Review

An Arsenic Removal Technology and Its Application in Arsenic-Containing Copper

Xiaowei Tang and Yuehui He

State Key Laboratory of Powder Metallurgy and Powder Metallurgy Research Institute, Central South University, Changsha 410083, China; txwisme@csu.edu.cn
State Key Laboratory of Synthetic Chemistry, Central South University, Changsha 410083, China

Abstract: The usage of copper (Cu) ores containing low or no arsenic (As) has reduced, and Cu ores containing high levels of As have emerged as vital mineral resources for Cu extraction and processing. The quality of the Cu ores has decreased from 1.6% to approximately 1.0%. The proportion of As to Cu in 15% of Cu resources currently reaches 1:5. However, during the extraction and processing of Cu ores, As presents significant environmental harm. Hence, safely and effectively removing As is paramount in Cu smelting and processing, holding substantial importance in fostering environmentally sustainable practices within the Cu extraction and processing industry. This article consolidates the resource distribution of As-containing Cu (ACC) ores, comprehensively and systematically evaluates the present advancements in extracting techniques for these minerals, and identifies the challenges inherent in pyrometallurgical and wet processes for treating ACC deposits. Pyrometallurgy is a simple primary roasting technique and has widespread applicability in the treatment of various ACC minerals. Its disadvantages are the emission of exhaust gas and the high treatment costs associated with it. The wet arsenic removal method boasts advantages including minimal air pollution and a high resource recovery rate, significantly aiding in Cu concentrate recovery; its major drawback is the production of As-containing wastewater. The hydrometallurgical removal of As from ACC mines involves extracting As through leaching. Recently, biometallurgy has presented innovative solutions using specialized microorganisms to bioleach or bioabsorb As, but large-scale industrial applications still lack specific practical implementation. This review explores the underlying causes of the challenges encountered in processing ACC minerals. Additionally, it highlights pyrometallurgical roasting coupled with high-temperature filtration as a pivotal advancement in the extraction and processing of ACC ores.

Keywords: Cu minerals; As removal; pyrometallurgy; hydrometallurgy; biometallurgy; As precipitation

1. Introduction

With societal progress and economic advancement, copper’s applications have expanded across diverse human endeavors. Copper has been used in integrated circuit (IC) devices in sizes less than 180 nm due to its low resistivity [1], resulting in a significant global surge in copper consumption. To meet the escalating demands, copper smelting capacity has increased rapidly, with a consistent annual increase in smelting scales. Nonetheless, the finite nature of copper resources poses a challenge, intensifying the reliance on Cu concentrates. Accordingly, a historic surge in the capacity of refined Cu has been witnessed in recent years [2–6]. Concurrently, the continued increases of resource utilization have resulted in a notable decline in high-quality Cu reserves. Global reports indicate a decrease in the average quality of Cu ores from 1.6% in 1990 to approximately 1.0% in recent years [7–9]. In China, more than half (56%) of Cu resources exhibit qualities under 0.7%. Against this background, as Cu production continues and high-grade Cu mineral resources diminish, Cu concentrates with low As contents decrease each year and...
there is a growing focus on As-containing Cu (ACC) minerals [10–12], which will inevitably be utilized for Cu smelting.

However, the processes for smelting ACC minerals generate various harmful substances, among which arsenic stands out as a common and particularly hazardous compound [13]. Arsenic’s toxicity to the human body can cause acute poisoning upon short-term exposure and can potentially lead to cancer upon prolonged contact [14]. Furthermore, the presence of arsenic poses threats not only to human health but also to the environment [13]. Arsenic exists widely in various minerals such as arsenopyrite, chalcopyrite, and tetrahedrite, and its presence in mineral formations such as these substantially diminishes the value of their Cu ores.

Nonetheless, as copper ore reserves deplete and mineral grades decline in copper smelting, the cost per unit of mined mineral escalates [11,12]. Rising operational costs prompt a reevaluation of the value of ACC minerals, despite their health and environmental hazards. From this standpoint, effectively and safely removing arsenic from copper minerals now seems to hold significant importance in fostering the sustainable and healthy development of China’s mineral raw material industry [12].

To address its potential, this review provides an overview of arsenic’s various forms and distribution in Cu ore and systematically explores arsenic treatment processes, predominantly focusing on typical treatment processes for ACC minerals. Following this, we outline the development trajectory of As extraction technologies that may be applied to minerals containing this compound, offering insights into the future possibilities for the efficient and safe utilization of ACC ores.

2. Current Status of ACC Minerals

2.1. Depletion of Cu Minerals

Recently, the intensified utilization of copper resources has significantly depleted high-quality and easily sorted Cu reserves [15]. Accordingly, reports indicate a pronounced decline in the average global Cu mineral grade, reducing from 1.6% in 1990 to around 1.0% in current assessments. This decrease is accompanied by a diminishing availability of high-grade Cu. Figure 1 visually tracks world Cu ore grade changes from 2000 to 2021 [16,17], with the graphical representation offering a clear illustration of the declining trend, emphasizing the tangible and concerning effects of prolonged and escalating resource exploitation on ore quality [18–20].

![Figure 1. Changes in copper grade worldwide from 2000 to 2021.](image)

This scenario presents a challenge in meeting the demand for copper production, as demand continues to grow while resources decline. One potential solution is the utilization of ACC resources. An ACC concentrate is the term used for a Cu concentrate containing more than 2% As. The resources to produce such a concentrate are readily available, with the
proportion of As to Cu in 15.0% of Cu resources standing at 1:5. Among these, tetrahedrite (Cu12As4S13) and arsenate (Cu3AsS4) are common As-bearing Cu deposits. While such Cu resources were previously overlooked, they are increasingly being considered as main materials for Cu metallurgy [21,22].

2.2. Hazards of ACC Minerals

In Cu metallurgy, along with the obvious shortcoming of Cu resources at present, an accompanying issue that must be faced is the increasing use of complex materials, particularly ACC minerals. There are options for processing these complex materials, such as residual arsenic treatment, but the costs of such approaches are increasing sharply. Furthermore, regardless of the Cu mineral properties and the sorting techniques used, it remains especially difficult to entirely separate As from Cu minerals, resulting in concentrates that contain amounts of As. As is severely toxic to human beings and other creatures. It causes direct damage to the nerve cells of the human body and can lead to peripheral neuritis, multi-organ carcinogenesis, and damage to the heart, liver, and other parenchymal organs [23]. The lethal dose for a human via acute poisoning is 0.2–0.6 g of arsenic [24]. Beyond its human impact, arsenic also pollutes the environment, necessitating investments in arsenic treatment [25]. Figure 2 presents a diagram of the chemical cycle of arsenic worldwide [26–28].

![Geochemical cycle of arsenic.](image_url)

Figure 2. Geochemical cycle of arsenic.

Given the increasing efforts being made to ensure environmental protection and develop sustainable strategies, the treatment of As-waste in Cu metallurgy is becoming a high priority, although there are costs associated with research and development [29,30]. Currently, arsenic smelting manufacturers have not yet devised an effective treatment method. While the options are being explored, large amounts of As waste are being discharged in three forms: gas, liquid, and solid. As shown in Table 1, according to United States Geological Survey (USGS) data, the annual output of arsenic is huge and growing [31,32]. However, when analyzing the data of the world’s two largest economies, the United States of America (USA) and China, it is found that the import and export quantities are relatively stable and account for only one-fifth of the output, which reflects the accumulation of this toxic waste and underscores the pressing short-term need for a solution. Until one is found, non-ferrous metallurgical enterprises will continue to have a highly adverse impact on their surrounding environments [13,14].
Table 1. Arsenic production, import, and export in China and the United States from 2015 to 2021 [31,32].

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<tr>
<td>Global</td>
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<td>37,000</td>
<td>37,000</td>
<td>33,400</td>
<td>32,300</td>
<td>60,000</td>
<td>59,000</td>
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<td>China Import</td>
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<td>16.98</td>
<td>3.31</td>
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<td>3555</td>
<td>2275</td>
<td>2008</td>
<td>1966</td>
<td>2601</td>
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<td>U.S.A Import</td>
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<td>5320</td>
<td>5980</td>
<td>5540</td>
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3. Technical Process of As Removal in ACC Minerals

The evolution of As removal technology in ACC mining has undergone several phases, marked by advancements in techniques aimed at efficiently eliminating As from ore. Initially, early methods relied on mechanical separation processes such as sorting and flotation, supplemented by pyrometallurgy. Pyrometallurgical processes offer simplicity, primarily involving roasting, and they have widespread applicability across various ACC minerals. However, a notable disadvantage is the challenging collection of exhaust gas, leading to high treatment costs due to environmental regulations governing waste gas management [33–37].

Subsequently, the introduction of wet smelting techniques revolutionized the process by utilizing chemical reactions to convert arsenic into soluble materials for extraction, thus markedly enhancing the removal efficiency. Wet arsenic removal methods boast advantages such as minimal air pollution and a high resource recovery rate, significantly aiding in Cu concentrate recovery. Nonetheless, a major drawback lies in the treatment of As-containing wastewater, which often necessitates additional As solidification, with associated costs typically surpassing those involved in treating As-containing waste gas [38,39]. Beyond these, recent advancements in biometallurgy have presented innovative solutions employing specialized microorganisms for the bioleaching or biosorption of As. However, large-scale industrial application remains theoretical, lacking specific practical implementation. Overall, this chronological progression from physical to chemical and biological methods reflects a continuous quest for more effective, environmentally sustainable, and thorough arsenic removal techniques in the realm of ACC mining.

4. Pyrometallurgy

The application of pyrometallurgy for As removal involves separating arsenic in its gaseous form from ACC mines. This may be achieved through the use of different roasting atmospheres, which includes reduction, oxidation, and sulfate/carbonate pyrometallurgies [15].

4.1. Reduction Pyrometallurgy

During anaerobic situations, chalcopyrite (Cu$_3$AsS$_4$) is initially decomposed at 550 °C, as described in Formula (1), reported previously [40–43]. Meanwhile, CuS is unstable at temperatures from 500 °C to 700 °C and changes into Cu$_2$S, as described by Formula (2) [40–43].

$$2\text{Cu}_3\text{AsS}_4(s) \rightarrow \text{Cu}_2\text{S}(s) + 4\text{CuS}(s) + \text{As}_2\text{S}_3(g) \quad (1)$$

$$2\text{Cu}_3\text{AsS}_4(s) \rightarrow 3\text{Cu}_2\text{S}(s) + \text{As}_2\text{S}_3(s) + \text{S}_2(g) \quad (2)$$

Another means of reaction is via the generation of perovskite (Cu$_{12}$As$_4$S$_{13}$) and its subsequent decomposition (3, 4) [36].

$$\text{(Cu}_3\text{AsS}_4)_{4}(s) \rightarrow \text{Cu}_{12}\text{As}_4\text{S}_{13}(s) + 3/2\text{S}_2(g) \quad (3)$$

$$\text{Cu}_{12}\text{As}_4\text{S}_{13}(s) \rightarrow 6\text{Cu}_2\text{S}_1+x(s) + \text{As}_4\text{S}_4(g) + (1.5-3x)\text{S}_2(g) \quad (4)$$
Moreover, a method that uses carbon monoxide to supply a reducing atmosphere may offer a useful means of As removal. In this pathway, when the CO₂ content reaches 15.5% in the exhaust gas, the As amount is decreased from 9% to 0.2% [44].

Wilkomirsky et al. [45] considered the possibility of neutral roast reactions for high-As Cu minerals and developed an Ellingham diagram accordingly. This was part of an attempt to simulate the thermodynamics and kinetics of the fluidized-bed neutral roasting of an enargite concentrate at the University of Concepcion’s pilot plant (Rajoria et al. [46]). In this simulation, the vast majority of the roasting reactions are exothermic. Enargite is directly broken down into Cu₂S (s) and As₂S₃ (g), which can also be achieved through a reaction with FeS.

4.2. Oxidation Pyrometallurgy

In the aerobic situation, chalcopyrite (Cu₃AsS₄) disintegrates into chalcopyrite (Cu₂S), sulfur dioxide, and As trioxide. This reaction may be described with the following Equation (5) [47]:

\[ 2\text{Cu}_3\text{As}_4\text{S}_4(s) \rightarrow \text{Cu}_2\text{S}(s) + 4\text{CuS}(s) + \text{As}_2\text{S}_3(g) \]  

(5)

After this reaction, the final Cu sulfide is converted into Cu oxide, which is described as follows (6, 7) [48]:

\[ 4\text{Cu}_3\text{As}_4\text{S}_4(s) + 22\text{O}_2(g) \rightarrow 6\text{Cu}_2\text{O}(s) + 16\text{SO}_2(g) + \text{As}_4\text{O}_6(g) \]  

(6)

\[ 4\text{Cu}_3\text{As}_4\text{S}_4(s) + 25\text{O}_2(g) \rightarrow 12\text{CuO}(s) + 16\text{SO}_2(g) + \text{As}_4\text{O}_6(g) \]  

(7)

In general, a high oxygen level results in the formation of Cu₃As and CuO phases, simultaneously transforms As₂O₃ into As₂O₅, and, finally, produces a copper-arsenate compound (3CuO-As₂O₅) with CuO in the condensate. This process is not conducive to arsenic removal.

Adham K and Harris CT analyzed the relationship between the equilibrium amount of gaseous As and the O₂ within the As-O-S system at 700 °C; their results are given in Figure 3 [49]. This reveals whether arsenic’s presence may be determined based on the oxygen potential and shows that arsenic mainly exists in three gaseous forms: As₂S₃, As₄S₄, and As₄O₆. Meanwhile, when the amount of oxygen increases, a considerable quantity of sulfur evaporates in the form of SO₂ (shown in Figure 3) [50].

![Figure 3. Thermodynamic equilibrium diagram for As-O-S system.](image-url)
4.3. Sulfate/Carbonate Roasting

Previous reports have stated that when the roasting temperature ranges from 400 to 550 °C, chalcopyrite (Cu$_3$AsS$_4$) undergoes a sulfation process, forming Cu sulfate, Cu, As, ferrum (Fe), sulfate (S), Fe$_2$O$_3$, and FeAsO$_4$. In this process, over 80% of As is fixed in the state of arsenate, and it only evaporates when the temperature rises above 650 °C [51].

Based on the above-mentioned process, Putra et al. proposed using sodium carbonate and arsenic fixed roasting to convert arsenic (Cu$_3$AsS$_4$) to sodium As, in which arsenic is dislodged at a temperature of 800 °C. This approach is described through the following Equations (8) and (9) [52].

$$4\text{Cu}_3\text{AsS}_4(\text{S}) + 5.5\text{Na}_2\text{CO}_3(s) + 8.75\text{O}_2(g) \rightarrow 3\text{CuO}(s) + \text{Na}_3\text{AsO}_4(s) \quad (8)$$

$$4\text{Cu}_3\text{AsS}_4(\text{S}) + 4\text{Na}_2\text{CO}_3(s) + 6\text{CO}_2(g) \rightarrow 1.5\text{Cu}_2\text{S}(s) + \text{Na}_3\text{AsO}_4(s) + 2.5\text{Na}_2\text{SO}_4 + 10\text{CO}(g) \quad (9)$$

5. Hydrometallurgy

Hydrometallurgy may be applied in the removal of arsenic from ACC mines, which mainly involves extracting arsenic through leaching. There are two main methods: alkali leaching and acid leaching [15].

5.1. Alkali Leaching

Alkali leaching is a frequently used method of As removal, in which the Cu in chalcopyrite is converted into Cu$_2$S or CuO by regulating the pH and increasing oxidants. Meanwhile, As is also changed into AsS$_4^{3-}$ or/and AsO$_4^{3-}$ [53,54]. The current alkaline leaching systems mainly include Na$_2$S-NaOH, NaHS-NaOH, and NaClO-NaOH.

The Na$_2$S-NaOH system is described using the following reaction Formula (10):

$$2\text{Cu}_3\text{AsS}_4 + 3\text{Na}_2\text{S} = 2\text{Na}_3\text{AsS}_4 + 3\text{Cu}_2\text{S} \quad (10)$$

This system has been applied in the treatment of arsenic tetrahedrite [55]. Under the conditions of a Na$_2$S concentration of 90–100 g/L, NaOH concentration of 70–80 g/L, a temperature 105 °C, and a liquid/solid ratio of 5:1, the rate of As removal can surpass 91.0%. Furthermore, using the approach mentioned above, Ruiz MC and Grandon L probed the co-effect of Na$_2$S and NaOH on chalcopyrite leaching. In doing so, they found that a rate of arsenic removal of over 97% could be achieved through the excessive use of Na$_2$S and NaOH at a temperature of 80 °C [56].

The NaHS-NaOH system, meanwhile, is described through the following reaction Formula (11):

$$2\text{Cu}_3\text{AsS}_4 + 6\text{H}^+ + 5.5\text{O}_2 \rightarrow 3\text{Cu}^{2+} + \text{Cu}_3(\text{AsO}_4)_2 + 8\text{S} + 3\text{H}_2\text{O} \quad (11)$$

A leaching study was conducted on chalcopyrite when using this system, which showed that chalcopyrite may be decomposed into Cu$_2$S, and arsenic may be removed at a rate exceeding 90% at a temperature of 80 °C and a pH of 12.5 [57].

Next, the equation for the NaClO-NaOH system is described as (12):

$$2\text{Cu}_3\text{AsS}_4 + 6\text{H}^+ + 5.5\text{O}_2 \rightarrow 3\text{Cu}^{2+} + \text{Cu}_3(\text{AsO}_4)_2 + 8\text{S} + 3\text{H}_2\text{O} \quad (12)$$

In a previous report, the results of a serial leaching experiment performed on high-As Cu minerals using the NaClO-NaOH system were presented. In this study, the experiment comprised a ratio of liquid/solid of 5:1, a temperature of 50 °C, and HClO concentration of 10%; the As removal rate was over 80% [58]. In another study, NaClO (0.13 mol/L) and NaOH were used to jointly act on chalcopyrite: a one-hour leaching experiment was conducted at 40–60 °C, and the As removal rate was over 80% [59]. In sum, applying
the proposed alkaline leaching method to removal arsenic requires an alkaline leaching solution and strongly alkali-resistant equipment, and the As removal rate is only 80.0%.

5.2. Acid Leaching

The leaching mode of high-As Cu minerals involves using reagents including H₂SO₄ and HCl to removal As (III) compounds [60,61]. In this method, a series of oxidants including H₂O₂, O₂, and Fe³⁺ must be added to the reaction setup to promote the reaction of As (III) with the oxidant. When taking this approach, the Cu in high-As Cu minerals changes into Cu²⁺ and Cu₃(AsO₄)₂ through the adjustment of the pH. This is represented by chemical Equations (13) and (14) [62]. Additionally, to promote the As leaching process, measures are taken such as adding NaCl or Fe³⁺, regulating the pH, and raising the temperature [63].

\[
\begin{align*}
2\text{Cu}_3\text{AsS}_4 + 6\text{H}^+ + 5.5\text{O}_2 & \rightarrow 3\text{Cu}^{2+} + \text{Cu}_3(\text{AsO}_4)_2 + 8\text{S} + 3\text{H}_2\text{O} \quad (13) \\
4\text{Cu}_3\text{AsS}_4 + 35\text{O}_2 + 10\text{H}_2\text{O} & \rightarrow 12\text{CuSO}_4 + 4\text{H}_3\text{AsO}_4 + 4\text{H}_2\text{SO}_4 \quad (14)
\end{align*}
\]

A previous report presented a study on high-As Cu minerals in Fe₂(SO₄)₃ media. The study showed that the arsenic leaching rate of high-As Cu minerals in Fe₂(SO₄)₃ medium, with a temperature of 80 °C and excessive Fe²⁺ [64], reached 100%. Furthermore, in a study on copper smelting, the As removal rate was close to 96% when polytetrafluoroethylene (PTFE) was added [65,66], in a process that also accelerated the change of arsenic into smectite, thus obtaining an arsenic solidification compound.

In summary, the acid extraction As removal method is actually a means of Cu extraction with a high rate of As removal, and As is solidified when carrying out this leaching method. However, a certain amount of waste is generated, and this method requires the addition of oxidants, which results in high costs in industrial production.

6. Biometallurgy

Generally, biometallurgy for As removal include two stages [67]. In this method, the first stage is dependent on the direct action of bacteria, which leads to the extraction and dissolution of As and S in H₃AsO₄ and H₂SO₄, respectively [15]. This reaction is described in Formula (15). In the second stage, the indirect reaction of bacteria dominates the entire process and accelerates the reaction set out in Equation (16).

\[
\begin{align*}
4\text{Cu}_3\text{AsS}_4 + 35\text{O}_2 + 10\text{H}_2\text{O} \text{ bacteria} & \rightarrow 12\text{CuSO}_4 + 4\text{H}_2\text{SO}_4 + 4\text{H}_3\text{AsO}_4 \quad (15) \\
\text{Cu}_3\text{AsS}_4 + 5.5\text{Fe}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O} \text{ bacteria} & \rightarrow 3\text{CuSO}_4 + 11\text{FeSO}_4 + 4\text{S} + \text{H}_3\text{AsO}_4 + 2.5\text{H}_2\text{SO}_4 \quad (16)
\end{align*}
\]

One study conducted a leaching experiment on high-As Cu minerals using mesophilic acidophilic Thiobacillus ferrooxidans, thermophilic acidophilic Thiothrix, and thermophilic Ferroplasia archaea. The study indicated that such bacteria have an accelerating effect on the extraction of arsenic [68]. In addition, a leaching experiment on ACC mines was conducted using moderately thermophilic bacteria. This experiment showed that under the conditions of pH 1.5 and 55 °C, when the slurry concentration was set as 5.0%, the As removal rates reached 78.21% [69]. Collectively, the research indicates that the biometallurgy method is a low-cost and low-polluting Cu extraction approach, but the As removal rate is relatively low.

7. Industrial Arsenic Removal

7.1. El Indio

In an example of the industrial-scale removal of arsenic, the El Indio (Chile Indio) [57] operation in Chile processed enargite concentrates comprising 23 wt.% Cu, 15 wt.% Fe, 35 wt.% S, 10 wt.% As, and 0.8 wt.% Sb. These concentrates underwent treatment in a 14-hearth, 6.5-m diameter Nicholas Herreschoff roaster, operating within the temperature
range of 500 to 700 °C while maintaining an oxygen content below 0.5%. This operational setup ensured a state of essentially neutral roasting. The El Indio roaster’s process flow is illustrated in Figure 4. The feed material was roasted within the roaster for approximately 3 h. The resultant outlet gases were collected using two cyclones, with the retrieved dust reintroduced into the roasting process and unoxidized gases (comprising sulfur and arsenic trisulfide) channeled into a combustion chamber. Here, excess air facilitated an exothermic reaction at temperatures of around 750 ± 25 °C. Following oxidation, the gases underwent cooling to 350 to 400 °C within a heat exchanger before entering an electrostatic precipitator. The dust, enriched with high-value precious metals, was blended with flotation concentrates. The dust-free gases then underwent additional cooling to roughly 120 ± 5 °C using cold air, prompting the condensation and removal of a significant portion of arsenic as arsenic trioxide, which took the form of a white powder within the gas phase. The resultant gas stream was ultimately discharged into the atmosphere.

![Figure 4. Schematic diagram of the El Indio flow.](image)

**Figure 4.** Schematic diagram of the El Indio flow.

### 7.2. CMI NESA Process

Oudenne [58] reviewed CMI NESA’s (Chartered Management Institute, NSW Education Standards Authority) three-decade-long efforts to treat arsenic, antimony-bearing concentrates, and other complex metallurgical byproducts. The review emphasized preliminary mineralogical characterization as being crucial for successful roasting. Their selective roasting, especially under reducing atmospheres, proved effective for removing arsenic from Cu-bearing materials such as tennantite, enargite, chalcopyrite, and pyrite. Variable factors, such as particle size, significantly influence the volatilization of cadmium (Cd), As, stibium (Sb), bismuth (Bi), and hydrargyrum (Hg) during this roasting. This selective roasting process aims for impurity removal, requiring specific conditions such as optimal temperature, a controlled heating rate, and a reducing atmosphere. However, employing a roasting furnace with a single atmospheric posed challenges for complex sulfide materials. Nonetheless, it was possible to eliminate volatile sulfides from nonvolatile minerals by using a reducing atmosphere. In a multi-stage reactor, independent temperature and atmosphere control in each hearth proved crucial for effective processing both above and within the material bed.

### 7.3. Ministro Hales

The processing of the Ministro Hales deposit in Chile by Codelco [59,60] commenced in 2013 with an annual throughput of 550,000 tons of Cu concentrate and concurrent production of 250,000 tons of sulfuric acid. This operation implements controlled oxidation, also termed neutral roasting, which is aimed at extracting arsenic in vapor form. The As-containing dust generated in the process undergoes collection and subsequent conversion into a disposable form or is stockpiled for management.
7.4. Others

Notably, Outotec in Frankfurt, Germany, manages a pilot plant employing roasting techniques to treat Cu concentrates, operating at a capacity of 25 kg/h. Beyond this, a few smelters process enargite concentrates directly, though most limit their arsenic intake for environmental reasons, preferring cleaner Cu concentrates (<0.5% As) [57]. The ASARCO (American Smelting and Refining Company) smelter in El Paso, Texas accepts Cu concentrates with a maximum As content of 0.2% [61]. Meanwhile, the Lepanto roaster of the Lepanto Consolidated Mining Company, the Philippines, treats about 180 t/d of enargite concentrates containing 11% As, 31% Cu, 15% Fe, and 34% S, and produces calcine containing 0.3% As, 43% Cu, 23% Fe, and 20% S [70]. Elsewhere, the Boliden roaster in Boliden Oy, Finland, with a capacity of up to 800 t/d, treats concentrates containing 1~2% As and typically produces a calcine containing about 0.1% As [57]. Dundee Precious Metals in Bulgaria, meanwhile, transports 175,000 t/a enargite concentrates to the NCS (Namibia Custom Smelters) smelter in Tsumeb, Namibia, known for processing high As and lead-bearing Cu concentrates, producing copper blister and arsenic trioxide (As2O3) [62].

8. Precipitation of Arsenic

8.1. Ferrihydrate Precipitation

As removal from solutions containing both dissolved Fe and As is commonly achieved through co-precipitation using ferrihydrate precipitation techniques [63]. Post-precipitation involves the elimination of As from solutions by introducing an aqueous solution containing ferric-bearing species at a pH range conducive to ferrihydrate formation (typically pH 7 to 8). Another method, adsorption, entails the extraction of arsenic from solutions through exposure to previously precipitated ferrhydrite solids. The effectiveness of precipitation is contingent upon various factors such as duration, temperature, pH levels, the mole ratio of Fe/As, agitation rate, the arsenic’s valence state, and associated ions, among others.

8.2. Ferric Precipitation

The United States Environmental Protection Agency (USEPA) has designated the precipitation of dissolved arsenic using ferric ions as “The Best Demonstrated Available Technology” (BDAT) [64]. The stability of any disposed As compound is influenced by various factors including the disposal location’s characteristics, the crystallinity and size distribution of the compound, and the presence of oxygen or any complexing agents.

9. Conclusions and Prospects

This study presented a comprehensive overview of the global copper landscape, shedding light on the escalating demand for copper and the formidable challenges stemming from diminishing high-grade copper resources. The rank of Cu ores has decreased from 1.6% to approximately 1.0%. The resulting rise in ACC minerals has surfaced as a significant concern. The proportion of As and Cu in 15.0% Cu resources is currently close to 1:5. The prevalence of arsenic in these minerals has raised concern regarding environmental and health hazards in Cu smelting operations.

Diverse methodologies, encompassing pyrometallurgy, hydrometallurgy, and biometallurgy, have been explored for As removal, with each method exhibiting distinct advantages and limitations. Pyrometallurgy, predominantly relying on roasting at high temperatures, encounters obstacles related to efficient gas-solid separation and environmental contamination. Hydrometallurgical techniques, meanwhile, such as alkaline and acid leaching, offer viable alternatives, albeit requiring expensive additives and posing challenges in solidifying arsenic in solution. Beyond these, biometallurgy, employing bacterial processes, emerges as a greener approach, but suffers from comparatively lower arsenic removal rates. Additionally, specific industrial As removal methods deployed in Cu smelting globally, such as neutral and selective roasting in various smelters, strive to curtail arsenic contents. However, substantial hurdles persist in achieving high-purity arsenic trioxide and implementing efficient gas-solid separation techniques.
As entering the smelting system can bring hazards to the smelting process, the process of treating arsenic after it enters the smelting system is extremely cumbersome. It is therefore essential to purify and remove As from the ore before it enters the smelting system. At this stage, there are two options for processing arsenic-containing ores: the wet method and the pyrometallurgical method. However, if the wet method is used to remove As, the As entering the solution cannot be effectively utilized, which is not useful for treating As pollution. The pyrometallurgical method mainly uses roasting to remove arsenic. The biggest challenge is associated with the high-temperature segregation of As-containing gas and dust, achieving gas-solid segregation in high-temperature conditions to obtain high-purity As trioxide and thereby realizing the resource utilization of arsenic. At this point, there are very few methods for gas-solid separation, such as electrostatic precipitation, baghouse filtration, and solid membrane filtration.

Electrostatic precipitation has limited collection ability for fine particles, and the smaller the particles, the higher the energy consumption. Baghouse filtration has the risk of bag burning at high temperatures. Solid membrane filtration includes various types of metal ceramics, generally resistant to high temperatures. Moreover, filter cake formed during the filtration process can effectively collect fine particles. Finally, the amount of energy consumed during nitrogen backflushing is much lower than that of electrostatic precipitation. Therefore, using solid membrane filtration can be said to be the only option for dust removal from roasting flue gas.

In summary, since the difficulty of handling arsenic is significantly increased after it enters a solution, we propose that using gas filtration is the most economical and effective method for separating arsenic from smoke. The electrostatic precipitation process used by El Indio can effectively remove arsenic and obtain arsenic oxide at the same time. Therefore, when seeking to improve gas solid separation methods, the use of high-temperature porous membrane separation can not only improve the purity of arsenic oxide after separation but can also save electricity. Accordingly, we predict that this will be the direction taken for ACC processing in the future.

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References


57. Tongamp, W.; Takasaki, Y.; Shibayama, A. Arsenic removal from copper ores and concentrates through alkaline leaching in NaHS media. *Hydrometallurgy 2009*, 98, 213–218. [CrossRef]


64. Rivera-Vasquez, B.F.; Dixon, D. Rapid atmospheric leaching of enargite in acidic ferric sulfate media. *Hydrometallurgy* 2015, 152, 149–158. [CrossRef]


67. Govindaiah, P.; Guerra, E.; Choi, Y.; Ye, Z. Pressure oxidation leaching of an enargite concentrate in the presence of polytetrafluoroethylene beads. *Hydrometallurgy* 2015, 157, 340–347. [CrossRef]


70. Flores, G.A.; Risopatron, C.; Pease, J. Processing of Complex Materials in the Copper Industry: Challenges and Opportunities Ahead. *Jom* 2020, 72, 3447–3461. [CrossRef] [PubMed]

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