

Effect of Cooling Rate on base Metals Recovery from Copper Matte Smelting Slags

N. Tshiongo , R K.K. Mbaya , K Maweja, L.C. Tshabalala

Abstract—Slag sample from copper smelting operation in a water jacket furnace from DRC plant was used. The study intends to determine the effect of cooling in the extraction of base metals. The cooling methods investigated were water quenching, air cooling and furnace cooling. The latter cooling ways were compared to the original as received slag. It was observed that, the cooling rate of the slag affected the leaching of base metals as it changed the phase distribution in the slag and the base metals distribution within the phases. It was also found that fast cooling of slag prevented crystallization and produced an amorphous phase that encloses the base metals. The amorphous slags from the slag dumps were more leachable in acidic medium (HNO₃) which leached 46% Cu, 95% Co, 85% Zn, 92% Pb and 79% Fe with no selectivity at pH0, than in basic medium (NH₄OH). The leachability was vice versa for the modified slags by quenching in water which leached 89% Cu with a high selectivity as metal extractions are less than 1% for Co, Zn, Pb and Fe at ambient temperature and pH12. For the crystallized slags, leaching of base metals increased with the increase of temperature from ambient temperature to 60°C and decreased at the higher temperature of 80°C due to the evaporation of the ammonia solution used for basic leaching, the total amounts of base metals that were leached in slow cooled slags were very low compared to the quenched slag samples.

Keywords—copper slag, leaching, amorphous, cooling rate

I. INTRODUCTION

DURING the production of copper, slag is produced as a waste product which was traditionally granulated and rapidly solidified in a high pressure high flow rate water jets during tapping from smelters. The historic and presently employed way of dealing with slag is dumping in the slag dumps or landfill sites. It has been estimated that for every tone of copper production, about 22ton of slag are generated each year from world copper production [5]. Slags are considered hazardous materials as they contain some base metals with concentrations higher than the required level in water and soil [2, 4,10 &12] in and around the dumping dams, some of these base metals have been proven to be toxic [9 & 10]. However, the composition of slag differs according to the source of generation, processing techniques employed and origin.

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When slags are leached with rain water [10], base metals are liberated from the slag and contaminate the soil and ground water system around the slag dumps. There are landfill site limitations and increasing disposal costs [4, 6 &7] involved in dumping slags that are untreated to recover toxic metals contents. So far slags have been used in the construction due to its high strength, durability and chemistry [13], and this has reduced the amounts of landfills. Rapid cooling of slag by water granulation results in an amorphous and glassy phased slag, encapsulating metal oxides and lowering the solubility of base metals [2, 5, 6 &13]. If the slag is cooled too fast, it passes from liquid state to a solid state without developing the crystal structure. Slow cooled slags displays chilled glassy outer margins and an increased crystallinity away from this margins towards the center of the mass [5,6 & 10]. Slags exhibited more homogenous matrix and lower bulk concentration of base metallic compounds [11]. Nevertheless, the formation of glassy matrix investigated by [13] was found insufficient to enclose the base metals and prevent them from being leached.

There have been various studies on the recovery of base metals from slags and other materials that were previously considered as waste using simple physical or chemical beneficiation techniques like classification, magnetic separation, floatation, leaching and roasting. Slags are no longer classified as waste materials but as secondary resource of metals [12]. Flotation of copper slag could be limited as it is the same as floating sulfide ores with which only metallic copper and sulfide minerals can be floated effective [12]. However, high recoveries of 88% Cu, 87% Co, 93% Zn & 83% Fe were achieved using a pyro-hydrometallurgy route (roasting followed by leaching) as an alternative for flotation [1]. Studies have been conducted to remove Pb, Cu, Co & Zn from dumped slags with direct reduction of copper matte smelting slag by using latent heat energy of molten slag [8], and It was proved that direct reduction using carbon is effective in simultaneous recoveries of Pb, Cu, Co & Zn from slag, with recoveries of 65-90% Cu, Co & Zn at coal to slag ratio of 5%. Higher base metals recoveries can be achieved in leaching using sulphuric acid, hydrochloric acid, ferric chloride, ammonia, cyanide etc [12]. Leaching of Ni/Co/Cu slags using sulphuric acid can result in recoveries as high as 85% Cu & 93% Zn with a large portion of Fe [3]. Silica gel has been shown to be a problem during leaching of slags with sulphuric acid. Although there are few studies on gel

formation, recoveries of around 60% Cu, 90% Co, 90% Zn & 90% Fe were achieved after 2 hours of leaching with sulphuric acid at 80°C, and the gel formation and Fe co-extraction are avoided [2]. Slow cooling of slags rendered to yield higher degrees of extraction (80-90% Ni & Co) and rapid cooling yielded lower extractions (20-40% Ni & Co) under similar leaching conditions [3].

In this study, the effect of cooling rate on the recovery of base metals from a copper smelting slag produced in a water jacket furnace was investigated, it was then done through leaching for 1200 minutes at different leaching mediums using nitric acid and ammonium solution for pH adjustments and agitating the solutions at 500 rpm.

II. MATERIALS

The kind of slag used for this study is a copper smelting slag produced in a water jacket furnace from DRC mine called GCM. The slag was sent for XRD analysis and the chemical composition of the slag used for the study is shown by table 1. The slags were leached (acidic and basic) using both nitric acid and ammonia solution. Standard glassware (500ml & 250ml beakers for leaching, 1000ml volumetric flask for solution preparation & 5ml pipette for sample taking), hot plate fitted with magnetic stirrer, contact thermometer and pH meter were used in running the experiments.

TABLE I CHEMICAL COMPOSITION IN WT% OF THE COPPER SMELTING SLAG PRODUCED IN A WATER JACKET FURNACE USED ON THIS STUDY

composition	Wt%
MgO	5.6
Al ₂ O ₃	6.0
SiO ₂	32
CaO	8.6
FeO	27
Co	1.7
Cu	0.2
Zn	5
PbO	0.9
S	0.4

III. EXPERIMENTAL PROCEDURE

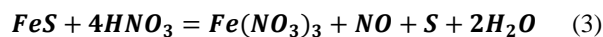
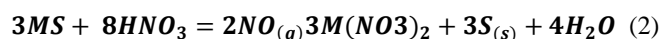
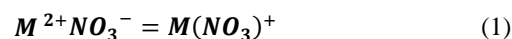
Annealing

The slag was divided into four parts of slags of which the first slag was left as it is when received (GCM1), the three other slags were heated in a muffle furnace for four hours to the melting temperature of copper smelting slag (between 1200-1300°C) and they were cooled in different cooling rates. The second slag was quenched in cold water (GCM2), the third slag was air cooled (GCM3) and the fourth slag was slowly cooled in the furnace (GCM4). A cross section of all slags samples were mounted in cold resin and finely polished and analyzed using scanning electron microscopy (SEM). And

the chemistry of phases was estimated by Energy-Dispersive X-ray (EDX).

Leaching

After annealing, samples were milled to 80% passing through a size 212µm screen. Batch leaching laboratory experiments on four annealed slags (GCM1, GCM2, GCM3, & GCM4) was carried out in 250ml beakers, parameters investigated were pH level and temperature. Three different pH levels (0, 3 & 12) and 4 different temperature ranges (25, 40, 60 & 80°C) were investigated. Nitric acid was used for the acidic pH 0 & 3 and ammonia solution was used for the basic pH 12. The procedure was heating the leach solution to the desired temperature and adding the slag sample at a solid to liquid ratio of 1:10. Agitating the solution at 500 rpm and taking the samples at five time intervals of which four were under 120 minutes and the last sample taken at 1200 minutes. The samples were then filtered and analyzed using atomic adsorption analysis. Leaching process of metals and metal sulphides with nitric acid occurs according to the following equation 1 & 2, and dissolution of iron from the slag to the leach liquor is shown by equation 3.



IV. RESULTS AND DISCUSSION

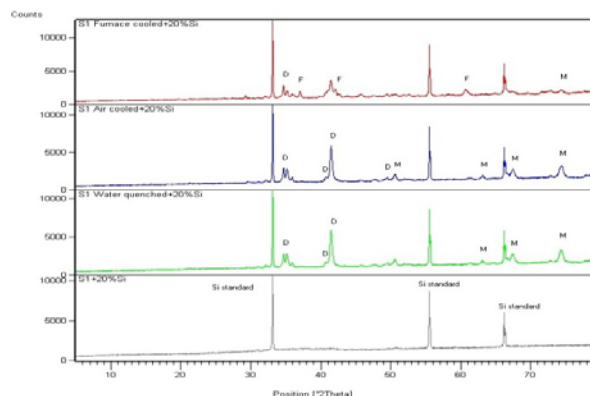


Fig. 1 XRD patterns of the amorphous and the crystallized products of copper smelting slag cooled in different cooling rates

The XRD patterns shown in figure 1 above shows that the as received water granulated slag was amorphous containing 6-4% of crystallized phases, whereas the other slags are about 80% crystallized after annealing. The crystallized phases of the annealed slags contains hedenbergite or diopside (D), magnetite (M) and fayalite (F) in various proportions depending on the annealing process employed as indicated in

figure1. The amount of total amorphous phases in the annealed slag decreased when the cooling rate decreases and at the same time the total amount of crystallized phases in the annealed slag has the opposite effect, and this is indicated by the increase in fayalite and the decrease in magnetite content in the slag.

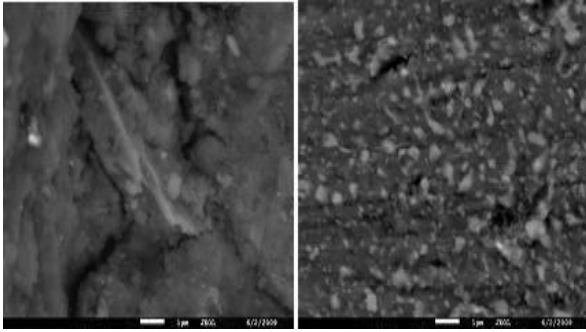


Fig. 2 SEM micrographs of (left) as received water granulated amorphous slag GCM1 and (right) the crystallized slag after annealing of the slag at 1200°C-1300°C and furnace cooled. The light areas are magnetite/fayalite matrix and the dark areas are the hedenbergite/diopside matrix.

The SEM micrographs in figure 2 shows that slow cooling of copper smelting slag produced a homogeneous structure where the magnetite phases present are evenly distributed in the diopside matrix. When cooling rate is faster, the magnetite phases will form smaller grains than that formed in the slow cooled slag. EDX estimates for chemical compositions of phase shows that the glassy phase formed during annealing was rich in Cu and Pb, and it was formed along the boundaries in between the large grains of magnetite for the annealed slag, and the crystallized phase of the annealed slag contains Cu, Zn and Fe.

The high overall base metal extraction is achieved when leaching GCM1 at pH0, as shown by figure 3 below. When the original slag is leached at high acidic medium, high base metals dissolution of 46% Cu, 95% Co, 86% Zn, 92% Pb and 79% Fe were achieved. In all the leaching experiments that were conducted, this was the only experiment were higher than 45% for all metals was dissolved to the acid. The only problem with these experimental results was that a lot of Fe co-extraction to the solution, and this can be problematic for solution purification step as the Fe extracted is even higher than the Cu extraction in this leaching condition. Water granulation of the slag during tapping of the slag causes an amorphous phase that encloses the base metals, but does not totally prevent leaching of base metals. After the slag has quenched, Cu and Pb are contained in the glassy phase at the margins of the phases that contains more of the other base metals as shown in the SEM micrographs in Figure 2.

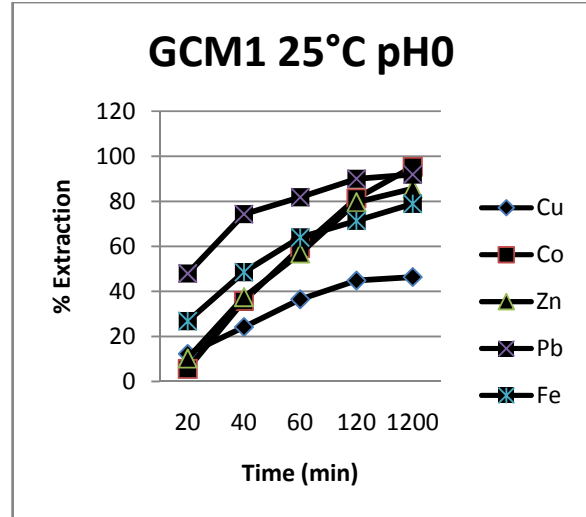


Fig. 3 Percentage leaching of base metals (Cu, Co, Zn, Pb & Fe) extraction for 1200 minutes of GCM1 slag at 25°C and pH 0

Fe co-extraction during leaching is a problem as it may cause problems in further processes like solvent extraction or electro-winning. Figure 4 shows the results of a leaching experiment of GCM2 slag that was leached at ammonia solution of pH12. Leaching of water quenched slag GCM2 shows a high selectivity of the dissolution of copper over the other base metals. Cu can be leached to a maximum of 90% with all the other base metals at less than 1% extraction. This process is perfect for further purification of Cu as the other base metals will be too low to interfere with Cu extraction and if there is interest in other base metals, the slag can be leached furthermore for remaining metals after leaching Cu. Due to Cu present in the margins, almost all the Cu is dissolved to the leaching solution before all the other base metals are reach in the middle of the matrix.

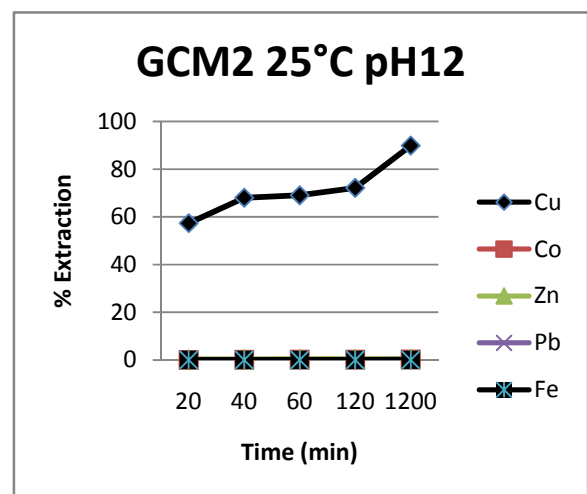


Fig. 4: Percentage leaching of base metals (Cu, Co, Zn, Pb & Fe) extraction for 1200 minutes of GCM2 at 25°C and pH 12.

When leaching GCM3 using the same conditions of ammonia solution at pH12, it resulted in the overall low base metals extraction but this condition provides lower Fe co extraction. Cu, Co, Zn & Pb at 22-36% were dissolved with a low amount of 5% Fe dissolved. Leaching of GCM3 at these conditions can be good to provide low Fe co-extraction.

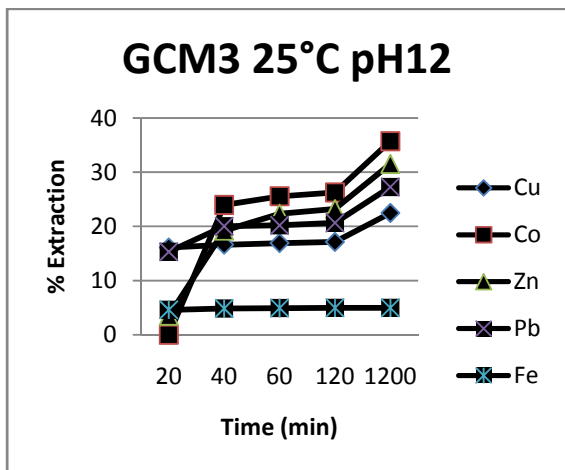


Fig. 5 Percentage leaching of base metals (Cu, Co, Zn, Pb & Fe) extraction for 1200 minutes of GCM3 at 25°C and pH 12.

The following figure 6 shows the effect of temperature on the extraction of copper from GCM4 slag. The base metals extraction followed the same trend as that of leaching GCM3 at the same conditions, it was selective over copper but the total extraction of all metals was very low at a maximum of 2% Cu at 80°C. This shows that slow cooling of the slag after tapping has advantages than water granulated slag as the slow cooled and crystallized slag leaches only a small amount of base metals it contains, therefore dumping of slowly cooled slag is not going to be too harsh on the environment and the surrounding underground water system. The results show that copper extraction increases with the increase in temperature.

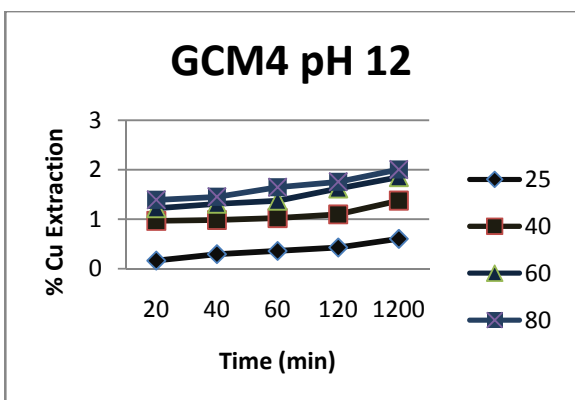


Fig. 6 Effect of temperature on Cu percentage extraction for 1200 minutes of GCM4 at 25°C and pH 12

Extraction of base metals increases with the increase of temperature and pH, But in most of the experiments, extraction increased until 60°C and decreased at 80°C and this can be due to the fact that the solution evaporates at a higher temperature of 80°C.

The results shows that fast cooling and development of a crystalline structure on a copper smelter slag enhances higher leaching of Cu and high selectivity, where as slow cooling results and uniformly distribution of base metals in the slag and decreases extraction of base metals and selectivity of the leach liquor is lowered. Slow cooling of the slag makes lower bulk concentrations of base metals in the homogeneous phase structure.

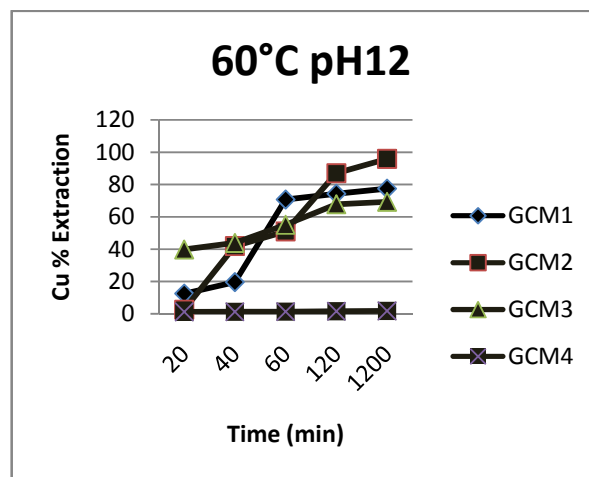


Fig. 7 Extraction percentages of Copper for all four slags cooled in different rates at 60°C and pH 12 for 1200 minutes leaching time.

When comparing the leaching percentages of copper from slags cooled in different rates it can be seen that after 120 minutes, the slag that was rapidly cooled by quenching in water had the most copper dissolution (95%) and the slag that was slowly cooled in the furnace had lower than 2% copper dissolution.

V. CONCLUSION

Annealing of copper smelting slag changes the phase arrangement in the slag, where the amorphous phase decreases as the cooling rate decreases and the crystallized phase increases with decrease in cooling rate employed in the annealing process. Leaching of the copper smelter slag without any modification resulted in the dissolution of 46% Cu, 95% Co, 86% Zn, 92% Pb and 79% Fe, which is the only slag yielding more base metals extraction at pH 0. Quenching of the slag causes an amorphous glassy phase which encloses most of the base metals and it does not enclose them enough to prevent leaching of base metals completely. In the more slow cooled and crystalline structure, the boundaries of the crystalline matrix are rich in copper but leaching of these slags is very low and this can be good if the slag is to be dumped. Water granulation of copper smelting slag has a positive

impact on the leaching of over 90% Cu extraction and selectivity over Co, Zn, Pb and Fe that are in the middle of the slag particles. Slow cooling the copper smelting slag changes the chemical structure of the slag and it will cause the slag to have a more evenly distributed composition of base metals and the leaching of this base metals and selectivity is increases with the increase in pH, but the extraction is lower than that of the water granulated slag.

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