



# Hydroxycalix[6]arenes with *p*-isononyl substituents for alkaline HLW processing

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## Abstract

Hydroxycalix[n]arenes possess high chemical and radiolytic stability, being promising extractants for long-lived radionuclides recovery from alkaline media. *P*-isononylcalix[6]arene shows the optimal combination of high extraction ability and good solubility in a paraffin diluent. During the static tests on real waste, high purification factors were achieved: 15,000 for <sup>137</sup>Cs and β-emitters and 100—for α-emitting radionuclides. Dynamic tests were carried out on a 16-stage test bench in countercurrent mode using model alkaline HLW. Purification factor > 500 was achieved for <sup>137</sup>Cs with its tenfold concentration in the re-extract. Test results confirm the possibility of using *p*-isononylcalix[6]arene for alkaline HLW processing.

**Keywords** Alkaline radioactive waste · Solvent extraction · *p*-isononylcalix[6]arene · Cesium-137 · Extraction processing of HLW

## Introduction

Modern radiochemistry usually applies extraction methods for highly active aqueous solutions processing. The main problem in the development of processing technology is the need for the simultaneous extraction of *s*- and *f*-elements of different chemical properties, for example, cesium and actinides. To date, many extractants have been proposed to solve this problem in acidic media [1–4]. Basically, polyfunctional compounds with phosphoryl and amide donor groups, forming strong complexes even with triply charged cations of transplutonium elements (TPE), are used as extractants. Functionalized calixarenes are of great interest for the TPE extraction from acidic media [5–8]. In addition to extraction, other methods of radionuclides recovery are being actively

developed: precipitation techniques [9], sorption [10–12] and others.

The main industrial method of extraction processing is the PUREX nitric acid process. However, its classical scheme is not ideal for modern production: the use of nitric acid in combination with solutions of tributyl phosphate (TBP) in a hydrocarbon diluent means dealing with an explosive and fire hazardous system that requires the use of appropriate safety measures. Extraction technology that allows reprocessing spent nuclear fuel (SNF) in alkaline-carbonate media is considered as an alternative way of SNF management [13, 14]. This approach would also solve the problem of processing accumulated alkaline waste, similar to those stored at FSUE “PA “Mayak” in Russia and in the USA (Hanford, Savannah River and Oak Ridge).

The world’s amount of accumulated alkaline HLW is significantly less than that of acidic ones, but their partitioning is a very difficult technological task due to the extremely high content of salts of non-radioactive elements [15]. FSUE “PA “Mayak” has accumulated a significant amount (more than 18,000 m<sup>3</sup>) of high level radioactive waste (HLW). These are alkaline systems of precipitates, suspensions and decantates with activity greater than 1 Ci L<sup>-1</sup>. The bulk of the precipitates are iron, aluminum, nickel, chromium hydroxides, iron and nickel sulfides, nickel-cesium and titanium-cesium ferrocyanides. Activity of precipitate is determined by <sup>137</sup>Cs, <sup>90</sup>Sr in equilibrium with <sup>90</sup>Y, as well as by

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$\alpha$ -emitting radionuclides. Solutions have high concentrations of hydroxide, nitrate, nitrite and sodium aluminate. Activity of liquid phase is determined mainly by  $^{137}\text{Cs}$  [16].

Extraction of cesium,  $\alpha$ - and  $\beta$ -emitters from alkaline HLW would make it possible to convert waste into the low level waste (LLW) and significantly simplify its management. In order to purify alkaline HLW to the levels, allowing their cementation and disposal in ground-level radioactive waste disposal sites (low-active solid radioactive waste of the 4th class on the Russian classification) it is necessary to recover at least 99.8% of  $^{137}\text{Cs}$ , 92% of  $^{90}\text{Sr}$  and 98% of actinides.

We have proposed calix[n]arenes with isononyl and *tert*-butyl substituents at the upper rim (Fig. 1) as promising extractants for alkaline HLW processing.

Preliminary studies of extraction properties of these calixarenes have shown that they efficiently recover cesium and americium from carbonate-alkaline media in the pH range of 12–14. The main obstacle of using *p*-alkylcalix[n]arenes in solvent extraction is their low solubility in organic diluents. The most lipophilic calixarene in the series of studied compounds—*p*-isononylcalix[8]arene, possesses solubility of less than  $0.006 \text{ mol L}^{-1}$  in hexane and about  $0.11 \text{ mol L}^{-1}$  in perchloroethylene [17].

Chlorinated hydrocarbons have proved impossible to be used as diluents [18, 19] because they are susceptible to radiolysis with the formation of radicals, interacting with the aromatic platform of calixarene and causing its disintegration. The only possible way is to use mixed diluents with additives that increase the solubility of the calixarene. Such a variant has already been tested by American scientists in the development of CSSX-process of alkaline HLW purification from cesium, who proposed phenoxy fluorine-containing alcohols as modifiers and solvating agents [20].

As a result of the studies [21], we have found that polar organofluorine compounds, including aromatic nitro compounds and aliphatic ethers, can be used as additives enhancing the solubility of the calixarenes. Taking into account the obtained data, an extractant based on *p*-isononylcalix[6]arene in *n*-tridecane with additions of

*m*-nitrobenzotrifluoride and diglyme was developed for dynamic tests on alkaline HLW of the FSUE “PA “Mayak”.

## Experimental

**Materials and techniques.** *P*-isononylcalix[6]arene (**IN6**, Fig. 1,  $n=0$ ,  $m=6$ ), was synthesized in the A.E. Arbusov Institute of Organic and Physical Chemistry of Russian Academy of Science (Kazan) according to the procedure described in [22]. The structure of *p*-isononylcalix[6]arene was characterized by NMR spectroscopy and MALDI mass spectrometry. Below are the main characteristics of this compound.

**IN6:** yield 32% (colorless powder). M.p: 102–104 °C.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ,  $\delta$ , ppm, Hz): 0.50–1.58 (m, 114H, –C<sub>9</sub>H<sub>19</sub>), 3.90 (m, 124 12H, Ar-CH<sub>2</sub>-Ar), 7.00–7.16 (m, 12H, ArH), 10.38 (s br, 6H, OH); IR  $\nu \text{ cm}^{-1}$ : 3172 (OH); Mass spectrum (MALDI): calculated  $[\text{M}^+]$   $m/z = 1394.1$ , found  $[\text{M} + \text{Na}]^+$   $m/z = 1417.1$ ,  $[\text{M} + \text{K}]^+$   $m/z = 1433.1$ .

The obtained *p*-isononylcalix[6]arene dissolves almost indefinitely in non-polar and weakly polar diluents (at least several orders higher than the requirements for industrial extractants). Solubility in polar diluents, such as *m*-nitrobenzotrifluoride, is about  $0.3\text{--}0.5 \text{ mol L}^{-1}$ .

Extractant solutions for the experiments were prepared by dissolving the calixarene sample in a mixture of polar diluent components (*m*-nitrobenzotrifluoride and diglyme) followed by the addition of *n*-tridecane. The extraction mixture was washed successively with  $1 \text{ mol L}^{-1} \text{ HNO}_3$  and  $1 \text{ mol L}^{-1} \text{ NaOH}$  (3 times each) prior to the test to remove residual products used in the synthesis of calixarene. The inorganic reagents used in the work were of analytical grade.

For carrying out the extraction experiments, required volumes of aqueous and organic phases of known composition were entered in polypropylene test tubes and mixed at 21–23 °C within 10 min. Preliminary experiments have shown that this time is sufficient to establish the extraction equilibrium. Phase separation was carried out by centrifugation or settling (tests on real HLW). Selected equilibrium samples of the aqueous phase were immediately acidified with  $3 \text{ mol L}^{-1} \text{ HNO}_3$  to prevent possible sorption of radionuclides on the surface of the tubes and transferred to radio-metric analysis.

Real alkaline HLW (decantate), containing  $2.6 \cdot 10^{10} \text{ Bq L}^{-1}$  of  $^{137}\text{Cs}$  and  $4.5 \cdot 10^7 \text{ Bq L}^{-1}$  of  $\alpha$ -active nuclides against the background of about  $6 \text{ mol L}^{-1}$  of salts of sodium (hydroxide, nitrate, nitrite, aluminate, chromate), was used for static tests. The test procedure with real HLW was similar to that, described in [21]. The extractant for the static tests was  $0.013 \text{ mol L}^{-1}$  **IN6** solution in a mixture of *m*-nitrobenzotrifluoride (13% vol.), diglyme (55% vol.) and *n*-tridecane (32% vol.).

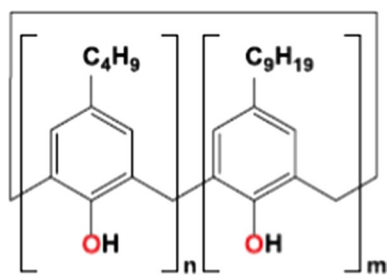


Fig. 1 Structural formulae of *p*-isononylcalix[n]arenes

Dynamic tests were carried out at a laboratory extraction plant (LEP), which included the following equipment:

- 2 extraction “mixer settler” blocks with pulsation mixing of the phases including 10 steps of extraction and 6 steps of re-extraction;
- 2 mechanical pulsators for mixing and transportation of the phases;
- proportional batcher with pressure head tanks for inactive technological solutions supply at the step of extractors;
- peristaltic pump Heidolph for initial model HLW serving.

The dynamic test extractant consisted of 0.038 mol L<sup>-1</sup> solution of calixarene **IN6** (Fig. 1, n=0, m=6) in a mixture of *m*-nitrobenzotrifluoride (10% vol.), diglyme (10% vol.) and *n*-tridecane (the rest). The density of the fresh extractant was 0.8037 g cm<sup>-3</sup>, after testing—0.7962 g cm<sup>-3</sup>.

The composition of the model HLW solution used for testing is presented in Table 1. As a stripping agent, 1 mol L<sup>-1</sup> HNO<sub>3</sub> was used.

An aliquot of the real alkaline decantate was added to the model HLW in a volume sufficient to achieve the specific activity of <sup>137</sup>Cs of about 10<sup>7</sup> Bq L<sup>-1</sup>.

The <sup>137</sup>Cs activity in the samples was determined by  $\gamma$ -spectrometry on a  $\gamma$ -ray energy spectrometer with a semiconductor detector “SEG-01 PPD”. The total activity of  $\alpha$ -emitting radionuclides was determined on a radiometer with a semiconductor detector by direct measurement of the count rate of external radiation pulses from the active operating surface of an open plane source. The measurement

time of the samples was chosen so that the inaccuracy of radiometric measurements did not exceed 15%.

The test flowsheet with real HLW under static conditions included 4 consecutive contacts of the initial solution with fresh portions of extractant at a volume ratio of organic and aqueous phases 1:1, as well as 4 additional contacts with fresh portions of extractant at a volume ratio of organic and aqueous phases 2:1. For radionuclides re-extraction, 2 mol L<sup>-1</sup> HNO<sub>3</sub> was used (2 contacts with a volumetric ratio of organic and aqueous phases 2:1).

The dynamic test scheme with model HLW provided:

- extraction of <sup>137</sup>Cs and  $\alpha$ -emitting radionuclides by 10 stages of the extraction unit;
- re-extraction of <sup>137</sup>Cs and  $\alpha$ -emitting radionuclides by 6 stages of the re-extraction unit.

In appliance with the process flow diagram (Fig. 2), the initial alkaline solution containing radionuclides entered the 10th stage of the extraction unit, where it was repeatedly contacted with the extractant supplied to the 1st stage, according to the countercurrent scheme. From the 1st stage of the extraction unit, raffinate, purified from radionuclides, was removed. The extract of <sup>137</sup>Cs and  $\alpha$ -emitting radionuclides, emerging from the 10th stage of the extraction unit by gravity entered the 1st stage of the re-extraction unit. In the 6th stage of the re-extraction unit, a stripping solution (1 mol L<sup>-1</sup> HNO<sub>3</sub>) was supplied. From the 1st stage of the re-extraction unit, the concentrated re-extract was derived. The spent extractant came out of the 6th stage of the re-extraction unit, which again entered the 1st stage of the extraction unit without any regeneration.

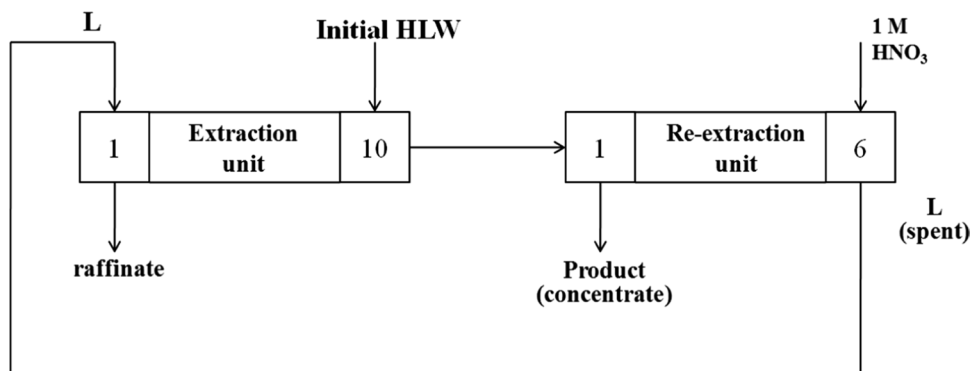
**Table 1** Composition of the model solution, simulating alkaline decantate of accumulated HLW

Cation	C (g L <sup>-1</sup> )	Anion	C (g L <sup>-1</sup> )
Na <sup>+</sup>	100	NO <sub>3</sub> <sup>-</sup>	110
Al <sup>3+</sup>	6.0	OH <sup>-</sup>	43
Cr <sup>3+</sup>	0.4	NO <sub>2</sub> <sup>-</sup>	35
Si <sup>2+</sup>	0.2	SO <sub>4</sub> <sup>2-</sup>	1.5

## Results and discussion

*Static tests.* The purpose was to determine the maximum possible depth of radionuclides extraction from the real alkaline HLW. In alkaline media, a part of  $\alpha$ -emitting actinides may exist in the colloidal state and do not pass into

**Fig. 2** Schematic diagram of dynamic tests



the organic phase. It was found that filtering real alkaline HLW through a paper filter “blue tape” with pore sizes of 1–2.5  $\mu\text{m}$  allows to remove up to 80% of the total  $\alpha$ -activity. Our experiments on the radionuclides extraction from real alkaline HLW using “mixed” calix[8]arenes with *tert*-butyl and isononyl substituents at the upper rim [21] confirmed the possibility of extracting up to 97.5% of  $\alpha$ -emitting radionuclides and 99.7% of  $^{137}\text{Cs}$ . These values are slightly lower than those required for the treatment of HLW to the category of LLW.

Therefore, for these tests, a more efficient extractant, containing 0.013 mol L<sup>-1</sup> **IN6** solution in a mixture of *m*-nitrobenzotrifluoride (13% vol.), diglyme (55% vol.) and *n*-tridecane (32% vol.) was proposed. The initial alkaline HLW was not diluted nor filtered before the experiment. Factor of HLW purification from  $^{137}\text{Cs}$  after 4 contacts with fresh portions of extractant was  $\sim 10^3$  (decrease from  $2.6 \cdot 10^{10}$  to  $2.9 \cdot 10^7$  Bq L<sup>-1</sup>). For additional 4 stages of extraction, the  $^{137}\text{Cs}$  activity in the raffinate decreases by one more order. The total factor of purification from  $^{137}\text{Cs}$  after 8 stages of extraction was  $1.5 \cdot 10^4$ , and from  $\alpha$ -emitting radionuclides—about 100.

Distribution ratios in the first three stages of extraction reached:

- for  $^{137}\text{Cs}$ —4.8/4.2/21.8, respectively;
- for  $\alpha$ -emitting radionuclides—5.7/0.5/0.4, respectively.

Low distribution ratios of  $\alpha$ -emitting radionuclides at the 2nd and 3rd stages of extraction confirm the assumption about the different forms of the existence of actinides in alkaline HLW.

High ratios of alkaline HLW purification from radionuclides, achieved in this experiment, make it possible to reliably convert waste to the category of LLW, which allows simplified disposal on the ground level.

In the tested extraction mixture, high extraction ability was combined with mean hydrodynamic characteristics: low separation rate due to the small density difference between the organic and aqueous phases. In this regard, to test a new extractant under dynamic conditions, the composition of the extraction mixture was optimized: the concentration of *p*-isononylcalix[6]arene **IN6** was increased, whereas the concentration of solvating additives—*m*-nitrobenzotrifluoride and diglyme—was reduced. The optimized extractant contained 0.038 mol L<sup>-1</sup> **IN6** in the mixture of 10% vol. *m*-nitrobenzotrifluoride and 10% vol. diglyme in *n*-tridecane, had a density of 0.8037 g cm<sup>-3</sup> and showed high separation rate both with alkaline HLW and with nitric acid stripping agent.

To determine the optimal consumption of operating solutions during dynamic tests, preliminary static experiment was conducted with a model HLW. It included 3

consecutive contacts of the extractant with fresh portions of the model HLW with a ratio O:A = 1:1 and a phase contact time of 10 min. Model HLW with an aliquote of real alkaline decantate and of  $^{137}\text{Cs}$  activity of  $7.3 \cdot 10^8$  Bq L<sup>-1</sup> was used. The  $^{137}\text{Cs}$  distribution ratios at 3 stages of extraction were: 3.1/2.3/1.9. The phases at all stages were separated rapidly (less than 2 min), interfacial films and precipitations were not formed. Thus, it was found that to extract 99.9% of  $^{137}\text{Cs}$  by 10 stages of extraction in the dynamic mode, it is necessary to maintain the ratio of the flows of the extractant and the model HLW not lower than 1:2.

*Dynamic tests.* The standard technological flowsheet for HLW extraction treatment includes two main operations: extraction and re-extraction of radionuclides, as well as two auxiliary processes: the extract washing and the spent extractant regeneration. When arranging the basic technological scheme of a specific process, it is necessary to minimize the number of auxiliary operations and the number of extraction stages in the main operations. In the American NG-CSSX-process for alkaline HLW purification of from  $^{137}\text{Cs}$ , the technological scheme includes 18 stages: 7 stages of extraction/re-extraction and 2 stages of washing/regeneration [23].

During static mode testing of our process, it was noted that extractant washes from degradation products spontaneously when it contacts with alkaline HLW solution. Experiments with the extractant containing 0.02 mol L<sup>-1</sup> of *p*-isononylcalix[6]arene in a mixture of 10% vol. *m*-nitrobenzotrifluoride and 10% vol. diglyme in *n*-tridecane showed that the fresh extractant recovers radionuclides from alkaline medium (1 mol L<sup>-1</sup> NaOH, pH = 13.3) with  $D_{\text{Cs}} = 3.5$  and  $D_{\text{Am}} = 1.8$ . The same extractant after contact with a stripping solution (2 mol L<sup>-1</sup> HNO<sub>3</sub> or H<sub>3</sub>PO<sub>4</sub>) recovers radionuclides with ratios  $D_{\text{Cs}} = 3.4$  and  $D_{\text{Am}} = 2.1$ . The extraction proceeds without gassing, the phases mix well and separate quickly. Thus, there is no need for washing the extract and regenerating the circulating extractant.

Refusal to wash the extract before the re-extraction operation allows avoiding an increase in the raffinate volume, but creates the danger of transferring a part of the HLW to the re-extract in the form of a microemulsion. To prevent this, an extra sedimentation stage was set between the extraction and re-extraction units (cylindrical container 30 × 150 mm with a lower feed and an upper outlet of the extract). After the experiment completion, less than 5 mL of the aqueous phase was found in it. Taking into account that more than 10 L of the model HLW were processed in the tests, the entrainment was less than 0.05%. Obviously, this value depends on the efficiency of the operating of extraction equipment, involved in the process. Nevertheless, we expect that in the future it is possible to refuse additional purification of the extract and immediately submit it for re-extraction.

Dynamic tests included two stages: at the first, the maximum extraction of radionuclides (mode I) was examined, and at the second, the maximum concentration of radionuclides (mode II) was examined.

The specified flows of technological products are shown in Table 2.

Dynamic tests were carried out around the clock, in four shifts of 6 h each. The total duration of tests in the maximum extraction mode was more than 58 h of continuous operation, in the maximum concentration mode—about 48 h of continuous operation. Analysis of samples of aqueous technological products (raffinate and re-extract) was carried out from averaged volumes collected per shift. If necessary, samples of these products were taken from the streams. In total, the test duration was 20 shifts. Excluding breaks for refueling containers with reagents, the test bench operated for 105 h. During this time, about 10.5 L of the initial solution were processed. The extractant run more than 10 circulations. The activity of  $^{137}\text{Cs}$  in the circulating extractant during the tests did not exceed  $10^5 \text{ Bq L}^{-1}$ . During the tests, the extraction system operated stably, there was neither formation of precipitates, nor poorly separated emulsions, nor mutual phase entrainment.

The actual flows of technological products during the tests are presented in Table 3.

The results of the analysis of technological products samples are presented in Table 4.

The initial HLW model solution contained  $(2.25 \pm 0.4) \cdot 10^7 \text{ Bq L}^{-1}$  of  $^{137}\text{Cs}$ . The content of  $\alpha$ -active radionuclides in the model HLW was below the detection limit.

Data on  $^{137}\text{Cs}$  distribution in the products of the technological scheme and the material balance of the process are presented in Table 5.

Analysis of the obtained data shows that 10 stages of extraction provide extraction of more than 99.8% of  $^{137}\text{Cs}$  from the model HLW, both in the maximum extraction mode (extraction with O:A = 1:1) and in the maximum concentration mode (extraction with O:A = 1:2). In the maximum extraction mode,  $\alpha$ -active radionuclides with activity of

**Table 2** The specified flows of technological products

Product	Consumption (mL/h)	
	Mode I (maximum extraction)	Mode II (maximum concentration)
Initial model HLW	94	94
Circulating extractant	94	45
Extract after extraction unit	94	45
Re-extractant	45	9

**Table 3** Actual flows of technological products

Duration (h)	Consumption of technological products (mL h <sup>-1</sup> )		
	Circulating extractant	Raffinate	Re-extractant
<i>Mode I</i>			
8.5	100	81.8	46.4
13.9	91	64	45
19.6	91	69	39
25	83.6	94.6	44
30.5	94.5	90.9	42.7
36	89.1	86.4	41
41.5	90.9	81.8	52.7
47	90.9	90.9	45.5
52.5	95.5	92.7	43.6
58	94.5	90.9	49.1
<i>Mode II</i>			
5.7	52.7	90.9	9.1
11.5	44.1	83.9	9.7
17	45.4	90.9	9.1
22.5	41.8	90.9	9.1
28	45.5	89.1	13.6
33.5	46.3	90.9	8.7
39	51.8	92.7	9.1
47.5	50	90.9	10

$(1.3 \div 4.0) \cdot 10^3 \text{ Bq L}^{-1}$  are detected in the re-extract containing significantly lower concentrations of stable salts than HLW. Activity of  $^{137}\text{Cs}$  in the re-extract exceeds the initial one by 9–11 times in the maximum concentration mode, whereas in the maximum extraction mode it exceeds initial

**Table 4** The results of the analysis of raffinate and re-extract

Duration (h)	$^{137}\text{Cs}$ activity (Bq L <sup>-1</sup> )	
	Raffinate	Re-extract
<i>Mode I</i>		
11	$(1.14 \pm 0.30) \cdot 10^4$	–
16.5	$(3.1 \pm 0.6) \cdot 10^4$	–
21.5	$(2.36 \pm 0.45) \cdot 10^5$	$(3.7 \pm 0.6) \cdot 10^7$
27	$(3.7 \pm 0.7) \cdot 10^4$	$(5.5 \pm 0.9) \cdot 10^7$
32.5	$(1.36 \pm 0.26) \cdot 10^5$	$(5.5 \pm 0.9) \cdot 10^7$
38	$(6.7 \pm 1.3) \cdot 10^4$	$(5.6 \pm 0.9) \cdot 10^7$
43.5	$(3.7 \pm 0.7) \cdot 10^4$	$(6.1 \pm 0.9) \cdot 10^7$
49	$(3.6 \pm 0.6) \cdot 10^5$	$(5.9 \pm 0.9) \cdot 10^7$
<i>Mode II</i>		
11.3	$(3.3 \pm 0.6) \cdot 10^4$	$(2.02 \pm 0.32) \cdot 10^8$
22.5	$(6.1 \pm 1.2) \cdot 10^4$	$(2.18 \pm 0.35) \cdot 10^8$
33.5	$(4.7 \pm 0.9) \cdot 10^4$	$(2.37 \pm 0.40) \cdot 10^8$
44.5	$(8.2 \pm 1.6) \cdot 10^4$	$(2.45 \pm 0.43) \cdot 10^8$



**Table 5** Distribution of  $^{137}\text{Cs}$  in the products of the technological scheme

Time from the start (duration) (h)	Product	$^{137}\text{Cs}$ activity	
		Bq	%
<i>Mode I: maximum extraction</i>			
21.5–27.0 (5.5)	Initial HLW	$1.15 \cdot 10^7$	100
	Re-extract	$1.05 \cdot 10^7$	91.3
	Raffinate	$0.7 \cdot 10^5$	0.61
	Sum (raffinate + re-extract)	$1.06 \cdot 10^7$	91.9
27.0–32.5 (5.5)	Initial HLW	$1.1 \cdot 10^7$	100
	Re-extract	$1.3 \cdot 10^7$	118
	Raffinate	$0.42 \cdot 10^5$	0.38
	Sum (raffinate + re-extract)	$1.30 \cdot 10^7$	118
32.5–38.0 (5.5)	Initial HLW	$1.04 \cdot 10^7$	100
	Re-extract	$1.4 \cdot 10^7$	135
	Raffinate	$0.21 \cdot 10^5$	0.20
	Sum (raffinate + re-extract)	$1.40 \cdot 10^7$	135
38.0–43.5 (5.5)	Initial HLW	$1.07 \cdot 10^7$	100
	Re-extract	$1.58 \cdot 10^7$	148
	Raffinate	$2.46 \cdot 10^4$	0.23
	Sum (raffinate + re-extract)	$1.60 \cdot 10^7$	148
43.5–49.0 (5.5)	Initial HLW	$1.13 \cdot 10^7$	100
	Re-extract	$1.48 \cdot 10^7$	131
	Raffinate	$1.0 \cdot 10^5$	0.88
	Sum (raffinate + re-extract)	$1.49 \cdot 10^7$	132
<i>Mode II: maximum concentration</i>			
0–11.3 (11.3)	Initial HLW	$2.21 \cdot 10^7$	100
	Re-extract	$0.214 \cdot 10^8$	96.8
	Raffinate	$3.24 \cdot 10^4$	0.14
	Sum (raffinate + re-extract)	$2.14 \cdot 10^7$	97
11.3–22.5 (11.2)	Initial HLW	$2.21 \cdot 10^7$	100
	Re-extract	$0.219 \cdot 10^8$	99
	Raffinate	$4.63 \cdot 10^4$	0.21
	Sum (raffinate + re-extract)	$2.19 \cdot 10^7$	99
22.5–33.5 (11)	Initial HLW	$2.23 \cdot 10^7$	100
	Re-extract	$0.28 \cdot 10^8$	125
	Raffinate	$5.35 \cdot 10^4$	0.24
	Sum (raffinate + re-extract)	$2.80 \cdot 10^7$	125
33.5–44.5 (11.0)	Initial HLW	$2.27 \cdot 10^7$	100
	Re-extract	$0.25 \cdot 10^8$	111.4
	Raffinate	$6.51 \cdot 10^4$	0.29
	Sum (raffinate + re-extract)	$2.54 \cdot 10^7$	112

HLW by 1.6–2.7 times, with the expected concentration factors of 10 and 2, respectively.

The radionuclides re-extraction with  $1 \text{ mol L}^{-1} \text{ HNO}_3$  in both tested modes was complete and the cesium activity in the circulating extractant was less than  $10^5 \text{ Bq L}^{-1}$ .

After completing the tests by the mode II, a stepwise sampling of organic and aqueous phases was carried out from the extraction unit. The results of the analysis of organic

**Table 6** Phase analysis results for stepwise sampling from the extraction unit for mode II

Stage number	$^{137}\text{Cs}$ activity ( $\text{Bq L}^{-1}$ )		$^{137}\text{Cs}$ distribution ratio (D)
	Organic phase	Aqueous phase	
1	$(2.59 \pm 0.45) \cdot 10^6$	$(9.1 \pm 1.7) \cdot 10^4$	28
2	$(2.4 \pm 0.4) \cdot 10^6$	$(1.85 \pm 0.35) \cdot 10^5$	13
3	$(2.18 \pm 0.35) \cdot 10^6$	$(4.0 \pm 0.7) \cdot 10^5$	5.5
4	$(4.2 \pm 0.7) \cdot 10^6$	$(8.0 \pm 1.4) \cdot 10^5$	5.3
5	$(7.5 \pm 1.3) \cdot 10^6$	$(1.52 \pm 0.24) \cdot 10^6$	4.9
6	$(1.07 \pm 0.18) \cdot 10^7$	$(3.3 \pm 0.6) \cdot 10^6$	3.2
7	$(1.5 \pm 0.23) \cdot 10^7$	$(4.0 \pm 0.7) \cdot 10^6$	3.8
8	$(2.05 \pm 0.35) \cdot 10^7$	$(4.3 \pm 0.7) \cdot 10^6$	4.8
9	$(3.5 \pm 0.6) \cdot 10^7$	$(8.3 \pm 1.4) \cdot 10^6$	4.2
10	$(6.6 \pm 1.1) \cdot 10^7$	$(1.45 \pm 0.23) \cdot 10^7$	4.6

and aqueous phases samples on  $^{137}\text{Cs}$  activity are presented in Table 6.

As it is expected,  $^{137}\text{Cs}$  distribution ratios decrease as the organic phase becomes saturated and this is in good agreement with the results of the static test with model HLW ( $D=3.1$ ). Anomalously high  $^{137}\text{Cs}$  distribution ratios (more than 10) at the first stages of the extraction unit are probably associated with uncertainty in the analysis of the  $^{137}\text{Cs}$  low activity in organic phase.

During dynamic tests, factor of HLW purification from  $^{137}\text{Cs}$  achieved  $> 500$ , with cesium tenfold concentration in the re-extract.

The test results confirm the principal possibility of using extractant based on *p*-isononylcalix[6]arene for the purification of alkaline HLW of the FSUE “PA “Mayak”, with obtaining cement compound of the LLW category, on the subsequent cementing stage.

## Conclusions

Based on the data obtained in experiments on real HLW, efficient purification from radionuclides can be achieved using extraction system based on *p*-isononylcalix[6]arene. The initial alkaline HLW solution in such a scheme will require only control clarification, re-extraction can be carried out with  $1\text{--}2 \text{ mol L}^{-1}$  solution of nitric or phosphoric acid—depending on whether it is supposed to solidify the obtained concentrate: in borosilicate or aluminophosphate glass. The examined technology does not require regeneration of the circulating extractant, since it involves its self-cleaning from radiolysis products in contact with a fresh portion of highly alkaline HLW.

High ratios of alkaline HLW purification from radionuclides, obtained as a result of testing both in static and dynamic conditions, make it possible, together with

subsequent cementing stage, to convert the waste into the category of LLW, which allows their simplified disposal on the ground level.

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