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Preliminary results on effect of H_2S on P265GH commercial material for natural gases and petroleum transportation

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ABSTRACT

A commercial Fe-C material (P265GH) used for natural gas delivery and transportation systems was analyzed in H_2S atmosphere in order to establish the corrosion resistance. In most of the industrial processes for gas purification the corrosion rate is speed up by the presence of sulphur (S) especially as ions (HS-, SO_3^{2-}) or different species like H_2S. The H_2S (hydrogen sulphide) is, beside a very toxic compound, a very active element in the acceleration of metallic materials deterioration. For experiments we used a three electrodes cell with $Na_2SO_4 + Na_2S$ solution at pH 3 for two different temperatures, room temperature ~ 25 °C (sample 1) and at 60 (sample 2) ±1 °C in order to realize EIS (electrochemical impedance spectroscopy) and potentiodynamic polarization. After electro-chemical tests and corrosion resistance characterisation the material surface was analyzed using scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS).

1. Introduction

The steels are the most used materials for the industrial equipment with a worldwide production of 1.55 billion tons in 2012 [1,2]. Depending of the alloy elements and microstructure it can be obtained a broad field of properties. The elements Cr, Ni and Mo are those added in percents to increase the corrosion resistance, while for the carbon steels and the low alloyed ones there are added additional elements in small concentrations in order to obtain specific mechanical properties. These materials are used in different industrial domains and different methods (for example the cathodic protection, coverings for carbon steels or alloying for the stainless steels) were applied to increase their resistance at corrosion when exposed at different mediums of degradation. Conventional low-carbon steels present a high corrosion in sulphur containing atmosphere because of a fast ionic diffusion [3]. In the petroliferous and gaseous industry, the steels are used for different appliances and are exposed constantly in different environments. In the process of production and manufacturing these substances we meet often H_2S in gaseous or dissolved forms. The physical-chemical state of H_2S will depend of ph, temperature and the partial pressure of the medium. A selection of the materials for different applications is made in agreement with the instructions of the standard NACE MR0175-ISO15156 (2003). Several specific conditions (physical and chemical) met in the systems of ducts are known as facilitating for the growth of bacteria and decrease of the sulphur consequently responsive for the generation of H_2S. Some carbon steels with high mechanical properties may be very sensitive at even very low levels of H_2S. The localized corrosion (pitting), but also cracking through stress crack corrosion (SCC) can be enhanced in the presence of H_2S and in the case of stainless steels. It is obvious that the presence of the compound H_2S leads to the degradation of the steels and represents a real menace for the exploitation of gases and petroleum or other applications where there are generated quantities of H_2S.

Conventional low-carbon steels present a high corrosion in sulphur containing atmosphere because of a fast ionic diffusion [4]. In most applications for transport or storage of oil or natural gaseous the corrosion rate of the metallic materials is accelerated by the present of S element as different ions (HS^-, $S_2O_4^{2-}$, SO_3^{2-}) or specific species of H_2S [5]. As common solutions can be used a higher corrosion resistance alloy (for example like stainless steels) as main production material or for metallic plating but both cases increase a lot the production expenses and in plating case also increase in weight the entire structure. Another solution can be the deposition

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of a thin protective layer of ceramic or polymer materials. Using thin films the costs of the materials will be low but the production cost can reach higher values so a versatile technique is required. Because the quality of the petroleum can't be better in the next 15–20 years we have to find proper solutions to improve the materials quality (properties). The commercial Fe-C steel (P265GH) has a rich background in the petroleum and natural gaseous industry. In Romania it is used and sold by S.C. TotalGaz Industry S.R.L. with markets like Eastern Europe, China, Iran or Russia. The necessity of high quality materials is obvious for everyone who will work with energy creation materials like petroleum or natural gaseous products [6].

The main purpose of this paper is to provide proper experimental data about the behaviour of low carbon steel in contact with an environment with H_2S in different percentages. The experiments were carried out at two different temperatures, in order to cover different real working conditions, 25 respectively 60 ±1 °C in solutions with 0, 10, 20 and 30 ppm/mole H_2S concentrations. Electrochemical impedance spectroscopy (EIS) was successfully used [5] for characterization of the metallic material surface in H_2S environment for 304L and 316L steels.

2. Experimental details

The material P265GH (according EN10028: C: max 0,2; Si: max 0,4; Mn: 0,8-1,4; Ni: max 0,3; Cu: max 0,3 and S: max. 0,015) is part of the class of the steels characterized by a good weld ability and a high resistance at high pressures tensile strength (MPa) 410–530 for 100 mm nominal thickness). There is also renowned for the high standard behaviour at high temperatures and it is used in the gas and petroleum industry, as well as the chemical and petrochemical industry. The material P265GH is used in manufacturing caldrons, radiators, heat exchangers, storing reservoirs, combustion funnels and gas discharge, recipients under pressure, filters, taps with sphere, flanges and for the production of the ducts which carry hot liquids. This material can be found as semi-manufactured under the form of steel plate, steel duct without welding, steel bar and steel band. The most renowned countries that provide steels of P265GH are the Saudi Arabia, Kuwait, Qatar, Yemen, The United Arab Emirates, Iran, Turkey, Kazakhstan, Greece, Singapore, Thailand, Indonesia, Vietnam, South Africa, Brazil, India, Australia and Egypt.

Analytic reactive Na_2SO_4, Na_2S, H_2SO_4 were used to obtain H_2S in an experimental precinct presented in Fig. 1. In order to carry out the experiments it was used an isolated enclosure with a volume of 500 cm^3. The precinct, presented schematically in Fig. 1 through 2D and 3D method, has four ways of access for: work electrode (the cylindrical sample with the diameter of 10 mm of P265GH built in teflon), the reference electrode (of saturated calomel), an counter electrode (platinum wire) and the way of access of the inert gas drained at 4-5 bar pressure.

The experiments were made in the experimental precinct in a solution of $Na_2S + H_2SO_4$, 1 M with the gradual obtaining of H_2S in the following percents 0, 10, 20 and 30 ppm/mol (respectively 0; 0.34; 0.68; 1.02 mg/l) at 25 and 60 °C with partial draining of argon. It was used for a litre of solution of Na_2SO_2 1 M: 142 g Na_2SO_4 which were made acetous with H_2SO_4 until a pH 3. Also it was used a litre of solution of NaCl 1 M: 58.44 g/mol/1 l solution that was made acetous with HCl until a pH = 3 and 100 ml solution (0.10%) Na_2S: 0.10 g NaS/100 ml or 0.338 g Na_2S $9H_20$/100 ml. In the presence of H_2SO_4 it takes place the reaction: $Na_2S + H_2SO_4 = H_2S + Na_2SO_4$.

In order to avoid the total contamination with oxygen and to recreate partially the conditions in which function these materials in real cases it was drained argon in the precinct. Because the real cases involve different conditions of running, there were carried out experiments at two different temperatures, respective 25 and 60 ±1 °C using a thermostating enclosure of the experimental cell. Both temperatures represent real work conditions of these materials from the transport and storage systems or the units of purification. In a future experiment it is desired to introduce also different values of pressure in the work precinct, but at present the tests were carried out at normal pressure. The inert gas drained has the role of reducing the role of cathodic reactions which might intervene in the analysis such as the reduction of oxygen or HS. After applying the inert gas for 20 min there were gradually introduced the necessary quantities of Na_2S to produce 10, 20, 30 ppm of H_2S(we mention that all the concentrations were related to ppm on mole). Forward Na_2S dissociates in H_2S in the acid solution: $Na_2S + 2H^+ \rightarrow 2Na^+ + H_2S$ [7,8]. As a result of this reaction, depending of the quantities of the reactive substances introduced, H_2S is formed at the interface with the experimental metallic material. On the whole duration of the experiments it was drained argon at the upper side of the precinct, at a distance of 100 mm of the solution/sample in order to avoid the excessive oxidation of the material, real work conditions of these materials in the industrial appliances with closed circuit and to maintain in work parameters the produced quantity of H_2S, avoiding thus the decrease of H_2S concentration.

The corrosion experiments were realized in the following order and exposing the material at 0, 10, 20 or 30 ppm/mol H_2S: a) 900 s to register the OCP, b) the resistance tests at polarization Rp with n domain of potential of ± 10 mV and a scanning speed of 0,5 mV/s, c) potentiometry tests EIS at OCP with an amplitude of 10 mV and a domain of frequencies between 10^{-2} and 10^5 Hz and d)linear and dynamic potentiometry tests with a scanning speed of 0,5 mV/s and a potential domain from −200 to 2000 mV taking into account the OCP. In order to insurance the reproducibility, all the experiments were carried out thrice.

Electrochemical measurements were performed (using Parstat 400 Princeton Applied Research, USA equipment) in the three electrode experimental cell, Fig. 1, connected with a potentiostat with the alloy sample (ground up to 2000 grit) with a rotating working electrode (500 rpm), saturated calomel electrode (SCE) as reference electrode and a platinum electrode as counter electrode. Electrochemical impedance spectra were measured over a frequency range from 100 kHz to 1 mHz using a 10 mV amplitude AC voltage signal. The test began with stabilizing the open circuit potential (OCP) for 30 min. Potentiodynamic polarization measurements were performed at a two scan rate of 1 mV/s and 5 mV/s from −0.15 V_{sce} up to +1.5 V_{sce}. Analysis of the spectra was performed in terms of equivalent circuit (EC) fitting using ZSimpWin software. After the electrochemical experiments (EIS, linear and cyclic potentiometry) the material was cleaned by sonication for 60 min in technical alcohol. The experimental samples surface was analyzed using SEM (scanning electron microscopy with VegaTescan LMH II, VegaT software for 2 and 3D characterization) equipment and EDAX (X-ray energy dispersive spectroscopy, Bruker type, Esprit software) for structural and chemical analyses. The electrochemical tests were carried out at various H_2S compositions (0, 5, 10 and 15 ppm). XRD determinations, using X'Pert equipment, on the expose surface at H_2S were done in order to establish the presence of FeS_x on the metallic material surface.

3. Experimental results

3.1. Microstructural results

In the aqueous solutions the weak alloyed steels and those with carbon are susceptible to corrosion that can take place through anodic or cathodic reactions. In the solutions without oxygen, such

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