GEOLOGICA CARPATHICA - SERIES CLAYS, 2, BRATISLAVA, DECEMBER 1992
77 - 82

WEATHERING PRODUCTS OF LOWER SILESIAN BASALTIC ROCKS AS SORBENTS OF HEAVY METALS

WANDA S. SIKORA and LEOKADIA BUDEK

Academy of Mining and Metallurgy, al. Mickiewicza 30, 30-059 Kraków, Poland

(Manuscript received September 4, 1992; accepted in revised form November 16, 1992)

Abstract: The sorption of Pb, Cd, Zn and Cu on the kaolinite and smectite-kaolinite products of basalt weathering has been studied. It has been found that the removability of these heavy metals from their solutions is relatively high. At low initial concentrations of solutions the metals studied were removed completely. The maximum sorption of all the metals by both investigated samples was higher than their CEC. The process of desorption with 1 *M* solution of ammonium acetate revealed that a certain part of the sorbed metals did not go back into solution. The quantity of these unremovable portions was influenced by the kind of metal and its concentration in the solution. The affinity of metals to the weathering products changes as follows: Cd>Pb>Cu≈Zn for kaolinite sample and Cd>Pb≈Cu>Zn for smectite-kaolinite one.

Key words: heavy metals, products of basalt weathering, sorbents, sorption, desorption.

Introduction

There are many aspects of heavy metals sorption by clay minerals. They constitutes a very important element in the process of heavy metals circulation in the natural environment. The clay minerals, accumulating heavy metals within the surface horizon of soils, influence their assimilation by plants. Due to the sorption properties the clays are also used as liners for various disposal sites to prevent pollution of ground and surface waters by liquid effluents from solid wastes.

The interaction between clay minerals and cations in water solutions is usually complex. According to Bruggenvert & Kamphorst (1979) several possible processes such as: reversible exchange of interlayer cations, selective and only partly reversible adsorption, chemisorption, particularly at the edges of clay minerals, adsorption of metal-ion complexes and precipitation of hydroxides or insoluble salts may be considered. Usually, there is no possibility to distinguish which process is the dominant one. Sposito (1984) suggests to describe as "sorption" the total process of removing metals from solution. In this meaning the term "sorption" will be used in the present paper.

The sorption properties of clays are mainly influenced by clay minerals but by iron minerals as well. The heavy metals sorption by clay suspensions depends on the specific surface area of the clay, the kind of metal used, pH and initial concentration of metal solution and the concentration of suspension (Helios Rybicka 1986; Kyziol 1991).

The weathering products of basaltic rocks have developed in the S - W part of Poland on the large area of Lower Silesia as Tertiary weathering crusts (Dyjor et al. 1991). They may be considered as ferruginous (up to 20 - 30 % Fe_2O_3), quartz-free clay sediments. Kaolinite (halloysite), and smectite are their main clay constituents. Their specific properties can be described by the large content of iron (crystalline and amorphous phases), the strong aggregation but low crystallinity of both clay and nonclay minerals and the presence of amorphous aluminosilicates. All the above descriptions suggest that the weathering products considered might appear as good sorbents of heavy metals. At first, the sorption of Pb, Cu, Zn and Cd on smectite and halloysite samples was studied (Budek et al. 1991). The aim of the present study was to estimate the sorption of those metals by other weathering products. The kaolinite sample from Dunino (Du-K) and the smectite-kaolinite from Mikolajowice (M-SmK) have been chosen.

Table 1: Mineralogical and chemical characteristics of samples.

Sample:		Du-K	M-SmK
mineral composition:		kaoliniteTc (about65%) hematite magnetite	kaolinite (about50%) smectite (about25%) magnetite
CEC [*meq*/100*g*]:		4.0	13.3
main exchangeable cations [*meq*/100*g*]	Ca	3.5	13.6
	Mg	0.5	1.1
	Na	0.3	0.5
	K	0.2	0.3
pH of suspension		7.2	6.7
main chemical constituents [wt %]	Al_2O_3	23.7	20.5
	Fe_2O_3	28.3	23.4
	TiO_2	5.22	5.04
heavy metals [*mg/kg*]	Pb	40	40
	Cu	100	100
	Zn	150	600
	Cd	5	5
fraction $<2\ \mu m$ [wt %]		50	31

Materials and methods

The mineralogical and chemical characteristics of the samples studied are presented in the Tab. 1.

The sorption of Zn, Cu, Pb and Cd was carried out using 2 % suspensions (20 g/dm^3) and nitrate metal solutions with initial concentrations (C_o) ranging 5 - 5000 mg/dm^3. The suspensions were equilibrated for 12 hours using a mechanical shaker. Then the suspensions were centrifuged and the concentration of metals in supernatant solution was measured by AAS method. Afterwards, the samples were washed by water and the desorption procedure using 1 *M* CH_3COONH_4 of pH 7 (12 hours shaking) was carried out. The concentration of released cations was determined by the AAS method. The pH of all metal solutions used before and after sorption procedure was also measured.

The removability (per cent of sorption - S) of metals by both investigated weathering products is in general high (Fig. 1). At low initial concentrations (C_o) of solutions up to 25 mg/dm^3 and for Pb even to 125 mg/dm^3 the metals were removed completely.

The shape of sorption curves is similar for all the metals. One can distinguish the three steps of the process. In the first step the removability is very high and decreases slightly while C_o is increasing (for Pb approximately to 250, for Cd to 125 and for Cu and Zn up to 25 - 50 mg/dm^3). In the second step, up to C_o about 2500 mg/dm^3, a considerable decrease of metal removability from solutions is observed. In the third step the removability of Pb and Cu slightly decreases again while for Cd and Zn an insignificant increase of removability is observed.

The pollution of aqueous systems by heavy metals is usually expressed in mg/dm^3. In order to compare the removability of Pb, Cd, Zn and Cu by investigated samples the equal initial concentration expressed in mg/dm^3 for all the metals was used. The removing for metal ions from water solutions by clay minerals occurs - as it is thought - mainly by cation exchange process. Then the process of sorption and desorption ought to be explained the light of number of the atoms involved (meq/dm^3). When the concentrations (C_o) are expressed in equivalent units (meq/dm^3) the maximum initial metal concentrations appeared to be different for particular metals. For Pb - the heaviest of all the investigated metals - the maximum C_o equals 50 meq/dm^3. That value then limits the range in which the sorption of all the metals may be compared.

The amount of metals sorbed by samples studied while C_o is below 50 meq/dm^3 changes in the following sequences: Cd>Pb>Cu≈Zn for kaolinite sample and Cd>PbŠCu>Zn for smectite-kaolinite sample (Fig. 2). The curves presented on Fig. 2 appear to be very similar for each metal of both samples studied, as far as the shape and the values of sorption are concerned. The sorption curves of Cd and Zn have two-step character; for C_o equal 40 - 70 meq/dm^3 they show a sharp change in slope.

It is worth to note that the amount of metals removed from solutions by both studied samples is higher than their CEC. The sorption reaches the CEC level by C_o about several meq/dm^3 (Figs. 3, 4; Tab. 1). It may suggest that the removing of Pb, Cd, Zn and Cu from solutions is not only a result of cation exchange process.

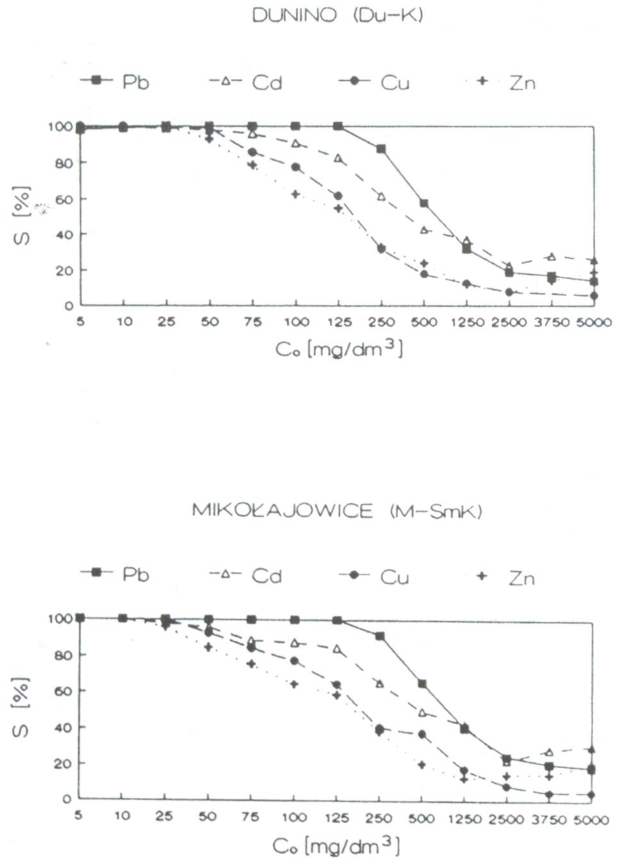

Fig. 1. Removability of Pb, Cd, Cu and Zn from solutions by Du-K and M-SmK samples.

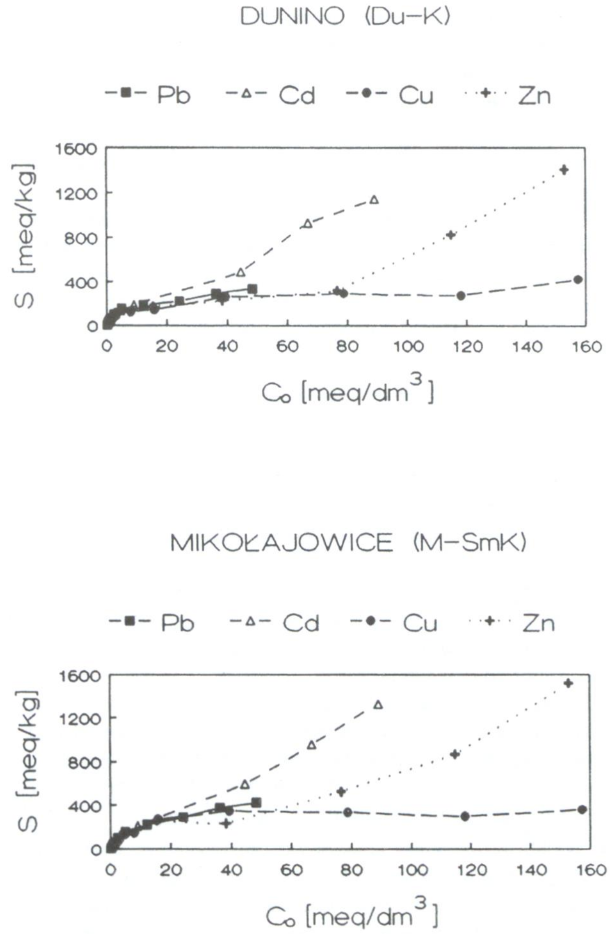

Fig. 2. Sorption (S) properties of Du-K and M-SmK samples.

Table 2: Changes in pH of Pb solutions.

Co $[mg/dm^3]$	pH		
	initial solution	after sorption	
		Du-K	M-SmK
5	5.7	7.2	7.2
10	5.8	7.3	7.2
25	5.8	7.4	7.2
50	5.8	7.2	7.1
75	5.7	7.1	6.8
100	5.7	6.8	6.5
125	5.5	6.9	6.0
250	5.4	5.7	5.5
500	5.5	5.4	4.7
1250	5.2	4.7	4.6
2500	5.2	4.5	4.7
3750	5.0	4.7	4.2
5000	5.0	4.3	4.1

Table 3: Changes in pH of Cd soultions.

Co $[mg/dm^3]$	pH		
	initial solution	after sorption	
		Du-K	M-SmK
5	6.4	7.3	7.5
10	6.4	7.4	7.3
25	6.6.	7.4	7.2
50	6.3	7.3	6.8
75	6.2	7.2	7.1
100	6.5	6.9	6.8
125	6.6	6.9	6.7
250	6.5	6.6	6.5
500	6.4	6.2	5.1
1250	6.2	6.5	5.2
2500	6.1	5.8	5.2
3750	6.1	5.7	5.1
5000	6.0	5.7	5.0

Table 4: Changes in pH of Cu solutions.

Co $[mg/dm^3]$	pH		
	initial solution	after sorption	
		Du-K	M-SmK
5	6.2	7.3	7.1
10	6.1	7.2	6.7
25	5.9	7.1	6.2
50	5.7	6.3	5.6
75	5.6	5.6	5.1
100	5.7	5.3	5.1
125	5.6	5.3	4.9
250	5.4	5.1	4.7
500	5.1	5.1	4.6
1250	4.9	4.7	4.2
2500	4.7	4.4	4.2
3750	4.6	4.3	4.3
5000	4.4	4.3	4.2

Table 5: Changes in pH of Zn solutions.

Co $[mg/dm^3]$	pH		
	initial solution	after sorption	
		Du-K	M-SmK
5	6.3	7.2	7.2
10	6.2	7.3	7.2
25	6.3	7.1	6.9
50	6.1	6.7	6.9
75	5.4	6.5	6.6
100	5.8	6.5	6.3
125	6.1	6.1	6.2
250	6.0	5.8	5.8
500	6.0	5.8	6.0
1250	5.9	6.0	5.7
2500	5.9	5.7	5.0
3750	6.0	5.5	5.0
5000	5.9	5.3	4.9

An interesting light was thrown on the course of sorption process by results of the desorption procedure. With increasing Co the amount of sorbed and desorbed metal increases (Figs. 3, 4). In the whole concentration range used, even at the lowest Co, there is not possible to desorb completely the previously sorbed metal. It indicates that irrespectively of Co used the metals are removed from solutions in, at least, two forms. One of them is easy to remove using CH_3COONH_4 solution (exchangeable form) while the other one is unremovable (unexchangeable form). The amount of the first form is measured by the value of desorption (D) while the amount of the second one by the difference value of sorption and desorption (S-D). At lowest C_o the unexchangeable form is the dominant one (more than 75 % of the total). It suggests that at first the metals are combined mainly with sites of higher energy and that is why they are difficult to remove. While the sorption is reaching CEC less than half of exchangeable sites are occupied by the sorbed metal.

It draws the attention that at low Co the pH of metal solutions after sorption is higher than that of initial solutions (Tabs. 2 - 5). It points out that at low metal concentration the hydrogen ions are preferably sorbed from solutions, resulting the increase of pH.

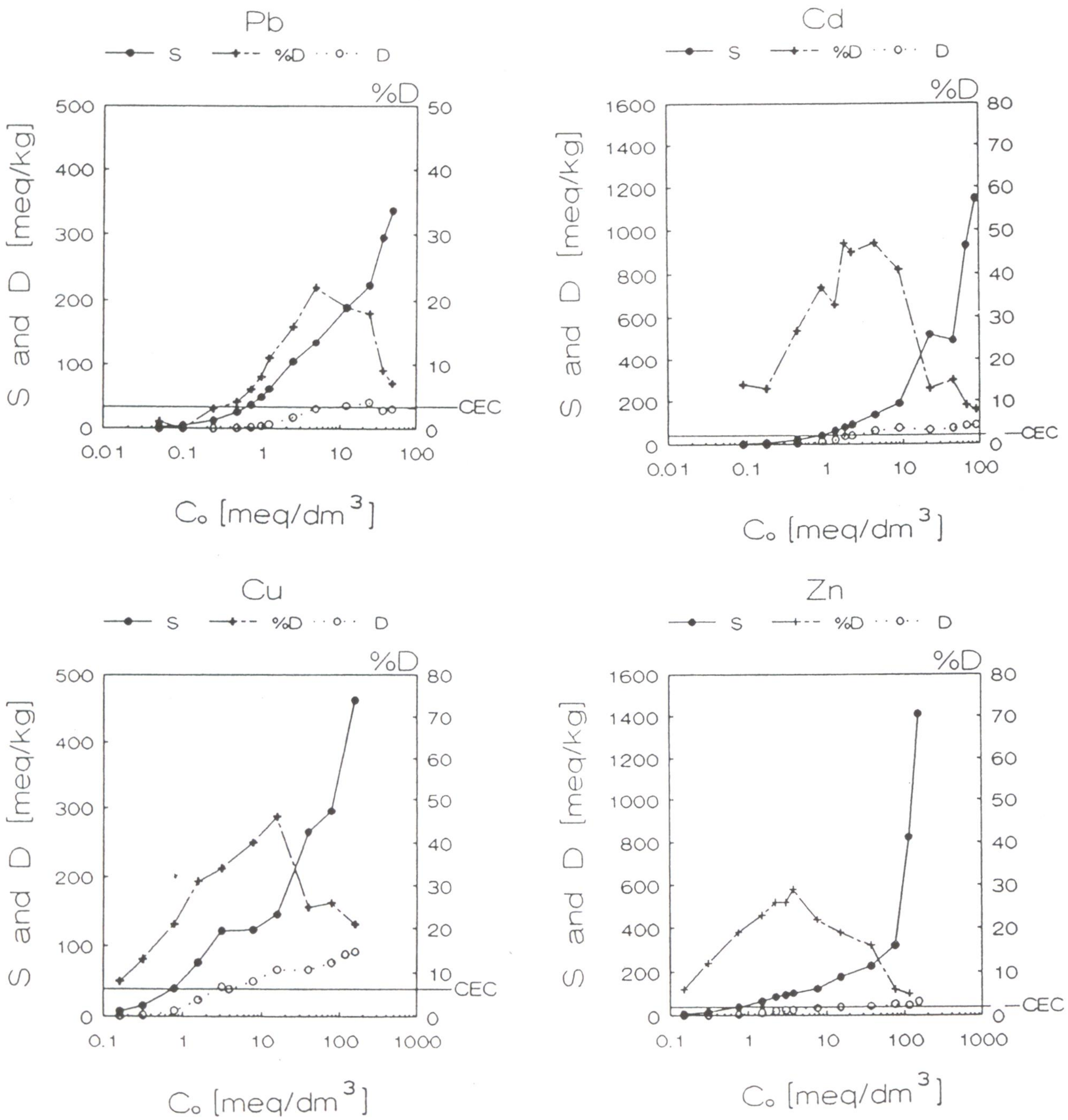

Fig. 3. Sorption (S) and desorption (D) properties of Du-K sample.

The increase of C_o causes the increase of the amount of metal sorbed in exchangeable as well as in unexchangeable form (Figs. 3, 4). At lower C_o the amount of the first form increases more than the second one - per cent of desorption (% D) increases. The maximum part of the exchangeable form (% D) does not exceed 60 % of the total amount of the sorbed metal. At certain C_o values, corresponding to maximum % D, desorption (D) stabilizes around the level of CEC. The further increase of sorption is predominantly covered by the unexchangeable form. It is therefore, most probable that the removal of metals from solutions occurs by precipitation of their hydrolyzed products.

The precipitation of metal ions in clay suspensions occurs at pH values which can be several unites lower than those predicted from tabulated solubility product values. This precipitation effect is not restricted to clay suspensions. For example, the pH for 50 % precipitation of Pb and Cd from 10^{-4} *M* solution has been reported as 6.0 and 7.4 on clays; 3.1 and 5.8 on hydrous iron oxides; 5.2 and 6.6 on hydrous aluminum oxide and 5.6 and 7.7 on goethite, respectively (fide Farrah & Pickerring 1979). All these values fall outside the range (6.1 - 9.1 for Pb and 8.8 - 9.8 for Cd) predicted from pK_{so} values.

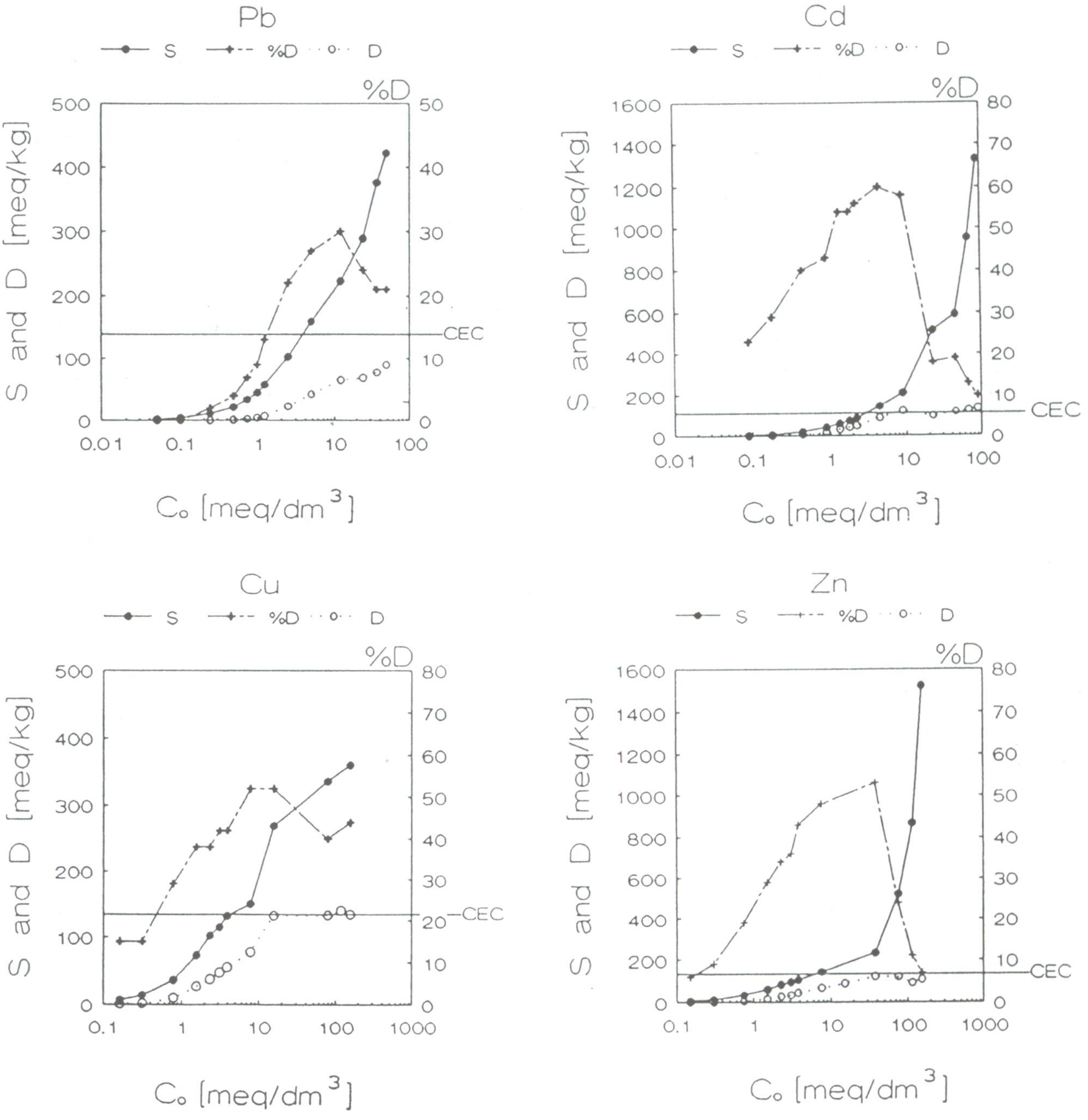

Fig. 4. Sorption (S) and desorption (D) properties of M-SmK sample.

The pH of metal ions precipitation may also be lowered while the concentration of metal is increasing. For example, in case of $Cd(OH)_2$ the beginning of precipitation takes place at pH equal to 8.2 for 10^{-2} *M* solution and 7.2 for 1 *M* solution.

In the investigated suspensions, in the range of presumed precipitation, C_o ranges from 0.6×10^{-2} *M* to 2.4×10^{-2} *M* for Pb and from 0.5×10^{-2} *M* to 5.0×10^{-2} *M* for Cd. At the same time the pH of suspensions ranges from 5.6 to 4.2 for Pb and from 6.5 to 5.7 (Du-K) and 5.0 (M-SmK) for Cd, respectively (Tabs. 2 - 5).

The pH after sorption is lower than the pH of the initial solutions. It seems to support the assumption that the precipitation of metal hydroxides takes place. It is not quite clear why the amount of Cd and Cu desorbed from the sample Du-K may be greater than its CEC (see Fig. 3).

The very similar sorption properties of both kaolinite (Du-K) and smectite-kaolinite (M-SmK) samples is rather surprising to authors. The smectite-kaolinite sample was expected to be more effective. Certain explanation of these observations can be done on the base of the grain size characteristics (Tab. 1). As already mentioned the Lower Silesian products of basalt weathering are strongly aggregated. Even a long lasting mechanical stirring does not break these aggregates. The part of the fraction $<2\,\mu m$ in the smectite-kaolinite sample is only 30 % (more aggregated sample) while that in the kaolinite sample is 50 %. It is very probable that in the more aggregated smectite-kaolinite sample the contact of metal solution with individual clay particles is more difficult than that in the kaolinite one.

Conclusions

1 - Both investigated weathering products of Lower Silesian basalts - kaolinite and smectite-kaolinite - are able to sorb very similar amounts of metals.

2 - The effectiveness of samples considered as sorbents of Pb, Zn, Cu and Cd from aqueous solutions is, in general, very high. At low concentration of metals up to 25 *mg/dm*^{3} - and in case of Pb even to 125 *mg/dm*^{3} - they are removed from solutions completely.

3 - The amount of metals removed from solutions is higher than CEC of studied samples.

4 - The metals are sorbed in exchangeable and in unexchangeable form.

5 - The proportion of both forms depends on initial concentration (C_o); the maximum of the exchangeable form does not exceed 60 % of the total sorbed metal.

6 - The affinity of metals to weathering products studied changes as follows: Cd > Pb≈Cu > Zn for kaolinite sample and Cd > Pb≈Cu > Zn for smectite-kaolinite one.

References

Bruggenwert M.G.M. & Kamphorst A., 1979: Survey of experimental information on cation exchange in soil systems. In: Bolt G. H. (Ed.): *Soil Chemistry. B. Physico-Chemical Models. Elsevier*, Amsterdam, 141 - 203.

Budek L., Helios Rybicka E., Kyziol J. & Sikora W. S., 1991: Preliminary studies on Lower Silesian weatheres basalts as sorbents of heavy metals. *National Conf. on Geological Aspects of Environment Protection*, 285 - 289 (in Polish).

Dyjor S., Kosciówko H. & Sikora W. S., 1991: Weathering products of Lower Silesian basaltic rocks - geological and mineralogical characteristics. In: Zabinski W. (Ed.): *Mineral sorbents of Poland*. 65 - 81 (in Polish).

Helios Rybicka E., 1986: The role of clay minerals in sorption of heavy metals by river sediments of Upper Vistula. *Z. Nauk AGH, Geol.*, 32 (in Polish).

Kyziol J., 1991: Sorption of some heavy metals by clay minerals. Dissertation AGH Kraków (in Polish).

Sposito G., 1984: The Surface Chemistry of Soils. *Oxford University Press*, New York.