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Electrochemical corrosion resistance and susceptibility of 12Cr martensitic stainless steel in H_2SO_4

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ABSTRACT

Corrosion susceptibility and inhibition of 12Cr martensitic stainless steel was evaluated in different sulphuric acid and the acid chloride concentrations. Corrosion inhibition of the tested samples in 1M H_2SO_4 was evaluated using potassium dichromate of different concentrations. The experiments were performed at ambient temperature using potentiodynamic polarization measurement. This paper reports the observed electrochemical response of the tested samples in the strong acid environments. Potentiodynamic polarization resistance technique was used to estimate the corrosion rate, the polarisation resistance and inhibition of the alloy samples tested. The results obtained showed some varied magnitude of corrosion susceptibility for the stainless steel at the different H_2SO_4 concentrations and also in the acid chloride test media. Corrosion inhibition of the tested samples was effectively achieved using the potassium dichromate inhibitor.

Keywords: Martensitic stainless steel, corrosion, polarization, sulphuric acid, potassium dichromate, inhibition.

INTRODUCTION

The need to gain more knowledge about the electrochemical corrosion reactions behaviour phenomena and the control and hence appropriate and better application/use of martensitic stainless steel has been of keen interest to corrosion researchers in recent time. Selection of materials for good performance in service and in the fabrication of equipment, components, applications and in the construction of industrial plants for the manufacture of acids, chemicals and their derivatives, is significantly important in ensuring the long life, dependability, serviceability, reliability, safety and economic viability of plants and industrial components. Several authors have reported on research studies using martensitic stainless steels in corrosion and protection [1-8].

Martensitic stainless steels can be high or are low carbon steels built around the Type 410 composition of iron, 12% Cr, and 0.12% C. They are usually tempered and hardened. Tempered martensitic stainless steel gives the steel good hardness and high toughness [9]. They are specific type of stainless steel alloys. They are a vital part of the stainless steel group of metallic alloys although not used in large quantities compared to austenitic and ferritic grades [10], These steel alloys possess combination of strength, toughness and moderate corrosion resistance characteristics which make them ideal for a wide range of applications. In comparison with the austenitic and ferritic grades of stainless steels, martensitic stainless steels are less resistant to corrosion. However, with at least 11.5% chromium, they are genuine stainless steels giving a significantly improved corrosion resistance compared to low alloy steels [11].

Martensitic stainless steels are used for surgical and dental instruments, wire, springs, blades, fasteners, gears and ball bearings. They are also used in the petrochemical industry for steam and gas turbines. The combination of high strength, good toughness and moderate corrosion resistance allow these steels to be used in a wide variety of applications including: razor strip, blades and cutting tools, surgical instruments, gears, valves, pumps, shafts, offshore oil and gas components, bearings, mixers and stirrers, turbine parts, and aerospace [12].

Sulphuric acid, the test medium in this work, is a highly corrosive, strong mineral acid with many industrial uses. Molecule of sulphuric acid, H_2SO_4 has more than one ionisable hydrogen atoms and is thus called polyprotic acid. The ionisation of this acid occurs in two steps, with the molecule losing one proton at a time [13]:

$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$
$$HSO_4^- \rightleftarrows H^+ + SO_4^{2-}$$

Sulphuric acid, H_2SO_4, which is a strong acid, is fully dissociated, and all the displaceable hydrogen in the acid is present in solution as hydrogen ion, H^+.

$$H_2SO_4 \quad ==> \; H^+ \; + \; SO_4$$
$$100\% \text{ as } H^+$$

Its complete dissociation enhances more reactive corrosion reactions. Sulphuric acid is a powerful protonating agent. It is also a moderately strong oxidizing agent. The acid is also a powerful dehydrating agent. In dilute solution, sulphuric acid is a strong dibasic acid forming two series of salts[14]. Its multifarious use in diverse areas of industry accounts for its being selected for use in this work.

Apparently, more sulphuric acid is produced than any other chemicals in the world [15]. 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[16]. 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[17]. Sulphuric acid at high concentrations is frequently the major ingredient in acidic drain cleaners[18].

This work investigates the corrosion resistance reactions phenomena of 12Cr martensitic stainless steel in varied concentrations of H_2SO_4. The higher concentrations of the acid were deliberately used to enhance more intense corrosion reactions. Potassium dichromate, a well- known chemical inhibitor was also intentionally chosen with the anticipation that a positive result might achieved. The acid test medium was further contaminated in part with sodium chloride (NaCl) at all the concentrations of H_2SO_4 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 and its corrosion inhibition. It also aims at determining its viable usefulness in this likely industrial and work environments.

EXPERIMENTAL SECTION

The composition of the martensitic stainless steel used in this experimental investigation is presented in Table 1. The samples in plate form (10mm wide and 10mm long) 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. For the monitoring, 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 test samples in plate form (10mm wide and 10mm long) used for this investigation were mounted in araldite resin and each connected with a flexible wire connection. They were further ground and polished to fine diamond (1μm) as mentioned above. The experiments were conducted in three different concentrations of sulphuric acid (H_2SO_4) and the acid contaminated with 3.5% sodium chloride, Table 2. All the chemicals used, were of the analytic reagent grade (AR). Potassium dichromate was used to evaluate the corrosion inhibition of the tested samples in 1M H_2SO_4.

Table 1: Spectrometer chemical composition of 12Cr martensitic stainless steel

Element	C V	Mn	Si	P	Mo	N	Ni Cr	Fe
Composition	0.197 0.32	0.66	0.18	0.022	1.63	0.0380	2.81 11.7	Balance

Table 2:Test Environments

Sulphuric acid, H_2SO_4	**H_2SO_4 + 3.5% NaCl**
1 M	1 M
3 M	3 M
5 M	5M

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.

SEM/EDS Characterisation

Some of the test samples of the martensitic stainless steel were separately examined for surface morphology, with the scanning electron microscope (SEM) equipped with the energy dispersive spectroscopy (EDS). SEM micrographs were made, Figs.8-10

RESULTS AND DISCUSSION

1M H_2SO_4 and 1 M H2SO4 + 3.5% NaCl test environment

The summary of the results obtained for all the result parameters used in the analysis of this work are given in Table 3. The results of the potentiodynamic potentiostatic polarization curves for the test specimens used respectively in 1M H_2SO_4 and the 1M H_2SO_4 + 3.5% NaCl test media are presented in Figures 1 and 2. The Ecorr value for the test in 1M H_2SO_4 was -0.41635V; the corrosion current density was 0.006334 A/cm^2; the polarization resistance, Rρ, was 139.21Ω and with a corrosion rate (CR) of1.3178V. Clearly, these results show very active corrosion reactions of the test samples in the test environments. With the addition of 3.5% NaCl to the H_2SO_4 test solution, the corrosion rate value obtained was 2.7275 mm/yr; the Ecorr value was -0.72602V; the polarization resistance, Rρ, was0.9624Ω and the corrosion current density was 0.007086 A/cm^2. The corrosion reactions here were that of severe corrosion. The H_2SO_4 dissociation ($H^+ + SO_4^{2-}$) and that of the NaCl ($Na^+ + Cl^-$) had no hindrance. It was a complete dissociation that gave the chemicals complete solubility and hence the apparent intense active corrosion reactions and the corrosion of the martensitic stainless steel. The acid chloride clearly, gave more active corrosion reactions and this could be due to the presence of chloride ions.

Table 3: Polarization results for the tests in H_2SO_4 and H_2SO_4 + NaCl environments

Sample	**i_{corr}(A)**	**ba**	**Bc**	**I_{corr} (A/cm^2)**	**R_P (Ω)**	**E_{corr} (V)**	**CR(mm/yr)**
1M H_2SO_4	0.006334	-	-	0.006334	139.21	-0.41635	1.3178
1M H2SO4 +3.5% NaCl	0.007086	-	-	0.007086	0.9624	-0.72602	2.7275
3M H_2SO_4	$9.27x10^{-4}$	0.2467	0.1478	$9.27\ x10^{-4}$	$4.30\ x10^{1}$	-0.4200	0.019
3M H_2SO_4 +3.5% NaCl	$8.29x10^{-5}$	0.0591	0.1598	$8.29\ x10^{-5}$	$2.26\ x10^{2}$	-0.3458	0.538
5M H_2SO_4	$2.39x10^{-3}$	0.3764	0.2340	$2.39\ x10^{-3}$	$2.60\ x10^{1}$	-0.4356	3.556
5M H_2SO_4+ 3.5% NaCl	$3.18x10^{-4}$	0.0815	0.1351	$3.18\ x10^{-4}$	$6.90\ x10^{1}$	-0.3826	2.064

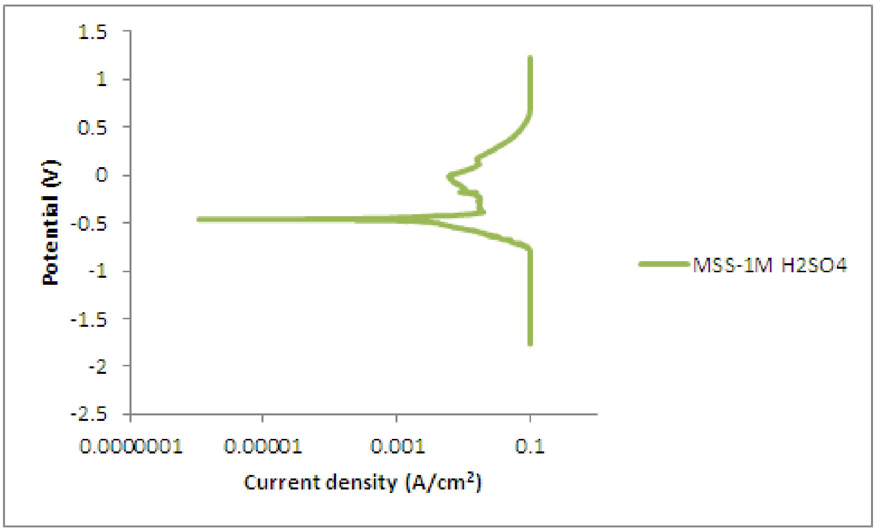


Figure 1.Polarization curve of martensitic stainless steel in 1M H_2SO_4

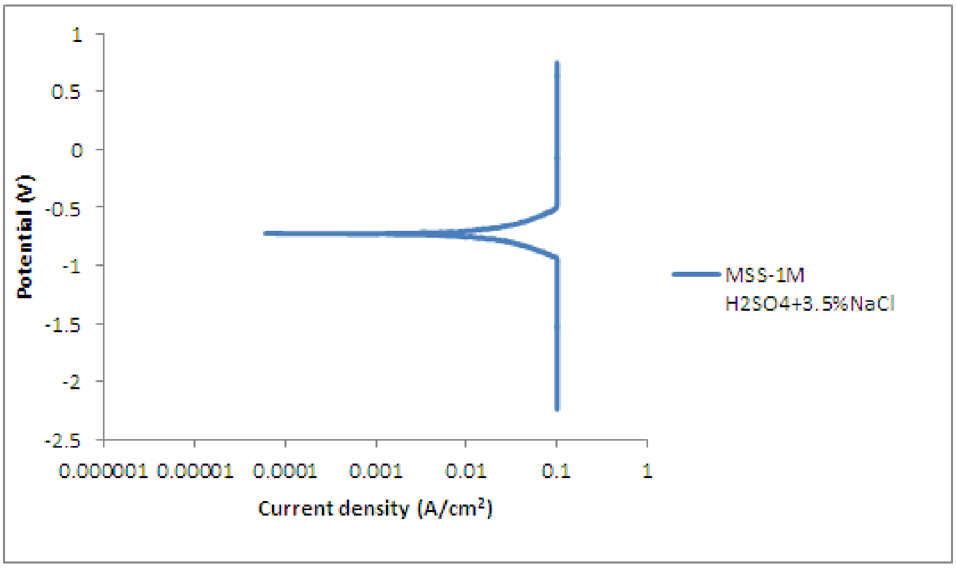


Figure 2.Polarization curve of martensitic stainless steel in 1M H_2SO_4 + 3.5% NaCl

3M H_2SO_4 test and 3M H_2SO_4 + 3.5% NaCl test environments

The polarization curves for the test specimen performed in 3M H_2SO_4 and the H_2SO_4 + 3.5% NaCl are presented in Figs. 3 and 4 respectively. Table 3 shows the results for these tests in the test environments. For the test reported in Fig. 3 for 3M H_2SO_4 alone, the Ecorr value as indicated in the Table was -0.4200 V, a relatively active corrosion reactions value.

The corrosion rate value obtained in this test medium was 0.019 mm/yr which gave increased corrosion rate, particularly when compared with the value of1.3178 mm/yr obtained for the test in 1M H_2SO_4 as given in Table 3. The recorded corrosion density was 9.27 $x10^{-4}$A/cm^2; and the polarization resistance was 4.30 $x10^1$ Ω. When compared with the 1M H_2SO_4 test results, the corrosion density decreased in value; there was decrease in polarization resistance; the open corrosion potential was slightly more negative in value; and the corrosion rate decreased significantly. However, with the addition of 3.5% NaCl, a different result was obtained. Here, the corrosion density (Icorr), 8.29 $x10^{-5}$ decreased and the polarization resistance (Ω), 2.26 $x10^2$, increased; the corrosion rate increased significantly at a value of 0.538 mm/yr. Also, there was decrease in the Ecorr with a recorded value of -0.3458V.

The addition of NaCl to the sulphuric acid, usually called acid chloride contributed to the breaking down of the steel's passive film that led to the anodic dissolution of the test electrode surface. Sulphuric acid reacts with sodium chloride to give hydrogen chloride gas (which in solution becomes hydrochloric acid) and sodium hydrogen sulphate:

$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

The dissociation of this reaction in solution gives sulphate ion and chloride ions – the two potent reacting species that promote active corrosion reactions.

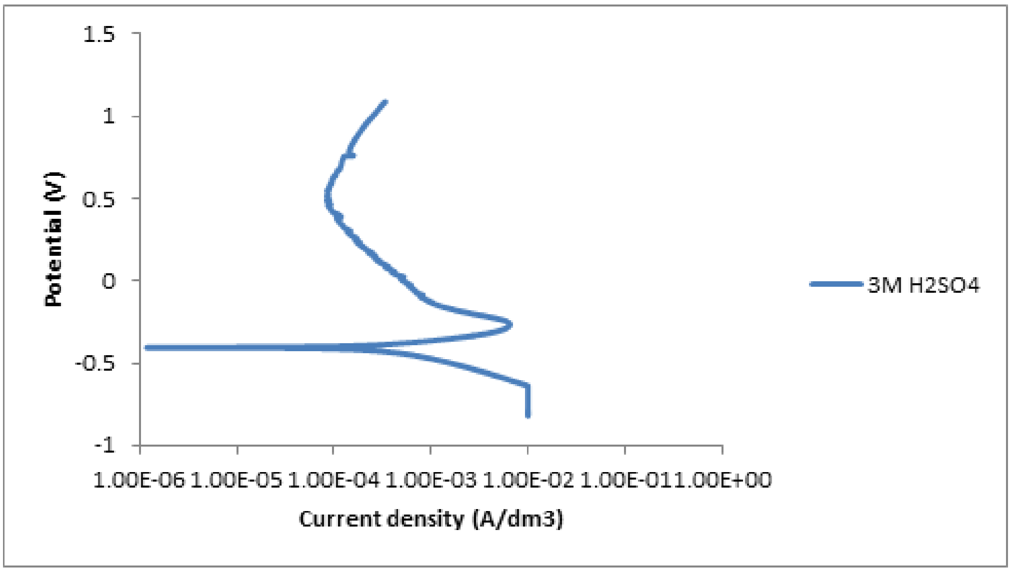


Figure 3.Polarisation curve of martensitic stainless steel in 3M H_2SO_4

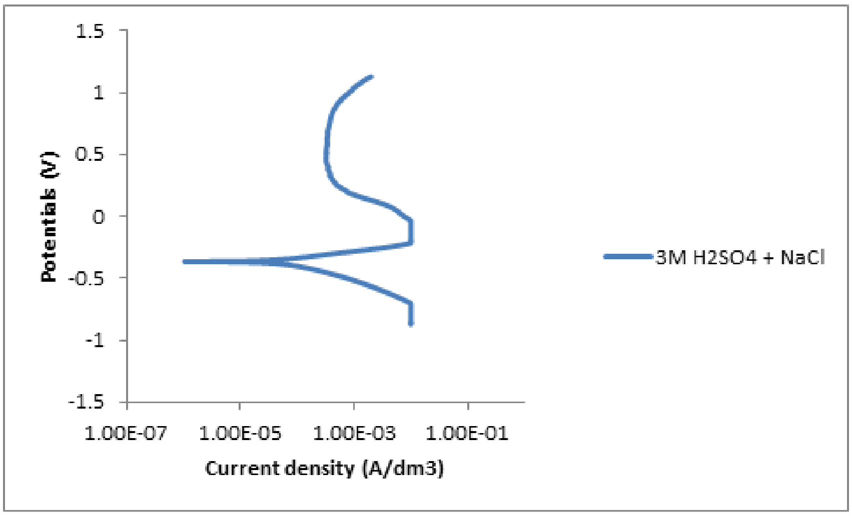


Figure 4.Polarisation curve of martensitic stainless steel in 3M H_2SO_4 + 3.5 NaCl

5M H_2SO_4 and 5M H_2SO_4 + 3.5% NaCl test environments

The potentiodynamic polarization corrosion curve of the martensitic stainless steel in 5M H_2SO_4 alone, presented in Figure 5, gave an open corrosion potential (OCP), Ecorr value of -0.4356 V. This medium had the highest molarity and hence the most concentrated but without added NaCl. From the Table 3, a polarisation resistance, Rρ, value of

2.60 x10^1 Ω; corrosion rate of 3.556 mm/year and current density of 2.39 x10^{-3} (A/cm^2), in addition to the OCP values stated above, showed active corrosion reactions that persisted throughout the monitoring period. The above results data changed with the use of the acid chloride, Fig. 6, that is, 5M H_2SO_4 + 3.5% NaCl. The polarization resistance, Rρ, value increased to 6.90 x10^1 Ω; and likewise the Ecorr value (-0.3826 V). The corrosion rate decreased to 2.664 mm/yr; and so also the current density value, 3.185x10^{-4} A/cm2. All these indicate comparative decrease in electrochemical active corrosion reactions. This was due to the oxidizing characteristic of the acid at high concentrations which tended to stifle the active corrosion reactions.

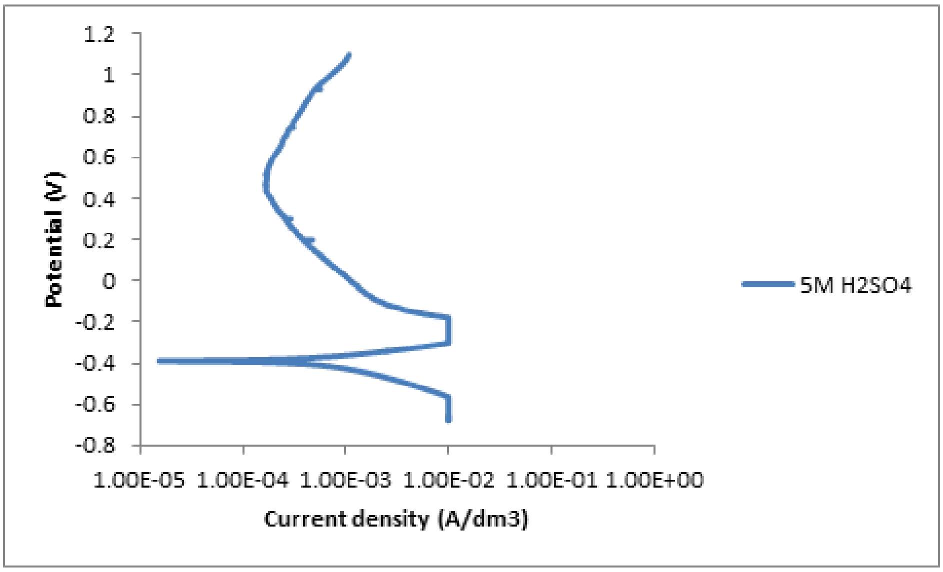


Figure 5.Polarization curve of martensitic stainless steel in 5M H_2SO_4

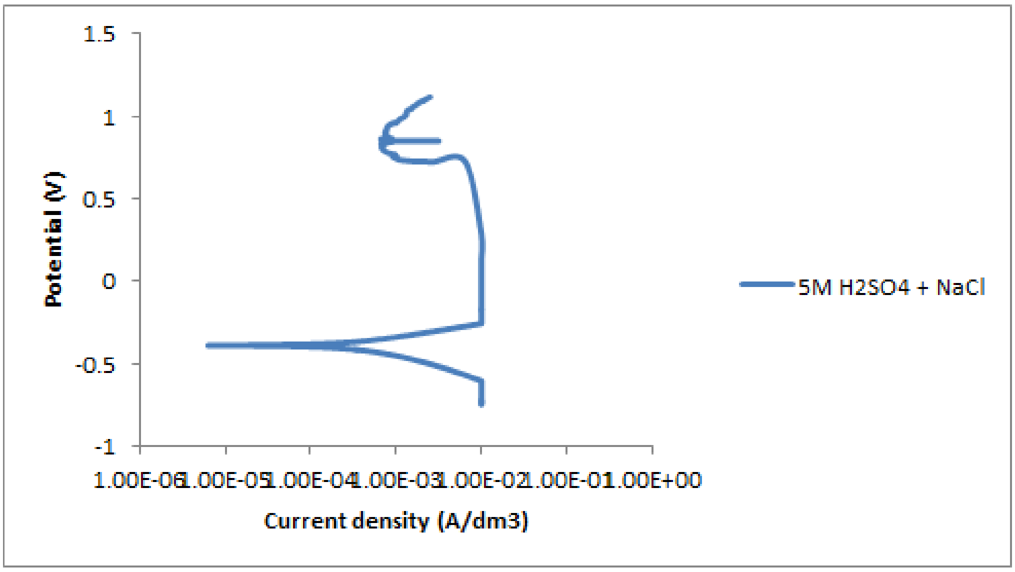


Figure 6.Polarization curve of martensitic stainless steel in 5M H_2SO_4 + 3.5% NaCl

In general, the tested martensitic stainless steel was susceptible to corrosion in the sulphuric acid which is a strong acid; and the susceptibility was further enhanced by the relatively high concentrations used as the test media. Corrosion was found to increase with the addition of NaCl to the acid. A further availability of the chloride ion reacting species increased the active corrosion reactions.

Inhibition of martensitic stainless steel in 1M H_2SO_4 medium

Presented in Fig. 7, are the potentiodynamic polarisation results obtained from the various concentrations of potassium dichromate inhibition of the martensitic stainless steel. The results obtained are also given in Table 4. Apart from the control experiment which was the test without the added inhibitor, the other tests contained the $K_2Cr_2O_7$ concentrations of: 0.5, 1.0, 1.5 and 2.0g respectively.

From Fig. 7 and Table 4, it is clear that the use of different concentrations of the inhibitor gave different results in terms of open circuit potential, Ecorr (V) though very close in potential values. Similarly, the corrosion rates (CR), polarisation resistance, Rρ (Ω), and corrosion current density, Icorr (A/cm^2), gave different results as explained below. The control experiment (test without inhibitor) did not only exhibit the highest corrosion rate (1.31780 mm/yr) but also had the lowest corrosion resistance (108.12Ω) and the highest corrosion current density 0.006334 A/cm^2) values. These values showed intense corrosion of the tested metal sample in the acid test environment without the use of the inhibitor.

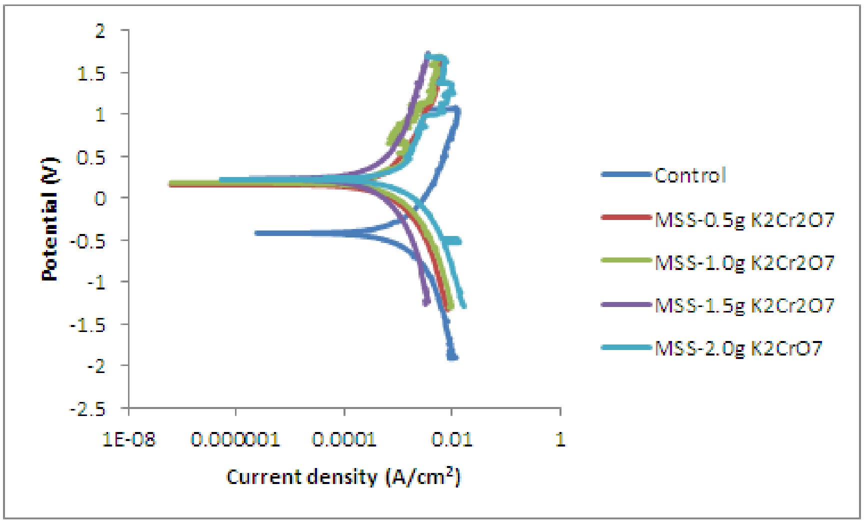


Figure 7: Polarisation curves of K_2CrO_7 inhibition of martensitic stainless steel in 1M H_2SO_4

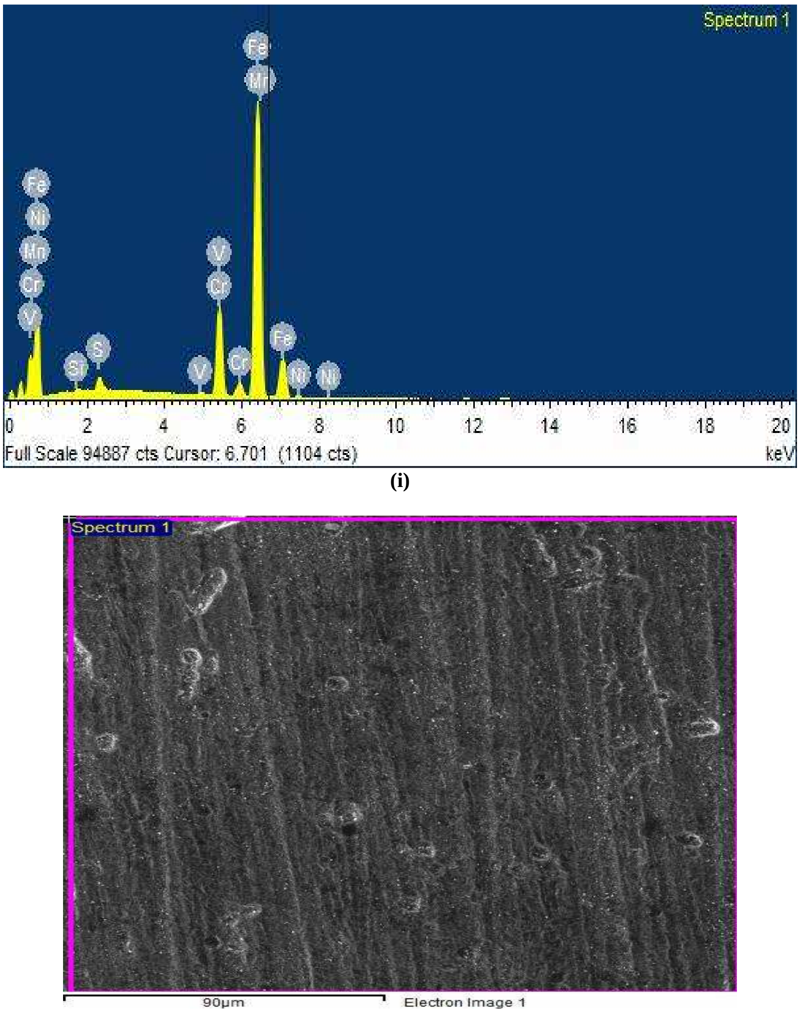
Table 4. Polarization results for the $K_2Cr_20_7$ inhibition tests in H_2SO_4

Sample	**Ecorr, Obs (V)**	**jcorr (A/cm²)**	**CR (mm/year)**	**Rp (Ω)**
Control	-0.41635	0.006334	1.31780	108.12
0.5g $K_2Cr_2O_7$	0.16145	0.000522	0.10859	444.47
1.0g $K_2Cr_2O_7$	0.18809	0.001269	0.26407	443.70
1.5g $K_2Cr_2O_7$	0.22788	0.002649	0.55112	139.21
2.0g $K_2Cr_2O_7$	0.18952	0.001788	0.37194	247.86

In these experimental tests, using the inhibitor, the lowest corrosion reactions were shown by the test with the 0.5g and 1.0g potassium dichromate, $K_2Cr_2O_7$respectively (Table 4).The inhibitor concentration of 0.5g $K_2Cr_2O_7$ gave the lowest corrosion rate, 0.10859 mm/yr; the highest corrosion resistance, 444.47Ω; the lowest corrosion current density, 0.000522 A/cm^2 values and lowest potential value of open corrosion potential (Ecorr), 0.16145V. These results showed indeed, appreciable magnitude of corrosion protection of the test electrode in the H_2SO_4environment with the use of the inhibitor.

SEM/EDS

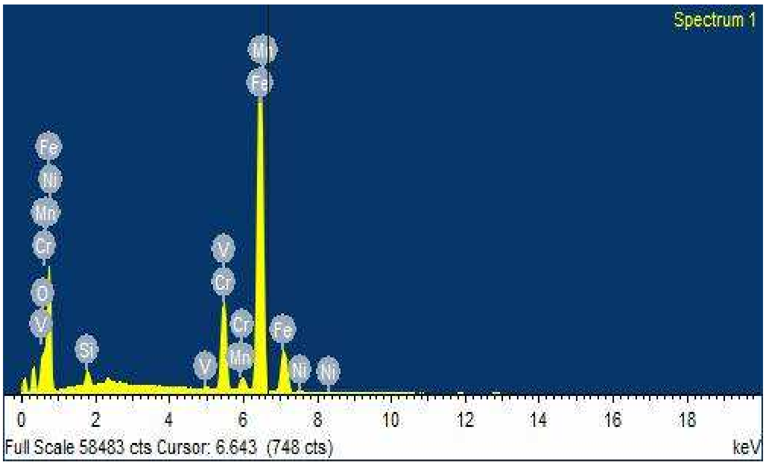
Presented in Figures 8 and 9 respectively are the results obtained for the SEM/EDS characterisation of the selected test samples.



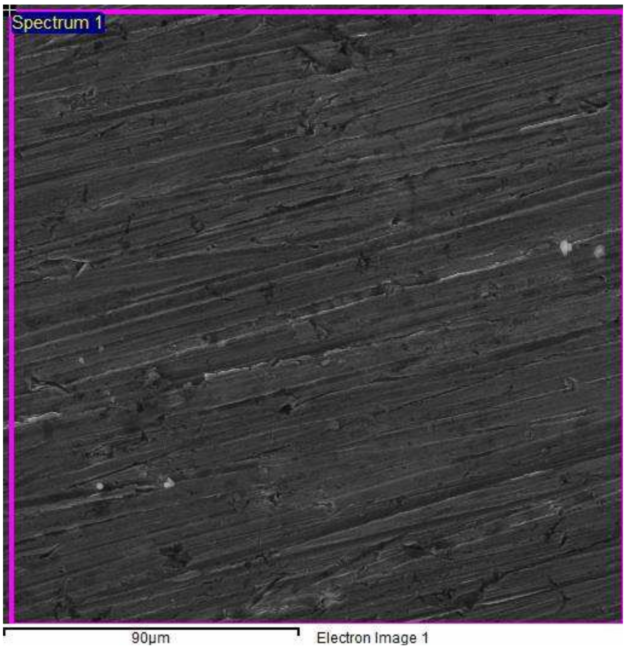
(i)

(ii)

Figure 8: EDS analysis and SEM micrograph of the uninhibited martensitic stainless steel in 1M H_2SO_4



(i)



(ii)

Figure 9: (i) EDS analysis and (ii) SEM micrograph of martensitic stainless steel in 1M H_2SO_4 with 1.5 K2Cr2O7 in1M H_2SO_4

In Fig. 8 (i), the EDS analysis confirmed the surface presence of Fe, Mn, Cr, V, and in lesser amounts, of S, Si and Ni. The surface feature of the test sample, Fig.8 (ii), was rough with grooves and corrosive degradation. In this test, the sample had no added inhibitor.

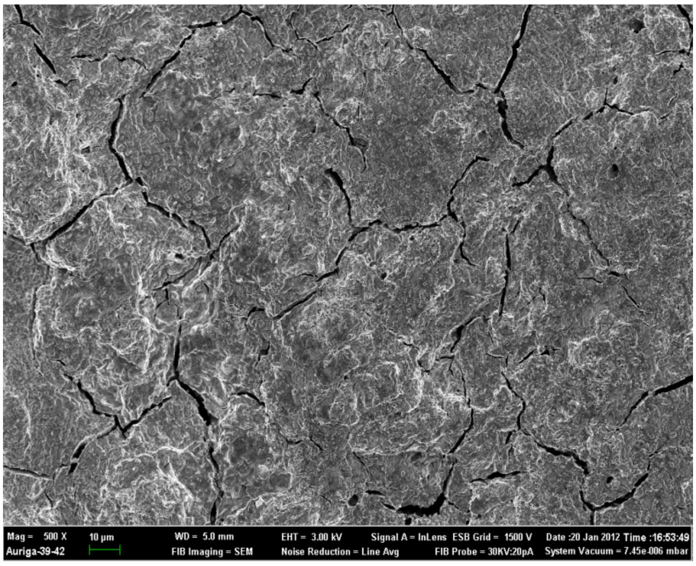


Figure 10. SEM micrograph of the steel sample surface immersed in 3M H_2SO_4 + 3.5% NaCl

In the test with the addition of $K_2Cr_2O_7$ inhibitor, Fig. 9 (i) shows the EDS analysis while Fig 9 (ii) shows the surface morphology of the selected test sample. The EDS analysis confirmed the presence of elements as presented in Fig. 8 (i) except the trace presence of Ni. There was the presence of Cl from NaCl. Figure 9 (ii) shows the smooth surface of the test samples with no apparent evidence of corrosion. This thus confirms the effectiveness of potassium dichromate inhibitor and even in all the concentrations used in the experiments.

The severely damaged surface of a representative sample immersed in 3M H_2SO_4 + 3.5% NaCl is presented in Fig. 10. It confirms the anodic dissolution corrosion reactions of the tested specimen in the strong acid without inhibitor after 6 hours.

CONCLUSION

1. Martensitic stainless steel was susceptible to corrosion in strong H_2SO_4 test environments.
2. Corrosion severity of the test electrodes, in general, increased with increase in molarity of the H_2SO_4 concentrations.
3. The susceptibility of the martensitic stainless steel test specimens to corrosion reaction was increased when the H_2SO_4 + NaCl solutions were used.
4. Very good and effective corrosion protection of the test electrodes (martensitic steel specimens) in the H_2SO_4 environment was achieved with the use of the $K_2Cr_2O_7$ at all the concentrations of the inhibitor used, but more significantly at the concentration of 0.5 Kg/L

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