#### Development of the Technology for Producing Industrial-Scale Batches of the Selective Sorbent for LRW Decontamination from Strontium and the Result of its Application

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# ABSTRACT

Currently in Russia ion exchange processes with various sorption media types are widely used for decontamination of liquid radioactive waste (LRW) from strontium radionuclides. However in most cases for decontamination of LRW with high hardness salt content the above mentioned sorbents are inefficient, which is associated with low selectivity of those with respect to strontium.

One of the most effective sorbents for decontaminating LRW from strontium radionuclides is the manganese (III, IV) hydroxide based inorganic sorbent possessing higher selectivity to strontium ions.

It is worth to mention that until recently an industrial-scale technology for producing batches of the manganese (III, IV) hydroxide based inorganic sorbent with predetermined operational and sorption-selective properties was not available.

In our paper the technological principles for synthesizing industrial-scale manganese (III, IV) hydroxide based sorbent batches are reported. Data on the main operational and sorption-selective characteristics of the sorbent as well as the results of LRW decontamination from strontium radionuclides at different objects are given and discussed.

## **INTRODUCTION**

Currently sorption techniques for decontamination of liquid radioactive waste (LRW) from strontium radionuclides are widely used with various sorption media types, namely, organic ion exchange resins, natural and synthetic zeolites, transition metal phosphates and hydroxides [1-3]. However for decontamination of LRW with high content of interfering ions, especially calcium, the sorbent media in question is inefficient, which is associated with the low selectivity of known sorbents with respect to strontium.

One of the most effective sorbents for decontaminating LRW from strontium radionuclides is the manganese (III, IV) hydroxide based inorganic sorbent possessing higher selectivity to strontium ions. We have developed a sorbent of the type with the MDM trade name intended for commercial use [4, 5]. However until recently a technology for producing industrial-scale batches of the sorbent with the required operational and sorption-selective properties was not available.

This work has focused on the elaboration of the technology for producing industrial-scale batches of MDM sorbent, on the determination of its sorption-selective characteristics, and on the full-scale tests of the sorbent for decontaminating actual LRW from strontium radionuclides.

# INDUSTRIAL-SCALE SORBENT PRODUCTION TECHNOLOGY

Synthesis of MDM sorbent consists of the following basic stages:

- 1. Interaction of divalent manganese and potassium permanganate salt solutions in alkaline medium with the formation of a suspension of manganese (III, IV) hydroxides;
- 2. Precipitate filtration;
- 3. Precipitate rinsing;
- 4. Precipitate drying and calcining;
- 5. Sorbent granulation.

Block diagram of the facility used for synthesizing industrial-scale batches of MDM sorbent is shown in Fig. 1.

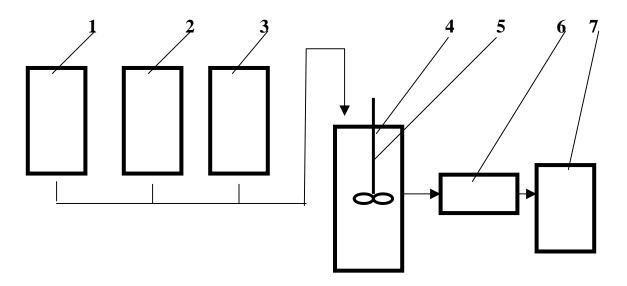


Fig. 1. Block diagram of the facility for MDM sorbent synthesis. 1, 2, 3. – metering tanks; 4 – reactor vessel; 5 - mechanical stirrer; 6 – nutsch filter; 7 – calcination furnace.

Technology of the synthesis consisted in the following. Solutions of 10 g/L potassium hydroxide, 20 g/L manganese sulfate, and 10% sodium hydroxide were prepared in measuring tanks 1, 2, and 3, respectively. Then 500 L of solution from metering tanks 1 and 2 each were transferred into the reactor vessel 4 of 1000 L operating volume under continuous stirring and the pH value was adjusted to 11.5-11.7 using sodium hydroxide solution from metering tank 3. After that a 1250 cm<sup>3</sup> portion of 10% aqueous polyvinyl alcohol solution was added into the reaction mix and the formed suspension was stirred for 2 more hours.

The resulting suspension was transferred onto the nutsch filter 6 with the effective filtering area of about 4 m<sup>2</sup> and vacuum-filtered to obtain wet paste. The paste was rinsed with hot water to get the neutral reaction, reloaded into trays and transferred into the calcinations furnace where it was calcined at  $250\pm10^{\circ}$ C for 6 hours. After cooling to the ambient temperature the calcined material was granulated by decrepitation by contacting the material with water at the liquid/solid phase ratio of (3-4)/1 for 2-3 hours. Obtained granulated material was elutriated from the fine grain size sorbent fraction by decanting, transferred into trays, and dried at the temperature of 100 °C to the constant weight. Gross weight of the sorbent produced in one cycle amounted 15 kg of the ready-to-use MDM sorbent.

Basic specifications of MDM sorbent are given in Table I [4, 5].

##	Parameter	Standard
1.	Appearance	Irregular shaped granules dark-brown in color
2.	Humidity, %, not less than	10
3.	Granule size, mm	0.25 - 3.00
4.	Content of the working fraction, %, not less than	95
5	Bulk density, g/cm <sup>3</sup>	0.5-0.8
6.	Batch capacity by calcium, mg-eqv/g, not less than	0.8
7.	Distribution coefficient of strontium, cm <sup>3</sup> /g, not less than	1000

 Table I. MDM Sorbent Specifications

# **RESULTS OF THE FULL-SCALE LRW DECONTAMINATION FROM STRONTIUM RADIONUCLIDES**

Full-scale demonstration of the MDM sorbent performance was conducted in 2004 at the State Russian Center for Nuclear Powered Shipbuilding at Severodvinsk City [6] and in 2005 at FSUE Rostovskii Special Combine "Radon" site located in southern Russia. Analytical data on the feed LRW for decontamination are given in Table II.

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Parameter	Value		
Dry residue, g/L	2.04		
Total hardness, mg-eqv/L	2.5		
COD by permanganate, mgO/L	59		
<sup>137</sup> Cs, Bq/L	180		
<sup>90</sup> Sr, Bq/L	180		
<sup>226</sup> Ra, Bq/L	158		
<sup>222</sup> Rn, Bq/L	7300		
$\Sigma \alpha$ by <sup>239</sup> Pu, Bq/L	97		

Table II. Chemical and Radionuclide Composition of Feed LRW at "Radon" Site

LRW was decontaminated using the mobile "ECO-2" facility. The facility was set up to operate as follows (see Fig. 2): submersible pump – filled mechanical filter F1 – cartridge microfilter – intermediate 500 L tank – ultrafiltration unit – sorption filter F2 – release of the decontaminated solution from the facility (see Fig. 2).

Facility filters were loaded with the following media:

- 100 L of quartz-sand-, 200 L of clinoptilolite, and 100 L of BAU activated carbon for F1 filled mechanical filter bed;
- 4 bulk-action polypropylene cartridges providing better than 4  $\mu$ m fine filtration in the microfilter;
- 12 ultrafiltration roll elements in the ultrafiltration module;
- 200 L of MDM sorbent for filled F2 sorption filter bed.

LRW was fed into the facility by the submersible drainage pump. For dosimetric, radiometric, and spectrometric monitoring the facility was equipped with necessary instrumentation, hardware and glassware.

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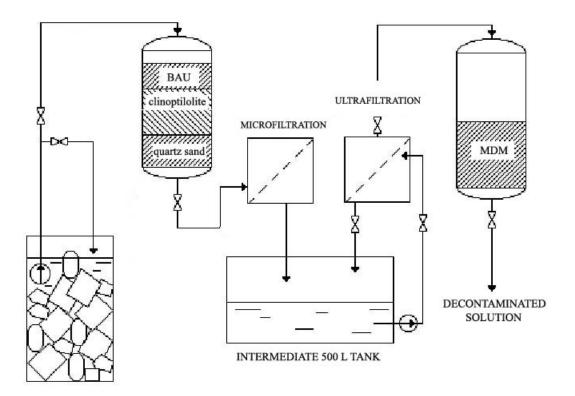


Fig. 2. General layout of "ECO-2" mobile facility

In the period of 09/28/05 through 10/11/05 LRW from the SRW repository tank of FSUE Rostovskii Special Combine "Radon" has been processed. General view of the facility in operation is shown in Fig. 3.

LRW decontamination performance was tested first with 4  $\text{m}^3$  of the feed. Sample of the decontaminated water showed gross beta-activity of 7.9 Bq/L, gross alpha-activity of 0.9 Bq/L, and volumetric <sup>90</sup>Sr activity of 1 Bq/L. Part of the beta activity value is attributed to the natural potassium leached from the concrete structure.

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Fig. 3. Location of "ECO-2" facility on site

During the facility operation the total LRW quantity of 58 m<sup>3</sup> has been decontaminated. MDM sorbent allowed the removal of  $^{90}$ Sr and  $^{226}$ Ra from LRW down below 1 Bq/L. The flow rate through the sorbent was maintained at 5-8 bed volumes per hour. After 290 bed volumes the sorbent resource was still not exhausted. When the analyses were completed, the decontaminated solution was dumped onto the ground.

#### CONCLUSIONS

1. The industrial-scale technology for producing MDM sorbent batches has been developed and the sorbent has been made.

2. Mobile ECO-2 and ECO-3 facilities with the selective MDM sorbent have been used for decontaminating LRW of the FSUE Rostovskii Special Combine "Radon" and the State Russian Center for Nuclear Powered Shipbuilding at Severodvinsk City.

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