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Abstract

Smelting is the main commercially viable route to process chalcopyrite, but alternate routes are investigated as ore bodies become more complex. Here, we propose processing chalcopyrite in an oxygen-free, sulfide regime. Using a molten sulfide electrolyte, liquid iron and liquid copper may be extracted in sequential steps while generating gaseous sulfur. Electrolysis experiments were scaled up to a 100A reactor capable of processing 2kg of material. Learnings from this scale-up process as well as a new process flow for a 100tpa demonstration will be presented. Overall, this route shows promise to supply the increasing demand for copper and byproduct metals with greater economic viability, fewer process steps and no noxious gases or oxidized by-products.

1 Introduction

From antiquity to contemporary copper smelting, oxygen has been the primary reactant to extract copper from its ore. When processing chalcopyrite, $CuFeS_2$, the most abundant copper mineral, oxygen combines with the other main constituents, Fe and S, to form iron oxide (collected in a silicate slag), and SO_2 (captured and converted to sulfuric acid in modern facilities) to yield metallic copper.[1] While this principle has supported tremendous growth in the industry over the last century, current economic and environmental challenges motivate the development of an alternative route. Copper demand is increasing[2] and a supply gap is projected within the next decade.[3] Increasingly complex ore deposits are surveyed,[4] while several open-pit operations are planning the transition to underground mining of more refractory copper ores.[5] Novel extraction routes are needed to generate greater value from

1

these lower grade ores and flexibly manage a range of impurities. Here, we present a vision to power the electrified economy through completely electrified copper production.

While alternative processing routes to smelting are available to process secondary copper -sulfides (Cu_2S) and -oxides, all are struggling to be viable for chalcopyrite, which is more refractory due to its high iron sulfide content. In designing a novel chemical metallurgy extraction pathway, electrolytic techniques are particularly attractive because electricity is utilized as the reductant to directly yield a metal product from ore.[6] High temperature electrolytic processes often exhibit competitive industrial productivity, due to high reaction rates and the ability to pass current continuously while the liquid metal product is periodically tapped.[7] The electrolytic challenge with chalcopyrite, and sulfides in general, is that they exhibit high electronic conductivity at intermediate and high temperatures. Electrons passed directly through a chalcopyrite matte conduct electronically between the electrodes, rather than participate in Faradaic reduction at the cathode and trigger oxidation at the anode. Design of a supporting electrolyte, which dissolves the mineral feedstock and reduces electronic conductivity while allowing for ionic movement, is integral to the success of electrolytic reduction.[6] In prior work, it was found that Cu_2S is highly soluble in a melt of BaS[8] and La_2S_3. The ionic bonding of this melt decreases electronic conductivity to such an extent that Faradaic reactions to decompose Cu_2S can occur.[9] The overall reaction describing the electrochemical decomposition of chalcopyrite to produce liquid copper is written below, for example at 1300ºC, with the corresponding standard state potential for decomposition of FeS to pure iron and Cu_2S to pure copper.[10]

$$CuFeS_{1.8} \rightarrow Cu(l) + Fe(s\ or\ l) + 0.9S_2(g)$$

$$E^0(Fe) = 0.36\ V, \qquad E^0(Cu) = 0.43\ V\ \ (1300ºC)$$
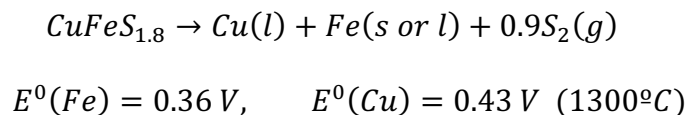
In recent work, it was shown that iron may be selectively deposited prior to copper due to differences in reaction voltage further accentuated by solution interactions with the supporting electrolyte, yielding separate metallic iron and copper products.[11] The proposed process flow to process chalcopyrite via this reaction (referred to as molten sulfide electrolysis, MSE) is shown in Figure 1. The analogous steps in the conventional smelting-converting-electro-refining route are shown below.

Molten sulfide electrolysis may substitute individual steps of the current process flow – for example, the feed from smelting may be processed in an electrolytic cell instead of a converter – or offer a completely alternative process from ore to copper product. To demonstrate feasibility and bring this process closer to industrial reality, a vision for scale-up is needed. In this paper, the design and construction of a laboratory scale 50-100A reactor, capable of handling 2kg of material (1 tpa Cu metal if operated continuously) is described. The

results for the first electrolytic extractions of iron and copper from a chalcopyrite concentrate are presented. A possible 100tpa pilot facility is proposed, based on these results.
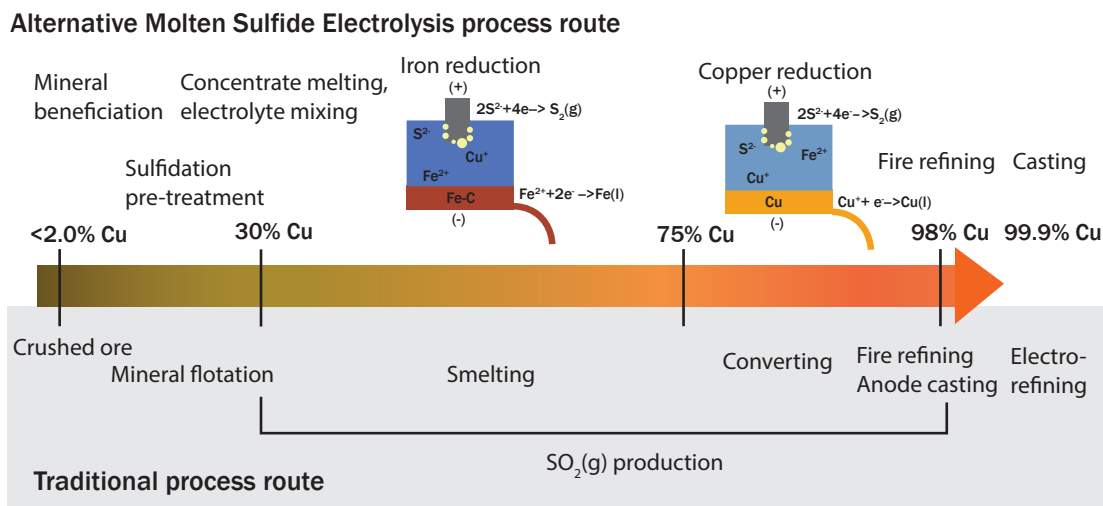

Figure 1 Proposed process flow from ore to finished product based on molten sulfide electrolysis (top) compared to the conventional smelting-converting-electrorefining route.

2 Building the 100A reactor

The main operating requirements for processing chalcopyrite as a molten sulfide are maintaining an oxygen-free atmosphere, and an operating temperature of 1,250-1,400ºC (such that both the electrolyte and copper metal product are liquid). Such an apparatus, to our knowledge, has not been built before. While not representative of the industrial version of MSE cells, we report our laboratory efforts that supported the operation of MSE up to 100A.

A sealed reactor chamber to contain the electrolytic cell was first designed. Ceramic tubes, such as alumina and mullite, are conventional choices for high temperature applications, but these materials are prone to cracking under high thermal gradients. In the event of cracking at high temperature, gaseous sulfur, evolved at the anode, may leak and react with ambient moist air to yield SO_2 and H_2S. To minimize this safety risk in our laboratory, a 304 stainless steel chamber, resistant to thermal shock and the sulfur atmosphere, was chosen. The maximum operating temperature of this chamber was approximately 1200ºC. To maintain an internal cell temperature of >1250ºC, without exceeding 1200ºC at the outer stainless steel chamber wall, two heat sources were used: an external furnace surrounding the chamber and an internal graphite heating coil, positioned below the electrolytic cell. Once the external steel wall reached 1200ºC, current was passed through the internal heating coil to increase the cell temperature to 1300ºC and was maintained during electrolysis. A PID on the external furnace ensured that the steel chamber never exceeded 1200 ºC while internal heating was active.

3

An inert atmosphere was maintained by flowing high purity argon (Airgas, ultra-high purity) through the reactor chamber and downstream gas handling system using a custom-designed gas rack. Sulfur produced at the anode is gaseous above 440ºC, and condenses as a fine powder downstream of the reactor. A gravity separator was designed to collect the sulfur powder. The output gas was neutralized through a 1M NaOH scrubber before being vented to exhaust. The reactor was located inside a plexiglass enclosure, directly connected to a building exhaust. H_2S and SO_2 gas sensors were positioned within and around the enclosure.

The electrochemical cell – the two electrodes and containment – must have appropriate chemical compatibility and electrical conductivity. Reaction-bonded magnesia-chromite refractory ('mag-chrome') (provided graciously by FRC Global and Harbison Walker) was selected due to its known compatibility with mattes and low electrical conductivity. To provide an electrical connection to the liquid metal cathode (either iron or copper), the base of the cell was utilized. Magnesia-graphite composite ('mag-carbon') (provided by FRC Global and Cera Techno Co., Ltd) was chosen as the base material, because it is both conductive and inert with liquid cast iron and copper. Graphite was used for the anode (EDM grade, GraphiteStore), which is inert during sulfur evolution in molten sulfide electrolysis.[9] All electrical connections inside the reactor, including to the internal heater and the electrolytic cell, were made using molybdenum rod, sheathed in alumina tubes. Figure 2 provides a schematic of the reactor and a photograph of the entire laboratory set up.
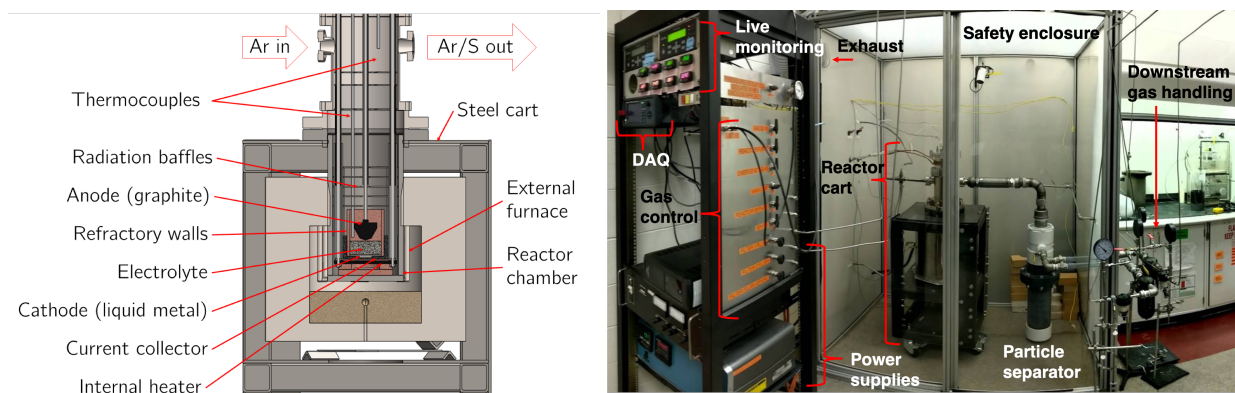

Figure 2 Schematic of the 50-100A reactor (left) and photograph of the full reactor set-up with process control and monitoring and gas handling systems (right).

3 Iron and copper extraction in the 50A reactor

3.1 In-house preparation of concentrate

Chalcopyrite concentrate, graciously provided by Freeport McMoRan, was used for both electrolysis trials. The original concentrate contained moisture (lost on ignition analysis indicated ~5wt% moisture), gangue oxides, and sulfates. To process chalcopyrite as a sulfide in

a controllable manner, oxygen and oxide phases were removed before mixing with the supporting electrolyte. Oxide and sulfide phases are typically immiscible, so the silicate oxide phase was removed by phase separation upon heating above the melting point of chalcopyrite. An induction heating system with a sealed quartz tube was used to melt, then quench the concentrate in a flowing Ar atmosphere. The glassy black silicate slag and the sulfide matte can be seen in Figure 3, which were easily physically separated. The elemental analysis of the sulfide matte, measured by ICP-MS, following this separation is also provided in Figure 3.
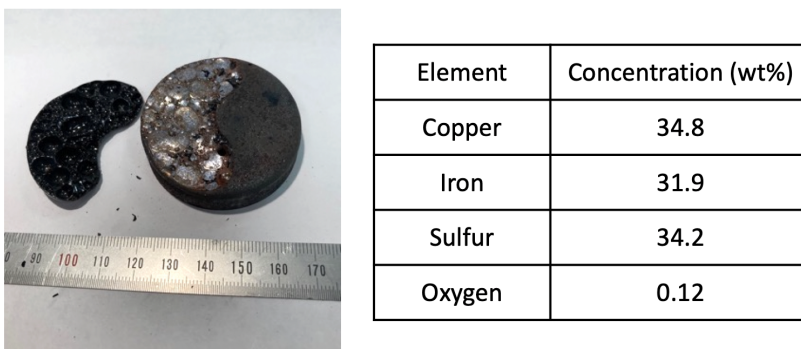

Element	Concentration (wt%)
Copper	34.8
Iron	31.9
Sulfur	34.2
Oxygen	0.12

Figure 3 Oxide slag phase separated from the sulfide matte after induction melting above 1,100ºC (left). Elemental composition of the sulfide matte after phase separation, measured by ICP-MS (right).

If the concentrate contains significant anionic impurities, such as As, Se, or Te, a sulfidation pre-treatment may be performed (see [12] in this volume) before, or in conjunction with pre-melting. The concentrate used in these experiments contained only minor impurities, and thus did not require further treatment. After oxide separation, the matte was crushed and mixed with BaS and La_2S_3, which had been synthesized from $BaSO_4$ and La_2O_3 precursors in-house [13], and melted in the induction furnace with a similar procedure described above, but to a higher maximum power output.

3.2 Iron extraction

Iron deposits preferentially from a chalcopyrite concentrate. Thus, iron must be removed first, until electrolysis of the iron-depleted electrolyte leads to liquid copper production. The feasibility of iron extraction was investigated with an electrolyte initially containing $CuFeS_2$ (18wt%) and a cast iron cathode (459.5g, 4.3wt% C). The total mass of the electrolyte (694.3g) allowed for an anode-cathode distance of approximately 3.5cm.

The temperature profile of the experiment and heating output from the furnace, internal heater and Joule heating from the electrolyte is shown in Figure 4 (top). The internal temperature of the electrolyte was estimated at ~1300ºC, sufficient to melt the electrolyte. Galvanostatic electrolysis was run at 40A, with a steady cell voltage of ~3V. After 20 minutes, the current was temporarily stepped up to a maximum of 120A, with a corresponding increase

in cell voltage. The electrolysis signals are shown in Figure 4 (bottom). In total, electrolysis was run for 60 minutes with 2 mol e$^-$ transferred.
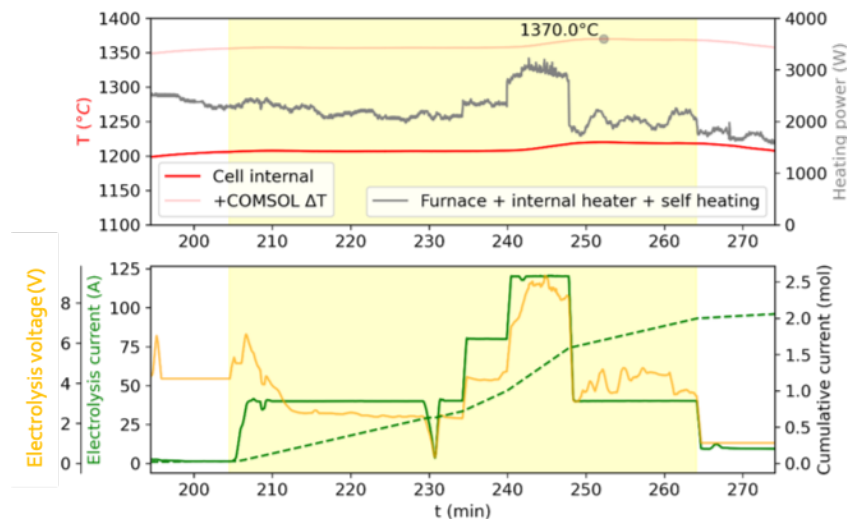

Figure 4 Measured temperature by thermocouple adjacent to cell and estimated cell internal temperature using Multiphysics (COMSOL) heat model. Heating power (sum of external furnace, internal heater and Joule heating) plotted in gray (top). Electrolysis signals: cell voltage (V, plotted in green solid line), applied current (A, plotted in solid yellow), and cumulative current (mol, plotted in dotted green) throughout the iron extraction trial (bottom).

After electrolysis, the cell was carefully deconstructed. A small amount of iron (~15g) had leaked from the cell to the bottom of the reactor chamber, likely due to mechanical displacement of refractory panels during cooling. Post-experiment observation shows that the electrolyte fully melted, and the anode made a clear indentation, as shown in Figure 5. Half of the cell was mounted in epoxy, ground and polished for metallography.

Figure 5 Images of the electrolysis cell following the iron extraction experiment.

3.3 Copper extraction

Previous work showed that copper deposition occurs once the electrolyte is enriched with copper sulfide, when the copper to iron molar ratio is 4:1.[11] Therefore, the electrolyte was

synthesized with a mix of chalcopyrite and Cu_2S (99.5% metals basis, Alfa Aesar), which together comprised 16wt% of the total electrolyte (768.6g, remainder BaS and La_2S_3). Copper (459.5g, 110 grade, McMaster-Carr) was placed in the bottom of the cell for the cathode. Galvanostatic electrolysis was conducted with a cathodic current density of ~0.8A/cm^2. The cell voltage was steady at 4V at the start of electrolysis, but increased to 6V over the course of the experiment (Figure 6).
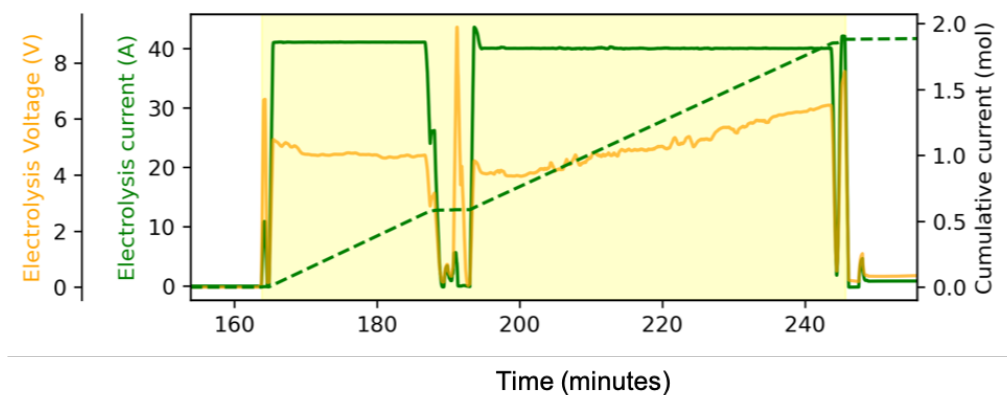

Figure 6 Electrolysis signals: cell voltage (V, plotted in solid yellow line), applied current (A, plotted in solid green), and cumulative current (mol, plotted in dotted green) throughout the copper extraction trial.

Upon cooling to room temperature, the cell was removed from the chamber. About 50 grams of solidified copper was recovered at the bottom of the chamber, again likely due to contraction of the refractory walls upon cooling. Leakage of the electrolyte was not observed. The cathode and electrolyte were similarly prepared for metallography (Figure 7). A representative sample of the electrolyte was ground with an alumina mortar and pestle and sieved through a series of meshes of increasing mesh size. Samples from each sieved portion were placed on a microscope slide and the metal content in the electrolyte was determined with a polarized filter. The weight percent of copper was estimated from the proportion of cross-sectional area of metal to electrolyte on the microscope slide.

4 Electrolysis results

In both the copper and iron experiments, significant metallic dispersion was found in the electrolyte, near the cathode, making the full recovery of the metal product difficult. Images of the cross-section from the iron (left) and copper (right) extraction experiments with metallic droplets ~1-50μm diameter can be seen in Figure 8. To determine the quantity of metal produced electrolytically, the composition of the electrolyte was measured using SEM-EDS to estimate depletion of the cation (Fe^{2+} and Cu^{1+}) species. Readings were taken at multiple points along the cross-section, taking care to measure the electrolyte in areas free from metallic particles. Gradually, the content of iron and copper increased towards the anode, indicating mass transfer limitations in the electrolyte.
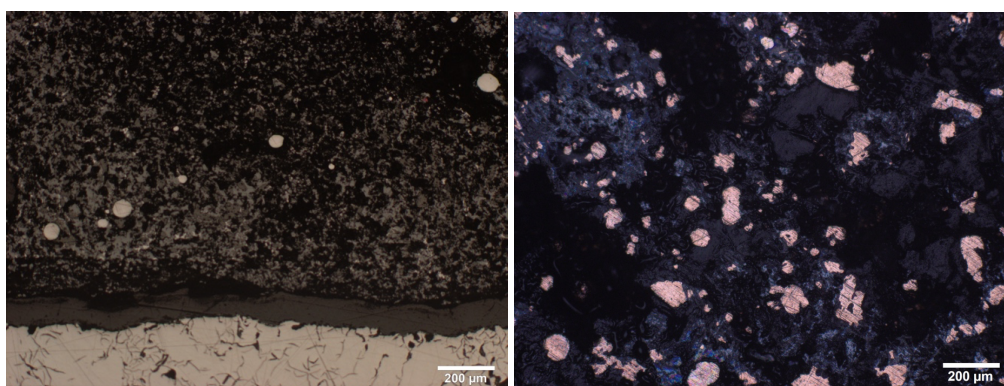

Figure 8 Images of the cross-section from the iron extraction (left) and copper extraction (right) experiments near the electrolyte – cathode interface, showing metallic dispersion.

In both the iron and copper extraction experiments, our conservative estimate based on the electrolyte depletion of iron and copper species suggest a cathodic Faradaic efficiency of about 40%. This efficiency is lower than previous work. Smaller scale (0.3A and 7A) experiments indicated a Faradaic efficiency of about 70%. [11,14]

One explanation of this observed decrease in efficiency is the concentration of electro-active species ($CuFeS_2$ and Cu_2S), which has a direct effect on the electronic conductivity of electrolyte (and the proportion of electrons conducted through the electrolyte without participating in Faradaic reactions). In these experiments, the proportion of electro-active species was increased to 16-20wt%, compared to experiments that yielded 70% faradaic efficiency (10wt% $CuFeS_2$). This shift in composition was necessary to lower the electrolyte melting point and achieve a fully molten electrolyte within the heating limitations of the reactor. The operating temperature of the stainless steel reactor chamber limited power output

of the external furnace, and the power of the internal heater was also constrained to avoid carbothermic reduction of the mag-carbon base. Heat management issues can be resolved with larger scale reactors, with one example described in Section 5 below.

The observed dispersion of the metallic cathode is likely a consequence of current distribution and surface tension effects, which are typically easier to manage in larger surface-to-volume cells. Operating with slightly higher operating temperature and greater anode-cathode distance was found to improve metal deposition in our trials. Given the batch operation in this reactor, there is high uncertainty in the efficiency of metal production. Ideally, the metallic product would be tapped periodically to prevent back-reaction with sulfur gas.

The composition of both cathodes measured by ICP can be seen in Table 1. In the copper metal, iron, sulfur and oxygen are the main impurities. This composition is similar to high-grade copper scrap, which is reported to be treatable in refining furnaces to achieve sufficient oxygen and sulfur concentrations by performing fire refining oxidation, followed by a reduction with natural gas or other hydrocarbons.[15] The slightly elevated concentration of iron can be readily treated in fire refining.[16] Sulfidation pre-treatments and the electro-deposition of electro-positive impurities in the iron extraction step [10,17] are new opportunities to recover, prior to the copper production step, a wide range of valuable and undesirable impurities.

Iron is a co-product of the electrolysis of $CuFeS_2$, produced without CO_2 emissions if C-free electricity is used. The iron metal will need to be refined to separate copper at ~2wt% and provide a product valuable to the steel industry. Recovering metallic iron without the environmental and GHG impact related to iron ore mining or iron smelting could provide a significant revenue stream and an opportunity to invest in refining processes to remove copper, and develop synergies with end-of-life steel scrap.[18]

Table 1 Composition of the iron and copper solidified cathodes following electrolysis, measured by ICP. Note: a small amount of Ba and La was detected in the copper sample due to occlusion of electrolyte, which was excluded from the composition below.

Element	wt% in iron cathode	wt% in copper cathode
Copper	1.9	98.9
Carbon	3.7	0
Sulfur	0.26	0.06
Oxygen	0.06	0.11
Iron	94.08	0.9

5 Toward a 100tpa facility

The scale-up process to 50-100A confirmed the feasibility of molten sulfide electrolysis to extract iron and copper from chalcopyrite. To further explore the industrial feasibility of this process, a 100tpa pilot is envisioned, the notional drawing of which is shown in Figure 9. The rotary kiln and pre-melting unit are proposed to investigate the impurity removal from the concentrate prior to entering the electrolysis reactor. It is indeed established that arsenic, antimony, tellurium, and selenium, and possibly a handful of other elements [12] can effectively be removed prior to smelting. The proposed reactor will support steady-state production of large quantities (~300 kg/day iron or ~700kg/day copper) of metal for further evaluation of the faradaic efficiency and the characterization of the metal quality. It will support investigation of the fate of more electro-positive (i.e. Ag, Au) and electro-negative elements (i.e. Se, Te) in the cathode and anode products, which are in very low concentration in the mineral feedstock.
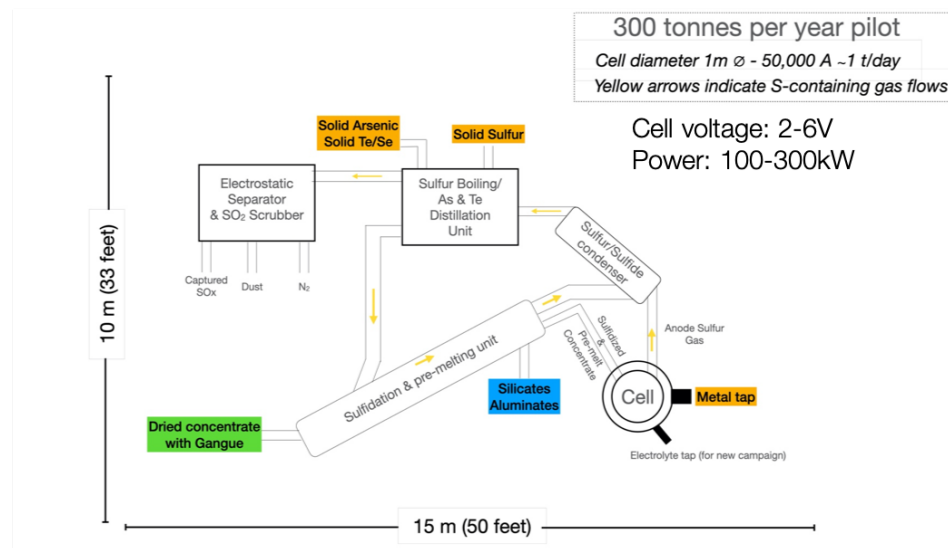

Figure 9 Notional sketch of the 100tpa pilot facility showing the sulfidation and pre-melting rotary kiln, the electrolysis cell with metal tapping, the condenser for gaseous sulfur, the distillation unit to recover solid arsenic and tellurium, and the scrubber for final treatment of the gas stream.

Utilizing the inherent resistance of the electrolyte (known as Joule heating) for a self-heating cell provides a great operational advantage. The proposed cell can run at an amperage of 50,000A, with characteristic diameter of 1m. The maximum current density for the 100tpa cell would be 6.4A/cm^2, though nominal operations are in the range of 0.5 to 2A/cm^2. A Multiphysics COMSOL simulation was developed and validated with probe temperature readings with the 100A reactor (agreement within 5ºC), to simulate the heating requirements for the 100tpa cell. The electrical resistance of the electrolyte measured at various anode-cathode distances was used to calculate heat generated over a range of cell voltages. The radiative, conductive, and convective (estimated with scaling laws to introduce a velocity field within the argon atmosphere) heat losses were estimated and balanced with the heat

generated. The dimensions, power and cell voltage proposed in Figure 9 provide excess heat in the cell to meet the self-heating requirement.

6 Conclusions

Molten sulfide electrolysis is proposed to pursue a unique processing space, with several objectives:

- High value by-product streams: iron may be tapped as liquid cast iron, rather than a fayalite slag, and sulfur is recovered in condensed, elemental form.
- Heat is efficiently provided by electricity. The supporting electrolyte dictates the heat needed for extraction, and is therefore independent of the iron to copper ratio in the feed, in contrast to conventional smelters.
- A new approach to flexibly manage impurities: conventionally, valuable cationic elements (metals) are recovered at low current densities downstream in aqueous electrorefining. In molten sulfide electrolysis, the difference in deposition potential can be exploited upstream, as shown herein for iron vs copper, and previously for molybdenum and rhenium vs copper,[17] or silver vs copper.[19]
- Oxides (slag) and sulfides (matte) phase-separate with limited copper losses in absence of oxygen. Gangue material may be skimmed off upon melting, to collect in condensed form, a new opportunity to handle a variety of chalcopyrite feedstock.
- Each process step is completely electrified. If powered using renewable energy sources, the process is decoupled from CO_2 emissions.
- Fire refining can treat the copper product, with the potential to by-pass electrorefining. A finished product may be cast in the same plant.
- No direct water consumption is required, such that facilities may be located closer to copper mines, typically in drier climates with abundant solar energy.
- Streamlined process flow with fewer unit operations for oxygen and by-product handling.

In this paper, a 50-100A reactor was constructed and the successful extraction of iron and copper from chalcopyrite concentrate was demonstrated. The essential parameters to achieve high efficiency were identified in this effort, in particular the need to achieve robust heat management, and ideally tap the liquid product. Those are very dependent on the engineering choices at the laboratory scale and may be resolved at a larger scale. Overall, the extraction process has scaled successfully from previous work (at the 0.3A and 7A scales), and pilot scale implementation is recommended to further advance industrial reality.

Acknowledgements

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