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# Recovery Of Germanium And Associated Base Metals From Copper Smelter Slag By Hydrochloric Acid Digestion

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***Abstract***
*The goal of this study was to recover germanium and its associated base metals from the copper smelter slag out from the Gécamines-Lubumbashi plant in DRC by digestion with hydrochloric acid followed by leaching with water. Prior to the tests, the slag was mineralogically and chemically characterized using XRD and ICP-OES respectively. The slag had an amorphous crystalline shape with germanium content of 0.01%. The granulometric analysis showed that approximately 55% of the slag was made up of grains in the range of 1 – 5 mm. Under optimal pH 2 and L/S = 4, leaching recovery of Co, Cu, Zn and Ge reached 80, 80, 86, and 90%, respectively, along with Fe at 72 %.*

***Keywords:*** *Copper smelter slag, germanium, associated base metals, hydrochloric acid digestion, water leaching.*

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## I. Introduction

With electrical characteristics halfway between those of a metal and an insulator, germanium is a hard, brittle, grayish-white, semi-conducting element. Germanium is essential to the operation of many commercial, industrial, and military applications due to its special qualities and metallic look. Depending on the use, it can be consumed as a pure element or as a compound [1, 3, 15].

Germanium is one of rare metal that is frequently extracted as a byproduct of the metallurgical operations of other nonferrous metals, like copper, zinc, lead, and aluminum, because there isn't currently an economically viable independent ore source of germanium in nature. Global production of germanium in 2011 was predicted to be 118 metric tons recovered mainly from zinc concentrates and from coal fly ash residues and recycled materials [2,3,4].

Canada extracted germanium on a global scale by using zinc concentrates transported from the United States. In Finland and Russia, zinc concentrates from the DRC were main sources, whereas in China, zinc leftovers and coal from various sources in China and other nations were utilized [7, 8, 15].

Pyrometallurgically treating sulfidic copper ores can provide blister copper, matte, and slag. In Haut-Katanga, Democratic Republic of the Congo (DRC), matte was produced at the Gécamines-Lubumbashi copper plant in a water-jacket furnace, along with some of valuable metals, namely Cu, Co, Zn, Fe and a significant amount of Ge being lost in the slag. This slag is granular because a cold-water jet suddenly cooled it. This leads to an uneven granulometry in this slag [9, 10, 13, 16].

Given the average market worth of the valuable metals in this slag, the introduction of new technologies, ecological change, and the fact that Ge, a strategic metalloid, represents around 20% of the entire value of these metals, the effort to recover germanium as additional value is necessary [11, 12, 14].

The purpose of this work is to recover the Ge present in the slag by hydrometallurgical method consisting of leaching with water after a pretreatment by digestion with hydrochloric acid.

The reaction assumed to take place during digestion is as follows:

$$MeFe_2O_{4(s)} + 8HCl_{(aq)} \rightarrow MeCl_{2(s)} + 2FeCl_{3(s)} + 4H_2O_{(vap)} \quad (1)$$

where Me (metal) stands for Cu, Co, Zn, Ge, and $MeFe_2O_4$ ferrites which is present in the slag.

## II. Materials And Methods

### Materials

The copper smelter slag was sourced from Gécamines copper smelter plant in Lubumbashi, DRC. The following analytical-grade chemicals were used: HCl (32%) and distilled water. All chemical reagents were obtained from Sigma Aldrich and used as received without further purification. A Vista MPX, CCD Simultaneous ICP-OES inductively coupled plasma atomic emission spectrometer, equipped with ICP-Expert software, was used to perform chemical analyses of raw slag and leach solutions following the indicated operating methods [16]. The tests and analyses were conducted at the Laboratory of Department 4 MAT of the Ecole Polytechnique de Bruxelles (Université Libre de Bruxelles, Belgique).

### Methods

As part of the experiment, the raw slag was digested by mixing it with concentrated hydrochloric acid for 24 hours at room temperature without stirring. The digested product was then put through a two-hour lixiviation process at 500 rpm with distillated water. At this point, just the pH, which has a value of 0.5 and ranges from 1 to 2.5, has been the adjusted parameter by adding a NaOH solution. The resulting leaching solutions were filtered and analyzed by ICP-OES.

## III. Results And Discussion

### Characterization of slag

The characterization of the slag was carried out by inductively coupled plasma optical emission spectrometry (ICP – OES) and XRD. Chemical analysis of the slag (Table 1) showed that the content of some metals was respectively: 2.4% Co, 0.9% Cu, 23.5% Fe, 5.6% Zn, and 0.01% Ge. Mineralogical analysis (XRD) reveals that this slag is amorphous (Figure 1); this may be explained by the fact that it was cooled suddenly by a jet of cold water after production in the water jacket furnace. The particle size range from 1 - 5 mm obtained by sieving accounted for almost 55% (Table 2) of the slag particles [17].

**TABLE 1:** Chemical Analysis of the copper smelter slag

| **Element** | **%** |
|---|---|
| Co | 2.4 |
| Cu | 0.9 |
| Fe | 23.5 |
| Zn | 5.6 |
| Ge | 0.01 |

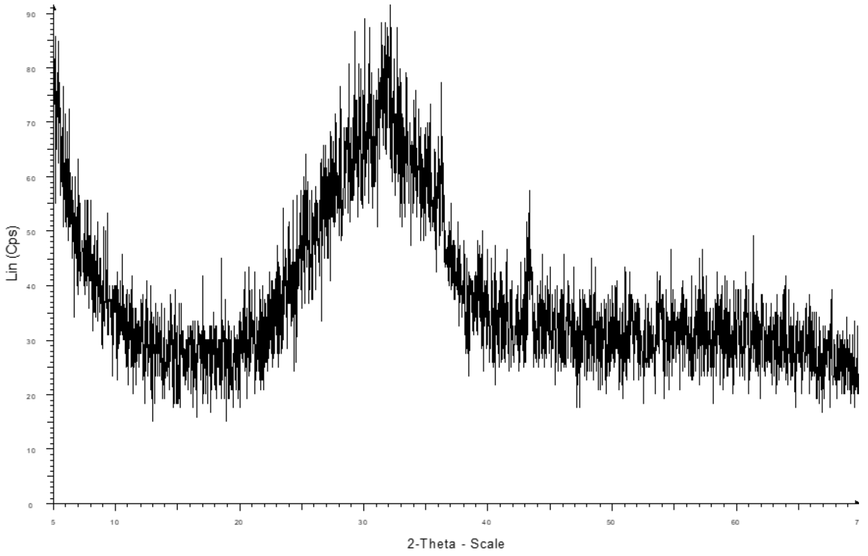

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**FIGURE 1:** Mineralogical analysis of the Slag (XRD)

**TABLE 2 :** Granulometric Analysis

| Fraction (mm) | < 0.5 | 0.5 – 0.85 | 0.85 – 1 | 1 - 5 | > 5 |
|---|---|---|---|---|---|
| Repartition (%) | 5.34 | 25.08 | 12.40 | 54.84 | 2.34 |

**Leaching Results**

After a 24h digestion process with HCl (32 %), leaching tests using distilled water as the leaching agent were carried out by varying two parameters: The liquid to solid (L/S) ratio (mL/g) and pH value. (Table 3) shows the experimental design and solubilization efficiency.

**TABLE 3:** Leaching design and Metal solubilization efficiency (%)

| pH | Run | L/S (mL/g) | Co | Cu | Fe | Zn | Ge |
|---|---|---|---|---|---|---|---|
| | | | % | % | % | % | % |
| 1.0 | 1 | 1 | 12 | 18 | 13 | 13 | 7 |
| | 2 | 2 | 27 | 36 | 28 | 28 | 15 |
| | 3 | 2.5 | 57 | 75 | 52 | 60 | 38 |
| | 4 | 4 | 73 | 96 | 66 | 80 | 45 |
| | 5 | 5 | 78 | 80 | 81 | 81 | 54 |
| 1.5 | 6 | 1 | 7 | 9 | 8 | 8 | 6 |
| | 7 | 2 | 25 | 30 | 21 | 25 | 15 |
| | 8 | 2.5 | 23 | 28 | 24 | 27 | 11 |
| | 9 | 4 | 83 | 92 | 85 | 95 | 65 |
| | 10 | 5 | 83 | 98 | 74 | 86 | 61 |
| 2.0 | 11 | 1 | 8 | 10 | 8 | 8 | 5 |
| | 12 | 2 | 43 | 58 | 39 | 51 | 27 |
| | 13 | 2.5 | 30 | 34 | 32 | 34 | 16 |
| | 14 | 4 | 80 | 80 | 72 | 86 | 90 |
| | 15 | 5 | 79 | 93 | 79 | 84 | 57 |
| 2.5 | 16 | 1 | 12 | 17 | 12 | 13 | 7 |
| | 17 | 2 | 44 | 56 | 40 | 59 | 31 |
| | 18 | 2.5 | 35 | 40 | 36 | 39 | 17 |
| | 19 | 4 | 79 | 86 | 77 | 77 | 78 |
| | 20 | 5 | 84 | 96 | 86 | 81 | 74 |

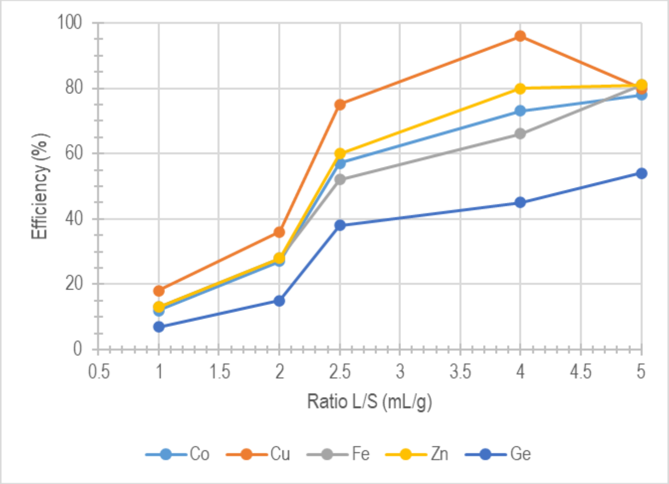

**FIGURE 2: Leaching efficiency at pH = 1.0**

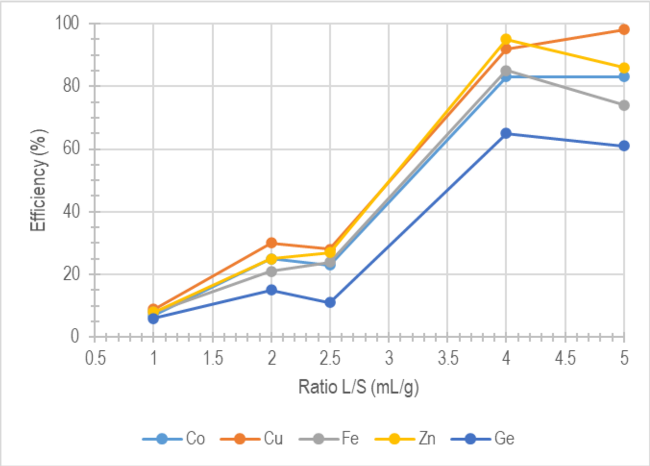

**FIGURE 3: Leaching efficiency at pH = 1.5**

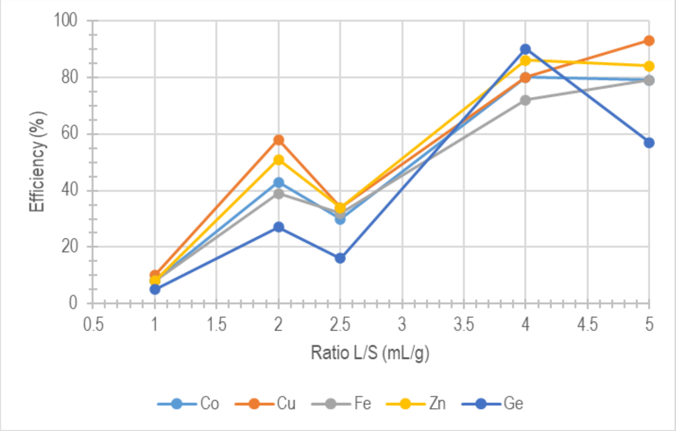

**FIGURE 4: Leaching efficiency at pH = 2.0**

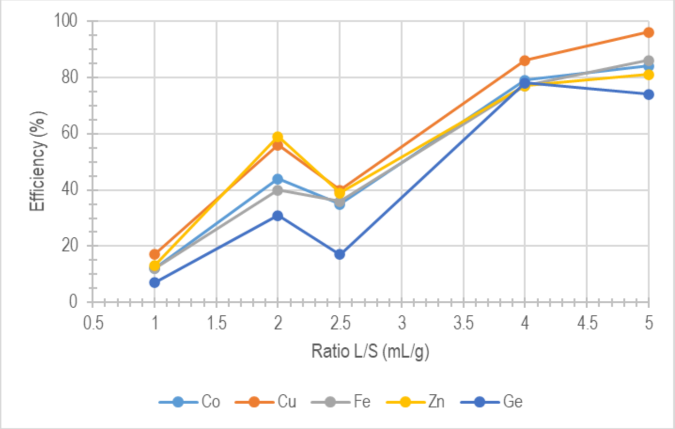

**FIGURE 5: Leaching efficiency at pH = 2.5**

This study looked at two parameters: the pH of the solutions at the leaching stage and the liquid-to-solid (mL/g) ratio during the digestion stage. It was discovered that the efficiency of metal solubilization was positively impacted by changing the liquid-to-solid ratio from 1 to 5 mL/g. (Figures 2 to 5) illustrate this, with each curve essentially rising. With a step of 0.5, the curves strictly increase between L/S = 1 and 2 and between 2.5 and 4 over the pH range of 1 to 2.5.

As L/S increases, more moles of HCl are needed to convert the recoverable metal compounds in the slag into water-soluble compounds. The reactions occur more or less fully during digestion, which raises the solubilization efficiency of the metals to be recovered at the leaching stage. This may help to explain this. The solubilization efficiency, however, hardly improves above L/S = 4. According to Harbuck *et al.*, 1991 [6], dissolved metals seem to start precipitating when the acid concentration in leaching solutions rises to extremely high levels, which lowers the yield of metal solubilization.

Therefore, figuring out the L/S ratio at which precipitation starts is essential in our situation. Additionally, the literature suggests that very high acid concentrations will necessitate lengthy digestion periods, which would not be beneficial from an industrial standpoint [5,6,17].

The solubilization efficiency for L/S ratios between 1 and 2.5 are comparatively low when compared to those obtained for ratios between 4 and 5. The digestion process was not completed because the slag contains other ineffective chemical elements that also consume acid, such as calcium, magnesium, etc. Additionally, this explains why the actual amount of acid absorbed is consistently higher than what a stoichiometric model would have suggested [17].

The L/S ratio of 4 mL/g may hold promise because of the encouraging efficiency that can be achieved with this ratio. The efficiency of recoverable metals may decrease if hydrolysis takes place above this ratio and small particles leftovers of insoluble compounds, such as tetragonal $GeO_2$, precipitate out of the solution. Since silicon is not dissolved during leaching, nearly all of the silicon remains in the slag. Silicon may reduce the solubilization efficiency by blocking metals that have a strong affinity for it in the leach residues, particularly germanium.

## IV. Conclusion

Recovering germanium from slag from Gécamines-Lubumbashi plants in the Democratic Republic of the Congo (DRC) was the goal of this study. Chemical analysis of the slag showed a germanium content of 0.01%, accompanied by a content of 2.4% Co, 0.9% Cu, 23.5% Fe, 5.6% Zn. Mineralogical analysis (XRD) revealed that the slag is amorphous and the particles between 1 and 5 mm make up nearly 55% of the slag particles. With an optimum pH of 2 and a S/L ratio of 4 mL/g, the leaching efficiency of germanium was 90%, while that of the associated metals Co, Cu, Zn and Fe reached 80, 80, 86 and 72%, respectively. The leach solutions were easily filtered and no trace of precipitate could be observed in the leach solutions after four months of observation. This confirms that the problem of silica gel was completely avoided by choosing to work in a hydrochloric medium, as not virtually all the silicon contained in the slag could be converted to water-soluble compounds during the digestion phase.

These results are encouraging for the future establishment of a suitable flowsheet for the recovery of the values contained in the leaching solution, paying attention to iron which requires appropriate treatment.

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