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Zn, Cd AND Mn SORPTION ON SOME CLAY MINERALS

A b s t r a c t. The studies of sorption properties were carried out on clay minerals of the smectite series, mixed-layer smectite/illite, illite and kaolinite. The sorption of heavy metals, such as Zn, Cd and Mn, was studied in water suspensions of clay minerals at a constant pH of 7. It was found that at low concentrations of metals in the solution (1—40 ppm), Zn, Cd i Mn are sorbed in an amount of 80—98% by clay minerals of the smectite series and illite and in about 50% by kaolinite. The sorption of these metals over the whole range of concentrations used follows Freundlich's sorption isotherm.

INTRODUCTION

Heavy metals accumulating in soil and in bottom sediments of water basins are major contaminants of the natural environment.

The sorption of heavy metals on the particles of soil and bottom sediments proceeds at a very rapid rate, especially in the case of metals such as zinc and cadmium. More than 90% of sorption takes place within 15 minutes, and the equilibrium state is reached after about 20 hours (Egozy 1980; Christensen 1980; Bourg, Filby 1974).

In the sorption of heavy metals in contaminated soil and water environments Fe and Mn oxy-hydroxides and clay minerals play a significant role (Jenne 1968; 1976; Huang 1980; Kabata-Pendias 1980). Studies of the sorption of heavy metals on clay minerals concern primarily the most toxic metals, such as Cd, Pb, Co and Zn (Christensen 1980; Bourg, Filby 1974; Shuman 1976; Salim, Cooksey 1980; Egozy 1980; Chester 1965; Navrot, Singer, Banin 1978).

Experimental evidence concerning the sorption of metals on clay minerals has been collected mainly for montmorillonites and to a less degree for illite and kaolinite. No studies have been made for mixed-layer smectite/illites and these, together with illite, are the most common minerals present in clay sediments.

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MATERIALS

The following clay minerals were subjected to investigation:

Wyoming montmorillonite (SWy-1), characterized by high cation exchange capacity (CEC) and a relatively small specific surface area (about 30 m²/g). The main exchangeable cations are Ca and Na. The sample contains a small amount of quartz and trace calcite.

Arizona montmorillonite (Cheto-SAz-1), showing both high CEC and a large specific surface area (ca 100 m²/g). The main exchangeable cation is Ca.

Konin smectite/illite < 2 μm. This fraction was isolated from the Poznań clay near Konin. The principal mineral is mixed-layer smectite/illite (up to 70%). The sample also contains illite, some kaolinite and trace quartz. The content of swelling layers, determined by X-ray method, is about 70%. The fraction in question is characterized by not very high CEC (45 meq/100 g) and its specific surface area is 45 m²/g. The main exchangeable cations are Ca and Mg.

Konin smectite/illite < 0.3 μm. This fraction was isolated from the < 2 μm fraction described above. It also contains illite and kaolinite in smaller amounts and trace quartz. The content of swelling layers is lower (60%) than in the < 2 μm fraction. CEC is equal to that in the < 2 μm fraction while the specific surface area is larger, being 70 m²/g. This sample was converted into a monoionic (Na) form.

Mikołajowice beidellite. The sample is the < 0.3 μm fraction isolated from the Mikołajowice weathering crust. Its principal phase is a swelling mineral referred to as beidellite (Wilgat 1982). It also contains small amounts of illite and kaolinite and trace quartz. It has a CEC of 59 meq/100 g and a specific surface area of 62 m²/g. The main exchangeable cation is Ca.

Silver Hill illite, Montana. The sample (below 2 μm fraction) is monomineral. No swelling layers have been detected by X-rays. The illite in question was described in detail by Hower and Mowatt (1966). Its cation exchange capacity is not very high, and the main exchangeable cations are Ca and Mg.

Georgia "poor" kaolinite, showing a low degree of structural ordering. It is medium-grained, its specific surface area being 16 m²/g.

Some physico-chemical properties of the samples studied are given in Table 1.

Table 1

Some physico-chemical properties of clay minerals

Sample	CEC meq/100 g	SSA m²/g	Fe₂O₃ wt.%	"Free" FeO wt.%
Wyoming montmorillonite	76	31	3.35	0.32
Arizona montmorillonite	120	97	1.42	0.08
Mikołajowice beidellite	45	62	12.64	3.44
Smectite/illite below 2 μm	45	49	7.39	0.26
Smectite/illite below 0.3 μm	43	72	5.18	0.62
Illite Montana	28	43	10.56	1.34
Georgia kaolinite	4.5	16	1.13	0.15

CEC — cation-exchange capacity, SSA — Specific surface area

EXPERIMENTAL

The sorption of heavy metals was carried out on samples with an original cationic complex on the exchange positions. The only exception was mixed-layer smectite//illite (below 0.3 μm fraction), in which exchangeable cations were replaced by Na ions. Clay minerals were prepared into water suspensions of a concentration of 100 mg clay/10 ml for minerals of the smectite series and 200 mg/10 ml for illite and kaolinite. At the constant pH 7, Zn, Mn and Cd were added in such proportions that their concentration in the initial solution would be 1, 3, 10, 20 and 40 ppm (0.1, 1, 3, 10 and 20 for kaolinite). Cd and Mn were added to illite, kaolinite and one sample of the smectite series, i.e. mixed-layer smectite/illite (Konin — below 2 μm fraction). Then the samples were shaken for 24 hours and the solid phase was separated from the solution by centrifuging. The content of unsorbed metal in solution was determined by atomic absorption spectrometry.

RESULTS

The above studies served as a basis for plotting sorption isotherms for respective metals. As is evident from Figure 1, 2 and 3, the sorption of metals over the whole range of concentrations used (1—40 ppm and 0.1—20 ppm for kaolinite) follows Freundlich's isotherm.

At the low concentration of Zn ions in solution, the sorption of this metal is similar for all the minerals studied except beidellite. At higher concentrations, dif-
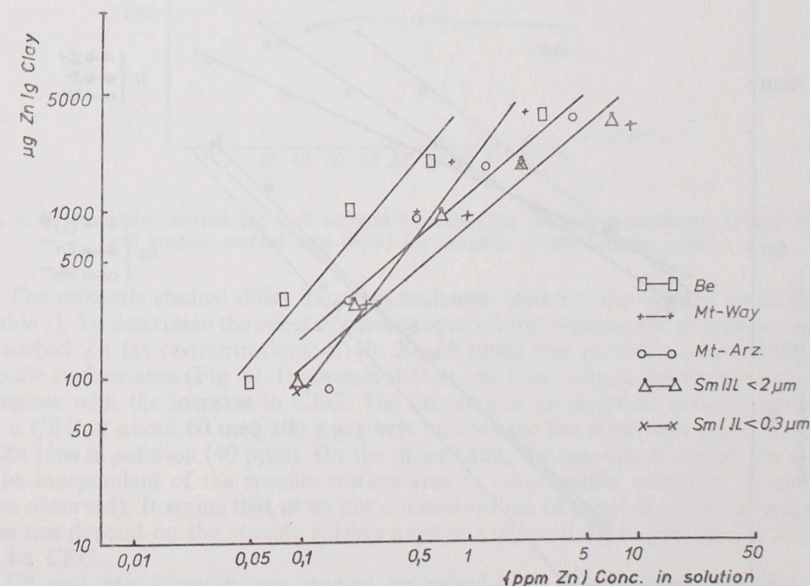

Fig. 1. Zn distribution between clay and solution

Be — beidellite, Mt-Way — Wyoming montmorillonite, Mt-Arz — Arizona montmorillonite, Sm/Il below 2 μm — smectite/illite, Sm/Il below 0.3 μm — smectite/illite
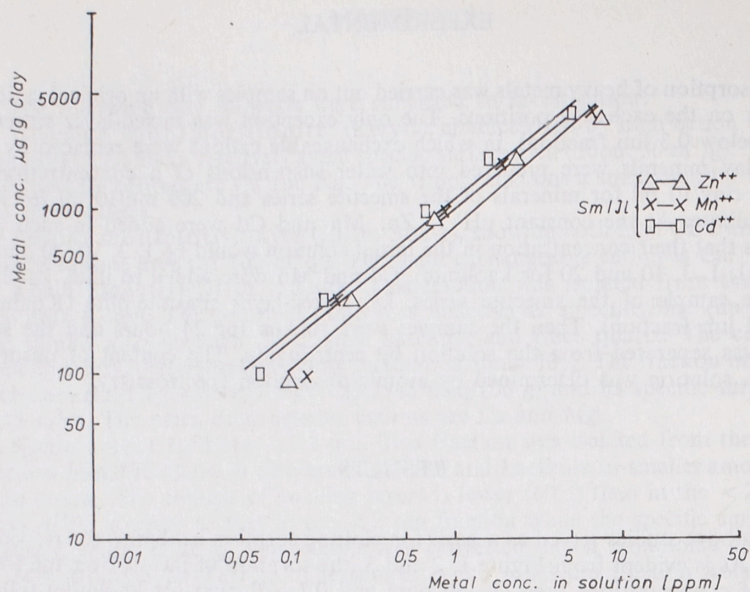
Fig. 2. Zn, Cd, Mn distribution between mixed-layer smectite/illite
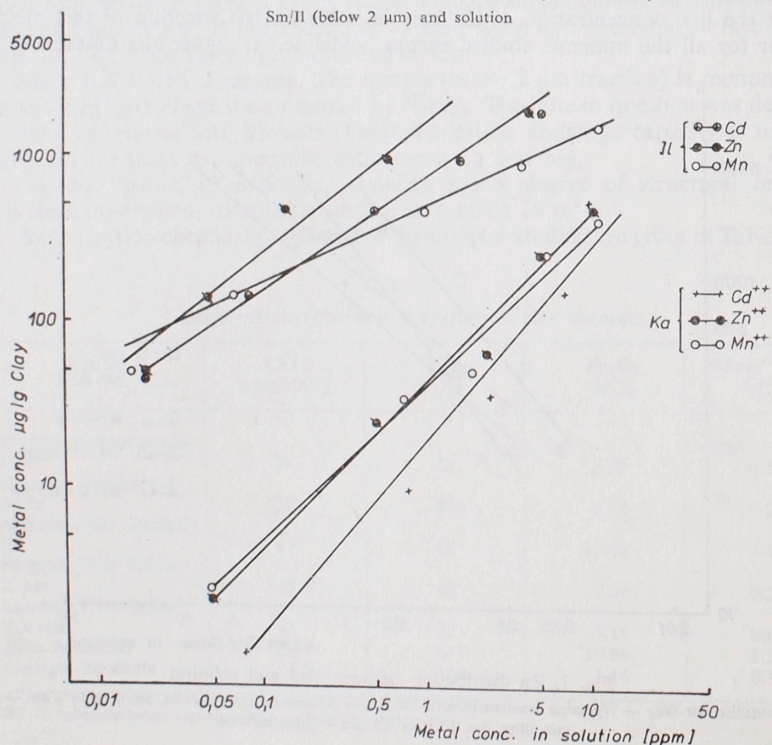Sm/Il (below 2 µm) and solution

Fig. 3. Zn, Cd, Mn distribution between illite and kaolinite and solution.
Il — illite, Ka — kaolinite

ferences in the shape of sorption isotherms become more pronounced. Zn sorption on mixed-layer smectite/illite (below 2 µm and 0.3 µm fractions) proceeds in a nearly similar way over the whole range of concentrations, which is presented by a single sorption isotherm. Zn is best sorbed by beidellite. The Wyoming and Arizona montmorillonites show a similar course of sorption, although at higher concentrations Zn sorption on the latter sample is somewhat lower. From Zn sorption isotherms it appears that minerals of the smectite series show certain differences in the sorption of this metal.
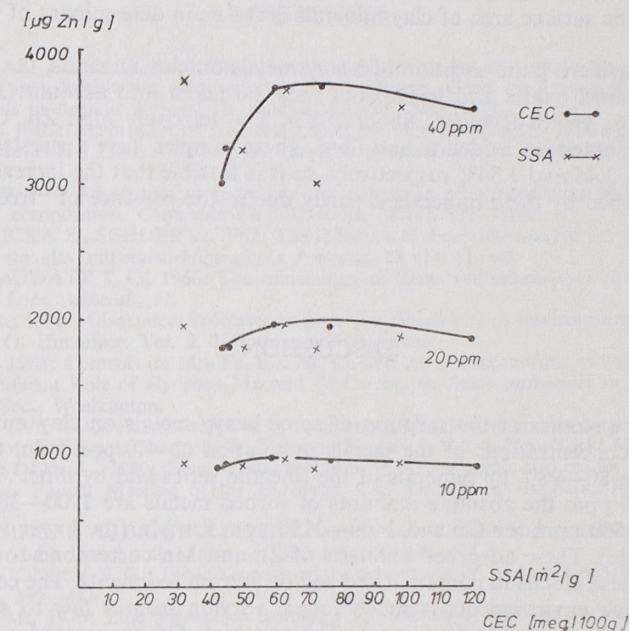

Fig. 4. Relationship between the total amount of sorbed Zn and cation-exchange capacity (CEC) and specific surface area (SSA) for minerals of the smectite series

The minerals studied differ in cation exchange capacity and specific surface area (Table 1). To determine the effect of these properties on sorption, the absolute amount of sorbed Zn (at concentrations of 40, 20, 10 ppm) was plotted against CEC and specific surface area (Fig. 4). It appears that at low CEC values, Zn sorption slightly increases with the increase in CEC. The increase in Zn sorption and its optimum for a CEC of about 60 meq/100 g are best marked for the maximum content ration of Zn ions in solution (40 ppm). On the other hand, the amount of sorbed Zn seems to be independent of the specific surface area (a considerable scatter of points has been observed). It seems that at so low concentrations of metal in solution, sorption does not depend on the specific surface area of a mineral or, to any greater extent, on its CEC.

Cd and Mn sorption was studied on mixed-layer smectite/illite, below 2 µm fraction. Figure 2 shows the sorption isotherms for these metals along with the Zn sorption isotherm. The three isotherms have a similar shape, but it has also been found that Cd is sorbed in the greatest and Zn in the least amount.

The isotherms obtained for Zn, Cd and Mn sorption on illite and kaolinite are presented in Fig. 3. Illite shows good sorption properties but also wide differences in the sorption of respective metals. Zinc is sorbed better and in greater amounts than cadmium. Manganese is sorbed in the least amount, which is well visible in its higher concentrations in solution. Kaolinite adsorbs the metals in question in considerably smaller amounts and also shows less differentiation in the sorption of respective metals. Zn and Mn are sorbed in similar amounts, greater than Cd.

The obtained results of Zn, Cd and Mn sorption on kaolinite and particularly on illite confirm the statement that at the metal concentrations used, neither the CEC nor the specific surface area of clay minerals is the main determinant of the amount of sorption.

When considering the sorption of heavy metals on clay minerals, the role played by hydrated iron oxides and hydroxides must be taken into account (Jenne 1968; Shuman 1976; Helios-Rybicka, Shoer 1982). The relatively high Zn, Cd and Mn sorption was noted on beidellite and illite. These samples have a substantial "free" iron content, 3.44 and 1.34% respectively, so it is feasible that the increased amount of metals sorbed by these minerals is partly due to the presence of "free" iron oxy-hydroxides.

DISCUSSION

The above studies of the sorption of some heavy metals on clay minerals show that at low concentrations of the metals in solution (1—40 ppm) Zn, Cd and Mn are sorbed in 80—98% by minerals of the smectite series and by illite. At a concentration of 40 ppm the absolute amounts of sorbed metals are 1700—3800 ppm for Zn, 1700—3500 ppm for Cd and 1400—3100 ppm for Mn (the lower values correspond to illite). These adsorbed amounts of Zn and Mn correspond to the average content of these metals in contaminated soil or bottom sediments. The concentration of Cd in such environments is much lower, varying from a few to some dozen, exceptionally to some hundred, ppm. The too high Cd concentrations were used in the present studies to make comparisons between metals.

Kaolinite shows much lower sorption. The absolute amount of metals sorbed by kaolinite at their concentration of 20 ppm varies from 400 to 500 ppm.

The observed differences in the sorption properties of minerals of the smectite series and the nearly equal Zn sorption on two different fractions of the same mixed-layer smectite/illite imply that the internal structure of a mineral affects essentially the sorption of metals at their low concentrations in solution. This statement is substantiated by the results of Zn, Cd and Mn sorption on kaolinite, and particularly on illite. Neither the CEC nor the specific surface area of clay minerals has any significant effect on the amount of sorption at the metal concentrations used in these studies.

In the case of minerals of the smectite series and also illite, the layer charge and its origin (from the tetra- or octahedral sheet) may play a significant role. In the case of kaolinite sorption may depend on the number of "active centres" originating from broken bonds at the edges or surfaces of kaolinite flakes.

The above results indicate that in the sorption of heavy metals not only minerals of the smectite series, characterized by high cation exchange capacity and large specific surface area, but also illite and kaolinite may play an important part. It seems,

therefore, that polymineral montmorillonite-illite-kaolinite clay rocks could be used instead of such sought-for sorbents as bentonites or montmorillonite clays to purify rivers and sewage contaminated by heavy metals.

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SORPCJA Zn, Cd I Mn NA WYBRANYCH MINERAŁACH ILASTYCH

Streszczenie

Kumulacja metali ciężkich m.in. w glebach oraz osadach dennych zbiorników wodnych jest jednym z ważniejszych czynników zanieczyszczenia środowiska naturalnego.

Sorpcja metali ciężkich na cząstkach gleb i osadów ilastych szczególnie w przypadku niektórych metali, takich jak Zn, Cd i Mn odbywa się bardzo gwałtownie.

Ponad 90% sorpcji ma miejsce w ciągu 15 minut, zaś stan równowagi zostaje osiągnięty po ok. 20 godz.

Przeprowadzono sorpcję Zn na minerałach ilastych, z grupy smektytu: montmorillonit Wyoming, montmorillonit Arizona, beidellit Mikołajowice, minerał o strukturze mieszanopakietowej smektyt/illit Konin, a także na illicie Montana i kaolinicie Georgia. Dla minerałów tych określono pojemność wymiany jonowej oraz całkowitą powierzchnię rozwiniętą, a także zawartość "żelaza wolnego".

Na próbkach illitu, kaolinitu oraz minerału o strukturze mieszanopakietowej smektyt/illit wykonano sorpcję Cd i Mn. Badania sorpcji Zn, Cd i Mn przeprowadzono przy ich koncentracji w roztworze 1—40 ppm, przy pH 7.

Uzyskane wyniki pozwoliły na wykreślenie izoterm sorpcji poszczególnych metali. W zakresie użytych stężeń metali w roztworze wyjściowym biegną one zgodnie z izotermą Freundlicha. Dla niskich stężeń Zn w roztworze, przebieg sorpcji jest podobny w przypadku wszystkich minerałów z wyjątkiem beidellitu. Minerał ten wykazuje najlepsze właściwości sorpcyjne.

Uzyskane izotermy sorpcji wskazują, że sorpcja metali w przypadku illitu jest również wysoka; zaznacza się też większe zróżnicowanie pomiędzy poszczególnymi metalami. Zn sorbowany jest lepiej i w większych ilościach niż kadm, zaś Mn w najmniejszych ilościach.

Kaolinit sorbuje te same metale w znacznie mniejszej ilości, wykazuje też niewielkie zróżnicowanie w sorpcji pomiędzy poszczególnymi metalami.

Uzyskane wyniki sorpcji Zn, Cd i Mn na minerałach ilastych wskazują, że dla użytych stężeń metali w roztworze, pojemność wymiany jonowej jak i całkowita powierzchnia rozwinięta minerałów nie mają decydującego wpływu na wielkość sorpcji. Jak się wydaje, sorpcja metali ciężkich na minerałach ilastych zależy od struktury danego minerału i jest różna dla różnych metali. Istotny wpływ w minerałach z grupy smektytu i w illicie mieć może wielkość ładunku pakietu i jego pochodzenie. W przypadku kaolinitu sorpcja może zależeć od ilości "centrów aktywnych" pochodzących od zerwanych wiązań na krawędziach lub powierzchniach blaszek tego minerału.

Stwierdzono, że w przypadku sorpcji metali ciężkich, obok minerałów ilastych z grupy smektytów, charakteryzujących się wysoką powierzchnią rozwiniętą oraz pojemnością jonowymienną, istotną rolę mogą odgrywać również illit a także kaolinit.

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СОРБЦИЯ Zn, Cd И Mn НА НЕКОТОРЫХ ГЛИНИСТЫХ МИНЕРАЛАХ

Резюме

Накопление тяжелых металлов в частности в почвах, а также в донных отложениях водоемов, является одним из важнейших факторов загрязнения окружающей среды.

Сорбция тяжелых металлов на частицах почв и глинистых отложений, особенно в случае некоторых металлов, таких как Zn, Cd и Mn, происходит очень стремительно. Свыше 90% сорбции имеет место в течение 15 минут, состояние же равновесия достигается примерно по истечении 20-и часов.

Проводилась сорбция Zn на минералах группы смектита: монтмориллонит — Вайоминг, монтмориллонит — Аризона, бейделлит — Миколаёвице, минерал со смешанно-пакетной структурой смектит/иллит — Конин, а также на иллите — Монтана и каолините — Джорджия. Для этих минералов определены емкость ионообмена, а также полная развернутая поверхность и содержание „свободного железа".

На образцах иллита, каолинита, а также минерала со смешанно-пакетной структурой смектит/иллит, проведена сорбция Cd и Mn. Исследования сорбции Zn, Cd и Mn проводились при их концентрации в растворе 1—40 ppm и pH7.

Полученные результаты позволили построить изотермы сорбции отдельных металлов. В пределах примененных концентраций металлов в исходном растворе они проходят согласно изотерме Фрейндлиха. Для низких концентраций Zn в растворе, ход сорбции у всех минералов похож, за исключением бейделлита. Этот минерал обнаруживает наилучшие сорбционные свойства.

Полученные изотермы показывают, что сорбция металлов в случае иллита тоже высока; отмечается также большее расхождение между отдельными металлами. Zn лучше сорбируется и в большем количестве чем кадмий, Mn же в наименьших количествах.

Каолинит сорбирует те же самые металлы в значительно меньшем количестве, обнаруживает также небольшое расхождение в сорбции отдельных металлов.

Полученные результаты сорбции Zn, Cd и Mn на глинистых минералах указывают, что для применяемых в выше представленных исследованиях концентраций металлов в растворе, емкость ионообмена, как и полная развернутая поверхность минералов, не оказывают решающего влияния на величину сорбции. Кажется, что сорбция тяжелых металлов на глинистых минералах зависит от структуры данного минерала и различна для разных металлов. Существенное влияние в минералах группы смектита и в иллите может иметь величина заряда пакета и его происхождение. В случае каолинита сорбция может зависеть от количества «активных центров», происходящих от разорванных соединений на ребрах, или поверхностях пластинок этого минерала.

Констатировано, что в случае сорбции тяжелых металлов, кроме глинистых минералов группы смектита, характеризующихся большой суммарной удельной поверхностью, а также ионообменной емкостью, существенную роль могут играть также иллит и каолинит.