

UDC 544.726.2; 621.039.735

DOI: 10.15372/CSD2020240

Sorption of $^{137}\text{Cs}^+$ from Aquatic Medium by an Illite-Containing Sorbent Obtained from the Clay-Salt Slimes of JSC “Belaruskali”

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(Received October 02, 2019; revised February 13, 2020)

Abstract

The results of a comprehensive study of an illite-containing sorbent (IS) are presented. The sorbent was obtained by means of acid-water treatment of the sample of clay-salt slimes, which are industrial wastes of JSC “Belaruskali” (the Republic of Belarus). The material composition of the IS is established, indicating that the main clay mineral is illite, the content of which is 65.2 mass %. The specific surface area of the IS is determined to be $(66 \pm 4) \text{ m}^2/\text{g}$. According to mineralogical composition, the IS refers to hydromica group. The sorption ability of the IS sample to extract $^{137}\text{Cs}^+$ from natural waters of different chemical composition was studied. It is shown that the major ions of natural waters, namely Ca^{2+} and Na^+ , do not have a significant effect on the sorption of $^{137}\text{Cs}^+$ by the IS for pH of water solution within the range of 5–9. It is determined that the IS has shown high selectivity with respect to $^{137}\text{Cs}^+$ sorption from aquatic medium, and the main competitor is K^+ ion. When K^+ concentration in the aquatic medium is higher than $0.5 \text{ mol}/\text{dm}^3$ in, the sorption of $^{137}\text{Cs}^+$ on the IS is completely inhibited. It is established that IS sorbs $^{137}\text{Cs}^+$ from natural water 2–4 times more efficiently than clinoptilolite of the Shivertuinskoye deposit (Chita region, Russia), which is currently used as a sorbent of $^{137}\text{Cs}^+$. The obtained results indicate the possibility and prospects of using CSS reserves accumulated in the Republic of Belarus to manufacture the IS and to use it for the purification of aquatic medium from $^{137}\text{Cs}^+$, as well as for solving a number of environmental problems, including rehabilitation of radioactively contaminated soils and territories.

Keywords: clay-salt slimes, illite-containing sorbent, natural water, $^{137}\text{Cs}^+$, sorption

INTRODUCTION

One of the urgent tasks of rational nature management is to solve the problem of the utilization of large-scale industrial waste. Potassium ores processing from large deposits in Canada, Russia, the Republic of Belarus, Germany, the USA and Spain, leads to the formation of large-scale industrial waste, independently of the processing method. This waste includes solid halite

and clay-salt slimes (CSS). The latter consist of suspended clay precipitate in the saturated solution of KCl and NaCl salts. The specific output of CSS at JSC “Belaruskali” (the Republic of Belarus) is $0.6\text{--}0.7 \text{ m}^3$ per 1 t of the final product. Clay-salt slimes are stored in slime depositories that occupy the area of more than 1100 ha of land and act as a source of environmental pollution, which worsens of the conditions of human life [1]. By 01.01.2019, the amount of CSS accu-

mulated in the depositories of JSC "Belaruskali" exceeds 119 million t, which allows us to consider this waste as secondary technogenic raw material resources.

On the other hand, search, development of new materials and improvement of the existing sorption materials for the recovery of radionuclides from aquatic media form an urgent research direction in connection with the aggravation of radioecological problems caused by the accumulation and spreading of radioactive pollution in the environment, especially after large accidents at the Chernobyl atomic power plant (Ukraine, 1986) and Fukushima-1 atomic power plant (Japan, 2011). The migration of ^{137}Cs and ^{90}Sr radionuclides in natural waters is connected with the high migration ability of these isotopes [2, 3].

The choice of a sorbent is determined not only by the parameters of radionuclide sorption but also by the economical reasonableness of its application if the deactivation of large amounts of radioactively polluted waters is considered [4]. Sorption-based modern technologies of aquatic environment purification from $^{137}\text{Cs}^+$ involve natural clays, which contain clay minerals of 2 : 1 structural type. Unlike synthetic sorbents, the application of natural clay in sorption is reasonable because of their wide availability, the low net cost in the case when large developed deposits are present, and efficiency with respect to $^{137}\text{Cs}^+$ [5–7].

It is known [7–9] that illite with densely compressed layers and broadened zones at their ends is characterized by the highest sorption properties with respect to $^{137}\text{Cs}^+$ among clay minerals of 2 : 1 structural type. It was established in [10] that the major minerals of CSS are illite, potassium feldspar and dolomite.

In connection with the aforesaid, one of the promising directions of CSS utilization is the production of illite-containing sorbent (IS) from them for the extraction of $^{137}\text{Cs}^+$ from aquatic media, which determines the relevance and necessity of the present study.

The goal of the present work was to evaluate the efficiency of $^{137}\text{Cs}^+$ extraction from aqueous media using the IS obtained from CSS formed at JSC "Belaruskali".

EXPERIMENTAL

The CSS sample taken from the depository of the Third mining factory of JSC "Belaruskali" (Soligorsk, the Republic of Belarus) was the ob-

ject of investigation. The major mineral phases in the water-insoluble precipitate of CSS are illite, dolomite and potassium feldspar, while the content of water-soluble salts KCl and NaCl is (5.4 ± 0.3) mass % [10]. It is demonstrated in this work that CSS is characterized by the low sorption capacity for the extraction of $^{137}\text{Cs}^+$ from tap water (Minsk, the Republic of Belarus). It is assumed to enhance the sorption capacity of the CSS sample with respect to $^{137}\text{Cs}^+$ both through its enrichment with illite by removing the waste material (carbonate minerals dolomite and calcite) and through a decrease of water-soluble salts (KCl and NaCl) and gypsum concentrations.

A sample of IS was obtained from the CSS sample by its acid-water treatment according to the procedure presented in [11]. The mineralogical and chemical composition of CSS and IS samples is also presented in the work.

The sorption characteristics of CSS and IS samples were determined using the sorption of micro-amounts of $^{137}\text{Cs}^+$. The specific activity of solutions prepared by adding $^{137}\text{Cs}^+$ as a radioactive label was $(5.2 \pm 0.3) \cdot 10^6$ Bq/dm³. The kinetics of $^{137}\text{Cs}^+$ sorption by the IS sample was studied under the conditions of limited volume at a temperature of (20 ± 2) °C. The radioactive solution with $^{137}\text{Cs}^+$ was prepared from the Minsk tap water. The weighted portions of the IS sample with a mass of 0.100 g were placed in centrifugal tubes, and 10 cm³ of the radioactive solution of $^{137}\text{Cs}^+$ was added into each tube. The resulting suspensions were periodically mixed. After the required time intervals (0.25, 0.5, 1, 3, 5, 10 h), the liquid phase was separated from the solid phase by filtering through the ashless paper filter after preliminary centrifuging (15 min, 6000 r.p.m.). Further experiments on $^{137}\text{Cs}^+$ sorption were carried out under the same conditions taking into account the time necessary for the equilibrium to be established in the sorbent – solution system. The specific activity of $^{137}\text{Cs}^+$ in the filtrate was determined using the direct spectrometric method relying on the line with quantum energy $E_\gamma = 662$ keV with the use of a multipurpose spectrometric complex RUS-91M (SPC Doza, Russia).

In the studies of the sorption of $^{137}\text{Cs}^+$, model and natural samples of aquatic media with different salt compositions were used as the liquid phase. In particular, we used tap water from Minsk with the following characteristics: pH 7.8, total mineralization (total dissolved solids) 294 mg/dm³, total alkalinity 3.1 mg-equiv/dm³, the concentration of Ca^{2+} , Mg^{2+} , Na^+ , K^+ cations 54, 17, 8 and

4 mg/dm³, respectively. The optimal conditions of ¹³⁷Cs⁺ sorption were determined: pH of the aqueous medium, the dose of sorbent sample. The required pH value was created using 0.1 M solutions of HCl and NaOH. Before experiments, indicator amounts of ¹³⁷Cs⁺ were added into solutions, and the solutions were kept for not less than 24 h for the radiochemical equilibrium to be established.

Model solutions were prepared by dissolving a weighted portion of the corresponding nitrates Ca(NO₃)₂, NaNO₃ and KNO₃ of >99 % purity in tap water. Experiments on ¹³⁷Cs⁺ sorption from model solutions with pH 6.9 were carried out under static conditions by mixing a weighted portion of the ground IS sample (0.100 g) with 20 cm³ of the solution for 4 h.

The degree of ¹³⁷Cs⁺ sorption (*S*, %), the coefficient of ¹³⁷Cs⁺ distribution (*K_d*, dm³/kg) and purification coefficient (*K_{pur}*) were calculated using the following formulas:

$$S = \frac{A_0 - A_e}{A_0} 100 \% \quad (1)$$

$$K_d = \frac{A_0 - A_e}{A_e} \frac{V}{m} \quad (2)$$

$$K_{pur} = \frac{A_0}{A_e} \quad (3)$$

where *A₀*, *A_e* are initial and equilibrium specific activity of ¹³⁷Cs⁺, respectively, Bq/dm³; *V* is the volume of the liquid phase, dm³; *m* is sample mass, kg.

RESULTS AND DISCUSSION

Clay minerals used for the purification of natural waters from ¹³⁷Cs⁺ differ from each other in texture and sorption characteristics. It was demonstrated in [7, 12, 13] that the sorption properties of clay are directly dependent on the content of clay minerals in them and on the structural features of these minerals. It was determined in [11] that the content of illite (65.2 mass %) and specific surface (66 ± 4 m²/g) of the IS sample are 1.4 and 2.4 times higher, respectively, than those of the CSS sample.

To evaluate the technological properties of the sorption material, a necessary criterion in addition to selectivity is the rate of the sorption process. This parameter allows one to determine the effective time of ¹³⁷Cs⁺ sorption, which provides a sufficient degree of its extraction into the sorbent from the aquatic medium. The dependence of the degree of ¹³⁷Cs⁺ sorption (*S*) from tap water

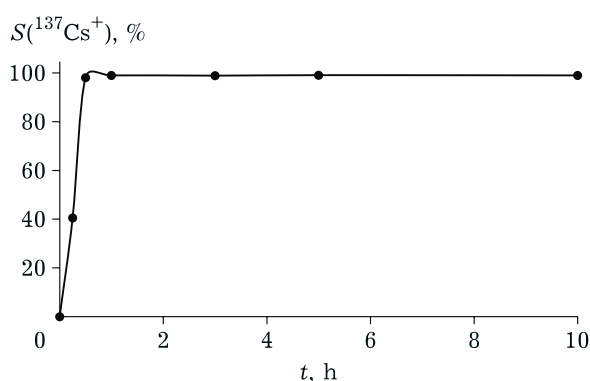


Fig. 1. Dependence of sorption degree (*S*) of ¹³⁷Cs⁺ from tap water (Minsk, pH 7.8) by the IS sample on time (*t*).

(Minsk) into the IS sample on the time of contact between the solid and liquid phases is shown in Fig. 1.

One can see that the sorption of ¹³⁷Cs⁺ proceeds most rapidly during the initial period of time. The shape of the kinetic curve shows that the degree of ¹³⁷Cs⁺ sorption increases during the first 30 min of the process. This is confirmed by a sharp upturn of the curve. Then the rate decreases rapidly, and the curve reaches its plateau corresponding to the level of the maximal sorption of ¹³⁷Cs⁺. It was determined (see Fig. 1) that the effective time of the achievement of a maximal degree of ¹³⁷Cs⁺ sorption (99 %) does not exceed 1 h, and then the equilibrium is reached, so the concentration of ¹³⁷Cs⁺ in tap water does not change.

Investigation of ¹³⁷Cs⁺ sorption from Minsk tap water by CSS and IS samples (solution volume 10 cm³, the mass of CSS or IS sample 0.100 g, sorption time 4 h) showed that the values of distribution coefficient (*K_d*) of ¹³⁷Cs⁺ for these samples are (503 ± 48) and (9700 ± 520) dm³/kg, respectively. Comparative analysis of *K_d* ¹³⁷Cs⁺ for CSS and IS samples revealed that the sorption of ¹³⁷Cs⁺ from tap water increased 19.3 times as a result of acid-water treatment of the initial CSS sample.

The value of pH in the aqueous solution is one of the essential parameters affecting *K_d* of radionuclides in the system "sorbent – aqueous solution" [14]. Surface and ground natural water differ not only in composition but also in acidity. It was demonstrated in [15, 16] that pH of surface water varies within the range 6.5–8.5, while pH of groundwater varies within the range 0 < pH < 12, but mainly it is 6.0–8.5.

Investigation of the effect of pH of aqueous solution on *K_d* ¹³⁷Cs⁺ was carried out within the pH range 5–9. The obtained dependence of *K_d* ¹³⁷Cs⁺

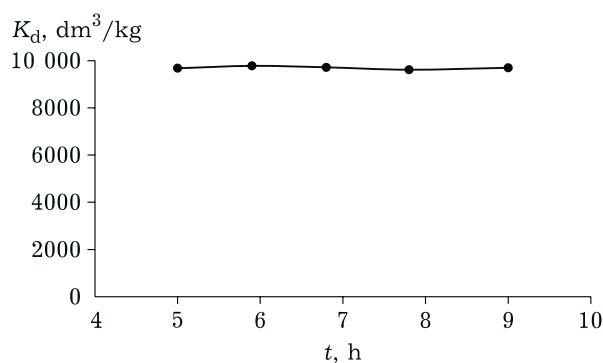


Fig. 2. Dependence of distribution coefficient (K_d) $^{137}\text{Cs}^+$ for the IS sample on pH of the aqueous solution (solution volume 10 cm^3 , IS sample mass 0.100 g, sorption time 4 h).

for IS on pH of an aqueous solution prepared using tap water is shown in Fig. 2. One can see that K_d $^{137}\text{Cs}^+$ changes insignificantly within the studied pH range and is equal to 9700 dm^3/kg on average.

The dose of sorbent, as well as pH of the aqueous solution, is an essential parameter that should be taken into account when choosing the optimal conditions for $^{137}\text{Cs}^+$ sorption because it affects the cost of purification of aquatic media. In this connection, to evaluate the efficiency of $^{137}\text{Cs}^+$ recovery from aqueous solutions by IS sample, we studied the sorption of $^{137}\text{Cs}^+$ from tap water with the variation of sorbent dose within the range from 0.5 to 10 g/dm^3 for sorption time 4 h, which is enough to reach the equilibrium in the system "sorbent – solution" (Fig. 3). It follows from the presented data that the maximal purification coefficient (K_{pur}) of tap water from $^{137}\text{Cs}^+$ is achieved for the dose of IS sample not less than 4 g/dm^3 and is equal to 98. In further experiments on the sorption of $^{137}\text{Cs}^+$ from aquatic media we used an IS dose equal to 5 g/dm^3 .

According to the data reported in [7, 17], the concentration of $^{137}\text{Cs}^+$ in natural aquatic media even with relatively high radioactivity level is substantially lower than the concentrations of Ca^{2+} , Mg^{2+} , Na^+ , K^+ ions typical for natural water. The major ions of natural waters among single- and divalent ions are Na^+ and Ca^{2+} , respectively. Potassium as a geochemical analogue of caesium has a substantial effect on the sorption of $^{137}\text{Cs}^+$ by clay minerals of the 2 : 1 structural type [7, 17]. In this connection, to evaluate the selectivity of the IS sample with respect to $^{137}\text{Cs}^+$, we studied the effect of the concentrations of competing ions Ca^{2+} , Na^+ and K^+ present in aquatic media on the extraction of $^{137}\text{Cs}^+$ from aqueous solutions.

During the sorption of $^{137}\text{Cs}^+$ from model solutions pH value was not changed. The specific ac-

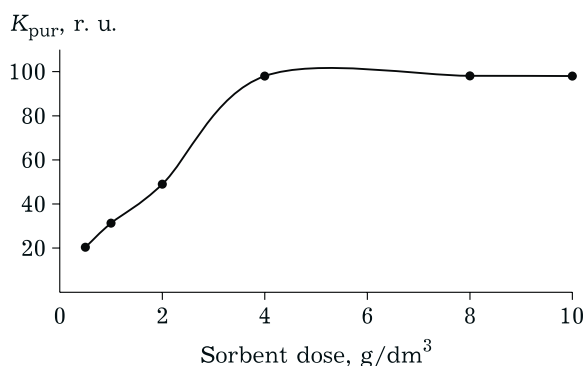


Fig. 3. Dependence of purification coefficient (K_{pur}) on IS dose (solution volume 10 cm^3 , IS sample mass 0.100 g, sorption time 4 h).

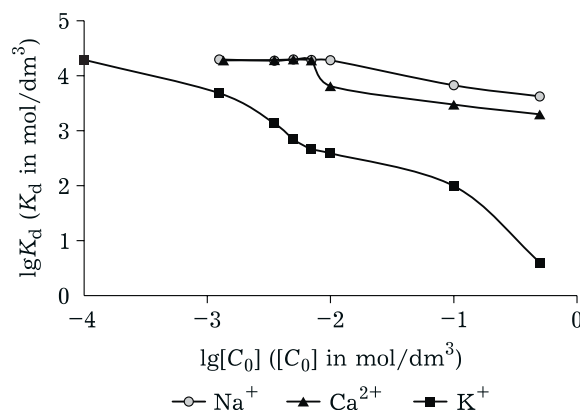


Fig. 4. Dependence of distribution coefficient (K_d) $^{137}\text{Cs}^+$ for IS sample on the concentration $[C_0]$ of Ca^{2+} , Na^+ and K^+ ions in the model solution in logarithmic coordinates.

tivity of $^{137}\text{Cs}^+$ in the initial solution was $(5.2 \pm 0.3) \cdot 10^6$ Bq/dm^3 , which is equivalent to $^{137}\text{Cs}^+$ concentration in solution $(1.2 \pm 0.1) \cdot 10^{-8}$ mol/dm^3 . The dependence of K_d $^{137}\text{Cs}^+$ for IS sample on the concentration $[C_0]$, mol/dm^3 of Ca^{2+} , Na^+ and K^+ ions in the model solution in logarithmic coordinates is shown in Fig. 4.

One can see that the selectivity of $^{137}\text{Cs}^+$ extraction by the IS sample is most substantially affected (among the studied ions) by the presence of K^+ , especially in the case of its high concentrations. The IS sample sorbs selectively $^{137}\text{Cs}^+$ from the model solution in the case if $[C_0](\text{K}^+)$ is less than 1 mmol/dm^3 , while for $[C_0](\text{K}^+) = 0.5$ mol/dm^3 the sorption of $^{137}\text{Cs}^+$ on IS is almost completely stopped. The effect of the competing ions Ca^{2+} , Na^+ and K^+ on $^{137}\text{Cs}^+$ redistribution in the system IS – natural water was studied with the samples of tap and underground water with different chemical compositions (Table. 1). Sample 1 (tap water, Minsk, the Republic of Belarus) is characterized by a low mineralization, in sample 2 (water

TABLE 1

Chemical composition of the samples of natural waters

Parameter	Sample		
	1	2	3
pH	7.8	7.4	7.1
Total dissolved solids, mg/dm ³	294	1950	6652
Total alkalinity, mg-equiv/dm ³	3.1	4.3	70.1
Ion content, mg/dm ³ :			
Ca ²⁺	54	475	121
Mg ²⁺	17	53	87
Na ⁺	8	18	1754
K ⁺	4	5	32

TABLE 2

Distribution coefficient K_d ¹³⁷Cs⁺ for the illite-containing sorbent and natural clinoptilolite

Sorbent	$K_d(^{137}\text{Cs}^+) \cdot 10^3$ for sample, dm ³ /kg		
	1	2	3
Illite-containing sorbent	19.2 ± 0.6	18.8 ± 0.7	8.5 ± 0.4
Natural clinoptilolite	8.8 ± 0.4	6.9 ± 0.3	2.1 ± 0.1

from a ground well, Vitebsk Region, the Republic of Belarus) prevailing ions are Ca²⁺, while sample 3 (water from a ground well, Borzhomi, Georgia) is characterized by the highest mineralization (total dissolved solids) among the studied samples and the higher concentration of Na⁺ ions in comparison with Ca²⁺ ions (see Table 1).

The values of distribution coefficient K_d ¹³⁷Cs⁺ for the IS sample for ¹³⁷Cs⁺ sorption from natural waters are presented in Table 2. To compare K_d values under similar conditions, sorption of ¹³⁷Cs⁺ on natural clinoptilolite from the Shivertuinskoye deposit (the Chita Region, Russia) was carried out. This mineral is presently used as a sorbent for ¹³⁷Cs⁺ [6, 18].

According to the obtained results the sorption of ¹³⁷Cs⁺ from natural water on IS proceeds 2–4 times more efficiently in comparison with natural clinoptilolite. A comparative analysis of the data (see Fig. 3 and Tables 1, 2) shows that they do not contradict each other and confirm the fact that Ca²⁺ and Na⁺ ions do not have a significant effect on the sorption of ¹³⁷Cs⁺ from natural water by the IS sample.

Thus, IS obtained from CSS of JSC “Belaruskali” is an efficient sorbent for the extraction of ¹³⁷Cs⁺ from natural water. In addition, a possible direction of its use may be rehabilitation of territories contaminated with ¹³⁷Cs, to reduce the migration of ¹³⁷Cs⁺ from the soil into agricultural plants.

CONCLUSION

As a result of the studies, it was demonstrated that CSS is a promising material for obtaining IS, which may be used for efficient purification of natural water from ¹³⁷Cs⁺. It was determined that the time within which the equilibrium is established in the system “sorbent – solution” during the sorption of ¹³⁷Cs⁺ from tap water (Minsk) by the IS sample is not more than 1 h. It was determined that IS exhibits high selectivity was ¹³⁷Cs⁺ during sorption from natural water, and K⁺ ion is the major competitor. For K⁺ concentration in the aquatic medium more than 0.5 mol/dm³ the sorption of ¹³⁷Cs⁺ on IS stops almost completely. A simple method to modify CSS was elaborated, including its enrichment with illite and a decrease in the content of water-soluble potassium. This allowed a 19.3 times increase in the sorption capacity of the material for ¹³⁷Cs⁺ and to obtain IS with the efficiency of ¹³⁷Cs⁺ extraction from natural water 2–4 times higher than that of clinoptilolite of the Shivertuinskoye deposit (the Chita Region, Russia), which is used at present as a sorbent for extraction of ¹³⁷Cs⁺. It was determined that the optimal conditions for the sorption of ¹³⁷Cs⁺ from natural water are: pH 5–9 and IS dose not less than 4 g/dm³ with sorption time 4 h.

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