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INTENSIFICATION OF SEPARATING PROCESSES OF HIGHLY CONCENTRATED URANYL SOLUTIONS AND FINE-DISPERSED SUSPENDED SOLIDS

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The investigations on intensifying separation processes of highly concentrated uranyl nitrate solutions and solid fine-dispersed suspended particles (ferric, silicon, molybdenum oxides and others) applying organic coagulants and flocculants have been carried out. It is shown that in the investigated regions of uranium concentrates of 300...450 g/l, nitric acid of 0,5...3,0 mole/l at optimal temperature 30...50 °C for effective phases separation the introduction of 100...200 mg/l of coagulant FLOQULAT™ FL 45 C (or an analogue VPK-402) and 5...10 mg/l of flocculant FLOPAM™ FO 4140 PWG type is enough.

Introduction

The perspective of the development of atomic power-producing complex of Russia is determined by Federal task program (FTP) «Development of atomic energy industrial complex of Russia for 2007–2010 and in perspective till 2015». The accelerated development of uranium production capacities and broad attraction of foreign companies uranium into Russia is planned in this program. Complication of enterprises producing uranium by refining redistributions as well as purchasing expensive nuclear-pure uranium compounds abroad decrease significantly economic efficiency of a fuel part of nuclear power [1].

Nuclear branch restructuring allows organizing refining operations of both domestic uranium concentrates and those bought on the world market at the plants have becoming available. In the past there were no plants for large-scale concentrates processing in USSR and Russia. At each ore enterprise there were as a rule its own refining scheme and obtaining pure uranium compounds.

At the present the task of mastering processing technique for concentrates of any composition with minimization of liquid radioactive waste is urgent in Russia. The most available minimization of liquid waste is the development of uranium processing purification with maximal concentration of uranyl nitrate solutions. The second stage after concentrates dissolution in nitric acid is separation of the obtained suspensions into solid and liquid components.

1. Selection of coagulant and flocculant for intensification of the extraction process of insoluble residue from the uranyl nitrate solution

For intensifying the separation processes of uranyl nitric acid solutions and fine-dispersed solid suspensions the influence of coagulants on this process was researched. Under the influence of coagulants fine-dispersed solids suspended in solution are gathered together into large mass – «flocks» which may be removed rather easily by such methods as precipitation, filtration, centrifugation. To exclude contamination in the given system the coagulants of organic origin without impurity cations may be used.

In highly concentrated solutions of uranyl nitrate (300...500 g/l by uranium), obtained at uranium concentrate dissolving in nitric acid, the fine-dispersed oxides and hydroxides of substances accompanying uranium in ore formation – this is mainly the compounds of iron, silicon, aluminum, molybdenum, are present in the form of solid suspensions. Due to their chemical nature metal oxides and hydroxides in acidic media have negative surface [2].

It is known that application of proper coagulants and flocculants allows intensifying the process of suspension separation into macro phases that is, in this case, obtaining pure solutions of uranyl nitrate.

It should be mentioned that we could not find in the published researches any information about coagulant application for purification of highly concentrated uranyl solutions from solid impurities with further uranium refining up to nuclear quality. All researches were carried out either with ore uranium leach (uranium concentration is less than 10 g/l) [3] or with strongly diluted solutions [4].

Searching for the proper coagulant produced in industrial scale the attention was paid to quaternary liquid polyamine applied for drinking water refining from solid impurities of inorganic and organic composition [5, 6].

On Russian market the polyamines of French and Russian production are sold. French coagulants are delivered to Russia by Co Ltd «Resurs ekologiya», Chelyabinsk. This company gave us some types of coagulants for studying. The coagulant of series FLOQULAT™ FL 45 C turned out to be the most efficient [7]. The similar coagulant is produced in Russia by CC «Kaustik», Sterlitamak known as «water-soluble cation polyelectrolyte of the type VPK-402».

Some properties of the applied coagulants: molecular weight is from 10 thousand to 1 million; nontoxic; noncombustible; fire-explosion safe; stable at storage.

To increase the efficiency of the process of liquid and solid phase separation the polymeric flocculants are often applied after processing colloid system with coagulant. Flocculants are used in very small quantities 0,01...1,00 mg/l and in this case precipitants are thicker and rapidly precipitated. Use of flocculants allows dec-

reasing coagulant dosage up to the minimal quantity required for suspension destabilization.

We did not find domestic producers of flocculants having the required characteristics. Therefore, French flocculants of ten denominations were applied in the researches: FO 4115, FO 4140, FO 4190, FO 4240, FA 920, AN 905, AN 910, AN 913, AN 923, AN 945 [8]. It is solid powdery substances soluble in water. Flocculants had different composition and were characterized by nonionic, anionic and cationic forms.

Experience in flocculants application at real technological solutions showed that the highest efficiency in separation of nitrate uranyl solutions and solid impurities was achieved using cationic polymer of the series FLOPAM™ FO 4140 PWG (PWG-Potable Water Grade – drinking water class). Some properties of flocculant FO 4140 PWG:

- molecular weight is from 3 to 15 m;
- charge density on a molecule is very low;
- solution viscosity with concentration of 1 g/l – 60 centipoise;
- storage temperature of flocculant powder is 0...35 °C;
- nontoxic.

2. Clarification of highly concentrated solutions of uranyl nitrate

The experiments were carried out in the direction of selection of separation optimal conditions for nitrate solutions of uranyl nitrate and insoluble residues of metal oxide compounds using coagulant of the type FLOQUALAT™ FL 45 C, further FL 45 C.

Suspensions for investigation were prepared solving uranium concentrate samples (uranium in the form of U_3O_8 , the amount of impurities is 12 % from batch weight) in nitric acid stirring at the temperature 90...95 °C. The obtained suspensions were of typical brown-orange color of ferric iron hydroxide against a background of yellow-green color of highly concentrated solution of uranyl nitrate. Mass of insoluble residue amounted to 0,6 % from batch mass. After finishing stirring solid impurities were distributed nonuniformly in the volume of solution. A part of insoluble residues was settled during two-three hours and represented very mobile, easily roiled sediment. The rest part of insoluble residues (about 2/3) formed with the solution the sediment stable system which was clarified by 25...30 % during 3–4 days. Such solutions were completely clarified neither by centrifugation nor by filtration.

Such solutions are not suitable for extraction processing as suspension presence in extraction devices results in trouble with process hydrodynamics and decrease of efficiency of target component extraction and refining. Coagulants and flocculants tenfold increasing the velocity of sedimentation were required for solution clarification.

To define coagulant optimal concentration 9 samples of suspension by 100 ml were prepared. Solution of coagulant FL 45 C was loaded into each sample supporting

coagulant concentration in the suspension 10, 50, 80, 100, 120, 150, 180, 200 and 500 mg/l. Coagulant was not added into check experiment. Operations were carried out at room temperature. Stirring was performed with compressed air by five minute. Then suspensions were poured into graduated cylinders and marked coagulant concentration at which suspension had maximal sedimentation velocity. At coagulant concentration from 0 to 50 mg/l solutions were not clarified, remain turbid; from 100 to 200 mg/l the solutions of uranyl nitrate were transparent, sediment was about 30 %; at 500 mg/l the solution of uranyl nitrate was transparent, sediment was 40 % of volume. At introduction of coagulant up to 80 mg/l concentration the solutions were clarified however sedimentation velocity was 0,3 % per minute from the volume. Sedimentation velocities in the experiments with coagulant concentration higher than 100 mg/l amounted to 2,2...2,8 % of the volume per minute.

Thus, it was stated that coagulant FL 45 C concentration at which highly concentrated solutions of uranyl nitrate are clarified with the maximal velocity is in the range from 100 to 200 mg/l.

The flocculant was selected in the following way.

Suspension consisting of uranyl nitrate solution and suspensions of oxides and hydroxides of impurity elements was prepared of uranium concentrate (uranyl nitrate concentration in suspension was 400 g/l, nitric acid concentration was 0,5...1,0 mole/l) the solution of coagulant FL 45 was prepared with concentration of 10 g/l and solutions of ten different flocculants with concentration 0,5 g/l. Then 10 glass cups were filled up with 50 ml of the prepared suspension each and coagulant FL 45 C were introduced into suspensions while stirring forming coagulant concentration in suspension of 200 mg/l.

Suspensions were actively stirred for 5 min then flocculants by 1,0 mg/l were added in them and stirred additionally during two minutes. Then suspensions were filtered through a layer of lavsan material applied for filtration. Flocculants presented for researches revealed flocculating properties in various degree. Cation forms of flocculants showed themselves in the best way (type FO) anionic showed themselves as the worth ones (type AN). So applying flocculants FO 4140 and FO 4240 not more than 2 % of sediments came into filtrate whereas application of the other flocculants, among the studied ones, resulted in breakthrough of sediments from 4 to 12 %. Sediments breakthroughs occur before formation of auto-filter bed and then the sediment is fully trapped at the filter.

At flocculants introduction just after coagulant FL 45 C addition and filtration through the lavsan the filtrates contained almost equal quantity of suspensions in all the experiments 5...6 %.

Solution soaking after coagulant and flocculant addition promoted better suspension separation. So next day after filtration all solutions were transparent regardless of applied flocculant.

In check experiments carrying out the same operations at suspensions the solutions turned out to be turbid without introducing coagulants and flocculants, sedi-

ments passed through the lavsan. Addition of coagulant FL 45 C into these suspensions (filtrates) supported rapid sedimentation of solid particles. Filtering these suspensions through a layer of material of polyethylene terephthalate (PETP) tissue (lavsan) first of all a part of sediment passed through the filter (till the formation of auto-filter bed) which rapidly settled then (sediment volume is 4 %).

Quality of solutions and sediment volumes depending on flocculant concentration with coagulant addition was determined with flocculant FO 4140 and coagulant FL 45 C; the results of researches are presented in Table 1.

Table 1. Dependence of solution quality and sediment volume on flocculant concentration

Concentration of flocculant FO 4140 in suspension, mg/l	Concentration of coagulant FL 45 C in suspension, mg/l	Type of solutions and sediments volume from the total volume of suspension
1,0	0	Turbid
5,0	0	Turbid
0,1	200	Transparent, sediment of 32 %
0,5	200	Transparent, sediment of 30 %
1,0	200	Transparent, sediment of 25 %
5,0	200	Transparent, sediment of 20 %
10,0	200	Transparent, sediment of 31 %

The maximal solution clarification was achieved at concentration of flocculant FO 4140 – 5 mg/l; in this case sediment volume from the total suspension volume amounted to 20 %.

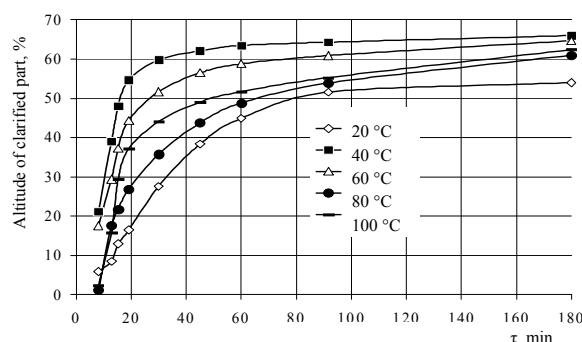


Fig. 1. Dependence of dimension of suspension clarified part on temperature and time of precipitation at coagulant and flocculant functioning

Dependence of coagulation speed on the temperature was defined with coagulant FL 45 C (Fig. 1). Addition of agents into suspension, stirring as well as suspension precipitation in uranyl nitrate solutions was carried out at temperatures: 20, 40, 60, 80 and 100 °C in the following way. Cylinder with suspension was put into thermostat with specified temperature. In 5 min coagulant was introduced into cylinder (admixture in cylinder was stirred 5 times by return movements of propeller mixer up and down) and then flocculant was added. Solution of flocculant FO 4140 was introduced into suspension at 5 mg/l. After the same stirring and exposure of admixture during 5 min at specified temperature heating was finished and then observations were carried out at room temperature. Each 5 minutes altitude of

clarified layer was recorded. Suspensions sedimentation velocity achieved maximum at 40 °C. At the next stage sediments were roiled, divided into two parts, centrifuged and filtrated through a layer of tissue of PETP. Joining was carried out at the test-tube centrifuge at 1000 rev/min up to 5 min; separation factor equals 210. It was stated that temperature increase results in converse effect that may be explained by speed acceleration of peptization (unaggregation) of floccules (aggregates, flocks) at temperature rise and probably destruction of coagulant and flocculent macro molecules. It should be mentioned that coagulant producer recommends preparing and storing solutions of these agents at temperature not higher than 50 °C.

Uranium concentration influence on coagulation and sedimentation process was defined at suspensions with uranium concentration in liquid phase 300, 350, 400 and 450 g/l, nitric acid concentration is 0,5...1,0 mole/l; temperature is 40 °C; stirring with propeller mixer during 10 s; measuring altitude of clarified layer each ten minutes.

The experiments showed that uranium concentration increase in the solution promotes increasing precipitant sedimentation volume that may be explained by the rise of dispersed medium viscosity.

Influence of solid phase quantity on amount of flocculant admixture supporting sedimentation was carried out in uranyl nitrate solutions with uranium concentration 400 g/l and nitric acid concentration 1 mole/l. Sediment obtained before was added into uranyl nitrate solution in the amount of: 0,6; 4,5; 8,2 % when stirring. Measuring cylinders were filled up with 50 ml of homogeneous sample and coagulant solution was introduced. The investigated suspension without coagulant was used as a test sample. Filtration velocity of investigated suspension with different content of coagulant FL 45 C was measured and after that the factor of filtration improvement as a quotient from division of filtration velocity of test samples (ml/min) by filtration velocity of suspension without coagulant (ml/min) was calculated. It was stated that in highly concentrated solutions of uranyl nitrate as well as in diluted solutions [2] coagulant concentration required for achieving coagulation threshold depends on solid phase concentration in suspension. So at 0,61 % of solid phase content in uranium solution has maximal magnitude 3,5 at coagulant concentration in suspension of 50...100 mg/l. At solid phase content of 4,5 % the improvement factor of filtration achieves maximum of 6,8...7,2 at coagulant concentration of 100...400 mg/l. At solid phase content of 8,2 % this factor has the magnitude of 6,8...7,2 at coagulant concentration of 750...1000 mg/l.

Thus, optimal coagulant concentration in suspension should be ascertained individually depending on solid suspensions content in suspension.

Influence of nitric acid concentration on sedimentation and coagulation processes was determined in suspension solutions, containing 0,7; 1,1; 1,7; 2,1 and 3,0 mole/l HNO₃. The obtained data are given in Table 2.

Table 2. Dependence of solution clarification time on nitric acid concentration

HNO ₃ , mole/l	Suspension sample with coagulant 100 mg/l			Test sample (without coagulant)		
	Sediment volume, %	Solution charac- teristic	The main time of clarification, min	Sediment volume, %	Solution characteristic	Clarification time, min
0,7	30,9	Transparent	39	0	Turbid, suspended particles by the whole volume	120
1,1	34,7	Transparent	31	0	Turbid, sediment at the bottom 9 %	120
1,7	38,0	Transparent	21	23,3	Dimmed	40
2,1	37,6	Transparent	18	28,3	Opalesce strongly	65
3,0	37,6	Transparent	17	34,5	Opalesce slightly	75

Table 3. Quality of solutions after jointing depending on nitric acid concentration

№ of the experiment	Concentration of HNO ₃ , mole/l	Jointing time, min						Filtration through a layer of tissue	
		1	2	3	4	5	10		
1	0,7	Turbid		Opalesce		Transparent		Filtrates in all samples are transparent, there is no sediment	
2	1,1	Turbid		Opalesce		Transparent			
3	1,7	Opalesce				Transparent			
4	2,1								
5	3.0	Transparent							

Conditions of experiments are: suspension with concentration 3,5 % of solid insoluble residues were stirred in cylinder during 5 min at temperature 40 °C then coagulant concentration 200 mg/l was formed in suspension, stirred during 10 s with propeller mixer then the solution was soaked at 40 °C 5 more min. Cylinder was taken off the thermostat and observations were carried out at room temperature. The main time of solution clarification after which sediment concentrates insignificantly shows considerable influence of acid concentration on sedimentation system characteristics. In 18...20 h sediment volume in cylinder relative to the total volume was defined.

In the samples with coagulant at the studied concentration of nitric acid the solutions of uranyl nitrate turned out to be transparent, the lowest percent of sediment is at concentration of HNO₃ 0,7 mole/l.

Suspension behavior after roiling was determined at jointing at test-tube centrifuge at 1000 rev/min, separation factor equal 210, and filtration through a layer of tissue of PETP. It is seen from the data given in Table 3 that increasing nitric acid concentration improves separation process of solid phase.

It should be noted that here the factor mentioned before is revealed when increasing nitric acid concentration velocity of solid particles sedimentation rises. This phenomenon may be explained by dissolving the finest particle fraction at peracidity and changing the interaction conditions of oxide particle surface with water molecules.

To confirm coagulating properties of VPK-402 produced in Russia the investigations by the same scheme as for FL 45 C were carried out. The carried out researches fully confirmed the similarity of FL 45 C and VPK-402 excluding the fact that concentration of coa-

gulant proper in VPK-402 is twice lower than in FL 45 C and impurity content, in particular sodium chloride, is twice higher that was stated in Russian coagulant certificate. Properties of solutions of coagulants FL 45 C and VPK-402 with concentration of 10 g/l do not change during the month at their soak at room temperature.

To check the coagulant influence on extraction purification of uranyl nitrate TBF the experiments at extraction laboratory setup consisting of 20 centrifugal extractors were carried out. The suspension obtained after uranium concentrate dissolving in nitric acid was clarified from solid impurities using coagulant FLOQU-LAT™ FL 45 C. Nitrate uranium solutions with uranium concentration of 450 g/l were filtered through the filter made of double cloth PETP. 5 experiments differing in modes of extraction and re-extraction processes of uranyl nitrate were carried out. Positive effect of coagulant introduction into highly concentrated solution of uranyl nitrate was noted (the results are given in the article «Extraction processing of concentrated solutions of uranyl nitrate with high content of impurities»).

Conclusion

1. Researches in intensification of separation processes of highly concentrated solutions of uranyl nitrate and solid fine dispersed suspended particles (oxides of iron, silicon, molybdenum etc.) showed high efficiency of applying organic coagulant FLOQU-LAT™ FL 45 C (the same as VPK-402) and flocculants.
2. In the studied regions of uranium concentration (300...450 g/l), nitric acid (0,7...3,0 mole/l) and solid impurities at optimal temperature 30...50 °C the addition of 100...200 mg/l of coagulant and 5...10 mg/l of flocculant into uranyl nitrate solutions is enough for efficient phase separation

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THE RESEARCH OF URANIUM MONOXIDE-OXIDE DISSOLUTION PROCESS IN NITRIC ACID

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The kinetics of concentrates of uranium monoxide-oxide dissolution process by nitric acid solutions of 5...9 mole/l in the range of 11...90 °C has been studied. It is stated that initial nitric acid concentration increasing results in some uranium dissolution degree increasing only at the first process stage. Temperature increasing significantly raises uranium dissolution degree at the first stage as well. Uranium dissolution degree increases for all studied temperatures with increasing of the process period. The main feature of the studied process is that while dissolving uranium monoxide-oxide the behavior of iron, molybdenum, silicon additives is adequate to that of uranium. The equation of the reducing sphere describes the uranium leaching process from its nitric acid concentrates.

To obtain uranium hexafluoride used for enrichment according to the demands of International standard ASTM C 787-03 uranium refined from soluble and insoluble impurities to the certain limits is required. Concentrates which represent oxides of uranium and impurities after thermal treatment (U_3O_8 , MoO_3 , SiO_2 , Fe_3O_4 , CaO , MgO , Al_2O_3 etc.) may be used as a material for obtaining uranium of the required purity degree. Dissolution (leaching) of U_3O_8 from the concentrates is reasonable to be carried out with nitric acid as the extractant tributyl phosphate used for refining U (VI) from impurities works efficiently in nitrate medium. In the process of triuranium octaoxide dissolution in nitric acid U(IV) is oxidized to U(VI) without oxidizer. Nitric acid has low corrosive activity relative to constructive materials, for example, to steel 12X18H10T. The task of investigations included defining influence of temperature, nitric acid concentration, time of concentrate dissolution on the degree of extraction of uranium and impurities from it (iron, molybdenum, silicon) as well as investigation of kinetics of uranium and impurities dissolution, calculation of velocity constant and activation energy, choice of limiting process stage.

Experimental part

Triuranium octaoxide concentrate which represents a dark-grey powder of the following composition: U – 83,14 wt. %; U-234 – 53 mkg/g; impurities (% of U): Fe – 0,070, SiO_2 – 0,170, Mo – 0,031, Ca – 0,004, $As \leq 0,004$, $B \leq 0,00003$, $F \leq 0,0005$, halogens – 0,002, Mg – 0,001, P – 0,006, K – 0,01, Na – 0,010, $Th \leq 0,003$, $Ti \leq 0,001$, $V \leq 0,001$, $Zr \leq 0,001$, $W \leq 0,001$ was used as a subject of inquiry. Apparent and metric densities of the powder are 1, 65 and 6, 83 g/cm³, respectively. Powder particle size determined at sedimentometer BC-3 did not exceed 50 mkm. Grain-size composition: 3 % of fractions of 0...10 mkm, 18 % of fractions of 10...20 mkm, 35 % of fractions of 20...30 mkm, and 22 % of fractions of 30...40 mkm and of 40...50 mkm each.

Influence of nitric acid concentrations (5...9 mole/l), temperature (11...90 °C) and time on dissolution degree of uranium oxides and impurities was studied at laboratory setup (Fig. 1). Reactor (3) was filled up with nitric acid of specified concentration. The solution was stirred with mechanical mixer. Solution temperature in