

RESEARCH ARTICLE

Selection, Modification, and Purification of Natural and Solidified Clays by a Patented Process: Analysis using ICP-MS and Rietveld

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Abstract: Background: The applications of the clay minerals in the various process industries are still relevant and closely related to their structure and composition.

Objective: to study ways of selection, purification and subsequent modification of mineral clays to ensure a specific industrial use, being proposed, developed and applied a separation method of clay fractions called *elutriation*.

Method: A granted process was based on the principle of *Stokes' Law* (BR Patent 102013016298). For this we used four glass columns in series in which were applied a high flow of deionized water, associated with a Venturi device to obtain purified *in natura* clays. We repeated this procedure adding NaCl to previous solution considering a fixed flux rate. This process enabled selective separation of clays and impurities by size and density.

Results: The efficient separation of crystalline phases has been verified qualitatively by both X-Ray Diffraction and Fluorescence. The main phases observed were montmorillonite, kaolinite and quartz. We also applied a quantitative analysis by means of the Rietveld refinement method of clay minerals, elutriated column by column, and also comparing elutriated and non-elutriated *in natura* samples.

Conclusions: Results showed that there was a purification process with increasing montmorillonite phase up to 96% in mass at the same time that was noted the decrease content of the kaolinite and quartz phases. ICP-MS results showed that there was sodium incorporation, especially in the last columns, when using NaCl added to water solution.

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1. INTRODUCTION

Clay minerals play an important role for industry in general, as pharmaceuticals, cosmetics, foods or ceramic, among others [1]. In this context, methods of identification and characterization of clay minerals are of high importance. The smectite clay group has variable interplanar distance d_{001} due to the characteristics of its crystalline structure. This **lattice** distance may vary according to certain conditions such as exposure to heat or special treatments as by adding solvents. It is possible to characterize such modifications by X-ray diffraction (XRD) [2].

Clays in general, and bentonites in particular are important nature materials that occupied places in different

types of industries and their specific properties. The applicability range of such materials just increased [2, 3], and these properties result from various groups of clay minerals. Its crystal lattices, the variety of chemical compositions, their isomorphous substitution possibilities allow, for example, the cationic modification which increases the degree of applicabilities [3]. The dispersion in water or many other solvents, the high power of swelling [2], high surface area, great ion exchange capacity [2-5], and the resulting rheological characteristics added to the fact that they are inexpensive **raw materials** to justify their choice while **resources** with enormous applications. Bentonite consists, in general of around eighty percent of montmorillonite [4, 5], and other minerals such as quartz and feldspar.

A wide variety of contaminations are found in bentonites, some of them originating in its genesis process – and other features are typical of the place where they were obtained. In general, we can mention the most common: kaolinite, quartz, pyrite, and calcite, among others, as well as organic matter, soluble minerals and amorphous [2, 3].

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George G. Stokes



Franz Ferdinand Schulze

Fig. (1). (a) Sir George Gabriel Stokes (1819 - 1903), Irish physicist and mathematician around 1860. Source: Smithsonian Institution Archives; (b) Franz Ferdinand Schulze (1815 - 1873), German chemist. Source: Deutsches Museum Archives, München. Both images are in public domain.

An important purpose of this study was to obtain bentonites with a richer montmorillonite phase by means of an easy, fast purification and selection of a patented process [6]. With the application of a pilot elutriation system based on Stoke's Law, named after the Irish physicist and mathematician George Gabriel Stokes (1819 - 1903, Fig. 1a). The schematic process is indicated in Fig. 2, and with this patented process [6], it was possible to control the solvent flow (in this case deionized water) and check the resulting materials collected column by column.

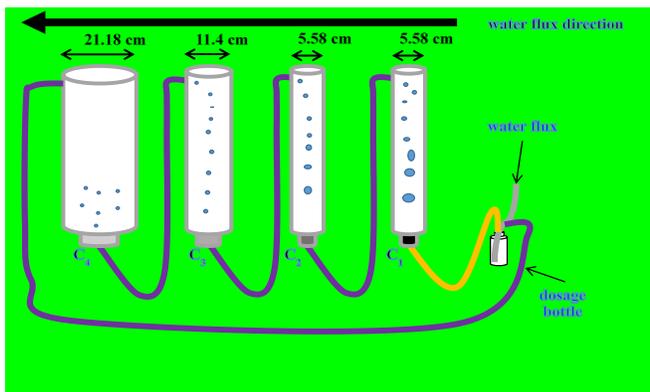


Fig. (2). Schematics of the elutriator used. Four borosilicate glass columns in series in a closed system, as indicated by C₁, C₂, C₃, and C₄. Flow rate occurs from the right (C₁) to left (C₄). The collected samples were obtained at the bottom of respective columns and analyzed. Venturi device is not shown, but close to bottle dosage. A simple pumping was also used (but not indicated). Patented process [6].

The montmorillonite expansion capacity is given by intercalating polar molecules or structures that may cause cationic substitution between their lamellae [2, 3]. This phenomenon causes a change in the density of the mineral, as consequence of the inclusion of larger molecules or chemical species which are able to increase the interlamellar distance. Since mineral contaminants, such as feldspar, mica, and quartz, among others, do not undergo this density modification due to water presence [3], a selection and purification process would occur.

Much of the knowledge about structural clays is due to the application of X-ray diffraction. From this technique, it is

possible to determine the crystalline phases present and to distinguish ceramic materials of the same crystal lattice owing to their dimensions, the degree of heterogeneity as well as properties like expansion or contraction. This is possible because in most crystalline solids the atoms are arranged in planes separated from each other by distances of the order of magnitude of X-rays wavelengths.

The objective of this work was to obtain the composition of purified and *in natural* clay minerals from a new mine in Bahia, a Brazilian Northeast state. For this task, we applied a high water flow (*i.e.*, few minutes processing) by means of the elutriation process, that follows Stoke's law [7]. More precisely, the solvent employed was deionized water. It was our intention to compare structures of *in natura* clays from the same elutriated material obtained in four different columns, as schematically shown in Fig. 2. We also considered the same material in a solution with deionized water but solidified with sodium chloride. Therefore, we applied the Rietveld method for a quantification analysis [8, 9] through software DBWS 9807a Tools 2.4, version beta [10].

2. BRIEF THEORY

The elutriation technique is quite old [11]. As far, authors know the German chemist Franz Ferdinand Schulze (1815 - 1873, Fig. 1b) published one of the first papers about this method, that has been first applied to inorganic materials, since the 1920s, it was used in experimental procedures for selecting and purifying clays [12, 13], which is based on Stoke's Law, that determines the terminal velocity of dispersed particles in a viscous medium [7].

The principle of this particular law states that a sphere of radius r , immersed in a fluid, is subject to the action of two opposing forces: the resistance R , due to the viscosity of the fluid given by η , resulting in $R = 6\pi r\eta v_f$ and to the gravity

force $F = \frac{4}{3}\pi r^3 \delta_p g$, where the density of the particle is δ_p ,

that is equilibrated by the upward buoyant force I , according to Archimedes Principle: $I = \frac{4}{3}\pi r^3 \delta g$, where δ is the fluid density.

Assuming that the sphere has initial zero velocity, motion only occurs when the resulting force $F - I$ overcomes the resistance R . The particle will then be a subject to accelerating movement until its speed in the fluid induces a resistance R which exactly equals the resulting force. The sphere will then fall with constant speed (called terminal velocity, v_f).

In the above conditions, the equation which represents the motion can be expressed as:

$$v_f = kg \frac{(\delta_p - \delta)}{\eta} r^2, \quad \text{Eq. (1)}$$

Where, g represents the gravitational acceleration, and k a constant with a value close to 2/9 for spherical particles. For this work, k equals a fraction somewhat smaller than this amount (about 1/18).

Briefly, the elutriation is basically a particle separation process which, depending on the flow is established with the elutriation column yields, a separation of particles with a certain radius. As the flux increases, there are separate particles with larger radii. This equation describes how fast it is necessary to establish a laminar flow of a fluid to drag particular spherical particle, in view of its radius and density. Terminal velocity v_f is directly proportional to the difference between the densities of the particle and fluid ($\delta_p - \delta$) and to the square of the particle radius (r^2), according to Eq. (1). The viscosity η , in turn, acts inversely proportional to v_f [7].

Stoke's law distinguishes terminal particle velocities by comparison between particle densities immersed in a solvent of density δ . In this work, other i particle types than clays should exist but is expected to have different densities δ_p^i . In particular, a specific clay phase, montmorillonite is expected which exists from a geological viewpoint (the mine where the sample was extracted has such natural deposits). This particular phase can also change its density by absorbing water into its lamellae and thus, modifying their lattice parameters.

In particular, well-dispersed clay suspension using water as a solution, when reached hydration equilibrium, is possible to observe different sedimentation velocities. Visually, one observes the turbidity change over time, being easy to notice that the rate of very fine particles settling is smaller than larger particles. The Stoke's Law quantifies such observation, following Eq. (1). Thus, if across flow (upstream) without turbulence is applied, with a known constant speed, and the given Stoke's Law, three situations are possible by setting the elutriation process (where U_f is the fluid velocity):

- Particles will settle ($v_f > U_f$);
- Particles will have zero velocity sedimentation ($v_f = U_f$);
- Particles will be transported to other column ($v_f < U_f$).

3. MATERIALS AND METHODS

The following calibration methods of the elutriation columns and the characterizations made by XRD as well as ICP-MS were done.

3.1. Materials Analyzed

The material used in this study corresponds to *in natura* clay from the national deposit "Serra do Vital" in Vitoria da Conquista, the southern city of Bahia, Brazil - from the Bentonite Brazilian Company (www.cbb.ind.br). More precisely, this study corresponds to the analysis of an elutriated bentonite *in natura* using deionized water. We also intended to compare this material in its natural state with a final stage where sodium chloride was added to deionized water.

Clay was previously milled and powdered up to about 200 grams on an analytical balance (precision 0.01 g). Subsequently, clay was mixed placing in a mixer initially using a volume of 1 liter with water, submitted to 750 rpm. This procedure took a time enough to obtain a homogeneous solution. Details of the procedure are available in ref. [4].

The suspension obtained was measured in the patented plant (60 l of deionized water) by means of a peristaltic

pump over a period of 30 minutes while the elutriation process using water already reached a steady state, according to a chosen flow rate. This operation has led to the purification process of clays as well as the best selection of the particle aggregation state, besides the separation of organic matter contamination as a natural ore.

3.2. Experimental Procedure for Elutriation in Series

Basically, the elutriation water ("solvent") applied in counter-flow carried different particle types through a series of columns C_i ($i = 1, 2, 3$ and 4) of different diameters which were dimensioned to cause, in a given fluid stream, an ascending speed, that was appropriate for the selection and enrichment of the ore. Fig. 2 summarizes the experimental apparatus, named "elutriator". The solvent used was recycled because the system was closed (there is a connector linking first and last columns, and a pumping machine was used to start all experiment). In a second step, we incorporated an additive to solvent (in this case NaCl).

The elutriation time varied with different kinds of clays and their state of aggregation [5]. In this way, we tried to adjust the main variable processes to favor separation. This adjusts are based on physical or chemical procedures as mentioned previously [4, 5]. In this system, it was even possible to make additions and modify treatments during elutriations [4], as for example modifying dosages in the water current flowing into columns. The four columns used in series were bi-diametric, and in their bottom, it was possible to collect materials. The end of the elutriation procedure was observed by the absence of moving particulates suspended in the fluid (a stationary regime). It was very important to control the flow through a rotameter to prevent acceleration or deceleration of the velocity v_f , thus modifying the result of selection [4].

The experimental procedure was performed to obtain elutriated samples, and followed five basic stages: *i*) mixed and pulverized clay in order to maintain a homogeneous texture - this procedure was done at a ratio of 700 ml of water for 200g of clay; *ii*) placing clay plus solvent in a container; *iii*) filling the elutriation columns C_1 to C_4 with purified water and then add clay solution into C_1 ; *iv*) specifying the flow rate and connecting the recirculation pump; and *v*) connecting pump to container.

Only after these steps, the elutriation started. The process was accompanied by a rotameter and a peristaltic pump calibrated mass flow, where a flow equals to 100g/min was applied [4]. To provide the best clay spray, we applied a Venturi tube in the system before reaching the clay columns. As a result, a reasonable elutriation was observed, more fast and efficient in comparison with previous results [4, 5].

The experimental procedure for solidified clay was also similar, first calculating the sodium chloride quantity to be used, given the maximum CTC of 1.2 meq/g for each clay sample. An excess of 20 wt.% based on the calculated value was added to ensure full replacement of the sodium into clay lamellae [4]. Sodium chloride was added to mixed and pulverized clay with deionized water. A flow chart describing experimental procedure is presented in Fig. 3.

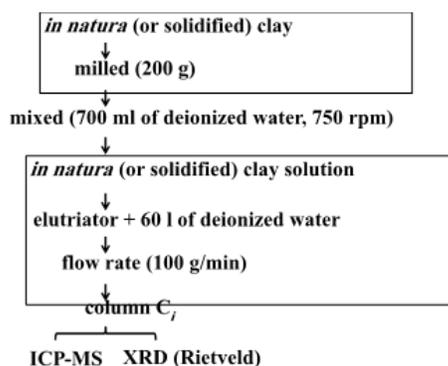


Fig. (3). Clay experimental procedure flow sheet.

3.3. Characterization by X-Ray Diffraction

By focusing a beam of X-rays in a crystal, it interacts with the atoms, yielding the diffraction phenomenon. The diffraction of X-rays occurs according to the Bragg's law [14]: $n\lambda = 2d_{hkl}\sin\theta$, the original work of two Nobel Prizes in 1915 [15]. This equation establishes the relationship between the diffraction angle and the distance between planes that rise - for each characteristic crystalline phase, where: n is an integer, λ is the wavelength of the incident X-ray, d_{hkl} is referred to the interplanar spacing (distance) with plane indices (hkl), and θ represents the diffraction angle.

Among the advantages of the XRD technique for the characterization phase, we highlight the simplicity and rapidity of the method, the reliability of the results will be obtained (mainly for the obtained diffraction profile, that is characteristic for each crystal phase). Further, it is possible to add the possibility of screening compound materials, a mixture of phases and a quantitative analysis thereof.

When characterizing clay minerals, the use of XRD technique becomes more suitable, because a chemical analysis would report the chemical elements present in the material, but not how they were joined. The chemical analysis could then be linked to rational analysis, but the results did not show a high reliability, and this procedure shall be indicated to identify polymorphic phases [3].

X-ray diffraction measurements were performed at room temperature using a Shimadzu diffractometer XRD-6000 X, using $\text{CuK}\alpha$ radiation ($\lambda = 1.542\text{\AA}$) of 30 kV and current 15 mA, 2θ ranging from 2° to 65° and a scan speed of 0.25° per step with a time of 1-second count per step. These samples were placed in powder form in the specimen holder cavity, lightly pressed to present a smooth surface and introduced into the goniometer of the diffractometer support. In all cases, a silicon pattern for the calibration procedure was used. The interpretation results were done by comparison with the existing standard database PDF2 (the International Centre for Diffraction Data, ICDD: www.icdd.com, 1996) using specific software. All qualitative analyses were later reviewed using the X-Pert High Score Plus version 3.0d (3.0.4).

To quantify, the data was applied Rietveld refinement method [8,9] using the DBWS 9807a Tools 2.4 software

[10]. This technique allows quantifying one or more phases from the result of the diffraction of X-rays peaks through an algorithm that involves the application of the method of least squares data [16]. As far as the setting is better, the result provides a new standard, calculated, which relates the mass fractions or mole fundamental components expected in the analyzed composite, column by column.

3.4. Characterization by ICP-MS

We have carried out characterizations by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) at the Institute of Physics at the University of São Paulo (IFUSP). It was used gas flux of 0.9 L/min, around 10 V for lens voltage and radio frequency power of 1100 W. These results were compared with experimental XRD data.

Table 1. Results of ICP-MS analysis in $\mu\text{g/g}$ for elutriation columns (N_i : in natura, S_i : solidified).

Column / Element	N_1	N_2	N_3	N_4	S_1	S_2	S_3	S_4
Li	2.12	2.36	1.33	1.54	4.06	0.95	1.27	1.82
Na	0.00	0.00	0.00	0.00	0.00	0.00	149.62	183.94
K	0.00	0.00	0.00	0.00	224.52	0.00	186.82	0.00
Ti	8.60	0.05	2.48	885.04	5.20	1403.50	2.22	906.68
V	82.25	83.83	91.64	76.93	141.34	77.95	44.33	88.71
Cr	570.18	641.87	717.82	519.63	549.58	182.54	385.56	719.64
Mn	13.62	19.84	12.97	12.16	28.74	19.42	11.29	15.91
Ni	152.24	168.27	198.59	189.49	228.72	126.66	88.48	225.76
Co	21.53	22.13	17.60	14.78	27.04	13.39	6.83	15.90
Cu	137.89	94.27	105.55	91.75	169.61	102.22	53.15	131.80
Zn	772.36	800.26	532.49	400.15	947.81	399.80	308.25	440.62
As	18.01	2.43	10.80	4.73	49.97	5.02	2.78	7.84
Cd	0.83	0.03	1.17	1.90	3.64	0.87	0.11	1.50
Ba	155.23	540.89	144.99	223.74	511.60	413.82	103.31	258.62
Pb	0.41	0.34	0.00	0.00	0.23	0.10	0.00	0.15
Th	0.00	0.02	0.00	0.00	0.07	0.25	0.00	0.00
U	0.23	0.00	0.00	0.23	0.12	0.10	0.18	0.88

4. RESULTS AND DISCUSSION

The ICP-MS results are shown in Tables 1 (for in natura samples, N_i) and 2 (for solidified samples, S_i) column by column. It is important to note the absence of sodium in elutriated samples for the four columns with deionized water only (N_i columns, Table 1). It was noted that sodium appeared in the last two columns of the elutriation experiment using sodium chloride (S_i columns, Table 2). Note that the values given in such tables as 0.00 were actually below the determination equipment limit. The calcium element was not observed due to experimental difficulties with this technique.

The elements copper, nickel, potassium, titanium, barium, vanadium, chromium, and zinc were observed at concentrations above 100 µg/g. Only traces of uranium, lead, and thorium were observed.

Table 2, in particular, shows the amounts in mass (wt.%) of iron and magnesium, quite common results considering clay minerals. A higher concentration in the last column (N₄, *in natura*; and S₄; solidified samples) in Tables 1 and 2 was also observed, both related to the phases with the highest concentration of montmorillonite, as described below.

Table 2. Results of ICP-MS analysis in mass (wt.%) for elutriation columns (N_i: *in natura*, S_i: solidified).

Column / Element	N ₁	N ₂	N ₃	N ₄	S ₁	S ₂	S ₃	S ₄
Fe	11.12	12.30	13.95	12.69	16.72	9.27	6.25	15.04
Mg	0.00	0.00	0.38	1.55	0.11	0.40	0.24	2.12

The X-ray diffraction has been widely used to determine crystalline phases in ceramic materials. In clays, a large amount of quartz and its high degree of orientation hinder the identification and characterization of the remaining phases [4].

Fig. 4 shows the diffractogram comparing the clays for each elutriation column with the *in natura* clay not elutriated. The largest peak in all the graphs, left-most, refers to montmorillonite phase (M), and more specifically to the plan *d*₀₀₁.

From these results, it is concluded that the column N₁ clay has a greater amount of impurities. This can demonstrate quartz peak intensity present in the column, which decreases in intensity in subsequent columns. The peak intensity of the montmorillonite phase in the fourth column is greater than in the other, validating the selection process, in accordance with the Rietveld analysis, presented below.

We note that in Fig. 5, the intensity peaks of the montmorillonite phase decreased as compared with Fig. 4. The main reason is due to the cation exchange process occurring during the elutriation columns in the solution with sodium chloride, as verified by the ICP-MS technique shown in Table 1. By modifying their *d*₀₀₁ spacing, which previously had alkali (mainly calcium) ions changed for sodium ions, there was a decrease in the intensity of the diffraction peak. Important to compare the intensities related to the quartz phase with elutriated in *solidified* clays, and also compared with the *in natura* clay (*i.e.*, not elutriated). Less quartz in the fourth column than previously validated the purification process [17] – such result is also in agreement with the calculations done by Rietveld method shown below.

A few comment results of particle size distribution in the literature involving this system should be done. In fact, the granulometric separation of samples of similar clays was previously conducted by Alves [4, 17] when noted a monomodal size distribution by means of simple optical microscopy observations, then checking the efficiency of the method. In that case, he considered low and average flows (between 15 and 60 g/min). The results obtained were very rea-

sonable for regulated flows and used and are within the average size limit of similar clays used in this study [2, 4].

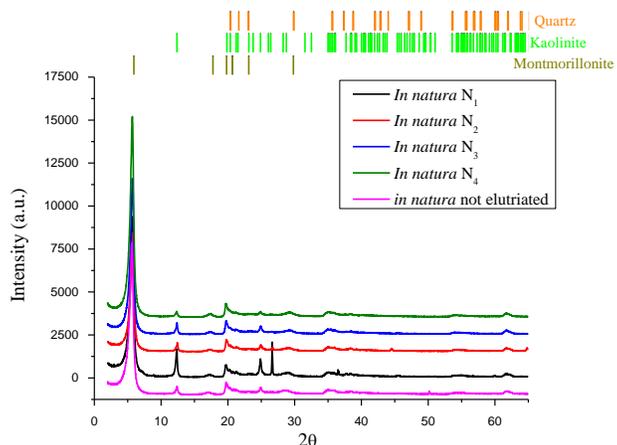


Fig. 4. Comparison of *in natura* elutriated clays and the same (but not elutriated) using deionized water flow of 100g/min by four columns in series, called N_i columns, *i* = 1, 2, 3 and 4. The vertical bars indicate the peak positions related to phases analyzed by Rietveld refinement [9, 10].

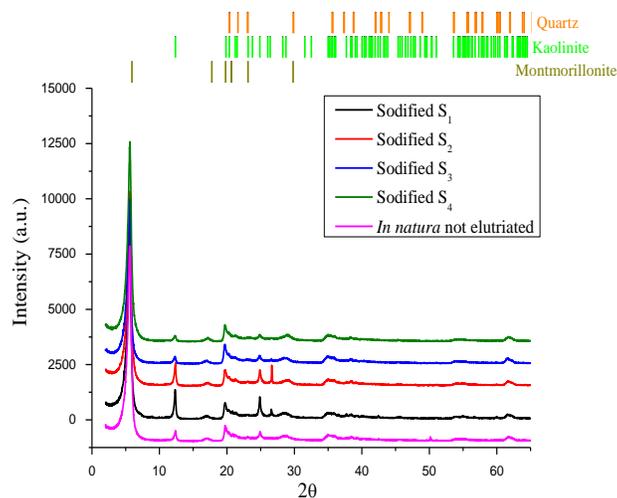


Fig. 5. Comparative of *solidified* elutriated clays and *in natura* (but not elutriated) using deionized water flow of 100g/min by four columns in series, called S_i columns, *i* = 1, 2, 3 and 4. The vertical bars indicate the peak positions related to phases analyzed by Rietveld refinement [9, 10].

About flow rate, it is important to say that the used flow of 100 g/min was proportional to terminal velocity *v_t*, as predicted by the Stoke’s Law because it provides water flow rate that is required to load a suspended particle, as shown in reference [7]. But when it comes to the separation at slightly larger flows (which would mean greater particle densities), some bimodal distributions was observed [4]. This particular result also suggests choosing *optimized* flows for a given particle size distribution, leading to an improved method and resulting successful particle separation.

Having in mind such results, it attempted to draw a comparison with a Stoke’s Law. The proposed method allowed clay separation by color difference – as seen column by column, and schematized in Fig. 2 (see bottoms of each col-

umn). Such result was also expected by Stoke's law because such visual differentiation was noted due to the reason that elutriated particles present densities and/or different diameters [4, 5].

The XRD patterns show that the elutriation was effective in purifying the clay, for example decreasing quartz (Q) and kaolinite (K) levels of the samples when compared elutriated first to last columns. It was also possible to compare such results with not elutriated *in natura* clays (as data shown in Table 3, obtained by Rietveld refinement [10]), which has reasonable quantities by mass (wt.%) of kaolinite (K) and quartz (Q), plus montmorillonite phase (M) where presented in higher quantity. The best-matching crystallographic information files were used for the refinement. For details see: montmorillonite [18], kaolinite [19] and quartz [20]. Although such comparative results are new in the literature due to the application of elutriation method, as far authors know, the characterization results of such clay samples are similar to those found in the literature [21-23].

Table 3. The mass percentage of the phases obtained from *in natura* clay (with no treatment by the elutriation process) via Rietveld refinement [9, 10].

Montmorillonite (wt.%)	Kaolinite (wt.%)	Quartz (wt.%)
75.37 ± 1.22	20.32 ± 4.66	4.30 ± 1.72

Table 4 shows the results of Rietveld refinement applied from first and last columns related to each of the three major phases. A tendency was observed, as the composite flows from column by column, that selection purification process occurred, resulting in a larger amount up to 96 wt.% of the M phase in the fourth column and a decrease of K and Q phases.

Table 4. Mass percentage of the phases obtained in first and last columns via Rietveld refinement [9, 10] for *in natura* elutriated clay.

Column	Montmorillonite (wt.%)	Kaolinite (wt.%)	Quartz (wt.%)
N ₁	56.53 ± 1.83	42.07 ± 3.29	1.4 ± 2.53
N ₄	95.98 ± 0.87	1.51 ± 0.80	2.51 ± 1.93

Table 5 shows results of the same elutriation experiment only including sodium chloride (NaCl) in deionized water. The phase separation shows a tendency of increase in the fraction of M phase between columns 1 and 4. However, the values of the mass concentrations differ from the previous table, probably due to the density change of montmorillonite phase. Note also that quartz distribution in the four columns was also different comparing both Tables 4 and 5 - since quartz has a density close to the M phase is expected that the sodium added at the solution promoted an ion exchange with cations naturally inserted in the interlamellar structure of *in natura* clay. The goodness-of-fit of the Rietveld final refinements was represented by $S(R_{wp}/R_{exp})$, and has shown S less than 1.3 as the best fit results for the last columns N₄ and S₄.

Table 5. Mass percentage of phases obtained in first and last columns via Rietveld refinement [9, 10] for *solidified* and elutriated clays.

Column	Montmorillonite (wt.%)	Kaolinite (wt.%)	Quartz (wt.%)
S ₁	55.79 ± 1.58	27.36 ± 4.12	16.85 ± 2.93
S ₄	78.58 ± 1.15	12.92 ± 2.44	8.51 ± 1.61

While there are some good commercial and free *softwares* dedicated to the Rietveld method as used in this work (we can mention the GSAS as another example [24]), many of them have a little friendly interface and require substantial knowledge of structural crystallography for the user. In particular, the difficulty of finding specific information on clays, mainly due to the hydration degree and cation types in their lamellar structures. However, it is possible to affirm the validity of this procedure because what was proposed was a comparative analysis, not taking into consideration issues such as the degree of hydration of clays and type of cations in the structure. In this sense, new studies aiming the proposal and inclusion of better structural models of clay minerals in Brazilian soils may contribute to the increased accuracy of the quantitative results provided by XRD-Rietveld approach.

CONCLUSION

In summary, the clay suspensions were poured within in series elutriation columns. It was then, applied a water counter-flow with a known constant flow rate, measured by calibrated rotameter. The smaller diameter of the bottom (settling zone), generally gives more turbulence to the flow, while avoiding agglomeration generates preferential paths the fluid. At the top, it reaches the selected speed or flow. Thus, a selective decantation is obtained.

The results showed that the patented procedure allows separation phases with good accuracy looking for optimum industrial utilization. For this, we applied the Stoke's Law in relatively short times (minutes) when using a Venturi tube in the system. Such selection may increase the performance of clays selection efficiency. Purification and modification of clays were shown by X-ray analysis by Rietveld Refinement method. It is found that the main phase characteristic peaks of quartz and kaolinite were retained in the first columns. We obtained 96wt.% of the montmorillonite phase in the last column using only deionized water. Just for comparison, the *in natura* sample had 75wt.% of the same phase, confirming the improvement of clay processing.

Although adjustments are still needed, the Rietveld method showed good potential as an alternative mineralogical quantification in the cases under study. The accurate determination of the mineral levels by Rietveld can contribute to the improvement of its use. However, it was experimentally verified that applying a sodification process, a difficult on drag particles from montmorillonite phase, as evidenced by flame spectrometry analysis.

ETHICS APPROVAL AND CONSENT TO PARTICIPATE

Not applicable.

HUMAN AND ANIMAL RIGHTS

No Animals/Humans were used for studies that are base of this research.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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