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# INVESTIGATION OF GERMANIUM EXTRACTION TECHNOLOGY FROM TECHNOGENIC METALLURGICAL WASTE

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**Abstract.** This study investigates the technological feasibility of extracting germanium (Ge) from technogenic waste generated by the Almalyk Mining and Metallurgical Complex. Due to the increasing industrial demand for Ge in semiconductor devices, infrared optics, fiber-optic communication systems, and solar energy technologies, secondary technogenic resources are becoming an important alternative source of rare metals. The investigated waste materials contained Ge associated with sulfide, oxide, and silicate phases, together with compounds of Fe, Zn, Cu, Pb, and Si. Combined pyrometallurgical and hydrometallurgical processing technologies were applied for germanium recovery. Preliminary preparation of technogenic materials included crushing, grinding, drying, and granulometric classification. Oxidative roasting was performed within the temperature range of 600–900 °C to facilitate sulfur removal and the transformation of Ge-bearing minerals into soluble oxide forms. Hydrometallurgical treatment was carried out using sulfuric acid and hydrochloric acid leaching systems under controlled technological conditions. Experimental investigations demonstrated that acidic oxidative media provided higher Ge extraction efficiency compared with alkaline systems. The highest recovery rates were achieved during oxygen-assisted and tartaric acid leaching processes. Solvent extraction and sorption methods ensured the selective separation of Ge from impurity elements such as Fe, Zn, Cu, and Pb. XRD, XRF, and AAS analyses confirmed the effectiveness of the developed processing technology and revealed a significant improvement in Ge recovery after the thermal activation of technogenic materials. The obtained results demonstrate that combined thermal and hydrometallurgical treatment technologies provide efficient and environmentally sustainable recovery of germanium from secondary industrial resources while simultaneously reducing industrial waste accumulation and expanding the utilization of technogenic raw materials.

**Keywords:** germanium, technogenic waste, hydrometallurgy, oxidative roasting, acid leaching, solvent extraction, rare metals.

**Аннотация.** В данном исследовании изучена технологическая возможность извлечения германия (Ge) из техногенных отходов Алмалыкского горно-металлургического комбината. В связи с возрастающим промышленным спросом на германий в производстве полупроводниковых приборов, инфракрасной оптики, волоконно-оптических систем связи и солнечной энергетики вторичные техногенные ресурсы становятся важным альтернативным источником редких металлов. Исследованные отходы содержали германий, связанный с сульфидными, оксидными и силикатными фазами, а также соединениями Fe, Zn, Cu, Pb и Si. Для извлечения германия были применены комбинированные пирометаллургические и гидрометаллургические технологии переработки. Предварительная подготовка техногенных материалов включала дробление, измельчение, сушку и granulometricкую классификацию. Окислительный обжиг

проводился в температурном интервале 600–900 °C с целью удаления серы и перевода германиевых минералов в растворимые оксидные формы. Гидрометаллургическая обработка осуществлялась с использованием систем сернокислотного и солянокислотного выщелачивания в контролируемых технологических условиях. Экспериментальные исследования показали, что кислые окислительные среды обеспечивают более высокую эффективность извлечения германия по сравнению со щелочными системами. Наибольшие показатели извлечения были достигнуты при кислородно-активированном и виннокислотном выщелачивании. Методы жидкостной экстракции и сорбции обеспечили селективное отделение германия от примесных элементов Fe, Zn, Cu и Pb. Анализы XRD, XRF и AAS подтвердили эффективность разработанной технологии переработки и выявили существенное повышение степени извлечения германия после термической активации техногенных материалов. Полученные результаты показывают, что комбинированные термические и гидрометаллургические технологии обеспечивают эффективное и экологически устойчивое извлечение германия из вторичных промышленных ресурсов, одновременно снижая накопление промышленных отходов и расширяя возможности использования техногенного сырья.

**Ключевые слова:** германий, техногенные отходы, гидрометаллургия, окислительный обжиг, кислотное выщелачивание, жидкостная экстракция, редкие металлы.

**Annotatsiya.** Ushbu tadqiqotda Olmaliq kon-metallurgiya kombinati tomonidan hosil qilinadigan texnogen chiqindilardan germaniy (Ge) ni ajratib olishning texnologik imkoniyatlari o'rganildi. Yarimo'tkazgich qurilmalari, infraqizil optika, tolali-optik aloqa tizimlari hamda quyosh energetikasi texnologiyalarida germaniyga bo'lgan sanoat talabi ortib borayotgani sababli, ikkilamchi texnogen resurslar noyob metallar uchun muhim muqobil manbaga aylanmoqda. Tadqiq qilingan chiqindilar tarkibida Ge sulfidli, oksidli va silikatli fazalar bilan bog'langan holda, shuningdek Fe, Zn, Cu, Pb va Si birikmalari bilan birga mavjudligi aniqlandi. Germaniyini ajratib olish uchun kombinatsiyalashgan pirometallurgik va gidrometallurgik qayta ishlash texnologiyalaridan foydalanildi. Texnogen materiallarni dastlabki tayyorlash maydalash, yanchish, quritish hamda granulometrik tasniflash bosqichlarini o'z ichiga oldi. Oksidlovchi kuydirish 600–900 °C harorat oralig'ida amalga oshirilib, oltingugurtni ajratish va germaniy saqlovchi minerallarni eruvchan oksid shakliga o'tkazish ta'minlandi. Gidrometallurgik ishlov berish sulfat va xlorid kislotalar asosidagi eritmalarda nazorat qilinadigan texnologik sharoitlarda olib borildi. Tajriba natijalari kislotali oksidlovchi muhitlar ishqoriy tizimlarga nisbatan Ge ni ajratib olish samaradorligini yuqori darajada ta'minlashini ko'rsatdi. Eng yuqori ajratib olish ko'rsatkichlari kislorod yordamida faollashtirilgan hamda vino kislotali eritmalarda kuzatildi. Eritmali ekstraksiya va sorbsiya usullari Ge ni Fe, Zn, Cu va Pb kabi qo'shimcha elementlardan selektiv ravishda ajratishni ta'minladi. XRD, XRF va AAS tahlillari ishlab chiqilgan texnologiyaning samaradorligini tasdiqlab, texnogen materiallarni termik faollashtirishdan so'ng Ge ni ajratib olish darajasi sezilarli oshganini ko'rsatdi. Olingan natijalar kombinatsiyalashgan termik va gidrometallurgik ishlov berish texnologiyalari ikkilamchi sanoat resurslaridan germaniyini samarali hamda ekologik barqaror tarzda ajratib olish imkonini berishini, shu bilan birga sanoat chiqindilari to'planishini kamaytirish va texnogen xomashyodan foydalanish darajasini kengaytirishini ko'rsatadi.

**Kalit so'zlar:** germaniy, texnogen chiqindilar, gidrometallurgiya, oksidlovchi kuydirish, kislotali eritishda ajratish, eritmali ekstraksiya, noyob metallar.

## INTRODUCTION

Germanium (Ge) is a strategically important rare metalloid that is widely used in semiconductor devices, infrared optics, fiber-optic communication systems, solar cells, and military electronics due to its unique physicochemical and electrical properties. The continuously increasing global demand for high-purity Ge has intensified scientific and industrial interest in the development of efficient technologies for its recovery from both primary mineral resources and secondary technogenic raw materials [7].

The average concentration of Ge in the Earth's crust is relatively low, amounting to approximately 1.0–1.7 ppm, while economically independent germanium minerals occur rarely in nature. Germanium is mainly associated with sulfide ores, coal deposits, zinc concentrates, copper-smelting products, and pyrite-containing technogenic waste. Therefore, industrial waste generated during mining and metallurgical processing is increasingly being considered a promising secondary source of Ge. The utilization of technogenic waste not only contributes to the expansion of the mineral resource base, but also promotes environmental sustainability through the reduction of industrial waste accumulation containing  $Fe_2O_3$ ,  $SiO_2$ ,  $Al_2O_3$ , Zn, Pb, Cu, and other trace elements [2, 13].

As illustrated in Figure 1, zinc refinery residues and coal fly ash represent important secondary industrial sources for germanium production. The growing contribution of recycling technologies and technogenic resources confirms the industrial significance of secondary raw materials in ensuring sustainable and resource-efficient Ge recovery processes (Figure 1).

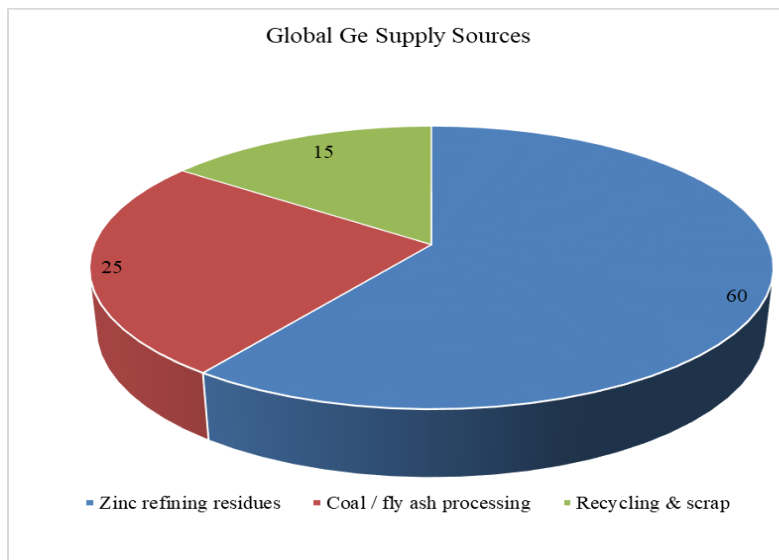
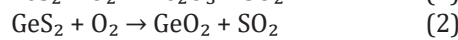
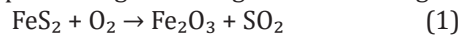


Figure 1. Main global secondary and industrial sources of germanium production

The Almalyk Mining and Metallurgical Complex generates significant quantities of flotation tailings, pyrite concentrates, smelting slags, and gas-cleaning dust during Cu–Mo ore beneficiation and metallurgical processing. These technogenic materials contain dispersed concentrations of Ge associated with sulfide phases such as  $\text{FeS}_2$ ,  $\text{CuFeS}_2$ , and  $\text{ZnS}$ . Hydrometallurgical and pyrometallurgical methods, including oxidative roasting, acid leaching, solvent extraction, and sorption, are considered effective approaches for the recovery of Ge from such secondary resources.

During oxidative roasting, sulfide compounds are transformed into oxide phases that exhibit higher solubility during subsequent hydrometallurgical processing according to the following reactions:



The efficiency of germanium extraction strongly depends on roasting temperature, leaching conditions, reagent concentration, and phase-transformation processes. Combined thermal and hydrometallurgical treatment technologies provide improved selectivity and higher recovery efficiency for low-grade technogenic materials. Therefore, this study investigates the technological feasibility of extracting germanium from technogenic waste generated at the Almalyk Mining and Metallurgical Complex using integrated processing technologies.

## LITERATURE REVIEW

The extraction of germanium (Ge) from technogenic waste and secondary raw materials has become an important area of modern hydrometallurgy and resource-saving technologies due to the growing demand for rare metals in the semiconductor, optical, and solar energy industries. Frenzel, Hirsch, and Gutzmer reported that Ge is mainly associated with sphalerite ( $\text{ZnS}$ ), pyrite ( $\text{FeS}_2$ ), and chalcopyrite ( $\text{CuFeS}_2$ ), while its concentration in natural ores remains relatively low. The authors concluded that technogenic waste generated during non-ferrous metallurgical processes represents a promising alternative source of germanium.

Wang, Chen, and Liu investigated sulfuric-acid leaching processes for Ge recovery from metallurgical dust and pyrite calcine. Their studies demonstrated that  $\text{H}_2\text{SO}_4$  leaching under optimized technological conditions ensures high germanium extraction efficiency while minimizing iron dissolution. The researchers also emphasized the importance of particle-size reduction and porous-structure formation for improving the efficiency of hydrometallurgical processing.

Moskalyk and Alfantazi extensively investigated hydrometallurgical purification technologies for rare metals, including germanium. Their studies demonstrated that solvent extraction using organophosphorus extractants such as D2EHPA and TBP provides effective selective separation of Ge from sulfate and chloride solutions. The authors also noted that ion-exchange sorption technologies improve the purity of germanium concentrates and reduce reagent consumption during processing.

Research conducted by Umarova, Umirzokov, and Makhmarezhabov demonstrated that technogenic waste generated at the Almalyk Mining and Metallurgical Complex contains valuable rare and dispersed elements such as Ge, Re, Se, and Te. The authors emphasized the importance of combined pyrometallurgical and hydrometallurgical technologies for the efficient processing of secondary raw materials and the reduction of environmental impacts.

Although numerous studies have investigated germanium recovery from industrial materials, the extraction of Ge from technogenic waste generated by the Almalyk Mining and Metallurgical Complex remains comparatively underexplored. Existing studies primarily focus on the recovery of Cu, Zn, and Fe, whereas the physicochemical behavior of Ge during roasting, leaching, and selective concentration processes has not yet been comprehensively investigated. Therefore, further research is required to determine optimal technological conditions for efficient and environmentally sustainable germanium recovery from secondary technogenic resources.

## RESEARCH METHODOLOGY

The research methodology for germanium extraction from technogenic waste generated by the Almalyk Mining and Metallurgical Complex was based on the application of combined pyrometallurgical and hydrometallurgical processing technologies. Technogenic materials containing Ge-bearing sulfide and oxide phases associated with Zn, Fe, Cu, and silicate compounds were selected as the primary objects of investigation. The collected waste samples underwent crushing, grinding, drying, and granulometric classification in order to obtain homogeneous materials suitable for subsequent experimental studies [1, 9, 15].

Thermal treatment was carried out through oxidative roasting within the temperature range of 600–900 °C to facilitate sulfur removal and the phase transformation of germanium-containing minerals into more soluble oxide forms [4]. Following the roasting process, the calcined materials were cooled and prepared for subsequent hydrometallurgical treatment.

Hydrometallurgical processing was performed using sulfuric-acid and hydrochloric-acid leaching systems under controlled technological conditions. The effects of leaching temperature, reagent concentration, solid-to-liquid ratio, and processing duration on germanium extraction efficiency were systematically investigated. In addition, oxygen-assisted and tartaric-acid leaching methods were applied to enhance the dissolution of Ge-bearing phases and improve metal recovery efficiency.

Selective separation and purification of germanium from impurity elements such as Fe, Zn, Cu, and Pb were carried out using solvent extraction and sorption technologies. Organophosphorus extractants and ion-exchange sorbents were employed to increase the selectivity and purity of germanium-containing solutions.

The phase composition and elemental characteristics of the investigated materials and processing products were analyzed using X-ray diffraction (XRD), X-ray fluorescence (XRF), and atomic absorption spectroscopy (AAS). The obtained experimental data were comparatively analyzed to determine the optimal technological parameters for efficient and environmentally sustainable germanium recovery from secondary technogenic resources (Figure 2).

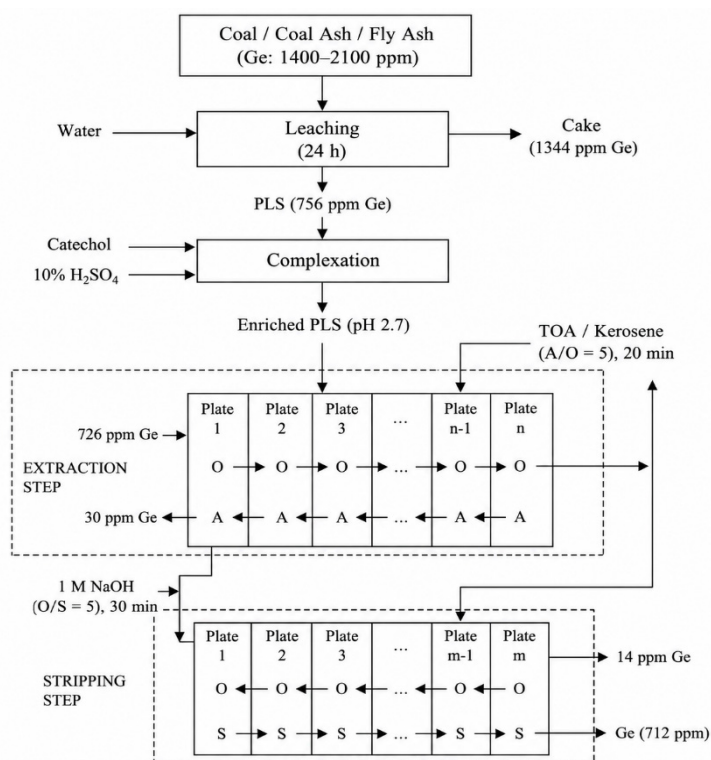


Figure 2. Technological Flow Diagram for Germanium Extraction from Technogenic Raw Materials

Hydrometallurgical processing of the roasted materials was carried out using  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$  leaching systems under controlled technological conditions. The separation of germanium from impurity elements such as Fe, Zn, Cu, and Pb was performed using solvent extraction, sorption, and selective-precipitation methods [6].

Chemical and phase-composition analyses were conducted using X-ray diffraction (XRD), X-ray fluorescence (XRF), and atomic absorption spectroscopy (AAS) techniques. The obtained experimental data were statistically processed in order to determine the optimal technological conditions for efficient and environmentally sustainable Ge recovery from technogenic raw materials [14].

## ANALYSIS AND RESULTS

The conducted experimental investigations demonstrated that technogenic waste generated by the Almalyk Mining and Metallurgical Complex represents a promising secondary raw material source for germanium recovery. Chemical and mineralogical analyses revealed that the investigated waste materials contained Ge mainly associated with sulfide and oxide phases, together with compounds containing Fe, Zn, Cu, Pb, and Si. X-ray fluorescence (XRF) and atomic absorption spectroscopy (AAS) analyses confirmed that germanium was unevenly distributed within pyrite concentrates, metallurgical dust, and flotation tailings, thereby necessitating preliminary thermal activation prior to hydrometallurgical processing [3].

Granulometric analysis demonstrated that fine fractions exhibited higher germanium concentrations due to their increased specific surface area and the more intensive association of Ge with sulfide particles [5]. As illustrated in Figure 3, the recovery efficiency of germanium from fly ash strongly depended on the type and chemical composition of the lixiviant used during the leaching process.

The obtained experimental results demonstrated that acidic oxidative systems provided higher Ge extraction efficiency compared with alkaline and neutral media. The highest recovery values were achieved in tartaric-acid and oxygen-assisted leaching systems, whereas NaOH solutions exhibited comparatively lower extraction efficiency. These findings confirm that the selection of an appropriate lixiviant plays a decisive role in enhancing germanium dissolution and improving the selective recovery of Ge from technogenic aluminosilicate materials (Figure 3).

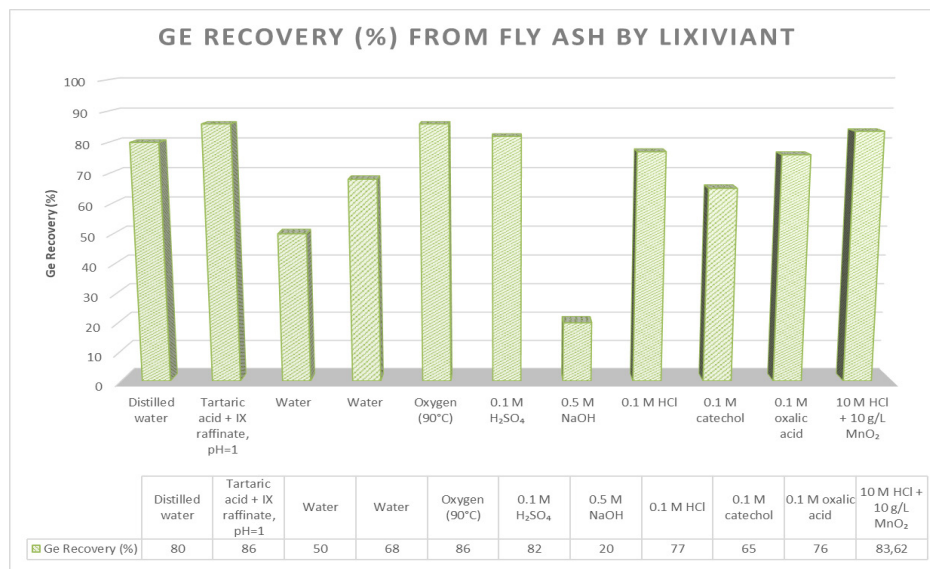


Figure 3. Effect of Different Lixiviants on Germanium Recovery from Fly Ash

During oxidative roasting, sulfur-containing compounds underwent thermal decomposition accompanied by the partial destruction of silicate and ferrite structures. The roasting process significantly improved the accessibility of germanium-bearing phases for subsequent acid leaching. Experimental results demonstrated that increasing the roasting temperature promoted sulfur removal and enhanced the transformation of Ge into soluble oxide forms [10].

However, excessively high roasting temperatures led to the partial sintering of the material and a decrease in leaching efficiency due to the formation of secondary phases. The optimal roasting conditions were observed within the temperature range of 700–800 °C, where the calcined products exhibited improved porosity and higher chemical reactivity (Figure 4).

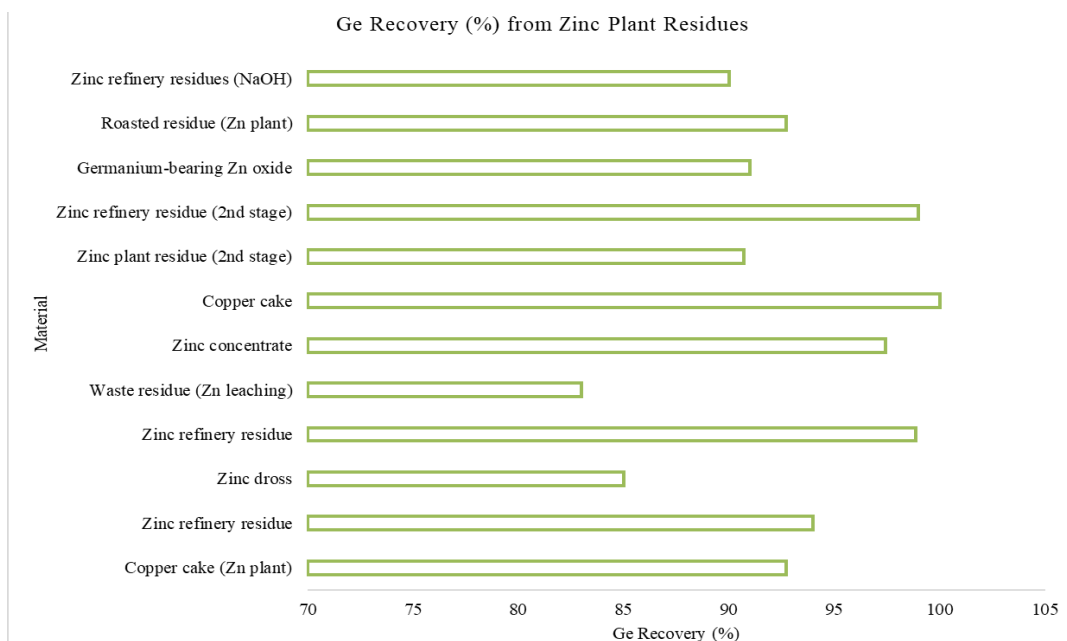


Figure 4. Recovery Efficiency of Germanium from Various Technogenic and Metallurgical Materials

As presented in Figure 4, the recovery efficiency of germanium from various technogenic and metallurgical materials varied depending on the mineralogical composition and processing conditions of the raw materials. The obtained results demonstrated that zinc-refinery residues, copper cake, and zinc concentrates exhibited the highest Ge recovery efficiencies due to the stronger association of germanium with sulfide and oxide phases that are readily accessible for hydrometallurgical treatment.

In contrast, waste residues generated after zinc leaching showed comparatively lower extraction efficiency because of the lower concentration and more complex distribution of Ge within silicate and ferrite structures. The experimental data confirm that metallurgical technogenic waste represents a promising secondary source for efficient germanium recovery and the development of resource-saving processing technologies.

Hydrometallurgical experiments demonstrated that sulfuric-acid and hydrochloric-acid leaching systems effectively dissolved germanium from roasted technogenic materials [12]. The leaching efficiency strongly depended on acid concentration, processing temperature, treatment duration, and solid-to-liquid ratio. Experimental observations indicated that moderate acid concentrations ensured the selective dissolution of Ge while limiting the transfer of impurity elements such as Fe and Si into the productive solutions.

The obtained pregnant leach solutions contained dissolved germanium together with Zn, Fe, and Cu ions, thereby requiring additional purification and selective concentration stages (Figure 5).

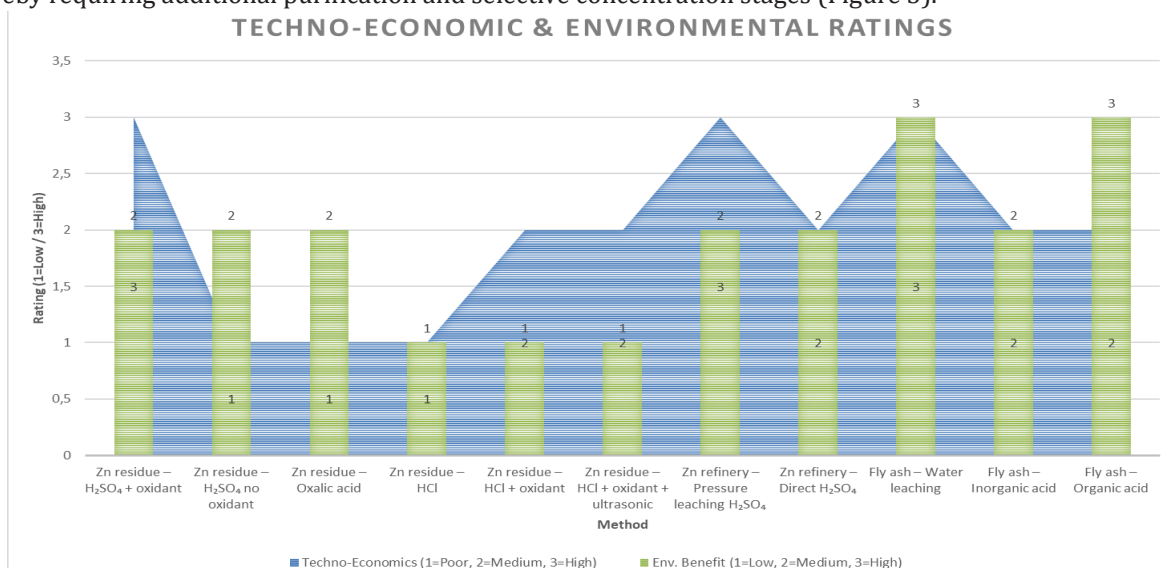


Figure 5. Comparative Techno-Economic and Environmental Assessment of Different Methods for Ge Extraction

## from Technogenic Materials

Selective extraction and purification experiments demonstrated that solvent extraction and sorption methods ensure efficient separation of Ge from impurity metals. The purification stage reduced the concentrations of Fe, Pb, and Cu compounds in the productive solutions and increased the purity of the germanium-bearing concentrate.

The obtained results confirmed that combined pyrometallurgical and hydrometallurgical treatment technologies significantly enhance the recovery efficiency of Ge from secondary technogenic resources [8]. Furthermore, the developed technological approach demonstrated important environmental and resource-saving advantages by reducing industrial waste accumulation and expanding the utilization of secondary mineral resources generated during metallurgical processing.

## CONCLUSION AND RECOMMENDATIONS

The conducted investigations demonstrated that technogenic waste generated by the Almalyk Mining and Metallurgical Complex represents a promising secondary source for germanium recovery. Chemical and mineralogical analyses confirmed the presence of Ge associated with sulfide, oxide, and silicate phases containing Fe, Zn, Cu, Pb, and other impurity compounds. Experimental results demonstrated that preliminary thermal treatment significantly improves the accessibility of germanium-bearing minerals for subsequent hydrometallurgical processing. Oxidative roasting within the optimal temperature range promoted sulfur removal and enhanced the transformation of Ge into soluble forms suitable for selective leaching.

The combined pyrometallurgical and hydrometallurgical processing technology developed in this study ensured efficient germanium extraction from technogenic raw materials. Acid leaching, solvent extraction, and sorption methods demonstrated high selectivity toward Ge while simultaneously reducing the concentration of impurity elements in productive solutions. The obtained results confirmed that integrated processing technologies not only improve Ge recovery efficiency, but also contribute to environmental sustainability through the utilization of industrial waste and the expansion of the secondary mineral-resource base.

The developed technological approach may be considered a promising solution for the sustainable processing of germanium-bearing technogenic materials. Furthermore, the implementation of integrated processing technologies can contribute to resource conservation, increased industrial efficiency, and the environmentally responsible utilization of secondary mineral resources generated during metallurgical operations.

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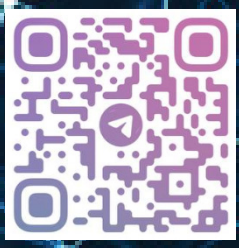
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