



## Research article

## Enhancing the flotation recovery of copper minerals in smelter slags from Namibia prior to disposal

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## ABSTRACT

Namibia Custom Smelters (NCS) process a range of copper concentrates in their three furnaces, namely; top submerged lance, copper converter and reverberatory furnaces, in order to produce mattes and fayalitic slags. The copper content of the slags range between 0.8 to 5 wt. % and this is considered too high for disposal to the environment. Currently, the slags are sent to a milling and flotation plant for liberation and recovery of residual copper. The copper recoveries realized in the plant are much lower than expected and it has been postulated that some copper minerals may be occurring in forms that are more difficult to float like oxides or fine disseminations in the gangue matrix. Mineralogical analysis of the slag samples was done using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) techniques. The analysis did not reveal the presence of copper oxide minerals, however most scans showed copper sulphide minerals as free grains and some finely disseminated in fayalite gangue. In the first phase of the present experimental studies, the slags were milled to 75% passing 45 microns, which is the degree of milling done in the existing plant mill-float circuit. A range of commercial flotation reagents that include xanthates, dithiophosphates, mercaptobenzothiazole, thionocarbamates, fatty acids, sulphides and sulphates were used in the flotation test-work. The copper recoveries obtained in the mill-float stage were between 70 - 80%. In the second phase of the study, the flotation tailings were further milled to 90% passing 45 microns and floated. The cumulative copper recoveries increased markedly to over 90%, which represents a significant improvement in comparison to the recoveries obtained from the mill-float process. Sodium alkyl dithiophosphate, mercaptobenzothiazole (FC7245) was found to be the secondary flotation reagent that gave the best copper recoveries.

## 1. Introduction

Slags that are produced from smelting of both ferrous and non-ferrous metal ores and concentrates together with other metallurgically generated residues like tailings dumps are increasingly becoming a subject of great environmental and ecological debate. The world now holds the view that economic and ecological considerations have to be integrated into the extraction process design, hence the emergence of the concept of sustainable metallurgy (Zander et al., 2013).

Sustainable metallurgy emphasizes on the point that recovery of valuable materials from waste residues, their reuse and recycling have a major advantage of saving the earth's finite resources and reducing the negative impact that waste has on the environment.

Slags are basically formed by fluxing agents used to aid high temperature liquid-liquid separation in furnaces. The gangue portion of the ore, with the help of fluxes, is absorbed in the slag phase during smelting while the valuable portion is tapped off as matte. Slags have found a wide range of applications in civil engineering, fertilizer production, road construction, cement production and in landfilling (Ziemkiewicz, 1998). Wang et al. (2011) reported that the main constituents of copper smelter slags found around the world are FeO and SiO<sub>2</sub>, which are components of fayalite, and each is present at about 20–55 wt. %. They also reported that the copper content of most smelter slags is normally around 1–2 wt. % while that of the converter slag lies between 2 and 2.5 wt. %. This higher content for the latter is due to over-oxidation and entrapment of metal droplets during the converting process.

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In the smelting process, the melt bath instability causes entrapment of valuable minerals in slags, resulting in slags that are enriched in mineral values. The mineral entrapment occurs partly due to mechanical entrapment of matte in the form of fine dispersions of metal sulphides (Herreros et al., 1998; Sun, 2006) or as heavy metals dissolving into slag as oxides chemically bound with silica in fayalite (Curlook and Papanagelakis, 2004; Toscano, 2001; Toscano and Utigard, 2003). These enriched slags are normally cleaned to remove wanted minerals and metals. Slag cleaning can be divided into two types, first being the pyrometallurgical reduction and settling of liquid slag, which is performed in slag-cleaning furnaces, and the second type being the mineral processing-based slag cleaning of solidified or granulated slag by crushing and/or grinding followed by gravity concentration or froth flotation (Davenport et al., 2002).

Pyrometallurgical cleaning of copper slags involves inducing conditions that encourage suspended matte ( $\text{Cu}_2\text{S}$ ) droplets to settle into the matte layer. The conditions are achieved by creating a low slag viscosity, low bath turbulence, longer residence time and a thin slag layer (Guo et al., 2016). These conditions are often difficult to obtain in the main smelting vessel, particularly the necessary residence time, hence some copper producers construct separate furnaces specifically for cleaning, smelting and converting slags that have a high residual copper mineral content (Davenport et al., 2002).

Flotation is a physical and chemical separation process that utilizes the difference in surface properties of the valuable minerals and the unwanted gangue minerals (Wills, 2006). Recovery of materials during flotation can be explained by the following three mechanisms: (i) selective attachment to air bubbles ("true flotation"); (ii) entrainment in water passing through froth; and (iii) physical entrapment between particles in the froth attached to air bubbles ("aggregation"). The majority of the recovery takes place via true flotation, as it is a highly chemically selective process. The separation efficiency between gangue and valuable mineral is also dependent on the degree of entrainment and physical entrapment. The two are not chemically selective processes, hence gangue and valuable minerals are both recovered by entrainment and entrapment. Wills (2006) noted that copper sulfide ( $\text{Cu}_2\text{S}$ ) minerals have good flotation response to anionic collectors such as amyl, iso-propyl and butyl xanthates, and the concentrations of collectors added usually vary between 3 and 300 g per tonne. Rougher concentrates and middlings are usually reground and floated for maximum recovery.

At the Namibia Custom Smelters (NCS), complex copper concentrates are smelted in plants that consist of a Top Submerged Lance (TSL) furnace, Copper converter and a Reverberatory furnace. The furnaces produce slags that generally have fayalite ( $\text{Fe}_2\text{SiO}_4$ ) as the dominant crystal phase followed by magnetite ( $\text{Fe}_3\text{O}_4$ ) and copper sulphide inclusions. The copper content of these slags has been found to range between 0.8 to 5 wt. % (Vojtech et al., 2009; Imris et al., 2000). According to Zander et al. (2011), Jackman and Hayward (1933), Mackey (1982) and Mihailova and Mehandjiev (2010), fayalitic slag generally contains up to 1 wt. % of copper as well as other valuable metals like nickel, cobalt and molybdenum. If the entrapped metal droplets and minerals content is above a threshold of about 1 wt. %, the slags are considered a secondary resource worthy of further beneficiation to recover the valuable constituents. In addition to the economic benefits of recovering metals from slags, the use of slags in other applications also requires them to be environmentally friendly by meeting regulatory limits of heavy metals. This makes the recovery of metals from slags an imperative precursor to use of slags.

The reclamation plant at NCS consists of a milling circuit, which produces a fine circuit product (75% passing 45 microns) at 25 tons per hour that is fed to a flotation circuit. The flotation circuit consists of a scalper section that is followed by a rougher section. The rougher concentrate is fed to cleaner cells and the cleaner tailings are returned to

the rougher cells. The rougher tails are fed to a series of scavenger cells before exiting the plant as final tailings. Potassium amyl xanthate (~300 g/t) is the primary flotation collector reagent used, and Sodium Di-alkyldithiophosphate (200 g/t) is added as a secondary collector. The main concern with the current process is that tailings grade in the excess of 0.9% Cu are consistently produced. This copper content is considered too high to be lost in the final waste stream. Therefore, the scope of the present work involves an investigation into how the flotation recoveries of the copper minerals can be enhanced by studying the mineralogy, milling and liberation profile of the slags and the flotation reagent suite that can be used to optimally recover the copper minerals from the slags.

## 2. Materials and methods

### 2.1. Feed material

The feed material used in this investigation was sourced from a mineral processing plant called the Namibian Custom Smelters (NCS) that is situated in a Southern African state called Namibia. Three homogenized samples were obtained from a reverberatory furnace slag, top submerged lance (TSL) slag and a converter slag, respectively. Laboratory tests were then carried out on these samples as well as on the combined slag, with the aim of recovering copper minerals.

### 2.2. Mineralogical tests

The prepared and homogenized sub-samples of reverberatory, TSL and converter slags were submitted for mineralogical analyses using X-ray diffraction (XRD) and scanning electron microscope (SEM) techniques. For XRD analysis, the different samples were prepared same as Ettler et al. (2009) by using a backloading preparation method. For SEM analysis, the procedure followed that in Ettler et al. (2009).

A chemical analysis was performed on different size classes of milled samples to determine the copper deportment across the spectrum of the size classes. Three slag samples (converter slag, TSL slag, reverb slag) were submitted to an external laboratory, SGS (South Africa). Mineralogical analyses on the slags were performed, particularly for the copper and zinc phases.

### 2.3. Milling and flotation test work

#### 2.3.1. Milling equipment

The following was used during the milling test work on the slag samples; a laboratory scale ball mill (400 mm by 300 mm), a Laarmann laboratory slurry press (size 13) for slurry filtration, a 1.0 L measuring cylinder for measuring and adding water, a drying oven to dry the slurry, steel grinding balls for milling, process water for milling and flotation, an analytical balance for sample weighing, test sieves (2800  $\mu\text{m}$ , 1400  $\mu\text{m}$ , 600 $\mu\text{m}$ , 300 $\mu\text{m}$ , 250  $\mu\text{m}$ , 150  $\mu\text{m}$ , 125  $\mu\text{m}$ , 106  $\mu\text{m}$ , 75  $\mu\text{m}$ , 45  $\mu\text{m}$ ) for size distribution determination, a vibratory sieve shaker to aid screening, a 20.0 L bucket to collect mill discharge.

#### 2.3.2. Milling experimental procedure

One kilogram of each of the three different slag samples (reverberatory furnace, TSL and converter slags) were weighed and placed in the ball mill loaded with 12.0 kg grinding steel balls. Measured 600 ml of plant process water was then also added to the charge in order to achieve a 62% solids by mass slurry. The samples were milled for 30, 60, 90, 120, 150 and 180 min. After milling, the mill discharge was washed out into the bucket over a wire mesh that served the purpose of retaining the grinding media. The product slurry was then dewatered using a filter press, dried in the oven set at a temperature of 65 °C for 45 min. This period was observed to be long enough for all the moisture to be driven

off without crusting the samples. Size analysis of the milled and dried slag samples was then carried out in order to develop milling curves. Using the milling curves, a milling duration of 2 h was found sufficient in order to achieve a 75% less than 45 microns product. The -45 microns product became the feed to the flotation cells, but samples used for flotation were not oven dried to avoid changing the surface properties. The water content of the milled samples was not measured as the oven dried samples were not used for flotation experiments but only for analysis.

### 2.3.3. Flotation experimental procedure

A Wemco fagergren mineral master (Model LA 500) flotation machine was used in carrying out the flotation tests. The milled slag was dewatered and placed into the flotation cell. Water was added to dilute the slurry up to approximately 30% solids by mass. Reagents specific to each test were added and a conditioning time of 3 min was allowed. Air was bubbled through the agitated slurry at a rate of 2–3 l/min and agitation was set at 1380 rpm. Concentrates were collected manually by scraping the froth using scraper blades. Each flotation experiment lasted 15 min. Firstly, each of the three slags was floated separately in order to study its individual flotation response. The second phase of the research involved regrinding and floating plant tailings. At that time, the reverberatory furnace had been decommissioned and only TSL slag and converter slags were evaluated. For the second series of tests, only reagents which delivered favorable results in the first phase were used. These were sodium alkyl dithiophosphate, mercaptobenzothiazole (FC 7245), Modified thionocarbocarbamate, methyl isobutyl carbinol (FC 4146), which are secondary collectors and 10% Na<sub>2</sub>S a sulphidising agent.

## 3. Results and discussions

### 3.1. Mineralogical analysis

Experimental analysis of the mineralogical composition of the three slag types i.e. converter, TSL and reverberatory slag is presented.

#### 3.1.1. X-ray diffraction (XRD) analysis

Results of the XRD analyses are given in Table 1.

Table 1 shows that chalcocite is the main copper bearing mineral in the converter slag. In the TSL slag, copper is in the form of chalcocite,

**Table 1.** Crystalline phases as determined by x-ray diffraction (XRD).

Converter Slag		
Mineral Name	Mineral Formula	Approximate Abundance
Fayalite	Fe <sub>2</sub> SiO <sub>4</sub>	20–50 %
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	20–50 %
Diopside	CaMgSi <sub>2</sub> O <sub>6</sub>	10–20 %
Quartz	SiO <sub>2</sub>	3–10 %
Sphene	CaTiSiO <sub>5</sub>	3–10 %
Chalcocite	Cu <sub>2</sub> S	3–10 %
TSL Slag		
Mineral Name	Mineral Formula	Approximate Abundance
Diopside	CaMgSi <sub>2</sub> O <sub>6</sub>	20–50 %
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	20–50 %
Chalcocite/digenite	Cu <sub>2</sub> S/Cu <sub>9</sub> S <sub>5</sub>	3–10 %
Bornite	Cu <sub>5</sub> FeS <sub>4</sub>	3–10 %
Reverberatory Slag		
Mineral Name	Mineral Formula	Approximate Abundance
Diopside	CaMgSi <sub>2</sub> O <sub>6</sub>	20–50 %
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	20–50 %
Quartz	SiO <sub>2</sub>	20–50 %
Plagioclase	NaAlSi <sub>3</sub> O <sub>8</sub>	10–20 %
Fayalite	Fe <sub>2</sub> SiO <sub>4</sub>	10–20 %

digenite and bornite. No copper containing minerals were detected in reverberatory slag, as it contains less than 1% copper. Some chalcocite was detected in the final tailings but not in the feed slag, this suggests that chalcocite was insignificant in the feed (<3%) and that it could have been very finely disseminated in the slag matrix but become concentrated in the tailings stream.

The slags investigated in this present work also show a content of fayalite in the similar range. However, a significant amount of iron also occurs in the form of magnetite (20–50% in Table 1). It is interesting to note that copper in the converter and TSL slags is generally much higher than the copper content found in primary copper ore, which is typically between 0.5 and ~2 wt%, making this material a potential secondary resource for copper.

Vojtech et al. (2009) studied the mineralogy and environmental stability of similar slags from Namibia smelters and reported that the slags were composed of mainly spinel oxides (CaMgSi<sub>2</sub>O<sub>6</sub>, CaTiSiO<sub>5</sub>, Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>SiO<sub>4</sub>), silicates (SiO<sub>2</sub>), glass (NaAlSi<sub>3</sub>O<sub>8</sub>) and sulphide-metallic inclusions. These same phases are confirmed in the XRD results as well.

#### 3.1.2. Scanning electron microscope (SEM) analysis

Figures 1, 2, and 3 shows the scanning electron micrographs obtained from the SEM analysis of the converter slag, TSL slag and reverberatory slag, respectively.

Figure 1(a) shows fayalite grain (3) with inclusions of partially exposed bornite and locked bornite (1 and 2 respectively) and magnetite (4). Figure 1(b) shows a liberated chalcocite grain (2) with small inclusions of galena (1). Figure 1(c) shows a fayalite grain (1) with locked and partially exposed bornite inclusions (3) and (4). There are also inclusions of magnetite (2). Scanning electron micrographs shown in the figure are for the converter slag. According to the XRD scans, chalcocite is the main copper mineral in the converter slag and Figure 1(b) confirms the presence of significantly liberated chalcocite grains. According to the XRD results, fayalite and magnetite are the dominant gangue phases in the converter slag. These are equally dominant in the corresponding SEM micrographs. The minerals bornite and galena were not picked up in the XRD analysis but are present in the SEM as finely disseminated grains. The absence of these minerals in the XRD could be due to that their relative abundance is below 3%.

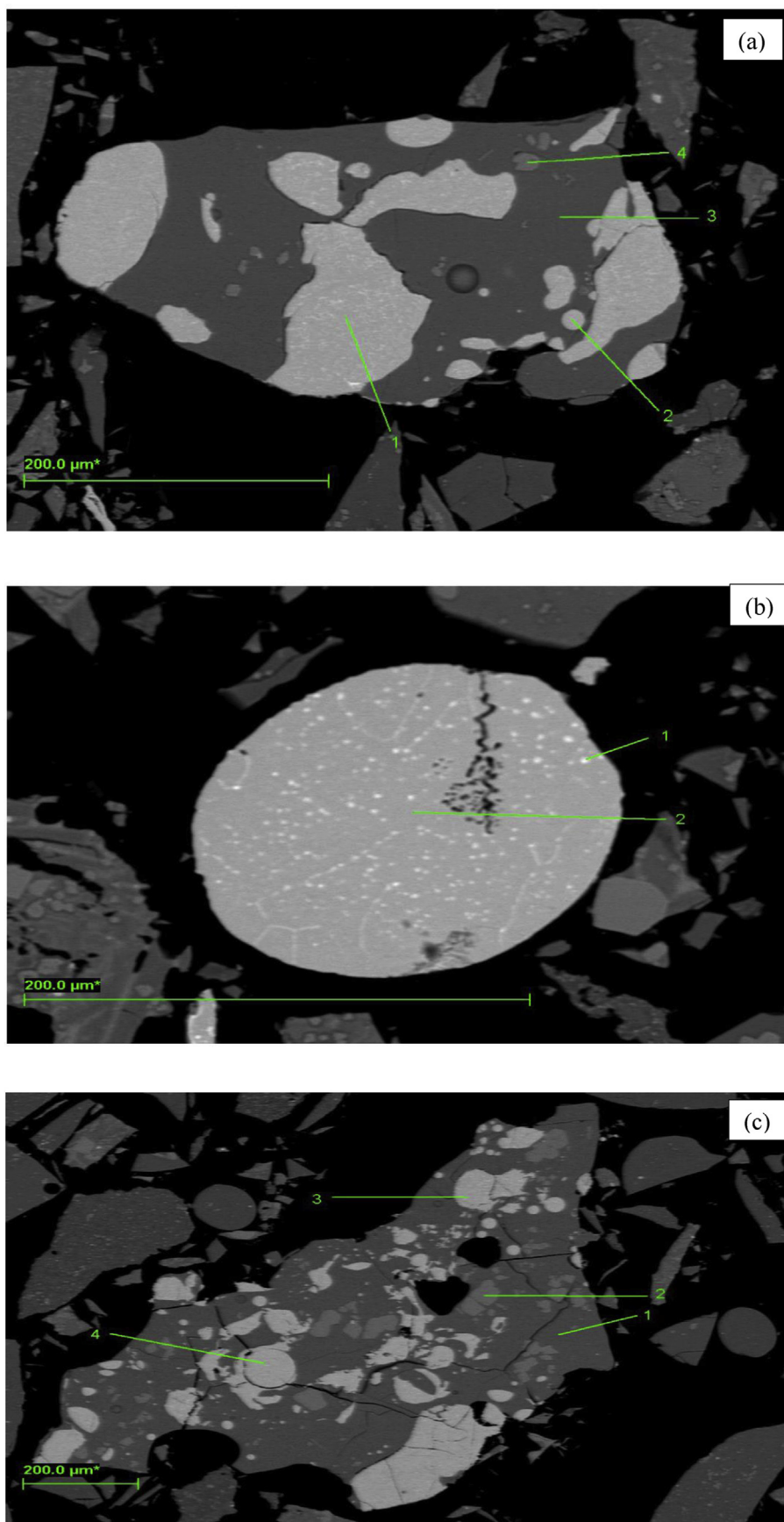
Figure 2 shows the scanning electron micrographs for TSL slags.

Figure 2(a) shows well exposed and liberated bornite grains (1) while Figure 2(b) shows liberated chalcocite grain (1). Bornite and chalcocite were also found to be the dominant copper bearing minerals in the TSL slag, according to the XRD analysis. Figure 2(c) and (d) show significant presence of diopside, which was also found to be the main gangue phase in the XRD analysis. Figure 2(c) shows a diopside grain (3) containing bornite (2 and 4) and magnetite inclusions (1). Figure 2(d) shows some chalcocite grains that are finely disseminated in diopside phase (3) as well as partially exposed chalcocite (1).

Figure 3 shows the scanning electron micrographs for the reverberatory slag. In these images it is evident that there is very little copper mineral content in this particular slag, confirming the XRD results, which indicate that the reverberatory slag has no copper minerals. This suggests that the reverberatory furnace is efficient in its recovery of copper and other values to the matte phase as it apparently produces a much cleaner slag.

Figure 3(a) shows a diopside grain (2) with locked and partially exposed bornite inclusions (3 and 1 respectively) while Figure 3(b) shows a diopside grain with inclusions of locked and partially exposed chalcocite (1) as well as magnetite (2).

Vojtech et al. (2009) suggests that spinels are the first crystallizing phase and they tend to form large zoned crystals (up to 50 μm). The scanning electron micrographs from this study also show fairly large and well-formed grains of diopside and fayalite, which are spinels. The presence of mattes (sulphide-rich materials) and speiss (arsenide-rich materials) were reported by Vojtech et al. (2009) to occur as droplets



**Figure 1.** Converter slag micrographs: (a) SEM microphotograph showing a fayalite grain, (b) SEM microphotograph showing a liberated chalcocite grain, and (c) SEM microphotograph showing a fayalite grain.

and fragments of various sizes composed of intergrowths of sulphides, metals and intermetallic compounds, and embedded within the spinels and silicate slag. Similar observations were also made where the occurrence of the copper bearing minerals in the scanning electron micrographs of Figure 3 appear as inclusions and imbeds of minerals in the diopside and fayalite grains.

### 3.2. Milling test work

Figure 4 shows the cumulative particle size distribution of the three slags as received into the milling plant from the crushing and screening circuit. All the slags are fed into the mill at 100% passing 2800  $\mu\text{m}$  Figure 5 shows the milling response of the three slags under identical laboratory milling conditions. Figure 5 suggests that the reverberatory slag crushes much more easily than the TSL slag and the converter slag as it has a much higher proportion of finer particles. Figure 6 shows the copper content from different particle size classes for the converter slag, TSL slag and reverberatory slag. The results from Figure 6 and the mineralogical studies suggest that there is an inverse relationship between the ease of crushing and the copper mineral content of the slag material.

Figure 4 shows the milling response of the three slags under identical laboratory milling conditions. Percentage passing 45 $\mu\text{m}$  was measured as a function of milling time at hourly intervals up to 3 h. The aim was to determine how long it would take to achieve the target of 75% passing 45 $\mu\text{m}$ , which is the size distribution required for the flotation tests. The results show that the TSL and converter slag require approximately the same milling time of 2 h and the reverberatory slag requires less milling time of 1 h and 40 min to achieve the same reduction in size.

A chemical analysis was performed on different size classes of milled samples to determine the copper department across the spectrum of the size classes. Figure 6 shows a size by assay analysis of the converter slag, TSL slag and reverberatory slag, respectively. The converter slag contains the highest amount of copper followed by the TSL slag while the reverberatory slag has the least copper content. This observation is consistent with what was reported in the work of Wang et al. (2011) that copper

content of converter slags are generally higher than that of other smelter slags due to over-oxidation and turbulence in the converting process, which encourages entrapment of metal droplets in the slag. The graph shows that as the particle size decreases from largest size fraction of 250–350  $\mu\text{m}$  to the finest size fraction of <45  $\mu\text{m}$ , the % content of copper generally increases for all the slags. Particles less than 45  $\mu\text{m}$  contain more copper than larger size classes and therefore the objective of milling would be to maximize on the class size that shows the greatest liberation, though a trade-off has to be made with the milling costs.

### 3.3. Flotation test work

Various flotation reagents that are commonly used for copper flotation were identified, selected and used during the flotation test work in order to identify the best reagent best suited to float the copper slags. Potassium amyl xanthate (PAX) and Flotanol CO 7 were used in all tests as the primary collector and frother. Different secondary collectors and sulphidizing agents were used to enhance the floatability of the target species. The different reagents used are tabulated in Table 2.

Table 3 illustrates the range of flotation tests performed, the flotation reagents, dosage and flotation time used. The main variables in the flotation tests were the type of secondary collector and the sulphidizing agents.

#### 3.3.1. Phase 1 – flotation of the original slags

This phase of the flotation test work involved the flotation of the original three slags and a composite mixture of all the slags at a ratio of 1:1:1, after grinding to 75% passing 45 microns. This was done so as to reduce the costs (save on time and chemicals that will be used) by floating all the slags at the same time and to see if the recoveries will be comparable to individual recoveries. In addition, mixing the slags helps to improve recoveries of reverberatory slags as reverberatory slags had low recoveries, typically less than 15% throughout the tests as compared to the mixed slags because it had less copper content (<1 wt.%). Figure 7 indicate the total recoveries obtained from the flotation of the different slags. The recovery was calculated using the following formula:

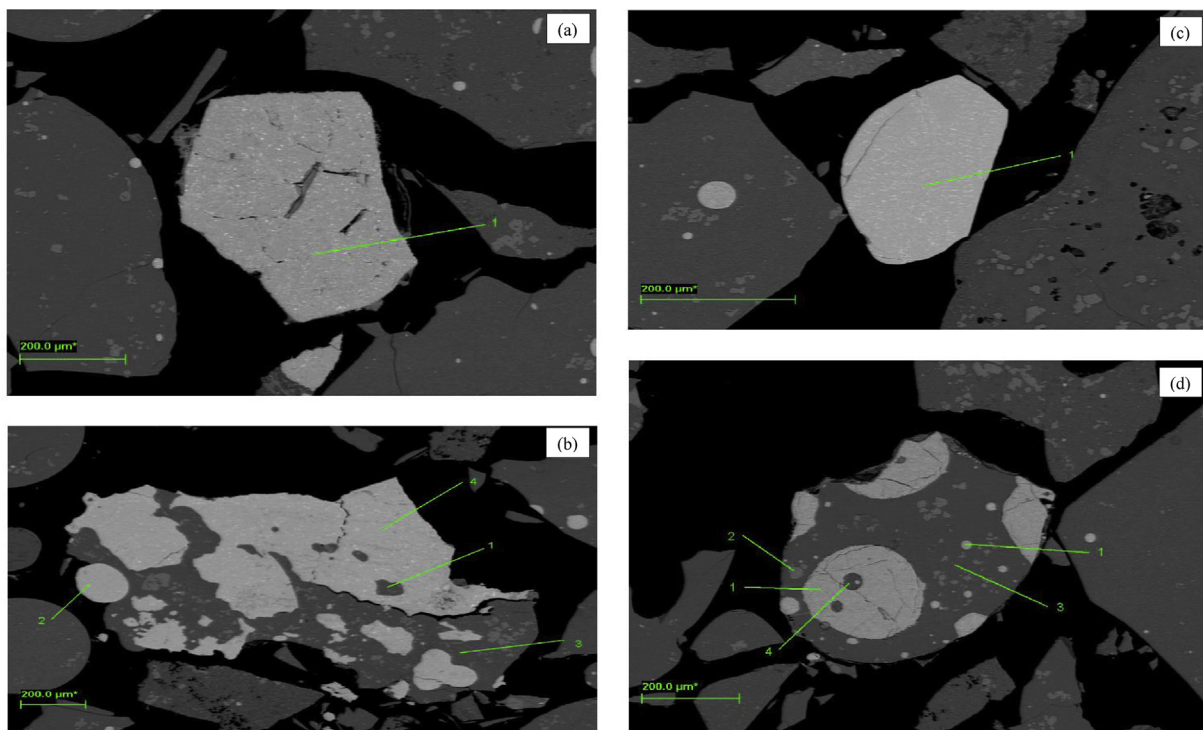
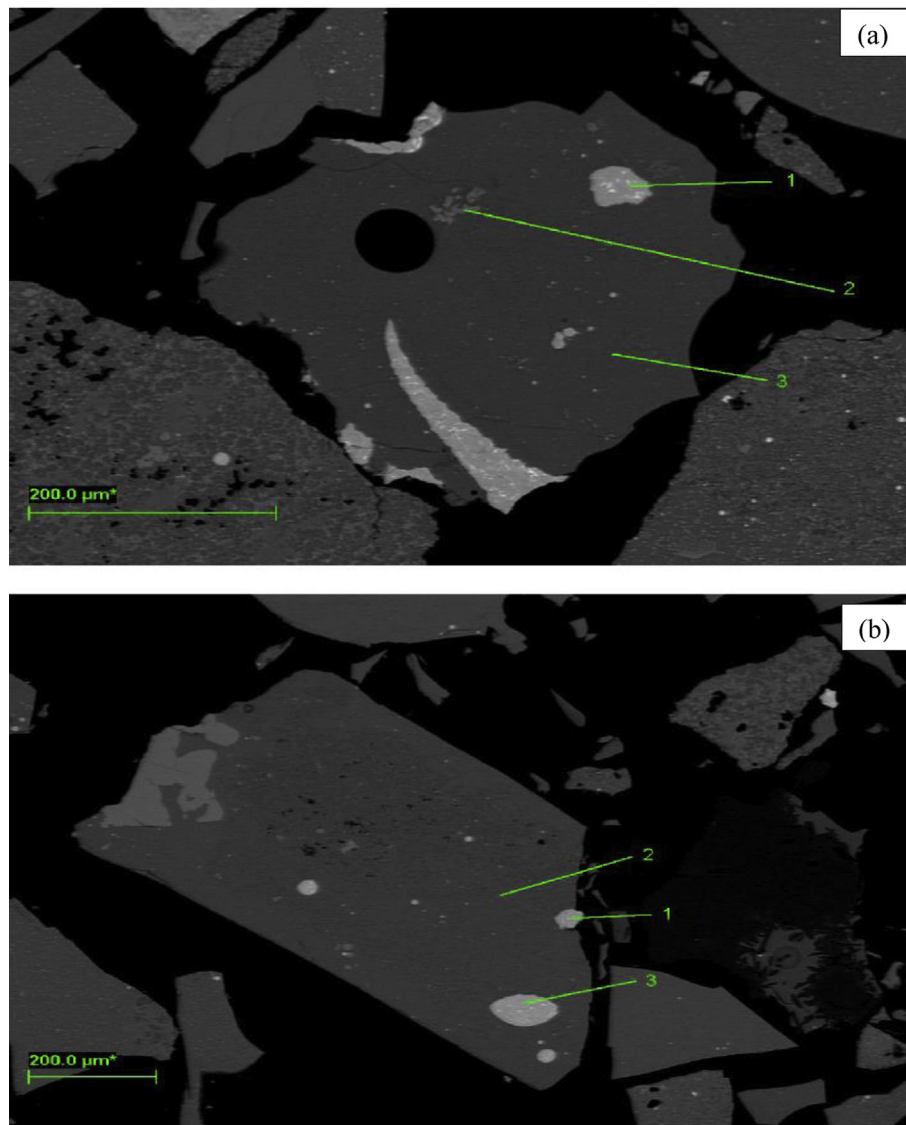


Figure 2. TSL Slag: (a) SEM microphotograph showing an exposed bornite mineral, (b) SEM microphotograph showing an exposed chalcocite grain, (c) SEM microphotograph showing a diopside grain, and (d) SEM microphotograph of diopside grain.



**Figure 3.** Reverberatory Slag: (a) SEM microphotograph showing a diopside grain, (b) SEM microphotograph showing a diopside grain.

$$\text{Recovery} = \frac{M_{\text{concentrate}} \times \%Cu_{\text{concentrate}}}{M_{\text{concentrate}} \times \%Cu_{\text{concentrate}} + M_{\text{tailings}} \times \%Cu_{\text{tailings}}} \quad 1$$

where  $M_{\text{concentrate}}$  is the weight (mass) of the concentrate in grams after flotation,  $\%Cu_{\text{concentrate}}$  is the copper content in the concentrate,  $M_{\text{tailings}}$  is the weight (mass) of the tailings in grams after flotation,  $\%Cu_{\text{tailings}}$  is the copper content in the tailings.

One of the results obtained after flotation and used to calculate recovery had concentrate and tailings grades of 31.6 and 0.38 % Cu, respectively. The concentrate and tailings weights were 12.4 and 337 g, respectively. This gave mass of copper in concentrate of 3.92 g and in the tailings, it was 1.28 g, to give a Cu recovery of 75.4%.

Figure 7 shows that the reverberatory slag yielded the lowest recoveries, typically less than 15% for all the tests conducted. The poor recoveries from the reverberatory slag are due to its low copper content, which is typically less than 1%. The XRD and the SEM analysis discussed in the earlier sections showed that the reverberatory slag has little or no copper mineral content. The recoveries from the converter slag and TSL slag are much higher; they were found to be consistently above 70%

whilst the recoveries from the mixed slag sample were also high but lower than those of TSL and converter slags respectively. Secondary collector FC4146 (Test 9), FC7245 (Test 2) yielded higher recoveries than other secondary collectors and 10%  $Na_2S$  (Test 12) yielded higher recoveries than other sulphidizing agents.

Test 9 in which FC 4146 was used as the secondary collector recorded the highest recoveries in comparison with other secondary collectors' tests, with recoveries of about 82% for the TSL slag, 79% for converter slag and 70% for a 1:1:1 mixture of the three slags. Test 12 in which  $Na_2S$  was used recorded the highest recoveries of about 86% for the TSL slag, 77% for converter slag and 75.1% for a 1:1:1 mixture of the three slags. This test also resulted in the lowest tailings grade of 0.64% Cu. The recoveries from the use of  $Na_2S$ , which is a sulphidizing agent were unexpected, considering the fact that mineralogical analysis showed no evidence of copper oxide minerals in the slag. A possible explanation could be that gangue oxides, with inclusion of copper minerals are sulphidized and picked up during flotation. Experiments with other sulphidizing agents used i.e.  $NaHS$ ,  $(NH_4)_2S$  and  $(NH_4)_2SO_4$  showed relatively low recoveries.

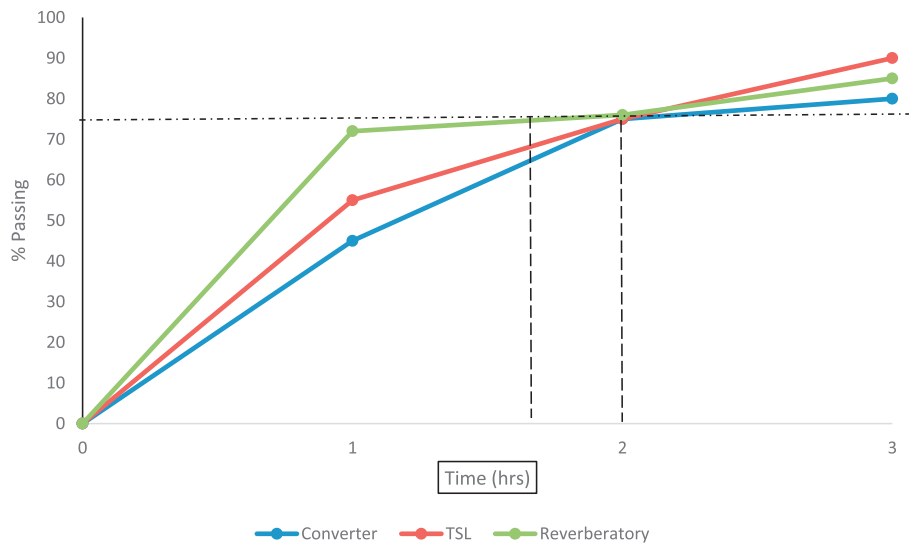


Figure 4. Cumulative particle size distribution of the three slags as received into the milling plant from the crushing and screening circuit

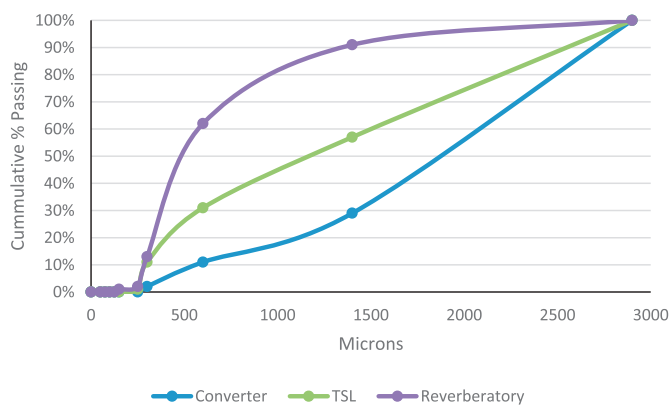


Figure 5. Milling response of the three slags under identical laboratory milling conditions.

### 3.3.2. Phase 2 – flotation of reground tailings

Phase 2 of the flotation test work involved regrinding the tailings from phase 1 experiments to 90% passing 45 microns and floating them, with the view that additional liberation will result in improved recoveries. Reagents for phase 2 tests were narrowed down to; Na<sub>2</sub>S, FC 4146 and FC 7245 i.e. the reagents that gave the best results in the phase 1 test work. Figures 8, 9, 10, and 11 show the results of the flotation tests after regrinding of the tailings.

Figures 9 and 10 show clearly that there was a marked increase in the overall recovery of copper after the tailings of the 1<sup>st</sup> stage flotation were milled to 90% passing 45 microns and floated. In the case of converter and mixed slag, increases of over 10% in the recovery were recorded when both FC4146 and FC7245 were used as secondary collectors or collector enhancers. The increase observed for the TSL slag was marginally lower than for the other slags. Figure 10 also reveals that flotation of the reground tailings with Na<sub>2</sub>S as a flotation collection enhancer did not produce any significant improvement in the overall recovery of Cu after regrinding of the tailings.

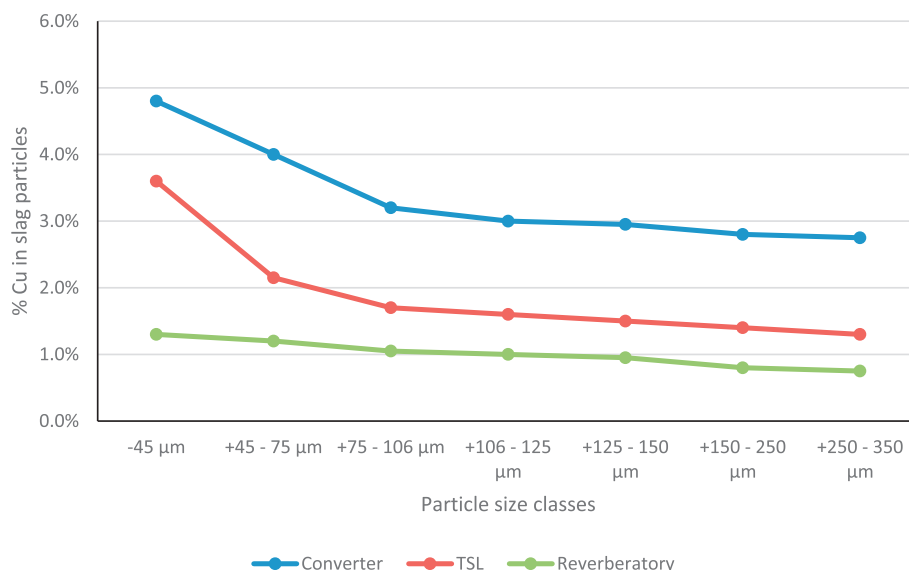


Figure 6. Size by assay analysis for the converter slag, TSL slag and reverberatory slag.

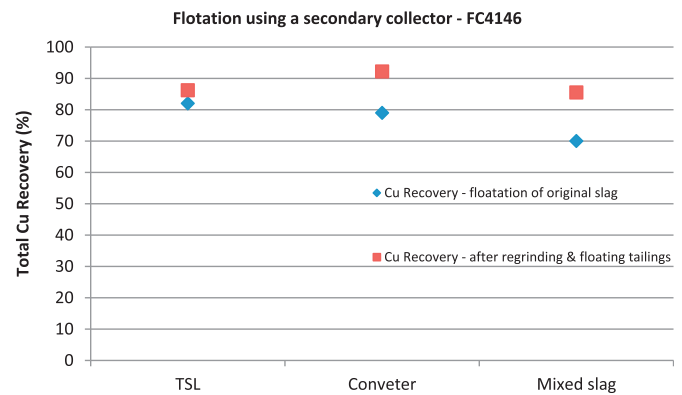
**Table 2.** Flotation reagents used.

Collectors	Frother	Sulphidizing agents
Potassium amyl xanthate (PAX)	Flotanol CO7	Sodium hydrosulphide (NaHS)
Sodium alkyl dithiophosphate, mercaptobenzothiazole (FC 7245)		Sodium sulphide (Na <sub>2</sub> S)
Isopropyl ethyl thionocarbamate (FC 4132)		Ammonium sulphate (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>
Sodium di-isobutyl dithiophosphate, sodium dibutyl dithiocarbamate, sodium hydrosulphide (FC 5473)		Ammonium sulphide (NH <sub>4</sub> ) <sub>2</sub> S
Allyl amyl xanthate ester, sodium diisoamyl dithiophosphate, sodium mercaptobenzothiazole, methyl isobutyl carbinol (FC 7412)		
Modified thionocarbocarbamate, methyl isobutyl carbinol (FC 4146)		
Thionocarbamate (Hostaflo E 703)		
Mercaptobenzothiazole (Hostaflo M 91)		
Flotiner fatty acids (FS-2)		
Flotiner fatty acids (FS-100)		

**Table 3.** Flotation tests matrix.

Test	Reagents			Flotation time	
	PAX (300 g/t)	Flotanol CO 7 (2ml)	Secondary collector (200 g/t)		
Test 1	10 % PAX	Frother	FC 4132	15 min	Secondary collector comparison
Test 2	10 % PAX	Frother	FC 7245	15 min	
Test 3	10 % PAX	Frother	FC 5473	15 min	
Test 4	10 % PAX	Frother	FS-100	15 min	
Test 5	10 % PAX	Frother	FC 7412	15 min	
Test 6	10 % PAX	Frother	E 703	15 min	
Test 7	10 % PAX	Frother	M91	15 min	
Test 8	10 % PAX	Frother	FS-2	15 min	
Test 9	10 % PAX	Frother	FC 4146	15 min	
Test 10	10 % PAX	Frother	(NH <sub>4</sub> ) <sub>2</sub> S	15 min	Sulphidizing agent comparison
Test 11	10 % PAX	Frother	10% NaHS	15 min	
Test 12	10 % PAX	Frother	10% Na <sub>2</sub> S	15 min	
Test 13	10 % PAX	Frother	10% NaHS, (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	15 min	

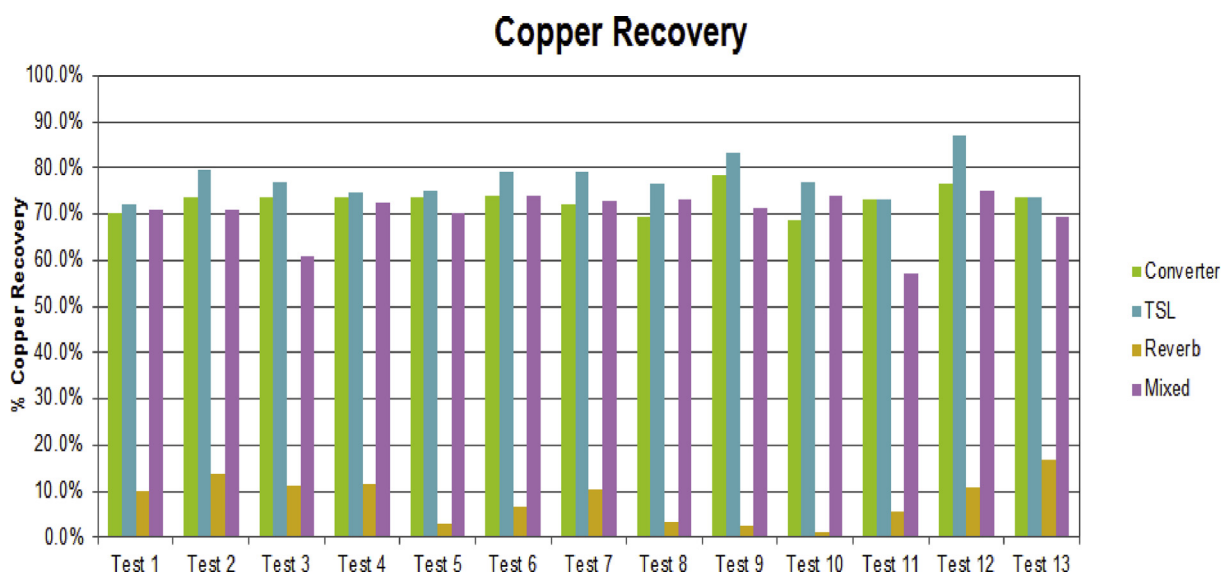
The results in Figure 11 show that FC7245 consistently caused greater increase in the Cu recovery after regrinding, with about 10% increase for TSL slag, 16.5% for converter slag and about 15% for mixed slag. FC4146 caused a 4% increase for TSL slag, about 13% for converter slag and



**Figure 8.** Total copper flotation recoveries before and after regrinding of the tailings using FC4146.

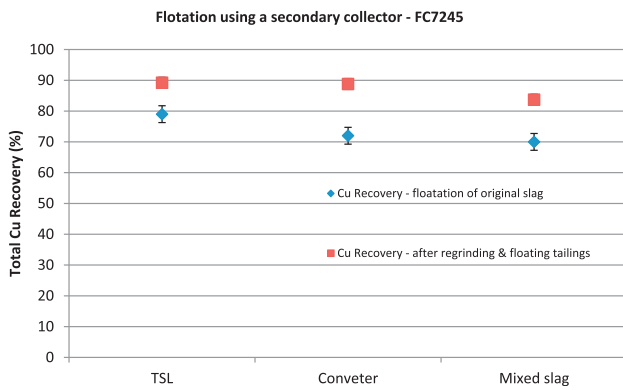
about 15% increase for mixed slag. Na<sub>2</sub>S caused minor improvements in recoveries of between 3 and 6 % for TSL, converter and mixed slag.

These results clearly demonstrate that when tailings of the slags that were initially floated at size 75µm are re-ground to 90µm, further liberation takes place, which frees up more copper minerals and render them floatable. The converter slag registered the highest recovery increase upon regrinding because of the higher copper department in the - 45 µm size class as observed in the size by assay analysis shown in Figure 6.

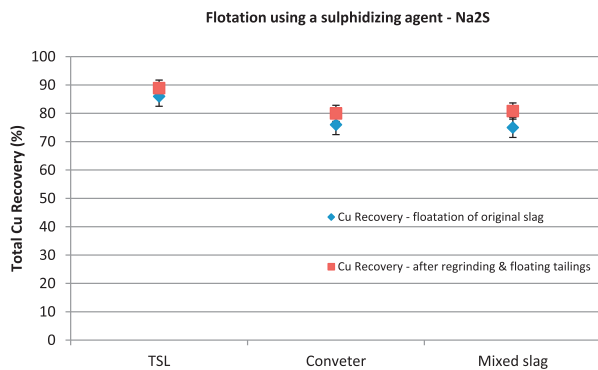


**Figure 7.** Copper recoveries from the Converter, TSL, Reverberatory and mixed slag at different flotation conditions.

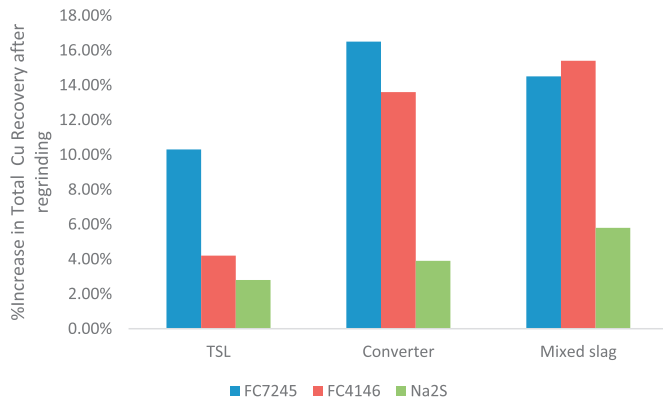




**Figure 9.** Total copper flotation recoveries before and after regrinding of the tailings using FC7245.



**Figure 10.** Total copper flotation recoveries before and after regrinding of the tailings using Na<sub>2</sub>S.



**Figure 11.** Percent increase in the flotation recovery of copper after regrinding.

#### 4. Conclusions

The mineralogical studies showed that the residual copper in slags from the Namibia Custom Smelters (NCS) is largely in the form of sulphide minerals i.e. Bornite, chalcocite digenite and traces of chalcopyrite, and that the gangue phases are mainly fayalite, magnetite and diopside. The slags produced from the NCS furnaces (TSL furnace, copper converter, reverberatory furnace) contain copper ranging between 0.8 to 5% w/w. Due to this high content of copper, the slags are milled and floated to recover the copper. The main drawback in the current process is that the final flotation tailings grades are in excess of 0.9% Cu. This copper content is considered too high to be lost in the final waste stream.

The milling response of the different slags showed that the reverberatory slag mills much more easily in comparison to the TSL slag and

the converter slag. The response also showed that there is an inverse relationship between the ease of milling and the copper mineral content of the slag material. Size by assay analysis showed that the content of copper generally increases with decrease in the particle size.

In Phase 1 of the flotation test work, the slags were initially milled to 75% passing 45 microns (which is a typical flotation grind used in the plant currently) and floated using a range of reagents. FC7245 (sodium alkyl dithiophosphate, mercaptobenzothiazole), FC4146 (modified thionocarbamate, methyl isobutyl carbinol) and Na<sub>2</sub>S were found to be the secondary flotation reagents that gave the best Cu recoveries for the 1<sup>st</sup> stage flotation. Phase 2 of the flotation test work involved regrinding the tailings from phase 1 tests to 90% passing 45 microns and floating them. Significant improvement in the overall Cu recoveries of up to 16% for the converter slag were recorded after regrinding using FC7245 as a secondary collector, proving that further liberation by grinding fines improves recoveries. It is recommended that a regrinding and secondary flotation circuit be incorporated as part of the plant modifications to maximize on the copper recovery subject to a favorable techno-economic analysis.

#### Declarations

##### Author contribution statement

Vusumuzi Sibanda: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Elias Sipunga: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Gwiranai Danha, Tirivaviri Augustine Mamvura: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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##### Competing interest statement

The authors declare no conflict of interest.

##### Additional information

No additional information is available for this paper.

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