CORROSION BEHAVIOUR OF AUSTENITIC STAINLESS STEEL GRADE 316 IN STRONG ACID SOLUTION

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Abstract: -

The resistance and susceptibility of austenitic stainless steel grade 316 exposed to strong acids solution (1M H_2SO_4, 4M H_2SO_4 and 1M HCl) at ambient temperature. Weight loss method was used to examine the corrosion rate of steel after immersion in the corrosive media or environment. During the research work reports observed severe general and pitting corrosion and the resistance of the steel to corrosion at different corrosive environment (concentration of the acid media). The result obtained showed the weak corrosion resistance / appreciable corrosion susceptibility of the austenitic stainless steel grade 316 to the test environment.

Key words: - Corrosion, Austenitic Stainless Steel Grade 316, 1M H_2SO_4, 4M H_2SO_4, and 1M HCl.

INTRODUCTION

Austenitic stainless steels are widely used in industrial applications due to their strength, corrosion resistance, mechanical workability, and excellent electrical and thermal conductivities. Among them, AISI 316 stainless steel is of great practical interest because it is employed in pharmaceutical, petrochemical, offshore drilling marine shipping, water desalination, marine environment etc. AISI type 316 stainless steels are used to handle much diluted acid at low temperature [1].

High corrosion resistance of austenitic stainless steels is primarily attributed to the passive oxide film formed on its surface that, exposed to an aqueous solution, 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 [2]. However, the resistance of this passive film is determined by the environmental conditions which the stainless steel is exposed to, as well as by the alloy composition.

It is well known that under the action of aggressive ions, i.e. chloride anion, local breakdown of passivity occurs, mainly at sites of local heterogeneities, causing pitting corrosion. The mechanism of pitting attack of stainless steel has been divided into three consecutive steps: initiation, metastable propagation and stable propagation of pits. The initiation step is mainly a local breakdown of the passivation oxide layer in presence of aggressive anions of the environment. The corrosion rate is increased by the fact that even more aggressive environment is produced by the corrosion reaction itself. However, at the earlier stages of pit propagation,when the pits are still very small, they can be repassivated spontaneously.This stage is often referred as metastable pit growth. Thestage of stable propagation is reached when spontaneous repassivation is no longer possible [3].

The reason for the good corrosion resistance of stainless steels is that they form a very thin, invisible surface film in oxidising environments. This film is an oxide that protects the steel from attack in an aggressive environment. As chromium is added to steel, a rapid reduction in corrosion rate is observed to around 10% because of the formation of this protective layer or passive film. In order to obtain a compact and continuous passive film, a chromium content of at least 11% is required. Passivity increases fairly rapidly with increasing chromium content up to about 17% chromium. This is the reason why many stainless steels contain 17-18% chromium.

The most important alloying element is therefore chromium, but a number of other elements such as molybdenum, nickel and nitrogen also contribute to the corrosion resistance of stainless steels. Other alloying elements may contribute to corrosion resistance in particular environments - for example copper in sulphuric acid or silicon, cerium and aluminium in high temperature corrosion in some gases.

Corrosion is the gradual destruction of material, usually metals, by chemical reaction with its environment. In the most common use of the word, this means electrochemical oxidation of metals in reaction with an oxidant such as oxygen. Corrosion degrades the useful properties of materials and structures including strength, appearance and permeability to liquids and gases. Corrosion can be concentrated locally to form a pit or crack, or it can extend across a wide area more or less uniformly corroding the surface. Because corrosion is a diffusion-controlled process, it occurs on exposed surfaces. As a result, methods to reduce the activity of the exposed surface, such as passivation and chromate conversion, can increase a material's corrosion resistance [4].

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 pitting [5].

Sulphuric acid causes numerous corrosion problems in consumer plant and industries where it is utilized under a variety of conditions.The resistance of austenitic stainless steels to 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 [6].

Sulphuric acid and hydrochloric acids are the two corrosion media used in this investigation. Apparently, more sulphuric acid is produced than any other chemicals in the world. It is used directly or indirectly in nearly all industries. It is principally used in the production of chemicals and their derivatives, pickling of steel and other metals, manufacture of fertilizers, dyes, drugs, pigments, explosives, synthetic detergents, rayon and other textiles, petroleum refining, and the production of rubbers. In making the acids, the problem of corrosion is significant in the production plants. The acid also causes major problem in consumers' plants when it is utilized under a wide variety of conditions. The resistance of austenitic stainless steels to sulphuric acid is complex due to the active-passive nature of the alloys [7].

Aqueous Corrosion Theory

Aqueous metallic corrosion is an electrochemical process that compromises metal oxidation (anodic) (Eq 1) and reduction (cathodic) reactions at the interface of a metal and aqueous electrolyte. Oxygen reduction (Eq 2) is observed in an aerated environment and\ hydrogen reduction (Eq 3) is observed in an acidic environment, both reduction reactions will occur in acidic, aerated environments.

$$M \rightarrow M^+ + ne^- \qquad (1)$$

$$\tfrac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^- \qquad (2)$$

$$2H^+ + 2e^- \rightarrow H_2 (g) \qquad (3)$$
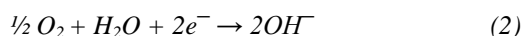
Standard immersion tests are useful for predicting a given alloy's service life in some environments. However these require long testing times, are expensive and are unable to reveal fundamental chemical processes occurring at the surface.

Pitting Corrosion

Pitting corrosion on a stainless steel surface is initiated by localized damage of thepassive film due to mechanical wear or environmental aggressiveness; this allows local anodicdissolution of iron before the passive film is re-formed. Instantaneous re-passivation kineticsprevents a majority of the initiated (meta-stable) pits from developing into growing (stable) pits.If the local pit environment becomes depleted in dissolved oxygen relative to the surroundingmetal, an area containing a small anode and large cathode and arises allowing stable pit growthgoverned by the following anodic (Eq 4) and cathodic (Eq 5) reactions.

$$Fe \rightarrow Fe^2 + 2e^- \qquad (4)$$

$$\tfrac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^- \qquad (5)$$

The aim of this study was to develop methods and procedures to clarify the localised corrosion risk of stainless steels in applications where solution concentration due to water evaporation is possible [8].

EXPERIMENTAL PROCEDURE

MATERIAL

Austenitic stainless steel AISI 316 plates have been used. Table 1 provides its nominal chemical composition. The composition of steels as analyzed by optical emission spectrophotometer is given in the Table 1.The material is rectangularwith a dimension 3 cm x 2 cm x 0.6 cm

Table 1 chemical composition of grade 316 austenitic stainless steel

Elements	C	Mn	Si	P	Cr	Ni	Mo	V	Cu	Sn	Al
Wt%	0.08	0.44	0.019	0.009	16.67	9.86	2.09	0.070	0.49	0.013	0.042

Test Media and preparation of solution

1M sulphuric acid, 4M sulphuric acid, 1M hydrochloric acids were used as the corrosive medium. Selected concentrations of hydrochloric or sulphuric acid were prepared by dilution of the corresponding concentrated solutions using twice-distilled water.

Preparation of Test Specimens

Plates of stainless steel were cut to dimensions 3 cm x 2 cm x 0.6 cm. The surface was ground employing a gradual sequence of emery papers of different grit sizes, namely 80, 120, 180, 220, 320, 400, 600, and 800 grades and then polished with $6.0u$m to $1.0u$m diamond paste. The ground specimen was rinsed, cleaned dried in air. All chemicals used in this work (namely HCl, H_2SO_4) were reagent grade.

Allspecimens were immersed at the same time in the experimental media which was sulphuric acid at concentrations of 1M, 2M and hydrochloric acid at concentration of 1M.

Weight-Loss Measurement

The weight loss technique which involves exposing a specimen of material to thecorroding environment for a given duration and then removing the specimen forweighing is the best known and the simplest of all corrosion measurement techniques.
The weight loss or gain is taken over the period of exposure, and later expressed as acorrosion rate. The determination of weight loss of a material in a corrosionexperiment has been one of the common methods used to calculate corrosion rates [9]. The weight loss technique is used so as to enable thecorrosion rate measurements to be done without disturbing the plant operation. The advantage of the weight loss technique is that the corrosion whichhas actually occurred can be observed on the sample. Moreover, this technique allows a visual examination, physical measurements and the chemical analysis of thecorrosion products.

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 12 days at ambient temperatures. Each of the test specimens was taken out every day (after 24 hours), washed with distilled water, rinsed with acetone, dried and re-weighed. Plots of weight-loss (mg) versus exposure time (days) (Figures 1, a, b, c) were produced. The corresponding corrosion rates were calculated from the formula:
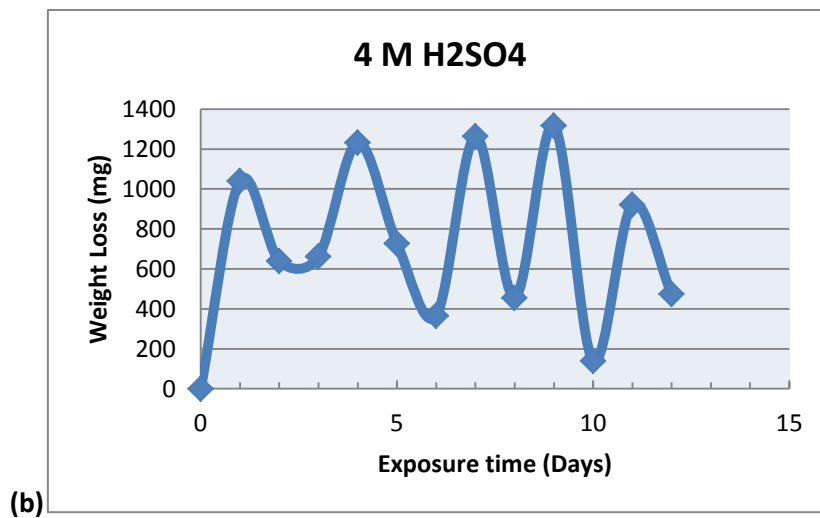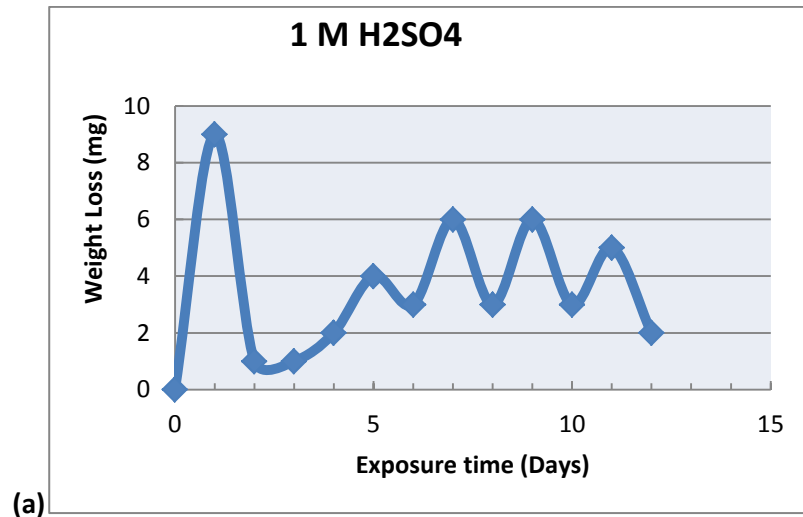
$$mm/yr = 87.6 \ W/DAT$$

Where W is the weight-loss (mg), D is the density (g/cm^2), A is the area (cm^2) and T is the time of exposure (hr).

The calculated corrosion rate values were used to plot the curves of corrosion rate versus exposure time (days) (Figures 2).

3. RESULTS AND DISCUSSION
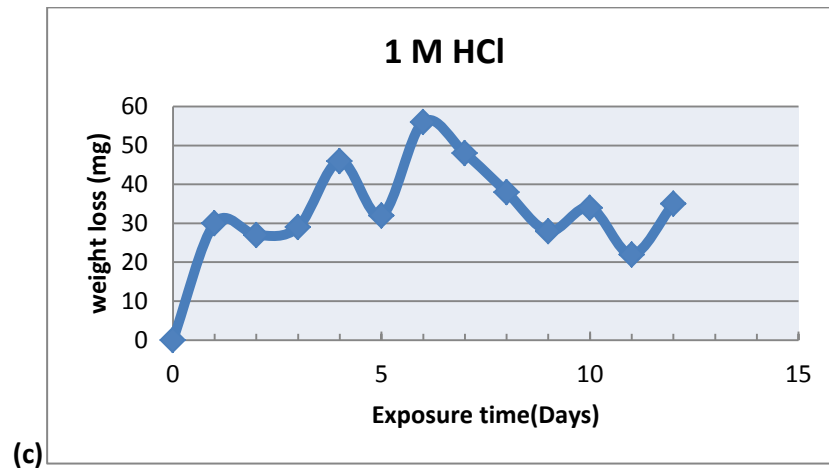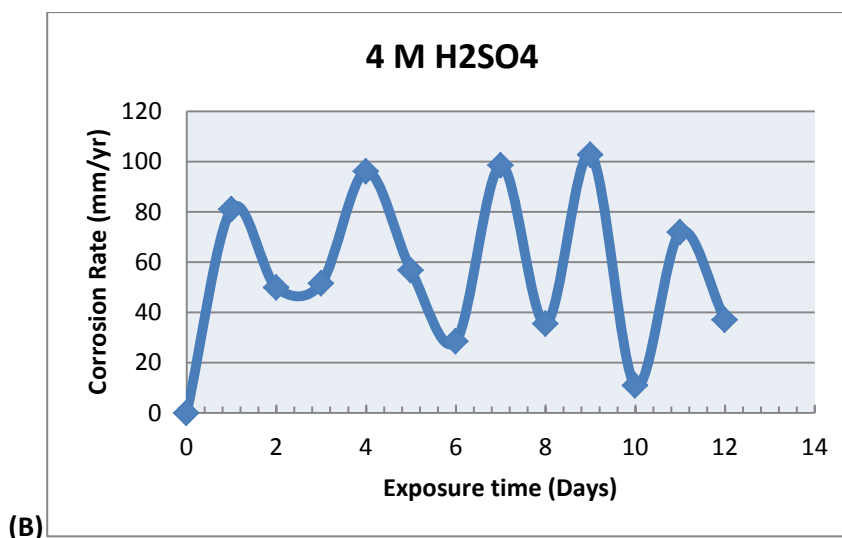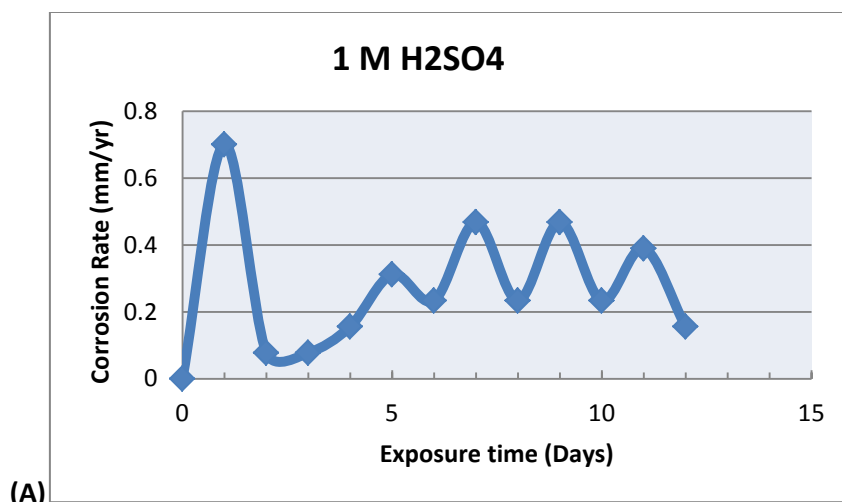
RESULTS

The results are shown in fig 1 to 4.

(a)

(b)

(c)

Figure 1 Variation of weight loss with exposure time for Grade 316 austenitic stainless steel specimen. (A) Specimen immersed in 1 M H_2SO_4 and (B) specimen immersed in 4 M H_2SO_4 (C) specimen immersed in 1 M HCl
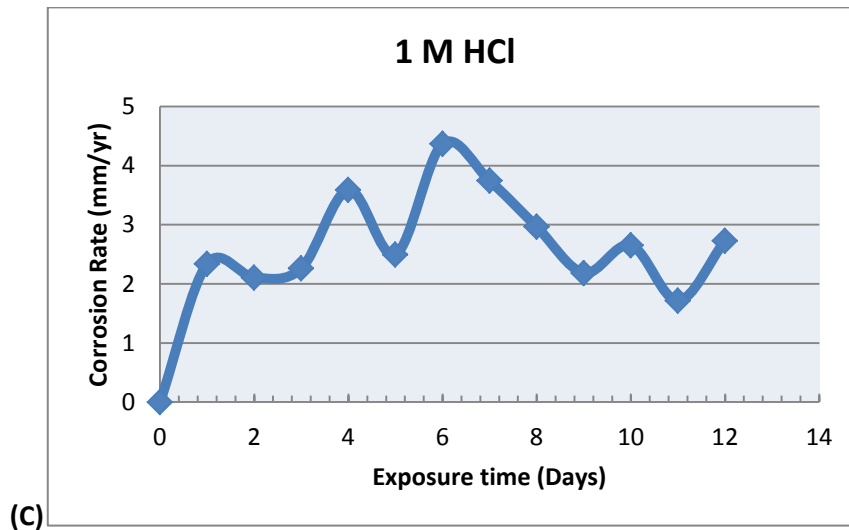

(A)

(B)

Figure 2 Variation of corrosion rate with exposure time for austenitic stainless steel specimen. (A) Specimen immersed in 1 M H2SO4, (B) Specimen immersed in 4 M H2SO4, and(C) Specimen immersed in 1 M HCl
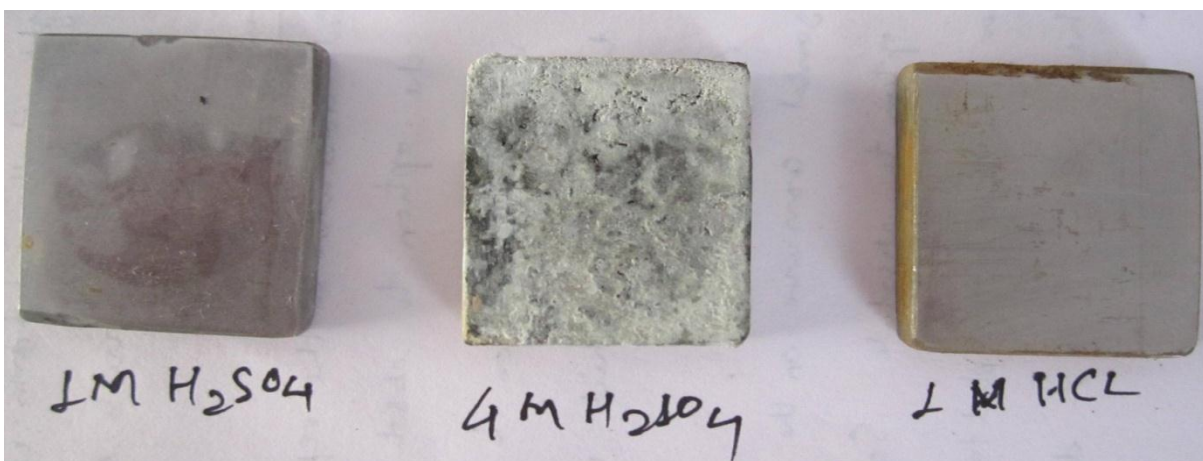

Fig.3 Photographs of sample before corrosion.

Fig.4 Photographs of sample after corrosion.

DISCUSSION

1 M H_2SO_4 acid corrosive environment

The results obtained for the weight-loss method and the corrosion rate in 1 M H_2SO_4 are as shown in Figures 1A and 2A, 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 29 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 2a, which is the corresponding curve of the corrosion rate calculated from data in Figure 1A, the corrosion rate was high achieving 0.70119 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 1M H_2SO_4 is slightly corrosive to Type 316 stainless steel.

4 M H_2SO_4 acid corrosive environment

The results obtained for the weight-loss method and the corrosion rate in 4M H_2SO_4 are as shown in Figures 1B and 2 B, 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 1.264 g. 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 2b, which is the corresponding curve of the corrosion rate calculated from data in Figure 1B, the corrosion rate was high achieving 96.085 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 4M H_2SO_4 is slightly corrosive to Type 316 stainless steel.

1 M HCl acid corrosive environment

Weight-loss of test specimen and corrosion rate in this environment is as shown in Figures 1C and 2C. The results showed a more significant increase in the weight-loss of the test specimen steadily with time within the first sixth days attaining a value of 56 mg which later increased insignificantly to the end of the experiment. In Figure 2C, the corrosion rate was high attaining 4.3675 mm/yr at the end of the experiment, thus this test environment is not safe for the use of the Type 316 stainless steel. 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 316 stainless steel.

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, 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 astringent condition is limited.

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