

## USE OF BIDENTATE ORGANOPHOSPHORUS COMPOUNDS AND AMPHOLITIES FOR RECOVERY OF TRANSPLUTONIUM ELEMENTS (TPE) FROM HIGHLY ACTIVE WASTES (HAW)

E. G. Dzekun

Production Association "Mayak", Chelyabinsk

V. M. Gelis and V. V. Milyutin

Institute of Physical Chemistry, Moscow

I. V. Smirnov and A. Yu. Shadrin

SPA "V. G. Khlopin Radium Institute", St. Petersburg

B. F. Myasoedov and M. K. Chmutova

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Moscow

### ABSTRACT

The report presents test results of the process for recovery of TPE from HAW with ampholities and subsequent fabrication of titanate and zirconate microspheres.

The use of bifunctional neutral organophosphorus compounds is considered as an alternative method for TPE recovery. The tests conducted on a test bench of centrifugal extractors have shown that the use of diphenyl dibutylcarbamoyl methyl phosphine oxide solution in polar fluororganic diluent affords the recovery of 95.0-99.5% RE and TPE without any solubilizer. Use of complexone provides fine purification from iron and zirconium.

Solid extractants on the basis of bifunctional neutral organophosphorus compounds impregnated into a styrol divinyl benzene matrix have been obtained and tested. These solid extractants permit to recover americium and curium (98.80 - 99.95%) from the solutions of 0.5 - 8.0 M HNO<sub>3</sub>. So, the capacity of the solid extractants has proved to be 0.1 - 0.2 Mm/l.

The problem of partitioning the long-lived radionuclides of rare earth, transplutonium and alkaline earth elements (AE) and manufacturing on their basis some materials possessing high chemical, thermal and radiation stability is rather urgent because of high radiotoxicity of above radionuclides and their wide application for fabrication of radioisotope electric batteries as well. (1)

For fraction partitioning the radioactive fission products, the methods of precipitation, extraction and ion-exchange are now used. (2) One of the most promising methods for group separation of RE, TPE and AE is ion-exchange chromatography using organic ion-exchange resins in the presence of complex-forming reagents. (3)

### THE USE OF ORGANOMINERAL SORBENTS FOR PARTITIONING HIGHLY ACTIVE WASTES AND FABRICATION OF MICROSPHERES FROM RE, TPE AND AE TITANATES AND ZIRCONATES

For the containment of radioactive wastes, vitrification method is presently most often used.

Concurrent with this method, some other solidification techniques are developed for fabrication of products which are thermodynamically more stable than glass. Among such new forms of wastes are different types of ceramic materials (phosphates, zirconates and titanates of corresponding elements). (4) Synthesis of the compounds mentioned-above proceeds on annealing a charge of certain composition at the temperatures 1000°C. After annealing the product is crushed and mould at high temperature. However this procedure is technologically complicated and ecologically hazardous.

The process developed by us makes it possible to recover the fractions of RE, TPE and AE ions from spent fuel reprocessing solutions and then to obtain titanates and zirconates of these elements as microspheric particles to be suitable for further processing.

The point of the method consists in the following. The solution containing radionuclides to be disposed of is passed through a layer of organomineral sorbent (OMS) made from ion-exchange resin impregnated with titanium or zirconium dioxide. After ion-exchange saturation, the OMS is annealed

in air at 1000°C. Annealed product represents titanates or zirconate of corresponding elements in the form of spheric particles.

As feed ion-exchange resins, we used sulphocationite KU - 2 X 8 (foreign analogue to Dowex 50 X 8), carboxyl cationite (analogue to Amberlite IRC-50), aminocarboxyl cationites of VPK and ANKB (analogues to Reillex 402 and Dowex A-1, Chelex-100 respectively).

Impregnation of titanium and zirconium dioxides was conducted by means of sorption of zirconium and titanium ions from chloride or nitrate solutions on a appropriate resin with subsequent hydrolysis of metals in ionite phase with alkaline solution. The described method of synthesis enables to obtain the OMS with content 7 - 15% wt of titanium and zirconium dioxides.

Sorption of RE (La as example), TPE (Am as example) and AE ions was studied on the obtained organomineral sorbents both from nitrate solution and simulated solution of Purex-process raffinate with the following composition (g/l): Fe - 10, Ni - 1.0, Cr - 1.0, Mn - 1.0, Al - 1.0, La - 25, Ca - 2.0, Sr - 1.0, Ba - 1.0, Cs - 2.0, HNO<sub>3</sub> - 3 M.

The obtained results show that on sorption from pure solutions the values of ion-exchange capacity agree reasonably well for the OMS and appropriate ion-exchange resins, what is indicative of non-exchange character of coupling between titanium or zirconium dioxides and ionite phase.

For the selective sorption of RE, TPE and AE ions from simulated solution, a method of ion-exchange chromatography in the presence of complexforming reagents (3) was used. Separation of RE, TPE and AE radionuclides from accompanying elements and their group fractionation could be attained by varying the composition of feed solution and sorption conditions. The main parameters to be varied involve type and concentration of complexforming reagents, pH and temperature of solution, filtration rate and ionite granulation.

So, on sorption of radionuclides from the simulated solution on VPK resin in the presence of citric acid, the selective sorption of RE and TPE occurs at pH = 2 - 4, AE - at pH = 6 - 8. Further intergroup separation of RE, TPE and AE ions could be performed by a method of displacement complexforming chromatography.

In order to study the behavior of the OMS saturated with radionuclides on heating, the sorbents were subjected to thermogravimetric analysis over the temperature range 22 - 1000°C at heating rate of 7.5°C/min. We studied the ionites KU - 2 x 8, VPK and KB - 4P - 2 in TiO<sub>2</sub>-form saturated with strontium, neodymium and americium ions, as well as ionite VP in ZrO<sub>2</sub>-form saturated with strontium and europium ions.

The conducted investigations disclosed that on heating the OMS the following processes take place: dehydration (22 - 300°C); decomposition and combustion of organic matrix (300 - 600°C); solid-phase synthesis of compounds (600 - 1000°C). X-ray phase analysis of specimens annealed at 1000°C indicates that on using the OMS on VPK and KB - 4P - 2 basis, solid phase consists of titanates and zirconates of corresponding metals, while the occurrence of extraneous phase being not observed. The annealed products are mechanically strong spheric particles of light grey color of 0.2 - 1.0 mm size.

After annealing of Sr-form KU - 2 X 8 (TiO<sub>2</sub>), in solid phase there were detected sulphate, sulphide and titanate of strontium, while the annealed products involving a sintered mass adherent to crucible walls, what is indicative of unsuitability of sulphocationites for solving the posed problem.

Hence, the complex of conducted investigations enables to offer more effective and safe method for fractionation of RE, TPE and AE radionuclides with subsequent transformation into ceramic materials in a form convenient for further processing.

## BIFUNCTIONAL ORGANOPHOSPHORUS COMPOUNDS

### Composition and Properties of Extraction Mixture

Bifunctional neutral organophosphorus compounds (BNOPC) such as diphosphine dioxides and carbamoylmethylene phosphine oxides (CMPO) are capable of extracting RE and TPE from strongly acidic media. Maximum extractability for RE and TPE and minimum one towards nitric acid are demonstrated by BNOPC with aryl substituents in phosphorus atom ("abnormal aryl effect"). Principal drawback of BNOPC as extractants is concerned with low solubility of their solvates with metals in routine diluents.

The usual way for improvement of compatibility of solvates with diluent is based on introduction of alkyl substituents into molecule of extractant or solvating additives of TBP type in diluent. This method was applied when elaborating the extraction system octylphenyl-N, N-diisobutyl methylene car-

bamoyl phosphine oxide - TBP - kerosene. However this system has also some disadvantages:

- synthesis and purification of extractant are very complicated;
- it is necessary to wash out acidic impurities formed on TBP hydrolysis from recycle extractant.

There is also another way for increasing the solubility of solvates with polar organic diluents. Such extraction system makes it possible:

- to abandon the solubilizers;
- to use the easily available and cheap diphenyl-N, N-dibutylmethylene carbamoyl phosphine oxide;
- to eliminate an operating of alkaline washing-out the recycle extractant;
- to decrease efficiently explosion and fire risk of the process.

High solvating ability of polar fluororganic diluents has a pronounced effect on the extraction properties of CMPO, increasing the distribution coefficients of metals and changing the dependence of distribution coefficients on acidity of aqueous phase (Fig. 1).

The use of polar fluororganic diluents permits to add solutions containing 1 M CMPO without occurring the third phase even under the complete saturation of extractant with metal.

### Test Results of the Flowsheet with BNOPC

The conducted investigations have indicated that for HAW processing it is reasonable to use solutions containing 0.25 - 0.45 M diphenyl-N, N-dibutylmethylene carbamoyl phosphine oxide in polar fluororganic diluent. The extractant

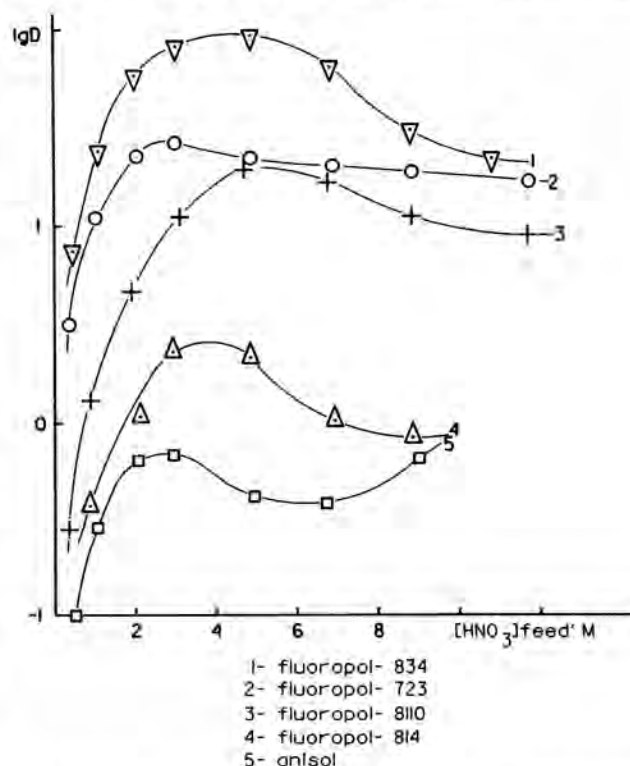


Fig. 1. Extraction of Eu (III) by 0.1 M solution of diphenyl-N, N-dibutylcarbamoyl methylene phosphine oxide in different diluents.

of such composition affords to recover rare-earth and actinide elements for 3 M HNO<sub>3</sub> with distribution coefficients of 100 - 10000. In this case, iron (III) and zirconium (IV) are coextracted to a considerable degree. For their separation, the introduction of complexone into feed or washing solution is needed.

Proceeding from the data on distribution of metals and acid under static conditions, two variants of the flowsheet for the recovery of RE and TPE from HAW were proposed in order to carry out the test within the continuous regime on 18-stage test bench of centrifugal extractors:

- selective stripping of iron and zirconium by a solution of complexone in acid (Fig. 2);
- selective extraction of RE from simulated solution containing a complexone which binds iron and zirconium (Fig. 3).

Aqueous simulated solution contained all the principal components of evaporated Purex-process raffinate (reprocessing of WWER fuel) as follows:

RE	14 g/l;
Fe	6 g/l;
Zr	3 g/l;
HNO <sub>3</sub>	4.6 M.

Extraction was performed at 5 stages, washing-out at 1 - 3, stripping at 6 - 10 stages. In all cases, washing solution contained 0.8 - 1 M HNO<sub>3</sub> with complexone addition, water was used for stripping.

The results of enlarged laboratory tests (reprocessed 40 l of simulated solution; organic phase subject to 50 recycles) have shown that both variants of the flowsheet provide 99.5 - 99.8% recovery of RE from HAW and production of strip solutions (reextracts) containing up to 10 g RE/l at pH 1 - 2. Purification coefficients of RE from iron are over 1000 and those from zirconium - over 100.

In the case of combination of wash solution and raffinate, the accumulation of zirconium on extraction stages was observed, what led periodically to the occurrence of PE in raffinate or zirconium in strip solution (reextract). The removal of wash solution into a separate flow provided more steady operation of equipment, but resulted in loss 6% RE with wash solution.

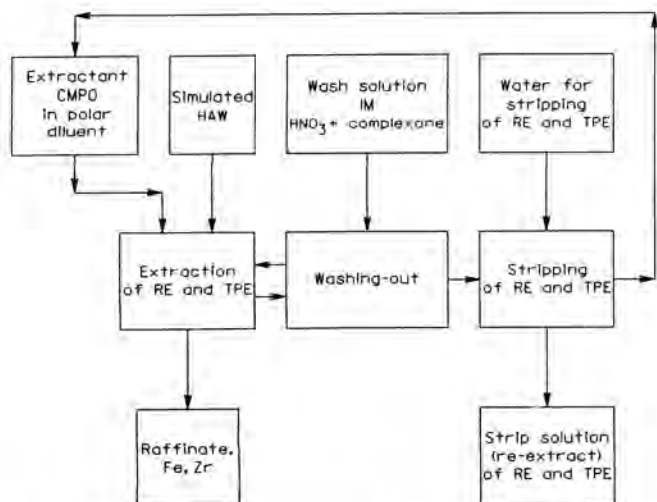


Fig. 2. Flowsheet for recovery of RE and TPE from HAW with separation from iron and zirconium.

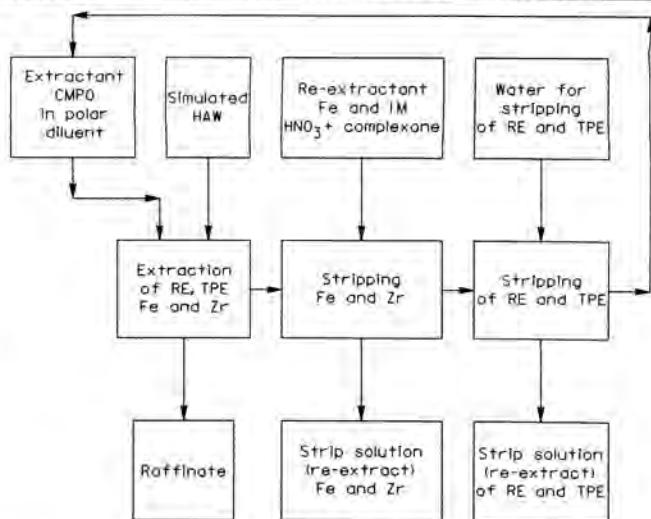


Fig. 3. Flowsheet for deep recovery of RE and TPE from HAW.

The obtained results enable to offer improved variant of extraction recovery of RE and TPE from HAW (Fig. 4). Realization of this flowsheet would allow to recover from strongly acidic media up to 99.8% RE and TPE, to purify them from iron and zirconium and transfer into weakly acidic strip solution (reextract).

Stripping of uranium, plutonium and neptunium which are practically not stripped with water could be performed by ammonium carbonate solution or complexone within periodical regime.

#### Using the Solid Extractants on BNOPC Basis

The attained degree of TPE recovery from HAW (99.8%) could be insufficient to assure the safety for final disposal. Further purification of raffinate is well to conduct by using the solid extractants on BNOPC basis.

We have developed a solid extractant on the basis of bifunctional extractant HA-231 which provides efficient recovery of RE and TPE from strongly acidic media (Fig. 5). Full capacity of solid extractant towards europium is about 50 mg/g. RE and TPE are desorbed by water, uranium, plutonium and neptunium - by a complexone solution. The above solid extractant features high radiation and chemical stability. By passing 1000 c. v. 3 M HNO<sub>3</sub> through the solid extractant, its extractability decreases by 10%, gamma-irradiation doses up to 10<sup>5</sup> Gy does not practically affect the extractant properties.

Possible use of the HA-231 solid extractant TPE and RE recovery has been tested for a real solution containing 100 mg/l Am, 12.5 mg/l Cm, 150 mg/l Pu and 170 mg/l RE in 1.2 M HNO<sub>3</sub>. From such solution (7 c. v.) up to 99% RE and TPE were recovered and about 90% - desorbed with 2 c. v. water. Desorption degree remained unaffected on increasing the exposure time before desorption from 1 hour up to 70 hours, although the radiation loading on the solid extractant was 20 kGy for 70 hours.

Besides RE and TPE, the HA-231 affords recovery of iron (III) and zirconium from strongly acidic media. Interfering effect of these elements can be overcome by introduction of adequate complexones into feed solution.

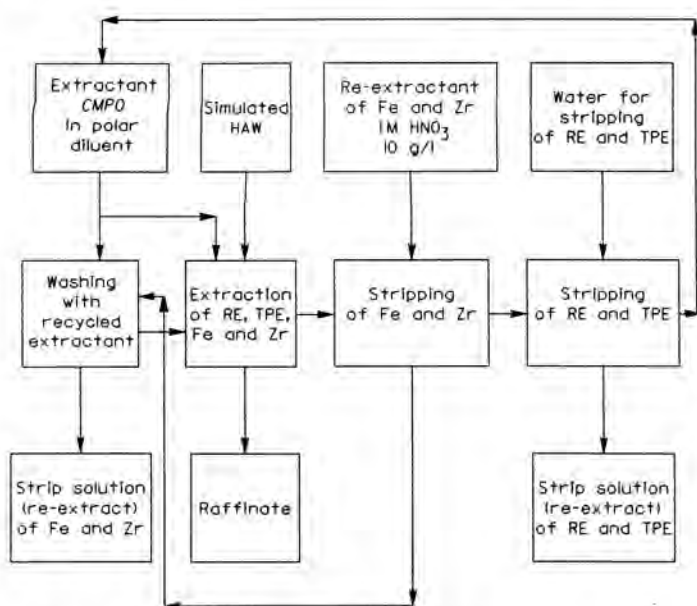


Fig. 4. Flowsheet for deep recovery of RE and TPE sum from HAW with purification from iron and zirconium.

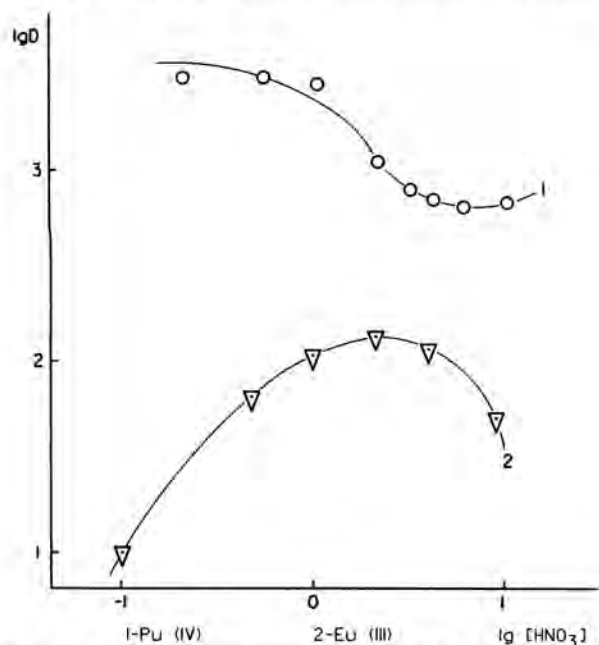


Fig. 5. Sorption of europium (III) and plutonium (IV) on impregnated solid extractant.

#### Using the Combination of Liquid Extraction and Solid Extractants on BNOPC Basis

The conducted investigations permit to suggest the following version for deep recovery of RE and TPE from strongly acidic media of complex salt composition:

- extraction of the major amount of RE and TPE (over 99.5%) with the solutions of diphenyl-N, N-dibutylcarbamoymethylene phosphine oxide in polar fluororganic diluent;
- further recovery of RE and TPE from raffinate on the HA-231 solid extractant with recycle of eluates to extraction reprocessing.

In our opinion, such flowsheet would afford the recovery ratio of RE and TPE from HAW over 99.998% and their transfer into strip solution (reextract) with pH 1 - 2, being convenient for subsequent processing. The proposal flowsheet for RE and TPE recovery could be used for radiochemical HAW reprocessing, as well as for purification of waste from laboratories and research centers.

Preliminary estimates have shown that the expenses for synthesis of extractants under laboratory conditions for the proposed flowsheet come up to the following:

- the extractant on the basis of CMPO and fluoropol-732 US \$600 per 1 kg, i. e. US \$2.5 per 1 l reprocessed HAW; the HA-231 solid extractant US \$2000 per 1 kg, i. e. US \$1 per 1 reprocessed HAW.

When passing from laboratory scale to semicommercial (pilot) synthesis of BNOPC, the expenses could be decreased by a factor of 2 - 5.

#### CONCLUSION

The conducted investigations have enabled to propose a method for fractionation of RE, TPE and AE by OMC with subsequent conversion into ceramic matrices in a form convenient for further processing.

Besides, a new approach to using BNOPC for RE and TPE recovery from HAW by means of extraction and sorption on solid extractants is offered. The use of polar diluents permits to employ BNOPC in two-component extraction systems suitable for the production of solid extractants without occurring the third phase of BNOPC solvate with RE.

The performed enlarged laboratory tests have confirmed promise for the proposed approaches to the problem solution.

#### REFERENCES

1. T. S. MURTHY, Proc. Nucl. Chem. and Radiochem. Symp. Andha Univ., Waltair, Febr., 25-28, 1980, p. 65-84.
2. K. W. CARLEY-VACACILY, "Solv. Extr. and Ion Exch. Nucl. Fuel Cycle", Chichester, 1985, p. 127-135.
3. L. TOTH, Radiochem. and Radioanal. Lett., 1983, v. 59; 4, p. 245-251.
4. YANG, LI J., K. SRIOHAR, R. RUSTUM, Nucl. Waste Manag. Prac., 2nd Internat. Symp., Chicago, III, Apr. 24-27, 1983, Columbus, Ohio, 1984, p. 159-169.