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DETERMINATION OF HEAVY METAL UPTAKE BY THE SODIUM FORM OF HEULANDITE USING RADIOCHEMICAL TECHNIQUES

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Abstract: The uptake of mercury, silver and cadmium ions from aqueous solutions by the sodium form of heulandite (NaHeu) has been studied at room temperature using radiochemical techniques. The concentration of the used solutions was varied approximately from 500 to 20000 mg/l. The concentration of the metal ions in the solutions after the treatments, determined by tracer techniques, was used for the determination of the uptake extend. At lower concentrations the uptake sequence of the investigated metal ions by the NaHeu is Ag > Hg > Cd, while at higher concentrations the sequence is Hg > Ag > Cd. The uptake is attributed not only to ion-exchange procedures but also to adsorption of some ionic species onto the surface of NaHeu grains.

Key words: sodium heulandite, radiochemical techniques, ion exchange and adsorption of Hg, Ag and Cd.

Introduction

Heulandite (Na, K)$Ca_4(Al_9Si_{27}O_{72})$.24 H_2O, along with clinoptilolite, stilbite, stellerite, barrerite and brewsterite belongs to the heulandite group of natural zeolites (Gottardi & Galli 1985). The structure of heulandite has been extensively investigated (Merkle & Slaughter 1968; Alberti 1972; Bartl 1973; Hambley & Taylor 1984; Smith 1988; Van Koningsveld 1991). Recent studies report, that heulandite belongs to a particular structural group (HEU) along with clinoptilolite and synthetic zeolite LZ-219 (Meier & Olson 1992).

The cation sieve properties of heulandite were investigated by Joshi & Rao (1983) and the structure of K-exchanged heulandite before and after dehydration was reported by Galli et al. (1983). The preparation of the hydrogen form of heulandite via thermal modification of its NH_4-exchanged form was investigated by Jacobs et al. (1978), while Mortier & Pearce (1981) determined the crystal structure of the partially NH_4-exchanged heulandite after dehydration. The thermal behaviour of Li-, Na-, K-, Rb-, Ca-, Sr-, Ba- and NH_4-exchanged heulandite was investigated by Alietti et al. (1974) and by Filizova et al. (1975). Roque-Malherbe et al. (1987) reported calorimetric measurements of ion-exchange heats of homoionic (Na, K, Mg, Ca, NH_4 and Ni) heulandite and the crystal structure of partially Rb-exchanged heulandite has been determined by Sugiyama & Takeuchi (1986).

Bresciani-Pahor et al. (1980, 1981) studied the Ag-exchanged natural heulandite and found that Ag^+ ions exchanged only univalent cations and that some Ag^+ ions were spread out in the zeolite pores. The aim of the present study is to investigate the uptake of Hg(II) and Cd(II) as well as of Ag(I) from their aqueous solutions of different concentrations by the sodium form of heulandite.

Sample preparation and characterization

The heulandite sample was used from the Poona, India (Sukheswala et al. 1974) and supplied by Albantakis Co, Athens Greece. The faintly white well-formed crystals of heulandite occur in basalt cavities on a drusy quartz matrix.

Pure crystals were detached carefully by hand-picking from the rock and were ground in an agate mortar. The grains produced were examined under stereomicroscope and thin sections of them were studied using petrographic microscope. Some grains were further ground and sieved in analytical sieves for the separation of the 20 - 90 μm size fraction. This crystalline powder was repeatedly washed and wet-sieved, using distilled water, in order to remove ultrafine particles that cling to the larger grains. After wet-sieving most, but not all, of the ultrafine particles were removed, as was revealed by Scanning Electron Microscopy (SEM). The X-ray powder diffraction analysis (XRD) showed only heulandite to be present in the separate. The X-ray powder diffraction patterns were obtained by a Philips (Model PW1820) diffractometer, Ni-filtered Cu$K\alpha$ radiation

Table 1: Chemical composition of heulandite (Heu) and its sodium form (NaHeu).

	wt.%			Calc. on 72 (O)			Trace elements of Heu	
	Heu	NaHeu		Heu	NaHeu		(μg/g)	det.limit$^+$
SiO_2	61.06	62.17	Si	27.99	28.15	Hg	<4.50	4.50
TiO_2	0.06	0.06	Ti	0.02	0.02	Ag	<0.37	0.37
Al_2O_3	14.17	14.54	Al	7.64	7.76	Cd	<5.50	5.50
Fe_2O_3	0.86	0.56	Fe^{3+}	0.30	0.19	Cr	2.24	0.75
MnO	0.32	0.06	Mn	0.12	0.02	Ta	1.93	0.06
MgO	0.08	0.01	Mg	0.05	0.01	As	1.80	0.13
CaO	6.71	0.06	Ca	3.30	0.03	U	1.69	0.20
SrO	0.35	0.06	Sr	0.09	0.02	Br	1.20	1.19
BaO	0.05	0.05	Ba	0.01	0.01	Sb	0.41	0.05
Na_2O	0.67	8.22	Na	0.60	7.22	Sm	0.24	0.007
K_2O	0.66	0.11	K	0.39	0.06	Au	0.09	0.002
H_2O^*	15.1	14.2	H_2O	23.1	21.4			
Total	100.09	100.10						
			Z	35.95	36.12			
Si/Al	3.81	3.78	X	4.56	7.37			
Si/Al^x	3.78	3.78	R	0.78	0.78			

$^+$ Calculated taking into account the irradiation conditions.

* Determined by thermogravimetric analyses.

^{x} Obtained by deconvolution of ^{29}Si MAS NMR spectra.

$Z = Si+Ti+Al+Fe^{3+}$; $X = Mn+Mg+Ca+Sr+Ba+Na+K$; $R = Si/Z$.

using silicon powder as external standard. The scanning speed was 1° per minute over the interval 3 - 70° of 2σ. The major elements of heulandite were determined by Atomic Absorption Spectrometry (AAS) using a Perkin Elmer (Model 5000) spectrophotometer. The trace elements were determined by Instrumental Neutron Activation Analysis (INAA) combined by high resolution gamma-spectrometry.

Sodium form of heulandite (NaHeu) was obtained by treating a specific quantity of initial heulandite (Heu) sample with NaCl solutions. Two preparation procedures were followed. In the first procedure 5 g of zeolite were treated, in a glass flask connected to a Liebig condenser rotating with 80 rpm, with 1000 ml 1M NaCl solution for 48 hours at 70 °C. The solution was renewed twice during the treatment (after 16 and 32 hours). In the second procedure also 5 g of heulandite were treated in the same way with 500 ml 4M NaCl solution at 100 °C for 30 hours. The rotation speed was in this case 100 rpm and the solution was also renewed twice during treatment (after 10 and 20 hours). The NaHeu sample obtained from both procedures was filtered in Gooch G4 and repeatedly washed with distilled water until no AgCl was formed in the filtrate by the addition of $AgNO_3$.

Preliminary experiments indicated, that both NaHeu samples bind higher amounts of the studied metal ions than Heu. In addition the NaHeu produced by the second procedure was found to take up higher amounts of the studied metal ions from their aqueous solutions. Therefore the NaHeu produced by the second procedure was chosen for the final experiments. The characterization of this NaHeu sample was performed by XRD, while its chemical composition was determined by AAS.

Reagents and methods

The reagents used (NaCl,$Hg(CH_3COO)_2$, $AgNO_3$and $Cd(NO_3)_2.4\ H_2O$) were of MERCK per analyse grade. The radioactive tracers were prepared by irradiation of mercury, silver and cadmium salts by thermal neutrons at the 5MW swimming pool type research reactor of the National Centre for Scientific Research *DEMOKRITOS* (Athens, Greece).

The identification and counting of the produced radionuclides has been performed using gamma-ray spectrometry. The same research reactor was used for the irradi-

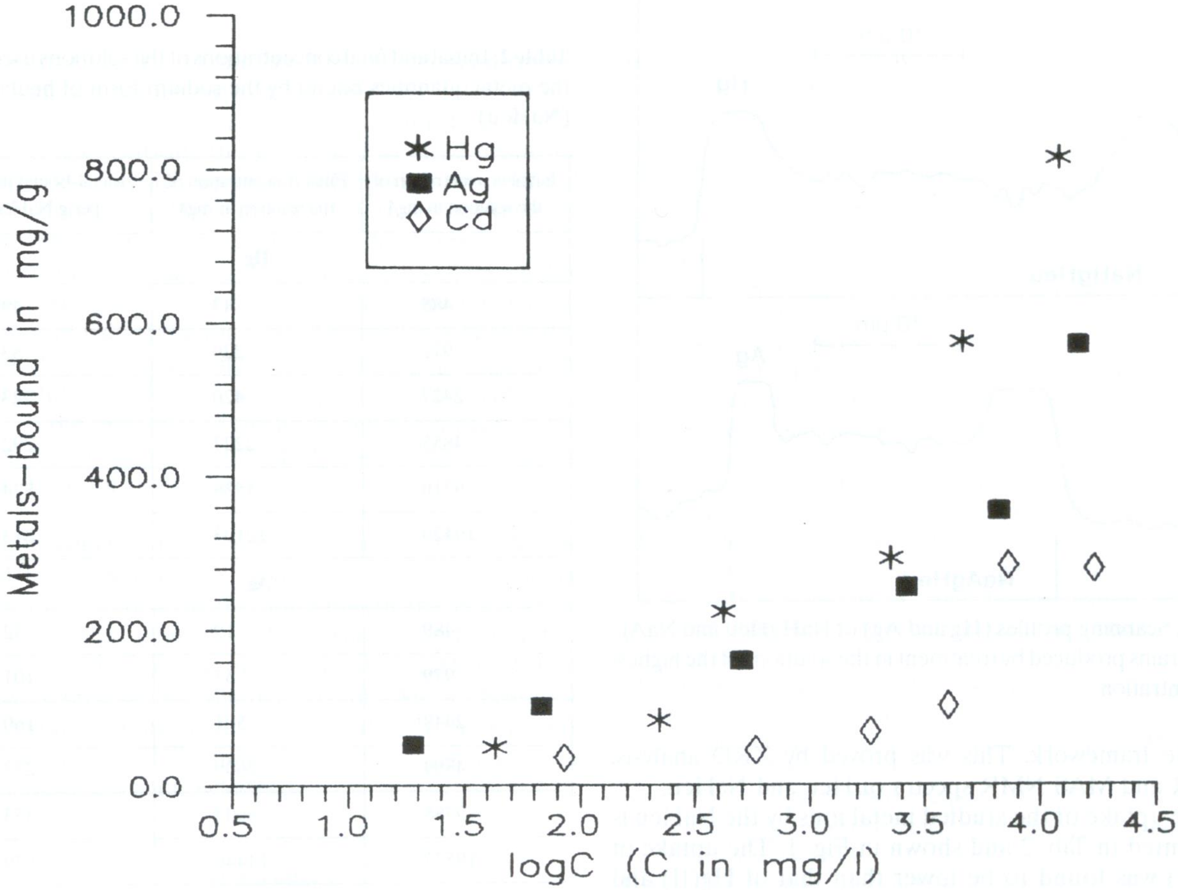

Fig. 1. The amount of metals bound, in mg/g NaHeu, *vs* the logarithm of their final concentrations (C) at room temperature. Initial pH of the solutions: Hg(II) = 4 - 5, Ag(I) = 6 - 7 and Cd(II) = 6 - 7.

ation of the zeolite samples used for the INAA of the material. About 50 mg of each sample were irradiated for 20 min by a thermal neutron flux of 3 x 10^{13} n/cm^2.sec. The samples were counted several times at different intervals after the end of the irradiation, using a gamma-spectrometry set-up consisting of a high purity Ge-detector (efficiency 20 %, resolution 1.8 KeV for the 1.332 MeV ^{60}Co line) connected to a CANBERRA S-35 Plus 8 K Multichannel Analyser. For the evaluation of the spectra the computer code SPECTRAN-AT has been used. The concentration of the elements has been calculated using the IAEA reference material Soil-7.

For the experimental procedure standard solutions of Hg(II), Ag(I) and Cd(II) with concentrations 19420, 19577 and 19500 mg/l (tested by AAS) were prepared by solving $Hg(CH_3COO)_2$, $AgNO_3$ and $Cd(NO_3)_2 . 4 H_2O$ respectively in twice distilled water. After pH measurement, the solutions were labelled by small amounts (a few kBq) of the radioactive tracers ^{197}Hg, ^{110m}Ag and ^{115}Cd respectively. Solutions with concentrations within the range of aprox. 20000 and 500 mg/l were prepared by dilution of the initial labelled standard solutions. The Hg(II), Ag(I) and Cd(II) uptake by NaHeu from the prepared solutions was studied by equilibration in glass centrifuge tubes of 0.09 g of the zeolite with precisely 10 ml solutions containing the respective cation. From preliminary experiments 24 hours shaking of the tubes were found to be sufficient for the achievement of equilibrium. After the equilibration and centrifugation (3000 rpm for 10 min) the radioactivity of 5 ml of clear supernatant solution was counted by gamma- spectrometry. The uptake was calculated from the difference of the determined radioactivity of the initial and the clear supernatant solution.

The same procedure was repeated using unlabelled solutions in order to investigate the distribution of the metals in the zeolite crystals using SEM (JSM 840S with a LINK AN 10000 EDS microanalyser).

Results

The major extraframework cation in the natural heulandite (Heu) used in this study is Ca, but considerable amounts of Na, K, and Sr are also present (Tab. 1). The INAA showed that the concentration of the trace elements Hg, Ag and Cd in Heu are below the detection limit of the analytical technique. On the other hand, the sodium form of heulandite (NaHeu) contains mainly Na as extraframework cation. Almost all Ca and K have been replaced by Na (Tab. 1). It must be emphasized, that this compositional modification did not cause changes to the initial alumino-

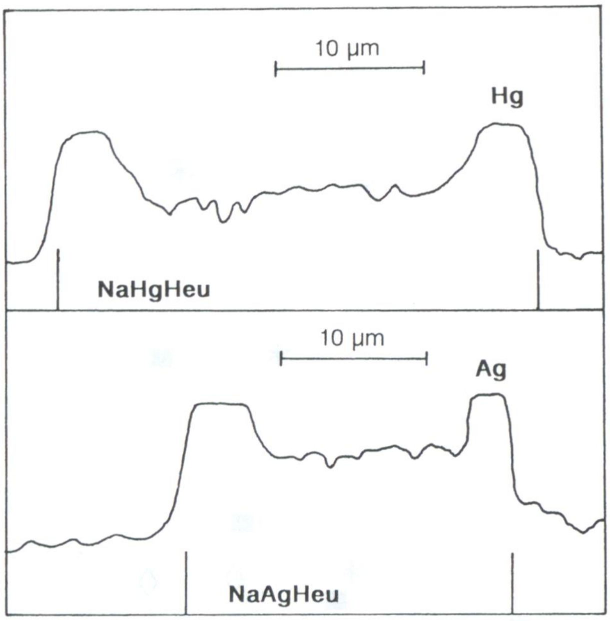

Fig. 2. Scanning profiles (Hg and Ag) of NaHgHeu and NaAgHeu grains produced by treatment in the solutions of the highest concentration.

Table 2: Initial and final concentrations of the solutions used and the metal quantities bound by the sodium form of heulandite (NaHeu).

Initial concentration of the solution in mg/l	Final concentration of the solution in mg/l	Metal-bound in mg per g NaHeu
	Hg	
485	43	49.1
971	220	83.4
2427	420	223.0
4855	2227	292.0
9710	4538	574.7
19420	12103	813.0
	Ag	
489	19	52.2
979	67	101.3
2448	501	160.0
4894	2609	253.9
9788	6603	353.9
19577	14446	570.1
	Cd	
487	185	35.5
975	572	44.8
2437	1815	69.1
4875	3951	102.7
9750	7208	282.4
19500	16995	278.3

silicate framework. This was proved by XRD analysis, FT-IR and MAS NMR spectra of Heu and NaHeu.

The uptake of the studied metal ions by the NaHeu is presented in Tab. 2 and shown in Fig. 1. The uptake of Cd(II) was found to be lower than that of Hg(II) and Ag(I) in the investigated concentrations. At lower concentrations the uptake of Ag(I) seems to be higher than that of Hg(II), whereas the opposite seems to happen at higher concentrations.

The scanning profiles of the studied metals, performed by SEM-EDS, on well polished grains of the final experimental products, clearly showed higher concentrations of Hg and Ag at the rims of the grains (Fig. 2). This phenomenon was found to be much weaker in the case of Cd, most probably due to its lower uptake. Further investigation is required in order to clarify this behaviour of cadmium.

Discussion and conclusions

The theoretical CEC, calculated from the chemical analyses (Tab. 1) and based on the exchangable cations, is 295 meq/100 g for Heu and 274 meq/100 g for NaHeu. According to the above CEC value of NaHeu the amounts of metal ions which could be absorbed by ion-exchange procedures were calculated to be *ca* 275 mg/g for Hg(II), *ca* 296 mg/g for Ag(I) and *ca* 154 mg/g for Cd(II). In the present experiments (Tab. 2) at the highest concentrations the amounts of the metal ions bound by the NaHeu reached 813 mg/g for Hg(II), 570 mg/g for Ag(I) and 278 mg/g for Cd(II). These values are higher than those calculated using the theoretical CEC, leading to the conclusion that the uptake of the investigated metal ions took place by several mechanisms including ion-exchange. The uptake of the studied metal ions could be attributed not only to ion-exchange but also to adsorption onto the surface of the NaHeu grains, as it is indicated by the scanning profiles (Fig. 2). The small ionic species are ion-exchanged penetrating into the lattice through the channels, while the large positively charged ionic species are adsorbed onto the zeolite surface. At the lower concentrations of the present experiments (Tab. 2), where the metal ion content is below the calculated theoretical CEC value for each metal, the uptake of the investigated metal ions is not complete. This phenomenon seems to be affected by several factors and more detailed experiments and the use of additional experimental techniques are required for the explanation of this behaviour.

On the basis of the effective hydrated ionic radius of Hg^{2+} (r = 1.51 A), Ag^{+} (r = 1.43 A) and Cd^{2+} (r = 1.53 A) the uptake sequence is expected to be Ag > Hg > Cd (Noyes 1962). This sequence is valid only for Cd in all the investigated concentrations, but only at the lower concentrations for Ag and Hg. At higher concentrations the uptake sequence for Ag and Hg is reversed. A possible explanation of this reversibility is that in those concentrations the formation of large positevely charged hydrolysation products of Hg(II) is pronounced. Furthermore, the large uptake difference between the two bivalent cations (Hg and Cd) could also be attributed to their bond character at the anionic sites of the zeolite. In the case of Hg(II) the covalent bond character, while in the case of Cd(II) the ionic bond character is favoured. It should be mentioned, that in the initial pH range of the used solutions ($pH_{Hg(II)} = 4 - 5$, $pH_{Ag(I)} = 6 - 7$, $pH_{Cd(II)} = 6 - 7$) the influence of the hydrogen ion concentration on the uptake of the metal ions by the NaHeu is believed to be of minor importance.

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