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Metallurgy

Innovative approaches to the processing of vanadium- and molybdenum-containing technogenic waste

[1]Yulusov S.B., [1]Sarsembayeva M.R., Khabiyev A.T.[1], [2]Retnawati H., [1*]Merkibayev Y.S., [1]Akbarov M.S., [1]Baltabay T.Y.

[1]Satbayev University, Almaty, Kazakhstan
[2]Yogyakarta State University, Indonesia

** Corresponding author email: y.merkibayev@satbayev.university*

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ABSTRACT
This article explores the consumption trends of vanadium and molybdenum across various industrial sectors, highlighting their strategic importance and the growing demand for a sustainable supply of raw materials. It analyses the sources of these elements of both natural and technogenic origin, including metallurgical slags, ashes, spent catalysts, and other industrial waste products. Particular attention is given to the environmental risks associated with the accumulation of vanadium and molybdenum compounds, which can have toxic effects on the environment. The study emphasises the need to incorporate secondary resources into industrial circulation to ensure the rational use of the mineral resource base and improve the efficiency of metal extraction from primary raw materials. A review is provided of existing chemical and hydrometallurgical methods for extracting vanadium and molybdenum, taking into account the composition of the processed material, technological conditions, and the limitations of specific approaches. The article underscores the potential of integrated waste processing, which enables the recovery of multiple valuable components and supports the transition to a circular economy.

Keywords: vanadium, molybdenum, ash and slag wastes, metallurgical slags, filtrate, hydrometallurgical methods, pyrometallurgical methods, bacterial leaching.

Information about authors:

Yulusov Sultan Baltabayevich	*Associate Professor of the Department of Metallurgy and Mineral Processing, O.A. Baikonurov Mining and Metallurgical Institute, Satbayev University, Almaty, Kazakhstan. Email: s.yulussov@satbayev.university; ORCID ID: https://0000-0001-8044-4186*
Sarsembayeva Marzhan Rahatovna	*PhD student of the Department of Metallurgy and Mineral Processing, O.A. Baikonurov Mining and Metallurgical Institute, Satbayev University, Almaty, Kazakhstan. Email: m.sarsembayeva@satbayev.university; ORCID ID: https://orcid.org/0009-0007-2315-3009*
Khabiyev Alibek Talgatbekuly	*Doctor Ph.D., Assoc. Professor, U. Joldasbekov Institute of Mechanics and Engineering, Almaty, Kazakhstan. E-mail: alibek1324@mail.ru; ORCID ID: https://orcid.org/0000-0001-9397-2367*
Heri Retnawati	*Professor, Yogyakarta State University, Indonesia. Email: heri_retnawati@uny.ac.id; ORCID ID: https://orcid.org/0000-0002-1792-5873*
Merkibayev Yerik Serikovich	*Ph.D., senior Lecturer of the Satbayev University, O.A. Baikonurov Mining and Metallurgical Institute, Almaty, Kazakhstan. Email: y.merkibayev@satbayev.university; ORCID ID: https://orcid.org/0000-0003-3869-6835*
Abarov Merey Sabituly	*Master of Engineering Sciences, Engineer of the Department of Metallurgy and Mineral Processing, O.A. Baikonurov Mining and Metallurgical Institute, Satbayev University, Almaty, Kazakhstan. E-mail: m.akbarov@satbayev.university; ORCID ID: https//orsid.org/0000-0002-4272-8038*
Baltabay Tamerlan	*4th year student of the Department of Metallurgy and Mineral Processing, O.A. Baikonurov Mining and Metallurgical Institute, Satbayev University, Almaty, Kazakhstan. Email: t.baltabay@satbayev.university*

Introduction

In the context of global growth in industrial production and raw material consumption, the issue of natural resource depletion is becoming increasingly pressing. The world's reserves of many strategically important metals, including vanadium and molybdenum, are limited. At the same time, vast amounts of technogenic waste are generated annually, containing residual quantities of valuable elements that remain unutilised and are disposed of in landfills, thereby adding to the environmental burden.

According to geological survey estimates, easily accessible reserves of vanadium and molybdenum are diminishing, and the concentrations of these elements in primary ores are decreasing. As a result, the costs of extraction and processing are rising, and the economic efficiency of traditional technologies is declining. This situation is driving the shift toward a circular economy, in which waste is viewed not as a burden but as a potential resource [1].

The integrated processing of secondary resources, such as metallurgical slags, fly ash, spent catalysts, and technological sludges, not only enables the recovery of strategically important metals into the production cycle but also reduces the volume of industrial waste. This approach addresses two key challenges simultaneously: ensuring resource security and mitigating environmental risks.

Vanadium and molybdenum are among the strategically important metals widely used across various industrial sectors. Their unique properties make them indispensable in metallurgy, the chemical and energy industries, as well as in high-tech sectors of the economy.

In recent years, global vanadium consumption has been steadily increasing due to the growing worldwide production of structural, stainless, and speciality steels. Beyond the metallurgical and chemical industries, vanadium and its compounds are also extensively used in nuclear and hydrogen energy applications and in the production of vanadium redox flow batteries.

The primary application of vanadium lies in the production of alloyed steels. The addition of vanadium significantly enhances the strength, wear resistance, and thermal stability of steel. Due to these properties, vanadium-containing alloys are widely used in construction, mechanical engineering, pipeline manufacturing, and the production of railway rails. Vanadium is also utilised in the production of armoured steels for the defence industry [[2], [3]].

In addition, vanadium pentoxide (V_2O_5) is used as a catalyst in the production of sulphuric acid and in various oxidation processes in the chemical industry. In recent years, increasing attention has been paid to the use of vanadium in the energy sector—particularly in vanadium redox flow batteries (VRFB), which are regarded as promising energy storage systems for renewable energy sources [4].

Molybdenum is primarily used as an alloying element in materials designed to operate under high temperatures and aggressive environments. It enhances strength, heat resistance, corrosion resistance, and wear resistance. Molybdenum-containing alloys are widely applied in the aerospace industry, power generation, the oil and gas sector, and nuclear energy.

A significant portion of molybdenum is used in the form of sulphides as catalysts in hydrotreating and hydrocracking processes in the petrochemical industry. Additionally, molybdenum compounds are utilised in the production of pigments, specialised lubricants, semiconductors, and glass enamels.

The limited availability of natural sources of vanadium and molybdenum, the high costs associated with their extraction, and geopolitical risks related to supply chains underscore the strategic importance of these metals. Both elements are included in the list of critical raw materials in several countries, including the European Union, the United States, and China.

Modern metallurgy and energy production generate substantial volumes of technogenic waste, which, despite the completion of the main production cycle, still contain residual amounts of valuable components, including vanadium and molybdenum. These waste materials are considered secondary resources that can be processed to obtain marketable products.

The most promising types of secondary raw materials for the extraction of vanadium and molybdenum include:

Fly ash and ash-slag waste: These are formed during the combustion of coal, fuel oil, and oil sludge at thermal power plants (TPPs). Such waste often contains vanadium in the form of oxides or complex compounds, particularly when the burnt fuel had a high content of vanadium and sulphur. In the ash from fuel oil combustion, vanadium concentrations can reach 5–10% [[5], [6], [7]].

Metallurgical slags: By-products of pig iron, steel, and alloy production. In converter slags and ferrovanadium slags, vanadium is typically present in the form of oxides or ferrites, with concentrations ranging from 1% to 15%. Some slags also contain molybdenum, especially when molybdenum-bearing ores have been processed.

Spent catalysts: Catalysts used in the oil refining and chemical industries often contain molybdenum and vanadium in the form of sulphides and oxides. After their operational lifespan ends, these materials become waste suitable for secondary processing. The molybdenum content in such catalysts can reach 10–20%, while vanadium content may be up to 5% [[8], [9]].

Sludges, filtrates, and dust residues: These are generated during filtration, wet gas scrubbing, and ore beneficiation processes. These materials often have a fine-grained structure, which facilitates subsequent metal recovery when properly pretreated.

Secondary resources represent a significant source of vanadium and molybdenum, with concentrations in certain waste streams comparable to—or even exceeding—those found in primary ores. Efficient processing of such materials could offer a sustainable alternative to conventional mining.

Classification of Secondary Resources Containing Vanadium and Molybdenum

The use of secondary resources is no longer merely an alternative—it has become a key strategic direction in modern metallurgy. In the coming years, metallurgists face the challenge of significantly reducing the energy and material intensity of production processes [10]. A critical solution to this challenge lies in the integration of secondary resources into various metallurgical technologies. The most effective results can be achieved when waste materials are returned to the very processes in which they were generated. When this is not feasible, such waste should be efficiently repurposed for other applications under economically favourable conditions.

Thermal Power Generation and Fuel Combustion. The combustion of solid fuels (coal, fuel oil, and petroleum) produces fly ash and ash-slag residues in which metal-containing components of the original raw materials accumulate. A significant quantity of vanadium is found in the waste from thermal power plants, particularly those burning fuel oil. The V_2O_5 content in such residues averages between 15% and 20% [11]. Another important source of secondary vanadium raw materials is spent catalysts from sulphuric acid production, which contain 5–10% V_2O_5. Additionally, the mining and beneficiation of vanadium-bearing ores generate massive volumes of tailings, classified as secondary vanadium resources, with V_2O_5 content up to 1%. Molybdenum can also be present in combustion residues, particularly when coal with high levels of mineral inclusions is used.

Metallurgical Slags and Dust Residues. During steelmaking, ferroalloy production, and the processing of vanadium- or molybdenum-bearing ores, a significant portion of these elements transfers into by-products such as slags, dust, and filtration sludges. For instance, the vanadium content in converter slags can reach 10–15%, depending on the ore composition and the specific technology employed [12]. These types of waste are generated in large volumes and accumulate over time at industrial sites, making them highly attractive for secondary processing and metal recovery.

Oil Refining and Chemical Industry. The widespread use of vanadium and molybdenum is largely due to their catalytic properties. These elements are key components of industrial catalysts employed in processes such as hydrotreating, hydrocracking, and desulfurisation of crude oil and petroleum products. Once their service life ends, these catalysts become highly concentrated waste materials: the molybdenum content can reach 10–20%, and vanadium up to 5–8% [13]. This makes them a particularly valuable type of secondary raw material.

Ore Beneficiation and Processing. During the processing of molybdenum- and vanadium-bearing ores, tailings, sludges, and spent solutions are generated, often retaining a substantial portion of valuable metals. This is mainly due to incomplete recovery of these elements during flotation, leaching, and filtration processes [14]. The presence of fine particles and chemically bound forms of Mo and V complicates their extraction, but modern technologies increasingly allow for efficient recovery even from such complex waste streams.

Vanadium and molybdenum enter secondary raw material flows from a wide range of industrial sources. Their further processing and extraction not only help to address the shortage of strategic metals but also contribute to reducing the accumulation of environmentally hazardous waste [15].

Technologies for Processing Vanadium- and Molybdenum-Containing Waste

As previously mentioned, technogenic waste from vanadium production includes sludges, ash, slags, and other solid residues containing oxides of vanadium, molybdenum, iron, aluminium, and other elements. The concentration of valuable components varies depending on the production technology and the characteristics of the original raw materials. The following key approaches are used for vanadium extraction from such waste:

- Hydrometallurgical Methods: These include both alkaline and acid leaching, which allow vanadium to be converted into a soluble form. For example, leaching with alkaline solutions such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) is effective for processing slags with high vanadium content. Studies have shown that using sulphuric acid (H_2SO_4) at concentrations of 45–50 g/L, combined with pre-grinding of the material to a particle size of 0.1 mm, significantly enhances the efficiency of vanadium extraction, enabling a high degree of solubility [16].

In a study on the hydrometallurgical processing of molybdenum-bearing industrial products from the Shatyrkul-Zhaysan ore cluster, experiments were conducted on atmospheric leaching using nitric acid in both single-stage and two-stage counter-current modes to optimise molybdenum recovery and minimise acid consumption. The most effective conditions for single-stage leaching were found to be a nitric acid concentration of 300 g/L and a sulphuric acid concentration of 100 g/L at 90 °C for 2 hours, resulting in a molybdenum recovery rate of 98.8%. The two-stage leaching process further improved efficiency, achieving a recovery rate of 94.3% using solutions with lower residual acidity and redox potential. Additionally, the solvent extraction stage was optimised using the molybdenum-specific extractant CYANEX® 600 and the diluent Elixore 205, based on the initial leach solution composition. The final product was commercial-grade calcium molybdate with a molybdenum content of 46.83%. This study demonstrated a successful method for producing market-grade calcium molybdate from copper-molybdenum ores, achieving high molybdenum recovery, reducing acid consumption, and minimising harmful emissions [17].

- Pyrometallurgical Methods: These include roasting and smelting processes. For example, roasting slags with alkaline additives at temperatures of 930–950 °C can achieve vanadium recovery rates of up to 30% [8].

While such methods are effective for preliminary vanadium concentration, they are associated with high energy consumption.

- Sorption Technologies: The use of ion-exchange resins and sorbents allows for the efficient extraction of vanadium from liquid waste streams. These methods are particularly advantageous for treating low-concentration solutions or for final purification steps in hydrometallurgical processes.

The methods for extracting molybdenum from technogenic waste are largely similar to those used for vanadium. Hydrometallurgical approaches, particularly leaching followed by precipitation, are considered the most promising. Specifically, acid leaching followed by the precipitation of molybdenum in the form of ammonium molybdate has proven effective in achieving high recovery rates [18].

Bacterial Leaching (Bioleaching): Bioleaching is an environmentally friendly method for metal extraction using microorganisms—typically bacteria such as *Acidithiobacillus ferrooxidans* or *Acidithiobacillus thiooxidans*—which convert metal-containing compounds into water-soluble forms. This approach reduces the use of aggressive chemical reagents and significantly lowers energy consumption.

Bioleaching strategies applied to the treatment of spent hydrodesulfurization catalysts highlight the considerable potential of microbe-driven biocycling for metal recovery. This method offers key advantages, including low capital and operating costs, reduced energy and reagent consumption, and mild operating conditions with minimal emissions. Bacteria such as *A. ferrooxidans* and *A. thiooxidans* play a critical role in metal dissolution through various mechanisms, including direct and indirect oxidation, as well as sulphur, thiosulphate, and polysulphide oxidation pathways. Similarly, fungi such as *Aspergillus niger* and *Penicillium simplicissimum* contribute to metal recovery through processes such as acidolysis, complexolysis, redox reactions, and bioaccumulation. In addition to factors such as pulp density, pH, and particle size, the toxicity of metals to microbial cultures is identified as one of the most significant parameters affecting metal mobilisation in bioleaching systems. Therefore, the use of adapted microbial strains is critical to reducing metal toxicity, enhancing microbial growth, and improving the overall efficiency of bioleaching processes [19].

The development of a technology for the integrated processing of technogenic waste from vanadium production, with the extraction of vanadium and molybdenum, represents an important step toward more sustainable and environmentally friendly production. These technologies not only offer economic benefits but also contribute to the conservation of natural resources, making them extremely valuable in the context of today's world [[20], [21], [22], [23], [24], [25]].

Table 1 – Analysis of Main Methods for Extracting Vanadium (V) and Molybdenum (Mo) from Secondary Resources, Including Hydrometallurgical and Pyrometallurgical Techniques:

Method	Type	Applicability	Advantages	Disadvantages	Recoverable Forms of V and Mo
Alkaline Leaching	Hydrometallurgy	Power plant ash, slags, spent catalysts	High selectivity for vanadium; mild conditions	Low molybdenum recovery; requires solution purification stage	$NaVO_3$, Na_2MoO_4
Acid Leaching (H_2SO_4, HCl, HNO_3)	Hydrometallurgy	Catalysts, sludges, slags	Suitable for simultaneous extraction of V and Mo	High corrosivity, formation of toxic gases	$VOSO_4$, MoO_3, $(NH_4)_2MoO_4$
Ammonium Leaching	Hydrometallurgy	Spent catalysts, ores	High selectivity for Mo (as ammonium salts)	Low vanadium solubility; long leaching time	$(NH_4)_2MoO_4$
Roasting with Na_2CO_3 or NaOH + Leaching	Hydro- and Pyrometallurgy	Slags, ash, ores	Conversion of V and Mo into soluble forms; high efficiency	High energy consumption, dust pollution	$NaVO_3$, Na_2MoO_4
Sulphidation + Leaching	Pyrometallurgy	Concentrates, slags	Enhanced Mo recovery as sulphides	Requires high temperatures; difficulty in selective separation	MoS_2 (with further processing), V_2O_5
Oxidative Smelting	Pyrometallurgy	Alloy steel waste, slags	Oxidises V and Mo into volatile or soluble compounds	High temperatures, high energy costs	V_2O_5, MoO_3
Sorption/Ion Exchange from Solutions	Physicochemical	Post-leaching solutions	High selectivity; purification of solutions	Requires pre-treatment of solution, expensive sorbents	V(V), Mo(VI)
Solvent Extraction with Organic Reagents	Physicochemical	Post-acid leaching solutions	Separation of V and Mo; high selectivity	Multi-stage process, organic waste generation	Organic complexes of V and Mo

- **Environmental and Economic Aspects of Involving Secondary Resources in Processing**

- The reuse of waste generated during vanadium production to extract valuable components such as vanadium and molybdenum represents a promising path toward improving production profitability and minimising environmental harm. Successful processing experiences in Kazakhstan and other countries demonstrate that modern recycling methods can yield significant economic and environmental benefits. Further progress requires new research and development aimed at improving processing technologies, enhancing their environmental safety, and creating universal solutions applicable to various types of waste.

- **Environmental Significance: Reduction of industrial waste volumes.** Ash, slags, dust residues, and spent catalysts are traditionally landfilled or stockpiled, occupying space and causing long-term environmental burdens. Their processing reduces the need for disposal sites and decreases soil, air, and water pollution.

- **Prevention of toxic component leaching.** Vanadium and molybdenum in industrial waste can transform into water-soluble forms and leach into groundwater. Recovering these elements minimizes the risks of bioaccumulation and toxic effects on the environment.

- **Reduction of carbon footprint.** Metal production from secondary raw materials requires significantly less energy than extraction from primary ores, contributing to lower greenhouse gas emissions.

- **Economic Efficiency:**

- **Increased recovery of valuable materials.** Integrated processing enables the extraction not only of the target element (e.g., vanadium) but also of associated components such as iron, nickel, cobalt, sulphur, and others. This significantly enhances the overall value of processing and the profitability of the project.

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- **Reduced dependence on imported raw materials.** Vanadium and molybdenum are classified as critical materials in many countries. Utilising domestic secondary sources strengthens raw material security and the resilience of the metallurgical sector.

- **Creation of new sectors in the waste recycling industry.** Entire industries focused on processing catalysts, slags, and ash are emerging, creating jobs and driving technological innovation at the intersection of metallurgy, chemistry, and environmental science.

Table 2 – Comparison of Main Methods for Extracting Vanadium (V) and Molybdenum (Mo) from Technogenic Feedstock Based on Efficiency, Environmental, and Economic Criteria

Method	Feedstock Type	V/Mo Recovery, %	Environmental Impact	Economic Efficiency	Comments
1. Alkaline Leaching	Slags, catalysts	V: 85–95%Mo: up to 98%	Moderate (alkaline effluents require neutralisation)	High (reagents are available, moderate energy consumption)	Simple, suitable for oxidised forms
2. Acid Leaching (H_2SO_4, HCl, HNO_3)	Slags, ash, catalysts	V: 80–95%Mo: 70–90%	Low (acidic effluents, corrosion)	High (inexpensive reagents)	Versatile, but low selectivity
3. Ammonium Leaching ($(NH_4)_2CO_3$, NH_4OH)	Catalysts, slags	V: 65–90%Mo: 80–95%	High (ammonia volatilises but can be captured)	Moderate (ammonium salts are more expensive)	Selective for Mo, forms complex salts
4. Roasting with Na_2CO_3 or NaOH + Leaching	Ash, slag, catalysts	V: 90–98%Mo: 90–99%	Low (high emissions and energy consumption)	Moderate (requires furnaces and additional equipment)	Suitable for hardly soluble phases
5. Sulphidation + Leaching	Molybdenum concentrates, catalysts	Mo: 80–95%V: 40–70%	Moderate (sulfur-containing emissions)	Moderate	Works better for Mo than for V
6. Oxidative Smelting (with $NaNO_3$, CaO)	Slags, ash	V: 85–95%Mo: 70–90%	Low (NO_x and CO_2 emissions)	Low (high energy consumption)	For complex matrices, but costly
7. Sorption / Ion Exchange	Leach solutions	V/Mo removal efficiency: >95%	High (closed-loop system, no liquid effluents)	Moderate (mixed sorbents are more expensive)	Reusable, high selectivity
8. Solvent Extraction with Organic Reagents	Leach solutions	V: up to 99.9%, Mo: 90–99%	Moderate (organic solvent vapors)	Moderate to high	High selectivity, but requires many stages

The integrated processing of vanadium- and molybdenum-containing waste is not only a way to improve the efficiency of metallurgical processes but also a powerful tool for the environmental modernisation of industry. A powerful and efficient tool like this integrated processing is essential [1]. It enables the simultaneous resolution of pollution issues, reduces dependence on natural resources, and fosters the creation of sustainable economic models within the framework of the green transition [26].

The ores of the Greater Karatau region represent a valuable but currently untapped source of rare and rare earth elements (REEs), even though technology is developing rapidly in the last 20 years [27]. To develop an integrated processing technology for the black shale ore, a series of chemical, X-ray phase, infrared, mineralogical, X-ray spectral, and electron microscopic studies were conducted. Rare and especially rare earth elements in the ore are present in various minerals as inclusions within a siliceous-carbonaceous matrix. This explains the failure of previously proposed processing methods, which resulted in either incomplete recovery of valuable components or uneconomical processes. New approaches are required to achieve more complete extraction. A method has been proposed for the preliminary treatment of the raw black shale ore by roasting with $(NH_4)_2SO_4$ in the presence of concentrated H_2SO_4, followed by leaching of the calcine with a dilute H_2SO_4 solution. Optimal conditions for each stage were determined. Kinetic studies of REE extraction from the sulphate calcine under the most favourable conditions showed maximum recovery rates of U – 98%, V – 92%, Mo – 89%, and REEs – 78%. The rate constant and effective activation energy for vanadium leaching, as a representative of rare and rare earth metals, were calculated. The process is diffusion-limited. After leaching valuable components, the remaining calcine can be used in a froth flotation enrichment process to extract carbon-containing material and subsequently as part of a charge for ferrosilicon production. The solution obtained from leaching the original calcine can be used for sorption recovery of U, Mo, V, and REEs [27, 28].

The authors of [29] proposed a technological scheme (Figure 1) for the processing of technogenic waste through integrated extraction of vanadium, molybdenum, and nickel, achieving a recovery rate of 87%. Meanwhile, during electrochlorination lasting 12 hours, the recovery rate of nickel was slightly lower—58%.

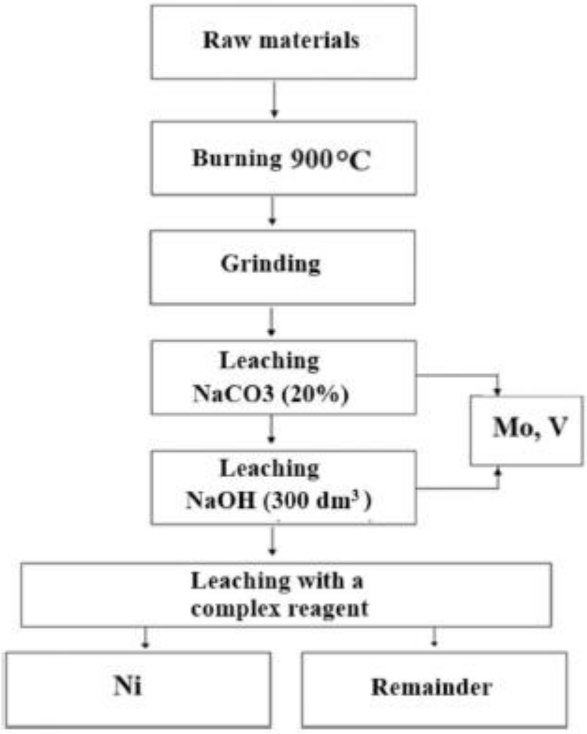

Figure 1 – Technological Flowchart for the Processing of Technogenic Waste with Integrated Extraction of Vanadium, Molybdenum, and Nickel

Conclusion

In the context of depleting high-grade natural ores and growing demand for strategic metals, the use of technogenic raw materials as an alternative source of vanadium and molybdenum is becoming increasingly relevant. Metallurgical slags, ash, spent catalysts, and other secondary resources not only contain high concentrations of valuable components but also pose a potential environmental threat when stored long-term or disposed of improperly.

The analysis shows that integrated waste processing technologies make it possible not only to efficiently extract vanadium and molybdenum but also to recover valuable by-products such as iron, nickel, sulphur, aluminosilicates, and others. This significantly enhances the economic viability of processing and helps reduce the environmental burden.

The most promising approaches are combined flowsheets that integrate pyrometallurgical, hydrometallurgical, and biotechnological methods. Their application should consider the specific waste composition, the chemical form of the metals, the level of contamination, and the final processing objectives. Particular attention must be given to the environmental safety of all stages of the technological process.

The development and implementation of such technologies align with the goals of sustainable development, resource conservation, and the transition to a circular economy. This enables the creation of closed production cycles and the effective integration of waste recycling into existing industrial systems.

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[1]Юлусов С.Б., [1]Сарсембаева М.Р., [1]Хабиев А.Т., [2]Retnawati H., [1*]Меркибаев Е.С., [1]Әкбаров М.С., [1]Балтабай Т.Е.

[1] Сәтбаев университеті, Алматы, Қазақстан
[2]Йогьякарта мемлекеттік университеті, Индонезия

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ТҮЙІНДЕМЕ
Мақалада өнеркәсіптің түрлі салаларында ванадий мен молибденді тұтыну бағыттары қаралды, бұл олардың стратегиялық маңыздылығы мен шикізатпен тұрақты қамтамасыз етудің өсіп келе жатқан қажеттілігін көрсетеді. Металлургиялық қождарды, күлдерді, пайдаланылған катализаторлар мен өнеркәсіптік процестердің басқа да қалдықтарын қоса алғанда, осы элементтердің табиғи және техногендік шығу көздері талданды. Қоршаған ортаға уытты әсер етуі мүмкін ванадий мен молибден қосылыстарының жиналуына байланысты экологиялық қауіптерге ерекше назар аударылады. Минералдық-шикізат базасын ұтымды пайдалану және бастапқы шикізаттан металдарды алудың тиімділігін арттыру үшін өнеркәсіп айналымына қайталама ресурстарды тарту қажеттігі атап көрсетілді. Өңделетін материалдың құрамын, технологиялық жағдайлардың ерекшеліктерін, сондай-ақ жекелеген тәсілдердің шектеулері мен кемшіліктерін ескере отырып, ванадий мен молибденді алудың қолданыстағы химиялық және гидрометаллургиялық әдістеріне шолу жасалды. Бірнеше құнды компоненттерді алуды қамтамасыз ететін және айналмалы экономикаға көшуге ықпал ететін қалдықтарды кешенді қайта өңдеудің перспективалылығына баса назар аударылды.

Түйін сөздер: *ванадий, молибден, күл-қож қалдықтары, металлургиялық шлактар, сүзгі, гидрометаллургиялық әдістер, пирометаллургиялық әдістер, бактериялық шаймалау.*

Авторлар туралы ақпарат:

Юлусов Султан Балтабаевич	*Юлусов Сұлтан Балтабайұлы PhD докторы, Ө.А. Байқоңыров атындағы Тау-кен-металлургия институтының Металлургия және пайдалы қазбаларды өңдеу кафедрасының доценті, Сәтбаев университеті, Алматы, Қазақстан. Email: s.yulussov@satbayev.university; ORCID ID: https://0000-0001-8044-4186*
Сарсембаева Маржан Рахатовна	*Металлургия және пайдалы қазбаларды өңдеу кафедрасының PhD докторанты, О.А. Байқоңыров атындағы тау-кен металлургия институты, Сәтбаев университеті, Алматы, Қазақстан. Email: m.sarsembayeva@satbayev.university; ORCID ID: https://orcid.org/0009-0007-2315-3009*
Хабиев Алибек Талгатбекұлы	*Ph.D докторы, ассоц. профессор, Академик У.А. Жолдасбеков атындағы Механика және машинатану институты, Алматы, Қазақстан. E-mail: alibek1324@mail.ru; ORCID ID: https://orcid.org/0000-0001-9397-2367*
Heri Retnawati	*Профессор, Йогьякарта мемлекеттік университеті, Индонезия. Email: heri_retnawati@uny.ac.id; ORCID ID: https://orcid.org/0000-0002-1792-5873*

Меркибаев Ерик Серикович	*Ph.D. докторы, Металлургия және пайдалы қазбаларды байыту кафедрасының аға оқытушысы, Ө.А. Байқоңыров атындағы Тау-кен-металлургия институты, Сәтбаев университеті, Алматы, Қазақстан. Email: y.merkibayev@satbayev.university; ORCID ID: https://orcid.org/0000-0003-3869-6835*
Әкбаров Мерей Сәбитұлы	*Техника ғылымдарының магистрі, Металлургия және пайдалы қазбаларды байыту кафедрасының инженері, Ө.А. Байқоңыров атындағы Тау-кен металлургия институты, Сәтбаев университеті, Алматы, Қазақстан. E-mail: m.akbarov@satbayev.university; ORCID ID: https//orsid.org/0000-0002-4272-8038*
Балтабай Тамерлан	*Металлургия және пайдалы қазбаларды өңдеу кафедрасының 4 курс студенті, О.А. Байқоңыров атындағы тау-кен металлургия институты, Сәтбаев университеті, Алматы, Қазақстан. Email: t.baltabay@satbayev.university*

Инновационные подходы к переработке техногенных отходов, содержащих ванадий и молибден

[1]Юлусов С.Б., [1]Сарсембаева М.Р., [1]Хабиев А.Т., [2]Retnawati H., [1*]Меркибаев Е.С., [1]Акбаров М.С., [1]Балтабай Т.Е.

[1]Satbayev University, Almaty, Kazakhstan
[2]Джокьякартский государственный университет, Индонезия

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ABSTRACT
В статье рассмотрены направления потребления ванадия и молибдена в различных отраслях промышленности, что подчёркивает их стратегическую значимость и растущую потребность в устойчивом обеспечении сырьём. Проанализированы источники этих элементов как природного, так и техногенного происхождения, включая металлургические шлаки, золы, отработанные катализаторы и другие отходы промышленных процессов. Отдельное внимание уделено экологическим рискам, связанным с накоплением соединений ванадия и молибдена, способных оказывать токсическое воздействие на окружающую среду. Подчёркнута необходимость вовлечения вторичных ресурсов в промышленный оборот для рационального использования минерально-сырьевой базы и повышения эффективности извлечения металлов из первичного сырья. Приведён обзор существующих химических и гидрометаллургических методов извлечения ванадия и молибдена, с учётом состава перерабатываемого материала, особенностей технологических условий, а также ограничений и недостатков отдельных подходов. Сделан акцент на перспективность комплексной переработки отходов, обеспечивающей извлечение нескольких ценных компонентов и способствующей переходу к циркулярной экономике.

Keywords: ванадий, молибден, золошлаковые отходы, металлургические шлаки, фильтрат, гидрометаллургические методы, пирометаллургические методы, бактериальное выщелачивание.

Информация об авторах:

Юлусов Султан Балтабаевич	*PhD, ассоциированный профессор кафедры Металлургии и обогащения полезных ископаемых, Горно-металлургический институт имени О.А. Байконурова, Satbayev University, Almaty, Kazakhstan. Email: s.yulussov@satbayev.university; ORCID ID: https://0000-0001-8044-4186*
Сарсембаева Маржан Рахатовна	*PhD докторант кафедры Металлургии и обогащения полезных ископаемых, Горно-металлургический институт имени О.А. Байконурова, Satbayev University, Almaty, Kazakhstan. Email: m.sarsembayeva@satbayev.university; ORCID ID: https://orcid.org/0009-0007-2315-3009*
Хабиев Алибек Талгатбекович	*Доктор Ph.D., ассоц. профессор, Институт механики и машиноведения имени академика У.А. Джолдасбекова, Алматы, Казахстан. E-mail: alibek1324@mail.ru; ORCID ID: https://orcid.org/0000-0001-9397-2367*
Heri Retnawati	*Профессор, Джокьякартский государственный университет, Индонезия. Email: heri_retnawati@uny.ac.id; ORCID ID: https://orcid.org/0000-0002-1792-5873*
Меркибаев Ерик Серикович	*PhD, старший преподаватель кафедры ʼМеталлургии и обогащения полезных ископаемых, Горно-металлургический институт имени О.А. Байконурова, Satbayev University, Almaty,Kazakhstan. Email: y.merkibayev@satbayev.university; ORCID ID: https://orcid.org/0000-0003-3869-6835*
Акбаров Мерей Сәбитұлы	*Магистр технических наук, инженер кафедры Металлургия и обогащения полезных ископаемых, Горно-металлургический институт имени О.А. Байконурова, Satbayev University, Алматы, Казахстан. E-mail: m.akbarov@satbayev.university; ORCID ID: https//orsid.org/0000-0002-4272-8038*
Балтабай Тамерлан	*Студент 4 курса кафедры Металлургии и обогащения полезных ископаемых, Горно-металлургический институт имени О.А. Байконурова, Satbayev University, Almaty, Kazakhstan. Email: t.baltabay@satbayev.university*

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