Recovery of Copper from Reverberatory Copper Slag and Production of a Leach Residue used as a Portland Cement Additive

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Large quantities of slag are produced every year and dumped on slag heaps around the world, posing a potential environmental threat due to contained heavy metals content. Slags are waste minerals produced during furnace smelting of minerals. The contained values of base metals may be released into the environment under natural weathering conditions polluting ground and underground water. Copper losses into slag are a continuous problem in pyrometallurgical smelting operations. Due to shortage of ore concentrate, various mining operations have initiated the recovery of copper from dumped slag. The typical process uses crushing, milling and flotation. These operations create excessive liner wear rates during crushing and milling because the bond work index of copper slag is 22 kWh/t and this is considered a very hard slag. The process also has reduced flotation recoveries and requires high flotation reagent consumption.

The present work shows that digestion of the milled copper slag slurry with concentrated sulphuric acid at a temperature of 250°C forms a solid cake and leaching of the solid cake with water is a possible option. However, the consumption of sulphuric acid can have a considerable cost on the recovery process. This can be limited by producing a leach residue containing gypsum and silicate materials as amorphous silica which are suitable for use as an additive for Portland cement. Laboratory results show that 90% copper recoveries can be achieved. The leaching is conducted to prevent silica gel formation and iron co-extraction. Leaching is optimum if silica gel-free solutions and good filterable residue are obtained.

INTRODUCTION

Slag is a waste by-product of smelting and converting operations in metallurgical plants. Both smelting and converting operations are aimed at iron separation from base metal sulphides in non-ferrous metallurgy. The iron sulphide component of the ore or concentrate is oxidized to iron oxide at higher temperatures in the molten form, and then fluxed with silica and other oxide rock minerals to produce fayalite ($2FeO \cdot SiO_2$) slag (Schlesinger et al., 2011). Slags are generally deposited on dumps and considered to be unreactive materials. Smelter copper slag contains significant concentrations of several potentially toxic elements, including arsenic, lead, cadmium, barium, zinc and copper. These elements can be released into the environment under natural weathering conditions and cause pollution of soils, surface waters and groundwater (David, 1998).

Recently smelter copper slags stockpiled in dumps are being reprocessed by crushing, milling and flotation to recover entrained copper contents. This technique produces a flotation concentrate copper grade of approximately 25 to 30% with copper recoveries of between 60 and 70%. However, the

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operational costs are excessively high due to crushing and milling liners wear rate which increase because copper slag has a bond work index of 22 kWh/t and is thus a very hard slag. The process also has reduced flotation recoveries and requires high flotation reagent consumption.

The present work shows that digestion of the milled copper slag slurry with concentrated sulphuric acid at a temperature of 250°C forms a solid cake and leaching of the solid cake with water is a possible option. The copper slag contains a high content of silica and iron. The solution final pH is the most important factor affecting the removal of iron and silica from the leach solution and the overall metal recovery. Fe removal from the leaching of copper slag is done by the formation of a metal hydroxide. Hydrolysis is the most common form of precipitation and production of a good filterable pulp is desirable. Sulphuric acid leaching of slag can form silica gel which results in blockages and problems during filtration, can prejudice the metal extraction and may form crud during solution purification. It is very important that the silica gel problem is managed because the residue must contain a higher content of amorphous silica which is a valuable additive in Portland cement manufacturing.

Copper slag is a form of olivine, a magnesium, iron and silicate mineral with the formula $(Mg^{+2}, Fe^{+2})_2SiO_4$. The production of nano silica from the dissolution of olivine is an economic option when compared with the traditional commercial method which requires high temperature vapourization of silica. Nano silica, silica fines and micro silica are added to commercial cements. It is imperative in the manufacturing process of cement to add these silica minerals because their addition reduces porosity, permeability and chemical attack and thus increases sulfate resistance, thermal stability, compressive strength and accelerated hydration (Quercia et al., 2014).

Olivine is dissolved in acid at low temperatures (50-95 °C) to form amorphous silica (Quercia et al., 2014). The dissolution produces a mixture of magnesium, iron and amorphous silica combined with inert minerals and unreacted olivine (Quercia et al., 2014). The unreacted olivine and inert minerals are removed from the leach residue by sedimentation.

MATERIALS AND METHODS

Copper slag was digested with concentrated sulphuric acid and distilled water. Digestion was carried out at a mass/volume ratio of 1:1 solid:liquid. The experiments were conducted with 100 g of copper slag. The temperature of digestion was 250°C. The residue was leached using a single volume of distilled water for 12 h. The slurry was stirred by magnetic stirrer. A schematic flow diagram of the leaching of copper from copper slag is shown in Figure 1.

RESULTS AND DISCUSSION

Table I gives the chemical composition of the copper slag; the results are obtained by using X-ray fluorescence analysis. It can be observed from the analysis that iron, silicon and calcium are the major constituents.

Table I. Chemical analysis of copper slag.

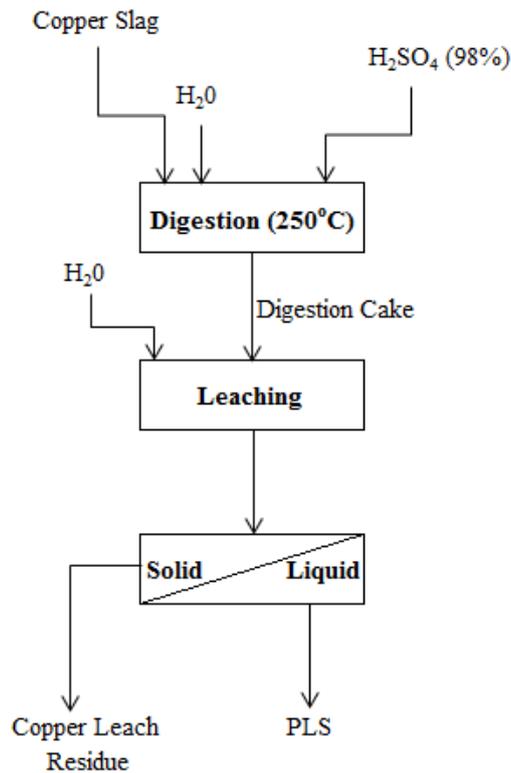| Oxide	Mass percent	Oxide	Mass percent
Cu	1.5 – 2.3	MgO	5.0 – 6.0
SiO_2	28.0 – 31.0	Al_2O_3	4.0 – 5.0
CaO	8.0 – 10.0	Co_3O_4	0.25 – 0.35
Fe_2O_3	40.0 – 42.0		

Figure 1. Schematic flow diagram for leaching of copper slag.

The mineral composition is given in Table II. The major phases are fayalite with silicates. The amorphous content of the copper slags is high, approximately 30%. The slag is a complex mixture of metals, sulphides, silicates and oxides with a glassy amorphous material. The screen analysis and chemical analysis of the pulverized sample are presented in Figure 2. The copper distribution reduces with an increase in particle size and the distribution of silica is evenly distributed at different size fractions.

Table II. Mineralogical composition of the slag.

Mineral	Chemical structure	Mass percent	Mineral	Chemical structure	Mass percent
Covellite	CuS	5.1	Magnetite	Fe_3O_4	22.51
Diopside	$CaMgSi_2O_6$	29.14	Periclase	MgO	0.93
Fayalite	Fe_2SiO_4	42.31	Amorphous	-	30 – 32

Leaching of the Copper Slag

Leaching of the copper slag with concentrated sulphuric acid and distilled water, without increasing the digestion temperature, resulted in leaching recoveries of 45%, with a final copper content in the leach residue of 1.24%. The reaction was exothermic and the measured temperature of the reaction was a maximum of 143°C. It was critical to increase the temperature of the digestion stage to increase the dissolution of copper. The temperature was increased to 250°C with the consideration that the melting point of concentrated sulphuric acid is 300°C (Habashi, 1999). The other reason why 250°C was selected as the digestion temperature is that the reaction when leaching chalcopyrite with concentrated sulphuric acid is slow below 150°C. The leaching reaction between 150°C and 250°C forms elemental sulphur, $CuSO_4$ and $FeSO_4$. Above 250°C, elemental sulphur and ferrous iron are oxidized (Habashi, 1999).
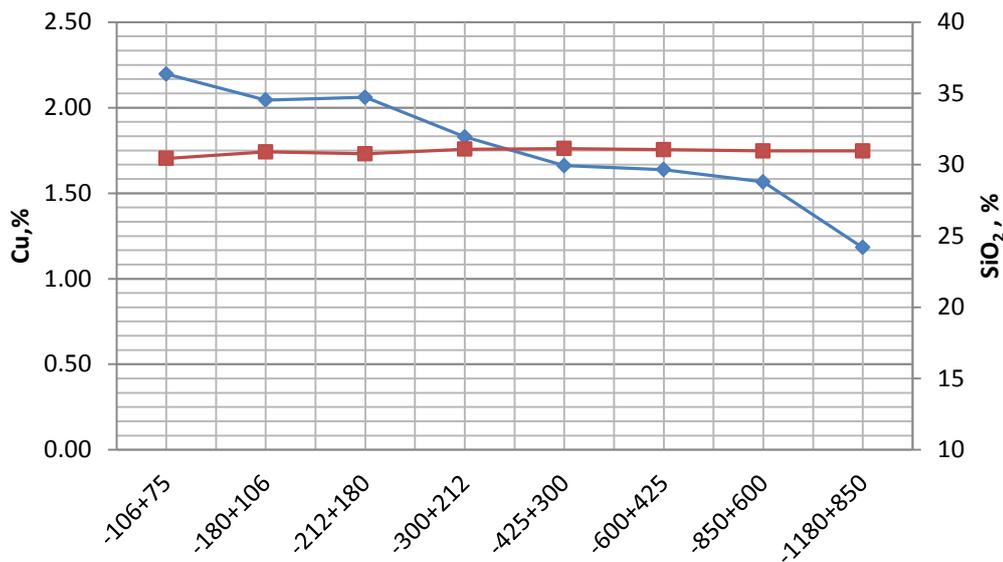
Figure 2.The screen analysis and chemical analysis of the pulverized sample of copper slag.

Effect of Acid Addition

Various amounts of acid were used to leach the copper slag. Figure 3 shows the effect of acid amount on the recovery of copper. The recovery of copper from the copper slag increased with an increase in the quantity of acid. The reaction was carried out with no water addition.
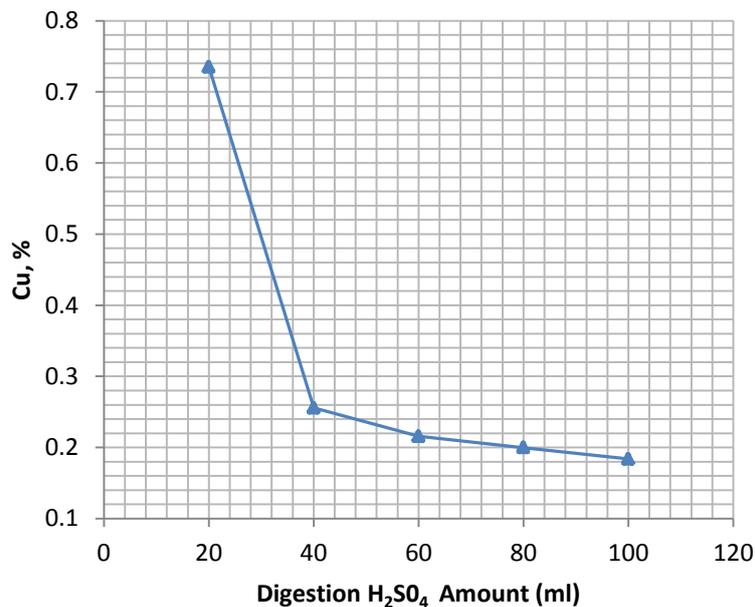

Figure 3. Copper in the residue for various quantities of acid addition to leach.

Effect of Acid Concentration

The effect of acid concentration was also investigated. Figure 4 shows that the copper recovery from the copper slag increases with an increase in acid concentration. An optimum recovery of copper is achieved at 70% H_2SO_4. The reaction was carried out with no water addition.
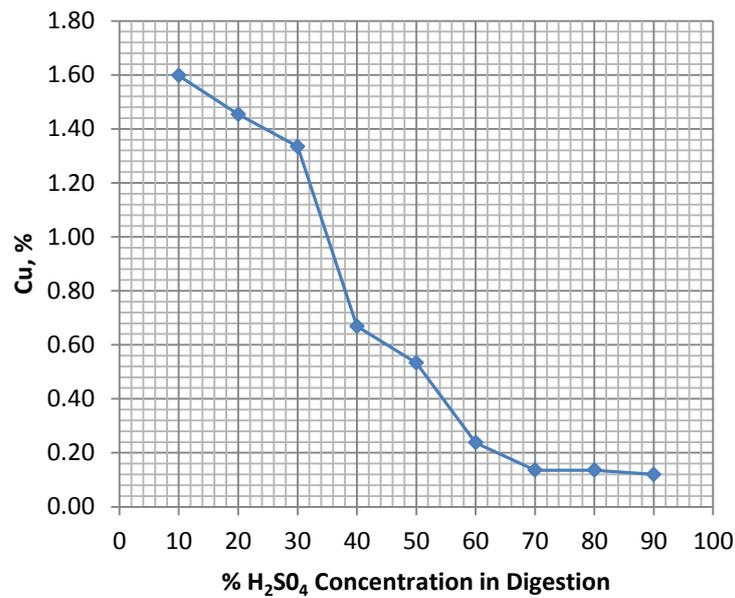
Figure 4. Copper in the residue for various concentrations of acid.

Effect of Water Addition on Digestion

It was found that water addition has a major effect on the extent of leaching under the experimental conditions employed. The recovery of copper increased dramatically with the addition of water up to 60 mL. The effect of water addition on the content of copper in the leach residue can be observed in Figure 5. A recovery of 95% was achieved when 60 mL of water was added during the digestion stage. The reaction was carried out with 100 mL of concentred sulphuric acid.
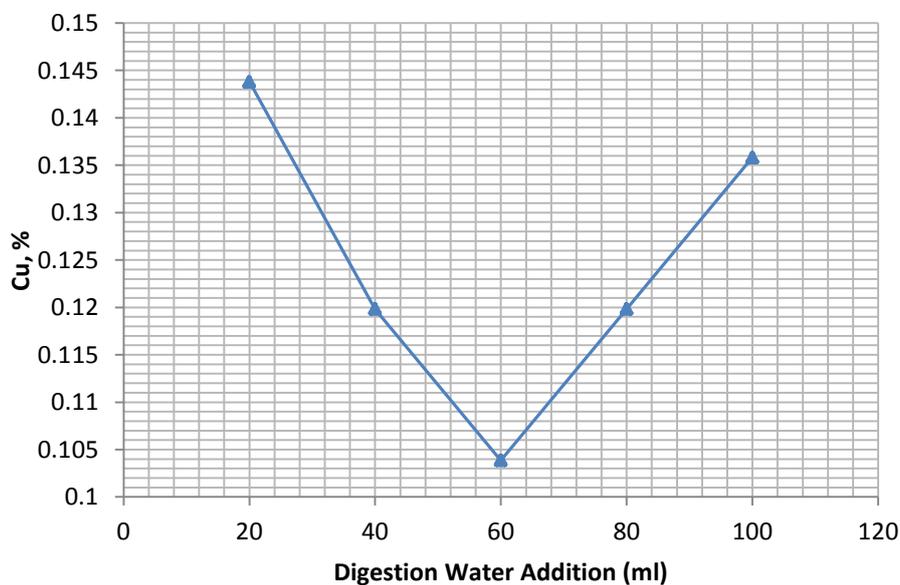

Figure 5. Copper in the residue for various water additions in digestion.

Figure 6 shows that at 60 mL water addition, the digestion temperature increased to 143°C. This is also the volume at which the high leaching results were obtained.
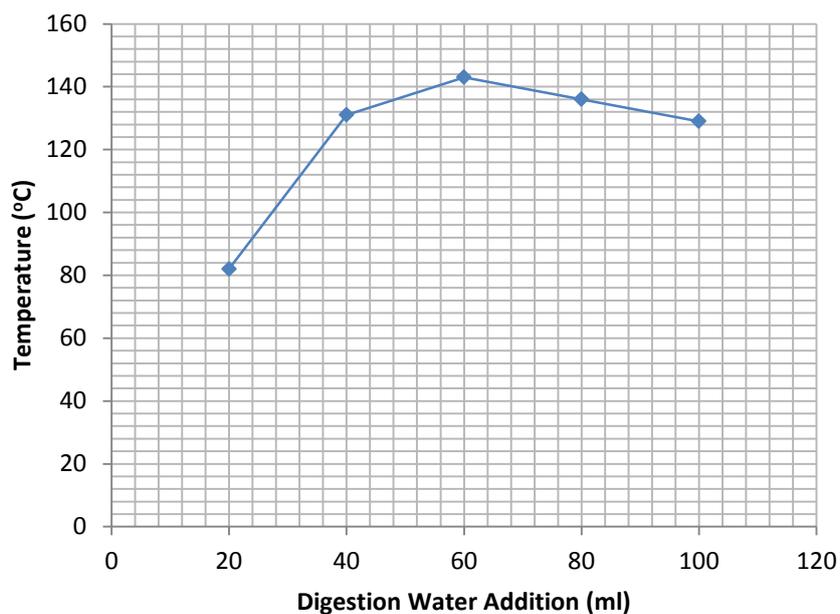
Figure 6. Effect of water addition to the digestion temperature.

Effect of Temperature

Figure 7 shows that the effect of digestion temperature is important when leaching copper from copper slag. The optimum digestion temperature is 250°C, at which a high recovery of copper from copper slag is achieved.
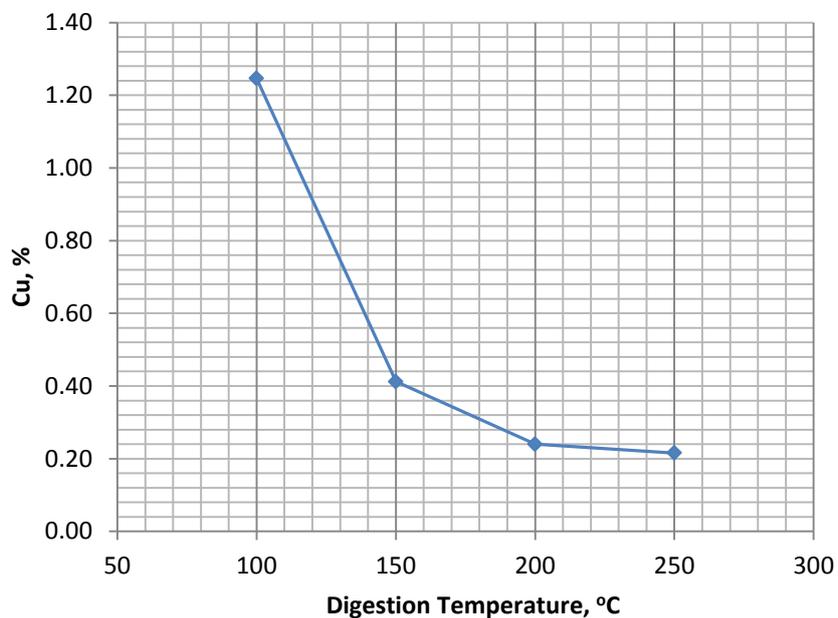

Figure 7. Copper in the residue at various digestion temperatures.

Effect of Digestion Time at 250°C

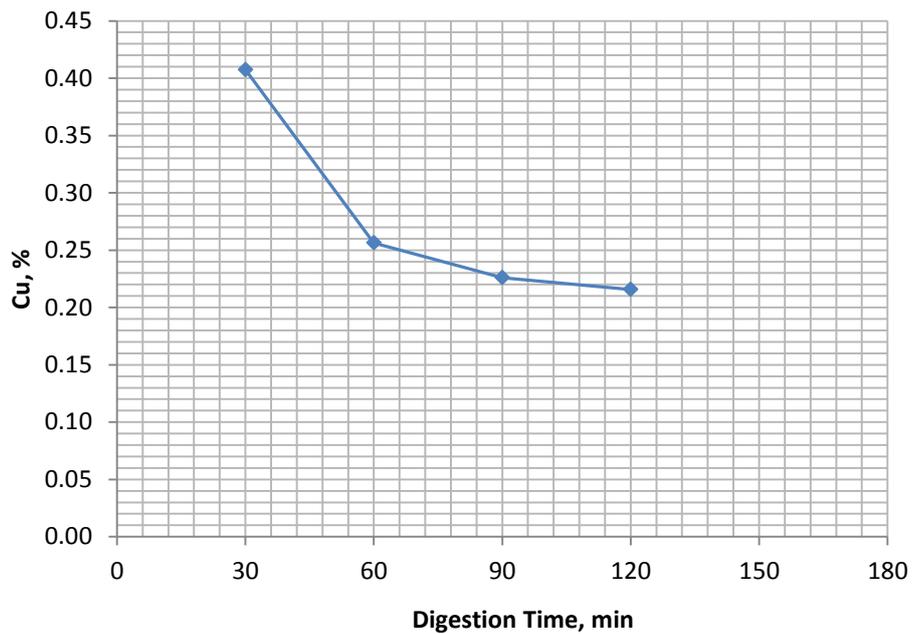Figure 8 shows that 2 hours of digestion at 250°C was adequate.

Figure 8. Copper in the residue at various digestion time.

Effect of Particle Size
Figure 9 shows the effect of particle size on the copper content in the leach residue. The recovery of copper at higher particles sizes was very low as all the copper particles were not exposed. The data show that the copper slag must be milled to a particle size of –106 μm to achieve the optimum recovery.
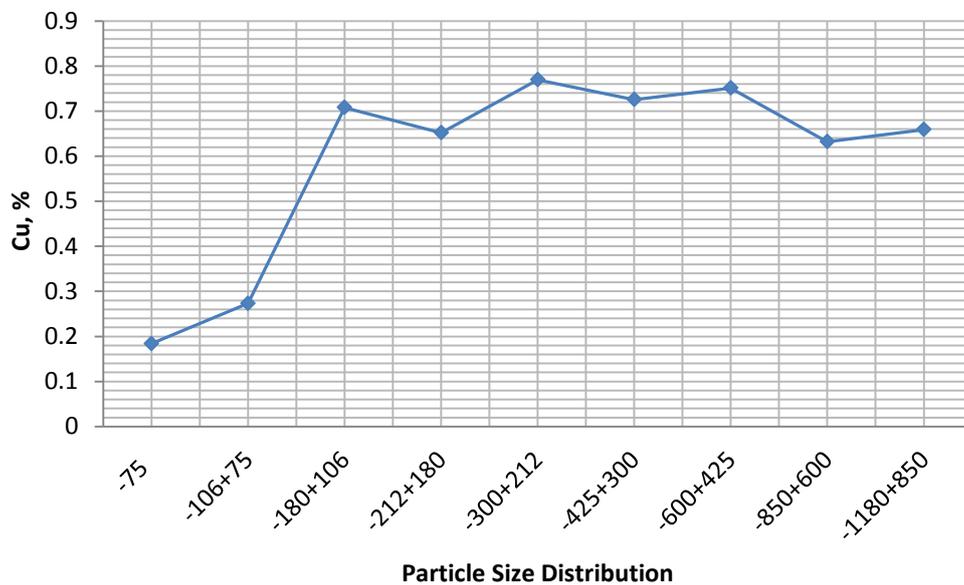

Figure 9. Copper in the residue at various particle sizes.

Pregnant Leach Solution and Leach Residue Analysis
The copper content in the pregnant leach solution was 2.9–3.3 g/L, as shown in Table III. This equates to a recovery of 80–90% of copper from the slag, depending on the number of leaching stages. Table IV gives the chemical composition of the leached residue and Table V gives the mineralogy. It can be

observed from the analysis that silicon is the major constituent. The iron and magnesium contents decreased. The major phases are amorphous material and diopside. The amorphous content of the residue is high, at approximately 48%.

Table III. Analysis of leach solution.

Cu (g/L)	Ni (mg/L)	Co (mg/L)	Ca (mg/L)	Mg (mg/L)	Fe (g/L)	Si (mg/L)
2.96	12.6	39.9	27.3	643	> 586	2.3

Table IV. Chemical analysis of leach residue.

Oxide	Mass percent	Oxide	Mass percent
Cu	0.10	MgO	0.796
SiO_2	52.7	Al_2O_3	2.86
CaO	14.3	Co_3O_4	0.25 – 0.35
Fe_2O_3	9.91		

Table V. Mineralogical analysis of leach residue.

Mineral	Chemical structure	Mass percent	Mineral	Chemical structure	Mass percent
Amorphous	-	48.31	Diopside	$CaMgSi_2O_6$	33.11
Anhydrite	$CaSO_4$	8.2	Spinel	$MgAl_2O_4$	12.77
Bassanite	$2CaSO_4 \bullet H_2O$	3.61			

The application of the leach residue in concrete is currently being investigated currently. Comparing the chemical composition of the leach residue with that of ferromanganese work conducted previously (Kazadi et al., 2013), this leach residue has a higher amorphous content and lower gypsum content.

CONCLUSIONS

This study shows that milled copper slag can be efficiently digested in sulfuric acid and distilled water at 250°C and the solid cake then water-leached. Leaching of the slag with concentrated sulphuric acid and distilled water, without increasing the digestion temperature, resulted in leach recoveries of 45%. The recovery of copper from the copper slag increased with an increase in the quantity of acid and with an increase in acid concentration. The recovery of copper increased dramatically with the addition of water up to 60 mL. The optimum digestion temperature and duration were 250°C and 2 h, respectively. The copper slag must be milled to a particle size of –106 μm to achieve optimum recovery. The highest extraction obtained was 95%, based on solids analysis. The copper leach solution can further undergo purification before recovery of the copper from solution. The high amorphous content, high silica content and low $CaSO_4$ content probably makes the copper slag leach residue a valuable additive for Portland cement. This work is ongoing and more tests are being conducted to optimize the digestion and leaching stages. The leach residue is being tested to determine if it is suitable to use as an additive for Portland cement manufacturing and to quantify how much the copper slag leach residue increases the strength of the cement.

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