SORPTION REMOVAL OF CS AND SR FROM RADIOACTIVE WASTEWATER BY MODIFIED BENTONITE CLAY

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Abstract Bentonite modified with ferrocyanides of Fe, Cu and CuK was tested for sorption of Cs-137 and Sr-90 and proved to be highly selective for Cs; ferrocyanides of Cu and CuK are also good sorbents for Sr. Bentonite modified with hydroxides of Ti, Sn and Sb are good for Sr removal.

Keywords: adsorption, modified clay sorbents, Cs-137, Sr-90, radioactive wastes

INTRODUCTION

Long-lived caesium and strontium radionuclides may be dispersed to the environment from repositories of radioactive wastes, during the reprocessing of spent nuclear fuel or as a result of accidents at nuclear power plants as at the Chernobyl nuclear power station. Many countries possess high volumes of liquid radioactive wastes. Hence the problem of radionuclide recovery from liquid wastes remains and attracts an ongoing research effort. Sorption technology enables a reduction in the volume of liquid wastes by concentration and solidification of radionuclides into immobile forms by means of concreting, bituminization and vitrification.

RESULTS AND DISCUSSION

In the last few years several inorganic sorbents were proposed for radionuclides removal. The most interesting are fibrous filled sorbents, ferrocyanides of transition metals and titanium compounds [1-6]. They have been successfully used for radionuclide separation. However, their utilization on an industrial scale is often limited by their susceptibility to different factors, such as concentration of competing ions, low resistance to radioactive damage and poor physical and mechanical properties (thermal stability, mechanical strength, and permeability). Since the quantity of radioactive wastes at nuclear power plants and test sites to be processed can be very large (sometimes thousands of cubic meters), the low cost of the sorbent becomes an advantage as well.

Many natural minerals (e.g. zeolites, clay, clinoptilollite, mordenite, tuffs) possess a number of the above mentioned characteristic advantages not normally found in inorganic materials and ion-exchange resins. Because of this they have been widely studied [7-12]. However, their recovery rates vary much depending on the chemical and mineral composition of the sorbent and the nature of the radionuclide. A study of the sorption characteristics of natural sorbents is of special interest as they are considered as backfill materials for nuclear waste repositories.

Several methods have been proposed to increase the selectivity of natural minerals towards caesium and strontium. Among these the most widely used methods are acid and alkali treatment, hydrothermal and thermal treatment, mechanical activation and pillaring [13-16].

In the last few years it has been proposed to chemically impregnate the carrier with specific inorganic compounds which show selectivity for the ion, or ions, of interest. The carrier might be ion-exchange resin, cellulose, active carbon, natural minerals. An application of this method resulted in the development of several new sorbents [17-19]. This approach is of great interest as it combines and enhances the sorption properties of the carrier and impregnated material and can improve their mechanical characteristics.

Sorption materials were synthesized on basis of bentonite clay which is waste from sulfur excavation in Yaziv sulfur mine (Lviv, Ukraine). The natural bentonite was modified by solutions of ferrous (III) and copper (II) ferrocyanides, and tin, titanium and antimony hydroxide.

The sorbents were tested for cleaning the simulated radioactive wastewater, contaminated with Cs-137 and Sr-90 in presence of high concentration of competing ions. Fig. 1,2 list sorption of Cs-137 in presence of Na^+. It is clear, that high concentrations of both Na^+ and Ca^{2+} do not inhibit Cs sorption, which enables usage of ferrocyanide-modified bentonites for decontamination of technological solutions. The kd values are 2000-15000 ml/g which is much higher than many types of natural minerals.
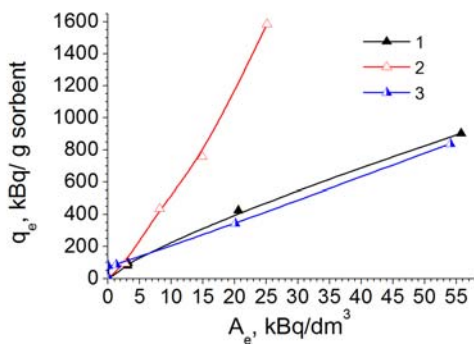

Figure 1. Sorption of Cs-137 on CPFC-bentonite in presence of Na^+ 1 – 2,3 ppm$^+$; 2 – 230 ppm; 3 – 2300 ppm
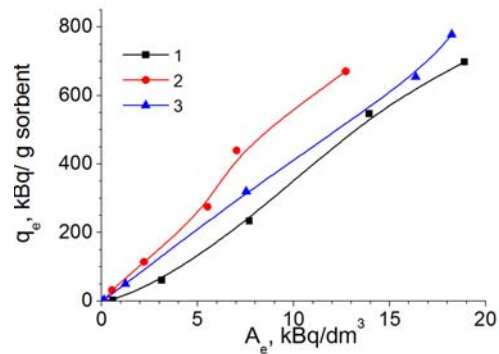
Figure 2. Sorption of Cs-137 in presence of Ca^{2+} 1 – FFC-bentonite; 2 – CFC-bentonite; 3 – CPFC-bentonite;

Sr-90 sorption is significantly inhibited by Ca^{2+} (Fig. 3,4). This is explained by lower selecitvity for Sr, than for Cs. CPFC and TH-bentonite show better sorption characteristics than SbH-bentonite, and S=90%. Maximum salt content for effective Sr-90 removal is 1 ppt (maximum 400 ppm Ca^{2+}).

Ions formed as a result of corrosion of apparatus and pipelines might compete for sorption center of the mineral. Hence, information of their influence on sorption is very important. As we can see from Table 1, presence of 5 ppm Co^{2+} and Mn^{2+} do not inhibit sorption of Cs-137 and Sr-90. Sorption of Cs-137 on CPFC-bentonite decreases only 2% even though it has high capacity for Co. Sorption of Sr-90 is inhibited maximum 5-10%.
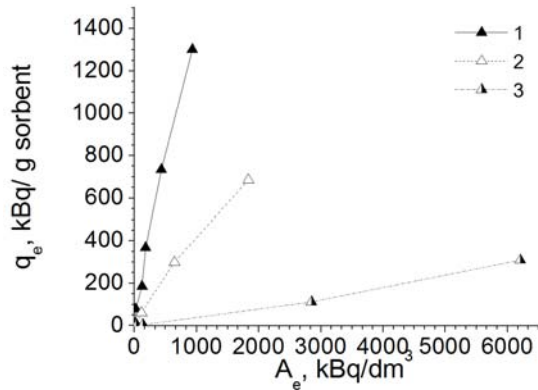
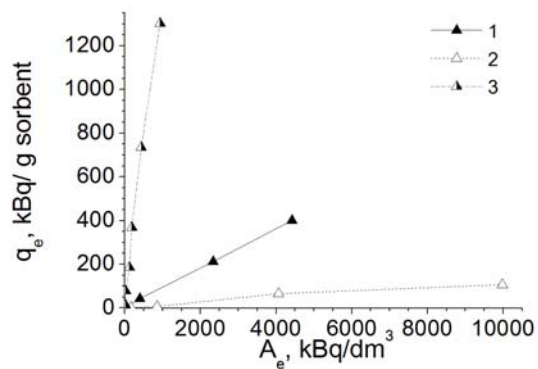Figure 3. Sorption of Sr-90 on CPFC-bentonite in presence of Na^+ 1 – 2,3 ppm^+; 2 – 230 ppm; 3 – 2300 ppm

Figure 4. Sorption of Sr-90 on CPFC-bentonite in presence of Ca^{2+}: 1 – 40 ppm Ca^{2+}; 2 – 400 ppm Ca^{2+}; 3 – 2,3 ppm Na^+

Table 1. Sorption characteristics of sorption recovery of Cs-137 and Sr-90 on modified clay minerals

Sorption characteristics	S,%	$k_d \cdot 10^{-3}$, см³/г	S,%	$k_d \cdot 10^{-3}$, см³/г	S,%	$k_d \cdot 10^{-3}$, см³/г
Sorption of Cs-137 in presence of corrosion products						
	FFC-bentonite		CFC-bentonite		CPFC-bentonite	
2,3 ppm Na^+	99,1-100	8-4970	99,4-100	17-6250	99,46-99,9	15-600
5 ppm Co^{2+}	98,5-99,5	5-20	99,1-99,7	10-25	98,9-99,7	7-26
5 ppm Mn^{2+}	98,8-99,7	7-20	99,2-100	12-3000	97,7-99,6	4-26
Sorption of Sr-90 in presence of corrosion products						
	CPFC-bentonite		TH-bentonite		SbH-bentonite	
2,3 ppm Na^+	70,8-97,7	0,2-3	81,6-92,2	0,5-1	77,0-93,2	0,2-1
5 ppm Co^{2+}	85,6-97,6	0,5-2,6	72,4-79,3	0,3	52,0-73,0	0,1-0,2
5 ppm Mn^{2+}	89,4-96,6	0,5-2	80,0-92,0	0,4-1,5	69,6-84,3	0,2-0,3

CONCLUSIONS

The research proves that the modified bentonite clay can be used for cleaning of cooling ponds of spent nuclear fuel during decomissioning of nuclear power plants, cleaning of radioactive wastes of power and medical industry etc., cleaning of ground waters and technological solutions and liquid radioactive wastes of soil decontamination. The latter is particularly important during decontamination of territories which underwent the act of nuclear terrorism, bombing with depleted uranium missile or nuclear accident.

Nomenclature
q_e Cs/Sr activity in sorbent phase at equilibrium, kBq g^{-1};
S   sorption rate;
kd   distribution koefficiend, ml/g

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