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Petroleum solid adherence on tubing surface

A. Cosultchi[a,b,*], E. Garciafigueroa[b,c], A. García-Bórquez[c], E. Reguera[d,e], H. Yee-Madeira[c,1], V.H. Lara[f], P. Bosch[f]

[a]*Department of Metallurgical Engineering, ESIQIE-IPN, Mexico City, Mexico*
[b]*Instituto Mexicano del Petroleo, 152 Eje Central "L. Cardenas", 07730 Mexico City, Mexico*
[c]*ESFM-IPN, UPALM, Ed. 9, Mexico City, 07738, Mexico*
[d]*Centro de Investigaciones en Ciencia Aplicada y Tecnológia Avanzada (CICATA-IPN), Mexico City, Mexico*
[e]*Universidad de La Habana, Cuba*
[f]*UAM-I, Av. Michoacan y Purisima, Iztapalapa, 09340, Mexico City, Mexico*

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Abstract

Blocking of the crude oil flow is induced occasionally by the presence of a black layer of material adhered along the internal walls of petroleum wells. A piece of tubing with a significant amount of organic material, collected from a Mexican oil well, was analyzed by Mössbauer Spectroscopy (MS), X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIRS). At room temperature, a fraction of the adherence detaches easily off from the tubing surface, but part of it remains firmly adhered. Non-stoichiometric iron oxides (oxidized magnetite or maghemite) and iron sulfides (pyrrhotite) and also small amounts of iron hydroxides and organic material were found on the tubing surface with adhered-material. This suggests a competitive adsorption of sulfur atoms and hydroxyl groups from petroleum, on the surface iron sites. Finally, the organic material, which contains alkyl chains and aromatic rings, is adsorbed non-dissociatively on the modified surface but only in the presence of non-stoichiometric iron sulfide.

Keywords: Petroleum; Deposition; Iron Compounds; Mössbauer spectroscopy

1. Introduction

The extraction of petroleum from a reservoir is made through a delivery duct, or tubing, which is a pipe placed within a productive oil well. The tubing used in petroleum wells is commonly manufactured according to API specifications [1], and its internal surface presents a uniform oxide layer as a result of thermal treatment [2]. This layer contains FeO and Fe_3O_4, with the FeO close to the bulk metal. Generally, the idea that the petroleum hydrocarbons preserve the tubing surface against corrosion is well-accepted [3,4]. Thus, the initial oxide layer composition is expected to prevail on the tubing surface after contact with petroleum hydrocarbons. However, when the tubing is working in extreme ambient with sour (H_2S) or sweet (CO_2) gases, it is damaged by corrosion or sulfide stress cracking [5–9]. Additionally, the presence of oilfield brine, water and salt (NaCl) within the crude oil flow induces corrosion of the metal matrix [10] and also dissociation of the adsorbed water on its surface [11]. Frequently, the tubing string of some wells shows heavy organic compounds adhered along the internal wall [12], which lead to clogging and reduction of the petroleum flow.

Several studies link the formation of petroleum sludge to the interaction of crude oil with iron compounds [13,14]. For instance, ferric ion (Fe^{3+}) contributes to increase the yield of precipitated material from crude oil [13] or from bitumen [14]. Consequently, iron minerals, which are present in the reservoir rocks as sandstone and limestone, promote the aggregation of the asphaltic material [15]. However, the importance of the presence of iron compounds on the tubing or pipe surface has been neglected. The type of the compounds, which are part of a solid deposit adhered on this surface is essential to provide a better understanding of the macroscopic phenomena of organic deposition. In this report we present the results of the characterization study of the material adhered to a low carbon steel tubing piece collected from a Mexican petroleum well. The data correlated to the way that petroleum compounds interact with the metallic surface of the tubing and cause deposit formation.

* Corresponding author. Address: Instituto Mexicano del Petroleo, 152 Eje Central "L. Cardenas", 07730 Mexico City, Mexico. Tel.: +52-5-337013; fax: +52-5-5678776.
E-mail address: acosul@imp.mx (A. Cosultchi).
[1] COFAA-Fellow.

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