

## REVIEW OF ALTERNATIVE TECHNOLOGIES FOR PRETREATMENT OF ACCUMULATED HLW

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### ABSTRACT

Accumulated liquid high-level wastes (HLW) from nuclear centers in Russia and the United States (U.S.) contain great amounts of nonradioactive salts; it is prudent to vitrify not the entire volume of these wastes, but only the concentrates of radionuclides recovered from them. For this purpose, different pretreatment technologies based on liquid-liquid extraction are under development. One such technology used chlorinated cobalt dicarbonyl (ChCoDiC) to attain the level of industrial implementation at the "Mayak" Production Association, Chelyabinsk, Russia, (Mayak) in 1996. This technology enables the recovery of cesium (Cs) and strontium (Sr) concentrate from HLW. Vitrifying the concentrated radioactive waste doubles the waste loading, thus reducing the cost of the vitrification process and subsequent monitored storage of glass canisters. However, the conversion of waste into a low-level category requires the recovery of not only Cs and Sr, but also actinides. V.G. Khlopin Radium Institute (KRI) collaborated with the Idaho National Engineering and Environmental Laboratory (INEEL) in developing two technologies that achieve this goal. The first technology uses two extractants: ChCoDiC extracts Cs and Sr in the early stage; the actinides are then recovered from ChCoDiC-process raffinate by different-radical phosphine oxide (POR-process). The second technology (UNEX-process) is based on the use of unified extractant for simultaneous recovery of Cs, Sr and actinides from HLW. This extractant is a mixture of ChCoDiC, carbamoylphosphine oxide (CMPO) and polyethylene glycol (PEG) in specially synthesized diluent – phenyltrifluoromethyl sulfone (FS-13). Both technologies have been subjected to a series of tests under dynamic conditions in multi-stage rigs of centrifugal contactors using actual HLW. Results have shown that both processes provide the conversion of waste bulk into a low-level category.

### INTRODUCTION

Among the different methods of HLW reprocessing (precipitation, sorption, chromatography, etc), the extraction processes are of special interest. As for now, the only method, which has found industrial use, is ChCoDiC extraction. Technological fundamentals of this process were jointly developed in the 1990s by the Czech and Russian specialists [1]; later, in 1996, KRI and Mayak brought the development up to industrial levels at the radiochemical plant [2]. At the Mayak industrial facility UE-35, more than 600 m<sup>3</sup> of HLW were reprocessed and about 25 million curies (Ci) of cesium and strontium were recovered. The Mayak plant is further tasked with creating a technology, which could provide recovery of actinides (U, Np, Pu, Am, Cm) and REE along with Cs and Sr.

Similar problems related to the reprocessing of accumulated acidic waste also exist at the INEEL. In the collaboration between KRI and INEEL, two flowsheets were developed and tested. One flowsheet employs ChCoDiC for Cs and Sr recovery at the first stage; the second stage involves the POR-process based on iso-amylodialkylphosphine oxide, which provides the recovery of actinides (U, Np, Pu, transplutonium elements [TPE], rare earth elements [REE] and Tc) over a rather wide range of acidities [3]. The other flowsheet is based on the so-called Universal Solvent Extraction Process (UNEX-process) intended for simultaneous recovery of actinides, REE, Cs and Sr from HLW [4]. As a result of laboratory studies, the best compositions of extraction systems meeting the requirements imposed on selectivity, chemical and radiation stability, and operational safety were established. Based on these data, flowsheets were developed and tested at pilot facilities under dynamic conditions using actual and simulated HLW.

### RESULTS AND DISCUSSION

#### Extraction of actinides, REE and technetium by iso-amylodialkylphosphine oxide

At the first stage of the flowsheet using two extractants, the ChCoDiC solution with added polyethylene glycol (PEG) is used. In the Russian practice, metanitrobenzofluoride is used as a diluent; however, because the use of nitroaromatic compounds is undesirable, a special diluent, phenyltrifluoromethylsulfone (FS-13), was developed for DOE application. This extractant was proven in a series of tests on Cs and Sr recovery from INEEL acidic waste. Raffinate arising from Cs and Sr extraction was used as feed solution for recovery of actinides, REE and Tc by different-radical phosphine oxide.

Among phosphine oxides, the short-chained phosphine oxides and the phosphine oxides with branched radicals possess rather high solubility in routine diluents; therefore, preference was given to iso-amylodialkylphosphine oxide (technical name – phosphine oxide different-radical, POR). Extraction, physical-chemical, and operational properties were studied for this extractant in different diluents.

When studying the radiation stability of POR, the extractant samples were irradiated by a dose of 2MGy. Slight changes of the extraction properties on such exposure were easily regenerated by treatment of the irradiated extractant with sodium carbonate solutions.

As a result of studying the properties of POR, some variants of its use were revealed, especially for recovery of all actinides, REE and Tc from raffinate generated upon Cs and Sr recovery by the ChCoDiC-extractant.

For application in reprocessing of accumulated HLW, scientists from KRI and INEEL tested this flowsheet using actual waste stored at the Idaho Nuclear Technology and Engineering Center (INTEC). The flowsheet involves combined extraction of actinides, REE and Tc with their subsequent combined stripping. Data on recovery of actinides and Tc are given in Table I.

Table I. Recovery of radionuclides from acidic INEEL HLW by POR-process

Element	Concentration in raffinate	Recovery
U	17 $\mu\text{g}/\ell$	99.98%
Np	4.4 $\mu\text{g}/\ell$	99.71%
Pu	< 30 Bq/ $\ell$	> 99.99%
Am	< 600 Bq/ $\ell$	> 99.99%
Tc	< 1 mg/ $\ell$	> 99%

The data of Table I show that, in combination with ChCoDiC-process for Cs and Sr recovery, the POR-process provides extraction of the main long-lived radionuclides from HLW and transforms the waste bulk into LLW category.

#### **Universal Solvent Extraction process (UNEX-process) for simultaneous recovery of cesium, strontium, actinides and REE from liquid acidic HLW**

The drawback of the POR - technology is that two extractants are needed for recovery of all the main radionuclides from HLW. Scientists from KRI and INEEL have jointly developed the Universal Solvent Extraction process (UNEX-process), which allows concurrent recovery of Cs, Sr, actinides and REE from acidic HLW. For this purpose the mixture of ChCoDiC, PEG and CMPO was chosen; it would be reasonable to assume that this mixture should extract Cs, Sr, actinides and REE. However, the mutual effect of each component on radionuclide extraction requires optimal components to be determined from among the selected class of compounds.

Based on preliminary UNEX tests results, preference was given to testing diphenyl-N,N-dibutylcarbamoylphosphine oxide (Ph2Bu2) and non-substituted PEG with short (8-10) oxyethyl chain (PEG-400), which, in combination with ChCoDiC, provide the simultaneous recovery of Cs, Sr, actinides and REE. Metanitrobenzotrifluoride or phenyltrifluoromethylsulfone can be used as diluents for this mixture. The molar ratio between ChCoDiC, CMPO and PEG is 5:1:1.

A series of studies was carried out for the selected composition of universal mixture and its efficiency was confirmed under operating conditions. The extraction properties of UNEX-extractant are shown on Fig. 1. Radiation-chemical stability, corrosion resistance and explosion-fire-safety were confirmed by special investigation, and extraction system stability was demonstrated in the course of prolonged process tests. Tests indicated that polyethylene glycol should be added at regular intervals because of its higher solubility in aqueous phase.

For stripping operation in the UNEX-process, different reagents were proposed to enable the simultaneous stripping of all the recoverable radionuclides or to produce individual fractions: Cs; Cs+Sr; actinides+REE. On the basis of these proposed reagents, the flowsheets were developed and tested under dynamic conditions on a centrifugal contactor rig using actual and simulated HLW at INTEC. One of the flowsheets with production of Cs+Sr and actinides+REE fractions is presented on Fig. 2.

The flowsheet, with combined extraction and subsequent stripping of all the recoverable radionuclides, was tested on actual INEEL HLW, because a technology capable of simultaneous extraction has been identified as a significant need by INEEL. Activity of  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$ , and gross  $\alpha$  in raffinate as a function of time is shown on Fig. 3. The test results are given in Table II.

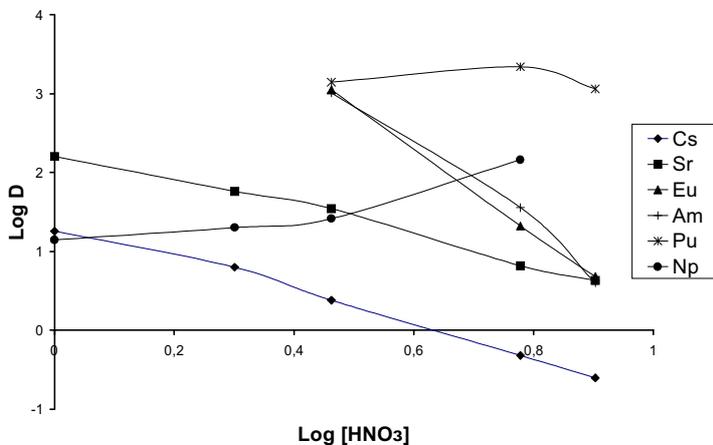


Fig. 1. Extraction of metals from HNO<sub>3</sub> by UNEX-extractant with composition of 0.08 M ChCoDiC + 0.02 M Ph<sub>2</sub>Bu<sub>2</sub> + 0.5% PEG-400 in FS-13

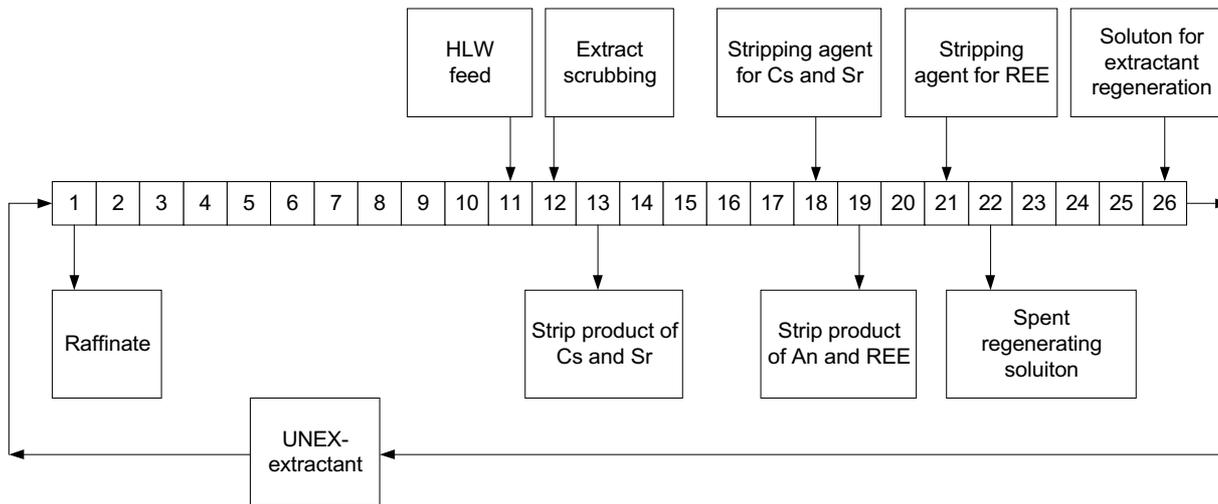


Fig. 2. UNEX-process flowsheet with recovery of fractions: Cs+Sr and actinides+REE

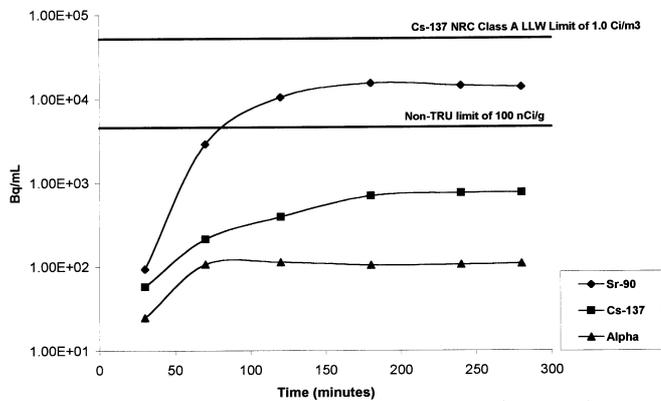


Fig. 3. Activity of <sup>90</sup>Sr, <sup>137</sup>Cs, and gross α in the raffinate as a function of time

Table II. Radionuclide distribution in UNEX-process flowsheet with combined extraction of Cs, Sr, actinides and REE

Product	<sup>137</sup> Cs	<sup>90</sup> Sr	$\alpha$	<sup>241</sup> Am	<sup>238</sup> Pu	<sup>239</sup> Pu	<sup>154</sup> Eu	<sup>99</sup> Tc
Raffinate	0.57%	0.0052%	0.040%	0.0002%	0.006%	0.002%	0.42%	81.2%
Strip product	100.6%	108.1%	100.4%	105.6%	96.9%	103%	78.6%	<0.14
Extractant	0.005%	0.005%	0.02%	0.2%	0.005%	0.0006%	0.075%	0.013%
Material balance	101.1%	108.1%	100.4%	105.8%	97.0%	103.9%	79.1%	81.3%

The data obtained on recovery of Cs, Sr, actinides and REE indicate the conversion of the majority of the waste into the low-level category suitable for near-surface storage; this classification drastically lowers the cost of HLW treatment, storage, and disposal.

## CONCLUSION

Scientists from KRI and INEEL developed flowsheets for recovery of Cs, Sr, actinides and REE from HLW. The ChCoDiC-process provides the efficient recovery of Cs and Sr at the first stage of the flowsheet based on two extractants. At the second stage, the use of iso-amylodialkylphosphine oxide (POR-process) enables the separation of actinides, TPE, REE and Tc from HLW. In combination with ChCoDiC-process for Cs and Sr recovery, the POR-process provides the conversion of most of the waste into a low-level category.

The UNEX-process, based on ChCoDiC, diphenyl-N, N-dibutylcarbamoylphosphine oxide and PEG in phenyltrifluoromethylsulfone, enables simultaneous recovery of Cs, Sr, actinides and REE from HLW. The following recovery degrees were attained in tests on actual HLW: Cs 99.4%, Sr 99.995%, and actinides 99.96%. The use of selective stripping agents in the UNEX-process allows individual radionuclide fractions (Cs, Cs+Sr, actinides+REE) to be obtained. This presents opportunities for using the UNEX-process not only for HLW management, but also for partitioning of long-lived radionuclides with the aim of their subsequent transmutation or geological disposal in the form of extremely strong matrices.

## REFERENCES

1. Galkin, B.Ya, V.N. Romanovsky, M. Kyrs, J. Rais *et al.* ISEC-88, Moscow, Nauka, 4, p. 215 (1988).
2. Dzekun, E.G, V.N. Romanovsky, V.M. Esimantovskiy, *et al.* Proceedings of SPECTRUM'96; Amer. Nucl. Society: La Grange Park, IL, p. 2138 (1996).
3. Law, V.J.D, V.N. Romanovskiy, B.N. Zaitsev *et al.* Proc. of Int. Topical Meeting on Nuclear and Hazardous Waste Management (SPECTRUM'96), Seattle, vol. 3, pp. 2308-2313 (1996).
4. Romanovskiy, V.N., V.A. Babain, T.A. Todd *et al.* "Solvent Extraction and Ion Exchange", 19(1), pp. 1-21 (2001).