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Effects of sodium hydroxide in a selective chemical treatment of Peruvian peloids

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The main purpose of this work is to apply the NaOH treatment to the silt and clay peloids in order to selectively concentrate iron oxides[1] by dissolving and removing phyllosilicates, for a better identification of oxides in the mineralogical composition of samples. For the mineralogical characterization of the samples that contain iron, especially for those that show magnetic ordering, transmission Mössbauer spectroscopy (TMS) was applied using the γ14.4 keV resonant nuclear transition in the the ^{57}Fe isotope; which allowed the detection od sesquioxides and other minerals that contain iron. For the identification of crystalline phases we use X ray diffractometry (XRD) technique. The NaOH treatment was applied sequentially to each sample and monitored by TMS and XRD. The results by TMS show paramagnetic doublets and the presence of partially oxidized magnetite. The XRD results of the samples without treatment show the presence of quartz and phyllosilicates such as vermiculite and halloysite. After selective chemical treatment the phyllosilicates were eliminated almost in their totality whereas the main (311) reflection beloging to iron oxide spinel was evident. As a general trend, the NaOH-treatment was significantly effective in concentrating iron oxide minerals in the studied peloids. The applied analytical techniques corroborate these results.

Keywords: Peloidss, Mössbauer spectroscopy, X ray diffractometry.

Efectos del hidróxido de sodio en un tratamiento químico selectivo de peloides peruanos

El propósito de este trabajo es la aplicación del tratamiento químico con NaOH en las fracciones de limo y arcilla de peloides a fin de concentrar óxidos de hierro y removeción de filosilicatos para una mejor identificación de los óxidos presentes en las muestras. Para la caracterización de muestras que contienen hierro y de manera particular aquellos que muestran ordenamiento magnético se aplicó la técnica de espectroscopia Mössbauer por transmisión (TMS) utilizando la transición nuclear resonante de γ14.4 keV en el isótopo ^{57}Fe, lo cual permitió la detección de sesquióxidos y otros minerales que contienen hierro. Para la identificación de fases cristalinas se utilizó difractometría de rayos X (XRD). El tratamiento con NaOH fue aplicado de manera secuencial a cada muestra, lo cual fue monitoreado por TMS y XRD. Los resultados por TMS muestran dobletes paramagnéticos y la presencia de magnetita parcialmente oxidada. Los resultados por XRD de las muestras sin tratamiento con NaOH muestra la presencia de cuarzo y filosilicatos como vermiculita y halloysita. Después del tratamiento se observa que algunos filosilicatos fueron eliminados en su totalidad, mientras la presencia de la reflexión principal (311) del óxido de hierro espinel se hace evidente. El tratamiento químico con NaOH fue significativamente efectivo en concentrar los minerales de óxidos de hierro presentes en los peloides estudiados. Estos resultados son corroborados por las técnicas aplicadas.

Palabras claves: Peloides, espectroscopia Mössbauer, difractometría de rayos X.

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1. Introduction

The peloids samples were extracted from *La Milagrosa* and *La Mellicera* salines located in the Chilca District, Cañete Province, near to Lima, Peru. The peloids are a natural product that forms in shallow layers at the bottom on hydric and saline deposits. Basically they are constituted by soil minerals and waters (Fe, Mg, Mn, S, Zn, P and Cu), oligoelements and geologic minerals (silicates, feldspars, quartz, mica and others); which in combination with natural sediments form a homogenous mass finely disperses [2,3]. The chemical selective treatment of the sodium Hydroxide (NaOH) was applied to the grain sized fractions silt and clay of peloid samples. An important step for this treatment is to determine the mineralogical composition of peloid samples. We began applying hydrogen peroxide to the samples in order to reduce the organic matter percentage and obtain better results[4-6]. The analysis of natural samples quite often requires concentrating the iron oxide minerals by selectively removing silicates or any mineral that contains aluminum[7]. This allows a better evaluation of the intrinsic properties of the iron oxides. The figure 1 shows the area map of the site from the samples were collected.

Figura 1: Location of *Las Salinas* site at Chilca District, Cañete Province, about 60 km south Lima, Peru.

2. Materials and methods

The samples were extracted in April 2006. The samples were collected from a 30 cm depth, approximately. After, were dried in a muffle furnace to 27°C and then sieved to 325 mesh in order to obtain grains of diameter <0.045 mm. The clay fraction (<0.002 mm) denominated MLG was obtained by sedimentation method[5] from *La Milagrosa* salines. Transmission Mössbauer spectroscopy (TMS) and X-rays diffractometry (XRD) were used as analytical techniques[8]. We used 200 mg of MLG sample for the MS analysis. The Mössbauer spectra were taken in a spectrometer in the mode transmission geometry using a ^{57}Co source in a Rh matrix and analyzed using the Normos program of Brand[9,10], making use of the version for crystalline sites (Normos Site) and of the version for distributions of hyperfine fields (Normos Distributions). The structural identification of mineral compounds of the samples were made by XRD, using a MINIFLEX RIGAKU diffractometer (which used the Cu-Kα radiation, λ=1.54178 Å) with a vertical goniometer[11]. The measurements were made with $4^\circ < 2\theta < 85^\circ$, 0.03° angular step and 2 s/step of counting time. About 500 mg of sample was used using a powder mount.

The physico-chemical analysis consisted of measuring pH of each sample using the instrument pHTester BNC/Oakton model 35624-10. For determining the organic matter percentage we used Walkley-Black method[5]. The organic matter removal was made using 30 % hydrogen peroxide (H_2O_2) (wt/wt)[6]. The NaOH treatments were applied in sequence. We made three successive steps, each step consist of adding 75 ml 5 M NaOH on 5 g sample that has to be under heat at 90°C by 1 hour. The collected remains were washed with diluted hydrochloric acid, HCl.

3. Results and discussion

The percentage of organic matter for the raw sample was 1.081 % and after H_2O_2 treatement was 0.3196 %. The pH value for the raw sample was 8.9. In the results for MLG sample, Fig. 2, the progressive enrichment of iron oxide is observed. In MLG2 without treatment, Fig.2.a, it does not display a hyperfine magnetic structure; in the same sample with a single NaOH treatment, Fig.2.b, an incipient hyperfine magnetic structure is observed, finally after the second NaOH treatment the presence of magnetic components with characteristics of being a magnetite partially oxidized -see Fig.2.c-, are observed. Magnetite is a member of the spinel group and has a mixture of $Fe^{3+,2+}$ valences in octahedral sites, we found a hyperfine magnetic field, $\langle B_{hf} \rangle = 45.98$ T, with an average isomer shift of relative to α-Fe, $\delta = 0.68$ mm/s, a quadrupole splitting of $2\varepsilon_Q = 0.02$ mm/s, with area of 7.39 %, and a contribution from Fe^{3+} in tetrahedral sites, with a maximum hyperfine magnetic field $\langle B_{hf} \rangle = 48.28$ T, $\delta = -0.206$ mm/s and $2\varepsilon_Q = -0.04$ mm/s, with area of 17.18 %. We also observed the presence of three doublets.

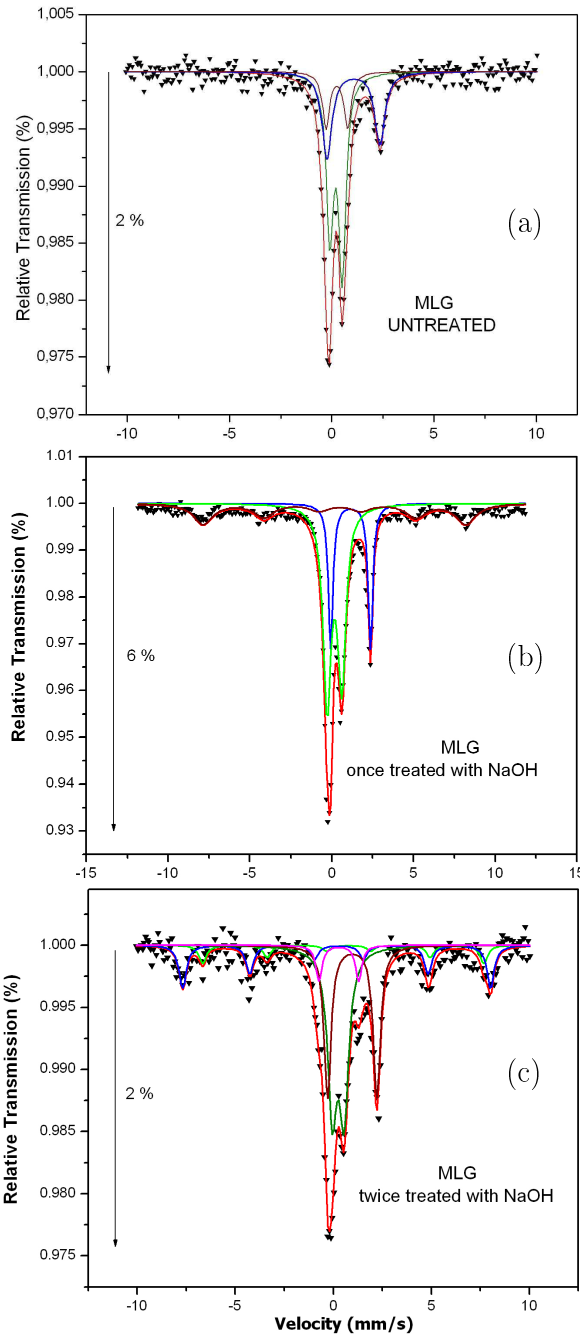

Figura 2: Mössbauer spectra of the MLG sample are shown. In (a) untreated sample, (b) after once, and (c) after two sequential NaOH treatments, respectively.

In the Fig. 3, we observe the evolution of the X ray difractograms MLG sample. The espectrum for untreated sample, see the upper, show the presence of quartz, illita, phyllosilicates like as vermiculite and halloysite. For the same sample under two and three sequential NaOH-treatment are show in the middle and lower spectra, respectively. We observe that phyllosilicates have been eliminated almost in their totality and the main (311) reflections of spinel iron oxide are observed. Drosdoff and Miles, in 1938, noted the destruction of mica and some vermiculite samples when was treated with 6 % and 30 % (wt/wt) H_2O_2[8]. The results obtained by TMS and XRD improve noticeble after the sequential NaOH treatments. Both techniques corroborate the presence of the iron oxide, magnetite.

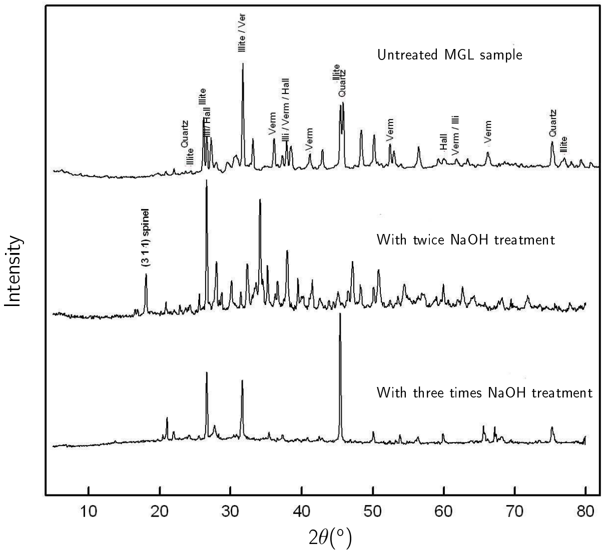

Figura 3: XRD spectra of the MLG sample are shown. The upper spectrum belong to an untreated sample, the middle is the same sample with twice NaOH treatment and the lower is with three sequential NaOH treatments. X-ray wavelength λ=1.54178 Å.

4. Conclusions

The NaOH treatment was significantly effective in eliminating the phyllosilicates and concentrating the iron oxide minerals peloids. The sample treated twice with NaOH and without adding hydrochloric acid for washing shows the (311) reflections of the iron oxide spinel; nevertheless the elimination of phyllosilicates is minimum. After three NaOH treatment and washed with hydrochloric acid we have observed that the phyllosilicates has been completely eliminated, moreover the presence of the (311) peak vanishes also. We know that the HCl acid treatment can modify the mineral structure and its adsorption capacity. We observed too that the sample with three NaOH treatment has a larger capacity for absorption of humidity. Therefore we could affirm that the followed NaOH method is fulfilled perfectly for the soil study; nevertheless for the peloid samples we must take into account two cases. First, with NaOH treatment without HCl washing is able to concentrate iron oxides, and second, the NaOH treatement with HCl washing eliminates the phyllosilicates and the spinel phase completely.

The NaOH treatment was efficient in the mineral concentration proccess of iron oxides from peloids samples with certain limitations.

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