

SELECTIVE GERMANIUM RECOVERY FROM FAYALITIC COPPER SLAG USING BIOLEACHING

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Abstract

Fayalitic copper slag (CS) from the reverberatory furnaces is an abundant metallurgical by-product containing trace amounts of critical elements such as germanium (Ge). This study investigates the integration of bioleaching and chemical leaching approach to recover Ge combining the micro-organism of *Bacillus subtilis* pretreatment with selective oxalic acid leaching in the presence of Hydrogen peroxide (H_2O_2). The characterization of CS used XRF, XRD, and SEM-EDS confirmed that the slag is predominantly composed of fayalite (Fe_2SiO_4) and magnetite (Fe_3O_4) with Ge dispersed within the silicate matrix. Bioleaching effectively mobilized Ge subsequently oxalic acid and H_2O_2 leaching selectively dissolved Ge into solution while iron (Fe) precipitated as ferric hydroxide ($Fe(OH)_3$). Kinetic leaching analysis revealed that Ge dissolution is diffusion-controlled with optimal Ge recovery of 50% achieved at 1.5 M oxalic acid over 30 minutes at fixed 25°C and 150rpm. After adding H_2O_2 , Ge recovery reached 28%, indicating that the system reached equilibrium and further dissolution slowed down recovery. This combined method demonstrates an environmentally friendly and efficient strategy for Ge recovery. Further work should focus on optimizing the leaching conditions and developing scalable recovery methods to make the residues of Fe-Si-rich to enhance resource utilization of the material for sustainability and reduce environmental impacts of critical metals lost.

Keywords: Bioleaching; copper slag; germanium

1. INTRODUCTION

Copper smelting using reverberatory furnaces generates large quantities of copper slag (CS) dominated by iron–silicate phases, mainly fayalite (Fe_2SiO_4) [1,2]. These slags are typically glassy and rich in FeO and SiO_2 , with trace elements such as Ge, Ga, In, and Zn incorporated within the silicate matrix [3]. Germanium is a critical element used in fibre optics, infrared optics, photovoltaic technologies, and its' limited primary supply has increased interest in recovery from secondary sources [4]. However, strong bonding within the fayalite structure makes Ge extraction challenging. Conventional methods are energy intensive and environmentally unfavorable [2]. Thus, prompting an interest in alternative approaches such as biological processes to enhance metal recovery from metallurgical slags.

2. METHODOLOGY

Copper slag (CS) was collected from a smelter in Katanga Province from Democratic Republic of Congo (DRC). Approximately 1 kg of CS was dried at 25 °C for 24 h and split using a spinning riffler into representative portions. A 500 g sample was subjected to particle size analysis using screens ranging from 2.0 mm to 0.075 mm, with less than 0.106 mm fraction selected for SEM-EDS analysis (JOEL JSM-840). A separate portion (200 g) was further split and selected samples were pulverized to less than 0.106 mm for XRF (Rigaku ZSX Primus II) and XRD (Rigaku Ultima V) analysis. The remaining material was recombined other 500 g was

milled for 2 h and sieved to achieve 100% passing 106 μm . A representative 100 g sample was used for bioleaching experiments.

For bioleaching 100 g of CS was mixed with 200 mL deionized water and 20 mL *Bacillus subtilis*, then stirred at 150 rpm and 25 °C for 24 h. A 20 mL aliquot was filtered for SEM-EDS analysis. The bioleached slurry was then treated with oxalic acid (0.5–2 M) at pH 4–5 (adjusted using NaOH) with samples collected every 30 min and analysed by ICP-OES. After leaching at 2 M, 15 mL of 30% H_2O_2 was added to oxidize Fe and promote its precipitation, while Ge remained in solution as a Ge–oxalate complex. The solid residue was analysed using XRD and SEM-EDS, and the leachate was analysed by ICP-OES to determine Ge recovery.

3. RESULTS

Characterization of Copper slag (CS) prior to bioleaching and kinetic leaching determines its elemental composition. The x-ray diffraction (XRD) identifies the sample mineral phases while the x-ray fluorescence (XRF) identifies its elemental composition, and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) examined the surface morphology and elemental distribution. There leachate elemental concentrations are measured using inductively coupled plasma of optical emission spectroscopy (ICP-OES). Bioleaching experiments were performed using *Bacillus subtilis* followed by oxalic acid leaching at pH 4–5 controlled using NaOH. After which leached residue were analysed by XRD and SEM-EDS while the leachate solutions were analysed using ICP-OES to determine Ge recovery.

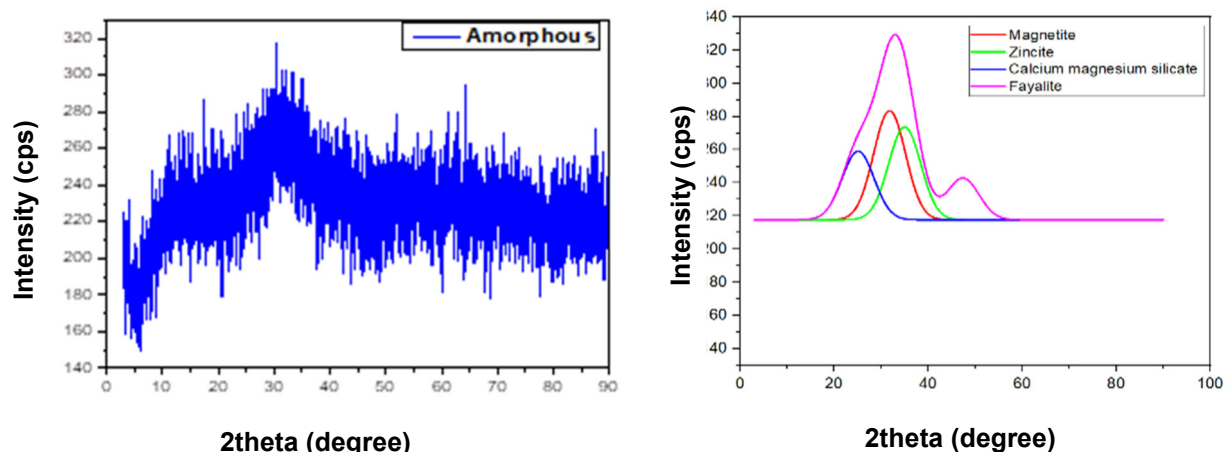


Figure 1 XRD pattern of CS sample and pattern decomposed of CS

The mineralogical composition of CS varies depending on furnace type and cooling rate. A reverberatory furnace slag is typically dark, glassy and mainly composed of fayalite and magnetite with occasional quartz [3]. An Amorphous CS sample using Origin software decomposition of **Figure 1** confirmed the presence of fayalite, magnetite, zincite and calcium magnesium silicate phases as illustrated in **Figure 1** of XRD analysis. The phase compositions present a correlation to the XRF elements within CS.

Table 1 XRF results of copper slag sample

Element	Fe	Si	Zn	Ca	Al	Cu	Mg	K	Co	Pb	Mn	S	Ti	Ni	Ba	P	Ge
%	22.41	10.97	16.20	7.90	2.21	1.91	1.03	0.74	0.61	0.55	0.32	0.31	0.27	0.19	0.17	0.13	0.04

These elemental composition phases correspond to the XRF analysis. There XRF results indicated that the dominate elements were Fe (22.41%), Zn (16.20%), Si (10.97%) and Ca (7.90%) with smaller concentrations of Aluminium (Al), Copper (Cu), Manganese (Mg) and trace elements of Ge (0.04%). These results agreed with previous studies reported in CS containing significant amounts of Cu, Co and trace metals including Ga,

Ge and Sb [5]. Showing the comparison of SEM analyses provided for the elemental and surface morphology of properties present in CS.

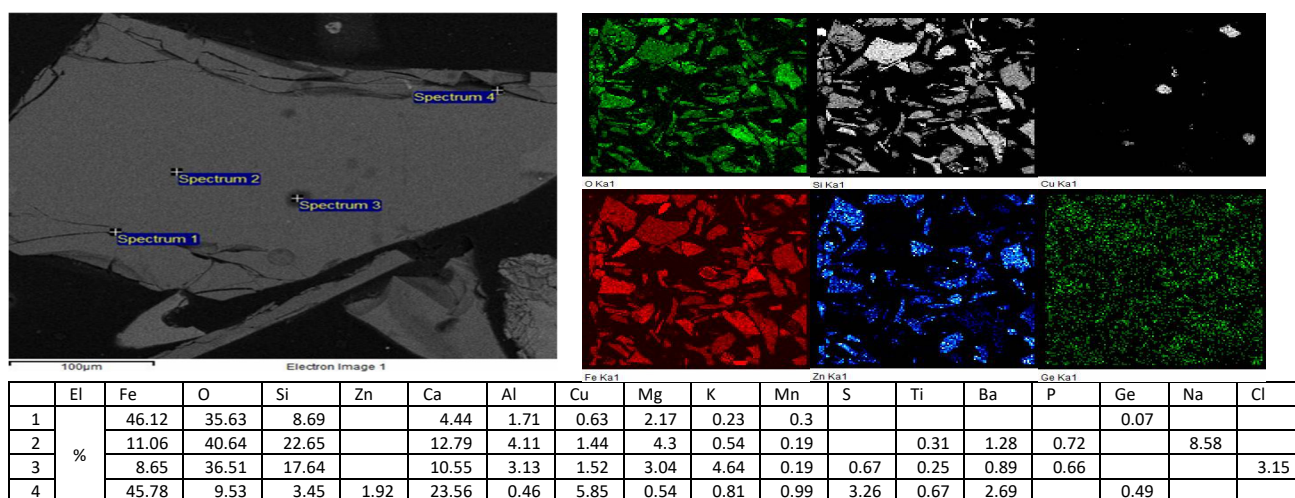


Figure 2 SEM microstructure of CS sample and EDS spectra of CS

The SEM-EDS analysis shown in **Figure 2** further confirmed the elemental distribution within the slag matrix. However, Ge was difficult to detect due to its very low concentration; therefore, an elemental mapping was used to identify its distribution. The mapping results indicated that Ge occurs in scattered regions within the fayalite matrix rather than in distinct high-intensity peaks, confirming its low abundance and strong association with iron silicate phases. Such encapsulation of trace metals within fayalite and magnetite structures has been widely reported for metallurgical slags [6]. Thus, it is essential to comprehend slag chemical characteristic and generation methods in order to maximize slag treatment to enhance the resource recovery and reduce environmental effect [7,1,8,2]. Bioleaching is beneficial in slag treatment not only reducing environmental hazardous materials but to lower energy consumption, low cost and high utilization of metal recovery making it environmentally friendly.

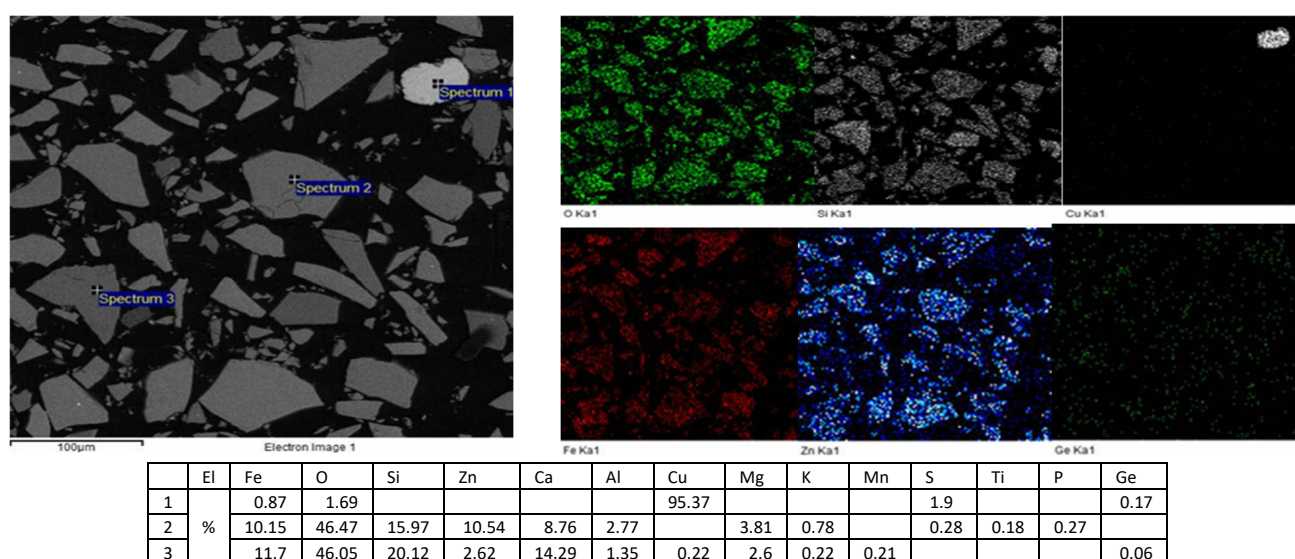


Figure 3 SEM microstructure and EDS spectra of Bioleached CS sample

Following CS characterization, bioleaching experiments were conducted to evaluate Ge release from the fayalite matrix. As shown in **Figures 3**, *Bacillus subtilis* enhanced Ge mobilization with SEM-EDS mapping

indicating more defined Ge distribution after 24 h compared to initial state. The pH decreased from 9.2 to 8 due to microbial organic acid production confirming active interaction with slag. EDS spectra showed increased Ge intensity, indicating improved liberation while Fe and Si remained largely in the residue due to the stability of fayalite structure. Kinetic modelling further indicated the governing dissolution behaviour for Ge recovery.

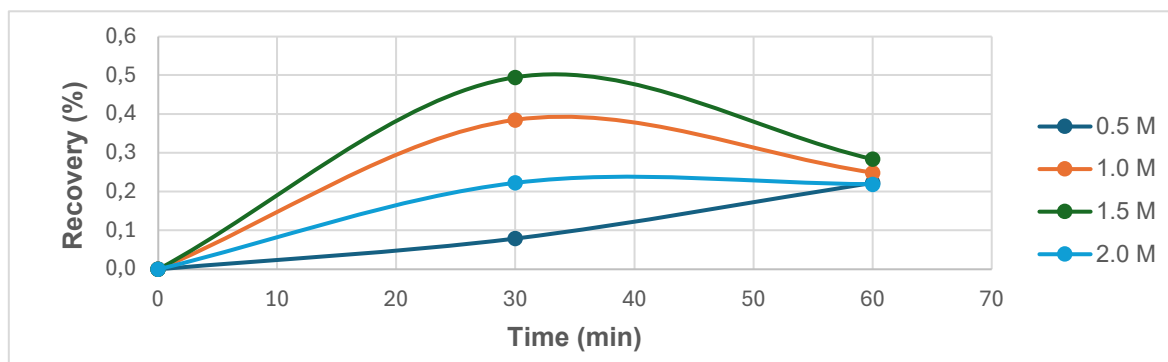


Figure 4 Recovery of Ge ion

The effect of oxalic acid concentration on Ge recovery is presented in **Figure 4**. The dissolution experiments were performed at a fixed temperature of 25 °C with oxalic acid concentrations ranging from 0.5 to 2 M while maintaining pH between 4 and 5. The results indicate that Ge recovery increased rapidly during the first 30 minutes and then decreased after 60 minutes. The optimal recovery of approximately 50% Ge was obtained at 1.5 M oxalic acid within 30 minutes. At higher concentrations or longer reaction times recovery decreased, with the lowest recovery of approximately 21% observed at 2 M after 60 minutes. These results suggest that increasing acid concentration enhances dissolution only up to an optimal point, after which secondary reactions or diffusion limitations reduce recovery efficiency.

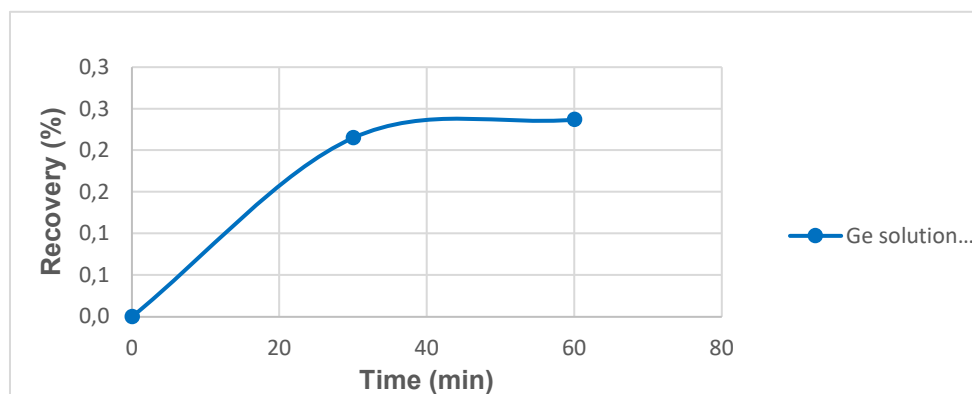


Figure 5 Recovery Ge solution using H₂O₂

The diffusion-controlled behaviour is further illustrated in **Figure 4**, where Ge recovery is plotted against time for oxalic acid concentrations between 0.5 to 2 M. This behaviour supports the hypothesis that Ge dissolution is primarily controlled by diffusion within the slag matrix rather than by chemical reaction kinetics [9]. The addition of hydrogen peroxide (H₂O₂) further improved separation between Fe and Ge, as shown in **Figure 5**. In the presence of 2 M oxalic acid and H₂O₂, Ge recovery increased steadily over 60 minutes, reaching approximately 28%. The oxidizing conditions promoted the conversion of Fe²⁺ to Fe³⁺, resulting in the formation of insoluble Fe(OH)₃ precipitates which removed Fe from solution and minimized interference with Ge dissolution [10]. Consequently, Ge remained in the aqueous phase as a soluble oxalate complex. These results demonstrate that using 2 M oxalic acid with oxide addition is an effective strategy for enhancing Ge recovery while simultaneously reducing Fe contamination.

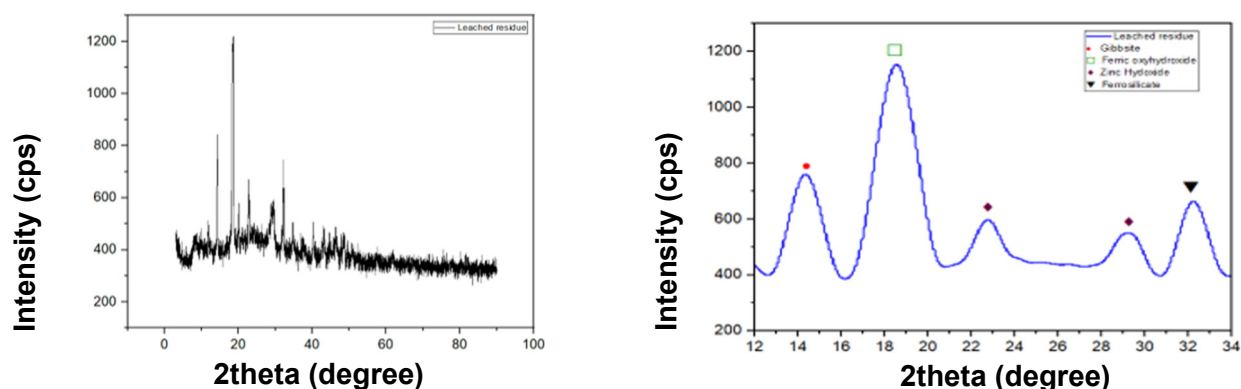
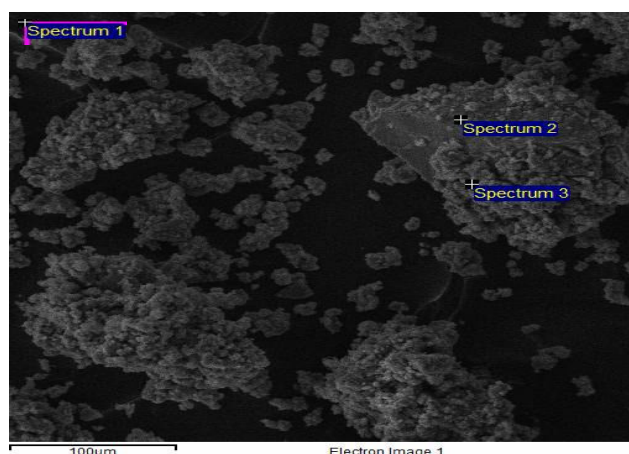


Figure 6 XRD Leaching residue

Figure 6 shows that the initial CS residue retains crystalline peaks despite its partially amorphous nature, consistent with Fe–silicate slag stability [11]. After treatment, **Figure 6** indicates formation of $\text{FeO}(\text{OH})$, $\text{Al}(\text{OH})_3$, $\text{Zn}(\text{OH})_3$, and residual Fe_2SiO_4 . The dominance of $\text{FeO}(\text{OH})$ confirms oxidation of Fe^{2+} to Fe^{3+} and precipitation of ferric hydroxide while reducing Fe_2SiO_4 intensity indicates partial matrix breakdown, enabling Ge release without complete dissolution [5]. These XRD results confirm that oxalic–peroxide treatment promotes Fe precipitation and selective Ge liberation, consistent with SEM observations of Fe retention and Ge release.



	El	Fe	O	Si	Zn	Ca	Al	Cu	Mg	K	Mn	S	Ti	Ba	P	Ge
1	%	13.16	46.93	12.74	8.36	5.67	2.53	0.58	1.73	0.71			0.46		0.29	
2		12.61	40.51	18.30	7.44	9.20	3.14		2.24	0.72		0.23	0.44		0.26	
3		23.82	20.93	15.92	15.36	15.38	2.32	0.68	0.98	1.26			1.11		0.29	

Figure 7 SEM-EDS of leached residue

The illustrates of SEM-EDS in **Figure 7** results showed a dominant percentage of Fe and Si in spectrum but no detectable Ge together with XRD patterns that highlight $\text{FeO}(\text{OH})$ and Fe_2SiO_4 as the main phases in the leach residue in **Figure 6**. This indicates that Fe remained largely in the solid phase, while Ge was selectively dissolved into the solution. The persistence of Fe-silicate spectrum suggests that fayalite underwent only partial decomposition under the applied leaching conditions. The formation of insoluble Fe compounds and the selective mobilization of Ge into the solution align with expected behaviour in oxalic acid and H_2O_2 leaching system [11]. This supported the observed distribution of elements between the residue and the solution. Thus, the overall combination of SEM-EDS and XRD data reflects a selective leaching process, where Fe remains trapped in solid silicate or oxyhydroxide network while Ge is mobilized into solution by soluble oxalate complexes explaining its absence within the solid residue.

4. CONCLUSION

Fayalitic copper slag from a reverberatory furnace represents a viable secondary source of germanium (Ge). The characterization using XRF, XRD, and SEM-EDS confirmed that the slag is dominated by Fe_2SiO_4 and Fe_3O_4 , with trace Ge distributed within the silicate matrix. Integrated bioleaching using *Bacillus subtilis* followed by oxalic acid leaching in the presence of H_2O_2 enabled selective Ge mobilization into solution. While Fe remained as ferric hydroxide in the residue. Germanium dissolution was found to be diffusion-controlled with the optimal recovery at 1.5 M oxalic acid within 30 minutes at 25 °C. Recovery increased with acid concentration and stabilized at approximately 28% indicating equilibrium limitations. These results demonstrate that combining microbial activation with mild chemical leaching provides an effective and environmentally sustainable approach for Ge recovery from metallurgical slags. Further work should focus on process optimization, scale-up and downstream Ge recovery techniques.

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