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MEMBRANE AND SORPTION MATERIALS AND TECHNOLOGIES: PRESENT AND FUTURE

KYIV 2018

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ArtOK publisher

KYIV 2018

UDC 544.726

CHAPTER 13

SORBENT ON THE BASIS OF Ti/Mn OXIDE AND Co CYANOFERRATE FOR ^{90}Sr AND ^{137}Cs SELECTIVE REMOVAL

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Abstract. *The complex oxides of $M_xMn_{1-x}O_2 \cdot nH_2O$ composition, (M-Zr, Ti, Sn) have been synthesized. Their surface was modified with phosphoric acid. phosphoric-molybdic acid and cobalt hexacyanoferrate. The sorption isotherms of Sr^{2+}, Cs^+ ions, as well as isotherms of sorption-desorption of such radionuclides as ^{90}Sr and ^{137}Cs were obtained. It was found that the most suitable sorbents for Sr^{2+} removal are $M_xMn_{1-x}O_2 \cdot nH_2O$ complex oxides. ZrO_2 modified by phosphate and molybdophosphate anions is effective towards Cs^+. The sorbent consisting of titanium dioxide and cobalt hexacyanoferrate can be recommended for extraction of both Sr^{2+} and Cs^+ ions.*
Keywords: *sorbent, composite, double oxides, hexacyanoferrate, strontium, cesium.*

Introduction. Radioactive waste from nuclear power plants (NPP) is one of the major problems, both in the field of NPP safety and industrial ecology. Today the objects of interest are full-cycle technologies. They give a recycled product that is suitable for disposal without any additional processing. The main chemical components of liquid radioactive wastes are borate and nitrate of Na^+ (~98%). The remaining 2 percents are the objects of our research, namely radioactive Cs^+ and Sr^{2+}. Cesium makes a major contribution to the amount of gamma activity, which is characterized by considerable radioactive toxicity. Strontium is of particular concern, because, it emits no gamma radiation (similarly to iron-55, carbon-14, tritium and plutonium), which is easy detectable. During the transfer from the original liquid radioactive wastes to the evaporator concentrates and further to solutions after deep evaporation plants, the salt content, alkalinity of the solutions (pH) and radioactivity increase in the first approximation according to the degree of concentration. Such salt content significantly increases the requirements for filtering material in the case of sorption and/or filtration technologies for their processing. Sorption technologies using selective inorganic ion exchange sorbents are the most promising for such applications. The relevant research is aimed at the development of technologies for the processing of radioactive waste that provides minimal disposal volumes [1]. Our investigations are devoted to synthesis and adsorption properties of double M/Mn and M/Al hydrated oxides

with various metals ratio (M – Zr(IV), Sn(IV), Ti(IV). In addition, the modification of oxide surface with phosphates (*Ph*), ammonium molybdophosphate (*Mo-Ph*) and hexacyanoferrate **(***HCF*) of Co(II) was made.

Experimental. Sol-gel synthesis was applied to preparation of a composite oxide sorbents [2]. Addition of anions of phosphates and molybdo-phosphates to oxide surface was performed by impregnation of oxide sorbents with solution of phosphoric acid and ammonium molybdo-phosphate [3]. Modification of oxide surface with hexacyanoferrate of Co(II) was performed by two way: classic precipitation and with usage of gel technology. Sorption capacity and distribution coefficients (K_d) were calculated from changing the concentration of Cs^+ and Sr^{2+} ions in model solutions (0.1 M Na^+, the concentration of Cs^+ and Sr^{2+} was varied) before and after sorption. Sorption was performed from the solutions containing radionuclides in an amount that corresponds to gamma-activity of 371 Bq for strontium-90 and of 16000 Bq for cesium-137. The sorbents were regenerated using a 1 M solution of ammonium acetate.

Results and discussion. The insertion of manganese dioxide to the hydrated oxides of metals of IV group leads to decrease of absorption capacity in relation to single charged K^+ ions compared with one-component oxides. This effect can be caused by increase of microporosity. The absorption capacity of synthesized oxides was determined towards ^{90}Sr radionuclides. The model solutions with a very low initial concentration of this component was used. It was found that the change of magnitudes of the distribution coefficients for double hydroxides is from 71200 (Sn/Mn) and 95000 (Zr/Mn). A very high level of radionuclides removal was found. The advantage of double oxides in comparison with manganese dioxide is follows: (i) coarse grains allowing us to reduce hydrodynamic resistance, (ii) much higher values of the coefficient of distribution of strontium ions, which indicate the possibility to use the sorbents for decontamination of very diluted solutions.

Figure 13.1 represents sorption data for $Ti_{0,3}Mn_{0,7}O_2 \cdot nH_2O$ double oxide and $Ti_{0,3}Mn_{0,7}O_2 \cdot nH_2O$/Co-*HCF* composite sorbent. Ti/Mn double oxide was chosen for surface modification due to the best sorption-desorption results concerning ^{90}Sr radionuclides (Tables 13.1 and 13.2). Modification of double oxide surface by hexacyanoferrate of Co(II) should increase sorption ability towards ^{137}Cs.

Table 13.1 gives sorption characteristics of the investigated composites iand some other ion exchange materials for comparison. Table 13.2 shows desorption results for some sorption materials loaded with radionuclides.

According to the Tables, manganese-containing sorbents are promising materials for the removal of ^{90}Sr radionuclides, and *Zr-Ph*, *Zr-Ph-Mo* sorbents are promising sorbents for the removal of ^{137}Cs radionuclides from water and liquid waste solutions. Ion exchange is the main mechanism of sorption, this provides high degree of regeneration with ammonium acetate. After surface modification

with hexacyanoferrate of Co(II), the $Ti_{0,3}Mn_{0,7}O_2 \cdot nH_2O$ sorbent can remove both ^{137}Cs and ^{90}Sr.

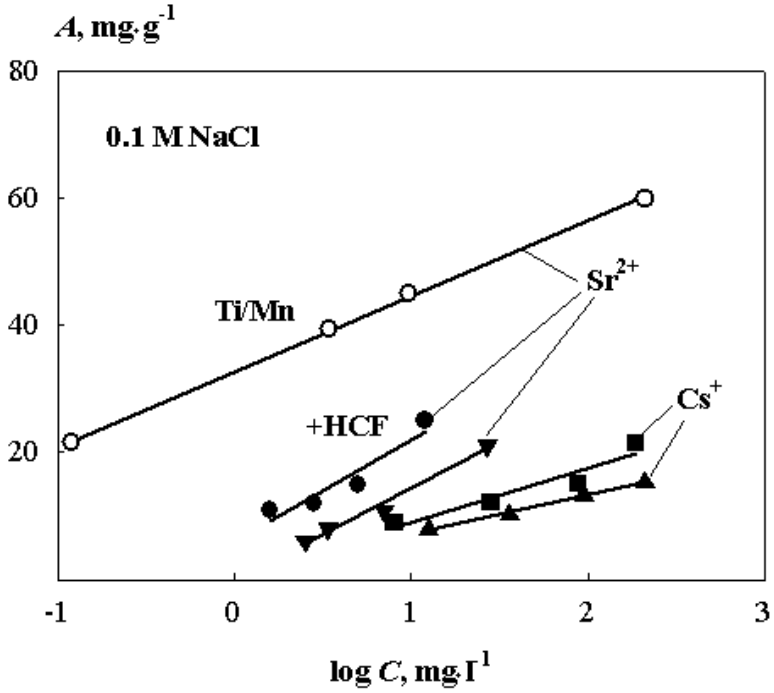

Fig. 13.1. *Sorption of Sr^{2+} and Cs^+ ions from model solution with 0.1 M NaCl with $Ti_{0,3}Mn_{0,7}O_2 \cdot nH_2O$ double oxide and $Ti_{0,3}Mn_{0,7}O_2 \cdot nH_2O$/Co-HCF composite sorbent:●,■ - synthesis using gel formation, ▼▲- synthesis by means of classic technique.*

Table 13.1. Sorption from model solutions containing Sr^{2+} and Cs^+ ions

Sorbent	$K_d \cdot 10^{-3}$	
	Sr^{2+}	**Cs^+**
Dowex 50*WX*-2	2	0.1-1
Dowex HCR-S	23	0.3
$M_{0,6}Mn_{0,4}O_2 \cdot nH_2O$	71-95	до 1.2
$TiO_2 \cdot nH_2O$/ *Dowex HCR-S*	50	4
Zirconium phosphate (*Zr-Ph*)	-	33
Zirconium phosphate modif. (*Zr-Ph-Mo*)	-	123
$Ti_{0,3}Mn_{0,7}O_2 \cdot nH_2O$ (+0.1M Na(I))	53	-
$Ti_{0,3}Mn_{0,7}O_2 \cdot nH_2O$/*HCF* (+0.1M Na(I))	20	7

Table 13.2. Degree of radionuclide desorption

Sorbent	**Degree of regeneration, %**	
	^{90}Sr	**^{137}Cs**
Zirconium phosphate (*Zr-Ph*)	-	67
Zirconium phosphate modif.(*Zr-Ph-Mo*)	-	47
$M_xMn_{1-x}O_2 \cdot nH_2O$	85-93	-

Conclusions. $M_xMn_{1-x}O_2 \cdot nH_2O$ oxides (M - Zr, Ti, Sn) of complex composition wre synthesized. Modification of their surface with various compounds such as phosphates, ammonium molybdophosphate and hexacyanoferrate was performed. The results for sorption-desorption concerning ^{90}Sr and ^{137}Cs confirm a suggestion about good perspective of the obtained materials for radionuclide removal from the solution containing high amount of salts.

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УДК 544.726

СОРБЕНТ НА ОСНОВІ Ti/Mn ОКСИДУ І ГЕКСАЦІАНОФЕРАТУ Co ДЛЯ СЕЛЕКТИВНОГО ВИДАЛЕННЯ ^{90}Sr ТА ^{137}Cs

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Резюме. *Синтезовано складні оксиди $M_xMn_{1-x}O_2 \cdot nH_2O$,(M - Zr, Ti, Sn). Поверхню оксидів модифіковано фосфорною та фосфорно-молібденовою кислотою, а також гексаціанофератом кобальту. Отримано ізотерми сорбції іонів Sr^{2+}, Cs^+, а також ізотерми сорбції-десорбції раділнуклідів ^{90}Sr та ^{137}Cs. Знайдено, що найбільш ефективними сорбентами для іонів Sr^{2+} є складні оксиди $M_xMn_{1-x}O_2 \cdot nH_2O$, а для Cs^+ - ZrO_2, модифікований фосфат- та молібдофосфат- аніонами. Сорбент $Ti_{0,3}Mn_{0,7}O_2 \cdot nH_2O$/Co-HCF селективно поглинає Sr^{2+}, Cs^+.*

Ключові слова*: сорбент, композит, подвійні оксиди, гексаціаноферат, стронцій, цезій.*