Synthesis and Properties of Strongly Basic Acrylate Polyfunctional Anion-Exchange Resin for Uranium Extraction

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Abstract—Some studies on the synthesis of strongly basic acrylate polyfunctional anion-exchange resins designed for the extraction of uranium from uranium ore leaching solutions were performed. The alkylation reaction conditions providing the synthesis of a polyfunctional anion-exchange resin with 55% of strongly basic groups were determined. Its sorption properties were studied using model solutions. The capacity of the alkylated polyfunctional anion-exchange resin with respect to uranium was shown to be highly competitive with foreign analogues using the comparative analysis of its ion-exchange characteristics with the parameters of known ion-exchange resins.

Strongly basic styrene anion-exchange resins with trimethylammonium (AM-p, A500U) diethanolamine (Ambersep920U), or pyridine (AMP) ionogenic groups are currently applied for the extraction of uranium from slurries and solutions. The synthesis of these sorbents obligatorily incorporates the polystyrene matrix chloromethylation stage, which is characterized by the application of hazardous reagents (chlorosulfonic acid, monochlorodimethyl ether) and a great amount of formed wastes (titanium tetrachloride, iron or tin chlorides) due to the use of Friedel−Crafts catalysts.

One of the promising directions in increasing the economic efficiency of hydrometallurgical methods for the extraction of uranium from complex lean ores and simplifying the sorbent synthesis technology is the use of polyfunctional ion-exchange resins [1]. Thus, some water treatment processes are performed using polyfunctional weakly basic acrylonitrile anion-exchange resins, such as Rossion-25 (Russia) and Relite MG1p (Resindion, Italy). They contain primary, secondary, and tertiary amino groups and are characterized by a chemically and mechanically strong porous matrix and a high ion-exchange capacity, which is nearly two times higher than for styrene anion-exchange resins. The technology of their synthesis is based on the copolymerization of acrylonitrile and divinylbenzene in the presence of various foaming agents and radical reaction initiators [2, 3]. Acrylic

acid ethers are sometimes added to a polymerization mixture to impart required properties to a commercial product. As a result, an ion-exchange resin matrix of a ternary copolymer is obtained. The further aminolysis of a formed intermediate product is performed with the use of diethylenetriamine in the presence of elementary sulfur as a catalyst to obtain a target anion-exchange resin in the end. To synthesize the polyacrylate weakly basic anion-exchange resin with cyclic (imidazoline) amino groups [4], porous acrylonitrile−divinylbenzene (8%) copolymer is subjected to aminolysis with ethylenediamine at 120−170°C and a pressure of 5−15 atm. This results in the anion-exchange resin with static and dynamic anion-exchange capacities of 7 and 1200 (g eqv)/m³, respectively. These anion-exchange resins were established to exhibit good sorption properties with respect to uranium, which can further be completely desorbed with the use of soda solutions. The sorption properties of Rossion-25 and Relite MG1p polyfunctional anion-exchange resins for water treatment and AMP commercial anion-exchange resin for uranium extraction are compared in Table 1 and Fig. 1.

To improve the sorption characteristics of acrylonitrile anion-exchanger resins with respect to uranium, we performed the studies on the introduction of strongly basic amino groups into a polyfunctional weakly basic sorbent. The Rossion-25 water treatment sorbent, whose synthesis was described in the patents

Table 1. Weight and volumetric capacity of anion-exchange resins with respect to uranium in the sorption from heap leaching model solutions

Anion-exchange resin grade	Weight capacity, mg/g	Volumetric capacity, mg/mL
AMP	157	74
Relite MG1p	116	58
Rossion-25	121	61

[2, 3], was selected as a weakly basic anion-exchange resin. Uranium sorption was performed from sulfuric acid model solutions (U, 0.5 g/L; Al, 1.0 g/L; SO_4^{2-}, 5.3 g/L; pH 3.5).

The objective of these studies was to develop a method for the introduction of quaternary amino groups into the structure of an acrylate polyfunctional anion-exchange resin containing primary, secondary, and tertiary amino groups for the purpose of improving its sorption properties with respect to uranium.
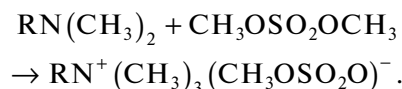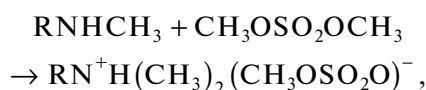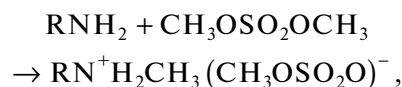
EXPERIMENTAL

The method of the synthesis of strongly basic polyfunctional anion-exchange resins consists in the creation of strongly basic ion-exchange groups in a weakly basic anion-exchange resin via the alkylation of primary and secondary amino groups to tertiary amino groups with their further quaternization to quaternary ammonium groups. The alkylation of ion-exchange resins has a number of specific features:

(1) The addition of a solvent to a reaction mass is required to provide the preliminary swelling of an ion-exchange resin and facilitate the diffusion of an alkylating agent deep into a sorbent grain;

Fig. 1. Resulting curves of uranium sorption from sulfuric acid solutions of heap ore leaching: (*1*) Rossion-25, (*2*) Relite MG1p, (*3*) AMP.

(2) Reactions with ion-exchange resins are preferably performed under the mildest conditions, which prevent the temperature and pH of a reaction medium from abrupt fluctuations and thereby preserve the integrity of grains and the strength characteristics of a sorbent.

In the course of studies, we used dimethylsulfate (DMS) (OOO ABRAZIVKhIM, Russia) to perform the alkylation of Rossion-25 anion-exchange resin containing the whole range of weakly basic amino groups, namely primary (~60−65%), secondary (~15−20%) and tertiary (~20−25%) amino groups. Water, methanol, and dioxane were used as solvents.

The interaction between different amino groups of the anion-exchange resin and dimethylsulfate represents a chain of serial and parallel reactions, which can be described by the following equations:

$$RNH_2 + CH_3OSO_2OCH_3$$
$$\rightarrow RN^+H_2CH_3(CH_3OSO_2O)^-,$$

$$RNHCH_3 + CH_3OSO_2OCH_3$$
$$\rightarrow RN^+H(CH_3)_2(CH_3OSO_2O)^-,$$

$$RN(CH_3)_2 + CH_3OSO_2OCH_3$$
$$\rightarrow RN^+(CH_3)_3(CH_3OSO_2O)^-.$$

Amino groups can react with dimethylsulfate only in a free base form, so a required amount of tartar salt (K_2CO_3, chemically pure grade; OOO ABRAZIVKhIM, Russia) was gradually added to the reaction mass to bond methylsulfuric acid formed in the alkylation reaction:
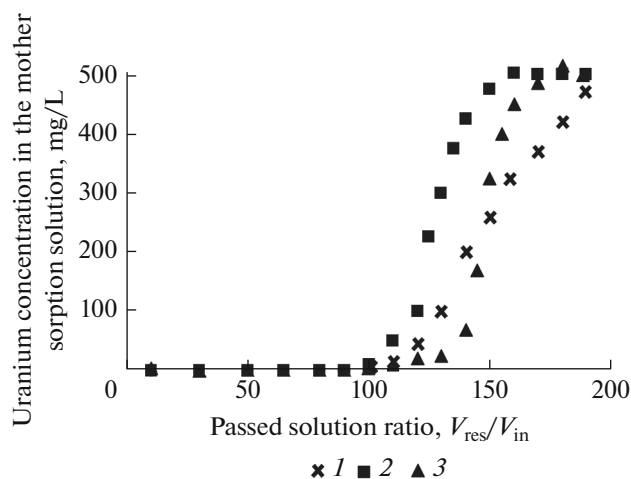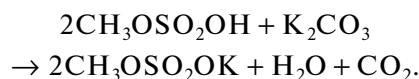
$$2CH_3OSO_2OH + K_2CO_3$$
$$\rightarrow 2CH_3OSO_2OK + H_2O + CO_2.$$

Experiments were performed using a four-necked flask equipped with an agitator, a thermometer, a reflux condenser, and a drop funnel. The flask was filled with calculated amounts of the Rossion-25 anion-exchanger resin in a free base form and a solvent (for anion-exchange resin swelling). The flask was further cooled on an ice bath to a temperature of 10−15°C, thereupon a stoichiometric dimethylsulfate amount of 1.85 g/(g dry anion-exchange resin) was added under stirring. An aqueous K_2CO_3 (~40%) solution was then introduced drop by drop at a certain rate in the amount of 1 mol of K_2CO_3 per 2 mol of dimethylsulfate until the reaction mass attained pH ~8. The alkylation process was performed for 8−10 h. The mother solution was then filtered out, and the anion-exchange resin was washed with water to neutral pH. The control of pH was performed using an EXPERT-pH pH meter (Econix EXPERT, Russia).

Table 2. Alkylation conditions for Rossion-25 anion-exchanger

Experiment no.	Solvent	Initial anion-exchanger humidity, %	Solvent volume, mg/g (initial anion-exchanger)	DMS amount, % of stoichiometric value
1	Water	50.0	1.0	1.0
2	Methanol	41.2	1.2	1.0
3	Dioxane	14.8	1.5	1.0
4	Water	50.0	0.5	0.5
5	Water	50.0	0.5	2.5
6	Water	50.0	–	1.0
7	Water	50.0	3.0	1.0

Table 3. Functional composition of alkylated acrylate anion-exchange resins

Experiment no.	TEC*, mg/g	Content of amino groups, %			
		primary	secondary	tertiary	quaternary
Rossion-25	6.3	64.0	20.2	9.0	6.8
1	5.1	12.5	9.5	33.4	44.6
2	5.3	11.9	12.0	33.5	42.6
3	5.2	10.3	10.2	32.1	47.4
4	5.5	36.6	16.3	18.5	28.6
5	4.9	4.1	11.3	31.9	52.7
6	5.5	10.4	10.0	34.0	55.6
7	5.6	16.3	6.0	43.5	34.2

* TEC is the total exchange capacity.

Table 4. Alkylation kinetics for Rossion-25 anion-exchange resin (experiment no. 3)

Parameter	Reaction time, h				
	0	2.5	6.5	7.5	10.0
TEC, mg/g	6.30	5.63	5.47	5.26	5.19
QSG, %	0.0	29.1	42.0	46.7	47.4

RESULTS AND DISCUSSION

The initial conditions of experiments on the alkylation of Rossion-25 anion-exchange resin are given in Table 2. Experimental results are presented in Table 3. From the data of Tables 2 and 3, it can be seen that the use of different solvents has barely produced any effect on the reaction result. The content of quaternary strongly basic groups (QSG) in the synthesized anion-exchange resins exhibits a small difference (42.2–47.4%) at the same ratio of reagents. The functional compositions of amino groups in the final products obtained with the use of water and methanol are also identical.

The content of strongly basic groups appreciably increases, when excess dimethylsulfate is used (experiment 5). However, a fivefold increase in its consump-tion in comparison with experiment 4 leads to a less than twofold increase in the content of strongly basic groups. A maximum content of strongly basic groups (55.6%) was attained only in experiment 6. In this experiment, no solvent was added, and water was introduced into the reaction system in a concentrated tartar salt solution and as moisture contained in the initial anion-exchange resin. The yield of strongly basic groups decreases at a water excess (experiment 7). In the course of experiment 3, samples for the estimation of alkylation process kinetics were taken each 2.5 h after the reaction began. Taken samples were analyzed for strongly basic groups. The results of studies are given in Table 4.

From the data of Table 4, it can be seen that the content of strongly basic groups slightly grows after 6.5 h
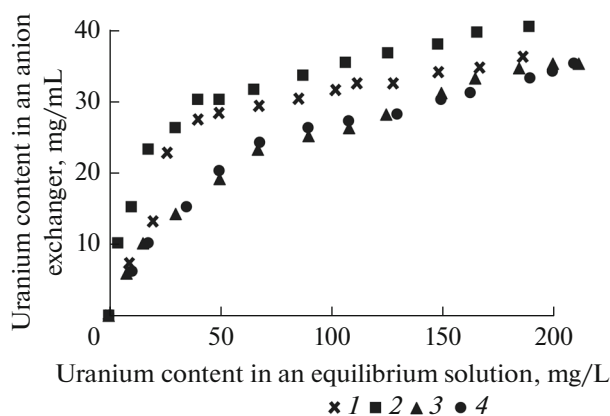
Fig. 2. Isotherms of uranium sorption from product solutions by (*1*) experimental and (*2*) AMP, (*3*) Ambersep 920U, and (*4*) Purolite A500U known commercial anion-exchange resins.

and barely changes after 7.5 h. Based on the obtained results, it is possible to conclude that 8—10 h are sufficient for the process of alkylation to complete.

Further studies were continued for the properties of the anion-exchange resin sample with a maximum content of quaternary amino groups (55.6%, experiment 6, Table 3) and the conditional name Rossion-25A. This anion-exchange resin was tested on a model solution, whose composition simulated the underground leaching uranium-containing product solutions from AO Dalur. The solutions had the following composition (g/L): U, 0.05; Fe_{tot}, 1.3; Al 2.0; Ca, 0.15; Mg, 0.07; Si, 0.05 (pH 1.75).

The uranium sorption isotherms for Rossion-25A and commercial AMP, Ambersep 920U, and Purolite A500U anion-exchange resins are plotted in Fig. 2.

The sorption isotherms indicate that Rossion-25A anion-exchange resin has high sorbability at small uranium concentrations and can provide low waste uranium concentrations in "tail" sorption solutions. At a uranium content of more than 120 mg/L, the sorption

properties of Rossion 25A anion-exchange resin are close to the characteristics of foreign Ambersep 920U and Purolite A500 anion-exchange resins. The comparative characteristics of the uranium sorption capacity of the above sorbents are given in Table 5.

As a result of performed studies, it has been shown that an anion-exchange resin with a high volumetric capacity with respect to uranium from underground leaching model solutions at a level, which is highly competitive with the capacity of known foreign strongly basic styrene anion-exchange resins applied in uranium extraction processes, can be obtained via the alkylation of a polyfunctional porous acrylate weakly basic anion-exchange resin with dimethylsulfate at 10—15°C, a stoichiometric consumption of dimethylsulfate, a minimum amount of water in the reaction system, and a process time of 8 h. Uranium can quantitatively be desorbed from such an anion-exchange resin with a solution of ammonium nitrate (NH_4NO_3) in sulfuric acid (H_2SO_4) to obtain a desorbate containing 25—30 g/L of uranium. The obtained

Table 5. Sorption capacity of experimental Rossion-25A and commercial anion-exchange resins with respect to uranium from underground leaching product solutions

Ino-exchanger grade	Ion-exchanger characterization	Sorption capacity with respect to uranium from a 50-mg/L solution	
		mg/g	mg/mL
Rossion-25A	Acrylate, porous, polyfunctional, 55% of strongly basic groups	61.7	27.6
AMP	Styrene, gel, moderately basic, pyridinium	79.0	30.4
Ambersep 920U	Styrene, porous, strongly basic, type II	58.5	19.5
Purolite A500U	Styrene, porous, strongly basic, type I	58.9	20.3

results allow us to recommend Rossion-25A alkylated anion-exchange resin for the selective extraction of uranium from underground leaching product solutions at its small concentration.

ACKNOWLEDGMENTS

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