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ZIRCONIUM AND TECHNETIUM RECOVERY AND PARTITIONING IN THE PRESENCE OF ACTINIDES IN MODIFIED PUREX PROCESS FOR ATW PROGRAM

Final report

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DISCLAIMER

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CONTENTS

ITRODUCTION

In previous report Modified Purex process has been proposed for reprocessing of spent actinide and technetium oxides, irradiated in water loop, as a part of ATW project. The flowseet is based on combination of all irradiated materials, their jont dissolution and reprocessing as a NPP spent fuel solution with abnormal plutonium content after addition of recycled depleted uranium concentrate.

Some groups of long-lived radionuclides could be completely recovered and localized even at the stage of extraction reprocessing using 30% TBP. Studies in this field were conducted for 10 years with the aim of developing the process for recovery, concentration and localization of U, Pu, Np, Tc and Zr within 1st extracton cycle. Transplutonium actinides are recovered from high-level raffinate of this cycle after evaporation and feed ajustment.

This technology has been specified as "Modified Purex process".

Modified Purex-process was based on four technological techniques:

1. Specific behviour of Pu and Np at high solvent loading with U.
2. Maximum recovery of Zr and Tc in the head extractor with their further removal into individual flows.
3. Stripping of Pu and Np by using a new salt-free complexing agent without interaction with Tc.
4. Separate stripping of Pu and Np with the use of U(IV) at various concentrations of Tc.

Originally this process has been developed (and is improved as yet) for new NPP spent fuel reprcessing plant RT-2 (Krasnoyarsk, Siberia) for treatment of highly burned-up nuclear fuel, securing on its ecological acceptability, including waste partitioning and their separate disposal. The aims of the process are in many aspects similar to ATW transmutation program; in this way recovery of uranium and plutonium with hard isotope proportion and their reuse in NPP fuel cycle is assumed to be a first step of total actinide transmuting.

Several variants of Modified Purex process, elaborated with the use of simulated solutions and tested on real solutions of LWR(WWER) spent fuel were reported previously. This paper is aimed to give some evidence on possibility of deep element recovering and initial step of their partitioning in the first cycle.

1. THEORETICAL AND EXPERIMENTAL BACKGROUND OF HEAD OPERATIONS

1.1 Interaction between actinides in extraction process

In the Purex process nitric acid, actinides, fission products and impurities are contacted with 30% TBP in diluent which is loaded with uranium from 0 to 100g/l and sometimes up to 110g/l. It corresponds to less than 90% of the maximum theoretical solvent loading. The reported data at high uranium content are not numerous, their number decreasing **with saturation level.**

The investigation were performed on extraction of nitric acid, actinides and some other elements by TBP at high loading with uranium up to full saturation in equilibrium with solid uranyl nitrate.

At the ultimate TBP loading and namely in equilibrium with solid uranyl nitrate, HNO_3 is dissolved in organic phase due to hydrogen bond with nitrate-group of uranyl nitrate-TBP disolvate. At lower uranium concentrations HNO_3 is extracted by means of formation of hydrogen bond with free P=O groups. In the range of uranium concentration 90-110g/l both variants of HNO_3 extraction by 30% TBP can take place. Consequently, HNO_3 distribution through extraction stages will deviate from the distribution predicted by classical model, the deviation increasing with uranium concentration in the solvent.

The equation of HNO_3 extraction for (5-100)% TBP solutions saturated with uranyl nitrate is as follows:

$$Y_H = [D_{nd}X_{nd}/C_w + 2K_dD^2_{nd}(X_{nd}/C_w)^2]S,$$ where

X_{nd}, C_w -concentrations of non-dissociated HNO_3 and water in aqueous phase, M;

Y_H - concentration of HNO_3 in organic phase, M;

S - concentration of uranyl nitrate solvate with TBP, M;

D_{nd} - distribution coefficient of undissociated HNO_3 monomer;

K_d - dimerization(association) constant of HNO_3 in organic phase, l/M.

Another important phenomenon that is peculiar to the zone of the high solvent loading with uranium, is connected with the significant difference between Np(IV) and Th(IV) distribution ratio (D), though they approximate to each other at lower uranium concentrations (Fig. 1.1). It has been also observed that the distribution ratios of Pu(IV) and Np(IV) depend on the concentrations of these elements at fixed uranium and nitric acid contents. For instance, the increase of Pu concentration from 100 to 500mg/l causes increase D_{Pu} by a factor of 1.5 (100g/l of uranium and 126g/l of nitric acid in aqueous phase). Under similar conditions, the increase of distribution ratio for tetravalent neptunium is 4-5 times (Fig. 1.2). For tetrava-

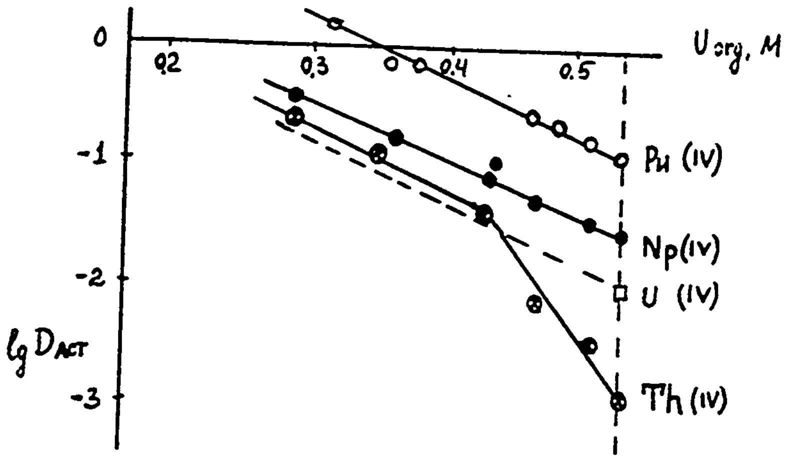


Fig.1.1. Dependence of tetravalent actinides distribution coefficients on uranyl nitrate concentration in organic phase at high loading.

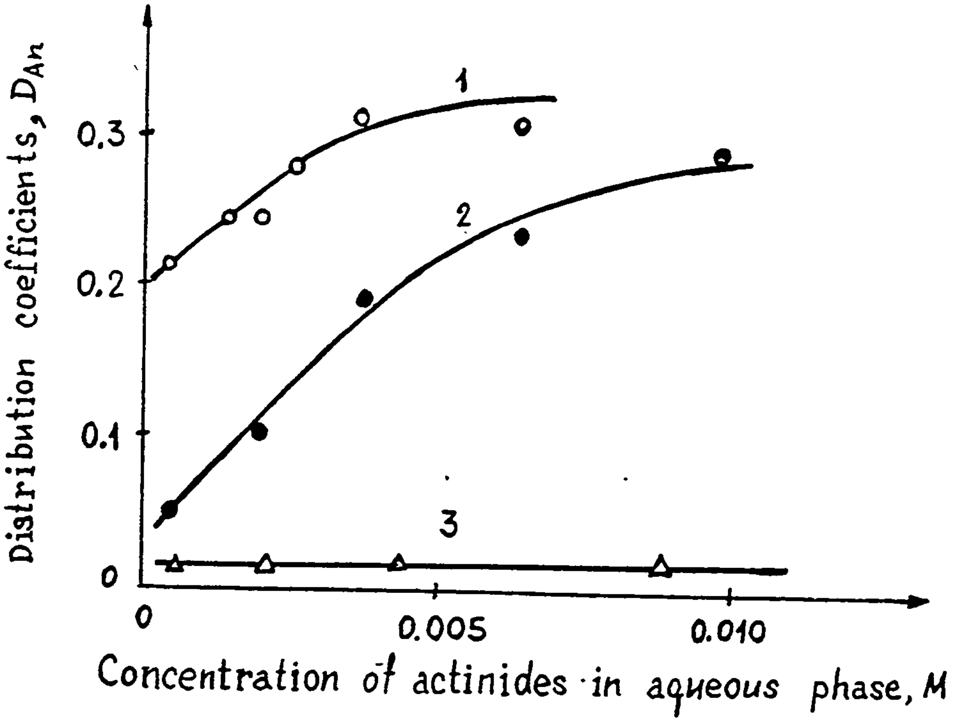


Fig.1.2

Extraction of tetravalent actinides by 30 % TBP in dodecane at

T = 20 °C; X_U = 0.42 M, X_{HNO_3} = 2 M.

1 - Pu (IV); 2 - Np (IV); 3 - Th (IV)

lent thorium the concentration dependence of distribution ratio has not been observed.

Neptunium exhibits the above effect in a definite acidity and temperature range. For Pu(IV) distribution the temperature dependence at high uranium saturation is under investigation.

On the base of the obtained experimental data a correction to mathematical model of extraction equilibria has been proposed with allowance for the behaviour of plutonium, and also neptunium in the range of high uranium concentations. Namely, the distribution of Pu(IV) at extraction by TBP from uranyl nitrate and nitric acid aqueous solutions is described by the ROZEN-ZELVENSKY model. The experimental verification showed that in the presence of uranium this model is quite correct at plutonium concentration below $4*10^{-3}$M. Processing of the experimental data at higher concentrations leads to the equation:

$$K^{*}_{Pu} = K_{Pu}[1 + (AX_{U}^{3}X_{Pu}/1+AX_{U}^{3}X_{Pu})],$$ where

K^{*}_{Pu} and K_{Pu} - concentration constants of Pu(IV) extraction equilibrium for the refined and original model, respectively;

X_{U}; X_{Pu} - concentrations of uranium and plutonium in aqueous phase, M;

A - coefficient.

Correction for Np(IV) has a more complicated form than for Pu(IV).

Application of corrected model is of importance for critical aspects. Uranium and plutonium distribution in the head extraction unit under normal conditions is well studied. However, with abnormal increase of the feed flow, uranium and plutonium concentration profiles start moving in the direction of raffinate exit. If the feed flow grows twice and higher as to the nominal value, uranium and plutonium rapidly fill all the stages of the mixer-settler and pass into raffinate. In this case, plutonium concentration in the unit does not come up to the critically dangerous limit. When the flow of the feed solutions is 110-130% of the normal value, the conditions are most unsafe due to plutonium accumulation. In the course of time the concentration of plutonium in the stages of extraction zone increases progressively and can become critically dangerous. At the same time, Pu content in raffinate does not differ essentially from the concentrations under normal conditions.

Fig. 1.3 exibits calculated profile of Pu concentration through the stages of the head mixer-settler in dynamics with the feed flow increasing by 22% as to the normal value.

Tests on U and Pu distribution and accumulation under abnormal conditions were conducted with the use of a laboratory extraction

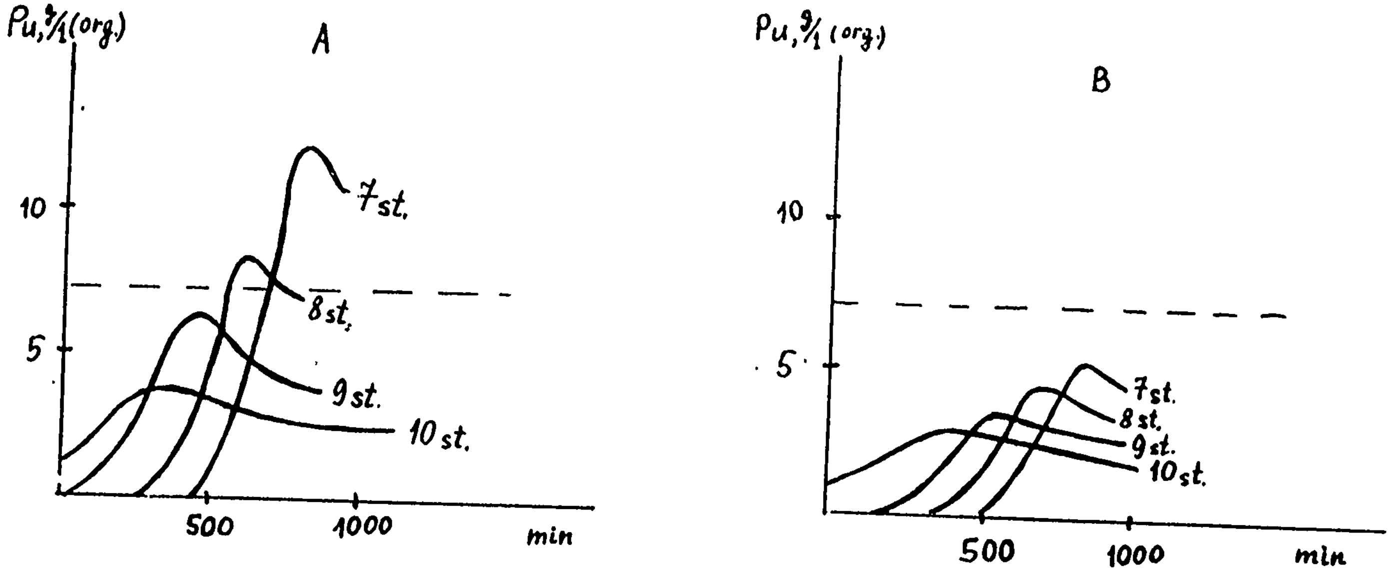


Fig. 1.3. Calculated profiles of Pu concentration in dynamics for the stages of head extraction mixer-settler unit at high uranium loading. Excess of feed solution flow is 22 %.
A - Routine model; B - with correction for extraction at high loading.
----- Permissible concentration level.

unit of mixer-settlers. It was found out that the formal values of distribution ratios for plutonium in the region of uranium front replacement are lower than those obtained at equilibrium. The breakthrough of plutonium into raffinate was observed to come earlier than it was predicted by the calculation, and plutonium is accumulated in lesser amounts. Later investigations in plant contactors showed that the rate of uranium and plutonium accumulation under abnormal conditions was determined by the hydrodynamic characteristics of the extraction equipment. The longer was the residence time of solutions in extraction stages, the better agreement was achieved with the calculated displacement of uranium and plutonium concentration fronts. The calculations with the use of a dynamic model produce most adequate results for the abnormal conditions of extraction process if the above-mentioned peculiarities of Pu extraction by 30% TBP at high loading are taken into account. From the results obtained it follows that plutonium breakthrough into the raffinate under similar conditions will be observed earlier in centrifugal contactors and later in mixer-settlers. The pulsed and reciprocating-plate columns take an intermediate position.

1.2 Zirconium and technetium extraction by TBP, loaded with uranium

Zirconium separation from uranium and plutonium during spent fuel reprocessing is an important but not easy task, and numerous investigations deal with the zirconium behaviour in various extraction systems. Some difficulties, however, hinder correlating the results of different researches. It is reasonable to note that the most of papers in this field treat of Zr-HNO_3-TBP system, the lesser part of them being dedicated to investigation of Zr-U-HNO_3-TBP, and, especially, Zr-Tc-U-HNO_3-TBP systems. At the same time technetium influences substantially on zirconium extraction.

The variety of zirconium forms in solution, in particular at low acidity (<3 M) complicates greatly the problem of the equilibrium data description and makes it practically unreal in the presence of uranium. So, it is essential to obtain own data base for zirconium extraction by TBP in Purex-process terms and to use it for direct calculations, may be without a reliable mathematical model of zirconium extraction and coextraction.

To standardize zirconium forms all solutions were prepared from salt concentrates. Zirconium salt was preliminary dissolved in 8 M NO_3, the concentrate was being heated for 6h up to boiling, diluted o 5 M HNO_3 and then stored.

Obtained data on zirconium and technetium distribution in the absence and in the presence of uranium are shown in Fig. 1.4 and 1.5, respectively. Firstly, the distribution ratio of zirconium apparently decreases with its own concentration and increases considerably with addition of technetium in comparable amounts. It can be seen also that the influence of technetium on zirconium distribution is diminished with the growth of organic phase loading by uranium.

Zirconium distribution coefficients are less than 1.0 at conditions of extraction unit, but the product of distribution coefficient multiplication by phase flow ratio may be just as less than 1.0 so more 1.0, depending on uranium content in the feed solution and solvent loading. The effect is strengthened by acid peak formation in the head extraction unit due to solvent loading with uranium. Taken together that leads either to extraction of zirconium, or to dumping the latter into waste. So, even preliminary correct prognose on zirconim behavior in the head extraction unit needs multy-component stage-by-stage computations.

As to technetium distribution it is not clear in what degree it is complexed and/or co-extracted with uranium and zirconium in the presence of both elements and so what part of last one ought to be extracted for complete recovery of technetium. Thus it also needs computation of its profile in the head extraction unit before process testing.

1.3 Computation of zirconium, technetium and uranium co-extraction

Calculations of Zr and Tc behavior in the head contactor were persued for 16 stage mixer-settler (Fig. 1.6), extraction zone consisting of 13 stages and scrubbing zone of 3 ones. The computations were made for alternate operating conditions that ensure different degree in Zr and Tc extraction.

In Table 1.1 the computation results are presented for the conditions corresponding to the "classic" Purex process where a bulk of zirconium is expected to pass into raffinate of the 1st extraction cycle. Though zirconium is practically absent in final solvent phase loaded with uranium, the conditions are favorable, according to the computation data, for Zr extraction in the stages with low uranium concentration and its reextraction in uranium extraction zone, being accumulated in the stages near uranium front. Zirconium accumulation contributes largely to technetium coextraction.

The way to extract Zr is analysed in Table 1.2 at constant solvent flow and loading with uranium up to 95g/l. It can be seen that

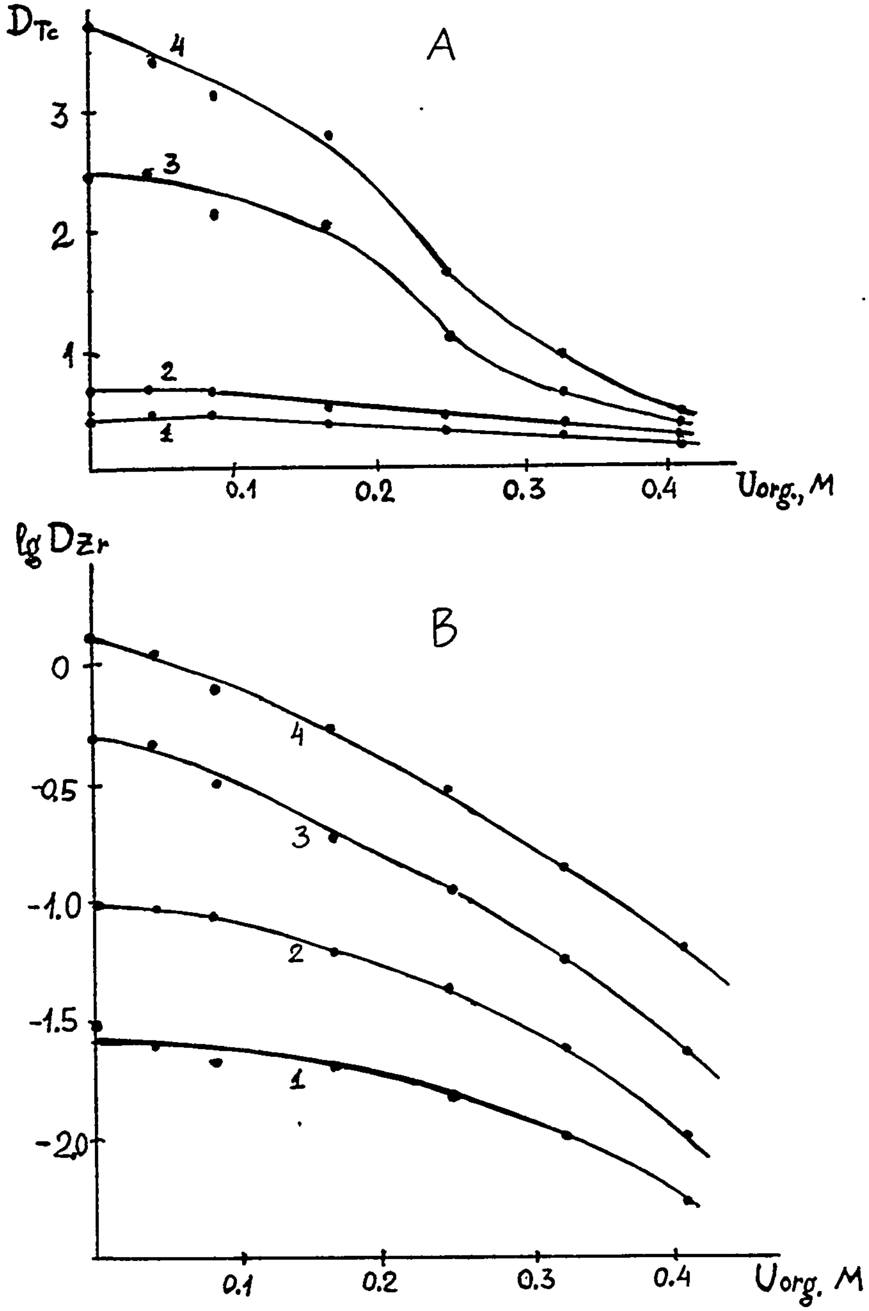


Fig.1.4 Distribution coefficients (D) dependence on uranyl nitrate concentration in solvent for technetium (A) and zirconium (B)
Initial concentration: 3g/l Zr; 0.1g/l Tc.
HNO_3 equilibrium concentration: 1- 2.0; 2- 3.0; 3- 4.0; 5- 5.0 M

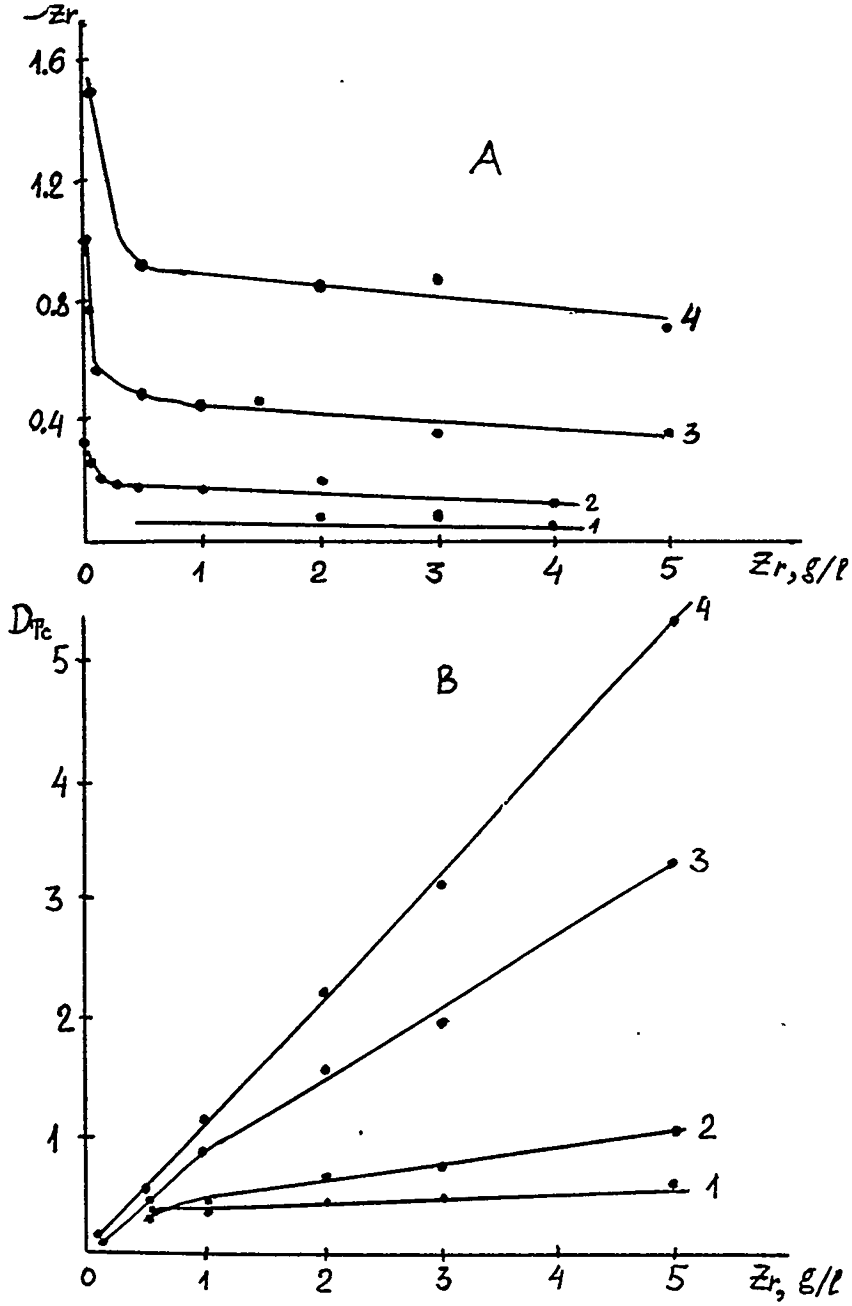


Fig. 1.5 Distribution coefficients (D) dependence on zirconium initial concentration in aqueous phase for zirconium (A) and technetium (B)

HNO_3 equilibrium concentration: 1- 2.0; 2- 3.0; 3- 4.0; 5- 5.0 M

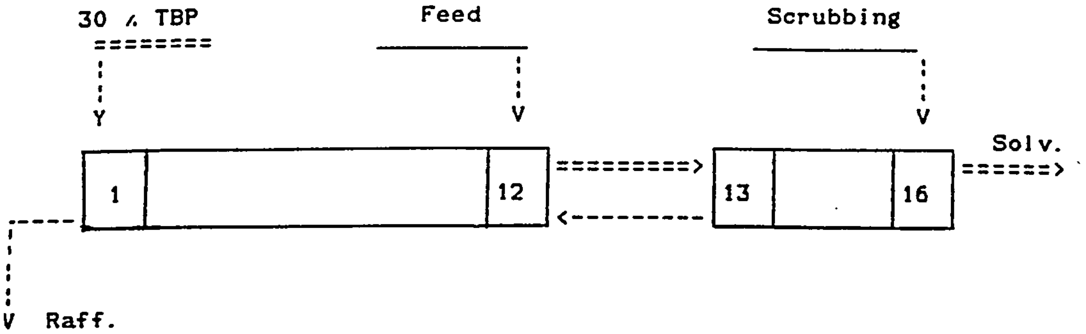


Fig.1.6 The structure of the head extractor unit.

Table 1.1.

alculated concentration profiles of HNO_3, U, Pu, Tc, in the head xtraction unit. Feed solution: 200 g/l U, 2 g/l Pu, 0.67 g/l Zr, 0.11 /l Tc, 3 M HNO_3. Relative flow of scrub (to feed): 0.21; 1 M HNO_3

age	Concentrations of components, g/l											
N	HNO_3		U		Pu		Zr		Tc		Tc #)	
	Aq.	Org.	Aq.	Org.	Aq.	Org.	Aq.	Org.	Aq.	Org.	Aq.	Org.
	160	38	0	0	0	0	0.55	0.08	0	0	0.02	0.004
	226	49	0	0	0	0	0.69	0.24	0	0	0.03	0.005
	245	51	0	0	0	0	0.97	0.44	0	0	0.03	0.008
	248	51	0	0	0	0	1.32	0.64	0	0	0.04	0.011
	249	51	0	0	0	0	1.65	0.82	0	0	0.04	0.015
	249	51	0	0	0	0	1.98	1.00	0	0	0.05	0.020
	248	51	0	0	0	0	2.28	1.18	0	0	0.06	0.027
	248	51	0	0	0	0	2.59	1.36	0	0	0.06	0.036
	248	51	0	0	0	0	2.90	1.55	0	0	0.08	0.046
	247	50	0.1	0.	0.	0.0	3.22	1.75	0.0	0.0	0.10	0.064
	247	45	0.3	14	0.03	0.54	3.56	1.56	0.00	0.03	0.11	0.081
	237	11	24.6	101	0.92	1.15	3.25	0.11	0.04	0.09	0.16	0.047
	133	7.1	47.3	102	1.93	1.20	1.07	0.01	0.32	0.08	0.10	0.045
	94	5.0	64.7	103	2.40	1.21	0.09	0.00	0.29	0.07	0.08	0.044
	73	4.0	71.3	102	2.52	1.16	0.00	0.00	0.19	0.07	0.07	0.043
	63	4.0	61.3	96	2.03	0.96	0.00	0.00	0.14	0.05	0.06	0.038

20 % stage efficience in coextraction with Zr

Table 1.2.

Effect of solvent-to-aqueous flow ratio and nitric acid concentration on extraction of Zr and Tc in the first extraction unit.

N	Composition of feed solution					Feed flow,	N = = S/A	N = = S/A	HNO$_3$ concent. M		Zr concent., g/l		Zr recovery,
	U, g/l	Pu, g/l	Zr, g/l	Tc, g/l	HNO$_3$, M	l/h	extr. zone	scrab. zone	Raff.	Extr.	Raff.	Extr.	%
1	200	2.0	0.67	0.11	3.0	0.240	1.72	10	2.54	0.065	0.55	0	0
2	250	2.5	0.83	0.14		0.190	2.08		2.42	0.075	0.35	0.15	50.5
3	300	3.0	1.00	0.17		0.160	2.38		2.35	0.075	0.075	0.29	90.1
4	350	3.5	1.17	0.19		0.134	2.72		2.23	0.077	0.009	0.32	98.9
5	400	4.0	0.22	0.22		0.119	2.96		2.17	0.077	0.002	0.32	99.8
6	200	2.0	0.67	0.11	3.0	0.240	1.89	20	2.62	0.103	0.35	0.14	42.4
7	250	2.5	0.83	0.14		0.190	2.35		2.52	0.103	0.022	0.31	97.0
8	300	3.0	1.00	0.17		0.160	2.70		2.45	0.103	0.004	0.32	99.7
9	350	3.5	1.17	0.19		0.134	3.14		2.32	0.104	0	0.32	100.0
10	400	4.0	1.33	0.22		0.119	3.47		2.27	0.104	0	0.32	100.0
11	350	3.5	1.17	0.19	2.0	0.134	2.72	10	1.51	0.076	0.65	0.08	25.4
12					2.5				1.88	0.077	0.10	0.28	88.0
13					3.0				2.23	0.077	0.009	0.32	98.9
14					3.5				2.60	0.077	0.001	0.32	99.9
15					4.0				2.96	0.077	0	0.32	100.0

S/A - solvent-to-aqueous flow ratio

the influence of solvent-to-aqeous flow ratio growth on Zr recovery is very essential, but it can't be achieved by decrease of solvent loading because of decontamination factor drop. The limiting value of S/A ratio in extraction zone is 2.9-3.0, which means uranium concentration in feed 320g/l and higher at HNO_3 concentration 3 M and also S/A flow ratio not less than 20 in scrubbing zone.

It should be noted that the algorithm for calculation was developed on the basis of ideal equilibrium equations. As to profiles through the apparatus, equilibrium in individual contactor stages may be not observed for all the elements. For example, calculated Tc recovery in "classic" Purex process is 100%, while in experiment (and plant process as well) it is of 85%, and agreement is achieved assuming that formal stage efficiency is about 20% - for Tc extraction only.

Therefore, there is a certain inaccuracy for expected values of :irconium and, especially, technetium accumulation in the contactor. lowever, obtained results allow to test directly the conditions of irconium and technetium total recovery on simulated and then on hot" solutions in series of rig trials.

2. PROCESS STUDY USING MIXER-SETTLERS

2.1. General information

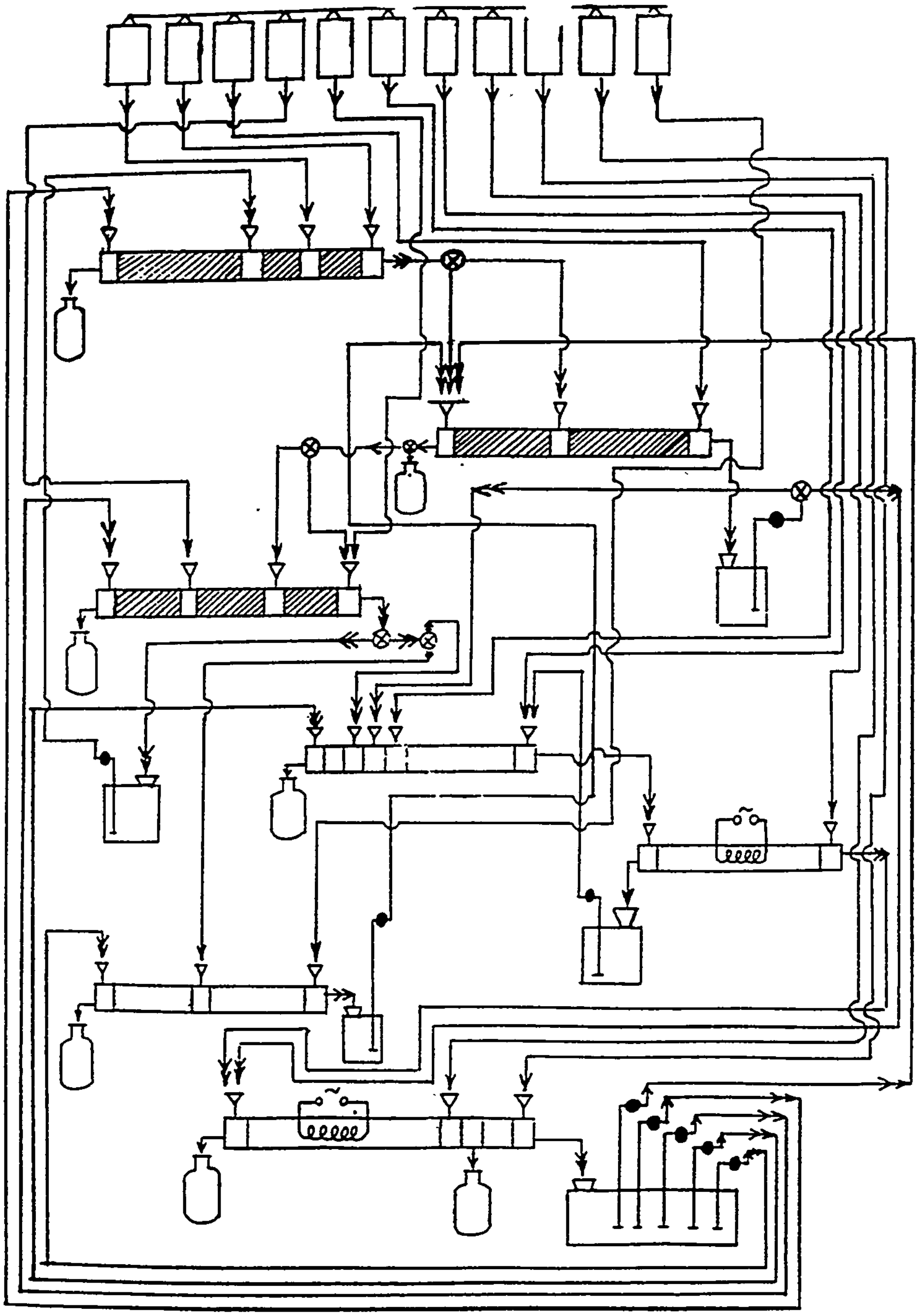
Most of experiments on Modified Purex process development has completed in miniature mixer-settlers. The contactors of this type are very convenient for radiochemical investigations using both simulate and real high-active solutions. Their construction is not complicated, they are reliable in operating.

The mixer-settlers are easily manufactured and installed in units and cycles with the aim to determine optimal perfomances of the process. Residence time (5-40 min. per stage) is high enough to obtain reproducible concentration profiles in the units, which permits to improve some operations at minimum data. Most of elements with variable oxidation state have enough time in any stage to come to equilibrium. Therefore, the interpretation of the process and its modelling are simplified significantly. Information obtained in miniature mixer-settlers with simulate solutions usually demands minimum number of expensive additional experiments with high-active solutions.

2.2. Miniature installation for testing the Purex process versions

The installation has been manufactured and assembled to perform verification of Purex-process modifications in miniature mixer-settler contactors. It includes seven multistage mixer units, which are made of stainless steel. The volume of liquids in each stage is equel to 15ml for mixing chamber (pulsed agitation) and 100ml for settling one. The schematic drawing of the instalation is presented in Fig.2.1.

Aqueous and solvent streams are shown by single-arrowed and double-arrowed lines, respectively. Besides mixer-settlers, the installation includes feed, intermediate and storage flasks, dosing equipment, taps, vents and valves. The flows of feed and reagent solutions are fixed by proportioner with smoothly lowered level of discharge. The flows of solvent are controlled by plunger dosator with ball valves and bellows hermetic sealing. Measures are taken to avoid overfilling in intermediate and storage tanks. It is possible to commutate or to switch of mixer-settles units by vents, to vary the number of stages in some units and, therefore, to design various versions of Purex process flowsheet. The mixer-settler units were mounted at different levels in order to organize gravity solvent flow from one unit to another at its maximum flow rate 1.5l/h. Some of the units were supplied with heaters to warm solutions upto50+5°C.



ig. 2.1 Schematic drawing of mixer-settler rig for Modified Purex process testing.

Units for Jont extraction and Zr/U-Tc partitioning are hatched.

Designation: ● dosing valve; ⊗ vent; receptacle; intermediate flask; heater; proportioner.

The feed simulate solution was prepared on the base of recycled uranyl nitrate, refined by extraction and concentrated by evaporation. The uranium solution contained considerable quantities of phosphate-ions as a result of TBP degradation during evaporation. So the procedure of feed solution preparation was as follows:

- concentrated solution of uranyl nitrate was analysed and diluted to obtain necessary uranium content (somewhat higher than final concentration);
- nitric acid concentration was adjusted;
- zirconium nitrate was added, its projected concentration being exceeded by 0.2-0.3 g/l;
- uranium - zirconium solution was kept for 50-80 hours to precipitate zirconium phosphates;

the residues were separated by solution decanting and all other components were added to the solution.

The described procedure of feed solution preparation prevented from phosphate precipitation in head extraction unit.

The miniature extraction installation allowed to investigate seve- ·al versions of Purex process with the use of simulate solutions.

This report includes the problems of optimization of the two operations, e.g. joint U, Pu, Np, Zr and Tc extraction and Zr selec- ive stripping. These units are hatched on the schematic drawing Fig. 2.1).

2.3. Studies of element distribution through the head operations using simulate solutions

Testing of zirconium-technetium coextraction in the head extrac- on unit of mixer-settler was started with the variant that envi- .ged no scrubbing in order to enable zirconium recovery at dimi- shed uranium feed concentration. The head unit included 10 stages, ile structure of 15 stage unit for zirconium stripping was rather mplicated (Fig.2.3).

Trials were carried out using simulate feed solution of NPP spent :l, but with lowered plutonium concentration, e.g. 300g/l U; 1g/l Pu; 0.05g/l Np(VI); 1.0g/l Zr; 0.1g/l Tc; 3.0 M HNO_3. Oxida- ·n states of Pu and Np, as well as Zr hydrolytic forms were sta- ized separately by heating or boiling in 8-12M HNO_3. Total samp- g was taken after 48h of continuous work.

xperimental profiles for Zr extraction and stripping are fixed Tables 2.1 and 2.2, respectively. It is seen Zr extraction to be :e successful; Tc is completely recovered as well due to coextrac-

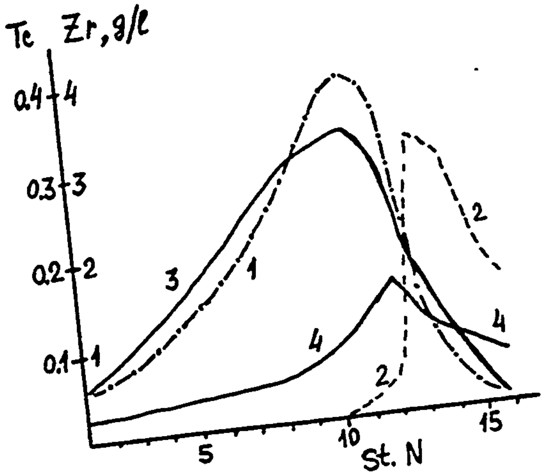


Fig. 2.2 Profiles of zirconium (1;3) and technetium (2;4) in aqueous phase of head extraction unit (simulated solution of NPP spent fuel at 33 GW*d/t burn-up) 1,2- as calculated; 3,3- real profile Input in mixer-settler stages: 1-Solvent, 12-Feed; 16-Scrub

Table 2.1

Distribution of U, Pu, Np, Zr, Tc and HNO_3 through the mixer-settler stages of the head extraction unit with no scrubbing

Feed: 300g/l U;0.01g/l Pu;0.05g/l Np(VI);1g/l Zr;0.1g/l Tc;3M HNO_3

Stage	Aqueous phase composition						Organic phase comp.		
	HNO_3 M	U g/l	Pu mg/l	Np mg/l	Zr mg/l	Tc mg/l	U g/l	Zr mg/l	Tc mg/l
1	2.9	0.01	-	0.05	3	1	-	-	0.4
3	4.7	0.01	-	0.2	7	1	-	6	0.4
6	4.9	0.01	0.1	1.0	10	1	0.7	12	0.4
8	5.0	0.07	0.1	-	525	-	3.5	300	8.4
9	4.7	8	0.3	7.8	1730	22	64	310	33
10	3.5	168	2.8	39	4520	119	108	280	36

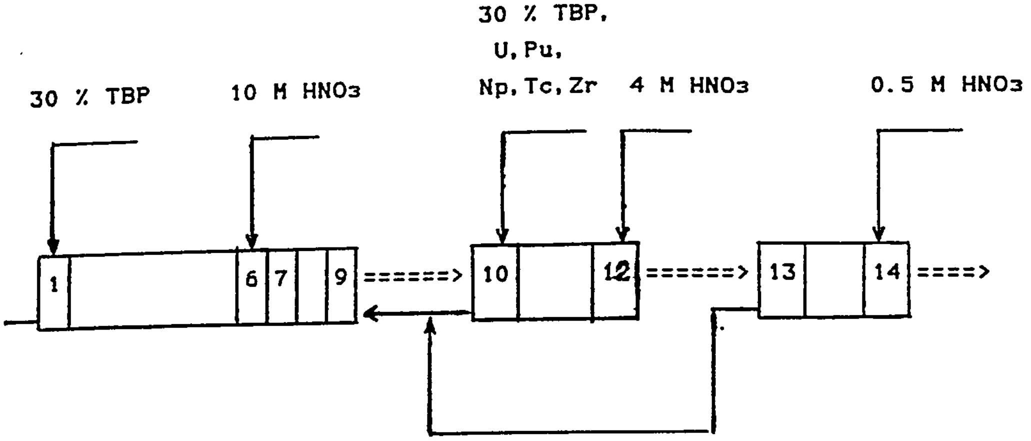


Fig.2.3 Structure of 2nd contactor for modified Purex-process flowsheet

Table 2.2

Distribution of elements and HNO3 through the stages of mixer-settler during zirconium stripping and actinide extraction from re-extract

age	Aqueous phase						Organic phase		
ber	U, g/l	Pu, mg/l	Np, mg/l	Zr, g/l	HNO_3, M	Tc, mg/l	Zr, g/d	Tc, mg/l	U, g/l
1	0.04	0.03	0.5	0.74	4.2	2.8	0.43	26	0.03
3	0.04	-	1.8	1.75	5.2	66	1.90	122	0.05
5	-	0.05	11.5	1.85	3.3	192	0.52	161	0.03
7	-	-	6.2	1.30	3.3	136	0.36	91.4	0.9
8	1.0	-	1.0	1.57	3.3	136	0.22	72.5	8.5
9	13.0	-	3.9	1.57	-	119	0.11	50.3	48.3
0	25.5	4.3	20	5.40	4.0	116	0.25	35	92
1	29.4	3.7	6.0	2.24	3.9	120	0.073	35	92
2	24.5	3.2	2.4	0.70	3.8	110	0.035	29	96
1	55	8.2	14	0.38	1.6	76	0.006	22	96
1	83	19.7	18	0.081	1.1	58	0.003	22	99
	82	15.4	30	0.011	0.6	87	-	20	96

tion with zirconium. Increased solvent loading with uranium also provides to Tc extraction without fail in actinide recovery, which may be expected from generally accepted point of view. Obtained results allowed to restore solvent product scrubbing, but with nitric acid of rather high concentration (3-4 M) at very low relative flow.

The second operation consist of two main parts, e.g. two-zone Zr stripping and actinide backextraction together with Tc. This process needs proper acidity and flow ratio control in order to separate correctly Zr from transmutable components. It must be mentioned that in further experimental series the operation was simplified, for RT-2 flowsheet needs now only U and Pu deep recovery from Zr strip, while the minor elements are finally combined for common solidification, using zirconium oxide as a matrix.

2.4 "Hot" rig trials

Two series of "hot" trials on Tc and Zr behaviour in the head ex-raction unit were carried out recently on mixer-settler rig, which as disposed in shielded cells of Gatchina Research Center. LWR WWER 440) fuel burn-up was 32 GW*d/t at cooling for 5 years.

In the first series only technetium behavior in "classic" process as examined. The structure of the head contactor and test results e shown in Fig.2.4 and 2.5. The results are compared to those, obtained with simulate solutions. They make evident, that Tc profile s a peak in feeding unit, and its recovery does not exeed 85%. Na- re of such effect was explained later by Tc-Zr co-distribution.

The second series was carried out in last few years for testing e reasonability of Purex process modification. Only some possible rrections were introduced in rig communications without its total construction. The improved flowsheet includes high acid scrubbing loaded solvent (Fig.2.6) at low relative flow to increase decon- nination from gamma-emitters without damage to zirconium recovery. feed contained 2.6 M HNO_3; 400 g/l U; 3.2 g/l Pu; 0.14 g/l Np; g/l Zr; 0.3 g/l Tc at 140 Ci/l total gamma-activity (mainly 134;137). The overall results on element partitioning were repor- previously.

e element profile is presented in Table 2.3. Zirconium extrac- n is connected with its large accumulation in extraction zone, h support technetium recovery. Content of the latter in high-le- raffinate was no more than 1% of initial amount, as well as of neptunium. Zirconium recovery was as high as 98%, its decon- nation factor being $1.5*10^{4}$.

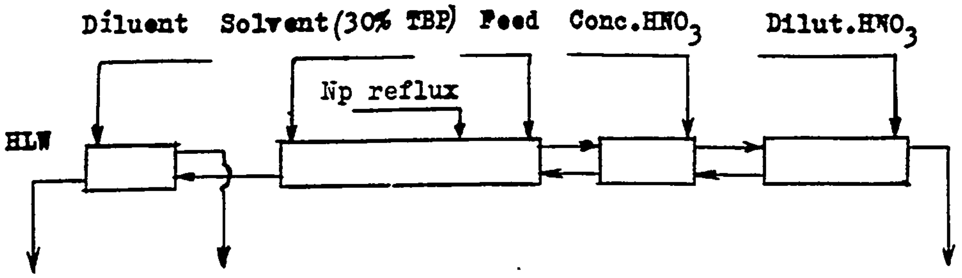


Fig. 2.4 Sketch of head extraction unit of the "hot" rig in Gatchina (1973 - 1986).

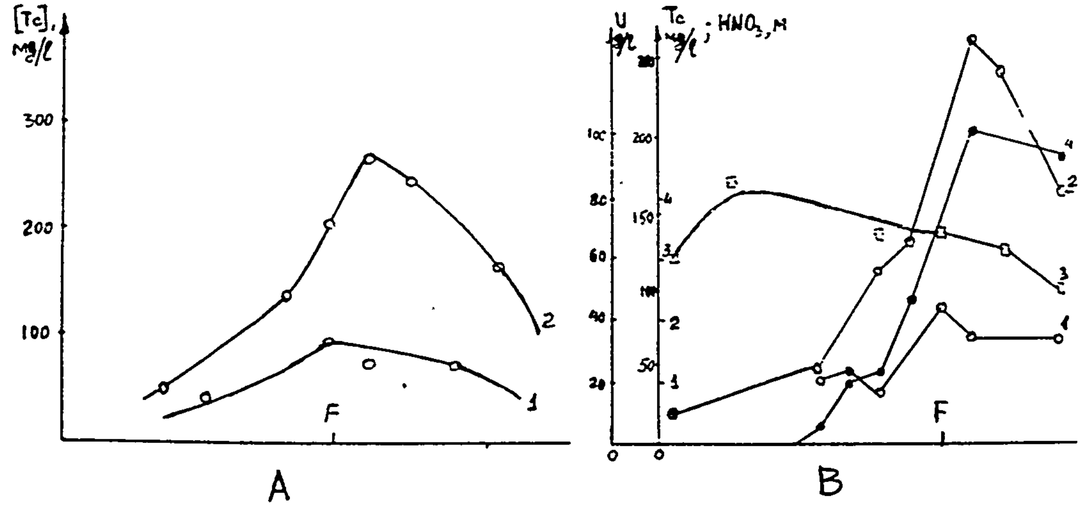


Fig. 2.5 The concentration profiles for Tc, U, HNO_3 in the head extraction unit (extraction and high acid scrubbing):
A - simulated solution;
B - NPP spent fuel solution (32,5 GW·d/t):
1 - Tc in organic phase; 2 - Tc in aqueous phase; 3, 4 - HNO_3 and U on aqueous phase

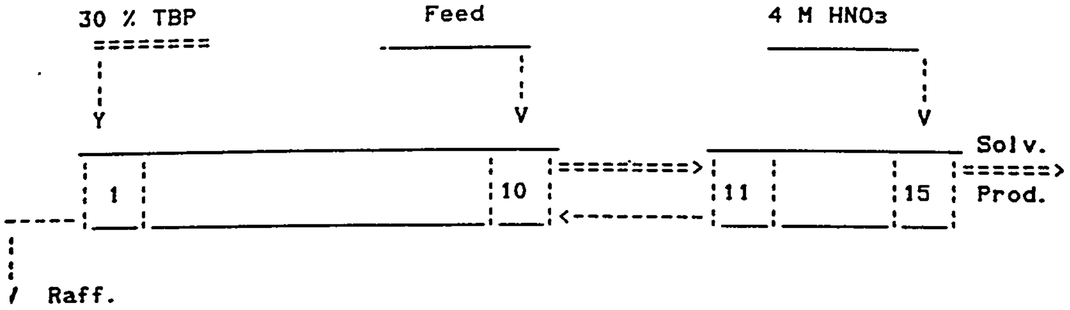


Fig.2.6 The structure of the head extraction unit of " hot " rig.

Table 2.3

Distribution of HNO$_3$, U, Pu, Zr, and Tc through the stages of the first mixer-settler unit in the trials with the use of NPP spent fuel

Stage	Aqueous phase HNO$_3$, M	U, g/l	Pu, g/l	Zr, g/l	Tc, mg/l	Organic phase U, g/d	Pu, g/l	Zr, g/l	Tc, mg/l
1	2.5	<0.06	<0.001	0.02	<1.0	<0.3	-	-	-
3	3.3	-	-	0.05	-	-	-	0.02	-
4	3.5	-	-	0.08	-	-	-	-	-
5	3.7	-	-	0.14	-	-	-	0.04	-
6	4.1	-	0.002	0.39	-	-	0.010	0.1	3
7	4.4	-	-	0.56	23	0.3	0.030	0.21	14
8	4.7	0.3	0.05	1.57	48	6.1	0.34	1.1	27
9	4.4	9.1	1.4	3.7	68	73	0.75	0.61	74
10	4.5	106	1.9	8.7	80	110	0.92	0.48	93
11	4.4	46	1.9	8.5	107	100	-	-	82
2	4.5	-	1.6	8.1	92	97	0.85	0.44	78
3	4.3	23	1.5	8.0	82	95	0.82	0.41	75
4	4.2	20	1.5	7.6	80	95	0.80	0.38	73
5	4.0	18	1.3	7.1	73	92	0.75	0.31	68

3. PROCESS TEST IN RECIPROCATING-PLATE COLUMNS USING SIMULATE SOLUTIONS

3.1. General information

The input of pulsating energy is used in column contactors to obtain higher rate of mass transfer. The principle of adding pulsating mechanical energy to an extraction column was originated by Van DiJck (US Pat 2011186, 1935). In accordance with Van DiJck's idea extraction efficiency of a perforated-plate column cou be improved:

- by pulsing the entire liquid content of the column;
- by reciprocating the plates in the column.

The first technique has been extensively utilized in various branches of industry, including radiochemical plants. The second technique has been widely exploited from the late 1950's.

The reciprocating-plate columns have gained increasing industrial application in chemical, pharmaceutical, petrochemical, hydrometallurgical and waste-water treatment industries. The apparatus of this type have demonstrated good performances and combine the advantages of high flow rates and mass transfer efficiency. The reciprocating-plate columns can be operated at high vibration level and low (2-4mm) amplitude, with easy and independent control for both amplitude and frequency of vibration, which is a complicated problem for pulsed columns. Besides, an attractive reason to use reciprocating-plate columns in radiochemical industry is in smaller volumes of contaminated air in comparison with the pulsed columns.

The use of reciprocating-plate columns for spent nuclear fuel reprocessing should enable the extraction processes to be conducted at higher specific flows and, consequently, solvent radiolysis should be minimized.

3.2 Testing rig description

Extraction process for RT-2 plant 1st cycle flowsheet have been investigated using simulate uranium-zirconium-technetium solutions at Radium Institute reciprocating-plate column test rig. The rig is disposed at Gatchina Research and Development Centre. The design of the rig allows to investigate mass-transfer and hydrodynamics of extraction operations with the use of corrosive, toxic and radioactive substances. Paraffine diluent for TBP is used, which contains mainy tri- and tetradecane.

The rig includes two reciprocating-plate columns. Each column is rovided with 3-meter height plate stack and top settlers. The plate

-stacks ..'e placed in glass shells with in. diameters 56 and 85mm respectively. The simplified scheme of the column rig ts depicted in Fig.3.1. Besides the columns A17 (56mm diameter) and A18 (85mm diameter) the test rig includes measuring tanks A3, A11, A12, A16, A24; tank-collectors A6, A7, A10, A14, A15; intermediate tanks A1, A2, A5, A8, A9, A21, A22; evaporator of uranium solution A20 and condenser A23. Solutions flowrates are fixed by rotameters R1, R2, R3 and R4.

The reciprocating-plate column A17 contains stack of 76 sieve plates with free area 44% (18 perforations of 8.7mm diameter), while plates are 55.4+0.1mm diameter. The central rod that supports the plate stack is reciprocated by means of electrical motor with geabox and crank mechanism. The drive is located at the top of the column. The double amplitude is adjusted in the range 3-6mm, and the vibration frequency is varied from 1.5 up to 8.5Hz.

A17 column has top and bottom settlers of 102mm diameter and 250-300 mm height. Sampling in the column A17 is performed with the use of sampling taps, which are located on lines of entering and outgoing solutions (taps S1-S4) and on levels 0.5-1.0-1.5-2.0-2.5m from the bottom settler along the column shell (taps S5-S9). The samples taken on those levels are used to determine not only component concentration, but also hold-up values.

3.3 Trials on the first extraction cycle process

In the course of experiments in column extraction of U, Zr and Tc from feed solution into 30% TBP was tested, as well as following Zr and then Tc backwashing. It was found out that both types of emulsion can be used on extraction, while aqueous continuous phase is preferable at stripping processes in order to ensure satisfactory hydrodynamic conditions.

The data on U, Zr, Tc and HNO_3 distribution through the column at steady-state conditions are presented in Tables 3.1 and 3.2. The uranium, zirconium and technetium profiles in aqueous phase along the column in course of extraction are shown in Fig.3.2.

It can be seen from the experimental data that extraction of uranium an technetium exeeds 99.99% and 99%, respectively. As for zironium about 70% of it is recovered. Calculations based on the above esults with allowance for the data on Zr equilibria show that in m height column 98% zirconium can be recovered, its concentration n high-level raffinate being lower than 30mg/l. At Zr stripping 8% zirconium passes into strip solution (1.2M HNO_3) when organic hase is dispersed. It can be expected that in 5-6m column about 98%

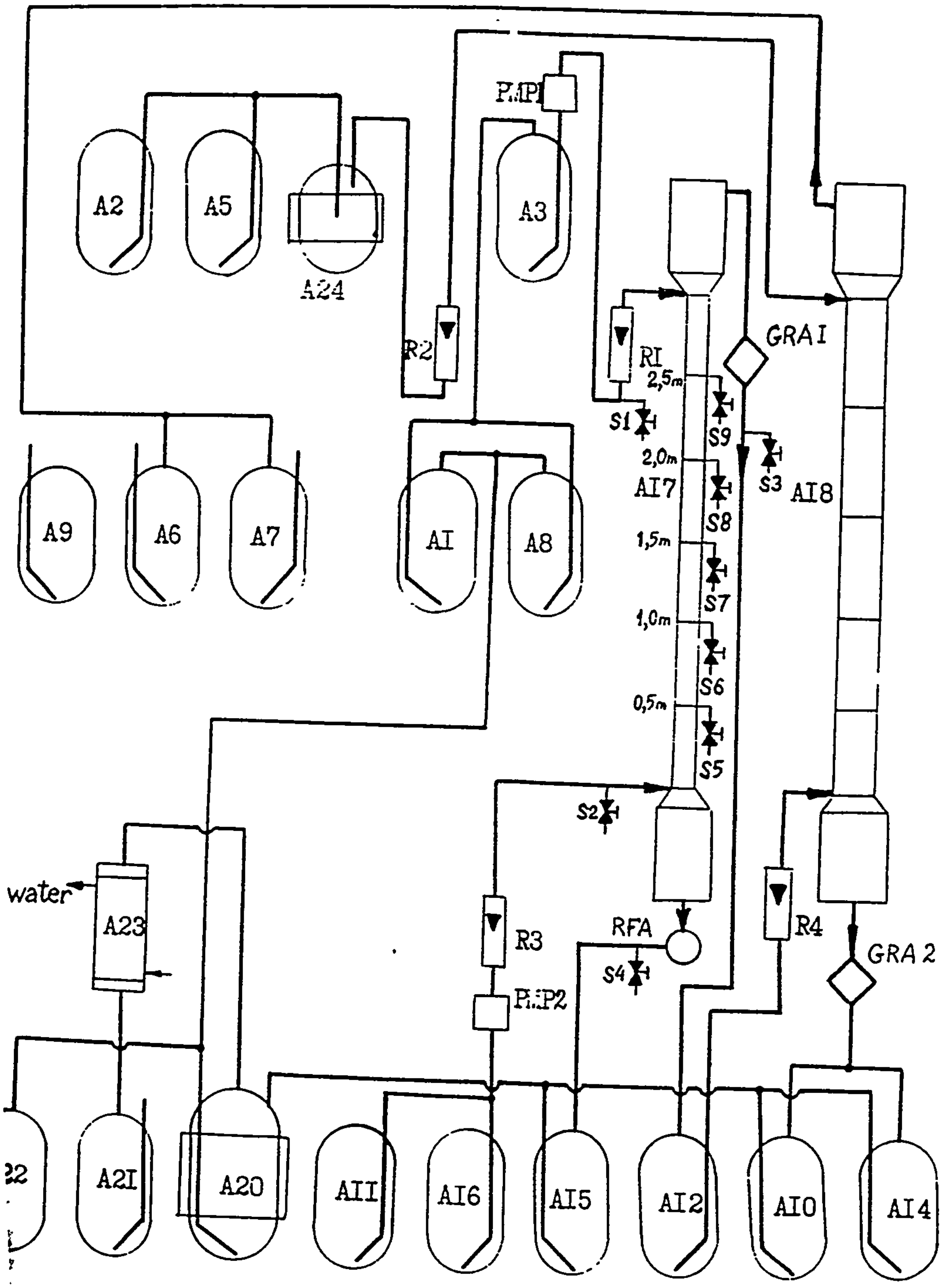


Fig.3.1. Reciprocating-plate column test rig.

Table 3.1

Concentration of U, Zr, Tc and HNO3 in entering and outgoing solutions. 3 meter height reciprocating-plate column.

Process	Emuls. type	Phase	Stream	Flow, l/h	Component concentration, g/l			
					U	Zr	Tc	HNO_3
Extraction	Org. dispersed	Aq.	In.	32	300	1.7	0.120	227
		Org.	In.	96	0	0	0	0
		Aq.	Out	32	0.030	0.05	<0.002	185
		Org.	Out	101	95	0.38	0.039	12
Extraction	Aq. dispersed	Aq.	In.	25	290	1.2	0.220	195
		Org.	In.	75	0	0	0	0
		Aq.	Out	25	0.022	0.40	<0.002	158
		Org.	Out	78	92	0.26	0.069	13
Zr - stripping	Org. dispersed	Aq.	In.	10	0	0	0	76
		Org.	In.	90	90	0.25	0.065	12
		Aq.	Out	10	22	1.88	0.070	85
		Org.	Out	90	88	0.03	0.057	10
[illegible] - stripping	Aq. dispersed	Aq.	In.	8	0	0	0	76
		Org.	In.	72	90	0.25	0.065	12
		Aq.	Out	8	15	1.12	0.035	90
		Org.	Out	72	88	0.12	0.062	10

Table 3.2

Profiles of U, Zr, Tc and HNO_3 concentrations, (g/l).
Reciprocating-plate column of 3 meter height.

Process emuls. type	Phase	Component	Sampling level (from the bottom of column), m				
			0.5	1.0	1.5	2.0	2.5
Extraction, org. dispers	Aq.	U	0.2	0.3	0.55	1.1	18
		Zr	0.96	1.35	1.80	2.23	2.65
		Tc	<0.002	<0.002	<0.002	0.012	0.036
		HNO_3	185	215	240	252	258
	Org.	U	0.06	0.10	0.18	0.37	6.0
		Zr	0.15	0.28	0.42	0.57	0.71
		Tc	<0.002	<0.002	<0.002	0.004	0.012
Extraction, aq. dispersed	Aq.	U	0.04	0.07	0.15	0.27	4.0
		Zr	0.7	0.95	1.31	1.62	1.8
		Tc	<0.002	<0.002	<0.002	0.012	0.045
		HNO_3	180	210	230	240	240
	Org.	U	0.1	0.2	0.45	0.8	12
		Zr	0.10	0.18	0.30	0.40	0.46
		Tc	<0.002	<0.002	<0.002	0.004	0.015
Zr - Stripping, org. dispersed	Aq.	U	22	21	19	17	14
		Zr	1.35	0.90	0.58	0.30	0.16
		Tc	0.055	0.052	0.045	0.035	0.020
		HNO_3	85	85	85	80	80
	Org.	U	90	89.9	89.7	89.5	89.3
		Zr	0.19	0.13	0.10	0.06	0.05
		Tc	0.064	0.064	0.062	0.061	0.059

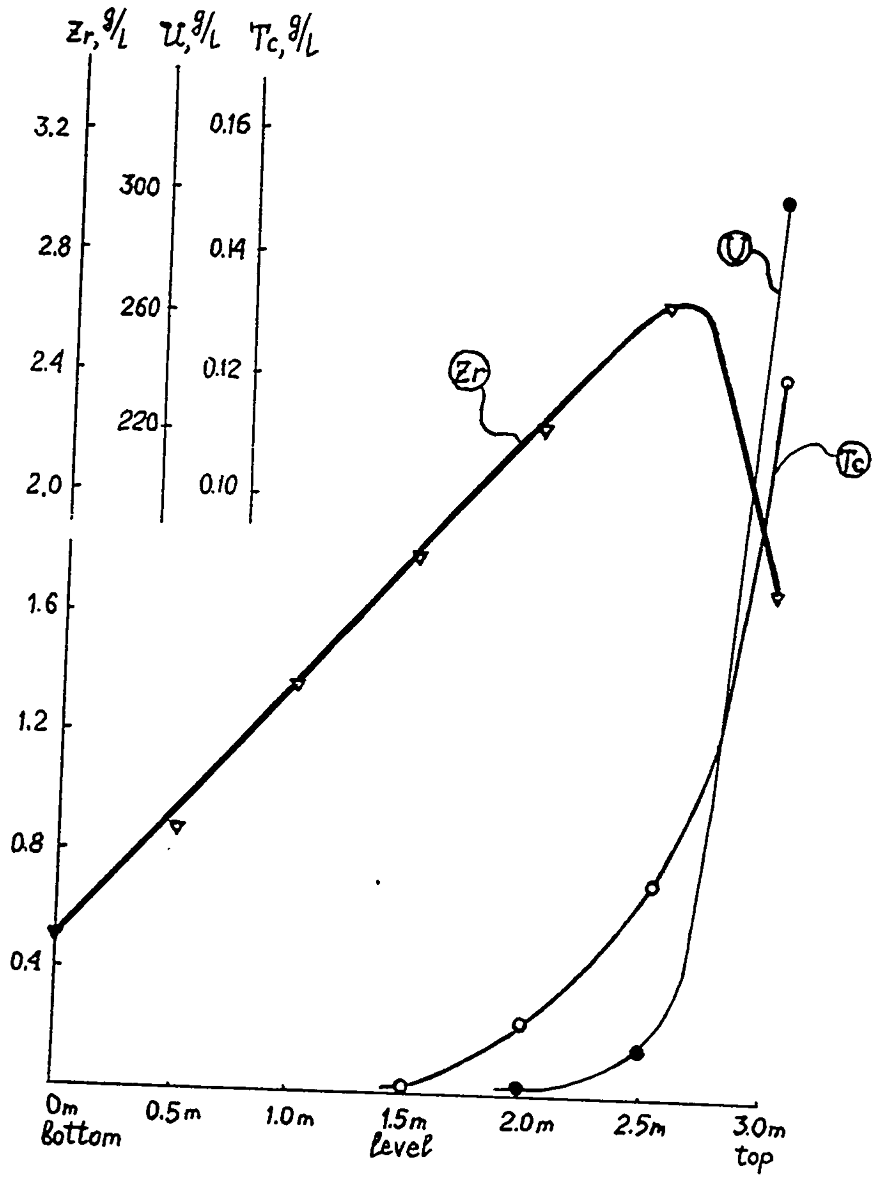


Fig.3.2. Uranium, zirconium and technetium concentration profiles in aqueous phase along the column in course of extraction

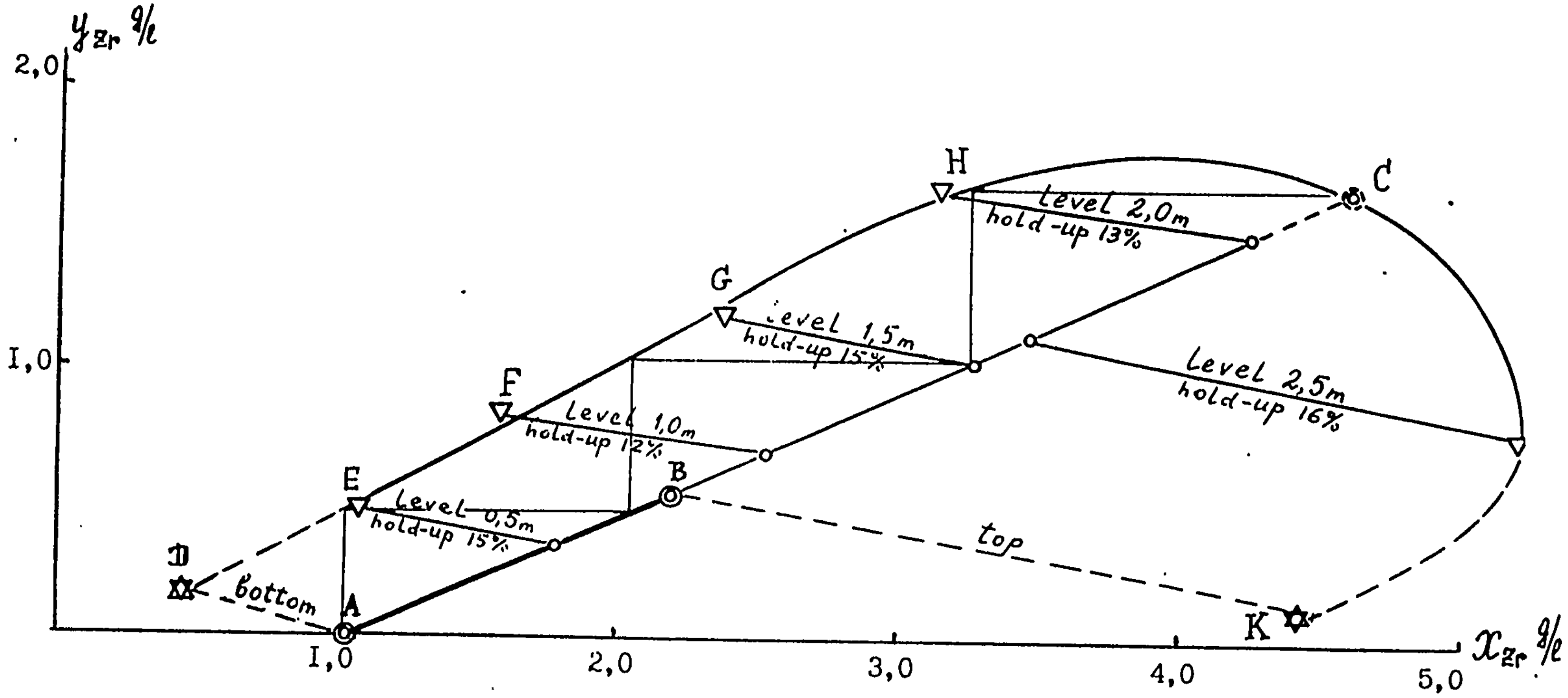


Fig. 3.3. Grafic-analitical determination of zirconium concentration in countercurrently flowing phases inside column.
ABC - operating line, EFGHJ - equilibrium curve.

zirconium will be stripped.

It is necessary to outline that the component concenrations presented in Table 3.2 are not the concentrations determined directly in samples of emulsion, which are taken out of the column. The aqueous and organic phases in the samples are practically in equilibrium to each other because of mass-transfer during sampling and phase separating prior analysis. So the procedure of grafic-analytical recalculation is used to determine real concentration profiles in countercurrently flowing phases inside the column. The recalculation method is described in:

Treybal R.E. Ind. Eng. Chem. 1955, v.47, p. 2435;

Treybal R.E. Liqid Extraction, 2 ed., p. 386, McGrow-Hill, London.

An example of recalculation for Zr profile is shown in Fig.3.3.

CONCLUSION

The above data give evidence for possibility of combined deep recovery of several elements from highly irradiated materials by means of TBP extraction in so-called Modified Purex process with the aim to further transmutation of these elements. Selective stripping of Zr from solvent phase containing U, Pu, Np and Tc is also quite effective. The nature of tested materials is in many respects similar to that of materials to be reprocessed after irradiation.

Further element partitioning stands apart of this paper framework and might be discussed in the next one. In order to choose the best partition variant it is necessary to know the optimal element combination for irradiation. It seems better to have minimum of loops and therefore less number of spent actinide products to be reprocessed at once.

The development of Modified Purex process has not been completed, and some new information would be aviable in next few years. The main technological problem to be solved should be oxide separation from the loop and admissible storage duration before their reprocessing and reuse in the loop.

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