

Electrochemical studies of the interaction of ethyl xanthate with Pd-Bi-Te

M.K.G. VERMAAK*, J.A. VENTER*, and P.C. PISTORIUS*

*Department of Materials Science and Metallurgical Engineering, University of Pretoria, Pretoria, South Africa

There are practical indications that flotation recovery of palladium bismuth tellurides is poor. This work tested whether this can be caused by a lack of interaction of the collector with the telluride. Impedance measurements, voltammetry and Raman spectroscopy were performed to determine the interaction of dithiocarbonate collectors (KEX) with Pd-Bi-Te. Impedance measurements showed lower capacitance values in solutions containing KEX indicating the formation of a continuous surface layer. Anodic and cathodic polarization diagrams show the mixed potential to be higher than the reversible potential of the xanthate-dixanthogen equilibrium reaction; hence the formation of dixanthogen on the surface is possible. Electrochemically controlled *in situ* Raman spectroscopy did indicate the presence of bulk diethyl dixanthogen on the surface. Raman spectroscopy has confirmed the co-presence of xanthate with dixanthogen, indicating that xanthate retains its molecular integrity when it adsorbs on the surface of the Pd-Bi-Te. As a result, the mineral surface is expected to be hydrophobic and a lack of collector interaction with the mineral is not the reason for low PGM recoveries experienced.

Keywords: Raman spectroscopy; Pd-Bi-Te; ethyl xanthate; platinum flotation; Great Dyke; Pd-bearing bismutho-tellurides and moncheite.

Introduction

Traditionally the Merensky and UG-2 reefs, located in the Bushveld Igneous Complex of South Africa, have been major sources of platinum-group minerals (PGMs)¹. Recent advances in beneficiation technologies have led to major expansions along the Eastern Limb of the Bushveld Igneous Complex. Even more recently we have seen expansions directed at altered platinum reserves, which are difficult to process. These reserves include the Platreef and the Great Dyke reserve in Zimbabwe. As a result of high temperature thermal alteration, the Great Dyke reserves contain unusually high levels of hydroxysilicates i.e. talc and chlorite². The high levels of hydroxysilicates in the Great Dyke reef result in excessive reagent consumption compared to the Merensky and UG-2 ores³.

The textural association of the PGMs will greatly influence their recovery potential during flotation. Good associations of base metal sulphides with PGMs are evident for the Merensky and UG-2 reefs, and as a result recoveries of 85% can be obtained. Because of the good PGM textural association, fundamental research was in the past focused mostly on the adsorption of dithiocarbonate collectors (xanthate) onto sulphide minerals (i.e. pyrrhotite, pentlandite and pyrite). However, the assumption that all PGMs remain associated with the base metal sulphides was challenged by the findings of Penberthy *et al.*⁴ who conducted a comprehensive study on the recovery of platinum-group elements from UG-2 chromite from the Bushveld Igneous Complex. Penberthy *et al.*⁴ found that up to fifty per cent of the PGMs were liberated during milling.

In addition, ores from the Great Dyke show poorer association of PGMs with the base metal sulphides and a significant portion is associated with the silicate minerals³.

Regrinding of the ore to liberate the PGMs is an important option to avoid significant losses to the tailings. Significant quantities of liberated PGMs were also observed in the flotation feed streams of Great Dyke ores³. As in the case of the Great Dyke, Wilson⁵ has indicated that high base-metal sulphide abundances in the Platreef do not necessarily indicate high PGM contents. The poor association of PGMs with the sulphides similarly results in the occurrence of large quantities of liberated PGMs in the flotation feed stream. Investigations are currently underway to treat UG-2 opencast pits by ultra-fine milling to liberate PGMs from the oxidized reef⁶. This clearly demonstrates the importance of studying the individual flotation response of the most abundant PGMs.

A comprehensive review of the PGM mineralogy of especially the Great Dyke and Platreef is given elsewhere⁷. Despite the obvious differences in the matrix mineralogy of the UG-2 and Merensky reefs, the PGM mineralogy is very similar. For both these reefs the (Pd,Pt)S class is by far the most abundant PGM class constituting sometimes up to 80% of the PGMs. Penberthy *et al.*⁴ found that this class of PGM did float but at lower rates than base metal sulphides. No indication was given on the flotation response of the Pd-Pt-Bi-Te. The PGM mineralogy of the Platreef and Great Dyke reef is in contrast to that of the UG-2 and Merensky ore in that a large portion of the minerals belongs to the Pd-Pt-Bi-Te and PGE-S-As and PGE-alloy classes^{5,8}. The occurrence of a large percentage of grains belonging to this class in the rougher and cleaner tails of concentrators along the Great Dyke shows that a fundamental understanding of the interaction of these minerals with collectors is essential.

The very small size (less than 10 μm in the case of the Great Dyke) and scarcity of individual grains contribute to

the complexity of studying fundamental interactions. It was therefore decided to perform fundamental work (i.e. electrochemical investigation, *in situ* Raman spectroscopy and electrochemically controlled contact angle measurements) on synthetic minerals. Contact angle measurements will not be possible on natural grains due to their small size. The same analytical techniques, except for contact angle measurements, will also be employed once natural grains are isolated. The comparison between natural and synthetic grains will be of great importance in evaluating synthetic grains as an alternative source of these grains. The main advantage of synthesizing these minerals in bulk is the ability to perform microflotation tests to evaluate the performance of different reagent suites.

To summarize, the aim of this study was to investigate the interaction of Pd-Bi-Te with dithiocarbonate collectors by employing electrochemical techniques and *in situ* Raman spectroscopy. The overall aim was also to assess whether the poor flotation response encountered in the Great Dyke of Zimbabwe can be related to poor collector-mineral interaction.

Interaction of thiols with metals

It was proposed that the interaction of thiols with metals (platinum, gold and copper) involved an electrochemical mechanism, with an anodic oxidation reaction involving the collector and a cathodic reduction reaction (i.e. reduction of oxygen)⁹:



X^- indicates the xanthate ion and X_2 dixanthogen. Woods *et al.*⁹ further proposed that Reaction 1 proceeds via an initial chemisorption step and that the multilayers of dixanthogen product are bound to the chemisorbed monolayer xanthate by the interaction of the hydrocarbon parts of the molecule. The main experimental advantage of the electrochemical nature of the reactions is that the reactions can be tracked by electrochemical techniques (i.e. potentiodynamic measurements and impedance measurements).

The possible interaction of dithiocarbonate collectors was hence determined through potentiodynamic measurements in the present work. Anodic and cathodic polarization diagrams were drawn for Pd-Bi-Te, to investigate the anodic oxidation and oxygen reduction reactions. The possibility of the formation of a surface layer of the collector was determined through impedance measurements. Impedance measurements allow *in situ* detection of the formation of surface layers of collector measured by a decrease in the circuit capacitance: a significant change in the capacitance value will indicate the formation of a continuous layer of the surfactant. Such a continuous layer of surfactant is expected to render the surface of the particle hydrophobic.

Impedance measurements are based on the modelling of an electrode in solution as an electronic circuit containing resistors, capacitors and inductors. A simplified version of such a circuit is shown in Figure 1. The equivalent circuit contains a resistor in series with a parallel circuit containing a capacitor and resistor.

The capacitance effect is a result of the double layer charging effect (C_D) and possible surface layers (C_s). The electrode capacitance is the series combination of the two effects as shown in Equation [3].

$$\frac{1}{C} = \frac{1}{C_D} + \frac{1}{C_s} \quad [3]$$

As shown by Equation [3], formation of a surface layer (with a finite value of C_s) will cause the electrode capacitance to decrease. In this way, the formation of surface layers can be detected when the mineral is anodically polarized in the presence of xanthate ions.

Experimental

Electrochemical investigations

The selection of the composition of the grains, the synthesis procedure and evaluation of the integrity of the synthetic crystal are given elsewhere⁷.

A conventional electrochemical cell with a three-electrode system was used. Potentials were measured against an Ag/AgCl reference electrode filled with saturated KCl, which has a potential of +0.20V against the standard hydrogen potential. The PGM crystal was mounted in resin and electrical contact was achieved between the contactor shaft and the mineral by employing a spring. The surface area of the Pd-Bi-Te sample was 0.14 cm². Two platinum wire electrodes (10 cm in length) were placed in glass tubes closed with porous glass discs at their ends. The platinum counter electrodes were placed at equal distances from the working electrode. The voltammograms were constructed with a Schlumberger model (1287) potentiostat and the potentiostat was interfaced with a Schlumberger model 1260 frequency response analyser for the impedance measurements. All experiments were conducted at 25°C ($\pm 1^\circ\text{C}$). Sodium borate at a concentration of 0.05M Na₂B₄O₇ was used to buffer the solution at a pH value of 9.3. Solutions were prepared using distilled water with a final resistivity of 18M Ω .cm. The solution was de-aerated for 2 hours with Argon gas (99.999%), from which oxygen was

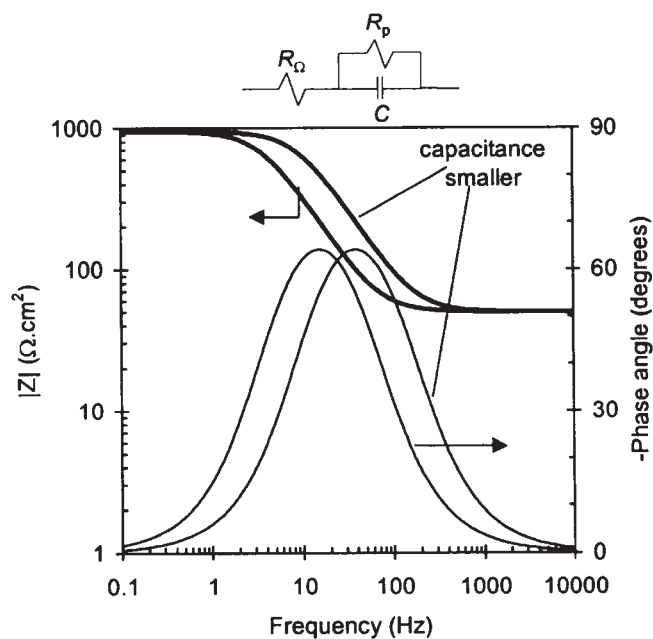


Figure 1. Equivalent circuit of a metallic electrode in a solution showing the different components. Also added is a Bode plot of the impedance as a function of the frequency. The effect of a decrease in capacitance is shown in the Bode plot. Drawn for $R_\Omega = 50 \Omega \cdot \text{cm}^2$, $R_p = 900 \Omega \cdot \text{cm}^2$ and $C = 50 \mu\text{F}/\text{cm}^2$ or $20 \mu\text{F}/\text{cm}^2$

removed by passing the gas over zirconia turnings heated at 600°C. The solution was replaced between experimental runs to avoid contamination. Purified potassium ethyl xanthate (KEX) was used in all the experiments. The PGM electrode was freshly prepared between experimental runs by wet abrasion on silica carbide paper (2400 grit) followed by a polishing stage using a 0.05 µm Micropolish Alumina-B suspension.

Raman spectroscopy

Raman spectroscopy provided valuable information regarding the nature of the species present on the surface of the mineral. A detailed description of the experimental set-up and procedure followed during the Raman spectroscopy is given elsewhere⁷. This technique probes the surface composition while the mineral is immersed in the electrolyte, under potential control.

Results and discussion

The variation of the current as a function of potential, obtained by changing the potential linearly with time between 0.1 (SHE) and 0.4 V (SHE) at a scan rate of 1 mV/s, is shown in Figure 2. The figure clearly indicates the enhanced anodic activity in the presence of xanthate. In addition to this, the figure shows that some oxidation of the mineral occurs in the absence of xanthate, at potentials more positive than 300 mV, as indicated by the anodic current. This anodic current does not originate from adsorption of oxygen only (or from other side reactions). Although anodic current from oxygen adsorption is observed on – for example – pure platinum in this potential range, the charge associated with such oxygen adsorption on platinum is in the range 120–400 µC/cm² (as found in sulphuric acid¹⁰, potassium hydroxide¹¹ and borate buffer solutions¹²), much less than the total anodic charge of 5.8 mC/cm² for the mineral in Figure 2.

Elvy *et al.*¹³ investigated the incongruent oxidation (in air) of minerals in the Pd-Te-Bi system leading to the

formation of a layer of tellurium and/or bismuth oxide covering the palladium-rich substrate. It was found that reactivity of the minerals increased in the order of: PdTe < PdTeBi < PdBi. This is in the same order as the reactivities of Pd, Te and Bi in the pure form. Figure 3 shows the anodic polarization curves of Bi, Te and Pd-Bi-Te in a deoxygenated solution containing 0.05 M Na₂B₄O₇.

Figure 3 clearly shows that Bi is more reactive than Te at potentials lower than 300 mV. It is thus expected that minerals containing higher levels of Bi should be more susceptible to oxidation. It is hence expected that the reactivity of the minerals should increase in the order of: PdTe < PdTeBi < PdBi, in agreement with Elvy *et al.*¹³. This implies that merenskyite (ideal formula: PdTe₂) should be more resistant to oxidation than michenerite (ideal formula: PdBiTe) due to its higher tellurium content. Although the reactive Bi and Te constitute 66.6 per cent (mole basis) of the Pd-Bi-Te mineral, its reactivity is appreciable lower than that of the pure constituents.

In order to investigate the formation of possible surface layers of collector, the Pd-Bi-Te electrode was polarized for 20 minutes at 0.3 V (SHE) in a 0.05 M Na₂B₄O₇ solution with or without 1 × 10⁻³ M potassium ethyl xanthate, following which impedance measurements were performed. The results of this experiment are shown in Figure 4.

The contribution of the capacitance value to the impedance is a maximum at intermediate frequencies i.e. where the phase angle is a maximum. The difference in the impedance values (with and without the collector) at intermediate frequencies, see Figure 4, is very significant. The fact that a change in the impedance values was observed indicates a change in the capacitance values due to the formation of a continuous layer on the surface. The formation of such a layer would tend to decrease the capacitance, see Equation [3].

These surface layers can possibly be multilayers of dixanthogen. Dixanthogen can only form if the mineral surface attains a potential higher than the equilibrium potential of the xanthate-dixanthogen couple. The reversible potential for the oxidation of ethyl xanthate to

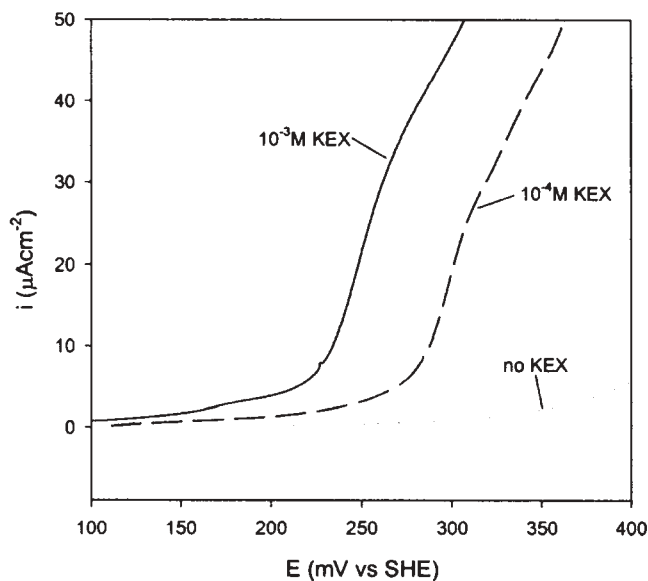


Figure 2. The influence of KEX on the anodic activity for Pd-Bi-Te. Current-potential curves for a Pd-Bi-Te electrode in a 0.05 M Na₂B₄O₇ solution at 25°C in the absence and presence of potassium ethyl xanthate. Potential sweep carried out at 1 mV/s

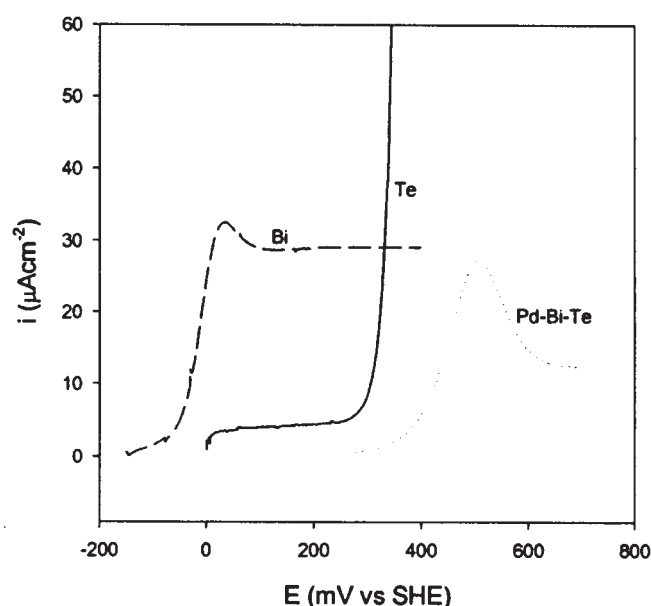


Figure 3. Anodic behaviour of selected metals and alloys in a deoxygenated solution containing 0.05 M Na₂B₄O₇ solution

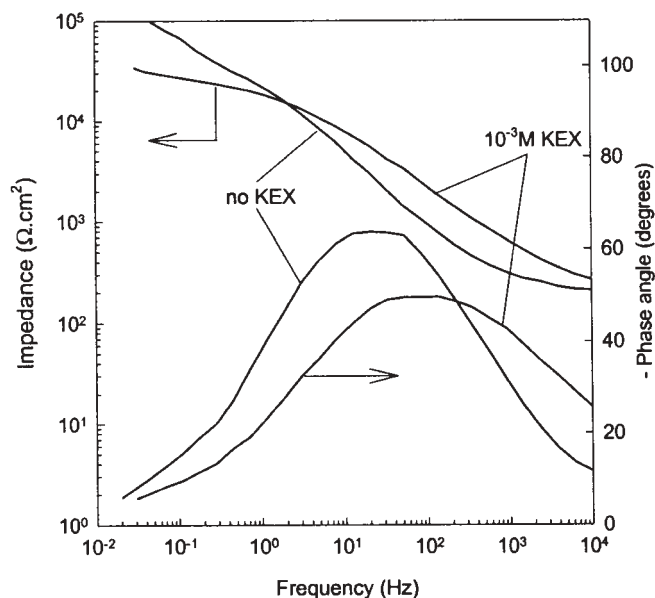


Figure 4. Bode plots for a Pd-Bi-Te electrode after anodic polarization for 20 min at 0.3 V (SHE) in a 0.05 M $\text{Na}_2\text{B}_4\text{O}_7$ solution containing zero and 1×10^{-3} M potassium ethyl xanthate

diethyl dixanthogen is 0.121 V (SHE) at a collector concentration of 10^{-3} M KEX⁹. Efficient cathodic reactions (i.e. reduction of oxygen on the surface of the mineral) would tend to increase the mixed potential. The cathodic polarization diagram showing the reduction of oxygen on the surface, in a borate solution only, is given in Figure 5.

The intersection of the cathodic and anodic polarization diagram (for 10^{-3} M KEX) in Figure 5, gives an estimate of the mixed potential (E_{mixed}) for this system. The actual measured mixed potential of the electrode in an oxygen-saturated solution containing 10^{-3} M KEX, is shown in Figure 6.

The true mixed potential was determined by freshly preparing the Pd-Bi-Te electrode by wet abrasion on silicon carbide paper (2400 grit) followed by a polishing stage. The borate solution was firstly aerated for 2 hours with oxygen gas whereafter the xanthate was added to obtain a concentration of 10^{-3} M KEX. The electrode was subsequently washed with double distilled water and quickly transferred to the electrochemical cell for measurements. The potential readings commenced the moment the electrode was immersed in the solution ($t=0$). The true mixed potential (see Figure 6) compares well (difference is less than 30 mV) with the value predicted from individual anodic and cathodic polarization diagrams (see Figure 5). This clearly demonstrates that the mixed potential of the system is higher than the equilibrium potential of the xanthate-dixanthogen couple. It is thus expected for dixanthogen to form on the surface of Pd-Bi-Te.

Complementing electrochemical investigations with studies using Raman spectroscopy has provided valuable information on the nature of the surface species (see Figure 7).

A detailed account of Raman spectroscopy performed on Pd-Bi-Te is given elsewhere⁷. The Raman spectrum in Figure 7 (see *in situ* spectrum) shows a clear band at 659 cm^{-1} (characteristic of xanthate), which confirms that ethyl xanthate retains its molecular integrity when it adsorbs on the surface of the mineral¹⁴. In addition to this, the band

that arises from the S-S stretching vibration of dixanthogen at 498 cm^{-1} is present in Figure 7 (see *in situ* spectra). Vermaak *et al.*⁷ showed that droplets form on the surface of the Pd-Bi-Te when polarized for extended periods at a potential of 0.3 V. The droplets showed the same Raman peaks as those of freshly synthesized dixanthogen. The formation of droplets on the surface of the Pd-Bi-Te electrode unambiguously shows that ethyl xanthate is oxidized to diethyl dixanthogen and that the 498 cm^{-1} band identified in Figure 7 does arise from the S-S stretching vibration. This result therefore confirms the formation of a product layer as suggested by the impedance measurements and mixed-potential measurements. The hydrophobicity of the surface was also quantified by conducting

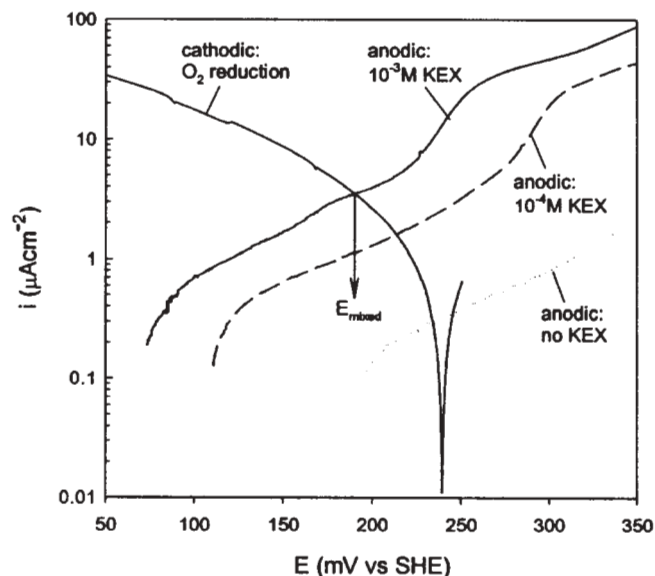


Figure 5. Current-potential curves for a Pd-Bi-Te electrode in a 0.05 M $\text{Na}_2\text{B}_4\text{O}_7$ solution at 25°C in the absence and presence of potassium ethyl xanthate. The cathodic polarization diagram was constructed in an oxygen-saturated 0.05 M $\text{Na}_2\text{B}_4\text{O}_7$ solution. Potential sweeps carried out at 1 mV/s

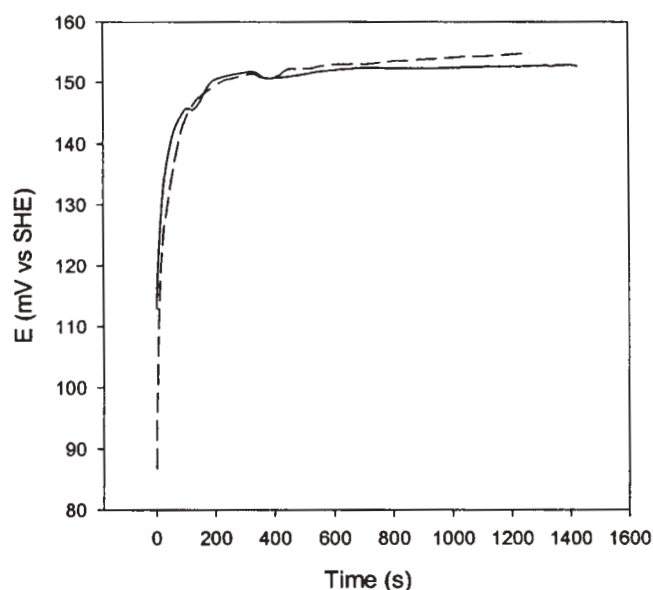


Figure 6. Mixed potential (for two runs) for Pd-Bi-Te in an oxygenated solution containing 10^{-3} M KEX, at a pH value of 9.2

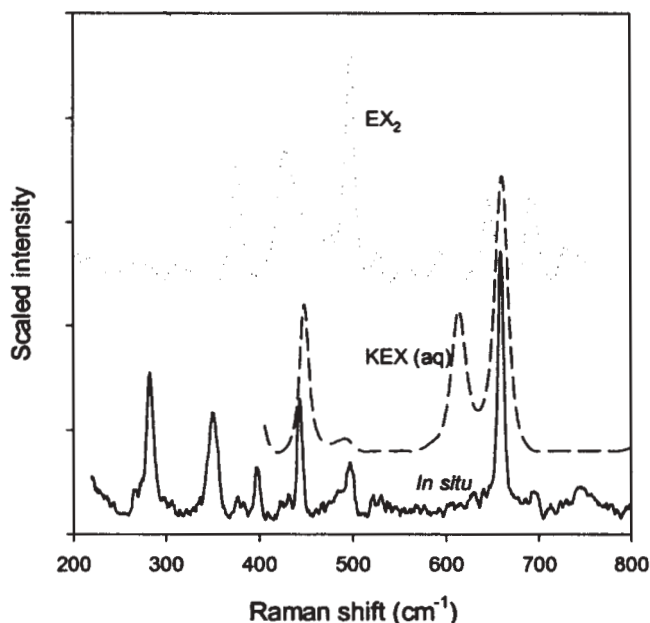


Figure 7. Raman spectra of freshly synthesized potassium ethyl xanthate, diethyl dioxanthogen and the *in situ* spectra of the surface of the Pd-Bi-Te in a 0.05 M Na₂B₄O₇ solution at 25°C containing 10⁻³ M KEX polarized at a potential of 0.3 V. Laser power rating of 100 mW and recording time of 120 seconds

electrochemically controlled contact angle measurements⁷. The results showed finite angles (maximum angle: 63 degrees) in the presence of xanthate. These results clearly indicate that the surface of the particle becomes hydrophobic and therefore the mineral should be recoverable if sufficient bubble attachment is achieved. The particle-bubble attachment is influenced by the particle size since the particle size influences the probability of attachment and the induction time (attachment after the collision)¹⁵. As a result, smaller particles show slower flotation rates compared to larger particles. Penberthy *et al.*⁴ found that small liberated platinum-group minerals did float, albeit at slower rates. Therefore, particle size could contribute to the poor flotation response in this case because the liberated PGM grains are usually less than 10 µm in size.

Conclusion

The adsorption of ethyl xanthate on Pd-Bi-Te has been studied using voltammetry, impedance measurements and Raman spectroscopy. Pd-Bi-Te shows very strong anodic activity when polarized at potentials > 0.2 V (SHE) in the presence of potassium ethyl xanthate. Prolonged exposure (20 minutes) of Pd-Bi-Te at this potential resulted in lower capacitance values. The lowering of the capacity value is a result of the formation of a continuous surface layer. Cathodic and anodic polarization curves predicted a mixed potential higher than that of the equilibrium xanthate-dioxanthogen couple. As a result, the increased anodic activity and the formation of the layer are likely to reflect the formation of diethyl dioxanthogen on the surface. This species was in fact identified on the surface of the Pd-Bi-Te by employing electrochemically controlled *in situ* Raman spectroscopy. The hydrophobic nature of the surface layer will render the minerals recoverable if adequate bubble

attachment is achieved.

References

1. MERKLE, R.K.W. and MCKENZIE, A.D. The Mining and Beneficiation of South African PGE ores — An Overview, *The Geology, Geochemistry, Mineralogy and Mineral Beneficiation of Platinum-Group Elements*, L.J. Cabri (ed.) Canadian Institute of Mining, Metallurgy and Petroleum, Special vol. 54, 2002, pp. 793–810.
2. PRENDERGAST, M.D. Platinum-group minerals and hydrosilicate ‘alteration’ in the Wedza-Mimosa platinum deposit, Greta Dyke, Zimbabwe—genetic and metallurgical implications. *Transaction of the Institution of Mining and Metallurgy (Section B: Earth Sciences)*, vol. 99, 1990, pp. B91–B105.
3. VAN WOUW, K. Internal report: Mineralogical investigation of the platinum-group minerals in flotation products from Mimosa Platinum Mine, 2003.
4. PENBERTHY, C.J., OOSTHUYZEN, E.J., and MERKLE, R.K.W. The recovery of platinum-group elements from the UG-2 chromitite, Bushveld Complex – a mineralogical perspective, *Mineralogy and Petrology*, vol. 68, 2000, pp. 213–222.
5. WILSON, M.G.C. *The mineral resources of South Africa*, Council of Geoscience, Sixth edition, 1998.
6. CIABERTA, S. Fast-tracked opencast projects yield more than expected, *Creamer Media’s Mining Weekly*, 5–11, December, vol. 9, 2003, pp. 21–22.
7. VERMAAK, M.K.G., PISTORIUS, P.C., and VENTER, J.A. Electrochemical and Raman spectroscopic studies of the interaction of ethyl xanthate with Pd-Bi-Te and PtAs₂, Submitted, 2004.
8. OBERTHÜR, T. Platinum-Group Element Mineralization of the Great Dyke, Zimbabwe, *The Geology, Geochemistry, Mineralogy and Mineral Beneficiation of Platinum-Group Elements*, L.J. Cabri (ed.). Canadian Institute of Mining, Metallurgy and Petroleum, Special vol. 54, 2002, pp. 793–810.
9. WOODS, R. and GARDNER, J.R. An Electrochemical investigation of Contact Angle and of Flotation in the presence of Alkylxanthates in Platinum and Gold Surfaces, *Australian Journal of Chemistry*, vol. 27, 1974, pp. 2139–2148.
10. ZOLFAGHARI, A., CONWAY, B.E., and JERKIEWICZ, G. Elucidation of the effects of competitive adsorption of Cl⁻ and Br⁻ ions on the initial stages of Pt surface oxidation by means of electrochemical nongravimetry. *Electrochimica Acta*, vol. 47, 2002, pp. 1173–1187.
11. DAMJANOVIC, A., YEH, L-S. R., and WOLF, J.F. Formation of thin oxides at platinum anodes in

alkaline solutions. III pH dependence. *Journal of the Electrochemical Society*, vol. 129, 1982, pp. 55–61.

12. WOODS, R. The oxidation of ethyl xanthate on platinum, gold, copper and galena electrodes. Relation to the mechanism of mineral flotation. *The Journal of Physical Chemistry*, vol. 75, 1971, pp. 354–362.
13. ELVY, S.B., WILLIAMS, P.A., and BUCKLEY, A.N. XPS evidence for the incongruent surface oxidation of minerals in the Pd-Te-Bi system. *Surface*

and interface analysis, vol. 24, 1996, pp. 641–646.

14. WOODS, R., HOPE, G.A., and BROWN, G.H. Spectroelectrochemical investigations of the interaction of ethyl xanthate with copper, silver and gold: II. SERS of xanthate absorbed on silver and copper surfaces, *Colloids and surfaces A: Physicochemical and Engineering Aspects*, vol. 137, 1998, pp. 329–337.
15. FENG, D. and ALDRICH, C. Effect of particle size