

Flotation of mixed oxide sulphide copper-cobalt minerals using xanthate, dithiophosphate, thiocarbamate and blended collectors



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ARTICLE INFO

Keywords:

Mixed oxide sulphide ore
Flotation
Copper
Cobalt
QEMSCAN

ABSTRACT

More than half of the global cobalt supply from primary sources is currently produced in the Democratic Republic of Congo (DRC) from ores containing copper-cobalt oxides or copper-cobalt sulphides. Where oxide and sulphide cobalt-bearing copper minerals occur together, efficient recovery of copper and cobalt is known to be extremely difficult. This study investigates the flotation behaviour of a mixed oxide-sulphide ore where copper is hosted in sulphides phases such as bornite, chalcopyrite and chalcocite, and oxide phases such as malachite and to a lesser extent chrysocolla. Three cobalt-bearing oxide minerals are observed in the mixed ore, *i.e.* heterogenite, kolwezite and cupro-asbolane, while carrollite is the only cobalt-bearing sulphide mineral. A two-stage rougher-scavenger flotation process is used in which sulphides are extracted from the ore first. In the second stage, oxides are activated using controlled potential sulphidisation followed by their recovery. Tests are performed with a range of collectors, including xanthate, phosphorodithioate, dithiophosphate, thiocarbamate, and a blend type. A dithiophosphate collector proved to be the most successful, achieving recovery of 94% of the carrollite, more than 90% of the copper sulphides, and 70% of the copper oxide minerals. The recovery of the cobalt oxides was less successful, with recovery of roughly half the kolwezite and only 20% of the heterogenite and cupro-asbolane. Despite the generally promising recoveries, the selectivity of the flotation process is relatively low with all the concentrates containing a significant amount of carbonate and silicate minerals. This suggests that a number of improvements require further investigation, notably the application of hydroxamate collectors, depressants and reverse flotation.

1. Introduction

Over the past two years the cobalt price has been volatile, varying by about 300% (London Metal Exchange, 2018) due to speculation that global cobalt consumption will triple in the next decade (Burton, 2018). According to the USGS (2017), about half of the world's cobalt land-based resources and reserves are found in the sediment-hosted Cu-Co deposits in the Democratic Republic of Congo (DRC), where cobalt is recovered as a by-product of copper. In the DRC, mining operations mainly focus on either the sulphide ore or the oxide ore for which effective metallurgical processes are well-established. However, less is known about processes for copper and cobalt extraction from mixed oxide-sulphide ore (Crundwell et al., 2011). From the perspective of beneficiation, mixed oxide-sulphide ores present a challenge, not least because physiochemical properties of sulphide minerals vary as a function of their oxidation state (Bulatovic, 2010; Gaudin, 1957). In DRC ores, common copper sulphides include bornite (Cu_5FeS_4) and chalcopyrite

(CuFeS_2). Copper oxides include malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$), chrysocolla ($(\text{Cu},\text{Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4\cdot n\text{H}_2\text{O}$) and pseudomalachite ($\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$). Cobalt minerals consist mainly of carrollite (CuCo_2S_4), heterogenite ($\text{Co}^{3+}\text{O}(\text{OH})$) and kolwezite ($(\text{Cu},\text{Co})_2\text{CO}_3(\text{OH})_2$). With only a limited number of operations extracting copper and cobalt from Congolese ores data about recovery of copper and cobalt is relatively scarce (Schmidt et al., 2016). Typically, 85% for copper and 75% for cobalt is recovered from sulphide ores while, for oxide ores, 75% of the copper and only 45% of the cobalt is recovered (Fisher and Treadgold, 2009). For mixed oxide-sulphide ores, up to 80% of the copper and 60% of the cobalt is recovered in the sulphide concentrate while for the oxide concentrate, only 60% of the copper and 40% of the cobalt are usually recovered (Crundwell et al., 2011). With mixed oxide-sulphide ores, it is accepted practice to concentrate sulphide and oxide minerals in separate flotation processes. While flotation is a common method to concentrate sulphide ore in the DRC, oxide ore requires sulphidisation prior to flotation with xanthate collectors (Crundwell et al., 2011). The flotation of sulphides and sulphidised oxides must be done separately as reagents

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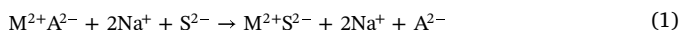
<https://doi.org/10.1016/j.mineng.2019.04.022>

Received 31 October 2018; Received in revised form 5 April 2019; Accepted 18 April 2019

Available online 27 May 2019

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used for sulphidisation of the oxide minerals will cause depression of sulphide minerals (Lee et al., 2009). Sulphidisation consists of activation of the oxidised surface using a sulphidising agent which releases sulphur ions in the solution by hydrolysis. The sulphur ions pass into the crystal lattice of the oxidized minerals, which then become receptive to sulphhydryl collectors (Bulatovic, 2010; Shungu et al., 1988). Common sulphidisers are sodium hydrogen sulphide (NaSH), sodium sulphide (Na₂S) and ammonium sulphide ((NH₄)₂S). The action of sodium sulphide on oxide minerals depends on heterogeneous reactions taking place between the sulphide ions in the solution and the oxide minerals compared with the sulphide ions and the gangue minerals (Malghan, 1986). Three steps were identified for copper oxides: adsorption of sulphide ions with the formation of copper sulphide, sulphide oxidation, and desorption of oxidised compounds by ion exchange (Castro et al., 1974). The net sulphidisation for sodium sulphide can be represented as given in Eq. (1) (Clark et al., 2002; Fuerstenau et al., 2007; Newell et al., 2007):



where M^{2+} represents a surface metal ion and A^{2-} an anion. Depending on the pulp chemistry conditions, either HS^- or S^{2-} are considered to be the active species. The minerals with freshly formed sulphide surfaces will become floatable using reagents for sulphide mineral flotation (Clark et al., 2002). Both for copper silicate and copper carbonate minerals, it has been suggested that Cu ions diffuse through the primary sulphide layer and form copper precipitates (Wright and Prosser, 1965; Zhou and Chander, 1993). A previous study by Lee et al. (2009) compared the use of a xanthate and n-octyl hydroxamate combination against a xanthate collector in a Controlled Potential Sulphidisation (CPS) process. When using CPS, an undefined dosage of sulphidiser is added to the pulp until the potential within the pulp reaches a desired level. A combination of the xanthate collector and hydroxamate collector showed superior performance to using a xanthate collector with CPS, as sulphide minerals were depressed by the sulphidising reagent (Lee et al., 2009). However, the oxide and sulphide ores were manually blended, avoiding possible issues due to oxide mineral association influencing the floatability of the sulphides and vice versa. The optimum potential range for the pulp has been recently evaluated, which showed that a pulp potential ranging of between -300 and -400 mV has similar recoveries to the potential between -450 and -550 mV, which was previously defined as the optimum range (Corin et al., 2017; Jones and Woodcock, 1978). While the CPS method recovered less than 30% of copper present in the oxide ore, a multistage sulphidisation approach was trialled, yielding a maximum recovery of 50% copper (Phetla and Muzenda, 2010). An alternative to CPS is slug sulphidisation, where a predefined dosage of sulphidising reagent is added. However, this can result in under-sulphidisation or depression of minerals due to over-sulphidisation (Corin et al., 2017). There is comparatively little published information on the flotation of cobalt minerals. Carrollite flotation has been studied in the presence of chalcopyrite, where a maximum cobalt recovery of 83% was obtained using a mixture of Potassium Amyl Xanthate (PAX) and Sodium Isopropyl Xanthate (SIPX) at ambient pH, whilst 93% of the copper was recovered (Musuku, 2011). Bulk flotation experiments with Zambian copper-cobalt sulphide ore showed superior flotation performance, with improved kinetics, when using Sodium Ethyl Xanthate (SEX) as a collector instead of a blend of alkyl dithiophosphate and thionocarbamate collectors, with copper sulphides floating more rapidly than cobalt sulphides (Mainza et al., 1999). Heterogenite has been successfully floated using a combination of sodium hydrosulphide and ammonium sulphide as sulphidisers, followed by flotation using a mixture of PAX and hydrolysed palm oil as collectors at a pulp potential between -450

and -550 mV (Kongolo et al., 2003). The combination of sodium hydrosulphide and ammonium sulphide showed better results for both copper and cobalt recovery compared to both sulphidisers being used individually, with a maximum recovery of 88% for both copper and cobalt.

In this study, a bulk sample of Cu-Co mixed oxide/sulphide ore from a major DRC operation is characterised and tested for flotation. The effectiveness and selectivity of a range of different collectors is studied for the recovery of sulphide and oxide copper-cobalt minerals. While the objective is to study the floatability of cobalt minerals, the concentration of copper-bearing minerals is also considered in view of its industrial relevance. Note that cobalt is only considered to be a by-product of copper production. However, with changing cobalt metal prices and an expected increase in cobalt consumption, a higher recovery of cobalt could prove beneficial from an economical perspective for the producers. This paper focusses on flotation technology to facilitate the growing importance of cobalt recovery.

2. Materials and methods

2.1. Materials

Test work was carried out with a sample of ore from an active mine site located in the Katanga province, DRC. The 60 kg sample was drawn from the oxide-to-sulphide transition zone and is assumed to be representative of a typical mixed oxide-sulphide copper-cobalt ore. To enable homogenisation, the ore was initially crushed below 2 mm and riffled into representative sub-samples of 500 g for test work. The relationship between grinding time and particle size was defined with a test performed on 500 g of the mixed ore sample at 60% solids content. The sample was ground in a belt driven stainless steel laboratory mill operating at 65 RPM. The mill chamber size was 300 mm by 160 mm and contained six 290 by 23 mm stainless steel rods with a mass of 1 kg each. The particle size distribution was analysed after 5, 10 and 15 min of grinding, using a Helium-Neon Laser Optical System Mastersizer 3000 (Malvern Instruments Ltd.) coupled with a Hydro Extended Volume (EV) sample dispersion unit. For each defined grinding time, a subsample was also collected for mineralogical analysis with QEMSCAN. The size distribution for the subsequent grinding times is shown in Fig. 1, which only was used to obtain indicative ore sizing data prior to QEMSCAN analysis.

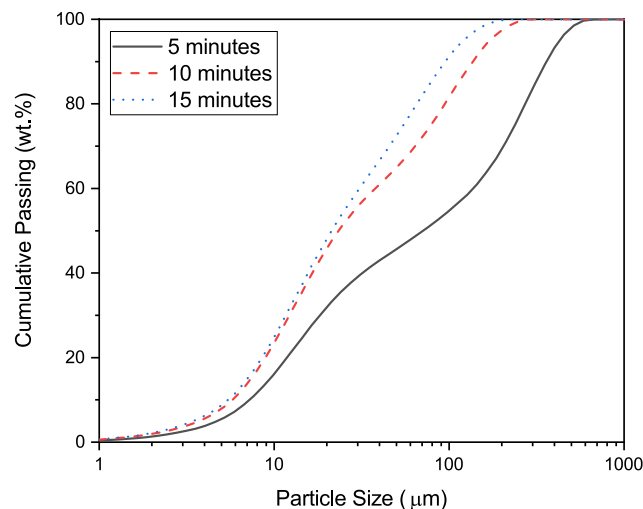


Fig. 1. Particle size distribution for 5, 10 and 15 min ground ore.

Based on product particle size and mineral liberation data obtained by QEMSCAN, a grind time of 10 min was selected which produces a particle size of 80% passing 95 μm.

2.2. Flotation tests

2.2.1. Flotation procedure

For the flotation experiments, a laboratory Denver D12 flotation cell was used with a volume of 1 dm³ with an impeller speed of 1200 RPM. All experiments were carried out at a pulp density of around 35% solids and ambient pH. Flotation experiments consisted of a succession of a rougher and scavenger stages, with both a sulphide flotation and sulphidisation – oxide flotation stage (Fig. 2). Five different collectors were evaluated. The aeration rate was 7 L/min using compressed atmospheric air. The potential was measured using a VWR U_H probe that was connected to a Jenway 3345 ion meter, which was calibrated using a 440 mV buffer solution from Mettler Toledo.

An overview of the flotation experiment conducted with each of the five investigated collectors, can be found in Table 1. No repeated measurements were done. Steps 1 and 10 only took place during the sulphidisation of the oxides and not when floating the sulphides. For each collector, a dosage of 30 g/t at a concentration of 1% was used, while the frother dosage was maintained at 50 g/t. Pulp potential was controlled by sulphidiser addition at a concentration of 10%. For both

sulphide and oxide flotation stages, eight different concentrates were collected. For each concentrate the copper and cobalt grade was measured using portable X-Ray Fluorescence (pXRF), after which the concentrates were combined into a sulphide and an oxide concentrate. The two concentrates and final tailings were analysed for mineralogy using QEMSCAN.

2.2.2. Reagents

The frother used in the experiment was Methyl Iso Butyl Carbinol (MIBC) while sodium hydrogen sulphide (NaSH) was used as a sulphidising reagent; both were provided by Acros Organics. Five different collectors were selected. Sodium IsoPropyl Xanthate (SIPX), supplied by Cheminova Agro A/S, was selected on the basis that it has been previously used as a collector for cobalt sulphides (Bell, 2011). Danafloat™ 068 (DF068) consists of sodium O,O-tolyl phosphorodithioate blended with cresols and is considered to be a selective collector for cobalt minerals at pH 4. Danafloat™ 245 (DF245) consists mainly of sodium O,O-diisobutyl dithiophosphate, and is known to be a bulk copper cobalt collector. Danafloat™ 507 (DF507B) is a blend of sodium O,O diisobutyl phosphorodithioate with O-isopropylethulthiocarbamate, and stated to be a selective copper mineral collector. Danafloat™ 571 (DF571) is a blend with MBT-Na and sodium O,O-diisobutyl phosphorodithioate and, as a collector, is considered to be suitable for concentrating sulphides with an oxidized surface. All the Danafloat

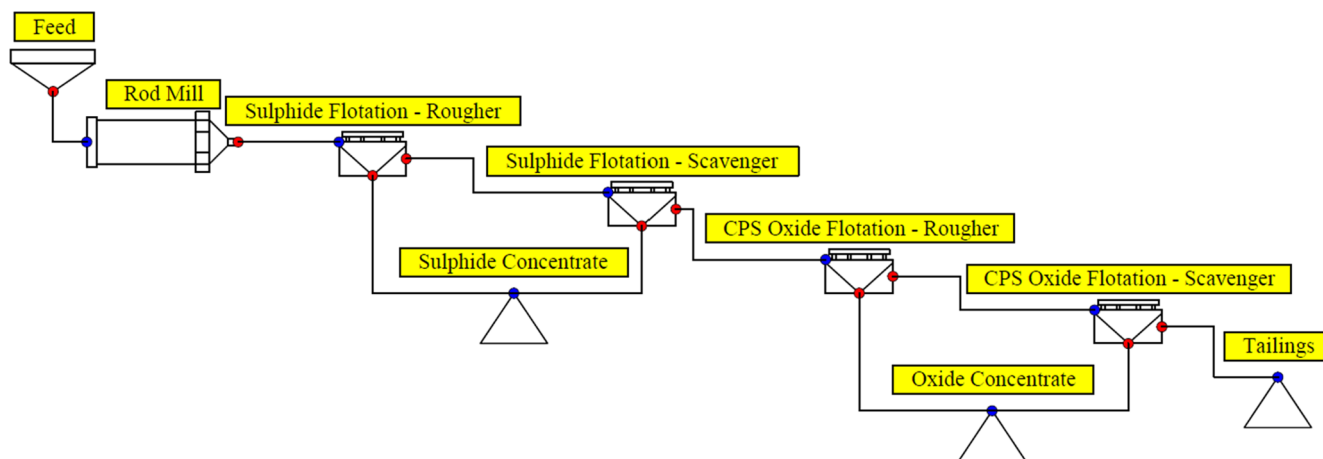


Fig. 2. Schematic overview of the flowsheet used throughout the flotation experiments.

Table 1
Flotation procedure for the experiments described in this study.

Stage	Conditioning time (min)	Flotation time (min)	Dosage
1. Sulphidisation	3		CPS range: – 300 and – 400 mV
2. Conditioning collector	3		30 g/t
3. Conditioning frother	1		50 g/t
4. Concentrate 1		0.5	
5. Concentrate 2		0.5	
6. Concentrate 3		1	
7. Concentrate 4		1	
8. Concentrate 5		2	
9. Concentrate 6		2	
10. Sulphidisation	3		CPS range: – 300 and – 400 mV
11. Conditioning collector	3		30 g/t
12. Concentrate 7		1	
13. Concentrate 8		2	

collectors contain a proportion of sodium hydroxide. The information on potential selectivity of each collector was obtained through personal communication with Danafloat.

2.3. Portable X-ray fluorescence

Portable X-Ray Fluorescence (pXRF) was used to analyse the copper and cobalt content of the individual flotation products. The device used was the Delta Premium Handheld XRF Analyser (Olympus, United Kingdom) in Geochemistry mode. Detection limits for copper and cobalt are 20 PPM for cobalt and 5 PPM for copper (Innov-X, 2010). The pXRF was set to analyse the sample for 1.5 min in total, with 45 s for beam 1 to detect the presence of heavier elements and 45 s for beam 2, to detect the lighter elements. The pXRF measurement area in the sample holder was fully covered with concentrates or tailings materials which were first dried, weighed and riffled. A minimum sample mass of 1.5 g was considered sufficient to obtain reliable measurements (Shand and Wendler, 2014). In order to improve the overall measurement accuracy, an external calibration was performed with an S4 Pioneer SQ-XRF (Bruker, United Kingdom) using 25 copper and cobalt standards. Comparison of measured and specified copper and cobalt grades yielded a correlation coefficient (R^2) of 0.98 with a Root Mean Square Error (RMSE) of 1.47% for copper and an R^2 of 0.99 with an RMSE of 0.32% for cobalt.

2.4. QEMSCAN

Quantitative mineralogical analysis was carried out using a QEMSCAN 4300 at Camborne School of Mines, University of Exeter, UK. This consists of a Zeiss EVO 50 Scanning Electron Microscope (SEM) platform and four light element Bruker silicon drift droplet (SDD) X-ray detectors (Gottlieb et al., 2000; Pirrie et al., 2004). Selected samples were mixed with pure graphite powder to minimise particle density settling effects, prepared into 30 mm diameter polished epoxy resin blocks and then analysed using the field scan or PMA mode to determine the mineral abundance and liberation of these samples. Standard settings were used following details outlined in Rollinson et al. (2011) with the fieldscan mode using a 10 μm scan resolution and the PMA mode using a 2–4 μm scan resolution matched to the particle size range. Data acquisition used iMeasure v4.2 software and data processing used iDiscover 4.2SR1 and 4.3. Data processing included development of a Species Identification Protocol (SIP) with minerals such as carrollite, heterogenite, chrysocolla, pseudomalachite, kolwezite and cupro-asbolane added, and the other mineral phases checked and refined.

3. Results

3.1. Characterisation of the Cu-Co mixed ore

Average abundance of 21 minerals present in the Cu-Co mixed ore sample is shown in Table 2. There are four copper sulphides, four copper oxides, one cobalt sulphide, and three cobalt oxides. Major gangue minerals consist of carbonates (magnesite, dolomite) and silicates (quartz, magnesiochlorite) and minor amounts of iron oxides, apatite and a range of minor gangue minerals, such as pyrite and rutile. Elemental copper and cobalt grades in the feed material are 1.65% and 0.09% respectively.

Copper and cobalt department is shown in Table 3. Six minerals

Table 2
Average QEMSCAN mineral abundance (wt%) obtained from five samples.

Mineral	Formula	Average abundance (wt%)	Standard Deviation
Carrollite	CuCo_2S_4	0.04	0.02
Chalcopyrite	CuFeS_2	0.59	0.17
Bornite	Cu_5FeS_4	0.89	0.44
Chalcocite	Cu_2S	0.23	0.09
Pyrite	FeS_2	0.02	0.01
Cu oxide	CuO	0.05	0.02
Malachite	$\text{Cu}_2\text{CO}_3(\text{OH})_2$	0.68	0.08
Chrysocolla	$(\text{Cu,Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4\text{nH}_2\text{O}$	0.67	0.10
Heterogenite	$\text{Co}^{3+}\text{O}(\text{OH})$	0.05	0.01
Kolwezite	$(\text{Cu,Co})_2\text{CO}_3(\text{OH})_2$	0.03	0.00
Cupro-asbolane	$(\text{Ni,Co})_{2-x}\text{Mn}^{4+}(\text{O,OH})_4\text{nH}_2\text{O}$	0.17	0.03
Goethite	$\text{FeO}(\text{OH})$	0.83	0.03
Rutile	TiO_2	0.08	0.01
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	17.65	0.96
Ankerite	$\text{Ca}(\text{Fe,Mg,Mn})(\text{CO}_3)_2$	1.10	0.04
Apatite	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	0.37	0.04
Magnesite	MgCO_3	51.67	2.85
Quartz	SiO_2	17.01	2.35
Magnesiochlorite	$(\text{Fe,Mg,Al})_6(\text{Si,Al})_4\text{O}_{10}(\text{OH})_8$	4.45*	0.29
Mg silicates	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	3.32	0.17
Others	–	0.10	0.02
Total		100.00	

make a significant contribution to the copper content: 54% of the copper is found in three sulphide minerals and 45% is present in three oxide minerals. There are four cobalt-containing minerals, of which two also contain copper, i.e., kolwezite and carrollite. 77% of the cobalt content is hosted in oxide minerals and 23% in carrollite, the only cobalt sulphide mineral.

A QEMSCAN measurement charts the surface area of a mineral species and translates this into a mineral mass by multiplying with the density and applying a stereological assumption. The percentage of the particle mass which consists of an individual mineral defines the degree of liberation for that mineral in a particle. In this study, the degree of liberation is recorded in ten equispaced classes, ranging from “ $\leq 10\%$ ” to “90–100%”. Particles in each liberation class are weighted with their total mass to reveal the proportion of the total mass of particles containing the mineral of interest in that class. Note that the liberation

Table 3
Copper and cobalt department.

Mineral	Cu department (wt%)	Co department (wt%)
Carrollite	0.4	22.7
Chalcopyrite	11.6	–
Bornite	31.6	–
Chalcocite	10.2	–
Malachite	27.0	–
Chrysocolla	15.8	–
Cu oxide	2.4	–
Kolwezite	0.9	11.9
Heterogenite	–	62.7
Cupro-asbolane	–	2.7
Total	100.0	100.0

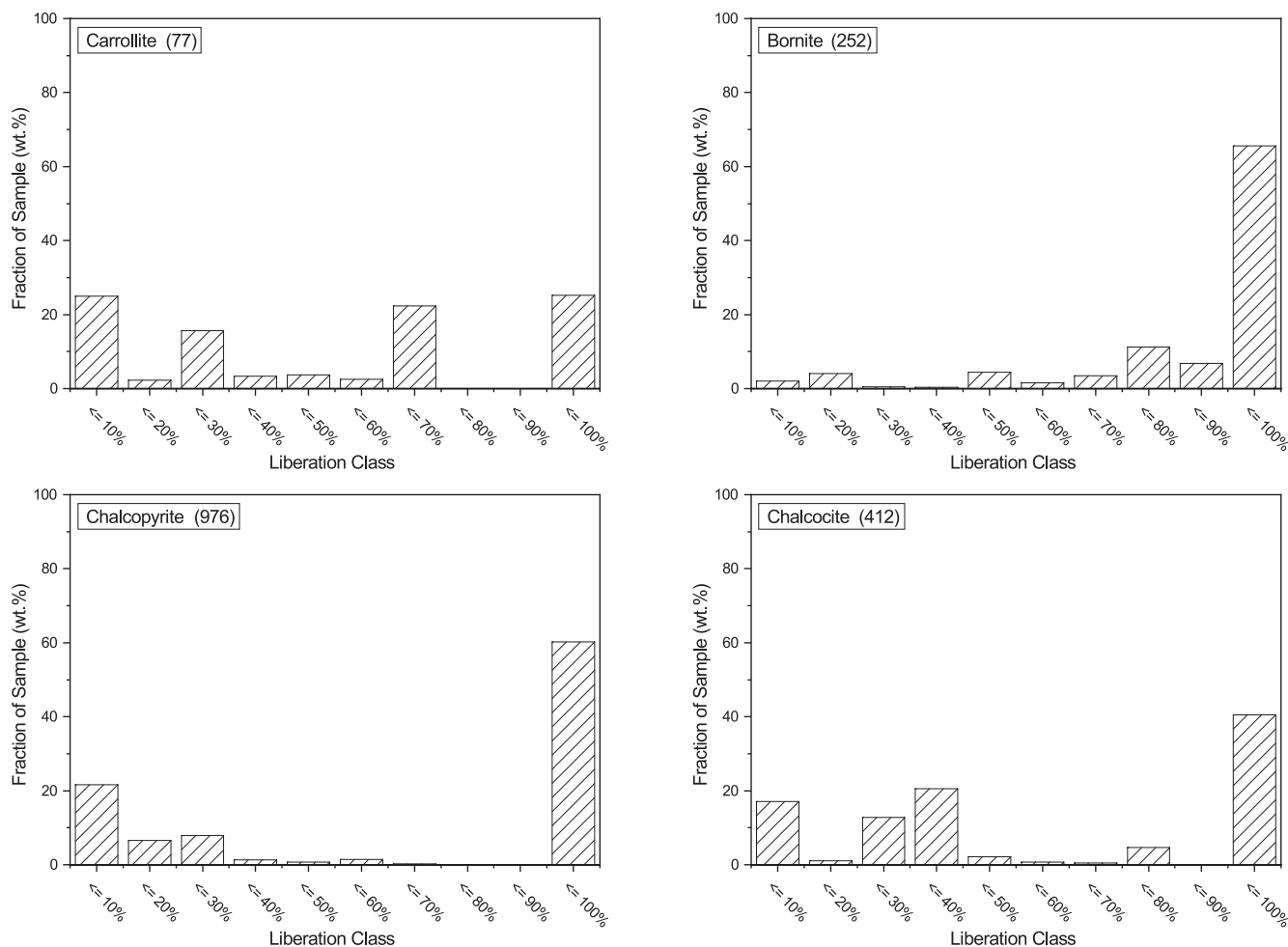


Fig. 3. Liberation of sulphide minerals in the mixed ore, with number of particles containing the mineral in brackets.

analysis may be biased (Leigh et al., 1993) - and should be considered as indicative only - because samples are not sized prior to QEMSCAN analysis. Fig. 3 shows the liberation classification of the sulphide minerals. Given the number of particles analysed with each mineral, the classification is considered to be fit-for-purpose (Leigh et al., 1993). Chalcopyrite and bornite grains are generally well-liberated, with about 60%, respectively 72% of the grains (on a mass basis) being more than 90% liberated. For carrollite, around a quarter is more than 90% liberated, whereas another quarter is less than 10% liberated. The remaining 50% of carrollite particles display a distribution of liberation spread between 70% and 30%. In view of the limited number of particles containing carrollite (77), industrial application would require analysis of more particles.

The liberation of the oxide minerals is shown in Fig. 4. Malachite is the only copper oxide mineral with a significant liberation, with 84% of the particles - on a mass basis - being more than 90% liberated. Liberation is much lower for the other copper oxides. However, analysis of Cu oxide, kolweziite and heterogenite are based on a small number of particles and thus should be interpreted with care.

The mineral association of sulphide minerals is shown in Fig. 5-A. Association with the background refers to the absence of actual mineral association. For example, on average 32% of the surface area of carrollite-bearing grains is associated with fully-liberated carrollite grains. The reported association hence exists between the fully-liberated mineral and the epoxy resin and graphite added at the sample preparation phase. This means that this fraction of the mineral surface is not associated with any other minerals and thus available for collector adsorption. Another 61% of carrollite-bearing particle surface is, on average, associated with other sulphide minerals, suggesting that, on average, 93% of the carrollite-bearing particles should be amenable to collector adsorption and separation through flotation. Chalcopyrite has a stronger association with both oxide minerals (14%) and Fe-oxides (4%) than the other sulphide minerals. This may lead to issues with chalcopyrite flotation, as oxides will be concentrated in the sulphide concentrate or chalcopyrite in the oxide concentrate. The mineral association of the oxide minerals is shown in Fig. 5-B. About 12% of the surface of particles which contain malachite is associated with sulphides, which could cause issues with malachite reporting to the

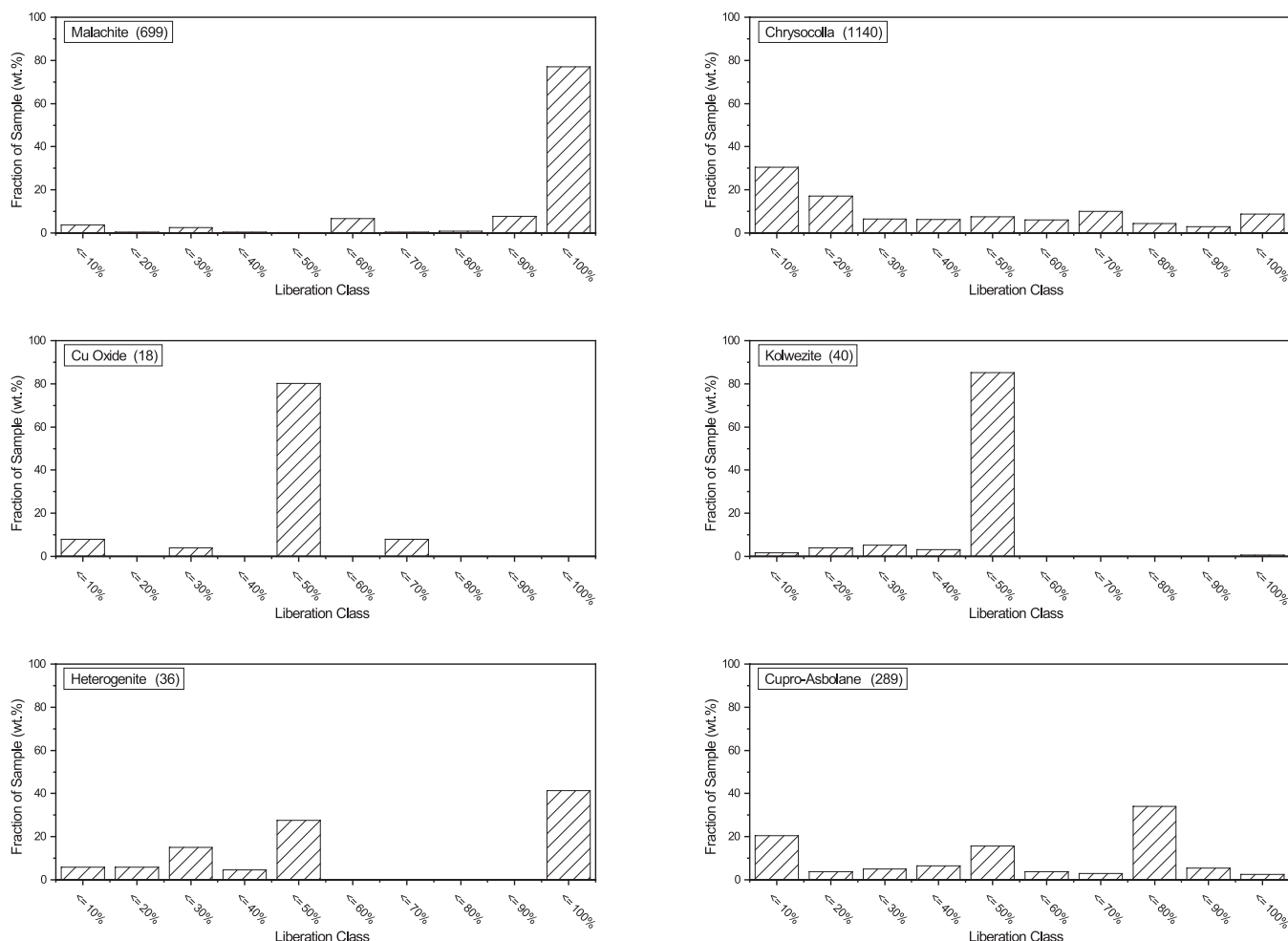


Fig. 4. Liberation of oxide minerals in the mixed ore, with number of particles containing the mineral in brackets.

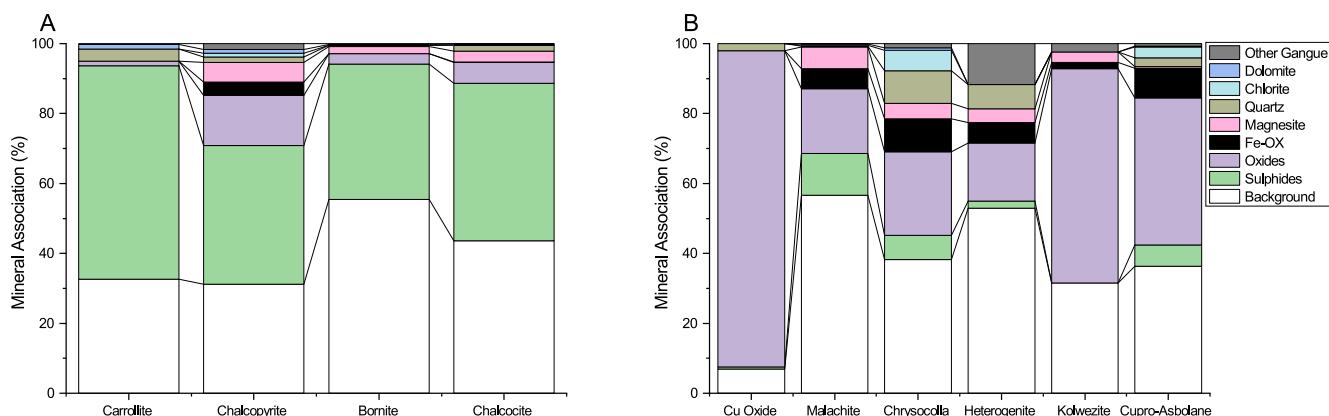


Fig. 5. Mineral association of sulphide (A) and oxide (B) minerals.

sulphide concentrate or sulphide minerals in the oxide concentrate. Compared to the sulphides, most oxide minerals are associated with Fe-oxides. In general, both oxide and sulphide minerals are associated with dolomite, chlorite, quartz and magnesite.

3.2. Flotation tests

3.2.1. Metal-based flotation performance

The recovery of copper in the sulphide flotation stage is shown as a function of time in Fig. 6-A. The type of collector is found to influence

the copper recovery. The best performing collector is the thiocarbamate collector (DF507B) with an overall recovery of 68%. Collector DF068, a phosphorodithioate-cresols blend, produces a relatively poor copper recovery. This was expected because this collector is specifically designed for selective cobalt flotation at an acidic pH. The kinetic curves for copper in the oxide flotation stage are shown in Fig. 6-B. Overall, a larger difference in performance between the collectors is observed in the oxide flotation stage. For the phosphorodithioate-MBT blend collector (DF571), the recovery only increases with 10% in the oxide flotation stage, whereas for the dithiophosphate (DF245) collector, the

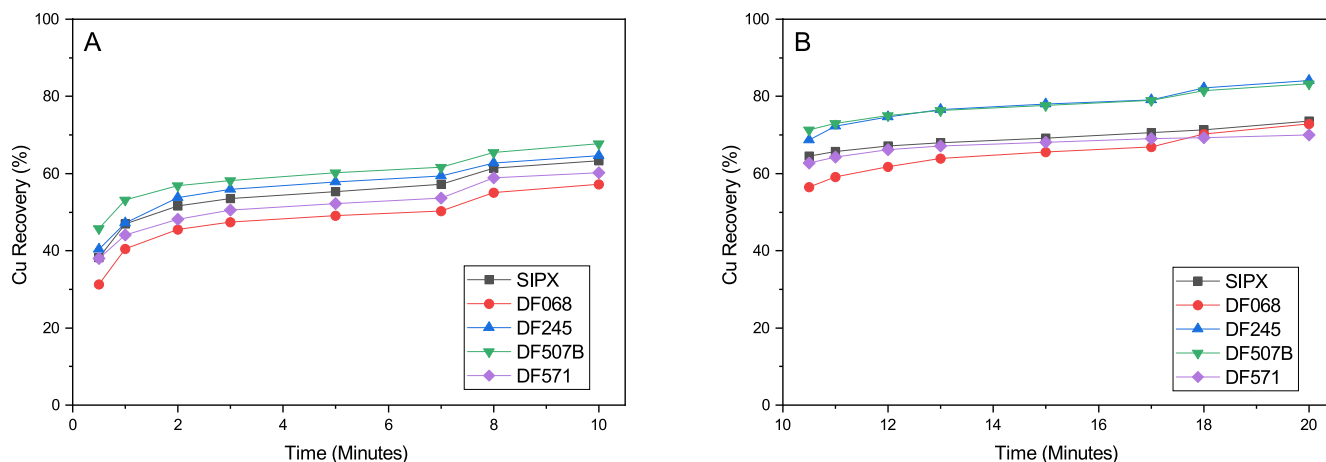


Fig. 6. Cobalt kinetic curves for the sulphide (A) and oxide (B) flotation stage for all collectors.

recovery increases with 20%. Of the total copper content, 38% can be found in copper oxide minerals and in the oxide flotation stage the maximum increase in copper recovery is 20%. Assuming that oxides are only recovered during the oxide flotation stage, Cu-oxide minerals recovery can be estimated at around 52%. That constitutes an increase of more than 20% compared to the cumulative copper recovery of less than 30% obtained when using SIPX and sulphidisation to float copper oxide ore (Corin et al., 2017). The dithiophosphate and thiocarbamate collectors (DF245 and DF507B) outperform the xanthate collector SIPX and both phosphorodithioate collectors (DF068 and DF571).

The time-dependent recovery of cobalt during the sulphide flotation stage is shown in Fig. 7-A. Cobalt recovery is relatively low for all collectors, with a maximum recovery of 31% cobalt for the stronger thiocarbamate collector (DF507B) and a minimum of 24% for DF068. The phosphorodithioate-MBT collector (DF571) returns a better performance for cobalt recovery than for copper recovery, extracting a larger amount of cobalt than the xanthate collector (SIPX) and dithiophosphate collector (DF245). The recovery of cobalt during the oxide flotation stage is shown in Fig. 7-B. In all cases, there is an increase in cobalt recovery, but differences between the response of cobalt oxide minerals to the selected collectors are larger than observed for the cobalt sulphide minerals. For dithiophosphate collector (DF245), the cobalt recovery increases with 18%, whereas for phosphorodithioate collector (DF571), the cobalt recovery only increases with 10%. The maximum increase in recovery is 18%. Recalling that 77% of the cobalt minerals are oxides, the increase in cobalt recovery is low. This indicates that the suggested direct sulphidisation process is not an optimal process for the concentration of cobalt oxides. The difference

between the performance of phosphorodithioate-MBT collector (DF571) in the oxide and sulphide flotation stage is interesting, as it is the worst performing collector for flotation of the activated oxides but the second-best performing collector for cobalt in the sulphide flotation stage.

The copper grade – recovery curves for the sulphide rougher - scavenger flotation stage are shown in Fig. 8-A. Collector DF245 shows superior metallurgical performance with an initial grade of 28%. This can be ascribed to the composition of collector DF245, as dithiophosphate collectors are known to be more selective. Collector DF507B has a thiocarbamate structure which is a strong but relatively unselective collector (Lotter and Bradshaw, 2010). This is evident from the first point of the grade-recovery curve, where DF245 produces the highest grade but DF507B the highest recovery. Towards the end of the grade-recovery curve, the difference in copper grade in the concentrate obtained with either DF245 and DF068 decreases, from 7.9% to 2.1%. That suggests that concentrates with a higher recovery will contain more dilution throughout the recovery process, as the selectivity of the collector decreases. The collector with the highest recovery (DF507B) also produces the lowest final copper grade in the copper concentrate, being 10% copper. The copper grade-recovery curves for the oxide flotation step are shown in Fig. 8-B. The dithiophosphate collector (DF245) is the best performing collector, with a relatively high copper recovery (83%) and grade (5.3%). The phosphorodithioate-MBT collector (DF571) initially produces a similar copper grade as DF245 and DF507B, but the effectiveness of the collector decreases as the flotation process continues, causing a decline in grade. An interesting observation is that the dithiophosphate and thiocarbamate collectors (DF245

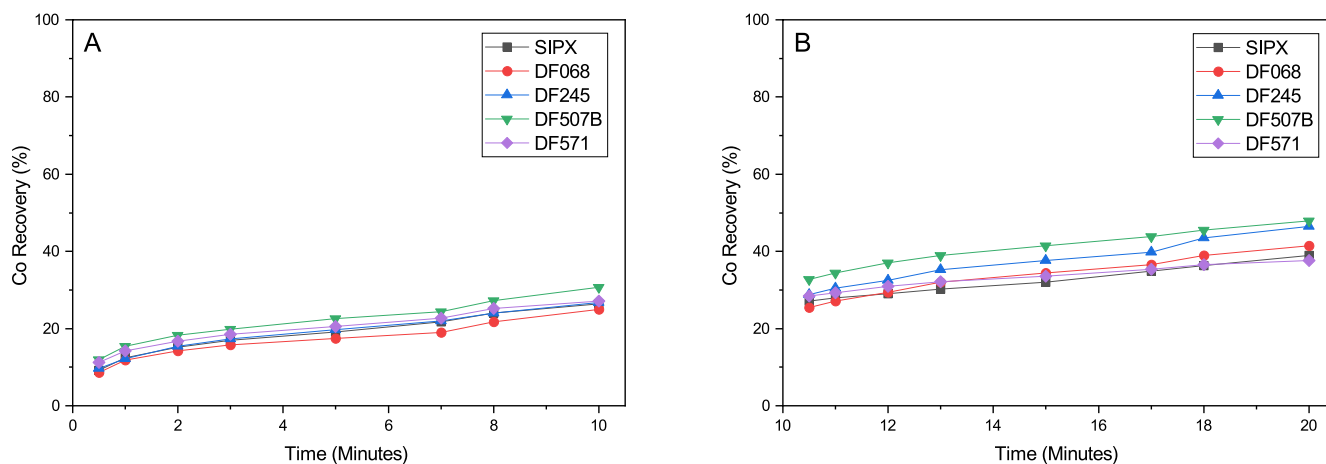


Fig. 7. Cobalt kinetic curves for the sulphide (A) and oxide (B) flotation stage for all collectors.

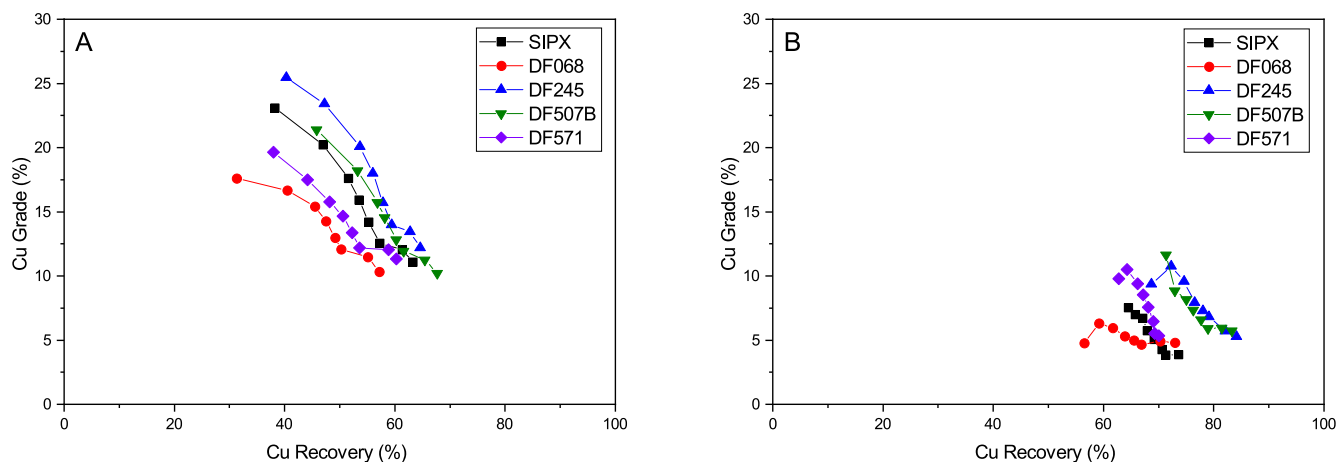


Fig. 8. Copper grade-recovery curves for the sulphide (A) and oxide (B) flotation stage for all collectors.

and DF507B) give a similar performance for activated oxide ore. When comparing grades in the oxide concentrates to the grades in the sulphide concentrate, it can be seen that both the initial and final copper content is lower for the oxide concentrate. This can be explained by the inefficiency of recovering the majority of the copper oxide minerals and the fact that the content of copper oxides in the feed is about half that of the copper sulphides.

The grade–recovery curves for cobalt in the sulphide flotation stage are shown in Fig. 9-A. Dithiophosphate collector DF245 allows for the highest overall cobalt content in the sulphide concentrate, which decreases from 4600 to 3800 ppm in the flotation process. This again confirms the selectivity of a dithiophosphate structure. The initial difference in grade between the best and worst performing collector for cobalt is around 683 ppm. The difference in grade decreases to 113 ppm whereas the difference in recovery is 1% for DF068 and DF245. This confirms what was observed in the copper sulphide flotation stage, where the main difference between the collectors is the difference in initial recovery while selectivity is reduced with longer flotation time. The grade–recovery curves for cobalt in the oxide flotation stage are shown in Fig. 9-B. The stronger thiocarbamate collector (DF507B) has the highest final grade, 5080 ppm, with an increase in cobalt oxide recovery of 16%. It is notable that the grade of the concentrate increases with time in the rougher phase and decreases again for the scavenger phase for all the collectors. This could indicate that if

a higher recovery of the cobalt oxides is desired, a longer flotation time is required due to slower kinetics of the minerals. Another explanation is that the sulphidised copper oxide minerals are concentrated initially and that the cobalt oxide minerals are only recovered when no sulphidised copper oxides remain.

3.2.2. Mineral-based flotation performance

The modal mineralogy of the combined sulphide concentrates is shown in Fig. 10-A. The phosphorodithioate-MBT collector (DF571) is the least selective collector, with only a small portion of the sulphide concentrate consisting of copper or cobalt sulphides. For the other collectors, the concentrates contain similar amounts of both valuable minerals and gangue minerals. In terms of gangue minerals, the magnesite content in the concentrate is in the same order of magnitude as it was in the feed (~50%). The concentrate also contains significant amounts of chlorite, quartz, dolomite, and magnesia silicates. None of the collectors appear to be selective with respect to recovery of gangue minerals. The modal mineralogy of the combined oxide concentrate is shown in Fig. 10-B. All collectors recovered oxide minerals, both copper and cobalt, and a small fraction of copper sulphides. Using a phosphorodithioate-MBT collector (DF571) led to recovery of a much larger fraction of chlorite than the other collectors, reducing the fraction of magnesite in the concentrate. However, as for the sulphide flotation stage, the majority of the oxide flotation concentrate consists of gangue

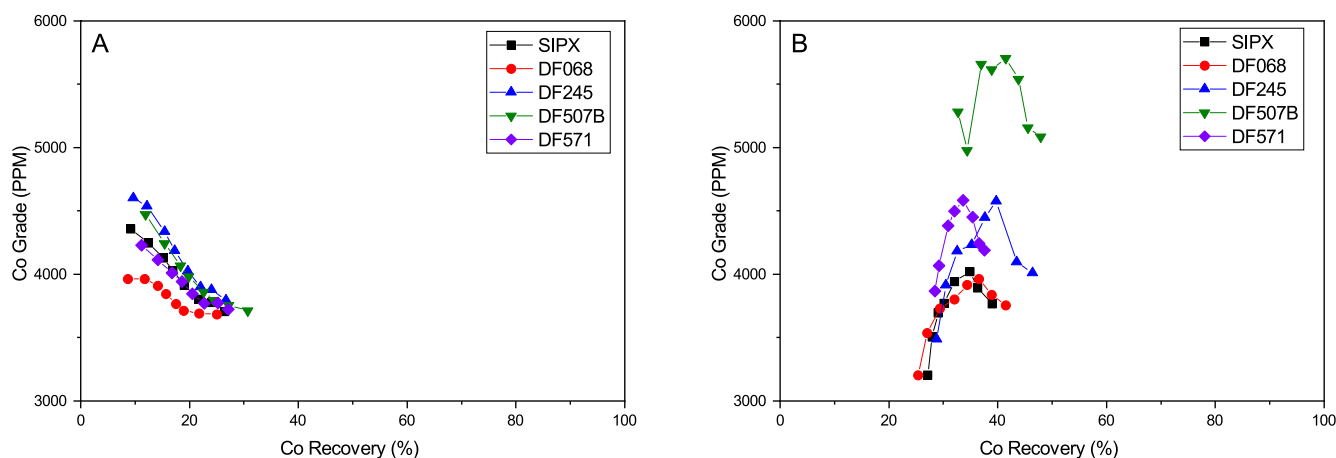


Fig. 9. Cobalt grade-recovery curves for the sulphide (A) and oxide (B) flotation stage for all collectors.

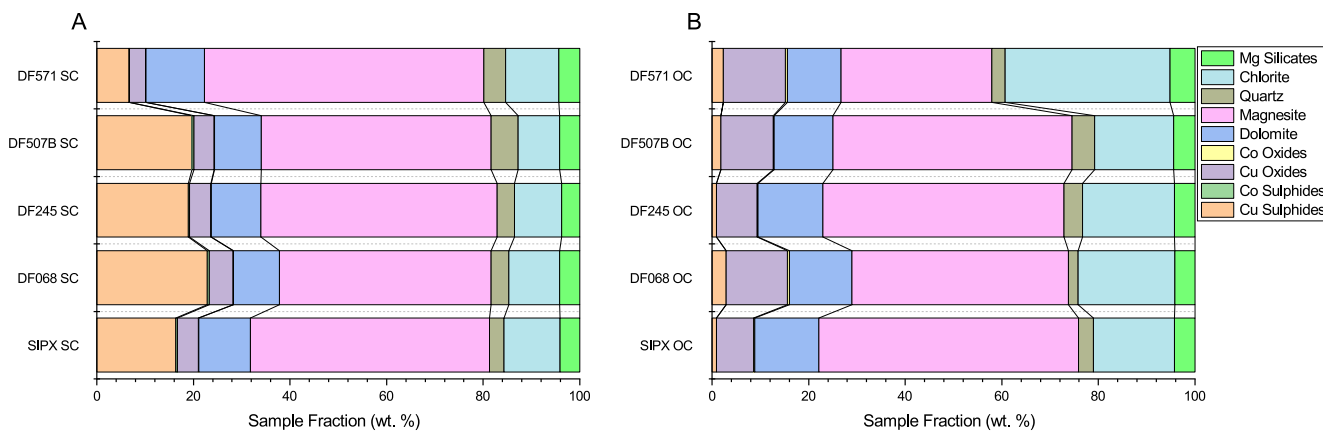


Fig. 10. Modal mineralogy of the cumulative sulphide concentrates (A) and oxide concentrates (B) for all collectors.

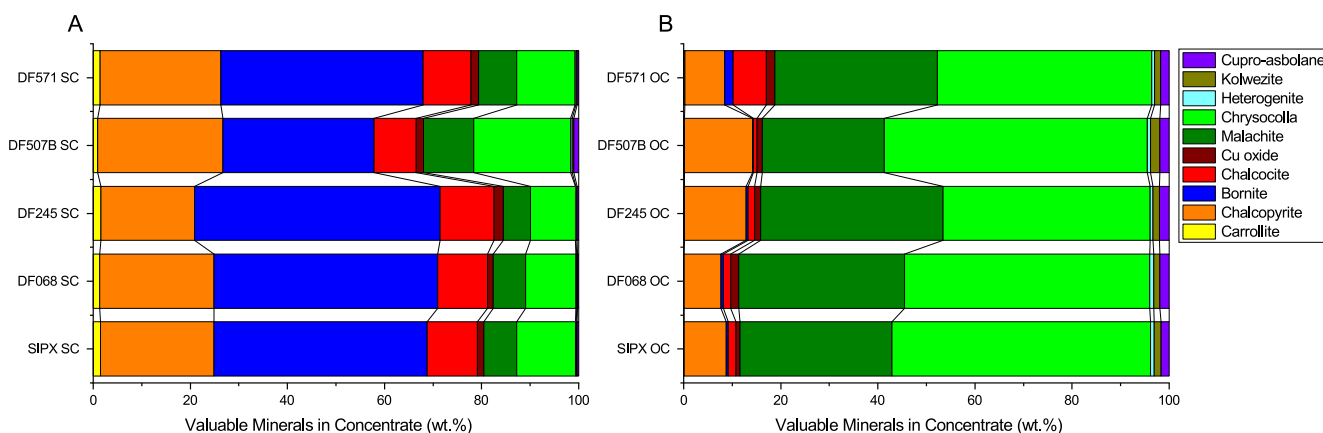


Fig. 11. Cumulative distribution of valuable minerals in the sulphide (A) and oxide concentrates (B) for all collectors.

minerals.

Fig. 11-A shows the content of valuable minerals in the sulphide concentrate as a function of the type of collector. The valuable minerals in the concentrates all consist of a small fraction of carrollite and more than 60% of copper sulphides. However, all concentrates also contain a non-negligible amount (up to 35%), of oxide minerals. Fig. 11 suggests that, with the exception of thiocarbamate collector DF507B, all collectors are equally selective for recovering sulphide minerals, as expressed in the sulphide-to-oxide ratio. The content of valuable minerals in the oxide concentrate is shown in Fig. 11-B. In all cases, some chalcopyrite reports to the oxide concentrate. Varying amounts of bornite and chalcocite are found in the oxide concentrate as well. For all collectors, valuable minerals in the oxide concentrate consist of at least 80% oxide minerals. From Figs. 10-B and 11-B, it can be concluded that a phosphorodithioate cresols blend collector (DF068) leads to the smallest fraction of copper sulphide minerals in the concentrate and is hence is the most selective collector for oxide flotation. Note that the presence of chalcopyrite may lead to reduction of the copper recovery when treated with sulphuric acid in a leaching process due to formation of a passivating layer (Hackl et al., 1995). In this case, the large quantity of gangue minerals found in the cumulative concentrates are the main concern.

The recovery per mineral for both the sulphide and oxide concentrate per collector is shown in Table 4. DF245 is the best performing collector for carrollite, bornite, chalcocite, malachite, and chrysocolla. Cupro-asbolane is poorly recovered with all the tested collectors. That is also the case for heterogenite, which can be seen as one of the main causes for the poor overall cobalt recovery: heterogenite accounts for 63% of the cobalt content. Heterogenite has been recovered using CPS and PAX before, with recoveries up to 90% at a pH of 10.5 (Kongolo

et al., 2003). It appears that the liberated fraction of heterogenite does not respond well to this flotation procedure. Furthermore, unliberated heterogenite is not associated with minerals that respond well to the flotation procedure. An explanation for the poor performance of the cobalt bearing oxide minerals is that cobalt ions become active at more

Table 4

Recovery of target minerals (wt%) per collector type for the sulphide and oxide concentrate.

Mineral	SIPX	DF068	DF245	DF507B	DF571
<i>Sulphide concentrate</i>					
Carrollite	70	73	92	76	49
Chalcopyrite	72	77	69	63	70
Bornite	86	95	98	86	85
Chalcocite	74	92	93	79	69
Cu Oxide	43	58	77	43	40
Malachite	15	19	24	18	19
Chrysocolla	32	32	34	28	32
Cupro-asbolane	4	3	7	5	3
Heterogenite	4	5	9	8	5
Kolwezite	10	8	16	11	9
<i>Oxide concentrate</i>					
Carrollite	1	1	2	7	2
Chalcopyrite	6	5	14	21	6
Bornite	0	0	0	0	1
Chalcocite	2	3	3	4	13
Cu Oxide	6	17	16	19	12
Malachite	15	20	50	27	22
Chrysocolla	31	32	48	47	32
Cupro-asbolane	4	4	12	6	4
Heterogenite	5	5	12	9	4
Kolwezite	16	15	34	38	18

alkaline pH, whereas copper ions are also active at ambient pH (Witika, 1995). It appears that cobalt ions did not diffuse through the sulphide layer to form a cobalt sulphide precipitate on the surface to allow for interaction with collectors. The observation that kolwezite responds better is due to the presence of copper ions in the mineral structure, which are activated by NaSH which allows for collector adsorption phenomena to take place. A higher recovery of oxide minerals with the dithiophosphate (DF245) collector is explained by a lower consumption rate of sulphidisation for that type of collector (Bulatovic, 2010). For both dithiophosphate (DF245) and thiocarbamate (DF507B) collectors, a larger fraction of chalcopryrite is recovered in the oxide concentrate. The collectors that produce a low oxide ore recovery, also have a lower chalcopryrite recovery in the oxide phase. This indicates that that a fraction of chalcopryrite is attached to the oxide ore that is passive in the sulphide flotation stage. More chalcocite is recovered by DF245 than DF507B, as the hydrophobicity of chalcocite is enhanced by the formation of cupric dithiolate due to adsorption of dithiophosphate (Hangone et al., 2005). In general, it is assumed that different collector types will be chemisorbed to metal ions on the mineral, forming a metal-thiolate (Bagci et al., 2007; Bhaskar Raju and Khangaonkar, 1984; Bradshaw, 1997). The exception is the adsorption of SIPX on chalcopryrite, where the a hydrophobic surface is created due to formation of dixanthogen on the mineral surface (Hangone et al., 2005).

The recovery of gangue minerals, shown in Table 5, are lower in the oxide concentrates. For pyrite and magnesioclhorite, the recovery exceeds the recovery of heterogenite. This is ascribed to the inactivity of cobalt ions. Even though dithiophosphate collectors are known to be more selective, DF245 does produce a relatively high recovery of gangue minerals compared to the xanthate and thiocarbamate types, which are known to be stronger and less selective (Lotter and Bradshaw, 2010). Considering this information and the grade-recovery curves in Section 3.2.1, it can be stated that the dithiophosphate is more selective in the beginning of the flotation process but that effect dissipates with increasing flotation time.

The enrichment factors for valuable minerals are shown in Table 6. All sulphide minerals and copper oxides are concentrated in the sulphide flotation stage, whilst cobalt oxides are less concentrated or equal to the content in the feed. When comparing the information from Table 6 with the recovery per mineral in Table 4, it follows that a higher recovery of valuable minerals is accompanied with a lower enrichment.

Table 5

Recovery of gangue minerals (wt%) per collector type for the sulphide and oxide concentrate.

Mineral	SIPX	DF068	DF245	DF507B	DF571
<i>Sulphide Concentrate</i>					
Pyrite	10	7	19	9	13
Goethite	7	8	12	11	9
Rutile	7	7	16	12	7
Dolomite	4	4	7	6	4
Fe Dolomite/Ankerite	7	8	11	10	9
Apatite	3	3	6	6	4
Magnesite	8	7	12	11	8
Quartz	1	2	4	3	2
Magnesioclhorite	21	17	23	22	18
Mg silicates	10	8	15	13	10
<i>Oxide Concentrate</i>					
Pyrite	2	1	3	3	3
Goethite	6	6	9	6	4
Rutile	4	5	9	6	3
Dolomite	2	3	5	2	2
Fe Dolomite/Ankerite	5	5	8	3	3
Apatite	2	2	4	1	1
Magnesite	4	4	7	2	2
Quartz	1	1	2	1	1
Magnesioclhorite	16	16	25	28	13
Mg silicates	5	5	9	6	4

Table 6

Enrichment factor per mineral for the sulphide and oxide concentrate.

Mineral	SIPX	DF068	DF245	DF507B	DF571
<i>Sulphide concentrate</i>					
Carrollite	9.3	9.7	7.2	7.8	5.9
Chalcopryrite	9.6	10.2	5.4	6.4	8.3
Bornite	11.5	12.6	7.6	8.8	10.1
Chalcocite	9.8	12.2	7.3	8.1	8.3
Cu Oxide	5.7	7.7	6.1	4.4	4.8
Malachite	2.0	2.6	1.9	1.9	2.2
Chrysocolla	4.3	4.3	2.7	2.9	3.8
Cupro-asbolane	0.5	0.4	0.6	0.5	0.4
Heterogenite	0.6	0.7	0.7	0.8	0.6
Kolwezite	1.4	1.0	1.2	1.1	1.0
<i>Oxide concentrate</i>					
Carrollite	0.2	0.2	0.3	1.7	0.7
Chalcopryrite	1.5	1.3	1.9	5.3	2.2
Bornite	0.0	0.1	0.0	0.1	0.3
Chalcocite	0.6	0.7	0.5	1.0	4.6
Cu Oxide	1.4	4.4	2.1	4.8	4.1
Malachite	3.8	5.3	6.9	6.8	7.5
Chrysocolla	7.9	8.3	6.5	11.9	11.1
Cupro-asbolane	1.1	1.1	1.7	1.6	1.5
Heterogenite	1.3	1.4	1.7	2.2	1.4
Kolwezite	4.3	3.8	4.7	9.5	6.1

Dithiophosphate collector (DF245) has the highest recovery but the enrichment factor is only about 7.4 for sulphide minerals. In contrast, the enrichment factor for SIPX is between 9.3 and 11.5, albeit with a lower recovery. The cobalt oxide minerals are concentrated in the oxide flotation stage, but at a low recovery. It is possible that the sulphidisation process is only partially successful. A stronger sulphidisation atmosphere or a larger dosage of collectors may be required to successfully concentrate and recover the cobalt oxides. In addition, moving towards a more alkaline pH may activate cobalt ions and prove to be beneficial for the recovery of cobalt minerals (Kongolo et al., 2003; Witika, 1995). For higher recovery of oxide minerals, hydroxamate collectors may be of interest. For reduction of the proportion of gangue minerals, the implementation of a depressant or reverse flotation could purify the concentrate.

4. Conclusions

The evaluation of a range of collectors for concentrating copper and cobalt with flotation from a DRC ore containing a mixture of oxide and sulphide minerals is reported. The flotation process consists of a sulphide flotation stage followed by an oxide flotation stage with controlled potential sulphidisation. QEMSCAN analysis of the ore shows that the metal department is complex, with seven copper-bearing minerals and four cobalt-bearing minerals associated with a complex gangue containing both carbonates and silicates. In all cases, the addition of NaSH leads to higher copper and cobalt recoveries. Differences in recovery of both copper and cobalt were observed, with copper recovery ranging from 70% to 83% and cobalt recovery ranging from 38% to 48%. The cobalt oxide minerals did not respond well to the designed flotation process: only small amounts of cobalt oxide minerals were recovered at low enrichment ratios. It was found that a dithiophosphate collector (DF245) produced the highest recovery of sulphide minerals and copper oxides after oxide sulphidisation. However, the proportion of cobalt oxide minerals recovered remained low. This study has shown that copper recovery can be increased by considering alternative collectors to the commonly applied xanthate collector. An alternative strategy is required for the concentration of cobalt oxide minerals and reduction of the gangue minerals in the concentrate. The application of hydroxamate collectors promises to improve the overall performance flotation of copper and cobalt from mixed sulphide-oxide ores. With regards to the problematic carbonate and silicate gangue,

reverse flotation to remove these minerals prior to copper-cobalt flotation or the use of depressants may prove useful. In summary, an enhanced understanding of the effect of collectors on mineral recovery with a flotation process supports the geometallurgically-informed extraction of copper and cobalt from complex ore types.

Acknowledgements

This work has been financially supported by the NERC project “Cobalt Geology, Geometallurgy and Geomicrobiology” (CoG3) [grant reference NE/M011372/1].

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