Electrochemical corrosion resistance and inhibition behaviour of martensitic stainless steel in hydrochloric acid

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ABSTRACT

Corrosion resistance behaviour of 12Cr martensitic stainless steel was evaluated in different hydrochloric acid and the acid chloride concentrations. Corrosion inhibition of the tested samples in 1M HCl was also evaluated using potassium dichromate. 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, the polarisation resistance and inhibition 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. Effective corrosion inhibition was also exhibited on the tested samples.

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

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INTRODUCTION

The increasing use of stainless steels in different environments and under different conditions necessitates the increased research interest in these groups of unique steels with particular attention to their performance, usability and viability in service. 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. Stainless steels may be classified by their crystalline structure into three main types: *Austenitic*, *Ferritic* and *Martensitic*. Several authors have reported on research studies using martensitic stainless steels in corrosion and protection [1-8].

Martensitic stainless steel is a specific type of stainless steel alloy.Martensitic stainless steels can be high or are low carbon steels built around the Type 410 composition of iron, 12% chromium, and 0.12% carbon. They are usually tempered and hardened. Tempered martensite gives steel good hardness and high toughness [9].Their combination of strength, toughness and moderate corrosion resistance makes them ideal for a wide range of applications. Since their invention, stainless steelshave come to be a vitally important material, its anti-corrosive qualities making it perfect for use in a huge range of different environments and circumstances.

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Martensitic stainless steels are similar to low alloy or carbon steels, having a structure similar to the ferritic steels. However, due to the addition of carbon, they can be hardened and strengthened by heat treatment, in a similar way to carbon steels. The main alloying element is chromium, typically 12 to 15%, molybdenum (0.2-1%), no nickel, except for two grades, and 0.1-1.2% carbon.Their structures are "body-centered tetragonal" (bct), and they are classed as a "hard" ferro-magnetic group [10]. In the annealed condition, they have tensile yield strengths of about 275 MPa and so they are usually machined, cold formed, or cold worked in this condition.

Optimum corrosion resistance is attained in the heat-treated i.e. hardened and tempered condition. 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 grades of stainless steels can be developed with the addition of nitrogen and nickel but with lower carbon levels than the traditional grades. These steels have improved toughness, weldability and corrosion resistance.

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]. Many of these applications are widely made open which probably explains why martensitic stainless steels do not have a prominent public profile. It is good, however, to make it known that much of our modern world rests on martensitic stainless steels.

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^+ [13-14].

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$
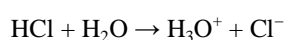
The other ion formed is Cl^-, the chloride ion. Hydrochloric acid is a strong acid, since it is essentially completely dissociated in water [13-14]. It is the most difficult of the common acids to handle from the standpoints of corrosion and materials of construction. This acid is very corrosive to most of the common metals and alloys [15]. 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 [16]. 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 [17].

Potassium dichromate used as inhibitor in this research work is not new in corrosion inhibition application. However, its use for this alloy in such HCl concentrations seems new. The inhibitor is a passivating type of inhibitor and does not require oxygen to be effective. Passivating inhibitors are known to increase the rate of anodic passivation to the extent that the anodes are polarized to a positive potential [18-19].

This work looks at the corrosion resistance reactions phenomena of 12Cr martensitic stainless steel in varied concentrations of HCl and under some potassium dichromate chemical inhibitor concentrations.The inhibitor had been previously used effectively in other related corrosion inhibition research [20 - 22]. 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.

MATERIALS AND METHODS

Martensitic stainless steel, with the composition as presented in Table 1was used in this investigation. The samples in plate form (10mm wide and 10mm long) were mounted in araldite resin and connected with a flexible wire

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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 experiments 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 were conducted in three different concentrations of hydrochloric acid (HCl) and the acid contaminated with 3.5% sodium chloride, Table 2. All the chemicals used, were of the analytic reagent grade (AR). Corrosion inhibition of the tested samples in 1M HCl was also evaluated using potassium dichromate.

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

Element	C	V	Mn	Si	P	Mo	N	Ni	Cr	Fe
Composition	0.197	0.3.	0.66	0.18	0.022	1.63	0.0380	2.81	11.7	Balance

Table 2.Test Environments

Hydrochloric acid, HCl	HCl + 35 g/L NaCl (3.5%)
5 M	5 M
3 M	3 M
1 M	1M

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 uninhibited and inhibited 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). Some SEM micrographs were made.

RESULTS AND DISCUSSION

3.1. 5 M HCl test environment
Table 3 shows the summary of the results obtained for all the result parameters used in the analysis of this work. The results of potentiostatic polarization curves for the test specimen used respectively in 5M HCl and the 5M HCl + 3.5% NaCl test media are presented in Figures 1 and 2. In Fig.1, the polarization corrosion curve of the martensitic stainless steel in 5M HCl alone, gave an open corrosion potential (OCP), Ecorrvalue of -0.4191 V. This medium had the highest molarity and hence the most concentrated but without added NaCl. From the Table, a polarisation resistance, Rρ, value of 9.70×10^1 Ω; corrosion rate of 1.579 mm/year and current density of 2.43×10^{-4} (A/cm^2), in addition to the OCP values stated above, showed active corrosion reactions that persisted throughout the monitoring period. 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, 5M HCl + 3.5% NaCl. The polarization resistance, Rρ, value was lowered to 4.02×10^2 Ω; and likewise the Ecorr value (-0.3603 V). The corrosion rate decreased to 0.314 mm/yr; and so also the current density value, 4.85×10^{-5} A/cm2. All these indicate comparative decreasein electrochemical active corrosion reactions. The chloride ions, Cl-, from the sodium chloride in combination with the dissociated Cl$^-$ from HCl did not increase the active corrosion reactions but rather decreased it. This was due to the less solubility of HCl at high concentrations and hence less dissociation of the acid into H$^+$ + Cl$^-$ when in combination with NaCl.

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

Sample	i_{corr}(A)	I_{corr} (A/cm^2)	R_P (Ω)	E_{corr} (V)	CR (mm/yr)
1M HCl	0.000957	0.000957	821.81	-0.55931	1.3933
1M HCl + 3.5%NaCl	0.033982	0.033982	2.1788	-0.82085	3.5351
3M HCl	2.44×10^{-4}	2.45×10^{-4}	8.60×10^1	-0.3811	1.585
3M HCl +3.5% NaCl	2.29×10^{-5}	2.29×10^{-5}	6.76×10^2	-0.3650	0.148
5M HCl	2.43×10^{-4}	2.43×10^{-4}	9.70×10^1	-0.4191	1.579
5M HCl + 3.5% NaCl	4.85×10^{-5}	4.85×10^{-5}	4.02×10^2	-0.3603	0.314
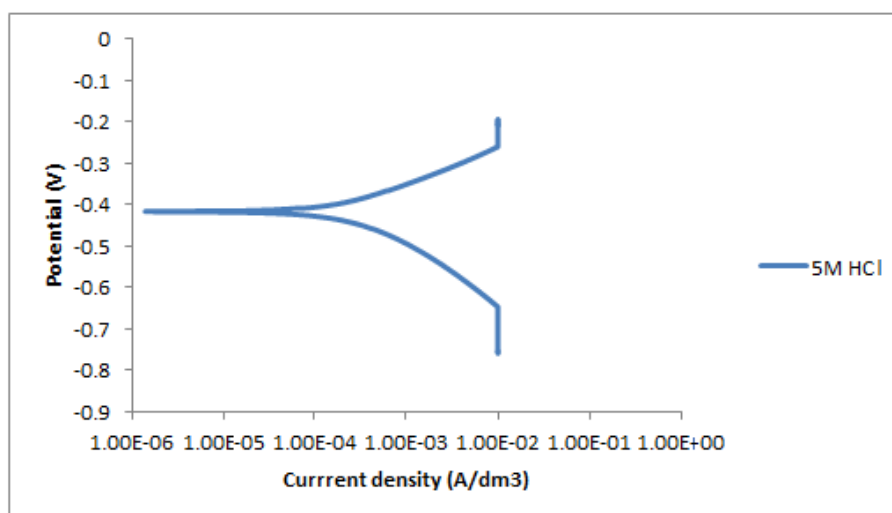
Figure 1.Polarization curve of martensitic stainless steel in 5M HCl
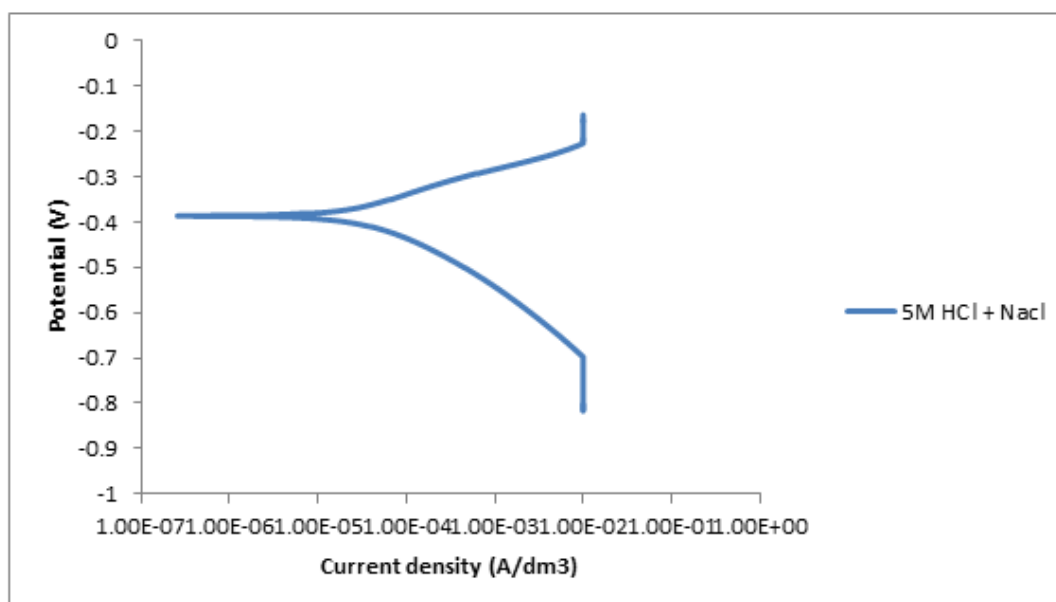
Figure 2.Polarisation curve of martensitic stainless steel in 5M HCl + 3.5% NaCl

3.2. 3 M HCl test and 3M HCl + 3.5% NaCl test environments
The polarization curves for the test specimen performed in 3M HCl and the HCl + 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 (3M HCl) alone, the Ecorr value as indicated in the Table was -0.3811 V, a relatively active corrosion reactions value.
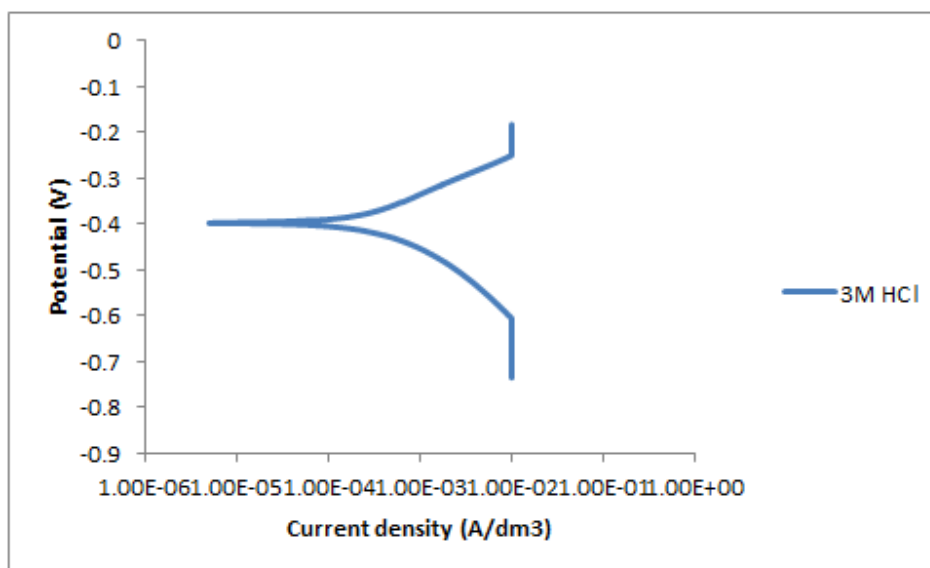
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Figure 3.Polarisation curve of martensitic stainless steel in 3 M HCl
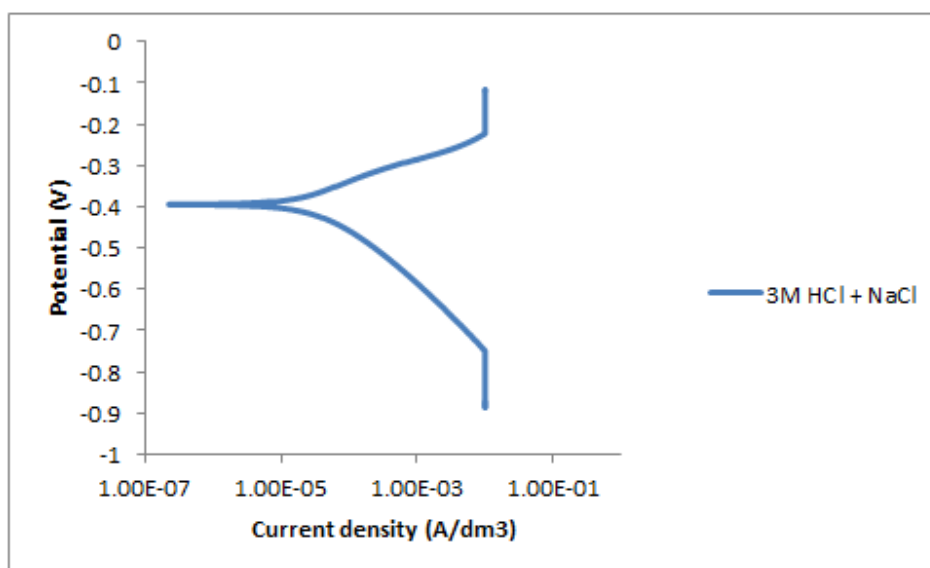

Figure 4.Polarisation curve of martensitic stainless steel in 3M HCl and 3MHCl + 3.5%NaCl

The corrosion rate value obtained in this test medium was 1.585 mm/yr which gave increased corrosion rate, particularly when compared with the value of. 1393 mm/yr obtained for the test in 1M HCl as given in Table 2. The recorded corrosion density was 2.45 x 10^{-4} A/cm^2; and the polarization resistance was 8.6 x 10^1Ω.When compared with the 5M HCl test results, the corrosion density was about the same value; there was decrease in polarization resistance; the open corrosion potential was more active; and the corrosion rate increased very slightly. However, with the addition of 3.5% NaCl, a different result was obtained. Here, the corrosion density (Icorr), 2.29 x 1010^{-5} decreased and the polarization resistance (Ω), 6.76 x 10^2, increased; the corrosion rate decreased significantly at a value of 0.148 mm/yr.Also, there was decrease in the Ecorr with a recorded value of -0.3650V. The dissociated chloride ions (Cl-) was therefore far more in 3M than in 3 M HCl + 3.5%NaCl due to the lower solubility of the HCl/NaCl in the solution and hence the less the active corrosion reactions.

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3.3. 1M HCl and 1 M HCl + 3.5% NaCl test environment
The polarization curve for the test specimen performed in 1M HCl and the 1M HCl + 3.5% NaCl are presented in Figs. 5 and 6 respectively. The summary of the results for these tests in these environments are presented in Table 2. The Ecorr value for the test in 1M HCl was -0.55931V; the corrosion current density was 0.000957 A/cm^2; the polarization resistance, Rρ, was 821.81Ω and with a corrosion rate (CR) of1.3933V.
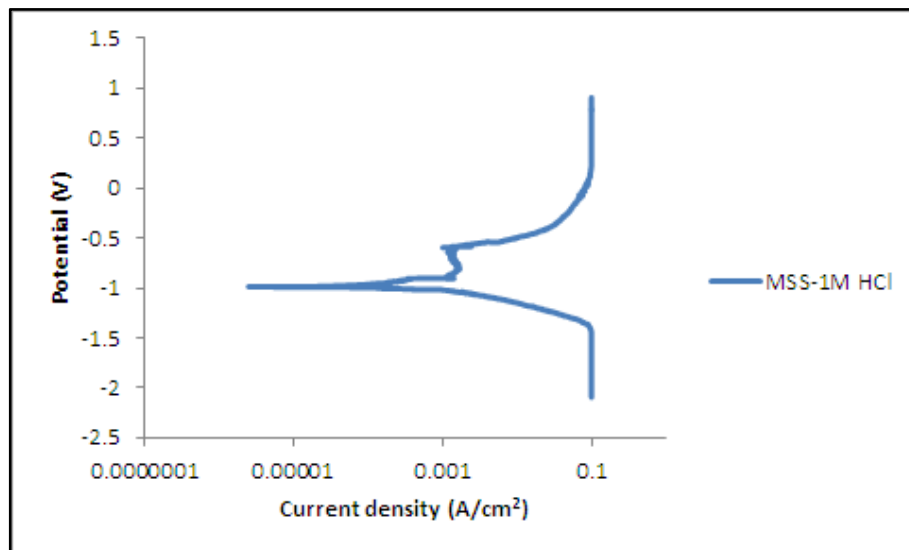
Figure 5.Polarisation curve of martensitic stainless steel in 1M HCl

These results show the very active corrosion reactions in these tests as presented in Table 2. With the addition of 3.5% NaCl to the HCl test solution, the corrosion rate value obtained was 3.5351 mm/yr; the Ecorr value was -0.82085V; the polarization resistance, Rρ, was2.1788 Ω and the corrosion current density was 0.033982 A/cm^2. The corrosion reactions here were that of severe corrosion. The HCl dissociation here (H$^+$ + Cl$^-$) 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.
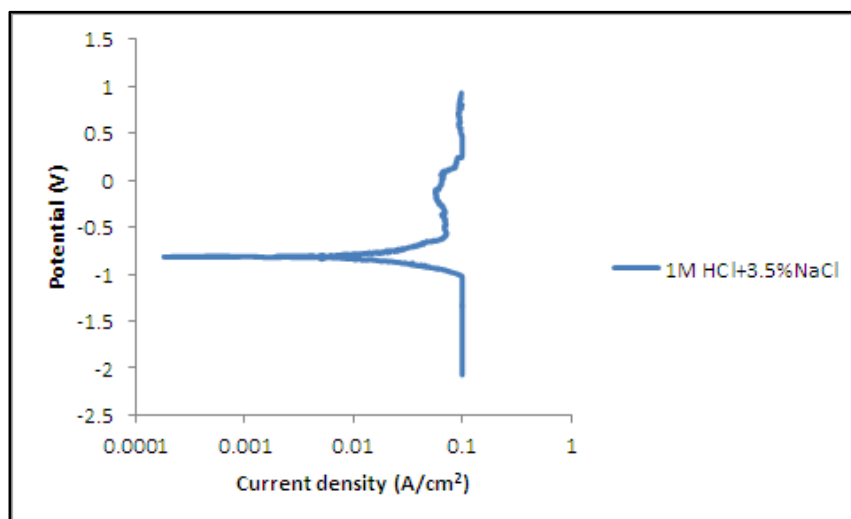

Figure 6.Polarisation curve of martensitic stainless steel in 1M HCl and 1M HCl + 3.5% NaCl

The overall corrosion trend from all the results above is that for all the tests in HCl alone, the corrosion severity increases with increase in molarity of the acid, thus 5M HCl >3M HCl >1M HCl. With the use of HCl + NaCl, the

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reverse was the case; the corrosion reactions severity was reversed thus: 1M HCl >3M HCl >5M HCl or 5M HCl< 3MHCl <1M HCl.

In general, due to the 'common ion effect' of the reactions between HCl and NaCl, there is no particular end reaction due to the common Cl⁻ ion. Addition ofHCl to solution of sodium chloride reduces the solubility of sodium chloride. The increased concentration of the acid at 5M apparently decreased the solubility of HCl/NaCl solution and hence reduction in corrosion reactions severity. The decreased solubility lowered the ionic dissociation of the chemicals.

3.4. Inhibition of Martensitic Stainless steelin 1M HCl medium
The potentiodynamic polarisation results obtained from the various concentrations of potassium dichromate inhibition of the martensitic stainless steel are presented in Fig. 7. The results obtained are also given in Table 4. Apart from the control experiment which was the test without inhibitor the other $K_2Cr_2O_7$ concentrations are: 0.5, 1.0, 1.5 and 2.0g respectively.
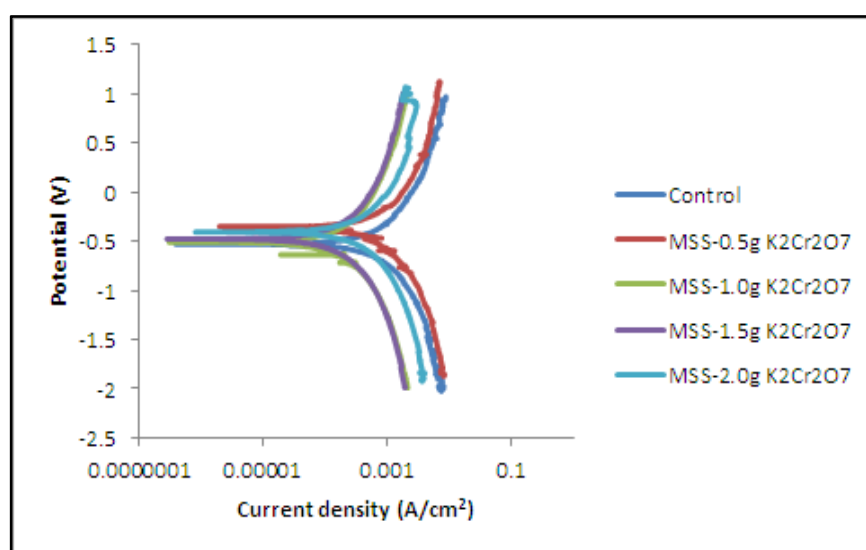

Figure 7: Polarisation curves of K_2CrO_7 inhibition of martensitic stainless steel in 1M HCl

It could be seen from Fig. 7 and Table 4, 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/cm²), give different results.

The control experiment (test without inhibitor) did not only exhibit the highest corrosion rate (0.76423 mm/yr) but also had the lowest corrosion resistance (403 Ω) and the highest corrosion current density 0.001079 A/cm²) values. These values showed intense corrosion of the tested metal sample in the acid test environment.

Table 4.Polarization results for the $K_2Cr_2O_7$ inhibition tests in HCl

Sample	Ecorr, Obs (V)	jcorr (A/cm²)	CR (mm/year)	Rp (Ω)
Control	-0.55931	0.001079	0.76423	403.69
0.5g $K_2Cr_2O_7$	-0.31732	0.000166	0.17225	880.88
1.0g $K_2Cr_2O_7$	-0.55932	0.000449	0.49330	735.12
1.5g $K_2Cr_2O_7$	-0.47790	0.000957	0.55233	821.81
2.0g $K_2Cr_2O_7$	-0.40720	0.000531	0.44878	865.01

In these experimental tests, using the inhibitor, the lowest corrosion reactions were shown by the test with the 0.5 Kg potassium dichromate, $K_2Cr_2O_7$.This inhibitor concentration gave the lowest corrosion rate, 0.17225 mm/yr; the highest corrosion resistance, 880.88 Ω; the lowest corrosion current density, 0.000166 A/cm² values and the least

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negative potential value of open corrosion potential (Ecorr), -0.31732V. These results showed indeed, appreciable magnitude of corrosion protection of the test electrode in the HCl environment with the use of the inhibitor.

Scanning Electron Microscopy/Energy Dispersive Spectroscopy Characterisation
The results obtained for the **S**canning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS) characterisation are presented in Figures 8 and 9 respectively. Inn Fig. 8 (i), EDS analysis confirmed the surface presence of Fe, Mn, Cr, V, less amount of S, Si and little presence of Ni. The surface feature of the test sample, Fig.8 (ii),was rough with grooves and corrosive damages. In this test, the sample had no inhibitor addition. In the test with the addition of inhibitor, Fig. 9 (i) shows the EDS analysis while Fig 9 (ii) shows the surface morphology. 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 and HCl.
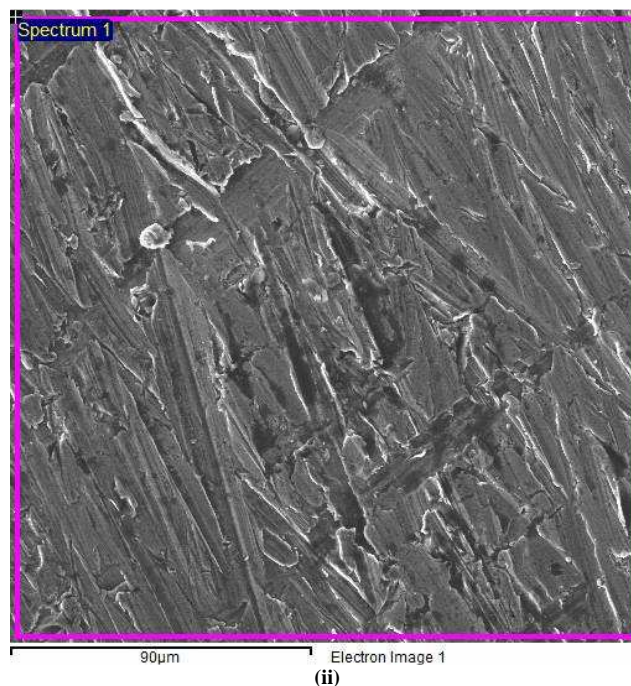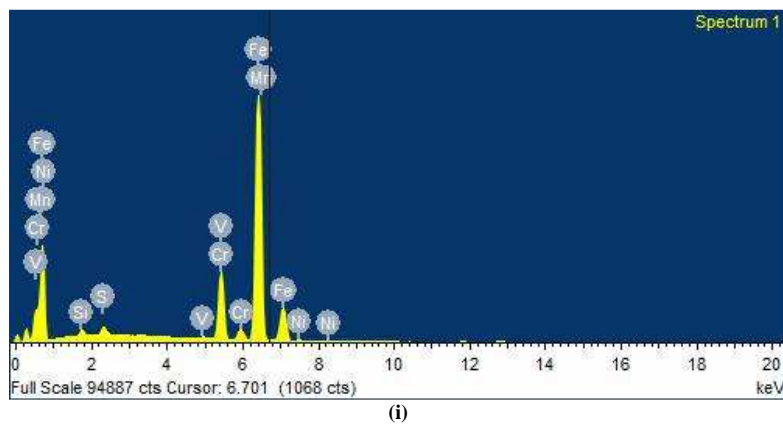

(i)

(ii)

Figure 8: EDS analysis and SEM micrograph of the uninhibited martensitic stainless steel in 1M HCl
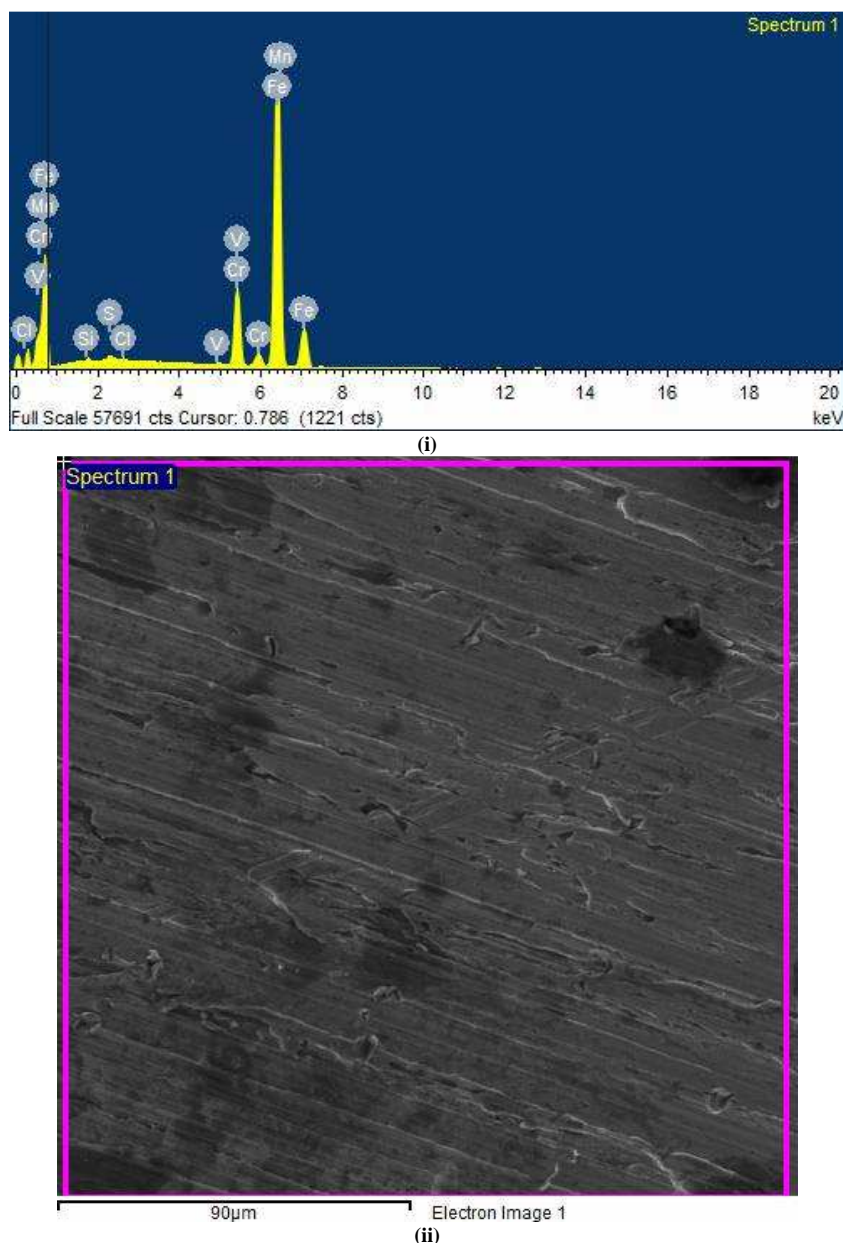
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(i)

(ii)

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

Figure 9 (ii) shows the smooth surface of the test samples with no apparent evidence of corrosion.

In summary, the mechanism by which chromate passivates steel has been studied extensively [18]. Like in this work, the inhibiting protection given by the $K_2Cr_2O_7$ on the tested steel could be said to be by a combination of adsorption and oxide formation on the steel surface. Adsorption helps to polarise the anode to sufficient potentials to form very thin hydrated ferric oxides which protect the steel.

CONCLUSION

1. Martensitic stainless steel suffered severe corrosion in strong HCl test environments.
2. Corrosion severity of the test electrodes increased with increase in molarity of the HCL concentrations.
3.The severity of the corrosion reactions of the martensitic stainless steel test specimens was reversed when the HCl + NaCl solutions were used. The corrosion severity decreasedwith increase in test solution molarity.

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4. Appreciable magnitude of corrosion protection of the test electrodes (martensitic steel specimens) in the HCl environment was achieved with the use of the $K_2Cr_2O_7$ inhibitor, particularly at the concentration of 0.5 Kg/L

Acknowledgement

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