The Electrochemical Behavior of Mild Steel in Sulfide Polluted NaCl at Different Velocities

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This paper studies the effect of solution speed and sulfide ion concentration present as a pollutant in 3.5% NaCl solution on the electrochemical behavior of mild steel. The weight loss/gain due to the interaction of the materials with the surrounded environments was calculated after rotating cylindrical-shape mild steel samples in sulfide polluted NaCl solution for 24 hrs at a speed of 0, 300, 600 and 900 ppm using a rotating disc electrode at room temperature. The effect of pollutant concentrations due to presence of sulfide ions on the electrochemical behavior was studied in NaCl solution containing 0.001, 0.005 and 0.010 M Na_2S. The presence of sulfide ions in NaCl solution enhanced the corrosion attack due to the localized replacement of the protective Fe-oxide film by a non-protective iron sulfide film. On the other hand, increasing the solution speed in presence of sulfide ions increased the corrosion attack which can be explained in the light of the synergistic action between the presence of sulfide and increasing the solution speed.

1. INTRODUCTION

The corrosion of steel in sulfide-containing solutions has received considerable attention for many years due to its importance in several industrial processes such as oil and gas production and transport. The evaluation of steel corrosion in sulfide environments is important in the petrochemical industry, as this phenomenon is responsible for costly economic and human loss [1].

Mild steel is a well-known structured material in the petroleum industry due to its low cost, good mechanical and corrosion resistant properties. The presence of some pollutants, mainly sulfide, in

the oil can affect the performance of mild steel in the petrochemical industry, as this phenomenon is responsible for costly economic and human loss [1-4].

Sulfide pollution of seawater can occur from the industrial waste discharge, biological and bacteriological process in seawater, which enhances the corrosion of steels. The solution speed in presence of suspended particles such as sand or fine waste particles and aggressive ions such as chloride and sulfide can have a marked effect on the corrosion protection performance of mild steel. The interaction of the suspended particles and aggrieve ions with the mild steel at high solution speed can result in erosion corrosion.

Erosion-corrosion occurs when a metal is exposed to flowing corrosive environment. The resulted mass loss is often much higher than ordinary summation of the mass loss due to pure erosion and that due to pure corrosion. The additional part is defined by the term of synergistic effect, which has a substantial contribution to the total material loss of the components suffering erosion-corrosion, especially in offshore systems. The weight loss of material in erosion-corrosion process is considered to be contribution due to electrochemical corrosion and mechanical erosion. Although the problem caused by the interaction of erosion and corrosion is very serious, the mechanism of synergy is still not thoroughly understood because of its complexity [5]. Therefore, the aim of this work is to investigate the effect of solution speed and sulfide ion concentration on the electrochemical behavior of mild steel in 3.5% NaCl solution.

2. EXPERIMENTAL PART

2.1. Materials

The electrodes used were cut from a mild steel rod and prepared in cylindrical form with diameter of φ0.85 cm and height of 3 cm. The chemical composition is 0.087 Si, 0.44 Mn, 0.013 Ti, 0.026 V, 0.005 Al, 0.002 Cr, 0.0005 Ni, 0.0009 Mo, 0.0006 Nb, 0.003 Cu, 0.029 Co, 0.011 W, 0.011 Pb, 0.05 C and Fe balance.

2.2. Surface preparation

Each specimen was abraded to a 800 grit finish with SiC paper, degreased in acetone, washed and dried in dry air. Laboratory grade chemicals were used to prepare all solutions.

2.3. Methods

2.3.1. Erosion-corrosion measurements

A series of samples were weighed before immersion in the electrolyte solution of NaCl containing 0, 0.001, 0.005, 0.010 M Na_2S. The solution pH was 6.5, 8.13, 8.60 and 10.88 respectively. All the samples were rotated for 24 hr at room temperature under different rotating speeds: 0, 300, 600,

and 900 rpm respectively. Then, the samples were rinsed with distilled water and acetone, dried with hot air, and weighed again.

2.3.2. Polarization tests

Liner polarization measurements of specimens, previously immersed for 30 minutes in the solutions (Table 2), were made using a scan rate of 0.07 mV/sec in the applied potential range from -0.15 V_{SCE} to 0.7 V_{SCE} with respect to E_{Corr} using an Autolab PGSTAT 30 galvanostat/ potentiostat. The exposed surface area was 25.4 mm^2. All curves were normalized to 1 cm^2.

2.3.3. Energy-dispersive spectrometry

SEM images of the cleaned samples were obtained using a digital scanning electron microscope, Model JEOL JSM 5410, Oxford Instruments. Microprobe analysis was performed using energy dispersive spectrometry, EDS, Model 6587, Pentafet Link, Oxford microanalysis group.

2.3.4. X-ray diffraction

After drying the corroded specimen (one week in corrosive solutions) with methanol, the solid surface corrosion products were characterized by an X-ray diffractometry (XRD). XRD analysis was performed using Bruker AXS, Model D8, 40 kV, 40 mA, Cu Kα ADVANCE.

2.3.5. Surface morphology

Corrosion morphology was examined with a metallographic microscope (LEICA DMR) with a Quips Programming window, LEICA Imaging Systems Ltd.

3. RESULTS AND DISCUSSION

3.1. Erosion-corrosion measurements

3.1.1. In absence of sulfide

In sulfide free 3.5% NaCl solution, increasing the rotation speed from 0 to 600 rpm has no marked effect on the corrosion rate due to the stability of the protective iron oxide layer to resist the chloride ions attach from the NaCl solution. Further increase in the solution speed up to 900 rpm increases the possibility to remove such protective layer and hence the corrosion rate will increase twice of that obtained at low speed (Fig.2).

3.1.2. In presence of sulfide

Generally, the presence of sulfide ions in NaCl solution resulted in a marked increase in the corrosion rates due to the local acidification caused by iron sulfide formation. The localized replacement of the protective Fe-oxide film by a non-protective iron sulfide film is responsible for increasing the pitting and erosion corrosion attack.

Under static conditions (zero solution speed), the corrosion rates based on weight-loss measurements increased dramatically from 25 MPY in sulfide-free solution to be 65, 80 and 100 MPY at 0.001, 0.005 and 0.010 M Na2S containing solution respectively.
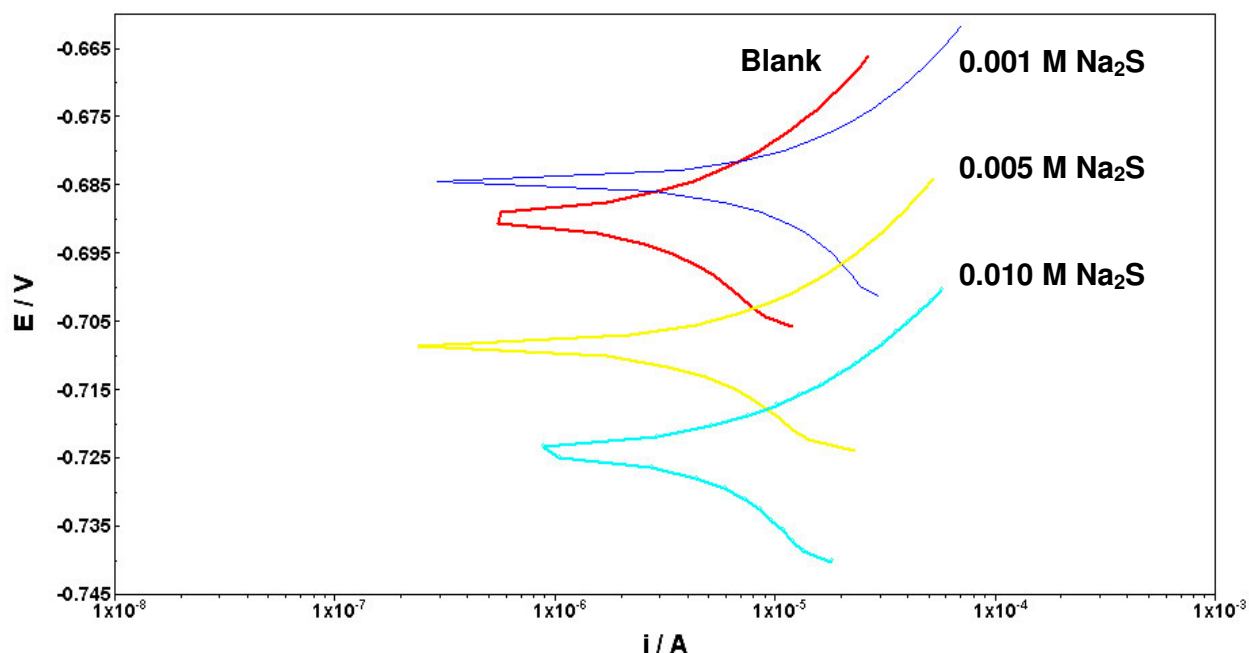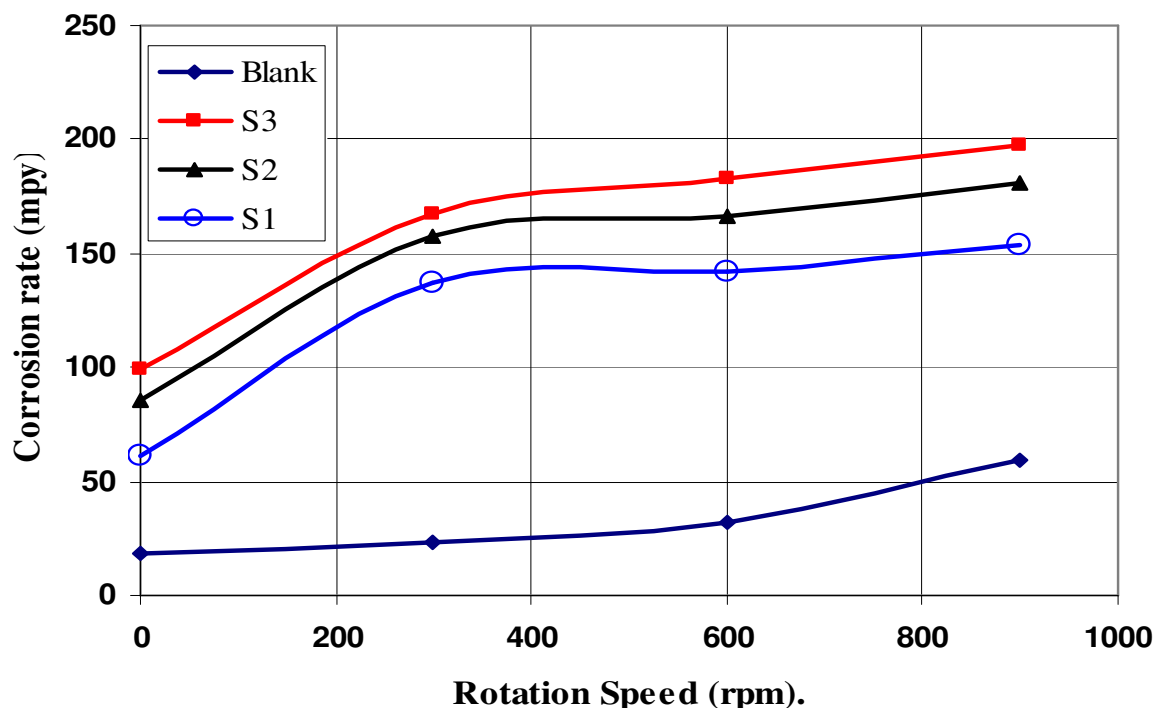

Figure 1. Effect of sulfide concentration on the corrosion rates in 3.5%NaCl solution

The electrochemical parameter calculated using the Tafel plots (Fig. 1) confirmed that the addition of sulfide increases the corrosion current, i_{corr} and corrosion rates and decreases the polarization resistances (R_p). The extent of increase in i_{corr} and corrosion rates is found to be a function of the concentration of Na$_2$S; higher the concentration of Na$_2$S, higher the values of corrosion rate and larger the increase in i_{corr} values.

The corrosion rate increases more than three times the value of blank samples when the sulfide concentration is increased from 0 to 0.010 M which is in a good agreement with the weight loss measurements in Fig. 2.

The corrosion rates increased sharply with the increase of solution speed from 0 to 300 rpm in presence of Na2S in NaCl solution. The higher the concentration of sulfide in NaCl solution is, the lower the resistance to erosion-corrosion. Increasing the rotation speed more than 300 rpm has no

detrimental effect on the corrosion rate. This can be attributed to the removal of sulfide ions from the surface at high speed preventing the local acidification which is the main source of corrosion. It has been reported that, solution speed affects the nature of the film of iron sulfide formed on steel surfaces exposed to sulfide solutions. Mackinawite is the predominant phase of the surface film formed at high fluid velocities, but it transforms into pyrrhotite and pyrite and at low velocities or in stagnant solution [6]. Other previous reports showed that the rate of release of iron from steel is controlled by the rate of dissolution of mackinawite, the initial corrosion product, and the diffusion of iron ions (FeSH+) from the solid-liquid interface to the bulk solution [7]. Moreover, the presence of iron sulfide promotes the anodic dissolution and accelerates local corrosion under the precipitate film [8,9].

Figure 2. Effect of solution speed and sulfide concentration on the corrosion rates (Blank) 0 M Na_2S; (S1) 0.001 M Na_2S; (S2) 0.005 M Na_2S; and (S3) 0.010 M Na_2S

3.2. Polarization measurements

Cyclic voltammetry data in Table 1 confirmed the previous observation where the pitting corrosion resistances decreased with increasing sulfide concentrations. The passivity domain of mild steel in pure NaCl solution (Blank) is -221 mV. The passivity domain gradually decreased to be -117, -24, and -4 mV after one week of immersion in NaCl solution containing 0.001, 0.005, and 0.010 M Na_2S respectively. These results are in agreement with the previous EIS results, visual inspection and microscopic examinations [10-12]. The pitting potential of the samples immersed in pure 3.5% NaCl solution was -523 mV. The pitting potential was shifted, due to the presence of sulfide, to more active

potential as shown in Table 1. This means that the pitting corrosion resistances decreased with increasing sulfide concentrations. The relative pit repassivation ability of mild steel in pure 3.5% NaCl solution (Epit-Ep) sharply decreased after the addition of 0.001, 0.005, and 0.010 M Na$_2$S respectively.

Table 1. Potentiodynamic polarization data for mild steel after one week of immersion in different corrosive solutions

Sample	E_{Corr} mV	E_{pit} mV	(E_{pit}-E_{Corr}) mV
Pure 3.5%NaCl	− 744	− 523	-221
3.5%NaCl + 0.001 M Na2S	− 813	− 696	-117
3.5%NaCl + 0.005 M Na2S	−769	− 745	-24
3.5%NaCl + 0.010 M Na2S	− 780	− 776	-4

3.3. Surface characterization

The surface examination of the sulfide polluted samples showed severe pitting and crevice corrosion after one week of immersion. The number of pits increases with increasing the sulfide contents. Few zones of crevice corrosion in addition to general corrosion were observed in the sample immersed in sulfide–free electrolyte.

XRD analysis revealed formation of iron sulfide and iron oxide (Fe$_2$O$_4$) in the surface layers of the sulfide polluted solutions. The blank samples revealed formation of both ferric and ferrous oxides. Energy dispersive spectrometry, EDS (Table 2), revealed presence of sulfur and oxygen for sulfide polluted samples. These results may indicate formation of mixture of iron sulfide and iron oxide compounds at the materials surface.

Table 2. EDS of mild steel after one week of corrosion

Sample	Fe Atomic ratio %	S Atomic ratio %	O Atomic ratio %
Pure 3.5%NaCl	31.49	-	68.46
3.5%NaCl + 0.001 M Na2S	41.13	1.93	55.24
3.5%NaCl + 0.005 M Na2S	30.62	0.66	66.80
3.5%NaCl + 0.010 M Na2S	34.27	5.13	60.43

The presence of sulfur inside the outer iron oxide layer decreases the resistance of the layer to corrosion attack due to the local acidification caused by iron sulfide formation. It was shown that the localized replacement of the protective Fe-oxide film by a non-protective iron sulfide (FeS$_{1-x}$) film is

responsible for the pitting corrosion. Therefore, blank samples showed the highest resistance to pitting corrosion [10-12].

4. CONCLUSIONS

1. The presence of sulfide ions as pollutants in NaCl solution results in a severe increase in the localize corrosion and erosion-corrosion attack on mild steel due to the local acidification caused by iron sulfide formation. The localized replacement of the protective Fe-oxide film by a non-protective iron sulfide film is responsible for increasing the pitting and erosion corrosion attack.

2. The corrosion rates increased sharply with the increase of solution speed from 0 to 300 rpm in presence of Na2S in NaCl solution. The higher the concentration of sulfide in NaCl solution is, the lower the resistance to erosion-corrosion. Increasing the rotation speed more than 300 rpm has no detrimental effect on the corrosion rate.

3. Increasing the sulfide concentration together with the solution speed has a synergistic effect on the corrosion resistance of mild steel.

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