

SILICA FOULING OF ANION-EXCHANGE RESINS IN URANIUM IN-SITU RECOVERY: CURRENT UNDERSTANDING AND REGENERATION APPROACHES

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Abstract. The growing share of in-situ leaching (ISL) in global uranium mining is increasing the demands on the efficiency of ion-exchange processing of pregnant solutions. Strongly basic anion exchange resins that sorb uranyl sulfate or uranyl carbonate complexes are typically used for uranium extraction. Over long periods of operation, their properties deteriorate due to the accumulation of silicon compounds released into the solution during the leaching of silicate rocks. This review examines the mechanisms of silicon fouling of anion exchange resins used in ISL, as well as existing methods for desilication and regeneration. An analysis of scientific publications and technical materials shows that fouling is primarily due to the penetration of silicic acid into the resin pores and its subsequent polymerization. With localized increases in pH, silicate anions can also interact with exchange sites. The formation of oligomeric and polymeric siloxane structures hinders mass transfer, blocks active sites, and reduces the uranium sorption capacity. Alkaline treatment with NaOH and fluoride-containing reagents are used for regeneration. Alkaline solutions are technologically simpler, but less effective against highly polymerized silica phases and, under harsh conditions, can damage the resin. Fluoride systems provide deeper silicon removal but place increased demands on the corrosion resistance of equipment and wastewater treatment. Therefore, the regeneration process must ensure silicon removal without significantly reducing the mechanical strength and sorption properties of the resin.

Keywords: uranium, in-situ recovery, sorption, silicon, desilication

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1. Introduction

Uranium retains a significant role in the global energy sector as the primary fuel for nuclear reactors generating electricity with low carbon emissions. According to the World Nuclear Association (WNA), global uranium demand is estimated at approximately 68,920 tU in 2025. In the baseline scenario, it could exceed 150,000 tU by 2040, driven by a projected increase in installed nuclear power capacity to 746 GW [1].

This demand growth is driven by the transition to sustainable energy systems and the goal of achieving carbon neutrality by 2050, as well as the need to diversify supplies in the face of geopolitical risks and a structural deficit in primary uranium production. In 2024, production covered only approximately 90% of global demand, with the remainder supplied by stockpiles and secondary sources [2]. Additional confirmation of the strategic role of nuclear energy is reflected in projections of the International Atomic Energy Agency (IAEA), according to which, under the high-growth scenario, global nuclear capacity may increase 2.6-fold, from 377 GW in 2024 to 992 GW by 2050 [3].

Uranium mining is one of the technologically complex areas of mining production, and the choice of method for developing a deposit is determined primarily by its lithological structure and hydrogeological conditions. In 2024, global uranium production amounted to about 60,000 tons. Underground in-situ leaching accounted for approximately 52% of this volume, or about 31,000 tons of uranium. With this method, the leaching solution is pumped into permeable, water-saturated ore-bearing horizons, where uranium is converted into a soluble form and then extracted through extraction wells. This makes it possible to significantly reduce the volume of overburden and underground mining operations. About 30 % of the world's uranium was extracted using the underground method, 14 % using the open-pit method, and about another 4 % was obtained as a by-product during the processing of other mineral raw materials. Kazakhstan maintains the world's leading position in terms of uranium production volume - about 39%, or 22,000 tons, with the bulk of production based on in-situ leaching. In Canada, which accounts for about 24% of global production, mainly the rich in-situ deposits of the Athabasca Basin are being developed. In Namibia and Australia, mainly open-pit and combined schemes are used; in Australia, uranium is also obtained as a by-product at the Olympic Dam deposit [4]. It is expected that the share of in-situ leaching may continue to grow as deposits suitable for this method are brought into development [5].

In in-situ leaching, the solution is injected through a system of injection wells into a mineralized aquifer. In the formation, uranium transitions from the solid phase into the solution, after which the productive solution is pumped to the surface through production wells. Depending on the composition of the ore, two main leaching systems are used - acidic and carbonate. In acid-based schemes, solutions of sulfuric acid are primarily used; in carbonate-based schemes, solutions of sodium carbonate and sodium bicarbonate, or ammonium-containing reagents, are used. The choice of medium depends on the mineralogical

composition of the ore-bearing rocks and, especially, on the content of carbonates, which consume the acid for neutralization [6, 7]. In some studies, a CaCO_3 content of up to 4 % is indicated as an approximate limit for applying an acid-based scheme. With a higher carbonate content, the acid consumption increases, so a carbonate-based scheme may turn out to be more technologically feasible [8].

To maintain oxidizing conditions in acidic systems, H_2O_2 , O_2 , Fe^{3+} , or hypochlorite are used. These reagents promote the conversion of uranium into the mobile hexavalent form U(VI) [9]. In carbonate systems, uranium recovery is based on the combination of oxidation and complex formation of uranyl with carbonate ions, resulting in the formation of the soluble complex $\text{UO}_2(\text{CO}_3)_3^{4-}$, which is widely applied in ISR operations in the United States. The World Nuclear Association also emphasizes the widespread use of the alkaline ISR variant in the United States due to the presence of acid-consuming minerals in host formations [10].

After the PLS is lifted to the surface, uranium is recovered by hydrometallurgical methods. For solutions with low and moderate mineralization, ion exchange is the most widely used method, whereas at high mineralization levels (approximately TDS above ~8000 mg/L) solvent extraction is preferred due to the decrease in resin efficiency [11]. In ion exchange schemes, the solution is sent to the sorption stage, where uranium is selectively fixed on anion exchange resins with high affinity for uranyl anionic complexes. The contact of the solution with the resin in the columns ensures the concentration of uranium in the sorbent granules, after which the purified solution is returned to the circulation circuit or sent for disposal [6, 12].

As the resin is saturated, an elution stage is carried out, during which uranium is displaced from the active centers by solutions of sodium or ammonium salts (chlorides or nitrates), which leads to the formation of concentrated uranium eluate, which is then sent to the precipitation stage [13]. In industrial practice, precipitation of ammonium diuranate with the addition of NH_3 , as well as precipitation of uranium peroxide using H_2O_2 , are widely used; the final product is usually obtained in the form of U_3O_8 (yellowcake) [14].

A significant operational limitation of ion exchange systems is the contamination and degradation of sorbents during repeated use. In addition to uranium, resins inevitably interact with the accompanying components of solutions, including iron, organic substances and silicon compounds. This leads to a decrease in exchange capacity, deterioration of sorption kinetics and an increase in reagent consumption at the desorption stage. In this regard, regular flushing, chemical cleaning and resin regeneration are considered as necessary elements of the technological scheme that ensure the stability of the sorption cycle [12].

Silicon compounds occupy a special place among pollutants. Silicic acid enters the solution during sulfuric acid leaching of aluminosilicate rocks and can accumulate in anion exchange resins to levels of about 12–17%, which is accompanied by a decrease in the sorption capacity of uranium and a deterioration

in the mechanical strength of resin granules [15]. The physico-chemical nature of this phenomenon is associated with the polymerization of SiO_2 and the formation of hard-to-remove deposits on the surface and inside the porous structure of the resin, which leads to blocking of active centers and slowing down the processes of mass transfer. Industrial practice shows that critical contamination can form after 15-20 sorption-desorption cycles, while the mass fraction of silicon impurities in the resin can reach tens of percent, which leads to a noticeable decrease in the efficiency of uranium extraction.

Thus, the purification and regeneration of sorbents in the uranium industry is not an auxiliary operation, but a system tool for maintaining the stability of the technological process. Alkaline desilication using NaOH solutions remains the most common approach; however, strongly basic anion-exchange resins have limited stability in alkaline environments, requiring strict control of process conditions and the use of protective technological measures. Increasing the NaOH concentration promotes increased silicon desorption but also increases the risk of degradation of the resin's polymer matrix [16].

In this context, analyzing the mechanisms of silicon contamination of ion-exchange resins and systematizing their purification methods used in industrial practice is particularly relevant, as silicon accumulation is considered one of the factors limiting the efficiency of uranium sorption extraction in ISR processes. However, an analysis of the literature shows that information on the influence of silicon compounds on the sorption properties of resins and the effectiveness of regeneration measures remains limited and fragmented, and the number of publications devoted to this issue in the context of uranium sorption extraction remains relatively small.

2. Modern Uranium Mining Methods and Their Influence on Market Structure

Modern uranium mining is a system in which the geology of deposits and the selected mining technology directly determine the stability of supply and, through contracting, shape the market cycle. In-situ leaching/in-situ recovery (ISL/ISR) dominates the current structure of global uranium mining: according to the World Nuclear Association, in 2024 approximately 52% of uranium was mined by ISL, approximately 44% by conventional methods (open-pit and underground mining), and approximately 4% is recovered as a by-product. This ratio should not be considered as a purely statistical characteristic; it reflects the technological shift of the market towards production schemes with lower capital intensity and higher scalability, which allows manufacturers to respond more quickly to changes in contract demand. A later WNA estimate places the ISL share above 55%, consistent with the forecast of 55–60% by 2026 cited above and indicates the continued strengthening of the role of ISR technologies in the global uranium industry [4].

Classical uranium mining includes open-pit and underground methods, the choice of which is determined by the depth of occurrence, geometry of the ore

body, and mining-geological conditions. In a fundamental review by the International Atomic Energy Agency (IAEA), it is emphasized that uranium extraction, depending on the depth of occurrence, may be carried out either by open-pit mining (with drilling-and-blasting preparation, bench systems, and radiometric grade control) or by underground mining [12]. From a practical perspective, this corresponds to the scheme shown in Figure 1, which illustrates three basic classes of uranium extraction: open-pit mining, underground mining, and ISL/ISR.

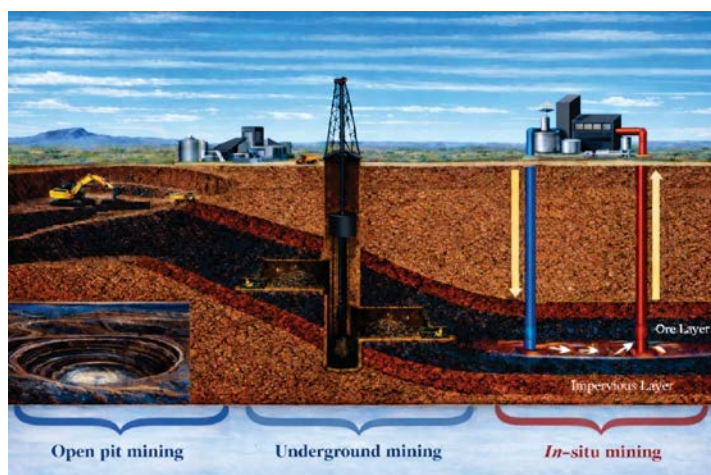


Figure 1 – Schematic representation of the main uranium mining methods (open-pit, underground, ISR).

Due to the high concentration of global uranium production within a limited number of supplier countries, not only the geographical distribution of mining but also the technological approaches used for deposit development acquire considerable importance. Leading producing countries employ fundamentally different mining methods – from in-situ recovery (ISR) to open-pit and underground mining of hard ores – which results in different sensitivities of their production systems to geotechnological, reagent-related, and infrastructural constraints. The systematization of countries according to dominant mining methods, based on national production profiles presented in the report OECD-NEA/IAEA Uranium 2024: Resources, Production and Demand [5], is presented in Table 1.

Table 1 – Distribution of Major Uranium-Producing Countries by Dominant Mining Methods (2024)

Country	Dominant mining method	Deposit type	Notes
Kazakhstan	ISR	Sandstone	Almost all production via ISR
Uzbekistan			ISR is the principal method
USA			ISR is the main operating method
Canada	Underground	High-grade	Underground mining

		unconsolidated ores	
Namibia	Open-pit	Granites, calcretes	Conventional mining
Australia	Underground / open-pit	Hard rock ores	Olympic Dam, Ranger, etc.
Russia	Underground / ISR	Sedimentary and hard rock	Mixed model
China		Various	ISR is being implemented
Niger	Underground / open-pit	Sedimentary	Conventional mining
Ukraine	Underground	Metasomatites	Underground mining
India	Underground / open-pit	Hard rock ores	Conventional mining
South Africa	Underground (as by-product)	Gold-bearing conglomerates	By-product uranium recovery

The transition toward ISR dominance is explained by a combination of technological-economic and geological factors. ISL is implemented through the circulation of leaching solutions within a permeable ore-bearing horizon and the recovery of pregnant leach solution (PLS) to the surface through production wells. For industrial feasibility, the presence of impermeable confining layers, controlled hydrodynamics, and regulated solution geochemistry are critical. As emphasized by the IAEA in its specialized publication on ISR operations, these requirements determine both the configuration of well fields and the monitoring regimes, and they also limit the applicability of the method according to deposit type [7].

At the global level, WNA also confirms its technological dominance: as early as 2022, a significant part of global uranium production was provided by enterprises using ISR technology, with the bulk of production in the USA, Kazakhstan and Uzbekistan coming from underground leaching [6]. This indicates that the technological leadership actually coincides with the geographical dominance of the sandstone uranium provinces and, consequently, with the concentration of market supply in a limited number of jurisdictions.

The uranium market is highly sensitive to changes in production because global supply is concentrated in a small number of countries. According to the WNA, Kazakhstan, Canada, and Namibia together accounted for about three quarters of global uranium production in 2024. Under these conditions, even relatively small changes in production plans, whether caused by delays in commissioning new capacity, logistical constraints, or regulatory factors, can noticeably affect market supply.

Kazakhstan plays a particularly important role in this structure. The country has remained the world's largest uranium producer since 2009 and also holds a substantial share of identified global uranium resources, according to the WNA country profile. The updated country profiles contain production and resource base indicators reflecting the long-term sustainability of supplies [17]. For the uranium market, not only the absolute volume of production is important, but also the technological nature of this supply: the dominance of ISR makes production rates more sensitive to hydrochemical constraints and the state of the reagent

infrastructure than to the traditional mining restrictions associated with the construction of underground mines.

The distribution of uranium production volumes among the main producing countries in 2024 is shown in Figure 2, while Figure 3 shows the distribution of production volumes among the ten largest uranium mining companies in the world according to WNA data for 2024.

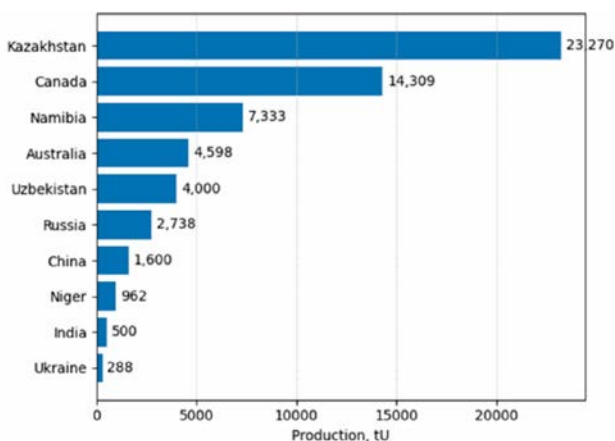


Figure 2 – Top-10 uranium-producing countries (2024), tU.

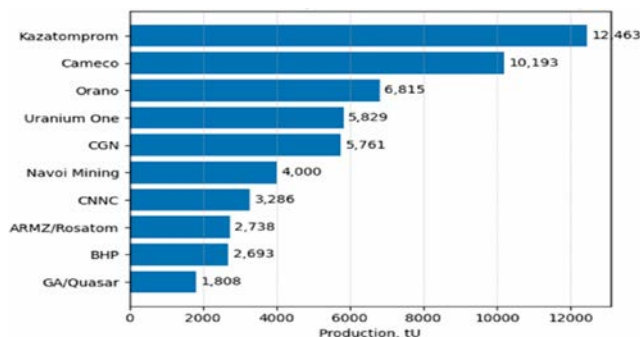


Figure 3 – Top-10 uranium-producing companies (2024), tU.

Along with the ranking of producers, the ownership structure of uranium mining companies is also of fundamental importance. According to an intergovernmental assessment presented in the Red Book (Uranium 2024 edition, data for 2022), of the total world uranium production national state-owned - companies, 15% (7,181 tons) by national private companies, 33% (16,400 tons) by foreign state-owned companies and 10% (4,970 tons) - by foreign private companies. Collectively, the Red Book indicates that in 2022, approximately 75% of global uranium production was associated with state-owned companies, while 25% was accounted for by the private sector [5, p. 95]. This configuration means

that a significant part of the uranium supply may be sensitive to national policy priorities and regulatory regimes, which is methodologically important to take into account when interpreting market signals (without assuming any political motivations beyond the information contained in the sources used).

Market data also shows that the observed spot price does not necessarily reflect the dominant segment of actual trading volumes. According to data provided by Yellow Cake, in the fourth quarter of 2024, the spot price of uranium decreased by 10.7%, decreasing from \$81.75/lb (September 30, 2024) to \$73.00/lb (December 31, 2024). After the end of the quarter, the decline continued, and as of January 27, 2025, the price of it amounted to \$67.30/lb, while the indicative long-term price for the same period decreased to \$79.00/lb. In terms of market liquidity, the quarterly trading volume was 11.1 million lb, while the cumulative annual volume in 2024 reached 45.6 million lb, compared with 56.7 million lb in 2023. At the same time, the average annual trading volume for the period 2020-2023 was 78.7 million lb, and the maximum value was recorded in 2021 (102.4 million lb) [18]. These indicators quantitatively confirm the thesis about the relatively small scale of the spot market segment and the potential volatility of price indicators in conditions of limited volume of “mobile stocks”; available for spot operations.

In terms of final demand, the contract structure of the uranium market is well illustrated by statistics for the United States. According to the U.S. Energy Information Administration (EIA), in 2024, U.S. nuclear power plant owners and operators purchased 55.9 million lb of U_3O_8 -equivalent, of which 49.8 million lb were delivered under short-, medium-, and long-term contracts, while 6.1 million lb were purchased under spot contracts. The weighted average purchase price in 2024 was \$52.71/lb, including \$71.92/lb for spot contracts and \$50.36/lb for contracts with a delivery period of more than one year. Furthermore, EIA data demonstrate the dominance of external supplies in the uranium procurement structure: of the 55.9 million lb, supplies from foreign producers accounted for 54.6 million lb, while U.S.-origin uranium accounted for only 4.3 million lb [19]. In the context of this review, these statistics serve as empirical confirmation that, even in the face of significant price fluctuations, major consumers primarily rely on multi-year contractual agreements, while the spot market serves primarily as an indicative measure.

These factors often cause discrepancies between planned production volumes and actual production levels. Energy policy creates an additional level of uncertainty. For example, in 2025, Reuters, examining the impact of government initiatives aimed at expanding nuclear energy in the United States, cited estimates indicating a possible acceleration in uranium demand growth due to reactor fleet expansion plans and the development of small modular reactors (SMR). Such trends may increase the likelihood of increased contracting activity and increase upward price pressure in the face of limited supply growth [20].

Taken together, the presented data allow us to conclude that the current structure of the uranium market-characterized by the technological dominance of

ISR, high production concentration, the return of long-term contracting, and limited spot market liquidity-increases the likelihood of periods of supply tightness as reactor fleet demand grows, even in cases where nominal production expansion plans appear sufficient on paper. The dynamics of World uranium production in 2010–2024 and the forecast of its change up to 2030 are presented in Figure 4 (according to data from [21]).

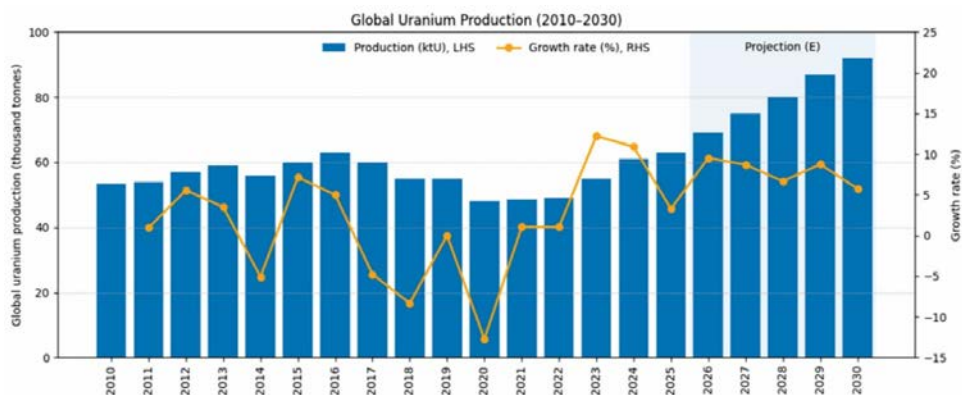


Figure 4 – World uranium production (2010–2030): production volumes (thousand tU) and growth rates (%)

As a result, the uranium market is entering a phase characterized by three interrelated characteristics: the technological dominance of ISR and its continued expansion to over half of global production; the high concentration of production in a limited number of countries and companies; and the restoration of long-term contracting as the primary mechanism for balancing supply and demand.

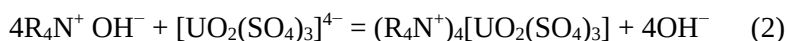
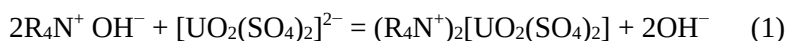
Taken together, these factors explain why even moderate changes in demand can quickly lead to a transition of the uranium market to a state of supply tension and increased price sensitivity. Under these conditions, the sustainability of uranium supplies is increasingly assessed not only in terms of resource availability but also in terms of the feasibility of production plans and the reliability of key mining centers.

3. Ion-Exchange Recovery of Uranium from Pregnant Leach Solutions of In-Situ Leaching

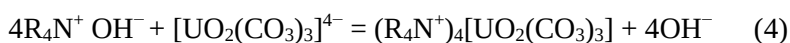
In industrial practice of uranium in-situ leaching, uranium recovery from pregnant leach solutions (PLS) is carried out by the ion-exchange method, which is based on the selective sorption of uranium(VI) anionic complexes on the functional groups of synthetic ion-exchange resins [22]. Depending on the chemical conditions of leaching, uranium in solution is present either in the form of uranyl sulfate complexes (in sulfuric-acid systems) or uranyl carbonate

complexes (in alkaline bicarbonate systems), which determines the requirements for the type of sorbent used [7].

Under conditions of acid in-situ leaching, which is widely applied at sandstone deposits in Kazakhstan where leaching is carried out with sulfuric acid, uranium (VI) is predominantly present in the form of anionic complexes $\text{UO}_2(\text{SO}_4)_2^{2-}$ and $\text{UO}_2(\text{SO}_4)_3^{4-}$ [23]. These complexes are recovered using strong-base anion exchange resins (SBA). Sorption of these complexes on the quaternary ammonium functional groups of SBA resins proceeds according to an ion-exchange mechanism that may be represented by the following reactions:



In contrast to acidic systems, at several ISR operations in the United States alkaline bicarbonate leaching is applied, in which uranium(VI) occurs predominantly in the form of uranyl-carbonate complexes $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ [24]. Their recovery on SBA anion exchange resins also occurs through exchange of the resin counter-ions for uranyl anionic complexes:



Under these conditions, such commercial strong-base anion exchange resins as Dowex 1X8, Purolite A-520E, Purolite A500, and Lewatit S6328A are widely used. These sorbents are applied both in resin-in-solution (RIS) column circuits and in resin-in-pulp (RIP) processes when solid particles are present in the productive solution.

For sulfuric-acid productive solutions it has been shown that the resin Dowex 1X8 provides a high sorption capacity and efficient desorption, enabling the production of eluates with uranium concentrations more than twenty times higher than those of the initial pregnant solution [25].

In carbonate ISR systems used at certain deposits in the United States, strong-base anion exchange resins resistant to high mineralization of groundwater are typically applied. In particular, column experiments have demonstrated that Dowex 21K resin can provide a loading capacity of up to 49.8 mg U g⁻¹ before breakthrough during treatment of carbonate groundwater solutions [26]. Similarly, Purolite A-520E is used in RIS processes for the recovery of uranyl-carbonate complexes from alkaline productive solutions [27].

A comparison of sorbents used in acidic and carbonate ISR circuits is presented in Table 2.

Table 2 – Sorbents Used in Acidic and Carbonate ISR Circuits

Resin brand	Sorbent type	Leaching medium	RIS	RIP
Dowex 1X8	SBA	H ₂ SO ₄	+	+
Purolite A-520E		H ₂ SO ₄ / NaHCO ₃	+	+
Purolite A500		H ₂ SO ₄	+	+
Lewatit S6328A			+	+
Dowex 21K		NaHCO ₃	+	-
Dowex 21K XLT			+	-

Thus, in modern technological schemes for uranium recovery from pregnant solutions of in-situ leaching, strong-base anion exchange resins are most widely used, providing effective sorption of uranium (VI) anionic complexes in both acidic and carbonate ISR systems. The choice of a specific resin grade is determined by the chemical composition of the pregnant solution, the type of leaching medium, and the engineering configuration of the sorption equipment.

4. The Problem of Silica Fouling of Ion-Exchange Resins in Uranium ISR Circuits

Under conditions of sulfuric-acid in-situ leaching of uranium (ISR/ISL), which is predominantly applied at sandstone deposits, pregnant leach solutions (PLS) inevitably contain, along with uranyl-sulfate complexes, significant concentrations of dissolved silicon originating from the acid decomposition of the silicate and aluminosilicate matrix of host rocks. Within the technological circuit of uranium recovery, silicon is present in a set of forms including orthosilicic acid, oligomeric polysilicic acids, and colloidal silica, and the transformation between these forms is primarily determined by pH, temperature, and the ionic composition of the solution.

Although at pH values typical of ISR solutions (pH $\approx$ 1.5–2.5) the rate of polycondensation of silicic acids may be relatively low, even minor local deviations in acidity that occur during mixing of process streams, washing zones, or interaction with hydrolyzing ions such as Fe³⁺ and Al³⁺ may initiate aggregation of low-molecular silicon species followed by the formation of hard-to-remove intrapore deposits on the surface and within the volume of ion-exchange sorbents [15, p.443].

As demonstrated by Chuuman et al. [28], the initial stage of interaction between silicon compounds and strong-base anion exchange resins proceeds through an ion-exchange mechanism between the functional quaternary ammonium groups of the polymer matrix of type R₄N⁺OH⁻ and the monosilicate anion Si(OH)₃O⁻, which may be described by the following reaction:



It should be noted that at the pH of 1.5–2.5 typical of ISR pregnant solutions and with a first dissociation constant of silicic acid of about $pK_{a1} \approx 9.8$, silicon is present mainly as the neutral species $\text{Si}(\text{OH})_4$. In the acidic sorption circuit, silica accumulation is therefore governed chiefly by polymerization and deposition of neutral silica within the pores, whereas the ion exchange described by reaction (5) is relevant primarily for the OH-form of the resin and for the alkaline regeneration stage. The sorbed monomeric forms of silicic acid subsequently undergo intrapore polycondensation with the formation of siloxane bonds (Si-O-Si), resulting in the formation of oligomeric and polymeric structures with different degrees of connectivity. According to NMR spectroscopy, these structures are identified as Q^1 – Q^3 silicate units. It has been shown that even when less than 10% of the ion-exchange capacity of the resin is occupied, monomeric forms (Q^0) transform into dimeric and linear polysilicates (Q^2 – Q^3), which is accompanied by a decrease in the mobility of the adsorbed silicon compounds and their subsequent fixation within the pore structure of the sorbent.

Practical observations in industrial ISR circuits demonstrate that the silicon content in strong-base anion exchange resins may reach 12–17 wt.%, which is accompanied by a decrease in uranium sorption capacity and deterioration of the mechanical strength of resin beads [15, p.435]. In this context, silica fouling of resins ceases to be considered a secondary analytical phenomenon and becomes a factor directly limiting the operational lifetime of sorption materials.

The mechanism of this phenomenon combines deposition of neutral silica inside the pores and competition of silicate anions with uranyl-sulfate complexes for the active sites of strong-base anion exchange resins. In the initial state, the resin exists in the hydroxide form $\text{R}_4\text{N}^+\text{OH}^-$. Upon contact with the pregnant solution of in-situ leaching, ion-exchange sorption of the anionic uranium complex $[\text{UO}_2(\text{SO}_4)_2]^{2-}$ occurs, resulting in the formation of a uranium-loaded resin form. At the same time, part of the dissolved silicon occurs as the anion $\text{Si}(\text{OH})_3\text{O}^-$, whose share rises in local zones of elevated pH and in the OH-form of the resin after regeneration and which then competes for the same quaternary ammonium sites; in the bulk acidic circuit the neutral form $\text{Si}(\text{OH})_4$ prevails and is retained mainly through intrapore polymerization.

During the desorption stage of uranium, uranyl-sulfate complexes are removed from the resin structure; however, silicon compounds may partially remain within the pores and on the functional groups of the resin. This leads to gradual accumulation of silicon in the anion-exchange matrix and to the formation of the so-called silica fouling effect, which is accompanied by a decrease in the availability of active sites and deterioration of the sorption properties of the material.

Schematically, the sequence of these stages – namely the initial state of the resin, sorption of uranyl-sulfate complexes with the competitive participation of silicates, and the subsequent partial retention of silicon after uranium desorption – may be represented as shown in Figure 5.

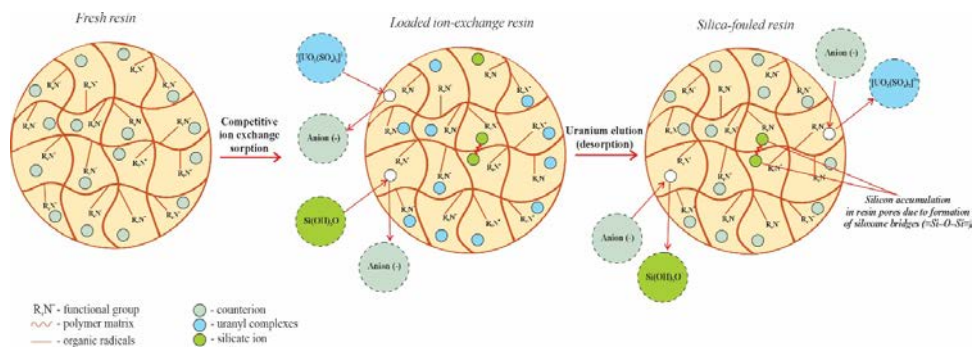


Figure 5 – Schematic representation of the competitive sorption of uranium and silicon on an anion-exchange resin.

The quantitative influence of accumulated silica on the sorption properties of resins was investigated in detail by Yahorava et al. [29]. The authors demonstrated that already at a silica content of about 6% SiO₂ in a gel-type RIP resin, the loss of maximum uranium loading after 24 hours exceeds 50%, whereas for macroporous resins a comparable decrease occurs only when silicon accumulation reaches 25–28%. At the same time, the authors reported differences in the morphology of deposits: in gel-type resins a diffusion film forms on the bead surface, whereas in macroporous resins silica penetrates deeper into the internal structure of the beads. This is confirmed by the increase in silicon concentration toward the center of the bead at high levels of contamination.

These results are consistent with the previously proposed mechanism of intrapore fouling, formulated by Zhang [30], according to which low-molecular polysilicic acids are capable of diffusing into the pore space of an anion-exchange resin, followed by aggregation and formation of intragranular deposits. In contrast, high-molecular polysilicate species are limited by pore dimensions and therefore predominantly precipitate on the resin surface. Taken together, these findings indicate that the critical factor in the degradation of sorption properties is not so much the total silicon concentration in solution but rather the presence of a reactive oligomeric silica fraction.

The obtained results also agree with experimental observations reported by Chuuman et al. [28, p.873], according to which the desorption of silicon from strong-base anion exchange resins strongly depends on the degree of polymerization of the silicate structures. Thus, structures of types Q⁰–Q² are relatively easily removed during treatment with 1–2% NaOH solutions, whereas more condensed Q³ structures are practically not desorbed even when the alkali concentration is increased. This indicates the necessity of breaking siloxane bridges during sorbent regeneration.

Additional confirmation of the influence of silica fouling on the kinetics of uranium sorption is presented in the work of Litvinenko et al. [31]. The authors showed that increasing the SiO₂ content in the Purolite A500U anion exchange

resin from 0 to approximately 19.6% leads to a substantial decrease in the degree of uranium saturation at a fixed contact time. For resin containing about 28% silica, achieving equilibrium loading requires an increase in contact time up to 24 hours, whereas a fresh sorbent reaches comparable values within 6 hours. Thus, the accumulation of silicon can shift the sorption process from a kinetically controlled regime to a diffusion-limited regime, which has direct technological implications for column ISR circuits.

It should be noted that the negative impact of silicon on the operational characteristics of sorption materials in ISR circuits is not limited to mechanical blockage of the porous structure of ion-exchange resins. According to the results reported by Sharafutdinov et al. [32], silica may participate in the formation of stable organo-silicon complexes with humic and fulvic acids present in pregnant leach solutions. These compounds subsequently sorb on the surface and within the volume of both anion-exchange and cation-exchange materials.

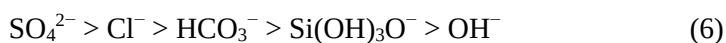
In this case, it is assumed that fixation of silicon within the ion-exchange matrix occurs not only in the form of polycondensed silicate particles but also as part of sulfoghumic compounds, which are capable of partial desorption during the regeneration stage. This results in secondary contamination of the commercial desorbate and deterioration of its technological characteristics during subsequent processing. Moreover, the sorbed organo-silicon complexes may serve as centers for further fixation of trivalent cations, particularly Fe^{3+} , predominantly in an irreversible form. This additionally reduces the efficiency of resin regeneration and promotes accumulation of ballast components within the ion-exchange phase.

Thus, the presence of silicon in ISR pregnant solutions may be considered a factor of complex chemical–physical contamination of strong-base anion exchange resins, leading to a progressive decrease in their working capacity and deterioration of cyclic stability during sorption–desorption operations.

Despite the established negative effects of silicon accumulation in ion-exchange resins, the scientific literature contains a comparatively limited number of studies devoted to the development of effective methods for its removal from the structure of sorbents. The most common approach remains alkaline desilication, based on the conversion of silica into soluble silicate forms [12, 33].

It should be taken into account that the efficiency of this process is determined not only by the concentration of alkali but also by the degree of polymerization of the adsorbed silicon compounds, since silicon removal in this case occurs mainly through alkaline hydrolysis of siloxane bonds (Si-O-Si) formed during intrapore polycondensation of silicic acid [28, p.871].

At the same time, the results of column experiments by Chuuman et al. [28, p.871] demonstrate that for the OH^- form of SBA anion exchange resin, the expected “reverse” desorption of silicon via displacement by more selective anions X^{n-} (such as Cl^- , HCO_3^- , SO_4^{2-}) is practically not realized, although the selectivity order for this system is given as:



The authors showed that regeneration of the column using H_2SO_4 , HCl , NaHCO_3 , and NaCl solutions results in incomplete elution of silicon, whereas noticeable elution occurs specifically when NaOH solution is used. This indicates that the dominant mechanism is hydrolytic destruction of polysilicates rather than simple ion exchange.

Consequently, alkaline regeneration should be considered a process limited by the rate of hydrolysis of siloxane bonds ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$) within the formed intrapore polysilicates rather than solely by the concentration of exchangeable silicon anions.

Earlier studies [15, p.436] established that treatment of anion exchange resin with NaOH solutions of $30\text{--}50\text{ g dm}^{-3}$ at $25\text{--}27\text{ }^\circ\text{C}$ allows the silicon content in the resin to be reduced to 2.91% and 1.15%, respectively, while maintaining mechanical strength of approximately 94%. However, increasing the alkali concentration above 100 g dm^{-3} leads to destruction of the polymer matrix of the sorbent. Similar concerns regarding chemical degradation of functional groups during intensive alkaline treatment were reported by Brown et al. [34], who emphasized the instability of certain strong-base anion exchange resins at high pH values.

Column experiments performed by Chuuman et al. demonstrated that increasing the concentration of NaOH increases silica elution within the range of 1–2%, whereas a further increase up to 5% practically does not produce additional improvement. Thus, a concentration of 2% NaOH may be considered sufficient for elution of adsorbed silicates.

The temperature factor exhibits a non-linear influence: increasing the temperature from $25\text{ }^\circ\text{C}$ to $45\text{ }^\circ\text{C}$ enhances the degree of elution, whereas at $55\text{ }^\circ\text{C}$ a decrease is observed. The authors attribute this to possible repolymerization or precipitation of silicon within the pores as a result of increasing local concentration of monosilicate during accelerated hydrolysis [28].

This effect is important for practical technological regulations, since it demonstrates that intensification of regeneration by heating has an optimum and exceeding this optimum may lead to the opposite effect.

In this context, the attention of researchers has been directed toward fluoride-containing reagent systems, which promote the formation of soluble fluorosilicate complexes. In the work of Spirin et al. [35], it was shown that the use of a regenerant composed of 10% HNO_3 + 5% HF allows the SiO_2 content in the resin to be reduced from an initial 36.8% to 2.8% at a solid-to-liquid ratio of 1:4, and to 0.4% at 1:5, while maintaining mechanical strength at the level of 75–76%.

In a direct comparative experiment using the same batch of resin, a three-stage alkaline treatment reduced the silicon content only to 11.5%, with residual mechanical strength of approximately 40%, whereas fluoride regeneration made it possible to achieve 6.2% SiO_2 with a strength of about 77%. This residual value is higher than the 0.4–2.8% reported by Spirin et al.; the difference should be attributed to the conditions of this comparative test (initial SiO_2 loading, reagent

concentration and number of contact stages) rather than to a discrepancy between the data.

Comparable results were reported by Litvinenko et al. [36], who showed that treatment of Purolite A500Y anion exchange resin with HF or HF + HNO₃ solutions at a sorbent-to-solution ratio of 1:5 for 3 hours results in a more pronounced decrease in residual SiO₂ content while causing less deterioration of mechanical strength compared with alkaline reagents.

Table 3 presents a comparative summary of the reported chemical methods for desilication of silica-fouled ion-exchange resins.

Table 3 – Chemical methods for desilication of silica-fouled ion-exchange resins

Method type	Reagent(s)	Optimal processing conditions	Desilication effect	Limitations	Source
Alkaline desilication	NaOH	30–50 g dm ⁻³ NaOH; 25–27 °C; L:S ≈3:1; ~2 h	SiO ₂ in resin reduced to 1.15–2.91 wt. %	NaOH > 100 g dm ⁻³ damages resin matrix Partial loss of mechanical strength High alkali consumption Possible silica gel formation in column	Kylyshkanov et al. [15]
		1–2% NaOH; ~45 °C; 5–10 min	Removal of monomeric and dimeric silica (Q ⁰ –Q ²); polymerized Q ³ silica remains		Chuuman et al. [28]
		150–200 g dm ⁻³ NaOH; ≤40 °C; 6–8 h	22–35% of silica removed from fouled resin		Molchanova et al. [16]
		3–6% NaOH; 8–16 h	SiO ₂ decreases from ~3–4% to 0.1–0.3% in resin		Ritcey [33]
Fluoride desilication	HF	~5–7% HF; S:L = 1:5; 3 h; RT	~13 g dm ⁻³ Si transferred to eluate	Fluoride corrosion and waste treatment Fluoride handling	Litvinenko et al. [31, 36]
	NH ₄ F	5–9% NH ₄ F; S:L = 1:5; 3 h; RT	Strong silica desorption; Si concentration in eluate ~13–14 g dm ⁻³		
Fluoride–acid treatment	NH ₄ F + H ₂ SO ₄	~10% NH ₄ F + dilute H ₂ SO ₄ ; ~3 h; RT	Moderate silica removal (~40–60%), mechanical strength ~90% retained	Changes sulfate balance	
Alkaline–salt desilication	NaOH + (NH ₄) ₂ SO ₄	9% NaOH + 15% (NH ₄) ₂ SO ₄ ; ~3 h; RT	28–35 g dm ⁻³ Si removed into eluate	Resin strength reduced to 63–68%	
Acid–fluoride treatment	HF + HNO ₃	10% HNO ₃ + 5% HF; S:L ≈1:4–1:5; 1–2 h	Residual SiO ₂ 0.4–2.8% in resin	Highly corrosive medium	Spirin et al. [35]

The data reported by Chuuman et al. [28, p.873] indicate that the limited efficiency of alkaline desilication is determined not only by diffusion factors but also by the degree of polycondensation of the adsorbed silicon compounds, since highly cross-linked Q^3 structures remain resistant to desorption even at elevated alkali concentrations.

Despite the relatively high efficiency of fluoride-based regeneration methods, their industrial application is associated with increased requirements for corrosion resistance of equipment and for handling fluoride-containing effluents. This significantly limits their use as a routine regeneration procedure.

In this regard, a number of authors are considering preventative approaches aimed at reducing the entry of reactive forms of silicon into the sorption circuit. For example, IAEA report TRS-359 notes that high-molecular-weight polymers can be used to remove colloidal silica from productive solutions before the sorption stage [12, p. 87]. Furthermore, Mikhaylenko and van Deventer [37] emphasizes the need to maintain a balance between the rate of silicon accumulation and its removal through partial regeneration of the resin flow in kidney-loop mode.

Another approach involves the use of macroreticular anion-exchange resins, which demonstrate higher stability when operating in environments with elevated silicon content. This is reflected in the patent [38], which demonstrates the applicability of such resins in long-term contact with solutions containing 500 – 700 mg/L SiO_2 . Overall, an analysis of the presented studies shows that existing desilication methods provide varying degrees of silicon removal and simultaneously have uneven effects on the mechanical integrity of resins. In this context, the depth of purification and the preservation of the resin granule structure act as competing criteria.

In many published studies, desilication efficiency is assessed primarily based on the residual SiO_2 content and the mechanical strength of the sorbent. Data on the recovery of uranium sorption capacity after regeneration are reported significantly less frequently, making direct comparisons of different regeneration methods difficult.

Additional complications arise from differences in the criteria for assessing silicon contamination and the analytical methods used. Therefore, the results of individual studies are not always comparable, and the transfer of laboratory data to industrial ISL conditions remains limited.

The available data are insufficient to fully evaluate the efficiency of desilication under ISL conditions. Further research should focus on regeneration modes that ensure silicon removal without significantly reducing the mechanical strength and uranium sorption capacity of ion-exchange resins during repeated use.

5. Conclusion

An analysis of current trends in global uranium mining reveals the consistent dominance of the in-situ leaching method, which accounts for a significant

portion of global production. When using this technology, the efficiency of processing pregnant solutions depends largely on the stable operation of the ion-exchange sorbents used for uranium extraction.

One of the reasons for the reduced efficiency of ISL sorption systems is the accumulation of silicon compounds in ion-exchange resins. Silicon enters the pregnant solutions through the interaction of the leach solution with silicate minerals in the host rocks. Its accumulation in the anion exchange resin structure can lead to a decrease in uranium sorption capacity and deterioration of mass transfer, which gradually reduces the efficiency of the sorption process.

Despite the practical significance of this problem, the mechanisms of contamination and regeneration of ion-exchange resins from silicon-containing compounds under uranium ISL conditions have not been sufficiently studied. The proposed purification methods provide varying degrees of silicon removal, but their impact on restoring the resins' sorption properties has been significantly less studied. Therefore, further research should focus on selecting regeneration modes that remove silicon with minimal damage to the sorbent, as well as developing measures to reduce silicon accumulation in ion-exchange materials during long-term operation.

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ЖЕР АСТЫ ШАЙМАЛАУ ПРОЦЕСІНДЕГІ АНИОНАЛМАСТЫРҒЫШ ШАЙЫРЛАРДЫҢ КРЕМНИЙМЕН ЛАСТАНУЫ: ҚАЗІРГІ ТҮСІНІКТЕР ЖӘНЕ РЕГЕНЕРАЦИЯ ӘДІСТЕРІ

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Түйіндеме. Уранды әлемдік өндіруде жер асты ұңғымалық шаймалау (ЖАШ) үлесінің артуы өнімді ерітінділерді ионалмасу әдістерімен тиімді өңдеуге қойылатын талаптарды күшейтеді. Уранды бөліп алу үшін әдетте уранил-сульфатты немесе уранил-карбонатты кешендерді сорбциялайтын күшті негізді аниониттер қолданылады. Ұзақ уақыт пайдаланғанда олардың қасиеттері силикатты жыныстарды шаймалау кезінде ерітіндіге өтетін кремний қосылыстарының жиналуына байланысты нашарлайды. Шолуда ЖАШ жағдайында қолданылатын анионалмастырғыш шайырлардың кремниймен ластану механизмдері, сондай-ақ десиликация мен регенерацияның қолданыстағы тәсілдері қарастырылды. Ғылыми жарияланымдар мен техникалық материалдарды талдау кремниймен ластану негізінен кремний қышқылының шайыр кеуектеріне енуі және одан әрі полимерленуімен байланысты екенін көрсетеді. рН жергілікті жоғарылаған жағдайда силикат аниондары ионалмасу орталықтарымен де әрекеттесуі мүмкін. Олигомерлі және полимерлі силоксан құрылымдарының түзілуі масса алмасуды қиындатады, белсенді орталықтарды бөгейді және уран бойынша сорбциялық сыйымдылықты төмендетеді. Регенерация үшін NaOH ерітіндісімен сілтілік өңдеу және құрамында фторид бар реагенттер қолданылады. Сілтілік ерітінділер технологиялық жағынан қарапайым, бірақ жоғары дәрежеде полимерленген кремнийлі фазаны жоюда тиімділігі төмен және қатаң режимдерде шайырды зақымдауы мүмкін.

Фторидті жүйелер кремнийді тереңірек жояды, алайда жабдықтың коррозияға төзімділігі мен ағынды суларды тазартуға жоғары талап қояды. Сондықтан регенерация режимі шайырдың механикалық беріктігі мен уранға қатысты сорбциялық қасиеттерін елеулі төмендетпей, кремнийді тиімді жоюды қамтамасыз етуі тиіс.

Түйінді сөздер: уран, жер асты шаймалау, сорбция, кремний, кремнийден тазарту

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ЗАГРЯЗНЕНИЕ АНИОНООБМЕННЫХ СМОЛ КРЕМНИЕМ В ПРОЦЕССЕ ПОДЗЕМНОГО ВЫЩЕЛАЧИВАНИЯ УРАНА: СОВРЕМЕННОЕ ПОНИМАНИЕ И ПОДХОДЫ К РЕГЕНЕРАЦИИ

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Резюме. Рост доли подземного скважинного выщелачивания (ПВ) в мировой добыче урана повышает требования к эффективности переработки продуктивных растворов ионообменными методами. Для извлечения урана обычно применяют сильноосновные аниониты, сорбирующие уранил-сульфатные или уранил-карбонатные комплексы. При длительной эксплуатации их свойства ухудшаются из-за накопления соединений кремния, поступающих в раствор при выщелачивании силикатных пород. В обзоре рассмотрены механизмы кремниевого загрязнения анионообменных смол, используемых в ПВ, а также существующие способы десиликации и регенерации. Анализ научных публикаций и технических материалов показывает, что загрязнение связано главным образом с проникновением кремниевой кислоты в поры смолы и ее последующей полимеризацией. При локальном повышении pH силикатные анионы также могут взаимодействовать с обменными центрами. Образование олигомерных и полимерных силоксановых структур затрудняет массоперенос, блокирует активные участки и снижает сорбционную емкость по урану. Для регенерации применяют щелочную обработку NaOH и фторидсодержащие реагенты. Щелочные растворы технологически проще, но менее эффективны при сильно полимеризованной кремнеземистой фазе и при жестких режимах могут повреждать смолу. Фторидные системы обеспечивают более глубокое удаление кремния, однако предъявляют повышенные требования к коррозионной стойкости оборудования и очистке стоков. Поэтому режим регенерации должен обеспечивать удаление кремния без существенного снижения механической прочности и сорбционных свойств смолы.

Ключевые слова: уран, подземное выщелачивание, сорбция, кремний, обескремнивание

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