

UDC 546.791.02.238:66.061.51

EXTRACTION PROCESSING OF CONCENTRATED SOLUTIONS OF URANYL NITRATE WITH HIGH IMPURITIES CONTENT

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Process flowsheet of recycling uranium concentrated solutions with its purification from insoluble impurities of iron, silicon, molybdenum, calcium oxides and hydroxides and soluble impurities with application of centrifugal extractors cascade has been developed and suggested for commercial introduction. The process was carried out at extractant saturation (30 % tributyl phosphate in hydrocarbon diluent) in extraction assembly lower than a limiting level (85...95 g/l) and in wash assembly – at limiting saturation (up to 120 g/l). As a result the waste uranium content in water-tail solutions 0,01...0,04 g/l and minimal content of impurities in re-extractors is provided.

Perspective program on development of nuclear power engineering proposes to involve wide range of raw materials from uranium ores to secondary uranium materials into processing at atomic enterprises. In this case the problem of reprocessing concentrated uranium solutions with high impurity content occurs.

One of the ways to separate target component from impurities is liquid extraction. Extraction is applied in the cases when direct techniques for admixture separation are not suitable or when expenses for other methods are higher. In the given paper after uranium concentrate dissolution in nitric acid and solution clarification by means of centrifuging and/or filtering highly concentrated nitrate uranium solutions are sent to extraction refining from soluble impurities using tributyl phosphate as an extractant (TBP).

Choice of extractant

Extraction processes are carried out in extractors of various constructions – mixer-settlers, extraction columns, centrifugal extractors etc. Wide use of mixer-settlers and column extractors is stipulated by their high capacity, arrangement simplicity, reliability in operation. Centrifugal extractors have a number of advantages over mixer-settlers and columns: high speed of achieving interfacial equilibrium at extraction, less radiation injury of reverse extractant, lower demand to the presence of suspensions in solutions, lower response of the process to the formation of 3^d phase owing to the presence of solid impurities in comparison with pulse columns. Centrifugal extractants operate practically without formation of substandard solutions that is the consequence of second equilibrium achieving in reaction zone of the device. Combination of intensive processes of solution stirring in attractive field and further emulsion separation in centrifugal force field in centrifugal extractors allows achieving high efficiency of mass transfer simultaneously with specific capacity with low uranium content in raffinate (0,010...0,015 g/l) [1]. High uranium extraction into extractant distinguishes profitably centrifugal extractors from the diagrams operating at other types of extractors where uranium content in raffinate is 1 g/l and more [2].

Extractors operate for years without failures and maintained easily and rapidly. The important criteria when estimating extractors availability in uranium

technology are also: reliability of hermetization, possibility of remote service, resistance to corrosive attack of structural materials, duration of overhaul period etc.

In Russia the centrifugal extractor of ECT-series with continuous extraction of solid phase [3], which may enter with initial solutions or may be formed at their contacting, was developed. Conical form of rotor and special construction of hydraulic lock promote continuous extraction of sediment from rotor with heavy phase (raffinate). Sediment weight in rotor accumulated in dynamic equilibrium mode depends on rotor angular velocity, liquid flow velocity in rotor, solid phase concentration in solution, slope angle of cone generatrix to the axis and finish of cone surface. Extractor may operate without hydrodynamic mode failures at solid phase content in solutions up to 5 g/l. Developing universal technology of refining uranyl nitrate (further uranium) solution from ballast impurities may be the most efficiently and effectively organized using centrifugal extractors.

In the given paper the centrifugal laboratory extractors EC33 produced at pilot plant NIKIMT in Moscow were applied for processing concentrated solutions of uranium with high content of impurities.

Some technical features of EC33 are: rotor speed is 50, s⁻¹; separating chamber diameter is 33 mm; capacity is 0,025 m³/h; active volume of mixing chamber is 0,025 l; active volume of separating chamber is 0,020 l.

Extraction refining of solutions obtained after uranium concentrate dissolution

At extraction processing of uranium concentrated solutions containing molybdenum, iron, silicon, and other impurities molybdenum causes the greatest difficulties that is defined by its rather high coefficient of distribution in tributyl phosphate [4]. Long-term experience of extraction processing of uranium solution showed that uranium purification from impurities including molybdenum rises at increasing extractant saturation with uranium up to the limiting value. The existing extraction schemes of processing uranium solutions allow achieving maximal uranium saturation however obtaining waste water-tail solutions by uranium content (0,01...0,04 g/l) is impeded at low amount of stages in extraction column and complicated by the fact that return cleansing solution with high uranium content is introduced into extraction column.

To increase uranium refining from molybdenum and other impurities obtaining waste solutions by uranium content the extractant is proposed to be saturated with uranium in extraction column up to the concentration of 80...110 g/l and extractant limiting saturation up to 120 g/l is occurred in scrub column. In this case, water solution is proposed to be removed from the scrub column into intermediate device and then into device-preparer for stirring with initial solution. To check the possibility of increasing efficiency of uranium solution refining from soluble ballast impurities and obtaining waste water-tail solutions by uranium content achieving the required uranium refining from impurities the experiments at laboratory device were carried out.

The device consisted of 20 centrifugal extractors. Concentrated uranium solutions obtained after uranium concentrate dissolution in nitric acid were used as initial solutions. For complete separation of uranium solution from insoluble residues they were treated with flocculant FLOQUALAT™ FL 45C (diallyl dimethyl ammonium).

The solutions were filtrated through a double lavsan filter and then uranium extraction refining was carried out. 5 solutions with the volume of 0, 5 l each were processed in all and correspondingly 5 experiments (I, II, III, IV, V) distinguishing in uranium extraction and re-extraction modes were carried out. All the experiments were carried out at room temperature – 25 °C. 30 % TBP in hydrocarbon diluent was used as an extractant.

The amount of stages and modes of single operations carrying out are as follows. Extraction block – 5 extractors, the ratio of flows of organic solution to aqueous one (O:A) was chosen at extractant saturation with uranium from 80 g/l to the limiting one, equal 120 g/l. Scrubbing block – 5 extractors, flows ratio is O:A=10:1. Evaporated re-extractors with uranium concentration of 450...500 g/l preliminary corrected by nitric acid content up to 30 g/l were used as scrub solutions. Re-extraction block – 8 extractors, flows ratio is O: A=1:1, 2 (experiment III) and O: A=1:1, 4 (experiments I, II, IV, V). The solution containing 3...5 g/l of nitric acid prepared with distilled water was used as re-extractant solution. Carbonate washing block – 2 extractors, flows ratio is O: A=10:1 (experiment III) and O: A=20:1 (experiments I, II, IV, V). The solution containing 50 g/l of sodium carbonate prepared with distilled water was used as a scrub solution. In the course of experiments uranium extractant samples escaping the extraction block were chosen for defining the content of uranium and impurities in them. The content of uranium and nitric acid in re-extractants, water-tail and scrub solutions, in organic solution, escaping the re-extraction block as well as in carbonate and organic solutions escaping the block of carbonate washing of extractant were also defined. Re-extractants of uranium were evaporated up to uranium concentration of 450 g/l and content of uranium, nitric acid and impurities in them was determined.

Basic technological diagram of extraction processing uranium solutions at laboratory device are given in the Figure.

The initial solution entered into the 5th extractor of extraction block and organic solution – into the 1st extractor of the same block. Water-tail solution escaping the 1st extractor was combined with carbonate solution for further researches. Uranium extract entered into the 6th extractor of the scrubbing block. Scrub solution prepared from evaporated uranium re-extractor entered into the 10th extractor of this block. Uranium extract escaping the 10th extractor of scrubbing block entered into the 11th extractor of re-extraction block and washing solution escaping the 6th extractor was removed into intermediate container and then it was proportionally added to the initial solution. Nitric acid solution (3...5 g/l) entered into the 18th extractor of re-extraction block. Uranium re-extract escaping the 11th extractor was evaporated up to 410...460 g/l after defining uranium and nitric acid in it. In the evaporated uranium extractor uranium and impurities contents were determined. Organic solution escaping the 18th extractor of re-extraction block entered into 19th extractor of carbonate washing block. The solution containing 50 g/l of sodium carbonate entered into the 20th extractor of the same block.

Carbonate solution in the mixture with water-tail solution was used for researching in preparing to burial and alkali concentration of uranium. Organic solution escaping the 20th extractor was used as a reverse extractant processing the next batches of uranium solution.

The carried out experiments showed that at extractant saturation with uranium up to concentration (85...94 g/l) uranium content in water-tail solutions amounted to <0,01...0,04 g/l. Further increase of extractant saturation with uranium up to 118...119 g/l (practically 100 % of saturation) resulted in increasing uranium content in water-tail solutions up to 1 g/l and uranium extraction into extracts decreased from >99,99 to 99,70 %. Impurity content in uranium extracts, in particular molybdenum and thorium, decreased according to the increase of extractant saturation with uranium. Increasing extractant saturation with uranium from 85 to 94 g/l molybdenum content in uranium extracts amounted to $1,0 \cdot 10^{-3}$ % at its content in initial solutions $(32...50) \cdot 10^{-3}$ %. Respectively, decontamination factors of uranium from molybdenum amounted to 30...50 (Table 1). Increasing extractant saturation with uranium up to 118...119 g/l resulted in decreasing molybdenum content in uranium extracts up to $<0,1 \cdot 10^{-3}$ % (decontamination factors of uranium from molybdenum is more than 500) [5] that corresponds to the standards ASTM C 787-03 for molybdenum content in commercial uranium hexafluoride.

Increasing extractant saturation degree with uranium resulted also in rise of uranium decontamination factors from other impurities. So changing extractant saturation with uranium from 85 to 119 g/l resulted in increasing uranium decontamination factors from tungsten from 1 to >20, aluminum from 50 to 100, calcium from 3, 3 to 15, 0. Uranium refining from such impurities as iron, manganese, tantalum did not depend on extractant saturation with uranium.

In the course of experiments regardless of extractant saturation with uranium the presence of fine-dispersed

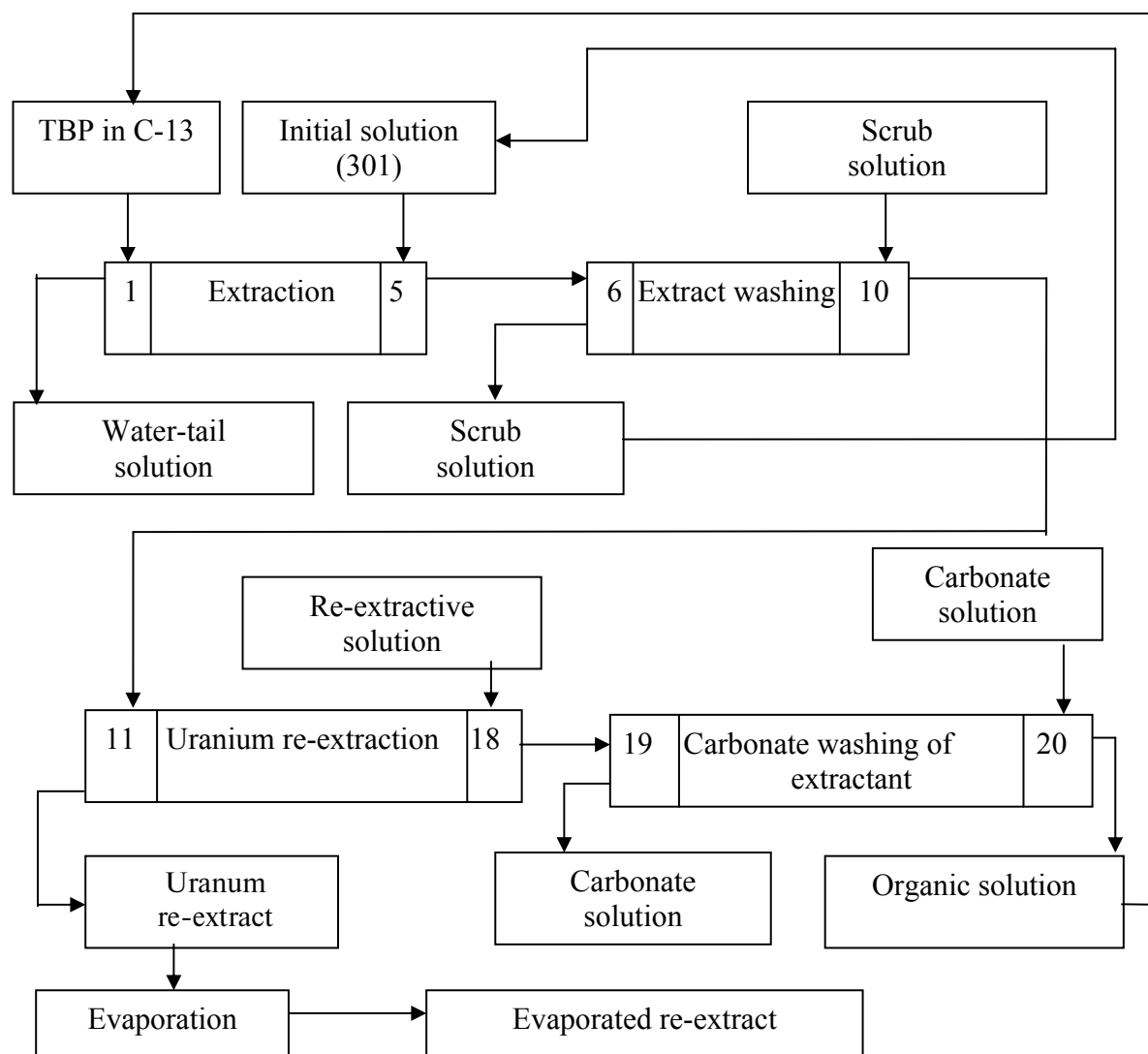


Figure. Basic technological diagram of extraction processing of uranium solutions

sediments uniformly distributes over the whole volume of the solution in water-tail solutions was noted. Presence of the same sediments in water-tail solutions was observed earlier when carrying out laboratory studies and industrial processing uranium solutions on the cascade of pulsating columns. Sediment sample analysis showed that their composition is mainly determined by calcium sulfate with silicon, molybdenum etc. Attempts to separate fine dispersed sediments by solution filtration through paper and lavsan filters as well as by jointing did not bring positive results. However, after keeping water-tail solutions during the day the solutions were clarified and a thin white layer of sediments was observed at the bottom of the container. It should be mentioned that fine dispersed sediments formed in centrifugal extractors did not influence negatively on their functioning. Uranium extracts escaping the extraction block were transparent. The apparent carryover of water phase as well as organic solution carryover with water-tail solutions was not observed. Failures of hydrodynamic operation modes (phase overflow, block of extractant channels of water and organic phases with sediments) were not noticed.

Table 1. Decontamination factors of uranium from impurities at extraction operation

Element	№ of the experiment				
	I	II	III	IV	V
Mo	32	32	50	>320	>320
Ti	>3	>3	>3	>3	>3
W	1	1	10	>20	>20
Al	50	100	50	100	100
Mn	>100	>100	>150	>100	>100
Fe	>30	>30	>40	>30	>30
Ca	3,3	4,3	13,3	15,0	15,0
Ta	>20	>20	>20	>20	>20

The investigations showed that the main factor determining the required uranium refining from impurities including molybdenum is limiting or close to the limiting extractant saturation with uranium. However, extraction block operation in the mode of limiting extractant saturation with uranium may result in increasing uranium content in water-tail solutions higher than waste standards that attracts processing water-tail solutions for additional recovery of uranium from them at a single node and correspondingly it demands additional agent consumption.

As the experiments showed the mode of limiting saturation of the extractant with uranium achieved in scrubbing block at extractant washing with nitrate solution containing 450...500 g/l of uranium allows obtaining the required uranium refining from impurities and extractant saturation with uranium in extraction block is lower than a limiting one (90...110 g/l) in the aggregate with extraction of scrub solution into intermediate container allows obtaining water-tail solutions waste by uranium content. So at uranium content of 94 g/l in extract 0,04 g/l remains in water-tail solution. As it was said above, extraction block of laboratory device consisted of 5 centrifugal extractors. In industrial variant which is in the design stage 7 centrifugal extractions are proposed to be used in extraction block that should support uranium content in water-tail solutions not more than 0,015 g/l.

Carrying out displacement washing of uranium extract allowed increasing saturation of organic solution, escaping the scrubbing block, with uranium up to the limiting (119...120 g/l) and owing to this obtaining additional uranium refining from impurities in scrubbing block that supported their content in uranium re-extracts meeting the requirements of ASTM C 787-03 for commercial uranium hexafluoride carrying out all 5 experiments. Let us note that the required uranium refining from impurities in experiments 4 and 5 was achieved just in extraction device block due to limiting extractant saturation with uranium. Content of impurities forming volatile and non-volatile fluorides obtained in the experiments are shown in Table 2.

Table 2. Impurity content

Element	Impurity content, wt. % to U	
	Achieved magnitude	Standard by ASTM C 787-03
Mo	$<0,1 \cdot 10^{-3}$	$0,14 \cdot 10^{-3}$
W	$<0,1 \cdot 10^{-3}$	$0,14 \cdot 10^{-3}$
Cr	$<0,3 \cdot 10^{-3}$	$1,0 \cdot 10^{-3}$
V	$<0,1 \cdot 10^{-3}$	$0,14 \cdot 10^{-3}$
Nb	$<0,1 \cdot 10^{-3}$	$0,1 \cdot 10^{-3}$
Ta	$<0,1 \cdot 10^{-3}$	$0,1 \cdot 10^{-3}$
Si	$<1,0 \cdot 10^{-3}$	$1,0 \cdot 10^{-2}$
Ti	$<0,1 \cdot 10^{-3}$	$0,1 \cdot 10^{-3}$

Notes: summary content of impurities forming non-volatile fluorides of aluminum, calcium, copper, zinc etc. in all 5 experiments amounted to $<3, 0 \cdot 10^{-2}$ %

Decontamination factors of uranium for extraction cycle in whole amounted to: from tungsten – more than 20, from aluminum – more than 50, from manganese – more than 150, from iron – more than 133; from magnesium – more than 10; from titanium – more than 10; from molybdenum – more than 320...500; from vanadium – more than 40.

Uranium content in organic solutions escaping the re-extraction block of centrifugal extractors is less than 0,01 g/l at flow ratio O: A=1:(1,4...1,5). Decrease of ratio of re-extractive solution flow to the flow of organic one (O:A=1:1,2) in the experiment III resulted in inc-

reasing uranium content up to 3 g/l in organic solution escaping re-extraction block that exceeds significantly the required value – not more than 0,015 g/l. However, it should be mentioned that in extraction diagram of uranium concentrate processing proposed for introduction 13 centrifugal extractors are stipulated in re-extraction block (there were used 8 in the laboratory device) that allows decreasing significantly uranium content in organic solutions escaping the re-extraction block. Besides, heating re-extractive solution up to 70 °C is stipulated that results in decreasing uranium distribution coefficients at each stage of re-extraction block and respectively in additional decreasing of uranium content in organic solution escaping the block.

At extractant carbonate washing there were no sediments in aqueous and organic phases. Uranium content in carbonate solutions escaping the block of extractant carbonate washing in the experiments I, II, IV, V amounted to less than 0, 01 g/l, in the experiment III it was 0, 28 g/l, in reverse extractants after soda washing was less than 0, 01 g/l. It should be mentioned that carbonate solutions escaping the scrubbing block of centrifugal extractors were of intensive-yellow color that, in our opinion, is explained by presence of coagulant or compounds entering into its composition in organic solution. When processing uranium solutions, untreated by coagulant, before the carbonate solutions were colorless. This circumstance demands studying in coagulant distribution in two-phase systems containing TBP as organic solution in hydrocarbon diluent as well as in coagulant or its compounds influence in extractant on technological data of extraction processing of uranium solutions during a long period of time.

Conclusions

1. The technology of processing concentrated uranium solutions with its refining from insoluble impurities of oxides and hydroxides of iron, silicon, molybdenum, calcium and soluble impurities using cascade of centrifugal extractors was developed and suggested for industrial introduction in laboratory environment.
2. The technological diagram consisting in extractant saturation with uranium in extraction block less than limiting level and in scrubbing one – limiting was suggested and tested at laboratory device consisting of centrifugal extractors.
3. It was shown that at processing solutions containing 370...450 g/l of uranium and 40 g/l of nitric acid, extractant saturation with uranium in extraction block up to concentration of 85...94 g/l (5 extraction stages) and 118...119 g/l in scrubbing block (5 scrubbing stages) uranium waste content 0,01...0,04 g/l in water-tail solutions and impurity content (including molybdenum) in re-extractors corresponding to ASTM C 787-03 at uranium hexafluoride for enriching and ASTM C 788-03 at uranyl nitrate of nuclear grade is supported.

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Received on 07.12.2006

UDC 622.374

TOPAZ CONCENTRATE DESILICONIZATION WITH AMMONIUM BIFLUORIDE

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Fluoridizing agent for the process of topaz concentrate desiliconization has been selected, topaz thermodynamic potentials have been appraised, thermodynamic probabilities of fluorination reaction of topaz concentrate main constituents have been calculated. The results of studying the concentrate desiliconization process with ammonium bifluoride by the methods of thermogravimetry, RFA, microphotography are presented.

The perspective of modern ceramic industry is the development of competitive product both on the basis of traditional raw material resources and involving new raw materials unused before. Development of technology of light mullite refractory obtaining from natural topaz concentrate allows meeting a demand on domestic market and decreasing significantly expenses for mullite goods production. Mullite represents aluminum silicate of the composition $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, stable at temperature up to 1700 °C, possessing a number of unique physicochemical properties and being one of the main crystal phases in many ceramic materials [1]. It is traditionally obtained by the method of solid-phase reactions (sintering aluminum and silicon oxides in stoichiometric ratio) as well as burning native minerals. Main natural raw material for mullite obtaining is kaolin and topaz [2].

Topaz is the mineral of island silicate subclass $\text{Al}_2[\text{SiO}_4](\text{F},\text{OH})_2$. The uniqueness of topaz is in the fact that it is the only native mineral which turns into mullite without intermediate phases when burning at 1100...1200 °C. Topaz refers to precious stones of the III class; this is the reason why mullite production from it is economically unpractical. However, there are ores containing topaz which can not be applied in jewelry industry it is so-called commercial topaz. The unique deposit of commercial topaz «Kopna» which is on the territory of Kemerovo region near settlement Ursk was explored in Siberia. On the basis of the deposit the ore-dressing and processing enterprise «Urskoe» is developed. Quartz is a dominant ore generating mineral of this deposit with the content from 60

to 92 %. Topaz forms from 7 to 38 % of ore; close relation with quartz is typical for it. After ore enriching topaz concentrate contains up to 50 % of excess silicon oxide which should be removed before mullite obtaining. Besides, in topaz constituent of ore there is up to 12 % of F which is segregated at burning in the form of SiF_4 [3]. Thus, there is a necessity of developing such technology which could allow removing excess quartz from topaz concentrate without touching topaz constituent. So it was necessary to chose desiliconizing agent to research the technique of desiliconization of topaz concentrate as well as mullitization processes of desiliconized topaz residual.

1. Selection of fluoridating agent

One of the efficient methods of silicon oxide removing (desiliconization operation) from ores is fluoride method. Main fluoridating agents in modern industry are elemental fluorine and fluorohydrogen as well as ammonium fluorides. Thermodynamic calculations carried out in the paper [4] showed that all three fluoridating agents may be used for desiliconization of topaz concentrate. However, there is a number of problems limiting F_2 and HF application for these purposes. In particular, using elemental fluoride requires development of fluoride additional production that increases expenses for ultimate goods production. Application of HF as well as F_2 results in emission of toxic gas SiF_4 which requires special conditions of working and utilization. Therefore, it is technologically more profitable to use ammonium bifluoride for desiliconization.