ALUMINOTHERMIC PROCESS FOR GERMANIUM RECOVERY USING FAYALITE COPPER SLAG

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Abstract

Because of a limited source of germanium and its high demand caused by growing technology industry, secondary sources become attractive and suited alternatives. In the present paper copper slag containing germanium was used as source and aluminothermic reduction was adopted as mode of reduction. To achieve the recovery of germanium from fayalitic slag, characterization of the as received copper slag, effect of varying basicity on Ge recovery and feasibility of Ge recovery through off-gas, effect of varying aluminium amount on Ge recovery at 1350°C for a two and half hour's residence time were investigated. A bench scale furnace was used for smelting. The characterization techniques of the raw slag included XRF, XRD, SEM-EDX, and AAS. Products were characterized using same techniques except XRF. The obtained results were analysed using statistical tools. Results showed that the slag was amorphous, predominantly fayalitic with the presence of low amount of magnetite. The highest recoveries of germanium in the metal increased significantly with slight increase of both the basicity and aluminium. The same behaviour was observed when the aluminium amounts increased, the recoveries increased significantly.

Keywords: Germanium, aluminothermic reduction, copper slag, metallurgy

1. INTRODUCTION

The progress noticed in the last decade demonstrates the need of recovering critical metals that take part in different applications. A list of so-called critical metals includes germanium used in the manufacturing of laser emitting diodes, solar panels, mobile phones, wireless systems and military [1-3].Kinetic analysis on carbothermic reduction of GeO_2 for germanium recovery from waste scraps and the reactions paths were thermodynamically explained [4]. The basicity has been found to be influential on the possibility of germanium to escape from the silicate matrix [5] while lime addition has been found to increase the activity coefficient of oxides in the slags [6-7]. The current investigation focused on the influence of basicity, aluminium amounts on the germanium recovery from copper slag and the generation of a model for germanium recovery.

2. METHODOLOGY

2.1 Material and equipment

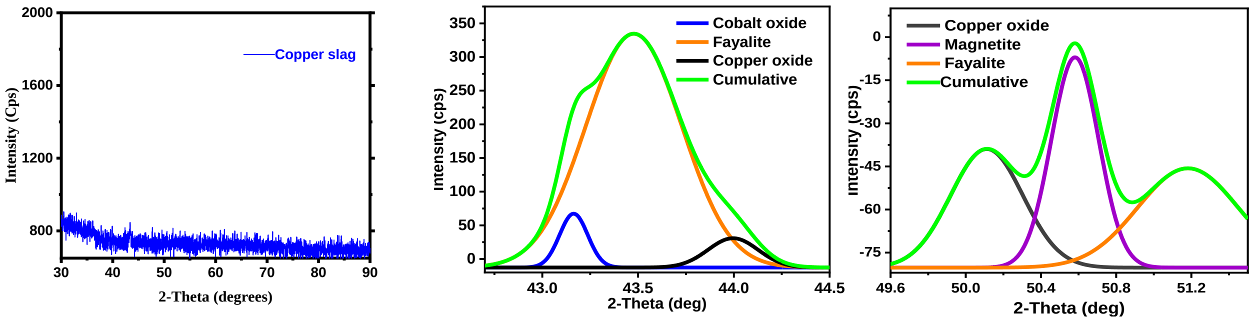
The copper slag sample that was utilized in this investigation came from the Societe de Traitement Du Terril de Lubumbashi Ltd, a copper smelter located in Lubumbashi, Katanga province, in the Democratic Republic of Congo. Aluminium 99.8%-powder-25 µm sourced from the pots of breweries; was used as reducing 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.

2.2 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 characterisation 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 characterisation. The remaining samples were recombined, homogenized, pulverized and used for experiments. The raw slag was mixed with 5 % of aluminium 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 using a vacuum to collect germanium gas and collected as an oxide and analysed.

3. RESULTS AND DISCUSSION

The XRD in **Figure 1a** depicts the mineralogy of the received copper sample slag while **Figures 1b** and **1c** are the decomposed peaks of the raw XRD results. The decomposition was conducted to better identify the minerals peaks that are present in the sample since it is amorphous which made a strait XRD results not easily unpacked.



a **b** **c**

Figure 1 XRD results of the raw copper slag sample

It transpires from the XRD results that cobalt oxide, copper oxide and a bit of magnetite were present, and the presence of fayalite confirmed that the slag was fayalitic.

Figure 2 and **Table 1** provide the SEM results and results analyzed respectively of the raw slag sample while **Table 2** presents XRF results. The combination of SEM and XRF results confirms that the raw slag is a fayalitic slag. The germanium is present in the sample as GeO_2 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.

Table 1 Analysis of the spectra in **Figure 2** (at% average of three points for each phase)

Spectrum	**Mg**	**Al**	**Si**	**S**	**Ca**	**Fe**	**Cu**	**Zn**	**Ge**
1	-	3.61	7.65	0.09	0.68	86.03	1.15	0.72	0.06
2	8.06	6.98	49.99	-	24.88	8.96	0.82	0.28	0.03
3	4.27	27.55	45.43	0.05	1.17	17.61	2.96	0.92	0.03

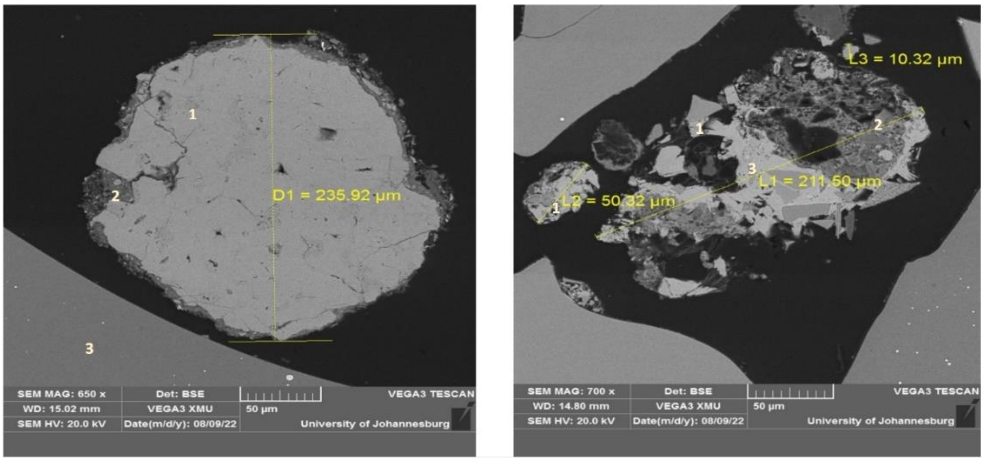


Figure 2 SEM of the copper slag sample

Table 2 XRF analysis of the copper slag sample

Oxide	**MgO**	**Al_2O_3**	**SiO_2**	**SO_3**	**CaO**	**FeO**	**Co_2O_3**	**CuO**	**ZnO**	**GeO_2**	**PbO**	
wt%	2.93	5.16	32.85	1.24	17.45	23.68	2.03	3.88	4.93	0.01	0.38	
Element	**Mg**	**Al**	**Si**	**S**	**Ca**	**Fe**	**Co**	**Cu**	**Zn**	**Ge**	**Pb**	**O**
wt%	1.76	2.73	15.36	0.50	12.47	18.41	1.44	3.10	3.96	0.01	0.33	37.9

Products results are regrouped per basicity used. The correlation between basicity combined with the amount of reductant and the germanium recovery is presented in **Table 3.**

Table 3 AAS results of the solution received from the fumes

Ge recovered through the fumes			
Basicity	Ge concentration (mg/L)	Recovery (%)	Reductant
0.6	0.2849	22.65	2g
1	0.4799	38.15	3g
1.2	0.4930	39.20	4g

Results in **Table 3** show that the increase in basicity under more reducing conditions led to increasing activity coefficients of all oxides being. Therefore, with further addition of aluminium powder the reduction of germanium oxide has been enhanced. Consequently, germanium recovery increased as well.

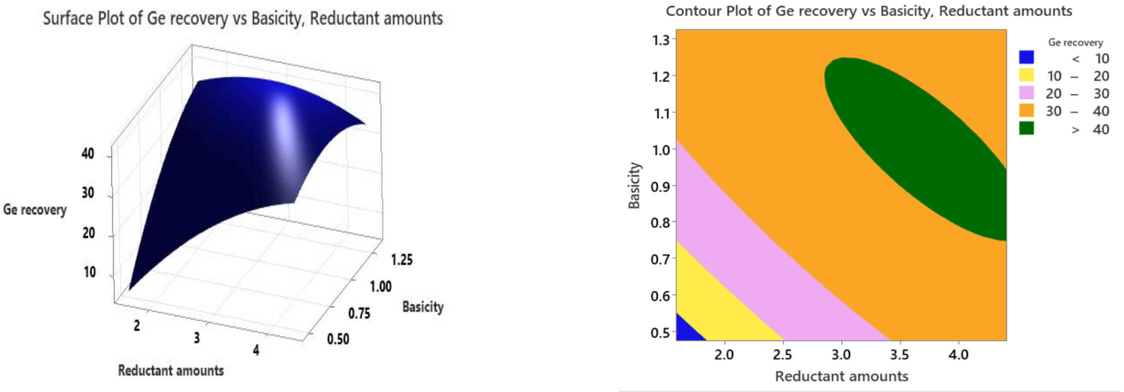


Figure 3 The response surface and contour plots of Ge recovery vs. aluminium amounts (grams)and basicity

Figure 3 below displays the response surface plot and the contour plots which highlighted generally the feasible region in which the highest or desired recovery was achieved.

As it can be seen, the highest recovery of 39.20 % was achieved a basicity range of 1 to 1.2 with an aluminium amount of 3 to 4 g in the green area on the contour plot. This feasible region is in accordance with the results obtained. A mathematical model of the process was generated from the software, and it provides the interaction between variables and is presented as follows:

Regression equation in uncoded units:

Ge recovery = -76.1 + 32.51x. Reductant amounts -112.9x. Basicity -2.517 x. Reductant amount - 30.9 Basicity -13.79 Reductant amount x Basicity (1)

To simplify equation (1) originally generated from the software, X stands for basicity while Y stands for amount of reductant amounts. The simplified equation (1) is as follows:

$\text{Ge recovery} = -76.1 + 32.51\,y + 112.9\,x - 2.517\,x^2 - 30.9\,y^2 - 13.79\,xy$

Table 4 Coefficients of determination of the model

R-sq	**R-sq (pred)**
91.80	41.71

The R^2 result in the model summary above indicates that the regression 91.80 % of the variance in strength, indicating that the model above adequately fits the data. The expected R^2 of 41.71% indicated that the model was not overfit.

Figure 4 below highlights the effects of the main variables on the process. It shows that the simultaneous increase in basicity and reductants amounts increased the mean recovery.

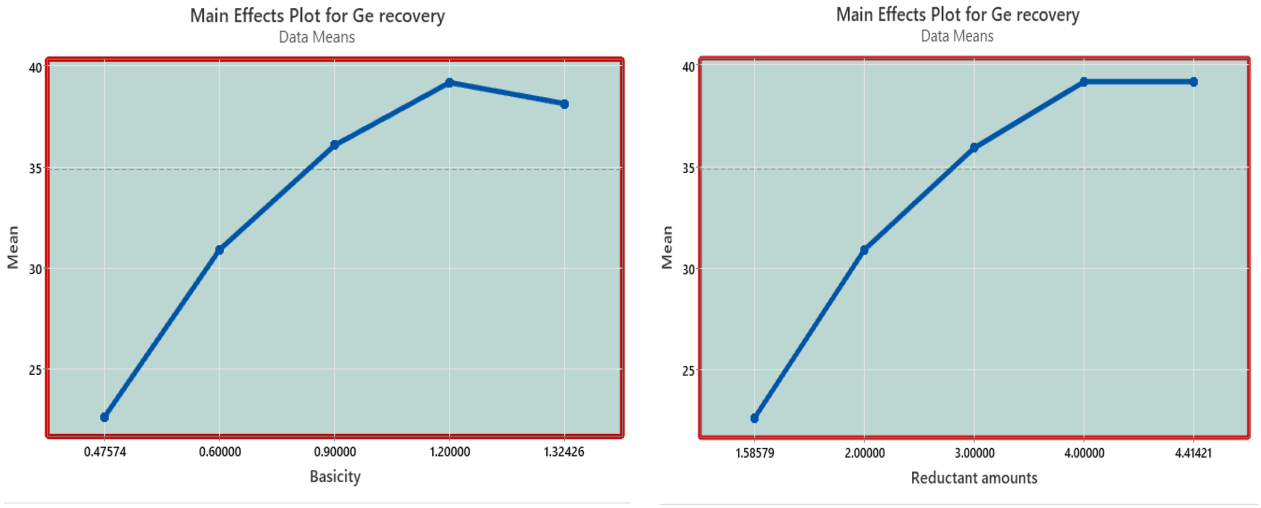


Figure 4 Influence of basicity and aluminium amounts on Ge recovery (per cent) against the mass of reductant used (g)

Table 4 displays the analysis of variance (ANOVA), which assisted to find whether a hypothesis is rejected or accepted based on its P-value or F-value. The P-value being the probability value whereas the F-value measures the significance of the overall ANOVA model for more than one explanatory variable. The lowest P-value of the model was found to be 0.001, one should understand that the lower the P-value (>0.05), the more fitted the model is. The higher the F-value, the more fitted a model is. The mathematical model generated by the software is a second-order model, inclusive of three parts, which are: linear, one-way interaction (square) which is an interaction between one parameter with itself, and 2-way interaction which is between two different parameters. It can be understood that the linear interaction and the one-way and two-way interactions were found all to be less than 0.05 when looking at the P-values, meaning the model is best suited for the process.

Table 4 ANOVA results

	Ge	
Source	**F-Value**	**P-Value**
Model	15.68	0.001
Linear	27.94	0
Reductant amounts	28.99	0.001
Basicity	26.89	0.001
Square	6.28	0.027
Reductant amounts x Reductant amounts	6.4	0.039
Basicity x Basicity	7.8	0.027
2-Way Interaction	9.95	0.016
Reductant amounts x Basicity	9.95	0.016

Figure 5 displays the Pareto Chart of the standardized effects and Interaction Plot for germanium recovery. From the Pareto Chart, it can be understood that all the variables are effective on germanium recovery whether used individually or together. On the other hand, the interaction plot for germanium recovery suggested that one can get a lower recovery as lower basicity and reductants are used and the recovery can increase as the two variables are increased until optimum recovery is achieved.

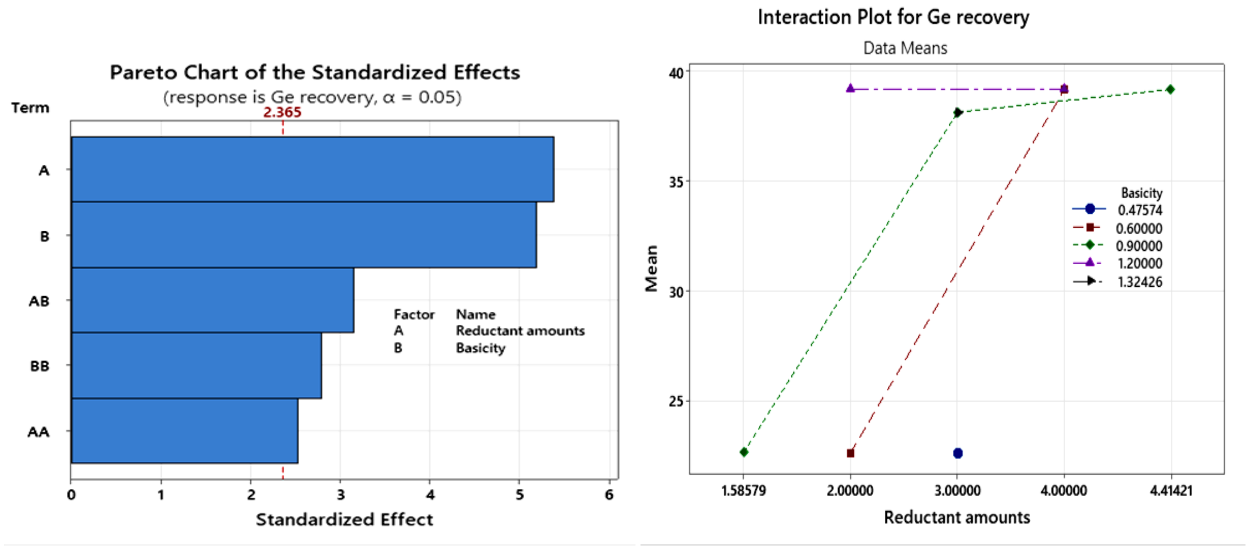


Figure 5 Pareto chart and interaction plot for Ge recovery

4. CONCLUSION

Results in this work showed the effects of aluminium addition on copper slag reduction and offered fresh perspectives on how to apply chemistry knowledge to improve metallothermic reduction for germanium recovery.

The following conclusions were drawn: 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 recovery was obtained at basicity of 3 and 4g of aluminium at 1350 °C. At lowest basicity which in this case was the basicity of the head slag, the recovery was low and the miscibility of metallic and slag phase was high. However, increasing the basicity improved the metal-slag separation by adding more lime to the slag. 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 separation shown in SEM-EDX results proved efficient. The response surface and contour plot for germanium recovery versus aluminium and basicity has successfully led to generate a regression equation in unicoded units. The generated model in this investigation is fit to predict germanium recovery using aluminothermic process and basicity.

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