

## **A Preliminary Study on Organoclays from Two Peruvian Clay Pits**

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### **ABSTRACT**

We studied two groups of samples called “La Calera” and “Amotape,” *in situ* from the Peruvian districts of Alto Laran and Amotape, respectively. Different techniques were needed to characterise them. By using X-ray diffractometry, we determined their phases as well as corroborated the cation exchange process in some samples; however, in other samples there was a large interplanar spacing. Through transmission Mössbauer spectroscopy, we obtained the valence state of iron. Consequently, we determined that the samples contained calcium and sodium clays. Additionally, we proceeded to optimise the calcium clays by cation exchange to obtain sodium clays, which can be used in wastewater treatment and other applications.

**Keywords:** Cation exchange, montmorillonite, Mössbauer spectroscopy, transmission X-ray diffraction,

### **INTRODUCTION**

Environmental conservation is of vital importance to living beings as it offers numerous benefits. Motivated by this fact, we began to think of developing procedures to obtain organoclays in the Soil Analysis Laboratory, Faculty of Physical Sciences, Universidad Nacional Mayor de San Marcos (UNMSM). Organoclays, better known commercially as organically-modified nanoclays, are clays modified with organic cations. These clays have applications in the agricultural, industrial and medicinal sectors (Uddin 2008; Perugachi 2006; Patel 2014; Aguilar *et al.* 2006). For example, their use in agriculture allows the extraction of contaminants because organoclays are excellent adsorbents and/or degraders of toxic substances like pesticides.

Through fieldwork, we obtained two groups of clayey rock samples. One group named *La Calera* (ARC-CAL), was collected in the Alto Larán district, Chincha Province, Ica Region, Peru. The other group of samples, named

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*Amotape* (ARC-AMOT), was collected in the Amotape district, Paita province, Piura Region. By using an extraction kit, all these samples were extracted *in situ* from several sites and placed into different containers for coding.

Preparation tests were carried out in the SAL following a sedimentation process for the production of clays, followed by another process for optimisation. These processes are based on two scientific works utilising the principle of cation exchange (Nigam *et al.* 2004; Lee and Lee 2004). Likewise, physico-chemical analyses were carried out to determine the degree of acidity of the samples (pH).

## MATERIALS AND METHODS

### *Sample Extraction and Preparation*

It is possible to obtain relatively pure montmorillonite from the respective sample. Certainly, there are several methods, some of which are better than others. In our experimental work, we have followed the procedures of Lee and Lee (2004), Nigam *et al.* (2004) and Perugachi (2006).

The samples were prepared in the Soil Analysis Laboratory, dried at room temperature, ground in a mortar, and sieved. Then the process of obtaining the nanoclay began. This process is divided into three stages: (i) obtaining the clay fraction; (ii) obtaining montmorillonite followed by the process of ion exchange; and (iii) preparation of the nanoclay.

### *Obtaining the Clay Fraction*

Using the usual sedimentation method, the clay fraction of a size less than 2  $\mu\text{m}$  was obtained (Lee and Lee 2004; Nigam *et al.* 2004). In this method a dispersing agent was used for suspension (water/sample/dispersant). Specifically, following the procedure indicated by Perugachi (2006), the organic matter was first removed as it acts as a cementing agent of the clay particles, i.e., it does not allow for easy dispersion of the clay particles. Then the clay fraction was recovered by using the aforementioned procedure of Perugachi (2006), dried in a 60°C oven, registered and finally deposited in a desiccant.

### *Obtaining the Montmorillonite*

Once the clay material was obtained (<2  $\mu\text{m}$ ), our objective was to increase the montmorillonite probably present in the aforementioned material. Using the cation exchange method, calcium cations were exchanged for sodium cations. Again, following the procedure indicated by Perugachi (2006), the sample was split into four equal parts and placed in the respective tubes of a PLC Series centrifuge of the UNMSM. This was followed by centrifugation and separation of the liquid from clay. Subsequently, the montmorillonite clay was collected, dried, stored in a desiccator, and finally registered.

### *Preparation of the Nanoclay*

For modification of the clay at nano molecular level, the organic modifier Arquad HTM8-MS was used (Dehydrogenated Tallow, 2-ethylhexyl quaternary ammonium). Alkyl ammonium ion was used as organic cation to substitute for the Na<sup>+</sup> inorganic cation.

The preparation of nanoclays was based on a procedure suggested by two scientific papers ( Lee and Lee 2004; Nigam *et al.*, 2004). It needs to be noted that Perugachi (2006) also adapted the procedures of the above cited authors. Specifically, these were the steps: (a) In a glass container, 1200 ml of a solution of water/ethanol (4/1, v/v), was prepared, then heated to 60 °C. Next, 15 g of sodium montmorillonite clay solution was added into the solution and shaken for 2 h at 60 °C. (b) In another container, to 100 ml of distilled water, 5 g of Arquad HTL8-MS was added and then stirred until homogenisation was achieved. (c) The substances from these two containers were thoroughly mixed with an ultrasonic processor for an hour. (d) The mixing was continued for a further 12 h at 60 °C with a magnetic stirrer. (e) The supernatant water was next removed. (f) The residue was washed with a solution of water/ethanol (1/1, v/v). (g) Finally, it was dried, stored and registered.

## **EXPERIMENTAL MEASUREMENTS**

### *Physico-chemical Measurements*

In the Soil Analysis Laboratory, we prepared the samples for the physico-chemical analysis. which was essentially measuring the degree of alkalinity by using a pHTester BNC/OAKTON(model 35624-10).

### *X-ray Diffractometry*

For structural analysis of the minerals present in the samples, a BRUKER diffractometer (D8-Focus model) was used, with Cu-K $\alpha$  radiation  $\lambda = 1.54178$  Å(40 kV and 40 mA), and a vertical goniometer. The angle scale interval of the goniometer was set at  $4^\circ < 2\theta < 70^\circ$  with the  $2\theta$  advance being  $0.02^\circ$  per step at intervals of 3s per step.

### *<sup>57</sup>Fe Mössbauer Transmission Spectrometry*

Utilising a conventional spectrometer which had a signal with sinusoidal velocity modulation, and 1024 channels, detailed information on minerals containing iron was obtained.. The Mössbauer spectra were taken at room temperature (~298 K) in the SAL. These spectra were obtained in transmission geometry by using a <sup>57</sup>Co source in an Rh matrix; subsequently, these same spectra were analysed by using the Normos program by Brand (2002).

## RESULTS AND DISCUSSION

### *Physico-chemical Analysis*

In relation to the degree of alkalinity of the samples, Table 1 shows the measurements of the hydrogen potential of these samples.

TABLE 1  
pH measurements of the samples

Samples pH	
ARC- CAL	8.36
ARC- AMOT	8.97

### *X-ray Diffractometry*

The results obtained through XRD are shown in Figs. 1 and 2. In Fig. 1, the ARC-CAL and ARC-AMOT untreated samples can be observed; in this figure, structural phases can be seen for each of these samples. With regard to ARC-AMOT, we observe an overlapping of Mont + Ili (Mont = montmorillonite; Ili = illite); likewise, we notice Ili + Non (Non=nontronite) and major peaks of nontronite. As opposed to ARC-CAL, where we can see definite and overlapped peaks of Mont + Ili, for the ARC-AMOT sample, the results infer that it is calcium clay. Therefore, the sample needs to be treated chemically to obtain sodium montmorillonite.

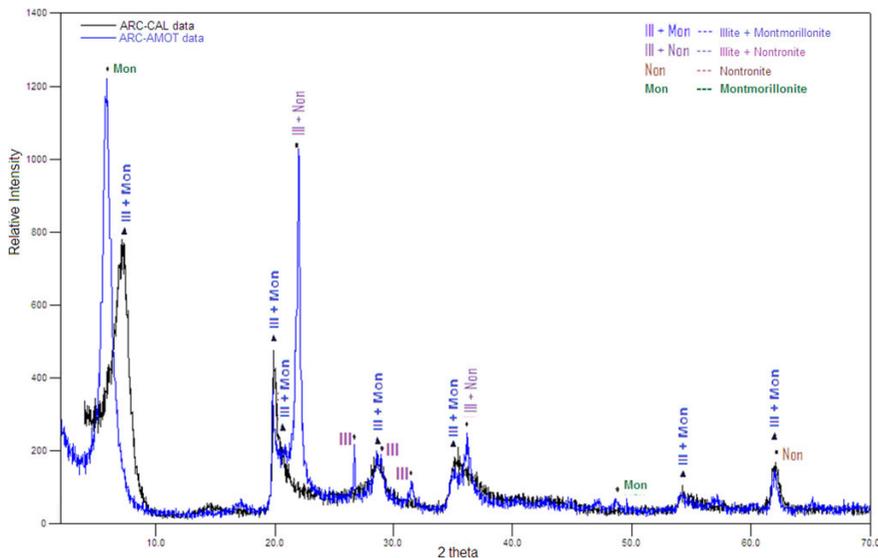


Fig. 1: Superimposed X-ray diffractograms of the ARC-AMOT and ARC-CAL untreated samples

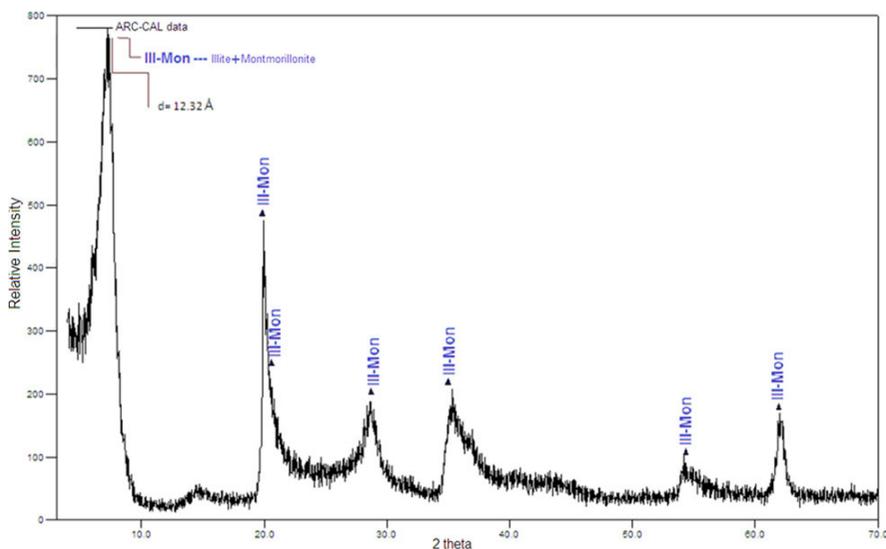


Fig. 2: X-ray diffractogram of the ARC-CAL treated sample; the observed interplanar distance  $d = 12.32 \text{ \AA}$  corresponds to sodium montmorillonite, after cation exchange treatment.

In Fig. 2, we can see that the ARC-CAL treated simple has two structural phases with their main peaks, illite and montmorillonite (typical clay phases). We also note the characteristic peaks of sodium montmorillonite, which has a simple layer of water at approximately  $d = 12.32 \text{ \AA}$ . In this regard, Roth (1951) and Williams *et al.* (1953) showed that at 50% relative humidity, sodium montmorillonite has a single layer of water, with  $d = 12.4 \text{ \AA}$ ; Murray (2007) has updated his book on these points. Also, the XRD results provides evidence that cation exchange has occurred; therefore, effectively, these are sodium montmorillonite clays. Furthermore, we observe that the peaks were wide, which could be due to the particle size.

Fig. 3 shows the evolution of the ARC-AMOT XRD diffractogram, where we had earlier observed overlapped peaks for both the treated and untreated samples. The interplanar distance is the same; however, the intensity of its peaks has decreased. In Fig. 4 we observe the final result: superposed peaks of ARC-AMOT, modified by the treatment. In this figure, on Amotape samples, specifically, we notice three curves: (a) ARC-AMOT ST (untreated sample, black colour); (b) ARC-AMOT TQ (with chemical treatment, pink color); (c) final ARC-AMOT (after cation exchange, blue color).

#### Transmission Mössbauer Spectroscopy

For a better fit of the hyperfine parameters, the results of TMS were registered at room temperature and at low speed (4 mm/s). In Fig. 5, we have the Mössbauer spectrum for the ARC-CAL sample. We can observe the presence of three

doublets: two of them associated with  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  sites, located in illite and montmorillonite, respectively (as already seen in the results by XRD). The third doublet is associated with a  $\text{Fe}^{3+}$  site.

In Fig. 6, we observe the TMS spectrum for the ARC-AMOT sample. We note the presence of three paramagnetic doublets: two of them associated to  $\text{Fe}^{3+}$

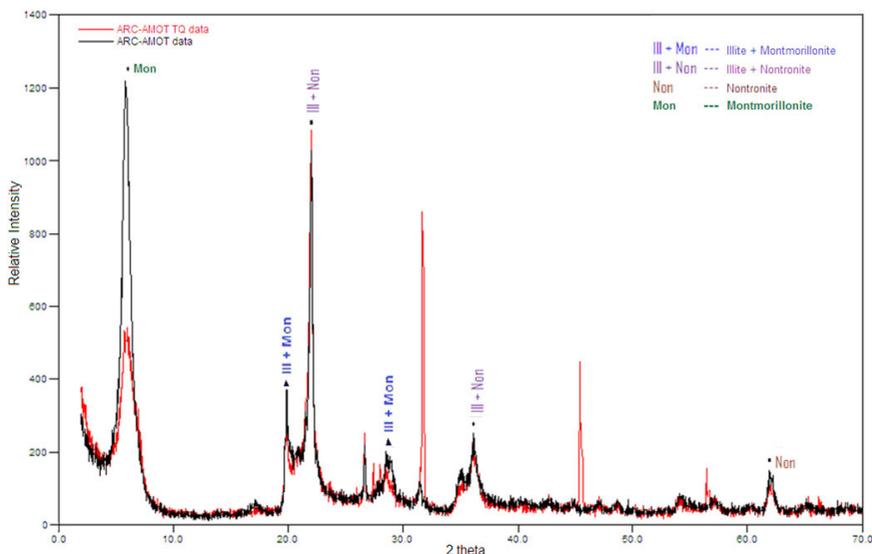


Fig. 3. Superimposed diffractograms of the ARC-AMOT samples. The treated and untreated samples are represented by red and black colours respectively.

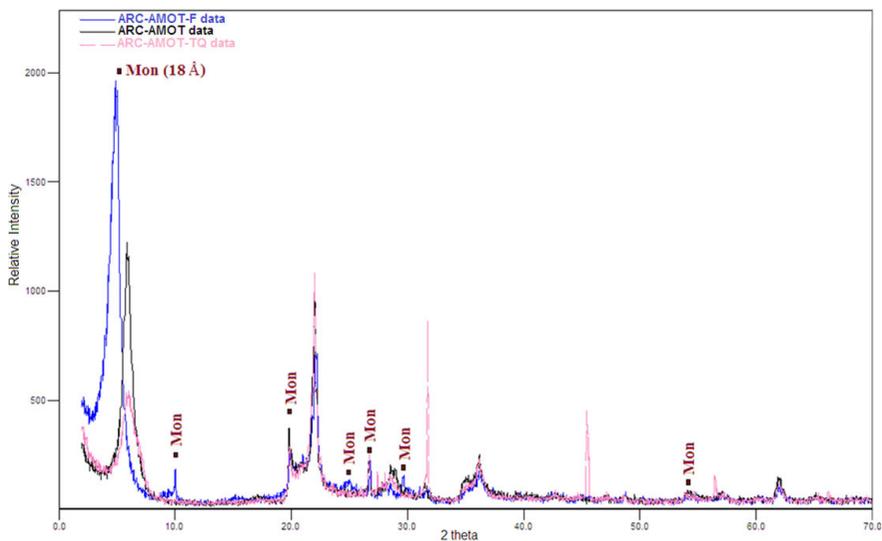


Fig. 4. Superimposed X-ray diffractograms of the Amotape samples: (1) untreated (ARC-Amot ST, black colour); (2) chemically treated (ARC-AMOT-TQ, pink colour); (3) after the cation exchange (ARC-AMOT-F, blue colour).

and  $\text{Fe}^{2+}$  sites, located in the illite and montmorillonite, respectively; the remaining doublet is associated with a  $\text{Fe}^{3+}$  site, which could be assigned to nontronite. These results corroborate the phases previously assigned by XRD.

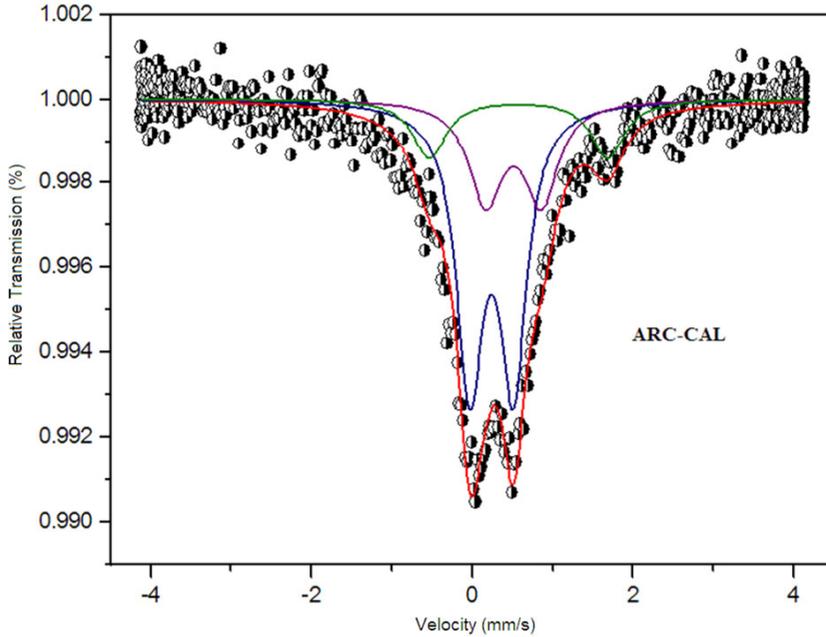


Fig. 5. ARC-CAL Mössbauer spectra registered at room temperature and at low speed (4 mm/s).

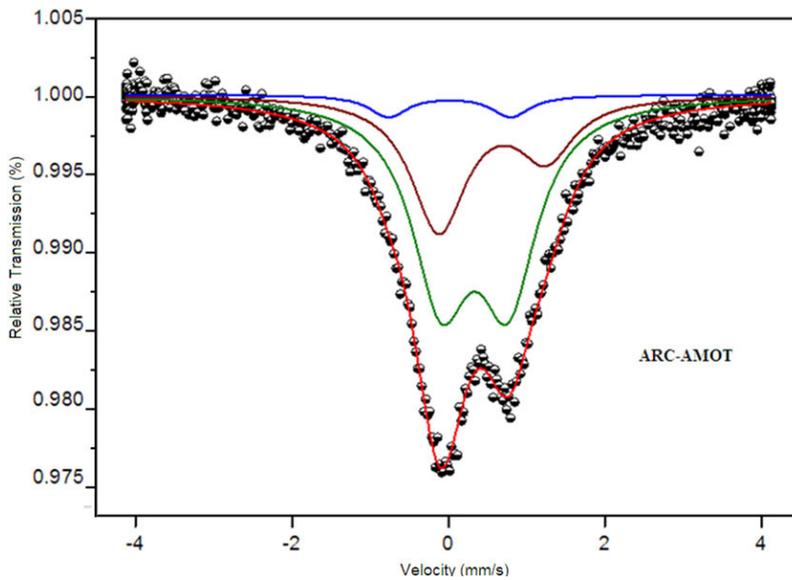


Fig. 6. ARC-AMOT Mössbauer spectra registered at room temperature and at low speed (4 mm/s).

## CONCLUSIONS

Through techniques earlier indicated, we have identified nanoclays in the Soil Analysis Laboratory in UNMSM. For the ARC-CAL sample, which was a sodium montmorillonite clay, we observed a peak with interlayer space  $d = 12.32 \text{ \AA}$ , a value very close to that obtained by other researchers ( $d = 12.4 \text{ \AA}$ ). For the ARC-AMOT IC sample, the interlayer space increased from 14.65 to 18.2  $\text{\AA}$ . This value offers a reason for continuing the investigation.

Finally, following up on this research will help in the implementation of protocols, optimal procedures and cost reduction. Consequently, all of these will lead to industrial production of nanoclay in the Republic of Peru.

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