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## Mechanisms of Pb (II) sorption and desorption at some clays and goethite-water interfaces

Mario BUSINELLI\*, Federica CASCIARI, Daniela BUSINELLI, Giovanni GIGLIOTTI

Dipartimento di Scienze Agroambientali e della Produzione Vegetale dell'Università degli Studi di Perugia, Borgo XX Giugno 72, 06121 Perugia, Italy

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**Abstract** – The aim of this research is to corroborate the results obtained with Pb (II) sorption and desorption macroscopic equilibrium studies on some soil minerals (montmorillonite, illite, kaolinite and goethite) using microscopic techniques. The sorption isotherms demonstrate that the adsorption capability of the substrates varies in the following sequence: illite > montmorillonite > kaolinite > goethite, and the desorption isotherms demonstrate the irreversibility of the bonds formed. pH adsorption edges on montmorillonite show that at a pH lower than the hydrolysis point the sorption edge is primarily due to ion exchange, while at a pH higher than the hydrolysis point, it is a combination of both ion exchange and precipitation. The EDS semi-quantitative analysis performed by SEM demonstrates that in the clays Pb replaced almost exclusively Ca ions. In the montmorillonite this replacement may also include the Ca ions in the interlayer space, and in the illite also, the replacement of protonated OH groups and the K ions situated at the edge of interlattice sites. Goethite shows an adsorption capability of the same magnitude as kaolinite.

lead / clays / goethite / sorption-desorption / microscopic techniques

**Résumé – Mécanismes d'absorption et de désorption du Pb (II) à l'interface entre solution aqueuse et certaines argiles et la goéthite.** L'objectif de cette recherche est d'étayer, au moyen de techniques microscopiques, les résultats obtenus par le biais d'études macroscopiques d'équilibre sur l'absorption et la désorption du Pb (II) sur certains composants minéraux du sol (montmorillonite, illite, kaolinite et goéthite). Les isothermes d'absorption ont montré que la capacité d'adsorption des substrats variait de la façon suivante : illite > montmorillonite > kaolinite > goéthite, et les isothermes de désorption ont démontré l'irréversibilité des liens formés. La variation du pourcentage de Pb adsorbé par la montmorillonite en fonction du pH montrait que, lorsque l'on a une valeur de pH inférieure au point d'hydrolyse, l'absorption est principalement due à une réaction d'échange ionique alors que, lorsque l'on a une valeur de pH supérieure au point d'hydrolyse, l'absorption est due à une combinaison de réactions d'échange ionique et précipitation. Les analyses semi-quantitatives effectuées au microscope électronique à balayage (MEB) couplé à la micro-analyse aux rayons X par dispersion d'énergie (EDS) ont démontré que, dans les argiles, le Pb remplaçait exclusivement les ions Ca. Dans la montmorillonite, cette substitution pourrait intéresser aussi les ions Ca de l'espace interlamellaire et, dans l'illite, il pourrait également y avoir substitution de groupes OH protonés et d'ions K situés au bord des sites interstrates. La goéthite a montré une capacité d'adsorption équivalente à celle de la kaolinite.

plomb / argiles / goéthite / absorption-désorption / techniques microscopiques

### 1. INTRODUCTION

Sorption reactions at soil-water interfaces decrease solute mobility, thus controlling the fate, bioavailability, and transport of trace metal ions in aquatic and soil environments. Correctly determining the sorption mechanism of metals on clay and other mineral surfaces is important for understanding the fate of such pollutants in contaminated soils and sediments, and will facilitate successful environmental remediation procedures [9].

The forces involved in adsorption can range from weak, physical, Van der Waals forces and electrostatic outer-sphere complexes (e.g. ion exchange) to chemical interactions. As the amount of a metal cation or anion sorbed on a surface increases to a higher surface coverage, a surface precipitate can form. There is a continuum between surface complexation (adsorption) and surface precipitation. At low surface coverages, surface complexation tends to dominate. As surface coverage increases, first nucleation and then precipitation occur. Another process is the diffusion of molecules or ions through

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\* Correspondence and reprints  
mbusinelli@unipg.it

crystalline solids that has to be interpreted to mean transfer through micropores, faults, or interfaces of the solid rather than through the lattice itself [8].

Another important process to evaluate the retention of metal ions from the soil constituents is the release of adsorbed species, often referred to as desorption. It is often observed that desorption is a more difficult process than adsorption and that not all of the adsorbate is desorbed, i.e., the reactions appear to be irreversible. Such irreversibility is commonly referred to as hysteresis or nonsingularity. In such cases, the adsorption and desorption isotherms corresponding to the forward and backward reactions would not coincide [14]. There are a number of reasons why “non-real hysteresis” may be observed, including artifacts related to experimental conditions and chemical transformations that occur during a particular experiment [11]. However, it appears that “real hysteresis” can occur, and this is affected dramatically by the type of the adsorbent, and the time over which the adsorption process has occurred [8].

Kinetic studies can also reveal something about reaction mechanisms at the soil particle/solution interface, particularly if energies of activation are calculated and stopped-flow or interruption techniques are employed.

In spite of many decades of intensive efforts by soil chemists to understand sorption processes, our understanding of the mechanisms of chemical reactions at the soil/liquid interface is still not definitive. One of the main reasons for this is that until quite recently, studies of the reactions between environmental particle surfaces and aqueous solutions were limited to macroscopic studies. Now it appears more and more evident that molecular and/or atomic resolution surface techniques should be employed to corroborate the proposed mechanisms hypothesized from equilibrium and kinetic studies. These techniques can be used either separately or, preferably, simultaneously with macroscopic investigations [8].

The aim of the present study is to corroborate the results obtained with Pb(II) sorption and desorption macroscopic equilibrium studies on three of the most representative clay minerals (montmorillonite, illite and kaolinite) and the most common iron oxide (goethite) present in the soil using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray microanalysis (EDS), X-Ray Powder Diffraction (XRPD) and Thermogravimetric Analysis (TGA).

## 2. MATERIALS AND METHODS

### 2.1. Materials

Montmorillonite (Upton, Wyoming), illite (Fithian, Illinois), kaolinite (Macon, Georgia) and goethite (Rheinland, Germany), were obtained from Ward's Natural Science Establishment, USA. The CEC, as determined by the Gillman method [7] and the external surface areas, as determined by BET-N<sub>2</sub> analysis [1] were 55.5 cmol·kg<sup>-1</sup> and 30 m<sup>2</sup>·g<sup>-1</sup> for montmorillonite, 20.5 cmol·kg<sup>-1</sup> and 52 m<sup>2</sup>·g<sup>-1</sup> for illite, 6.0 cmol·kg<sup>-1</sup> and 18 m<sup>2</sup>·g<sup>-1</sup> for kaolinite and 2.5 cmol·kg<sup>-1</sup> and 10 m<sup>2</sup>·g<sup>-1</sup> for goethite.

The montmorillonite sample was Na-saturated by washing 0.1 g of sample with 20 ml of 1 M NaCl three times, then four times with deionized water to remove excess salts. Impurities were removed from the clay by centrifugation. Carbonates in the smectite were decomposed by rapidly lowering the pH of a stirred clay slurry to 3.5 with 0.1 M HCl. After the carbonates were decomposed, the pH of the slurry was raised to pH 7.0 with 0.1 M NaOH. The clay slurry was then washed twice with deionized water to remove any residues. The clay fraction ( $\leq 2 \mu\text{m}$ ) was freeze-dried before being used in the experiments [10].

The Ca-clays were prepared by washing 0.1 g of the fraction  $< 2 \mu\text{m}$  three times with 20 ml of 1 M Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and removing the excess salt by washing and centrifugation with distilled water until the test for NO<sub>3</sub><sup>-</sup> was negative [3].

The Pb-clays and Pb-goethite were prepared from 0.1 g of Ca-clays and goethite samples, respectively, by washing the samples three times with 20 ml of 1 M Pb(NO<sub>3</sub>)<sub>2</sub> and removing the excess salt by centrifugation as above.

### 2.2. Sorption and desorption isotherms

For the sorption isotherm, about 0.1 g of Na-montmorillonite, illite, kaolinite and goethite were separately weighed into 50 ml centrifuge tubes and each mixed with 20 ml solutions of 0.1 mM, 0.5 mM, 1 mM, 5 mM and 10 mM Pb(NO<sub>3</sub>)<sub>2</sub> in solutions with an ionic strength of 10 mM NaNO<sub>3</sub>. The isotherm data were obtained at pHs which were not kept constant, but which were verified to remain  $< 6.5$ . The tube was flushed with N<sub>2</sub> gas for 1 minute and capped tightly before being shaken at 60 rpm at 23 °C for four days. The suspension was removed, the pH was measured with a glass electrode and the Pb concentration in the solution was determined by Atomic Adsorption at 283.3 nm in an air-acetylene flame using a Perkin Elmer model 560 spectrophotometer. Pb sorbed by the soil was calculated as the difference between the initial and the equilibrium concentrations [10]. Desorption was initiated from each sorption soil suspension by replacing the removed 10 ml aliquot with 10 ml of 10 mM NaNO<sub>3</sub>. The mixture was resuspended by vigorous agitation and shaken under N<sub>2</sub> for four days. The suspension was centrifuged and 10 ml of the supernatant were removed for Pb analysis. This procedure was repeated five times, resulting in a total of six desorptions for each adsorption sample tested.

### 2.3. Lead sorption pH-edge

For the determination of the pH-edge, about 0.1 g of Na-montmorillonite sample was mixed with 20 ml of 0.5, 1 and 2 mM Pb(NO<sub>3</sub>)<sub>2</sub> in 10 mM NaNO<sub>3</sub>. The mixture was titrated to different pHs ranging from pH 2.5 to pH 8.8 using 0.1 M NaOH or 0.1 M HNO<sub>3</sub> and shaken under N<sub>2</sub> for four days. The reaction was stopped by centrifugation and the supernatant saved for Pb determination [10].

### 2.4. Scanning electron microscopy (SEM) and energy dispersive X-ray microanalysis (EDS)

The Ca-samples and Pb-samples were placed in a vacuum desiccator containing CaCl<sub>2</sub> to be dried before being viewed with a scanning electron microscope.

SEM examinations and EDS semi-quantitative analyses were performed on a Philips XL30 scanning electronic microscope fitted with a LaB<sub>6</sub> electron gun and an EDAX/DX4 analyzer. The samples were prepared by taking a small amount (~25 mm<sup>2</sup>) from the conditioned substrates. All samples were coated with a thin carbon layer in order to obtain a conductive surface.

EDS analyses were carried out on a cross-section of 400 μm<sup>2</sup>, the same for all samples.

### 2.5. X-ray powder diffraction (XRPD)

Relative changes in the basal spacings of Ca-clays and Pb-clays, prepared as in Section 2.1, were measured by X-ray powder diffraction (XRPD) to determine whether Pb intercalated the clay minerals. XRPD patterns at 25 °C were recorded with a computer-controlled Philips PW1710 diffractometer using a Ni-filtered CuKα radiation (40 kV, 30 mA). All the samples were previously conditioned at 75% relative humidity (r.h.).

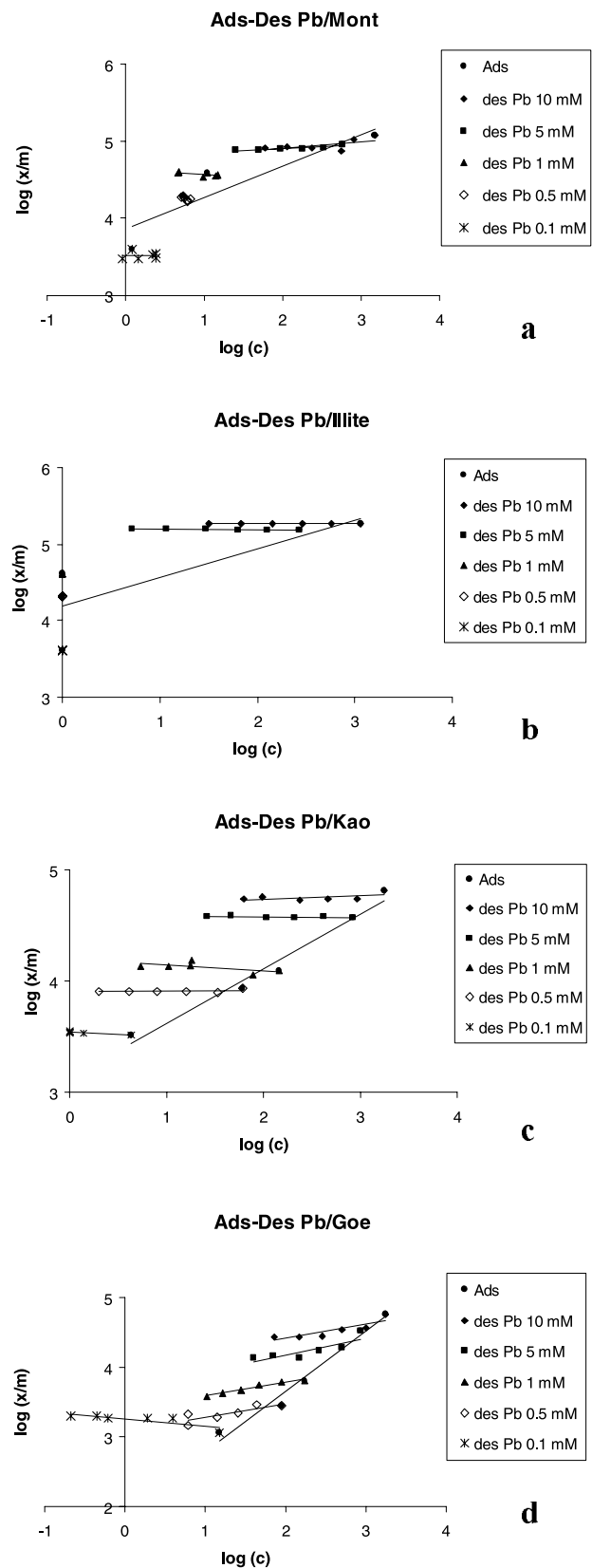
### 2.6. Thermogravimetric analyses (TGA)

The Ca-montmorillonite and Pb-montmorillonite samples observed with XRPD were also examined with thermogravimetric analysis (TGA). This is a technique whereby a sample is continuously weighed as it is being heated at a controlled rate. The change in weight is recorded against the temperature and yields information on the thermal stability and composition of the material under investigation. Thermal analyses were performed in air using a Stanton Redcroft Thermal Analyzer STA781 at a heating rate of 5 °C/min.

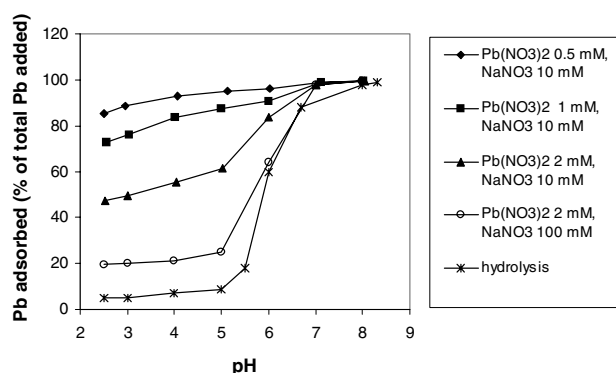
## 3. RESULTS AND DISCUSSION

As Strawn et al. [12] showed that adsorption kinetics of Pb(II) at the aluminum oxide-water interface at pH 6.5 were initially fast, resulting in 76% of the total sorption occurring within 15 min., followed by a slow continuous sorption reaction likely resulting from diffusion through micropores, and Shen et al. [10] showed that all the Pb sorption in the smectite took place within 0.1 h, after which the sorption kinetics exhibited a plateau, a time period of four days was considered adequate to reach equilibrium conditions in pH-edge and isotherm studies.

Figure 1 shows the Pb Freundlich adsorption and desorption isotherms [6] on montmorillonite, illite, kaolinite and goethite. The study was performed using solutions of Pb(NO<sub>3</sub>)<sub>2</sub> of different concentrations with uncontrolled pH values varying from 5.87 to 4.30. All the isotherms are L-type with 1/n similar values for clays (0.40, 0.37 and 0.49 for montmorillonite, illite and kaolinite, respectively) and an approximately double value for goethite. This means that the lead adsorption on goethite is more sensitive to the changing of lead concentration in the equilibrium solution. The clay K<sub>F</sub> values are, on the contrary, 183, 87 and 16 times higher for illite, montmorillonite and kaolinite, respectively, than the goethite K<sub>F</sub> value (84 ml·g<sup>-1</sup>). This means that the adsorption capability of clay is higher than that of iron oxide. Each point



**Figure 1.** Adsorption and desorption isotherms of Pb on (a) montmorillonite, (b) illite, (c) kaolinite and (d) goethite.



**Figure 2.** The pH edge of Pb retention in montmorillonite from lead nitrate.

of the adsorption and desorption isotherms was obtained at a different pH value due to the different lead solution concentration used to fit the isotherms.

To evaluate the effect of the pH-adsorption edges for lead sorption on the montmorillonite, another experiment as described in Section 2.3 was performed (Fig. 2). At the same ionic strength (10 mM), the edge was shifted to a higher pH when lead concentration increased. The percentage of lead sorption on the montmorillonite increased with decreasing Pb concentration at a pH below the Pb hydrolysis point. At the same concentration of Pb (2 mM), increasing ionic strength from 10 to 100 mM sensibly decreased lead adsorption at the pH below the Pb hydrolysis point (Fig. 2). This indicated that the Pb sorption mechanism in the low pH range was primarily ionic exchange. Pulse et al. [5] and Shen et al. [10] reported a similar behavior in Pb sorption with increasing ionic strength. Above the Pb hydrolysis point, almost all the Pb was retained by montmorillonite, regardless of the Pb concentration and ionic strength (Fig. 2). This means that above this pH value chemisorption and precipitation are the main causes of Pb retention.

As the pH is an important parameter that affects the magnitude and the quality of the Pb sorption, we have shown in Table I the pH corresponding to the Pb sorption percentages of the points used to fit the isotherms given in Figure 1. Obviously, for all the substrates the sorption percentage

decreases as the initial solution concentration increases. The high total sorption obtained at low concentrations up to 1 mM for illite is due to the high pH values of the experiment (from 7.5 to 7.9) that cause Pb precipitation. This behavior is also found in montmorillonite and, to a lesser extent, in kaolinite, but only with the 0.1 mM solution. This effect is not found in goethite, where the pH values are always around four. The data referring to 5.0 and 10.0 mM concentrations that are obtained at low pH values (from 3.6 to 5.1) enable us to evaluate the adsorption capability of the substrates, that varies in the following sequence: illite > montmorillonite > kaolinite > goethite.

The desorption isotherms that show a complete hysteresis (Fig. 1) testify to the irreversibility of the bonds formed between Pb and the substrates, also for the pH below the hydrolysis point. Thus the Pb retention on the substrates examined can be attributed to the formation of inner-sphere complexes.

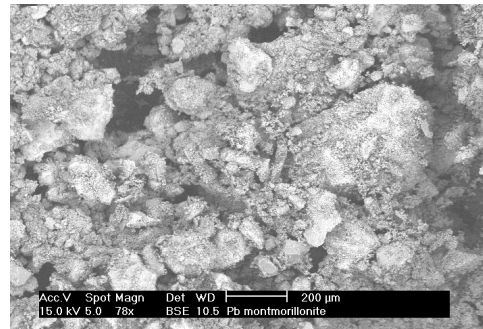
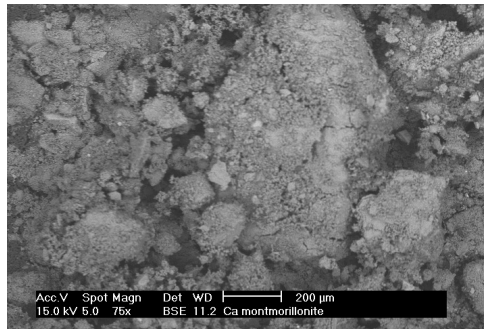
As the aim of our work was to clarify the bonds involved in Pb retention on different substrates, we did our next study (SEM-EDS, XRPD and TGA analysis) at a pH lower than the Pb hydrolysis point, where the interference of the Pb precipitation does not occur. The study was performed on the dried solid obtained from a suspension prepared by mixing the substrate with 1 M  $\text{Pb}(\text{NO}_3)_2$  solution in the solid/solution ratio =  $5 \text{ g} \cdot \text{L}^{-1}$ .

Figure 3 shows the SEM back-scattered electron images of the four substrates before and after the Pb saturation. As can be seen, the presence of lead is evidenced by the brightness of the images. In the case of goethite, this difference in brightness cannot be seen because Fe also causes brightness. In Table II, EDS semi-quantitative analyses of Ca- and Pb-clays and untreated and Pb-treated goethite are reported. The data show that in the montmorillonite, Pb ions mainly replaced Ca and Mg ions, probably with an exchange mechanism. In the illite, the Pb sorbed is not balanced by equivalent cation desorption as only Ca decreases, but this decrease is not enough to justify a simple exchange process. This behavior may be explained both by a chemisorption process involving protonated OH groups that are displaced as  $\text{H}_2\text{O}$  molecules and replaced by Pb ions, leading to the formation of inner-sphere metal complexes through a ligand exchange process [2], and also

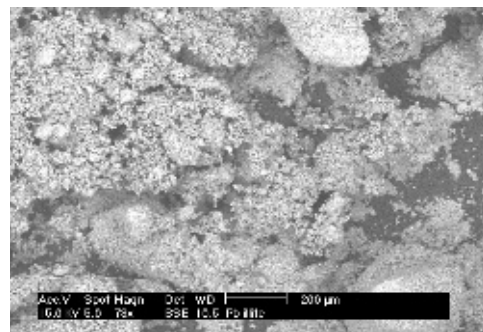
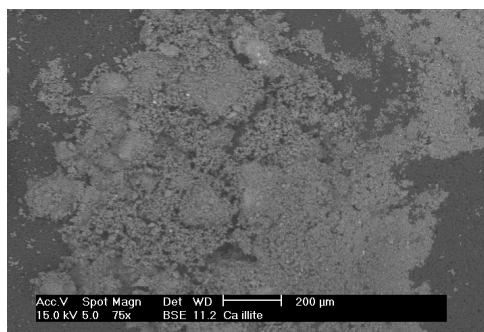
**Table I.** pH and adsorption percentage values of the liquid phase of the suspensions prepared by mixing 0.1 g of the various adsorbents (M = montmorillonite, I = illite, K = kaolinite, G = goethite) with 20 ml of solutions with different Pb concentrations.

Initial solution concentration (mM)	pH and adsorption percentage values							
	M		I		K		G	
	pH	% ads.	pH	% ads.	pH	% ads.	pH	% ads.
0.1	7.2	94.5	7.9	100	5.9	79	4.4	27.5
0.5	6.3	94.8	7.6	100	5.3	41.2	4.0	13.5
1.0	6.0	94.7	7.5	100	5.1	30	3.9	15.7
5.0	5.0	43.6	5.1	74.2	4.8	17.9	3.7	15.9
10.0	4.9	28.4	4.8	44.5	4.8	16.7	3.6	13.9

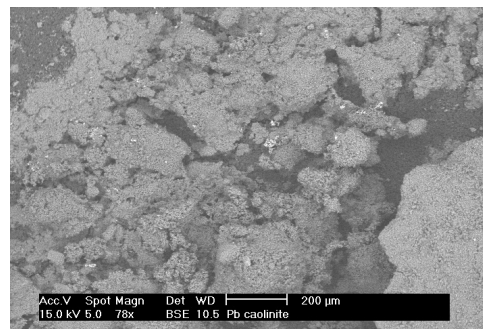
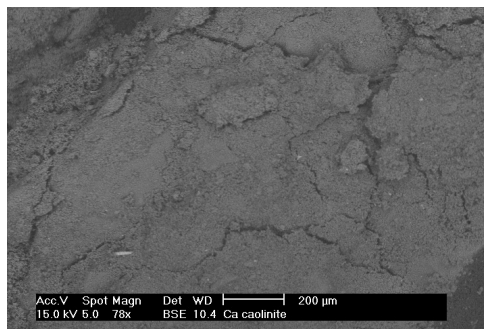
## Montmorillonite



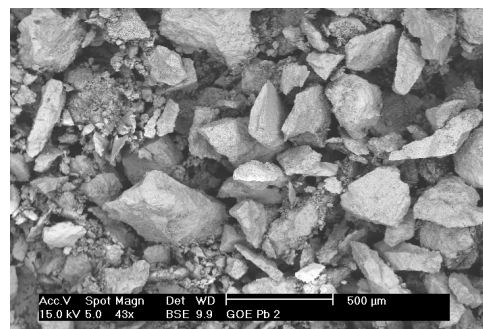
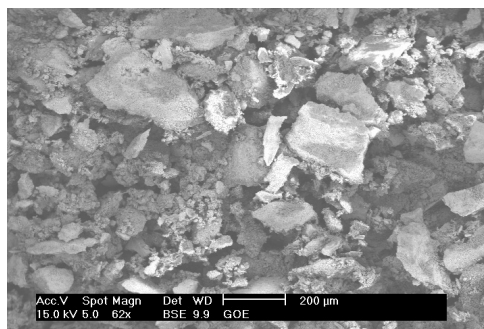
## Illite



## Kaolinite



## Goethite



**Figure 3.** SEM back-scattered electron images of the Ca-clays and untreated goethite (on the left) and the respective Pb-clays and Pb-goethite (on the right).

**Table II.** Elemental compositions of Ca- and Pb-clays (M = montmorillonite, I = illite, K = kaolinite) and untreated and Pb-treated goethite (G) from EDS microanalysis. The results are expressed as moles of element on 100 g of substrate.

Element mol/100 g	M		I		K		G	
	Ca	Pb	Ca	Pb	Ca	Pb	untreated	Pb
Si	1.1588	1.0102	0.9975	0.7840	0.8985	0.8878	0.1587	0.4292
Al	0.3843	0.3443	0.4808	0.4137	0.8224	0.8116	0.0596	0.2729
Na	0.0232	0.0235	0.0403	0.0416	0.0184	0.0126	0.0252	0.0465
K	0.0106	0.0081	0.1004	0.0836	0.0053	0.0045	-	-
Mg	0.0814	0.0712	0.0821	0.0752	0.0236	0.0208	0.0816	0.5491
Ca	0.0470	0.0050	0.0304	0.0039	0.0050	-	-	-
Pb	-	0.0672	-	0.0840	-	0.0090	-	0.0033
Fe	0.0400	0.0284	0.0411	0.0489	0.0028	0.0049	1.0249	0.4329
Si/Al	3.0154	2.9341	2.0747	1.8951	1.0925	1.0939	-	-

because the edge situated in interlattice sites became occupied by Pb ions other than K, presumably leading to partial opening of the interlattice space [4].

Kaolinite and goethite have a similar behavior. This is not surprising, because in this clay, the sorption of aqueous species and the development of a surface charge are controlled mainly by amphoteric reactions at oxygen sites on aluminol and siloxane surfaces that are conceptually similar to surface reactions on oxide minerals. Compared with 2:1 clays the Pb sorption of kaolinite and goethite is almost ten times lower. This can be explained because it has been demonstrated [12] that the bonds between Pb and aluminol sites are weak compared with the bonds formed between Pb and the functional groups of 2:1 clays; moreover, this may be due to the low pH of kaolinite and goethite suspensions; the surface charge is likely to be positive, so that a repulsion of Pb may occur.

Excepting Ca, all the other elements of the clays do not show notable variations going from the Ca-clays to the Pb-clays. The Si/Al ratios also remain the same. On the contrary, the goethite shows a notable decrease in Fe content. This may be due to the dissolution process that occurs on the  $\alpha$ -FeOOH (goethite) in acidic media [13] such as the  $\text{Pb}(\text{NO}_3)_2$  solution. This dissolution that causes a decrease in Fe content in goethite, and consequently an apparent increase in the other elements (Si, Al, Na and Mg), may also contribute to the lowering of the sorption of Pb on the oxide surfaces.

XRPD spectra of the clays before and after Pb saturation (Fig. 4) testify that no modification occurred in illite (Fig. 4a) and kaolinite (Fig. 4b) and the only change in montmorillonite (Fig. 4c) is the decrease in the interlayer spacing from 1.7 to 1.4 nm. This decrease could be due to the replacement of hydrated Ca ions (radius 0.6 nm) with Pb ions (radius 0.45 nm) in the interlayer space, lowering its water content, as shown by the TGA curves of Pb- and Ca-montmorillonite given in Figure 4d. As concerns illite, the similar diffraction pattern of the Ca- and Pb-saturated clay does not exclude the possibility of a penetration of Pb ions inside the interlayer space through the edge sites at the border of the illite sheets, replacing K ions,

that cannot be evidenced by the XRPD spectra. This could explain the higher Pb retention capability of illite as compared with the montmorillonite clay.

#### 4. CONCLUSIONS

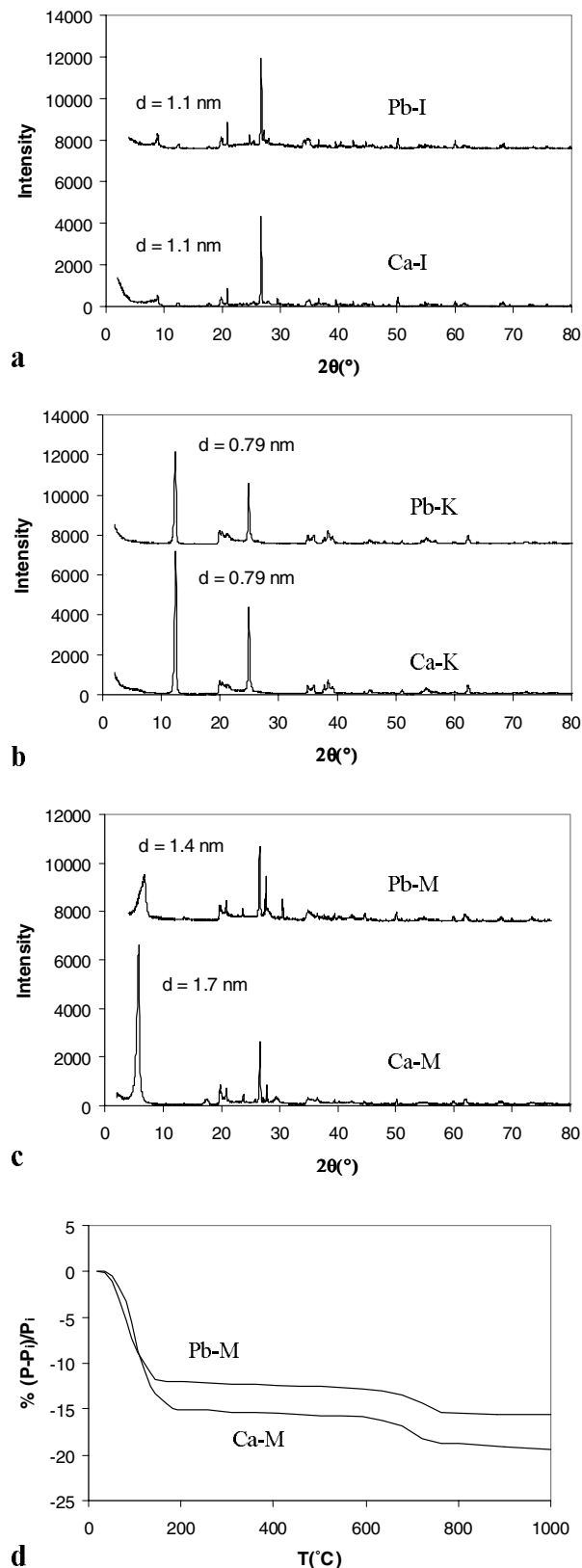
The sorption isotherms under uncontrolled pH conditions fitted with the Freundlich equation on montmorillonite, illite, kaolinite and goethite demonstrate that the adsorption capability of clays was higher than that of iron oxide, and can be classified in the sequence illite > montmorillonite > kaolinite.

The desorption isotherms demonstrate the irreversibility of the bonds formed between Pb and the substrates that we examined, supporting the hypothesis of a chemisorption process.

pH adsorption edges for lead on montmorillonite demonstrate that at a pH below the hydrolysis point the sorption edge is primarily due to ion exchange and is affected by ionic strength, while at a pH above the hydrolysis point it is due to a combination of both ion exchange and precipitation.

The EDS semi-quantitative analysis performed by SEM demonstrates that in the clays Pb replaces almost exclusively Ca ions. This supports the hypothesis of an exchange mechanism, that in montmorillonite also involves the Ca ions in the interlayer space, as demonstrated by the XRPD spectra and confirmed by the TGA curves. In illite the Pb sorbed is not balanced by equivalent Ca desorption. This behavior may be explained by a chemisorption process involving protonated OH groups that are displaced as  $\text{H}_2\text{O}$  molecules and replaced by Pb ions, leading to the formation of inner-sphere metal complexes, and/or because the edge situated in interlattice sites became occupied by Pb ions other than K, presumably leading to a partial opening of the interlattice space.

Goethite shows an adsorption capability of the same magnitude as kaolinite and a notable decrease in Fe content, probably due to a dissolution process caused by the acidic media used in the experiment.



**Figure 4.** XRPD spectra of (a) I = illite, (b) K = kaolinite, (c) M = montmorillonite jointly with the (d) TGA curves of M = montmorillonite, before and after Pb saturation.

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