

Research paper

Clean and efficient extraction of copper ions and deposition as metal

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Abstract

A simple, clean and efficient one-pot process is offered as an alternative to the conventional complex processing presently used to extract copper ions from copper containing materials, like copper concentrate or slag, and to form copper metal. The alternative process uses a eutectic molten salt of potassium chloride, sodium chloride and zinc chloride as the reaction fluid which is recyclable, low in cost, environmentally benign, low melting (melting point 204°), high boiling (vapor pressure is only a few psi at 800°) and chemically, thermally and physically stable. The metal completely dissolves out of copper concentrate or slag in the aerobic eutectic molten chloride salt in a graphite or glassy carbon pot, which serves as a cathode, with a graphite anode, to reduce the metal ions to metal which sinks to the bottom of the graphite pot. The total efficiency for extraction and deposition is virtually 100% as determined by elemental and gravimetric analyses.

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1. Introduction

Copper, silver and gold are valuable metals prized for their desirable properties such as ductility, strength, electrical conductivity as well as stability and durability. Accordingly, these materials are used when a stable metal is required for commercial applications such as in the electronics, plumbing and jewelry industries. The reason for the chemical stability of copper, silver and gold is similar; it is due to the high reduction potential of the ions of these metals. Because these valuable metals have high reduction potentials, they have similar processing. The conventional processing that is presently used to extract metal ion from ore involves toxic and aggressive chemical reagents in water, followed by application of electrical energy to electrodes in aqueous solution of complex copper silver or gold ions, which decomposes the metal ion complexes leading to the deposition of the desired metal [1]. The conventional processing is expensive and environmentally invasive, but is tolerated because of the value

of these metals [2–4]. These metals are often found in the same ore. Typically, gold is the least abundant; silver is more abundant and copper is the most abundant naturally occurring species. The conventional processing is used to produce copper on a large scale, which leads to the accumulation of a substantial amount of toxic materials, which time to time is dumped into the environment (soil and ground water) due to accidents, such as flooding from violent weather. A new approach for extracting copper from copper concentrates (20–30% Cu) is presented here. This new approach uses molten salts as a medium for metal extraction instead of the conventional pyro- or hydro- or pyro–hydro-extraction processes. The new molten salt process for metallic copper production uses unreactive, non-toxic neutral chloride salts as the processing fluid, so it virtually eliminates the chance of toxic emissions during the processing of copper concentrates to copper metal. The processing salt is specific eutectic molten salt discussed used here to illustrate the new processing is a mixture of potassium chloride, sodium chloride and zinc chloride. This particular reaction fluid is environmentally benign, recyclable and so low in cost (<\$1 per kilogram), as well as low melting (melting point 204°), high boiling (800°) and chemically, thermally and physically stable, which are properties the molten salt needs to have to be a practical lixiviant and plating electrolyte.

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2. Experimental

The reagents used were sodium chloride (NaCl), potassium chloride (KCl), zinc chloride (ZnCl_2), silver chloride, 99.99% silver wire (Alfa Aesar, Premion grade), and cupric chloride from Sigma Aldrich (reagent grade). Concentrated copper ore and copper slag samples were provided by Mexicana de Cobre. The apparatus used were a heating mantle (Glas Col), 99.9% graphite crucibles (Wang Xueping, Singapore), glassy carbon crucibles (SPI Supplies/Structure Probe, Inc., West Chester, PA), graphite rods (McMaster Carr), power supply (Circuit Specialists, Tempe, AZ), BioLogic potentiostat (Oak Ridge, TN). A home made reference electrode was made of silver wire in a solution of silver chloride in potassium chloride in a quartz vessel with a zirconia rod sealed into the quartz on the side of the vessel immersed the molten salt to make a tortuous ion flow path, and this Ag/AgCl electrode (SSE) was found to have a potential of 0.2 V versus NHE, details of the reference electrode are beyond the scope of this paper and will be discussed elsewhere [5]. The ternary molten salt mixture used in “one-pot” as lixiviant and plating electrolyte had a composition of 13.4 mol% NaCl—33.7% KCl—52.9% ZnCl_2 with a melting point (T_m) of 204° [6,7]. This extraction and plating cell was a conductive carbon crucible as a cathode filled with molten salt and copper concentrate with a graphite rod inserted as anode. An electrical power supply was used to impose a voltage between the anode rod and cathode crucible with the cathode biased negative. A minimum potential difference of about 2.0 V was applied between the anode (graphite rods) and the cathode (graphite crucible) based on thermodynamic calculations and was adjusted to give desired current levels based on cell geometry (electrode area and separation). Since copper is the densest material in the melt, copper sinks and collects on the bottom of the graphite crucible (cathode). For the purpose of analysis, the copper electrodeposited from the molten salt (above) was collected from the bottom of the graphite crucible and washed several times with deionized water (DI water) to remove all salt and soluble impurities, weighed and then sent for elemental analysis. Elemental analyses were performed by Galbraith laboratories, Knoxville, TN, USA.

3. Results and discussion

The copper extraction and metal formation is a “one-pot” process using a molten eutectic mixture of NaCl, KCl and ZnCl_2 as both the lixiviant (to dissolve copper and copper oxide from copper concentrate ore or slag) and as an ionically conductive electrolyte medium for electrodeposition of copper ions as copper metal. Several eutectic molten halide salt mixtures form when NaCl, KCl and ZnCl_2 are in an approximate ratio of 1 mol of NaCl, 1 mol of KCl and 1 mol ZnCl_2 ; mixed and heated to melt at around 200°. The salt is open to the atmosphere when used because it has low-vapor pressure (~1 psig at 500°) and oxygen and water in air assist the metal extraction. The particular ternary mixture used here had a composition of 13.4 mol% NaCl—33.7% KCl—52.9% ZnCl_2 with a melting point (T_m) of 204° and was used at temperatures in the range between 400 and 500° while extracting and

electroplating copper. Copper metal was electroplated from the copper that dissolved in the molten salt from the copper concentrate, slag or authentic sample (like copper chloride).

3.1. Electrodeposition of copper metal from copper(II)-chloride in molten salt

Cupric chloride was added to the molten NaCl—KCl— ZnCl_2 eutectic salt and then attempts made to electrodeposit copper metal. This was done a first step to check if copper ions dissolve in molten NaCl—KCl— ZnCl_2 eutectic salt and if this molten salt mixture can be used as an electrolyte for reductive electrodeposition of these ions as copper metal. A precisely weighed amount (3 g) of copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) was added to the molten NaCl—KCl— ZnCl_2 salt in a quartz crucible (similar to Fig. 1). The copper chloride dihydrate was seen to readily dissolve in the molten salt. The open circuit voltage (OCV) between a copper metal wire electrode in the NaCl—KCl— ZnCl_2 salt with CuCl_2 was measured versus a silver/silver chloride reference electrode (SSE) immersed in the same salt mixture at 350°. The OCV between the copper wire and the SSE reference was initially found to be -0.14 V, but slowly drifted to more positive values and was about -0.12 V after several minutes. Therefore, the potential of the Cu/Cu²⁺ couple in the molten salt mixture was estimated to be about -0.12 V vs. SSE.

Next, two graphite rods, serving as anode and cathode, with a SSE reference electrode were put in the molten NaCl—KCl— ZnCl_2 salt with the 3 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in the quartz crucible which was heated using a resistive heating tape, as shown in Fig. 1. Since the OCV for a copper wire in cupric chloride salt was found to be around -0.12 V vs. SSE, a constant potential of -0.5 V vs. SSE was applied to the working graphite rod (cathode), and a cell current of

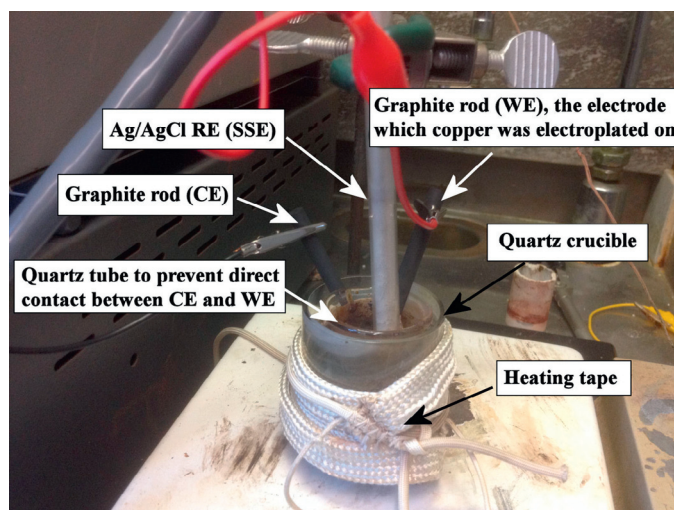


Fig. 1. Cell for reduction of cupric chloride in molten NaCl—KCl— ZnCl_2 salt in a quartz vessel in air. Graphite working electrode (cathode), graphite counter electrode, silver/silver chloride reference electrode (SSE). Cathode potential: -0.5 V vs. SSE.

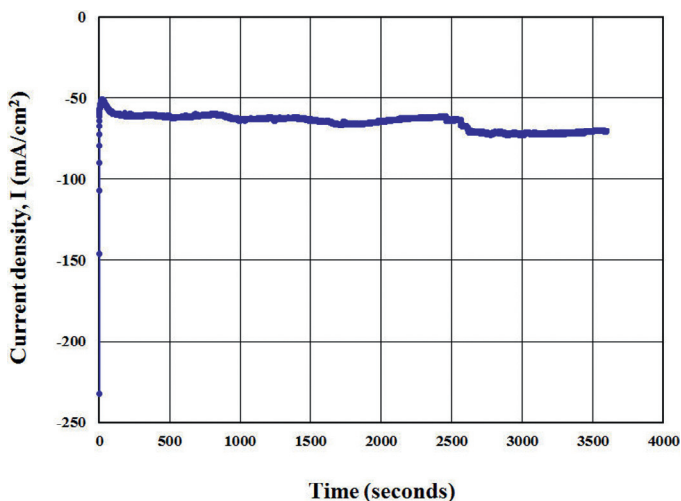


Fig. 2. Current density as a function of time as copper metal is electrodeposited from molten NaCl—KCl—ZnCl₂ salt containing 3 g added CuCl₂ · 2H₂O at 300°. WE: graphite. CE: graphite. RE: SSE. Applied potential to WE was -0.5 V vs. Ag/AgCl.

about 60 mA/cm² developed between the graphite working (cathodic) and counter (anodic) electrodes. The overpotential is approximately 0.38 V (0.5–0.12 V). At such high reducing overpotentials, the current is expected to be limited by mass transport of copper ions to the working electrode, which is consistent with the constant current observed in the plot of I vs. t shown in Fig. 2. Since the working graphite electrode was the negative pole, it was the cathode, and – as expected – copper metal was seen to electroplate onto the working graphite electrode as current passed in the cell. The graphite counter electrode was an anode so its potential was more positive than the working graphite electrode serving as a cathode.

Next, an attempt was made to make a practical cell design for the electrodeposition of copper metal with a simple power supply. A graphite rod electrode was immersed into a new mixture of copper salt (3 g of CuCl₂ · 2H₂O) and molten NaCl—KCl—ZnCl₂ salt in a graphite crucible. An ordinary power supply was used to apply a constant voltage (2.0 V) between the graphite crucible cathode (negative pole) and the graphite rod anode (positive pole).

When the voltage was applied, a current between 40 and 60 mA/cm² developed. The voltage was applied for 2 h at temperatures ranging from 250° to 300°, and copper metal was electrodeposited at the bottom of the graphite crucible. The measured amount of electrodeposited copper was 1.09 g, which indicates that the conversion of copper ions to copper metal was effectively 100%, within experimental error.

Fig. 3 shows the experimental setup for the plating of copper metal from copper chloride in molten Na—K—Zn chloride salt. Fig. 4 shows the plated metallic copper formed from this experiment. The main conclusion from this experiment is that copper metal can be quantitatively extracted from ionic copper compounds when using the molten chloride salts as a reaction medium (electrolyte) and the cell design of Fig. 3.

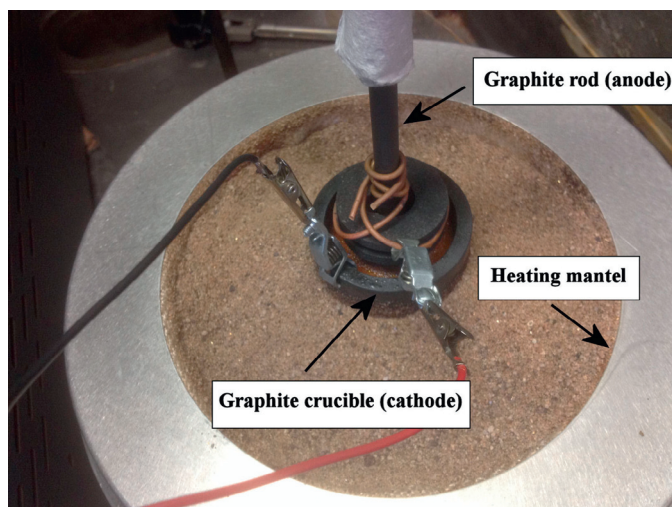


Fig. 3. Setup for electroplating of copper metal from copper chloride in molten chloride salts.

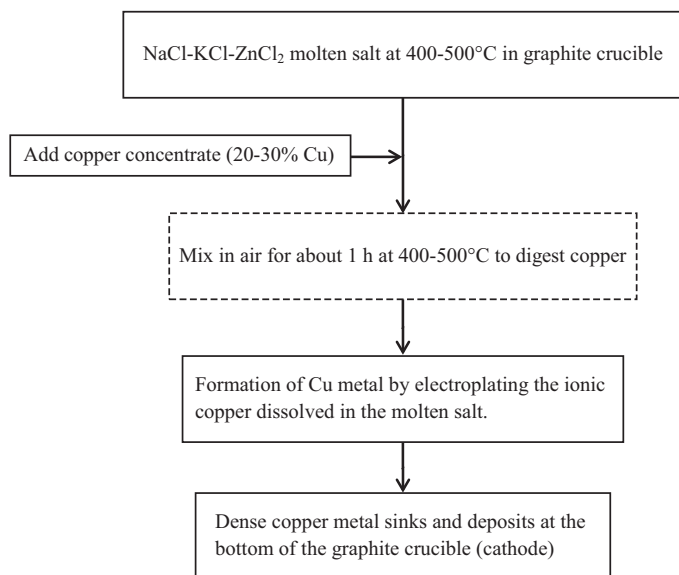


Fig. 4. Copper metal at the bottom of a conducting carbon crucible serving as a cathode. The copper was electrodeposited from a molten NaCl—KCl—ZnCl₂ salt containing pure CuCl₂ · 2H₂O.

3.2. Extraction of copper from copper concentrate using molten metal halide salts

After verifying the feasibility of the new approach for depositing copper metal from a molten NaCl—KCl—ZnCl₂ salt with dissolved CuCl₂ ions, the next step was to see if copper could be extracted from copper rich earths, and if the extracted copper could be plated as metallic copper. The copper rich earths studied here were authentic copper concentrate and copper slag, obtained from Mexicana de Cobre.

Success in this experiment is considered a proof of concept for a new “green” technology in which copper is extracted from copper concentrate (or slag) using molten salt and electrodepositing pure copper metal from this molten salt. A flow chart showing the essential steps to extract and deposit copper is given in Scheme 1.



Scheme 1. Simplified flowchart showing essential steps during copper extraction from copper concentrate in molten salt.

This new process uses chloride salts (NaCl , KCl and ZnCl_2) which are inexpensive, environmentally-benign chemicals compared to the highly toxic and hazardous chemicals, like cyanides and sulfuric acid, presently used in the conventional process for copper extraction. The extent of conversion in new molten salt process was found to be virtually 100% (vide infra), as previously confirmed by using the pure chemical $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Fig. 4). Essentially, copper extraction occurs from copper earths, because oxygen (or protons on water) dissolved in the salt oxidizes any metallic compounds in the melt and the chloride in the salts break down any oxides thereby dissolving metallic copper and copper oxide found in ore or slag. Electrodeposition of copper metal occurs, because the molten NaCl-KCl-ZnCl_2 salt is highly ionically conductive, allowing reduction of dissolved copper ions to copper metal, when a graphite anode is inserted in the salt and a proper external voltage is applied between this anode and the graphite crucible, which acts as the cathode. The two steps (copper extraction and deposition) are done in the same graphite crucible, which gives a simple “one-pot” reactor for processing copper rich earths to copper metal. Reaching this result required some optimizations.

The same setup (Fig. 3) and conditions optimized for electrodepositing metallic copper (Fig. 4) from molten salt loaded with cupric chloride were used in the first attempt to extract copper from a real copper containing mining sample and to electrodeposit the extract copper as copper metal. However, when real copper concentrate sample was used, it was seen that further optimization was required. For example, during the processing of a copper concentrate sample, copper was deposited on the crucible wall and bottom, and even into the wall of porous graphite, as can be seen by inspecting Fig. 5. Furthermore, the appearance of the electrodeposited copper was dull suggesting the presence of impurities.

Changes in the copper extraction (time, temperature) and electrodeposition conditions (potential, temperature, time) were

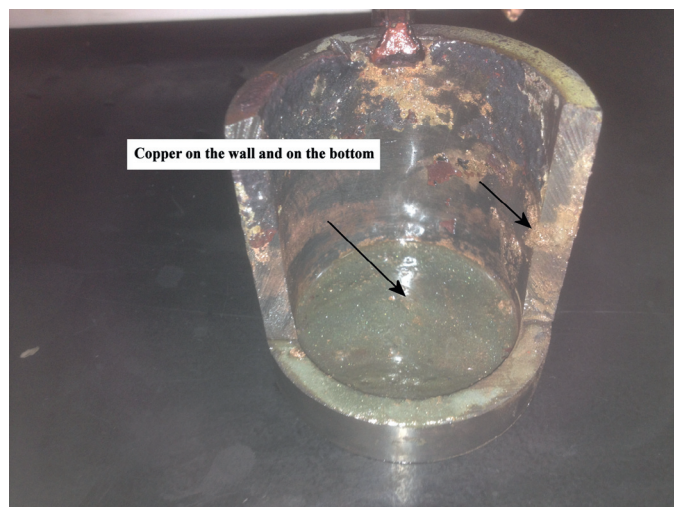


Fig. 5. Copper plated on the side wall and bottom of a graphite crucible cathode.

done to optimize conditions of the processing of the copper concentrate in terms of the experimentally determined percent of copper metal formed versus the copper assayed in the copper rich earth (concentrate or slag). The goal was to change conditions and raising the conversion efficiency (which is the extent copper metal recovered from the copper concentrate ore or slag) which was the criterion used to determine that the change in a condition was an improvement.

After much trial and error, a suitable cell was found for processing copper extraction and deposition of metallic copper with high efficiency. This cell was changed from pure (but porous) graphite to a non-porous glassy conducting carbon crucible to hold the molten NaCl-KCl-ZnCl_2 salt with copper rich earth. The temperature of molten salt mixture was at least 400° to lower viscosity of the melt. Stirring was found essential. A setup with these features is shown in Fig. 6.

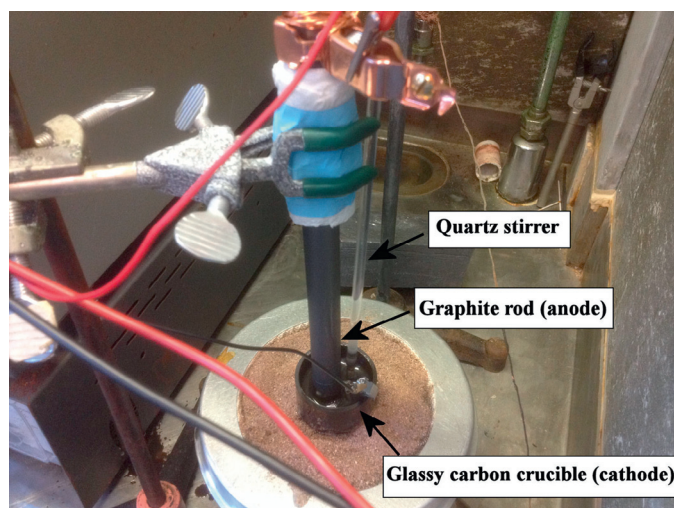


Fig. 6. Setup for electroplating copper from copper concentrate dissolved in molten NaCl-KCl-ZnCl_2 salt.



Fig. 7. Deposited copper from copper concentrate dissolved in molten NaCl–KCl–ZnCl₂ salt. The copper was electroplated at 3.5 V at 450° for 4h.

After processing a copper rich earth (Cu concentrate or slag), copper was not in the wall of the crucible but could be seen clearly deposited on both the wall and the bottom of the crucible as can be seen by inspecting Fig. 7.

Fig. 8 shows the copper formed after process optimization. This copper was formed using the glassy carbon crucible as a cathode and was collected and transferred to a glass beaker then washed with DI water. The copper was plated at high overpotential and so other elements were co-plated with copper during the extraction and plating process. Fig. 9 shows the recovered powder containing copper and other co-plated metals.

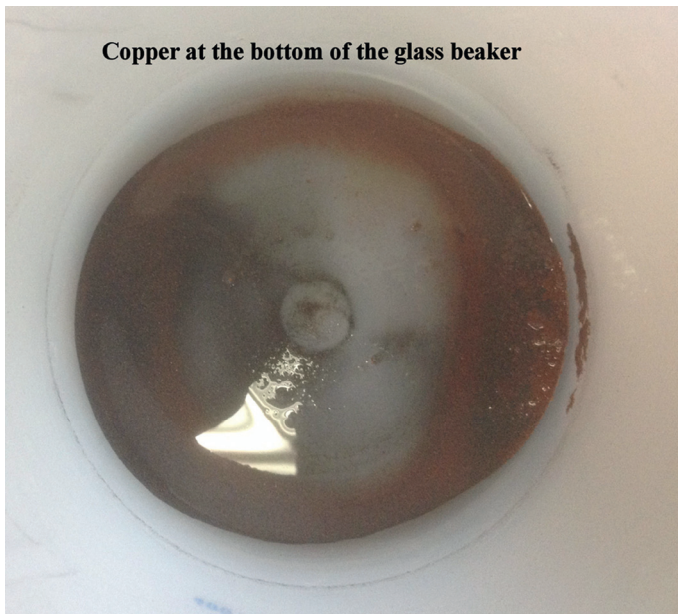


Fig. 8. Cu formed after process optimization.



Fig. 9. Copper plus other co-plated elements.

In order to determine the extent the copper extracted from the copper rich sample, unprocessed sample materials were sent to a third party (Galbraith Laboratories, Inc., TN, USA) for chemical analysis. The analysis was to provide the percent of copper in the as received unprocessed sample (Cu concentrate) and of the material that was collected after processing (the extracted material). Three replicate samples of copper concentrate and extracted material were analyzed. The extent of copper conversion was estimated. Table 1 shows the results of the analyses.

As shown in Table 1, the experimentally determined extent of conversion of copper from the copper ore is **98.36%**.

3.3. Extraction of copper from copper slag using metal halide salts

Copper metal was extracted from a copper containing slag using the same optimized procedure for extracting copper

Table 1
Assay of copper concentrate ore and corresponding electrodeposited copper.

Sample	Amount used in analysis (mg)	% Cu
Cu concentrate sample	153.42	19.9
	158.39	21.7
	152.77	20.8
Average (sum/3)	154.86	20.8
Normalization to 1 g (1000 mg)	Then each 1 g (1000 mg) of Cu concentrate contains 208 mg of Cu	
Extracted material (Cu + other co-plated elements)	156.33	19.2
	152.13	19.5
	155.76	22.7
Average (sum/3)	154.74	20.46
Normalization to 1 g (1000 mg)	Then each 1 g (1000 mg) of extracted material contains 204.6 mg of Cu	
Extent of conversion	Extracted Cu weight in 1 g/Cu weight in 1 g of Cu concentrate = $204.6/208 \times 100 = 98.36\%$	

Table 2
Analysis of the extracted material from the slag.

Sample	Amount used (mg)	% Cu
Cu slag extract	151.58	1.61
	152.48	2.09
	151.21	2.14
Average (sum/3)	151.75	1.94
Normalization to 1 g (1000 mg)	Then each 1 g of the extracted material contains 19.4 mg Cu	

metal from Cu concentrate. The starting amount of slag was 50 g. After the optimized dissolution and electro-deposition procedure was performed, 1.3 g of metallic material was extracted from the slag. This metallic material (1.3 g) was sent to the Galbraith Laboratories for analysis. Table 2 shows the percentage of copper (% Cu) Galbraith found to be in the 3 replicate samples taken from the 1.3 g of metallic material extracted from the 50 g of the slag. The balance of the replicate samples is others metals like, mainly, iron and possibly traces of silver, gold, etc.

From the result in Table 2, it is clear that in the 1.3 g of metallic metals extracted from 50 g of slag, there are 25.22 mg of Cu. So for each kilogram of slag, a half of a gram of Cu can be recovered, which is considered a significant amount with considerable economic value, considering the millions of tons of slag per year which are generated from conventional copper extraction processes [1].

4. Conclusions

This work is a positive proof-of-concept that an alternative process to the conventional process can be used for extracting copper from a copper-rich concentrate or slag and for depositing the extracted copper as copper metal. This new process is done in one-pot using a eutectic molten chloride salt, i.e., molten NaCl—KCl—ZnCl₂ salt, as both the copper extracting fluid (**lixiviant**) and the electrolyte for electrodeposition of copper metal. The NaCl—KCl—ZnCl₂ salt is environmentally benign since it is made of non-toxic elements and emits no toxic vapors.

The copper completely dissolves from the concentrate or slag, when these are added to the aerobic eutectic molten chloride salt contained in a graphite or glassy carbon crucible. After the copper concentrate or slag is digested, a graphite rod is inserted in the molten salt mixture to serve as an anode. A power supply is connected to the graphite rod and the graphite crucible, which serves as the cathode, and then the copper ions in the molten salt are reduced and deposited as copper metal,

which sinks to the bottom of the graphite crucible, since copper is much denser than the salt. On a large scale, opening a valve at the bottom of a production crucible would allow harvesting of the copper metal product by simply draining the copper out of crucible. The total efficiency for extraction and deposition is virtually 100% as determined by elemental and gravimetric analyses.

Electrodepositing the copper from the molten NaCl—KCl—ZnCl₂ salt essentially regenerates the molten NaCl—KCl—ZnCl₂ salt. Since the NaCl—KCl—ZnCl₂ salt can be regenerated, the new processing is not just environmentally benign but also can be both sustainable and economical. This processing is well suited to processing earthen materials rich in silver and gold as well as copper and mixtures of all three metals.

Although the results are quite new, there seems to be no reason that the conventional hydrometallurgical processing cannot be replaced by the new molten salt processing which at this time appears to be a more economic, efficient, sustainable and environmentally benign alternative.

Acknowledgement

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