Technical Report

Electrochemical Corrosion Resistance Evaluation of Ferritic Stainless Steel in HCl

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Corrosion resistance behaviour of S43903 ferritic stainless steel was evaluated in different hydrochloric acid and the acid chloride concentrations. The experiments were performed at ambient temperature using potentiodynamic polarization measurement. This paper reports the observed electrochemical response of the experimental tests. Different concentrations of the test media were used with sodium chloride addition. Tafel and polarization resistance techniques were used to estimate the corrosion rate and the polarisation resistance of the alloy samples tested. The results obtained showed some magnitude of corrosion susceptibility for the stainless steel at higher HCl concentrations and also in the acid chloride test media.
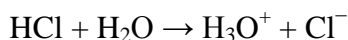
1. INTRODUCTION

Stainless steel is the name given to a family of corrosion and heat resistant steels containing a minimum of 10.5% chromium. Just as there is a range of structural and engineering carbon steels meeting different requirements of strength, weldability and toughness, so there is a wide range of stainless steels with progressively higher levels of corrosion resistance and strength. These result from the controlled addition of alloying elements, each offering specific attributes in respect of strength and ability to resist different environments. The available grades of stainless steel can be classified into five basic families: ferritic, martensitic, austenitic, duplex and precipitation hardenable. A lot of research studies in corrosion and protection had been done [1-8] and are still being done on these groups of metallic alloys because of their use in all important facets of engineering infrastructural, production and manufacturing processes.

Ferritic stainless steels have a "body-centred-cubic" (bcc) crystal structure, which is the same as pure iron at room temperature. The main alloying element is chromium, with contents typically between 11 and 17%, although a higher chromium content of about 29% is found in one specialised grade. Carbon is kept low which results in these steels having limited strength. They are not hardenable by heat treatment and have annealed yield strengths in the range of 275 to 350 MPa.

Ferritic grades have been developed to provide a group of stainless steel to resist corrosion and oxidation, while being highly resistant to stress corrosion cracking. These steels are magnetic but cannot be hardened or strengthened by heat treatment. They can be cold worked and softene.id by annealing. As a group, they are more corrosive resistant than the martensitic grades, but generally inferior to the austenitic grades. Like martensitic grades, these are straight chromium steels with no nickel. They are used for decorative trim, sinks, and automotive applications, particularly exhaust systems.

Ferritic grades offer a wide range of corrosion resistance properties from non-severe conditions inside the home to rough outdoor conditions. At the high-end, ferritics surpass even some austenitic grades in corrosion resistance [9-11]. It must be noted, however, that the corrosion resistance of stainless steel is determined more by chemical composition than by austenitic or ferritic atomic structure. These grades can be used in atmospheric environments of widely varied corrosive severity. The nickel-free ferritic grades have excellent resistances to chloride induced stress corrosion cracking. The molybdenum-alloyed ferritic steels, e.g. 4521, have largely the same corrosion resistance as 4401 / 4404 but are superior to most austenitic steels in terms of their resistance to stress corrosion cracking. The ferritics, including the superferritics, group of stainless steel alloys had generated increased research interest, particularly in the recent time [12-16].

Hydrochloric acid, the test medium in this work, is a highly corrosive, strong mineral acid with many industrial uses. Hydrogen chloride (HCl) is a monoprotic acid, which means it can dissociate (*i.e.,* ionize) only once to give up one H^+ ion (a single proton). In aqueous hydrochloric acid, the H^+ joins a water molecule to form a hydronium ion, H_3O^+ [17-18].

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

The other ion formed is Cl^-, the chloride ion. Hydrochloric acid is a strong acid, since it is essentially completely dissociated in water [17-18]. It is the most difficult of the common acids to handle from the standpoints of corrosion and materials of construction. This acid is very corrosive to most of the common metals and alloys [7]. Hydrochloric acid is used in many industrial processes such as pickling of steel; production of organic and inorganic compounds, pH control and neutralization, and regeneration of ion exchangers. Hydrochloric acid is used for a large number of small-scale applications, such as leather processing, purification of common salt, household cleaning and building construction [19]. Oil production may be stimulated by injecting hydrochloric acid into the rock formation of an oil well, dissolving a portion of the rock, and creating a large-pore structure. Oil well acidizing is a common process in the North Sea oil production industry [20].

This work looks at the corrosion resistance reactions phenomena of S43903 ferritic stainless steel in varied concentrations of HCl. The acid test media were further contaminated with sodium

chloride (NaCl) at all the concentrations of HCl used to further enhance the breakdown of passivity by the chloride ions. The work aims at evaluating the corrosion resistance of the stainless steel at different concentrations of the acid and the acid-chloride test media. It also aims at determining its viable usefulness in this likely industrial and work environments particularly with respect to materials selection.

2. EXPERIMENTAL METHOD

Ferritic stainless steel, – S43903 samples in plate form (10mm wide and 10mm long) used for this investigation were mounted in araldite resin and connected with a flexible wire connection, ground and polished to fine diamond (1μm), cleaned and rinsed/degreased in an ultrasonic bath using acetone. The samples were immediately kept in a desiccator for subsequent corrosion experimental studies. Potentiostatic polarisation experiments were performed using each of the flat plate specimens in turns, in which 1 cm^2 surface area of the specimen was exposed to the test solution at room temperature. The experiments were performed using a polarisation cell of three – electrode system consisting of a reference electrode (silver chloride electrode– SCE), a working electrode (WE); and two carbon rod counter electrodes (CE). The potentiodynamic studies were made at a scan rate of 0.00166V/s from -1.5 to +1.5V and the corrosion currents were recorded. The experiments were conducted in four different concentrations of hydrochloric acid (HCl) and the acid contaminated with 3.5% sodium chloride, Table 1. The chemicals used: sodium chloride (NaCl) and hydrochloric acid (HCl) were prepared from analytic reagent grade (AR).

Table 1. Test Environments

Hydrochloric acid, HCl	HCl + 35 g/L NaCl (3.5%)
4 M	4 M
2.5 M	2.5 M
1.5 M	1.5M
1.0 M	1.0M

The polarisation cell was connected to a potentiostat (Autolab PGSTAT 30 ECO CHIMIE) and interfaced with a computer for data acquisition and analysis. For reproducibility of results, three different experiments were performed for each of the samples under the same conditions; a scan rate of 1 mV/s was maintained throughout the experiment. The experiments were performed in turns in de-aerated condition using nitrogen gas.

3. RESULTS AND DISCUSSION

3.1. 4 M HCl test environment

For all the experimental tests performed, the summary of the results for all the major result parameters used in the analysis for this work are presented in Table 2. The potentiostatic polarization curves' results for the test specimen recorded in 4 M HCl and the 4M HCl + 3.5% NaCl test media are presented in Figures 1 and 2 respectively. Fig.1 shows the polarization corrosion curve of the S43903 ferritic stainless steel in 4M HCl alone. The open corrosion potential (OCP), Ecorr was -0.29249 V. This medium had the highest molarity and hence the most concentrated but without added NaCl. From the Table, a polarisation resistance, $R\rho$, value of 288.04 Ω; corrosion rate of 0.59091 mm/year and current density of 5.53E-05 (A/cm2), in addition to the OCP values stated above, showed active corrosion reactions that persisted throughout the monitoring period. From Fig.1, the primary passive potential (Epp) value was 0.0991821 V, the critical current density (icr) value was 0.052475 (A/cm^2); the passive current density (ipass) was 0.00118805 (A/cm^2); the critical pitting potential (EB) was 0.982971 V and passive potential range value was 0.798340 V. These values will be subsequently used comparatively for the values obtained for the other tests where applicable. The above results data changed with the use of the acid chloride, Fig. 2, that is, 4 M HCl + 3.5% NaCl. The polarization resistance, $R\rho$, value was lowered to 135.76 Ω; and likewise the Ecorr value (-0.19152 V). The corrosion rate increased to 0.8136 mm/yr; and so also the current density value, 7.62E-05 A/cm^2. All these indicate increased electrochemical active corrosion reactions. The chloride ions, Cl$^-$, from the sodium chloride would have added to this increased active corrosion reactions and hence increase in corrosion magnitude.

Table 2. Corrosion polarisation results for the test in HCl

Test Environment	Ecorr, Obs (V)	icorr (A/cm²)	icorr (A)	Corrosion rate (mm/yr	Polarization resistance (Ω)
4 M HCl	-0.29249	5.53E-05	7.47E-05	0.59091	288.04
4 M HCl + 3.5%NaCl	-0.19152	7.62E-05	9.94E-05	0.8136	135.76
2.5 M HCl	-0.2058	3.31E-05	3.57E05	0.35341	295.55
2.5 M HCl + 3.5% NaCl	-0.16347	3.61E-05	4.71E-05	0.38495	124.75
1.5 M HCl	-0.22009	9.79E-06	1.23E-05	0.10376	1571.8
1.5 MHCl + 3.5% NaCl	-0.1951	3.48E-05	4.07E-05	0.37177	140.68
1 M HCl	-0.16246	8.43E-06	7.21E-06	0.090036	4275.9
1 M HCl + 3.5% NaCl	-0.19314	2.89E-05	3.24E-05	0.30875	101.41

From Fig.2, the primary passive potential (Epp) value was -0.00335693 V, the critical current density (icr) was 0.0788025 (A/cm^2); the passive current density (ipass) was 0.00203308 (A/cm^2); and the critical pitting potential (EB) was 0.96344 V. All these pointed towards increase in active corrosion reactions when compared with the Figure 1 values.
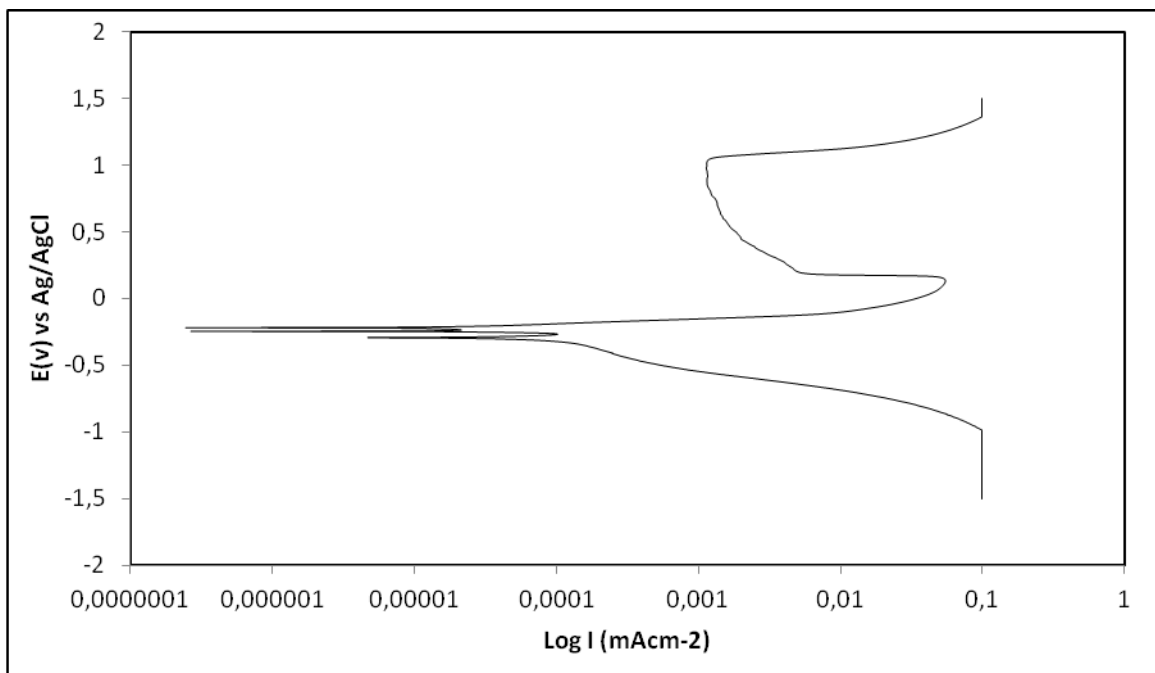

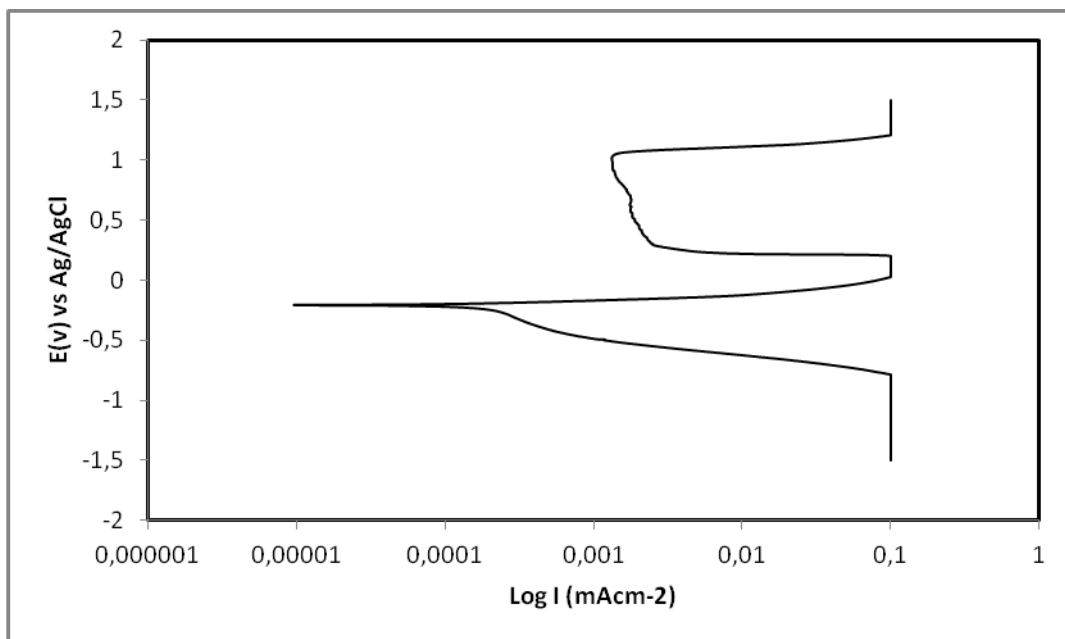**Figure 1.** Polarization curve of ferritic stainless steel in 4M HCl

Figure 2. Polarisation curve of ferritic stainless steel in 4 M HCl + 3.5% NaCl

In general, the corrosion resistance, the passivation characteristics and the anodic protectibility improve as the primary passive potential becomes more active; as the critical current density and the passive current densities decrease, and as the passive potential range becomes broader.

3.2. 2.5 M HCl and 2.5 M HCl + 3.5% NaCl test environment

Figs. 3 and 4 show the polarization curve for the test specimen performed in 2.5 M HCl and the HCl + 3.5% NaCl respectively. The summary of the results for these tests in these environments are presented in Table 2. The Ecorr value from the Table was -0.2058 V, a relatively active corrosion reactions value.
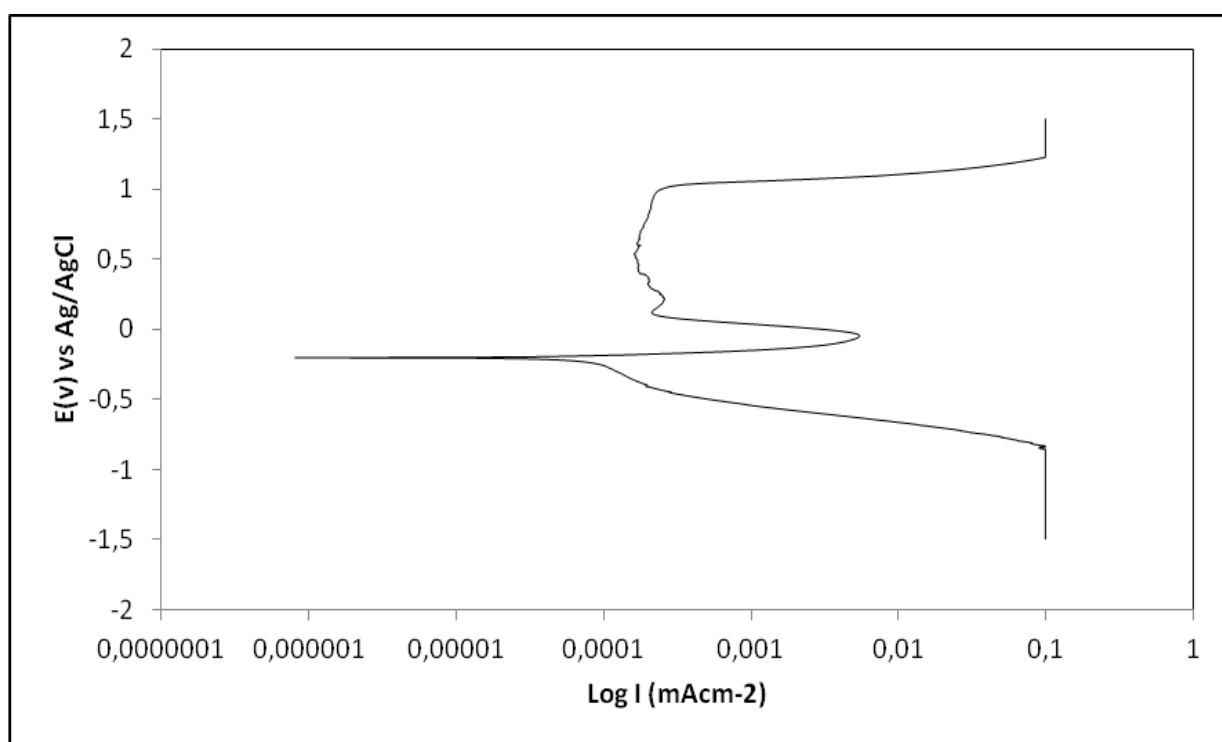

Figure 3. Polarisation curve of ferritic stainless steel in 2.5 M HCl

In this medium, the corrosion rate value obtained was 0.35341 mm/yr which was low, particularly when compared with the value of 1.7116 mm/yr obtained for the test in 4 M HCl (Table 2). The dissociated chloride ions (Cl⁻) was therefore far more in 4M than in 2.5 M HCl and hence the more intense active corrosion reactions. The polarization resistance, Rρ, value obtained was 295.55 Ω which was far more than as obtained for 4 MHCl (288.04Ω) and hence the lower corrosion values obtained. A value of 3.31×10^{-05} A/cm^2 current density was recorded and this was a far lower corrosion current than in the 4 M HCl. This value also showed corrosion - reactions which were less significant than in 4 M HCl test environment.
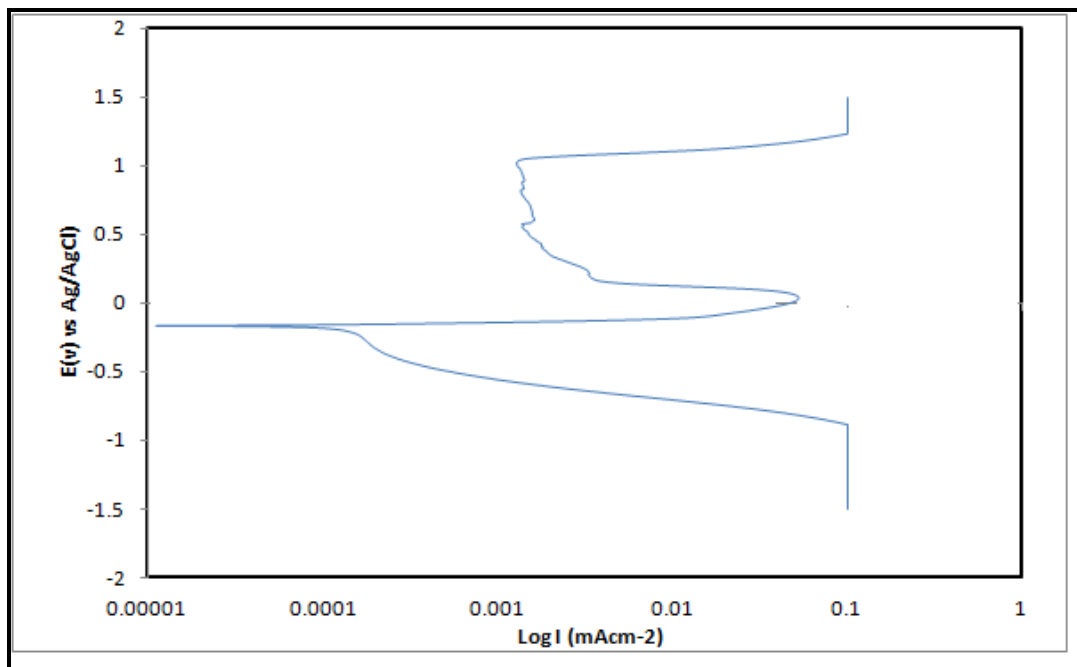
Figure 4. Polarisation curve of ferritic stainless steel in 2.5M HCl + 3.5% NaCl

From Fig.3, the primary passive potential (Epp) value was 0.0981579 V, the critical current density (icr) value was 0.00494415 (A/cm^2); the passive current density (ipass) was 0.000171265 (A/cm^2); the critical pitting potential (EB) was 0.960999 V and passive potential range value was 0.866 V. When compared with the similar values obtained in Fig. 1, for the test in 4 M HCl, it could be seen that the primary potential value becomes more active; the critical current density and the passive current density decrease in values and the passive potential range becomes broader comparatively, and these could be associated with the improvement in the corrosion resistance, passivation characteristics and anodic protectibility of the stainless steel in 2.5 M HCl, a lower concentration test environment than in the former (4 M HCl).

Just like in Fig. 2, the use of NaCl in addition to the HCl, Fig. 4, brought about changes in the corrosion reactions profile. The polarization resistance, Rρ, value was lowered to 124.75 Ω; the Ecorr was -0.16347 V, a lower negative value. The corrosion rate increased to 0.38495 mm/yr when compared with Fig. 3 – the HCl test environment alone; and so also the current density value, 3.61E-05 A/cm^2 increased slightly. These values indicate increasing loss of anodic protectibilty, reduction in corrosion resistance and decrease in passivation characteristics when compared with the HCl environment alone, Fig. 3. In Fig. 4, the primary passive potential (Epp) value was 0.0186157 V, the critical current density (icr) was 0.0568575 (A/cm^2); the passive current density (ipass) was 0.00144531 (A/cm^2); and the critical pitting potential (EB) was 0.978088 V. All these are indication of increasing active corrosion reactions when compared with the Figure 3 values.

3.3. 1.5 M HCl test environment

Fig. 5 shows the curve obtained from the corrosion measurement of the specimen tested in 1.5 M HCl. The Ecorr (OCP) value obtained was -0.22009 V; and the polarisation resistance, Rρ, was 1571.8 Ω.The corrosion current density value obtained was 9.79×10^{-6}; and a corrosion rate value of 0.10376 mm/yr was recorded. These data showed minimal corrosion reactions magnitude. These values gave lower active corrosion reactions and hence lower magnitude of corrosion when compared with the test experiments in 4 M and 2.5 M HCl respectively. This result was not unexpected due to the very lower concentration of the acid used. Further data values obtained from Fig.5 also pointed towards better corrosion performance in this low concentration of the acid. These values include: the primary passive potential (Epp) value was -0.0790405 V, the critical current density (icr) value was 0.00138184 (A/cm^2); the passive current density (ipass) was 5.02×10^{-05} (A/cm^2); the critical pitting potential (EB) was 0.960999 V and passive potential range value was 0.842286 V. A comparison with the similar values obtained in Figs. 1 and 3 for the tests in 4 M and 2.5 M HCl respectively, showed that the primary potential value becomes more active; the critical current density and the passive current density decrease in values greatly. These could be associated with the improvement in the corrosion resistance, passivation characteristics and anodic protectibility of the stainless steel in 2.5 M HCl, a lower concentration test environment than the former (4 M HCl) as earlier indicated.
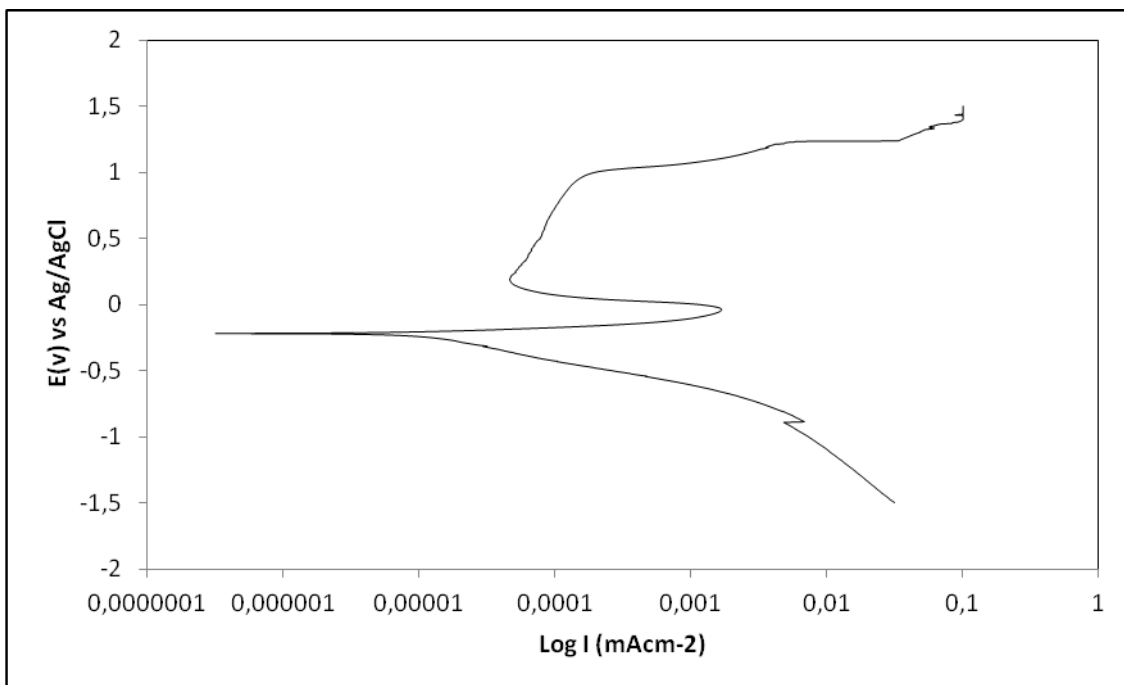

Figure 5. Polarisation curve of ferritic stainless steel in 1.5 M HCl

3.4. 1.5 M HCl + 35 g/l NaCl (3.5%) test environment

When 35g/l (3.5%) sodium chloride was separately added to the same concentration (1.5M HCl) of the test environment as in Fig. 5, there was apparent increased active corrosion reactions

behaviour observed in the corrosion polarization values obtained, as shown in Table 2 and Fig. 6. From both the Table 2 and Fig. 6, it could be seen that a much higher corrosion current density (icorr) value of 3.48×10^{-05} A/cm^2 was achieved that was even much higher than in 2.5 M HCl. A lower value of polarization resistance, Rρ, of 140.68 Ω that was even lower than that obtained in the test with 4M HCl was achieved. Also a much higher corrosion rate of 0.37177 mm/yr that was even much higher than obtained in the tests with 1.5 and 2.5 M HCl without NaCl addition was obtained. These values are apparent indication of increased corrosion reactions, due to the action of the added NaCl that increased Cl$^-$ ions concentration in the test medium. The increased Cl$^-$ ions acted to further depassivate the steel specimens' protective film, initiated the metal's surface anodic dissolution and hence increased corrosion of the tested specimens. From Fig.6, the primary passive potential (Epp) has a value of - 0.0692749 V, the critical current density, (icr) is 4.523×10^{-3} A/cm^2 ; and the passive current, (ipass), is 2.14×10^{-4} A/cm^2.
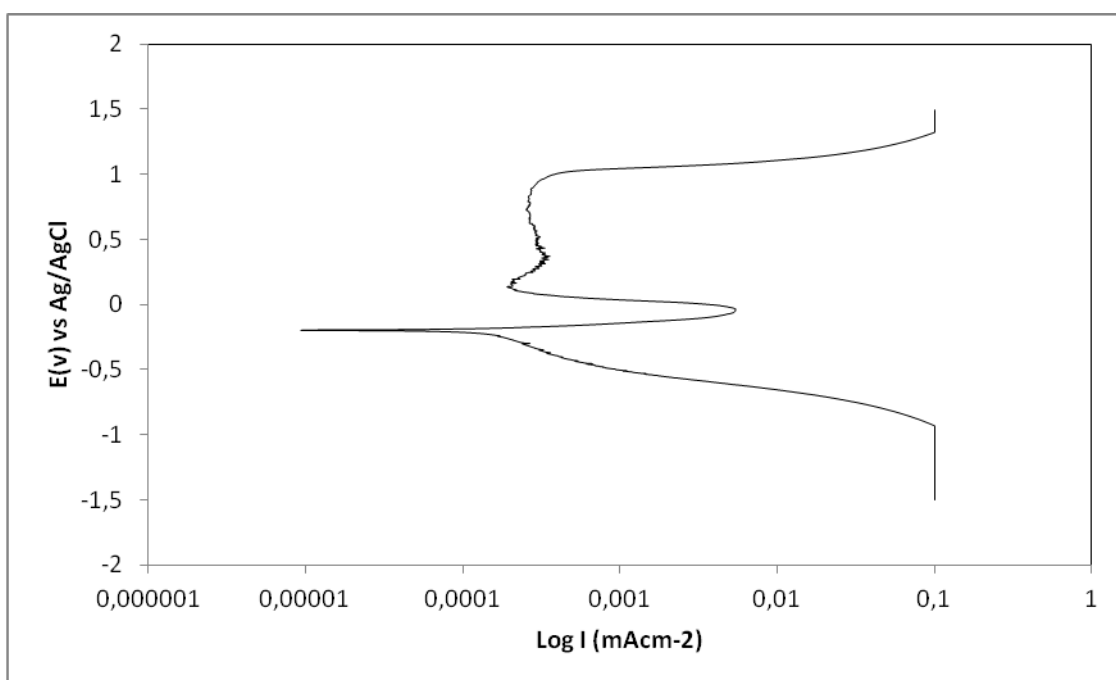

Figure 6. Polarisation curve of ferritic stainless steel in 1.5 M HCl + 3.5% NaCl

The critical pitting potential is 0.948972 V. From these data values, the primary passive potential becomes less active, and the critical current and the passive current densities increase. These are indications of increased active corrosion reactions due to the increased Cl$^-$ ions concentration from the addition of NaCl as mentioned above.

3.5. 1 M HCl and 1 M HCl + 3.5% (35 g/l) NaCl test environment

The potentiostatic polarization curves and tables of measurement results for the test specimens recorded in different concentrations of HCl with and without the addition of 35g/l NaCl are presented

in Figs. 7 and 8 and Table 2 respectively. Fig.7 shows the polarization corrosion curve of the ferritic stainless steel in 1M HCl alone. The open corrosion potential (OCP), Ecorr was 0.57387V. The specimen can be described to be protected with this potential value throughout the experimental period.

This medium serves as the control for the subsequent experiment in which there was the addition of 3.5% NaCl (35g/l) to the HCl. A summary of the overall result data is presented in Table 2 The corrosion rate recorded was 0.090036 mm/yr and the corrosion polarisation resistance, $R\rho$, was 4275.9 Ω. At this 1 M HCl concentration, it appears that though there was corrosion reactions behaviour, the ferritic stainless steel specimen was very corrosion resistant. The primary passive potential, Epp, value obtained was 0.150452 V and the critical current density value was 1.53×10^{-4} A/cm^2. These two values put the corrosion behaviour more in the passive reactions state.
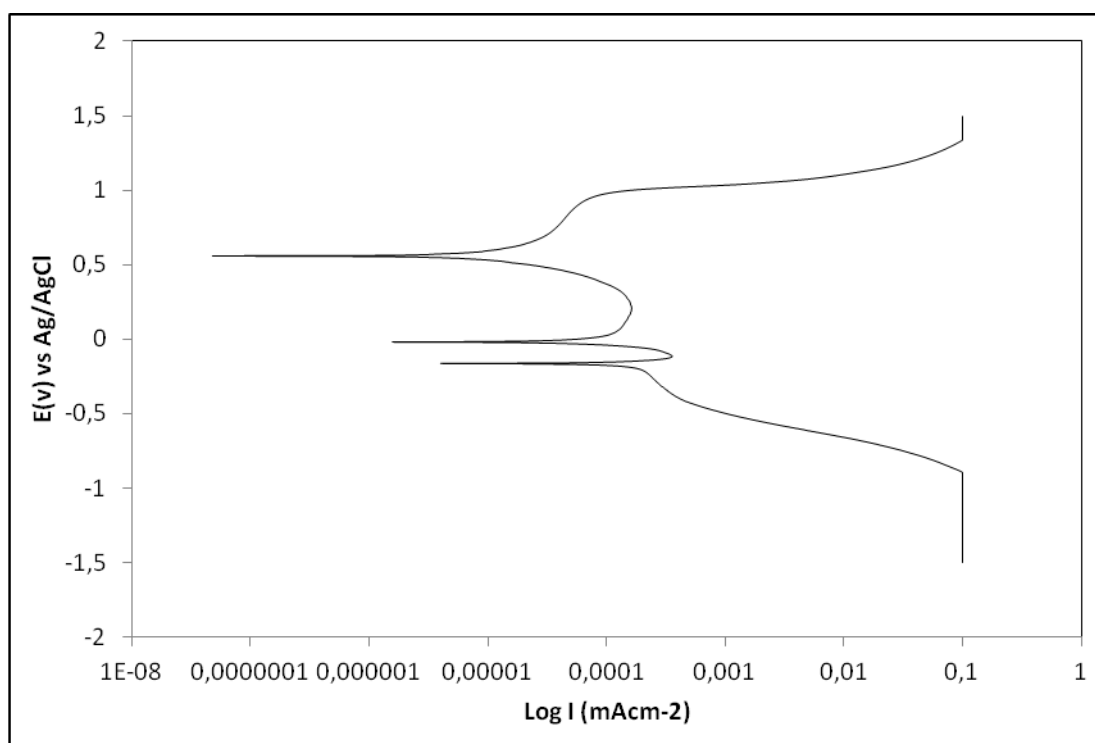

Figure 7. Polarisation curve of ferritic stainless steel in 1 M HCl

Fig. 8 and the relevant data in Table 2 show the corrosion polarisation curve and the summary of the results obtained for the test specimen in 1 M HCl + 35 g/l (3.5%) NaCl. The open circuit potential (Ecoor) recorded was -0.20027 V (Table 7). The corrosion rate value was 0.30875 mm/yr and the corrosion polarization resistance, $R\rho$, was 101.41 Ω. When compared with the test in 1 M HCl alone, these results data confirmed that there was increase in corrosion reactions when NaCl was used in addition, with the acid at that same concentration. The corrosion resistance, in comparison became very low and the corrosion rate increased drastically.
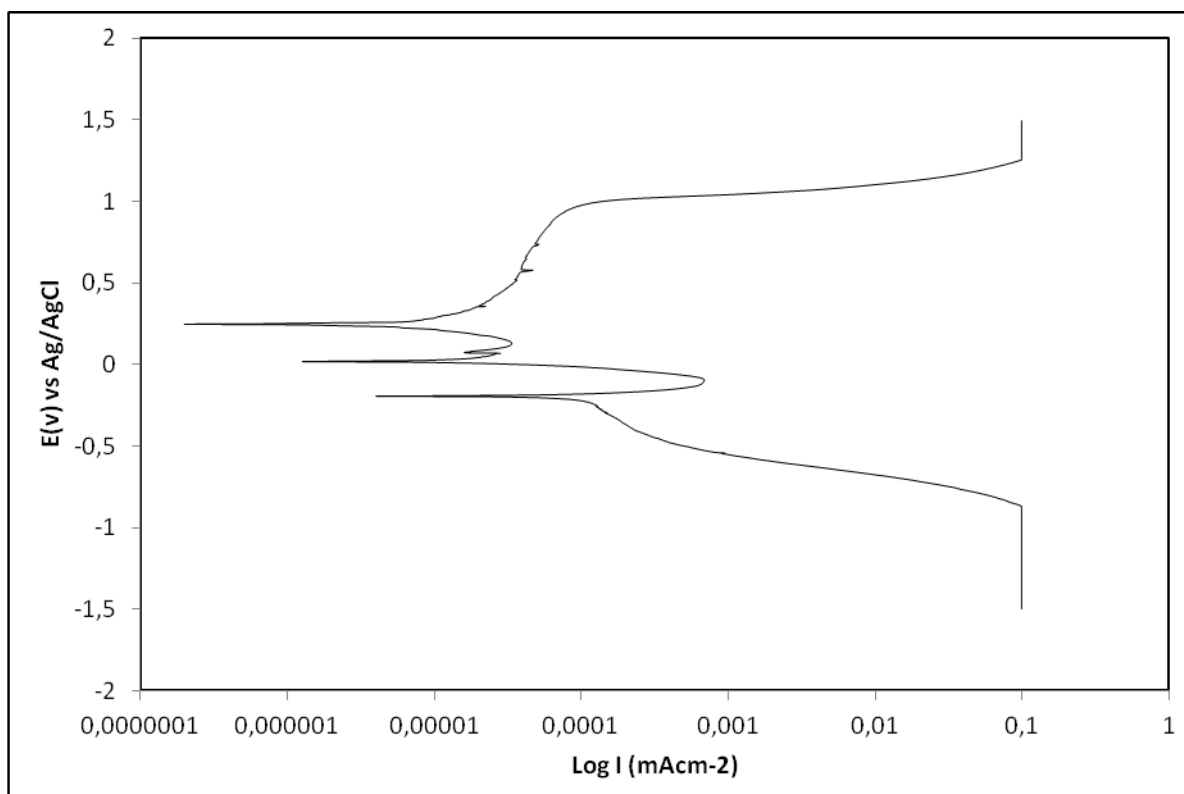
Figure 8. Polarisation curve of ferritic stainless steel in 1 M HCl + 3.5% NaCl

The results obtained in the HCl and HCl + NaCl test media showed varied corrosion magnitudes. The effect of Cl⁻ ions, in particular, was significant in the active corrosion reactions phenomena causing the protective film rupture and initiation of anodic dissolution of the test electrodes. The overall corrosion polarisation behaviour showed the ferritic stainless steel electrode to have a measure of corrosion resistance in the HCl test environment alone at lower concentrations. The HCl- acid chloride solution increased the corrosion rate and reduced the corrosion resistance of the steel. The ferritic stainless steel also was susceptible to corrosion at the higher concentration(s) of HCl without NaCl as indicated by the test in the 4 M HCl.

4. CONCLUSION

Appreciable corrosion resistance of the tested S43903 stainless steel specimens was exhibited in the hydrochloric acid test environments alone at the low concentrations (1 M and 1.5 M), particularly in the test environments that did not contain added NaCl. The addition of sodium chloride, however, shifted the polarisation behaviour into active corrosion reactions at these two mentioned concentrations. The corrosion polarisation behaviour for the tests performed in 4 M HCl showed active corrosion reactions that were similar to the tests with added NaCl at the lower concentrations. There was reduced corrosion resistance of the steel at this concentration of the acid alone. Addition of NaCl to this concentration increased the corrosion rate further and lowered the corrosion resistance. The

steel gave a fairly good corrosion resistance performance in 2.5 M HCl without sodium chloride addition. The stainless steel should be used with caution in the HCl environment that contains sodium chloride.

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