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DESILICATION OF MACROPOROUS ANION-EXCHANGE RESINS USING HYDROFLUORIC ACID IN URANIUM HYDROMETALLURGY

Abstract. Macroporous anion exchange resins of the «Ambercept 920», «Purolite 500» and «APM» grades were used. The thermodynamic parameters of the ion exchange reaction were calculated using a modified Debye-Hückel model, considering the limita-tions of its applicability at high ionic strength. It has been established that ammonium bifluoride (NH_4HF_2) effectively desilicifies macroporous anion-exchange resins used in uranium hydrometallurgy. At a concentration of 30–50 g/dm³, a degree of desiliconisation of 96,3 ± 1.2% is achieved, with a reduction in strength of no more than 10–12%. The process follows pseudo-second-order kinetics (R^2 = 0,992). The formation of a stable SiF_6^{2-} complex (ΔG = −7,3…−13,0 kJ/mol) has been demonstrated. The results obtained confirm the high efficiency and technological feasibility of using NH_4HF_2 for the regeneration of ion-exchange resins.
Keywords: *anion-exchange resins, uranium hydrometallurgy, desiliconisation, mechanical strength, ammonium bifluoride, thermodynamic analysis.*

Уран гидрометаллургиясында макрокеуекті анионалмастырғыш шайырларды фторсутек қышқылының көмегімен кремнийден тазарту

Аңдатпа. «Ambercept 920», «Purolite 500» және «APM» маркалы макрокеуекті анион алмастыратын шайырлар қолданылды. Ион алмасу реакциясының термодинамикалық параметрлері жоғары иондық күшті қолдану шектеулерін ескере отырып модификацияланған Дебай-Хюкель моделі арқылы есептелді. Амоний бифториді (NH_4HF_2) уран гидрометаллургиясында қолданылатын макрокеуекті анион алмастыратын шайырларды тиімді десиликациялайтыны анықталды. 30–50 г/дм³ концентрацияда кремнийден тазарту дәрежесі 96,3 ± 1,2%-ға жетеді, ал беріктік 10–12%-дан артық төмендемейді. Процесс псевдоекінші реттік кинетикаға бағынады (R^2 = 0,992). Тұрақты SiF_6^{2-} кешенің ($\Delta G°$ = −7,3…−13,0 кДж/моль) түзілуі дәлелденді. Алынған нәтижелер NH_4HF_2-ні ион алмастыратын шайырларды регенерациялау үшін қолданудың жоғары тиімділігі мен технологиялық мүмкіндігін растайды.
Түйінді сөздер: *анион алмастыратын шайырлар, уран гидрометаллургиясы, кремнийден тазарту, механикалық беріктік, аммоний бифториді, термодинамикалық талдау.*

Обескремнивание макропористых анионообменных смол при помощи фтороводородной кислоты в гидрометаллургии урана

Аннотация. Использовались макропористые анионообменные смолы марок «Ambercept 920», «Purolite 500» и «APM». Термодинамические параметры реакции ионного обмена были рассчитаны с использованием модифицированной модели Дебая-Хюккеля с учетом ограничений ее применимости при высокой ионной силе. Установлено, что бифторид аммония (NH_4HF_2) эффективно удаляет кремний из макропористых анионообменных смол, используемых в гидрометаллургии урана. При концентрации 30–50 г/дм³ достигается степень десилицификации 96,3 ± 1,2%, при этом снижение прочности составляет не более 10–12%. Процесс протекает по кинетике псевдовторого порядка (R^2 = 0,992). Доказано образование стабильного комплекса SiF_6^{2-} (ΔG° = −7,3…−13,0 кДж/моль). Полученные результаты подтверждают высокую эффективность и технологическую осуществимость использования NH_4HF_2 для регенерации ионообменных смол.
Ключевые слова: *анионообменные смолы, гидрометаллургия урана, обескремнивание, механическая прочность, бифторид аммония, термодинамический анализ.*

Introduction

Ion-exchange technologies are widely used in uranium extraction, particularly in in-situ leaching (ISL). During operation, polystyrene-divinylbenzene anion exchangers become contaminated with silicon and silicates, reducing exchange capacity and impairing hydrodynamic characteristics. Silica precipitates or adsorbs on the granule surface, penetrates the macroporous resin and increases towards the granule centre [1]. As poisoning impurities accumulate, regeneration is required to restore sorption capacity.

The main silica-removal methods are coagulation (including heterocoagulation), flocculation, baromembrane treatment and sorption. Recent studies (2022–2025) identify coagulation, adsorption and membrane filtration as the principal approaches [2], although their technological implementation is complex. Therefore, adapting established treatment methods to the specific composition of productive uranium solutions is preferable to developing a new sorbent.

Literature data indicate that silicon can be removed using adsorbents and absorbents (aluminium oxide, aluminium and iron hydroxides, magnesium dioxide), complexing agents (potassium fluoride, hydrofluoric acid, ammonium molybdate), resins (Duolite A-102, Geon, Purolite) and coagulants (gelatin, gum arabic, guar gum) [3]. Sorbents and coagulants may cause uranium co-precipitation; fluorine-containing reagents are therefore promising because they form stable ***SiF6²⁻*** complexes [4].

The most effective methods for removing silicon from ion-exchange resins are alkaline desiliconisation and bifluoride treatment. Conventional alkaline treatment uses ***NaOH*** at pH 12,8–13,2 with protective additives [5]. Increasing ***NaOH*** from 20 to 60 g/dm³ raises desilication from 52% to 84%; the optimal 40–60 g/dm³ range reduces silicon to 1,6–3,5%. At 40 g/dm³, one treatment removes 79,7% of silicon, while a second treatment can achieve complete removal.

Repeated alkaline treatment partly restores exchange capacity but degrades the polymer matrix and lowers mechanical strength: by more than 5% after one treatment and by about 18% after a second. Protective salts can reduce this effect, but their type and concentration require additional study for modern resin grades.

Fluorine-containing additives for silica removal are less extensively studied. Reported reagents include ammonium bifluoride (***NH4HF2***), ammonium fluoride (***NH4F***), sodium tetrafluoroborate (***NaBF4***) and disodium fluorophosphate (***Na2PO3F***) [6]. Hydrofluoric acid and its salts are effective but their use is constrained by equipment corrosion and possible product contamination [7]. Studies [8, 9] describe ***HF*** formation from ammonium bifluoride and sulphuric acid and its subsequent reaction with silica, aluminosilicates and quartz:

$$NH_4HF_2 + H_2SO_4 \rightarrow NH_4SO_4 + HF. \quad (1)$$

$$6HF + SiO_2 \rightarrow SiF_4 + 2HF + 2H_2O. \quad (2)$$

$$CaAl_2SiO_8 + 16HF \rightarrow 2AlF_3 + 2SiF_4 + 8H_2O + CaF_2. \quad (3)$$

Hydrofluoric acid therefore destroys silica-bearing and aluminosilicate deposits, improving effective porosity and filtration characteristics; ***HF*** is largely consumed by reaction with quartz.

Given that, in aqueous solutions, silicon exists mainly in the form of weak orthosilicic acid

$$H_4SiO_4 \leftrightarrows H_3SiO_4^- + H^+ \quad (4)$$

and anion exchangers in the sulphate form interact in the technological cycle with the dissociated form of silicic acid and sorb silica in the form of a hydrosilicate ion:

$$R\text{-}N^+(CH_3)_3HSO_4^- + H_3SiO_4^- \rightarrow R\text{-}N^+(CH_3)_3HSiO_3^- + HSO_4^- + H_2O. \quad (5)$$

When bifluoride reacts with sorbed silica, a hexafluorosilicate ion is formed:

$$HSiO_3^- + 6HF \rightarrow SiF_6^{2-} + 3H_2O + H^+. \quad (6)$$

The fluorosilicate formed displaces the silicate from the ion exchange resin phase:

$$2(R\text{-}N^+HSiO_3^-) + 6HF_2^- \rightarrow (R\text{-}N^+)2SiF_6 + 2HSiO_3^- + 6HF. \quad (7)$$

A simplified overall ionic equation for the interaction process between anion ex-changers that have sorbed silica with bifluoride would take the following form:

$$R\text{-}N^+HSiO_3^- + 6\,HF_2^- \rightarrow R\text{-}N^+F^- + SiF_6^{2-} + 5HF + 3H_2O. \quad (8)$$

Although fluoride-containing reagents are known to dissolve silica, their use for regenerating macroporous anion-exchange resins under real uranium-hydrometallurgical conditions remains insufficiently studied. In particular, the effects of ***NH4HF2*** concentration on desilication, sorbent mechanical strength and process thermodynamics require evaluation.

Materials and Methods

A method for studying the desilication of ion exchangers with ammo-nium bifluoride

Ammonium bifluoride reacts with sulphuric acid to form hydrofluoric acid and ammonium sulphate. The resulting ***HF*** is highly reactive toward silica-containing compounds and can therefore remove silicon and fouling deposits from ion-exchange resins.

The effect of ***NH4HF2*** concentration was studied under static conditions using the setup in Figure 1: sorbent volume 0.2 dm³; L:S = 3:1; contact time 10–180 min; temperature (20 ± 2) °C. Experiments were performed in triplicate (n = 3); results are mean ± standard deviation, with 95% confidence intervals calculated using Student's t-distribution.

Kinetic data for 10–180 min were fitted to first- and second-order models and the Weber-Morris intradiffusion model.

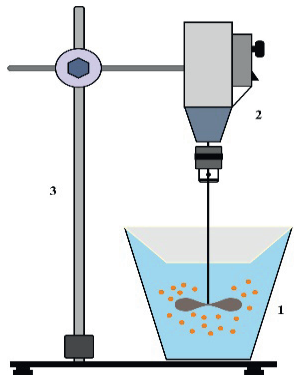


Figure 1. Laboratory setup for the removal of silicon from anion exchangers under agitation:
1 — laboratory beaker; 2 — stirrer; 3 — stand.

Сурет 1. Араластырғыш арқылы анион алмастырғыштардан кремнийді кетіруге арналған зертханалық қондырғы:
1 — зертханалық мензура; 2 — араластырғыш; 3 — штатив.

Рис. 1. Лабораторная установка по удалению кремния из анионитов в агитационном режиме:
1 — лабораторный стакан; 2 — мешалка; 3 — штатив.

Desilication tests used a sorbent from a NAC Kazatomprom JSC facility consisting of a mixture of «Ambercept 920», «Purolite 500» and «APM» anion-exchange resins.

Electron microscopy was used to compare silicon-saturated (~20–22 wt % ***SiO2***) and silicon-depleted sorbent samples.

Analytical-grade ammonium bifluoride (***NH4HF2***) was used; working solutions of 20–70 g/dm³ were prepared with distilled water.

NH4HF2 concentration was determined titrimetrically and silicon gravimetrically.

Mechanical strength was assessed by a drum abrasion test simulating operational loads and expressed as relative sorbent-volume loss after the standard test.

Sorbent morphology and elemental composition were studied by SEM-EDS using a JSM 6610 LV microscope (JEOL, Japan) with an INCA Energy 450 system (Oxford Instruments), comparing initial silicon-saturated and treated samples.

Results and Discussion

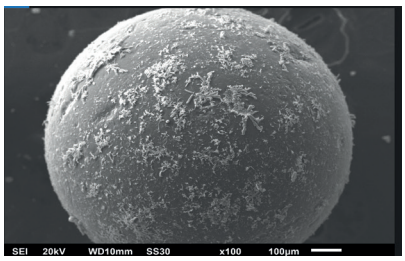
Figure 2 compares silicon-saturated sorbent with samples treated using ammonium bifluoride (SEM, JSM 6610 LV, JEOL).

Figure 2*(a)* shows a developed surface with fine inclusions and needle- and plate-like silicon-containing deposits, confirming saturation of the sorbent with silicon compounds.

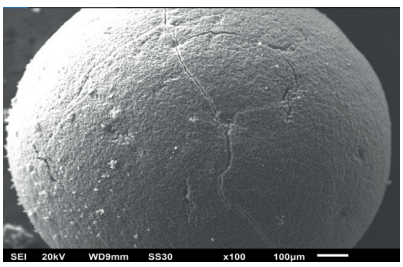
After ***NH4HF2*** treatment (Figure 2*(b)*), the surface becomes more uniform and contains fewer crystalline deposits, indicating silicon removal. Isolated microcracks are also visible, probably due to reagent action on the surface layer.

According to electron microscope images, the grains of the silicon-saturated sorbent are covered with «flakes» of various sizes and shapes (Figure 3).

Silicon-saturated particles are covered by unevenly distributed «scaly», needle- and plate-like formations that create a rough surface layer attributable to silicon-containing compounds.

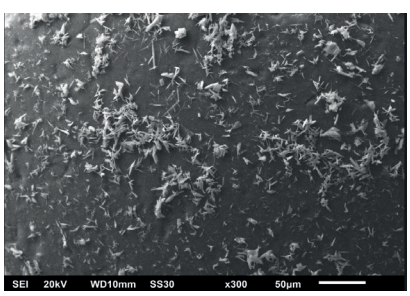


(a)

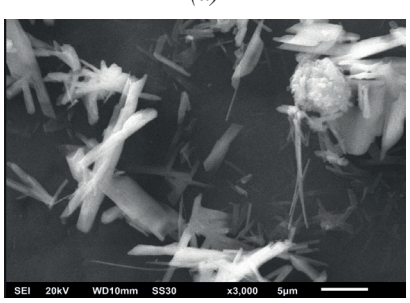


(b)

Figure 2. The microstructure of sorbent samples saturated with silicon *(a)* and after treatment with ammonium bifluoride *(b)*.
Сурет 2. Кремниймен қаныққан сорбент үлгілерінің микроқұрылымы *(а)* және аммоний бифторидімен өңдегеннен кейінгі микроқұрылымы *(b)*.
Рис. 2. Микроструктура образцов сорбентов, насыщенных кремнием *(а)* и после очистки бифторидом аммония *(б)*.



(a)



(b)

Figure 3. Microstructure of the «flakes» on the surface of the sorbent grains at different magnifications: *a – ×300; b – ×3000.*
Сурет 3. Сорбент түйіршіктерінің бетіндегі «қабыршақтардың» микроқұрылымы әртүрлі үлкейтулерде: *а – ×300; б – ×3000.*
Рис. 3. Микроструктура «чешуек» на поверхности зерен сорбента при различных увеличениях: *а – ×300; b – ×3000.*

At higher magnification (Figure 3*(b)*), the «flakes» appear as elongated plate- and needle-like crystals of heterogeneous size, sometimes grouped together. This confirms formation of a silicon-containing surface layer. Table 1 and Figures 4 and 5 present their chemical composition.

Table 1
Results of chemical analysis of the «flakes» on the grains of silicon-enriched sorbent, wt. %
Кесте 1
Кремниймен байытылған сорбенттің дәншелеріндегі «жалпақшалардың» химиялық талдау нәтижелері, салмақ бойынша %
Таблица 1
Результаты химического анализа «чешуек» на зернах насыщенного кремнием сорбента, вес. %

Spectrum	*Fe*	*O*	*Al*	*Si*	*S*	*U*	*W*	*Cl*
5	0,6	58,2	0,7	39,8	0,4	0,3		
6	0,3	35,8		46,3	1,7		7,0	0,3
7	0,4	56,1	0,5	38,5	0,5		4,1	

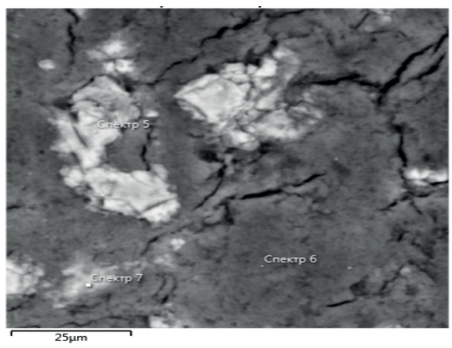


Figure 4. Electron micrograph of the surface of a silicon-saturated sorbent.
Сурет 4. Кремниймен қаныққан Сорбент бетінің электронды бейнесі.
Рис. 4. Электронное изображение поверхности сорбента, насыщенного кремнием.

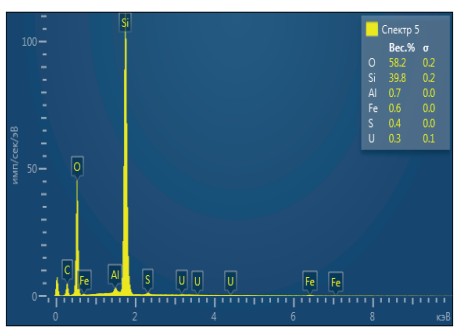


Figure 5. Spectral image of the chemical analysis results for a silicon-saturated sorbent.
Сурет 5. Кремниймен қаныққан сорбентті химиялық талдау нәтижелерінің спектрлік бейнесі.
Рис. 5. Спектральное изображение результатов химического анализа насыщенного кремнием сорбента.

Chemical analysis shows that the «flakes» contain mainly silicon, sulphur and iron. SEM-EDS confirms that the initial silicon-saturated ion exchanger is covered by complex deposits that block pores and impair mass transfer (Table 1). After ***NH4HF2*** treatment, the granule surface changes markedly; local microanalysis results are given in Table 2 and Figures 6 and 7.

Table 2

Results of chemical analysis of the sorbent surface during purification with ammonium bifluoride, % by weight

Кесте 2

Аммоний бифторидімен тазарту процесінде сорбент бетін химиялық талдау нәтижелері, салмақ бойынша %

Таблица 2

Результаты химического анализа поверхности сорбента в процессе очистки бифторидом аммония, вес. %

Spectrum	*W*	*Ca*	*F*	*Si*	*S*	*Cl*
3	1,4	20,5	62,7	11,0	3,6	0,8
4	2,6		61,6	14,4	9,4	2,1

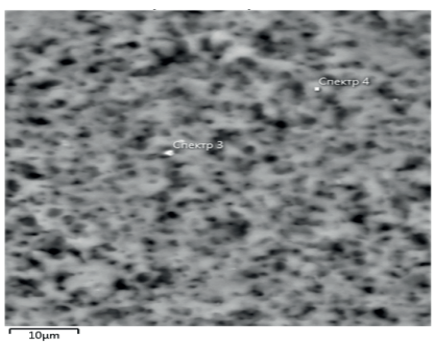


Figure 6. Electron micrograph of the sorbent surface during purification with ammonium bifluoride.
Сурет 6. Аммоний бифторидімен тазарту процесінде сорбент бетінің электронды бейнесі.
Рис. 6. Электронное изображение поверхности сорбента в процессе очистки бифторидом аммония.

After ***NH4HF2*** treatment, the granule surface becomes smoother and silicon decreases to 11–14% (Table 2). Fluorine

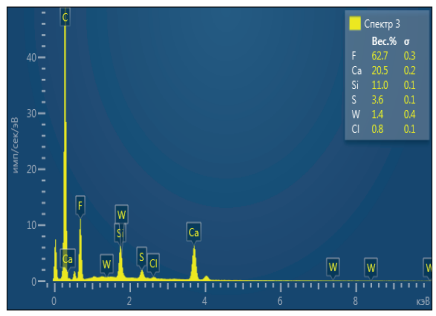


Figure 7. Spectral image of the chemical analysis results of the sorbent during the purification process using ammonium bifluoride.
Сурет 7. Аммоний бифторидімен тазарту процесінде сорбентті химиялық талдау нәтижелерінің спектрлік бейнесі.
Рис. 7. Спектральное изображение результатов химического анализа сорбента в процессе очистки бифторидом аммония.

in the EDS spectra (61–62%) confirms participation of $HF2^-$ in the reaction.

The results indicate chemical conversion of silicates into soluble fluorosilicate complexes rather than simple mechanical removal. Silicon depletion correlates with restoration of the pore structure. Table 3 summarises solution and resin composition after purification and the mechanical strength of the treated sorbent.

Table 3 and Figures 8–10 show that 20–70 g/dm³ ***NH4HF2*** provides high silicon removal. At 40–50 g/dm³, residual ***SiO2*** in the ionite is negligible. Increasing concentrations of $HF2^-$ and ***HF*** convert silicate groups into stable, soluble $SiF6^{2-}$, shifting equilibrium toward silicon desorption in accordance with reaction (8). The limiting stage is the surface chemical reaction between $HF2^-$ and silicate groups.

Kinetic fitting showed that the desilication process is best described by the pseudo-second-order model (R^2 = 0,992), consistent with the conclusion that the surface chemical reaction between $HF2^-$ and silicate groups controls the process.

An important advantage is preservation of resin integrity: 30–50 g/dm³ ***NH4HF2*** provides effective desilication while maintaining acceptable mechanical strength.

Table 3

Results of the desiliconisation process of the ion exchange resin using NH_4HF_2

Кесте 3

NH_4HF_2 көмегімен иониттің кремнийсіздену процесінің нәтижелері

Таблица 3

Результаты процесса обескремнивания ионита с NH_4HF_2

Sample №	Concentration of NH_4HF_2, g/dm³	SiO_2 in solution, g/dm³	SiO_2 in the resin, %	Degree of desiliconisation, %	Mechanical strength, %
1	20	3,26 ± 0,10	2,7 ± 0,08	77,96 ± 1,20	93,5 ± 1,5
2	30	5,60 ± 0,15	1,57 ± 0,05	87,18 ± 1,20	92,0 ± 1,3
3	40	7,53 ± 0,20	0,42 ± 0,03	96,57 ± 1,20	84,0 ± 1,8
4	50	8,51 ± 0,25	not found	100,0 ± 0,5	79,5 ± 2,0
5	60	8,28 ± 0,25	not found	100,0 ± 0,5	79,5 ± 2,0
6	70	8,51 ± 0,15	not found	100,0 ± 0,5	79,0 ± 1,8

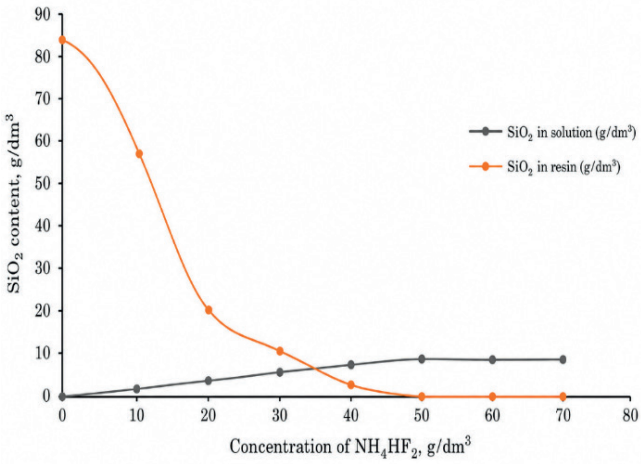


Figure 8. Effect of the mass concentration of NH_4HF_2 on the silicon content in the solution (mean ± standard deviation, n = 3).
Сурет 8. NH_4HF_2 массалық концентрациясының ерітіндідегі кремний құрамына әсері (орташа ± стандартты ауытқу, n = 3).
Рис. 8. Влияние массовой концентрации NH_4HF_2 на содержание кремния в растворе (среднее ± стандартное отклонение, n = 3).

Figure 9 shows how the sorbent's purification efficiency varies with the mass concentration of the bifluoride solution used.

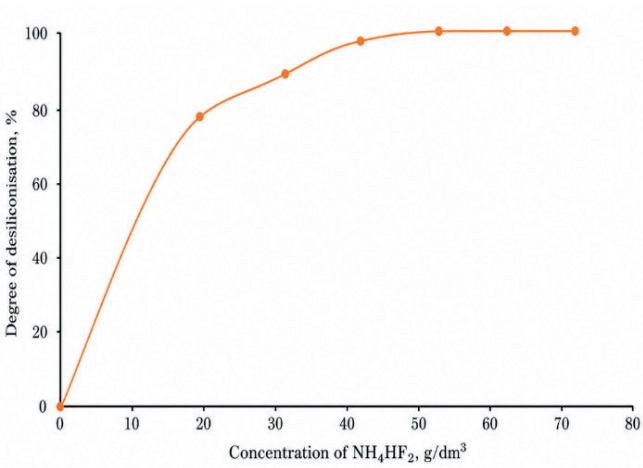


Figure 9. Relationship between the degree of desiliconisation of the anion exchange resin and the concentration of NH_4HF_2 (mean ± standard deviation, n = 3).
Сурет 9. Аниониттің кремнийсіздену дәрежесінің NH_4HF_2 концентрациясына тәуелділігі (орташа ± стандартты ауытқу, n = 3).
Рис. 9. Зависимость степени обескремнивания анионита от концентрации NH_4HF_2 (среднее ± стандартное отклонение, n = 3).

Figure 10 illustrates the effect of the mass concentration of the ammonium bifluoride solution on the mechanical strength of the regenerated sorbent.

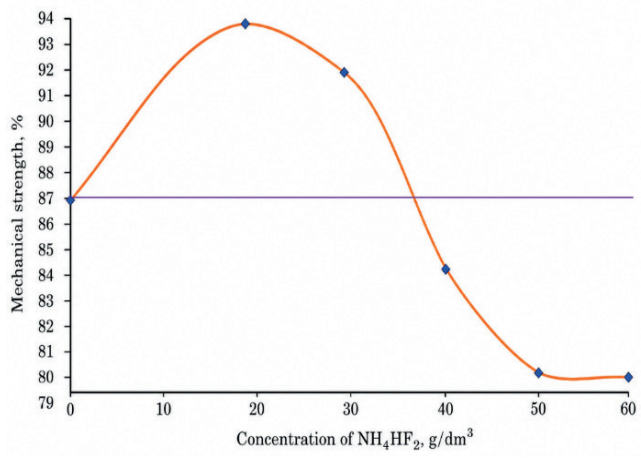


Figure 10. Effect of NH_4HF_2 concentration on the mechanical strength of the anion exchanger (mean ± standard deviation, n = 3).
Сурет 10. NH_4HF_2 концентрациясының аниониттің механикалық беріктігіне әсері (орташа ± стандартты ауытқу, n = 3).
Рис. 10. Влияние концентрации NH_4HF_2 на механическую прочность анионита (среднее ± стандартное отклонение, n = 3).

As shown in Figure 10, resin mechanical strength remains above 79% even at the highest reagent concentrations. At lower ***NH4HF2*** concentrations it increases slightly from 87% to 91–93%, probably because removal of surface deposits reduces structural defects.

Table 4 presents the performance criteria for bifluoride purification in comparison with alkaline desiliconisation.

Table 4
Quantitative criteria for purification using various reagents
Кесте 4
Әртүрлі реагенттермен тазалаудың сандық критерийлері
Таблица 4
Количественные критерии очистки различными реагентами

Parameters	Reagent	
	NH_4HF_2	NaOH
Degree of desiliconisation, %	96–100	80–84
Number of cycles	1	2–3
Loss of strength, %	10–12	15–-20
Reagent consumption, kg/m³	90–150	similarly
Mechanism	complex formation	alkaline hydrolysis

Bifluoride treatment achieves a high degree of desiliconisation in one stage, whereas alkaline treatment usually requires several cycles. At L:S = 3:1, ***NH4HF2*** consumption is 90–150 kg per 1 m³ of sorbent, comparable with alkaline desilica-

tion. Fewer regeneration cycles reduce total operating costs by 20–25%. In addition, bifluoride treatment is less destructive to the polymer matrix, extends sorbent service life and is thermodynamically favoured by formation of $SiF6^{2-}$.

Thus, bifluoride treatment is preferable where repeated regeneration would accelerate sorbent abrasion and degradation. Alkaline treatment remains applicable when reagent economy is prioritised, provided the number of cycles and protective additives are controlled.

To further evaluate the driving force of the process, thermodynamic parameters were calculated using the extended Debye-Hückel equation.

For ion-exchange equilibrium, the thermodynamic equilibrium constant K and standard Gibbs free energy $\Delta G°$ were determined for reaction (8); water activity was taken as 1:

$$K = \frac{a_{R-N^+F^-} \cdot a_{SiF_6^{2-}} \cdot a_{HF}^5}{a_{R-N^+HSiO_3^-} \cdot a_{HF_2^-}^6}.$$

Since the sorbent's ion-exchange groups are in the solid phase, their activities can be expressed in terms of the ratio of equivalent fractions in the sorbent:

$$\frac{a_{R-N^+F^-}}{a_{R-N^+HSiO_3^-}} \approx \frac{X_F}{X_{Si}},$$

where X_F is the equivalent fluorine content in the sorbent;

X_{Si} — equivalent silicon content in the sorbent.

The activity of the dissolved particles was calculated as:

$$a_i = \gamma_i C_i,$$

where a_i — the activity of the i-th component;

γ_i — activity coefficient of the i-th component;

C_i — the molar concentration of the i-th component.

For a solution of ammonium bifluoride with a mass concentration of 30 g/dm³, the molar concentration is:

$$C = \frac{30}{57} = 0{,}526 \text{ mol/dm}^3.$$

The ionic strength was calculated using the following equation:

$$I = \frac{1}{2}\sum C_i z_i^2,$$

where C — molar concentration, mol/dm³;

z — ion charge.

For NH_4^+ and HF_2^- ions, the ionic strength is:

$$I = \frac{1}{2}(0{,}526 + 0{,}526) = 0{,}526.$$

The activity coefficients were determined using the extended Debye-Hückel equation:

$$\log \gamma_i = \frac{-Az_i^2\sqrt{I}}{1+Ba_i\sqrt{I}},$$

where A — the Debye–Hückel constant, equal to 0,509 (298 K);

B — the Debye-Hückel constant, equal to 0,328 (298 K);

a_i — effective ionic radius, Å;

I — ionic force.

The activity coefficient for HF_2^- at $z = -1$ and a ≈ 4 Å will be:

$$\log \gamma = \frac{-0{,}509 \times 1 \times 0{,}725}{1+0{,}328 \times 4 \times 0{,}725} = -0{,}189$$

$$\gamma_{HF_2^-} = 0{,}65$$

The activity coefficient for SiF_6^{2-} at $z = -2$ and a ≈ 5 Å will be:

$$\log \gamma = \frac{-0{,}509 \times 4 \times 0{,}725}{1+0{,}328 \times 5 \times 0{,}725} = -0{,}676$$

$$\gamma_{SiF_6^{2-}} = 0{,}21$$

The effective radii adopted for $HF2^-$ (4 Å) and $SiF6^{2-}$ (5 Å) follow literature data for hydrated ions [10, 11] and permit estimation of activity coefficients at an ionic strength of about 0.5 mol/dm³.

Given a mass concentration of ammonium bifluoride of 30 g/dm³, a mass concentration of SiO_2 in the solution of 5,6 g/dm³, and a molar mass of SiF_6^{2-} of 144 g/mol, the molar concentration of SiF_6^{2-} will be

$$C_{SiF_6^{2-}} = \frac{5{,}6}{144} = 0{,}0389 \text{ mol/dm}^3,$$

and the activity:

$$a_{SiF_6^{2-}} = 0{,}21 \times 0{,}0389 = 0{,}00817.$$

Given that the molar concentration of HF_2^- is ≈ 0,526 mol/dm³ and the activity coefficient $\gamma = 0{,}65$, the activity of HF_2^- is:

$$a_{HF_2^-} = 0{,}65 \times 0{,}526 = 0{,}342,$$

Then $a^6_{HF_2^-} = (0{,}342)^6 = 0{,}0016$.

The equilibrium coefficient was calculated using the equation:

$$K \approx \frac{(X_F/X_{Si}) \times 0{,}00817}{0{,}0016}.$$

At a recovery rate of ≈ 87 %, the ratio

$$\frac{X_F}{X_{Si}} \approx \frac{0{,}87}{0{,}13} \approx 6{,}69.$$

Then $K = \frac{6{,}69 \times 0{,}00817}{0{,}0016} = 34{,}2.$

$\Delta G°$ was calculated using the equation:

$\Delta G° = -RT \ln K,$

where R — the gas constant, equal to 8,314 J/(mol*K);

T — process temperature 298 K;

$\ln K = 3{,}53$.

$\Delta G° = -8{,}314 \times 298 \times 3{,}53 = -8740$ J/mol = – 8,74 kJ/mol.

The results of calculations for the equilibrium constant and standard Gibbs energy of reaction (8) at different concentrations of ammonium bifluoride, using the extended Debye-Hückel equation, are presented in Table 5.

Table 5

Results of thermodynamic calculations for the desiliconisation of ion exchange resin using NH4HF2

Кесте 5

NH4HF2 қолдана отырып ион алмастыру шайырын десиликанизациялау бойынша термодинамикалық есептеулердің нәтижелері

Таблица 5

Результаты термодинамических расчетов процесса обескремнивания ионита с NH4HF2

Concentration NH_4HF_2, g/dm^3	Molar concentration, mol/dm^3	Ionic force	Activity coefficient for HF_2^-	Activity coefficient for SiF_6^{2-}	Equilibrium coefficient	Standard Gibbs energy, kJ/mol
20	0,351	0,351	0,69	0,28	18,4	- 7,3
30	0,526	0,526	0,65	0,21	34,2	- 8,7
40	0,702	0.702	0,61	0,17	62,5	- 10,3
50	0,877	0.877	0,58	0,14	95,8	-11,3
60	1,053	1,053	0,55	0,12	138,0	- 12,3
70	1,228	1,228	0,52	0,10	185,0	-13,0

With increasing ***NH4HF2*** concentration, K rises from 18,4 to 185 and $\Delta G°$ decreases from −7,3 to −13,0 kJ/mol (Table 5), demonstrating increasing thermodynamic favourability. Negative $\Delta G°$ values confirm stable formation of $SiF6^{2-}$ and a shift of equilibrium toward silicon removal.

The Debye-Hückel equation has limitations at elevated ionic strength. At $I > 0,5$, a possible error of 8–12% should be considered; nevertheless, the model is suitable for qualitative trends and ΔG° estimation. For greater accuracy, the Pitzer model may be used [12].

Thus, the values of K and $\Delta G°$ indicate a significant thermodynamic advantage, the stability of SiF_6^{2-} formation, and the high selectivity of the process.

Conclusion

Experiments confirmed that ammonium bifluoride effectively regenerates silicon-saturated anion exchangers.

The optimal ***NH4HF2*** concentration of 30–50 g/dm³ provides up to 100% silicon removal while preserving acceptable resin mechanical strength.

Using the extended Debye-Hückel equation at $I = 0,526$ mol/l gives $K \approx 34$ at 298 K. As ***NH4HF2*** increases from 20 to 70 g/dm³, $\Delta G°$ changes from −7.3 to −13.0 kJ/mol, confirming increasing stability of $SiF6^{2-}$ formation and high selectivity of bifluoride regeneration.

Thermodynamic and experimental data indicate the following regeneration mechanism:

- penetration of $HF2^-$ and ***HF*** into the macroporous resin and access to active sites;
- reaction with silicate groups fixed in the polymer matrix;
- formation of stable soluble $SiF6^{2-}$:

$$SiO_2 + 6HF \rightarrow SiF_6^{2-} + 2H_2O, \qquad (9)$$

which shifts equilibrium toward silicon removal;

- desorption of $SiF6^{2-}$ and restoration of ion-exchange capacity.

The method is technologically feasible and can reduce operating costs by extending resin service life in uranium-solution processing.

The results correspond to current hydrometallurgical trends (2022–2025) toward selective impurity removal with minimal damage to sorbents. Unlike alkaline hydrolysis, fluorine-containing reagents selectively convert silica into a soluble, thermodynamically stable form.

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