

# CLAY-SALT SLIMES OF THE «BELARUSKALI» - PROSPECTIVE SORBENTS FOR MANAGEMENT OF THE LIQUID RADIOACTIVE WASTES AND DECONTAMINATION OF AQUEOUS SOLUTIONS

## ПЕРСПЕКТИВНЫЕ СОРБЕНТЫ ПРИ ОБРАЩЕНИИ С ЖИДКИМИ РАДИОАКТИВНЫМИ ОТХОДАМИ И ДЕЗАКТИВАЦИИ ВОДНЫХ РАСТВОРОВ ГЛИНИСТО-СОЛЕВЫХ ШЛАМОВ ОАО «БЕЛАРУСЬКАЛИЙ»

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Clay-salt slimes, production wastes from the JSC “Belaruskali”, have been tested as a low-cost, eco-friendly potential sorbent for the removal of radionuclides from aqueous solutions, and may be a component of the cement filling of drums used in the storage of radioactive wastes. The efficiency of sorptive removal of caesium (I) -137, strontium (II) -90, europium (III) -152, and americium (IV) -241 was examined with respect to the time of phase equilibration, pH, sorbent dosage, and the presence of salts and complexing agents. Irradiation stability of the material was also studied. It was found that uptake of the radionuclides is almost complete. A procedure for the removal of technetium-99 has been also proposed. Experimental results obtained within the presented work confirm our expectations.

Глинисто-солевые шламы, относящиеся к отходам производства ОАО «Беларуськалий», были испытаны как недорогой, экологически чистый потенциальный сорбент для удаления радионуклидов из водных растворов и могут быть одним из компонентов цементного наполнителя контейнеров, используемых для хранения радиоактивных отходов. Эффективность сорбционного удаления цезия (I) -137, стронция (II) -90, европия (III) -152 и америция (IV) -241 была исследована в отношении времени фазового уравнивания, pH, дозы сорбента, и присутствием солей и комплексообразующих агентов. Также было изучено облучение материала. Было установлено, что поглощение радионуклидов практически завершено. Предложена также технология удаления технеция-99 из водного раствора. Экспериментальные результаты, полученные в рамках представленной работы, подтверждают наши предположения по данному исследованию.

*Keywords:* radioecology, waste management, radioactively contaminated water, clay-salt slimes, radionuclides, sorbents.

*Ключевые слова:* радиоэкология, утилизация отходов, глинисто-солевые шламы, радиоактивно загрязненная вода, радионуклиды, сорбенты.

In Poland, low- and medium-level short-lived radioactive wastes (LLRW and MLRW, respectively) are conditioned in the near-surface National Radioactive Waste Repository (NRWR in Rozan) operated by the Radioactive Waste Management Plant. In 2016 NRWR collected about fifty cubic meters of wastes, with about 40% being liquid. Also collected, were about 24,000 smoke detectors and 1,300 decommissioned sealed radioactive sources [1]. In Belarus, in turn, in the near future LLRW and MLRW will be stored in an area near the nuclear power plant (at present, under construction) before being removed to the repository. This will be constructed by 2028 [2].

Great problem related to LLRW and MLRW management is the possibility of leaching of radioactive elements by different aqueous streams present in the repository, which may result in dangerous health effects in both humans and animals within the local environment. To prevent the abovementioned release of hazardous radioactive elements from storage locations into the environment, a well-known multi-barrier system was put into effect. Typically, the main retardation barrier for the release of radionuclides is the immobilization of radioactive wastes in different mixtures of cement and sorbents [3].

The presently realized Polish-Belarusian joint project is aimed at determining sorption characteristics of clay-salt slimes (CSS), a waste product created during the fabrication of potash fertilizers in Belaruskali (Soligorsk, Belarus).

Experiments were performed with clay-salt slimes (CSS-1 and CSS-3) samples withdrawn from the clay-salt slime repositories No. 1 and No. 3, respectively. The mineralogical composition of this material is iolite – 51.1 %; dolomite – 19.6 %; potassium feldspar – 14.0 %; quartz – 7.4 %, and other minor minerals – 7.1 %. The raw materials were converted

into the form of sorbent according to the procedure described elsewhere [Braun, to be published]. By this procedure we have obtained two different fractions, assigned as A and B materials.

The specific surface area of the CSS-3B material was determined by low-temperature nitrogen adsorption and utilising Brunauer–Emmett–Teller theory (BET) to be about 66 m<sup>2</sup>/g, and is twice greater than that of the CSS-3A (28 m<sup>2</sup>/g) [4].

Sorption experiments were performed in the batch experiments by changing only one parameter in any series of experiments. Such methodology allows for identifying the optimum experimental conditions for sorption. List of the parameters, ranges of the studied values and the optimum sorption conditions are listed in Table 1.

Table 1 – Controllable factors and their values

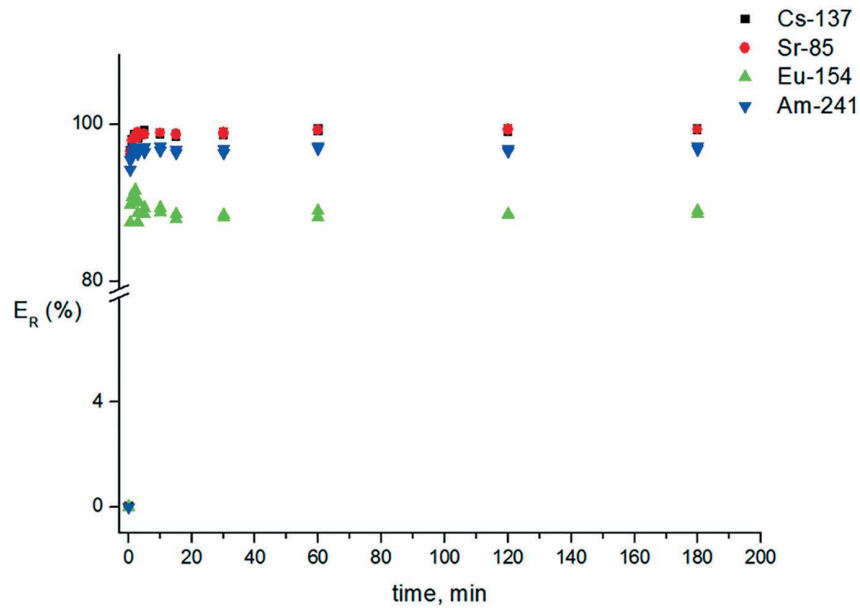
No	Description	Studied values	Optimum value	Units
1	Initial metal concentration	nca *		mol dm <sup>-3</sup>
2	Initial salt concentration	ca. 10 <sup>-2</sup> M NaNO <sub>3</sub>		M
3	Temperature	Room temperature		°C
4	Time of contacting phases	0 – 180	60	min
5	Mass of sorbent used	from 1 to 20	5	g dm <sup>-3</sup>
6	pH	2–10	5.5	
7	Presence of salts	Na <sup>+</sup> , K <sup>+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup> chlorides: 583, 32, 129 and 182		mg dm <sup>-3</sup>
8	Presence of chelating agents (no/yes)	oxalic and citric acids and Na-EDTA: 2·10 <sup>-3</sup> , each		M
9	Irradiation dose	250	no	kGy

**Note:** \* No-carrier added (nca) radioisotope: extremely small amount of the radioactive isotope (usually in the range of 10<sup>-6</sup>–10<sup>-7</sup> mol) which is not stabilized with weight amount of its stable isotopes [1].

Efficiency of the solution purification, ( $E_r$ , %), was calculated with the formula:

$$E_r = \frac{(A_0 - A_{\epsilon q})}{A_0} \cdot 100\% \quad (1)$$

The representative results of removal efficiency ( $E_r$ ) vs. time and mass of the sorbent used are given in the following Figure.



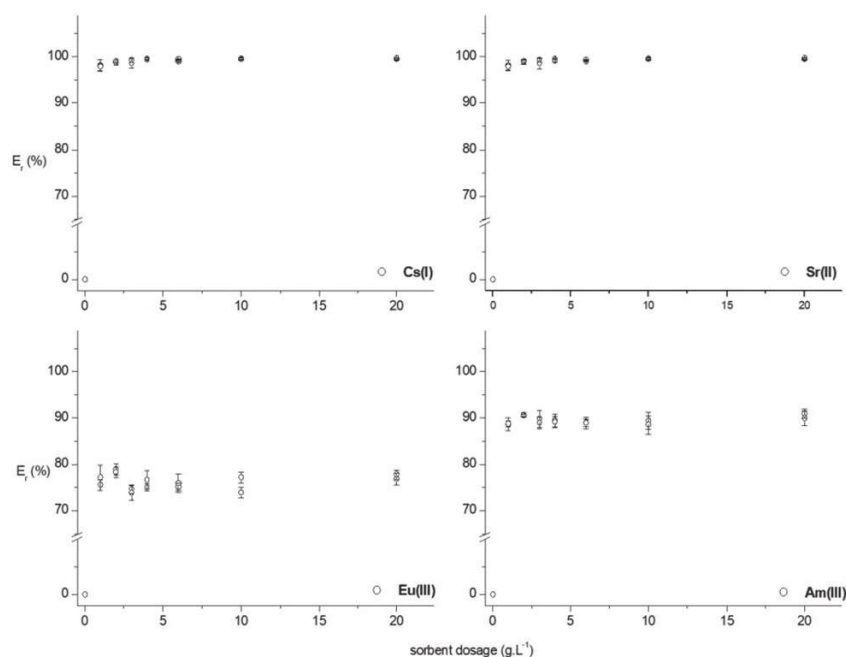


Figure – Effect of contacting time and mass of the sorbent used on sorption of the radionuclides onto CSS-3A

Summary data for caesium (I), strontium (II), europium (III), americium (IV) and technetium (VII) sorption obtained in the presented project show that they are of the same range as these of another natural sorbents. Main results are presented in Table 2.

Table 2 – Main results obtained for the CSS-1 and CSS-3 sorbents

	CSS-1A	CSS-1B	CSS-3A	CSS-3B
Proposed time to reach equilibrium (min)	10 min	10 min	10 min	10 min
Proposed sorbent dosage (g·dm <sup>3</sup> )	2	2	2	5
Optimum pH	Does not change significantly within the pH range 2–12		Does not change significantly within the pH range 2–12	
Zeta potential* (pH=4); mV	–20.1	–22.5	–25.5	–24.4
Main components [4]:	iolite	44.2 %	61.2 %	48.2 %
	dolomite	23.0 %	0	17.0 %
Radiation stability	very high	very high	very high	very high
E <sub>r</sub> (%) of the initial radionuclide content in the solution**	Cs (I)	99.0±0.3	98.6±0.2	98.8±0.4
	Sr (II)	99.0±0.4	98.4±0.3	98.8±0.4
	Eu (III)	91.1±0.6	87.0±0.5	89.1±1.0
	Am (IV)	97.4±0.2	92.3±0.2	96.8±0.4
	Tc (IV) / SnCl <sub>4</sub>	not studied	not studied	99.6±0.3

Notes: \* – Electric charge of the surface; \*\* – For the conditions listed in Table 1 as optimum.

So, it may be stated, that are industrial wastes in the activity of the “Belaruskali”, may be accounted as a perspective sorbent for treatment of aqueous solutions containing the radioactive metals.

Conflict of interest. The authors state that there is no conflict of interest in presented work.

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