SURFACE AND INTERFACE ANALYSIS
Surf. Interface Anal. 2002; **34**: 384–388
Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/sia.1322

SIA

Formation of petroleum organic deposits on steel surfaces

A. Cosultchi,[1,2]* A. García-Bórquez,[3] J. Aguilar-Hernandez,[3] H. Yee-Madeira,[3†] E. Reguera,[4] V. H. Lara[5] and P. Bosch[5]

[1] Dept. of Metallurgical Engineering, ESIQIE-IPN, 07738 Mexico City, Mexico
[2] Instituto Mexicano del Petroleo, 07730 Mexico City, Mexico
[3] ESFM-IPN, 07738, Mexico City, Mexico
[4] Universidad de La Habana, Cuba
[5] UAM-Iztapalapa, 09340, Mexico City, Mexico

Received 16 July 2001; Revised 30 November 2001; Accepted 24 December 2001

An adhered organic deposit, formed within the petroleum well on the steel surface of the tubing walls, was systematically characterized following a sequence of bulk and surface techniques. The results allowed the identification of the tubing wall and its internal surface structures. As a consequence of the contact with sulphur-bearing compounds such as H_2S and brine from petroleum, the pre-oxidized steel surface was modified by non-stoichiometric iron compound formation. These new iron phases favour adsorption and chemisorption of the petroleum polar compounds on the steel surface. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: petroleum well; carbon steel surface; adherence; SEM-EDS; AES; XRD; Mössbauer; FTIR; Raman; spectroscopy

INTRODUCTION

When materials such as steel are exposed to multicomponent environments, as in the petroleum well, several processes such as oxidation, sulphidation or carburization may occur not only at the gas/metal interface but also within the scale that preserves the reaction products.[1] In addition to the new iron phases formed in such an environment, organic material was found adhered on the internal surface of some petroleum wells.[2] The study of this material is difficult, because the adhered layer is irregular and consequently the compositional information obtained only by means of surface-specific techniques could be incomplete. For instance, the type of carbon steel used for the tubing and its manufacturing process could affect the tubing wall composition and structure. In addition, the hydrocarbon ambient modifies the steel surface[3] and, furthermore, its complexity increases when the internal surface of the tubing is petroleum- or brine-wetted. Moreover, extraction of the tubing piece from the well implicated the formation of other iron compounds as a consequence of its exposure to the atmosphere.[4]

In this work, the identification of elements, their chemical bonding and concentrations as well as the particular morphologies observed in the bulk structure and on the tubing border was carried out by means of several bulk and surface-specific techniques. Additionally, a discussion concerning the interpretation of results as well as mechanisms of formation of the identified compounds is presented.

*Correspondence to: A. Cosultchi, Instituto Mexicano del Petroleo, 152 Eje Central ''L. Cardenas,'' Mexico City 07730, Mexico.
E-mail: acosul@imp
Contract/grant sponsor: Instituto Mexicano del Petroleo;
Contract/grant number: FIES 97-06-I.
†CO FAA Fellow

EXPERIMENTAL

Metallic coupons with an adhered layer of black material were cut from a piece of tubing removed from a Mexican well. A cross-section of a metallic coupon was polished and prepared for microscopic observations by gold coating. Energy-dispersive spectroscopy (EDS; Jeol JSM 6300 with Noran Microanalyst spectrometer at 15 kV and a working distance of 39 mm) and Auger electron spectroscopy (AES; Jeol JAMP 30 at 10 kV) registered the chemical compositions across the wall section of the tubing.[5] These techniques also provide elemental compositions at different depths. Auger spectra of the sample were registered after sputtering with argon. Element quantification was accomplished using sensitivity factors from the literature.[6] Fourier transform infrared (FTIR; Perkin-Elmer 2000 FT-IR) and Raman spectroscopies in reflection mode, as well as x-ray diffraction (D500 Siemens diffractometer with Cu K_α source) results were acquired from the surface with the adhered layer. The Raman spectrum was obtained with the 514.5 nm line of an Ar^+ laser (40 mW) focused to an area of $\sim$0.5 mm^2. The outcoming radiation was analysed by a double monocromator (1403-SPEX) and detected by a thermoelectrically cooled photomultiplier tube (RCA-C3104) connected to a photon counting system.

Additionally, Mössbauer spectroscopy was applied to the scraped powder of the steel surface in order to