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## **Electrolytic production of copper from chalcopyrite**

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**Key words:** copper, extraction, electrowinning, chalcopyrite, aqueous solutions, hydrometallurgy, ionic liquids, molten salts, sulfides, electrochemical engineering, renewable energy

### **Abstract**

The transition to renewable energy infrastructure necessitates rapid growth in copper production, averaging at least 3.5% annually to 2050. The current smelting-converting-electrorefining route must be revisited considering these future prospects as ore grades deplete and the costs to mitigate emissions to the environment increase. Here, we investigate electrolytic alternatives, reviewing the background and recent developments for four classes of electrolytes to directly decompose the most important industrial copper mineral, chalcopyrite: aqueous solutions, ionic liquids, molten salts and molten sulfides. These electrolytes are discussed in the framework of electrochemical engineering, as applied to the electrolytic decomposition of chalcopyrite. A vision is proposed in which an electrolytic technique, integrated with low cost and sustainable power, enables the production of unprecedented annual tonnages of copper from low-grade chalcopyrite, with valuable by-products and enhanced selectivity for impurities.

### **1. Introduction**

The swift transition to clean energy infrastructure is undertaken today by society with the aim to mitigate the effects of climate change [1]. The infrastructure to generate, transmit and store power requires unprecedented quantities of copper, steel and minor, precious metals [2]. However, the production of these metals is questioned considering their environmental impact [3]. For non-ferrous metals, ore grades are reported to decrease, and the ability to treat more diverse and traditionally problematic mineral deposits would be a great advantage [4]. As more metal must be extracted with greater efficiency and flexibility, novel extraction routes may be pursued.

Fundamentally new routes to decouple metal production from greenhouse gases at an affordable cost are required for all major metals. Electrowinning, in particular if it can be directly applied to the metal-containing compound from the ore, is an especially relevant option, providing sustainable and cost-effective power is available. Such compounds for iron are iron oxides, e.g. hematite ( $\text{Fe}_2\text{O}_3$ ), today mostly traded as iron concentrate of high purity (+98% iron oxide). Low [5], medium [6] or high [7] temperature direct electrowinning of oxides to produce only metal (e.g. Fe) and oxygen ( $\text{O}_2$ ) have received significant attention, some of those approaches being now at the stage of small pilot operations. In this opinion piece, the electrolytic processing of the other major rock-forming compound, sulfide, is explored. The focus is on the production of copper, a bulk commodity with superior electrical properties, key to the proliferation of electric vehicles and smart electricity grids. The approaches highlighted here are transferable to a range of other metal sulfides.

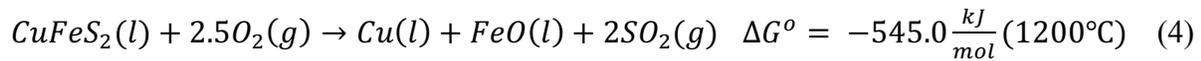
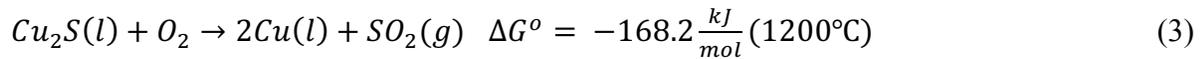
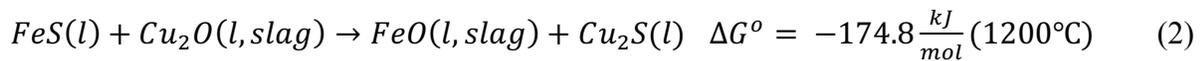
The race against climate change sets an ambitious timeline for future copper production. Elshkaki et al. [8] predict that global copper demand will increase between 275 and 350% by 2050, if the United Nations Environment Programme GEO-4 scenarios are pursued. 90% of global copper resources are sulfide ores, where most of the copper is in the form of covellite ( $\text{CuS}$ ), chalcocite ( $\text{Cu}_2\text{S}$ ), chalcopyrite ( $\text{CuFeS}_2$ ) and bornite ( $\text{Cu}_5\text{FeS}_4$ ). Covellite and chalcocite are surface deposits and can be treated economically, but these resources are largely exhausted. Typically formed at greater depths, chalcopyrite is the major copper mineral remaining, constituting over 70% of the global copper reserve [9]. Here, we seek to review the recovery of copper from iron and sulfur in chalcopyrite (equation 1,  $\Delta G_f^\circ$  as reported by Conrad et al. [10]), and whether a novel electrochemical route could be developed to contribute to the vast quantity of copper required for global electrification.



One metric tonne of  $\text{CuFeS}_2$  contains 330 kg of Cu, 290 kg of Fe and 330 kg of  $\text{S}_2$ . Clearly, the chemical nature of the compound imposes constraints on possible processes, both the conventional pyrometallurgy routes, as well as direct electrowinning approaches.

## 1.1 Convention

In conventional pyrometallurgy, a reducing agent is used in conjunction with the decomposition reaction (1), both to provide the necessary thermodynamic driving force, as well as additional energy to maintain the heat balance in the reactor. Reductants common in metallurgical extraction, carbon or hydrogen, are not suitable to reduce sulfide ores because the stability of H<sub>2</sub>S and CS<sub>2</sub> are less than the sulfides. Instead, oxygen can be employed as a reductant, as well as a separating agent to remove iron. Upon melting, chalcopyrite forms a matte containing Cu<sub>2</sub>S and FeS. The key equilibrium reaction exploited during smelting with oxygen is shown in equation 2, indicating that the preferential oxidation of iron is highly favored. FeO is collected in a silicate slag, so the matte containing primarily Cu<sub>2</sub>S can then be converted to liquid copper and gaseous SO<sub>2</sub>, as shown in equation 3. The total simplified reaction for these steps is shown in equation 4. These reactions are discussed in greater detail by Seetharaman et al. [11], while Schuhmann [12] provides a classic resource on the topic.



The smelting-converting-electrorefining route in practice, as detailed by Schlesinger et al. [13], suffers from the generation of by-products, and high capital costs. SO<sub>2</sub> (~2 tonnes per tonne of copper, as shown in equation 4) is toxic to humans and environmentally harmful, and must be collected and converted to sulfuric acid. The silicate slag containing iron (2.2 tons/ton copper [14]), is typically disposed. While oxygen offers effective control over the main constituents, it offers limited selective control over the numerous trace elements in the chalcopyrite ore. Most notably, arsenic oxidizes and volatilizes, dispersing amongst the slag, matte, dust, as well as precipitates (slimes) of the later electrorefining state – all of which require further treatment to neutralize the toxicity of arsenic compounds [15]. Precious trace metals, such as silver, gold, or elements such as tellurium or selenium contained in chalcopyrite typically report to the matte, then to liquid copper metal upon conversion. After fire refining, copper is cast to anodes and aqueous electrorefining is used to recover these valuable elements. While largely effective, this later step is the slowest of copper production, and costly.

Auxiliary processes are required to handle and treat by-products, but the conventional route also dictates significant investment and rigidity in feedstock selection and preparation. Arsenic can only be tolerated at low concentrations ( $<0.5\text{wt}\%$ ). To maintain the proper heat balance in the smelter and converter, copper and iron must be at a sufficiently high concentration (and still, around 30 GJ/tonne copper energy is consumed during copper smelting, converting and refining [16]). Besides, copper ores are largely gangue (minerals such as pyrite, alumina, limestone and silica), and only  $\sim 0.6\%$  copper, such that mining products must be crushed, ground and floated to concentrate the chalcopyrite and other sulfide fraction (containing 25-35 wt% Cu). These comminution and floating processes are costly and energy-intensive, and this energy intensity increases exponentially as ore grades deplete below 0.5% [3]. Meanwhile, plentiful high-copper, but arsenic-rich deposits remain unviable for processing [17].

## 2. Electrolytic alternatives

A variety of methods exist to extract copper from chalcopyrite, alternative to the current route, which conceptually dates back to antiquity. Indeed, Baba et al. [9] reviews novel techniques for processing chalcopyrite, as well as Prasad et al. [18]. Both surveys focus on hydrometallurgical extraction. Here, electrolytic methods are the focus, for the possibility to directly and efficiently decompose sulfides to their elemental constituents. When electrons provide the energy requirements for equation (1), the use of reductants or oxidants and the generation of sulfuric acid are avoided, with the potential to streamline the whole production chain, from raw ore to refined products.

Conventional direct electrolytic methods can be described with several basic steps, as presented by Allanore [19]. First, the copper sulfide compound must be dissociated into its constitutive anions ( $\text{S}^{2-}$ ) and cations ( $\text{Cu}^{1+}/\text{Cu}^{2+}$  and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  for chalcopyrite). A supporting electrolyte then acts as a solvent for the sulfide feedstock. Alternatively, solid chalcopyrite concentrate may be employed as an electrode, while the electrolyte acts to transport the cation, or anion. In both situations a potential difference is necessary across the electrodes to drive the ions separation. At the anode and cathode, electrons are transferred to form a neutral species, the metal at the cathode and typically a gas at the anode. Both then need to be removed from the electrolyte solution and the electrolysis reactor (cell).

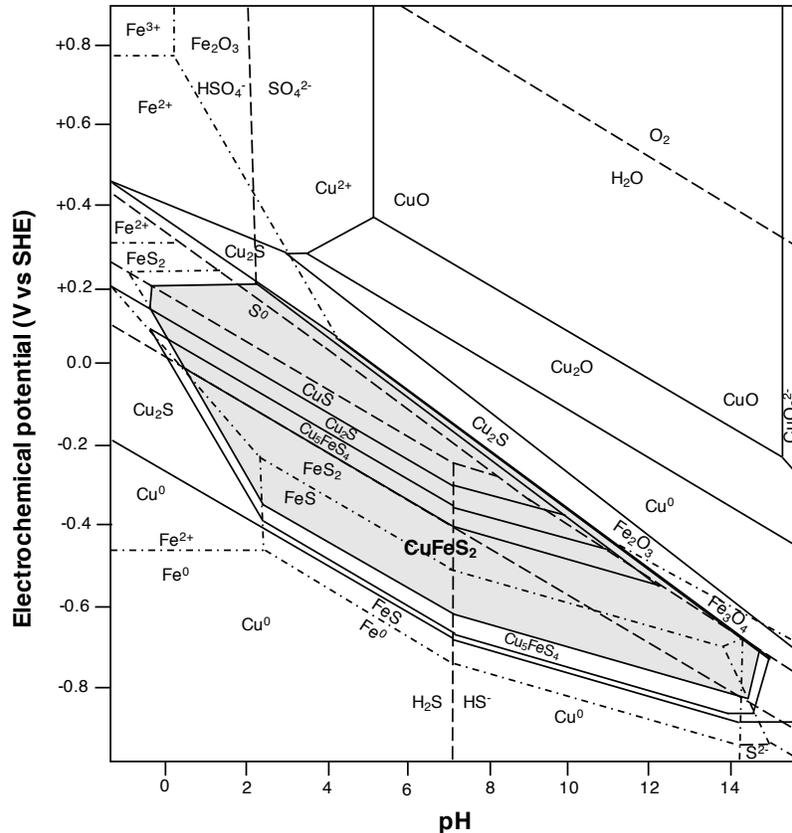
To carry out these steps, the choice of electrolyte is key, and requirements include:

- High ionic conductivity
- High rates of mass transport
- Chemical and thermal stability
- High solubility for the feedstock

The electrolyte composition ultimately determines the operating parameters and the physical arrangement of the cell, and thus electrolytic processes may be classified based on the electrolyte nature. The electrolytic decomposition of chalcopyrite has been investigated in several electrolytes: aqueous solutions, ionic liquids, molten salts and molten sulfides. The background and recent advancements for these electrolyte categories are summarized below. Given these categories, the distinction between low and high temperature processes is important to consider as well. Distinct challenges exist for both, due to the semiconducting nature of metal sulfides. Prior to melting, chalcopyrite is in a strong lattice formation, and is difficult to dissociate. As temperature increases, bond energy decreases, so the decomposition of chalcopyrite requires relatively lower potentials, but efforts for molten-state processing have been hindered by the persistence of high electronic conductivity of chalcopyrite.

## 2.1 Aqueous solutions

Hydrometallurgical techniques are in industrial operation to extract copper from oxide and secondary sulfide ores, but the treatment of chalcopyrite remains challenging. Chalcopyrite is the most refractory copper mineral. Harsh conditions (highly acidic solutions, high pressure and temperature, or thermal and chemical pretreatments) are required. Direct electrochemical leaching attempts to improve the limited chemical dissolution, for example by using chalcopyrite slurry as a massive electrode (which has sufficiently low resistivity). The Pourbaix diagram for the  $\text{CuFeS}_2\text{-H}_2\text{O}$  system, shown in Figure 1, illustrates the various pathways for decomposing chalcopyrite via reduction or oxidation, in an acidic or basic solution. In this diagram, theoretical reactions that may occur over geological timescales or at high pressures, but known not to occur in the laboratory (the consumption of  $\text{H}_2\text{S}$  as a reactant and the formation of  $\text{FeS}_2$ ), are eliminated to show a more realistic stability of  $\text{CuFeS}_2$  [20].



**Figure 1:** Eh-pH diagram of the Cu-Fe-S-H<sub>2</sub>O system at 25°C and 1atm. All solutes at 0.1M activity except Cu<sup>2+</sup>=0.01M. The stability of CuFeS<sub>2</sub> assumes H<sub>2</sub>S is not available as a reactant and FeS<sub>2</sub> cannot appreciably form (consistent with laboratory observations). Redrawn from Peters [20].

Reductive decomposition is attractive for the direct recovery of metallic copper. Particularly, an acidic solution may retain iron in solution for effective separation. The electroreduction of chalcopyrite has been conducted with sulfuric acid as the electrolyte, but the reaction was hindered by the co-evolution of hydrogen. In an alternative approach by Fuentes-Aceituno et al. [21], monoatomic hydrogen is supposedly formed at the cathode to act as the reducing agent. Martinez-Gomez et al. [22] studied this system and found the electro-assisted reduction kinetics were considerably hindered by passivation of the chalcopyrite particles with elemental sulfur. Recent work by Martinez-Gomez et al. [23] investigated several operating variables in HCl media, and an operating window to avoid passivation was demonstrated. Low energy consumption was reported as an advantage, but operational difficulties include the generation of H<sub>2</sub>S (which must be electro-oxidized at the anode to prevent emission of this highly toxic gas), as well as the reactivity of the copper product upon exposure to air.

The other main approach, oxidative processing, has been widely explored. In such a process, a slurry of chalcopyrite powder is employed as the anode to then liberate elemental sulfur or sulfate ions in solution, depending on the oxidizing potential and pH. Such slurry electrolysis is analogous to the alkaline process for iron oxide where solubility is limited [5], though in the latter iron is directly electrowon, while for the former the outlet solution would then undergo electrowinning in a different cell. The main challenge for chalcopyrite processing is the formation of a metal-deficient-sulfide (i.e. a sulfur enriched) layer, which greatly inhibits leaching kinetics. Despite significant academic study, the composition of this layer and the exact mechanism of passivation remain unclear [24]. Various agents have been tested in an attempt to penetrate the film and improve dissolution. Processing routes can largely be divided into sulfate-based (the current industry standard) and halide-based (mostly chloride, less commonly bromide) processes, but nitric acid, ammoniacal and biological systems have also been explored. These processes are reviewed by Dreisinger [25]. Overall, electrochemical processing in aqueous solutions may be profitable for low-grade concentrates not amenable to floatation, but due to the numerous steps and by-products as a result of employing an oxidizing agent, the applicability remains limited.

Research in this area is active, and several new approaches have been recently introduced. Reagents may be added to act as catalysts during leaching. For example, copper recovery is significantly increased with additives to a ferric sulfate leaching solution: thiocarbonyl functional groups in the Jetti process [26] and iodide as investigated by Granata et al. [27]. As chalcopyrite dissolution is notoriously complex and highly dependent on specific surface chemistry, Yang et al. [28] demonstrate a high-throughput “ore-on-a-chip” method to study and optimize leaching conditions for specific deposits. Microfluidic platforms enable fast and efficient testing, so the mechanisms behind chalcopyrite oxidation may be further elucidated. Another approach is to simply accept the slow copper extraction rates, and utilize chalcopyrite primarily for energy storage. Deen and Asselin [29] demonstrate a fixed bed flow cell, where the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox reaction in the presence of Cu is the charge/discharge process. Coulombic efficiency decreased by ~20% (from 80% initially) over 400 cycles. This decrease in efficiency during cycling was accompanied by the extraction of pure copper (10-13% of the copper contained in chalcopyrite) – the profits of which may incentivize the adoption of this technology, and allow copper production in remote sites with minimal capital costs.

## 2.2 Ionic liquids

In response to the low dissolution of chalcopyrite in conventional aqueous solutions, ionic liquids, a relatively new generation of solvents, have been gaining attention. Ionic liquids are mixtures of organic and inorganic salts that are liquid at low temperatures. These solvents are promising for extracting reactive metals and alloys because they exhibit a wide liquid temperature range with no vapor pressure up to the decomposition temperature (typically  $\sim 400^{\circ}\text{C}$ ), as well as a wide electrochemical window ( $\sim 4.0\text{V}$ ) [30]. Properties such as viscosity, ionic conductivity and chemical reactivity can be manipulated by combining cations and anions of different size and structure [31]. Here, ionic liquids are categorized separately from aqueous solutions, but these solvents are often mixed with  $\text{H}_2\text{O}$  to reduce cost and viscosity.

There have been a number of recent studies applying ionic liquids to chalcopyrite, summarized by Rodriguez et al. [32]. Results from the first study by Whitehead et al. [33] showed copper leaching rates increased from 55% to 87% when increasing the concentration of ionic liquid (1-butyl-3-methyl-imidazolium hydrogen sulfate) from 10 to 100% in aqueous solution, at  $70^{\circ}\text{C}$ . It was proposed that these improvements were due to improved oxygen solubility capacity of ionic liquids in aqueous sulfuric acid, and that Brønsted acidity was important to provide the proton present in the  $\text{HSO}_4^-$  counter ion. However, recent research presents a contrasting theory, stating that in fact ionic liquids are not strong oxidants, and the oxygen solubility in ionic liquids is lower than in water. Instead, the hydrophobicity of ionic liquids has been proposed as a key feature for improved dissolution. Ionic liquids may have a higher affinity for sulfur and sulfidic-hydrophobic surfaces, decreasing resistance at the solid-liquid interface, to then improve the solution-solid surface electron transfer processes or aid in removing oxidation products [34].

Still, the precise mechanisms promoting dissolution of chalcopyrite in ionic liquids, and whether they offer sufficient advantages over simple  $\text{H}_2\text{SO}_4$  systems remain debated. Carlesi et al. [35] observed a synergistic effect between ionic liquids and sulfuric acid above  $60^{\circ}\text{C}$ , and proposed that ionic liquids promote decomposition of sulfidic intermediates that passivate the surface of chalcopyrite. Al-Zubeidei et al. [36] studied the leaching of chalcopyrite with several structurally simple ionic liquids, and found that the progression of leaching was similar to that of  $\text{H}_2\text{SO}_4$  solutions, and that more polar cations improve extraction. Kuzmina et al. [37] studied

chalcopyrite leaching in a series of ionic liquids in the absence of oxidants, and the 1-butylimidazolium hydrogen sulfate composition showed the best performance. Still, the leaching ability of ionic liquids alone was insufficient to extract copper from chalcopyrite. The ideal combination of ionic liquid and oxidant is being investigated. For example, Rodriguez et al. [32] built on the work by Kuzmina et al. [37] to add bromide as an oxidant to the 1-butyl-3-methylimidazolium hydrogen sulfate system, and confirmed superior leaching to  $H_2SO_4$  leaching with chloride ions.

A slightly different electrolyte class, deep eutectic solvents (DES), may offer a pathway for direct extraction, as well as cheaper cost and lower toxicity. DES's have similar properties to ionic liquids, but are primarily chloride based, with hydrogen-bond donors [38]. These electrolytes have been used to directly decompose a range of metal sulfides: Ru et al. [39] demonstrated the deposition of lead powders and sulfur nanoparticles from solid PbS in choline chloride-ethylene glycol solution at  $80^\circ C$ , and Wang et al. [40] showed the desulfurization of  $Sb_2S_3$  to antimony powders is possible in the same solution. Such systems have been applied to chalcopyrite as well. Anggara et al. [34] successfully demonstrated the electrowinning of copper from chalcopyrite in mixed DES of 20wt% choline chloride-oxalic acid and 80wt% choline chloride-ethylene glycol. The authors hypothesized favorable dissolution was due to the high Cl<sup>-</sup> content and low water content, and the authors noted that the DES electrolyte can be further optimized to increase the selectivity of copper over iron by changing solute speciation, and therefore redox properties.

### **2.3 Molten salts and borates**

A beacon in electrochemical engineering based on molten salt is the Hall-Héroult process for aluminum. Molten salts have been investigated for a wide range of systems over the last century [41]. Interest in those electrolytes was re-invigorated by Chen et al. [42], upon successfully demonstrating the electro-deoxidation of  $TiO_2$  using a  $CaCl_2$  electrolyte to produce titanium powder as an alternative to pyrometallurgy (Kroll). Electrolysis conducted in molten alkali halides can be applied to many metal systems, due to the wide electrochemical window, as well as high ionic conductivity and low viscosity that the salts offer. In particular molten salts can act to suppress electronic conductivity if the supporting alkali or alkaline-earth metals are not produced at the cathode.

Early work by Garbee and Flengas [43] show the addition of copper chloride (CuCl) to copper sulfide (Cu<sub>2</sub>S) sufficiently decreases electronic conductivity. Copper metal was selectively recovered from a Cu-Fe-S matte dissolved in molten CuCl. At operating temperatures between 450 and 600°C, sulfur gas was evolved, but copper deposited as solid dendrites at the cathode, resulting in low productivity. The approach has since been modified to employ copper sulfide powder as a solid cathode to avoid the formation of dendrites. The electrolyte does not dissolve the metal sulfide, but supports the transfer of the S<sup>2-</sup> ions evolved at the electrolyte-cathode interface to the anode (typically graphite). With sufficiently low oxygen partial pressure and anode current density, elemental gaseous sulfur is the main anodic product. CaCl<sub>2</sub>-based electrolytes have been investigated by Ge et al. [44], but CaCl<sub>2</sub> has a low solubility for S<sup>2-</sup> ions, is prone to hydrolysis (leading to problematic side reactions), and CaS forms as an intermediate product. Noting the high solubility of S<sup>2-</sup> ions (~39 mol/L in NaCl at 712°C), and low solubility for O<sup>2-</sup> ions, Tan et al. [45] used an equimolar NaCl-KCl melt at 700°C to desulfurize chalcopyrite, after a series of insertion reactions between NaCl-KCl and CuFeS<sub>2</sub> for L<sub>x</sub>CuFeS<sub>2</sub> compounds. Overall, the experimental results suggest high current efficiency (85%) and low process energy consumption. Nemeth [46] successfully treated natural chalcopyrite concentrate with this process. Altogether, NaCl-KCl melts remain difficult to scale-up for continuous metal production, and in particular the avoidance of Cl<sub>2</sub>(g) or other chlorinated gases evolution.

Kartal and Timur [47] employ molten borax to decompose liquid copper sulfide. Due to immiscibility and density differences, liquid copper sulfide was decomposed at 1200°C, collecting as liquid copper at the cathode below, while S<sup>2-</sup> ions were transferred through the molten borax above to the anode. While such an arrangement is promising for semi-continuous operation, reactions between the S<sup>2-</sup> ion and Na<sup>+</sup> to form Na<sub>2</sub>S were observed, due to the inherently limited solubility of sulfides in acidic oxide melts. While controlling side reactions involving sodium may ultimately limit the productivity of copper production, borate remains amongst the less studied electrolytes for metal electrowinning.

## 2.4 Molten sulfides

The principle behind sulfide-based electrolytes is “like dissolves like.” A sulfide-based electrolyte could act as a solvent for copper sulfide feedstock, with high solubility to support high current density, and thus high productivity. However, since the first demonstration of the

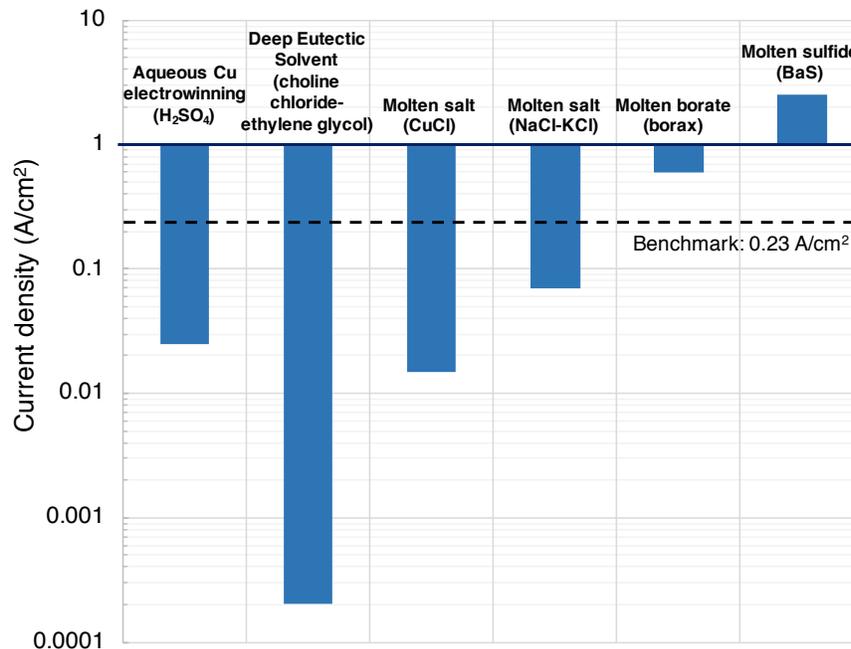
decomposition of metal sulfides in the molten state by Townsend in 1906 [48], the high electronic conductivity has been prohibitive for Faradaic reactions to be controlled. Alkali and alkali earth metals exhibit the largest electronegativity difference versus sulfur, and may exhibit ionic bonding. Therefore, Sokhanvaran et al. [49] selected BaS, due to its large electronegativity difference, large bandgap and small electrical conductivity. With a binary BaS-Cu<sub>2</sub>S electrolyte, cathodic electrochemical reactions were demonstrated and for the first time liquid copper was extracted from a molten sulfide melt. Molten sulfide electrolysis is promising not only for the single-step extraction of copper, but to also selectively extract other elements contained in the ore concentrate. Sahu et al. [50] used a BaS-based electrolyte (with La<sub>2</sub>S<sub>3</sub> addition to improve the faradaic efficiency) and showed the selective reduction of copper, molybdenum and rhenium in a BaS-La<sub>2</sub>S<sub>3</sub> electrolyte, confirming the Ellingham diagram prediction. Indeed, not only does the BaS-La<sub>2</sub>S<sub>3</sub> supporting electrolyte sufficiently inhibit electronic conductivity, the decomposition potential of BaS and La<sub>2</sub>S<sub>3</sub> is also several volts lower than most metal sulfides. Further, common anion impurities: arsenides, tellurides and selenides, may be selectively oxidized at the anode. Currently, the electrolysis of natural chalcopyrite concentrate in a BaS-La<sub>2</sub>S<sub>3</sub> supporting electrolyte is being investigated to understand the extent to which trace elements can be selectively extracted, as well as iron. Iron is present in equimolar proportion, and iron sulfide (FeS) exhibits a very similar decomposition potential to copper sulfide (Cu<sub>2</sub>S). With this challenging circumstance, there is a unique opportunity to explore co-deposition and distribution of the metal species as the electrolyte composition changes during processing.

### **3. Current reality**

Given this overview of the developments for each type of electrolyte, we return to the original motivation—could these electrolytes enable the production of unprecedented annual tonnages of copper from low-grade chalcopyrite without by-products or noxious emissions? Here, the four electrolyte classes are compared considering three electrochemical engineering aspects: current density; the management of iron, sulfur and impurities; and state (solid/liquid) of the feedstock and product.

#### **3.1 Current density**

Due to the commodity nature of bulk metals, conversion cost is the key determining factor for industrial feasibility. Using the Hall-Héroult process as a benchmark for the commodity production of metal by electrolysis, Allanore [19] provides metrics a hypothetical electrolytic cell must achieve for industrial copper production. Current density is key, directly determining the rate of metal production. Figure 2 compiles reported current densities for various electrolyte systems. High solubility of the species in the electrolyte enables high current density. Non-sulfide electrolytes are ultimately limited by the fact that electrolyte species may react with the sulfide or  $S^{2-}$ , or may compete for reduction. For aqueous solutions, the solubility of metal species is limited by the tendency for water to react, precipitating oxides and hydroxides. Ionic liquids offer a non-aqueous alternative, and higher concentrations of metal ions may be achieved by designing ionic liquids that have a coordinating group covalently linked to the cation, or by incorporating a metal complex into the composition. Brooks et al. [51] demonstrate this concept, obtaining high electrodeposition rates ( $0.25 \text{ A/cm}^2$ ) with a synthesized ionic liquid containing copper(I). This solution was synthesized by treating copper(II) oxide, as well as adding copper metal to a solution of copper(II) salt in acetonitrile; however, such an approach is likely not applicable to chalcopyrite. For molten salts, NaCl-KCl shows limited improvement in current density over CuCl, while borax may be promising from this standpoint. Comparatively, in molten sulfides, the current density can be improved by yet another order of magnitude ( $2.5 \text{ A/cm}^2$ ), due to the large miscibility of chalcopyrite in BaS [52].



**Figure 2:** Current densities for various electrolyte systems plotted on a logarithmic scale, plus the benchmark to match the industry standard for liquid metal production with an electrolysis cell [19]. Reported values used for aqueous copper electrowinning [13], deep eutectic solvent [34], CuCl [43], molten borax [47] and molten sulfide [49]. Current density for NaCl-KCl system calculated by dividing average operating current by reported sample surface area [45].

### 3.2 Management of iron, sulfur and impurities

Current density determines the rate of metal production at the cathode, but for chalcopyrite it is important to focus on the liberation and collection of the other constituents: iron and sulfur. Copper extraction is limited primarily by the ability to manage iron and sulfur in the system. The Pourbaix diagram in Figure 1 illustrates the fundamental challenge of decomposing chalcopyrite in aqueous solutions: many intermediate phases form. Any effective leachant for copper will most likely leach iron. Indeed, initial leaching studies proposed that iron preferentially leached from chalcopyrite at first, and a diffusion polysulfide layer formed due to the slower diffusion of copper than iron in the solid state [9]. Recent research by Nyembwe et al. [53] further confirms that sulfur and iron precipitates (goethite, jarosite), as well as gangue minerals hinder dissolution. Sulfur is not efficiently extracted during leaching, but instead forms a non-conducting layer around chalcopyrite. While higher temperatures and pressures typically enhance leaching, the passivating effect of sulfur becomes particularly problematic at temperatures above the sulfur melting point (115°C), and surfactants are required to decrease wetting phenomena [54]. While ionic liquids are a possibility to overcome passivation, future work must investigate the speciation and collection of iron and sulfur in these systems. Abbott et al. [55] explains that “relatively little is known about anodic reactions in ionic liquids and very little data has been published on anodic dissolution efficiencies.” Typically, the anodic reaction (dependent on the activity of the anion ligand and the viscosity of the liquid) is slower than the cathodic reaction in ionic liquids. Meanwhile, the separation and collection of elemental iron (at the cathode) and sulfur (gaseous, at the anode) have been demonstrated successfully in molten salt and molten sulfide systems. In fact, in a recent thesis Chmielowiec [56] studied the anodic gas evolution in various electrolyte systems to inform the design of an electrochemical cell, showing for example how molten sulfides may support high anodic current densities.

Copper concentrates also contain gangue materials (alumina and silica, totaling ~10wt%) and a wide range of impurities. Tan et al. [45] and Nemeth [46] extracted copper and iron from natural concentrate in a NaCl-KCl electrolyte. Nemeth [46] showed As, Sb, Pb and Zn, could be

removed in the exhaust gas due to evaporation. Silicates and oxides were collected in the iron-rich and copper-rich deposit powders. While results for treating natural concentrate in molten sulfide electrolytes are yet to be published, a sulfide-based electrolyte may offer improved selectivity compared to non-sulfide systems. Chalcopyrite concentrate can be completely dissolved in a molten sulfide supporting electrolyte, such that compounds present may then be selective decomposed. Additionally, as the system is molten, any oxides present will phase separate as lighter, immiscible liquid (slag), and can be skimmed. Enhanced selectivity and removal rates are necessary to enable electrochemical method to be competitive and accommodate varied feedstock compositions.

### **3.3 State of the feedstock and product**

The state (solid/liquid) of the feedstock and product has critical implications on the productivity and energy consumption of industrial processes. When treating a solid feedstock that has a limited solubility, the rate of metal extraction depends on particle size, necessitating extensive feedstock preparation. These crushing and grinding steps may be reduced when operating at a temperature where the feedstock is molten. Upon melting, mass transport and kinetic relations are drastically improved. While molten processing requires high temperatures, this does not necessarily equate to high energy consumption. The heat balance in a molten electrolytic cell operating at high current density can be efficiently managed – the Joule effect overcomes heat losses and provides self-heating. The conventional smelting-converting process requires that gangue is minimized to maintain the delicate heat balance and reduce fuel consumption, but with a self-heating cell, more gangue may be tolerated, significantly lowering the ore treatment costs. Finally, the production of a liquid product allows tapping for continuous operation. Alternatively, solid copper powder deposits require subsequent rinsing, careful handling (as they are highly reactive to water and air), and must be melted and cast for manufacturing commercial products. Overall, a process utilizing a molten feedstock and generating a liquid product would minimize temperature discontinuities and enable a highly streamlined processing route.

## **4. A future vision**

Challenges certainly exist in the development of an efficient, fully electrolytic process for copper production. As noted in previous reviews, “there is a general lack of understanding and study of the physical chemistry, thermodynamic and electrochemical properties of electrolytes” [57]. Without a fundamental understanding, progress will remain relatively empirical, on a trial-and-error basis, which is regrettable given the urgency of current societal challenges. The opportunity to synergize electrolytic metal production with the proliferation of renewable energy should be earnestly pursued. Currently, Chile is installing renewable energy at mine sites [58]. Electrolytic processes could also be deployed at such sites, if they can offer fewer process steps, smaller footprints, and lower capital costs. Electrolytic cells would be complementary to the intermittent nature of renewable energy, with the ability to switch between metal production and energy storage as necessary [59]. We hope this ambitious vision motivates innovation in electrolyte and cell design to enable the use of electrons to selectively decompose the primary constituents of chalcopyrite (copper, iron and sulfur), as well as trace elements.

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