

# Contribution to the Metal-Slag Equilibrium Study During Carbothermic Reduction of Copper Slag for Cobalt Recovery

Seya Kabamba Alex, Michel Kalenga wa Kalenga, and Willie Nheta

**Abstract**— In today's mining industry, the growing demand for high-tech materials and the diminishing primary cobalt resources have compelled the industry to turn to recycling slag as a secondary source of cobalt. Cobalt has been discovered in copper slag originating from the water-jacket furnace in the Katanga Province of the Democratic Republic of Congo. This study aimed to optimize cobalt content and investigate whether the system reached equilibrium during the carbothermic reduction of the slag. The primary fayalitic slag was analysed using XRD, XRF, and SEM. To influence the cobalt activity, lime was added to adjust the basicity to unity, affecting the activities of other oxides. The smelting process was conducted at 1400°C, with coke serving as the reductant, and carbon monoxide was blown into the furnace to create strong reducing conditions. The sample spent two hours in the furnace, which was deemed sufficient to reach full equilibrium if possible. The outcomes included a secondary slag and an alloy, which were analysed using XRD, XRF, and SEM. The results indicated that the metallic phase contained copper, cobalt, iron, and minor traces of zinc, while the secondary slag phase consisted of SiO<sub>2</sub>, CaO, and some FeO. The recovery of cobalt fell short of the calculated equilibrium amount, suggesting that the system did not reach full equilibrium but was very close to it.

**Keywords**— Equilibrium, Cobalt reduction, Copper slag.

## I. INTRODUCTION

In recent years, environmental challenges, depletion in high metal grade ores and dumping space availability constraints have prompted researchers to investigate the treatability of mineralogical waste materials for the generation of utilizable products from secondary sources [1,2]. The mining and metallurgical industry have long been the object of criticism for the environmentally destructive nature of their waste materials. Many studies have been conducted to address the issue. The hydrometallurgical or pyrometallurgical recycling of copper slags to produce valuable metals and a secondary slag of adequate mechanical properties for its utilization elsewhere is a good example [3].

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Slag is the molten waste material produced during the pyrometallurgical treatment of ores or concentrate. It is fundamentally a mixture of gangue (oxides) and flux. Copper slags are the principal non-ferrous slag. It is estimated that 2.2 tons of slag are discharged for each ton of copper metal produced [4-7]. The chemical composition of the slag depends on the original composition of the ore processed and the type and efficiency of the techniques employed in its beneficiation. The slag phase composition also depends on its quenching rates [8-9]. Several metallurgical plants, through various methods, target specific metals while discarding any other metals of no interest as gangue material, residue or slag. The volatility of the prices of mineral commodities is such that one mineral of no economic interest may suddenly become profitable and goads metallurgists to reevaluate its possible extraction from previously considered useless waste or uneconomical ore reserves. In addition, technological breakthroughs have made possible the recovery of formally untreatable minor amounts of metals in ores or gangues. Several millions of tons of slag are produced each year during the pyrometallurgical treatment of copper. Copper slag can be harmful to the ecology and often contain non-negligible proportions of values. The reasons behind the treatment of copper slag can thus be summarized as the retrieval of metallic values (Cu, Co etc.) and the generation of reusable secondary slag to cut down the mineral industry environmental footprint. During the pyrometallurgical processing of copper slag, several chemical and thermodynamic factors can be used to characterize the slag-metal-gas system. Such factors include the equilibrium constant, entropy, enthalpy, etc. The present investigation assesses the equilibrium between the secondary slag, metal and gaseous phase during the pyrometallurgical extraction process of Cobalt from a Water jacket furnace copper slag using Coke as a reductant.

## II. EXPERIMENTAL PROCEDURE

### A. Materials

A copper slag from Katanga, in the Democratic Republic of Congo was reduced with coke for the recovery of cobalt.

Flux: Lime (95% purity), from Protea Chemicals; was added to adjust the slag basicity with a view to produce a slag of low melting point and viscosity.

Reductant: Coke originating from South Africa was used as

reductant and was characterized through proximate analysis.

### B. Equipment

XRF, XRD and SEM-EDS were used as analytical techniques for elemental, mineralogical and superficial analysis of the raw slag and the products after reduction process. An alumina tube furnace THM 15 with a heating rate of 7°C/min was used for the experiments conducted in a graphite crucible embedded in a silica crucible to prevent any spillages and avoid possible interaction with the alumina tube.

### C. Methodology

The slag was milled to -75µm and dried at 105°C in an oven for an hour. 10 g were taken from the dried material and mixed with 5g of Sasol wax in a mortar with pestle for analysis. For better qualitative and quantitative analysis of different phases, the sample was ground to 1- 5 µm. Finally, the sample was coated with a thin layer of gold in a gold sputter coater and was analysed using SEM. Proximate and ultimate analysis were performed on the coke for characterization. The mix of slag, flux and coke were milled together for 15 minutes for homogenization, then placed the crucible for smelting in the tube furnace set at 1400°C for 150 minutes. The products subjected to XRD, XRF and SEM-EDS analysis for characterization.

## III. RESULTS AND DISCUSSION

Table I below provides the XRF results of the slag head sample. Results reveal that cobalt in the head sample amounts to around 1.39%, 3.67% copper while Fe is 20.44% and silicon 12.71%.

TABLE I  
XRF ANALYSIS OF THE HEAD SLAG SAMPLE

Oxide	Mean mass %	Element	Mean mass %	Std dev.	Min	Max
Al <sub>2</sub> O <sub>3</sub>	4.402	Al	2.330	0.048	2.279	2.401
CaO	20.744	Ca	14.826	0.042	14.780	14.882
Co <sub>2</sub> O <sub>3</sub>	1.891	Co	1.388	0.024	1.352	1.415
CuO	4.619	Cu	3.690	0.105	3.581	3.832
FeO	29.233	Fe	20.446	0.313	19.976	20.776
MgO	3.667	Mg	2.212	0.063	2.152	2.307
MnO	0.352	Mn	0.273	0.010	0.260	0.282
SiO <sub>2</sub>	27.186	Si	12.708	0.243	12.442	13.055
ZnO	4.791	Zn	3.849	0.083	3.727	3.932

From the chemical composition it transpires that the basicity is less than unity. This simply means that the slag is acidic. Further, the amount of silica and iron oxide presumes the slag to be fayalitic.

Fig. 1 below depicts the SEM-EDS results of the slag head sample. Three spots were analysed and have been shown in Table II

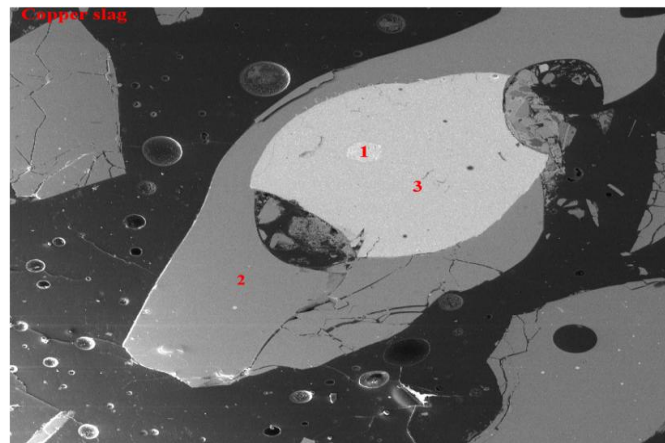


Fig. 1 SEM-EDS image of the slag head sample

TABLE II  
SPECTRA ANALYSIS OF THE SEM-EDS OF THE SLAG HEAD SAMPLE (%)

Spot	O <sub>2</sub>	Na	Mg	Al	Si	S	Ca	Fe	Co	Cu
1	81.0			1.2	3.31	12.8		1.5		0.2
2	75.9	2.7	3.3	1.9	10.5	2	0.9	1.4	0.1	
3	79.9		1.8		4.2	13.5		1.1		0.1

From the spectra, it is observed that cobalt content remains at 0.1%, silicon at 10.5% as the highest while sulphur has been detected. The presence of sulphur means that matte was entrained during slag tapping in the water-jacket furnace.

Fig. 2 below provides the XRD results of the slag head sample. Due to the sample being amorphous there was extensive peak overlapping in the diffractogram. The diffractogram was therefore deconvoluted at two theta degrees and some of the overlapped peaks were isolated. As displayed in Fig. 2 below, there was overlapping at around 21, 26, 38 and 43 °. Fayalite, Iron Oxide, Cobalt oxides etc. peaks were hence deconvoluted using Origin 8.5 pro software.

Table III and Fig. 3 present the XRF and XRD results of the secondary slag.

TABLE III  
XRF RESULTS OF THE SECONDARY SLAG SAMPLE

Oxides	Mass %	Elements	Mass %
Al <sub>2</sub> O <sub>3</sub>	6.4	Al	3.4
CaO	36.1	Ca	25.8
Co <sub>2</sub> O <sub>3</sub>	0.7	Co	0.7
CuO	1.1	Cu	0.8
Fe <sub>2</sub> O <sub>3</sub>	9.7	Fe	6.8
MgO	6.2	Mg	3.8
MnO	0.3	Mn	0.3

The XRF of the secondary slag shows that cobalt content in the final slag is low, therefore the carbothermic reduction was efficient. The mass balance could not be performed efficiently due to the difficulties encountered during the separation

between the alloy produced and the secondary slag. The immiscibility was not complete.

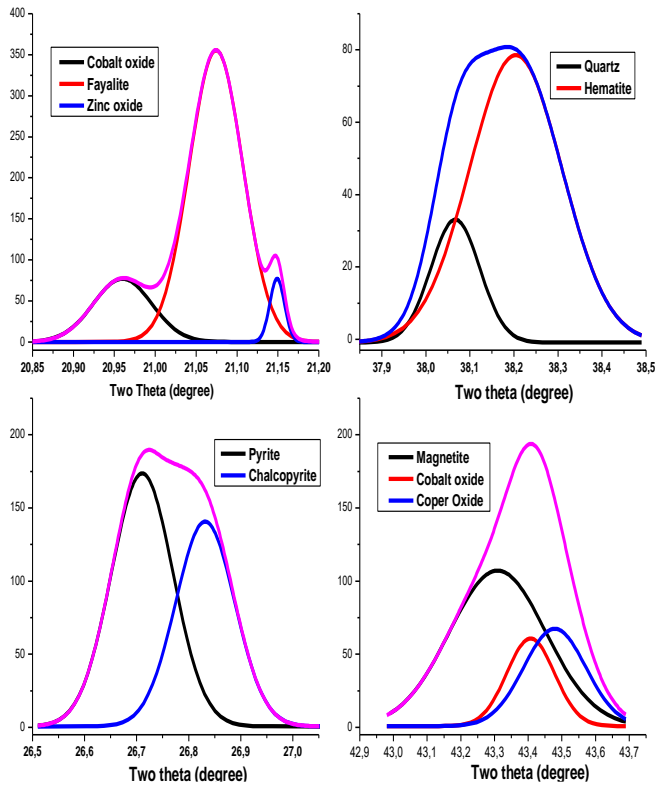


Fig. 2 Deconvoluted XRD patterns of the primary slag

Table IV and Fig. 4 demonstrate that copper was predominantly reduced. This is in line with the composition of the head sample slag and supported by the Ellingham diagram. The amount of cobalt in the alloy is significant which attests that cobalt recovery was high although not calculated.

Fig. 5 depicts the SEM-EDS results of the secondary slag while Table V provides the composition of different spectra analysed.

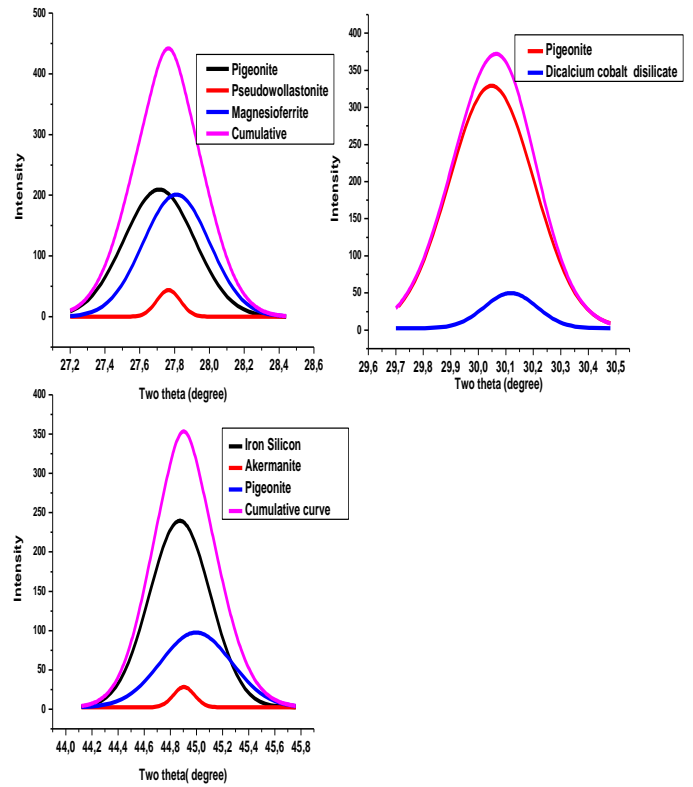


Fig.3: Deconvoluted XRD patterns of the secondary slag

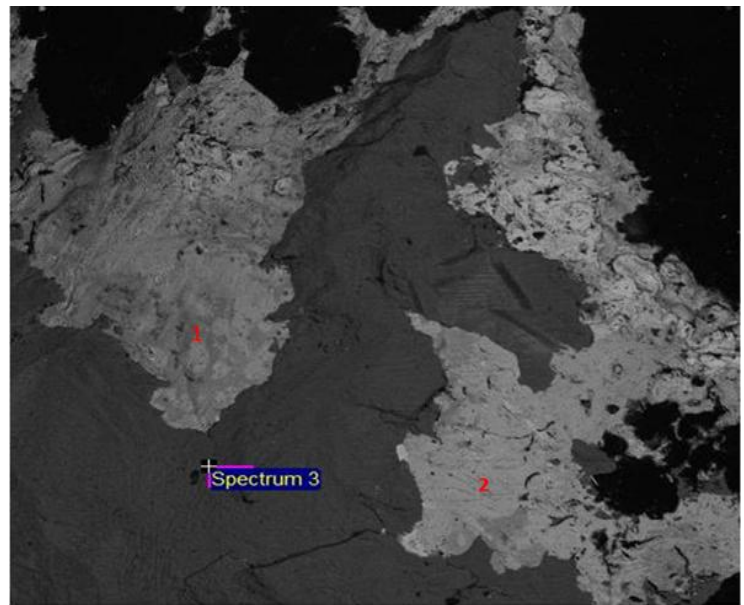


Fig 4: SEM-EDS of the secondary slag

TABLE V  
COMPOSITION OF SPECTRA ANALYSED ON THE SEM

Spot	O	Na	Al	Si	S	Ca	Fe	Co	Cu	Zn
1	15.6			0.5	0.2	0.3	12.6	0.9	62.9	5.0
2	14.5		0.2	0.4			9.5	0.8	72.2	2.1
3	46.1	0.3	3.3	1.94	0.4	25.4	0.6	0.3		

#### IV. CONCLUSION

The aim of the study was to theoretically assess a phase equilibrium in the system comprising a metallic, a slag and a gaseous phase during the carboreduction smelting of a copper slag. The primary slag was characterised through XRF, XRD and SEM before smelting was carried out in an alumina tube furnace at 1400°C for 2.5 hours at a basicity of about 1. The products of smelting including a metallic phase and a slag phase were equally characterised using the above-mentioned techniques. The recovery of cobalt was deemed low, and it was attempted to link it to the possibility of a phase equilibrium. After careful consideration of the data, including low cobalt recovery and high iron content in the metallic phase, this hypothesis was rejected, and a classic cause was postulated. It is recommended that further studies be conducted on the same slag under more optimised conditions in order to reassess the possibility of a phase equilibrium. The results of this work have not been coupled with any thermodynamic calculations using a software.

#### ACKNOWLEDGMENT

Authors thank the Societe de Traitement du Terril de Lubumbashi General Manager, Mr Grant Dempsey for his kindness to provide the copper slag samples and permission to conduct this investigation. The University of Johannesburg and the National Research Foundation of South Africa [**Grant number 132291**] for the financial support of this project.

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