

Electro-Chemical Behavior of Low Carbon Steel Under H₂S Influence

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Abstract. A commercial low carbon steel material (P265GH) with application at industrial scale for natural gas delivery and transportation systems was analyzed in H₂S 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 H₂S. The H₂S (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 Na₂SO₄ + Na₂S solution at pH 3 at room temperature (~ 25°C) to realize EIS (electrochemical impedance spectroscopy) and potentiodynamic 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 (CO₂), hydrogen sulfide (H₂S), water and chemical components [3]. At the moment when these gaseous pass through dissolution into water compose a weak acid that is very corrosive.

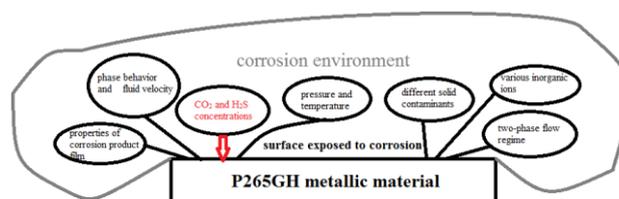


Figure 1. Factors that influence the metallic material corrosion resistance exposed to an environment with CO₂+H₂S.

This corrosive environment will cause high intensity corrosion (generalized, pitting, cracking or combinations). Having CO₂, H₂S 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 CO₂+H₂S on the commercial steel P256GH for different concentrations of H₂S (0, 10, 20 and 30 ppm/mol).

2. Experimental setup

Analytical grade Na₂SO₄, Na₂S, and H₂SO₄ reagents were used. To prepare the solution, 1 M Na₂SO₄ solution was buffered by H₂SO₄ to a pH of 3. Usually, if is necessary to analyze the H₂S 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 O₂ and HS⁻ reduction). We proposed for the article four analyze cases which depend on the quantity of produced Na₂S, initial case with 0 and producing 10, 20 and 30 ppm/mole of H₂S, through addition to the solution (concentrations are in ppm/mole). In this case next reaction will occur based on the dissociation of Na₂S to H₂S 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 H₂S is locally generated at the vicinity of alloy surface. An isolated electro-chemical cell (600 cm³ volume) was used for adding adding Na₂S. During the experiment the Na₂S was continuously added in order to produce H₂S also an inert gas (argon) was purged above the experimental cell with a very low pressure control and prevent the decreasing in H₂S concentration during the experiment. The sample, P256 was mounted cylindrical specimens with 1 cm (diameter) have the role of working element.

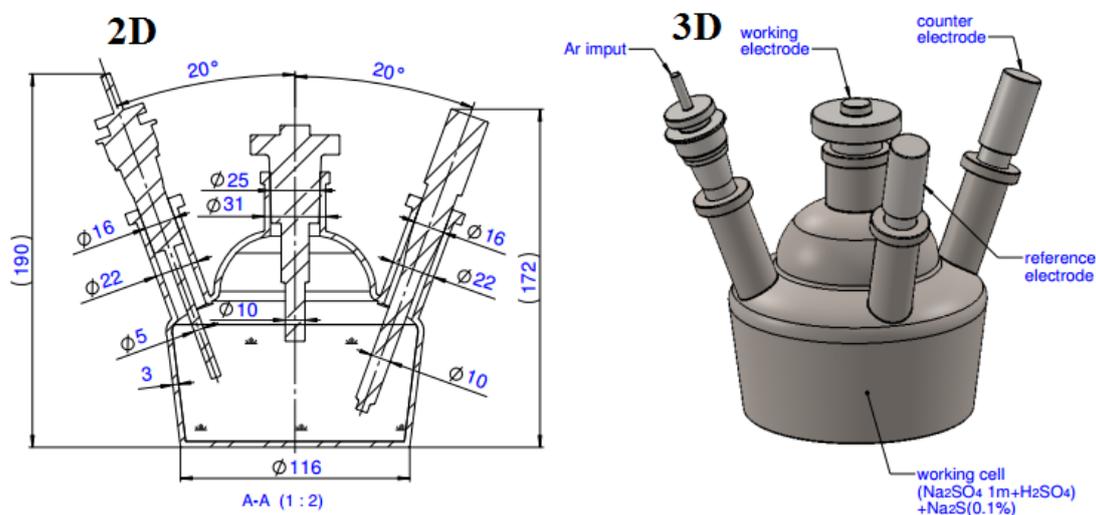


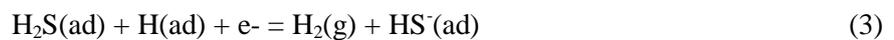
Figure 2. Experimental cell for study the H₂S influence.

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.

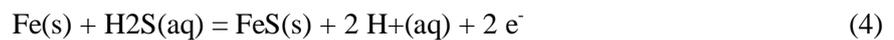
The experimental sample was, after the electro-corrosion tests, analyzed on the surface by scanning electron microscopy (SEM VegaTescan LMH II, SE detector, 30 kV) and X-ray dispersive energy spectroscopy (EDAX Bruker, XFlash).

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].



At anode the main reaction is the oxidation of iron. A reaction mechanism for solid materials in case of reaction between H_2S 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.



The results of OCP variations are presented in figure 1 a). The increase in H_2S concentration decreases the OCP from -590 mV (0 ppm/mole) to -630 mV (36 ppm/mole). Decrease in OCP with the increase of H_2S 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_2S concentration on LPR (polarisation resistance, RP) values.

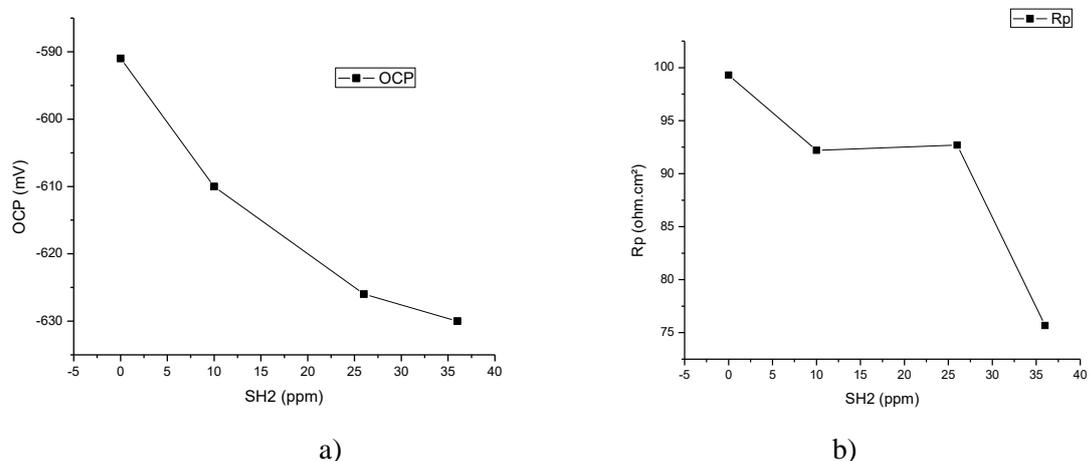


Figure 3. a) OCP variations of P265GH alloy vs. H_2S concentration (ppm by mole) in $Na_2SO_4 + Na_2S$ (pH 3). b) LPR (R_p) variations of P265GH H_2S concentration (ppm by mole) in $Na_2SO_4 + Na_2S$ (pH 3).

During the increase of the H_2S 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_2S 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_2S 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 $\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}$, pH 3, at various H_2S concentrations (ppm by mole), $T \approx 25^\circ\text{C}$ and b) cyclic polarization curve of P265GH steel in $\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}$, pH 3, at various H_2S concentrations (ppm/ mole), $T \approx 25^\circ\text{C}$. Linear polarization, figure 4 a), present the increasing character of the corrosion rate with the percentage of H_2S with near values for 0 and 10 ppm/mole samples and bigger values of corrosion for 20 and 30 ppm/mole samples.

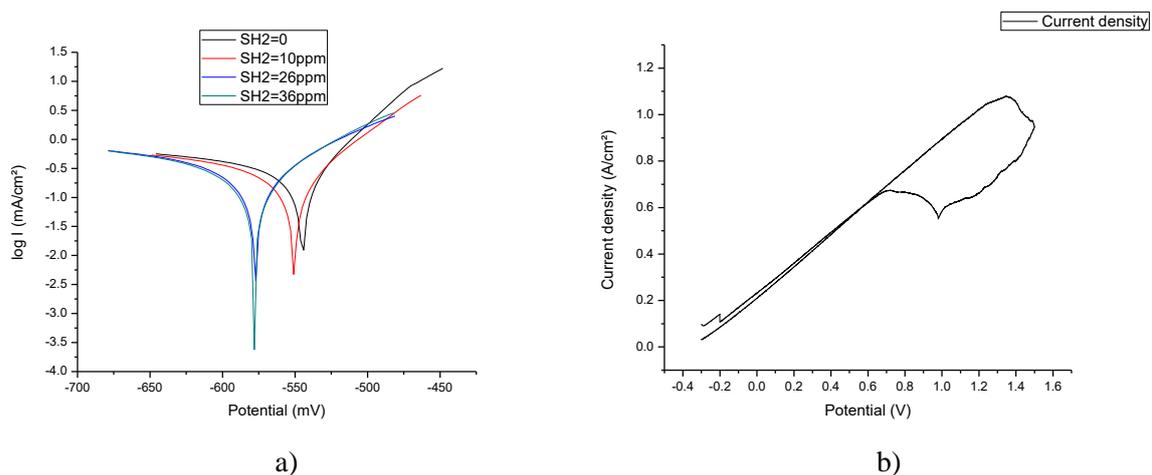


Figure 4. a) Linear polarization curves of P265GH steel in $\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}$, pH 3, at various H_2S concentrations (ppm by mole), $T \approx 25^\circ\text{C}$ b) Cyclic polarization curve of P265GH steel in $\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}$, pH 3, at various H_2S concentrations (ppm/ mole), $T \approx 25^\circ\text{C}$.

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 $\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}$, pH 3, at various H_2S concentrations (ppm by mole), $T \approx 25^\circ\text{C}$. 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].

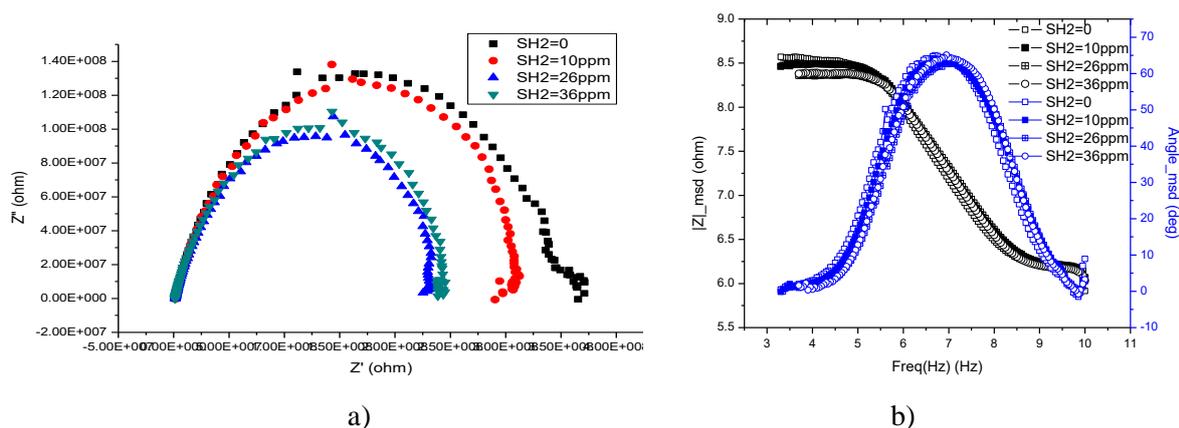


Figure 5. (a) Nyquist and (b) Bode plots of P265GH in $\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}$, pH 3, at various H_2S concentrations (ppm by mole), $T \approx 25^\circ\text{C}$.

During the increase in the H_2S concentration, RP of the experimental alloy reduce more or less with the same trend. The participation of H_2S 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_2S concentration. The EIS results are proper to be used to identify the corrosion and electro-corrosion mechanisms by the presence of H_2S .

The reactions between H_2S 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_2 evolution reaction.

Hydrogen could appear as a result of the reduction reaction of H_2S 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 .

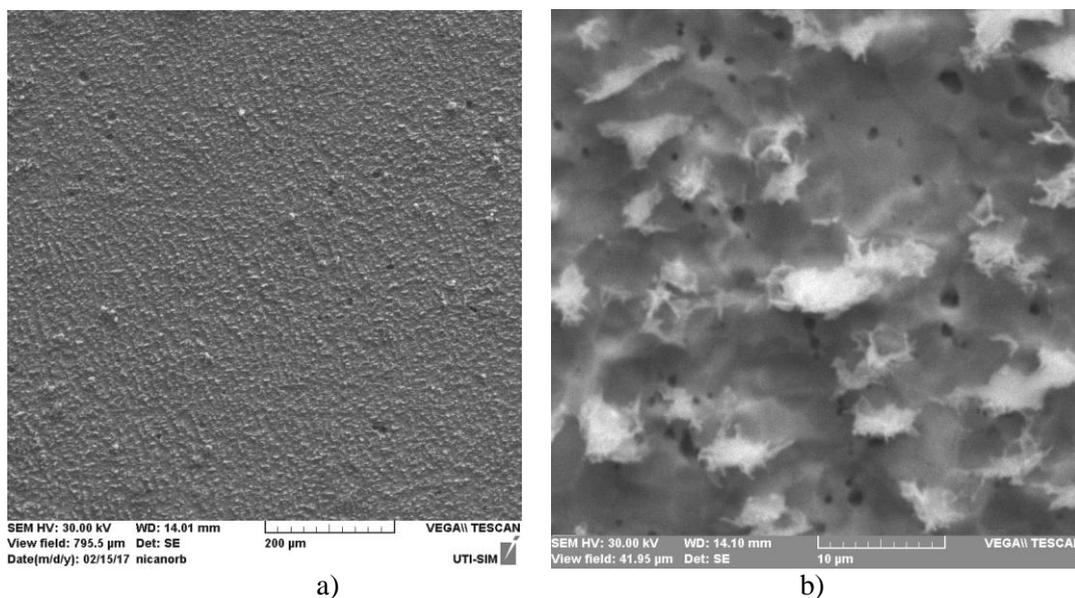


Figure 6. SEM images of the P265GH surface after the electro-chemical tests a) 250x and b) 5000x.

Analyzing the electrochemical corrosion reactions between H_2S 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.

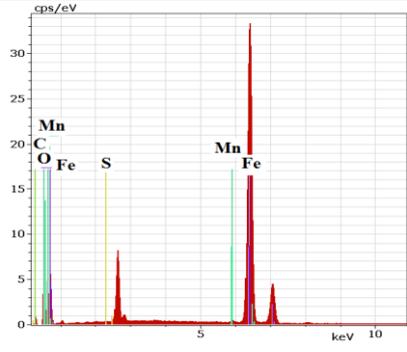
In table 1 is presented the chemical composition of the metallic material surface after the electro-chemical test made on a 4 mm² area. Comparing to the C-steel used for tests we observe a decrease of iron and manganese chemical elements mass percentages which probably pass to oxides and detach from 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_2 was adsorbed on the steel surface prior to H_2S and the H_2S adsorption reduced.

Based on the chemical composition result, table 1, and the literature [18] the compound CO_2 corrosion was the main process at the beginning of corrosion process and the main product is probably $FeCO_3$. Based on cyclic curve and EIS experiments the structure form at the beginning, probably $FeCO_3$ and precipitated on the metal surface was not compact at the start of the corrosion. In this case the specie Fe^{2+} has the ability to penetrate through the scales by diffusion.

After that Fe^{2+} reached the surface film / liquid interface, the compound iron sulfide form when combining with the S^{2-} anion and then precipitated on $FeCO_3$.

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 Nizar I, Heah C Y 2011 *Australian Journal of Basic and Applied Sciences* **5** (9) 441-449
- [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, Nestic 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, Trinca L C, Dascalu 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 714920
- [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