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THE INFLUENCE OF Fe-OXIDE COATINGS ON THE ADSORPTION OF Zn ONTO CLAY MINERALS

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Abstract. The influence of Fe-oxide coatings on the adsorption of zinc onto clay minerals was investigated in three experimental series: 1. natural standard clay minerals: kaolinite, illite and smectite, 2. the same clay matrices after sequential extraction with hydroxylamine hydrochloride, oxalate buffer and dithionite/citrate buffer solutions. 3. clay matrices with artificial coatings of Fe-oxohydrates. Results obtained indicate that in respect to the adsorption of zinc, Fe-oxides have some influence on kaolinite, but only little influence on illite and smectite and that structural and other characteristics such as CEC (cation exchange capacity) and SSA (specific surface area) are more important for the adsorption behavior of zinc (and other transition elements) on trioctahedral clay minerals.

INTRODUCTION

Characteristic for clay minerals is their large surface area of 10—800 m²/g which is said to be the major reason for the enrichment of heavy metals on clays.

Jenne (1966) suggested that this enrichment occurs less as a direct adsorption onto clay mineral surfaces, rather being adsorbed onto coatings, which, in addition to organic substances, consist of iron and manganese oxyhydrates. Thus, in extraction experiments with sediments containing a high percentage of clay minerals, the greater part of heavy metals was released from the iron and manganese oxide phases, even though the relative weight of these phases amounted to only a few percent (Schmoll, Förstner 1979; Förstner, Patchineelam 1980). On the other hand, Shuman (1976) investigating soils, found that the removal of iron oxides increases the capacity to adsorb Zn in more instances than it was decreased.

In order to gain further information on the significance of oxidic phases during the adsorption of heavy metal ions on various clay minerals the adsorption of Zn²⁺ on standard samples — kaolinite, illite and smectite — was assessed.

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In addition, by extraction with hydroxylammonium chloride, oxalic acid buffer and dithionite solution, these samples were freed of iron to various degrees. The influence of these processes and the artificial coating with Fe-oxides on the adsorption of Zn^{2+} was then analyzed.

MATERIALS AND METHODS

The following standard clay minerals were used for the present investigations:

- kaolinite KGa-2-Georgia
- illite, IMt-1, Montana, fraction $<2 \mu m$
- smectite, Poznanski clay (Poland), fraction $<2 \mu m$

In order to coat the clay minerals used with oxidic iron phases according to methods for the production of pure goethite or haematite (Atkinson 1967), their aqueous suspensions were injected with Fe^{3+} , shaken and the solid phase isolated. A small amount of water was then added and a) the solution was boiled for 24 hours under reflux (haematite) and b) the pH was raised to 12 with KOH and the solution was tempered at $60^\circ C$ for 24 hours. Both samples were centrifugated and the solid phase dried at $60^\circ C$.

The physical and chemical characteristics of all materials used is compiled in Table 1.

Table 1

Chemical and physical properties of samples investigated

	Kaolinite			Smectite			Illite		
	SSA	CEC	NS-Fe ¹ (ppm)	SSA	CEC	NS-Fe ¹ (ppm)	SSA	CEC	NS-Fe ¹ (ppm)
Untreated samples	16.3	4.3	411 ⁺	49.2	45.1	1000 ⁺	43.3	28.4	2058 ⁺
Extracted samples:									
HY	18.9	4.9	20	51.5	47.3	550	44.9	24.2	800
OX	20.1	5.4	150	55.6	45.9	650	49.0	23.3	1200
DI	16.5	6.2	1000	15.3	41.5	1420	44.0	22.2	200
Coated samples:									
Haematite	18.1	—	1647	55.6	—	11.428 ⁺	52.6	—	13.142 ⁺
Goethite	22.1	—	3092	51.0	—	10.857	45.7	—	13.142 ⁺

key: SSA (specific surface area — N_2 area in m^2/g), CEC (cation exchange capacity in meq/100 g) and non-silicate (NS) iron content extraction solution for clay minerals.

⁺ iron content in dithionite solution for untreated and coated clay minerals.

¹ non-silicate iron

The selective release of non-silicate iron oxides was attained by shaking a 100 mg sample with 10 ml extraction solution (0.1 m hydroxyl-ammonium chloride in 0.01 m nitric acid — HY — Chao 1972); 0.4 m oxalic acid) ammonium oxalate buffer — OX — (Schwertmann 1964); and 0.05 m sodium dithionite in 0.27 m Na-citrate solution — DI (Holmgren 1967) for 12 hours. In respect to the adsorption studies, 100 mg of the various solid substances were injected with 10 ml of 1, 10, 20 and 40 ppm zinc solution, adjusted at pH 7, shaken for 12 hours and centrifugated. The solution was analyzed for zinc content with AAS (atomic adsorption spectrometry).

RESULTS AND DISCUSSION

Figures 1a, b, c show the adsorption of zinc from a 10 ppm solution onto standard clay minerals after consecutive treatment with the various extraction reagents. Also shown are the development of cation exchange capacity (CEC), the specific surface area (SSA) and the amount of Fe remaining on the standard clay after each extraction. Here, the extractable amount for all reagents ("non-silicate iron") is set at 100%. For all other parameters, the values of the untreated sample is 100. The relations between the adsorbed amount of zinc and the parameters already mentioned can be summarized as follows:

- for kaolinite, a correlation between the zinc adsorption and the iron amount in the clay particles is apparent,
- for illite, there is a highly significant correlation between CEC and the amount of adsorbed zinc,
- for smectite, a correlation between zinc adsorption and SSA seems to be most probable.

These findings — confirmed for various zinc concentrations between 1 and 40 ppm — become understandable upon consideration of the structure of the various standard clay minerals.

Kaolinite shows no distinct adsorption characteristics; thus, changes on the mineral surface — for example, Fe-oxide coatings — could evoke marked changes of adsorption capacity. On the other hand, the significance of CEC for the adsorption characteristics of illite can be explained by surface charge, a result of isomorphic substitution in tetrahedral layers. Smectite clay minerals, which have lower surface charge, indicate — due to the much larger surface area — an influence by Fe-oxides only to the extent that their specific surface area is also increased.

All together it was shown during the present investigations that Fe oxides play a role for the adsorption of zinc onto kaolinite, have no relevance for the same onto illite and, in respect to the adsorption onto smectite, no specific influence of Fe oxides is visible.

To test these preliminary results, further adsorption experiments were made with clay standards that were coated with goethite or haematite layers. Results are shown in Fig. 2a—c. An improvement in the adsorption capacity of kaolinite is attained with Fe-oxide coatings. These can be traced chiefly to the increased SSA, but in the case of goethite there is a certain specific improvement of the adsorption capacity.

For illite, there is no visible influence by the Fe amount and the surface charge, which agrees with the results given above.

Smectite shows an improvement in the adsorption capacity, which corresponds proportionally to the increase in the surface area. The importance of Fe layers seems to become greater as the concentration of zinc increases.

In order to ascertain if there is a specific influence of oxidic Fe coatings on the adsorption of zinc on clay minerals, the mean values of the quotients from the amounts adsorbed onto the 3 untreated clay minerals and from the goethite- and haematite-coated samples (mean of the adsorption from 1, 10, 20, 40 and 100 ppm solutions) were set in ratio with the specific surface areas of each untreated and mineral phase:

$$\frac{Ads_{UN}}{Ads_{G,H}} \cdot \frac{SSA_{UN}}{SSA_{G,H}} \quad K, I, S$$

The mean value of the 6 quotients named in Table 2 was 1.00 ± 0.14 . An influence of Fe-oxidic coating other than a surface area effect cannot be determined.

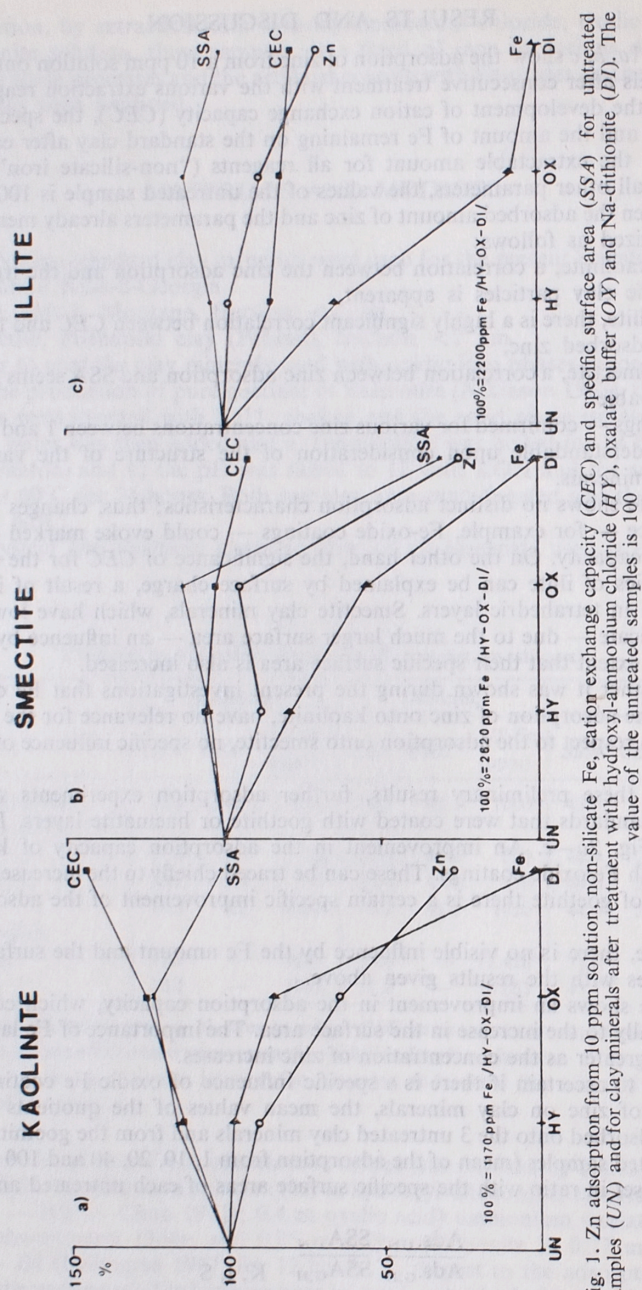


Fig. 1. Zn adsorption from 10 ppm solution, non-silicate Fe, cation exchange capacity (CEC) and specific surface area (SSA) for untreated samples (UN) and for clay minerals after treatment with hydroxyl-ammonium chloride (HY), oxalate buffer (OX) and Na-dithionite (DI). The value of the untreated samples is 100

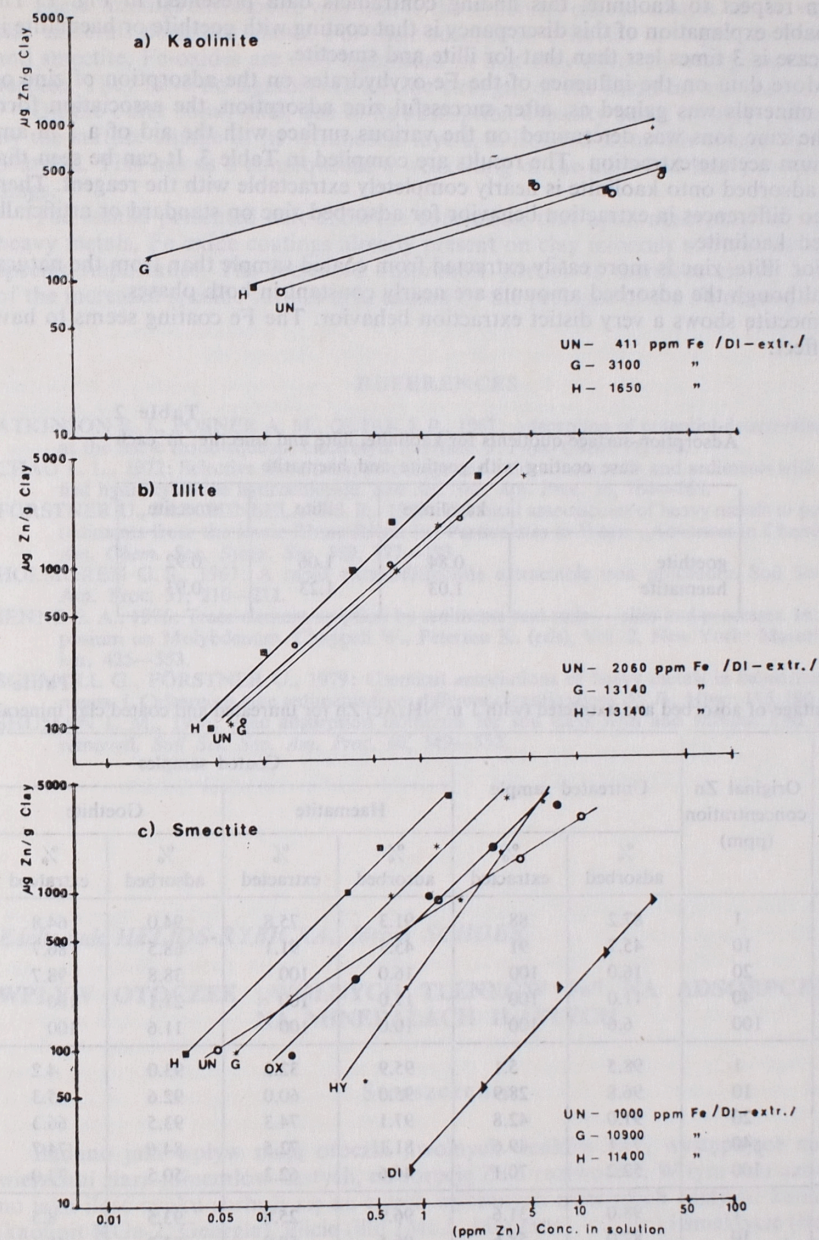


Fig. 2. Freundlich adsorption isotherms (a, b) for untreated and coated clay minerals and additional isotherms (c) for smectite after treatment with the extraction reagents.

Key: UN — untreated samples, H — haematite coated, G — goethite coated, Extraction reagents: HY — hydroxylammonium chloride, OX — oxalate buffer, DI — Na dithionite

In respect to kaolinite, this finding contradicts data presented in Fig. 1. The probable explanation of this discrepancy is that coating with goethite or haematite in this case is 3 times less than that for illite and smectite.

More data on the influence of the Fe-oxyhydrates on the adsorption of zinc on clay minerals was gained as, after successful zinc adsorption, the association form of the zinc ions was determined on the various surface with the aid of a 1 M ammonium acetate extraction. The results are compiled in Table 3. It can be seen that zinc adsorbed onto kaolinite is nearly completely extractable with the reagent. There are no differences in extraction behavior for adsorbed zinc on standard or artificially coated kaolinite.

For illite, zinc is more easily extracted from coated sample than from the natural one although the adsorbed amounts are nearly constant in both phases.

Smectite shows a very distinct extraction behavior. The Fe coating seems to have no effect.

Table 2
Adsorption-surface quotients for kaolinite, illite and smectite; in each case coating with goethite and haematite

	kaolinite	illite	smectite
goethite	0.84	1.06	0.92
haematite	1.03	1.23	0.93

Table 3
Percentage of adsorbed and extracted (with 1 M NH_4Ac) Zn for untreated and coated clay minerals

Minerals	Original Zn concentration (ppm)	Untreated sample		Coated samples			
		% adsorbed	% extracted	Haematite		Goethite	
				% adsorbed	% extracted	% adsorbed	% extracted
Kaolinite	1	87.2	88	91.3	75.8	94.0	64.8
	10	45.7	91	45.7	91.1	68.5	86.7
	20	16.0	100	16.0	100	38.8	98.7
	40	11.0	100	11.0	100	21.1	100
	100	6.6	100	10.0	100	11.6	100
Illite	1	98.5	5.1	95.9	32.3	93.0	4.2
	10	96.8	28.9	95.0	60.0	92.6	45.3
	20	91.0	42.8	97.1	74.3	93.5	66.3
	40	77.1	49.6	81.1	72.5	84.6	74.7
	100	52.2	70.1	46.6	62.3	50.5	73.0
Smectite	1	98.0	31.6	96.9	25.8	93.5	8.5
	10	87.0	58.6	96.5	58.0	93.3	45.1
	20	77.4	67.2	97.2	67.9	93.5	65.1
	40	71.4	70.3	96.1	75.7	90.7	71.6
	100	53.3	76.5	80.0	74.2	67.8	72.1

These findings correspond very well to the structural characteristics of the various clay minerals described above. For their adsorption behavior in respect to kaolinite and smectite, Fe-oxides are only significant in that they effect an enlargement of the surface. They have no significance for the strength of the chemical association.

On the other hand, illite, due to its adsorption capacity being strongly influenced by the surface charge of its tetrahedral layers, is isolated from this charge by its Fe coatings. This has as a consequence a weakening of the adsorbed heavy metal bondings.

The results presented here allow the conclusion that upon adsorption of soluted heavy metals, Fe oxide coatings already present on clay minerals surfaces have little specific importance. The increased adsorbable portion is therefore chiefly a result of the increased specific surface area caused by the presence of the Fe coatings.

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WPLYW OTOCZEK „WOLNYCH TLENKÓW Fe” NA ADSORPCJĘ Zn NA MINERAŁACH ILASTYCH

Streszczenie

Badano jaki wpływ mają otoczki „wolnych tlenków Fe”, występujące na powierzchni ziarn mineralów ilastych, na sorpcję Zn z roztworów. W tym celu oznaczano jaką ilość cynku sorbuje się na trzech wybranych mineralach ilastych: kaolinicie (kaolinit KGa-2, Georgia), illicie (illit IMt-1, Montana, $<2\text{ }\mu\text{m}$) i smektycie (frakcja $<2\text{ }\mu\text{m}$ iłu poznańskiego). Prowadzono także sorpcję Zn na tychże mineralach, po ekstrakcji „wolnych tlenków Fe” (*non-silicate Fe*) kolejno następującymi odczynnikami: chlorowodorkiem hydroksylaminy, buforem szczawianowym i ditioninem sodowym. Po każdym etapie ekstrakcji oznaczano pojemność wymiany kationów (CEC).

и поверхность właściwą (SSA) próbek. W ostatniej serii badań sorbowano cynk na badanych minerałach ilastych po pokryciu ich powierzchni hematytom i goethytom.

Badania wykazały, że obecność „wolnych tlenków Fe” ma wyraźny wpływ na sorpcję Zn przez kaolinit; mniej wyraźnie wpływ ten zaznacza się w przypadku smektytu, natomiast jest problematyczny w przypadku illitu. Ilość Zn sorbowanego przez illit i smektyt w większym stopniu zależy od pojemności wymiany kationów i powierzchni właściwej.

OBJAŚNIENIA FIGUR

Fig. 1. Adsorpcja Zn z roztworu o stężeniu 10 ppm, Fe niezwiązane w krzemianach, pojemność wymiany kationów (CEC), powierzchnia właściwa (SSA) dla próbek wyjściowych (UN) i po obróbce: chlorowodorowym hydroksylaminą (HY), buforem szczawianowym (OX) i ditioni-
nem sodowym (DI). Dla próbek wyjściowych przyjęto wartości 100

Fig. 2. Izotermy adsorpcyjne (a, b) Freundlicha dla próbek wyjściowych i pokrytych hematytom i goethytom oraz dodatkowe izotermy (c) dla smektytu poddanego działaniu odczynników ekstrakcyjnych;

UN — próbki wyjściowe, H — pokryte hematytom, G — pokryte goethytom. Odczynniki ekstrakcyjne: HY — chlorowodorek hydroksylaminy, OX — bufor szczawianowy, DI — ditionin sodowy.

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ВЛИЯНИЕ ОБОЛОЧЕК «СВОБОДНЫХ ОКИСЛОВ Fe» НА АДсорбЦИЮ НА ГЛИНИСТЫХ МИНЕРАЛАХ

Резюме

Изучалось влияние оболочек «свободных окислов Fe», присутствующих на поверхности зерен глинистых минералов, на сорбцию Zn из растворов. С этой целью определено, какое количество Zn сорбируется на трех избранных глинистых минералах — каолините (каолинит KGa-2, Джорджия), иллите (иллит IMt-1, Монтана, < 2 мкм) и смектите (фракция < 2 мкм познаньской глины). Проводилась также сорбция на этих же минералах после экстракции «свободных окислов Fe» (несиликатного Fe) последовательно следующими реагентами: хлористоводородным гидроксиламинном, оксалатным буфером и натриевым дитионинном. После каждого этапа экстракции определялись величина обменной способности катионов (CEC) и удельная поверхность образцов (SSA). В последней серии исследований цинк сорбировался на изучаемых глинистых минералах после покрытия их поверхности гематитом и гётитом.

Исследованиями обнаружено, что присутствие «свободных окислов Fe» имеет явное влияние на сорбцию Zn каолинитом; менее четкое в случае смектита, а проблематично в случае иллита. Количество Zn, сорбированного иллитом и смектитом, в большей степени зависит от катионной обменной способности и удельной поверхности.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Fig. 1. Адсорбция Zn из раствора, содержащего 10 г/г, несиликатное Fe, катионная обменная способность (CEC), удельная поверхность (SSA) для исходных образцов (UN) и после обработки: хлористоводородным гидроксиламинном (HY), оксалатным буфером (OX) и натриевым дитионинном (DI). Для исходных образцов принято значение 100

Fig. 2. Адсорбционные изотермы Фрейндлиха (a, b) для исходных, а также покрытых гематитом и гётитом образцов и дополнительные изотермы (c) для смектита, подверженному воздействию экстрагирующих реагентов

UN — исходные образцы, H — покрытые гематитом, G — покрытые гётитом. Экстрагирующие реагенты: HY — хлористоводородный гидроксиламин, OX — оксалатный буфер, DI — натриевый дитионин