

Technical Report

Corrosion Polarization Behaviour of Type 316 Stainless Steel in Strong Acids and Acid Chlorides

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Received: 18 February 2012 / Accepted: 19 March 2012 / Published: 1 April 2012

The corrosion resistance and/or susceptibility of Type 316 austenitic stainless steel was separately performed at ambient temperature in different concentrations (the intermediate and the concentrated) of sulphuric acid, H₂SO₄, and phosphoric acid, H₃PO₄. Similar tests were also performed by the addition of 2% (20g/l) sodium chloride, NaCl, to each of the specified acid concentrations to form their acid chlorides. Potentiostatic polarization method was used for the corrosion investigation. The electrochemical corrosion reactions exhibited both the passive and active corrosion reactions characteristics. The acids at the intermediate concentrations show more obvious active corrosion reactions; while in the concentrated form they were relatively passive – the passivity that was associated with the oxidizing nature of the concentrated acids. The addition of 2% NaCl to each of the test medium concentration gave increased active corrosion reactions that could be due to the test electrodes' surface protective film rupture by anodic dissolution. In all the tests, however, the magnitude of corrosion could be considered to be low.

Keywords: corrosion resistance, sulphuric and phosphoric acids, sodium chloride, polarization.

1. INTRODUCTION

The exorbitant amount spent on corrosion and protection of engineering components, structures/facilities annually has created a lot of interest in continually seeking for techniques and methods to efficiently combat corrosion. This is of particular interest to corrosion scientists and engineers worldwide, to gain more knowledge about the corrosion phenomenon and its control, and with the aim of finding appropriate and better utilization of austenitic stainless steels and other alloys.

For the fabrication of equipment components, and for the construction of industrial plants for the manufacture of acids, chemicals, and their derivatives, it is important to make the appropriate selection of the materials used. This will ensure long life, dependability, safety, reliability and economic viability of plant and industrial engineering components. The selection of appropriate metal or alloy for a particular corrosion service is, therefore, the most common method of preventing or reducing corrosion damage. In this regard, austenitic stainless steels are frequently used [1-4].

As previously reviewed [5, 6], the austenitic stainless steels comprise a large and varied group of iron-based alloys containing 18% or more chromium and sufficient nickel to assume a fully austenitic metallurgical structure. The most common group is referred to as “18-8” stainless steel 918%Cr and 8%Ni of which Type 316 stainless steel belongs. These alloys are of major importance in the chemical process industries and in other industrial applications. They are the alloys of choice for many of the applications which require a higher level of corrosion resistance than the type 304 stainless steel. In composition, type 316 consists of about 2% Mo to improve the resistance to pitting attack by strengthening the passive film and imparting improved corrosion resistance in reducing acids (7, 8).

Austenitic stainless steels have a wide spectrum of resistance to corrosion by chemical environments. The alloys form a film which protects the underlying metal from attack in many environments. This film is very thin, essentially transparent and self-healing; if it is damaged mechanically or chemically, it will reform very rapidly [9]. However, in a situation where the rate of damage is more than the rate of repair, a progressive active corrosion reaction will occur, which may cause corrosion degradation of the alloy. Such a phenomenon has been caused in acid environments containing sodium chloride.

Sulphuric acid and phosphoric acids are the two corrosion media used in this investigation. Apparently, more sulphuric acid is produced than any other chemicals in the world [10]. It is used directly or indirectly in nearly all industries. It is principally used in the production of chemicals and their derivatives, pickling of steel and other metals, manufacture of fertilizers, dyes, drugs, pigments, explosives, synthetic detergents, rayon and other textiles, petroleum refining, and the production of rubbers. In making the acids, the problem of corrosion is significant in the production plants. The acid also causes major problem in consumers' plants when it is utilized under a wide variety of conditions. The resistance of austenitic stainless steels to sulphuric acid is complex due to the active-passive nature of the alloys.

Phosphoric acid, the second test environment used in this investigation was chosen because of its industrial applications. Corrosion by phosphoric acid depends to a large extent on the methods of manufacture and the impurities present in the commercial finished products. Fluorides, chlorides and sulphuric acid are the main impurities present in the manufacturing process and in some marketed acids [11].

This present investigation looks at the corrosion resistance reactions phenomena of type 316 stainless steels in varied concentrations of the acids used. The acids test media were further contaminated with sodium chloride (NaCl) to further enhance the breakdown of passivity by the chloride ions. The work aims at evaluating the corrosion resistance of Type 316 stainless steel at different concentrations of sodium chloride contaminated strong acids to determine its viable

usefulness in this type of harsh environments which simulate many industrial applications/conditions. The work will also make a contribution to the on-going research work in the use of stainless steels in simulated industrial environments such as the very strong acids in this investigation.

2. EXPERIMENTAL METHOD

Austenitic stainless steel –SS316 samples in cylindrical form (10mm dia 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 (1 μ m), cleaned and rinsed/degreased in an ultrasonic bath using acetone. The samples were immediately kept in a desiccator for subsequent corrosion experimental studies.

Potentiostatic polarization experiments were performed using each of the cylindrical specimens in turns, in which 1 cm² surface area of the specimen was exposed to the test solution at room temperature. The experiments were performed using a polarization cell of three – electrode system consisting of a reference electrode (saturated calomel – SCE), a working electrode (WE); and a counter electrode (CE) made of platinum mesh. The experiments were conducted in six different solutions for each stainless steel sample. All the chemicals used: sodium chloride (NaCl), sulphuric acid (H₂SO₄) and phosphoric acid (H₃PO₄) were prepared from analytic reagent grade (AR). The test environments are presented in Table 1:

Table 1. Test Environments

| Sulphuric acid, H ₂ SO ₄ | Sulphuric acid + 20g/L NaCl (2%) | Phosphoric acid, H ₃ PO ₄ | Phosphoric acid, H ₃ PO ₄ + 20g/L NaCl (2%) |
|--|----------------------------------|---|---|
| 9.1M (48.5%) | 9.1 M + 2% NaCl | 7.4M (42.5%) | 7.4M + 2% NaCl |
| 18.2M (97%) | 18.2 M + 2% NaCl | 14.8M (85%) | 14.8M + 2% NaCl |

The polarisation cell was connected to a potentiostat (EG & G 273A) 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 Sulphuric acid and sulphuric acid – sodium chloride environments

The potentiostatic polarization curves and table of measurement results for the test specimen recorded in different concentrations of H₂SO₄ with and without the addition of 20g/l NaCl are

presented in Figs. 1-4 and Table 2 respectively. Fig.1 shows the polarization corrosion curve of the 316 stainless steel in 9.1M H₂SO₄ alone. The open corrosion potential (OCP), E_{corr} was 0.305V. 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 2% NaCl (20g/l) to the H₂SO₄. A summary of the overall result data is presented in Table 2.

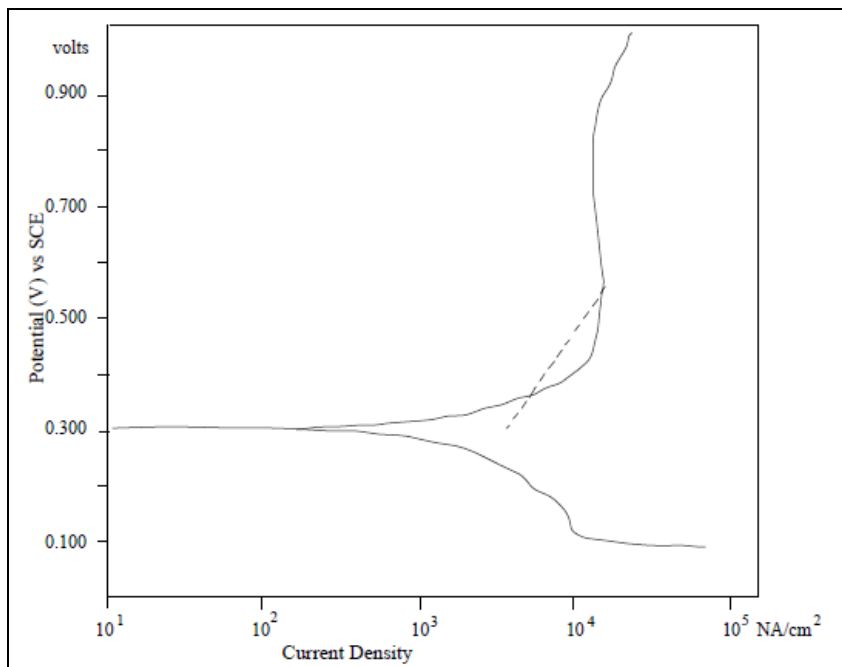


Figure 1. Polarization Curves of 316L stainless steel in 9.1M H₂SO₄ (48.5%)

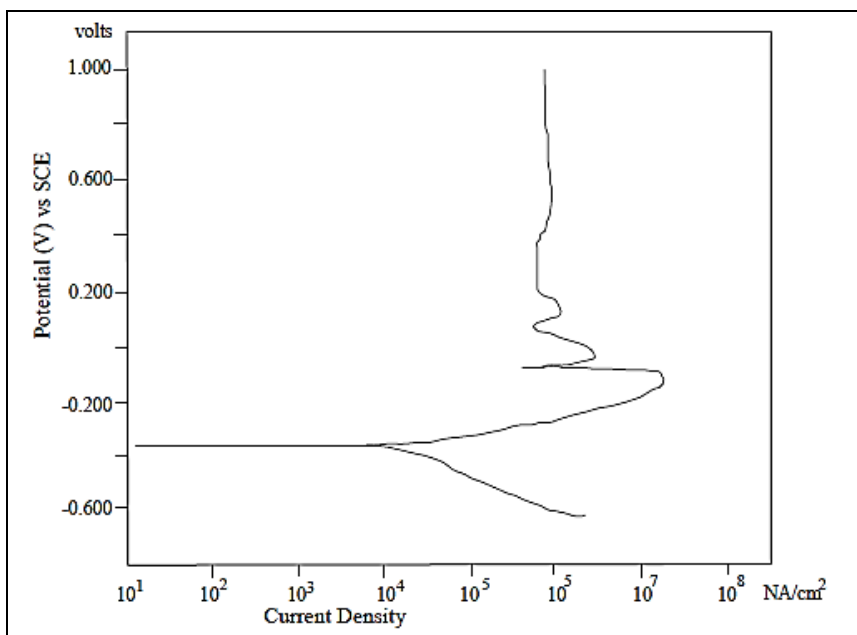


Figure 2. Polarization curves of 316L stainless steel in 9.1M H₂SO₄ and 20g/l NaCl

Further results summary for the test in 9.1M H₂SO₄ presented in Table 1 showed that the corrosion rate is 2.09×10^{-5} mm/yr and the corrosion polarization resistance (R_p) is $-3.8 \times 10^{-7}\Omega$. The corrosion current density of 5×10^{-6} A/cm² was low and the corrosion current is 3.56×10^{-7} A which was also very low. All these results data confirmed the corrosion of the test specimen in H₂SO₄ to be very low.

Fig. 2 shows the polarization curve as in Fig. 1, but with the addition of 20g/l NaCl to the acid environment. The results obtained here were quite different from those of the Fig.1 as also presented in Table 2. There was increased corrosion rate 4.84×10^{-2} (mm/yr) and the E_{corr} (OCP) of -0.380V. The polarization resistance value was -2.3×10^{-5} and with a corrosion density of 1.2×10^{-4} A/cm². The corrosion current recorded was 8.25×10^{-5} A. Comparatively these corrosion reactions data indicated more corrosion occurrence than in the environment without NaCl (Fig.1). These results showed less corrosion resistance and a decrease in passivation characteristics. These effects are, apparently, due to the chloride ions (Cl⁻) penetrating the passive film, causing film breakdown and initiating anodic dissolution of the alloy. The addition of 2% NaCl caused a shift in potential toward increasing negative values.

Table 2. Summary of corrosion polarization results for the test specimen in H₂SO₄

| Sample | i_{corr} (A) | I_{corr} (A/cm ²) | R _p (Ω) | E _{corr} (V) | Corrosion rate (mm/yr) |
|--|------------------------|--|-----------------------|-----------------------|------------------------|
| H ₂ SO ₄ 9.1M +NaCl 20g/l | 8.25×10^{-5} | 1.2×10^{-4} | -2.3×10^{-5} | -0.380 | 4.84×10^{-2} |
| H ₂ SO ₄ 9.1M | 3.56×10^{-7} | 5×10^{-6} | -3.8×10^{-7} | 0.300 | 2.09×10^{-5} |
| H ₂ SO ₄ 18.2M +NaCl 20g/l | 5.69×10^{-3} | 8×10^{-2} | -5.0×10^{-2} | -0.400 | 3.34×10^{-7} |
| H ₂ SO ₄ 18.2M | -1.18×10^{-4} | -1.66×10^{-3} | -3.9×10^{-9} | 0.320 | -6.92×10^{-6} |

Presented in Fig. 3 is the corrosion polarization curve for the stainless steel specimen immersed in 18.2MH₂SO₄ (87%) which was a very strong acid of high strength (concentration). The results obtained such as the E_{corr} of 0.320V; polarization resistance (R_p) of $-3.9 \times 10^{-9}\Omega$, corrosion rate (CR) - 6.92×10^{-6} mm/yr.; corrosion current density (I_{corr}) -1.66×10^{-3} A/cm² showed that there was more corrosion resistance of the steel specimen in this medium. The corrosion resistance observed in this test medium and also as reported in Figs. 1 and 2 above could be associated with the fact that sulphuric acid is oxidizing when concentrated but it is reducing at low and intermediate concentrations. The response of most stainless steel types is that, in general, they are resistant at either low or high concentrations, but are attacked at intermediate concentrations [12].

Fig. 4 shows the corrosion polarization curve for the same acid concentration as in Fig. 3 above but with the addition of 20g/l NaCl. With an E_{corr} value of -0.400V, the corrosion reactions here had far less corrosion resistance when compared with the test medium without NaCl addition. The polarization resistance value of -5.0×10^{-2} Ω was much higher than in Fig.3; and so also, a very high

Icorr value of $8 \times 10^{-2} \text{ A/cm}^2$. The addition of Cl^- would have caused a depassivation of the adherent chromium film and that of dense concentrated H_2SO_4 .

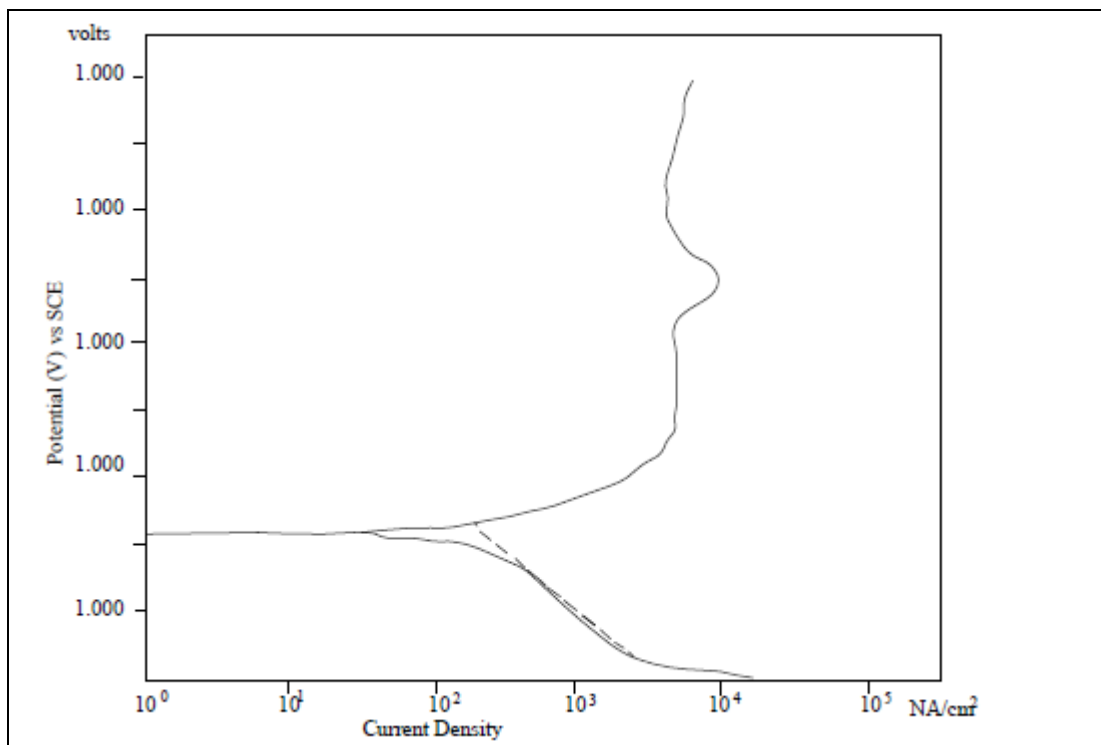


Figure 3. Polarization Curves of 316L stainless steel in 18.2M H_2SO_4 (97%)

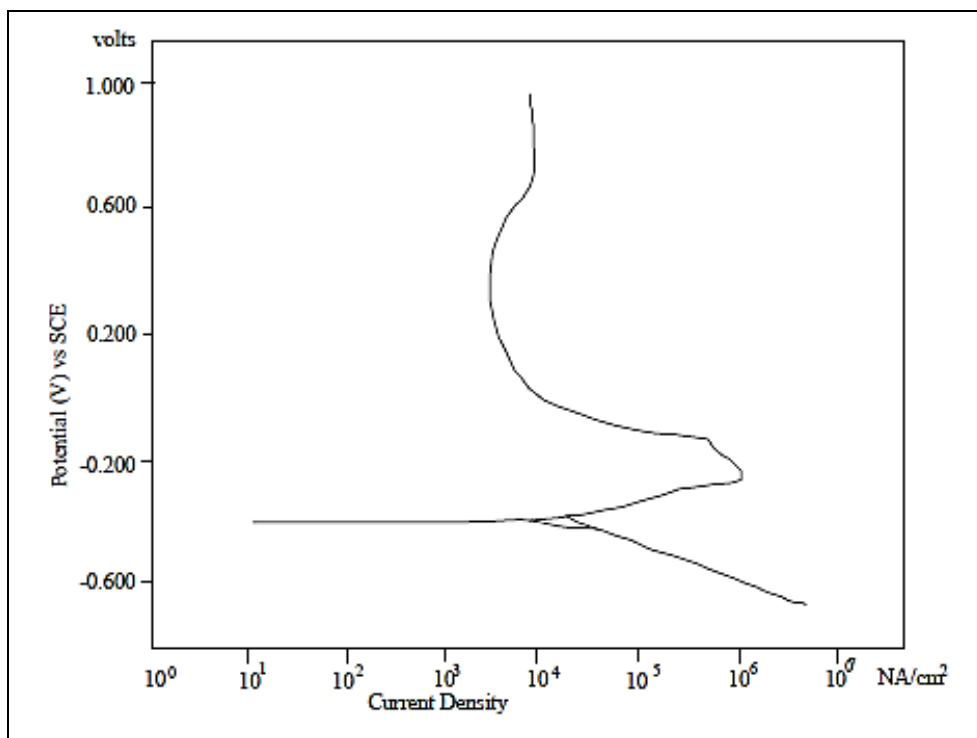


Figure 4. Polarization Curves of 316L stainless steel in 18.2M H_2SO_4 and 20g/l NaCl

3.2. Phosphoric acid and phosphoric acid – NaCl environments

The corrosion polarization curves for the 316 austenitic stainless steel specimens immersed/tested in varied concentrations of phosphoric acid (H₃PO₄) and phosphoric acid-sodium chloride environments are presented in Figs. 5 – 8. The summary of the polarization measurement results are presented in Table 3.

Table 3. Summary of corrosion polarization results for the test specimen in H₃PO₄

| Sample | <i>i</i> _{corr} (A) | <i>I</i> _{corr} (A/cm ²) | R _P (Ω) | E _{corr} (V) | Corrosion (mm/yr) | rate |
|---|------------------------------|--|----------------------|--------------------------|-----------------------|------|
| H ₃ PO ₄ 7.4M +NaCl 20g/l | 1.02x10 ⁻³ | 1.2x10 ⁻² | 2.2x10 ⁻³ | -0.300 | 5.02x10 ⁻³ | |
| H ₃ PO ₄ 7.4M | 7.12x10 ⁻⁷ | 1.0x10 ⁻⁵ | 2.5x10 ⁻⁶ | 0.050 | 3.34x10 ⁻⁶ | |
| H ₃ PO ₄ 14.8M +NaCl 20g/l | 1.19x10 ⁻³ | 1.7x10 ⁻² | 2.4x10 ⁻³ | -0.400 | 5.59x10 ⁻³ | |
| H ₃ PO ₄ 14.8M | 1.42x10 ⁻⁵ | 2.0x10 ⁻⁴ | 1.0x10 ⁻⁴ | 0.100 | 6.67x10 ⁻⁵ | |

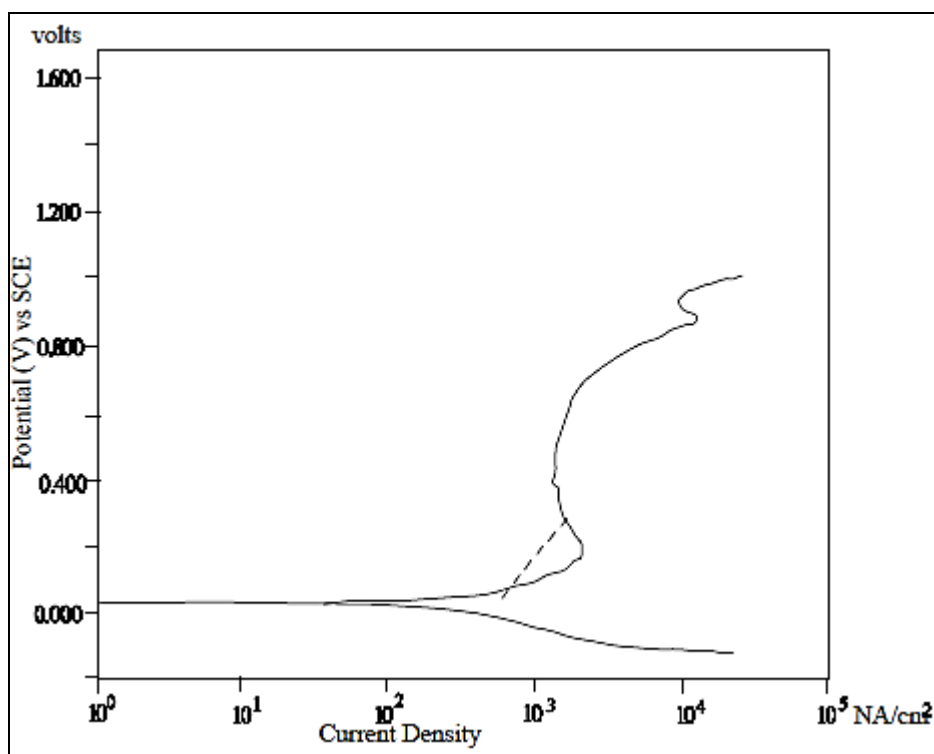


Figure 5. Polarization Curves of 316L stainless steel in 7.4M H₃PO₄ (42.5%)

Fig. 5 shows the curve obtained during the corrosion measurement of the specimen tested in 7.4M H₃PO₄. The E_{corr} (OCP) value obtained was 0.050V; and the polarization resistance, R_p, was

$2.5 \times 10^{-6} \Omega$. The anodic corrosion current value obtained was 1.0×10^{-5} ; and a corrosion rate value of 3.34×10^{-6} mm/yr was recorded. These data showed minimal corrosion reactions magnitude.

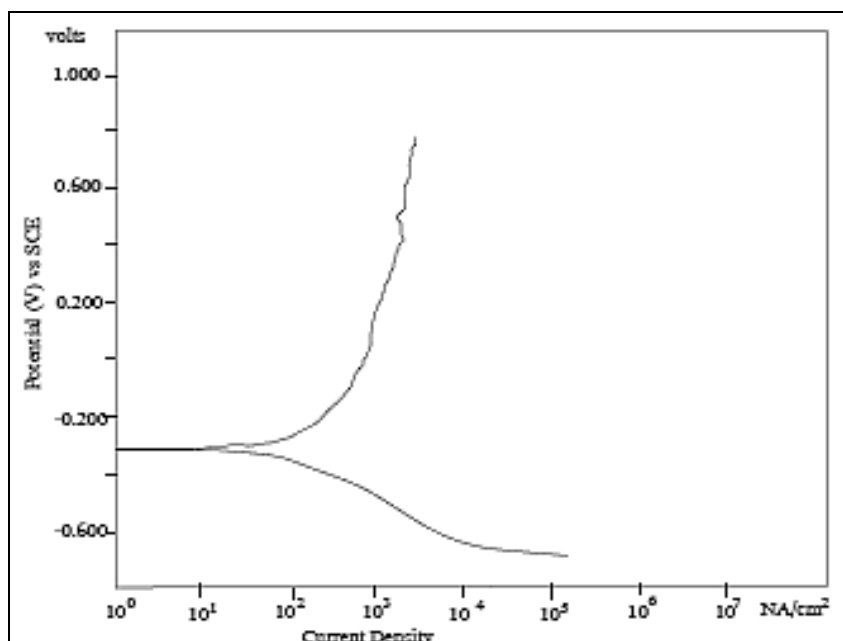


Figure 6. Polarization Curve of 316L Stainless steel in 7.4M H_3PO_4 and 20g/l NaCl

Presented in Fig. 6, is the same test as in Fig. 5 but with the addition of 20g/l of NaCl to the H_3PO_4 test medium. The obtained corrosion polarization measurement results, presented in Table 3 showed relatively increased corrosion reactions characteristics when compared with the test without NaCl addition. There were increased values of corrosion rate (5.02×10^{-3} mm/yr); corrosion polarization resistance ($2.2 \times 10^{-3} \Omega$); anodic corrosion current density (1.2×10^{-2} A/cm²); corrosion current (1.02×10^{-3} A); and a more negative value of E_{corr} (OCP) (-0.300V). All these results data are indications of increased corrosion reactions phenomena. The addition of sodium chloride, NaCl, to the test medium, no doubt, could be associated with these corrosion reactions characteristics. The reacting species of this acid, the PO_4^- and Cl^- ions at the strength of 7.4M had depassivated and penetrated (by film rupture) the stainless steel's chromium protective film and initiate active corrosion reactions by anodic dissolution.

In Fig. 7, which shows the polarization curve for the test performed in 14.8 H_3PO_4 , the E_{corr} value was 0.0100V, a relatively passive corrosion value. In this medium, the corrosion rate value obtained was 6.67×10^{-5} mm/yr which was also low. The polarization resistance value obtained was $1.0 \times 10^{-4} \Omega$ which was also not significant. A value of 2.0×10^{-4} A/cm² anodic current density was recorded and with a low corrosion current (i_{corr}) of 1.42×10^{-5} A. These values also showed corrosion reactions which were not significant.

When 20g/l sodium chloride was separately added to the same concentration of the test environment, Fig. 8, apparent increased active corrosion reactions behaviour was observed as showed

by the polarization measurement values obtained. Here a much higher corrosion current (i_{corr}) value of $1.19 \times 10^{-3} \text{ A}$ was achieved.

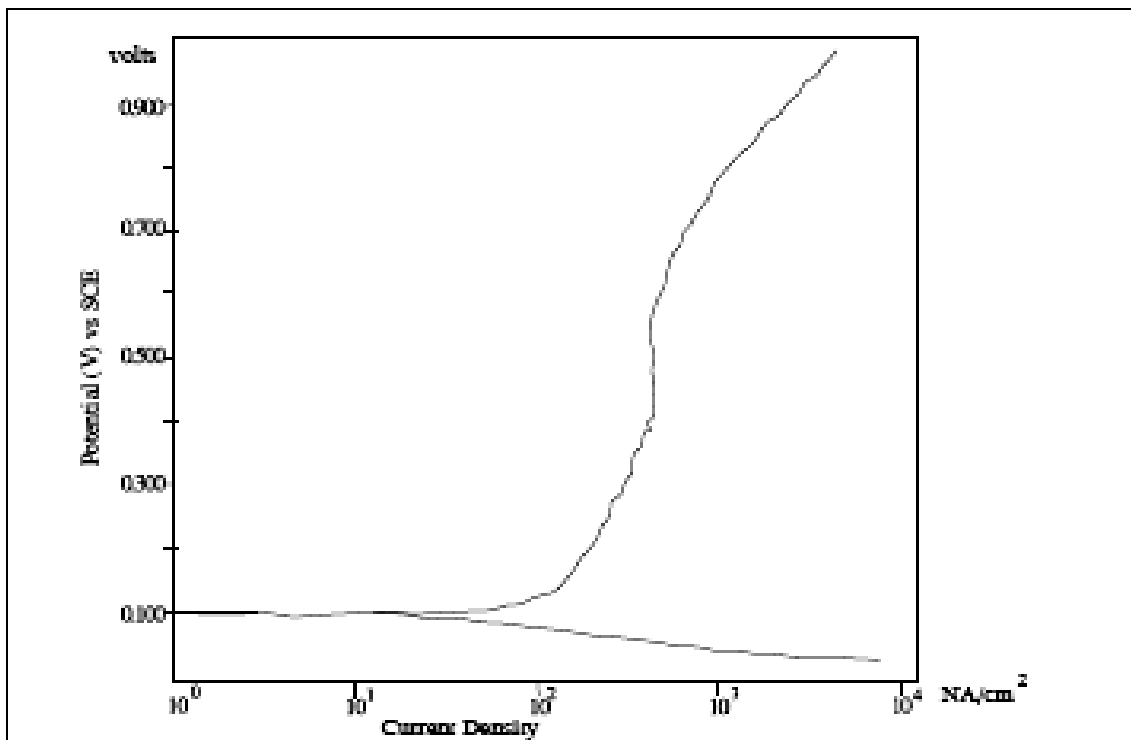


Figure 7. Polarization Curve of 316L stainless steel in 14.8M H₃PO₄

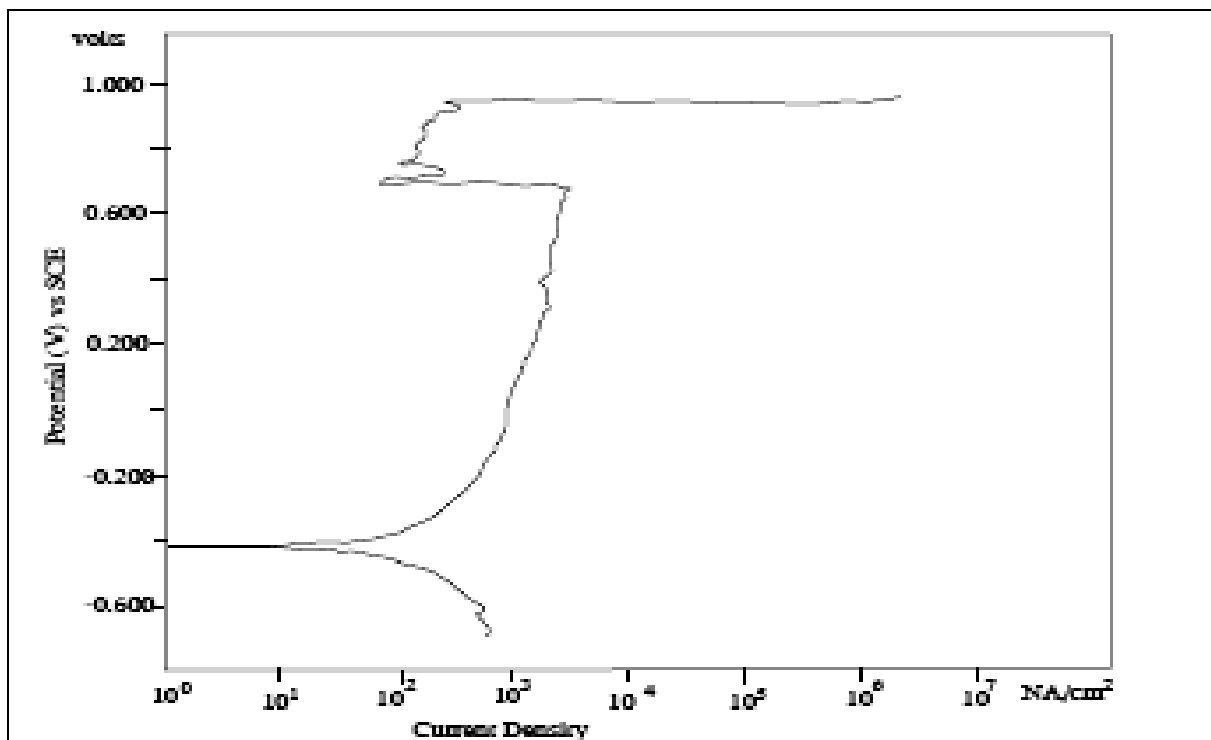


Figure 8. Polarization Curve of 316L stainless steel in 14.8M H₃PO₄ and 20g/l NaCl

The anodic current density (I_{corr}) value, $1.7 \times 10^{-2} \text{ A/cm}^2$ obtained was also of an order of 2 degrees higher than in Fig. 7. A very significant result was the open corrosion potential (OCP), E_{corr} , value of -0.400V which indicated increased active corrosion reactions. A higher value of polarization resistance of 2.4×10^{-3} ; and a corrosion rate of $5.59 \times 10^{-3} \text{ mm/yr}$ values were obtained. These values are apparent indication of increased corrosion reactions, due to the combined actions of PO_4^- and Cl^- ions that depassivated the steel specimens' protective film, initiated the metal's surface anodic dissolution and hence increased corrosion of the tested specimens.

The results obtained both in the H_2SO_4 and H_3PO_4 test media showed very low corrosion magnitude. 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. Corrosion reactions in the concentrated H_2SO_4 (18.2M) was apparently insignificant due to the oxidizing nature of this test medium. With the addition of NaCl, however, a tendency towards active corrosion reactions was observed. The overall corrosion polarization behaviour showed the 316 stainless steel electrode to have a measure of corrosion resistance in the strong acidic / acid chloride test environments, and hence fair/good passivation characteristics and anodic protectibility enhanced by the self- generated protective film.

4. CONCLUSION

Appreciable corrosion resistance of the tested 316 austenitic stainless steel specimens was exhibited in the sulphuric acid test environments at both the intermediate (9.1M; 48.5%) and at the high concentrations (18.2M; 97%), particularly in the test environments that did not contain added NaCl. The concentrated H_2SO_4 (18.2M) showed near absolute passivity. The addition of sodium chloride, however, shifted the polarization behaviour into active corrosion reactions, though still minimally.

The corrosion polarization behaviour for the tests performed in phosphoric acid, H_3PO_4 , also showed active corrosion reactions behaviour at all the used concentrations (7.4M; 42.5% and 14.8M; 85%). The addition of NaCl gave less corrosion resistance of the test electrode as indicated by the obtained results data.

The overall corrosion resistance performance of this alloy in the test environments can be rated as fair to good.

ACKNOWLEDGEMENT

The authors acknowledge the graphic work contributions of Dr John Samuel and O. Oladoyinbo, Covenant University, Ota, Nigeria.

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