Effect of the Sour Water H$_2$S on the Corrosion of Oil Pipelines.

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ABSTRACT

The experiments were performed at atmospheric pressure in glass cells filled with a sour water (oil wells water) and H$_2$S gases (H$_2$S concentrations in the gas inlet: 0.01 M to 10.0M). Rectangular specimens made from steel pipeline exposed to H$_2$S gases for a test period ranging from one hour to twenty-four hours at temperature ranges from 30°C to 90°C with flow rates ranging from 0.0 to 4.0 m/s peripheral speed. The potentiodynamic polarization technique is applied. The effect of the polarization technique parameters on detecting the oil pipelines corrosion carried out at various test conditions. A microstructure examination proved that Mackinawite scale forms on the steel surface as a product of H$_2$S corrosion. The corrosion rate clearly increases with velocity and the effect much pronounced for shorter exposure times. Very weak temperature dependence observed even for the shorter-term exposure that disappears for the longer exposure times. The potential values reduced with electrodes area increment at different exposure periods. The smaller tipped probe has more influence than the larger-tipped probe. The electrodes distance decreases its corrosion current increment due to its nearest position effect that leads to the strong exposure.

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INTRODUCTION

Steel is the most important engineering and construction material in the world. It used in every aspect of our lives, from automotive manufacture to construction products, from steel toecaps for protective footwear to refrigerators and washing machines and from cargo ships to the finest scalpel for hospital surgery, [1]. Ashraf and Hala [2], and Heakal et al. [3] showed that because of its hardness and low cost, carbon steel is a metallic constructional material commonly used for the majority of pipelines and vessels in oil production and refinery plants. Quej-Aké et al. [4] mentioned that corrosion process of carbon steel in acid sour environments, representative of atmospheric distillation plants, is a very important scientific and technological topic in the oilfield industry. Ashraf et al. [5] and Bhat, and Alva [6] concluded that corrosion is a thermodynamically feasible process as it is associated with decrease in Gibb's free energy. Corrosion is an afflicting problem associated with every use of metals. The damage by corrosion results in high cost for maintenance and protection of materials used. Development of methods to control corrosion is a challenge to scientists working in this area. Martinez, et al. [7] illustrated that corrosion process can be influenced, in different ways, by the relative movement between the metal and the corroding environment. This relative movement can increase the heat and mass transfer of reactants towards and from the surface of the corroding metal, with a consequent increase in the corrosion rate.

Ashraf and Abo-Dief [8] and Shahid and Faisal [9], deduced that corrosion is one of the major problems faced by the oil and gas industry, especially in wells. Hydrogen sulfide (H_2S) gas causes severe corrosion of equipment, in particular piping. Dadgarinezhad and Baghae [10] showed that hydrogen sulfide is a very dangerous, toxic and corrosive gas. It can diffuse into drilling fluid from formations during drilling of gas and oil wells. Hydrogen sulfide removed from this fluid to reduce the environmental pollution, protect the health of drilling workers and prevent corrosion of pipelines and equipments. Koteeswaran , [11] showed that the internal corrosion of carbon steel in the presence of hydrogen sulfide represents a significant problem for both oil refineries and natural gas treatment facilities. Surface scale formation is one of the important factors governing the corrosion rate. The scale growth depends primarily on the kinetics of scale formation. In an H_2S environment many types of iron sulfide may form such as amorphous ferrous sulfide, mackinawite, cubic ferrous sulfide, smythite, greigte, pyrrhotite, troilite and pyrite, among which mackinawite is considered to form first on the steel surface by a direct surface reaction. Choi et al. [12] evaluated the effect of low-level hydrogen sulfide (H_2S) on carbon dioxide (CO_2) corrosion of carbon steel in acidic solutions, and investigated the mechanism of sulfide scale formation in CO_2/H_2S environments.

Ashraf et al. [13], illustrated the effect of the electrostatic process variables on the corrosion of aluminium and hot work tool steel using NaCl corrosion medium at a corrosion period of; 15 min, 30 min, 45 min and 60 min. Lucio-Garcia et al., [14] evaluated the H_2S corrosion resistance of a C–Mn pipeline steel with three different microstructures using electrochemical techniques with a 3% wt. NaCl solution at 50 ^{o}C. Microstructures included martensite, ferrite, and ferrite + bainite. All techniques showed that the highest corrosion rate corresponded to the steel with a martensitic microstructure; up to one order of magnitude higher than the corrosion rate for steels with a ferritic + bainitic microstructure, whereas the steel with the ferritic microstructure showed the lowest corrosion rate. Samide et al. [15] investigated the effect of an antibacterial drug, sulfacetamide, IUPAC name *N*-[(4-aminophenyl) sulfonyl] acetamide (APSA) on the corrosion of carbon steel in 1.0 M HCl solution. Heakal et al. [16] synthesized and used three new thiadiazole derivatives (TDADs), to protect grade 1018 carbon steel from corrosion in naturally aerated 0.5 M NaCl solution (~ 3% by wt.). The object of this work was to study the effect H_2S gases with various concentrations for a test period ranging from one hour to twenty-four hours at temperature ranges from 30°C to 90°C with flow rates ranging from 0.0 to 4.0 m/s peripheral speed. The variation of the electrostatic polarization parameters on the H_2S corrosion of mild steel pipelines in the sour water obtained.

EXPERIMENTAL WORK

The experiments were performed at atmospheric pressure in glass cells filled with a sour water (oil wells water) and H2S gases (H2S concentrations in the gas inlet: 0.01 M to 10.0M). The H_2S concentrations in the liquid phase (in mol/l) under different test conditions shown in Fig. 1. Rectangular specimens made from steel pipeline exposed to H_2S gas for 1-24h at 30-90°C at a flow rates ranging from 0.0 to 4.0 m/s peripheral speed. Each mild steel tubing of the following percentage composition: 0.09% P, 0.38% Si, 0.01% Al, 0.05%

Mn, 0.21% C, 0.05% S and the remainder iron was prepared by mechanically pressed into sheets of 2mm thickness. The mild steel sheet mechanically cut into specimens of 20mm length and 10 mm width, having a hole of 2mm uniform diameter to facilitate suspension in the test solution. The specimens mechanically cleaned followed by grinding with emery paper of 600±1200 grit, and finally polished with a diamond paste of fine quality to expose shining polished surface. To remove any oil and organic impurities, they degreased in absolute ethanol, dried in acetone and stored in moisture-free desiccators prior to use. Accurate weight of the samples taken using electronic balance. Triple experiments performed in each case and the mean value of the weight loss reported. Micrographs of the corroded mild steel surface specimens taken. Weight change measurement used to obtain both the corrosion rate of mild steel and the retention rate of iron sulfide scale.
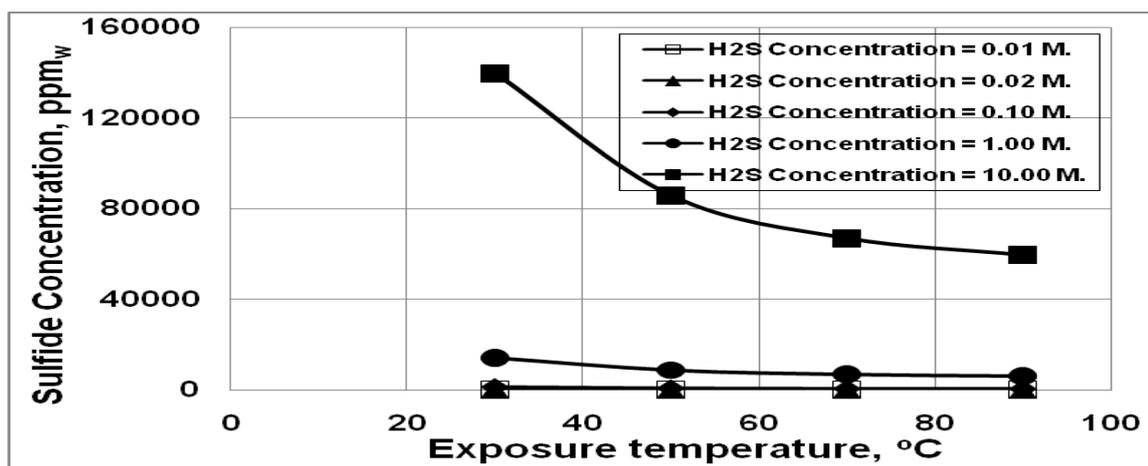
Fig. 1. Sulphide concentration at different H_2S concentrations and temperatures.

For potentiodynamic polarization studies, the electrochemical cell was assembled in a 250 ml round-bottomed flask consisting of mild steel coupon as working electrode; Pt sheet as a counter electrode and a and a saturated calomel electrode (SCE) was used as reference. All three electrodes were connected to a potentiostat (Model 283, EG&G PARC). The electrodes diameters are 2 mm, 4 mm and the distances taken to be 1 cm, and 2-cm. Potential range of ±250 mV with respect to open circuit potential and a scan rate of 0.166 mV/s applied. The polarization measurements run on a computerized potentiostat (Radiometer model VoltaLab 40) and VoltaMaster 4 program. Power levels of 20, 35 and 50 W cm^{-2} used, Polarization curves and spectra were recorded 1hr to 24 hrs after the initial immersion when a sufficiently good steady state had reached such that the corrosion potential was almost invariant over the time scale of the experiment. Electrodes carefully polished, before each experiment, using silicon carbide abrasive paper, down to 1200 grade.

3. RESULTS and DISCUSSIONS

3.1 H_2S Corrosion Process Variables

The effect of flow rate investigated by varying the rotation rate of the cylindrical working electrode up to 4m/s peripheral velocity. The corrosion rate as a function of reaction time at different velocities shown in Figure 2. The corrosion rate clearly increases with velocity and the effect much pronounced for shorter exposure times. For longer exposures in flowing conditions, the corrosion rates decrease significantly due to a buildup of a protective iron sulfide scale. This suggests that at higher flow rates, much larger fraction of the iron sulfide scale formed in the corrosion process is lost to the solution due to the hydrodynamic stresses induced by the flow. The effect of temperature on both the corrosion rate and the scale retention rate   in Figures 3 and 4 at an exposure periods ranging from 1 hour to 24 hours at 10% vol. H_2S gas concentration. Very weak temperature dependence observed even for the shorter-term exposure, which disappears for the longer exposure times. This seems to suggest that the corrosion rate predominantly controlled by the presence of the iron sulfide scale, with the effect increasing over time. The increase of the corrosion rate with increasing temperature can be explained on the basis that at high temperature, the adsorbed molecules on the metal

surfaces become unstable with a consequent decrease in the protection film, i.e., the ability to form a protective film on the metal surface is decreased with increasing temperature.
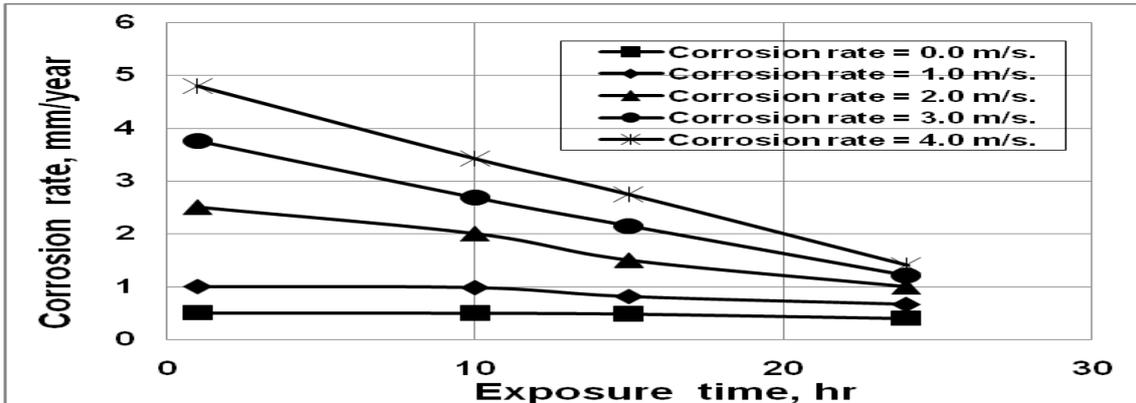
Fig. 2. Corrosion rate at various velocities at 0.01 Vol. H_2S concentration at 25 °C.
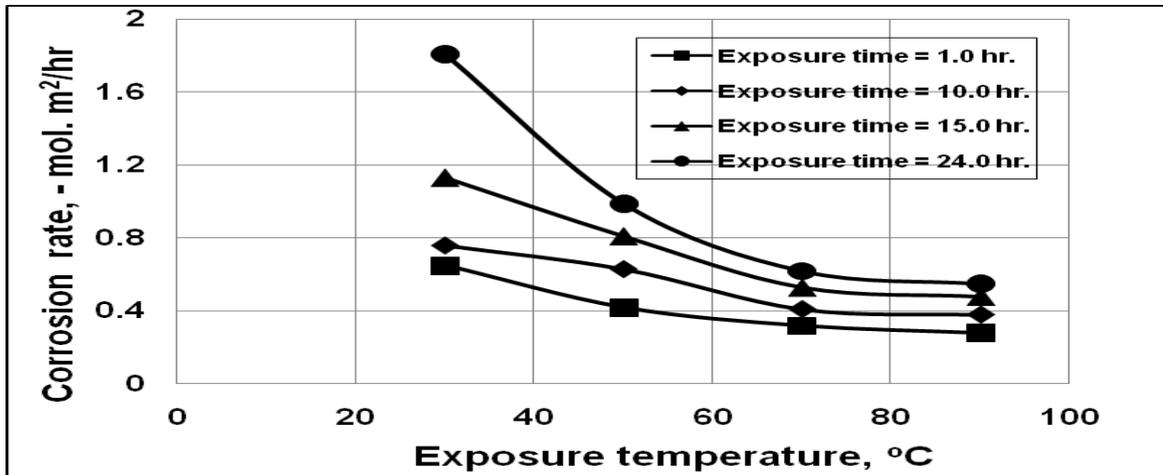
Fig. 3. Corrosion rate at 10%H_2S and 4m/s at various exposure time and temperatures.
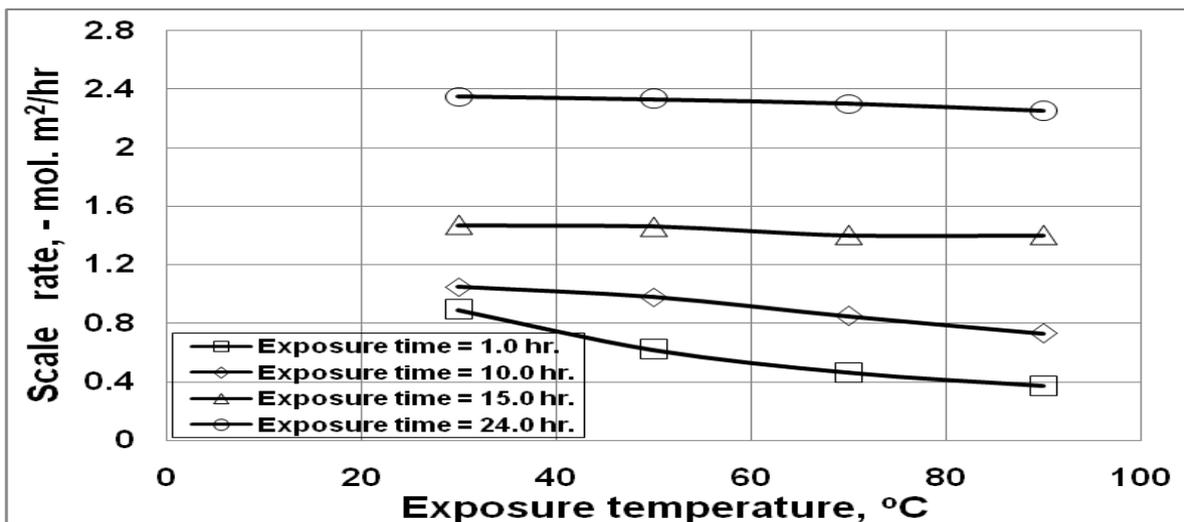
Fig. 4. Scale retention rate at 10%H_2S&4m/s at various time and temperatures.
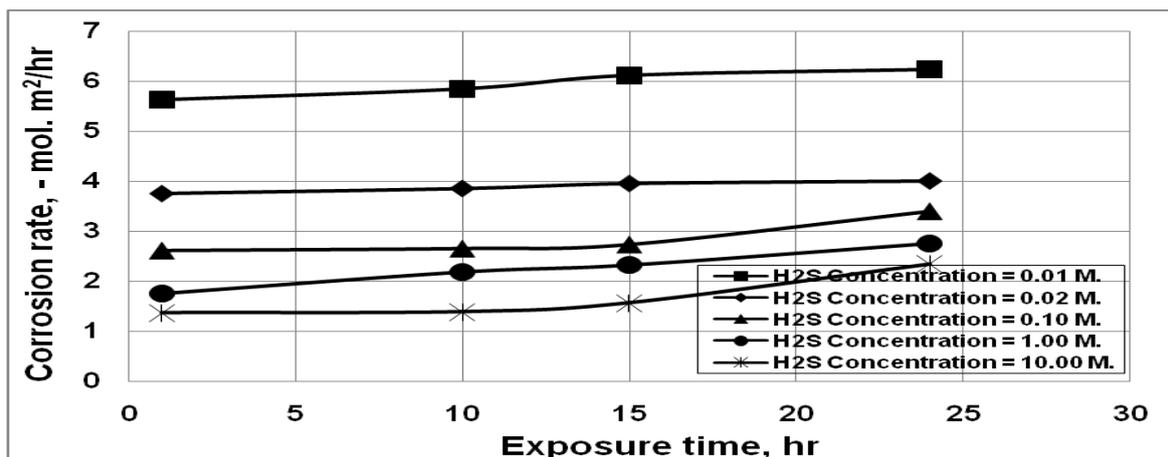
Fig. 5. Corrosion rate at 90 °C and 4m/s at various exposure time and concentrations.
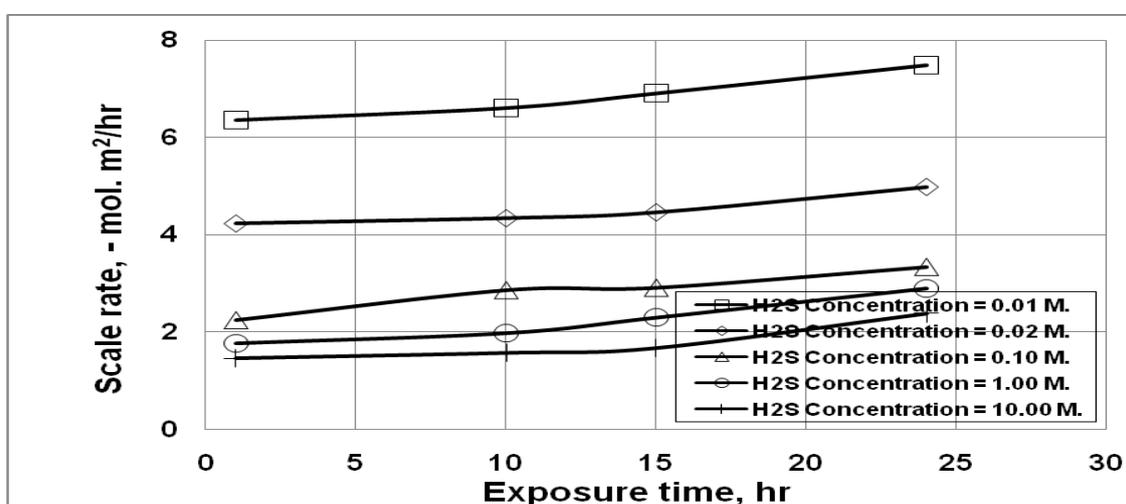
Fig. 6. Scale retention rate at 90°C & 4m/s at various time periods and concentrations.

Figures 5 and 6 show the comparison of corrosion rate and scale retention rates expressed in the same molar units vs. H_2S gas concentrations at various exposure periods at 90°C and 4.0 m/s. The comparison indicates that both the corrosion rate and scale retention rate increase with the increase of H_2S gas concentration, however, the corrosion rate is always higher than the scale retention rate. The scaling tendency under the test conditions indicates that the iron consumed by corrosion ended up as iron sulfide on the steel surface, with the balance lost to the solution. As a very small increase in the dissolved Fe^{2+} was measured in the solution it was concluded that some of the iron sulfide that formed on the steel spalled off in a spontaneous process probably due to intrinsic growth stresses (since no flow was present in these experiments that would impose extrinsic hydrodynamic stresses), in agreement with [14]. As observed of the loss in weight, the corrosion rate of steel with increasing H_2S concentration, and increasing time of immersion, as shown in Figs. 5 and 6. It is clear that the corrosion rate of steel increases with increasing the H_2S concentration. This attributed to that the exposure of the metal to sulphide ions results in the formation of porous, non-protective iron sulphide on the metal surface. Thus, relatively high corrosion rate maintained, [12]. The corrosion behaviour of iron in presence of S ions depends upon the concentration of H_2S. The corrosion rate increases with increasing concentration of H_2S as given in Fig. 5. It found that in aerated sulphide polluted light fraction, the accelerated metal corrosion appears to be the result of the sulphide that preventing the formation of a protective oxide corrosion product layer, [15].

3.2. Electrostatic Process Variables

Figure 7 illustrated that the initial values of potential reduced with increasing the electrodes area at different exposure periods. It is shown that the corrosion effect increases with the exposure periods increment which can be ascribed to the formation of an oxide film. The smaller tipped probe has more influence than the larger-tipped probe because it is much more effective in destroying (or preventing formation of) the oxide layer. While, the variation of potential power causes the potential to change abruptly to a more negative value, which can be attributed to destruction of the oxide layer. The potential tends to move in the negative direction. Here it well known that oxide is not easily formed. Large potential spikes appear which are probably due to the mass transport effect removing any loosely bound oxide from the surface. The effect of H_2S concentration and probe tip distance summarized in Fig. 8. It showed that the increment of the H_2S Concentration increases the corrosion rate due to concentration effect on the steel corrosion while the decrement of the electrode distance has the same effect due to the distance decrement that leads to the strong exposure on the steel surface. The figure show that the corrosion currents parallel the values of corrosion potential decreases with the exposure periods.
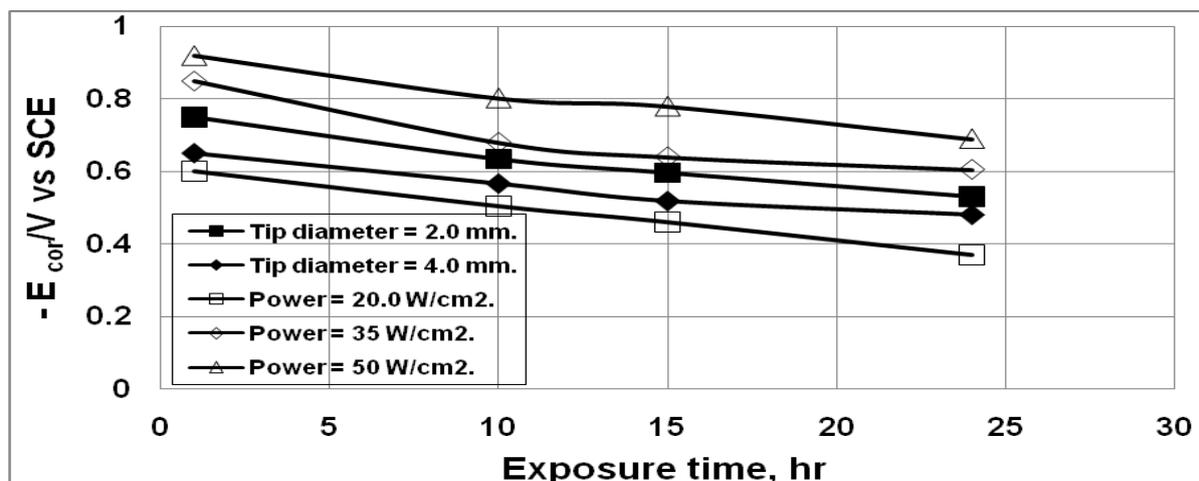
Fig. 7. Effect of potential power and tip diam. on E_{cor}/V at 2cm distance, 90°C and 10M H_2S.
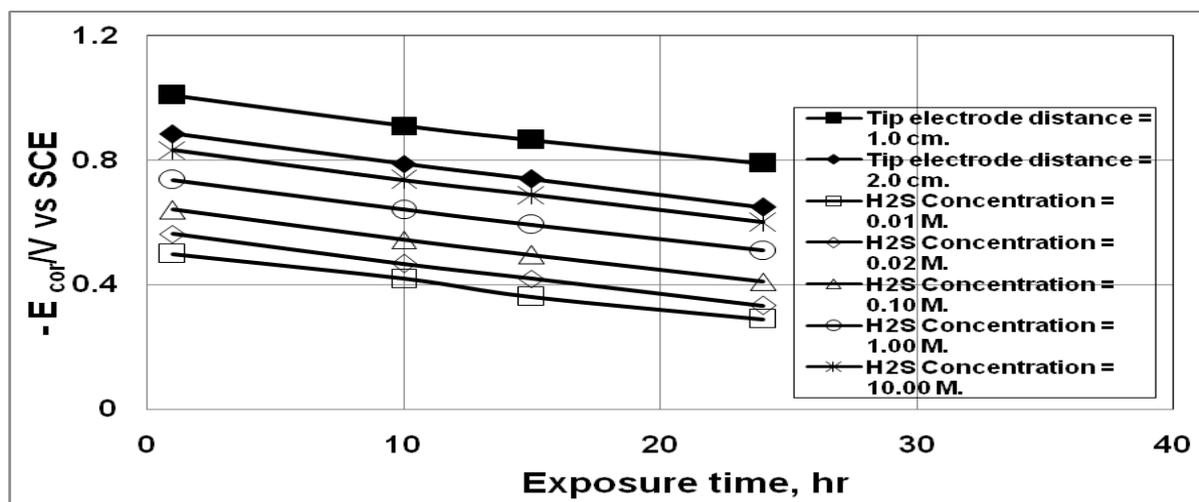
Fig. 8. Effect of tip distance and H_2S concentrations on E_{cor}/V at 4cm² area, 90°C and 50W/cm².
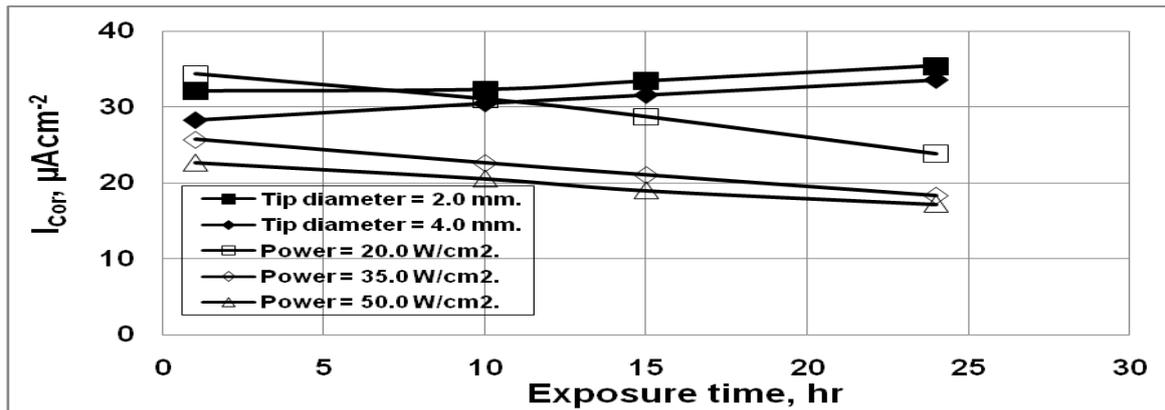
Fig. 9. Effect of potential power and tip diam. on ($I_{cor}/\mu A\ cm^{-2}$) at 2cm distance, 90°C and 10M H_2S.
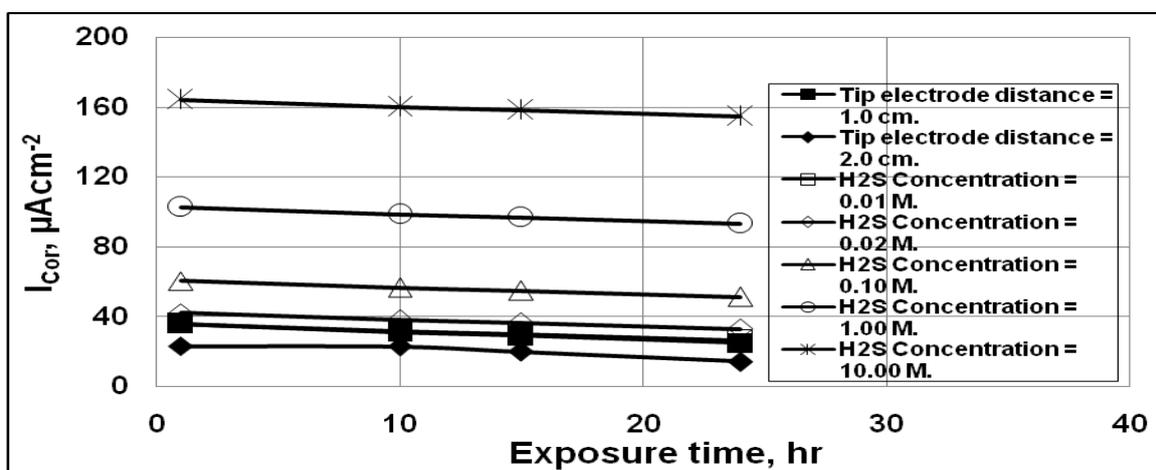
Fig. 10. Effect of tip distance and H_2S oncentrations on ($I_{cor}/\mu A\ cm^{-2}$) at 4cm² area, 90°C and 50W/cm².

Fig. 9. Shows the effect of the electrodes tip diameters and potential power on the corrosion current at different exposure periods. It is clear that as the tip diameter decreases the concentration of the current increases and there effect increases with the exposure period increment. The figure shows that the corrosion currents parallel the values of corrosion potential decreases with the exposure periods. The values of the corrosion currents tend to increase, then. After 1 h immersion, the values are lower than after 10min immersion due to the film is thicker or less porous than that formed initially, [16]. Fig. 10 showed the effect of the tip electrodes distance and the H_2S concentration on the corrosion current at different exposure periods. It is clear that as the electrodes distance decreases its corrosion current increment due to its nearest position effect that leads to the strong exposure. Also as the H_2S concentration increases its corrosion current increases. As the exposure period increases, its effect decreases due to the surface structure, morphology and the formed film becomes thicker and less porous than that formed initially.

3. 3. Metallographic Examination

There seems to be a consensus that mackinawite scale forms on the steel surface as a product of H_2S corrosion, [11]. Mackinawite scale found to be the dominant iron sulfide species. Clearly, other types of iron sulfide film observed on steel surfaces attacked by H_2S, particularly in long exposures. Mackinawite formation via a direct heterogeneous chemical reaction with iron on the steel surface seems to be the more relevant mechanism, [8]. Many pieces of evidence seem to support this conclusion: layered structure of mackinawite scale often containing cracks and delaminations, with steel surface imprint visible even after rather long exposures. When the mechanical limit of the Mackinawite exceeded micro cracking of the film occurs, thereby relieving the internal stresses and the process starts all over again. These micro-cracks, which most likely occur at mackinawite grain boundaries, serve as preferred pathways for more rapid penetration of sulfide species that fuel the solid-state reaction. It expected that in some instances, at stress concentration points, large

cracks in the film may appear and an obvious change in macroscopic fracture morphology found at a H$_2$S flow rate of 1m/s. Except for the fast fracture region, predominantly flat fracture with secondary cracks on the fracture surface observed as displayed in Fig. 11. The changes in macroscopic fracture morphology also reflected the detrimental effect of hydrogen embrittlement. For instance, the embrittled area of the specimen increased as the flow rate increases to 2m/sec. causes pits, Fig. 12. The results showed that the studied steel presented maximum corrosion rates at 90°C in the laboratory corrosion tests. These results related to the presence of non-protective films constituted by products precipitated on the samples and as the Mackinawite film goes through the growth/micro-cracking cycle, it thickens. As larger crack appear, whole layers of the film may partially delaminate from the steel surface starting another cycle of rapid film growth underneath, as shown in Figure 13. The SEM observation showed the presence of blisters uniformly distributed on the exposed samples surface but in the last case, the blisters more rounded in agreement with Ashraf and Hala [8].
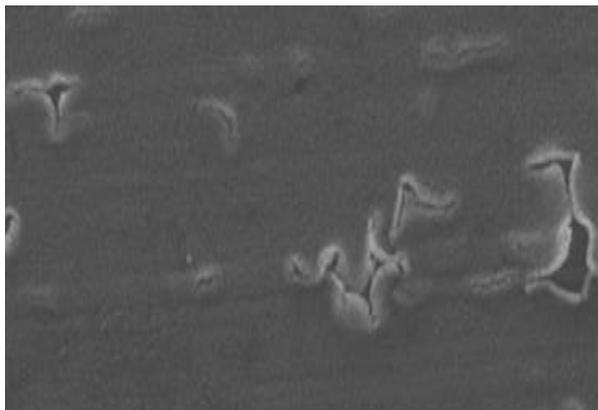
Fig. 11. Cracks on the mild steel sulphide film (1000 X).

Fig. 12. Iron sulphide pitting localized attack. (500 X).
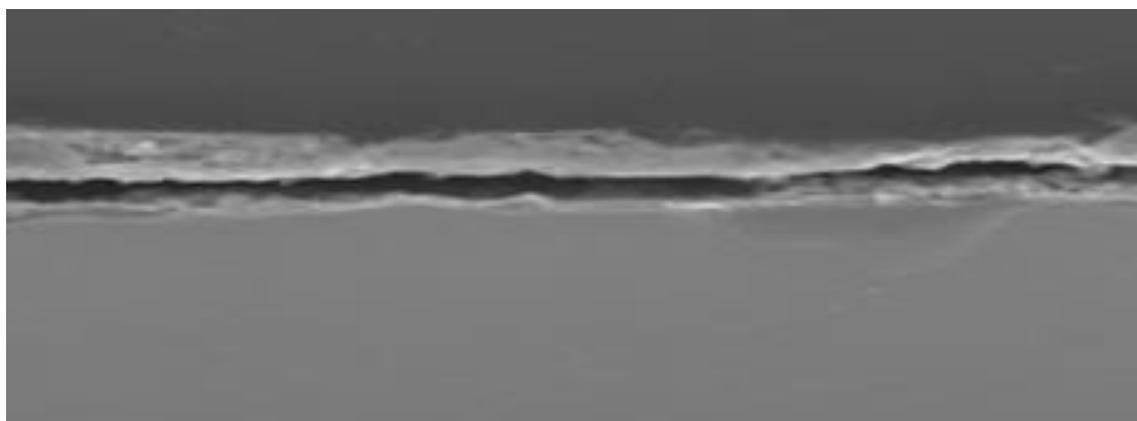
Fig. 13. Larger crack and scale formed on the mild steel surface (1000 X).

4. CONCLUSIONS

From the present work, the following conclusions obtained:

1. The corrosion rate increases with velocity increment for shorter exposure times. For longer rate exposures, the corrosion rates decrease.
2. Very weak temperature dependence observed even for the shorter-term exposure, which disappears for the longer exposure times.
3. The smaller tipped probe has more influence than the larger-tipped probe.
4. The tip diameter decreases the concentration of the current increases and there effect increases with the exposure period increment.
5. The corrosion currents parallel the values of corrosion potential decreases with the exposure periods increment.

6. The electrodes distance decreases its corrosion current increment due to its nearest position effect that leads to the strong exposure.
7. The corrosion rate of mild steel in H_2S corrosion affected by H_2S gas concentration, temperature, velocity, and the exposure periods.
8. Mackenawite is the predominant iron sulfide formed on the steel surface by solid-state reaction.

5. REFERENCES

[1] Ashraf T. Mohamed, and Hala M. Abo-Dief, "Effect of The Exposure Period in The Carbon Steel Corrosion using Organic Sulfur Compounds", The 14th Asian-Pacific Corrosion Control Conf. (14APCCC), Shanghai, PR China, 21-24 Oct. 2006.

[2] Ashraf T. Mohamed and Hala M. Abo-Dief, "Natural Corrosion Treatment of Mild Steel Pipelines", The Int. Eng. Conf. (IECHAR), Al-Ahsa, KSA, pp. 263-269, May 1-2, 2010.

[3] F. El-Taib Heakal, A.S. Fouda, and M.S. Radwan, "Some New Thiadiazole Derivatives as Corrosion Inhibitors for 1018 Carbon Steel Dissolution in Sodium Chloride Solution", Int. J. Electrochem. Sci., Volume 6, pp. 3140 – 3163, 2011.

[4] L. Quej-Aké, R. Cabrera-Sierra, E. Arce-Estrada, and J. Marín-Cruz, "EIS Evaluation of The Effect of Neutralizing and Inhibitor Compounds on Corrosion Process of 1018 Carbon Steel in Acid Solutions Typical of Atmospheric Distillation Plants", Int. J. Electro-chem. Sci., 3, pp. 56-66, 2008.

[5] Ashraf T. Mohamed, Fahd A. Al-Zahrani, and H. M. Abo-Dief, "Conventional Extrusion, Wear And Corrosion Of Aluminium And Aluminium/Copper Composites", Part I. Compaction and wear of Al &Al/Cu Composites, The Int. Conf. on Innovative Techn. (IN-TECH 2011), Bratislava- Slovakia Republic and Vienna, Austria, 1/9-4/9, 2011.

[6] J. Ishwara Bhat, and Vijaya D. P. Alva, "Meclizine Hydrochloride as a Potential Non-Toxic Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Medium", Archives of Applied Science Research, Volume 1, pp. 343-356, 2011.

[7] R. Galvan-Martinez, R. Orozco-Cruz, J. Mendoza-Flores, A. Contreras and J. Genesca, "Study of the Mass Transport on Corrosion of Low Carbon Steel Immersed in Sour Solution Under Turbulent Flow Conditions", Hydrodynamics – Optimizing Methods and Tools, México, pp. 353-372, 2011.

[8] Ashraf T. Mohamed, and H. M. Abo-Dief, "Environmental and Metal Protection from H_2S Pollution", The Twenty-Six Annual Meeting of The Saudi Community for Life Science, Al-Taif University, Al-Taif, May 10-12, 2011.

[9] M. Shahid and M. Faisal, "Effect of Hydrogen Sulfide Gas Concentration on The Corrosion Behavior Of "ASTM A-106 Grade-A" Carbon Steel In 14% Diethanol Amine Solution", The Arabian J. for Science and Eng., V. 34, No. 2C, pp. 179-186, Dec. 2009.

[10] A. Dadgarinezhad, and F. Baghae, "A New Synthesized Corrosion Inhibitor for Mild Steel in 0.5 M H_2SO_4", Gazi Univ. J. of Sci. GU J Sci, 24(2), pp. 219-226, 2011.

[11] M. Koteeswaran, "CO2 and H2S Corrosion in Oil Pipelines", Master Thesis, University of Stavanger, June 2010

[12] Yoon-Seok Choi, Srdjan Nesic, Shiun Ling, "Effect of H_2S on the CO_2 Corrosion of Carbon Teel in Acidic Solutions", Electrochimica Acta, V. 56, pp. 1752–1760, 2011.

[13] Ashraf T. Mohamed, Fahd A. Al-Zahrani, Mohammed A. Saif and H. M. Abo-Dief, "Effect of the Electrostatic Polarization Variables on Aluminium and Hot Work Tool Steel Corrosion", The 2nd Int. Conf. Energy, Eng., Aswan, Egypt, Dec. 27-29, 2010.

[14] M.A. Garcia, J.G.G. Rodriguez, M. Casales, L. Martinez, J.G.C. Nava, M.A.N. Flores, and A.M. Villafañe, "Effect of Heat Treatment on H_2S Corrosion of A Micro-Alloyed C–Mn Steel", Corrosion Science 51, pp. 2380–2386, 2009.

[15] A. Samide, B. Tutunaru, C. Negrilaa, I. Trandafir, and A. Maxut, "Effect of Sulfacet Amide on The Composition of Corrosion Products Formed Onto Carbon Steel Surface in Hydrochloric Acid", Digest Journal of Nanomaterials and Biostructures, Vol. 6, No.2, pp. 663-673, April - June 2011.

[16] F. E. Heakal, A.S. Fouda, and M.S. Radwan, "Some New Thiadiazole Derivatives as Corrosion Inhibitors for 1018 Carbon Steel Dissolution in Sodium Chloride Solution", Int. J. Electrochem. Sci., Volume 6, pp. 3140 – 3163, 2011.