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MODEL STUDIES ON IMMOBILIZATION OF CERTAIN HEAVY METALS BY SYNTHETIC ZEOLITE

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INTRODUCTION

In modern world there are many sources of heavy metals emissions, which have been deposited in our environment mainly in soil. This type of the environment contamination still has risen.

To solve the problem many methods were proposed most of which are very expensive and onerous. One of a new possible way to achieve this goal is to use zeolites as „reconstituent traps” of soils heavy metals [1, 2]. It is well known that zeolites — primarily natural occur in soils [5, 7], now natural and synthetic molecular sieves [4] — possess many interesting properties connected with their fine defined crystal structure and intracrystalline cavities. The particular properties e.g. large ion exchange and adsorption capacities course that use of zeolites in soil improves some properties of soil and at the same time zeolites act as good traps for the metals presented in soil. Practical methods of the use of synthetic molecular sieves as the traps in soils were worked out [6].

Borowiak [3] studies the dynamic of changes of heavy metals content in soils in a system „zeolite—soil”. It was found the dynamic depends on properties of the soils. More detail model studies on this problem were suggested.

There is just the purpose of the present paper to describe results of the model studies on synthetic zeolite type 4A competed for heavy metals ions (Zn(II), Cu(II), Pb(II)) with some mineral soils components.

MATERIALS AND METHODS

Systems: the zeolite — a model mineral soil component were studies separately. 100 g of a sample of the air — drying component and

5 g of the zeolite were placed in quartz beaker. Next the solid mixture was covered by a solution of the nitrates with $\text{pH} = 5$ (1 mm up the solid phase). After mixing 3 drops of chlorophorm were added and the beaker was shut close. Each studied system contained 12 000 ppm Zn(II), 3000 ppm Cu(II) and 6000 ppm Pb(II). A conservation time of the systems was one, six and twelve months in a dark place and a room temperature. Each experiment was four time repeated.

After and of the experiment the solid phase was separated from the solution, dried in room temperature and next the zeolite phase was separated from the component phase.

For the metals extractions from the zeolite after the experiment the following media were used: 1) re-distillated water, 2) aqueous solution 1 M $\text{CH}_3\text{COONH}_4$ ($\text{pH} = 7,2$), 3) aqueous solution 0,1 M HCl, 4) aqueous solution 20% HCl.

To extract the metals a sample of zeolite was consecutively treated with 1., 2., 3., and 4 media during 24 hours. The ASA technique was used for analysis of the metals in solutions, Zn(II) and Cu(II) were analyzed in the aqueous solutions, and Pb(II) — after extracting from the solutions to organic phase.

RESULTS

Zinc. The results of the zinc extractions from the zeolites after the experiments are presented in Table 1. A total content of zinc in the zeolites were calculated as a sum of the four consecutive extractions and an amount of exchangeable zinc in the zeolites, available in the natural soil conditions for an ion exchange and for plant was assumed to be a sum of extracted with H_2O , 1 M $\text{CH}_3\text{COONH}_4$, and 0,1 M HCl.

The biggest total content of zinc was found in the experiments with quartz sand (92,35—99,06% of added zinc, depends on the conservation time), the same order was found for $\text{Fe}_2\text{O}_3 \times n\text{H}_2\text{O}$ after 12 months (98,54%) starting from 66,43% after 1 month. In the present of kaolinit the content was found to be lower (46,43—56,65%) but still much more higher as compare with bentonite (0,28—0,91%) and beidelite (1,65—1,96%). These latter results probably may be explained taking into account large sorption capacities of bentonite and beidelite which are about 7—26 times greater than that of kaolinite. The affinity of zinc for the minerals may also play a role.

A percent portion of exchangeable zinc expressed as a ratio of the amount and the total content of zinc in the zeolite was found to be greatest in the present of kaolinite (29,27—38,96%) and lowest in the present of $\text{Fe}_2\text{O}_3 \times n\text{H}_2\text{O}$ (7,40—10,28).

Tabela 1

Results of zinc extractions

Item	Time [months]	The extracting media, ppm				$\Sigma_{1,2,3,4}$ ppm	CT^a	Ex^b
		1	2	3	4		%	
Quartz sand	1	0,6	1680	516	10000	11196,6	92,85	10,69
	6	0,9	1900	1820	8200	11920,9	98,89	31,21
	12	0,8	1440	2000	8500	11940,8	99,06	28,82
Kaolinite	1	0,6	1680	502	3420	5602,6	46,43	38,96
	6	0,6	1640	552	4660	6852,6	56,65	32,00
	12	0,9	1280	656	4680	6616,9	54,69	29,27
Bentonite	1	0,8	8,6	10	144	163,4	0,91	11,82
	6	1,2	6,7	5,2	74	87,1	0,28	15,04
	12	1,0	8,9	6,2	107	123,0	0,57	13,01
Beidelite	1	0,6	26,0	66	160	252,6	1,65	31,95
	6	0,6	21,2	48	220	289,8	1,96	31,73
Fe ₂ O ₃ x nH ₂ O	1	1,2	512	312	7200	8025,2	66,43	10,28
	6	1,8	528	363	10200	1109,8	91,98	8,05
	12	1,2	466	412	11000	11879,2	98,54	7,40
Zeolite before experiments	traces		0,4	1,4	52,7	54,5	—	—

^a $CT = (\Sigma_{1,2,3,4} - \Sigma_{zeolite}) \cdot 100 / \text{amount of added zinc.}$

^b $Ex = \Sigma_{1,2,3} \cdot 100 / \Sigma_{1,2,3,4}.$

Copper. The results of the copper extraction from the zeolites after the experiments are presented in Table 2. The total content of copper in the zeolites was found to decrease in order: quartz sand (72,28—77,33^{0/0}); kaolinite (39,47—43,77^{0/0}); $\text{Fe}_2\text{O}_3 \times n\text{H}_2\text{O}$ (29,52—36,99^{0/0}); beidelite (0,37—0,47^{0/0}) and bentonite (0,17—0,51^{0/0}).

The percent portion of exchangeable copper was found to be greatest in the present of kaolinite (44,33—47,51^{0/0}) and lowest in present of hydrated iron (III) oxide (7,96—15,49^{0/0}).

Lead. The results of the lead extraction from the zeolites after the experiments are presented in Table 3. All of the lead added to the quartz sand — zeolite system was found to be in the zeolite after 1 month (the total content 99,27^{0/0}). In the present of kaolinite the content was 63,45—75,08^{0/0} depends on the conservation time. Only a small content of lead was in zeolite in present of bentonite, beidelite and $\text{Fe}_2\text{O}_3 \times n\text{H}_2\text{O}$: 1,17—2,92^{0/0}; 0,72—0,75^{0/0}; 0,42—1,00^{0/0}, respectively.

The percent portion of exchangeable lead was found to change from 10,12^{0/0} to 55,77^{0/0} depends on the mineral components and time.

DISCUSSION

There are many types of possible interactions between zeolite and soil in any zeolite-soil system but it seems reasonable to assume that most of the interactions occur through a natural aqueous solution in a wet soil. The solution may be in an equilibrium with the exchangeable ions of heavy metals there are on mineral and organic components of soil. The interactions between the natural component of soil as also between the natural component and zeolite may change this equilibrium state replaced ions on sites more thermodynamic favourable. For the same reason in zeolite interacted with a solution salt occlusion or imbibition of heavy metals compounds are possible too [4]. Water and small organic compounds would be adsorbed very strong by zeolites also. The latter adsorption may be eliminate if a zeolite with small windows will be used.

In the present studies a first step was made to model the complicated system zeolite-soil. The models used in our studies represent „zeolite-aqueous solutions component of soil” system as simple as possible (e.g., the solutions contains only four types of ions, three metals ions and nitrate ion), a component of soil in the beginning of experiments did not contain contaminations of heavy metals studied it was used the zeolite 4A with narrow windows (about 4A, etc.). To model the natural conditions at the end of any experiment no wash and only drying were used. It means that the obtained total content

Table 2

Results of copper extractions

Item	Time [months]	The extracting media, ppm				$\Sigma_{1,2,3,4}$ ppm	CT^a	Ex^b
		1	2	3	4			%
Quartz sand	1	0,3	566	253	1360	2179,3	72,28	37,59
	6	0,8	357	451	1540	2348,8	77,93	19,20
	12	tr	279	486	1460	2225,0	73,81	34,38
Kaolinite	1	tr	390	197	737	1324,0	43,77	44,33
	6	tr	322	205	684	1211,0	40,01	43,52
	12	tr	309	260	626	1195,0	39,47	47,52
Bentonite	1	tr	4,4	1,8	19,9	26,1	0,51	23,75
	6	tr	2,9	1,0	12,0	15,9	0,17	24,53
	12	tr	4,0	1,1	17,9	23,0	0,41	22,17
Beidelite	1	tr.	4,6	4,4	12,8	21,8	0,37	41,28
	6	tr	6,0	3,0	15,8	24,8	0,47	36,29
$Fe_2O_3 \cdot x n H_2O$	1	0,8	36,9	33,7	825	896,4	29,52	7,96
	6	0,9	73,2	61,0	870	1005,1	33,14	13,44
	12	1,4	74,0	98,2	947	1120,6	36,99	15,49
Zeolite before experiments		tr.	tr.	tr.	11,0	11,0	--	--

^{a,b} See Table 1, tr = trace.

Table 3

Results of lead extractions

Item	Time [months]	The extracting media, ppm				$\Sigma_{1,2,3,4}$ ppm	CT ^a	Ex ^b %
		1	2	3	4			
Quartz sand	1	0,8	958	781	4318	5957,8	99,27	27,53
	6	0,8	954	1586	3492	6033,8	100	42,13
	12	0,8	922	1730	3385	6037,8	100	43,94
Kaolinite	1	0,8	918	888	2019	3825,8	63,45	47,23
	6	0,8	1237	949	2338	5423,8	75,08	48,33
	12	0,8	1290	1138	1776	4205,8	69,77	57,77
Bentonite	1	tr.	tr.	20	69	89	1,17	22,47
	6	tr.	tr.	23	118	141	2,03	16,31
	12	tr.	tr.	25	169	194	2,92	12,87
Beidelite	1	tr.	6	20	36	62	0,72	41,93
	6	tr.	6	18	40	64	0,75	37,50
Fe ₂ O ₃ xH ₂ O	1	tr.	8	tr.	50	58	0,65	13,79
	6	tr.	8	tr.	71	79	1,00	10,12
	12	tr.	6	tr.	38	44	0,42	13,64
Zeolite before experiments		tr.	tr.	tr.	19	19	—	—

^{a,b} See Table 1.

of heavy metals in zeolites results not only from the studied interactions in the system but from the drying operation, also.

The model studies presented in this paper illustrate that an effectiveness of action of the zeolite as heavy metals trap is depend on type of the component of soil and of metal. It is easy for the zeolite to compete for heavy metals ions with quartz sand and—less—with kaolinite. The largest effect was found with quartz sand for lead (about 100% added lead was trapped very quickly by zeolite), a little lower—for zinc (95%) and for copper (75%). Only a little effect was observed for bentonite and beidelite. From this point of view it seems not reasonable to expect this type of zeolite may be a good trap of the metals in heavy soils. On the other hand, using the type of zeolite in soil from Katowice (with very large contamination of heavy metals) about 80% of lead was removed from the soil after three months [1]. This problem need more detail studies.

It seems that about 78% of zinc, 70% of copper and 68% of lead trapped in zeolite should be not available in natural conditions for plants, as indicate the results of percent portion of exchangeable metals in zeolite.

REFERENCES

- [1] Borowiak M., Górny M., Kot B., Lewandowski W. Study on distribution of heavy metals in anthropogenic soil-zeolite systems. Prep. Pap. of Sc. Meeting PTChem., Katowice 1983.
- [2] Borowiak M., Czarnowska K., Lewandowski W., Kot B. Study on dynamic of changes of heavy metals contents in anthropogenic soils in present of zeolites. III Nat. Conf. „Influence of contaminations of trace metals on natural conditions of agriculture”. Pulawy 1985.
- [3] Borowiak M., Czarnowska K., Lewandowski W., Kot B. Study on dynamic of changes of heavy metals contents in anthropogenic soils in present of zeolites. Roczn. Glebozn. 1986, 37 (4), 67.
- [4] Breck D. W. Zeolite molecular sieves. Willey, New York 1974.
- [5] Brogowski Z. The possibility of zeolites occurrence in the soils of Poland. Zesz. Prob. Post. Nauk Rol. 1983, 220.
- [6] Gworek B., Borowiak M. Zgt. Pat. No 283821 (RP). 1990.
- [7] Sandy L. B., Mumpton F. A. Natural zeolites. Occurrence, properties, uses. Pergamon Press, New York 1978.

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МОДЕЛЬНЫЕ ИССЛЕДОВАНИЯ ПО СОРБЦИИ ТЯЖЕЛЫХ МЕТАЛЛОВ СИНТЕТИЧЕСКИМИ ЗЕОЛИТАМИ

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Резюме

Проводились модельные исследования по сорбции тяжелых металлов (Pb, Zn и Cu) синтетическими цеолитами в единичных системах с кварцевым песком (стекольным), каолинитом, бейделитом, бентонитом и гидратированной окисью железа. Указанные минеральные компоненты смешивали с цеолитом в весовом соотношении 20 : 1 и заливали раствором нитратов Pb(II), Zn (II) и Cu (II) в количествах соответственно 6000, 12000 и 3000 мг/кг сухого вещества минерального компонента. Инкубация системы продолжалась 1, 6 и 12 месяцев.

В системе цеолит — кварцевый песок исследуемый материал сорбировал 99,27 — 100% прибавленного свинца, 92,35 — 99,06% цинка и 72,28 — 77,89% меди; в системе с каолинитом соответственно 63,45—75,08 Pb, 46,43 — 56,65% Zn и 39,47 — 43,77% Cu; в системе с бентонитом соответственно 1,17 — 2,92% Pb, 0,28 — 0,91 % Zn и 0,17—0,51% Cu; в системе в бейделитом соответственно 0,72 — 0,75% Pb, 1,65 — 1,96% Zn и 0,37 — 0,47% Cu; в системе с гидратированной окисью железа соответственно 0,65 — 1,00% Pb, 66,43 — 98,54% Zn и 29,52 — 36,99% Cu.

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MODELOWE BADANIA NAD SORPCJĄ METALI CIĘŻKICH PRZEZ SYNTETYCZNE ZEOLITY

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Streszczenie

Przeprowadzono modelowe badania nad sorpcją metali ciężkich (Pb, Zn i Cu) przez syntetyczne zeolity w układach pojedynczych z piaskiem kwarcowym (szklarskim), kaolinitem, beidelitem, bentonitem oraz uwodnionym tlenkiem żelazowym. Wymienione komponenty mineralne zmieszano z zeolitem w stosunku wagowym 20 : 1 i zalano roztworem azotanów Pb(II), Zn(II) i Cu(II) w ilości odpowiednio 6000, 12000 i 3000 mg/kg suchej masy komponenta mineralnego. Inkubacja układu trwała 1, 6 i 12 miesięcy.

W układzie zeolit — piasek kwarcowy badany minerał zasorbował 99,27—100% dodanego ołowiu, 92,35—99,06% cynku i 72,28—77,93% miedzi; w układzie z kaolinitem odpowiednio 63,45—75,08% Pb, 46,43—56,65% Zn i 39,47—43,77% Cu; w układzie z bentonitem odpowiednio 1,17—2,92% Pb, 0,28—0,91% Zn i 0,17—0,51% Cu; w układzie z beidelitem odpowiednio 0,72—0,75% Pb, 1,65—1,96% Zn i 0,37—

0,47% Cu; w układzie z uwodnionym tlenkiem żelaza odpowiednio 0,65—1,00% Pb, 66,43—98,54% Zn i 29,52—36,99% Cu.

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