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Technical note

Selective reduction of Cu from aqueous solutions through hydrothermal route for production of Cu powders

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ABSTRACT

Selective reduction of Cu from aqueous solutions containing Ni and Fe to produce Cu powders was investigated through hydrogen gas reduction. The reduction kinetics was found to depend on temperature, hydrogen gas pressure as well as trace amount of iron. Under optimum precipitation condition (solution pH: 3.5, temperature: 180 °C, time: 90 min., and hydrogen pressure: 30 kg/cm^2), copper powders (purity > 99.9%) was obtained with more than 99% precipitation efficiency. The SEM images revealed that the precipitated Cu particles have irregular shapes at lower precipitation temperatures, while spherical Cu particles form at higher reduction temperature. Addition of a surfactant modified the morphology of copper powders and also prevented their coating on the reactor's surface. Precipitated Cu powders are fine sized (more than 80% particles below 45 μm) and have lose and green densities of 3.28 g/cm^3 and 8.45 g/cm^3, respectively.

1. Introduction

Recovery of base metals such as Cu, Ni and Co from low grade ores (Lazaro et al., 2011), secondaries (Davies, 1975), wastes (Yang et al., 2012), residue/sludge (Kuchar et al., 2006), effluent streams (Nenov et al., 2008), etc. has gained lots of importance from the environmental point of view. Rapid depletion of high grade ores makes this subject even more relevant. Hydrometallurgical processes by far, have been considered to be the most efficient one for treatment of such low grade and waste materials. The major advantages of hydrometallurgical processes include their flexibility, adaptability, and low capital and energy requirement. Conventional hydrometallurgical processes based on leaching – solvent extraction – electrolysis though are successful in producing metals from such low grade ores and waste sources, but new approaches still need to be explored to make these processes more economically competitive. One of the options in this regard is to produce high pure metal powders, rather than metal sheets or ingots (Agrawal et al., 2006a; Meshram et al., 2013). Copper powder with desired purity, size and shape found enormous high value powder metallurgical applications such as: specialty alloys, composites & infiltrates, self-lubricating bearings, welding electrodes, numbers of electric and electronic components, medicines, etc.

A survey of literature indicated that number of methods are being practiced for production of such metal powders, which include ionic precipitations (Abdel-Aziz, 2011), chemical & electrolytic reductions (van der Weijden et al., 2002), and gaseous reductions under atmospheric as well as under temperature–pressure conditions (Togashi and Nagai, 1983). Among these processes, H_2 gas reduction processes are found to be most successful in terms of selectivity, energy consumption and their ability to produce tailored powders through the addition of additives or modifiers. From literature it was also realized that, selective reduction of metals from aqueous solutions depends on several factors, notably the solution composition (type & concentration of impurities). Therefore, each individual system needs to be studied thoroughly and accordingly; the process has to be optimized to get high pure metal powders with desired purity and characteristics. The main objective of this study is to produce high pure Cu powders from a typical synthetic solution containing Cu^{2+}, Ni^{2+} and traces of Fe^{3+}. The composition of the solution was chosen to match the composition of leach solution that would be generated by processing of polymetallic manganese nodules through an integrated hydro-metallurgical processing route.

For efficient treatment of sea nodules, nodules are initially smelted to produce alloys rich in Cu, Ni, Fe and Co while rejecting most of the gangue minerals in the slag. These alloys are then sulfidized to make friable mattes, which are leached in sulphuric acid under high temperature–pressure condition (Parhi et al., 2011). During leaching most of the iron was rejected as iron oxide in the residues. Other metals such

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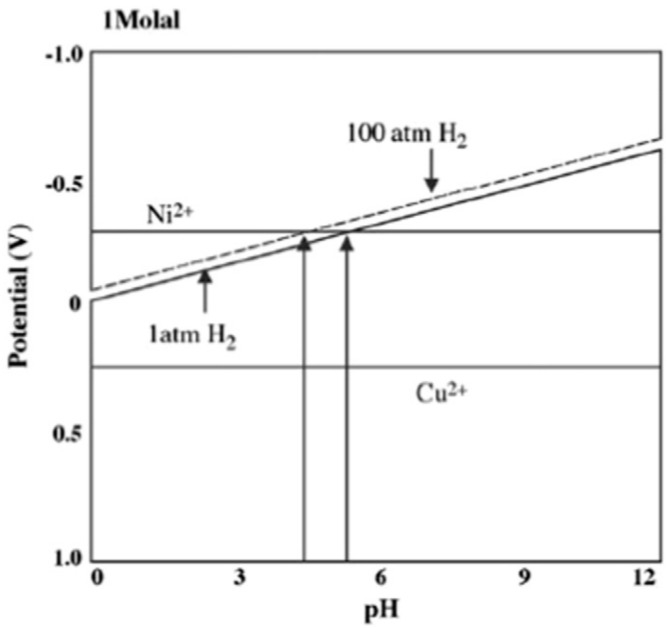

Fig. 1. Variation of reduction potentials of Cu & Ni w.r.t. pH & H_2 partial pressure. (1 Molal conc.)

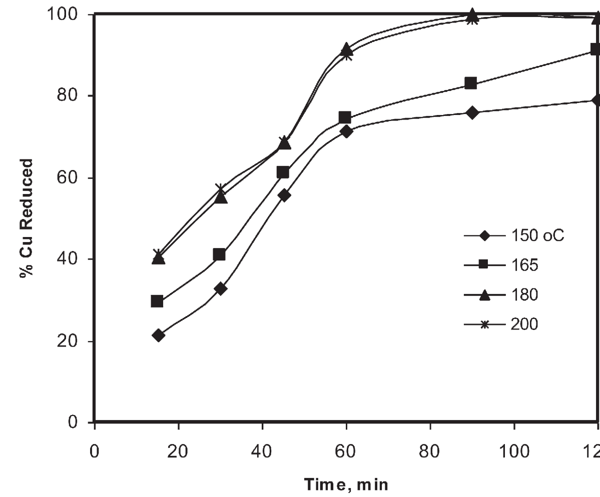

Fig. 3. Effect of reaction temperature on Cu reduction ($PH_2 = 25$ kg/cm^2).

as copper, nickel and cobalt are found in the solution. The present investigation is focused to develop and optimize selective production of Cu powders from such leaching solutions of sulfide mattes derived from manganese nodules.

2. Materials and methods

Initial copper reduction studies were carried with synthetic solutions having similar compositions as that of leach solutions i.e.: 25 g/L Cu, 30 g/L Ni and 0–100 ppm Fe. These solutions were made by dissolving calculated quantities respective metal sulfates (A.R. Grade) in distilled water. The pH of these solutions was adjusted to 3.5 by addition of 20% Na_2CO_3 or H_2SO_4. Six-hundred milliliters of this synthetic solution was transferred in to an autoclave (PARR 1 L capacity, Model No. 4530) having a titanium lined container and reduction experiments were carried out under varying reaction temperature, hydrogen gas partial pressure and reaction time. The effect of these reaction parameters on percentage reduction of Cu was studied by analyzing the mother (filtrate) liquor.

Reduction kinetics of Cu^{2+} was monitored by withdrawing samples from the autoclave at desired time intervals (after attainment of desired temperature & feeding of H_2). These samples (~15 mL) were filtered and the filtrate was analyzed for Cu and Ni by AAS (Atomic Absorption Spectrophotometry). After completion of each reduction experiment, the autoclave was allowed to cool to room temperature and the solution and metal powders were taken out. The powder was properly washed with distilled water followed by sodium carbonate solution to neutralize the acid and finally with distilled water. It was then treated with sodium potassium tartarate (to protect from surface oxidation) and dried at 100 °C.

3. Results and discussion

The effect of hydrothermal reduction temperature, time and H_2 gas partial pressure on percentage reduction of Cu was studied. Variation of Cu^{2+}/Cu & Ni^{2+}/Ni potential with respect to solution pH and H_2 partial pressure is presented in Fig. 1. This figure indicates that, under ambient conditions selective reduction of Cu over Ni is possible below pH 5.5. However, in view of the actual leach solution pH, all the reduction experiments were carried out at an initial pH of 3.5.

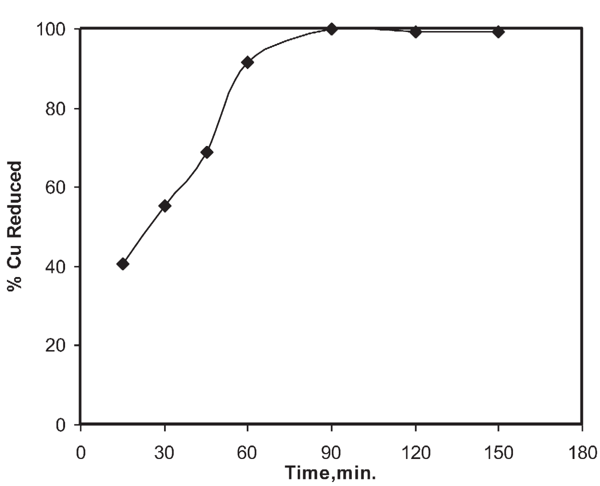

Fig. 2. Effect of reaction time on Cu reduction (180 °C, $PH_2 = 25$ kg/cm^2).

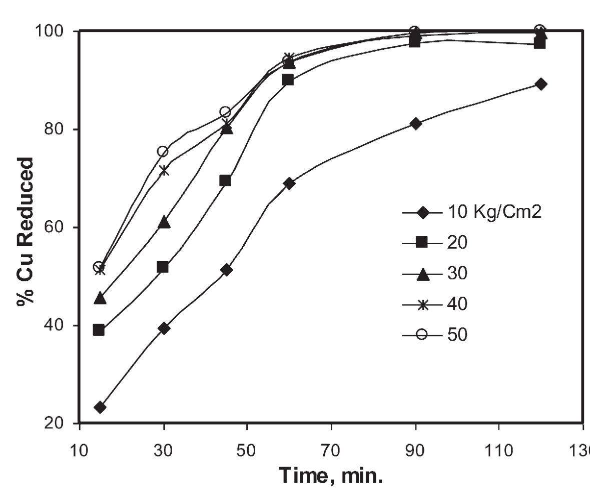

Fig. 4. Effect of H_2 gas pressure on Cu reduction (180 °C).