The flotation of auriferous pyrite with a mixture of collectors

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Abstract

Dithiocarbonates (xanthates) have been the most widely used collectors in sulphide mineral flotation. More recently, research has resulted in the use of trithiocarbonate (TTC) collectors. The present study focuses on the effect of mixtures of C_{12} trithiocarbonate (C_{12} TTC) and sodium *iso*-butyl xanthate (SIBX) in the flotation of auriferous pyrite and the associated gold and uranium from cyanidation tailings. Improved gold and uranium flotation responses were observed with collector mixtures than with SIBX alone. Sulphur recoveries were not affected. Mineralogical analysis of flotation concentrates showed that gold and uranium were also hosted by kerogen. It was therefore proposed that the improved recoveries could have been mostly due to higher kerogen recovery rather than synergism in pyrite flotation. This mechanism opens possibilities into maximising uranium recoveries in auriferous flotation circuits where low recoveries are common.

Article Outline

1. Introduction

Gold in reclaimed tailings dump material from the Witwatersrand basin in South Africa is recovered by alkaline cyanide leaching. Occurrences in which metal values are encapsulated in insoluble minerals like pyrite are not uncommon. Typically, as much as 20% can be associated with the sulphide, which scarcely constitutes more than 4% of the ore (Botelho De Sousa et al., 1986). This occluded gold is refractory to cyanidation and has been traditionally recovered by flotation of pyrite from leach residues. The concentrate produced is calcined at close to 700 °C, liberating gold values that are then leached in cyanide.

Xanthates [dithiocarbonates (DTCs)] have been the collectors of choice for the bulk flotation of sulphide minerals. Recent advances in collector development have resulted in the development and application of trithiocarbonate (TTC) collectors. Early bench-scale flotation research has shown TTCs to be effective in the bulk flotation of sulphides ([Coetzer, 1987], [Coetzer and Davidtz, 1989], [Du Plessis and Davidtz, 1998], [Du Plessis, 2003] and [Breytenbach et al., 2003]). At present, there is a growing interest in the flotation behaviour of TTCs when used in combination with other sulphide collectors. The improved flotation response is believed to be the result of synergism between collectors, similar to that of dithiocarbamate and dithiocarbonate mixtures reported by Bradshaw and O'Connor (1994). The work conducted by Du Plessis et al. (2000) also reported better sulphide flotation response with a mixture of 25% C_{12} TTC and 75% SIBX when compared to SIBX alone.

Anglogold Ashanti's No. 2 Gold Plant at Orkney (South Africa) recovers gold from cyanidation tailings by flotation of pyrite using sodium *iso*-butyl xanthate (SIBX) as a

collector. Uranium is recovered as a by-product of the flotation process. Trial runs using a mixture of SIBX and C_{12} TTC, first in the laboratory and then at a full plant scale conducted over a ten-month period showed increases in gold, uranium, and sulphur recoveries (Davidtz, 2000). This developed interest in the role played by TTC collectors and prompted further research ([Du Plessis et al., 2000], [Du Plessis, 2003], [Breytenbach et al., 2003] and [Makanza and Davidtz, 2005]). Some of the areas of interest included the effect of functional group changes [O–CS_2 (in DTCs) versus S–CS_2 (in TTCs)] on auriferous pyrite flotation response and definition of relevant mechanisms using electrochemistry and spectroscopy.

Previous studies indicated significant differences between the adsorption mechanisms of dithiocarbonates (xanthate) and trithiocarbonates (TTC). The xanthate adsorbs via a charge transfer process and as a result will only adsorb in the presence of an anodic current. More recent investigations ([Venter and Vermaak, 2007a], [Venter and Vermaak, 2007b] and [Venter and Vermaak, 2007c]) indicated the adsorption of TTC onto the substrate in reducing conditions — it appears that TTC decomposes on the surface and the decompositional products render the surface hydrophobic. In case of potentials more positive than equilibrium potential of the TTC monomer–dimer couple some oxidation of the TTC occurs ([Du Plessis, 2003], [Venter and Vermaak, 2007a] and [Venter and Vermaak, 2007b]).

The present work attempts to quantify the effect of SIBX/TTC collector mixtures on the flotation of auriferous pyrite from oxidised material such as No. 2 Gold Plant feed.

2. Experimental

2.1. Ores and reagents

The auriferous pyrite ore (80% passing 100 μm) used in this study was collected from the feed to the flotation circuit at No. 2 Gold Plant. Typical chemical and mineralogical compositions are shown in Table 1 and Table 2. After filtration, approximately 500 kg of the material was dried at about 60 °C for 48 h, screened at 850 μm to break any lumps

and thoroughly mixed. It was first divided into 50 kg batches, and then further divided into 2 kg samples using the cone and quartering technique.

Table 1.

Typical chemical composition of the bulk ore sample from No. 2 Gold Plant

mass %					ppm			
Si	Ca	Fe	S	Zr	Au	Pb	U_3O_8	Zn
39.62	0.46	3.06	1.03	0.03	0.4	109	140	213

Table 2.

Typical minerals contained in No. 2 Gold Plant feed

Mineral	Chemical formula
Quartz	SiO_2
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$
Clinochlore	$(Mg,Fe)_6(Si,Al)_4O_{10}(OH)_8$
Muscovite	$(K,Na)(Al,Mg,Fe)_2(Si_{3.1}Al_{0.9})O_{10}(OH)_2$
Hematite	Fe_2O_3
Pyrite (cubic)	FeS_2
Gypsum	$CaSO_4 \cdot 2H_2O$

Pulp pH was adjusted with reagent grade sulphuric acid and caustic soda. 20 g/t GEMPOLYM GM4 was used as a depressant, 16 g/t Dowfroth 200 as a frother and 70 g/t copper sulphate ($CuSO_4 \cdot 5H_2O$) as an activator. The collectors used in this work were sodium *iso*-butyl xanthate, C_{12} TTC and C_{12} mercaptan ($C_{12}SH$). Unless stated otherwise,

the TTC and mercaptan were dosed from undiluted solutions while the rest of the reagents were used in the form of 1 wt.% solutions.

2.2. Effect of SIBX/C$_{12}$ TTC mixtures on auriferous pyrite flotation

The effect of SIBX/C$_{12}$ TTC mixtures on the flotation of auriferous pyrite was studied through bulk flotation tests where 20 g/t SIBX was used as a standard. Part of the SIBX dosage was substituted with C$_{12}$ TTC on a molar basis (Table 3).

Table 3.

SIBX/C$_{12}$ TTC mixtures calculated for a 2 kg ore sample

SIBX			C$_{12}$ TTC		
mol%	µmol	1 wt.% solution (ml)	mol%	µmol	20 wt.% TTC (µl)
100	232.6	4.0	0	0	0.0
92	214.0	3.7	8	19	27.9
84	195.3	3.4	16	37	55.8
75	174.4	3.0	25	58	87.2

A 2 kg sample of ore was transferred into a 5 l Denver flotation cell and pulped to 40 wt.% solids using tap water. It was agitated at 1200 rpm for 1 min before any reagents were added. The pulp was conditioned with copper sulphate for 5 min, followed by the simultaneous addition of the collectors and 5 min of conditioning. The frother and lastly the depressant were added, each followed by 1 min of conditioning. Thereafter, the pulp was aerated and flotation was carried out for 6 min, during which froth was scraped in 15-second intervals at a constant depth. Throughout the experiment, pulp pH was maintained at 7.2. Froth height was maintained using an automatic level controller throughout the test.

Experiments using each collector mixture were repeated in triplicates. The tailings and bulk concentrates collected from each test were filtered, dried and weighed. Samples were analysed for sulphur using a 114 Series Leco Sulphur Analyser. Uranium content was determined with a sequential XRF spectrometer ARL 9400-241 XP+ and gold by fire assay with lead collection.

2.3. Effect of using diluted and aged C12 TTC on the auriferous pyrite flotation

The effect of using diluted and aged TTC on the flotation of auriferous pyrite was investigated by means of release curve experiments. The flotation performance of SIBX/fresh C_{12} TTC mixture was compared with that of a mixture in which the TTC was diluted to 1 wt.% and aged for 24 h. A mixture of C_{12} mercaptan and SIBX was tested for reference purposes. In all the experiments, SIBX substitutions were done at 8 mol%. A 4 kg ore sample was transferred into a 10 l Denver flotation cell where it was made up to a pulp of 40 wt.% solids. After aeration, concentrates were collected at 0–1, 1–2, 2–4, 4–8, and 8–20 min intervals. At the end of the each test, concentrates and tailings were filtered, dried at 60 °C and analysed for sulphur, uranium and gold and water recovery was also determined. All tests were carried out in duplicates. Experimental data were fitted using empirical first order kinetics outlined by (Cullinan et al., 1999) and (Agar et al., 1980):

$$R=R_{max}[1-e^{-kt}]. \tag{1}$$

Where R (%) is the recovery at time t (min), k (min^{-1}) is the initial rate and R_{max} (%) is the final recovery.

3. Results and discussion

3.1. Effect of SIBX/C12 TTC mixtures on auriferous pyrite flotation

Fig. 1 shows sulphur, gold and uranium recoveries plotted against C_{12} TTC molar concentration. Throughout the range of collector compositions, uranium and gold recoveries followed similar trends. At 8 mol%, uranium recovery was higher than the standard by 2 percentage points and gold by 4.8. These are equivalent to 7% and 10% of

the standard respectively, and are significant. At 16 mol% TTC, recoveries were statistically similar to those observed at 8 mol% and were followed by lower responses at 25 mol%. Sulphur recovery was almost constant throughout — the lower response at 25 mol% is insignificant. When long-chain collectors adsorb, very little collector is needed to saturate all surface active sites. High adsorption density does not necessarily mean an increase in hydrophobicity. With long-chain collectors, secondary adsorption by hydrophobic bonding may produce micelle structures with more polar sites exposed and decreased floatability.
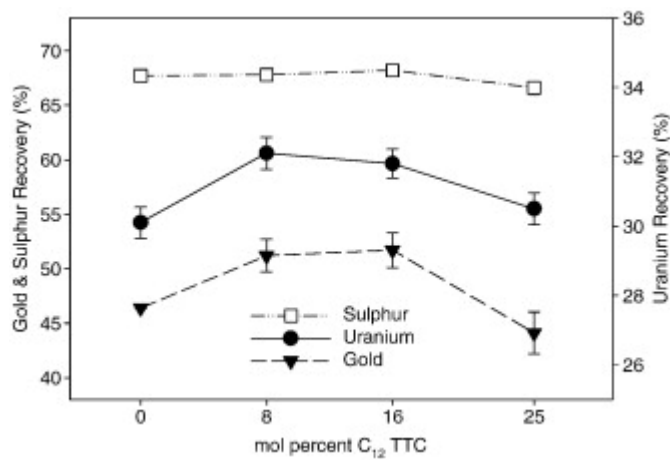

Fig. 1. Response of sulphur, uranium and gold recoveries to C_{12} TTC concentration in the collector mixture.

The enhancement of gold and uranium flotation at 8 mol% TTC compared to SIBX alone could be explained in terms of collector interactions and the nature of minerals that host the valuable metals. Even though the actual mechanisms are not clearly established (Bradshaw, 1997) two theories have been proposed in literature to account for flotation enhancement in applications utilising collector mixtures. Mitrofanov et al. (1985) attributed better performance to the summation of individual contributions of the respective collectors. Valdiviezo and Oliveira (1993) however ascribed it to synergism, the working together of two collectors to yield flotation performances greater than the sum of the individual reagents. According to Bradshaw (1997) this is due to improved adsorption characteristics of the mixed collectors on mineral surfaces as compared to pure collectors. The author highlighted the work conducted by Mellgren (1966) who

proposed that when one of the collectors adsorbs by chemisorption, it provides sites on the mineral surface for the subsequent adsorption of the second collector, which is comprised of more hydrophobic neutral molecules, thereby increasing the overall hydrophobic properties of the mineral. For the SIBX–TTC mixtures being tested in this present work, since TTC oxidises more readily than SIBX (Du Plessis et al., 2000), it could initially irreversibly adsorb and the dithiolate of SIBX could then increase the density of collector packing by physisorption, increasing the hydrophobic state of the valuable minerals. Surface plasmon resonance (SPR) spectroscopy on gold for approximately the same alkyl chain length analogue of TTC and DTC, indicated extremely high values of SPR response obtained for the trithiocarbonate (Groot et al., 2005). These results indicated a very strong interaction of the TTC with the gold surface. As a result of this one would expect longer chain TTCs to show a similar strong interaction compared to the long-chain DTCs.

In Witwatersrand ores, gold refractory to cyanidation and uranium are generally believed to be hosted by pyrite (Ford, 1993). This means that gold, uranium and sulphur recoveries should follow fairly similar trends. Fig. 1 shows a significant increase in gold and uranium recoveries at 8 mol% TTC that is not evident in sulphur recovery. Uranium is present in the form of oxide minerals uraninite (UO_2) and brannerite ($U_{1-x}Ti_{2+x}O_6$) (Ford, 1993) that are not expected to respond to flotation with thiol collectors by true flotation — entrainment due to changes in the froth structure cannot be ruled out. Since the presence of liberated gold is unlikely, both metals are probably associated with a mineral that responded more to SIBX/C_{12} TTC mixtures than SIBX alone.

In the cyanidation process, milled ores are contacted with activated carbon, which adsorbs dissolved gold from solution in a process called the carbon-in-leach (CIL) process. Activated carbon has a tendency of breaking down to sizes small enough to pass through inter-stage screens placed between leach columns, allowing it to escape into the tailings stream. The presence of fine particles of loaded activated carbon in cyanidation tailings such as the material treated in this present work is not unusual. Secondly, literature has shown that most Witwatersrand ores contain carbonaceous matter known as

kerogen, which is sometimes associated with gold and uranium ([Simpson and Bowles, 1977], [Anhaeusser et al., 1987], [Robb and Meyer, 1995] and [Parnell, 2001]). Both activated carbon and kerogen are organic and possess natural hydrophobicity so that they are likely to influence gold and uranium flotation recoveries.

Back-scattered electron imaging (BEI) and energy dispersive spectroscopy (EDS) were employed to investigate the presence of carbonaceous matter recovered in the flotation concentrates. An EDS spectrum (Fig. 3A) of phase A in the electro-micrograph in Fig. 2 shows that it contains $78.95 \pm 0.83\%$ by weight uranium and must be uraninite since no titanium peak could be identified. The occurrence of gold in phase A could not be determined, most likely because it is below detection limits of the instrument. Phase B (Fig. 2) contains mostly sulphur and iron (Fig. 3B) and must be pyrite. The darkest particles (phase C for instance) are high in aluminium and silicon (Fig. 3C) and could be aluminosilicates and pyrophyllite.
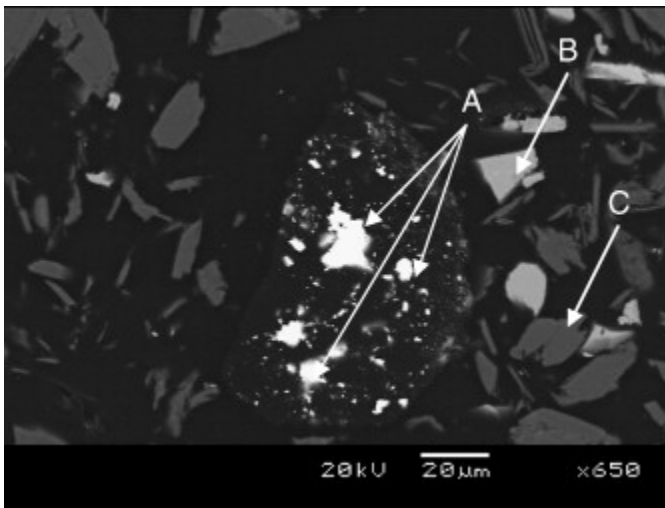

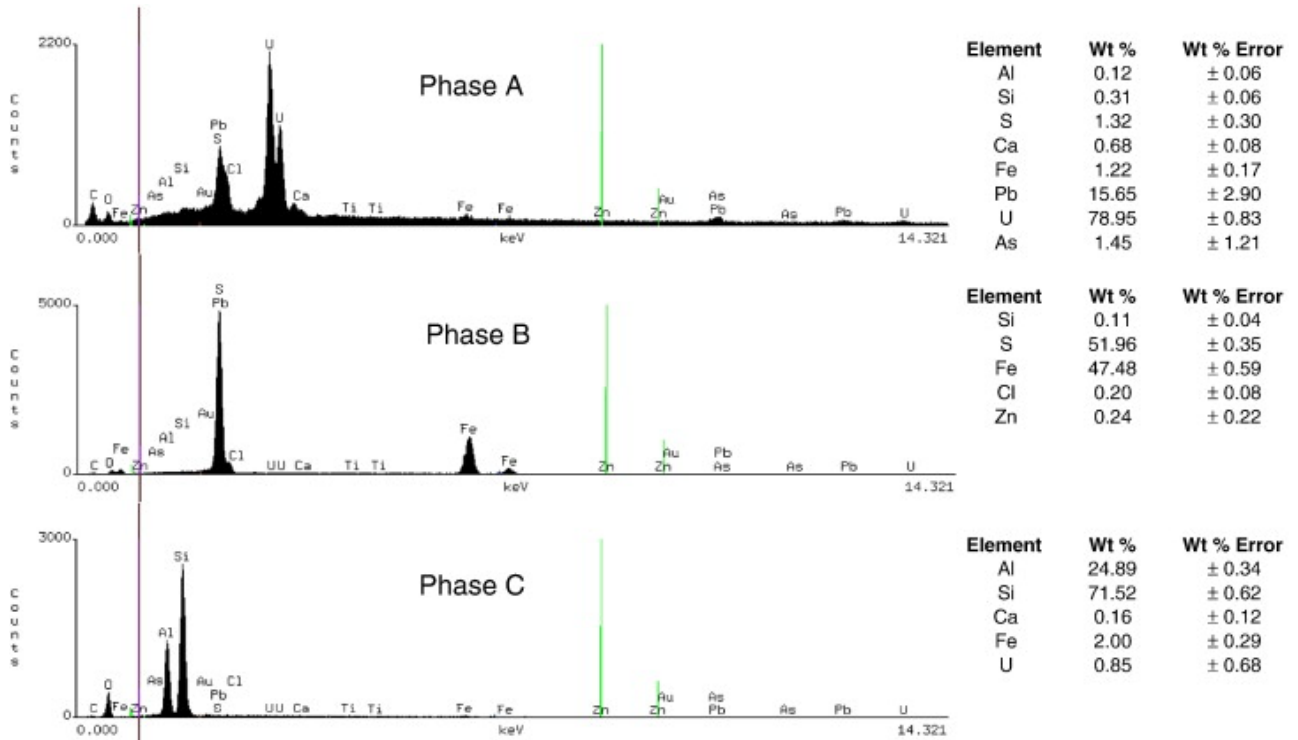Fig. 2. A back-scattered electron image taken from a concentrate recovered with 8 mol% C_{12} TTC.

Fig. 3. (A), (B) and (C): EDS spectra showing the elemental compositions of the corresponding phases in **Fig. 2**.

The presence of lead (15.65 ± 2.90 wt.%) and sulphur (1.32 ± 0.30 wt.%) in the EDS spectra in Fig. 3(A) suggests the presence of galena and (or) lead in the uranium-containing particle. Ford (1993) has reported that uraninite, one of the most important carriers of uranium in the Witwatersrand, sometimes contains minute specks of up to 20% by mass of galena per grain. The author postulated this to originate from lead formed by the radioactive decay of uranium. Lead and galena respond very well to flotation with xanthates ([Tolun and Kitchener, 1963], [Woods, 1971] and [O'Dea et al., 2001]). Presumably the presence of lead and/ore galena may act as a good substrate for thiol collector interactions and synergism. In this case the dual function of long-chain TTCs becomes more interesting. A hydrophobic tail will prefer non-polar surfaces such as kerogen, as well as a strong sulphide interaction with lead. With regard to gold and uranium recovery, unique structural features of long-chain TTCs can at least partly explain improvements in recovery — gold not associated with the base metal sulphides is

expected to show a strong flotation response as indicated by the strong interaction of TTC with gold surfaces investigated employing SPR spectroscopy (Groot et al., 2005).

The particles labelled A in Fig. 2 are part of a dispersion of fine particles that is surrounded by a dark matrix. If the borders of the latter are traced, they compound to a particle. During microprobe analysis of a similar particle (Fig. 4) this matrix remained unchanged while the surrounding resin was charred by the electron beam of the instrument. This suggests that it differs from resin used to mount the sample. The EDS spectra generated during microprobe analysis also showed a significant carbon peak (Fig. 5b) indicating the dark matrix is carbonaceous in nature and could be kerogen. Mounting the samples in bromine containing resins would have aided the identification of the carbonaceous matter in these particles.
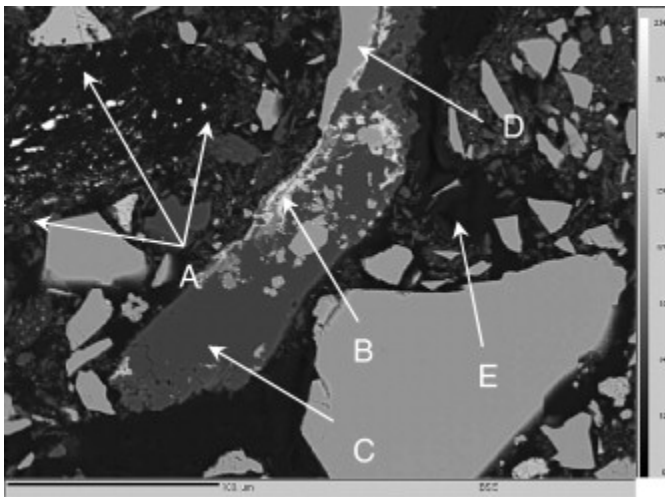

Fig. 4. A back-scattered electron image taken from the microprobe analysis of concentrates floated with 8 mol% C_{12} TTC (A) boundaries of a dark matrix carrying a fine dispersion of uranium particles, (B) uranium particles, (C) siliceous phase, (D) pyrite and (E) charring of resin after exposure to electron beam.
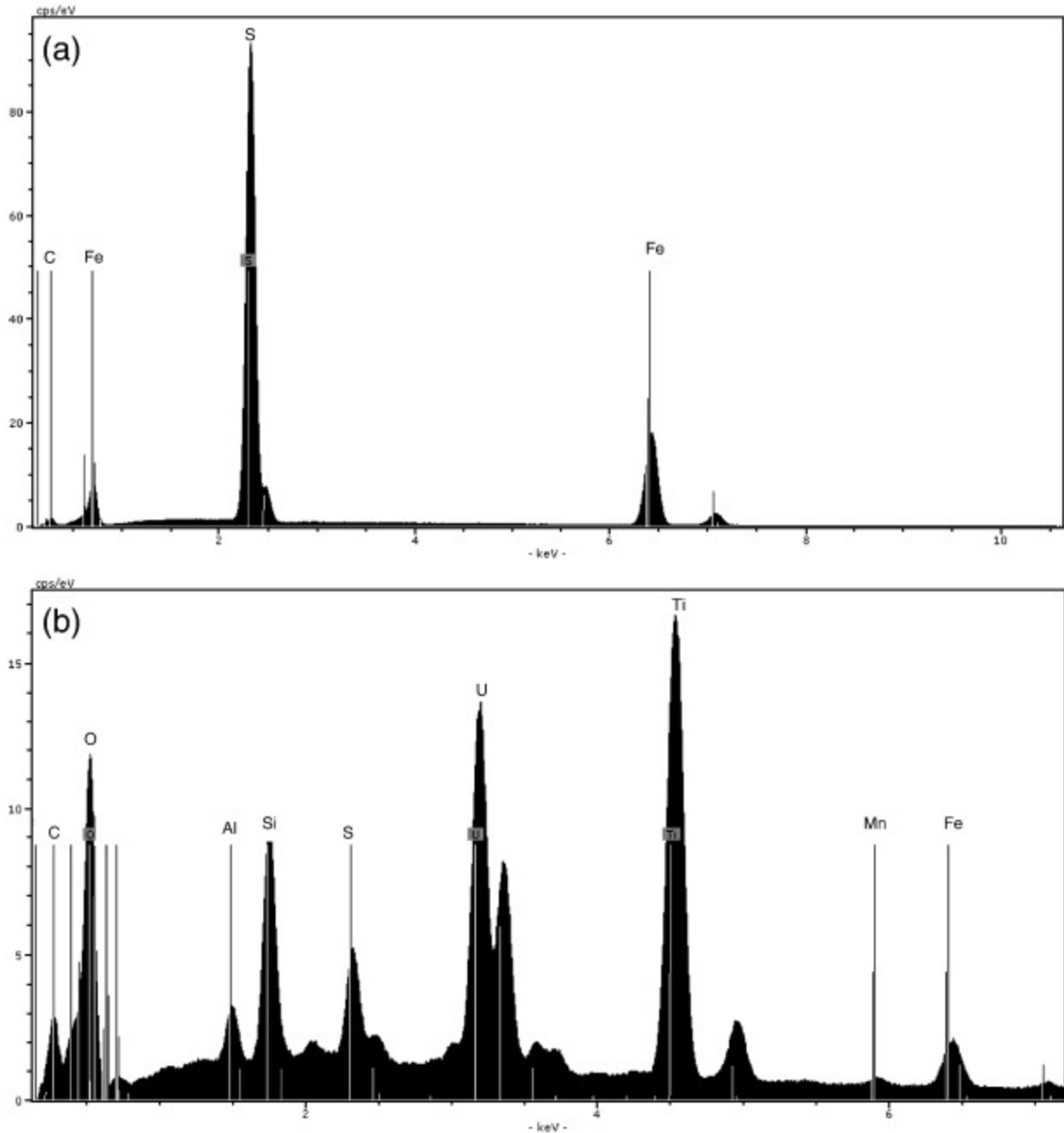
Fig. 5. EDS spectra generated from the microprobe analysis of (a) an iron sulphide and (b) the dark particle carrying uranium particles found in flotation concentrates.

Another observation from the back-scattered electron image in Fig. 4 is that uranium and pyrite (see Fig. 5a) co-exist in a single particle. This implies that uranium could at least be partially recovered with pyrite. Because sulphur recovery was relatively constant throughout, the higher uranium recovery at 8 mol% TTC was probably due to a mineralogical association with kerogen and to a lesser extent with pyrite.

Fig. 6 shows sulphur, gold and uranium concentrate grades plotted versus C_{12} TTC concentration. All grades generally decreased as the concentration of TTC was increased.
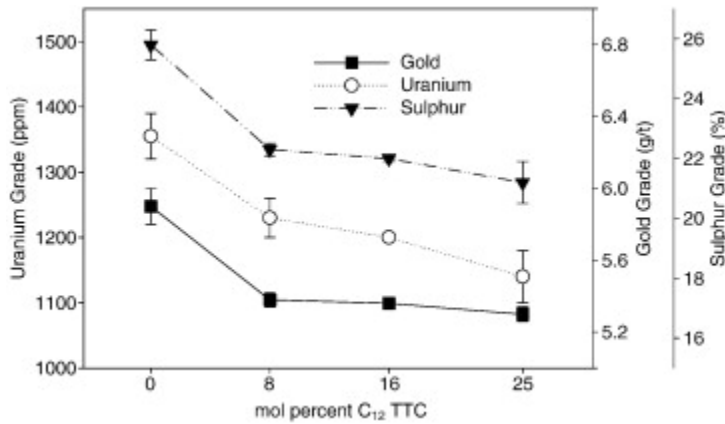

Fig. 6. Sulphur, uranium and gold grades for different C_{12} TTC concentrations in the collector mixture.

In Fig. 7, mass recovery displayed the opposite. Such trends are typical of gangue flotation. More gangue was recovered as the amount of TTC dosed was increased. This diluted the concentrates; hence the continuous decrease in grades. A plot of water recovery versus TTC concentration has also been included in Fig. 7, and it follows a similar trend with mass recovery. Gangue flotation through entrainment has been known to be proportional to water recovery ([Engelbrecht and Woodburn, 1975], [Kirjavainen, 1996] and [Savassi et al., 1998]). The correlation between mass and water recoveries suggests that higher gangue recoveries were more likely to be due to entrainment than poor selectivity. During experiments, more frothing was observed with SIBX/TTC mixtures than with SIBX. The behaviour increased with increased TTC concentration. Gangue collection by long-chain TTC molecules is a possibility. Naturally hydrophobic gangue minerals such as pyrophyllite and fine particle with activating exchangeable ions such as cations on muscovite may be collected by true flotation. The long hydrophobic tail of C_{12}TTC conceivably can attach to the non-polar surface of hydrophobic minerals and increase entrainment with poorer drainage.
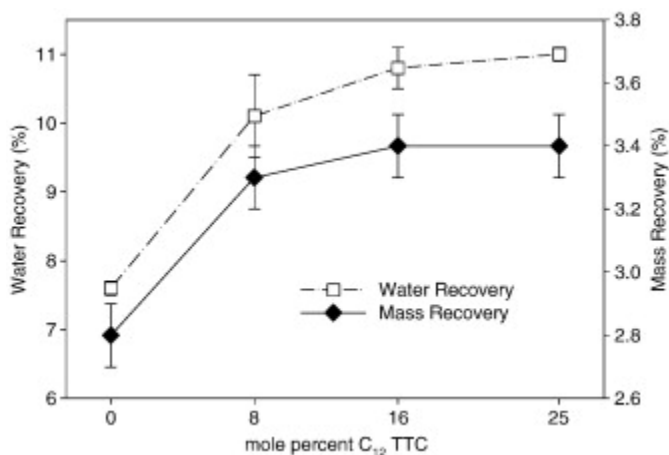
Fig. 7. Variation of water and mass recovery with C_{12} TTC concentration in the collector mixture.

3.2. Effect of diluted and aged C12 TTC on auriferous pyrite flotation

In most flotation processes, it is common practice to dilute collectors prior to their application. Spectroscopic studies conducted by Du Plessis (2003) and Venter and Vermaak (2007) have shown that trithiocarbonates decompose to form the respective mercaptan and carbon bisulphide. The effect of floating pyrite with a diluted (1 wt.%) and aged C_{12} TTC (aged for 24 h at a neutral pH) was therefore investigated. Fresh C_{12} TTC consisting of 20 wt.% solution was used for comparison. A mixture of SIBX and C_{12} mercaptan was tested for reference purposes.

The sulphur recovery-grade curves in Fig. 8 show that 8 mol% fresh TTC showed the best performance. This was followed by the mercaptan mixture, and diluted TTC/SIBX combination and lastly, the standard. The inability of the thiol (on its own) to act as a collector was reported by Keller et al. (1994) that found that at low thiol concentrations (on copper) no significant flotation was possible. Clearly by using a mixture of the thiol and xanthate good recoveries were realised since the xanthate aids the adsorption of the thiol. Table 4 contains initial rates and final recovery data. The R^2 term shows that all the data fitted well into first order kinetics described by Eq. (1). Both TTC/SIBX combinations recorded better sulphur flotation responses than the standard. Between the TTC mixtures, higher initial rates and final recoveries were obtained with fresh TTC.
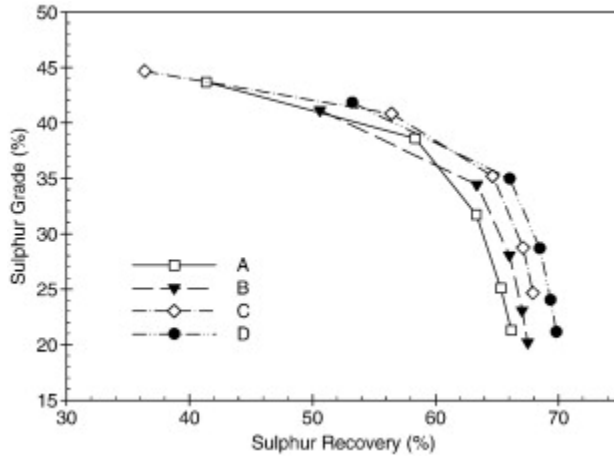
Fig. 8. Sulphur recovery-grade curves for [A] the standard, [B] 8 mol% C_{12} TTC — diluted and aged for 24 h, [C] 8 mol% C_{12} mercaptan and [D] 8 mol% fresh C_{12} TTC.

Table 4.

Sulphur initial rates and final recoveries

Collector composition	R^2	k (min^{-1})	R_{max} (%)
Standard (20 g/t SIBX)	0.9953	1.03	65.52
8% C_{12} mercaptan	0.9982	0.82	67.70
8% diluted C_{12} TTC and aged for 24 h	0.9997	1.42	67.02
8% fresh C_{12} TTC	0.9998	1.47	69.39

Uranium initial rates and final recoveries are shown in Table 5. Both TTCs (fresh and aged) had higher initial rates than the standard. The initial rate recorded with fresh TTC was higher than that for diluted and aged TTC by a factor of 10%. A plot of grade-recovery curves in Fig. 9 shows that the final recoveries for the standard and the two TTC mixtures were almost similar. The fresh TTC/SIBX mixture was more superior because it recorded the highest initial rate. The mercaptan mixture showed the lowest initial rate and final recovery.

Table 5.

Uranium final recoveries and initial rates

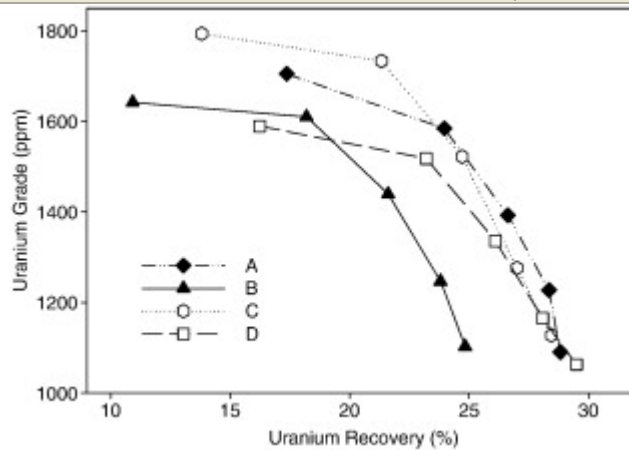| Collector composition	R^2	k (min^{-1})	R_{max} (ppm)
Standard (20 g/t SIBX)	0.9953	0.70	27.47
8% C_{12} mercaptan	0.9962	0.62	24.30
8% diluted C_{12} TTC and aged for 24 h	0.9952	0.83	28.40
8% fresh C_{12} TTC	0.9966	0.92	28.30

Fig. 9. Uranium recovery-grade curves for [A] 8 mol% fresh C_{12} TTC, [B] 8 mol% C_{12} mercaptan [C] the standard and [D] 8 mol% C_{12} TTC — diluted and aged for 24 h. Gold recovery-grade curves are shown in Fig. 10. The respective kinetics data are shown in Table 6. Initial rates for both SIBX/TTC mixtures differed by 0.03 units and their final recoveries by 2.4 percentage points. This is equivalent to only 4% and 5% respectively. The initial rate for the fresh TTC/SIBX mixture was higher than the standard by 0.11 units and considering that this translates to 17% — it is significant.
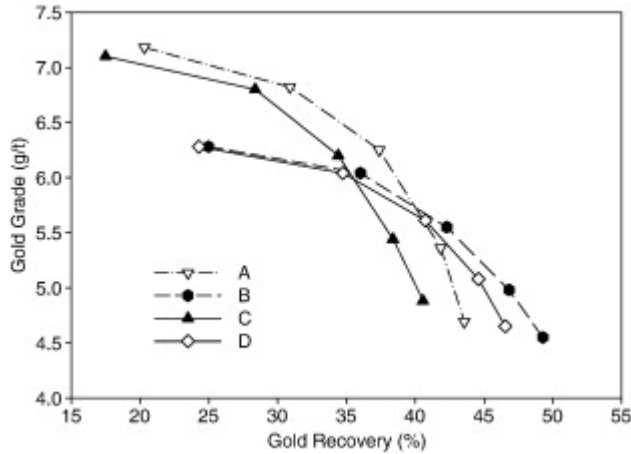
Fig. 10. Gold recovery-grade curves for [A] the standard, [B] 8 mol% fresh C_{12} TTC, [C] 8 mol% C_{12} mercaptan and [D] 8 mol% C_{12} TTC, diluted and aged for 24 h.

Table 6.

Gold flotation responses for 8 mol% substitution of the standard

Collector composition	R^2	k (min^{-1})	R_{max} (g/t)
Standard (20 g/t SIBX)	0.9967	0.63	42.4
8% C_{12} mercaptan	0.9961	0.59	39.4
8% diluted C_{12} TTC and aged for 24 h	0.9942	0.71	45.0
8% fresh C_{12} TTC	0.9956	0.74	47.4

Based on the measurement of flotation initial rates and final recoveries, together with comparison between plotted recovery-grade curves, it is clear that by combining SIBX and fresh C_{12} TTC, a better flotation activity is obtained than with SIBX alone. This is in agreement with earlier plant trials by Davidtz (2000). Previous conclusions have been that the surface density of collector packing of dixanthogen is promoted by the long-chain TTC ([Davidtz, 1999] and [Breytenbach et al., 2003]) implying a synergistic effect. Furthermore, the addition of TTC at the dosage levels studied does not reduce the effectiveness of SIBX. The 1 wt.% solution of TTC marginally lost activity when compared to the fresh TTC solution. This is in good agreement with a microflotation

study performed by Venter and Vermaak (2007a) indicating that decomposed TTC looses its effectiveness but still has a higher initial rate compared to xanthate. This is probably due to the hydrolysis of TTC, forming a mercaptan ([Du Plessis, 2003] and [Venter and Vermaak, 2007a]). The mercaptan/SIBX reference sample generally showed a distinct reduction in grade recovery and kinetics. Although there was not much difference between the fresh and aged TTC, it is likely that the decrease in activity could be more severe if the concentrations were lower.

4. Conclusions

The effects of replacing mole fractions of SIBX with C_{12} TTC were investigated. From bulk flotation tests, it was observed that better gold and uranium flotation performance was obtained from SIBX/C_{12} TTC mixtures than with SIBX alone. Sulphur recovery was comparatively constant throughout all SIBX/TTC mixtures tested. The highest uranium and gold recoveries were recorded at 8 mol% TTC. Scanning electron and microprobe investigations showed the presence of a carbonaceous matter called kerogen and is in agreement with literature. Most of the uranium bearing particles encountered in flotation concentrates occurred as a fine dispersion in kerogen — a small percentage co-exits with pyrite in a single particle. The better flotation performance was therefore mainly attributed to enhanced collection of kerogen particles by collector mixtures compared to SIBX alone. Gold concentrations were below detection limits of the instruments used, but since literature shows that it is associated with kerogen, the mechanisms described for uranium be assumed to be common.

Correlation between mass and water recoveries showed that flotation with collector mixtures was characterised by gangue entrainment. Because kerogen is naturally hydrophobic, high recoveries of the associated gold and uranium could have been a result of mass pull but the galena associated with the uranium particles could also enhance the recovery of the valuables. Measurement of initial rates and final recoveries showed a marginal decrease in activity of SIBX/TTC mixtures in which TTC has been diluted and aged compared to fresh TTC.

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