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## SORPTION OF Zn AND Pb BY MONOIONIC FORMS OF SMECTITE

**Abstract.** The authors studied sorption of Zn and Pb from nitrate solutions by smectite clay with different interlayer cations. The relation between the sorption and kind of interlayer metal was slightly different for various ranges of initial concentration of the nitrate solution. The quantity of metal possible to be desorbed after sorption changed, in general, as follows: Na-smectite  $\cong$  K-smectite < Ca-smectite  $\leq$  Mg-smectite.

**Key-words:** smectite clay, sorption, desorption, Zn, Pb.

## INTRODUCTION

The environment pollution with toxic heavy metals is a very serious problem nowadays. The most important processes affecting the behaviour of metals in the environment are those associated with the adsorption of metals from the liquid phase on the solid phase. The term "adsorption" refers here to all phenomena at the solid-solution boundary, including cation exchange (non-specific adsorption), specific adsorption, co-precipitation and organic complexation. It is frequently difficult to identify which particular process is responsible for the retention of metals (Alloway 1995). Soils and aquifer solids provide surfaces available for heterogeneous reactions with solutes present in soil interstitial water and groundwater (Bourg 1995).

Many heavy metals, like lead, zinc, cadmium and copper, tend to be strongly sorbed on solids. Consequently, the amount of many contaminants in the environment and their transport pathways, cycling, and ultimate removal are controlled not only by solubility, but also by sorption-desorption reactions on sedimentary particulate matter (Velde 1995).

Sorption depends on many variables, such as pH, geochemical properties of the metal and its concentration, competing cations versus ionic strength of the solution,

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aqueous speciation, kind of sorbent, surface complexation, surface area and site density, time dependency of reaction (Jenne 1998). The major sorbents of heavy metals in the environment include organic matter, hydrated metal oxides, and clay minerals.

Potentially toxic effects and bio-availability of heavy metals depend on how they are sorbed on the clay-size material, and how this may be altered by changes in the chemical environment, i.e. pH and Eh, either during transport or after deposition. Transport of pollutants by clay materials is not only important in surface environments, but also during subsurface colloidal transport through the porous media of soils and aquifers (Velde 1995).

Affinity of cations towards sorbents increases with increasing oxidation number (valence effect) and the decreasing diameter of their hydrated forms (Förstner, Wittmann 1979). Helfferich (fide Sparks 1995) has given the following selectivity sequence of some cations:  $\text{Ba}^{2+} > \text{Pb}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Mg}^{2+} > \text{Ag}^+ > \text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Li}^+$ .

Sorption of Zn and Pb by a smectite clay saturated with different interlayer cations was the aim of these investigation.

## MATERIALS AND METHODS

The fraction  $< 63 \mu\text{m}$  of the smectite clay from Chmielnik containing dioctahedral montmorillonite (Żabiński 1991) was used as a sorbent. It was saturated with  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  cations to obtain homoionic forms (Na-smectite, K-smectite, Ca-smectite and Mg-smectite).

Zinc and lead were sorbed using smectite clay suspensions in  $\text{Zn}(\text{NO}_3)_2$  and  $\text{Pb}(\text{NO}_3)_2$  solutions; the initial metal concentrations ( $C_0$ ) ranged from 0.05 to 2.5 mM. The suspensions were agitated on an automatic shaker for 12 hours, and the solution was next separated out from the solid phase by centrifugation. Afterwards, the metals were desorbed from the solid phase by shaking it for 12 h with 1 M ammonium acetate solution. The concentration of the clay suspension in both experiments (sorption and desorption) was 20 g/l. The pH of the solutions after sorption and desorption was controlled and concentration of metals in solution measured by AAS.

## RESULTS

Sorption took place at pH that was stabilized in the clay suspensions in metal nitrate solutions of different concentration. The pH values of the initial  $\text{Zn}(\text{NO}_3)_2$  and  $\text{Pb}(\text{NO}_3)_2$  solutions were 5.8–6.3 and 5.3–5.8, respectively; the pH of solutions separated out from the solid phase after sorption generally was higher (Table 1). Thus, sorption of Zn and Pb took place at different pH ranging from slightly acidic (5.3) to close to neutral (7.5), depending on the kind and concentration of the metal sorbed and interlayer cations of smectite.

TABLE 1

Form of smectite	pH of the $\text{Zn}(\text{NO}_3)_2$ solution		pH of the $\text{Pb}(\text{NO}_3)_2$ solution	
	initial	after sorption	initial	after sorption
Na-smectite	5.8–6.3	6.5–7.5	5.3–5.8	6.4–7.1
K-smectite	5.8–6.3	5.3–6.2	5.3–5.8	5.6–6.2
Ca-smectite	5.8–6.3	5.9–6.6	5.3–5.8	5.3–6.6
Mg-smectite	5.8–6.3	5.9–6.6	5.3–5.8	5.5–6.1

The quantity of metal taken up from the solution depended on pH of the solution (Fig. 1). The higher pH, the smaller was sorption for all smectite forms, but, simultaneously, the smaller was initial metal concentration ( $C_0$ ) in the solution. Then one cannot say that pH was the essential parameter that influenced sorption.

Sorption of both metals by smectite clay was high; more than 80% of each was taken up from the solution during experiments. Percentage of the metal sorbed (%S) depended on the kind of interlayer metal of smectite (Fig. 2, 3) and was different for various ranges of  $C_0$ .

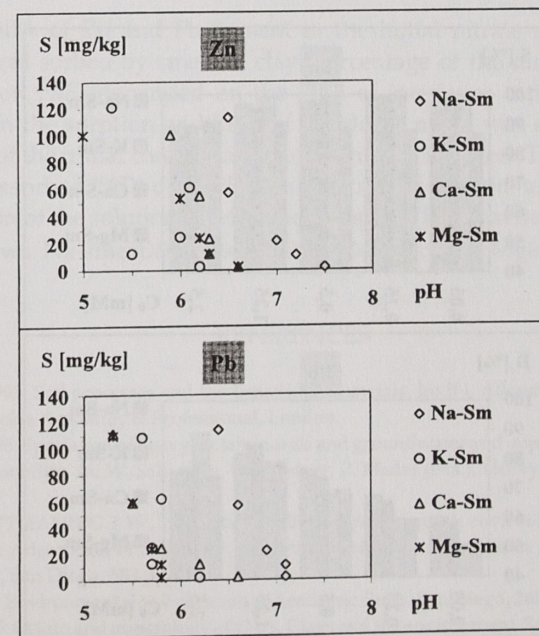


Fig. 1. Relation between metal sorption and pH of the suspension



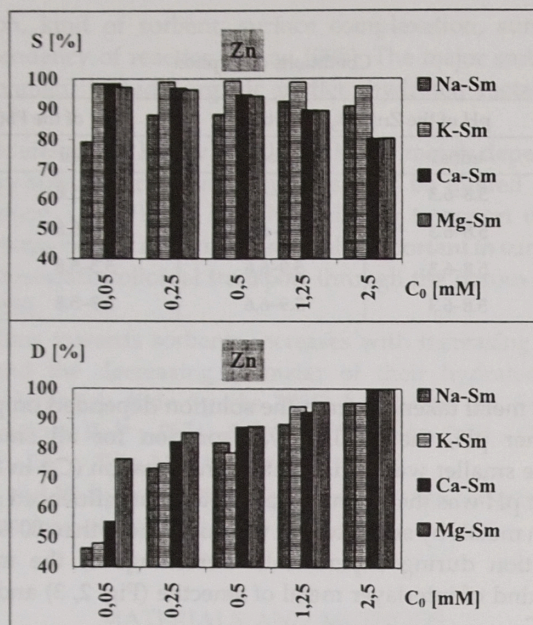


Fig. 2. Percentage sorption (S) and desorption (D) of Zn by the various forms of smectite

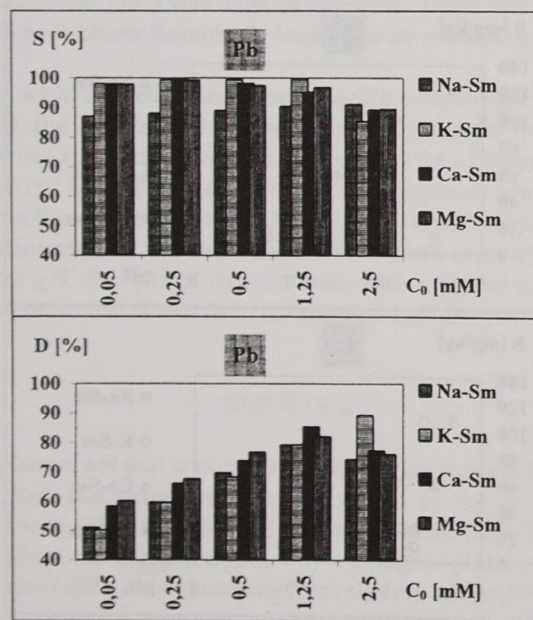


Fig. 3. Percentage sorption (S) and desorption (D) of Pb by the various forms of smectite

In the  $C_0$  range 0.05–0.5 mM particular smectite forms took up Zn in quantities (%S) changing in the following sequence: Na-smectite < Mg-smectite  $\approx$  Ca-smectite  $\leq$  K-smectite (Fig. 2). The sequence in the range 1.25–2.5 mM was different: Ca-smectite  $\approx$  Mg-smectite < Na-smectite < K smectite. In the case of Pb sorption (Fig. 3), in the  $C_0$  range 0.05–1.25 mM the succession was the same as for lower (0.05–0.5 mM) initial concentrations of Zn, but for  $C_0 = 2.5$  mM  $\text{Pb}(\text{NO}_3)_2$  it changed as follows: K-smectite < Ca-smectite  $\approx$  Mg-smectite < Na-smectite.

Quantity of the metal that could be subsequently desorbed (%D) depended on the form of smectite used as a sorbent and on the concentration of the solution in which sorption had been previously carried out (Fig. 2, 3). In general, metals sorbed from solutions of higher concentrations, could be easier desorbed, it means they had been weaker bound to the sorbent. Only the Pb sorbed from the solution of the highest concentration ( $C_0 = 2.5$  mM) was desorbed in the lower percentage than the Pb sorbed at  $C_0 < 2.5$  mM (except for K-smectite).

Pb was stronger bound to the smectite than Zn: it was desorbed in lower relative quantities (%D) than the latter. In general, percentage of the metal possible to be desorbed changed as follows for particulate forms of smectite: Na-smectite  $\approx$  K-smectite < Ca-smectite  $\leq$  Mg-smectite.

## CONCLUSIONS

More than 80% of Zn and Pb present in the initial nitrate solution of different concentration was sorbed by smectite clay. Percentage of the metal that was sorbed from the solution (%S) depended on the kind of interlayer cation of smectite. The relation between the sorption and kind of interlayer metal was slightly different for various ranges of the initial concentration of the nitrate solution. The quantity of metal possible to be desorbed (%D) depended on the form of smectite used as a sorbent and the concentration of the solution in which sorption had been carried out. It changed, in general, as follows: Na-smectite  $\approx$  K-smectite < Ca-smectite  $\leq$  Mg-smectite.

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## SORPCJA Zn I Pb PRZEZ MONOJONOWE FORMY SMEKTYTU

### Streszczenie

Badano sorpcję, a następnie desorpcję cynku i ołowiu przez sodową, potasową, wapniową i magnezową formę smektytu. Stwierdzono, że procentowa usuwalność tych metali z roztworu przez różne, monojonowe formy smektytu zależy nie tylko od formy smektytu (rodzaju kationów w przestrzeniach międzypakietowych), lecz także od początkowego stężenia metali w roztworze. Z kolei procentowa ilość metalu, jaka może być zdesorbowana po procesie sorpcji, generalnie zmienia się w kolejności: Na-smektyt  $\approx$  K-smektyt < Ca-smektyt  $\leq$  Mg-smektyt.

### CONCLUSIONS

More than 80% of Zn and Pb present in the initial metal solution of different concentration was sorbed by smectite clay. The change in the metal that was sorbed from the solution (%) depended on the kind of monovalent cation of smectite. The relation between the sorption and desorption was slightly different for various ranges of the initial metal concentration. The quantity of metal possible to be desorbed after sorption was the least of what was used as a sorbent and the concentration of the solution. In the case of Na-smektyt, the concentration of the solution, as follows: Na-smektyt  $\approx$  K-smektyt < Ca-smektyt  $\leq$  Mg-smektyt.

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