Characterization Of Oil Shale Residue And Rejects From Irati Formation By Electron Paramagnetic Resonance[*]

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In this study, sedimentary organic matter of oil shale rejects, calschist, shale fine and the so called retorted shale from Irati formation was characterized. EPR was used to analyse the samples regarding loss of signal in $g = 2.003$ associated to the organic free radical with the calcined samples and washing with hydrogen peroxide. The radical signal was detected in all samples, however, for the calschist and shale fine samples another signal was identified at $g = 2.000$ which disappeared when the sample was heated at 400 ^{0}C. Hydrogen peroxide washing was also performed and it was noted that after washing the signal appeared around $g = 2.000$ for all samples, including retorted shale, which might be due to the quartz E_1 defect.

1. INTRODUCTION

The pyrobituminous shale, as it is best known, is an oily sedimentary rock, which contains bitumen and kerogen, an organic complex that when heated decays and produces several products, residues and rejects.

According to conventional Geology, the Formation is a sedimentary Bay that marked the Permian Period and its deposition might have occurred in shallow sea water, in largely confined bays, in a climate suitable to calcarium precipitation and physico-chemical conditions favorable to the accumulation of organic matter, which generate pyrobitumen [1]. The Irati formation presents defined layers, which vary in thickness from 5.5 m to 3.5 m with 15% organic matter content intercalated by deposits rich in carbonates. In the region of São Mateus do Sul, Parana State, southern Brazil, there are oil shale formations, called Irati Formation.

In 1970 a mineral (shale) exploration program was established, the Petrosix [1,2]. The mill which processes 1660 tons of "raw shale", firstly mined and crushed, then taken to the retorter, where it is pyrolized, cooked at about 500 ^{0}C releasing the contained organic matter and leaving behind 1376 tons of the residue called retorted shale. Besides the residue, retorted shale, the Petrosix extraction process generates a large amount of rejects, mainly shale fines (less than 0.25 inch) with an oil content of about 15%, and calschist.

In Brazil, the oil shale has been produced since the end of XVIII century, however, very little is known about its residue (retorted shale) and rejects (calschist and shale fine), which

together represent 82% of the total. They constitute a double problem, both contaminating the environment and contributing to higher oil and gas extraction costs [2].

The literature presents some works with shale and also with the retorted residue, however, there are no works with calschist and shale fine. Adams et al. (2005) [3] analyzing oil shale showed that Multivariate calibration modelling has proved to be effective and efficient tool combined with DRIFTS for predicting oil content from oil shale.

Sousa et al. (1997) [4] showed that the oil shale free radical transformation (production and decomposition) mechanism can be described as: $A_i \Rightarrow B_i \Rightarrow C_i$ where B_i are paramagnetic species and A_i e C_i are diamagnetic species. Working with Electron Paramagnetic Resonance (EPR) on retorted shale samples Sousa et al. (1994) [5] analyzed the effects produced on the retorted shale samples at temperatures from 100 a 1000 ^{0}C. They showed that the resonance signal in $g = 4.2$ associated to the ion Fe^{3+} with 5/2 spin, presents a decrease in the samples line width of the samples heated at 900 ^{0}C e 1000 ^{0}C, indicating the appearance of a glass phase.

The Electron Paramagnetic Resonance (EPR) is used in this work [6] to characterize the sedimentary organic matter obtained from the Irati Formation, observing the organic radical signal of shale residue in the Petrosix process, also called retorted shale, as well as the rejects called shale fine and calschist which did not undergo the process.

2. MATERIAL AND METHODS

The samples of the rejects and residue were the region of São Mateus do Sul, Parana State, Brazil, Irati Formation. The retorted shale samples (RS), calschist (CS) and shale fine (SF) were milled and calcined in oven for 2 hours at 200 ^{0}C and then at 400 ^{0}C and finally at 700 ^{0}C. They were also washed

with hydrogen peroxide to eliminate part of the organic matter of the samples. During the washing 1 g of sample for 10 mL of H_2O_2 was used, each sample underwent 40 washings. The samples were put in quartz tube with about 20 mg of non-calcined samples, calcined samples and washed with Hydrogen peroxide.

EPR spectra were recorded for freeze-dried at room temperature in X Band (9.4 GHz). Experimental conditions were: modulation frequency of 100 kHz; microwave power (0.2 mW) in order to avoid semiquinone-type free radicals signal saturation, adequate modulation amplitude (0.1 mT) and time constant (2.56 ms) that was $1/4$ of the conversion time to guarantee no signal deformation by increasing line width. The central field was 338 mT, with 5 mT scanning and modulation amplitude de 0.1 mT peak to peak (H_{pp}). A patterned sample Cr^{3+} with $g = 1.9797$ was added to the sample in the resonant cavity, in order to determine the g value for each sample [7].

The X-Ray Diffraction (XRD) analyses were carried out using an automatic horizontal diffractometer, rotating anode RIGAKU ROTAFLEX generator, Ru-200B model, with Cu$K\alpha$ radiation ($\lambda k_{\alpha 1} = 1.54433$, Å $\lambda k_{\alpha 2} = 1.54051$ Å) operating at 50 kV and 100 mA, in the continuous scanning mode with speed of 2 °/min., within the range of $5^0 \leq 2\theta \leq 100^0$, with divergence slit (DS): 1.00^0, reception slit (RS): 0.30^0, scattering slit (SS): 1.00^0 and the samples were powdered and sieved (53 μm aperture) and were placed on the sample holder and lightly pressed.

3. RESULTS AND DISCUSSION

Figure 1 presents the CS sample spectra without calcination and with the calcined samples at 200 ^{0}C and 400 ^{0}C (similar signals occurred for the SF and RS). The appearance of resonance signal in $g = 2$ of Fe^{3+} with large line width was noticed due to the dipolar interaction between the ferromagnetic structures when the sample was calcined at 400 ^{0}C. Such result confirms what was verified by Fonseca et al. (1984) [8] and Sousa et al. (1994) [6] when they worked with RS samples, those authors attributed the Fe^{3+} signal to the oxidation of Fe^{2+} found in (Fe_2S_3) pyrite and the generation of Fe^{3+} in hematite (Fe_2O_3). The Fe^{3+} signal can be observed in $g = 4.3$ associated to the Fe^{3+} ion with 5/2 spin which can occupy either tetrahedral or octahedral sites of silicate structures. [5]

The spectrum also shows (NC and 200^{0}C) a sextet of lines centered at $g = 2.00$ with a hyperfine coupling constant (A) of 9 mT generated by Mn^{2+} ions with 5/2 nuclear spin [2].

The organic radical spectra for the non-calcined samples, for the three samples: calschist, shale fine and retorted shale, are shown in Figure 2a. The signal for the retorted shale presents a characteristic similar to the organic radical with value in $g = 2.003$ [8] and line width about 5.5 G. The signal for calschist and shale fine present the signal in $g = 2.003$, however, there is another signal in $g = 2.000$. There were no changes in the spectra obtained from samples heated at 200 ^{0}C (Figure 2b) emphasizing that the organic matter related to the organic radical is stable at this temperature once the free radical signal in $g = 2.003$ increased in relation to the spectra at room temperature. Figure 2c shows the spectra after the samples were heated at 400^{0}C. It is possible to observe that the signal around $g = 2.000$ disappears, the organic radical signal
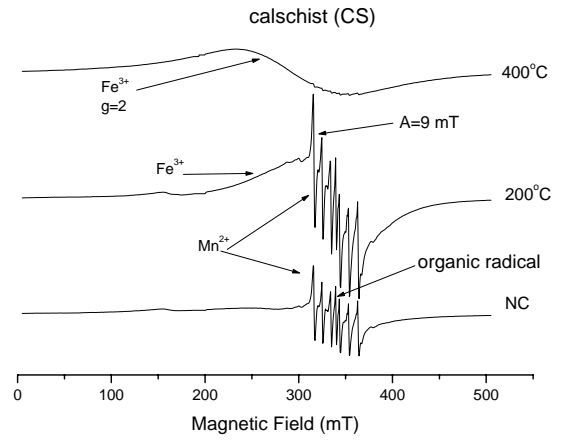

FIG. 1: EPR signals for the calschist sample with variation of magnetic field (B) 500 mT at non calcined (NC) 200^{0}C and 400^{0}C. The Fe^{3+} signal for the three calcination temperatures. At 400^{0}C the gain in signal is lower, however, the intensity of Fe^{3+} signal is higher.

becomes noisier highlighting decrease in the signal to noise ratio. When samples were heated at 700^{0}C, organic radical signal was not observed (data not shown) indicating loss of organic radical due to samples calcination.

The spectra of samples washed with hydrogen peroxide are shown in Figure 3 together with the non-calcined samples. The signal around g=2.000 is observed to increase in calschist and shale fine samples and also appeared in the retorted shale sample. Souza et. al (1994) [5] working with retorted shale did not identify the signal in $g = 2.000$ since this signal only appears when the part of organic matter that contains the organic radical in $g = 2.003$ is extracted. This is only possible when the sample is washed with hydrogen peroxide as shown in Figure 3.

The signal around $g = 2.000$ can be due to the quartz as it was also proposed by Bayer et al. (2000) [9] when studying soil physical fractions (oxisol) and identifying the organic signal due to the semiquinone radical and a signal in g=2.000. S. Botis (2005) [10] employing the EPR data reveal the presence of six paramagnetic defects: one oxygen vacancy center (E1), three silicon vacancy hole centers $\left[O_2^{3-}/H^-(I).O_2^{3-}/H^+(II).O_2^{3-}/M^+\right]$ and two O_2^- peroxy centers, in the Athabasca quartz.

Figure 4 shows the XRD of retorted shale (RS) identifying the quartz as principal mineral, in accordance with the most intense peak and others, all indicated with *hkl* indexes [11], such result was also presented by Pimental et al. (2006) [12]. In this analysis was possible to verify three more intense diffraction peaks associated with the kaolin group and three more intense diffraction peaks associated with pyrite, all indicated with label and hkl indexes [11]. The signal in the region $g = 2.000$ is (using the Cr^{3+} pattern) 2.00043 which can be due to the unpaired electron in a vacancy of oxygen in which the electron occupies a silicon hybrid orbital sp^3 which is linked to three oxygen atoms in quartz sample as proposed by Botis S. (2005) [10].

FIG. 2: Signals in the $g = 2.003$ and 2.000 regions of samples CS, SF, RS: a) non-calcined; b) calcined at 200^0C; c) calcined at 400^0C. The signal disappears in the 2.000 region at 400^0C.

FIG. 3: Signals in the $g = 2.003$ and 2.000 region: a) non-treated; b) treated with H_2O_2. showing the appearance of signal in the 2.000 region for the RS sample.

the presence of another signal in $g = 2.00043$, in the samples
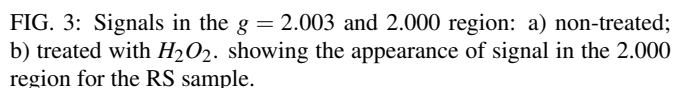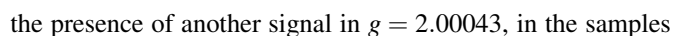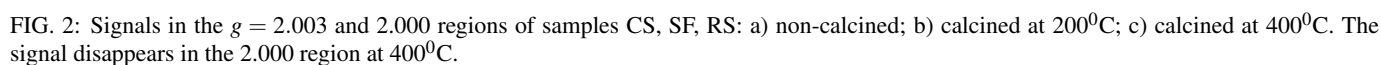

FIG. 4: XRD analysis of the non-calcined RS sample showing quartz as principal mineral and respective peaks indicated with *hkl* indexes, kaolin group (label: KG) and pyrite (PY) indicated with label and indexes *hkl*.

4. CONCLUSIONS

The spectra of EPR of the samples of CS, SF and RS showed the sign of Fe^{3+}, Mn^{2+} and organic free radical. It was identified one signal characteristic similar of organic radical with value in $g = 2.003$. The samples de CS and SF were observed non-calcined and calcined. Through washes with H_2O_2 the presence of the other signal in $g = 2.00043$ was observed in all the samples including XR and this signal is probably due to quartz (vacancy of Oxygen) in agreement with XRD analysis.

[1] http://www2.petrobras.com.br/minisite/refinarias/ petrosix/portugues/processo/index.asp acesso in 05-29-2008.

[2] A.S. Mangrich, L.C. Tessaro, A. Dos Anjos, F. Wypych, J.F. Soares Environmental Geology **40**, 1030 (2001).

[3] M.J. Adams, A. Waja, S. Bhargava, S. Grocott and M. Romeo Fuel **84**, 1991 (2005).

[4] J.J.F. Sousa, N.V. Vugman and C. Costa Neto. Organic Geochemistry **26**, 183 (1997).

[5] J.J.F. Sousa, L. M. Diehl, N. V. Vugman, M. V. A. Fonseca and C. Costa Neto Anais da Academia Brasileira de Ciências **66**, 13 (1994).

[6] C. P. POOLE Jr. Electron spin resonance: a comprehensive treatise on experimental techniques. New York, Wiley-Interscience, (1967) 921p.

[7] M.L. Simões, W.T.L. da Silva, S. C. Saab, L. M. Santos and L. Martin-Neto Revista Brasileira de Ciência do Solo **31**, 1319 (2007).

[8] A. Marchand and J. Conard Electron paramagnetic resonance in kerogen studies. In: B. Durant, ed. kerogen; insoluble organic matter from sedimentary rocks. Paris, Technip, (1980) 243p.

[9] C. Bayer, L. Martin-Neto, S. C. Saab and J. Mielniczuk Revista Brasileira de Ciência do Solo **24**, 11 (2000).

[10] S. Botis S. M. Nokhrin, Y. Pan, Y. Xu, T. Bonli and V. Sopuck The Canadian Mineralogist **43**;1565 (2005).

[11] G.W. Brindley and G. Brown (eds.) Crystal Structures of Clay Minerals and Their X-ray Identification. London, Mineralogical Society, (1980) 495p.

[12] P.M. Pimentel, C. N. Silva Jr, D. M. A. Melo, G. Maldonado and D. M. Henrique Cerâmica **52**, 194 (2006).