Recovery of Cu and Zn from Complex Sulphide Ore

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Abstract
Complex Sulphide Ores are often found to be a close mutual association with each other and with the nonmetallic gangue. The beneficiation experiments showed that it would be very difficult to recover Cu and Zn from the lean complex Sulphide ores using traditional ore beneficiation methods. In the present work, leaching of complex sulfide ores in sulfuric acid was investigated by the Electro hydrometallurgy process. The lab-scale experiments were conducted to investigate the influences of pulp-density, electrolyte concentration, particle size, current density and time on recovery of Cu and Zn. The leach liquor obtained after electrolysis was subjected to Atomic Absorption Spectroscopy analysis for the recovery of minerals.

1. Introduction
The processing of complex Sulphide ores depends on the nature of the gangue material and percentage composition of various nonferrous metals present in the ores or in the bulk concentrates. As Zinc and copper often occur together, the separation of one metal from the other has presented problems to the nonferrous metallurgists [1].

Sulphide ores are extremely complicated mineralogical associations of the inter grown of their constituent minerals [2] comprising mainly chalcopyrite (CuFeS2), sphalerite (ZnS), and galena (PbS), these ores do not allow the recovery of metal by direct chemical leaching due to their low solubility in most leaching reagents[3]. In such cases, the ore must be pre-treated in order to release the desired metals physically and to make the ore amenable to leaching reagents. Processes available for the treatment of complex Sulphide ores involve Sulphide oxidation to form water soluble sulphates or oxides. The sulphur oxidation processes include roasting, pressure oxidation, chemical oxidation and bioleaching. The processes that are traditionally used are complex and expensive. Hence attention has been drawn to the use of easily available and cheap reagents like sulphuric acid for base metal recovery and means of optimizing the dissolution kinetics. Although sulphuric acid may not be as effective as other stronger oxidizing acids like nitric acid, it is, however, preferred to all other reagents in terms of cost, corrosion wear and the ease of regeneration during electro winning [4].

The ore minerals in poly-metallic and complex deposits are often found to be in close mutual association with each other and with the nonmetallic gangue. In many cases, attempts to concentrate these ores have run in to problems because it is either difficult to obtain a suitable grade of the
concentrate by conventional flotation methods or the recovery of metals in the respective concentrate is poor. Zinc that finds its way to a copper concentrate is always discarded in the slag as a waste, while copper in a lead concentrate leads to serious smelting problems.

The major step in hydrometallurgical methods involves the absorption of the nonferrous metallic values in a solution and leaving behind a major part of the iron in the leach residue. The next steps are solution purification, separation of the nonferrous metals by electrolysis. During the metal extraction, the bulk of the metal is separated from impurities present in the compound which invariably comprises more than one phase. The driving force for the reactions involved in metal extraction depends on the differences in the chemical potentials of the elements.

The scanning electron microscope (SEM) is one of the most versatile and widely used tools of modern science as it allows the study of both the morphology and composition of materials [5]. It has been extensively applied in mineralogical studies of sulphide ores and their residues [6, 7, 8, 9,10]. The main purpose of this work is to study the various parameters (time, particle size, pulp density, current density, concentration) on recovery of Cu and Zn from complex Sulphide ores.

2. Experimental procedure
A standard 500 ml beaker is taken in which graphite (anode) and copper (cathode) electrodes are placed. The positive terminal of the D.C. source is connected to the ammeter the then connected to graphite anode. The negative terminal of D.C. source is connected to cathode copper sheet by a rheostat. The inter-electrode distance was maintained at 6cm.

For each experiment a known weight of sample of specific size fraction was taken. The thermometer and electrodes were set in the position. As soon as the sample was added a constant amount of current was passed from D.C. power supply. The stirring of the slurry was provided with Teflon covered magnetic stirring bar. The slurry was stirred in just fast enough to maintain suspension of the solids. The leaching is continued for a specific amount of time, after leaching it was filtered and the leach liquor was analyzed for copper, lead and zinc. The effect of current density, the effect of time, the effect of concentration, effect of pulp density and the particle size were studied.

![Figure 1. Experimental setup used for electro leaching](image)

MS+H₂SO₄+0.5O₂ → MSO₄+SO²⁺+H₂O, [11] Where M can be Zn, Cu

2.1 Atomic absorption spectroscopy (AAS)
The technique of atomic absorption developed by Sir Alan Walsh of C.S.I.R.O in the mid 1950 has become the preferred method of elemental analysis. Walsh discovered that the majority of free atoms in the commonly used flame were in the ground state, but that the flames did not also have enough energy to excite these atoms. A light source emitting a narrow spectral line of the characteristic energy is used to excite the free atoms formed in the flame. The decrease in energy (absorption) is
then measured. The absorption is proportional to the concentration of free atoms in the flame, given by the Lamberts Beer Law.

\[
\text{Absorbance} = \log_{10} \frac{I_0}{I_t} = K.C.L
\]  

(1)

Where,
- \(I_0\) = intensity of incident radiation emitted from the light source
- \(I_t\) = intensity of transmitting radiations
- \(C\) = concentration of sample
- \(K\) = constant
- \(L\) = path length.

Atomic Absorption Spectroscopy uses the absorption of light to measure the concentration of gas phase atoms. Since samples are usually liquids or solids, the analyte atoms or ions must be vaporized in a flame or graphite furnace. The atoms absorb UV or Visible light and make the transition to higher electronic energy levels. The analyte concentration is determined from a working curve after calibrating the instrument with standards of known concentration. Atomic absorption is similar to Ultraviolet Spectroscopy in that similar wavelength and the same relationship are used, but differs in the fact that a line source is used, and the sample compartment (a flame or electro thermal atomizer) is positioned before the monochromatic and not after it. In practical atomic absorption analysis the Lamberts Beers Law can be reduced to

\[
\text{Absorbance} = \log_{10} \frac{I_0}{I_t} \propto c
\]  

(2)

2.2 Analytical procedure

2.2.1 Calibration Curve:
This is the most common method where interference effects are known to be absent. Usually at least three standards and a blank are used to cover the range 0.1 to 0.8 ABS. The calibration is performed by using the blank solution to zero the instrument. The standards are then analyzed with the lowest concentration first, and the blank run between standards, to ensure the base line (zero point) has not changed. Samples are then analyzed and their absorbance recorded. A graph of absorbance VS concentration is plotted.

![Figure 2. Calibration curve](image-url)
3. Results and Discussions:
The SEM image and the chemical composition of complex sulphide ore is mentioned below.

![SEM image of complex sulphide ore](image)

**Figure 3.** SEM image of complex sulphide ore

**Table 1:** Chemical composition of sulphide ore

| Element | (Kev) | Mass% | Error% | At%  | K    |
|---------|-------|-------|--------|------|------|
| C K     | 0.277 | 30.17 | 0.08   | 52.34| 9.2782 |
| O K     | 0.525 | 26.55 | 0.11   | 34.58| 26.4518 |
| Mg K    | 1.253 | 1.31  | 0.06   | 1.12 | 1.0728 |
| Si K    | 1.739 | 2.97  | 0.05   | 2.21 | 3.7332 |
| S K     | 2.307 | 6.50  | 0.04   | 4.23 | 11.2963 |
| Fe K    | 6.398 | 2.62  | 0.14   | 0.98 | 4.0928 |
| Cu K    | 8.040 | 0.83  | 0.29   | 0.27 | 1.2601 |
| Zn K    | 8.630 | 6.18  | 0.37   | 1.97 | 9.4144 |
| Pb M    | 2.342 | 22.87 | 0.18   | 2.30 | 33.4003 |
| Total   |       | 100.00|        | 100.00|      |

3.1 Atomic Absorption Spectroscopy Readings in PPM for all Parameters

After electrolysis, the samples are subjected to Atomic Absorption Spectroscopy to recover Cu and Zn from leach liquor.

**Table 4:** AAS readings for time

| Time (HR.) | Cu    | Zn    |
|------------|-------|-------|
| 1          | 1.61  | 0.876 |
| 2          | 1.754 | 1.915 |
| 3          | 2.18  | 2.361 |
| 4          | 2.364 | 3.69  |
### Table 5: AAS readings for particle size

| Particle size (μm) | Cu  | Zn  |
|-------------------|-----|-----|
| 150               | 0.88| 0.708|
| 105               | 1.16| 1.199|
| 75                | 1.46| 2.454|
| 53                | 1.56| 3.092|

### Table 6: AAS readings for pulp density

| Pulp density (g/l) | Cu  | Zn  |
|--------------------|-----|-----|
| 10.10              | 1.46| 4.32|
| 20.40              | 1.22| 4.14|
| 30.92              | 1.20| 3.08|
| 41.65              | 1.09| 2.33|

### Table 7: AAS readings for concentration

| Concentration (M) | Cu  | Zn  |
|-------------------|-----|-----|
| 1                 | 2.69| 5.40|
| 2                 | 1.557| 2.13|
| 3                 | 1.247| 1.82|

### Table 8: AAS readings for Current density

| Current density (amps/dm²) | Cu  | Zn  |
|----------------------------|-----|-----|
| 3.75                       | 1.085| 2.45|
| 5                          | 1.116| 2.615|
| 6.25                       | 1.51 | 2.940|
3.2. Percentage recovery of Cu and Zn for various parameters

3.2.1. Effect of Time on Electro Oxidation

**Operating conditions:**
- Pulp Density: 30.92 g/l
- Electrolyte concentration: 1 M H₂SO₄
- Temperature: 30°C
- Particle size: 150 μm
- Current Density: 2.5 amps/dm²

| Time (hrs) | % Copper Recovery | % Zinc Recovery |
|-----------|------------------|-----------------|
| 1         | 32.38            | 4.730           |
| 2         | 35.24            | 10.33           |
| 3         | 43.89            | 12.74           |
| 4         | 47.48            | 19.95           |

**Figure 4.** Percentage recovery of copper and zinc Versus Time (hrs)

3.2.1.1. Effect of Time:

The effect of time on the rate of copper and Zinc recovery was investigated at different Time intervals of 1, 2, 3, and 4 hrs respectively. The experiments were conducted at 30°C (room temperature), 1 M H₂SO₄ concentration at a pulp density of 30.92 g/l and particle size of 150 μm. Increase in time of leaching increased recovery of both copper and Zinc from 32.38% to 47.48% and 4.730 % to 19.95%. The increase in dissolution with the increase in time at 30°C is a direct consequence of the prolonged exposure of the mineral surface to the acid medium.
3.2.2. Effect of particle size on Electro Oxidation

Operating conditions:

- Pulp Density: 30.92 g/l
- Time: 1 hour
- Temperature: 30°C
- Electrolyte Conc: 1 M H₂SO₄
- Current Density: 2.5 amps/dm²

| Particle size (μm) | % Copper Recovery | % Zinc Recovery |
|-------------------|------------------|-----------------|
| 100               | 17.69            | 3.824           |
| 140               | 23.37            | 6.472           |
| 200               | 29.47            | 13.24           |
| 270               | 31.40            | 16.68           |

Table 10: % recovery of Cu and Zn verses particle size

Figure 5. Percentage recovery of copper and zinc versus particle size in μm

3.2.2.1. Effect of particle size:

The effect of time on the rate of copper and Zinc recovery was investigated at different mesh size 100, 140, 200, and 270 μm respectively. The experiments were conducted at 30°C (room temperature), 1 M H₂SO₄ concentration at a pulp density of 30.92 g/l for 1 hr. The finer the particle size, recovery of both copper and Zinc increased from 17.69 to 31.40% and 3.824 % to 16.68%. As particle size decreases more surface area is available for reaction, so recovery will be more.

3.2.3. Effect of Pulp Density on Electro Oxidation

Operating conditions:

- Current Density: 2.5 amps/dm²
- Time: 1 hour
- Temperature: 30°C
- Electrolyte concentration: 1 M H₂SO₄
- Particle Size: 100 μm
3.2.3.1. Effect of pulp Density:

The effect of pulp density on the rate of copper and Zinc recovery was investigated at different pulp density of 10.10, 20.40, 30.92 and 41.65 g/l. The experiments were conducted at temperature 30°C 1 M H₂SO₄ concentration at a current density of 2.5amps/dm² and particle size of 100 μm. Pulp density had the minimum effect on the Cu and Zn extraction, an increase in pulp density will cause difficulties for agitation, slurry filtration operation etc.

3.2.4. Effect of Concentration on Electro Oxidation

Operating conditions:

- Pulp Density: 30.92 g/l
- Time: 1 hours
- Temperature: 30º C
- Particle size: (100 mesh) 150 μm
- Current Density: 2.5 amps/dm²

| Concentration (M) | %Copper Recovery | % Zinc Recovery |
|------------------|------------------|-----------------|
| 1                | 54.05            | 29.14           |
| 2                | 3.28             | 11.51           |
| 2.5              | 25.05            | 9.84            |
3.2.4.1. Effect of Concentration:

The effect of concentration on the rate of copper and zinc recovery was investigated at different concentration intervals of 1, 2, and 2.5 molars respectively. The experiments were conducted at 30°C (room temperature), 1 M H₂SO₄ concentration at a pulp density of 30.92 g/l and particle size of 150 μm. The dissolution of both Cu and Zn decreases, as the concentration increases. The rate was independent of the concentration of the acid.

### Operating conditions:

- **Pulp Density**: 30.92 g/l
- **Time**: 1 hours
- **Temperature**: 30°C
- **Electrolyte concentration**: 1 M H₂SO₄
- **Particle Size**: (100 mesh) 150 μm

#### Table 13: % recovery of Cu and Zn versus current density

| Current density amps/ dm² | % Copper Recovery | % Zinc Recovery |
|---------------------------|-------------------|-----------------|
| 3.75                      | 21.80             | 13.25           |
| 5                         | 22.42             | 14.11           |
| 6.25                      | 30.46             | 15.86           |
3.2.5.1. Effect of Current Density:

The effect of the rate of current density on the rate of copper and Zinc recovery was investigated at different current density of 3.75, 5, and 6.25 amps/ dm². The experiments were conducted at 30°C and 1 M H₂SO₄ concentration at a pulp density of 30.92g/l and particle size of 150μm. As current density increases ionic movement will be more which favors the reaction to take place faster and recovery will be more.

4. Conclusions:

• The increase in dissolution with the increase in time is a direct consequence of the prolonged exposure of the mineral surface to the acid medium; intern increases the recovery of Cu and Zn.
• As particle size decreases more surface area is available for reaction, so recovery will be more.
• Pulp density had the minimum effect on the Cu and Zn extraction, an increase in pulp density will cause difficulties for agitation, slurry filtration operation etc.
• The dissolution of both Cu and Zn decreases, as the concentration increases. The rate was independent of the concentration of the acid.
• As current density increases ionic movement will be more which favors the reaction to take place faster and recovery will be more.
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