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Influence of morphology and surface charge on the suitability of palygorskite as drilling fluid

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ABSTRACT

This study investigates the influence of physical chemistry properties of three palygorskites from Brazil on the suitability of the dispersions for use as a component of drilling fluid. Characterization and technological tests have been carried out.

The analysis were done with X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), Thermo Gravimetric Analysis (TGA), Scanning Electronic Microscopy (SEM), Laser Particle Sizer and Electro Kinetic Sonic Amplitude (ESA). The samples were prepared as recommended by Petrobras' Normalization Standard (N-1967, 1984).

Both the morphology and surface charge of the particles have a major effect on the suitability as the drilling fluid. The dark São Pedro palygorskite sample showed the best suitability in both fresh and salt water. The dark and white São Pedro samples were classified as type 1 palygorskite and are of high yield. The Boa Vista sample was classified as medium yield.

1. Introduction

Palygorskite is a clay mineral that belongs to the hormite group, with the approximate formula:

$$R_5Si_8O_{20}(OH)_2(OH_2)_4.4H_2O$$

where *R* is mainly the Mg^{2+} cation, but can be partially substituted by Al^{3+}, Fe^{2+} or Fe^{3+} cations in the octahedral sheet (Souza Santos and Souza Santos, 1984).

The main properties of palygorskite are high specific surface area, usually, in the range of 125 m^2/g and 210 m^2/g), high adsorption capacity, considerable bleaching power, chemical inertness and ability to become thixotropic in the presence of electrolytes.

These properties make to palygorskite of great commercial interest for several industrial applications (Luz et al., 1988; Almeida, 1994; Oliveira, 2004). In the case of oil well drilling fluids, palygorskite is used as a thixotropic agent and viscosity controller, and could act as a inhibiting agent for circulation loss (Darley and Gray, 1988; Luz and Baltar, 2003).

The oil wells drilling fluids should include a thixotropic component. This is important because it allows the drilling "mud" to flow freely while remaining in suspension under movement, and assuming the form of a gel when under stationary conditions. The gel-like structure blocks the return of rock fragments to the bottom of the well. Bentonite is the most used clay for this purpose, since it presents excellent thixotropy in fresh water. However, when in contact with salts, bentonite tends to coagulate reducing its viscosity and losing its thixotropic properties. Palygorskite, in contrast, remains a viscous dispersion in the presence of dissolved salts (Baltar et al., 2003). It is thus used as a component of drilling fluids for wells drilled off shore or those that cross layers of soluble salts.

2. Experimental

2.1. Materials

2.1.1. Samples

This study was carried out with three samples of palygorskite originating from Boa Vista and São Pedro mines, in the state of Piauí, Brazil, which show the largest economical potential with reserves in the order of 20 million tons.

Two samples were collected at the São Pedro mine, named white and dark São Pedro. One sample was collected at the Boa Vista mine.

2.1.2. Equipment

The equipments used in the clay mineral analysis and characterization, were:

(1) Siemens — Bruker axs X-Ray Diffratomer D5000
(2) Bruker axs S4 — Explorer X-Ray Fluorescence
(3) Bruker maxs S4 — Explorer SEM,
(4) FRITSCH Model 14 Pulverizer
(5) Fann Instruments Hamilton Beach Shaker Model 936

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Table 1
Chemical composition of the palygorskite samples from Piauí, Brazil

Oxide	Samples (%)		
	White São Pedro	Dark São Pedro	Boa Vista
SiO_2	68.5	66.7	57.9
Al_2O_3	10.3	9.1	12.1
Fe_2O_3	4.0	3.7	7.2
MgO	5.6	7.4	4.9
CaO	0.17	0.17	0.10
K_2O	1.2	0.83	2.2
Na_2O	0.10	0.11	0.14
L.O.I.*	9.50	11.06	13.37

*L.O.I. — loss on ignition.

(6) Fann Instruments Viscosimeter Model 35-A
(7) Malvern Master Sizer 2000 Laser Diffractometer
(8) Matec Instruments ESA-9800 System Zeta Potential.

2.2. Procedure

The chemical composition of the palygorskite samples was determined by X-Ray Fluorescence (XRF) analysis. The mineralogical composition was determined by X-Ray Diffraction analysis (XRD), complemented by Thermo Gravimetric Analysis (TGA), Thermo differential Analysis (TDA), Infrared (IR) and Scanning Electron Microscopy (SEM) analysis. The measurement of the specific surface area was done by nitrogen adsorption at 77 K.

2.2.1. Sample preparation

The clay samples were submitted to a pre-hydration period of 24 h, using 2 L of distilled water per kg of sample. The material was then scrubbed at 1920 rpm for 1 h. For the scrubbing process, a 20% solid by weight pulp was used.

2.2.2. Granulometric size distribution

After scrubbing, the size distribution of the coarse fraction was measured by sieving, using 0.417, 0.208, 0.147, 0,074 mm sieves. The size distribution of the fine fraction was determined using the laser diffractometer.

2.2.3. Electrokinetic mobility

The influence of pH (2 to 9) on the electrokinetic mobility was investigated by the electro acoustic method.

2.2.4. Viscosity

The $<74\ \mu_m$ fraction of the palygorskite was heated to 100 °C, then disaggregated and homogenized. The pulp was stirred for 20 min and the viscosity was recorded at 600 rpm.

2.2.5. Dispersions in salt water

Type 1 — A saturated 400 g/L NaCl dispersion was prepared at first. The solution was filtered and 420 mL of it were introduced into the mixer, together 34.6 g of type I palygorskite. The mixer was maintained at low stirring speed for 20 min. After stirring, the dispersion was left at rest for 24 h at room temperature.

Type 2 — The same procedure used in the preparation of the type I dispersion was used for the type II, except that 24 g of palygorskite that were added to the 420 mL of the saturated solution.

3. Results and discussion

3.1. Palygorskite characterization

3.1.1. Chemical and mineralogical composition

The chemical compositions of the three representative samples of palygorskite show little differences (Table 1) except for the higher content of Fe_2O_3 and lower SiO_2 grades of the Boa Vista palygorskite.

The X-Ray diffractograms indicate the presence of palygorskite and quartz in all samples. The São Pedro Mine samples contain small amounts of kaolinite and diaspore as well.

Comparing the intensity of the quartz reflections to those of the palygorskite, the content of quartz decreases as follows: White São Pedro>Dark São Pedro>Boa Vista. This is in agreement with the content of silica (Table 1).

Based on the chemical and mineralogical analyses, the content of quartz was estimated and a chemical formula for each of the palygorskite samples was derived (Table 2). These calculated chemical formulas show that:

Table 2
Estimated quartz content and chemical formula of the palygorskite samples

Sample	Quartz content (%)	Chemical formula
White São Pedro	18.0	$K_{0,2}(Mg_{1,3}Al_{1,9}Fe_{0,5}{}^{+3})Si_8O_{20}(OH)_2$
Dark São Pedro	15.5	$K_{0,2}(Mg_{1,7}Al_{1,7}Fe_{0,4}{}^{+3})Si_8O_{20}(OH)_2$
Boa Vista	8.2	$K_{0,4}(Mg_{1,1}Al_{2,0}Fe_{0,8}{}^{+3})\ Si_{7,8}Al_{0,2}O_{20}(OH)_3$

(1) Potassium is the main structural cation (unlike other palygorskites);
(2) Iron is an important component of the octahedral sheet (especially in the sample from the Boa Vista mine);
(3) The Boa Vista palygorskite shows such a high level of trivalent cations that its stoichiometry is different from the other two samples (three structural hydroxyls instead of two) and it also shows aluminum atoms at tetrahedral sites.

In TGA analyses (Table 3) the palygorskites show the following transformations:

- Endothermic mass loss at $T_{max}<100$ °C;
- Endothermic mass loss at $T_{max}\approx200$ °C;
- Endothermic mass loss at $T_{max}\approx450$ °C;
- Endothermic crystalline transformation $T\cong570$ °C;
- Exothermic crystalline transformation $T>700$ °C.

The endothermic transformations up to 570 °C indicate the presence of quartz in all samples. The exothermic solid phase transformations starting at 700 °C, indicate the formation of crystalline phases such as olivine (Mg_2SiO_4), spinel ($MgAl_2O_4$), enstatite ($MgSiO_3$), sillimanite (Al_2SiO_5) and crystobalite (SiO_2).

The three ranges of temperature in which mass loss took place are in agreement with palygorskite behavior. The first is associated with the desorption of water adsorbed on the external surface; followed by loss of zeolitic water; and the third is due to the elimination of coordination water and structural hydroxyls (Mackenzie, 1957). The values of mass loss are lower than those found in literature, not only due to the presence of quartz, but also of the high content of Fe in the structure.

3.1.2. Morphology

The images of the São Pedro Mine samples (Fig. 1A and B) show a large number of particles of acicular habit (similar to images found in the literature), while the Boa Vista palygorskite (Fig. 1C) consists of few fibers and irregular, round particles.

3.1.3. Electrokinetic mobility

The Boa Vista palygorskite shows an isoelectric point at pH 2.6 (more acidic in relation to the others) (Fig. 2). The White and Dark São Pedro samples showed isoelectric points at pH 3.7 and 3.3, respectively. The Boa Vista palygorskite presented a lower mobility in the whole pH range.

Table 3
TG analysis of the palygorskites samples

Palygorskite	Range (°c)	Mass loss (%)	Range (°c)	Mass loss (%)	Range (°c)	Mass loss (%)
Boa Vista	Room temperature to 150	8.8	150 to 250	1.7	300 to 600	4.0
White São Pedro	Room temperature to 130	6.1	130 to 240	1.9	240 to 600	4.4
Dark São Pedro	27.2 to 150	7.7	150 to 250	2.4	250 to 600	4.2