

# THE SEARCH FOR ALTERNATIVE EFFECTIVE ION EXCHANGE RESINS FOR URANIUM RECOVERY FROM IN-SITU LEACHING PREGNANT SOLUTIONS

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**Abstract** Sorption characteristics of ion exchange resins D402-II, S500, EDE-10P and CG8 were investigated during uranium extraction in static conditions from pregnant solutions of uranium ISL. Sorption from sulfuric, nitric and hydrochloric acids model solutions were also investigated. It was identified that S500 and EDE-10P are of greatest interest. Uranium sorption from pregnant solution of uranium ISL on resins S500 and EDE-10P in dynamic conditions had been carried out and that allowed us to achieve the capacity of 74.6 and 80.7 mg/g respectively after passing of 850 BV. In static conditions the process of uranium desorption from S500 and EDE-10P resins was investigated with using of the following solutions, mol/dm<sup>3</sup>: H<sub>2</sub>SO<sub>4</sub> 1.0; NH<sub>4</sub>NO<sub>3</sub> 0.6, 1.3, 1.8; (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> 0.3, 0.6; HNO<sub>3</sub> 1.6; NaCl 0.8, 1.6, 2.4. It was identified the prospects of using of ammonium nitrate and sodium chloride based solutions. The tests of uranium desorption under dynamic conditions with the use of NH<sub>4</sub>NO<sub>3</sub> 1.8 mol/dm<sup>3</sup> solution determined by the efficiency of extraction of uranium recovery using the reverse desorption solution. That will allow to consider favorably integration of chelating resin S500 in the existing technology of uranium ISL enterprises.

**Keywords** uranium ISL, chelating ion exchange resin, sorption, desorption

## 1 Introduction

At present time anion exchange resins are mainly used for uranium in-situ leaching (ISL) enterprises, that in general due to the high affinity of uranium complexes with functional groups specified type of ion exchange resins. At the same time anion exchange resins have some shortcomings: they are characterized by organic, silicon and other anions "poisoning", which determines regular purification from contaminants. The specified complexity, combined with the high value of the anion exchange resin to create preconditions for the search for alternative ion exchangers, which allow to extract uranium with similar efficiency.

As we know from various sources, uranium in sulfuric acid solutions could be in the form of uranyl cation, medicationabana molecule uranysulfate and sulfate complex anions, the ratio between which depends on the concentration of sulfate ions and uranyl-ions in accordance with the reaction:



It is possible to assume, conditionally, that there is a dynamic equilibrium in solution:



Thus cation exchangers (extract uranyl cations) as well as anion exchangers (extract sulfate anion complexes) could be used for uranium extraction. As far as  $\text{UO}_2^{2+}$  or  $[\text{UO}_2(\text{SO}_4)_3]^{4-}$  ions to remove from the solution in the phase resin, shift the equilibrium towards the extracted ion will be followed.

Strongly acid ion-exchangers couldn't be used for uranium extraction from pregnant solution of uranium ISL due to the sharp decrease of resin capacity (up to zero) by increasing the concentration of sulfate-ions up to 10-15 g/dm<sup>3</sup>. This is related with the fact that, as far as sulfate-ions concentration increasing the above mentioned equilibrium shifts toward the formation of sulfate anion complexes and the activity coefficient of uranyl cation in external solution decreases.

Weak acid ion-exchanger can operate in these conditions (e.g. SG-1), since the reduction of activity coefficient of uranyl-ion is compensated by decreasing of activity coefficient of uranyl-ion in the resin phase.



The acidity increases and shift the equilibrium to the left, therefore capacity of the uranium is equal to zero at low pH values, while increasing the pH above 1.2 the capacity begins to increase and achieve the maximum at pH 3-5. Because ion exchange acid (H<sup>+</sup>) is released and the pH is reduced, in order to maintain the right pH value (2.8 to 3.5) are added alkaline agents

Doubly charged cations of impurities (Fe<sup>2+</sup>, Mn<sup>2+</sup>) can't compete with uranyl-ion due to smaller size of hydration shell and low activity coefficient in resin of the latter.

Ferric ions are capable to compete with uranyl-ion, but ferric sulfate hydrolysis begins at pH 2.5, whereby the resin capacity by iron is not high. The presence of nitrate-ion has no effect on uranium capacity in contrast to anion exchange resins.

Because of high selectivity of the resin to hydrogen-ion, desorption can be performed by any acid at pH < 1, and, in addition, by increasing the acid concentration leads to the decrease of the volume of received commodity desorbate.

The results of research of uranium sorption on carboxyl cation exchange resin KM-2p from bicarbonate-chloride solution are known [1].

Initial resin KM-2p was transferred from H<sup>+</sup> form to Na<sup>+</sup>-NH<sub>4</sub><sup>+</sup>-H<sup>+</sup> with using of 10 % NaCl + 0,3 % HNO<sub>3</sub> solution. Initial sodium-chloride regenerate (pH 6.0-6.5; HCO<sub>3</sub><sup>-</sup> – 8-10 g/dm<sup>3</sup>) with contents of uranium 4.2 g/dm<sup>3</sup> and molybdenum 3.0 g/dm<sup>3</sup> was fed to sorption column – the chain of 3-4 columns, each of which was loaded by 100 cm<sup>3</sup> of cation exchange resin KM-2p. As the result of resin capacity by uranium was 140-150 g/kg. The column with saturated resin was regenerated. Before it the resin have been washed (2 BV) to displace sorption solution. 10 % sulfuric acid solution used as regenerating solution.

Polyampholytes containing iminodiacetate groups in the structure could be prospective replacement for anion exchange resins [2]. The presence of these groups in the structure allows not only to extract uranium selectively from solutions of various compositions, but also to regenerate ampholytes effectively.

The efficiency of using of iminodiacetate polyampholyte ANKB-35 for uranium recovery form pregnant solution of ISL was proved.

This leads to sorption of uranium cation, anion resins and polyampholytes. The relevant data on dependence of volume distribution coefficient of all three types of resins are given in a number of articles and books [3].

It is shown that aminocarboxylic ampholytes could be used for uranium recovery from pregnant solutions with subsequent concentrating on desorption stage. The most efficient desorbent was nitric acid. Uranium capacity on ampholyte would be significantly increased, if uranium sorption was carried out at higher pH values of pregnant solution. It is recommended to use mentioned ampholytes for additional recovery of uranium from circulating solutions.

In the study [4] describes the prospects of using weak acid cation exchange resin to extract uranium from pregnant solution of uranium carbonate ISL.

The main reaction:



The result found that the use of weak cation-exchange resins is promising for the recovery of uranium from high and low concentrated solutions and during groundwater restoration. Waste volumes are minimized and lime softening is eliminated as a pretreatment.

The behavior of cation exchange resin with sulphonic acid functional groups Amberlite® IRN77, anion exchange resin with 2,N-dimethylpyridinium groups Varion AP during uranium sorption from underground water were investigated [5]. The results of sorption in dynamic conditions on cation exchange resin from model solutions showed the efficiency of IRN 77.

There was performed a study of uranium sorption on phosphorus-modified poly(sterene-co-divinylbenzene) polyamidoamine PAMAM [6]. The maximum sorption capacity (99.89 mg/g) observed at the pH 5.0 and initial uranium (VI) concentration 100 mg/dm<sup>3</sup> and adsorbent dose 1 g/dm<sup>3</sup>. Sorption capacity hadn't any noticeable loss after 27 cycles in a fixed bed.

During researches of efficient methods of uranium removal from contaminated groundwater, batch and field column tests were carried out [7]. It is shown that strong base anion exchange resins were more effective in removing uranium from both near-neutral pH (6.5) and high pH (8) low nitrate-containing groundwaters than chelating resins, that were extracted uranium from acidic (pH 5) solutions. Chelating resins were presented by Eichrom Diphonix (diphosphoric acid) with approximate cost of \$3000/ft<sup>3</sup> and BioRad Chelex 100 (paired iminodiacetate ions) with \$265/ft<sup>3</sup> cost.

The problem of uranium (VI) recovery from water and nuclear industry wastewater on amine-modified biomaterial (tamarind fruit shell) was studied, while uranium is formed chelate complexes with material functional groups [8]. Promising results on sorption kinetics and relatively high capacity (100.79 mg/g) allowed to consider this material as prospective.

The experiments with ion-imprinted magnetic chitosan resin for uranium sorption from aqueous solutions at different pH, sorbent amount, initial uranium concentration, mixing time and temperature were carried out [9]. It was shown high capacity and selectivity for uranium.

Sorption and desorption characteristics of Purolite S957, D5041 and Lewatit TP260 were studied [10] at uranium extraction from nitric acid solutions. During sorption on resins Purolite S957 and D5041 there were observed negative influence of impurities – oxalic acid (from 0.2 g/dm<sup>3</sup>), DTPA (from 25 g/dm<sup>3</sup>), calcium and sodium ions (from 2 g/dm<sup>3</sup>), iron (Fe<sup>3+</sup>) (from 1 g/dm<sup>3</sup>), ammonium (from 2 g/dm<sup>3</sup>) and chromium (from 0.05 g/dm<sup>3</sup>). The most negative impact is shown by ions of Fe<sup>3+</sup>. The presence of ions of calcium, Fe<sup>3+</sup> and chromium in solution also decrease the distribution coefficient of uranium on resin Lewatit TP260. In static conditions is shown the possibility of uranium desorption from saturated samples of resin by solution of ammonium carbonate and sodium carbonate with share of 5 %.

Thus, there is considerable potential for ion exchangers identification, that would be alternative to anion exchange resins and allow to extract uranium efficiently from complex solution.

It should be noted that the efficiency of resin usage in each particular case depends on number of factors – sorption capacity, degree and complexity of regeneration, mechanical stability and cost.

The evaluation of the sorbent efficiency is based on its sorption and desorption characteristics. Desorption solution should provide a high level of target components recovery to the liquid phase and the possibility of recycling. The last is indispensable condition from ecological and economical points of view.

## 2 Experimental

### 2.1 Reagent and materials

The ion exchange resins (Table 1) were provided by manufacturers for laboratory tests:

- D402-II (Jiangsu Suqing Water Treatment Engineering Group Co., Ltd.) – chelating resin;
- S500 (Anhui Sanxing Resin Technology Co., Ltd.) – chelating resin;
- EDE-10P (“Uralchimplast”, JSC) – middle base anion exchange resin;
- CG8 (ResinTech, Inc.) – sulfonated cation resin.

Table 1 Characteristics of ion exchange resins

Resin	Functional groups	Structure	Size in air-dry condition, mm	Total exchange capacity, mol/dm <sup>3</sup>
D402-II	CH <sub>2</sub> NHCH <sub>2</sub> PO <sub>3</sub>	Macroporous	0.40÷0.70	≥ 1.45
S500	CH <sub>2</sub> NHCH <sub>2</sub> PO <sub>3</sub>	Macroporous	0.40÷0.70	-
EDE-10P	secondary and tertiary amine groups of aliphatic series and about 20 % of quaternary ammonium groups	Gel	0.40÷2.00	2.30
CG8	R-(SO <sub>3</sub> ) <sup>-</sup> M	Gel	0.80	1.85

The experiments in static conditions were carried out on several model solutions (Table 2) in order to determine the influence of nature of uranium complexes on efficiency of its extraction to resin phase.

Table 2 Composition of initial solutions for static conditions experiments

Parameter / Element	Initial solution №1	Initial solution №2	Initial solution №3	Initial solution №4
Media	H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> SO <sub>4</sub>	HNO <sub>3</sub>	HCl
pH	2.2	4.0	2.1	2.0
U, mg/dm <sup>3</sup>	47.6	48.3	41.6	42.4
Fe, mg/dm <sup>3</sup>	420	420	420	420

The experiments of sorption in dynamic conditions were carried out on solution filtrate of uranium at the one of the enterprises of “NAC” Kazatomprom”, JSC. The composition of the solution is shown in Table 3 (analyzed components).

Table 3 The composition of analyzed components in the initial solution under dynamic conditions experiments

Element	U	Fe	pH
Concentration, mg/dm <sup>3</sup>	47	420	2.2

All other chemical substances used were of analytical grade. During the realization of the experiments were used distilled water.

### 2.2 Instrumentation

The analysis of solution and resins on uranium content has been realized by complexometric titration. The weight measurements realized on laboratory analytical balances Mettler Toledo ML54. The multimeter MM40 Crison instruments is used for the pH measurements in solutions.

### 2.3 Sorbent preparation

Ion exchange resins had subjected to conditioning before use. In the separating funnels, sorbents treated in series by 2 mol/dm<sup>3</sup> HCl until complete removal of iron, by water and 5 % NaOH for elimination of organic residue of synthesis. In addition, ionites had been prepared to work conditions by holding during 24 h in appropriate medium and by distilled water washing until pH 3.0–3.5.

### 2.4 Experiments on sorption and desorption in static conditions

Within the study of uranium sorption in static conditions a prepared solution with volume of 3 dm<sup>3</sup> was filled in agitator with stirring device. Then a conditioned swollen resin (3 cm<sup>3</sup>) added into the solution.

Within the study of uranium desorption at static conditions a prepared solution with volume of 0.5 dm<sup>3</sup> was filled in agitator with stirring device. Then a conditioned saturated resin (5 cm<sup>3</sup>) added into the solution. Desorption was carried out with using of different solutions (Table 4).

Table 4 Eluent solutions for experiments at static conditions

Eluent solution	H <sub>2</sub> SO <sub>4</sub>	NH <sub>4</sub> NO <sub>3</sub>		(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>		HNO <sub>3</sub>	NaCl			
Concentration, mol/dm <sup>3</sup>	1.0	0.6	1.3	1.8	0.3	0.6	1.6	0.8	1.6	2.4

Prepared mixture stirred at 120 rpm for 12 hours at room temperature (25±1 °C).

Uranium extraction degree into the phase of resin/solution and sorption capacity were evaluated by the following equations:

$$E = \frac{C_0 - C_e}{C_0} \times 100\% \quad (4)$$

$$Q = \frac{(C_0 - C_e)V}{m} \quad (5)$$

where E – degree of sorption; Q – sorption capacity, mg/g; C<sub>0</sub> and C<sub>e</sub> – are uranium concentrations in initial and equilibrium conditions in solution (sorption) and resin (desorption), mg/dm<sup>3</sup>; m – weight of wet resin, g; V – total volume of solution, dm<sup>3</sup>.

## 2.5 Experiments on sorption and desorption in dynamic conditions

For studying the sorption and desorption processes in dynamic conditions, the pre-soaked resin, transformed into the desired ionic form, was placed in columns (20 mm × 200 mm) made of Plexiglas, and the studied solution was passed through a packed bed resin until the complete uranium saturation.

The input of solution was realized by peristaltic pump insuring a constant flow rate of 5 BV/hour during sorption and a constant flow rate of 1 BV/hour during desorption. The eluates were fractionally sampled for analysis.

Desorption was carried out with using of 1.8 mol/dm<sup>3</sup> NH<sub>4</sub>NO<sub>3</sub> solution. All the experiments were performed at room temperature (25±1 °C).

## 3 Results and discussion

### 3.1 Sorption in static conditions

The experiments on uranium sorption in static conditions had the following goals:

- to identify the most prospective resins of different types for uranium extraction from sulfuric acid solution with capacity by uranium, comparable with widely strong anion exchange resins, that is used at enterprises of “NAC “Kazatomprom”, JSC, for subsequent feasibility evaluation of its industrial application;
- study of kinetic and capacity parameters of prospective resins at uranium extraction from alternative to sulfuric acid media, that support uranyl cation formation, which leads to intensification of ion exchange process.

In Table 5, the results of estimation of resin capacity by uranium in equilibrium with researched model solutions are shown.

Table 5 Resin capacity after sorption in static condition

Resin	Initial solution №1	Initial solution №2	Initial solution №3	Initial solution №4
	Estimated capacity by uranium, mg/g			
D402-II	-	-	-	-
S500	55.2	55.9	0.3	5.9
EDE-10P	44.9	41.4	4.5	22.7
CG8	0.3	0.3	0.5	0.4

It could be seen that chelating resin D402-II and sulfonic resin CG8 hardly extract uranium within the frame of the experimental conditions. There is a regularity of slight effect of pH of sulfuric acid solution on uranium exchange capacity of the resins S500 and EDE-10P. Significantly lower capacity during operation of mentioned resins in hydrochloric acid solution and especially in nitric acid solution are observed.

On the basis of obtained results S500 and EDE-10P are selected for further experiments on real pregnant solution of uranium ISL.

### 3.2 Sorption in dynamic conditions

The breakthrough curves of sorption demonstrate the correlation between the changes of the target component contents in the filtrate and the volume of solution which passes through the sorbent layer. Besides, the relationship between the target element concentration in the eluate ( $C_e$ ) and in the input solution ( $C_0$ ) was used as a function of time or of volume of passed solution. The calculation of the integral under the breakthrough curve allows to find the quantity of sorbed target element. The total number of sorbed element can be calculated in experimental conditions by the equation:

$$Q = \int_0^{V_e} \frac{(C_0 - C_e)}{m} dV_e \quad (6)$$

where  $V_e$  – volume of solution, which was passed through the column,  $\text{cm}^3$ .

In Table 6 the results of estimation of researched resins capacity by uranium are shown.

Table 6 Resin capacity after sorption in dynamic condition

Resin	Estimated capacity by uranium, mg/g
S500	74.6
EDE-10P	80.7

It should be noted that uranium breakthrough (over  $3 \text{ mg/dm}^3$ ) on S500 resin occurs much latter, than on EDE-10P.

Presented results confirm the comparable efficiency of the resins S500 and EDE-10P for uranium sorption from process solutions of uranium ISL.

### 3.3 Desorption in static conditions

The evaluation of the sorbent efficiency is based on its sorption and desorption characteristics. Desorption solution should provide a high level of target components recovery to the liquid phase and the possibility of recycling [11].

The results of uranium desorption from phase of resins S500 and EDE-10P in static conditions by different eluent solutions are presented on Fig. 1 and 2 respectively.

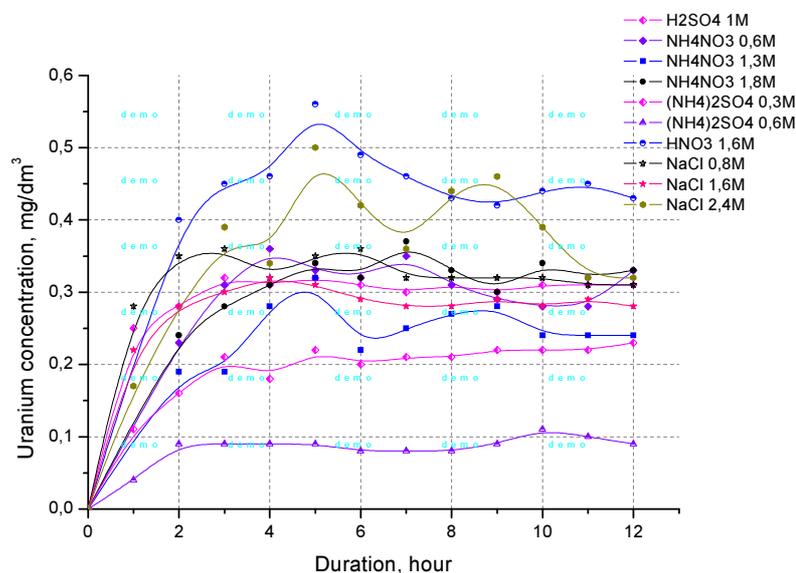


Fig. 1 Kinetic curves of uranium desorption on S500

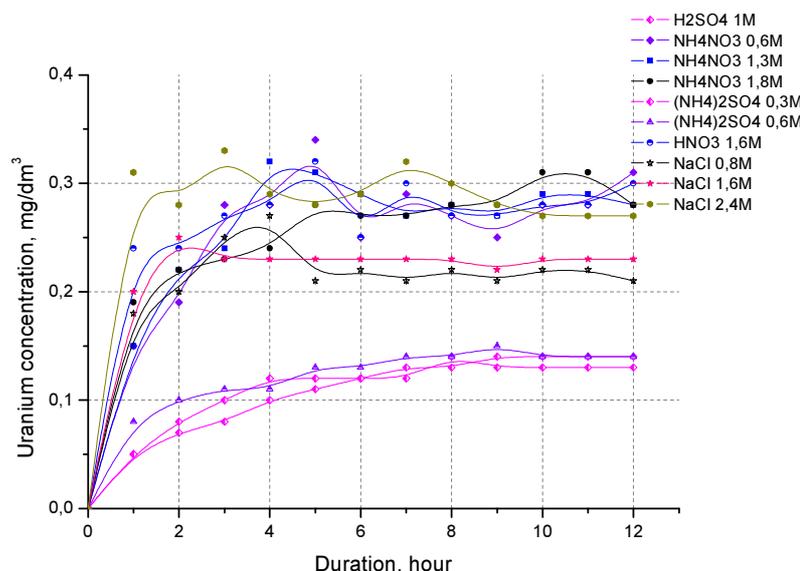


Fig. 2 Kinetic curves of uranium desorption on EDE-10P

In Table 7 the results of calculation of uranium desorption degree are shown.

Table 7 The results of estimation of uranium desorption degree

Eluent solution	H <sub>2</sub> SO <sub>4</sub>	NH <sub>4</sub> NO <sub>3</sub>			(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>		HNO <sub>3</sub>	NaCl		
Concentration, mol/dm <sup>3</sup>	1.0	0.6	1.3	1.8	0.3	0.6	1.6	0.8	1.6	2.4
Desorption degree, %:										
- S500;	96	66	71	82	31	34	99	92	99	99
- EDE-10P	72	64	96	97	71	96	98	96	99	99
Equilibrium condition achievement time, hour:										
- S500;	4	6	6	6	4	4	3	5	5	5
- EDE-10P	4	7	7	7	6	6	3	4	4	4

From Table 7 it could be seen, that it is possible to use both acids and its salts for uranium extraction from resin phase. The use of sulfuric and nitric acids provide sufficient desorption, however subsequent technological operation should avoid neutralization for economic reasons. Ammonium sulfate within studied concentrations is not of sufficient interest.

It should be noted that it is advisable to consider the possibility of integration of obtained technological solutions to existing technology of uranium ISL enterprises. Therefore, the obtained eluate should provide selective uranium precipitation that is efficient from technological and economic points of view.

The Table 7 shows that using of ammonium nitrate provides sufficiently fully extract uranium. Wide application of this reagent on existing uranium ISL enterprises increases the possibility of its successful integration.

Sodium chloride has a lower cost and at the same time demonstrates comparable desorption degree, however provided primary tests in dynamic conditions were unsatisfactory. In this regard, the following experiments were carried out with solution of ammonium nitrate.

### 3.4 Desorption in dynamic conditions

Table 8 shows estimated degree of uranium recovery at resin desorption.

Table 8 Uranium recovery at desorption

Resin	Initial uranium content in resin, %	Desorption degree, %
S500	8.7	82.0
EDE-10P	7.0	70.3

Breakthrough curve of S500 desorption has a higher peak and not so stretched as EDE-10P curve, and sufficient recovery degree is achieved by passing 11 BV. Performed tests of uranium sorption and desorption on chelating resins S500 confirm considerable attractiveness of this resin for application on uranium ISL enterprises.

#### 4 Conclusion

Provided research demonstrates the prospects of S500 and EDE-10P resins for uranium recovery from complex solutions, which are pregnant solutions of uranium ISL, due to reduction of “poisons” influence on exchange capacity and lower cost at comparable technological parameters.

It was identified that S500 and EDE-10P resins could be used effectively at uranium ion exchange recovery from pregnant solutions of uranium ISL. Further experiments determined that there is the possibility of integration of S500 resin in existing technology of uranium ISL enterprises by using circulating desorption solution, which is prepared on the basis of ammonium nitrate.

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