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Study of scandium sorption on a phosphorus-containing cation exchange resin from solutions generated during uranium extraction

Zhiger Kenzhetayev [1*], Bolatbek Toksanbayev [1], Umit Yessimkanova [1],
Mukhametkali Mataev [2]

[1] *Ascore, Almaty, Kazakhstan*
[2] *Institute of High Technologies, Almaty, Kazakhstan*
**Corresponding author: e-mail kzhiger@yahoo.com*

Abstract

Purpose. This study aims to develop an efficient method for scandium recovery from barren solutions generated during the in-situ leaching of uranium ores, using a phosphorus-containing cation exchange resin, and to determine the optimal sorption conditions.

Methods. The research employed static and dynamic sorption techniques and kinetic modeling of ion exchange processes. Elemental analysis was performed using ICP-MS spectrometry following microwave-assisted sample digestion. Gel diffusion coefficients, kinetic parameters of the pseudo-first and pseudo-second order models, and half-exchange times were calculated. The efficiency of the sorption process was assessed across a range of solution acidities (H_2SO_4 = 5-15 g/dm^3).

Findings. Phosphorus-containing ion exchange resins with strong complexation properties demonstrated high potential for extracting rare earth elements. Experimental variation of the feed solution pH revealed a significant influence of acidity on scandium uptake. It was found that increasing the solution acidity to 15 g/dm^3 resulted in the maximum sorption capacity for scandium (0.384 mg/g), while simultaneously reducing the uptake of impurities. The sorption process followed a pseudo-second-order kinetic model with a high coefficient of determination ($R^2 = 0.999$). Gel-phase diffusion was identified as the rate-limiting step. The calculated half-exchange time was 1884 seconds.

Originality. A comprehensive kinetic and phase-chemical study of scandium sorption from uranium-bearing solutions onto a phosphorus-containing cation exchanger has been conducted for the first time. The applicability of the Ho and McKay kinetic model has been confirmed, and key exchange parameters have been determined.

Practical implications. The results of this study can be applied in the design and optimization of scandium and other rare earth element recovery processes from leach solutions generated during uranium ore processing, enabling their further use in various industrial sectors.

Keywords: *scandium, sorption, cation exchange resin, ion exchange, kinetics, gel diffusion, uranium leach solution*

1. Introduction

Kazakhstan's uranium industry plays a significant role in the global economy, as the country ranks among the world's leading uranium producers [1], [2]. The complex chemical and technological processes in uranium extraction and processing [3], [4] result in substantial volumes of liquid waste containing various elements, including rare earth metals such as scandium. Consequently, developing efficient methods for recovering scandium from solutions generated during uranium mining and processing has become a pressing research priority.

One of the promising materials for this purpose is phosphorus-containing cation exchange resin, which has demonstrated favorable sorption properties toward a wide range of cations, including rare earth elements [5]. Sorption of scandium onto such resins may offer a practical recovery approach from wastewaters produced during uranium-related operations. However, a detailed investigation of the sorption behavior and kinetics of scandium interaction with phosphorus-functionalized resins is required to optimize this process. Key factors such as scandium concentration, pH, temperature, and other process parameters must be examined to understand the sorption mechanism better and develop efficient recovery technologies [6], [7]. A comprehensive study of these processes can significantly enhance scandium recovery efficiency, which is of both environmental and economic importance for Kazakhstan's uranium sector [8]-[10].

In addition, potential ecological and hygienic risks associated with anthropogenic solutions must be considered, as highlighted by studies in molybdenum production [11] and by environmental monitoring models based on robust algorithmic frameworks [12]. Related chemical engineering research also increasingly addresses energy efficiency improvements, optimization of equipment operating modes, and industrial safety aspects reflected in modern approaches to the modeling and design of engineering systems [13]-[16].

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The in-situ leaching (ISL) method also holds considerable potential for the recovery of rare earth elements (REEs) such as scandium, which is one of the by-products of uranium mining [17], [18]. For this purpose, it is necessary to take into consideration recent studies on drilling [19]-[22]. Scandium is widely used in sectors such as aerospace and aviation, as well as in the production of lightweight metal alloys, making it a strategically essential and high-value element [23]-[25]. One of the primary secondary sources of REEs, including scandium, is the barren (raffinate) solution generated after uranium has been sorbed onto ion exchange resins. The recovery of scandium from these raffinate solutions mustn't interfere with the primary uranium extraction process or compromise the overall efficiency of the production system [26]-[28].

Kazakhstan, accounting for approximately 27% of global uranium production, plays a pivotal role in the international uranium market, underscoring the relevance of extracting scandium and other REEs. Various technologies have been developed to improve the efficiency of REE recovery, contributing to the uranium industry's sustainable and environmentally responsible advancement [29]. The application of scandium extraction technologies enhances the economic performance of mining operations and mitigates the environmental risks associated with uranium extraction and processing [30]. Comparable challenges in the integrated recovery of rare metals and the development of efficient processing schemes for mineral resources have been addressed in studies on placer platinum-group minerals [31], as well as in research into the comprehensive processing of natural tuffs and zeolite-bearing rocks [32], [33].

The scandium concentration in productive solutions varies from 0.09 to 0.31 mg/dm^3, indirectly indicating its content in the ore and confirming the feasibility of scandium recovery at various stages of uranium solution treatment. These findings also suggest that scandium extraction can be implemented without significantly disrupting the core uranium production process [34]. The primary source of scandium remains the raffinate solution generated after uranium sorption. Samples of productive and raffinate solutions were collected at the mining operations of JSC NAC "Kazatomprom" from January to December 2024 to assess the composition of such solutions. The obtained data enable a more detailed analysis of REE concentrations, including scandium, in uranium-bearing ores [35].

Figure 1 and 2 present the average concentrations of scandium, rhenium, and the total rare earth elements (REEs) in process solutions. Figure 1 shows the mean contents across various technological streams, while Figure 2 illustrates the annual dynamics of scandium, rhenium, and REE concentrations at Mine No. 6.

Based on the data shown in Figures 1 and 2, the annual fluctuations in scandium content in productive solutions range from 0.0044 to 17.43% relative to the yearly mean. The scandium concentration remains within this range throughout the year, with no indication of seasonal variability.

The highest scandium concentrations were recorded at Mine No. 6 in productive and barren solutions – 321.54 and 324.75 μg/L, respectively. The scandium concentration in the total REE fraction at this site reaches 0.32 mg/dm^3. These elevated values suggest Mine No. 6 is the most promising site for further scandium recovery. The concentrations of other rare earth elements, including lanthanides, are significantly lower.

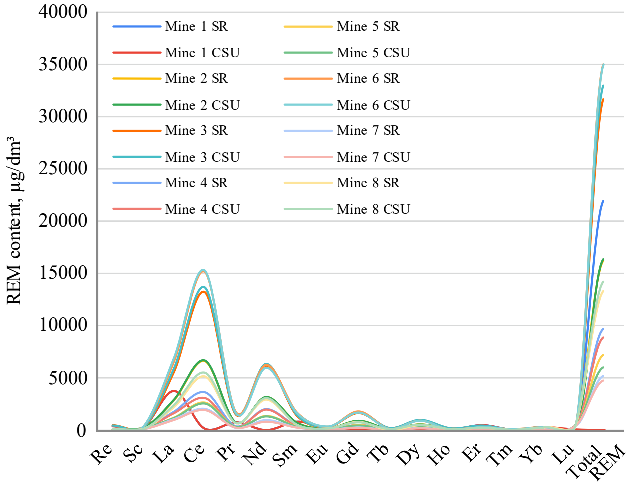

Figure 1. Average concentrations of scandium, rhenium, and total REEs in process solutions

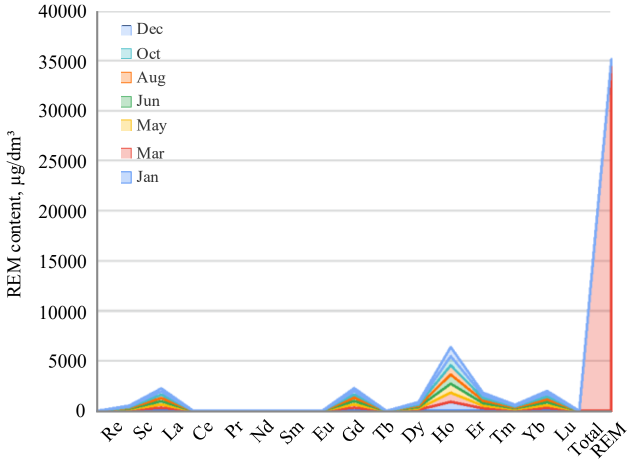

Figure 2. Annual variation in scandium, rhenium, and total REE concentrations in process solutions at Mine No. 6

The difference in scandium content between productive and barren solutions is negligible for most deposits. No significant retention of scandium by conventional ion exchange resins has been observed, indicating its stable presence in solution and making direct recovery without prior separation feasible.

Based on these findings, Mine No. 6 was selected for further process development. A phosphorus-containing cation exchange resin was used as the sorbent due to its capacity to concentrate scandium from multicomponent solutions selectively. Despite its effectiveness, this method is limited by the resin's relatively low sorption capacity for scandium and the co-extraction of impurities in the eluate.

To enhance sorption capacity, a series of experiments were conducted using barren solutions with varying levels of acidity (H_2SO_4 concentrations of 5, 10, and 15 g/dm^3). Additionally, the kinetics of scandium sorption onto the phosphorus-containing cation exchange resin were studied to assess the process dynamics under different environmental conditions.

2. Methodology

2.1. Sample preparation and analysis

A quadrupole inductively coupled plasma mass spectrometer (ICP-MS), ICAP-Qc, manufactured by Thermo Fisher Scientific, was employed to accurately determine elemental concentrations in liquid solutions and ion exchange resins. This highly sensitive analytical instrument enables precise quantification of trace elements with minimal measurement error, not exceeding 0.4%. The choice of this method was driven by its ability to reliably analyze complex multicomponent solutions, a crucial feature when studying the composition of uranium processing solutions and extracting rare earth elements such as scandium. Using the ICAP-Qc ICP-MS ensured reproducible and robust results, which were essential for evaluating ion exchange efficiency and accurately measuring element concentrations at various stages of the experiments.

Ion exchange resin decomposition for subsequent analysis was performed using a Mars 6 microwave digestion system. This technique was selected due to its high speed and efficiency. Microwave-assisted digestion ensures uniform sample heating, enabling complete matrix breakdown and efficient extraction of all analyzable components under controlled temperature conditions.

Preconditioning the ion exchange resins before use was a critical step, as it helped remove residual impurities, particularly iron, that could otherwise interfere with measurement accuracy. For this purpose, the resins were treated with a 2N HCl solution and subsequently rinsed with deionized water. A 5% NaOH solution was applied to eliminate any remaining organic residues. Following this conditioning procedure, the resins were equilibrated in the working medium for 24 hours to stabilize their properties before the sorption experiments. The working medium was flushed until the pH stabilized in the range of 5.0-5.5, which was found to be optimal for scandium recovery while minimizing undesirable side reactions.

2.2. Scandium sorption methodology under static conditions

A phase volume ratio of 1000:1 was employed for the sorption experiments to ensure sufficient contact time for effective scandium uptake. This ratio was selected to achieve maximum sorption capacity with minimal reagent consumption and time investment. The total experiment duration was 24 hours, sufficient for equilibrium to be reached under varying acidity conditions.

During each experiment, 5 cm^3 of ion exchange resin was placed in a vessel containing 5 dm^3 of barren solution (raffinate). Mechanical stirring was applied throughout the process to ensure uniform phase contact. The initial time point was recorded, and solution samples were collected at regular intervals: 1, 2, 4, 6, 8, 12, 16, 20, and 24 hours. This approach enabled the construction of a dynamic sorption curve and allowed scandium concentration changes to be tracked over time.

Upon completion of the sorption process, the resin was separated from the solution and rinsed with distilled water to remove any residual impurities that could interfere with subsequent analysis. Following the rinsing step, the scandium content and concentrations of accompanying elements were determined. These measurements were used to evaluate the process's overall efficiency and refine key sorption parameters.

The laboratory setup (Fig. 3) included components for precise control of temperature, solution pH, phase contact time, and mixing intensity. The parameters recorded during each experiment, including the change in scandium concentration in solution and the amount sorbed onto the resin, served as the basis for calculating sorption capacity and constructing kinetic curves.

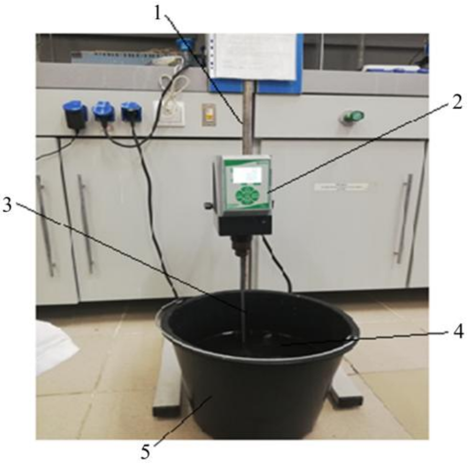

Figure 3. Laboratory setup for scandium sorption experiments under static conditions: 1 – stand; 2 – motor; 3 – stirrer; 4 – container with barren solution; 5 – ion exchange resin

This approach provided reliable insights into the interaction behavior of scandium with the phosphorus-containing cation exchange resin under conditions approximating industrial practice. The resulting data were used to assess the effect of solution acidity on sorption efficiency and to select the optimal conditions for subsequent experiments.

2.3. Calculation of static ion exchange capacity (SIEC)

To evaluate the efficiency of the ion exchange resin in extracting target elements from solution, the static ion exchange capacity (SIEC) is calculated. This parameter reflects the resin's ability to exchange ions with solution components and is a key metric in optimizing sorption process conditions. The calculation is based on the initial and equilibrium concentrations of the target element in the solution, the volume of solution in contact with the resin, and the mass of the sorbent used.

The experiments were conducted under fixed parameters: constant solution volume and known resin mass, ensuring reproducibility of conditions. Upon completion of the sorption process, the element concentrations before and after contact with the resin were measured, and the exchange capacity was then calculated.

The static ion exchange capacity (SIEC) is determined using Equation (1):

$$ECOE = \frac{\left(C_0 - C_\infty\right) \cdot V}{m}, \tag{1}$$

where:

C_0 – initial concentration of the target element in solution, mg/dm^3;

C_∞ – equilibrium concentration after sorption, mg/dm^3;

V – volume of the solution, dm^3;

m – mass of the ion exchange resin used in the sorption process, g.

The difference ($C_0 - C_\infty$) represents the amount of ions sorbed by the resin. At the same time, normalization by the solution volume and sorbent mass ensures comparability of results across different experimental conditions and resin types.

The calculated *SIEC* values were used for the quantitative assessment of sorption efficiency and to compare the sorption capacity under varying pH conditions and scandium concentrations. These results formed the basis for further analysis of how external factors influence the sorption behavior of the phosphorus-containing cation exchange resin.

2.4. Kinetics of scandium (Sc(III)) sorption on ion exchange resins

The sorption kinetics of scandium ions (Sc(III)) on the selected ion exchange resin were studied using a limited-volume method with a constant ratio of solution volume to resin mass (V:m). For the experiments, a column packed with 2 mL of resin was used, through which 1 L of working solution containing a predefined Sc(III) concentration was passed. The contact time between the solution and the resin was varied across the following intervals: 9000, 4800, 1800, 1200, and 780 seconds. After each interval, the concentration of Sc(III) in the solution and on the resin was measured to determine the degree of sorption and the amount of scandium sorbed at each time point. Based on the collected data, a dynamic sorption curve was constructed, showing the relationship between the amount of sorbed scandium and contact time.

The models proposed by Boyd, Meyers, and Adamson [2], [3]were applied to analyze sorption kinetics. These models describe diffusion-controlled processes occurring through the liquid boundary layer. In this case, the kinetic equation takes the following form:

$$-\log\left(1-F\right)=\frac{3D}{2,3\cdot r\cdot \Delta r\cdot \lambda}\cdot t=kt\,. \tag{2}$$

For processes controlled by gel-phase (intraparticle) diffusion, the following equation is used:

$$F=1-\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{D_G t\pi^2 n^2}{r_0^2}\right), \tag{3}$$

where:

F – degree of exchange, defined as the ratio of the amount of ions sorbed at time t to the amount sorbed at equilibrium;

r – resin particle radius;

Δr – thickness of the liquid boundary layer;

D – diffusion coefficient of the substance within the resin particles;

λ – distribution coefficient of ions between the solution and the resin;

D_G – gel diffusion coefficient;

$\frac{D_\Gamma \pi^2}{r_0^2}=B$ – kinetic rate constant;

r_0 – average radius of the resin particle.

Analysis of the kinetic data enables identification of the rate-limiting step in the sorption process. It supports selecting an appropriate mass transfer model for accurately interpreting the interaction mechanisms between Sc(III) ions and the ion exchange resin.

Applying the above equations allows for a more precise interpretation of sorption kinetics, taking into account the influence of film (boundary layer) and gel-phase diffusion. This approach considers parameters such as diffusion coefficients and specific ion–resin interaction characteristics. Correlating the experimental data with mathematical models provides insight into the mechanisms limiting the sorption rate. It facilitates the determination of optimal operating parameters for ion exchange systems used in scandium and rare earth element recovery. Contemporary approaches to diffusion and mass transfer in solid porous media also account for radiative and thermodiffusion effects, as demonstrated in research on ceramic materials and concretes [36]-[39].

A laboratory setup was used to investigate sorption kinetics under dynamic conditions, the schematic of which is shown in Figure 4.

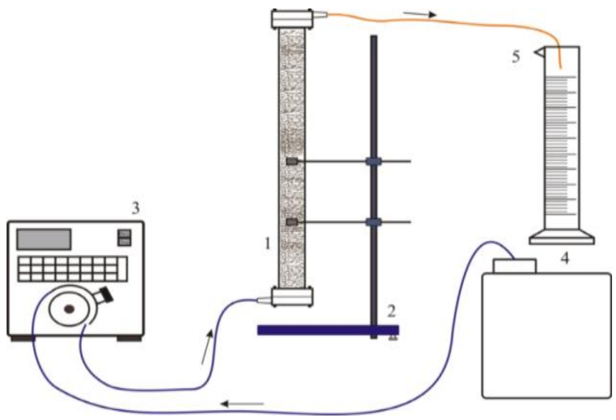

Figure 4. Laboratory setup for kinetic experiments under dynamic conditions: 1 – sorption column; 2 – stand; 3 – peristaltic pump; 4 – buffer tank; 5 – graduated cylinder for collecting raffinate

The system allows for precise control of experimental conditions and enables continuous monitoring of the system's behavior over time. This approach provides a reliable basis for the quantitative evaluation of kinetic parameters and for improving technological solutions to recover target components from solutions.

3. Results and discussion

The object of study was a phosphorus-containing ion exchange resin characterized by pronounced complexation properties and high selectivity toward scandium [10]. Due to these properties, the material is considered a promising sorbent for recovering rare earth elements, including scandium, from complex multicomponent solutions.

One of the practical approaches to enhancing the exchange capacity of weakly acidic cation exchangers is adjusting the acidity of the initial solution. Increasing the acid concentration promotes activation of the functional groups on the resin surface, enhancing ion exchange and increasing the degree of sorption of target components. A series of experiments was conducted using barren solutions (raffinate) with varying acidity to evaluate the effect of pH on scandium recovery.

A series of static tests was performed to gain a deeper understanding of the sorption behavior of the phosphorus-functionalized resin. These experiments examined scandium uptake and the co-sorption of impurities under different acidity conditions. The results provided insight into the influence of pH on the sorption efficiency of both the target element and unwanted components, allowing the identification of conditions that ensure selectivity in the process.

The scandium sorption kinetics curves obtained during the experiments are presented in Figure 5. These curves illustrate the dynamics of scandium concentration reduction in solution over time at different acidity levels, revealing the influence of pH on the rate and completeness of scandium uptake. Analyzing the kinetic profiles shown in Figure 5 makes it possible to determine the optimal conditions for achieving maximum scandium recovery efficiency while minimizing the co-sorption of undesirable impurities.

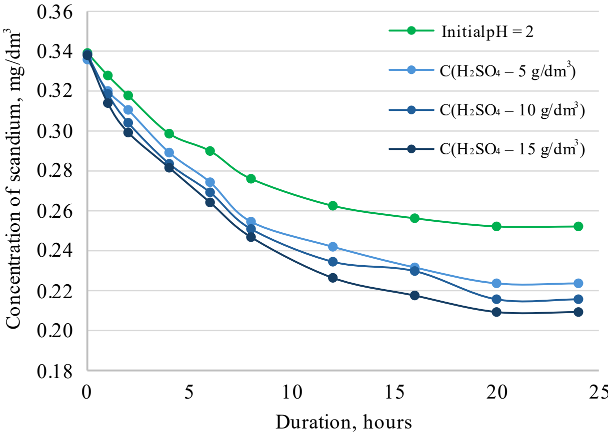

Figure 5. Scandium sorption onto the cation exchange resin under static conditions at varying acidity levels of the initial solution

According to the data presented in Figure 5, the best results were achieved when the raffinate solution was pre-acidified to a sulfuric acid concentration of 15 g/dm^3. Increasing the solution's acidity led to a faster sorption process and more complete scandium uptake, indicating enhanced ion exchange activity of the resin. At higher acid concentrations, equilibrium was reached significantly faster, making this condition the most favorable for practical implementation. These findings confirm the critical role of solution acidity in intensifying sorption interactions and highlight the feasibility of controlling the rate and extent of scandium recovery by adjusting pH. Such an approach can be effectively integrated into industrial schemes for concentrating rare earth elements.

Additionally, Table 1 presents comparative values of the static ion exchange capacity (SIEC) of the phosphorus-containing cation exchange resin, obtained for scandium and accompanying impurities from solutions with varying acidity levels (5, 10, and 15 g/dm^3 H_2SO_4). Changes in acid concentration were found to have a marked effect on ion exchange efficiency. As the acidity increased, the resin's capacity for scandium also increased, while the sorption of most co-occurring rare earth elements decreased, thus improving process selectivity. Comparative analysis of these data makes it possible to determine optimal conditions for maximizing scandium recovery while minimizing competition from other ions.

Table 1. Static ion exchange capacity of the cation exchange resin for scandium and co-existing impurities at different acidity levels (mg/g)

Element	pH ≈ 2 (initial raffinate)	H_2SO_4 – 5 g/dm^3	H_2SO_4 – 10 g/dm^3	H_2SO_4 – 15 g/dm^3
Sc	0.144	0.185	0.285	0.384
Ce	0.032	0.020	0.011	0.009
Dy	0.013	0.011	0.006	0.004
Er	0.006	0.004	0.003	–
Eu	0.002	0.001	0.00079	0.00059
Gd	0.023	0.023	0.014	0.013
La	–	–	–	–
Nd	0.005	–	–	–
Fe	6.915	7.891	5.601	5.705
Th	0.098	0.137	0.097	0.130
U	0.366	0.443	0.532	0.581
Al	0.093	0.073	0.047	0.039
Ca	0.410	0.343	0.531	0.429

At an H_2SO_4 concentration of 15 g/dm^3, the maximum sorption capacity for scandium (0.384 mg/g) was achieved, accompanied by a decrease in the sorption of Ce, Dy, Gd, and other lanthanides. This indicates improved selectivity of the ion exchange resin and confirms the effectiveness of acidity regulation as a tool for controlling the extraction process. The observed trends can be applied to tailor the sorption technology to the specific composition of productive or barren solutions.

The data presented in Table 1 indicate a clear dependence of the sorption capacity of the phosphorus-containing cation exchange resin on solution acidity. As the sulfuric acid concentration in the initial solution increases, scandium sorption rises significantly. Simultaneously, the capacity for rare earth elements and certain impurities decreases, suggesting enhanced selectivity of the material toward Sc^{3+} ions.

The scandium sorption process proceeds via a cation exchange mechanism involving functional phosphorus groups. This mechanism can be represented by the reaction in Figure 6, where the Sc^{3+} ion interacts with hydroxyl groups of phosphoric acid moieties on the resin surface, displacing protons and forming stable coordination bonds [40].

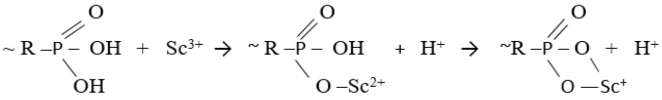

Figure 6. Mechanism of Sc^{3+} sorption by phosphorus-containing functional groups of the ion exchange resin

A kinetic study was additionally conducted to investigate this interaction in greater detail and to assess its rate quantitatively. This approach made it possible to track the concentration changes over time and identify the rate-limiting steps affecting the overall process dynamics. The results served as the basis for calculating kinetic parameters required for subsequent optimization of scandium extraction technology. In recent years, increasing attention has been devoted to ion exchange processes, as evidenced by several review articles and experimental studies exploring general patterns and specific kinetic features of rare earth element sorption [41]-[43].

Ion exchange on granular resins proceeds through several sequential stages, each influencing the overall rate and efficiency of the process. In the initial stage, the sorbed ions diffuse across the liquid film surrounding the resin particle (external or film diffusion). Subsequently, the ions penetrate the interior of the grain, where internal (gel-phase) diffusion occurs toward the active functional groups. Upon reaching the sorption sites, the ion exchange reaction involves the displacement of counterions. These displaced counterions then diffuse back from the interior of the resin particle to its surface (reverse gel diffusion) and re-enter the bulk solution through the same boundary layer. This sequence of stages collectively defines both the kinetic behavior of the system and the factors that constrain the extent and selectivity of sorption.

By electroneutrality, the influx of cations from the solution and the release of counterions from the resin matrix must occur synchronously. Therefore, the external diffusion stages (Stages 1 and 5) are mirror processes occurring at equal rates. For each ion diffusing toward the resin surface, there is a corresponding counterion leaving the resin particle. A similar balance is maintained within the resin bead itself, where the outward migration of displaced ions compensates the inward movement of sorbed ions toward active sites.

As a result, the entire ion exchange process can be simplified into three principal stages: external (film) diffusion, internal (gel-phase) diffusion, and the ion exchange reaction. Among these, the slowest stage determines the overall rate of the ion exchange process.

An acidified solution was prepared for the scandium sorption kinetics study based on the raffinate obtained after uranium sorption. The scandium concentration in the solution was 0.31 mg/dm^3, the sulfuric acid concentration was 15 g/dm^3, and the liquid-to-solid phase ratio (L:S) was 500. The initial experimental parameters were as follows: specific volume of the cation exchange resin – 3.0 cm^3/g, and static exchange capacity for scandium (Q_e) – 0.384 mg/g. At each time interval, the concentration of scandium retained in the resin was measured and denoted as Q_t (mg/cm^3), enabling the construction of kinetic sorption curves. The experimental results on scandium sorption kinetics are presented in Table 2 and illustrated in Figure 7.

Table 2. Characteristics of scandium sorption on the cation exchange resin at L:S = 500, H_2SO_4 = 15 g/dm^3

V_{resin}, cm^3	$V_{solution}$, cm^3	t, s	B_t	C_{Sc} in solution, mg/dm^3	Q_t, mg/cm^3
2	1000	9000	1.340	0.090	0.107
		4800	0.703	0.142	0.089
		1800	0.210	0.205	0.055
		1200	0.1147	0.226	0.042
		780	0.0473	0.247	0.029

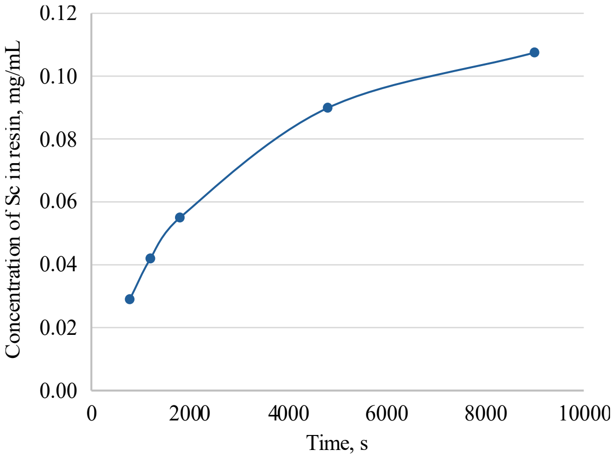

Figure 7. Kinetic sorption curve of scandium on the cation exchange resin from raffinate (15 g/dm^3 H_2SO_4, L:S = 500, C_{Sc} = 0.3 mg/l)

The dynamics of scandium concentration changes in both the solution and the resin over time, as shown in Figure 7, exhibit a characteristic kinetic curve profile, with a pronounced initial phase of rapid sorption followed by a plateau. The obtained Q_t values, combined with kinetic model equations, allow for the calculation of diffusion coefficients and the identification of the rate-limiting step in the process.

The Boyd model is used to describe the ion exchange kinetics under conditions where internal (gel-phase) diffusion is the limiting stage. This model is widely applied in the analysis of sorption and ion exchange processes in porous materials, including cation exchangers, as it provides a quantitative framework for assessing the contribution of intraparticle diffusion to the overall mass transfer mechanism.

The model describes the kinetics of ion penetration into the resin particle interior, where the rate is controlled by diffusion within the ion exchange phase rather than by the exchange reaction itself. Assuming spherical geometry and a uniform distribution of active sites, the equation derived by Boyd takes the following form:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-Btn^2\right), \tag{4}$$

where:

$F = Q_t / Q_e$ – degree of exchange at time t;

B_t – dimensionless kinetic parameter;

Q_t – concentration of sorbed scandium at time t, mg/cm^3;

Q_e – equilibrium concentration of sorbed scandium, mg/cm^3.

Equation (4) is applied to approximate the experimental data and enables the calculation of the gel-phase diffusion coefficient by comparing the theoretical and empirical sorption curves.

The values of B_t were determined based on tabulated data corresponding to various experimentally obtained exchange degrees, $F = Q_t / Q_e$ [44]. The corresponding B_t was identified for each value of F, and a plot of B_t versus time t was constructed. This approach allows for visualization of the kinetic behavior of the system and identification of the mechanism limiting the sorption rate.

The linear nature of this relationship, with a high coefficient of determination (R^2 = 0.9997), confirms that the gel-phase diffusion model governs the scandium sorption process onto the cation exchange resin under the studied conditions. The slope of the line is used to calculate parameter B, which is then used to determine the gel-phase diffusion coefficient using the following Equation:

$$B = \frac{D_G \pi^2}{r_0^2}. \tag{5}$$

In cases where the initial portion of the plot deviates from linearity, it may indicate the influence of external (film) diffusion. Under such conditions, a logarithmic dependence of $-\log(1 - F)$ on time t should be used, characteristic of the film diffusion-controlled model. The slope of the corresponding straight line reflects the kinetic constant of external diffusion, which can then be used to calculate the respective diffusion coefficient.

The plot of the Boyd-Adams model parameter B_t versus time is shown in Figure 8. The experimental data presented in Figure 8 show a linear relationship between B_t and time, indicating that the sorption rate is controlled primarily by gel-phase diffusion processes. To further verify this, an additional analysis was carried out by plotting $-\log(1-F)$ versus contact time (Fig. 9), a method commonly used to assess the contribution of film diffusion.

The curve in Figure 9 deviates from linearity, particularly in the initial stages, confirming that film diffusion plays only a minor role in the overall process. Thus, under the studied conditions, the sorption of Sc^{3+} onto the phosphorus-containing ion exchange resin proceeds under diffusion control, with internal (intraparticle) diffusion being the primary rate-limiting factor. Equation 5, based on the Boyd model, was applied for the quantitative evaluation of the process.

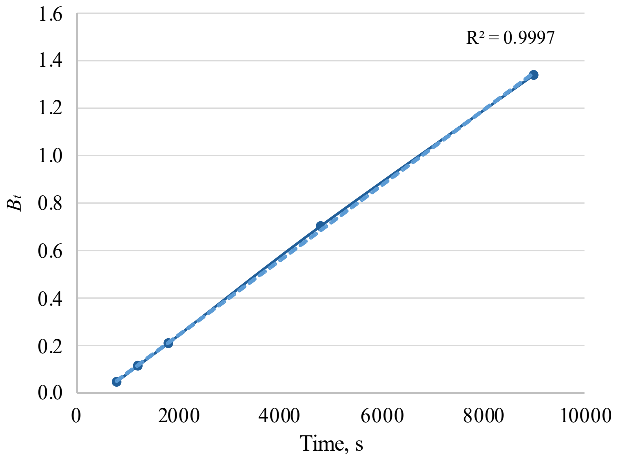

Figure 8. Time dependence of the Boyd-Adams model criterion for Sc sorption from raffinate onto the cation exchange resin (H_2SO_4 = 15 g/dm^3, L:S = 500, C_{Sc} = 0.3 mg/l)

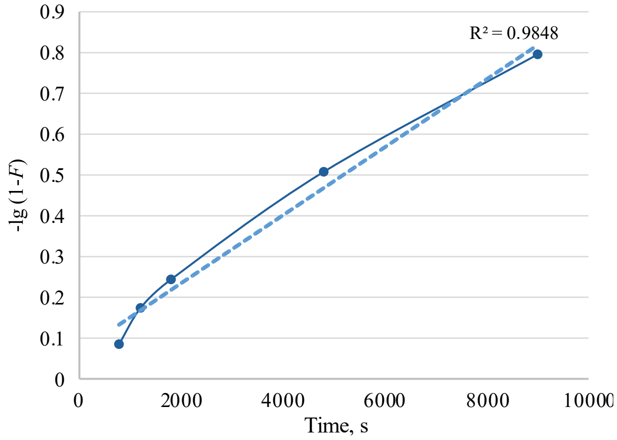

Figure 9. Dependence of −log(1−F) on phase contact time during Sc^{3+} sorption from raffinate onto the cation exchange resin (L:S = 500, C_{Sc} = 0.3 mg/l)

An analysis of the ion exchange resin's adequate particle size was carried out to calculate the diffusion coefficient per GOST 10900-84. According to the standard, the proper particle size corresponds to the sieve aperture through which no more than 10% of the material passes. For the resin under study, this value was determined to be 0.5 mm (0.05 cm), which was used as the average particle radius for subsequent calculations.

Based on the experimentally derived dependence $B_t = f(t)$, the kinetic parameter was calculated as $B = 15.7 \cdot 10^{-5}$, from which the gel-phase diffusion coefficient was determined to be $D_G = 3.98 \cdot 10^{-8}$ cm^2/s. These values characterize the rate of ion transport within the resin particle and are critical for modeling and scaling up ion exchange processes.

To estimate the characteristic time of the process, the equation for half-exchange time under gel-phase diffusion control was used [45], [46]:

$$\tau_{1/2} = \frac{0.03 \cdot r_0^2}{D_G}, \tag{6}$$

where:

r_0 – average radius of the resin particle;

D_G – effective intraparticle diffusion coefficient.

The calculated half-exchange time $\tau_{1/2}$ for scandium sorption on the investigated phosphorus-containing cation exchange resin was 1884 seconds. This value represents the time required to reach half of the equilibrium sorption capacity. It can select geometric and process parameters for ion exchange equipment, including particle size, contact time, and solution flow rate.

Additional kinetic models, namely, the pseudo-first-order and pseudo-second-order models, were applied to describe sorption kinetics more accurately and identify rate-limiting steps. These models help to determine the sorption mechanism and to assess the influence of factors such as ion concentration, temperature, and solution composition on the rate and extent of the sorption process. One of the earliest models used to describe sorption kinetics is the pseudo-first-order model proposed by Lagergren. The sorption rate in this model is described by a logarithmic equation [45]:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t, \tag{7}$$

where:

Q_t – sorption capacity at time t, mg/cm^3;

Q_e – equilibrium sorption capacity, mg/cm^3;

k_1 – pseudo-first-order rate constant 1/s.

The applicability of the Lagergren model is assessed based on several criteria. Most importantly, a high degree of agreement with experimental data (with a coefficient of determination R^2 close to 1) and the linearity of the plot passing through the origin are considered essential [47]. If either of these conditions is not met, it suggests that the sorption process is governed not by a single mechanism but by a combination of factors. On heterogeneous surfaces, overlapping effects of diffusive mass transfer and the ion exchange chemical reaction are commonly observed, making them difficult to distinguish experimentally.

The sorption kinetics were also analyzed using the pseudo-second-order model, which is widely used to describe ion exchange processes involving chemical interaction between solute ions and the active sites of the sorbent. The linear form of the Ho and McKay equation is expressed as follows [45]:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t = \frac{1}{h} + \frac{1}{Q_e} t, \tag{8}$$

where:

k_2 – pseudo-second-order rate constant, cm^3/(mg·s);

$h = k_2 Q_e^2$ – initial sorption rate, mg/(cm^3·s).

From a physical standpoint, the model assumes that the rate-limiting step is a chemical interaction between the solute ion and a functional group of the sorbent in a 1:1 molar ratio. If the plot of t/Q_t versus t is linear, the process follows the pseudo-second-order kinetic model.

The plot $t/Q_t = f(t)$, shown in Figure 10, demonstrates a high degree of linearity ($R^2 = 0.9992$), confirming the model's applicability. From the slope and intercept of the linear plot, the values of Q_e and k_2 can be determined, which are then used to calculate the initial sorption rate h. A comparison of the experimental data fitting using both models shows that the Ho and McKay model provides a better fit and can be reliably used to describe the sorption kinetics in the studied system.

Processing the kinetic data using the linearized forms of the pseudo-first-order and pseudo-second-order models enabled the determination of the ion exchange rate constants for scandium sorption onto the phosphorus-containing cation exchange resin Purolite MTS 9580. A comparative analysis of the calculated parameters is presented in Figure 11.

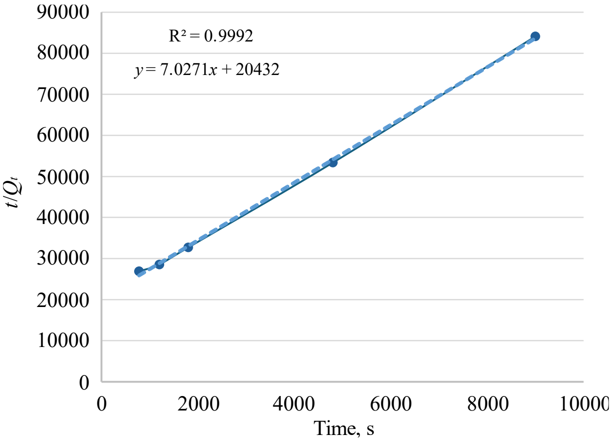

Figure 10. Dependence of $t/Qt = f(t)$ during scandium sorption onto the cation exchange resin

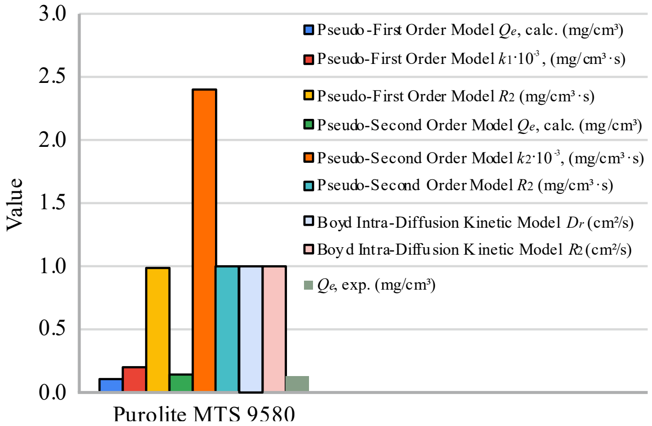

Figure 11. Kinetic characteristics of scandium sorption on the cation exchange resin based on different kinetic models

The results confirm that the dominant factor in the sorption process is internal (gel-phase) diffusion. The high coefficient of determination ($R^2 > 0.99$) obtained for the Boyd model supports the conclusion that diffusion is the prevailing mechanism governing scandium ion transport to the active sites. At the same time, the pseudo-second-order model proved to be the most adequate for describing the kinetics of the process. This is supported by the high correlation coefficient ($R^2 = 0.999$) and the close agreement between the calculated equilibrium capacity Q_e and the experimentally measured value.

These findings indicate that the rate-limiting step is chemical and that intermolecular interactions within the sorbent phase may be significant. Thus, using the Ho and McKay model is justified for describing scandium sorption under the investigated conditions, and the derived parameters can be applied to predict system behavior during process scale-up.

4. Conclusions

The experimental results confirmed the high efficiency of phosphorus-containing ion exchange resins for scandium recovery from raffinate solutions generated during the in-situ leaching of uranium ores. Increasing the solution acidity to 15 g/dm^3 H_2SO_4 significantly enhances the sorption capacity of the resin for scandium, thereby improving both the selectivity and purity of the recovered component. At the same time, the sorption of accompanying rare earth elements and other impurities is reduced, further reinforcing the process selectivity.

Kinetic analysis revealed that the rate-limiting step of scandium sorption is internal (gel-phase) diffusion. The application of pseudo-first-order and pseudo-second-order kinetic models demonstrated a high degree of agreement with experimental data ($R^2 > 0.99$), confirming their suitability for describing the sorption mechanism. The calculated parameters, including rate constants and diffusion coefficients, can be employed in designing and optimizing ion exchange systems.

The findings of this study highlight the practical potential for scandium, a by-product of uranium processing, to be integrated into industrial applications, contributing to improved economic performance and environmental sustainability of hydrometallurgical operations. The optimal sulfuric acid concentration for achieving maximum scandium recovery efficiency is 15 g/dm^3. The data obtained provides a foundation for process scale-up and the implementation of efficient solution purification strategies in existing industrial facilities.

Author contributions

Conceptualization: ZK, UY; Data curation: UY, MM; Formal analysis: ZK, MM; Funding acquisition: ZK, BT; Investigation: ZK, UY; Methodology: MM, UY; Project administration: ZK; Resources: BT, UY; Software: UY; Supervision: ZK; Validation: ZK, UY; Visualization: BT; Writing – original draft: ZK, BT, UY; Writing – review & editing: ZK, MM. All authors have read and agreed to the published version of the manuscript.

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Conflicts of interest

The authors declare no conflict of interest.

Data availability statement

The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

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Дослідження сорбції скандію на фосфоровмісному катіонітів з розчинів, одержуваних при вилученні урану

Ж. Кенжетаєв, Б. Токсанбаєв, У. Єссімканова, М. Матаєв

Мета. Розробка ефективного методу вилучення скандію з маткових розчинів, що утворюються при переробці уранових руд методом підземного свердловинного вилуговування, із використанням фосфоровмісного катіоніту та визначення оптимальних умов сорбції.

Методика. У роботі використано методи статичної та динамічної сорбції, а також кінетичне моделювання процесів іонного обміну. Аналіз вмісту елементів проводився із застосуванням ІСП-МС спектрометрії та мікрохвильової мінералізації зразків. Розраховано коефіцієнти гелевої дифузії, параметри моделей псевдопершого та псевдодругого порядків, а також час напівобміну. Ефективність процесу оцінювалася при варіюванні кислотності розчину (H_2SO_4 = 5-15 г/дм^3).

Результати. Використання фосфоровмісних іонітів з високими комплексоутворюючими властивостями для вилучення рідкісноземельних елементів продемонструвало значний потенціал. Експерименти, що проводилися при зміні вихідного розчину pH, показали вплив кислотності на процес сорбції. Встановлено, що підвищення кислотності розчину до 15 г/дм^3 забезпечує максимальну ємність сорбенту скандію (0.384 мг/г) при одночасному зниженні сорбції домішок. Процес сорбції описується моделлю псевдодругого порядку з високим коефіцієнтом детермінації (R^2 = 0.999). Обмежувальною стадією є гелева дифузія. Розрахунковий час напівобміну склав 1884 секунди.

Наукова новизна. Вперше проведено комплексне кінетичне та фазово-хімічне дослідження сорбції скандію з уранових розчинів на фосфоровмісному катіоніті, підтверджено застосування моделі Хо та Маккею, а також розраховано ключові параметри обміну.

Практична значимість. Результати дослідження можуть бути використані для проєктування та оптимізації схем вилучення скандію та інших рідкісноземельних елементів з розчинів, що утворюються при переробці уранових руд, з метою їх подальшого використання в різних галузях промисловості.

Ключові слова: *скандій, сорбція, катіоніт, іонний обмін, кінетика, гелева дифузія, уранові розчини*

Publisher's note