

## **4. Experimental procedure**

This chapter gives brief descriptions of the experimental methods which were used in the present study.

### **4.1. X-ray diffraction and Scanning Electron Microscopy**

A Siemens D-501 X-ray diffraction (XRD) instrument was used to identify the crystalline phases in the synthetically prepared minerals (Pd-Bi-Te and PtAs<sub>2</sub>) and the natural minerals (pyrrhotite, chalcopyrite and pyrite). Each sample was milled for 10 minutes in a swing mill and subsequently pressed into Siemens sample holders (1 – 2 grams of sample) using a glass slide. The specifications on the XRD instrument and settings are shown in Table 7.

**Table 7:** Instrument and data collection parameters.

Instrument	Siemens D-501
Radiation	Cu $K\alpha$
Temperature	25°C
Specimen	Flat-plate rotating (30 rpm)
Power setting	40 kV, 40 mA
Soller slits	2° (diffracted beam side)
Divergence slits	1°
Receiving slits	0.05°
Monochromator	Secondary, graphite
Detector	Scintillation counter
Range of $2\theta$	5 – 80° $2\theta$
Step width	0.04 ° $2\theta$
Time per step	1.5s

The microstructures of the synthetic and natural mineral samples and samples from flotation concentrates were investigated by employing a scanning electron microscope

(SEM) (JSM-6300). All the mineral and flotation concentrate samples were polished using a 0.05 $\mu$ m Micropolish Alumina-B suspension and chemically analysed by EDX (energy dispersive X-ray analysis). The non-metallic samples were mounted in epoxy resin (impregnated under vacuum) and gold coated by sputtering. The different phases were identified by examining the sample with back-scattered electron imaging using a Centaurus back-scatter detector. The analyses were performed using a Voyager analysis system using a Si (Li) (lithium-drifted silicon) detector with a Norvar window analysing X-rays produced at 25kV acceleration voltage with a working distance of 10mm, using 100 seconds of analysis time.

#### **4.2. Synthesis of selected platinum group minerals**

In any fundamental study of a surface the starting material must be clearly defined and as free from impurities as possible. The draw-back of using synthetic materials is the uncertainty about the correspondence between the synthetic crystal and the natural mineral. This is a concern for especially the PGMs considering the host of impurities found in PGMs such as Fe, Ni and Cu. However, the very small size (less than 10  $\mu$ m 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 (electrochemical investigation, *in situ* Raman spectroscopy and electrochemically-controlled contact angle measurements) on synthetic minerals. Contact angle measurements (using Equilibrium Capillary Pressure techniques) could be possible on natural grains, but too many hand-picked grains would be required to form a packed bed. The main advantage of synthesizing these minerals in bulk is the possibility of performing microflotation tests to evaluate the performance of different reagent suites. The minimum particle size was fixed by the constraints of contact angle measurements, which required mineral particles with exposed diameters of 6-10  $\mu$ m. (Smaller diameters would have been sufficient for electrochemical and Raman investigations, but the same working electrodes – large enough for contact angle measurements – were used in all three types of tests.)

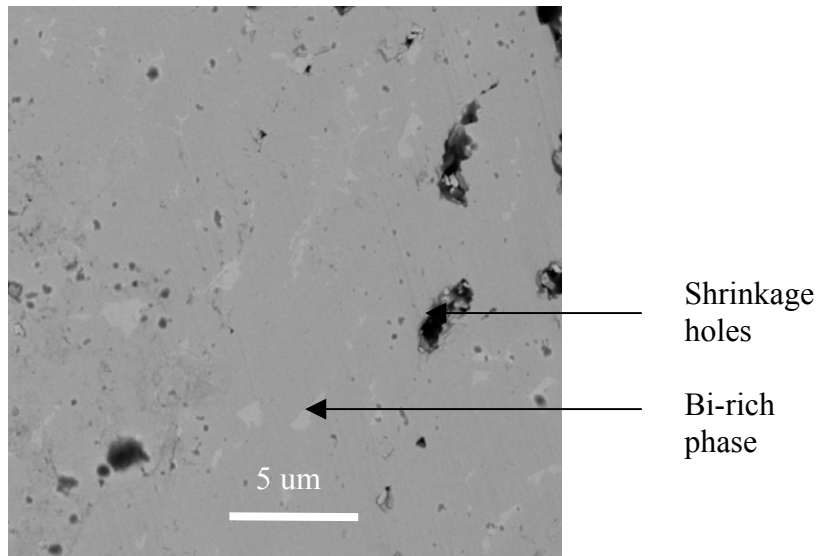
Sperrylite ( $\text{PtAs}_2$ ), and Pd-bearing bismuthotelluride (michenerite) were synthetically prepared since – as discussed in Chapter 2 – these are the most abundant PGMs in the orebody which is the subject of the current study.

Each material was synthesised by reacting stoichiometric quantities (accurately weighed to 3 decimal places) of its constituent elements (total about 1g) in an evacuated silica tube. Palladium wire (diameter 0.5mm, 99.99+%), platinum wire (diameter 1.0 mm, 99.99+%), tellurium lump (99.999+%), bismuth rod (99.997%) and arsenic lump (99.9999%) were used. All these constituents were supplied by Goodfellow.

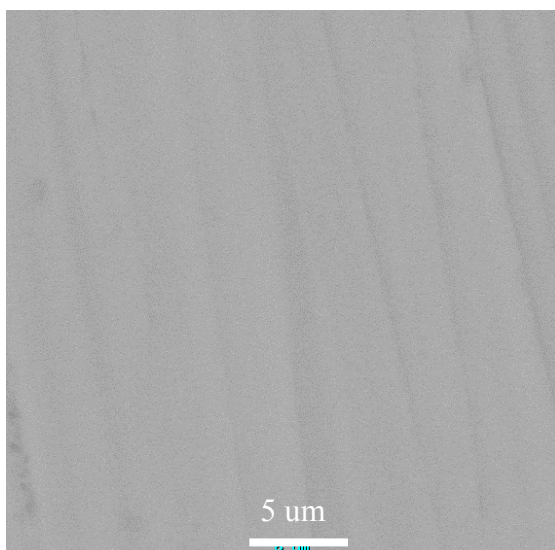
The michinerite (equimolar mixtures of Pd, Bi and Te) was heated to a sufficiently high temperature ( $700^\circ\text{C}$ ) to melt the Bi and Te and to dissolve the Pd before the final heat treatment in the muffle furnace was applied. In the first step, the Pd-Bi-Te was held at  $700^\circ\text{C}$  for 20 hours followed by slow cooling over 6 hours. Despite using the same procedure as been described by Evans *et al.* (1996), homogeneity of the synthetically prepared sample was not achieved. Back-scattered electron images showed the presence of three phases. Energy dispersive X-ray analysis (EDS) performed on the phases indicated the presence of a Bi-rich phase, Pd-rich phase and that of a phase with a composition approximating that of the target phase (that is, equimolar Pd-Bi-Te). The same heat treatment was repeated on the same sample in an attempt to produce a single solid solution phase. The microstructure that was obtained resembles that of the previous back-scattered electron image (three phases were present). It was concluded that a peritectic transformation reaction had to take place to consume the Bi-rich (liquid) and Pd-rich (solid) phases. The rate of this reaction will be greatly enhanced if a very fine microstructure is obtained before the onset of the final heat treatment stage at  $480^\circ\text{C}$ . This was accomplished by heating the sample to the required melting temperature followed by cooling in still air for a few seconds before being subjected to heat treatment at  $480^\circ\text{C}$ .

It can clearly be seen from the back-scattered electron image shown in Figure 16 that the microstructure after the  $480^\circ\text{C}$  heat treatment is much more homogeneous with only two phases clearly visible. EDS analysis performed on the light phase indicated this phase to be rich in bismuth. Following the positive outcome of this heat treatment the sample was treated for another 100 hours at  $480^\circ\text{C}$  to ensure phase integrity and

homogeneity. A fully homogeneous microstructure was only obtained by employing the heat treatment at 480°C for up to 60 days. The electron back-scattered image and XRD spectra of the microstructure are shown in Figure 17 and in Appendices 5 and 6. To summarise, samples used for the microflotation tests were treated for 60 days at 480°C, while the samples for the rest of the test work were treated for 100 hours at the same temperature.

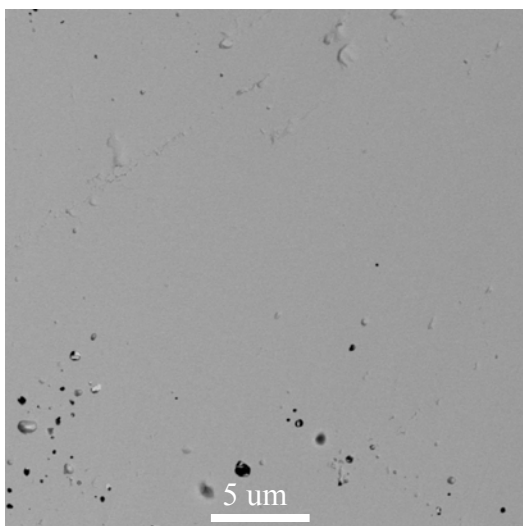


**Figure 16:** Back-scattered electron micrograph showing the two most prominent phases of the synthetically prepared michenerite (Pd-Bi-Te) heated to 700°C, followed by cooling in still air and heat treatment at 480°C for 100 hours. Accelerating voltage 25kV.



**Figure 17:** Back-scattered electron micrograph of the synthetically prepared michenerite (Pd-Bi-Te) heat-treated at 480°C for 60 days. Accelerating voltage 25kV.

Sperrylite ( $\text{PtAs}_2$ ) was prepared by heating stoichiometric amounts of the constituents to 800°C in a sealed silica ampoule (1 gram total sample mass). The ampoule could not be heated to a high enough temperature to melt the contents because of concern around elevated partial pressure of arsenic at high temperatures. (The melting point of pure arsenic is 817°C [at 28 atm] and the sublimation point is 613°C [Weast, 1982]). The constituents were held for 6 hours at 800°C before being slowly cooled to room temperature over a period of 5 hours. The synthetic sperrylite was subsequently investigated by electron-back scattering and XRD analysis to verify the integrity and identity of the phase sought. A back-scattered electron image and XRD pattern of the synthetic sperrylite are shown in Figure 18 and Appendix 7, respectively. These examinations provided no evidence of minor concentrations of other phases.



**Figure 18:** Back-scattered electron micrograph showing the single solution phase of the synthetically prepared sperrylite. Accelerating voltage 25kV.

### **4.3. Electrochemical measurements**

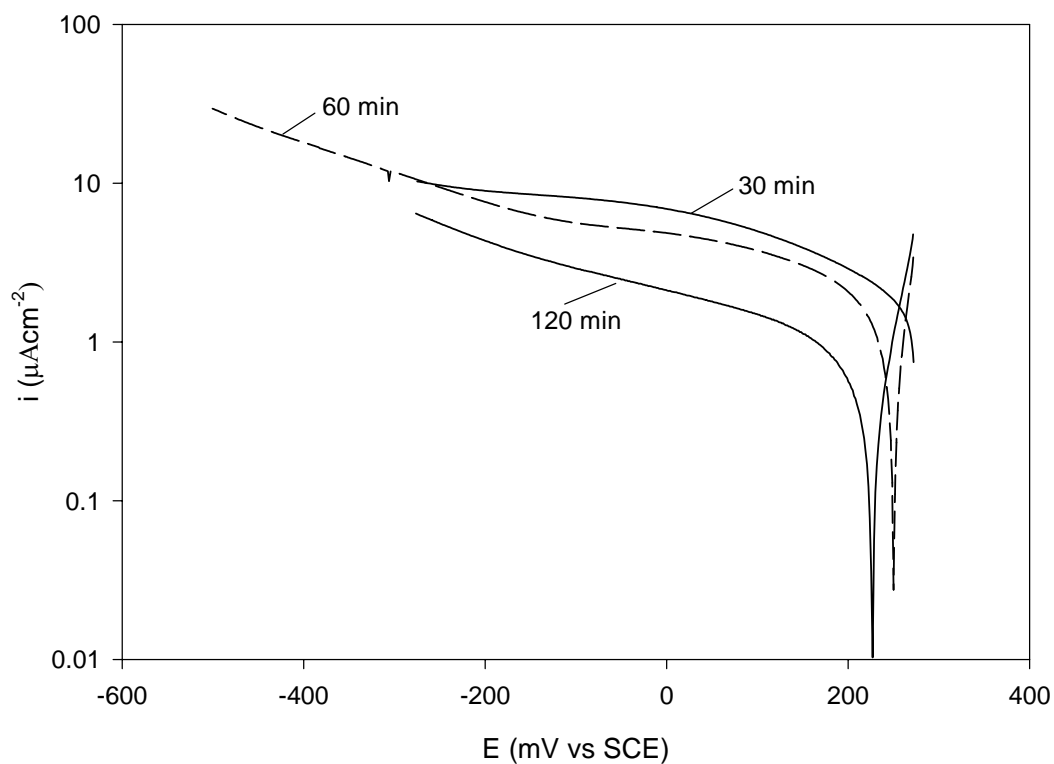
A conventional electrochemical cell with a three-electrode system was used. Potentials were measured against a Ag/AgCl reference electrode filled with saturated KCl, which has a potential of +0.20V against the standard hydrogen electrode. The PGM crystals were mounted in resin and electrical contact was achieved between the contactor shaft and the mineral by employing a spring. The surface area of the Pd-Bi-Te and the PtAs<sub>2</sub> sample was 0.12 cm<sup>2</sup> and 0.14 cm<sup>2</sup>, respectively. Two platinum wire electrodes (10 cm in length) were placed in glass tubes closed with porous glass discs at their ends to serve as counter electrodes. The platinum counter electrodes were placed at equal distances (3 centimetres) from the working electrode. The voltammograms were constructed with a Schlumberger 1287 potentiostat and the potentiostat was interfaced with a Schlumberger 1260 frequency response analyzer for the impedance measurements. All experiments were conducted at 25°C (± 1°C). Sodium borate at a concentration of 0.05M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> was used to buffer the solution at a pH value of 9.3.

A large ohmic resistance between the working and reference electrode is undesirable because it masks the effective overpotential applied to the system. As a result the *IR* effects need to be evaluated to determine whether they affect the polarisation

measurements. High-frequency impedance spectroscopy (see Chapter 5 for more detail) was used to calculate the solution resistance whereas low-frequency impedance measurements resulted in the sum of the solution and polarisation resistances. The solution resistance was subtracted from the impedance value obtained at the low frequency measurements yielding the polarisation resistance of the system. A typical solution resistance of  $200\Omega\cdot\text{cm}^2$  was measured for a Pd-Bi-Te electrode polarised at 0.3V (SHE) in a 0.05 M  $\text{Na}_2\text{B}_4\text{O}_7$  solution containing  $1 \times 10^{-3}$  M potassium ethyl xanthate (see figure 25); the relatively low value of the solution resistance should not affect the polarisation measurements significantly since this value is much lower than the polarisation resistance ( $> 10^4 \Omega\cdot\text{cm}^2$ ).

Distilled water with a final resistivity of  $18\text{M}\Omega\cdot\text{cm}$  was used to prepare solutions. Prior to measurements, the solution was de-aerated for 2 hours with argon gas (99.999%), from which oxygen was removed by passing the gas over zirconia turnings at  $600^\circ\text{C}$ . The solution was replaced between experimental runs to avoid contamination. Purified potassium ethyl xanthate (KEX) was used in all the experiments. The xanthate was purified on a regular basis by dissolving in acetone, filtering the solids and subsequent evaporation of the acetone in a vacuum (De Wet *et al.*, 1996). The xanthate solutions were prepared minutes prior to the commencement of the experimental run to avoid decomposition. The PGM working electrode was freshly prepared before each experiment by wet grinding to 2400 grit silicon carbide paper followed by wet polishing using a  $0.05\mu\text{m}$  Micropolish Alumina-B suspension. Distilled water with a final resistivity of  $18\text{M}\Omega\cdot\text{cm}$  was used to make up the polishing suspension. This polishing treatment gave reproducible results. After polishing the samples were thoroughly washed with distilled water and immediately transferred to the electrochemical cell for measurements.

Figure 19 shows the reduction halfcycles on a Pt-electrode after different gas purging times, when using de-aerated argon gas for oxygen removal. Clearly a longer de-aeration period results in lower oxygen reduction currents, which is the desired effect when performing anodic polarisation measurements. This effect of the de-aeration period on the anodic polarisation measurement was confirmed by measurements on Pd-Bi-Te for the deaeration periods shown in figure 19.



**Figure 19:** Reduction of oxygen on platinum for different de-aeration periods in a 0.05 M  $\text{Na}_2\text{B}_4\text{O}_7$  solution at 25°C. Potential sweep carried out at 1mV/s.

The anodic polarization curve for the 120-minute de-aeration period showed the most detail (the least interference from cathodic reactions), and hence all solutions were de-aerated for 2 hours before electrochemical measurements.



## **4.4. Raman spectroscopy**

### **4.4.1. Introduction**

In 1928, Professor C.V. Raman discovered the inelastic scattering of light by which a molecule scatters a single photon which loses energy in the process. The difference between the higher energy state produced by the incident beam and the photon of lower energy released corresponds to the vibrational energy of the molecule of interest (Woods *et al.*, 2000). The vibrational energy is a unique characteristic of the species of interest.

The quantised vibrational changes that are associated with the scattering of the light are similar to those of the IR absorption spectrum, but there are enough differences between the two techniques to make the techniques complementary. The Raman microprobe is capable of achieving a spatial resolution 10 times better than that of IR microprobes, because the spatial resolution is proportional to the wavelength of the incident beam. The spatial resolution is typical of the order of a 1 $\mu$ m (Woods *et al.*, 2000). In contrast to the IR microprobe samples for the Raman microprobe do not have to be dry. In addition to this Raman spectroscopy has the advantage that the incident and scattered beams can have wavelengths in the region not strongly absorbed by water molecules (Woods *et al.*, 2000). This makes the technique ideal to perform *in situ* investigations in an aqueous medium using glass or – preferably - silica windows.

A major limitation of the Raman technique is that it has a lower sensitivity than most systems which stems from the fact that only one photon out of 10<sup>8</sup> photons from the incident flux will undergo scattering (Woods *et al.*, 2000). However, the Raman technique can provide valuable information on organic and inorganic species on the surface of many minerals, mineral identity, and species in aqueous solution.

Surface enhancement Raman scattering spectroscopy (SERS) involves the enhancement of the scattering intensity of species, which are adsorbed onto or are close to a roughened surface. The intensity is enhanced by a factor of some 10<sup>4</sup> to 10<sup>5</sup>.

Because of this extremely high surface sensitivity monolayers and sub-monolayers can be investigated making it an indispensable tool for the studying of collector interactions with surfaces. Especially the potential dependency of the collector adsorption on the metal of interest is of great importance to fundamental research. Unfortunately only three noble metals (Au, Ag and Cu) provide large enhancement. However roughening techniques performed on metals (Pt, Pd, Cr and Fe) can generate SERS on these metals with an enhancement factor between 1 and 4 orders in magnitude (Zhong-Qun *et al.*, 2002). The roughening technique involves oxidation-reduction cycles (by variation of the potential) in a chloride or sulphate medium.

#### **4.4.2. Experimental**

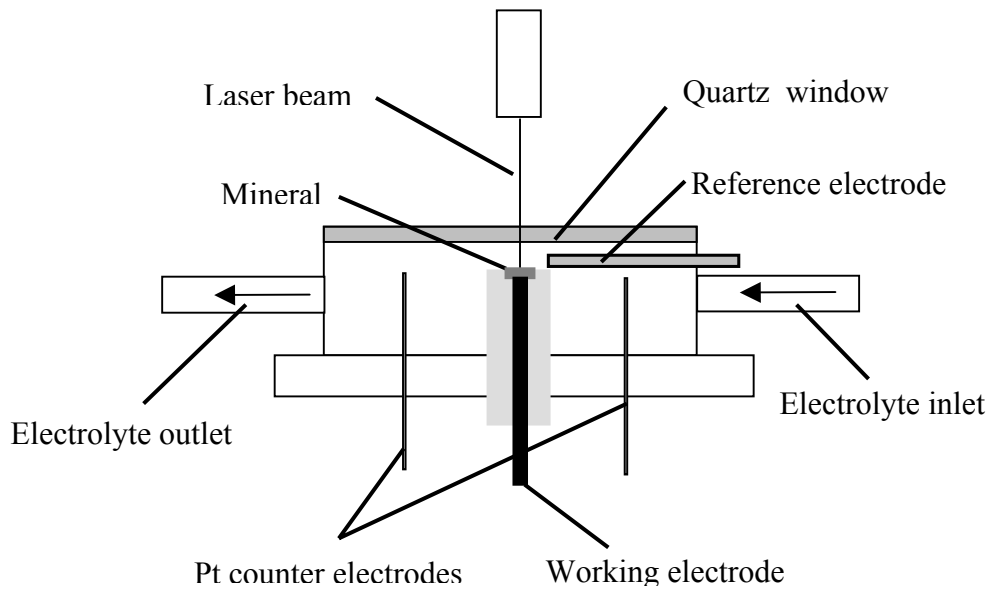
The Raman measurements were taken with an XY Raman spectrometer from Dilor, using the  $\lambda = 514.5$  nm laser line of a Coherent Innova 90 Ar<sup>+</sup>-laser as exciting line. The spectra were recorded in a backscattering configuration with a long working distance 50x objective of an Olympus microscope attached to the instrument. The instrument is equipped with a nitrogen cooled CCD detector and the spectral resolution was at least  $2\text{ cm}^{-1}$  for all the measurements. A low laser power of 50-100 mW was used for all measurements to avoid decomposition of species on the sample surface.

As for electrochemical measurements, sodium borate at a concentration of 0.05 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> was used to buffer the solution at pH value of 9.3. The solution was de-aerated for 2 hours with Argon gas (99.999%), from which traces of oxygen were removed by passing the gas over zirconia turnings heated at 600°C. The PGM working electrode was freshly prepared between experimental runs by wet abrasion using a 0.05  $\mu\text{m}$  Micropolish Alumina-B suspension. The electrode was subsequently washed by double distilled water and quickly transferred to the electrochemical cell for measurements. The system was flushed thoroughly with the de-aerated argon to prevent oxidation of the minerals once the mineral was positioned in the electrochemical cell. Once flushed the system was sealed (using rubber plugs) and kept at a positive pressure to avoid the ingress of air.

All experiments were conducted at 25°C ( $\pm 1^\circ\text{C}$ ) by immersing the electrolyte reservoir (700 ml in volume) in a water bath. The liquid phase was pumped at a constant rate of 100 ml/min over the working electrode by employing a peristaltic pump. The electrochemical cell (8cm long and wide and 2cm deep) consisted of a quartz window (2mm thick) at the top, two platinum counter electrodes, and the Luggin tube. The platinum wire counter electrodes (1.5 cm long and 0.5mm in diameter) were placed at equal distances (1cm) from the working electrode. The working electrode was placed close to the quartz window (approximate distance of 3mm) to facilitate easier focusing. The surface potential was controlled using a Schlumberger 1287 potentiostat while measuring the current as a function of time. The surface of the mineral was reduced at  $-0.4\text{V}$  (SHE) for about 5 minutes before the commencement of the experiments

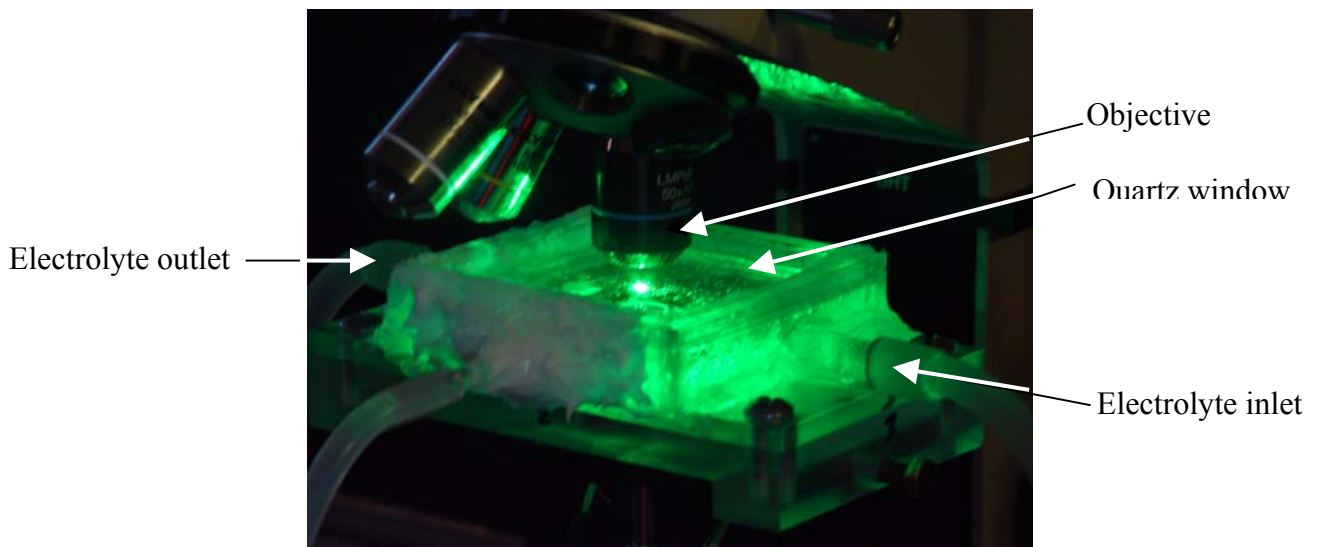
The laser beam was focused on the sample by means of an optical microscope fitted with a video camera. The continuous radiation of a laser focused for extended periods on one spot can lead to the decomposition of surfactants. The decomposition of the surfactants is very sensitive to the surface properties of the mineral: both pure tellurium and pure bismuth showed interaction with the laser in the presence of xanthate even at low radiation powers, but the interaction of the laser with the surfactants on the Pd-Bi-Te was not nearly as evident. Because of the possibility of laser-induced surface changes each Raman spectrum (recording time of about 120 seconds) was taken at a site away from the previous site (but remaining in the same general area) to prevent the gradual decomposition of the surfactants by continuous radiation.

The electrochemical cell employed for Raman spectroscopy is shown in Figure 20.



**Figure 20:** Schematic of the *in situ* electrochemical cell used for Raman spectroscopy.

Figure 21 shows the laser focused on the mineral placed in the *in situ* electrochemical cell.



**Figure 21.** Optical image of the laser focused on mineral while the Raman spectrum is recorded.

#### **4.5. Contact angle measurements**

A modified electrochemical cell with two parallel plate windows was used to perform contact angle measurements under potentiostatic control. The same polishing procedure was used as described earlier. The electrochemically controlled contact angle measurements were performed under the same conditions as mentioned in the section on electrochemical measurements. The electrochemical cell was placed on the optical bench of the Ramé-Hart contact angle goniometer (Model: 100-00-230) and the captive bubble arrangement (The nitrogen bubble was introduced to the downward facing mineral surface in the electrolyte).

Woods *et al.* (1977) showed that residual polishing agents and any form of organic contamination have a serious effect on the contact angle measurements (for example: washing of a polished gold electrode with ethanol and distilled water produced a contact angle of 70° instead of the expected 0°). As a result care had to be taken during this investigation to avoid any form of contamination when performing contact angle measurements. Organic contamination of the distilled water was minimised by using the Simplicity<sup>TM</sup> water system of Millipore. The water system employs purification media and an UV lamp to produce distilled water with extremely low levels of organic contamination (< 15 ppb) and a final resistivity of 18MΩ.cm.

A glass capillary with a very small opening was used to place the small nitrogen bubbles (approximately 0.5mm in diameter) on the mineral surface. The contact angle measurement procedure involved stepping the potential to the required value for 5 minutes. The contact angle was measured directly after polarization was terminated, measuring contact angles on both sides of the bubble. At least 5 bubbles were placed as quickly as possible on the surface from which contact angles were measured. The electrode was subsequently withdrawn from the cell and a new surface was generated, by employing the same polishing routine as mentioned above. The contact angle measurements were subsequently repeated at the same potential. A standard deviation and 95% confidence interval were determined from the measurements of the two runs. For cases where zero contact angles were found (indicating no attachment), a bubble protruding from the glass capillary was placed on the surface and then slowly

withdrawn from the surface, to test whether attachment was indeed absent. Lack of attachment characterizes a zero contact angle. Latex gloves were worn throughout the experiments to avoid the contamination of the mineral surfaces. After the completion of the contact angle measurements the glassware was thoroughly washed using purified distilled water and placed in drying oven to prevent organic contamination.

## **4.6. Microflotation measurements**

### **4.6.1. Natural and synthetic minerals**

The most abundant base metal sulphides found in Merensky ore are pyrrhotite (approximately 45%), pentlandite (approximately 32%), chalcopyrite (approximately 16%) and pyrite (approximately 2-4%) (Feng and Aldrich, 1999), and hence the flotation of some of these common sulphides was compared with that of the palladium bismuth telluride. Massive crystals of pentlandite (a typical fast-floating mineral) could not be sourced, but natural pyrrhotite and pyrite samples were obtained from the Wards Natural Science Company, and natural chalcopyrite was obtained from the hand-picked mineral collection of the Department of Geology, University of Pretoria. X-ray diffraction (XRD) analysis confirmed the phase composition of the natural samples and identified the monoclinic crystal structure of pyrrhotite (see Appendices 8-10 for XRD spectra).

Pd-bearing bismutho-telluride (michenerite, representative of the most abundant PGM found in the flotation feed) was prepared synthetically. The synthesis procedure is given in paragraph 4.2. The Pd-Bi-Te mineral samples were stored under purified argon once removed from the evacuated, sealed quartz tubes.

### **4.6.2. Flotation**

A microflotation cell (capacity of 250 ml) as described before (Bradshaw and O'Connor, 1996) was used to determine the flotation response of the selected minerals. The microflotation cell consists of a cylindrical tube with a lower conical (tapered) section with air introduced through a needle valve located at the base of the cell. During the study flotation tests were carried out at a constant gas flow rate of 3.5

cm<sup>3</sup>/min. The pulp was kept in suspension and circulated by employing a peristaltic pump. A cone at the top of the flotation cell deflects the mineral-loaded bubbles whereupon the bubbles burst, resulting in the collection of the mineral in the concentrate launder.

Purified sodium isobutyl xanthate (SIBX) was obtained from SENMIN. Other chemicals were of analytical grade quality. It was decided to use sodium isobutyl xanthate as collector instead of potassium ethyl xanthate since the former is used in industry and the aim of the microflotation experiments was to keep as many variables as close as possible to plant conditions in order to establish the true flotation response of the Pd-Bi-Te minerals. The potassium ethyl xanthate (at a concentration of 10<sup>-3</sup> M) is most frequently used in fundamental studies involving functional groups and surfaces, hence the selection for the fundamental work of this thesis (see sections 4.3, 4.4 and 4.5).

All mineral samples (initial mass of around 3.5 grams) were freshly ground in an agate mortar prior to each experiment. The crushed products were screened to produce a particle size distribution of +38 µm-106 µm for microflotation tests. Microflotation experiments were carried out on a 2 gram single mineral sample added to 250 cm<sup>3</sup> of solution. Sodium carbonate (0.1 M) and hydrochloric acid (0.1 M) were used for pH adjustments prior to the flotation tests. Microflotation tests were performed in synthetic water containing the major ions found in plant process water ( Mg<sup>2+</sup> 80 ppm, Ca<sup>2+</sup> 80 ppm, Na<sup>+</sup> 135 ppm, Cl<sup>-</sup> 270 ppm, SO<sub>4</sub><sup>2-</sup> 250 ppm, NO<sub>3</sub><sup>-</sup> 135 ppm, NO<sub>2</sub><sup>-</sup> 40 ppm and CO<sub>3</sub><sup>2-</sup> 40 ppm). The mineral samples were conditioned for 1 minute in the synthetic water followed by SIBX addition (giving a 5×10<sup>-5</sup> M concentration) and conditioning for a further 3 minutes. During subsequent batch flotation the concentrates were collected at total times of 3, 6, 10 and 20 minutes. The concentrates and non-floated fraction were allowed to air-dry and were weighed. All flotation tests, except on the Pd-Bi-Te, were performed in triplicate to ascertain the repeatability of the microflotation test procedure.