

CHAPTER 3: RESULTS

3.1 MECHANICAL TESTING

3.1.1 Fracture Surfaces

Figures 47–50 portray photomicrographs of a typical fracture, as well as different types of fracture surfaces, examined in the SEM. Figure 48 shows the fracture surface of a ductile specimen ($\epsilon = 8.3\%$) revealing the characteristic dimple appearance associated with microvoid coalescence. Figure 49 depicts the fracture surface of an embrittled specimen ($\epsilon = 3.9\%$), whilst Figure 50 displays the fracture surface of an extremely embrittled specimen ($\epsilon = 1.4\%$) revealing a brittle cleavage mode of failure.

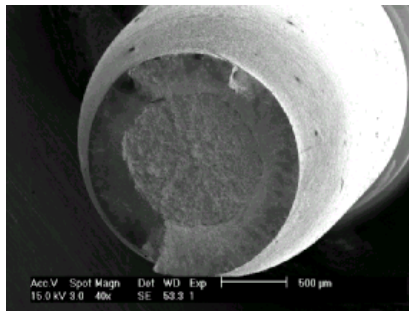


Figure 47. Fractured end of a Cd plated de-embrittled steel tensile specimen

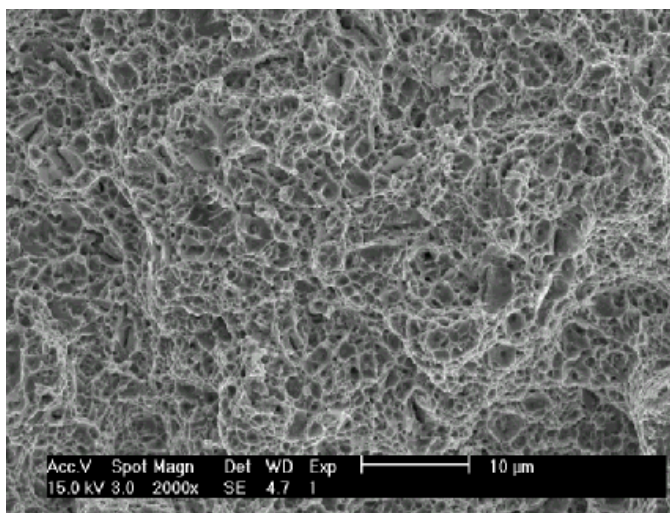


Figure 48. Ductile fracture surface of an unplated AISI 4340 steel tensile specimen

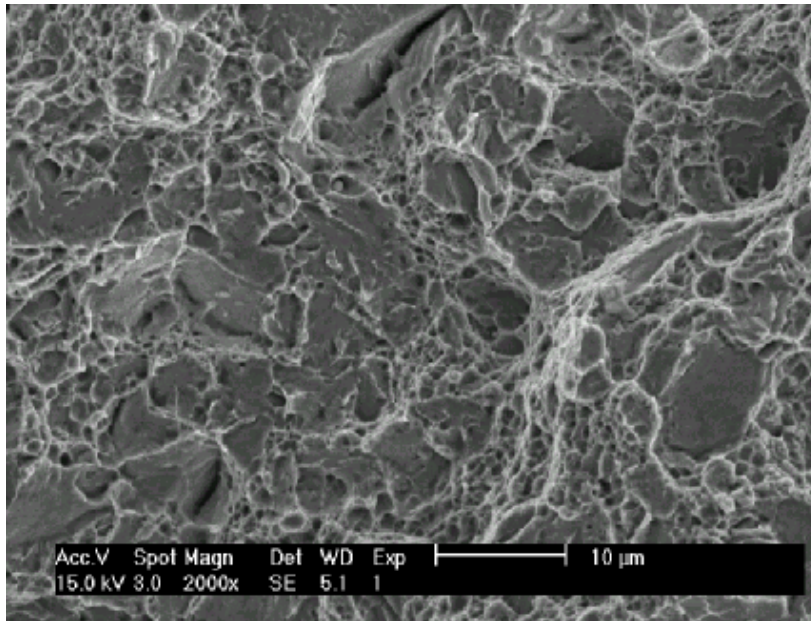


Figure 49. Fracture surface of a partly embrittled specimen ($\epsilon = 3.9\%$) showing decreased microvoid coalescence (re-embrittled Alcotec coated steel tensile specimen corroding in 3.5 % NaCl solution)

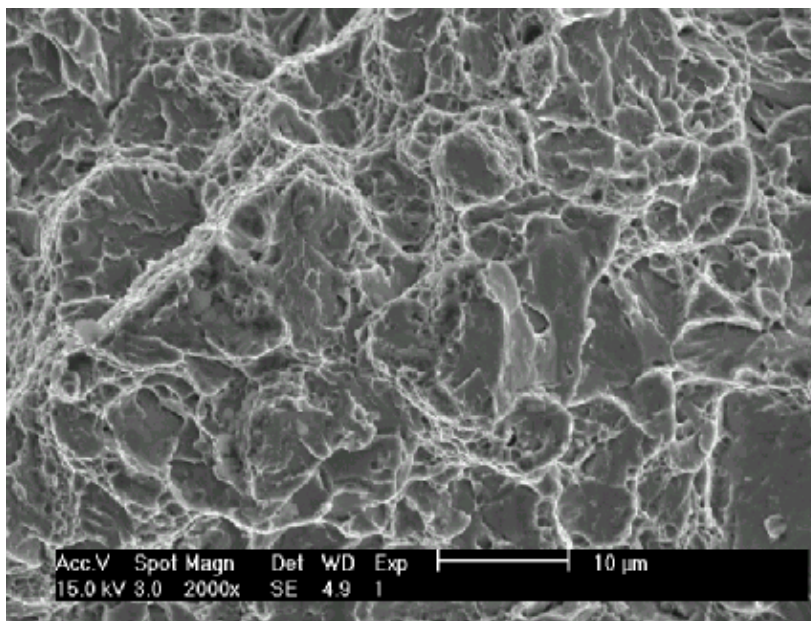


Figure 50. Brittle fracture surface ($\epsilon = 1.4\%$) showing transgranular cleavage and some microvoid coalescence (Cd plated steel specimen)

3.1.2 Slow Strain Rate Test Results

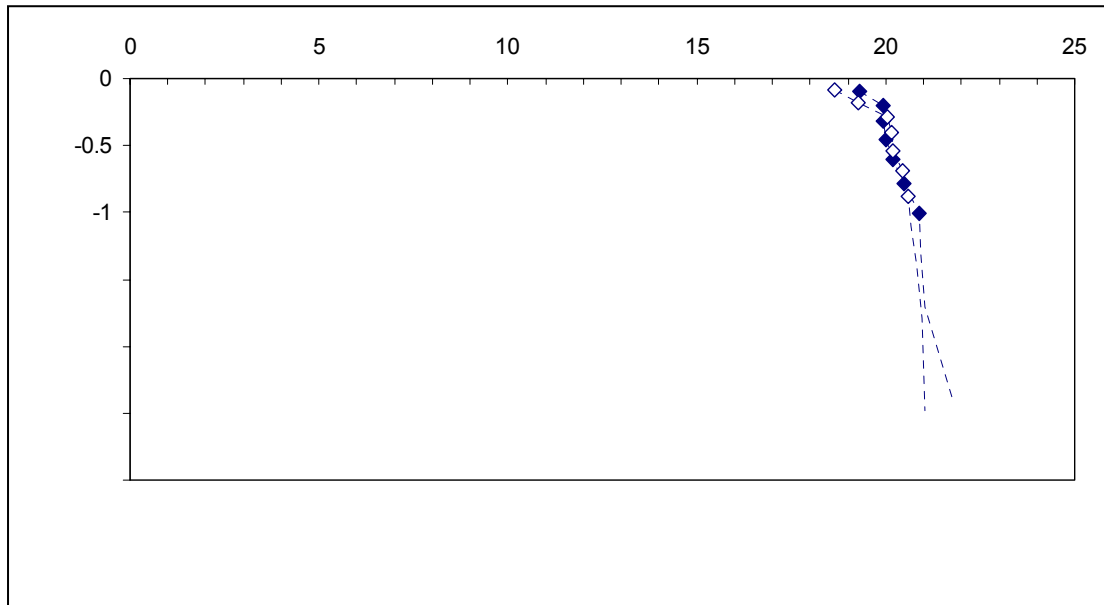


Figure 51. Weibull plot of times to failure for each batch of unplated specimens

Figure 51 shows the SSRT results for the heat treated unplated AISI 4340 steel tensile specimens on a Weibull graph. As seen in Table 5, the mean times to failure for both batches were close to each other. A Student's *t*-test for non-normal distributions (Appendix), like the Weibull distribution, was performed to check if these two sets of results were part of the same population. For a percentage of confidence of 95% and 19 degrees of freedom ($10+11-2=19$) the limiting value of the *t*-statistic, determined from tables of the *t*-distribution, is 2.09. As viewed in Table 6, the value of tabular *t* is greater than the value of *t* calculated from experimentally determined values. Hence, the SSRT results for these two batches of steel specimens cannot be assumed to belong to different populations.

Specimens	Mean T_{failure} (h)	n	SD
Unplated a	20.45	10	0.72
Unplated b	20.26	11	0.73

Note: n is the number of tested specimens, and SD is the standard deviation

Table 5. Mean times to failure for each batch of unplated specimens

Sets of Results	t statistic	v	α	t tabular	Compare	Accept?
Unplated a / b	0.6	19	0.05	2.09	$t_s < t_{tab}$	Yes

Table 6. Comparison of batches a and b using the student's t-test

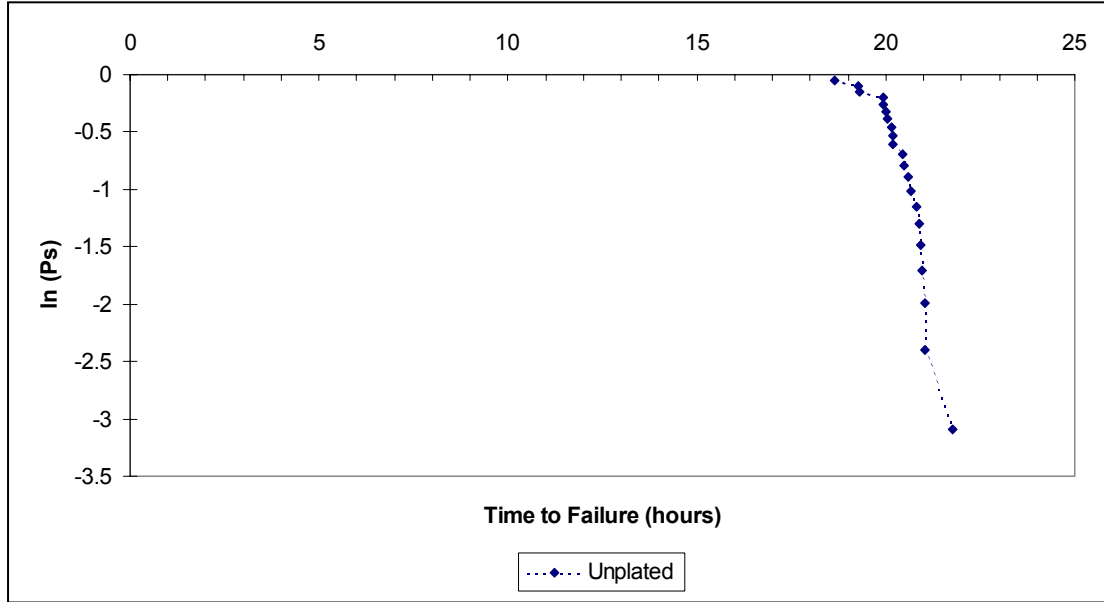


Figure 52. Weibull plot of all the unplated control specimens

The SSRT results for both batches of AISI 4340 steel specimens are depicted in Figure 52 as a single set of data. The unplated specimens are the control specimens, with which all other specimens will be compared. For this reason, the results of the unplated specimens will be present in every single Weibull plot for all the treated tensile specimens. Moreover, the times to failure of all the other specimens will be compared with the mean time to failure of the control specimens, provided in Table 7, in order to quantify the extent of embrittlement through the embrittlement index (EI).

Specimens	Mean $T_{failure}$ (h)	n	SD
Unplated	20.35	21	0.71

Table 7. Mean time to failure for all the unplated control specimens

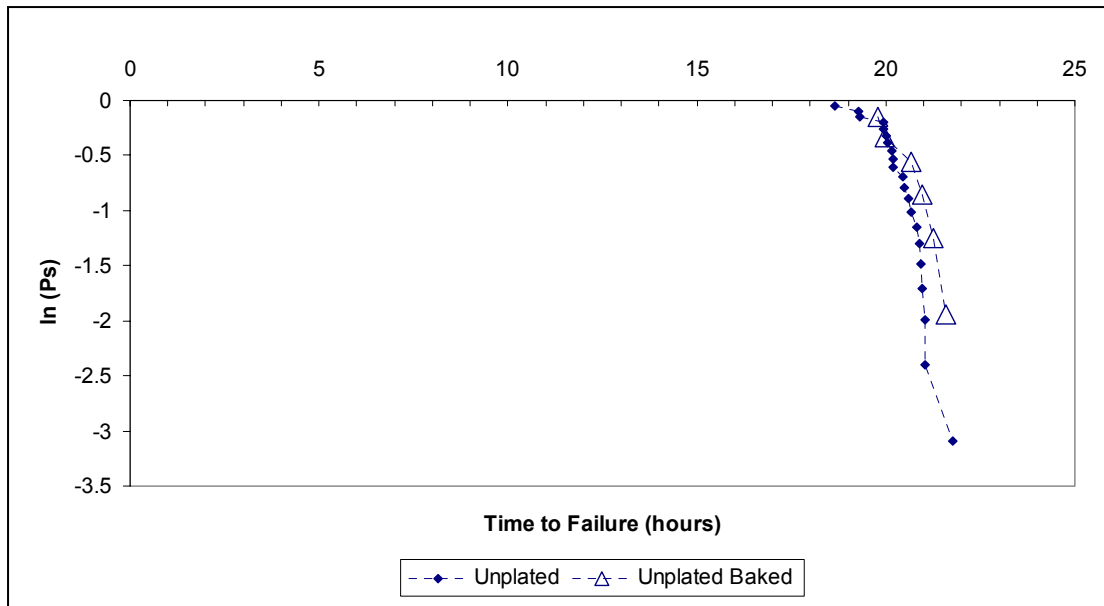


Figure 53. Weibull plot of the effect of baking on unplated control specimens

Figure 53 demonstrates that there was no significant effect of baking at 200°C for 24 hours before testing on unplated steel specimens. Although the mean time to failure for baked specimens was slightly higher than the mean time for unbaked specimens (Tables 7 and 8), a Student's t-test compared these two sets of results, and it could not be assumed that they were part of separate populations. (Table 9) As a result, it is concluded that there is no likelihood for such an applied baking treatment to affect the tensile properties of any other treated AISI 4340 steel tensile specimen.

Specimens	Mean T_{failure} (h)	EI (%)	n	SD
Unplated Baked	20.70	-1.73	6	0.70

Table 8. Mean time to failure for the unplated baked specimens

Sets of Results	t statistic	v	α	t tabular	Compare	Accept?
Baked / Unbaked	1.08	25	0.05	2.06	$t_s < t_{\text{tab}}$	Yes

Table 9. Student's t-test for baked and unbaked control specimens

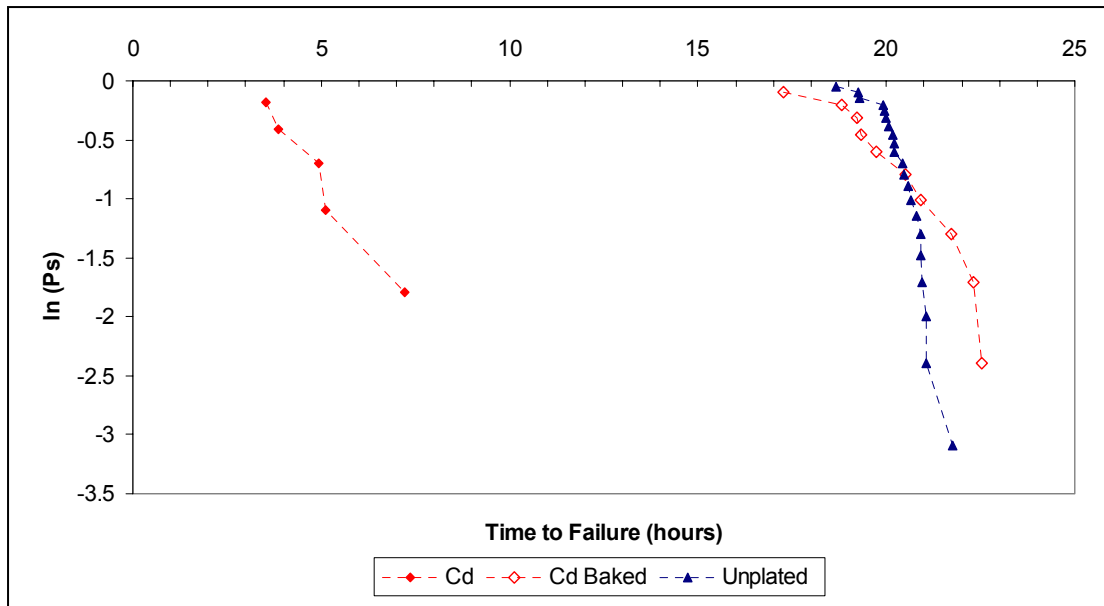


Figure 54. Weibull plot of the effect of Cd electroplating

As depicted in Figure 54, the time to failure of specimens that had been plated with 8 μm of Cd was considerably decreased compared to the unplated specimens. (Table 10) Cd plated specimens that had been immediately baked at 200°C for 24 hours showed similar times to failure as in the unplated control, but with more scatter. Baking proved to be almost fully effective in the recovery of the ductile properties of the steel specimens by promoting the loss of hydrogen from the surface of the coating. According to a Student's t-test, the results of Cd plated and baked specimens could be assumed to belong to the same population as the results for the unplated control. (Table 11)

Specimens	Mean T_{failure} (h)	EI (%)	n	SD
Cd	4.93	75.75	5	1.45
Cd Baked	20.23	0.58	10	1.67

Table 10. Mean times to failure of baked and unbaked Cd plated specimens

Sets of Results	t statistic	v	α	t tabular	Compare	Accept?
Cd Baked / Unplated	0.22	29	0.05	2.05	$t_s < t_{\text{tab}}$	Yes

Table 11. Student's t-test for baked Cd plated specimens

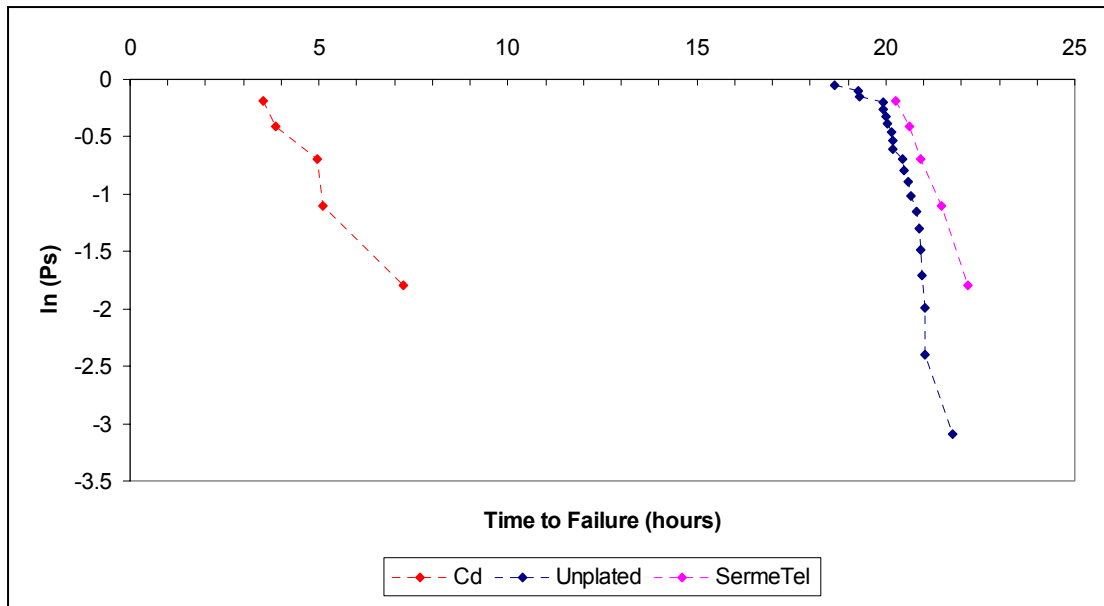


Figure 55. Weibull graph for SermeTel coated specimens

From Figure 55 it appeared that the SermeTel coating treatment alone, unlike cadmium plating, did not promote HE of the steel substrate, as the mean time to failure for SermeTel coated specimens was higher than that for the unplated case. Hence, no further baking treatment was implemented. According to a Student's t-test the results of SermeTel coated steel tensile specimens and those of the unplated control were assumed to belong to the same population. (Table 13)

Specimens	Mean T_{failure} (h)	EI (%)	n	SD
SermeTel	21.10	-3.66	5	0.75

Table 12. Mean times to failure of SermeTel coated specimens

Sets of Results	t statistic	v	α	t tabular	Compare	Accept?
SermeTel / Unplated	2.03	24	0.05	2.06	$t_s < t_{\text{tab}}$	Yes

Table 13. Student's t-test for SermeTel coated specimens

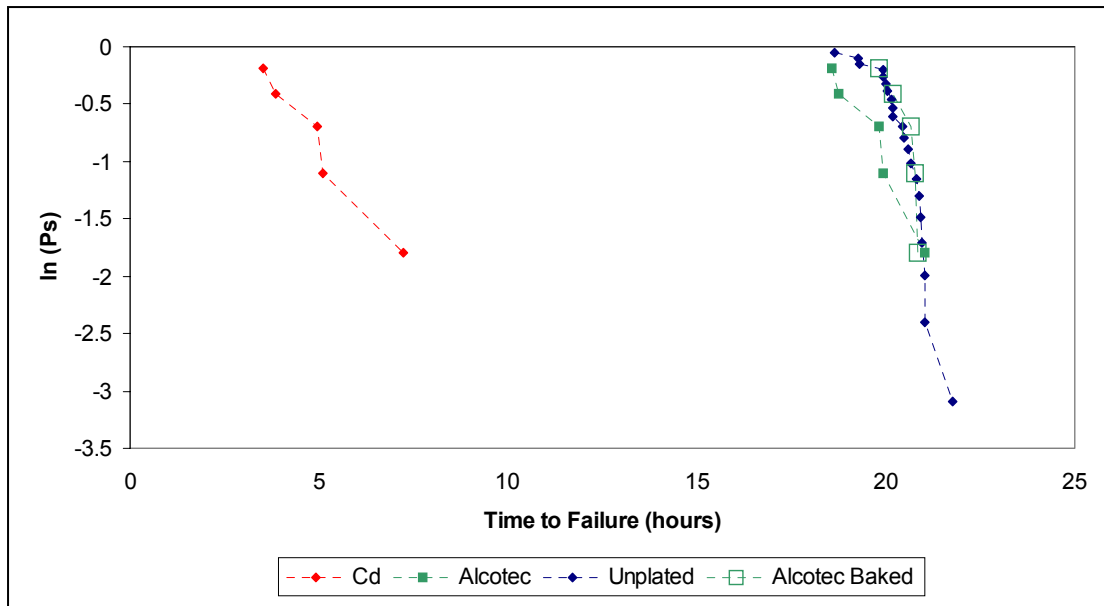


Figure 56. Weibull graph for Alcotec coated specimens

As illustrated in Figure 56, the Alcotec coating treatment promoted a small amount of HE of the steel emphasising the need for a subsequent baking treatment. Alcotec coated steel specimens baked at 200°C for 24 hours displayed a full recovery of their tensile properties proving the effectiveness of the de-embrittlement process. (Table 14) From a statistical point of view, both results for Alcotec coated and Alcotec coated, as well as baked, specimens could not be presumed to belong to a different population than the air tests results. (Table 15)

Specimens	Mean T_{failure} (h)	EI (%)	n	SD
Alcotec	19.63	3.54	5	1.01
Alcotec Baked	20.46	-0.54	5	0.44

Table 14. Mean times to failure of Alcotec coated specimens

Sets of Results	t statistic	v	α	t tabular	Compare	Accept?
Alcotec / Unplated	1.51	24	0.05	2.06	$t_s < t_{\text{tab}}$	Yes
Alcotec Baked / Unplated	0.44	24	0.05	2.06	$t_s < t_{\text{tab}}$	Yes

Table 15. Student's t-test for Alcotec coated specimens

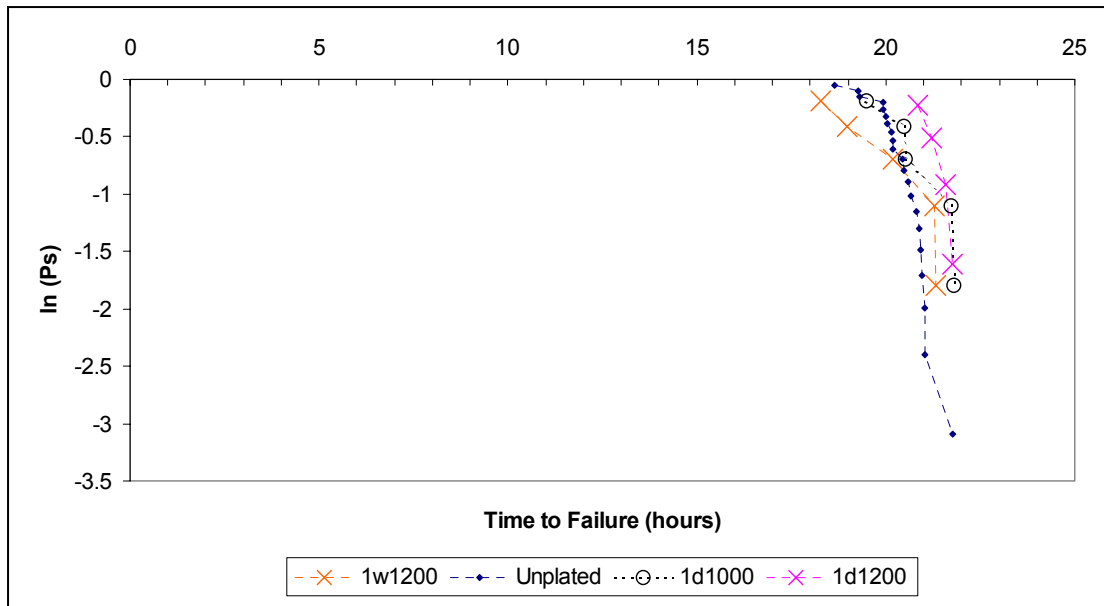


Figure 57. Weibull graph for unplated specimens tested after having been potentiostatically charged in 3.5 % NaCl solution for one day and one week

The Weibull plot in Figure 57 shows the SSRT results for AISI 4340 steel specimens that were potentiostatically charged at the electrochemical potentials of corroding coatings for either one day or one week, and then they were tested. The attempt was to simulate the mechanical behaviour of coated specimens that were tested after their coatings had corroded in 3.5% NaCl solution for either a day or a week. In all cases the times to failure were close to those of the air tests. (Table 16) Although the tensile specimens needed less than 7 hours to be filled with hydrogen [47], it appeared that its embrittling action could not be detected, as hydrogen had enough time to diffuse out of the cylindrical gauge length of the tensile specimens.

Student's t-tests, carried out to check if each of these sets of results belongs to the same population as the unplated control results, proved that the SSRT data for specimens charged at -1000 mV (SCE) for one day, and at -1200 mV (SCE) for one week were part of the same population as the results for the unplated control. On the contrary, specimens charged at -1200 mV (SCE) for one day proved to be considered as part of a different population from the population of the unplated control specimens. (Table 17)

Specimens	Mean T_{failure} (h)	EI (%)	n	SD
1d (-1000 mV[SCE])	20.81	-2.26	5	0.96
1d (-1200 mV[SCE])	21.36	-4.96	4	0.41
1w (-1200 mV[SCE])	20.01	1.66	5	1.37

Table 16. Mean times to failure of unplated specimens tested after having been potentiostatically charged in 3.5 % NaCl solution for one day and one week

Sets of Results / Unplated	t statistic	v	α	t tabular	Compare	Accept?
1d (-1000 mV[SCE])	1.01	24	0.05	2.06	$t_s < t_{\text{tab}}$	Yes
1d (-1200 mV[SCE])	3.93	23	0.05	2.07	$t_s > t_{\text{tab}}$	No
1w (-1200 mV[SCE])	0.54	24	0.05	2.06	$t_s < t_{\text{tab}}$	Yes

Table 17. Student's t-test for unplated specimens tested after having been potentiostatically charged in 3.5 % NaCl solution for one day and one week

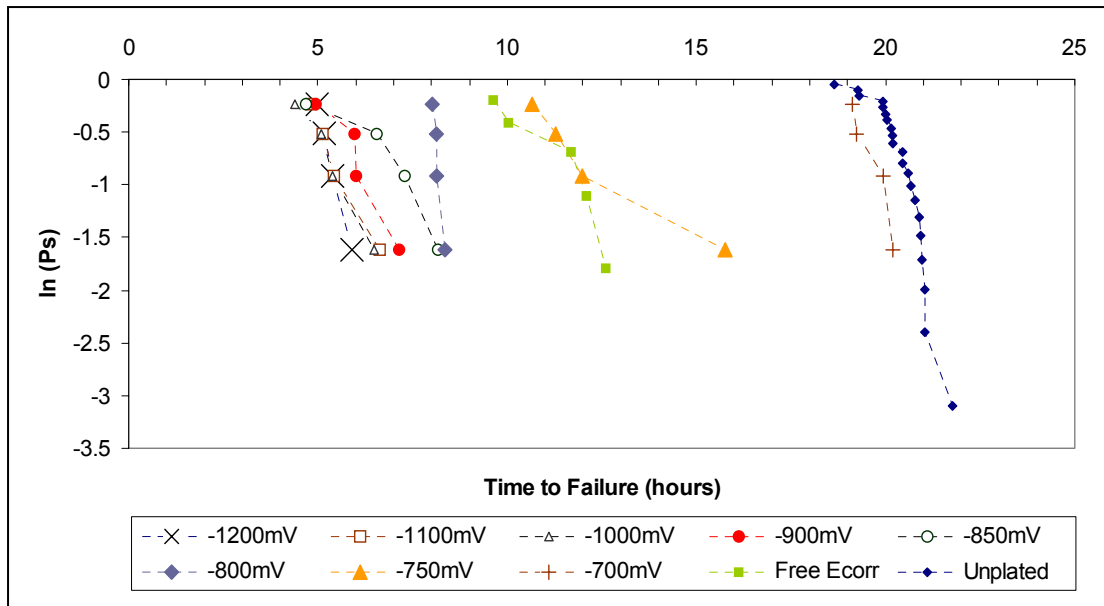


Figure 58. Weibull graph for unplated specimens tested and simultaneously charged in 3.5% NaCl solution at various potentials

Figure 58 illustrates the SSRT results for unplated AISI 4340 steel specimens, which were strained while being surrounded by a 3.5% NaCl solution, as well as being potentiostatically charged at the above range of potentials. The times to failure for these specimens were very different from those of the unplated control, indicating that charging whilst straining poses a higher risk of embrittlement than charging and testing afterwards. (Table 18)

The more active the potential was, the higher the EI appeared. Only at -700 mV (SCE) the degree of observed embrittlement was low with times to failure close to those of the air test. The highest embrittlement was detected between -1000 and -1200 mV (SCE) implying that the benefits of the cathodic protection were overridden by the detrimental embrittling effects of a larger hydrogen absorption at these potentials. Concerning the tests for freely corroding specimens, their potential eventually reached values between -620 and -640 mV (SCE), with times to failure slightly smaller than those at -750 mV (SCE). (Table 18)

Specimens	Mean T_{failure} (h)	EI (%)	n	SD
-1200 mV (SCE)	5.37	73.61	4	0.39
-1100 mV (SCE)	5.51	72.94	4	0.78
-1000 mV (SCE)	5.35	73.71	4	0.87
-900 mV (SCE)	6.02	70.43	4	0.90
-850 mV (SCE)	6.68	67.19	4	1.49
-800 mV (SCE)	8.16	59.90	4	0.14
-750 mV (SCE)	12.42	38.98	4	2.29
-700 mV (SCE)	19.63	3.53	4	0.51
Free E_{corr}	11.22	44.87	5	1.30

Table 18. Mean times to failure for strained unplated specimens, which were simultaneously charged at the electrochemical potentials of corroding coatings in 3.5% NaCl solution.

As the charged specimens at -700 mV (SCE) showed SSRT results closer to the unplated control case, a Student's t -test was implemented for these two sets of results indicating that these groups belong to different populations. (Table 19)

Sets of Results	t statistic	v	α	t tabular	Compare	Accept?
-700 mV (SCE) / Unplated	2.41	23	0.05	2.07	$t_s > t_{\text{tab}}$	No

Table 19. Student's t -test for unplated specimens, stressed and simultaneously charged in 3.5% NaCl solution at -700 mV (SCE)

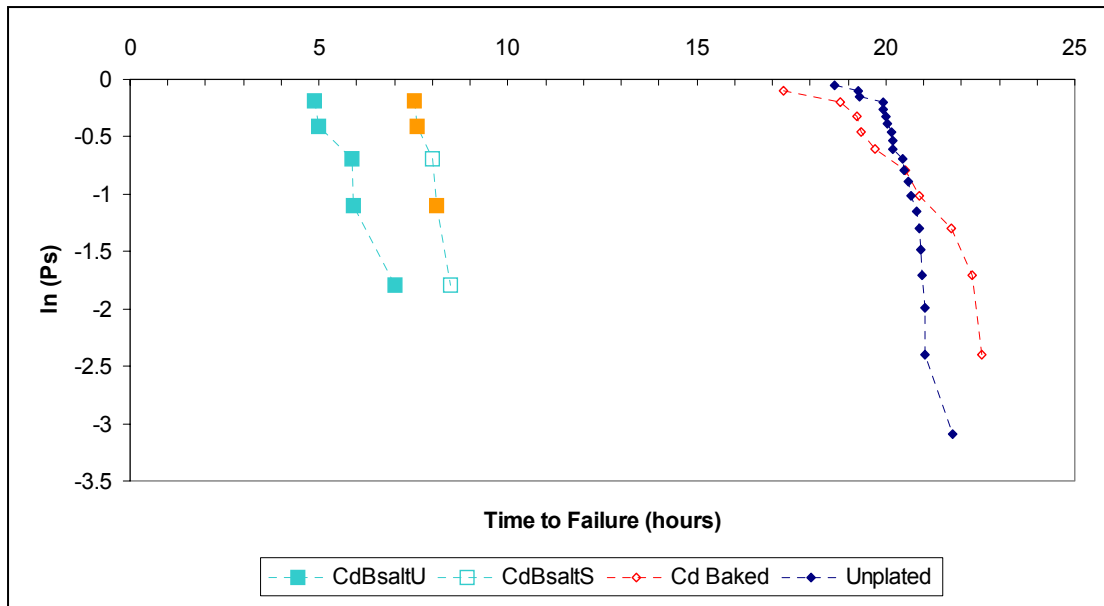


Figure 59. Weibull analysis for Cd plated and baked specimens (scribed and unscribed) strained in 3.5% NaCl solution (Specimens failing out of the scribe are with orange colour.)

Figure 59 demonstrates that significantly large amounts of hydrogen re-embrittlement were detected for both unscribed and scribed specimens due to the corrosion of the Cd coating, the dissolution of which was accompanied by the cathodic reaction of water reduction. In both cases the measured corrosion potentials varied between -740 and -780 mV (SCE) approximately. (Table 20) Cadmium scribed specimens failed at longer times than unscribed, thus indicating that Cd was a pervious coating to hydrogen, and for this reason it was not coincidental that three out of five scribed specimens failed out of the scribe, as the most significant microstructural flaws, at which HE would occur, were not necessarily located at the position of the scribe. In these specimens, sufficient hydrogen was absorbed at pores and coating defects for embrittlement to take place outside the scribed area at the largest flaw present.

Specimens	Potential range [mV _{SCE}]	Mean T _{failure} (h)	EI (%)	n	SD
CdBsaltU	(-760, -740)	5.73	71.83	5	0.87
CdBsaltS	(-780, -760)	7.94	60.99	5	0.40

Table 20. Mean times to failure and potential ranges for Cd plated and baked specimens freely corroding in 3.5% NaCl solution whilst tested

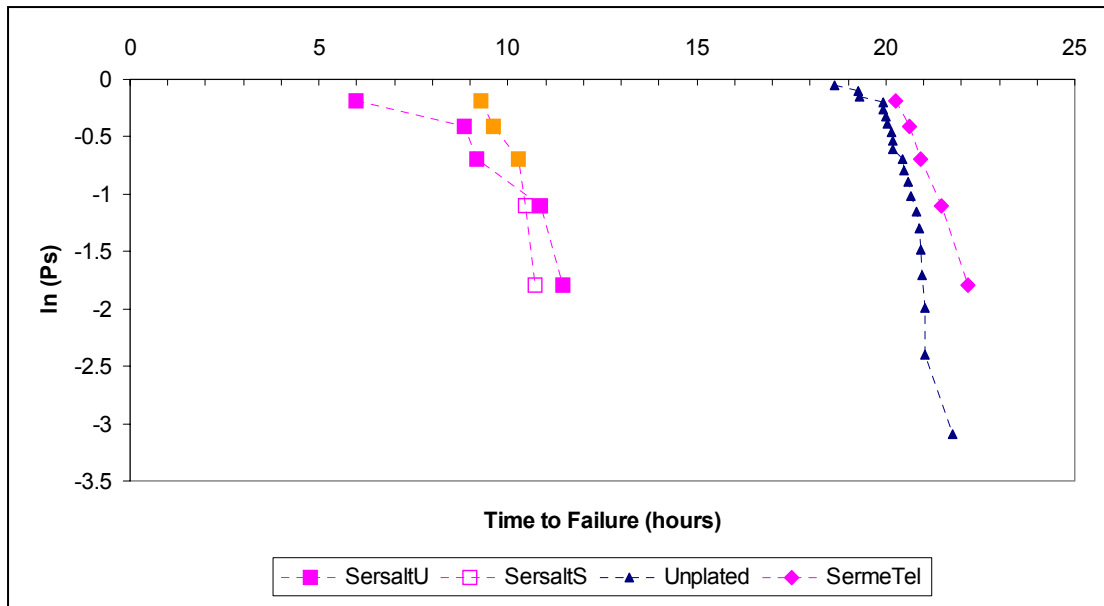


Figure 60. Weibull analysis for SermeTel coated specimens strained in 3.5% NaCl solution (Specimens failing out of the scribe are with orange colour.)

Figure 60 shows the re-embrittling effect of the corrosion of SermeTel on coated steel specimens, strained while charged in 3.5% NaCl solution. Scribed specimens failed at longer times than unscribed, with three out of five specimens failing out of the scribe, at the position of the most significant microstructural flaws, thus showing the permeability of SermeTel to hydrogen. (Table 21) In both cases the potential of SermeTel was round -750 mV (SCE). According to the Student's t -test below, these sets of results cannot be assumed to belong to different populations. (Table 22)

Specimens	Potential range [mV _{SCE}]	Mean T_{failure} (h)	EI (%)	n	SD
SersaltU	(-755, -745)	9.27	54.44	5	2.14
SersaltS	(-770, -740)	10.05	50.64	5	0.62

Table 21. Mean times to failure and potential ranges for SermeTel coated specimens freely corroding in 3.5% NaCl solution whilst tested

SermeTel Specimens	t statistic	v	α	t tabular	Compare	Accept?
Unscribed / Scribed	0.79	8	0.05	2.31	$t_s < t_{\text{tab}}$	Yes

Table 22. Student's t -test for SermeTel coated specimens freely corroding in 3.5% NaCl solution whilst tested

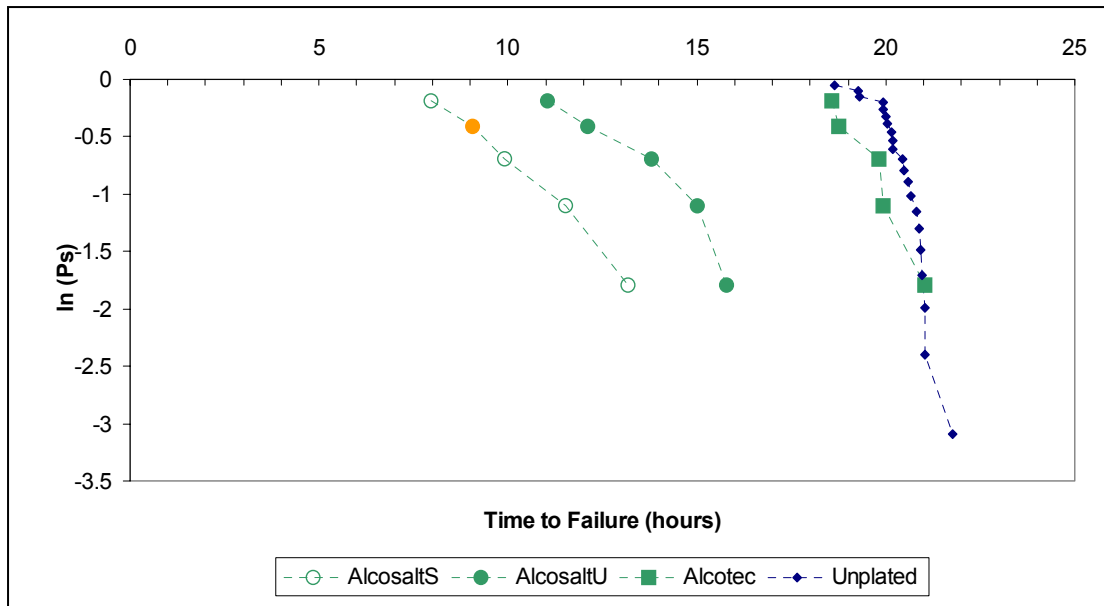


Figure 61. Weibull analysis for Alcotec coated specimens strained in 3.5% NaCl solution (Specimens failing out of the scribe are with orange colour.)

Figure 61 shows that the corrosion of the Alcotec coating promoted the hydrogen re-embrittlement of the coated steel tensile specimens, either scribed or unscribed. In this case, scribed specimens failed at shorter times than unscribed suggesting that Alcotec was a less pervious coating to hydrogen than Cd and SermeTel. The last proposal was further strengthened by the fact that just one out of five scribed specimens failed out of the scribe. Finally, as seen in Table 23, the free corrosion potential range for Alcotec coated specimens was more active than that of Cd and SermeTel coated specimens with values round -800 mV (SCE) for either the scribed or the unscribed case.

Specimens	Potential range [mV _{SCE}]	Mean T _{failure} (h)	EI (%)	n	SD
AlcosaltU	(-820, -800)	13.55	33.42	5	1.97
AlcosaltS	(-820, -780)	10.30	49.37	5	2.07

Table 23. Mean times to failure and potential ranges for Alcotec coated specimens freely corroding in 3.5% NaCl solution whilst tested

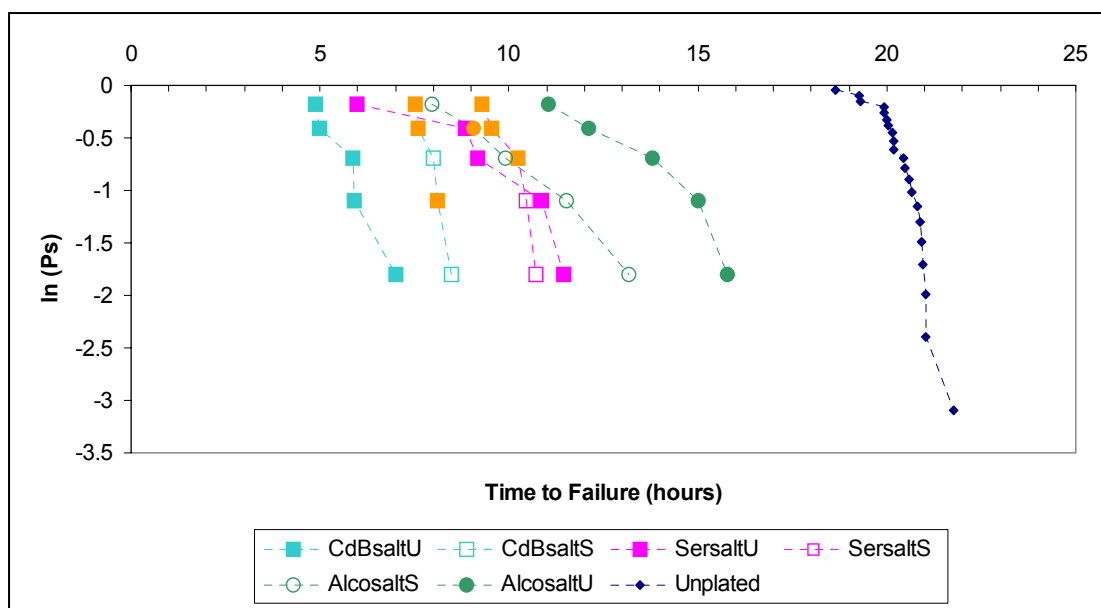


Figure 62. Weibull analysis for all coated specimens strained in a 3.5% NaCl solution (Specimens failing out of the scribe are with orange colour.)

The Weibull plot in Figure 62 is practically a summary of the SSRT results for all the coated steel tensile specimens that were strained while their coatings, i.e. Cd, SermeTel and Alcotec were corroding in a salt solution. The corrosion of Alcotec incurred less re-embrittlement than the dissolution of the other two coatings on both scribed and unscribed steel specimens, and SermeTel coated specimens displayed longer times to failure than the Cd plated tensile specimens. The first finding was unexpected, as Alcotec displayed more active corrosion potentials suggesting more hydrogen uptake, and thus more embrittlement. The previous expectation was also based on the SSRT results for cathodically protected and simultaneously stressed, unplated steel specimens, where specimens charged at -800 mV (SCE) showed more embrittlement than those held at -750 mV (SCE). However, the corrosion of Cd and SermeTel caused more loss of the steel ductile properties than the corrosion of Alcotec, implying, therefore, that these two coatings were more permeable to hydrogen than Alcotec.

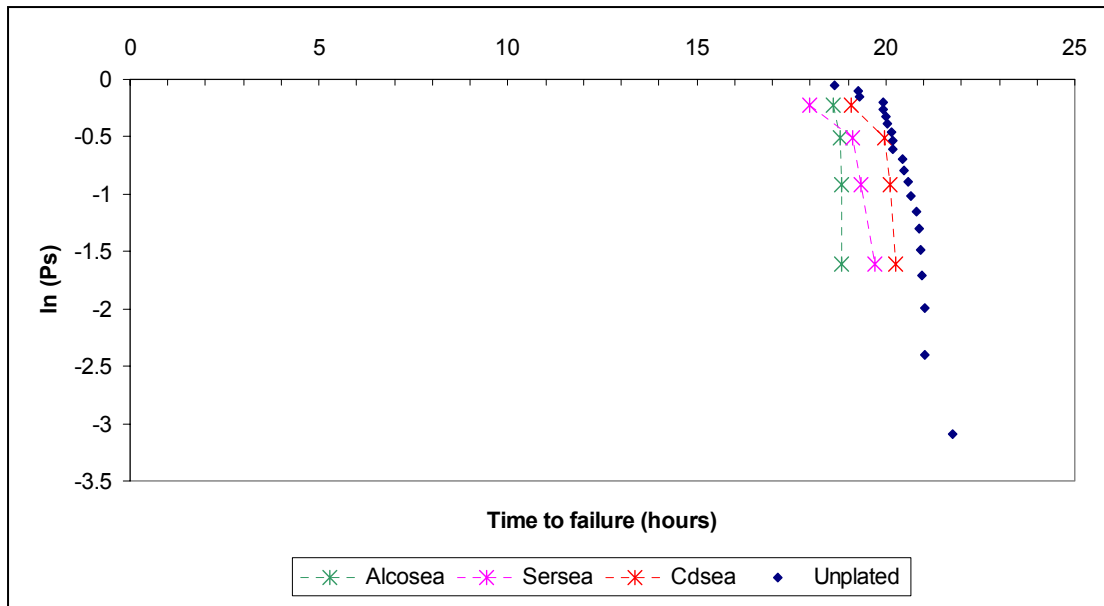


Figure 63. Weibull plot for coated tensile specimens exposed to marine atmosphere for two years

Figure 63 illustrates the effect of marine atmosphere exposure on the ductile properties of AISI 4340 steel tensile specimens. As viewed on the above Weibull plot, there were very small amounts of re-embrittlement introduced as a result of the corrosion of the applied coatings. This case was different from the previous one analysed in Figures 59–61. This time coatings were firstly corroded, and then the specimens were tested, whilst, previously, corrosion and testing were taking place simultaneously. Cd plated and baked specimens displayed the least degree of re-embrittlement, being followed by SermeTel, and Alcotec had the shortest times to failure, but still with a limited effect on the ductility of steel. (Table 24)

Specimens	Mean T_{failure} (h)	EI (%)	n	SD
Alcosea	18.77	7.75	4	0.10
Sersea	19.04	6.45	4	0.75
Cdsea	19.87	2.35	4	0.53

Table 24. Mean times to failure for coated specimens exposed to marine atmosphere for two years

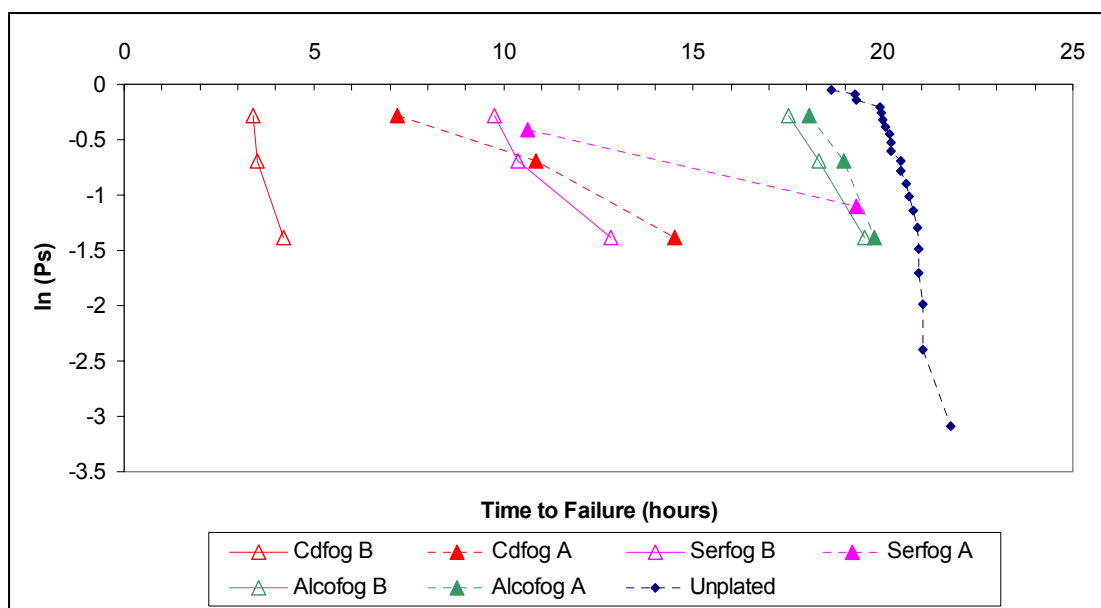


Figure 64. Weibull plot for coated specimens tested after being held under salt spray testing conditions for 1000 hours (2 tests performed, A and B)

Figure 64 demonstrates the re-embrittling effect of the corrosion of the applied coatings on the steel ductile properties, as a result of the salt spray conditions. Two salt spray tests were performed, and only in the case of the Alcotec coated specimens, a Student's t-test proved that the two sets of results could not be assumed as part of different populations. (Table 26) Moreover, the corrosion of Alcotec produced the smallest degree of embrittlement among all treatments examined. (Table 25)

In the other two coatings, the mechanical properties of the steel substrate were more affected by the hydrogen re-embrittlement caused by their corrosion, and additionally, the results of the two repeats were very different from each other, thus considering them as separate groups. Cd plated and baked specimens displayed the highest amount of re-embrittlement among all treatments, and especially in the second repeat. SermeTel coated specimens behaviour in the salt spray test was laying between that of Cd and Alcotec for both runs. (Table 25)

Specimens	Mean T_{failure} (h)	EI (%)	n	SD
Cdfog A	10.85	46.67	3	3.65
Cdfog B	3.71	81.79	3	0.45
Serfog A	14.97	26.46	2	6.13
Serfog B	10.98	46.03	3	1.62
Alcofog A	18.94	6.93	3	0.86
Alcofog B	18.43	9.42	3	1.01

Table 25. Mean times to failure for coated specimens tested after being held under salt spray testing for 1000 hours (2 tests performed, A and B)

Sets of Results	t statistic	v	α	t tabular	Compare	Accept?
Alcofog A / B	0.67	4	0.05	2.78	$t_s < t_{\text{tab}}$	Yes

Table 26. Student's t-test for Alcotec plated specimens placed in salt fog cabinet for 1000 hours (Comparison between batches A and B)

3.2 PERMEATION MEASUREMENTS

Figure 65 depicts a typical depletion transient. Depleting the steel shim of hydrogen present prior to any permeation testing was necessary in order to achieve a low hydrogen background level. It is this background flux value that is subtracted from the plateau value, in order to calculate from every transient the steady-state flux J_{∞} .

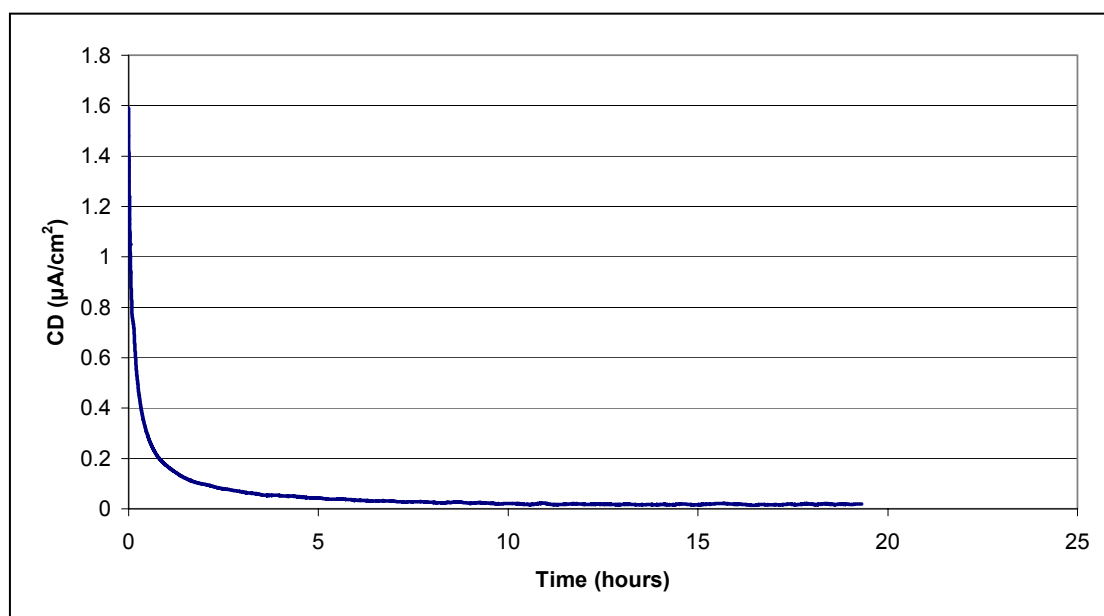


Figure 65. Typical depletion transient

Figures 66–74 show transients for hydrogen permeation tests for an unplated steel membrane held at –1200, –1100, –1000, –900, –875, –850, –825, –800 mV (SCE) and at the free corrosion potential of steel, the trend of which is displayed in Figure 75. Figure 76 portrays all the previously depicted transients in Figures 66–74 in one graph. These transients are representative for each of the aforementioned potentials, at which several permeation measurements were performed. Table 27 summarises the results of the steady-state fluxes J_{∞} from all the performed permeation measurements at the above potentials, referring to the mean J_{∞} values as well.

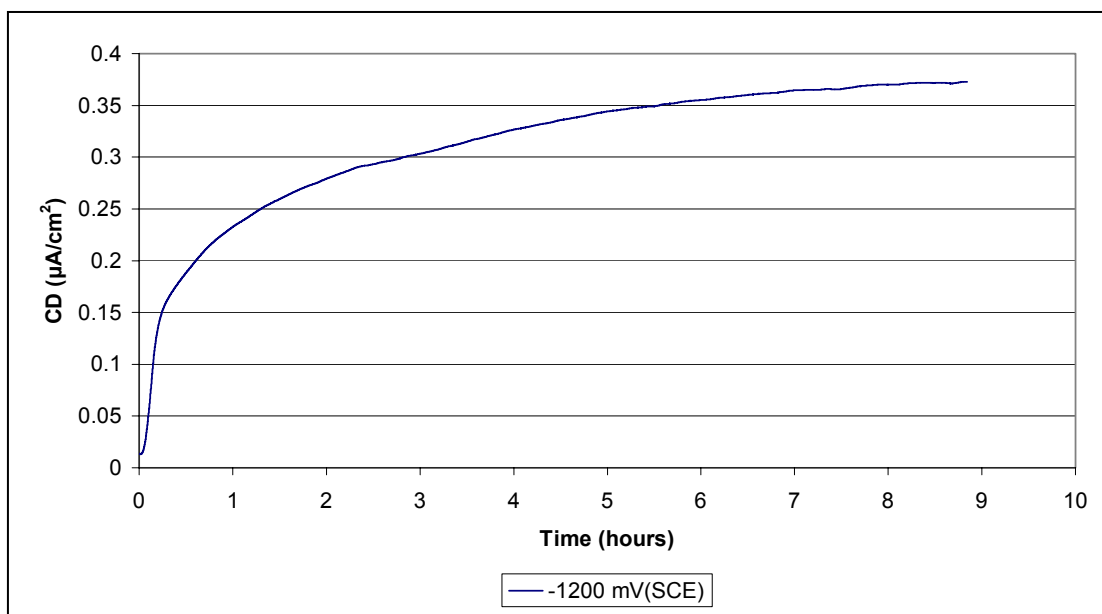


Figure 66. Permeation transient at -1200 mV (SCE)

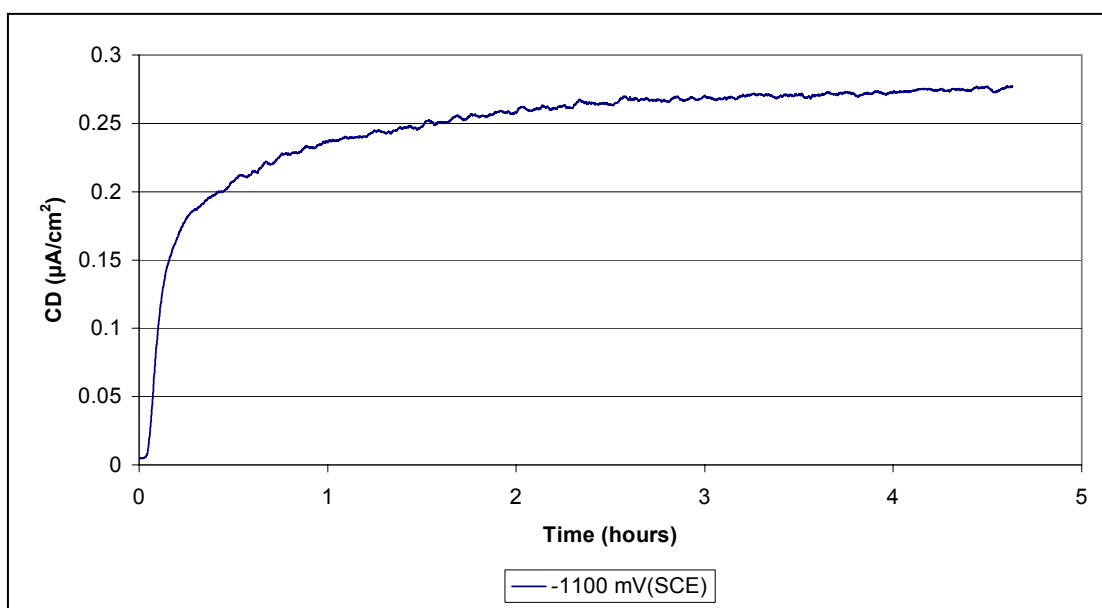


Figure 67. Permeation transient at -1100 mV (SCE)

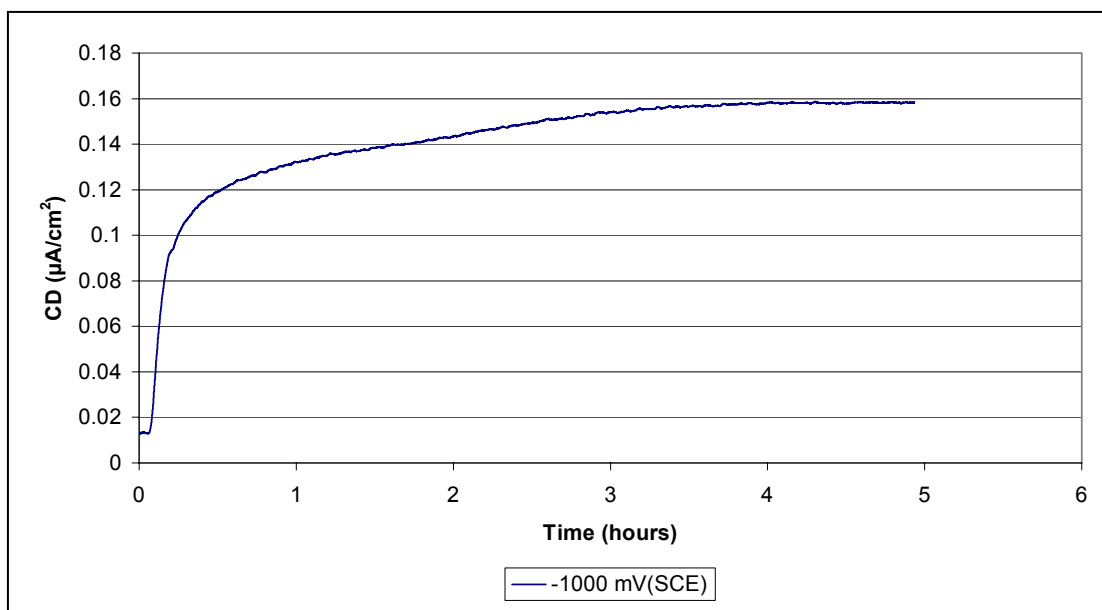


Figure 68. Permeation transient at –1000 mV (SCE)

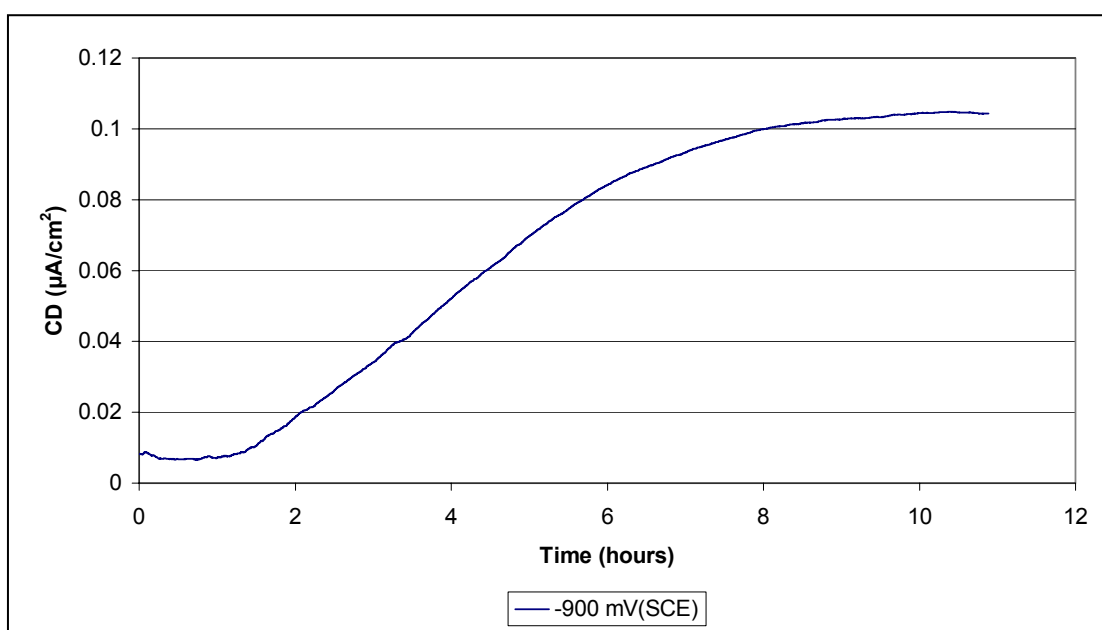


Figure 69. Permeation transient at –900 mV (SCE)

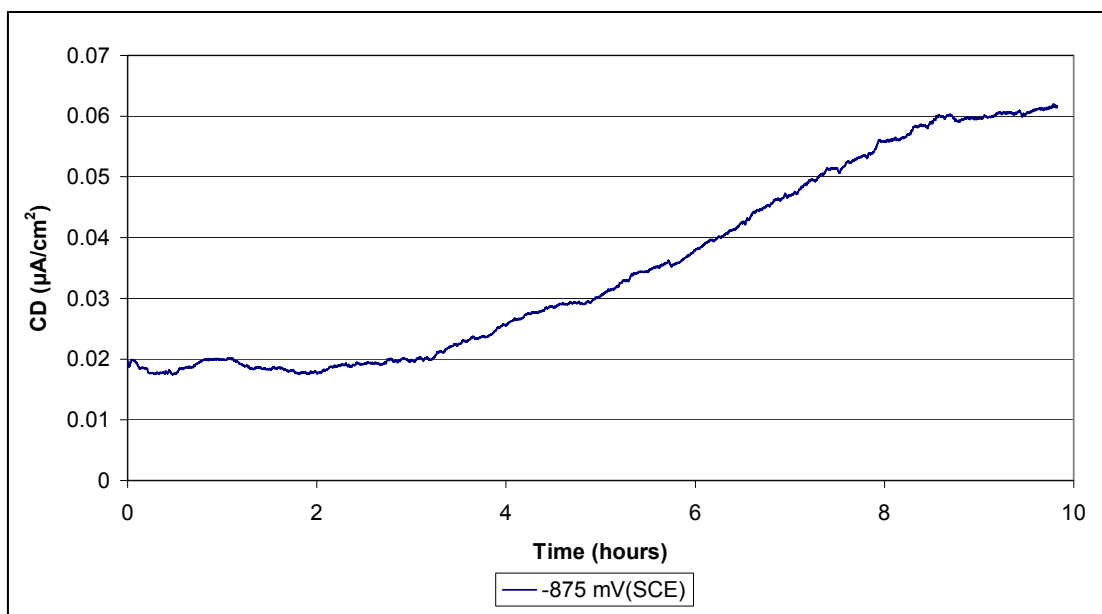


Figure 70. Permeation transient at -875 mV (SCE)

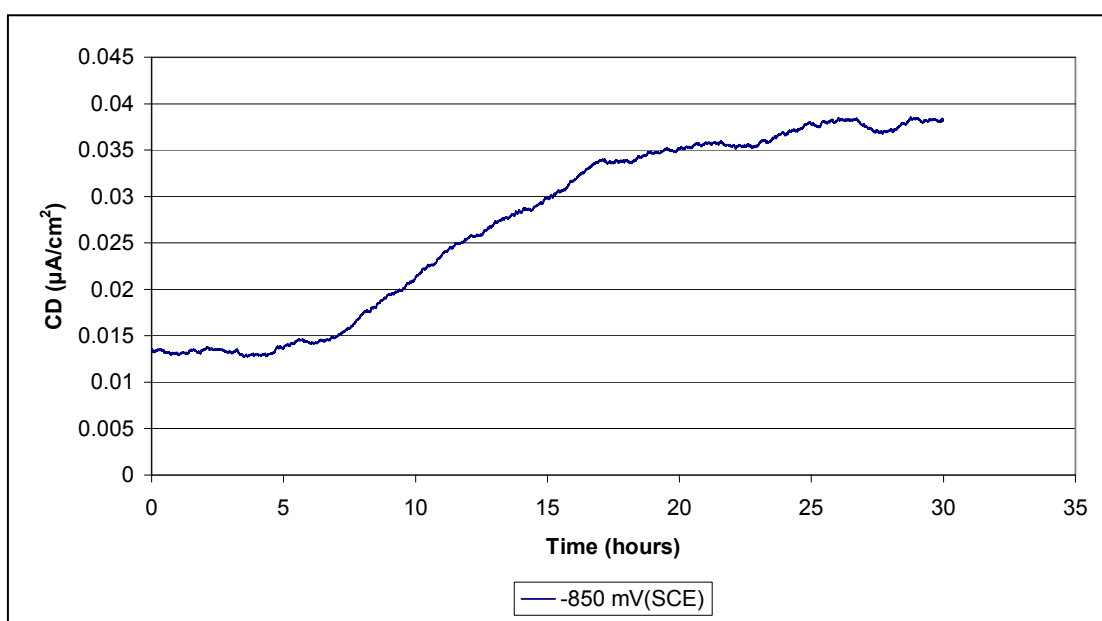


Figure 71. Permeation transient at -850 mV (SCE)

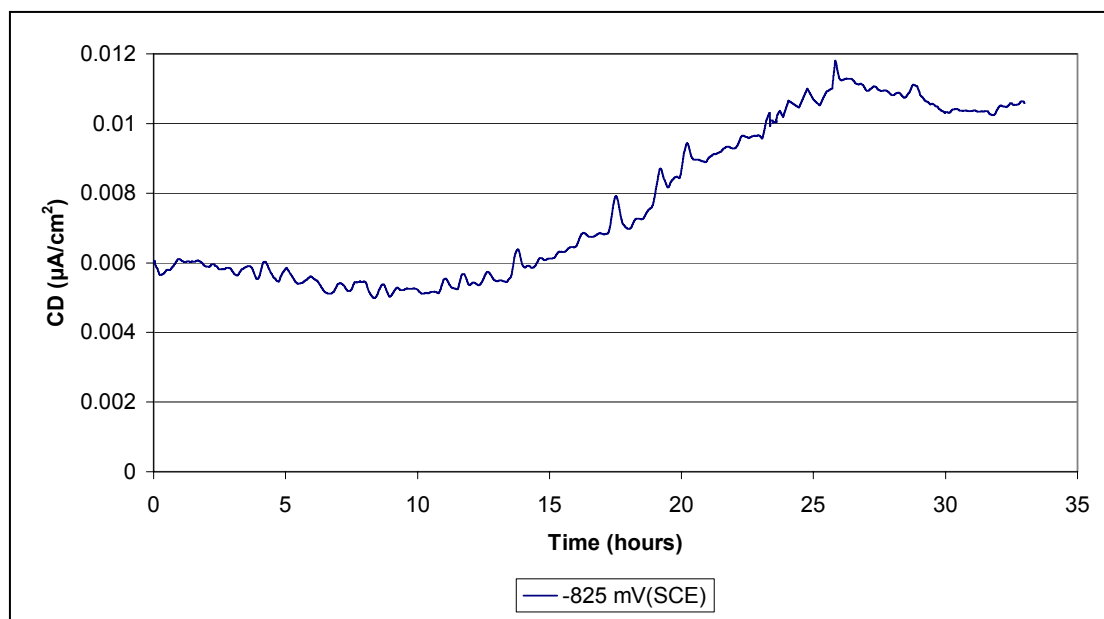


Figure 72. Permeation transient at -825 mV (SCE)

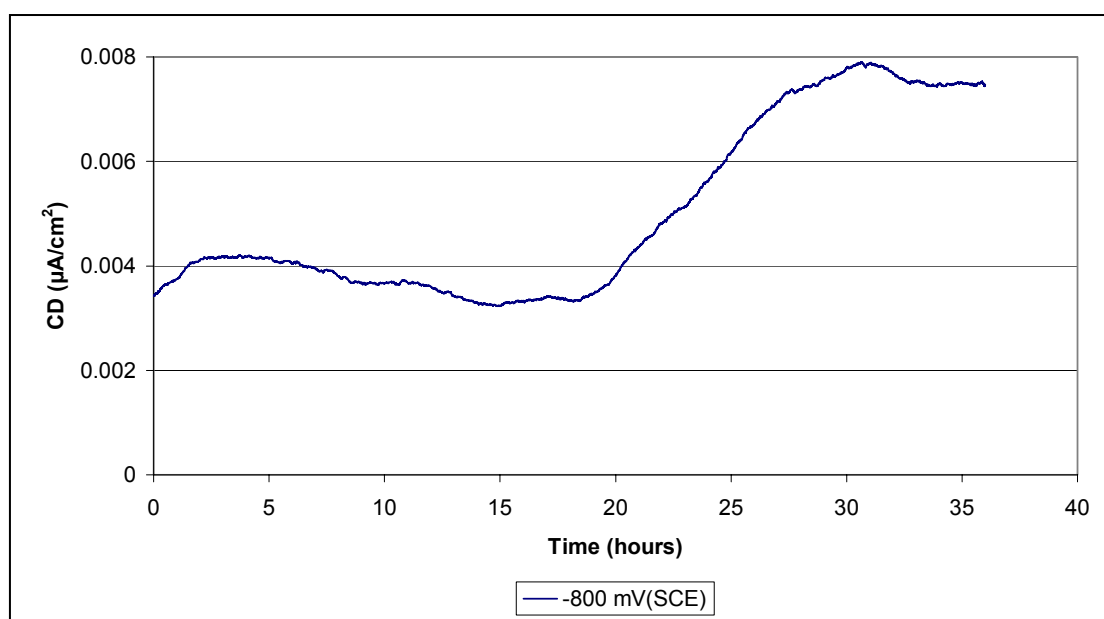


Figure 73. Permeation transient at -800 mV (SCE)

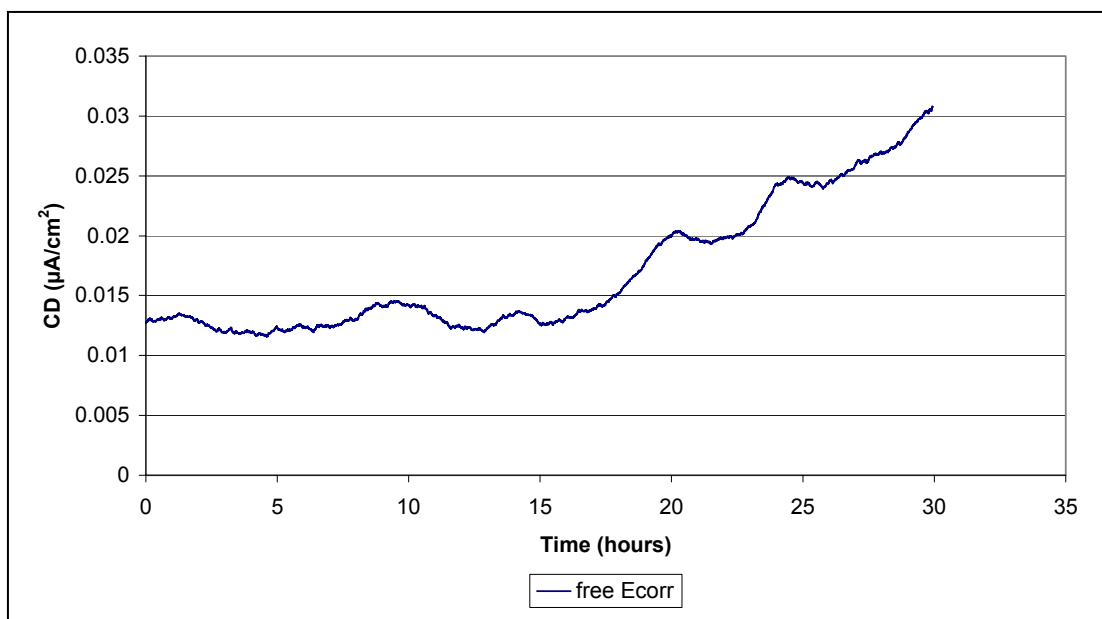


Figure 74. Permeation transient at free corrosion potential of the membrane

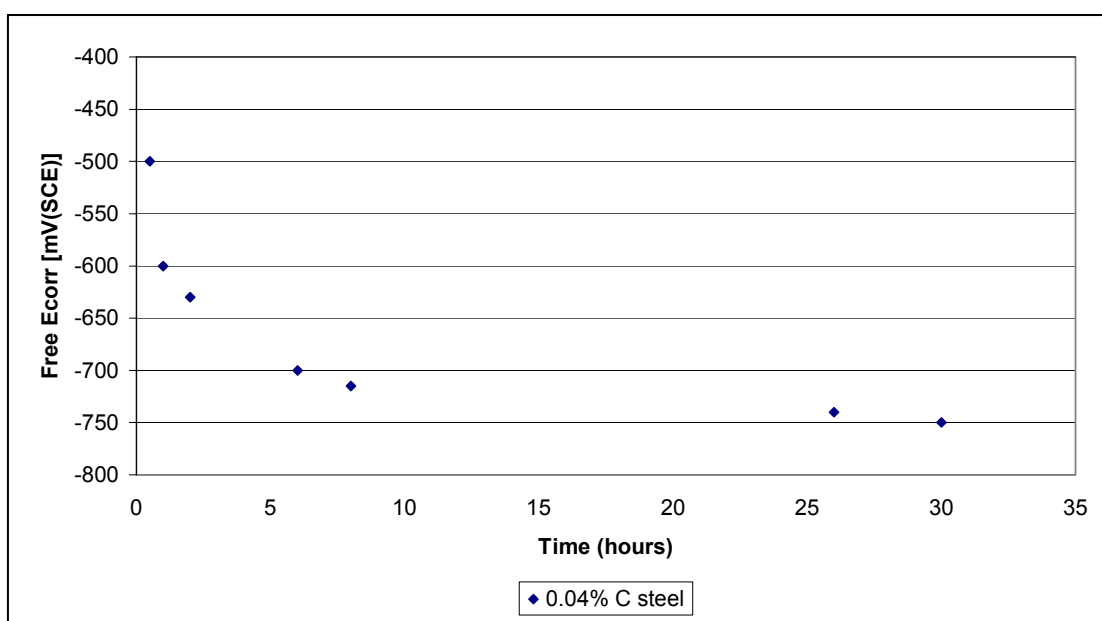


Figure 75. Free corrosion potential of the steel in the transient of Figure 74

Potential	J_{∞} values ($\mu\text{A}/\text{cm}^2$)	SD
-1200 mV (SCE)	0.383 0.281 0.272 0.257 0.359	
Mean -1200 mV (SCE)	0.31	0.057
-1100 mV (SCE)	0.272 0.271 0.178 0.16	
Mean -1100 mV (SCE)	0.22	0.06
-1000 mV (SCE)	0.265 0.215 0.146	
Mean -1000 mV (SCE)	0.209	0.06
-900 mV (SCE)	0.136 0.10 0.098	
Mean -900 mV (SCE)	0.111	0.021
-875 mV (SCE)	0.044	
-850 mV (SCE)	0.030 0.025	
Mean -850 mV (SCE)	0.0275	0.0035
-825 mV (SCE)	0.006	
-800 mV (SCE)	0.009 0.004	
Mean -800 mV (SCE)	0.0065	0.0035
Free Ecorr	0.019	

Table 27. Steady-state fluxes (including mean values) at each potential

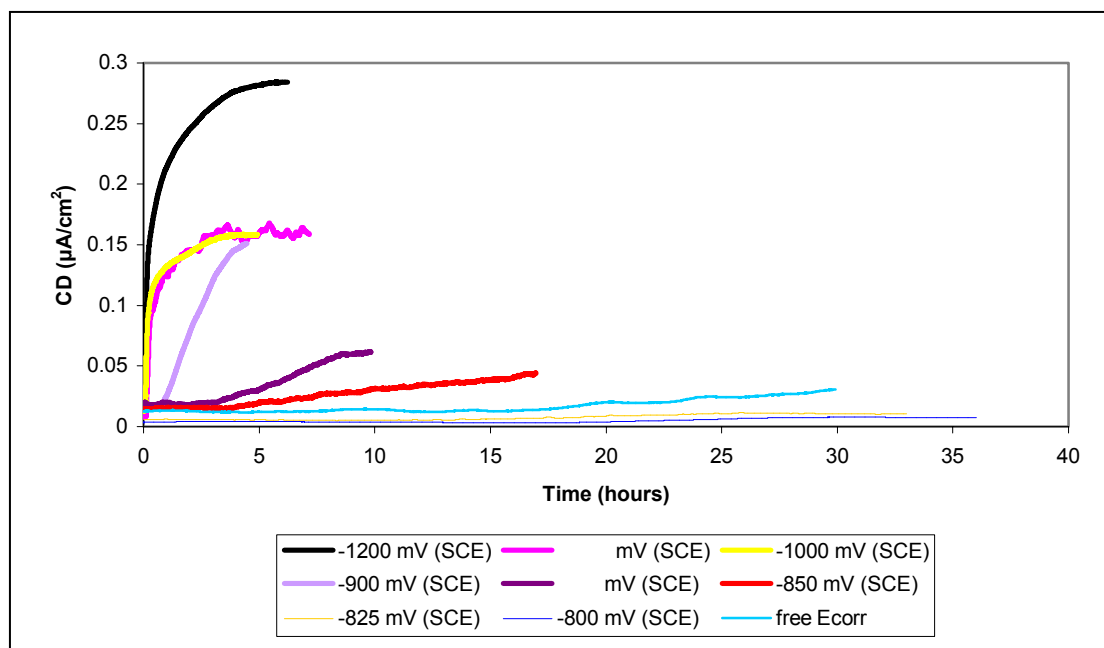


Figure 76. Summary of all permeation transients shown in Figures 66–74

The general trend from the previous results is that the more negative the charging potential is, the greater the amount of hydrogen that permeates the membrane. This is shown more pictorially in Figure 76, as well as in the bar chart of Figure 77. From this remark, it can be concluded that a more active coating is likely to promote more hydrogen re-embrittlement due to its corrosion than a less active coating. Moreover, this trend is in agreement with the findings of the mechanical testing results, where at more active potentials there is more observed embrittlement for unplated steel tensile specimens, strained and charged at the same time.

At values of -750 and -700 mV (SCE) no hydrogen permeation could be detected, as the hydrogen background level was higher than the permeating flux of hydrogen at these potentials. However, even at these potentials hydrogen might have entered and permeated the membrane, as in the SSRTs for unplated steel specimens, which were strained and simultaneously charged at these potentials, embrittlement was detected. Concerning the free corrosion potential of the steel shim, this was observed to reach values between -750 and -700 mV (SCE) for most time of the experiment. Despite this fact, hydrogen uptake was detected in the permeation test for a freely corroding membrane, confirming that the higher EI in SSRTs for freely corroding strained

specimens compared to the embrittling effect of straining and charging at -750 and -700 mV (SCE) was not coincidental.

Another remark from the previous permeation transients (Fig. 66–74, 76) is that the more active the potential is the shorter the breakthrough time appears to be. At potentials between -1200 and -1000 mV (SCE) the first hydrogen needed from just a few seconds up to a few minutes to permeate the membrane. At -900 mV (SCE) it needed at least one hour, and at more noble potentials the breakthrough time was in the range of hours. Consequently, the background level could affect the apparent breakthrough time, and if at more negative potentials could have had no effect whatsoever, at more noble values, such as between -850 and -800 mV (SCE), the smallest possible background level was essential to be achieved, so as to clearly detect hydrogen the soonest possible.

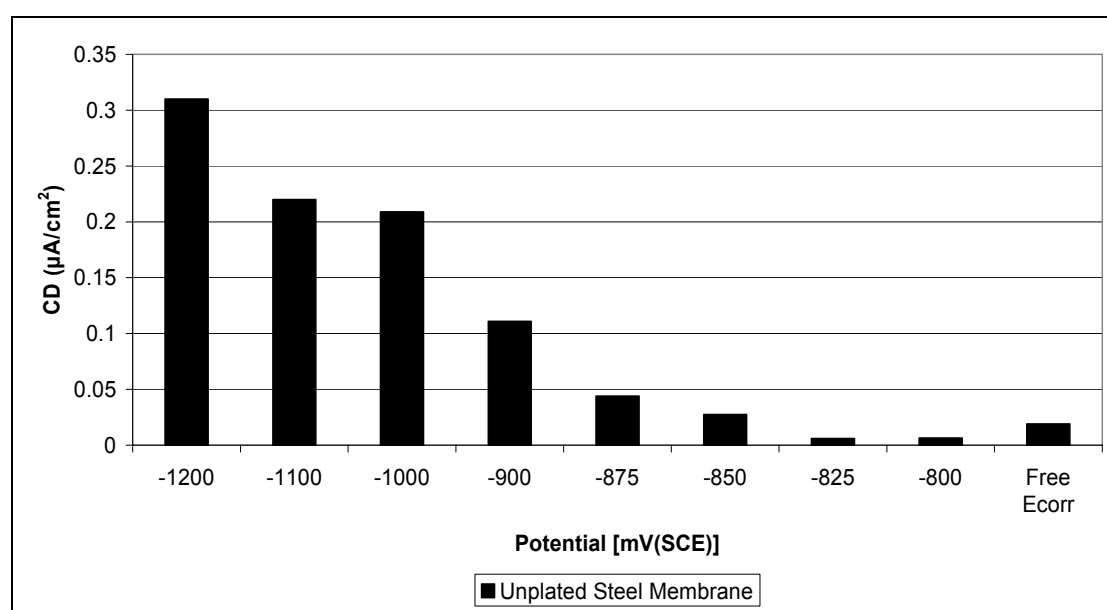


Figure 77. Bar chart of mean steady–state fluxes at each potential

3.3 LINEAR POLARISATION RESISTANCE RESULTS

Stern and Geary [122, 123] derived an expression for the calculation of corrosion currents from linear polarisation resistance (LPR) measurements. Their relationship was based on a detailed analysis of the polarisation curves of the anodic and cathodic reactions occurring during the corrosion of a metal, and the assumption that both reactions are charge-transfer controlled. According to this expression, at potentials close to E_{corr} (± 10 mV) the corrosion current (I_{corr}) is proportional to the reciprocal of the polarisation resistance (R_p) that is the slope of the potential–current curves (Equation 31 in the Experimental) obtained from the LPR experiment. Given the anodic and cathodic Tafel constants, a value for I_{corr} can be calculated using the following equation.

Equation 32:

$$I_{corr} = \frac{b_a b_c}{2.3(b_a + b_c) \left(\frac{\Delta E}{\Delta I} \right)_{E_{corr}}} = \frac{B}{R_p}$$

where:

I_{corr} corrosion current density ($A\ cm^{-2}$)

E_{corr} corrosion potential (mV)

R_p polarisation resistance ($\Omega\ cm^2$)

b_a, b_c anodic, cathodic Tafel constants

B Stern–Geary constant (mV)

B is taken to be 18 mV for the Al–based coatings [120] and 16 mV for Cd [10], and is related to the anodic and cathodic Tafel constants as follows ;-

Equation 33:

$$B = \frac{b_a b_c}{2.3(b_a + b_c)}$$

The corrosion rate of a coating is calculated from the corrosion current using Equation 34. The expressed corrosion rate in cm/year can easily be converted into $\mu m/year$.

Equation 34:

$$\text{Corrosion Rate} = \frac{I_{\text{corr}} M t}{F z \rho}$$

where:

I_{corr} corrosion current density (A cm^{-2})

M atomic mass (g mol^{-1})

t time (31.536×10^6 seconds/year)

F Faraday's constant ($96500 \text{ Cb mol}^{-1}$)

z number of electrons in oxidation reaction

ρ density (g cm^{-3})

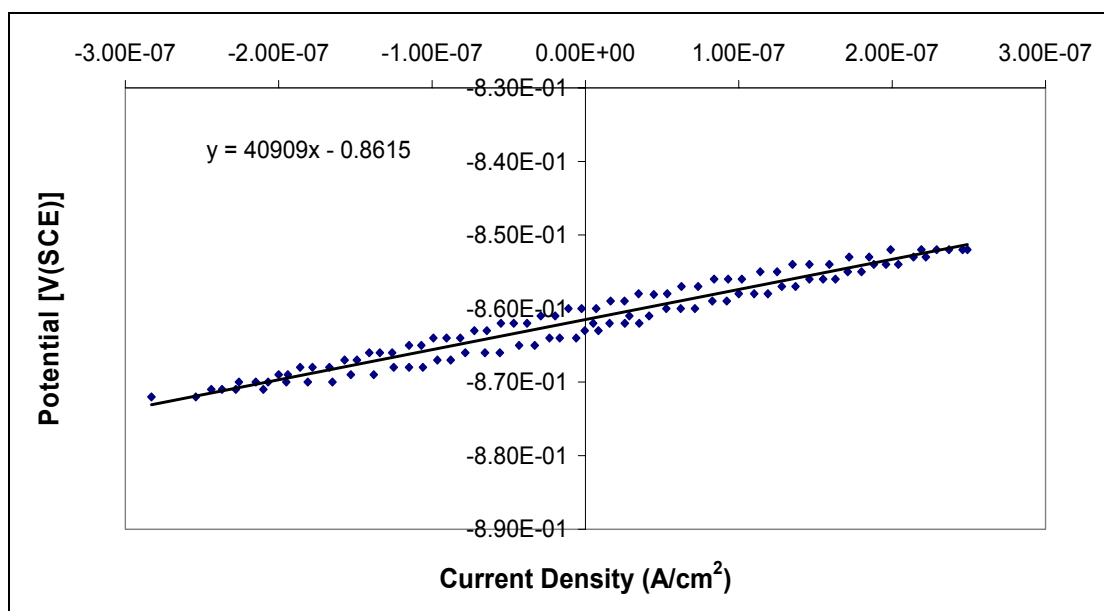


Figure 78. Typical LPR plot for the SermeTel coating

A typical LPR plot is shown in Figure 78, where $R_p = 40,900 \Omega \text{ cm}^2$ for the SermeTel coating. This corresponds to an I_{corr} value of $4.4 \times 10^{-7} \text{ A cm}^{-2}$ and a corrosion rate for the SermeTel of $4.8 \mu\text{m/year}$. Calculated R_p values from LPR plots are depicted in graphs presenting the trend in R_p for SermeTel, Alcotec and Cadmium over a period of 3000 hours. (Fig. 80, 82, 84) In addition, graphs showing the trend in E_{corr} for the same coatings contain data, measured at the same time as the available R_p values, and over the same period of time. (Fig. 79, 81, 83)

3.3.1 SermeTel CR984–LT

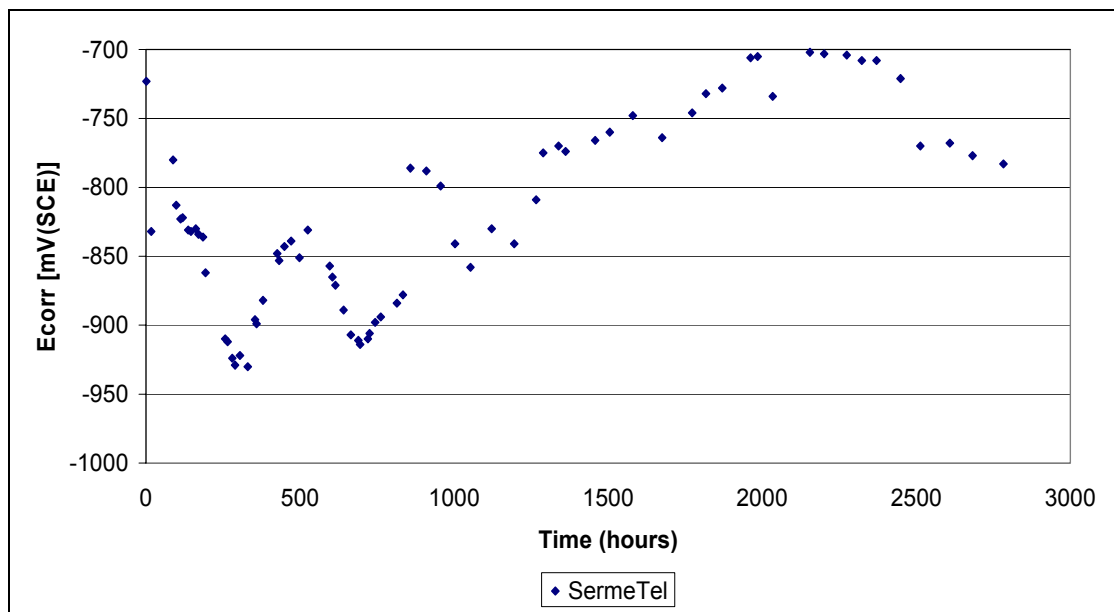


Figure 79. Trend in E_{corr} for the SermeTel coating

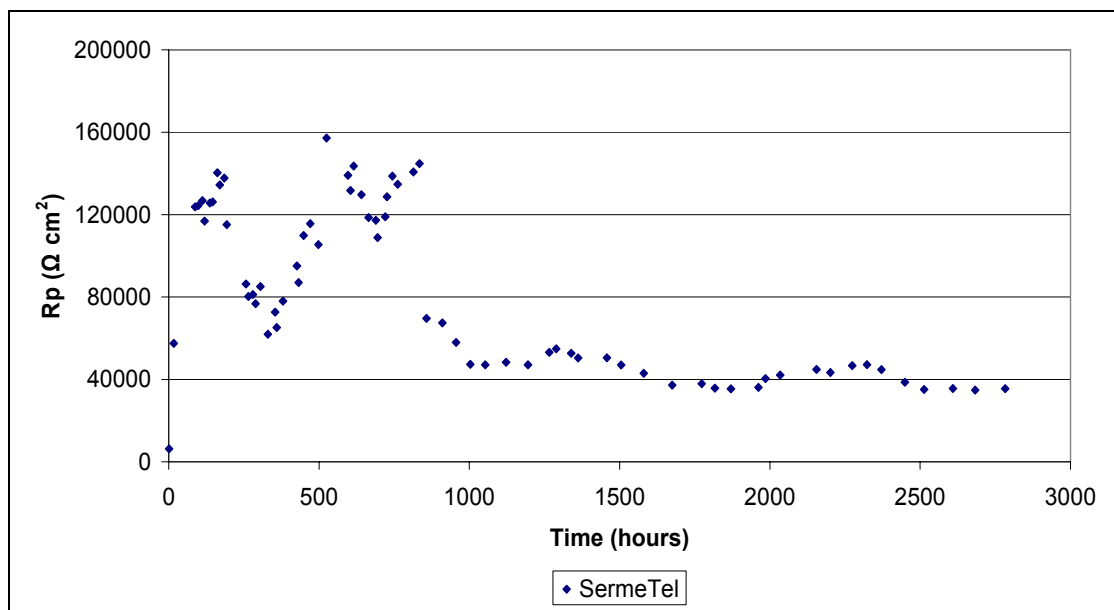


Figure 80. Trend in R_p for the SermeTel coating

As viewed in Figure 79, the corrosion potential of the SermeTel coating started from values in the range between -800 and -700 mV (SCE) and shifted afterwards towards more active values, as corrosion of the aluminium particles in the coating occurred. After 300 hours the trend reversed with the potential moving towards the noble direction due to the formation of an aluminium oxide barrier film. Eventually, it resulted in ranging again between -800 and -700 mV (SCE), as new areas of bare aluminium became exposed and were, in turn, corroded and partially protected by corrosion products. Concerning the morphology of the SermeTel coating, first signs of grey and black spots appeared at 250 hours, which spread throughout the panel by the completion of 600 hours. Afterwards, neither significant change in the panel's appearance was observed nor red rust corrosion products ever appeared.

Figure 80 shows the trend in the polarisation resistance for the SermeTel coating over a period of 3000 hours. It can be viewed that a maximum R_p value of approximately $160,000 \Omega \text{ cm}^2$ was reached for SermeTel after 500 hours of exposure, and hence, the SermeTel self-corrosion rate reached its minimum, as the corrosion of the aluminium particles in the coating surface produced a barrier film of aluminium oxide that reduced the subsequent rate of attack. However, it seems that this barrier layer broke down at a later stage, and consequently, the polarisation resistance decreased and stabilised at the level of approximately $40,000 \Omega \text{ cm}^2$, which corresponds to an increased corrosion rate of 4.8 microns per year for SermeTel.

3.3.2 Galvano–Aluminium Alcotec

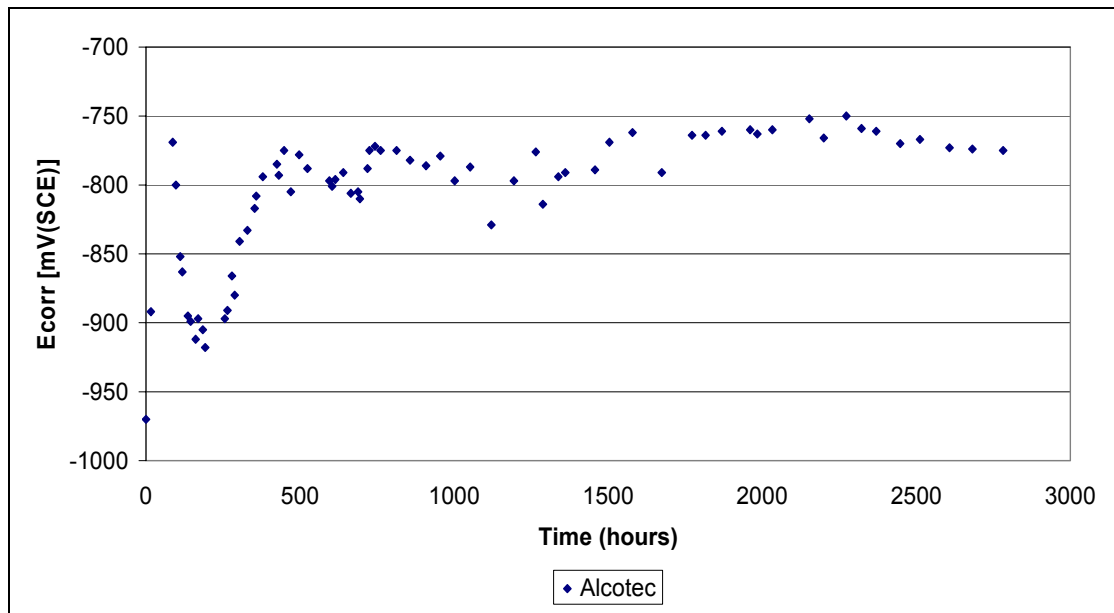


Figure 81. Trend in E_{corr} for the Alcotec coating

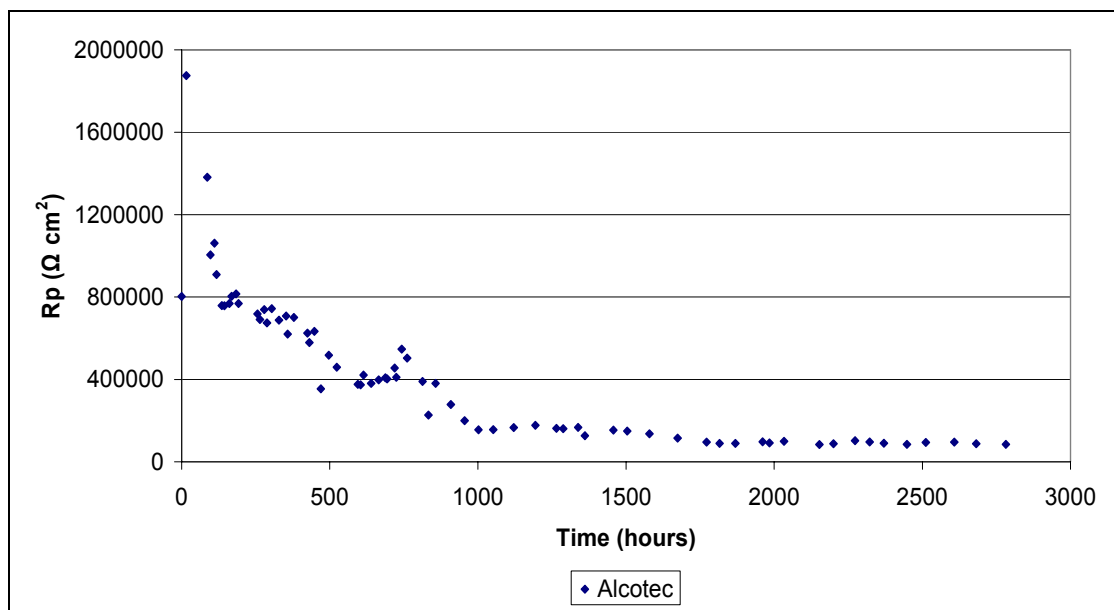


Figure 82. Trend in R_p for the Alcotec coating

Figure 81 depicts the trend in E_{corr} for the Alcotec coating. As seen, the firstly measured potential values for the Alcotec were very negative, but after 200 hours the corrosion potential values started shifting towards the noble direction. After 500 hours the Alcotec corrosion potential was fluctuating within the range between -800 and -750 mV (SCE).

On the same time, as viewed in Figure 82, the initially observed R_p values of nearly $2,000,000 \Omega \text{ cm}^2$ gradually decreased to a level of approximately $100,000 \Omega \text{ cm}^2$. This suggests a 20fold increase of the Alcotec self-corrosion rate, which from the initial value of 0.1 microns per year resulted in 2 microns per year that was still smaller than the eventually observed rate for SermeTel. These changes in polarisation resistance are supported by the observations in the appearance of the Alcotec coating. According to these remarks, Alcotec started losing its Chromium VI passivation treatment colour (yellow) at 200 hours, while by 600 hours the colour was completely lost. Hence, this passive layer breaking down resulted in the R_p drop and the increase of the corrosion rate.

3.3.3 Cadmium

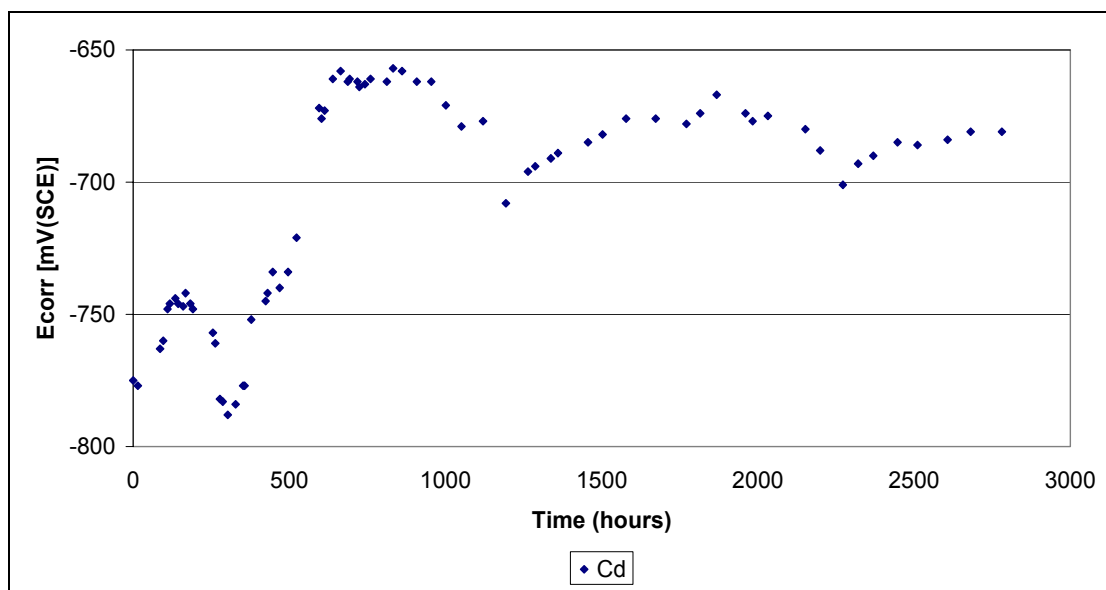


Figure 83. Trend in E_{corr} for Cd

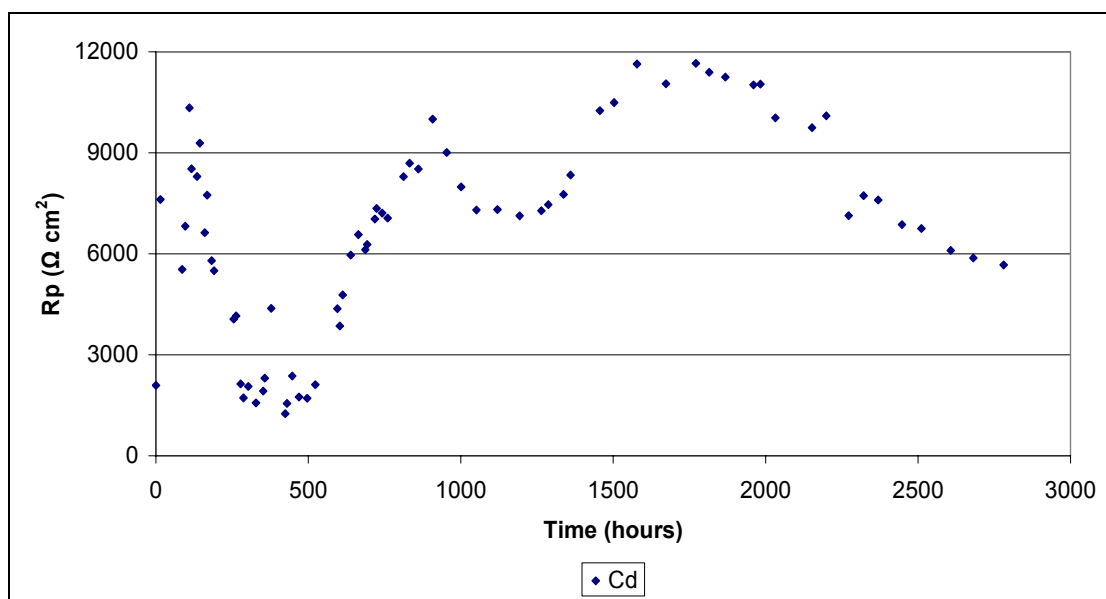


Figure 84. Trend in R_p for Cd

Figure 83 portrays the trend in the corrosion potential for the cadmium coating. Its potential started with values between -800 and -750 mV (SCE) and shifted towards more noble values later, resulting in a fluctuation within the range of -700 to -650 mV (SCE). Concerning the polarisation resistance, depicted in Figure 84, it dropped from the initially observed level of $10,000 \Omega \text{ cm}^2$ to $2,000$ at 500 hours. Afterwards, it increased again to the maximum of $12,000 \Omega \text{ cm}^2$ at $1,500$ hours of exposure. At a later stage, the R_p dropped to the eventually observed level of approximately $6,000 \Omega \text{ cm}^2$ that corresponded to a corrosion rate of 57 microns per year for the cadmium coating. This was a very high corrosion rate, by far higher than in both previously observed cases, and for this reason, it is not coincidental that it was the only case, where red rust corrosion products appeared. First signs of red rust emerged on the boundary of cadmium with Lacomit at 1200 hours, while red rust covered up to 20% of the panel's area after 2000 hours. Afterwards, the area covered by red rust did not expand any more and shortly before the 3000 -hour period the experiment was ceased.

3.4 GALVANIC COUPLING RESULTS

3.4.1 SermeTel CR984-LT

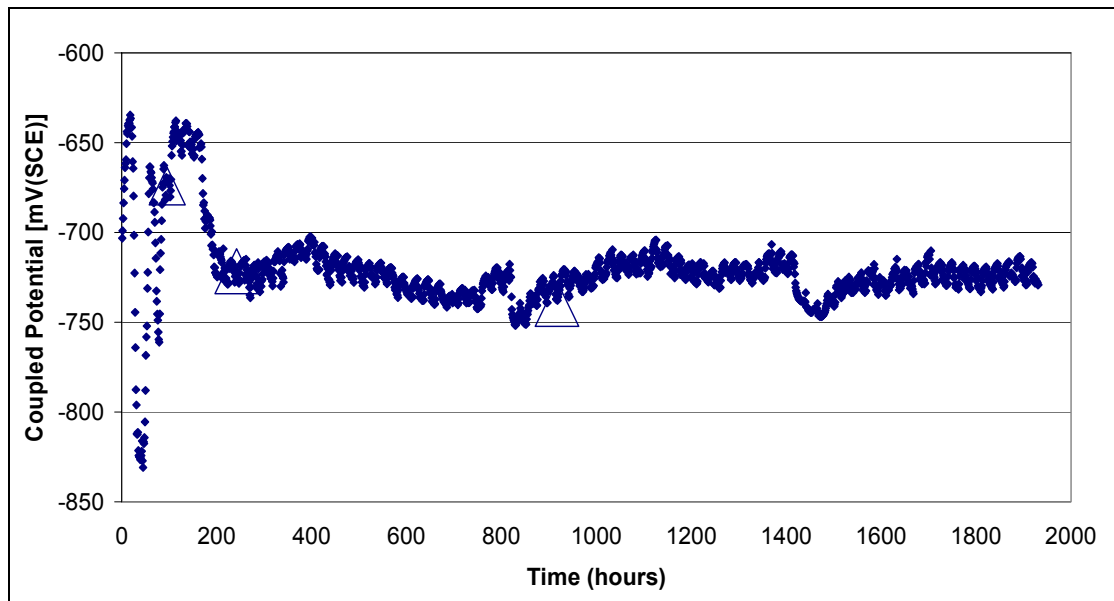


Figure 85. Coupled potential of SermeTel with steel

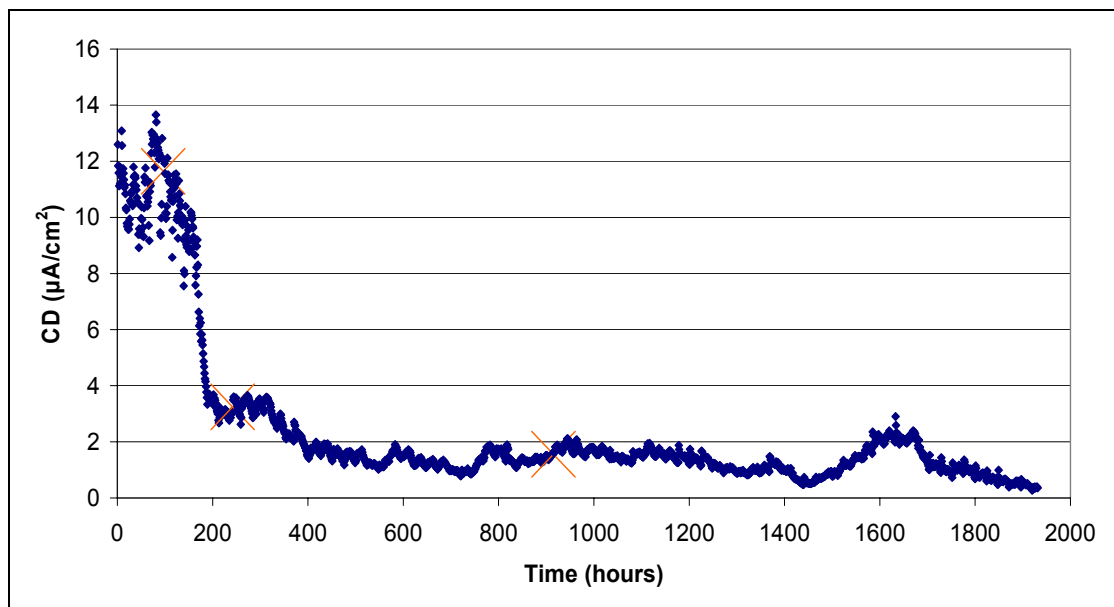


Figure 86. Galvanic current density of SermeTel coupled with steel

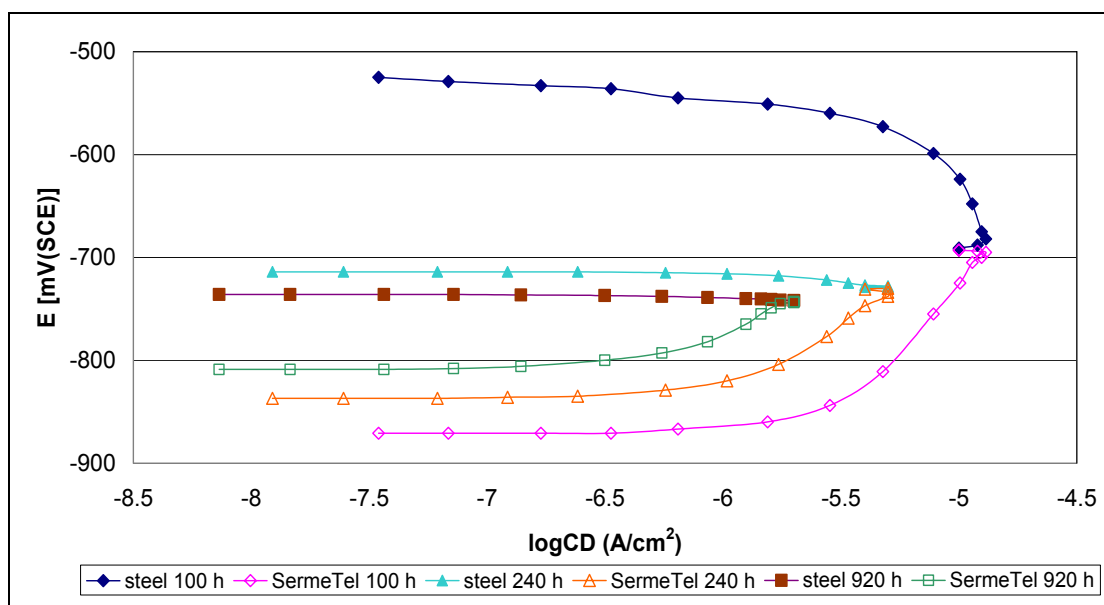


Figure 87. Electrochemical polarisation curves for the couple SermeTel–steel

Figure 85 depicts the trend of the coupled potential of SermeTel with steel. This potential displayed more active values initially, then headed towards the noble direction before eventually ranging between -700 and -750 mV (SCE) after 200 hours of experimentation. Concerning the appearance of both panels of the couple, first signs of red rust appeared on steel after 150 hours, while after 700 hours the steel panel was completely rusty. The SermeTel panel displayed first signs of white corrosion products after 600 hours without any further deterioration of its appearance.

Figure 86 shows the galvanic current density of SermeTel coupled with steel. Its positive value indicates that the SermeTel coating is the sacrificial anode in this couple. As viewed, the initially large current rapidly decayed at round 200 hours before stabilising in the range between 1 and 2 $\mu\text{A}/\text{cm}^2$, which corresponds to a corrosion rate of SermeTel between 10 and 20 μm per year, and an approximately similar corrosion rate for steel. Hence, there was a deceleration of the corrosion rate of SermeTel, which was still theoretically adequate to provide protection to the steel panel. The rate was quite high, but the case of the 1:1 anode/cathode area ratio is a worse case than that expected in service, where a large coating/steel area ratio would exist at a scratch or coating defect.

Figure 87 shows the electrochemical polarisation curves for SermeTel coupled with steel at various times. These times are marked on both graphs of coupled potential and galvanic current density versus time, and it is seen that the points where each pair of curves intersect at each time correspond to the marked coupled potential and current density of the relevant graphs. From the plot of Figure 87, it is concluded that there has initially been a mixed control in the electrochemical phenomenon, which gave place afterwards to more active coupled potential values, smaller current densities and an anodic control, imposed by the dissolution of aluminium particles in the SermeTel coating.

3.4.2 Galvano–Aluminium Alcotec

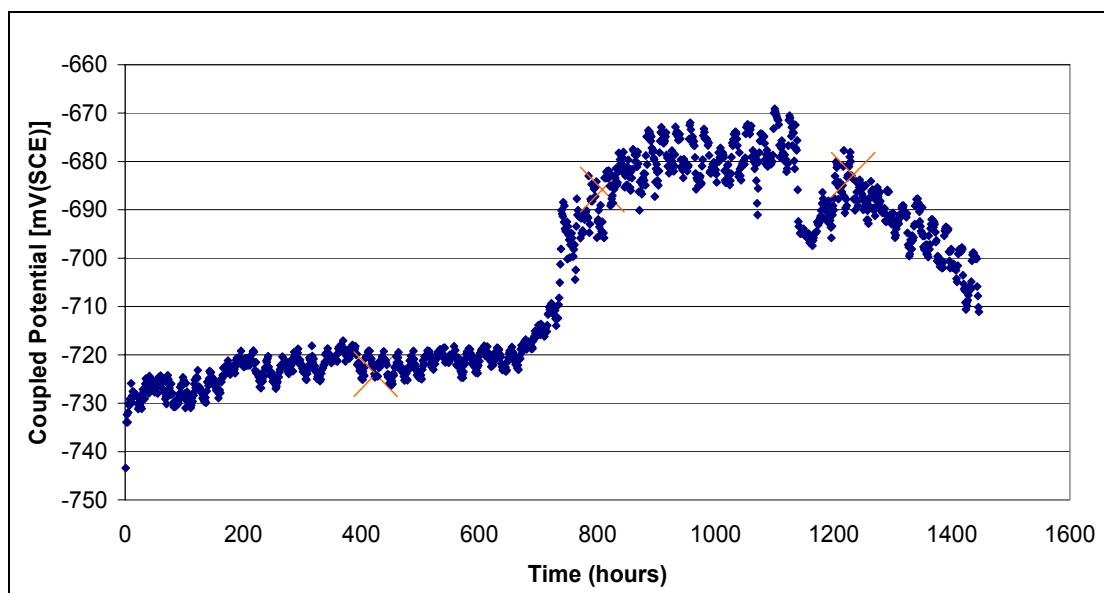


Figure 88. Coupled potential of Alcotec with steel

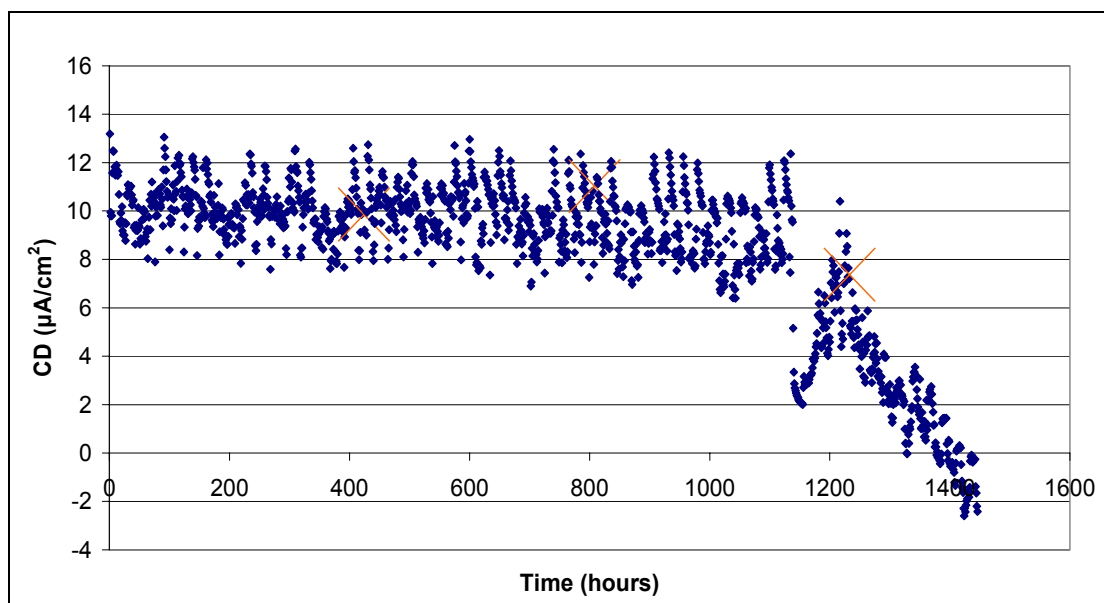


Figure 89. Galvanic current density of Alcotec coupled with steel

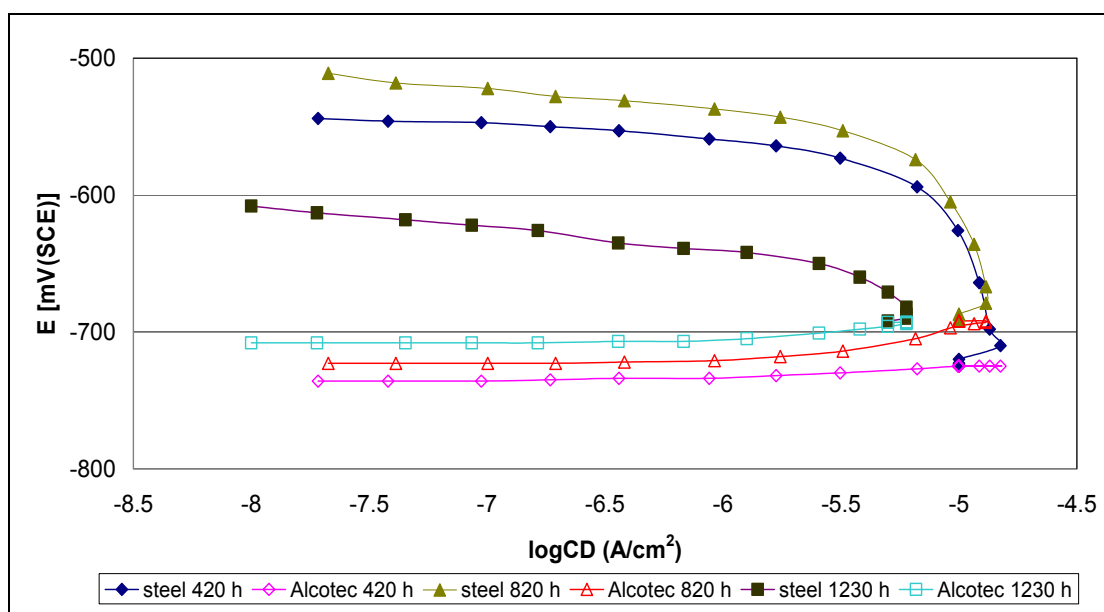


Figure 90. Electrochemical polarisation curves for the couple Alcotec–steel

According to Figure 88, the coupled potential of Alcotec with steel started with values in the range between -730 and -720 mV (SCE). After 700 hours the potential shifted towards more noble values at the level of -680 mV (SCE) before becoming more active again towards the end of the experiment. Concerning the appearance of the panels of this couple, the Alcotec coating started losing its passivation treatment colour at 250 hours, and by the completion of 900 hours the colour had entirely disappeared. At 1000 hours the Alcotec panel was rusty, and at 1200 hours first signs of red rust appeared on the steel panel.

Figure 89 portrays the galvanic current density of Alcotec coupled with steel. Its values were high for a longer period of time compared to the SermeTel–steel couple, as up to 1000 hours the galvanic current density was round $10 \mu\text{A}/\text{cm}^2$, corresponding to a corrosion rate for steel of $103 \mu\text{m}$ per year, and $97 \mu\text{m}$ per year for Alcotec. Previous remarks on SermeTel about such high corrosion rates apply to Alcotec as well. However, the current decreased afterwards, and at 1400 hours it changed direction showing that the sacrificial corrosion protection of steel, provided by the Alcotec coating, ceased. It was then that the steel panel started behaving as the anode and the Alcotec as the cathode, and the experiment was stopped.

Figure 90 demonstrates the electrochemical polarisation curves for Alcotec coupled with steel at various times. As explained earlier for the SermeTel coating, these curves are related to the coupled potential and galvanic current density graphs against time. According to these curves, at all times there is preponderance of a cathodic control on the coupling of Alcotec with steel, as oxygen reduction on steel controls the whole electrochemical phenomenon.

3.4.3 Cadmium

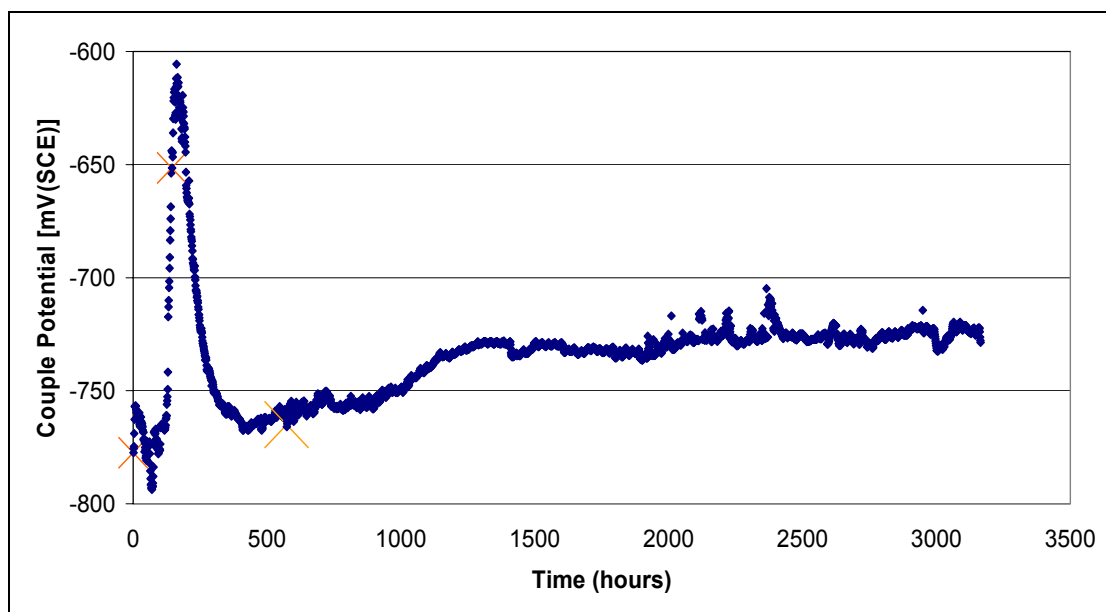


Figure 91. Coupled potential of Cd with steel

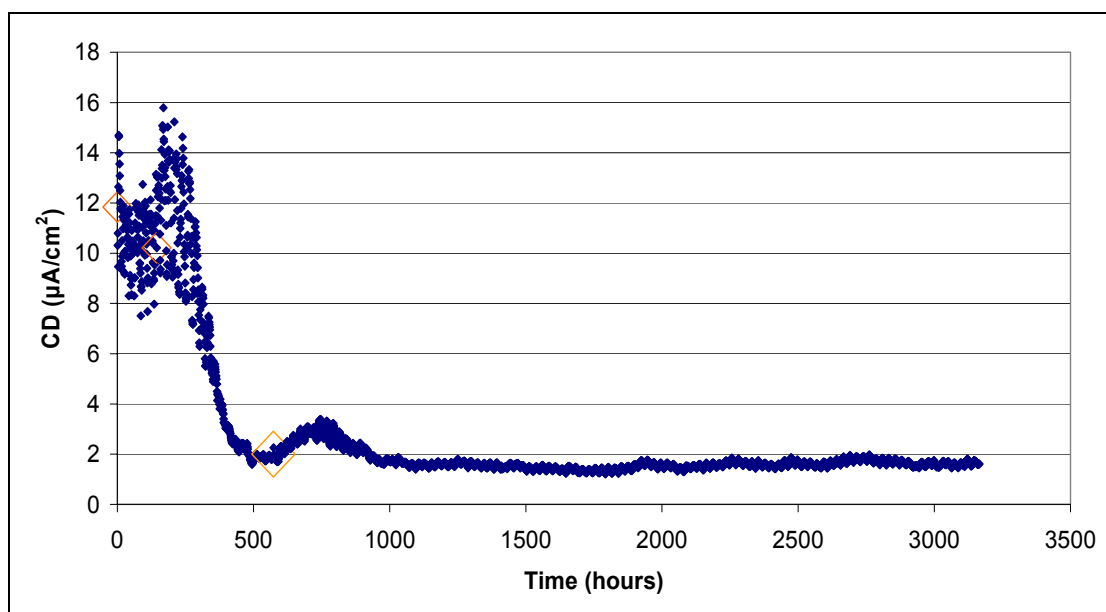


Figure 92. Galvanic current density of Cd coupled with steel

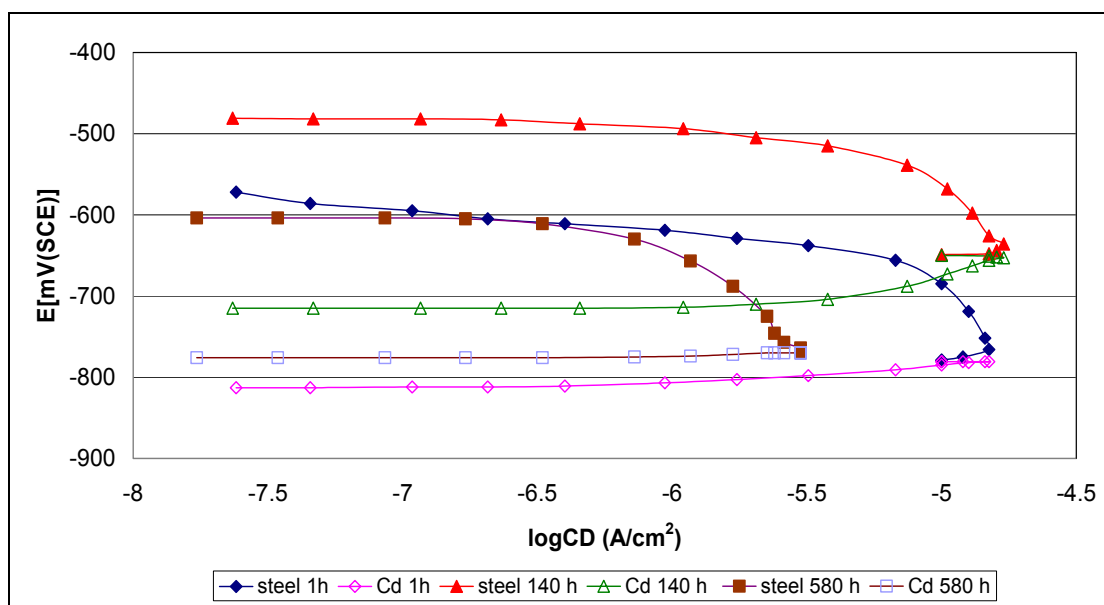


Figure 93. Electrochemical polarisation curves for the couple Cd–steel

Figure 91 shows the potential of the Cd–steel couple against time. As viewed, the coupled potential started at more active values near -800 mV (SCE), headed towards more noble values at -600 mV (SCE), and it eventually stabilised at a level of -730 mV (SCE) after 1000 hours of experimentation. As far as the appearance of the panels of this couple is concerned, no signs of red rust were observed on the steel panel. On the other hand, by the completion of 600 hours the Cd panel was completely rusty.

Figure 92 depicts the trend in the galvanic current density of Cd coupled with steel. Initial large values between 8 and $14 \mu\text{A}/\text{cm}^2$ gave place to smaller current densities of $2 \mu\text{A}/\text{cm}^2$ after 500 hours and for the rest of the experiment. This value corresponds to a corrosion rate of $37 \mu\text{m}/\text{year}$ for Cd and $20 \mu\text{m}/\text{year}$ for steel. Concerning the electrochemical polarisation curves for Cadmium coupled with steel, these are shown in Figure 93 at various times. As seen, the whole phenomenon was proved to be under cathodic control in all cases.

3.5 SALT SPRAY TESTING RESULTS

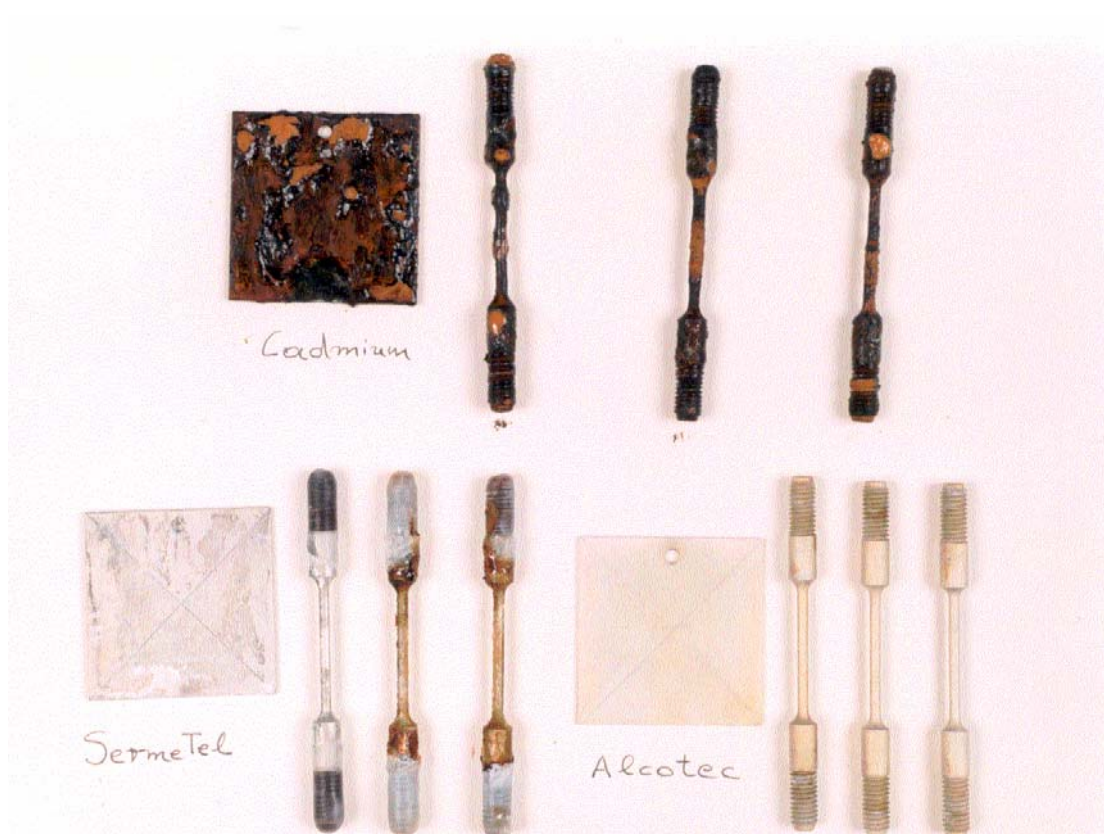


Figure 94. Photograph of coated panels and tensile specimens after 1000 hours of salt spray testing (first case)

Figure 94 shows the tensile specimens and panels, coated with SermeTel, Alcotec and Cadmium, that had submitted salt spray conditions for 1000 hours in a salt fog cabinet according to the ASTM B117-94 standard. The above photograph and the following remarks concern the first performed salt spray test.

Concerning the Cadmium plated steel panel, first signs of red rust appeared at 300 hours of exposure. At 350 hours of testing first signs of red rust appeared on the Cd plated tensile specimens. Both Cd panels and tensile specimens were completely covered by red rust by the completion of 500 hours of experimentation, and by the end of the test their appearance deteriorated even more resulting in that shown in Figure 94.

In terms of the Alcotec plated specimens, after 250 hours of exposure the Alcotec panel lost entirely its characteristic Cr VI passivation treatment colour, and towards the end of the test this occurred also to all the Alcotec plated tensile specimens. However, at the end of the test no signs of corrosion products were detected on any of the tensile specimens and the panel, neither on its surface nor on its scribed marks.

As far as the SermeTel specimens are concerned, two out of three tensile specimens displayed first signs of red rust on their gauge length at 600 hours of testing, while the third one showed no signs of red rust degradation whatsoever, as it can be viewed on Figure 94. Finally, the SermeTel coated panel bears signs of white rust on its surface, but there are no traces of red rust on its scribed marks.

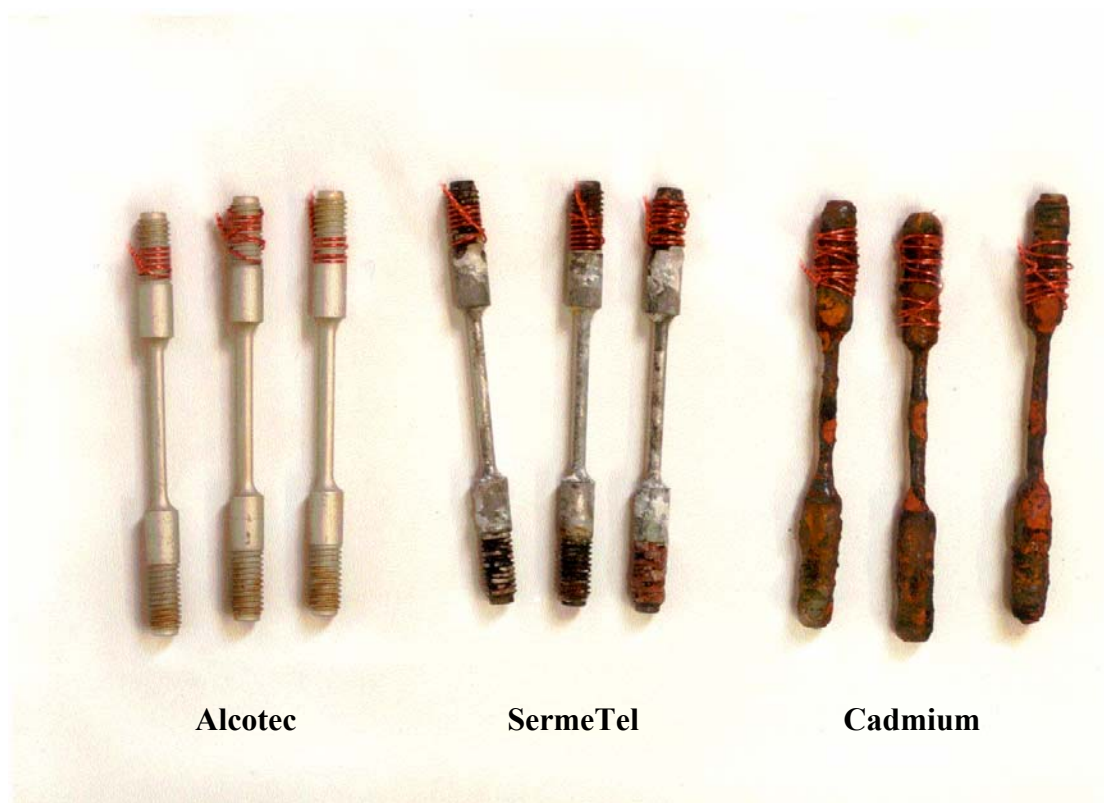


Figure 95. Photograph of coated tensile specimens after 1000 hours of salt spray testing (second case)

Figure 95 portrays coated tensile specimens that had submitted salt spray conditions in a second test. Cd plated tensile specimens showed first signs of red rust after 120 hours, and after 250 hours rust had covered the whole of both their gauge lengths and

their threaded parts. By the end of the test their appearance deteriorated even more. Alcotec tensile specimens started losing their characteristic passivation treatment colour at 250 hours and by the completion of 400 hours they had completely lost it. By the end of the experiments no signs of corrosion degradation ever appeared on Alcotec plated specimens. Finally, SermeTel coated specimens showed first signs of white spots on their gauge length at 250 hours. By the end of the test, no red rust traces had been observed at all, and only white corrosion products were conspicuous, as seen on Figure 95.

3.6 MARINE ATMOSPHERE EXPOSURE TESTING RESULTS



Figure 96. Unscribed coated panels exposed to marine atmosphere for 2 years

Figure 96 shows the appearance of the unscribed coated panels that have been exposed to marine atmosphere in a coastal test site for 2 years. By the completion of 8 months of exposure, the Alcotec coated panels had lost their yellow passivation treatment colour, and the SermeTel panels had shown their first signs of white rust corrosion products. At the end of the experiment no signs of corrosion products were present on the Alcotec and Cadmium panels, while SermeTel panels displayed white corrosion products throughout their surfaces, as well as some red rust covering a very small part of their surfaces.

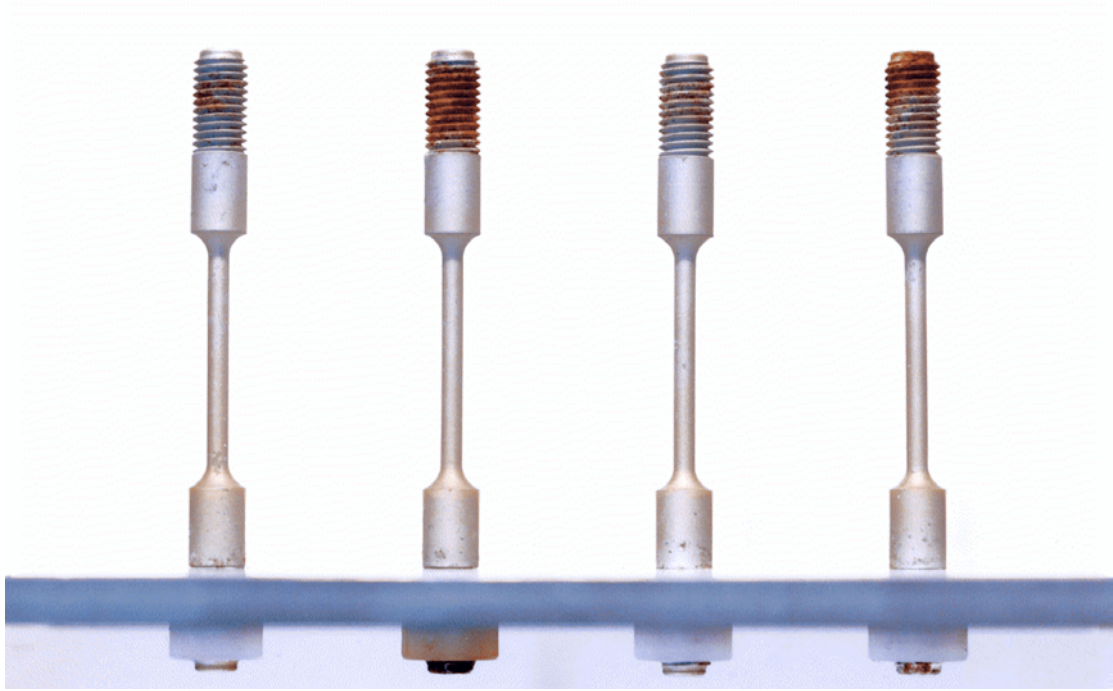


Figure 97. Alcotec coated tensile specimens exposed to marine atmosphere for 2 years

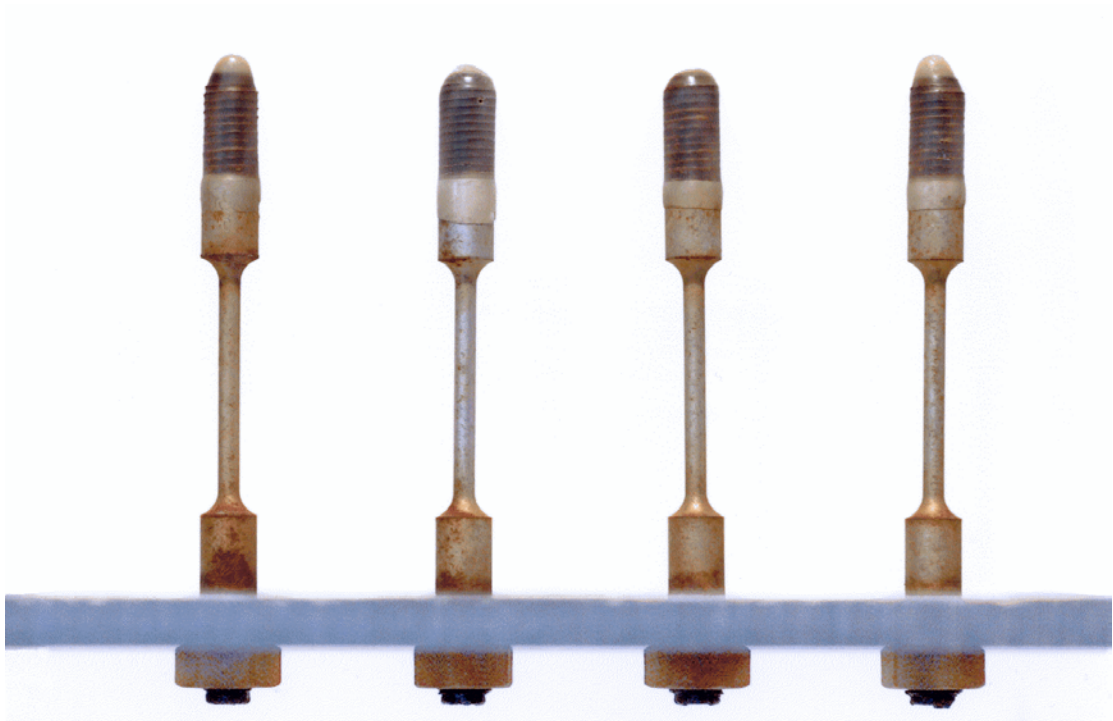


Figure 98. SermeTel coated tensile specimens exposed to marine atmosphere for 2 years

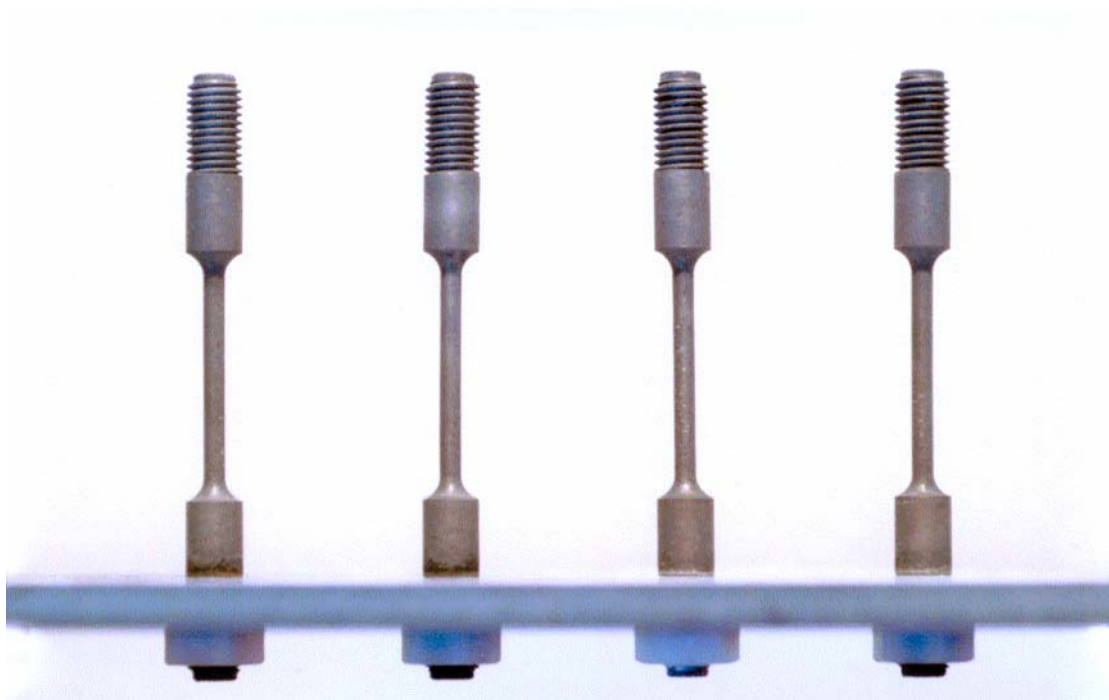


Figure 99. Cd plated tensile specimens exposed to marine atmosphere for 2 years

During the first year of the marine atmosphere testing there were no signs of deterioration for the coated steel tensile specimens. For this reason, the exposure continued for another year, at the end of which the tensile specimens were tested, with their SSRT results presented in the Mechanical Testing Results section. As seen, extremely small amounts of re-embrittlement were observed, and this is further strengthened by the corrosion appearance of these specimens in Figures 97–99. Alcotec specimens had lost their passivation treatment colour at 8 months of testing, as the unscribed Alcotec panels did, but by the end of the tests they did not display any signs of red rust on their gauge length apart from some red rust appearing on some of their threaded parts. SermeTel specimens showed some signs of red rust near and round their gauge length by the completion of the second year of experimentation. Finally, Cadmium plated tensile specimens showed no signs of degradation at the end.

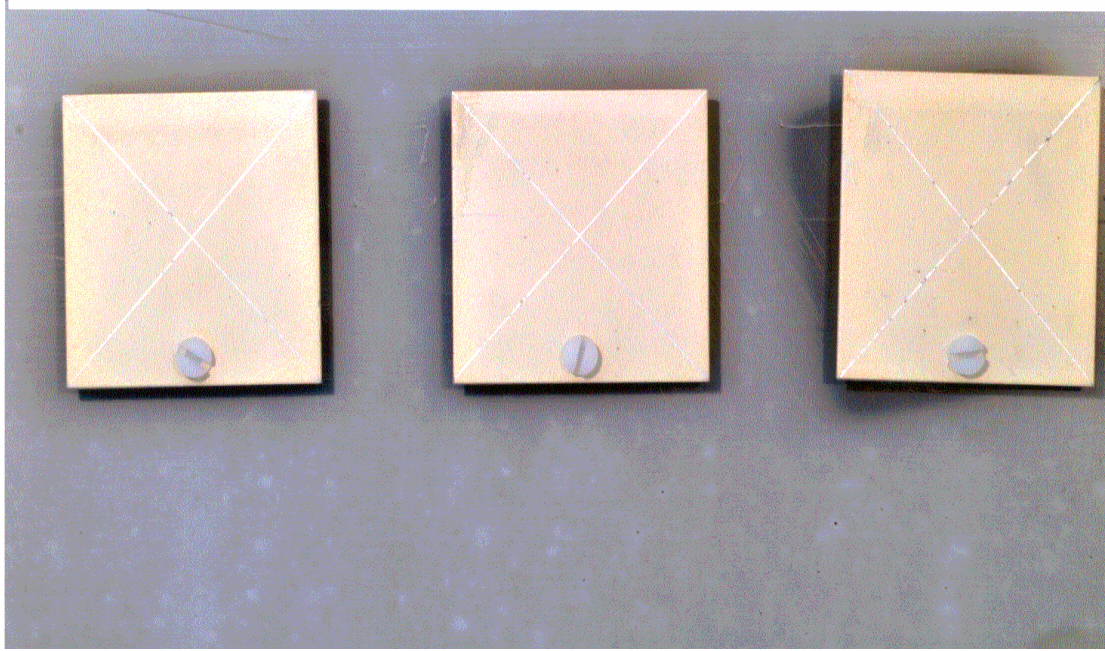


Figure 100. Scribed Alcotec coated panels after 12 months of marine atmosphere exposure



Figure 101. Scribed SermeTel coated panels after 12 months of marine atmosphere exposure



Figure 102. Scribed Cd coated panels after 12 months of marine atmosphere exposure

Figures 100–102 display the appearance of the scribed coated panels that had experienced the marine atmosphere exposure at a coastal test site for 12 months. Alcotec scribed panels did not show any signs of corrosion products, either white or red rust, neither on their scribed marks nor on their surfaces. Moreover, they preserved their passivation treatment colour. On the other hand, all SermeTel scribed panels displayed some signs of red rust on their scribe marks, with two out of three showing more corrosion products of this type than the third one. Moreover, in all SermeTel panels' surfaces appeared white rust corrosion products. Finally, Cd scribed panels did not display any signs of corrosion degradation either on their surfaces or on their scribed marks.