Lead and Copper Adsorbed Montmorillonites in Wetting and Drying Cycles

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INTRODUCTION.

It is well known that potassium-montmorillonite undergoes illitization when subjected to cyclic wetting and drying (Eberl et al., 1986). The use of K-fertilizers cause the fixation of K^+ in vermiculites and smectites structure thus changing their physico-chemical properties (expansion and adsorption capacity). The most important clay mineral factor affecting K-fixation is the layer charge of the original swelling clay mineral (Horváth and Novák, 1975). Later, similar effects of other cations have been demonstrated, such as NH_3 (Sucha and Siranova, 1991) and Cs (Cuadros, 2002). Clay liners under waste deposits and soils close to traffic lines and industrial sites are subjected to heavy metal contamination and alternating wet and dry conditions. Therefore, it became very important to know wether heavy metal ions have similar effects on the clay mineral properties in wetting and drying cycles than potassium.

In this work preliminary results of Cu and Pb adsorption and wetting–drying experiments on two montmorillonite with different layer charge are presented.

MATERIALS AND METHODS.

International standard montmorillonite from Wyoming (SWy-2) as typical low charged smectite and a higher charged natural Na-montmorillonite (VCB) from a romanian bentonite deposit were used in the study. Both samples consist almost purely of montmorillonite, VCB has minor amount of cristobalite. The studied montmorillonites in their initial sodium form have a perfect expansion capacity.

The adsorption experiments were performed by mixing 400 mg of montmorillonite with 40 ml of solutions containing various concentrations of copper and lead nitrates. The initial metal concentrations were set to 20, 40, 50, 80, 100, 200, 500, 1000, 1500 and 2000 mg/l. The samples were shaken for 48 hours at room temperature, then they were centrifuged. The equilibrium concentrations of Cu and Pb were measured by atomic absorption spectrometry (PERKIN ELMER 5000). The amounts of adsorbed metals were calculated from the difference between concentration of the starting and equilibrium solutions. Initial pH of the solutions was adjusted to 4.5–5.0 by adding some drops of dilute HNO_3. For the wetting and drying experiments approximately three grams of samples have been prepared with 1000 mg/l metal solutions. The samples were wetted by 50 ml distilled water and then dried on water-bath on 80°C. Samples for XRD and spectroscopic analyses were taken after the 0, 1st, 2nd, 5th, 10th, and 20th wetting–drying cycle.
Cation saturation (3 times) using 1N Mg and K chlorides was carried out on the adsorbed samples after the experiments. The solid phase was washed by distilled water and then sedimented on a glass slide for the XRD analysis. The samples were air dried and stored under controlled humidity conditions (RH = 25–30%) in a dessiccator. The XRD measurements were carried out by a PHILIPS PW 1710 diffractometer, using 45kV accelerating voltage and 35mA current, and Cu Kα radiation. The samples were glycolated in vapour at 60°C overnight and glycerol solvated at 95°C overnight. Electron spin resonance (ESR) was applied to study the chemical speciation of adsorbed copper on the montmorillonites. The CEC values were determined on the basis of Ba-exchange.

RESULTS AND DISCUSSION.

Maximum adsorption capacities of the samples for copper and lead are shown in Table 1.

	Layer charge	Adsorbed Pb(mg/kg)	Adsorbed Cu(mg/kg)
SWy-2	0.305	68373	22241
VCB	0.355	76660	21606

Table 1. *Mean layer charge and Pb and Cu adsorption capacity of the studied montmorillonites.*

The studied montmorillonites have very large adsorption capacity both for Cu and Pb. Based on the change of basal spacing and on the chemical analyses of the metal adsorbed montmorillonites, the main mechanism of adsorption is ion exchange, and the main site of the sorption is the interlayer space.

Both Cu and Pb adsorbed montmorillonites have about 13–14 Å basal spacing in case of small concentration and high pH, while in case of high metal ion concentration and low pH the montmorillonites tend to have 12.5 Å basal spacing (one layer water arrangement) (Fig.1).
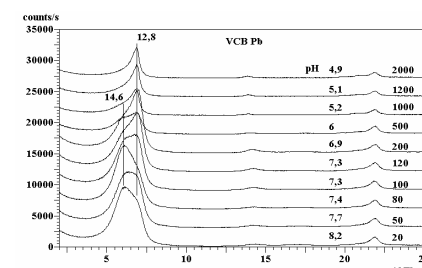

fig 1. *X-ray patterns of VCB montmorillonite adsorbed with different concentration lead solutions (20–2000 mg/l).*

One of the most important properties of montmorillonites is expandibility. In a previous study the partial loss of expansion capacity was found in case of Cu adsorbed SWy-2 montmorillonite, but

not in the case of high charged VCB sample (Németh et al. 2005).

The same phenomenon was found for lead in the present study: adsorbed Pb decrease the swelling capacity of the low charged SWy-2 montmorillonite, but does not effect drastically the expansion of the high charged sample. The basal spacing of glycerol solvated Pb adsorbed SWy-2 decreased from 18 to 14 Å (Fig. 2).
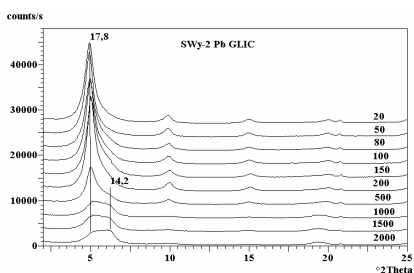

fig 2. X-ray patterns of Pb adsorbed VCB montmorillonite after glycerol solvation.

The initial basal spacing of the metal ion adsorbed samples does not change significantly after ten wetting-drying cycles. However, there is some important changes in the X-ray patterns when the samples were solvated by ethylene-glycol (Fig. 3).
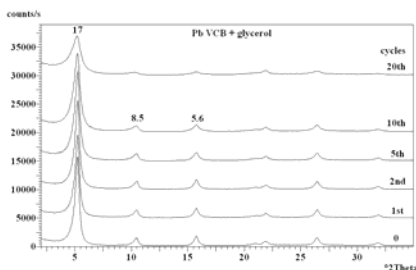

fig 3. X-ray patterns of ethylene-glycol solvated Pb adsorbed VCB montmorillonite after 0–20 wetting-drying cycles.

In all cases the half-width of the 001 peak increases with the number of the wetting–drying cycles. However, the amount of this increase depends on the adsorbed metal ion and on the layer charge of the montmorillonite. The higher charged VCB montmorillonite exhibited almost twice wider peak width than low charged SWy-2 montmorillonite. Moreover, the effect of lead on the peak profile is larger than that of copper. This peak widening can suggest the partial loss of expansion or the decomposition of the particles during the wetting–drying. This effect occured strictly after ten cycles or more, it also depends on the nature of metal ion and on the clay.

The heavy metal adsorbed samples were saturated by Mg^{2+} and K^+ after the wettng–drying experiments and XRD measurements were carried out to check the ion exchange. No significant change in the basal spacing of Mg-saturated samples have been found, only a slight increase of half-width could be observed. However, in the case of K-saturation the basal spacing increased gradually. After cycles 0 to 5 VCB montmorillonite exhibited 11.8 Å, after the 10th cycle 12 Å, and after the 20th cycle 12.3 Å basal spacing. This change occured also for SWy-2 but the value of the increase was smaller. Simoultanously, an increase of peak width can be observed. This indicates the strengthening of the fixation of Pb in the montmorillonite structure during the wetting and drying. It also suggests that there is a competition for the adsorption sites between Pb^{2+} and K^+ which is due to their similar ionic radius. The effect is more intensive in the case of higher charged montmorillonite, similarly to the case of potassium and vermiculite, K-fixation being stronger in high charged vermiculites then in low charged smectites.

CONCLUSIONS.

Copper and lead adsorbed montmorillonites were studied after wetting and drying cycles. The first twenty cycles caused some significant change in the properties of the montmorillonites. The most important is that potassium adsorption has been inhibited by the fixation of lead in the structure during the wetting—drying cycles.

Knowledge of the mineralogical, crystal structural, crystal chemical and physical changes due to the wetting–drying cycles is essentially important in the characterization of clay liners under waste deposits and of the clay mineralogy of soils, mainly from the aspect of their potassium supply. Therefore, further wetting–drying studies of heavy metal adsorbed clay minerals are needed. In addition to this, the results can be useful in the geological, mineralogical, and geochemical interpretation of weathering and diagenetic processes.

The results of wetting and drying cycles experiments contribute to the knowledge of the real structure of smectites.

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