Contents lists available at ScienceDirect

Spectrochimica Acta Part B

Analytical Note

Double-pulse laser-induced breakdown spectroscopy analysis of scales from petroleum pipelines

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ARTICLE INFO

ABSTRACT

Pipeline scales from the Campos Bay Petroleum Field near Rio de Janeiro, Brazil have been analyzed by both Raman spectroscopy and by laser-induced breakdown spectroscopy (LIBS) using a double-pulse, calibration-free approach. Elements that are characteristic of petroleum (e.g. C, H, N, O, Mg, Na, Fe and V) were detected, in addition to the Ca, Al, and Si which form the matrix of the scale. The LIBS results were compared with the results of micro-Raman spectroscopy, which confirmed the nature of the incrustations inferred by the LIBS analysis. Results of this preliminary study suggest that diffusion of pipe material into the pipeline intake column plays an important role in the growth of scale. Thanks to the simplicity and relative low cost of equipment and to the fact that no special chemical pre-treatment of the samples is needed, LIBS can offer very fast acquisition of data and the possibility of in situ measurements. LIBS could thus represent an alternative or complementary method for the chemical characterization of the scales by comparison to conventional analytical techniques, such as X-ray diffraction or X-ray fluorescence.

1. Introduction

Formation of mineral scales is one of the major problems in the oil production industry. Scales may be defined as chemical compounds of inorganic nature which grow as a result of unwanted material deposition and chemical reactions on metallic parts of equipment used in petroleum fields. The harmful effect of fouling of the pipes is a flux reduction or a complete obstruction of the pipeline, an event that can produce important downtimes, loss of profits, and repairing and replacing costs. Barium/strontium/calcium sulfates and calcium/magnesium carbonates can be found as insoluble inorganic scales, but the most predominant scales are the barium sulfate ($BaSO_4$) and calcium carbonate ($CaCO_3$) [1]. There are interests in methods, chemical and mechanical, to remove or prevent scales formation, such as continuous injection of scale inhibitors through the gas-lift system, desulfation of seawater and sand screening with gravel packs impregnated with inhibitors [2].

In this work the LIBS technique [3] was used to perform a stratigraphic analysis on some scales coming from an oil field at Campos Bay – Rio de Janeiro – Brazil. The analysis of the scales composition by LIBS aims to improve the understanding of the fundamental mechanisms involved in the fouling growth on the oil pipelines. Recently, LIBS analysis was employed successfully to analyze metal traces in

Saudi Arabian crude oils [4] and the use of LIBS as a promising technique in area of petroleum analysis was demonstrated by Fortes et al. [5].

2. Samples and experimental details

Fig. 1 shows the four types of samples investigated in this work. The sample labeled as I_1 consists of drag-products adsorbed on the tube wall. In fact, sample I_1 is basically made of little pieces of rocks having silicon as the major component. Sample I_2 is a pellet of white scale having as major component $CaSO_4$. The sample labeled as I_3 is a pellet of multilayer scale representing a calcareous fouling. This sample was extracted and processed by Soxhlet extraction technique [6] to completely remove the organic phase, thus allowing the study of the formation of fouling, its morphology and chemical composition. Sample I_4 consists of a section of a pipe placed after the three-phase separator (gas, oil and water) with a thick calcareous deposit on the internal surface [7]. This pipeline exclusively conducts seawater contaminated with very little organic material. Chloroform was used to remove the remains of crude oil from all the samples; after that, the samples were rinsed in hot water (60 °C) in an ultrasonic chamber and then dried.

The samples were analyzed using the Modì LIBS instrument [8] manufactured by Marwan Technology, in the "Advanced" configuration. This device delivers two collinear laser pulses at Nd:YAG fundamental wavelength of 1064 nm and adjustable energy per pulse with a FWHM of about 10 ns. The focusing lens had a focal length of

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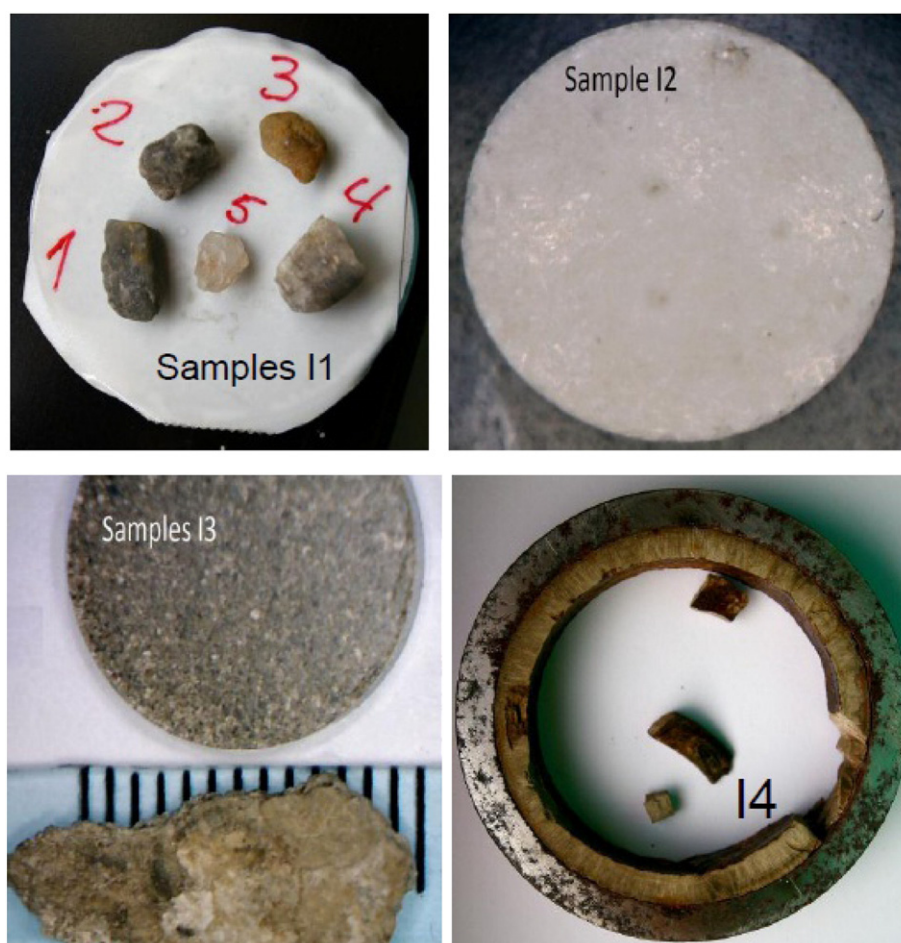 E-mail address: vincenzo.palleschi@cnr.it (V. Palleschi).

Fig. 1. Four kinds of scales removed of tube wall of gas lift system and three phase separator.

10 mm. For the present work the interpulse delay was set at 1 μs and the energy per pulse was adjusted at 60 mJ. The spectra were recovered 1 μs after the second pulse with an Andor Mechelle Spectrometer with spectral range from 200 nm to 975 nm having a resolution: $\lambda/\Delta\lambda = 5000$ with a slit entrance of 50 μm. The acquisition time used was 1 μs.

The Raman analysis was made using a Renishaw InVia Spectrometer associated with Leica DLML microscope and 50× microscope objective. He–Ne laser ($\lambda = 633$ nm), laser power = 30 mW (0.1 mW effective power on the sample) and acquisition time of 10s in 100 accumulation were used.

3. The experimental procedure

For all the samples, 25 spectra were acquired, each one corresponding to a double laser pulse. The first five spectra were discarded in order to avoid possible surface contamination due to the sample manipulation. The remaining 20 spectra were averaged into a single spectrum. Three different spots at each sample were probed, to check the sample homogeneity.

Particular attention was given to the sample I_4, for which a stratigraphic analysis of its elemental chemical composition was performed. Probing points can be clearly see in the Fig. 2 because of the craters produced by the laser ablation. The stratigraphic probing was made radially starting from the radial position at 15 mm, which is on the Fe–Mn pipe, at 1 mm steps up to reach the external surface of the scale (5 mm). The radial position 14 mm is on the wall-incrustation boundary, while the remaining points are on the scale internal layer.

4. Results

Atomic spectra were analyzed using the LIBS++ program [9] and the concentrations calculated with the calibration-free method, due
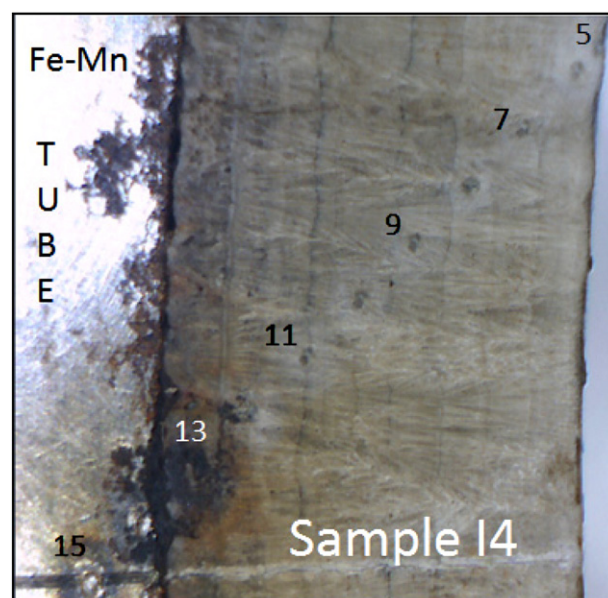

Fig. 2. Enlarged view of cross section of an iron tube used after three-phase separator where the probing points are marked in millimeter.

to the lack of suitable standards for building calibration curves for the elements in the scales [10,11]. Fig. 3 shows a typical spectrum taken from sample I_4 where some atomic lines of Ca I and Sr II are shown. LIBS analysis of the sample reveals trace of Cu, Al, Ba, Fe, K, B and Sr. Silicon and calcium are the major components of samples I_1, I_2 respectively. Sample I_3 is a rust deposit, which is resulting from the corrosive action of oxygen and H_2S. As expected, the LIBS spectrum of this sample showed high levels of Fe and Al, typical of this kind of incrustation.

Concerning sample I_4, the pipe is made with a high strength carbon steel alloy type API (American Petroleum Institute) 5L X-80 whose chemical composition in mass% is $C_{Max} = 0.08\%$; $Si_{Max} = 0.26\%$; $Mn_{Max} = 1.75\%$; $P_{Max} = 0.001\%$; $S_{Max} = 0.0005\%$; $Mo_{Max} = 0.27\%$ and $Ni_{Max} = 0.22\%$. This tube has been operating for about 10 months at the well in Campos Basin – Rio de Janeiro – Brazil. The deposit on the inner surface of the pipe is very sticky; the main component of the incrustation is calcium carbonate ($CaCO_3$) deposited on a thin corrosion layer of the pipe composed of a mixture of Fe_3O_4 and FeOOH (hydrated ferric oxide) [12].

On sample I_4 there are both radial and azimuthal reddish striations that are visible at bare eye. These striations may occur as a consequence of radial diffusion of metals from the pipe to the scale and its azimuthal deposition in a ox-reduction process induced by systematic or random pressure variations into the oil reservoir which may influence the bicarbonate/carbonate equilibrium equation $2HCO_3^- \rightarrow CO_3^{2-} + CO_2 + H_2O$.

The Raman spectrum reveals the presence of the calcium carbonate 1087 cm^{-1} band in the white part of sample I_4. In the reddish zones, and in particular close to the boundary with the iron pipe, the Raman spectrum evidences the presence of ferric oxide. Figs. 4 and 5 show the Raman spectra obtained from the white and red parts of the sample I_4, respectively.

The chromatographic analysis [13] of water used after the three-phase separator revealed only traces of iron and iodine, high levels of sodium ($Na^+ = 33,500$ mg/l), chlorine ($Cl^- = 59,100$ mg/l), calcium ($Ca^{2+} = 2,600$ mg/l) and sulfur. The chemical analysis also reveals the presence of ions potentially responsible for pipe fouling, as the cations Sr^{2+}(315 mg/l), Ba^{2+}(30 mg/l) and Mg^{2+}(270 mg/l) and the anions carbonate (130 mg/l), bicarbonate (830 mg/l) and sulfate (15 mg/l).
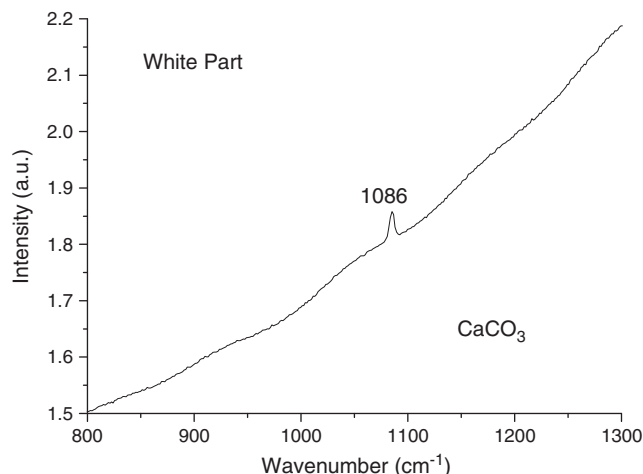

Fig. 4. Raman spectrum of white phase of sample I_4.

The pH of water was 7.95 and during the operation time the water temperature ranged from 60 to 80 °C.

The stratigraphic analysis of the incrustation was made by "shooting" the laser on several points of the cross-section, placed 1 mm apart from each other. At each point, spectra were acquired cumulating 20 laser shots, after 5 cleaning shots, and analyzed using the LIBS++ program. The analysis of sample I_4 revealed the presence of iron, calcium, sodium, magnesium, barium, potassium, manganese and strontium. Fig. 6 shows the radial profile of the concentration of these elements. The concentration of iron significantly decreases in the first 2 mm within the deposit and then remains approximately constant at about 1%. A similar behavior is observed for manganese, whose concentration goes to zero 3 mm away from the tube wall. As the chemical analysis did not reveal substantial amounts of iron in the seawater, it is highly plausible that the significant presence of iron in the scale could derive from its diffusion from the Fe–Mn pipe to the incrustation. The corrosion and diffusion of iron [14] could play a fundamental role in the development of this kind of scale, with the visible radial striations acting as diffusion channels of
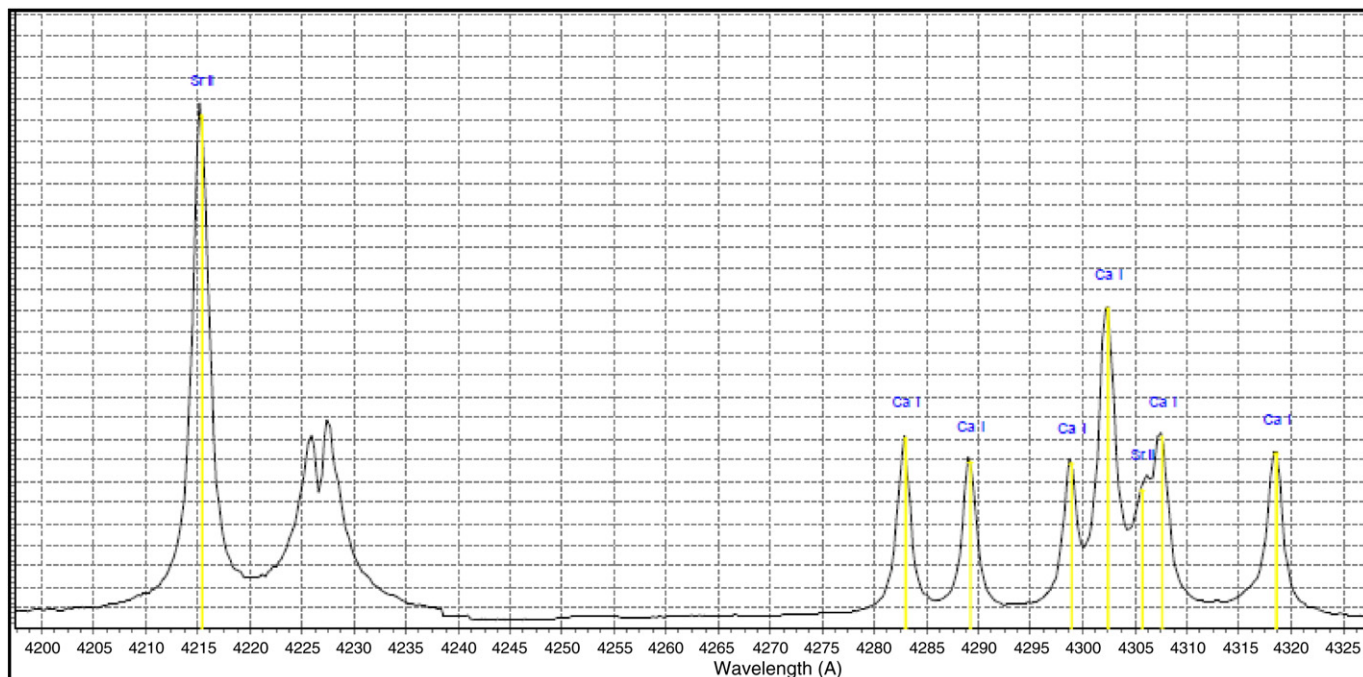

Fig. 3. Typical LIBS spectrum of Sample I_4 at radial position 8 mm showing Ca I and Sr II lines.
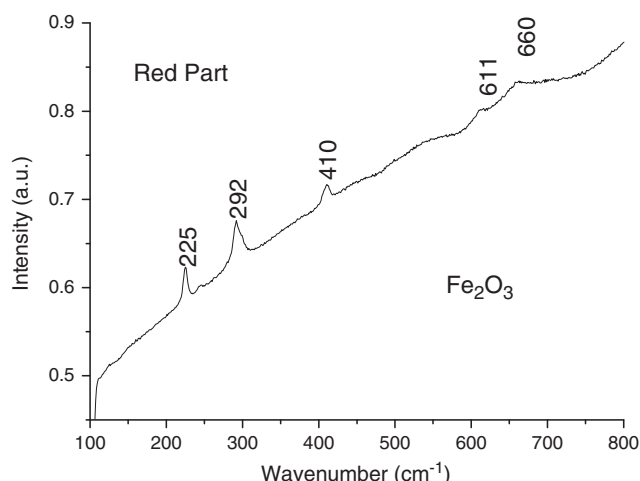
Fig. 5. Raman spectrum of red phase of sample I₄.

iron to the incrustation. The similarity of iron and manganese profiles indicates that also this element diffuses from the pipe to the scale.

It should be noted in Fig. 6 that sodium has a singular behavior, reaching a maximum concentration 1 mm away from the tube-scale interface. This non monotonic behavior of sodium is a clear sign that the chemical composition of seawater had changed during the ten months of operation. If this finding will be confirmed by further analysis on the plant, a routine analysis on the inner part of the pipes to be performed with a micro-LIBS system could provide a mean for correlating the environmental changes with the growth of fouling. Moreover, further compositional studies on the internal deposit of the pipes could provide the data for developing a transport model describing the Fe and Mn leaching from the pipe to the incrustation.

5. Conclusions

The preliminary results here presented suggest that the diffusion of pipe material into the incrustation has an important role in the growth of scales. The analysis of the growth process of the incrustations is important and further studies must be done for better understanding the basic processes of their formation. In this work, the spatial behavior of sodium as showed in Fig. 6, for example, is a clear indication that the chemical composition of the medium (seawater) changed

during the growth of the scale. That change in turn influenced the precipitation process, leaving a "mark" in the scale. This kind of micro-analysis could be done at the oil field through a continuous water analysis and a posteriori micro-LIBS analysis [15,16] of the scale composition. In other words, by monitoring the temporal variation in the seawater of specific elements, like sodium or calcium for example, and measuring the scale growth, a correlation between medium composition and pipe fouling could be determined and, on the basis of the information obtained, better strategies for preserving the pipeline integrity could be devised.

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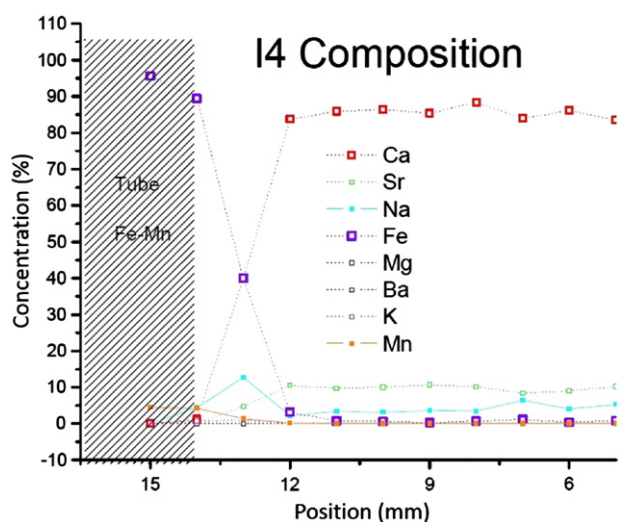

Fig. 6. Concentration profile of scale I₄.