

APPLICATION OF INORGANIC ADSORBENTS AND ION EXCHANGE RESINS FOR DECONTAMINATING SOLUTIONS FROM CESIUM AND STRONTIUM RADIONUCLIDES

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ABSTRACT

Adsorption and selective characteristics of a number of inorganic adsorbents, namely, natural and modified aluminosilicates; synthetic zeolites; hydrated metal oxide-based adsorbents; polyvalent metal and multi-basic acid salts; carbon adsorbents and organic ion exchange resins have been investigated with respect to strontium and cesium ions. The highest selectivity with respect to cesium has been observed for ferrocyanide-based adsorbents FS, NGA, NGS, MGA, MGS (K_d values being $> 10^4$ cm³/g). From solutions with low salt content (0.1 mole/l NaNO₃ and 0.01 mole/l Ca(NO₃)₂) high K_d values for cesium were also observed for natural aluminosilicates, various types of synthetic zeolites, and zirconium and titanium phosphates. Ion exchange resins, hydrous metal oxide and carbon adsorbents revealed the lowest adsorption characteristics with respect to cesium.

For strontium different influence of sodium and calcium macro amounts upon the uptake of Sr ions has been detected. Synthetic shabazite of KG-13 type possessed the unique selectivity to strontium in the presence of sodium ions ($K = 4.3 \times 10^3$ cm³/gin 0.5 mole/l NaNO₃ solution). Under the same conditions rather efficient adsorption of Sr occurred on aminocarboxylic amphotites of ANKB-type (analogous to U.S. made Dowex A-1), synthetic zeolites of A and X-type, and on manganese dioxide-based adsorbent ISMA-3. Natural aluminosilicates, certain synthetic zeolites, transition metal phosphates and ferrocyanides, carbon adsorbents showed relatively low selectivity to strontium.

In the presence of Ca ions the above characteristics with respect to strontium appeared to be approximately the same for the entire set of adsorbents studied. Hence, the efficiency of Ca-Sr pair separation on the adsorbents investigated should be comparatively low.

The above study facilitated the choice of adsorbents for decontamination of industrial reservoirs at IA "Mayak" (Chelyabinsk, Russia) from cesium and strontium radionuclides. The pilot plant comprised 2 adsorption columns of 20 l each, connected in series. Specific activity value for ¹³⁷Cs and ⁹⁰Sr in feed water amounted (0.2-1.0) $\times 10^{-6}$ and (1-2) $\times 10^{-6}$ Bq/l, respectively, calcium and magnesium concentration varied within the range 100:130 and 60:85 mg/l, respectively, pH value equalled 7.5-8.5. As the result of the pilot plant tests it was found that the efficient removal of Cs could be done using synthetic zeolites of A-type (decontamination factor $D_f > 10^3$ at the installation throughput $T > 1000$ bed volumes).

Decontamination from Sr on the same adsorbent was markedly worse owing to the presence of calcium ions ($D_f = 3$ at $T < 100$ b.v.). To improve the removal of Sr the preliminary precipitation of hardness salts with soda was conducted, thus increasing D_f up to 10^3 at $T = 1000$ b.v.

It can be concluded, the research reported allows to choose the most efficient adsorbents for decontamination of solutions having different chemical and radionuclide composition.

INTRODUCTION

Large volumes of different level radioactive wastes (LLRW, ILRW, HLRW) arise in the course of operation of spent nuclear fuel reprocessing facilities. This paper reports the results of studying the decontamination of natural reservoir water and ground water migrating from the open surface HLRW repository (the so called Karachay lake, IA "Mayak", Chelyabinsk, Russia).

The process of decontamination was conducted using various inorganic and organic adsorbing media. Two different approaches were used for radwaste treatment. First, the isolation of radionuclides by the ion exchange material was followed by the disposal of the exhausted exchanger, and second, the exhausted ion exchanger was regenerated and the radionuclide concentrate was solidified by means of the suitable conventional technique (cementation, bituminization, vitrification).

Decontamination of radwaste solutions using inorganic ion exchangers is discussed in a number of publications (Gelis,

1991, Hooper, 1985, Pekarek, 1972, Sipos-Galiba, 1980). However, it appeared to be rather difficult to make the comparative study of the data reported on account of those investigations were performed under different conditions. To facilitate the choice of an ion exchange media suitable for any situation the extensive study of the whole set of adsorbent species have been performed. As long as the salt background usually governs the efficiency of decontaminating radwaste by means of ion exchange technique, the resulting data are classified in terms of sodium and calcium salt concentration in the feed.

EXPERIMENTAL

Adsorption and selective characteristics were studied in the batch mode, using Sr and Cs as tracers. Ion exchange material used for study is listed below.

1. KU-2x8 - strong acid sulfocationite (analogous to Dowex 50x8);

2. KB-4P2 weak acid carboxylic cationite (analogous to Amberlite IRC-50, carboxylic functional groups);
3. KU-1 - phenolphormaldehyde sulfocationite (analogous to Amberlite IR-100, sulfonic functional groups);
4. ANKB-2 - aminocarboxylic amphotite (analogous to Dowex A1, Chelex-100, iminodiacetic functional groups);
5. Natural vermiculite, Kovdor deposit (Apatity, Russia);
6. Natural Clinoptilolite, "Dzegvi" deposit (Republic of Georgia);
7. NaA (CaA), NaX, (CaX) - sodium (calcium) forms of synthetic A and X zeolite type, respectively;
8. KG-13 - synthetic zeolite of shabazite type, potassium form;
9. IE-95, A-51 - synthetic zeolites of shabazite and A type, respectively;
10. Pirolusite - natural manganese dioxide, Chiatur deposit (Republic of Georgia);
11. SKK-3 - antimony-silicon cationite of the brutto-formula $Sb_2O_5 \cdot nSiO_2 \cdot x mMeO \cdot x kH_2O$;
12. Termoxid-5 - hydrated titanium dioxide-based adsorbent;
13. ISMA-3 - modified manganese dioxide;
14. FT and FZ - spherically granulated titanium and zirconium phosphates;
15. FS-1, FS-2, FS-3 - composite nickel, copper, and zinc ferrocyanide-based adsorbents, respectively;
16. MGA and NGA - aluminosilicate-supported copper and nickel ferrocyanides, respectively;
17. BAU - charcoal adsorbent

The pilot plant tests were performed on the installation comprising 2 stainless steel columns of 20 l operation volume, connected in series. The pilot plant was installed at the IA "Mayak" and used for treatment of industrial reservoir water.

RESULTS AND DISCUSSION

The distribution coefficient values of ^{85}Sr and ^{137}Cs for all the materials investigated are listed in Table I.

The highest selectivity to ^{137}Cs has been observed on ferrocyanide-based adsorbents ($K_d > 10^4$) in all the media investigated. Moreover, the efficient adsorption of ^{137}Cs from solutions with low salt content occurs on synthetic zeolites, and titanium and zirconium phosphates ($K_d > 10^3$). It should be mentioned, however, that all those ion exchangers are suitable for direct disposal of the exhausted material only.

When studying the uptake of Sr, different influence of alkaline and alkaline earth elements in the waste content on the adsorption characteristics has been found. In the presence of Na ions aminocarboxylic amphotites of ANKB-type, synthetic zeolites, and ISMA-3 adsorbent revealed increased selectivity to Sr, but from Ca-containing solutions adsorption

of Sr strongly decreases. Taking into account rather high calcium content in contaminated natural reservoirs (up to 250 mg/l of Ca) it appeared to be necessary to remove the bulk of calcium ions from feed water prior to ion exchange treatment. Preliminary precipitation of hardness salts in the form of carbonates seemed to be the solution providing sufficient increase in decontamination efficiency and installation throughput values. The pilot plant tests at the IA "Mayak" proved this approach to be effective (D_f with respect to ^{90}Sr reached 10^3 at the throughput $T = 1000$ bed volumes). However, taking into account huge volume of water to be decontaminated (above $5 \cdot 10^8 m^3$) the said procedure could be considered only as a temporary one.

Special efforts were devoted to the search of adsorbents capable to uptake Sr selectively from the solutions under study. Modification of natural manganese dioxide under certain conditions appeared to be very promising resulting in the adsorbent of ISMA-3 type. This material adsorbs Sr from solutions with up to 1.2 g/l Ca concentration (see Table I). Moreover, it could be easily regenerated and used in a multi-cycle mode of operation.

CONCLUSIONS

Our investigations allow to conclude that the adsorption technique could be effectively used for the treatment of natural reservoir water contaminated with long lived radionuclides. Ferrocyanide-based adsorbents used for the uptake of cesium radionuclides possess throughput values up to 100000 b.v. and are disposed of without regeneration thus providing simultaneous immobilization of the radionuclide in the solid state. Adsorbents for strontium, on the contrary, are used in a multi-cycle mode, while the strontium concentrate is treated by means of any conventional immobilization technique.

REFERENCES

1. GELIS, V.M. et al., 1991, *Proceedings of the XIII Seminar on Chemistry and Technology of Inorganic Adsorbents* (in Russian), Minsk, p. 15.
2. GELIS, V.M. et al., 1991, *Proceedings of the VII All-Union Conference on the Application of Ion Exchange Material in Industry and Analytical Chemistry* (in Russian), Voronezh, p. 253.
3. HOOPER, E.W., 1985, "The Application of Inorganic Ion Exchangers to the Treatment of Medium Active Effluents", *Solvent Extraction and Ion Exchange in Nuclear Fuel Cycle*, Chichester, p. 145-155.
4. PEKAREK, V., and VESELY, V., 1972, "Synthetic Inorganic Ion Exchanger-II", *Talanta*, Vol. 19, pp.1245-1283.
5. SIPOS-GALIBA, J., and LIESER, K.H., 1980, "Comparison of the Properties of Inorganic Ion Exchangers with Respect to the Separation of the Fission Products Cesium and Strontium", *Radiochemical and Radioanalytical Letters*, Vol. 45, pp. 329-340.

TABLE I
Distribution Coefficient Values of ^{85}Sr and ^{137}Cs Tracers on
Inorganic Adsorbents and Ion Exchange Resins

Ion exchanger	Ionic form	K_d ^{137}Cs in solution of			K_d ^{85}Sr in solution of		
		0.1 M sodium nitrate	1.0 M sodium nitrate	0.01 M calcium nitrate	0.1 M sodium nitrate	0.5 M sodium nitrate	0.01 M calcium nitrate
KU-2x8	Na (Ca)	390	10	130	2000	175	310
KB-4P2	--"	82	-	115	11000	530	125
ANKB-2	--"	70	-	46	55000	5800	36
KU-1	--"	540	-	390	1200	45	105
Vermiculite	--"	1000	105	4400	50	2	17
Clinoptilolite	--"	4100	600	14000	1100	75	520
NaA (CaA)	--"	500	20	3200	25000	1600	106
NaX (CaX)	--"	600	40	2600	7900	515	345
KG-13	K (Ca)	300	30	2100	250000	43000	250
A-51	Na (Ca)	160	16	1800	1600	640	68
IE-95	--"	4800	480	4900	750	4	340
ISMA-3	--"	290	5	2900	38000	5500	500
Pirolusite	--"	175	-	495	1000	325	16
SKK-3	H (Ca)	4100	-	1000	750	170	50
Termoxid-5	H	44	< 2	90	49	-	9
FT	NH ₄	3600	770	7400	60	30	50
FZ	--"	7300	700	15000	< 2	-	< 2
FS-1	K	-	86000	83000	-	-	-
FS-2	--"	28000	20000	10000	150	-	48
FS-3	--"	-	-	5800	-	-	-
MGA	--"	32000	86000	-	-	-	-
NGA	--"	20000	76000	-	145	-	55
BAU	--	43	< 2	44	1200	46	< 2