DEVELOPMENT OF A SELECTIVE SORBENT FOR LIQUID RADIOACTIVE WASTE DECONTAMINATION FROM STRONTIUM

S. A. Dmitriev, D. V. Adamovich
State Unitary Enterprise "Radon"

V. M. Gelis, V. V. Milyutin, O. A. Kononenko
Institute of Physical Chemistry of the Russian Academy of Sciences
Moscow, Russia

ABSTRACT

The types of sorption media widely used nowadays for decontaminating liquid radioactive waste (LRW) from strontium are the following: organic ion exchange resins, natural and synthetic zeolites, as well as phosphates and hydrous oxides of various transition metals. The experience accumulated to date shows the majority of the above-mentioned sorbents to be not effective enough for decontaminating LRW with the salt bearing over 1 g/L. The latter phenomenon is connected with the low selectivity of those sorbents towards strontium in the presence of interfering ions, especially calcium ions.

In the paper we present the development of a technique for synthesizing the manganese (III, IV) hydroxide based selective sorbent; results of the sorbent characterization, basic operational and sorption-selective parameters with respect to strontium; results of its practical application.

INTRODUCTION

Sorption methods based on different sorption media types, namely, organic ion exchange resins, natural and synthetic zeolites, as well as various transition metal phosphates and hydroxides are widely used nowadays for decontaminating liquid radioactive waste (LRW) from strontium [1-3]. However in most cases the above mentioned sorbents are not effective enough for decontaminating the LRW with a high content of interfering ions, especially calcium ions. The adverse effect is associated with the low selectivity of the known sorbents with respect to strontium.

One of the most efficient sorbents known for decontaminating LRW from strontium radionuclides is based upon the manganese hydroxides (III, IV) and possesses a higher selectivity towards strontium ions [4].

However a technology for producing large batches of the sorbent in question that would provide the operational and sorption-selective characteristics required has not been developed until recently.

The goals of our work were as follows:

- to develop a technology for producing large batches of the manganese hydroxide (III, IV) based sorbent;
- to produce a test batch of the sorbent,
- to determine the sorption-selective characteristics of the sorbent;
- to test the sorbent for decontaminating actual LRW from strontium radionuclides.

Development of the Sorbent Production Technology

Synthesis of the manganese hydroxide (III, IV) sorbent consists of the following basic stages:

1. The interaction of solutions of a divalent manganese salt and the potassium permanganate in alkaline medium resulting in the formation of the manganese hydroxide (III, IV) precipitate suspension;
2. Filtering of the precipitate;
3. Rinsing of the precipitate;
4. Drying and calcining of the precipitate;
5. Granulating of the sorbent.

Our experiments allowed us to determine the optimum conditions for each stage of the sorbent synthesis as follows:

- concentrations of a divalent manganese salt and the potassium permanganate solutions within the range of 0.1-0.2 and 0.1-0.15 mole/L, respectively;
- the Mn(II)/$KMnO_4$ mole ratio of 1.3-1.6;
- the stirring time not less than 1 hour;
- the temperature of 20-60 ^oC;
- the reagent mix pH value within the range of 10.0-12.0

To provide higher mechanical strength of the sorbent granules an organic polymer, for example, the polyvinyl alcohol was added into the reagent mix in the amount of 1-5% of the manganese hydroxide (III, IV) precipitate formed. The optimal calcination temperature was 230-250 ^oC and the calcinations time was 4-6 hours.

Granulating of the sorbent was performed by decrepitation through contacting the calcined precipitate with water.

Production of an Experimental Sorbent Batch

To determine a possibility of synthesizing large manganese hydroxide (III, IV) based sorbent batches we have performed the synthesis of an enlarged batch of the sorbent.

The block diagram of an experimental facility set up for the sorbent synthesis is shown in Fig. 1.

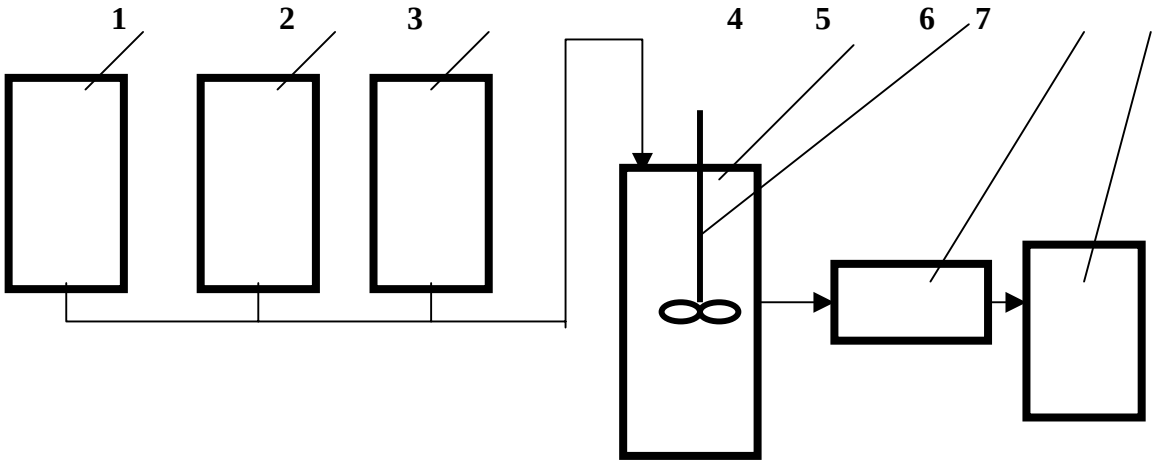

Fig. 1. Block diagram of the experimental facility for synthesizing the MDM sorbent. 1, 2, 3 – metering tanks; 4 – the reactor vessel; the mechanical stirrer; 6 – the nutsch filter; 7 – the calcination furnace.

The technology of the synthesis consisted in the following. The 10 g/L potassium permanganate, 20 g/l manganese sulfate, and 10% sodium hydroxide solutions were prepared in the metering tanks 1, 2, and 3, respectively.

One hundred liter portions of the solutions from the metering tanks 1 and 2 were transferred into the reactor vessel under the continuous stirring; the sodium hydroxide solution from the metering tank 3 was added to adjust the reaction mix pH value to 11.5-11.7. After that a 200 cm^3 portion of the 10% aqueous polyvinyl alcohol solution was added and the mix was stirred for 2 hours more.

The suspension was transferred to the nutsch filter 5 with the effective filtration area of about 0.8 sq. m and vacuum-filtered to get a wet paste. The paste was rinsed on the filter with hot water to get the neutral pH, put into trays and transferred into the calcination furnace 7, where the thermal treatment of the sorbent was conducted for 6 hours at the temperature of 250±10 ^oC. After the calcination the material was allowed to cool to the ambient temperature and granulated by the decrepitation through contacting the material with water at the liquid/solid phase ratio of (3-4)/1 for 2-3 hours. The obtained granulated material was elutriated from the small grain size sorbent fraction by decanting, transferred into trays, and dried at the temperature of 100 ^oC to the constant weight. The gross weight of the sorbent produced in one cycle amounted 2.2 kg (the trade name assigned to the sorbent was MDM).

Determination of the Physicochemical and Sorption Characteristics of the Sorbent

Basic physicochemical characteristics of the MDM sorbent are listed below:

1. Appearance – irregular-shaped granules, dark-brown in color;
2. Bulk density – 0.52 g/cm^3;
3. Grain size distribution:
   fraction content, % by weight:
   3 mm – 59.1;
   3+2 mm – 20.9;
   2+1 mm – 13.1;
   1+0.5 mm – 3.0;
   0.5+ 0.25 mm – 3.1;
   < 0.25 mm – 1.3.

The produced sorbent has been characterized both under the batch and flow conditions.

In batch mode we determined the distribution coefficient values (K_d) of the tracer ^{85}Sr radionuclide quantities and the batch capacity value (BC) with respect to calcium according to the following technique:

Aliquot sorbent weight of 0.1 g was brought into contact with 20 cm^3 of 0.02 g-eqv/L solution of calcium nitrate with the pH value of 6.0 containing tracer (≈10^5 Bq/L) quantities of the ^{85}Sr radionuclide and was continuously shaken for 48 hours. Equilibrated mix was filtered through the paper filter and the filtrate was analyzed for the calcium ion concentration and the specific radioactivity of ^{85}Sr.

Results of the analyses were used to calculate the distribution coefficient (K_d) values of ^{85}Sr and the batch capacity (BC) values with respect to calcium according to the following formulas:

$$K_d = \frac{a_o - a_e}{a_e} * \frac{V}{m} \ [cm^3/g]$$

where a_o, a_e – starting and equilibrium radioactivity of ^{85}Sr in solution, Bq/cm^3;

V – liquid phase volume, cm^3;
m – weight of the sorbent, g.

$$BC = (C_O - C_e) * \frac{V}{m}$$

where C_o, C_e – starting and equilibrium concentrations of calcium ions in the solution, mg-eqv/cm^3.

To obtain comparative data for the MDM sorbent we determined K_d and BC values under similar conditions for the following sorbents:

- KU-2x8 – strong acidic sulfocationite;
- Cln – natural clinoptilolite.

The results obtained are given in Table I.

Table I. Distribution coefficient values (K_d) for ^{85}Sr and the batch capacity (BC) values with respect to calcium on various sorbents

Sorption characteristics	Type of the sorbent		
	KU-2x8	Cln	MDM
Kd ^{85}Sr, cm^3/g	220	300	1500
BC, mg-eqv/g	3.60	0.68	1.30

The data given in Table 1 show that the manganese hydroxide (III, IV) based MDM sorbent possesses the best sorption-selective characteristics with respect to strontium.

The flow tests of the sorbents were performed according to the following technique. A glass column with the internal diameter of 10 mm was loaded with 3 cm^3 of a sorbent bed. The solution was passed through the column with the flow rate of 15 cm^3/hr. The sorption process was conducted with the solution containing 0.02 g-eqv/L of calcium nitrate, ^{85}Sr radionuclide with the specific radioactivity value of ~ 10^5 Bq/L at pH=6.0. The emerging filtrate was fractionated and analyzed for the content of calcium ions and the specific radioactivity of ^{85}Sr.

Results of the analyses were used to determine the value of the total dynamic capacity (TDC) with respect to calcium and a volume of the solution passed through the column until the 1% and 5% breakthrough of strontium into the filtrate (V_1 and V_{50}, respectively) expressed in terms of the bed volumes (bv).

The results obtained are given in Table 2.

Table II. Results of the flow sorption tests of strontium on different sorbents

Sorbent characteristics	Type of the sorbent		
	KU-2x8	Cln	MDM
TDC, mg-eqv/cm^3	2.0	0.60	1.28
V_1, bv	80	40	200
V_{50}, bv	140	125	440

The results given in Table 2 confirm the conclusion of the highest selectivity of the MDM sorbent with respect to strontium radionuclides.

Tests of the Actual LRW Decontamination from Strontium and Cesium Radionuclides

To examine a possibility of the inorganic sorbent application for the liquid radioactive waste decontamination from strontium and cesium radionuclides the tests have been performed with the actual LRW of the State Russian Atomic Shipbuilding Center.

Chemical composition of the waste was as follows: the total salt bearing – 2.9 g/L, total hardness – 8.2 mg-eqv/L, the concentration of Ca^{2+} ions – 0.4 mg-eqv/L; the concentration of Mg^{2+} ions – 7.8 mg-eqv/L, the chloride ion concentration – 1.5 g/L, pH=8.3.

Radionuclide composition of the waste was as follows: gross beta-activity – $4.3 \cdot 10^4$; ^{137}Cs-$2{,}3 \cdot 10^4$; ^{90}Sr – $7.5 * 10^3$; ^{60}Co–110.

The MDM sorbent was used for decontaminating LRW from strontium radionuclides, and the composite nickel ferrocyanide – based NGS sorbent deposited on the silica gel carrier was used for decontaminating LRW from cesium radionuclides [5].

The flow tests of the sorbents were performed according to the following technique. A glass column with the internal diameter of 10 mm was successively loaded with 3 cm^3 of the MDM and the same quantity of the NGS sorbent bed. The grain size of both sorbents was within the range of 0.25-0.5 mm. The solution was passed through the column with the flow rate of 12-15 cm^3/hr. The emerging filtrate was fractionated and analyzed for the content of ^{137}Cs, ^{90}Sr, and ^{60}Co.

During the tests the total of 13.8 L (4600 bv with respect to each individual sorbent) of LRW was passed through the column. During the entire test the specific radioactivity values of ^{137}Cs, ^{90}Sr, and ^{60}Co in the filtrates were 30-60; <2 and 80-100 Bq/L, respectively. Decontamination factors from cesium, strontium, and cobalt radionuclides amounted 380-770, > 3800, and 1.1-1.3 respectively.

Thus, the tests showed the high efficiency of the MDM sorbent for decontaminating LRW from strontium and of the NGS sorbent – from cesium radionuclides.

CONCLUSIONS

1. Optimum conditions have been determined for synthesizing manganese hydroxide (III, IV) based granulated MDM sorbent intended for the selective removal of strontium from solutions. The production technology for large batches of the MDM sorbent has been developed and used for obtaining the test sorbent batch.

2. Sorption-selective characteristics of the MDM sorbent have been determined under the batch and flow conditions. It has been shown that the efficiency revealed by the sorbent under study for the strontium radionuclide sorption in the presence of macroamounts of calcium ions excelled greatly all the sorbents known for the purpose.

3. The inorganic NGA and MDM sorbent tests have been conducted for the actual LRW decontamination from cesium and strontium radionuclides. High efficiency of MDM and NGA sorbents has been shown for decontaminating LRW from strontium and cesium radionuclides, respectively; the decontamination factors exceeded 3800 for strontium and 380-770 for cesium.

REFERENCES

1. V.M. Gelis, V.V.Milyutin. Proc. of Forth Int. Conf. on Rad.Waste Manag. and Envir. Remed. Prague,1993, v.1, p.379-381.

2. V.M. Gelis, V.V.Milyutin. Proc. of Firth Int. Conf. on Rad.Waste Manag. and Envir. Remed. Berlin,1995, v.2, p.1159-1160.

3. V.V.Milyutin,V.M. Gelis. Journal of Applied Chemistry (*in Russian*), v.67, 11, p.1776-1779.

4. Patent of the Russian Federation No. 2094115, 1999.

5. V.V.Milyutin,V.M. Gelis., R.A.Penzin. Radiochemistry (in Russian), 1993, 3, p.76-82.