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Environmentally Friendly Leaching of Antimony from Mining Residues Using Deep Eutectic Solvents: Optimization and Sustainable Extraction Strategies

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Abstract: This paper focuses on the environmental leaching of antimony, a critical mineral, using deep eutectic solvents. Mining residues often contain embedded antimony, posing environmental risks. Deep eutectic solvents, known for being low in toxicity, cost-effective, and environmentally friendly, present a promising avenue for sustainable antimony extraction. The study focuses on optimizing the leaching process through experimental analysis by considering variables such as temperature, time, and percentage of solids. Different deep eutectic solvent (DES) compositions are being studied, including choline chloride with malonic acid, thiourea, and ethylene glycol in different molar ratios, to identify the most effective solvent system for antimony extraction. A sample, originally obtained from mining waste produced via the flotation of antimonite ore, was used to test these three types of DESs. By optimizing the leaching process by changing the ratio of solid and liquid components, as well as the amount of oxidizing agent up to 3 g, iodine, yields of up to 100% were achieved after leaching for 4 h at 100 °C. The aim of the study is to advance sustainable resource management by providing knowledge on an ecological and feasible method of extracting antimony from mine waste, leading to more conscious and efficient resource practices in the mining sector.

Keywords: hydrometallurgy; solvometallurgy; antimony; leaching; critical raw materials; deep eutectic solvents; mining waste

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1. Introduction

Commodities are essential for the global economy, supporting industries and technological advancement [1]. Both EU and global focus on steady raw material supply is critical [2]; the EU lists 34 critical raw materials, such as copper and nickel, that, while not meeting CRM criteria, are considered strategic under EU law due to their economic value. Key sectors include electronics, automotive, aerospace, defense, healthcare, and steel [3,4]. The concentration of critical raw materials in certain countries and their heavy reliance on imports pose significant supply risks. Their scarcity stems from their unique properties that make them essential for various applications in clean technologies, such as solar panels, wind turbines, electric vehicles, and energy-efficient lighting [5]. Access to these materials is crucial for technological advancement and improving quality of life, but their supply is at risk due to low production. There is a growing focus on innovative recycling, extracting resources from waste (mining, water treatment, industrial processes, discarded products). The emphasis placed on recovery is expected to increase in future [6,7].

The extraction of antimony from ore is usually conducted via either hydrometallurgical or pyrometallurgical methods. While both approaches have their advantages and disadvantages, hydrometallurgical techniques are better suited to low-grade ores. The raw material needs to be prepared before leaching, often resulting in the formation of a concentrate. At this stage, valuable minerals are typically concentrated using flotation or gravity separation techniques [8]. Antimony is usually extracted from ore using either hydrometallurgical or pyrometallurgical processes. While both approaches have their advantages and disadvantages, hydrometallurgical processes are more suitable for low-grade ores [9].

Chemical processes are used for low-grade or complex ores that are difficult to treat, as well as for ores containing trace elements and secondary materials (waste). Traditional treatment methods may not always be sufficient to extract metal concentrates, making the use of chemical treatments crucial. Recently, we have seen an increase in the use of chemical treatments in the management of secondary raw materials. The drive to recycle metal-bearing secondary raw materials is driven by the scarcity of primary resources and the need to protect the environment. Addressing the global challenge of recovering metals from secondary raw materials and reducing environmental impact through recycling is inherently complex. A holistic, interdisciplinary approach is essential when dealing with different types of primary or secondary raw materials, requiring the integration of different methods and processes [10,11].

The hydrometallurgical process of raw material processing is complex and consists mainly of two basic phases: leaching and precipitation. This complex process integrates various factors, such as temperature, time, agitation, concentration of leaching agent, and material-specific variables, that together determine the efficiency of the process. Choosing the right leaching matrix is critical, and the choice of leach has a significant impact on the overall efficiency of the process. Although many leaching agents are available, there is growing concern about their effectiveness, toxicity, and environmental impacts [12]. For example, in the past, cyanide and strong acid solutions were widely used for gold leaching, but due to environmental concerns, many countries have banned cyanidation, leading to the adoption of alternative reagents, such as thiourea, sodium thiosulphate, bacteria, and others [13].

Leaching is a process used to extract valuable metals from ores or materials containing them by dissolving them in a solvent. Antimony, a metalloid element, can undergo different types of leaching depending on the specific conditions and reagents used. Here are some common types of leaching processes for antimony:

Acid leaching involves using acidic solutions to dissolve antimony from its ores or concentrates. Sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) are commonly used as leaching agents. The general reaction for acid leaching of antimony ore can be represented as follows:

$$Sb_2S_3 + 2HCl \rightarrow 2SbCl_3 + 3H_2S \tag{1}$$

This method has gained widespread adoption in many countries due to its effectiveness. Initially, crude antimony is leached in a solution, resulting in the formation of a thin layer of Sb_2O_3 on its surface over time. The antimony layer is then removed, and the purified antimony is dissolved in a more dilute mineral acid solution. Overall, leaching with mineral acids remains one of the most established methods for extracting antimony metal [14,15].

Alkaline leaching involves using alkaline solutions to dissolve antimony. Sodium hydroxide (NaOH) and ammonia (NH_3) solutions are often employed as leaching agents. Alkaline leaching may be preferred in certain cases where acid leaching is not suitable due to the nature of the ore or to avoid the formation of unwanted precipitates. The reaction used for the alkaline leaching of antimony depends on the specific conditions but generally involves the dissolution of antimony oxide minerals [16].

Cyanide leaching is a method commonly used for extracting gold and silver, but it can also be applied to certain antimony ores. Sodium cyanide (NaCN) is typically used as the leaching agent in cyanide leaching. Cyanide leaching of antimony can be complex and requires careful control of conditions to prevent the formation of toxic species. The reaction involves the formation of soluble antimony cyanide complexes [17].

Oxidative leaching involves using oxidizing agents to enhance the dissolution of antimony. Common oxidizing agents include hydrogen peroxide (H_2O_2) and nitric acid

(HNO_3). Oxidative leaching can be particularly effective for refractory antimony ores or concentrates that are difficult to treat via conventional methods. The reaction mechanisms in oxidative leaching are complex and can involve the oxidation of antimony sulfide minerals to soluble antimony species.

These are some of the main types of leaching processes that can be used for extracting antimony from its ores or concentrates. The choice of leaching method depends on factors such as the nature of the ore, desired product specifications, environmental considerations, and economic feasibility [18].

The process must be carefully monitored using worldwide guidelines based on a contemporary understanding of toxicity and environmental principles to comply with current environmental regulations. All solvents must be removed before they are discharged into the environment [19]. The recovery of metals from solution is typically achieved using one of four key methods: cementation, precipitation, ion exchange, or electrolysis. Electrolysis is a commonly used approach, particularly for metals including copper, silver, and gold [20]. However, there are significant challenges associated with metal recovery from solution, including the need to carefully control the deposition process by maintaining pH levels and relying on complex agents like cyanide or ammonia.

As demand for metals grows, the metals industry is increasingly reliant on low-grade ores. There is currently a focus on recovering metals from industrial process residues or mine tailings, previously considered waste. Due to the low metal concentrations, pyrometallurgical methods often are not economically viable for processing these residues. Similarly, most hydrometallurgical processes struggle to recover metals from low-grade ores, tailings, or industrial residues with minimal valuable metals due to the lack of specificity of leaching with aqueous acid solutions. In cases where conventional pyrometallurgical or hydrometallurgical processes cannot effectively extract metals from low-grade ores, mine tailings, industrial residues, and, possibly, municipal wastes, solvometallurgy emerges as a potential alternative [21,22].

Ionic liquids and deep eutectic solvents have provided a new, innovative approach and given rise to new branches of hydrometallurgy called ionometallurgy and solvometallurgy. In contrast to hydrometallurgy, solvometallurgy utilizes non-aqueous solutions that blend Lewis and Bronsted acids and bases. These mixtures offer novel opportunities for the extraction of mineral resources and are appropriate for use in processing lower-grade ores. Currently, due to the depletion of high-grade raw materials containing larger quantities of useful resources, there is a pressing need to switch to processing lower-grade ores. An environmentally acceptable solution to this issue is solvometallurgy [22].

Deep eutectic solvents are mixtures of Lewis or Brønsted acids and bases that produce liquids. DESs are commonly classified as a form of ionic liquids due to their shared properties such as high thermal stability, low volatility, and low vapor pressure, among others. These desirable attributes make DESs an excellent substitute for various volatile organic compounds utilized in both research and practice. In contrast to ionic liquids, the majority of which are costly reagents that are neither biodegradable nor environmentally friendly, DESs offer a more cost-effective alternative. Additionally, their preparation is comparatively uncomplicated, their toxicity is minimal, and, in contrast to ionic liquids, they are also biodegradable [23,24]. DESs comprise large asymmetric ions with low lattice energy. They are primarily synthesized through the coupling of a quaternary ammonium salt with a hydrogen bond donor (HBD). Most of the DESs that have been studied and produced can be divided into four categories:

Type I—Quaternary ammonium salt and metal chloride;
Type II—Quaternary ammonium salt and metal chloride hydrate;
Type III—Quaternary ammonium salt and HBD;
Type IV—metal chloride hydrate and HBD [23].

In industrial processes, a combination of choline chloride and hydrated metal halides (type II) is utilized due to their low cost and tolerance to air and moisture. Type III DESs, obtained from a blend of choline chloride and HBD, exhibit the capacity to dissolve a diverse array of metal species, rendering them a point of interest. Various HBDs, such as amides, carboxylic acids, and alcohols, were studied. These liquids are easily prepared and do not react much with water. Additionally, many of them are biodegradable and can be obtained at low cost [23]. The production processes for DESs involve merely mixing the components with slight heating. HBA and HBD serve as the components in this case. During the preparation, no chemical reaction occurs, which indicates their low production expenses and extensive range of potential applications [25,26]. Although DES is considered the least toxic of the leaching agents, it is not completely non-toxic. Types I, II, and IV contain metal salts that have some degree of toxicity. However, Type III DESs contain various amides and polyols like urea, glycerol, ethylene glycol, fructose, and other chemicals, which exhibit a remarkably low degree of toxicity. Moreover, some Type III DESs can even be produced by using food additives [23]. When compared to aqueous solutions of acids and bases that are commonly used in hydrometallurgy, DESs present several advantages. Notably, they exhibit a high solubility for metal salts, as well as an important level of conductivity. DESs also offer a wider range of potential applications in mineral processing than aqueous solutions, although their applications are not as broad as those provided by certain ionic liquids [23,27].

Thus, this study aims to experimentally validate the use of deep eutectic solvents as leaching agents in the leaching process of the raw material extracted from Čučma tailings. The primary objective of this study is to experimentally validate the efficacy of DESs in extracting antimony from the flotation waste derived from the tailings pond at Čučma. By optimizing parameters such as leaching time and temperature, we aim to maximize the recovery of antimony from this secondary raw material. This optimization process will not only enhance the efficiency of antimony extraction but also contribute to reducing the environmental footprint associated with traditional extraction methods. The successful implementation of DES-based leaching for antimony recovery holds significant implications for sustainable resource utilization. By minimizing reliance on harsh chemicals and energy-intensive processes, this approach aligns with the principles of green chemistry and the circular economy. Moreover, the eco-friendly nature of DES-based leaching mitigates potential environmental risks and ensures the responsible management of mineral resources. In conclusion, our study seeks to advance the understanding of DES as a viable leaching agent for antimony recovery, particularly from complex secondary raw materials like flotation waste. Through systematic experimentation and optimization, we aim to establish a robust and eco-friendly extraction process that contributes to the sustainable management of antimony resources while minimizing environmental impact [28,29].

2. Materials and Methods

2.1. Specific Information of the Sample

The raw material we used originated from the Čučma tailings. The Čučma tailings pond is situated in the Rožňava district, receiving flotation waste from the antimonite mine's raw material treatment. Previously, this mine was a significant manufacturer of antimony and contributed to making the former Czechoslovakia one of the primary global antimony producers. Mining operations at the Čučma site ceased several years ago, and the Čučma tailings pond has subsequently been a considerable environmental burden. Table 1 below displays the essential dimensional characteristics of the Čučma tailings pond.

Table 1. Basic characteristics of the Čučma tailings pond.

Area of the Tailings Pond	Volume of the Tailings Pond	Quantity of Sludge	Quantity of Sb
34,000 m^2	166,692 m^3	333,384 t	1265 t

In the flotation waste obtained from the Čučma tailings, pyrite was the most abundant of all the minerals contained. Other important minerals were antimonite and arsenopyrite.

Antimonite was present in less than 1% of the samples, and its amount is shown in Table 2. This is explained by the considerable instability of antimonite, which dissolves under the influence of external factors and subsequently recrystallizes as oxides or hydroxides. Arsenopyrite was the least abundant of the minerals. Abundantly occurring, in addition to sulfides, were oxides and hydroxides of iron, antimony, and, to a lesser extent, arsenic, calcium, and lead. Their composition is highly variable. The antimony oxides found at the site included senarmonite, valentinite, and stibiconite. The antimony content of these minerals ranged from 56.56 to 73.06 wt.%. In the antimony oxides, in which elevated concentrations of As, Ca, and Pb were measured, the antimony content was significantly lower. It ranged from 13.48 to 53.10 wt.%. As far as ore minerals are concerned, carbonates, micas, and quartz accounted for the largest proportion. Tetrahedrite, barite, zircon, magnetite, and rutile were also noted, albeit in tiny amounts. The proportions of clays increased at greater depths in the tailings. Among the elements, iron was the most abundant in the raw material. Other elements with more significant amounts were aluminum, sulfur, manganese, antimony, calcium, and, in smaller amounts, zinc, arsenic, lead, cobalt, nickel, silicon, gold, and silver.

Table 2. Antimony amount in the original sample.

Element	Amount of the Element in the Sample
Antimony	6000 $g \cdot t^{-1}$

Before leaching, the raw material underwent crushing and grinding of its mineral grains to achieve a certain grain size suitable for leaching. If the raw material contained grains that were too large, the useful mineral (antimony) may not have been adequately liberated from them during the leaching process. Similarly, if the grains were too small, the viscosity would increase, which was also undesirable. Therefore, the optimum grain size was an especially important factor in the leaching process. We used raw materials for leaching whose grains did not exceed 315 µm and whose d80 (d80 in mineralurgy refers to the particle size at which 80% of the material is finer and 20% is coarser. It serves as a critical parameter for understanding the distribution of particle sizes in mineral processing, aiding the optimization of grinding and separation processes) value was equal to 150 µm.

2.2. Experiments

Deep eutectic solvents type III were used, and they are shown in Table 3. The main component was choline chloride. The leaching agents were used to leach the mixture in specific leaching molar ratios for choline chloride and ethylene glycol (1:2), choline chloride and malonic acid (1:1), and choline chloride and thiourea (1:1). In this experiment, the hydrogen bond acceptor was choline chloride (purity < 98%), and the hydrogen bond donors were ethylene glycol (purity 99.9%), malonic acid (purity 99%), and thiourea (purity 99%).

Table 3. Proportions of different hydrogen bond donors used in ChCl-based DESs.

Hydrogen Bond Donor (HBD)	ChCl/HBD (Molar Ratio)	Density
Ethylene glycol	1:2	1.12 $g \cdot cm^{-3}$
Malonic acid	1:1	1.25 $g \cdot cm^{-3}$
Thiourea	1:1	1.36 $g \cdot cm^{-3}$

After mixing ethylene glycol and choline chloride, we heated this mixture until the choline chloride was completely dissolved, giving us a transparent homogeneous liquid, as can be seen in Figure 1.

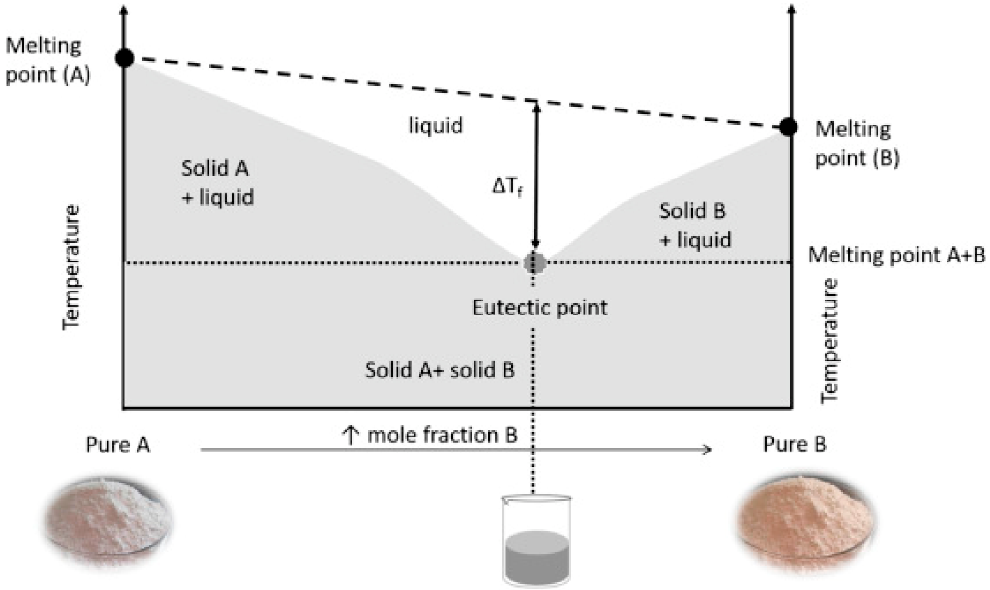


Figure 1. Formation of the homogeneous liquid after heating a mixture of choline chloride and ethylene glycol [30].

Leaching experiments were carried out at temperatures of 60 °C, 80 °C, and 100 °C. The prepared mixture was heated using a magnetic stirrer. During the whole heating process, the mixture was stirred at the same time. The speed was set at 300 rpm. When the desired temperature was reached, a sample of 50 g was added to the solution to obtain an optimum density of between 30% and 50% of the solid in solution. We also added 2 g of iodine as a strong oxidizing agent for solubilizing metals in the DES. The factors that we tried to control, and which we gradually changed, were the temperature and time of the antimony leaching process. After each leaching stage, the sample was filtered and washed with distilled water at a 2:1 ratio against the liquid eutectic mixture.

2.3. Analysis

The input sample was analyzed using AAS, XRF and XPS. Solid leached samples were dried at 60 °C for one hour after washing and analyzed using AAS and XRF to identify leached elements. Liquid samples (DESs) were analyzed using AAS only. Subsequent research focused on determining the influence of the solid component percentage on the antimony leaching dynamics. Experiments that yielded optimum antimony yields were retested with varying times, temperatures, and iodine concentrations. After leaching, the solid samples were washed and analyzed using an XPS machine to determine the composition of the sample.

AAS (iCE 3300 AA-ThermoFisher Scientific, Grand Island, NY, USA) was performed using an extract consisting of 1 g of solid material and 25 mL of 0.5 mol·L^{-1} HCl. Solid samples (filtrate of the leached sample) were analyzed via X-ray photoelectron spectroscopy (XPS) (SPECS Surface Nano Analysis GmbH, Berlin, Germany). XPS was performed using the SPECS instrument equipped with a PHOIBOS 100 SCD hemispherical energy analyzer and a non-monochromatic X-ray source. The survey surface spectrum was measured at a pass energy of 70 eV and the core spectra at 20 eV at room temperature, with a base pressure of 10^{-8} millibar and AlKα excitation at 10 kV (200 W). The base pressure was 10^{-8} millibar, with AlKα excitation at 10 kV (200 W).

3. Results

In the first series of experiments, 50 g of a sample from the Čučma tailings ponds was leached in a deep eutectic solvent consisting of choline chloride and ethylene glycol at a volume of 154.51 mL and a molar ratio of 1:2. The percentage of the solid component was 30.45%. The experiments were carried out at temperatures of 60 °C, 80 °C, and 100 °C.

Each sample was filtered after the specified time interval. The filtered samples (i.e., solid residue and liquid leachate) were analyzed via atomic absorption spectrometry (AAS) and X-ray fluorescence (XRF), the average results of which are shown in Table 4. The antimony yields at 60 °C, 80 °C, and 100 °C were calculated from the XRF measurements of the solid residue, which are shown in Figure 2.

Table 4. The antimony concentrations in the solution and the solid residue after leaching in a mixture of choline chloride and ethylene glycol at different temperatures (60 °C, 80 °C, and 100 °C).

Duration of Leaching	**The Concentration of Sb in the Solution g·t^{-1} at 60 °C**	**The Concentration of Sb in the Solid Residue g·t^{-1}**	**The Concentration of Sb in the Solution g·t^{-1} at 80 °C**	**The Concentration of Sb in the Solid Residue g·t^{-1}**	**The Concentration of Sb in the Solution g·t^{-1} at 100 °C**	**The Concentration of Sb in the Solid Residue g·t^{-1}**
0 min	0	6000	0	6000	0	6000
5 min	1789	4211	1996	4004	2376	3624
15 min	2365	3635	2778	3222	2905	3095
30 min	3134	2866	3237	2763	3576	2424
1 h	3500	2500	3329	2671	3537	2463
2 h	3502	2498	3657	2343	3792	2208
3 h	3763	2237	3833	2167	4180	1820
4 h	3999	2001	4042	1958	4496	1504
6 h	4015	1985	4146	1854	4497	1503
10 h	4144	1856	4178	1822	4498	1502
12 h	4315	1685	4318	1682	4499	1501
24 h	4480	1520	4447	1553	4500	1500

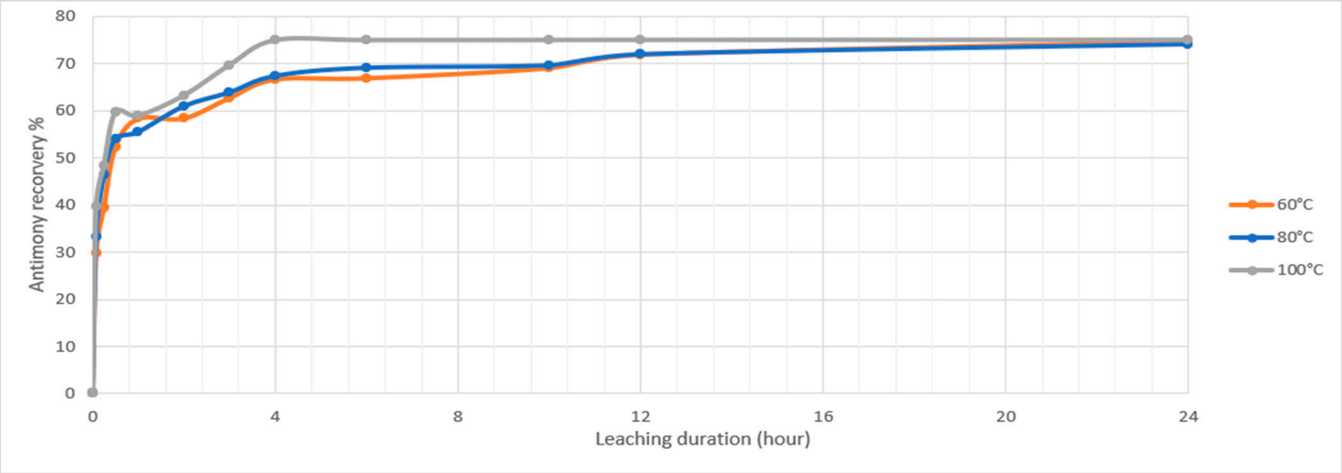


Figure 2. Antimony yields at 60 °C, 80 °C, and 100 °C were calculated from XRF measurements of the solid residue after leaching in a mixture of choline chloride and ethylene glycol (1:2) at time intervals of 5 min, 15 min, 30 min, 1 h, 2 h, 3 h, 4 h, 6 h, 12 h, and 24 h.

The highest antimony yield was 74.15%, which was achieved at a temperature of 100 °C and by leaching for 4 h.

In the second series of experiments, 50 g of the sample from the Čučma tailings impoundment was leached in a deep eutectic solvent consisting of choline chloride and malonic acid at a volume of 124.66 mL and a molar ratio of 1:1. The percentage of solid component was 33.02%. The experiments were carried out at 60 °C, 80 °C, and 100 °C. Each sample was filtered after the specified time interval. The filtered samples (i.e., solid residue and liquid leachate) were analyzed via atomic absorption spectrometry (AAS) and X-ray fluorescence (XRF), the results of which are shown in Table 5. The antimony yields at 60 °C, 80 °C, and 100 °C were calculated from the XRF measurements of the solid residue, which are shown in Figure 3.

Table 5. The antimony concentrations in the solution and the solid residue after leaching in a mixture of choline chloride and malonic acid at different temperatures (60 °C, 80 °C, and 100 °C).

Duration of Leaching	**The Concentration of Sb in the Solution g·t^{-1} at 60 °C**	**The Concentration of Sb in the Solid Residue g·t^{-1}**	**The Concentration of Sb in the Solution g·t^{-1} at 80 °C**	**The Concentration of Sb in the Solid Residue g·t^{-1}**	**The Concentration of Sb in the Solution g·t^{-1} at 100 °C**	**The Concentration of Sb in the Solid Residue g·t^{-1}**
0 min	0	6000	0	6000	0	6000
5 min	20	5980	72	5928	741	5259
15 min	100	5900	112	5888	800	5200
30 min	100	5900	159	5841	814	5186
1 h	400	5600	600	5400	876	5124
2 h	700	5300	964	5036	1015	4985
3 h	764	5236	999	5001	964	5036
4 h	900	5100	913	5087	1015	4985
6 h	1126	4874	1058	4942	1179	4821
10 h	1129	4871	1350	4650	1179	4821
12 h	1130	4870	1400	4600	1248	4752
24 h	1150	4850	1438	4562	1253	4747

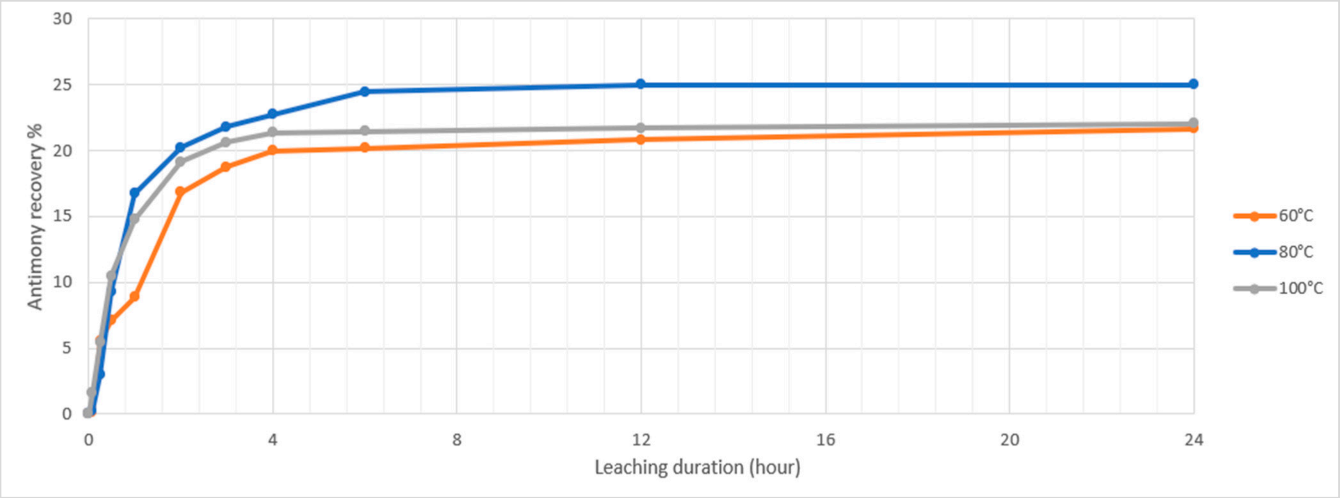


Figure 3. Antimony yields at 60 °C, 80 °C, and 100 °C were calculated from XRF measurements of the solid residue after leaching in a mixture of choline chloride and malonic acid (1:1) at time intervals of 5 min, 15 min, 30 min, 1 h, 2 h, 3 h, 4 h, 6 h, 12 h, and 24 h.

The highest antimony yield was 25.05%, which was achieved at a temperature of 100 °C and leaching for 24 h.

In the last series of experiments, 50 g of the sample from the Čučma tailings was leached in a volume of 118.60 mL of a deep eutectic solvent consisting of choline chloride and thiourea in a molar ratio of 1:1. The percentage of solid component was 37.27%. The experiments were carried out at 60 °C, 80 °C, and 100 °C. The filtered samples (i.e., solid residue and liquid leachate) were analyzed via atomic absorption spectrometry (AAS) and X-ray fluorescence (XRF), the results of which are shown in Table 6. The antimony yields at 60 °C, 80 °C, and 100 °C were calculated from the XRF measurements of the solid residue, and they are shown in Figure 4.

Table 6. The antimony concentrations in the solution and the solid residue after leaching in a mixture of choline chloride and thiourea at different temperatures (60 °C, 80 °C, and 100 °C).

Duration of Leaching	The Concentration of Sb in the Solution g·t^{-1} at 60 °C	The Concentration of Sb in the Solid Residue g·t^{-1}	The Concentration of Sb in the Solution g·t^{-1} at 80 °C	The Concentration of Sb in the Solid Residue g·t^{-1}	The Concentration of Sb in the Solution g·t^{-1} at 100 °C	The Concentration of Sb in the Solid Residue g·t^{-1}
0 min	0	6000	0	6000	0	6000
5 min	100	5900	150	5850	200	5800
15 min	286	5714	178	5822	326	5674
30 min	726	5274	557	5443	831	5169
1 h	286	5714	1003	4997	885	5115
2 h	734	5266	1215	4785	1248	4752
3 h	940	5060	1308	4692	1323	4677
4 h	960	5040	1364	4636	1370	4630
6 h	990	5010	1500	4500	1500	4500
10 h	1450	4550	1480	4520	1750	4250
12 h	1400	4600	1500	4500	1400	4600
24 h	1300	4700	1400	4600	1500	4500

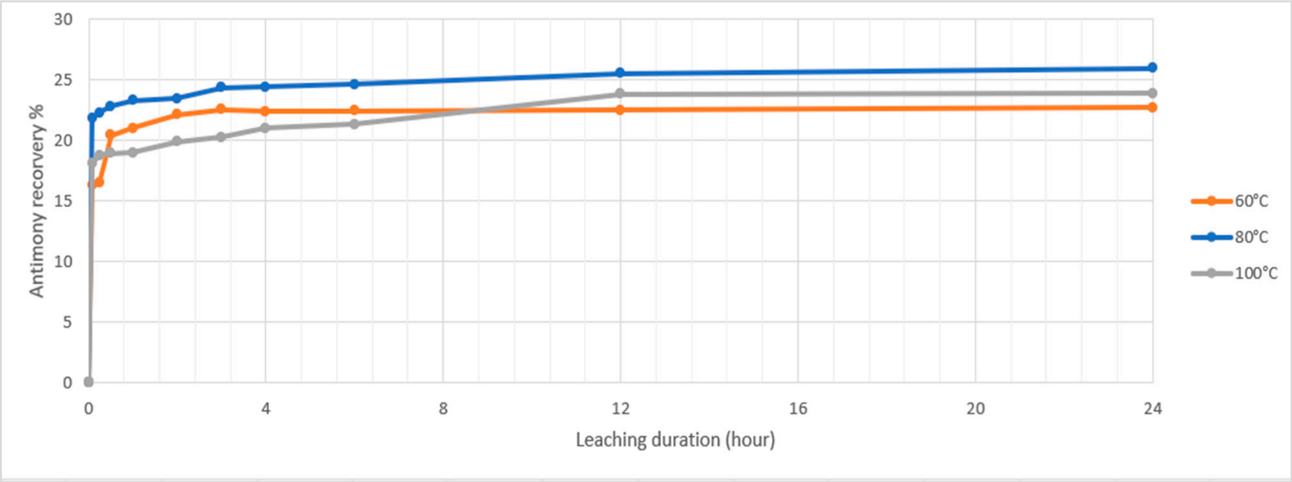


Figure 4. Antimony yields at 60 °C, 80 °C, and 100 °C were calculated from XRF measurements of the solid residue after leaching in a mixture of choline chloride and thiourea (1:1) at time intervals of 5 min, 15 min, 30 min, 1 h, 2 h, 3 h, 4 h, 6 h, 12 h, and 24 h.

The highest antimony yield was 25.97%, which was achieved at a temperature of 80 °C and by leaching for 24 h.

In a meticulous quest to optimize antimony leaching methods, recent experiments conducted at a constant temperature of 100 °C for 4 h—identified as the optimum condition for achieving the highest yield—focused on the integration of deep eutectic solvents (a mixture of choline chloride and ethylene glycol with the best yield 74.15%). These tests aimed to unravel the intricate effects of the varying concentrations of solid component percentage on antimony yield.

The dried samples were analyzed by AAS. Table 7 presents a comprehensive overview of the data, which illustrates the impact of the solid component percentage on antimony yield. Figure 5 shows the dependence of the percentual fraction of the solid component on the antimony yield at 100 °C and 4 h of incubation in a mixture of choline chloride and ethylene glycol, where it can be seen that from a 12.18–30.45 percent concentration, the antimony yield does not change, while the addition of more solid component causes a decrease in the yield.

Table 7. Percentage representation of the solid sample component in the solution and the yield of antimony.

Sample Quantity **g**	**Antimony Yield** **%**
20	74.15
40	74.15
50	74.15
60	66.67
80	58.33
100	53.33
150	35.00
200	28.33

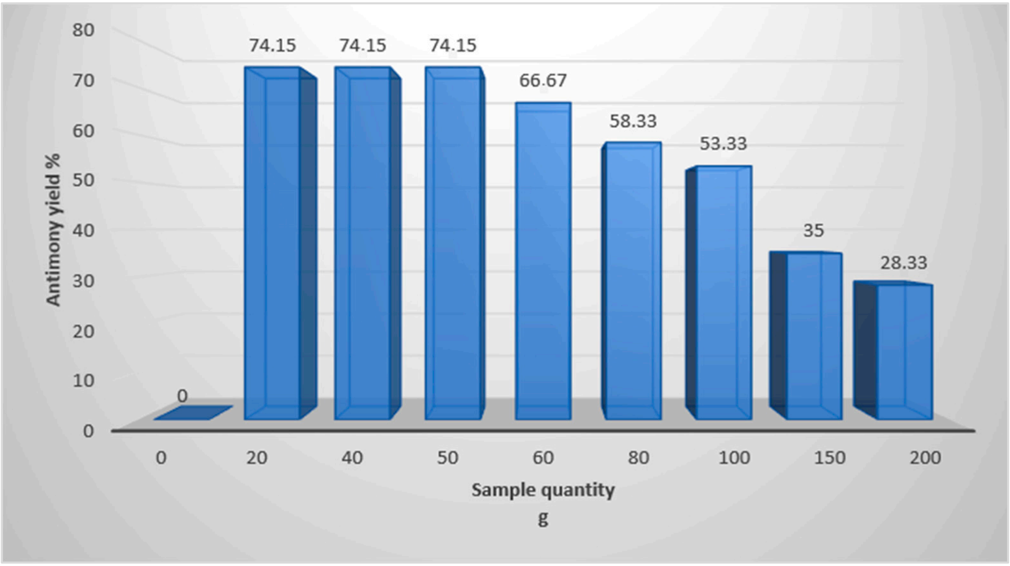


Figure 5. The dependence of the percentage of the solid component on the antimony yield at 100 °C and 4 h of leaching with choline chloride and ethylene glycol.

The overall tests showed that the highest antimony yield was up to 74.15% using a mixture of choline chloride and ethylene glycol at 100 °C for 4 h with 50 g of solid component.

The experiments were repeated at 100 °C for 4 h with a sample quantity of 50 g, and the concentration of iodine (as the oxidizing agent) was changed and monitored—identified as the optimum condition for achieving the highest yield—by focusing on the integration of deep eutectic solvents. These tests aimed to unravel the intricate effects of varying concentrations of iodine, an essential oxidizing reagent, set at 3 g, 2 g, and 1 g, and the absence of iodine (0 g) on the leaching process. Figure 6 displays the outcomes of tests examining the effect of the iodine amount on antimony yield, as analyzed via AAS.

The overall tests showed that the highest antimony yield was 100% when using a mixture of choline chloride and ethylene glycol at 100 °C with 3 g of iodine as the oxidizing agent.

The XPS analysis was used to confirm the presence of Sb, and it can also confirm the oxidation or reduction of antimony as it desorbs from the material. The raw input sample was analyzed before beginning the process and then after leaching. In Figure 7, the survey spectra of the input sample show that antimony is bound to antimony trioxide (Sb_2O_3) in an amount of 4.9 At%.

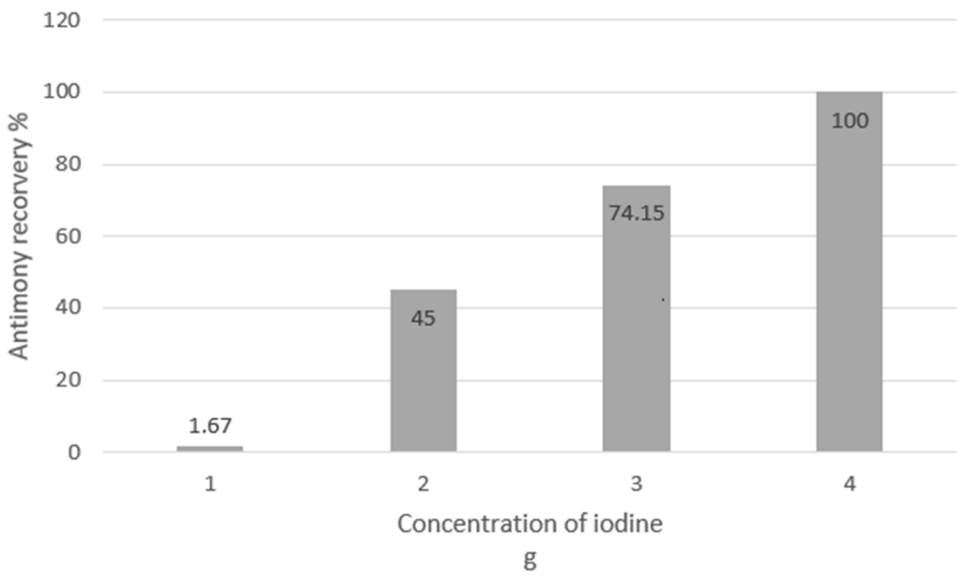
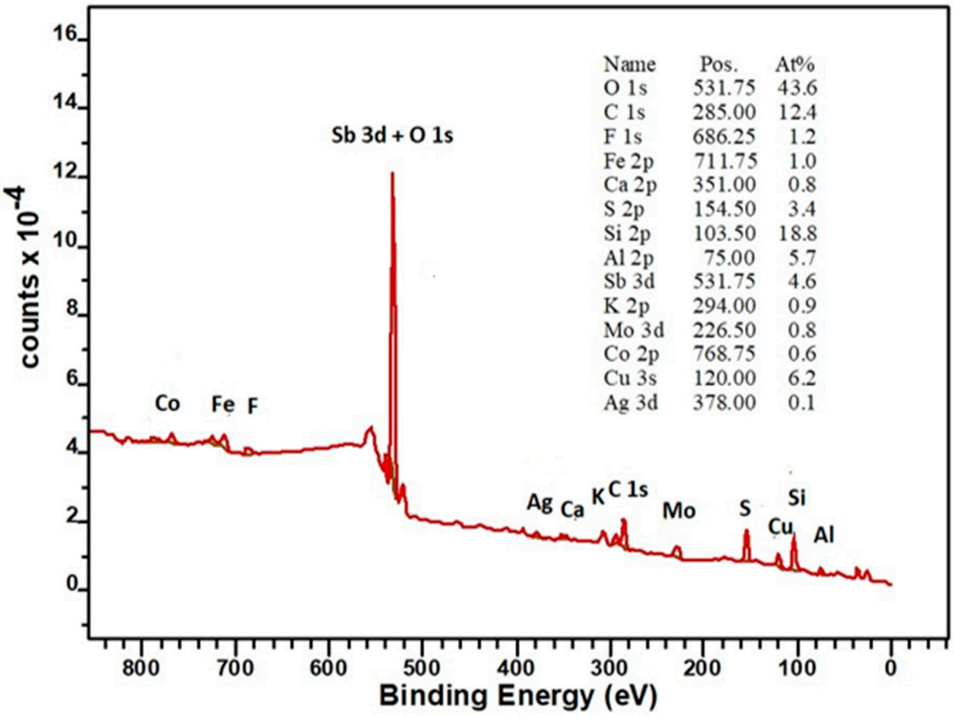


Figure 6. Dependence of the amount of iodine on the antimony yield.



Name	Pos.	At%
O 1s	531.75	43.6
C 1s	285.00	12.4
F 1s	686.25	1.2
Fe 2p	711.75	1.0
Ca 2p	351.00	0.8
S 2p	154.50	3.4
Si 2p	103.50	18.8
Al 2p	75.00	5.7
Sb 3d	531.75	4.6
K 2p	294.00	0.9
Mo 3d	226.50	0.8
Co 2p	768.75	0.6
Cu 3s	120.00	6.2
Ag 3d	378.00	0.1

Figure 7. Survey spectrum of the input sample.

Figure 8 shows that after leaching with a solids concentration of 12.18%, the sample also contains antimony in the form of Sb_2O_3.

After leaching the sample with a solids concentration of 12.18%, a change in the analytical results is evident, as shown in Figure 9. Antimony trioxide is no longer present in the leached sample, instead being replaced by antimony in its elemental form, which is easier to work with.

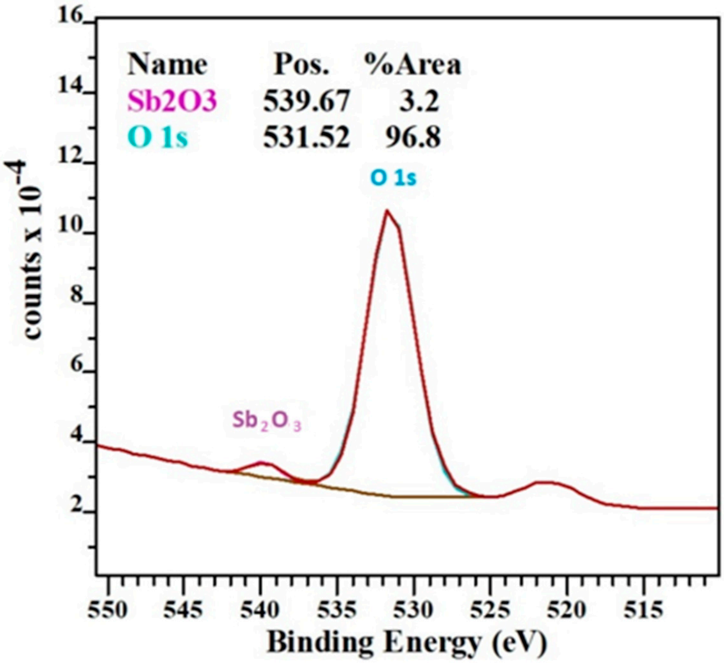


Figure 8. X-ray photoelectron spectrum of antimony before leaching.

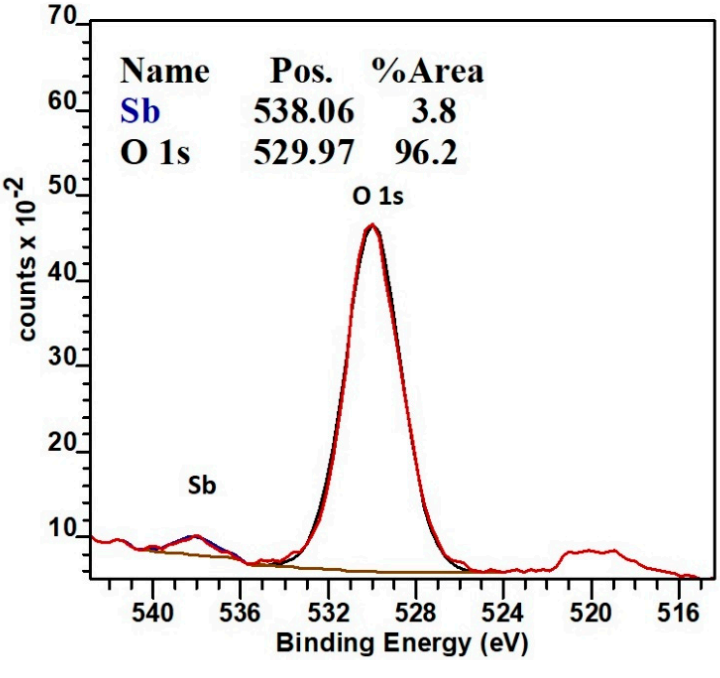


Figure 9. X-ray photoelectron spectrum of antimony after leaching.

4. Discussion

The results obtained in this study have prompted extensive discussion regarding their consistency with previous research and the original working hypotheses that deep eutectic solvents are suitable for metal oxide extraction. These results have implications that extend to a broader context and shed light on the potential applications and limitations of the parameters studied.

When considered in the context of existing studies, our results are consistent with trends observed in previous research and confirm the efficacy of deep eutectic solvents (DESs) in the environmental leaching of metal oxides. Our research investigation centered on antimony, a critical mineral, where we used three types of deep eutectic solvents, such as choline chloride with ethylene glycol, malonic acid, and thiourea at different molar ratios. The process of optimization, which involved varying parameters such as temperature, time, quantity of oxidizing agent, and percentage of solids, revealed the correlation with solvent efficiency and pinpointed a promising amalgamation for achieving the highest extraction efficiency. To improve process optimization, we observed the percentage of the solid component in the solution. Experiments showed that the best and equal results were at concentrations of 12.18%, 24.36%, and 30.45%, respectively. To make leaching effective, the best result for the percentage representation of the solid component was 30.45%. As another indicator, we focused on the amount of the oxidizing agent, iodine, that was used. The best efficiency was obtained when using 3 g of iodine.

The implications of our findings extend beyond the laboratory setting, providing insights into eco-friendly practices for extracting antimony in real-world mining scenarios. With critical minerals becoming increasingly vital, the use of DESs in resource management has the potential to promote a more sustainable and environmentally conscious approach in the mining sector. As such, this study adds to the ongoing discourse on the use of green technologies in mineral extraction.

While our study offers valuable insights, there are inherent limitations, since it is limited to specific DES compositions and parameters and may not encompass all conceivable variations in environmental leaching conditions or the complexities of real-world mining waste. Moreover, our investigation is confined to antimony extraction, and the wider use of DESs to extract other metals requires further research. It is important to consider these limitations when evaluating the wider implications of this study, as overlooking subtleties could affect industrial applications on a larger scale.

To enhance our understanding of DESs' applications in metal leaching, future studies should explore additional DES compositions, investigate their effectiveness under diverse conditions, and assess the scalability and economic feasibility of the extraction process. The kinetics of the leaching process also require further exploration. These recommendations aim to guide future research efforts, facilitating practical implementation and progress in sustainable metal extraction technology.

Moreover, the implications of these findings extend beyond their immediate applications, prompting further research directions for the future. This study contributes to the ongoing discussion of eco-friendly extraction methods for critical minerals from mining wastes and provides a feasible pathway toward more sustainable resource management in the mining sector. Additionally, assessing the scalability and economic viability of DES-based antimony extraction may pave the way for practical implementation on a larger scale.

In our next study, we will focus on the extraction of antimony, as it has been shown in other studies that the extraction of metal oxides has been successful. Deep eutectic solvents (DESs) have been suggested as innovative electrolytes, offering various benefits compared to traditional electrolytes like concentrated mixtures of phosphoric acid and sulfuric acid. These advantages include milder acidity, enhanced surface quality on cast items, and increased efficiency in current utilization. Combining DES extraction with electro-deposition processes has been recognized as a promising approach for metal retrieval. This method capitalizes on the notable solubility of metal salts in DES, enabling both the targeted dissolution and subsequent electro-deposition of metals [23]. Numerous research works have documented the retrieval of metals via the combination of DES-mediated extraction and electro-deposition. This electro-deposition process enables the direct conversion of target metals from their oxide or complex forms within the DESs to a pure metallic state on solid electrodes, significantly streamlining the practical utilization of reclaimed metals [23]. For example, Poll et al. (2016) introduced a technique aimed at reclaiming lead from Pb-based hybrid organic–inorganic perovskite (HOIP) photovoltaic devices through a process that concurrently dissolves and electro-deposits using a mixture of choline chloride and ethylene glycol [24]. Above all, in our aforementioned conditions, we would specialize in electrolysis to obtain pure antimony.

5. Conclusions

In summary, this study represents a significant step forward in the quest for sustainable resource management within the mining industry. The best yield, 100%, was obtained with a mixture of choline chloride and ethylene glycol at 100 °C for 4 h of leaching with a solids content of 30.45% and an oxidant of 3 g of iodine, highlighting the promise of these solvents for the sustainable extraction of antimony from mine tailings. By using deep eutectic solvents for the environmentally friendly extraction of antimony from mining waste, the study not only demonstrates a successful methodology but also opens doors to more responsible and efficient resource practices. This comprehensive approach promises to address the environmental risks associated with mining residues while maximizing the extraction of critical minerals such as antimony.

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