

The feasibility of 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 from the application of de-icing salts, from cast-in chlorides or from seawater as in marine structures. . Traditional repair techniques of chloride contaminated concrete involve the cutting and removal of all contaminated concrete, an intrusive and mainly unnecessary action. Electrochemical extraction is the removal of chlorides from the vicinity of the reinforcement leaving all sound concrete intact. In a relatively short period (6 to 10 weeks) a relatively high potential is applied to the structure. The chloride ions migrate away from the reinforcement towards the external anode. The critical threshold for hydrogen generation of $0.94 V_{SCE}$ in concrete is exceeded by electrochemical chloride extraction. Thus atomic hydrogen is created at the surface of the cathodically polarised reinforcement. High strength steels in prestressed concrete structures are susceptible to adsorb hydrogen and suffer from brittle fracture since they contain alloys, which facilitate the adsorption of hydrogen. The application of electrochemical chloride extraction on prestressed concrete structures has therefore been questioned. This article reviews the causes of hydrogen embrittlement in steel and relevant experiments on prestressed concrete. It can be concluded that the risk of hydrogen embrittlement in prestressed and post-tensioned concrete structures is overestimated and the application of electrochemical chloride extraction is feasible.

Keywords: Electrochemical chloride extraction, prestressed concrete, hydrogen embrittlement, corrosion, concrete repair

Introduction

Steel in reinforced concrete is usually protected from corrosion due to the formation of a protective surface film in alkaline milieu ($pH > 12.5$). At the presence of chloride this protective layer breaks down. This can be attributed to the solution of intermediate iron salt and subsequent breakdown of the passive layer. The iron salt reacts with oxygen in water, the chloride is set free again and can dissolve more iron in the passive film. This process takes place even in non-carbonated concrete at a pH around 12.5 when a critical chloride threshold in concrete is exceeded.

Chloride was used in the early 60's and 70's as hydration accelerator. In the form of sodium chloride it is still used as de-icing salt. Replacement is not economically viable. In the Northern Hemisphere structures that suffer from chloride induced deterioration are bridges, park decks or retaining walls.

The application of electrochemical chloride extraction (ECE) is now commonly accepted as rehabilitation method for ordinary reinforced concrete. Steel rebars of ordinary reinforced concrete structures do not suffer from brittle fracture since they don't contain alloys, which in turn provide trapping sites for hydrogen. High strength steel on the other hand contains alloys. Therefore irregularities in the metal matrix occur to facilitate hydrogen uptake. A high proportion of bridges contain prestressed steel.

Prestressed concrete

In the United States more than 200 000 tons of prestressing steel are used per annum, worldwide approximately 1 million tons. The most wide spread corrosion problems in the U.S. exist in post-tensioned parking garage decks and in post-tensioned structures involving unbonded tendons. In the period between 1950 and 1979, 242 cases of damage were reported in prestressed and post-tensioned concrete. [9]

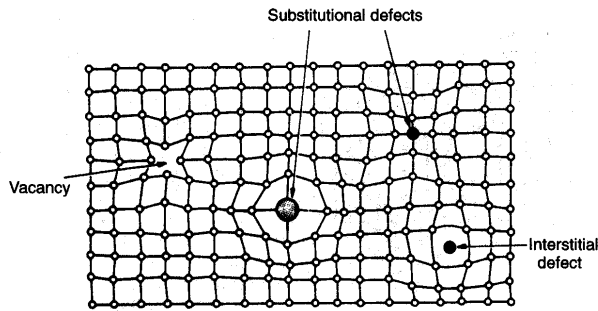


Figure 1 Point defects in a lattice [18]

ductility and the material's sensitivity to heat treatment. [21]

Steel is basically iron with the addition of small amounts of carbon up to a maximum of 1.67% by weight, and other elements added to provide particular mechanical properties. Above 1.67% carbon the material generally takes the form of cast iron. As the carbon level is increased, the effect is to raise the strength level, but reduce the

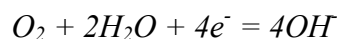
There are several types of high strength steel used for prestressing, covered by British Standards BS 5896 for wires and strands and BS 4486 for bars. Wires have a carbon content of 0.7 – 0.85%. Their nominal tensile strength varies between 1230 and 1770 N/mm². [13] The most common is cold drawn eutectic carbon-manganese steel. [9]

High strength steels do not process the same well defined yield point as mild steel, and so the proof stress is defined as the stress at which, when load is removed, there is a given permanent deformation. The deformation specified in British Standards for prestressing steel is 0.1% elongation. Although the modulus of elasticity for various types of prestressing steel varies, for design purposes it is given in EC2 as 200 x 103 N/mm² for all types of steel. [13]

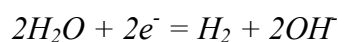
The causes of hydrogen generation

Hydrogen on the surface of reinforcement in concrete can be produced as a result of electrochemical processes such as corrosion, cathodic protection or electrochemical chloride extraction.

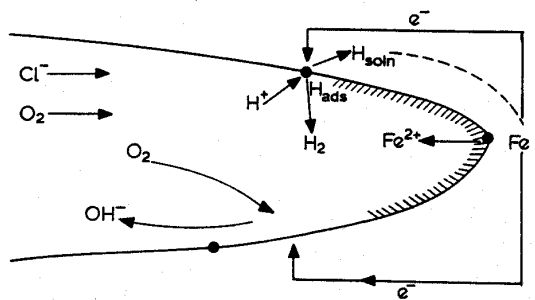
For concrete under atmospheric exposure condition the reaction at low current densities, as they are typical for **cathodic protection** is:



The hydrogen evolution reaction is typical for high current densities as they are applied in **electrochemical chloride extraction**:



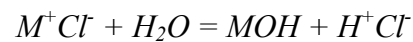
Both reactions produce one mole of hydroxide ions for each Faraday of charge. [4]



Schematic diagram of corrosion mechanisms occurring at crack tip during environmentally induced cracking

Figure 2 Corrosion process of steel, with local anode at the crack tip^[17]

During **corrosion** hydrogen is generated and can cause hydrogen embrittlement.^[10] The occurrence of hydrogen in the presence of chloride ions is made possible because chlorides break down the passivity of steel and at damaged 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^- . The hydrolysis of these products generates atomic hydrogen as follows:



The acidity in the pit is increased by hydrogen atoms to a pH of 3.5 and due to the lack of oxygen as a depolariser at the cathode, hydrogen ions act as depolarisers in the pit:



Once produced the atoms do not rapidly recombine at low pressures because the energy released by their union immediately causes them to separate again.^[8] Thus, recombination of hydrogen does not take place entirely and at favourable locations the hydrogen migrates into the steel thereby causing brittle fracture.^[26]

The presence of oxygen is crucial to suppress hydrogen generation on the cathode. Therefore, once the oxygen is reduced the electrochemical equilibrium moves towards a lower potential as proposed by the *Pourbaix*-Diagram. Oxygen diffusion and migration through concrete could play an important role in the hydrogen generation process.

Oxygen diffusion decreases with increasing moisture content and increases with increasing w/c ratio i.e. porosity.^[3] Alonso et al. (1993) identified oxygen availability in the surrounding solution to be relevant for the onset of hydrogen embrittlement reaction. Cold drawn prestressing wire 7-mm diameter was tested in aerated 0.1M $NaHCO_3$ solution. The reduction in area was 16% compared to 35% in de-aerated solution.^[1]

Previous experimental studies

Investigations on high strength steel specimens using the electroplating technique related the susceptibility of steel to hydrogen embrittlement only to its hardness, other factors such as composition and structure were not found to be important. During the electroplating process the combination of inhibitors and current densities between 1 A/dm^2 and 3 A/dm^2 made the steel specimens less sensitive to hydrogen uptake than lower or higher treatment rates.^[5] However, the effect of cathodic polarisation is dependent on the applied stress level and the nature of the cracking process, which in turn is related to the size of the crack.^[27] Based on statistical analysis, Toribio, developed an equation for the susceptibility of steels to brittle fracture in relation to the applied stress level.^[23]

Above the critical potential at applied current densities of 224 mA/m^2 to the steel surface (1862 N/mm^2) the observed hydrogen embrittlement due to corrosion was greater than the hydrogen embrittlement due to applied current.^[10] This is contrary to

general opinion according to which conventional cathodic protection is not suitable for the application on structures containing high strength steel, since hydrogen is produced at the steel at potentials greater than -0.9mV .^{[12][15]} Therefore pulse cathodic protection was developed, which in contrast to conventional cathodic protection, applies very short duration (less than 10% of the total lifetime), but very high voltage DC pulses to the structure. Oxygen molecules and the hydrogen ions absorbed on the metal surface are instantaneously reduced.^[7] Transferred to ECE this would mean relatively short application periods followed by long out-gas periods.

Experiments on 1910 N/mm^2 steel at a potential of -1.3V showed that the maximum charging time was 9 hrs in deaerated, Ca(OH)_2 saturated solution to reach the full extent of hydrogen embrittlement.^[11] 50 hrs after the stop of charging hydrogen diffuses out of the steel and no effects of hydrogen are evident any more.^[10]

In cold drawn steels exposed to calcium hydroxide solutions with added chloride at some pH's and at potentials below $-0.90\text{ V}_{\text{SCE}}$ steels undergo brittle fracture due to hydrogen. At higher potentials above $-0.60\text{ V}_{\text{SCE}}$ a second regime of cracking is encountered. A range of potentials in which environment sensitive fracture is not observed separates the two regimes. The fracture surfaces produced at the higher potentials are result of dissolution of the ferrite in the perlite structure of the steel and the fractography is substantially different from that produced at potentials around $-0.90\text{ V}_{\text{SCE}}$. The mechanism is called active path dissolution.^[9]

Using constant extension rate tests (CERT), Hartt et al. (1993) found a similar threshold potential of $-0.90\text{ V}_{\text{SCE}}$ for steel (UTS 1910 N/mm^2 , cold drawn, 7 wire strand) specimens in a deaerated calcium hydroxide solutions. With the exception of the lowest pH = 5.4 investigated, the greatest embrittlement occurred at the highest pH = 12.4 for given potentials. Potential was found to be the most important criterion on HE whilst the influence of pH, chloride content and precharging time was only marginal.^[12]

Ihekwa and Hope (1998) tested eight concrete specimens containing untensioned high strength steel with a tensile strength of 585 MPa ($=\text{ N/mm}^2$) and Brinell Hardness of 212 maximum. A titanium mesh anode was installed using 0.1M sodium borate Na_3BO_3 as electrolyte. A current density of 1.0 A/m^2 and 3.0 A/m^2 was applied to the surface for eight weeks. After the treatment period the specimens were subjected to slow strain-rate tension tests in accordance with ASTM E8M-91. A general reduction in strength of about 50% from control values was recorded.^[14]

Ashida and Ishibashi (1993) subjected high strength steel bars (1500 N/mm^2), prestressed to 60% of the ultimate strength to ECE treatment at current densities between 1 and 2 A/m^2 for a period of 4 to 8 weeks. The stress-strain behaviour, the yield and ultimate strength were not influenced by the ECE treatment.^[2]

The effect of different cathodic potentials (-0.8 , -1 , -1.2V) on hydrogen embrittlement of high strength steel and mechanical behaviour of prestressed steel wire ($\varnothing 9.3\text{mm}$) using slow strain rate test and a exposure period of 3 years was investigated. Static and dynamic loading showed that the applied potential had no effect on proof stress, ultimate tensile stress or breaking strength for the prestressed steel wire. The elongation of strands in uncharged, and therefore corroded beams was smaller since the fracture zone of a strand is in the pitting corrosion area which in turn decreases the elongation.^[16]

Treadaway (1971) prepared prestressed concrete specimens with and without calcium chloride additions and with tension stressed to 70 to 80% of the UTS. These were exposed to freely outdoors in an industrial environment for 2 to 27 months and in hot 0.02M sodium hydroxide solutions of different NaCl content with pH in the range of 10.2 to 11.6. No indication of hydrogen embrittlement (cracking) was detected. However, no direct current was applied to the samples.^[24]

Scannell, et al.(1987), polarised a prestressed steel tendon cathodically in concrete to $-1.30 V_{SCE}$ for 36 days. When the tendon was recovered, notched and tested in three-point bending, no distinction in failure load between polarised and non polarised tendons was detected even though embrittlement was observed when heat treated and comparably polarised in aqueous solution.^[19]

Steels that are hardened by cold-working show a better resistance to hydrogen induced brittle fracture compared to quenched and tempered steels.^{[22] [25]}

The influence of hydrogen on the properties of high strength steel - measurement techniques

Three types of mechanical tests are available. The *constant stress test* (1) applies a constant stress to a specimen. It is either used for testing of samples already containing hydrogen or of samples in environments causing hydrogen entry. The specimen can be notched to develop a region of triaxial stress at the tip of the notch thereby concentrating the hydrogen at this region. Smooth samples can be used for sustained load testing. However, in this case the defects responsible for hydrogen entry normally will be surface or near-surface non-metallic inclusions. Usually a huge scatter of results is obtained from these tests. Hydrogen can diffuse approximately 10 μm in 1s. Therefore failure times of the order of a second can be obtained for severe hydrogen exposure conditions. Service life predictions cannot be obtained from sustained load tests. Failure will occur after approximately one month of exposure to the hydrogen exposure. Stress-corrosion cracking processes are dependent on plastic strain in the material. *Controlled strain-rate tests* (2) offer the benefit that due to the slow ingress of stress, any stress-corrosion cracking phenomena is given time to occur. Therefore, the slow strain-rate test can show any tendency to cracking in a metal-environment combination. Typical test duration for steels are in the order of one week. This test type overstates the susceptibility of materials to hydrogen embrittlement, because the enforced plastic deformation provides a very severe test condition. Structural steels will fail even under conditions with very low rates of hydrogen entry. *Fracture mechanics tests* (3) provide the possibility to assess materials, which already contain defects.

A method to calculate the mobile hydrogen is proposed by DeLuccia and Berman. After the uptake period the steel is anodically polarised. The hydrogen cation is therefore pushed out of the steel and migrates to the external cathode. The resulting current flow indicates the amount of hydrogen that was adsorbed into the steel.^[6]

Acoustic emission of steel during electrochemical hydrogen charging (5-40 mA/cm²) and during tensile testing of uncharged and hydrogen charged specimens was recorded and found to be substantially different from uncharged specimens. Materials without hydrogen embrittlement show acoustic emission in the second load phase only if the level of the first load is exceeded (Kaiser-effect). This effect is omitted for hydrogen charged specimens.^[20]

Conclusion

From this brief literature review the following conclusions can be drawn: Hydrogen uptake takes place in high strength steels because the microstructure provides trap sites for hydrogen. Cold drawn and hardened steels are less susceptible to brittle fracture than tempered and quenched steels. Mechanical tests such as the constant extension rate tests overestimate the risk of hydrogen embrittlement, particularly when they are carried out in concrete simulating solutions rather than real concrete. Tests of high strength steel in real concrete showed much better performance and their properties remained largely unchanged. Therefore, the application of ECE on prestressed concrete structures seems to be feasible and will be investigated in a subsequent test program.

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