

*Corrosion Polarization and $K_2Cr_2O_7$
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Stainless Steel in H_3PO_4 and $H_3PO_4 + 3.65$
% NaCl Environments*

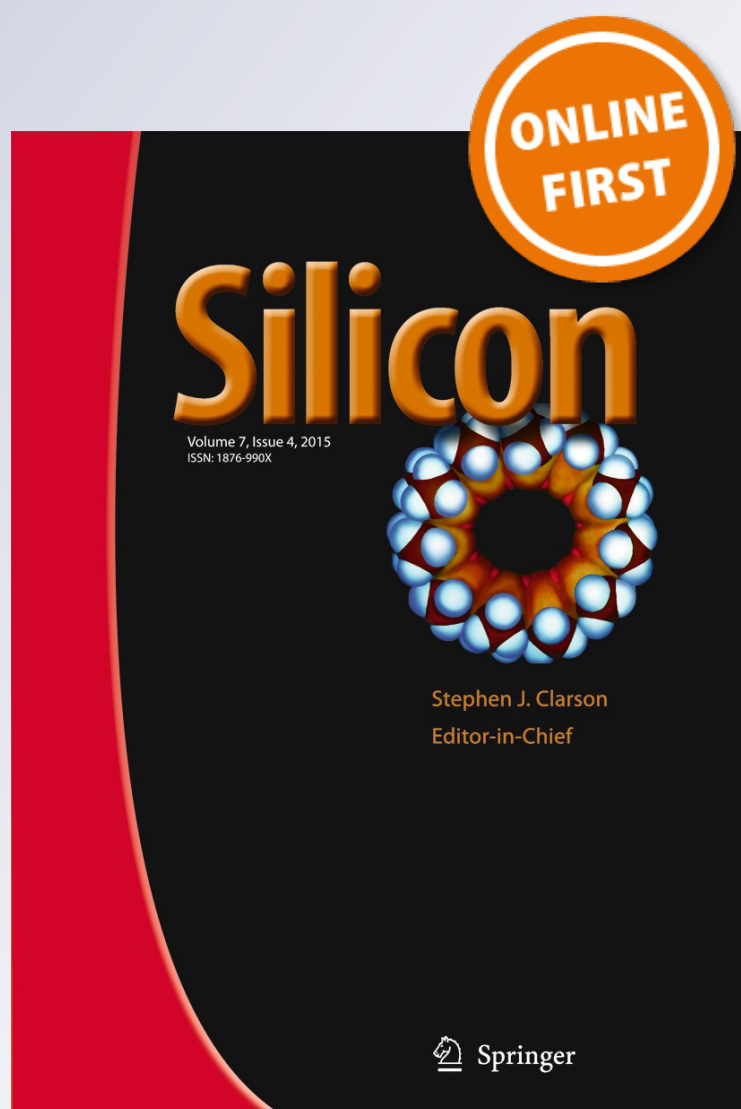
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Corrosion Polarization and $K_2Cr_2O_7$ Inhibition Behaviour of Martensitic Stainless Steel in H_3PO_4 and $H_3PO_4 + 3.65\%$ NaCl Environments

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Abstract The corrosion resistance behaviour of 12Cr martensitic stainless steel was evaluated in different concentrations of H_3PO_4 and $H_3PO_4 + NaCl$. Corrosion inhibition of the tested samples in 1M H_3PO_4 was also evaluated using potassium dichromate. The experiments were performed at ambient temperature of 27° using potentiodynamic polarization measurements. 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 showed some magnitude of corrosion susceptibility for the stainless steel at higher H_3PO_4 concentrations and also in the acid chloride test media. Effective corrosion inhibition was also exhibited on the tested samples.

Keywords Corrosion · Phosphoric acid · Potassium dichromate · Polarization · Inhibition · Martensitic stainless steel

1 Introduction

The importance of stainless steels in industrial applications drives the interest in this present work. Stainless steel

belongs to a family of corrosion and heat resistant steels containing a minimum of 10.5 % chromium. There is a wide range of stainless steels with progressively higher levels of corrosion resistance and strength that also meets with other mechanical characteristics. 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. These are *austenitic*, *ferritic* and *martensitic stainless* steels. The use of steel, its characteristics and its corrosion resistance has been reported [1]. Several authors [2–9] have reported studies using martensitic stainless steels in corrosion and protection. Martensitic stainless steel is a specific type of stainless steel alloy. Martensitic stainless steels can be high or low carbon steels built around a type that is not used in large quantities compared to austenitic and ferritic grades. They are a vital part of the 410 composition of iron, 12 % chromium, and 0.12 % carbon. Martensitic stainless steels are usually tempered and hardened. Tempered martensitic stainless steel has good hardness and high toughness [10].

Martensitic stainless steels are a vital part of the stainless steel group of metallic alloys although they are not used in large quantities compared to austenitic and ferritic grades. Their combination of strength, toughness and moderate corrosion resistance makes them ideal for a wide range of applications. Since their invention, stainless steels have come to be a vitally important material, their anti-corrosive qualities making them perfect for use in a huge range of different environments and circumstances.

This group of stainless steels is 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

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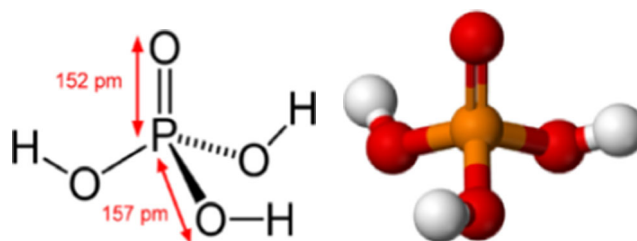
carbon steels. The main alloying element is chromium, typically 12 to 15 %, molybdenum (0.2–1 %), no nickel, except for two grades, and 0.1–1.2 % carbon. Their structures are “body-centered tetragonal” (bct), and they are classed as a “hard” ferro-magnetic group [11]. In the annealed condition, they have tensile yield strengths of about 275 MPa and so they are usually machined, cold formed, or cold worked in this condition. The strength obtained by heat treatment depends on the carbon content of the alloy. Increasing the carbon content increases the strength and hardness potential but decreases ductility and toughness.

In the heat-treated i.e. hardened and tempered condition, optimum corrosion resistance is attained. When compared with the austenitic and ferritic grades of stainless steels, martensitic stainless steels are less resistant to corrosion. With at least 11.5 % chromium, however, they are genuine stainless steels giving a significantly improved corrosion resistance compared to low alloy steels [12]. 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 components [13]. Many of these applications are not widely known which may explain 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.

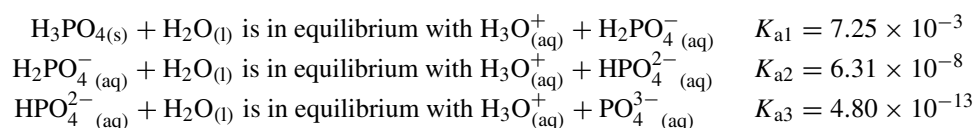
Phosphoric acid, the test medium in this work is a mineral acid having the chemical formula H_3PO_4 . Orthophosphoric acid molecules can combine with themselves to form a variety of compounds which are also referred to as phosphoric acids.



Structural formula of H_3PO_4 [14]

Ball and stick model [14]

Orthophosphoric acid is a very polar molecule. It is infinitely soluble in water. The oxidation state of phosphorus (P) in ortho- and other phosphoric acids is +5; the oxidation state of all the oxygen atoms (O) is -2 and all the hydrogen atoms (H) is $+1$. Triprotic means that an orthophosphoric acid molecule can dissociate up to three times, giving up an H^+ each time, which typically combines with a water molecule, H_2O , as shown in these reactions [15]:



In addition to being a chemical reagent, phosphoric acid has a wide variety of uses, including as a rust inhibitor, food additive, dental and orthopedic etchant, electrolyte, flux, dispersing agent, industrial etchant, fertilizer feedstock, and component of home cleaning products [16–20].

This work looks at the corrosion resistance reactions of 12Cr martensitic stainless steel in varied concentrations of H_3PO_4 and in different concentrations of $\text{K}_2\text{Cr}_2\text{O}_7$ inhibitor. Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, is a common inorganic chemical reagent, most commonly used as an oxidizing agent in various laboratory and industrial applications. It had been previously used effectively in other corrosion inhibition research [21, 22]. Inhibitors can affect protection by affecting the anodic reaction or the cathodic

reaction or both reactions (mixed) [23, 24]. By the reaction mechanism, inhibitors can be classified as: passivation, precipitators, vapor - phase, cathodic, anodic, neutralizing and absorbents [25]. Note also that the chemical structure of the inhibitor molecule plays a significant role in the inhibition mechanism and often determines whether or not such compounds will give effective inhibition in a specific corrosion system [24].

The acid test media were further contaminated with sodium chloride (NaCl) at all the concentrations of H_3PO_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. It also

Table 1 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	0.038	2.81	11.7	82.443

aims at determining its usefulness in likely industrial and work environments particularly with respect to materials selection.

2 Material and Methods

Martensitic stainless steel, with the composition shown in Table 1 was used in this investigation. The samples in plate form (10 mm wide and 10 mm long) were mounted in araldite resin and connected with a flexible wire connection, ground and polished to fine diamond size (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 polarisation experiments were performed using each of the flat plate specimens. For examination, 1 cm² surface area of the specimen was exposed to the test solution at room temperature. The experiments were performed using a polarisation cell with a 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 0.00166 V/s from –1.5 to +1.5 V and the corrosion currents were recorded. The experiments were conducted in three different concentrations of phosphoric acid (H₃PO₄) and also subsequently repeated in the acid test environment 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 H₃PO₄ was also evaluated using potassium dichromate.

The polarisation cell was connected to a potentiostat (Autolab PGSTAT 30 ECO CHIMIE) and interfaced with a computer for data acquisition and analysis. For repro-

ducibility 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 a de-aerated condition using nitrogen gas.

2.1 SEM/EDS Characterisation

Some of the uninhibited and inhibited test samples of the martensitic stainless steel were separately examined for surface morphology, with a scanning electron microscope (SEM) after the experiments and representative micrographs are shown in Fig. 8(a, b and c).

3 Results and Discussion

Table 3 shows the summary of the results obtained.

3.1 1M H₃PO₄ and 1M H₃PO₄ + 3.65 % NaCl Test Environments

Figures 1 and 2 represent the corrosion polarisation curves for the martensitic stainless steel in 1M H₃PO₄ and 1M H₃PO₄ + 3.65 % NaCl solution respectively. The other corrosion results for various test parameters are contained in Table 3. The tests in 1M H₃PO₄ alone showed appreciable active corrosion reactions and hence appreciable corrosion which could be associated with anodic dissolution of the test electrodes. However, the corrosion magnitude as indicated by the corrosion rate was not very severe based on the results obtained. The corrosion rate (CR) value was 1.3703 mm/yr; the open corrosion potential (E_{corr}) value was –0.44587 V while the corrosion polarisation resistance, R_p, value recorded was 27.722 Ω and a value of 0.00356 A/cm² was recorded for corrosion current density (I_{corr}). All these results confirm the very active corrosion reactions on the test electrode/acid interface. Addition of 3.65 % NaCl to the acid in another test gave an apparent increase in corrosion reactions based on the results shown in Table 3 and the corrosion profile presented in Fig. 2. The corrosion rate increased to 2.5483 mm/yr; the polarisation resistance R_p decreased significantly with a value of 3.5028 Ω . The corrosion cur-

Table 2 Test environments

Phosphoric acid, H ₃ PO ₄	H ₃ PO ₄ + 35 g/L NaCl (3.5 %)
5 M	5 M
3 M	3 M
1 M	1M

Table 3 Polarization results for the tests in H₃PO₄ and H₃PO₄ + NaCl environments

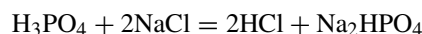
Sample	i_{corr} (A)	ba	bc	I_{corr} (A/cm ²)	R_p (Ω)	E_{corr} (V)	CR (mm/yr)
1M H ₃ PO ₄	0.00356	–	–	0.00356	27.722	–0.44587	1.3703
1M H ₃ PO ₄ + 3.65 % NaCl	0.006621	–	–	0.006621	3.5028	–0.64999	2.5483
3M H ₃ PO ₄	3.75×10^{-4}	0.1932	0.1136	3.76×10^{-4}	1.24×10^2	–0.4173	2.436
3M H ₃ PO ₄ + 3.65 % NaCl	1.19×10^{-3}	0.3270	0.6194	1.19×10^{-3}	7.70×10^1	–0.3954	7.750
5M H ₃ PO ₄	1.01×10^{-5}	0.1687	0.1612	1.02×10^{-5}	3.36×10^3	–0.4148	0.065
5M H ₃ PO ₄ + 3.65 % NaCl	1.03×10^{-3}	0.2444	0.3678	1.03×10^{-3}	6.10×10^1	–0.4177	6.730

rent density (I_{corr}) A/cm² also increased while the open corrosion potential, OCP, gave a more negative value of –0.64999 V. The reacting chloride ion, Cl⁻, species from the sodium chloride in the solution contributed to the increase in the corrosion observed based on the various results obtained.

3.2 3M H₃PO₄ and 3M H₃PO₄ + 3.65 % NaCl Test Environments

The results of potentiodynamic polarization curves for the test specimen used respectively in 3M H₃PO₄ and the 3M H₃PO₄ + 3.65 % NaCl test media are presented in Figs. 3 and 4. The open corrosion potential (OCP), E_{corr} value for the test in 3M H₃PO₄ environment alone as presented in Table 3 and Fig. 3, is –0.4173 V. The corrosion rate (CR) value of the specimen was 2.436 mm/yr and the corrosion polarisation resistance, R_p value was $1.24 \times 10^2 \Omega$. A corrosion current density, I_{corr} value of 3.76×10^{-4} was also achieved. The active corrosion reactions and hence the corrosion of the specimen in this test medium was apparent. With the addition of 3.65 % NaCl to the test medium, Fig. 4, i.e., with 3M H₃PO₄ + 3.65 % NaCl, the corrosion profile changed significantly with an appreciable increase in corrosion as indicated by the values obtained for the various

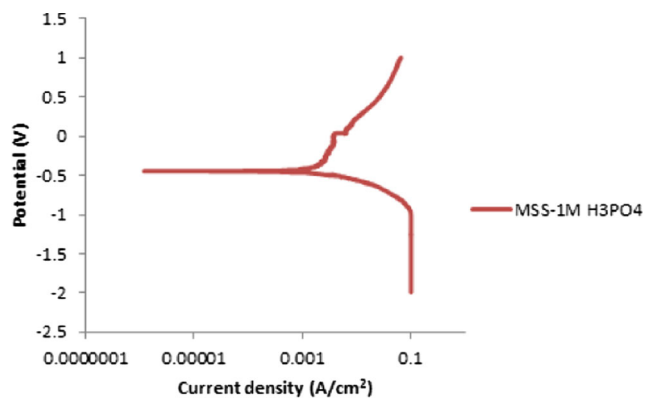
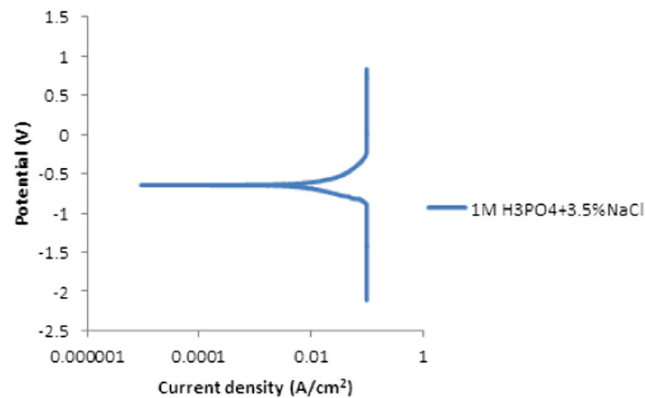
parameters. Thus the corrosion rate (CR) value increased to 7.750 mm/yr and the polarisation resistance, R_p decreased drastically to a value of 7.70×10^1 . The open corrosion potentials (OCP) values recorded also changed with the latter being –0.3954 and its current density value was 1.19×10^{-3} an order of 1 magnitude when compared with the former. All these results point towards increased corrosion of the test specimen(s) in the acid chloride medium. The reaction of phosphoric acid with sodium chloride is given by the equation:



Phosphoric or orthophosphoric acid is a weaker acid when compared with HCl and hence the tendency of increased corrosion when sodium chloride was added to the H₃PO₄ as observed in this experimental result.

3.3 5M H₃PO₄ and 5M H₃PO₄ + 3.5 % NaCl Test Environments

Figures 5 and 6 show the results of potentiostatic polarization curves for the test specimens used respectively in 5M H₃PO₄ and the 5M H₃PO₄ + 3.65 % NaCl test media. In Fig. 5, the polarization corrosion curve of the marten-

**Fig. 1** Corrosion polarization curve of martensitic stainless steel in 1M H₃PO₄**Fig. 2** Corrosion polarization curve of martensitic stainless steel in 1M H₃PO₄ + 3.65 % NaCl

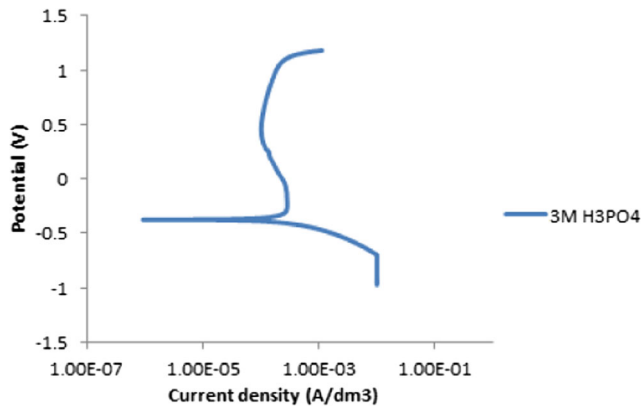


Fig. 3 Corrosion polarization curve of martensitic stainless steel in 3M H₃PO₄

sitic stainless steel in 5M H₃PO₄ alone, gave an open corrosion potential (OCP), E_{corr} value of -0.4148 V. This medium had the highest molarity and hence the most concentrated but without added NaCl. From Table 3, a polarisation resistance, R_p , value of $3.36 \times 10^3 \Omega$; corrosion rate of 0.065 mm/year and current density of 1.02×10^{-5} (A/cm²), in addition to the OCP values stated above, showed very little active corrosion reactions that persisted throughout the monitoring period. These values can be considered very safe for the use of the metallic alloy under test. This corrosion phenomenon could be associated with the oxidizing nature of the very oxidizing nature of the acid at such a high concentration. The above results changed with the use of the acid chloride, Fig. 6, i.e., 5M H₃PO₄ + 3.65 % NaCl. The polarisation resistance, R_p , value was lowered to $6.10 \times 10^1 \Omega$; and the E_{corr} value was -0.4177 V. The corrosion rate increased to 6.7306 mm/yr; and so also the corrosion current density value, 1.03×10^{-3} A/cm². All these indicate a comparatively significant increase in electrochemically active corrosion reactions. The chloride ions, Cl⁻, from the sodium chloride in combination with the dissociated PO₄²⁻ from H₃PO₄ did increase the active corrosion

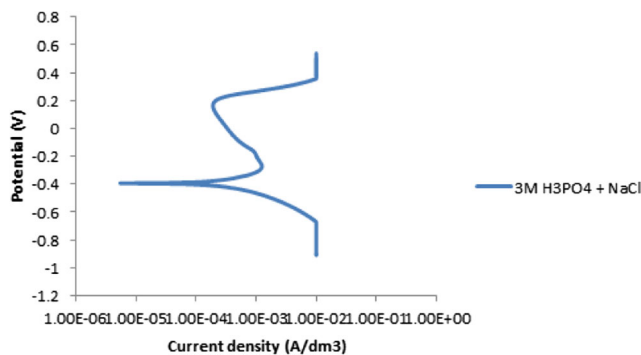


Fig. 4 Corrosion polarization curve of martensitic stainless steel in 3M H₃PO₄ + 3.65 % NaCl

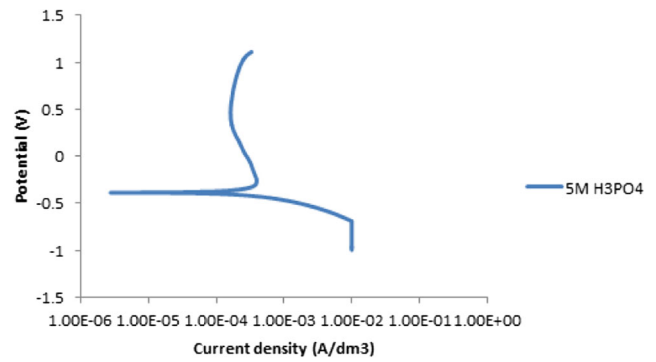


Fig. 5 Corrosion polarization curve of martensitic stainless steel in 5M H₃PO₄

reactions and hence the significant corrosion magnitude as indicated by the corrosion rate, corrosion current density and the decreased polarization resistance.

3.4 Inhibition of Martensitic Stainless Steel in 1M H₃PO₄ Medium

The potentiodynamic polarisation results obtained from the various concentrations of potassium dichromate inhibition of the martensitic stainless steel in 1M H₃PO₄ 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 K₂Cr₂O₇ concentrations are: 0.5, 1.0, 1.5 and 2.0 g respectively.

It can 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, E_{corr} (V) though very close in potential values. Similarly, the corrosion rates (CR), polarisation resistance, R_p (Ω), and corrosion current density, I_{corr} (A/cm²), give different results. The control experiment (test without inhibitor) did not only exhibit the highest corrosion rate (1.370300 mm/yr) but also had

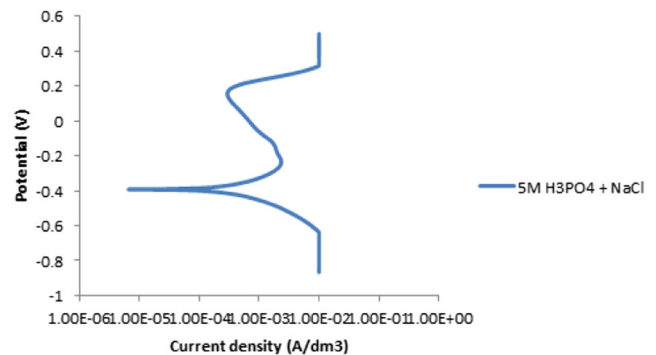


Fig. 6 Corrosion polarization curve of martensitic stainless steel in 5M H₃PO₄ + 3.65 % NaCl

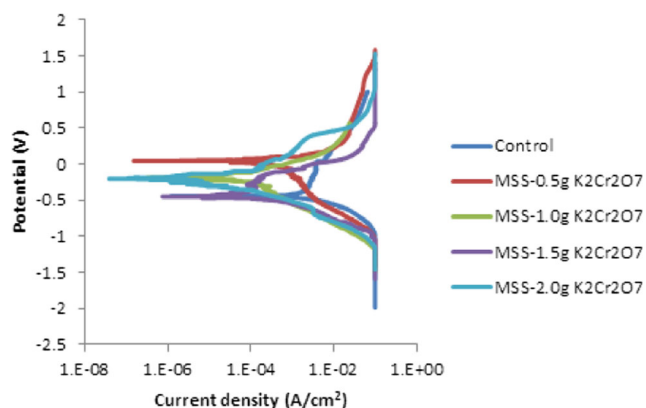
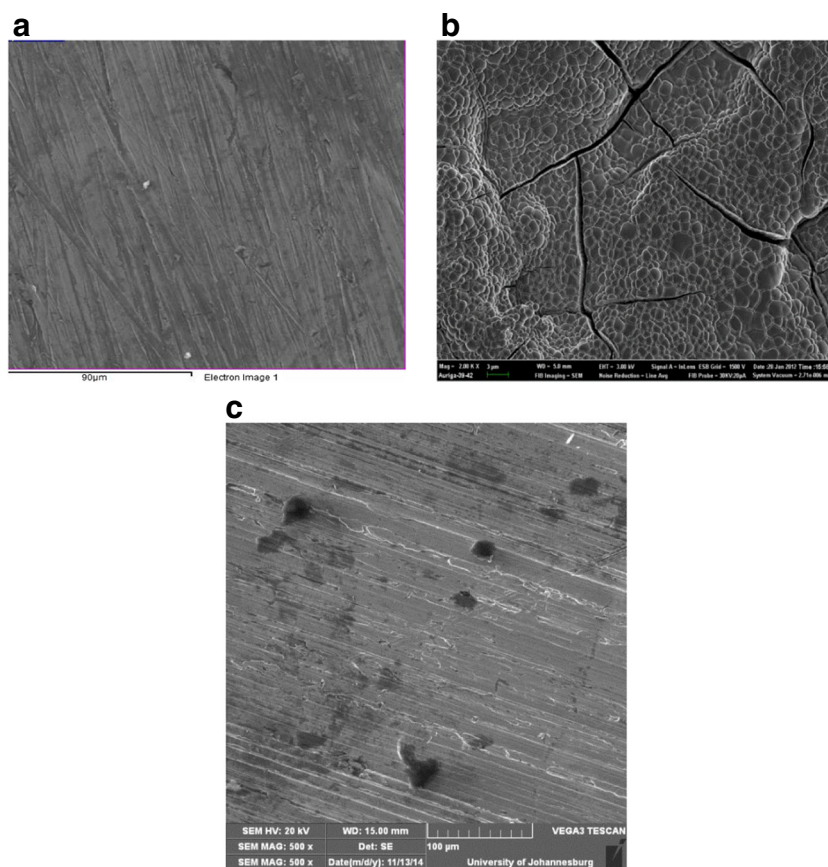


Fig. 7 Polarisation curves of K_2CrO_7 inhibition of martensitic stainless steel in 1M H_3PO_4

the lowest corrosion resistance (27.722Ω) and the highest corrosion current density ($0.003560 A/cm^2$) values. These values show intense corrosion of the tested metal sample in the phosphoric acid environment.

In these experimental tests, using the inhibitor, the lowest corrosion reactions were shown by the test with 0.5 kg potassium dichromate, $K_2Cr_2O_7$. This inhibitor concentration gave the lowest corrosion rate, $0.095564 mm/yr$; the

Fig. 8 SEM micrographs of the surface of martensitic stainless steel test specimens: **a** before immersion, **b** specimen immersed in 5M H_3PO_4 + 3.65 % NaCl, and **c** inhibited with 1.5M $K_2Cr_2O_7$



highest corrosion resistance, 390.16Ω ; the lowest corrosion current density, $0.000248 A/cm^2$ values and the least negative potential value of open corrosion potential (E_{corr}), $-0.029513 V$. The use of this inhibitor, from these results, showed an appreciable magnitude of corrosion protection of the test specimens in the H_3PO_4 environment.

4 Surface Morphology

The representative test samples of the uninhibited and inhibited martensitic stainless steel examined for surface morphology, with the scanning electron microscope (SEM) after the experiments, are presented in Fig. 8a, b and c. Surface corrosive degradation could be observed in Fig. 8b due to the phosphoric acid chloride attack. The chloride ions reacting species in combination with the phosphate ions would have penetrated the steel's passive film to initiate corrosion by anodic dissolution of the test electrodes surface. In Fig. 8c, the test sample was inhibited with 1.5M $K_2Cr_2O_7$. There could be some corrosion reactions, however, no apparent corrosion was observed on the specimen's surface. This seems to indicate that the inhibitor was effective in providing surface inhibition for the steel in such an aggressive test environment.

Table 4 Polarization results for the $K_2Cr_2O_7$ inhibition tests in 1M H_3PO_4

Sample No	Ecorr, Obs (V)	jcorr (A/cm ²)	Corrosion rate (mm/year)	Polarization resistance Ω
Control	-0.445870	0.003560	1.370300	27.722
0.5g $K_2Cr_2O_7$	-0.029513	0.000248	0.095564	390.16
1.0g $K_2Cr_2O_7$	-0.198670	0.000348	0.134120	241.70
1.5g $K_2Cr_2O_7$	-0.452030	0.002696	0.279000	136.69
2.0g $K_2Cr_2O_7$	-0.450610	0.000638	0.245630	122.31

5 Conclusion

1. Martensitic stainless steel is susceptible to corrosion in 1M H_3PO_4 test environment but not severely; the corrosion, however, becomes intense with increase in molarity of the acid concentration up to 3M H_3PO_4 concentration.
2. With further increase in the acid molarity, particularly at 5M H_3PO_4 , the intense corrosion of the martensitic stainless steel test specimens was reversed. The corrosion severity decreased significantly to a safe level for use with an increase in test solution molarity, almost behaving like an inhibitor. This behaviour could be due to the oxidising power of the acid at higher concentrations.
3. At all the levels of concentrations used, the inhibitor - $K_2Cr_2O_7$, gave good and effective corrosion protection of the test electrodes (martensitic steel specimens) in the acid and acid chloride test environments used.

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References

1. Davies JR (ed) (2000) Corrosion: understanding the basics. ASM International, p 231
2. Bourgin C, Chaveau E, Arnaud A (2006) Metall Res Tech 103:32
3. Agrawal R, Namboodhri TKG (1990) Corrosion Sci 30:37
4. Falleiros A, Magri M, Falleiros IGS (1999) Corrosion 55:769
5. Xr Y, Liu D, Han D (2008) Surf Coatings Technol 202:2577
6. Fierro G, Ingo GM, Manaa F (1989) Corrosion 45:814
7. Li CX, Bell T (2006) Corrosion Sci 48:2036
8. Zang H, Zhao YL, Jiang ZD (2005) Mater Lett 59:3370
9. Kwok CT, Lo KH, Cheng FT, Man HC (2003) Surf Coatings Techn 166:221
10. Tabatabae BA, Ashrafzadeh F, Hassanli AM (2011) ISIJ Int 51:471
11. British Stainless Steel Association (BSSA). Martensitic stainless steels, www.bssa.org.uk/topics.php?Article=253. Retrieved 15-03-2015
12. Sedriks AJ (1996) Corrosion of stainless steels, 2nd edn. Wiley, New York
13. AK Stainless steels, AK Steels Corporation. www.aksteel.com/markets_products/stainless.aspx. Retrieved: 15-03-2015
14. Phosphoric acid-Wikipedia. http://en.wikipedia.org/wiki/Phosphoric_acid. Retrieved 25-04-2015
15. Klement R (1963) Orthophosphoric acid. In: Brauer G (ed) Handbook of preparative inorganic chemistry. 2nd edn, vol 1. Academic Press, NY, p 543
16. Schrödter K, Bettermann G, Staffel T, Wahl F, Klein T, Hofmann (2008) Phosphoric acid and phosphates. In: Ullmann's encyclopedia of industrial chemistry. Wiley-VCH, Weinheim. doi:10.1002/14356007.a19_465.pub3
17. Toles C, Rimmer S, Hower JC (1996) Carbon 34(11):1419. doi:10.1016/S0008-6223(96)00093-0
18. Wolf S, Tauber RN (1986) Silicon processing for the VLSI era: Volume 1 – Process technology. p 534 ISBN 0-9616721-6-1
19. Ingredient dictionary: P Cosmetic ingredient dictionary. Paula's Choice. Retrieved 16 November 2007
20. Current EU approved additives and their E Numbers. Foods Standards Agency. 14 March 2012. Retrieved April 25, 2015
21. Loto CA, Adeleke AH (2004) Corro Prev Control 6:61
22. Loto CA, Omoosho OA, Popoola API (2011) Intl J Phys Sci 6(9):2075
23. John PB (1997) Corrosion of steel in concrete: understanding, investigation and repair. E & FN, An Imprint of Routledge, London and New York
24. Fontana MG (1978) Corrosion engineering. McGraw Hill International Book Co
25. Landroum RJ (1989) Fundamentals of designing for corrosion control. A corrosion aid for the designer. NACE, Houston, p 352