

Full Length Research Paper

Corrosion resistance of austenitic stainless steel in sulphuric acid

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The resistance and susceptibility of austenitic stainless steel, Type 304, exposed to strong tetraoxosulphate (VI) acids (2 and 5 M concentrations) contaminated with sodium chloride at ambient temperatures was investigated by gravimetric and metallographic/scanning electron microscopy surface characterization methods. Scanning electron microscope (SEM) was used to examine and characterize the test specimen's surface morphology after immersion in the corrosive media. Surface corrosion deposit composition was analyzed with the SEM paired with energy dispersive spectrometer (EDS). This paper reports the observed severe general and pitting corrosion and the resistance of the steel to corrosion at different concentrations of the acid chloride media. The results obtained showed the weak corrosion resistance/appreciable corrosion susceptibility of the stainless steel alloy to the test environments.

Key words: Stainless steel, corrosion, sulphuric acid, acid chloride.

INTRODUCTION

Material deterioration occurs all around us when we look at many metallic items of common use e.g. in chemical industries numerous corrosion problem occurs, some so serious as to cause the shutdown of plants and collapse of structures causing hazards to human life, as such, billions of dollars are lost each year because of corrosion. Corrosion is therefore a matter of great concern due to the enormous cost involved in the replacement of metallic parts in all kinds of applications (Hajra, 1997).

Corrosion can often be predictable or totally unpredictable and catastrophic, such as hydrogen embrittlement or stress corrosion of critical structural members and pressure vessels in the aerospace and chemical process industry (Key to Metals AG, 1999 to 2011). Corrosion process occurs secretly and is difficult to notice until extensive damage has occurred.

The basic cause of corrosion is the inherent instability of metals in their refined forms, thus refined metals being in a much higher energy state than in their corresponding ores tends to return to their original forms of lower energy state. Corrosion cannot be totally eliminated, but its

severity reduced, most especially with the selection of appropriate materials in various applications, especially in aggressive environments.

The desire to gain more knowledge about the corrosion phenomena and their control, hence, appropriate better utilization of engineering alloys, especially austenitic stainless steel, particularly Type 304–UNS S304 008 has been of utmost concern and interest to scientist and engineers worldwide due to their wide spectrum of application in harsh environments, such as in the process industries. Corrosion occurs in many forms in structures made of these steels during service in various media. Some of these forms are intergranular (Wilson, 1995; Zheng et al., 2005) pitting, sulphide stress cracking, chloride stress cracking (Aydogdu et al., 2006; Chen et al., 2006) and stress corrosion cracking (Okpala et al., 2004; Nishimura et al., 2006; Loto et al., 1988). Weld decay is also common in sensitized stainless steel structures (Walker, 1993; Parvathavarthini et al., 2006). The consequences of these forms of corrosion are obvious; varying from enormous material losses to unreliability of operating the equipment which may lead to catastrophic consequences involving both men and money (Ayo et al., 2009).

The corrosion properties of Type 304 stainless steel

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have been studied by a great number of authors and relevant data can be found in a number of publications (Roberge, 2002; Streicher, 2000; Loto et al., 2005; Active Library® on Corrosion, 1992). High corrosion resistance of austenitic stainless steels is primarily attributed to the passive oxide film formed on its surface, exposed to an aqueous solution, which is a mixture of iron and chromium oxides, with hydroxide and water-containing compounds located in the outermost region of the film, and chromium oxide enrichment at the metal-film interface (Marcus et al., 1988). However, the resistance of this passive film is determined by the environmental conditions which the stainless steel is exposed to, as well as the alloy composition.

Dissolution and passivation of 304 stainless steel in deaerated sulphuric acid has shown that chromium content exhibits two stable corrosion potentials, one related to the active, bare chromium surface, and the second one self-establishing on the passive surface of Chromium. In many studies of the structure of the passive film on chromium stainless steels it has been demonstrated that the properties of chromium stainless steels are due to the selective dissolution of Cr alloy and accumulation of Cr_2O_3 on the surface of passive layer, i.e., practically to the formation of a Chromium passive layer (Shreier et al., 2000; Kaesche, 1979; Sato and Okamoto, 1981).

The most effective method of preventing corrosion is the selection of appropriate alloy for a particular corrosion service, 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 austenite metallurgical structure (Brubaker, 1986). The most common form is referred to as "18 – 8" stainless steel (18% Cr and 8% Ni) of which the Type 304 stainless steel belongs.

Stainless steel forms a film which protects the underlying metal from attack in many environments. This film is very thin, transparent and self healing; if damaged mechanically or chemically, the protective film will be reformed very rapidly, however, in a situation in which the rate of damage is more than the rate of repair, a progressive active corrosion occurs.

A large number of corrosion failures can be directly attributed to the indiscriminate selection of stainless steels for construction on the basis that they are all round viable. Austenitic stainless steel represents a class of highly corrosion resistant materials of relatively low cost, whose application should be carefully selected for optimal performance and extended usage.

Tetraoxosulphate (VI) acid (Sulphuric) is the corrosive media used in this work. It is produced more than any other chemical in the world. It has large scale uses covering nearly all industries, such as fertilizer industries, petroleum refinery, paint industry, steel pickling, extraction of non-metals, manufacture of explosives, etc., (Fontana et al., 1978). In chemical industries, it is used

for the production of dye stuffs, pharmaceuticals and fluorine.

Sulphuric acid causes numerous corrosion problems in consumer plant and industries where it is utilized under a variety of conditions. Acid is a very important commodity material and indeed a nation's sulphuric acid production is a good indicator of its industrial strength. It is a constituent of acid rain formed by atmospheric oxidation of sulphur dioxide. The resistance of austenitic stainless steels to tetraoxosulphate (VI) acid is complex due to the active passive nature of the alloys. Any compound capable of donating free chlorine ions (Cl^-) to an aqueous (water-based) solution has the potential for causing failure in austenitic stainless steels. Chlorine ion is extremely electronegative, and therefore, very reactive with certain compounds and elements. This reactivity is part of its usefulness in certain situations, but becomes a double-edged sword where stainless steel is concerned.

In this work, the acid used is further contaminated with sodium chloride (NaCl) to further enhance the breakdown of passivity by the chloride ions. This present investigation aims at evaluating the corrosion resistance of Type 304 austenitic stainless steel at different concentrations of tetraoxosulphate (VI) acid contaminated with sodium chloride to determine its viability and usefulness. It is hoped that the results from this investigation will make a further contribution to the existing knowledge in the selection of Type 304 stainless steel for further industrial and environmental use.

EXPERIMENTAL PROCEDURE

Material

The steel used in this work was the Type 304 austenitic stainless steel of nominal composition; 18.11% Cr, 8.32% Ni and 68.32% Fe. The energy dispersive spectrometer analysis (EDS) of the steel specimen before immersion is as shown in Figure 1A. The material is cylindrical and has a diameter of 0.65 cm (65 mm).

Test media

The test media are: (1) 2 M tetraoxosulphate (VI) acid, (2) 5 M tetraoxosulphate (VI) acid, (3) 2 M tetraoxosulphate (VI) acid + 5% NaCl and (4) 5 M tetraoxosulphate (VI) acid + 5% NaCl. All acids were of Analar grade.

Preparation of test specimens

The cylindrical stainless steel (0.65 cm diameter) was cut into a number of test specimens of different dimensions in length ranging from 1.78 to 1.88 cm. The two surface ends of each of the specimen were ground with silicon carbide abrasive papers of 240, 320, 400 and 600 grits. They were then polished with 1.0 μm diamond paste, washed with distilled water, rinsed with methyl alcohol, dried and stored in a dessicator for further weight-loss test and scanning electron microscopy surface examination and characterization.

EDS analysis

The EDS analysis is as shown in Figure 1A as earlier mentioned. Further EDS analysis of the test specimen's surfaces after the immersion test was performed on the surface film and corrosion deposits. The representative results obtained are as shown in Figure 1B to E.

Weight-loss experiments

Weighted test specimens were fully and separately immersed in each of the two different concentrations of the test media contained in separate 100 ml beakers for 16 days at ambient temperatures. Each of the test specimens was taken out every three days, washed with distilled water, rinsed with acetone, dried and re-weighed. Plots of weight-loss (mg) versus exposure time (days) (Figures 2 and 3) were produced. The corresponding corrosion rates were calculated from the formula:

$$\text{mm/yr} = 87.6 W/\text{DAT} \quad (1)$$

where W is the weight-loss (mg), D is the density (g/cm^3), A is the area (cm^2) and T is the time of exposure (h). The calculated corrosion rate values were used to plot the curves of corrosion rate versus exposure time (days) (Figures 4 and 5).

Scanning electron microscopy (SEM) examination

The polished surface of the steel was etched with oxalic acid and the microstructure examined in the SEM. The obtained micrographs are as shown in Figure 6A and B. Further SEM characterizations of the corroded surfaces were made after many days of immersion of the test specimens in the acid media. Micrographs of the representative areas were made as shown in Figure 7, 8, 9, 10 and 11. All micrographic images were made with JEOL 840 SEM.

RESULTS AND DISCUSSION

Energy dispersive spectrometer analysis

The energy dispersive spectrometer analysis of the steel composition (Figure 1A) gave the nominal compositions of Type 304 austenitic stainless steel used. Apart from the compositional analysis, the micrographs of the steel microstructure, that is, the cross section and the side surface (Figure 2A and B) made from the polished and etched specimen surface confirmed the stainless steel used. The analysis of the corrosion deposit on the surface of the specimen after immersion are as shown in Figure 1B to E for the 2 M tetraoxosulphate(VI) acid, 2 M tetraoxosulphate (VI) acid contaminated with sodium chloride, 5 M tetraoxosulphate(VI) acid and 5 M tetraoxosulphate (VI) acid contaminated with sodium chloride environments, respectively. The elemental sulphur from the acid test media is indicated as a peak in the earlier mentioned figures. Iron and chromium are also present. The sulphur and silicon peak signals represent the analysis of the corrosion deposits on the surface of the specimen immersed in the acidic environments.

Weight-loss method

2 M tetraoxosulphate (VI) acid environment (H_2SO_4)

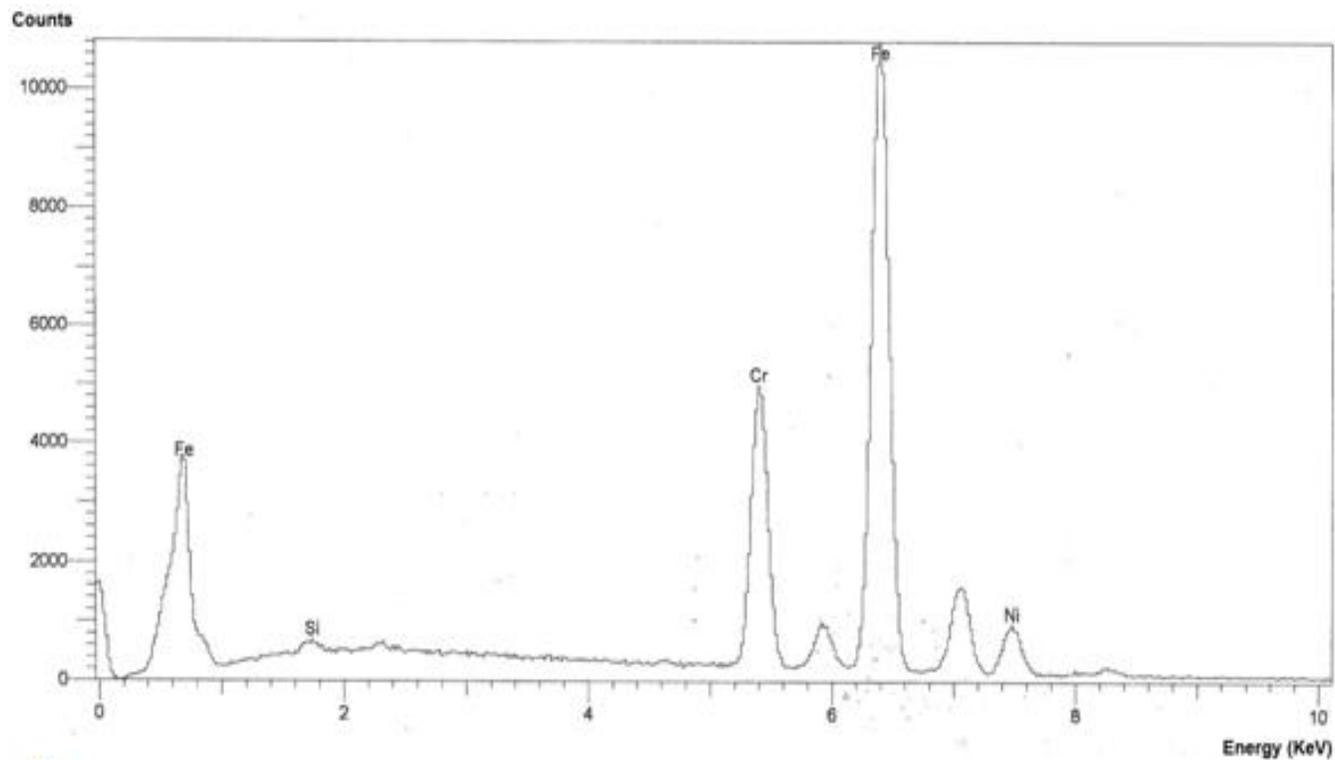
The results obtained for the weight-loss method and the corrosion rate in 2 M H_2SO_4 are as shown in Figures 2A and 4A, and there was a significant increase in the weight-loss of the test specimen with time in the first eight days of the experiment which got to 1.2 mg. After this period and to the end of the experiment, a slightly steady state corrosion reactions phenomenon was maintained and small weight-loss of the test specimen was observed. This observation could be explained to be due to the stifling effect of the corrosive medium by the corrosion deposit which has weakened the acid test environment. In Figure 4a, which is the corresponding curve of the corrosion rate calculated from data in Figure 2A, the corrosion rate was high achieving 0.011 mm/yr within the first four days of the experiment. This was maintained for another four days, from this period the corrosion rate decreased rapidly with time to the end of the experiment. These results are indications that 2 M H_2SO_4 is slightly corrosive to Type 304 stainless steel.

2 M tetraoxosulphate (VI) acid environment (H_2SO_4) + 5% sodium chloride (NaCl)

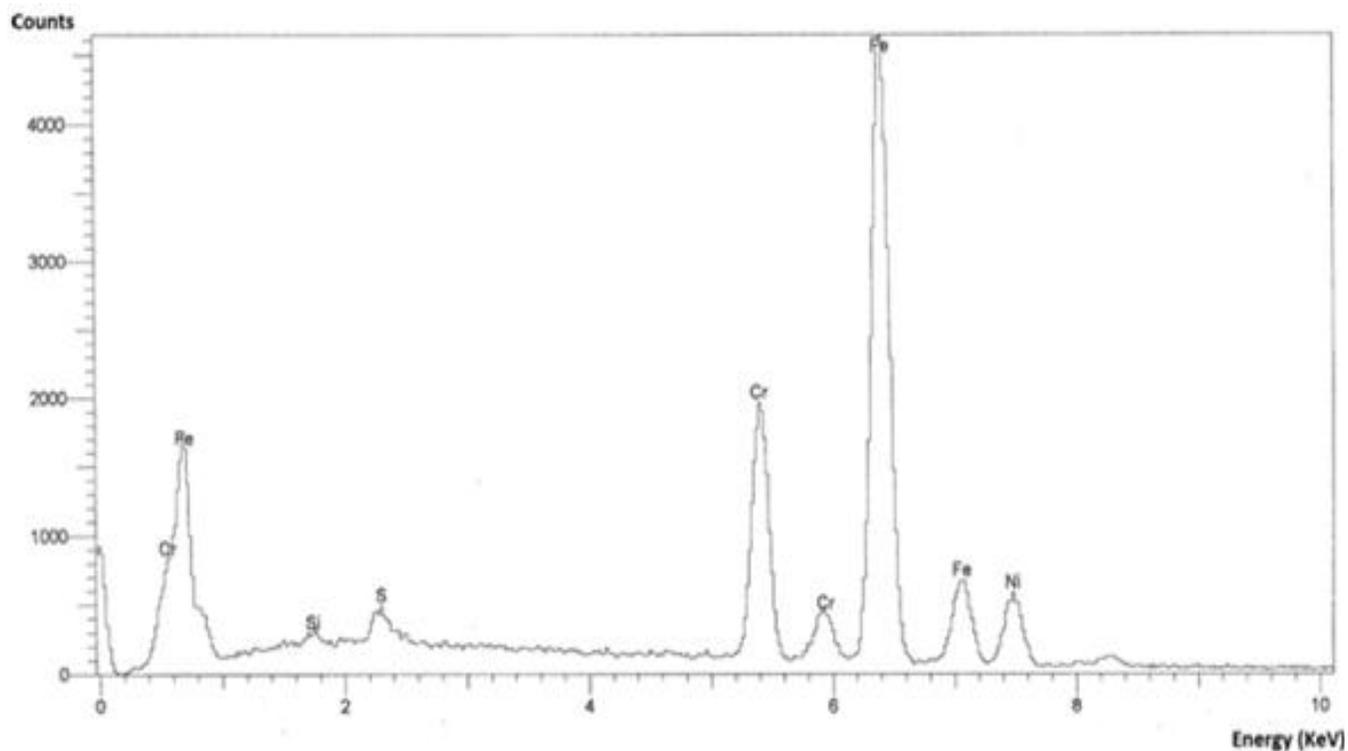
Weight-loss of test specimen and corrosion rate in this environment is as shown in Figures 2B and 4B. The results showed a more significant increase in the weight-loss of the test specimen steadily with time within the first twelve days attaining a value of 38.75 mg which later increased insignificantly to the end of the experiment. In Figure 4b, the corrosion rate was high attaining 0.25 mm/yr at the end of the experiment, thus this test environment is not safe for the use of the Type 304 stainless steel as the 5% sodium chloride further enhanced the corrosion reactions, hence the corrosion rate. The chloride ions (Cl^-) would have made a contribution in breaking down the steel's passive film for Cl^- to react with the steel specimen's surface. The result would be that of initiating active corrosion reactions. This environment is indeed very corrosive to Type 304 stainless steel.

5 M tetraoxosulphate (VI) acid environment (H_2SO_4)

The results for the variation of weight-loss with exposure time for the stainless steel specimen immersed in 5 M H_2SO_4 acid are as shown in Figure 3A. Also presented in Figure 5A are the results of corresponding corrosion rate for the steel specimen immersed in the same acidic environment. Weight-loss in this acid concentration is high for the first nine days achieving a maximum of 1.51 mg before decreasing slightly, after which steady state reactions occurred for another seven days. The corrosion

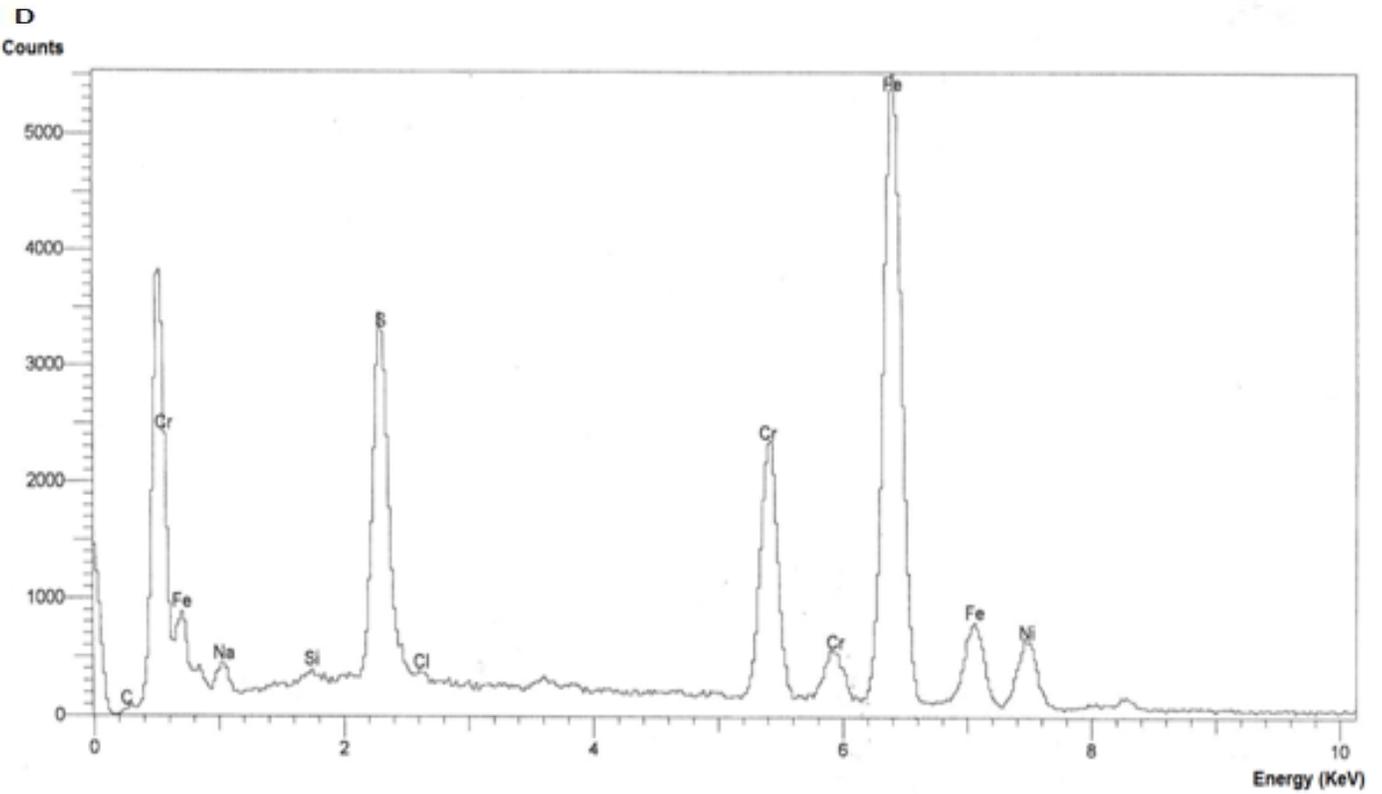
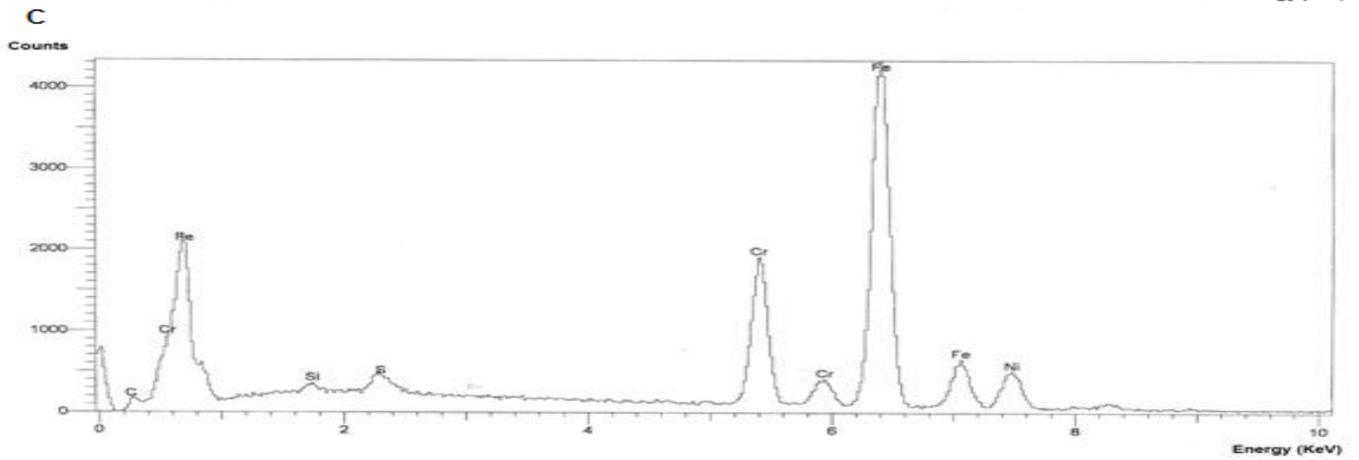
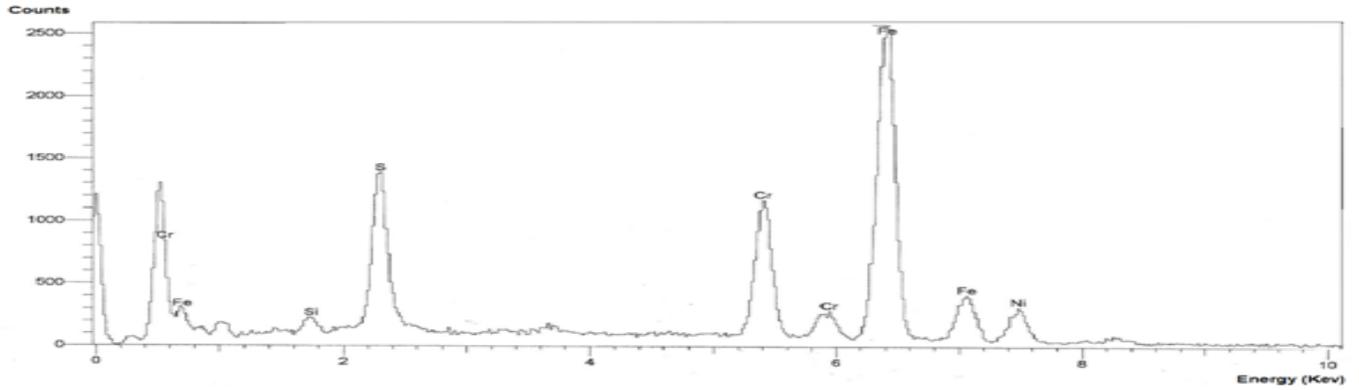


A



B

Figure 1. Energy dispersive spectrometer analysis of Type 304 stainless steel. (A) Untested 304 stainless steel surface, (B) after immersion in 2 M H₂SO₄, (C) after immersion in 2 M H₂SO₄ + 5% NaCl, (D) after immersion in 5 M H₂SO₄ and (E) after immersion in 5 M H₂SO₄ + 5%NaCl.



E

Figure 1. Contd.

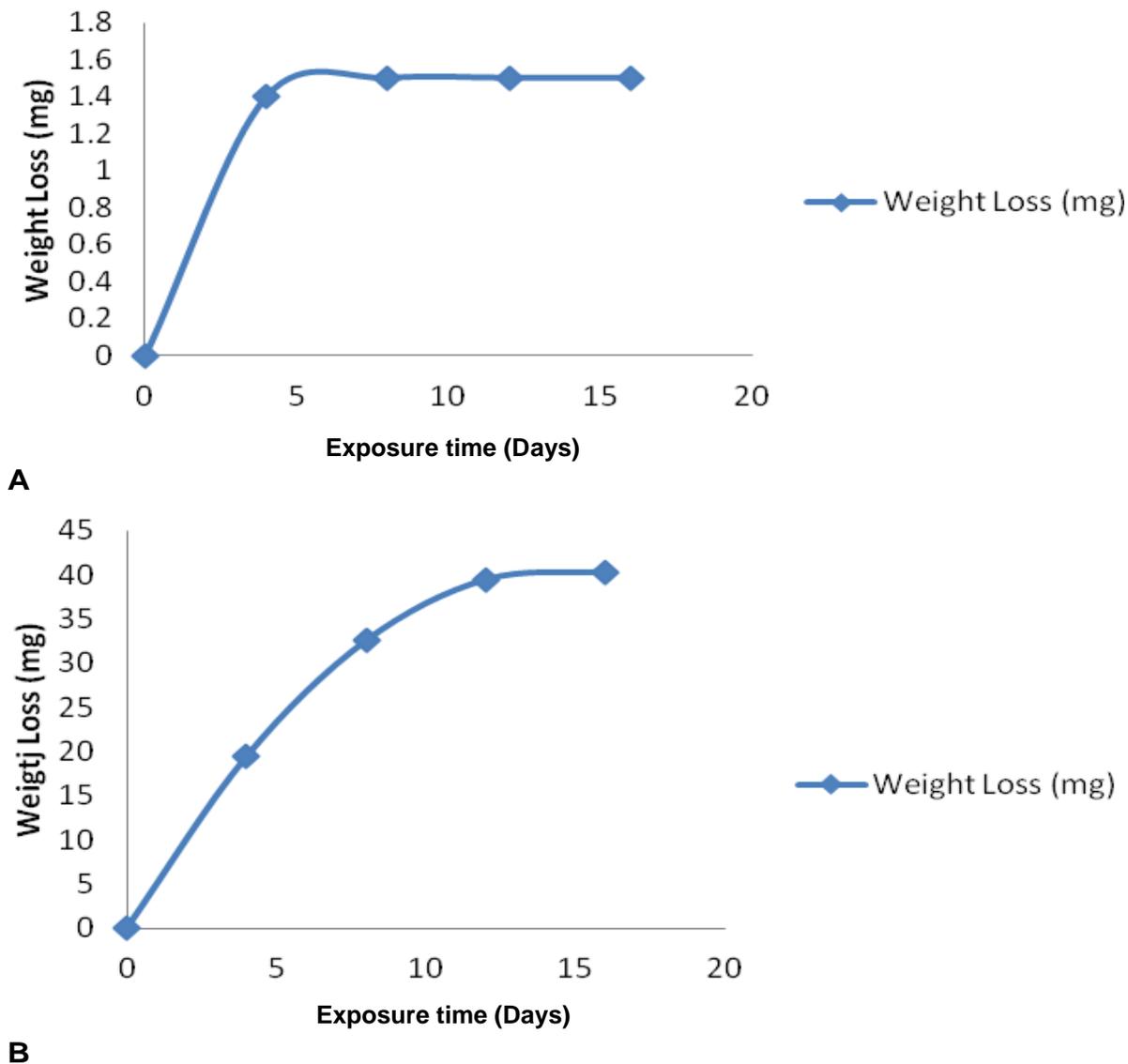


Figure 2. Variation of weight loss with exposure time for austenitic stainless steel specimen. (A) Specimen immersed in 2 M H₂SO₄ and (B) specimen immersed in 2 M H₂SO₄ + 5% NaCl.

rate as shown in Figure 5A indicates a decrease all through the experimental period, due to the weakening effect of the corrosive medium by the corrosion deposits.

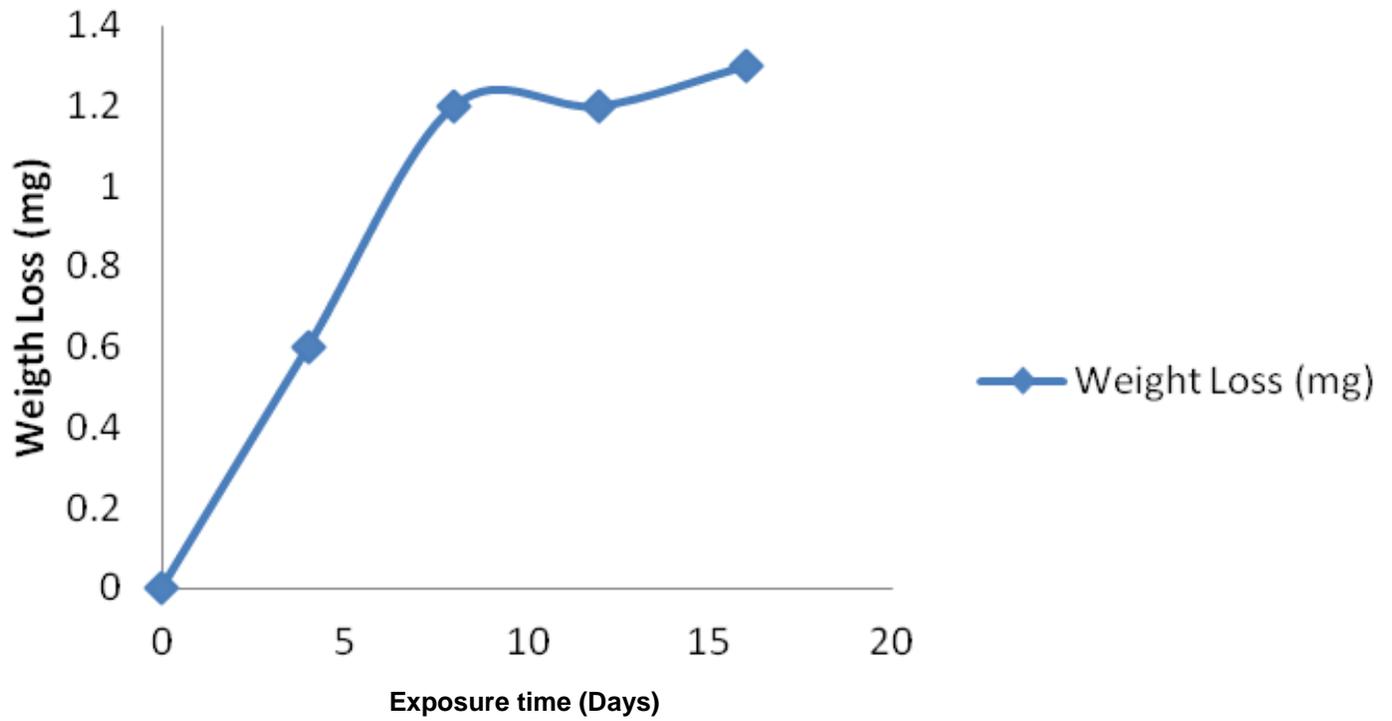
5 M tetraoxosulphate (VI) acid environment (H₂SO₄) + 5% sodium chloride (NaCl)

In this environment, weight-loss was very significant as shown in Figure 3B achieving a maximum of 20 mg in sixteen days of the experiment. This result is observed to be quite different from what was obtained in the 5 M concentration acid media. The corresponding curve of corrosion rate to time (days) in Figure 5B shows drastic decrease in corrosion rate with time throughout the

experimental period from 0.225 mm/yr for the first four days to 0.1 mm/yr at the end of the next twelve days, also due to the reduction in strength of acid medium by the corrosion deposits from the corroding metal specimen.

Comparison of the four different test media

A comparison of the weight-loss and corrosion rate of the four specimens shows that the weight-loss and corrosion rates of 2 and 5 M H₂SO₄ are very low as compared to the media contaminated with 5% sodium chloride (NaCl). This observation is simply due to their close molar concentrations, thus no appreciable difference in weight-loss and corrosion rate results; however, the 2 M H₂SO₄ +



A

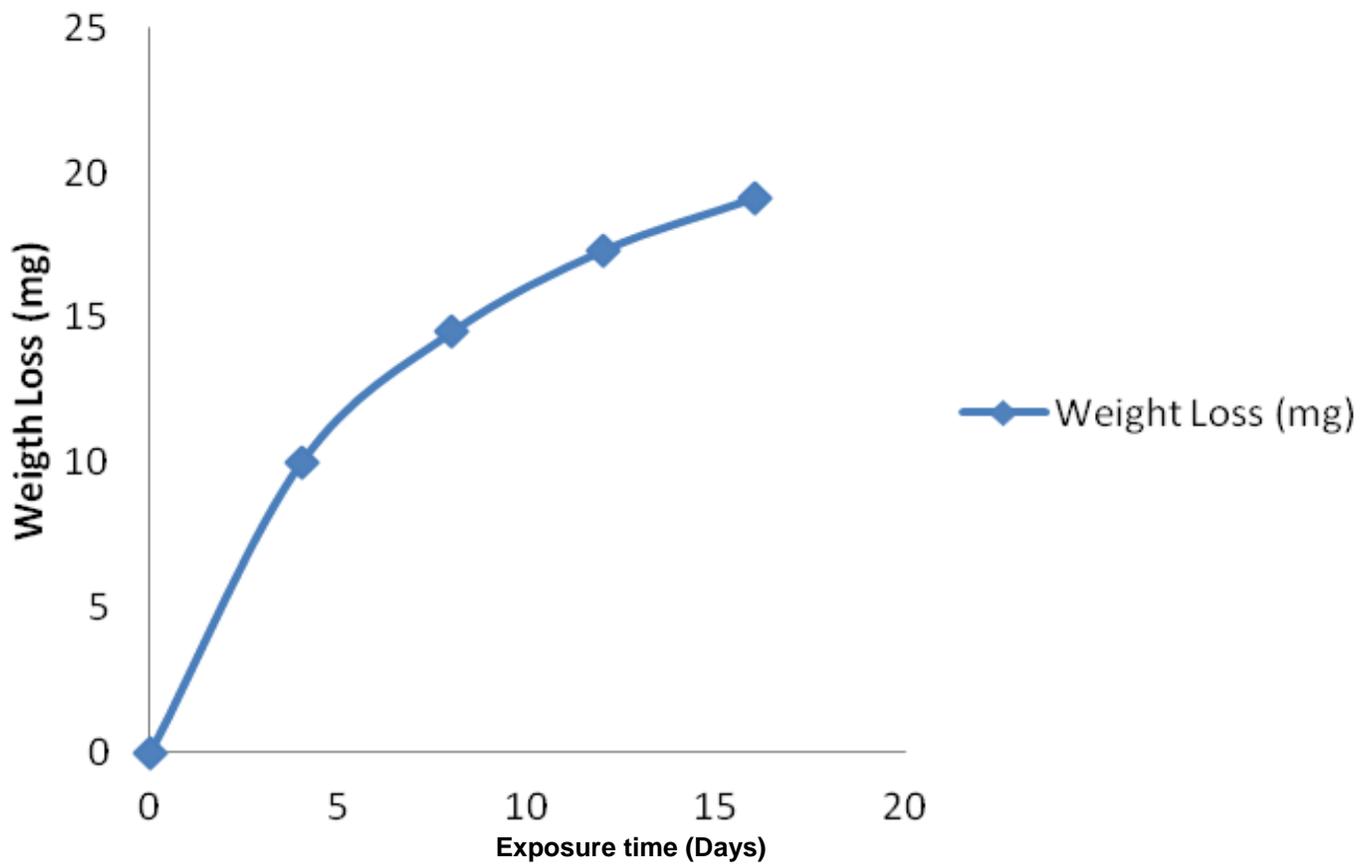
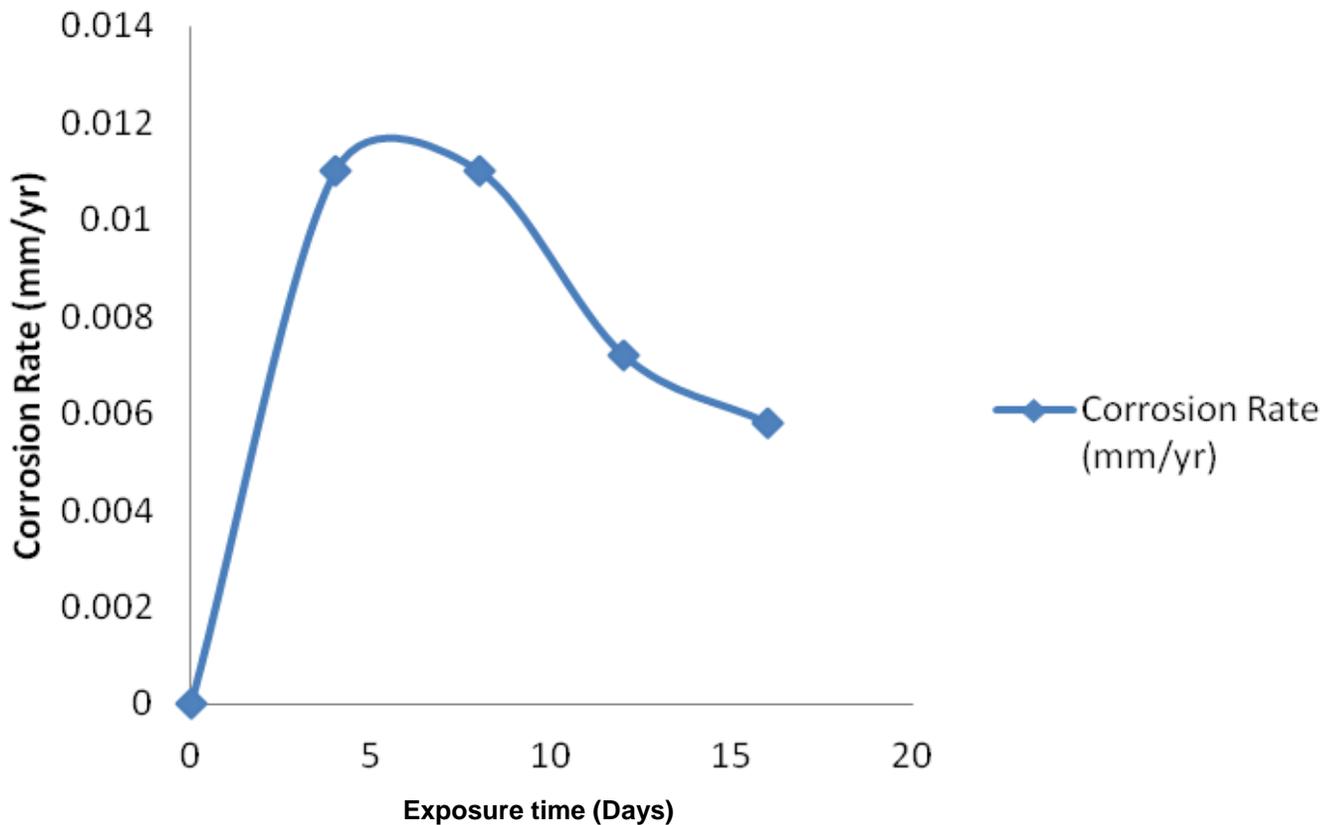
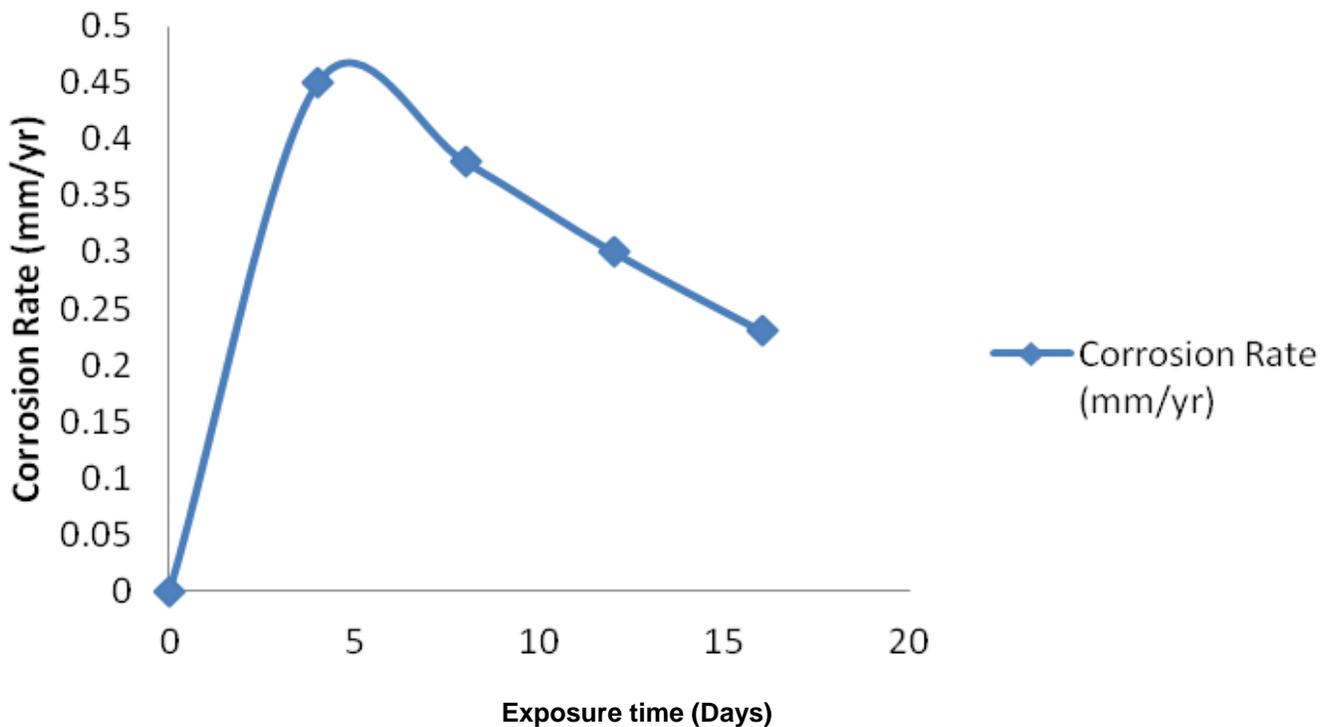


Figure 3. Variation of weight loss with exposure time for austenitic stainless steel specimen. (A) Specimen immersed in 5 M H₂SO₄ and (B) specimen immersed in 5 M H₂SO₄ + 5% NaCl.

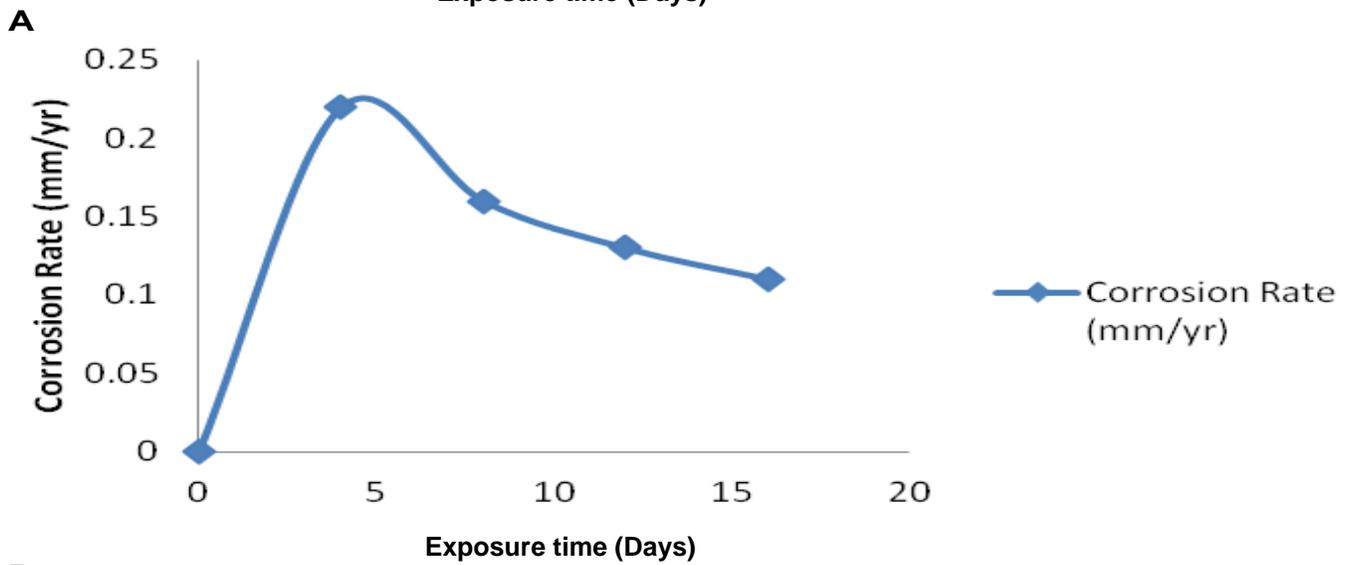
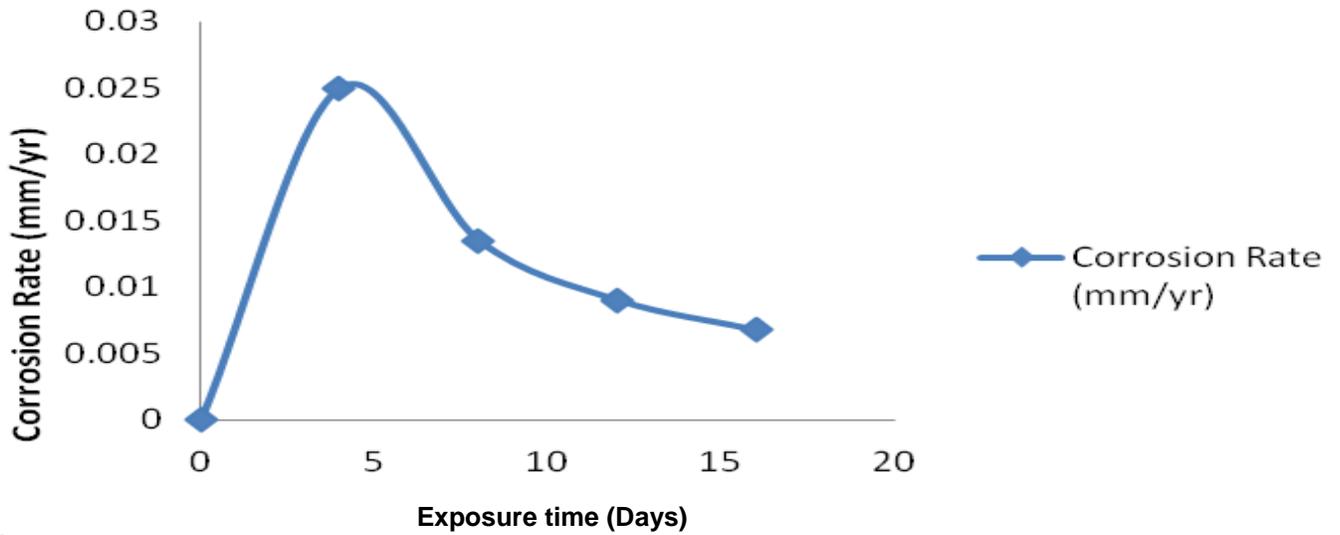


A



B

Figure 4. Variation of corrosion rate with exposure time for austenitic stainless steel specimen. (A) Specimen immersed in 2 M H₂SO₄, and (B) specimen immersed in 2 M H₂SO₄ + 5% NaCl.



B

Figure 5. Variation of corrosion rate with exposure time for austenitic stainless steel specimen. (A) Specimen immersed in 5 M H₂SO₄, and (B) specimen immersed in 5 M H₂SO₄ + 5% NaCl.

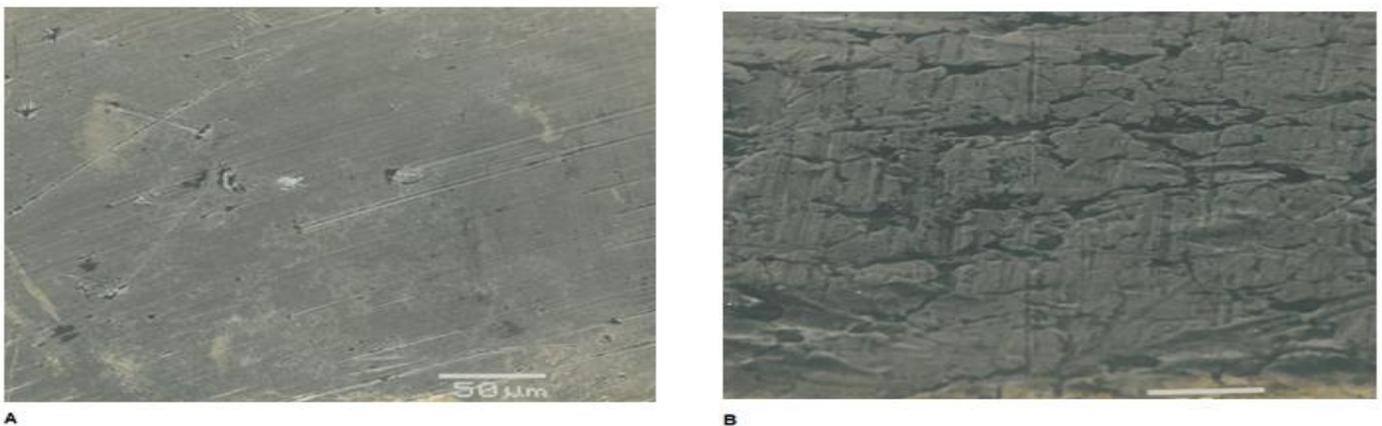


Figure 6. Specimen before immersion. (A) Cut surface (cross section) and (B) side surface of the specimen.

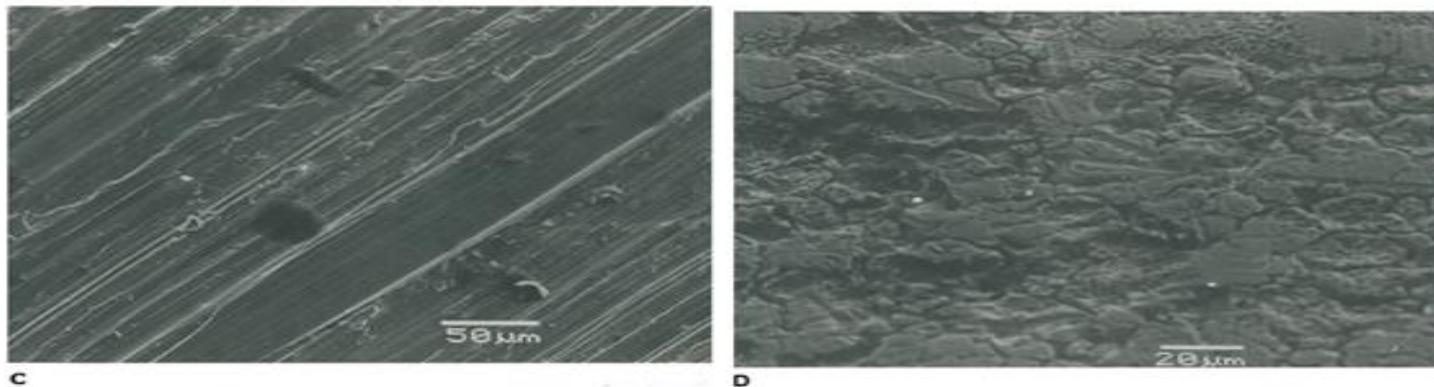


Figure 7. SEM micrographs of steel test specimen's surface after immersion in 2 M H₂SO₄. (C) Cut surface (cross section) (×300) and (D) side surface (×600).

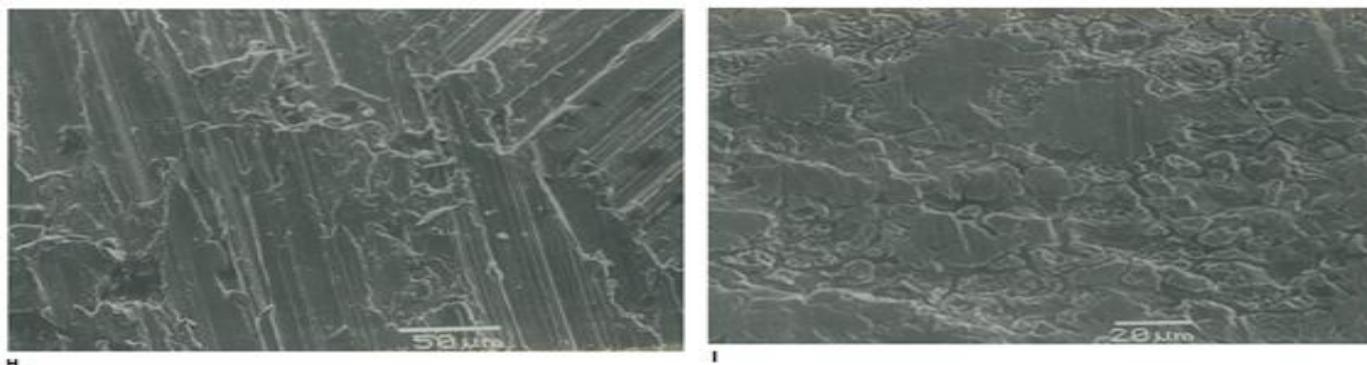


Figure 8. SEM micrographs of steel test specimens after immersion in 5 M H₂SO₄. (H) Cross section (×300) and (I) side surface (×600).

5% NaCl and 5 M H₂SO₄ + 5% NaCl showed a marked difference due to the effect of sodium chloride (NaCl) which greatly assists in depassivating the chromium film, thus exposing the austenitic stainless steel to attack by the corrosive medium. From Figure 2b and d, it can be deduced from the low molar concentration of H₂SO₄ acid contaminated with NaCl, that the weight-loss is higher increasing exponentially with time to the end of the experiment when compared with 5 M H₂SO₄ + 5% NaCl. The corrosion rate of 2 M H₂SO₄ + 5% NaCl is also higher as compared to 5 M H₂SO₄, though, both decreasing progressively with time. From these observations, low molar concentration of the acid media is more aggressive as compared to higher molar concentration, thus it is relatively unsafe for austenitic stainless steel application.

Scanning electron microscopy (SEM)

Specimen examination before Immersion

The representative polished cross-section surface and the side view (lengthwise) of the cylindrical test

specimens (Figure 6A and B) were examined in the scanning electron microscope before the immersion test for the weight-loss method. Two micrographs were taken to reveal the specimens appearance before the corrosion test as shown in Figure 6.

Steel specimen immersed in 2 and 5 M H₂SO₄ test media

The SEM micrographs made for the steel test specimen immersed in 2 and 5 M H₂SO₄ acid are as shown in Figures 7C and D and 8H and I. Figure 7C shows the cross-section surface after the weight-loss immersion test at a low magnification ×300, while Figure 7D is a portion of Figure 7C, but at a higher magnification ×600 for the 2 M H₂SO₄. Figure 7C and D shows the topographic image of the corroded surface. The severe corrosive degradation of the acid test media is very apparent. The corrosion mode was that of severe general corrosion. This is also slightly similar to the micrographs obtained from 5 M H₂SO₄ (Figure 8H and I), though the extent of damage is less when compared to 2 M H₂SO₄ test media.

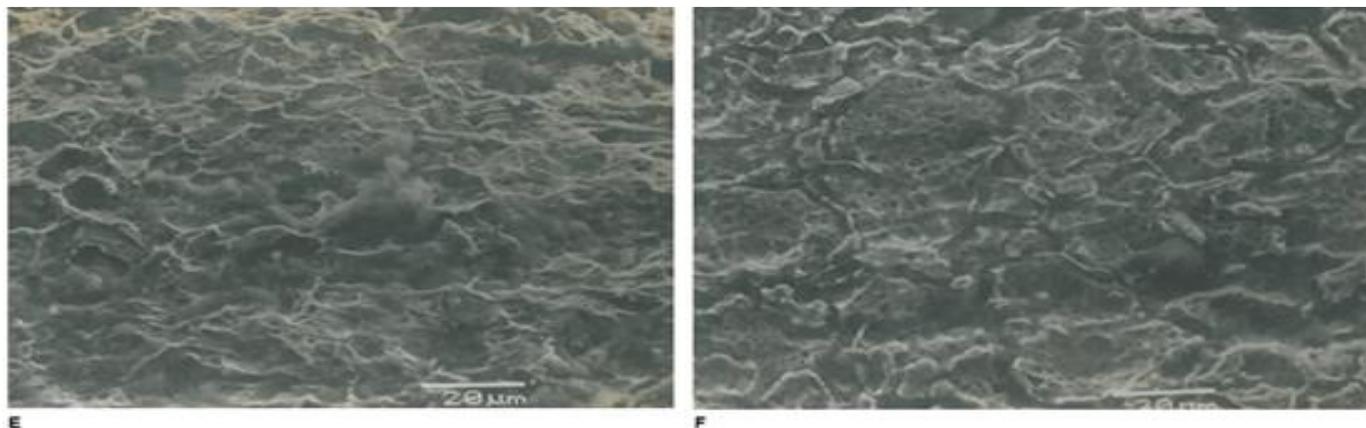


Figure 9. SEM micrographs of steel test specimens after immersion in 2 M H₂SO₄ + 5 NaCl, (E) side surface of the specimen (x800) and (F) cut surface (cross section) (x800).

In both acid media, the corrosion reaction species are sulphate ions (SO₄⁻) from the tetraoxosulphate (VI) acid. These ions breakdown the chromium protective film on the stainless steel surface (film rupture) achieved by penetrating through the passive film to begin the process of active interfacial corrosion reactions at the specimen surface.

Steel specimen immersed in 2 M H₂SO₄ + 5% NaCl and 5 M H₂SO₄ + 5% NaCl

The SEM micrographs of the specimens immersed in 2 M H₂SO₄ + 5% NaCl and 5 M H₂SO₄ + 5% NaCl acid medias contaminated with NaCl are as shown in Figures 9E and F and 10G and 11J at magnification x300 and x800, respectively. The corrosion damage in the micrographs was immense (complete corrosion degradation). This was due to the effect of sulphate ions (SO₄⁻) in addition to chloride ions (Cl⁻) which further assists in the accelerated breakdown of the chromium film similar to those earlier discussed, but the extent of damage was more severe in test media 2 M H₂SO₄ + 5% NaCl.

Mechanism of corrosion failure

It could be observed that the stainless steel specimen failed in the test media and with greater intensity in the acid chloride. The combined chloride and sulphate ions would undoubtedly cause more deleterious corrosion reactions. Their ability to penetrate the stainless steel formed film on the surface of the metal to initiate, perpetrate and sustain corrosion reactions would be more drastic. The consequence of this was that of severe active corrosion reactions of anodic dissolution of this tested alloy. In the presence of these reacting species,

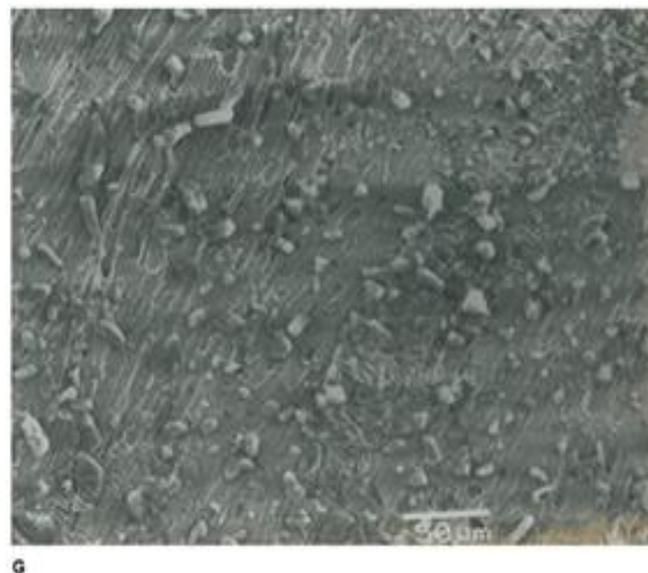


Figure 10. SEM micrographs of steel test specimens cut surface (cross section) after immersion in 2 M H₂SO₄ + NaCl (x300).

Cl⁻ and SO₄⁼ at high concentrations, the ability of the stainless steel to repair its film was drastically reduced and the protection was hence lost.

Conclusion

Austenitic stainless steel is susceptible to dilute sulphuric acid environments, with significant pitting corrosion and extensive damage of the surface topography, though, the steel tends to be more resistant at higher molar concentrations of the acid media as compared to the lower concentration; however, its viability in such stringent condition is limited.

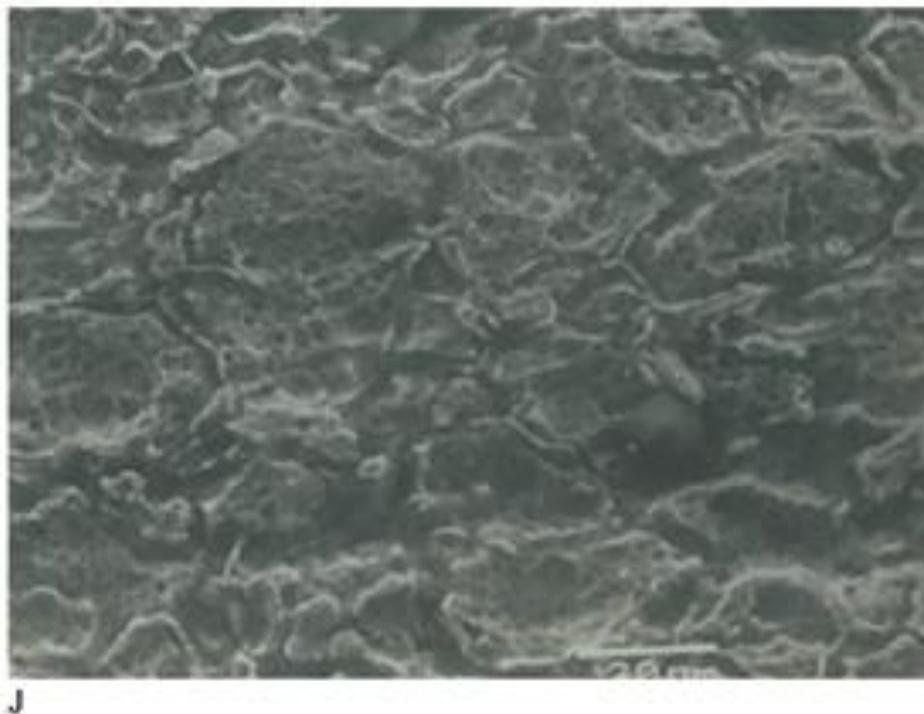


Figure 11. SEM micrograph of steel test specimens after immersion in 5 M H₂SO₄ + 5 NaCl (side surface) (x800).

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