Investigations into the Recovery of Platinum Group Minerals from the Platreef Ore of the Bushveld Complex of South Africa

Copper sulfate addition shown to be of limited value for treatement of Platreef ore

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In the flotation of platinum group minerals (PGMs) it has generally been assumed that they will behave similarly to base metal sulfides and thus sulfide reagent regimes are generally used in such flotation plants. However the tellurides and arsenides of platinum and palladium contribute about 50% of the PGMs present in the Platreef ore, located in the northern limb of the Bushveld Complex of South Africa, and there is evidence of these minerals reporting to the flotation tailings. The present investigation was aimed at studying the flotation behaviour of tellurides, arsenides and sulfides of Pt and Pd and relating these observations to their surface characteristics. Microflotation, zeta potential determinations, time-of-flight secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS) analyses were used to study the synthesised samples after various treatments. It was shown that in almost all cases the addition of a typical sulfide collector, sodium isobutyl xanthate (SIBX), increased the recovery of all the Pt and Pd minerals investigated but that the presence of copper sulfate widely used to activate sulfide minerals caused the recoveries to decrease. These results may question the value of adding copper sulfate in the treatment of Platreef PGM-bearing ore.

Introduction

Most of the world's supply of Pt and Pd and associated elements comes from mines within four major layered igneous intrusions: the Bushveld Complex in South Africa, the Stillwater Complex in the USA, the Great Dyke in Zimbabwe and the Noril'sk-Talnakh Complexes in Russia (1).

The Bushveld Complex in South Africa is a vast repository of value minerals which spreads over an area of 65,000 km^2 and has a thickness of 7 km to 9 km (2). It is a layered intrusion of variable

mineralisation of mafic to ultramafic rocks associated with two felsic intrusive suites. The Bushveld Complex consists of five main limbs, known as the Far Western, Western, Northern, Eastern and Southeastern Limbs respectively (**Figure 1**). The Bushveld Complex's upper zone has the largest concentration of platinum group elements (PGEs): platinum, palladium, rhodium, iridium, osmium and ruthenium. These are contained in the Upper Group Chromitite No. 2 (UG2), the Merensky Reef and the Platreef. The mineral ores from these reefs differ according to grain size, association and concentration of the PGEs.

The Merensky Reef contains base metal sulfide grains and associated PGMs. The rock-forming silicate minerals of the Merensky Reef consist of orthopyroxene (~60%), plagioglase feldspar (~20%), pyroxene (~15%), phlogopite (~5%) and occasional olivine. Interspersed in the mineral rock are secondary minerals of talc, serpentine, chlorite and magnetite. The base metal sulfides are pyrrhotite (~40%), pentlandite (~30%), chalcopyrite (~15%) and trace amounts of millerite, troilite, pyrite and cubanite (1, 4).

The UG2 reef consists of chromitite layers in the Bushveld Complex which are localised in the Critical Zone. They are further subdivided, according to their height in the Critical Zone, into three groups: Lower Group (LG), Middle Group (MG) and Upper Group (UG). The UG2 chromitite layer presents the second layer of the Upper Group and lies between 20 m to 400 m below the Merensky Reef (1). UG2 is a platiniferous chromitite layer whose mineralogy varies depending on the geographic location within the complex. UG2 contains chromite (60% to 90%) with interstitial orthopyrexene (5% to 25%). Minor amounts, less than 5%, of subordinate minerals such as clinopyroxene, biotite, phlogopite, talc, chlorite, quartz and serpentine are also present. Chalcopyrite, pyrrhotite, pyrite and pentlandite are the major base metal sulfide minerals, usually present in trace amounts (<0.1%) (1, 4).

The Platreef is located in the Northern Limb of the Bushveld Complex. This reef consists of a complex assemblage of rock types, with pyroxenites, serpentinites and calc-silicates being the most abundant. The predominant PGMs in the mined area of the Platreef are the PGE tellurides, arsenides, sulfides and alloys. The Pt and Pd tellurides, being the most important, may contribute between 20% and 45% of the PGMs present in the Platreef ore, followed by the alloys (26%), arsenides (21%) and sulfides (19%). Their abundances vary from north to south and from section to section. The major sulfide minerals are pyrrhotite, pentlandite and chalcopyrite (5). Non-sulfide gangue minerals consist mainly of pyroxene and feldspar along with quantities of chlorite, tremolite,
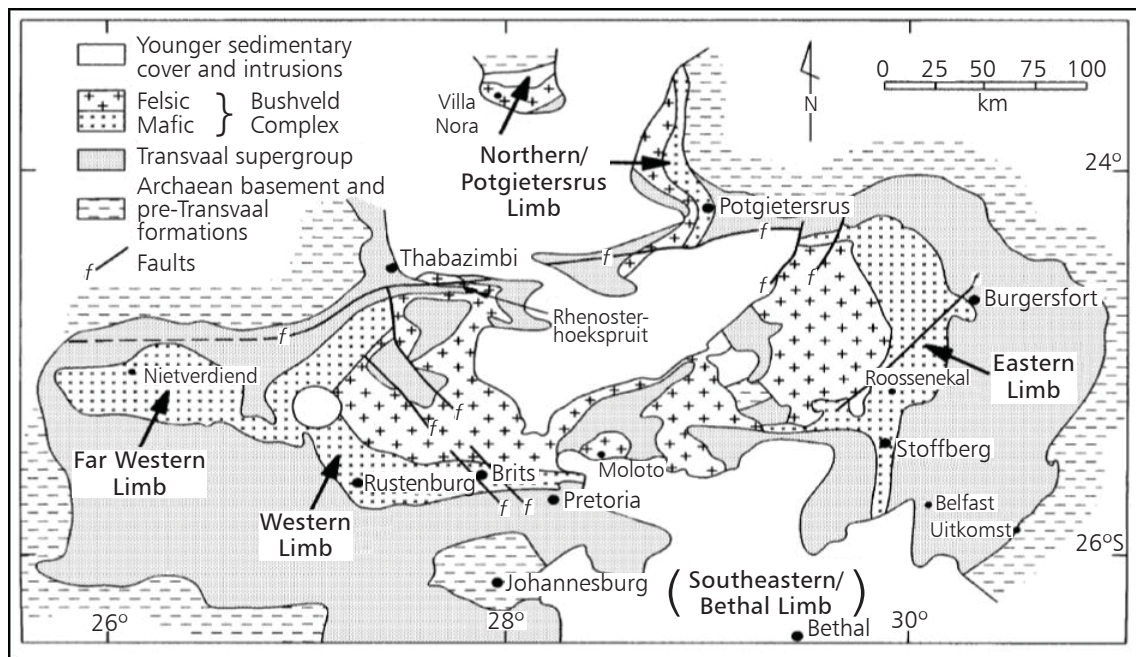

Fig. 1. Geological map of the Bushveld Complex, South Africa (3)

talc and mica. **Table I** summarises the approximate occurrences of the major PGMs in the various reefs.

The telluride minerals present in the Platreef ore are moncheite ((Pt,Pd)(Bi,Te)$_2$ and PtTe$_2$) and merenskyite ((Pd,Pt)(Bi,Te)$_2$ and PdTe$_2$) and the arsenides are mainly sperrylite (PtAs$_2$) and palladoarsenide (Pd$_2$As). The high concentrations of these minerals make it necessary to explore opportunities to maximise the recovery of these minerals by flotation. Presently the current flotation practice is to treat these minerals using reagent suites typical of sulfide flotation but this may not be the optimal approach.

The present paper describes recent investigations into the flotation behaviour of tellurides, arsenides and sulfides. Given the fact that it is inordinately difficult to obtain natural samples of these minerals the study required the synthesis of the relevant minerals. The prepared samples were then investigated in terms of their surface charges using measurements of their zeta potential and of their hydrophobicity when exposed to different reagent suites in a microflotation cell.

Experimental Procedures

The specific Pt minerals synthesised for the purposes of the present investigation were sperrylite (PtAs$_2$), moncheite (PtTe$_2$) and cooperite (PtS), and the Pd minerals were merenskyite (PdTe$_2$), palladoarsenide (Pd$_2$As) and vysotskite (PdS). The synthesis of the samples has been described elsewhere (6, 7). **Table II** summarises the results of the synthesis procedure used for the various minerals.

The minerals were subsequently characterised using X-ray diffraction (XRD) with Rietveld refinement. Back scattered electron (BSE) micrographs of all samples were obtained. Microflotation, zeta potential determinations and ToF-SIMS and XPS analyses were used to characterise the surface of the minerals

and their flotation behaviour. These techniques and experimental methods have been described elsewhere (6, 7). The compositions of all samples were obtained using energy dispersive spectroscopy (EDS) obtained from the scanning electron microscope investigation. BET surface areas were also determined. In the microflotation tests, purified SIBX was used as a collector and sodium carbonate (0.1 M) or hydrochloric acid (0.1 M) were used for pH adjustment. Copper sulfate was used as an activator on the basis of the assumption that the tellurides and arsenides would behave like sulfides which are activated by using this reagent. For these tests synthetic plant water was used (ionic strength = 3.5 E–02) and the particles were in the 38 μm to 106 μm range.

Results and Discussion

The main question being addressed in this investigation was the floatability of the different minerals and to what extent they respond to the reagents currently in use on the flotation plants in the various concentrators. Given the very small amounts of mineral available it was necessary to use microflotation tests to carry out this investigation. Since microflotation does not incorporate any froth phase it is really a measure of the mineral's hydrophobicity after treatment with the collector molecules. In other words, it merely gives an indication, important as that is, of the extent to which a mineral exposed to different chemical environments will adhere effectively to a bubble and report to the launder at the top of the cell.

The cell used in this study has been described elsewhere (8). The results of the microflotation studies are summarised in **Table III**. The results with no reagent reflect the natural hydrophobicity of the mineral. It can be seen that sulfides and tellurides were both reasonably floatable in the absence of any collector whereas the arsenides were hardly

Table I

Platinum Bearing Minerals in the Different Reefs of the Bushveld Complex

Reef	Mineral composition, %				
	Sulfides	**Tellurides**	**Arsenides**	**Alloys**	**Others**
Merensky	36	30	7	7	20
UG2	70	<5	<5	20	<5
Platreef	3	30	21	26	20

Table II

Synthesis Procedures for the Platinum Minerals Used in this Study

Mineral	Stoichiometric composition	Thermal treatment	Yield and phase purity by XRD
Cooperite PtS	$Pt_{2.00}S_{2.00}$ (34.35 g Pt, 5.65 g S)	Ampoule heated to 1000°C at a rate of 20°C min^{-1}, held for 96 hours, then allowed to cool at a rate of 10°C min^{-1}. Break tube, regrind, reseal and reheat to 1000°C at a rate of 20°C min^{-1}, held for 96 hours, then allowed to cool at a rate of 10°C min^{-1}	40 g >99% purity
Vysotskite PdS	$Pd_{8.00}S_{8.00}$ (30.74 g Pd, 9.26 g S)	Ampoule heated to 800°C at a rate of 20°C min^{-1}, held for 30 minutes, subjected to controlled linear slow cooling down to 350°C over 60 hours	40 g 97.4% purity
Sperrylite PtAs$_2$ (Sample 1)	$Pt_{4.00}As_{8.00}$ (33.93 g Pt, 26.06 g As)	Ampoule heated to 800°C at a rate of 10°C min^{-1}, held for 6 hours then slowly cooled to ambient temperature at a rate of 5°C min^{-1}	60 g 90.6% purity
Sperrylite PtAs$_2$ (Sample 2)	$Pt_{4.00}As_{8.00}$ (33.93 g Pt, 26.06 g As)	Ampoule heated to 800°C at a rate of 10°C min^{-1}, held for 12 hours then slowly cooled to ambient temperature at a rate of 5°C min^{-1}	60 g 93.5% purity
Palladoarsenide Pd$_2$As	$Pd_{2.65}As$ (44.38 g Pd, 15.62 g As)	Ampoule heated to 800°C at a rate of 10°C min^{-1}, held for 12 hours then slowly cooled to ambient temperature at a rate of 5°C min^{-1}	60 g >95% purity
Moncheite PtTe$_2$	$Pt_{1.00}Te_{2.00}$ (20 g Pt, 40 g Te)	Ampoule heated to 1150°C at a rate of 20°C min^{-1}, held for 30 minutes, subjected to controlled linear slow cooling down to 350°C over 60 hours, then slowly cooled to ambient temperature at a rate of 10°C min^{-1}	60 g 75.7% purity
Merenskyite PdTe$_2$	$Pd_{1.00}Te_{2.00}$ (20 g Pd, 40 g Te)	Ampoule heated to 800°C at a rate of 20°C min^{-1}, held for 30 minutes, subjected to controlled linear slow cooling down to 350°C over 60 hours, then slowly cooled to ambient temperature at a rate of 10°C min^{-1}	60 g 68.7% purity

Table III

Recoveries of Various Platinum and Palladium Tellurides, Arsenides and Sulfides in a Microflotation Cell at pH = 9 in Synthetic Plant Water

Mineral	No reagent[a]	SIBX[b]	CuSO$_4$ + SIBX[c]
PtTe$_2$	50	99	50
PdTe$_2$	61	99	98
PtAs$_2$ (Sample 1)	4	72	68
PtAs$_2$ (Sample 2)	0	2	8
PdAs$_2$	24	95	66
PtS	94	94	89
PdS	64	95	99

[a] Natural hydrophobicity
[b] Sodium isobutyl xanthate
[c] Treatment with copper sulfate before addition of SIBX

floatable. Addition of SIBX improved the floatability of all the minerals except for the sample labelled PtAs$_2$ (Sample 2). **Figures 2** and **3** show plots of the recovery *vs.* time for the case of Pd$_2$As and PtTe$_2$ with no reagent, the addition of SIBX and the addition of SIBX after conditioning in copper sulfate. These plots show clearly the decrease in both the recoveries and the rates of flotation of the mineral when copper sulfate is present.

The microflotation results of the Pt arsenides are of particular interest. Empirical observations on plants have suggested that PtAs$_2$ (sperrylite) is a poorly floatable mineral. This is shown to be the case for Sample 2 in this study, but not significantly
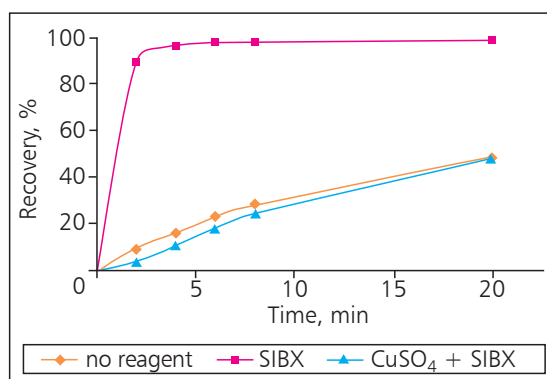
Fig. 3. Platinum telluride (PtTe$_2$) recovery-time curves at pH 9 comparing no reagents, SIBX and CuSO$_4$ + SIBX in synthetic water, ionic strength = 3.5 E–02
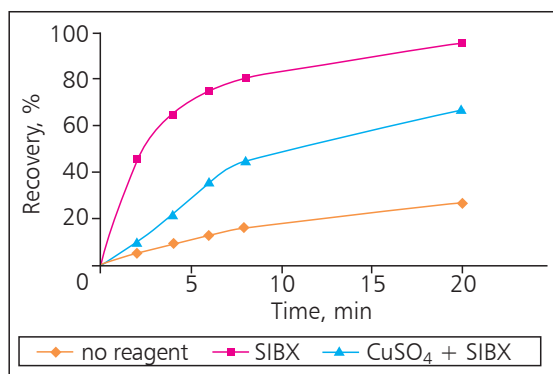
Fig. 2. Palladoarsenide (Pd$_2$As) recovery-time curves at pH 9 comparing no reagents, SIBX and CuSO$_4$ + SIBX in synthetic water, ionic strength = 3.5 E–02

for Sample 1. It is clear that samples prepared using different synthesis times have quite different flotation behaviour. The BSE micrographs of PtAs$_2$ (Sample 1) prepared using a synthesis time of 6 h (**Table II**) show the presence of Pt blebs with a size range of 2 μm to 5 μm within the sperrylite phase (**Figure 4(a)**). Sample 2, which was synthesised for 12 h, showed fewer such Pt blebs on the surface (**Figure 4(b)**).

The EDS results show that the Pt blebs in Sample 2 were much richer in arsenic relative to those in Sample 1. These treatments were repeated and the results were found to be reproducible. It appears that the longer synthesis time resulted in a sample in which the Pt was more homogeneously distributed and that
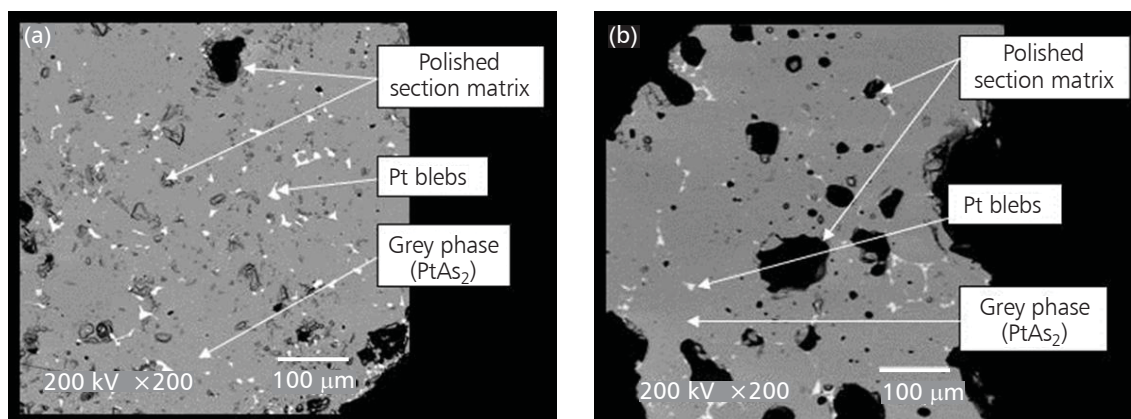
*Fig. 4. Back scattered electron (BSE) micrograph of PtAs$_2$: (a) Sample 1; (b) Sample 2. (See **Table II** for synthesis procedures)*

a type of annealing process may have occurred. The higher recoveries of Sample 1 are ascribed to the ease of interaction of the SIBX collector molecules with the Pt blebs. Such an interaction was much less in the case of Sample 2.

Zeta potential measurements over the range pH 6 to pH 10 showed that the surface charges on each sample were very similar. ToF-SIMS on samples treated with SIBX showed a higher degree of adsorption of xanthate on Sample 1, which correlates with the flotation results. It is also possible that the high concentration of arsenic in the Pt blebs in Sample 2 may be due to the arsenic inhibiting, through poisoning of Pt, the conversion of xanthate to dixanthogen which is known to be catalysed by the surfaces of metallic sulfides (9). It is interesting to note that when Sample 2 was ground to 38 μm its recovery increased to 40%. This increase in recovery may have been due to the exposure of new free Pt blebs.

Compared to the samples of PtAs$_2$, PdAs$_2$ was much more floatable especially when treated with SIBX. This sample had a zeta potential value of almost 0 over the entire pH range which in itself is a remarkable observation. ToF-SIMS showed a high coverage of xanthate after exposure to SIBX and this is consistent with the high flotation recoveries.

The sulfides, as expected, showed high recoveries after treatment with SIBX although the relative differences between the natural floatability of PtAs$_2$ and Pd$_2$As are interesting. The differences, although small, are opposite to that observed for PtTe$_2$ and PdTe$_2$ and so it is not possible to ascribe these differences to the relative roles of the Pt and the Pd. Differences in crystal structures have also been invoked to explain such differences (10) but this is purely speculative. It is most likely that such relatively small differences are due to the variabilities in the product of the synthesis process. Both the sulfides and the tellurides floated readily when treated with SIBX with recoveries between 94% and 99%.

The role of copper sulfate is of great interest since copper sulfate is generally used on sulfide concentrators given its widely known function as an activator (11). As can be seen from **Table III** the addition of copper sulfate resulted in a significant decrease in the recovery of all the Pt compounds, especially PtTe$_2$. PtAs$_2$ also showed a marked decrease in recovery. In the flotation of PGMs it is general practice to add copper sulfate for reasons referred to above. However, as noted here, copper sulfate caused a decrease in the recovery of minerals typical of PGMs occurring in the Platreef ore.

The addition of copper sulfate to the pure mineral during this study always resulted in an increase in the zeta potential of the mineral. At pH>7 the species Cu(OH)$^+$ is dominant and the adsorption of this species to the surface may explain this increase. At higher pHs the dominant species becomes Cu(OH)$_2$ and precipitates of this species may essentially mask the surface, which may explain the more positive zeta potential. When copper sulfate was added after the SIBX collector the zeta potential became more negative relative to copper sulfate alone. This may be due to formation of Cu(OH)X. ToF-SIMS showed that in the case of the tellurides the addition of SIBX after treatment with CuSO$_4$ resulted in a much lower concentration of xanthate on the surface compared to addition of xanthate alone.

What is clear from the flotation experiments is that the presence of copper sulfate, added as an activator for the sulfide minerals, significantly decreased the recovery of PtTe$_2$ and of PtAs$_2$. This may be due to the deposition of Cu(OH)$_2$ colloids which could inhibit access of xanthate ions to the surface. The effect on PdTe$_2$ was less significant. The zeta potential measurements do not predict the flotation behaviour and there were no obvious correlations observed between the zeta potential values and the percentage recoveries. The xanthate concentrations on the surface in the absence or presence of copper were not significantly different and hence the mere detection of xanthate species on the surface is not an indicator of floatability. It can therefore be concluded that it is the chemical nature of the xanthate species which is crucial to promoting flotation. XPS analysis on PtTe$_2$ suggests that part of the xanthate is converted *via* a redox reaction with Cu(II) to Cu(I)X which appears not to contribute to rendering the surface hydrophobic. It is also clear that the theories proposed for the role of copper sulfate as an activator are not necessarily relevant to the case of the tellurides and arsenides.

The unexpected negative effect of copper sulfate addition may thus be ascribed to either the preferential occupation of specific sites by colloidal Cu(OH)$_2$ species, inhibiting the adsorption of xanthate, or the slow conversion of the hydrophilic Cu(OH)$_2$ colloids present on the mineral surfaces to the hydrophobic Cu(I)X species. This has potential major ramifications for the operation of flotation plants since it is inevitable that recycled process water will contain copper species and these may interact with the mineral surfaces before they are exposed to the xanthate collector, thus reducing the recoveries.

Conclusions

This study has examined the floatability of synthetic tellurides, arsenides and sulfides of Pt and Pd. It has been shown that these minerals float readily when treated with SIBX. Unlike base metal sulfides, the addition of copper sulfate as an activator resulted in a decrease in both the rate of flotation and, especially in the case of PtTe$_2$ and PtAs$_2$, in the final recoveries. There were no clear correlations between the observations made of the surface charges of the minerals and their flotation behaviour. XPS and ToF-SIMS results showed xanthate adsorption on the mineral surfaces, although in lesser concentrations in the presence of copper sulfate, using the addition sequence of CuSO$_4$, followed by xanthate. There were indications that Cu(I)X was formed but this was associated with a lowering in flotation recovery.

It is inferred from the results that the active species for flotation was dixanthogen and the presence of copper sulfate in some way inhibited this formation. In the case of the PtAs$_2$ it was suggested that the relatively small number of Pt blebs on the surface, as well as their high arsenic concentration, may have reduced the extent of xanthate conversion to dixanthogen. It is speculated that the negative effect of copper on the recovery may be due to Cu(OH)$_2$ precipitation on the mineral surfaces occurring in patches and thus when xanthate ions are subsequently added, most of the active sites are already occupied by the hydrophilic Cu(OH)$_2$ which reduces the degree of xanthate adsorbing directly onto the vacant Pt and Pd mineral surface sites. Given that the minerals float readily in the presence of xanthate alone, processes which minimise the exposure of these minerals to copper sulfate would probably result in higher recoveries.

Acknowledgements

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