

Sulfide Tailings as Potential Secondary Sources of Critical Minerals: Tellurium

Fardis Nakhaei

Missouri University of Science & Technology, Rolla, MO, USA

Jose L. Corchado-Albelo

Missouri University of Science & Technology, Rolla, MO, USA

Noelia Munoz-Garcia

Université de Sherbrooke, Quebec, Canada

Lana Alagha

Missouri University of Science & Technology, Rolla, MO, USA

Michèle Heitz

Université de Sherbrooke, Quebec, Canada.

ABSTRACT

Sulfide tailings from past and present mining activities are important hosts of critical elements and precious metals. This review paper presented a literature survey on the recovery practices of some critical minerals containing Te from sulfide tailings with a special focus on the physical beneficiation and hydrometallurgical separation methods. Finally, a conceptual framework and possible processing flowsheets were proposed. The findings of this review will be useful for the researchers in the field of geochemistry, mineral processing, and metallurgy to evaluate the separation processes for reprocessing of mine tailings for the recovery of critical minerals.

INTRODUCTION

Tellurium (Te), with a concentration as low as 1–5 ppb in the Earth's crust, is even more scarce than Au, Ag, Pt, and REEs [1]. Except for a standalone Te deposit in China, [2], Te is typically found in association with other minerals like pyrite, chalcopyrite, galena, and sphalerite and usually recovered as a byproduct of copper ore processing. Given the increasing global demand for Te, its limited reserves, and relatively low recovery, it has been classified as a critical element in several countries [3–5]. Most of the Te production occurs in China (61%), Japan (11%), Sweden (9%), Russia (8%), and Canada (8%) [6,7]. Determining global

Te production precisely is challenging due to the incomplete reporting by companies and countries, but the world's current production for refined Te is estimated to be 500 to 550 tons per year [7–9].

Because of their outstanding thermal, optical, and electrical characteristics, Te and Te-containing compounds find broad applications across diverse industries. Over the past decade, there has been a substantial global increase in the production of cadmium telluride (CdTe) thin-film solar cells, rising from negligible levels in the mid-2000s to surpassing 6 gigawatts in 2020 alone, according to the Fraunhofer Institute for Solar Energy Systems (2022) [10]. This increase in CdTe production led to a corresponding rise in Te demand, making up approximately 40% of global Te usage and standing as its most substantial application [11–13]. Te is also employed in various other industry sectors including thermoelectric production (constituting 30% of global Te production), metallurgical alloys (15%), color ceramics and glass fibers (10%), and heat-resistant rubber (5%) [14,15].

The escalating worldwide demand for Te in recent years has led to increased focus on recovering tellurium from ores, tailings, and metallurgical by-products [16,17]. According to Ojebuoboh's research [18], about 90% of Te in ores is typically lost to tailings during the concentration processes of copper-containing sulfide minerals at mining

sites. However, despite this loss, these sources currently make a minor contribution to the overall global Te supply. To address both the scarcity of Te resources and the issue of tailing pollution, there is a need for viable, efficient, and cost-effective technologies for the recovery of Te from mine tailings.

Over 90% of the global Te supply is derived from anode slimes, a byproduct generated during the electrolytic refining of copper [19]. In this process, an electric potential is applied to copper anodes (<99% pure copper), releasing Cu^{2+} cations into the electrolyte. These cations migrate and deposit on the cathode, resulting in the production of copper metal with a purity exceeding 99.99%. Meanwhile, insoluble impurities settle at the bottom of the tank, forming anode slimes. A significant portion of Te, more than 98%, in the anode is insoluble in the electrolyte and, consequently, is found in the anode slimes along with other insoluble impurities [19, 20]. To evaluate how much Te production can be enhanced, it is crucial to calculate how much is potentially available from copper operations in which Te is present but currently not recovered.

While several recent studies have discussed the recovery of some critical minerals in tailing streams, [21, 22], there is a conspicuous absence of comprehensive review reports encompassing the existing techniques for extracting and recovering tellurium from tailings generated during the copper concentration and extractive metallurgy processes. Hence, it is necessary to contribute to Te research by providing a comprehensive study that explores essential aspects such as production, primary applications, available sources, and separation techniques for extracting Te. This review aims to provide a concise overview of the present status of tellurium recovery from tailing streams, with a focus on the latest and most notable achievements in this field. It also covers challenges and opportunities in Te recovery, offering a valuable reference for the full exploitation and utilization of tailings and industrial development.

TAILING STREAMS OF COPPER CONCENTRATION, SMELTING, AND REFINING PROCESSES

Copper sulfides constitute the primary source of metallic copper, comprising 80% of copper resources [23]. The major copper sulfide ores include chalcopyrite (CuFeS_2), bornite (Cu_5FeS_4), covellite (CuS), and chalcocite (Cu_2S). Pyrite (FeS_2) is the most abundant sulfide mineral and is considered a gangue mineral in the flotation of copper sulfides. It gains significance only when associated with precious metals such as gold. Typically, copper concentrate from sulfide ores is generated through comminution, classification, and flotation operations and it is subsequently subjected to pyrometallurgical or hydrometallurgical processes to remove impurities and extract the pure copper metal [24]. Tailings are the solid and fluid products generated in mine, mineral processing, and extractive metallurgy operations [25]. Figure 1 shows a generalized flowsheet of the processing of copper sulfide ores.

The initial tailings generated in open pit and underground mining operations consist of discarded rocks, overburden, and discharged water. Copper sulfide minerals are typically concentrated through flotation processes, resulting in tailings that contain mainly gangue minerals [26]. Tailings are produced in extractive metallurgical processes including slags, flue dust, slimes, and electrolyte solution. They are generated during the extraction of pure copper metal from high-grade copper concentrate [26].

As the metal markets continue to grow in both scope and scale, the waste products and residues generated during the entire extraction process evolved into valuable sources of critical metals like Te. Reprocessing these waste materials not only contributes to meeting the increasing demand for critical metals in the future but also aligns with the broader goal of transitioning the mining industry towards a circular economy system.

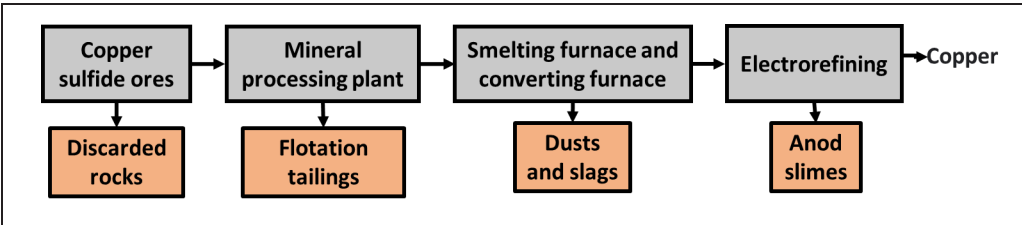


Figure 1. Generalized flowsheet of different processes utilized to recover copper from copper sulfide ores.

RECOVERY OF TE FROM COPPER CONCENTRATION TAILINGS

According to the available literature, Te minerals are present in nature associated with sulfide minerals as micron or submicron inclusions [27]. The enrichment of Te minerals might increase in the concentrates during the processing of the raw copper sulfide ores, or they could be lost to the tailings. If Te is found in copper sulfide minerals, it could be captured using selective chemical reagents, which may recover significant amount of Te minerals in the copper concentrate. On the other hand, if the Te is found in gangue minerals such as pyrite, it would end up in tailings as pyrite is depressed in the flotation process of copper ores. The behavior of Te minerals through the initial separation processes of copper sulfide ores is influenced by various factors, including the liberation degree, surface characteristics, and chemistry of the flotation pulp [28].

Although, few studies investigated Te concentration in copper ore deposits, the distribution of Te minerals within the tailing streams in a copper processing plant is poorly understood. Yano [29] discovered a correlation between Te concentration and the concentrations of Ag, Bi, Pb, and Au and described that Te is present in chalcopyrite in the form of telluride mineral nanoparticles. Reich [30] identified trace amounts of Te (approximately 5 ppm) associated with pyrite in a porphyry copper deposit.

The only published research that quantified Te concentration in copper processing tailings implied that the lost Te, Au, and Ag minerals were mostly hosted as micro-inclusions (less than 10 μm) in pyrite grains that were depressed during the bulk flotation of copper sulfides [31]. The major Te bearing minerals in processing tailings were tetradymite ($\text{Bi}_2\text{Te}_2\text{S}$), petzite (Ag_3AuTe), hessite (Ag_2T), goldfieldite ($\text{Cu}_{12}(\text{Te},\text{Sb},\text{As})_4\text{S}_{13}$), Altaite ($(\text{Bi},\text{Pb})\text{Te}$), and cervellite (Ag_4TeS). Tetradymite was the main Te-bearing mineral which often coexisted with chalcopyrite and pyrite [31]. The images acquired using TESCAN Integrated Mineral Analyzer (TIMA) illustrated that the pyrite particles contain several inclusions of petzite, hessite, goldfieldite, and bornite (Figure 2). Since Te is associated with Au, Ag minerals, it is beneficial to develop economically feasible processes that enhance the simultaneous recovery of Te, Au, and Ag from these resources. Using new reagents, modification of the process flowsheet and the optimization of technological parameters may help recover Te from the tailings. Re-processing of these tailings provides one avenue to meet Te demand and aligns with the drive to transform the mining industry into a circular economy system.

Although there are some investigations on the recovery of Te from Te-bearing ores or Te-bearing gold concentrates

[32, 33], there is no study on the recovery of Te from copper sulfide tailings. Wei et al., [33] conducted a comprehensive study on the recovery of valuable elements from telluride-type gold and silver deposits (Xiaoqinling, China). They acquired tellurium-gold-silver mixed concentrates through one rougher, two cleaning, and two scavenging flotations steps. Isoamyl xanthate and ethyl thiocarbamate (1:1, 120 g/t) were used in the flotation process. The resulting concentrate contained Te, Au, and Ag, with average grades of 241, 90, and 92 g/t, respectively. The recoveries were notably high, reaching 95% for Te, 97% for Au, and 94% for Ag. Despite these achievements, additional research is required to investigate the separation of Te from precious metals.

RECOVERY OF TE FROM ANODE SLIMES

Most of the Te is produced exclusively as by-products of pyrometallurgical and hydrometallurgical treatment of copper concentrate. The smelting process of copper sulfide concentrate is divided into several stages, such as smelting, converting, dust and slag treatment, refining and electrorefining [34]. The first four steps are pyrometallurgical operations and the final one is an electrochemical/hydrometallurgical process. The initial stage of the smelting process involves heating the concentrate to temperatures exceeding 1200°C in the flash furnace, accompanied by the presence of oxygen gas and silica minerals. The reaction between silicates and iron oxide produces an iron-rich slag (Fe_2SiO_4), which is then removed, leading to the creation of low-iron copper matte.

The copper-rich matte is subsequently transferred to a converter furnace, where it undergoes further oxidation to facilitate the continued separation of copper from iron and sulfur. The resulting blister copper is then subjected to treatment in an anode furnace using a non-oxidizing

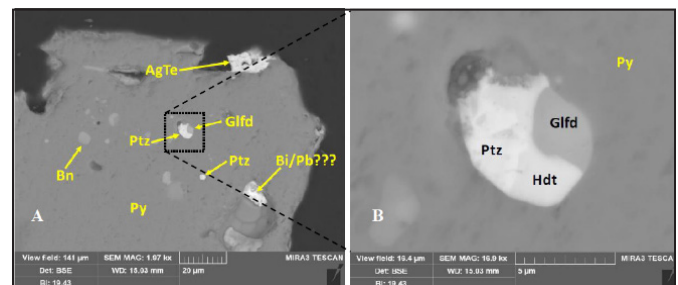


Figure 2. (A) A Scanning Electron Microscopy (SEM) image showing pyrite grains that host several micro inclusions of Te minerals like petzite (Ptz), hessite (AgTe), goldfieldite (Gifd), bornite (Bn), and a bismuth-lead grain. (B) High magnification SEM image of an inclusion that contain petzite, goldfieldite, and hodrushite (Hdt) [31].

gas to eliminate excess oxygen. Following this, the copper is cast into copper anodes through fire refining. These anodes, comprising 98–99% pure copper, may contain minor impurities such as Au, Ag, PGE, Se, and Te. Copper cathode (99.9% pure) can be produced from the copper anodes via electrorefining in a copper sulfate-sulfuric acid electrolyte tank. A thorough explanation of the copper production processes has been summarized by Moskalyk and Alfantazi [35].

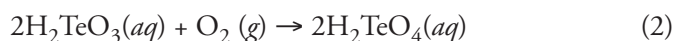
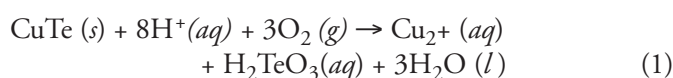
Anode slimes are collected from the bottom of the electrolytic tanks during the refining of copper [36]. The type of ore and the method of copper extraction significantly impact the distribution of elements and the composition of the anode slimes. Copper anode slimes typically consist of Cu, Ni, Se, Te, Ag, Au, and PGE metals. The Te content usually falls within the range of 1–4 wt%, occasionally reaching higher levels, such as 8–9 wt%. A significant portion of Te (often exceeding 80%) is found as inclusions at the grain boundaries of silver-copper-selenide-telluride compounds in the copper anode slimes. The anode slimes need to be further treated for the extraction of the precious and critical metals. These slimes are regularly processed to recover additional Cu and then to recover precious metals, as well as minor elements including Se and Te.

While Te is considered as an impurity in electrolytic copper and as a harmful substance in its natural form if improperly disposed, represents a highly valuable by-product when recovered efficiently from copper anode slimes [37]. From a statistical perspective, 90% of the world's total pure Te production is derived from the processing of copper anode slimes. Processing 1000 tons of copper ore generally results in the production of approximately 1 kg of Te [38]. Table 1 displays the composition of anode slimes originating from various copper refinery plants worldwide.

Te present in anode slime can be extracted through either pyrometallurgical or hydrometallurgical procedures. Pyrometallurgical methods for treating anode slime encompass processes such as oxidizing roasting, soda ash

smelting, cupellation, and sulphation roasting [41]. Within the pyrometallurgical techniques, Te can be transformed into soluble or insoluble forms based on the requirements of successive operations. Subsequently, in the hydrometallurgical phase, Te is extracted through leaching, purification, and electrowinning. Nevertheless, the recovery of Te is typically below 70% due to the lengthy nature of the process [42,43].

The leaching process can be broadly categorized into two main groups: acid leaching and alkaline leaching. In the treatment of copper anode slime, sulfuric acid-oxygen pressure leaching stands out as one of the main separation techniques [43] (Wang, 2011). The use of oxygen as an oxidizing agent plays a crucial role in enhancing the leaching efficiency. Hoffmann and Westrom [44] employed the typical conditions of selective oxidative acidic leaching, which involved a temperature of 120°C and a partial oxygen pressure of 345 kPa, for the separation of Te and Se. Given that Se and seleno-compounds exhibit higher resistance to oxidation, the majority of Se remained in the residue, while Te compounds were dissolved in the oxidative acidic environment. The dissolution of Te compounds can be represented by the following chemical reactions, as explained by Hoffmann [40]:



Apart from oxygen, various other oxidizing agents, including H_2O_2 , NaClO_3 , FeCl_3 , and MnO_2 , have been examined for the leaching of Te with H_2SO_4 [45–49]. Hait et al. [45] discovered that the leaching efficiency of Te in copper anode slime remained consistently below 10% when using H_2SO_4 without oxidizing agents, but it significantly improved manganese dioxide (MnO_2) was added. In addition to the use of oxidative agents, microwave technology has been employed to reduce leaching time and enhance solvent heating rates. Ma et al. [50] investigated the decomposition of copper anode slime when subjected to microwave energy in H_2SO_4 environment. They reported impressive leaching efficiencies, achieving 99.56% for Cu and 98.68% for Te, all within less than 5 minutes under the optimized conditions of microwave-assisted leaching.

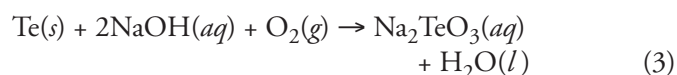
Despite the widespread use of H_2SO_4 as a lixiviant in acid leaching process of Te, other acids have also been used including HNO_3 at high dosage serving as an oxidizing agent as well. In this context, while copper can be effectively leached by HNO_3 , the associated Te could undergo oxidation, forming TeO_2 , which is soluble in HCl.

Table 1. Anode slime composition in different refineries [34, 39–40]

Plant	Country	Te (%)
Saganoseki	Japan	3.9
Las Ventanas	Chile	0.8
Townsville	Australia	0.5
Amarillo	USA	1.4
Montreal	Canada	2
Boliden	Sweden	0.9
Kayseri	Turkey	0.4
Sarcheshmeh	Iran	0.7
Kennecott	USA	3.5

Sun et al. [51] demonstrated that in a high-dosage HNO₃ solution, nearly 99% of the Cu was successfully leached, whereas only 3% of the Te was extracted. Subsequently, the leaching efficiency of Te was significantly improved, reaching 99%, when treated with HCl.

Given that Te can be dissolved in both acidic and alkaline environments whereas Cu is only soluble in an acidic media, the use of alkaline leaching represents a potentially promising approach for separating copper and tellurium. Moreover, the low corrosiveness of alkaline solutions to reaction equipment presents a distinct advantage, as it helps reduce the costs associated with process maintenance. This aspect holds significant economic value and practical importance for industrial applications. The selective leaching of Te and Cu is achieved through an aerated alkaline leaching method in which NaOH is frequently employed as the leaching agent. In this process, Te is transformed into a soluble Te(IV) compound, while Cu remains in solid form within the residue, although it undergoes oxidation to CuO. The reactions involved are as follows [52]:



Oxygen can be introduced by blowing air into the solution, although the quantity of oxygen must be kept in the optimum value, as extreme oxygen levels can result in the oxidation of soluble Te (IV) into its insoluble form (VI) within the alkaline environments. The separation between Te and Se can be accomplished through the high levels of oxidation and transformation of Te and Se into hexavalent valence forms. In this process, Se(VI) takes the form of sodium selenate, which is soluble in alkaline solutions, while Te(VI) forms sodium tellurate, which remains insoluble in the residue, allowing for the efficient separation of Se and Te [53].

Based on the Cu–Te–Se–H₂O system's Pourbaix diagram, Fan et al. [38] proposed a method for the selective alkaline pressure leaching of Cu, Te, and Se. They noted that approximately 90% of the Te can be oxidized to a soluble form, sodium tellurite (IV), while the Cu remains in the residue. Within an alkaline environment, both Te and Se were dissolved in the forms of TeO₃²⁻ and SeO₄²⁻. Consequently, the alkaline pressure oxidation leaching process with NaOH could effectively separate Te and Se from Cu and other impurities, provided the conditions were carefully controlled. The challenge of separating Te from Se was addressed by neutralization of the alkaline solution, in which TeO₃²⁻ ions were hydrolyzed to TeO₂, while Se

remained in the solution. Multiple tests conducted under various conditions revealed that the leaching efficiencies of Te and Se were significantly influenced by reaction's pressure and temperature. Optimal conditions for the process included an L/S ratio of 6:1, 30- 40 g/L NaOH, total pressure of compressed air of 1 MPa, 120 °C, agitation rate of 400 rpm for 6 hours.

In various industrial facilities like Luilu Metallurgical Plant in Congo [54], Freeport's Refinery in the USA [55], Naoshima's Smelter and Refinery in Japan [56], and several major copper smelters in China such as Zhongyuan Gold Smelter and Tongling Nonferrous Metals Smelter, the elimination of Te from the leaching solution is typically achieved through the reduction of Te (IV/VI) forms using metallic copper, leading to the production of insoluble copper telluride (Cu₂Te) [57,58]. This method allows for the enrichment of Te by more than tenfold from anode slime to Cu₂Te. However, many companies opt to store or sell the Cu₂Te at low costs instead of pursuing the individual recovery of Te and Cu. This decision is largely taken because of the intricate physicochemical characteristics of Te, which pose significant technical challenges in the process of Cu-Te separation. Cu₂Te remains stable over a broad pH range. The development of an affordable and environmentally friendly process for Te and Cu extraction from Cu₂Te is of paramount importance for the copper smelters.

Xu et al. [59] introduced both atmospheric and high pressure oxidizing alkaline leaching techniques with O₂ serving as the oxidant for the recovery of Te and Cu from the Cu₂Te. The process mechanisms for the leaching of Cu₂Te at atmospheric pressure are depicted in Figure 3 (a). Initially, the Cu₂Te reacts with NaOH and O₂, leading to a selective dissolution of Te into the solution, while Cu remains in the solid phase as Cu₂O. As the reaction progresses, the unreacted Cu₂Te core diminishes, and the Cu₂O layer gradually thickens. Because of the limited kinetic conditions at atmospheric pressure, the diffusion of NaOH and O₂ toward the surface of the unreacted Cu₂Te becomes increasingly challenging, resulting in the formation of a dense outer Cu₂O surface. Meanwhile, the Cu₂O on the surface undergoes more oxidation by O₂, forming a fresh outer layer of Cu(OH)₂, which subsequently reacts with the dissolved Na₂TeO₃ at the liquid-solid interface, leading to the production of insoluble CuTeO₃ on the particle's surface. This prompts the reverse transfer of the dissolved Te from the solution to the solid phase, thereby contributing to the low Te leaching rate of the alkaline leaching operation at atmospheric pressure. The mechanisms of the pressure oxidizing alkaline leaching operation of Cu₂Te at 0.7 MPa are depicted in Figure 3. At first, Te

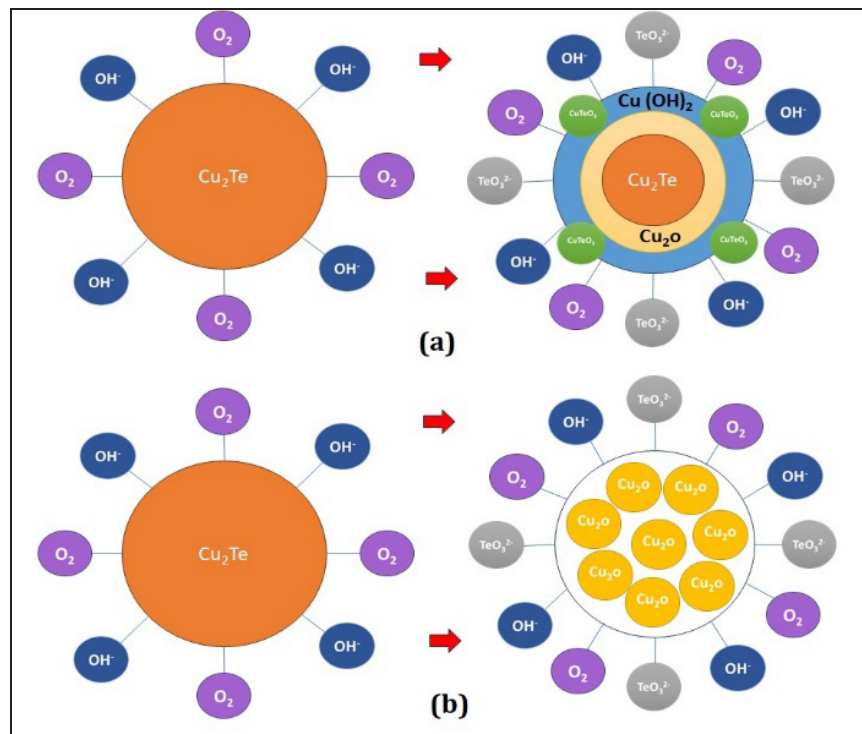


Figure 3. Mechanisms of the oxidizing alkaline leaching process at (a) atmospheric pressure, and (b) pressure at 0.7 MPa. Regenerated from [59]

reacts with NaOH and O_2 , resulting in the formation of soluble Na_2TeO_3 , which is then transported to the solution, while the Cu remains in the residue, forming a layer of Cu_2O . As the reaction time increases, the unreacted Cu_2Te particle core diminishes, and the Cu_2O residue layer slowly thickens. The high-pressure conditions expedite the diffusion of NaOH and O_2 reactants toward the reaction interface, along with the outward transportation of the Na_2TeO_3 product to the solution until the Te selective dissolution process from Cu_2Te is complete.

Xu et al. [60] introduced an innovative alkaline leaching method utilizing H_2O_2 as an oxidizing agent for the effective extraction of Te and Cu from Cu_2Te , with no production of solid or liquid waste. The process, as illustrated in Figure 4, involved two stages of atmospheric alkaline leaching for the separation of Cu and Te, followed by neutralizing precipitation with H_2SO_4 to recover Te. A comprehensive investigation into various factors impacting the alkaline leaching operation was conducted, resulting in the identification of optimal conditions: 5 mol/L NaOH, L/S ratio of 5 mL/g, 25°C, H_2O_2 / Cu_2Te mole ratio of 5 for 5 hours. The optimal alkaline leaching conditions facilitated the reduction of Te content in the solid phase from 31.75 wt% to 4.63 wt%, achieving an impressive Te leaching rate of around 91%. Following Te leaching, H_2SO_4 was employed to modify the pH to 4.5 for effective TeO_2

precipitation. TeO_2 crystallization was accomplished within 1 hour, leading to an overall Te recovery rate of nearly 90%.

Relying solely on the leaching process is inadequate for the efficient separation of Te, necessitating additional steps to obtain pure Te. Selective precipitation stands as one of the commonly utilized purification techniques for the separation of Te from leachate solutions. The specific flowsheets and precipitation agents employed are contingent on the types of leaching processes involved. Notably, various approaches have been employed to extract Te from the solution, including copper displacement, reduction precipitation, pH adjustment through neutralization, and electrolysis [40, 61, 62]. However, it is important to note that, with a few exceptions, Te is predominantly precipitated from a solution in the form of compounds that demand subsequent extraction and purification to achieve higher-purity Te. Various chemical agents, including copper, cuprous ions [63], hydrazine hydrate [64], and sodium sulfite [65], have been employed for the precipitation of Te from sulfuric acid media. Notably, copper stands out as a highly cost-effective reducing agent, with reports demonstrating its effectiveness for Te and Te/Se cementation from aqueous solutions [55].

After the alkaline leaching process, Te remains in the leaching solution as sodium tellurite (Na_2TeO_3), a soluble compound in the liquid phase, and can be subsequently

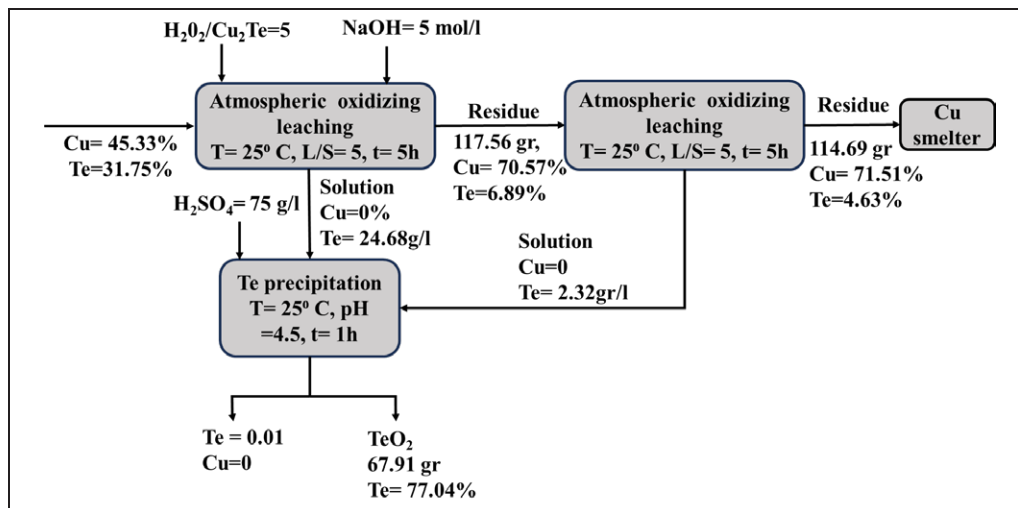
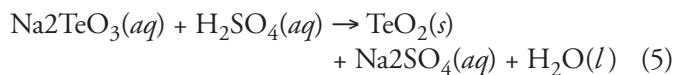


Figure 4. The proposed flowsheet for extraction of Te and Cu from Cu_2Te [60]

precipitated as TeO_2 . According to Mokmeli et al. [58], Te (IV) has the lowest solubility in a solution in pH of 4.5 at 25 °aC. To neutralize the alkaline leaching solution, H_2SO_4 is commonly employed. Consequently, Te can be recovered as TeO_2 precipitate by changing the pH to 4.5, and the reaction is as follows:



Xu et al. [59] employed an oxidizing alkaline leaching method to achieve the separation of Cu and Te, followed by the neutralization of the alkaline leaching solution for the precipitation of TeO_2 . Through the neutralization process using H_2SO_4 to adjust the pH to 4.5, they successfully recovered tellurium with a TeO_2 precipitation efficiency exceeding 95%, closely aligning with the anticipated theoretical value of approximately 97%.

Shao et al., [49] investigated the impact of several factors like reducing agent concentration, reaction time, temperature, and agitation speed, on the selective precipitation of Te from the leaching solution. Na_2SO_3 excess coefficient (NEC) was employed to quantify Na_2SO_3 concentration based on the research of Xu et al., [66]. They found that under suitable conditions, including 16 of NEC, 10 minutes of reduction time, and 80 °C of temperature, approximately 99.83% of Te in the leaching solution was reduced to crude Te. According to the microscopic morphology analysis presented in Figure 5 at 90 °C for 60 minutes, when NEC was less than 13, there were no corresponding SEM images due to the low precipitation rate of Te. However, as the Na_2SO_3 dosage increased, the number of crude Te particles gradually raised and reached a peak at 16. Alongside, needle-like crystals composed primarily of Ca,

S, and O appeared on the crude Te surface. The needle-like or rod-shaped crystals were mainly CaSO_4 , which was a result of the saturation of Ca^{2+} and SO_4^{2-} in the leaching solution. Although their saturation state could be disrupted due to the formation of some SO_4^{2-} after the reduction of Na_2SO_3 , it led to the precipitation of CaSO_4 . Increased Na_2SO_3 content generated more SO_4^{2-} , further which facilitated the growth and coarsening of CaSO_4 . Hence, a minimal Na_2SO_3 dosage could be beneficial to inhibit the generation of CaSO_4 when Te(IV) in the leaching solution is reduced into crude Te.

In the fields of PVC and semiconductors, achieving a higher purity of Te is essential, as even minor contaminations can negatively impact the operation of these equipment. The electrowinning process is broadly used in industry for this purpose [67]. Additionally, the electrodeposition-redox

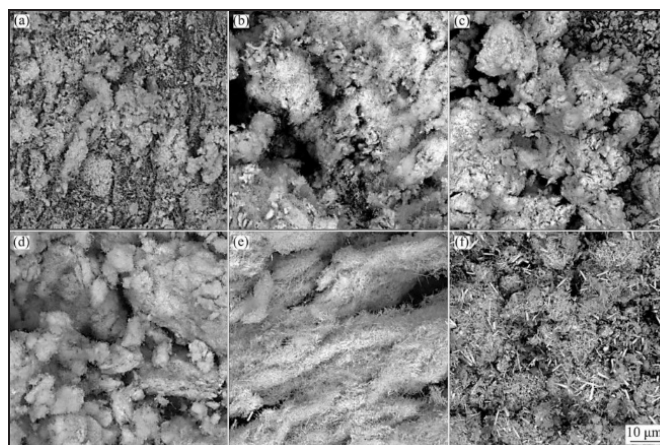
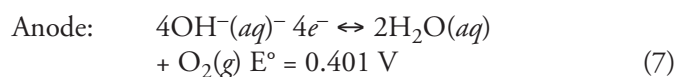
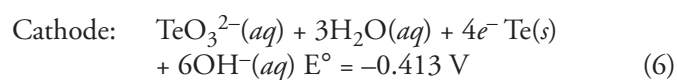


Figure 5. SEM images of Te after selective reduction of leaching solution with different NEC values: (a) 13; (b) 16; (c) 18; (d) 20; (e) 24; (f) 32 [49]

replacement (EDRR) technique has recently gained attention for the recovery of Te with lower concentrations.

Rhee et al. [52] outlined a process for the extraction of Te including leaching, precipitation, and electrowinning stages. Initially, more than 95% of the Te was recovered in the form of TeO_3^{2-} in alkaline leaching solution, while the remaining impurities, such as Cu and Pb, were primarily precipitated using Na_2S . Subsequently, nearly 99.9% of the Te was recovered through electrowinning from the relatively purified pregnant solution. The cathodic and anodic reactions within the electrowinning of Te in an alkaline solution were stated as follows: pH of 14, temperature of 25°C, TeO_3^{2-} concentration of 1 mol/L, and oxygen pressure of 1 atm):



To address the limitations associated with high reagent dosage and low recovery efficiency in traditional methods, Jin et al. [68] introduced an innovative and effective electrochemical extraction technique for Te and Cu from HCl solutions using stainless steel electrodes. The high mobility of Te in HCl solutions led to favorable electrodeposition behavior of Te (IV) based on both thermodynamic and kinetic considerations.

The conventional electrolytic extraction process involved an initial Te concentration of 100–300 g/L and a current density of 50–60 A m², yielding a current efficiency of 70–80% over a period of approximately 25 days [69]. Various efforts have been carried out towards the development of novel electrowinning methods. Cyclone electrowinning has been invented to effectively recover Te from electrolytes with substantially lower concentrations and higher impurity levels. Cyclone electrowinning achieves efficient electrowinning by facilitating high-speed liquid injection, increasing mass transfer near the electrode surface, and enhancing current density [70].

A number of research studies have concentrated on the recovery of Te from aqueous solutions using cyclone electrowinning. One of these studies, conducted by Jin et al. [68], successfully produced fine Te powder from a HCl system including 2 g/L Te, with a cathode current efficiency of only 84.3%. Another study, conducted by Xu et al. [70], demonstrated that the efficient electro-deposition of 99.94% pure Te from a sodium tellurite alkaline solution with a current efficiency of 95.25%. The Te concentration

in the solution was notably high at 100 g·L⁻¹, and the solution contained almost no impurities.

Tian et al. [69] primarily examined the utilization of cyclone electrowinning to extract Te from alkaline solutions. Their findings indicated that optimal conditions involved an electrolysis time of 24 hours, a current density of 60 Am², and an electrolyte flow speed of 300 Lh⁻¹. Approximately 82.89% of Te was extracted with a purity of 99.90% and a current efficiency of 95.61%. The results of the pilot-scale experiments indicated that Te was achieved with a purity of 99.99% with a current efficiency of 97.1% [71]. Nonetheless, some challenges persist in the practical application of cyclone electrowinning, including issues concerning test conditions and equipment for large scale production.

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

The demand for tellurium (Te) is on the rise due to its extensive applications ranging from traditional metallurgy to emerging electronics. The disparity between the limited reserves and yield of Te and the growing market demand underscores the need for the development of highly efficient and large-scale recovery technologies. The recovery of Te from tailings and metallurgical wastes of copper sulfide processing holds promise in offsetting a significant portion of primary Te extraction, thus helping to alleviate potential supply risks in the future. This comprehensive review offered insights into recent advancements in Te recovery from these resources and indicated a heightened focus on research endeavors aimed at devising effective recovery technologies. Given that currently over 90% of the global Te supply originates from anode slimes, a byproduct of copper electrorefining, various promising hydrometallurgy techniques that are commonly utilized for Te recovery, were discussed in this review including leaching, precipitation, and electrolysis. Successful extraction of Te can be achieved from both acidic and alkaline solutions. Despite their reduced energy consumption and diminished air pollution, the proposed methods are still plagued by prolonged processes, elevated equipment corrosion, and challenging liquid-solid separation. Efforts are underway to enhance leaching efficiency and selectivity through the utilization of eco-friendly oxidants, the incorporation of organic solvents and resins, and the optimization of effective parameters. Overall, efficient Te recovery mandates the creation of environmentally sustainable, economically feasible, fully integrated, and logistically streamlined recovery flowsheets. This goal can only be realized by integrating the benefits

of diverse technologies. Based on this review, some potential research thrust areas and challenges associated with Te recovery from tailings can be put forward:

1. Future technologies for reprocessing should prioritize increasing the Te content in low-waste materials. Despite numerous efforts to develop recovery technologies, there remains significant potential for achieving environmentally friendly, fully integrated, and sustainable Te recovery. The separation of Te from tailings, aligning with environmental protection standards and societal requirements, is anticipated to be realized in the foreseeable future.
2. Due to the low Te concentrations in copper flotation tailings, there is insufficient documentation on the distribution of Te-bearing minerals in these resources. This includes a lack of process mineralogy to identify the host minerals containing Te, which could be targeted for recovery. In extractive metallurgical processes, the behavior of Te is comprehensively understood, particularly for anode slimes. Consequently, research that encompasses the mineralogical characteristics of flotation tailings and technologies for recovering Te is recommended. Given that the tailings predominantly consist of fine-grained particles, flotation and hydrometallurgical techniques emerge as potentially viable routes for Te recovery. Therefore, forthcoming research should concentrate on investigating these methods for recovering Te from sulfide tailings.

REFERENCES

- [1] Mahmoudi, A., Shakibania, S., Mokmeli, M. 2020. Tellurium, from copper anode slime to high purity product: A review paper. *Metall. Mater. Trans. B* 51, 2555–2575.
- [2] Yang, W., Lan, X., Wang, Q., Dong, P., Wang, G., 2021. Selective pre-leaching of tellurium from telluride-type gold concentrate. *Front. Chem.* 9 (101), 593888.
- [3] Bo, L., Yuanfeng, P., Qi, Z., Zhihong, H., Jie, L., Huining, X., 2019. Porous cellulose beads reconstituted from ionic liquid for adsorption of heavy metal ions from aqueous solutions. *Cellulose*, 26, 9163–9178.
- [4] Gulley, A.L., Nassar, N.T., Xun, S., 2018. China, the United States, and competition for resources that enable emerging technologies. *Proc. Natl. Acad. Sci.* 115, 4111.
- [5] Jowitt, S.M., Mudd, G.M., Werner, T.T., Weng, Z.H., Barkoff, D.W., McCaffrey, D., 2018. The critical metals: an overview and opportunities and concerns for the future. *Society of Economic Geologists Special Publications*, 21, 25–38.
- [6] Addicks, L., 2008. Copper Refining. *Dabney Press*.
- [7] Anderson, C.S., 2021. Selenium and Tellurium - 2019 Annual Tables. *In 2019 Minerals Yearbook*. U.S. Geological Survey: Reston.
- [8] Willis, P., Chapman, A., Fryer, A., 2012. Study of By-Products of Copper, Lead, Zinc and Nickel: Tellurium Information. *Oakdene Hollins*: Aylesbury, UK.
- [9] Feng, J., 2017. China's minor metals and the supply and demand of gallium, selenium, and tellurium. *In Minor Metals Trade Association Conference; China Nonferrous Metals Industry Association - Gallium Selenium and Tellurium Branch*: Dublin, Ireland, 2017.
- [10] Fraunhofer Institute for Solar Energy Systems. Photovoltaics report www.ise.fraunhofer.de/content/dam/ise/de/documents/publications/studies/Photovoltaics-Report.pdf. 2022.
- [11] Grygoy'c, K., Jabło'nska-Czapla, M., 2021. Development of a tellurium speciation study using IC-ICP-MS on soil samples taken from an area associated with the storage, processing, and recovery of electrowaste. *Mol.*, 26 (9).
- [12] Zweibel, K., 2010. The impact of tellurium supply on cadmium telluride photovoltaics. *Science* 328 (5979), 699–701.
- [13] Liu, Y., Liu, P., Jiang, Q., Jiang, F., Liu, J., Liu, G., Liu, C., Du, Y., Xu, J., 2021. Organic/ inorganic hybrid for flexible thermoelectric fibers. *Chem. Eng. J.* 405, 126510.
- [14] Lide, D.R., 2005. CRC Handbook of Chemistry and Physics, 86th ed. *CRC Press*, Boca Raton, Florida.
- [15] El-Mallawany, R.A.H., 2011. Tellurite Glasses Handbook: Physical Properties and Data, 2nd ed. *CRC Press*, Boca Raton, Florida.
- [16] Candelise, C., Winkler, M., Gross, R., 2012. Implications for CdTe and CIGS technologies production costs of indium and tellurium scarcity. *Prog. Photovolt. Res. Appl.* 20, 816–831.
- [17] Rocchetti, L., Beolchini, F., 2015. Recovery of valuable materials from end-of-life thinfilm photovoltaic panels: environmental impact assessment of different management options. *J. Clean. Prod.* 89, 59–64.

- [18] Ojebuoboh, F., 2008. Selenium and tellurium from copper refinery slimes and their changing applications. In *World of Metallurgy - ERZMETALL* 61, 33–39.
- [19] U.S. Geological Survey, 2021. Mineral Commodity Summaries. U.S. Geological Survey: Reston, 2021.
- [20] Davenport, W.G., King, M., Schlesinger M., and Biswas, A.K. 2002. *Extractive Metallurgy of Copper*, 4th edition, *Pergamon*.
- [21] Suppes, R., Heuss-Aßbichler, 2021. Resource potential of mine wastes: A conventional and sustainable perspective on a case study tailings mining project. *J. Cleaner Prod.* 297, 126446.
- [22] Van der Ent, A., Parbhakar-Fox, A., Erskine, P.D., 2021. Treasure from trash: Mining critical metals from waste and unconventional sources. *Sci. Total Environ.* 758, 143673.
- [23] Bilal, M., Park, I., Hornn, V., Ito, M., Hassan, F.U., Jeon, S., Hiroyoshi, N. 2022. The challenges and prospects of recovering fine copper sulfides from tailings using different flotation techniques: A review. *Minerals*, 12, 586.
- [24] Ghodrati, S., Nakhaei, F., VandGhorbany O., & Hekmati, M. 2020. Modeling and optimization of chemical reagents to improve copper flotation performance using response surface methodology, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 42:13, 1633–1648.
- [25] Hudson-Edwards, K.A., Jamieson, H.E., Lottermoser, B.G., 2011. Mine Wastes: Past, Present. Future. *Elements*, 7, 375–380.
- [26] Lottermoser, B.G., 2010. *Mine Wastes: Characterization, Treatment and Environmental Impacts*, 3rd Edition. 2010, *Springer*, Berlin, Heidelberg.
- [27] König, S., Lissner, M., Lorand, J-P., Bragagni A., Luguët, A. 2015. Mineralogical control of selenium, tellurium and highly siderophile elements in the Earth's mantle: Evidence from mineral separates of ultra-depleted mantle residues. *Chem Geol.* 396,16–24.
- [28] Moats, M., Alagha, L., Awuah-offei, K. 2021. Towards resilient and sustainable supply of critical elements from the copper supply chain: A review. *Journal of Cleaner Production*, 307: 127207.
- [29] Yano, R., Trace element distribution in chalcopyrite-bearing porphyry and skarn deposits. 2012, University of Nevada, Reno.
- [30] Reich, M., Deditius, A., Chryssoulis, S., Li, J.W., Ma, C.Q., Parada, M.A., Barra, F., Mittermayr, F., 2013. Pyrite as a record of hydrothermal fluid evolution in a porphyry copper system: A SIMS/EPMA trace element study. *Geochimica et Cosmochimica Acta* 104, 42–62.
- [31] Corchado-Albelo, J. and Alagha, L. 2023. Characterization of tellurium, gold, and silver in copper porphyry processing streams, *MINEXCHANGE SME*, Conference; Denver, CO, March 1 2023.
- [32] Yu, H., Zhang, T., Jing, Z., Xu, J., Qiu, F., Yang, D., Yu, L., 2019. In situ fabrication of dynamic nano zero-valent iron/activated carbon nanotubes membranes for tellurium separation. *Chem. Eng. Sci.* 205, 278–286.
- [33] Wei, X., Liu, C., Cao, H., Ning, P., Jin, W., Yang, Z., Wang, H., Sun, Z., 2019. Understanding the features of PGMs in spent ternary automobile catalysts for development of cleaner recovery technology. *J. Clean. Prod.* 239, 118031.
- [34] Schlesinger, M. E. Sole, K. C. Davenport G. W. 2011 Davenport WG. *Extractive metallurgy of copper*. 5th Edition - July 26, 2011 Elsevier; <https://www.elsevier.com/books/extractive-metallurgy-of-copper/schlesinger/978-0-08-096789-9>. Accessed Mar 2020.
- [35] Moskalyk, R.R., Alfantazi, A.M, 2003. Review of copper pyrometallurgical practice: today and tomorrow. *Miner. Eng.* 16:893–919.
- [36] Chen, Y., Zhao, Z., Taskinen, P., Liang, Y., Ouyang, H., Peng, B., Jokilaakso, A., Zhou, S., Chen, T., Peng, N., Liu, H., 2020. Characterization of copper smelting flue dusts from a bottom-blowing bath smelting furnace and a flash smelting furnace. *Metall. Mater. Trans. B*, 51B, 2596–2608.
- [37] Mei, Q., Tian, R., Shi, Y., Hua, Q., Chen, C., Tong, B., 2016. A series of selective and sensitive fluorescent sensors based on a thiophen-2-yl-benzothiazole unit for Hg²⁺. *New J. Chem.* 40, 2333–2342.
- [38] Fan, Y., Yang, Y., Xiao, Y., Zhao, Z., Lei, Y., 2013. Recovery of tellurium from high tellurium bearing materials by alkaline pressure leaching process: thermodynamic evaluation and experimental study. *Hydrometallurgy*, 139, 95–99.
- [39] Mahmoudi, A., Shakibania, S., Mokmeli, M., Rashchi, F., 2020. tellurium, from copper anode slime to high purity product: A review paper. *Metall. Mater. Trans. B* 51 (6), 2555–2575.

- [40] Hoffmann, J.E., 1989. Recovering selenium and tellurium from copper refinery slimes. *J. Occup. Med.* 41 (7), 33–38.
- [41] Makuei, F.M., Senanayake, G., 2018. Extraction of tellurium from lead and copper bearing feed materials and interim metallurgical products—a short review. *Miner. Eng.* 115, 79–87.
- [42] Ludvigsson, B.M., Larsson, S.R., 2003. Anode slimes treatment: the Boliden experience. *JOM* 55, 41–44.
- [43] Wang, S., 2011. Tellurium, its resourcefulness and recovery. *JOM* 6, 90–93.
- [44] Hoffmann, J.E., Westrom, B., 1994. Hydrometallurgical Processing of Refinery Slimes at Phelps Dodge: Theory to Practice, Hydrometallurgy '94. *Springer Netherlands*, Dordrecht, pp. 69–105.
- [45] Hait, J., Jana, R.K., Kumar, V., Sanyal, S.K., 2002. Some studies on sulfuric acid leaching of anode slime with additives. *Ind. Eng. Chem. Res.* 41, 6593–6599.
- [46] Aydogan, S., Aras, A., Canbazoglu, M., 2005. Dissolution kinetics of sphalerite in acidic ferric chloride leaching. *Chem. Eng. J.* 114, 67–72.
- [47] Fthenakis, V.M., Wang, W., 2006. Extraction and separation of Cd and Te from cadmium telluride photovoltaic manufacturing scrap. *Prostate*, 14, 363–371.
- [48] Shao, L., Diao, J., Ji, C., Li, G., 2020. A novel and clean process for extracting tellurium and bismuth from Dashuigou tellurium ore by oxidizing leaching. *Hydrometallurgy* 191, 105205.
- [49] Shao, L.X., Diao, J., Liu, L., Xie, B., 2023. Selective reduction separation and recovery of tellurium and bismuth from acidic leaching solution, *Transactions of Nonferrous Metals Society of China*, 33 (2), 596–608.
- [50] Ma, Z.-y., Yang, H.-y., Huang, S.-t., Lü, Y., Xiong, L., 2015. Ultra fast microwave-assisted leaching for the recovery of copper and tellurium from copper anode slime. *Int. J. Miner. Metall. Mater.* 22 (6), 582–588.
- [51] Sun, Z.-m., Zheng, Y.-j., 2011. Preparation of high pure tellurium from raw tellurium containing Cu and Se by chemical method. *Trans. Nonferrous Metals Soc. China* 21 (3), 665–672.
- [52] Rhee, K.I., Lee, C.K., Ha, Y.C., Jeong, G.J., Kim, H.S., Sohn, H.J., 1999. Tellurium recovery from cemented tellurium with minimum waste disposal. *Hydrometallurgy* 53 (2), 189–201.
- [53] Li, Z., Qiu, F., Tian, Q., Yue, X., Zhang, T., 2022. Production and recovery of tellurium from metallurgical intermediates and electronic waste—A comprehensive review. *J. Clean. Prod.* 366, 132796.
- [54] Charles, Ph., Hannaert, P., 1970. Fluid-bed cementation of selenium contained in a copper electrolyte. Copper metallurgy proceedings. *AIME, Denver*, pp. 240–259.
- [55] Wang, S., Westrom, B., Fernandez, J., 2003. A novel process for recovery of Te and Se from copper slimes autoclave leach solution. *J. Miner. Mater. Charact. Eng.* 2 (1), 53–64.
- [56] Shibasaki, T., Abe, K., Takeuchi, H., 1992. Recovery of tellurium from decopperizing leach solution of copper refinery slimes by a fixed bed reactor. *Hydrometallurgy* 29 (1), 399–412.
- [57] Dutton, W.A., Cooper, W.C., 1966. The oxides and oxyacids of tellurium. *Noranda Research Center*, pp. 657–674.
- [58] Mokmeli, M., Dreisinger, D.B., Wassink, B., 2014. Thermodynamics and kinetics study of tellurium removal with cuprous ion. *Hydrometallurgy* 147, 20–29.
- [59] Xu, L., Xiong, Y., Song, Y., Zhang, G., Zhang, F., Yang, Y., Hua, Z., Tian, Y., You, J., Zhao, Z., 2020. Recycling of copper telluride from copper anode slime processing: toward efficient recovery of tellurium and copper. *Hydrometallurgy* 196, 105436.
- [60] Xu, L., Xiong, Y., Zhang, G., Zhang, F., Yang, Y., Hua, Z., Tian, Y., You, J., Zhao, Z., 2020. An environmental-friendly process for recovery of tellurium and copper from copper telluride. *J. Clean. Prod.* 272, 122723.
- [61] Liu, W., Yang, T., Zhang, D., Chen, L., Liu, Y., 2014. Pretreatment of copper anode slime with alkaline pressure oxidative leaching. *Int. J. Miner. Process.* 128, 48–54.
- [62] Xiao, L., Wang, Y.L., Yv, Y., Fu, G.Y., Han, P.W., Sun, Z.H.I., Ye, S.F., 2018. An environmentally friendly process to selectively recover silver from copper anode slime. *J. Clean. Prod.* 187, 708–716.
- [63] Mokmeli, M., Dreisinger, D., Wassink, B., 2015. Modeling of selenium and tellurium removal from copper electrowinning solution. *Hydrometallurgy* 153, 12–20.
- [64] Zhang, F.Y., Zheng, Y.J., Peng, G.M., 2017. Selection of reductants for extracting selenium and tellurium from degoldized solution of copper anode slimes. *Trans. Nonferrous Met. Soc. China* 27 (4), 917–924.
- [65] Guo, X.Y., Xu, Z.P., Li, D., Tian, Q.H., Xu, R.Z., Zhang, Z., 2017. Recovery of tellurium from high tellurium-bearing materials by alkaline sulfide leaching followed by sodium sulfite precipitation. *Hydrometallurgy*, 171, 355–361.

- [66] Xu, Z., Guo, X., Li, D., Tian, Q., Zhu, L., 2020. Selective recovery of Sb and Te from the sodium sulfide leach solution of Te-bearing alkaline skimming slag by drop-wise H_2O_2 addition followed by Na_2S – Na_2SO_3 precipitation. *Hydrometallurgy* 191, 105219.
- [67] Bouroushian, M., 2010. Electrochemistry of the chalcogens. In: Bouroushian, M. (Ed.), *Electrochemistry of Metal Chalcogenides*. Springer, Berlin, Heidelberg, pp. 57–75.
- [68] Jin, W., Su, J., Chen, S., Li, P., Moats, M.S., Maduraiveeran, G., Lei, H., 2018. Efficient electrochemical recovery of fine tellurium powder from hydrochloric acid media via mass transfer enhancement. *Separ. Purif. Technol.* 203, 117–123.
- [69] Tian, Q., Li, J., Guo, X., Li, D., Yang, Y., Xu, Z., Li, W., 2021. Efficient electrochemical recovery of tellurium from spent electrolytes by cyclone electrowinning. *J. Sustain. Metall.* 7 (1), 27–45.
- [70] Jin, W., Hu, M., Hu, J., 2018a. Selective and efficient electrochemical recovery of dilute copper and tellurium from acidic chloride solutions. *ACS Sustain. Chem. Eng.* 6 (10), 13378–13384.
- [71] Hong, J., Xu, Z., Li, D., Guo, X., Yu, D., Tian, Q., 2020. A pilot study: efficient electrowinning of tellurium from alkaline solution by cyclone electrowinning technology. *Hydrometallurgy*, 196, 105429.

Testing of Ground Truth Instruments for Use in Evaluating Haul Truck Collision Warning and Avoidance Systems

J. Bickson, Chenming Zhou, Yongjun Zhang, J.R. Srednicki,
J.L. Carr, M. Girman, J. A. Galanko, C.R. DeGennaro, and B. Lambie
CDC NIOSH, Pittsburgh, PA

ABSTRACT

Between 2005 and 2021, surface mining haul trucks were involved in 54 fatal incidents in the United States [1]. Collision warning and avoidance systems (CXS) can help haul truck operators navigate their route safely. The evaluation of CXS object detection performance for surface mining haul trucks relies on the positional accuracy of the ground truth instrument. As part of a holistic approach, researchers from the National Institute for Occupational Safety and Health (NIOSH) characterized the accuracy of a global navigation satellite system (GNSS) that serves as the ground truth instrument to determine object position and velocity in CXS object detection performance testing. We used precision surveying equipment to establish ground truth points for comparison with GNSS data collected for static positional measurements and reduced-scale straight-line vehicle dynamic tests. We conducted these tests with real-time kinematics (RTK) and then satellite-based augmentation systems (SBAS). For the dynamic tests, we measured a distance error of 1.34 m (4.40 ft) using RTK and 1.50 m (4.92 ft) using an SBAS. This research will provide CXS manufacturers and CXS researchers a basis for evaluating the positional accuracy of CXS. Note that we did not evaluate any CXS in this experiment.

INTRODUCTION

Background

For surface mine haul trucks, the main function of collision warning and avoidance systems (CXS) is to assist drivers at avoiding accidents in their travel that can lead to collateral damages, injuries, or fatalities. Because detection

performance is critical, the ground truth instrument (GTI) used to assess positional accuracy of CXS must be reliable. Modern GNSS receivers can be considered as a GTI because of their reported centimeter level of accuracy, under static condition [2]. Researchers from the National Institute for Occupational Safety and Health (NIOSH) designed an experiment to validate the positional accuracy of GNSS receivers for our intended purpose which is to use GNSS receivers as ground truth to assess detection of CXS, specifically while GNSS receivers are in motion.

Limited literature exists describing dynamic test measurements of GNSS receivers. However, two relevant standards exist that discuss the accuracy of GNSS receivers for static measurements or testing methods for GNSS while in motion. These are ISO 12188-1 and ISO 12188-2. These standards provide detailed instructions on how to test the positional accuracy of GNSS receivers in the agricultural industry. ISO 12188-1 specifies common parameters to assess and compare different GNSS receivers in dynamic conditions [3]. ISO 12188-2 covers how to assess automated guidance systems based on GNSS technologies for agricultural vehicles [4]. NIOSH researchers modified the static and dynamic test methods described in these standards to make them more suitable to our application. Our test method differed in terms of test course requirement, test procedure and test report and calculations.

Approach in the Current Study

Using ISO 12188-1 and ISO 12188-2 as reference, we took measurements to evaluate the positional accuracy of GNSS receivers we used in a separate experiment to assess