

## CHAPTER 4: DISCUSSION

The discussion of the experimental results of this work will firstly be based on the findings of mechanical testing for hydrogen charged unplated steel tensile specimens, and secondly on the hydrogen permeation results for unplated steel membranes. Conclusions drawn from these results apply to all tested coatings, i.e. Cd, SermeTel and Alcotec, as potentiostatic charging of unplated tensile specimens or membranes at a specific potential attempts to simulate the case of coated specimens or membranes corroding at the same potential. Following this discussion, each coating will be individually assessed and compared to each other, based on its hydrogen embrittlement, de-embrittlement and re-embrittlement behaviour, as well as its corrosion performance in a variety of environments.

### 4.1 HE OF CHARGED UNCOATED AISI 4340 STEEL SPECIMENS

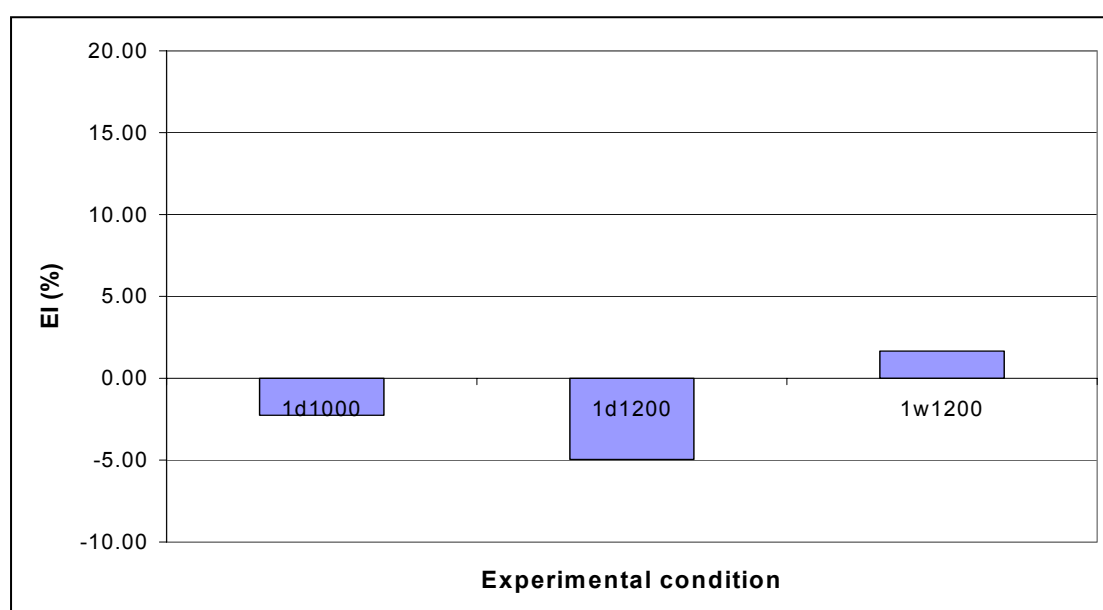
As stated earlier, uncoated steel tensile specimens potentiostatically charged at the corrosion potential of various coatings can simulate the behaviour of coated steel specimens that corrode at the value of this imposed potential. The range of potentials for the coatings, either coupled or uncoupled to steel, is between  $-650$  and  $-900$  mV (SCE), as seen from the results of LPR measurements and galvanic coupling to steel. (Fig. 79, 81, 83, 85, 88, 91). At these potentials, as well as at more cathodic ones, there is concern for hydrogen entry responsible for any potential hydrogen re-embrittlement of corroding coated steel components.

According to the Pourbaix diagram for the iron–water system at  $25\text{ }^{\circ}\text{C}$  [95], depicted in Figure 24, the line **a** of the hydrogen ion reduction sets the boundary of potentials below which the hydrogen evolution reaction is possible at a given pH. In our experiments a 3.5% NaCl solution was used as a corrosive environment for the re-embrittlement testing, and the expected values of pH are between 5 and 7. For these pH values hydrogen evolution is possible for potentials between  $-200$  and  $-400$  mV in the hydrogen scale, or roughly between  $-450$  and  $-650$  mV (SCE). Consequently, from a thermodynamic point of view, hydrogen entry is possible for potentials below

–650 mV (SCE) for the tested environment of the steel tensile specimens, and hence the corrosion potentials of the examined coatings lie within this range of potentials.

The range of potentials for charging the uncoated AISI 4340 steel specimens was targeted to be between –700 mV and –1200 mV (SCE), in order to examine the effects of cathodic charging at even more negative potentials simulating more electronegative coatings, like zinc for instance. Two approaches were followed in the slow strain rate testing of these specimens. The first was precharging specimens with hydrogen for a specific period of time and then mechanically testing them, and the second was to simultaneously charge the specimens with hydrogen and strain them.

#### 4.1.1 Specimens Tested Subsequent to Precharging

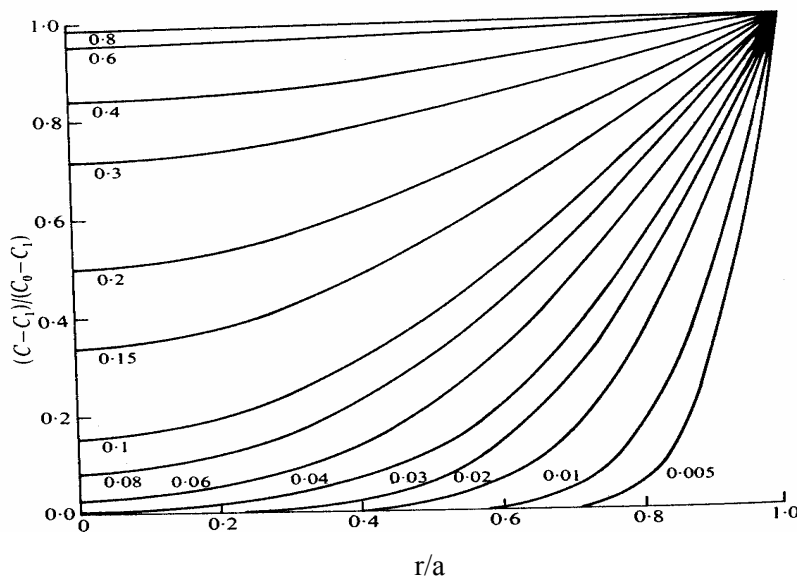


**Figure 103. Bar chart of EI for precharged, and then tested uncoated specimens at various potentials for one day and week**

Unplated 4340 steel tensile specimens were potentiostatically precharged at –1000 mV (SCE) for one day, and at –1200 mV (SCE) for one day and one week in a 3.5% NaCl solution, and then tested in a SSRT. According to the results presented in Figure 57 in Chapter 3, the times to failure for these specimens were very close to the air test results, and therefore, the EI values for specimens tested under these experimental

conditions were round zero. (Figure 103) Based on these results no further precharging at more anodic values (closer to the potentials of the aluminium-based coatings) was performed.

As seen from these experiments no embrittling effect of hydrogen was detected, although 24 hours were more than enough for hydrogen to be uniformly distributed in the cylindrical gauge length of the tensile specimens. More in detail, Figure 104 depicts the concentration distributions for the case of hydrogen diffusion in a solid cylinder for a non-steady state, a constant surface concentration  $C_0$  and an initial uniform distribution of the diffusing substance  $C_1$  throughout the cylinder. The hydrogen concentration is given for a cylinder of radius  $\alpha$  in terms of two dimensionless parameters  $Dt/\alpha^2$  and  $r/\alpha$ , where  $D$  is the diffusion coefficient of hydrogen in the 4340 steel. [64]



**Figure 104. Concentration distributions at various times ( $Dt/\alpha^2$ ) with initial concentration  $C_1$  and surface concentration  $C_0$ . [64]**

Supposing the diffusion coefficient of hydrogen into the AISI 4340 steel equal to  $4 \times 10^{-7} \text{ cm}^2/\text{s}$  [66, 124], we can estimate the time at which the concentration of hydrogen in the middle of the cylinder ( $r/\alpha = 0$ ) will approximately be the same as at the surface. Hence, from the above graph, for  $C-C_1/C_0-C_1$  approaching unity the dimensionless number  $Dt/\alpha^2$  has to be at least 0.8. In the case of the tested tensile

specimens  $\alpha = 0.1125$  cm and hence, 7 hours is assumed to be the appropriate time for the specimen to be filled with an almost uniform distribution of hydrogen.

Precharging with hydrogen for one day or one week proved to be ineffective in the detection of HE, and therefore, questions arose concerning the detrimental action of hydrogen without the simultaneous effect of stress. Both the fact that hydrogen permeation does occur at active potentials like  $-1000$  and  $-1200$  mV (SCE) (Figures 66, 68, 77 and Table 27), and the sufficient time for hydrogen to be uniformly distributed in the whole specimen before the completion of the precharging time led to the assumption that hydrogen had enough time to diffuse out of the specimens before sufficient stress levels were reached, thus no embrittlement could be detected.

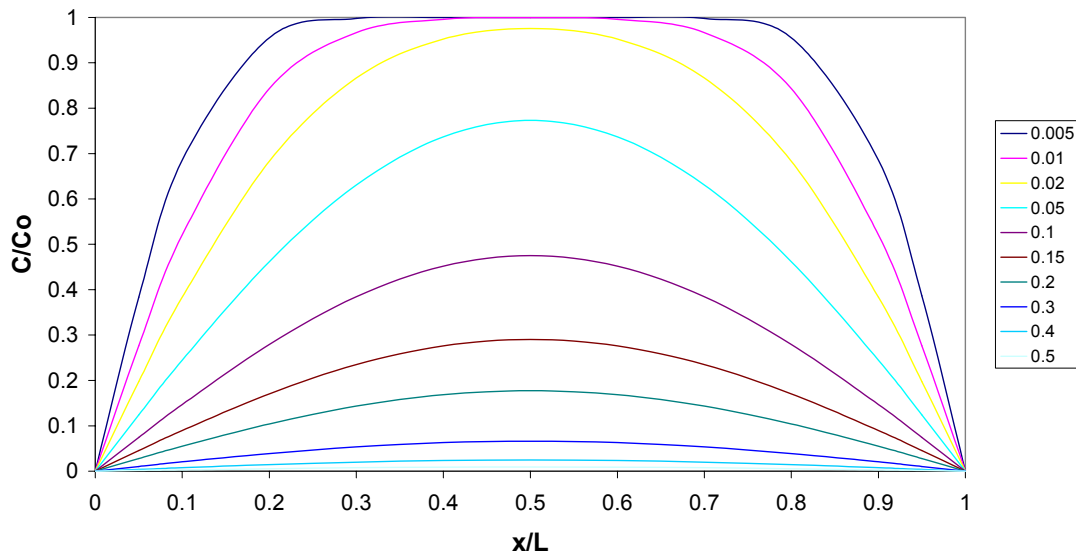
The previous assumption could be confirmed from the desorption curves for hydrogen diffusing out of plane sheet, as diffusion in cylindrical tensile specimens can be simulated with diffusion in plane sheets. The analytical solution for a plane sheet is much easier to be found and presented in a graph compared to the solution for the solid cylinder, and this is the reason why this approach is followed for the current problem. Given a plane sheet with initial hydrogen distribution  $C_o$ , zero hydrogen concentrations at the surfaces of both sides of the membrane, and the fact that oxides have no effect neither on hydrogen concentration in the plane sheet nor on the escape of hydrogen to the atmosphere, then, according to Crank [64] and Shewmon [125], the concentration  $C(x,t)$  at a specific position  $x$  and at a specific time  $t$ , is given by the following equation :-

Equation 35:

$$C(x,t) = \frac{4C_o}{\pi} \sum_{m=0}^{\infty} \frac{1}{2m+1} \sin \frac{(2m+1)\pi x}{L} \exp \{-D(2m+1)^2 \pi^2 t / L^2\}$$

Solutions of the Equation 35 are presented in Figure 105 for various times  $Dt/L^2$  and at various depths  $x/L$  of the membrane. As viewed, for the dimensionless number  $Dt/L^2$  equal to 0.4, the hydrogen concentration inside the cylinder has almost become zero, i.e. the membrane is depleted of hydrogen. For the same time it could be assumed that hydrogen would have been depleted from a solid cylinder, like the tensile specimens in the SSRTs. If the radius of the specimens in the dimensionless

number is considered instead of  $L$  (membrane length), it is derived that hydrogen has almost completely diffused out of the tensile specimens after approximately 3.5 hours. This is the time when the specimens are still in the elastic region in the stress–strain diagram. Consequently, there is not enough hydrogen concentration to cause any HE, and this is confirmed by the experimental results of precharged and then stressed uncoated steel specimens.



**Figure 105. Concentration distributions for a plane sheet at various times ( $Dt/\alpha^2$ ) with initial uniform concentration  $C_0$  and zero surface concentration at both sides of the membrane, resulting in desorption of the diffusing substance.**

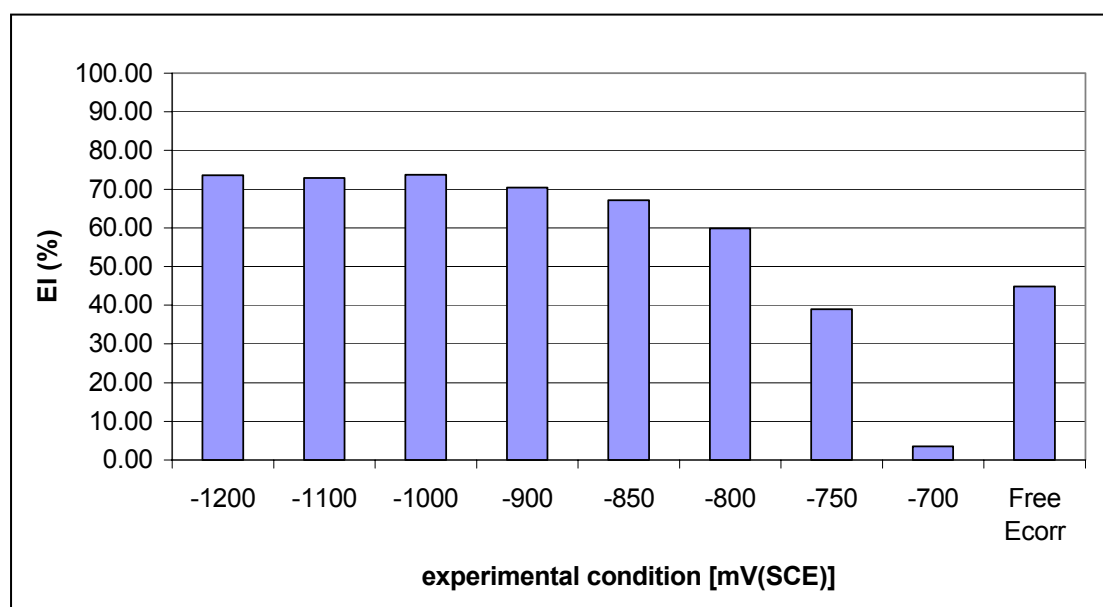
On the other hand, these findings were in agreement with the results of Yoshizawa and Yamakawa [126] on high strength steels of less than 1500 MPa in UTS. Although they implemented constant load tests, they concluded that precharged steel specimens that were afterwards tested had longer time to failure than specimens simultaneously charged and loaded. This difference was attributed to the hypothesis that if during precharging hydrogen takes a uniform distribution, then the tip of any pre-existing microcrack rounds out to prevent any stress concentration, thus resulting in longer life of the specimens.

#### 4.1.2 SSRT Specimens Charged Whilst Tested

A number of investigators have raised the issue of the detrimental effect of the combination of stress with a minimum level of hydrogen concentration, in order to result in the deterioration of the load bearing properties of various metals and alloys, including steels. [23, 27, 33, 34, 55, 57, 66, 88, 90, 91, 103, 111, 126–130]

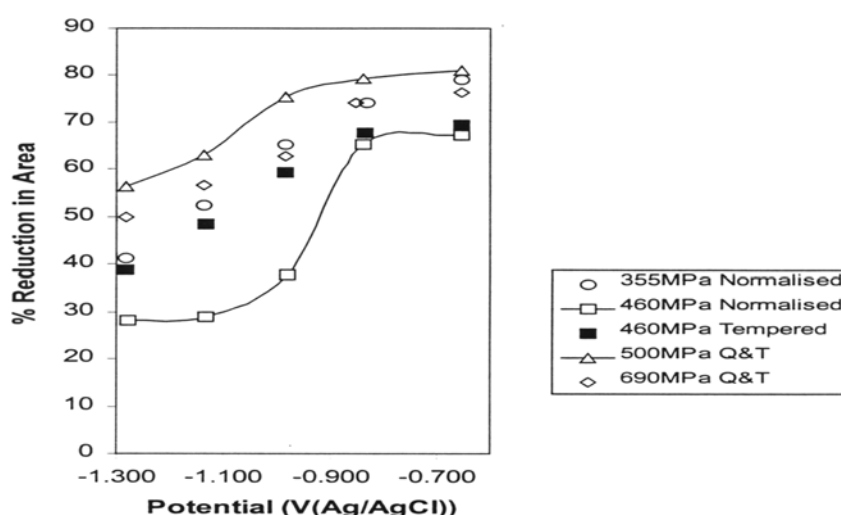
Based on and encouraged by the previous thoughts, uncoated steel tensile specimens were potentiostatically charged and strained at the same time. From Figure 58 in Chapter 3, it is apparent that the combination of hydrogen charging whilst straining proved to be detrimental to the tensile properties of the AISI 4340 steel. The times to failure at all the checked potentials were found to be shorter than in the air tests. More in detail, only at  $-700$  mV (SCE) was the average time to failure close to that for the air tests. In all the other cases substantial amounts of embrittlement were introduced as a result of the cathodic protection of the steel substrate.

##### Potential Versus Degree of Embrittlement



**Figure 106. Bar chart of Embrittlement Indices for strained and charged AISI 4340 steel tensile specimens at various potentials**

Figure 106 portrays pictorially the EI for specimens stressed whilst charged at various potentials. According to this bar chart, it can be concluded that at more negative potentials there are shorter times to failure, and therefore, the more active the potential is the higher the observed EI. This is an expected finding, as from the permeation results (Figures 66–74) it is evident that at more active potentials the permeating amount of hydrogen is higher (Figure 77), and it is exactly this type of hydrogen that can easily diffuse in the steel microstructure and impair its mechanical properties [91, 103]. However, more discussion combining both SSRTs of cathodically protected uncoated steel specimens and hydrogen permeation testing of unplated steel membranes will be presented in a following section. However, at this stage the findings of this work can be compared with other studies, where the role of the applied potential in cathodic protection schemes has been underlined. [57, 70, 103, 131]

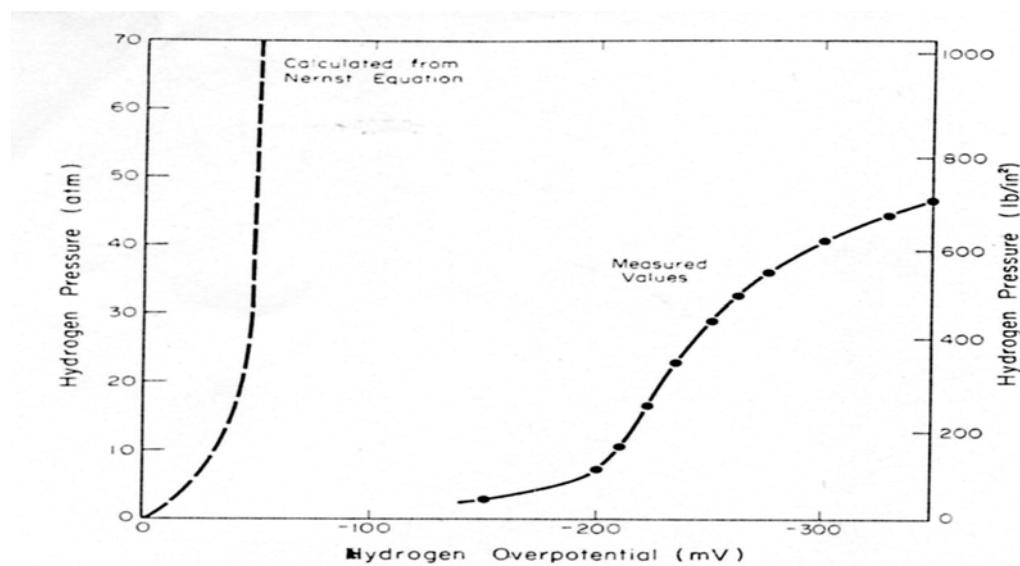


**Figure 107. Percentage reduction in area in SSRTs for carbon–manganese steels showing the effect of applied potential in seawater [70]**

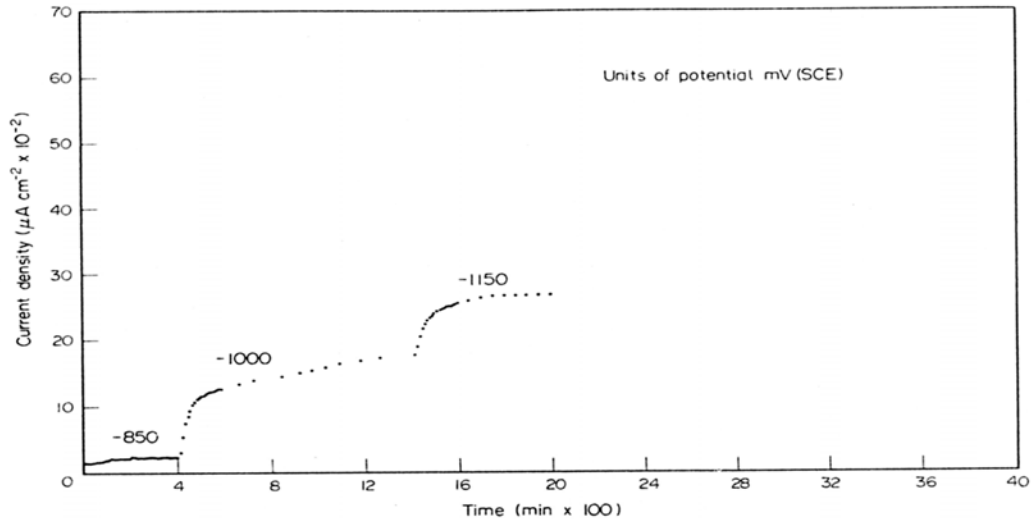
Particularly, Robinson and Kilgallon [70], in a review of the effects of microstructure on the HE of high strength offshore steels, provided examples of the embrittling effect of cathodic overprotection for various materials and environments, reported by different investigators. Specifically, normalised, as well as quenched and tempered carbon–manganese steels, cathodically protected in natural seawater, exhibited smaller RA (Reduction in Area), and thus higher EI, at more active values. (Figure

107) Despite the fact that these steels are low strength steels with lower HE susceptibility compared to the high strength AISI 4340 steel of the present study, they could be at risk in some environments, if overprotected.

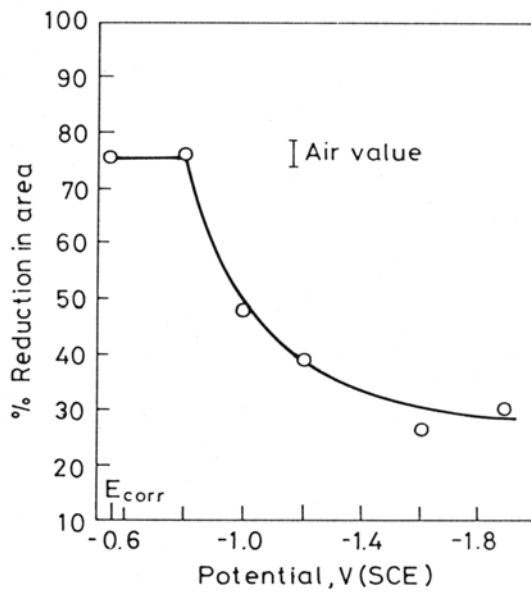
Other reported examples include the increase in hydrogen pressure with increasing cathodic polarisation of iron in 0.1 N  $\text{H}_2\text{SO}_4$  (Figure 108) [57], and the increase in hydrogen permeation by lowering the applied potential of 50D steel exposed to 3.5% NaCl solution (Figure 109) [103]. In the last case decrease of the potential causes a reduction in the threshold stress intensity for cracking,  $K_{th}$ , in crack velocity measurements, as  $K_{th}$  is inversely proportional to the hydrogen concentration. Finally, Procter [131], reporting detrimental effects of cathodic protection, referred to the decreased ductility of potentiostatically charged X65 pipeline steel specimens strained at  $10^{-6} \text{ s}^{-1}$  in 3.5% NaCl solution with the lowering of the applied potential. (Figure 110) Although the examined material was different from the AISI 4340 steel of the current study, the experimental conditions concerning the corrosive environment and the strain rate were similar.



**Figure 108. Relationship between theoretical and measured hydrogen gas pressures and overpotential of an iron cathode polarised in 0.1 N  $\text{H}_2\text{SO}_4$  [57]**



**Figure 109. Permeation transients for 50D steel cathodically polarised in aerated 3.5% NaCl solution [103]**



**Figure 110. Percentage reduction in area against potentiostatically controlled potential for X65 pipeline steel specimens subjected to tensile testing at a strain rate of  $10^{-6} \text{ s}^{-1}$  in 3.5% NaCl solution [131]**

There are some other direct remarks from the trend shown in the bar chart of Figure 106. No EI exceeded a 75% value in any circumstances, as specimens charged at  $-1200$ ,  $-1100$  and  $-1000$  mV (SCE) failed at approximately 5.5 hours. This is probably due to the fact that some minimum stress levels need to be reached for

hydrogen re-embrittlement to occur. The interpretation of this issue is directly related to the effect of hydrogen concentration and stress on the HE risk of metallic materials and will follow later in the Discussion.

Concerning the SSRTs of uncoated steel specimens at their free corrosion potential, it should be noted that the potential started with values round  $-500$  mV (SCE) before settling to a value round  $-630$  mV (SCE) for the majority of the tested time. In this case, the measured EI was between the EI recorded values corresponding to  $-750$  and  $-800$  mV (SCE) (Figure 58, Table 18). In other words, substantial amount of HE was detected at the free corrosion potential, and if this were an unexpected finding of the present study, it would have not been for Smith et al. [132] who studied the electrochemical conditions at the tip of an advancing stress corrosion crack in AISI 4340 steel, the same material as in this work. According to them, the electrochemical conditions at the advancing edge of a crack are not the same as those of the bulk solution. They supported the view that hydrogen is involved in the cracking of AISI 4340 steel under all the studied conditions, i.e. free corrosion potential, anodic polarisation and cathodic polarisation. The difference between their study and the present lies in the fact that at free corrosion potential they found the least hydrogen generation, whilst in this study a higher EI was found at free corrosion potential compared to  $-700$  and  $-750$  mV (SCE) (Figure 58, Table 18). Concerning anodic polarisation, which was not studied in this work, they found times to fracture markedly longer than for the freely corroding conditions.

#### Re-Embrittlement of Corroding Coated AISI 4340 Steel Specimens

At this point, it should be reminded that the reason for performing mechanical testing with potentiostatically charged uncoated steel tensile specimens is to simulate and draw some first conclusions about the re-embrittlement of coated steel specimens corroding at the same potentials. Our coatings of interest, i.e. the aluminium-based coatings are corroding within the range of  $-900$  to  $-700$  mV (SCE) (Figures 79, 81), and consequently, based on the previously concluded remarks on cathodically protected bare steel specimens, a high risk of re-embrittlement of coated steel specimens is posed. This risk exists when the tensile specimens are simultaneously charged and strained, and it is possible in service conditions that fasteners and

undercarriage components are stressed and corroded at the same time. For this reason, the results discussed in this section will be correlated with the results of re-embrittlement testing of each one of the coatings, with which the steel specimens were coated.

### Stress and Hydrogen Content

Comparing the SSRT results for precharged and strained specimens (Figure 57) with those for charged, as well as stressed, specimens (Figure 58), it is concluded that hydrogen charging cannot have damaging effects on high strength steel mechanical properties with the absence of stress. Although coated tensile specimens, pre-exposed in salt spray or marine atmosphere, both exhibited some re-embrittlement without the simultaneous effect of corrosion and straining, the following discussion will focus on the relationship between stress and hydrogen concentration based on the SSRT results for charged uncoated steel specimens. According to McCright [57] the variables controlling the hydrogen absorption are the potential of the metal, the pH and composition of the solution, the presence of certain species that catalytically promote hydrogen absorption ('promoters'), the temperature and finally, the presence or absence of stress.

Concerning the effect of stress, McCright reiterated and underlined points suggested by Beck et al. [66] that tensile strain increases the concentration of absorbed hydrogen as a result of the dilation of the interstitial lattice sites where hydrogen accommodates, but it does not affect the diffusivity of hydrogen. The hydrogen concentration in stressed material is given by the following formula:

Equation 36:

$$C_{\sigma} = C_o \exp\left(\frac{6\sigma^2 V}{2YRT}\right)$$

where  $C_{\sigma}$  is the concentration under tensile stress  $\sigma$ ,  $C_o$  is the concentration in the absence of stress,  $Y$  is Young modulus and  $V$  the molar volume of iron. The factor 6 comes from the coordination of octahedral interstitial sites and the term  $\sigma^2/2Y$  represents the elastic strain energy per unit volume.

As stated earlier a substantial number of investigators underlined the crucial role of both hydrogen content and stress for crack initiation and occurrence. Some of them [33, 93, 111, 127] highlighted that a critical combination of stress state and hydrogen concentration must be attained for the initiation of a crack. In other words, in the current study, hydrogen re-embrittlement cannot occur if deformation and hydrogen charging do not take place simultaneously.

At this stage, the question is focused on which of these two combining factors, stress or hydrogen concentration, plays the most crucial role in the hydrogen embrittlement and re-embrittlement phenomena. From the formulation of this question the obvious answer seems to be hydrogen content or solubility in the steel microstructure, and particularly in microstructural defects, like surface inclusions, grain boundaries, interfaces, dislocations etc., where one of several possible mechanisms of embrittlement can take place. No matter which is the preponderant mechanism hydrogen diffuses to regions of high triaxial stress, where the hydrogen concentration is sufficiently high to cause crack propagation. Consequently, the prerequisite for hydrogen re-embrittlement or HE in general is a critical hydrogen concentration, adequate to initiate a crack. [23, 88, 89, 103]

In this context, the critical issue is not the combination of hydrogen with stress, but the role of stress to assist the production of a critical amount of hydrogen grouping in the region where a fracture embryo exists. [23, 130] On the other hand, for the attainment of a critical hydrogen concentration some minimum levels of stress are necessary. Thus, Beachem [27] paid attention to the fact that increasing hydrogen concentration causes a lowering of applied loads required for cracking, and increasing stress lowers the amount of hydrogen required for cracking. In the frame of the previous contention, the issue to be always remembered is that, despite this inversely proportional relationship between stress and hydrogen concentration, high levels of stress cannot eliminate the need for some hydrogen for the occurrence of HE, and high levels of hydrogen content cannot eliminate the need for a minimum stress for the accommodation of this hydrogen (lower critical stress) [89, 130]. For this reason, embrittlement of charged and strained specimens could not result in shorter times to failure and higher EI for even more cathodic potentials below  $-1000$  mV (SCE) (Table 18), as HE requires a combination of stress and hydrogen concentration.

Other investigators contributed their ideas to this discussion by examining the hydrogen redistribution over the metal body and its accumulation near microcracks by the applied load [128], whilst Robinson and Sharp [91] suggested that the incubation time in SSRTs, i.e. the time below which failure is unlikely to occur, may be regarded as the minimum time required to produce a critical hydrogen concentration at a critical depth. Finally, Tabata and Birnbaum [55] supported the view that the localisation of the slip process in the HELP model results in the greater concentration of hydrogen absorbed in the triaxial stress field of the crack tip. This concentration could be further increased by the interaction between solute hydrogen and the stress fields of the dislocations and in some cases by increased transport of hydrogen by dislocation dragging.

Finally, in this discussion about the role of hydrogen content and stress, it should be emphasised that this issue was raised and examined by investigators supporting different views on HE mechanisms. Supporters of the Hydride Induced Cracking as a viable mechanism of HE emphasised the role of the combination of stress and hydrogen concentration for the formation and the stabilisation of the embrittling hydrides. [33, 34] As seen earlier, Troiano [23], one of the first proponents of the Lattice Decohesion Theory as the basis for the interpretation of the HE mechanism, explained the role of stress in increasing the critical hydrogen concentration necessary to initiate a crack. Moreover, in the perspective of the Surface Energy Theory of HE, Petch and Stables [38] raised doubts about the created stresses of accumulating molecular hydrogen in internal cavities as the source of HE, and expressed the view that a small hydrogen quantity is necessary to make the embrittlement mechanism operative provided some stress concentration exists. Finally, Beachem [27] and Birnbaum [55], lending support to the Localised Slip Model referred to the role of stress as a factor that increases the hydrogen concentration in high triaxial stress sites.

## 4.2 HYDROGEN PERMEATION TESTING

Electrochemical permeation measurements were used in this study to determine the amount of absorbed hydrogen by unplated steel membranes, potentiostatically charged at the potential of a corroding coating, in order to simulate the hydrogen absorption during the re-embrittlement of corroding coated tensile specimens. The double cell permeation technique applied in this work is just one of the various available electrochemical methods. Other examples comprise the gel filled hydrogen probe [104, 133] and the barnacle electrode [134], both of them employed in hydrogen measurements in various types of steel. All these methods measure the level of the mobile hydrogen, i.e. both the mobile lattice hydrogen and that held in reversible traps, and it is this type of hydrogen that can diffuse to defect sites, like high triaxial stress areas within the microstructure and cause embrittlement. [85, 91, 104, 133, 134] In contrast, vacuum extraction measures the total hydrogen content of steels, including that which is irreversibly trapped, but this type of trapping is not responsible for embrittlement phenomena. Consequently, the hydrogen permeation results can be both discussed on their own, as well as in conjunction with hydrogen re-embrittlement testing results.

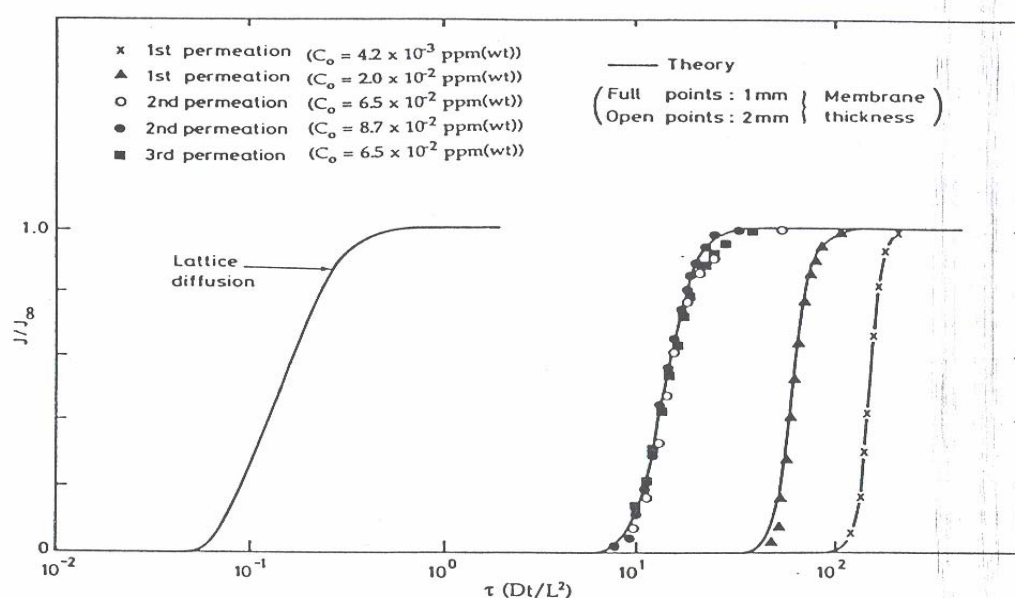
### 4.2.1 Shape of Permeation Transients

The shape of every permeation transient produced is the result of the interaction between the charging hydrogen passing through a metal membrane and the microstructure of the membrane. Consequently, the transient shapes can disclose information on microstructural characteristics related to reversible or irreversible trapping, as well as charging conditions, like applied potential and hydrogen concentration. For uncoated steel membranes that are cathodically charged there are various conditions that may alter the shape of the curve from a theoretical one describing pure lattice diffusion of hydrogen without trapping effects.

#### The Effect of Trapping

An obvious remark from the Permeation Results (Fig. 66–74) is that the more negative the charging potential is the shorter the breakthrough time appears to be. As

a result, breakthrough time ranged from a few seconds at  $-1200$  mV (SCE) to several hours at potentials above  $-900$  mV (SCE). In connection with the previously referred trend, the application of more noble potentials resulted in less steep transients compared to those obtained at  $-1200$  and  $-1100$  mV (SCE), presented in Figures 66 and 67. The reasons hidden behind the deviations from a typical permeation transient like that one of Figure 17 in Literature Review are related to the effect of trapping, and some explanations could be sought in the work of Turnbull with various types of charged uncoated stainless steel membranes, such as BS 970 410S21 [127, 135] and AISI 410 [72].



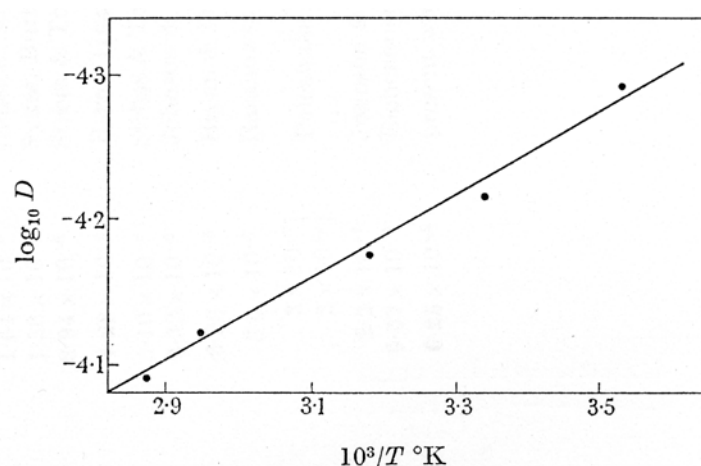
**Figure 111. Rising permeation transients for BS 970 410S21 stainless steel in acidified NaCl at 77 °C. Results show irreversible trapping (1<sup>st</sup> transient) and dependency on charging conditions ( $C_o$  value). [127, 135]**

Turnbull observed that if a specimen is charged with hydrogen and then recharged after enough time to allow the diffusible hydrogen to escape, then the breakthrough time of the second transient is shorter than that of the first, as seen in Figure 111 [127, 135]. This can be ascribed to the fact that irreversible traps in the microstructure are filled during the first charging experiment (permeation), and thus, the hydrogen passing through the metallic membrane in the second permeation has no longer to fill these traps. Moreover, Hillier [11] mentioned that if a specimen is charged for a

second time, then the slope of the rising transient becomes earlier and steeper, resulting in a reduction in the rise time of the curve.

Other observations referred to by Turnbull [127, 135] include that a less steep permeation transient than that predicted from Fick's law is often an indication of unsteady surface conditions, and that, to the contrary, a steeper permeation transient suggests significant trap occupancy. Finally, if there is a peak in the steady-state flux of the transient followed by a decrease in the height of the transient, this could be attributed to surface filming or void formation, as a result of which hydrogen can be trapped into voids. Consequently, there is a reduction in the hydrogen quantity that is detected at the exit side of the cell over time.

As viewed, various factors like experimental variables and microstructural parameters can have an effect on the shape of the permeation transients. The theoretical lattice diffusion coefficient in most of the experiments of this work was the same, as there were membranes from the same low carbon steel and in the same range of temperatures round 25°C. For some permeation experiments that were performed throughout the day temperatures could be up to 10 degrees Celsius less overnight. These temperature differences would explain discrepancies of around 25% in the  $D$  value of hydrogen in AISI 4340 steel, bearing in mind that this diffusion coefficient is given as a function of temperature by the following plot (Figure 112) [66]:



**Figure 112. Arrhenius plot of hydrogen diffusion coefficient  $D$  in AISI 4340 steel [66]**

Although the applied steel membrane in the permeation experiments was not the AISI 4340 steel, which was used in mechanical testing, the previous remarks about the effect of temperature on the hydrogen diffusivity in this type of steel are useful to be taken into account, as the hydrogen diffusivity in the steel membranes of the permeation experiments can be a similar function of temperature, implying that a change of approximately 10 degrees in temperature could change the value of the hydrogen diffusion coefficient by 25%.

Applying the time lag method for the calculation of D values [64, 65], i.e. based on Equation 6, there were found so different D values for hydrogen that they could not be explained only based on temperature differences, suggesting that the calculated D value is not the theoretical lattice diffusion coefficient, but an effective diffusion coefficient which has incorporated the effects of irreversible trapping.

| Condition      | $J_{\infty}$ ( $\mu\text{A}/\text{cm}^2$ ) | $T_{\text{lag}}$ (s) | D ( $\times 10^{-8} \text{ cm}^2/\text{s}$ ) |
|----------------|--------------------------------------------|----------------------|----------------------------------------------|
| -1200 mV (SCE) | 0.383                                      | 620                  | 0.67                                         |
| -1100 mV (SCE) | 0.271                                      | 770                  | 0.54                                         |
| -1000 mV (SCE) | 0.146                                      | 1600                 | 0.26                                         |
| - 900 mV (SCE) | 0.098                                      | 18000                | 0.023                                        |
| - 875 mV (SCE) | 0.044                                      | 24000                | 0.0174                                       |
| - 850 mV (SCE) | 0.025                                      | 52000                | 0.0080                                       |
| - 825 mV (SCE) | 0.006                                      | 72000                | 0.0058                                       |
| - 800 mV (SCE) | 0.004                                      | 86000                | 0.0048                                       |

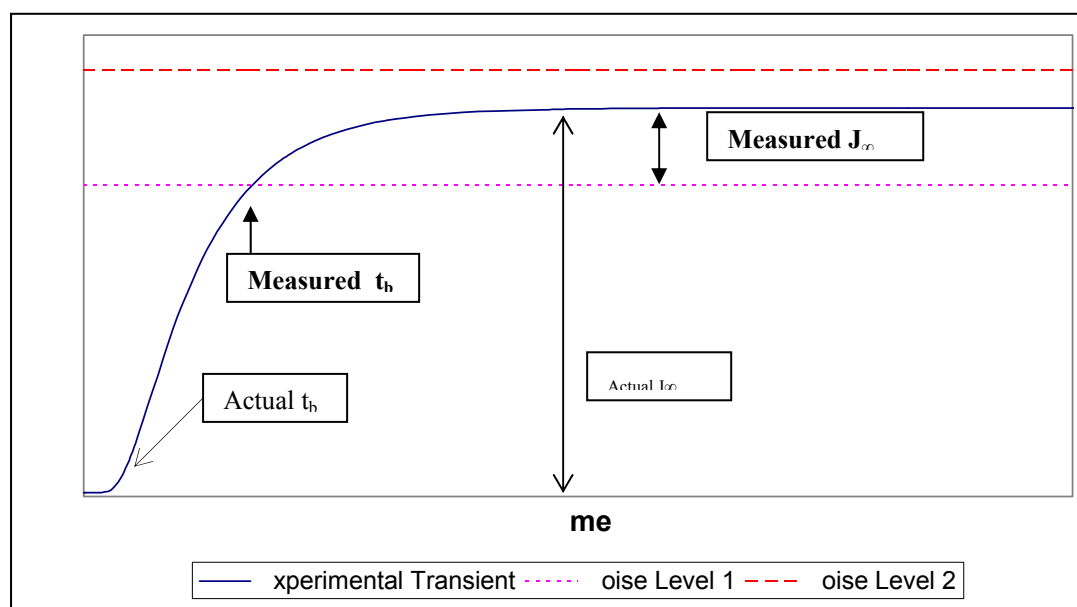
**Table 28. Calculated D values at various potentials displaying the effect of different time lag values**

The above Table 28 presents the calculated D values for the permeation transients presented in Figures 66–74. Only values at –1200 and –1100 mV (SCE) are close to the D value of  $2 \times 10^{-8} \text{ cm}^2/\text{s}$ , calculated by Kilgallon [22] and Hillier [11] for a charged unplated shim of the same steel composition. On the other hand, there are huge discrepancies in the effective D values for the whole studied range of potentials between –1200 and –800 mV (SCE). These disagreements cannot be accounted for

based on any temperature effect, as the effective diffusion coefficient at  $-1200$  mV (SCE) was found to be 140 times higher than the  $D$  value at  $-800$  mV (SCE). This is firstly attributed to the differences in the time lag values, and secondly, it reveals the effect of filling traps at more noble values.

At more positive potentials the hydrogen concentration at the surface of the membrane is smaller compared to surface hydrogen concentration at more active values. On the other hand, this is obvious from the steady-state flux values that were higher at more negative potentials. Charging hydrogen with higher concentration can have the effect of filling traps easier and quicker, thus allowing the permeated hydrogen to reach its final value quicker, and in that case this is depicted with a steeper increase on the permeation transient, as well as a shorter breakthrough time. These thoughts are in agreement with the case of BS 970 410S21 stainless steel [127, 135], presented in Figure 111, where charging at 0.02 ppm (wt) hydrogen produced a shorter breakthrough time than when charging at 0.0042 ppm wt).

### Background Noise Effect



**Figure 113. Permeation transient showing the effect of various background noise levels on the breakthrough time  $t_b$  and the steady state flux  $J_\infty$ .**

Apart from trapping phenomena, permeation experiments had to face the effect of background noise current. Bearing in mind the increasing difficulty in filling traps at more noble values, as well as the smaller steady-state fluxes at these potentials, it can be concluded how difficult it was to detect permeable hydrogen at potentials above  $-800$  mV (SCE), where in SSRTs for charged and stressed unplated steel specimens there was observed embrittlement (Figure 58). As a result, no permeation transients at potentials higher than  $-800$  mV (SCE) were produced, as the smallest achieved background current of  $0.004 \mu\text{A}/\text{cm}^2$  (Figure 73) was still enough to hide the hydrogen permeating current density at such potential values.

The previous remarks can be shown more pictorially in Figure 113, where the effect of two different background current levels is depicted on the obtained permeation transient. If there is a noise level 1, then the recorded breakthrough time is different from the actual that would have been obtained without noise. Moreover, the shape of the obtained transient is different, as all the information below the noise level 1 line is not recorded. If there is a higher noise level 2, then no permeating hydrogen can be recorded whatsoever, as all the information that would have been acquired is below the noise level line 2. Finally, the problem of the background current deterred the performance of permeation measurements with coated steel membranes that would have been scratched. Apart from the apparent difficulty of accurately measuring the scratch surface, the produced permeation currents from the corrosion of the coatings would have been extremely small and difficult to measure.

### Film Formation Effect

Concerning the permeation transients at  $-825$  and  $-800$  mV (SCE) (Figures 72 and 73), it was observed that after a long period of time the permeating flux was decreased. Based on Turnbull's [127, 135] observations on similar cases, this drop in the current density could be attributed to the film formation on the charging side of the membrane. Hydrogen can be trapped in these films, and consequently, the permeation flux is decreasing from its plateau value. This phenomenon was also observed at other more active values, but these transients were not amongst the typical ones presented in Figures 66–74. However, their highest values were shown in Table

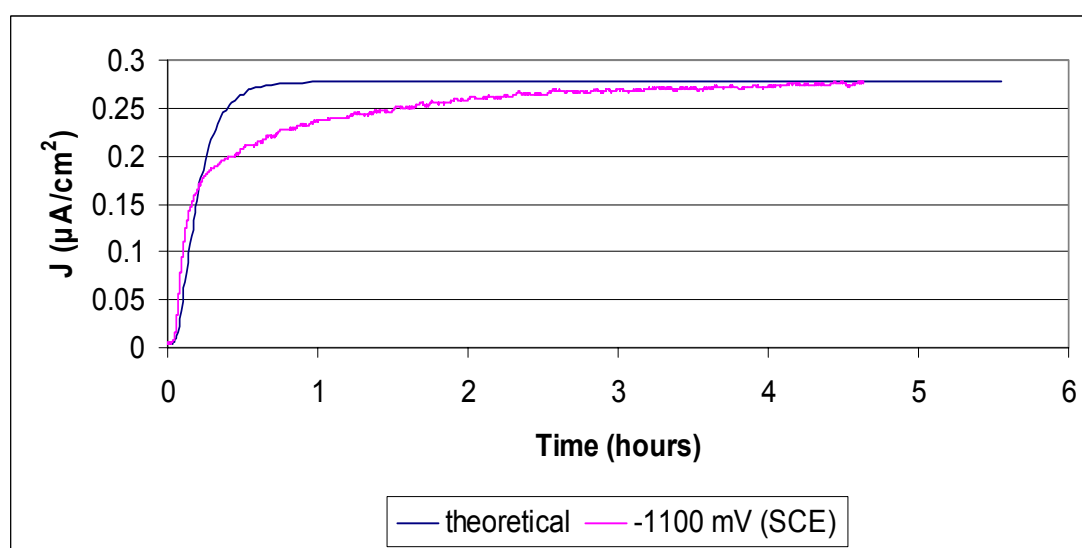
27 of the Permeation Results and were taken into account for the calculation of the mean steady-state flux values.

### Theoretical and Experimental Transients

Finally, in the discussion about the transients shape, there was an attempt to show the differences between the experimentally obtained curves and some theoretical ones based on potentiostatic charging [67]. Using Equation 12 of Boes and Züchner [67] – presented again here – for the prediction of a rising permeation transient under non-steady state potentiostatic conditions, someone can obtain a theoretical transient and compare it with the experimental one.

Equation 12:

$$J = J_{\infty} \left\{ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(-\frac{Dn^2\pi^2 t}{L^2}\right) \right\}$$



**Figure 114. Theoretical and experimental transients at –1100 mV (SCE)**

However, it should be noted that even this theoretical transient is different for each experiment, as its plotting is based on the calculated  $J_{\infty}$  and  $D$  values from the experimental transient. Despite this fact, this is a useful comparison between the theoretically expected and the experimentally obtained. A typical example of such a

comparison is shown in Figure 114, where there are both the experimental and the theoretical transients at  $-1100$  mV (SCE).

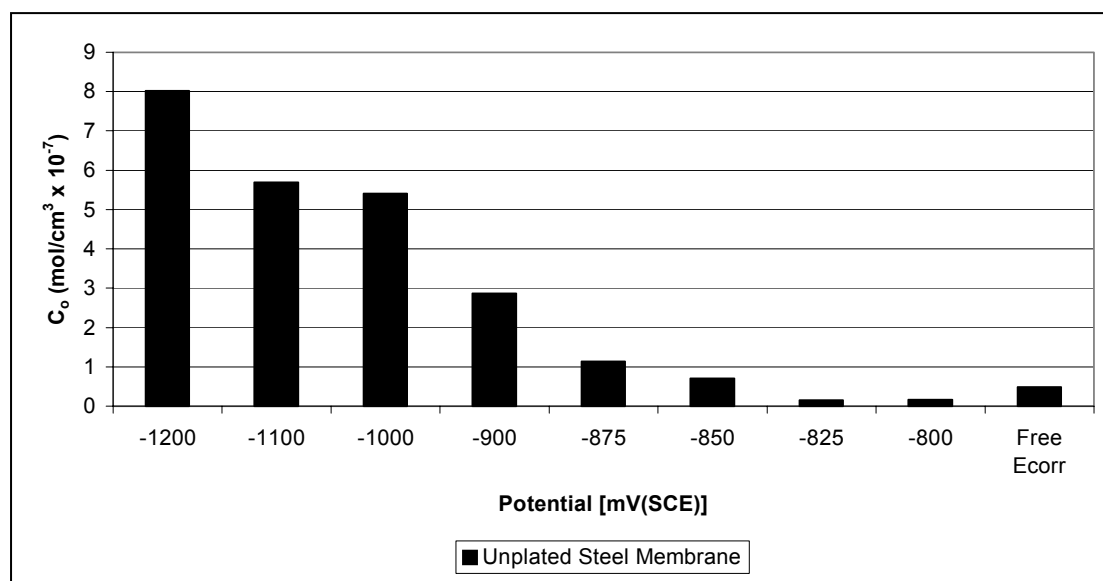
As viewed from Figure 114 there is no close agreement between the experimental and theoretical transients at  $-1100$  mV (SCE). The plotting of the theoretical line was based on the values of Table 28 for  $-1100$  mV (SCE), where  $J_{\infty}=0.271$   $\mu\text{A}/\text{cm}^2$  and  $D=0.54 \times 10^{-8}$   $\text{cm}^2/\text{s}$ . The discrepancy would have been larger if, instead of the calculated  $D$  value, a more widely accepted [11, 22] constant value of  $2 \times 10^{-8}$   $\text{cm}^2/\text{s}$  was used. No matter which is the followed approach, this disagreement is expected, as other investigators [68, 69], as well, found deviations from theoretical transients.

More specifically, Archer and Grant [68] supported the view that experimentally obtained transients lie between those expected for potentiostatic and galvanostatic conditions, because hydrogen entry does not depend only on the charging conditions, but also on the various steps involved in hydrogen evolution at the entrance face and its diffusion through the membrane. As potentiostatic conditions, widely assumed to lead to constant surface concentration, necessitate the entrance of a small fraction of hydrogen in the membrane, and galvanostatic conditions, widely assumed to lead to a constant flux, necessitate that the whole charging hydrogen enters, both conditions seem unlikely to apply to the same membrane. Moreover, Allcock [69] (Figure 21) found his experimental transients, obtained under galvanostatic conditions, to be in closer agreement with theoretical transients for constant surface coverage instead of the expected constant flux model when galvanostatically charging.

#### **4.2.2 Potential and Hydrogen Concentration**

Charging an unplated steel shim at more negative potentials causes more hydrogen to permeate to the exit side of the shim, as higher current densities are recorded. This trend was shown in Figure 77. At the same time, the higher hydrogen permeating fluxes correspond to higher surface hydrogen concentrations on the charging side of the membrane. Taking the hydrogen diffusion coefficient into the steel membrane as  $2 \times 10^{-8}$   $\text{cm}^2/\text{s}$  [11, 22] and with a membrane thickness of  $50$   $\mu\text{m}$ , the surface hydrogen concentration values can be calculated by Equation 4, according to which

$C_o = J_{\infty}L/FD$ . Figure 115 depicts the trend of higher surface hydrogen concentrations at more active potentials.



**Figure 115. Bar chart of surface hydrogen concentration against potential**

This trend was expected in general, and similar relationship between hydrogen permeation and potential was found in other works. More in detail, Lucas and Robinson [103] reported the increase in permeation current density at more negative potentials for 50D steel cathodically protected in aerated 3.5% NaCl solution, as seen in Figure 109. Moreover, as viewed in Figures 116 and 117, Robinson and Kilgallon [136] showed that at more negative potentials there is increased hydrogen permeation and higher hydrogen surface concentration for a cathodically protected low C steel membrane – with the same composition as in this study – in both sterile and biologically active seawater. Comparing the permeation results of the present study in 3.5% NaCl for a range of potentials with the results of Figure 116 in sterile seawater and for the same type of low carbon steel membrane, it is concluded that these two sets of permeation flux data are of the same order of magnitude in the same range of potentials. (Figure 118)

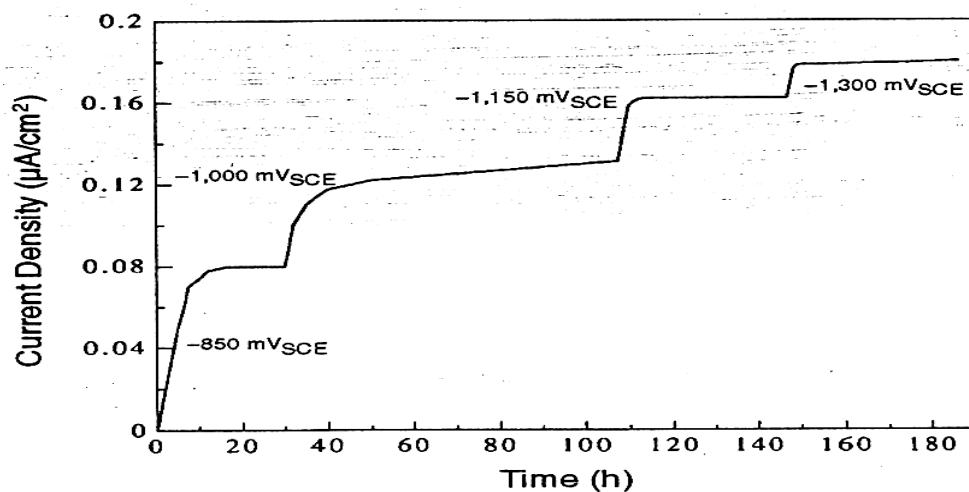


Figure 116. Hydrogen permeation transients for a low-carbon steel membrane exposed to sterile seawater showing the effect of applied potential [136]

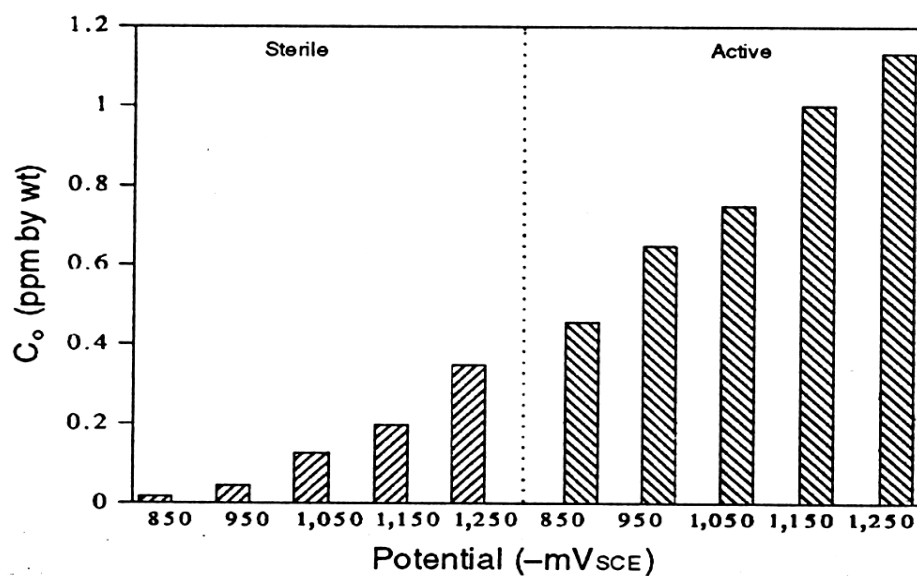
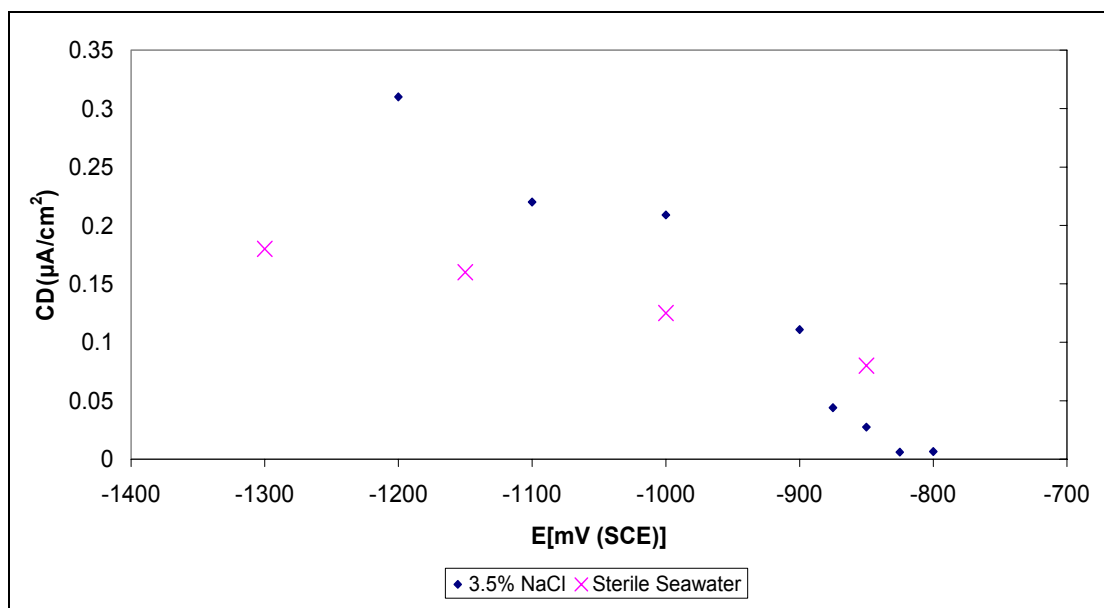


Figure 117. Effect of applied potential on surface hydrogen concentration of the low-carbon steel membrane in sterile and biologically active seawater [136]



**Figure 118. Comparison of permeation results in potentiostatically charged low-carbon steel membranes in 3.5% NaCl solution in the present study with results in sterile seawater [136] for the same membrane material**

#### Hydrogen Permeation and Re-embrittlement of Corroding Coated Steel Specimens

From the above trend of the permeation experiments, it is apparent that more active corroding coatings will be responsible for more hydrogen uptake by the steel substrate, and for this reason, a zinc coating, for example, is more likely to cause higher extent of re-embrittlement than cadmium. Moreover, in terms of the aluminium-based coatings of interest, there is a clear indication that hydrogen definitely permeates steel at potentials below  $-800$  mV (SCE) (Figure 73), and very probably even at  $-750$  mV (SCE), although a certain amount of background noise prevented the detection of any permeating hydrogen at this more noble potential value. SSRTs of stressed and charged uncoated steel specimens showed that re-embrittlement is a concern at  $-750$  mV (SCE) (Table 18), and therefore, hydrogen should diffuse and permeate at this potential too, which, on the other hand, lies within the range of potentials, at which corrosion of the aluminium-based coatings occurs.

In general, the drawn conclusion from the permeation measurements is that the re-embrittlement of steel specimens, coated with aluminium-based coatings is a real

concern. This conclusion is in line with the conclusions from SSRTs with charged and stressed unplated specimens, and all observations made, based on both types of experimentation, will be used as a basis, with which SSRT re-embrittlement results will be compared for each coating separately. Before attaining this level of discussion, further comments on the relationship between the results of SSRTs and permeation measurements are developed in the following section.

#### **4.2.3 Hydrogen Permeation Measurements and SSRTs**

So far, based on both SSRTs on charged uncoated steel tensile specimens, as well as hydrogen permeation measurements with charged uncoated steel membranes, there is a clear indication that hydrogen is extremely likely to impair the mechanical properties of coated high strength steel components when the coatings corrode in service, and while these components are stressed. The aim of this section is to show how the results, the comments and the conclusions from both types of testing are correlated with each other in the light of the examination of the measured re-embrittlement.

##### Similarities and Differences in the Experimental Procedure

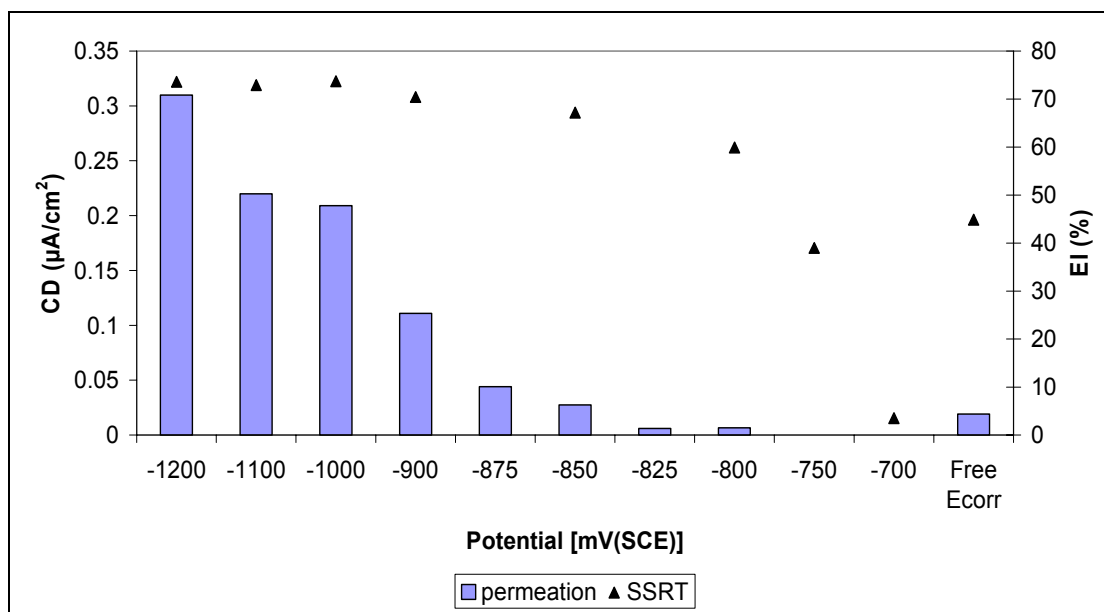
Attempting to proceed with this comparison, it is firstly essential to highlight some of the differences and similarities between the two techniques. Firstly, in SSRTs the employed grade of steel was the AISI 4340, while in the permeation tests it was 0.04% C steel. The hydrogen diffusion coefficient in the first material is reported to be between  $2$  and  $4 \times 10^{-7} \text{ cm}^2/\text{s}$  [124, 137, 138], whilst in the second to be  $2 \times 10^{-8} \text{ cm}^2/\text{s}$  [11, 22]. Moreover, charging in SSRTs was performed during or prior to straining, whilst in permeation measurements there was absence of stress. However, as some similarities in trends were found between permeation tests and SSRTs with charged and simultaneously strained specimens, these two sets of experimental results are going to be compared. Finally, another common aspect in both tests was the same corrosive environment of 3.5% NaCl solution, which was responsible for the ingress of hydrogen into the steel structure in both cases.

### Role and Objectives of Each Test

Concerning the role and goal of each experimental procedure, permeation tests measure quantitatively the amount of hydrogen, which enters the steel membrane, diffuses through it, and finally permeates. As pointed out earlier, it is exactly this hydrogen that will be available to migrate to areas of high triaxial stress in a stressed component, and cause embrittlement following one or several possible proposed HE mechanisms. [85, 91, 104, 133, 134] It is the hydrogen that will not be trapped into irreversible traps, unable then to freely diffuse within the microstructure, but it is the hydrogen that is either readily diffusible or reversibly trapped, and thus potentially able to be available to freely diffuse after its limited residence time within the trap. [78] On the other hand, SSRTs deal with the effect of the embrittling action of the previously described type of hydrogen, and their results can be easily quantified by providing an EI value, which shows the degree or extent of the embrittling action. From the above, it can be inferred that while permeation measures quantitatively the embrittler, i.e. hydrogen, SSRTs quantify its embrittling effects on various materials, including high strength steels, and it is in the context of this relationship between these two tests that their results will be compared.

### Comparison Between Permeation and SSRT Results

The graph in Figure 119 summarises hydrogen permeation and SSRT results for uncoated specimens, potentiostatically charged in the range between  $-700$  and  $-1200$  mV (SCE). By decreasing the applied potential more hydrogen permeates the membrane and a higher extent of re-embrittlement for the tensile specimens is observed.



**Figure 119. Mixed graph showing steady-state flux and EI values at various potentials**

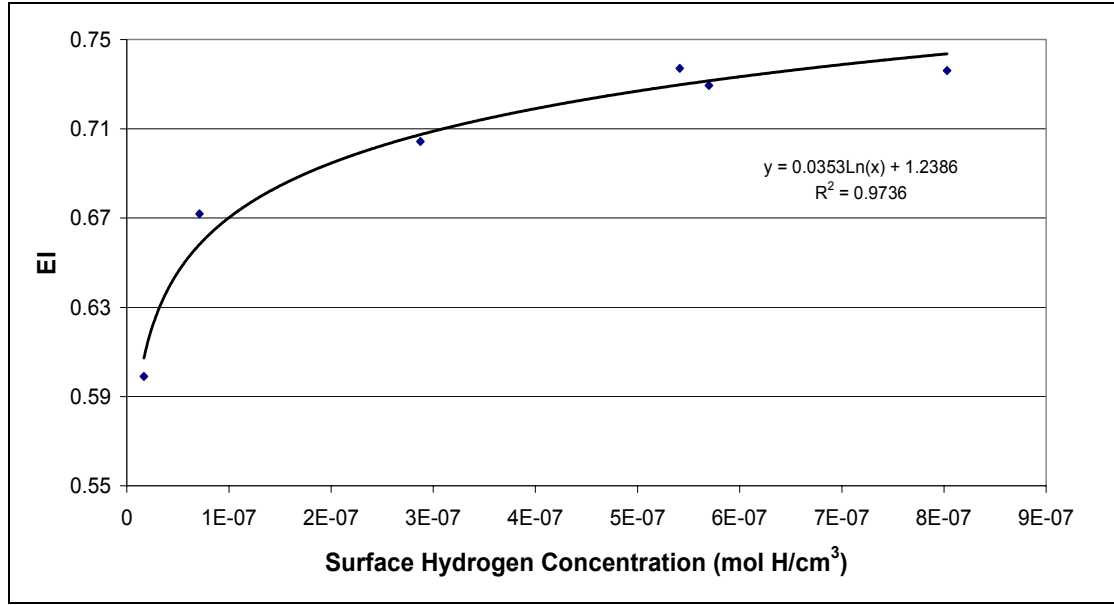
Various remarks can be mentioned from the comparison of these two sets of results. Firstly, at very negative potentials, between  $-1200$  and  $-1000$  mV (SCE), the high rates of permeating hydrogen correspond well with the increased EIs. As stated earlier, it is impossible to obtain even higher ductility losses before attaining a minimum stress level, and this is the reason why below  $-1000$  mV (SCE) there cannot be observed even more embrittlement, although even more hydrogen is permeating. Secondly, it is observed that the occurring embrittlement when steel freely corrodes is confirmed by the detected rate of hydrogen permeation in the respective permeation test. However, it should be noticed that the measured potential in a SSRT resulted in  $-630$  mV (SCE), whereas in a permeation test in  $-750$  mV (SCE). (Figures 74 and 75) Finally, applying cathodic potential of  $-700$  mV (SCE) suggests not only the partial protection of steel against corrosion, but also a very small extent of hydrogen embrittlement, which is corroborated by the lack of a measurable amount of hydrogen in the permeation tests.

Concerning the degree of embrittlement and the permeation rates at potentials between  $-750$  and  $-900$  mV (SCE), it should be emphasised that there was an increase in permeating hydrogen, as well as in its consequent embrittling effects,

towards more cathodic potential values. However, despite the fact that at  $-750$  mV (SCE) no hydrogen permeation was detected, in the respective SSRT the EI value approached 40%, suggesting that hydrogen should permeate at this potential too, but the background current density in combination with strong trapping effects made it impossible to detect any hydrogen.

The previously referred lack of permeating hydrogen at  $-750$  mV (SCE) with the detection of substantial embrittlement at the same potential should not be considered as a unique case of discrepancy between permeation measurements and SSRTs. Careful examination of the graph in Figure 119 suggests that there is no linear correlation between the observed EIs and the detected permeation rate at a specific potential. For example, at  $-800$ ,  $-850$  and  $-900$  mV (SCE) the embrittlement indices are roughly 60%, 67% and 70%, respectively. However, the steady-state hydrogen permeation rate, as well as the surface hydrogen concentration, at  $-900$  mV (SCE) is four times higher than at  $-850$  mV (SCE) and 17 times higher than at  $-800$  mV (SCE). Despite this fact, the embrittling effects of these extremely unequal rates are lying within very close range. On the other hand, it should be remembered that the hydrogen permeation rates account for concentrations of hydrogen created in unstressed situations, while in the SSRTs the concentrations of hydrogen responsible for the observed embrittlement were formed under stress.

As seen in Figure 120, applying linear regression analysis between EIs (Figure 119) and surface hydrogen concentration  $C_o$  data (Figure 115), which correspond to potentials between  $-1200$  and  $-800$  mV (SCE), the following logarithmic equation was fitted best between these data, according to which higher hydrogen concentrations were leading to greater degree of embrittlement.



**Figure 120. Embrittlement Indices against surface hydrogen concentration**

Equation 37:

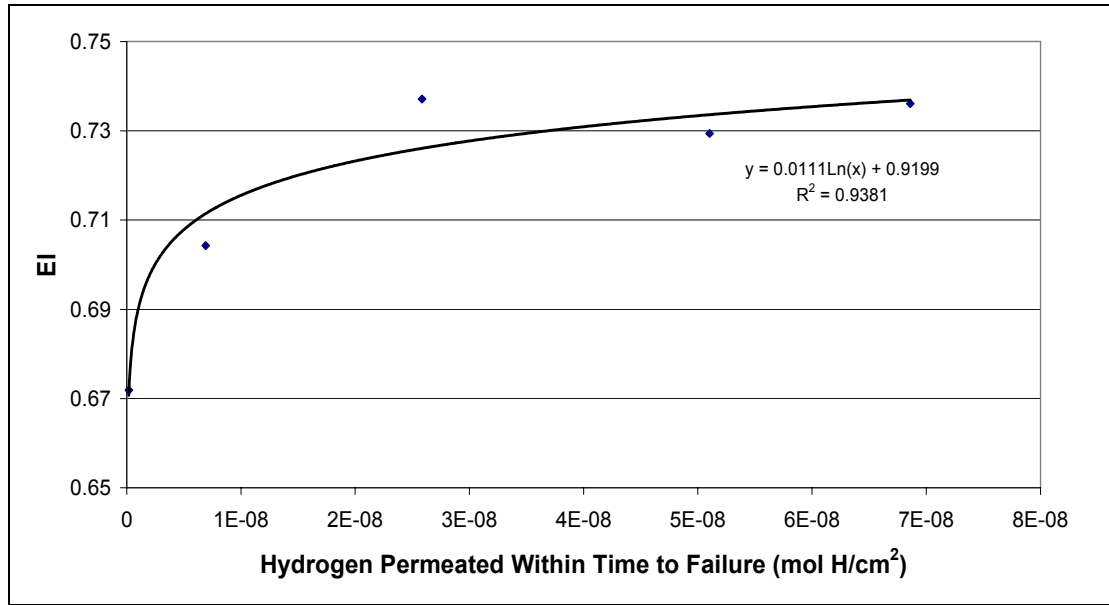
$$EI = 1.24 + 0.0353 \ln C_0, \text{ where } C_0 \text{ in mol/cm}^3.$$

This should not be considered as an unexpected finding, as some other investigators [103, 136] have also found logarithmic (or exponential) relationships between hydrogen concentration and variables applied in various kinds of mechanical testing, like the threshold stress intensity for cracking,  $K_{th}$ , used in fatigue testing. Lucas and Robinson [103] measured  $K_{th}$  for BS4360 grade 50D C–Mn steel in the hardened condition and showed that it was related to hydrogen concentration by the equation  $K_{th} = 91.2e^{-0.49C_0}$ . On the other hand, for quenched and tempered low alloy steel with yield strength of 690 MPa, Robinson and Kilgallon [136] found a linear relationship between  $C_0$  and  $\log K_{th}$ , according to which  $\log K_{th} = 1.6 - 0.65C_0$ . Although, in the present study it was the EI that was logarithmically related to hydrogen concentration, it seems to be not coincidental that such relationships are applied between hydrogen concentration and the variable that changes as a result of the hydrogen action, i.e. time to failure, reduction in area or threshold stress intensity for cracking.

| <b>E [mV (SCE)]</b> | <b>EI (%)</b> | <b>Tf (hours)</b> | <b>mol H/cm<sup>2</sup> (10<sup>-8</sup>)</b> |
|---------------------|---------------|-------------------|-----------------------------------------------|
| -1200               | 73.61         | 5.37              | 6.86                                          |
| -1100               | 72.94         | 5.51              | 5.10                                          |
| -1000               | 73.71         | 5.35              | 2.59                                          |
| -900                | 70.43         | 6.02              | 0.69                                          |
| -875                |               |                   |                                               |
| -850                | 67.19         | 6.68              | 0.02                                          |
| -825                |               |                   |                                               |
| -800                | 59.9          | 8.16              | 0                                             |
| -750                | 38.98         | 12.42             | 0                                             |
| -700                | 3.53          | 19.63             | 0                                             |
| Free Ecorr          | 44.87         | 11.22             | 0                                             |

**Table 29. EI values, times to failure and permeated hydrogen within Tf at various potentials**

The absence of stress during permeation measurements could be further highlighted by the data presented in Table 29. The amount of absorbed hydrogen at a particular potential in a permeation test was calculated for the time to failure observed at the same potential in a SSRT. Again, and in a more conspicuous way, it is evident that there is not an accurately described correlation of the amount of hydrogen from permeation tests and the subsequent extent of embrittlement from the SSRTs. Although there are two different materials, a low carbon steel and the AISI 4340 steel, with different D values for hydrogen in each material, conclusions can be drawn from the relative amounts of permeation at various potentials. For instance, it seems difficult to explain how the times to failure for specimens strained and charged at -900 and -850 mV (SCE) are so close, when, on the other hand, the permeated amount of hydrogen up to the failure time is almost 35 times higher at -900 mV (SCE) compared to -850 mV (SCE). If the hydrogen diffusivity in the AISI 4340 steel was used in the calculation of the amounts from permeation, then these permeated amounts would have been higher, but still at -900 mV there would have been 35 times more permeated hydrogen compared to -850 mV (SCE).



**Figure 121. Embrittlement Indices against hydrogen permeated within time to failure**

Applying linear regression analysis (Figure 121) between EIs and the quantity of permeated hydrogen  $Q_{TF}$  within the time to failure of uncoated steel specimens charged at potentials between  $-1200$  and  $-850$  mV (SCE), the following logarithmic equation was fitted best between these data, according to which higher hydrogen permeation was responsible for greater degree of embrittlement. (Figure 74)

Equation 38:

$$EI = 0.92 + 0.0111 \ln Q_{TF}, \text{ where } Q_{TF} \text{ in mol H/cm}^2$$

The trend in Equation 38 is similar to that in Equation 37, and if there is a logarithmic relationship between EI and surface hydrogen concentration, a similar relationship could easily be justified between EI and permeated quantity of hydrogen, which is exactly that amount of embrittler responsible for a specific degree of embrittlement.

## The Role of Stress in the Comparison Between Permeation Measurements and SSRTs

From the previously referred observations and comparisons, it is apparent that the presence or absence of stress is the main difference between SSRTs and permeation tests. The attainment of a high critical amount of hydrogen is a prerequisite for the initiation of a crack [70], but this is easily facilitated when a critical combination of hydrogen concentration and stress exists [33, 93, 111, 127]. Concerning the effect of stress, Beck et al. [66] suggested that tensile strain increases the concentration of absorbed hydrogen as a result of the dilation of the interstitial lattice sites where hydrogen accumulates, but it does not affect the diffusivity of hydrogen. For this reason, if the permeation experiments of this work were carried out under stress, there would have been an increase in hydrogen permeation rate, but as a result of an increase in hydrogen solubility with stress, and not due to the unaffected diffusion coefficient of hydrogen.

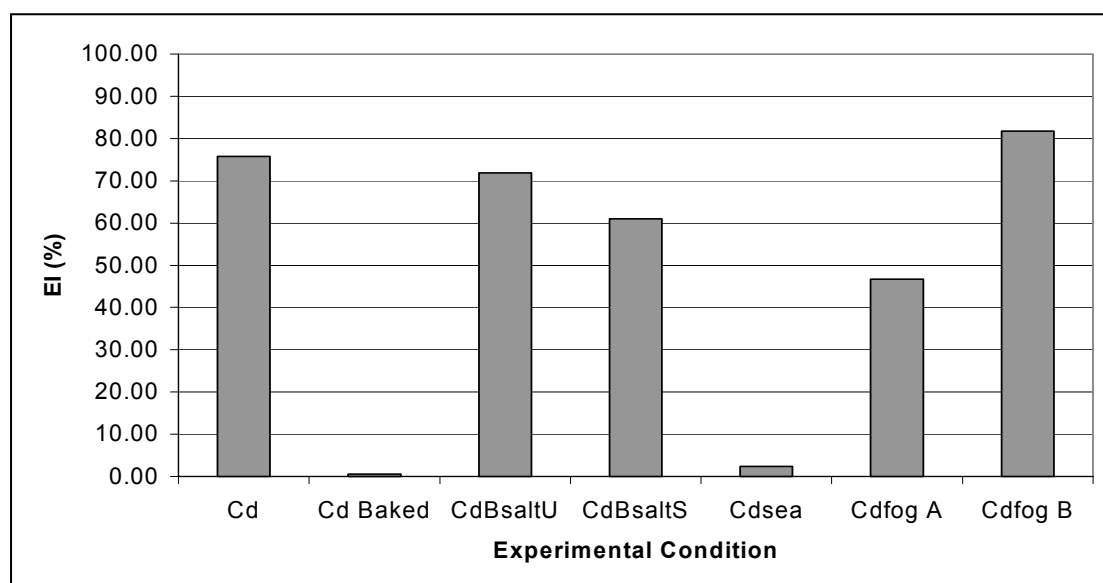
Zakroczymski [56] referred to the effect of straining on hydrogen transport in iron, nickel and stainless steel. Related to the effect of strain on permeation rate and diffusivity, he distinguished two cases, elastic and plastic deformation. In studies with Armco iron, he observed for the elastic region a slight increase in permeation rate with no change in diffusivity, and for the plastic region both diffusivity and permeability of hydrogen were substantially reduced irrespective of the strain rate, but depending on strain. Thus, it was suggested that enhanced trapping of hydrogen was caused, which in turn was responsible for the behaviour in the plastic region.

Bearing in mind the above points, it is clear that hydrogen permeation measurements would have been better correlated with SSRTs for charged and stressed uncoated specimens, if permeation was taking place in stressed membranes. However, conclusions about a possible re-embrittlement of corroding coated steel components can be still drawn even in the light of the performed permeation and mechanical tests, as their similarities and differences were critically discussed. Based on their conclusions, it will be easier to predict and understand the re-embrittlement behaviour of Cd and Al-based coated steel specimens.

### 4.3 DISCUSSION CADMIUM

Electroplated cadmium is the material used at present as coating for the sacrificial corrosion protection of high strength steel components in aerospace applications. As the aim of this work was to evaluate aluminium-based coatings as alternatives to cadmium, it is the role of cadmium in the degradation of steel mechanical properties under various conditions, as well as its corrosion performance, that are going to be discussed first. The performance of the aluminium-based coatings will follow and will be compared with that of cadmium.

#### 4.3.1 Mechanical Testing



**Figure 122. Bar chart displaying the EI for all Cd plated specimens at all the experimental conditions**

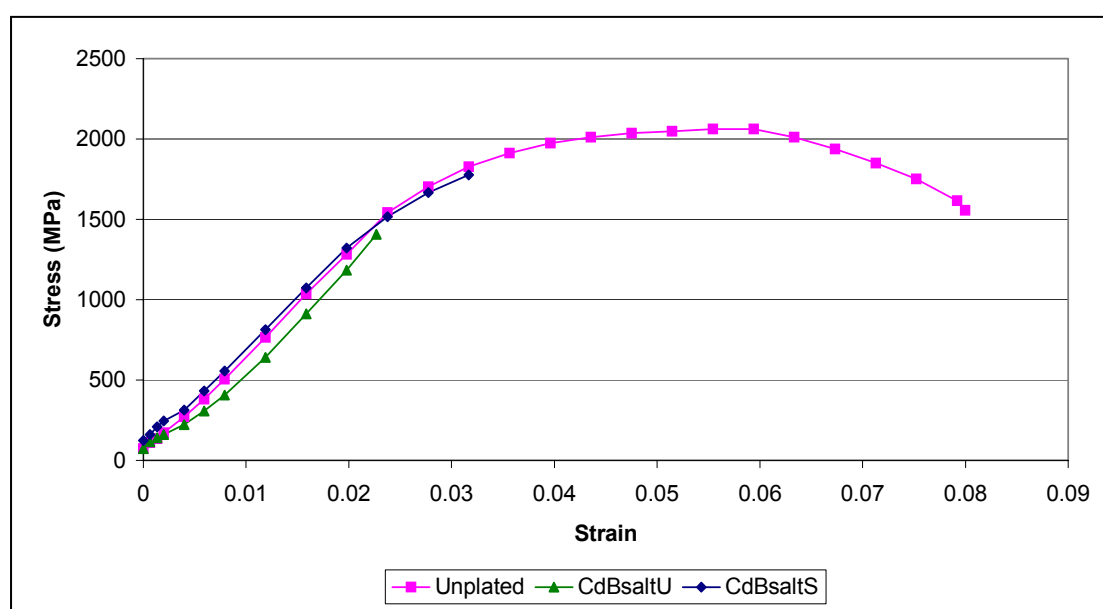
#### Hydrogen Embrittlement and De-Embrittlement of Cadmium Coated Specimens

Figure 122 summarises the effect of Cd electroplating on AISI 4340 steel tensile specimens at a range of treatments and corrosive environments. As viewed, Cd plating caused a substantial amount of embrittlement to the steel substrate (EI=75.8%) (Table 10), as the electroplating procedure has generally less than 100% current efficiency with a small fraction of the current causing the generation of hydrogen. However, an

immediate post-plating baking process at 200°C for 24 hours almost fully de-embrittled the tensile specimens (EI=0.6%) (Table 10). This was not an unexpected finding, as previous studies at Cranfield [9, 11, 13] had shown that the embrittlement of Cd plated AISI 4340 steel specimens could be overcome by de-embrittlement treatment consisting of baking at a temperature between 190 and 230°C for 24 hours [2–4].

### Hydrogen Re-embrittlement of Cadmium Coated Specimens

#### Tests in 3.5% NaCl solution



**Figure 123. Stress–strain diagram showing the re-embrittlement of scribed and unscribed Cd plated and baked specimens, corroded in 3.5% NaCl solution**

Cd coated tensile specimens were stressed in 3.5% NaCl solution, so that a simultaneous effect of stress and corrosion of the Cd coating occurs. As seen in Figures 122 and 123, both scribed (EI=61%) and unscribed specimens (EI=71.8%) were substantially re-embrittled as a result of the hydrogen entry due to the cathodic reaction of water reduction whilst the anodic reaction of cadmium dissolution was simultaneously taking place. No matter how large the extent of the re-embrittlement was, it should be noted that its occurrence was not unexpected, as various investigators had addressed the issue of hydrogen embrittlement of steels as a result of

the corrosion of the coating, taking place under the influence of corrosive environments or even corrosive fluids, e.g. paint strippers. [2, 18, 19, 139] For instance, Pollock [19] studied the embrittling effect of maintenance products, like paint strippers, on Cd plated and baked AISI 4340 steel specimens, both notched and unnotched, and he detected small embrittlement caused by some of them.

From the stress–strain diagram of Figure 123 it is proved that the phenomenon occurring during these tests was hydrogen embrittlement as a result of the corrosion of the coating, i.e. hydrogen re–embrittlement, as, in general, hydrogen does not change the yield point [11, 21, 24] or the UTS of high strength steels, but merely cuts the stress–strain curve at reduced values of strain.

#### Marine Atmosphere Exposure Trials

As seen from Figure 122, Cd plated and baked specimens that had been exposed to marine atmosphere conditions for 2 years, showed an insignificant amount of re–embrittlement ( $EI=2.4\%$ ) failing at 19.9 hours on average (Table 24). Marine atmosphere was the environment, where the Cd coating performed by far better than in 3.5% NaCl solution, as there was by far less amount of re–embrittlement observed. However, in the case of marine exposure, the tensile specimens were firstly corroded, and then tested in SSRTs, allowing plenty of time for hydrogen to diffuse out of the specimens. In other words, there was not the simultaneous effect of stress and hydrogen diffusion, as in the case of 3.5% NaCl solution. Finally, the excellent mechanical performance of Cd plated specimens in the marine atmosphere was confirmed by their appearance after two years of exposure, according to which no signs of degradation were observed at the end of this long experiment.

#### Salt Spray Testing

This type of testing was the most aggressive corrosive environment, to which the Cd coated and baked tensile specimens were submitted. As viewed from the bar chart of Figure 122, in both salt spray tests, significant amounts of re–embrittlement were introduced into the high strength steel specimens, although the specimens were firstly corroded and then tested. The fact that a high extent of embrittlement was recorded

without the simultaneous effect of stress and hydrogen diffusion indicates the degree of the aggressiveness of the salt spray test. More specifically, in the first case the EI was almost 47% corresponding to an average time to failure of 10.9 hours (Table 25), whilst in the second case this index value reached roughly 82% or a mean time to failure of 3.7 hours (Table 25), displaying the highest extent of embrittlement observed in any SSRT in this work.

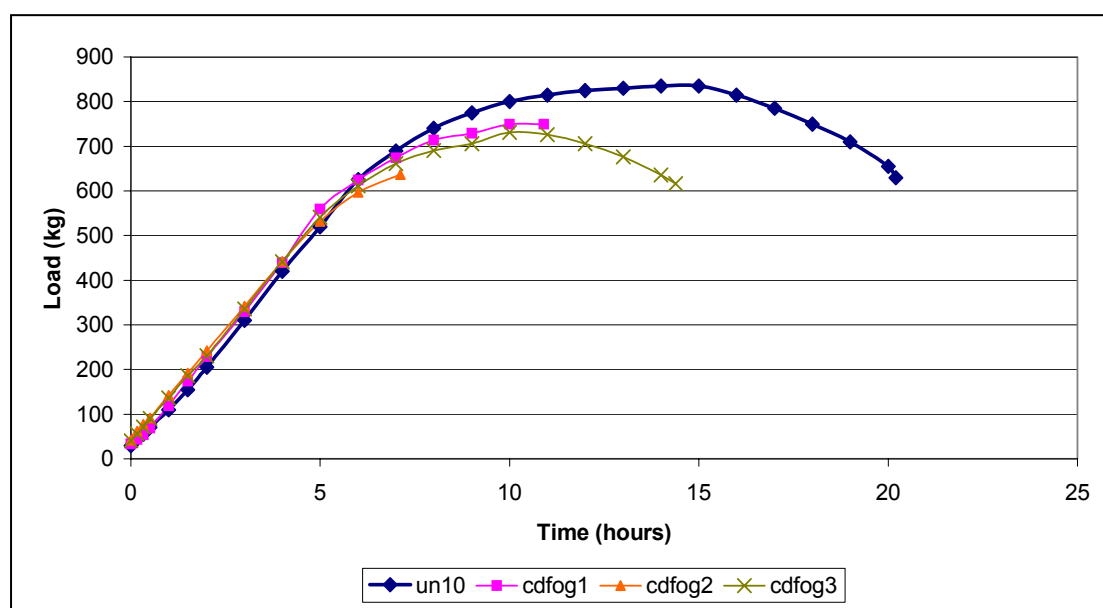
In the first case the three tested specimens exhibited quite a lot of scatter in the times to failure ( $SD=3.65$ ), while in the second case a smaller one ( $SD=0.45$ ) was recorded. (Figure 64 and Table 25) Any observed scatter could be ascribed to some variation of the salt fog distribution in the cabinet, although the specimens had been moved regularly to different positions. A further possibility is that the range in times to failure was a consequence of different amounts of corrosion in the gauge lengths of the specimens, suggesting that the final degradation of the mechanical properties of the Cd coated steel was not only the result of the cathodic reaction of water reduction leading to hydrogen entry, but also due to an anodic reaction of the iron dissolution when the coating was no longer protecting the steel.

#### *Physical Appearance of Cd Plated Specimens During Salt Spray Test*

The previously expressed concern about iron anodic dissolution should be given further consideration, if the recorded time for the first appearance of red rust on tensile specimens in each repeat is taken into account, as well as the time when the tensile specimens were totally covered by corrosion products. More in detail, as seen in the Salt Spray Testing results, in the first case, Cd coated and baked specimens displayed first signs of red rust at 350 hours, and were totally covered by corrosion products at 500 hours. (Figure 94) For the remaining 500 hours the steel was left to freely corrode with no remaining Cd coating to sacrificially protect it. On the other hand, in the second repeat of the test, the specimens showed first signs of red rust at 120 hours, and red rust covered totally their threaded parts and gauge lengths at 250 hours. (Figure 95) As a result, steel was freely corroding, and was totally unprotected for 750 hours. This could possibly be an explanation for the huge observed differences in the times to failure between the specimens of both cases, lending

support to the view that the degradation of the mechanical properties was the result of both hydrogen re-embrittlement and corrosion.

*Information from Load–Time and Stress–Strain Diagrams about Hydrogen Re-Embritlement and Corrosion of Cd Plated Specimens*



**Figure 124. Load–time diagram for Cd plated and baked specimens held for 1000 hours in a salt spray cabinet (first case)**

Load–time diagrams combined with stress–strain diagrams could shed more light on the attempt to understand if corrosion or hydrogen re-embrittlement was responsible for the degradation of the steel mechanical properties. It was the first case of salt spray testing that was chosen for analysis, as the obtained times to failure exceeded the yield point and ranged between 7.1 and 14.4 hours. Consequently, it was easier in that case to detect if hydrogen embrittlement could be the unique cause for the observed degradation. From Figure 124, it is seen that Cd plated specimens failed in all cases at reduced loads for the same strain as in the unplated specimens, suggesting that the reduction of the load–bearing properties of steel occurred not only because of hydrogen re-embrittlement, but also due to corrosion of unprotected iron, which reduced the area under load.

At this point, it should be emphasised that among all coated specimens, tested in the salt spray cabinet, only the Cd plated ones submitted a reduction in their diameters along their gauge lengths, and hence, this means that there was a reduced area under load during the SSRTs, incurring changes in the position of the stress–strain curves for these specimens. The following Table 30 shows the diameters of the specimens after the salt spray test and before the SSRT ( $D_b$ ), the diameters after the SSRT ( $D_a$ ), the reductions in area after the SSRT (RA%), and the times to failure ( $T_{\text{failure}}$ ).

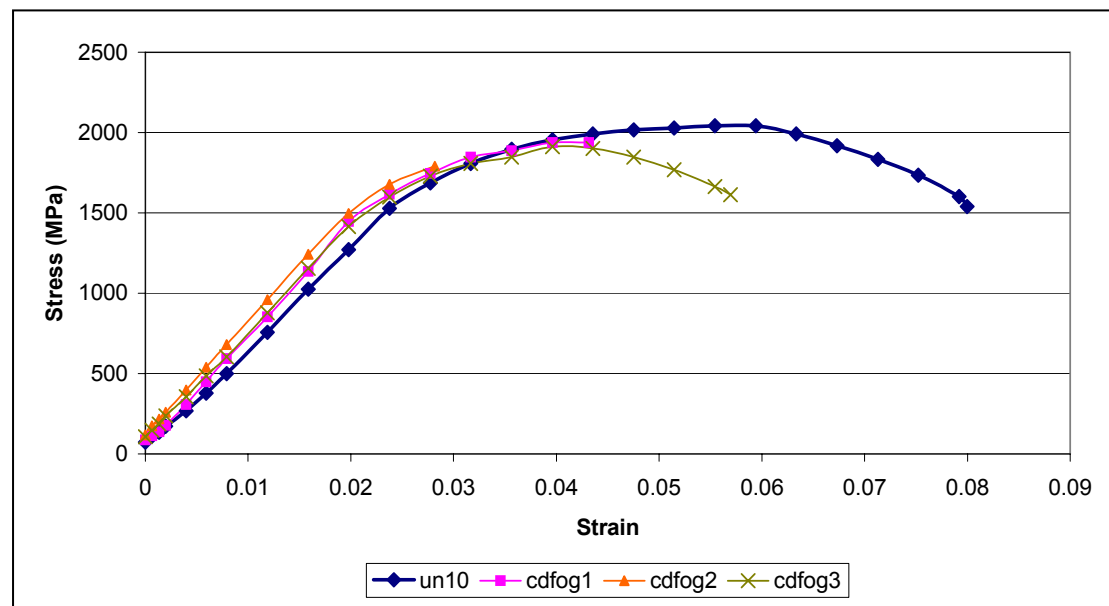
| Specimen | $D_b$ (mm) | $D_a$ (mm) | RA (%) | $T_{\text{failure}}$ (h) |
|----------|------------|------------|--------|--------------------------|
| Cdfog1   | 2.197      | 1.905      | 19.5   | 14.4                     |
| Cdfog2   | 2.111      | 2.107      | 0.3    | 7.1                      |
| Cdfog3   | 2.185      | 2.054      | 11.6   | 10.9                     |

**Table 30.  $D_b$ ,  $D_a$ , RA and  $T_{\text{failure}}$  for Cd plated and baked specimens, held in salt spray testing for 1000 hours (first case)**

From Table 30 there was information on the diameters, and thus the areas under stress of the Cd plated and corroded specimens. By obtaining this piece of information the load–time diagrams were transformed to the stress–strain diagrams. Moreover, it was observed that specimens with larger diameters, after the salt spray test and before the SSRT, displayed longer times to failure, while, totally expectedly, those with the higher reduction in area showed more elongation and longer times to failure.

Figure 125 depicts the stress–strain diagrams for the three Cd plated specimens that were submitted to salt fog conditions, and these curves are compared with one of unplated steel specimen. As seen, the position of the curves, compared to that for the unplated control, changed from the load–time to the stress–strain diagram, as the corroded specimens had smaller diameters and areas under load in the SSRTs than the unplated specimens. Although two out of three specimens failed at the same stress as the unplated specimen for the same strain, the third specimen failed at a stress of 400 MPa lower compared to the unplated control, suggesting that hydrogen re–embrittlement acted first, while after the dissolution of cadmium both hydrogen re–embrittlement and corrosion of the steel occurred. It could be suggested, that ending

the salt spray test when the specimens display the first signs of red rust, and then performing the SSRT could lead to the detection of the pure effect of re-embrittlement on the high strength steel. However, the purpose of the salt fog test was to examine the effect of these corrosive conditions for a specific period of time on a range of coated steels, in order to compare their performance as ‘embrittlers’ and sacrificial coatings.



**Figure 125. Stress–strain diagram for Cd plated and baked specimens held for 1000 hours in a salt spray cabinet (first case)**

### 4.3.2 Corrosion Testing

#### LPR Measurements

LPR measurements yielded information in two aspects; firstly, monitoring of the free corrosion potential of cadmium, and secondly, recording of its polarisation resistance value that is useful for the estimation of the corrosion rate trend of the coating.

#### Potential Recording

As already seen in the LPR Results, Cadmium's potential shifted from values slightly more noble than  $-800$  mV (SCE) up to values in the range between  $-700$  and  $-650$  mV (SCE). (Figure 83) After 1200 hours of exposure the Cd coating displayed its first signs of red rust, which covered 20% of its area at 2000 hours and onwards. This means that after this time the recorded potential was not that for a detached Cd coating. However, the previous remarks on potential trend were definitely valid up to 1200 hours, and therefore, the drawn conclusion is that the potential shifted towards more noble values, as Cd was not passivated with chromium, and for this reason it was more active initially. This trend was also observed by Hillier [11] in polarisation scans and LPR measurements for unpassivated cadmium.

#### Polarisation Resistance

Concerning the polarisation resistance trend, after an initial level of  $3,000 \Omega \text{ cm}^2$ , the  $R_p$  increased and then fluctuated between  $6,000$  and  $12,000 \Omega \text{ cm}^2$ . (Figure 84) Bearing in mind that the  $R_p$  results for cadmium are valid up to 1200 hours, it is concluded that there was an increase of the  $R_p$  compared to the initial LPR measurement, and this corresponded to a decrease of the self-corrosion rate of cadmium. This trend was observed also in Hillier's work [11], although the increase of the  $R_p$  value for Cd after three months of immersion in that case was by far higher.

### Galvanic Coupling Measurements and Polarisation Curves

In this type of corrosion testing, the couple of Cd with steel showed no signs of red rust up to 600 hours. Afterwards, although the steel panel remained intact, the Cd panel was totally covered with corrosion products. As a result, any useful conclusions about the coupled potential and the galvanic current density are worth drawing for that period only. The coupled potential started with values between  $-750$  and  $-800$  mV (SCE), close to that for detached cadmium, and after a short deviation to the more noble level of  $-600$  mV (SCE), the potential reached a level round  $-750$  mV (SCE). (Figure 91) Excluding this observed deviation that was short in time, these results could be compared with those of Baldwin [10] who found the coupled potential of Cd with steel in 0.6 M NaCl solution starting at  $-800$  mV (SCE) and approaching  $-750$  mV (SCE) after 150 hours of immersion. Moreover, the observed trend in coupled potential in the present study was confirmed by the determination of polarisation curves in each of the isolated electrodes of the couple. According to these curves (Figure 93), presented in the Galvanic Coupling Results, in all cases the coupled potential was closer to the Cd value, as the whole phenomenon was under cathodic control, imposed by the cathodic reaction of oxygen reduction on the steel panel that remained the cathode in this couple throughout the whole experiment.

The fact that Cd was the anode and steel remained the cathode in this couple is confirmed by the positive value of the galvanic current density. (Figure 92) No change in the polarity of the current was observed, and this was also confirmed by the obtained polarisation curves. From the same curves there was also confirmation of the drop in the galvanic current density, as the change from approximately 10 to  $2 \mu\text{A}/\text{cm}^2$  was verified by the change from  $-5$  to roughly  $-5.5$  in the logarithm of the current density in the polarisation curves. (Figure 93) In general, it is concluded that Cd was sacrificially protecting steel till the end of the experiment, and this is confirmed by the lack of signs of red rust on the steel panel.

### Salt Spray Testing

In both neutral salt spray tests, the scribed Cd plated steel panel and the Cd plated tensile specimens displayed the poorest performance among all tested coatings. In the

first experiment they showed signs of red rust at 300 hours and became totally rusty at 500 hours (Figure 94), while in the second case first signs of red rust appeared at 120 hours and by 250 hours all specimens were totally covered with rust. (Figure 95) These results were not coincidental in the light of the current study, as exceptionally high self-corrosion rates were measured for Cd in LPR measurements. On the other hand, this type of electroplated Cd was not passivated with chromium treatment, and this could be a reason for its poor corrosion performance under these conditions.

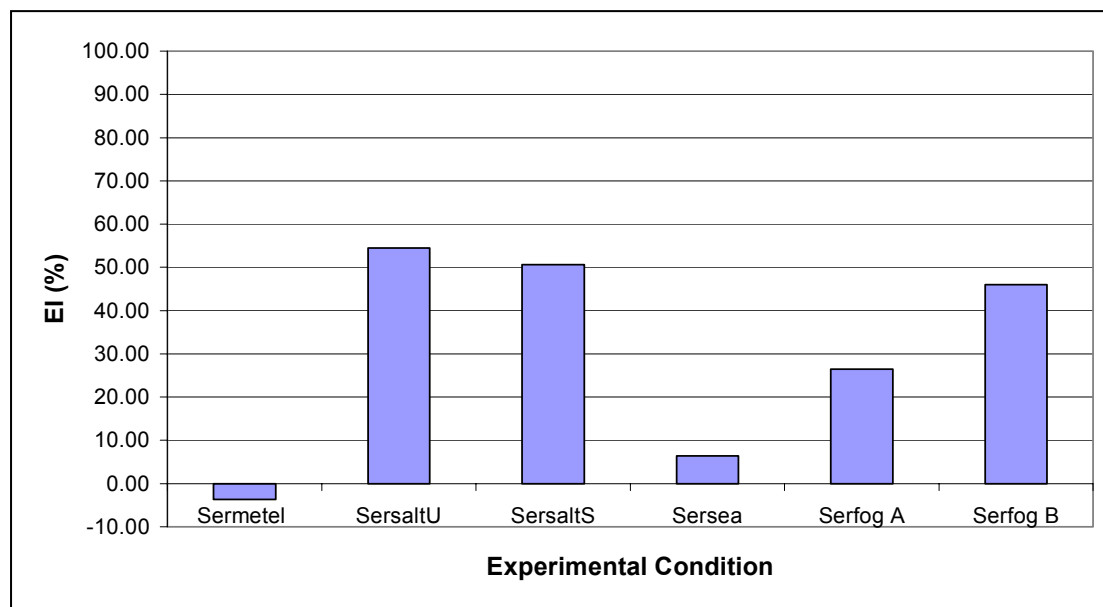
However, Baldwin and Smith [1] reported a good performance in neutral salt spray for pure electroplated Cd that had good barrier properties. These properties could be an explanation for the poor performance of Cd in salt fog in the present study, as the Cd coating in this study was proven to have poor barrier properties, because three out of five Cd plated and baked steel tensile specimens failed out of the scribe in SSRTs performed in 3.5% NaCl solution, as seen in Mechanical Testing Results. (Figure 59) Previous studies on sacrificial coatings [1, 140, 141] established that in neutral salt fog environment barrier properties tend to dominate over sacrificial properties. In this context, it is not coincidental that the Cd coating, referred to by Baldwin and Smith [1], performed better in salt fog than the Cd coating in the present study.

#### Marine Atmosphere Exposure Trials

Unscribed Cd plated steel panels displayed no signs of red rust after two years of marine exposure. (Figure 96) The same appearance was observed for Cd plated steel tensile specimens, where the coating remained intact as well. (Figure 99) In the last case the duration of the exposure was two years too. Finally, scribed Cd plated panels showed no signs of red rust either on the scribed marks or on the coating surface after just one year of marine exposure. (Figure 102) As seen, Cd performance was exceptionally good in marine atmosphere compared to other corrosive environments, corroborating the less re-embrittling influence of Cd on the steel mechanical properties in this environment in comparison with other corrosive conditions.

## 4.4 DISCUSSION SERMETEL CR984–LT

### 4.4.1 Mechanical Testing



**Figure 126. Bar chart displaying the EI for all SermeTel coated specimens at all the experimental conditions**

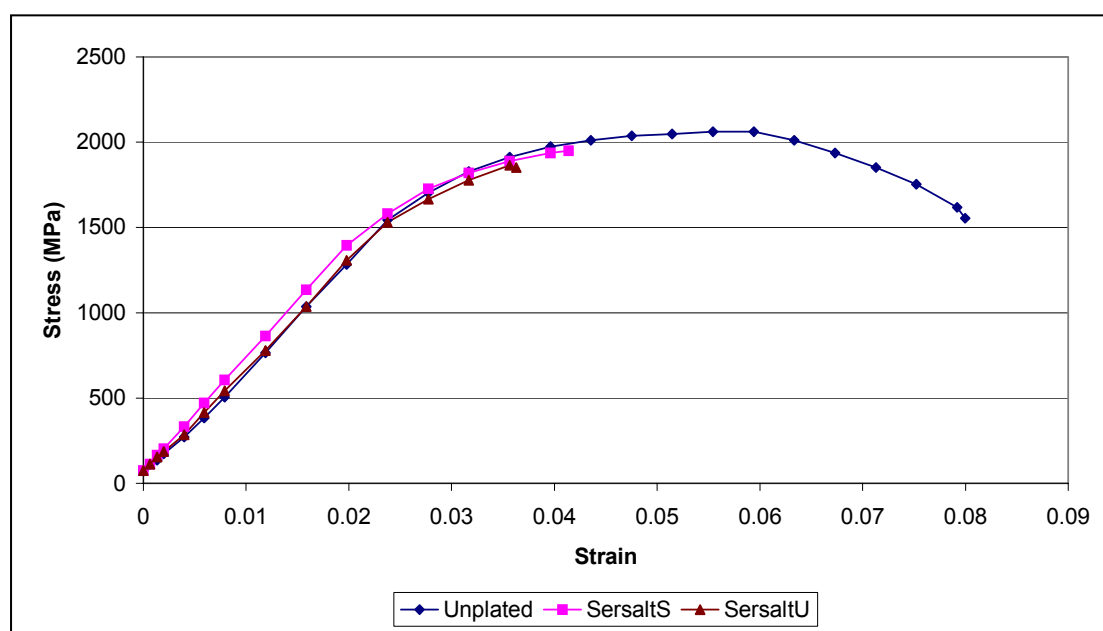
#### Hydrogen Embrittlement of SermeTel Coated Specimens

Figure 126 summarises the effect of SermeTel coating on the mechanical properties of the AISI 4340 steel tensile specimens at a range of treatments and corrosive environments. As seen in Chapter 3 (Figure 55, Table 12), the application of the SermeTel coating did not cause any embrittlement to the steel substrate, as the mean time to failure of the SermeTel coated specimens was higher than that for the unplated specimens ( $EI = -3.7\%$ ). This observed non-embrittling effect of SermeTel confirms the view of Mosser [5] that dense pack metallic–ceramic coatings, among which SermeTel CR984–LT, are not causing any embrittlement. As no HE was detected, there was no need to bake SermeTel coated specimens as in the case of Cd. For this reason, from an embrittlement point of view, SermeTel appears to behave better than Cd.

## Hydrogen Re-embrittlement of SermeTel Coated Specimens

### Tests in 3.5% NaCl solution

Scribed and unscribed SermeTel coated steel tensile specimens showed a high extent of re-embrittlement when they were strained in 3.5% NaCl solution, suggesting the embrittling effect of simultaneously straining and charging with hydrogen. Scribed specimens failed at 10.1 hours (EI=50.6%) on average, while the mean time to failure for the unscribed specimens was 9.3 hours (EI=54.4%). (Table 21, Figure 126) Three out of five scribed specimens failed out of the scribe, at the site of the most significant microstructural flaw where there was at least a critical amount of hydrogen concentration. As in the case of Cd, these findings suggest that SermeTel is a pervious coating to hydrogen. However, SermeTel was found to cause less re-embrittlement than Cd.



**Figure 127. Stress-strain diagram showing the re-embrittlement of scribed and unscribed SermeTel coated specimens, corroded in 3.5% NaCl solution**

From the stress-strain diagram of Figure 127 it is proved that the phenomenon occurring during these tests was hydrogen re-embrittlement. SermeTel coated specimens failed at a reduced fracture stress, and their stress-strain diagrams almost

followed the diagram for the unplated control specimens with the only difference that they were cut off at the times to failure. This is exactly what Troiano [21] emphasises as the real effect of hydrogen embrittlement on metals. Moreover, no yield point change was observed in Figure 127, and this is another issue related to embrittlement. As discussed in the case of cadmium, re-embrittlement could be potentially expected in the case of the corrosion of SermeTel as well, as various investigators had highlighted the effect of embrittlement on coated components when coatings corrode in service. [2, 18, 19, 139]

### Marine Atmosphere Exposure Trials

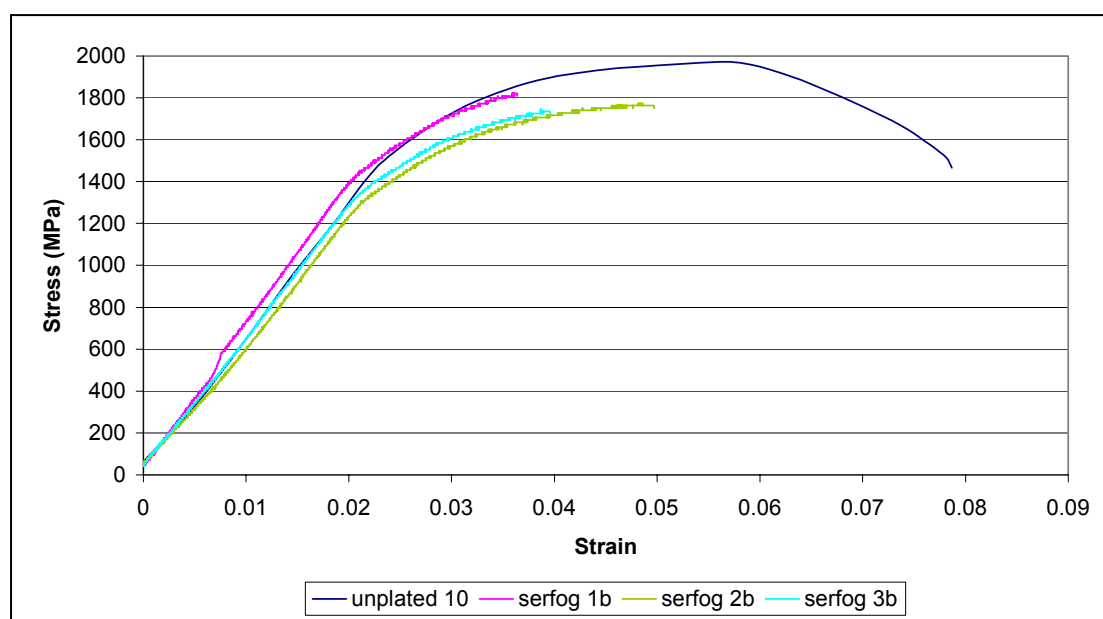
As viewed from Figure 126, SermeTel coated specimens that had been exposed to marine atmosphere conditions for 2 years, showed a very small amount of re-embrittlement (EI=6.5%) failing at 19 hours on average (Table 24). Marine atmosphere was the environment, where the SermeTel coating caused less embrittlement than in 3.5% NaCl solution. However, as earlier seen for cadmium, in the case of marine exposure, the tensile specimens were firstly corroded, and then tested in SSRTs, allowing plenty of time for hydrogen to diffuse out of the specimens, thus failing to detect any embrittlement to the extent it would be expected. Finally, SermeTel coated tensile specimens showed some red rust corrosion products on their threaded parts after two years of marine atmosphere exposure, and in this context, it is not coincidental that SermeTel corroded specimens in the marine environment failed slightly shorter compared to the Cd plated specimens that did not exhibit any signs of corrosion products whatsoever.

### Salt Spray Testing

AISI 4340 steel specimens, coated with SermeTel and tested in salt fog cabinet for 1000 hours, experienced less corrosion damage than the Cd plated steel specimens. (Figure 64, Table 25) Only two specimens from the first repeat exhibited some red rust corrosion products at the end of the experiment, while all the rest of the specimens showed just some white rust corrosion products. Moreover, the diameter of the specimens along the gauge length was not reduced in any case, and the extent of re-embrittlement for SermeTel coated specimens, corroded and then tested, was

smaller than in the case of Cd. However, in both salt fog tests there were substantial amounts of ductility loss observed for the SermeTel coated specimens, showing the aggressiveness of the salt spray environment. The average EI in the first test was 26.5% and in the second test it was 46% (Figure 126, Table 25).

Even in the case of SermeTel there was quite a lot of scatter observed in the salt spray testing results. As discussed with cadmium, this could be attributed to some variation of the salt fog distribution in the cabinet, although the specimens were regularly moved to different positions, and as a result to different amounts of corrosion in the gauge lengths of the specimens. In order to distinguish if the finally reduced times to failure of the corroded specimens were the result of corrosion or re-embrittlement, Figure 128 depicts the stress–strain diagram for SermeTel coated specimens, which is a useful tool in the attempt to answer this question.



**Figure 128. Stress–strain diagram for SermeTel coated specimens held for 1000 hours in a salt spray cabinet (second case)**

From the above stress–strain diagram it is concluded that the main reason for the degradation of the mechanical properties of the AISI 4340 steel is the hydrogen entering and diffusing into the steel substrate as a result of the cathodic reaction of water reduction while SermeTel corrodes according to its anodic reaction of

aluminium dissolution. Up to the yield point there were no many differences in the stress–strain curve of all coated and uncoated specimens. Some deviations from the unplated control curve were observed for two specimens in the plastic region lending support to the view that corrosion of SermeTel might have occurred and slightly influenced the final result, but definitely not to the extent seen with cadmium. Indeed, some corrosion has definitely occurred, as white rust corrosion products were observed on all the three SermeTel coated specimens tested in the second salt spray test.

#### **4.4.2 Corrosion Testing**

##### LPR Measurements

##### Potential Recording

The free corrosion potential of SermeTel fluctuated between  $-800$  and  $-700$  mV (SCE) for most of the time of its 3000 hour–exposure to 3.5% NaCl solution (Figure 79), as a result of the formation and breaking down of Al corrosion products. Moreover, this is the range within which Mosser [5] gave a free corrosion potential value of  $-740$  mV (SCE). The last value is close to the recorded values for SermeTel in the SSRTs in NaCl solution (Table 21), where the experiment lasted for a few hours instead of the weeks of the LPR measurements.

In any case of testing, the recorded potentials can reassure that SermeTel CR984–LT is sacrificial towards steel. The only arisen concern is that in longer exposure to corrosive environments there is a likelihood for a provisional deviation towards potential values between  $-900$  and  $-800$  mV (SCE), suggesting that at that time an exposed SermeTel coating could re–embrittle the steel substrate even more than the observed extent in SSRTs, where potential values round  $-750$  mV (SCE) prevailed (Table 21).

### Polarisation Resistance

Based on the LPR results for SermeTel, initially reached levels of  $160,000 \Omega \text{ cm}^2$  were reduced to a level of  $40,000 \Omega \text{ cm}^2$  as the formation of corrosion products, which reduced the SermeTel corrosion rate, gave place to a breaking down of this barrier protective film, and as a result the self-corrosion rate of SermeTel increased. (Figure 80) However, it was never as high as the corrosion rate of non-passivated cadmium, which resulted in corroding at least six times faster than SermeTel towards the end of the experiment, as the polarisation resistance for Cd was eventually  $6,000 \Omega \text{ cm}^2$  and for SermeTel it was  $40,000 \Omega \text{ cm}^2$ .

### Galvanic Coupling Measurements and Polarisation Curves

SermeTel displayed signs of white corrosion products after 600 hours of coupling with steel and exposure to 3.5% NaCl solution with no further deterioration of its appearance. However, the steel panel started corroding quite early, with first signs of red rust at 150 hours, and by 700 hours it was completely covered with red rust, and thus, SermeTel sacrificial corrosion protection towards steel ceased. Nevertheless, according to the positive value of the galvanic current, SermeTel was always the anode and the steel the cathode in this couple, suggesting that steel should have theoretically been protected till the end of the experiment. (Figure 86)

Moreover, the coupled potential was between  $-750$  and  $-700$  mV (SCE) (Figure 85) for most of the time of the experimentation, and this range of potentials was very close to the observed values for the detached SermeTel coated steel panel in the LPR measurements. However, according to the electrochemical polarisation curves (Figure 87) the whole coupling phenomenon was initially under mixed control giving later place to an anodic control, imposed by the dissolution of aluminium particles in SermeTel. From the same curves it is viewed that the potential for the isolated SermeTel was in a quite active range between  $-900$  and  $-800$  mV (SCE), but as anodic control was predominant, the mixed potential appeared between  $-750$  and  $-700$  mV (SCE).

### Salt Spray Testing

In both salt spray tests performed for this study (Figures 94 and 95), SermeTel coated tensile specimens and panels displayed white corrosion products, and only in the first salt fog test (Figure 94) red rust corrosion products were spotted on the gauge length of the tensile specimens. No signs of red rust were observed on the scribed mark of the SermeTel coated panel in the first test. This means that the corrosion performance of SermeTel CR984-LT was in general better compared to Cd, where red rust corrosion products appeared in every single specimen and panel. These findings are in agreement with the results presented by Mosser [5] who mentioned no base metal corrosion on the scribe of scribed SermeTel coated panels.

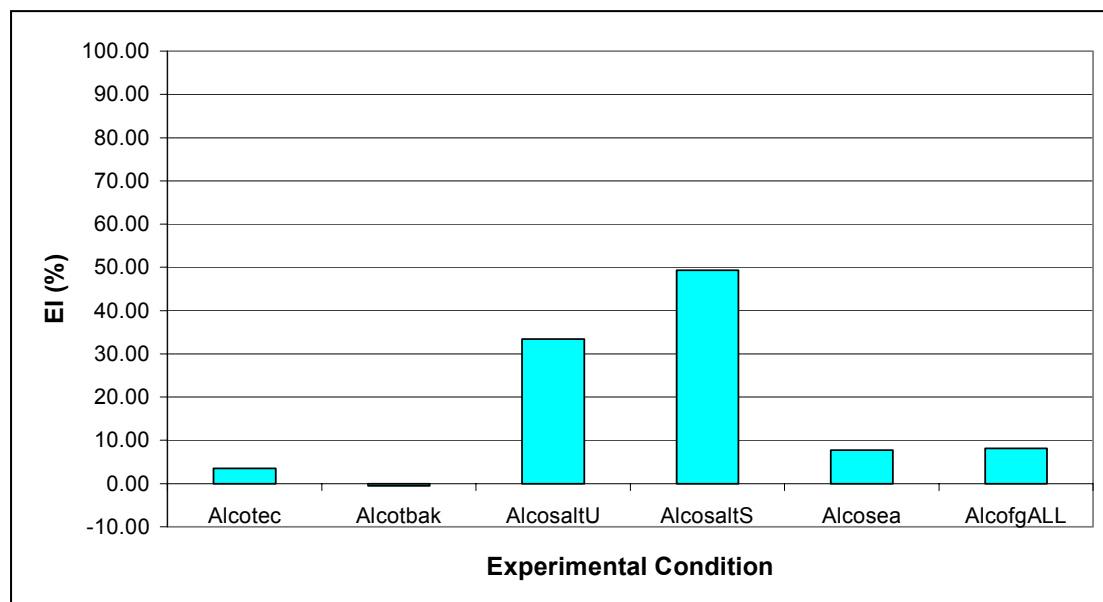
### Marine Atmosphere Exposure Trials

Unscribed SermeTel coated panels showed white rust corrosion products and some red rust on a very small part of their surfaces after two years of exposure in marine atmosphere conditions. (Figure 96) Some signs of red rust were seen on the gauge length of the SermeTel coated tensile specimens after two years of exposure (Figure 98), while scribed SermeTel coated panels displayed white corrosion products on their surfaces and red rust on their scribes after one year of exposure (Figure 101).

The performance of SermeTel under these conditions was poorer compared to cadmium. Moreover, it was worse compared to SermeTel under salt spray conditions, and despite the fact that salt fog conditions are considered as a more aggressive environment than the marine atmosphere. However, the performance of SermeTel in marine atmosphere should be seriously taken into account, as this environment is considered to closely simulate service conditions experienced by aircraft.

## 4.5 DISCUSSION GALVANO–ALUMINIUM ALCOTEC

### 4.5.1 Mechanical Testing



**Figure 129. Bar Chart Displaying the EI for All Alcotec Coated Specimens at All the Experimental Conditions**

#### Hydrogen Embrittlement and De–Embrittlement of Alcotec Coated Specimens

Figure 129 summarises the effect of Galvano–Aluminium Alcotec coating on AISI 4340 steel tensile specimens at a range of treatments and corrosive environments. As viewed from this bar chart, the electrodeposition of Alcotec incurred a small amount of embrittlement (EI=3.5%) (Table 14), but a subsequent baking treatment at 200°C for 24 hours was fully effective in the recovery of the ductile properties of the AISI 4340 steel, as the EI was –0.5% (Table 14), i.e. the times to failure for Alcotec coated and baked specimens were slightly longer than for the unplated control.

The electrodeposition of Alcotec is claimed as non–embrittling to high strength steels by its producers [14, 15]. However, a limited extent of embrittlement was found in this study, and this could be attributed to pretreatments that may involve the immersion of components in aqueous solutions of mineral or organic acids, which can

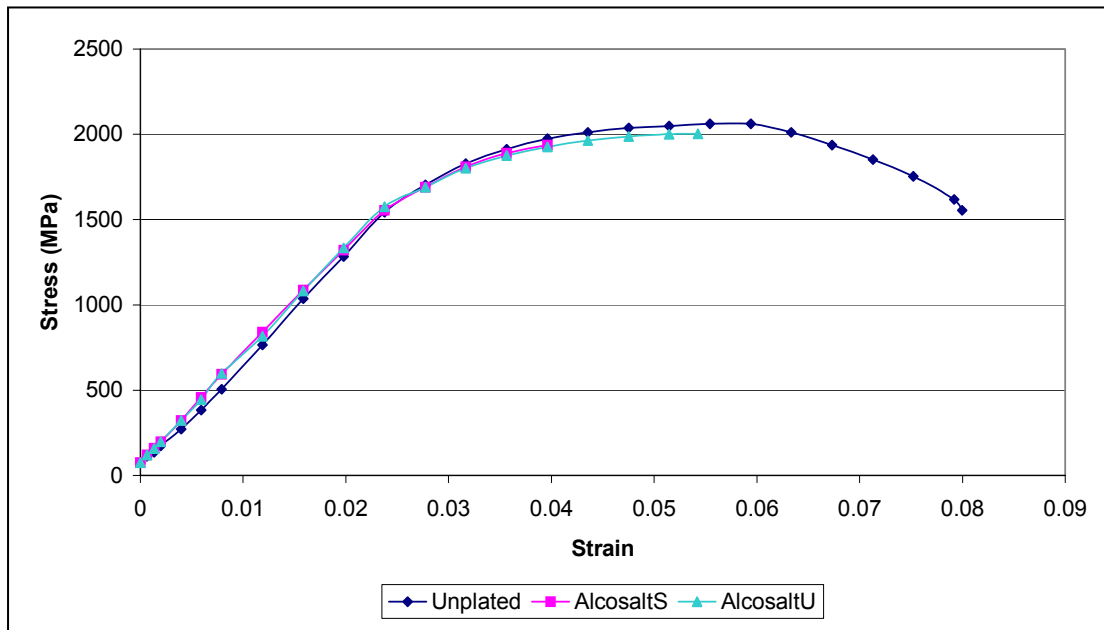
embrittle high strength steels. [15] The applied de-embrittlement baking procedure at 200°C in this work is a recommended treatment, as the Alcotec Galvano-Aluminium electroplate film is deposited from a toluene solution at approximately 100°C, and this film is reported to be stable in working environments up to 500°C. [15] On the other hand, 200°C is an acceptable baking temperature, at which the microstructure of the AISI 4340 steel is not affected, as tempering of steel takes place at 250°C.

### Hydrogen Re-embrittlement of Alcotec Coated Specimens

#### Tests in 3.5% NaCl solution

Scribed and unscribed Alcotec coated steel tensile specimens showed a substantial amount of re-embrittlement when they were strained in 3.5% NaCl solution, highlighting the embrittling effectiveness of a corrosive environment combined with stress. Scribed specimens failed at 10.3 hours (EI=49.3%) on average, while the mean time to failure for the unscribed specimens was 13.6 hours (EI=33.4%). (Figure 129, Table 23) Only one out of five scribed specimens failed out of the scribe, suggesting that the Alcotec coating was less pervious to hydrogen compared to Cd and SermeTel, where unscribed specimens failed in shorter times than scribed, and moreover, most of the scribed specimens failed out of the scribe.

The stress-strain diagram of Figure 130 proves that the occurred effect on the degradation of the tensile properties of AISI 4340 steel was re-embrittlement, as the stress-strain curves of Alcotec coated and corroded steel specimens followed up to the point of their fracture the curve for the unplated control specimens. Moreover, this conclusion is further strengthened by the fact that the yield point of the coated specimens was not altered compared to the yield point of the unplated specimens. As with the embrittling effect of the corrosion of Cd and SermeTel on steel, it was not surprising that Alcotec coated specimens could potentially suffer from re-embrittlement, as various investigators had underlined the effect of embrittlement on coated components when coatings corrode in service. [2, 18, 19, 139]



**Figure 130. Stress–strain diagram showing the re–embrittlement of scribed and unscribed Alcotec coated specimens, corroded in 3.5% NaCl solution**

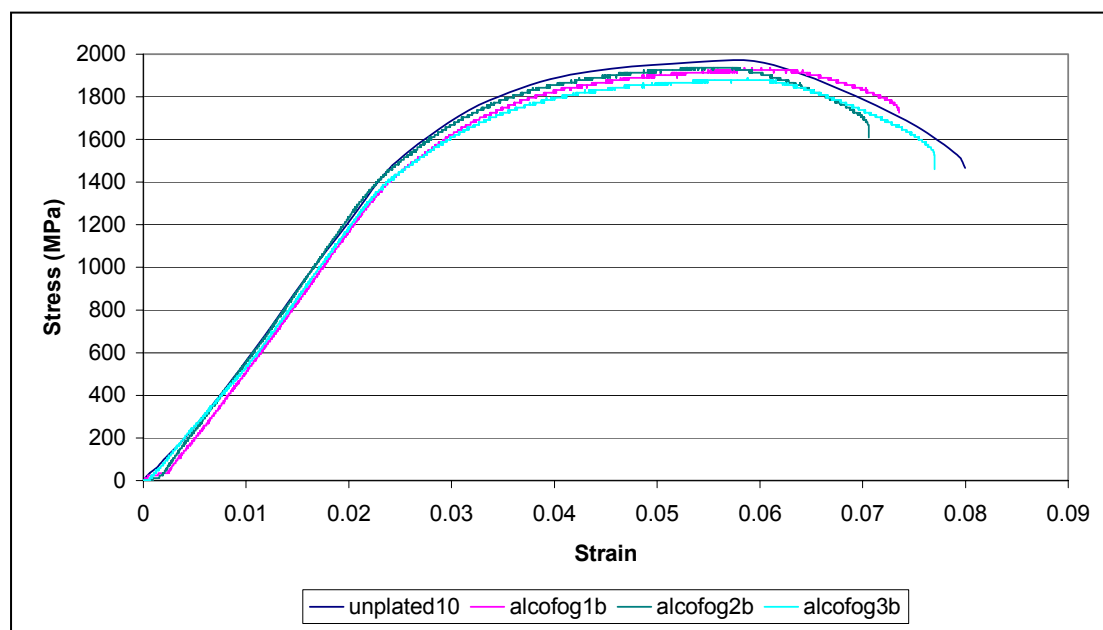
#### Marine Atmosphere Exposure Trials

As seen from Figure 129, Alcotec coated specimens that had been exposed to marine atmosphere conditions for 2 years, exhibited a very small amount of re–embrittlement (EI=7.8%) failing at 18.8 hours on average (Table 24). This mean time to failure was shorter compared to that for Cd and SermeTel coated specimens in the same environment. Furthermore, it should be re–emphasised that all coated specimens were firstly corroded in the marine atmosphere for two years, and then tested in the SSRTs. Finally, Alcotec coated tensile specimens showed some signs of red rust on their threaded parts, and this could probably be a visual sign to explain why they might have failed at shorter times compared to Cd coated specimens that did not exhibit any signs of red rust at all.

#### Salt Spray Testing

Alcotec coated tensile specimens corroded in a salt spray test for 1000 hours, and then tested in SSRTs, showed a very limited degree of re–embrittlement, as they failed at

18.7 hours on average (EI=8.2%). (Figure 129, Table 25) This was approximately the same extent of re-embrittlement as in the case of marine atmosphere exposure trials, and moreover, Alcotec was the coating, with which the least amount of steel mechanical degradation was observed in salt spray testing compared to Cd and SermeTel.



**Figure 131. Stress–strain diagram for Alcotec specimens held for 1000 hours in a salt spray cabinet (second case)**

No signs of corrosion products were developed on both Alcotec coated panels and tensile specimens (Figures 94 and 95), and from Figure 131 it is apparent that the tensile specimens were just re-embrittled, as no significant differences were observed on the shape of the obtained stress–strain curves between the unplated control and Alcotec coated specimens. Finally, it should be noted that in both salt spray tests close times to failure were recorded, allowing, after checking with a Student's t-test (Table 26), the treatment of their populations as a single one, presented in Figure 129. Moreover, Alcotec coated specimens showed a very small scatter in their results in this particular type of corrosive environment. (Table 25)

## 4.5.2 Corrosion Testing

### LPR Measurements

#### Potential Recording

As viewed in the LPR results for Alcotec (Figure 81), its first recorded potential values were very active, e.g.  $-950$  mV (SCE), as it could be expected for pure aluminium. However, the formation of aluminium oxide made the potential shift towards more noble values, close to  $-750$  mV (SCE). Afterwards, breaking down of the protective oxide layer might have taken place, and at 200 hours discoloration because of the loss of chromium passivation treatment started to occur, which made the potential head towards more negative values before stabilising between  $-800$  and  $-750$  mV (SCE). This range of potentials suggests that Alcotec can offer sacrificial corrosion protection to steel substrates.

The previously referred potential values are close to the observed range in the SSRTs for Alcotec coated specimens. (Table 23) Moreover, they suggest that re-embrittlement of high strength steels is likely to happen when the corrosion of applied Alcotec coating takes place, as it was indicated from both SSRTs for cathodically protected unplated steel tensile specimens (Figure 58) and permeation measurements on cathodically protected steel membranes (Figures 66–74).

#### Polarisation Resistance

The polarisation resistance of Alcotec displayed an almost 20fold decrease during the experiment of 3000 hours, suggesting that the self-corrosion rate of Alcotec increased by the same order of magnitude in the same time. (Figure 82) This increase could be attributed to the loss of the chromium passivation treatment of Alcotec. This was observed through its discoloration, as a yellow chromated passivation post-treatment was applied to Alcotec. The discoloration started at 200 hours when the self-corrosion rate was at least as double as its initial value, with  $R_p$  values of  $800,000 \Omega \text{ cm}^2$  at 200 hours and  $1,900,000 \Omega \text{ cm}^2$  initially. (Figure 82) The yellow colour was

completely lost after 600 hours of experimentation, when the self-corrosion rate ( $R_p$  value of  $400,000 \Omega \text{ cm}^2$ ) was five times higher than its initial value ( $R_p$  value of  $1,900,000 \Omega \text{ cm}^2$ ) (Figure 82). Although by the end of the experiment Alcotec was corroding twenty times faster than at the beginning, the final self-corrosion rate ( $R_p$  of  $80,000 \Omega \text{ cm}^2$ ) was approximately two times slower than that of SermeTel ( $R_p$  of  $40,000 \Omega \text{ cm}^2$ ) and at least 30 times slower than that of cadmium ( $R_p$  of  $6,000 \Omega \text{ cm}^2$ ). (Figures 80, 82 and 84)

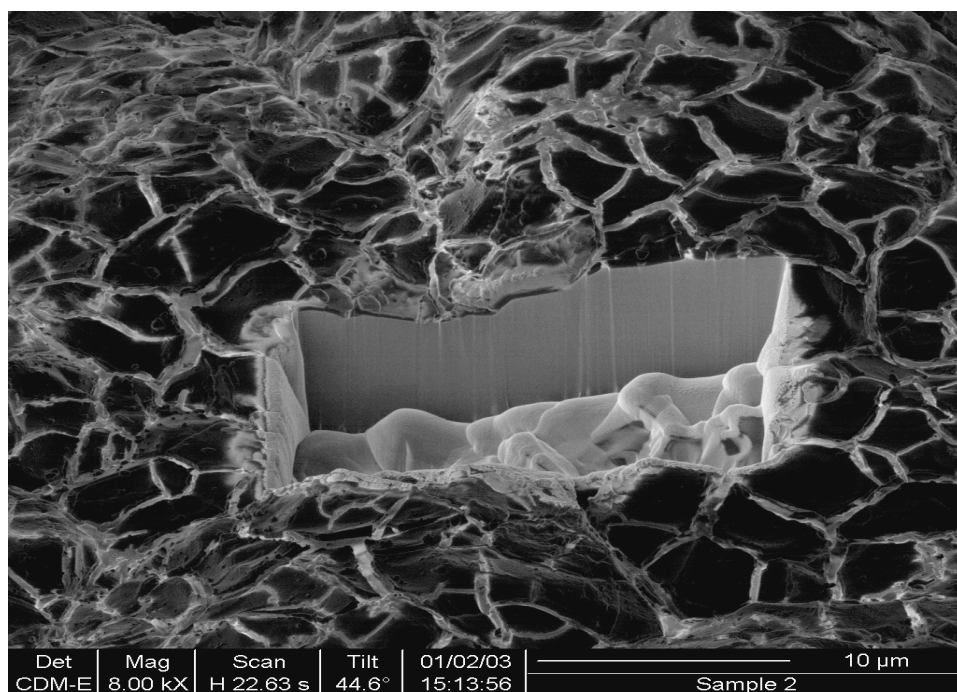
### Galvanic Coupling Measurements and Polarisation Curves

As seen in Galvanic Coupling Results (Figure 88), the coupled potential of Alcotec with steel ranged between  $-730$  and  $-680 \text{ mV (SCE)}$ . This result could be justified by the appearance of the polarisation curves for the detached electrodes (Figure 90), according to which the whole phenomenon was under cathodic control, imposed by the oxygen reduction on steel. Steel behaved as the cathode up to 1400 hours of experimentation when the polarity of the galvanic current was reversed, proving that the sacrificial corrosion protection of Alcotec towards steel was ceased. (Figure 89) This was accompanied by the fact that the steel panel showed first signs of red rust at 1200 hours, while earlier, at 1000 hours, the Alcotec coated panel was already completely covered by corrosion products.

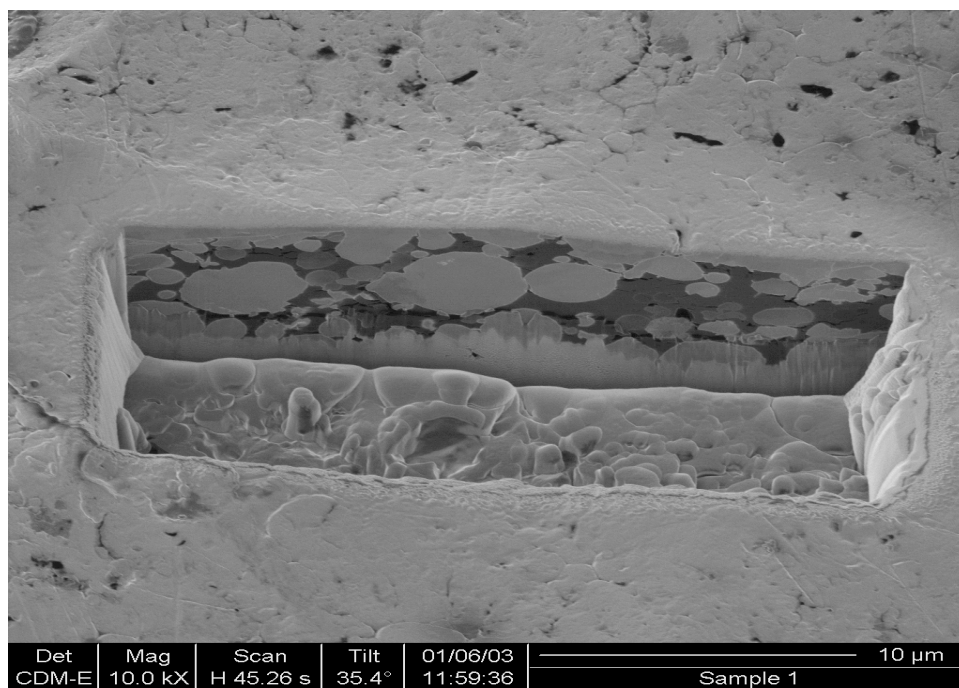
### Salt Spray Testing

Alcotec coated steel panel and tensile specimens displayed no signs of corrosion products on them after the end of both salt spray tests performed in this study. (Figures 94 and 95) Moreover, all these specimens started losing the yellow colour of their chromium passivation treatment at 250 hours, and by the end of the experiment complete discoloration had taken place. Alcotec coated specimens performed by far better than Cd and SermeTel in salt spray testing. An explanation could be its barrier properties that mainly influence a coating's performance in salt spray conditions, as Baldwin, Smith and Robinson support [140, 141]. Alcotec was proven to have the best barrier properties among all coatings examined, as it was less pervious to hydrogen than the other two coatings, based on the SSRT results for coated specimens

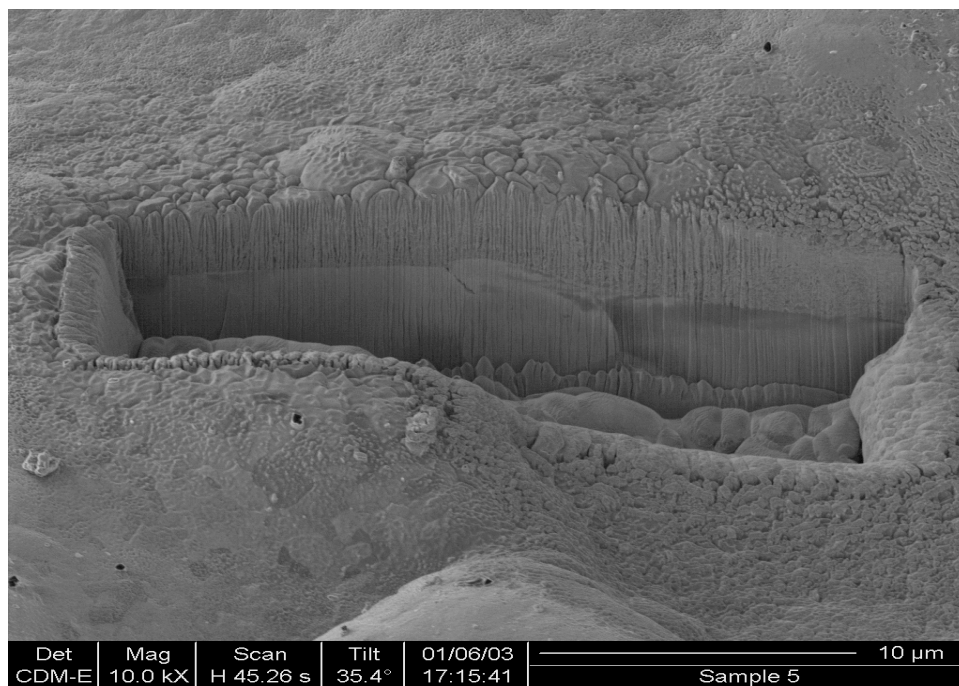
strained in 3.5% NaCl solution. (Figure 62) Furthermore, Figures 132–134 display the microstructures of Alcotec, Cd and SermeTel, revealed with the help of Focused Ion Beam (FIB) technique. [142] Viewing these pictures, Alcotec appears as a dense coating with few visible pores, compared to Cd and SermeTel, supporting further the view of its better barrier properties in comparison with the other two coatings. In this context, it was not coincidental that Alcotec plated tensile specimens showed the least re-embrittlement in SSRTs for coated specimens that had submitted salt fog conditions. The excellent performance of Galvano–Aluminium Alcotec in salt spray environments was also confirmed by other research studies [15], where only complete or slight discoloration was observed.



**Figure 132. Alcotec microstructure revealed by Focused Ion Beam etching**



**Figure 133. SermeTel microstructure revealed by Focused Ion Beam etching**



**Figure 134. Cadmium as revealed by Focused Ion Beam etching**

### Marine Atmosphere Exposure Trials

Scribed Alcotec coated panels preserved their passivation colour during marine atmosphere exposure trials lasting for one year, and they did not display any corrosion products at all. (Figure 100) On the other hand, unscribed Alcotec plated panels exposed to marine atmosphere for two years submitted discoloration, but did not show any signs of corrosion products. (Figure 96) Only Alcotec coated tensile specimens (Figure 97), exposed to marine environment for two years, did exhibit signs of red rust on their threaded parts only, whilst their passivation treatment colour was already lost after 8 months of experimentation. To summarise, the performance of Alcotec coating in the marine environment was overall satisfactory, and it could be classified as the second best coating after cadmium, the performance of which was excellent, as no signs of red rust ever appeared in any type of Cd plated specimens.

## 4.6 GENERAL DISCUSSION OF COATINGS

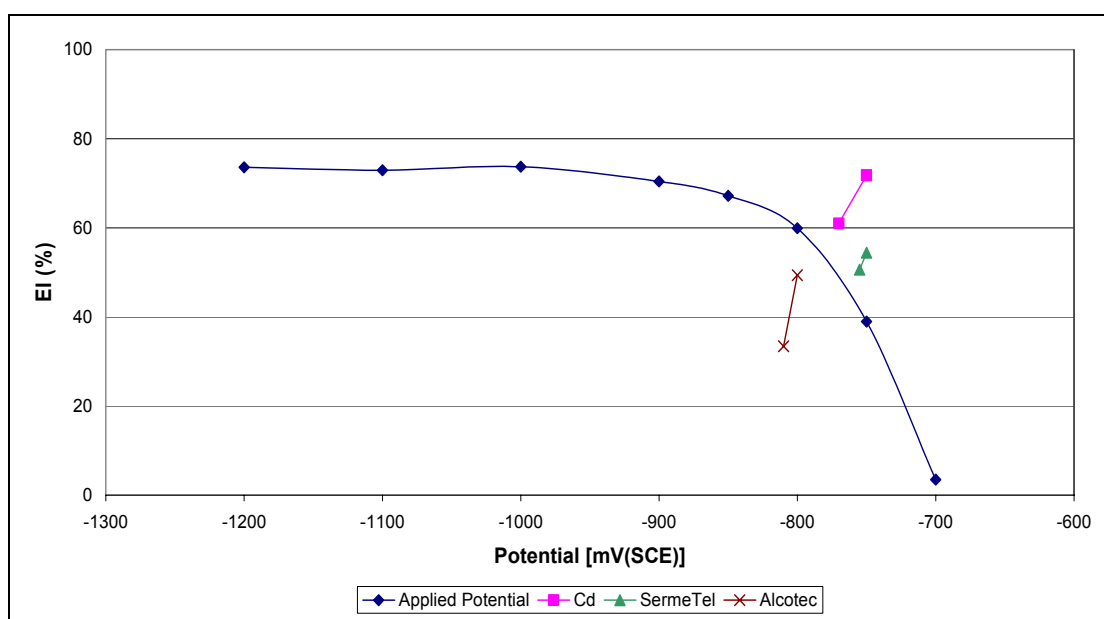
The present section aims to compare and rank the investigated coatings based on their effect upon the mechanical properties of the AISI 4340 high strength steel, as well as their corrosion behaviour, either detached or coupled to steel. Through this comparison conclusions can be drawn concerning the suitability of each of the examined Al-based coatings as possible replacements of Cd as sacrificial coatings for the corrosion protection of high strength steels.

| Coating  | HE   | DeE  | ReE (3.5% NaCl) | ReE (Marine) | ReE (Salt Fog) |
|----------|------|------|-----------------|--------------|----------------|
| Cadmium  | 75.6 | 0.6  | 61 – 71.8       | 2.4          | 46.7 – 81.8    |
| SermeTel | -3.7 |      | 50.6 – 54.4     | 6.5          | 26.5 – 46      |
| Alcotec  | 3.5  | -0.5 | 33.4 – 49.4     | 7.8          | 6.9 – 9.4      |

**Table 31. EIs for mechanically tested (SSRTs) coated AISI 4340 steel specimens at different experimental conditions, including direct hydrogen embrittlement (HE), post-application de-embrittlement baking treatment (DeE), re-embrittlement (ReE) in 3.5% NaCl solution, ReE after marine atmosphere exposure, and ReE subsequent to salt spray (fog) testing**

According to Table 31, both Al-based coatings showed a better embrittlement and re-embrittlement behaviour than Cd, apart from the case of SSRTs after marine atmosphere exposure. The Alcotec coating had on average the best embrittlement behaviour towards the AISI 4340 high strength steel, as it caused just a very small amount of direct embrittlement (HE) from its application, and it incurred in most corrosive environments a clearly smaller extent of re-embrittlement compared to the other two coatings. More in detail, Alcotec coated specimens exhibited a limited loss of their ductility, which was recovered after a subsequent baking treatment at 200°C for 24 hours. Although SermeTel did not cause any HE as a result of its application, its re-embrittlement behaviour was worse than Alcotec in 3.5% NaCl solution and subsequent to salt spray testing. Only in SSRTs after marine atmosphere exposure did SermeTel coated specimens display a slightly smaller degree of re-embrittlement compared to Alcotec.

From re-embrittlement SSRTs in 3.5% NaCl solution and SSRTs after salt spray testing, it is concluded that Alcotec had by far better barrier properties than Cd and SermeTel. Alcotec was the most active amongst the examined coatings, as seen from Table 32, where its potential is depicted at various corrosion measurements. For this reason, it was expected to display an increased propensity towards re-embrittlement, as unplated steel specimens, which were cathodically charged during SSRTs, submitted more re-embrittlement at more active values, as seen in Figure 135. Contrary to these expectations, Alcotec coated specimens showed less embrittlement than the unplated steel specimens that were cathodically charged at its free corrosion potential range. Moreover, Cd and SermeTel coated specimens exhibited more embrittlement than the unplated steel specimens that were cathodically charged at the free corrosion potentials of these coatings.



**Figure 135. Comparison of EIs of freely corroding coated steel specimens with cathodically protected unplated steel specimens**

It would have been ideal if we could measure the free corrosion potential of a coating and then correlate this potential with its embrittling effect when cathodically applied to protect a bare piece of a given substrate. However, what could be gained from such a connection of these two cases is just an indication of a trend for a corroding coating to re-embrittle a steel substrate in a particular corrosive environment.

Various reasons could be related to the disagreement of these two supposedly equivalent cases. These can be the relative rates of the various steps involved in hydrogen evolution reaction and entry into a substrate and how the presence of a given coating can affect any of these steps. Particularly, the porosity of a coating is an important factor, as hydrogen diffusion occurs first through that coating before the diffusion of hydrogen into the steel. In addition, another factor to take into account are the mechanical properties of the coatings concerning their continuity under stress.

Finally, another aspect in the re-embrittlement of steel could be the presence of elements acting as hydrogen promoters. For instance, SermeTel consists of Al particles in an inorganic chromate and phosphate binder. Phosphorus is one among the elements characterised as hydrogen or cathodic promoters because in very small additions they can cause substantial increase in the hydrogen entry kinetics and hydrogen absorption. [40] For this reason, it is likely that when SermeTel corrodes the presence of phosphorus in the inorganic binder can result in the absorption of larger amounts of hydrogen that could embrittle the specimens under the simultaneous effect of stress.

| <b>Coating</b> | <b>Potential Range (SSRTs) [mV(SCE)]</b> | <b>Potential Range (LPR) [mV(SCE)]</b> | <b>Final Self-Corrosion Rate (<math>\mu\text{m}/\text{yr}</math>)</b> | <b>Coupled Potential [mV(SCE)]</b> | <b>Galvanic Corrosion Rate (<math>\mu\text{m}/\text{yr}</math>)</b> |
|----------------|------------------------------------------|----------------------------------------|-----------------------------------------------------------------------|------------------------------------|---------------------------------------------------------------------|
| Cadmium        | (-780, -740)                             | (-790, -660)                           | 57                                                                    | -750                               | 37                                                                  |
| SermeTel       | (-770, -740)                             | (-900, -700)                           | 4.8                                                                   | -730                               | 20                                                                  |
| Alcotec        | (-820, -780)                             | (-900, -750)                           | 2                                                                     | -680                               | 103                                                                 |

**Table 32. Summary of corrosion behaviour of the isolated coatings and coatings coupled to steel after 1000 hours exposure to 3.5% NaCl solution**

Table 32 summarises the corrosion testing results for the investigated coatings, either detached or coupled to steel, after 1000 hours of experimentation. As stated earlier, Alcotec was the most active among the examined coatings. Furthermore, it had the smallest self-corrosion rate, confirming a low consumption rate when being detached. Moreover, salt spray results (Figures 94 and 95) showed that Alcotec had the best corrosion performance in that aggressive environment, underlining its excellent

barrier properties, as past studies on sacrificial coatings [1, 140, 141] established that in neutral salt fog environment barrier properties tend to dominate over sacrificial properties. In addition, Alcotec had the second best performance after Cd in marine atmosphere exposure trials (Figures 96, 97 and 100), displaying satisfactory sacrificial corrosion properties, as Baldwin, Smith and Robinson support [140, 141] that sacrificial properties take over barrier properties in marine atmosphere. However, Alcotec displayed an exceptionally high galvanic corrosion rate, which can definitely result in its accelerated consumption when sacrificially protecting steel substrates.

SermeTel exhibited the smallest galvanic corrosion rate, but its performance in salt spray tests was poorer than Alcotec indicating its inferior barrier properties. Moreover, marine atmosphere exposure trials showed the poorest performance for SermeTel, highlighting its increased risk for passivation, tending to leave steel unprotected to corrode.

From the previous remarks, it can be concluded that SermeTel and Alcotec showed an improved behaviour towards embrittlement and re-embrittlement compared to Cd. From this perspective both investigated Al-based coatings can be considered as potential replacements to Cd. However, Alcotec suffers from a high galvanic corrosion rate when coupled to steel, while SermeTel has poor barrier properties, and is likely to passivate in marine atmosphere. Bearing in mind the aforementioned demerits of the studied coatings, Alcotec can be regarded, compared to SermeTel, as a more suitable alternative to Cd for the sacrificial corrosion protection of high strength steels for aerospace applications, for it has better barrier properties and incurs on average the smallest re-embrittlement among all coatings. SermeTel might have smaller galvanic corrosion rate than Alcotec, but this becomes useless taking into account its risk of passivation that is not observed with Alcotec.