

RESEARCH ARTICLE

Flame Photometry Characterization Procedure for Sodium Content in Brazilian Bentonites for Nanotechnology Applications

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Abstract: Background: Brazilian bentonites have a low sodium concentration in their inter-layer structure. This is a problem with most of the industrial applications that demand the characteristics of sodium bentonites.

Objective: As a solution for this limitation, sodium carbonate is added to *in natura* clays, promoting ion exchange between other interlayer cations with sodium.

Method: A process was used based on the principle of Stokes' Law (BR Patent 10 2013 016298). For this, we used four glass columns in series, in which a high water flow was considered to obtain purified clays. It was proposed as a simple, fast and economical method for sodium determination that was developed and applied in bentonites by flame photometry. The equipment calibration was performed with a NaCl standard solution in concentrations between 80 and 110 ppm. The bentonites in the suspension were separated by means of centrifugation, being thus analyzed by a flame photometer.

Results: The samples were prepared according to the manufacturer's specifications to contain detectable amounts of sodium by means of flame photometry. A resulting linear relationship between the average value readings *versus* sodium standard content solution (both in ppm) was obtained by the logarithmic scale, as expected.

Conclusion: The procedure allowed to define a method that could be used in the sodification control process, thus making it possible to differentiate the sodium cation content in terms of the value of cation exchange capacity (CEC) from bentonite. X-ray analysis of *in natura* and the sodified clays showed nanostructural differences related to interlayer distance.

Keywords: Clay, bentonite, sodium procedure characterization, flame photometry, nanotechnology, cation exchange capacity.

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1. INTRODUCTION

The term bentonite has usually been employed to describe volcanic clays of certain origin [1]. However, in Brazil, this term is used in a generic form, *i.e.*, a clay that consists essentially of one or

more clay minerals of the smectite group, specially montmorillonite – and is not necessarily related to its geologic origin [2]. Thus, bentonites can be described as all clays with high amounts of montmorillonite, presenting almost the same rheological behavior to the ones from volcanic origin [1].

Bentonites have, in their crystalline structure, anionic charges generated by the isomorphous substitution of Al^{3+} into Mg^{2+} ions [1]. These (and other) cations can be substituted according to empirical rules [1]. The stoichiometric value related to such exchange is called CEC (cation exchange capacity). The Brazilian bentonites, specially obtained from Bahia, are in general polycationics, that is, they present low or even no sodium concentration with a predominance of alkaline earth metals in their interlayers [3]. The majority of the industrial applications demand proper rheological behaviors of sodium bentonites, being totally or partially sodified. Sodium cation (CT-Na) has the property to increase thixotropy in bentonite-water suspensions, being one of its most important properties in diverse industrial clay applications. However, reaching the viscosity adjusted for one determined application does not require the complete sodification, that is, lesser CT-Na than CEC. Thus, a bentonite of determining type will be able to conserve part of its original cationic composition in its structure, which is called *partial* sodification [4]. To enrich sodium industrially by means of cationic modification, sodium carbonate is simply added into bentonites (*bulk*: US\$ 275.00 per ton for Na_2CO_3) [5]. In Brazil, it is an imported raw material with a higher value as compared to bentonite mass (US\$ 41.33 per ton for bentonite *in natura*) [6]. Logistic factors such as importation, economic (costs) and industry (as scale and high production) demand in laboratories, new and dynamic methods of easy execution being economically viable, to promote the sodification process in Brazilian bentonites.

A quantitative and fast determination of the alkaline metal content in watery solutions is by means of flame photometry [7]. The operation starts with the “photoemission” process, that takes place by the excitement of the atom in question (in this work, sodium). When such solution is added to the flame of combustible gases such as the GLP and the combustion supporter - compressed air, in adjusted ratios, it is possible to obtain a flame free of soot

and with constant intensity. In this case, two characteristic spectral lines appear: $D_1 = 588.995 \text{ nm}$ and $D_2 = 589.592 \text{ nm}$ (an emission of recognized yellow color – see Ref. [8] for more details).

Application of this method has been observed in diverse areas, as in the analyses of drinking waters [7], ground, foods [9] and some biological materials of interest [10, 11]. Its sensitivity allows detecting a small amount (in ppm) of metals and the intensity of the emission is always a function of the cationic concentration. However, authors claim that no specific application of the sodium content as a process control has been carried out in nanostructure modified clays using flame photometry. As mentioned, any cation of this crystalline system could be determined in the quantitative form using this technique which is based on the cation replacement from its interlayers and its precise evaluation. Such modification occurs at the nano scale, due to the interlamellar distance d_{001} between the montmorillonite planes.

The quantification analyses conducted, in this work, and calibration curves were drawn using the external standard method (following Ref. [12]).

2. EXPERIMENTAL PROCEDURE

We present in this section the materials and the experimental procedure employed.

2.1. Materials

We used the following materials:

2.1.1. Glassware

Twelve centrifugal machine tubes were used in this work (with 15 mL superior capacity each); one 50 mL volumetric pipette; one 1000 mL volumetric flask; four 50 mL volumetric flasks; one 50 mL beaker; one glass funnel with a short pipe; one glass baton; four 125 mL Erlenmeyers; four watch glasses.

2.1.2. Reagents

For the execution of this work, the following reagents were used: *a*) ammonium acetate P.A. (VETEC); *b*) sodium chloride P.A. (VETEC); *c*) distilled water. The reagent ammonium acetate and distilled water had previously been tested in the flame photometer to verify the absence of contamination with sodium. The purity of sodium chloride was considered acceptable.

Two Brazilian clay samples were used, taken from Serra do Vital region (Vitoria da Conquista, Bahia, Brazil):

- i) Sample A – The previously treated under patented process with four percent of sodium carbonate;
- ii) Sample B – The previously treated under patented process with three percent of sodium carbonate.

The application of a pilot elutriation system, that selects and purifies natural clays, based on Stokes' Law [3, 4], was proposed and patented [13]. In this granted process, it was possible to control the solvent flow (e.g. water) and check the resulting materials collected.

2.1.3. Equipment: Flame Photometer

The instrument used for sodium content in clays was a flame photometer, *Analyser* trademark, model 910, that is relatively low-cost equipment and is very easy to use, considering both the operation as well as result interpretation – which means there is no need for a high specialized analyst. The equipment consists of an emitting system (burning with a sprinkler), an optical system that includes filters that prevent measurement interferences, thus avoiding other cations emissions, and a sensor system that determines the intensity of the cation emission. Its applicability can be extended to alkaline metals and alkaline earth metals [7].

In the experimental procedure, an analytical balance with double scale (trademark *Shimadzu*, model AUW-D), an ultrasound bath (trademark *Unique* group, USc-2800 model, frequency: 50/60Hz) and a centrifugal machine (*FANEM*, model 206 BL, 3500 RPM rotation, 1944g force) were also used.

2.1.4 Equipment: X-ray Diffractometer

X-ray diffractograms of *in natura* and sodified samples were also compared by an X-ray diffractometer *Shimadzu* XRD-6000 model, with a copper anode ($\lambda = 1.54\text{\AA}$), 30 kV tension, at 15 mA current. The goniometer speed was set as 0.05° for each step, with 1s being counted for step with a typical interval of 2.5 and 35° . Samples were prepared in powder form. In all cases, a silicon pattern was used for equipment calibration. The result

interpretations were performed by comparison with reasonable patterns as found in the database PDF02 (ICDD, 1996) using specific *software*.

2.2. Methodology

Following the instructions of the photometer manual, all measurements were performed in order to guarantee a steady-state operation.

Analytical calibration curve was calculated with sodium standard solution at the following concentrations: 80, 90, 100 and 110 ppm (y_{Na} , in ppm). The sodium chloride masses x_{NaCl} (in mg) corresponding to each one of these concentrations were calculated according to Eq. (1), that involves molecular sodium chloride mass (z_{NaCl}) and Na atomic mass (w_{Na}):

$$x_{\text{NaCl}} = \frac{y_{\text{Na}} \times z_{\text{NaCl}}}{w_{\text{Na}}} \quad (1)$$

The bentonite samples were collected and divided into four parts to guarantee their representation. After that, they underwent specific procedures for the preparation of each sample: a) The material was washed and rinsed with distilled water to eliminate possible sodium residues. b) Followed by this a 1000 mL of solution with 0.5 mol/L ammonium acetate was prepared.

Considering the CEC results from samples A and B, which were 68.39 (CEC/100meq) and 66.12 (CEC/meq), respectively, it was possible to establish a formula that relates the sodium carbonate content and the sodium concentration obtained from clay solution.

Thus, the bentonite mass was weighed to determine the sodium carbonate content, according to Eq. (2), with the intention that the sodium value would be between the minimum and maximum and a calibration curve of 80-110 Na ppm.

$$w_{\text{Bentonite}} = \frac{k_{\text{Na}} \times eq_{\text{chem}}(\text{Na}_2\text{CO}_3) \times 5}{\rho_{\text{Na}_2\text{CO}_3} \times w_{\text{Na}}} \quad (2)$$

where $w_{\text{Bentonite}}$ corresponds to the bentonite mass (in mg) to be weighted; k_{Na} is to the desired sodium concentration (in ppm); $eq_{\text{chem}}(\text{Na}_2\text{CO}_3)$ is the half of the sodium carbonate molecular mass; and, is the percentage of sodium carbonate declared by the manufacturer. The constant 5 was obtained

from the volumetric measurements and the conversions involved.

The resulting mass was added into a 50 ml calibrated flask followed by the addition of an ammonium acetate solution to approximately 1 cm below the gauging flask line. Following this, the sample suspension was placed in the ultrasound device, at 60 Hz frequency by 40 minutes at room temperature. After ultrasound application, the calibrated flask was removed from the bath. Then, 50 ml of the flask was then filled with the ammonium acetate solution. This suspension, after shaking, was used for centrifugation to decant the bentonite fraction, thus, avoiding the obstruction of the photometer fine-spray system. Finally, readings of the different solutions were identified corresponding to the sodium standards and bentonites.

3. RESULTS & DISCUSSION

Following are the results of the flame photometer calibration and the content of the sodified bentonites.

3.1. Flame Photometer Calibration

The first step of the analysis was the calibration of the equipment, following the methodology presented in the previous section. Thus, after established the following sodium solution concentrations (starting from NaCl) for the procedure of curve calculation, the following results were obtained (Table 1).

The distilled water reading was considered as the “zero” value of sodium concentration, being verified before each reading of standards and/or samples.

Figure (1) presents the average values from photometer measurements and the corresponding

error bars are shown in Table 1. The resulting curve tends to be logarithmic in a larger scale, for example, between 50 and 150 ppm, as shown in previous results based on diverse materials [7, 9-11, 14]. However, a considerable linearity was observed in short intervals, for the particular case of the materials analyzed in this work. Thus, such results are in accordance with the limitation of the equipment and the presented experimental procedure.

It is important to observe that the pressure, the amount of solution and the compressed air humidity would influence the results [7, 9-11, 14]. The concentrations used were selected considering the fact that high solution levels present the auto-absorption effect, *i.e.*, the absorption of the light of the emitted sodium from the interior (hotter, also called the oxidant zone) as compared with the peripheral part (colder temperatures, *i.e.*, a reducing zone). This temperature difference could modify the detector sensitivity [7]. It is important to affirm that, while using much diluted solutions, extreme care must be taken to avoid spectral interferences leading to contamination of other elements [7]. But this was not the case in this study as the solutions were kept at high *pH* values, because the determined alkaline solutions cannot be kept in usual laboratory glassware for too long, because some glasses have in their compositions diverse alkaline metals and alkaline earth metals [15] which possibly would cause some contamination.

3.2. Sodium Content Analysis in Clays Modified Nanostructurally

The resultant values for each sample, obtained from the flame photometer, were used to calculate the sodium percentage, as well as to calculate the percentages of sodium oxide and sodium carbonate, considering the linear approach between

Table 1. Results of the flame photometer calibration (values in ppm). The reading values of each measurement are presented. The experimental error of the equipment was assessed as ± 0.5 ppm.

Concentration (ppm)	1° Measure	2° Measure	3° Measure	Average Value
80	80	82	79	80.3
90	86	85	88	86.3
100	92	92	93	92.3
110	97	97	96	96.7

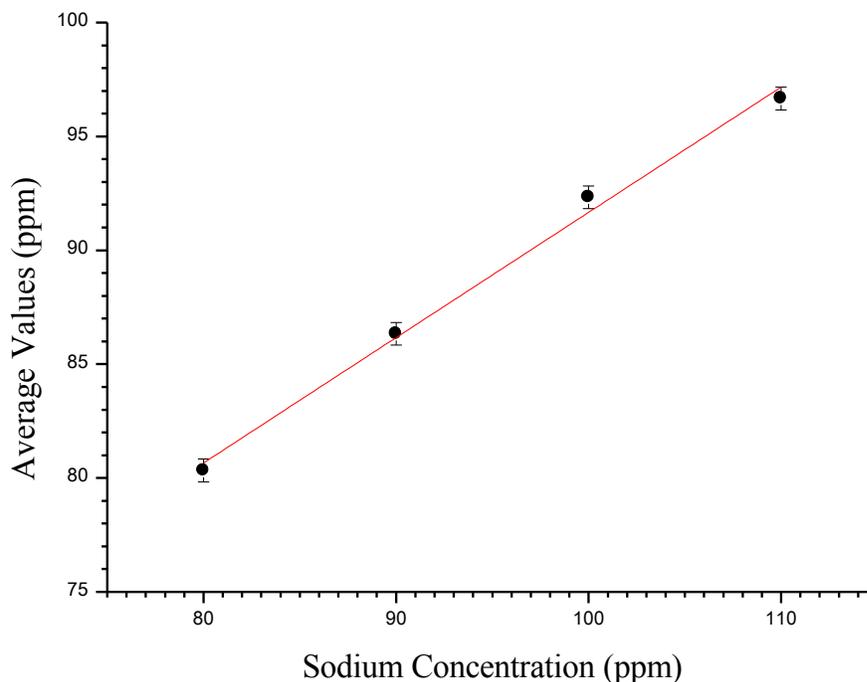


Fig. (1). Calibration curve of sodium content and the corresponding reading of the flame photometer, considering the average values (in ppm) presented in Table 1.

80 and 110 ppm of sodium presented in Fig. (1), by the following expression, Eq. (3):

$$\text{Na}(\%) = \frac{k_{\text{Na}} \times 5}{w_{\text{Bentonite}}} \quad (3)$$

From the equation above, it is possible to calculate sodium oxide percentage from a simple linear dependence: $\text{Na}_2\text{O}(\%) = 1.348\text{Na}(\%)$, where the constant 1.348 results from the quotient between the sodium oxide molecular mass and the sodium atomic mass multiplied by two. It is easy to note that the sodium carbonate percentage corresponds to: $\text{Na}_2\text{CO}_3(\%) = 1.71\text{Na}_2\text{O}(\%)$, where constant 1.71 results from the quotient between the sodium carbonate molecular mass and sodium oxide molecular mass.

Considering also that clays possess different humidity contents, the expression results are referred to dry clays, as shown in Eq. (4):

$$w_{\text{Bentonite}} = w_{\text{Wet Bentonite}} \frac{100 - p_{\text{H}_2\text{O}}}{100} \quad (4)$$

where $w_{\text{Bentonite}}$ corresponds to the mass of weighing bentonite, $p_{\text{H}_2\text{O}}$ is the water percentage (H_2O) and $w_{\text{Wet Bentonite}}$ is related to the mass of humid bentonite.

Based on previous equations, the results are shown in Table 2. Others ions - as for example Mg^{2+} and Ca^{2+} , that also form part of polycationic smectites, could be quantified by this method if there is equipment that allows such analyses. This procedure would be also applied for similar equipment and/or techniques.

3.3. X-ray Diffraction of *in natura* and Sodified Clays

Analysis of X-ray diffraction was performed for *in natura* and sodified clays. X-ray diffractogram was performed between 2.5° to 35° , as shown in Fig. (2).

Results show the efficiency of the sodification process because the montmorillonite peak (M) increased substantially as compared to *in natura* clay (by seven times). There were also observed quartz (Q) and kaolinite (C) phases in both the samples as usual impurities in this system.

The highest peak, on the left side of Fig. (2), is referred to montmorillonite (M), more precisely to (001) plane. It is noticeable that the interlayer distance changed from 14.84 \AA for 15.17 \AA , basically due to the sodification process. This result is similar to the literature data [16-18]. Figure (3) presents the schematic diagram of the sodification process.

Table 2. Result calculations of sodium content from analysis of sodified bentonites using a calibrated flame photometer. Essays 1 and 2 correspond to the results of the analyses of the *A* sample and essays 3 and 4 correspond to the result analyses of *B* sample.

Essay	$p\text{H}_2\text{O}$ (%)	$w_{\text{Wet Bentonite}}$ (mg)	k_{Na} (ppm)	$w_{\text{Bentonite}}$ (mg)	Na (%)	Na_2O (%)	Na_2CO_3 (%)
<i>A</i>	1	13.79	272.5	88	234.9	1.87	4.32
	2	13.79	294.1	95	253.5	1.87	4.32
<i>B</i>	3	13.18	332.5	80	288.7	1.39	3.19
	4	13.18	389.6	95	338.3	1.40	3.24
Conversion factor from Na to Na_2O						1.348	
Conversion factor from Na_2O to Na_2CO_3						1.710	

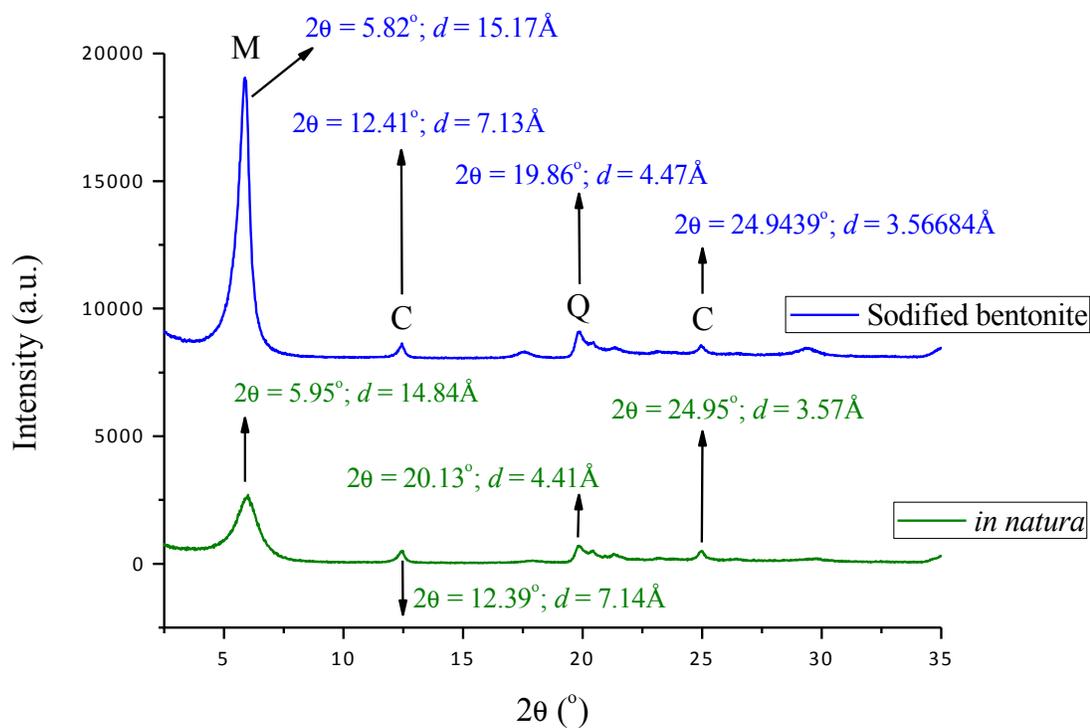


Fig. (2). XRD results from sodified and *in natura* clays. From this analysis is possible to note structural differences in both samples due to montmorillonite phase (M), as well as the minor phases – kaolinite (C) and quartz (Q).

Figure (3) shows how montmorillonite nanostructure changes with the addition of sodium, as observed by Alves *et al.* [4]. The basal distance measured in Fig. (2) shows no water between tetrahedral sheets. After sodium intercalation, the nanostructure should expand.

CONCLUSION

This is a practical method because it does not require complex techniques and gives fast results.

The results obtained by the proposed procedure gave reasonable values, with simple methodology. Moreover, it is of low cost and performs evaluation of the sodium clay amounts in materials being nanostructurally modified. The sample preparation does not demand time, and the calibration curve is easy to obtain. Such a curve provides a straight line in small sodium concentration intervals or even serves as a logarithmic function in larger concentration intervals. In fact, one expects that

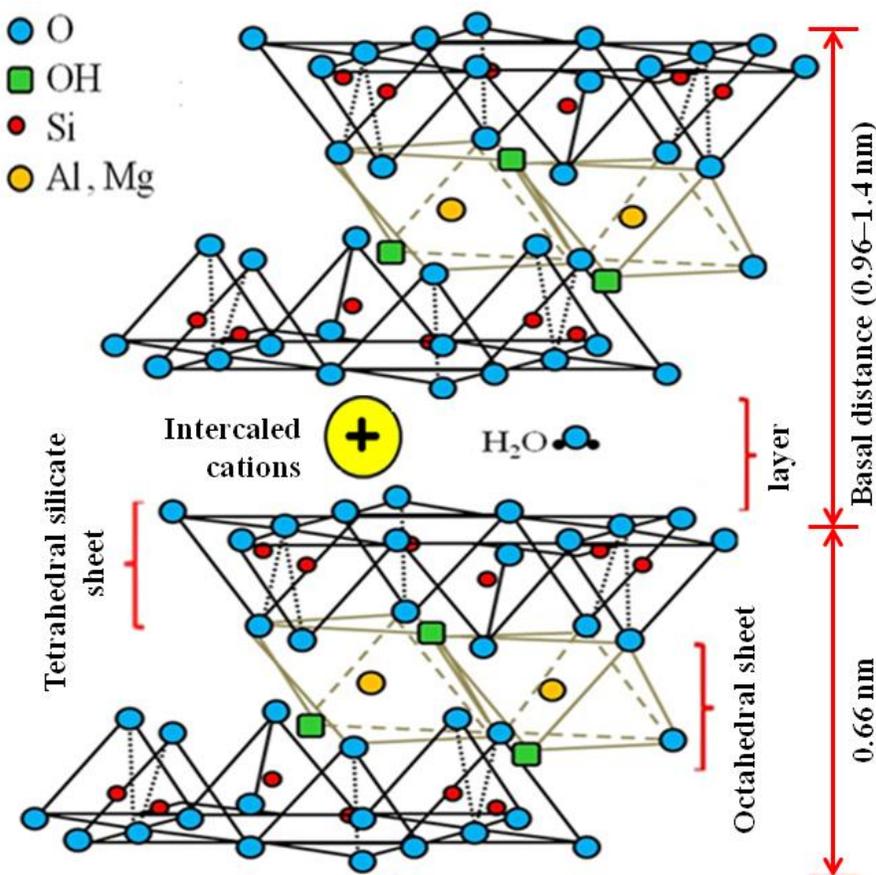


Fig. (3). Schematic diagram of the smectite structure, particularly montmorillonite.

for small intervals, the calibration curve must approximately be linear considering small variations of concentration of the alkaline metal.

X-ray characterization showed the occurrence of nanostructural modification at the largest peak, corresponding to interlayer 001 distance, related to montmorillonite phase that increased by means of the sodification process.

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

Not applicable.

FUNDING

None.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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