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STUDY OF THE RELATIONSHIP BETWEEN THE MINERALOGICAL COMPOSITION AND THE DISINTEGRATION OF SHALES FROM PARAÍBA AND CEARÁ STATES OF BRAZIL

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Abstract. *The problem of instability of wells in shale formations has been a major concern for oil engineers since the beginning of oil well drilling. Shales present an instability behavior when drilled with aqueous fluids, which is often associated to their mineralogical composition; shales that have a higher amount of hydratable clay minerals tend to be unstable in the presence of water. In view of this, this work has as objective to relate the mineralogical composition of the shales with their disintegration. In order to do so, five samples of shales from the Rio do Peixe Basin, located in the State of Paraíba, were characterized. These samples were named as S1, S2, S3, S4 and S5. For comparison purposes, a clay sample of industrialized Bentonite Sodium, named as BS, was also characterized. The characterization was performed by methods of cation exchange capacity (CEC), particle size analysis by laser diffraction and X-ray diffraction (XRD). In addition, studies of disintegration, in the presence of deionized water, aqueous solution of potassium citrate (salt employed as a swell inhibitor of aqueous drilling fluids), and drilling fluid, were performed following API (American Petroleum Institute) standards. The results suggest that the phenomenon of disintegration is manifested in the presence or absence of reactive clay minerals. Moreover, the results obtained showed that the disintegration behavior does not present direct relation to the content of clay fraction. And, finally, it can be concluded that, the samples of shales studied showed considerable disintegration when in the presence of deionized water. However, this disintegration is widely reduced in the presence of potassium citrate salt or aqueous drilling fluids inhibited with the potassium citrate salt.*

Keywords: *shales, instability, disitegration, characterization*

1. INTRODUCTION

In the process of oil well drilling different subsurface rock layers are destroyed by the rotation and weight on bit, which is located at the end of a drill string. The drilling fluid, also called mud, continuously remove the rock fragments generated by this process. The drilling fluid is injected into the drill string and returns through the annular space formed by the wellbore walls and the drill string (Thomas, 2001).

The rocks most commonly found in oil well drilling are shales, sedimentary rocks of fine granulometry formed by quartz, silicates, carbonates and clay. The clay content makes the rock shales reactive to water-based fluids. (Nmegbu and Ohazuruike, 2014; Boul, et al., 2017).

When in contact with water, the clay fraction minerals - or clay minerals - tend to swell (increase the space between layers) following basically two mechanisms: crystalline swelling and osmotic swelling. The first is related to surface hydration (adsorption of water molecules) and can occur in all types of clay minerals, being characterized by the low increase in interlamellar space (ranging from 9 Å to 20 Å). The second occurs only in some types of clay minerals that exhibit large increases in interlamellar space (ranging from 20 Å to 130 Å) (Medjimurec and Pasic, 2013).

The stability or integrity of oil wells using oil or synthetic base fluids can be easily achieved. However, for aqueous-based fluids, which are environmentally less impacting, shale stability is strongly affected by the physical-chemical interaction between the drilling fluid and the fluids in the rock pores. Usually, the chemical properties of the water phase of the drilling fluid are different from those found in the fluids of the drilled rock (Asef and Farrokhouz, 2013).

In the case of shales, these interactions are associated with the movement of water and ions from the well to formation or from the formation to the well, which result, respectively, in hydration and dehydration processes of the clay minerals (Medjimurec and Pasic, 2013).

Disintegration is one of the possible problems of instability of shales during drilling with aqueous based fluids. Besides this, the shales can experience a tendency to form caves, swelling of the formation, among others (Wilson and Wilson, 2014; van Oort et al., 1996).

Badger et al. (1956) studied the disintegration of shales immersed in water and concluded that the degree of disintegration of the samples is a function of the type of clay, the properties of the fluid used in the immersion, as well as the fluid capacity of penetrating the rock and accessing the rocks.

The most important consequence of well instability is non-productive time (NPT) and additional unexpected costs. The oil industry spends more than a billion dollars annually to solve well instability problems (Tare et al., 2002; Zhang et al., 2004, Khodja et al., 2010, Asef and Farrokhrouz, 2013).

According to Boul *et. al*. (2017), the different types of clay minerals provide different levels of shale reactivity when in the presence of water. According to the authors, shale with high smectite content, presenting a high degree of swelling, will typically have a higher reactivity to water than shales with high content of ilite-type, which have no associated swelling.

Thus, from the point of view of well stability, it is therefore agreed that the nature of the clay mineral and its content in shale formations are the main factors that allow its instability. Therefore, the main mechanism for shale instability is the volume increase by osmotic swelling of smectites. However, shales with high concentrations of ilite and kaolinite may also have unstable behavior, as well as shales with predominant smectite clay contents may or may not have unstable behavior, showing that interlamellar swelling cannot be considered as the universal mechanism for swelling of shales (Wilson and Wilson, 2014).

2. OBJECTIVE

This work aims to relate the mineralogical composition of Brazilian shales from the Rio do Peixe and Araripe Basins to their disintegration.

3. METHODOLOGY AND MATERIALS

3.1 Materials

For the accomplishment of this research five samples of shales, identified in Table 1, and a sample of industrialized sodium bentonite clay, identified as SB, were studied.

Table 1. Nomenclature e location of shale samples

Sample	Nomenclature	Location
Shale 1	S1	Rio do Peixe Basin, Sousa - PB
Shale 2	S2	Rio do Peixe Basin, Sousa - PB
Shale 3	S3	Araripe Basin, Nova Olinda-CE
Shale 4	S4	Rio do Peixe Basin, Sousa - PB
Shale 5	S5	Rio do Peixe Basin, Sousa - PB

3.2 Procedure

3.2.1 Cation Exchange Capacity (CEC) and Specific Area (SA)

The determination of cation exchange capacity (CEC) and specific area was performed using the methylene blue adsorption test. For this technique, initially 0.5g of the shale sample, milled and sieved in ABNT No. 200 sieve, is slowly mixed with 300mL of deionized water under constant shaking. The pH meter was then contacted with the suspension formed, and 1N solution of Na_2CO_3 was added dropwise to pH 9.0. Then, 1N HCl was added dropwise until reach 3.5 pH. After the pH stabilization at 3.5, 2mL of aqueous methylene blue solution (3.7g / L) was added to the mixture and after 5 minutes a drop of the mixture was placed on filter paper using a stick. When a very intense bluish circular crown was formed on the filter paper, it was another 15 minutes to drip another drop to confirm the circular crown, closing the test. Otherwise, 2mL of methylene blue was added and after 5 minutes another drop was dripped onto the filter paper until the previously described phenomenon occurred.

With the total volume of methylene blue (V) used to form the very intense bluish circular crown, the molar concentration (C) of 3.7 g / L and the sample mass (m) of 0.5 g, the cation exchange capacity (CEC) and the specific area (SA) are calculated, using Equations 1 and 2, described below (Chen *et al*., 1974).

$$CEC = \frac{C.V.100g}{m} = \left(\frac{meq\ of\ blue\ methylene}{100g\ of\ dry\ clay}\right) \tag{1}$$

$$SA = CEC\ \times 7{,}8043\ \left(\frac{m^2}{g}\right) \tag{2}$$

3.2.2 Granulometric analysis by laser diffraction

The granulometric analysis by laser diffraction uses the method of dispersion of particles in liquid phase associated with an optical measurement through laser diffraction. In this method, the proportional relationship between the laser diffraction and the concentration and particle size is combined. To carry out this characterization, the samples were sieved in ABNT No. 200 (0.074mm) sieve, and dispersed in 250mL of distilled water on a Hamilton Beach shaker at a speed of 17,000 rpm for 10 minutes. These dispersions were then placed in the equipment CILAS model 1064, using the wet function, until reaching the ideal concentration, which is 150 diffraction units / incidence area.

The analyzes were carried out in the Material Characterization Laboratory of the Materials Engineering Academic Unit, at the Science and Technology Center of the Federal University of Campina Grande.

3.2.3 X Ray Diffraction

For the identification of mineralogical constituents of the samples through a qualitative study, the X-ray diffraction technique (XRD) was used. X-ray diffraction (XRD) is a widely used method for the characterization of crystalline structures, so it is a very useful method for the qualitative identification of some components in the shales to be studied in this work.

The analyzes of X-ray diffraction (XRD) of the samples, in the samples dried and treated with ethylene glycol, were performed on a SHIMADZU X-ray diffraction equipment, model XRD-6000 operating with copper k-alpha radiation, with a voltage of 40kV and 30mA current and wavelength $\lambda = 1.5406$Å. The samples were analyzed with scanning between 2θ (3 °) and 2θ (70 °), the speed of the goniometer was 2 ° / minute.

The tests were carried out in the Material Engineering Characterization Laboratory of the Science and Technology Center - CCT of the Federal University of Campina Grande.

3.2.4 Disintegration

The disintegration test was developed by the oil industry in order to simulate the impacts of cuttings (shale fragments) on the drill string. These impacts promote the disintegration of the fragments, known as dispersion. The equipment used to carry out the test was the Fann Roller Oven, model 704 ES, composed of cells of stainless steel with capacity for 400 mL. For the disintegration tests, the shale samples were milled and sieved between ABNT No. 4 and ABNT No. 8 sieves, apertures between 4.75 mm and 2.36 mm, respectively.

For the accomplishment of this research three aqueous systems were used: deionized water, aqueous solution of potassium citrate and drilling fluid. Tables 2 and 3 show the concentration of the additives for the aqueous solution of potassium citrate and for the drilling fluid, respectively. The basic formulation for the drilling fluids was obtained by Lucena (2014).

Table 2. Formulation for the aqueous solution of potassium citrate.

Additive	Function	Concentration (/350mL of water)
Potassium citrate	Swelling Inhibitor	20,0g

Table 3. Base formulation for drilling fluids.

Additive	Function	Concentration (/350mL of water)
Silicone based fluid	Defoamer	0,084g
Xanthan Gum	Viscosifier	1,5g
Low viscosity carboxymethyl cellulose	Filtrate Reducers	3,5g
Magnesium oxide	pH controller	1,0g
Potassium citrate	Swelling Inhibitor	20,0g
Tetrakis(hydroxymethyl) phosphonium	Bactericide	0,7g
Calcite	Sealant	15,0g

To this, 350 mL of a fluid was added to each cell of the Roller Oven, and then 20 g of the previously prepared sample (milled and sieved) was added. The rotation of the cells was maintained at 50 rpm at 150 ° F for 16 hours. Figure 1 shows the simplified scheme of disintegration assay in the rotary cell.

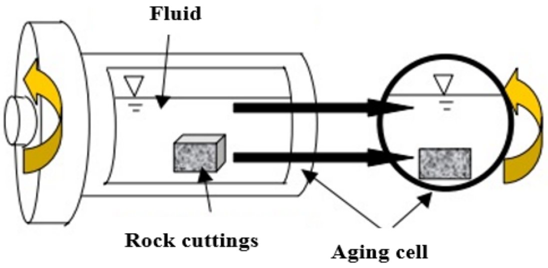

Figure 1: Simplified scheme of disintegration assay in the rotary cell. Source: Perez, 1997

After 16 hours, the samples were cooled to room temperature. Then the cell contents (fluid + shale) were carefully filtered on No. 200 ABNT sieve, with fresh water flow of approximately 2 L / min to promote sample washing. The shale with a particle size less than 0.074 mm was not retained in the sieve and was considered dispersed. The material retained followed into a greenhouse where it was subjected to a temperature of 140 °F for 24 hours. After 24 hours, the material was weighed in a high precision analytical balance. Equation 3 provides the disintegration of the sample tested.

$$D = \frac{(mi - mr) \times 100}{mi} \quad (3)$$

Where D is the disintegration or disintegration rate (%), mi is the initial mass of the sample and mr is the mass of shale retained in the sieve (API, 2009).

4. RESULTS AND DISCUSSION

4.1 Cation exchange capacity (CEC) and specific area (SA)

The cation exchange capacity of a clay mineral can be defined as the ability of clay to absorb cations in its molecular structure. Determination of this property for shale formations reflects their levels of reactivity with aqueous fluids.

The values of cation exchange capacity (CEC) and specific area (SA) for the shale samples analyzed and the reference values for different clay minerals, according to Souza Santos (1989), are presented, respectively, in Tables 4 and 5.

Table 4. Cation exchange capacity (CEC) and specific area (SA).

Sample	CEC (meq/100g of dry clay)	SA (m^2/g)
S1	23,1	180,3
S2	32,4	144,4
S3	41,6	324,7
S4	27,8	217,0
S5	27,8	217,0
SB	92,5	721,9

Table 5. Values of CEC and SA for the main clay minerals.

Clay mineral	CEC (meq/100g of dry clay)	SA (m^2/g)
Kaolinite	3-15	5-10
Illite	10-40	100-200
Vermiculite	100-150	300-500
Smectite	80-150	700-800

Based on Table 4, it can be seen that the results of cation exchange capacity for the shale samples were in the range of 23.1 and 41.6 meq / 100g of dry clay and for the sodium bentonite clay a capacity of cation exchange of 92.5 meq / 100 g of dry clay.

Comparing the results obtained in Table 4 with the typical values (Table 5), it can be inferred that, probably, the shale samples present considerable amount in their composition of the illite clay, while the clay that essentially composes the SB sample is the smectite.

Consequently, shale samples indicate a low reactivity potential, while the sodium bentonite clay sample has a higher capacity to absorb water and, consequently, higher rates of expansion.

With regard to SA, values for shales from 144.4 m² / g up to 324.7 m² / g and for the SB sample of 721.9 m² / g are observed. It is emphasized that the higher the SA, the greater the area for hydration and probable swelling.

4.2 Granulometric analysis by laser diffraction

Table 6 shows the average particle diameter (μm) of the samples under study, as well as the accumulated particle content (%) with a size of less than 2 μm, obtained from the particle size analysis data. Since, according to Souza Santos (1989), the clay fraction is in the size range of less than 2 μm, this accumulated content must provide the volume of clay fraction present in each sample.

Table 6: Average diameter and accumulated content particle with a size of less than 2 μm from the samples studied.

Sample	Average diameter (μm)	Accumulated content (%)
S1	7,02	34,40
S2	7,98	24,55
S3	6,52	16,56
S4	8,39	30,26
S5	11,23	20,33
SB	4,52	35,31

Based on Table 6, it can be seen that the average particle diameter of the S1 sample is 7.02 μm, the S2 sample is 7.98 μm, the S3 sample is 6.52 μm, the S4 sample is 8.39 μm, the S5 sample is 11.23 μm and, for the SB sample, the average diameter is 4.52 μm.

The highest accumulated particle content (Table 6) with a diameter smaller than 2μm is present in the SB sample, with 35.31% of the particle volume. The shale samples showed particle sizes smaller than 2μm ranging from 16.56% (S3) to 34.40% (S1).

4.3 X Ray diffraction

Figures 2 to 7 show the diffractograms of the samples studied. X-ray diffraction tests were performed on the samples in the absence and presence of ethylene glycol. For the samples in the presence of ethylene glycol, the EG symbol was added after their regular nomenclature. The symbols used in the graphs for the different minerals found in the samples are: E - Smectite Group; I - Illite; M-Mica; C - Kaolinite; Q - Quartz; F - Feldspar.

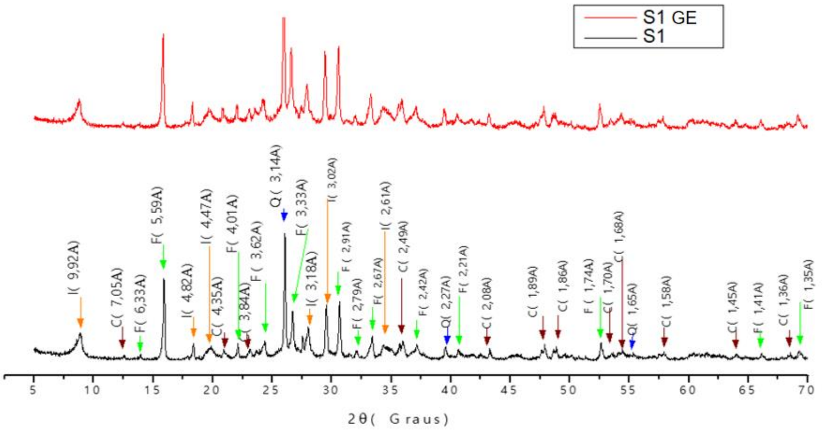

Figure 2: X-ray diffractogram for the S1 sample with and without ethylene glycol, respectively.

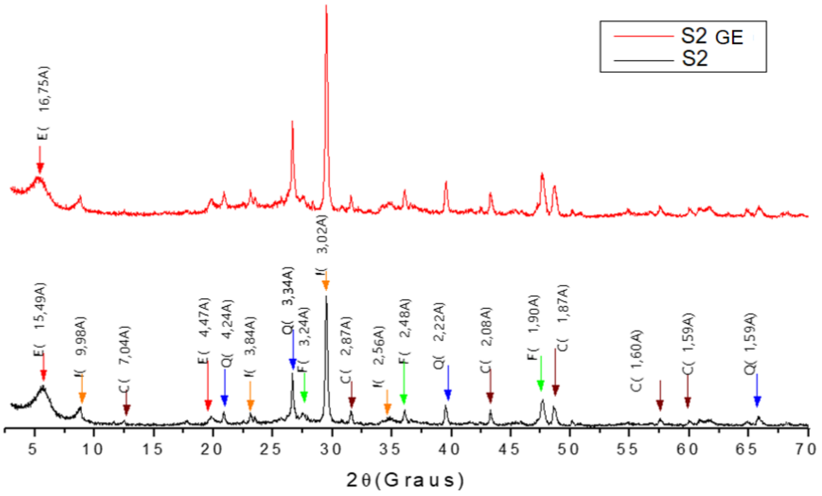

Figure 3: X-ray diffractogram for the S2 sample with and without ethylene glycol, respectively.

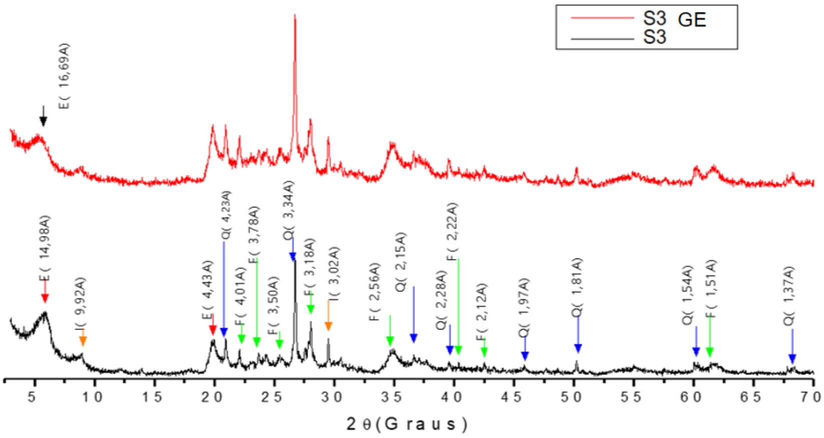

Figure 4: X-ray diffractogram for the S3 sample with and without ethylene glycol, respectively.

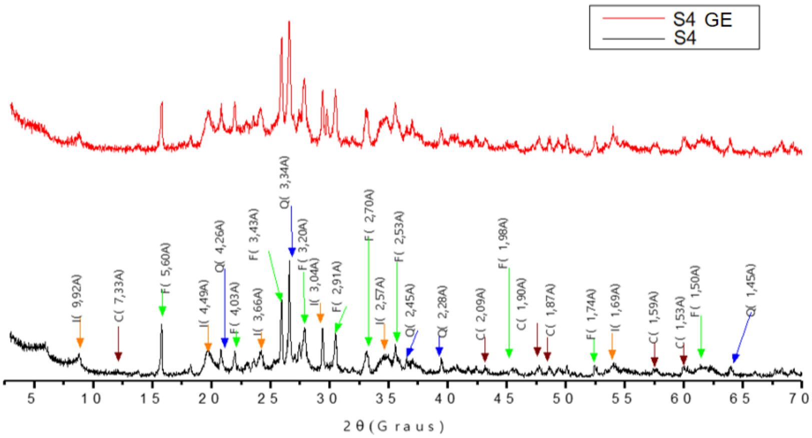

Figure 5: X-ray diffractogram for the S4 sample with and without ethylene glycol, respectively.

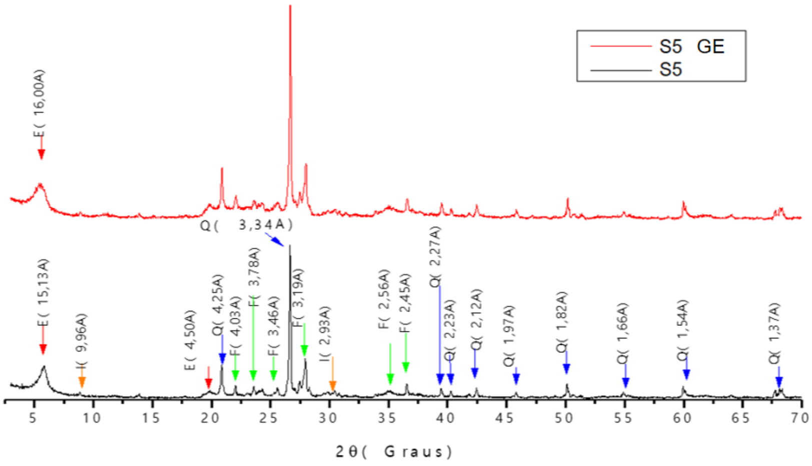

Figure 6: X-ray diffractogram for the S5 sample with and without ethylene glycol, respectively.

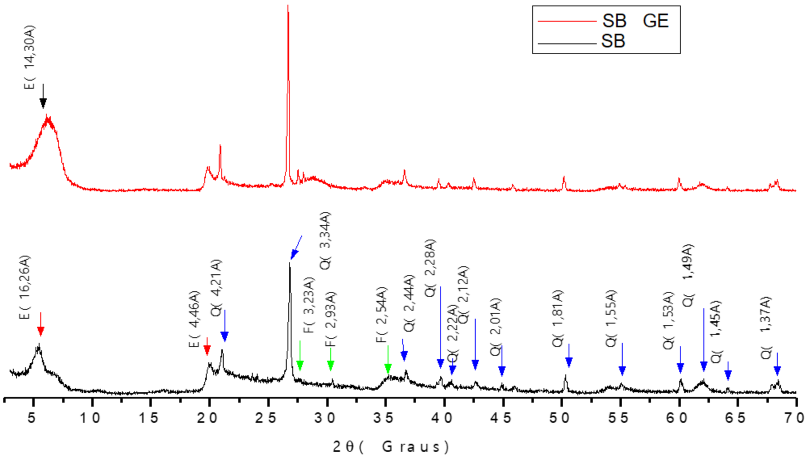

Figure 7: X-ray diffractogram for the SB sample with and without ethylene glycol, respectively.

According to the diffractograms presented in Figures 2 and 5, peaks that indicate the presence of illite and kaolinite in the shale samples S1 and S4 are observed, as well as the presence of feldspar and quartz in their composition. In the sample S2, the peaks observed indicate the presence of smectite, illite and kaolinite, in addition to the presence of quartz and feldspar in its composition (Figure 3). For samples S3 and S5 (Figures 4 and 6, respectively), the presence of the clay minerals of the smectite and illite group is verified, besides the presence of feldspar and quartz.

In this way, the diffractograms confirm the presence of the illite in all samples studied. For the shale samples, the XRD results together with the CEC and SA values show that the predominant clay mineral might be the illite. For the SB sample, the XRD results together with the CEC and SA values show that the predominant clay mineral is smectite.

4.4 Disintegration

Figure 8 shows the disintegration values for the shale samples (S1 to S5) and for the SB sample in different fluids.

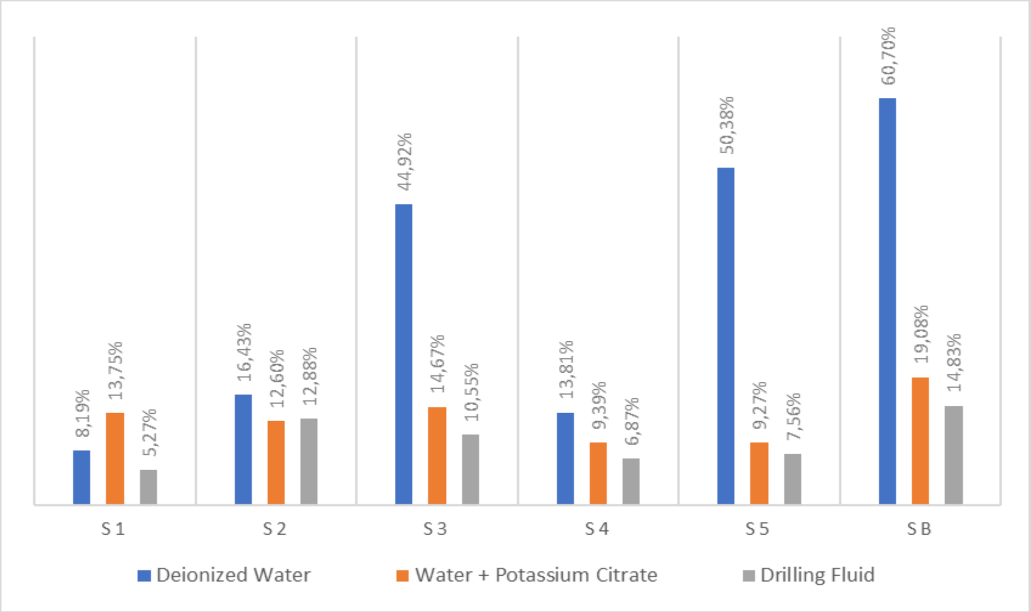

Figure 8: Disintegration of shale samples in different aqueous fluids.

The disintegration values shown in Figure 8 for the shale samples indicate that the percentage disintegrated in deionized water is, for most samples, higher than the disintegrated percentage measured in the other fluids. This behavior shows that, for the samples studied, the presence of potassium citrate reduced the disintegration potential of the samples studied.

In the other hand, when comparing the tests of cation exchange capacity (CEC) and specific area (SA), X-ray diffraction (XRD) and disintegration, the results suggest that the phenomenon of disintegration is manifested in the predominance or not of reactive clay minerals, but that their presence accentuates the phenomenon. The SB sample presented high values of CEC and SA and their disintegration measured in the presence of deionized water was, in a very significant way, the highest among the studied samples (63.7%). However, shale samples that presented low values of CEC and SA, obtained disintegrations varying between 8.19% and 50.38%, with the highest values of disintegration (16.43%, 44.92 and 50, 38%) found in the samples containing clay minerals from the smectite group (S2, S3 and S5, respectively).

It was possible to notice that, for the studied samples, the amount of clay fraction and the level of disintegration did not have directly related behavior. The SB sample, which presented the highest disintegration, has 35.31% of grains with grain size less than 2µm, higher grain content in this range among the studied samples. However, the shale samples S3 and S5, which presented the greatest disintegration among the shales, have, respectively, 16.56% and 20.33% of grains with particle size less than 2µm, while the shale samples S1 and S4, which showed low levels of disintegration, respectively, with 34,40% and 30,26% of grains with grain size less than 2µm, approximately equal to that found in sample SB.

Table 7 shows the effect of the inhibited fluids on the disintegration of the samples. Negative values reflect reduction in disintegration and positive values reflect increase in disintegration, when compared with values measured in deionized water.

Table 7: Effect of inhibited fluids on the disintegration.

Sample	Water + Potassium Citrate (%)	Drilling Fluid (%)
S1	+67,89%	-20,79%
S2	-23,41%	-21,58%
S3	-67,41%	-76,53%
S4	-31,88%	-50,36%
S5	-84,16%	-87,07%
SB	-70,02%	-76,69%

Based on Table 7, it can be seen that, for the samples studied, the swelling inhibitor (potassium citrate) proved to be efficient in inhibiting the disintegration of the sample. The highest reduction in disintegration occurred in sample S5 (87.07%) and the lowest in sample S1 (20.79%), both in drilling fluid.

The results show that the samples with the highest inhibition rates, both in the drilling fluid and in water with inhibitor (BS, S3 and S5), were those with the highest disintegration rates in deionized water. The same behavior occurs with the samples that obtained lower values of disintegration in deionized water (S2, S4), being also the samples with smaller reductions in the disintegration rate. The shale S1 presented an anomalous behavior, reduction in drilling fluid and increase in water with inhibitor, and it was not used for comparative purposes

5. CONCLUSION

The shale samples from the Rio do Peixe and Araripe basins can be considered as formations of low reactivity potential, while the bentonite sodium clay sample has high potential. In relation to the disintegration behavior, it was possible to conclude that the studied shales present considerable disintegration when in the presence of deionized water. However, its disintegration was considerably reduced when in the presence of the potassium citrate salt. The same was evidenced when the shale disintegration was measured in aqueous drilling fluids inhibited with the potassium citrate salt. In addition, it was concluded that inhibition of disintegration was more efficient in the samples with higher disintegration rates. Finally, the studies showed that, for the studied samples, the content of clay fraction and the disintegration of the shales do not have directly related behavior. For further studies, it is suggested to perform tests that show the amount of clay minerals present in the samples.

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