

Research paper

# Clean and efficient extraction of copper ions and deposition as metal

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Received 30 May 2015; received in revised form 21 June 2015; accepted 22 June 2015

Available online 17 July 2015

## 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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**Keywords:** Copper; Extraction; Deposition; Refining

## 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 ( $\text{ZnCl}_2$ ), 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%  $\text{ZnCl}_2$  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  $\text{ZnCl}_2$  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  $\text{ZnCl}_2$  are in an approximate ratio of 1 mol of NaCl, 1 mol of KCl and 1 mol  $\text{ZnCl}_2$ ; 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%  $\text{ZnCl}_2$  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— $\text{ZnCl}_2$  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— $\text{ZnCl}_2$  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— $\text{ZnCl}_2$  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— $\text{ZnCl}_2$  salt with  $\text{CuCl}_2$  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/Cu<sup>2+</sup> 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— $\text{ZnCl}_2$  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

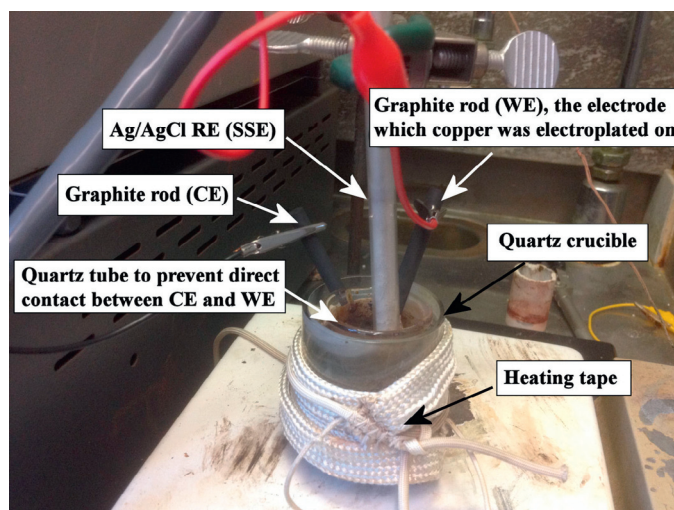


Fig. 1. Cell for reduction of cupric chloride in molten NaCl—KCl— $\text{ZnCl}_2$  salt in a quartz vessel in air. Graphite working electrode (cathode), graphite counter electrode, silver/silver chloride reference electrode (SSE). Cathode potential:  $-0.5$  V vs. SSE.

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