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Sorption of actinides on natural Fe-Mn oceanic crusts from seawater

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Under normal conditions we carry out static experiments on the sorption of U-233, Np-237, Pu-238, Am-241 from aqueous solution corresponding to seawater model on crushed samples of ferromanganese ore crusts taken from the Magellan seamountains guyots. The kinetics of sorption was studied on the example of uranium, which was already adsorbed on 96.0% in the first hour, and after the first day it was reached the level closed to the ultimate extraction 99.0%. The equilibrium sorption degree of studied radionuclides for the "young" crust was slightly higher than for the "old" one and increased for both samples among Np<U<Pu<Am from 96.7% to 99.6%.

Key word: actinides, radioactive waste, sorption, ferromanganese crusts

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Search of new effective natural sorbents for toxic waste, in particular radioactive, is very important task. Besides that in geochemistry of oceanic processes there is unexplored a behavior of radionuclides at long-living sediment processes and geochemical cycles elements. All these questions have forced us to spend studying sorption characteristics oceanic Fe-Mn ores. There are some publications specifying on high effective properties of Fe-Mn crusts concerning elements having artificial long-living isotopes [*Scott, et al.,2005; Duff, et al., 2002, Koschinsky, & Hein, 2003*]. However, direct experimental researches on sorption characteristics of radionuclides aren't known for Fe-Mn crusts. Definition of radionuclides (U-233, Np-237, Pu-238, Am-241) sorption parameters was a problem of the present research in conditions close to natural oceanic ones.

We used close to neutral (pH=8.0) a solution haven salt structure as seawater (Table 1) under normal conditions. Radionuclides were entered in the form of nitrates, their abundance in working solutions were: Am – $3.27*10^{-9}$, Np – $5*10^{-6}$, Pu – $5*10^{-10}$, U – $2*10^{-7}$ M.

Table 1. Salt composition of the solution (bulk salinity 35 ‰)

Na	468 mM
Mg	53 mM
S	28 mM
Cl	546 mM
K	10.2 mM
Ca	10.3 mM
$N(NO_3^-)$	45 μM
$N(N_2)$	610 μM
Sr	90 μM

As a sorbent we used average combine samples Fe-Mn crusts taken from the Magellan seamountains guyots. We have created average bulk probe of the top "young" type of ores (III layer) - sample T2 and average bulk probe from the bottom "ancient" layers I-1, I-2 – sample RT. In experiments we used fractions of 0.2–0.04 mm. Composition of samples are given in Table 2.

To determine the phase composition the powder samples were examined by X-ray diffractometer D/MAX-2500 (Rigaku). XRPD patterns of the samples have been removed in CuKα-

radiation at a rate of 10°/min and with step 0.02°2Θ. Predominant phases in both samples were vernadite and asbolan-buserite (Fig. 1). In addition to them in the ancient layer, it was better crystallized, there were carbonates, hematite, barite, analcime, goethite, and in the young - a large number of probably terrigenous quartz.

Table 2. The chemical composition of the used sorbents

Sample/ element	RT (ancient)	T2 (young)	Sample/ element	RT (ancient)	T2 (young)
wt.%			ppm		
SiO_2	4.64	9.06	V	577	2
TiO_2	1.39	1.54	Co	2880	4350
Al_2O_3	1.38	2.02	Ni	2476	3396
CaO	11.71	3.24	Cu	1220	1080
Fe_2O_3	19.48	21.31	Zn	591	511
K_2O	0.45	0.60	Sr	1557	1136
MgO	1.14	1.35	Zr	637	550
MnO	20.45	22.15	Mo	546	361
Na_2O	1.91	1.86	Nb	58	49
P_2O_5	4.72	1.15	La	212	173
S	0.27	0.17	Ce	1228	766
Total	67.55	64.45			
ppp	31.09	34.2			
Sum	98.64	98.65			

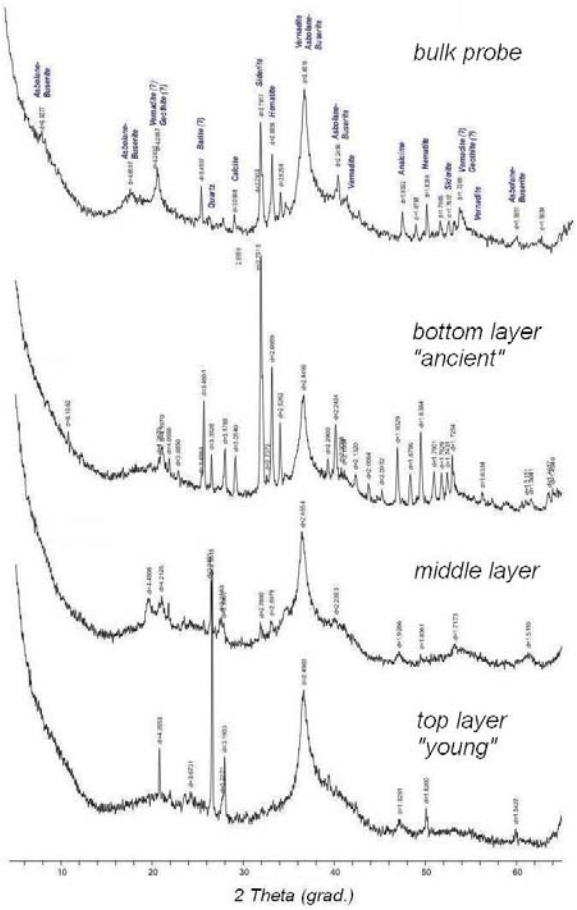

Fig. 1. XRPD patterns and mineral composition of the Fe-Mn crusts, CuKα radiation

Experiments on the leaching and sorption were carried out under static conditions in polypropylene tubes with periodic stirring. Ratio of solid and liquid phases was 1:20 (0.5 g : 10 ml). Aliquots for analysis were collected after centrifugation. The contents of Fe and Mn were determined by atomic absorption spectrometer AAnalyst-400 (Perkin Elmer). Activities of radionuclides were determined by liquid scintillation alpha-, beta-spectrometer SKS-07P-B11 with the detection unit UDBT-003 (Green Star Instruments). As liquid scintillator was used Optiphase HiSafe III (Perkin Elmer).

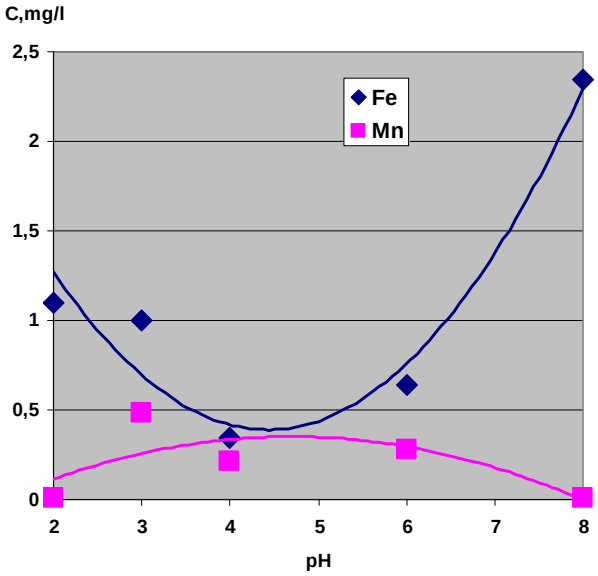

Fig. 2. The dependence of Fe and Mn concentrations in solution vs. pH on leaching of the sample T2 for 1 day

To estimate the resistance of the crust material in environment conditions with various pH we have studied the leaching of Fe and Mn from the sample T2 in HNO_3 solutions with pH = 2, 3, 4, 6 and NaOH solution with pH = 8. The contact time was 1 day. It is established that the investigated elements behave the opposite way (Fig. 2). Leaching of Mn is lower than Fe, and has, in contrast to the latter as a tendency to increase with increasing and with decreasing pH.

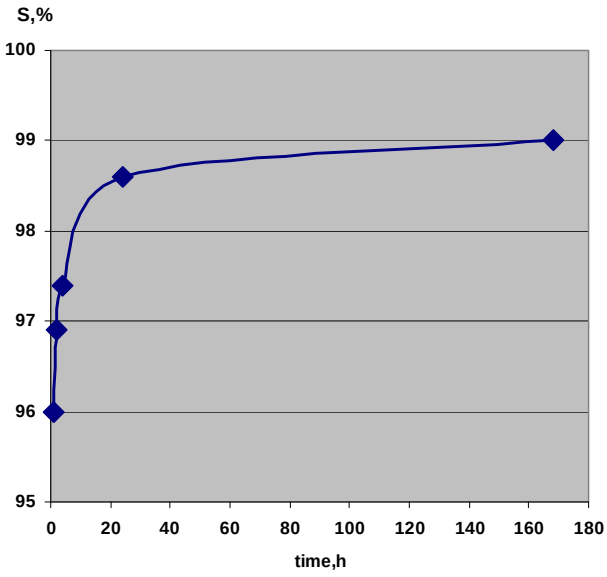

Fig. 3. The kinetic curve of uranium sorption on the sample T2

The speed of the process has been studied on the example of uranium sorption on the sample T2. A plot of the extraction of uranium from the solution against the time of contact with the sample is shown in Fig. 3. As can be seen from the plot, uranium was rapidly adsorbed by crust material: already in the first hour it was absorbed 96.0% of substance from the solution, and after the first day it was reached the level closed to the ultimate extraction 99.0%.

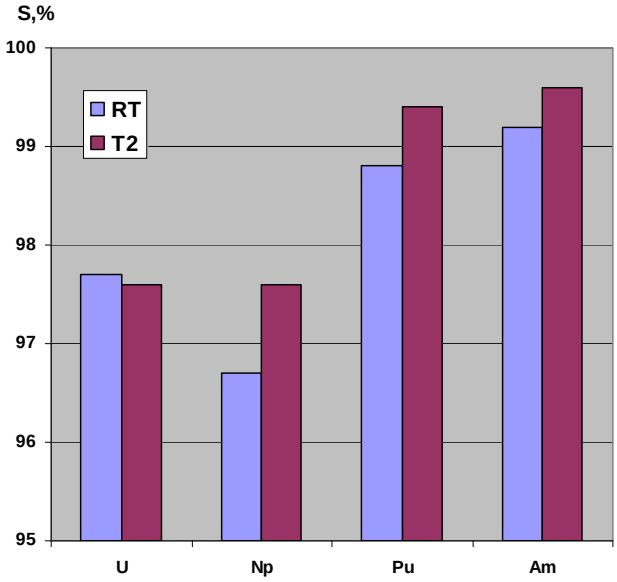

Fig. 4. The degree of radionuclides extraction from the working solution by samples RT and T2 in 10 days of contact

Experiments to determine the sorption of all four radionuclides on both samples have spent at time duration 10 days, certainly more than it was necessary for the establishment of sorption equilibrium (Fig. 4). Degree of sorption reaction for "young" crust was a little above than for "ancient" one also increased for both samples among Np<U<Pu<Am from 96.7 % to 99.6 %.

Thus, the received experimental results have shown perspectives to use natural material of Fe–Mn ore crusts as effective sorbent for extraction of radionuclides from liquid radioactive salt solutions with pH close to the neutral. Besides, thanks to activity of sorption interaction, it is necessary to recognize possibility of self-cleaning of oceanic waters at pollution of ocean by radionuclides. In the presence of powerful geological processes of Fe-Mn ore mineralization radioactive deposits intruding into oceanic water are concentrated on the surfaces of seamountains and an oceanic bottom and deduced quickly from a geochemical cycle.

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