Manganese Oxide-Based Sorbent for Sr-90 Radionuclide Removal from Seawater

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Abstract. The morphology, specific surface area, and sorption properties toward Sr-90 radionuclides in seawater of a sorption material based on manganese oxide have been investigated. The material was fabricated through interaction of $KMnO_4$ and H_2O_2 with subsequent annealing at 500 °C. The sorbent is characterized with the mechanical strength sufficient for using under dynamic sorption conditions: here, the efficiency of Sr-90 removal at feeding of 150 bed volumes exceeds 95 %. The values of Sr-90 distribution coefficients are equal to $0.8–1.2 \times 10^3$ ml/g in the real seawater and to $1.6-1.8 \times 10^3$ ml/g in the simulated one.

1. Introduction

The importance of creating novel sorption materials for Sr-90 removal from seawater is caused by active construction works and operation of nuclear powers plants (NPPs) located in the coastal area – some of them use seawater for direct cooling. The latter created potential risks of the release of anthropogenic radionuclides into the World Ocean with formation of huge amounts of liquid radioactive waste (LRW) streams of complex chemical compositions in case of emergency. Presently, formation of such LRW comprising the radioactively contaminated seawater (SW) occurs in the process of operation, repair, service, and decommissioning of nuclear-powered ships.

The most hazardous radionuclides include Cs-137 and Sr-90 belonging to the group of high-toxicity isotopes. The increased content of these radionuclides in the environment, especially in natural water basins, creates risks of elevated radiation doses for human population. Whereas the task of Cs-137 removal from SW can be solved through application of ferrocyanide sorbents and phenol-aldehyde resins, the Sr-90 removal is still an urgent problem.

The developed and successfully applied technology of seawater decontamination from Sr-90 using the sorption-reagent material (barium silicate) [1–3] has an essential disadvantage – formation of significant amounts of secondary wastes in the form of spent material. That is why to develop an efficient technology of decontamination of seawater from Sr-90 with formation of minimal amounts of secondary wastes, it is necessary to create materials characterized with high selectivity to Sr and the possibility of extended used in the sorption–elution–regeneration cycle. The radionuclide concentrate obtained in the form of eluate can be evaporated down to the minimal volume or reprocessed using smaller amounts of the sorbent, which will allow reducing the volume of radioactive waste to be sent for final disposal.

To solve the task of the removal of Sr-90 from seawater, the most promising are sorption materials based on manganese oxides and characterized with an acceptable selectivity toward Sr^{2+} ions in the

presence of Mg^{2+} and Ca^{2+}. The sorbed Sr can be eluted by solution of a strong mineral acid with a repeated application of the sorbent in the sorption process. However, despite a large number of works in this field, just a small part of them are devoted to strontium removal from seawater, while there are virtually no works on studying the possibility of application of manganese oxide in the sorption–elution–regeneration cycle. In our opinion, the layered modification of manganese oxide, which can be synthesized through a relatively simple procedure, is the most efficient in solution of the problem of decontamination of LRW streams comprising the radioactively contaminated seawater [4]. The present work was devoted to studies of the Sr sorption from seawater by the layered modification of manganese's oxide in the sorption–elution–regeneration mode.

2. Experimental

The sorbent was obtained through mixing of concentrated solutions of $KMnO_4$ and H_2O_2 under constant stirring at heat and reaction gaseous products removal. The produced precipitate was washed with deionized H_2O and annealed, after preliminary drying, at 500 °C for 6 h in air. The produced sorbent comprises granules of irregular shapes and black color with characteristic metallic gloss; its bulk weight is equal to 1.56 g/ml.

The strontium sorption under static conditions was carried out under constant joint stirring of the sorbent and the liquid medium – the stirring duration was 24 hours, V/m = 1000 ml/g, and the sorbent weight was 0.01 g. The initial solutions activity was 1000 Bq/ml. The distribution coefficient of Sr-90 (K_d of Sr-90) was determined upon determination of the solution residual activity.

The Sr-90 distribution coefficient was calculated according to the formula (1):

$$K_d = \frac{A_0 - A_1}{A_1} \times \frac{V}{m} \qquad (1),$$

where A_0 – the liquid medium initial activity (Bq/ml), A_1 – the liquid medium residual activity after sorption (Bq/ml), V – the liquid medium volume at sorption (ml), m – the sorbent weight (g).

The sorption under dynamic conditions was studied by feeding the liquid medium through a column of an internal diameter of 0.5 cm containing 1 ml of the sorbent with grain sizes of 0.1-0.2 mm. The feeding rate was 10 bed volumes per hour (BV/h). Elution of the adsorbed strontium was made using 0.5 M HCl solution at a rate of 10 BV/h. Thereafter, the sorbent was regenerated by 100 ml of 1.0 M NaOH solution and washed with 30 ml of distilled H_2O, and the sorption cycle was repeated.

The Sr-90 desorption was calculated according to the formula (2):

$$Desorption\% = \left(\frac{\sum_1^i V \times A_1}{A_x + A_{x-1}} \right) \times 100 \qquad (2)$$

where A_1 – the eluate activity (Bq/ml), V – the eluate volume (ml), A_x – the activity of Sr-90 removed at the sorption stage (Bq), A_{x-1} – the residual activity of Sr-90 from the previous cycle (Bq), x – the cycle number, i – the number of the eluate fraction.

Seawater (SW) taken at the Amursky bay (Primorsky Territory) and preliminarily filtered through two "blue ribbon" cellulose filters was used. To study sorption-selective characteristics, seawater samples containing the Sr-90 tracer of an activity of 100–300 Bq/ml were used. To prepare the simulated seawater (S-SW), the composition suggested in [5] was used.

3. Results and Discussion

The materials notations and their sorption characteristics and specific surface areas as well as Na and K contents are presented in Table 1.

Table 1. Characteristics of manganese oxide samples used in the present work.

Sample	Thermal	Treatment by	$\omega(Na^+)$,	$\omega(K^+)$,	Specific	K_d of Sr-90

No.	treatment temperature (℃)	HCl+NaOH solutions	wt.%	wt.%	surface area (m^3/g)	SW	S-SW
1	105	No	Not determined		13.4	520	950
2	500	No	4.1	4.37	9.4	890	1690
3	500	Yes	6.06	0.34	12	1240	1830

The XRD spectra of the samples 1, 2, and 3 were recorded (Figure 1). The materials are characterized with low degree of crystallinity, which complicates correct identification of the phase composition. However, the obtained XRD patterns allow assuming the presence of several phases, mainly K- and Na-birnessite.
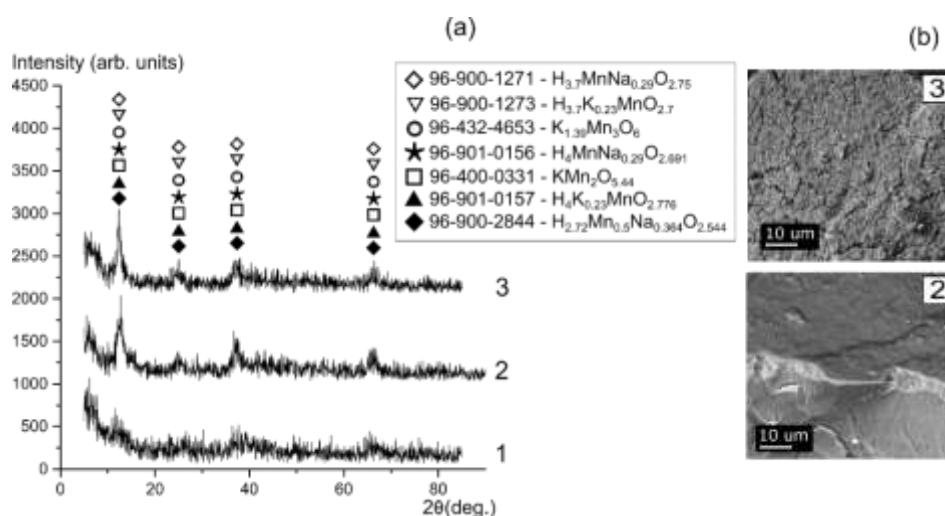

Figure 1. XRD-spectra of the synthesized samples (a) and REM images of their surfaces (b); 1 – sample 1, 2 – sample 2, 3 – sample 3.

It was revealed that the increase of the temperature of thermal treatment from 105 to 500 °C resulted in the increase of the Sr-90 K_d more than 1.5-fold. Probably, this is related to formation of a clearly expressed phase of birnessite at higher heating temperatures. Preliminary sequential treatment of the samples by HCl and NaOH solutions also results in the increase of the efficiency of Sr-90 removal. Such results can be explained by high content of potassium (Table 1) having high competing impact on the sorption (as compared to sodium) in the initial sample. That is why the potassium removal from the manganese oxide composition has a positive effect on the efficiency of Sr-90 removal. Besides, the treatment by HCl and NaOH solutions yields the increase of the specific surface area from 9.4 to 12 m^3/g, which could also increase the Sr-90 K_d values.

In the presence of Na^+, the sorbents based on manganese oxides are known to be efficient materials for strontium removal [6]. However, since it is evident that the most pronounced effect on sorption is provided by Ca^{2+} and Mg^{2+} ions, we studied their effect on the efficiency of Sr-90 removal by manganese oxide (the results are shown in Table 2). The obtained results indicate to the fact that Ca^{2+} ions decrease the strontium sorption to the highest degree, as compared to Mg^{2+} ions. However, in the simulated solution containing 0.01 mol/L of Ca^{2+}, the Sr-90 K_d values remain rather high, which indicates to the selectivity of manganese oxide that is sufficiently high to remove this radionuclide from seawater.

Table 2. Effect of Ca^{2+} and Mg^{2+} ions concentrations on the efficiency of Sr-90 sorption by manganese oxide.

Ca^{2+} concentration, mol/l	Sr-90 K_d, ml/g	Mg^{2+} concentration, mol/l	Sr-90 K_d, ml/g
0,0001	40.2×10^3	0,0001	18.9×10^4

0,001	13.7×10^3	0,001	5.4×10^4
0,01	1.9×10^3	0,01	2.2×10^4
0,01	0.7×10^3	0,01	0.6×10^4

The manganese oxide sorption characteristics under dynamic conditions were investigated. Figure 2 shows the output curves of sorption of non-active strontium from S-SW, and the calculated values of full dynamic exchange capacity were equal to 9.16, 7.82, and 6.85 mg/g in the first, second, and third cycles, respectively. Such a capacity reduction can be related to a gradual material dissolution. For example, the height of the sorption layer decreased by 20 % after three cycles. The dissolution can be explained by disproportionation of Mn^{3+} in acidic media with formation of Mn^{4+} and soluble Mn^{2+}.
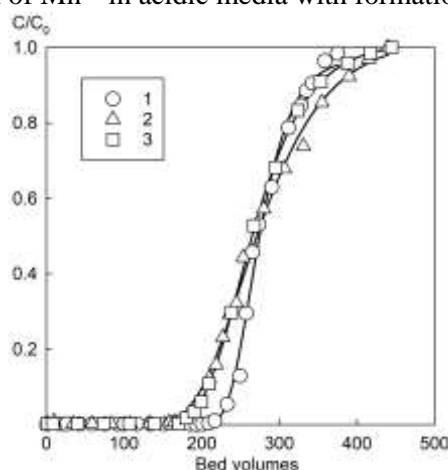

Figure 2. Sorption of non-active strontium from S-SW by manganese oxide under dynamic conditions, initial Sr concentration 50 mg/l: 1 – sample 1, 2 – sample 2, 3 – sample 3.

The sorption and desorption of Sr-90 micro-quantities from real seawater under dynamic conditions were investigated and the results are shown in Fig. 3. In the course of removal of Sr-90 micro-quantities from SW, the sorbent resource, taking into account the real strontium content, decreases and does not attain its maximal capacity. The reason of the decrease of the sorbent resource could consist in the presence of organic contaminants and organic carbon in SW, which promote Mn reduction until lowest oxidation states, and suspensions.

The Sr-90 removal from SW is characterized with low efficiency in the first cycle (Fig. 3a, curve 1), which is related to the sorbent achievement of the working mode, transition into the Na-form, and formation of a developed surface. During the second and further cycles, the sorbent resource exceeds 150 bed volumes, while no changes in the sorbent or filtrate color were observed at the sorption stage.

Figure 3b shows the curves of elution of Sr-90 sorbed from real SW under dynamic conditions. The obtained results indicate to instability of radionuclide elution, but after 4 cycles the residual activity of Sr-90 did not exceed 4 % of total activity absorbed by the sorbent.
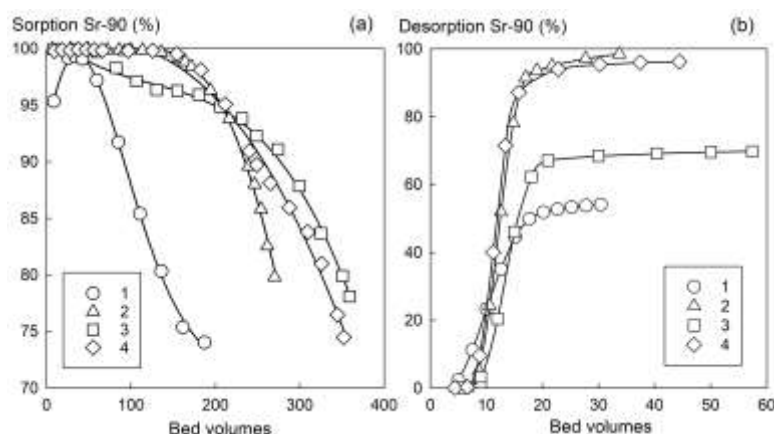
Figure 3. Sorption (a) and desorption (b) of Sr-90 from real seawater under dynamic conditions.

4. Conclusions

The interaction of $KMnO_4$ and H_2O_2 with subsequent treatment by 1 M NaOH solution and annealing at 500 ℃ produced the material with the structure of birnessite characterized with high selectivity toward Sr-90. In the presence of 0.4 g/l of Ca^{2+} ions, the Sr-90 distribution coefficient is equal to 1.9×10^3 mg/g, which enables one to use this material for seawater decontamination from this radionuclide. The Sr-90 distribution coefficients is equal: in real seawater – to 0.8–1.2×10^3 mg/g, in simulated seawater – to 1.6–1.8×10^3 mg/g. Under dynamic sorption conditions, the material is mechanically stable and preserves the grain structure. However, at prolonged functioning, the material dynamic exchange capacity decreases due to its dissolution, and a regular addition of new sorbent batches is required. Under dynamic sorption conditions, the average value of the volume of seawater fed until the Sr-90 breakthrough of 95 % and higher exceeds 150 bed volumes at a filtering rate of 10 BV/h. The produced material can be applied in decontamination of liquid radioactive waste streams containing seawater from Sr-90.

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