

On a Probable Catalytic Interaction between Magnetite (Fe₃O₄) and Petroleum

A. Cosultchi,^{*,†} J. A. Ascencio-Gutiérrez,[†] E. Reguera,^{‡,§} B. Zeifert,^{||} and H. Yee-Madeira[⊥]

Instituto Mexicano del Petróleo, 152 Eje Central "L. Cardenas", 07730 Mexico City, Mexico, Institute of Materials and Reagents, University of La Habana, Cuba, Center of Applied Science and Advanced Technologies of IPN, Mexico, Department of Metallurgical Engineering, ESIQIE-IPN Mexico City, Mexico, and ESFM-IPN, Mexico City, Mexico

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Magnetic and nonmagnetic iron compounds were detected as part of asphaltene deposits formed on tubing wall surface. To shed light on the probable role of the iron compounds in the formation of such deposits, magnetite (Fe₃O₄), one of the intrinsic components of the iron oxide multilayer scale of any carbon steel surface, was contacted with crude oil at 170 °C, a temperature similar to that of the bottom well, and subsequently aged at room temperature. Characterization of the samples was made by using XRD, Mössbauer, IR, TGA, EDS, and microscopic (SEM and TEM) techniques. Small amounts of new iron phases, magnetic (oxidized magnetite) and nonmagnetic (iron oxyhydroxides), an increase in the content of C=C and C–O bonds of the organic phase, and an increase of the thermal stability of the organic phase indicated the formation of iron complexes of Fe ions and FeOOH with the oxygen functionalities.

Introduction

The C–Mn steel tubing is normally covered by a firmly adhered scale of iron oxides rich in magnetite (Fe₃O₄),¹ as a consequence of the manufacturing process. This iron oxide contains both Fe²⁺ and Fe³⁺ ions within a compact bulk, and in the presence of the oxidizing agents, it has a low surface reactivity given by surface sites where ferrous ions are accessible.² Magnetite is also susceptible to corrosion in wetted environments, forming iron (3+) oxyhydroxides, a process known as atmospheric corrosion.³

At the bottom-well conditions, such tubing contacts crude oil, and consequently, chemical changes other than atmospheric corrosion occur depending on the temperature, pressure, and fluid composition, as shown in previous studies.^{4,5} As crude oil flows up through the tubing well, the fluid pressure progressively decreases until gas phase and water, if any, separate from the liquid one. Reactive gases such as H₂S, CO₂, and methane, once separated from the liquid phase, also contribute to change the composition of the initial iron oxide layer of the tubing surface.^{1,6,7} Thus, on a tubing surface exposed to crude oil

contact, compounds such as nonstoichiometric iron sulfides (Fe_{1–x}S), siderite (FeCO₃), maghemite, and iron oxyhydroxides (akaganeite, β-FeOOH; lepidocrocite, γ-FeOOH; and goethite, α-FeOOH) can normally be detected.⁶

In addition, all these compounds are concurring with organic material; organic (asphaltene) deposits have been reported as related to most of the mentioned iron phases as well as to other minerals.^{4,8,9} However, interaction between the oxide layer and the organic phase and the mutual effect that they can have on their respective composition and morphology remain poorly documented.^{10,11} It is highly important that the reactivity of iron compounds and their selectivity toward some of the crude oil polar compounds are studied in order to understand the formation of asphaltene deposits in petroleum wells and the role of tubing steel composition in such process.

Thus, in this contribution, this subject is studied from samples of magnetite that have been contacted with crude oil following two steps: (a) at high temperature (170 °C) and for a short period of time (170 h) and, (b) at room temperature and for a long period of time (two years). The phase transformation of the magnetite was followed by XRD and Mössbauer spectroscopy, while the organic phase was observed by FTIR. In addition, electron microscopy techniques were used to evaluate the mutual effect of the interaction between organic and inorganic phases.

* Corresponding author. E-mail: acosul@imp.mx.

[†] Instituto Mexicano del Petróleo.

[‡] University of La Habana.

[§] Center of Applied Science and Advanced Technologies of IPN.

^{||} ESIQIE-IPN.

[⊥] ESFM-IPN.

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