Electro-Chemical Behavior of Low Carbon Steel Under H$_2$S Influence

M G Zaharia$^1$, S Stanciu$^1$, R Cimpoesu$^*$, C Nejneru$^1$, C Savin$^1$, V Manole$^1$ and N Cimpoeșu$^1$

Technical University “Gheorghe Asachi” of Iași, Faculty of Material Science and Engineering, Prof. Dr. Doc. Dimitrie Mangeron Street, number 67, Iași, 700050, Romania

E-mail: ramonahanu@yahoo.com

Abstract. A commercial low carbon steel material (P265GH) with application at industrial scale for natural gas delivery and transportation systems was analyzed in H$_2$S atmosphere. The article proposed a new experimental cell in order to establish the behavior of the material in sulfur contaminated environment. In most of the industrial processes for gas purification the corrosion rate is speed up by the presence of S (sulfur) especially as ions or species like H$_2$S. The H$_2$S (hydrogen sulfide) is, beside a very toxic compound, a very active element in the acceleration of metallic materials deterioration especially in complex solicitations like pressure and temperature in the same time. For experiments we used a three electrodes cell with Na$_2$SO$_4$ + Na$_2$S solution at pH 3 at room temperature (~ 25°C) to realize EIS (electrochemical impedance spectroscopy) and potentio-dynamic polarization experiments. Scanning electron microscopy and X-ray dispersive energy spectroscopy were used to characterize the metallic material surface exposed to experimental environment.

1. Introduction

Human race demand energy in an increasing way which will reach with a plus of 55% by 2030 manly because of the industry consume and the population growth [1,2]. The main important energy source remain the oil and natural gas for at least 30-50 years even progresses in the renewable energy were recorded most of all in strong industrialized and very good research programs countries. Most of the natural gas or oil production and transport domains encountered the appearance of various quantities of carbon dioxide (CO$_2$), hydrogen sulfide (H$_2$S), water and chemical components [3]. At the moment when these gaseous pass through dissolution into water compose a weak acid that is very corrosive.

![Figure 1](image_url). Factors that influence the metallic material corrosion resistance exposed to an environment with CO$_2$+H$_2$S.
This corrosive environment will cause high intensity corrosion (generalized, pitting, cracking or combinations). Having CO$_2$, H$_2$S and water products the corrosion process in gas and oil production operations is conditional on different factors that act separately or together on the metallic parts, figure 1. The influence of these parameters and interactions among them is a very important aspect in the corrosion research on oil and gas production systems.

In this article we proposed an experimental cell to analyze the effects of an environment with CO$_2$+H$_2$S on the commercial steel P256GH for different concentrations of H$_2$S (0, 10, 20 and 30 ppm/mol).

2. Experimental setup
Analytical grade Na$_2$SO$_4$, Na$_2$S, and H$_2$SO$_4$ reagents were used. To prepare the solution, 1 M Na$_2$SO$_4$ solution was buffered by H$_2$SO$_4$ to a pH of 3. Usually, if is necessary to analyze the H$_2$S corrosion mechanism, experimentally we have to purge an inert gas into the solution to remove dissolved oxygen [4] but in our experimental case we analyze the behavior of the material in an atmosphere with oxygen, this case being recognized in few industrial applications. In this case few cathodic chemical reactions will interfere (like O$_2$ and HS$^-$ reduction). We proposed for the article four analyze cases which depend on the quantity of produced Na$_2$S, initial case with 0 and producing 10, 20 and 30 ppm/mole of H$_2$S, through addition to the solution (concentrations are in ppm/mole). In this case next reaction will occur based on the dissociation of Na$_2$S to H$_2$S in a solution with pH smaller than 7 [5]:

$$\text{Na}_2\text{S} + 2\text{H}^+ \rightarrow 2\text{Na}^+ + \text{H}_2\text{S}$$

now a reduce amount of H$_2$S is locally generated at the vicinity of alloy surface. An isolated electro-chemical cell (600 cm$^3$ volume) was used for adding Na$_2$S. During the experiment the Na$_2$S was continuously added in order to produce H$_2$S also an inert gas (argon) was purged above the experimental cell with a very low pressure control and prevent the decreasing in H$_2$S concentration during the experiment. The sample, P256 was mounted cylindrical specimens with 1 cm (diameter) have the role of working element.

![Experimental cell for study the H$_2$S influence.](image)

We perform more corrosion experiments keeping the order: (I) 300 s OCP recording, (II) LPR test with potential domain of ± 100 mV and the rate of 1 mV/s, (III) potentiostatic EIS test at OCP with amplitude of 10 mV and normally a frequency range of $10^2$ to $10^5$ Hz, and (IV) linear and cyclic tests with a rate of 1 mV/s and potential range from 200 to 1500 mV with respect to OCP. All measurements were repeated 3 times for results reproducibility. The corrosion experiments were realized by EG201 Potentiostat equipment, using saturated calomel and Pt wire as reference and counter electrodes, respectively. The equipment software was used to extract the EIS equivalent circuit components. Simulated data was fitted by less than 2% error in calculation.
The experimental sample was, after the electro-corrosion tests, analyzed on the surface by scanning electron microscopy (SEM VegaTescan LMH II, SE detector, 30 kV) and X-ray dispersive energy spectroscopy (EDAX Bruker, XFlash).

3. Experimental results
The diffused H atoms can react to form H$_2$ inside the steel, causing hydrogen bubbles on the surface of the material [6].

$$H_2S(aq) = H_2S(ad)$$ (1)

$$H_2S(ad) + e^- = H(ad) + HS(ad)$$ (2)

$$H_2S(ad) + H(ad) + e^- = H_2(g) + HS(ad)$$ (3)

At anode the main reaction is the oxidation of iron. A reaction mechanism for solid materials in case of reaction between H$_2$S and Fe is presented in equation (4). During the reaction, characterized mainly by loss of iron contribute at the metallic material destroying and to decrease the strength.

$$Fe(s) + H_2S(aq) = FeS(s) + 2 H^+(aq) + 2 e^-$$ (4)

The results of OCP variations are presented in figure 1 a). The increase in H$_2$S concentration decreases the OCP from -590 mV (0 ppm/mole) to -630 mV (36 ppm/mole). Decrease in OCP with the increase of H$_2$S indicate that the alloy suffer a deterioration and the activity on the surface is accelerated. In figure 3 b) is represented the influence of H$_2$S concentration on LPR (polarisation resistance, Rp) values.

Figure 3. a) OCP variations of P265GH alloy vs. H$_2$S concentration (ppm by mole) in Na$_2$SO$_4$ + Na$_2$S (pH 3). b) LPR (Rp) variations of P265GH H$_2$S concentration (ppm by mole) in Na$_2$SO$_4$ + Na$_2$S (pH 3).

During the increase of the H$_2$S concentration the RP values decrease, fact that confirm the results of OCP measurements are follow a similar trend. Between initial sample and the one expose to 36 ppm/mole H$_2$S the RP suffer a high decrease which is relative smaller for 10 and 26ppm/mole samples. Based on the experimental results the corrosion rate increase. The increase in corrosion rate by introducing H$_2$S in contact with P256GH can collaborate with the increase in proton reduction, equations (2)–(4) and automatically the anodic dissolution. In the same time the elements based on sulfide ions can have an important role as surface catalysts and to increase the anodic dissolution.
presented in both in LPR and OCP results. In figure 4 are presented in a) linear polarization curves of P265GH steel in Na$_2$SO$_4$ + Na$_2$S, pH 3, at various H$_2$S concentrations (ppm by mole), T ≈ 25°C and b) cyclic polarization curve of P265GH steel in Na$_2$SO$_4$ + Na$_2$S, pH 3, at various H$_2$S concentrations (ppm/ mole), T ≈ 25°C. Linear polarization, figure 4 a), present the increasing character of the corrosion rate with the percentage of H$_2$S with near values for 0 and 10 ppm/mole samples and bigger values of corrosion for 20 and 30 ppm/mole samples.

![Image of polarization curves](image)

**Figure 4.** a) Linear polarization curves of P265GH steel in Na$_2$SO$_4$ + Na$_2$S, pH 3, at various H$_2$S concentrations (ppm by mole), T ≈ 25°C b) Cyclic polarization curve of P265GH steel in Na$_2$SO$_4$ + Na$_2$S, pH 3, at various H$_2$S concentrations (ppm/ mole), T ≈ 25°C.

The cyclic curve present definitely a pitting corrosion type with a trend to generalization of the pitting on the entire material surface.

In figure 5 are presented in (a) Nyquist and (b) Bode plots of P265GH in Na$_2$SO$_4$ + Na$_2$S, pH 3, at various H$_2$S concentrations (ppm by mole), T ≈ 25°C. In all conditions, the Nyquist curves indicate a single capacitance loop having a time constant in Bode plots. Therefore, the alloy-electrolyte interface can be simulated by a Randles equivalent circuit [7-17].

![Image of Nyquist and Bode plots](image)

**Figure 5.** (a) Nyquist and (b) Bode plots of P265GH in Na$_2$SO$_4$ + Na$_2$S, pH 3, at various H$_2$S concentrations (ppm by mole), T ≈ 25°C.

During the increase in the H$_2$S concentration, RP of the experimental alloy reduce more or less with the same trend. The participation of H$_2$S didn’t induce any other time constants on the graphs presented in figure 5, in the same time a decrease in the capacitance loop diameter and charge transfer
resistance can be observed by an increase in the H\textsubscript{2}S concentration. The EIS results are proper to be used to identify the corrosion and electro-corrosion mechanisms by the presence of H\textsubscript{2}S.

The reactions between H\textsubscript{2}S and P256GH has an determining role on the initiation and propagation of cracking and failure. It can be observed from figure 6 a) and b) the formation of corrosion pits on the surface of material and the tendency to connect and form a crack. In conditions of a higher pressure (for example in transport of oil and gas products) these cracks can produce the material failure. As cathodic reaction can be considered the H\textsubscript{2} evolution reaction.

Hydrogen could appear as a result of the reduction reaction of H\textsubscript{2}S on the steel surface. The produced hydrogen atom can penetrate into the metallic lattice and diminish the mechanical properties of carbon steels, causing Hydrogen Induced Cracking (hydrogen embrittlement). The corrosion pits, after an entire corrosion cycle, describe in experimental part, have diameters between 1-3 µm.

![Figure 6. SEM images of the P265GH surface after the electro-chemical tests a) 250x and b) 5000x.](image)

Analyzing the electrochemical corrosion reactions between H\textsubscript{2}S and Fe will improve the understanding of the initiation and propagation of cracking. It is important in this applications field where the corrosion mechanism act in time or long time like decades to analyze if we can correlate a higher corrosion rate of metallic materials tends to provoke a higher susceptibility of C-steel to cracking.

In table 1 is presented the chemical composition of the metallic material surface after the electro-chemical test made on a 4 mm\textsuperscript{2} area. Comparing to the C-steel used for tests we observe a decrease of iron and manganese chemical elements mass percentages which probably pass to oxides and detach from the material. On the surface remain oxides which are still attached to the surface, indicated by the presence of oxygen with 1.47 wt%. In the same time the lost percentages of iron and manganese are connected also with the presence of sulfur on the surface. The compound CO\textsubscript{2} was adsorbed on the steel surface prior to H\textsubscript{2}S and the H\textsubscript{2}S adsorption reduced.

Based on the chemical composition result, table 1, and the literature [18] the compound CO\textsubscript{2} corrosion was the main process at the beginning of corrosion process and the main product is probably FeCO\textsubscript{3}. Based on cyclic curve and EIS experiments the structure form at the beginning, probably FeCO\textsubscript{3} and precipitated on the metal surface was not compact at the start of the corrosion. In this case the specie Fe\textsuperscript{2+} has the ability to penetrate through the scales by diffusion.

After that Fe\textsuperscript{2+} reached the surface film / liquid interface, the compound iron sulfide form when combining with the S\textsuperscript{2-} anion and then precipitated on FeCO\textsubscript{3}.
Table 1. Chemical composition after the experimental test.

| Element   | wt.[%] | at.[%] | Error in % |
|-----------|--------|--------|------------|
| Iron      | 96.43  | 88.98  | 0.95       |
| Oxygen    | 1.47   | 4.72   | 0.41       |
| Carbon    | 1.27   | 5.45   | 0.35       |
| Manganese | 0.75   | 0.69   | 0.16       |
| Sulfur    | 0.1    | 0.16   | 0.04       |

4. Conclusions
OCP, LPR and EIS results showed almost similar trends in corrosion behavior of the material. By an increase in H₂S concentration from 0, 10, 20 and then 30 ppm, the corrosion resistance of the material decrease, substantially for sample in 30 ppm/mole solution. The compound H₂S have the effect to retard the formation of passive layer from the substrate. Linear potentiometry confirm the increase of corrosion rate with the increase of H₂S percentage. Cyclic potentiometry present a clearly pitting corrosion of the surface at the beginning and with a general character at the end. The pitting corrosion is confirmed by the SEM images.

References
[1] Holditch S A and Chianelli R R 2008 MRS Bull. 33 317
[2] Liew Y M, Kamarudin H, Mustafa Al Bakri A M, Luqman M, Khairul Nizari I, Heah C Y 2011 Australian Journal of Basic and Applied Sciences 5 (9) 317
[3] Perju M C, Vizureanu P 2014 REV. CHIM. (Bucharest) 65(6) 694-696
[4] Ma H, Cheng X, Li G, Chen S, Quan Z, Zhao S, Niu L 2000 Corros. Sci. 42, 1669
[5] Betova I, Bojinov M, Hyökyvirta O, Saario T 2010 Corros. Sci. 52 1499
[6] Lee K L J, Nesic S 2005 NACE proceedings 05630
[7] Izquierdo J, Bolat G, Cimpoesu N, Trinca L C, Mareci D, Souto R M 2016 Applied Surface Science 385 368
[8] Chelariu R, Mareci D, Bolat G, Peptu C A, Cailean D 2015 Materials and Corrosion-Werkstoffe Und Korrosion 66 573
[9] Cimpoesu N, Trincă L C, Dascălu G, Stanciu S, Gurlui S O, Mareci D 2016 Journal of Chemistry Article ID 9520972
[10] Chelariu R, Bolat G, Izquierdo J, Mareci D, Gordin D M, Gloriant T, Souto R M 2014 Electrochimica Acta 137 280
[11] Bolat G, Mareci D, Iacoban S, Cimpoesu N, Munteanu C 2013 Journal of Spectroscopy ID 719420
[12] Zhenguang L, Xiuhua G, Linxiu D, Jianping L, Ping L, Chi Y, Misra R D K, Yuxin W 2017 Electrochimica Acta 232 528
[13] Wang P, Wang J, Zheng S, Qi Y, Xiong M, Zheng Y 2015 International Journal of Hydrogen Energy 40 11925
[14] Davoodi A et al. 2011 Corrosion Science 53 399
[15] Zepon G et al., 2015 Materials & Design 83 214
[16] Ziomek-Moroz M, Hawk J A, Thodla R, Gui F 2013 ECS Trans. 50, 79
[17] Holditch S A and Chianelli R R 2008 MRS Bull. 33 317
[18] Wu H B, Liu L, Wang L, Liu Y 2014 Journal of iron and steel research international 21 76