Crossref **DOI**: [10.31643/2026/6445.08](https://doi.org/10.31643/2026/6445.08) Metallurgy

Transformation of mining and metallurgical waste into functional materials: overview of technologies and applications

¹Beisebayeva A.S., 2 Zhantikeyev U.Ye., ²Kunarbekova M.S., ²Azat S., 1*Merkibayev Y.S.

¹ O.A. Baikonurov Mining and Metallurgical Institute, Satbayev University, Almaty, Kazakhstan ² Laboratory of Engineering profile, Satbayev University, Almaty, Kazakhstan

** Corresponding author email[: y.merkibayev@satbayev.university](mailto:y.merkibayev@satbayev.university)*

ABSTRACT

Introduction

The mining and metallurgical industry plays a pivotal role in the global economy, supplying essential metals and materials to nearly all industrial sectors. However, the activities of this industry are

associated with the generation of significant volumes of waste, which have a detrimental impact on the environment. Globally, more than 100 billion tons of mining and metallurgical waste are produced annually, much of which is stored in dumps and tailing ponds, posing environmental risks and

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occupying vast areas. Addressing the problem of waste disposal and recycling is becoming increasingly urgent in light of growing demands for environmental sustainability and the rational use of resources.

Modern waste processing technologies not only minimize their negative environmental impact but also enable the extraction of valuable components, transforming them into useful materials. Hydrometallurgical and pyrometallurgical processes occupy a central role in strategies for the recycling of mining and metallurgical waste due to their ability to extract metals and synthesize functional materials. These processes allow for the production of materials such as nanoporous silica, rare earth metals, catalysts, and sorbents, which have broad applications across various industries, including electronics, energy, and chemistry.

Despite significant progress in the field of mining and metallurgical waste recycling, numerous unresolved challenges remain, particularly concerning the economic feasibility of the processes, their environmental impact, and the quality of the resulting products. The implementation of a circular production cycle, in which waste becomes a valuable raw material, requires the development of innovative technologies and strategies that ensure maximum efficiency and minimal environmental risks.

The aim of this article is to provide a comprehensive review of current achievements and challenges in the recycling of mining and metallurgical waste, with a focus on hydrometallurgical and pyrometallurgical processes. The article examines modern methods for extracting valuable components and synthesizing functional materials and analyzes their environmental and economic aspects. Special attention is given to the prospects for applying these technologies in industry and their contribution to sustainable development.

Thus, this work seeks to highlight the importance of mining and metallurgical waste recycling and to discuss strategies that promote the efficient use of natural resources and the reduction of environmental burdens.

Processing of silicon from silicon slag

In the context of global sustainable and lowcarbon development, the recycling of silicon from metallurgical-grade refined silicon slag (MGRSS) has become increasingly important. The elemental silicon (Si) content in MGRSS plays a crucial role in silicon extraction processes, directly influencing the

choice and economic efficiency of recovery technologies.

In a study [1], a method was developed for separating and quantifying silicon content and other silicon phases in MGRSS. First, the silicate present in MGRSS was dissolved using hydrochloric acid to extract its content, leaving behind a mixture of silicon and silicon carbide (SiC) particles. Next, silicon was dissolved using a combination of nitric and hydrofluoric acids (HF/HNO3), separating the SiC particles. The respective contents of silicon and SiC were then measured. Over two stages, the effects of dissolution and the repeatability of silicate and silicon extraction in different acids were analyzed. Ultimately, the silicon content in MGRSS, determined through this two-step chemical method, was found to be 21.84 ± 0.53 %. This was achieved using an acid mixture with a 1:1 volume ratio of HNO3 to HF and a reaction time of 1 hour.

This approach challenges conventional methods of estimating elemental silicon content in MGRSS, which often rely on experiential techniques. By providing a more precise assessment, the method contributes to improving silicon extraction processes and reducing the volume of MGRSS, which primarily contains silicate, silicon, and SiC. Traditional methods are insufficient for accurately measuring silicon content and other phases in MGRSS. For the first time, a technological process for determining silicon content in MGRSS was proposed and implemented in this study.

Figure 1 - Schematic diagram of the experiments: **a** block diagram, **b** principle scheme [1]

The experimental procedure is shown in Figure 1. To further verify the reaction between silicate and hydrochloric acid, corrosion tests were conducted on bulk MGRSS samples. The results, illustrated in Figure 2, reveal that in the original MGRSS (Figure 2a), light gray areas corresponded to silicate, spherical gray regions with distinct boundaries represented silicon, and dark black regions were SiC, with clearly defined phase boundaries. Figures 2b–d demonstrate the reaction of silicate with hydrochloric acid, showing leaching from cracks and the silicon/silicate boundary. The corroded surface exhibited noticeable gullies and pits, with pronounced grooves surrounding Si and SiC. The silicate surface displayed visible white honeycomblike patterns, likely caused by hydrochloric acid washing the silicate surface for a short period without forming deep trenches.

Figure 2 - EPMA analysis of in-situ corrosion of MGRSS by hydrochloric acid: an MGRSS before corrosion; **b**-**d** MGSRS after corrosion [1]

Using a two-step dissolution method, silicon and other phases in MGRSS were successfully separated and quantified. In the first step, silicates were completely dissolved with hydrochloric acid. In the second step, silicon particles were fully dissolved using the HF/HNO3 mixture, separating the SiC. The silicon content determined via this method was 21.84%, with a standard deviation of 0.53%, demonstrating high analytical accuracy. This method holds significant potential for enhancing silicon recycling technologies and supporting the sustainable development of metallurgical-grade silicon (MG-Si) smelting [1].

This research also explored the separation of silicon slag produced using both high-temperature resistance furnaces and medium-frequency induction furnaces. Key factors such as melting temperature, melting duration, gas purging, stirring methods, and the addition of slagging agents were systematically analyzed for their impact on the efficiency of silicon and slag separation. Chemical

composition analysis and microscopic morphology studies revealed that the primary components of silicon slag included Si, Fe, Al, Ca, Ti, Mg, and K. These impurities mainly occurred in oxide forms, such as SiC, Ca($Al₂Si₂O₈$), and Fe $₂SiO₄$.</sub>

When using a high-temperature resistance furnace, the efficiency of silicon separation varied significantly depending on whether argon stirring was employed. Argon stirring notably enhanced the separation process, enabling a more complete separation of silicon and slag. At 1550°C, optimal separation was achieved by blowing argon into the molten slag and stirring for 2 hours. Experimental results indicated that the viscosity and fluidity of the melt were critical factors influencing separation efficiency. Effective silicon extraction could be achieved by increasing the melting temperature and extending the purging time.

In medium-frequency induction furnaces, silicon and slag separation occurred more rapidly. Adding a slagging agent composed of $CaO-SiO₂-CaCl₂$ to the molten material facilitated complete separation in a shorter time. Microscopic morphology and ICP-AES analyses of elemental silicon demonstrated that both argon stirring and electromagnetic stirring significantly enhanced the extraction and purification of silicon. These processes also contributed to reducing environmental pollution by improving the efficiency of separation and reducing waste [2].

Currently, numerous industries produce waste or byproduct streams, which are either stored or utilized as secondary products. In sectors such as photovoltaics and semiconductors, the cutting and grinding of metallic silicon generate valuable metallic powder byproducts. ReSiTec (Portugal) has been actively engaged in research and development projects aimed at advancing innovative technologies for the recycling and purification of these metal powders. Particular emphasis has been placed on metallic silicon powder produced during cutting and grinding operations.

A novel process has been developed to recover fine metallic silicon particles, ranging from 0 to 150 microns, from highly diluted wastewater streams. Established separation and classification techniques have been modified and optimized to efficiently clean and recycle metallic silicon powder, transforming it from waste into valuable new products. Experimental evaluations demonstrated a substantial increase in silicon purity, from an initial 50% to levels exceeding 99%, with an acceptable yield. This advancement suggests that the

technology could be extended to other industrial processes involving metallic powder waste streams.

ReSiTec now plays a key role in supporting the recycling industry by offering research and development services and producing over 500 tons of high-purity recycled metallic silicon powder annually. Despite this progress, large quantities of metallic silicon powder—exceeding 100,000 tons continue to be discarded as industrial waste. Over the past several years, ReSiTec has refined its recycling process, particularly for metallic silicon powders originating from the production of solargrade silicon. Notably, the energy consumption of this recycling process is less than 1 kWh/kg, significantly lower than that of traditional metallic silicon production methods, highlighting its economic and environmental advantages [3].

A waste-free process for extracting extremely pure nanoporous silica particles from phosphoric slag

This study focuses on the recycling of phosphorus slag as a cost-effective source for silica (SiO₂) extraction, addressing both resource recovery and environmental pollution mitigation. The primary objective was to establish a zero-waste process for extracting high-purity nanoporous silica particles (NPSP) as a valuable product. The process involved leaching phosphorus slag using nitric acid under specific conditions: acid concentration (C8M), liquidto-solid ratio (r1:3), duration (t2h), and temperature (T75°C). Calcium oxide (CaO) was also extracted as a byproduct using oxalic acid. The resulting $SiO₂$ and CaO products achieved purities of 99.16% and 98.65%, respectively. Additionally, the process demonstrated sustainability through the recovery and reuse of reagents: approximately 77% of oxalic acid was reclaimed by cooling the nitric acid solution containing oxalate to 5°C, and around 85% of nitric acid was recovered.

The article further reports the outcomes of phosphorus slag processing using both alkaline and acidic reagents. Autoclave leaching experiments with sodium hydroxide and sodium carbonate solutions revealed silicon extraction efficiencies of 1.1% and 16.6%, respectively. Investigations into nitric acid leaching for extracting rare earth metals (REM) from phosphorus slag were also conducted. Optimal leaching conditions included a nitric acid concentration of 7.5 mol/ dm^3 , a liquid-to-solid ratio

of 2.6 cm³/g, a temperature of 60 $^{\circ}$ C, a process duration of 1 hour, and a stirrer speed of 500 rpm. Under these conditions, extraction efficiencies for REM, calcium, aluminum, and iron were 98%, 99.1%, 99%, and 18.8%, respectively. The remaining siliconcontaining residue was suitable for producing precipitated silica, containing approximately 75-80% SiO₂.

Subsequent leaching of the residue obtained from nitric acid treatment was performed using sodium hydroxide in a thermostated cell at 98°C and in an autoclave at 220°C. The most efficient extraction occurred in the thermostated cell at 98°C, achieving a silicon recovery rate of 97.9%. A comprehensive technological scheme for phosphorus slag processing was proposed, enabling the production of rare earth metal concentrates, precipitated silica (white soot), construction materials, and fertilizers.

This research provides an in-depth assessment of phosphorus slag as a resource for extracting rare earth metals and precipitated silica. It characterizes the chemical and phase composition of the slag, identifying the primary elements and trace components, as well as the forms of siliconcontaining compounds present, demonstrating its potential for sustainable and resource-efficient applications [4].

Figure 3 - Technological scheme for the comprehensive processing of phosphorus slag [4]

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Physicochemical studies have demonstrated that slags resulting from electrothermal phosphorus production represent a valuable raw material for the extraction of rare earth metals (REEs) and precipitated silicon dioxide (SiO₂). The application of hydrometallurgical methods, including lowtemperature treatment with acids and alkalis, facilitates a comprehensive processing approach. This enables the extraction of valuable components into solution, ensuring the efficient utilization of raw materials.

Based on the findings of phosphorus slag processing, a technological scheme (Figure 3) has been proposed. This scheme aims to enable the production of REE concentrates, precipitated SiO₂, construction materials, and fertilizers. Such an integrated processing framework has the potential to significantly enhance the value derived from phosphorus slag.

Despite substantial research efforts, primarily at the laboratory scale, recycling rates for REEs remain alarmingly low, with less than 1% of REEs recycled as of 2011. This inefficiency is attributed to factors such as inadequate collection systems, technological barriers, and the absence of economic incentives. Addressing these challenges necessitates paradigm shift toward the development of highly efficient, fully integrated recycling processes.

This article reviews existing literature on REE recycling, focusing on three critical applications: permanent magnets, nickel-metal hydride batteries, and lamp phosphors. It examines the current state of pre-processing for end-of-life materials containing REEs and the subsequent extraction methods. Both pyrometallurgical and hydrometallurgical pathways for separating REEs from non-rare-earth elements in recycled materials are analyzed in detail. Furthermore, the importance of life cycle assessment (LCA) in evaluating the environmental and economic impact of REE recycling is emphasized.

The review highlights that efficient REE recycling not only reduces supply chain risks but also mitigates the significant environmental issues associated with traditional REE mining and processing. By adopting integrated recycling technologies informed by the existing body of research, significant advancements in resource efficiency and environmental sustainability can be achieved.

The most prevalent rare earth element (REE) magnets are predominantly composed of neodymium-iron-boron (NdFeB) alloys. These magnets feature a matrix phase of $Nd_2Fe_{14}B$,

encompassed by a grain boundary phase enriched with neodymium. Additionally, they contain trace quantities of other elements, including praseodymium, gadolinium, terbium, and notably dysprosium, alongside various transition metals such as cobalt, vanadium, titanium, zirconium, molybdenum, and niobium [5].

The recycling and reuse of metals are pivotal for fostering a resource-efficient economy. While efficient recycling pathways are well-established for base metals (e.g., iron, copper, aluminum, zinc) and precious metals (e.g., gold, silver, platinum group metals), the recycling rates for end-of-life REEs were notably low, with less than 1% being recycled as of 2011. A life cycle assessment conducted in 2007 estimated global REE reserves to be approximately four times the annual extraction volume [6].

Mining industry waste, including acid mine drainage (AMD), represents a significant environmental challenge due to its potential to contaminate surface and groundwater systems. AMD poses a critical threat to ecosystems and water resources. Simultaneously, the synthesis of advanced nanomaterials has become an integral aspect of modern technological advancements. However, traditional methods for producing nanomaterials are associated with high costs and environmental concerns due to the reliance on hazardous chemicals and energy-intensive processes.

An emerging and promising solution lies in the utilization of mining waste and AMD as raw materials for nanomaterial production. This approach not only facilitates the detoxification and valorization of waste but also yields functional nanomaterials with properties comparable to those synthesized from pure chemical precursors. For instance, this strategy has been successfully applied in the synthesis of iron- and copper-based nanomaterials, which exhibit substantial potential for diverse applications. This study emphasizes the production of nanoparticles and nanocomposites derived from mining waste and AMD, demonstrating the dual benefits of environmental remediation and resource recovery [7].

The initial precursor material predominantly comprised iron sulfate, derived from tailings produced by the company's iron mining operations. The second precursor material was obtained via acid extraction from iron-rich sludge, which was collected from the Doser River following the collapse of the Fundão Dam in Mariana in 2015. The synthesis of hybrid materials was carried out as follows: cobalt

chloride hexahydrate (CoCl₂·6H₂O) and spent iron salts were dissolved in water containing natural organic matter. The resulting solution was alkalized to a pH of 9 using a 1M sodium hydroxide (NaOH) solution. The precipitate was subsequently washed and dried. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses revealed the formation of nanostructures, while Xray diffraction studies confirmed the formation of a cobalt ferrite phase (CoFe₂O₄). The synthesized hybrids (NOMCoFe₂O₄) achieved a remarkable 99% conversion of nitrophenol within 1–2 minutes.

In another investigation, manganese ferrite (MnFe₂O₄) was synthesized from low-grade mining waste containing both iron and manganese. The precursor material was initially heated to 700°C, followed by leaching in a sulfuric acid (H_2SO_4) solution. The filtrate was purified, and its composition was adjusted to maintain a molar Fe:Mn ratio of 2:1. The synthesis of MnFe $_2O_4$ nanoparticles was conducted by precipitation at 90°C. The resulting nanoparticles, with an average size of 45 nm, exhibited a saturation magnetization of 51.03 emu/g and demonstrated potential for energy storage applications.

Research over the past two decades has shown the following:

1. Mine tailings can serve as a valuable source of iron for synthesizing diverse nanoparticles, including magnetite, interconnected α -Fe₂O₃, ferrites, and their composites, as well as copper and selenium nanoparticles. These materials exhibit properties and potential applications comparable to those synthesized from pure chemical precursors.

2. Acid mine drainage (AMD) has been utilized as a source of iron for synthesizing various magnetic nanoparticles, such as magnetic zero-valent iron, goethite, and hematite, as well as copper, zinc, and lead sulfide nanoparticles and their respective nanocomposites. AMD has also shown potential for silicon nanoparticle (SiNP) synthesis. Moreover, the materials produced from AMD have demonstrated their capacity to remove a wide range of pollutants from contaminated water. Notably, many studies have used real waste as raw materials.

Despite these promising results, several limitations remain. Most experiments have been conducted on a small laboratory scale. The use of strong acidic solutions for leaching mining waste and strong alkaline solutions (e.g., NaOH) to adjust the pH during AMD treatment is a common practice, raising environmental and safety concerns. Furthermore, the stabilization of non-magnetic

nanoparticles within various composites or on different supports (e.g., clay or zeolite) has been insufficiently explored, despite its potential to enable easier separation and reuse of these nanocomposites.

In conclusion, the synthesis of nanoparticles and nanocomposites from mining waste and AMD offers a promising, environmentally sustainable approach to mitigating the environmental impact of these waste streams while generating valuable materials. However, the full-scale implementation of this approach remains a challenge and requires further research and development [8].

The extraction of silica from waste materials or by-products has recently emerged as a significant focus in scientific research. A substantial volume of silica-rich materials, including agricultural, industrial, and mining residues, is frequently discarded. Table 1 provides a detailed list of silicacontaining waste materials, their respective sources, and the amount of silica present prior to processing. The silicon or silica content in these wastes varies depending on multiple environmental factors.

As waste volumes continue to rise, their reuse is gaining increasing importance, particularly given the environmental challenges posed by waste disposal and pollution. In this context, silica-rich waste is increasingly regarded as a renewable and sustainable resource with the potential to serve as a cost-effective precursor for the extraction of silicon nanoparticles (SiNPs). Over the past decade, significant progress has been achieved in producing mesoporous SiNPs from waste materials, with numerous simple and efficient methods being proposed for this purpose [9].

Synthesis of functional materials from solidified slags

Metallurgical slags represent a promising resource for the development of novel functional materials due to their rich composition and availability. These by-products of metallurgical processes have been successfully utilized in the production of various advanced materials, including sintered glass-ceramics [[10], [11]], porous ceramic materials [[12], [14]], ceramic bricks [13], functional zeolites for wastewater treatment [14], and refractory materials [15].

Among these applications, the synthesis of functional glass-ceramics and zeolites stands out as particularly significant. Glass-ceramics produced

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from metallurgical slags exhibit unique structural and mechanical properties, making them suitable for applications such as construction materials, wear-resistant surfaces, and even specialized industrial tools. Similarly, zeolites derived from slags have demonstrated exceptional capabilities in environmental remediation, particularly in wastewater treatment, owing to their high surface area, ion-exchange capacity, and adsorption properties.

This study focuses on exploring and advancing the utilization of metallurgical slags for the synthesis of these functional materials, emphasizing their potential to contribute to sustainable material development and waste valorization strategies.

Previous studies [16] investigated the solubility, reactivity and nucleation behavior of $Cr₂O₃$ in the CaO-MgO-Al₂O₃-SiO₂ glassy system. The experiments were conducted by melting the slag containing up to 5 mol% Cr_2O_3 at 1400°C to study the effect of magnesium content on spinel formation. At the melting temperature, it was assumed that the reaction between $Cr₂O₃$ and MgO resulted in the formation of stable $Mg₂Cr₂O₄.$

In a related study [17], the mineralogical and petrological properties of CaO-SiO₂-Al₂O₃-MgO-Fe-Cr slags obtained during the production of highcarbon ferrochrome were investigated. The results showed that the slag solidified into a semi-crystalline structure comprising hypidiomorphic spinel crystals ((Mg, Fe)(Fe, Al, Cr)₂O₄) dispersed in a homogeneous glassy matrix.

Figure 4 - Phase composition and mineralogy of aircooled ferrochrome slags [17]

This study focused on the selective dissolution of zinc, gallium and germanium from zinc smelter residues using a staged leaching process. Thermodynamic analysis confirmed that the selective leaching of Zn, Ga and Ge could be achieved by optimizing the pH conditions. The first stage used sulfuric acid solutions (2 mol/L $H₂SO₄$) with a liquid to solid ratio of 10 ml/g at 80°C for 4 hours, which resulted in the leaching of more than 93% of Zn, nearly 100% of Ga and less than 8% of Ge. The second stage used sodium hydroxide solutions (1 mol/L NaOH) with a liquid to solid ratio of 20 ml/g at 80°C for 4 hours [18].

Based on the comprehensive characterization of zinc refining residues, a two-stage leaching process was implemented in this work. In the first stage, Zn and Ga were selectively leached by adjusting the concentration of sulfuric acid, resulting in Ge being enriched in the sulfuric acid leaching residue. In the second stage, Ge was efficiently extracted into sodium hydroxide solution by breaking its bond with Si. The leaching mechanisms were further elucidated by analyzing changes in the mineral phase composition [[19], [20]].

Точка	Фаза/зона	O	Mg	Al	Si	К	Ca	Cr	Fe
$\overline{2}$	Стекло	47.51	7.02	10.06	28.69	0.96	3.61	1.11	
3	Mg-Cr-Al-Sp	40.08	16.69	27.69				15.82	0.94
4	Пироксен	45.79	21.94	3.09	26.11			2.04	0.50
5	Mg-Al-Sp	43.67	17.33	38.53					0.47
7	Стекло	47.13	6.84	10.18	28.80	0.91	3.54	1.57	
8	Фостерит	43.10	34.01		20.30			1.60	0.99
13	Стекло	47.46	6.70	11.11	28.42	1.20	3.73	1.28	
14	Пироксен	45.50	21.62	3.46	26.05			2.24	0.50

Таблица 1 - Перечень кремнеземсодержащих отходов с указанием их источников и количеством кремнезема

Conclusion

Mining and metallurgical waste represents a significant source of valuable materials, including metals, oxides, and silicate compounds, which can be effectively recycled into functional materials. Their recycling not only helps minimize environmental impact but also creates new economic opportunities.

To further advance the recycling of mining and metallurgical waste, research focused on improving existing technologies and developing new approaches is essential. Special attention should be given to integrating a circular economy into production processes, which will enable the most efficient use of resources and minimize environmental risks.

The transformation of mining and metallurgical waste into functional materials is a promising field that combines environmental responsibility with economic benefits and innovative solutions. Success

in this area requires the integration of scientific research, industrial collaboration, and governmental support to achieve sustainable development and efficient use of natural resources.

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

CRediT author statement. **A. Beisebayeva:** Data curation, Writing-Original draft preparation; **U.Zhantikeyev:** Conceptualization, Methodology; **M.Kunarbekova:** Visualization, Investigation; **S. Azat:** Supervision; **Ye.Merkibayev:** Writing-Reviewing and Editing.

Acknowledgements. This research is funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. BR21881939 on the topic: "Development of resource-saving energy-generating technologies for the mining and metallurgical complex and the creation of an innovative engineering center", 2023- 2025).

Cite this article as: Beisebayeva AS, Zhantikeyev UYe, Kunarbekova MS, Azat S, Merkibayev YeS. Transformation of mining and metallurgical waste into functional materials: Overview of technologies and applications. Kompleksnoe Ispolzovanie Mineralnogo Syra = Complex Use of Mineral Resources. 2026; 336(1):86-95[. https://doi.org/10.31643/2026/6445.08](https://doi.org/10.31643/2026/6445.08)

Тау-кен металлургия қалдықтарын функционалды материалдарға айналдыру: технологиялар мен қосымшаларға шолу

¹Бейсебаева А.С., ²Жантикеев Ұ.Е., ²Кунарбекова М.С., ²Азат С., ¹Меркібаев Е.С.

¹ Ө.А. Байқоңыров атындағы Тау-кен металлургия институты, Сәтбаев Университеті,, Алматы, Қазақстан ² Инженерлік бейіндегі зертхана, Сәтбаев Университеті, Алматы, Қазақстан

ТҮЙІНДЕМЕ

Мақала келді: *4 қыркүйек 2024* Сараптамадан өтті: *4 қазан 2024* Қабылданды: *17 желтоқсан 2024* Мақалада кремний, сирек кездесетін металдар, нано-кеуекті кремний диоксиді және басқа да құнды компоненттерден тұратын функционалды материалдарды алу үшін тау-кен металлургиялық қалдықтарды өңдеудің заманауи әдістеріне шолу жасалады. Өңдеу және тазарту технологиялары, оның ішінде гидрометаллургиялық және пирометаллургиялық процестер, сондай-ақ олардың тау-кен металлургиялық кешенінде түзілетін қалдықтардың әртүрлі түрлеріне қолданылуы қарастырылады. Қалдықтарды қайта өңдеудің экологиялық аспектілері мен экономикалық тиімділігіне, сондай-ақ қоршаған ортаның ластануын төмендетуді қамтамасыз ететін қалдықсыз процестерді енгізу мүмкіндіктеріне ерекше назар аударылады. Инновациялық технологияларды сәтті енгізудің мысалдары келтірілген және әртүрлі салаларда екінші реттік материалдарды пайдалану перспективалары сипатталған. Авторлар қоршаған ортаның ластануын азайту үшін қалдықсыз процестерді енгізудің маңыздылығын атап көрсетеді. Мақалада сонымен қатар соңғы өнімдердің қасиеттерін айтарлықтай жақсартуға мүмкіндік беретін кремний мен кремнийді алу және өңдеу әдістері талқыланады. Тау-кен металлургия өндірісінің қалдықтарын қайта өңдеудің инновациялық технологиялары қалдықтар көлемін азайтуға ғана емес, сонымен қатар жаңа экономикалық тиімді материалдар жасауға да ықпал етеді. Зерттеу қалдықтарды қайта өңдеудің маңыздылығына назар аударуға бағытталған және оларды табиғи ресурстардың тұрақты дамуы мен тиімді пайдаланылуына ықпал ететін құнды шикізат ретінде пайдалану әлеуетін көрсетеді. Авторлар сонымен қатар қайта өңдеу технологияларын одан әрі дамыту перспективаларын, соның ішінде жаңа әдістерді әзірлеуді және бар процестерді оңтайландыруды талқылайды, Бұл тиімділікті арттыруға және қайта өңдеу шығындарын азайтуға мүмкіндік береді.

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Преобразование горно-металлургических отходов в функциональные материалы: обзор технологий и применений

¹Бейсебаева А.С., ²Жантикеев Ұ.Е., ²Кунарбекова М.С., ²Азат С., ¹Меркибаев Е.С.

¹ Горно-металлургический институт имени О.А. Байконурова, Satbayev University, Алматы, Казахстан ² Лаборатория инженерного профиля, Satbayev University, Алматы, Казахстан

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