

The effect of potassium dichromate inhibitor on the corrosion of stainless steels in sulphuric acid mixed with sodium chloride

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THE EFFECT OF potassium dichromate as an inorganic inhibitor on the corrosion behaviour of Types 316 and 304 austenitic stainless steels in dilute sulphuric acid mixed with sodium chloride was studied at ambient temperature. The experiments were performed using potentiodynamic polarization, and this paper reports the observed electrochemical response. Different concentrations of the inhibitor were used. The results obtained show the effective corrosion-control performance of the inhibitor at the optimum level of concentration for the two stainless steels. Tafel and polarization resistance techniques were used to estimate the corrosion rate of each of the alloy samples tested.

TECHNIQUES AND METHODS to efficiently combat corrosion are continually being sought as a result of the exorbitant amount spent on corrosion annually. It has been of interest to corrosion scientists and engineers worldwide to gain more knowledge about the corrosion phenomenon and its control, and thus appropriate and better utilization of austenitic stainless steels, among other alloys.

To ensure long life, as well as dependability, reliability, safety, and economic viability of plant and industrial components, it is vital to make the appropriate selection of the materials used. This is absolutely necessary for the fabrication of equipment components, and for the construction of industrial plants for the manufacture of acids, chemicals, and their derivatives. The selection of the appropriate metal or alloy for a particular corrosion service is therefore the most common method of preventing or reducing corrosion damage.

Austenitic stainless steels are frequently-used alloys in this regard.

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 (18% Cr and 8% Ni), and these alloys are of major importance in the chemical process industries. The types 304 and 316 stainless steels used in this work belong to this group. In composition, however, type 316 consists of about 2% Mo to improve resistance to pitting attack by strengthening the passive film and imparting improved corrosion resistance in reducing acids [1, 2].

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

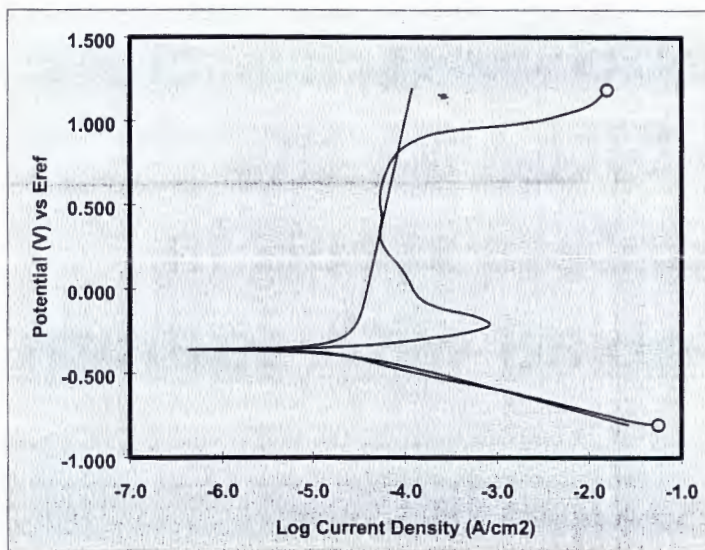


Fig.1. Polarization curves of 316 stainless steel in 1M H₂SO₄

film is very thin, essentially transparent and self-healing; if it is damaged mechanically or chemically, it will reform very rapidly [3]. 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. In this situation, additional protection for the stainless steels could be economically beneficial, and is therefore desirable. The effective use of inhibitors could then be viable, and this is the object of the present investigation.

The application of inhibitors is one of the means of combating corrosion in acid,

aqueous, and process-industry environments. An inhibitor is a substance which retards a chemical reaction; thus, a corrosion inhibitor is a substance which, when added to an environment decreases the rate of attack by the environment on a metal [4]. Numerous papers have been published on the protective action of corrosion inhibitors on metals in aqueous and acidic solutions [5-9].

Potassium dichromate as an inhibitor has been chosen in this work: the chemical was found to be effective as an inhibitor against corrosion of mild steel reinforcement in concrete [10]. It is envisaged that the results obtained here will be of benefit to industries and researchers in the field of corrosion and protection studies.

Experimental techniques

The two types of stainless steel – SS304 and SS316 samples in cylindrical form (10mm dia and 10mm long) – used for these studies were ground and polished up to fine diamond (1µm), cleaned, and rinsed/degreased in an ultrasonic bath using acetone. They were immediately kept in a desiccator for subsequent corrosion studies.

Potentiodynamic experiments were performed using each of the cylindrical specimens in turn, in which 1cm² surface area of the specimen was exposed to the test solution at room temperature. The experiments were performed using a polarization cell of a three-electrode system

Sample	Temp (°C)	Corrosion current I _{corr} (µA/cm ²)	OCP(V)	Beta anodic β _a (V/decade)	Beta cathodic β _c (V/decade)	Tafel corrosion rate (mm/yr)
1M H ₂ SO ₄ only	Room temp.	27.94	-0.3098	0.2465	0.1491	0.332
1M H ₂ SO ₄ + 4%NaCl		29.94	-0.3379	0.1253	0.1573	0.356
1M H ₂ SO ₄ + 4%NaCl + 0.5% K ₂ Cr ₂ O ₇		141.0	-0.1766	0.5080	0.2350	1.673
1M H ₂ SO ₄ + 4%NaCl + 1.0% K ₂ Cr ₂ O ₇		13.42	-0.0502	0.4967	0.2973	0.159
1M H ₂ SO ₄ + 4%NaCl + 2.0% K ₂ Cr ₂ O ₇		121.3	-0.1649	0.4963	0.1175	1.44

Table 1. Tafel calculation of corrosion data.

consisting of a reference electrode (a saturated calomel electrode – SCE), a working electrode (WE); and a counter electrode (CE) made of platinum mesh.

The experiments were conducted in five different solutions for each stainless steel samples. All the chemicals used were prepared from AR-grade analytical reagent: sulphuric acid (H_2SO_4), sodium chloride (NaCl), and potassium dichromate ($K_2Cr_2O_7$). The test environments were:

- 1M H_2SO_4
- 1M H_2SO_4 + 4% NaCl
- 1M H_2SO_4 + 4% NaCl + 0.5% $K_2Cr_2O_7$
- 1M H_2SO_4 + 4% NaCl + 1% $K_2Cr_2O_7$
- 1M H_2SO_4 + 4% NaCl + 2% $K_2Cr_2O_7$

The polarization cell was connected to a potentiostat 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 2.5mV/s was maintained throughout the experiment. Tafel and polarization techniques were used to estimate the corrosion rate of each of the tested alloy samples. The experiments were conducted in turns in de-aerated condition using nitrogen gas.

Results and discussion

Type 316 stainless steel

The potentiodynamic polarization curves

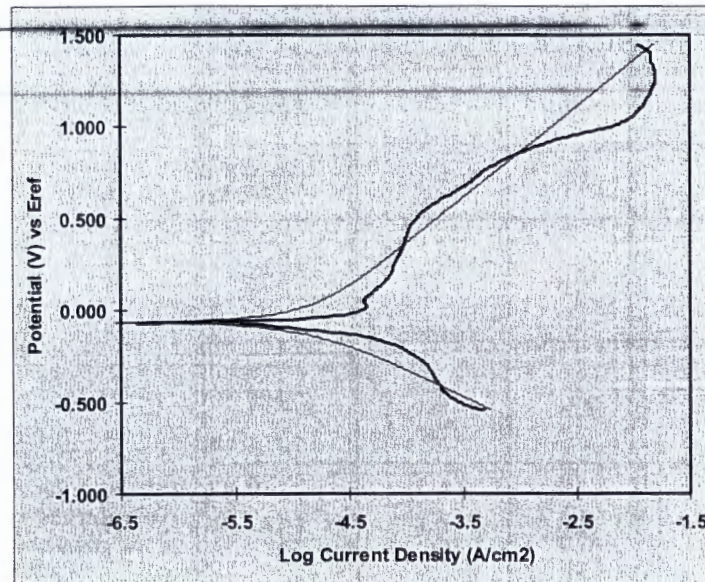
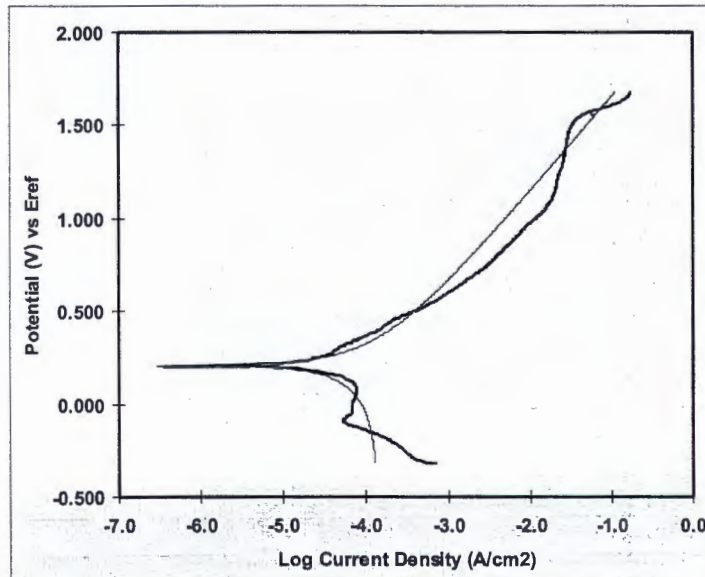
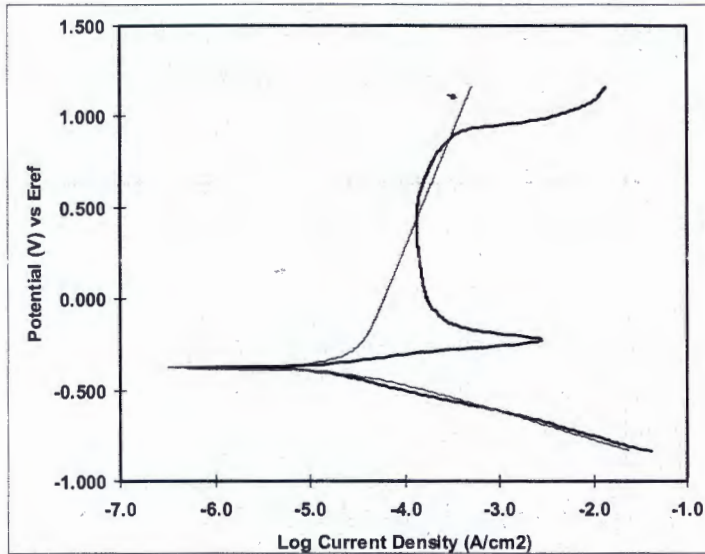
of the type 316 austenitic stainless steel electrode recorded in 1M dilute H_2SO_4 containing 4% NaCl concentration with and without different concentrations (0.5%, 1% and 2%) of $K_2Cr_2O_7$ as inhibitor, at room temperature, are presented in Figs 1-5. The data obtained were analyzed and calculation made as presented in Tables 1 and 2.

Fig.1 shows the polarization corrosion curve of 316 stainless steel in dilute H_2SO_4 alone. The data and the polarization curve show that the corrosion of the steel was minimal throughout the duration of the experiment. The corrosion rate, by Tafel calculation, was 0.332mm/yr, and the open corrosion potential was -0.3098mV. In general, this medium serves as the control for the experiment to which other results will be compared for this particular test electrode.

The addition of NaCl solution to H_2SO_4 increased the corrosion rate (0.356mm/yr by Tafel calculation, and 0.568mm/yr by polarization resistance technique). The primary passive potential (E_{pp}), Fig.2, becomes less active when compared with the same in Fig.1. The critical current density (i_{cr}) and the passive current density (i_{pass}) increased and the passive potential range became smaller. All these observations indicate 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

Sample	Temp (°C)	Corrosion current i_{corr} ($\mu A/cm^2$)	OCP(V)	Beta anodic β_a (V/decade)	Beta cathodic β_c (V/decade)	R_p corrosion rate (mm/yr)
1M H_2SO_4 only	Room temp.	56.24	-0.3186	0.1	0.1	0.4908
1M H_2SO_4 + 4%NaCl		60.11	-0.3388	0.1	0.1	0.5682
1M H_2SO_4 + 4%NaCl + 0.5% $K_2Cr_2O_7$		148.22	-0.1820	0.1	0.1	1.8638
1M H_2SO_4 + 4%NaCl + 1.0% $K_2Cr_2O_7$		36.46	-0.0682	0.1	0.1	0.2054
1M H_2SO_4 + 4%NaCl + 2.0% $K_2Cr_2O_7$		128.40	-0.1851	0.1	0.1	1.478

Table
2. Polarization
resistance
calculation of
the observed
data.



dissolution of the alloy. The addition of 4% NaCl caused a shift in potential towards increasing negative values. This is an indication of increased active corrosion. The open corrosion potential (OCP) now becomes 0.3378V (Tafel) and 0.3388V (polarization resistance). The corrosion current (I_{corr}) increased to $29.94\mu\text{mA}/\text{cm}^2$ (Tafel) as compared with $27.94\mu\text{mA}/\text{cm}^2$ for the sulphuric acid test medium alone.

There was a complete change in the polarization curve profile when the 0.5% potassium dichromate inhibitor was added to the $1\text{M H}_2\text{SO}_4 + 4\% \text{NaCl}$ solution (Fig.3). The critical current density (i_{cr}); the primary passives potential (E_{pp}); the passive current density (i_{pass}); and the passive potential range become difficult to distinguish. The OCP is 0.1766V, and the corrosion rate (Tables 1 and 2) is 1.673mm/yr (Tafel results) and 1.8638mm/yr (polarization resistance calculation). The corrosion current became very high at $141.00\mu\text{mA}/\text{cm}^2$ (Tafel). All these changing phenomena suggest, to a large extent, the reduction in the corrosion resistance, the passivation characteristics, and reduction in the anodic protectibility of the alloy. The susceptibility of the alloy to corrosion in this test medium is, therefore, very apparent. Instead of corrosion inhibition, there was corrosion acceleration of the test electrodes. The inference, therefore, is that the 0.5% potassium dichromate inhibitor has a negative effect on the corrosion inhibition of type 316 stainless steel in $1\text{M H}_2\text{SO}_4 + 4\% \text{NaCl}$ solution. This result is usually characteristic of inhibitors in general: that is, the tendency to accelerate corrosion of alloys if the concentration of the inhibitor used is below the level or above the level (optimum level) at which the inhibitive effect can be achieved.

When the concentration of the inhibitor addition was changed from 0.5 to 1%, the same trend of the polarization curve profile as in Fig.3 was obtained, and is presented in Fig.4. However, the passive potential

Fig.2 (left, top). Polarization curves of 316 stainless steel in $1\text{M H}_2\text{SO}_4 + 4\% \text{NaCl}$.

Fig.3 (left, centre). Polarization curve of 316 stainless steel in $1\text{M H}_2\text{SO}_4 + 4\% \text{NaCl} + 0.5\% \text{K}_2\text{Cr}_2\text{O}_7$ solution.

Fig.4 (left, bottom). Polarization curves of 316 stainless steel in $1\text{M H}_2\text{SO}_4 + 4\% \text{NaCl} + 1\% \text{K}_2\text{Cr}_2\text{O}_7$ solution.

range is better defined than in Fig.3. In addition, the critical pitting potential, the critical current density, and the primary passive potential zones of the curve could be identified, though not distinctly. The OCP is -0.0502 , an indication of passivity when compared with the test in H_2SO_4 alone. The corrosion rate is 0.159mm/yr (Tafel results) and 0.2054mm/yr (polarization resistance). The corrosion current (I_{corr}) is $13.42\mu\text{A/cm}^2$. A clear case of corrosion inhibitor characteristic is exhibited here. The inhibitor (potassium dichromate) concentration at 1% addition, therefore, has a good inhibition performance in this test medium.

The addition of 2% potassium dichromate solution as inhibitor to the 1M H_2SO_4 and 4% NaCl solutions (test medium) did not inhibit the corrosion of 316 stainless steel but, rather, accelerated it. The corrosion polarization curve profile is presented in Fig.5. The OCP is -0.1649V and the corrosion rate is 1.44mm/yr (Tafel results) and 1.478mm/yr (polarization resistance method). This observed phenomenon is in agreement with inhibitor characteristic in which the corrosion of alloy is accelerated when the added inhibitor has a concentration more (or less) than the optimum level.

Type 304 stainless steel

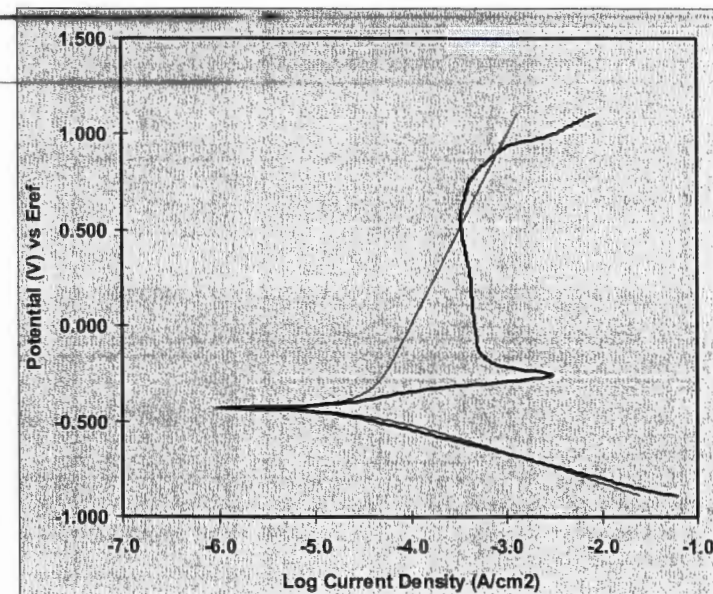
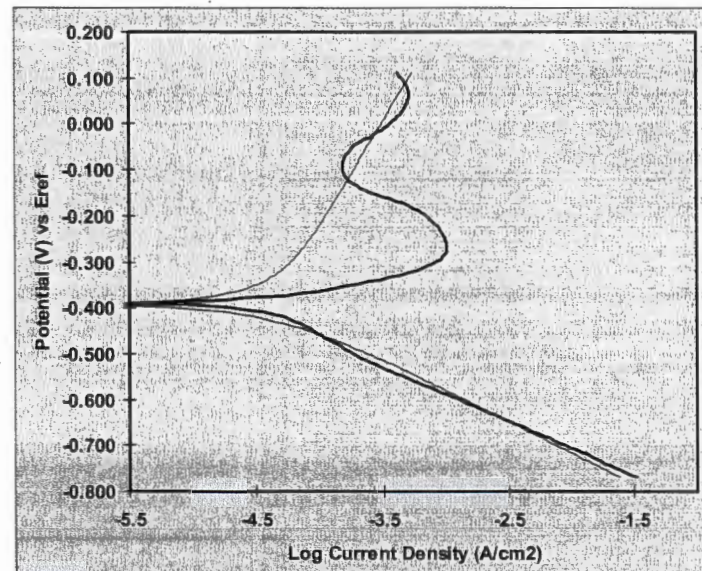
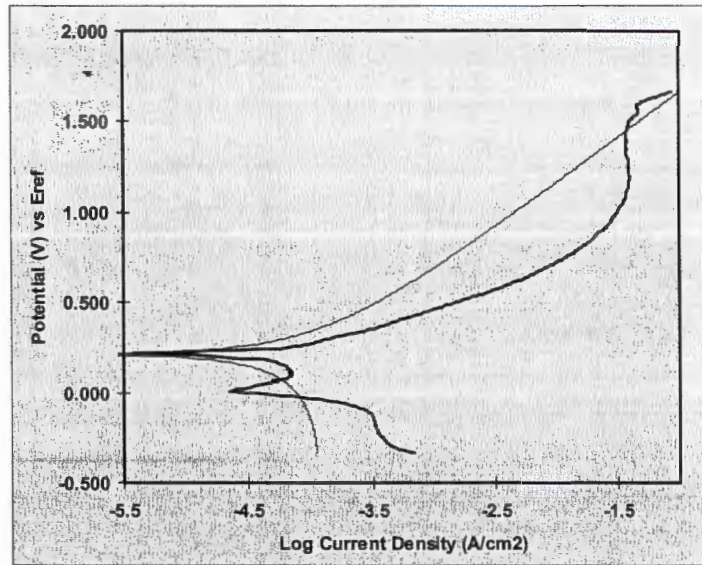
The potentiodynamic polarization data for Type 304 austenitic stainless steel in 1M H_2SO_4 , with and without sodium chloride and potassium dichromate inhibitor, are presented in Figs 6-10. All the other recorded and analyzed data are shown in Tables 3 and 4.

The polarization corrosion profile for the specimen in H_2SO_4 alone is presented in Fig.6. With an OCP of -0.3922V and a corrosion current density, I_{corr} of $42.91\mu\text{A/cm}^2$, the calculated corrosion rate (Tafel) is 0.5106mm/yr and by polarization resistance, the corrosion rate is 0.6911mm/yr .

Fig.5 (right, top). Polarization curves of 316 in 1M H_2SO_4 + 4% NaCl + 2% $K_2Cr_2O_7$ solution.

Fig.6 (right, centre). Polarization curves of 304 stainless steel in 1M H_2SO_4 .

Fig.7 (right, bottom). Polarization curves of 304 stainless steel in 1M H_2SO_4 + 4% NaCl solution.



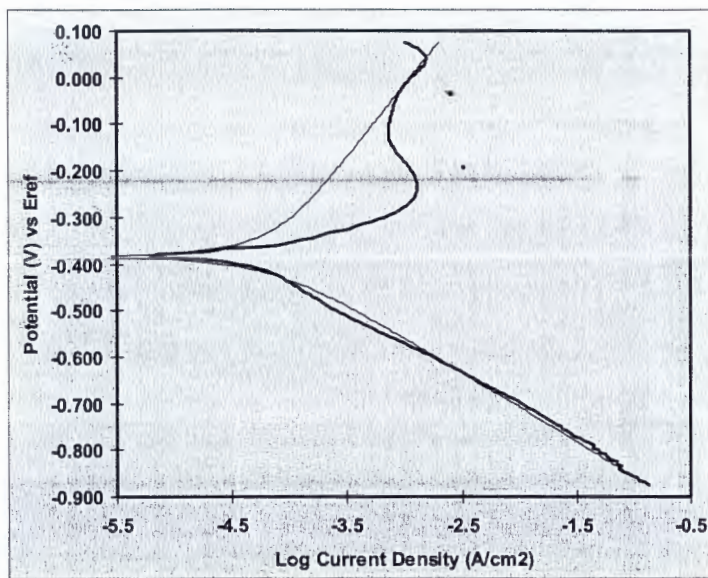


Fig. 8. Polarization curves of 304 stainless steel in 1M H₂SO₄ + 4% NaCl + 0.5% K₂Cr₂O₇ solution.

yr. The recorded data (Tables 3 and 4) show the corrosion of this steel in 1M H₂SO₄. The recorded corrosion rate cannot be described as significant. The passive film of the stainless steel gave some measure of corrosion protection. The polarization corrosion curve profile did not show a stable or defined transpassive region, and the passive potential range is not well defined, either. This could be due to active and passive corrosion reactions of this steel in the acid, in which a steady-state corrosion phenomenon could not be achieved.

A more-defined polarization corrosion curve profile was obtained when 4% sodium

chloride solution was added to the 1M H₂SO₄. When compared with the results obtained with the use of the acid alone, the corrosion current density (I_{corr}) and the primary passive potential decreased, while the passive potential range becomes broader (Fig.7). These observations indicate corrosion resistance of the steel in this mixed test solution. The corrosion rates of 0.436mm/yr (Tafel) and 0.6098mm/yr (polarization resistance) also confirm that there was less corrosion here, compared to Fig.6. The chloride ion (Cl⁻), instead of increasing the corrosion susceptibility of the alloy, rather increased the resistance to corrosion. This result is in conformity with other results in other studies [8]. When 0.5% potassium dichromate was added to the test solution as inhibitor, there was an acceptable corrosion rate. The corrosion rate increased from 0.436mm/yr (Tafel) and 0.6098mm/yr (polarization resistance) to 0.7913 and 1.1294mm/yr, respectively. There was drastic increase in corrosion current, achieving a value of 66.50µmA/cm² (Tafel) and 78.43µmA/cm² (polarization resistance). These changes also reflected in the polarization corrosion curve profile, Fig.8. It is difficult to explain this increase in corrosion with the addition of 0.5% potassium dichromate inhibitor. It is important to know that this inhibitor is an oxidizer; if used at a level not at optimum level, there is a tendency for the reaction to increase corrosion reactions as observed. This is a type of reaction which is characteristic of inhibitors when used at a

Table 3. Tafel calculation of the observed corrosion data.

Sample	Temp (°C)	Corrosion current I_{corr} ($\mu A/cm^2$)	OCP(V)	Beta anodic β_a (V/decade)	Beta cathodic β_c (V/decade)	Tafel corrosion rate (mm/yr)
1M H ₂ SO ₄ only	Room temp.	42.91	-0.3922	0.4593	0.1373	0.5106
1M H ₂ SO ₄ + 4%NaCl		36.68	-0.4350	0.9910	0.1606	0.4365
1M H ₂ SO ₄ + 4%NaCl + 0.5% K ₂ Cr ₂ O ₇		66.51	-0.3838	0.3118	0.1492	0.7913
1M H ₂ SO ₄ + 4%NaCl + 1.0% K ₂ Cr ₂ O ₇		30.72	-0.1098	0.5420	0.2360	0.3655
1M H ₂ SO ₄ + 4%NaCl + 2.0% K ₂ Cr ₂ O ₇		70.54	-0.3802	0.6032	0.1542	0.8390

concentration which is insufficient for corrosion inhibition. The corrosion reduction (oxidizing) process, enhanced by the low concentration of the inhibitor, could contribute to the depassivation of the steel's protective film for the chloride ions to penetrate to initiate corrosion reactions on the steel's surface.

The addition of 1% potassium dichromate solution as inhibitor to the 1M H₂SO₄ and 4% NaCl test medium, shifted the open corrosion potential (E_{corr}) to -0.1099V. The polarization corrosion curve profile, Fig.9, changed and without any particular definition vis-à-vis the primary passive potential, the critical current density, the passive current density, and the passive potential range. The critical pitting potentials also become difficult to define in the curve profile. The recorded corrosion current density (I_{corr}) decreased to 30.72µmA/cm². The corrosion rate recorded for both the Tafel and polarization resistance calculations decreased to 0.3665mm/yr and 0.4330 mm/yr respectively in comparison with the values mentioned above for 0.5% inhibitor addition to the test medium. These observations show the 304 stainless steel electrode to have a measure of protection, that is, showing corrosion resistance in the solution, and hence improvement in passivation characteristics and anodic protectibility. The inference of these results is that the concentration of 1% potassium dichromate inhibitor additions to the acid-chloride test solution was fairly effective

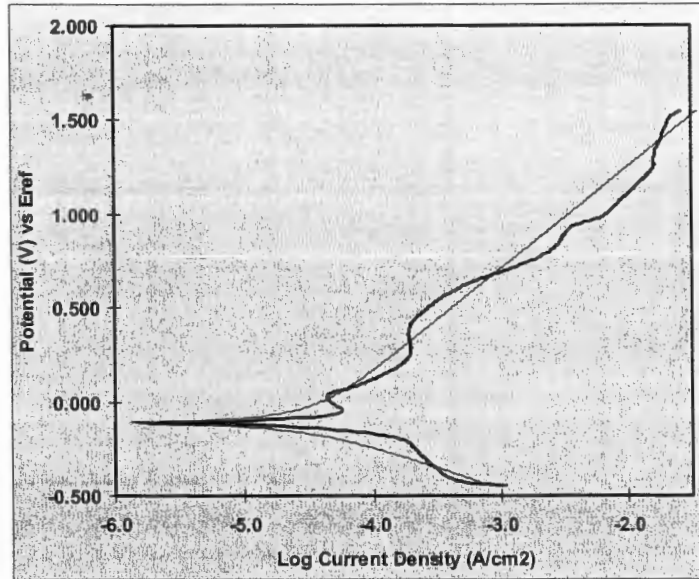


Fig.9. Polarization curves of 304 stainless steel in 1M H₂SO₄ + 4% NaCl + 1% K₂Cr₂O₇ solution.

in inhibiting the corrosion of the steel (304 stainless steel) in 1M H₂SO₄ + 4% NaCl solution.

The addition of 2% potassium dichromate solution as inhibitor to the 1M H₂SO₄ and 4% NaCl solution accelerates the corrosion rate from the previous values of 0.3655 and 0.4330mm/yr to 0.839 and 1.6505mm/yr, respectively (Tafel and polarization resistance results). This is shown in Tables 3 and 4. It could be seen also that there was a change in the polarization corrosion curve profile, Fig.10. The open corrosion potential decreases negatively to the values of -0.3802V (Tafel calculation) and -0.3843V

Sample	Temp (°C)	Corrosion current I _{corr} (µA/cm ²)	OCP(V)	Beta anodic β _a (V/decade)	Beta cathodic β _c (V/decade)	R _p corrosion rate (mm/yr)
1M H ₂ SO ₄ only	Room temp.	44.10	-0.4012	0.1	0.1	0.6911
1M H ₂ SO ₄ + 4%NaCl		45.72	-0.4480	0.1	0.1	0.6098
1M H ₂ SO ₄ + 4%NaCl + 0.5% K ₂ Cr ₂ O ₇		78.43	-0.3840	0.1	0.1	1.1294
1M H ₂ SO ₄ + 4%NaCl + 1.0% K ₂ Cr ₂ O ₇		36.28	-0.1102	0.1	0.1	0.4330
1M H ₂ SO ₄ + 4%NaCl + 2.0% K ₂ Cr ₂ O ₇		84.32	-0.3842	0.1	0.1	1.6505

Table 4. Polarization resistance calculation of the observed corrosion data.

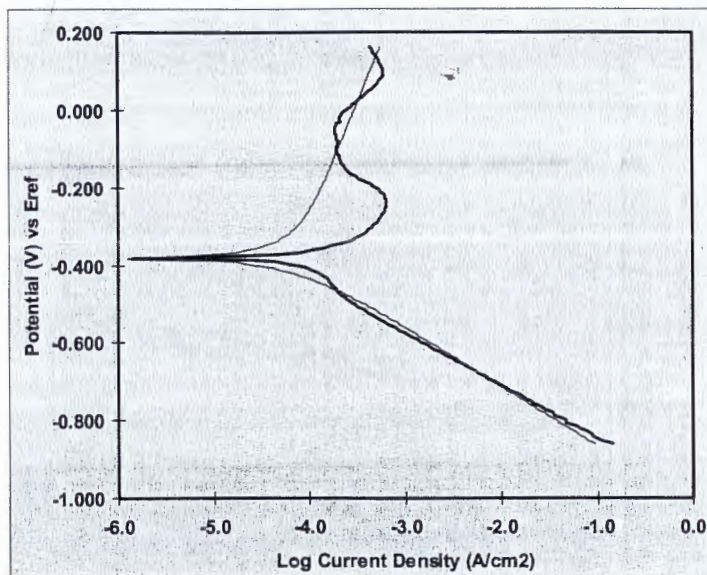


Fig.10. Polarization curves of 304 stainless steel in $1M H_2SO_4 + 4\% NaCl + 2\% K_2Cr_2O_7$

(polarization resistance). There was a drastic increase in corrosion current density (I_{corr}) which now achieves the values of $0.54 \mu A/cm^2$ (Tafel) and $84.32 \mu A/cm^2$ (polarization resistance). The polarization corrosion curve profile now resembles that of Fig.6, in which only $1M H_2SO_4$ was used. With these results, the concentration of 2% potassium dichromate inhibitor did not inhibit corrosion reactions in the test medium. It could, therefore, be inferred that this concentration is probably more than the optimum level required for this particular test medium.

Conclusions

The results show that potassium dichromate, at the concentrations used, in addition to $1M H_2SO_4 + 4\% NaCl$ has effective corrosion inhibition performance in both the two grades of stainless steel – 316 and 304 – at the concentration of 1% at ambient temperature.

Potassium dichromate inhibitor has better protective performance with 316 than 304 at 1% concentration in the test medium (sulphuric acid + 4% sodium chloride).

The optimum level of performance for this inhibitor in the test medium used, will be about 1% inhibitor concentration where the least corrosion rate (mm/yr) was achieved for both types 316 and 304 stainless steel.

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Professor Cleophas A Loto (pictured, left) received his BSc in chemistry from the University of Lagos, Nigeria, in 1977, an MSc in metallurgy from Brunel University, UK in 1982, and a PhD in corrosion science and engineering from the University of Manchester Institute of Science and Technology, UK in 1984. He is at present working with the Center for Engineering Research, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia. Prior to joining the Research



Institute of the University, Professor Loto was a full professor and Head of the Department of Mechanical Engineering, Ladoké Akintola University of Technology, Ogbomoso, Nigeria (1997/98). Before this, he was associate professor at Bayero University, Kano, Nigeria (1995-1996); a senior lecturer at the University of Lagos (1989-1995); and a lecturer at the Obafemi Awolowo University, Ile-Ife (1985-1989). He also worked with the Nigerian Steel Development Authority / Ajaokuta Steel Co, Nigeria, as a senior metallurgist / chemist from 1978 to 1984.

Professor Loto was a guest research scientist at the Department of Engineering Metals, Chalmers University of Technology, Gothenburg, Sweden, as a Council of Europe / Swedish Institute Scholar in 1988, and in 1991/92, he was a visiting professor and research associate at the Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada. He was also a senior visiting research fellow at the South Bank University, London, in 1995.

Professor Loto has worked on several research projects, which include corrosion in concrete; stress-corrosion cracking of ferrous and non-ferrous alloys; electroless nickel plating of iron powders; failure analysis of failed metallic materials; corrosion inhibitors; pitting and crevice corrosion of super-austenitic and austenitic

stainless steels in seawater and in strong acids; cathodic protection; electrodeposition of zinc; coatings for corrosion protection; and the structure / property relationship of metals / alloys.

Adeyinka Adeleke (pictured, right) is currently working on the near-neutral pH stress-corrosion cracking of Canadian pipeline steels, in a project sponsored by IPSCO, at the University of Alberta, where he is also a research and teaching assistant. Prior to this, in 2001-2002, he worked at the University of British Columbia, Vancouver, Canada on bio-hydro-metallurgy research, where he also undertook various forms of experimental work to further investigate the leaching kinetics of copper mineral concentrates.

From 1998-2001, Mr Adeleke was involved with research into corrosion and materials development, using SEM and TEM to analyze intermetallic phases in materials, at the King Fahd University of Petroleum and Minerals, Saudi Arabia. His earlier work in industry included general maintenance of mechanical equipment and monitoring of the corrosion rate of oil-carrying pipes for the Agip Oil Co in Port-Harcourt, Nigeria, and inspection of raw materials (billets) and rolling products, involving metallographic studies of failed and normal rolling products, for the Oshogbo Steel Rolling Co, Oshogbo Nigeria.

