Morphological characterization of Brazilian organ clays using AFM and SEM studies

A. Tejedor De León[1], G. Navarro[2], J. Rubio[2]

[1]*Depto de Materiales y Metalurgia, Centro Regional de Veraguas – Universidad Tecnológica de Panamá*
[2] *Laboratorio de Processamento Mineral – Depto. de Metalurgia – Universidade Federal do Rio Grande do Sul - Brasil*
[3] *Laboratorio de Tecnologia Mineral e Ambiental – Escola de Engeharia – Universidade Federal do Rio Grande do Sul - Brasil*

ABSTRACT: *A combination of SEM (Scanning Electron Microscopy) and AFM (Atomic Force Microscopy) techniques was used to characterise the morphology of Brazilian montmorillonites before and after intercalation of some organic compounds. AFM revealed that the layers are staked over above the others. The surface of the particles consisted of layers bounded with smooth flat basal planes and larger edges ending in some cascade-like steps 184 µm wide. Some micro and macro valleys (0.6 µm deep) are distributed throughout the whole area and irregularities on basal planes may be attributed to the crystallographic conditions of the genesis of these Brazilian montmorillonites. The mapping performed over 20 x 40 areas showed adhesion forces of 11 nN magnitude on bare clay mineral in the Na+ form and 40 nN for the calcium form. Forces between 10 and 6 nN were found after organic intercalation. In general, the intercalation caused significant changes in the surface properties of clay mineral. The combination of AFM and SEM studies provided evidence about the poorl crystallinity of the Brazilian montmorillonites.*

Keywords: *Atomic Force Microscopy, organoclays, montmorillonites, Scanning Electron Microscopý Volume 3, Issue 2, Mar. – Apr. 2013.*

I. INTRODUCTION

Although the production of modified montmorillonites by the intercalation of organic compounds has been recognised in many areas [1-4], little is known about the influence on its morphology.

The morphology of clay mineral was studied by electron microscopy [5] [6] and these studies revealed a multiplicity of microsteps on the clay mineral surfaces.

Atomic Force Microscopy [7] has rapidly spread throughout many fields of science [8-10] [5] due to its high versatility. While height images provided quantitative topographic information, deflection images often revealed finer surface details. The AFM can also record the force felt by the cantilever as the probe tip is brought close to - and even into - a surface and then pulled away [10]. This technique can be used to measure long range attractive or repulsive forces between the probe tip and the surface, elucidating local chemical and mechanical properties and even the thickness of adsorbed molecular layers or bond rupture lengths [7].

The aim of this work was to characterise the surface morphology of a Brazilian motmorillonite in the calcium and sodium form and after intercalation of two organic compounds using a combination of SEM and AFM techniques.

II. MATERIALS AND METHODS

2.1 Materials

BRASGEL, an industrial Brazilian montmorillonite in Na^{1+} form Campina Grande – Paraiba, Brazil, BENTOCAL, a montmorillonite saturated with calcium cations. The organoclays used in these studies (FENAN and ETIL) was obtained by the intercalation of two organic compounds, 1.1 ortho phenantroline and Ethylenediamine respectively.

2.2 Atomic force microscopy studies

The morphological structure of different montmorillonites samples and its contact force curve were determined by AFM by the contact mode (Digital Nanoscope IIIa, 3000 system, Si_3N_4 micro cantilever). The force curve obtained for each bentonite sample was utilised to calculate the nominal contact force of the tip on the surface samples, defined by the equations:

$$F = k\Delta z \qquad (1)$$

$$\Delta z = ADP \qquad (2)$$

where: F = Contact force in nN; k = spring constant of the micro cantilever, 0.6 Nm^{-1}; Δz = distance from de control point, nm; A = number of divisions of the cantilever deflection; D = potential applied, V/divisions; P = piezo sensitivity constant, 2 nmV^{-1}.

2.3 Scanning electron microscopy studies

SEM studies were performed with a Phillips XL-30 ESEM scanning microscope operating normally with up to 30 kV acceleration voltage field emission gun. The samples were attached to a metal mount by carbon tape. Due to the insulating nature of the materials, the samples were coated with a 20 nm thick layer of gold (Balzer Union SCD 040 Sputter Coater system under argon vacuum.)

III. RESULTS AND DISCUSION

3.1 Topographical analysis

The nanotopography of BRASGEL sample is shown in Figure 1.

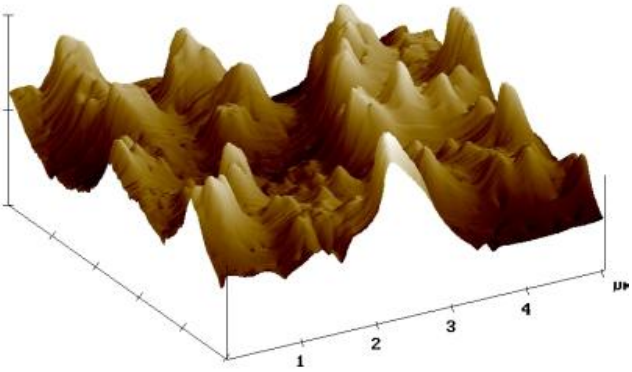

Figure 1: Contac Mode Atomic Force Microscopy (CM-AFM) images of sodium Brazilian montmorillonite (BRAGEL)

The 3D images of the sample, obtained by AFM studies, show different topography at various levels. The surface of BRASGEL shows complex morphological features with irregular and elongated edges, well-defined “hills” and several depressions, suggesting a surface with great roughness; the edges of the flakes, not clearly defined, are ragged and irregular. It also shows a successive “mountain range” with intermittent micro and macrovalleys (~ 0.6 µm deep). This observation may be linked to a poorly crystallisation conditions [5] whereby the Brazilian bentonites were formed [11].

Figure 2 for the Ca-montmorillonite (BENTOCAL) shows the presence of a large jagged and an irregular edge and an isolated volcano (~184 nm height)in the surface.

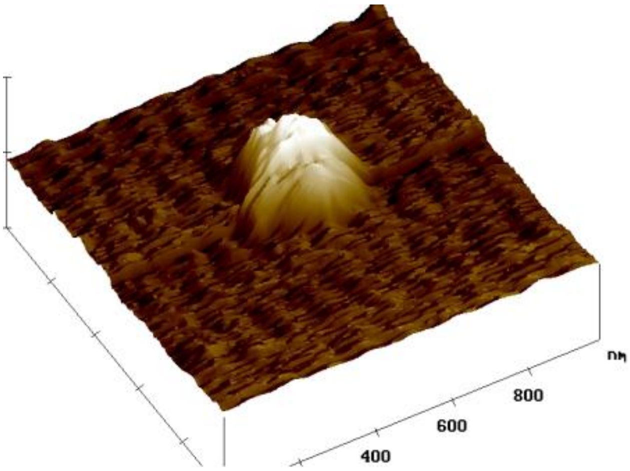

Figure 2: AFM micrographs from the surface of BENTOCAL

In the middle of the figure appears a defect caused by the tip – tip artefacts during image acquisition. Nevertheless microvalleys and grooves are seen (arrow marks). The surface is continuous and appears smooth. Also seen are the cascade.-like step structures, 280-345 nm wide as described by [5] who studied the nanomorphology of well and poorly crystallized kaolinites.

Figure 3 obtained after Phenanthroline intercalation shows an apparently smooth surface unlike the non-treated montmorillonite.

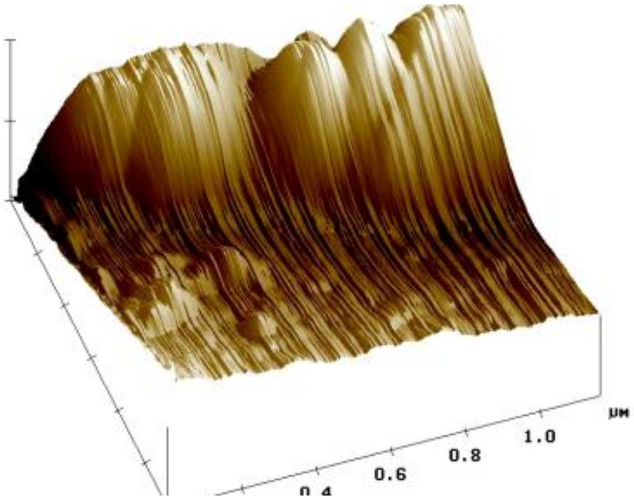

Figure 3: AFM micrographs on well-ordered montmorillonite after phenanthroline intercalation (FENAN)

The overall topography is relatively regular and the basal planes are staked one above the other. The surface topography of the organoclay became smoother and presented a massive cascade-like structure at the layer edges.

Figure 4 shows a typical F-E (force vs. extension) curve obtained on the BRASGEL surface. The the slope of the curve suggests that the tip moved on a hard surface, and a typical large adhesion interaction curve was represented [10].

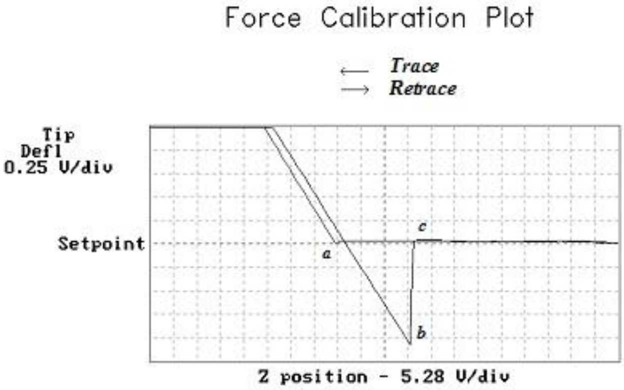

Figure 4: Computing contact force obtainen by AFM to the BRASGEL montmorillonite.

The force curve represents the deflection signal for each complete trace-retrace cycle of the piezo. At point *a*, the cantilever is not deflected but due to attractive forces between the tip and the bentonite surface, the tip sticks to the sample, and the cantilever is pulled down as the piezo continues to retract. Eventually, the spring force of the bent cantilever overcomes the attractive forces, and the cantilever quickly returns to its non-deflected, non-contact position. This is represented by point *c.* At point **b**, the spring force of the cantilever equals the attractive forces between the tip and the surface. The indentation in the surface was extremely "rough" (677.32 nm) and the extension of the sample was in the range of 5 x 5 μm. The contact forces for the other samples were calculated by employing equations 1 and 2 (Table 1).

Table 1: Contact forces onto Brazilian motmorillonites.

Samples	*Resulting conctac force, nN*
BRASGEL	11
BENTOCAL	40
FENAN	10
ETIL	6

The BRASGEL sample presents an attactive contact force of 11 nN, between the sodium motmorillonite surface and the silicon nitride tip. In the case of alcium montmorillonite (BENTOCAL) the force increased to 40 nN. After the intercalation of Orthophenanthroline and Ethylenediamine the significantly reduced.

3.2. Micro structural analysis

The SEM image of BRASGEL bentonite shows a continuous surface, even though it contains small particles and the edges of the lamellar are jagged and irregular (Fig. 5). The presence of a greater number of smaller size particles between the lamellar make the sample less compact and less rigid (Frost et al., 2002). The form presented by the Brazilian bentonites, is a typical "terraces landform" [11]

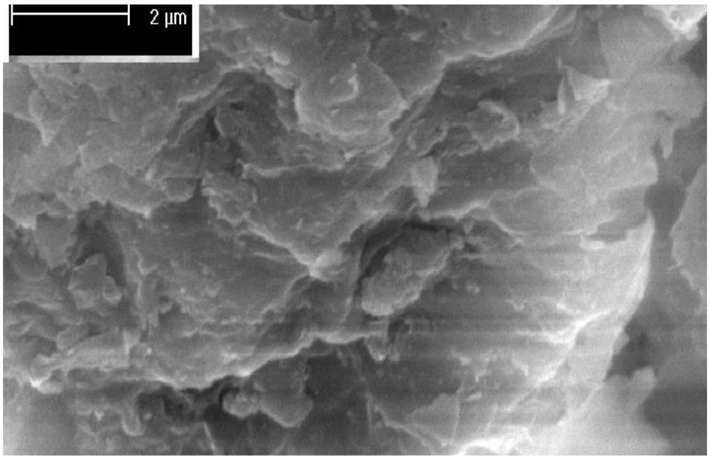

Figure 5: SEM micrographs of the motmorillonite (sodium form) - BRASGEL

IV. CONCLUSIONS

The results of these studies reveal that AFM and SEM are important complementary tools while investigating clay mineral surfaces.

Intercalation of EP and OP molecules caused a significant change in the surface properties of the Brazilian montmorillonite.

The correlation between the AFM and SEM studies provided information about the poor crystalline of the Brazilian bentonite particles which, despite the poor crystallinity, the bentonites were very easy to grafted with OP.

The resulting OP organoclays shown more stability in terms of the resulting contact force performed in the sequence works: intercalation, copper ions adsorption and desorption experiments than the bentonites grafted with ET.

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REFERENCES

[1] De León, A.T.; Nunes, D.G. and Rubio, J. Adsorption of Cu ions onto a 1.10 phenanthroline-grafted Brazilian bentonite. *Clays and Clay Minerlas*. 1, 2003, 58 -64.
[2] Krishna, B.S.; Murty, D.S.R.; Jai Prakash, B.S. Surfactant-modified clay as adsorbent for chromate. Applied *Clay Science*. 20, 2001, 65-71.
[3] Mortland, M.M.; Berkheiser, V. Triethylene diamine-clay complexes as matrices for adsorption and catalytic reactions. *Clays and Clay Minerals*. 24, 1976, 60-63.
[4] Cox, M.; Rus-Romero, J.R.; Sheriff, T.S. The application of montmorillonite clays impregnated with organic extractants for the removal of metals from aqueous solution Part I. The preparation of clays impregnated with di-(2-ethylhexyl) phosphoric acid and their use for the removal of copper (II). *Chemical Engineering Journal*. 84, 2001. 107-113.
[5] Zbik, M.; Smart, R.St.C. Nanomorphology of kaolinites: comparative SEM and AFM studies. *Clays and Clay Minerals*. 46, 1998, 153-160.
[6] Thompson, D.W.; Macmillan, J.J.; Wyatt, D.A. Electron microscope studies of the surface microstructures of layer-lattice silicates. *Journal of Colloid and Interface Science*. 82, 1981, 362-372.
[7] Binnig, G.; Quate, C.F.; Gerber, Ch. Atomic force microscope. *Physical Review Letters*. 56, 1986, 930-933.
[8] Senna, L.F.; Achete, C.A.; Simão, R.A.; Hirsch, T. Comparative study between the electrochemical behavior of TiN, TiCxNy and CrN hard coatings by using microscopy and electrochemical techniques. *Materials Research*. 4, 2001, 137-141.
[9] Oréfice, R.L.; Brennan, A. Evaluation of the interactions between polymeric chains and surfaces with different structures performed by an atomic force microscope. *Materials Research*. 1, 1998, 19-28.
[10] Ikai, A.; Afrin R.; Itoh, A.; Thogersen, H.C.; Hayashi, Y.; Osada, T. Force measurements for membrane protein manipulation. Colloids and Surfaces B*: Biointerfaces*. 23, 2002, 165-171.
[11] Gopinath, T.R.; Schuster, H-D.; Schuckmann, W.K. (1981). Modelo de ocorrência e gênese da argila bentonítica de Boa Vista, Campina Grande, Paraíba. *Revista Brasileira de Geociências*. 11, 1981, 185-192.