Characterisation of a Secondary Copper Slag Produced Through Aluminothermic Process

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Abstract— Due to the limited availability of Germanium and its high demand driven by the expanding technology sector, secondary sources have become appealing alternatives. This paper explores the use of copper slag as a source of germanium, employing aluminothermic reduction for extraction. The study investigates the recovery of germanium from fayalitic slag by analysing the characteristics of the copper slag, the impact of varying basicity on germanium recovery, the feasibility of recovery through off-gas, and the effect of different aluminium amounts on recovery at 1350°C with a residence time of two and a half hours. A bench-scale furnace was utilized for the smelting process. Characterization of the raw slag involved techniques such as XRF, XRD, SEM-EDX, and AAS, while the products were analysed using the same methods, excluding XRF. Statistical tools were employed to analyse the results. The findings revealed that the slag was primarily amorphous and fayalitic, with a minor presence of magnetite. Notably, germanium recovery in the metal improved significantly with slight increases in both basicity and aluminium content, demonstrating a consistent trend of enhanced recovery with higher aluminium amounts.

Keywords— Aluminothermic Reduction, Copper Slag, Germanium Recovery, Pyrometallurgy, Metal Refining.

I. INTRODUCTION

This paper provided light on the recovery of germanium from fayalite copper slag using aluminium as a reductant. Germanium has always been very important to the industry as it is highly demanded in different technologies. Hence the recovery of this metal is very important not only because of its market price but also because it forms part of heavy metals that are very dangerous to the environment on a health level [1]. Recovery of heavy metals from the slag keeps the environment away from different types of pollutions as well as makes the slag dumb harmless [2]. One of the most pressing issues confronting human society in our century is resource scarcity. Improving living standards, along with a world population projected to reach 9 billion by 2050 and possibly 10 billion by the end of the century, are likely to push resource demand into uncharted territory. Mineral resources such as Cu, Co, Ni, Ge, and Fe, common metals in modern culture, are one of these resources [3].

Germanium is widely recognized for its role in semiconductors, particularly in transistors and integrated circuits, but its transparency at certain wavelengths also makes it valuable in infrared optical systems. The germanium industry has gained significant attention due to advancements in telecommunications and computing, which have increased the demand for germanium and its derivatives [4]. Copper slag, a by-product of copper production, is now regarded as a source of various metals that can be recovered through a range of techniques. It is estimated that for every ton of copper produced, 2 to 3 tons of slag are generated. The accumulation of copper slag over the years has created waste management challenges, as it is classified as hazardous waste due to its heavy metal content. Consequently, environmental policies aimed at copper production focus on reducing slag generation and promoting the recycling of slag into valuable products [5]. In pyrometallurgy, several reduction processes exist, including carbothermic reduction, where carbon facilitates the reduction, and metallothermic processes, where a metal reduces an oxide to yield pure metal or matte. This study investigates the recovery of germanium using pure aluminium as a reductant. With many ore bodies being depleted, secondary sources such as scraps, slag, and effluents are increasingly processed for metal recovery. Slag, a by-product of pyrometallurgical smelting, often contains metals that can be extracted, making it a viable secondary source [6]. This research specifically targets the extraction of germanium from fayalitic copper slag, which serves as an alternative supply due to the trace amounts of germanium in primary sources. By utilizing copper slag, pyrometallurgical smelters can minimize their environmental impact. Numerous studies indicate that valuable metals are often entrained in slag during melting processes [7]. As a result, there have been concerted efforts to recover these metals and repurpose slag for industrial use, thus enhancing sustainability. The iron oxide and silica (SiO_2) content in fayalitic slags from copper smelting typically ranges from 30% to 40% [6]. Recovery methods for metals from fayalitic slag, including flotation, magnetic separation, direct reduction, and other techniques such as smelting and sulfation roasting, have been investigated in recent studies [8].

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II. METHODOLOGY

A. Material and equipment

The copper slag sample that was utilized in this investigation came from the Societe de Traitement Du Terril de Lubumbashi Ltd, a copper smelter located in Lubumbashi, Katanga province, in the Democratic Republic of Congo. Aluminum 99.8%-powder-25 μm sourced from the pots of breweries; was used as reducing agent. Calcium oxide (56.08%) sourced from the Department of Metallurgy at the University of Johannesburg; was used as flux and Argon 99.96 % from Afrox.A THM 15 vertical furnace equipped with an alumina tube was used for the experiment. X-ray spectroscopy (XRF) Rigaku Primus II for elemental analysis, X-Ray diffraction spectroscopic Rigaku Ultima IV for mineralogical analysis, Scanning electron microscopy (SEM) TESCAN for morphological analysis.

B. Experimental Procedure

Approximately 1.5 kg of copper slag was split into two using the jones riffler, then one fraction of the sample was taken to the spinning riffler for further sample splitting of which about 75 g was obtained and taken for characterization and experiment. Prior to analysis, about 75 g of the representative sample was further split into 7.5 g and enough sample was used for the characterization. The remaining samples were recombined, homogenized, pulverized and used for experiments. The raw slag was mixed with 5 % of aluminum powder and lime to adjust the basicity to unity. To improve homogenization, the mix was milled for 15 minutes. To avoid any oxidation, argon was blown into the furnace during the entire duration of the experiment. Experiments were conducted at 1400 ℃ and kept at this temperature for two hours. During the smelting at the mentioned temperature, the off gas was bubbled into the water mixed with KI using a vacuum to collect Germanium gas and collected as an oxide and analyzed.
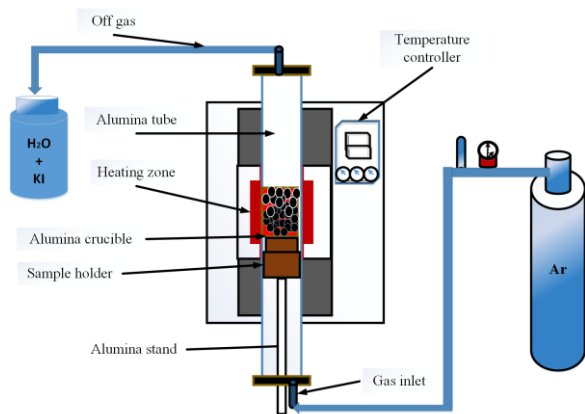

Fig. 1:: Experimental setup plotted using Visio 2013

III. RESULTS AND DISCUSSION

A. Characterization results of the as received slag prior to the smelting process

Chemical composition of the raw slag X-ray Fluorescence (XRF)

For the major constituent elements, the XRF results are summarized in the table below. The analysis that was done on the material that was received yielded these XRF results. The XRF apparatus is utilized to ascertain the sample's elemental composition, as was indicated in the methods section.

TABLE 1: RAW SLAG XRF ANALYSIS

Compound	%Mass
MgO	2.93
Al_2O_3	5.16
SiO_2	32.85
SO_3	1.24
CaO	17.45
FeO	23.68
Co_2O_3	2.03
CuO	3.88
ZnO	4.93
GeO_2	0.01
Balance	5.84

Phase mineralogic of the as received cupper slag using the X-ray diffraction spectroscopy

The peaks overlapped because of the amorphous nature of the slag. Then, using OriginPro software 9.0, a deconvolution was required to see the true peaks. According to Figure 10, the decomposition was carried out at angles of 43 and 51 degrees, respectively.
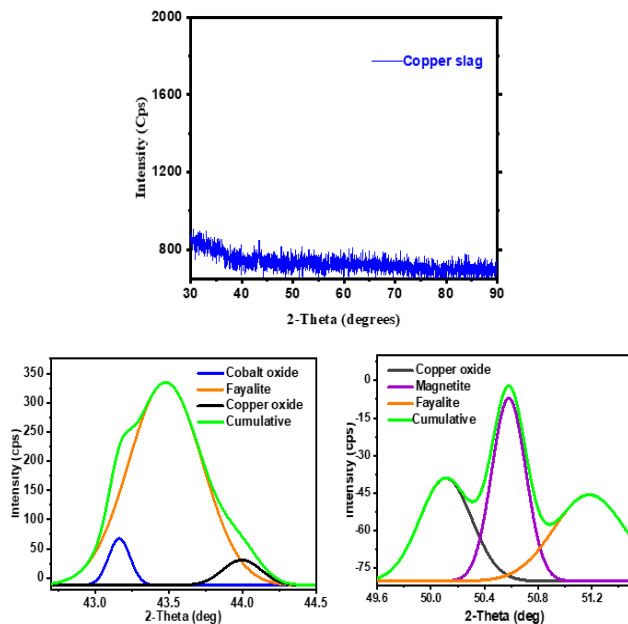

Fig. 2: XRD results of the as received slag prior to deconvolution

During the study, peaks including fayalite, chalcopyrite, magnetite, copper oxide, and cobalt oxide were found at the two theta values.

Morphology and mineral distribution of the as received cupper slag using SEM-EDX

Fig. 3 depicts the structure of slag. There is an uneven distribution of components throughout the slag that work to balance one another out.
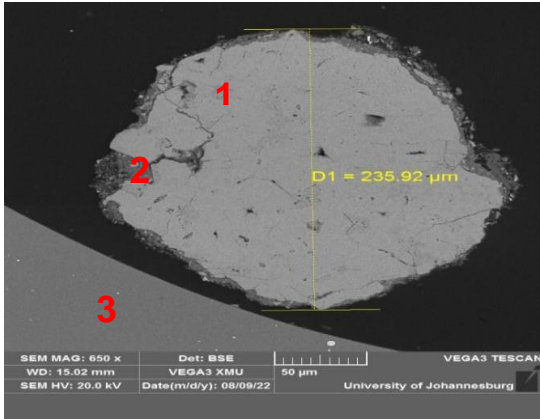

Fig. 3: SEM-EDS result of the raw slag

The quality of Ge in the slag is poor which agrees with the grade of the Ge found in the XRF and AAS results which are very low. The mapping in Figure 4 also proves that as the Ge distribution throughout the slag is very low and dispersed poorly.
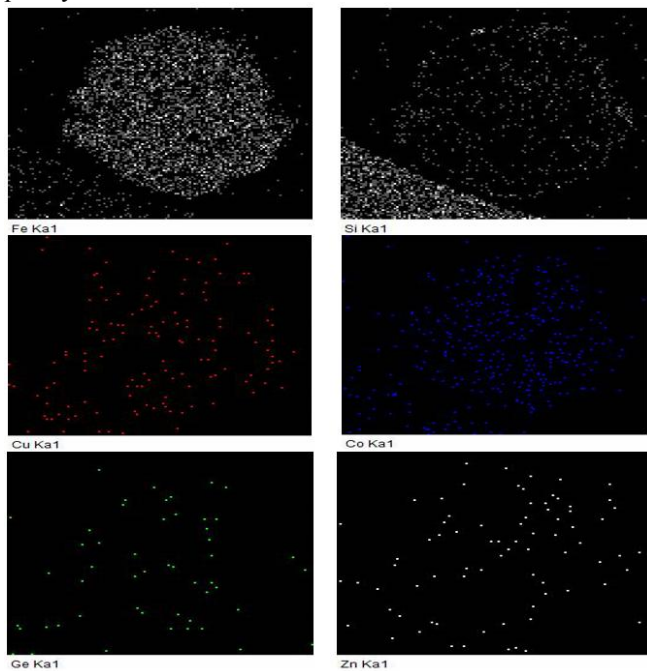

Fig. 4: Mapping of the As-received sample.

TABLE II: SEM-EDS RESULTS OF THE RAW SLAG

Spec No	Mg	Al	Si	S	Ca	Fe	Cu	Zn	Ge
Spec 1	-	3.6	7.7	-	1	86	1	1	0.06
Spec 2	8.1	6.9	50	-	25	8.9	1	0.3	0.03
Spec 3	4.3	28	45	-	1.2	18	3	0.9	0.03

The combination of SEM results confirms that the raw slag is a fayalitic slag. The germanium is present in the sample as GeO2 in the silicate matrix and is considerably low. Therefore, because of the low amount of germanium in the raw copper slag sample, it requires a more selective pyrometallurgical concept with well-chosen and targeted variables such as activities and reducing conditions.

Atomic Adsorption spectrometer (AAS) of the as-received sample

To get the grade of the sample, the slag was digested using HCl. After obtention of the results, the results agreed with the XRF results when looking at the grade of Germanium. In XRF results, Ge has a grade of 0.02% whereas in the AAS results of the feed Ge has a grade of 0.01715 which is nearly the same if not the same.
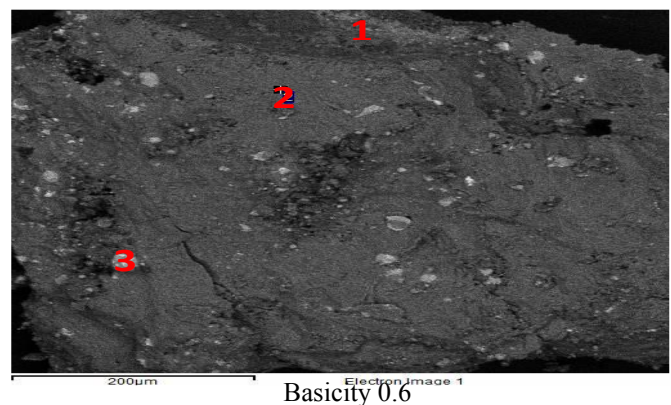
TABLE III: AAS RESULTS OF THE AS RECEIVED SAMPLE

	Head samples	
SAMPLE ID	CONC (mg/L)	Grade (%)
Feed	3.76	0.017

B. Characterisation results of the products

The reduction process was performed in conditions already set and both smelting products were analyzed using the same analytical techniques as the as received sample.

Morphology and mineral distribution of the secondary slag at different basicity

Below is the microstructure of the secondary slag after SEM-EDS analysis performed on the said slag at different basicity.
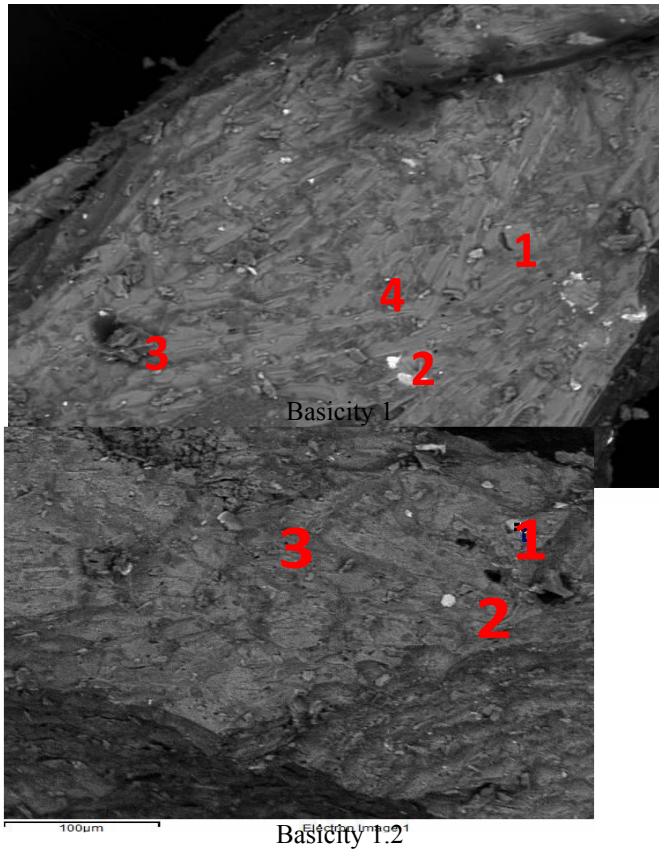

Basicity 0.6

The metallic phase consisted of a fine layer of metals surrounding the slag. The hardness of this layer coupled to its fine thickness presented difficulties to scratching. It was therefore decided to separate the metallic phase for SEM analysis. Instead, the bloc was crashed into small pieces to fit the aluminum pin for the analysis of the metal-covered surface by SEM. The results obtained are presented below at various basicity. The concentration of metals at specific spots in the metallic layer is seen to have increased because of change in reductant amount and basicity adjustment.

Fig. 5: Microstructure of the secondary copper slag at various basicity

TABLE IV: SEM-EDS RESULTS OF THE SECONDARY SLAG AT BASICITY OF 0.6

SpecNo	Fe	Zn	Mg	Cu	Al	Si
Spec 1	0.45	-	013.8	0.45	63.2	0.97
Spec 2	-	-	10.8	-	46.6	22.2
Spec 3	14.5	1.17	0.46	16.7	3.21	62.3

TABLE V: SEM-EDS RESULTS OF THE SECONDARY SLAG AT BASICITY OF 1

SpecNo	Fe	Ge	Mn	Cu	Al	Si
Spec 1	2.35	-	0.16	0.21	0.5	94.6
Spec 2	-	-	-	-	0.8	98.2
Spec 3	-	-	-	-	35.1	31.9
Spec 4	-	-	-	-	67.3	5.54

TABLE VI: SEM-EDS RESULTS OF THE SECONDARY SLAG AT BASICITY OF 1.2

Spec No	Fe	Mn	Mg	Ca	Si
Spec 1	22.15	0.14	0.4	2.5	61.2
Spec 2	-	-	0.43	36.4	16.7
Spec 3	-	-	35.1	35.1	15.6

From basicity of 0.6 in 5 to basicity of 1, the difference can already be seen as the slag quality differs as the mattes entrained in the secondary slag are fewer in basicity of 1 than they are in basicity of 0.6. the secondary slag structure at basicity of 1.2, there was much difference between the slag highlighted below and the secondary slag at basicity of 0.6 and 1.

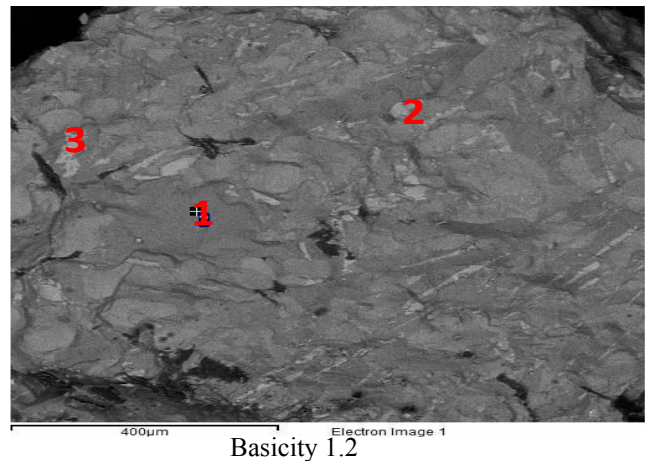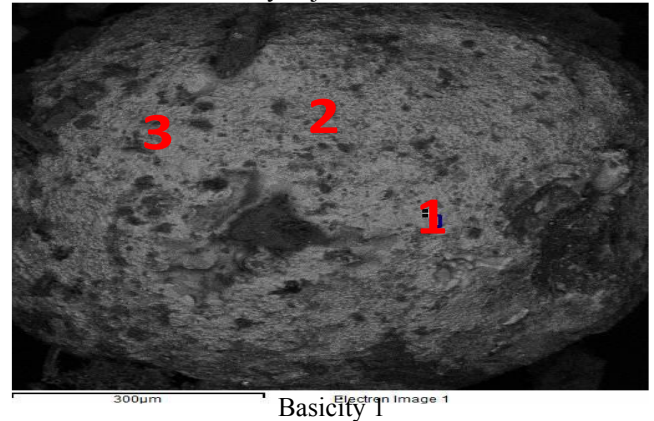*Morphology and mineral distribution of the metal*

Fig. 6: SEM-EDS result of the matte at basicity at different basicity

The quality of the different metals produced from the smelting process conducted at 1350 ºC in a horizontal alumina tube furnace is shown above and the spectrums detected are displayed with their elemental composition in the said table 7, 8, 9.

TABLE VII: SEM-EDS RESULTS OF THE MATTE AT BASICITY OF 0.6

SpecNo	Fe	Ge	Cu	Si	Co
Spec 1	5.18	0.12	87.3	5.47	0.4
Spec 2	61.7	0.02	3.14	30.4	4.36

TABLE VIII: SEM-EDS RESULTS OF THE MATTE AT BASICITY OF 1

Spec No	Fe	Ge	Cu	Co
Spec 1	1.75	-	22.9	0.13
Spec 2	8.21	0.13	79.4	0.76
Spec 3	1.84	-	2.28	0.4

TABLE IX SEM-EDS RESULTS OF THE MATTE AT BASICITY OF 1.2

Spec No	Fe	Ge	Cu	Co
Spec 1	2.12	0.04	55.8	0.44
Spec 2	3.74	-	70.1	0.6
Spec 3	2.04	0.04	55.4	0.4

Phase mineralogic of the products at different basicity

To be able to see the difference in the phases at different phases, the XRD results of the products were plotted using OriginPro 9.0, the results are plotted as follows the raw slag at the bottom, followed by the secondary slag, the metal at the top of the graph, respectively at each basicity.
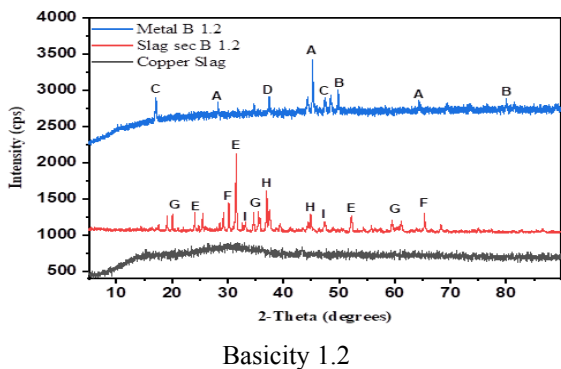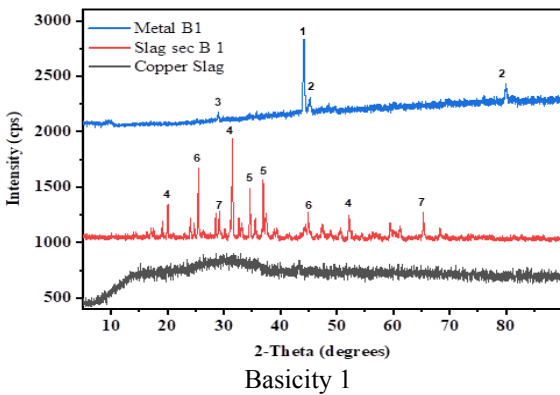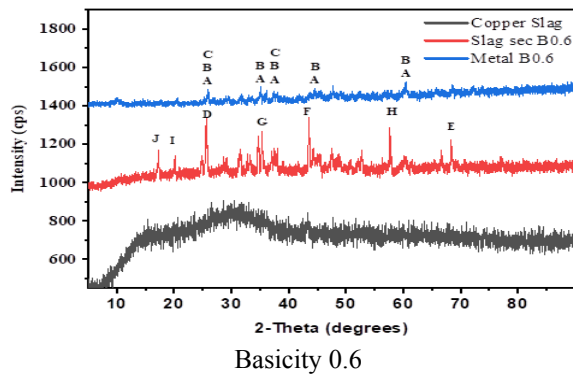

Basicity 0.6

Basicity 1

Basicity 1.2

Fig. 7: XRD patterns of the raw slag, secondary slag, and the metal at various basicity

At a basicity of 0.6, separation proved challenging. While the difference in shape between the secondary slag and the

metal was minimal, a notable distinction existed between the raw slag and the smelting products. In contrast, at a basicity of 1, a significant difference emerged among the matte produced, secondary slag, and as-received slag. The metal pattern indicated that separation was more effective under these neutral conditions, where the feed was neither too acidic nor too basic. This balance reduced the viscosity of the slag, facilitating better separation. At a basicity of 1.2, although the separation improved compared to that at 0.6, it was still not as effective as at a basicity of 1. The following are the legends of the graphs in Fig. 7.

Basicity 0.6

A: Magnesium Iron Silicate ($Mg_{0.56} Fe_{0.44}$) O Si O_2
B: Magnesium Iron Silicate [Mg Fe (SiO_4)]
C: Aluminium Iron Nickel ($Al_{75} Ni10 Fe_{15}$)
D: Sodium Hydrogen Phosphate Hydrate ($Na_2HPO_{3.5}H_2O$)
E: Silicon Oxide (SiO_2)
F: Lead Silicate (Pb_3SiO_5)
G: Iron Silicate Oxide Fayalite ($Fe_2 Si O_4$)
H: Iron Oxide Hematite ($Fe_2 O_3$)
I: Germanium Lanthanum Manganese (La Mn Ge)
J: Aluminium Oxide (Al_2O_3)

Basicity 1

1: Iron Sulphide (Fe_7S_8)
2: Aluminium Copper ($A_{13.892} Cu_{6.10808}$)
3: Aluminium Cobalt (Al_3Co)
4: Iron Oxide (Fe_3O_4)
5: Copper Nickel Tin Sulphide ($Cu_2 Ni Sn S_4$)
6: Calcium Aluminium Silicate [$Ca_2Al (AlSiO_7)$]
7: Calcium Aluminium Oxide (Ca Al_4O_7)

Basicity 1.2

A: Iron Silicon (FeSi)
B: Copper Sulphide (Cu_2S)
C: Arsenic Copper Oxide Hydrate ($As_2O_{54}CuO.7H_2O$)
D: Aluminium Copper ($Al_{3.892} Cu_{6.10808}$)
E: Silicon Oxide (SiO_2)
F: Iron Oxide (Fe_2O_3)
G: Calcium Aluminium Silicate ($Ca_2Al_2SiO_7$)
H: Calcium Aluminium Oxide ($CaAl_4O_7$)
I: Calcium Aluminium Oxide [Ca $(AlO_2)_2$]

Atomic Adsorption spectrometer (AAS) of the solution collected from the fumes

The increase in basicity under more reducing conditions led to increasing activity coefficients of all oxides being. Therefore, with further addition of aluminum powder the reduction of Germanium oxide has been enhanced. Consequently, germanium recovery increased as well.

TABLE X: AAS RESULTS OF THE SOLUTION RECEIVED FROM THE FUMES

	Ge recovery in the off gas		
Sample ID	Basicity 0.6	Basicity 1	Basicity 1.2
Conc (mg/L)	0.2849	0.4799	0.4930

IV. CONCLUSION

To summarize, before the real experiment was carried out in the laboratory, the lime and the reductant underwent various types of characterizations. When the makeup of the samples was known, stoichiometric calculations were made to determine the proper amount of copper slag, lime, and aluminum to add while considering the size of the crucible that would be employed. The sample was ready and fed into the alumina tube furnace at a temperature of 1350 ºC for 2h30 minutes after the parameters were known. Following the smelting process, the sample was again analyzed using sample analytical techniques that were used on the raw slag to determine how the composition and structure of the metal produced as well as the secondary slag had changed. The discussion part of the report will go into detail about the outcomes that were just mentioned. The analysis of the dissolved head sample, solution recovered from the fumes was done using XRF, XRD, SEM-EDX and AAS. The results from each analytical technique are shown above.

As a result, the findings enabled the following conclusions to be taken, and the following suggestions were made regarding the methodology and potential future research areas:

• The XRD results revealed that the slag was mainly amorphous and dominantly composed of the fayalite phase with magnetite, suggesting that FeS was oxidized to FeO and that FeO was then partially oxidized to Fe_3O_4. There was also cobalt oxide and copper oxide. These findings were enhanced by high levels of Fe, Si, Cu, and Co that the XRF study revealed.

• The highest recoveries were obtained at high basicity and higher reductant amount at a fixed temperature of 1350 °C for a fixed time of 2h30 minutes. At lowest basicity which in this case was the basicity of the slag, the recoveries of germanium and the matte were low since the separation between the slag and matte was difficult regardless of the temperature due to the slag being more viscous. Nevertheless, increasing the basicity made the separation very easy as the viscosity of the slag was decreased by adding more lime to the slag.

• The microstructure of the matte differed significantly as the basicity increased from acidic to basic. At the basicity of 0.6 the matte was found to be dissolved into the slag which proved that the separation was not easy in acidic environment. But as the basicity increased from 0.6 to 1 then to 1.2, the quality of the matte improved and the separation seemed to be easy as shown in the SEM-EDX results.

ACKNOWLEDGMENT

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