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Solvent Extraction of Germanium from Fe-Cu-Co-Ge Alloy: The Role of Isobutyl Methyl Ketone in a Ferric Iron-Containing Medium

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ABSTRACT

This study focuses on the selective extraction of germanium from a leachate of a Fe-Cu-Co-Ge alloy, using isobutyl methyl ketone (MIBK) as a solvent in an environment rich in ferric iron. Tests were conducted by varying several operational parameters, including the organic-to-aqueous phase ratio and the pH of the solution. The results showed a germanium extraction yield of 55.48% at a pH of 1.5. By optimizing the phase ratio, an additional yield of 15.5% was achieved at a ratio of 5/1. As the germanium extraction yield increased, that of ferric iron decreased by 6.16%, a reduction that did not have a significant impact, given that the concentration of ferric iron was 100 times higher than that of germanium. The removal of iron in the aqueous phase improved the germanium extraction yield by approximately 9%. Through multiple extraction steps, the germanium extraction yield reached 99.2%, although this led to a decrease in the extractant's selectivity towards other metals. These results highlight the effectiveness of solvent extraction for germanium recovery, while also underscoring the complex interactions between metals during the extraction process.

Keywords: solvent extraction, alloy, ferric ion, hydrometallurgy and polymetallic leachate

INTRODUCTION

The Democratic Republic of Congo (DRC) is renowned for its vast and rich polymetallic deposits, which are found in almost all its provinces. It stands out as one of the world's leading producers of cathode copper, as well as cobalt, zinc, tin, coltan, germanium, and gold concentrates. Furthermore, the country is famous for its diamond production, along with other precious and semi-precious stones.

This mineral wealth represents a strategic asset for the economic development of the DRC and attracts interest from investors worldwide (Mbuyi, 2021; Tshibanda, 2020; Ngoy, 2022; Kambale, 2019; Moke, 2023). Its subsoil also contains a wide variety of minerals, including abundant iron, nickel, platinum, calcium, mercury, silver, lead, zirconium, uranium, and rare earth elements (Kande, 2021; Lubala, 2020; Mbuyi, 2022; Senga, 2019; Makasi, 2023).

The primary germanium-bearing minerals notably include argyrodite (Ag_8GeS_6), germanite ($(Cu,Fe)_2GeS_4$), and gehlenite ($Ca_2Al_2GeSiO_7$). Zincite (ZnO) and coal fly ash, which contain traces of germanium, can also be added to this list. The only exploited germanium deposit in the DRC is located in the Haut-Katanga province, more precisely in Kipushi (Mworozi, 2018; Ntamakou, 2015; Christman et al., 2010; McGowan, 2007; Oden, 2000). However, the DRC is not among the leading producers of germanium despite the renown of its Kipushi deposit (Muyej, 2020; Tshibanda, 2017; Mbuyi, 2015; Kambala, 2010; Kambundji, 2001).

Due to its semiconducting and optical properties, germanium is of great interest to industry. It also plays a crucial role in the composition of optical fibers, particularly in infrared optical systems used in electronics (Hernández et al., 2006; Kayembe et al., 2023; Li et al., 2021; Smith & Zhang, 2018; Rogers et al., 2015; Mahmood & Xu, 2010).

Germanium is sold on international markets in two main forms: pure germanium and germanium dioxide (Blazy, 2021; Jdid, 2020; Pungwe, 2022; Kambale, 2019; Mbuyi, 2023). Indeed, the production of germanium is a matter of raw material supply, which primarily consists of residues from zinc and copper metallurgy, coal fly ash, and the recycling of optical fibers.

Furthermore, several methods are used for its production, including gravity separation combined with low-temperature sintering and chlorination distillation (Kambale, 2019), leaching (Jdid, 2020), precipitation (Blazy, 2021), solvent extraction (Kambale, 2019), and electrolysis (Blazy, 2021).

Thus, the objective of this study was to develop and optimize an effective extraction method for the separation and purification of germanium from a complex aqueous solution containing several other metals, including iron in high concentration, while minimizing germanium losses. Specifically, the study was conducted to investigate the effect of pH on the extraction efficiency of germanium and the other metals present in the initial aqueous solution, to determine the optimal concentration of MIBK for efficient germanium extraction, to evaluate the impact of the organic/aqueous ratio on the yield, to separate iron from other metals by extraction with ammonium thiocyanate diluted in isopropanol, and to optimize the conditions for the final extraction of germanium after iron removal to achieve maximum yield.

MATERIALS AND METHODS

Origin of the Studied Sample

The aqueous solution used in this study was collected on April 17, 2024, from the facilities of the Société de Traitement de Terril de Lubumbashi (STL), specifically from the company's hydrometallurgical plant. At this facility, the alloy is first crushed to increase the surface area of contact, which enhances the efficiency of chemical reactions and maximizes the recovery of germanium and other present metals. After crushing, a first leaching step is performed, primarily aimed at recovering cobalt while removing other undesirable metals from the residues. This step uses sulfuric acid to selectively dissolve the cobalt. Following this initial leaching, the germanium remains in the solid residue. The resulting pulp is then filtered to separate the solid residue, which contains the germanium, from the sulfuric acid solution. This residue is then subjected to a second leaching with sulfuric acid, allowing the germanium to be dissolved into solution. After this step, the pulp is filtered again to recover the solution containing the dissolved germanium. This two-step leaching approach optimizes germanium recovery while minimizing the loss of precious metals. The solution used in this study comes from the second leaching step carried out at the hydrometallurgical plant of the Lubumbashi tailings processing company (STL). It was carefully stored in a 20-liter plastic container and kept in the chemistry laboratory of the Faculty of Science and Technology. This storage ensures the stability of the solution for subsequent analyses.

Readjustment of the Aqueous Phase pH

To prepare the aqueous phase for the extraction of germanium using MIBK, the pH of the solution was adjusted to values between 1 and 2.5, in increments of 0.5. The protocol followed was as follows: four 60 ml samples of the initial solution, with a pH of 0.8, were collected and transferred into four separate beakers. A few drops of 0.1 M sodium carbonate were added to each beaker to achieve the desired pH.

Preparation of the Organic Phase

The organic phase consisted of methyl isobutyl ketone (MIBK) as the extracting agent and kerosene as the diluent, in a 1:3 ratio, corresponding to 25% MIBK and 75% kerosene. To prepare this solution, 750 ml of kerosene were poured into a 1000 ml volumetric flask, which was then filled to the calibration mark with MIBK. The solution was thoroughly mixed by stirring for several minutes to ensure optimal homogeneity.

Iron Removal Test

To test iron removal, 60 ml of the aqueous phase were measured using a graduated cylinder and poured into a 250 ml separatory funnel. An equivalent volume of the organic phase, composed of ammonium thiocyanate and isopropyl alcohol in a 1:1 ratio, was added. Additionally, 4 g of NaCl were incorporated. The separatory funnel containing the mixture was sealed tightly and shaken vigorously for at least 5 minutes. After shaking, the mixture was allowed to separate, and the separation time was recorded (Gracia, 2022). Once a clear separation was observed, the aqueous phase was carefully decanted into a clean flask.

Experimental Procedure for Germanium Extraction

Two types of extraction were performed: the first on the solution as sampled from the plant, and the second on the solution that had undergone iron ion extraction tests, following this procedure: using a graduated cylinder, a volume of the aqueous phase was measured and poured into a 250 ml separatory funnel. A corresponding volume of the organic phase was added, respecting the planned organic/aqueous ratios for each test (1/5, 1/2, 1/1, 2/1, and 5/1). The separatory funnel containing the mixture was sealed tightly and shaken vigorously for at least 5 minutes. After shaking, phase separation was observed, and the time required for this separation was recorded. Once the mixture was fully separated, the aqueous phase was recovered into a clean and suitable flask.

Chemical Analyses

Chemical analyses were carried out at the Office of Control of the Congo (OCC) in Lubumbashi, using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). These analyses determined the concentrations of metallic elements at different pH levels. The table below presents these concentrations, providing crucial information for understanding the impact of pH on metal extraction and the efficiency of the separation processes. These data are essential for optimizing extraction conditions and improving the recovery of target elements.

Table I. Concentrations (mg/L) of metals in aqueous solutions at different pH levels

Phase aqueous	Ge	Co	Cu	Fe	Mn	Ni	Zn
pH 1	184.2	2181	433	18340	5.174	25.49	252.2
pH 1.5	183.5	2181	431.8	18335	5.108	25.45	245.7
pH 2	181.4	2181	429.1	18327	5.052	25.31	238.8
pH 2.5	176.1	2176	422.3	18255	5.027	25.07	228

F	*P-value*	*F crit*
1.14E-05	1	3.008787

The results presented in Table I above were analyzed using one-way ANOVA. This statistical treatment reveals that the calculated F-value (1.14×10^{-5}) is significantly lower than the critical F-value (3.01). This indicates that there is no significant difference in the extraction procedure across different pH levels. The addition of sodium carbonate did influence metal concentrations, as shown in the study by Mohamed et al. (2018), which reports a slight effect at pH 2.5. At this pH, the concentration of germanium decreased by 4.39%, copper by 2.47%, iron by 9.59%, and cobalt by 5%. However, these variations are not considered significant. Similarly, nickel and zinc did not experience any negative impact on their concentrations as pH increased relative to their initial levels. The addition of carbonate led to the precipitation of some metals and the basification of the solution. Carbonate is commonly used as a precipitating agent in extractive metallurgy to facilitate metal separation.

RESULTS AND DISCUSSION

Solvent extraction of germanium represents a promising technique for the recovery of this metal from aqueous solutions. This method, often favored for its selectivity and efficiency, enables the separation of germanium from other elements present in the solutions. In this study, we evaluated extraction performance based on various parameters, such as pH and reagent concentrations. The results obtained provide valuable insights into the extraction mechanisms, as well as the optimal conditions for maximizing germanium recovery while minimizing losses of other metals. These data are essential for developing more efficient and sustainable extraction processes in the context of extractive metallurgy.

Variation of pH in Solvent Extraction of Germanium

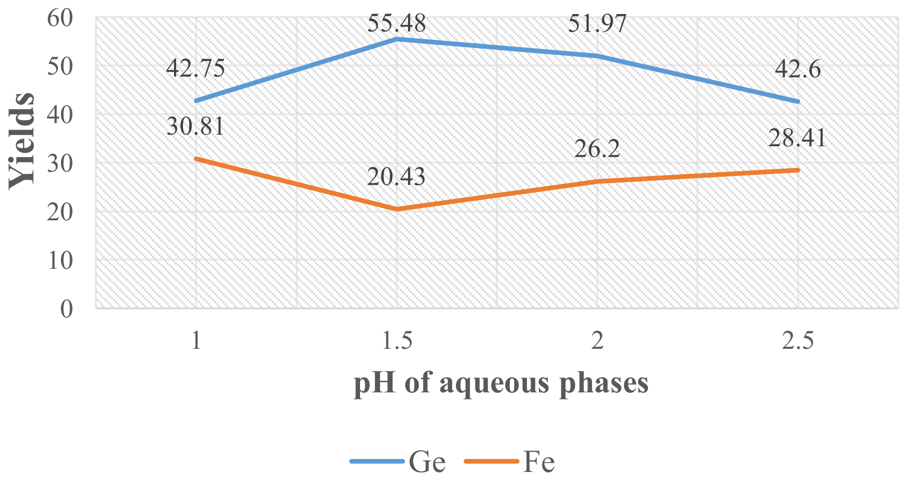

Figure 1. Evolution of the extraction yield of germanium at different pH levels of the aqueous phases

The extraction yield of iron decreases at pH 1.5 and shows slight variations at pH 2, stabilizing from pH 2.5 onwards. In contrast, germanium reaches a maximum yield of 55.48% at pH 1.5, then decreases at lower pH levels. This effect of pH on the extraction yield of germanium has been illustrated by Elena et al. (2016) and Oka et al. (1955). The results obtained are consistent with those of other studies, such as those by Xie et al. (2018), Antonio et al. (2012), Jiri et al. (2010), Hilebrant and Hoste (1958), and Ayres (1949), which also showed that germanium can be efficiently extracted in most cases at pH levels between 1 and 2. These observations largely depend on the physicochemical properties of the complexing agent used.

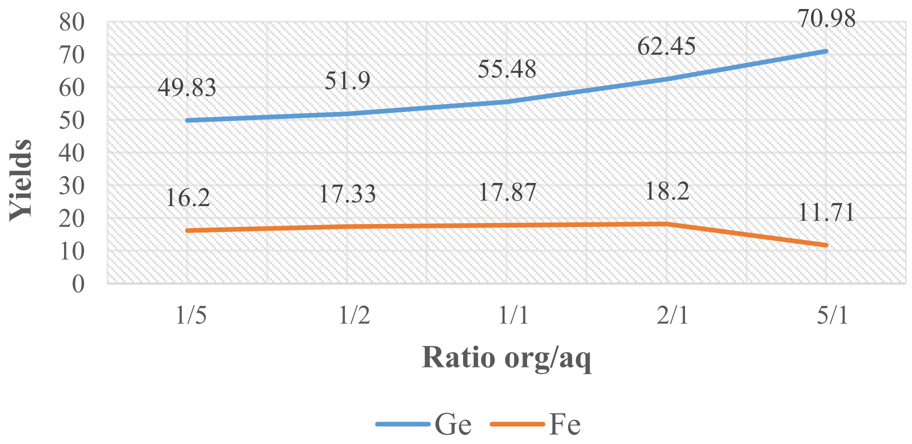

Figure 2. Evolution of the extraction yield of germanium at different organic/aqueous (Org/Aq) ratios

Analysis of the extraction yield trends presented in Figure 2 clearly shows that the extraction yield of germanium increases with the organic/aqueous ratio, reaching a maximum of 70.98% at a ratio of 5/1. This observation underscores that higher organic/aqueous ratios, such as 2/1 and 5/1, favor germanium extraction, as indicated by Smith (2007). Concurrently, the yield of iron decreases at these same ratios, dropping from 18.21% to 11.71%.

This demonstrates that increasing the organic ratio not only enhances germanium recovery but also reduces the co-extraction of iron, which is crucial for optimizing selectivity. The selectivity of germanium relative to iron increases with higher organic/aqueous ratios, suggesting that MIBK becomes more selective for germanium at higher concentrations of the organic phase.

These results align with the work of Xie et al. (2018), Elena et al. (2016), Jiri et al. (2010), Pierre (2008), Smith (2007), Hilebrant and Hoste (1958), and Oka and Kanno (1955), all of whom reported similar behaviors during germanium extraction.

The high presence of iron during the extraction process led to trials of iron removal using ammonium thiocyanate. This strategy aims to improve germanium selectivity by reducing the concentration of iron in the aqueous phase, which could promote even more efficient germanium extraction. These results highlight the importance of optimizing extraction conditions to maximize germanium recovery while minimizing interference from other metals, particularly iron.

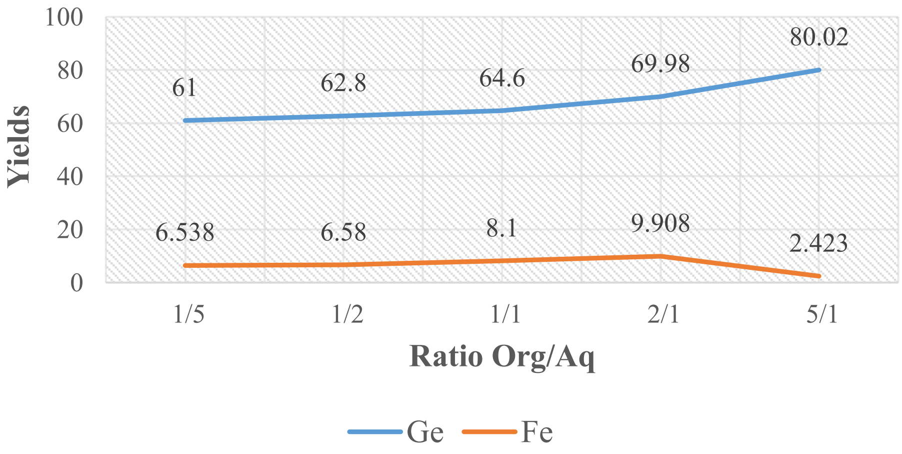

Figure 3. Germanium extraction yield after iron removal

Following iron separation, the final extraction of germanium using a solution containing 25% MIBK and 75% kerosene as diluent increased the extraction yield by 10% compared to previous conditions. This significant improvement highlights the importance of optimizing extraction conditions to maximize germanium recovery.

The selectivity for germanium was significantly enhanced after the initial iron removal using ammonium thiocyanate. This crucial step not only reduced the iron concentration in the aqueous phase but also created a more favorable environment for selective germanium extraction. Studies by Zaitsev et al. (2021), Tang et al. (2020), Perry et al. (2019), Chagnes et al. (2018), Damaye et al. (2016), and Zhang et al. (2006) corroborate these findings, indicating that preliminary separation of impurities, such as iron, is essential to enhance the selectivity of extracting agents.

This approach demonstrates that managing metallic interferences is fundamental in the germanium extraction process. By reducing iron presence, not only is the yield increased, but the purity of the recovered germanium is also optimized. These results suggest that implementing impurity removal techniques should become a standard step in germanium extraction protocols to improve overall efficiency and cost-effectiveness of industrial processes.

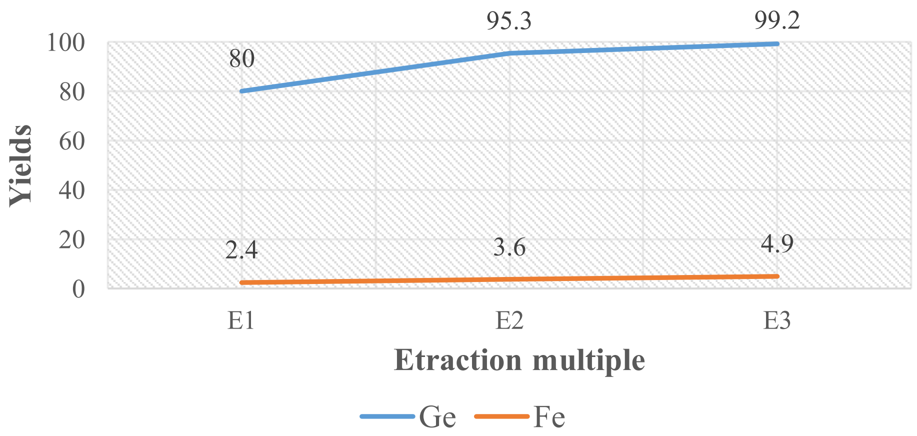

Figure 4. Multiple extraction yield

The cumulative yields of germanium extraction show a significant increase, reaching 99.2% after three cycles, demonstrating the high efficiency of the extraction process for this metal. This exceptional performance highlights not only the viability of solvent extraction but also the importance of the optimized extraction conditions that were implemented.

In contrast, the yield of iron showed a slight increase, with cumulative values of 3.6% for the second extraction and 4.9% for the third extraction. This trend indicates that, although germanium recovery is highly efficient, there are challenges associated with the co-extraction of impurities, particularly iron. The slight increase in iron yield suggests that residual amounts of iron persist even after multiple extraction cycles, which may require additional strategies to minimize its presence.

The effect of multiple extraction on yield is well documented in the literature, as shown by the work of Zaitsev et al. (2021), Tang et al. (2020), Perry et al. (2019), Chagnes et al. (2018), and Damaye et al. (2016). These studies confirm that repeated extraction cycles can improve overall yield, but they also emphasize the importance of managing selectivity to avoid unwanted recovery of other metals.

Thus, although multiple extraction proves beneficial for maximizing germanium recovery, it is crucial to explore methods to reduce the co-extraction of iron and other impurities. This could include preliminary removal steps or the use of more selective extracting agents. In summary, optimizing these processes is essential to ensure not only high yield but also the purity of the recovered germanium, which is fundamental for industrial applications.

CONCLUSION

This study demonstrated the effectiveness of solvent extraction of germanium from a complex leachate containing iron, copper, and cobalt, using isobutyl methyl ketone (MIBK) as the solvent. The results obtained highlight the importance of operational parameters on extraction yield. At pH 1.5, a maximum yield of 55.48% was achieved for germanium. By optimizing the organic-to-aqueous phase ratio to 5/1, an additional yield of 15.5% was obtained, bringing the total yield to 70.98%.

Iron removal improved the germanium extraction yield by approximately 10%, while multiple extraction led to an impressive cumulative yield of 99.2% after three cycles. These results underscore not only the effectiveness of the solvent extraction method but also the complex interactions between metals during the extraction process.

However, the decrease in extractant selectivity during multiple extractions highlights the need for further research to optimize the separation of germanium from other metals. Improving extraction methods could have significant implications for industry, particularly in the context of valorizing mineral resources in the Democratic Republic of Congo, a country rich in precious metals but still under-exploited. Future studies should focus on exploring other extracting agents and refining extraction processes to maximize the selective recovery of germanium and associated metals.

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