluble corrosion products M^+Cl^-. With the hydrolysis of these products, atomic hydrogen is generated: $M^+Cl^- + H_2O = MOH + H^+Cl^-$. The formation of hydrogen atoms in the pit causes an increase in acidity (pH 3.5). Due to the lack of oxygen at the cathode, hydrogen ions act as depolarisers in the pit: $H^+ + e \rightarrow H_{ad}$ and $H_{ad} + H_{ad} \rightarrow H_2$. The recombination of hydrogen does not take place entirely and at favourable locations the adsorbed hydrogen migrates into the steel where it can cause brittle fracture (Vehovar et al, 1998).

Despite extensive research on the subject, the mechanism of hydrogen embrittlement remains uncertain. As matrix concentrations are very low the concentration of hydrogen in the steel is typically of the order of one hydrogen atom for every 10^6 iron atoms. Two possible effects of hydrogen can be identified:

- The strength of the metal-metal bond is decreased by hydrogen, enabling brittle fracture. Surface energy and decohesion models are based on this premise.

- The stress that is required to produce dislocations from the crack tip is increased by hydrogen. Consequently ductile fracture is made more difficult.

Currently, there are several theories to explain hydrogen embrittlement. The *planar pressure theory* suggests that hydrogen gas in the voids creates high pressure thereby causing fracture failure. Other defects in the metal contribute to the effect. However this theory cannot explain the hydrogen embrittlement of steels in equilibrium with hydrogen at a very low pressures. The role of hydrogen in *decohesion models* is to weaken the atomic steel bonds. Cleavage crack growth and grain boundary separation is the mode of failure according to this model. However, transgranular cracking cannot be sufficiently explained by the decohesion theory. The surface energy of a newly formed crack is lowered by hydrogen. The stress intensity necessary for brittle fracture is thereby reduced. This failure mechanism is proposed by the *surface energy theory*. To be effective in lowering the energy required for fracture, hydrogen adsorption must occur at the same time as the fracture. There is almost no evidence for the *hydride formation* in steels. However, this mechanism might be of importance for the induction of cleavage by a brittle surface hydride film. *Local plastic theories* describe a mechanism that involves the dislocation emission at the crack tip. The crack growth thereby occurs by a localised plastic deformation at the crack tip (Parkins, 1994).

Hydrogen may enter steel from the gas phase or from an aqueous solution when substances containing hydrogen are reduced electrochemically. Hydrogen embrittlement originates in the thin outer surface layers of high strength steels (Sastri, 1995). The process important for hydrogen embrittlement due to ECE, is where atomic hydrogen is created by the Volmer reaction. The pH value of the solution determines the type of reaction and in a more alkaline solution electrocatalysis of water into hydroxyl ions and atomic hydrogen protons is the dominant process. The entry of atomic hydrogen into the steel from the surface adsorbed state is controlled by the diffusion rate and at crack tips, where hydrogen can be transported into the bulk by dislocation motions, this enables very high rates of hydrogen entry. The hydrogen concentration below the surface is directly related to the surface concentration or coverage because the hydrogen entry reaction is in equilibrium. Hence, the balance of the Volmer reaction and the Heyrovský reaction control the rate of entry of hydrogen into steel. Increases in cathodic current raise the subsurface hydrogen concentration by the square root of the cathodic current.

Hydrogen exists in metals in its monatomic form and is described as atomic hydrogen. It occupies the tetrahedral site in the body centred cubic (bcc) iron lattice. Hydrogen atoms are also attracted to defect-sites in metal, the so-called traps. Important trap sites in steel are phase boundaries, dislocations, voids and non-metallic inclusions. Grain boundaries trap very little hydrogen unless there is segregation due to carbon or other impurity atoms.

Trap types can be classified into four categories:

- Saturable, where the number of sites for hydrogen atoms is fixed;

- Non-saturable, where the number of sites for hydrogen atoms in the trap varies according to the fugacity;

- Reversible, where the trap binding energy is small and the hydrogen can escape as well as entering the trap;

- Irreversible, where the trap binding energy is large, and hydrogen will not leave the site at ambient temperature.

According to Suresh (1998), the inducement of hydrogen embrittlement involves three key steps:

- The adsorption of hydrogen on the freshly created slip step or fatigue crack surface;

- The dissociation of the hydrogen molecule into atomic hydrogen;

- The transport of hydrogen by random walk diffusion through the lattice, grain boundaries or by transport along with mobile dislocations in plastically deforming regions to critical sites in the lattice or to regions of high triaxial stress ahead of the crack tip.

Hydrogen in traps consists of molecular hydrogen H_2 in the void and adsorbed hydrogen on the walls of the void. High pressures may develop due to the trapped hydrogen. This may lead to the growth of cracks around the void. Such cracks develop around non-metallic inclusions, which have been flattened by rolling (Lukito, 1997).

Elastic constants of steel do not change because of hydrogen and the effect on yield stress is unpredictable as it may increase as well as decrease. Plastic behaviour of iron and steel is influenced but the effects are rather complex since hydrogen may harden or soften the material according to the structure and the mode of slip. Hydrogen is of the utmost importance in the creation of brittle fracture where the steel would normally behave in a ductile fashion. Concentrations of less than 1 ppm of hydrogen may cause embrittlement of high strength steels (Cottis, 1994). As the strength of steel increases, the damage due to dissolved hydrogen tends to become more intense (Kishtal, 1984). Although grain boundaries do not act as major sites for trapping of hydrogen, segregation of impurities and carbide precipitation at the boundary will alter the behaviour. Small changes in tempering treatment can give large variations in hydrogen embrittlement resistance. Therefore steels that are hardened by cold-working show a better resistance compared with quenched and tempered steels (Slater 1983). It has been indicated that when the rolling direction of the steel is perpendicular to the tensile axis, the steel is more prone to hydrogen embrittlement due to the presence of elongated non-metallic inclusions in the matrix (Tsuboi, 1996). Conversely, since the phase boundaries of cold-drawn perlitic wires (BS 5896) lie parallel to the tensile axis, they may incorporate large quantities of hydrogen without suffering from brittle fracture (Cottis, 1994).

RESEARCH SIGNIFICANCE

Electrochemical chloride extraction is a well-established procedure for the removal of chlorides from ordinary reinforcement. Its application on structures containing high strength steels has been questioned in the past because of the danger of hydrogen embrittlement. The phenomenon of hydrogen embrittlement during ECE has not been well studied and a review of the few items of literature on the subject showed inconsistency of published results. However, if ECE and other electrochemical processes could be applied to prestressed and post-tensioned structures there would be considerable economical benefits.

EXPERIMENTAL PROGRAMME

Six prestressed concrete specimens were cast at the workshop of the Breton Group Ltd., Belfast and temperature cured for 48 hrs. The 3-day and 28-day compressive strengths of the concrete were obtained to calculate the level of prestressing of the wires in the concrete. After initial heat curing the samples were transported to the concrete laboratory of the University of Ulster and further cured at ambient temperature at a relative humidity of 55%. The mix proportions per 1 m³ of concrete consisted of 182 kg mixing water, 460 kg cement CE 42.5 (w/c ratio 0.4), 755 kg sand, 391 kg fine aggregate, 586 kg coarse aggregate and 11.37 kg of sodium chloride. The strands were prestressed to 80% of their ultimate tensile strength.

To quantify the hydrogen uptake during the ECE phase, two hydrogen oxidation cells were installed on each of the specimens and hydrogen induced current flow was measured.

The samples were not corroded to allow the effects of hydrogen generated during ECE to be investigated separately from the effects of any corrosion process.
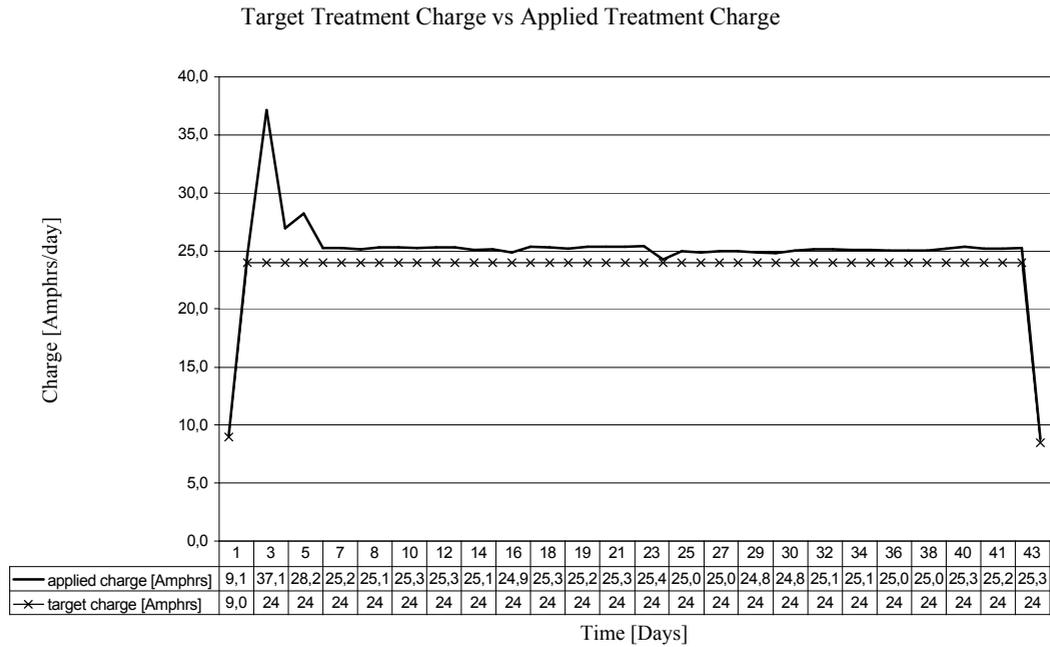
Target Treatment Charge vs Applied Treatment Charge

	1	3	5	7	8	10	12	14	16	18	19	21	23	25	27	29	30	32	34	36	38	40	41	43
applied charge [Amphrs]	9,1	37,1	28,2	25,2	25,1	25,3	25,3	25,1	24,9	25,3	25,2	25,3	25,4	25,0	25,0	24,8	24,8	25,1	25,1	25,0	25,0	25,3	25,2	25,3
target charge [Amphrs]	9,0	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24

Time [Days]

Figure 1 Applied Charge Distribution of Sample 1

The corrosion potential of the strands was monitored prior to treatment to ensure that the strands were un-corroded. ECE treatment was applied to the samples for periods between 44 and 55 days. A current density of 1 Amp/m² of the steel surface was applied (see Figure 1).

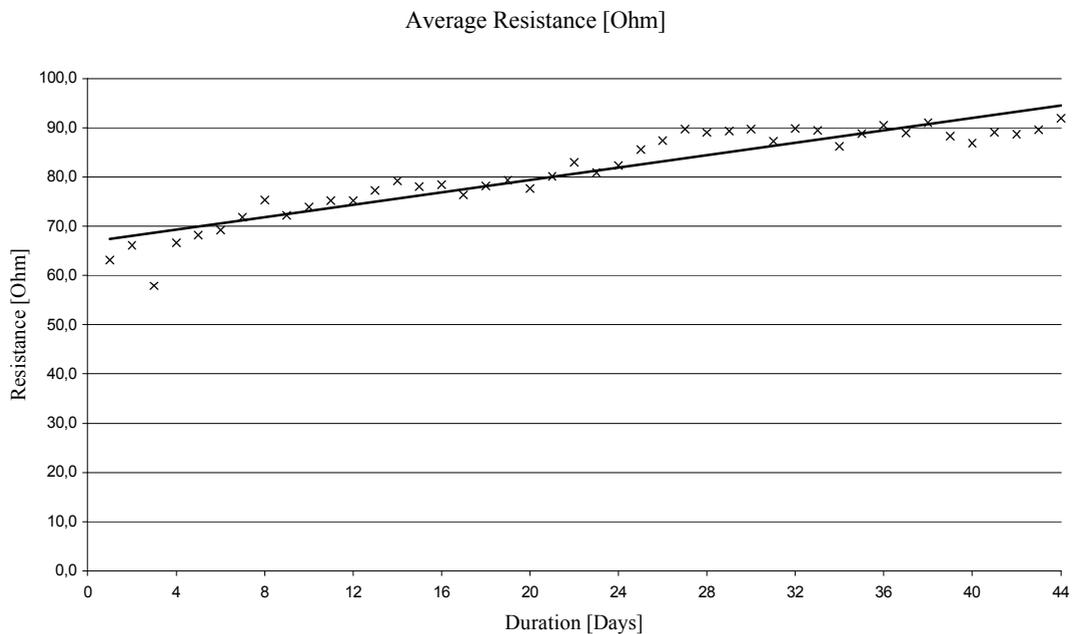The increasing resistance of the concrete due to the extraction of ions from the bulk is shown in Figure 2.

Average Resistance [Ohm]

Figure 2 Resistance of Sample 1 During ECE Treatment

EXPERIMENTAL RESULTS AND DISCUSSION

ECE treatment of the first sample was stopped after 44 days when a charge of 1056 Amp-hrs was applied to the steel surface. The sample was sliced to remove the steel which was then subjected to constant extension rate tests (CERT) and a fatigue test programme. The aim was to minimise the time between

ECE-treatment and mechanical tests of the steel in order to maintain any hydrogen-induced effects. An upper limit of 0.1 mm/min was used for the CERT (Cherry, Price, 1980) and it took approximately two hours to complete each test. The load during the fatigue tests was cycled between 65 kN and 85 kN at a frequency of 4 Hz. Time until failure was between three and four hours. The fractured surfaces were analysed using a scanning electron microscopy (SEM).
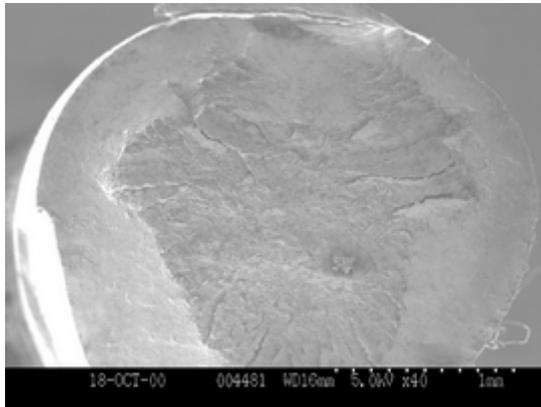

Plate 3 Fractured Surface of Steel treated in K₂CO₃ Electrolyte

No differences were found in CERT or fatigue tests in five of the six samples compared to untreated steel samples. Only the specimen treated in potassium carbonate electrolyte showed reduced fatigue life and reduced ductility (see Figure 4). The ultimate tensile strength, however, remained unchanged. The fractured surface was substantially different from the fractured surfaces of other steel specimens (see Plate 3). Both, ductility and fatigue life recovered within 48 hrs of the end of treatment.

Current densities for ECE treatment are given in Amperes per metre of treated steel surface. Rates of 1-2 A/m^2 are reported in the literature. ECE was originally applied to structures with a high reinforcement content so that the ratio of steel to concrete surface was almost equal to 1. However, some structures, or laboratory specimens in particular may have a ratio of steel to concrete surface area, which may be significantly less. For these structures a treatment of 1A/m^2 of concrete surface results in much higher treatment rates for the steel surface. Of greatest importance for electrochemical reactions such as migration of ions during ECE, is the surface area of the electrode (the reinforcement) and not the surface area of any extended membrane such as the concrete surface. This is due to the fact that the current flow (or potential difference) induces electrochemical reactions between two electrodes.

Strain [%] of CERT Directly and 48 hrs After End of ECE Treatment

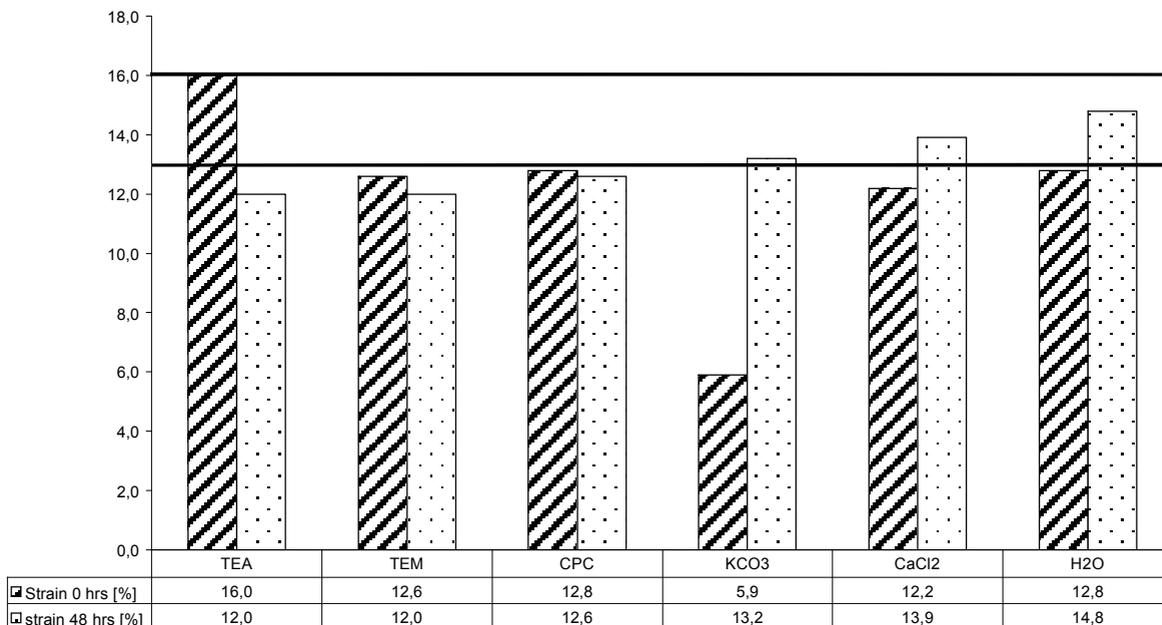|	TEA	TEM	CPC	KCO3	CaCl2	H2O
Strain 0 hrs [%]	16,0	12,6	12,8	5,9	12,2	12,8
strain 48 hrs [%]	12,0	12,0	12,6	13,2	13,9	14,8

Figure 4 Strain Rate of Samples Directly and 48 hrs after end of ECE Treatment.

Field applications of ECE mainly use 1 A/m^2 of steel surface. The treatment current density during the experiment was thus adjusted to this rate. Furthermore, higher current densities do not necessarily result

in higher extraction rates. The initial chloride content of 1.2 % cement content was reduced to 0.2% close to the reinforcement (see Figure 5).
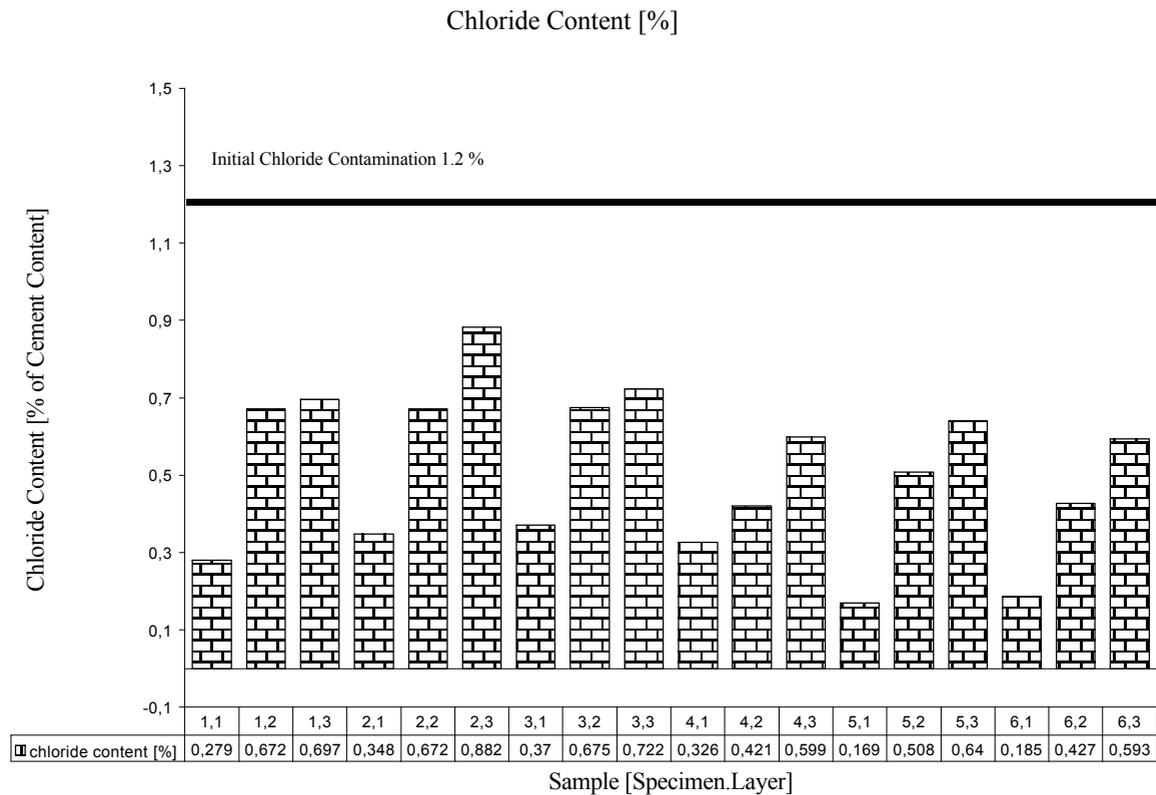
Chloride Content [%]

Figure 5 Chloride Content of Samples

The charge on the specimens varied between 1040 Ahrs and 1340 Ahrs. The charge on the specimen where HE was observed was 1080 Ahrs. It is therefore questionable whether the charge was the cause of the embrittlement reaction (see Table 1).

Sample [Number]	Electrolyte [Name]	Charge [Ahrs]
1	Tetraethylammonium iodide	1055
2	Tetramethylammonium chloride	1041
3	Cethylpiridinium chloride	1055
4	Potassium carbonate	1080
5	Calcium chloride	1340
6	Tap-Water	1320

Table 1 Charge During ECE Treatment

The electrolyte would seem to play an important role in the susceptibility of high strength steels to hydrogen embrittlement and these results are in agreement with findings of recent studies. Fullea (2000) tested steels in simulated concrete pore water and environments that are recommended for hydrogen embrittlement tests for prestressing wire. The steel showed no susceptibility to HE in concrete pore water.

Potassium carbonate is used in re-alkalisation treatment of concrete. It is transported through electro-osmosis close to the cathode where the equilibrium condition between carbondioxide in the air and the potassium carbonate eventually results in the production of hydroxide ions. It might be possible that during the production of hydroxide, additional hydrogen was generated at the steel surface resulting in brittle fracture of the steel.

CONCLUSIONS

From the experimental programme the following conclusions can be drawn:

1. The most commonly used high strength steel in prestressed concrete, the 7-wire-super-strand (BS 5896) with an ultimate tensile strength of 1860 N/mm^2 did not appear to be affected by hydrogen charging due to the application of ECE when the strands were un-corroded. The ductility, the ultimate tensile strength and the fatigue life of five of the six specimens tested were not adversely affected;

2. The electrolyte used when undertaking ECE may be important in the susceptibility of high strength steels to hydrogen embrittlement. The CERT and fatigue test programme of the fractured surface of the potassium carbonate treated sample would suggest hydrogen induced brittle failure.

ACKNOWLEDGEMENTS

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