

**EXTRACTION AND RECOVERY OF CRITICAL METALS (Ga
AND Ge) FROM INDUSTRIAL WASTE**

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**EXTRACTION AND RECOVERY OF CRITICAL METALS (Ga
AND Ge) FROM INDUSTRIAL WASTE**

by

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submitted

in fulfilment of the requirements of the degree of

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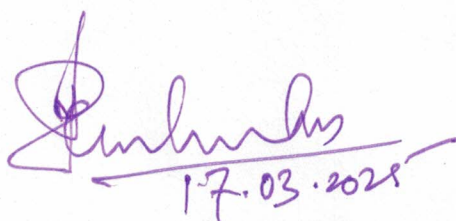
JULY 2025

Dedicated to my mother, father and my sister

CERTIFICATE

This is to certify that the thesis entitled “**Extraction and recovery of critical metals (Ga and Ge) from industrial waste**”, being submitted by **Ms Priyanka Dubey** to the **Indian Institute of Technology, Delhi**, for the award of the degree of ‘**Doctor of Philosophy**’ in the Department of Biochemical Engineering and Biotechnology is a record bonafide research work carried out by her under our supervision and guidance. We believe the thesis work has reached the requisite standards to fulfil the Doctor of Philosophy degree requirement.

The material contained in the thesis is original and has not been submitted in part or full to any other University or Institute for the award of any other degree or diploma.



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A handwritten signature in black ink, reading 'Priyanka Dubey' in a cursive style. The signature is written on a white background.

Priyanka Dubey

ABSTRACT

Gallium (Ga) and germanium (Ge) are categorised as technology-critical elements and play an indispensable role in advanced technologies, including semiconductors, military applications, photovoltaics and polymerisation catalysis. However, the supply risk associated with these metals is driven by their limited primary sources, import dependency and increasing industrial demand, necessitates further exploration of secondary sources for sustainable recovery. This study investigates the extraction of Ga and Ge and the selective recovery of Ga from copper sulfide flotation tailings, an underutilised but promising secondary source.

A comprehensive approach was used, with a detailed characterisation of copper ore, rough feed, concentrate and flotation tailings from Hindustan Copper Ltd. (Khetri Copper Complex, Rajasthan) to determine the occurrence and distribution of metals. Scanning Electron Microscopy and Energy-Dispersive X-ray Spectroscopy (SEM-EDX) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) were used to determine the elemental composition, and Mineral Liberation analysis (MLA) was used to determine modal mineralogy, particle size distribution, elemental department, mineral association, and liberation. Subsequently, chemical leaching using—hydrochloric acid (HCl), nitric acid (HNO₃), and sulfuric acid (H₂SO₄)—and organic acid (oxalic acid, citric acid) was conducted for the tailings. Bioleaching was performed with iron- and sulfur-oxidising microorganisms (*Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*) with both pure and mixed consortia. The study further explored solvent extraction techniques using di-tridecylamine (DTDA) for the removal of Fe from H₂SO₄ Pregnant leaching solution (PLS) and Trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104) for the selective extraction of Ga and Ge from HCl PLS. Ga was further selectively stripped into H₂SO₄ solution, which was subsequently used for its recovery via complexation with siderophores, utilising the GaLIophore technology to achieve high selectivity.

The results of the finding showed that the ore from Khetri Copper Complex (KCC) is mainly a sulfide ore, and the main minerals detected were chalcopyrite, pyrite and silicates (micas and quartz). Ga and Ge were detected in all four samples and accumulated in tailings to a certain extent. MLA results showed the association and interlocking of minerals, and the particle size analysis showed that the minerals were more liberated in small-size fractions. The chemical leaching results indicated that HCl and HNO₃ were suitable for leaching Ga and Ge from sulfide tailings, and organic acid was unsuitable for leaching metals from complex tailings. Ga leaching was 95% in 2M HNO₃ after 7 days, and the maximum Ge leaching of 78% was observed in 2M HCl after 7 days of leaching at 30°C and 150 rpm. Bioleaching results showed very low leaching of metals in both individual and mixed consortia. It showed that the adaptation of the organisms enhanced the leaching of the metals. Still, the tailings sample imposed specific toxicity on organisms' growth, affecting the overall leaching of metals.

The recovery of metals by solvent extraction using DTDA and Cyphos IL 104 showed promising results; DTDA extracted 89% of Fe from the H₂SO₄ leaching solution. However, 7% Ga and 14% Ge coextraction also occurred. Cyphos IL 104 effectively extracted approximately 85% of Ga at 3M HCl leaching solution and 80% of Ge at 10M HCl leaching solution. However, the addition of ascorbic acid—used to suppress Fe extraction—negatively impacted Ge extraction. Selective stripping of Ga was achieved using 0.5 M H₂SO₄, resulting in a final Ga recovery of 83% in the stripping solution under optimised conditions (0.005 M Cyphos IL 104, room temperature). While Ge extraction by Cyphos IL 104 reached 80%, its recovery remains a subject for future work and may be achieved through the application of suitable technologies. Further, GaLliphore technology was tested for the recovery of Ga from stripping solution containing a scarce amount of metal, where Ga from the stripping solution—containing 53 mg/L of Fe—was recovered through complexation with desferrioxamine B (DFOB), resulting in approximately 44% recovery of Ga. The research contributes to

developing an efficient, sustainable process for recovering Ga and Ge from secondary sources, addressing supply chain vulnerabilities. By integrating mineralogical insights and hydrometallurgical methods, this study paves the way for optimising resource utilisation while mitigating environmental concerns associated with mining waste.

Keywords: Critical metals, gallium, germanium, flotation tailings, bioleaching, solvent extraction, sustainable metal recovery.

गैलियम (Ga) और जर्मनियम (Ge) का औद्योगिक कचरे से निष्कर्षण और पुनर्प्राप्ति

सार

गैलियम (Ga) और जर्मनियम (Ge) को प्रौद्योगिकी-महत्वपूर्ण तत्वों के रूप में वर्गीकृत किया गया है और ये अर्धचालकों, सैन्य अनुप्रयोगों, फोटोवोल्टेइक्स तथा पॉलिमराइज़ेशन उत्प्रेरण सहित उन्नत तकनीकों में एक अनिवार्य भूमिका निभाते हैं। हालांकि, इन धातुओं से जुड़ी आपूर्ति जोखिम उनके सीमित प्राथमिक स्रोतों, आयात निर्भरता और बढ़ती औद्योगिक मांग के कारण उत्पन्न होती है, जो सतत पुनर्प्राप्ति हेतु द्वितीयक स्रोतों की और अधिक खोज को आवश्यक बनाती है। यह अध्ययन कॉपर सल्फाइड फ्लोटेशन टेलिंग्स से Ga और Ge की निष्कर्षण और Ga की चयनात्मक पुनर्प्राप्ति की जांच करता है, जो एक कम उपयोग किया गया लेकिन संभावनाशील द्वितीयक स्रोत है।

इस हेतु एक व्यापक दृष्टिकोण अपनाया गया, जिसमें हिंदुस्तान कॉपर लिमिटेड (खेड़ी कॉपर कॉम्प्लेक्स, राजस्थान) से प्राप्त तांबा अयस्क, रफ फीड, कंसंट्रेट और फ्लोटेशन टेलिंग्स का विस्तृत विशेषता निर्धारण किया गया ताकि धातुओं की उपस्थिति और वितरण को समझा जा सके। स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी और एनर्जी-डिस्पर्सिव एक्स-रे स्पेक्ट्रोस्कोपी (SEM-EDX) तथा इंडक्टिवली कपल्ड प्लाज़्मा मास स्पेक्ट्रोमेट्री (ICP-MS) का उपयोग तत्वीय संरचना निर्धारण हेतु किया गया, जबकि मिनेरल लिबरेशन एनालिसिस (MLA) का उपयोग मोडल मिनेरलॉजी, कण आकार वितरण, तत्वीय वितरण, खनिज संघटन और मुक्तता का आकलन करने हेतु किया गया।

इसके पश्चात, टेलिंग्स के लिए रासायनिक लीचिंग—हाइड्रोक्लोरिक अम्ल (HCl), नाइट्रिक अम्ल (HNO₃), और सल्फ्यूरिक अम्ल (H₂SO₄)—तथा जैविक अम्ल (ऑक्सैलिक अम्ल, साइट्रिक अम्ल) से की गई। जैवलीचिंग में लौह- और गंधक-ऑक्सीकारक सूक्ष्मजीवों (*Acidithiobacillus ferrooxidans* और *Acidithiobacillus*

thiooxidans) का उपयोग शुद्ध और मिश्रित दोनों समूहों में किया गया। अध्ययन में इसके अतिरिक्त डाई-ट्राइडेसाइलैमाइन (DTDA) द्वारा H₂SO₄ प्रेग्नेंट लीचिंग सोल्यूशन (PLS) से Fe हटाने और ट्राइहेक्सिल(टेट्राडेसाइल)फॉस्फोनियम बिस(2,4,4-ट्राइमेथिलपेंटिल)फॉस्फिनेट (Cyphos IL 104) द्वारा HCl PLS से Ga और Ge के चयनात्मक निष्कर्षण की सॉल्वेंट एक्सट्रैक्शन तकनीकों की भी पड़ताल की गई। Ga को आगे 0.5M H₂SO₄ में चयनात्मक रूप से स्ट्रिप किया गया, जिसे बाद में साइडरोफोर्स के साथ उसके कॉम्प्लेक्सेशन द्वारा पुनर्प्राप्त किया गया, जिसमें GaLiophore तकनीक का उपयोग कर उच्च चयनशीलता प्राप्त की गई।

परिणामों से ज्ञात हुआ कि खेड़ी कॉपर कॉम्प्लेक्स (KCC) से प्राप्त अयस्क मुख्यतः सल्फाइड प्रकार का है, और इसमें प्रमुख खनिजों के रूप में चालकोपाइराइट, पाइराइट और सिलिकेट्स (माइका व क्वार्ट्ज) पाए गए। Ga और Ge सभी चार नमूनों में मौजूद थे और कुछ सीमा तक टेलिंग्स में संचित पाए गए। MLA के परिणामों ने खनिजों की संगति और इंटरलॉकिंग को दर्शाया, जबकि कण आकार विश्लेषण से पता चला कि छोटे आकार वाले अंशों में खनिज अधिक मुक्त हुए थे। रासायनिक लीचिंग परिणामों से ज्ञात हुआ कि HCl और HNO₃, सल्फाइड टेलिंग्स से Ga और Ge के निष्कर्षण हेतु उपयुक्त थे, जबकि कार्बनिक अम्ल जटिल टेलिंग्स से धातु निष्कर्षण में अप्रभावी रहे। 2M HNO₃ में 7 दिनों के बाद Ga का 95% निष्कर्षण हुआ, और 2M HCl में 30°C तापमान और 150 rpm पर 7 दिनों में Ge का अधिकतम 78% निष्कर्षण प्राप्त हुआ।

जैवलीचिंग के परिणामों से यह स्पष्ट हुआ कि व्यक्तिगत और मिश्रित समूहों में धातुओं का निष्कर्षण बहुत कम था। हालांकि, सूक्ष्मजीवों की अनुकूलन प्रक्रिया ने धातु निष्कर्षण में कुछ वृद्धि दिखाई, फिर भी टेलिंग्स के नमूनों ने उनके विकास पर विशिष्ट विषाक्तता प्रभाव डाला, जिससे कुल निष्कर्षण प्रभावित हुआ।

DTDA और Cyphos IL 104 द्वारा सॉल्वेंट एक्सट्रैक्शन से धातुओं की पुनर्प्राप्ति के परिणाम आशाजनक रहे; DTDA ने H₂SO₄ लीचिंग सोल्यूशन से Fe का 89% निष्कर्षण किया, लेकिन साथ ही 7% Ga और 14% Ge का सह-निष्कर्षण भी हुआ। Cyphos IL 104 ने 3M HCl लीचिंग सोल्यूशन से लगभग 85% Ga और 10M HCl से 80% Ge को प्रभावी रूप से निष्कर्षित किया। हालांकि, Fe निष्कर्षण को दबाने हेतु जोड़ी गई एस्कॉर्बिक एसिड ने Ge निष्कर्षण पर प्रतिकूल प्रभाव डाला। 0.5M H₂SO₄ द्वारा Ga का चयनात्मक स्ट्रिपिंग किया गया, जिससे अनुकूलित स्थितियों में स्ट्रिपिंग सोल्यूशन में 83% Ga की अंतिम पुनर्प्राप्ति प्राप्त हुई (0.005M Cyphos IL 104, कमरे के तापमान पर)। जबकि Cyphos IL 104 द्वारा Ge का निष्कर्षण 80% तक पहुंचा, उसकी पुनर्प्राप्ति अभी भी भविष्य के अनुसंधान का विषय बनी हुई है और उपयुक्त तकनीकों के उपयोग से प्राप्त की जा सकती है।

आगे, स्ट्रिपिंग सोल्यूशन से Ga की पुनर्प्राप्ति हेतु GaLliphore तकनीक का परीक्षण किया गया, जिसमें Fe की 53 mg/L उपस्थिति वाले स्ट्रिपिंग सोल्यूशन से *Desferrioxamine B (DFOB)* के साथ कॉम्प्लेक्सेशन द्वारा लगभग 44% Ga पुनर्प्राप्त किया गया। यह शोध द्वितीयक स्रोतों से Ga और Ge की पुनर्प्राप्ति के लिए एक कुशल, टिकाऊ प्रक्रिया के विकास में योगदान करता है, जिससे आपूर्ति श्रृंखला की कमजोरियों को संबोधित किया जा सके। खनिज विज्ञान और हाइड्रोमेटलर्जिकल विधियों के एकीकरण के माध्यम से यह अध्ययन संसाधनों के इष्टतम उपयोग और खनन अपशिष्ट से संबंधित पर्यावरणीय समस्याओं को कम करने की दिशा में मार्ग प्रशस्त करता है।

कीवर्ड्स: महत्वपूर्ण धातुएँ, गैलियम, जर्मेनियम, फ्लोटेशन टेलिंग्स, जैवलीचिंग, सॉल्वेंट एक्सट्रैक्शन, सतत धातु पुनर्प्राप्ति.

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