Interpreting the role of reagents in the flotation of platinum-bearing Merensky ores

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Synopsis
Reagents are added to the flotation process of Merensky Reef ores to achieve specific functions that enable the separation of valuable minerals from gangue minerals on the basis of the difference in their surface properties. However, due to the complexity of the process, the various interactions that occur as well as the incomplete liberation of the ore and range of minerals present, it is difficult to quantify the behaviour of each of the reagents. More specifically, changes made to achieve a particular outcome may have secondary effects that can override the desired effect. If all the effects and interactions can be accounted for, it is possible to manipulate reagent suites and obtain better overall metallurgical performance. This paper discusses the effect of the addition of copper sulphate at different operating points of the recovery of the sulphide minerals. Batch flotation tests indicated that the recovery of chalcopyrite was not affected when operating conditions were varied, whereas pentlandite recovery was strongly affected by the point of reagent addition, and pyrrhotite recovery was enhanced by copper sulphate addition, irrespective of the point of addition, with the extent being dependent on the ore source. Floatable gangue was activated by copper sulphate in the presence of the dithiophosphate collector. Froth stability was also affected by copper sulphate addition.

Introduction
The platinum group elements (PGE) in the Merensky Reef in the Bushveld Complex are strongly associated with the base metal sulphide (BMS) minerals present in the Reef, either as discrete platinum group minerals (PGM) included or attached to the sulphides, or in solid solution with these sulphides (Peyerl, 1983, Schouwstra et al., 2000, Ballhaus and Sylvester, 2000; Cawthorn et al., 2002). In general, the BMS content of the reef is in the region of 1%. This is made up of approximately 45–55% pyrrhotite, 30–35% pentlandite and 15–20% chalcopyrite, and with minor pyrite. The nature of the mineralization of these ores is such that the natural pH of the ore slurries is always alkaline, at a pH of around 9.

The PGEs are recovered by flotation and the flotation of the BMS is treated as a bulk sulphide recovery. In order to maximize PGE recovery, the recovery of all the BMS needs to be optimized. It is known, however, that the flotation rate of chalcopyrite is very rapid, whereas pyrrhotite is generally considered to be a slow floating sulphide, with the flotation rate for pentlandite being in between. It has also been observed that the minerals have varying responses to different conditions (Ekmeç et al., 2005, 2006, Bradshaw et al., 1999, 2006). The addition of copper sulphate is the most controversial and causes the widest range of response.

Reagents are added to perform specific roles that manipulate the pulp chemistry and enhance the differences in mineral surface hydrophobicity to facilitate the separation. The reality is not so straightforward. In addition to the primary role of a reagent, various reagent interactions and competing effects as well as the varying responses of the different minerals have to be taken into account. It is necessary to assess the reagent’s behaviour holistically and evaluate its effects both in the pulp and froth phases, as material is recovered by true flotation as well as by entrainment (Bradshaw et al., 2005).

The role of copper ions in the activation of sulphide minerals, particularly sphalerite, has been well documented (Jain and Fuerstenau, 1985). However, the majority of these studies have been conducted in the acidic region. The mechanism of activation of sulphide minerals in the alkaline region is complicated by the fact that almost all of the activating ions (Cu²⁺) are present in the form of an insoluble metal hydroxide as soon as the reagent is added. In some studies it was recognized that because of copper hydroxide precipitation in alkaline
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media, the mechanism of activation in this pH range may be via the reaction of the collector with hydroxide precipitates (Ralston and Healy, 1980; Laskowski et al., 1997).

Buswell and Nicol (2002) carried out an electrochemical investigation of the activation of pyrrhotite in both acid and alkaline media. They found that the reaction of pyrrhotite with xanthate was enhanced in acidic solutions due to the formation of CuS at the surface, there was no evidence for the formation of CuS in alkaline conditions. In the study of the copper adsorption mechanism on pyrite using various surface techniques by Weisener and Gerson (2000), it was shown that the activation occurred even in the alkaline range via the reaction of Cu²⁺ with surface sulphur sites to the reduced form Cu⁺ together with an over layer of colloidal Cu(OH)₂.

In the classical understanding of the activation process, the copper ions are added to the system initially to allow the adsorption of the copper ions on the surface of the sulphide minerals. Collector is then added, which reacts with the copper ions at the surface to form a hydrophobic species and results in flotation. It has been postulated that the following reactions are likely to occur at the mineral surface (Fuerstenau, 1982, Wesseldijk et al., 2006), which may cause inevitable activation of gangue minerals (such as the silicates and oxides) has also been shown to occur via the adsorption of metal hydroxy and hydroxide species at alkaline conditions in the flotation of platinum bearing ores (Mailula, 2003; Shackelton et al., 2003; Martinovic, 2004; Fornasiero and Ralston, 2005). Consequently the use of copper sulphate as an activator for recovery of the valuable minerals from the Merensky Reef may also lead to activation of gangue minerals.

Over the years each operation has developed a suitable (but not necessarily optimum) reagent suite. The primary collector added to enhance the valuable mineral hydrophobicity is always a xanthate, either sodium isobutyl xanthate (SIBX) or sodium isopropyl xanthate (SIPX). This is often used in conjunction with a secondary collector such as diithiophosphate (DTP). Copper sulphate (CuSO₄·5H₂O) is sometimes added as an activator (Hochreiter et al., 1985). Frothers include the polyglycol ethers as well as the TEB range. MIBC, a commonly used frother elsewhere in the world, is not used in the SA platinum industry. Where necessary, concentrators use a depressant to reduce the naturally floating gangue minerals (NFG), such as talc, that are present in the ore. This is of particular importance to the occurrence of talc rims on pyroxene and chromite (Gottlieb and Adair, 1991, Becker et al., 2006), which may cause further dilution of the concentrate because of the flotation of these composite particles. Two types of polysaccharides, namely modified guar gum (guar) and carboxymethyl cellulose (CMC), are commonly used depressants.

This paper draws on various detailed publications covering a substantial amount of work undertaken by the MPRU to demonstrate the varying responses of the base metal sulphide minerals chalcopyrite, pentlandite and pyrrhotite to selected operating conditions and reagent regimes for copper sulphate addition, the interaction with a collector mixture, and the effect of the point of addition. The depressant type and dosage was kept constant. The effect of depressants has been investigated in other publications (Wiese et al., 2005a,b), but not included in this analysis. No platinum group element analysis was done.

Experimental

Two ores (A and B) from different operations on the Merensky Reef in the Bushveld Complex were obtained. The bulk samples were crushed, blended, riffled, and split using a rotary splitter into 1 kg samples in the MPRU at the University of Cape Town. A stainless steel rod mill with a diameter of 200 mm was used to mill 1 kg portions of the ore. The mill was charged with 20 stainless steel rods of varying diameter in the following ratios: 6 x 25 mm, 8 x 20 mm and 6 x 16 mm. Both ore samples were milled at 66% solids in synthetic plant water (Wiese et al, 2005a) to achieve a grind of 60% passing 75 µm.

The milled slurry was transferred to a modified 3 L Leeds flotation cell, where the volume was made up using synthetic plant water to produce 35% solids. The cell was fitted with a variable speed drive and the pulp level was controlled manually. The impeller speed was set at 1 200 rpm. The depressant Depramin 267 was added at a dosage of 100 g/t irrespective of active ingredient. The air was maintained at a flow rate of 7 L/minute in all the tests. The froth height was kept constant at 2 cm throughout. Four concentrates were collected at 2, 6, 12 and 20 minutes of flotation time by scraping the froth into a collecting pan every 15 seconds. Water recoveries were measured for each test. Feeds, concentrates, and tails were filtered, dried, and weighed before analysis. Copper and total nickel analysis of each sample was done after acid digestion using an atomic absorption spectrophotometer. It should be noted that some nickel in the feed is associated with the gangue minerals (e.g. olivine), and therefore the sulphide nickel recoveries from the concentrates would actually be higher than the total nickel recoveries reported here. It is assumed that the nickel present in all concentrates is entirely sulphide nickel (pentlandite) and that the contribution of the nickel from the gangue is negligible, but it was not possible to report the work in terms of pentlandite recoveries as the non-sulphide nickel in the gangue was not measured. Sulphur analysis was carried out using a LECO sulphur analyser. Pyrrhotite was back calculated from the amount of copper (chalcopyrite) and nickel (pentlandite) in the concentrates, so that its performance could be assessed in terms of mass of pyrrhotite recovered. However, the amount in the tails was unknown, so that overall recoveries could not be calculated. It has been
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assumed that the analysis of the sulphide minerals recovered in the concentrates gives an indication of PGE recovery owing to the strong association between the sulphides and PGEs in these particular ores. All tests were conducted in duplicate.

Results and discussion

The effect of ore sample and sequence of addition on the role of copper sulphate

Six flotation tests were conducted in duplicate using a standard reagent suite. CuSO\textsubscript{4} \cdot 5H\textsubscript{2}O was added at a dosage of 40 g/t. The collector used was sodium normal propyl xanthate (SNPX) at a dosage of 150 g/t. The frother DOW 200 was added at a dosage of 200 g/t. A CMC depressant, Depramin 267, was used at a constant dosage of 100 g/t. As specified, CuSO\textsubscript{4} \cdot 5H\textsubscript{2}O was added prior to the collector, after the collector or omitted from the test. The dosages of SNPX and CuSO\textsubscript{4} were such that there was more than 300% excess of collector present than that required to react with the copper to form CuX\textsubscript{2} stoichiometrically.

The copper grade recovery curves for the three conditions are shown in Figure 1. Very little difference was seen in the copper recoveries for the three conditions, although the lower grades obtained for ore B than for ore A were expected from the higher floatable gangue (pyroxene) content and were consistent with the increased concentrate masses obtained from batch flotation tests. The slightly higher copper recoveries observed for both ores with the ‘No Cu’ condition are within the reproducibility of these results. The nickel grade recovery curves shown in Figure 2 indicate a very similar behaviour for the conditions with copper sulphate addition. However, in the absence of copper sulphate addition there was a significant decrease in grade and a slight decrease in recovery for ore A, with a larger decrease in recovery for ore B. For all conditions there was again a higher nickel recovery from ore A than from ore B.

Figures 3, 4, and 5 show the recovery of copper (chalcopyrite), nickel (pentlandite) and pyrrhotite as a function of water recovery recovered to the concentrate. This shows the ‘effective rate of flotation’, which takes into account froth stability effects, and is more representative of the true floatability of minerals in a batch flotation system.
than recovery versus time (Bradshaw et al., 2005). Whereas copper sulphate addition did not affect chalcopyrite recovery (Figure 3), it had a slight effect on pentlandite recovery (Figure 4), and a strong influence on the calculated amount of pyrrhotite reporting to the concentrate (Figure 5). In addition, there was some difference in the pyrrhotite response between the two ores. When copper sulphate was added (whether before or after the collector), more pyrrhotite was recovered from ore A than from ore B. In the absence of copper (‘No Cu’), the recovery of pyrrhotite from ore B was reduced by at least 50%, whereas there was only a small decrease in the pyrrhotite recovery from ore A. The reason for the differences in the performance of the pyrrhotite depending on ore type is a topic for further investigation to ascertain whether it is dependent on the crystallographic nature of pyrrhotite (hexagonal or monoclinic), texture or extent of intergrowths with pentlandite and nickel in solid solution.

When the collector was added before the copper, it would be anticipated that all of the copper would react in solution with the excess collector and form CuX₂ before any copper ions could actually reach the mineral surface. Consequently, in this case, if activation occurred, the activation process would be different from the classical activation process. The flotation results show that activation did occur with both ores when the collector was added before the copper, and that the extent of activation (or improvement in recovery) was similar. This implies that the formation of hydrophobic precipitates in solution can still lead to activation, presumably via the adsorption of these species at the mineral surface. Hydrophobic bonding forces on surfaces that already have some hydrophobicity from reaction with the collector will tend to adsorb these hydrophobic precipitates. These precipitates would not be expected to lead to an activation of gangue or hydrophilic particles. No activation of gangue was observed in these tests. Figure 6 shows that the amount of floating gangue calculated using the entrainability value of Robertson (2003) as a function of the water recovery indicates that within the accuracy of the test work changing the sequence of addition or the presence of copper sulphate had no significant influence on the amount of floating gangue for both ores. Modal analysis conducted on the two ores using automated quantitative mineralogy showed that ore B contained almost double the amount of naturally floatable gangue (pyroxene) than ore A (Wiese et al., 2005a, Becker et al., 2006).

![Figure 3— Copper recovery versus water recovery for the two ores (A and B) using the three options of copper sulphate addition](image)

![Figure 4— Nickel recovery versus water recovery for the two ores (A and B) using the three options of copper sulphate addition](image)
A series of batch flotation tests was conducted using ore B to investigate the use of lead ions (Pb(NO₃)₂) instead of copper ions (CuSO₄·5H₂O) as an activator for pyrrhotite. These tests were conducted at pH 9, the natural pH for the system, as well as at pH 8 and 10 (Wiese et al., 2006). The use of CuSO₄·5H₂O as an activator was effective at all pH values tested. The use of Pb(NO₃)₂ was not effective as an activator for pyrrhotite. Similar recoveries were obtained for conditions when no activator was used.

The effect of co-collector (dithiophosphate) and point of addition on the role of copper sulphate

Batch flotation tests were conducted to investigate the role of dithiophosphate (DTP) (37.5 g of a 50% solution) as a collector, together with 37.5 g sodium isobutyl xanthate (SIBX), on the flotation response of Merensky ore (B). If no DTP was added, the SIBX dosage was 50 g/t. The role of the point of collector addition was also evaluated, with the collector added to the mill prior to grinding and to the cell where specified. A 100 g/t dosage of Depramin 267 CMC was used as the depressant and 40 g/t DOW 200 as the frother. Where specified, 40 g/t of copper sulphate (CuSO₄·5H₂O) was added. In these tests, the collector addition was only sufficient to react stoichiometrically with 90% of the copper to form CuX₂ and was added to the mill before the copper sulphate, so that if the collector was reacting with the sulphide minerals during milling, there would always be an excess of copper ions for the classical activation to occur despite the order of addition of collector before activator.

Figure 7 shows that there was no effect on chalcopyrite recovery of copper sulphate addition or point of collector addition. Figure 8 shows a reduction in the effective flotation rate of nickel when the collectors were added to the cell compared to when they were added to the mill, and that there was no effect of copper sulphate addition, which is in contrast to Figure 4, where a slight effect was observed. The deleterious effect of collector addition to the cell is consistent with the rapid oxidation of newly liberated pentlandite surfaces and the effect on collector adsorption and floatability. This has been shown by Newell et al., (2005) on oxidized pentlandite, which required more extreme sulphidation conditions than chalcopyrite or pyrrhotite to restore its floatability. The addition of copper was not found to overcome this initial decrease in the flotation, although the positive effect of copper sulphate addition on the recovery of pentlandite has been seen with the addition of higher
dosages of copper sulphate (Buswell et al., 2006). In contrast, the flotation rate of pyrrhotite was not dependent on point of collector addition (Figure 9), but was dependent on the addition of copper sulphate as an activator.

However, it should be noted that the deleterious ‘oxidation’ effect of the pentlandite can also be influenced by the type of depressant used (Wiese et al., 2006). The use of a modified guar depressant, which is a stronger depressant than a CMC, was shown to reduce the effect of oxidation of the pentlandite, presumably because its strong hydrogen-bonding forces remove the iron hydroxides that are likely to be present. However, the stronger nature of the depressant may also lead to some depression of pentlandite, particularly the unliberated particles, leading to lower recoveries, which may counteract the improved rate. It should be noted that, although the effective rate of recovery of the pentlandite has been reduced, the time of flotation was sufficient to ensure that the final recovery was not affected (Wiese et al., 2006).

Figure 10 shows that the addition of copper sulphate, at the collector:copper ratio of 90%, made it possible that adsorption of copper ions on gangue minerals could occur and lead to activation and increased gangue recovery. However, comparison with Figure 11 shows that activation of gangue occurred only when DTP was used in combination with the xanthate. When xanthate alone was used, no gangue activation with copper sulphate addition was observed.

DTP addition also led to increased frothability and mass recovery for all conditions tested. There was no enhancement of sulphide (chalcopyrite, pentlandite or pyrrhotite) floatability when DTP was used in conjunction with xanthate, as there was when xanthate was used on its own.

If copper sulphate is added in excess it would be expected that the collector concentration in solution would be reduced to close to zero. Thus, if enhanced flotation was observed after copper addition, it would imply that hydrophobic species on the surface must then provide the source of the xanthate needed to react with the newly adsorbed copper ions in order to lead to the enhanced recovery. There is too little information available to speculate on the mechanisms taking place. Nevertheless it suggests that the copper activation observed in practice is far more complex than that suggested by the classical mechanisms, and should be investigated further.
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Figure 9—Comparison of pyrrhotite mass recovery versus water recovered for X/DTP added to mill and cell for ore B

Figure 10—Calculated floating gangue versus water recovered for the flotation tests to evaluate the effect of the SIBX/DTP collector combination conditions on flotation performance for ore B

Figure 11—Calculated floating gangue versus water recovered for the flotation tests to evaluate the effect of the SIBX alone collector conditions on flotation performance for ore B
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Conclusions

The different base metal sulphide minerals in Merensky ores (chalcopyrite, pentlandite and pyrrhotite) respond differently to different reagents and operating conditions, particularly those affecting froth stability, so that optimizing overall recovery is not trivial and a holistic understanding is needed. The overall effect of copper sulphate addition is dependent not only on its primary intended role (activating valuable minerals) but also on its interactions with the other reagents and the varying mechanisms occurring on the mineral surfaces.

The floatability of chalcopyrite was not affected, and appears to be more consistent than that of other minerals. Its recovery is affected by froth stability and probably by liberation, although this has not been explicitly shown by this research.

The floatability of pentlandite was affected by the point of collector addition. The best results (floatability) were achieved when the collector was added to the mill. The response of pentlandite to copper sulphate addition was varied, and depended on the collector:copper ratio as well as operating conditions. This may be a function of its particular mineralogy, association with pyrrhotite, depressant type or other reagent dosage, and should be investigated further.

The addition of copper sulphate affected the floatability of pyrrhotite, and more so in the case of ore B than ore A. However, the point of copper sulphate addition did not affect the improvement in pyrrhotite recovery, showing that the activation mechanism was not the classic well-established mechanism as for sphalerite, but possibly by selective precipitation of hydrophobic species.

Naturally floatable gangue could be activated by copper sulphate addition in the presence of DTP, but not with xanthate alone. DTP addition also increased frothability and mass recovery without affecting sulphide mineral floatability.

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