Thiol collector blends for improved PGM recovery: a case study of a UG2 ore

M.G.Moja[1], I.O. Otunniyi[1], and P. Mendonidis[1]

Affiliation:
[1]Department of Metallurgical Engineering, Vaal University of Technology, Vanderbijlpark, South Africa.

Correspondence to:
M.G. Moja

Email:
mojamg@yahoo.com

Synopsis
Different thiol collectors are widely used to improve the flotation performance of PGM-containing ore. They are used either as a single collector or as a collector blend. The performance of sodium n-propyl xanthate (SNPX), dithiocarbamate (DTC), and O-isopropyl-N-ethyl thionocarbamate (IPETC) collectors was evaluated in order to improve the recovery of PGMs from UG2 ore. SNPX was used as single collector, followed by SNPX blends with DTC and IPETC. The best blend improved the 3PGM + Au recovery from 81% to 86% without compromising the grade. As thiols remain the most widely used collectors in the recovery of PGMs from sulphide ores, particularly with leaner and more complex occurrences, there is room for continued research on the most effective blends.

Keywords
froth flotation, collector, thiol blends, PGMs, recovery.

Introduction

Platinum group metals (PGMs) are one of the main sources of mineral revenue in South Africa. The orebodies are located in the Bushveld Complex in Limpopo, North West, and Mpumalanga provinces. The PGMs are found in the UG2 Reef, Merensky Reef, and Platreef and are associated with sulphides, base metals, and gangue minerals (Cawthorn, 1999). The different orebodies are distinguished by their mineralogical composition. The Merensky Reef consists mainly of approximately 60% orthopyroxene, 20% plagioclase feldspar, 15% pyroxene, 5% phlogopite, and some olivine. The Platreef is comprised of a complex suite of serpentines, calc-silicates, and pyroxenites (McFadzean, 2014). The UG2 Reef has a high content of chromite and silicates.

UG2 ore is dominated by chromite gangue, comprising 60–90% by volume, with some silicate minerals (5–30% pyroxene and 1–10% plagioclase) (McLaren and de Villiers, 1982; McFadzean, 2014). Chromite is hydrophilic by nature, but it can report to the flotation concentrates through entrainment and this can be detrimental to the downstream smelting process (Wesseldijk *et al.*, 1999; McFadzean, 2014). The maximum limit recovery and grade for chromite are 2.5% and less than 5% respectively (Wesseldijk *et al.*, 1999; Valenta, 2007; McFadzean, 2014). It is therefore important to recover a high percentage of the valuable minerals and leave as much chromite as possible in the tailings. Hence the effect of different parameters on the recovery and grade of PGMs has to be taken into consideration during optimization of a flotation plant (Valenta, 2007), and this poses quite a challenge for a metallurgist. Considering the fact that UG2 ore has a high chromite content, thiol collectors tend to be very effective in achieving the desired results, and the use of blends can bring about improved recovery without compromising grade.

Thiol collectors have been around for over 100 years and they are still relevant in the froth flotation industry. Thiols are compounds containing a –SH group in combination with an organic radical (Bulatovic, 2007), and they play a significant role during flotation of valuable minerals. Thiol collectors, which are also known as sulphydryl compounds, are widely renowned for being selective and powerful in the flotation of sulphide minerals (Wills and Napier-Munn, 2006).

Xanthate hydrolyses and forms unstable xanthic acids in the presence of moisture; it further decomposes into carbon disulphide and alcohol (Bulatovic, 2007; Fuerstenau, 1982a). In solution, xanthate decomposition increases with decreasing pH, and xanthates are stable in alkaline media (Bulatovic, 2007; Wills and Napier-Munn, 2006). The length of the carbon radical determines the dissociation of xanthates in an acid medium, and xanthates with a shorter hydrocarbon radical dissociate faster than those with longer carbon chains (Bulatovic, 2007; Fuerstenau, 1982b), hence sodium n-propyl xanthate (SNPX) was used as the primary collector in this study.

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Dithiocarbamates have some comparable properties with xanthates but are more expensive, hence they are used as secondary collectors. They are stable over a wide pH range (from pH 5–12) and can achieve flotation rates which are faster than xanthates (Ngobeni and Hangone, 2013). Thionocarbamates belong to the family of xanthates and dithiocarbamates, due to the similarity of the surface coordinating solidophilic groups in these compounds. They are selective collectors of copper sulphides. They are stable in acid media down to a pH of 4 (Ackerman *et al.*, 1984; Jiwu, Longllng, and Kuoxiong, 1984; Wills and Napier-Munn, 2006). The thionocarbamates have an outstanding selectivity against pyrite and pyrrhotite (Nagaraj *et al.*, 1988; Liu, 2004).

Collectors can be used either as a single reagent or a mixed system. Glembotskii (1958), Lotter and Bradshaw (2010), and Ngobeni and Hangone (2013) have proven that it is beneficial to mix or blend collectors. These benefits included faster kinetics, increased carrying capacity of the froth phase, and recovery of middling and coarse particles (Lotter and Bradshaw, 2010). The performance benefits are derived from the interaction between various components of the mixed collectors rather than the singular main effects. According to Bradshaw (1997) and Makanza, Vermaak, and Davidtz (2008), the adsorption of xanthates onto the mineral surface occurs through charge transfer between the collector and the mineral surface, whereas dithiocarbamates adsorb through the formation of metal-thiolate on the mineral surface. Therefore when dithiocarbamate and xanthate collectors are blended, the blends will manifest adsorption characteristics of both collectors, and as a result bring about improved adsorption characteristics resulting in an improved coverage of the mineral surface.

Three different types of thiols, namely sodium n-propyl xanthate (SNPX), dithiocarbamate (DTC), and O-isopropyl-N-ethyl thionocarbamate (IPETC) were evaluated in this work, and a case study of their application as collector blends is presented. The aim was to investigate the performance of SNPX, DTC, and IPETC, with DTC and IPETC as co-collectors to improve the recovery of PGMs from a UG2 ore from the western Bushveld Complex (North West Province). This work is part of a postgraduate study with Vaal University of Technology aimed at improving the recovery of PGMs through blending collectors.

Experimental details

Sample collection and preparation

The UG2 ore sample was obtained from a mine in the western limb of the Bushveld Complex. The bulk sample was crushed, blended, riffled, and split into portions of 2 kg. The 2 kg samples were wet milled at 67% solids by mass in a laboratory rod mill for 60 minutes to 75% passing 75 μm. The rod mill was charged with 28 stainless steel rods, ten of which were 20 mm × 310 mm, another ten were 15 m × 310 cm, and eight were 9 mm × 310 mm.

Reagents

SNPX was received in powder form, and DTC and IPETC were received as liquids. All these collectors were of analytical grade. SNPX was dosed at 150 g/t, as a single collector, but at 100 g/t with a 50 g/t complementary dose of either DTC or IPETC as the co-collector. Copper sulphate as an activator for sulphide minerals, and carboxyl methylcellulose (CMC) as depressant for gangue minerals, were received in powder form, and were dosed at 40 and 60 g/t respectively. Polypropylene glycol (22 g/t) was used as the frother.

Flotation procedure

The wet-milled slurry was transferred into a 5 litre Denver batch flotation cell, and flotation was carried out at a pulp density of 35% solids. The impeller was operated at a speed of 1200 r/min throughout the test. The pulp pH was first regulated to 8.0. Reagent conditioning was done in the following order: copper sulphate at 40 g/t for 5 minutes; SNPX or SNPX co-collector at 150 g/t or 100 g/t and 50 g/t respectively for 2 minutes; CMC at 60 g/t for 2 minutes; and lastly polypropylene glycol at 22 g/t for 1 minute. Thereafter, air was introduced into the cell at a flow rate of 5 l/min.

Four concentrates were collected into a pan by scraping off the froth at intervals of 15 seconds for collection times of 1, 2, 5, and 12 minutes. The collected concentrates and the tailings were weighed, filtered, dried, and weighed again. The dried concentrates and tailings were analysed for four elements (4E: Pt, Pd, Rh, and Au) and chromite using fire assay (by lead collection with an inductively coupled plasma–optical emission spectrometry finish). Since the focus of this study was on blending collectors, all other reagents and their dosages were kept constant during the tests. Each test was conducted in triplicate. To ensure procedural precision, mass pulls were compared and any runs that deviated by more than 5% were rejected and repeated.

Results and discussion

The effects of collector blending (SNPX, SNPX plus IPETC blend, and SNPX plus DTC blend) are presented in this section. The 4E built-up and assayed head grades of the UG2 ore used, cumulative 3PGE + Au (4E) recoveries *versus* time, cumulative 3PGE + Au recoveries *versus* cumulative 3PGE + Au grades, and chrome recoveries *versus* water recoveries, were used to quantify these results.

Table I indicates the built-up (reconstituted) head grade which was calculated, and assayed head grade measured at Mintek, for different conditions.

Figure 1 shows the cumulative 3PGE + Au recoveries *versus* flotation time using SNPX and SNPX-IPETC and SNPX-DTC blends. With SNPX at a dosage of 150 g/t the recovery increased rapidly for the first 8 minutes, and thereafter increased gradually until the twentieth minute, when the last concentrate was collected. The overall cumulative recovery was 81%, which is the same as the overall cumulative recovery of the SNPX-DTC blend. This may be due to the fact that SNPX is a short hydrocarbon chain xanthate, and therefore the reaction between the xanthate and the minerals may have been faster than with the SNPX-DTC blend but slower than with the SNPX-IPETC blend.

According to Glembotskii (1958), and Lotter and Bradshaw (2010), blends of xanthates and DTCs exhibit synergistic effects. However, the SNPX-DTC blend achieved an overall cumulative recovery similar to that of SNPX alone (Figure 1). By twenty

Table I

4E built-up (reconstituted) head grade and assayed head grade (measured) of the UG2 ore

	4E head grade (reconstituted) (g/t)	4E head grade (as analysed) (g/t)	Standard deviation
SNPX	3.53	3.69	0.11
SNPX-DTC	4.14	3.69	0.32
SNPX-IPETC	3.78	3.69	0.06

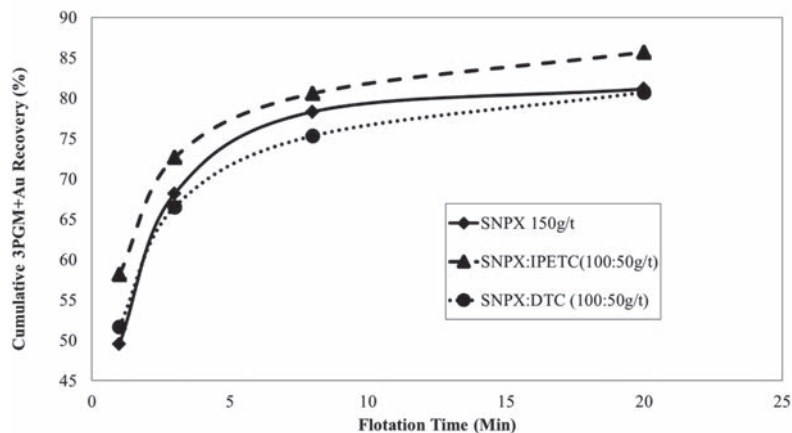# Thiol collector blends for improved PGM recovery: a case study of a UG2 ore

Figure 1—Cumulative 3PGM + Au recoveries obtained with SNPX and SNPX blended with IPETC and DTC
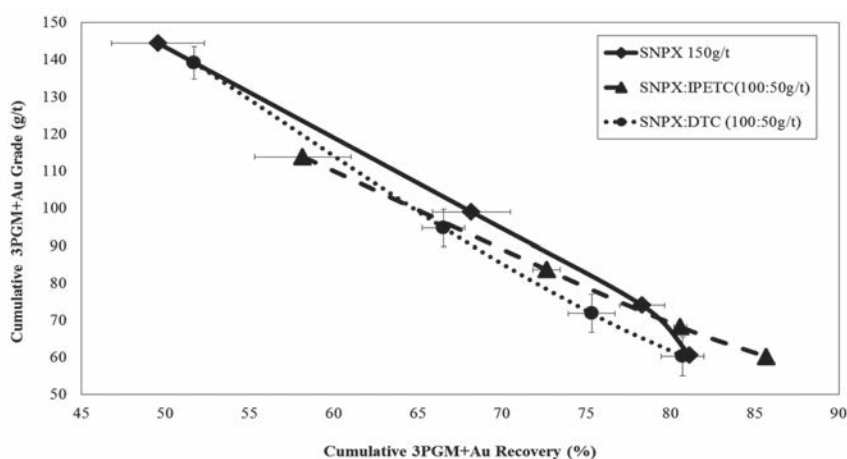

Figure 2—Cumulative 3PGM + Au grade *versus* cumulative 3PGM + Au recovery obtained with SNPX and SNPX blended with IPETC and DTC

minutes, the maximum recovery had been attained for the SNPX condition, and it was apparent that additional flotation time would not improve the recovery (as indicated by the asymptotic curve); while the SNPX-DTC blend curve continued with a positive gradient, indicating that a further increase in flotation time would result in increased recovery. This is evidence of a synergistic effect. However, such further increase in recovery generally compromises grade disproportionately (see discussion on Figure 2). It is also notable that the kinetics under SNPX alone is faster than that under SNPX-DTC. This agrees with the known effects of chain length and branching of hydrocarbon group in collector ions. The linear and shorter group in SNPX results in a higher reaction rate compared to the dialkyl structure in $R_2NCS_2–$ from DTC. The DTC blend therefore does not present a clear indication of improvement in flotation performance.

The SNPX-IPETC blend, however, gave an improved overall cumulative recovery of 86%, which is 5% higher compared to the SNPX-DTC blend. Inferring from Figure 1, this improved recovery is also accompanied by a higher recovery rate over the entire duration of the test. The rate and recovery improvements are positive indicators of desired synergistic effects from a collector blend. It can be inferred that the different interaction obtainable from the thionocarbamate (ROCSNHR) effectively complements that from the dithiocarbonate ion (ROCS$_2^-$) to achieve more collector interaction at surface sites otherwise interactable for xanthate only. A recent study (Bu *et al.*, 2018) indicated that

IPETC is able to remove hydroxide ions from the mineral surface and interact at such freshly activated site.

Figure 2 illustrates the cumulative 3PGM + Au grade *versus* cumulative 3PGM + Au recovery from SNPX, SNPX-IPETC, and SNPX-DTC. The SNPX-IPETC and SNPX-DTC blends show overall concentrate grades of 60.1 g/t and 60.2 g/t respectively, while SNPX shows higher grades from the start of flotation until dropping markedly to 60.53 g/t after recovery stagnated between 12 and 20 minutes (Figure 1). Although Figure 1 shows an improvement in recovery could be expected with extended flotation time, Figure 2 shows that this will be accompanied by a trade-off in grade. Bhaskar Raju and Forsling (1991) state that because dithiocarbamate loses electrons easily, resulting in a stronger but less selective collector, xanthate can be more selective than DTC. This can explain the cumulative grades curve under SNPX-DTC being below those for the other conditions (Figure 2).

IPETC, on the other hand, has an advantage over xanthate due to its higher selectivity for base metal sulphides and long-term storage stability, yet it is not considered a powerful collector (Nagaraj, Wang, and Frattaroli, 1986). But since the overall cumulative grades for all three conditions are within 1 g/t, while the overall cumulative recovery of the SNPX-IPETC blend is 5% higher than for the other conditions, the SNPX-IPETC blend clearly performs better in improving PGM beneficiation from this ore.

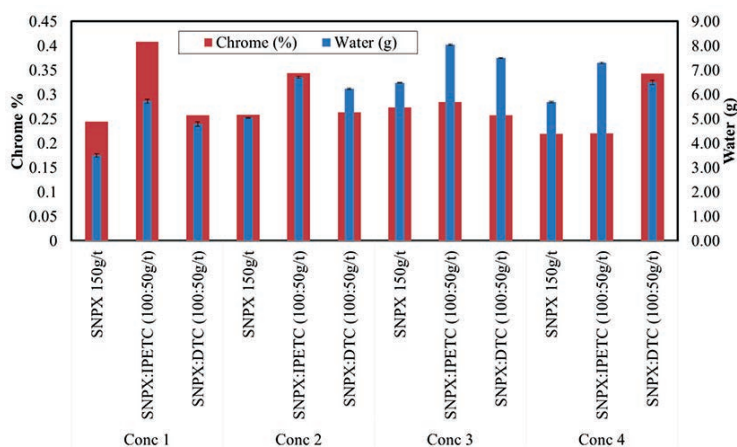# Thiol collector blends for improved PGM recovery: a case study of a UG2 ore

Figure 3—Chrome recovery *versus* water recovery obtained with SNPX and SNPX blends with DTC and IPETC

Figure 3 shows the relationship between the chromite and water recoveries at each stage of flotation under different conditions. The recovery of chromite increased in the order SNPX < SNPX-DTC < SNPX-IPETC. The cumulative chromite recoveries were 1%, 1.1%, and 1.3% respectively. At the beginning of the flotation procedure chrome was mostly entrained and recovered together with finer particles, but over time chromite recovery decreased, supporting the notion that chromite is hydrophilic. Furthermore, the SNPX-IPETC blend yielded the highest mass recovery of water together with percentage chromite recovery, supporting the trends shown in Figure 1.

Conclusion

This study established conditions under which flotation recoveries of 3PGE + Au from a Bushveld UG2 PGM ore can be improved by introducing the appropriate blend of collectors, specifically the SNPX-IPETC blend. The synergistic adsorption characteristics of SNPX and IPETC improved recovery without compromising the grade. The SNPX-DTC blend did not give such improvement. Au+3PGE recovery increased from 81% with SNPX alone to 86% with the SNPX-IPETC blend. The accompanying chromite recovery was minimal (0.4% maximum during the first few minutes of flotation). Although the cost of using two collectors may be more than that of a single collector, the increase in recovery may compensate for the extra cost.

Acknowledgements

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