

# TECHNOLOGICAL TESTS OF HAW PARTITIONING WITH THE USE OF CHLORINATED COBALT DICARBOLYDE (CHCODIC); MANAGEMENT OF SECONDARY WASTES

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## ABSTRACT

The main results of technological tests with different variants of ChCoDiC using for HAW reprocessing in test facilities in hot boxes are presented. Technological flowsheets are developed for separating fractions of strontium, cesium, transplutonium elements and rare earths from HAW.

The results of technological tests in a pilot facility of radiochemical plant on reprocessing of highly active raffinates arising from the recovery of metallic uranium, oxide fuel and aluminum-containing fuel are given. It is shown that the technology provides the separation into individual flows of strontium, cesium, TPE and RE up to 99.5%. Millions Curies of strontium and cesium have been obtained and used for fabrication of test lots of isotope sources.

High chemical and radiation stability of extraction system based on ChCoDiC were demonstrated in the course of prolonged HAW reprocessing.

The results of investigating the secondary wastes arising in the flowsheet with using ChCoDiC and the proposals on management of these wastes are considered.

## INTRODUCTION

The technology of HAW partitioning which provides separation into individual fractions of cesium, strontium, transplutonium (TPE) and rare-earth (RE) elements is at the initial stages of its development. Slow progress is caused primarily by high activity of feed solutions, complex salt composition of them, components similar to their chemical behavior (TPE and RE) etc.

New extractants of higher selectivity towards certain elements or groups of elements are proposed for HAW reprocessing. Among these extractants, Crown ethers, acidic salts of organophosphorus acids, bidentate organophosphorus extractants (dioxides, diphosphines, carbamoylphosphine oxides) (1-4) etc. In our works we paid most attention to chlorinated cobalt dicarbolyde proposed by the Soviet and Czechoslovak scientists as extractant for reprocessing of liquid HAW. (5, 6)

In the last few years the specialists of Radium Institute and radiochemical plant "Mayak" brought the level of these studies up to commercial tests.

## RECOVERY OF CESIUM AND STRONTIUM

On the basis of data on systematical study of properties of chlorinated cobalt dicarbolyde and on investigation of possible use of ChCoDiC for HAW reprocessing, a technological flowsheet for recovery of strontium and cesium was developed and tested in counter-flow extraction facility in hot boxes.

The flowsheet envisaged recovery of cesium by extractant consisting of 0.06 M ChCoDiC in the mixture of nitrobenzene and carbon tetrachloride, washing of extract and stripping of cesium. From the raffinate strontium was recovered by the same extractant but with addition of 1% vol. of SlovafoI-909.

The recovery of strontium and cesium was performed directly from acidic solutions of highly active raffinate arising from extraction reprocessing of spent WWER fuel. The yields of cesium and strontium into reextracts were 99.8% and 99.7%, respectively. Decontamination factors of strontium

and cesium from accompanying gamma-emitters exceeded  $5 \cdot 10^2$ .

Principal drawback of the flowsheet consisted in using two extraction systems for the selective recovery of strontium and cesium.

Further development of the method for the recovery of strontium and cesium with ChCoDiC involved the elaboration of the flowsheet on the basis of four-component system. Key flowsheet is shown on Fig. 1. On testing the flowsheet in hot boxes, highly active wastes of different types were used as feed solution. In all cases rather high indices were achieved for recovery, yield and purification of strontium and cesium from impurities. So, for example, on testing the flowsheet with evaporated raffinate arising from reprocessing of irradiated metallic uranium, the recovery of strontium and cesium into

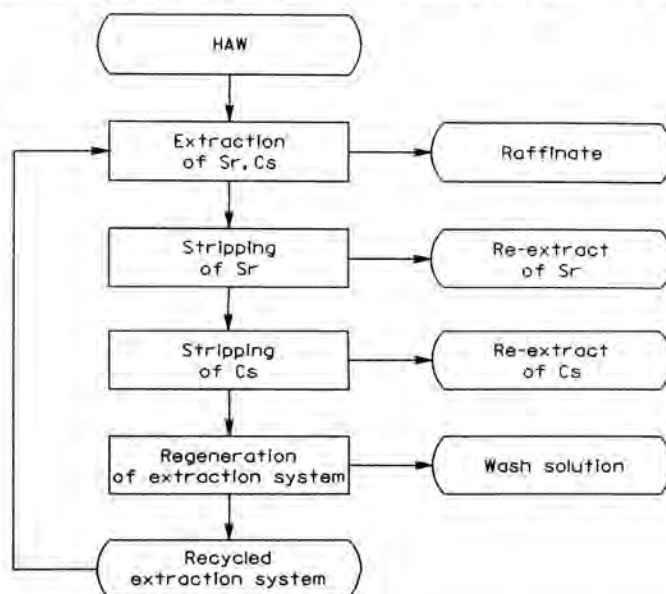


Fig. 1. Key flowsheet for recovery of cesium and strontium on the basis of one extraction system.

extract was 99.4% and 99.6%, respectively. Direct yield of strontium and cesium into corresponding reextracts was 98.4% and 99%. The concentration degree of strontium and cesium was 10 and 2.5. Decontamination factor of strontium from gamma-emitters attained  $10^3$ . The content of measurable macroimpurities in strontium strip solution (reextract) did not exceed their content in strips (reextracting solution).

The results of multilateral laboratory investigations and bench tests in hot boxes enabled to proceed to full-scale verification of extraction technology for separation of strontium and cesium.

It should be noted that the full-scale tests were preceded by commercial synthesis of components for the extraction system.

In extraction facility equipped by apparatus of mixer-settler type with the use of four-component extraction mixture, over  $480 \text{ m}^3$  (throughput  $2\text{-}3.5 \text{ m}^3/\text{d}$ ) of raffinates arising from Purex-reprocessing of the following types of irradiated fuel was processed without preliminary adjustment and preparation:

- metallic uranium (including evaporated raffinates with additions of different liquid radioactive wastes);
- NPP oxide fuel with burn-up to  $40 \text{ MW}\cdot\text{d}/\text{kg U}$  (including evaporated raffinates);
- fuel containing considerable amounts of aluminum.

On reprocessing of above raffinates, the recovery of strontium and cesium into extract was 97.8-99.6% (with regard to departures from process regulation). In all cases the concentration was attained for strontium by 7-10 times and for cesium by 2-2.5 times.

Besides, the second cycles for concentration of strontium and cesium were carriers out;  $60 \text{ m}^3$  of strontium reextracts and more than  $30 \text{ m}^3$  of cesium reextracts were reprocessed.

In the course of investigations aimed at the improvement of HAW partitioning technology conducted along with full-scale tests, a three-component extraction system on the basis

of ChCoDiC was elaborated and tested in hot-box facilities by the use of mixer-settlers and centrifugal extractors. This extraction system is not corrosion-aggressive to construction materials. It was established that on integral dose of  $10^5\text{-}10^6$  Gystainless-steel was practically free to corrosion. According to examination (on the basis of standards currently in force), the improved technology with using ChCoDiC is fire- and explosion-proof.

During full-scale tests of the improved flowsheet with three-component extraction system more than  $90 \text{ m}^3$  of HAW were reprocessed, including  $54 \text{ m}^3$  of raffinate arising from reprocessing of spent WWER fuel. In Table I the data are cited on averaged content of strontium, cesium and impurities in feed solution (raffinate from WWER fuel reprocessing) and reextracts of strontium and cesium. Losses of strontium and cesium with raffinate were below 0.6%. Losses of cesium with strontium reextract were 0.4%, those of strontium with cesium reextract - 2.5%. Concentration of strontium and cesium for an extraction cycle was increased by 8.7 times and 8 times, respectively. Decontamination factors of strontium and cesium from gamma-emitters and macroimpurities are given in Table II.

For additional concentration of strontium and purification from admixture, the second extraction cycles were conducted. As feed solution strontium reextract of the first cycle was used. Data on averaged content of strontium and admixtures in feed solution and strontium reextract of the second cycle are shown in Table I. Losses of strontium with raffinate accounted for 1.5% of strontium content in feed solution. Concentration degree of cesium on the second cycle was about 5. The data on additional purification of strontium from impurities on the second cycle are given in Table II.

In the course of testing, the three-component extraction system performed about 70 cycles. The results of reference tests showed that the extraction and hydrodynamic properties of organic solution were practically unaffected. This is

TABLE I

Content of Strontium, Cesium, and Impurities in Feed Solution and Reextracts

Product	Nitric Acid g/l	Content of Radionuclides, Ci/l					Content of macroimpurities, mg/Ci Sr (mg/Ci Cs)							
		Sr <sup>90</sup>	Cs <sup>137,134</sup>	Ce <sup>144</sup>	Ru <sup>106</sup>	Eu <sup>154</sup>	Fe	Cr	Ni	Al	Ca	Pb	Ba	Na
Feed Solution	192	4.6	15.4	3.0	2.6	0.5	174 (52)	6.5 (1.9)	22 (6.5)	430 (130)	6.5 (1.9)	2.2 (0.65)	65 (19)	540 (162)
Reextract of Sr	128	40.2	0.51	0.07	0.06	0.01	0.7	0.2	0.2	0.2	0.7	0.2	3.7	25
Stripping (Reextraction) of Cs	246	0.9	122	-	-	-	(0.25)	(0.08)	(0.08)	(0.08)	(0.25)	(0.08)	(4.9)	(0.4)
Stripping (Reextraction) of Sr on the second extraction cycle	118	202	0.06	0.02	0.09	-	0.25	0.05	0.05	0.05	0.25	0.05	0.25	0.50

TABLE II

Decontamination Factors of Cesium and Strontium from Impurities

Element	<sup>90</sup> Sr	<sup>137,134</sup> Cs	<sup>144</sup> Ce	<sup>106</sup> Ru	<sup>154</sup> Eu	Fe	Cr	Ni	Al	Ca	Pb	Ba	Na
Decontamination Factor of Cesium	-	-	-	-	-	210	24	80	$1.6 \cdot 10^3$	8	3	4	400
Decontamination Factor of Strontium on I cycle	-	260	375	380	440	250	30	110	$2.1 \cdot 10^3$	9	11	17	22
Decontamination Factor of Strontium on II cycle	-	40	17	3	-	3	4	4	4	3	4	15	50

ative of high chemical and radiation stability of the extraction system.

Systematical analysis of aqueous products revealed that the losses of ChCoDiC due to solubility are negligible, less than 20 mg/l.

During the full-scale testing of the technology with using the four- and three-component extraction system on the basis of ChCoDiC, more than 570 m<sup>3</sup> of different highly active raffinate were reprocessed and Mega-Curium amount of strontium-90 and cesium-137,134 was recovered.

The problem of waste partitioning coincides with the necessary recovery of strontium-90 and cesium-137 for further utilization. In the frames of complex full-scale tests, the concentrates of strontium-90 and cesium-137 resulted from reprocessing of HAW with low content of cesium-134 were successfully used for manufacturing the test lots of isotope sources being now under commercial tests.

#### FRACTION RECOVERY OF CESIUM, STRONTIUM, TPE AND RE

Concurrent with the development of strontium and cesium recovery, the investigations were carried out in the field of extraction of trivalent elements. It was established that the extraction system on the basis of ChCoDiC could be also used for the recovery of TPE and RE on higher content of ChCoDiC in organic solution and at concentration of 0.5 M HNO<sub>3</sub> in initial solution of HAW.

Proceeding from the results of preliminary experiments, a combined flowsheet was elaborated for coextraction of cesium, strontium, RE and TPE and subsequent selective stripping (reextraction) of TPE-RE strontium-cesium sum. This flowsheet was tested in laboratory facility in hot boxes. A simulator of 5-fold evaporated raffinate arising from reprocessing of WWER fuel with 0.4 M HNO<sub>3</sub> was used as feed solution. Under experimental conditions by using the tetracomponent extraction system, the recovery of cesium and strontium into extract was over 99.9%, that of RE and TPE - 99.6%. The overall losses with yielding products did not exceed 4.3% for cesium, 1.5% for strontium, 0.5% for TPE and RE. The most losses of cesium were observed with strontium reextract (3.8%) and those of strontium-with cesium reextract

(1.1%). Concentrating degree of the recovered elements was about 3. The proposed flowsheet for HAW partitioning affords rather high recovery, separation of strontium, cesium, RE and TPE, as well as their purification from the impurities. At the same time, the flowsheet has some significant disadvantages: excess (3 times) of the volume of removed products as compared with the volume of feed solution, RE and TPE are not separated, low degree of concentrating the elements.

Further development of the method for the recovery of strontium, cesium, TPE and RE with using ChCoDiC resulted in the elaboration of a modified HAW partitioning flowsheet, see Fig. 2. An important distinguishing characteristic of the flowsheet is the preliminary recovery of strontium and cesium by a low flow of extractant and separate stripping (reextraction) of TPE and RE.

The extraction flowsheet for HAW partitioning was tested in the facility in hot boxes by the use of simulated solution, as well as evaporated raffinate and raffinate diluted to 0.35 M HNO<sub>3</sub> arising from spent WWER fuel. In the course of testing the flowsheet with three-component extraction system, the recovery of cesium into extract was 99.8%, strontium - 99.9%, RE - 97.8%, TPE - 99.5%. The direct yield into corresponding reextract was for cesium - 98.2%, strontium - 97.8%, RE - 97%, TPE - 97.5%. The most losses of cesium occur with reextract of strontium, and those of strontium - with cesium RE with raffinate and TPE with reextract of RE.

The concentrating degree of strontium, cesium, TPE and RE was 9.2, 9.8, 3.3 and 3.2, respectively. Losses of ChCoDiC with aqueous product range from 20 to 50 mg/l. The proposed flowsheet for complete HAW partitioning provides efficient recovery, separation of strontium, cesium, TPE and RE and purification of these elements from impurities.

Full-scale testing of HAW partitioning flowsheet including recovery and separation of RE and TPE was conducted with three-component extraction system in the same facility as in the case of testing the flowsheet for strontium and cesium recovery.

In the process of testing the partitioning flowsheet, 40 m<sup>3</sup> of 0.45 M HNO<sub>3</sub> raffinate was reprocessed which was obtained after the recovery of strontium and cesium from evaporated solution of HAW from regeneration of WWER fuel

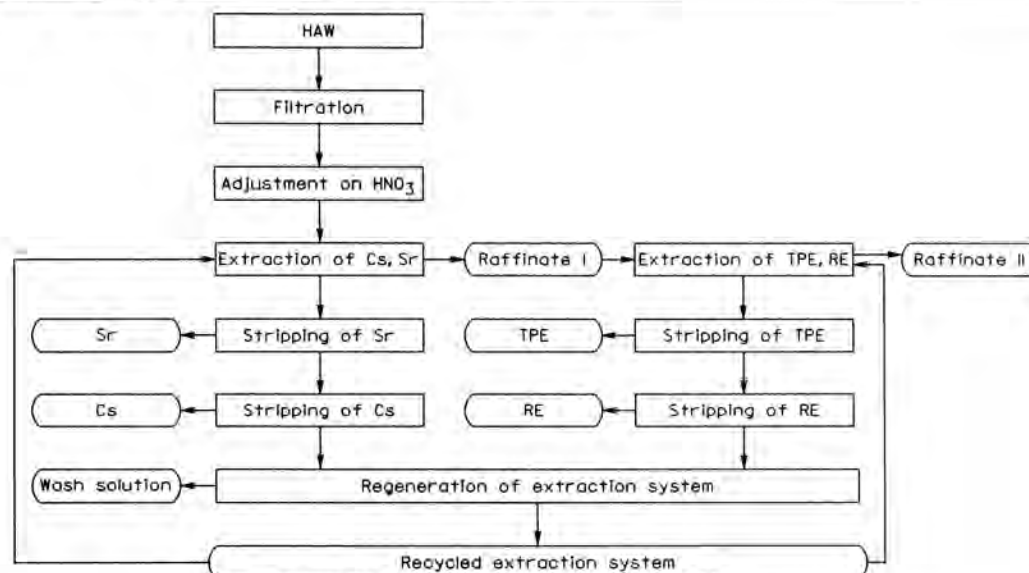


Fig. 2. Key flowsheet for HA partitioning.

and adjustment of acid content by water dilution. In the course of reprocessing, the recovery of TPE and RE into extract was 98.1%. The direct yield of TPE and RE into corresponding reextracts was 95.6% and 97.1%, respectively (according to measured losses). Rather low indices for the recovery of TPE, RE and the purification of RE from TPE are caused by design features of the extraction facility, as the number of stages in some batteries was not optimum. In the course of reprocessing, TPE concentrate was produced which contained 21 g of curium-244 and 240 g of americium-241.

#### MANAGEMENT OF SECONDARY WASTES

On realizing the partitioning flowsheets with ChCoDiC, the following products are considered as secondary wastes:

- raffinates;
- reextracts of cesium, strontium, TPE and RE;
- solutions arising from intercycle regeneration of extractant;
- recycle extractant.

Aqueous solutions are, as a rule, subject to evaporation with subsequent solidification of residues and with using distilled nitric acid for preparation of different technological products.

On testing these processes, the content and behavior of ChCoDiC and other dissolved components of the extraction system were monitored. The tests of the evaporation processes did not reveal any appreciable corrosion effect of chloride ion arising from ChCoDiC destruction on construction materials. Similar results were obtained testing the processes of subsequent solidification of residues.

According to the data of examination, the processes for treatment of aqueous products of the HAW partitioning flowsheet with ChCoDiC are fire-, explosion- and corrosion-proof.

The prolonged technological tests brought out no deterioration in quality of the extraction system on its multiple recycling. The tests have shown that it is possible not to remove the extractant from the process, but to adjust periodically its composition, as the dissolution of its components proceeds.

From the standpoint of effect on organism, polyethylene glycol, as a component of the extraction system, falls to the class of low-hazardous substances. Permissible concentration of other components of the extraction system, including ChCoDiC, is  $1 \text{ mg/m}^3$ .

#### CONCLUSION

Effective extraction technology for recovery and separation of radionuclides of strontium, cesium, rare-earths and transplutonium elements from acidic highly active wastes by using chlorinated cobalt dicarbolyde has been developed.

The proposed technology provides the recovery and separation of strontium, cesium, RE and TPE into individual flows to the degree of 99%.

The flowsheet is versatile with respect to different liquid HAW from radiochemical production. One of the important aspects of this technology is its possible use for separation of long-lived radionuclides from salted highly active wastes, what alleviates significantly the solution of problems concerning the subsequent management of these wastes. Reactants giving rise to additional accumulation of metal salts in radioactive wastes are not used in this technology.

The program of mastering the technology and synthesis of required reactants have been solved on a commercial scale.

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