

PHYSICO-CHEMICAL AND EXTRACTION PROPERTIES OF CHLORINATED COBALT DICARBOLYDE (CHCODIC), EXTRACTION MECHANISM, MATHEMATICAL SIMULATION OF THE PROCESS

V. N. Romanovskii and L. N. Lazarev
SPA "V. G. Khlopin Radium Institute"

V. V. Romanovskii
Leningrad Technological Institute
St. Petersburg, Russia

ABSTRACT

Physico-chemical and extraction properties of ChCoDiC are reviewed. It is shown that ChCoDiC exhibits some features which enable to use it in extraction technology of liquid HAW processing with the obtained fractions of cesium, strontium, rare earth (RE) and transplutonium elements (TPE).

Synergetic effect of polyethylene glycols on extraction of alkaline-earth and rare-earth elements is investigated. The introduction of them into extraction systems makes it possible to develop a combined flowsheet for nitric-acidic HAW reprocessing which provides selective and complete recovery of long-lived radionuclides fractions.

The data on the investigation of complex formation of these elements by means of conductivity, high-frequency dielectricity and infrared spectroscopy are presented. Stoichiometry of cesium, strontium and cerium complexes with ChCoDiC is revealed.

On the basis of spectroscopy and extraction data, the flowsheets of extraction equilibria are proposed, and the programs for calculation of extraction flowsheets and mathematical model of the process are developed.

INTRODUCTION

Closed nuclear fuel cycle (NFC) envisages the management of liquid HAW including the major part of spent fuel radioactivity with the most hazardous long-lived radionuclides.

Concepts for management of long-lived radionuclides which are now under development in our country involve preliminary stage of HAW partitioning with separation into individual fractions of cesium, strontium, transplutonium (TPE) and rare-earth (RE) elements. (1)

The development of a combined flowsheet for HAW partition remains up to now the urgent problem of spent nuclear fuel reprocessing. One of such flowsheets is based on the extraction process with ChCoDiC as extractant which was advanced for these purposes by Soviet and Czechoslovak investigators. (2, 3)

For the last 10 years, the scientists of Radium Institute in cooperation with the specialists of radiochemical plant have brought up this design up to the tests on commercial scale. (4) At the same time the improvement of extractant blend, some operations in the process and control system requires thorough study of physico-chemical basis of carborane extraction, process mechanism and stoichiometry, as well as development of mathematical simulation of extraction equilibrium.

The subject matter of the report is generalization of recent studies of physico-chemical fundamentals for extraction by carborane extractants based on ChCoDiC.

SYNTHESIS OF CHCODIC

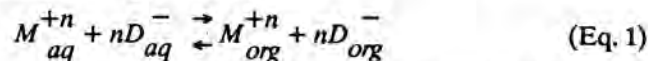
Carborane complex in anion form is synthesized from orthocarborane by the elimination of BH-group when boiling in methanol in the presence of sodium alkaline and by the reaction of formed acid with cobalt chloride in strongly alkaline medium. Reactant is obtained as cesium salt and then is converted into acidic form by contacting nitrobenzene solution with 8 M nitric acid.

Halogen derivatives of polyhedral carborane complex (6-7 chlorine or bromine atoms have stronger chemical and radiation stability) (6); therefore, mastering the chlorination reaction of cobalt dicarbolyde (2) allows next to use chlorinated cobalt dicarbolyde for radiochemical purposes.

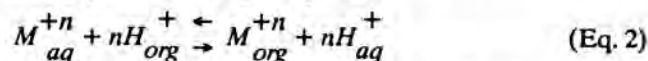
DESCRIPTION OF THE EXTRACTION PROCESS OF METALS BY CHCODIC

Salts of dicarbolyde complex anions, in particular cobalt salts dissolved in polar solvents of nitrobenzene type, are dissociated to a great extent and are very stable in chemical and radiation respect. (5) These properties permit to use these compounds as extractants, of metal cations.

In the presence of cobalt dicarbolyde in anion form (D^-), cations are extracted into nitrobenzene as ion pairs according to the following reaction:



Extraction process runs by substitution of H^+ for M^{+n} between aqueous and organic phases:



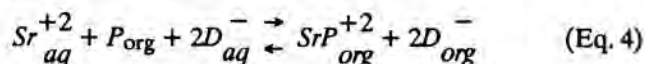
In case $C_{M+n} \ll C_{H+D}$; $H^+_{org} = D^-_{org} + C_{H+D}$ distribution coefficient is

$$D_M = K_{nH}^M \cdot \frac{C_{H^+D}^n}{C_{Haq}^n} \quad (\text{Eq. 3})$$

where K_{nH}^M - equilibrium constant of extraction exchange.

For cesium $\lg K_{nH}^{Cs} \sim 10^2$. This indicates that for efficient recovery of cesium from acidic solutions (up to 4-6 M HNO_3) the concentration of extractant could be about 0.01-0.1 M.

For the recovery of strontium from 0.5 M HNO₃ with distribution coefficient of about 2, the concentration of extractant should be rather high (0.5 M). In the course of further investigation a synergetic effect has been observed which results in complexformation between cations of strontium, barium and trivalent elements (TPE and RE) and compounds of polyethylene glycols type. The formed complexes pass to organic phase more efficiently than free ions according to the reaction:



where P - molecule of polyethylene glycol (PEG).

In the case of TPE and RE extraction at low concentrations of polyethylene glycol, the complexes of MD₃P type predominate. At higher concentrations of PEG, these complexes react further with 1-2 molecules of PEG and the compounds of expected composition MD₃P₂ and MD₃P₃ are formed.

STOICHIOMETRY OF CHCODIC EXTRACTION

Optimizing the combined flowsheet for HAW processing by experimental means is hindered by large amounts of components in aqueous and organic phases. The simulation of process calls for the development of specific calculation programs of equilibrium constants and equilibrium composition in extraction systems. This, in turn, involves using not only extraction data, but also spectroscopic ones for refinement of reaction stoichiometry in a two-phase system.

On analyzing the spectra of metal extracts in near IR-region, regular change of optical density is revealed depending on changes in metal concentration of 1920 nm line assigned to B-H bond overtone. This dependence proved to be a linear function:

$$\begin{aligned} d_{Cs} &= -3.355 C_{Cs} + 0.62 \\ d_{Sr} &= -4.56 C_{Sr} + 0.58 \\ d_{Ce} &= -3.15 C_{Ce} + 0.62 \end{aligned} \quad (\text{Eq. 5})$$

It can be shown that the average number of ChCoDiC molecules added to metal ion is determined from the expression:

$$n = \frac{d_{MDn}}{d_{HD}^{\rho}} \cdot \frac{C_{HD}^{\rho}}{C_{MDn}} - A \frac{C_{HD}^{\rho}}{d_{HD}^{\rho}} \quad (\text{Eq. 6})$$

where

- HD - denotes ChCoDiC in H-form;
- MD_n - complex of metal with ChCoDiC; the index "o" refers to solution without any metal;
- d - optical density;
- C - concentration of component in solution;
- A - angle coefficient in expression (5).

According to the expression (5), the following values of averaged number of ligands were obtained:

- Cs - 1.01 ± 0.02
- Sr - 1.96 ± 0.04
- Ce - 3.01 ± 0.02

So, the spectroscopic data have confirmed the stoichiometry of complexformation of ChCoDiC with cesium, strontium

and cerium (III), which was earlier determined by extraction method. These data were used for the development of mathematical model for the extraction system on ChCoDiC basis.

DIELECTRIC CONSTANT OF CHCODIC SOLUTIONS

For calculating the extraction constants, the dependence of dielectric constant of ChCoDiC solutions in nitrobenzene on extractant concentration was studied (Table I).

TABLE I

Dielectric Constant of ChCoDiC Solutions (E) in Nitrobenzene at 90 MHz Frequency, T = 298°K

C, $\frac{M}{dm^3}$	0.029	0.059	0.08	0.097	0.12	0.159	0.21	0.23	0.27	0.30
E	33.2	31.0	29.8	28.3	26.3	24.9	22.8	20.3	19.6	17.6

The dependence is linear and could be described by the equation:

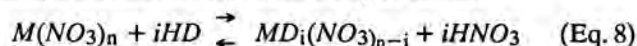
$$E = 34.06 - 55.9 \cdot C \quad (\text{Eq. 7})$$

The maximum deviation of calculated values from experimental one is no more than 5%. On mathematical simulation for extraction distribution of metals, non-ideality of organic phase is taken into account by introduction into calculation of concentration constant of activity coefficient depending on dielectric penetrability of medium.

MATHEMATICAL MODEL FOR EXTRACTION OF METALS BY CHCODIC

On the basis of extraction, spectroscopic and dielkometric data, a mathematical model has been developed for the extraction system on the basis of ChCoDiC with the aim of calculating separate cascades and flowsheet as a whole and designing the automatized system for the control of technological process.

The mathematical model is based on matrix representation of chemical equilibria which occur in the system between metal ions to be extracted, protons, nitrate-ions and ChCoDiC anion. (7) Extraction of metals proceeding through the ion-exchange mechanism is presented by equation:



The influence of changes in dielectric constant of solution on metal extraction was allowed for according to the equation:

$$\lg K_{ex}^M = \lg K_{ex}^{M,O} + A (E_o - E) \quad (\text{Eq. 9})$$

where

- $\lg K_{ex}^{M,O}$ - constant of metal extraction in infinitely diluted diluent;
- A - parameter;
- E_o and E - dielectric constant of diluent and solution respectively.

Mass action law in a matrix form is presented as follows:

$$A \cdot \bar{E} = \bar{E}C \quad (\text{Eq. 10})$$

where

\overline{EC} - concentration logarithm vector of obtained forms;

\overline{E} - concentration logarithm vector of base forms.

The equation of material balance could be described as:

$$A^T \cdot 10^A \cdot \overline{E} + 10^{\overline{E}} = C \quad (\text{Eq. 11})$$

where C - vector of analytical concentrations of base forms.

At each point of concentration dependence of distribution coefficients the equation system (11) should be solved, and metal distribution coefficient is calculated as the ratio of equilibrium metal concentrations in organic and aqueous phases.

For determining the concentration constants of extraction by means of Fletcher-Powell method (8), end function is minimized and distribution coefficients are calculated.

Concentration constants were determined for wide region of extractant and nitric acid concentrations. Then the approximation of logarithms for concentration constants of cesium extraction was conducted by the following expression:

$$K_{ex} = K_{ex}^T A (E_0 - E) + B\sqrt{I} \quad (\text{Eq. 12})$$

where

K_{ex}^T - thermodynamical constant of extraction;

A and B - parameters of approximation for change in dielectric constant of extractant and for ionic strength of aqueous phase;

I - ionic strength of aqueous phase.

As a result, the following values of extraction constant and parameters were obtained:

$$K_{ex}^T = 2.73 \pm 0.04; A = -0.009 \pm 0.002; B = 0.30 \pm 0.002.$$

The obtained data were used particularly for calculation of distribution coefficients cesium macroamounts, which agreed closely with experimental data (Table II).

With regard to the formation of some forms of complex compounds of TPE and RE in the systems containing ChCoDiC and PEG in nitrobenzene, analogous models were elaborated on americium and europium examples. (9) As in the case of cesium, the results have confirmed the satisfactory predicative features of the model.

EFFECT OF COMPLEXONES ON EXTRACTION OF METALS BY CHCODIC

The subject of improving the flowsheet for separation of cesium, strontium, TPE and RE from HAW is optimizing the stripping operation for cesium exhibiting the most affinity to organic phase. For efficient scrubbing of cesium from extractant, strong nitric acid solutions of hydrazine are used (2), which involve many technological difficulties. Therefore, some attempts were undertaken in order to suppress the cesium extraction by introduction of complexones in the system.

Investigating the influence of 0.03 M sodium diethylenetriamine pentaacetate (DTPA) on extraction of cesium and RE has shown, that at 0.3-0.5 M HNO₃ in aqueous phase the introduction of complexone decreases the distribution coefficients of cesium by a factor of 7, while the distribution coefficients of cerium (III) do not practically change. It is hoped that the difference in behavior of the elements under these conditions is connected with the formation of ChCoDiC-DTPA complexes and with the different complexformation between metals of I and III groups and DTPA.

Such complexones as ethylenediamine diacetic acid (EDDA) and nitrilotrimethylene phosphonic acid (NTP) suppress extraction more efficiently, decreasing the distribution coefficients of cesium by factors of 20 and 40, respectively.

The use of a particular complexone enables to strip cesium effectively under rather soft conditions and to concentrate it in small volumes.

TABLE II

Dependence of Cesium Distribution Coefficients (D_{Cs}) on Initial Concentration of Cesium in Aqueous Phase When Extraction by 0.097 M ChCoDiC Solution in Nitrobenzene from Nitric Acid

C_{Cs} , M/dm ³	CHNO ₃ , M/dm ³	D_{Cs}^{calc}	D_{Cs}^{exp}	Error, %
0.001	5.0	3.503	3.74	6.3
0.01		3.268	3.27	0.06
0.05		2.268	2.56	11.4
0.1		1.728	1.63	-6.0
0.5		0.223	0.259	14.1
0.001	0.5	272.7	242.0	-12.7
0.01		257.1	247.5	-3.9
0.1		113.1	128.9	12.3
0.001	1.0	133.8	126.3	-5.9
0.01		133.7	116.9	-14.3
0.1		63.3	54.1	16.9

ON SOME PROMISING MIXTURES OF CHCODIC WITH CROWN ETHERS

Further improvement of HAW reprocessing technology with using ChCoDiC involves also search for polyoxocompounds as alternatives to polyethylene glycol Slovafo-909 nonylphenylpolyethylene glycol), the most widely used in flowsheets with ChCoDiC.

For this purpose, a variety of polyoxocompounds, ethylene glycol ethers, oxyethyl amines and Crown ethers (10) was studied. In HAW reprocessing, principal interest may be expressed in the mixtures of ChCoDiC with 15-Crown-5 which provide the most complete recovery of europium and americium, as well as the mixtures of ChCoDiC with 18-Crown-6 which provide separation factors of 4-6 for "europium-americium" pair.

For these mixtures, the dependences of distribution coefficients and separation factors on concentration of europium nitrate in aqueous phase were determined which disclosed the preservation of selective properties of mixtures when passing from microconcentrations to macroconcentrations.

The obtained results give grounds for consideration of the investigated modified systems on ChCoDiC basis as promising ones for extensive use of this method for HAW partitioning.

CONCLUSION

Investigation of physico-chemical and extraction properties of the systems on ChCoDiC basis has revealed the possibilities for using them in recovery of cesium, strontium, TPE and RE fractions from HAW.

Extraction, spectroscopic and dielkometric data on ChCoDiC extractants make it possible to develop a mathematical model of the process for calculating the optimum flowsheets and designing the control system.

For improvement of individual operations in the flowsheet, the effect of complexones has been studied. So, it was shown that such complexones as DTPA, EDDA a. o. could be used for suppression of cesium extraction on the stage of scrubbing from organic phase.

For optimizing the composition of extractants on ChCoDiC basis, the mixtures with some polyoxocompounds have been studied; the most promising proved to be mixtures

with 15-Crown-5 resulting the most complete recovery of europium and americium and mixtures with 18-Crown-6 providing the high separation factors of TPE and RE (4+6).

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