Electrochemical Behaviour of Low Carbon Steel in Aqueous Solutions

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ABSTRACT - *An effective way of assessing corrosion in pipelines before serious consequences occur is to use tools that can predict the future of a pipeline through an understanding of its present state and the mechanisms of corrosion. In this work electrochemical methods such as liner and tafel polarization resistance were used to evaluate corrosion. Most metal corrosion occurs via electrochemical reactions at the interface between the metal and an electrolyte solution and, therefore, since corrosion occurs via electrochemical reactions, electrochemical techniques are ideal for the study of the corrosion processes. This particular study has examined the corrosion that occurred in different grades of low carbon steels with particular aggressive solutions. Corrosion rate measurements were obtained using different aqueous environments such as a plain sodium chloride solution, a sodium chloride and carbon dioxide solution, and a sodium chloride and sulphuric acid solution that also contained a small amount of carbon dioxide. The corrosion morphology was examined using a scanning electron microscopy (SEM) in which the surfaces examined showed general corrosive attack with some shallow pits.*

1. INTRODUCTION

The metallurgy of pipelines, vessels, etc in oil and gas-producing systems is usually based on carbon steel. This is because carbon steel has good mechanical properties and is also relatively cost effective. However, carbon steel is strongly susceptible to corrosion attack from the dissolved gases (CO_2 and H_2S) that are present in the produced fluids. As such, the presence of the two acid gases carbon dioxide CO_2 and hydrogen sulphide H_2S with partial pressures and condensed water chemistry [1], the corrosivity of the material is generally caused to increase. A quantative understanding of the corrosion rate of steel under these conditions will be a key factor in providing an accurate risk assessment of the attack of pipelines by internal corrosion.

Corrosion in gas gathering and transmission pipelines has been reported in the presence of H_2S and CO_2 in the gas and high chloride concentrations or sulphur/polysulfide sludge from the formation water [2-3]. The earliest studies of the combined effects of CO_2 and H_2S were carried out by Greco and Wright and Sardico, et al. [4] who found that a protective sulphide film formed at concentrations of H_2S <1,700 ppm, which corresponds to a gas pressure of <0.1

psi. At higher concentrations, a non-protective sulphide film was reported. In their work It was observed that small concentrations of H_2S (0.02 mole or 0.0065 psi) decreased the corrosion rate of steel at 70°C and 80°C in a 1M sodium chloride solution with 10 psi CO_2 [5-8]. However, it was noticed that pitting occurred in these solutions, possibly caused by selective dissolution of the ferrite phase. At higher H_2S concentrations (0.002 psi to 0.0082 psi), considerable scatter in corrosion rate results was observed, with the corrosion rate generally increasing with H_2S concentration [4].

Certain corrosion phenomena show maximum severity at ambient temperature. In particular, this is true for all the damage mechanisms involving hydrogen cracking: sulphide stress cracking (SSC), stepwise cracking (SWC) and stress oriented hydrogen induced cracking (SOHIC). However, today's problems often concern traces of H_2S at partial pressure <1 atm [1]. Furthermore, CO_2 acts largely via its effect on pH, which readily can be measured or calculated at low temperatures. The objective of the research presented in this paper is to measure the corrosion rate for five types of normal carbon steel in three different aqueous solutions which were (a) plain sodium Chloride (sea water), a second solution of sodium chloride with added carbon dioxide gas, and a third solution of sodium chloride with added sulphuric acid and a small amount of carbon dioxide. This study involved linear polarization resistance (LPR) and analytical techniques scanning electron microscopy (SEM).

2. EXPERIMENTAL PROCEDURE

Electrochemical polarization tests were accomplished using a computer controlled potentiostat. The potentiostat was programmed to apply a continuously varying potential to the sample at a scan rate of 0.5mV/s. The potentiostatic technique is performed by plotting the resulting current density against the applied potential.

Linear polarization resistance (LPR) measurements have been used to assess the corrosion behaviour of the various steel specimens in the various solutions, the first solution containing only sodium chloride at a concentration of 4.5% by weight. The second solution used contained the same

level of sodium chloride but with the addition of carbon dioxide gas. Finally, the third also contains the same level of sodium chloride but with an addition of sulphuric acid H_2SO_4. The LPR measurements were used to draw curves that supply information on the susceptibility of the steels to different types of corrosion, specifically to pitting corrosion.

The experiments were performed using cylindrical specimens of normal carbon steel, such as 070-M20, 080-M40, 070-M55, API 5L Gr. A/B and A106 Gr. A/B; the composition specifications for these steels is shown in Table below. It should be noted that there was little difference in these steels in respect of their silicon, sulphur phosphorus contents but there were differences in respect to their carbon contents. The specimens required were machined into different sizes and this was due to the material availability. The cylindrical bars used for 070-M20, 080-M40 and 070-M55 were machined from the stock into bars 12 mm in diameter by 20 mm in length. The other two specimens API 5L Gr. A/B and A106 Gr. A/B were machined out of stock consisting of tubular pipes 8" in diameter, schedule 80. In these cases the specimens were narrower but longer at 6mm diameter by 50 mm in length.

Each sample was prepared with No80 Emery paper so that conditions prior to exposure were the same for each steel sample; at the same time accurate dimension measurements were taken to determine the exposed surface area. Nitrogen purging of the apparatus was used prior to each experiment and the tests were carried out in a corrosion cell.

The specimens used in the polarisation scans were carefully examined using optical microscopy at a magnification of x 500 in each case and the results are shown in Figs. 6.

3. EXPERIMENTAL RESULTS

The various corrosion rates were determined by the linear polarization resistance (LPR) method i.e. through Tafel calculations and the results obtained are shown in Table 2. Also, polarisation curves were obtained and these are shown in Fig. 1 using the three solutions described earlier in the Introduction.

Steel	C	Mn	P	S	Si
070-M20	0.16-0.24	0.50-0.90	0-0.05	0-0.05	0.10
080-M40	0.36-0.44	0.60-1.0	0-0.05	0-0.05	0.10-0.40
070-M55	0.50-0.60	0.50-0.90	0-0.05	0-0.05	0.10-0.40
A 106 Gr A/B	0.25- 0.30	0.27~0.98/0.29~1.06	0-0.025	0-0.025	-
API 5L Gr A/B	0.21-0.27	0.90/1.15	0-0.04	0-0.05	-

Table 1- Specimens chemical composition specifications

Results Obtained	Specimens				
	070-M20	080-M40	070-M55	A106 Gr A/B	API5L Gr A/B
NaCl					
Corrosion rate	2.620 mpy	0.938 mpy	1.108 mpy	2.815 mpy	2.442 mpy
Weight reduction	0.0788 g	0.0481 g	0.0206 g	0.0798 g	0.0701 g
NaCl+CO$_2$					
Corrosion rate	12.62 mpy	85.47 mpy	95.36 mpy	13.34 mpy	11.98 mpy
Weight reduction	0.1403 g	0.4568 g	0.4347 g	0.1520 g	0.0985 g
NaCl+CO$_2$+H$_2$SO$_4$					
Corrosion rate	150.7 mpy	196.1 mpy	266 mpy	178.3 mpy	163.3 mpy
Weight reduction	0.6791 g	0.7829 g	0.8216 g	0.6895 g	0.6883 g

Table 2- Effects of NaCl, CO_2 and H_2SO_4 on corrosion rates and weight reductions
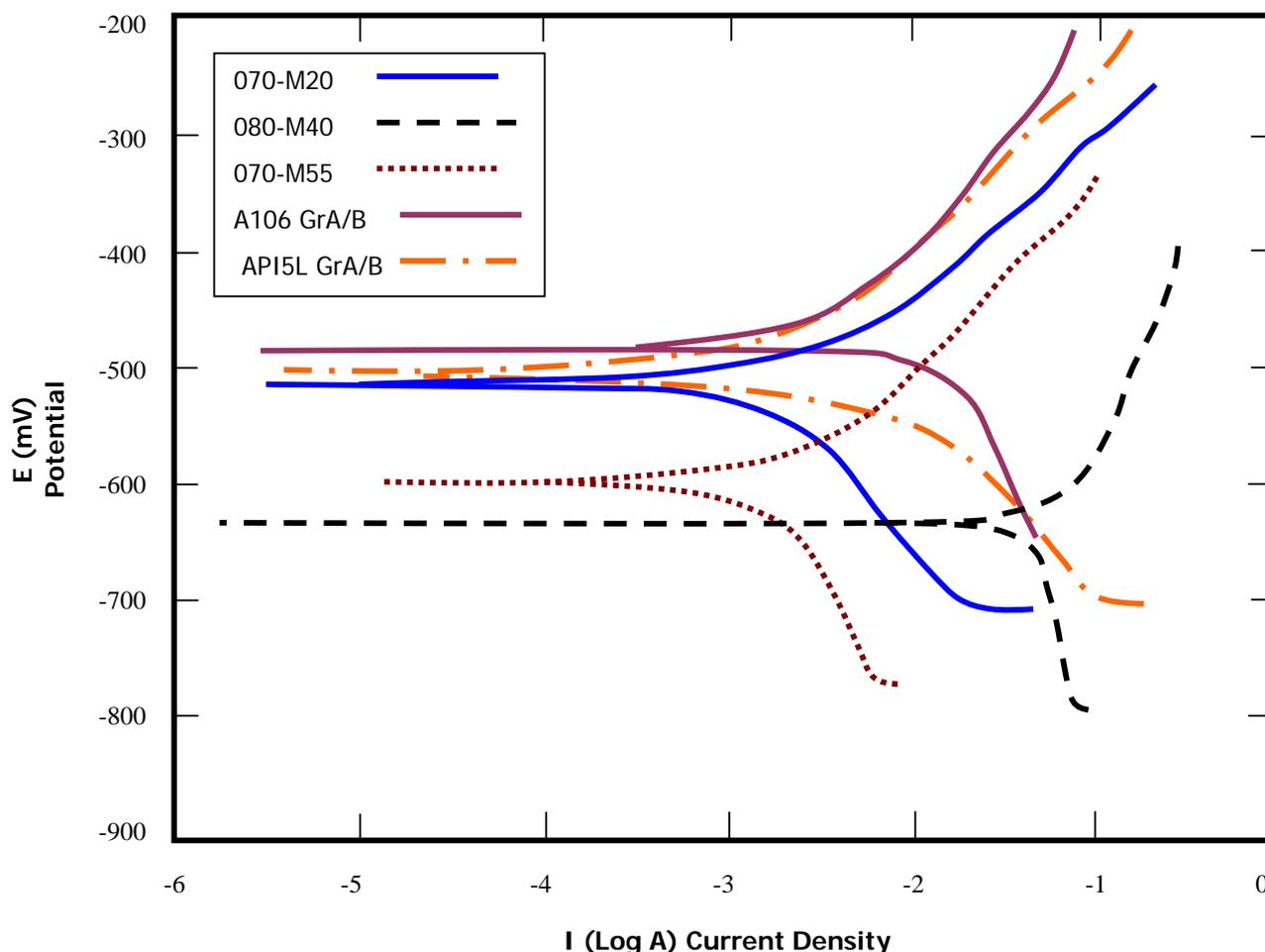
Figure -1 Anodic Polarization Curves of mild steel in NaCl, CO_2 and H_2SO_4 solution

The polarisation curves obtain from the experiment results for the steels in aqueous NaCl, H_2SO_4 and purged CO_2 gas solutions are illustrated in Fig. 1. Although the curves are again very similar for the weight reduction in Table 2, they still show quite significant differences. For example, the lower carbon steel material 070-M20, A106 and API5L showed high corrosion rates from 2.442 to 2.815 mpy in NaCl 4.5% respectively whereas for the rest of the materials, such as 080-M40 and 070-M55, the corrosion rates take place from 0.938 mpy to 1.108 mpy (refer to Fig. 2 for more details). In the case of the second aqueous solution, namely sodium chloride and carbon dioxide CO_2 gas, the corrosion rates were found to be quite low for the low carbon steels but with higher corrosion rates for the medium and high carbon content steels (refer to Table 2 and to Fig. 3). Finally, for the third aqueous solution which consists of sodium chloride, sulphuric acid and purged CO_2 gas the highest corrosion rates 266 mpy was obtained from high carbon content specimen 070-M55, then the second corrosion rate 196.1 mpy was obtained from the medium carbon content steel 080-M40. The low carbon content steels such as 070-M20, A106 and API5L gave results with the corrosion rates ranging from 150.7 mpy to 178.3 mpy respectively (refer to Fig. 4).

On the other hand, the weight reduction measurements showed quite significant results from the three main aqueous solutions used (refer to Fig. 5). For the first solution, plain sodium chloride, the low carbon content steels such as 070-M20, A106 and API5L showed higher weight reductions from 0.0701 g to 0.0788 g than the medium and high carbon content (080-M40 and 070-M55) which gave values of 0.0206g to 0.0481 respectively. The second solution, sodium chloride and carbon dioxide gas, the medium and high carbon content showed higher weight reductions of 0.4568g and 0.4347g. However, the low carbon content specimens in the same solution showed a weight reduction from 0.0985g to 0.1403g respectively. For the third solution, namely sodium chloride, sulphuric acid and purged CO_2 gas, the medium and high carbon content steels, such as 080-M40 and 070-M55, showed weight reductions of 0.7829g and 0.8216g. The low carbon content steel specimens, such as 070-M20, A106 and API5L, showed values of weight reduction from 0.6791g to 0.6883g respectively.
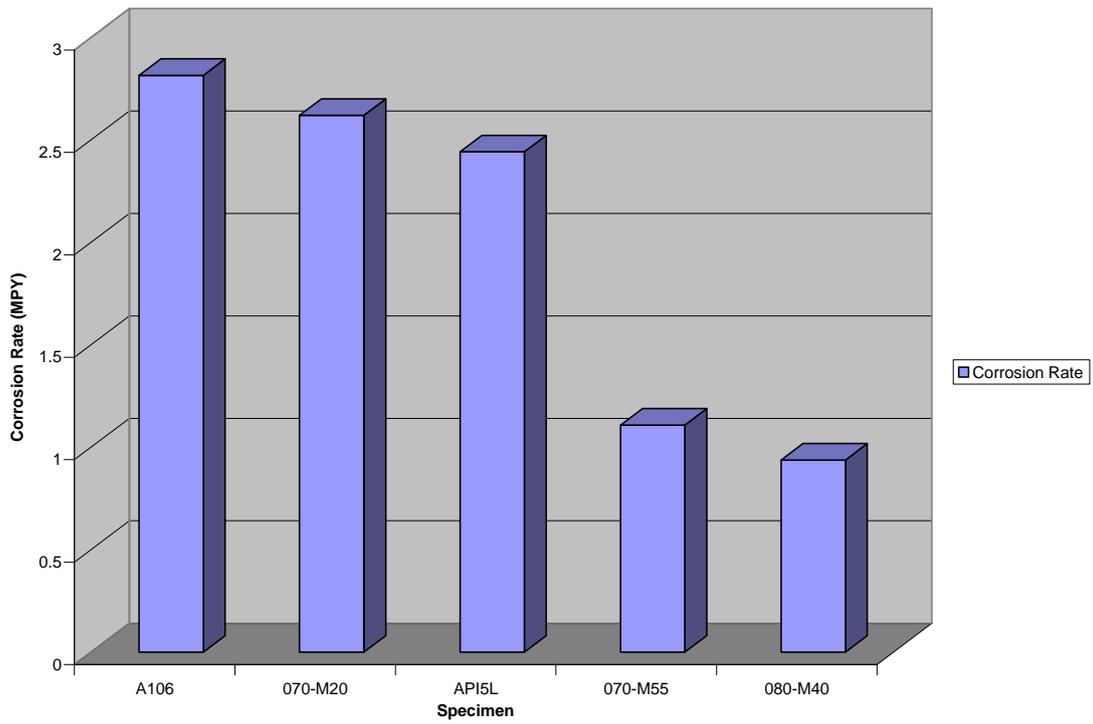
Figure 2 – Effect of NaCl solution on corrosion rate
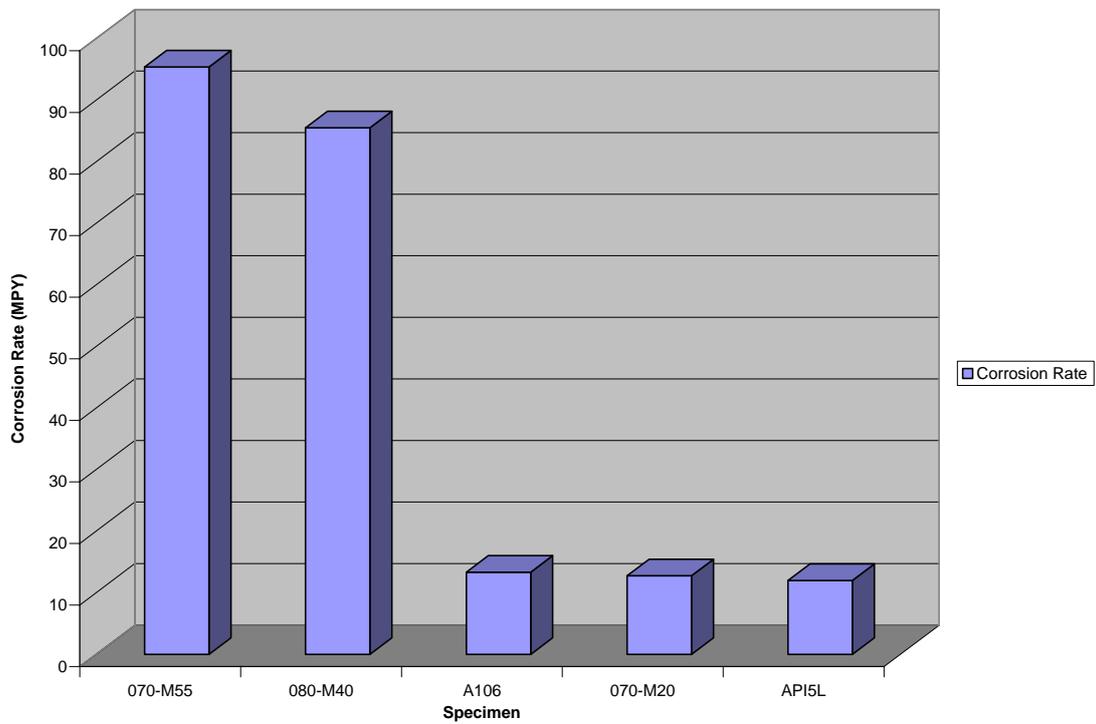
Figure 3 – Effect of the NaCl and CO_2 solution on corrosion rate
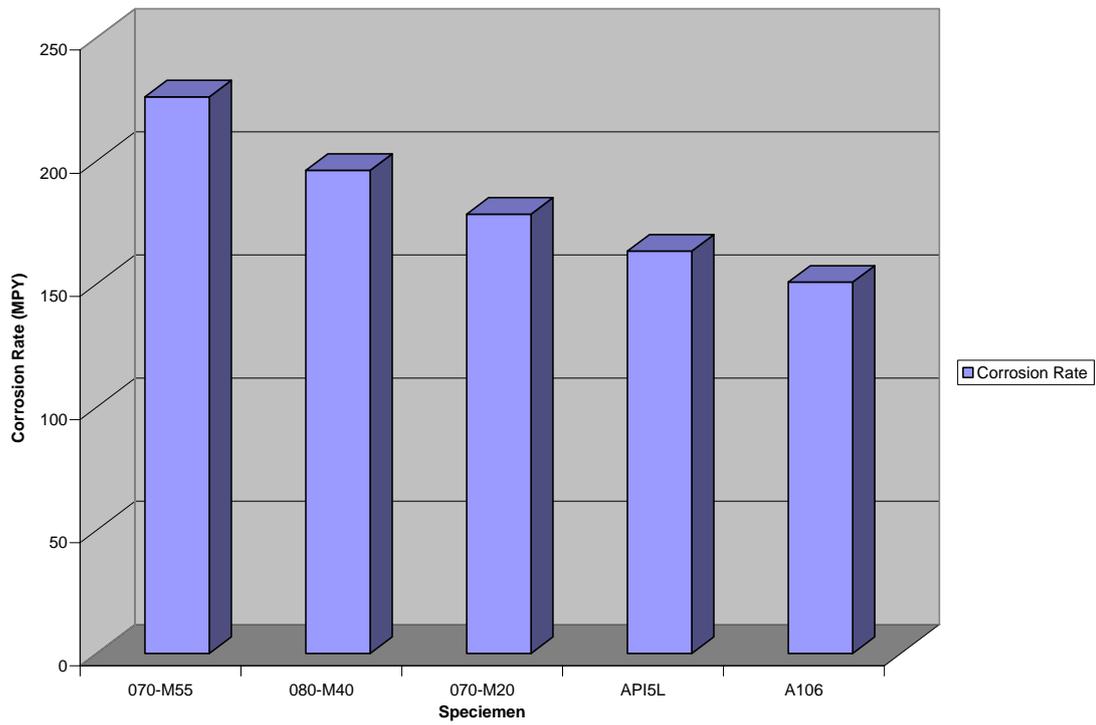
Figure 4 – Effect of the NaCl and H_2SO_4 solution on corrosion rate
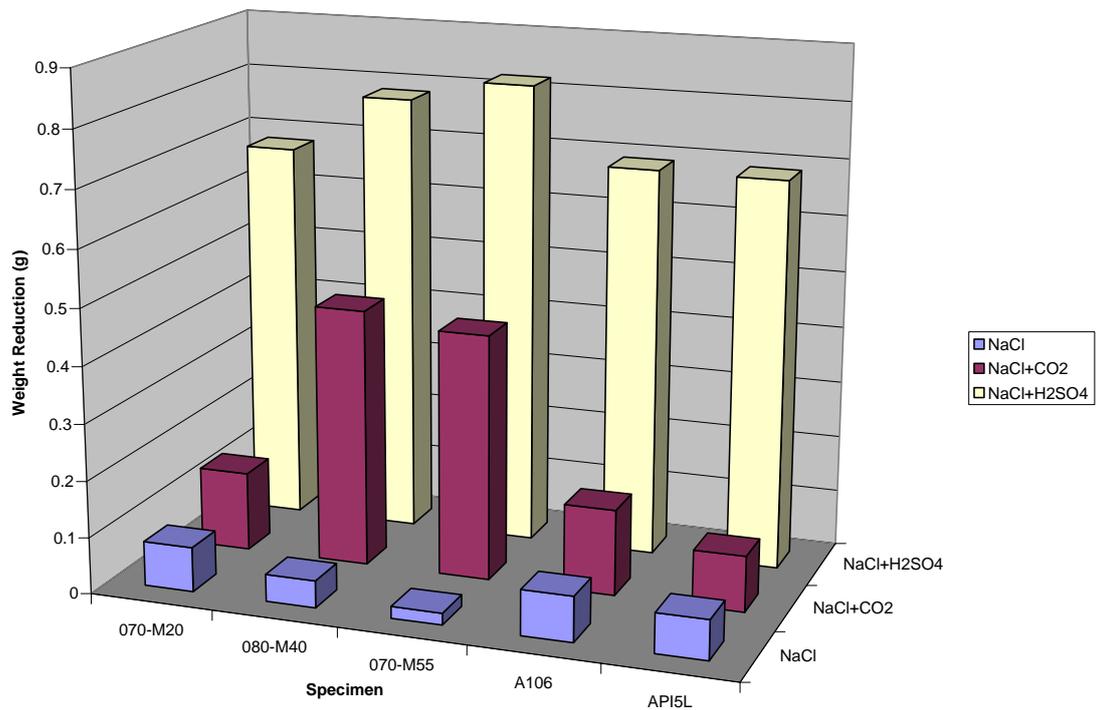
Figure 5 – Effect of NaCl, CO_2 and H_2SO_4 solution on weight reduction

| A106 | API5L | 070-M20 | 080-M40 | 070-M55 |
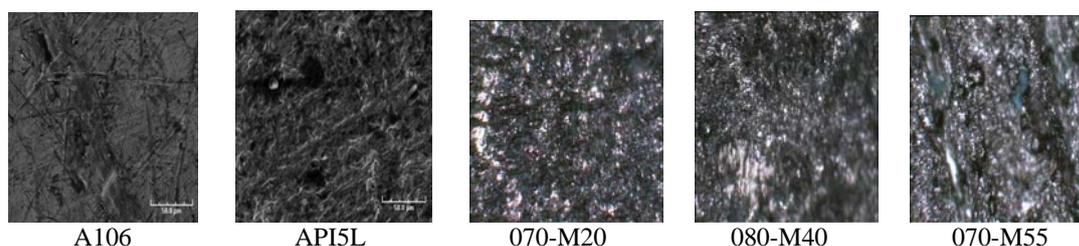
Figure 6 – SEM of the carbon steel specimen in NaCl, CO_2 and H_2SO_4

Corrosion morphology was examined using scanning electron microscopy (SEM) at a magnification of x 500 in each case in which the surface showed with uniform attack with some shallow pits with general corrosion (refer to Figs. 6).

4. CONCLUSIONS

The main conclusion to be drawn from these results is that the carbon contents of the steels used played a part in the corrosion process, especially in the acidic solutions (solutions 2 and 3). The mechanism involved in this effect is not clear at this time but one possibility is the setting up of an electrolytic cell in the surface of the steels exposed to the solution where the carbon contents become significant. One hypothesis would be that the electrolytic cell arose between the ferrite phase and the iron carbide particles with the anode in the cell becoming the Fe_3C. It is well known that the proportion of Fe_3C steadily increases as the carbon content rises and, hence, the higher carbon steels will inevitably offer a greater micro-area of the constituent to the solution during the experiment. However, the results in the plain NaCl solution were the opposite of those in solutions 2 and 3 with the low carbon steels performing badly, presumably because the electrolytic cells were not set up in this environment and other, unknown, factors applied.

The work is continuing and it is hoped that the experiments will be repeated with more varieties of steel, particularly with some medium-carbon steels with, say, 0.5% C or thereabouts, and some with very low carbon contents, such as BOS process steels that typically have only 0.07 – 0.09%C. Also, other varieties of steel could be used such as the typical low alloy C-Mo types to see how they perform in relation to these results.

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