Extraction of copper by leaching of electrostatic precipitator dust and two step removal of arsenic from the leach liquor

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Abstract−The paper deals with the extraction of copper from the deposited material of the liner of the electrostatic precipitator (ESP) of the copper smelter plant. These precipitates of ESP liner (ESP dust) generally contain mixed phases of copper and arsenic. An attempt is made to extract copper from ESP dust, subsequently removing arsenic from the leach liquor. The ESP dust containing paramelaconite ($6CuO \cdot Cu_2O$), α-domeykite (Cu_3As), metadomeykite (Cu_3As), enargite (Cu_3AsS_4) and $(Cu,Fe) SO_4 \cdot H_2O$ is not a naturally occurring geological mineral; thus comparatively high acid concentration and temperature are required to break the matrix of this mixed material so as to liberate the content. The leaching efficiency of copper was 97% at 97 °C. The acid concentration of 1.5 M and pulp density of 20% was found to be optimum. The removal of arsenic as ferric arsenate was carried out in two stages: increasing the pH and precipitation of arsenic by adjusting pH of the solution and by adding ferrous sulfate and hydrogen peroxide. The optimum removal of arsenic was 95% when pH was raised to 2.35 followed by precipitation. The key progression of the process is the recovery of copper from ESP dust as well as removal of arsenic from the leach liquor.

Key words: ESP Dust, Copper Arsenide, Leaching, Arsenic, Ferric Arsenate

INTRODUCTION

In the smelters of copper plants, copper dusts get deposited as complex compounds in the electrostatic precipitator (ESP) walls and in the liner of waste heat boiler. These precipitates of electrostatic precipitator liners having different mineralogy than the naturally occurring ones generally contain mixed phases of copper and arsenic. Arsenic is generally discarded from aqueous effluents or smelter gases as a waste. In the gaseous form while going out, it gets accumulated in the liner of electrostatic precipitators and forms compounds with copper. Arsenic is one of the major contaminants in many non-ferrous metallurgical processes and the removal is still a major challenge for researchers. Arsenic-bearing compounds find very limited market due to severe toxicity. Disposal of arsenic in the last few decades has been a serious environmental challenge for the metallurgical industries, especially for copper smelters, due to and the numerous environmental regulations imposed.

Generally Cu exists as oxide, carbonate and sulfide or in mixed phases in nature. So, extraction processes of copper from these materials are different than the minerals available normally. Due to the depletion of high grade ores, it is now an appropriate time to recover and reuse metals from the low and lean grade sources. To extract copper from these secondary sources is essential in view of the increasing demand for the metal. Several investigations have been reported previously on leaching of oxidized Cu ores/malachite ores in NH_3 media [1-3], and in H_2SO_4 media [4,5]. Attempt has also been made to use ultrasonics to increase the rate of leaching of oxidized copper ore in ammonia [6] as well as in acid media [7]. Use of aqueous ammonia as the leaching agent is advantageous for its selectivity towards copper. Gangue minerals are not attacked by aqueous ammonia, thus reducing reagent consumption, but in this case the overall kinetics is slow. Sulfuric acid is most widely used acid for leaching due to the following advantages: (i) high solubility of copper, (ii) low price, (iii) well established technology for solvent extraction/electro-winning in sulfate media, and (iv) regeneration of acid after solvent extraction. Copper from copper arsenides can be extracted through acid leaching by using different oxidants [8] like O_2, H_2O_2, Fe^{3+}, Ce^{4+}, hypochlorite leaching [9], chloride leaching [10], sulfidation and pressure leaching in sulfuric acid media [11], alkaline leaching with NaHS media [12] etc. Janin et al. have studied selective recovery of metals from the leachate [13].

The dissolved arsenic in the leach liquor causes the real menace. Arsenic can also be removed via adsorption [14-18] when it is in lower quantity. But when arsenic is there in heavy dose, precipitation of ferric arsenate is one of the safe ways to remove arsenic. In the precipitation system the effects of temperature, seeding, acidity, valency, presence of third ion and dissolution rate of scorodite (ferric arsenate) in environmental conditions were studied by various investigators [19-22]. The experimental conditions for arsenic removal and precipitation are different for different investigators. Arsenic can either be extracted directly from acidic solution with ferrous sulfate and O_2 gas [22] or air [23] (below 100 °C). It can also be extracted with oxidative alkaline leaching of As bearing solids followed by precipitation of calcium arsenate. Dissolution of calcium arsenate brings back As into solution in acidic medium where it is precipitated as scorodite with ferrous sulfate and oxygen gas [24]. Arsenic fixation was also carried out *in situ* from contaminated soil with ferrous sulfate, potassium permanganate and calcium hydroxide [25,26]. Arsenic was also precipitated from fresh water organic matter [27] or by stabilization of arsenic by precipitating arsenic natroalunite from waste calcium arsenate [28]. Moreover, investigations related to metals extraction from flue dust with arsenic stabilization [29], smelter residue treatment with arsenic removal and copper

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extraction [30] and smelter dust treatment with pressure leaching [31] are also there. Apart from these studies, basic studies on synthesis of scorodite are also there. For example, studies related to prescorodite species [32,33], nanocrystalline scorodite [34] are there. The experimental methods in all the aforesaid investigations include the precipitation of ferric arsenate from ferrous sulfate with oxidant below 100 °C either with synthetic arsenic solution or industrial effluents.

Arsenic removal is a necessary step for the down stream processes. The solution to this problem is not only the removal of arsenic from the leach liquor for the downstream processes, but also to find a solution to the disposal problems like the synthesis of arsenic-bearing compound having environmental stability. From the above literatures it is found that arsenic can be removed by adsorption or precipitations, which are two important chemical engineering applications. In the present paper, an attempt is made to recover copper from ESP dust of the copper smelter plant, which is not a natural geological mineral and also has different compositions like mixed phases of copper oxide and copper arsenide using chemical engineering application of leaching technique. Secondly, removal of arsenic from the leach liquor via pH increment followed by atmospheric scorodite precipitation, which is another chemical engineering application below 100 °C with hydrogen peroxide.

EXPERIMENTAL

1. Material

The original material is a deposit on the liner of the electrostatic precipitator of a copper smelter plant. The material was used without any chemical or thermal treatment as the raw material. It was ground and sieved. The bulk size was ≤100 μm. The chemical composition of the material was found to be 31.77% Cu, 14.92% Fe, 0.061% Co, 0.052% Ni, 1.56% Zn, 0.068% Mn along with this 6.1% As, 9.98% S. The balance amount may be attributed to the presence of oxygen and gaseous components. The chemicals like ferrous sulfate hepta hydrate and hydrogen peroxide used in the study were obtained from Merck (India) and Finar (India), respectively. For analysis the chemicals used were acetic acid (Finar, India), potassium iodide (Merck, India) and sodium thiosulfate (Merck, India).

2. Method

2-1. Leaching

The leaching experiments were carried out by taking required amount of sulfuric acid in a glass beaker of 500 ml capacity placed on a magnetic stirrer with hot plate. The concentration of sulphuric acid was varied from 0.8 M to 2 M. The pulp density was varied from 10% to 30%. The temperature of all the experiments was maintained at 97 °C except where it was varied between 25 °C to 97 °C. Time of leaching was varied from 1 h to 8 hrs. The rate of leaching was monitored in terms of leaching efficiency calculated as-

$$([W]_t/[W]_c) \times 100 = \text{leaching efficiency in \%} \qquad (1)$$

Where, $[W]_t$=Wt. of the metal dissolved in solution after a particular time period
$[W]_c$=Total wt. of the metal in the sample taken.

2-2. Removal of Arsenic

Two steps were chosen to remove arsenic from the leach liquor:

1) Increasing the pH of the solution upto 2.3 by dropwise addition of 6 M sodium hydroxide, and 2) precipitation of ferric arsenate from this solution. The precipitation was carried out in a 250 ml conical flask where 100 ml of leach liquor containing copper and arsenic was mixed with calculated amount of ferrous sulfate so as to maintain the required ratio of Fe/As 1.0, and 10 mL of hydrogen peroxide was added and stirred for 4 hrs at 97 °C. The yellowish brown precipitate of ferric arsenate was collected, washed and dried at 80 °C in a hot air oven for 24 hrs. The sample was collected and characterized.

2-3. Analyses

Copper was analyzed by chemical analyses following standard iodometry method [35]. Arsenic and other impurities in the leach liquor were analyzed by atomic absorption spectrophotometer (model no. SHIMADZU-AA6300).

3. Characterization

Phase determination by XRD was determined by using an X-Ray diffractometer model PW 1830 X'pert system in the 2θ range of 10 to 40° with voltage of 30 kV, and MoKα was used to characterize the samples. The morphology of the precipitated ferric arsenate was studied by scanning electron microscopy (model no. HITACHI S-3400 N).

RESULTS AND DISCUSSION

1. Mineralogy

The XRD of the mineral is given in Fig. 1(a). The 100% peak refers to paramelaconite (6CuO·Cu₂O) [JCPDS-3-879], indicating the major phase. Other minor phases present were α-domeykite (Cu₃As) [JCPDS-9-333], metadomeykite (Cu₃As) [JCPDS-2-1251], enargite (Cu₃AsS₄) [JCPDS-10-436] and (Cu,Fe) SO₄·H₂O [JCPDS-15-120].

2. Leaching

Leaching of the material was carried out to extract copper from the matrix. This material is not a naturally occurring geological ma-
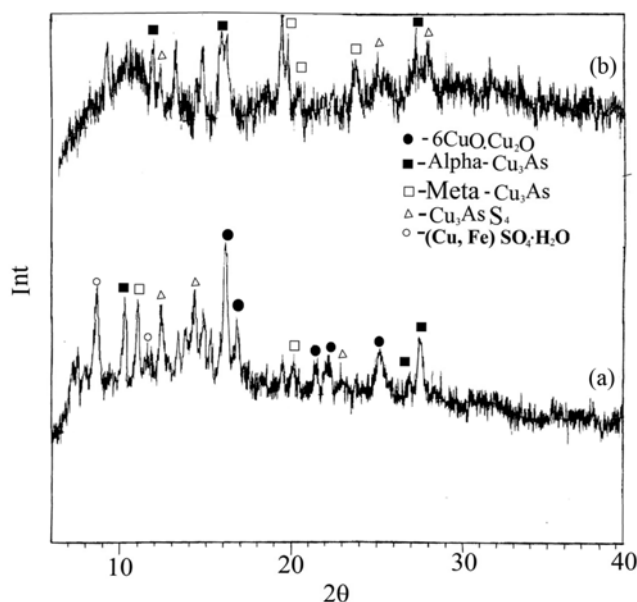

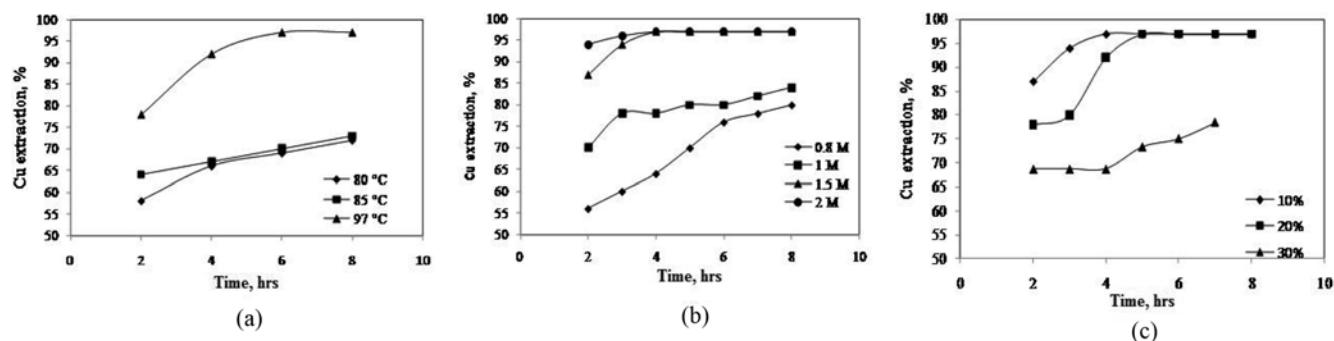Fig. 1. XRD of the samples (a) raw, (b) leach residue (1.5 M acid).

Fig. 2. Extraction of copper at different conditions; (a) Effect of temperature on leaching, 1.5 M acid, 20% pulp density, (b) Effect of acid concentration on leaching, 10% pulp density, 97 °C, (c) Effect of pulp density on leaching, 1.5 M, 97 °C.

terial. It is an industrial deposition. So, its mineralogy and leaching behaviour are quite different from the normal ores and minerals. It is a secondary material of copper industries. Variation of parameters was studied and optimized. The results are given in following sections.

2-1. Effect of Temperature

The effect of temperature was studied for the liberation of metal values. It was found that increase in temperature increases the liberation factor. The plots in Fig. 2(a) reveal the effect of temperature on the leaching of copper oxide and copper arsenide.

The maximum leaching efficiency at 80 °C was 69% at 8 h for 20% pulp density, while it was 97% when the temperature was increased to 97 °C. Copper arsenides require high temperature for leaching as examplified by enargite leaching (Padilla et al., 2010) via sulfidation at a temperature of 350-400 °C followed by pressure leaching at 95 °C. However, hypochlorite leaching of enargite requires 40-50 °C for maximum recovery (Viñals et al., 2003). In the present case 97 °C is found suitable for leaching of a material containing a mixture of copper oxide, arsenide, and arsenic sulfide for obtaining a significant leaching efficiency. The leach liquor was found to be Cu: 61.3 g/L, As: 11.7 g/L, Fe: 13.6 g/L, Zn: 2.8 g/L, Co: 180 ppm, Ni: 12 ppm, Mn: 12 ppm, Pb: 25 ppm.

2-2. Effect of Acid Concentration

The concentration of the acid is one of the major parameters for recovery of copper. Acid breaks the complex to release the metal values. In the present study acid concentration was varied from 0.8 M to 2 M. Fig. 2(b) shows that when the concentration of the acid was 0.8 M the maximum leaching at the end of 8 h was around 80% for 10% pulp density. With the increase in the acidity to 1.5 M the leaching efficiency was increased to 97% within 4hrs for the same pulp density. Similarly, 97% recovery was achieved within three hours when acid concentration was increased to 2 M. The high acid concentration indicates the material deposited in the liner has acquired a very stable complex of copper oxide with arsenic. It needs high temperature and high acidity to break the complex so as to liberate the content. Some of the acid is consumed in breaking down the matrix, by gangues and by liberating the metal values. The residual acids in all the cases are calculated and found that 62.75 g/L, 80.95 g/L, 128.38 g/L and 175.42 g/L in case of 0.8 M, 1 M, 1.5 M and 2 M initial acid concentrations, respectively. The unreacted acids also prove that the leaching is an acid-starving system.

The X-ray diffraction pattern of the 1.5 M sulfuric acid leach residue is given in Fig. 1(b). After leaching with 1.5 M sulphuric acid

it was found that oxide part and majority of the arsenide part were leached out, leaving behind the phase enargite (Cu₃AsS₄) and small parts of copper arsenides also.

2-3. Effect of Pulp Density

The solid to liquid ratio (w/v) is termed the pulp density. The effect of pulp density on copper extraction is given in Fig. 2(c). It is clear that in both 10% and 20% pulp density 97% extraction was achieved. But when the pulp density was increased to 30%, the recovery was reduced to around 75%. Hence in this case 20% may be taken as the optimum pulp density for optimal recovery of copper.

3. Removal of Arsenic

Arsenic is a menace, a serious threat to the biosphere. It cannot be discharged as such with the effluents. It seriously needs some treatment. In this case arsenic is removed from the leach liquor via two steps.

3-1. pH Increment

It is the pH which rules the whole precipitation. The pH of the leach liquor used in this case was less than 1. The pH of the solution was increased by adding 6 M NaOH dropwise and very carefully to avoid local precipitation.

The arsenic content of the original leach liquor was 11.7 g/L. With increase in the pH of the solution some of the arsenic is removed. At pH 1.0, arsenic removed was 24%, with pH 2.0 the removed arsenic was 47% and after increasing the pH to 2.35 the arsenic removed was 58% and the balance arsenic remained in solution was 4.91 g/L.

3-2. Precipitation

Arsenite (AsO_3^{3-}) is released when leaching with acid releases arsenic in the form of ferric arsenate is readily formed by coprecipitation of ferric ion and arsenate (AsO_4^{3-}) ion. The role of oxidant is to oxidize As (III) (arsenite) to As (V) (arsenate) and simultaneously oxidizing ferrous ions to ferric ions which combined to precipitate ferric arsenate as described in Eqs. (2) to (4).

$$AsO_3^{3-}+[O] \rightarrow AsO_4^{3-} \qquad (2)$$

$$Fe\,(II)+[O] \rightarrow Fe\,(III) \qquad (3)$$

$$Fe\,(III)+AsO_4^{3-} \rightarrow FeAsO_4 \qquad (4)$$

The precipitated ferric arsenate so obtained was characterized with XRD. The XRD pattern as shown in Fig. 3 matches fairly well with standard XRD pattern of scorodite (FeAsO₄·2H₂O) (JCPDS-26-778). All the peaks are identified and matched with scorodite, except

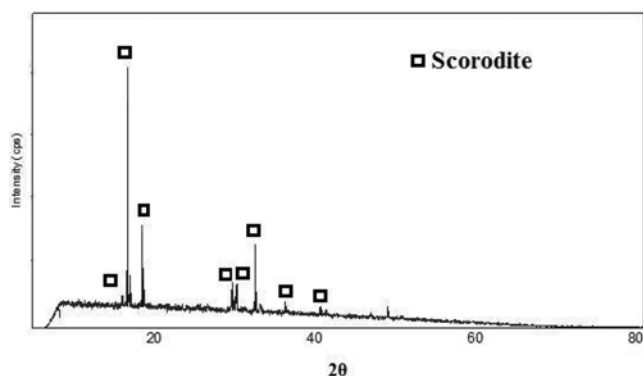Fig. 3. XRD of the precipitated ferric arsenate (Scorodite).

Fig. 5. Effect of time on scorodite precipitation, 97 °C.

two tiny unidentified peaks at 2θ value of around 48°. The SEM images of the precipitate (Fig. 4) exhibit uniformly distributed crystals of scorodite.

3-2-1. Effect of Time on Precipitation

The solution after the first step of arsenic removal was treated with ferrous sulfate at pH 2.5 and temperature 95-97 °C to precipitate scorodite crystals. The arsenic was removed successfully through precipitation of ferric arsenate, and the final arsenic in the solution was 1.35 g/L after 2 hrs and 0.585 g/L after 4 hrs as described in Fig. 5. The decrease in the arsenic concentration is attributed to the formation of the scorodite.

3-2-2. Effect of Temperature

Temperature was found to be effective for the precipitation of ferric arsenate. With the increase in the temperature from 30 °C to 97 °C, the arsenic that remained in the solution after precipitation was 2.5 g/L at 30 °C, 1.5 g/L at 60 °C and 0.585 g/L at 97 °C (Fig. 6).

It is also reported for an induction period at lower temperature (85 °C) with seeded scorodite precipitation [14]. Similar phenomenon was observed in this case also; the increase in the yield of ferric arsenate with temperature was slow upto 60 °C, but beyond that temperature a rapid enhancement in the yield was observed. Fujita et al. 2008 have reported that the precipitation yield at 70 °C and 95 °C is the same. But the development in crystallinity in the precipitates of 95 °C is much higher as compared with the same obtained at 70 °C. So, it can be concluded that arsenic removal through ferric
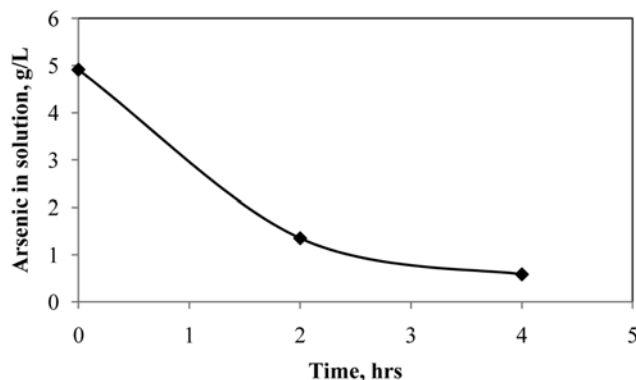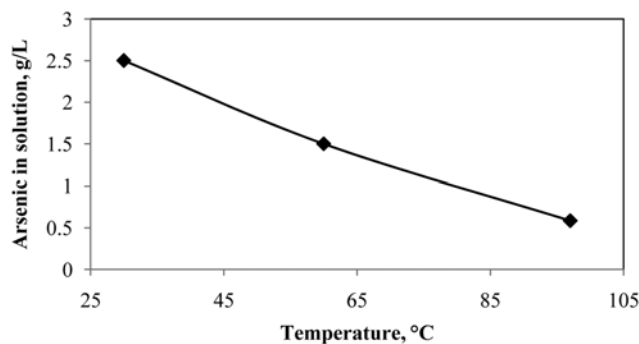

Fig. 6. Effect of temperature on scorodite precipitation, 8 h.

arsenate precipitation is directly related to temperature.

CONCLUSIONS

The ESP dust of copper smelter plant containing paramelaconite, α-domeykite, meta-domeykite enargite and copper iron sulfate hydrate was leached in sulfuric acid medium at different temperature and acid concentrations. The leaching efficiency of copper was 97% at 97 °C. The acid concentration of 1.5 M and pulp density of 20% was found to be optimum under the present conditions. High acid concentration and temperature are essential to break the matrix of
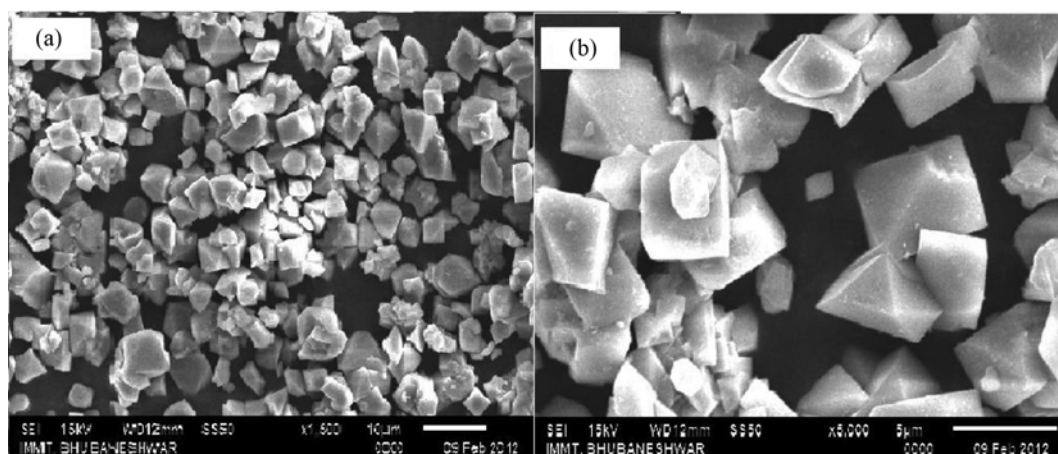

Fig. 4. SEM of the precipitated ferric arsenate (Scorodite); (a) 1,500 times magnification, (b) 5,000 times magnification.

this mixed material so as to liberate the content. High concentration of acid could dissolve the oxide part, but a few of the arsenides could not get dissolved at this acid concentration. The arsenic content in the material also leached along with copper. The leach liquor contains almost 94% of the total arsenic.

Arsenic is removed from the leach liquor in two subsequent steps: 1) increasing the pH to 2.35, and 2) precipitation of ferric arsenate from the pH adjusted liquor. The maximum arsenic removed was 95%. The advantage of the process is that it not only offers recovery of copper from an ESP dust but also suggests a remedy for arsenic removal from the leach liquor producing ferric arsenate.

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