



DOI: 10.31643/2024/6445.44

Metallurgy



## Overview of Technologies Used to Extract Scandium from Secondary Raw Materials

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<p>Received: December 10, 2023 Peer-reviewed: December 19, 2023 Accepted: January 17, 2024</p>	<p><b>ABSTRACT</b> The exceptional mechanical and chemical properties exhibited by scandium, characterized by its low density, high strength, and remarkable resistance to corrosion, have positioned it as a sought-after metal in diverse industrial applications. Consequently, a surge in market demand for scandium has been observed, highlighting its unique attributes compared to other metals. The Republic of Kazakhstan has identified potential sources of scandium in the waste generated by the titanium, uranium, and aluminum industries. By implementing efficient processing techniques for these production wastes, the country can effectively address the deficit of scandium while also mitigating man-made emissions, thus significantly improving the environmental landscape. This article aims to explore and evaluate contemporary methodologies that have been employed for the recovery of scandium from the aforementioned secondary sources. By examining and analyzing these techniques, we can gain insights into the most effective and sustainable approaches to harnessing scandium from waste materials in Kazakhstan. This research not only contributes to meeting market demands but also ensures the responsible utilization of scandium, benefiting not just the country's economy but also its environmental sustainability.</p>
	<p><b>Keywords:</b> titanium wastes, rare metals, scandium, rare earth elements, leaching, chlorination</p>
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### Introduction

The global market demand for rare and rare earth metals (REM) in the development and production of mineral resources is growing each year, driven by scientific and technological advancements [[1], [2], [3]]. Scandium, a rare and expensive metal, is primarily found dispersed in nature, although it also exists in its mineral called tortveitite. The extraction and purification of scandium involve multiple processes, which significantly contribute to its high price. In 2016, for example, scandium oxide cost reached \$4,200 per kilogram [[4], [5], [6]]. Scandium possesses unique properties such as low density, high strength, and excellent corrosion resistance, making it crucial for various industries including aviation, electronics, and energy. However, the natural sources of

scandium are limited, leading to increased research on its extraction [[7], [8]].

Although scandium is more prevalent in the Earth's crust compared to precious metals like gold and silver, it is a scattered element that does not form distinct deposits. Instead, scandium is widely distributed as a minor impurity in ores and minerals containing zircon, wolframite, beryl, cassiterite, uranium, and titanium [9]. Scandium is extracted from these ores as well as from waste generated during mineral production. In recycled mineral raw materials, scandium can constitute a fraction of around a dozen percent or more. Therefore, scandium concentrate is initially obtained from secondary raw materials, enabling the production of pure scandium through subsequent processing. Possible sources of secondary raw materials include slag, sludge, chlorine melts, and reverse solutions from underground leaching. The

processes for separating scandium from solutes are complex and may involve deposition, extraction, and ion exchange methods [[10], [11]].

The primary objective of this study is to provide an overview of industrial waste categories and the technological interventions employed in the extraction of scandium.

### Extraction from uranium raw materials

Scandium is primarily sourced from uranium ores, which typically contain concentrations of 0.001-0.0001% of this element. Higher concentrations of scandium can be found in specific minerals such as davidite (0.02%), xenotime (0.08-0.1%), and obrucheveite (0.08-0.2%) [12]. The annual production of scandium oxide ( $\text{Sc}_2\text{O}_3$ ) from uranium ores ranges from 50 to 500 tonnes, and the worldwide reserves of such ores are estimated to be around 600 million tonnes. When uranium ores are leached with sulphuric acid, scandium is transferred into the solution.

A technology scheme for the simultaneous extraction of scandium during the processing of uranium has been outlined in references [[12], [13]] (Figure 1). The process begins with leaching uranium ore using sulphuric acid, resulting in a solution containing up to 1 mg/l  $\text{Sc}_2\text{O}_3$ . Dodecylphosphoric acid (0.1 M) is used to fully extract uranium from this solution. Notably, scandium, thorium, and titanium are commonly co-extracted but remain in the organic phase after uranium re-extraction through a 10 M HCl solution.

Hydrofluoric acid treatment is employed to extract scandium and thorium from the organic solution. As a result, scandium and thorium form solid deposits (10%  $\text{Sc}_2\text{O}_3$  and 20%  $\text{ThO}_2$ ). The resulting precipitate is dissolved in a 15% sodium hydroxide solution at 75-90 °C for 4 hours, leading to the formation of scandium oxide. After filtration, the scandium hydroxide is dissolved in hydrochloric acid, and impurities such as titanium, zirconium, iron, and silicon are removed through hydrolysis. Subsequently, an oxalate purification method is applied.

Uranium is sorbed by anionites from these solutions while scandium remains in the solution. According to reference [14], the sorption of scandium can be achieved using ion exchange resins containing phosphorus, such as Lewatit TR 260. Laboratory experiments using authentic solutions have successfully achieved an overall dynamic capacity of scandium of 0.049 kg/m<sup>3</sup>. Desorption of scandium from a fully saturated sorbent, using eight specific volumes of  $\text{Na}_2\text{CO}_3$  solution (200 g/L), resulted in an 80% desorption efficiency. The desorbed substances were then subjected to the next stage of scandium absorption using the highly alkaline anion exchange resin Amberlite 920. From this resin, scandium is desorbed using a nitric acid solution containing ammonium nitrate. Additionally, an additional phase involves the precipitation of scandium oxalate from the desorbate of the second phase, followed by calcination to obtain  $\text{Sc}_2\text{O}_3$ .

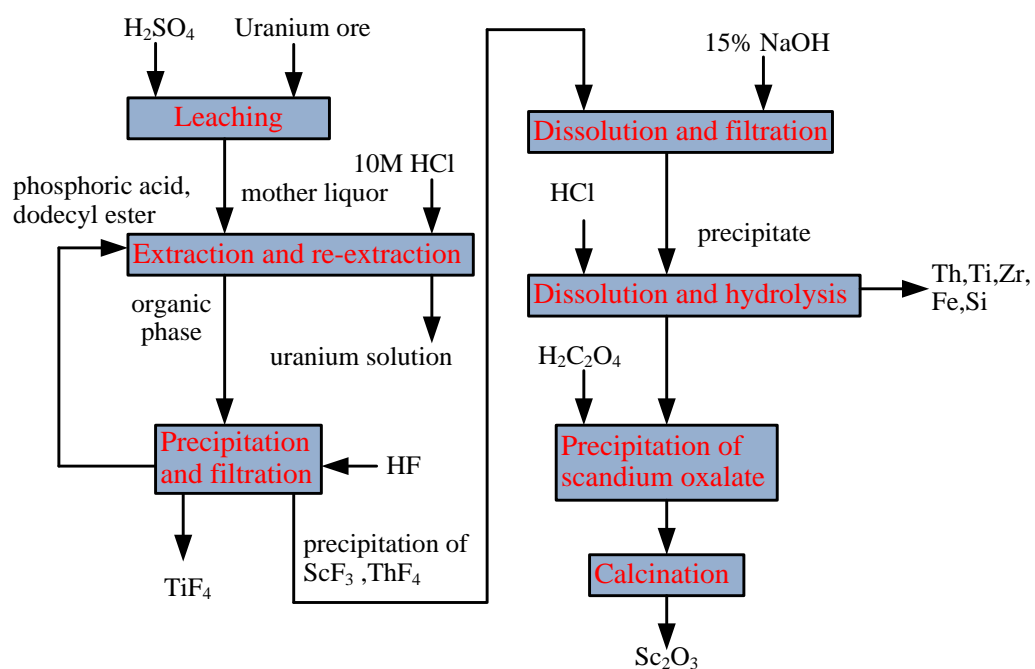


Figure 1 - Technological flow sheet of associated scandium extraction in uranium processing

In article [15], the authors examined the sorption capacities of Lewatit TP260 and Purolite MTS9580 sorbents. The results indicated that MTS9580 resin had an advantage over TP260, with an exchange capacity of 200 mg Sc/dm<sup>3</sup> compared to 59.7 mg Sc/dm<sup>3</sup> for TP260. It is important to note that Purolite MTS9580 has a significantly reduced dynamic exchange capacity for undesirable impurities such as Al, Fe, Ca, and others.

**Extraction of scandium from red mud.** A waste by-product of the Bayer bauxite treatment process presents a challenging technological task. Red mud production is significant, with approximately 1.1-1.2 tonnes generated for every tonne of bauxite alumina. Currently, red muds are typically deposited in designated lagoons due to limited disposal options. However, this practice poses environmental challenges and occupies large areas of land [[14], [15], [16]]. The global accumulation of red mud resulting from alumina production has reached around 1.5 billion tonnes, with this quantity increasing annually [[17], [18], [19]]. Despite current storage methods, environmental contamination from toxic substances contained in red mud remains a persistent issue. The extraction and recycling of metals from this waste can help mitigate these concerns.

Scandium, an essential component found in red mud, requires complex technological processes for retrieval. With the rapidly growing global consumption of scandium, there is a need to develop techniques to extract it in various chemical forms, such as oxide or fluoride.

A study conducted in [20] investigated the extraction of scandium from red mud obtained in Greece (see Figure 2). The red muds underwent sintering using sodium carbonates or sodium borates at 1100 °C for 20 minutes, followed by leaching with a 1.5 M HCl solution. The resulting solution was then subjected to ion exchange using Dowex 50W-X8 sulphocationite resin, enabling scandium and a significant portion of impurities to be extracted. The impurities were eluted with a 1.75 M HCl solution, and scandium was quantitatively desorbed using a 6 M HCl solution. The solution was subsequently neutralized with ammonia and passed through a liquid-liquid extraction step using a 0.05 M solution of D2EHPA in hexane. Scandium re-extraction was achieved using a 2 M NaOH solution. However, this recovery method is not cost-effective due to its lack of selectivity, requiring additional purification operations, and resulting in significant costs. To address this issue, the authors of [[21], [22]] have developed methods allowing for more selective leaching of scandium from red mud. The leaching of lanthanides, scandium, and yttrium from red mud was investigated using sulphuric, nitric, and hydrochloric acid solutions. Dilute HNO<sub>3</sub> (approximately 0.5 M) at room temperature provided the best results, with recoveries of 80% for scandium, 96% for yttrium, and 70% for ytterbium. Importantly, only 3% of iron was introduced into the solution.

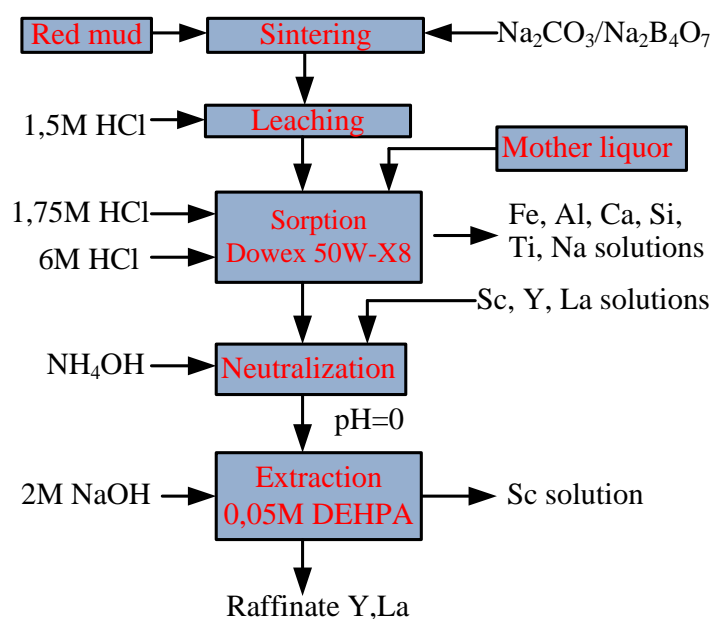


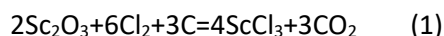
Figure 2 - Technological flow sheet of scandium extraction from red mud

Furthermore, in [23], the alkaline method for scandium extraction from red sludge is described. The process involves treating red sludge with a  $\text{Na}_2\text{CO}_3$  solution, followed by hydrolytic precipitation of Sc(III) using a carrier (aluminium or zinc oxide solution in sodium hydroxide). The resulting precipitate is then treated with concentrated sodium hydroxide solution, transferred to the hydrochloric acid solution, and the filtrate is treated with an excess of stoichiometric proportions of ammonia or hydrofluoric acid solution. Experimental results indicate that this technique allows for the production of a scandium concentrate containing 10-30%  $\text{Sc}_2\text{O}_3$  in oxide form and 30-50%  $\text{ScF}_3$  in fluoride form.

When scandium is precipitated from an acidic solution using an ammonia solution, the recovery rate of scandium in the precipitate reaches 94-100%. Alternatively, when precipitation is done with hydrofluoric acid, the recovery rate ranges from 92-100%. However, it is important to acknowledge that this method involves multiple precipitation and filtration steps, which results in low productivity and complexity in terms of automation.

#### Extraction of Scandium from titanium production waste

Titanium concentrate is typically processed using two primary methods: sulfuric acid, which produces titanium oxide, and chlorination, which produces titanium tetrachloride. During the chlorination of titanium slag, a significant portion of scandium accumulates in the remaining melt of titanium chlorate. Scandium oxide undergoes chlorination through the reaction (1).



Scandium chloride is well soluble in water and hydrochloric acid solvents. Figure 3 shows the technology of the recovery of scandium. The bulk melt containing 0.01-0.03% scandium is alkalized in a weak solution of hydrochloric acid (20-40 g/l HCl). Scandium, located in the bulk melt in the form of chloride, is filtered and sent for extraction, adjusted for the content of ferric chloride. Scandium extraction is carried out with a 70% solution of tributyl phosphate in kerosene; the resulting scandium-enriched organic phase is washed from impurities with strong hydrochloric acid (220-240 g/l HCl); then the scandium extract is transferred to the aqueous phase (reextract) with a 7% hydrochloric acid solution. From the reextraction of oxalic acid, oxalates of scandium

and other metals are precipitated, the resulting pulp is filtered, a solid precipitate of oxalates is dried and heated at 700°C and a technical oxide containing 40-60%  $\text{Sc}_2\text{O}_3$  is obtained [[24], [25]].

The extraction of scandium from ilmenite slags obtained after smelting ilmenite concentrates is described in the referenced work (Figure 4). The proposed method involves grinding the slag and sintering it with  $\text{Na}_2\text{CO}_3$  at temperatures between 900-1000°C. The sintered material is then leached with a 30% HCl solution, maintaining a S:L ratio of 1:2 and a temperature of 80°C. Using an extraction solution of 30% D2EHPA in kerosene, 94% of scandium is extracted from the solution at a W:O ratio of 20:1. Iron is removed by washing the extracted solution with a 5M HCl solution, and scandium is further re-extracted with a 2M NaOH solution. The  $\text{Sc}(\text{OH})_3$  precipitate is dissolved in an HCl solution, and scandium oxalate is obtained through precipitation. The total recovery of scandium achieved is 90%.

Figure 4 provides an example of a process for obtaining scandium from the residual chlorination melt of titanium slag, as documented in previous research [20]. The process is based on the extraction of scandium as TBF from chloride solutions obtained through leaching with a 6M hydrochloric acid solution. The solution is then purified from radium by precipitating it together with newly formed barium sulfate. Scandium is subsequently extracted as a hydroxide by precipitating it with an  $\text{NH}_4\text{OH}$  solution after re-extraction with a 0.1M hydrochloric acid solution. Finally, the precipitate is heated to obtain  $\text{Sc}_2\text{O}_3$ .

The work [26] describes a method for processing a melt of titanium chlorators by obtaining  $\text{Sc}_2\text{O}_3$  and concentrating it in the aqueous phase of yttrium and manganese. The solution is based on the results of research on the extraction of Scandium, Yttrium, aluminum, iron(III), Titanium and manganese with a new nitrogen extractant N(2-hydroxy-5-nonylbenzyl)- $\beta$ ,  $\beta$ -dihydroxyethylamine (NBEA-1) in an organic thinner.

The method of separation of scandium and titanium is based on the use of an organic solution of NBEA for extraction [27]. For this process, a chloride solution containing titanium and scandium is used, to which hydrogen peroxide is added in a certain ratio with a titanium concentration from 0.8 to 10. Then the solution is neutralized, after which extraction is performed using a solution of NBEA in octanol with a concentration of 0.25 mol/l for 30 minutes at a pH of 2.25 to 3.45. This method allows to increase the metal separation coefficient from 450 to 26440.

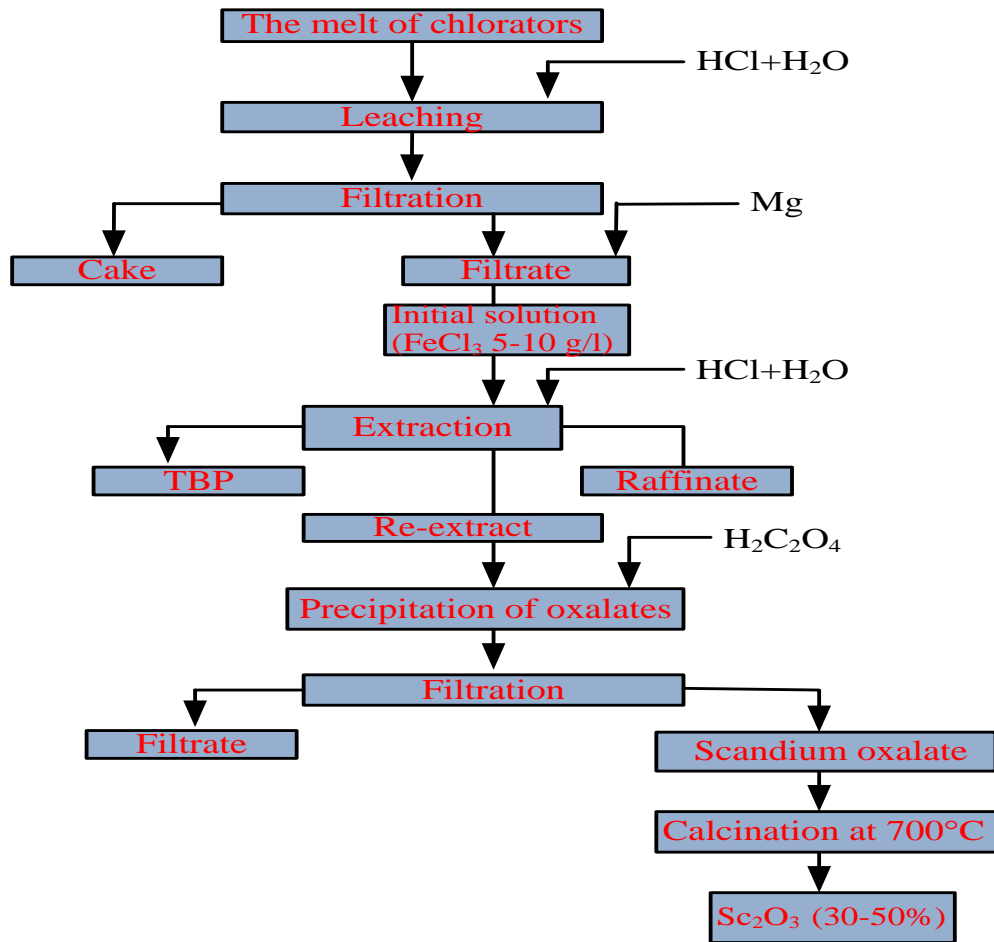


Figure 3 - Technological flow sheet for recovery scandium oxide from the spent melt of titanium chlorators

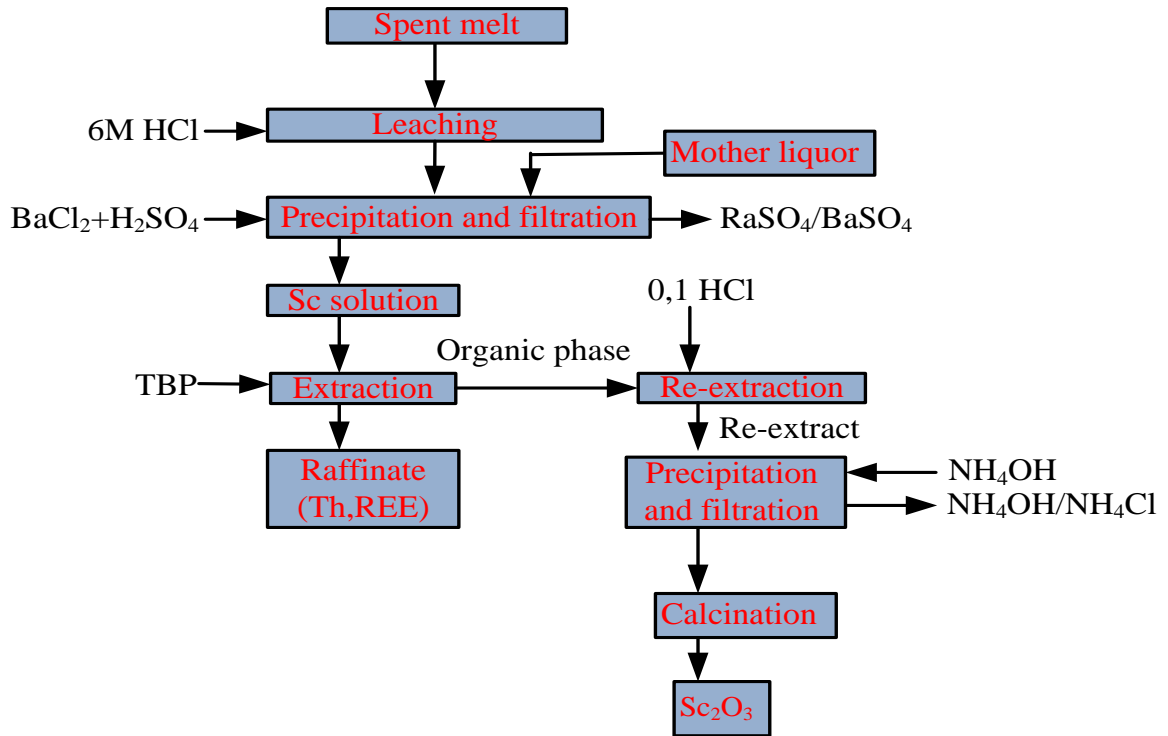


Figure 4 -Technological flow sheet for recovery scandium oxide from the spent melt of titanium chlorators

## Conclusion

In conclusion, the development of extraction technologies for scandium from secondary raw material sources is an important area of research, as it allows for improved resource efficiency and the recovery of valuable metals from waste materials. Effective methods for extracting scandium from feedstocks, with high recovery rates ranging from 85-90%, often involve sorption or extraction steps utilizing phosphorus-containing substances. These steps can be applied during the primary concentration of scandium as well as in subsequent

processing to remove unwanted impurities. Sorbents such as Lewatit TP260 and Purolite MTS9580 have shown promising selectivity towards scandium, and Dowex 50W-X8 has demonstrated high recovery not only of scandium but also other impurities. Further research will focus on the sorption capacities of Lewatit TP260 and Purolite MTS9580 in titanium waste solutions following aqueous leaching.

**Conflict of interest.** The corresponding author declares that there is no conflict of interest.

**Cite this article as:** Orynbayev BM, Baigenzhenov OS, Turan MD. Overview of Technologies Used to Extract Scandium from Secondary Raw Materials. *Kompleksnoe Ispolzovanie Mineralnogo Syra = Complex Use of Mineral Resources*. 2024; 331(4):109-116. <https://doi.org/10.31643/2024/6445.44>

## Скандийді қайталама шикізаттан алу үшін қолданылатын технологияларға шолу

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<p>Мақала келді: 10 желтоқсан 2023 Сараптамадан өтті: 19 желтоқсан 2023 Қабылданды: 17 қаңтар 2024</p>	<p><b>ТҮЙІНДЕМЕ</b> Скандийдің тығыздығы төмен, беріктігі жоғары және коррозияға төзімділігімен ерекшеленетін ерекше механикалық және химиялық қасиеттері оны әртүрлі өнеркәсіптік салаларда сұранысқа ие металға айналдырды. Осыған байланысты скандийге нарықтық сұраныстың күрт өсуі байқалады, бұл оның басқа металдармен салыстырғанда қасиеттерінің ерекше екендігін көрсетеді. Қазақстан Республикасында титан, уран және алюминий өнеркәсібінің қалдықтарындағы скандийдің әлеуетті көздері анықталды. Осы өндіріс қалдықтарын өңдеудің тиімді технологияларын енгізу арқылы біздің ел скандий тапшылығы мәселесін тиімді шеше алады және сонымен бірге техногендік қалдықтарды азайтады, осылайша экологиялық жағдайды айтарлықтай жақсартады. Бұл мақаланың мақсаты – жоғарыда аталған қайталама шикізат көздерінен скандийді алу үшін қолданылатын заманауи әдістерді зерттеу және бағалау. Осы әдістерді зерделеп, талдай отырып, біз скандийді Қазақстандағы қалдықтардан алудың неғұрлым тиімді және орнықты тәсілдері туралы түсінік ала аламыз. Бұл зерттеу нарықтың қажеттіліктерін қанағаттандыруға ықпал етіп қана қоймайды, сонымен қатар скандийді жауапкершілікпен пайдалануды қамтамасыз етеді. Бұл елдің экономикасына ғана емес, оның экологиялық тұрақтылығына да пайда әкеледі.</p>
	<p><b>Түйін сөздер:</b> титан қалдықтары, сирек металдар, скандий, сирек жер элементтері, шаймалау, хлорлау</p>
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## Обзор технологий, использовавшихся для извлечения скандия из вторичного сырья

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<p>Поступила: 10 декабря 2023 Рецензирование: 19 декабря 2023 Принята в печать: 17 января 2024</p>	<p><b>АННОТАЦИЯ</b></p> <p>Исключительные механические и химические свойства скандия, характеризующиеся низкой плотностью, высокой прочностью и удивительной устойчивостью к коррозии, сделали его востребованным металлом в различных промышленных областях. В связи с этим наблюдается резкий рост рыночного спроса на скандий, что подчеркивает его уникальные свойства по сравнению с другими металлами. Республика Казахстан выявила потенциальные источники скандия в отходах титановой, урановой и алюминиевой промышленности. Внедрив эффективные технологии переработки этих отходов производства, страна сможет эффективно решить проблему дефицита скандия и одновременно снизить техногенные выбросы, тем самым значительно улучшив экологическую обстановку. Цель данной статьи - изучить и оценить современные методики, применяемые для извлечения скандия из вышеупомянутых вторичных источников. Изучив и проанализировав эти методы, мы сможем получить представление о наиболее эффективных и устойчивых подходах к извлечению скандия из отходов в Казахстане. Данное исследование не только способствует удовлетворению потребностей рынка, но и обеспечивает ответственное использование скандия, принося пользу не только экономике страны, но и ее экологической устойчивости.</p>
	<p><b>Ключевые слова:</b> титановые отходы, редкие металлы, скандий, редкоземельные элементы, выщелачивание, хлорирование</p>
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