Review

The Use of Acid Leaching to Recover Metals from Tailings: A Review

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Abstract: Mine tailings deposits are often overlooked by the industry, posing significant environmental challenges due to chemical hazards and inadequate maintenance. Nevertheless, such mineral deposits hold considerable economic potential for processing, and the adoption of innovative technologies may also address critical chemical and physical stability issues. Existing research has demonstrated the feasibility of recovering target metals—i.e., copper, iron, manganese, cobalt, zinc, and others—through the application of acid leaching techniques with consistently high yields and metal recovery rates. Therefore, a compilation was carried out from 2008 onwards, on working conditions such as leaching agent, acid concentration, oxidizing-reducing reagent, particle size, O2 pressure, stirring speed, solid–liquid ratio, temperature, and leaching time. At present, there are no reviews on the recovery of metals via acid leaching in tailings, so this study can serve as support for future researchers who want to project themselves in this area, ordering the procedures and the results obtained by the research carried out. Regarding the evaluation, it can be commented that research has shown that acid leaching of tailings has achieved recoveries of over 90% in different metals, such as Zn, Cu, and Fe, which indicates that the treatment is efficient and recommended for different types of tailings.

Keywords: mine tailings; tailings reprocessing; acid leaching; hydrometallurgy; metal recovery

1. Introduction

In copper mining, various physicochemical processes [1,2] are employed to treat ores and extract valuable commercial materials. The choice of ore processing depends on mineral composition, whether oxide or sulfide-based; though for both, material liberation processes must involve different particle sizes. Generally, oxide-rich materials are subjected to hydrometallurgical treatment, while sulfide-rich materials are concentrated [3] before undergoing pyrometallurgical treatment. Both processing routes yield the desired products but generate mining waste [4], much of which poses environmental and human health hazards [3,5–12].

One particularly significant and recently studied waste stream is mine tailings, a byproduct of sulfide ore concentration procedure [13]. These tailings are transported to tailings deposits [14] with a focus on achieving chemical and physical stability [2,6]. To meet these objectives, it is imperative to remove toxic agents and potential sulfuric acid producers, including pyrite, which is the precursor of acid mine drainage (AMD) formation due to oxygen and water exposure, where it is a serious environmental problem for industries due to its low pH, less than pH 3, coupled with a high concentration of heavy metals such as cadmium (Cd), Cu, iron (Fe), manganese (Mn), lead (Pb), and zinc (Zn), and toxic metalloids such as arsenic (As) and selenium (Se) [15], and to ensure a robust structural integrity to prevent spillage and leakage within the deposit. Further, emphasizing the chemical stability of mine tailings is paramount since insufficient stability within a tailings deposit significantly heightens the risk of environmental contamination [6].
composition of the tailings deposit may vary depending on the ore processing sector [16]. Furthermore, considering the state of the waste—active, non-active, or abandoned [6]—is crucial, as it impacts the treatment approach. Many of these deposits are solely under physical control, prompting current research into the chemical stability and the potential extraction of valuable materials for use in fields like construction [17,18]. Finally, the concentrated chemical composition of these tailings may hold economic value, particularly for the steel and electromobility industries [14,19–21].

Since these deposits are exposed to the elements, contact with atmospheric oxygen can lead to surface oxidation, which may have occurred over an extended period [22]. Consequently, the application of hydrometallurgical treatment methods has been explored for such materials. The uncertainty surrounding the behavior of tailings deposits has spurred the implementation of metallurgical procedures. Indeed, researchers have proposed diverse methodologies for recovering valuable minerals from these tailings, including bioremediation [23], bioleaching [4,24], phytostabilization [6,25], flotation [5,26], geopolymers [27], agitated acid leaching [22,28–46]—both in columns [47,48] and in autoclave [49,50]—and even utilizing this waste as a raw material for cement production in the construction industry [51–53].

As the processing of tailings material is being evaluated, it is important to consider the provenance of this sample. It is known that tailings are a residue from the mineral concentration stage, so their mineralogy will be composed mostly of unwanted compounds, e.g., quartz (SiO₂), carbonates (CaCO₃), some oxides (Al₂O₃, MgO, Fe₂O₃ and Fe₃O₄), and pyrite (FeS₂). To mitigate the inconveniences that these impurities can generate, it is recommended to implement pre-treatments to the tailings sample such as milling, to release trapped minerals and, thus, increase the contact surface of the tailings and to promote the development of the tailings.

To mitigate the inconveniences that can generate these impurities, it is also recommended to implement pre-treatments to the tailings sample such as grinding, to release trapped mineral and, thus, increase the contact surface of this and promote the interaction between the metal and the leaching agent. Another treatment is mineral flotation, in which the valuable mineral will be concentrated and the inert material can be separated from the material of interest. It is also possible to float pyrite in neutral environments, so that in the future it will not be a problem. In the case of having an impurity rich in iron, specifically magnetite, it is advisable to implement a magnetic treatment in order to remove most of this iron oxide in a physical way.

This paper was written to satisfy the need for a review of the work carried out by authors on the acid tailings leaching process and, thus, to be able to provide ordered information for future researchers who require parameters and variables to carry out their scientific research.

2. Bibliographic Review

As non-renewable resources, ore grades are declining, prompting increased consideration of reprocessing for mining waste material within the mining industry. Mine tailings harbor trace metals of interest, amenable to recovery via hydrometallurgical methods, such as acid leaching. Various researchers have tackled tailings materials from their respective regions, achieving substantial recoveries of copper, iron, cobalt, zinc, gold, and silver through acid leaching techniques. The extractions of these metals help the chemical stability of the tailings, because when the concentration of these species decreases, the formation of AMD is interrupted, avoiding acid seepage and overflows. In addition, the reprocessing of tailings helps sustainable mining; it reduces polluting emissions and is friendly to the ecosystem.

In 2008, Antonijevic [28] proposed copper recovery from Bor copper mine tailings through acid leaching. The tailings had around 21% sulfide content and 0.2% copper, with a particle size of approximately 0.074 mm. He used a 1-L beaker with mechanical and magnetic agitators, employing 500 mL of leaching solution and 100 g of sample
Antonijevic investigated the effects of initial pH, pulp density, agitation speed, particle size, Fe$_2$(SO$_4$)$_3$ oxidant concentration, and temperature. Using three sulfuric acid concentrations (1 M, 5 M, and 9 M), he achieved copper extractions of 62%, 65%, and 70% approximately within about 120 min. Varying pulp densities (20–50%) resulted in copper recoveries of 60–64% and iron recoveries of around 2%. Agitation speed variation (300–900 RPM) consistently yielded 60% copper recovery and approximately 2% iron recovery. Particle size-based leaching showed recoveries below 10% for particle sizes larger than +74 µm, roughly 57% copper recovery for −74 µm, and recoveries exceeding 70% for −36 µm particle sizes. Concerning temperature, experiments at 20 °C, 40 °C, and 60 °C with 0.1 M acid, 20% solids, and an oxidizing agent at 5 g/L concentration demonstrated that higher temperatures led to increased dissolution of Cu and Fe, achieving 80% recovery, up from 68% at 20 °C, in just 2 h, with 88% Cu extraction after 32 h.

In 2012, Guo [29] investigated heavy metal leaching from Dexing Copper mine tailings. Material characterization was performed using acid digestion, ICP (AES), and XRD, revealing contents of 455 ppm Cu, 31,750 ppm Fe, 775 ppm Mn, and 215 ppm Zn. Acid leaching (25 g material, 250 mL HCl, room temperature, 50 days) explored pH, temperature, and particle size. Lower pH (pH < 3) led to greater metal dissolution for all metals, with pH = 2 (0.01 M hydrochloric acid concentration) yielding the highest extractions (Zn 5.4%, Cu 5.8%, Fe 11.1%, Mn 34.1%). Elevated temperatures (5 and 27 °C) over 10 days increased recoveries (Zn 70%, Cu 60%, Fe 86%, Mn 63%). Smaller particle sizes (1700 µm and 150 µm) had higher metal recoveries.

In 2014, Chen [30] focused on Dabaosan Mine tailings directly from flotation. Digestions, atomic absorption, ICP-MS, SEM-EDX, QUEMSCAN, and Bond moisture analysis showed 18% of the flotation tail contained metals of interest, with Cu, Zn, Fe, and Mg concentrations of 2923.15, 1638.21, 108,671.20, and 590.80 ppm, respectively. The tailings had about 4.43% oxidized iron, zinc was in sphalerite form, and copper existed as a mix of oxides and sulfides (31.62% and 68.34%, respectively). Leaching experiments involved varying sulfuric acid concentrations, agitation at 400 RPM, and assessing temperature, acid dosage, leaching time, and solid–liquid ratio. Initial tests at temperatures from 30 °C to 80 °C, with 0.24 mL/g of sulfuric acid, 1:2 S:L ratio, and 2 h of treatment, resulted in similar recoveries for Cu, Mn, Zn, and Fe, approximately 99%, 55%, 28%, and 15%, respectively. Changing acid concentrations (0.18 to 0.40 mL/g) at a constant 30 °C, 1:2 S:L ratio, and 2-h duration led to consistent recoveries for all metals except copper, which increased from 70% to nearly 98% at higher acid levels. Assessing leaching time at 0.24 mL/g (0.05 M) H$_2$SO$_4$, 1:2 S:L ratio, and 30 °C showed stable recoveries after 2 h, reaching almost 100% for copper, 55% for manganese, 30% for zinc, and less than 20% for iron. Examining solid–liquid ratios from 1:9 to 1:1, corresponding to pulp densities of 10% to 50%, revealed varying extraction behavior. Iron remained stable at around 20% recovery, while zinc recovery increased linearly as pulp density decreased, reaching about 40%. Copper and manganese recoveries increased and stabilized as the S:L ratio decreased (1:2–1:9), with maximum recoveries of 98.40% for Cu and 65% for Mn.

In 2015, Wang [31] conducted leaching experiments on Yangla, Yunnan Province, China tailings. Wang characterized the material with XRD and SEM-EDS, revealing 0.41% Cu, mostly oxidized (80.49%). Wang explored the influence of concentration, temperature, solid–liquid ratio (S:L), and agitation speed. Testing a range of initial acid concentrations (0.230–0.494 M) with 400 RPM agitation, 1:3 S:L ratio, 62 °C, and a 60-min cycle, he observed that higher acid concentration, up to 0.428 M H$_2$SO$_4$, led to a peak copper extraction of around 50%. Wang also found a positive correlation between higher temperatures (75–88 °C) and increased copper recovery when using 0.428 M H$_2$SO$_4$. Regarding S:L ratios (1:1 to 1.5) at 75 °C, 0.428 M acid, and agitation, lower pulp densities yielded stable, high extractions, while higher densities slowed extraction. Maximum copper extraction occurred at 300 RPM, with constant recoveries beyond that speed. Wang concluded that an efficient leaching process involved 0.428 M H$_2$SO$_4$, 75 °C, 1.3 S:L ratio, 300 RPM agitation, and a 60-min cycle, resulting in a 53.8% copper recovery with 12.85 tons of acid consumption.
In 2015, Santos [32] processed tailings material from the Rio Doce Magnesio (RDM) Company-Morro do Mina Unit in Conselheiro Lafaiete (MG, Brazil). The material was characterized using sieving, XRD, acid digestion, ICP-AES, gravimetry, LOC, and the Volhard–Wolff method, revealing a total Mn content of 24.8%, with 86.6% of particles measuring less than 250 μm. Santos employed a 2\(^3\) factorial experimental design to evaluate the variables of acid concentration, leaching time, and waste amount, considering two particle size ranges, sulfuric acid, 100 RPM agitation, and a solution volume of 10 mL. The acid concentration, time, and amount of waste were varied in the ranges of 9.8–54\% w/w, 1–6 h, and 0.5–1.5 g, respectively. The experimental setup resulted in eight leaching experiments, with five replicates of the midpoint levels for each variable. The findings indicated that smaller particle sizes led to improved manganese recovery. Santos subsequently employed a Doehlert experimental design to optimize the leaching process, identifying ideal parameters: 9.8% H\(_2\)SO\(_4\) (w/w) (1M of sulfuric acid), 10 h of leaching, 0.1 g of tailings, 10 mL of solution, and 100 RPM agitation, achieving a remarkable 95.5% manganese recovery.

In 2016, Liu [33] delved into copper recovery from tailings material abundant in calcium salts. The material, sourced from Chuxiong, Yunnan Province, China, contained 0.68% copper and 3.15% iron, with 91.2% of the copper oxidized. Additionally, the sample contained substantial acid-consuming impurities like CaO, MgO, and Al\(_2\)O\(_3\). To address the high acid consumption, Liu proposed a reverse flotation pretreatment using oleic acid to separate these impurities. This pretreatment significantly reduced acid consumption from 0.367 tons to 0.126 tons, enabling the recovery of 66.74% of the copper through acid leaching. The leaching process utilized a 1:2 solid–liquid ratio (S:L), agitation at 300 RPM, and a 30-min leaching time.

In 2017, Asadi [34] conducted leaching experiments on tailings from the Bama processing plant in Isfahan, Iran. The material underwent crushing and grinding to reduce particle size to less than 150 μm, with XRF revealing an 8.26% Zn content. Asadi employed a CCRD experimental design with 32 iterations considering factors like agitation speed, sulfuric acid concentration, H\(_2\)SO\(_4\):Fe\(_2\)(SO\(_4\))\(_3\) ratio, L:S ratio, and temperature. Initial experiments focused on the effect of the oxidizing agent, Fe\(_2\)(SO\(_4\))\(_3\), showing that zinc recovery increased up to 0.5 M Fe\(_2\)(SO\(_4\))\(_3\). Further analysis highlighted that higher H\(_2\)SO\(_4\):Fe\(_2\)(SO\(_4\))\(_3\) ratios and temperatures led to increased Zn dissolution, with temperature being the most influential factor. Low L:S ratios, increased stirring speeds, and higher H\(_2\)SO\(_4\) concentrations enhanced Zn extraction. The interaction of L:S, temperature, and stirring speed had a significant impact. Optimizing Zn leaching, Asadi identified ideal parameters as 320 RPM agitation, 1.14 M H\(_2\)SO\(_4\) concentration, 2.49 H\(_2\)SO\(_4\):Fe\(_2\)(SO\(_4\))\(_3\) ratio, L:S ratio of 10.10 mL/g, and 80 °C temperature, resulting in a remarkable 94.3% zinc recovery.

In 2018, Guiming [35] examined tailings material using two metallurgical methods. The sample consisted of 93–94% non-metallic and 5–7% metallic components, with 0.5192% copper, of which 93.64% was oxidized. Initially, a flotation process recovered 0.489% copper. Subsequently, an agitated acid leaching process assessed the effects of acid concentration, temperature, and time. The first analysis employed a 1-h leaching period, room temperature, 500 g of material, and 1 L of solution, resulting in copper recoveries of 15.49%, 18.84%, 32.82%, and 53.11% for acid concentrations of 40, 60, 80, and 100 kg/t (0.2, 0.3, 0.4, and 0.5 M), respectively. The second analysis maintained the conditions but increased acid concentrations and a temperature range of 45–55 °C. Copper recoveries were 33.27%, 73.23%, 75.51%, and 91.71% for sulfuric acid dosages of 80, 100, 130, and 160 kg/t (0.4, 0.5, 0.65 M, and 0.8 M). In the third analysis, sulfuric acid remained at 160 kg/t, with equal S:L ratios, a temperature range of 45–55 °C, and a 2-h leaching time. The impact of time was evaluated in 30-min intervals, yielding recoveries of 91.34%, 91.71%, 92.10%, and 92.86% for leaching times of 0.5, 1, 1.5, and 2 h.

In 2018, Bai [36] worked with chrysocolla-rich tailings material from Zambia, Africa. Characterization through XRD and SEM-EDS identified a 0.91% copper content, with 93.41% in oxidized form, primarily as chalocite, malachite, and chrysocolla compounds. Notably, 64.84% of the copper presented a challenging extraction profile. Consequently, Bai...
employed agitated acid leaching, investigating the effects of acid concentration, temperature, and leaching time, with a constant agitation speed of 700 RPM and S:L ratio of 1:2. Through experimental design and data analysis, the study identified optimal parameters: 0.01 M acid concentration, 68.51 °C temperature, and a 4.36-h leaching time, resulting in an impressive 85.86% copper recovery.

In 2018, researcher Rogowski [37] conducted a study on radiotracer application in tailings acid leaching using material from the Polish Geological Institute-National Research Institute, characterized with 10,686.7 ppm copper content. Rogowski employed various acids—H$_2$SO$_4$ (98% pure), HNO$_3$ (65% pure), C$_6$H$_5$O$_7$ (pure), C$_6$H$_8$O$_6$ (pure), and CH$_3$COOH (99% pure)—at 25 °C, with 20 g of material, 300 mL of acid solution, and leaching times ranging from 24 to 48 h. Sulfuric acid concentrations of 2–8 M resulted in initial and final copper recoveries of 15% and 22%, respectively. Nitric acid, in concentrations from 0.01 to 14 M, yielded maximum copper extraction at 10.5 M, achieving 71% Cu recovery, with around 50% recovery within the 3–9 M HNO$_3$ range. The other acids, except ascorbic acid, achieved approximately 20% copper recovery.

In 2018, Stanković [38] conducted a comprehensive study on old tailings from the Mining and Smelting Copper Co. Bor in Serbia. His analysis encompassed the physical, mineralological, and chemical properties of the tailings, employing wet granulometry and polarized microscopy techniques. This characterization revealed that a substantial portion, exceeding 75%, had a particle size of −37 µm. The tailings composition was identified as 90% gangue, 6% pyrite, 0.4% chalcopyrite, and 0.13% cuprite, with a total copper content of 0.192%, primarily in the oxidized form at 55.21%. Later, Stanković [39] introduced a copper extraction process involving two metallurgical stages: an initial acidic agitated leaching followed by flotation of the insoluble solids from the leaching step. In the first phase, he applied parameters of 0.2 M H$_2$SO$_4$, an S:L ratio of 1:2, agitation at 300 RPM, a temperature of 20 °C, and a 1-h leaching duration. Subsequently, in the second stage, the aim was to concentrate the insoluble solids from the leaching step to enhance copper recovery from the tailings. Utilizing acid leaching alone, Stanković achieved a commendable 70% copper recovery; however, with the incorporation of the flotation stage, the overall recovery significantly improved to 80%, highlighting the effectiveness of the integrated process.

In 2018, researcher Han [49] investigated high-pressure leaching of tailings from the Bor mining area in Serbia, characterized through ICP-OES, XRF, XRD, SEM-EDS, revealing 0.34% Cu, 8.96% Fe, and mineral compounds like SiO$_2$, FeS$_2$, and Al$_2$Si$_2$O$_5$(OH)$_4$. Han’s study comprised several phases: initially, a mineral concentration pretreatment increased copper content from 0.34% to 0.65%. Subsequently, the influence of pyrite on copper leaching was explored. High-pressure leaching tests examined factors like acid concentration, oxygen pressure, temperature, pulp density, free acid, and iron precipitation. Conducted in a 2 L autoclave, the experiments revealed that using distilled water resulted in 98.1% Cu and 67.4% Fe extraction. Parameters like oxygen pressure, temperature, and pulp density significantly impacted copper and iron recovery, with higher values leading to increased extraction rates. The optimized conditions included 0 M H$_2$SO$_4$, i.e., without the presence of acid, only leaching with distilled water, 2 MPa O$_2$ pressure, 180 °C temperature, 60-min leaching, and a pulp density of 400 g/L, yielding 2.9 g/L Cu recovery suitable for subsequent solvent extraction processes.

In 2019, Pazhoohan [39] conducted leaching experiments on tailings from Dehne Siah Zangaloo, Anabad, Iran, revealing a mineral composition of 3.44% iron and 0.62% oxidized copper, primarily as azurite (13%) and malachite (87%). The tailings had a particle size less than or equal to 100 µm. Pazhoohan conducted leaching tests with solids percentages ranging from 30% to 45%, using 1000 mL of leaching solution, a 90-min leaching time, and an agitation speed of 100 RPM. Two acid addition methods were employed. In the first method, gradual acid addition resulted in 90% copper and 12% iron recoveries after 40 min. In the second method, instantaneous acid addition achieved 93% copper and 11% iron recoveries within the first 15 min.
In 2019, Constantin [22] evaluated acid leaching for precious metal extraction from tailings sourced from the Baia Mare Central Flotation Pond, which contained chalcopyrite, sphalerite, galena, and pyrite. Characterization through ICP-OES and FAAS revealed trace amounts of gold and silver (<0.7 ppm and <10.8 ppm, respectively). Constantin’s investigation involved two steps, each using different acid leaching techniques. In the first step, with an S:L ratio of 1:1.5, 120 RPM agitation, a 7-day leaching time, and 2 M H₂SO₄ or 2 M HNO₃ solutions, only silver was recovered, yielding 1 ppm and 12.5 ppm for H₂SO₄ and HNO₃, respectively. In the second step, insolubles from the first step underwent a second acid leaching with 2 M H₂SO₄, an S:L ratio of 1:1.5, 120 RPM agitation, and a 7-day leaching time, resulting in recoveries of 12.5 ppm silver and 0.5 ppm gold for H₂SO₄, and 1 ppm gold for HNO₃. Constantin also investigated the impact of oxidizing agents (H₂O₂ and Fe₂(SO₄)₃) on H₂SO₄ leachates but observed no significant effect, likely due to the already oxidized nature of the tailings.

In 2020, Shengo [40] developed a comprehensive approach to recover copper and cobalt from tailings originating in Luanshi, Democratic Republic of Congo, Africa. Characterization revealed that the tailings contained 0.74% copper and 0.37% cobalt, primarily in the oxidized form, with the highest concentrations in particles below ~38 µm. To facilitate mineral liberation, wet milling was employed, reducing the d80 particle size to 138 µm in just 11 min. Shengo’s dual-pronged mineral processing strategy encompassed acid leaching and flotation for ore concentration. Acid leaching experiments involved optimizing parameters such as time, temperature, and the addition of reducing agents, achieving notable recoveries of 75% Cu and 62% Co at 120 min, with further enhancement to 79% Cu and 56% Co at 60 °C. The introduction of Na₂S₂O₅ (10–15 g) at 120 min and 60 °C yielded promising results with 70% Cu and 80% Co recovery. Concurrently, ore concentration via flotation, utilizing chemical reagents in both rougher and cleaner stages, resulted in recoveries of 56% Cu and 59% Co in the rougher stage, followed by improvements to 35% Cu and 43% Co in the cleaner flotation stage.

In 2020, Conić [41] undertook a study focused on efficiently extracting copper from tailings material sourced from Copper Mine Bor, Serbia. Characterization encompassed chemical analysis, XRD, and particle size measurement, revealing a p80 particle size of 75 µm and a composition of 7.78% Fe, 10.52% S, and 0.24% Cu, with 0.12% existing as oxidized forms and the remainder as sulfides. Conić employed three hydrometallurgical techniques: acid leaching, bioleaching, and leaching with biogenic agents. In acid leaching, utilizing 1 M H₂SO₄, 300 RPM agitation, 30% pulp density, 80 °C temperature, and 120 min of leaching time, a 55% copper recovery was achieved within the first 30 min, maintained throughout the process. Bioleaching, with 10% pulp density, 45 °C temperature, 250 RPM agitation, 15 days of leaching, air and CO₂ injection, reached its peak with an 84% copper recovery on the ninth day. Leaching with biogenic agents involved a 240-min process using ferrous sulfate pentahydrate, salts, and bacteria, extracting a maximum of 80% copper within 10 min.

In 2021, Alvarez [42] processed tailings from Ramba del Real, Murcia, Spain, characterized with WDXRF and XRD, revealing Zn and Cu contents of 1.38% and 0.0435%, respectively. Alvarez conducted nine leaching trials using carbon-based materials (AC and VC) and three H₂SO₄ concentration levels (0.25, 0.5, and 1 M) at 90 °C, 250 RPM, and a 6-h processing time. Each experiment involved 2.5 g of tailings and 50 mL of leaching solution, except for carbon-based tests with a 1:1.5 w/w tailings-AC/VC ratio. The highest zinc extraction (99%) was achieved with tailings-1 M H₂SO₄-VC, tailings-0.5 M H₂SO₄-AC, and tailings-0.25 M H₂SO₄ after 6 h. For copper, the top extractions (48–61%) occurred with tailings-1 M H₂SO₄-AC, tailings-1 M H₂SO₄-VC, and tailings-0.5 M H₂SO₄-AC combinations.

In 2021, Tao [43] processed tailings from Yunnan Tin Group (Holding) Company Limited, China, utilizing acid leaching to extract iron. Before leaching, Tao characterized the tailings with various techniques, revealing a composition of 0.26% copper and 36.76% iron. Tao’s investigation analyzed the impacts of temperature, acid concentration, solid-to-
liquid (S:L) ratio, and agitation speed. Temperature experiments ranged from 20–60 °C, with other parameters held constant (400 RPM, 0.53 M sulfuric acid, and an S:L ratio of 1:10). Recoveries increased from 49.53% at 20 °C to 69.18% at 60 °C. For acid concentration, experiments at 40 °C with varying concentrations (0.31–0.64 M) resulted in recoveries of 46.87% and 67.83% at 20 °C and 60 °C, respectively. S:L ratio variations (1:4, 1:6, 1:8, 1:10, and 1:12) at 40 °C, 0.53 M acid, and 400 RPM showed recoveries of approximately 40%, 50%, and 55% for the first three ratios and 65% for the last two ratios. Assessing agitation speed at 40 °C, 0.53 M H$_2$SO$_4$, and an S:L ratio of 1:10, recoveries increased with speeds of 100, 200, 300, 400, and 500 RPM, reaching 67% at 400 and 500 RPM.

In 2021, researcher Schueler [44] conducted leaching experiments on tailings material from Neves Corvo, Portugal, with initial characterization revealing significant copper, zinc, lead, and arsenic contents. Employing a Box–Behnken experimental design, Schueler investigated the impacts of sodium chloride concentration, sulfuric acid concentration, and temperature on the leaching process. The experiments maintained agitation at 250 RPM, an S:L ratio of 1:10, a NaCl reducing agent dosage of 10–35–60 g/L, temperature ranges of 20–45–70 °C, and H$_2$SO$_4$ concentrations of 0.01–0.5–1 M. The most favorable outcome, achieved in just 4 h, involved conditions of 60 g/L NaCl, 0.01 M H$_2$SO$_4$, 45 °C, an S:L ratio of 1:10, resulting in a 55% lead extraction. A second leaching process for the solid residue using conditions from the highest Pb recovery tests (60 g/L NaCl, 0.5 M H$_2$SO$_4$, 70 °C, S:L ratio of 1:10) produced recoveries of 66.8% Cu, 84.1% Zn, 93.9% Pb, and 47.8% As after 1 and 24 h.

In 2021, Godirilwe [50] conducted leaching experiments on tailings material from Bor Copper Mine, Serbia, considering both raw tailings and a concentrated tailings variant. Characterization of the samples revealed differences in copper and iron content, with the raw tailings containing 0.24% Cu and 3.51% Fe, while the concentrated tailings had higher levels at 0.65% Cu and 35.20% Fe, with a D50 particle size of 27 µm. High-pressure leaching was performed for both conditions, featuring parameters such as 700 RPM agitation speed, H$_2$SO$_4$ concentrations ranging from 0.2 to 1 M, 2 MPa O$_2$ pressure, a 1-h leaching time, a temperature of 180 °C, and varying pulp densities (100 g/L for raw tailings and 400 g/L for concentrated tailings). Analysis of the resulting PLS, conducted using ICP-OES and XRD, showed copper recoveries of 98.72% and 94.4% for the raw and concentrated tailings, respectively, along with iron recoveries of 16.31% and 65.9% for the same conditions.

In 2022, researcher Santibáñez-Velasquez [45] conducted comprehensive leaching experiments on tailings material from northern Chile to extract iron and other metals. The tailings underwent meticulous chemical characterization involving SEM-EDS, XRD, and granulometric analysis using Ro-Tap equipment. The experimental phase was characterized by hydrochloric acid leaching, with varying concentrations (3, 6, 9, and 12 M), agitation set at 550 RPM, 1 g of homogenized sample in 250 mL of solution, leaching times spanning 6, 16, and 62 h, and a temperature range from 25 °C to 70 °C. The experiments were systematically divided into three distinct phases, each honing in on specific variables. In the initial phase, the focus was on hydrochloric acid concentration, with a fixed time of 16 h at 25 °C. The second phase incorporated the concentration that yielded the best recovery (9 M HCl) while maintaining a temperature of 25 °C and examining leaching times of 6, 16, and 62 h. The third phase involved 9 M HCl concentration, a 16-h leaching time, and temperature variations from 25 °C to 70 °C. The optimized parameters discerned by Santibáñez-Velasquez included a 9 M acid concentration, a 16-h leaching duration, and a temperature of 60 °C, ultimately resulting in notable recoveries of 749.40 mg/L of Fe, 3.30 mg/L of Cu, 38.78 mg/L of Mg.

In 2022, Zamarreño [46] utilized tailings from the Culebrón wetland in Coquimbo, Chile, containing 15.3% iron and 1452 ppm cobalt. After pretreatment to remove magnetic material and recording an initial pH of 7.11, two leaching experiments were conducted. The first experiment involved four leachings using 50 g of sample, 60-h resting periods, and 100 mL HCl solutions at 20% and 25% concentrations by weight, with results analyzed gravimetrically. The second experiment utilized 200 mL of 0.5 M tartaric acid solution with
5 M H₂O₂ addition for every 10 g of sieved and unsieved samples over 48 h. The outcomes demonstrated an average cobalt recovery of 58.14% ± 26.27% and an iron recovery of 21.87%. Notably, unsieved material achieved a 91.06% cobalt recovery, while sieved material exhibited an even higher 95% cobalt recovery rate.

3. Discussion

Our review shows that acid leaching has become a dominant method for metal extraction, consistently delivering high recovery rates. Several authors agree with the implementation of this hydrometallurgical method, since by extracting metals from these deposits, two high impact problems are mitigated. One of them is the one that has been constantly mentioned at the beginning of this paper, which is environmental pollution, and the second problem addressed by the processing of mine tailings is the reuse of mining resources. It is known worldwide that mineral reserves are decreasing their grades, so it is attractive to process mining waste material in order to make the industrial process more efficient and reduce the environmental impacts that mining has caused.

After this analysis, it is important to consider the following aspects in order to carry out an efficient study on hydrometallurgical treatment of mine tailings.

3.1. Chemical Composition of Tailings

Before implementing a metallurgical process, it is essential to know the chemical and mineralogical composition of the sample, so that it is possible to choose the suitable agents and parameters to obtain the desired extraction. The table below summarizes the chemical composition used from the study.

Table 1 shows that each tailings material differed in chemical and mineralogical composition, due to the fact that they are found in different geographical locations and originate from different metal flotation processes. In addition, the researchers implemented methodologies that, while all focused on the extraction of metals from an acid leaching process, these techniques differed in the variables of leaching agent, acid concentration, oxidizing/reducing reagents, stirring speed, S:L ratio, temperature, and leaching time.

Researchers have effectively optimized key parameters such as temperature, agitation, and acid concentration. The following table (Table 2) shows the optimal parameters and corresponding metal recoveries in each study.
Table 1. Chemical composition of tailings from the bibliographic review (wt. %).

<table>
<thead>
<tr>
<th>Author</th>
<th>Type of Tailings</th>
<th>Mine Location</th>
<th>Cu</th>
<th>Fe</th>
<th>S</th>
<th>Co *</th>
<th>Ag *</th>
<th>Au *</th>
<th>Mg</th>
<th>Mn</th>
<th>Zn</th>
<th>Al</th>
<th>Sb *</th>
<th>Pb</th>
<th>As</th>
<th>Cd *</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Fe₂O₃</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>[28]</td>
<td>Flotation tailings</td>
<td>Bor Copper Mine, Serbia</td>
<td>0.20</td>
<td>8.69</td>
<td>10.58</td>
<td>3.0</td>
<td>0.35</td>
<td>0.003</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>0.014</td>
<td>----</td>
<td>----</td>
<td>8.52</td>
<td>53.34</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>[29]</td>
<td>Mine tailings</td>
<td>Dexing Copper Mine, China</td>
<td>0.046</td>
<td>3.175</td>
<td>1.12</td>
<td>0.078</td>
<td>0.022</td>
<td>8.354</td>
<td>≤5*</td>
<td>≤5</td>
<td>----</td>
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</tr>
<tr>
<td>[30]</td>
<td>Copper sulfide tailing</td>
<td>Dabaoshan Mine region, China</td>
<td>0.292</td>
<td>10.87</td>
<td>8.81</td>
<td>2.528</td>
<td>0.059</td>
<td>0.164</td>
<td>9.45</td>
<td>0.018</td>
<td>8.48</td>
<td>15.06</td>
<td>----</td>
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</tr>
<tr>
<td>[31]</td>
<td>Copper flotation tailings</td>
<td>Yangla Copper Mine, China</td>
<td>0.41</td>
<td>20.21</td>
<td>0.27</td>
<td>1.54</td>
<td>24.76</td>
<td>0.013</td>
<td>5.49</td>
<td>&lt;24</td>
<td>0.005</td>
<td>0.009</td>
<td>7.59</td>
<td>62.81</td>
<td>11.28</td>
<td>5.69</td>
<td>21.75</td>
<td>16.77</td>
<td>2.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[32]</td>
<td>Manganese ore tailing</td>
<td>MG, Brazil</td>
<td>0.024</td>
<td>4.72</td>
<td>0.689</td>
<td>198</td>
<td>0.19</td>
<td>----</td>
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</tr>
<tr>
<td>[33]</td>
<td>Copper flotation tailings</td>
<td>Chuxiong, China</td>
<td>0.68</td>
<td>3.15</td>
<td>0.07</td>
<td>----</td>
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</tr>
<tr>
<td>[34]</td>
<td>Tailings from lead-zinc flotation</td>
<td>Bama processing plant, Iran</td>
<td>0.027</td>
<td>4.72</td>
<td>0.689</td>
<td>198</td>
<td>0.19</td>
<td>----</td>
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</tr>
<tr>
<td>[35]</td>
<td>Tailings from oxy-sulfur copper ore</td>
<td>Zambia, Africa</td>
<td>0.91</td>
<td>4.34</td>
<td>0.035</td>
<td>----</td>
<td>----</td>
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<td>----</td>
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</tr>
<tr>
<td>[36]</td>
<td>Flotation flotation tailings</td>
<td>Polish Geological Institute</td>
<td>0.024</td>
<td>4.72</td>
<td>0.689</td>
<td>198</td>
<td>0.19</td>
<td>----</td>
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</tr>
<tr>
<td>[37]</td>
<td>Old flotation tailings</td>
<td>RTB Bor, Serbia</td>
<td>0.217</td>
<td>4.72</td>
<td>5.41</td>
<td>1.45</td>
<td>0.36</td>
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</tr>
<tr>
<td>[38]</td>
<td>Flotation tailings</td>
<td>Bor Mining, Serbia</td>
<td>0.34</td>
<td>8.96</td>
<td>11.2</td>
<td>----</td>
<td>----</td>
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</tr>
<tr>
<td>[39]</td>
<td>Flotation tailings</td>
<td>Deine Stah Zangaloos, Iran</td>
<td>0.62</td>
<td>3.44</td>
<td>9.4</td>
<td>----</td>
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</tr>
<tr>
<td>[40]</td>
<td>Flotation tailings</td>
<td>Central Flotation, Romania</td>
<td>0.056</td>
<td>7.04</td>
<td>1.882</td>
<td>15.8</td>
<td>≤10.8</td>
<td>≤0.7</td>
<td>0.586</td>
<td>0.620</td>
<td>0.589</td>
<td>3.207</td>
<td>150</td>
<td>0.235</td>
<td>0.061</td>
<td>8.4</td>
<td>----</td>
<td>----</td>
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<td>----</td>
</tr>
<tr>
<td>[41]</td>
<td>Flotation tailings</td>
<td>Luisswiishi, Africa</td>
<td>0.74</td>
<td>0.20</td>
<td>0.37</td>
<td>----</td>
<td>----</td>
<td>----</td>
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<td>----</td>
</tr>
<tr>
<td>[42]</td>
<td>Flotation tailings</td>
<td>Bor Copper Mine, Serbia</td>
<td>0.24</td>
<td>7.78</td>
<td>10.52</td>
<td>3.0</td>
<td>0.5</td>
<td>0.016</td>
<td>0.01</td>
<td>6.58</td>
<td>&lt;50</td>
<td>&lt;0.03</td>
<td>0.022</td>
<td>&lt;10</td>
<td>----</td>
<td>----</td>
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<td>----</td>
</tr>
<tr>
<td>[43]</td>
<td>Flotation tailings</td>
<td>Yunnan Tin Group, China</td>
<td>0.26</td>
<td>36.76</td>
<td>0.17</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>1.03</td>
<td>0.11</td>
<td>2.06</td>
<td>2.45</td>
<td>----</td>
<td>----</td>
<td>1.17</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
</tbody>
</table>

---

* denotes the concentration is less than 5%.
<table>
<thead>
<tr>
<th>Author</th>
<th>Type of Tailings</th>
<th>Mine Location</th>
<th>Cu</th>
<th>Fe</th>
<th>S</th>
<th>Co *</th>
<th>Ag *</th>
<th>Au *</th>
<th>Mg</th>
<th>Mn</th>
<th>Zn</th>
<th>Al</th>
<th>Sb *</th>
<th>Pb</th>
<th>As</th>
<th>Cd *</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Fe₂O₃</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>[44]</td>
<td>Sulfidic tailings</td>
<td>Neves Corvo, Portugal</td>
<td>0.401</td>
<td>28.62</td>
<td>24.9</td>
<td>211</td>
<td>20</td>
<td>---</td>
<td>0.946</td>
<td>0.064</td>
<td>1.032</td>
<td>3.041</td>
<td>251</td>
<td>0.365</td>
<td>0.432</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>[45]</td>
<td>Copper tailings</td>
<td>Vallenar, Chile</td>
<td>0.160</td>
<td>17.70</td>
<td>0.783</td>
<td>---</td>
<td>40</td>
<td>---</td>
<td>1.706</td>
<td>0.014</td>
<td>0.026</td>
<td>3.320</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>[46]</td>
<td>Mining tailings</td>
<td>Humedal Culebrón, Chile</td>
<td>0.42</td>
<td>7.77</td>
<td>---</td>
<td>1404</td>
<td>8</td>
<td>---</td>
<td>1.17</td>
<td>---</td>
<td>0.007</td>
<td>7.3</td>
<td>---</td>
<td>0.004</td>
<td>0.004</td>
<td>---</td>
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<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

* corresponds to ppm.
In the studies mentioned, sulfuric acid consistently stands out as a preferred option for leaching due to its cost-effectiveness and widespread accessibility [37]. It is noteworthy that when sulfuric acid is combined with agitation in the process, it consistently delivers highly efficient copper extractions, typically ranging from 50% to nearly 100%. Moreover, it often allows for shorter processing times compared to acids like HCl and HNO$_3$.

### Table 2. Metal extractions from mine tailings via acid agitated leaching.

<table>
<thead>
<tr>
<th>Author</th>
<th>Leaching Agent</th>
<th>Acid Concentration</th>
<th>Oxidizing/Reducing Reagent</th>
<th>Stirring Speed (RPM)</th>
<th>S.L Ratio</th>
<th>Temperature (°C)</th>
<th>Leaching Time (h)</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>[28]</td>
<td>H$_2$SO$_4$</td>
<td>0.1 M</td>
<td>Fe$_2$(SO$_4$)$_3$</td>
<td>600</td>
<td>1:5</td>
<td>60</td>
<td>2</td>
<td>80% Cu</td>
</tr>
<tr>
<td>[29]</td>
<td>HCl</td>
<td>0.01 M (pH 2) *</td>
<td>---</td>
<td>---</td>
<td>1:10</td>
<td>27</td>
<td>1200</td>
<td>34.1% Mn, 11.1% Fe, 5.8% Cu, 5.4% Zn</td>
</tr>
<tr>
<td>[30]</td>
<td>H$_2$SO$_4$</td>
<td>0.05 M (0.24 mL/g) *</td>
<td>---</td>
<td>400</td>
<td>1:2</td>
<td>30</td>
<td>2</td>
<td>98.45% Cu, 56.13% Mn, 21.41% Zn, 17.25% Fe</td>
</tr>
<tr>
<td>[31]</td>
<td>H$_2$SO$_4$</td>
<td>0.428 M</td>
<td>---</td>
<td>300</td>
<td>1:3</td>
<td>75</td>
<td>1</td>
<td>53.8% Cu</td>
</tr>
<tr>
<td>[32]</td>
<td>H$_2$SO$_4$</td>
<td>1 M (9.8% p/p) *</td>
<td>---</td>
<td>100</td>
<td>---</td>
<td>25</td>
<td>10</td>
<td>95.5% Mn</td>
</tr>
<tr>
<td>[33]</td>
<td>H$_2$SO$_4$</td>
<td>---</td>
<td>---</td>
<td>300</td>
<td>1:2</td>
<td>25</td>
<td>0.5</td>
<td>66.74% Cu</td>
</tr>
<tr>
<td>[34]</td>
<td>H$_2$SO$_4$</td>
<td>1.14 M</td>
<td>Fe$_2$(SO$_4$)$_3$</td>
<td>320</td>
<td>1:10</td>
<td>80</td>
<td>1</td>
<td>94.3% Cu</td>
</tr>
<tr>
<td>[35]</td>
<td>H$_2$SO$_4$</td>
<td>0.8 M (160 kg/t) *</td>
<td>---</td>
<td>---</td>
<td>1:3</td>
<td>45–55</td>
<td>0.5</td>
<td>91.34% Cu</td>
</tr>
<tr>
<td>[36]</td>
<td>H$_2$SO$_4$</td>
<td>0.01 M (85 kg/t) *</td>
<td>---</td>
<td>700</td>
<td>1:2</td>
<td>68.51</td>
<td>4.36</td>
<td>85.86% Cu</td>
</tr>
<tr>
<td>[37]</td>
<td>HNO$_3$</td>
<td>10.5 M</td>
<td>---</td>
<td>---</td>
<td>1:1.5</td>
<td>25</td>
<td>24–48</td>
<td>71% Cu</td>
</tr>
<tr>
<td>[38]</td>
<td>H$_2$SO$_4$</td>
<td>0.2 M</td>
<td>---</td>
<td>300</td>
<td>1:2</td>
<td>20</td>
<td>1</td>
<td>70% Cu</td>
</tr>
<tr>
<td>[39]</td>
<td>H$_2$SO$_4$</td>
<td>0.5 M (110 kg/t) *</td>
<td>---</td>
<td>100</td>
<td>1:2.5</td>
<td>30</td>
<td>1.5</td>
<td>92.67% Cu</td>
</tr>
<tr>
<td>[40]</td>
<td>HNO$_3$</td>
<td>2.5 M</td>
<td>---</td>
<td>120</td>
<td>1:1.5</td>
<td>25</td>
<td>168</td>
<td>12.5 ppm Ag</td>
</tr>
<tr>
<td>[41]</td>
<td>H$_2$SO$_4$</td>
<td>0.1 M</td>
<td>---</td>
<td>300</td>
<td>1:3</td>
<td>80</td>
<td>2</td>
<td>50% Cu</td>
</tr>
<tr>
<td>[42]</td>
<td>H$_2$SO$_4$</td>
<td>1 M</td>
<td>VC and H$_2$O$_2$</td>
<td>250</td>
<td>1:2</td>
<td>90</td>
<td>6</td>
<td>99% Zn, 61% Cu</td>
</tr>
<tr>
<td>[43]</td>
<td>H$_2$SO$_4$</td>
<td>0.53 M</td>
<td>---</td>
<td>400</td>
<td>1:10</td>
<td>40</td>
<td>2</td>
<td>66.45% Fe, 65.32% Cu, 59.95% Zn</td>
</tr>
<tr>
<td>[44]</td>
<td>H$_2$SO$_4$</td>
<td>0.01–0.5 M</td>
<td>NaCl</td>
<td>250</td>
<td>1:10</td>
<td>45–70</td>
<td>1–24</td>
<td>93.9% Pb, 84.1% Zn, 66.8% Cu, 47.2% As</td>
</tr>
<tr>
<td>[50]</td>
<td>H$_2$SO$_4$</td>
<td>1 M</td>
<td>Pressure O$_2$</td>
<td>700</td>
<td>1:2.5</td>
<td>180</td>
<td>1</td>
<td>94.4% Cu, 65.9% Fe</td>
</tr>
<tr>
<td>[45]</td>
<td>HCl</td>
<td>9 M</td>
<td>---</td>
<td>550</td>
<td>---</td>
<td>60</td>
<td>16</td>
<td>82.61% Fe, 82.5% Cu</td>
</tr>
<tr>
<td>[46]</td>
<td>HCl and C$_4$H$_4$O$_6$</td>
<td>20–25% and 0.5 M H$_2$O$_2$</td>
<td>---</td>
<td>25</td>
<td>---</td>
<td>60–48</td>
<td>91.06% Co, 21.87% Fe</td>
<td></td>
</tr>
</tbody>
</table>

* corresponds to the original research values.
3.2. Effect of Leaching Agent

The selection of a leaching agent will depend on a set of conditions regarding the material to be processed. It is imperative to consider the type of material, its surface condition, its chemical and mineralogical composition, the process from which it was generated, as well as other details.

In addition to the above, depending on the leaching efficiency it is possible to confirm the choice of leaching agent. It should be noted that for each metal to be extracted, the investigation should be approached in a different way.

The extractions obtained from the studies reviewed above are shown in Table 3, where the concentrations obtained after using an agitated leaching technique with the optimum parameters for some of the studies can be visualized.

<table>
<thead>
<tr>
<th>Author</th>
<th>Leaching Agent</th>
<th>Cu</th>
<th>Fe</th>
<th>Co</th>
<th>Ag</th>
<th>Mg</th>
<th>Mn</th>
<th>Zn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>[29]</td>
<td>HCl</td>
<td>4.0</td>
<td>145</td>
<td>---</td>
<td>---</td>
<td>19</td>
<td>0.26</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>[32]</td>
<td>H$_2$SO$_4$</td>
<td>66.3*</td>
<td>9320</td>
<td>110.7*</td>
<td>---</td>
<td>8100 *</td>
<td>128,600*</td>
<td>63.3*</td>
<td>2557*</td>
</tr>
<tr>
<td>[38]</td>
<td>H$_2$SO$_4$</td>
<td>364</td>
<td>---</td>
<td>---</td>
<td>---</td>
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<td>---</td>
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</tr>
<tr>
<td>[49]</td>
<td>H$_2$SO$_4$</td>
<td>2890</td>
<td>103,000</td>
<td>---</td>
<td>---</td>
<td>---</td>
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</tr>
<tr>
<td>[22]</td>
<td>HNO$_3$</td>
<td>450</td>
<td>8 *</td>
<td>12.5 *</td>
<td>3490</td>
<td>4460</td>
<td>---</td>
<td>1780</td>
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</tr>
<tr>
<td>[40]</td>
<td>H$_2$SO$_4$</td>
<td>2530</td>
<td>1400</td>
<td>1 *</td>
<td>---</td>
<td>---</td>
<td>300</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>[41]</td>
<td>H$_2$SO$_4$</td>
<td>360</td>
<td>5450</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>[50]</td>
<td>H$_2$SO$_4$</td>
<td>2900</td>
<td>102,900</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>[45]</td>
<td>HCl</td>
<td>3.3</td>
<td>749.4</td>
<td>---</td>
<td>38.78</td>
<td>---</td>
<td>25.11</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>[46]</td>
<td>HCl and H$_2$O$_6$</td>
<td>---</td>
<td>---</td>
<td>11.58*</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

* corresponds to ppm.

The incidence of the leaching agents H$_2$SO$_4$ and HCl will be evaluated by their reaction mechanisms.

3.2.1. Sulfuric Acid

Copper within a tailings deposit can be found in silicate, oxidized, and sulfide forms, so the following mechanisms were used to demonstrate the dissolution of the copper species in the presence of H$_2$SO$_4$. Table 1 shows that the copper content in the tailings analyzed in each study does not exceed 1%, so some of the researchers used sulfuric acid as a leaching solution, since it can generate soluble compounds and copper ions.

\[
\text{CuFeS}_2(s) + 1/2\text{O}_2(g) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{CuS}(s) + \text{FeSO}_4(s) + \text{H}_2\text{O}(l) + S^0(s) \quad (1)
\]

\[
\text{CuS}(s) + 1/2\text{O}_2(g) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{CuSO}_4(s) + \text{H}_2\text{O}(l) + S^0(s) \quad (2)
\]

\[
\text{CuCO} \cdot \text{Cu(OH)}_2(s) + 2\text{H}_2\text{SO}_4(aq) \rightarrow 2\text{CuSO}_4(s) + 3\text{H}_2\text{O}(l) + \text{CO}_2 \uparrow \quad (3)
\]

\[
\text{CuSiO}_3 \cdot 2\text{H}_2\text{SO}_4(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{CuSO}_4(s) + \text{H}_2\text{SiO}_3(aq) + 2\text{H}_2\text{O}(l) \quad (4)
\]

\[
\text{CuO}(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{CuSO}_4(s) + \text{H}_2\text{O}(l) \quad (5)
\]
CuO(s) + 2H⁺(aq) → Cu²⁺(aq) + H₂O(l)  \hspace{1cm} (6)

Equation (1) shows the decomposition of chalcopyrite to form chalcocite, which later (Equation (2)) will form copper sulfate, which is soluble in water and decomposes in acid environments (pH < 4.5). Equations (3) and (4) show how complex copper compounds decompose, forming a soluble product while Equations (5) and (6) show the behavior of an oxidized copper material in the presence of sulfuric acid.

Regarding the amount of iron, it can be said that the tailings have a high iron content, so the extraction of iron is a tentative idea. The nature of this metal will depend on the conditions in which the tailings deposit was left, so within this material iron can be found as an ion, hydroxide, silicate, or oxide.

Fe³⁺(aq) + H₂O(l) → FeOH²⁺(aq) + H⁺(aq)  \hspace{1cm} (7)

2Fe(OH)₃ + 3H₂SO₄(aq) → Fe₂(SO₄)₃(s) + 6H₂O(l)  \hspace{1cm} (8)

Fe₃O₄(s) + H₂SO₄(aq) → FeSO₄(s) + Fe₂O₃(s) + H₂O(l)  \hspace{1cm} (9)

Fe₂SiO₄(s) + 2H₂SO₄(aq) → 2FeSO₄(s) + H₄SiO₄(aq)  \hspace{1cm} (10)

When iron compounds come into contact with sulfuric acid they decompose forming iron sulfates (Equations (8)–(10)), in the case of silicates, a silicic acid is formed (Equation (10)) and in the case of an oxide, such as magnetite, an iron oxide (hematite) is formed (Equation (9)).

There are tailings that stand out for their high Zn content, so the use of H₂SO₄ for the leaching of this residue has also been carried out. The reaction mechanisms for zinc compounds in contact with sulfuric acid are as follows:

ZnS(s) + H₂SO₄(aq) → ZnSO₄(s) + H₂S(g)  \hspace{1cm} (11)

ZnS(s) + H₂SO₄(aq) + 1/2O₂(g) → ZnSO₄(s) + H₂O(l) + S⁰(s)  \hspace{1cm} (12)

Zn₂SiO₄(s) + 2H₂SO₄(aq) → 2ZnSO₄(s) + Si(OH)₄(aq)  \hspace{1cm} (13)

Zn₄SiO₇·(OH)₂·H₂O(s) + 4H₂SO₄(aq) → 4ZnSO₄(s) + Si₂O(OH)₆ + 3H₂O(l)  \hspace{1cm} (14)

ZnO(s) + H₂SO₄(aq) → ZnSO₄(s) + H₂O(l)  \hspace{1cm} (15)

For all Zn compounds, when leached with sulfuric acid, ZnSO₄ is formed, but depending on the mineralogy of the compound, the reaction will have different products, such as the leaching of spharelite, H₂S (Equation (11)), and S⁰ in the presence of oxygen (Equation (12)); silicon hydroxides for zinc silicates (Equations (13) and (14)) and water formation for Zn oxides (Equation (15)).

One of the most common impurities in tailings, besides quartz, are carbonates, which are commonly known to be high acid consumers disrupting the efficiency of valuable metal extraction.

CaCO₃(s) + H₂SO₄(aq) → CaSO₄(s) + H₂O(l) + CO₂↑  \hspace{1cm} (16)

CaO(s) + H₂SO₄(aq) → CaSO₄(s) + H₂O(l)  \hspace{1cm} (17)
It can be seen that the reactions between carbonate compounds and calcium oxides (Equations (16) and (17)) and the product formed is anhydrite, which directly affects the leaching of metals.

There are toxic metals that need to be extracted to avoid further environmental contamination. One of them is lead. The mechanisms associated with the leaching of lead in the presence of sulfuric acid are shown in Equation (18).

\[
PbS(s) + H_2SO_4(aq) \rightarrow PbSO_4(s) + H_2S(g) \quad (18)
\]

3.2.2. Hydrochloric Acid

The second acid to be evaluated is hydrochloric acid, which is decomposed by the mechanism provided by Equation (19).

\[
6HCl(aq) \rightarrow 6H^+(aq) + 6Cl^-(aq) \quad (19)
\]

The manganese compounds in the tailings are mostly complex compounds that can be separated into ions, thereby releasing the metal of interest.

\[
Ca_3Mn(SO_4)_2(OH)_6(H_2O)_3(s) + 6H^+(aq) \rightarrow 3Ca^{2+}(aq) + Mn^{4+}(aq) + 2SO_4^{2-} + 9H_2O(l) \quad (20)
\]

\[
Ca_3Mn(SO_4)_2(OH)_6(H_2O)_3(s)+6HCl(aq) \rightarrow 3Ca^{2+}(aq)+ Mn^{4+}(aq)+2SO_4^{2-} + 6Cl^- + 9H_2O(l) \quad (21)
\]

In Equations (20) and (21), it can be seen how the use of hydrochloric acid allows this ion separation without contaminating the desired metal and allowing an efficient extraction.

In the case of lead, which is a toxic metal, the chlorine ion allows the formation of PbCl\(_2\) (seen in Equation (22)), which can encapsulate the metal and, thus, reduce the damage caused by this metal in solution.

\[
PbSO_4(s) + 2Cl^-(aq) \rightarrow PbCl_2(s) + SO_4^{2-} \quad (22)
\]

\[
PbCl_2(s) + 2Cl^-(aq) \rightarrow PbCl_2^-(aq) \quad (23)
\]

Further processing of the lead compound in contact with the chlorine ion will result in a lead compound in solution (Equation (23)), which can be recovered by leach solution refining processes.

3.3. Leached Solution Refining Processes

The product recovered from acid leaching of mine tailings material has a high content of metals in solution, which are recovered by electrochemical, chemical, and metallurgical processes, such as fractional precipitation [30] and solvent extraction with subsequent electrowinning [49,50]. With the above processes it is possible to recover the metal from the leached solution and deliver a solid commercial product for direct industrial use.

4. Conclusions

This comprehensive review consolidates procedures, parameters, and data for recovering metals from mine tailings, serving as a foundational resource for related research. Prior to processing tailings, conducting chemical and physical characterizations is essential. This deep understanding of tailings composition, species, and quantities forms the basis for designing experiments to optimize metal extraction efficiently.

The choice of chemical agents for leaching depends on various factors, including tailings’ chemical composition, oxidation state, valuable material percentage, acid-consuming impurities, particle size, and more. Tailoring each acid leaching operation meticulously involves adjusting acid concentration, agitation parameters, and pulp density to suit material-specific characteristics. Depending on material requirements, introducing chemi-
cal agent dosages, applying elevated temperatures, and controlling particle sizes, preferably on a micron scale, may be necessary.

Moreover, evaluating whether tailings processing steps like grinding, additional leaching, ore concentration (flotation), roasting, magnetic separation, or other metallurgical processes should precede or follow leaching is crucial. This assessment ensures alignment with recovery goals and material characteristics in the chosen processing sequence.

In the future, and depending on the metal being extracted, it is necessary to select the correct refining process to obtain a final product, such as the implementation of solvent extraction plus electrowinning for copper or fractional precipitation in the case of refining multiple metals.

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