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STUDY OF THE PETROLOGY OF THE SHALE ROCK FROM THE PARANA BASIN

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ABSTRACT

In the present work, the characteristics of shale rock, collected in the surrounds of Limeira, in the interior of São Paulo, were studied. Shales are rocks formed by the consolidation of layers of clay, silt or mud, and are composed of minerals derived from mechanical abrasion materials, weathering final product and chemical and/or biochemical additions [1]. Shales are mostly fine granules, susceptible to the mineralogical rearrangement, and their chemical composition is quite varied due to the geomorphology and the tectonism undergone by the sedimentary basins. They are impermeable structures, formed by the consolidation of layered clay with thin laminations. Because of these characteristics presented, together with the decline of petroleum production, a growing interest in the better understanding and knowledge of the physical-chemical properties of the interior of shale rocks has been demonstrated. In this work, different methodologies were used to characterize them, using the Gamma Ray Computed Industrial Tomography technique along with other complementary procedures, such as Scanning Electron Microscopy (SEM), X-Ray Fluorescence and X-Ray Diffraction. Several characteristics have been studied, such as the analysis of the particle morphology, the contrasts and distributions of these particles in the internal structure of the rock, identification of the types of elements present (quantitative analysis), as well as establishing a proportion in which each element is present in the mineral through its crystalline structure and obtaining images of the rock internal structure.

1. INTRODUCTION

In the current world scenario, where there is a growing demand for energy resources, due to an accelerated development of technology and means of production, one of the main raw materials that drive this cycle is oil, but in a few years, the conventional procedures for production will no longer be able to correspond to that increase. For this reason, the study and exploration of non-conventional alternatives become necessary. It is at this point that shale reservoirs are on the agenda because they are rocks that have a great exploration potential, even with some countries already making use of this method.

Shales are one of the most abundant sedimentary rocks found in sedimentary basins. Brazil is classified by the IEA (International Energy Agency) as the 10th shale reserve in the world, behind countries such as China, the United States and Argentina [2]. These rocks are formed by the consolidation of silt, mud or clay, having a granulation that varies from thin to very thin, with impermeable layers with their structures originated from rocks exposed to erosion and weathering. Their chemical composition is quite varied according to the geomorphology of the places where they have been formed, however, even when this variation is present, shales are rocks rich in organic matter, when compared to rocks of other types, and they may be a great source of hydrocarbons (HC) [3]. Thus, the study and the exploitation of this resource end up being of great economic interest for the countries.

The deposits of known shales vary from the Cambrian to the Tertiary period and may be found in several depositional environments such as marshes, marine basins, freshwater lakes, saline lakes, as well as in coastal zones. These deposits may contain little organic matter, being of low economic value and without much interest in their study, or they may contain enormous amounts, attracting attention to their exploitation, which becomes very attractive [4].

Although there are other sources of cheaper energy and a greater focus on investment in other areas, such as mining, shales may represent a very important resource because, according to studies in some countries, standing out among them Germany, China, Israel, Estonia and even Brazil, showing that besides oil and gas, it is possible to obtain other resources from these reservoirs such as electricity, heat, cement, chemicals and others, all of them reasonably priced, allowing competitiveness in the market, in addition to an increase in the generation of jobs in various sectors [5]. Both the internal structure and the composition of shales are already known when referring to sealing rocks or trying to maintain the stability of wells drilled in these structures. Nevertheless, little or almost nothing is known when it comes to the shales presented as reservoir rocks, taking into account that the techniques used in conventional reservoirs cannot be simply transferred to the shales because of the greater complexity in their properties.

The reservoir rocks are those that have good porosity and permeability, propitious to the accumulation and production of oil, gas and/or water, depending on the interest, whereas these fluids are among the grains of the rocks. Therefore, a greater and better knowledge of the physical properties of these rocks, such as the filling of fluids in their pores, their stratigraphy and their internal geometry are necessary, having a fundamental role in increasing the recovery factor in the extraction of hydrocarbons. There is already a great deal of information about rocks such as sandstones and carbonates, which are the most common types of reservoirs. However, in addition to these common types, unconventional reservoirs such as bituminous shales are also found. Because of this, the more information is collected, the more tools the engineers and others involved will have to improve their work. With this information in hand, there may be an optimization in the extraction of the desired material, as previously mentioned, besides a reduction in the time of the operations and the final costs involved.

The shale samples analyzed in this work were collected from the surrounds of Limeira, in the countryside of São Paulo. Because they are rocks that have impermeable structures, formed by the consolidation of clay in layers with thin laminations, being different from the structures usually explored, a more detailed characterization is necessary. For the analysis, Gamma Ray Computed Industrial Tomography technique was used, in conjunction with other complementary techniques, such as Scanning Electron Microscopy (SEM), X-ray Fluorescence and X-ray Diffraction.

The Scanning Electron Microscope (SEM) is an instrument widely used to perform the microstructural analysis of several types of solid materials since it has very high resolution. With its use, the morphology, topography and elemental chemical composition of the rocks were evaluated, with the possibility to observe the homogeneity and structural quality in a magnification scale of 10-20,000X [6]. X-ray diffraction has been developed and used to study all the states of matter, from nanometric particles to powder and solids, allowing a characterization of the crystalline structure of materials, being very useful for a more detailed description of the shales structure. Thus, data have been obtained allowing the analysis of the rocks chemical composition, their crystalline structure as already mentioned, the size and thickness of the crystals and the arrangement of the layers [7]. X-ray fluorescence is an analytical technique with which it is possible to identify elements present in the samples. It is, also, possible to establish the concentration in which each element is present (qualitative and quantitative analysis) [8].

Gamma ray industrial computer tomography may be considered a technological innovation in the analysis of these samples, since it permits to overcome the limitations of geophysical and micro-tomographic techniques, as the samples do not need to be processed. It is a non-destructive technique for measuring rocks of different dimensions and formats. With this technique it is possible to visualize the porosity and its distributions in the rock, the inter connectivity between the pores, the permeability, the density and the structural textural properties [9].

2. MATERIALS AND METHODS

The samples of the shale rock studied in this work have hydrocarbons in their empty spaces and were taken from Limeira city, in the countryside of São Paulo. Specific petrographics hammers and sledge hammers were used for field work on outcrops (surface exposed rocks). Analyzes were performed using X-ray diffraction (XRD) with and without the use of dispersive energy spectroscopy (DES), X-ray fluorescence, scanning electron microscopy (SEM) and Gamma ray industrial computer tomography.

2.1. Sample preparation

For the preparation of the sample used, small fragments of the rock were used as well as a quantity of it pulverized. For the Fluorescence technique, 9g of powdered shale were used, mixed with 1g of micro crystalline wax and, then, pressed into tablet form in a matrix of 36 mm of diameter to be analyzed in semi-quantitative form in the equipment. In the case of the Electron Microscopy technique, the powder samples were dispersed on a carbon adhesive and also covered with carbon to be inserted in the equipment. For the X-ray diffraction technique, the samples were only placed in powder form, in glass sample pot and then placed in the equipment. And lastly, for the tomography technique it was not necessary to perform any previous preparation, the only necessary measure was to adjust the sample so that the whole structure was in the path of the radiation beam, not to lose any "edge".

2.2. Scanning Electron Microscope (SEM)

In order to evaluate the morphology, topography and elemental chemical composition of the shale, a scanning electron microscope was used to observe the homogeneity and the structural quality with a high resolution (magnification of 10-20,000X), presenting a scale with order values of 2 to 5 nanometers (20 - 50 A°) in commercial instruments and it may be obtained measurements up to 1 nanometer (10 A°) if advanced research instruments are used. The principle of a scanning electron microscope (SEM) consists of the use of a beam of small-diameter electrons to be incident on the surface of the sample for the production of electrons and photons, which may be collected by suitable detectors and, subsequently, converted into a signal of video. Later, this signal is transmitted to a cathode screen whose scanning is perfectly synchronized with that of the incident beam. In order to be detected, the electromagnetic rays resulting from this interaction between the beam and the sample have to be returned to the detector, their results being influenced by the intensity of the energy that the particles are incident on the detector or being captured by the detector. Most of these instruments used, as source of electrons, a heated tungsten (W) filament, operating in a range of 1 to 50 kV acceleration voltages. The great advantage of SEM in relation to other types of microscopes is the possibility of combining a microstructural analysis with a chemical microanalysis, as well as the possibility of generating images with a large focus, with a three-dimensional appearance [6, 10]. It was, also, used the dispersive energy spectroscopy (EDS) analysis, which is a very important tool of the SEM, since it allows the characterization of metallic and semiconductor materials, identifying the composition of the sample, even if qualitatively, in specific points of the image. In this study, the equipment used for analyzes was the Scanning Electron Microscope, brand LX-30 of Philips and the measurements were made in the CCTM of IPEN/CNEN-SP.

2.3. X-ray Fluorescence

The X-ray fluorescence technique is very useful for the detection and quantification of heavy metals, based on the measurement of the characteristic X-ray intensities that are emitted by the chemical elements contained in the sample. The mode of operation of this technique consists in the use of a source of controlled excitation, in order to cause an increase in the agitation of the molecules of the atoms present in the analyzed substances, obtaining a fluorescence emission spectrum characteristic of the chemical element present in the sample. The source used may be alpha or gamma particles from radioactive sources or even a bundle of charged particles from accelerators or x-ray tubes. After the molecules are excited, the atom absorbs a large amount of energy and moves to an unstable state, causing its electrons to transition between the energetic layers (layer L and M for layer K, layer M and N for layer L and/or in outer layers). Due to these movements between the layers, characteristic spectra of the elements are emitted and may be measured qualitatively and quantitatively [8, 11]. The X-ray Fluorescence equipment used to carry out the measurements was the EDX-900HS model, from SHIMADZU brand.

2.4. X-ray Diffraction

X-ray diffraction is a rapid analysis technique mostly often used to identify the crystalline phase of the rock. The equipment used, the diffractometer, consists of three basic elements: an X-ray emitting tube, an X-ray detector and a holder for the sample to be placed. For the execution of the technique, the sample of interest is placed in the support where it will be bombarded by fast electron beams. A cathode ray emitting tube will emit X-rays that will heat a filament; electrons are produced and, then, accelerated toward the target of interest. When the emitted electrons reach enough energy to remove the electrons present in the target material, electronic transitions will start in the energetic layers of the sample and a single-layer electron will be pulled out; when it is filled again, there will be emission of radiation with a length of the characteristic wave of this transition (diffracted rays). As the sample and the detector are rotated, the intensity of the reflected X-rays is recorded, being the ratio between the angle that the electrons were bombarded and collected the most important component of the diffraction. When the geometry of the incident X-rays contemplates the Bragg Equation ($n\lambda = 2d \sin \theta$), there is a constructive interference and a peak of intensity is generated. This signal is collected and processed by a detector that sends it to equipment where it may be seen or printed. The instrument that is used to hold the angle and rotate the sample is called a goniometer; this sample rotates in the path of the X-ray beam at an angle θ, while the detector rotates at an angle of 2θ [7, 12]. The X-ray diffraction equipment used to carry out measurements was the Bruker D8 Advance 3kW diffractometer, equipped with a copper radiation tube, 250mm goniometer, a graphite monochromator and a scintillation detector.

2.5. Industrial Gamma Ray Computed Tomography

Computed tomography consists of the transmission of gamma rays through a heterogeneous medium accompanied by attenuation, which will provide the integral measure of the mass distribution line through the path traveled by the beam. The measurement of several beams with different orientations, both spatial and angular in relation to the studied volume, followed by an image reconstruction process, provides the density distribution of the phases with a high degree of spatial resolution [13]. With this technique it is possible to generate images that are not influenced by the internal structure, being able to obtain detailed information of the internal structure of the object of interest with high precision and accuracy. The set consists of a source that is the radiation emitter, the sample used, which in the case of this work will be the shale, and a set of eight 12.5mm diameter x 50mm thick NaI (TI) detectors, positioned diametrically opposite to the tungsten source port, and which may contain one or more radioactive sources of different energies. The detector and source assembly will rotate 360º, making measurements every 0.79º (1 step), to obtain an accurate image of the entire sample. The main factors that should be considered in the use of this technique is (a) the choice of the appropriate radioactive source for the penetration of the studied object, being it possible to be mono-energetic or multi-energetic and (b) the time the sample will be exposed, since the larger the time, the better the image will be. The tomograph used was developed and belongs to the Center for Radiation Technology (CTR), IPEN/CNEN-SP [9].

3. RESULTS AND DISCUSSION

By X-ray fluorescence, it was possible to analyze the composition of the elements present in the sample. In the case of shale, the elements determined by the technique are presented in Table 1 through their oxides. As it may be observed, the main elements that constitute this sample (concentration> 1%) are SiO_2 (22.4%) and other elements, such as Fe2O3 (5.9%), MgO (5.6%) and CaO 6%), with very close concentrations. Also, elements with lower concentrations, called trace elements (concentration <1%), such as Na_2O (0.3%), SrO (0.2%), P_2O_5 (01%) and BaO (0,1%) have appeared.

Table 1: Concentration of the elements present in the shale through the fluorescence method.

Z	ELEMENTO	ÓXIDO	CONCENTRAÇÃO
14	Silicon	SiO_2	22,4%
26	Iron	Fe_2O_3	5,9%
12	Magnesium	MgO	5,6%
20	Calcium	CaO	4,6%
13	Aluminium	Al_2O_3	2,6%
16	Sulphur	SO_3	1,2%
19	Potassium	K_2O	1,1%
11	Sodium	Na_2O	0,3%
22	Titanium	TiO_2	0,3%
38	Strontium	SrO	0,2%
15	Phosphorus	P_2O_5	0,1%
25	Manganese	MnO	0,1%
56	Barium	BaO	0,1%

In the diffractogram of the shale sample shown in Figure 1, several intensity peaks could be observed, however, three of these peaks stand out with higher values. Figures 2 and 3 shows a diffractogram with standard peak elements existing in the EVA software database, serving as a parameter to identify the elements present in the sample. From the analysis of these diffractograms, specifically in larger intensity peaks, it may be proposed that the element presenting a greater concentration is the quartz, shown with a red circle in Figure 1, in order to highlight it from the others. At smaller peaks, it is possible to note the presence of pyrite (FeS2) with the blue line, and some silicates as calcium silicate (Ca_2SiO_4) (shown as a green circle on Figure 1) plus potassium, magnesium and aluminum silicate with the light and dark green lines, respectively, shown in Figures 2 and 3, compared with Figure 1. From the results of the X-ray fluorescence and those of the X-ray diffraction, it may be stated that both present similar results as to the chemical composition present in the sample.

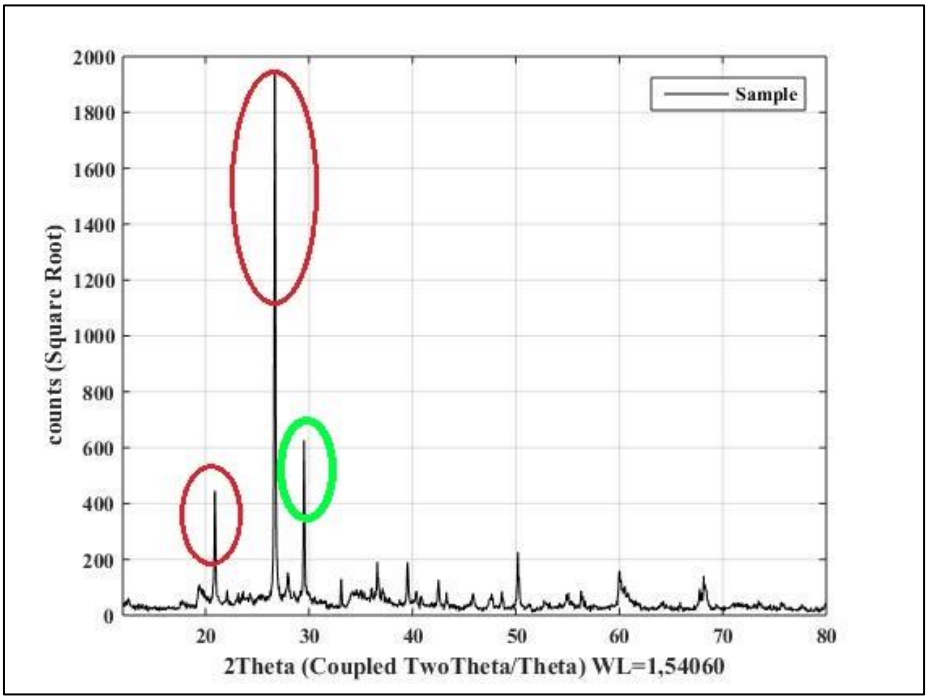


Figure 1: Diffractogram of the shale sample.

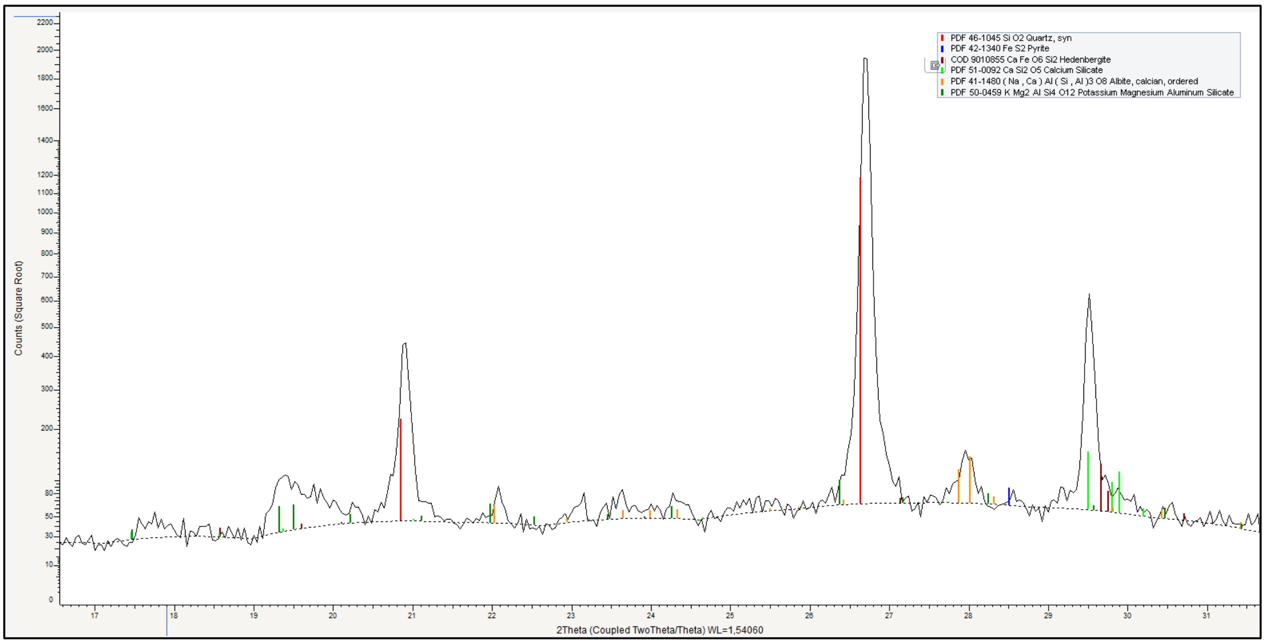


Figure 2: Diffractogram with the patterns of elements and the peak of the coupled shale (black line).

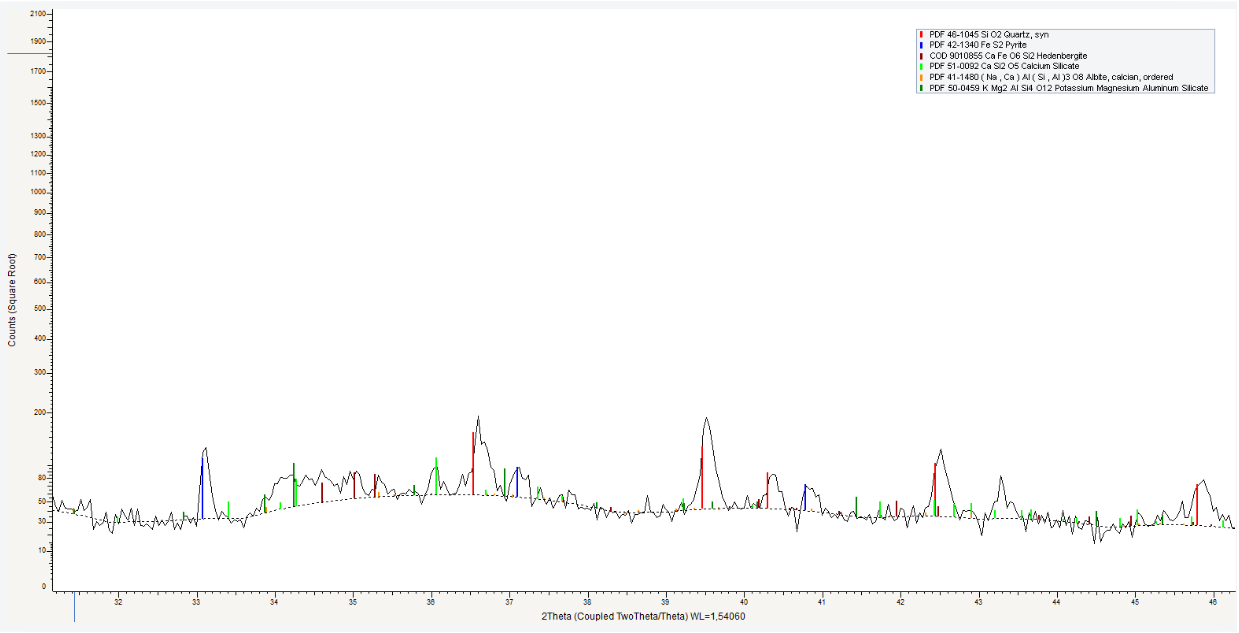
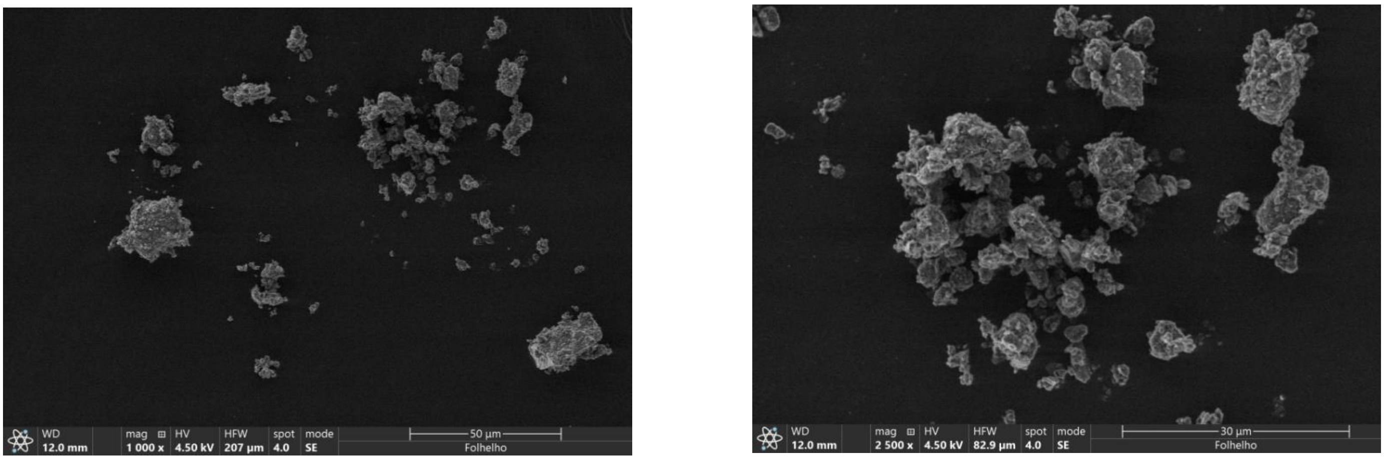


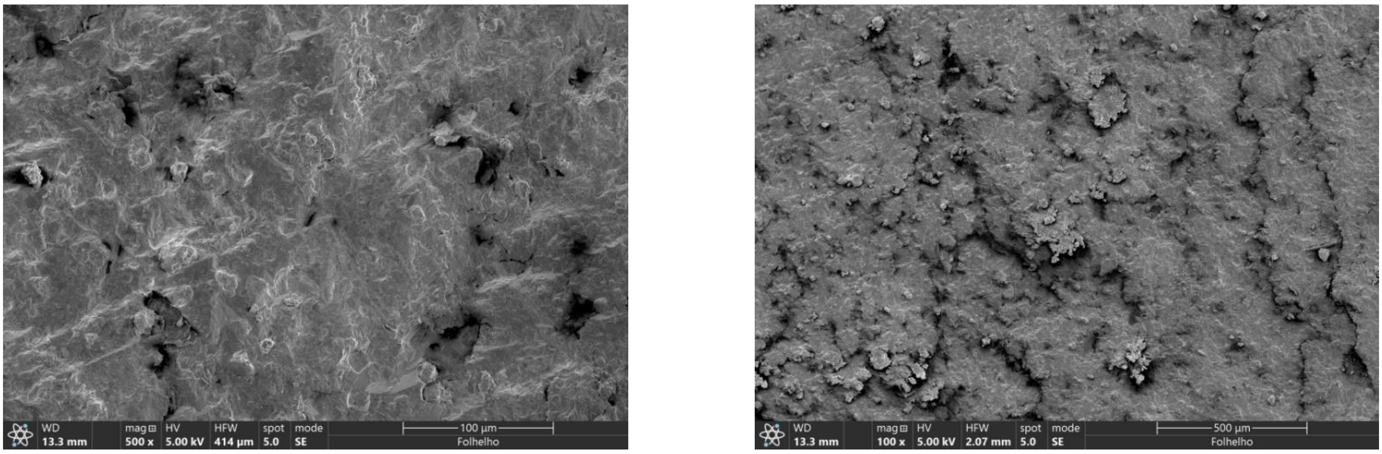
Figure 3: Diffractogram with the patterns of elements and the peak of the coupled shale (black line).

In the images obtained by the scanning electron microscope, it was possible to observe that the sample is composed of a fine granulation, characteristic of the shales, with grains dispersed as it may be seen in Figure 4, increasing in 1000x its normal size and Figure 5, increasing 2500x, apparently not presenting cementation, thus, being able to present a quantity of void spaces that confer to this rock the condition to store hydrocarbons. From these images it is, also, possible to notice that the structure of the grains does not follow a defined pattern, with grains of several formats (sub-angular, rounded, sub-rounded).



Figures 4 and 5: Shale structure images increased by 1000x and 2500x.

The images increased 500x (Figure 6) and increased 100x (Figure 7) are showing the surface of a grain present in the sample. As it may be seen, the images present two colors in highlights, one with a lighter tone and the other with a darker tone. This signal contrast may be an indication of different compositions, with light areas with high atomic number indication and dark areas indicating materials with low atomic numbers. In this case, the clear area is the rock matrix, as seen in the other techniques, composed mainly of SiO_2 and the dark part being hydrocarbon.



Figures 6 and 7: Enlarged images of the structure of a grain present in the sample.

Using the dispersive energy spectroscopy tool, which image is shown in Figure 8, it was possible to identify, in the sample, the presence of silicon elements (yellow color), in greater quantity and the elements calcium and magnesium (green and blue color, respectively) as previously measured by X-ray fluorescence and X-ray diffraction techniques. It is, also, possible to notice a dark color in the image, where there is a porous zone, containing or it may contain hydrocarbon.

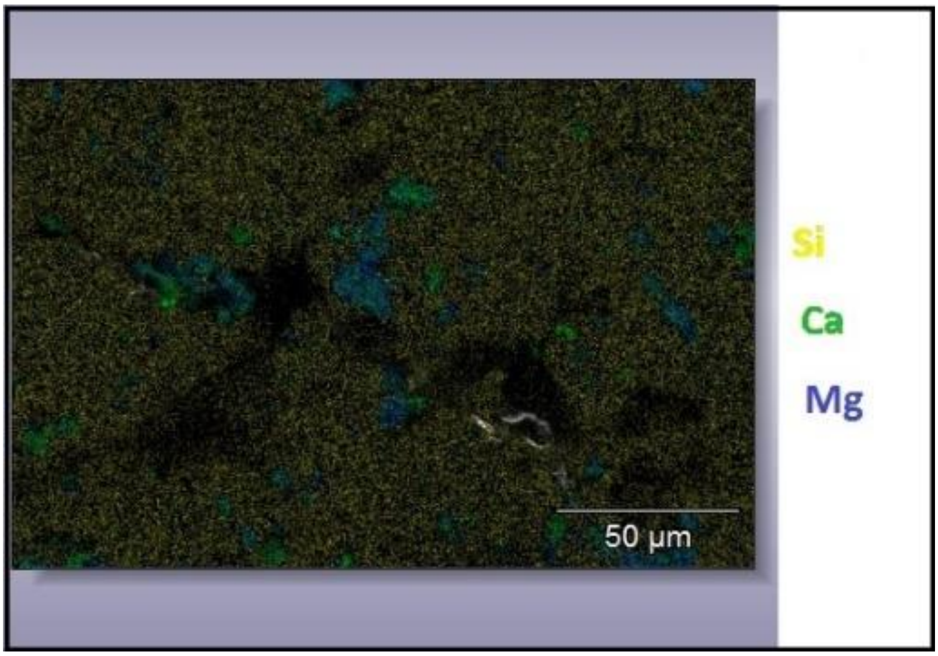


Figure 8: Dispersive energy spectroscopy (DES) map performed on a sample grain.

From the analysis of the results obtained by the gamma ray computed tomography, presented in Figure 9, it may be stated that the rock has a denser and consolidated matrix, having pink hue in the image, composed by silica (Si), the main element that constitutes the sample. There is a small amount of red dots positioned on its surface, and from the scale shown in the image, it could be confirmed that it is an element with a high density value, in this case, iron (Fe). It is also possible to notice the presence of other elements with different densities, represented by the dark blue color; these elements may be calcium (Ca) and magnesium (Mg), which have similar density values, but lower than Si and Fe. All these elements were verified and confirmed by comparison with other auxiliary identification techniques presented above. Finally, it is possible to see some well-spread and poorly connected pores (water-green color), having some material inside, with lower densities, thus it is possible to state that this substance is hydrocarbon.

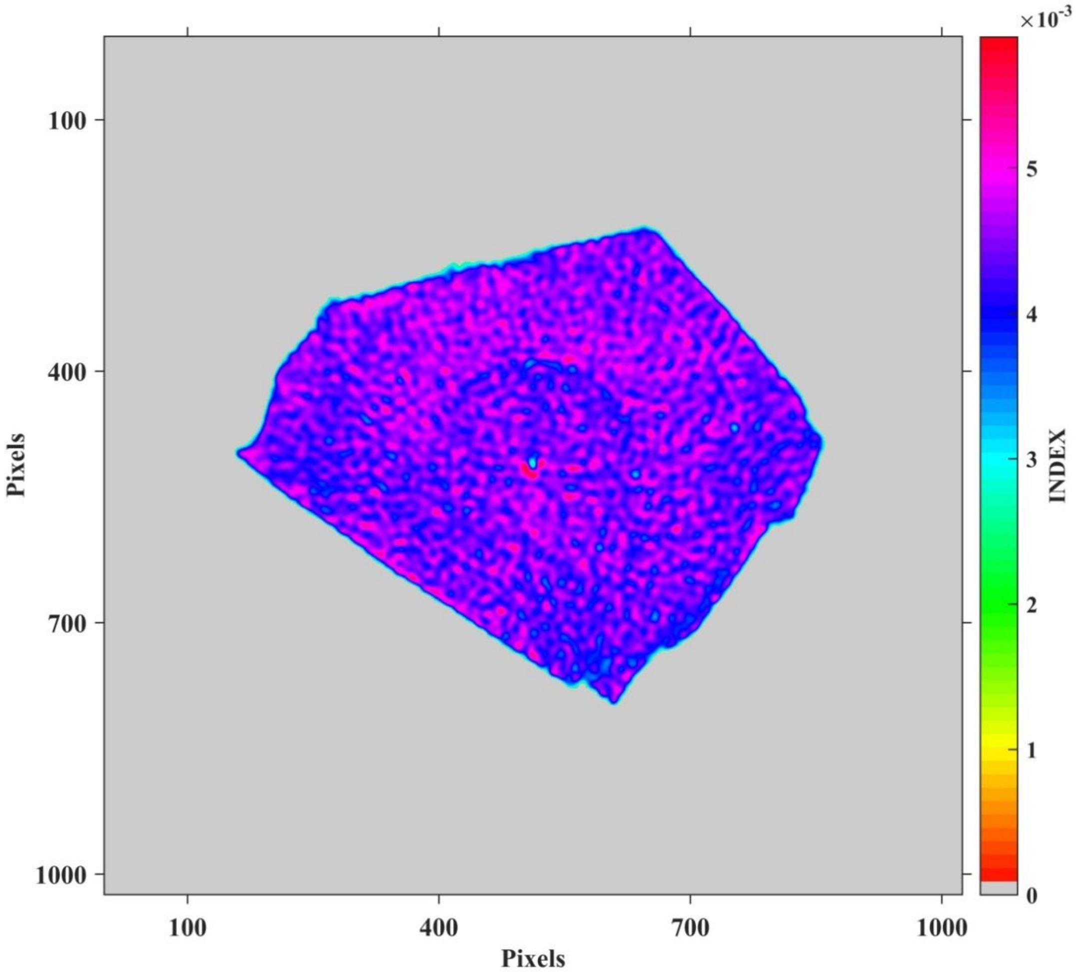


Figure 9: Image generated by the tomography showing the constituent elements of the sample surface through the density difference among them.

4. CONCLUSIONS

From the diffraction analysis it was possible to conclude that the main components of this shale sample are Silica (Si), with very high diffraction peaks, followed by other elements such as iron, magnesium and calcium, but in smaller amounts. The presence of all these elements could be confirmed by the results obtained by the fluorescence method, which determined that the present silica value is approximately 22.4%, while as to the other elements is between 4% and 6%. Also, dispersive energy spectroscopy technique corroborated the results of these elements in the shale sample. These auxiliary techniques proved to be effective as complementary methods in the interpretation of the image generated by the gamma ray industrial tomograph, allowing the differences in structures to be inferred with greater accuracy.

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