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Copper Slag Valorisation: Recovery of Cobalt by Sulfurization and Flotation

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Abstract **-** The recovery of cobalt from the copper smelter slag by sulfurization and flotation was investigated. The copper smelter slag was characterized using XRF, XRD and SEM analysis. The slag was reduced using coke and sulfurized using gypsum. The coke was characterized to know the volatile matter, moisture content, ash content and the percentage fixed carbon. A determined amount of copper smelter slag, gypsum and coke were blended together and were investigated for the sulfurization process. The gypsum contained 97.3% $CaSO_4$. The sulfurization experiments were carried out at 950 °C using a tube furnace. The products of the sulfurization experiments were characterized by XRD and XRF analysis and floated using a micro-flotation. The products of the flotation experiments were characterized using XRF. It was found that the raw copper slag contained 2.30% Co, 5.27% Cu and 35.13% Fe. After flotation, a concentrate containing 0.88% Co was produced. The highest recovery of cobalt was obtained at pH 8 with a recovery of 38.37%. Sulfurization and flotation of copper smelter slag has potential in valorisation of slag and help to mitigate the release of hazardous heavy metals into the environment.

Keywords**:** Copper slag, cobalt, sulfurization, flotation

1. Introduction

Copper smelting slag is a secondary waste manufactured in the copper smelting industry. Almost 30 million tons of copper slag are discharged annually into the environment around the world [1]. Copper slag contains many harmful heavy metals and is considered as hazardous waste. Many plants have tried to mitigate this problem by retreatment of slags to recover base metal entrained in the slag. Base metals can be recovered through flotation and leaching processes [2, 3]. Other researchers have worked on the use of slag as a raw material for cement production and for road construction [4]. Several studies have been carried out extensively in order to study the manner to be used by metallurgists to extract copper, cobalt and iron from copper slag [2, 3, 5, 6]. Cobalt is usually produced as a by-product of copper or nickel processes.

Copper slag reduction for cobalt recovery is fundamentally a chemical process accompanied by chemical reactions. Depending on the oxide species present in the copper slag, several reactions can be expected to happen based on the thermodynamic stability information provided by the Ellingham diagram. Cobalt is generally extracted as a side product during or after the recovery processes of primary metal with which it naturally associates with. There exist very few mining activities in the world having cobalt as their primary metal production. Currently, Bou Azer (Morocco) is home to the only Co-dominant mine in the world. The methods involved in the beneficiation of cobalt depends on the type of the host ore, the environmental legislation, the final cobalt product required as well as the attractiveness of the market.

Copper smelting slags are complex materials comprising of oxides, sulphides, silicates, and glassy amorphous materials. They can contain appreciable amounts of valuable metals such as copper, cobalt, and zinc, as well as iron. Mineralogical studies have shown that cobalt is present as CoO in copper reverberatory furnace slag. Copper in the slag is attributed mainly to the presence of copper-rich sulphides. The cobalt oxide, and, to a lesser extent, the copper oxide associated with the silicate/oxide phases, is reduced by Fe from the alloy to form metallic Co (and Cu), resulting in the formation of FeO in the slag [6]. The discarded slag can contain large amounts of copper and other base metals, and the recovery of these metals is not easy as mineral processing procedures are necessary in order to retrieved values from the slag. The reason why the slags are not easy to process is because of their complex mineralogy, metal occurrence morphology and metal phase distribution [1]. In order to achieve higher recoveries, it depends on the grindability of the slag and liberation, and whether the metal of interest is in the form of sulphide or oxide. The hydrometallurgical recovery of cobalt from slag, although experimentally efficient, is uneconomical due to high operational costs and high iron recovery [7]. In comparison, flotation of Cobalt from slags is unresponsive because of the common difficulties in floating oxide minerals.

The objective of this study is to investigate the sulfurization of copper smelter slag with the aim of recovering Cobalt and reduce the impact of slag to the environment.

2. Materials and Methods

2.1 Materials

Copper smelter slag used in this research was sourced from Katanga Province, Democratic Republic of Congo. The gypsum which was used as a sulfurization agent was obtained from an impurity removal process in a Cobalt production plant and it contained 97.3% $CaSO_4$. The coke used was obtained from a foundry laboratory and it contained 79.451% fixed carbon. The flotation reagents used were Potassium amyl xanthate (PAX) as collector, Copper sulphate as depressant and Dowfroth 200 as a frother sourced from Merck, South Africa, and they were all of AR grade.

2.2 Mineralogical and morphology characterisation of the slag sample

The chemical composition of the copper smelter slag was determined using X-ray fluorescence (XRF) Rigaku ZSX Primus II with SQX analysis software (Japan) and the major phase components were determined using X- Ray Diffraction (XRD) Rigaku UltimaIV with PDXL analysis software (Japan). The diffraction beam monochromatic operates at 40 KVA and 30 mA with step size of 0.02 to generate the x- ray patterns with enough intensities to produce lines in order to identify minerals in the scanning range of 5^{O} to 90^{O}. Scanning rate was 1 degree per minute while the source of energy was copper with CuKα radiation = 1.5418Å. Mineral phases were identified using the PDXL analysis software of the International Centre for Diffraction Data (ICDD).

To observe the distribution of the heavy metals and phases in the copper smelter slag sample, the samples were prepared using epoxy resin and their surfaces polished. The samples were then analysed using TESCAN scanning electron microscope (SEM). It is incorporated with EDX analysis software performance in Nano space at accelerating voltage of 20KVA. Images, grain boundaries and grain sizes were made using the backscattering electron detectors while chemical elements of the sample were determined by the EDS. The images were shown with point analysis at the positions of the ore particles.

2.3 Coke characterisation

To determine the moisture content of the coke, an empty vessel was dried by heating at 108±2 ºC. It was then left to cool down before it was weighed on an electronic mass balance. A total of 1 g of pulverised coke was then uniformly spread in the vessel. The mass of the sample containing vessel was also recorded before the vessel was transferred to an oven where the sample was heated at 108±2 ºC for 1.5 hours to evaporate all the moisture. Cooling of the vessel with the heated sample was done in a desiccator before its mass was recorded. The coke moisture content was finally computed by subtracting the mass of the vessel with sample after heating from the one before heating.

The volatile matter content of the coke was determined by heating a crucible at 900±10 ºC for 7 minutes to drive off all volatiles. It was then cooled in a desiccator before a total of 1.5 g of coke was added to it. The crucible with the sample were then placed into a muffle furnace where the temperature was set to 900±10 for 7 minutes. The crucible with heated sample were subsequently cooled down before their mass was recorded. Subtracting the moisture content from the mass loss after heating gave the volatile matter content of the metallurgical coal. The ash content of the coke was determined by heating 1g of coke for I hour at 900^{O}C, cooled and weighed. Subtracting the mass of the empty crucible from the latter mass gave the ash content of coke. The percentage of fixed carbon was computed by difference according to equation (1)

$$F = 100\% - (M + V + A) \tag{1}$$

Where F is the % fixed carbon, M is % moisture, and V is % volatile matter and A is the % ash.

2.4 Sulfurization experiments

The sulfurization tests were conducted in a tube furnace. 300g of the slag was blended with pre-determined amount of coke and gypsum, and stored in 3 separate bags. Each bag had 100g of copper slag, 10g of coke and 10g of gypsum. The blended sample was milled using a rod mill to achieve a product with a PSD of 80% passing 75 microns. 20g of the sample was transferred into 3 different graphite crucibles. The graphite crucible was then transferred into the tube furnace and heated for one hour at 950 °C. The sample was left in the furnace to cool down. The products obtained were prepared and analysed using XRD and XRF. The remaining samples were then floated in a micro flotation cell.

2.5 Flotation experiments

A Micro-flotation cell was used for the flotation experiments. The cell was filled with running water at natural pH of 7 to the maximum mark of the column. Air was blown from the bottom using a compressor while adding 10g of the sulfurized ore. 0.20g/t of Potassium Amyl Xanthate (PAX) and copper sulphate were added and conditioned for 5 minutes. 5 drops of Dowfroth 200 was added and everything was allowed to condition for 10 minutes. The compressor was adjusted to maintain the particle and bubbles in suspension. The froth product was collected. The process was performed to a point where there was no froth overflowing. The concentrates and the tailings were filtered using a vacuum filter. The products were analysed using XRF.

3. Results and discussion

3.1 Chemical composition of the raw copper smelter slag

The chemical composition of the as received copper smelter slag is shown in Table 1. The raw copper smelter slag shows a high percentage of iron, calcium, silicon and zinc. All these heavy elements will end up in the environment if they are not well disposed [1]. The slag contain 2.3% Wt Co which can be recovered. The high content of Fe (35.13%) and Si (17.64%) indicates that this is a fayalite slag.

Table 1: Elemental composition of the copper smelter slag

Element	Mg	Al	Si	P	S	Ca	Ti	Mn	Fe	Cu	Co	Zn	Cr
% Wt	3.26	3.09	17.64	0.21	0.20	21.13	0.53	0.37	35.13	5.27	2.300	8.07	0.24

3.2 Mineralogical composition of copper smelter slag

The XRD pattern of copper smelter slag is very complex, with several peaks overlapping as a result of many minerals present in the slag. In order to have a clear understanding of the mineral phases present, the peaks were decomposed using Origin 8.5 software and the results are shown in Fig. 1. Five major crystalline phase were identified which are: Fayalite, Zhanghengite, Magnetite, Copper oxide and Cobalt oxide. Zhanghengite is a mineral consisting of copper, zinc, iron, chromium and aluminium. Fig. 1 shows that cobalt exist as an oxide in the slag and there is need for it to be sulfurized before flotation process.

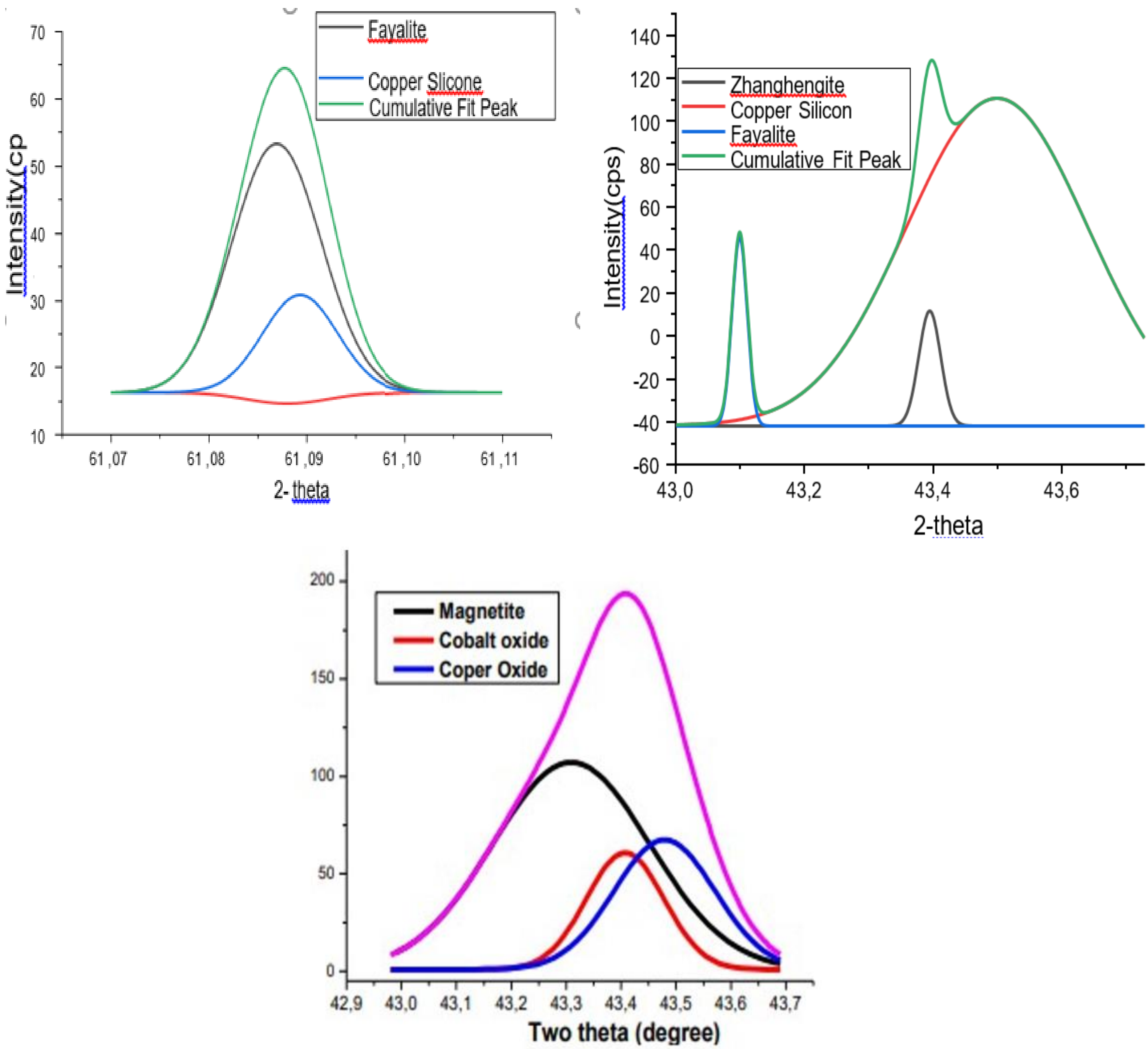

Fig. 1: XRD pattern of the copper smelter slag sample

3.3 Surface morphology of the sample

In order to determine the bound relationship between the main phases and the heavy metals, the surface morphology of the copper smelter slag sample was determined using SEM – EDS and the results are shown in Fig. 2 and Table 2.

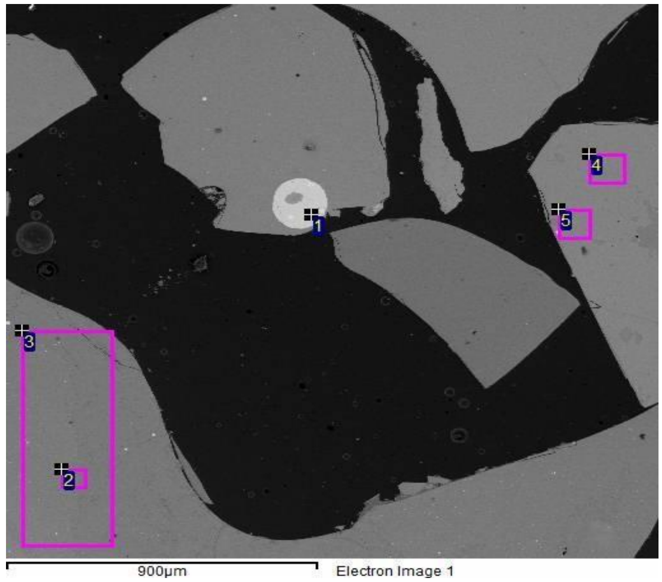

Fig. 2: SEM image of polished surface of copper smelter slag

Table 2: The elemental composition of selected points on the polished surface

Spot	N	O	Mg	Al	Si	S	Cl	K	Ca	Ti	Fe	Cu	Co	Zn
1	6.1	86.14				1.69	4.55				0.74	0.49	0.29	
2		47.0	2.53	2.73	18.92			0.57	12.08	0.18	10.20	3.31		2.40
3		51.05	2.39	2.60	17.86		0.33	0.51	11.0	0.21	9.75	1.59	0.50	2.21
4		46.0	3.14	3.17	16.92	0.66		0.66	2.98	0.23	17.18	0.28	0.67	8.16
5		44.97	3.96	2.84	16.08	1.65		0.60	2.66	0.21	16.94	2.43		7.65

Cobalt is found on points 1, 3 and 4 which have a very high content of oxygen and a low concentration of sulphur indicating that most of the cobalt is incorporated in the slag rather as an oxide than a sulphide. Oxide mineral are more hydrophilic and float very poorly. There is need to change this oxide mineral into a sulphide mineral which is more hydrophobic and easier to float [2].

3.4 Coke characterisation

The coke, which was used as a reducing agent was characterised for moisture, volatile matter and ash content, and the results were 1.732, 5.132 and 13.685% respectively. The percentage of fixed carbon was computed using equation (1) and the coke contained 79.451% fixed carbon.

3.5 Sulfurization experiments results.

After sulfurization experiments in a tube furnace at 950^{o}C, the product was analysed using XRF for elemental composition and the results are shown in Table 3. The mass percentage of Co, Fe, Zn and Cu decreased, compared to the results of the raw copper slag in Table 1. This might be explained by the increase of the values of sulphur and calcium as a results of addition of the sulfurizing agent.

Table 3: XRF results of the sulfurized slag at 950 °C

Element	Mg	Al	Si	P	S	Ca	Ti	Mn	Fe	Cu	Co	Zn	Cr
% Wt	0,67	1,08	4,41	0,06	9,82	28,62	0,18	0,12	10,89	1,83	0,86	1.8	0,03

The sulfurized slag sample was analysed using XRD for mineral phases identification and the results are shown in Fig. 3. The results revealed that Cobalt was present in the form of cattierite (CoS_2). The formation of cobalt sulphide and copper sulphide minerals demonstrate that the slag can be floated. Copper is in the form of covelite (CuS). Hedenbergite ($CaFeSi_2O_6$) is the iron rich end member of pyroxene. It is difficult to find the mineral as a pure substance; it needs to be synthesized in the laboratory. Akermanite contains calcium, magnesium, silicon and oxygen.

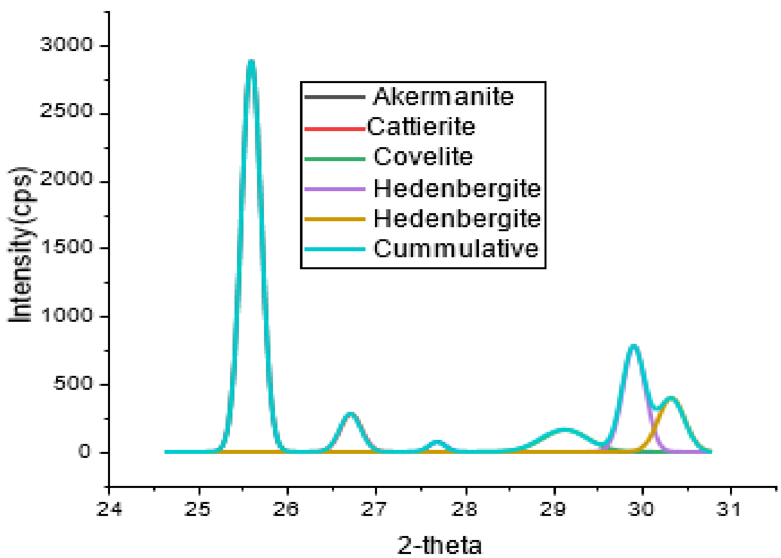

Fig. 3: XRD pattern of the sulfurized copper smelter slag

3.6 Flotation experiments results.

3.6.1 Effect of pH on the grade of the concentrate

Feasibility studies on the flotation of cobalt sulphide from the sulfurized slag was done in a micro-flotation cell. The effect of pH on the recovery of cobalt into the concentrate was investigated and the results are shown in Table 4. The results revealed that as pH increased from pH 3 to 8, the Co grade increased from 0.26 to 0.33%. Further increase of pH from 8 to 13, the grade of cobalt decreased to a grade of 0.19%. This similar trend was observed with Zn grade. Zn increased from a grade of 0.49 to a grade of 0.60 % with increase in pH from 3 to 8. With further increase in pH, the grade decreased to a grade of 0.40% at pH 13. Cu grade also increased with increase in pH from 3 to 8. The highest Cu grade of 2.49% was obtained at pH 6. At pH 8, the highest Fe grade of 4.59% and Si grade of 9.32% was observed. The sulfurized copper slag should be floated at pH 8 because it shows better recoveries of Co, Cu and Zn. However, higher grades of Fe and Si were also observed at this pH and there is need to investigate other reagents suites that will increase selectivity.

Table 4: Chemical composition of the floated sulfurized slag at different pHs

Element	Mg	Al	Si	P	S	Ca	Ti	Mn	Fe	Cu	Co	Zn
% Wt at pH 3	1.00	2.02	7,66	0.11	8.59	35.5	0.21	0.05	3.26	0.66	0.26	0.49
% Wt at pH 4	0.71	1.40	12.02	0.09	12.02	31.57	0.19	0.05	2.90	0.77	0.23	0.45
% Wt at pH 5	0.78	1.68	7.74	0.11	7.94	35.50	0.24	0.05	3.73	0.48	0.21	0.45
% Wt at pH 6	0.78	1.68	5.92	0.09	11.37	31.49	0.21	0.05	3.04	2.49	0.22	0.45
% Wt at pH 7	0.91	1.77	6.71	0.10	10.06	34.30	0.17	0.05	2.95	0.69	0.23	0.45
% Wt at pH 8	1.53	2.13	9.32	0.14	10.06	32.19	0.35	0.08	4.59	0.88	0.33	0.60
% Wt at pH 9	1.38	1.96	9.03	0.13	6.77	34.76	0.29	0.06	3.68	0.57	0.28	0.56
% Wt at pH 10	0.70	1.45	4.49	0.09	11.74	31.65	0.18	0.05	2.87	0.49	0.22	0.43
% Wt at pH 11	0.82	1.62	6.13	0.09	11.17	32.69	0.21	0.04	2.67	0.57	0.21	0.42
% Wt at pH 12	0.73	1.16	4.65	0.09	11.15	37.57	0.17	0.05	2.45	0.57	0.20	0.41
% Wt at pH 13	1.33	1.39	4.53	0.05	9.98	34.94	0.23	0.05	3.87	1.63	0.19	0.40

4. Conclusion

In this work, in order to comprehensively understand to the mineralogical characteristics of a copper smelter slag, XRF, XRD and SEM-EDs was used for analysis. Industrial symbiosis was demonstrated by the use of gypsum which is a waste from another stream for sulfurization of copper smelter slag at 950^{O}C. After sulfurization, oxides of Cu, Co and Zn were converted to sulphides. The flotation results illustrated that pH plays a major role when floating sulfurized slag using PAX as a collector. With optimisation of reagent suites, better selectivity can be achieved. Sulfurization of copper smelter slag followed by flotation has potential in the valorisation of copper smelter slag and reduce quantity of hazardous materials dumped into the environment. Further investigations are required to optimise both the sulfurization and flotation process.

Acknowledgements

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