
**MATERIALS OF POWER ENGINEERING
AND RADIATION-RESISTANT MATERIALS**

Combined Matrixes for Solidification of Organic Radioactive Liquid Wastes Containing Cs-137 and Sr-90

A. V. Nikitin*, Yu. V. Kondakova**, and A. B. Sazonov***

Mendeleev University of Chemical Technology of Russia, Moscow, 125047 Russia

*e-mail: nikitin_89@mail.ru

**e-mail: yuliochik@mail.ru

***e-mail: absazonov@mail.ru

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Abstract—Combined cement matrixes are proposed for petrification of organic liquid radioactive liquid wastes (spent tributyl phosphate in hydrocarbon solvent, process oil) containing radionuclides ^{137}Cs and ^{90}Sr . The high level of filling of the matrixes with waste is achieved by premixing thermally expanded graphite with the latter. To confine cesium firmly, bentonite clay additions with a montmorillonite content not less than 65 vol % should be included in the compounds. It is demonstrated that the desired content of extracting agent in the compound is 25 vol % and that of oil is 20 vol %. The minimum time of aging of the compounds before transportation for long-term storage or burial should be not less than 42 days from the moment of cement mixing. The moisture-resistant enamel coating of the surface of compounds does not prevent substantial diffusion of ^{137}Cs . However, it slows down the water absorption by the cement, thus postponing the beginning of transition ^{137}Cs and other radionuclides to the liquid phase. The strength of the compounds obtained in the paper complies with the standardized values (GOST R 51883-2002). The average leaching rate of ^{137}Cs is not more than 1 mg/(cm² day) and that of $^{90}\text{Sr} + ^{90}\text{Y}$ is not more than 0.1 mg/(cm² day). The leaching kinetics of cesium radionuclides from the compound has a diffusive character. The leaching kinetics of strontium and yttrium radionuclides from the compound has a sorption-desorption character. The leaching rates of radionuclides of elements of groups I, II, and III form the following series: $R(^{137}\text{Cs}) > R(^{90}\text{Sr}) \gg R(^{90}\text{Y})$.

Keywords: radioactive oils, cesium, strontium, cement compounds, thermally expanded graphite, mechanical strength, leaching rate

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INTRODUCTION

Organic radioactive liquid wastes (RLW) (organic RLW—ORLW) form a specific group of radioactive wastes. The feature of ORLW is that they cannot be efficiently or in some cases even subjected to conventional reprocessing methods used for water systems.

Organic wastes are represented mostly by used extracting agents, their solvents, and process oils contaminated with uranium and plutonium isotopes, fission products, tritium, and other radionuclides. As a rule, this type of ORLW represents the mixture of various kinds of oils containing hydrocarbons of lighter fractions, water, and solid particles. These used oils are beyond decontamination and recirculation. Their conversion by oxidation is ineffective because of formation of the coke fraction. That is why long-term storage in metal storage tanks is at present moment the only method to handle radioactive oils.

Extraction is the main industrial method of spent nuclear fuel (SNF) reprocessing: selective recovery of metal ions from aqueous solutions by certain organic

compounds, for example, by tributyl phosphate (TBP) hydrocarbon solvent in its mixture with hydrocarbon solvent. The spent extracting agent containing TBP, solvent, and their products of radiation, thermal, and chemical decomposition belongs to ORLW of moderate activity level. As well as the spent oils, it is contaminated for the most part with uranium, plutonium, and fission products. Unfortunately, at radiochemical plants, not much attention is paid to deactivation of such type waste. The controlled storage in the liquid state directly on site is used as a temporary response to the problem.

According to the national health and safety regulations, all liquid radioactive wastes should be subjected to solidification before transportation/shipment for long-term storage or burial. During solidification of organic RLW, it is possible to use practically any solid matrixes synthesized by the cold procedure. Portland cement is the most available material possessing such properties. However, the simple cementation of ORLW has a major drawback: only a small quantity of waste (up to 10–12 vol %) can be included in the

cement under the condition that its monolithic form will be retained. It is possible to achieve a high level of inclusion in a cement compound with preliminary absorption of ORLW by porous carbon-based materials: for example, by thermally expanded graphite (TEG). Thus, a cohesive product able to form compounds with cementing materials [1] is obtained as a result of petroleum oil absorption by TEG.

Low leaching rates of radionuclides and high mechanical strength are basic requirements applicable to the cement compounds containing radioactive wastes.

In the present study, the following problems were formulated: to determine the retentive capacity of compounds of the general composition "OLRW–TEG–cement–bentonite" in relation to ^{137}Cs and ^{90}Sr (long-lived fission products) and the mechanical characteristics of these compounds; to recommend the formula of a compound that complies with the standardized document (GOST R 51883-2002).

EXPERIMENTAL

To obtain TEG, the chromium sulfate synthetic method was used. This method is economical and can be easily implemented in industrial conditions [2]. Foundry graphite GF-1 (GOST 5279-74) was used as the raw material. Synthesis included the following stages: graphite surface oxidation by a saturated aqueous solution of crude chromic anhydride, chemical intercalation of 94% sulfuric acid (reagent grade), hydrolysis of the obtained graphite bisulfate, leaching of graphite oxide by distilled water, drying at 120°C , and expansion by microwave heating. The synthesized TEG bulk density was 10 g/L. The characteristics of graphite obtained by such method are presented in [3].

The radioactive solutions simulating two main types of ORLW (extracting agent and oil) were prepared in the following manner. Aqueous solutions of $^{137}\text{CsNO}_3$ or $^{90}\text{SrCl}_2$ (radionuclides without a carrying agent) were emulsified with a nonionized surfactant triton X-100 (Sigma-Aldrich) in 30% TBP solution (>99%, Merck) in *n*-dodecane (pure grade). To simulate partial decomposition of the extracting agent when subjected to hydrogen nitrate and ionizing radiation [4], in some cases, dibutylphthalate acid (DBPA, 97%, Acros) in the amount of 10–30 vol % of TBP was added. In a similar way, the imitator of the spent radioactive oil was prepared: salt solutions of $^{137}\text{CsNO}_3$ and $^{90}\text{SrCl}_2$ were emulsified in vacuum oil VO-1 with triton X-100.

The obtained solutions were absorbed by the powder TEG; the latter was taken in amount of 1 g per 20 g of the imitator ORLW. After 3 days of curing, the formed solid material was mixed with a cement dough. Portland cement M-500 was used for preparation of cement compounds. The water–cement ratio (WC) against the advice [5] was varied in the range from 0.3

to 0.4, which was sufficient for a complete hydration of cement minerals, but in this case, layering of the included materials and cement dough was still not observed during the setting time. To improve the retentive capacity in relation to radionuclides, bentonite clays in the amount of 3–9% of dry cement mass was added to some compounds. Two samples of different origin with a significantly different content of montmorillonite (the main source material of bentonite clays) were used for comparison: B4 (Dashukovka region of the Cherkassy deposit, Ukraine, montmorillonite content of 65–85% [6]) and BT (Tagansk deposit, Kazakstan, montmorillonite content >90% [7]). To determine whether the moisture-resistant coating of cement stone produces additional resistance to diffusion of radionuclides, several cement blocks were coated with enamel with chlorinated rubber base (Dufa) at the concrete strength development stage. Cement compounds were aged in the forms during 28 (in some cases 42) days for strength development. The solid cement blocks were in the form of monolithic cylinders of height equal to the diameter (3.2 cm); the geometrical area of the blocks was about 48 cm^2 and mass was around 30 g. The range of the initial activities of the blocks was 0.03–8 MBq from ^{137}Cs and 0.1–0.8 MBq from $^{90}\text{Sr} + ^{90}\text{Y}$ in equilibrium. Radionuclides were not added in the samples prepared for structural tests.

The content of the obtained compounds is presented in Table 1. Blocks of batches of Cs and Sr were prepared for experiments on leaching of the corresponding radionuclides. Blocks of batches P1–P5 were subjected to a shatter test. Here, the blocks of batch P1 were not subjected to any preliminary stresses. The blocks of batch P2 were tested by 30 freezing cycles down to -18°C and defrosting up to $+22^\circ\text{C}$ (defrosting was performed with complete immersion of the blocks in tap water. Duration of stay of the blocks of batch P3 in water at 22°C (for shatter tests) was 90 days. Duration of stay of the blocks of batch P4 in water at same temperature was increased to 180 days. Certain blocks of batch P5 were subjected to irradiation by γ rays of ^{60}Co with dose rate of 0.08 Gy/s. During irradiation, these blocks received a dose a bit more 250 kGy, that is, one-fourth of the dose specified by GOST. However, according to the estimation, for the spent extracting agent with specific activity of 10^7 Bq/kg , this dose will be accumulated in 1000 years, even though all this activity is due to long-lived α -emitting radionuclides (which is unlikely). Another part of the blocks of batch P5 was exposed to γ radiation as well and received the GOST specified dose (1 MGy). The compression strength of samples was determined with a hydraulic press; the compression strength measurement error was $\sim 0.05\text{--}0.1\text{ MPa}$.

The samples of compounds that contained radionuclides were introduced in closed fishbowls with 200 mL of distilled water. Leaching of ^{137}Cs and $^{90}\text{Sr} + ^{90}\text{Y}$ was

Table 1. Composition of cement compounds and character of test carried out

No.	Imitator ORLW	Composition of imitator	WC	Additives, vol %	Batch
1*	Exraction agent	8.5	0.3		Cs, Sr
2*		11	0.3		Cs, Sr
3*		14	0.3		Cs, Sr, P1, P3, P5**
4*		17	0.3		Cs, Sr
5*		20	0.3		Cs, Sr, P1, P2, P3, P5**
6*		20	0.3		3% B4 Cs, P2
7*		20	0.3		6% B4 Cs, P2
8*		20	0.3		9% B4 Cs, Sr, P2
9		20	0.3		5% B4 Cs, P1***
10		20	0.3		5% BT Cs, P1***
11		21	0.3		Cs***
12		25	0.3		P1, P3, P5**
13		25	0.3		10% DBPA Cs
14		25	0.3		20% DBPA Cs
15		25	0.3		30% DBPA Cs
16		30	0.3		P1, P3, P5**
17		35	0.3		P1, P3, P5**
18		35	0.3		6% B4 P1, P3, P5**
19		15	0.35		P1
20		20	0.35		P1
21		25	0.35		P1
22		15	0.4		Cs, Sr, P1, P2, P3, P4, P5
23		20	0.4		Cs, Sr, P1, P2, P3, P4, P5
24		25	0.4		Cs, Sr, P1, P2, P3, P4, P5
25		15	0.4		5% BT Cs, P1, P2, P3, P5
26		20	0.4		5% BT Cs, P1, P2, P3, P5
27		25	0.4		5% BT Cs, P1, P2, P3, P5
28		25	0.4		3% BT P1
29		25	0.4		6% BT P1
30	Oil	15	0.35		Cs, Sr, P1, P2, P3, P4, P5
31		20	0.35		Cs, Sr, P1, P2, P3, P4, P5
32		25	0.35		Cs, Sr, P1, P2, P3, P4, P5
33		15	0.35		5% BT Cs, P1, P2, P3, P5
34		20	0.35		5% BT Cs, P1, P2, P3, P5
35		25	0.35		5% BT Cs, P1, P2, P3, P5
36		20	0.35		3% BT P1
37		20	0.35		6% BT P1
38		20	0.35		5% B4 Cs, P1***
39		20	0.35		5% BT Cs, P1***
40		15	0.4		5% B4 P1
41		20	0.4		5% B4 P1
42		25	0.4		5% B4 P1

* Blocks were coated with chlorinated rubber enamel; concrete strength development was prolonged to 42 days.

** Absorbed dose was about 250 kGy.

*** Concrete strength development was prolonged to 42 days.

performed at the room temperature (22°C) in static conditions.

Measurements of ^{137}Cs activity were performed on a MKS-01A scintillation γ spectrometer (RDC Amplituda) with a Na(Tl) detector for 1 h for each sample. The leaching water of each sample was decanted in a separate Marinelli beaker, and after the measurement was completed, it was drained into the RLW receptacle. Then the compound was flooded with fresh water. The statistical error of measurement of ^{137}Cs activity was not more than 10%. Water samples with volume of 20 mL from each specimen were sampled and 20 mL of distilled water was added to the leaching water to measure the activity of $^{90}\text{Sr} + ^{90}\text{Y}$. Activity measurement was performed using Cherenkov radiation on an 300-SL liquid scintillation spectrometer (Hidex) for 1 h. The statistical error of the activity measurement was not more than 5%.

The specific activity of the initial imitators of ORLW was determined in a similar way.

RESULTS AND DISCUSSION

Strength Tests

The compressive loads tests of the blocks without preliminary exposures (ultimate compression strength P_1) and also blocks preliminarily subjected to 30 freezing–defrosting cycles (P_2), stay in water for 90 days (P_3) and 180 days (P_4), and exposure to γ radiation (P_5) are presented in Table 2.

The results of structural tests demonstrate that, for compounds with WC = 0.3, 0.35, and 0.4 containing the extracting agent in the amount of 15–25 vol % and not subjected to any preliminary exposures, the compression strength is not less than the specified norms ($P_1 \geq 4.9$ MPa). At the same time, no positive results were obtained for the blocks containing the extracting agent in the amount of 30–35 vol %.

Comparing the strength characteristics of compounds with WC = 0.3 (samples 3, 5, 12, 16–18), one can note a general tendency of the strength improvement for the samples subjected to irradiation, freezing, or long stay in water in comparison with the samples that were not subjected to such exposures. However, the compression strength of samples with WC = 0.4 (samples 22–27) after thermal, immersion, and radiation exposures decreases in comparison with the samples with control compounds, though staying within the specified norms.

The blocks that stayed in water for 180 days are an exception: here, in some cases, an increase in strength is observed. Upon compression of such samples (25–27) on a hydraulic press, it was observed that plastic deformation precedes their shattering.

For compounds containing a mineral oil as ORLW, the strength of some samples is higher than the acceptable limit even after temperature and other exposures

(excluding compound 32 containing 25 vol % oil). By and large, the strength of compounds with the extracting agent is higher than those containing the same quantity of the oil. This is explained by the capacity of oil to be adsorbed more securely on solid surfaces, making the coating impervious to water. Hydration of minerals of cement in such conditions at first slows down and then eventually stops, resulting in failure of concrete strength development. Thus, the results demonstrate that the desired content of the extracting agent in a cement compound is up to 25 vol %, and that of oil is up to 20 vol %: a lower content ORLW is not worthwhile owing to the considerable increase in solidified waste, and a higher content is not appropriate because of the decrease in strength below the specified limit.

The impact of bentonite clays on the strength of compounds can be characterized as a negative one (nevertheless, as will be seen in what follows, selective sorption properties of bentonite in relation to cesium make its inclusion in the compound worthwhile. The property of bentonite to bind large quantities of water causes a deficit of free water available for hydration of clinker minerals. In this case, the more hydration is hindered, the less quantity of bentonite will produce the specified effect. Nevertheless, water will bind to clinker minerals much more strongly than to bentonite. There is reason to believe that the given water deficit is temporary and an increase in the holding period of cement blocks for concrete strength development will make it possible to obtain samples complying with GOST standards. From these considerations, the strength development for compounds 9, 10, 38, and 39 was prolonged to 42 days. As follows from the results (Table 2), the given assumption was confirmed: the strength of the blocks that had not been subjected to preliminary exposures proved to be more than two times higher than the minimum permissible value. In the given case, the composition of the bentonite clay was irrelevant. Taking into consideration that a decrease in strength of the studied compounds is not observed with any kind of impacts (thermal, immersion, radiation), one can conclude that the increase in the curing time by half instead of the usually accepted 28 days will guarantee sufficient mechanical strength after such impacts as well.

Leaching of ^{137}Cs

The level of leaching of radionuclides was determined by the formula

$$S = \frac{A_{\Sigma}}{a_0 V}, \quad (1)$$

where A_{Σ} is the total activity that passed into the water from the moment of the first sampling, Bq; a_0 is the initial volume activity of the imitator ORLW, Bq/mL; and V is the volume of the imitator ORLW in the block, mL.

Table 2. Compression strength limits of cement compounds, MPa

Compound	Compression strength limits of cement compounds subjected to the following factors, MPa				
	without exposure	30 cycles of freezing–defrosting	water 90 days	water 180 days	γ radiation
	P_1	P_2	P_3	P_4	P_5
3	16.39		9.45		20.06
5	6.75	13.40	6.94		8.68
6		6.27			
7		5.01			
8		6.75			
9	10.81				
10	10.83				
12	4.82		5.79		7.71
16	2.89		3.47		5.79
17	**		2.51		3.28
18	**		1.93		1.74
19	14.63				
20	11.46				
21	7.31				
22	14.63	13.65	12.19	16.83	9.03
23	11.46	10.24	12.92	15.12	9.27
24	8.53	9.01	7.56	19.98	10.49
25	6.83	7.07	15.86		11.71
26	6.58	6.09	12.92		11.47
27	4.88	5.85	4.88		6.83
28	7.13				
29	6.09				
30	12.19	9.01	7.56	12.44	9.51
31	8.29	5.36	5.36	6.34	7.07
32	4.87	3.41	4.63	5.12	4.39
33	7.07	4.14	6.59		11.95
34	5.12	3.09	3.90		3.66
35	2.68	3.42	3.17		2.68
36	4.14				
37	3.66				
38	11.83				
39	11.04				
40	4.14				
41	5.85				
42	5.36				

* Numbering corresponds to Table 1.

** Blocks were destroyed immediately after extraction from the form.

The kinetic curves of leaching (dependences of S on time t) of ^{137}Cs from blocks 1–5 containing the extracting agent and coated with a chlorinated rubber enamel are presented in Fig. 1. The moment of first appearance of ^{137}Cs in the water at the detection level t_1 (1 day) is (henceforward) the time reference point.

For compounds 1–7, this moment occurs on days 9–10 of the contact with the water, while the egress of cesium from all other compounds is already observed during the first day of leaching. The kinetic curve of leaching of ^{137}Cs from sample 11 not coated with the enamel is presented in the same figure. Comparing it

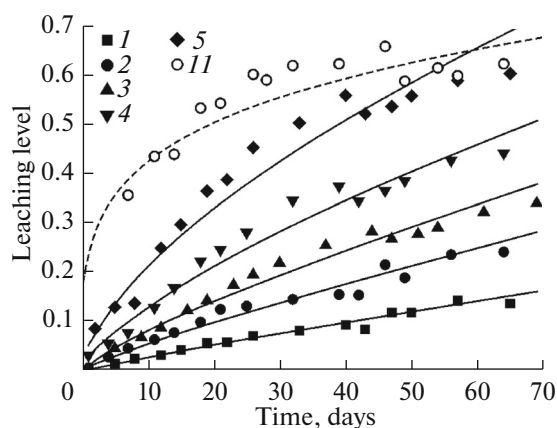


Fig. 1. Leaching curves of ^{137}Cs from compounds 1–5 covered with enamel and compound 11.

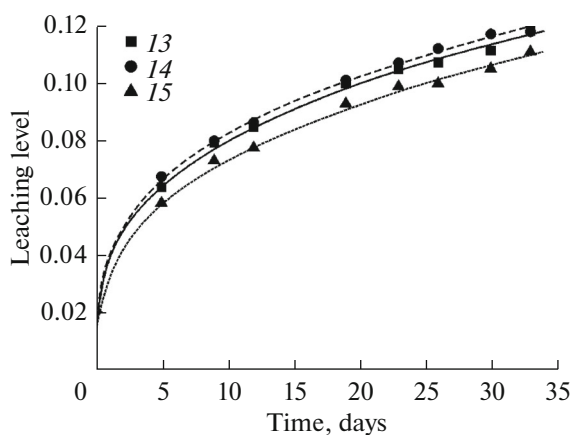


Fig. 2. Leaching curves of ^{137}Cs from DBPA-containing compounds 13–15.

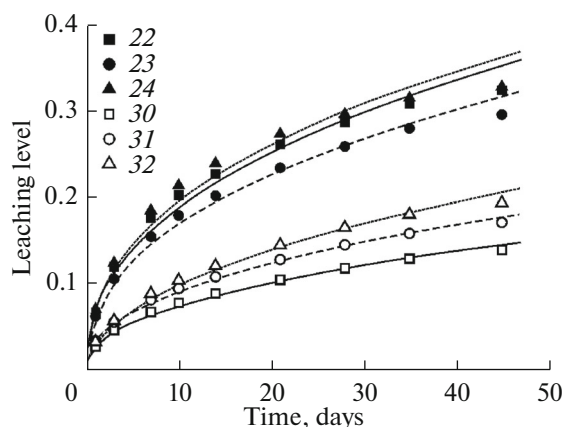


Fig. 3. Leaching curves of ^{137}Cs from extractant-containing compounds 22–24 and oil-containing compounds 30–32.

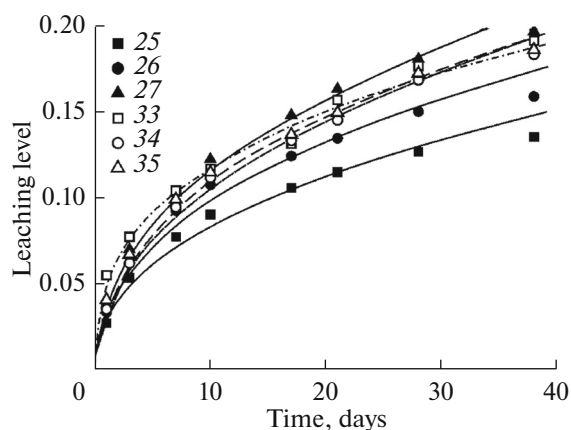


Fig. 4. Leaching curves of ^{137}Cs from compounds 25–27 containing extracting agent and compounds 33–35 containing oil (all compounds contain bentonite).

with the curve for sample 5 containing practically the same amount of extracting agent, one can notice that cesium leaching rates are pretty close in both cases as well. The given results indicate that cesium leaching from the compound occurs only owing to water absorption by it and that the enamel coating prevents its penetration into the cement stone; the coating itself is not a barrier to cesium diffusion.

When comparing cesium leaching rates from blocks 22–24 and 30–32 (Fig. 2), one can observe a monotonic dependence of the speed of the process on the content of ORLW: it grows with filling of the compound with organic matter. Here, radionuclide leaching from the compound with oil is slower than that from the compound with the extracting agent evidently because of the different viscosity of these liquids (the viscosity of oil is higher by one to two orders of magnitude), which depends inversely on the diffusion coefficient. Increasing the water–cement ratio from 0.3 to 0.4 (Figs. 1 and 2) will improve fixation of

cesium in the compounds containing the extracting agent. Nevertheless, as will be seen in what follows, the general result remains inadequate in this case as well.

The presence of the spent extracting agent DBPA in the imitator (Fig. 3) affects (positively) the cesium fixation in the compound apparently because of formation of this metal salt, which has lower diffusion mobility than the hydrated ion. Here, the samples with 10, 20, and 30% DBPA in TBP demonstrate close cesium leaching rates with their tendency to decrease upon increasing the ratio of additive. It should be noted that concentrations of the spent extracting agent in DBPA are incommensurably smaller [4]. With this consideration in mind, one can deduce that in actual systems formation DBPA will not result in an increase in cesium leaching.

As anticipated, the presence of bentonite clays has the greatest effect on retention of cesium in the composition of the compound. However, for compounds 25–27 and 33–35, a decrease in the leaching rate is observed

only when filling the matrix with the extracting agent instead of oil (Fig. 4). This difference is due to the lower diffusion mobility of cesium in the oil than in the extracting agent. Consequently, diffusion of cesium to particles of montmorillonite in the first case takes more time.

Thus, the cement compounds studied in this work after 28 days of curing even approximately cannot be considered as equilibrium systems. Besides hydration of clinker minerals and the strength development stage, processes of migration of the radionuclide from one phase to another one take place there. This idea is confirmed also by the results presented in Fig. 5. Increasing the content of bentonite clay B4 in compounds 6 and 7 from 3 to 6% of dry cement weight results in a five- to sevenfold decrease in the leaching rate. Moreover, cesium leaching from compound 8 containing 9% B4 was not observed over a period of 50 days at all. The curing of these samples before the tests lasted 50% longer, i.e., 42 days. Hence, sorption of cesium is a rather lengthy process. Its rate spikes with an increase in the bentonite content. However, as noted above, the strength of the compound can become inadequate with too high a bentonite content.

The difference in sorbing properties of bentonite clays B4 and B5 is clearly seen when comparing the results obtained with samples 9, 10 and 38, 39. Bentonite from the Tagansk deposit containing a large quantity of montmorillonite (the most active cesium sorbent) decreases the leaching rate better at the matched content of the clay in the compound. This difference is the most striking in the case of the compounds with the extracting agent. Low mobility of cesium in the oil is the reason.

Thus, for full implementation of the sorbing properties of bentonite clays in relation to cesium and improvement of mechanical strength of the matrix, one should increase the curing time of the real cement compounds with ORLW before transportation for long-term storage or burial.

The results of approximation of kinetic curves by the power function [3]

$$S(t) = \text{const } t^P \quad (2)$$

are presented in Figs. 1–5 by solid lines. The exponent P in most cases is far from 0.5, suggesting a complicated character of diffusion of ^{137}Cs in the matrix. Thus, for the compounds not coated with an enamel and not containing bentonite, the value of P is in the range of 0.35–0.45. For compounds containing bentonite, it is much less—0.2–0.3. Here, one can see that the last experimental points are situated below the approximating curve. This implies that diffusion inside the compound is the limiting stage of the process, and the effective diffusion coefficient decreases gradually owing to additional hydration of cement minerals upon contact with water and continuing sorption of cesium by montmorillonite.

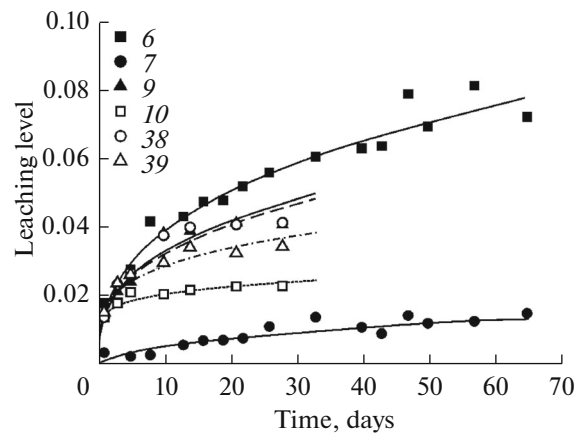


Fig. 5. Leaching curves of ^{137}Cs from compounds 6–10 containing extracting agent and compounds 38–39 containing oil (all compounds contain bentonite; curing time was increased to 42 days).

For compounds 1–5 coated with the chlorinated rubber enamel, the exponent P grows from 0.6 to 1 with decrease in the content ORLW in the compound. In this case, the transfer of the radionuclide from the solid state to the liquid one is limited by the permeability of the coating and the active force of the process (the concentrated pressure) stays practically constant until the leaching level becomes significant.

According to GOST R 51883-2002, the value that determines the radionuclide fixation reliability in the composition of the compound is the leaching rate R , which can be obtained via the leaching level as

$$R = S \frac{m}{Ft}, \quad (3)$$

where m is the weight of the block and F is the area of the open geometrical surface.

As calculated according to Eq. (3), the average leaching rates ^{137}Cs corresponding to $t = 28$ days are presented in Table 3. One can see that the leaching rate not exceeding the standard of 1 mg/(cm² day) by GOST is observed only for the compounds containing bentonite in an amount not less than 5% (samples 7–10, 38, 39).

Leaching of ^{90}Sr and ^{90}Y

The leaching level of the sum of radionuclides ^{90}Sr and ^{90}Y was calculated by formula (1). The leaching kinetic curves are presented in Figs. 6 and 7. The moment of first contact of the compound with water is the time reference point. For compounds 1–6 and 8 (Fig. 6), a multitude of irregular jumps on the dependence of the leaching level on time was observed during the whole experiment. Most likely, they were caused by the presence of suspended particles, which

Table 3. Average leaching rate of ^{137}Cs after 28 days

Compound*	R , mg/(cm ² day)	Compound*	R , mg/(cm ² day)
1	1.60	22	8.85
2	2.80	23	9.81
3	6.26	24	10.1
4	4.91	25	4.40
5	10.2	26	5.20
6	1.34	27	6.25
7	0.21	30	4.02
8	< 0.05**	31	4.95
9	0.92	32	5.63
10	0.52	33	6.15
11	16.5	34	5.84
13	4.12	35	5.96
14	4.16	38	0.94
15	3.82	39	0.80

* Numbering corresponds to Table 1.

** Cesium activity proved to be lower than the detection level.

induced a significant error when determining minor activity.

Comparing the curves for samples 5 and 8, one can notice that leaching of ^{90}Sr and ^{90}Y in the last case proceeds 1.5–2 times slower. Hence, inclusion of the bentonite clay in the compound results in sorption of not only cesium but also strontium, which complies with the data [5]. As for ^{137}Cs , the enamel coating slows down the water absorption by cement: the start of the

observed output of activity from blocks 1–5 and 8 was on days 5–10 of the contact with water. At the same time, comparison of the results presented in Figs. 6 and 7 demonstrates that the coating significantly decreases the leaching rate of ^{90}Sr and ^{90}Y . The values of the average leaching rates of these radionuclides are presented in Table 4.

From the results, one can deduce that the leaching rate of ^{90}Sr and ^{90}Y does not exceed 0.1 mg/(cm² day) for all compounds in contrast to ^{137}Cs . In this case, it grows insignificantly when filling the compound with ORLW. A reliable dependence of the leaching rate on the type on ORLW has not been obtained.

As is well known, in conditions of radioactive equilibrium of ^{90}Sr and ^{90}Y , yttrium makes the main contribution (more than 95%) to the apparatus spectrum of Cherenkov radiation [8]. Measurement of water samples performed by us over 2–3 days of leaching do not demonstrated any noticeable changes of activity in comparison with the first measurements. Therefore, ^{90}Sr and ^{90}Y are present in samples in an equilibrium amount. This being the case, one can estimate the individual leaching rates of strontium and yttrium.

If we assume the rates of transition of ^{90}Sr and ^{90}Y to the liquid state to be constant (which can be done because of the linear character of the kinetic curves), then the quantity of atoms of radionuclides N_{Sr} and N_{Y} in the leaching water as a function of time t will be governed by the following differential equations:

$$\frac{dN_{\text{Sr}}}{dt} = r_{\text{Sr}} - \lambda_{\text{Sr}}N_{\text{Sr}}, \quad (4)$$

$$\frac{dN_{\text{Y}}}{dt} = r_{\text{Y}} - \lambda_{\text{Y}}N_{\text{Y}} + \lambda_{\text{Sr}}N_{\text{Sr}}, \quad (5)$$

where r_{Sr} and r_{Y} are the rates of transition to the liquid phase of ^{90}Sr and ^{90}Y , respectively, s⁻¹; and λ_{Sr} and λ_{Y} are the decay constants of ^{90}Sr and ^{90}Y , respectively.

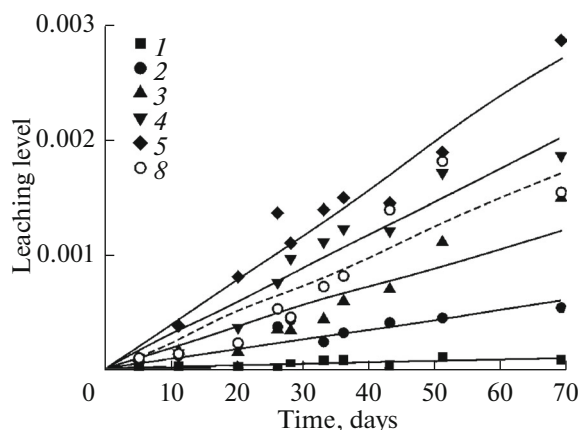


Fig. 6. Leaching curves of ^{90}Sr + ^{90}Y from enamel-covered compounds 1–5 and compound 8 (containing bentonite).

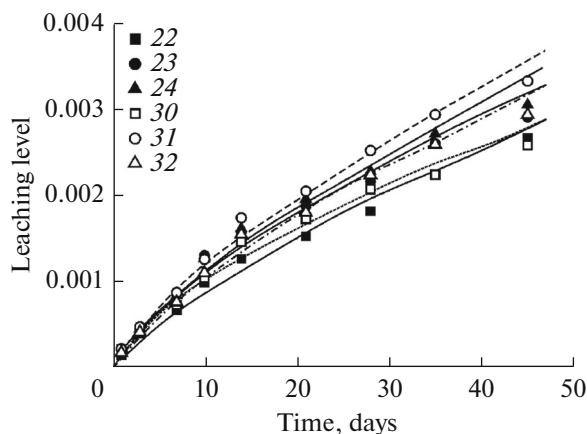


Fig. 7. Leaching curves of ^{90}Sr + ^{90}Y from compounds 22–24 containing extracting agent and compounds 30–32 containing oil.

Table 4. Average leaching rate of $^{90}\text{Sr} + ^{90}\text{Y}$ after 28 days

Compound*	R , mg/(cm ² day)	Compound*	R , mg/(cm ² day)
1	0.001	22	0.063
2	0.012	23	0.074
3	0.009	24	0.079
4	0.027	30	0.071
5	0.031	31	0.077
8	0.012	32	0.087

* Numbering corresponds to Table 1.

The solution of the system of these equations for the current activities A_{Sr} and A_{Y} in the water has the following form:

$$A_{\text{Sr}} = r_{\text{Sr}} (1 - e^{-\lambda_{\text{Sr}}t}), \tag{6}$$

$$A_{\text{Y}} = r_{\text{Y}} (1 - e^{-\lambda_{\text{Y}}t}) + r_{\text{Sr}} \left(1 + \frac{\lambda_{\text{Y}}e^{-\lambda_{\text{Sr}}t}}{\lambda_{\text{Sr}} - \lambda_{\text{Y}}} + \frac{\lambda_{\text{Sr}}e^{-\lambda_{\text{Y}}t}}{\lambda_{\text{Y}} - \lambda_{\text{Sr}}} \right). \tag{7}$$

It follows that the ratio of activities $A_{\text{Y}}/A_{\text{Sr}}$ will with good accuracy be equal to one in the case where their transition rates to the liquid phase are related in the same way as the half-lives, or

$$r_{\text{Y}}/r_{\text{Sr}} = \lambda_{\text{Sr}}/\lambda_{\text{Y}} = 0.0002536.$$

The dependence of the ratio $A_{\text{Y}}/A_{\text{Sr}}$ on time at various values of $x = r_{\text{Y}}/r_{\text{Sr}}$ (Fig. 8) makes it possible to establish that the leaching rate of ^{90}Y is 0.02–0.03% of the leaching rate of ^{90}Sr , i.e., negligibly small. Comparing the results obtained in this study, one can notice that the leaching rates of radionuclides of elements of groups I, II, and III from cement compounds with ORLW form the following series:

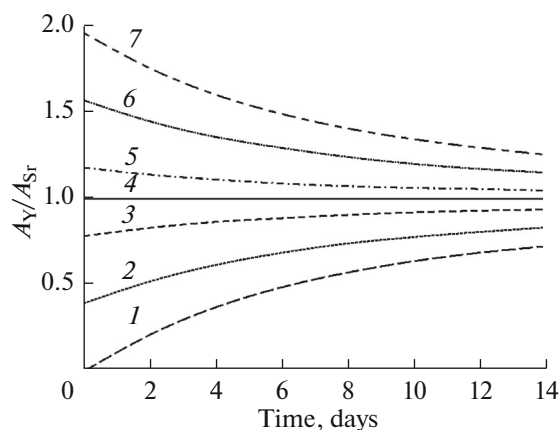


Fig. 8. Ratio of ^{90}Y and ^{90}Sr activities plotted against the ratio of their leaching rates.

$$R(^{137}\text{Cs}) > R(^{90}\text{Sr}) \gg R(^{90}\text{Y}).$$

We note that the approximation of the curves of strontium leaching from compounds 22–24 and 30–32 by Eq. (2) gives values $R = 0.65–0.75$. In this case, the first points in time keep a linear dependence ($R = 1$) best. This and a relatively small leaching rate suggest that in the given case the process is limited not by diffusion but by the transition of radionuclides from one phase to another. Inasmuch as strontium is a chemical analog of calcium, its observed small leaching rate from the cement compounds is a result of exchange processes of calcium to strontium in the composition of minerals of the cement matrix: $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, etc. The retention mechanism of yttrium by the compound appears to be similar.

CONCLUSIONS

It is proposed to use combined cement compounds containing ORLW preliminarily mixed with TEG at the weight ratio of 20 : 1 and Portland cement M-500 with a bentonite clay additive (5% of dry cement weight) with montmorillonite content not less than 65% and water ($\text{WC} = 0.3–0.35$) for petrification of such ORLW as spent TBP in hydrocarbon solvent and process oil. The optimal filling of the compound with extracting agent is 25%, and with oil, it is 20 vol %. The minimum aging time of the compounds before transportation for long-term storage or burial should be not less than 42 days from the moment of mixing of cement.

The strength of the compounds with the given composition complies with the standardized values (GOST R 51883-2002). The average leaching rate of ^{137}Cs is not more than 1 mg/(cm² day); for $^{90}\text{Sr} + ^{90}\text{Y}$, it is not more 0.1 mg/(cm² day).

It has been established that leaching kinetics of cesium radionuclides has a diffusional character and that of strontium and yttrium is of sorption-desorption nature. The leaching rates of radionuclides of elements of groups I, II, and III form the following series: $R(^{137}\text{Cs}) > R(^{90}\text{Sr}) \gg R(^{90}\text{Y})$.

The moisture-resistant enamel coating of the surface of compounds does not create a significant barrier to diffusion of ^{137}Cs . However, it slows down the water absorption by cement, thus postponing the beginning of transition of ^{137}Cs and other radionuclides to the liquid phase.

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