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CONTENTS

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© A. Kuttybayev[1], O. Khayitov[2], L. Saidova[3*], A. Umirzokov[2], Y. Makhat[1], 2025.
[1]Satbayev University, Almaty, Kazakhstan;
[2]Tashkent State Technical University named after Islam Karimov, Tashkent, Uzbekistan;
[3]Navoi Branch of the Academy of Sciences of the Republic of Uzbekistan, Navoi, Uzbekistan.
E-mail: lolasaidova75@gmail.com

THE INFLUENCE OF CHLORIDE IONS ON URANIUM SORPTION FROM PRODUCTIVE SOLUTIONS OF SULFURIC ACID LEACHING OF ORES

Aidar Kuttybayev — Candidate of Technical Sciences, professor, Satbayev University, Almaty, Kazakhstan,
E-mail: a.kuttybayev@satbayev.university, https://orcid.org/0000-0003-3997-8324;
Odiljon Khayitov — Doctor of geological-mineralogical sciences, professor, academician of the Turan Academy of Sciences, Tashkent State Technical University named after Islam Karimov, Tashkent, Uzbekistan,
E-mail: o_hayitov@mail.ru, https://orcid.org/0000-0002-7735-5980;
Lola Saidova — PhD, Navoi Branch of the Academy of Sciences of the Republic of Uzbekistan, Navoi, Uzbekistan,
E-mail: lolasaidova75@gmail.com, https://orcid.org/0000-0001-6236-0288;
Azamat Umirzokov — PhD, Tashkent State Technical University named after Islam Karimov, Tashkent, Uzbekistan,
E-mail: a_umirzoqov@mail.ru; https://orcid.org/0000-0002-9609-179X;
Yernur Makhat — Master's student, Satbayev University, Almaty, Kazakhstan,
E-mail: mahaternr@gmail.com, https://orcid.org/0009-0004-6252-6507.

Abstract. The article investigates sorption methods for uranium extraction using ion-exchange resins, with a focus on the influence of chloride ions in productive solutions. The relevance of the study stems from the negative impact of elevated chloride content on resin capacity and uranium recovery efficiency. Analytical methods were applied to both solutions and ion-exchange resins, and experiments were conducted on uranium sorption using anion and cation exchangers under varying acidity conditions. The key hypothesis is that increasing chloride ion concentration significantly reduces the sorption capacity of the resins. The results confirm that when chloride content exceeds 3 g/L, uranium recovery efficiency decreases substantially, making the use of certain anion exchangers economically

unfeasible. In exogenous ore-forming processes, geochemical barriers play an important role-these are zones in the Earth's crust where the intensity of chemical element migration sharply decreases over a short distance, leading to their accumulation. This definition of a barrier is given by A.I. Perelman, the founder of the theory of geochemical barriers. Nearly all exogenous ore deposits are formed at some type of geochemical barrier. In particular, uranium mineralization can form at evaporative, neutralization, sorption, and most commonly-at redox barriers, which are typically divided into two subtypes: gley and hydrogen sulfide barriers. The obtained data can be used to optimize uranium extraction technologies, which is important for improving the efficiency of hydrometallurgical processes and reducing processing costs. It is recommended to continue research on the influence of other anions and environmental conditions to develop more effective uranium sorption methods.

Key words: desorption, ion exchange, resin, depressant, chloride, ion, sorbent

© А. Құттыбаев[1], О. Хайитов[2], Л. Саидова[3*], А. Өмірзақов[2], Е. Махат[1], 2025.

[1]Satbayev University, Алматы, Қазақстан;

[2]Ислам Каримов атындағы Ташкент мемлекеттік техникалық университеті, Ташкент, Өзбекстан;

[3]Өзбекстан Республикасы ғылым академиясының Навои филиалы, Навои, Өзбекстан.

E-mail: lolasaidova75@gmail.com

ХЛОРИД ИОНДАРЫНЫҢ КЕНДЕРДІҢ КҮКІРТ ҚЫШҚЫЛЫН СІЛТІЛЕНДІРУДІҢ ӨНІМДІ ЕРІТІНДІЛЕРІНЕН УРАННЫҢ СОРБЦИЯСЫНА ӘСЕРІ

Айдар Құттыбаев — техника ғылымдарының кандидаты, профессор, Satbayev University, Алматы, Қазақстан,
E-mail: a.kuttybayev@satbayev.university, https://orcid.org/0000-0003-3997-8324;
Одильжон Хайитов — геология-минералогия ғылымдарының докторы, профессор, Тұран ғылым академиясының академигі, Ислам Каримов атындағы Ташкент мемлекеттік техникалық университеті, Ташкент, Өзбекстан,
E-mail: o_hayitov@mail.ru, https://orcid.org/0000-0002-7735-5980;
Лола Саидова — PhD, Өзбекстан Республикасы ғылым академиясының Навои филиалы, Навои, Өзбекстан,
E-mail: lolasaidova75@gmail.com, https://orcid.org/0000-0001-6236-0288;
Азамат Өмірзақов — PhD, Ислам Каримов атындағы Ташкент мемлекеттік техникалық университеті, Ташкент, Өзбекстан,
E-mail: a_umirzoqov@mail.ru; https://orcid.org/0000-0002-9609-179X;
Ернұр Махат — магистрант, Satbayev University, Алматы, Қазақстан,
E-mail: mahaternr@gmail.com, https://orcid.org/0009-0004-6252-6507.

Аннотация. Мақалада хлорид иондарының өнімді ерітінділердегі әсеріне назар аудара отырып, ион алмастырғыш шайырларды қолдана отырып, уранды

алудың сорбциялық әдістері зерттелген. Зерттеудің өзектілігі хлоридтің жоғарылауының шайырдың сыйымдылығына және уранды қалпына келтіру тиімділігіне кері әсерінен туындайды. Аналитикалық әдістер ерітінділерге де, ион алмастырғыш шайырларға да қолданылды, әр түрлі қышқылдық жағдайында анион мен катион алмастырғыштарды қолдана отырып, уранды сорбциялау бойынша тәжірибелер жүргізілді. Негізгі гипотеза – хлорид иондарының концентрациясының жоғарылауы шайырлардың сорбциялық қабілетін айтарлықтай төмендетеді. Нәтижелер хлоридтің мөлшері 3 г/Л-ден асқанда уранды қалпына келтіру тиімділігі айтарлықтай төмендейтінін растайды, бұл кейбір анион алмастырғыштарды пайдалануды экономикалық тұрғыдан мүмкін емес етеді. Экзогендік кен түзілу процестерінде геохимиялық кедергілер маңызды рөл атқарады – бұл Жер қыртысындағы химиялық элементтердің миграциясының қарқындылығы қысқа қашықтықта күрт төмендеп, олардың жиналуына әкелетін аймақтар. Кедергінің бұл анықтамасын геохимиялық кедергілер теориясының негізін қалаушы А.И. Перельман енгізген. Экзогендік кен орындарының барлығы дерлік геохимиялық тосқауылдың қандай да бір түрінде түзіледі. Атап айтқанда, уранның минералдануы булану, бейтараптандыру, сорбция және көбінесе тотығу-тотықсыздану кедергілерінде пайда болуы мүмкін, олар әдетте екі кіші түрге бөлінеді: глей және күкіртсутек кедергілері. Алынған мәліметтер уранды алу технологияларын оңтайландыру үшін пайдаланылуы мүмкін, бұл гидрометаллургиялық процестердің тиімділігін арттыру және өңдеу шығындарын азайту үшін маңызды. Уранды сорбциялаудың неғұрлым тиімді әдістерін жасау үшін басқа аниондардың және қоршаған орта жағдайларының әсері туралы зерттеулерді жалғастыру ұсынылады.

Түйін сөздер: десорбция, ион алмасу, шайыр, депрессант, хлорид, ион, сорбент

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[1]Satbayev University, Алматы, Казахстан;

[2]Ташкентский государственный технический университет имени Ислама Каримова, Ташкент, Узбекистан;

[3]Филиал Навоийской академии наук Республики Узбекистан, Навои, Узбекистан.

E-mail: lolasaidova75@gmail.com

ВЛИЯНИЕ ХЛОРИД-ИОНОВ НА СОРБЦИЮ УРАНА ИЗ ПРОДУКТИВНЫХ РАСТВОРОВ СЕРНОКИСЛОТНОГО ВЫЩЕЛАЧИВАНИЯ РУД

Айдар Куттыбаев — кандидат технических наук, профессор, Satbayev University, Алматы, Казахстан,

E-mail: a.kuttybayev@satbayev.university, https://orcid.org/0000-0003-3997-8324;

Одилжон Хайитов — доктор геолого-минералогических наук, профессор, академик Академии наук Турана, Ташкентский государственный технический университет имени Ислама Каримова, Ташкент, Узбекистан,
E-mail: o_hayitov@mail.ru, https://orcid.org/0000-0002-7735-5980;
Лола Саидова — PhD, Филиал Навоийской академии наук Республики Узбекистан, Навои, Узбекистан,
E-mail: lolasaidova75@gmail.com, https://orcid.org/0000-0001-6236-0288;
Азамат Умирзоков — PhD, Ташкентский государственный технический университет имени Ислама Каримова, Ташкент, Узбекистан,
E-mail: a_umirzoqov@mail.ru, https://orcid.org/0000-0002-9609-179X;
Ернур Махат — магистрант, Satbayev University, Алматы, Казахстан,
E-mail: mahaternr@gmail.com, https://orcid.org/0009-0004-6252-6507.

Аннотация. В статье исследуются сорбционные методы извлечения урана с использованием ионообменных смол, с акцентом на влияние хлорид-ионов в продуктивных растворах. Актуальность исследования обусловлена негативным воздействием повышенного содержания хлоридов на ёмкость смол и эффективность извлечения урана. Применены методы анализа растворов и ионообменных смол, а также проведены эксперименты по сорбции урана анионитами и катионитами при различных кислотностях. Ключевая гипотеза заключается в том, что увеличение концентрации хлорид-ионов значительно снижает сорбционную ёмкость смол. Результаты подтверждают, что при содержании хлоридов выше 3 г/л эффективность извлечения урана существенно падает, что делает использование некоторых анионитов экономически нецелесообразным. В экзогенных процессах рудообразования важную роль играют геохимические барьеры – те участки земной коры, где на коротком расстоянии происходит резкое уменьшение интенсивности миграции химических элементов и, как следствие, их концентрация. Такое определение барьера дает А.И. Перельман – основатель учения о геохимических барьерах. Практически все экзогенные рудные месторождения сформированы на том или ином геохимическом барьере. В частности, урановая минерализация может формироваться на эвапорационном (испарительном), нейтрализационном, сорбционном и, наиболее часто – восстановительном барьере (или редокс–барьере), который принято делить на два подвида – глеевый и сероводородный. Полученные данные могут быть использованы для оптимизации технологий извлечения урана, что важно для повышения эффективности гидрометаллургических процессов и снижения затрат на переработку. Рекомендуется продолжить исследования влияния других анионов и условий среды для разработки более эффективных методов сорбции урана.

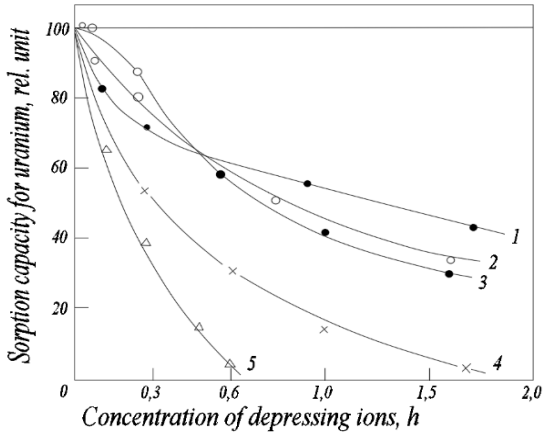
Ключевые слова: десорбция, ионообмен, смола, депрессант, хлорид, ион, сорбент

Introduction. Sorption methods for uranium and associated component extraction are based on ion-exchange processes using ion-exchange resins (Kassenov, 2016:6). Ionites are solid, practically insoluble artificial (or natural) materials in

aqueous solutions of acids, alkalis, and organic media, enabling the extraction of metals from solutions in cationic or anionic forms (Adamaev, 2015:4). The process of sorption-based extraction and concentration of valuable components consists of two stages: Saturation of the sorbent, Desorption of valuable components from it. At the first stage, the productive solution interacts with the sorbent, and valuable components are selectively absorbed by the ionite. Once equilibrium capacity for one or more metals is reached, the sorbent undergoes the desorption stage, during which it contacts a solution whose ions replace the metal ions from the ionite. After desorption, the sorbent is returned to the sorption stage (Mussin, 2023:9).

The concentrated solution, in the form of a commercial desorbate, is then sent for further processing. The volume of the desorbed solution containing valuable components is significantly smaller than the initial volume subjected to sorption, which facilitates further concentration (Matayev, 2024:10). The sorption exchange process follows the law of mass action. The primary requirements for effective sorption include selectivity towards the extracted metals (Petrov, 2021:15), maximum resin capacity, and good kinetic parameters for both sorption and regeneration. The efficiency of the sorption process is evaluated based on the sorption capacity of the resin, the degree of metal extraction from productive solutions (PS), the number of sorption stages, the single-time ionite loading, the duration of solution contact with the ionite, and desorption conditions. These parameters are interrelated, reflecting the fundamental physicochemical principles of sorption and depending on the process design (Eshonova, 2023:5; Petukhov, 2015:14). At several uranium deposits, a trend has been observed that reduces metal sorption efficiency-an increased concentration of chlorides in productive uranium solutions (Abdeli, 2018:1; Abdeli, 2024:2).

It is well known that chloride ions are strong depressants for uranium sorption by strongly basic anionites (Figure 1). As seen in Figure 1, at a chloride ion concentration of 0.6 N (21.3 g/L), uranium is practically not sorbed (Maslov, 2007:9).



1 – Phosphate ion; 2 – Nitrate ion; 3 – Fluoride ion; 4 – Sulfate ion; 5 – Chloride ion

Figure 1. Dependence of the Sorption Capacity of a Strongly Basic Anionite for Uranium on the Concentration of Depressing Ions

At the same time, the main properties of the solutions remain unchanged and are returned to the cycle. In leaching technology, the conditions for the further processing of solutions are considered, including residual acidity, total salt content, and the presence of depressing components during sorption. For uranium extraction from solutions, anionites are primarily used. Impurities in productive solutions behave differently (Rakishev, 2020:17). Cations of alkali and alkaline earth metals, as well as copper, iron, cobalt, and manganese ions, are practically not sorbed. Meanwhile, sulfate, nitrate, chloride, fluoride, and phosphate ions are well sorbed and act as depressants. Additionally, some anions can accumulate on anionites and "poison" them, as their affinity or the resin is extremely strong (Rakishev, 2014:16; Khayitov, 2025:7).

The sorption of uranium from the productive solution obtained from the leaching of waste at the Northern Mining Department of Navoi Mining and Metallurgical Company (Sharafutdinov, 2014:18 Khayitov, 2025:8) (NMMC) using VO-020 anionite is presented in Table 1. The sorption process was conducted under static conditions, with a resin-to-solution volume ratio of 1:1000 over 24 hours.

As shown in Table 1, regardless of the solution's pH, uranium is practically not sorbed, while the capacity of the saturated resin for chloride ions approaches the theoretically possible value (3 mEq/g or 106 mg/g).

Additionally, the possibility of increasing the sorption capacity of the anionite by diluting the initial productive solution with water was studied (Abdeli, 2021:3).

Table 1. Dependence of the Static Exchange Capacity of the Resin on the pH of the Solution
Initial solution concentration: Chloride ions: 15,000 mg/L, Metal: 50 mg/L

Concentration in the solution, mg/L					Content in the saturated resin, mg/g	
Before sorption			After sorption			
pH	Me	Cl	Me	Cl	Me	Cl
1,8	50,0	15 000	48,5	13900	0,71	102,1
5,0	50,0	15 000	50,0	14000	0,24	101,2
7,7	50,0	15 000	49,0	14000	0,73	101,2

The studies were conducted both under static and dynamic conditions using laboratory columns. The results are presented in Table 2.

Table 2. The dependence of resin capacity on the dilution of the productive solution
Concentration in the initial solution: chloride ions 11,700 mg/L, metal – 20 mg/L

Dilution, solution: water	pH	Concentration Cl, g/L	Concentration Me, mg/L	Static exchange capacity, mg/g	Dynamic exchange capacity, mg/g
Initial solution	1,7	11,7	20,0	1,4	1,4
1 : 1	2,1	5,9	10,0	2,7	2,98
1 : 2	2,3	3,9	6,7	2,7	2,98
1 : 3	2,4	2,9	5,0	2,7	2,98
1 : 4	2,9	2,3	4,0	2,7	2,98

As seen from the results in Table 2, diluting the initial productive solution by half leads to an approximately twofold increase in the resin's capacity for uranium. Further dilution does not affect the resin's capacity. However, the obtained resin capacity values remain low.

The sorption of uranium from productive solutions was also studied using cationites: Strongly acidic sulfonic cationite KU-2, Weakly acidic carboxyl cationite D-5201.

The results are presented in Tables 3, 4, and 5.

Table 3. Results of uranium sorption by cation exchangers
Chloride ion concentration 15,000 mg/L

pH of the solution	Cation exchanger D-5201		Cation exchanger KU-2	
	[Me] in the solution, mg/L	Cation exchanger capacity, mg/g	[Me] in the solution, mg/L	Cation exchanger capacity, mg/g
1,6	35,0	0,0	35,0	0,15
6,3	7,0	13,0	7,0	0,18

Table 4. Dependence of cation exchanger KU-2 capacity on the dilution of the productive solution
Concentration in the initial solution: chloride ions 15,000 mg/L, metal – 35 mg/L

Dilution, solution: water	pH	Concentration Cl, mg/L	Concentration Me, mg/L	Static exchange capacity, mg/g
Initial solution	3,2	15 000	35,0	0,36
1 : 1	7,8	7 500	17,5	0,72
1 : 2	8,4	5 000	11,7	0,02

As seen from the results in Tables 3, 4, and 5, cationite KU-2 is unsuitable for uranium sorption from productive solutions due to its low capacity. Cationite D-5201 provides a satisfactory uranium capacity when sorption is conducted in pH-neutral media (pH = 6.3).

Table 5. Dependence of cation exchanger KU-2 capacity on the pH of the productive solution
Concentration in the initial solution: chloride ions 15,000 mg/L, metal – 35 mg/L

pH	1,6	3,2	5,4	6,6
Capacity, mg/g	0,15	0,36	2,24	0,14

Studies were conducted on uranium leaching from tailings using technical water (Rakishev, 2020:17). In the water sample taken from quarry No. 8, the concentrations of elements were as follows, mg/L: Me – 2.0; Cl^- – 1775; HCO_3^- – 195; Si – 1.8; P – 1.1. For the leaching experiments and subsequent metal sorption using the anion exchanger BD-706, a sample of off-balance ore from tailing pile No. 10 was used, with a metal content of 0.024%, and a sample of off-balance ore from the roadside stockpile with a metal content of 0.110%.

The results of metal leaching and subsequent sorption by the anion exchanger are presented in Table 6.

Table 6. Results of metal leaching and subsequent sorption by the anion exchanger
Metal sorption at chloride concentration Cl^- 1775 mg/L

Off-balance ore sample	Concentration of H_2SO_4 for leaching, g/L	Leaching and sorption results			
		Final pH	[Me] in solid tailings, %	[Me] in the solution, mg/L	Anion exchanger capacity, mg/g
Roadside stockpile, [Me]=0.110%	30,0	0,9	0,010	780	55,2
	15,0	1,6	0,012	620	99,3
	8,0	3,0	0,095	34	91,9
Tailing pile No. 10, [Me]=0.024%	30,0	1,0	0,0036	88	9,0
	15,0	1,4	0,0039	67	18,2
	8,0	3,0	0,0100	40	22,5

As seen from the results in Table 6, leaching of off-balance ores using water from Pit No. 8 with a chloride concentration of 1,775 mg/L, followed by uranium sorption with the anionite BO-020, provides positive results both in terms of the residual uranium content in the leaching tailings and the saturation of the resin (Matayev, 2024:10).

Materials and methods of research. The relevance of this study lies in the fact that during the development of some uranium deposits, where ores contain a high concentration of chlorine minerals, productive solutions are formed with chloride ion concentrations exceeding 1.0 g/L (Omarbekov, 2020:11). This significantly affects the capacity of ion-exchange resins. Detailed studies on the impact of chloride ion concentration on the sorption capacity of resins have not been conducted, especially regarding bicarbonate solutions. The objective of this study was to investigate the effect of chloride ion concentration in productive solutions of various acidities on uranium sorption efficiency using both anionites and cationites. State of the Problem.To date, studies on the influence of chloride ion concentration have been conducted only for AMP and AM anionites, and only in acidic media. Research on the use of modern anionites and cationites for uranium extraction from chloride-rich solutions has not been carried out. Additionally, no data exist on uranium sorption from bicarbonate solutions with high chloride concentrations.

The research methods include: Analysis of scientific and technical literature, analytical methods for solution and ion-exchange resin composition,experimental studies on uranium sorption using various modern anionites and cationites.The effectiveness of uranium sorption is determined by the degree of uranium extraction, purification, and concentration-which are the main objectives of sorption. The primary requirement for the process is: Maximum resin capacity, selectivity, good kinetic parameters for sorption and regeneration of uranium. Sometimes, increasing selectivity results in deterioration of kinetic parameters or reduced desorption efficiency. From a technological perspective, it is more beneficial to use a less selective ionite with better kinetic characteristics for ion exchange and desorption. The minimum key parameters that a technologist should consider include: Sorption capacity, number of sorption stages, single-time ionite loading,duration of solution or pulp contact with the ionite, desorption conditions. These parameters are

interrelated and reflect the fundamental physicochemical laws of sorption statics and kinetics, as well as depending on the technological process design.

Key Stages in the Development of Sorption Technology for Uranium Extraction:

1. Selection of the ionite type, based on the physicochemical properties of the liquid phase and the general principles of ion exchange statics and kinetics;

2. Qualitative and quantitative assessment of various physicochemical factors affecting sorption and desorption kinetics (e.g., temperature, pH, impurity concentration) (Sanakulov, 2024:18; Sharafutdinov, 2024:19);

3. Determination of optimal parameters for sorption, desorption, and preceding stages of hydrometallurgical processing, influencing sorption efficiency.

The composition and properties of the liquid phase (initial solution) play a crucial role in both sorption and desorption processes (Wang, 2019:20).

Results.

Typically, the liquid phase contains: Macro-impurities: SO_4^{2-}, HSO_4^-, CO_3^{2-}, HCO_3^-, Ca^{2+}, Mg^{2+}, Fe^{3+}, Fe^{2+}, NO_3^-, Al^{3+}, etc. Micro-impurities: Mo^{6+}, As, Cu, Ni, Co, P, F, Ti, Th, rare earth elements (REEs), and other naturally occurring radioactive elements. Therefore, another important requirement for ionites is minimal exchange constants for micro-impurities. The improvement of existing technologies to address depressing agents during uranium chemical concentrate production is highly relevant (Oryngozhin, 2021:12; Oryngozhin, 2022:13). For uranium deposits such as Meilisay, Kukhnur, Yogdu, and Northern Kanimekh, in-situ leaching (ISL) presents several challenges, including:low uranium extraction kinetics due to the dominance of U(IV) over U(VI), high reducing capacity of rocks, requiring increased oxidant consumption, complex mineral composition, complicating processing and increasing costs. Depressing impurities include anion species that strongly sorb onto anionites, competing with uranium ions. These include:Sulfate (SO_4^{2-}) and bisulfate (HSO_4^-) ions, Nitrate (NO_3^-), chloride (Cl^-), fluoride (F^-), and phosphate (PO_4^{3-}) ions. Sulfate ions, in particular, exhibit strong depressive effects, accumulating in recirculating sulfuric acid solutions during underground and surface processing cycles. Their presence depends on the ore composition, forming soluble sulfate salts of alkali metals, magnesium, aluminum, divalent iron, manganese, and other impurities.

Discussion

Studies on the effects of depressing anions in productive solutions revealed the following impacts on uranium sorption:

1. Increasing Cl^- concentration from 0.5 g/L to 5.0 g/L significantly reduces sorption capacity.

2. Phosphorus ion concentrations above 1.2 g/L reduce the equilibrium uranium content on resin from 50.5 mg/g to 35 mg/g. When phosphorus concentration is 0.1-0.12 g/L, simultaneous sorption of uranium and phosphorus occurs.

3. Accumulation of SiO_4^{2-} up to 2.8 g/L decreases resin sorption capacity by 30%.

4. Nitrate concentrations of 0.8 g/L and above result in uranium breakthrough in sorption mother liquors, reducing sorption efficiency.

5. Increasing sulfate ion concentration from 10 to 40 g/L reduces ionite capacity from 37.0 to 17.0 kg/t.

Thus, increasing depressing ion concentrations above 0.1 N for nitrate ions, 0.2 N for chloride ions, and 0.4 N for phosphate ions leads to a 10-80% decrease in uranium sorption capacity.

Conclusions.

Scientific analysis indicates that during uranium extraction with anionites, the primary depressing impurity is chloride ions (Cl^-). At chloride concentrations of 3 g/L, nearly all anionites exhibit extremely low uranium sorption, making their industrial application economically unviable.

Therefore, this study focuses on the influence of chloride ion concentration in underground leaching solutions of various acidities on uranium sorption efficiency using anionites and cationites. The research aims to identify the optimal ion-exchange resin brands for uranium sorption (Saidova, 2024:10).

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