



Centre for Minerals Research
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An investigation into the floatability of platinum group arsenides and tellurides under varying collector and solution chemistries

By
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A thesis submitted to the University of Cape Town as fulfilment of the requirement for the degree of **Doctor of Philosophy in Chemical Engineering**



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Date: 03 June 2024

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List of Publications and Conferences

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Synopsis

The Platreef is a Ni-Cu-PGE deposit located in the northern limb of the Bushveld Igneous Complex in South Africa. This ore deposit is host to some of the world's largest reserves of platinum group elements (PGE). In particular, PGE tellurides and arsenides constitute about 30% and 21% of the platinum group mineral (PGM) assemblage in the Platreef, respectively, thus making these minerals the most abundant and economically important PGMs in the Platreef. Therefore, the beneficiation of the Platreef ore bodies is projected to play a key role in the PGM industry in the foreseeable future, especially with the growing demand for platinum driven by the transition to green energy.

It has been found that there are major losses of PGMs during the processing of Platreef ore bodies, with most of these losses being attributed to sperrylite (PtAs_2). The losses of sperrylite are due to the poor recovery of this mineral by flotation where it has been shown to be poorly floatable with xanthate collectors. The main objective of this study was to investigate the floatability of PGE arsenides and tellurides, viz. sperrylite, palladoarsenide (Pd_2As), moncheite (PtTe_2) and merenskyite (PdTe_2), with the primary focus being to understand and improve the floatability of sperrylite by exploiting flotation chemistry. The other minerals (palladoarsenide, moncheite and merenskyite) were chosen for their common elements and used as comparative minerals by which to highlight differences in sperrylite behaviour. This study focused on the role of the collector, solution, and mineral chemistries in relation to how these affect the floatability of sperrylite and the other minerals. To achieve the objectives of this study, this research was organised into three phases, with each phase focusing on the role of the collector, solution, and mineral chemistry, respectively.

Phase One focused on the use of collectors with greater electron-donating properties than the traditionally used xanthate collectors under the assumption that these collectors will bond more readily with the sperrylite surface and induce floatability of this poorly floating mineral. The collectors investigated included potassium n-butyl trithiocarbonate (PNBTTC), propyl thiourea (PTU), potassium n-butyl xanthate (PNBX) and potassium amyl xanthate (PAX). In order to better understand the extent of interaction of the collectors with the sperrylite surface and the resultant flotation performance, adsorption studies using UV-vis spectroscopy were performed and compared with flotation recoveries. This was further supported by determining the collector-mineral energy of interaction, as measured using calorimetry.

The results showed that the PNBTTTC and TU collectors had a higher energy of interaction with sperrylite compared to the PAX and PNBX collectors. However, none of these collectors significantly improved the recovery of this mineral at pH 9 and a collector dosage equivalent to 1 pseudo-monolayer (ML) surface coverage. These collectors yielded similar and low sperrylite recoveries of 15.5% (PNBTTC), 15.4% (PAX), 16.1% (PNBX) and 18.1% (PTU). Increasing the dosage of a strong xanthate collector, PAX, significantly improved the recovery of sperrylite. However, the recovery of the mineral approached a maximum of only 45% at a very high collector dosage of 20 ML PAX. This illustrates and confirms the difficulty of obtaining

good flotation recoveries of sperrylite at the conditions observed in typical PGM concentrators, such as pH 9.

Phase Two of this study focused on the effect of pH and electrochemical potential (Eh) on the floatability of sperrylite. This was investigated on the basis of emerging evidence suggesting that the adsorption of xanthate collectors on sperrylite, hence its floatability, could be improved at lower pH and/or higher Eh conditions. Rest potential measurements were used to determine the electrochemical interactions between the collector PAX and sperrylite at different Eh-pH conditions. The chemical speciation resulting from these interactions on the sperrylite surface was characterised using surface characterisation techniques including zeta potential measurements and spectroscopic studies. This was used to understand the flotation performance of sperrylite, as determined using microflotation studies, under varying Eh-pH conditions.

It was shown that sperrylite floats better at acidic conditions, where its recovery increased from 22% at pH 9 to 61% at pH 3 using 5 ML of PAX collector. It was shown that the hydrophobicity of sperrylite is governed by both the amount of collector that is adsorbed, and the amount of the adsorbed collector that is adsorbed as dixanthogen. In addition to dixanthogen, PAX could also be co-adsorbed as the metal xanthate on the mineral. However, it is the specific presence of dixanthogen that ultimately strongly promotes the hydrophobicity of the mineral. Both the formation of dixanthogen and the amount of collector adsorbed on sperrylite were improved by decreasing pH which also corresponded to an increase in Eh. However, it was found that it was not conducive to chemically increase Eh using NaClO, for example, since this resulted in a reaction between NaClO and PAX, and/or caused an excessive oxidation of sperrylite which in fact hindered the ability of the collector to impart hydrophobicity.

Finally, **Phase Three** of this study focused on comparing the floatabilities of PGE arsenides and tellurides in order to gain further insights into why sperrylite has such a poor floatability relative to other similar PGE minerals including Pd₂As, PtTe₂ and PdTe₂. The floatability of the minerals was investigated using microflotation and batch flotation studies. Supplementary test work conducted to better understand the floatability of these minerals included rest potential measurements, zeta potential measurements and spectroscopic studies.

PtAs₂ was found to exhibit a higher degree of natural hydrophilicity compared to the other PGE arsenides and tellurides investigated. The differences in the natural floatability of these minerals were attributed to the crystal structure effects and/or the ability of the minerals to acquire self-induced hydrophobicity. In the presence of PAX at pH 9, the microflotation recoveries of the minerals followed the order Pd₂As (95%) > PtTe₂ (88%) > PdTe₂ (81%) > PtAs₂ (22%). The PGE tellurides generally had a better interaction with the xanthate collector which contributed to their better floatability. On the other hand, a contributing factor to the poor floatability of sperrylite was found to be its higher affinity for OH⁻ adsorption compared to the other PGE minerals, which inhibited collector adsorption on this mineral. All the recoveries of the minerals were improved at lower pH, where the concentration of the inhibitory OH⁻ is

lower. The exception to this was Pd_2As whose recovery decreased from 95% at pH 9 to 85% at pH 3. Both the microflotation and batch flotation studies showed that operating at pH 3 improved the recovery of PtAs_2 to a greater extent compared to that of the other PGE minerals investigated.

Another major contributing factor to the poor floatability of PtAs_2 at pH 9 was proposed to be its weak electrochemical interaction with xanthates as a result of its electronic properties. It is postulated that the large band gap of sperrylite makes it a poor semi-conductor, unlike the other PGE minerals that have a smaller band gap and, therefore, have more of the properties of a semi-conductor material, allowing electron transfer between mineral and collector. This presents opportunities for further research in this area.

Ultimately, this study contributes to the understanding of the reasons for the poor floatability of sperrylite and possible remedies for improving the flotation recovery of this economically important mineral.

Table of Contents

Declaration	ii
Acknowledgements.....	iii
List of Publications and Conferences	iv
Synopsis.....	v
List of Figures	xii
List of Tables	xx
Nomenclature	xxii
CHAPTER 1: Introduction and Literature Review	1
1. Introduction and Literature Review.....	1
1.1. Background.....	1
1.2. Scope of Research	2
1.3. Mineralogy of the Platreef	3
1.4. Mineral processing of PGMs.....	4
1.4.1. Principles of froth flotation	6
1.5. Role of collectors	7
1.5.1. Collector adsorption mechanism of xanthate collectors.....	8
1.5.2. Collector chemistry	9
1.5.2.1. Effect of the functional group of the collector	9
1.5.2.2. Effect of length and structure of the alkyl chain of the collector	11
1.5.2.3. Effect of collector dosage	12
1.6. Role of solution.....	12
1.6.1. Effect of ionic strength	12
1.6.2. Effect of electrochemical potential	13
1.6.3. Effect of pH.....	14
1.6.3.1. Competitive effect between collector and hydroxy species	15
1.6.3.2. Effect of pH on potential at which the mineral and collector are oxidised	15
1.7. Role of mineral	17
1.7.1. Natural floatability of minerals.....	17
1.7.1.1. Crystal structure effect	17
1.7.1.2. Thermodynamics of adhesion of water	20
1.7.1.3. Self-induced hydrophobicity at specific pulp conditions	21
1.7.2. Effect of the electronic properties of the minerals	21
1.8. Summary and Gap Analysis	24
1.9. Hypotheses	26
CHAPTER 2: Research Objectives	27
2. Research Objectives	27
2.1. Research Objectives	27

2.2.	Key Questions.....	27
2.3.	Research Approach.....	28
2.3.1.	Phase One: Investigation of collectors on flotation of sperrylite	29
2.3.2.	Phase Two: Effect of pH-Eh on floatability of sperrylite	30
2.3.3.	Phase Three: Comparisons of floatability of PGE arsenides and tellurides	31
CHAPTER 3: Experimental Details		34
3.	Experimental Methods.....	34
3.1.	Mineral Synthesis	34
3.2.	Mineral Characterisation.....	35
3.2.1.	X-Ray diffraction	36
3.2.1.1.	Sperrylite.....	36
3.2.1.2.	Palladoarsenide.....	36
3.2.1.3.	Merenskyite	37
3.2.1.4.	Moncheite.....	38
3.2.2.	Scanning electron microscopy and energy-dispersive X-ray spectroscopy	38
3.2.2.1.	Sperrylite.....	39
3.2.2.2.	Palladoarsenide.....	40
3.2.2.3.	Moncheite.....	41
3.2.2.4.	Merenskyite	42
3.2.3.	BET analysis.....	43
3.3.	Ore preparation and information	43
3.4.	Reagents.....	45
3.4.1.	Collectors	45
3.4.2.	Frothers.....	48
3.4.3.	pH and Eh modifiers.....	48
3.4.4.	Synthetic Plant Water	49
3.5.	Microflotation.....	49
3.5.1.	Microflotation procedure	50
3.5.2.	Microflotation reproducibility tests.....	52
3.6.	Rest potential measurements	54
3.6.1.	Electrode manufacturing	55
3.6.2.	Rest potential experimental procedure.....	56
3.6.3.	Rest potential measurements reproducibility tests.....	57
3.7.	Isothermal Titration Calorimetry	58
3.7.1.	ITC experimental procedure	59
3.7.2.	Blank ITC experimental procedure.....	59
3.7.3.	ITC reproducibility tests	60
3.8.	Ultraviolet spectroscopy.....	62
3.8.1.	UV-vis spectroscopy experimental procedure	62
3.8.2.	Standard Absorbance vs Concentration curves	63
3.8.3.	UV-vis spectroscopy reproducibility tests.....	64
3.9.	Mineral surface characterisation	65
3.9.1.	Fourier Transform Infrared Spectroscopy.....	65
3.9.2.	X-Ray photoelectron spectroscopy.....	66
3.9.3.	Raman spectroscopy.....	66
3.9.4.	Zeta potential measurements.....	67
3.9.4.1.	Zeta potential measurements calibration.....	69
3.10.	Batch Flotation.....	70

3.10.1.	Milling	70
3.10.2.	Batch Flotation.....	72
3.10.3.	X-Ray fluorescence.....	76
3.10.4.	Inductively coupled plasma-mass spectrometry (ICP-MS).....	76
3.11.	Preliminary Experiments	77
3.11.1.	Collector screening	77
3.11.2.	Effect of NaClO addition on pH.....	78
CHAPTER 4: Investigation of the performance of various collectors on the flotation of sperrylite.....		79
4. Investigation of the performance of various collectors on the flotation of sperrylite . 79		
4.1.	Introduction.....	79
4.2.	Results.....	79
4.2.1.	Isothermal Titration Calorimetry (ITC) - Heats of adsorption measurements.....	79
4.2.2.	The extent of collector adsorption	80
4.2.3.	Microflotation	83
4.2.4.	Batch Flotation	86
4.3.	Discussion	89
4.3.1.	Effect of collector ligand type on the heat of adsorption	89
4.3.2.	Effect of alkyl chain length on the heat of adsorption	90
4.3.3.	Microflotation response of sperrylite with the different collectors.....	91
4.3.4.	Effect of collector dosage on the floatability of sperrylite	92
4.3.5.	Effect of ionic strength on the floatability of sperrylite	93
4.3.6.	Microflotation vs batch flotation of sperrylite	94
4.4.	Conclusions.....	95
CHAPTER 5: Effect of pH-Eh on the floatability of sperrylite		97
5. Effect of pH-Eh on the floatability of sperrylite.....		97
5.1.	Introduction.....	97
5.2.	Results.....	97
5.2.1.	Microflotation	97
5.2.2.	The extent of collector adsorption	101
5.2.3.	Rest potential measurements	105
5.2.4.	Surface Characterisation	107
5.2.4.1.	Fourier Transform Infrared Spectroscopy (FTIR)	107
5.2.4.2.	X-Ray photoelectron spectroscopy.....	110
5.2.4.3.	Zeta potential measurements.....	111
5.2.4.4.	Raman spectroscopy.....	112
5.3.	Discussion	120
5.3.1.	Effect of pH and Eh on the floatability of sperrylite	120
5.3.2.	The extent of collector adsorption	121
5.3.3.	Nature of collector adsorption.....	122
5.3.4.	Chemical control of redox potential.....	124
5.4.	Conclusions.....	126

CHAPTER 6: Comparisons of floatability of PGE arsenides and tellurides.....	128
6. Comparisons of the floatability of PGE arsenides and tellurides	128
6.1. Introduction.....	128
6.2. Results.....	128
6.2.1. Microflotation	128
6.2.2. Rest potential measurements of PGE arsenides and tellurides	133
6.2.3. The extent of collector adsorption	136
6.2.4. Surface characterization.....	136
6.2.4.1. Zeta potential measurements.....	136
6.2.4.2. Fourier Transform Infrared Spectroscopy.....	139
6.2.4.3. Raman spectroscopy.....	141
6.2.5. Batch Flotation.....	145
6.3. Discussion.....	150
6.3.1. Natural floatability of the PGE arsenides and tellurides	150
6.3.2. Collector-induced floatability of the PGE arsenides and tellurides	153
6.3.2.1. PGE arsenides	153
6.3.2.2. PGE Tellurides	154
6.3.3. Effect of the electronic properties of the minerals	155
6.3.4. Application of pH reduction in batch flotation.....	156
6.4. Conclusions.....	158
CHAPTER 7: General Conclusions	159
Recommendations for future work	162
CHAPTER 8: References	164
CHAPTER 9: Appendices.....	A
A. APPENDIX A: Collector surface coverage calculation	A
B. APPENDIX B: Heat of adsorption profiles	C
C. APPENDIX C: XPS results.....	D
D. APPENDIX D: Rest potential measurement profiles.....	O
E. APPENDIX E: Batch flotation	P

List of Figures

Figure 1.1: Scope of current research work.....	2
Figure 1.2: Generalised stratigraphy of the northern limb of the Bushveld Complex (McDonald et al., 2005)	4
Figure 1.3: Generic flowsheet of PGM processing showing the value chain and losses during each stage of the process (Gibson et al., 2023)	5
Figure 1.4: Typical MF2 circuit for processing Platreef ores (Engelbrecht, 2012)	5
Figure 1.5: Schematic representation of a froth flotation cell showing the principle of flotation (Wills & Finch, 2015)	6
Figure 1.6: Schematic representation of collector adsorption onto a mineral surface	7
Figure 1.7: Generic molecular structure of a xanthate, trithiocarbonate and thiourea collector, where E represents electronegativity.....	11
Figure 1.8: Contact angles of sperrylite as a function of Eh in the presence of 10^{-03} M KEX at pH 9 (Vermaak, Pistorius, et al., 2007)	14
Figure 1.9: Flotation domains of sulfide minerals: Py = pyrite, Cpy = chalcopyrite, Bor = bornite, Cc = covellite; with Pourbaix diagrams of butyl xanthate and ethyl dithiophosphate overlain (Lotter et al., 2016)	16
Figure 1.10: Crystal structure of Melonite Group minerals ($PtTe_2$ and $PdTe_2$). Legend: grey = Pt or Pd, green = Te (commons.wikimedia.org)	18
Figure 1.11: a) Bulk crystal structure, b) working surface of $PtAs_2$. Legend: blue = Pt, purple = As (Waterson, 2015)	19
Figure 1.12: Crystal structure of Pd_2As (Nemutudi, 2020).....	20
Figure 1.13: Relationship between the natural floatability and surface energy of PGM and sulfide minerals (Pikinini, 2022).....	21
Figure 1.14: Schematic representation of band gap energy of metallic, semiconductor and insulator minerals	22
Figure 1.15: Mechanism of collector adsorption illustrated using butyl xanthate (BX) and diethyl dithiocarbamate (DDTC) adsorption on pyrite (Hu et al., 2009).....	23
Figure 2.1: Focus of Phase One, Two and Three of this thesis.....	29
Figure 2.2: Research approach used in Phase One	30
Figure 2.3: Research approach used in Phase Two	31
Figure 2.4: Research approach used in Phase Three	32
Figure 3.1: Mineral synthesis procedure of the PGMs investigated in this study.....	34
Figure 3.2: Diffractogram of the synthesised sperrylite sample	36

Figure 3.3: Diffractogram of the synthesised palladoarsenide sample	37
Figure 3.4: Diffractogram of the synthesised merenskyite sample	37
Figure 3.5: Diffractogram of the synthesised moncheite sample.....	38
Figure 3.6: BSE micrograph of the synthesised sperrylite.....	39
Figure 3.7: BSE micrograph of the synthesised palladoarsenide	40
Figure 3.8: BSE micrograph of the synthesised moncheite.....	41
Figure 3.9: BSE micrograph of the synthesised merenskyite	42
Figure 3.10: QXRD Bulk mineralogy of the Platreef flotation feed samples (Nyaruwata, 2022)	44
Figure 3.11: PGM distribution in the Platreef flotation feed samples determined using QEMSCAN. Total number of PGM -bearing particles = 565 (Nyaruwata, 2022)	44
Figure 3.12: PGM mode of occurrence in the feed Platreef ore samples at a grind of 80% passing 45 µm. Total number of PGM-bearing particles = 565 (Nyaruwata, 2022).....	45
Figure 3.13: Schematic of the UCT microflotation rig used in this study (Bradshaw & O'Connor, 1996)	50
Figure 3.14: UCT microflotation rig used in this study.....	51
Figure 3.15: Electrochemistry experimental set-up.....	54
Figure 3.16: Electrodes used in this study	56
Figure 3.17: Schematic representation of the rest potential profile obtained from the electrochemical experiments.....	57
Figure 3.18: Duplicate rest potential profiles of sperrylite with PAX at pH 3	58
Figure 3.19: Isothermal Titration Calorimetry instrument set-up	59
Figure 3.20: ITC reproducibility tests using pyrite with PNBX at pH 9	61
Figure 3.21: UV-vis spectrophotometer and quartz cuvettes used in this study.....	62
Figure 3.22: Standard absorbance vs concentration curves for a) PAX, b) PNBX, c) SIBX and d) PTU collectors. Absorbance at 301 nm for the xanthates and 288 for PTU.....	64
Figure 3.23: FTIR spectrometer used in this study.....	65
Figure 3.24: Experimental set-up for the Raman spectroscopy analyses	67
Figure 3.25: Experimental set-up for the zeta potential measurements.....	68
Figure 3.26: Procedure for performing zeta potential measurements.....	69
Figure 3.27: Stainless steel grinding mill.....	71
Figure 3.28: Milling curve of the Platreef ore used in this study	72

Figure 3.29: 8-L modified Leeds batch flotation cell	73
Figure 3.30: Batch flotation experimental procedure used in Phase One	74
Figure 3.31: Batch flotation experimental procedure used for Case 0 in Phase Three	75
Figure 3.32: Batch flotation experimental procedure used for Case 1 in Phase Three	75
Figure 3.33: Batch flotation experimental procedure used for Case 2 in Phase Three	76
Figure 3.34: Microflotation recoveries of pyrite with xanthate, trithiocarbonate and thiourea collectors; with 1 pseudo-monolayer of collector dosed at pH 9	77
Figure 3.35: Effect of NaClO addition on pH	78
Figure 4.1: Extent of adsorption of the different collectors on sperrylite at an initial collector concentration equivalent to 1 pseudo-monolayer surface coverage, in pH 9 water. PAX and PNBX absorbance peak = 301 nm, PTU absorbance peak = 288 nm.....	81
Figure 4.2: UV-vis spectra of a PNBTTTC solution initially containing 2.9×10^{-5} M PNBTTTC at pH 9 recorded at 10-minute intervals for 60 minutes.....	82
Figure 4.3: PNBTTTC decomposition plot as a function of time at pH 9; with an initial concentration of 2.9×10^{-5} M of PNBTTTC	82
Figure 4.4: Microflotation recoveries of sperrylite with different collectors at pH 9. ML = collector dosage equivalent to a pseudo-monolayer mineral surface coverage and k = first-order rate constant. $RSE_{\text{pooled}} = 3.79\%$	83
Figure 4.5: Microflotation final cumulative recoveries (i.e., after 20 minutes) of sperrylite with different collectors at a dosage equivalent 1 pseudo-monolayer surface coverage in de-ionised water and 0.12 M NaCl solution at pH 9; 15 ppm frother. $RSE_{\text{pooled}} = 3.79\%$	84
Figure 4.6: Final cumulative microflotation recoveries of sperrylite with different dosages of PAX at pH 9. ML = collector dosage equivalent to a pseudo-monolayer surface coverage and k =first-order rate constant; 15 ppm frother. $RSE_{\text{pooled}} = 3.79\%$	85
Figure 4.7: Final cumulative microflotation recoveries and amount of collector adsorbed on sperrylite as a function of the number of PAX pseudo-monolayers added at pH 9	86
Figure 4.8: Pt and As recovery vs solids recovered from batch flotation tests comparing the standard case conditions with increased ionic strength, 10 SPW; and collector with a different functional group, PNBTTTC.....	88
Figure 5.1: Microflotation recoveries of sperrylite conditioned at varying pH conditions with 5 monolayers of PAX or no collector where specified; in 0.12 M NaCl and with 15 ppm frother. $RSE_{\text{pooled}} = 3.79\%$	98
Figure 5.2: Measured Eh values of the sperrylite pulp corresponding to the different pH and NaClO concentrations. $RSE_{\text{pooled}} = 3.79\%$	99

Figure 5.3: Final cumulative microflotation recoveries of sperrylite as a function of pH and NaClO concentration; PAX collector dosage equivalent to 5 pseudo-monolayers; in 0.12 M NaCl; and with 15 ppm frother. $RSE_{pooled} = 3.79\%$	100
Figure 5.4: Final cumulative recoveries of sperrylite comparing the effect of 0.01 M NaClO and H_2O_2 at pH 3 and pH 9; with 5 pseudo-monolayers of PAX, 15 ppm frother and 0.12 M NaCl. $RSE_{pooled} = 3.79\%$	100
Figure 5.5: Effect of pH on the decomposition of PAX; with an initial PAX concentration = 7.24×10^{-5} M; PAX absorbance peak = 301 nm	101
Figure 5.6: Amount of PAX collector and/or reacted on sperrylite in the presence and absence of 0.001 M NaClO as a function of pH; with an initial PAX concentration = 7.24×10^{-5} M; PAX absorbance peak = 301 nm	102
Figure 5.7: UV-vis spectra of PAX with 0.001 M NaClO and without NaClO at different pH conditions in the absence of a mineral; Initial PAX concentration = 7.24×10^{-5} M	104
Figure 5.8: Amount of PAX collector reacted with 0.001 M NaClO in the absence of a mineral. Initial PAX concentration = 7.24×10^{-5} M; PAX absorbance peak = 301 nm	105
Figure 5.9: Rest potential profiles of sperrylite at different pH conditions with 0 M NaClO; 6.24×10^{-4} M PAX added at 600 seconds	106
Figure 5.10: Rest potential profiles of sperrylite at different pH conditions with 0.01 M NaClO; 6.24×10^{-4} M PAX added at 600 seconds	107
Figure 5.11: FTIR spectra of sperrylite conditioned at pH 9 without and with 5×10^{-4} M PAX collector	108
Figure 5.12: FTIR spectra of sperrylite conditioned at pH 3 without and with 5×10^{-4} M PAX collector	109
Figure 5.13: FTIR spectra of sperrylite conditioned at pH 9 with 0.01 M NaClO and without or with 5×10^{-4} M PAX collector	109
Figure 5.14: S 2p spectra of sperrylite conditioned with 5×10^{-4} M PAX at a) pH 9 and b) pH 3	110
Figure 5.15: S 2p spectra of sperrylite conditioned with 5×10^{-4} M PAX at pH 3, with peak fitting	111
Figure 5.16: Zeta potentials of sperrylite in 0.12 M KCl without and with 5×10^{-4} M PAX... ..	112
Figure 5.17: in-situ Raman spectra of sperrylite conditioned at pH 3 from 1 minute to 10 minutes. Spectra of dry sperrylite ('as is') and reference solution included at second-from-bottom and bottom, respectively. NB: The left and right diagrams represent different ranges on the electromagnetic spectrum and have different y-axis scales	114
Figure 5.18: in-situ Raman spectra of sperrylite conditioned at pH 9 from 1 minute to 10 minutes. Spectra of dry sperrylite ('as is') and reference solution included at the bottom and	

second-from-bottom, respectively. NB: The left and right diagrams represent different ranges on the electromagnetic spectrum	115
Figure 5.19: in-situ Raman spectra of sperrylite conditioned at pH 3 with 5×10^{-04} M PAX from 1 minute to 10 minutes. Spectra of dry sperrylite ('as is') and reference solution included at the top and second-from-top, respectively. NB: The left and right diagrams represent different ranges on the electromagnetic spectrum and have different y-axis scales.....	116
Figure 5.20: in-situ Raman spectra of sperrylite conditioned at pH 3 with 5×10^{-04} M PAX from 1 minute to 10 minutes. Spectra of dry sperrylite ('as is') and reference solutions included at the bottom and the top, respectively. NB: The left and right diagrams represent different ranges on the electromagnetic spectrum and have different y-axis scales.....	117
Figure 5.21: in-situ Raman spectra of sperrylite conditioned with 0.01 M NaClO at pH 9 from 1 minute to 10 minutes. Spectra of dry sperrylite ('as is') and reference solutions included at the bottom and at the top, respectively. NB: The left and right diagrams represent different ranges on the electromagnetic spectrum and have different y-axis scales.....	118
Figure 6.1: Collectorless recoveries of PtAs ₂ , PtTe ₂ , Pd ₂ As, and PdTe ₂ at pH 9; frother at 15 ppm. RSE _{pooled} = 3.79%.....	129
Figure 6.2: Collectorless recoveries of PtAs ₂ , PtTe ₂ , Pd ₂ As, and PdTe ₂ at pH 3; frother at 15 ppm. RSE _{pooled} = 3.79%.....	129
Figure 6.3: Recoveries of PtAs ₂ , PtTe ₂ , Pd ₂ As, and PdTe ₂ at pH 9 with 1.69×10^{-06} M PAX collector; frother at 15 ppm. RSE _{pooled} = 3.79%.....	131
Figure 6.4: Recoveries of PtAs ₂ , PtTe ₂ , Pd ₂ As, and PdTe ₂ at pH 3 with 1.69×10^{-06} M PAX collector; frother at 15 ppm. RSE _{pooled} = 3.79%.....	132
Figure 6.5: Rest potential profiles of PtAs ₂ , PtTe ₂ , Pd ₂ As and PdTe ₂ at pH 9; 6.24×10^{-04} M PAX added at 600 seconds	134
Figure 6.6: Rest potential profiles of PtAs ₂ , PtTe ₂ , Pd ₂ As and PdTe ₂ at pH 3; 6.24×10^{-04} M PAX added at 600 seconds	135
Figure 6.7: a) Initial rest potential b) change in potential upon collector addition; of PtAs ₂ , PtTe ₂ , Pd ₂ As and PdTe ₂ as a function of pH	135
Figure 6.8: Amount of PAX adsorbed onto PtAs ₂ , Pd ₂ As, PtTe ₂ , and PdTe ₂ at pH 9 and; with an initial PAX concentration = 5.79×10^{-06} mol/g	136
Figure 6.9: Zeta potential measurements of PtAs ₂ without and with 5×10^{-04} M PAX, using 0.12 M KCl as a background electrolyte	137
Figure 6.10: Zeta potential measurements of Pd ₂ As without and with 5×10^{-04} M PAX, using 0.12 M KCl as a background electrolyte.....	137
Figure 6.11: Zeta potential measurements of PtTe ₂ without and with 5×10^{-04} M PAX, using 0.12 M KCl as a background electrolyte.....	138

Figure 6.12: Zeta potential measurements of PdTe ₂ without and with 5x10 ⁻⁰⁴ M PAX, using 0.12 M KCl as a background electrolyte.....	138
Figure 6.13: Zeta potential measurements of PtAs ₂ , Pd ₂ As, PtTe ₂ and PdTe ₂ a) without PAX b) with 5x10 ⁻⁰⁴ M PAX	139
Figure 6.14: FTIR spectra of PtAs ₂ conditioned at pH 9 and 3	139
Figure 6.15: FTIR spectra of Pd ₂ As conditioned at pH 9 and 3.....	140
Figure 6.16: FTIR spectra of PtTe ₂ conditioned at pH 9 and 3	141
Figure 6.17: FTIR spectra of PdTe ₂ conditioned at pH 9 and 3.....	141
Figure 6.18: in-situ Raman spectra of PtAs ₂ conditioned at pH 9 from 1 minute to 10 minutes. Spectra of dry PtAs ₂ ('as is') and reference solution are included at the bottom and second-from-bottom, respectively. NB: The left and right diagrams represent different ranges on the electromagnetic spectrum.....	142
Figure 6.19: in-situ Raman spectra of Pd ₂ As conditioned at pH 9 from 1 minute to 10 minutes. Spectra of dry Pd ₂ As ('as is') and reference solution are included at the bottom and second-from-bottom, respectively. NB: The left and right diagrams represent different ranges on the electromagnetic spectrum.....	143
Figure 6.20: in-situ Raman spectra of PtTe ₂ conditioned at pH 9 from 1 minute to 10 minutes. Spectra of dry PtTe ₂ ('as is') and reference solution are included at the bottom and second-from-bottom, respectively. NB: The left and right diagrams represent different ranges on the electromagnetic spectrum.....	144
Figure 6.21: in-situ Raman spectra of PdTe ₂ conditioned at pH 9 from 1 minute to 10 minutes. Spectra of dry PdTe ₂ ('as is') and reference solution are included at the bottom and second-from-bottom, respectively. NB: The left and right diagrams represent different ranges on the electromagnetic spectrum.....	145
Figure 6.22: Grade-Recovery curves of Pt from batch flotation tests comparing the flotation performance at the natural pH of 9 and adjusted pH of 3	146
Figure 6.23: Grade-Recovery curves of Pd from batch flotation tests comparing the flotation performance at the natural pH of 9 and adjusted pH of 3	147
Figure 6.24: Grade-Recovery curves of As from batch flotation tests comparing the flotation performance at the natural pH of 9 and adjusted pH of 3	148
Figure 6.25: Grade-Recovery curves of Te from batch flotation tests comparing the flotation performance at the natural pH of 9 and adjusted pH of 3	148
Figure 6.26: Final upgrade ratios of Pt, Pd, As and Te for the different batch flotation test conditions investigated.....	149
Figure 6.27: Relationship between the collectorless recoveries and the initial rest potentials of the PGE minerals investigated in this study at pH 9	152

Figure B.1: Heat of collector adsorption on sperrylite as a function of monolayer coverage for the PNBTC, PAX, PNBX and PTU collectors at pH 9	C
Figure C.1: XPS wide scan of sperrylite conditioned at pH 9	D
Figure C.2: XPS wide scan of sperrylite conditioned at pH 3	E
Figure C.3: XPS wide scan of sperrylite conditioned with 5×10^{-04} M PAX at pH 9.....	E
Figure C.4: XPS wide scan of sperrylite conditioned with 5×10^{-04} M PAX at pH 3.....	F
Figure C.5: Pt 4f XPS spectra from sperrylite conditioned at pH 9 without PAX.....	F
Figure C.6: As 3d XPS spectra from sperrylite conditioned at pH 9 without PAX	G
Figure C.7: O 1s XPS spectra from sperrylite conditioned at pH 9 without PAX	G
Figure C.8: C 1s XPS spectra from sperrylite conditioned at pH 9 without PAX.....	H
Figure C.9: Pt 4f XPS spectra from sperrylite conditioned at pH 3 without PAX.....	H
Figure C.10: As 3d XPS spectra from sperrylite conditioned at pH 3 without PAX	I
Figure C.11: O 1s XPS spectra from sperrylite conditioned at pH 3 without PAX	I
Figure C.12: C 1s XPS spectra from sperrylite conditioned at pH 3 without PAX.....	J
Figure C.13: Pt 4f XPS spectra from sperrylite conditioned at pH 9 with 5×10^{-04} M PAX.....	J
Figure C.14: As 3d XPS spectra from sperrylite conditioned at pH 9 with 5×10^{-04} M PAX	K
Figure C.15: O 1s XPS spectra from sperrylite conditioned at pH 9 with 5×10^{-04} M PAX	K
Figure C.16: C 1s XPS spectra from sperrylite conditioned at pH 9 with 5×10^{-04} M PAX.....	L
Figure C.17: Pt 4f XPS spectra from sperrylite conditioned at pH 3 with 5×10^{-04} M PAX.....	L
Figure C.18: As 3d XPS spectra from sperrylite conditioned at pH 3 with 5×10^{-04} M PAX	M
Figure C.19: O 1s XPS spectra from sperrylite conditioned at pH 3 with 5×10^{-04} M PAX	M
Figure C.20: C 1s XPS spectra from sperrylite conditioned at pH 3 with 5×10^{-04} M PAX.....	N
Figure D.1: Rest potential profiles of PtAs ₂ , PtTe ₂ , Pd ₂ As and PdTe ₂ at pH 5; 6.24×10^{-04} M PAX added at 600 seconds	O
Figure D.2: Rest potential profiles of PtAs ₂ , PtTe ₂ , Pd ₂ As and PdTe ₂ at pH 7; 6.24×10^{-04} M PAX added at 600 seconds	O
Figure E.1: Recovery of Pt as a function of time for the different batch flotations tests conducted	P
Figure E.2: Recovery of Pd as a function of time for the different batch flotations tests conducted	Q
Figure E.3: Recovery of As as a function of time for the different batch flotations tests conducted	Q

Figure E.4: Recovery of Te as a function of time for the different batch flotations tests conducted R

List of Tables

Table 1.1: Microflotation recoveries of PGE tellurides and arsenides at pH 9 (Shackleton, 2007)	24
Table 2.1: Experiments conducted to address the key questions and hypotheses in Phase One	32
Table 2.2: Experiments conducted to address the key questions and hypotheses in Phase Two	33
Table 2.3: Experiments conducted to address the key questions and hypotheses in Phase Three	33
Table 3.1: Thermal treatment procedure used to synthesise the PGMs investigated in this study	35
Table 3.2: Rietveld quantification of the synthesised sperrylite sample	36
Table 3.3: Rietveld refinement of the synthesised palladoarsenide sample	37
Table 3.4: Rietveld refined of the synthesised merenskyite sample	38
Table 3.5: Rietveld refinement of the synthesised moncheite sample	38
Table 3.6: EDS results showing the elemental composition of the synthesised sperrylite	39
Table 3.7: EDS results showing the elemental composition of the synthesised palladoarsenide	40
Table 3.8: EDS results showing the elemental composition of the synthesised moncheite	41
Table 3.9: EDS results showing the elemental composition of the synthesised merenskyite	42
Table 3.10: Surface areas of the minerals determined using BET analysis	43
Table 3.11: Xanthate collectors considered in this study	46
Table 3.12: Trithiocarbonate collectors considered in this study	47
Table 3.13: Thiourea collectors considered in this study	48
Table 3.14: pH buffers used for the rest potential measurements	49
Table 3.15: Ion compositions of synthetic plant water at two different ionic strengths (Wiese et al., 2005)	49
Table 3.16: Microflotation reproducibility test results showing the average recoveries and associated errors	53
Table 3.17: Enthalpy of dilution for the collectors investigated	60
Table 3.18: ITC reproducibility test results showing average enthalpies and the associated errors	61
Table 3.19: Reproducibility test results of UV-vis spectroscopy using PNBX and sperrylite	65

Table 3.20: Formulation of a 1-litre TiO ₂ reference dispersion solution	70
Table 3.21: Details of the grinding mill used in this study	71
Table 3.22: Reagents used for the different flotation conditions investigated	74
Table 3.23: Method for microwave-assisted acid digestion	77
Table 4.1: Heat of adsorption of different collectors, at a dosage equivalent to 1 pseudo-monolayer surface coverage, on sperrylite at pH 9	80
Table 4.2: Batch flotation samples submitted for ICP-MS showing the variability of the assays of Pt and As for the different cases investigated. Samples were analysed in triplicates.....	87
Table 4.3: Upgrade ratios of Cu, Ni, Pt, and As obtained from batch flotation tests comparing standard case conditions with increased ionic strength, 10 SPW, and PNBTTTC	88
Table 5.1: Absorbance peaks of xanthate at 226 nm and 301 nm, with calculated X ₂₂₆ :X ₃₀₁ ratios for PAX-only and NaClO-PAX solution for different pH conditions.....	103
Table 5.2: Summary of the initial rest potentials and change in potential of sperrylite after collector addition, without and with 0.01 M NaClO	107
Table 5.3: Assignment of vibrational spectra of sperrylite (Muller & Lutz, 1991)	113
Table 5.4: Summary of Raman vibrational bands of sperrylite and their assignment in the absence of a collector at pH 3 and pH 9	119
Table 5.5: Summary of Raman vibrational bands of sperrylite and their assignment in the presence of 5x10 ⁻⁰⁴ M PAX collector at pH 3 and pH 9	119
Table 6.1: Number of collector monolayers equivalent to 1.69x10 ⁻⁰⁶ mol/g dosage and BET surface areas of the minerals.....	130
Table 6.2: Summary of the microflotation recoveries of the PGE arsenides and tellurides at pH 9 and 3, with and without PAX collector.....	132
Table 6.3: Pt, Pd, As, and Te flotation rate constants for flotation tests conducted at pH 9 and 3	147
Table 6.4: Final recoveries and grades of Pt, Pd, As and Te for the different batch flotation test conditions investigated	150
Table 6.5: Comparison of batch flotation recoveries at pH 9 and 3	157

Nomenclature

ΔH	Change in enthalpy or heat
A	Absorbance
$a_{\text{oxidation}}$	Activity of oxidised species
$a_{\text{reduction}}$	Activity of reduced species
BET	Brunauer-Emmett-Teller
BMS	Base metal sulfides
BSE	Back-scattered electron
CMC	Carboxymethyl cellulose
EDS	Energy-dispersive X-ray spectroscopy
Eh	Electrochemical redox potential
FeS_2	Pyrite
FTIR	Fourier Transform Infrared spectroscopy
HOMO	Highest occupied molecular orbital
ICP-OES	Inductively coupled-optical emission spectrometry
ICP-MS	Inductively coupled plasma-mass spectrometry
ITC	Isothermal Titration Calorimetry
k	First-order rate constant
K	Barsky Equilibrium Constant
LUMO	Lowest unoccupied molecular orbital
MTC	Monothiocarbonate
MX_2	Metal xanthate
PAX	Potassium amyl xanthate
PGE	Platinum group elements
PGM	Platinum group minerals
pKa	-log of the acid dissociation constant
PNBTTC	Potassium n-butyl trithiocarbonate
PNBX	Potassium n-butyl xanthate
Pd_2As	Palladoarsenide
PdTe_2	Merenskyite
PPG	Polypropylene glycol
PTU	Propyl thiourea
PtAs_2	Sperrylite
PtTe_2	Moncheite
QEMSCAN	Quantitative Evaluation of Minerals by Scanning Electron Microscopy
SEM	Scanning electron microscopy
Senfroth	Polypropylene glycol based frother
Senkol 3	Dithiophosphate collector
SEX	Sodium ethyl xanthate
SHE	Standard hydrogen electrode

SIBX	Sodium iso-butyl xanthate
SPW	Synthetic plant water
TOF-SIMS	Time of Flight Secondary Ion Mass Spectroscopy
UV-vis	Ultraviolet visible
X ⁻	Xanthate ion
X ₂	Dixanthogen
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence

CHAPTER 1: Introduction and Literature Review

1. Introduction and Literature Review

1.1. Background

The Bushveld igneous Complex in South Africa is host to the largest reserves of platinum group elements (PGE) in the world. The major PGE ore deposits found in the Bushveld Complex include the Merensky Reef, Upper Group-2 (UG-2) and Platreef.

The Platreef, which is the reef type of interest in this study, contains the highest composition of PGE tellurides and arsenides. It is envisaged that the beneficiation of the Platreef will play an integral role in the PGM industry for the foreseeable future. PGE tellurides and arsenides constitute about 30% and 21% of the platinum group mineral (PGM) assemblage in the Platreef, respectively (Shamaila & O'Connor, 2008). This makes these minerals the most abundant and economically important class of PGMs in the Platreef. However, it has been established that during the processing of the Platreef ores there are major losses of these PGMs, with the losses being mainly attributed to PtAs₂ (sperrylite). The reason for these losses is mainly attributed to the poor recovery of the minerals by froth flotation (Shackleton, 2007).

Much of the research on the flotation of PGMs has primarily focused on base metal sulfides (BMS). This is because of the general association of PGMs with BMS. As such, the reagent suites that have been used are those typical of sulfide-bearing ores. However, the Platreef has a much more complex and diverse mineralisation. In general, this reef is almost barren of PGE sulfides and the association of PGMs with BMS is quite erratic (Armitage et al., 2002; Holwell et al., 2006). Therefore, the flotation reagent suites typically used for sulfide ores may not be effective in the flotation of PGMs from the Platreef. Studies have shown that sperrylite has a poor flotation recovery even after being treated with xanthate collectors, the typical collectors used in the flotation of PGM-sulfide bearing ores (Shackleton et al., 2007; Pikinini, 2022). This has been mainly attributed to the poor adsorption of xanthate collectors onto the surface of sperrylite.

There is evidence that sperrylite may be electrochemically inert at pH 9, the typical operating pH in PGM concentrators (Pikinini, 2022). This may explain the poor interaction of sperrylite, hence floatability, with xanthate collectors. Exploring different operating pH conditions may offer benefits in improving the floatability of sperrylite. In addition to pH, studies have shown that sperrylite may require very anodic conditions (>200 mV) for it to be rendered sufficiently hydrophobic by a xanthate collector (Vermaak, Pistorius, et al., 2007). This suggests that the optimal flotation domain of sperrylite may be outside the typical pH-Eh conditions observed in PGM flotation.

In contrast to sperrylite, other PGMs which share some similarities with sperrylite such as PtTe₂ (moncheite) or Pd₂As (palladoarsenide) have been shown to float relatively well. The reasons for the difference in the floatability of these three minerals are not yet clearly

understood. Through the work of Shamaila & O'Connor (2008) which compared the floatability of synthetic PGE tellurides and arsenides, mineralogical factors such as particle size, association or liberation have been eliminated as primary causes for the differences observed in the floatability of these minerals. It is of interest to determine the reasons for the poor floatability of sperrylite when compared with other PGE arsenides and tellurides which have a relatively much better floatability.

1.2. Scope of Research

The factors that affect flotation can usually be categorised into the chemical, operational and equipment factors. This study focuses on the chemical factors with specific reference to collector and solution chemistry. Operational factors with specific reference to mineral type are also investigated. In this study, sperrylite is the primary mineral of interest as the largest losses in the processing of the Platreef come from this mineral. Other PGMs, including Pd_2As , PtTe_2 and PdTe_2 which share some similarities with sperrylite are investigated for comparative purposes to gain insights into the poor floatability of sperrylite. The scope of this study is illustrated in Figure 1.1.

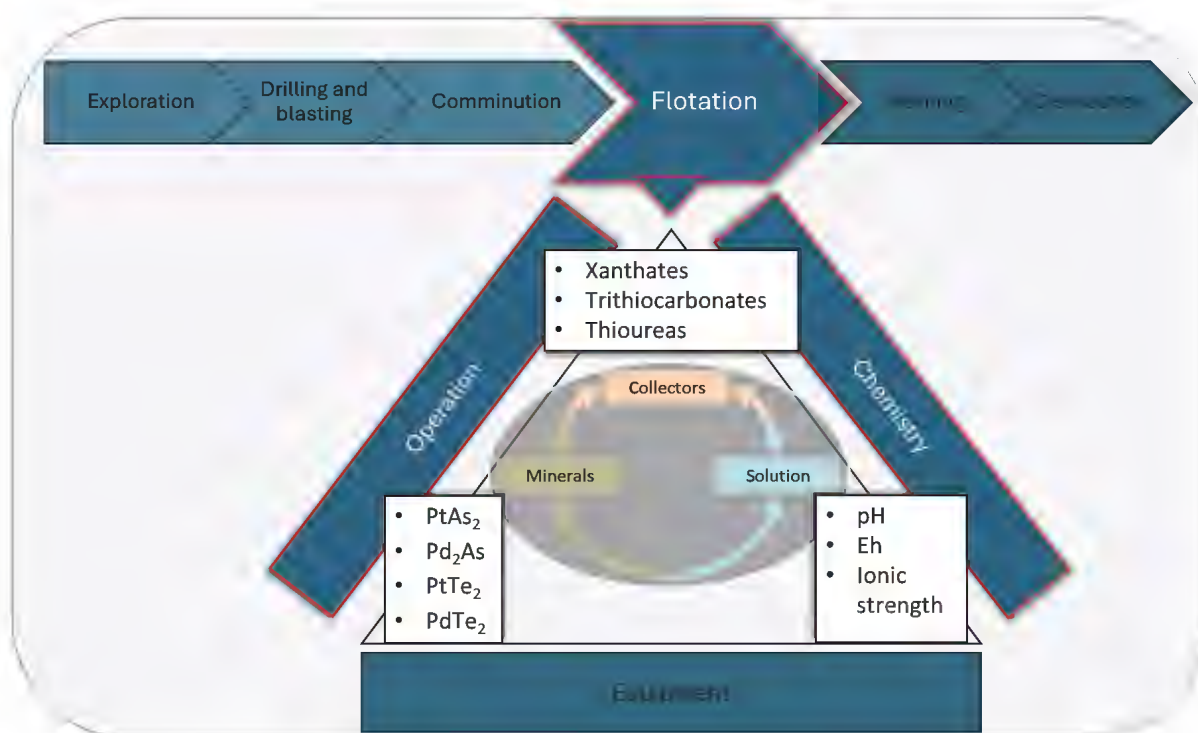


Figure 1.1: Scope of current research work

1.3. Mineralogy of the Platreef

The Platreef is a Ni-Cu-PGE deposit characterised by a mafic-ultramafic tabular body located at the base of the northern limb of the Bushveld Complex. It is dominated by a complex assemblage of pyroxenites, serpentinites and calc-silicates. Unlike the Merensky reef and UG-2, the mineralisation in the Platreef is much more complex and diverse. In particular, the base metal mineralisation and PGE concentrations are highly variable both in terms of value as well as distribution (Schouwstra et al., 2000). Although the PGM distribution is variable, there is a consensus that the PGM assemblage in the Platreef is dominated by PGE tellurides, arsenides and alloys (Kinloch, 1982; Armitage, 2011). The mineralisation varies depending on the strike along the Platreef. A generalised stratigraphy of the northern limb of the Bushveld Complex in which the Platreef is found is illustrated in Figure 1.2. The overall composition of the PGM assemblage in the Platreef has been reported to be 30% Pt-Pd tellurides, 26% alloys, and 21% PGE arsenides (Viljoen & Schurmann, 1998).

The PGE tellurides consist of merenskyite and moncheite which in their simplest form can be represented by PdTe_2 and PtTe_2 , respectively. The composition of these minerals is often variable and can occur in association with bismuth such as $(\text{Pt,Pd})(\text{Bi,Te})_2$. On the other hand, the composition of PGE arsenides is less variable compared to that of the tellurides. The PGE arsenides in the Platreef are dominated by sperrylite (PtAs_2), with this mineral being the only platinum-bearing mineral of any significance from the arsenide group. Furthermore, sperrylite is typically the only source of arsenic in Platreef ores (Holwell et al., 2006; Shamaila & O'Connor, 2008).

Compared to the Merensky and UG-2 reefs, the Platreef generally shows a scarcity of PGE sulfides. Viljoen & Schurmann (1998) reported the PGE sulfide content can be as much as 19% of the PGM assemblage. However, Armitage et al. (2002) and Holwell et al. (2006) found the PGM assemblages in the Platreef to be virtually free of PGE sulfides. This is indicative of the erratic nature of the occurrence of PGE sulfides in the Platreef. In addition, the PGMs in this reef show a relatively poor association with BMS. The main BMS mineralisation in the Platreef occur as, in order of decreasing abundance, primary pyrrhotite, pentlandite, chalcopyrite, and minor secondary pyrite and bornite. These mostly occur as disseminated interstitial blebs throughout the pyroxenite rock types. Overall, the BMS content in the Platreef typically ranges between ~0.21 and ~0.5% of the host lithology (Gibson et al., 2023).

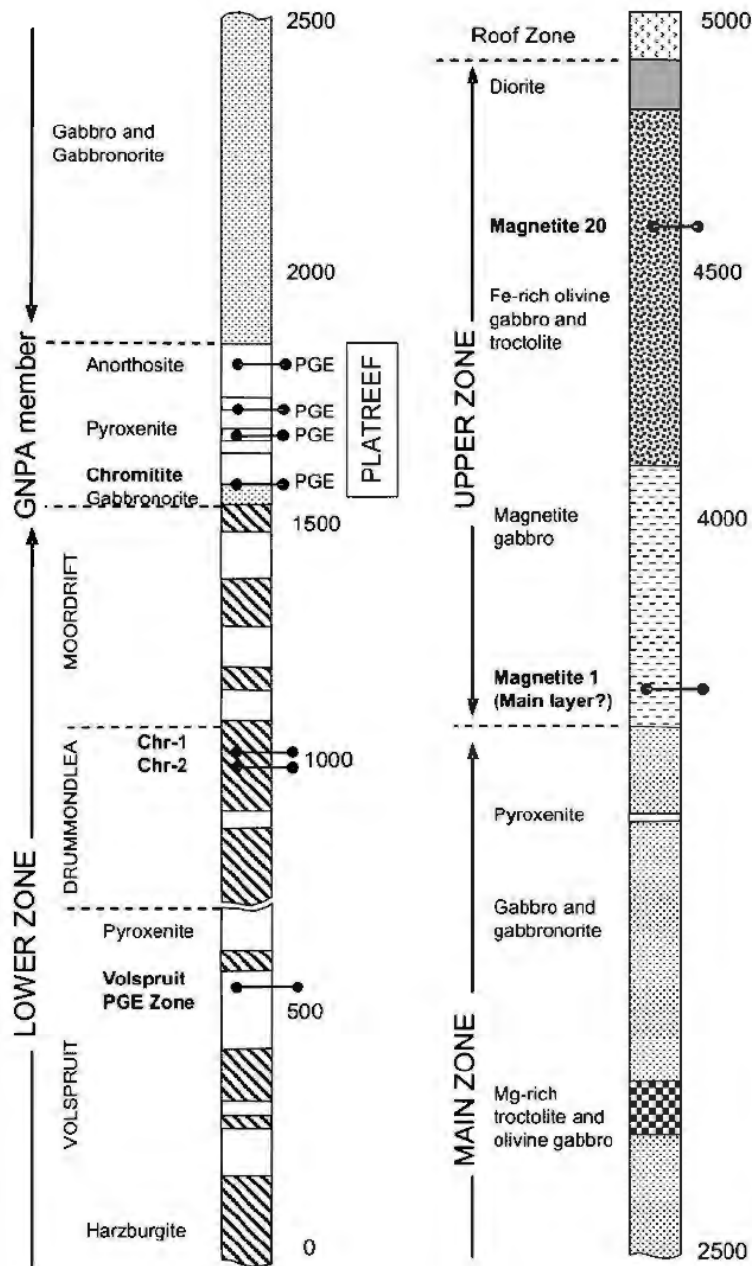


Figure 1.2: Generalised stratigraphy of the northern limb of the Bushveld Complex (McDonald et al., 2005)

The complexities in the mineralogy of the Platreef compared to the Merensky and UG-2 reefs have contributed to the challenges encountered when recovering the PGMs from this reef. For instance, the poor association of PGMs with BMS has meant that the collectors typically used in the flotation of sulfide minerals are not as successful in recovering PGMs from the Platreef.

1.4. Mineral processing of PGMs

The processing of PGM ore bodies includes processes such as i) comminution which involves size reduction to liberate valuable minerals, ii) concentration of valuable minerals using flotation, iii) smelting and conversion to obtain the BMS and PGE, and iv) refining to obtain a

Chapter 1: Introduction and Literature Review

saleable metal. This generic flowsheet is illustrated in Figure 1.3. One of the major challenges during the beneficiation is the high losses of PGMs. Approximately 27-28% of platinum losses occur during mining, while 13 – 20% occur during the comminution and concentration stages (Gibson et al., 2023). In part, these losses can be attributed to factors such as complex mineralogy, PGM speciation and poor liberation.

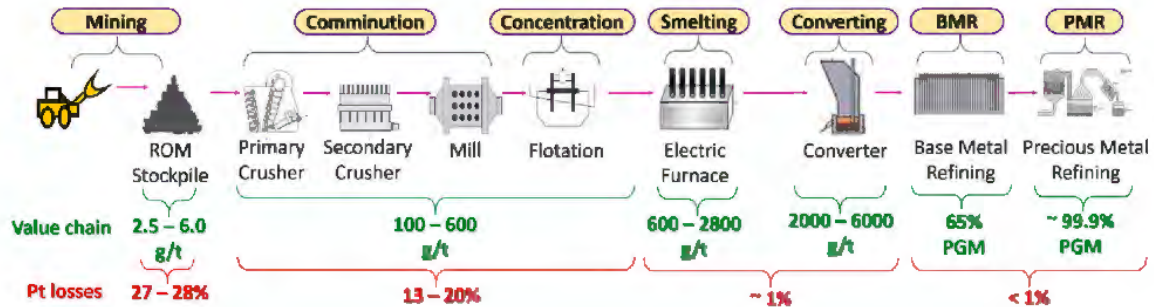


Figure 1.3: Generic flowsheet of PGM processing showing the value chain and losses during each stage of the process (Gibson et al., 2023)

Due to the complex nature and mineralogy of PGM ores, typical circuits for processing Platreef ores incorporate a multiple liberation/beneficiation configuration such as MF2 (mill-float-mill-float) flow sheets. An example of an MF2 flow sheet is illustrated in Figure 1.4. The principle behind this circuit configuration is to improve process efficiency by incremental recovery of the liberated minerals, thereby minimising the risk of overgrinding (Engelbrecht, 2012). To enable this, the primary milling circuit produces a coarser primary grind to enable flotation of the already liberated PGMs before overgrinding occurs. Thereafter, the tails from the primary circuit are reground to a finer grind in the secondary circuit to liberate PGMs from the silicates.

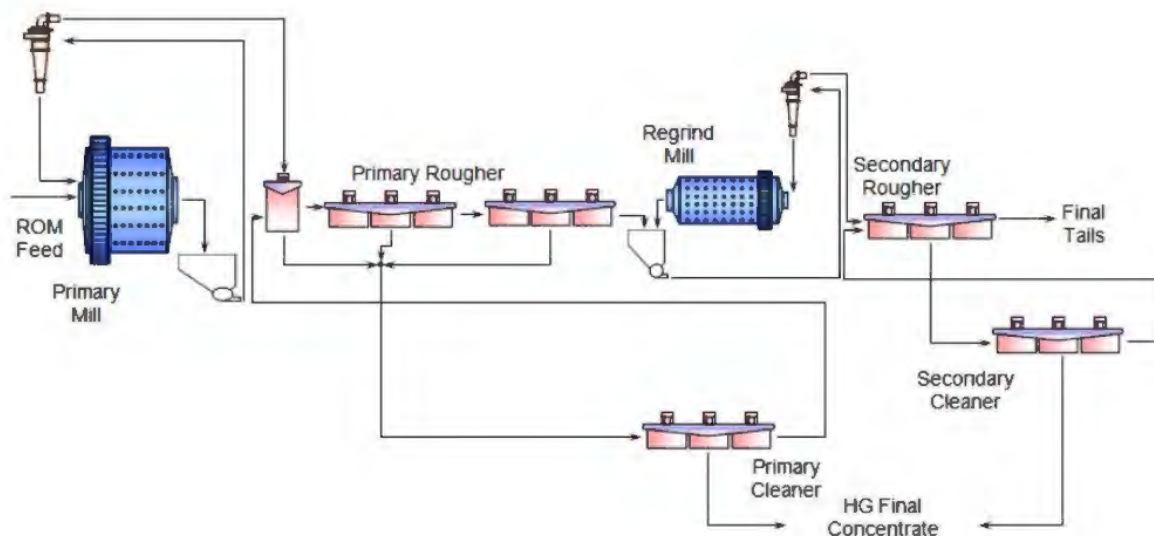


Figure 1.4: Typical MF2 circuit for processing Platreef ores (Engelbrecht, 2012)

Despite the added advantages of MF2 circuits such as the increased liberation, there are still major losses of PGMs such as sperrylite during the processing of the Platreef ores even when sperrylite is fully liberated (Shamaila & O'Connor, 2008). As mentioned before, these losses are mainly attributed to the poor flotation of sperrylite. Therefore, there is a need to understand this aspect of the beneficiation process in relation to the recovery of sperrylite, and PGMs in general.

1.4.1. Principles of froth flotation

Froth flotation is a fundamental step that is necessary for the recovery of commercially valuable minerals from ore bodies. It is a physicochemical process that is concerned with separating valuable minerals from gangue material based on differences in the surface properties of minerals such as hydrophobicity. Hydrophobic minerals can attach to bubbles and be floated, thus separating them from those that are hydrophilic or readily wetted by water. A schematic representation of this principle is shown in Figure 1.5.

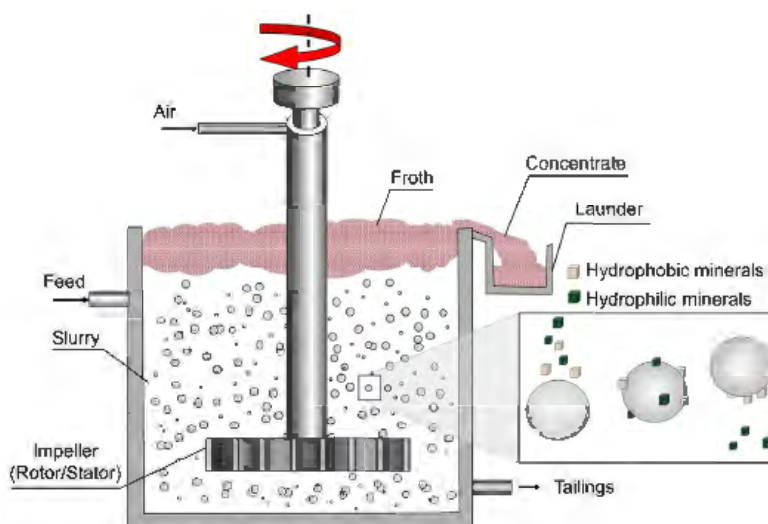


Figure 1.5: Schematic representation of a froth flotation cell showing the principle of flotation (Wills & Finch, 2015)

The flotation cell requires a high-speed impeller to provide enough turbulence for the mineral particles in the pulp phase. The agitation promotes the collision of mineral particles with bubbles which are introduced by injecting air into the cell near the impeller, thereby generating bubbles under the turbulence created by the impeller. The collision of the particles with the bubbles results in the attachment of hydrophobic particles which are then carried by the rising bubbles to the froth phase. The valuable minerals reporting to the froth phase are then conveyed into the launders where they are concentrated and collected. On the other hand, the hydrophilic particles left in the pulp phase are rejected into the tailings.

There are three sub-processes by which mineral particles can report to the froth phase (Wills & Finch, 2015):

- a) Selective attachment of mineral particles to air bubbles. This is known as “true flotation”;
- b) Entrainment of particles in the water which passes through the froth
- c) Physical entrapment between the particles attached to the air bubbles

This work is mainly concerned with the first sub-process. The selective attachment of particles to bubbles represents the majority of the particles that are recovered in the concentrate. It is this process that exploits the differences in the surface properties of the minerals. It is a major pre-requisite for the particles to be hydrophobic in order to be selectively attached to air bubbles. The hydrophobicity of the minerals can be native, self-induced or collector-induced (Rao, 2004). Flotation is a complex process which can be influenced by several factors which, as already mentioned, have been categorised into chemical, operational and equipment factors (Dowling et al., 1985).

This study focuses on the role of the collector, solution and mineral properties in relation to how these affect the floatability of minerals.

1.5. Role of collectors

Some minerals are naturally hydrophobic and can therefore be recovered by flotation with little assistance. However, in most cases, the difference in the hydrophobicity between the valuable mineral and gangue material is not high enough to achieve selective bubble-particle attachment. In these cases, the use of chemical reagents known as collectors is necessary. Collectors selectively impart hydrophobicity to the surface of the valuable mineral. The collector interacts with the mineral surface either by physical or chemical adsorption or both (Rao, 2004).

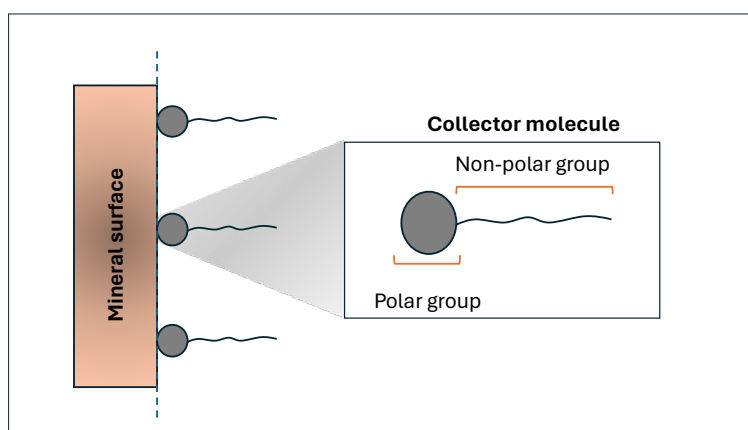


Figure 1.6: Schematic representation of collector adsorption onto a mineral surface

The molecular structure of a collector is made up of a polar and non-polar group. This is illustrated in Figure 1.6. The non-polar group, which comprises an alkyl chain, is responsible for the hydrophobic character of the collector. The polar group is responsible for adsorbing onto the mineral surface. Thiol collectors are the most commonly used types of collectors in

sulfide and PGM flotation. These are organosulfur compounds containing the sulfhydryl functional group. The most common thiol collectors include xanthates, dithiocarbonates and dithiophosphates.

Xanthate collectors have been extensively used in the flotation of sulfide minerals. However, in the case of sperrylite, these collectors have not been as successful in improving its recovery by flotation. For instance, Shackleton et al. (2007) found that the addition of sodium iso-butyl xanthate (SIBX) hardly had any effect on the recovery of sperrylite. This was despite surface analyses of the samples, using zeta potential measurements and Time of Flight Secondary Ion Mass Spectroscopy (TOF-SIMS), showing that there was some adsorption of the collector onto the mineral, albeit to a very limited extent. Furthermore, electrochemical investigations conducted by Pikinini (2022) showed that sperrylite had the least extent of interaction with xanthate collectors compared to sulfide minerals such as pyrite, arsenopyrite and platarsite.

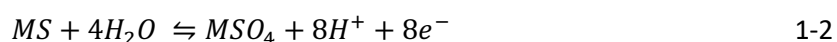
1.5.1. Collector adsorption mechanism of xanthate collectors

The adsorption of xanthate collectors onto the mineral surface is considered to occur via an electrochemical mechanism in which there is a transfer of electrons (Rao, 2004). The collector may undergo various anodic oxidation reactions coupled with the simultaneous cathodic reduction of oxygen. The oxidation reactions can yield at least three collector products that can then adsorb onto the mineral surface to impart hydrophobicity, viz. chemisorbed xanthate, metal xanthate or dixanthogen (Woods, 1996).

In the formation of the chemisorbed xanthate, electrostatic adsorption of the xanthate ion on the mineral surface takes place first (Leja, 1982). This is then followed by the chemisorption of the xanthate which is a single-step anodic charge transfer reaction described by reaction 1-1, where X^- refers to the xanthate ion and X_{ads} refers to the chemisorbed xanthate.



It has been found that the chemisorbed xanthate usually does not suffice to induce hydrophobicity on its own. A metal xanthate or dixanthogen needs to be co-adsorbed on the first layer of the chemisorbed xanthate (Leja, 1982). The formation of the metal xanthate occurs through a combination of chemical and electrochemical reactions (Fuerstenau et al., 2007). First, there is an electrochemical reaction in which the mineral surface is oxidised which subsequently releases metal cations as described by reaction 1-2 ; where M refers to the metal cation from the mineral surface and S refers to sulfide.



Thereafter, an ion exchange reaction takes place between the metal cations and the xanthate to form a metal xanthate complex according to reaction 1-3.



Chapter 1: Introduction and Literature Review

The third collector product that forms on the mineral surface is dixanthogen, the dimer of xanthate. Dixanthogen is formed through the catalytic oxidation of the collector, as described by reaction 1-4, where X_2 refers to dixanthogen.



In reaction 1-4, the mineral itself is not involved in the reaction. However, the presence of the mineral catalyses the rate of this reaction, which is otherwise a slow reaction (Woods, 1971). The mineral surface provides a pathway for the transfer of electrons between the cathodic and anodic sites. The dixanthogen that is formed is then weakly attached to the mineral surface through physisorption. Despite its relatively weak physisorption, dixanthogen has been recognised as the most hydrophobic collector product formed from the reaction schemes shown above (Leja, 1982).

The reduction of oxygen has been recognised as the cathodic reaction that allows the anodic reactions of the collector presented above to proceed (Woods, 1996; Fuerstenau et al., 2007). The reduction of oxygen at the mineral surface occurs according to reaction 1-5.



The type of collector species formed as described by the reaction scheme above depends on several factors, including collector chemistry, pH, Eh, availability of metal ions, type of mineral, dissolved oxygen and presence of any catalytic species that may favour specific reactions (Hu et al., 2009).

1.5.2. Collector chemistry

Collector chemistry depends on the type of functional group, length and structure of the alkyl chain. These factors affect the nature of the adsorption of the collector onto the mineral, and hence the resulting hydrophobicity. Hydrophobicity may also be affected by the amount of the collector (i.e. dosage) that is present in the system.

1.5.2.1. Effect of the functional group of the collector

As mentioned in 1.5.1, the adsorption of xanthate collectors involves a transfer of electrons. In general, this phenomenon is affected by the structure and/or composition of the functional or polar head group of the collector which bonds to the mineral surface. The electron-releasing or electron-withdrawing tendency of the collector depends on the electronegativity of the atoms that constitute the polar group. Atoms with high electronegativity tend to be electron-withdrawing (electron acceptors) while those with lower electronegativity tend to be electron-releasing (electron donors) ((Somasundaran & Nagaraj, 1984). In turn, this affects the reactivity of the collector with the mineral surface, with collectors that have a higher electron-releasing tendency being more reactive due to their greater availability of electrons to form bonds. However, the reactivity of collectors increases at the expense of their selectivity (Lotter & Bradshaw, 2010). Therefore, based on this, there are collectors such as trithiocarbonates

(TTC) and thioureas (TU) that could be considered to be more reactive, but less selective, compared to the conventional xanthate collectors.

TTC collectors differ from xanthates in that the functional group contains three divalent sulfur atoms that are bonded to the carbon atom, as opposed to two divalent sulfur atoms in xanthates. A schematic representation of the molecular structures of these collectors is shown in Figure 1.7. TTC collectors have been shown to be more beneficial in recovering sulfide minerals by flotation compared to conventional xanthate collectors (Breytenbach et al., 2003; Venter & Vermaak, 2008). Furthermore, TTC collectors are considered to interact with the mineral surface through both an electrochemical and non-electrochemical action. This was shown by Venter & Vermaak (2008) who found that TTC collectors could adsorb onto the mineral surface irrespective of the surface potential. That is, it could adsorb both under oxidising and reducing conditions, unlike xanthate collectors which require oxidising conditions for the charge transfer to take place.

Thiourea collectors are organosulfur compounds with the functional group -NHC(S)NH_2 as shown in Figure 1.7. These collectors are known to be strong chelating agents. They interact with the mineral surface through a complexation reaction between the metal cation from the mineral surface and the collector molecule/ion (Xu et al., 2021). Fairthorne et al. (1998) performed spectroscopic studies investigating the adsorption of butyl ethoxycarbonyl thiourea (BECTU) on chalcopyrite. Their work showed that the mechanism of thiourea adsorption involved multilayer adsorption by forming Cu-BECTU complexes. In the case of platinum-bearing minerals, the thiourea collector could adsorb on the mineral by forming a Pt-TU surface complex, where Pt is coordinated to the S and N atoms thus forming a 4-membered Pt-N-C-S ring structure (Somasundaran & Nagaraj, 1984; Henderson et al., 2001).

The molecular structures of a generic xanthate, trithiocarbonate and thiourea collector are shown in Figure 1.7 for comparison. The group electronegativity of the functional group of the collectors, calculated by averaging the electronegativities of the atoms constituting the polar head group, are also shown in Figure 1.7. Based on the electron-releasing tendency, hence reactivity with the mineral surface, of these collectors their collecting ability can be ranked as follows:

$$\text{TU} > \text{TTC} > \text{Xanthates}$$

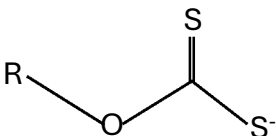
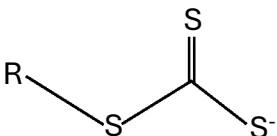
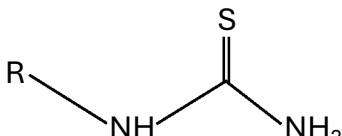
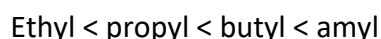
Xanthate	Trithiocarbonate	Thiourea
 R = alkyl chain		
$E_{\text{polar group}} = 2.79$	$E_{\text{polar group}} = 2.57$	$E_{\text{polar group}} = 2.20$

Figure 1.7: Generic molecular structure of a xanthate, trithiocarbonate and thiourea collector, where E represents electronegativity

1.5.2.2. Effect of length and structure of the alkyl chain of the collector

The alkyl chain is the non-polar group of the collector which is responsible for the hydrophobic character of the collector. Increasing the alkyl chain has been shown to increase the adsorption and collecting ability of the collector (e.g., Ackerman et al., 1987; Taguta et al., 2017; McFadzean et al., 2023). This is related to the inductive effect that the alkyl group exerts on the polar group of the collector. Inductive effect refers to the shifting of the electrons in response to the electronegativity of nearby atoms (McMurry, 2012). Longer alkyl chains exert a stronger inductive effect thus increasing the electron density and availability of electrons around the polar group. This results in the collector being more reactive with the mineral surface (Somasundaran & Nagaraj, 1984).

The inductive effect as the alkyl chain length increases also affects the ease with which dixanthogen forms. Dixanthogen forms at lower redox potentials as the alkyl chain length of the collector increases (Hamilton & Woods, 1979). This means that the collector can be more easily oxidised to dixanthogen, thus increasing the ability of the collector to impart hydrophobicity. Therefore, the collecting ability of the collector based on the length of the alkyl chain length can be arranged as follows:



Although increasing the alkyl chain length increases the collecting ability of the collector, this also depends on the structure of the alkyl chain. That is, whether the alkyl chain is branched or straight. Collectors with straight alkyl chains have been shown to outperform their branched-chain equivalents (Taguta et al., 2017; Özün & Ergen, 2019). This is due to the steric hindrance that is caused by the branched structure of the collector which results in lower surface coverage of the mineral. The collecting ability of branched collectors becomes progressively worse as the alkyl chain increases (Ackerman et al., 1987). Therefore, both the length and structure of the alkyl chain are important factors that determine the efficacy of the collector.

1.5.2.3. Effect of collector dosage

The hydrophobicity imparted to the mineral is also determined by the availability of the collector in the system. Collector dosage is an important factor to consider during flotation (Blake & Ralston, 1985; Crawford & Ralston, 1988). In single-mineral systems, collector dosage is often quoted in terms of surface coverage which refers to the number of collector molecules covering the mineral surface. For most minerals, collector dosage equivalent to a monolayer surface coverage or less is typically sufficient to render the mineral hydrophobic (Rao, 2004). However, there are minerals on which a monolayer surface coverage is not sufficient. For example, in a study conducted by Henwood (1995), it was reported that up to 20 to 30 monolayers of collector surface coverage may be required to obtain reasonably good recoveries. This was attributed to the irregularity of the pyrite structure where some sites are more active than others. Therefore, it is possible that dosages in excess of monolayer coverages would be required such that both the relatively strong and weaker sites are coated with the collector.

Pyrite and sperrylite share a similar crystal structure. Therefore, it is possible that sperrylite, like pyrite, may also require high collector dosage to obtain reasonably good flotation recoveries, although the similarity in the crystal structures of these minerals does not necessarily suggest a similar energetic heterogeneity of sites on the surface. A study conducted by Pikinini (2022) showed that adding 30 monolayers of a sodium n-butyl dithiocarbonate collector improved the recovery of sperrylite to 45% from 24% at 1 monolayer.

1.6. Role of solution

The scheme of reactions presented in section 1.5.1 suggests that the interaction of xanthate with minerals is a strong function of electrochemical potential (Eh) and pH, both of which determine the thermodynamic stability of the collector species formed. In general, the quality of the process water used in flotation will affect the interactions occurring at the mineral-solution interface. Factors that describe water quality include Eh, pH, type of ions present and ionic strength.

1.6.1. Effect of ionic strength

Ionic strength can be understood as the measure of the average electrostatic interactions of the ions in the solution. It depends on the molality (m_i) and charge (z_i) of the ions according to equation 1-6.

$$I = \sum_{i=1}^n m_i z_i^2 \quad 1-6$$

Ionic strength has been shown to have an influence on factors including bubble-particle attachment efficiency, induction time, bubble size and critical hydrophobicity (Blake & Ralston, 1985; Crawford & Ralston, 1988; Hewitt et al., 1995). The effect of ionic strength on slow floating or weakly hydrophobic minerals is of particular interest in this study.

Increasing ionic strength improves the kinetics of flotation by decreasing the bubble-particle attachment induction time (Hewitt et al., 1995). This improvement is considered to be due to the reduction in the electrostatic repulsion between the mineral particle and the bubble, thus enabling easier and more efficient bubble-particle attachment. The improved flotation kinetics can also be attributed to reduced bubble coalescence at higher ionic strength thus resulting in smaller bubble sizes, of which this is essential for efficient bubble-particle attachment (Michaux et al., 2018). The following events must occur for bubble-particle attachment to occur (Crawford & Ralston, 1988; Hewitt et al., 1995):

- i) The liquid film between the particle and bubble must be drained and ruptured,
- ii) The gas-liquid-solid contact lines must expand to form a wetting perimeter

The time taken for these two events to occur is referred to as the induction time. It is during these events that the hydrophobicity and ionic strength play a role. Studies (e.g., Crawford & Ralston, 1988; Hewitt et al., 1994, 1995) have shown that the effect of increasing ionic strength is more effective in weakly hydrophobic particles, as is the case for sperrylite. For instance, Hewitt et al. (1995) found that the effect of increasing ionic strength in improving bubble-particle attachment efficiency was more noticeable for quartz particles with lower degrees of hydrophobicity. Similar findings have been reported by Shackleton et al. (2012). In their study, it was shown that increasing ionic strength improved the flotation recovery of moncheite (a relatively less hydrophobic PGM) to a larger extent than it did for pentlandite (a relatively more hydrophobic sulfide). Therefore, the effect of ionic strength on sperrylite which is much more hydrophilic compared to these minerals is of interest.

1.6.2. Effect of electrochemical potential

The anodic sites where collector oxidation occurs and the cathodic sites where oxygen reduction occurs are both hosted at the mineral-solution interface. They are related through the potential across the mineral-solution interface (Woods, 1971). When the rate of the anodic reactions equals the rate of the cathodic reactions, the resulting potential is referred to as the rest potential or mixed potential for multiple reactions (Rao, 2004).

Allison et al. (1972) studied the type of collector species formed on the surface of sulfide minerals as a function of rest potential. They found that if the rest potential of the mineral in a solution is higher than the equilibrium potential of the xanthate/dixanthogen couple, then dixanthogen is more likely to form. On the other hand, if the rest potential is lower, then chemisorbed xanthate or metal xanthate are more likely to form on the mineral surface. The formation of chemisorbed xanthate, often referred to as underpotential deposition, is thermodynamically favoured at lower potentials than the equilibrium potential for the formation of metal xanthate. Ultimately, this suggests that increasing potential should promote the oxidation of xanthate to dixanthogen, hence increasing the imparted hydrophobicity and floatability of the mineral (Buckley & Woods, 1997). In general, whether the conditions are oxidising or reducing will determine whether the mineral may be recovered by true flotation (Gardner & Woods, 1979).

In the case of sperrylite, Vermaak et al. (2007) measured the hydrophobicity of this mineral using contact angles and showed it is hydrophilic at low potentials. In their study, sperrylite was found to have a contact angle of zero at potentials less than 200 mV vs SHE. Vermaak et al. (2007) showed that increasing the potential to at least 100 mV vs SHE above the equilibrium potential of the xanthate/dixanthogen couple increased the hydrophobicity of the mineral. This is illustrated in Figure 1.8.

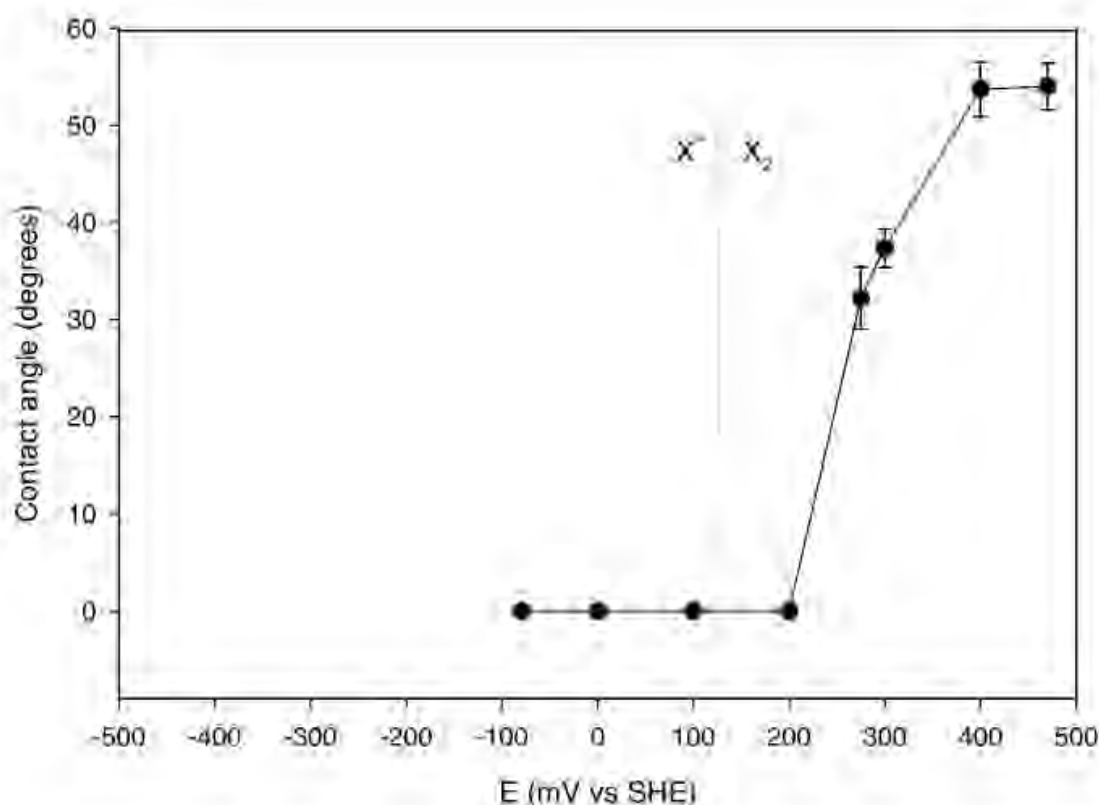


Figure 1.8: Contact angles of sperrylite as a function of Eh in the presence of 10^{-3} M KEX at pH 9 (Vermaak, Pistorius, et al., 2007)

The limitation of the study by Vermaak et al. (2007) is that potentiostatic control of Eh was employed where anodic polarization of the mineral was achieved by passing a current through the mineral. Although this method of Eh control is appropriate, since it does not introduce redox reagents, it is not applicable to plant practice (Hayes & Ralston, 1988). Therefore, it is not clear whether the hydrophobicity of sperrylite would be enhanced at higher Eh conditions if Eh was controlled via the addition of redox reagents

1.6.3. Effect of pH

The pH of the solution has various effects on the interactions at the mineral-solution interface. Similar to Eh control, pH control is often used to selectively float minerals while depressing others. This is because different minerals respond differently to changes in Eh-pH conditions.

1.6.3.1. Competitive effect between collector and hydroxy species

At high pH conditions, there is a high concentration of OH^- that are present in the solution. These ions can react with the metal cations from the mineral to produce hydrophilic hydroxides according to reaction 1-7.



In the same instance, the reaction scheme presented in section 1.5.1 showed that the collector also reacts with the mineral surface. Therefore, both the collector and hydroxy species compete for adsorption sites on the mineral surface. This competitive effect can be described by the Barsky relationship, defined by reaction 1-8 (Somasundaran & Wang, 2006).

$$K = \frac{[\text{X}^-]}{[\text{OH}^-]} \quad 1-8$$

The lower the Barsky constant, K, the higher the inhibition of collector adsorption due to the adsorption sites on the mineral surface being taken by the hydrophilic hydroxy species. This is the case at high pH conditions where the concentration of OH^- ions is high. The inhibitory effect of OH^- can be countered by increasing the concentration of the xanthate collector (Janetski et al., 1977).

Different minerals have different affinities for OH adsorption. Therefore, the amount of collector required to counter the effect of OH is different for different minerals. Waterson et al. (2016) have shown through computational modelling that OH^- preferentially adsorb on sperrylite with a binding energy of -473.8 kJ/mol compared to -299.5 kJ/mol for ethyl xanthate or -51.5 kJ/mol for diethyl dixanthogen. This high affinity of sperrylite for OH adsorption probably plays a role in the low degree of hydrophobicity of this mineral at pH 9.

In a study conducted by Pikinini (2022), it was shown that the adsorption of potassium n-butyl xanthate (PNBX) on sperrylite could be significantly improved by lowering the pH from 9 to 4. However, despite the improved collector adsorption at the lower pH, this did not result in a correspondingly high sperrylite recovery. This is probably due to the fact that a collector dosage equivalent to 1 monolayer surface coverage was used, which was deemed not sufficient to render sperrylite significantly hydrophobic as mentioned in section 1.5.2.3. The work of Pikinini (2022) provides preliminary evidence that sperrylite may require high collector dosages and/or low pH conditions for it to be floatable using xanthate collectors.

1.6.3.2. Effect of pH on potential at which the mineral and collector are oxidised

The suitable anodic conditions required for the oxidation of xanthate can be achieved by controlling the Eh of the system as mentioned in section 1.6.2. However, for systems that involve H^+ and OH^- ions such as those encountered in flotation, pH and Eh are related through the Nernst relationship described by equation 1-9 (Archer, 1989; Cheng & Iwasaki, 1992)

$$E_h = E^0 - 0.0592\text{pH} - \frac{0.0592}{n} \log \left(\frac{a_{\text{oxidation}}}{a_{\text{reduction}}} \right) \quad 1-9$$

Chapter 1: Introduction and Literature Review

where:

- E_h - Redox potential
- E^0 - Standard electrode potential
- n - Number of electrons transferred
- a - Activities of the oxidised and reduced species

Therefore, the formation of dixanthogen can also be affected by changes in pH. Tadie et al. (2015a,b) found that the formation of dixanthogen from sodium ethyl xanthate (SEX) was not thermodynamically favoured on the surface of $PtTe_2$ at pH 9. However, at pH 4.2 the formation of dixanthogen was thermodynamically favoured. They attributed this to increased electro-catalytic activity of the mineral to facilitate dixanthogen formation at lower pH. This phenomenon is also true in the case of sulfide minerals. For instance, dixanthogen formation has been shown to be inhibited at high pH conditions (pH 11.4) on pyrite (Janetski et al., 1977; Göktepe, 2002).

Linking this to flotation, it can be established that there is a critical pH above which the flotation of the mineral will be inhibited. The optimum flotation range will depend on several factors including type of mineral, type of collector and concentration, E_h and pH. In flotation, the challenge is often to find the conditions suitable for the selective flotation of the mineral of interest. There is extensive literature on how most sulfide minerals respond to changes in E_h -pH conditions and these relationships are generally represented as Pourbaix diagrams (Pourbaix, 1974). For instance, the flotation domains of some sulfide minerals have been empirically arranged as illustrated in Figure 1.9.

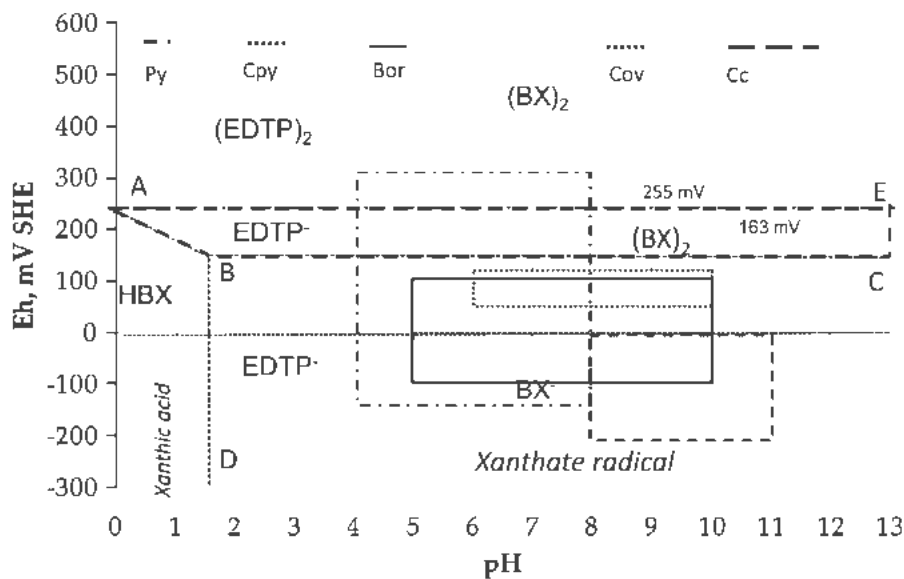


Figure 1.9: Flotation domains of sulfide minerals: Py = pyrite, Cpy = chalcopyrite, Bor = bornite, Cc = covellite; with Pourbaix diagrams of butyl xanthate and ethyl dithiophosphate overlain (Lotter et al., 2016)

For PGMs, there is only very limited information on such relationships. The reviewed literature suggests that the operating conditions (e.g. pH 9) in a typical PGM concentrator are not conducive for xanthate adsorption on sperrylite. Therefore, it is possible that the optimal flotation domain of sperrylite, as a function of Eh and pH, lies outside the typical operating conditions.

1.7. Role of mineral

As mentioned before, some minerals are naturally hydrophobic and often do not require the addition of collectors during flotation. Other minerals are naturally hydrophilic and the addition of collectors is necessary to induce hydrophobicity. This depends on the mineral properties such as crystal structure, surface and electronic properties of the mineral.

1.7.1. Natural floatability of minerals

Over the years, many views have been proposed regarding the natural floatability of minerals. The factors that have been proposed to affect natural floatability may be summarised into 1) crystal structure features, 2) thermodynamics of adhesion of water to the mineral surface, and 3) self-induced hydrophobicity of the mineral under specific pulp conditions.

1.7.1.1. Crystal structure effect

Minerals can be naturally hydrophobic due to the crystal structure features of the mineral. For instance, molybdenite is the most well-known sulfide mineral that exhibits native hydrophobicity. Native hydrophobicity can be acquired when the mineral is cleaved resulting in the exposure of a hydrophobic surface (Rao, 2004). The crystal structure of molybdenite consists of S-Mo-S layers held by Van der Waals forces. It exhibits two types of surfaces when cleaved, viz. 1) non-polar faces that result from the breakage of S-S bonds, 2) polar edges that result from the breakage of strong Mo-S covalent bonds (Castro et al., 2016). Molybdenite preferentially cleaves along its non-polar face and this is considered to play a role in the native hydrophobicity exhibited by this mineral.

In the case of PtTe_2 and PdTe_2 , these minerals crystallize into the trigonal CdI_2 -type crystal structure and belong to the Melonite Group. A schematic representation of the crystal structure of these minerals is shown in Figure 1.10.

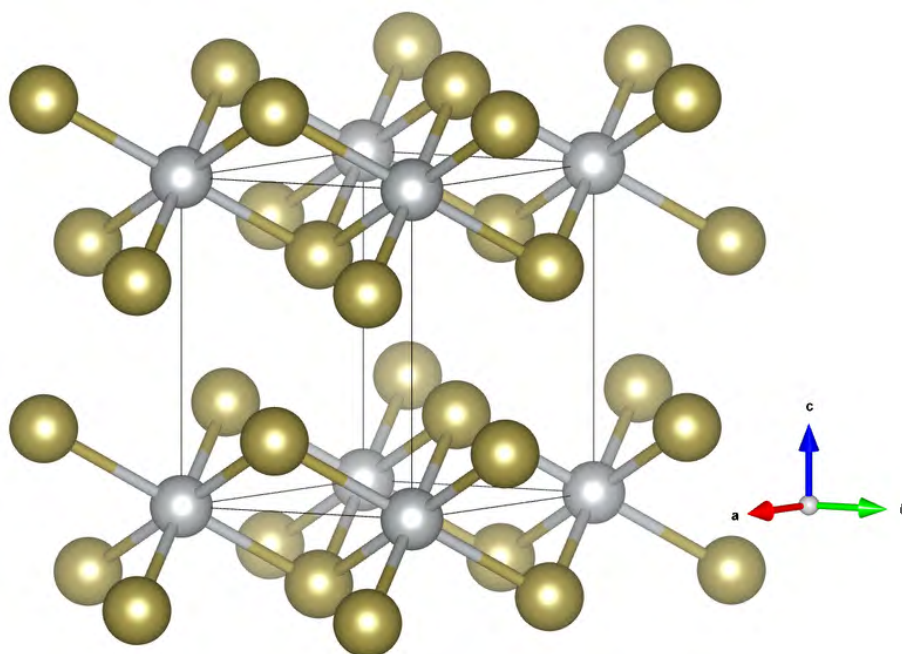


Figure 1.10: Crystal structure of Melonite Group minerals (PtTe₂ and PdTe₂).
Legend: grey = Pt or Pd, green = Te (commons.wikimedia.org)

This is a layer-lattice structure where the Pt or Pd atoms are surrounded by six Te atoms forming sheets of MTe₆ (M = Pt or Pd) octahedra along the basal plane. The sheets are held together by Van der Waals forces (Politano et al., 2018). The weak interlayer interactions on the crystal structure of these minerals provide a likely plane of cleavage by which the mineral surface can interact with the prevailing solution environment.

Sperrylite crystallizes into the isomeric system and shares a similar crystal habit and structure with pyrite. Its crystal structure belongs to the Pa3-T_h⁶ space group (Muller & Lutz, 1991). A unit cell of sperrylite is shown in Figure 1.11a. This crystal structure is characterised by distorted tetrahedral coordination around the As atoms and distorted octahedral coordination around the Pt atoms. The exposed surface of sperrylite consists of 'clefts' and 'ridges' where the Pt atoms occupy the clefts between the ridges made by the As atoms. This is shown in Figure 1.11b

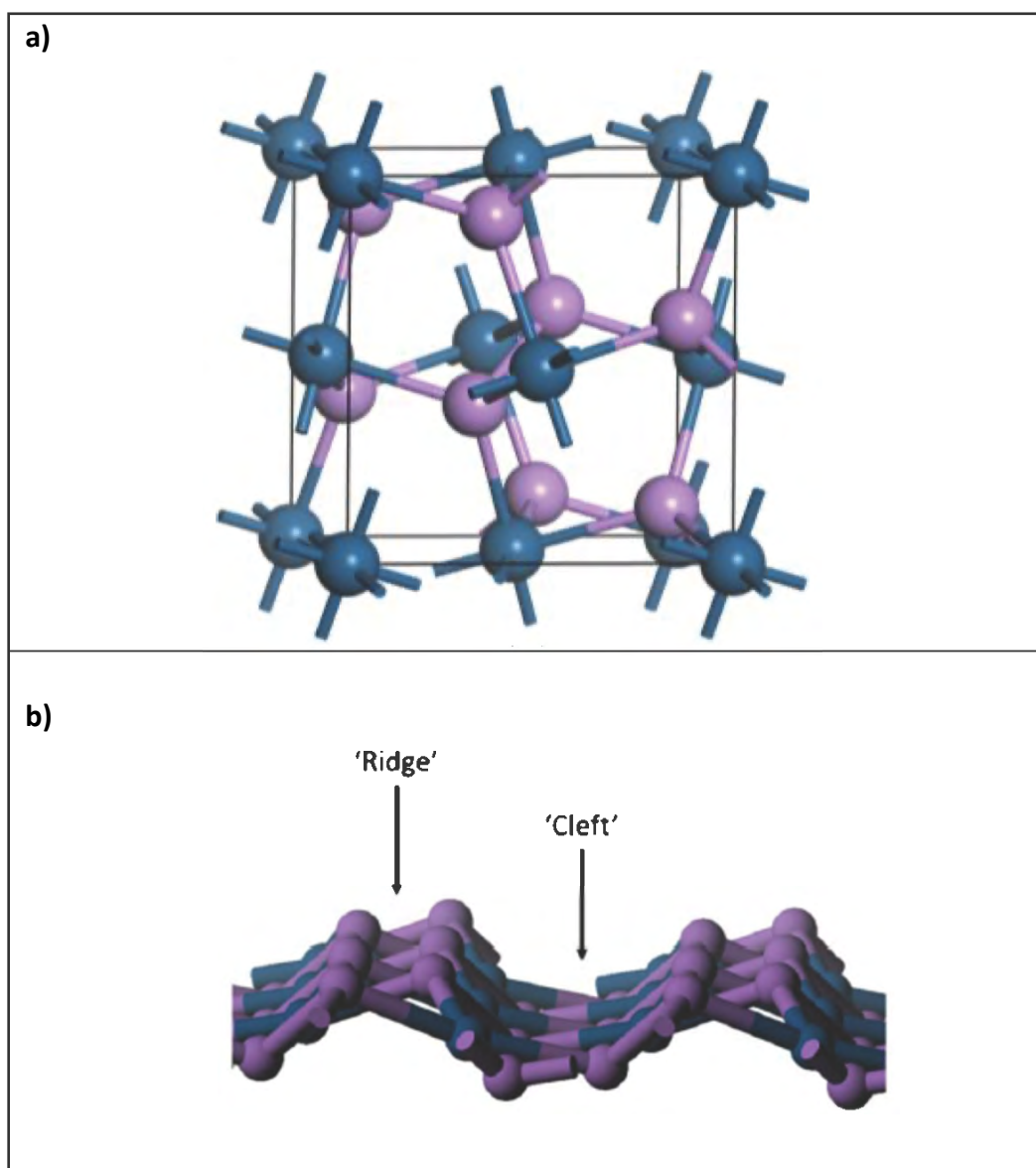


Figure 1.11: a) Bulk crystal structure, b) working surface of PtAs₂. Legend: blue = Pt, purple = As (Waterson, 2015)

The surface of sperrylite suffers from both steric hindrance caused by the raised As atoms as well as electronic hindrance caused by the As lone pairs. Due to the lack of exposure of the Pt atoms, these atoms may be hindered from interacting with collector ligands during flotation (Waterson et al., 2016). Waterson et al. (2016) proposed that the surface structure of sperrylite may contribute to its poor flotation performance that has been observed by other authors (e.g. Shackleton et al., 2007; Shamaila & O'Connor, 2008; Pikinini, 2022). However, the study by Shackleton et al. (2007) did not find a correlation between the crystal structure of the PGMs and their flotation performance. On the other hand, a study by Pikinini (2022) proposed that the floatability of sperrylite could be linked to its crystal structure and the As atoms on the surface which can act as electron acceptors which would increase the number of collector adsorption sites thereby reducing the overall collector binding energy on the Pt atoms.

Palladoarsenide crystallizes in the monoclinic crystal structure system (Saini et al., 1964). The crystal structure of this mineral is shown in Figure 1.12.

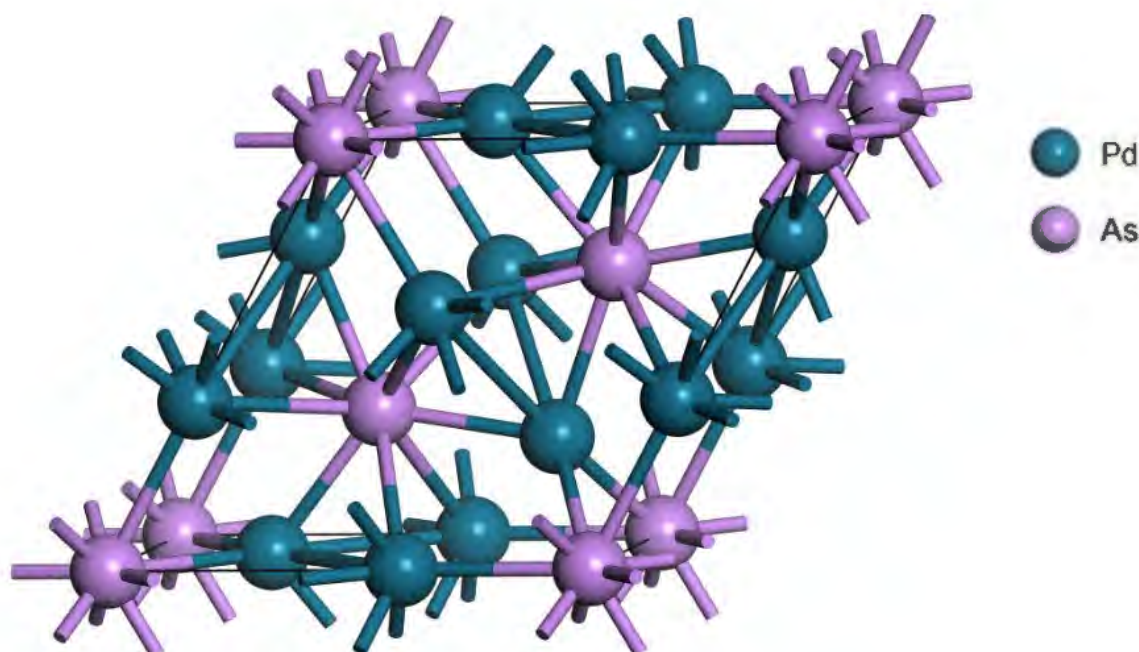


Figure 1.12: Crystal structure of Pd_2As (Nemutudi, 2020)

1.7.1.2. Thermodynamics of adhesion of water

In terms of thermodynamics, a hydrophilic mineral is one in which the energy of adhesion of water exceeds that of the cohesion of water at the mineral surface (Rao, 2004). In such a case, the mineral is completely wetted by the water phase. On the other hand, a hydrophobic mineral is only partially wetted by the water phase. As a result, the hydrophobicity of minerals is often measured in terms of wettability. This phenomenon can be readily related to the surface energy of the mineral, where minerals with a lower surface energy tend to be less wettable and hence more hydrophobic (Taguta et al., 2018, 2019). In this context, surface energy refers to the excess energy per unit area when the mineral is cleaved by breaking the inter-planar chemical bonds thereby exposing polar and non-polar sites on the mineral surface (Gao et al., 2019).

The surface energy of minerals can be correlated to their natural floatability. This is shown in Figure 1.13 for some PGM and sulfide minerals. In general, the natural floatability of the mineral increases with a decrease in its surface energy. For instance, sperrylite with its relatively higher surface energy (about 1.04 J/m^2) has a poor natural floatability. A similar relationship between the heat of immersion, which is a measure of wettability, and floatability has been found by Taguta et al. (2018). In their study, Taguta et al. (2018) found that there is

a critical heat of immersion beyond which no flotation occurs which was reported to be around 0.2 J/m^2 .

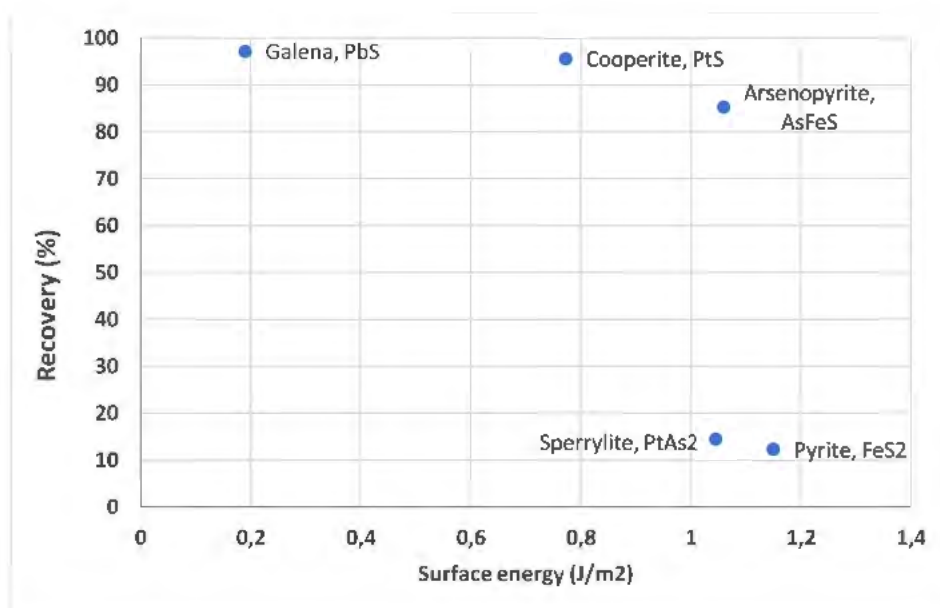


Figure 1.13: Relationship between the natural floatability and surface energy of PGM and sulfide minerals (Pikinini, 2022)

1.7.1.3. Self-induced hydrophobicity at specific pulp conditions

Minerals can acquire hydrophobicity when exposed to specific pulp conditions (e.g. pH and Eh) resulting in a chemical reaction on the mineral surface with water or dissolved oxygen. For instance, elemental sulfur and/or a metal-deficient surface which are formed through mild oxidation are considered to be necessary for the self-induced hydrophobicity of sulfide minerals (Rao, 2004; Hu et al., 2009). The ability of minerals to form a hydrophobic layer via mild oxidation and the stability of this hydrophobic layer is generally linked to their natural floatability (Heyes & Trahar, 1977, 1979; Hayes et al., 1987).

1.7.2. Effect of the electronic properties of the minerals

As already established, the reactions between the collector, solution and the mineral are predominantly electrochemical in nature. This involves the transfer of electrons from the oxidation of the collector at the anodic site which are accepted by oxygen at the cathodic site. The mineral is required to be conductive in order to sustain this transfer of electrons. Therefore, the electronic properties of the mineral play a major role in this regard. A fundamental property of the conductivity of electrons is the band gap energy. The band gap energy arises from the energy that is required for electrons to migrate from the valence band to the conduction band of the mineral. This migration of electrons is what allows conduction and is necessary during xanthate adsorption (Leja, 1982). A schematic representation of the band gap energy for different types of minerals is illustrated in Figure 1.14.

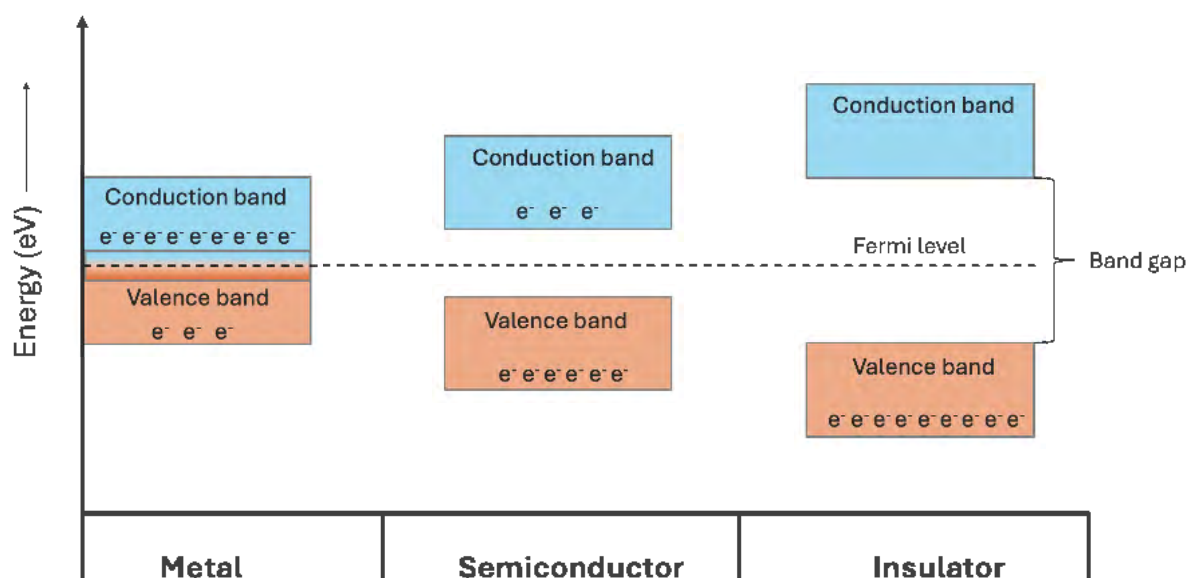


Figure 1.14: Schematic representation of band gap energy of metallic, semiconductor and insulator minerals

The Fermi level corresponds to the energy level that has an equal probability of being occupied or unoccupied (Leblanc et al., 1986). That is, it lies halfway in the band gap. The bigger the band gap, the more energy is required for the electrons to migrate into the conduction band. Minerals with larger band gaps have poor conducting properties, and therefore poor catalysts for xanthate adsorption.

The electrochemical reactions describing collector adsorption presented in section 1.5.1 can now be understood in terms of molecular orbitals and band gap energy. This is illustrated in Figure 1.15 using the adsorption of butyl xanthate and diethyl dithiocarbamate on pyrite as an example.

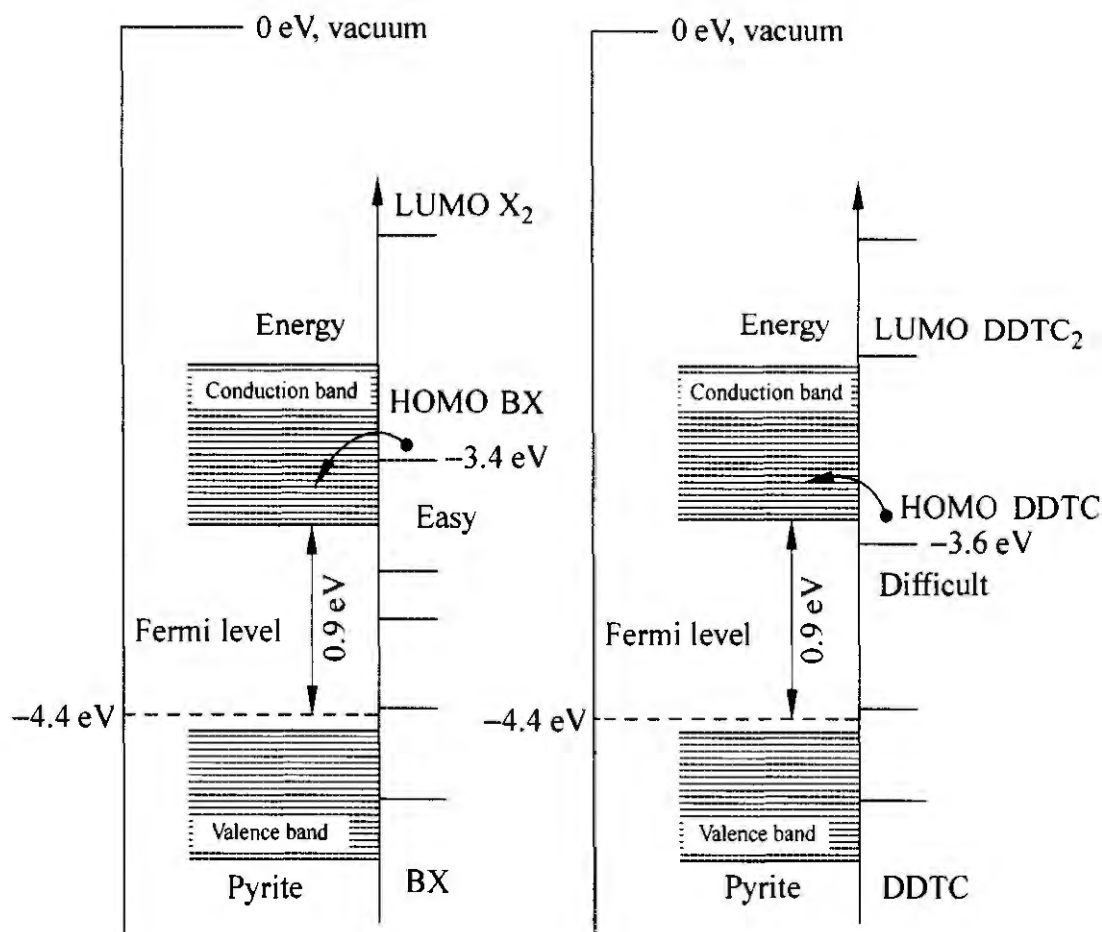


Figure 1.15: Mechanism of collector adsorption illustrated using butyl xanthate (BX) and diethyl dithiocarbamate (DDTC) adsorption on pyrite (Hu et al., 2009)

HOMO refers to the highest occupied molecular orbital while LUMO refers to the lowest unoccupied molecular orbital. For electron transfer to be thermodynamically favourable, electrons are transferred from the HOMO level of the collector (higher energy) to the LUMO level of the mineral (lower energy). In Figure 1.15, the HOMO level of xanthate is higher than the bottom of the conduction band of pyrite (i.e. LUMO of pyrite). Therefore, the transfer of electrons from xanthate to pyrite resulting in the formation of dixanthogen is thermodynamically favoured. However, in the case of DDTC its HOMO level is lower than the LUMO level of pyrite and therefore the formation of the dimer of DDTC on pyrite is not thermodynamically favoured (Hu et al., 2009). The formation of the dimer of DDTC on pyrite could be promoted by operating under stronger oxidizing conditions or shifting the Fermi level to more negative values. The Fermi level is similar to the electrochemical potential in that they both describe the tendency of the mineral to accept or donate electrons. The more negative the Fermi level, the higher the electrochemical potential and therefore the greater the tendency to accept electrons (Hu et al., 2009).

Following from this, the interaction of xanthate with the PGMs to be investigated in this study can be related to the electronic properties of these minerals. PdTe_2 and PtTe_2 have good

conductive properties due to the bonding nature within these minerals. Bonding in these metal dichalcogens occurs between the p-orbitals from the chalcogen (Te) and d-orbitals from the metal (Pt or Pd). The small band gap energy between the p-d orbitals gives PdTe₂ and PtTe₂ their metallic properties (Guo et al., 1986; Dai et al., 2003). Therefore, these minerals can be expected to have good electron-conducting properties which is a requirement during xanthate adsorption. On the other hand, bonding within PtAs₂ occurs between the 5d orbitals of Pt and 4p orbitals of As. Non-metallic behaviour has been reported for PtAs₂ with a semi-conductor band gap of 0.34 eV wherein this originates from the hybridization effect between the d-p orbitals of Pt and As (Nguyen-Manh et al., 1999). Electrochemical investigations performed by Pikinini (2022) showed that PtAs₂ may be electrochemically inert and this is probably due to the poor conductive properties of this mineral.

The better conducting properties of the PGE tellurides may explain their better floatability with xanthate collectors compared to PGE arsenides reported by (Shackleton, 2007) and Shamaila & O'Connor (2008). The recoveries of these PGMs reported by Shackleton (2007) are shown in Table 1.1.

Table 1.1: Microflotation recoveries of PGE tellurides and arsenides at pH 9 (Shackleton, 2007)

Mineral	No Collector	With 6.25x10 ⁻⁰⁶ mol/g SIBX
PtAs ₂ (NS145)*	7.14%	74%
PtAs ₂ (NS146)	0.9%	1.9%
Pd ₂ As	27%	96%
PtTe ₂	49%	>99%
PdTe ₂	63%	>99%

*The characterisation of this mineral showed high unreacted Pt phases, and the high recovery of this mineral was attributed to this in the study by Shackleton (2007)

1.8. Summary and Gap Analysis

There is only a rather limited understanding of the floatability of PGMs. Much of the previous research on the recovery of PGMs has focused on the recovery of base metal sulfides due to the association of these minerals with PGMs. However, the PGMs in the Platreef ore body generally have a poor association with base metal sulfides as well as a scarcity of PGE sulfides. As a result, the typical reagents suites and flotation conditions that have been optimised for recovering sulfide-bearing minerals have not been as effective in recovering the PGMs from the Platreef. In particular, the floatability of sperrylite has been shown to be poor when using xanthate collectors at pH 9, the typical collectors and operating in PGM concentrators. This has raised the need to improve the understanding of the role of the collector, the solution and the mineral in relation to how these affect the floatability of PGMs, especially sperrylite.

The poor flotation of sperrylite has been shown to be mainly due to the poor adsorption of xanthate collectors on the surface of this mineral at pH 9 (Shackleton et al., 2007; Pikinini, 2022). For instance, electrochemical investigations performed by Pikinini (2022) showed that

PNBX had a minimal extent of interaction with sperrylite at pH 9. Therefore, the use of collectors capable of stronger interactions is a research area of interest in this regard. Trithiocarbonate and thiourea collectors have been shown to potentially offer some benefits compared to the conventional xanthate collectors. This can be attributed to the functional groups of the trithiocarbonate and thiourea collectors which have a greater electron-releasing tendency, and hence better reactivity with the mineral surface, compared to the conventional xanthate collectors.

The efficacy of xanthate collectors is a strong function of solution conditions such as pH and Eh. There is extensive literature on how the floatability of sulfide minerals with xanthate collectors changes as a function of pH and Eh. For PGMs, there is only very limited information on such relationships. There is some evidence which suggests that the optimal flotation domain of sperrylite, as a function of pH and Eh, lies outside the typical operating PGM flotation conditions. For instance, preliminary investigations by Pikinini (2022) showed that the adsorption of xanthate on sperrylite could be improved at acidic conditions. With regards to Eh, Vermaak et al. (2007) showed that increasing the potential to at least 100 mV vs SHE above the equilibrium potential of the xanthate/dixanthogen couple increased the hydrophobicity of sperrylite, presumably due to an increase in the formation of and adsorption of dixanthogen. However, in the study by Vermaak et al. (2007) the Eh was controlled via anodic polarization achieved by passing a current through the mineral which is not readily applicable to plant practice. Therefore, it is not clear whether the hydrophobicity of sperrylite would be enhanced at higher Eh conditions if Eh was controlled via the addition of redox reagents which is more readily applicable to plant practice.

Finally, the role of the properties of sperrylite and how they contribute to the poor floatability of this mineral are not clearly understood. This is especially true when viewed in the context of other similar PGMs such as palladoarsenide or merenskyite which have a relatively much better floatability compared to sperrylite. Computational studies have suggested that the poor floatability of sperrylite is due to the inaccessibility of the Pt atoms on the surface structure of this mineral, thus hindering them from interacting with collector ligands during flotation (Waterson et al., 2016). However, there has been no clear evidence that relates the crystal structure of PGMs with their flotation performance. For instance, the study by Shackleton et al. (2007) did not find a correlation between crystal structure and the flotation performance of PGE arsenides and tellurides (i.e. sperrylite, palladoarsenide, moncheite and merenskyite). On the other hand, a study by Pikinini (2022) proposed that the floatability of sperrylite could be linked to its crystal structure and the As atoms on the surface which can act as electron acceptors which would increase the number of collector adsorption sites thereby reducing the overall collector binding energy on the Pt atoms. In general, it is known that the floatability of minerals may be influenced by crystallographic, electronic, surface characteristics, as well as the solution environment. Therefore, it is of interest to compare the floatability of sperrylite with other PGMs under different solution conditions in order to

establish how the inherent mineral properties (e.g. crystal structures, electronic properties) and solution conditions affect the floatability of these minerals.

1.9. Hypotheses

In carrying out the present research, it was necessary at the outset to propose appropriate hypotheses to be addressed in the experimental programme. These are presented below.

Hypothesis 1:

The trithiocarbonate and thiourea collectors will bond more strongly with sperrylite and improve the floatability of this mineral to a greater extent compared to xanthate collectors. This is because the functional groups of the trithiocarbonate and thiourea collectors have a greater electron-releasing tendency resulting in a greater availability of electrons to form bonds with the mineral surface.

Hypothesis 2:

Sperrylite will have a better floatability at lower pH and/or higher Eh conditions compared to the current operating conditions of pH 9 and Eh $\approx$ 160 mV vs SHE. This is because:

- Lowering pH reduces the concentration of OH⁻ ions that would otherwise compete with the collector for adsorption sites on the mineral surface
- At lower pH, the formation of dixanthogen is thermodynamically favoured and this is required to impart sufficient hydrophobicity on sperrylite
- At higher Eh conditions, at least 100 mV vs SHE above the xanthate/dixanthogen equilibrium potential, the formation of dixanthogen is thermodynamically favoured

Hypothesis 3:

Sperrylite has a poorer floatability compared to other PGMs including palladoarsenide, moncheite and merenskyite. It is hypothesised that this is due to sperrylite being more electrochemically inert and therefore less conducive to sustaining electron charge transfer between the collector and the mineral.

CHAPTER 2: Research Objectives

2. Research Objectives

2.1. Research Objectives

The main objective of this study was to investigate the floatability of PGE arsenides and tellurides, viz. sperrylite, palladoarsenide, moncheite and merenskyite, with the primary focus being to understand and improve the floatability of sperrylite by exploiting flotation chemistry.

The key objectives of the study were:

- To determine the floatability of sperrylite using collectors with different functional groups, including xanthate, trithiocarbonate and thiourea collectors;
- To determine the effect of pH and Eh on the floatability of sperrylite to find its optimal flotation domain
- To determine the reasons for the poor floatability of sperrylite compared to other PGMs such as palladoarsenide, moncheite and merenskyite
- To determine the applicability of the results by comparing the microflotation results, which provide ideal mineral floatabilities, with the results obtained from batch flotation studies which provide a more realistic scenario
- To develop an alternative technique of assaying Pt, As, Pd, and Te without relying on mineralogical analysis, which is often time-consuming, costly and statistically compromised

2.2. Key Questions

The key question driving this research was:

“How can flotation chemistry, as determined by the mineral, collector and solution, be exploited to improve the hydrophobicity of sperrylite?”

From this, other key questions which guided the research towards answering this question were:

On collector chemistry:

- What is the flotation response of sperrylite using xanthate, trithiocarbonate and thiourea collectors?
- What is the effect of collector ligand type on the heat of collector adsorption on sperrylite which is a measure of the strength of collector adsorption?
- What is the effect of alkyl chain length on the heat of collector adsorption on sperrylite?
- What is the effect of the ionic strength of the process water used in flotation and the collector dosage on the floatability of sperrylite?

Chapter 2: Research Objectives

- How do the mineral flotation results obtained from microflotation studies compare with those obtained from batch flotation studies?

On solution chemistry:

- How do pH and Eh affect the floatability of sperrylite?
- What is the extent and nature of xanthate collector adsorption on sperrylite under varying pH and Eh conditions?
- How does the chemical control of Eh using a modifier such as NaClO affect the floatability of sperrylite?

On mineral comparisons:

- How do the natural floatabilities of the PGE arsenides and tellurides compare under varying pH conditions?
- How do the collector-induced floatabilities of the PGE arsenides and tellurides compare under varying pH conditions?
- What is the relationship between the electrochemical potential, as determined by rest potential measurements, and electronic properties, such as band gap energy, of the PGE arsenides and tellurides?
- Can pH reduction be applied in a more realistic scenario which includes the froth phase, a complex ore and complex cell hydrodynamics such as in batch flotation tests?

2.3. Research Approach

This study was organised into three phases, with each phase designed to address specific research questions as outlined in section 2.2. The areas of focus in each phase are shown in Figure 2.1. **Phase One** focused on the use of collectors with different functional groups on sperrylite. **Phase Two** focused on the effect of pH and Eh on the floatability of sperrylite. Finally, **Phase Three** focused on comparing the floatabilities of the PGE arsenides and tellurides.

Chapter 2: Research Objectives

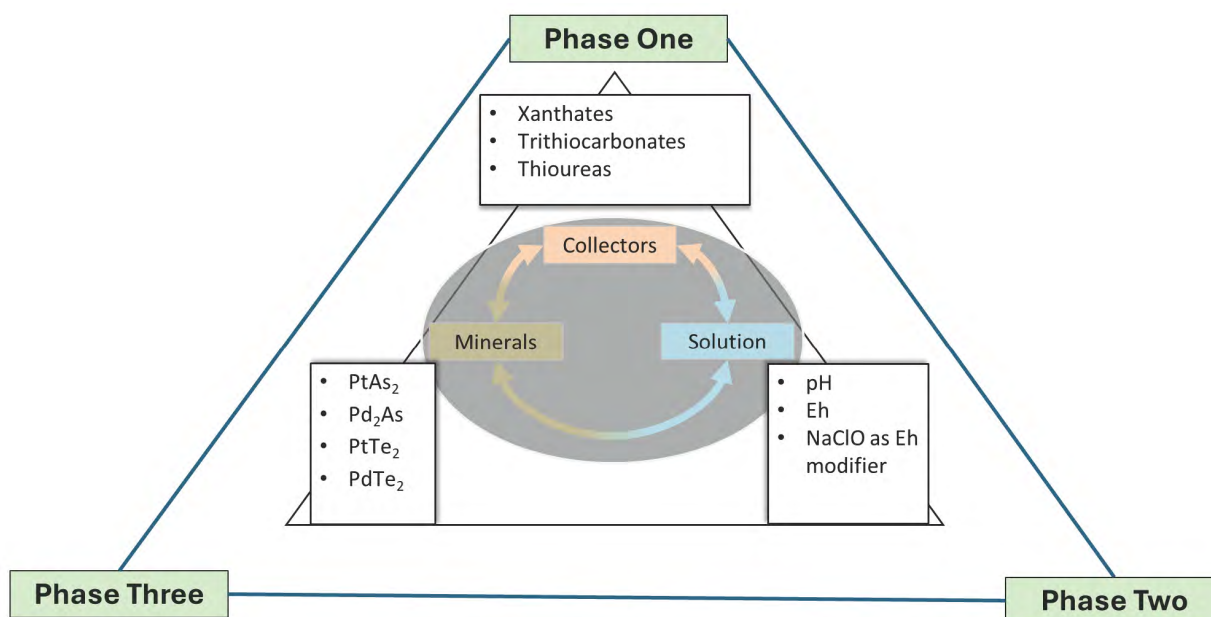


Figure 2.1: Focus of Phase One, Two and Three of this thesis

2.3.1. Phase One: Investigation of collectors on flotation of sperrylite

The research approach used in **Phase One** is illustrated in Figure 2.2. The effects of collector type, collector dosage and ionic strength on the floatability of sperrylite were investigated. The floatability of the pure mineral was investigated using microflotation. In order to better understand the extent of interaction of the collectors with sperrylite and the resultant performance, adsorption isotherms obtained using UV-vis spectroscopy were compared with the microflotation recoveries. This was further supported by determining the collector-mineral energy of interaction, as measured using isothermal titration calorimetry. Thereafter, selected conditions including collector type and ionic strength were investigated in batch flotation tests to compare the flotation results with those obtained from microflotation.

Chapter 2: Research Objectives

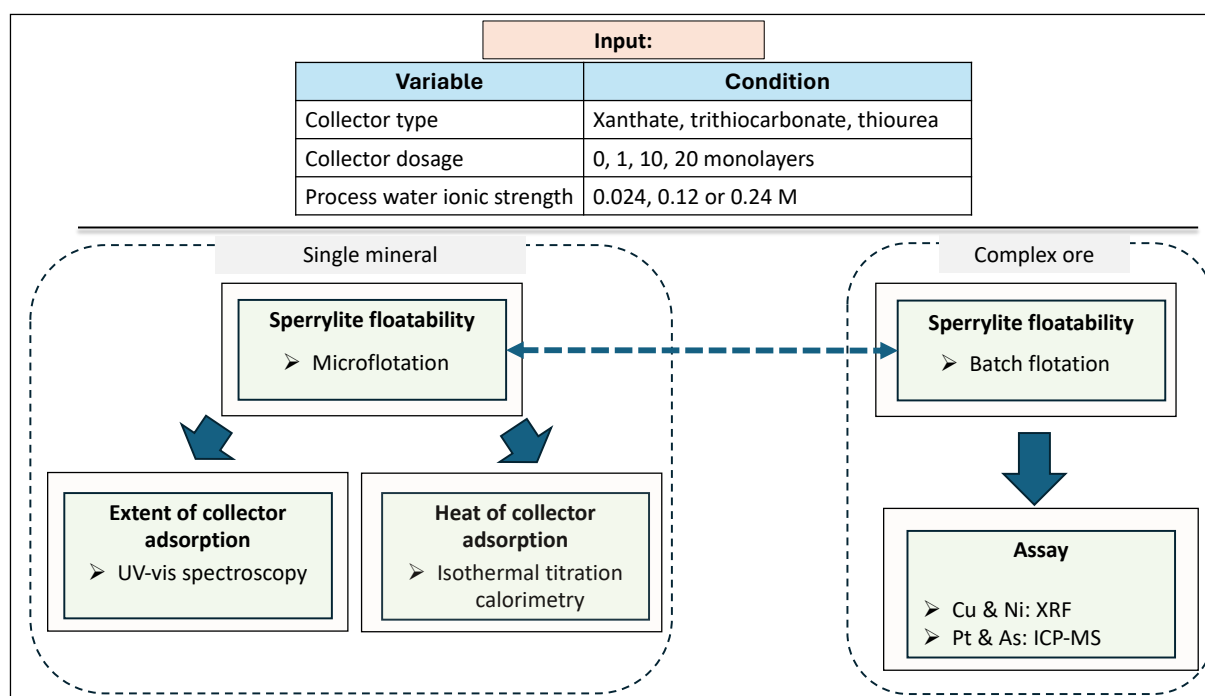


Figure 2.2: Research approach used in Phase One

2.3.2. Phase Two: Effect of pH-Eh on floatability of sperrylite

The research approach used in **Phase Two** is illustrated in Figure 2.3. The floatability of sperrylite, as determined using microflotation, was investigated under varying pH and Eh conditions. The use of a redox reagent, NaClO, to chemically control the Eh was also investigated. Rest potential measurements were employed to determine the electrochemical interactions that may be occurring between sperrylite and PAX collector at different pH and Eh conditions. The chemical speciation resulting from these interactions on the surface of sperrylite was characterised using surface characterisation techniques including zeta potential measurements and spectroscopic studies.

Chapter 2: Research Objectives

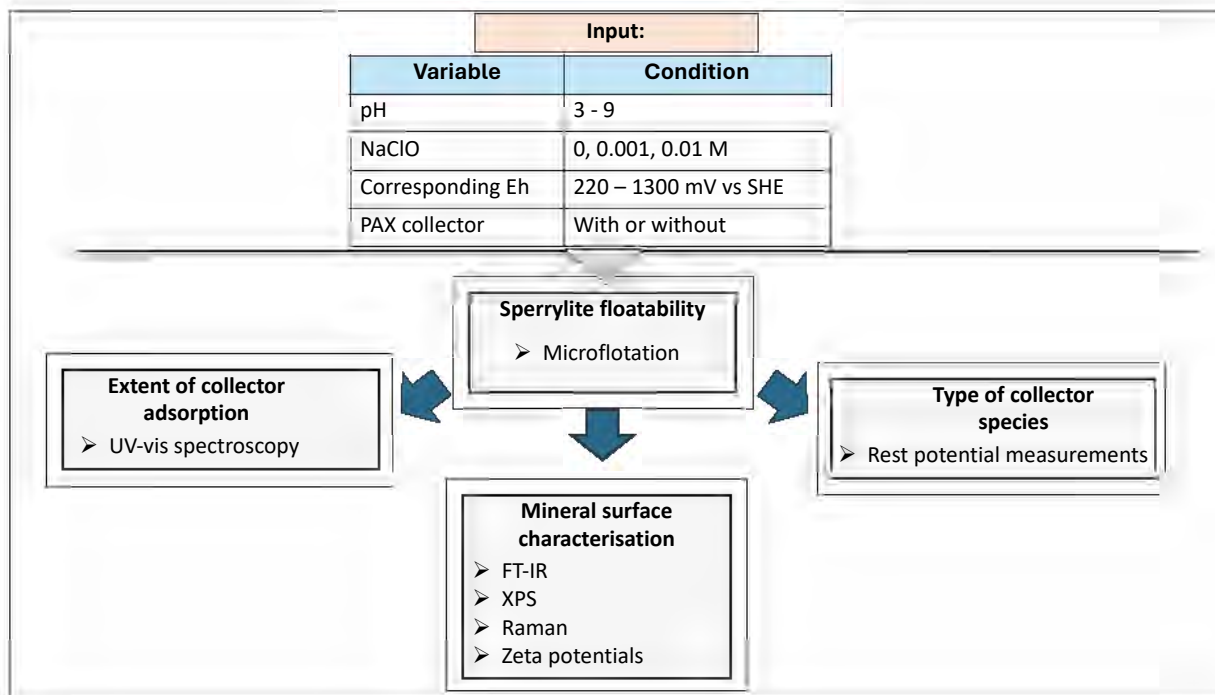


Figure 2.3: Research approach used in Phase Two

2.3.3. Phase Three: Comparisons of floatability of PGE arsenides and tellurides

The research approach used in **Phase Three** is illustrated in Figure 2.4. The natural and collector-induced floatabilities of the PGMs were investigated using microflotation. The extent and nature of collector adsorption on the surface of the PGMs were characterised using UV-vis spectroscopy and rest potential measurements. To better understand the chemical speciation at the surface when the minerals are treated at the various solution conditions, zeta potential measurements and spectroscopic studies were performed. The application of pH reduction in a complex ore was investigated using batch flotation tests and the results obtained were compared with those obtained from microflotation tests.

Chapter 2: Research Objectives

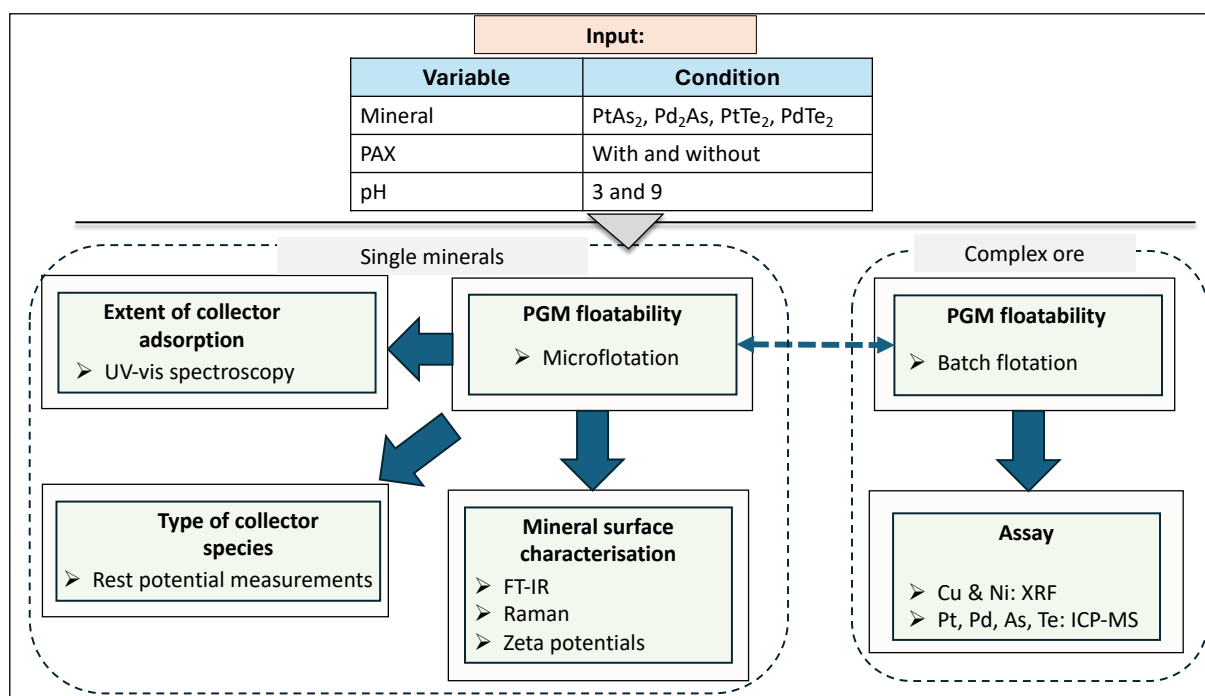


Figure 2.4: Research approach used in Phase Three

The experiments conducted to address the hypothesis and key questions of this research work are summarised in Table 2.1 (Phase One), Table 2.2 (Phase Two) and Table 2.3 (Phase Three).

Table 2.1: Experiments conducted to address the key questions and hypotheses in Phase One

Hypothesis	Key Questions	Experiments
The trithiocarbonate and thiourea collectors will bond more strongly with sperrylite and improve the floatability of this mineral to a greater extent compared to xanthate collectors. This is because the functional groups of the trithiocarbonate and thiourea collectors have a greater electron-releasing tendency resulting in a greater availability of electrons to form bonds with the mineral surface	➤ What is the flotation response of sperrylite using xanthate, trithiocarbonate and thiourea collectors?	➤ Microflotation
	➤ What is the effect of collector ligand type on the heat of collector adsorption on sperrylite which is a measure of the strength of collector adsorption?	➤ UV-vis spectroscopy
	➤ What is the effect of alkyl chain length on the heat of collector adsorption on sperrylite?	➤ Isothermal Titration Calorimetry
	➤ What is the effect of the ionic strength of the process water used in flotation and the collector dosage on the floatability of sperrylite?	➤ Batch flotation
	➤ How do the mineral flotation results obtained from microflotation compare with those obtained from batch flotation?	

Chapter 2: Research Objectives

Table 2.2: Experiments conducted to address the key questions and hypotheses in Phase Two

Hypothesis	Key Questions	Experiments
Sperrylite will have a better floatability at lower pH and/or higher Eh conditions compared to the current operating conditions of pH 9 and Eh $\approx$ 160 mV vs SHE. This is because: ➤ Lowering pH reduces the concentration of OH⁻ ions that would otherwise compete with the collector for adsorption sites on the mineral surface ➤ At lower pH, the formation of dixanthogen is thermodynamically favoured and this is required to impart sufficient hydrophobicity on sperrylite ➤ At higher Eh conditions, at least 100 mV vs SHE above the xanthate/dixanthogen equilibrium potential, the formation of dixanthogen is thermodynamically favoured	➤ How do pH and Eh affect the floatability of sperrylite? ➤ What is the extent and nature of xanthate collector adsorption on sperrylite under varying pH and Eh conditions? ➤ How does the chemical control of Eh using NaClO affect the floatability of sperrylite?	➤ Microflotation ➤ UV-vis spectroscopy ➤ Rest potential measurements ➤ Zeta potential measurements ➤ FT-IR spectroscopy ➤ XPS ➤ Raman spectroscopy

Table 2.3: Experiments conducted to address the key questions and hypotheses in Phase Three

Hypothesis	Key Questions	Experiments
Sperrylite has a poorer floatability compared to other PGMs including palladoarsenide, moncheite and merenskyite. It is hypothesised that this is due to sperrylite being more electrochemically inert and therefore less conducive to sustaining electron charge transfer between the collector and the mineral.	➤ How do the natural floatabilities of the PGE arsenides and tellurides compare under varying pH conditions? ➤ How do the collector-induced floatabilities of the PGE arsenides and tellurides compare under varying pH conditions? ➤ What is the relationship between the electrochemical potential and electronic properties of the PGE arsenides and tellurides? ➤ Can pH reduction be applied in a more realistic scenario in batch flotation where a complex ore is used?	➤ Microflotation ➤ UV-vis spectroscopy ➤ Rest potential measurements ➤ Zeta potential measurements ➤ FT-IR spectroscopy ➤ Raman spectroscopy ➤ Batch flotation

CHAPTER 3: Experimental Details

3. Experimental Methods

This chapter describes the materials and experimental methods used to address the hypotheses and key questions of this study.

3.1. Mineral Synthesis

Obtaining naturally occurring PGMs in sufficient quantities is not possible due to their low concentration and small grain size in PGM ores. This is a challenge which has been faced in all previous investigations into the behaviour of these minerals. However, it has been shown that synthetic PGE arsenides and tellurides have a similar behaviour to their natural equivalents and can be used to simulate their behaviour (Shamaila & O'Connor, 2008). Therefore, the PGMs investigated in this study were synthesised from their pure constituents. PtAs_2 (sperrylite), Pd_2As (palladoarsenide), PtTe_2 (moncheite), and PdTe_2 (merenskyite) were synthesised using the thermal treatment procedure developed by Shackleton (2007).

Pure platinum and palladium were supplied by Anglo-American Platinum. Pure arsenic and tellurium were supplied by Alfa Aesar and Sigma-Aldrich, respectively. The procedure used to synthesise the four PGMs investigated is illustrated in Figure 3.1. Stoichiometric masses of the pure constituents of the respective minerals were weighed into a silica tube to make up a 20 g sample. The ampoule was evacuated under near-vacuum conditions over at least 4 days to remove oxygen. Thereafter, the ampoule was sealed and transferred to a furnace where it was thermally treated.

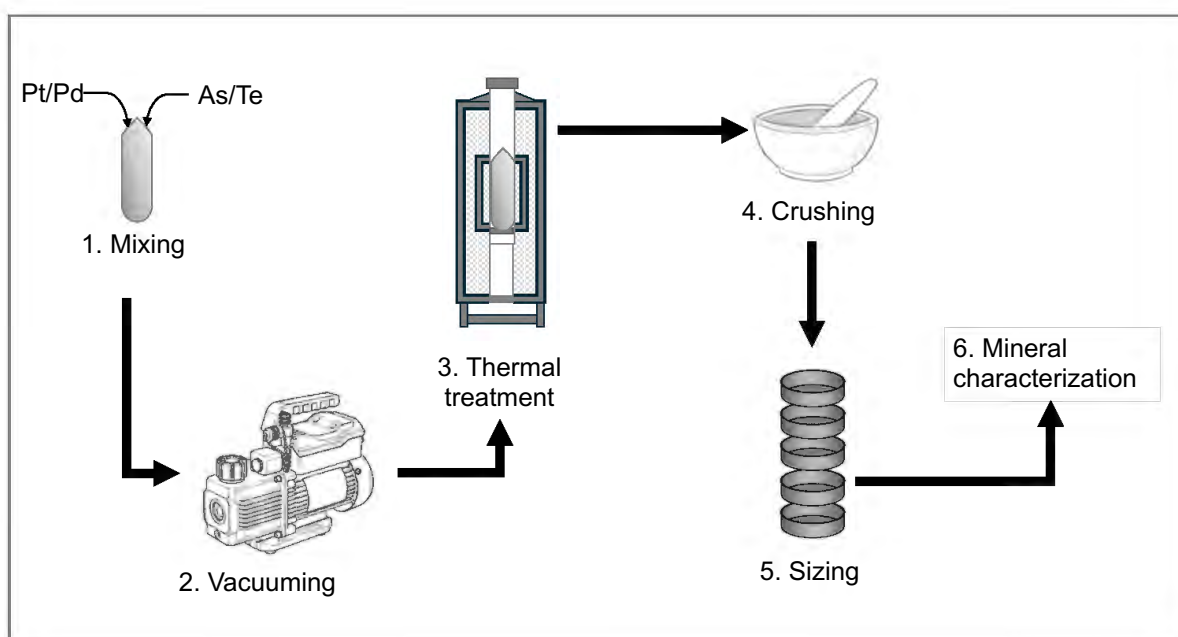


Figure 3.1: Mineral synthesis procedure of the PGMs investigated in this study

Chapter 3: Experimental Details

The thermal treatment procedures for each mineral are described in Table 3.1. During thermal treatment, the gases from the furnace were purged using an inert gas, nitrogen, and directed to a gas scrubbing unit containing NaOH and water. After thermal treatment, the minerals were taken out of the furnace and ground using a mortar and pestle. A mortar and pestle, instead of a pulveriser, was used in order to have controlled grinding and maintain the structural integrity of the minerals. After grinding, sperrylite was thermally treated for a second time to ensure a complete reaction of platinum and arsenic. The synthesised minerals were crushed into two size fractions, viz. +38-106 μm and -38 μm .

Throughout the synthesis and storage of the minerals, precautions were taken to minimise oxidation of the samples. During the synthesis, the oxygen in the ampoule was evacuated over at least a period of 4 days and in the furnace, the gases were purged using nitrogen. The synthesised minerals were stored under nitrogen in a freezer in sealed sample vials.

Table 3.1: Thermal treatment procedure used to synthesise the PGMs investigated in this study

Mineral	Stoichiometric composition	Thermal Treatment
Sperrylite PtAs_2	$\text{Pt}_{1.00}\text{As}_{2.00}$ (11.31 g Pt; 8.69 g As)	-Ampoule heated to 800°C at a rate of 2.5°C/min -Held at 800°C for 84 hours -Cooled to 400°C at a rate of 0.5°C/min -Held at 400°C for 24 hours -Cooled to 30°C at a rate of 0.4°C/min
Palladoarsenide Pd_2As	$\text{Pd}_{2.00}\text{As}_{1.00}$ (22.19 g Pd; 7.81 g As)	-Ampoule heated to 800°C at a rate of 2.5°C/min -Held at 800°C for 84 hours -Cooled to 400°C at a rate of 0.5°C/min -Held at 400°C for 24 hours -Cooled to 30°C at a rate of 0.4°C/min
Moncheite PtTe_2	$\text{Pt}_{1.00}\text{Te}_{2.00}$ (13.0 g Pt, 17.0 g Te)	-Ampoule heated to 1150°C at a rate of 5°C/min -Held at 1150°C for 30 minutes -Cooled to 350°C at a rate of 0.5°C/min -Held at 350°C for 60 hours -Cooled to 30°C at a rate of 0.4°C/min
Merenskyite PdTe_2	$\text{Pd}_{1.00}\text{Te}_{2.00}$ (8.83 g Pd; 21.17 g Te)	-Ampoule heated to 1150°C at a rate of 5°C/min -Held at 1150°C for 30 minutes -Cooled to 350°C at a rate of 0.5°C/min -Held at 350°C for 60 hours -Cooled to 30°C at a rate of 0.4°C/min

3.2. Mineral Characterisation

The synthesised minerals were characterized to determine the composition, homogeneity and surface area of the minerals.

3.2.1. X-Ray diffraction

XRD analysis was used to identify the phases present and the quantity of those phases in the synthesised samples. The XRD analyses were conducted using a Bruker D8 Advance powder diffractometer featuring a LynxEye silicon-drift detector, fixed divergence slits and a Co- α radiation source (1.78897 Å). Phase identification was performed using the Bruker EVA software. Diffractograms were acquired as coupled $2\theta/\theta$ scans on the 0-70° 2θ range. Thereafter, Rietveld refinement was performed using the Bruker Topas software to quantify the phases present.

3.2.1.1. Sperrylite

The diffractogram of the synthesised sperrylite sample is shown in Figure 3.2. This sample was composed of sperrylite as the major phase and a minor phase of platinum. The Rietveld Quantification results are shown in Table 3.2, where it can be seen that 96.1% of the identified phases was sperrylite with the rest being platinum.

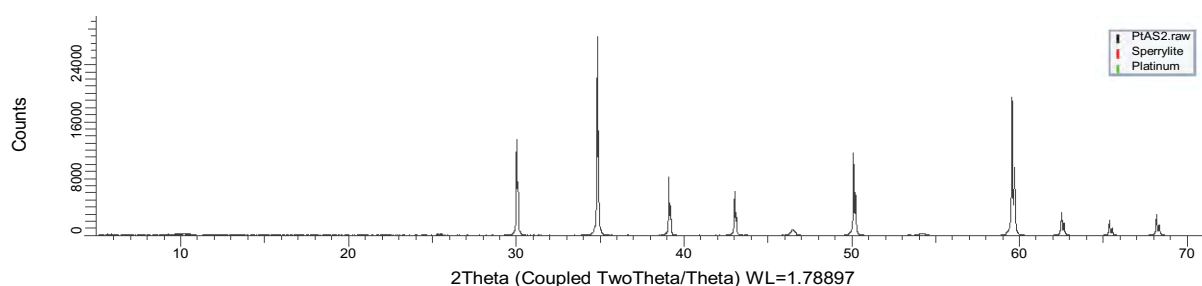


Figure 3.2: Diffractogram of the synthesised sperrylite sample

Table 3.2: Rietveld quantification of the synthesised sperrylite sample

Expected phase	Identified phase	Rietveld Quantification (%)
Sperrylite (PtAs ₂)	Sperrylite	96.1
	Platinum	3.9

3.2.1.2. Palladoarsenide

The diffractogram of the synthesised palladoarsenide sample is shown in Figure 3.3. Although it was possible to perform a Rietveld quantification of the palladoarsenide sample, this sample produced a poor diffractogram with broad and diffuse signals in the XRD pattern rather than sharp peaks. This suggests that this sample has a low degree of crystallinity, and possibly has some amorphous content. Furthermore, the broadening of the peaks can overlap with or obscure smaller crystalline peaks, thus making it difficult to accurately determine all the phases present and the purity of the sample. Similar findings on the XRD analysis of

synthesised palladoarsenide have been reported (Shackleton, 2007). Two phases were identified in the sample in the present study, viz. a palladoarsenide and iron oxide hydrate phase. Table 3.3 shows that 93.3% of the synthesised mineral was palladoarsenide and 6.7% was an iron oxide impurity. However, it is difficult to determine the accuracy of this quantification as mentioned. Therefore, in the context of the poor diffractogram of this sample and, therefore, the accuracy of the Rietveld quantification, it is only possible to conclude qualitatively that the main phase of this sample was palladoarsenide.

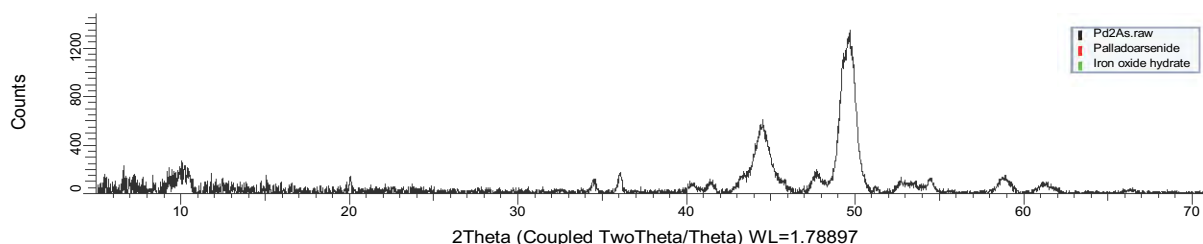


Figure 3.3: Diffractogram of the synthesised palladoarsenide sample

Table 3.3: Rietveld refinement of the synthesised palladoarsenide sample

Expected phase	Identified phase	Rietveld Quantification (%)
Palladoarsenide (Pd ₂ As)	Palladoarsenide	93.3
	Iron oxide hydrate	6.7

3.2.1.3. Merenskyite

The diffractogram of the synthesised merenskyite sample is shown in Figure 3.4. The sample was composed of merenskyite, tellurium and iron oxide hydrate phases. A relatively high tellurium phase was identified with a composition of 17.8% as shown by the Rietveld Quantification results shown in Table 3.4. The expected phase, merenskyite, was identified with a composition of 80.8%. The impurity, iron oxide hydrate, had a composition of 1.5%.

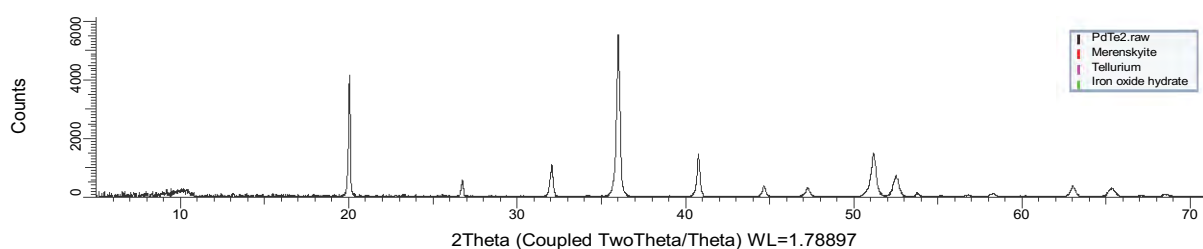


Figure 3.4: Diffractogram of the synthesised merenskyite sample

Chapter 3: Experimental Details

Table 3.4: Rietveld refinement of the synthesised merenskyite sample

Expected phase	Identified phase	Rietveld Quantification (%)
Merenskyite (PdTe_2)	Merenskyite	80.75
	Tellurium	17.76
	Iron oxide hydrate	1.49

3.2.1.4. Moncheite

The diffractogram obtained for the synthesised moncheite sample is shown in Figure 3.5. Two phases were identified for this sample, viz. moncheite and emmonsites, with a composition of 89% and 11%, respectively, as shown in Table 3.5.

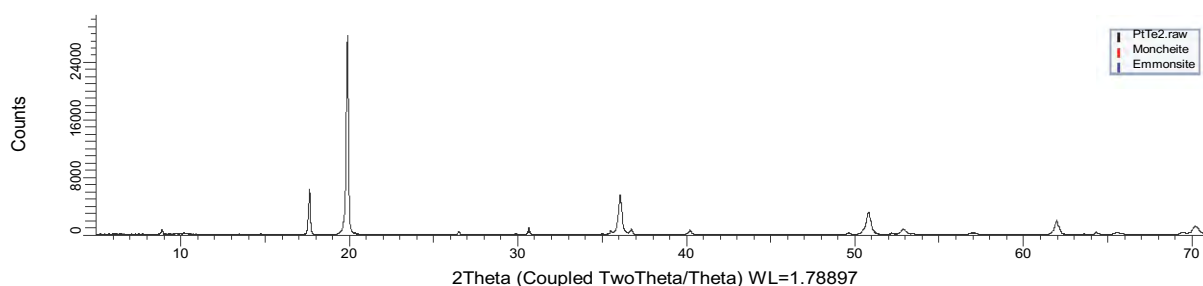


Figure 3.5: Diffractogram of the synthesised moncheite sample

Table 3.5: Rietveld refinement of the synthesised moncheite sample

Expected phase	Identified phase	Rietveld Quantification (%)
Moncheite (PtTe_2)	Moncheite	89.0
	Emmonsites	11.0

3.2.2. Scanning electron microscopy and energy-dispersive X-ray spectroscopy

Scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDS) were used to determine the elemental composition of the synthesised samples. This is a semi-quantitative technique which uses electron-excited characteristic peaks that can be used to identify the elemental composition of minerals. In these analyses, the search criteria were limited such that only the expected elements constituting the respective minerals were displayed. However, elements such as carbon and oxygen were also added to the search criteria to allow phases resulting from the oxidation of the minerals to be captured. The back-scattered electron (BSE) micrographs obtained from the samples were analysed for the phases present for each mineral.

3.2.2.1. Sperrylite

The BSE micrograph of sperrylite in Figure 3.6 shows that mainly two phases were formed, viz. grey phase and bright phase. It should be noted that the black colour in these micrographs represents the polished section matrix and not the mineral. The grey phase, which makes up the majority of the sample, is PtAs_2 with the composition shown in Table 3.6. The obtained phase is very close to the expected phase of PtAs_2 . The expected phase was calculated using the stoichiometric quantities of Pt and As as given by the empirical formula of sperrylite.

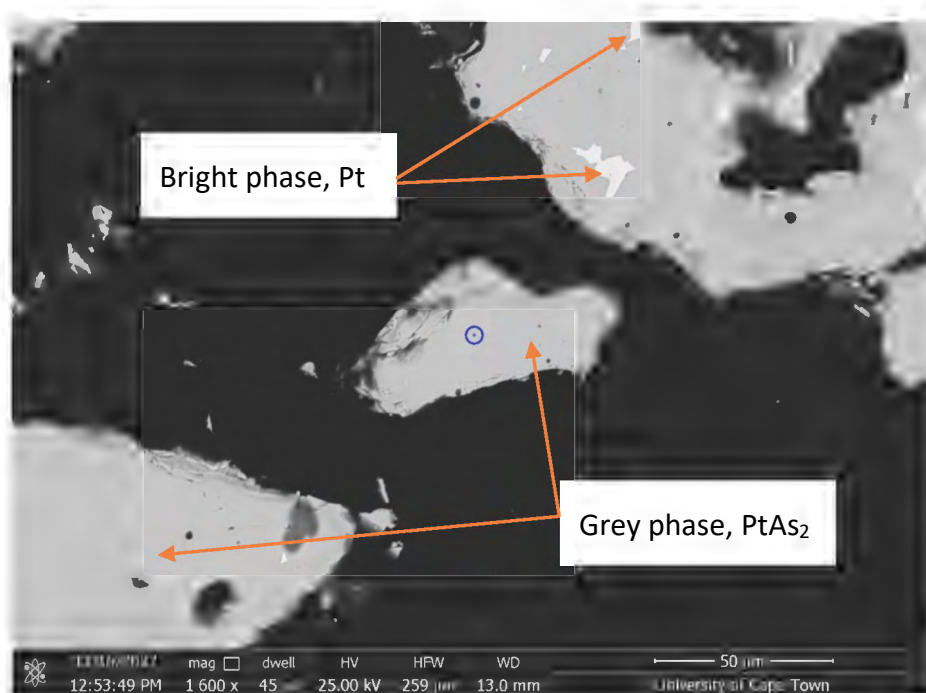


Figure 3.6: BSE micrograph of the synthesised sperrylite

There are trace amounts of oxygen which may have resulted from oxygen that was not evacuated from the ampoule or from oxidation. This oxygen probably resulted in trace amounts of an arsenolite (As_4O_6) phase. However, this phase or oxygen was not identified by the XRD analysis of this mineral. The bright phase represents unreacted Pt. The sperrylite samples were thermally treated twice in an attempt to drive the reaction between Pt and As to completion. This minimised the unreacted Pt phase but did not eliminate it. However, the XRD analysis showed that only 3.9 wt.% of the mineral was Pt, with the rest being PtAs_2 (see section 3.2.1.1).

Table 3.6: EDS results showing the elemental composition of the synthesised sperrylite

Phases	Phase ID	Pt (wt.%)	As (wt.%)	O (wt.%)
Expected phase	PtAs_2	56.6	43.4	-
Grey phase	PtAs_2	55.1	44.6	0.2
Bright phase	Pt	100.0	0.0	0.0

Chapter 3: Experimental Details

3.2.2.2. Palladoarsenide

The BSE micrograph of the synthesised palladoarsenide is shown in Figure 3.7. Six spectra of the mineral sample were taken, and the elemental compositions obtained are shown in Table 3.7.

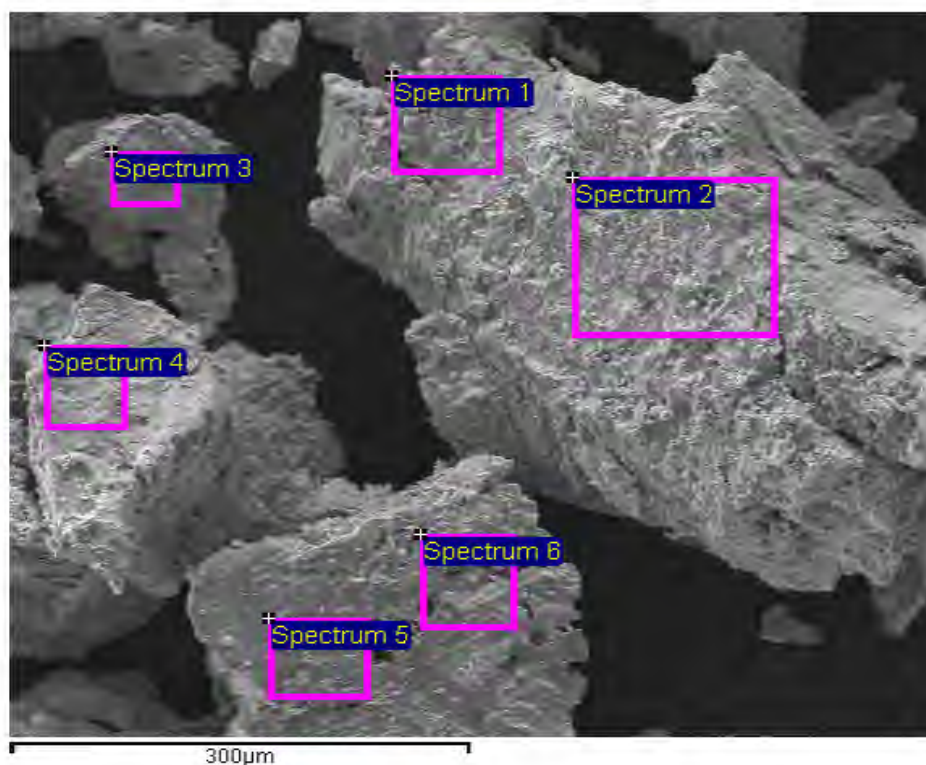


Figure 3.7: BSE micrograph of the synthesised palladoarsenide

The compositions shown in Table 3.7 indicate that there were likely two phases obtained, viz., an oxygen-rich phase and an oxygen-deficient phase. The XRD analysis identified the oxygen-rich phase as an iron oxide hydrate. Although iron was not identified by the EDS analysis, these results show that oxygen was present in the palladoarsenide sample. The presence of this oxygen-rich phase may indicate the presence of some amorphous content and/or oxidation of the palladoarsenide sample. The main phase of this sample was identified as palladoarsenide. The phases were quantified using XRD analysis (see section 3.2.1.2).

Table 3.7: EDS results showing the elemental composition of the synthesised palladoarsenide

Phases	Phase ID	Pd (wt.%)	As (wt.%)	O (wt.%)
Expected phase	Pd ₂ As	74.0	26.0	-
Spectrum 1		55.4	32.9	11.6
Spectrum 2		50.5	34.9	14.6
Spectrum 3		55.9	32.4	11.8
Spectrum 4		64.9	30.1	5.1
Spectrum 5		69.1	25.4	5.5
Spectrum 6		65.8	27.8	6.4

3.2.2.3. Moncheite

The BSE micrograph of the synthesised moncheite is shown in Figure 3.8. The elemental compositions obtained from the different spectra of the mineral particles were close to the expected stoichiometric composition of PtTe_2 . The elemental compositions obtained are shown in Table 3.8.

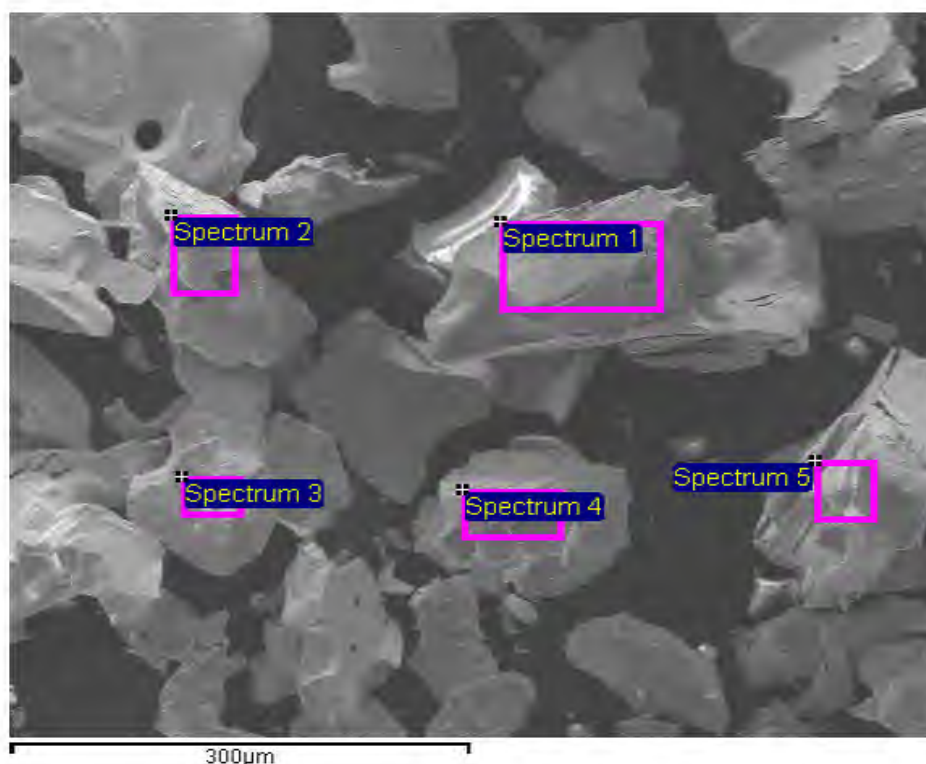


Figure 3.8: BSE micrograph of the synthesised moncheite

Table 3.8 shows that carbon was also detected in addition to the expected elements for moncheite. However, this carbon likely came from the instrument rather than the mineral. The samples were mounted on SEM stubs using double-sided conductive carbon tape, which would be the likely source for carbon. The identification and quantification of the phases present in the mineral were determined using XRD analysis (see section 3.2.1.4).

Table 3.8: EDS results showing the elemental composition of the synthesised moncheite

Phases	Phase ID	Pt (wt.%)	Te (wt.%)	C (wt.%)
Expected phase	PtTe_2	43.0	57.0	-
Spectrum 1		41.2	52.7	6.1
Spectrum 2		40.7	50.8	8.5
Spectrum 3		40.1	52.2	7.7
Spectrum 4		40.1	51.1	8.8
Spectrum 5		38.7	51.2	10.1

Chapter 3: Experimental Details

3.2.2.4. Merenskyite

The BSE micrograph of the synthesised merenskyite is shown in Figure 3.9. At least two phases were formed during the synthesis of this mineral, viz., a Te phase and a PdTe_2 phase.

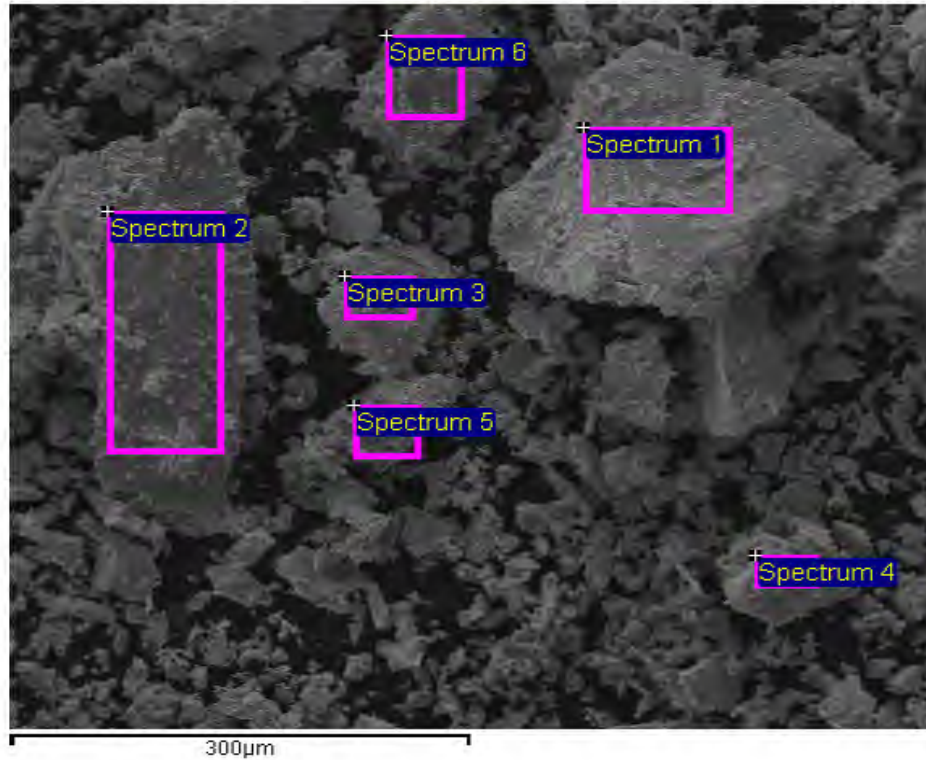


Figure 3.9: BSE micrograph of the synthesised merenskyite

The elemental compositions of the phases obtained are shown in Table 3.9. The Te-rich phase is indicated by spectra 4 and 5. This phase likely resulted from an incomplete reaction of Pd and Te during the mineral synthesis. The second phase is PdTe_2 indicated by spectra 1, 2, 3 and 6. The quantification and validation of the phases present in the mineral were performed using XRD analysis (see section 3.2.1.3).

Table 3.9: EDS results showing the elemental composition of the synthesised merenskyite

Phases	Phase ID	Pd (wt.%)	Te (wt.%)	C (wt.%)	B (wt.%)
Expected phase	PdTe_2	29.0	71.0	-	
Spectrum 1		24.4	66.9	5.3	3.5
Spectrum 2		23.4	68.6	3.9	4.1
Spectrum 3		20.9	70.0	4.7	4.5
Spectrum 4		1.2	89.8	4.0	5.0
Spectrum 5		2.3	93.6	0.0	4.0
Spectrum 6		20.1	71.6	4.4	3.0

3.2.3. BET analysis

The Brunauer-Emmett-Teller (BET) analysis was used to determine the surface areas of the synthesised PGMs. The specific surface areas of the minerals obtained for the +38-106 μm and -38 μm size fractions are shown in Table 3.10. In this study, pyrite was used to perform scoping and reproducibility tests. The surface areas obtained from the BET analysis were used to calculate the collector surface coverages where this was used such as in the microflotation, UV-vis spectroscopy and microcalorimetry studies.

Table 3.10: Surface areas of the minerals determined using BET analysis

Mineral	BET surface area of +38-106 μm size fraction (m^2/g)	BET surface area of -38 μm size fraction (m^2/g)
Sperrylite (PtAs_2)	0.06	0.20
Palladoarsenide (Pd_2As)	0.18	0.28
Moncheite (PtTe_2)	0.14	0.65
Merenskyite (PdTe_2)	0.11	0.39
Pyrite (FeS_2)	0.10	1.20

3.3. Ore preparation and information

The batch flotation experiments were conducted using a Platreef ore, which is the ore of interest in this study. The ore was obtained using belt-cut samples of run-of-mine ore from a South African Platinum Mine located in the Limpopo Province in South Africa. The dried ore was delivered to the Centre for Minerals Research at the University of Cape Town for use in this study. The ore was prepared by crushing to a top size of 2.6 mm using a jaw crusher. Thereafter, it was blended, riffled and split into 3.7 kg representative samples. The riffler and rotary splitter used were supplied by Dickie & Stockler (Pty) Ltd. The samples were split into 3.7 kg masses as these were the masses required to obtain 35 wt.% solids in an 8 L batch flotation cell used in this study.

The mineralogical characterisation of the feed Platreef ore samples used in this study was performed by Nyaruwata (2022). The bulk modal mineralogy was performed using quantitative X-ray diffraction (QXRD), while the PGM mineralogy was performed using Quantitative Evaluation of Minerals by Scanning Electron Microscopy (QEMSCAN). The bulk mineralogy of the samples is shown in Figure 3.10. The samples are dominated by pyroxenes, which is consistent with the Platreef rock type being classified as pyroxenite (McDonald et al., 2005; Schouwstra et al., 2017). The BMS and PGMs were below the detection limit of the QXRD which is typically 2 wt.%.

Chapter 3: Experimental Details

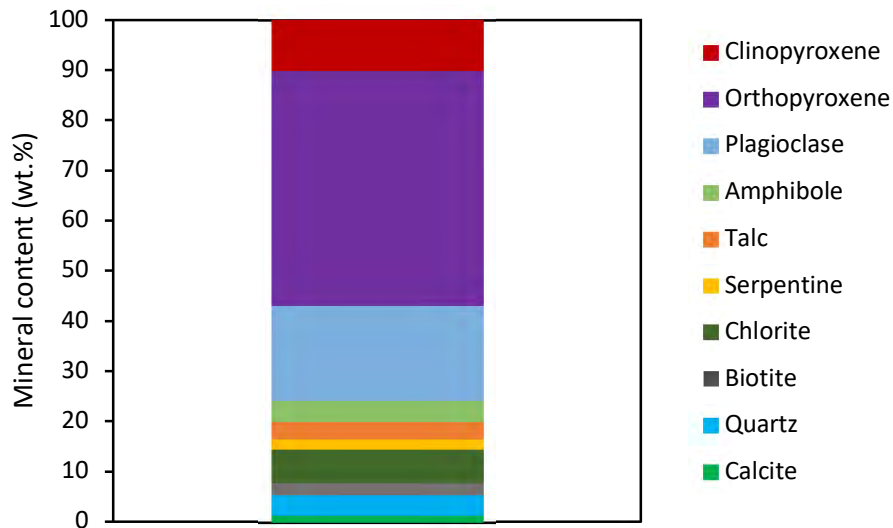


Figure 3.10: QXRD Bulk mineralogy of the Platreef flotation feed samples (Nyaruwata, 2022)

The PGM distribution in the flotation feed samples quantified using QEMSCAN is shown in Figure 3.11. The flotation feed samples are dominated by PGE sulfides, arsenides and bismuthotellurides. Of particular interest in this study are the PGE arsenides which are predominantly composed of sperrylite, as well as the PGE tellurides (classified under PGE bismuthotellurides) from which minerals such as moncheite and merenskyite are found.

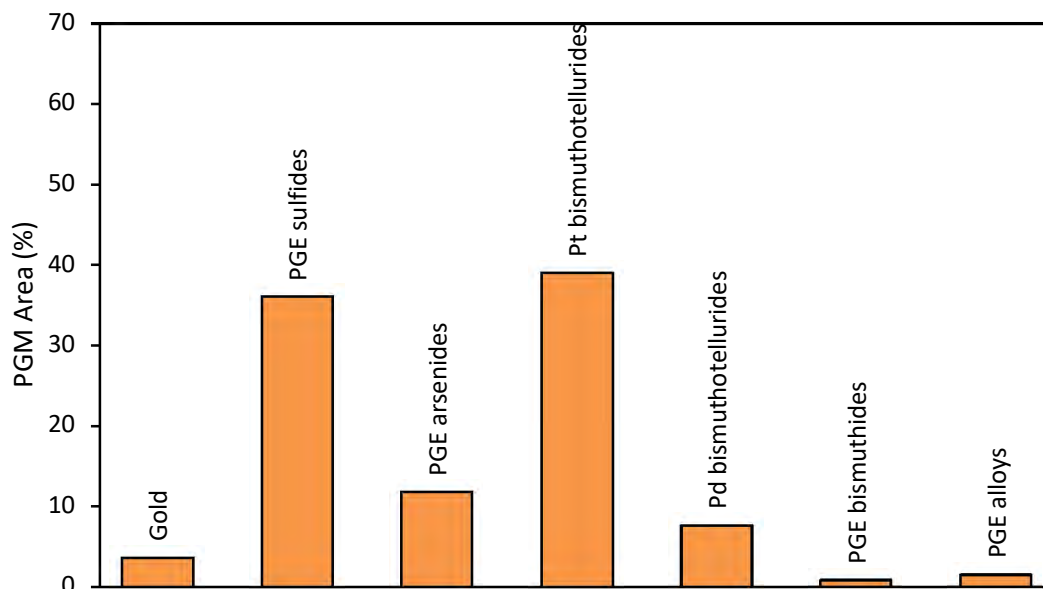


Figure 3.11: PGM distribution in the Platreef flotation feed samples determined using QEMSCAN. Total number of PGM -bearing particles = 565 (Nyaruwata, 2022)

At the grind of 80% passing 45 μm used in this study, the majority of the PGMs can be expected to be liberated as shown in Figure 3.12. However, some of the PGMs are associated with silicates which would make it difficult for them to be recovered by true flotation. It should be noted that for the purposes of recovery, the PGMs associated with BMS can be considered to be “liberated” since these can be recovered by association.

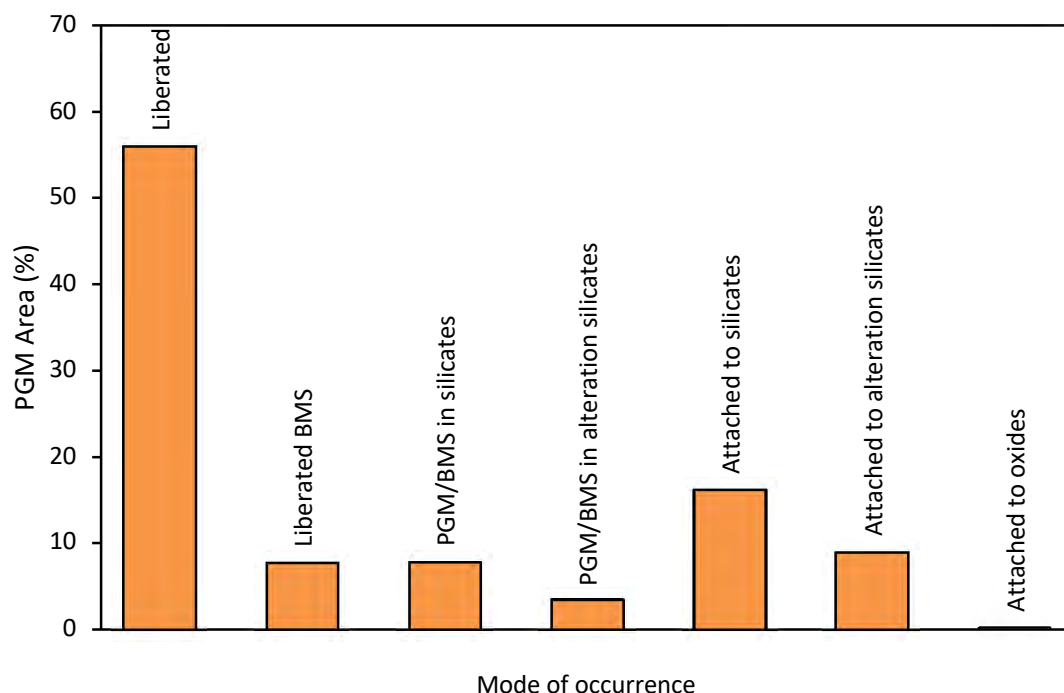


Figure 3.12: PGM mode of occurrence in the feed Platreef ore samples at a grind of 80% passing 45 μm . Total number of PGM-bearing particles = 565 (Nyaruwata, 2022)

3.4. Reagents

Several reagents were used in this study. Information regarding the reagents used for the different types of experiments conducted is provided in the following sections.

3.4.1. Collectors

In **Phase One** of this study, the use of three types of collectors on sperrylite was investigated, viz., xanthate, trithiocarbonate and thiourea collectors. For each type of collector, the length of the alkyl chain was considered. Due to the limited availability of sperrylite, only the best-performing collector from each type was used with sperrylite. The collectors were screened using pyrite to determine the best-performing collector (see section 3.11.1). The collectors used on sperrylite or during the batch flotation experiments are highlighted in Table 3.11 to Table 3.13.

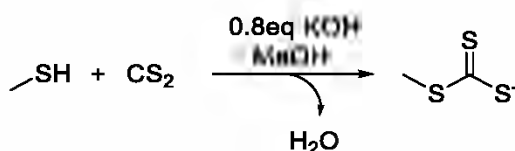
The xanthate collectors used in this study were supplied by AECI Mining Chemicals (Pty) Ltd. The information on these collectors is presented in Table 3.11.

Chapter 3: Experimental Details

Table 3.11: Xanthate collectors considered in this study

Structure	Collector Name	Collector Abbreviation	Molecular Weight (g/mol)
	Sodium ethyl xanthate	SEX	144.15
	Sodium n-propyl xanthate	SNPX	158.16
	Potassium n-butyl xanthate	PNBX	188.29
	Sodium iso-butyl xanthate	SIBX	171.18
	Potassium amyl xanthate	PAX	202.37

The trithiocarbonate collectors considered in this study are presented in Table 3.12. These collectors were synthesised in the Chemistry Department at the University of Cape Town and were provided for investigation in this study. The method for synthesising the trithiocarbonate collectors has been detailed by Drake & Yang (1994), and only a brief description is provided here. The synthesis was achieved through the nucleophilic addition of CS₂ which had been deprotonated with a base (KOH). Thereafter, the compounds were isolated by precipitation and suction filtration. The general reaction scheme for TTC formation can be described by the following reaction scheme:



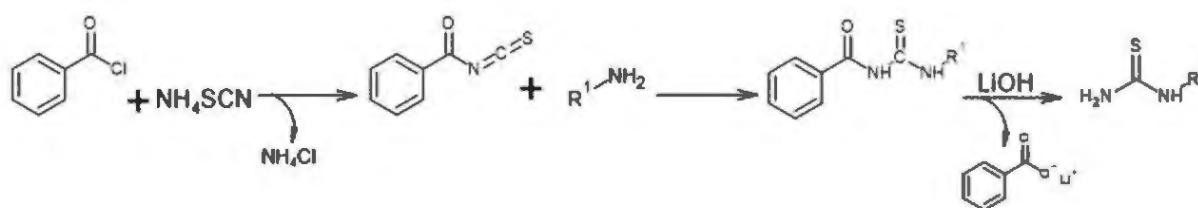
The purity of the synthesised collectors was verified by proton and carbon nuclear magnetic resonance.

Chapter 3: Experimental Details

Table 3.12: Trithiocarbonate collectors considered in this study

Structure	Collector Name	Collector Abbreviation	Molecular Weight (g/mol)
	Potassium ethyl trithiocarbonate	PETTC	176.36
	Potassium propyl trithiocarbonate	PPTTC	190.39
	Potassium n-butyl trithiocarbonate	PNBTTC	204.42
	Potassium tert-butyl trithiocarbonate	PTBTTC	204.42
	Potassium iso-amyl trithiocarbonate	PIATTC	218.44

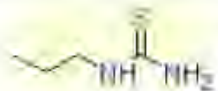
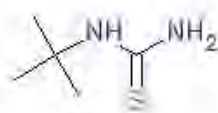
The thiourea collectors were also synthesised in the Chemistry Department at the University of Cape Town. The method for synthesising these collectors has been detailed by Milosavljević et al. (2015). The general reaction scheme for the formation of thiourea can be described by the following reaction scheme:



The alkyl thiourea formed was collected by suction filtration. The purity of the synthesised collectors was verified by proton and carbon nuclear magnetic resonance. The thiourea collectors considered in this study are presented in Table 3.13.

Chapter 3: Experimental Details

Table 3.13: Thiourea collectors considered in this study

Structure	Collector Name	Collector Abbreviation	Molecular Weight (g/mol)
	Propyl thiourea	PTU	118.2
	Tert-butyl thiourea	TBTU	132.23

For the experiments in which the collector dosage was based on surface coverage, the dosage was calculated based on the surface area of the mineral and the footprint area of the collector molecule. Surface coverage refers to the number of molecules of the collector required to cover the available surface area of the mineral, and this is reported in terms of pseudo-monolayers covering the mineral surface.

Surface coverage was calculated as the total area covered by the collector divided by the total mineral surface area. The surface area of the mineral was determined using BET analysis (see section 3.2.3). The area covered by the collector was calculated using the footprint area of one collector molecule which was assumed to be 28.8 Å (Grano et al., 1997). A sample calculation of the collector surface coverage is shown in APPENDIX A. In reality, the area covered by each collector, and hence the number of pseudo-monolayers, is likely to be slightly different. However, in this study (i.e. Phase One), it was assumed to be the same for all collectors. This assumption is relevant only in so far as it allows an estimate to be made about the number of pseudo-monolayers of the collector required. In this way, the actual number of moles of the collector is constant.

3.4.2. Frothers

For the microflotation experiments, the frother used was Senfroth 200, a polypropylene glycol (PPG) based frother supplied by AECI Mining Chemicals (Pty) Ltd. The frother was used at a dosage of 15 ppm which is the dosage just above the critical coalescence concentration (Cho & Laskowski, 2002). This dosage was used to ensure that bubble size remained essentially constant throughout the microflotation experiments.

3.4.3. pH and Eh modifiers

pH was adjusted by using either 0.1 M NaOH or 0.1 M HCl for all the experiments unless otherwise stated. The NaOH and HCl were supplied by Merck (Pty) Ltd. These modifiers were deemed suitable as they have a minimal effect on the mineral-collector interactions (Taguta, 2015) and would, therefore, not interfere with the results obtained other than modifying pH.

Chapter 3: Experimental Details

In the rest potential measurement experiments, pH regulation was achieved using pH buffers. The buffers shown in Table 3.14, supplied by Merck (Pty) Ltd, were used to achieve the various pH values.

Table 3.14: pH buffers used for the rest potential measurements

pH	Buffer(s)
3	0.01 M H ₂ SO ₄
5	0.1 M KH ₂ PO ₄ and 0.1 M NaOH
7	0.1 M KH ₂ PO ₄ and 0.1 M NaOH
9	0.05 M Na ₂ B ₄ O ₇

For the experiments in which chemical Eh modification was investigated, 10% sodium hypochlorite (NaClO), supplied by KIMIX Chemical & Lab Supplies, was used. This was investigated at 0.001 M and 0.01 M concentrations.

3.4.4. Synthetic Plant Water

The batch flotation experiments were conducted using synthetic plant water (SPW). The SPW was made by dissolving salts containing the ions indicated in Table 3.15 in de-ionised water to mimic typical water compositions of South African PGM concentrators.

Table 3.15: Ion compositions of synthetic plant water at two different ionic strengths (Wiese et al., 2005)

Ion	[Ca ²⁺] (ppm)	[Mg ²⁺] (ppm)	[Na ⁺] (ppm)	[Cl ⁻] (ppm)	[SO ₄ ²⁻] (ppm)	[NO ₃ ²⁻] (ppm)	[CO ₃ ²⁻] (ppm)	TDS (mg/L)	IS (mol/L)
1 SPW	80	70	153	287	176	176	17	1023	0.0242
10 SPW	800	700	1530	2870	1760	1760	170	10230	0.2426

3.5. Microflotation

Microflotation was used to measure the floatability of the minerals investigated at varying collector and solution chemistries. Microflotation measures the floatability of single minerals without the influence of other minerals or the presence of the froth phase. Recovery is purely an indication of the hydrophobicity of the mineral, thus making this technique a good indicator of mineral hydrophobicity. In this study, the UCT microflotation rig was used to conduct the microflotation experiments. A schematic diagram of the UCT microflotation rig is illustrated in Figure 3.13.

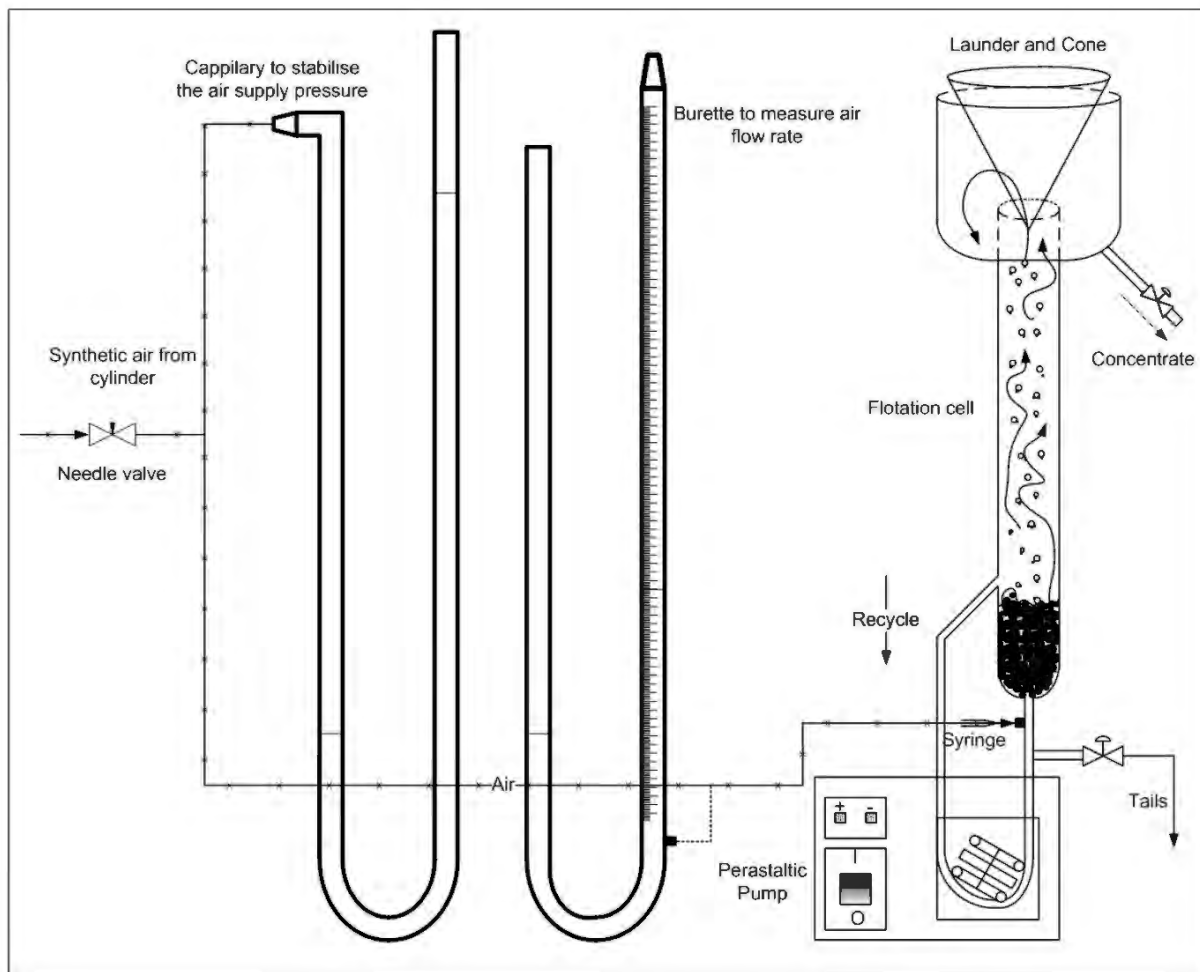


Figure 3.13: Schematic of the UCT microflotation rig used in this study (Bradshaw & O'Connor, 1996)

During an experiment, the mineral particles were kept in suspension using a Watson Marlow 505U peristaltic pump to circulate the slurry. Air was introduced at the bottom of the microflotation cell to create bubbles on which hydrophobic particles could attach and rise to the concentrate launder to be recovered.

3.5.1. Microflotation procedure

2 ± 0.1 g of the mineral in the +38-106 μm size fraction was weighed out into a 50 ml beaker. A 50 ml solution was then added, and the slurry was ultra-sonicated in a water bath for 5 minutes to disperse the slurry. The added solution was de-ionised water adjusted to the desired pH, Eh and/or ionic strength. 0.12 M NaCl was used to adjust the ionic strength of the process water. NaCl was chosen because the Na^+ and Cl^- ions have a minimal interaction with the mineral surface or other reagents. This ensures that the effect observed is related to the ionic strength rather than the type of ions present (Shackleton et al., 2012). After adjusting the slurry for pH, Eh and/or ionic strength, the collector at the desired dosage was added using an auto pipette. This was conditioned for 5 minutes by stirring, whereafter, a frother at a

Chapter 3: Experimental Details

dosage of 15 ppm was added and conditioned for a further 5 minutes. Thereafter, the conditioned slurry was transferred into the 250 ml microflotation cell shown in Figure 3.14. Top-up water at the conditions of interest was added to the 250 ml level.



Figure 3.14: UCT microflotation rig used in this study

Throughout the experiments, the airflow rate was maintained at 8 ml/min and the peristaltic pump was maintained at a speed of 65 rpm. Concentrates were collected at 2, 6, 12 and 20 minutes. The tails were collected at the end of the experiment (i.e. after 20 minutes). The concentrates were filtered, dried and weighed to calculate recoveries.

The cumulative recoveries were calculated using equation 3-1.

$$R_j = \frac{\sum C_j}{F} \quad 3-1$$

where:

- $\sum C_j$ - sum of the concentrates at time interval $j = 2, 6, 12$ or 20 minutes (g)
- F - Total feed (g)
- R_j - recovery at time interval j (g)

Chapter 3: Experimental Details

The flotation kinetics were calculated using the Klimpel rate equation by using the least squares method on the recovery-time data (Dowling et al., 1985). The Klimpel rate equation is given by equation 3-2. In this equation, k and R_{inf} are fitted parameters.

$$R = R_{inf}(1 - e^{-kt}) \quad 3-2$$

where:

- R - Recovery
- R_{inf} - Maximum possible recovery
- k - first-order rate constant (min^{-1})
- t - time (min)

3.5.2. Microflotation reproducibility tests

Due to the limited availability and high cost of the PGMs, experiments were conducted in singles. However, reproducibility tests were conducted using pyrite to determine the reliability of the experimental procedure used.

Reproducibility tests were conducted to determine the reliability of the equipment and experimental method. The reproducibility and error analysis includes conditions that are representative of the variability that would be expected across the different sets of microflotation tests. In general, the microflotation tests produced reproducible and reliable results across the different conditions, with the highest relative standard error obtained being 10.16% as shown in Table 3.16.

In order to determine an estimate of the error that could be used for the experiments in which only single tests could be performed, a pooled (or combined) standard error was calculated from the errors presented in Table 3.16. The pooled standard error is essentially an average of the error of multiple groups of data sets which assumes homogeneity of variance across the experimental conditions. Since the conditions were similarly controlled for the different sets of experiments, this is a reasonable assumption. That is, there are no conditions that have an inherently different variability. The pooled relative standard error was calculated using equation 3-3.

$$RSE_{pooled} = 100\% \times \frac{1}{Mean_{overall}} \sqrt{\frac{\sum_{i=1}^m (n_i - 1) s_i^2}{\sum (n_i - 1)}} \quad 3-3$$

Where:

- RSE_{pooled} - Pooled relative standard error
- s_i^2 - sample variance
- n_i - sample size

Chapter 3: Experimental Details

From the reproducibility tests presented in Table 3.16, the pooled RSE was calculated to be 3.79% which was deemed acceptable as an estimate of reproducibility of the microflotation test results.

Table 3.16: Microflotation reproducibility test results showing the average recoveries and associated errors

Conditions	Time (min)	RUN 1 Rec.	RUN 2 Rec.	Ave.	Std. Dev.	Std. Err.	RSD
1 ML PNBX, pyrite, pH 9	2	46.2%	47.6%	0.47	0.01	0.01	1.45%
	6	79.4%	77.2%	0.78	0.02	0.01	1.41%
	12	92.1%	90.4%	0.91	0.01	0.01	0.92%
	20	96.4%	95.3%	0.96	0.01	0.01	0.55%
Conditions	Time (min)	RUN 1 Rec.	RUN 2 Rec.	Ave.	Std. Dev.	Std. Err.	RSD
1 ML SEX, pyrite, pH 9	2	23.9%	20.1%	0.22	0.03	0.02	8.59%
	6	56.7%	52.1%	0.54	0.03	0.02	4.18%
	12	83.5%	79.3%	0.81	0.03	0.02	2.55%
	20	92.5%	90.9%	0.92	0.01	0.01	0.87%
Conditions	Time (min)	RUN 1 Rec.	RUN 2 Rec.	Ave.	Std. Dev.	Std. Err.	RSD
1 ML PNBTC, pyrite, pH 9	2	49.0%	56.2%	0.53	0.05	0.04	6.76%
	6	87.9%	88.2%	0.88	0.00	0.00	0.17%
	12	96.7%	96.9%	0.97	0.00	0.00	0.12%
	20	98.4%	98.7%	0.99	0.00	0.00	0.14%
Conditions	Time (min)	RUN 1 Rec.	RUN 2 Rec.	Ave.	Std. Dev.	Std. Err.	RSD
5 ML PAX, sperrylite, pH 3, 0.01 M NaClO	2	9.4%	10.8%	0.10	0.01	0.01	6.99%
	6	14.7%	17.8%	0.16	0.02	0.02	9.58%
	12	20.0%	21.6%	0.21	0.01	0.01	3.93%
	20	23.5%	26.1%	0.25	0.02	0.01	5.22%
Conditions	Time (min)	RUN 1 Rec.	RUN 2 Rec.	Ave.	Std. Dev.	Std. Err.	RSD
No Reagent, Pyrite, pH 9	2	1.1%	1.2%	0.01	0.00	0.00	4.54%
	6	2.8%	2.8%	0.03	0.00	0.00	0.76%
	12	5.0%	4.5%	0.05	0.00	0.00	5.37%
	20	7.4%	6.0%	0.07	0.01	0.01	10.16%

3.6. Rest potential measurements

Electrochemical rest potential measurements were conducted to determine the type of collector species likely to form on the mineral surface under the different conditions investigated.

The instrument set-up used for the rest potential measurements is shown in Figure 3.15. The rest potential measurements were conducted in a 500 ml double-jacketed reaction vessel filled with 450 ml solution at the conditions of interest. During an experiment, this was agitated using a Freed Electric magnetic stirrer to ensure homogeneous mixing. The temperature in the reaction vessel was regulated at $25 \pm 1^\circ\text{C}$ using a Shinha DCS Model 300 temperature controller equipped with an ABB water bath. A three-electrode system was used to measure the rest potentials of the minerals. This consisted of a working, counter and reference electrodes. The working electrodes were manufactured using the synthetic mineral of interest (see section 3.6.1). The counter electrode was made from a Pt wire. A double junction Ag/AgCl electrode containing a 3 M KCl solution supplied by Metrohm was used as the reference electrode. The potential measured was corrected by +0.207 V to obtain the potential relative to the standard hydrogen electrode (SHE). The electrodes were connected to a Gamry Instrument™ potentiostat which was interfaced to a computer via a USB connection.

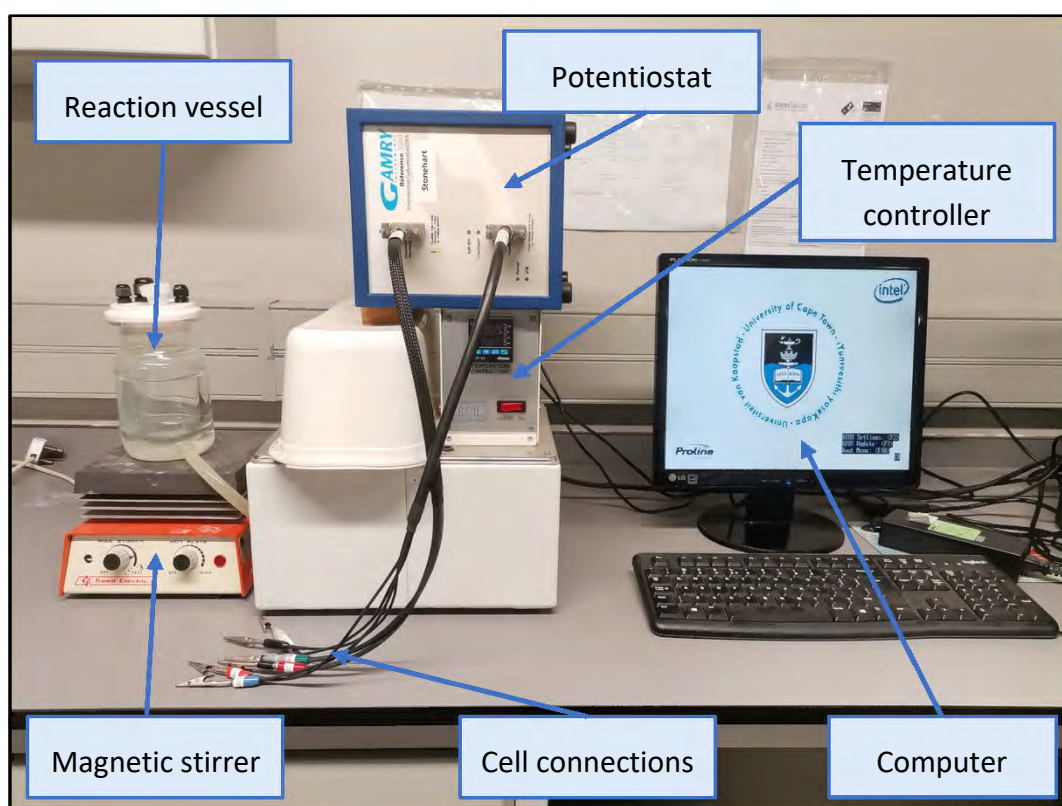


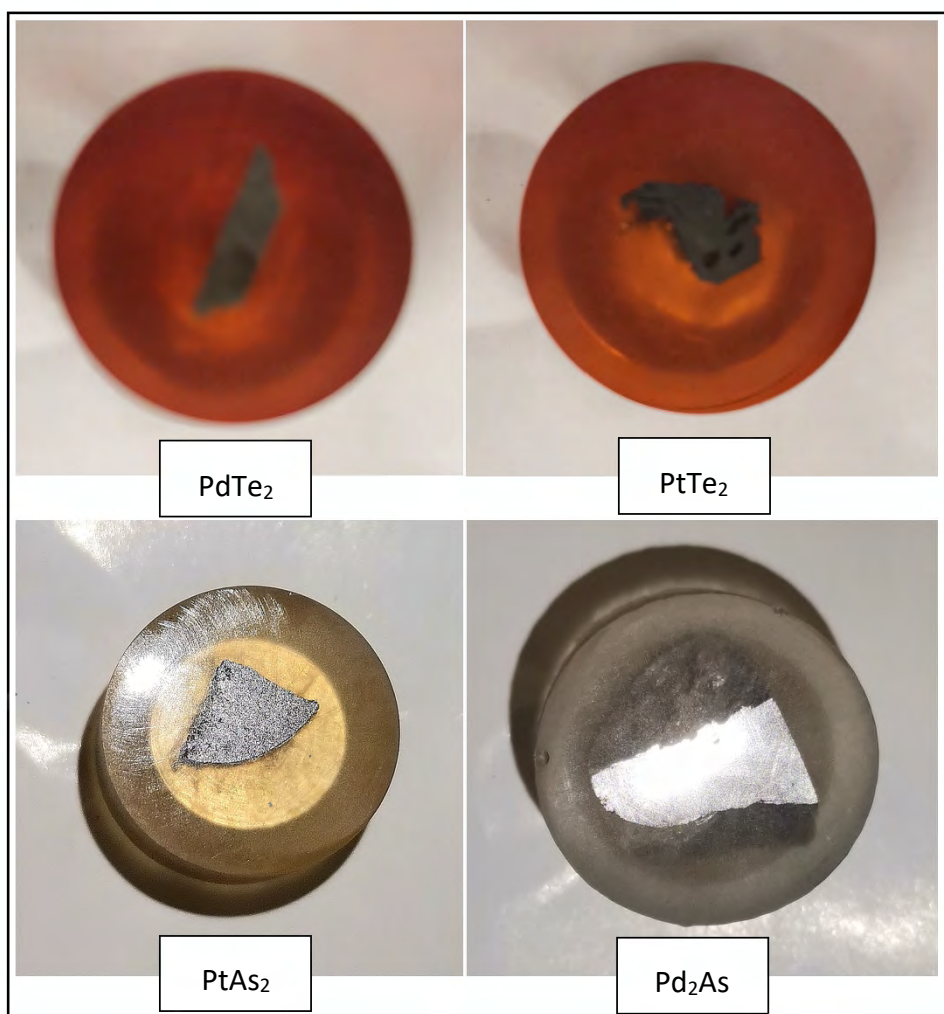
Figure 3.15: Electrochemistry experimental set-up

Chapter 3: Experimental Details

3.6.1. Electrode manufacturing

The working electrodes were manufactured using the synthetic mineral of interest. The PtTe_2 and PdTe_2 were manufactured at Murdoch University, Perth, Western Australia and were provided for use in this study (Tadie, 2015). The Pd_2As and PtAs_2 electrodes were manufactured in-house in the Centre for Minerals Research labs.

To manufacture these electrodes, the synthetic mineral was attached to a threaded copper SEM stub using conductive silver glue. This was then embedded in an epoxy mould. The epoxy resin was mixed with an EcoFix hardener at a ratio of 2:1 (resin: hardener). The epoxy with the embedded mineral was left to harden overnight. Thereafter, the exposed mineral surface was polished using a Grit Silica Carbide paper. Progressively smaller sizes of carbide paper were used to polish the mineral until a smooth surface was observed under a microscope. The electrodes used in this study are shown in Figure 3.16.



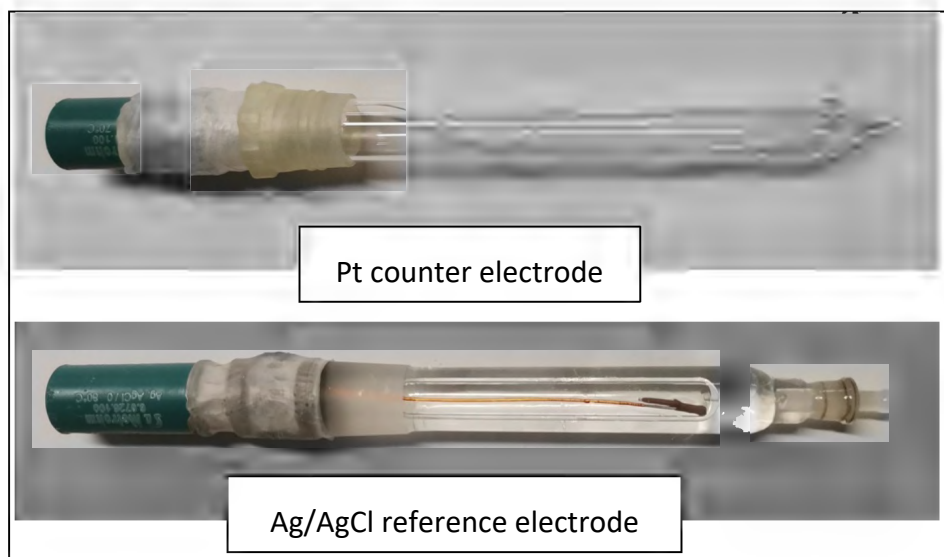


Figure 3.16: Electrodes used in this study

3.6.2. Rest potential experimental procedure

Before the commencement of each rest potential measurement, the working electrodes were polished. The electrodes were wet-polished using a 600 Grit Silica Carbide paper. Thereafter, they were polished using a Struers deagglomerated gamma alumina powder mixed with ultra-pure water. The electrodes were polished starting with a 1 μm powder, followed by 0.5 μm , then finishing with 0.05 μm . Thereafter, they were rinsed with ultra-pure water and dried by lightly dabbing with a paper towel before being transferred into the reaction vessel.

The reaction vessel contained a 450 ml solution made of 0.1 M Na_2SO_4 , pH buffer of interest (see Table 3.14), and/or NaClO . All the solutions were made using ultra-pure water. Measurements were performed using the Module PHE™ 200 run in open circuit in the absence of a collector for 10 minutes to obtain the rest potential of the mineral. After 10 minutes, 6.24×10^{-4} M collector was injected into the reaction vessel and the rest potentials were measured for a further 10 minutes.

Measurements of the equilibrium potential of the xanthate/dixanthogen couple were performed in a similar manner, except that in this case the mineral electrode (i.e. working electrode) was replaced by a Pt counter sensor electrode in the three-electrode system. The equilibrium potential of the xanthate/dixanthogen couple was obtained by taking the final rest potential after 20 minutes. A schematic of the rest potential profiles obtained from these experiments is shown in Figure 3.17.

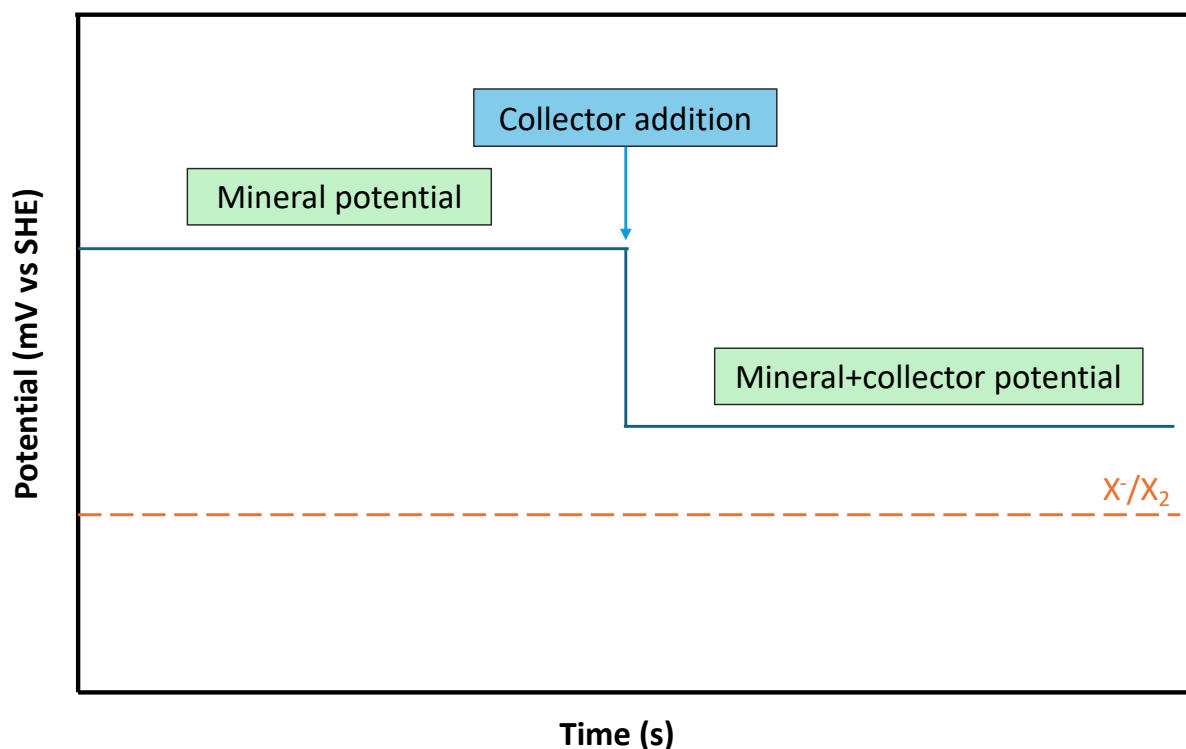


Figure 3.17: Schematic representation of the rest potential profile obtained from the electrochemical experiments

3.6.3. Rest potential measurements reproducibility tests

All the rest potential measurements were conducted in duplicates and the average potentials are reported in mV vs SHE in this thesis. The rest potential measurements conducted on sperrylite with PAX are used as an example to illustrate the reliability of the results obtained. This is shown in Figure 3.18.

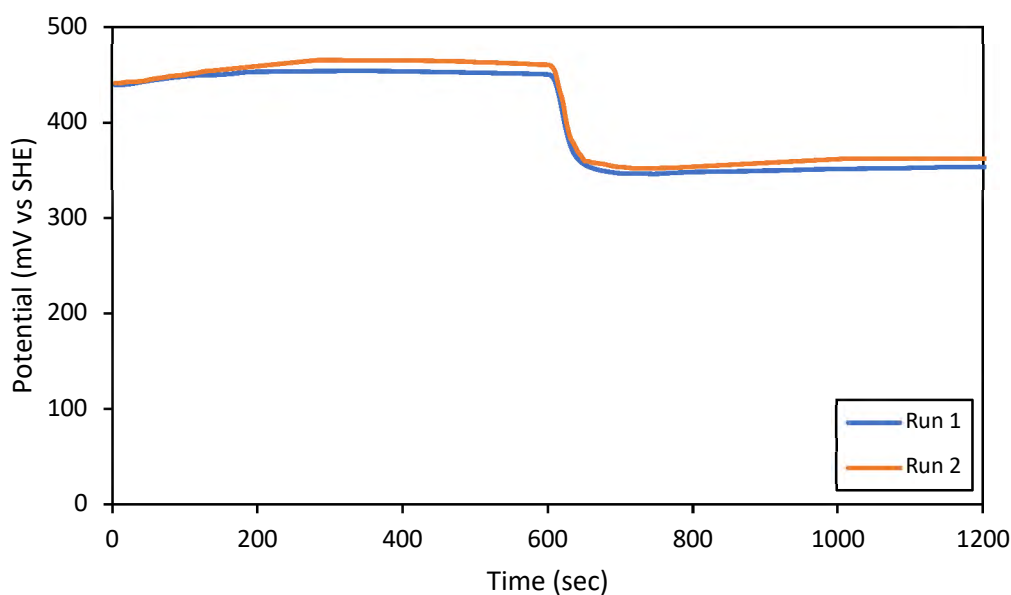


Figure 3.18: Duplicate rest potential profiles of sperrylite with PAX at pH 3

3.7. Isothermal Titration Calorimetry

The reactions (physical or chemical) that occur during collector adsorption on a mineral surface are accompanied by a change in enthalpy (or heat). The magnitude of this change in heat gives information on the strength of the adsorption of the collector. In this study, the heat of collector adsorption was measured using isothermal titration calorimetry (ITC). These measurements were performed using a TAM III microcalorimeter from TA Instruments. The ITC experiments were conducted at 25°C, wherein the temperature was controlled within a precision of 0.0001°C.

The microcalorimeter setup used for the ITC experiments is illustrated in Figure 3.19. This consists of the microcalorimeter, a Lund syringe pump and a titration accessory. The titration accessory is equipped with a titration tube, a gold-plated propeller stirrer that fits onto the titration shaft and a stainless steel sample ampoule. During an experiment, the reaction ampoule is placed onto the titration ampoule accessory equipped with the stirrer. A reference ampoule is placed onto a reference ampoule. Both the reaction and reference ampoule contain exactly the same mineral slurry, except that the reaction ampoule is stirred and titrations are made into this ampoule. Titrations are made using a syringe equipped with a cannula that is inserted into the reaction ampoule via the titration tube. During an experiment, the titrations from the syringe are controlled using a Lund pump.

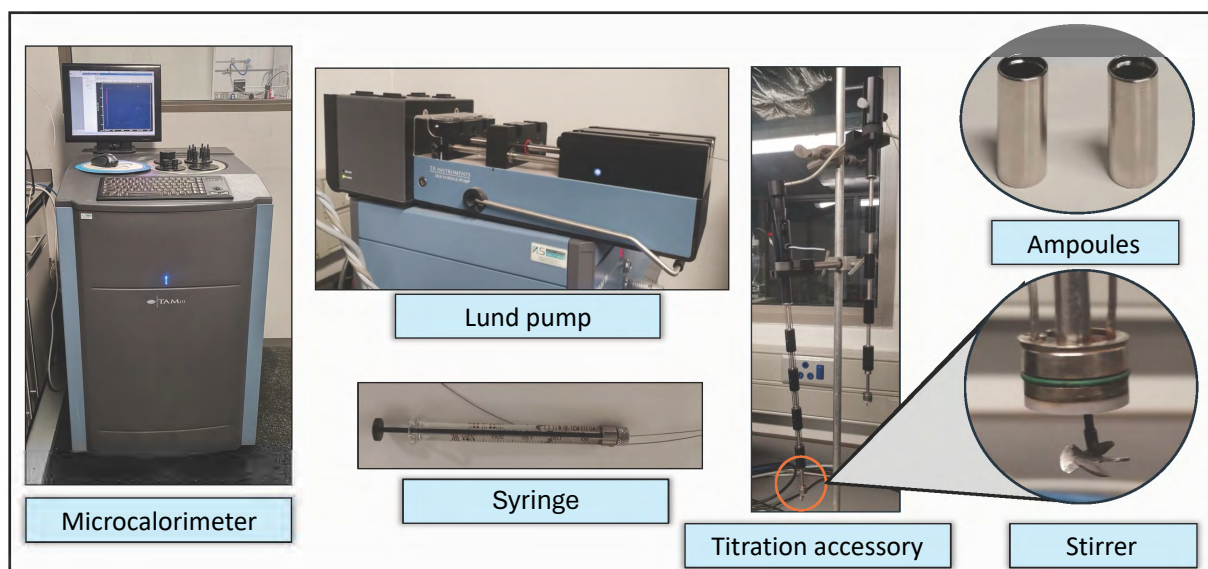


Figure 3.19: Isothermal Titration Calorimetry instrument set-up

3.7.1. ITC experimental procedure

0.2 ± 0.0004 g of the synthetic mineral in the -38 μm size fraction was weighed into the reaction and reference ampoules. Thereafter, 0.7 ml de-ionised water adjusted to pH 9 was added to each ampoule and ultra-sonicated in a water bath for 30 s to disperse the slurry. The pH of the de-ionised water was adjusted drop-wise using 0.1 M NaOH before being added into the ampoules. The ampoules were then loaded into the calorimeter and the heat flow was allowed to equilibrate. The collector solution was loaded into a titration syringe and 2 μl titrations were made at 1-hour intervals, totalling 20 titrations. Each titration contained a collector concentration equivalent to approximately 25% of a pseudo-monolayer.

In this thesis, the enthalpies are reported at a collector concentration equivalent to 1 pseudo-monolayer surface coverage (i.e. 4 titrations). The full details of the heat of collector adsorption vs collector dosage profiles for the different collectors investigated are shown in APPENDIX B.

Calibration of calorimeter

The calorimeter was operated in dynamic mode for the ITC experiments. Before the experiments, a dynamic calibration of the sample and reference titration ampoules with the titrand was performed. This was done to correct for the thermal inertia of the ampoules which arises from the difference between the heat detected by the calorimeter and the heat produced by the sample. The thermal inertia depends on the heat capacity and heat transfer from the sample to the surroundings. Dynamic calibration uses a known power input to determine a gain factor and two-time constants which are then used to correct for the thermal inertia of the ampoules.

3.7.2. Blank ITC experimental procedure

The enthalpy measured by the microcalorimeter consists of a change in enthalpy from the interaction of the collector with the mineral, a change in enthalpy resulting from stirring and

Chapter 3: Experimental Details

mixing, and a change in enthalpy when the collector is exposed to a larger volume (i.e., enthalpy of dilution). This can be given by the equation 3-4.

$$\Delta H_{Total} = \Delta H_{collector+mineral} + \Delta H_{dilution} + \Delta H_{mixing} \quad 3-4$$

In this study, the heat of stirring and mixing was assumed to be negligible (Zogg et al., 2004). Therefore, the total enthalpy measured consists of a change in enthalpy from the collector-mineral interactions and enthalpy of dilution. The enthalpy of dilution was measured using a similar procedure as that described in section 3.7.1, except that in this case there was no mineral present. The enthalpy of dilution was then subtracted from the total enthalpy of interaction to give the enthalpy of interaction between the collector and the mineral surface. The enthalpies of dilution obtained for the different collectors are shown in Table 3.17. All enthalpies reported in this thesis have been corrected for the enthalpy of dilution.

Table 3.17: Enthalpy of dilution for the collectors investigated

Collector	Enthalpy of dilution (kJ/mol)
PAX	17.45
PNBX	26.25
PNBTTC	28.54
PTU	18.10

3.7.3. ITC reproducibility tests

Due to the limited availability of sperrylite, the ITC tests were conducted in single tests. Reproducibility tests to determine the reliability of the ITC tests were conducted using pyrite with PNBX at pH 9. The results obtained showing the specific enthalpy of collector adsorption as a function of collector dosage are presented in Figure 3.20.

Chapter 3: Experimental Details

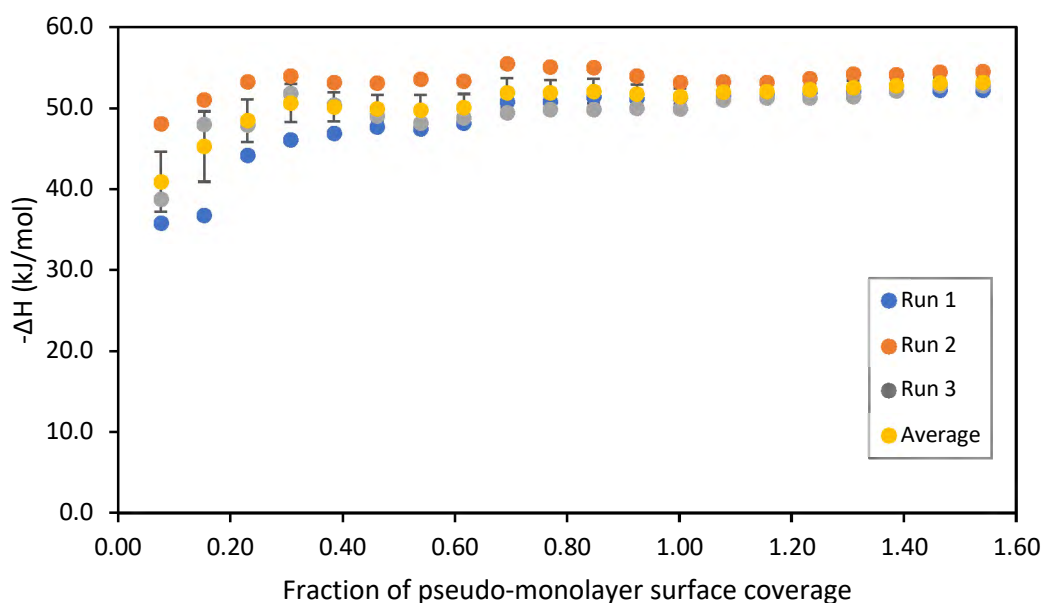


Figure 3.20: ITC reproducibility tests using pyrite with PNBX at pH 9

The highest relative standard error was found to be 9.5% as shown in Table 3.18. At 1 pseudo-monolayer surface coverage, the relative standard was found to be 1.8% which was deemed acceptable.

Table 3.18: ITC reproducibility test results showing average enthalpies and the associated errors

Fraction of monolayer	Cumulative specific enthalpy of adsorption (kJ/mol)				Std. Dev.	Std. Error	Relative Std. Error
	Run 1	Run 2	Run 3	Average			
0.08	-35.9	-48.1	-38.9	-41.0	6.4	3.7	9.0%
0.15	-36.8	-51.0	-48.0	-45.3	7.5	4.3	9.5%
0.23	-44.2	-53.2	-48.0	-48.5	4.5	2.6	5.4%
0.31	-46.1	-53.9	-51.8	-50.6	4.0	2.3	4.6%
0.38	-46.9	-53.2	-50.4	-50.2	3.1	1.8	3.6%
0.46	-47.7	-53.1	-49.1	-50.0	2.8	1.6	3.3%
0.54	-47.5	-53.5	-48.2	-49.7	3.3	1.9	3.8%
0.62	-48.2	-53.4	-48.8	-50.1	2.8	1.6	3.3%
0.69	-50.8	-55.4	-49.4	-51.9	3.1	1.8	3.5%
0.77	-50.8	-55.0	-49.8	-51.9	2.8	1.6	3.1%
0.85	-51.4	-55.0	-49.9	-52.1	2.6	1.5	2.9%
0.92	-51.2	-53.9	-50.0	-51.7	2.0	1.2	2.3%
1.00	-51.3	-53.2	-49.9	-51.5	1.6	0.9	1.8%
1.08	-51.6	-53.3	-51.1	-52.0	1.2	0.7	1.3%
1.15	-51.7	-53.2	-51.3	-52.1	1.0	0.6	1.1%
1.23	-51.9	-53.7	-51.2	-52.3	1.2	0.7	1.4%
1.31	-52.1	-54.2	-51.5	-52.6	1.4	0.8	1.6%
1.39	-52.1	-54.2	-52.2	-52.8	1.2	0.7	1.3%
1.46	-52.2	-54.4	-52.7	-53.1	1.2	0.7	1.3%

3.8. Ultraviolet spectroscopy

UV-visible spectroscopy experiments were conducted to determine the extent of collector adsorption onto the mineral surface. These experiments were conducted using an Ultrospec™ 2100 Pro UV-visible spectrophotometer from Amersham Biosciences shown in Figure 3.21. Quartz cuvettes with an internal width of 10 mm were used to hold the samples for the spectroscopic measurements.

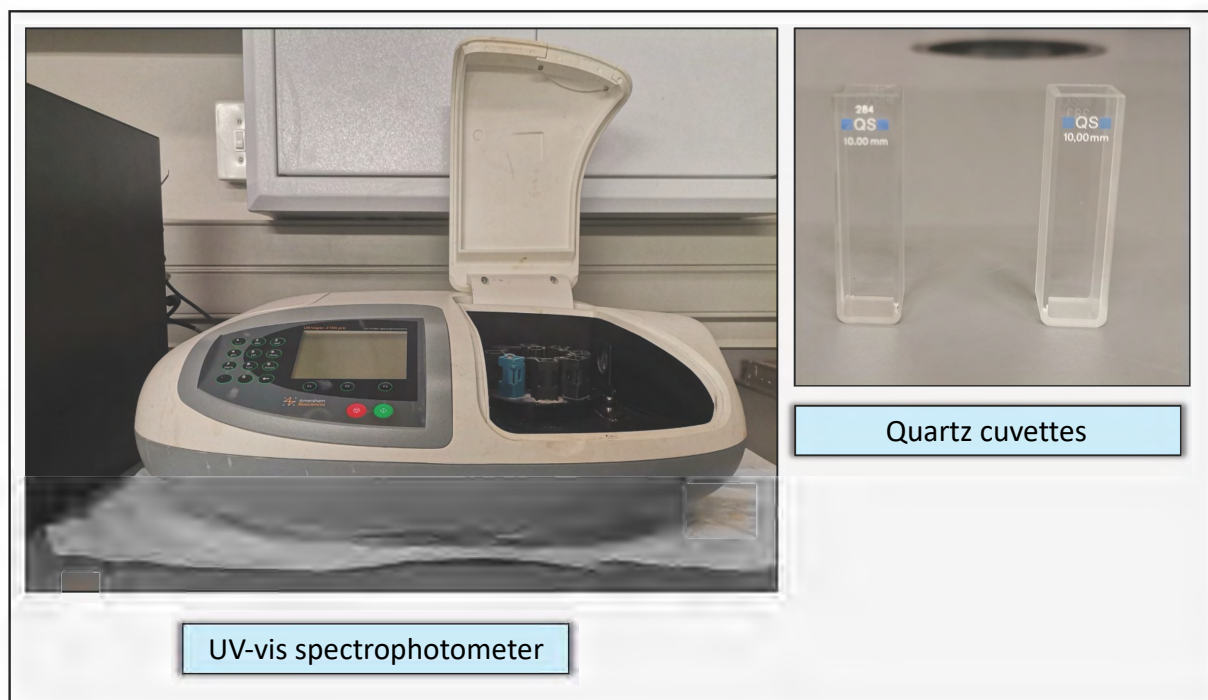


Figure 3.21: UV-vis spectrophotometer and quartz cuvettes used in this study

3.8.1. UV-vis spectroscopy experimental procedure

Mineral solutions were prepared using 1 ± 0.001 g of the synthetic mineral in the $-38 \mu\text{m}$ size fraction and 40 ml de-ionised water. The pH of the slurry was adjusted drop-wise using 0.1 M NaOH or HCl. The slurry was conditioned using a magnetic stirrer. For the experiments in which Eh was chemically modified, NaClO at a concentration of 0.001 M was used. After conditioning the slurry at the desired conditions, the collector was added at the required dosage.

In **Phase One**, the conditioning time of the PAX, PNBX and PTU collectors was chosen to be 20 minutes to allow sufficient time for the different collectors to adsorb onto the mineral surface. The spectra of the PNBTTTC collector could not be measured due to the very fast decomposition rate of this collector. In **Phase Two** and **Three**, where the effect of pH was investigated, a shorter conditioning time was selected. At lower pH, the rate of collector decomposition is faster. Therefore, a conditioning time of 5 minutes was chosen in **Phase Two** and **Three** to minimise collector decomposition while allowing sufficient time for collector adsorption.

Chapter 3: Experimental Details

After collector conditioning, the slurry was filtered using a Millipore Stericup vacuum filter and filter paper with a pore size of 0.45 μm . The filtered solutions were transferred into quartz cuvettes, after which the absorbance spectra were measured from 190 to 600 nm wavelength using a UV-vis spectrophotometer. The UV-vis spectrophotometer measures the concentration of the collector remaining in the solution. The amount of the collector adsorbed onto the mineral surface was determined by subtracting the residual collector concentration from the known initial collector concentration dosed.

3.8.2. Standard Absorbance vs Concentration curves

As already mentioned, the UV-vis spectrophotometer measures the absorbance of the collector remaining in the solution. In order to calculate the residual collector concentration from these absorbances, standard collector absorbance vs concentration curves were first determined. Standard collector solutions of known concentration were prepared and their absorbance spectra were measured. The collector concentration of the standard solutions was then calculated from their absorbances using Beer-Lambert's Law which states that absorbance is directly proportional to concentration according to equation 3-5 (Swinehart, 1962).

$$A = \epsilon lc \quad 3-5$$

where:

- A - Absorbance (-)
- ϵ - molar absorptivity $\left(\frac{L}{\text{mol.cm}}\right)$
- l - path length of the cuvette (cm)
- c - concentration (mol/L)

A plot of A vs c gives a linear relationship in the form $y = mx$ where the slope can be expressed by ϵl . The A vs c plots for the different collectors are shown in Figure 3.22, where the characteristic peaks at 301 nm for the xanthates and 288 nm for the PTU collector are plotted.

Chapter 3: Experimental Details

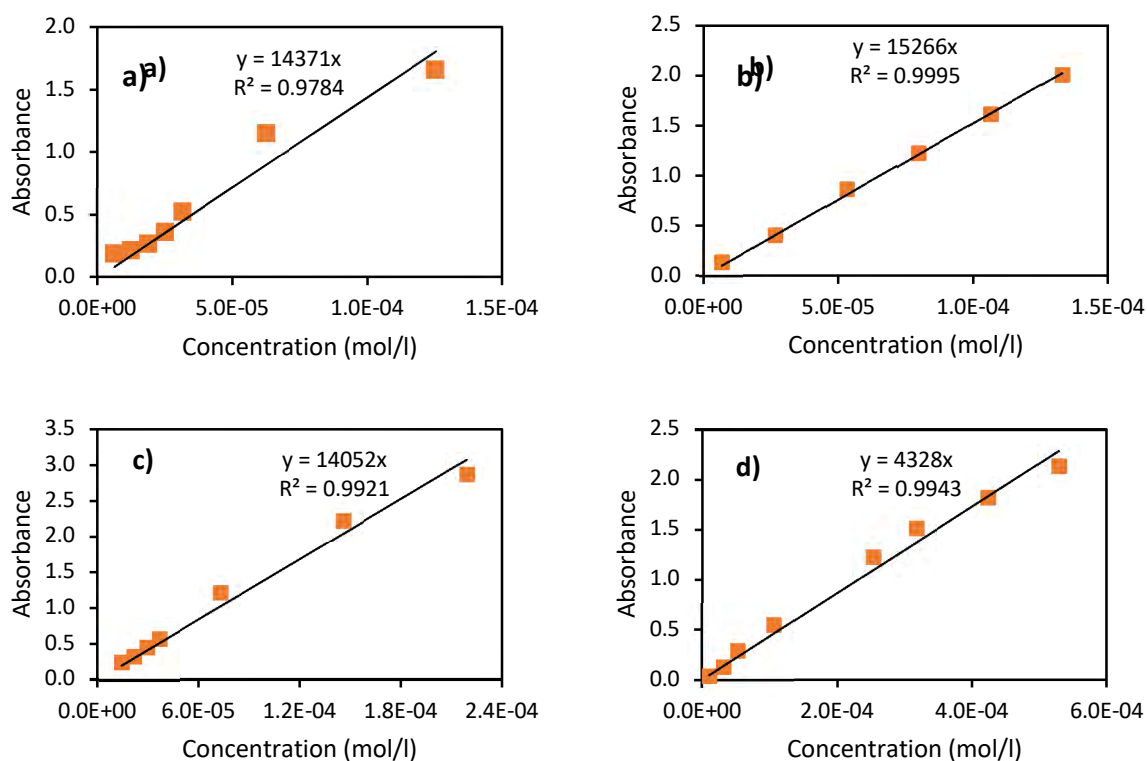


Figure 3.22: Standard absorbance vs concentration curves for a) PAX, b) PNBX, c) SIBX and d) PTU collectors. Absorbance at 301 nm for the xanthates and 288 for PTU

For the UV-vis spectroscopy adsorption tests on the minerals, the initial collector concentration was known, and the absorbance, hence the concentration, of the residual collector could be determined. Therefore, the amount of collector adsorbing onto the mineral could be determined by difference.

3.8.3. UV-vis spectroscopy reproducibility tests

Reproducibility tests were conducted to determine the reliability of the results obtained from the UV-vis spectroscopy experiments. These tests were conducted using the adsorption of PNBX on sperrylite at pH 9. The reproducibility test results are presented in Table 3.19, showing the residual average absorbances of PNBX at 301 nm and the associated errors. The reproducibility test results show that reliable results could be obtained from the UV-vis spectroscopy tests, with the relative standard error being 1.8%. Subsequent UV-vis adsorption tests were conducted in single tests owing to the limited availability of the PGMs.

Table 3.19: Reproducibility test results of UV-vis spectroscopy using PNBX and sperrylite

Description	Value
A ₃₀₁ Sample 1	0.272
A ₃₀₁ Sample 2	0.259
A ₃₀₁ Sample 3	0.257
Average absorbance	0.263
Standard deviation	0.0083
Standard error	0.0048
Relative standard error	1.8%

3.9. Mineral surface characterisation

3.9.1. Fourier Transform Infrared Spectroscopy

The FTIR analyses were performed at the GeoRessources Faculty of Sciences and Technologies laboratories, at the University of Lorraine, in order to characterise the surface of the minerals investigated. The analyses were performed using a Bruker FTIR EQUINOX IFS 55 spectrometer shown in Figure 3.23. The spectrometer comprises two compartments attached to an IRScope 1 infrared microscope with a temperature-controlled stage.

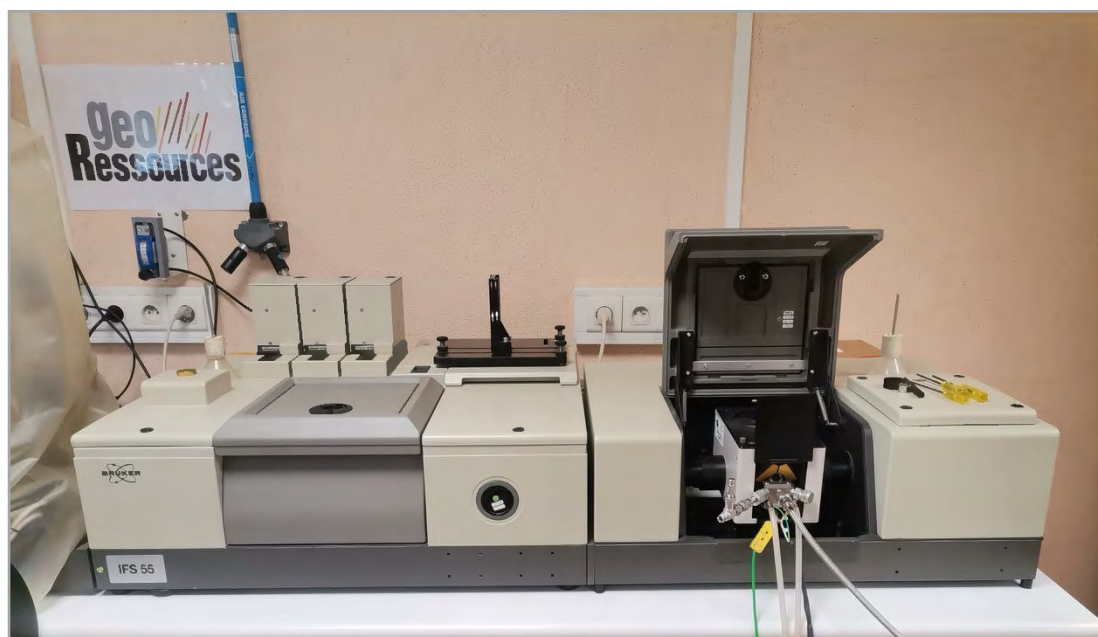


Figure 3.23: FTIR spectrometer used in this study

1 g of the synthetic mineral in the $-38\ \mu\text{m}$ size fraction was weighed and mixed with 50 ml ultra-pure water or 0.01 M NaClO solution. The slurry was ultra-sonicated for 5 minutes to disperse the particles. The pH of the slurry was adjusted drop-wise using either 0.1 M HCl or NaOH. In the cases where a collector was used, 5×10^{-4} M PAX was added and conditioned by

stirring using a magnetic stirrer for 10 minutes. Thereafter, the slurry was filtered using a Buchner funnel. The filtered samples were transferred into a desiccator where they were dried under near-vacuum conditions and stored until analysis.

The analyses were performed using KBr of spectral grade as the medium which was stored in the oven at 80°C to prevent moisture absorption. The conditioned mineral sample was transferred into a mortar and mixed with KBr at a ratio of 1.5 wt.% mineral sample. The mixture was finely ground into a powder using a pestle and mortar after which it was transferred into a pellet press capsule where it was pressed using a bolt press to evenly distribute the particles. Thereafter, the pellet press capsule was transferred into a manual hydraulic press to make a sample pellet.

Prior to loading the sample pellet into the spectrometer, a blank KBr pellet was prepared in order to perform a background scan. The preparation of the blank KBr pellet followed the same procedure as that of the sample pellet, except that in this case there was no mineral sample mixed with the KBr. The blank KBr pellet was loaded into the spectrometer and a background scan was performed. Thereafter, this was removed, and the sample pellet was loaded to perform the FTIR analyses where 200 scans in 2 minutes were performed for each sample. The capsule press accessory, mortar and pestle were thoroughly cleaned in-between analyses using chloroform and dried using paper towels.

3.9.2. X-Ray photoelectron spectroscopy

The sample preparation for the XPS analyses followed the same procedure as that for the FTIR experiments. XPS analyses were conducted at the Laboratory of Physical Chemistry and Microbiology for the Environment (LCPME), University of Lorraine. XPS spectra were acquired at room temperature under a pressure of $\sim 10^{-7}$ using a KRATOS Axis Ultra DLD (Kratos Analytical, U.K.) X-ray photoelectron spectrometer with a monochromatic Al K α X-ray source (1486.6 eV). The instrument was calibrated using metallic copper with a binding energy of 932.62 eV for the Cu $_{3/2}$ line. Spectra were recorded either in low-resolution mode with 1.0 eV steps and 160 eV analyzer pass energy or in high-resolution mode with 0.05 eV steps and 20 eV pass energy. Quantification was performed using the photoemission cross sections and coefficients provided in the *Vision* package. Calculations of the XPS elemental compositions based on the main peak areas measured from the high-resolution spectra were performed using the *Kratos Vision* 2.2.11 software.

3.9.3. Raman spectroscopy

The Raman spectroscopy analyses were performed at the GeoRessources laboratories, at the University of Lorraine. These analyses were performed using a Raman Rxn4 spectrometer supplied by Kaiser Optical Systems, Inc., with a laser excitation wavelength of 532 nm and a fibre-optic Raman sampling probe. The set-up used to perform the Raman analyses in this study is shown in Figure 3.24.

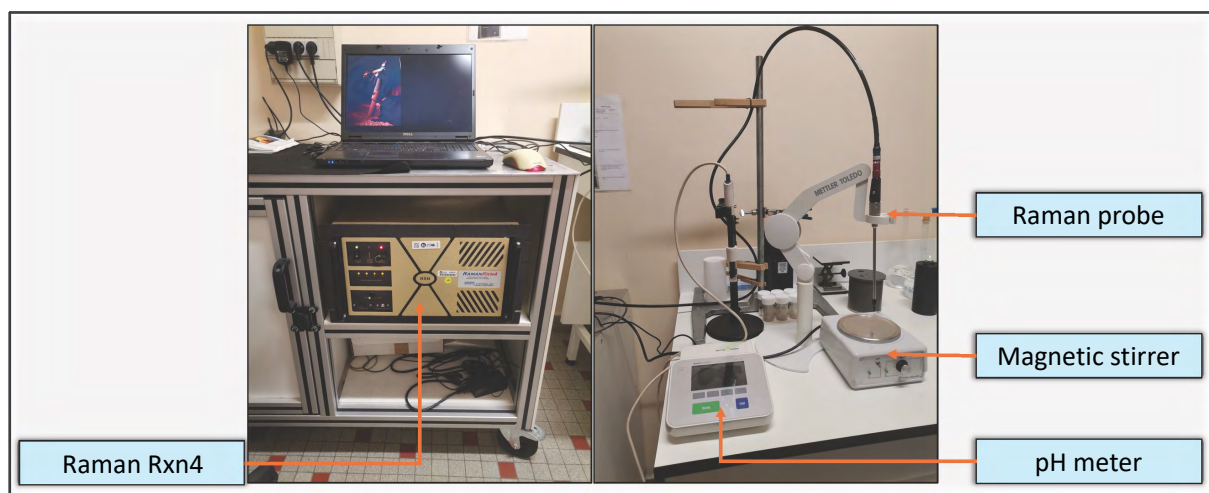


Figure 3.24: Experimental set-up for the Raman spectroscopy analyses

Three separate sets of spectra were recorded for each condition investigated:

1) Solution only spectra

A 50 ml solution was prepared using ultra-pure water or 0.01 M NaClO and the pH was adjusted to 9 or 3. The pH was adjusted drop-wise using 0.1 M NaOH or HCl. In the cases where a collector was used, 5×10^{-4} M PAX was added. The Raman spectra of the solution were then recorded.

2) Dry mineral ('as is') spectra

1.5 g of the synthetic mineral in the $-38 \mu\text{m}$ size fraction was weighed into a sample holder and the spectra of the dry mineral were recorded.

3) Slurry spectra

1.5 g of the mineral was mixed with 50 ml ultra-pure water or 0.01 M NaClO and the pH was adjusted to 9 or 3. Thereafter, 5×10^{-4} M PAX was added where this was investigated. *In-situ* Raman spectra of the slurry were recorded at 1-minute intervals for 10 minutes.

3.9.4. Zeta potential measurements

Zeta potential measurements were conducted to measure the surface charge of the PGM minerals investigated. These measurements were performed at the GeoRessources laboratories, at the University of Lorraine. A ZetaPhoremeter VI[®] supplied by CAD instruments was used to measure the electrophoretic mobility of the minerals. The experimental set-up used for the zeta potential measurements is shown in Figure 3.25.

The ZetaPhoremeter was equipped with a quartz cell connecting a pair of platinum electrodes (anode and cathode), a digital video image capture (CCD camera), and a laser-illuminator. The video capturing the electrophoretic mobility of the particles was analysed using the

Chapter 3: Experimental Details

Zetacompact software and converted to zeta potentials using the Smoluchowski equation shown in equation 3-6 (Sze et al., 2003).

$$v_E = 4\pi\epsilon_0\epsilon_r \frac{\zeta}{6\pi\mu} (1 + \kappa r) \quad 3-6$$

where:

- v_E - electrophoretic mobility
- ϵ_0 - relative dielectric constant
- ϵ_r - electrical permittivity of a vacuum
- μ - solution viscosity
- κ - Debye-Hückel parameter
- ζ - zeta potential

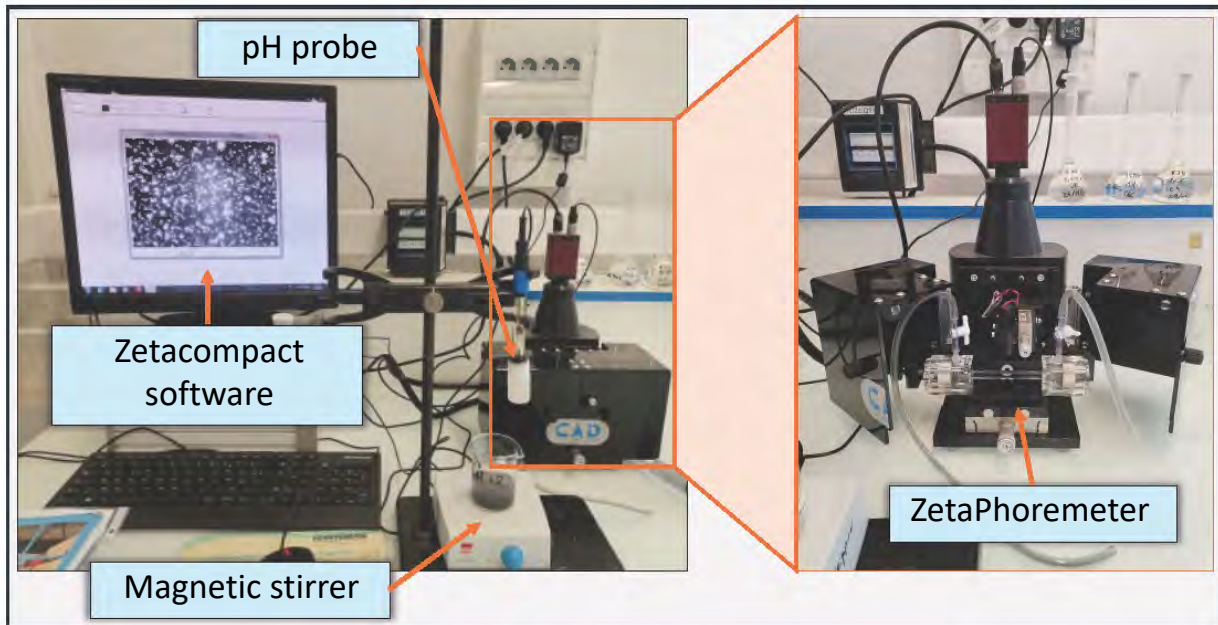


Figure 3.25: Experimental set-up for the zeta potential measurements

The procedure followed in conducting the zeta potential measurements is illustrated in Figure 3.26. The synthetic PGMs in the $-38 \mu\text{m}$ size fraction were further ground to $-20 \mu\text{m}$ using a mortar and pestle. 0.075 g of the mineral was weighed and mixed with 60 ml of 0.12 M KCl in a beaker. KCl was used as the background electrolyte. The slurry was ultra-sonicated for 5 minutes to disperse the particles. Thereafter, the slurry was conditioned by using a magnetic stirrer at the relevant pH where this was adjusted using either 0.1 M NaOH or HCl. Experiments were conducted in the pH range 2 to 12 at increments of 2 pH units, without and with 5×10^{-4} M PAX collector. The collector was conditioned for 10 minutes for the experiments in which it was added. The conditioned slurry was allowed to settle for 3 to 5 minutes before taking a supernatant sample for the electrophoretic mobility measurement.

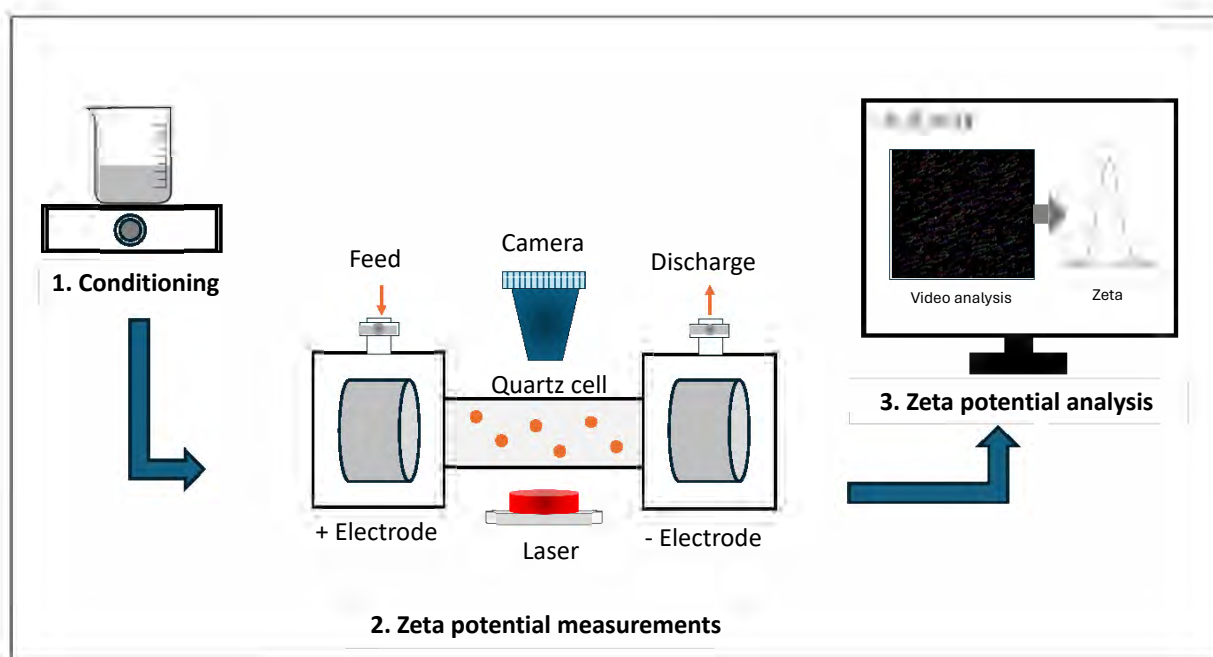


Figure 3.26: Procedure for performing zeta potential measurements

The sample was filled into the cell of the ZetaPhoremeter via the feed tube, ensuring that there were no bubbles formed in the tank. The electrophoretic mobility of the particles was captured by the CCD camera, and this was converted to zeta potentials in the *Zetacompact* software using the Smoluchowski equation. All experiments were conducted in duplicates and the average zeta potentials are reported in this thesis.

3.9.4.1. Zeta potential measurements calibration

Two types of calibration tests were performed daily before using the ZetaPhoremeter, viz. conductivity calibration and stationary plane calibration.

a) Conductivity calibration

The conductivity calibration was performed using 10^{-02} M KCl with known conductivity at the temperature in which the experiments were conducted, i.e. room temperature. The conductivity calibration is essentially a calibration of the effective distance between the two electrodes.

b) Stationary plane calibration

Prior to performing zeta potential measurements, the ZetaPhoremeter was tested daily using a reference dispersion of TiO_2 (Aeroxide® TiO_2 from Evonik-Degussa, Germany). The composition for a 1-litre TiO_2 dispersion solution is shown in Table 3.20.

Table 3.20: Formulation of a 1-litre TiO₂ reference dispersion solution

Description	Volume added (ml)
Stock solution of KCl at 1 g/l	100
Stock solution of sodium pyrophosphate (Na ₂ P ₂ O ₇) at 1 g/l	10
Stock solution of TiO ₂ at 1 g/l	0.1
Ultra-pure water	889.9

To perform a TiO₂ reference dispersion test, 50 ml of the reference dispersion solution was added to a beaker. The beaker was then placed in an ultrasonic chamber where it was sonicated for 1 minute. Thereafter, the zeta potential of the reference dispersion solution was measured. The measured zeta potential should be between 30 and 40 mV at pH 7.

3.10. Batch Flotation

Microflotation tests are ideal for measuring the hydrophobicity of specific minerals since, when properly controlled, there are no interfering effects from the froth phase, hydrodynamics, and the presence of other minerals. To test whether any benefits observed in microflotation are sustained in a more realistic scenario, batch flotation experiments were conducted.

3.10.1. Milling

A Platreef ore was used for the batch flotation experiments. The preparation of the ore to 3.7 kg representative samples with a top size of 2.6 mm has been described in section 3.3. Milling of the ore to the desired grind for flotation was performed using a 3 kg stainless steel grinding mill pictured in Figure 3.27. The grind chosen in this study was 80% solids passing 45 µm. This grind was chosen as typical of a PGM concentrator secondary in order to ensure substantial liberation of the fine-grained PGM particles.

Chapter 3: Experimental Details



Figure 3.27: Stainless steel grinding mill

A milling curve was produced to determine the milling time required to achieve the desired grind. This was done by wet milling the 3.7 kg ore sample at 66 wt.% solids using tap water. The mill was charged with 22 stainless steel rods as the grinding media. The ore and the water were loaded into the mill and this was milled for 20 minutes. A summary of the details of the mill used in this study is provided in Table 3.21.

Table 3.21: Details of the grinding mill used in this study

Stainless steel grinding mill	
Mass (kg)	3.0
Speed (rpm)	56.4
Inner diameter (mm)	303
Length (mm)	301
Stainless steel grinding media (rods)	
No. of rods	22
Mass of each rod (kg)	0.79
Diameter of each rod (mm)	21
Length of each rod (mm)	285

The milled slurry was filtered using a filter press and the filtered pulp cake was cut into four equal quarters. One-quarter of the pulp cake was dried in an oven (EcoTherm^e, Labotec) at 110°C for about three hours. The rest of the pulp cake was dried at 80°C overnight. The dried

quartered pulp cake was weighed and wet-screened using a sieve with an aperture size of 45 μm . The solids passing through 45 μm were filtered and dried, and their masses were recorded. Thereafter, all the solids were recombined into 3.7 kg and this process was repeated for a milling time of 45 and 80 minutes. The milling curve showing the %solids passing 45 μm as a function of time is shown in Figure 3.28. To achieve an 80% solids passing 45 μm grind, a milling time of 105 minutes is required (extrapolated).

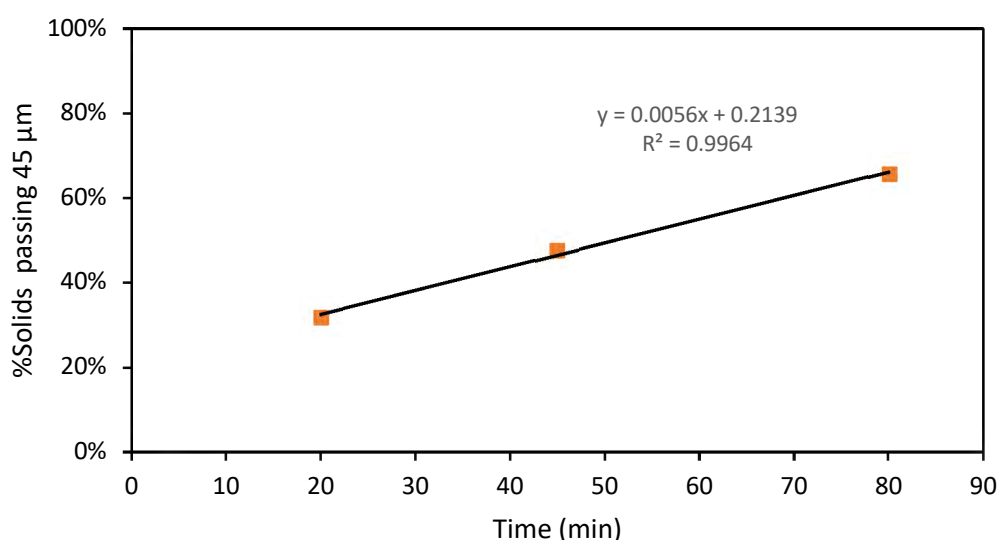


Figure 3.28: Milling curve of the Platreef ore used in this study

It should be noted that in real process milling, mild still/grinding media would typically be used instead of stainless steel/media. Mild steel is more susceptible to corrosion/dissolution, and this consumes oxygen in the mill, thus lowering the pulp Eh. As a result, the conditions in the mill may not be sufficiently anodic to allow for the adsorption of the collector (e.g. oxidation of xanthate to dixanthogen). In addition, the use of mild steel could lead to galvanic interactions between the media and the mineral, where electrons flow from the mild steel to the mineral. This could result in an accelerated rate of corrosion/dissolution of the media leading to reactions at the mineral/solution interface and the subsequent formation of hydrophilic metal hydroxides on the mineral surface (Rao, 2004). Therefore, the type of mill/media is an important consideration if the findings of this work were to be applied in a real process.

3.10.2. Batch Flotation

The batch flotation experiments were conducted in an 8-L modified Leeds flotation cell pictured in Figure 3.29. The flotation cell was fitted with a variable speed drive which was set to 1200 rpm during the experiments to provide agitation. Air was introduced at the bottom of the cell, and this was maintained at 12 L/min for the batch flotation experiments.

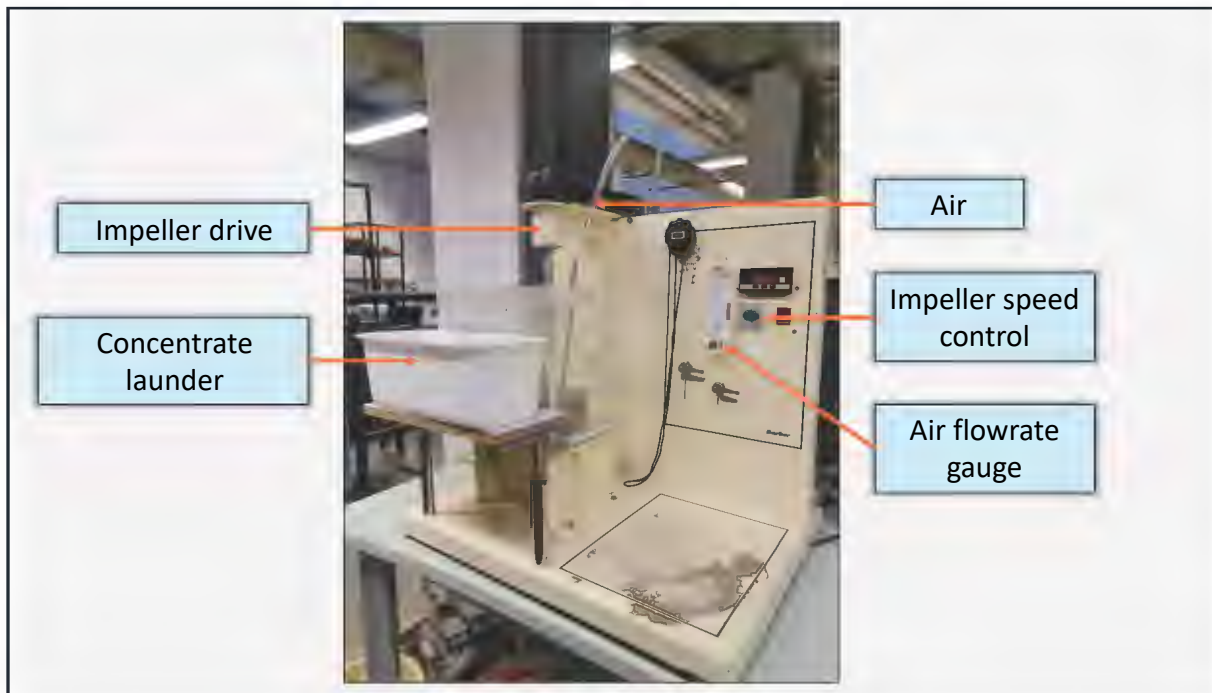


Figure 3.29: 8-L modified Leeds batch flotation cell

The procedure followed in conducting the batch flotation experiments for **Phase One** of this study is illustrated in Figure 3.30. The milled slurry was transferred into the flotation cell and topped up with synthetic plant water with the appropriate composition (see Table 3.15 for synthetic water composition). The slurry was conditioned in the cell with the reagents shown in Table 3.22 for the different conditions investigated. In Table 3.22, it should be noted that Senkol 3 is a dithiophosphate-based collector used as a co-collector and CMC Norilose 6064 is a carboxymethyl cellulose depressant, both of which were supplied by AECI Mining Chemicals (Pty) Ltd. Thereafter, flotation was started with the introduction of the air and the froth was scraped off into the concentrate launder every 15 seconds. Throughout the experiments, the pulp level was controlled manually by topping up with synthetic plant water to maintain a constant froth height of 2 cm. Only a single concentrate was collected, after 6 minutes of flotation. The decision to collect only a single concentrate was based on minimising cost, while not allowing excess residence time that would have allowed all the PGMs to float. It was important to capture the differential in recoveries of the different PGMs and the choice of residence time was based on previous experience in PGM flotation kinetics.

Chapter 3: Experimental Details

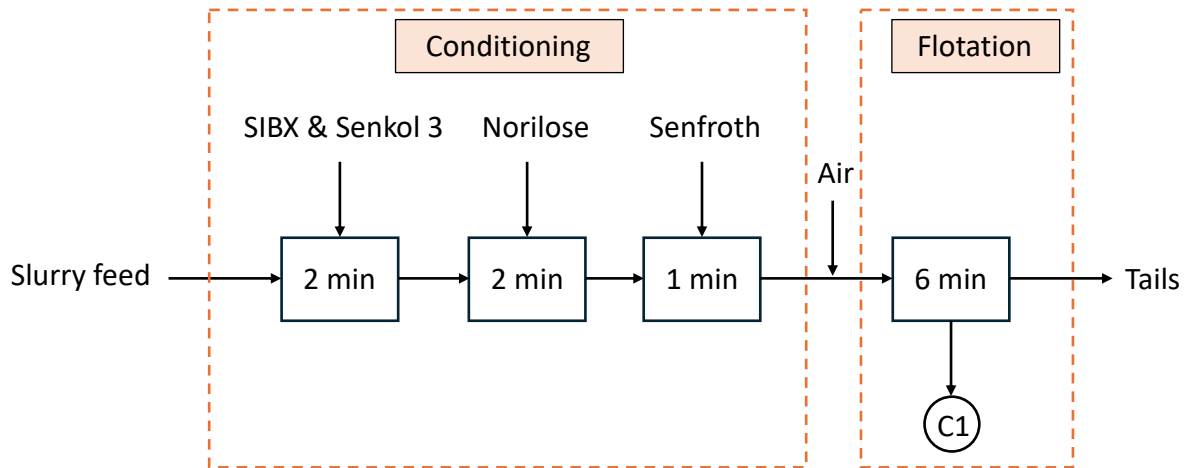


Figure 3.30: Batch flotation experimental procedure used in Phase One

After flotation, both the wet and dry masses of the concentrate were recorded to determine the water recovery. The concentrate and the tails were filtered and dried in an oven at 80°C. The dried masses were recorded and used to determine the solid recoveries.

Table 3.22: Reagents used for the different flotation conditions investigated

Reagent	Standard case	PNBTTC case	High ionic strength case
SIBX	140 g/t	-	140 g/t
Senkol 3	47 g/t	-	47 g/t
PNBTTC	-	140 g/t	-
CMC Norilose 6064	80 g/t	80 g/t	80 g/t
Senfroth 516	40 g/t	40 g/t	40 g/t
Synthetic plant water (SPW)	1 SPW	1 SPW	10 SPW

In **Phase Three** of this study, three cases were investigated in the batch flotation experiments, viz.:

- 1) Case 0: pH 9 (standard case),
- 2) Case 1: pH 3
- 3) Case 2: Two-stage flotation (stage 1 = pH 9, stage 2 = pH 3)

The procedure used to conduct these batch flotation experiments was the same as that used in **Phase One**, except that in this case four concentrates were collected instead of one. The four concentrates were collected for 2, 4, 6 and 8 minutes, respectively. The procedure used to conduct the batch flotation experiments for Phase Three is illustrated in Figure 3.31 (Case 0), Figure 3.32 (Case 1) and Figure 3.33 (Case 2).

Chapter 3: Experimental Details

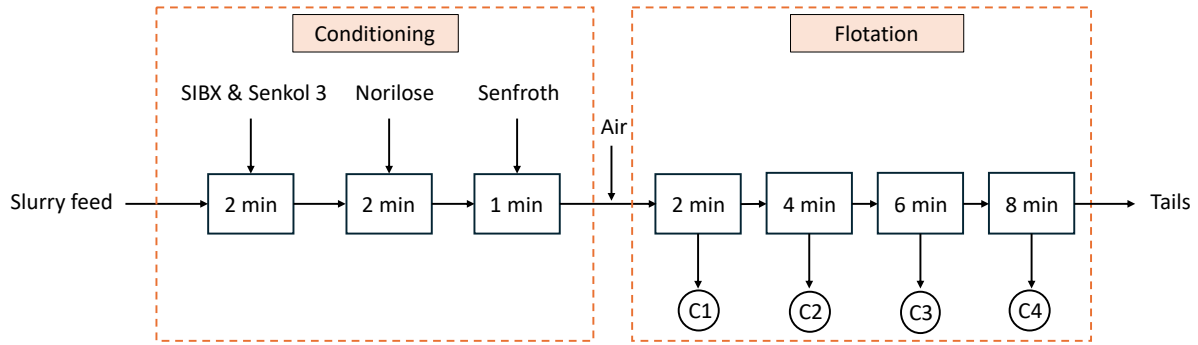


Figure 3.31: Batch flotation experimental procedure used for Case 0 in Phase Three

Case 0 was conducted at the natural pH of the Platreef slurry which is pH 9. In Case 1, the pH of the slurry was adjusted to pH 3 using H_2SO_4 before conditioning with the flotation reagents.

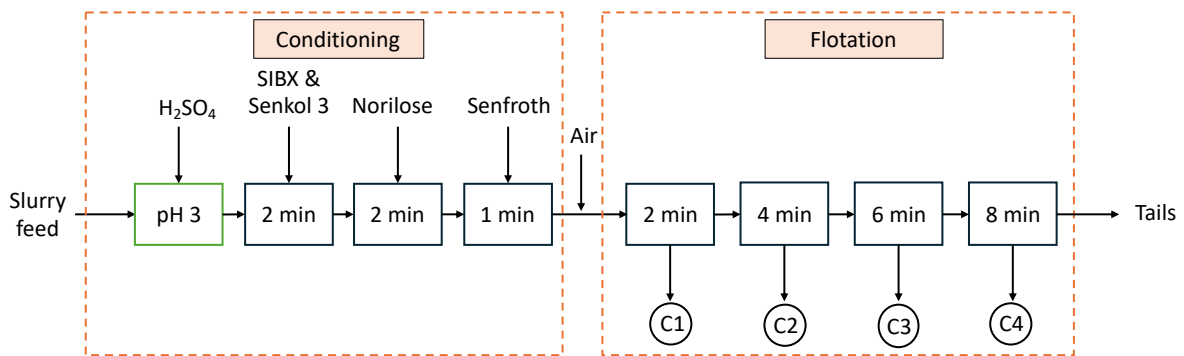


Figure 3.32: Batch flotation experimental procedure used for Case 1 in Phase Three

In Case 2, the air was switched off to pause flotation after collecting the fourth concentrate. Thereafter, the pH of the slurry remaining in the cell was adjusted to pH 3 using H_2SO_4 . After pH adjustment, the slurry was conditioned with the flotation reagents as shown in Figure 3.33. The same flotation reagents and dosages as those shown in Table 3.22 for the standard case were used in **Phase Three**. However, in stage 2 of Case 2; SIBX at 100 g/t, Senkol 3 at 33.6 g/t and Senfroth 516 at 20 g/t were used. Flotation was re-initiated with the introduction of air and four concentrates with the same residence times as those in stage 1 were collected. All experiments were conducted in duplicates and the averages are reported in this thesis with the error bars representing the calculated standard errors.

Chapter 3: Experimental Details

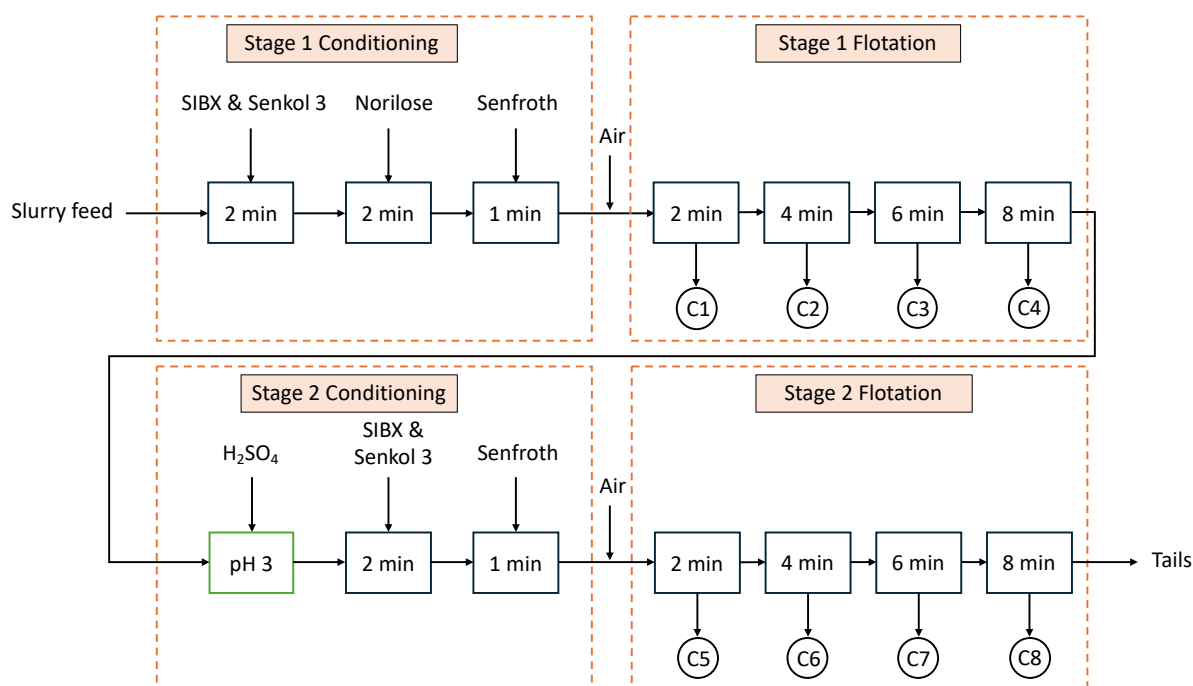


Figure 3.33: Batch flotation experimental procedure used for Case 2 in Phase Three

After filtering and drying, the feed concentrates and tails were collected and sub-sampled for analytical work.

3.10.3. X-Ray fluorescence

XRF was used to analyse for Cu and Ni. XRF was conducted using a handheld Olympus Vanta™ C Series analyzer. The assays obtained from XRF were used to calculate the Cu and Ni recoveries.

3.10.4. Inductively coupled plasma-mass spectrometry (ICP-MS)

The feed, concentrates and tails samples were analysed for Pt, Pd, As and Te using ICP-MS. ICP-MS is a novel method for determining differences in PGM species recovery. The standard assay method for PGM ores is to assay only for the metals (usually Pt, Pd, Rh and Au) which is typically done by fire assay concentration followed by Inductively coupled-optical emission spectrometry (ICP-OES). The ICP-MS route was chosen in order to assay for As and Te to differentiate between improvements in recovery for all Pt and Pd minerals, or PGE arsenides and tellurides selectively, without the need for mineralogical analysis which is costly and often difficult to obtain statistically significant data.

Before sub-sampling for ICP-MS, it was necessary to micronise the samples to remove any nugget effects. After micronising, the samples were split using a Rotary Micro Riffler into representative samples of 0.2 g. These samples were subsequently acid-digested using a Mars 6 Microwave Digester. The method used for microwave-assisted digestion is summarised in Table 3.23.

Chapter 3: Experimental Details

Table 3.23: Method for microwave-assisted acid digestion

	Acids	Ramp time (minutes)	Hold time (minutes)	Final temperature (°C)
Digestion	8 ml Aqua Regia, 2 ml HF	30	45	220
Neutralisation	20 ml H ₃ BO ₃	30	10	170

The digested sample was transferred accurately to a 50 ml volumetric flask and filled to the mark with 2 wt.% HNO₃. Thereafter, the samples were sent for ICP-MS analysis.

3.11. Preliminary Experiments

This section presents important considerations that were undertaken before commencing the experimental work.

3.11.1. Collector screening

In **Phase One** of this study, eleven collectors were considered, including four xanthate, five trithiocarbonate and two thiourea collectors. However, only the best-performing collectors from each collector type were used on sperrylite due to the limited availability of the mineral sample. The collectors were screened using the flotation performance of pyrite with these collectors in microflotation. Pyrite was selected as a readily available proxy for sperrylite since these minerals belong to the same crystal group. The microflotation recoveries of pyrite obtained with the collectors are shown in Figure 3.34, where the best-performing collectors from each collector type are highlighted. The PNBX, PAX, PNBTTTC and PTU collectors were selected for the investigations on sperrylite in **Phase One**.

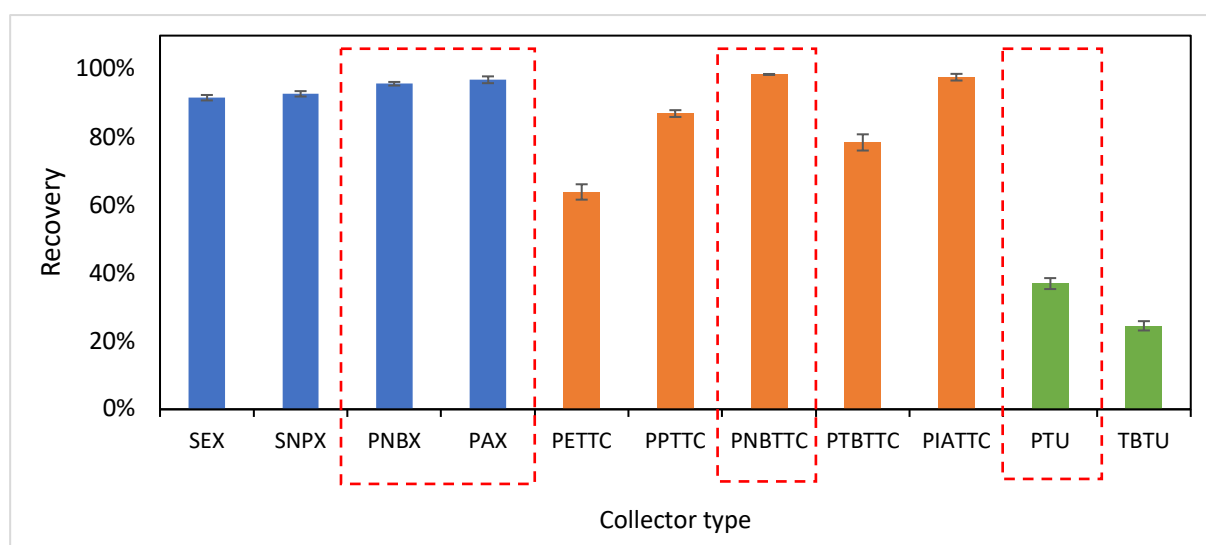


Figure 3.34: Microflotation recoveries of pyrite with xanthate, trithiocarbonate and thiourea collectors; with 1 pseudo-monolayer of collector dosed at pH 9

3.11.2. Effect of NaClO addition on pH

NaClO was used as an Eh modifier for the experiments where chemical control of potential was investigated in Phase Three. It was important to establish whether Eh could be studied at a constant pH to de-couple the effect of pH from Eh when the Eh is controlled chemically. Beaker tests were conducted using de-ionised water adjusted to pH 9 and 4 where 10 % NaClO was added drop-wise and the Eh-pH was measured. It can be seen in the results presented in Figure 3.35 that the pH was fairly constant with the addition of NaClO both at pH 9 and 4. Therefore, the effect of Eh when it is controlled using NaClO could be studied at a constant pH.

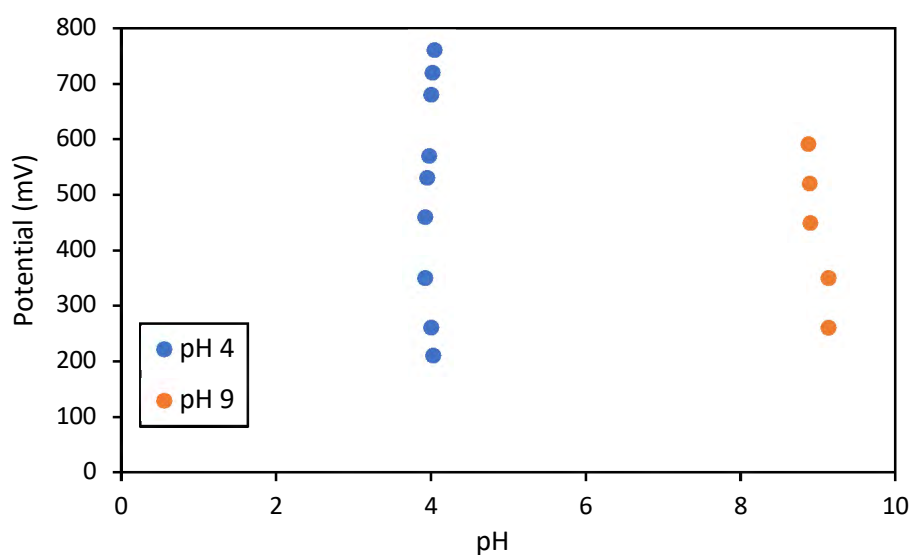


Figure 3.35: Effect of NaClO addition on pH

CHAPTER 4: Investigation of the performance of various collectors on the flotation of sperrylite

4. Investigation of the performance of various collectors on the flotation of sperrylite

4.1. Introduction

This chapter presents the results and discussion of **Phase One** of this work. This phase focused on investigating the flotation performance of sperrylite with collectors such as trithiocarbonate and thiourea collectors that have greater electron-donating properties compared to the conventional xanthates. It was hypothesised that these collectors would bond more readily with the sperrylite surface because the functional groups of the trithiocarbonate and thiourea collectors have a greater electron-releasing tendency, resulting in a greater availability of electrons to form bonds with the mineral surface and thus induce floatability of this poorly floating mineral. The collectors investigated include potassium n-butyl trithiocarbonate (PNBTTC), propyl thiourea (PTU), potassium n-butyl xanthate (PNBX) and potassium amyl xanthate (PAX). In addition, the effect of increasing the ionic strength of the process water used was investigated in an attempt to improve the bubble-particle attachment efficiency of sperrylite.

To better understand the extent of interaction of the collectors with the sperrylite surface and the resultant flotation performance, the extent of adsorption of the collectors as determined using UV-vis spectroscopy was compared with flotation recoveries. This was further supported by determining the collector-mineral energy of interaction, as measured using isothermal titration calorimetry. Finally, batch flotation tests were conducted to determine whether the results obtained in a microflotation cell could be extrapolated to a more realistic scenario as typified by batch flotation of a more complex ore in which a froth phase is present.

4.2. Results

4.2.1. Isothermal Titration Calorimetry (ITC) - Heats of adsorption measurements

ITC experiments were conducted to measure the heat of the interaction of the trithiocarbonate, thiourea and xanthate collectors with sperrylite. These experiments were conducted at pH 9. Table 4.1 shows the heats of adsorption for the different collectors with sperrylite. It should be noted that these heats of adsorption have been corrected for the heat of dilution.

Chapter 4: Investigation of the performance of various collectors on the flotation of sperrylite

Table 4.1: Heat of adsorption of different collectors, at a dosage equivalent to 1 pseudo-monolayer surface coverage, on sperrylite at pH 9

Collector	Heat of adsorption (mJ)	Specific heat of adsorption (kJ/mol)	Corrected specific heat of adsorption (kJ/mol)
PNBTTC	-8.66	-41.80	-
PAX	-6.24	-30.13	-39.92
PNBX	-4.19	-19.96	-60.06
PTU	-7.04	-34.15	-149.53

For collectors with the same functional group, viz., the xanthates, the collector with the longer alkyl chain length had a higher heat of adsorption. This can be seen when comparing the heat of adsorption of PAX and PNBX which have 5 and 4 carbon atoms in their alkyl chains, respectively. On the other hand, for collectors with different functional groups, the order of heat of adsorption depends on the nature of the donor atoms in the polar group of the collector. The heats of adsorption followed the order: TTC>TU>Xanthates.

It should be noted that “kJ/mol” refers to the heat evolved per mole of collector added when the collector adsorbs onto the mineral surface. This is indicated by the specific heat of adsorption. The analysis above assumes that all the moles of the collector added are adsorbed onto the mineral. However, as will be shown by UV-vis spectroscopy (see section 4.2.2), not all moles of the collector added are adsorbed. Therefore, the heat of adsorption should be corrected for the moles of the collector that are actually adsorbed. One way of correcting the heat of adsorption would be to divide by the number of moles of collector that adsorb onto the mineral surface obtained from UV-vis spectroscopy. These are shown as the ‘corrected specific heat of adsorption’ in Table 4.1, where it can be seen that the TU collector has a much higher heat of adsorption compared to the xanthates.

The limitation of using UV-vis data with the ITC data is that the environments in these two types of experiments are most likely different during the experiment. In the UV-vis tests, the pH was regulated at pH 9 throughout the experiments. However, for the ITC tests, it was only possible to regulate pH before the experiment and not during the experiment, since the ampoule used is very small and inaccessible during the 20-hour duration of the experiment. As a result, the effect of pH which may be changing during the ITC experiments is not known. The effect of pH on collector adsorption on sperrylite is investigated in **Phase Two** of this study.

4.2.2. The extent of collector adsorption

The amount of collector that is adsorbed on the surface of sperrylite was studied using UV-vis spectroscopy. The results obtained for each of the collectors are shown in Figure 4.1.

Chapter 4: Investigation of the performance of various collectors on the flotation of sperrylite

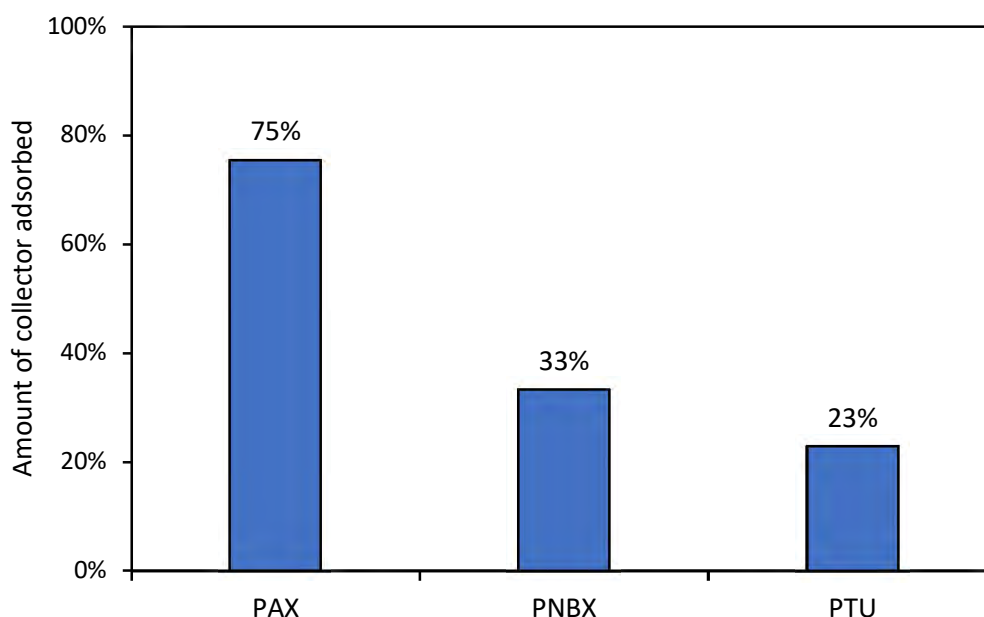


Figure 4.1: Extent of adsorption of the different collectors on sperrylite at an initial collector concentration equivalent to 1 pseudo-monolayer surface coverage, in pH 9 water. PAX and PNBX absorbance peak = 301 nm, PTU absorbance peak = 288 nm

Of the collectors that were studied, Figure 4.1 shows that PAX had the highest extent of adsorption onto sperrylite, with an adsorption of 75% of the original PAX in solution. PTU had the least extent of adsorption, with only 23% of the collector adsorbed. The adsorption of PNBTTTC, which is part of the collector set being studied, could not be measured due to its fast decomposition rate and by the time the post-adsorption concentration was to be measured, most of the collector had decomposed to form carbon disulfide.

The full UV-vis spectra showing the decomposition of PNBTTTC over time are shown in Figure 4.2. It is evident from these spectra that the peaks at 303 nm and 333 nm, which are characteristic of TTC (Du Plessis et al., 2003; Venter, 2008), show a decrease in concentration over time, thus indicating the decomposition of the collector. The TTC decomposes to form carbon disulfide (CS_2) which can be assigned to the peak at 206 nm (Sun & Forsling, 1997) that increases over time.

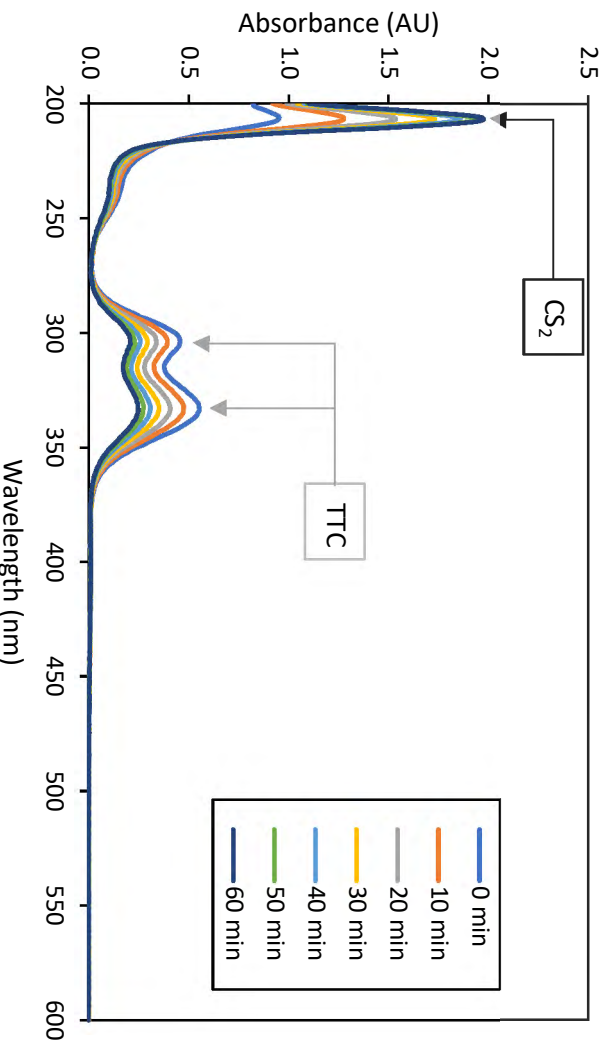


Figure 4.2: UV-vis spectra of a PNBTTTC solution initially containing 2.9×10^{-5} M PNBTTTC at pH 9 recorded at 10-minute intervals for 60 minutes

The decomposition of TTC follows a first-order reaction rate (Venter & Vermaak, 2008). A plot of $\ln(\Delta\text{Abs})$ vs time, where Abs indicates Absorbance, produces a straight line with a slope of $-k$ which is the first-order reaction rate constant. This plot is shown in Figure 4.3 where it can be seen that PNBTTTC has a decomposition rate of 0.0136 min^{-1} .

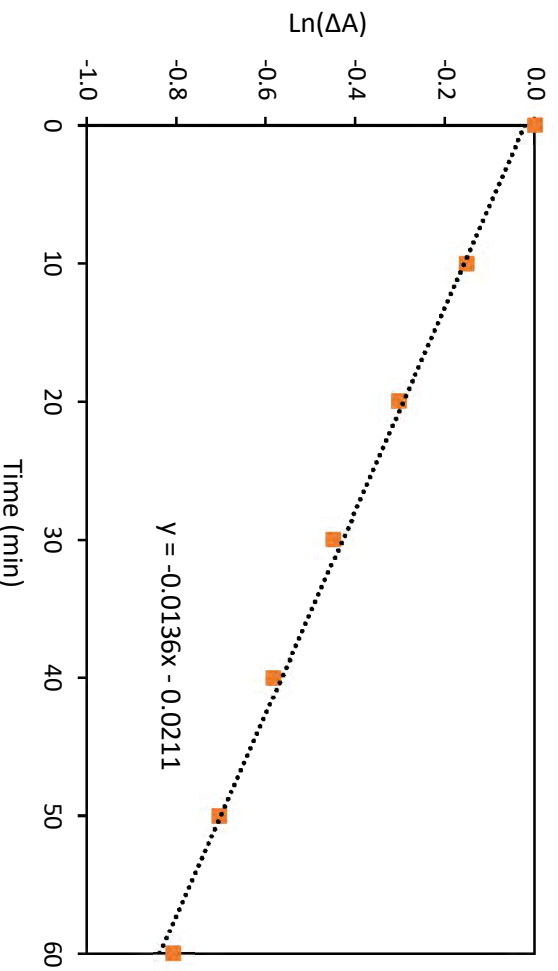


Figure 4.3: PNBTTTC decomposition plot as a function of time at pH 9; with an initial concentration of 2.9×10^{-5} M of PNBTTTC

Chapter 4: Investigation of the performance of various collectors on the flotation of sperrylite

4.2.3. Microflotation

Microflotation experiments were conducted at pH 9 to investigate the flotation response of sperrylite using the various collectors. The effect of collector type, collector dosage, and ionic strength of the slurry was investigated.

Figure 4.4 shows the recovery-time curves of sperrylite with the different collectors conditioned at 1 pseudo-monolayer surface coverage using de-ionized water adjusted to pH 9. A frother was added at a dosage of 15 ppm, which is the dosage just above the critical coalescence concentration to keep the bubble size constant. A test was also conducted with no collector added to determine the natural floatability of sperrylite. As can be seen from Figure 4.4, the natural floatability of sperrylite was very low, with a recovery of 4.8%. The addition of collectors resulted in a modest improvement in the recovery of sperrylite. However, none of the collectors resulted in significantly high recoveries, with the recoveries ranging from 15.5 – 18.1%. From the analysis of the flotation kinetics, sperrylite is clearly slow floating at this pH, with the maximum first-order rate constant being 0.11 min^{-1} . The flotation rate constant was determined using the Klimpel model (see section 3.5.1) For comparison, chalcopyrite with PAX has a rate constant of 0.2 min^{-1} (Taguta, 2015).

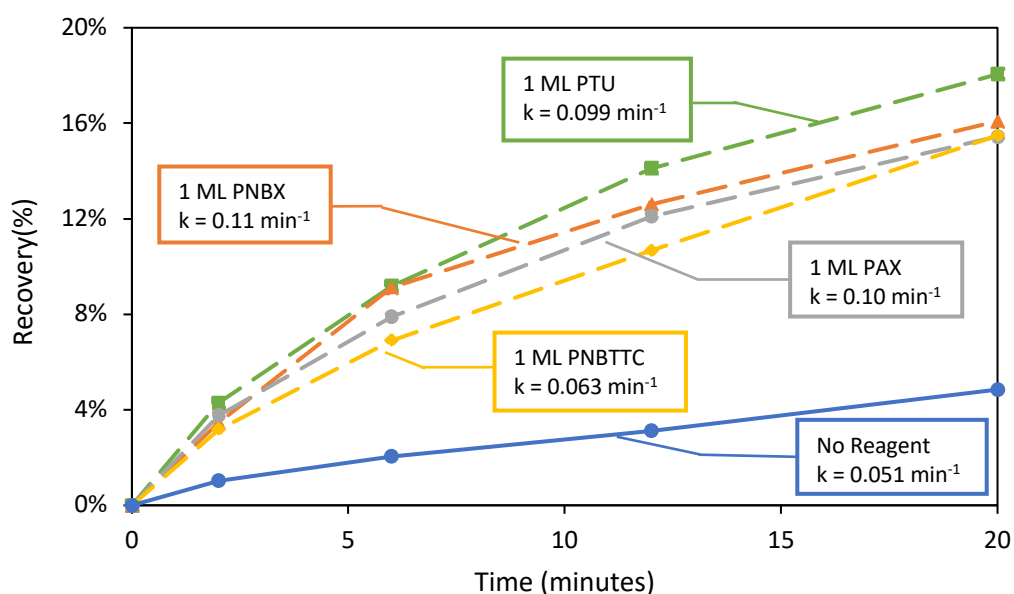


Figure 4.4: Microflotation recoveries of sperrylite with different collectors at pH 9. ML = collector dosage equivalent to a pseudo-monolayer mineral surface coverage and k = first-order rate constant. $RSE_{\text{pooled}} = 3.79\%$

Figure 4.5 shows a comparison of the final cumulative recoveries of sperrylite, with no added electrolyte, and in 0.12 M NaCl solution with the different collectors studied. The results show that, generally, increasing the ionic strength of the slurry improved the flotation recovery of sperrylite. The highest improvement observed was for the PAX collector, resulting in an increase in sperrylite recovery from 15.4% to 20.6%.

Chapter 4: Investigation of the performance of various collectors on the flotation of sperrylite

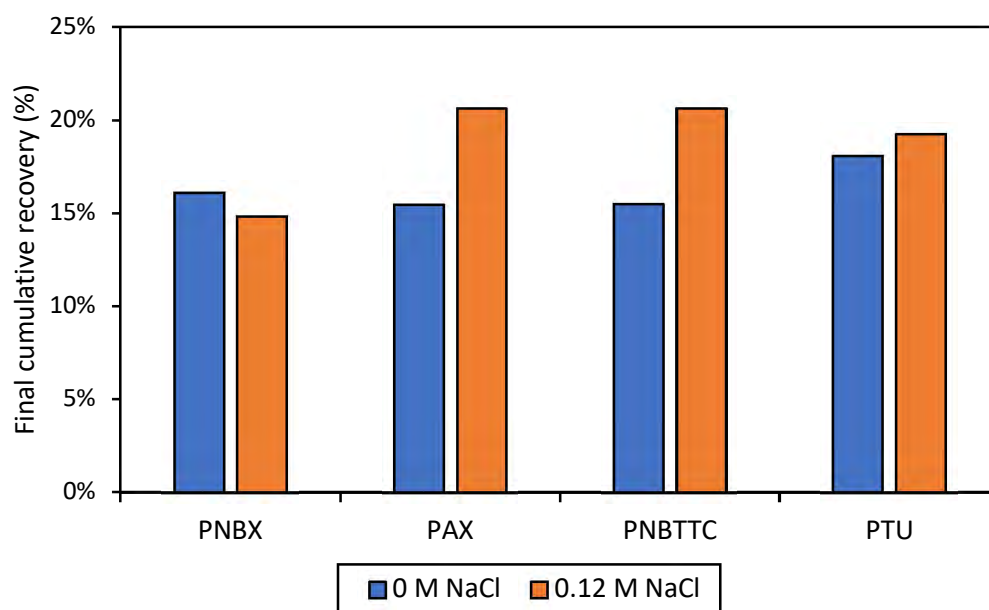


Figure 4.5: Microflotation final cumulative recoveries (i.e., after 20 minutes) of sperrylite with different collectors at a dosage equivalent 1 pseudo-monolayer surface coverage in de-ionised water and 0.12 M NaCl solution at pH 9; 15 ppm frother. $RSE_{pooled} = 3.79\%$

Figure 4.6 shows the effect of increasing collector dosage on the recovery of sperrylite. PAX was chosen to study the effect of dosage and its dosage was increased from 1 ML to 20 ML (ML = collector dosage equivalent to a pseudo-monolayer coverage). PAX was chosen because of its longer alkyl chain length and because it is readily available. The results show, as expected, that sperrylite recovery increased with an increase in PAX dosage, with the recovery increasing to 45.2% at 20 ML. However, the recovery of sperrylite reached a point beyond which no further improvement was observed with an increase in collector dosage as shown by the developing plateau in the recovery-dosage profile. With increased collector dosage, the flotation kinetics of sperrylite were improved indicating that sperrylite floats faster at higher collector dosages.

Chapter 4: Investigation of the performance of various collectors on the flotation of sperrylite

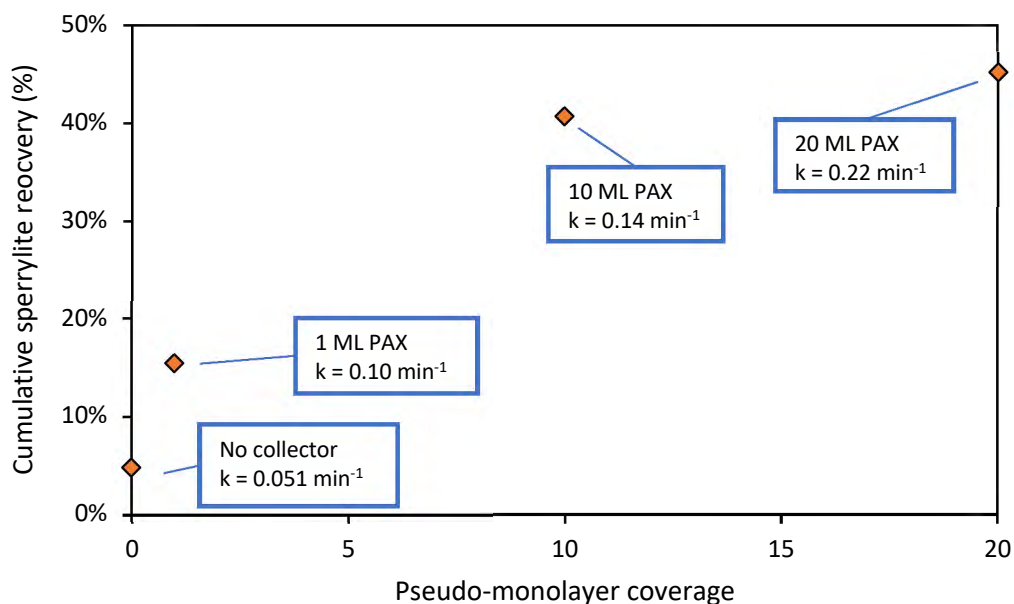


Figure 4.6: Final cumulative microflotation recoveries of sperrylite with different dosages of PAX at pH 9. ML = collector dosage equivalent to a pseudo-monolayer surface coverage and k = first-order rate constant; 15 ppm frother. $\text{RSE}_{\text{pooled}} = 3.79\%$

UV-vis adsorption measurements were conducted to determine the amount of PAX that adsorbs on sperrylite as a function of collector dosage. The adsorption isotherm obtained is shown in Figure 4.7 where it has been superimposed on the microflotation recovery data. The figure shows that the increased collector dosage resulted in higher amounts adsorbed onto the sperrylite surface, thus causing an increase in recovery. The data shows that only 20% to 50% of the added collector was actually adsorbed onto the mineral surface and that approximately 20 ML needed to be added to achieve the highest observed recovery of 45.2%.

Chapter 4: Investigation of the performance of various collectors on the flotation of sperrylite

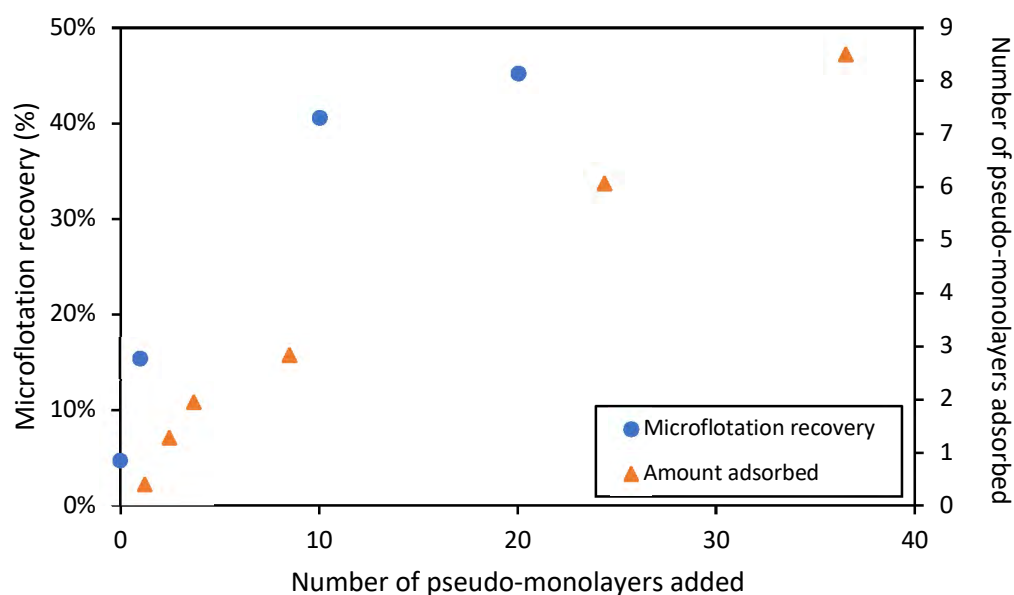


Figure 4.7: Final cumulative microflotation recoveries and amount of collector adsorbed on sperrylite as a function of the number of PAX pseudo-monolayers added at pH 9

4.2.4. Batch Flotation

The flotation response obtained from microflotation is an ideal case, without the influence of the froth phase, the presence of other minerals, or complex cell hydrodynamics. However, the energy input in the microflotation cell is low, which may reduce the bubble-particle collision process. Therefore, to test whether the results obtained in a microflotation cell could be extrapolated to a more realistic scenario, batch flotation tests were conducted. Three conditions were investigated, viz. 1) Standard case, 2) high ionic strength of 0.242 M which is equivalent to ten times the concentration of the standard synthetic plant water (10 SPW), and 3) collector with a different functional group, PNBTTTC.

ICP-MS was used to assay for Pt and As as an alternative to the time-consuming, costly and often statistically compromised mineralogical analysis. The assay results are presented in Table 4.2, showing the reproducibility and viability of the ICP-MS technique.

Chapter 4: Investigation of the performance of various collectors on the flotation of sperrylite

Table 4.2: Batch flotation samples submitted for ICP-MS showing the variability of the assays of Pt and As for the different cases investigated. Samples were analysed in triplicates

	As		Pt	
	Average grade (g/t)	Relative Standard Error	Average grade (g/t)	Relative Standard Error
Feed	0.67	6.7%	1.68	13.1%
Std. Case Conc.	2.21	6.5%	4.68	0.6%
Std. Case Tails	0.56	10.7%	0.62	5.2%
10 SPW Conc.	1.27	4.4%	3.54	16.2%
10 SPW Tails	0.43	1.4%	0.55	4.9%
PNBTTC Conc.	1.88	6.9%	6.06	6.1%
PNBTTC Tails	0.53	4.4%	0.95	4.9%

As can be seen from Table 4.2, there is some variability in the assayed samples, particularly in the case of the Pt assays with one case having a relative standard error of 16.2%. These variations most likely came from having to use very small sample masses, 0.2 g, during acid digestion thus making it difficult to ensure the representativity of the sample. This was addressed to an extent by micronizing the samples to very fine particle sizes, viz. 100% passing 38 μm , in an attempt to minimise the ‘nugget effect’ and improve reproducibility. However, the As assay, which is most relevant to this part of the study, showed relatively better reproducibility with the highest standard error being 10.7%.

Figure 4.8 shows that the recovery of Pt and As increased with an increase in the mass of solids recovered, with the case of the higher ionic strength (10 SPW) yielding the highest recoveries. It can also be observed that the recovery of Pt was always higher than that of As. This is likely because there are other Pt-bearing minerals in the ore other than PtAs_2 such as Pt tellurides and alloys. These are more easily recovered compared to PtAs_2 . In addition to this, there did not seem to be any selective improvement for PtAs_2 recovery in any of the cases studied. An analysis of the As:Pt ratios for each condition studied would show whether there was any selective increase in the As recovery. The As:Pt ratios for the different conditions were found to be in the sequence 10 SPW>Standard case>PNBTTC (0.77>0.71>0.68). The difference between these ratios is not statistically significant, thus indicating that there was not much selective improvement in the recovery of As, hence PtAs_2 . The assumption made here is that As only comes from PtAs_2 in the Platreef ore as discussed in section 1.3 (Shamaila, 2007).

Chapter 4: Investigation of the performance of various collectors on the flotation of sperrylite

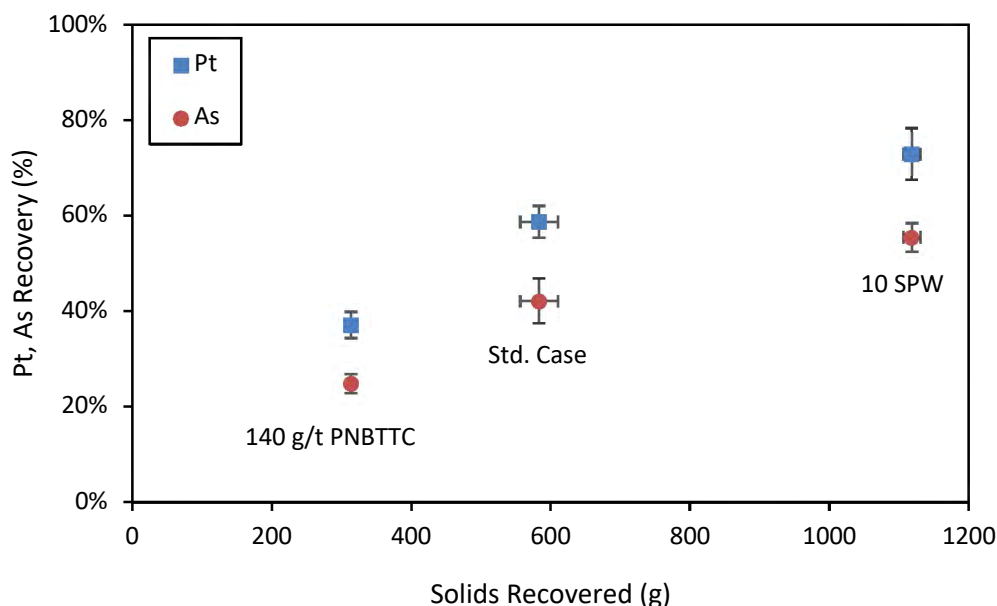


Figure 4.8: Pt and As recovery vs solids recovered from batch flotation tests comparing the standard case conditions with increased ionic strength, 10 SPW; and collector with a different functional group, PNBTTT

Table 4.3 shows the upgrade ratios of Pt and As, along with those of Cu and Ni, from the corresponding batch flotation tests. The upgrade ratio represents the ratio of the concentration of metal in the concentrate to that in the feed. The PNBTTT collector yielded high upgrade ratios for Cu and Ni, showing that this collector is highly selective towards these minerals. With regards to Pt and As, the '10 SPW' case yielded the lowest upgrade ratio.

Table 4.3: Upgrade ratios of Cu, Ni, Pt, and As obtained from batch flotation tests comparing standard case conditions with increased ionic strength, 10 SPW, and PNBTTT

	Upgrade ratio (-)			
	Cu	Ni	Pt	As
Standard Case	4.81	3.29	3.15	3.11
10 SPW (0.242 M)	2.86	2.29	2.98	1.78
140 g/t PNBTTT	7.60	3.74	4.08	2.64

4.3. Discussion

This phase of the study investigated the effect of using different collectors on the recovery of sperrylite by flotation. Trithiocarbonate and thiourea collectors, in addition to xanthates, were studied as these collectors have been shown to potentially offer some benefits over the conventional xanthate collectors (Fairthorne et al., 1997; Venter, 2008; Venter & Vermaak, 2008). Of particular interest in this study was the extent to which these collectors adsorb onto the mineral surface and whether the strength or extent of their adsorption could be used to predict the flotation response of sperrylite. In the collector structure, two major factors are responsible for the strength of collector adsorption onto a mineral surface and the resulting hydrophobicity, viz. the composition of the polar head group of the collector, and the length and structure of the non-alkyl group of the collector. In general, these collectors adsorb onto the mineral surface via a redox chemical reaction which can be described by the electron donor/electron acceptor model. It is in the context of this model that the factors mentioned above affect collector adsorption.

4.3.1. Effect of collector ligand type on the heat of adsorption

The effect of ligand type on the adsorption of the collector onto sperrylite was compared between PNBTTTC and PNBX. These two collectors have the same alkyl chain length of 4 linear CH₂ groups, but different ligand types. Therefore, a comparison can be made of the effect of ligand type. The heat of adsorption of these two collectors showed that PNBTTTC has a stronger adsorption onto sperrylite compared to PNBX, with the heats of adsorption being -41.80 kJ/mol and -19.96 kJ/mol, respectively. This difference can be attributed to the difference in the electron-withdrawing tendency of the O and S atoms in the functional group of these collectors. The tendency of the polar group of the collector to release or withdraw electrons affects the electron density around the donor atoms. Consequently, the electron density affects the electrons available to form bonds between the collector and the mineral surface.

Collectors whose functional group has a low electronegativity are less electron-withdrawing and can easily form bonds (i.e., are more reactive) with the mineral due to the high electron density around the donor atoms (Somasundaran & Nagaraj, 1984; Raju & Forsling, 1997). The functional groups of PNBTTTC and PNBX are -SCS₂ and -OCS₂, respectively. The S atom, which has replaced the O atom from the xanthate, is less electronegative. This makes the trithiocarbonate collector less electron-withdrawing, and hence more reactive with the sperrylite surface as evident from its higher heat of adsorption.

The fact that PNBTTTC has a higher heat of adsorption compared to PNBX can also be explained using the pK_a values of these collectors. The pK_a value represents the tendency of the collector to donate electrons to metal atoms and is one of the major factors that determine the strength of the collector-mineral bond. Other factors include the nature of the donor atoms, substituents and central metal atom (Somasundaran & Nagaraj, 1984), some of which have been discussed above. The pK_a values of PNBTTTC and PNBX are 2.59 (Thiart & Gammon,

Chapter 4: Investigation of the performance of various collectors on the flotation of sperrylite

2022, personal communication) and 2.22 (Hayashi et al., 1984), respectively. Since the pKa value of the PNBTTTC collector is higher, it indicates that this collector is more reactive.

It was mentioned in the UV-vis results presented in section 4.2.2 that the residual concentration and hence adsorption of PNBTTTC could not be measured due to its very rapid rate of decomposition. Therefore, it is of interest to know what is being measured by the ITC. Venter (2008) has studied the decomposition of TTC collectors and proposed that TTC decomposes into CS₂ and R-S⁻ according to reaction 4-1, where R represents the alkyl chain



In the case of the PNBTTTC used in this study, the R-S⁻ species would be CH₃(CH₂)₃S⁻. The decomposition product CS₂ was detected and measured by UV-vis spectroscopy in this study (cf. Figure 4.2). According to Shen (2016), the decomposition products of the collector could adsorb on the mineral surface. This could happen through sequential or parallel interactions between the mineral surface and the decomposition products, in addition to the interactions between the collector and the mineral surface. Therefore, these interactions are possibly what is being measured by the ITC tests. However, it should be noted that even though CS₂ may adsorb onto the mineral surface, it does not impart hydrophobicity to the mineral.

The decomposition of TTC follows a first-order reaction rate (Sun & Forsling, 1997; Venter & Vermaak, 2008). The first-order rate constant was calculated from the decomposition plot of PNBTTTC and was found to be 0.0136 min⁻¹ (cf. Figure 4.3). This is the rate constant in the aqueous phase. In the presence of the mineral, it is expected that the decomposition rate of the collector would be slower, and most of the collector would instead be adsorbed (Fredriksson et al., 2006). For the microflotation tests performed in this study, the TTC collector was always prepared fresh before each test and used immediately to minimise decomposition.

Returning to the discussion on the effect of ligand type, the last collector that was studied is the PTU collector. This collector also behaves according to the electron donor/electron acceptor model (Fairthorne et al., 1997; Xu et al., 2021) and had a heat of adsorption of -34.15 kJ/mol. However, a direct comparison between the PTU and TTC or the xanthates cannot be made because the PTU collector has both a shorter alkyl chain length and a different ligand type. The comparison of the effect of alkyl chain length is instead made between PAX and PNBX (cf. section 4.3.2). In that regard, it is interesting to note that despite the PTU having a shorter alkyl chain length, it still had a higher heat of adsorption compared to the xanthate collectors. This is most likely due to the amine group in PTU which is less electron-withdrawing compared to the O atom in the xanthate collectors.

4.3.2. Effect of alkyl chain length on the heat of adsorption

Aside from the ligand type, the length of the alkyl chain can also affect the strength of collector adsorption onto the mineral surface. PAX and PNBX which are both xanthate collectors but have 5 and 4 linearly configured CH₂ groups, respectively, were compared for the effect of

Chapter 4: Investigation of the performance of various collectors on the flotation of sperrylite

alkyl chain length. The ITC experiments showed that PAX had a higher heat of adsorption, viz. -30.13 kJ/mol, compared to -19.96 kJ/mol for PNBX (cf. Table 4.1). The alkyl group is known to exert a positive inductive effect on the polar group of the collector. This affects the electron density around the polar group of the collector. Longer alkyl chains exert a stronger positive inductive effect which increases the electron density, hence the reactivity of the collector with the mineral surface (Somasundaran & Nagaraj, 1984; McMurry, 2012; Taguta et al., 2017). This is consistent with PAX having a higher heat of adsorption compared to PNBX.

It should be noted that the discussion above assumes that all the moles of the collector added in the ITC experiments contribute to the heat evolved when the collector adsorbs onto the mineral surface. In this context, it is worth noting that the heat of adsorption of these collectors on sperrylite is relatively low compared to other mineral-collector systems. For instance, Taguta et al. (2017) found that the heat of adsorption of PAX onto pyrite was -59.2 kJ/mol. Another example of a different mineral is PNBX on chalcopyrite which produced a heat of adsorption of -51.1 kJ/mol. In fact, even the collector with the shortest alkyl chain length, SEX, produced a heat of adsorption of -57.1 kJ/mol on pyrite. All of these are much higher than the heats of adsorption obtained in the present study for the sperrylite-collector system. There is therefore evidence that while there may be varying degrees of interaction of the different collectors with sperrylite, these interactions are relatively weak compared to those observed with other minerals such as pyrite and chalcopyrite.

4.3.3. Microflotation response of sperrylite with the different collectors

Having established the reactivity of the collectors with sperrylite, it is instructive to determine whether these results correlate with the flotation response of sperrylite.

The collectorless recovery of sperrylite showed that this mineral has a very low natural floatability, with a final cumulative recovery of 4.8%. This is consistent with the findings from the work of Shackleton et al. (2007). Therefore, sperrylite needs to be treated with collectors to induce hydrophobicity so that it can be recovered by flotation. The collectors used to treat sperrylite in this study did not yield any significantly high recoveries. PNBX, PNBTTT and PAX all yielded similar results with the final cumulative recoveries of 16.1%, 15.5% and 15.4%, respectively (cf. Figure 4.4). One important aspect to note about this set of results is the similarly low recoveries despite ITC and UV-vis spectroscopy experiments showing that these collectors had different extents and strengths of adsorption on sperrylite. The extent of adsorption of the collectors was found to be 75% for PAX, 33% for PNBX, and 23% for PTU where these percentages indicate the amount of collector adsorbed from the initial concentration equivalent to 1 pseudo-monolayer. It may therefore have been expected that with an increased extent of collector adsorption, the recovery of the mineral should also increase. However, this was not the case.

One possible explanation for this is that 1 pseudo-monolayer surface coverage is below the dosage required to reach critical hydrophobicity for sperrylite. This is sometimes equated to a critical contact angle below which flotation is not possible. In the region below critical

Chapter 4: Investigation of the performance of various collectors on the flotation of sperrylite

hydrophobicity, the amount of the collector adsorbed on the mineral surface would increase without necessarily increasing the recovery of the mineral. This would explain why the collectors used in this study had different amounts adsorbed onto sperrylite but yielded similar recoveries. Therefore, it is likely that this low recovery may be due to underdosing of the collector. In a study conducted by Henwood (1995), it was shown that some minerals such as pyrite required collector dosage greatly in excess of 1 pseudo-monolayer surface coverage to float. In that study, this was attributed to the high irregularity of the pyrite surface structure, where some sites are more reactive than others. It is possible, therefore, that larger collector dosages would be required so that both the relatively strong and weaker sites on the mineral surface are coated with a collector. Sperrylite has a similar crystal structure to that of pyrite, making it possible that sperrylite, like pyrite, may also require larger collector dosages to obtain reasonable flotation recoveries although the similarity of crystal structures does not necessarily imply a similar energetic heterogeneity of sites on the mineral surface. The effect of collector dosage on the recovery of sperrylite was explored further in the present study and this is discussed in 4.3.4 below.

As already indicated, there seems to be no correlation between the strength of collector adsorption and the flotation response of sperrylite, at least not at 1 pseudo-monolayer surface coverage. For instance, the PTU collector resulted in the highest sperrylite recovery out of the collectors investigated with a recovery of 18.1% but did not have the strongest adsorption according to the ITC results which showed that PTU had a heat of adsorption of -34.15 kJ/mol. The same is true for the other collectors which had varying strengths of adsorption but yielded similar sperrylite recoveries. The fact that there was no correlation between how strongly the collector adsorbed onto the mineral surface and the flotation response of the mineral has been reported by others (e.g. Maier et al., 1997; Taguta et al., 2017). In particular, Taguta et al. (2017) showed that the strength of collector adsorption, as predicted by ITC in this case, is not a good predictor of hydrophobicity when different collector ligand types are used but more useful for collectors of the same type which may have different alkyl chain lengths.

Ultimately, the microflotation results showed that sperrylite is slow floating and that there may be a problem of collector underdosing at 1 pseudo-monolayer surface coverage. Further microflotation tests were conducted which investigated the effect of collector dosage as well as ionic strength. The effect of ionic strength was explored in an attempt to improve the flotation kinetics of this otherwise slow-floating mineral. Increasing ionic strength has been shown to result in faster flotation rates of minerals (Michaux et al., 2018). Only microflotation tests were conducted to test these effects owing to the limited availability of sperrylite.

4.3.4. Effect of collector dosage on the floatability of sperrylite

One pseudo-monolayer surface coverage, or even less, has been used extensively in previous studies and is considered sufficient to induce floatability to most minerals (McFadzean et al., 2012; Taguta et al., 2017; Pienaar et al., 2019). However, for sperrylite, there is a possibility that it may be underdosed at 1 pseudo-monolayer coverage. Therefore, the effect of

Chapter 4: Investigation of the performance of various collectors on the flotation of sperrylite

increasing collector dosage on the recovery of sperrylite was examined. The results (cf. Figure 4.6) showed that there was a significant increase in the recovery of sperrylite with increasing PAX collector dosage, with the recovery increasing to 45% at 20 pseudo-monolayers. The recoveries reached a point beyond which a further increase in collector does not result in any significant increase in recovery. With increasing collector dosage, there is also an improvement in the flotation kinetics of sperrylite as evident from the first-order rate constants which increased from 0.051 min^{-1} with no collector to 0.22 min^{-1} with 20 pseudo-monolayers of PAX. These findings suggest that for sperrylite, an optimum collector dosage well above 1 pseudo-monolayer surface coverage is necessary to impart sufficient hydrophobicity to the mineral. It was seen in Figure 4.7 that increasing the number of collector pseudo-monolayers added resulted in an increase in the absolute amount of collector adsorbed, and hence the hydrophobicity of the mineral. This correlated with an increase in sperrylite microflotation recoveries.

The mechanism by which multilayer adsorption occurs is not clearly understood. Possible explanations have been put forward (Leja, 1982; Wills & Finch, 2015). One such explanation is that at pseudo-monolayer surface coverage, the collector is considered to adsorb onto the mineral surface at isolated sites. The sites on which the collector adsorbs depend on both the selectivity of the collector and the nature of the adsorption sites. Due to the adsorption sites being isolated, this results in a discontinuous collector layer which may not be enough to render the mineral sufficiently hydrophobic. On the other hand, multilayer adsorption is considered to probably result in a continuous layer of collector molecules that coat the mineral rendering it more hydrophobic. These multilayers are adsorbed on the mineral surface by chemisorption, as well as through lateral Van der Waals forces between the alkyl chains of the collector (Leja, 1982).

4.3.5. Effect of ionic strength on the floatability of sperrylite

The effect of ionic strength, which was varied using NaCl, was investigated in this study in an attempt to improve the floatability of sperrylite. When comparing the recoveries obtained with the collectors at 0 and 0.12 M ionic strength (cf. Figure 4.5), the results showed that ionic strength influences the flotation response. Generally, the recovery of sperrylite increased at higher ionic strength. The highest improvement observed was for the PAX collector where the recovery of sperrylite increased from 15.4% to 20.6% as a result of increasing ionic strength.

Ionic strength has been shown to improve the kinetics of flotation by decreasing bubble-particle induction time (Hewitt et al., 1995; Shackleton et al., 2012). Higher ionic strength results in a more rapidly thinning liquid film and therefore higher rate of drainage at the boundary interface when a particle collides and attaches to a bubble. This higher rate of liquid film thinning is considered to be due to the reduction in the electrostatic repulsion between the mineral particle and the bubble. That is, higher salt concentrations reduce the energy barrier for bubble-particle attachment. This has been related to faster flotation kinetics (Laskowski & Yoon, 1991; Michaux et al., 2018). Studies (e.g. Crawford & Ralston, 1988; Hewitt

Chapter 4: Investigation of the performance of various collectors on the flotation of sperrylite

et al., 1994, 1995) have shown that this effect of increasing ionic strength is more effective in weakly hydrophobic minerals, as is the case for sperrylite. In addition to the reduction in induction time, the increased ionic strength may decrease the critical hydrophobicity required to initiate flotation (Crawford & Ralston, 1988). It may also be speculated that increasing ionic strength improved the adsorption of the collectors onto the sperrylite surface, thus improving the floatability of this mineral.

The study of the bubble-particle interactions is beyond the scope of the present work. However, it should be noted that ionic strength may also affect bubble size and density. At higher ionic strength, bubble coalescence is inhibited thus leading to smaller bubbles per unit volume. There is therefore a higher number of bubble-particle collisions per unit time (Blake & Ralston, 1985). Bubble size decreases until the critical coalescence concentration is attained beyond which a further increase in ionic strength will not decrease bubble size. Therefore, to ensure that bubble size remained constant during the microflotation test work in this study, a frother was added at a dosage just above the critical coalescence concentration. Therefore, the results obtained concerning the effect of ionic strength can be attributed to more efficient bubble-particle attachment at higher ionic strength as discussed above.

4.3.6. Microflotation vs batch flotation of sperrylite

Finally, tests were conducted to determine the batch flotation responses of sperrylite in a more realistic scenario that includes the froth phase, complex ore and complex hydrodynamics. The batch flotation response of sperrylite was investigated under standard conditions, with PNBTTTC, and with high ionic strength (10 SPW) conditions.

A comparison of the effect of higher ionic strength showed that this results in an increase in recovery of Pt and As both in microflotation and batch flotation. This increase in the batch flotation recoveries at higher ionic strength is most likely due to an increase in both the kinetics of bubble-particle attachment, as well as the froth stability. It has been shown that water recovery increases with an increase in ionic strength, thus indicating that the ions have a froth-stabilizing effect (Manono et al., 2012). High froth stability is generally associated with a higher mass pull, which was the case for the test at higher ionic strength. However, this results in a decrease in the grade and thus increasing ionic strength does not lead to a selective recovery of Pt and As (Table 4.3). In addition to this, an analysis of the As:Pt ratios of the different conditions investigated showed that there is minimal selective improvement in the recovery of sperrylite.

The other case that was studied was that of using a collector with a different functional group, PNBTTTC. In this case, the recovery of Pt and As obtained in batch flotation was lower compared to the standard case, where SIBX was used. In the microflotation cell, it was observed that PNBTTTC yielded similar recoveries as the xanthate. A case can be made that in the batch flotation tests, PNBTTTC is more selective towards other minerals present in the system. This is evident in the upgrade ratios of Cu and Ni which were higher compared to those obtained for the standard case conditions, and generally higher than the upgrade ratios of Pt and As. Thus,

Chapter 4: Investigation of the performance of various collectors on the flotation of sperrylite

this suggests that this collector is more selective towards the base metal sulfides, which is consistent with PNBTTTC being a sulfur-based collector.

From these results, it can be generally concluded that comparisons can be made between the microflotation and batch flotation responses. However, other factors such as froth stability or collector selectivity in batch flotation do affect the ultimate performance. It is also worth noting that the recoveries obtained in batch flotation are generally higher than those from microflotation. This is most likely due to the higher turbulent energy in batch flotation. However, the batch flotation tests confirmed that the naturally occurring sperrylite has a lower flotation recovery than the other naturally occurring platinum group minerals in the Platreef and that the slow floatability observed in the microflotation studies was not simply a synthetic mineral effect.

It is worth noting that in this study it was shown that assaying for arsenic by ICP-MS was a viable alternative to the time-consuming, costly, and often statistically compromised mineralogical analysis.

4.4. Conclusions

This phase of the study sought to investigate the effect of the use of PNBTTTC, PTU, PAX and PNBX collectors on the floatability of sperrylite. The PNBTTTC and PTU collectors were chosen as they have been shown in systems such as base metal sulfides to have stronger collecting ability compared to the conventional xanthate collectors.

This study has confirmed that the recovery of sperrylite by flotation is generally poor. The PNBTTTC and PTU collectors, which have stronger collecting ability than xanthates, showed little improvement in the recovery of sperrylite at pseudo-monolayer surface dosages despite the collectors having varying degrees of adsorption. None of the collectors investigated yielded sperrylite recoveries greater than 18%. Very high collector dosages (20 ML) of a strong collector such as PAX increased the overall adsorption of the collector onto sperrylite but only improved the recovery to a maximum of 45%. Ultimately, this implies that the surface of sperrylite does not appear to be amenable to strong interactions with these collector types that would induce sufficient hydrophobicity and hence recovery at 1 pseudo-monolayer surface coverage. However, even when multiple monolayers have adsorbed, the resultant coverage is not sufficient to induce a high hydrophobicity and recovery.

Microflotation tests showed that the recovery of sperrylite can be increased by increasing collector dosage or ionic strength. However, other factors should be considered as shown by the batch flotation tests. The batch flotation studies showed that the recoveries of Pt and As increased at higher ionic strengths of the process water to 73% and 56%, respectively, but at the cost of increased solids recoveries and hence lower grades. However, it should be noted that in PGM flotation, recovery is the more important indicator for determining flotation performance. The batch flotation studies also showed that the use of PNBTTTC selectively

Chapter 4: Investigation of the performance of various collectors on the flotation of sperrylite

improved the grades of the base metal sulfides present in the ore to a larger extent compared to the grades of Pt and As.

A useful outcome of the study was the application of an arsenic assay by ICP-MS as a proxy for sperrylite recovery as an alternative to a mineralogical analysis. This may have further application as an online technique if the XRF technique can be refined as it has been for palladium. This study provides further insights into the flotation response of sperrylite to improve the recovery of this economically important mineral.

CHAPTER 5: Effect of pH-Eh on the floatability of sperrylite

5. Effect of pH-Eh on the floatability of sperrylite

5.1. Introduction

Phase One of this work showed that the surface of sperrylite does not appear to be amenable to strong interactions with the collectors typically used in PGM flotation. Even collectors with stronger collecting ability did not significantly improve the floatability of this mineral. The evidence obtained suggested that it is the surface of sperrylite or the pulp chemistry, rather than the type of collector, that primarily renders this mineral difficult to float; although there are avenues for improving collector chemistry to target this mineral.

In a flotation system, minerals behave differently under varying pulp pH and redox conditions as indicated by Eh. In flotation, the challenge is often to find the Eh-pH conditions that are suitable for the selective flotation of the mineral of interest. While the flotation response of most base metal sulfides to changes in Eh-pH conditions is well-documented, such information is limited for PGMs. The optimum flotation Eh-pH domain of sperrylite is likely to be outside the conditions typically used in PGM concentrators, e.g. pH 9. Therefore, **Phase Two** of this study focuses on investigating the effect of pH and Eh on the floatability of sperrylite. The results and discussion of this phase are presented in this chapter.

In this phase, rest potential measurements are used to determine the electrochemical interactions that may be occurring between sperrylite and PAX at different pH and Eh conditions. PAX was chosen as being a conventional, but relatively strong, xanthate collector. The chemical speciation resulting from these interactions on the surface of sperrylite is characterized using surface characterization techniques including zeta potential measurements and spectroscopic studies. All of these are used to understand the flotation behaviour, as determined using microflotation, of sperrylite under varying Eh and pH conditions. Ultimately, this study aims to determine the Eh-pH regions where the adsorption of the collector, and hence imparted hydrophobicity and floatability of sperrylite, are optimized.

5.2. Results

5.2.1. Microflotation

Microflotation tests were conducted to establish the effect of pH and Eh on the recovery of sperrylite using PAX as the collector. Figure 5.1 shows the recoveries obtained at varying pH (i.e. pH 3, 5, 7, and 9) in the absence of any Eh modifying agent. The results show that the collectorless recovery of sperrylite only increased from 7% at pH 9 to 8% at pH 3, thus showing that changing pH did not have much effect on the natural hydrophobicity of the mineral on its

Chapter 5: Effect of pH-Eh on the floatability of sperrylite

own. When sperrylite was conditioned with PAX, the recoveries significantly improved from 22% at pH 9 to 61% at pH 3. This shows that sperrylite floats better under acidic conditions.

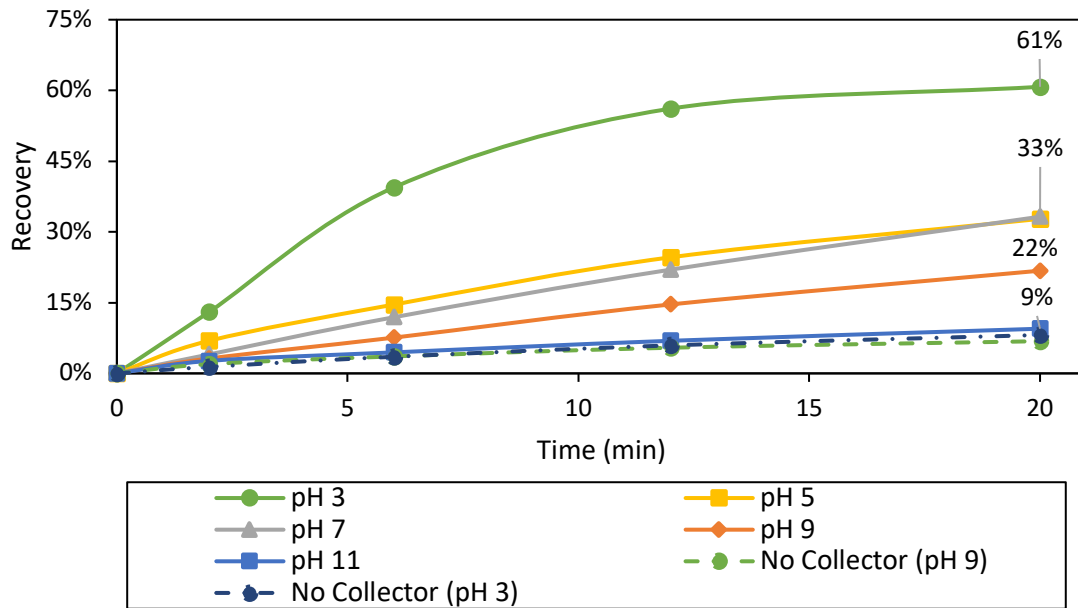


Figure 5.1: Microflotation recoveries of sperrylite conditioned at varying pH conditions with 5 monolayers of PAX or no collector where specified; in 0.12 M NaCl and with 15 ppm frother. $RSE_{\text{pooled}} = 3.79\%$

Figure 5.2 shows that the measured Eh using a platinum electrode significantly increased when pH was decreased (blue line: 0M NaClO). Experiments were then carried out in which the Eh was chemically modified at constant pH by using different concentrations of NaClO which is an oxidizing agent. It should be noted that NaClO has a natural pH of ~ 11 , and the various pH conditions were achieved using HCl or NaOH. This shows that the 0.01 M concentration of NaClO drastically increased the Eh of the sperrylite pulp. On the other hand, it can be seen that 0.001 M of NaClO resulted in similar Eh values compared to the case without an oxidizing agent.

Chapter 5: Effect of pH-Eh on the floatability of sperrylite

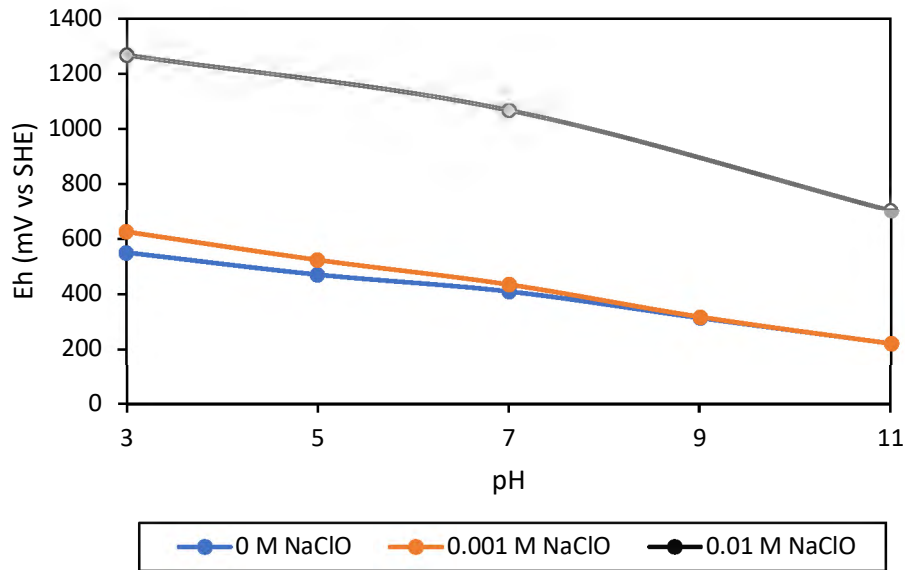


Figure 5.2: Measured Eh values of the sperrylite pulp corresponding to the different pH and NaClO concentrations. $RSE_{\text{pooled}} = 3.79\%$

The microflotation recoveries of sperrylite obtained using varying NaClO concentrations and pH conditions are shown in Figure 5.3. Contrary to the expectation that increasing Eh would improve the floatability of sperrylite due to the promotion of dixanthogen formation at higher Eh conditions (see section 5.2.3), it was found that the addition of NaClO to chemically modify Eh was detrimental to the recovery of this mineral. As shown in Figure 5.3, the recovery of sperrylite generally decreased with increasing concentration of NaClO. It can be seen that the addition of 0.001 M NaClO significantly decreased the recovery of sperrylite despite having similar Eh values compared to the case without an oxidizing agent.

Chapter 5: Effect of pH-Eh on the floatability of sperrylite

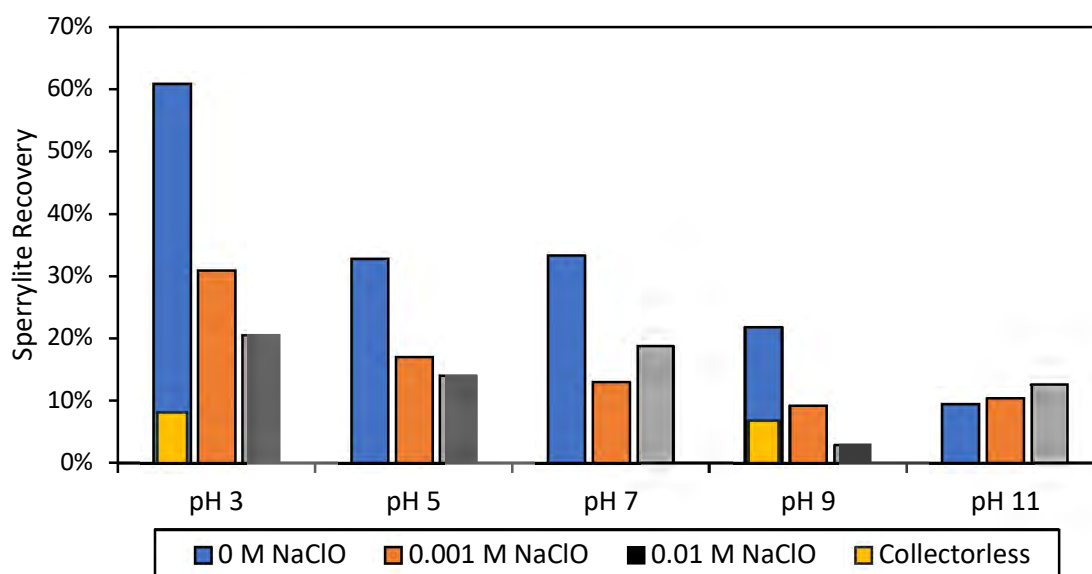


Figure 5.3: Final cumulative microflotation recoveries of sperrylite as a function of pH and NaClO concentration; PAX collector dosage equivalent to 5 pseudo-monolayers; in 0.12 M NaCl; and with 15 ppm frother. $RSE_{\text{pooled}} = 3.79\%$

The effect of using a different oxidizing agent, H_2O_2 , which is commonly used in some flotation processes, was also investigated to determine whether the detrimental effect observed with NaClO was due to the formation of surface-adsorbed reaction products from the reduction of NaClO. This is shown in Figure 5.4 where it can be seen that the addition of H_2O_2 also had a detrimental effect on the recovery of sperrylite.

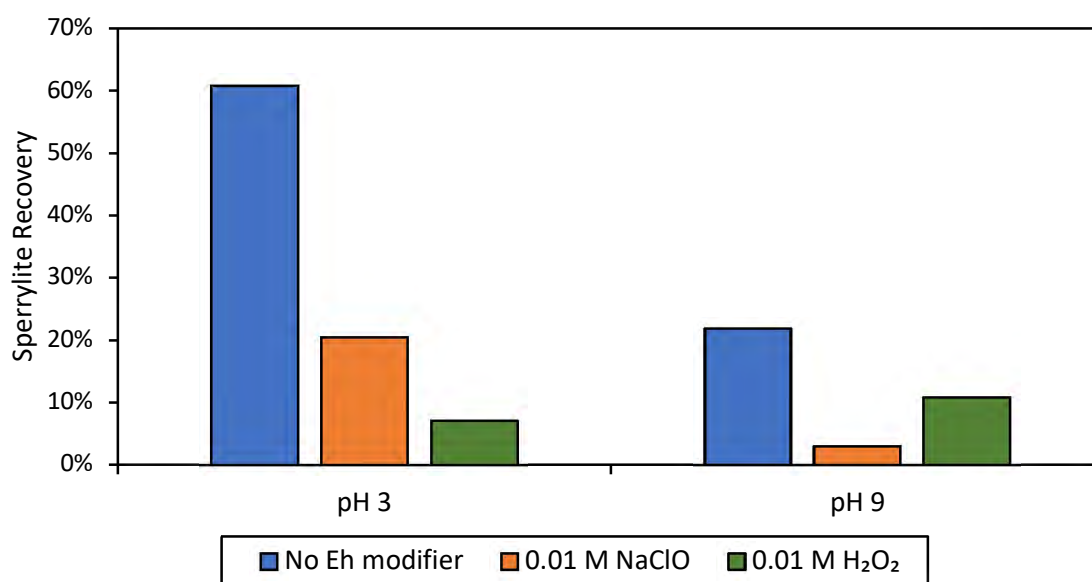
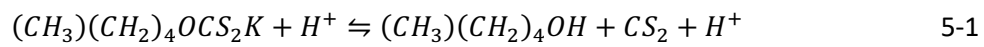


Figure 5.4: Final cumulative recoveries of sperrylite comparing the effect of 0.01 M NaClO and H_2O_2 at pH 3 and pH 9; with 5 pseudo-monolayers of PAX, 15 ppm frother and 0.12 M NaCl. $RSE_{\text{pooled}} = 3.79\%$

Supplementary test work was undertaken to attempt to explain the interactions occurring at the surface of sperrylite with changes in Eh and pH. The results of these tests are presented in the subsequent sections.

5.2.2. The extent of collector adsorption

The amount of PAX collector that is adsorbed onto sperrylite at the different Eh-pH conditions was measured using UV-vis spectroscopy. Xanthate collectors are known to be susceptible to decomposition in water, where pH plays a critical role in determining the rate of decomposition of the collector. Therefore, it was necessary to first measure the decomposition of the collector used as a function of time and pH. The decomposition of PAX was measured at pH 3, 7 and 11. As evident from Figure 5.5, there was no measurable decomposition of the collector at pH 7 and 11 within 60 minutes. However, at pH 3 the collector decomposed rapidly. At acidic conditions, xanthate collectors can decompose to form carbon disulfide and an alcohol (Shen et al., 2016). For PAX, the decomposition can be described by reaction 5-1:



The appearance of a peak at 206 nm that increased with time was identified from the UV-vis spectra observed at pH 3. This peak can be attributed to CS_2 (Rao, 2004). Therefore, in order to minimise the decomposition of the collector while allowing sufficient time for the collector to adsorb onto the mineral, a conditioning time of 5 minutes was chosen when conducting the tests to measure the amount of collector adsorbed onto the mineral.

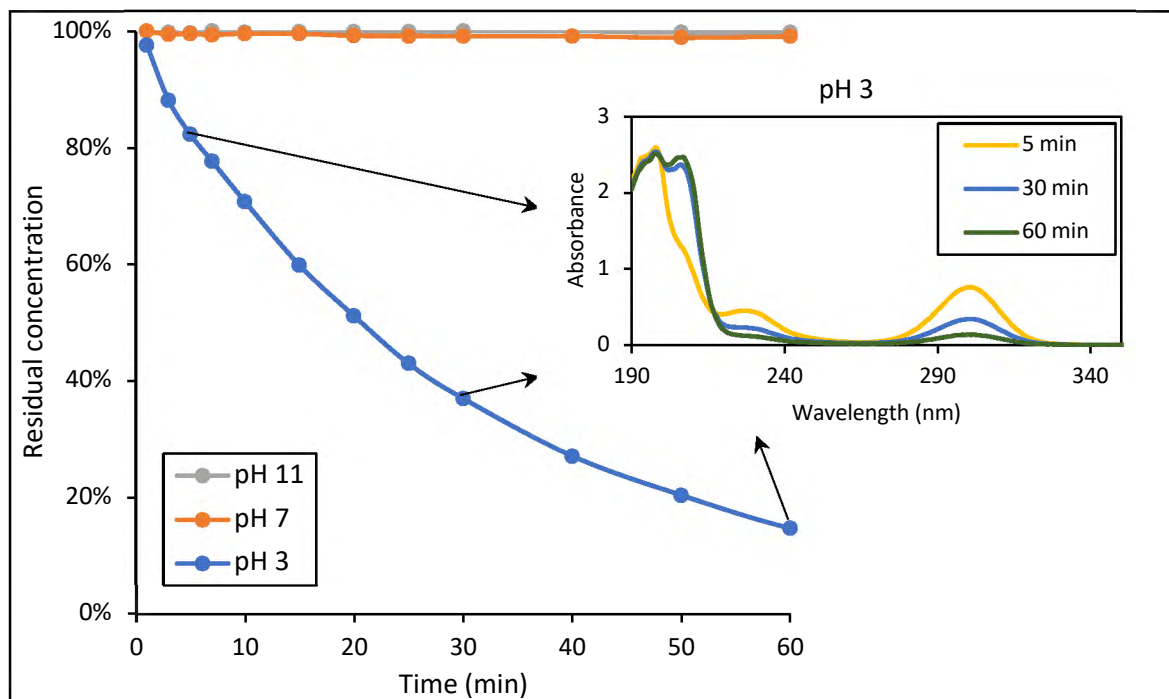


Figure 5.5: Effect of pH on the decomposition of PAX; with an initial PAX concentration = 7.24×10^{-5} M; PAX absorbance peak = 301 nm

The extent of adsorption at different Eh-pH conditions, as measured by UV-vis spectroscopy, is shown in Figure 5.6. The results show that the amount of collector adsorbed onto sperrylite increased with a decrease in pH.

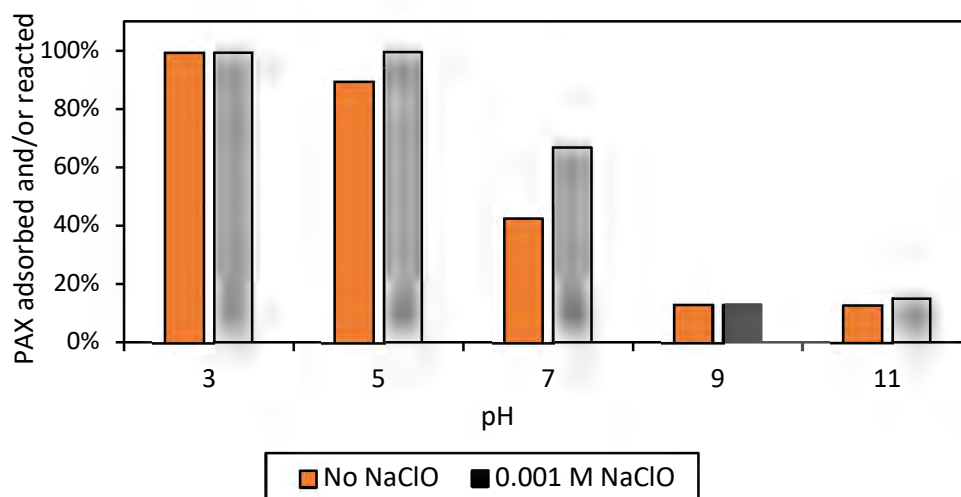


Figure 5.6: Amount of PAX collector and/or reacted on sperrylite in the presence and absence of 0.001 M NaClO as a function of pH; with an initial PAX concentration = 7.24×10^{-5} M; PAX absorbance peak = 301 nm

The effect of NaClO on the adsorption of the collector on sperrylite is more complicated. The UV-vis spectra observed for PAX in a 0.001 M NaClO solution in the absence of the mineral showed that NaClO and PAX reacted with each other. The UV-vis spectra obtained without and with NaClO are shown in Figure 5.7 where it can be seen that a significant amount of PAX was consumed (denoted by the reduction in the absorbance peak at 301 nm) in the presence of NaClO.

Although the exact nature of the product of the reaction between PAX and NaClO could not be explicitly identified by the UV-vis spectroscopy tests performed in this study, it is possible to infer that a monothiocarbonate (MTC) ion is the likely product of this reaction based on an analysis of the UV-vis spectra obtained with NaClO. The absorbance peak of MTC on the UV-vis spectrum is found at 223 nm (Rao, 2004). However, xanthate also has an absorbance peak at 226 nm which overlaps with the absorbance peak of MTC, thus making it difficult to deconvolute the peaks and hence to identify the MTC species. To decouple this, the ratio of the absorbance of xanthate (A_{226}) to that at 301 nm (A_{301}) was calculated for a PAX solution to determine the characteristic $A_{226}:A_{301}$ of PAX at the different pH conditions. If this ratio increases in the presence of NaClO, this suggests that there is a species other than xanthate contributing to the peak in the 223 – 226 nm region. This analysis is presented in Table 5.1, and this showed that the $A_{226}:A_{301}$ ratio in the presence of NaClO was always greater than in the absence of NaClO for all the pH conditions investigated. Therefore, it can be inferred from this that there is a species other than xanthate that contributes to the absorbance peak in the 223 – 226 nm region, and it is proposed that this species is MTC.

Chapter 5: Effect of pH-Eh on the floatability of sperrylite

Table 5.1: Absorbance peaks of xanthate at 226 nm and 301 nm, with calculated X226:X301 ratios for PAX-only and NaClO-PAX solution for different pH conditions

	PAX-only solution			NaClO-PAX solution		
	A ₂₂₆	A ₃₀₁	A ₂₂₆ :A ₃₀₁ ratio	A ₂₂₆	A ₃₀₁	A ₂₂₆ :X ₃₀₁ ratio
pH 3	0.45	0.76	0.60	0.35	0.55	0.63
pH 5	0.50	0.90	0.55	0.46	0.58	0.79
pH 7	0.55	0.94	0.59	0.49	0.54	0.91
pH 9	0.52	0.90	0.57	0.47	0.46	1.01
pH 11	0.55	0.97	0.57	0.56	0.60	0.94

Chapter 5: Effect of pH-Eh on the floatability of sperrylite

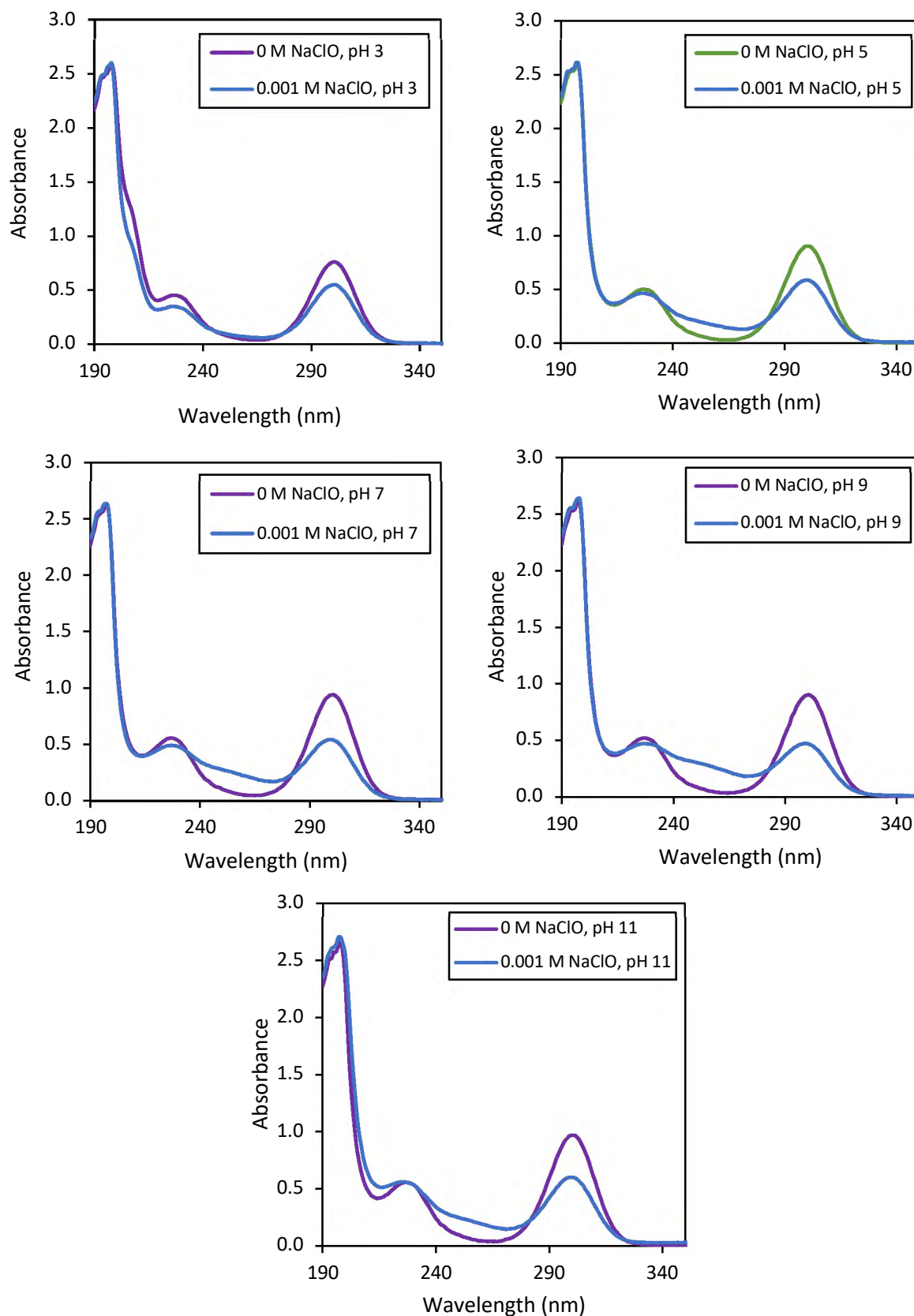


Figure 5.7: UV-vis spectra of PAX with 0.001 M NaClO and without NaClO at different pH conditions in the absence of a mineral; Initial PAX concentration = 7.24×10^{-5} M

The UV-vis spectra presented in Figure 5.7 show that the amount of PAX reacted with NaClO generally increased with an increase in pH. This is better illustrated in Figure 5.8. However, when there is a mineral present, it is not possible to distinguish how much of the collector reacts with NaClO and how much reacts with sperrylite. The rate of each reaction will determine which of the competing reactions will dominate. To that end, it should be noted that Figure 5.6 shows the total amount of collector either reacted with NaClO and/or adsorbed onto sperrylite. The only conclusion that can be drawn from this is that less collector is adsorbed onto the mineral surface when NaClO is present. This may be due to a reaction of PAX with NaClO and/or due to excessive oxidation of the mineral surface by NaClO, thus inhibiting collector adsorption.

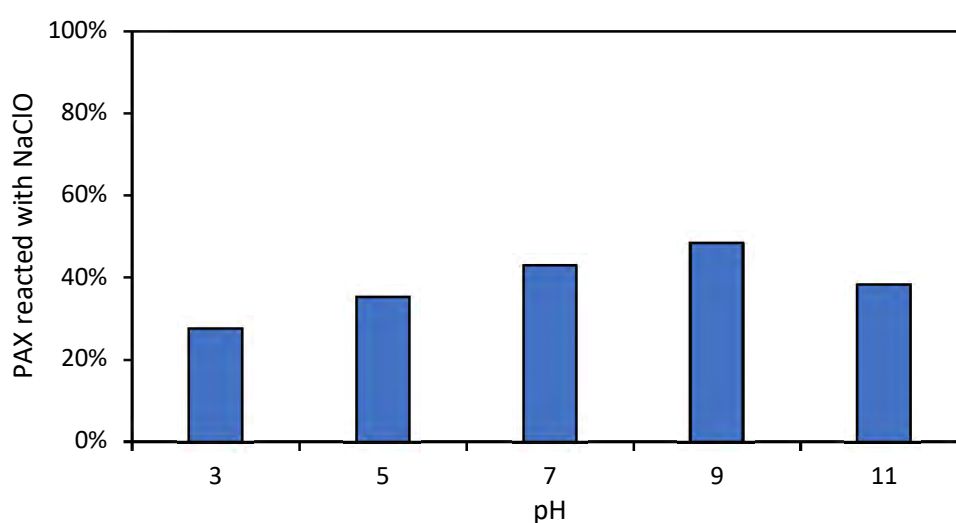


Figure 5.8: Amount of PAX collector reacted with 0.001 M NaClO in the absence of a mineral. Initial PAX concentration = 7.24×10^{-5} M; PAX absorbance peak = 301 nm

5.2.3. Rest potential measurements

The formation of the xanthate collector species responsible for imparting hydrophobicity to the mineral surface is driven by the electrochemical potential across the mineral-solution interface. Therefore, rest potential measurements were carried out to determine the type of collector species that is likely to form on the surface of sperrylite at the different Eh-pH conditions. The results obtained are shown in Figure 5.9.

In determining the interactions between the mineral surface and the collector, the region after 600 seconds is most relevant. This is the point at which the collector was added. Upon the addition of the PAX collector, Figure 5.9 shows that the rest potential of sperrylite decreased which signifies an interaction between the collector and the mineral surface. The magnitude of this change in potential is considered to indicate how reactive the mineral surface is with the collector (Bozkurt et al., 1998; Buswell et al., 2002). From the rest potential profiles, the reactivity of sperrylite with PAX increased with a decrease in pH. At pH 9, there was practically no electrochemical interaction between the collector and the mineral surface

in the absence of NaClO. Nevertheless, the final rest potential of sperrylite was above the equilibrium potential for the xanthate/dixanthogen couple (89 mV vs SHE) at all tested pH conditions, thereby indicating that the formation of dixanthogen, as opposed to the xanthate ion, was thermodynamically favoured which is generally considered to be highly conducive to imparting sufficient hydrophobicity to the mineral.

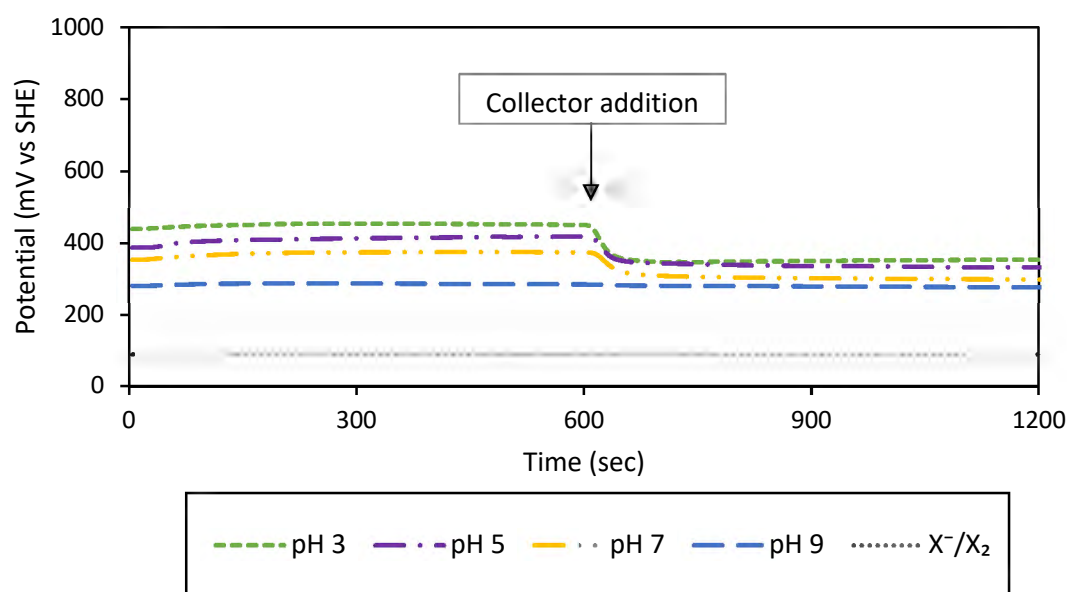


Figure 5.9: Rest potential profiles of sperrylite at different pH conditions with 0 M NaClO; 6.24×10^{-4} M PAX added at 600 seconds

In the presence of NaClO (Figure 5.10), the rest potential profiles show that there was a greater change in the magnitude of the rest potential of the mineral upon collector addition at 600 seconds compared to the case without NaClO. In addition, the final rest potential of sperrylite in the presence of PAX and NaClO was greater than the equilibrium potential of the xanthate/dixanthogen couple, thus signifying that the formation of dixanthogen on sperrylite should be thermodynamically favoured. However, even though increased formation of dixanthogen should be thermodynamically favoured according to the rest potential measurements in the presence of NaClO, it is unlikely that xanthate was predominantly oxidized to this species since neither the spectroscopic studies nor the floatability studies supported increased amounts of dixanthogen in the presence of NaClO. It is more plausible that the greater magnitude of change in potential upon collector addition in Figure 5.10 was as a result of a sperrylite-catalyzed oxidation of PAX to MTC in the presence of NaClO. The oxidation of MTC has been shown to be favoured at high Eh conditions such as those obtained in Figure 5.10 (Forson et al., 2021). The formation of MTC in the presence of NaClO is supported by the UV-vis spectroscopic studies (see Section 5.2.2).

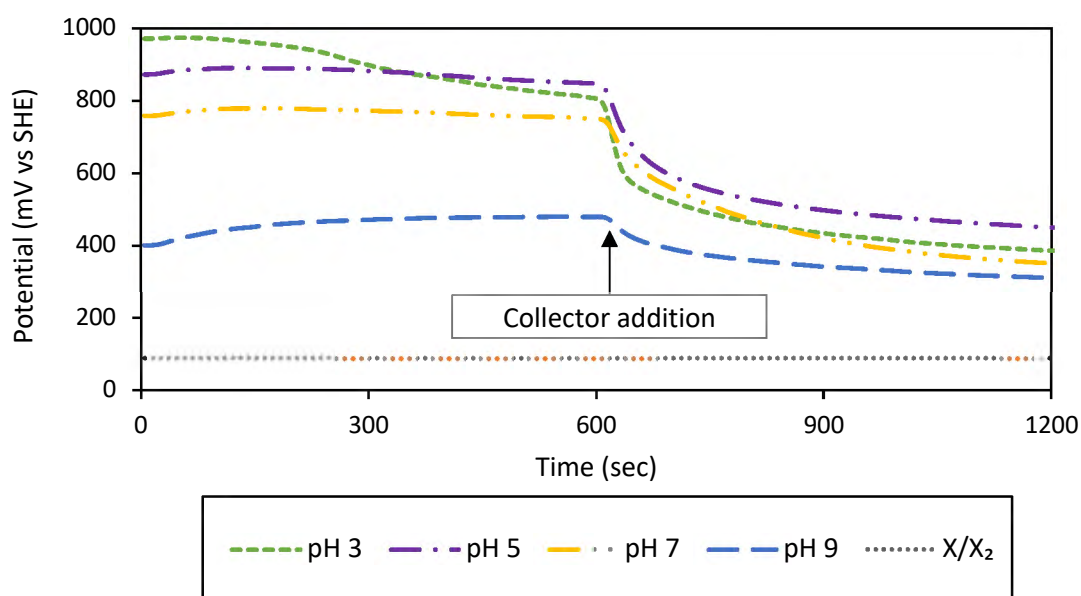


Figure 5.10: Rest potential profiles of sperrylite at different pH conditions with 0.01 M NaClO; 6.24×10^{-4} M PAX added at 600 seconds

The oxidation of the mineral surface can be determined by referring to the rest potential of the mineral before collector addition. It can be observed in Figure 5.9 and Figure 5.10 that both decreasing pH and the addition of NaClO oxidized the mineral surface. This is indicated by the increase in the rest potential of the mineral before collector addition. However, NaClO oxidized the mineral surface to a larger extent. The initial rest potentials and change in potential after collector addition are summarized in Table 5.2.

Table 5.2: Summary of the initial rest potentials and change in potential of sperrylite after collector addition, without and with 0.01 M NaClO

	Initial rest potential (mV vs SHE)		Δ Potential after PAX addition (mV vs SHE)	
	No NaClO	0.01 M NaClO	No NaClO	0.01 M NaClO
pH 3	450	806	96	419
pH 5	418	848	86	397
pH 7	374	750	75	398
pH 9	285	480	8	169

5.2.4. Surface Characterisation

5.2.4.1. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analyses were conducted to study the effect of Eh and pH conditioning on the surface of sperrylite and its interaction with PAX. The spectra of sperrylite conditioned at pH 9 and 3 are shown in Figure 5.11 and Figure 5.12, respectively. The FTIR spectra show that pH did not

seem to have much effect on the mineral surface itself as can be seen by the similar spectra of sperrylite conditioned at pH 3 and 9. However, pH did have an effect on the adsorption of the collector onto the mineral surface. At pH 9, there were no bands that appeared when sperrylite was treated with PAX which probably indicates little or no collector adsorption. This is supported by the data from the UV-vis experiments (cf. section 5.2.2) and rest potential measurements (cf. section 5.2.3).

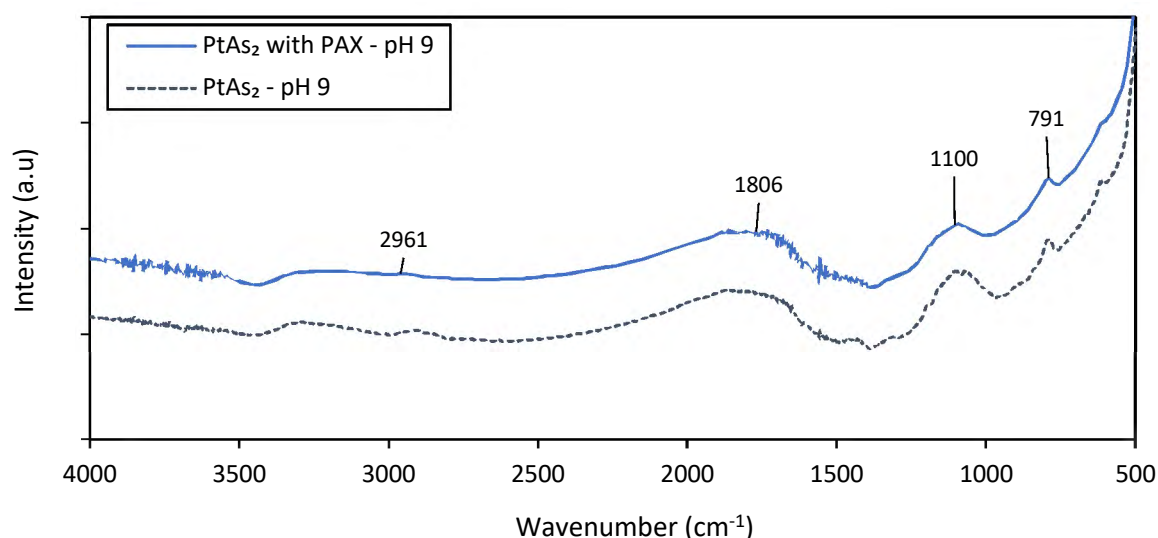


Figure 5.11: FTIR spectra of sperrylite conditioned at pH 9 without and with 5×10^{-4} M PAX collector

On the other hand, at pH 3, there was a clear indication that PAX had adsorbed as can be seen by the appearance of new bands on the sperrylite treated with PAX shown in Figure 5.12. The first indication of collector adsorption was the appearance of the bands at 2961, 2933 and 2873 cm^{-1} which can be attributed to alkyl C-H stretches of the collector (Rao, 2004). The band at 1264 cm^{-1} , attributed to C-O-C stretching, is characteristic of dixanthogen (Little et al., 1961) while the band at 1026 cm^{-1} , associated with C=S stretching, is characteristic of the xanthate monomer (Watt & McCormick, 1965).

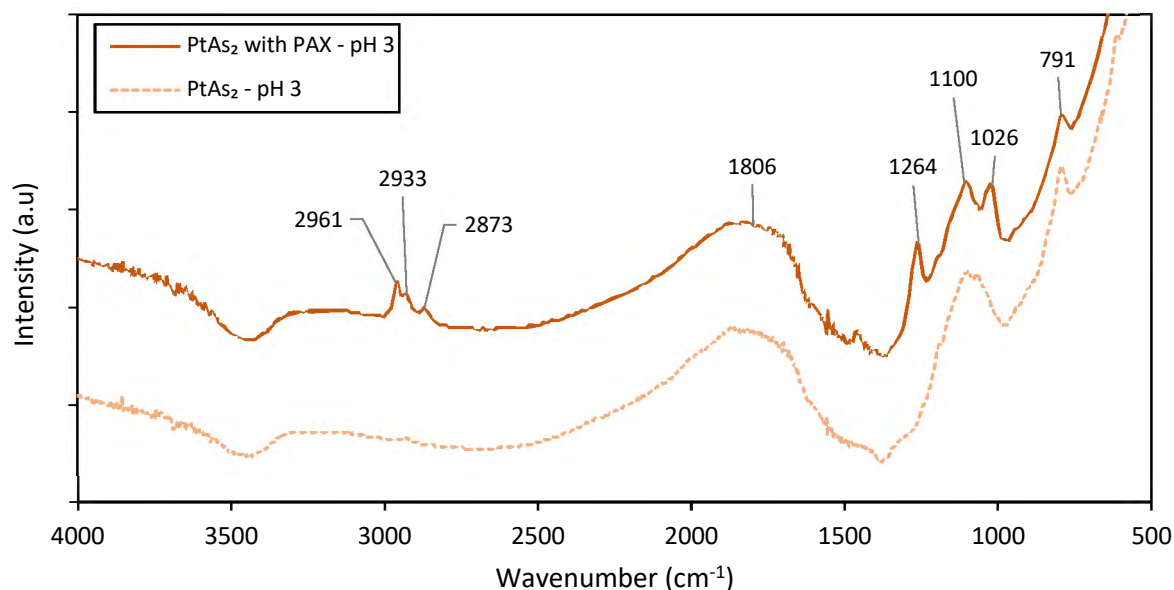


Figure 5.12: FTIR spectra of sperrylite conditioned at pH 3 without and with 5×10^{-4} M PAX collector

The effect of adding NaClO was investigated at pH 9 and the spectra obtained are shown in Figure 5.13. The spectra show that PAX was poorly adsorbed when sperrylite was treated with NaClO. The only band that changed with the addition of NaClO was the band at 1100 cm^{-1} which decreased slightly in its intensity. From the FTIR results alone, it is inconclusive what this change signifies. Therefore, Raman spectroscopy which provided *in-situ* measurements was used to aid the investigation of the changes to the surface of sperrylite when conditioned with NaClO (see section 5.2.4.4). In the presence of NaClO, both FTIR and Raman spectroscopy showed no evidence of PAX adsorption on sperrylite at pH 9.

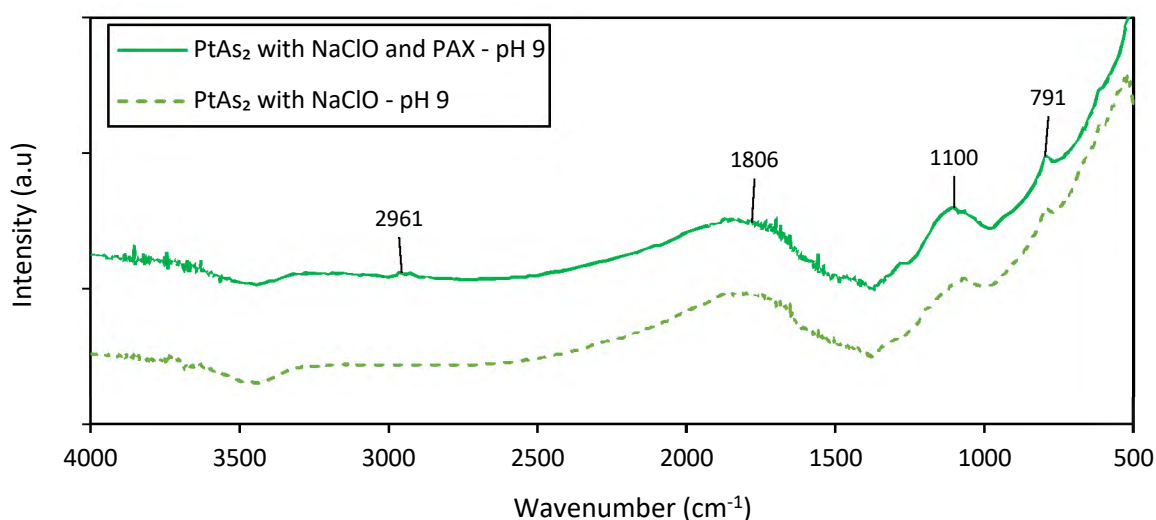


Figure 5.13: FTIR spectra of sperrylite conditioned at pH 9 with 0.01 M NaClO and without or with 5×10^{-4} M PAX collector

5.2.4.2. X-Ray photoelectron spectroscopy

Similar to the FTIR results presented in section 5.2.4.1, XPS analysis showed that PAX adsorbed as dioxanthogen at pH 3. The adsorption of the collector on sperrylite can be determined from the S 2p spectra generated from XPS analysis. These spectra are shown in Figure 5.14 where it can be seen that there was a clear difference in the S 2p spectra at the different pHs, with pH 3 having a well-defined peak. This is due to better adsorption of the collector at pH 3 compared to pH 9. Only the S 2p spectra are presented in this section as these are directly relevant to determining the nature of collector adsorption on sperrylite. The Pt, As, O and C spectra are shown in APPENDIX C as these did not contribute further information to what is presented in this result section.

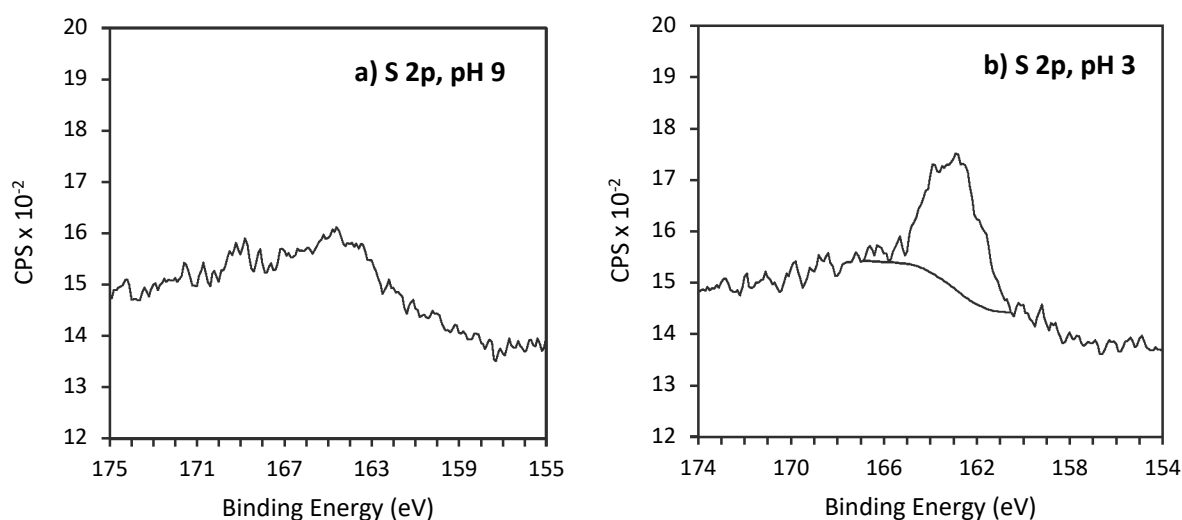


Figure 5.14: S 2p spectra of sperrylite conditioned with 5×10^{-4} M PAX at a) pH 9 and b) pH 3

Peak fitting was only performed for the S 2p spectra obtained at pH 3 due to the high noise-to-signal ratio of the S 2p spectra at pH 9. Several constraints such as energy separation, spin-orbit intensity (i.e. area constraints), FWHM (full width at half maximum), and peak shape were considered when fitting the peaks. From these considerations, two pairs of doublets had a better fit compared to a single doublet pair. Given the broad nature of the S 2p peak ranging from about 161 to 166 eV, it is unlikely that xanthate would be present in a single chemical oxidation state. Typically, for single oxidation state xanthate species, a narrower S 2p peak would be expected (Pillai et al., 1983; Mikhlin et al., 2016). The broad S 2p peak suggests that xanthate is present in multiple oxidation states on the surface of sperrylite at pH 3.

The S 2p spectrum of sperrylite conditioned with PAX at pH 3 was fitted, as shown in Figure 5.15, with two S 2p_{3/2} and S 2p_{1/2} doublet pairs with an intensity ratio of 2:1, a spin-orbit energy splitting of 1.16 eV and full width at half maximum (FWHM) values of 1.7 eV (species A) and 1.6 eV (species B). It can be seen from the fitted spectra that there were at least two collector species present on the surface of sperrylite at pH 3.

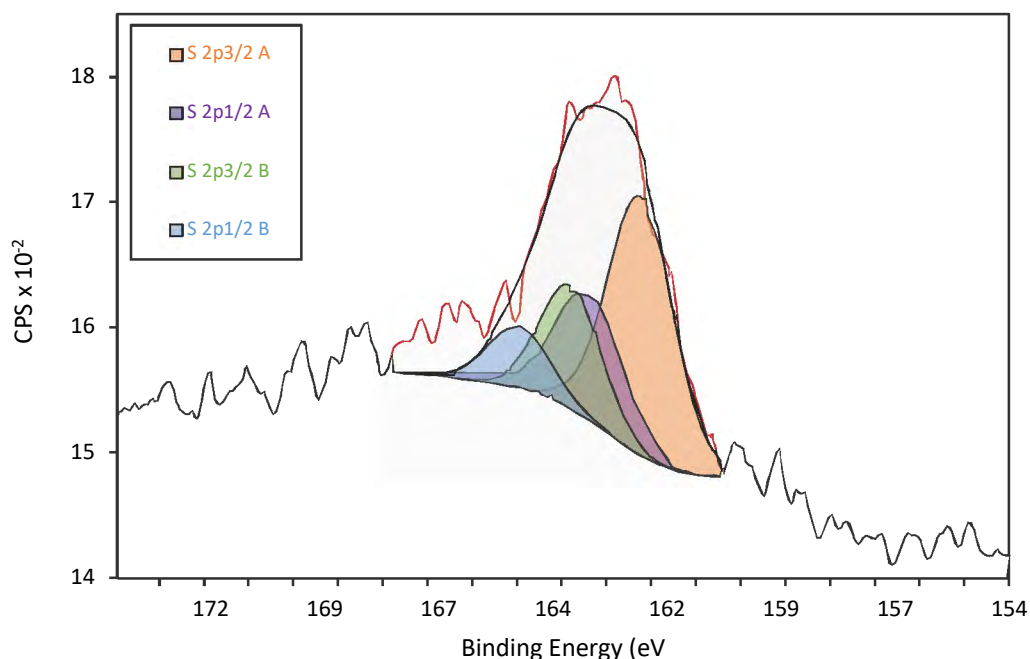


Figure 5.15: S 2p spectra of sperrylite conditioned with 5×10^{-4} M PAX at pH 3, with peak fitting

The peak at 164.03 eV is a signature bridging of S atoms in dixanthogen. On the other hand, the S 2p peak at 162.48 eV may be attributed to monosulfide species on the mineral surface (Szargan et al., 1992; Mikhlin et al., 2016; Ejtemaei & Nguyen, 2017). This signal is likely to be a contribution from the terminal S atoms originating from a species of the monomer of xanthate adsorbed onto the mineral surface. The presence of this second species on the mineral surface, in addition to dixanthogen, is supported by the zeta potential measurements presented in the following section.

5.2.4.3. Zeta potential measurements

Zeta potential measurements were conducted to determine the surface charge of sperrylite in the absence and presence of PAX across a pH range from 2 to 12. The results shown in Figure 5.16 show that sperrylite is negatively charged and that the zeta potentials became more negative with an increase in pH, ranging from 0 to -29 mV. This can be attributed to the increase in the concentration of OH^- ions at higher pH conditions. In the presence of the collector, the zeta potentials of sperrylite shifted to more negative values ranging from -2 to -38 mV. Since dixanthogen, which has been identified by FTIR and XPS, has a neutral charge, it is unlikely to be the cause of this negative shift. The shift to more negative zeta potentials, when PAX is added, may be due to the interaction of xanthate ions with the positively charged metal cations on the mineral surface, thereby shifting the charge balance towards the anionic species.

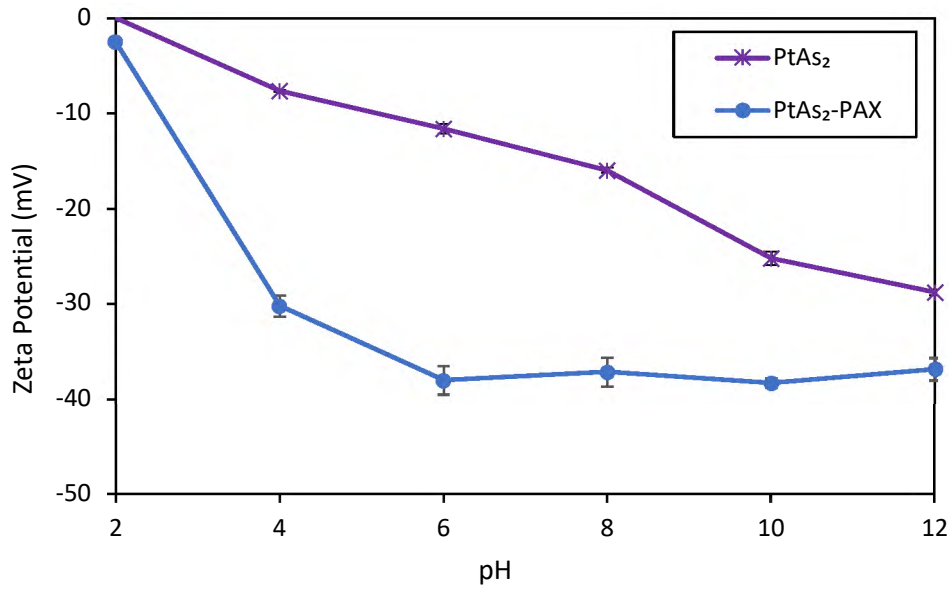


Figure 5.16: Zeta potentials of sperrylite in 0.12 M KCl without and with 5×10^{-4} M PAX

5.2.4.4. Raman spectroscopy

The Raman spectra of dry sperrylite (measured 'as is'), the respective reference solutions and sperrylite conditioned at pH 3 and pH 9 in the absence of PAX at increasing time intervals are shown in Figure 5.17 and Figure 5.18, respectively. The assignment of spectra of sperrylite was based on the five Raman-active zone centre phonon modes of pyrite-compounds, to which sperrylite belongs. According to the group theory of crystal structures, the vibrations of the Raman-active phonon modes of sperrylite can be represented by equation 5-2 (Muller & Lutz, 1991; Chen et al., 2022):

$$\Gamma = Ag + Eg + 3Fg \quad 5-2$$

where Γ is the gamma character in the simple cubic Brillouin zone, which corresponds to long-wavelength vibrations and defined as the sum of the Raman-active phonon modes. This expression indicates that sperrylite has one symmetric mode (Ag, As-As in-phase stretches), a double degenerate mode (Eg, As₂ librational mode), and a triple degenerate mode (3Fg) which consists of coupled librational and stretching modes. The description and assignment of these phonon modes are presented in Table 5.3.

Table 5.3: Assignment of vibrational spectra of sperrylite (Muller & Lutz, 1991)

Phonon mode	Vibration/bond	Raman shift (cm ⁻¹)
Ag	As-As symmetric stretches	278
Eg	As ₂ liberations	214
Fg1	Coupled stretches and liberations	295
Fg2	As-As out-of-phase stretches	262
Fg3	Coupled stretches and vibrations	223

The Raman spectra of sperrylite with no collector or NaClO (i.e. Figure 5.17 and Figure 5.18) show that the phonon modes were slightly more defined at pH 3 compared to pH 9. For instance, the vibrational bands of the Ag species which represents As-As in-phase symmetric stretches were more intense at pH 3. The spectra show that there were differences in the manner in which sperrylite interacts with the solution. The broad band at 3415 cm⁻¹ can be assigned to OH stretching vibrations, which result from OH species bonded to the mineral surface (Woods et al., 1998). At pH 9, this band was very intense and its rate of disappearance with time was slower compared to that at pH 3. This could signify a stronger interaction of OH species at pH 9 with the sperrylite surface.

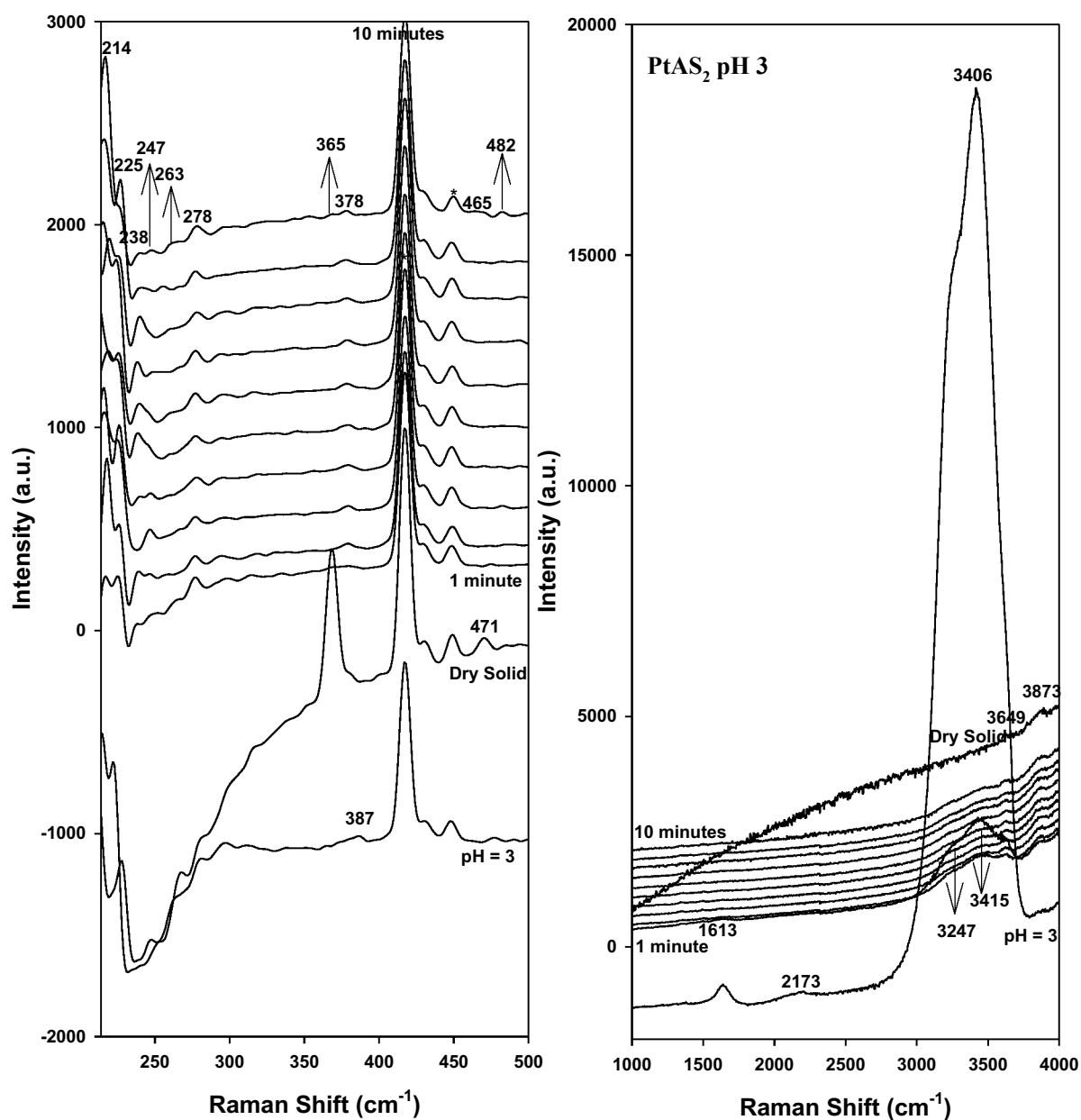


Figure 5.17: in-situ Raman spectra of sperrylite conditioned at pH 3 from 1 minute to 10 minutes. Spectra of dry sperrylite ('as is') and reference solution included at second-from-bottom and bottom, respectively. NB: The left and right diagrams represent different ranges on the electromagnetic spectrum and have different y-axis scales

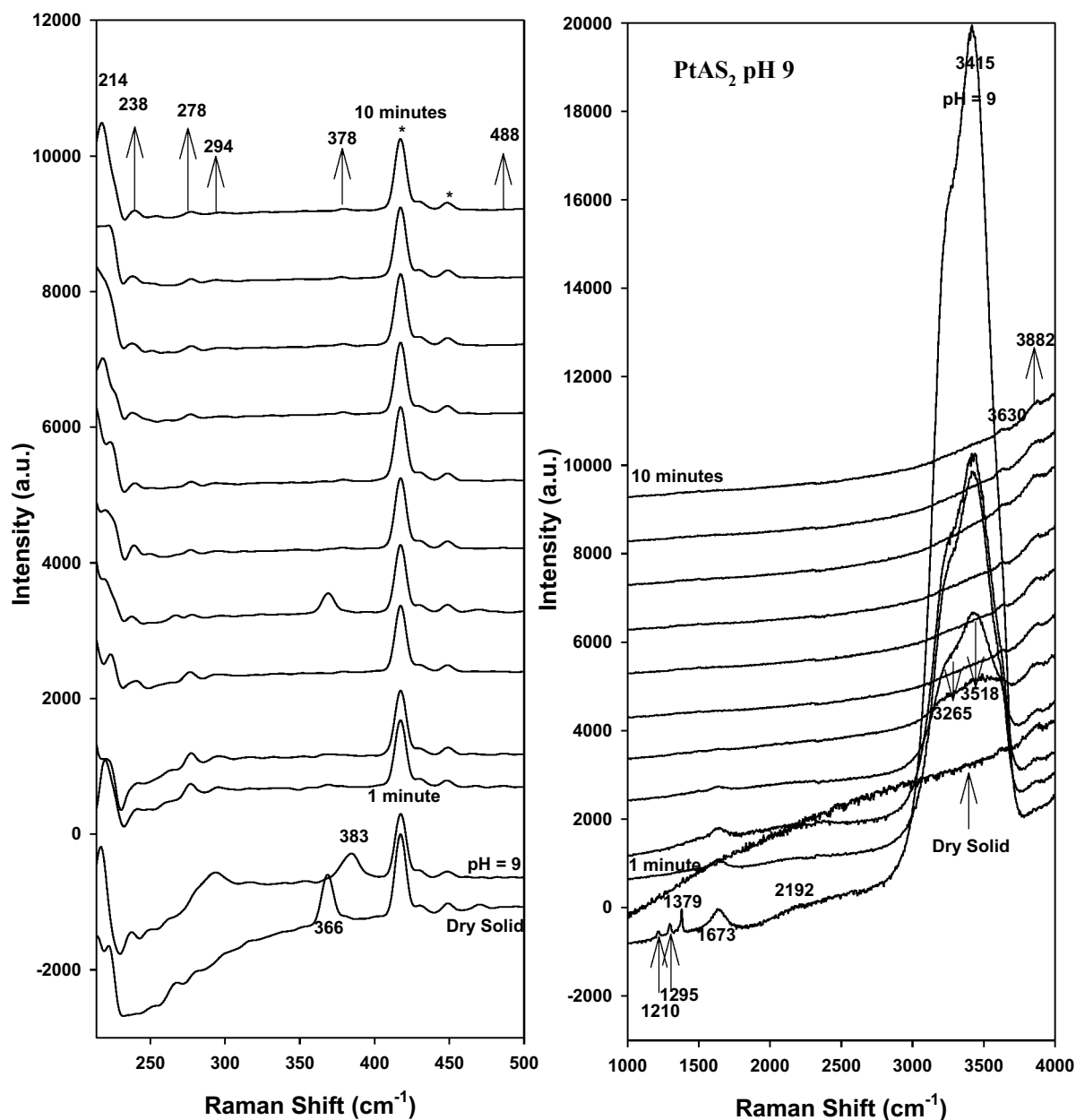


Figure 5.18: in-situ Raman spectra of sperrylite conditioned at pH 9 from 1 minute to 10 minutes. Spectra of dry sperrylite ('as is') and reference solution included at the bottom and second-from-bottom, respectively. NB: The left and right diagrams represent different ranges on the electromagnetic spectrum

The Raman spectra of sperrylite conditioned with PAX collector at pH 3 and pH 9 are shown in Figure 5.19 and Figure 5.20, respectively. Similar to the FTIR and XPS results, the Raman spectra of sperrylite conditioned with PAX showed no evidence of collector adsorption at pH 9 as evident from there being no vibrational bands that belong to the collector on the surface of sperrylite at this pH (see Figure 5.20). At pH 3, there were vibrational bands that appeared after about 8 minutes at 1350 cm^{-1} and 1621 cm^{-1} (see Figure 5.19) which indicate the

presence of the collector. The band at 1350 in particular can be assigned to CH wagging vibrations which have been found in dixanthogens (Andreev & Barzev, 2003).

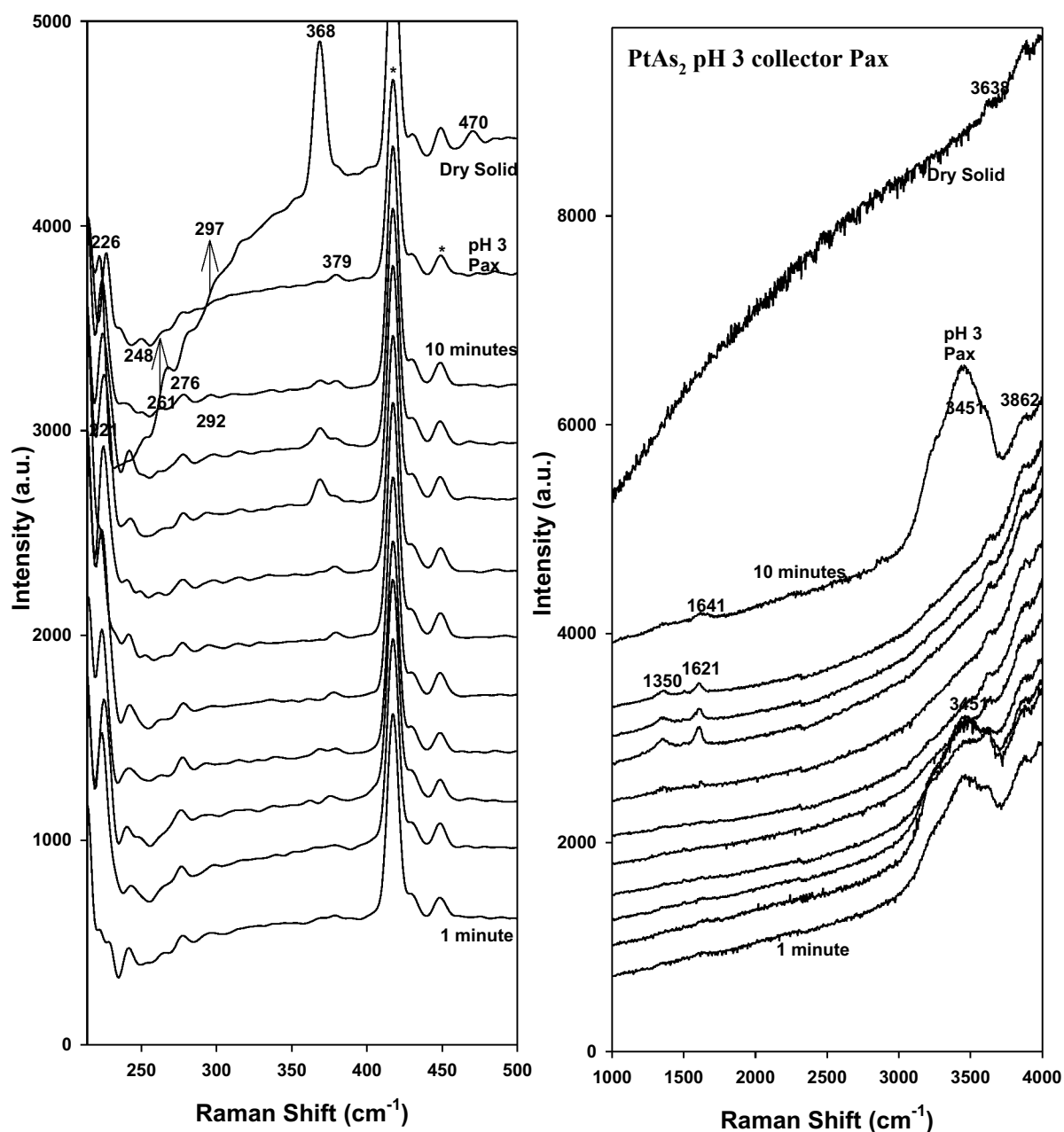


Figure 5.19: in-situ Raman spectra of sperrylite conditioned at pH 3 with 5×10^{-4} M PAX from 1 minute to 10 minutes. Spectra of dry sperrylite ('as is') and reference solution included at the top and second-from-top, respectively. NB: The left and right diagrams represent different ranges on the electromagnetic spectrum and have different y-axis scales

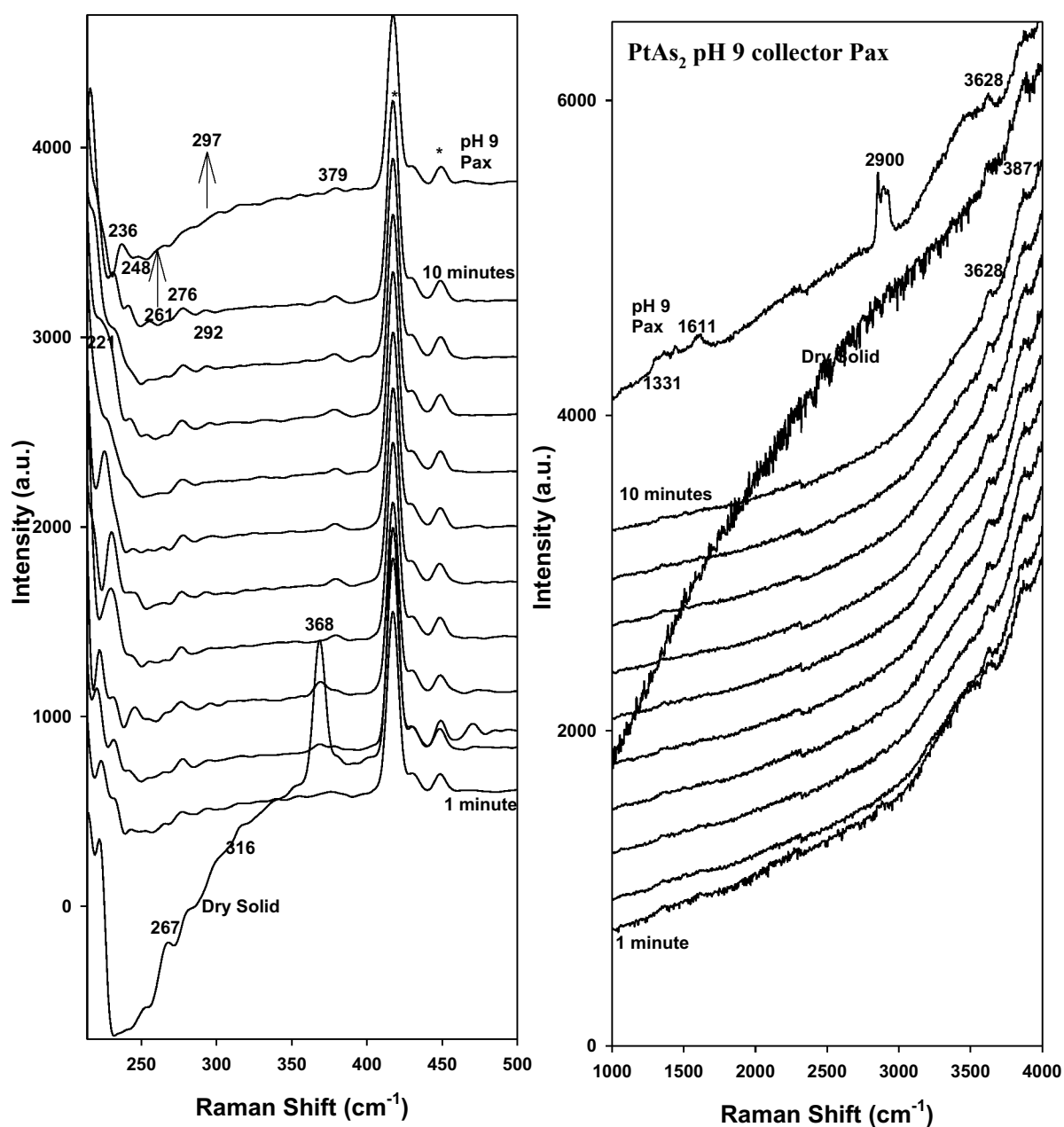


Figure 5.20: in-situ Raman spectra of sperrylite conditioned at pH 3 with 5×10^{-4} M PAX from 1 minute to 10 minutes. Spectra of dry sperrylite ('as is') and reference solutions included at the bottom and the top, respectively. NB: The left and right diagrams represent different ranges on the electromagnetic spectrum and have different y-axis scales

When sperrylite was conditioned with NaClO, there was a clear change in the surface composition of the mineral. This is shown in Figure 5.21 where it can be seen that all the five phonon modes characteristic of sperrylite disappeared and/or were replaced by a very intense band at 250 cm^{-1} . This band can be assigned to As-O-As vibrations (Bahfenne, 2011) which are indicative of the oxidation of sperrylite in the presence of NaClO. This is consistent with the rest potential measurements which showed that sperrylite had an initial rest potential of 480 mV vs SHE in the presence of NaClO compared to 285 mV vs SHE without NaClO (cf. Table 5.2),

thus indicating a high degree of oxidation when sperrylite is conditioned with NaClO. This is different to the hydroxylation that occurs at high pHs that introduces a peak at 3415 cm^{-1} as shown in Figure 5.18.

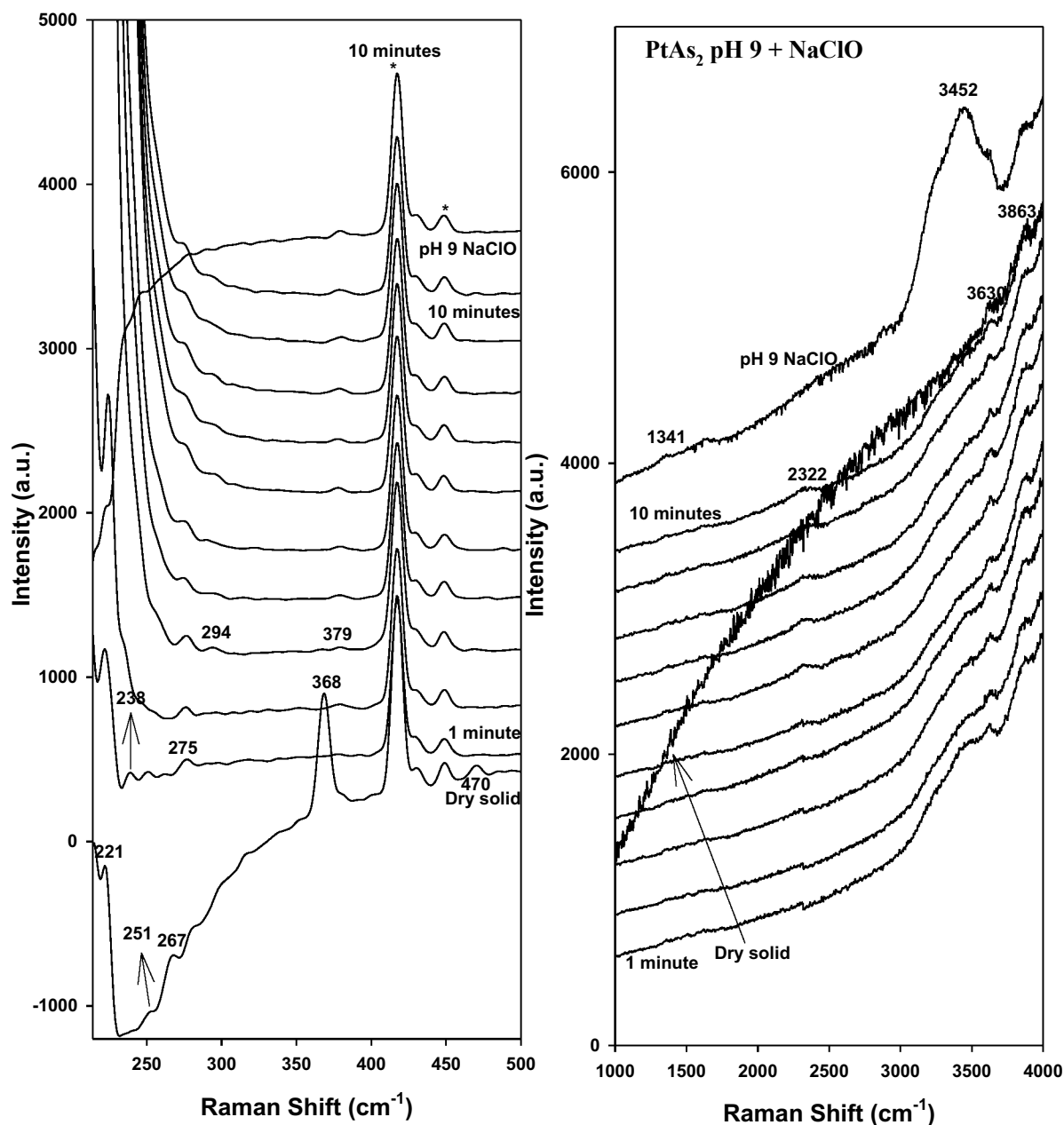


Figure 5.21: in-situ Raman spectra of sperrylite conditioned with 0.01 M NaClO at pH 9 from 1 minute to 10 minutes. Spectra of dry sperrylite ('as is') and reference solutions included at the bottom and at the top, respectively. NB: The left and right diagrams represent different ranges on the electromagnetic spectrum and have different y-axis scales

The relevant vibrational bands and their assignments for the different conditions are summarised in Table 5.4 and Table 5.5. It should be noted that the *in-situ* bands refer to the final spectra (i.e. at 10 minutes) of the sperrylite slurries.

Chapter 5: Effect of pH-Eh on the floatability of sperrylite

Table 5.4: Summary of Raman vibrational bands of sperrylite and their assignment in the absence of a collector at pH 3 and pH 9

Vibration ^a	Dry solid	<i>In-situ</i> at pH 3	pH 3 ref. solution	<i>In-situ</i> at pH 9	pH 9 ref. solution	<i>In-situ</i> with NaClO at pH 9	0.01 M NaClO ref. solution at pH 9
Ag	278	278		278			
Eg	214	214		214			
Fg1	295	-	N/A	-	N/A	250	N/A
Fg2	262	263		-			
Fg3	223	225		225			
vOH	-	3247-3415	3406	3265-3416	3415	3630	3452
vCH	-	-	-	-	-	-	-
δOH	-	-	2173	-	2192	2322	-
	-	-	1613	1673	1673	-	-
	-	-	-	-	1379	-	-
ωCH, X ₂	-	-	-	-	-	-	-
ωCH, X	-	-	-	-	-	-	-

Table 5.5: Summary of Raman vibrational bands of sperrylite and their assignment in the presence of 5x10⁻⁰⁴ M PAX collector at pH 3 and pH 9

Vibration ^a	Dry solid	<i>In-situ</i> with PAX at pH 3	pH 3 + PAX ref. solution	<i>In-situ</i> with PAX at pH 9	pH 9 + PAX ref. solution
Ag	278	276		276	
Eg	214	214		214	
Fg1	295	292	N/A	292	N/A
Fg2	262	261		261	
Fg3	223	221		221	
vOH	-	3451	3451	3628	3628
vCH	-	-	-	-	2900
	-	-	-	-	-
δOH	-	1621	1641	-	1611
	-	-	-	-	-
ωCH, X ₂	-	1350	1350	-	-
ωCH, X	-	-		-	1331

^aVibrational bands: v, stretching; δ, bending; ω, wagging

5.3. Discussion

Sperrylite has been shown to be poorly floatable at pH 9, the typical conditions used in PGM flotation. For systems that involve H^+ or OH^- ions, such as those encountered in flotation, pH and Eh are related to one another through the Nernst relationship (Archer, 1989), which can be described by equation 5-3:

$$E_h = E^0 - 0.0592pH - \frac{0.0592}{n} \log \left(\frac{a_{oxidation}}{a_{reduction}} \right) \quad 5-3$$

where ' E_h ' is the redox potential, ' E^0 ' is the standard electrode potential, ' n ' is the number of electrons transferred and ' a ' is the activity of the oxidised or reduced species.

The efficacy of collector adsorption, hence imparted hydrophobicity, has been shown to be a strong function of these Eh-pH relationships. Different minerals have different optimal Eh-pH regions of floatability (López-Valdivieso et al., 2006; Lotter et al., 2016; Zanin et al., 2019). This phase of the study aimed to find the optimal flotation Eh-pH region for sperrylite, and to link the flotation performance to the mineral-collector interactions occurring on the mineral surface.

5.3.1. Effect of pH and Eh on the floatability of sperrylite

The microflotation test work showed that the recovery of sperrylite with PAX improved from 22% at pH 9 to 61% at pH 3 (cf. Figure 5.1). Correspondingly, the Eh associated with these pH conditions increased from 313 mV vs SHE at pH 9 to 550 mV vs SHE at pH 3 (cf. Figure 5.2). Given that the collectorless recovery of sperrylite only changed from 7% at pH 9 to 8% at pH 3, this suggests that changes in pH have little effect on the natural hydrophobicity of sperrylite. Rather, pH predominantly affects the ability of the collector to impart hydrophobicity to the mineral.

The interaction of xanthate collectors with minerals is largely governed by electrochemical reactions where the collector is oxidized to produce three possible collector products which are then adsorbed onto the mineral surface, viz., chemisorbed xanthate, metal xanthate or dixanthogen (Woods, 1996). The oxidation of the collector is coupled with the reduction of oxygen. These oxidation (anodic) and reduction (cathodic) reactions are related through the potential across the mineral-solution interface referred to as rest potential or mixed potential (Woods, 1971). In the context of these electrochemical interactions, there are at least three explanations that can be put forward for the increased sperrylite recoveries observed at decreasing pH, viz., that this:

- i) Increases the Eh and provides oxidizing conditions thus making the formation of dixanthogen thermodynamically favourable, or
- ii) Cleans the surface of the mineral by removing hydrophilic OH^- species that would otherwise compete with or inhibit collector adsorption on the mineral surface, or
- iii) Reduces the concentration of OH^- ions thus driving the cathodic reduction of oxygen forward which promotes the oxidation of xanthate

In essence, changing the pH-Eh conditions changes the amount of collector that can be adsorbed and/or the nature of the collector species that can form on the mineral surface. These propositions were explored by performing electrochemical rest potential measurements, zeta potential measurements and spectroscopic studies. The first point addressed is with regard to the extent to which the collector adsorbs on the sperrylite surface at the different conditions investigated.

5.3.2. The extent of collector adsorption

UV-vis spectroscopy studies performed at varying pH conditions showed that the amount of PAX adsorbed on sperrylite increased with decreasing pH, with 99% of the added collector adsorbed at pH 3 compared to only 13% at pH 9 (cf. Figure 5.6). This is equivalent to 4.95 and 0.65 pseudo-monolayers of PAX adsorbed at pH 3 and 9, respectively. This trend corroborates the microflotation recoveries. That is, the improved sperrylite recoveries as a result of decreasing pH correspond to higher amounts of collector adsorbed on the sperrylite surface.

The poor adsorption of the collector with increasing pH is likely due to an increase in the concentration of OH^- species that preferentially adsorb onto sperrylite thus inhibiting collector adsorption. Waterson et al. (2016) have shown through computational modelling that OH^- ions preferentially adsorb on sperrylite with a binding energy of -473.8 kJ/mol compared to -299.5 kJ/mol for ethyl xanthate or -51.5 kJ/mol for diethyl dioxanthogen. Therefore, at high pH there is a strong competition between OH^- ions and xanthate for adsorption on the mineral surface. This competition is typically described by the Barsky relationship, the ratio of xanthate and OH^- ions in solution, represented by equation 5-4 (Somasundaran & Wang, 2006).

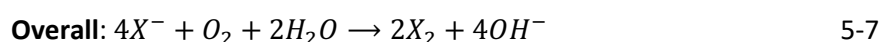
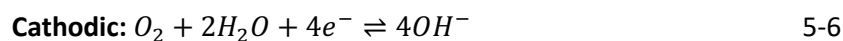
$$K = \frac{[\text{X}^-]}{[\text{OH}^-]} \quad 5-4$$

Lowering the pH essentially cleans the surface of the mineral by removing the OH^- ions, thereby allowing for more collector to be adsorbed. In the present study, this cleaning effect was demonstrated using Raman spectroscopy where *in-situ* Raman spectra of sperrylite were taken at 1-minute intervals for 10 minutes at pH 3 and 9 (cf. Figure 5.17 and Figure 5.18). In this context, the most relevant vibrational band is the one at 3415 cm^{-1} which can be assigned to OH stretching vibrations resulting from OH species bonded to the sperrylite surface (Woods & Hope, 1998; Woods et al., 1998). At pH 9 the intensity of this band is much stronger compared to that at pH 3. Furthermore, the rate of disappearance of this band is slower at pH 9. It can be concluded from this that the interaction between the sperrylite surface and OH^- species, hence competition with the collector for adsorption, is stronger at pH 9.

Having established the extent of collector adsorption on the sperrylite surface, the next key question addressed is with regard to the nature of the collector adsorption.

5.3.3. Nature of collector adsorption

As mentioned earlier, the adsorption of xanthate collectors can be described by electrochemical reactions where different collector products could be formed on the mineral surface. Vermaak et al. (2007) have shown through electrochemical studies that dixanthogen is the likely species required on the surface of sperrylite to impart hydrophobicity. The formation of dixanthogen proceeds according to reaction 5-7.



A necessary condition for the formation of dixanthogen to be thermodynamically favourable is that the rest potential of the mineral in a solution of xanthate should be greater than the equilibrium potential of the xanthate/dixanthogen couple which was 89 mV vs SHE for PAX in this study (Allison et al., 1972). The rest potential measurements of sperrylite with PAX performed in this study showed that the formation of diamyl dixanthogen was thermodynamically favoured across the tested pH range. However, at pH 9 it was found that there was very little interaction between PAX and sperrylite (cf. Figure 5.9). This may explain the poor recovery of this mineral that has been observed at pH 9 by others (e.g. Shackleton et al., 2007; Shamaila & O'Connor, 2008; Pikinini, 2022), which was also confirmed in the present study. At pH 9, this study has shown that sperrylite may be electrochemically inert as evident from there being minimal electrochemical interaction between the collector and the mineral surface. In order to increase the interaction between PAX and sperrylite, it is necessary to decrease pH.

Decreasing the pH from pH 9 to 3 resulted in an increase in the rest potential of sperrylite from 285 to 450 mV vs SHE, respectively (cf. Table 5.2). This is indicated by the region before collector addition (at 600 seconds) in the rest potential profiles shown in Figure 5.9. The reduction in pH is necessary as it provides a suitable surface for the oxidation of xanthate to dixanthogen. With further lowering of pH, the interaction between PAX and sperrylite increased as indicated by the magnitude of the change in potential upon collector addition.

It would be expected that if dixanthogen is the species adsorbed on the mineral surface as predicted by the rest potential measurements, the surface charge of sperrylite treated with PAX should remain unchanged due to dixanthogen being neutrally charged, or that the surface charge would shift to a more neutral value as the double layer is compressed. However, it was observed in this study that the zeta potential of sperrylite, which is indicative of surface charge, became more negative when treated with PAX compared to the untreated surface. The zeta potentials shifted from a range of 0 to -29 mV for the untreated sperrylite to a range of -2 to -38 mV for the collector-treated sperrylite in the tested pH range (cf. Figure 5.16). This shift is likely due to an interaction between the xanthate ions and the metal cations present on the mineral surface. This would shield the positively charged cations on the mineral surface

and shift the surface charge balance towards the anionic species. Therefore, it is likely that the adsorption of PAX on sperrylite takes place through co-adsorption of the metal xanthate and dioxanthogen.

A similar mechanism of xanthate adsorption has been proposed by various authors (Fuerstenau et al., 1990; López Valdivieso et al., 2003; Zhang et al., 2013; Multani et al., 2018). López Valdivieso et al. (2003) performed zeta potential, rest potential and cyclic voltammetry studies and proposed that the adsorption of isopropyl xanthate on arsenopyrite occurred first as isopropyl dioxanthogen, then followed by the co-adsorption of isopropyl xanthate ions adsorbed via hydrophobic bonding with the dioxanthogen in the first layer. Similarly, for a pyrite-xanthate system, Zhang et al. (2013) have found that xanthate adsorption on pyrite occurs via a reaction of xanthate ions in solution with ferric ions on the pyrite surface. Subsequently, a co-adsorption of dioxanthogen occurs by hydrophobic bonding between the xanthate radicals in the dioxanthogen and ferric xanthate complex. The adsorption of PAX on sperrylite likely follows a similar mechanism to the co-adsorption of dioxanthogen and metal xanthate on pyrite.

In the present study, the co-adsorption of dioxanthogen and metal xanthate is further supported by the XPS analyses. The XPS results showed that there are at least two collector species present on the sperrylite surface at pH 3, viz. a xanthate monomer species and a dioxanthogen. The first species was identified by the peak at 162.48 eV which may be attributed to terminal S atoms originating from xanthate. The second species was identified by the peak at 164.03 eV which is characteristic of S-S bridging in dioxanthogen (Szargan et al., 1992; Mikhlin et al., 2016; Ejtemaei & Nguyen, 2017).

The hydrophobicity imparted to sperrylite is most likely governed by the amount of collector adsorbed and/or relative proportions of the adsorbed dioxanthogen and metal xanthate. At pH<4, the zeta potential measurements showed that there is a smaller shift between the zeta potentials of the untreated and PAX-treated sperrylite. This either indicates poor adsorption of the collector or that the collector is adsorbed primarily as dioxanthogen both of which would result in minimal changes to the zeta potential of the mineral. The former is unlikely to be true since the UV-vis spectroscopy tests showed that there is high adsorption of the collector at pH 3, with 99% of the added collector adsorbed. Therefore, the collector must be adsorbed primarily as dioxanthogen. The presence of dioxanthogen at pH 3 was confirmed by FTIR spectroscopy, in addition to the evidence already discussed.

FTIR spectroscopy showed a clear difference between the adsorption of PAX on sperrylite at pH 9 compared to pH 3. At pH 9, there was no evidence that the collector had adsorbed on the mineral surface as there were no new vibrational bands detected with the addition of PAX (cf. Figure 5.11). This is likely due to the poor adsorption of the collector at this pH which could not be registered by the spectrometer. On the other hand, new vibrational bands belonging to the collector were detected at pH 3 (cf. Figure 5.12). Of particular interest are the bands at 1264 and 1026 cm^{-1} which can be assigned to C-O-C asymmetric stretching and C=S stretching

vibrations, respectively. The C=S band at 1026 cm^{-1} is characteristic of the monomer of xanthate (Shankaranarayana & Patel, 1965; Watt & McCormick, 1965; Rao, 2004).

The C-O-C bond is found in both the xanthate and dixanthogen molecules. However, it is possible to distinguish the species from which this bond originates depending on its vibration frequency. When the C-O-C is from the monomer xanthate, its vibration frequency is found at $1100\text{-}1140\text{ cm}^{-1}$ and 1200 cm^{-1} . However, when these vibrations are from dixanthogen, they shift to about $1250\text{-}1270\text{ cm}^{-1}$. This shift is related to the difference in electronegativity between the sulfur and the metal from the mineral which affects how the collector is bonded to the mineral surface (Rao, 2004). Therefore, in this study, the vibrational band at 1264 cm^{-1} is assigned to C-O-C and this originates from dixanthogen. This assignment is consistent with those of Little et al. (1961) and Leppinen et al. (1989).

It has been established that it is necessary to lower pH, which corresponds to increasing Eh, to provide a suitable sperrylite surface for the oxidation of xanthate to dixanthogen. Eh can also be increased using an oxidizing agent. The use of NaClO to chemically increase the Eh of sperrylite at constant pH was investigated, with the expectation that increased Eh would promote dixanthogen formation according to the electrochemical model of xanthate adsorption (Woods, 1996).

5.3.4. Chemical control of redox potential

Microflotation test work conducted in the presence of NaClO showed that the addition of NaClO is detrimental to the recovery of sperrylite. For instance, at pH 3 the recovery of sperrylite was found to be 61% without NaClO. The addition of 0.001 M NaClO decreased the recovery to 31%, and an addition of 0.01 M NaClO further decreased the sperrylite recovery to 21%. This trend was found to be true for most of the pH conditions investigated (cf. Figure 5.3). Microflotation tests performed using an alternative oxidizing agent, H_2O_2 , showed that this effect is not unique to NaClO. That is, the use of these oxidizing agents to chemically modify the Eh of sperrylite is detrimental to its recovery. However, this is likely a chemical effect and not necessarily the effect of Eh as demonstrated by the rest potential measurements.

Rest potential measurements indicated that dixanthogen should be thermodynamically favoured and that the reactivity of PAX with sperrylite is increased in the presence of NaClO (cf. Figure 5.10). From this, it could be deduced that the presence of NaClO may lead to enhanced collector adsorption, and hence hydrophobicity of sperrylite. However, as evident from microflotation results, this was not the case. Furthermore, increased collector adsorption in the presence of NaClO was not observed in the spectroscopic studies performed. Therefore, it is clear that the thermodynamically favoured formation of dixanthogen as predicted by the rest potential measurements is not the only criterion by which interactions between the collector and the mineral should be evaluated. According to Leja (1982), the surface of the mineral does not become sufficiently hydrophobic if the requisite amount of

dixanthogen is not adsorbed or if the conditions are such that other hydrophilic products that preferentially adsorb onto the mineral surface are formed.

The more likely explanation for the greater magnitude of the change in the rest potential of sperrylite upon collector addition in the presence of NaClO is that this resulted from a surface-catalyzed reaction of PAX to a hydrophilic MTC ion, rather than dixanthogen. This explanation is consistent with the microflotation studies which showed reduced floatability of sperrylite in the presence of NaClO, as well as UV-vis spectroscopic studies which showed that there was a reaction between PAX and NaClO. Several studies have shown similar findings where the addition of NaClO or H₂O₂ did not result in an improvement in the floatability of minerals despite there being an increase in pulp potential which should favour dixanthogen formation (e.g. López-Valdivieso et al., 2006; Chimonyo et al., 2017). Chimonyo et al. (2017) concluded that there was no significant change to the recovery of copper and nickel when the Eh was changed to a higher potential using NaClO. Similarly, López-Valdivieso et al. (2006) reported decreases in arsenopyrite recoveries at high Eh values in the presence of H₂O₂. The authors proposed that the decrease in arsenopyrite recovery at high Eh values was due to the surface oxidation of the mineral which led to the production of arsenate species that subsequently interact with ferric hydroxide and inhibit the formation of dixanthogen. Ultimately, in the present study, it is proposed that the addition of NaClO results in excessive oxidation of sperrylite and/or reacts with the collector, thus limiting the adsorption of the collector to the mineral.

The reaction of NaClO with PAX was confirmed by UV-vis spectroscopy where it was found that some of the collector reacts with NaClO even in the absence of the mineral (cf. Figure 5.8). It has been reported that in the presence of an oxidant such as NaClO or H₂O₂, xanthate can be converted to a hydrophilic monothiocarbonate (MTC) ion on the surface of sulfides (Harris & Finkelstein, 1975; Chen et al., 2019; Forson et al., 2021). The UV-vis spectra obtained in this study did not explicitly show the presence of MTC in the presence of NaClO. This is likely because the absorbance peak of MTC, which is found at 223 nm, overlaps with that of xanthate found at 226 nm; and this peak at 226 nm was detected. The characteristic absorbance peak of xanthate is also found at 301 nm. Therefore, a xanthate solution has a ratio of the peak at 226 and 301 nm ($X_{226}:X_{301}$) that is characteristic of that solution. The $X_{226}:X_{301}$ ratio of the xanthate-only solution was used as the reference and compared with the ratio obtained when both NaClO and PAX were present in the solution.

The analysis of these ratios revealed that the $X_{226}:X_{301}$ ratio when NaClO is present is always higher than that characteristic of a xanthate-only solution. For instance, at pH 9 this ratio was found to be 1.01 for a PAX-NaClO solution compared to 0.57 for a PAX-only solution (cf. Table 5.1). This suggests that there is a species other than xanthate that contributes to the peak at 226 nm in the presence of NaClO. It is proposed that the formation of MTC is the likely product (Harris & Finkelstein, 1975). The formation of MTC increases with pH as evident from the increasing $X_{226}:X_{301}$ ratio (cf. Table 5.1). This is consistent with the findings by Harris & Finkelstein (1975) and Montalti et al. (1991) who have shown that the formation of MTC

increases with pH. Ultimately, it has been shown that there is a bulk consumption of xanthate in the presence of NaClO thus reducing the amount of collector available to adsorb onto sperrylite.

The other proposed explanation of the poor collector adsorption and recovery of sperrylite in the presence of NaClO is that NaClO results in “excessive” oxidation of the mineral. It should be noted that flotation generally occurs in mildly oxidizing conditions which is necessary to induce some degree of hydrophobicity in the minerals (Heyes & Trahar, 1977; Chen et al., 2014). However, excessive oxidation can be detrimental to the floatability of minerals (Senior & Trahar, 1991; Smart, 1991). In this study, no attempt is made to quantify “mild” and “excessive” oxidation as has been done, for instance by Moimane et al. (2020). In the context in which this is herein used, “excessive” oxidation may be defined as that which is detrimental to the adsorption of the collector and hydrophobicity of the mineral.

The proposition that NaClO results in “excessive” oxidation is supported by Raman spectroscopy. The Raman spectra of sperrylite in the presence of 0.01 M NaClO showed that the phonon vibrational modes that are characteristic of sperrylite were replaced by a very intense band at 250 cm^{-1} (cf. Figure 5.21). This is attributed to the oxidation of the mineral by NaClO. Density Functional Theory calculations have shown that sperrylite oxidizes through the As sites where oxidation occurs via As-O-As bridging of oxygen (Nemutudi et al., 2022). In the present study, the band appearing at 250 cm^{-1} is assigned to As-O-As vibrations. This is consistent with the Raman spectra assignment for As_2O_3 species by Bahfenne (2011).

5.4. Conclusions

This study sought to investigate the effect of pH and Eh on the floatability of sperrylite, with the aim of finding the Eh-pH conditions that are suitable for this mineral. It was shown that sperrylite floats better at acidic conditions, where the recovery increased from 22% at pH 9 to 61% at pH 3. This was shown to be due to the extent to which the collector adsorbs on sperrylite as well as the nature of the collector adsorption. The extent of PAX adsorption on sperrylite was found to be 99% of the dosed collector at pH 3 compared to only 13% at pH 9. The collector was found to be primarily adsorbed as dixanthogen at pH 3. A metal xanthate species was also found at pH 3 and it was proposed that this is co-adsorbed on the sperrylite surface along with dixanthogen. On the other hand, at pH 9, there was no evidence of these collector species on the surface of sperrylite probably due to their low adsorption.

It can be concluded that the hydrophobicity of sperrylite is governed by the amount of the collector that is adsorbed on the mineral surface, and the relative proportion of the adsorbed collector that is adsorbed as dixanthogen. Both the amount of collector adsorbed and the formation of dixanthogen can be improved by decreasing pH which also corresponds to an increase in Eh. However, it was found that it was not conducive to increase Eh chemically using, for example, NaClO since in this case there is a reaction between NaClO and PAX, and/or excessive oxidation of sperrylite occurs which ultimately reduces the ability of the collector to impart hydrophobicity to the mineral. In the presence of 0.01 M NaClO, the recovery of

Chapter 5: Effect of pH-Eh on the floatability of sperrylite

sperrylite was reduced from 61% to 21% at pH 3, thus indicating that its hydrophobicity had decreased.

This study provides important experimental evidence to support our understanding of the poor floatability of sperrylite, which may provide guidance for research into remedial steps that can be taken to improve the flotation recovery of this economically important mineral.

CHAPTER 6: Comparisons of floatability of PGE arsenides and tellurides

6. Comparisons of the floatability of PGE arsenides and tellurides

6.1. Introduction

This chapter presents the results and discussion of **Phase Three** of this work. This phase focused on comparing the floatability of PGE arsenides and tellurides, the latter of which share some similarities with PtAs_2 . This was done in order to get insights into the poor floatability of PtAs_2 compared to other PGE minerals. The other PGE minerals investigated include Pd_2As (palladoarsenide), PtTe_2 (moncheite) and PdTe_2 (merenskyite).

In order to compare the natural and collector-induced floatabilities of the minerals, microflotation test work was conducted. These tests were supplemented by determining the extent of collector adsorption onto the minerals which was measured using UV-vis spectroscopy as well as determining the nature of this collector adsorption using rest potential measurements. Furthermore, spectroscopic studies including FTIR and Raman spectroscopy were used to better understand the nature of the surface of these minerals. Finally, batch flotation studies were conducted using a complex ore to determine the flotation performance of these minerals in a more realistic scenario.

6.2. Results

6.2.1. Microflotation

Microflotation test work was conducted to investigate and compare the floatability of PtAs_2 (sperrylite), Pd_2As (palladoarsenide), PtTe_2 (moncheite) and PdTe_2 (merenskyite). These tests were conducted at pH 9 and pH 3. Figure 6.1 shows the collectorless recoveries of the different PGE minerals at pH 9. It can be seen that all the PGE minerals except PtAs_2 had relatively good natural floatability. In particular, Pd_2As was found to have a collectorless recovery of 74% at pH 9. The tellurides, on the other hand, both had similar recoveries, with a recovery of 46% for PtTe_2 and 49% for PdTe_2 .

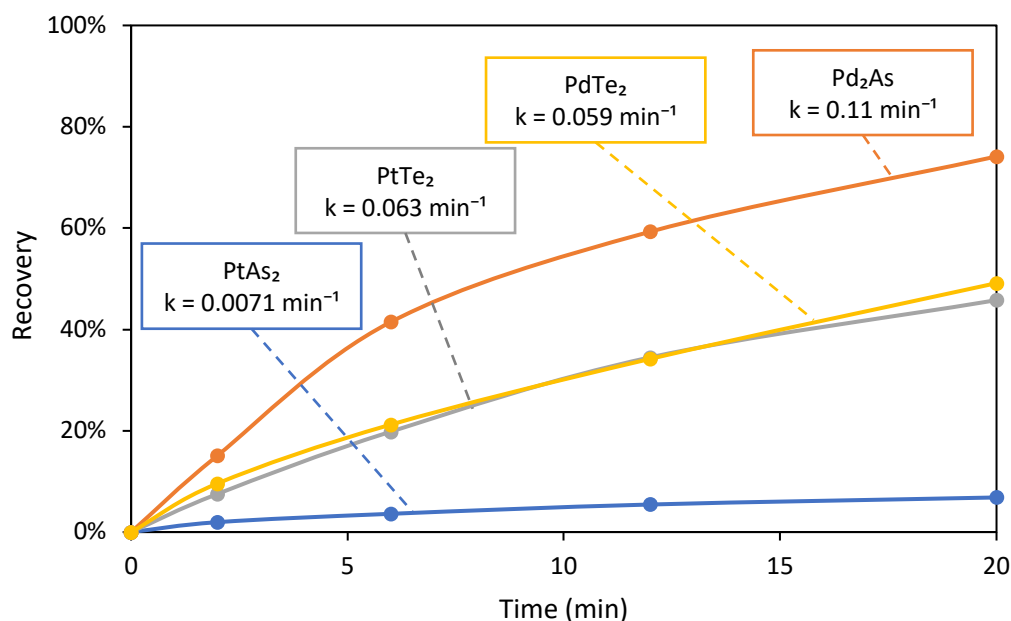


Figure 6.1: Collectorless recoveries of PtAs₂, PtTe₂, Pd₂As, and PdTe₂ at pH 9; frother at 15 ppm. RSE_{pooled} = 3.79%

Figure 6.2 shows that trends in recovery at pH 3 are similar to those observed at pH 9 except that in this case, the PGE minerals, other than PtAs₂ had greater recoveries at pH 3 than at pH 9. The collectorless recoveries increased to 81% for Pd₂As, 63% for PtTe₂, and 58% for PdTe₂. This is in contrast to PtAs₂ for which the collectorless recovery hardly changed (7% at pH 9 and 8% at pH 3). In addition to the recoveries, the flotation rates of all the minerals were greater at pH 3 as evident from the first-order rate constants. The first-order rate constants were determined using the Klimpel model.

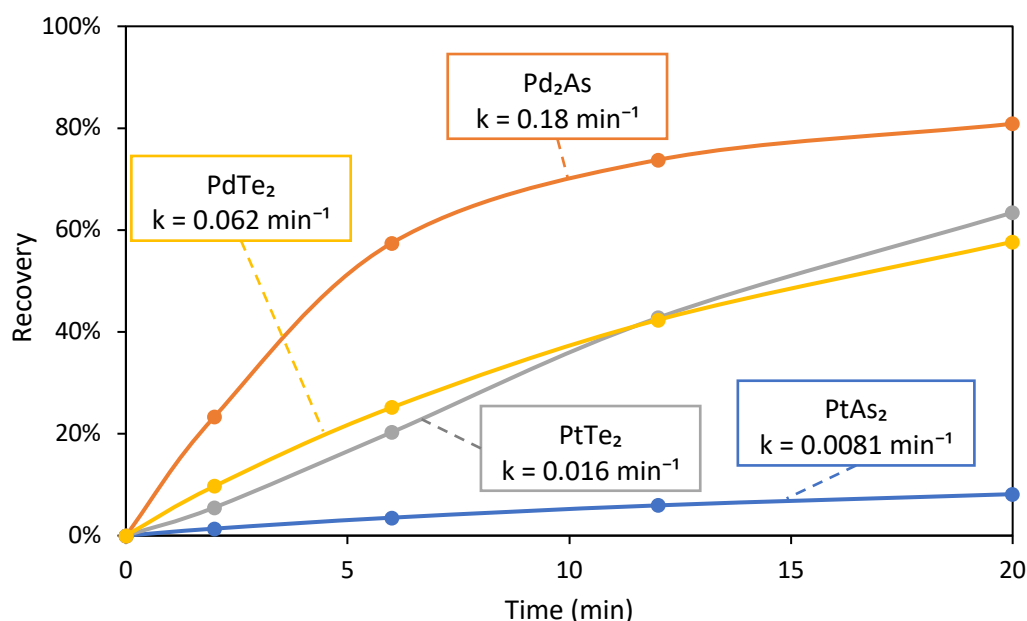


Figure 6.2: Collectorless recoveries of PtAs₂, PtTe₂, Pd₂As, and PdTe₂ at pH 3; frother at 15 ppm. RSE_{pooled} = 3.79%

Chapter 6: Comparisons of the floatability of PGE arsenides and tellurides

When studying the effect of the collector on the floatability of the minerals, it was deemed appropriate to use the same molar dosage of PAX, rather than surface coverage, despite the minerals having different BET surface areas. The dosage used was based on a molar equivalent of 5 pseudo-monolayers of PAX required for sperrylite. It was important to determine the differences in the responses of the minerals. Since the other PGE minerals investigated, namely, Pd_2As , PtTe_2 and PdTe_2 already had relatively good natural floatability, adding 5 pseudo-monolayers of collector based on their BET surface areas would have been too high to show any differences in the recoveries of these minerals. Thus, a constant molar dosage of 1.69×10^{-6} mol/g was used for all the minerals used in the microflotation tests. The equivalent number of monolayers to this collector dosage and BET surface areas of the respective minerals are shown in Table 6.1. It should also be noted that the method of using pseudo-monolayer coverage was always meant as an estimate to get the collector dosage into the correct region since BET values at such low surface areas may be somewhat variable.

Table 6.1: Number of collector monolayers equivalent to 1.69×10^{-6} mol/g dosage and BET surface areas of the minerals

Mineral	Equivalent no. of monolayers	BET surface area (m^2/g)
PtAs_2 (Sperrylite)	5.0	0.06
Pd_2As (Palladoarsenide)	3.1	0.18
PtTe_2 (Moncheite)	2.4	0.14
PdTe_2 (Merenskyite)	1.9	0.11

The recoveries of the PGE minerals in the presence of PAX at pH 9 and 3 are shown in Figure 6.3 and Figure 6.4, respectively. In the presence of PAX at pH 9, the recoveries obtained were in the order: Pd_2As (95%) > PtTe_2 (81%) > PdTe_2 (81%) PtAs_2 (22%). In general, the tellurides had a greater response to the addition of PAX compared to the arsenides at pH 9, relative to their respective collectorless recoveries.

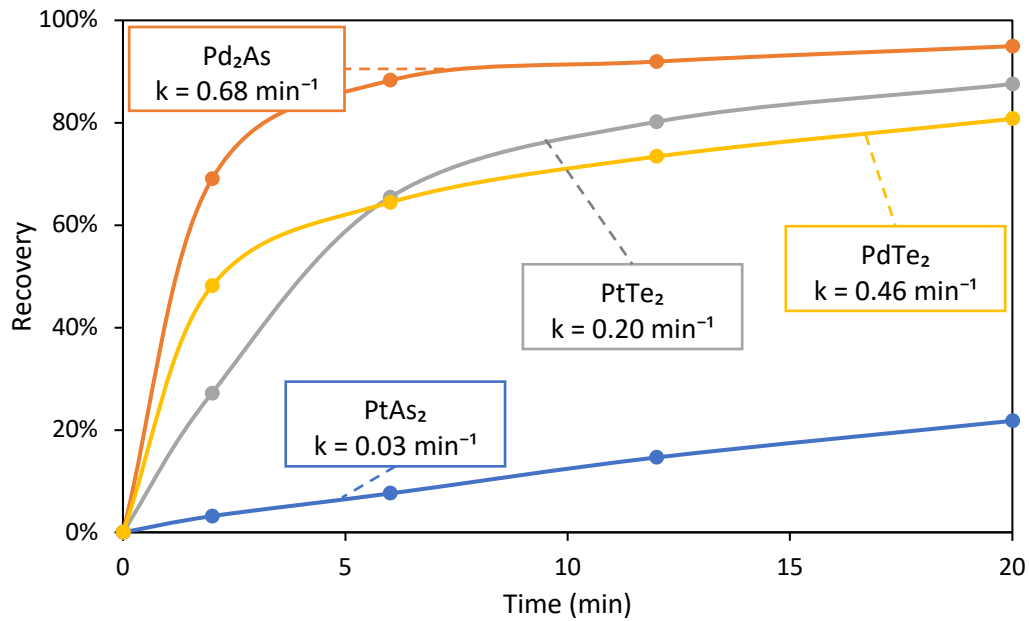


Figure 6.3: Recoveries of PtAs₂, PtTe₂, Pd₂As, and PdTe₂ at pH 9 with 1.69×10^{-6} M PAX collector; frother at 15 ppm. $RSE_{\text{pooled}} = 3.79\%$

Lowering the pH to pH 3 in the presence of PAX improved the recoveries of all the minerals, except for Pd₂As whose recovery decreased from 95% at pH 9 to 85% at pH 3. In contrast, PtAs₂ had the greatest improvement with the change in pH, where its recovery increased from 22% at pH 9 to 61% at pH 3, almost a three-fold improvement. It can thus be seen that while Pd₂As and PtAs₂ are both PGE arsenides, their behaviour in terms of floatability is quite different. The two PGE tellurides, on the other hand, generally had fairly similar final recoveries. However, their rates of flotation were found to be different with PdTe₂ always having higher rates of flotation compared to PtTe₂.

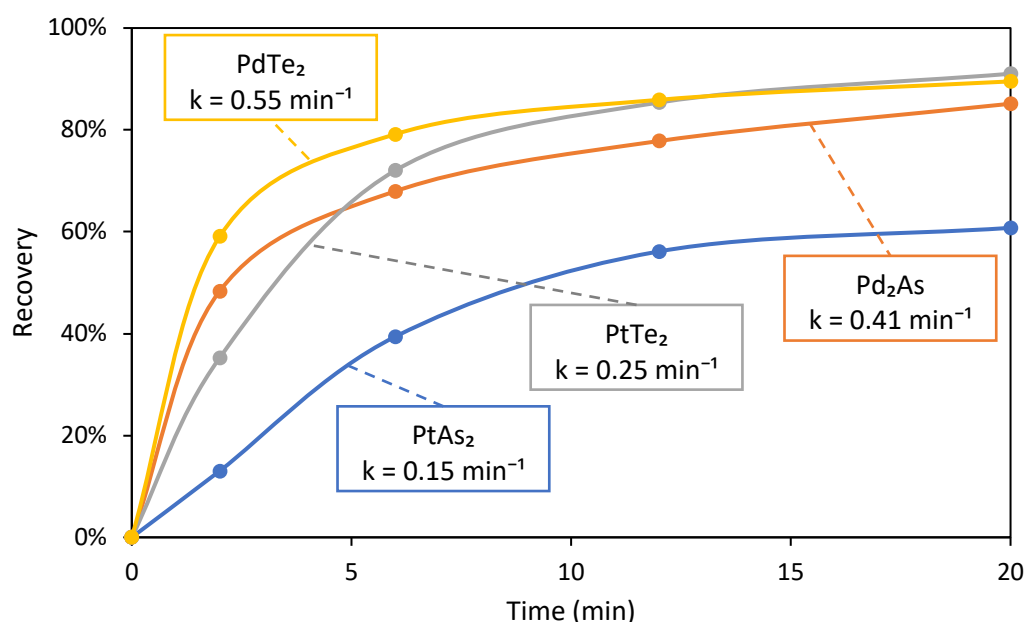


Figure 6.4: Recoveries of PtAs₂, PtTe₂, Pd₂As, and PdTe₂ at pH 3 with 1.69×10^{-6} M PAX collector; frother at 15 ppm. $RSE_{\text{pooled}} = 3.79\%$

These results are summarised in terms of the effect of collector addition, as well as the effect of changing pH in Table 6.2 where the ‘Effect of collector’ is the change in recovery between that without the collector and that with the collector present at constant pH, and the ‘Effect of pH with PAX’ is the change in the collector-assisted recovery between pH 9 and 3. The PGE tellurides have the greatest response to the addition of PAX compared to the arsenides, except at pH 3 where PtAs₂ had the greatest response. Furthermore, lowering pH seems to benefit PtAs₂ much more than the other PGE minerals.

Table 6.2: Summary of the microflotation recoveries of the PGE arsenides and tellurides at pH 9 and 3, with and without PAX collector

Mineral	pH 9			pH 3			Effect of pH with PAX
	No collector	With PAX	Effect of collector	No collector	With PAX	Effect of collector	
PtAs ₂	7%	22%	15%	8%	61%	53%	39%
Pd ₂ As	74%	95%	21%	81%	85%	4%	-10%
PtTe ₂	46%	88%	42%	63%	91%	28%	3%
PdTe ₂	49%	81%	32%	58%	90%	32%	9%

6.2.2. Rest potential measurements of PGE arsenides and tellurides

Rest potential measurements of the different PGE arsenides and tellurides were conducted at pH 3, 5, 7, and 9. However, the full rest potential profiles are only shown for the conditions at pH 3 and 9 in this section (see APPENDIX D for the full details of rest potential profiles at pH 5 and 7). The effect of collector addition on the rest potentials of the minerals was also investigated.

Figure 6.5 shows the rest potential profiles of the PGE minerals at pH 9 where it can be seen that the most anodic rest potential was that of PtAs_2 (285 mV v SHE), followed by PdTe_2 (246 mV vs SHE), PtTe_2 (237 mV vs SHE), and then Pd_2As (153 mV vs SHE). This is indicated by the region before 600 seconds in Figure 6.5. The two PGE tellurides had similar initial rest potentials, which may indicate similar oxidation behaviour in the absence of a collector. The addition of PAX at 600 seconds changed the potential of the PGE tellurides to a greater extent compared to the PGE arsenides, thus indicating a greater interaction of these minerals with PAX.

The final rest potential of all the minerals, except PdTe_2 , in a solution of PAX lay above the equilibrium potential of the xanthate/dixanthogen couple which suggests that the formation of dixanthogen is thermodynamically favoured on the surface of these minerals. On the other hand, the rest potential of PdTe_2 sharply decreased upon collector addition and subsequently increased to a final value below the xanthate/dixanthogen equilibrium potential. This suggests that the formation of metal xanthate, as opposed to dixanthogen, is thermodynamically favoured on the surface of PdTe_2 . Interestingly, it was found that Pd_2As behaved very similarly to PtAs_2 with regard to the change in potential upon collector addition. Both minerals had a minimal change in potential, thus indicating limited interaction with the collector, even though the flotation response was much greater for Pd_2As .

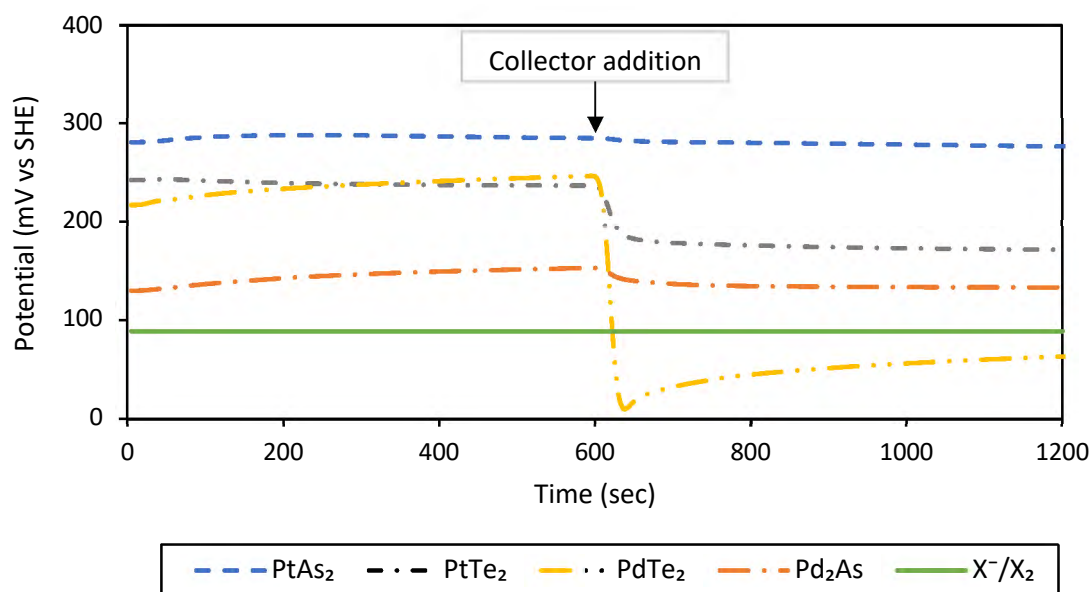


Figure 6.5: Rest potential profiles of PtAs₂, PtTe₂, Pd₂As and PdTe₂ at pH 9; 6.24x10⁻⁴ M PAX added at 600 seconds

At pH 3, the rest potential measurements of the minerals obtained are shown in Figure 6.6. At the lower pH, the initial rest potentials of all the minerals became more anodic compared to those at pH 9. The most anodic rest potential at pH 3 was that of PtTe₂, followed by PdTe₂, then PtAs₂ and Pd₂As. The interaction between PAX and the minerals, indicated by the change in potential upon collector addition, was found to be greater for all the minerals compared to that at pH 9. Furthermore, the final rest potential of all the minerals was above the equilibrium potential of the xanthate/dixanthogen couple. In particular, PdTe₂ had a final rest potential above the xanthate/dixanthogen equilibrium potential, unlike at pH 9. Therefore, different collector species may be responsible for the flotation of PdTe₂ depending on the pH.

Chapter 6: Comparisons of the floatability of PGE arsenides and tellurides

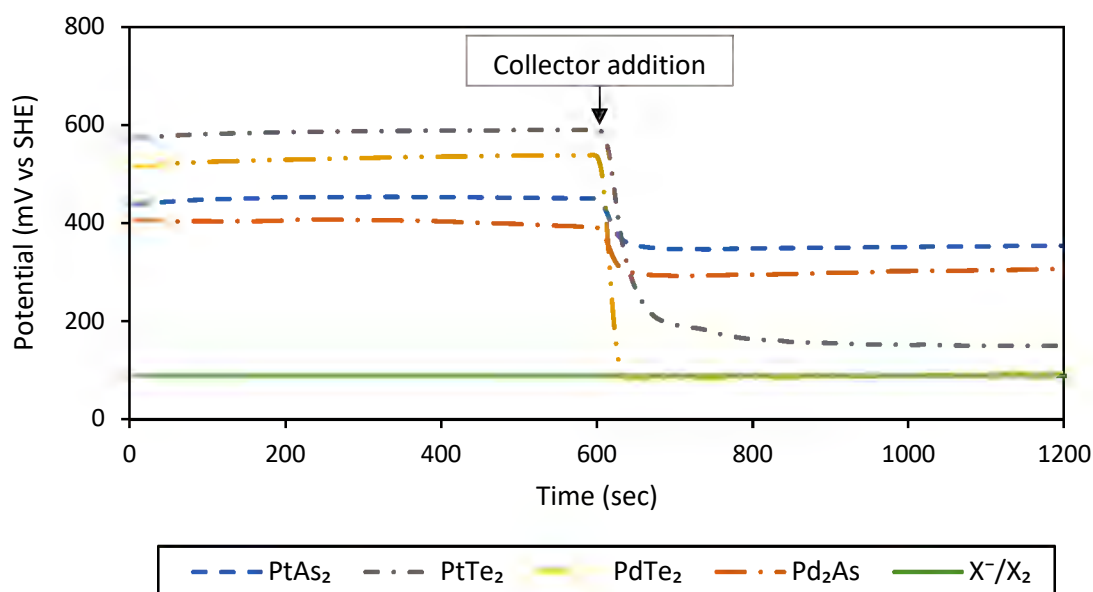


Figure 6.6: Rest potential profiles of PtAs₂, PtTe₂, Pd₂As and PdTe₂ at pH 3; 6.24×10^{-4} M PAX added at 600 seconds

The initial rest potential and change in potential of the mineral upon collector addition are summarised in Figure 6.7. In general, the initial rest potentials (i.e. without collector) of the PGE tellurides had a greater response to changes in pH compared to those of the PGE arsenides. The initial rest potential of PtAs₂ as a function of pH is a relatively flat response, meaning that pH had little effect on the redox potential of this mineral. Furthermore, these results have shown that the PGE tellurides had a greater interaction with PAX as shown by the change in potential upon collector addition for these minerals.

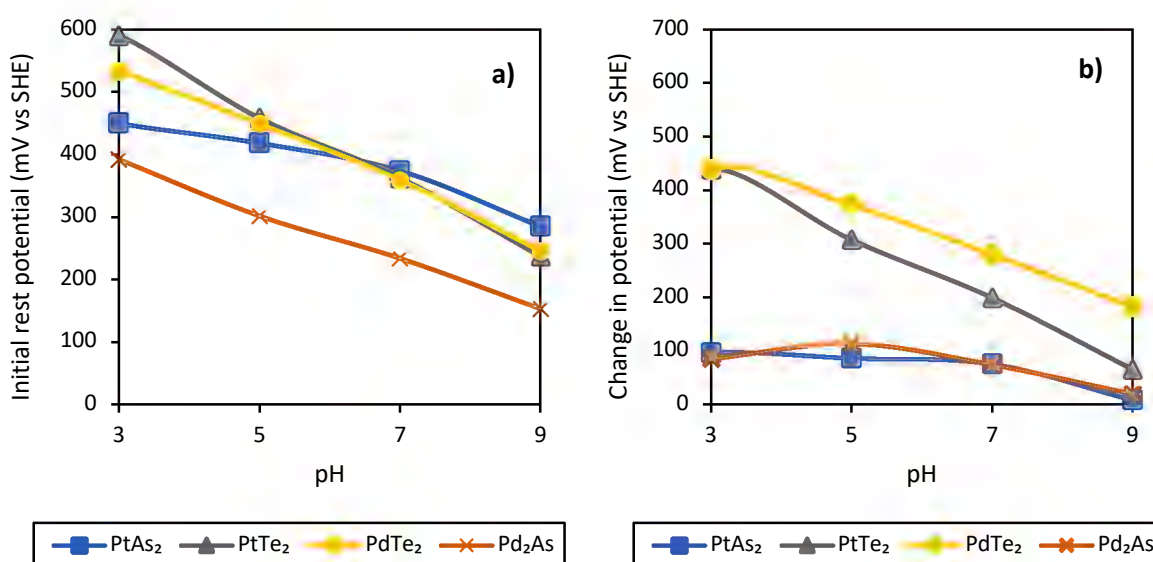


Figure 6.7: a) Initial rest potential b) change in potential upon collector addition; of PtAs₂, PtTe₂, Pd₂As and PdTe₂ as a function of pH

6.2.3. The extent of collector adsorption

UV-vis spectroscopy tests of solutions before and after reagent contact with the minerals were carried out to determine the amount of collector that adsorbs onto the different PGE minerals. These tests were carried out at pH 9 and 3, using 5.79×10^{-6} mol/g of PAX for all the minerals. This concentration is based on a dosage equivalent to 5 pseudo-monolayer surface coverage of PtAs_2 .

Figure 6.8 shows that essentially the total amount of the initial collector added was adsorbed onto the surface of all the minerals both at pH 9 and 3, except for PtAs_2 . For PtAs_2 , it was only at pH 3 where 99% of the dosed collector was adsorbed. These results show that while the adsorption of the xanthate collector may be poor for PtAs_2 at pH 9, the typical operating pH, this is not the case for the other PGE minerals. Despite the poor electrochemical response of Pd_2As (cf. Figure 6.7b), there was a high extent of collector adsorption on this mineral.

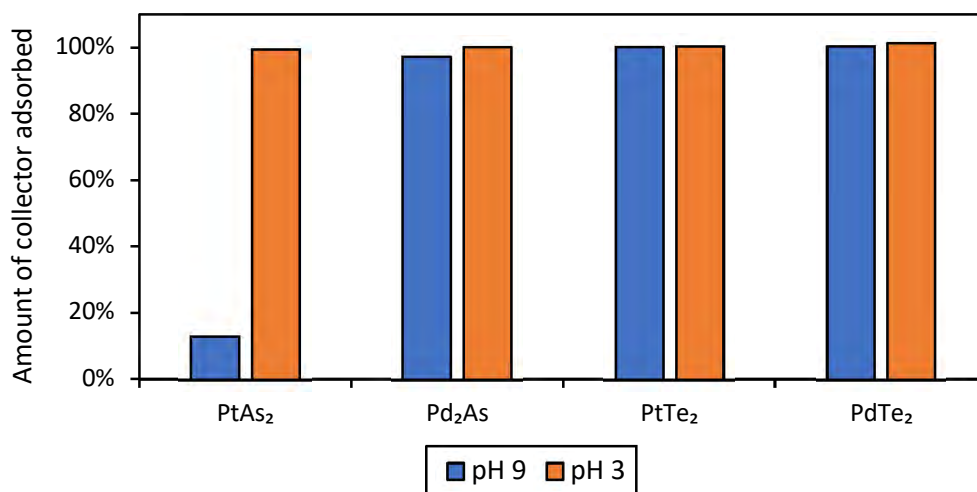


Figure 6.8: Amount of PAX adsorbed onto PtAs_2 , Pd_2As , PtTe_2 , and PdTe_2 at pH 9 and; with an initial PAX concentration = 5.79×10^{-6} mol/g

6.2.4. Surface characterization

6.2.4.1. Zeta potential measurements

Zeta potential measurements were used as a proxy for measuring the surface charge of the minerals without and with 5×10^{-4} M PAX collector across a pH range from 2 to 12. The results obtained are presented in Figure 6.9 to Figure 6.12 for the different minerals investigated. In general, all the minerals were found to be negatively charged both with and without collector addition, with the surface charge becoming more negative with increasing pH.

PtAs_2 , Pd_2As , and PtTe_2 were found to have a similar surface charge in the absence of a collector, with their zeta potentials ranging from 0 to -29 mV in the pH range from 2 to 12. On the other hand, PdTe_2 had the most negative surface charge with zeta potentials ranging from -9 to -43 mV in the pH range from 2 to 12.

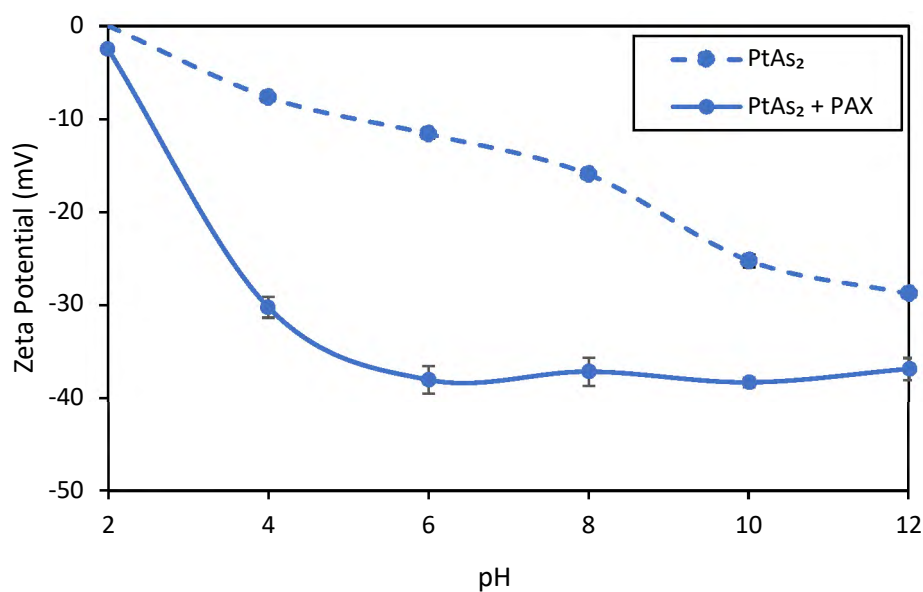


Figure 6.9: Zeta potential measurements of PtAs₂ without and with 5×10^{-4} M PAX, using 0.12 M KCl as a background electrolyte

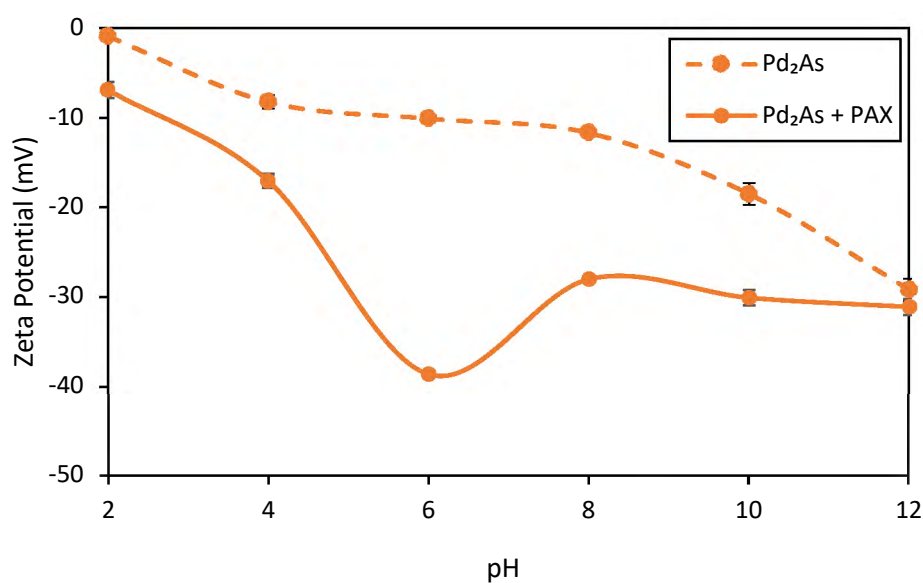


Figure 6.10: Zeta potential measurements of Pd₂As without and with 5×10^{-4} M PAX, using 0.12 M KCl as a background electrolyte

When the minerals were treated with PAX, the zeta potentials of the PGE arsenides and PtTe₂ shifted to more negative zeta potentials. This suggests either an increase in negatively charged species or a decrease in positively charged species on the surface of these minerals when the minerals are treated with PAX. The shift in zeta potential is more pronounced between pH 4 and 8 for these minerals.

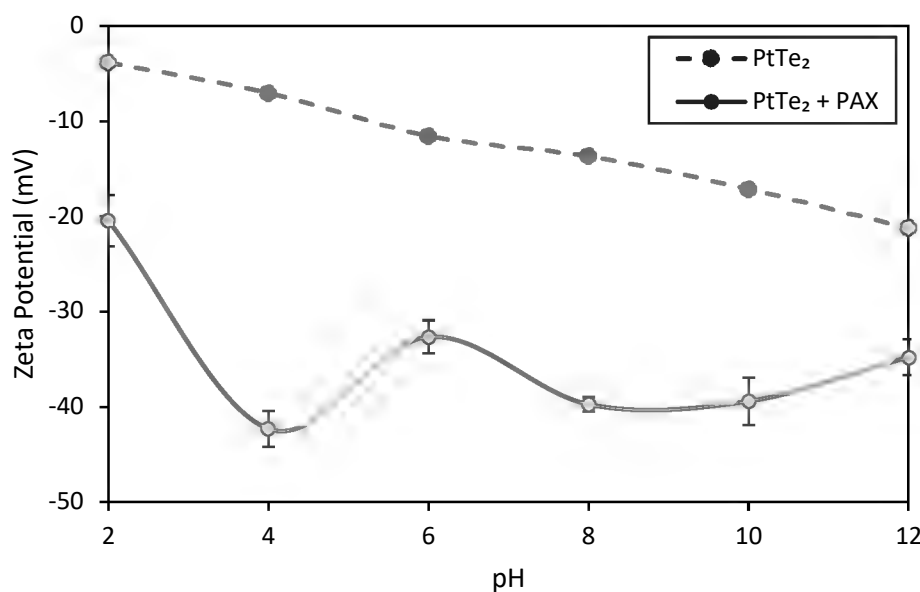


Figure 6.11: Zeta potential measurements of PtTe₂ without and with 5×10^{-4} M PAX, using 0.12 M KCl as a background electrolyte

The response of the surface charge of PdTe₂ when treated with PAX was found to be quite different compared to that of the other three PGE minerals. At pH's above 8, the zeta potential of the collector-treated PdTe₂ was found to shift to less negative values relative to the untreated surface as shown in Figure 6.12. For instance, at pH 10 the zeta potential of this mineral was found to be -37 mV without collector compared to -26 mV in the presence of PAX.

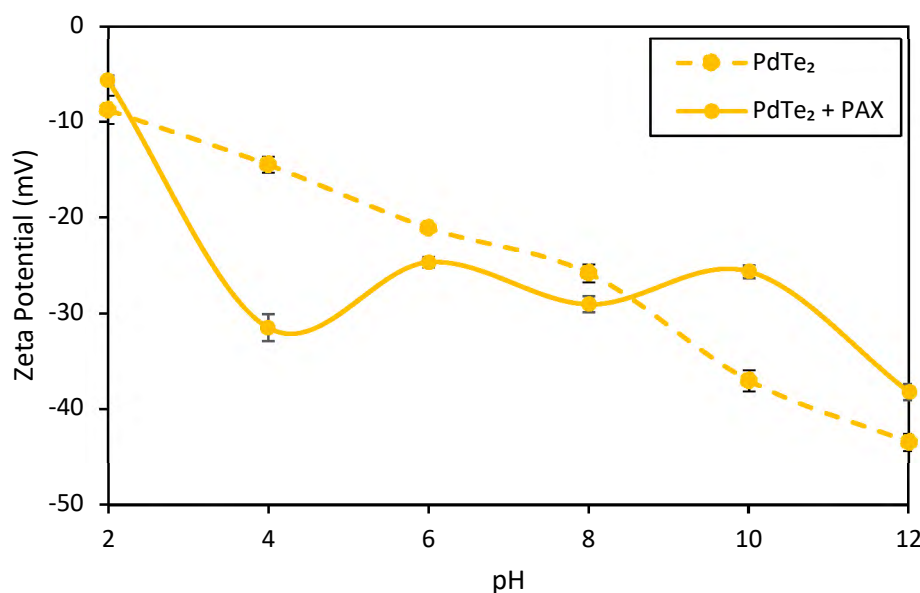


Figure 6.12: Zeta potential measurements of PdTe₂ without and with 5×10^{-4} M PAX, using 0.12 M KCl as a background electrolyte

In summary, the zeta potential measurements showed similarities in the surface charge of the PGE arsenides and PtTe₂. PdTe₂ had the most negative zeta potentials compared to the other minerals. These comparisons are shown in Figure 6.13a. The most striking difference in the

presence of PAX was between the zeta potentials of PdTe₂ compared to those of the other three minerals, where it was found that the zeta potentials of this mineral shifted to less negative values when treated with PAX at pH values above 8.

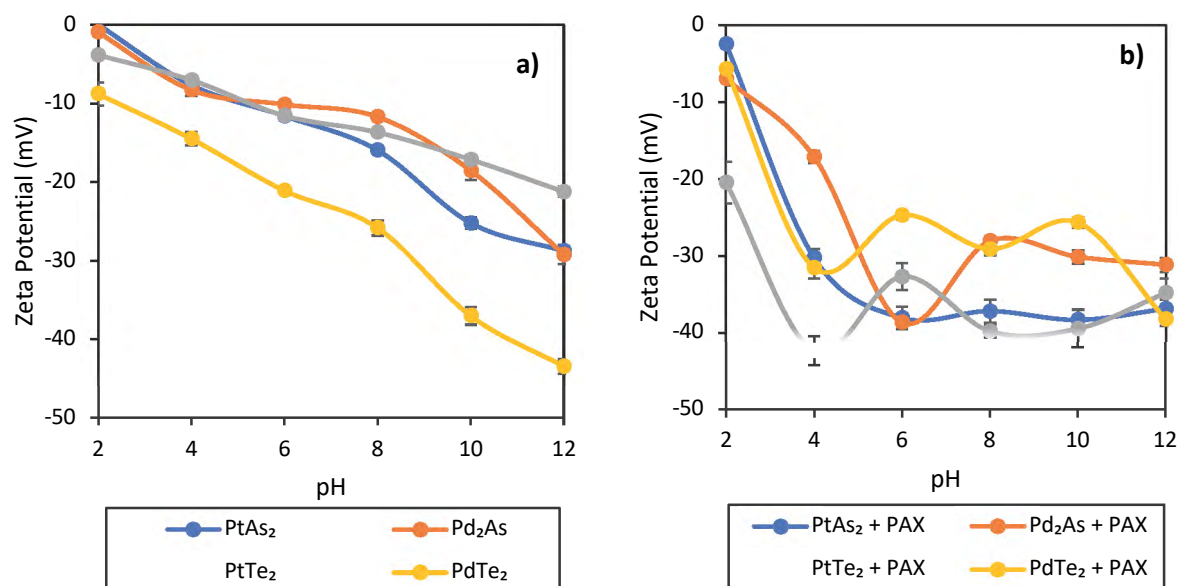


Figure 6.13: Zeta potential measurements of PtAs₂, Pd₂As, PtTe₂ and PdTe₂ a) without PAX b) with 5x10⁻⁴ M PAX

6.2.4.2. Fourier Transform Infrared Spectroscopy

FTIR studies were conducted to compare the nature of the surface of the minerals in the absence of a collector. The spectra obtained at pH 9 and 3 are shown in Figure 6.14 (PtAs₂), Figure 6.15 (Pd₂As), Figure 6.16 (PtTe₂) and Figure 6.17 (PdTe₂). Compared to the other minerals it can be observed that PtAs₂ showed the most activity on its surface as evident from the number of peaks or bands observed in the spectra.

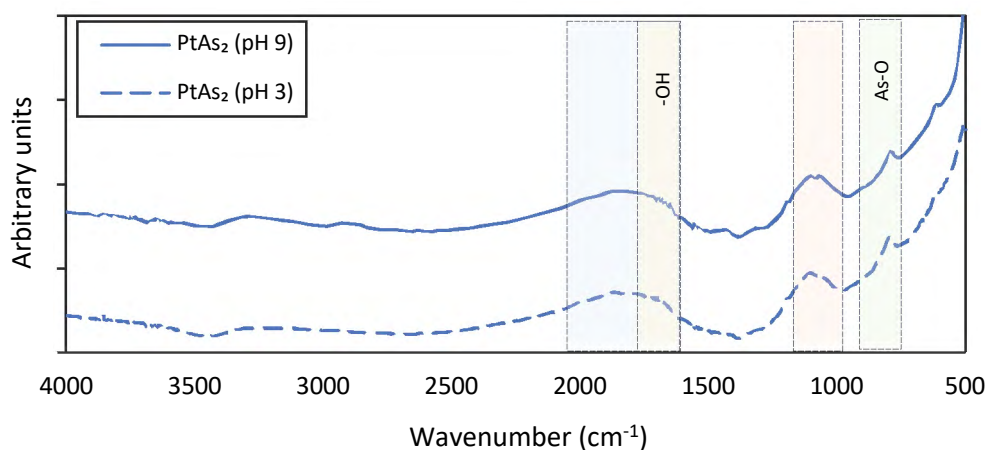


Figure 6.14: FTIR spectra of PtAs₂ conditioned at pH 9 and 3

The band at 797 cm^{-1} can be assigned to As-O vibrations (Cowen et al., 2008; Ait-khouia et al., 2023). OH stretching and bending vibrations are known to occur at $3200\text{--}3800\text{ cm}^{-1}$ and 1630 cm^{-1} , respectively (Coker et al., 1982; Vrancken et al., 2017; Amari et al., 2021). Therefore, there may be OH bending vibrations as evident from the peak at $1600\text{--}2000\text{ cm}^{-1}$ on PtAs_2 . Furthermore, the OH vibrations in the region between $1600\text{--}2000\text{ cm}^{-1}$ may be from hydrogen-bonded molecular water, rather than free OH^- ions, since these vibrations appear with the same intensity both in alkaline and acidic conditions. Given the broad nature of this peak, it is likely that there are other interactions besides OH interactions occurring in this region. It is interesting to note that these vibrations, which include OH interactions, only appeared on the surface of PtAs_2 and were not observed on the spectra of the other minerals. This suggests that sperrylite has a greater affinity with water and may be more naturally hydrophilic than the other PGE minerals investigated. The presence of OH interactions was also shown by Raman spectroscopy (see section 6.2.4.3).

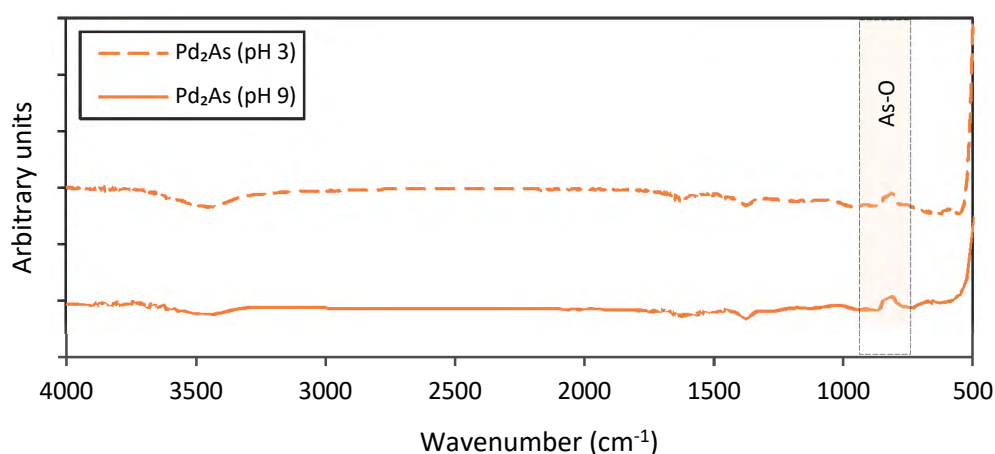


Figure 6.15: FTIR spectra of Pd_2As conditioned at pH 9 and 3

For the two PGE tellurides, two vibrational bands were observed, at $\sim 780\text{ cm}^{-1}$ and $\sim 690\text{ cm}^{-1}$, respectively. These bands have been assigned to Te-O stretching vibrations (Arnaudov et al., 1982; Carotenuto et al., 2015; Amari et al., 2021). For the PtTe_2 mineral, these bands only appeared at pH 3 and not at pH 9 (cf. Figure 6.16). On the other hand, the Te-O vibrations appeared both at pH 3 and 9 on PdTe_2 (cf. Figure 6.17) with a stronger intensity compared to those on PtTe_2 . In general, the FTIR spectra of all the minerals investigated did not show any differences between the surfaces conditioned at pH 9 compared to pH 3; the exception being PtTe_2 .

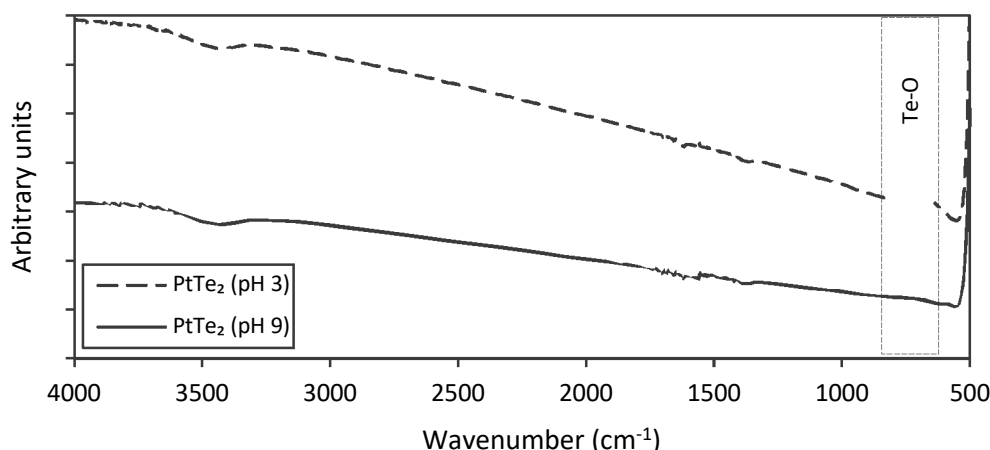


Figure 6.16: FTIR spectra of PtTe₂ conditioned at pH 9 and 3

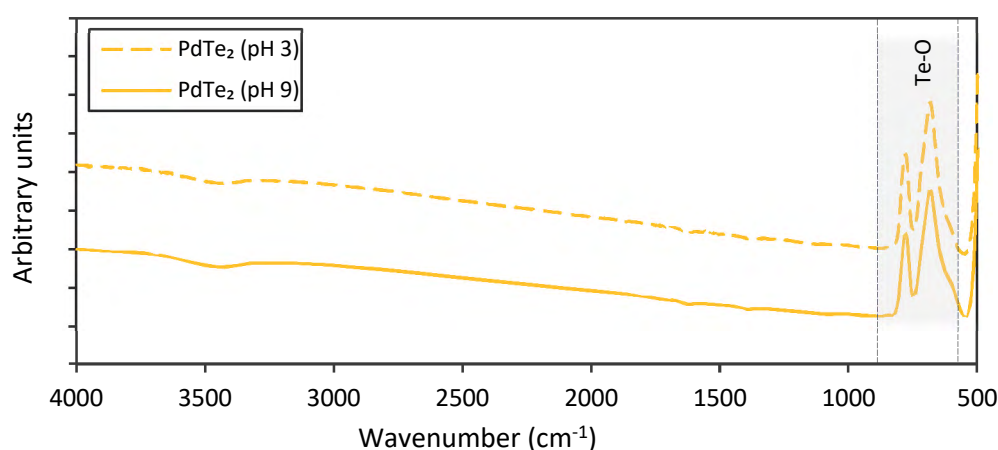


Figure 6.17: FTIR spectra of PdTe₂ conditioned at pH 9 and 3

6.2.4.3. Raman spectroscopy

In order to complement the FTIR studies, Raman spectroscopy was used to provide valuable information on the nature of the surface of the minerals in the absence of a collector. The spectra obtained at pH 9 are shown in Figure 6.18 (PtAs₂) Figure 6.19 (Pd₂As), Figure 6.20 (PtTe₂) and Figure 6.21 (PdTe₂). It should be noted that the results for each of the minerals include three sets of spectra, viz. *in-situ* spectra taken at 1-minute intervals for 10 minutes, spectra of the dry mineral ('as is') and spectra of the reference solution (i.e. solution without the mineral).

The most noteworthy difference between the spectra of these minerals is the presence of the OH vibrations at 3200-3600 cm⁻¹. These vibrations were found to have a stronger intensity only on PtAs₂ (cf. Figure 6.18). On the other minerals, there was a minimal presence of OH vibrations. This suggests that PtAs₂ has a stronger affinity for OH interactions, which is consistent with the FTIR studies (cf. Figure 6.14).

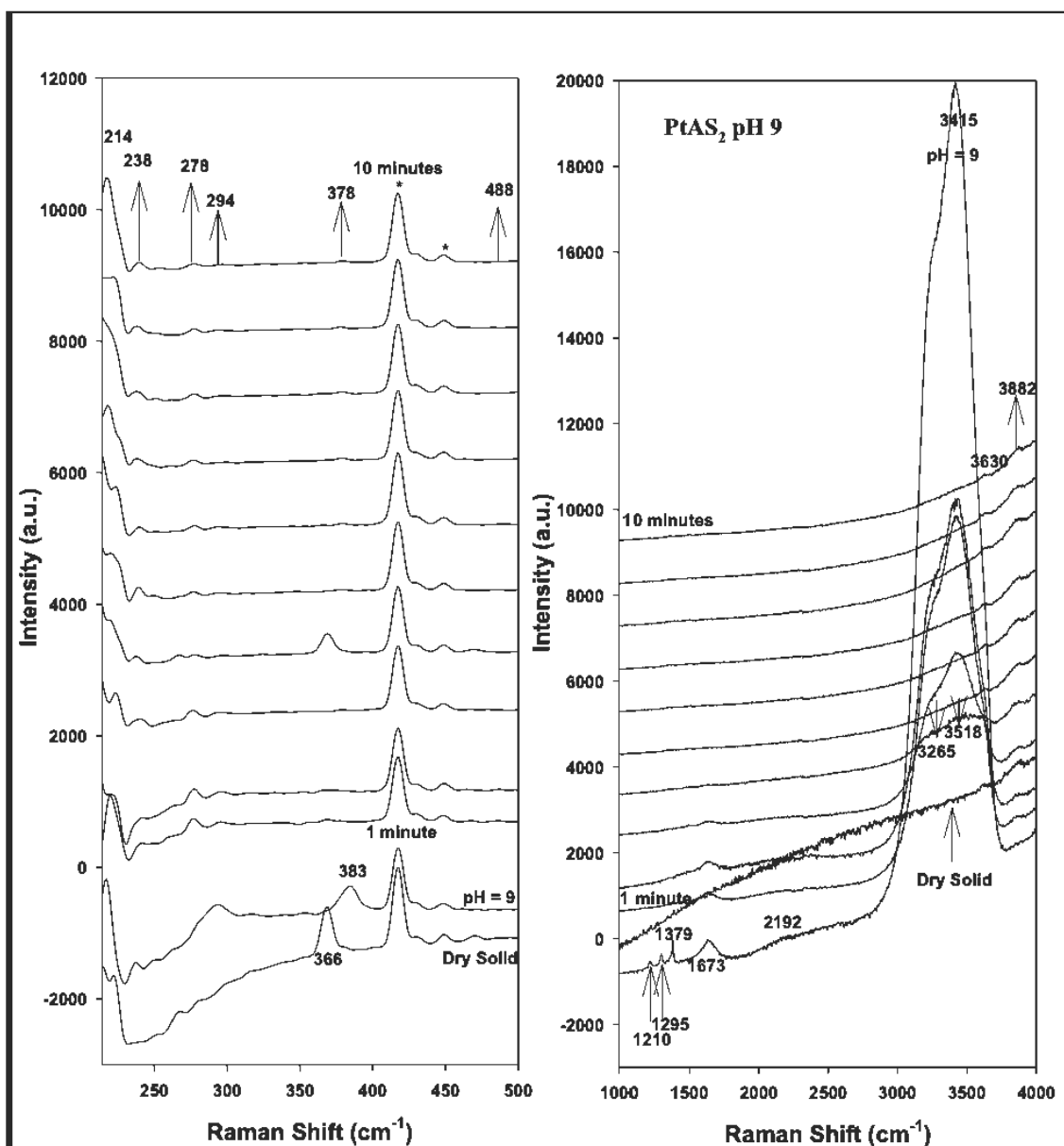


Figure 6.18: in-situ Raman spectra of PtAs₂ conditioned at pH 9 from 1 minute to 10 minutes. Spectra of dry PtAs₂ ('as is') and reference solution are included at the bottom and second-from-bottom, respectively. NB: The left and right diagrams represent different ranges on the electromagnetic spectrum

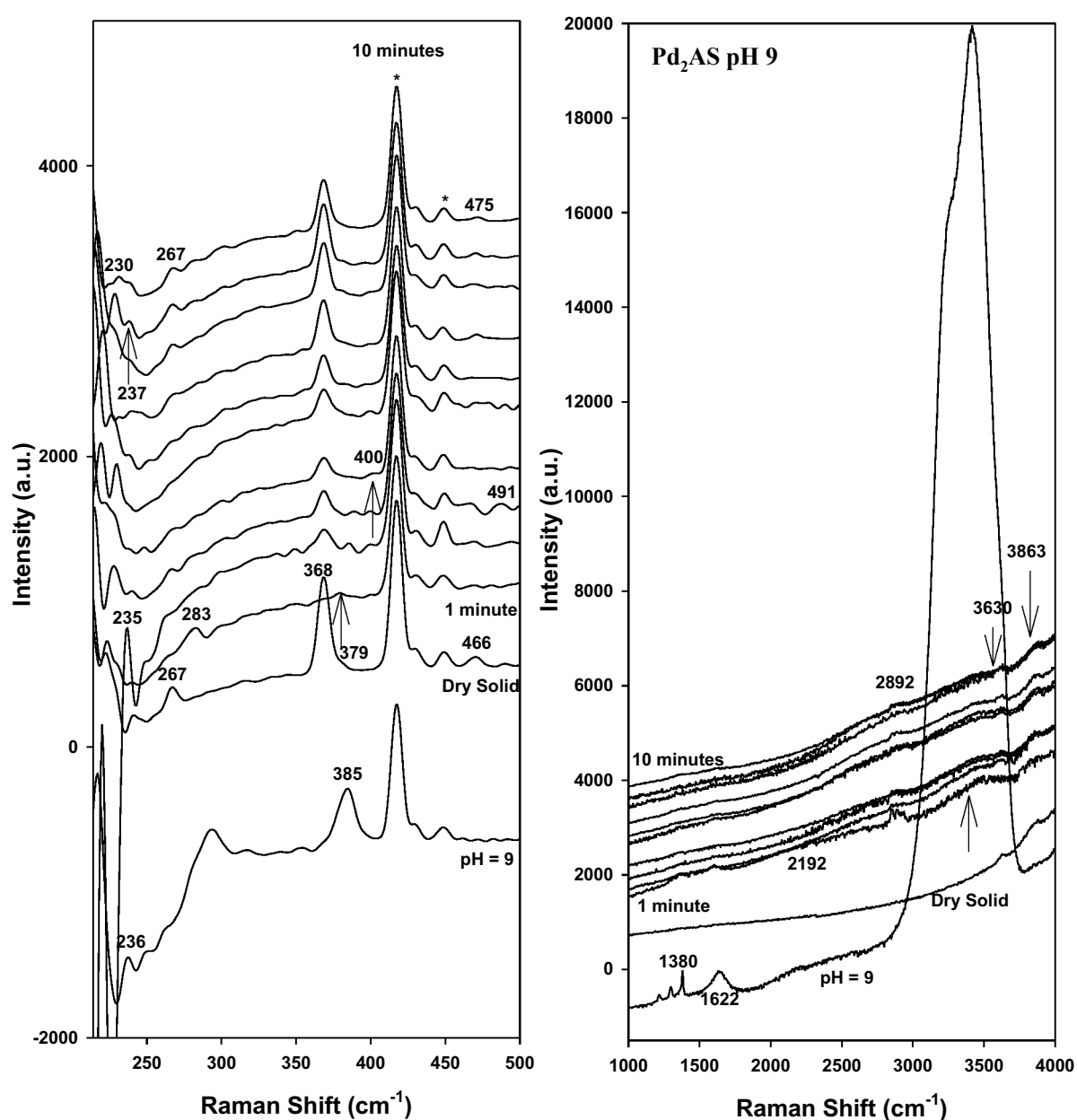


Figure 6.19: in-situ Raman spectra of Pd_2As conditioned at pH 9 from 1 minute to 10 minutes. Spectra of dry Pd_2As ('as is') and reference solution are included at the bottom and second-from-bottom, respectively. NB: The left and right diagrams represent different ranges on the electromagnetic spectrum

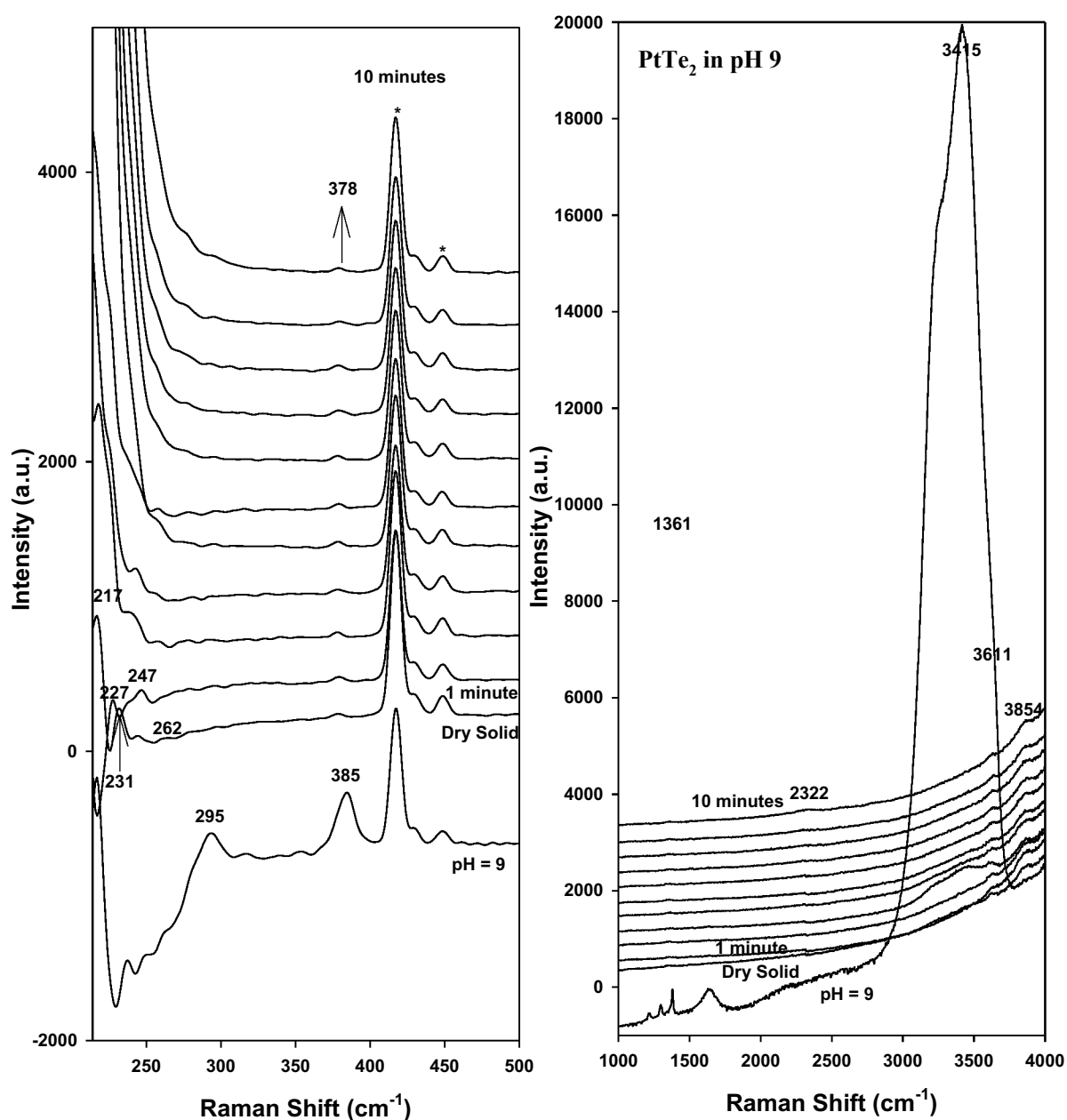


Figure 6.20: in-situ Raman spectra of PtTe₂ conditioned at pH 9 from 1 minute to 10 minutes. Spectra of dry PtTe₂ ('as is') and reference solution are included at the bottom and second-from-bottom, respectively. NB: The left and right diagrams represent different ranges on the electromagnetic spectrum

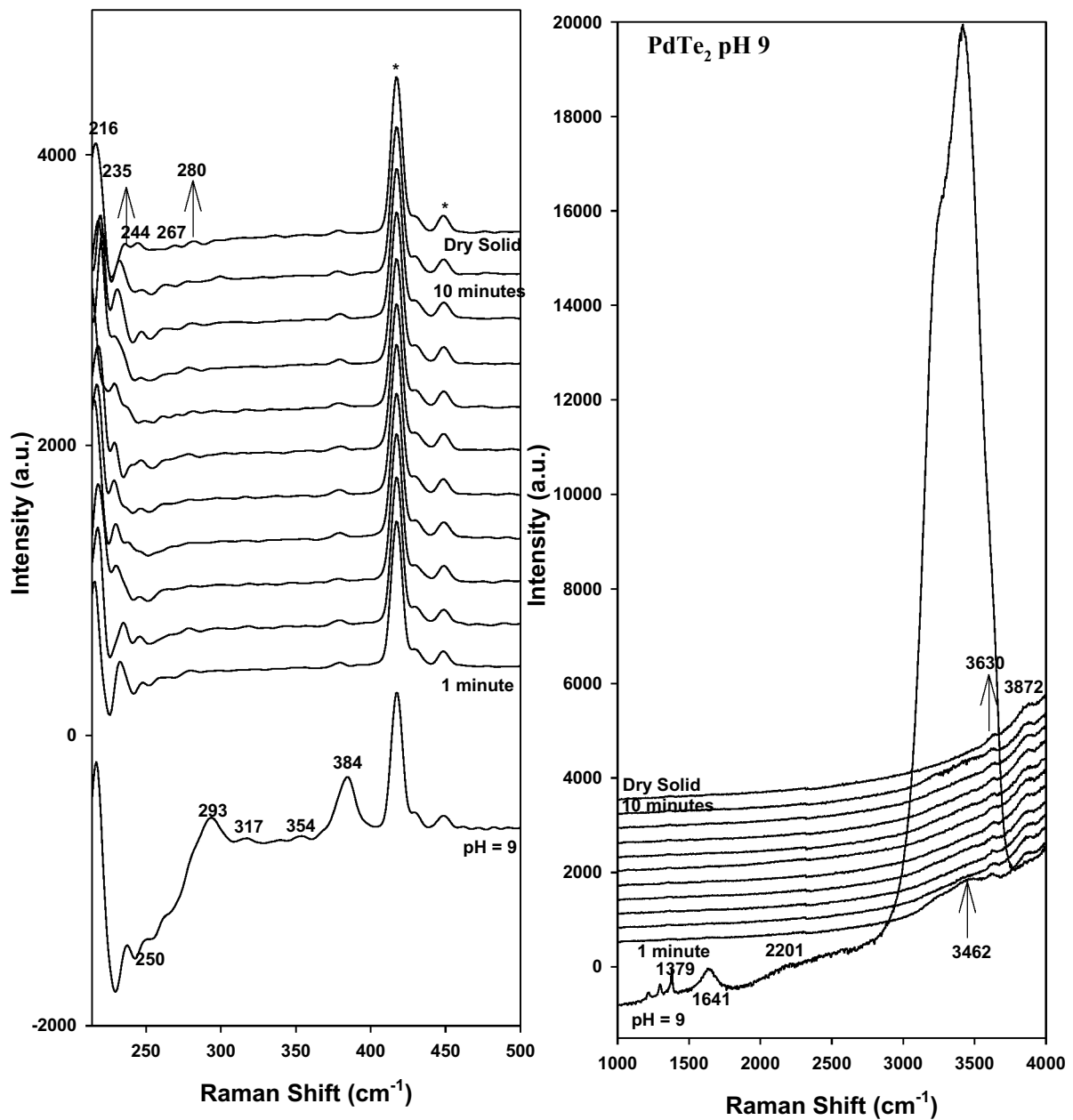


Figure 6.21: in-situ Raman spectra of PdTe₂ conditioned at pH 9 from 1 minute to 10 minutes. Spectra of dry PdTe₂ ('as is') and reference solution are included at the bottom and second-from-bottom, respectively. NB: The left and right diagrams represent different ranges on the electromagnetic spectrum

6.2.5. Batch Flotation

Batch flotation tests were conducted to determine the applicability of pH reduction in a more realistic scenario where a complex ore is used. Three tests were conducted, viz.:

- 1) Case 1: pH 3
- 2) Case 2: Two-stage flotation (stage 1 = pH 9, stage 2 = pH 3)

Chapter 6: Comparisons of the floatability of PGE arsenides and tellurides

The experimental set-up used for these tests has been described in detail in section 3.10.2. The tests compared the flotation performance obtained at pH 9 and 3. The tests also compared the performance obtained based on two different circuit configurations. The pH was adjusted from the natural pH (i.e. pH 9) to pH 3 either at the incoming rougher feed stream (Case 1) or on the tailings of the first rougher stage (Case 2).

The Grade-Recovery curves of Pt and Pd are shown in Figure 6.22 and Figure 6.23, respectively. Pt and Pd were used to track the flotation performance of the overall Pt and Pd minerals. These results show that changing the pH of the incoming rougher feed to pH 3 improved both the grades and recoveries of the Pt and Pd minerals. This can be seen when comparing the Pt and Pd recoveries in Case 1 and Case 2 – Stage 1. The final Pt recoveries increased from 58% at pH 9 to 79% at pH 3 while those of Pd increased from 78% at pH 9 to 86% at pH 3. Similarly, the final grades of these minerals increased from 2.6 to 3.4 g/t for Pt and 5.1 to 5.7 g/t for Pd when the pH was decreased from pH 9 to 3. These results show that the Pt minerals had a greater response to the change in pH compared to the Pd minerals, even though the Pd minerals had a better flotation performance overall.

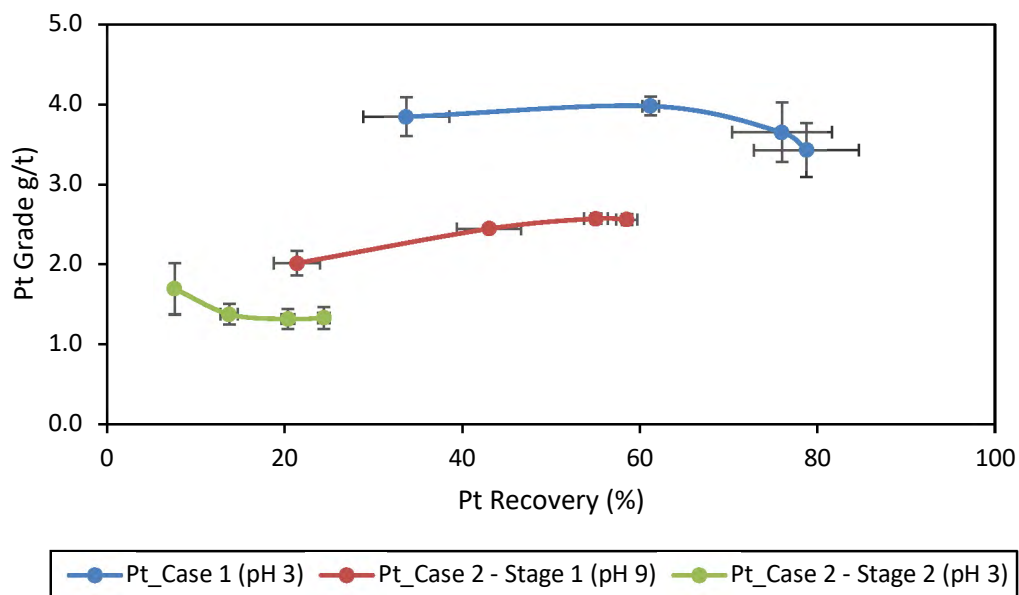


Figure 6.22: Grade-Recovery curves of Pt from batch flotation tests comparing the flotation performance at the natural pH of 9 and adjusted pH of 3

Chapter 6: Comparisons of the floatability of PGE arsenides and tellurides

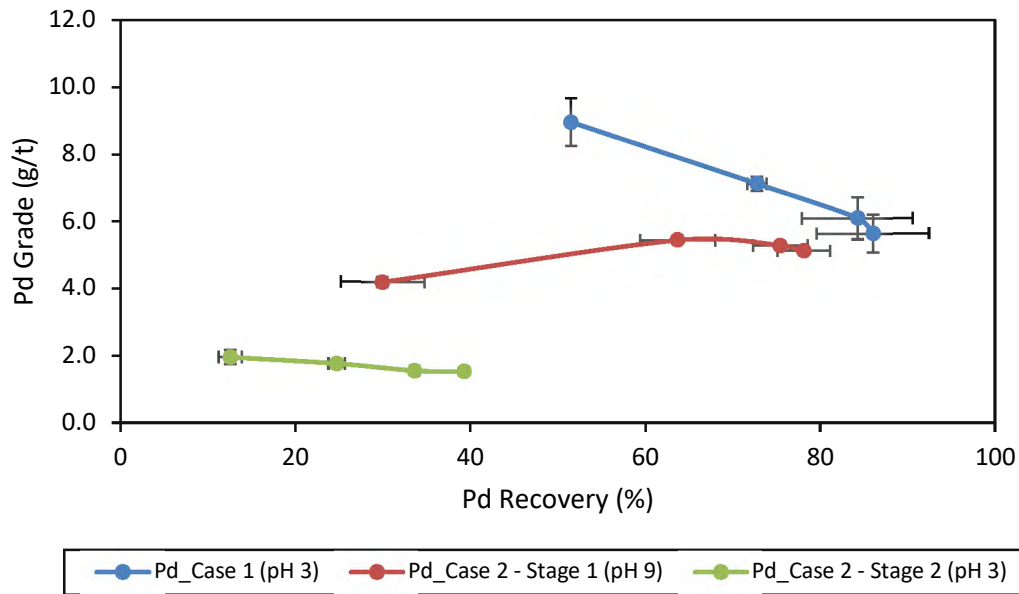


Figure 6.23: Grade-Recovery curves of Pd from batch flotation tests comparing the flotation performance at the natural pH of 9 and adjusted pH of 3

An analysis of the flotation kinetics showed that there are differences in the flotation performance at pH 9 compared to pH 3. The flotation rates of the Pt and Pd minerals were found to be significantly better at pH 3. The flotation rates, which were determined using the Klimpel model, are shown in Table 6.3. The flotation recoveries as a function of residence time used to determine the flotation kinetics are presented in APPENDIX E. In general, these results have shown that the Pd minerals had a better flotation performance compared to that of the Pt minerals.

Table 6.3: Pt, Pd, As, and Te flotation rate constants for flotation tests conducted at pH 9 and 3

Test	Pt		Pd		As		Te	
	R_{inf} (%)	k (min^{-1})	R_{inf} (%)	k (min^{-1})	R_{inf} (%)	k (min^{-1})	R_{inf} (%)	k (min^{-1})
Case 1 (pH 3)	78.9	0.26	83.7	0.44	58.7	0.33	84.0	0.31
Case 2 - Stage 1 (pH 9)	59.1	0.22	79.1	0.26	43.4	0.25	75.4	0.22
Case 2 - Stage 2 (pH 3)	25.6	0.14	40.0	0.17	16.7	0.11	34.8	0.11

To determine the flotation performance of the PGE arsenides and tellurides specifically, their performance was tracked using As and Te, respectively. In the Platreef ore, As and Te occur separately and are predominantly present in the form of PGE arsenides and tellurides (Shamaila & O'Connor, 2008; Nyaruwata, 2022). Therefore, the assays of these elements can be used to infer the flotation performance of the PGE arsenides and tellurides.

Similar to the microflotation results (see section 6.2.1), Figure 6.24 (showing As) and Figure 6.25 (showing Te) show that the flotation performance of the PGE tellurides was better compared to that of the PGE arsenides. The recoveries of these minerals were improved from pH 9 to 3, with an increase from 43% to 60% for the PGE arsenides and 74% to 85% for the

Chapter 6: Comparisons of the floatability of PGE arsenides and tellurides

PGE tellurides. Similar to the performance of PtAs_2 in the microflotation studies, the batch flotation studies have also shown that this mineral (represented by the PGE arsenides) had a greater response to the change in pH compared to the PGE tellurides.

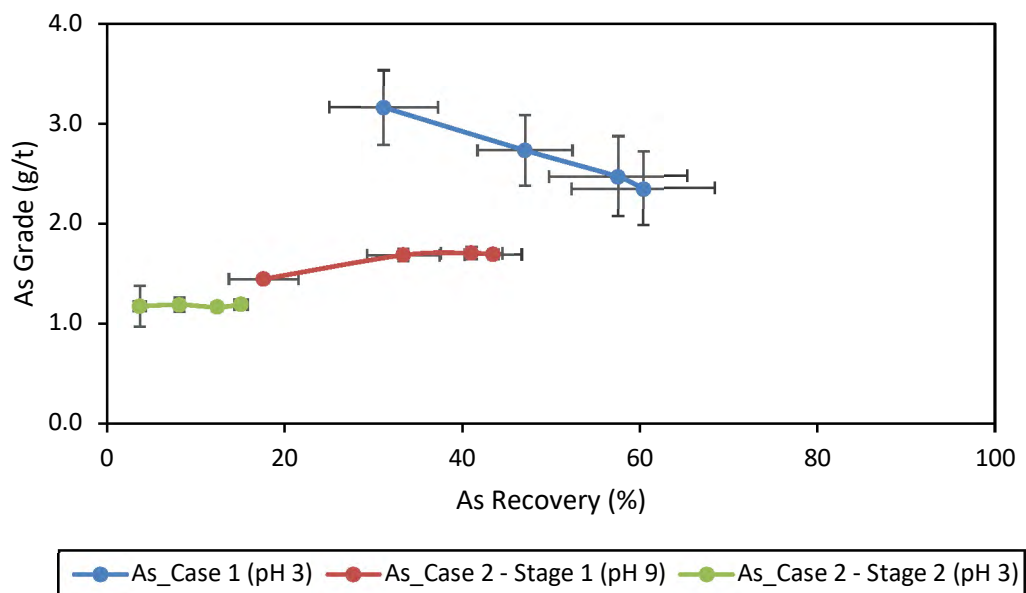


Figure 6.24: Grade-Recovery curves of As from batch flotation tests comparing the flotation performance at the natural pH of 9 and adjusted pH of 3

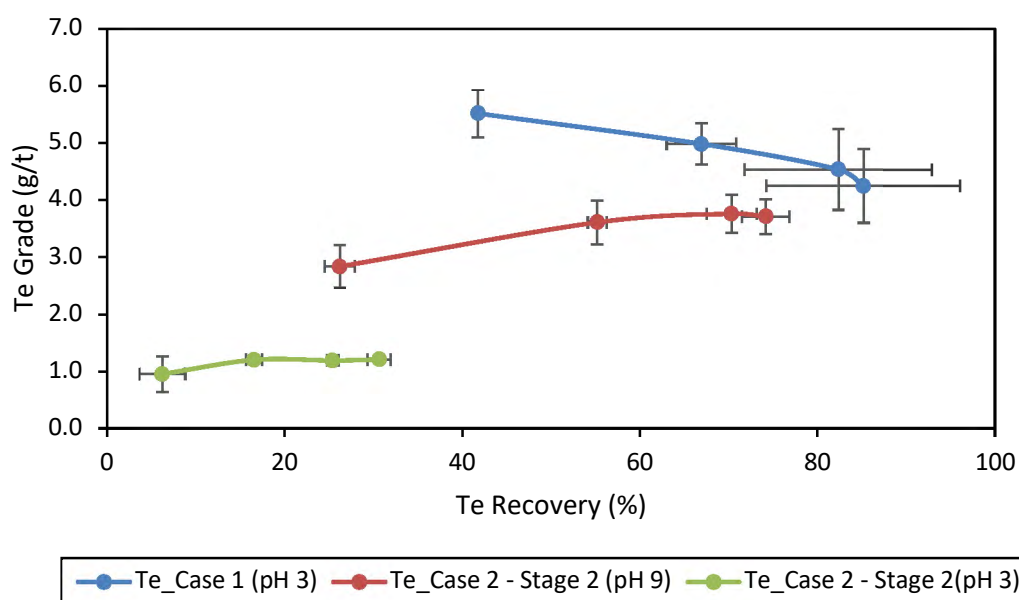


Figure 6.25: Grade-Recovery curves of Te from batch flotation tests comparing the flotation performance at the natural pH of 9 and adjusted pH of 3

With regards to the two-stage flotation operated at pH 9 followed by pH 3, these results have shown that a further 15% As and 31% Te recovery could be achieved in the second stage from the tails of the first rougher stage. The upgrade performance of the second stage of flotation in Case 2 is best illustrated using upgrade ratios, where this represents the ratio of the concentration of the metal in the concentrate to that in the feed. Representing the data in this way eliminates the effect of the differences in the feed grade. The final upgrade ratios of the minerals of interest are presented in Figure 6.26. The highest upgrade ratios of the overall Pt and Pd minerals were found in Case 2 – Stage 2. However, the upgrade performance in this flotation stage was not selective to the PGE arsenides and tellurides since the upgrade ratios of these minerals remained relatively similar as those in Case 2 – Stage 1.

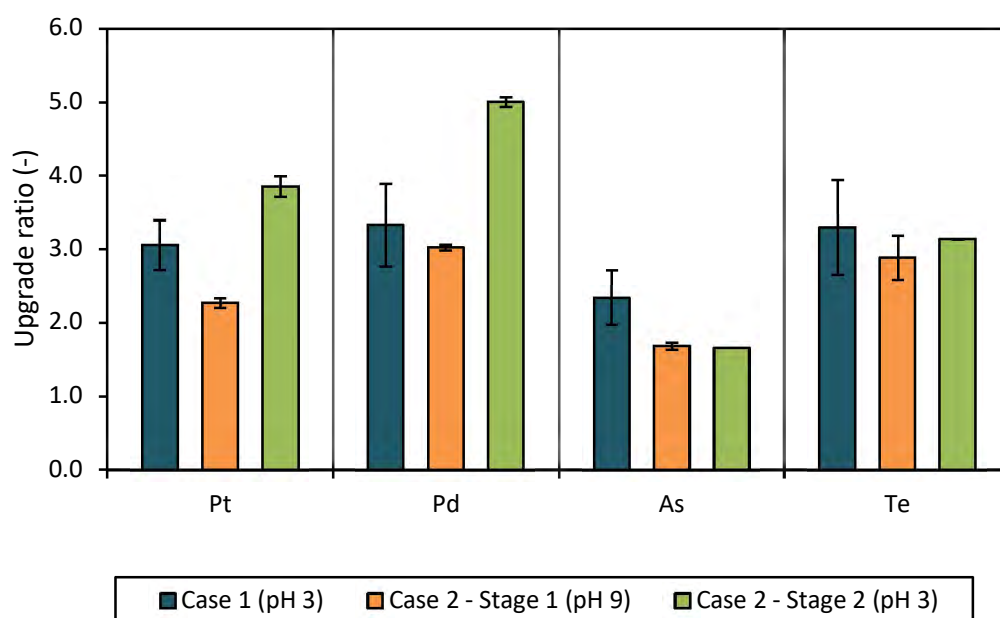


Figure 6.26: Final upgrade ratios of Pt, Pd, As and Te for the different batch flotation test conditions investigated

The final recoveries and grades of the two circuit configurations are summarised in Table 6.4. In summary, the batch flotation results have shown that Case 1, which was operated at pH 3, had the better flotation performance of all the minerals in terms of their flotation recoveries, grades and kinetics. In particular, the recovery of the PGE arsenides was improved from 43.5% at pH 9 to 60% at pH 3. Despite the longer residence time in the second circuit configuration (i.e. Case 2), it is interesting to note that it was still outperformed by Case 1. This is evident from the comparison of the Case 1 and Case 2 global performance shown in Table 6.4. Global response refers to the overall performance of the two stages in Case 2.

Chapter 6: Comparisons of the floatability of PGE arsenides and tellurides

Table 6.4: Final recoveries and grades of Pt, Pd, As and Te for the different batch flotation test conditions investigated

Test	Recovery (%)				Grade (g/t)			
	Pt	Pd	As	Te	Pt	Pd	As	Te
Case 1 (pH 3)	78.7	86.0	60.4	85.1	3.4	5.7	2.4	4.2
Case 2 - Stage 1 (pH 9)	58.5	78.0	43.5	74.1	2.6	5.1	1.7	3.7
Case 2 - Stage 2 (pH 3)	24.5	39.2	15.1	30.6	1.3	1.5	1.2	1.2
Case 2 global response	65.9	83.6	50.9	79.9	2.3	4.4	1.6	3.2

In summary, the results presented in this phase of the study showed that PtAs_2 is poorly floating compared to the other PGE arsenides and tellurides as shown by the microflotation results. The better flotation performance of the PGE tellurides was further shown using batch flotation tests. Compared to the other minerals, the supplementary test work conducted in this study showed that PtAs_2 :

- Has poor interactions with the collector
- Is relatively electrochemically inert
- Has a strong affinity for OH^- and H_2O adsorption

The floatability of the minerals, as determined by microflotation and batch flotation studies, and the supplementary test work, can be improved by lowering pH. Lowering the pH benefited PtAs_2 to a greater extent relative to the other PGE arsenides and tellurides.

6.3. Discussion

This phase of the study aimed to investigate and compare the floatability of PGE arsenides and tellurides, to get insights into why PtAs_2 has such a poor flotation performance relative to that of other similar PGE minerals. To this end, the natural and collector-induced floatability of PtAs_2 , Pd_2As , PtTe_2 , and PdTe_2 minerals were compared.

6.3.1. Natural floatability of the PGE arsenides and tellurides

The recoveries of the minerals in the absence of a collector were determined using microflotation to establish the natural floatability of the PGE minerals investigated. PtAs_2 was found to have the lowest collectorless recovery, with a recovery of 7% at pH 9. On the contrary, the PGE tellurides and Pd_2As were found to have higher collectorless recoveries, with recoveries reaching 46% for PtTe_2 , 49% for PdTe_2 , and 74% for Pd_2As at pH 9 (cf. Figure 6.1). This corroborates the findings by Shackleton et al. (2007) which showed that the PGE tellurides and arsenides have relatively good natural floatability with the exception of PtAs_2 .

To explain these findings, it is instructive to note that natural hydrophobicity, and hence floatability, may be native or self-induced. Native hydrophobicity depends on the crystal structure features of the mineral and is independent of the pulp conditions. That is, it is inherent to the mineral. Self-induced hydrophobicity, on the other hand, refers to hydrophobicity that is acquired when the mineral is exposed to specific pulp conditions (e.g. Eh and pH) resulting in a chemical reaction on the mineral surface with water or oxygen (Hu

et al., 2009). Examples of sulfide minerals that exhibit native hydrophobicity include molybdenite, realgar and stibnite (Hayes et al., 1987; Rao, 2004). The native hydrophobicity exhibited by these minerals is independent of the pulp conditions. Following this, it can be surmised that PtAs_2 is naturally hydrophilic since its collectorless recovery was found to be very low and this was found to be the case at all pH conditions investigated. The collectorless recovery of PtAs_2 only changed from 7% to 8% with a change in pH from 9 to pH 3.

PtAs_2 being naturally hydrophilic can be supported by surface energy calculations of this mineral. Hydrophobicity is often measured in terms of the wettability of the mineral surface, where minerals with a high surface energy tend to have high wettability and hence are hydrophilic (Taguta et al., 2018, 2019). In this context, surface energy refers to the excess energy per unit area when the mineral is cleaved thereby exposing polar and non-polar sites on the mineral surface (Gao et al., 2019). The surface energy of PtAs_2 has been calculated to be about 1.01 J/m^2 (Ngoepe et al., 2005; Nemutudi, 2020). This is higher than the surface energy of 0.2 J/m^2 which has been reported to be the critical surface energy above which no flotation occurs for most minerals (Taguta et al., 2018).

The other PGM minerals, on the other hand, exhibited some degree of native hydrophobicity and/or were capable of self-induced hydrophobicity. Native hydrophobicity is considered to result in minerals with open sheet/layered structures held by Van der Waals forces or from the breakage pattern of the mineral structure which exposes a hydrophobic cleavage surface (Rao, 2004). PtTe_2 and PdTe_2 have a layer-lattice structure consisting of 'faces' and 'edges', and belong to the trigonal CdI_2 -type crystal system. The layers are linked by Van der Waals gaps and weak interlayer interactions which provide a likely point of cleavage (Dai et al., 2003; Politano et al., 2018). The exposure of this cleavage could result in these minerals being natively hydrophobic. This is similar to how the layered structure of molybdenite acquires its native hydrophobicity where it preferentially cleaves along its hydrophobic 'face' (Castro et al., 2016).

In addition to the crystal features that can be used to explain the natural floatability of the minerals investigated, it is noteworthy that there seems to be a correlation between the collectorless recoveries and the collectorless ('initial') rest potentials of the minerals. This is indicated in Figure 6.27 where it can be seen that the collectorless recoveries of the minerals followed the order shown below, with the rest potentials in *mV vs SHE* indicated in brackets:

$$\begin{array}{ccccccc} \text{Pd}_2\text{As} & > & \text{PdTe}_2 & \gtrsim & \text{PtTe}_2 & > & \text{PtAs}_2 \\ (153) & & (246) & & (237) & & (285) \end{array}$$

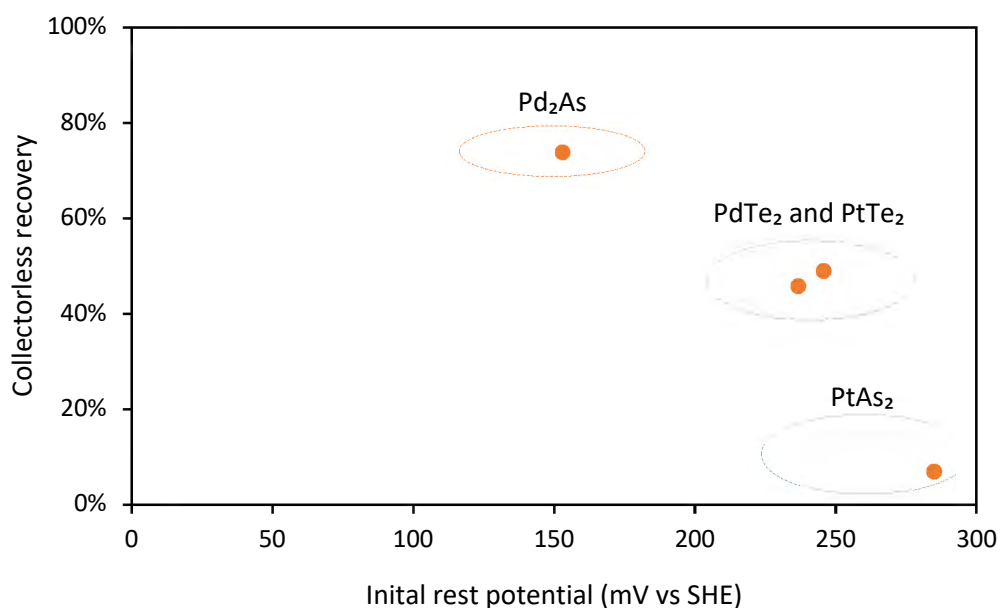


Figure 6.27: Relationship between the collectorless recoveries and the initial rest potentials of the PGE minerals investigated in this study at pH 9

If rest potential is taken to indicate the ease with which the mineral is oxidised (Wills & Finch, 2015), then it can be deduced that collectorless recovery increases with ease of oxidation (i.e. decreasing rest potential). Such a relationship has been used to rank the natural floatability of sulfide minerals (e.g. Heyes & Trahar, 1977; Hayes et al., 1987; Hayes & Ralston, 1988). The ability of sulfide minerals to form a hydrophobic layer via mild oxidation and the stability of this hydrophobic layer is generally linked to the ease of their collectorless flotation. For instance, elemental sulfur and/or a metal-deficient surface which are formed through mild oxidation are considered to be necessary for the self-induced hydrophobicity of sulfide minerals (Rao, 2004; Hu et al., 2009).

The resulting natural hydrophobicity (whether native or self-induced) may be considered to be a balance between the hydrophobic and hydrophilic species or sites found on the mineral surface (Hayes et al., 1987; Shuiyu et al., 1994). This relationship is similar to the classical Barsky relationship, $[\text{X}^-]/[\text{OH}^-] = \text{constant}$, describing the competition between OH^- and xanthate adsorption. This study did not identify the hydrophobic species responsible for the natural hydrophobicity of the PGE minerals. However, the presence of OH species, which may be considered to represent the hydrophilic species, was found.

It was found that PtAs_2 has a stronger affinity for OH adsorption compared to the other PGE tellurides and arsenides. This was shown by the FTIR and Raman spectroscopy studies. The FTIR spectra of PtAs_2 showed the presence of a broad peak in the region between 1600 and 2000 cm^{-1} . It is known that the OH bending vibrations are found at 1630 cm^{-1} (Coker et al., 1982; Vrancken et al., 2017; Amari et al., 2021), which falls within this region and thus indicating that there may be OH adsorption on PtAs_2 . Since these vibrations were found at both basic and acidic conditions with the same intensity, it is likely that they are OH vibrations

from molecular water which implies that sperrylite has a greater natural hydrophilicity. These vibrations were not observed on the spectra of the other PGE minerals. The presence of OH species on the surface of PtAs_2 was also confirmed by Raman spectroscopy. The *in-situ* Raman spectra of PtAs_2 showed that there was a stronger intensity of OH stretching vibrations, which are found at $3200\text{--}3800\text{ cm}^{-1}$ (Woods & Hope, 1998; Woods et al., 1998). On the other hand, there was only a minimal presence of these OH stretching vibrations on the Raman spectra of the other PGE minerals. Based on this, it can be deduced that the stronger adsorption of OH species PtAs_2 compared to the other PGE arsenides and tellurides plays a role in the hydrophilicity of this mineral.

In summary, the collectorless floatability of the PGE minerals may be influenced by crystal features and/or chemical interactions occurring on the surface of these minerals. The overall natural floatability is likely to be a combination of these two factors. In this context, PtAs_2 has been shown to have a much lower degree of natural hydrophobicity compared to the other PGE arsenides and tellurides.

6.3.2. Collector-induced floatability of the PGE arsenides and tellurides

The differences in the floatability of the PGE arsenides and tellurides originate, in part, from the differences in their natural hydrophobicity as already discussed. However, there are also differences in the way these minerals interact with the collector to render the mineral hydrophobic and thus bring about collector-induced floatability.

6.3.2.1. PGE arsenides

The two PGE arsenides, PtAs_2 and Pd_2As , had very different flotation behaviours. Pd_2As had the highest collector-induced recovery, with a recovery of 95% at pH 9. In contrast, PtAs_2 only had a recovery of 22% at pH 9. At pH 3, the recovery of PtAs_2 was significantly improved to 61% while the recovery of Pd_2As decreased to 85%. Although there are some differences in the adsorption of the collector onto these minerals, the big differences in their collector-induced recoveries are largely due to Pd_2As having a high natural floatability as discussed in section 6.3.1. Therefore, the collector-induced recoveries of these minerals should be viewed within this context. For instance, the addition of PAX increased the recovery of Pd_2As by 21% (from a collectorless recovery of 74%) while it increased the recovery of PtAs_2 by 15% at pH 9.

The relatively higher improvement in the recovery of Pd_2As when a collector is added may be explained by the fact that this mineral had a higher extent of collector adsorption compared to PtAs_2 . The adsorption experiments showed that >99% of the dosed collector was adsorbed on Pd_2As at pH 9 compared to 13% for PtAs_2 . This difference in the extent of collector adsorption is likely due to the high degree of hydroxide adsorption on the PtAs_2 surface, as shown by Raman spectroscopy, which hinders collector adsorption.

Despite the different extent of collector adsorption on these minerals, the rest and zeta potential measurements showed that the adsorption of PAX on PtAs_2 and Pd_2As probably follows a similar pathway. The rest potential measurements showed that the formation of dixanthogen is thermodynamically favoured on both these minerals as indicated by the values

of their final rest potentials in the presence of PAX (cf. Figure 6.5). Furthermore, the changes in rest potential of PtAs₂ and Pd₂As upon collector addition were similar across the pH ranges tested, viz. between 3 and 9 (cf. Figure 6.7b). Therefore, a similar xanthate adsorption mechanism as that proposed in Phase Two of this work for PtAs₂ is likely true for Pd₂As. That is, xanthate adsorption occurs via a co-adsorption of dixanthogen and xanthate ions bonded to the metal cations on the mineral surface. This is further supported by the fact that both these minerals had similar zeta potentials both with and without a collector.

6.3.2.2. PGE Tellurides

Unlike the PGE arsenides, the two PGE tellurides (PtTe₂ and PdTe₂), had similar microflotation recoveries. The recoveries of PtTe₂ were found to be 88% at pH 9 and 91% at pH 3, while those of PdTe₂ were found to be 81% at pH 9 and 90% at pH 3 in the presence of PAX. Even though the final recoveries of these two minerals were similar, their first-order rate constants as obtained from the Klimpel model were quite different. For instance, PtTe₂ had a rate constant of 0.2 min⁻¹ compared to that of 0.46 min⁻¹ for PdTe₂ at pH 9. This difference in kinetics only appeared when these minerals were treated with PAX, which suggests that there may be differences in the way that PtTe₂ and PdTe₂ interact with the collector.

The adsorption experiments showed that both PGE tellurides have a high extent of collector adsorption, with >99% of the dosed collector being adsorbed at both pH 9 and 3. However, there were differences in the nature of the collector adsorption as shown by the rest and zeta potential measurements. The final rest potential of PtTe₂ was found to lie above the equilibrium potential of the xanthate/dixanthogen couple at pH 9. Therefore, the formation of dixanthogen on this mineral is thermodynamically favoured at these conditions. At acidic conditions (pH 3), the formation of dixanthogen was still thermodynamically favoured; however, the interaction between PAX and the PtTe₂ surface was greater at pH 3 as indicated by the greater change in potential upon collector addition. In general, the interaction of xanthate with the PGE tellurides was greater compared to that with the PGE arsenides (cf. Figure 6.7b).

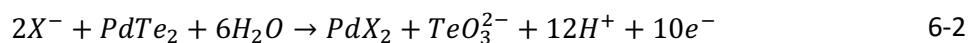
The adsorption of the collector on PtTe₂ possibly occurs via an initial chemisorption of xanthate ions on the Pt atoms followed by further oxidation of the collector to form dixanthogen. The initial chemisorption step can be described by reaction 6-1.



According to Buckley & Woods (1997), this reaction can occur as a precursor to the formation of dixanthogen. The occurrence of the initial reaction is supported by the zeta potential measurements which showed that the zeta potentials of PtTe₂ shifted to more negative values when treated with PAX relative to the untreated surface (cf. Figure 6.11). The shift of the zeta potentials to more negative values suggests an increase in the adsorption of negatively charged species or a decrease in positively charged species on the surface of the mineral when treated with PAX. This would be the case if the xanthate ions were chemisorbed on the Pt atoms. These findings are consistent with the rest potential measurements and cyclic

voltammetry studies conducted by Tadie et al. (2015a,b) which showed that the adsorption of xanthate on PtTe₂ and PdTe₂ possibly occurs via two reactions in series, viz., chemisorption of xanthate followed by adsorption of metal xanthate or dixanthogen. The adsorption of dixanthogen on PtTe₂ has also been confirmed by *ex-situ* FTIR spectroscopy studies performed by Vermaak et al. (2007).

The nature of collector adsorption on PdTe₂ was found to be different compared to that on PtTe₂. At pH 9, the rest potential measurements showed that the rest potential of PdTe₂ sharply decreased upon collector addition at 600 seconds (Figure 6.5), and subsequently increased to a final value below the equilibrium potential of the xanthate/dixanthogen couple. The value of the final rest potential suggests that chemisorbed xanthate or metal xanthate, and not dixanthogen, are the thermodynamically favoured species to form on the surface of PdTe₂. A similar two-step reaction as that on PtTe₂ has been proposed by Tadie et al. (2015a,b), except that in the case of PdTe₂ the chemisorption of xanthate is followed by the adsorption of metal xanthate, PdX₂, described by reaction 6-2.



At pH 3, the final rest potential of PdTe₂ almost coincided with the equilibrium potential of the xanthate/dixanthogen couple. Therefore, there is a possibility that dixanthogen, as opposed to metal xanthate at pH 9, may be the active collector species on PdTe₂ at acidic conditions. The difference in the nature of collector adsorption on PdTe₂ at different pH can also be supported by the zeta potential measurements. These measurements showed that the zeta potentials of the PAX-treated PdTe₂ were less negative relative to the untreated surface at pH >8, whereas at pH <8 they became more negative. This suggests that the nature of collector adsorption on PdTe₂ may be different above and below pH 8.

6.3.3. Effect of the electronic properties of the minerals

Ultimately, this study has shown that the collector-induced recovery of PtAs₂ can be significantly improved by lowering pH. This had to do with the high affinity of PtAs₂ for OH adsorption at high pH which hindered collector adsorption. Despite the improvement in the recovery of PtAs₂ at pH 3, the recovery of this mineral was still found to be lower compared to that of the PGE tellurides. It was shown that the PGE tellurides generally have a higher affinity for xanthate adsorption compared to the PGE arsenides. The fundamental reason as to why this is the case remains unclear. Although an investigation of the solid-state properties of the minerals is beyond the scope of the current study it may be postulated that the solid-state properties of these minerals play a role in this regard.

It is known that the adsorption of thiol collectors, such as xanthates, involves a transfer of electrons from the collector's HOMO at the anodic site, where the collector is oxidised, through the mineral surface to the cathodic site where oxygen is reduced (Woods, 1996). This requires that the mineral is conductive to facilitate this transfer of electrons. For instance, most sulfide minerals are semiconductors and can therefore sustain this transfer of electrons. The semi-conductive properties of minerals can be quantified by the band gap between the

valence and conduction bands of the mineral. The bigger the band gap, the more energy is required for the electrons to migrate (Leja, 1982; Yu & Cardona, 2010). In the context where the collector adsorbs via an electrochemical mechanism, this means that minerals with larger band gaps will be poor semiconductors, and therefore poor catalysts for xanthate adsorption. A rudimentary analysis of the band gaps of the minerals investigated in this study showed this to be the case.

The valence band involves the orbitals of the mineral anions, while the conductive band primarily involves the orbitals of the mineral cations. Therefore, the band gap can be modelled as a function of some parameter of the cation and anion. For instance, in binary compounds, there is a linear relationship between the band gap and electronegativities of the anion and cation (Hooge, 1960; Dagenais et al., 2013). That is, band gap increases with increasing electronegativity. Applying this to the PGE arsenides and tellurides, their band gaps can be expected to follow the trend shown below:

$$\begin{array}{cccc} \text{PdTe}_2 < & \text{PtTe}_2 < & \text{Pd}_2\text{As} < & \text{PtAs}_2 \\ (2.13) & (2.16) & (2.19) & (2.21) \end{array}$$

where the numbers in brackets refer to the group electronegativities of the minerals obtained by averaging the individual electronegativities making up the group (Clifford, 1959). From this, it can be deduced that PtAs_2 should have the largest band gap and hence poorest semi-conductive properties. It is interesting to note that this trend follows the same order as the interaction of the minerals with PAX that was shown by the rest potential measurements performed in the present study. This was shown by the change in the rest potential of the minerals upon collector addition (cf. Figure 6.7b).

This is also consistent with the intramolecular bonding within the structures of PtTe_2 and PdTe_2 . Bonding in these metal dichalcogens occurs between the p-orbitals from the chalcogen (Te) and d-orbitals from the metal (Pt or Pd). The small energy gap between the p-d orbitals gives PtTe_2 and PdTe_2 their metallic electronic properties (Guo et al., 1986; Dai et al., 2003). Therefore, these minerals can be expected to have good electron-conducting properties.

6.3.4. Application of pH reduction in batch flotation

Batch flotation tests were conducted to determine the applicability of pH reduction in a more realistic scenario that includes the froth phase, complex ore and complex cell hydrodynamics. The flotation performance of the PGE arsenides and tellurides was investigated using two circuit configurations, viz. Case 1 (pH 3) and Case 2 (two-stage flotation where stage 1 = pH 9, stage 2 = pH 3). In this study, flotation performance was determined using recoveries, grades and flotation kinetics, of which recovery is the most important indicator in PGM flotation.

The flotation performance of the PGE tellurides was found to be better than that of the PGE arsenides. For instance, the final recovery of the PGE tellurides at pH 9 was found to be 31% higher than that of the PGE arsenides (cf. Table 6.4). This is consistent with the findings obtained by Shamaila & O'Connor (2008) who found that the recovery of PGE tellurides in a Platreef ore was 37% higher. This is also consistent with the findings in the present study from

the microflotation studies which showed that PtTe_2 and PdTe_2 had a better floatability compared to PtAs_2 . In this study, this was attributed to the better interaction of the xanthate collector with the PGE tellurides, as well as their better natural floatability in general. Of particular interest in this study was whether the recovery of PtAs_2 could be selectively improved by lowering pH.

The improvements in batch flotation recoveries obtained when the pH was change from pH 9 (Case 2 – Stage 1) to pH 3 (Case 1) are shown in Table 6.5. While both the PGE arsenide and telluride recoveries were improved at pH 3, it can be seen that the PGE arsenide recoveries were improved to a greater extent. The PGE arsenide recoveries were improved by 17% while those of the PGE tellurides were improved by 11%. Therefore, it can be concluded that operating at pH 3 was more selective in improving the recoveries of the PGE arsenides, which are dominated by PtAs_2 . This is consistent with the microflotation tests conducted in this study which showed that operating at pH 3 improved the recovery of PtAs_2 to a greater extent compared to Pd_2As , PtTe_2 and PdTe_2 .

Table 6.5: Comparison of batch flotation recoveries at pH 9 and 3

Mineral	Recovery (%)		Improvement in recovery (%)
	pH 9	pH 3	
Overall Pt minerals	58	79	20
Overall Pd minerals	78	86	8
PGE arsenides (As)	43	60	17
PGE tellurides (Te)	74	85	11

In addition to the recoveries, the batch flotation studies further showed that the grades and flotation kinetics of all the PGE arsenides and tellurides can be improved at pH 3.

When the pH was adjusted to pH 3 on the tails of the first rougher stage after floating at pH 9 (i.e. Case 2 - Stage 2), it was found that a further 15% PGE arsenides and 31% PGE tellurides could be achieved (cf. Table 6.4). These lower recoveries are probably due to the lower mass pull of the floatable material in the second stage of flotation in Case 2. However, it was noted that higher upgrade ratios of the PGMs could be achieved in this stage. Interestingly, it was found that Case 1 outperformed the global response of Case 2 (i.e. stage 1 and 2) despite the longer residence time in Case 2. For instance, recoveries of 60% for the PGE arsenides and 85% for the PGE tellurides were obtained in Case 1, while in Case 2's global response, 51% and 80% recoveries were obtained for the PGE arsenides and tellurides, respectively. Therefore, it can be concluded that a better flotation performance can be achieved when the pH is adjusted to pH 3 in the incoming feed of the first rougher.

Ultimately, the batch flotation studies have corroborated the findings from the microflotation studies in showing that the flotation performance of PtAs_2 can be selectively improved by operating at pH 3 even in the presence of the froth phase, complex ore and complex cell hydrodynamics.

6.4. Conclusions

This phase of the study sought to investigate and compare the floatability of PGE arsenides and tellurides in order to gain insights into the possible reasons for the poor floatability of PtAs_2 compared to other PGE minerals. The collectorless and collector-induced floatability of these minerals were compared. The collectorless recoveries at pH 9 followed the order: Pd_2As (74%) > PdTe_2 (49%) > PtTe_2 (46%) > PtAs_2 (7%). The differences in the natural floatabilities of these minerals were attributed to the crystal effects of the minerals and/or chemical reactions occurring on the mineral surface which contributed to the self-induced hydrophobicity of the minerals. In this regard, PtAs_2 was found to be naturally hydrophilic compared to the other PGE minerals as shown by the strong interaction with water and hydroxide ions in FTIR and Raman spectroscopy experiments.

In the presence of PAX at pH 9, the recoveries of the minerals followed the order: Pd_2As (95%) > PtTe_2 (88%) > PdTe_2 (81%) > PtAs_2 (22%). It was shown that the PGE tellurides generally have a better interaction with PAX which likely contributed to their better floatability compared to the PGE arsenides. The adsorption of xanthate involved the formation of dixanthogen as the dominant species on all the minerals, except for PdTe_2 on which the dominant species was found to be the metal xanthate, PdX_2 . It is likely that the poor interaction of PtAs_2 with xanthate is due to the solid-state electronic structure of the mineral, since it appears that PtAs_2 has a larger band gap and is more electrochemically inert than the other minerals that were studied.

Both the collectorless and collector-induced recoveries of all the minerals were improved at lower pH, except Pd_2As whose collector-induced recovery decreased from 95% at pH 9 to 85% at pH 3. The microflotation response of PtAs_2 was improved to a greater extent compared to that of the other PGMs investigated, where the recovery of this mineral increased from 22% at pH 9 to 61% at pH 3. This was corroborated by the batch flotation studies which showed that the flotation performance of PGE arsenides (which are dominated by PtAs_2) can be selectively improved by operating at pH 3 even in the presence of the froth phase, complex ore and complex cell hydrodynamics.

CHAPTER 7: General Conclusions

The beneficiation of the Platreef ore deposit, with its abundant PGE tellurides and arsenides, is expected to play a key role in the PGM industry for the foreseeable future. With the growing demand for platinum driven by the transition to green energy, there is a rising need for sources of platinum. One such source is sperrylite (PtAs_2) which is found in relative abundance in Platreef ore bodies. However, it has been found that there are major losses of sperrylite during the processing of Platreef ores with these losses being mainly attributed to the poor recovery of this mineral by flotation. This study contributes fundamental knowledge to the understanding of the reasons for the poor floatability of this economically important mineral and possible remedies for improving the recovery of this mineral.

The main objective of this study was to investigate the floatability of PGE arsenides and tellurides, viz. sperrylite, palladoarsenide, moncheite and merenskyite, with the primary focus being to understand and improve the floatability of sperrylite by exploiting flotation chemistry. In particular, this study focused on the role of collector, solution and mineral chemistries in relation to how these affect the floatability of sperrylite. At the outset of this research, three hypotheses were proposed, and the general conclusions derived from the evidence collected in addressing these hypotheses are summarised in this chapter.

“The trithiocarbonate (TTC) and thiourea (TU) collectors will bond more strongly with sperrylite and improve the floatability of this mineral to a greater extent compared to the xanthate collectors. This is because the functional groups of the trithiocarbonate and thiourea collectors have a greater electron-releasing tendency resulting in a greater availability of electrons to form bonds with the mineral surface.”

It was found that the TTC and TU collectors did indeed adsorb more strongly on the sperrylite surface compared to the xanthate collectors. The heat of adsorption of the collectors on sperrylite at pH 9 and a collector dosage equivalent to 1 pseudo-monolayer (ML) surface coverage followed the order:

$\text{PNBTTC} (-41.80 \text{ kJ/mol}) > \text{PTU} > (-34.15 \text{ kJ/mol}) > \text{PAX} (-30.13 \text{ kJ/mol}) > \text{PNBX} (-19.96 \text{ kJ/mol})$

However, none of the collectors significantly improved the floatability of sperrylite. PNBTTTC, PAX and PNBX all yielded similar microflotation recoveries of 15.5, 15.4 and 16.1%, respectively. A slightly higher recovery of 18.1% was obtained using the PTU collector. These findings imply that these collector types did not sufficiently improve the hydrophobicity of sperrylite at 1 ML and pH 9.

Microflotation studies showed that the recovery of sperrylite could be improved to some extent by increasing the ionic strength of the process water and to a greater extent by increasing collector dosage. Increasing the collector dosage of a strong collector, PAX, resulted in a significant improvement in the recovery of sperrylite. However, the recovery of the

mineral approached a maximum of only 45% at a very high collector dosage of 20 ML PAX. On the other hand, increasing ionic strength from 0 to 0.12 M NaCl only resulted in modest improvements in sperrylite recovery. For instance, the recovery of the mineral with 1 ML PAX improved from 15.4% at 0 M NaCl to 20.6% at 0.12 M NaCl.

These findings highlight the difficulties in obtaining good recoveries of sperrylite at the typical conditions in PGM concentrators such as pH 9. Given that the floatability of sperrylite could be improved to some extent at higher ionic strength and collector dosages, this study further investigated the flotation behaviour of sperrylite at 5 ML PAX and 0.12 M NaCl which are slightly higher than the typical conditions. However, in this case, the focus was on how Eh-pH conditions affect the floatability of sperrylite.

"Sperrylite will have a better floatability at lower pH and/or higher Eh conditions compared to the current operating conditions of pH 9 and $Eh \approx 160$ mV vs SHE. This is because:

- Lowering pH reduces the concentration of OH^- ions that would otherwise compete with the collector for adsorption sites on the mineral surface,*
- At lower pH, the formation of dixanthogen is thermodynamically favoured and this is required to impart sufficient hydrophobicity on sperrylite,*
- At higher Eh conditions, at least 100 mV vs SHE above the xanthate/dixanthogen equilibrium potential, the formation of dixanthogen is thermodynamically favoured."*

It was shown that sperrylite floats better at acidic conditions, where the recovery increased from 22% at pH 9 to 61% at pH 3. This was attributed to better adsorption of the collector at acidic conditions. In this study, the adsorption of PAX on sperrylite was proposed to be a co-adsorption of metal xanthate and dixanthogen. However, it is the specific presence of dixanthogen that strongly promotes the hydrophobicity of the mineral. Therefore, it can be concluded that the hydrophobicity of sperrylite is likely to be governed by the amount of collector that is adsorbed on the mineral surface, and the relative proportion that is adsorbed as dixanthogen.

Both the formation of dixanthogen and the amount of collector adsorbed were improved by decreasing pH which also corresponded to an increase in Eh. The formation of dixanthogen is thermodynamically favoured at potentials above 89 mV vs SHE for PAX. Sperrylite in a solution of PAX had a rest potential of 276 and 354 mV vs SHE at pH 9 and 3, respectively, thus showing that the formation of dixanthogen was thermodynamically favoured at both conditions, but more favoured at pH. However, it was found that it was not conducive to increase Eh chemically using, for example, NaClO or H_2O_2 since in this case there is a reaction between NaClO and PAX, and/or excessive oxidation of sperrylite occurs which ultimately reduces the ability of the collector to impart hydrophobicity to the mineral. In the presence of the 0.01 M NaClO, the recovery of sperrylite was reduced from 61% to 21% at pH 3, thus indicating that the hydrophobicity of the mineral had decreased. Furthermore, a reduction in the recovery of

Chapter 7: General Conclusions

sperrylite was observed even though the Eh stayed relatively constant when adding lower concentrations of NaClO. For instance, an addition of 0.001 M NaClO resulted in the recovery of sperrylite being reduced from 61% to 31% at pH 3 despite the pulp Eh only changing from 550 to 625 mV vs SHE. This illustrates that NaClO has a deleterious chemical effect on the floatability of sperrylite.

Furthermore, this study investigated and compared the floatability of PGE arsenides and tellurides to get further insights into why sperrylite has such a poor flotation performance relative to that of other similar PGE minerals. To this end, the floatability of sperrylite, palladoarsenide, moncheite, and merenskyite minerals was compared to determine the possible reasons for their differences in floatability.

"Sperrylite has a poorer floatability compared to other PGMs including palladoarsenide, moncheite and merenskyite. It is hypothesised that this is due to sperrylite being more electrochemically inert and therefore less conducive to sustaining electron charge transfer between the collector and the mineral."

This study confirmed the lower degree of the natural and collector-induced floatability of sperrylite compared to the other PGE arsenides and tellurides investigated, namely, palladoarsenide, moncheite and merenskyite. For instance, the collectorless recoveries at pH 9 followed the order: palladoarsenide (74%) > merenskyite (49%) > moncheite (46%) > sperrylite (7%). In the presence of PAX at pH 9, the recoveries of the minerals followed the order: palladoarsenide (95%) > moncheite (88%) > merenskyite (81%) > sperrylite (22%). A contributing factor to the lower degree of floatability of sperrylite is that this mineral has a higher affinity for hydroxide and water interaction compared to the other PGMs investigated which inhibits collector adsorption on this mineral. All the recoveries of the minerals were improved at lower pH, where the concentration of OH⁻ ions is low. The exception to this was palladoarsenide whose collector-induced recovery decreased from 95% at pH 9 to 85% at pH 3.

It was shown that decreasing the pH improved the collector-induced recovery of sperrylite to a much greater extent compared to that of the other PGMs investigated. The microflotation recovery of sperrylite improved from 22% at pH 9 to 61% at pH 3, almost a three-fold increase. The reduction of pH which resulted in an improvement in the recovery of sperrylite was shown to be also applicable in batch flotation. The batch flotation studies showed that the recovery of the PGE arsenides (which are dominated by sperrylite) increased from 43% at pH 9 to 60% at pH 3. In addition to the recoveries, the grades and flotation kinetics were improved at the lower pH conditions. This shows that even in the presence of froth effects, complex ore and more complex cell hydrodynamics, the recovery of sperrylite can be improved by operating at pH 3.

Another major contributing factor to the lower degree of floatability of sperrylite is its poor electrochemical interaction with the collector compared to the other PGMs. The rest potential

measurements showed that the interaction of the minerals with PAX at pH 9 followed the order: merenskyite (182.2 mV vs SHE) > moncheite (65.4 mV vs SHE) > palladoarsenide (19.6 mV vs SHE) > sperrylite (8.3 mV vs SHE), where the magnitude of the interaction is indicated in brackets.

The poor electrochemical interaction of sperrylite with PAX is suggestive of a poor flow of electrons through the mineral surface to enable dixanthogen formation and its adsorption. Interestingly, a rudimentary analysis of band gap energy which is a measure of the ability of the mineral to conduct electrons showed that there was a correlation between the mineral-collector electrochemical interactions as measured by rest potentials and the band gap energies of the mineral. For instance, this analysis showed that sperrylite has a wide band gap energy (i.e. poor conductor) and this correlated with the poor electrochemical interaction of this mineral with the collector determined by the rest potential measurements. Although band gap energies were not measured in this study but inferred from electronegativity differences between mineral cations and anions, there is evidence to suggest the poor conductivity of sperrylite plays a major role in its poor floatability with xanthate collectors.

This work has shown that the optimal flotation domain of sperrylite, as a function of pH and Eh, is not the same as that of the other PGE arsenides and tellurides such as palladoarsenide, moncheite and merenskyite. The optimal flotation conditions of sperrylite have been shown to be at pH 3, with a corresponding natural Eh of 550 mV vs SHE.

Ultimately, the findings obtained in this study contribute to an understanding of the requirements for improving the hydrophobicity of sperrylite using xanthate collectors. One such requirement is that it is necessary to have a mineral surface that will catalyse the formation of dixanthogen and enhance collector adsorption. This presents an opportunity for further research avenues that could be explored to achieve this. One such avenue is the exploration of the conductive properties of sperrylite such as band gap energy and how this can be exploited to improve xanthate adsorption on this mineral.

This work has made a significant contribution to the understanding of the poor floatability of sperrylite, a major component of the largest PGM ore body in the world. It has, for the first time, shown spectroscopic evidence of strong water and hydroxide interactions with sperrylite that are not present for other platinum group minerals. In addition, this work has made findings on improving flotation recoveries of PGMs at acidic pH conditions. Very importantly, this work has laid a fundamental foundation for a greater understanding of the flotation of platinum group minerals, which was previously missing from the scientific literature.

Recommendations for future work

This PhD has contributed to the fundamental understanding of the interactions of platinum group minerals with water, hydroxide species and collectors. From this has emerged one key element that appears to affect the reactivity of sperrylite, which is the surface electronic

Chapter 7: General Conclusions

structure of this mineral. To capitalize on this finding, future work should be focused on efforts to modify the mineral's surface electronic structure through the use of adsorbents that can create a conducive surface for collector adsorption. This will necessitate finding suitable adsorbents such as co-collectors or ions.

This study has also shown that lower pH plays a critical role in improving the floatability of sperrylite, mainly due to improved adsorption of the xanthate collector. It was shown that this is true even in the case of batch flotation studies where a real ore was used. There is an opportunity for future work to consider the feasibility of exploring this further at pilot or plant scale, although it is important to note that such a change in operational procedure would have other major implications on the overall process and would probably ultimately be decided as much by economic as flotation performance considerations.

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CHAPTER 9: Appendices

A. APPENDIX A: Collector surface coverage calculation

Collector surface coverage refers to the number of molecules of the collector covering the available surface area of the mineral, and this was reported in terms of pseudo-monolayers in this thesis. Surface coverage was calculated as the total area covered by the collector divided by the total mineral surface area. The surface area of the mineral was determined using BET analysis. The area covered by the collector was calculated using the footprint area of one collector molecule which was assumed to be 28.8 Å (Grano et al., 1997). A sample calculation of the surface coverage is shown in this appendix using sperrylite and PAX collector as an example.

Total available mineral surface area:	
Mass of sperrylite (g)	2
BET specific surface area of sperrylite (m ² /g)	0.06
Available mineral surface area (m ²)	$2 \times 0.06 = 0.12$

Moles of collector required for 1 pseudo-monolayer	
Footprint area of one collector molecule (m ²)	2.88×10^{-19}
No. of collector molecules required for 1 pseudo-monolayer	$\frac{0.12}{2.88 \times 10^{-19}} = 4.07 \times 10^{17}$
Avogadro's number	6.02×10^{23}
No. of moles of collector required for 1 pseudo-monolayer (mol)	$\frac{4.07 \times 10^{17}}{6.02 \times 10^{23}} = 6.76 \times 10^{-7}$

The number of moles of collector required for 1 pseudo-monolayer coverage was then used to determine the collector volume dosage based on the molecular mass of the collector.

Chapter 9: Appendices

Collector amount dosed:	
Molecular weight of PAX (g/mol)	202
Purity of PAX (%)	>99
Concentration of collector stock solution (g/ml)	0.01
Amount of collector dosed (μl)	$\frac{(6.76 \times 10^{-06})(202)(1000)}{(> 99\%)(0.01)} = 13.65$

B. APPENDIX B: Heat of adsorption profiles

In CHAPTER 4: Investigation of the performance of various collectors on the flotation of sperrylite, the heats of adsorption of the collectors are reported at 1 pseudo-monolayer surface coverage. The full details of the heat of adsorption as a function of collector surface coverage are presented in Figure B.1. The slope of these curves is indicative of the affinity that the collector has with the sperrylite surface, which follows the order:

$$\text{PNBTTC} > \text{PAX} > \text{PNBX} > \text{PTU}$$

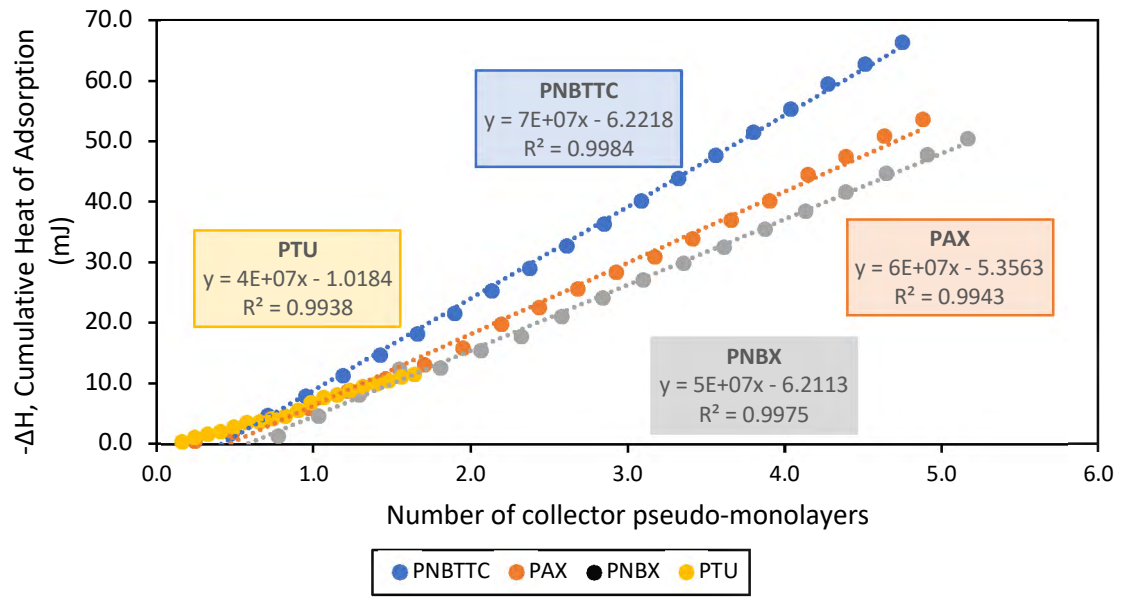


Figure B.1: Heat of collector adsorption on sperrylite as a function of monolayer coverage for the PNBTTTC, PAX, PNBX and PTU collectors at pH 9

C. APPENDIX C: XPS results

In CHAPTER 5: Effect of pH-Eh on the floatability of sperrylite, only the S 2p spectra were discussed as these were directly relevant for determining the nature of collector adsorption on sperrylite at pH 9 compared to pH 3. The spectra showing the C, O, Pt and As peaks for sperrylite conditioned at pH 9 and 3, with and without PAX are shown in this appendix in Figure C.1 to Figure C.20.

These spectra do not show much additional information to what has already been presented and discussed in **Chapter 5**, other than that pH does not seem to have much effect on the sperrylite mineral itself. All else being equal, a shift in the Binding Energy (BE) of the bonds would indicate a change in the chemical state of the atoms. However, these spectra show that there was hardly any change in the chemical states of the atoms.

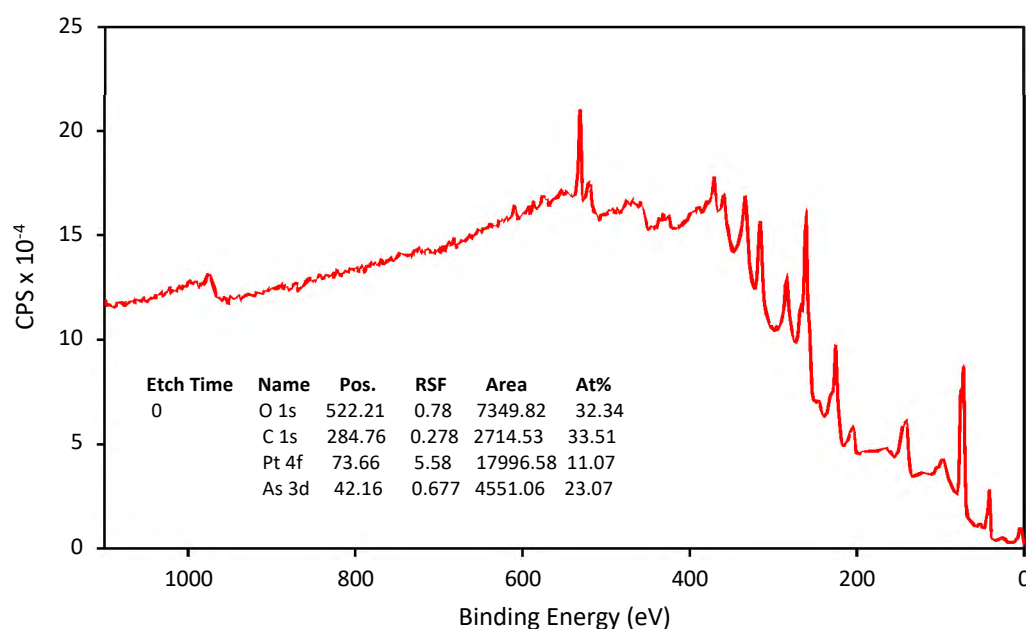


Figure C.1: XPS wide scan of sperrylite conditioned at pH 9

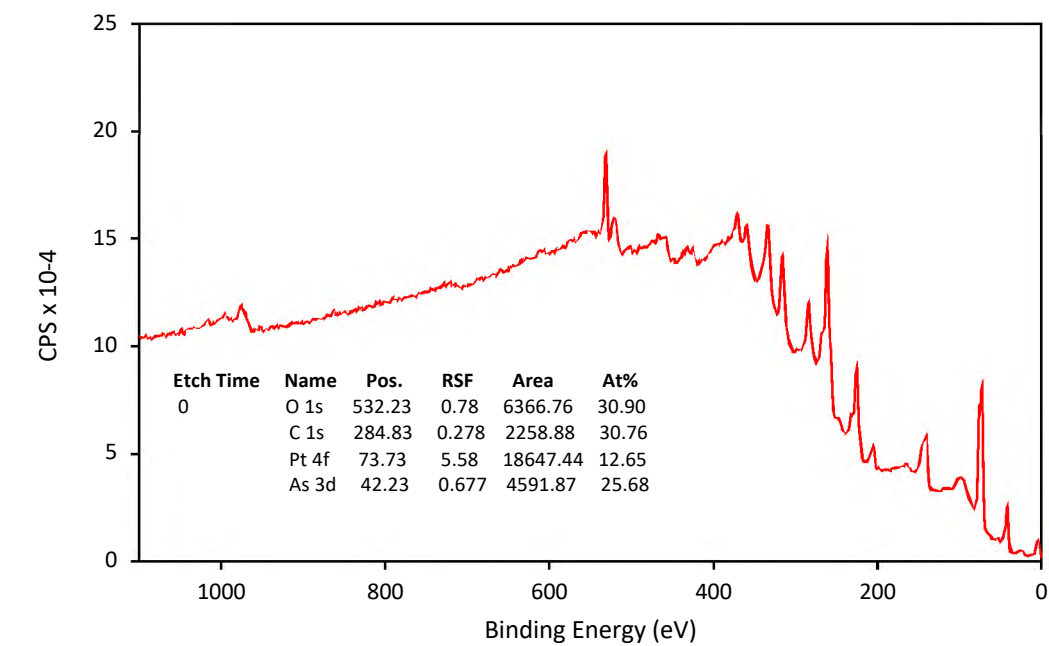


Figure C.2: XPS wide scan of sperrylite conditioned at pH 3

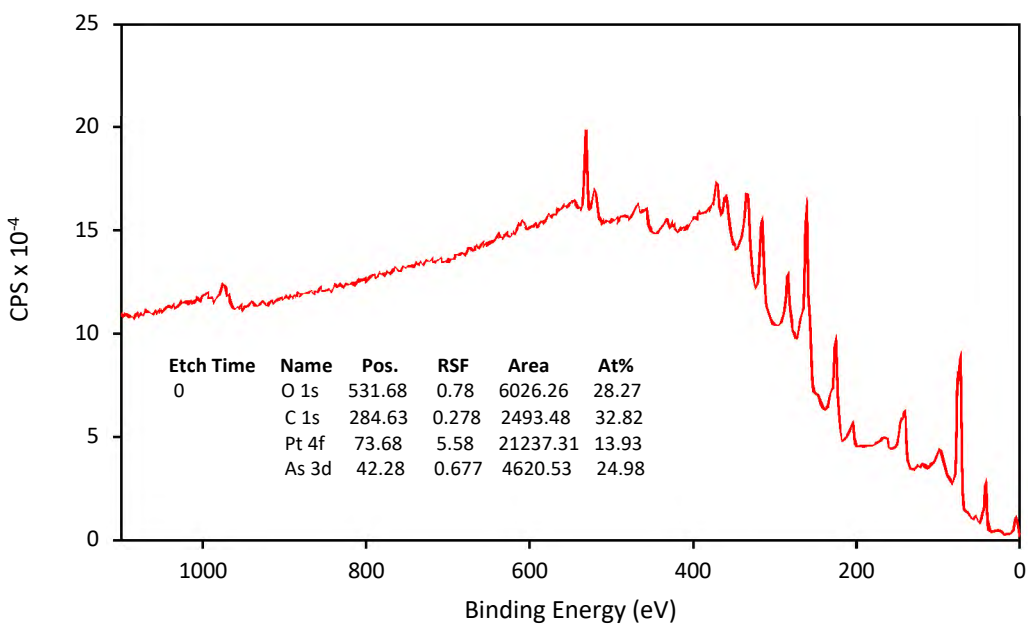


Figure C.3: XPS wide scan of sperrylite conditioned with 5×10^{-4} M PAX at pH 9

Chapter 9: Appendices

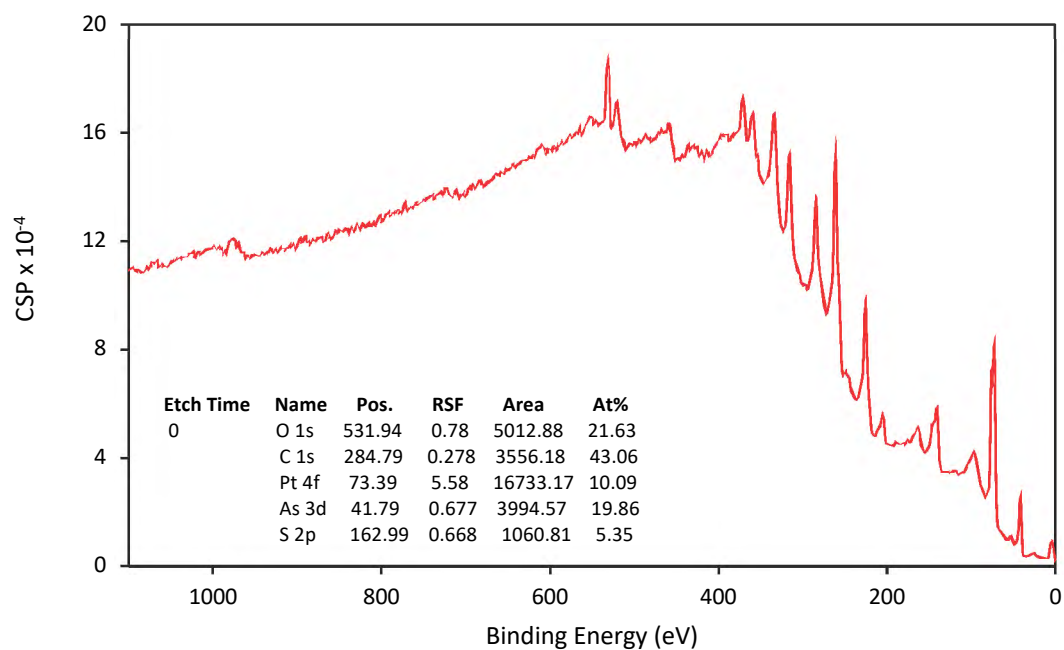


Figure C.4: XPS wide scan of sperrylite conditioned with 5×10^{-4} M PAX at pH 3

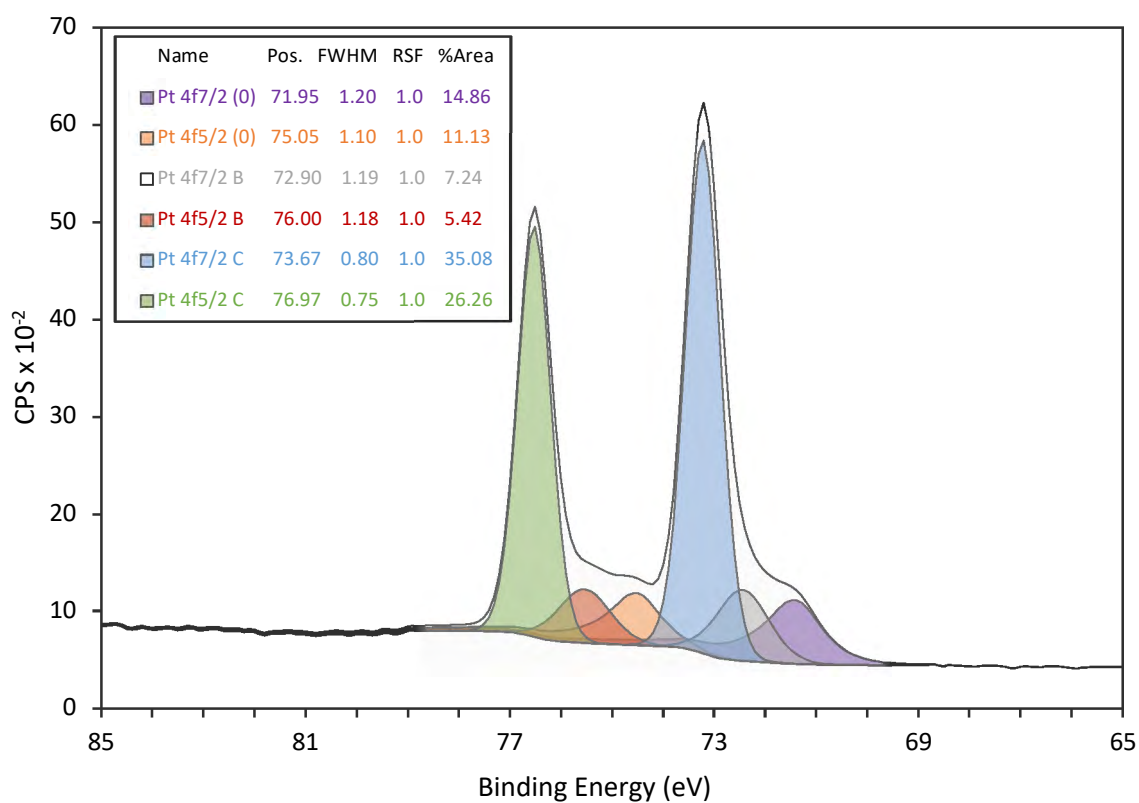


Figure C.5: Pt 4f XPS spectra from sperrylite conditioned at pH 9 without PAX

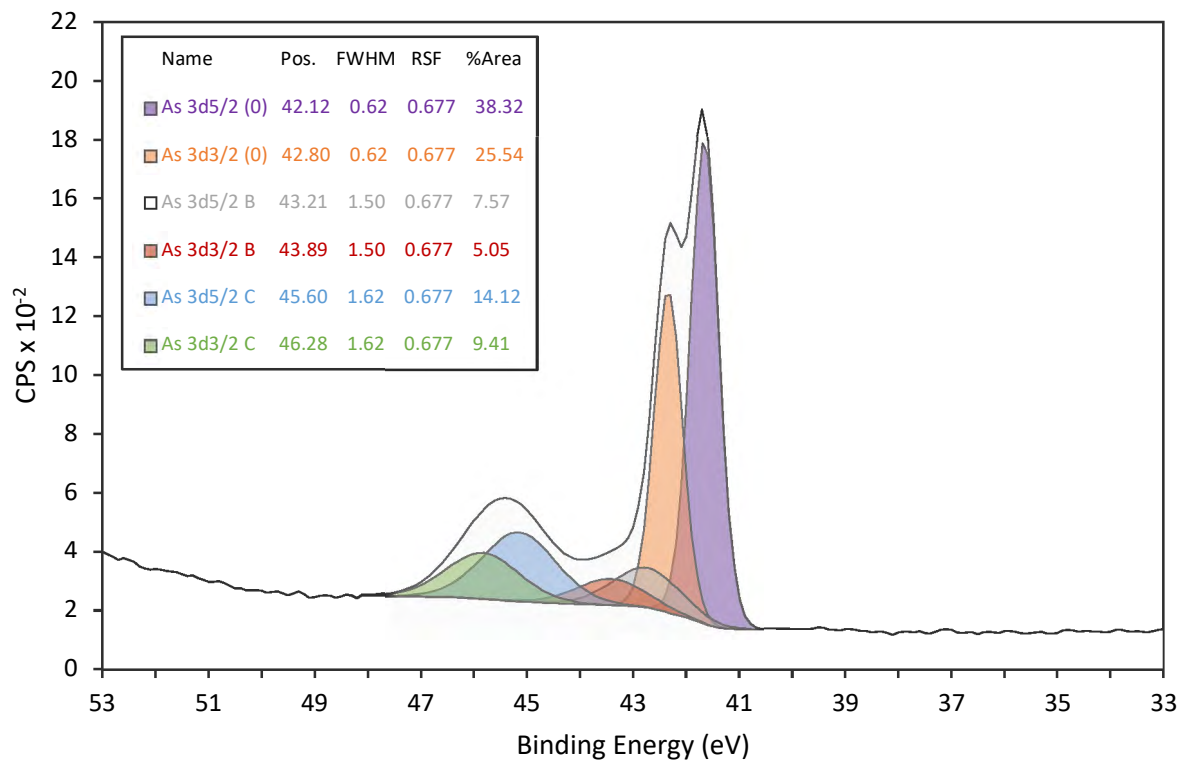


Figure C.6: As 3d XPS spectra from sperrylite conditioned at pH 9 without PAX

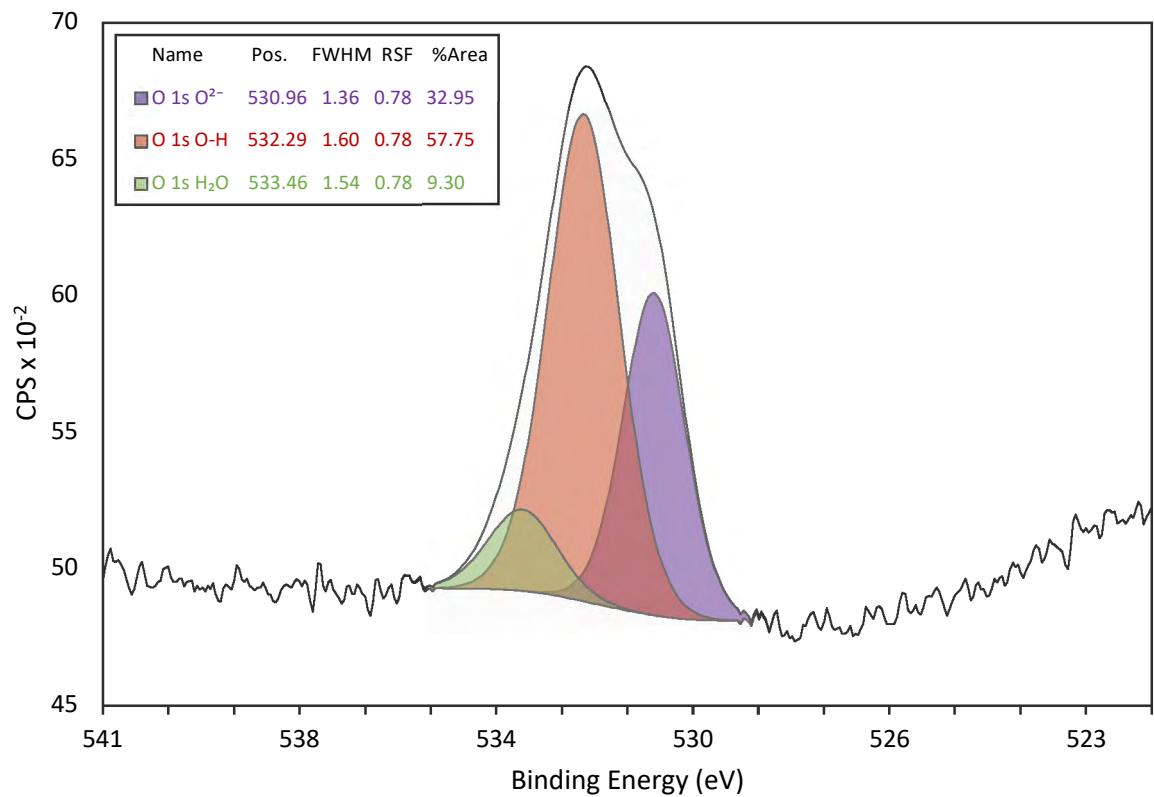


Figure C.7: O 1s XPS spectra from sperrylite conditioned at pH 9 without PAX

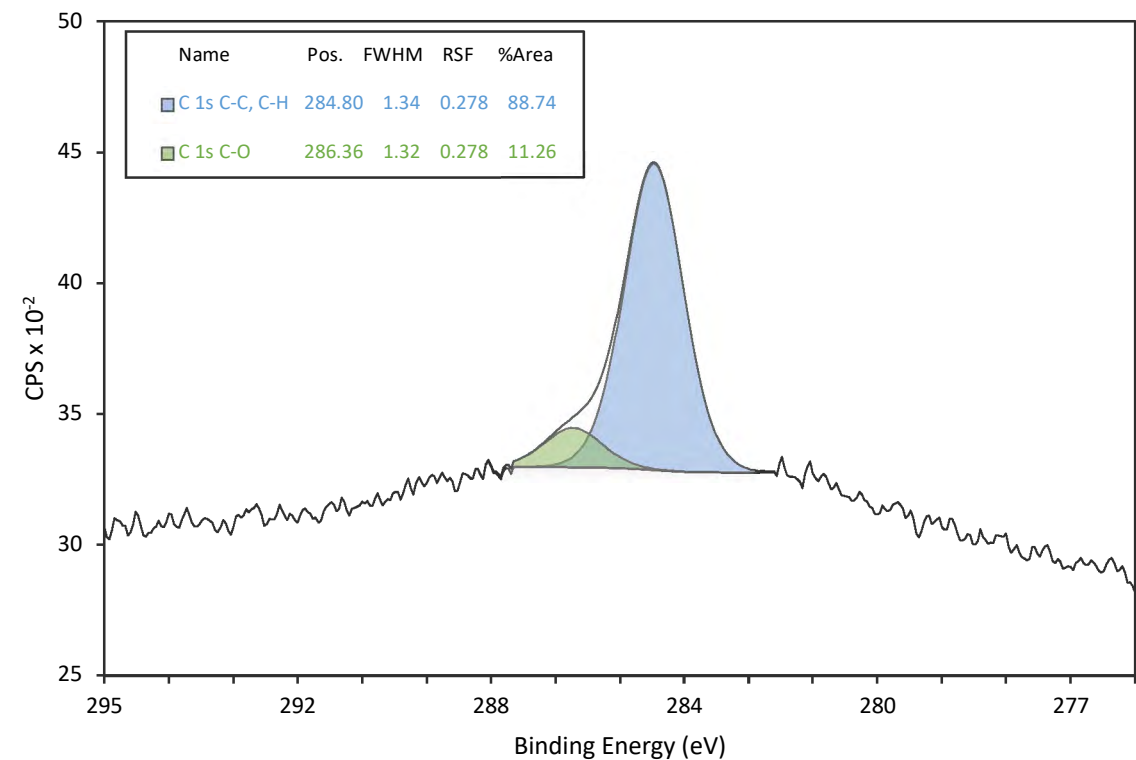


Figure C.8: C 1s XPS spectra from sperrylite conditioned at pH 9 without PAX

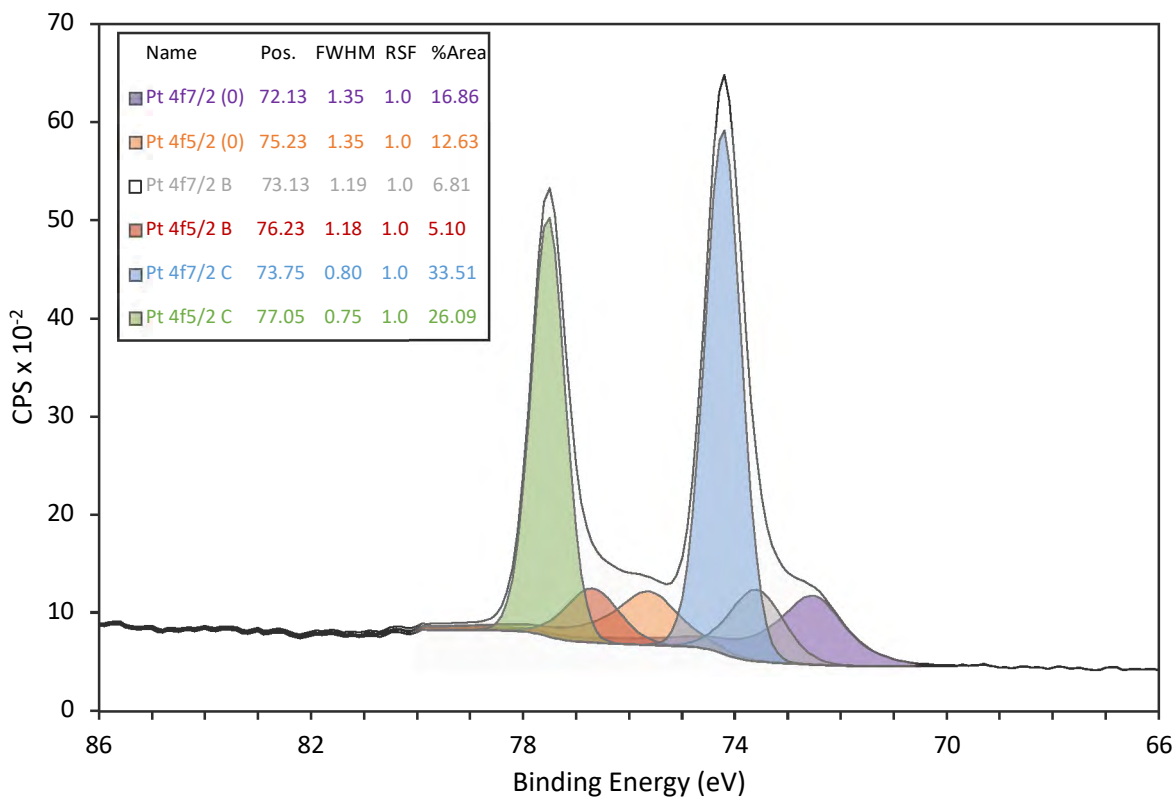


Figure C.9: Pt 4f XPS spectra from sperrylite conditioned at pH 3 without PAX

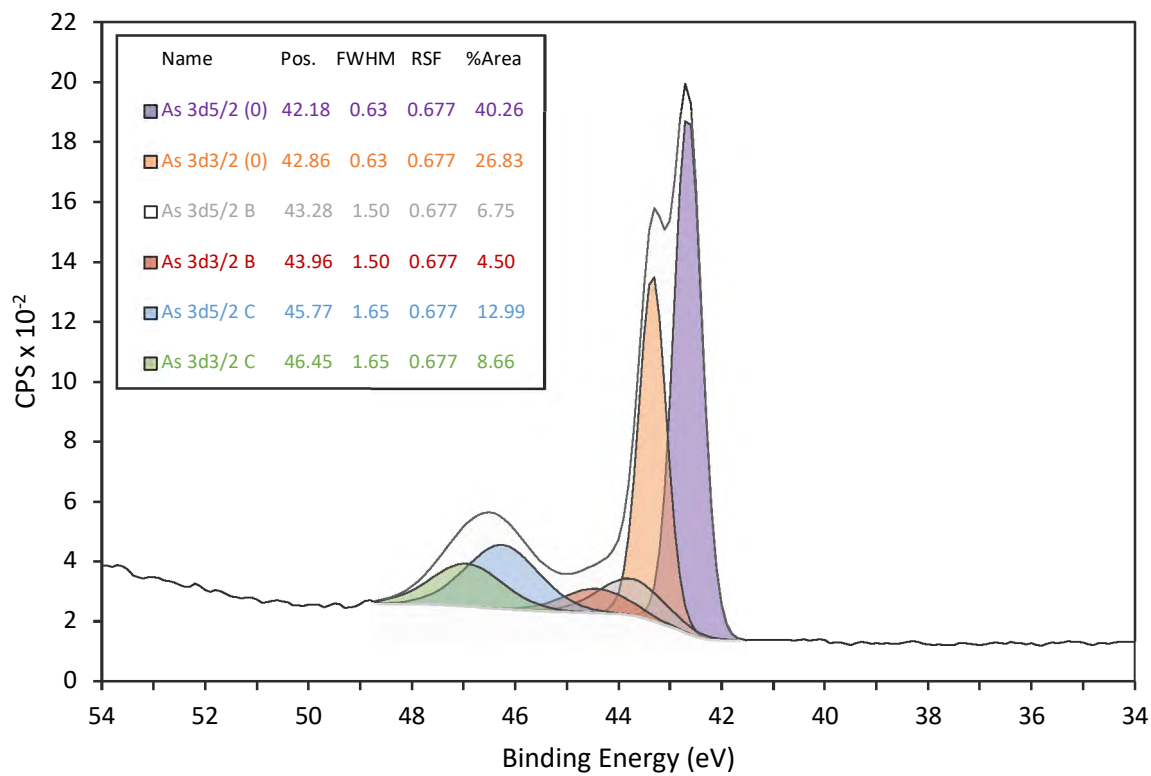


Figure C.10: As 3d XPS spectra from sperrylite conditioned at pH 3 without PAX

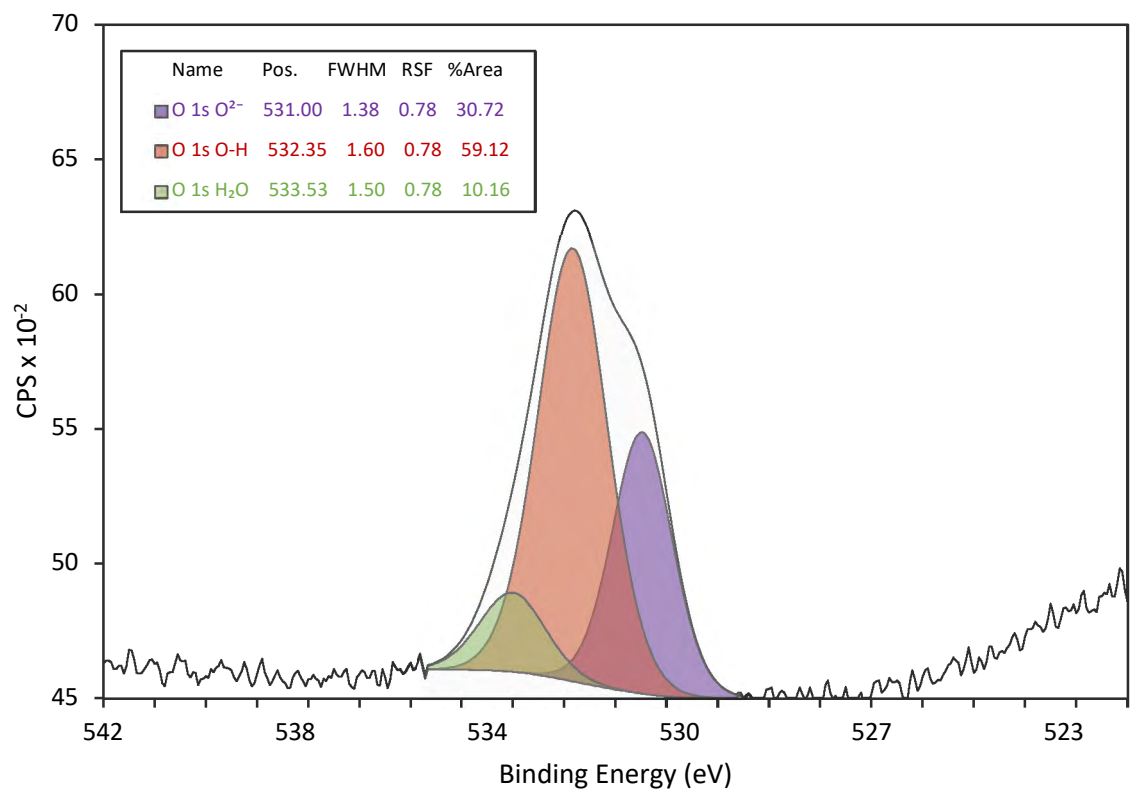


Figure C.11: O 1s XPS spectra from sperrylite conditioned at pH 3 without PAX

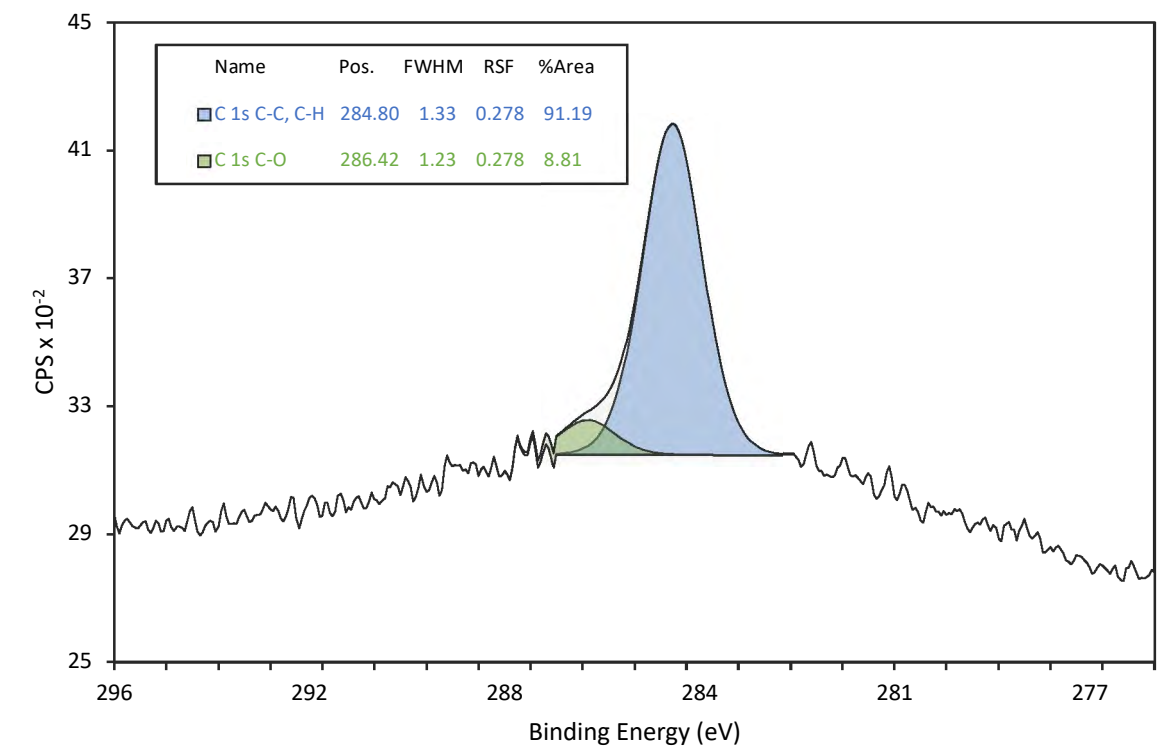


Figure C.12: C 1s XPS spectra from sperrylite conditioned at pH 3 without PAX

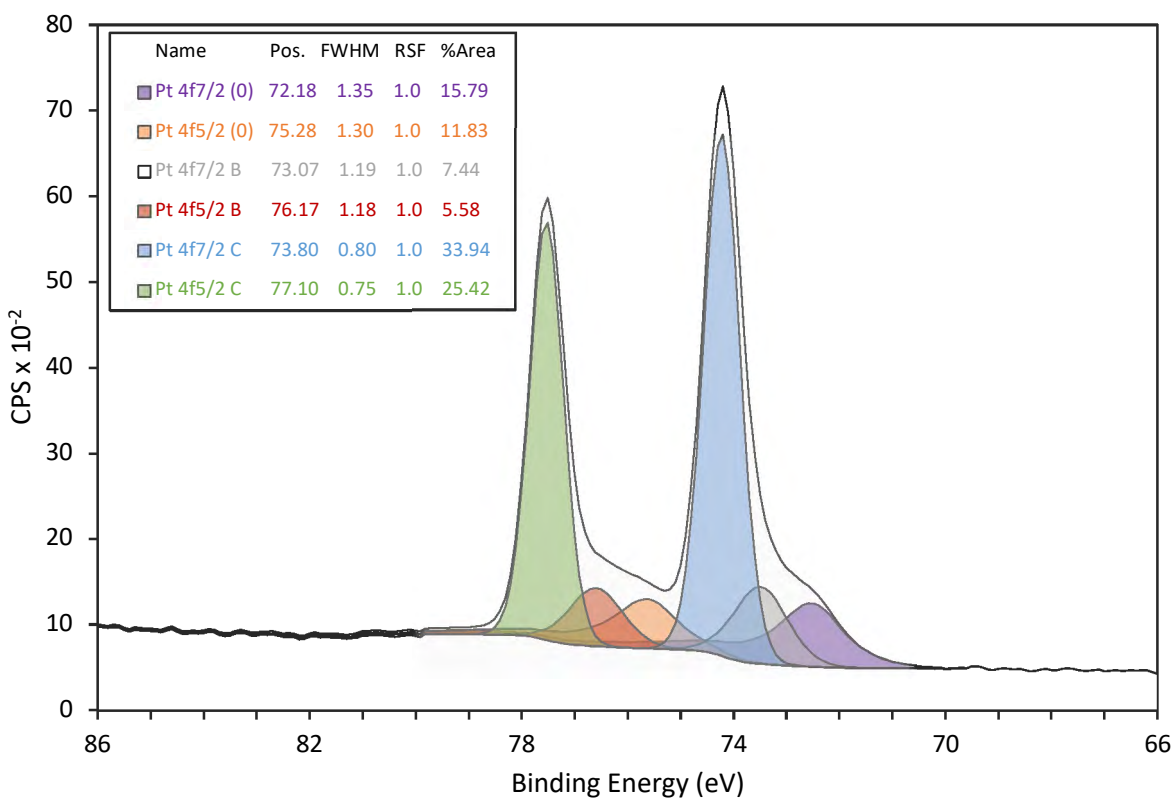


Figure C.13: Pt 4f XPS spectra from sperrylite conditioned at pH 9 with 5x10⁻⁰⁴ M PAX

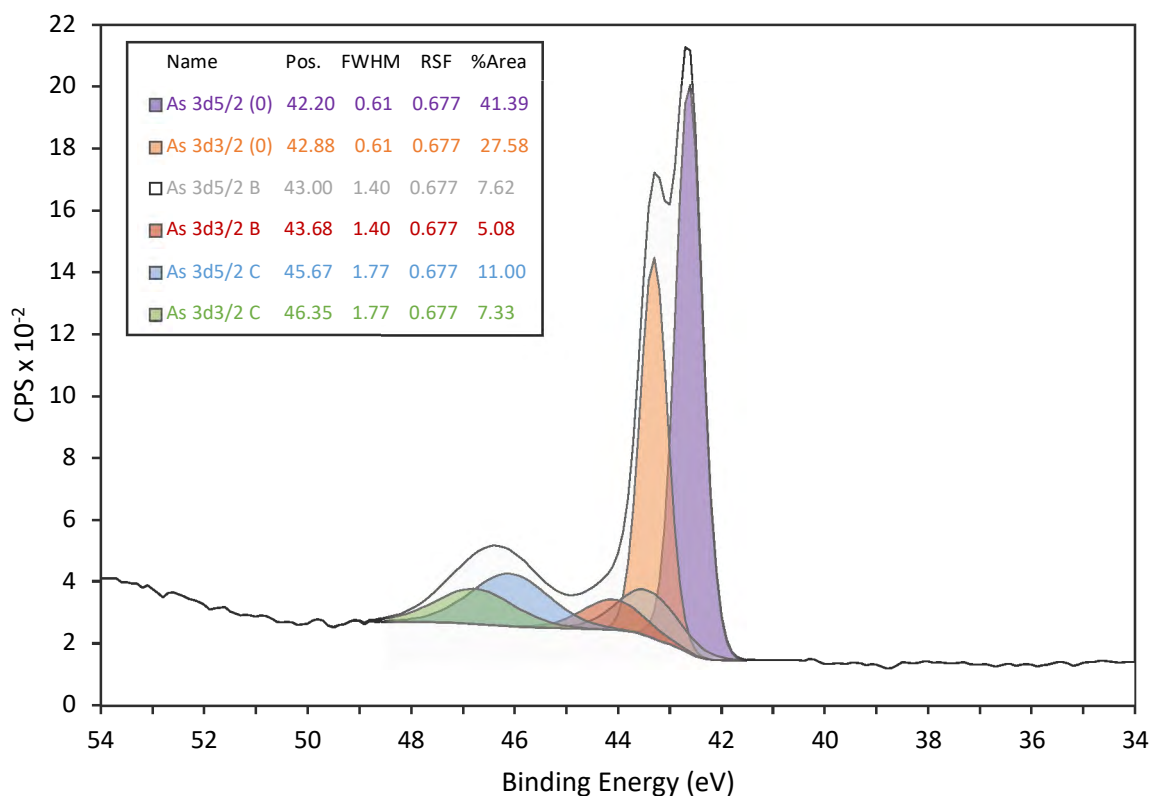


Figure C.14: As 3d XPS spectra from sperrylite conditioned at pH 9 with 5×10^{-4} M PAX

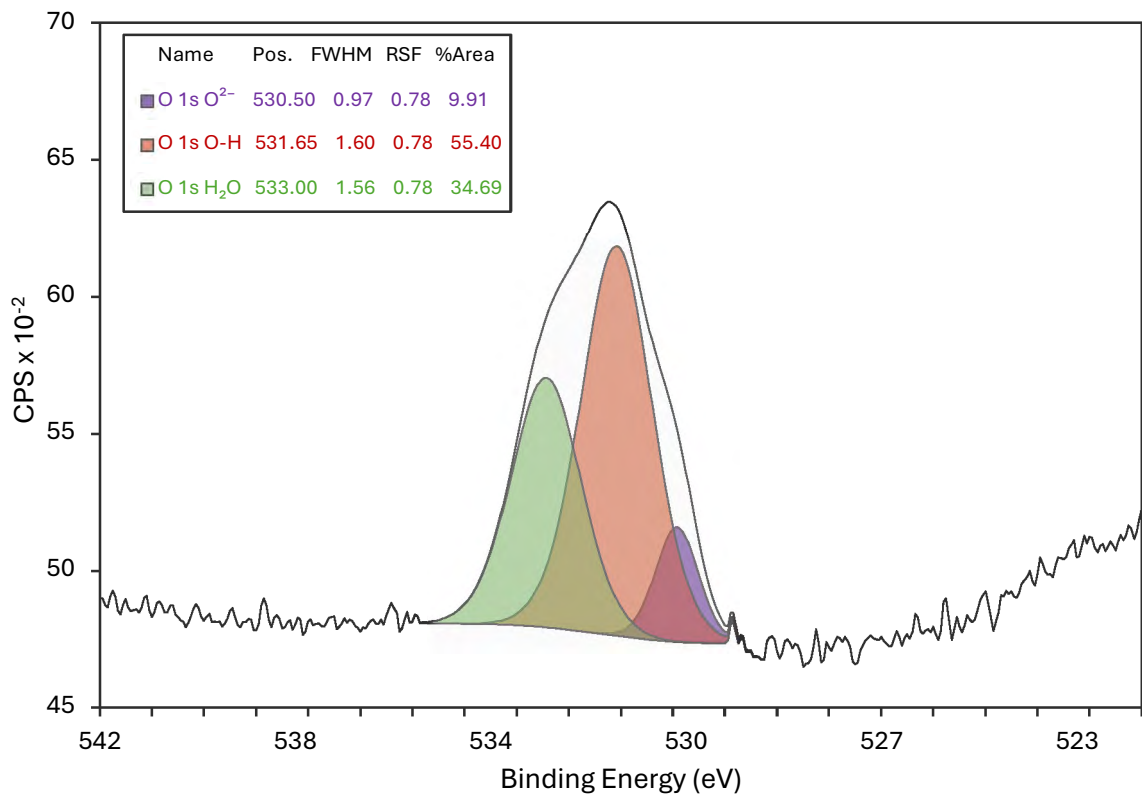


Figure C.15: O 1s XPS spectra from sperrylite conditioned at pH 9 with 5×10^{-4} M PAX

Chapter 9: Appendices

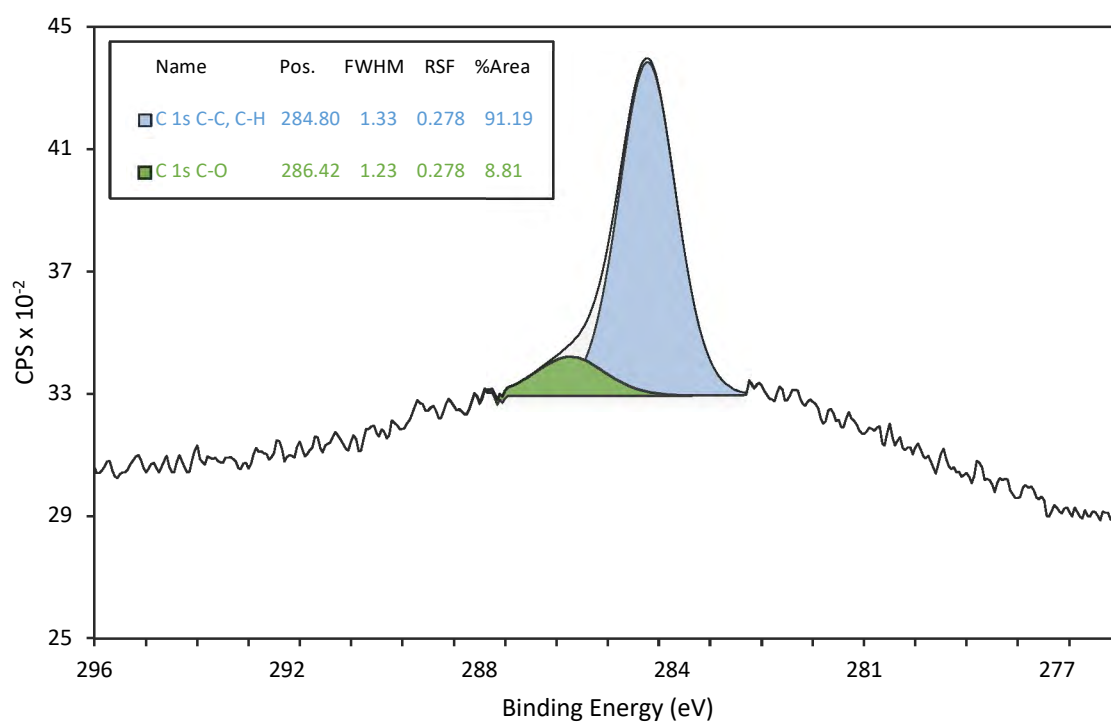


Figure C.16: C 1s XPS spectra from sperrylite conditioned at pH 9 with 5×10^{-4} M PAX

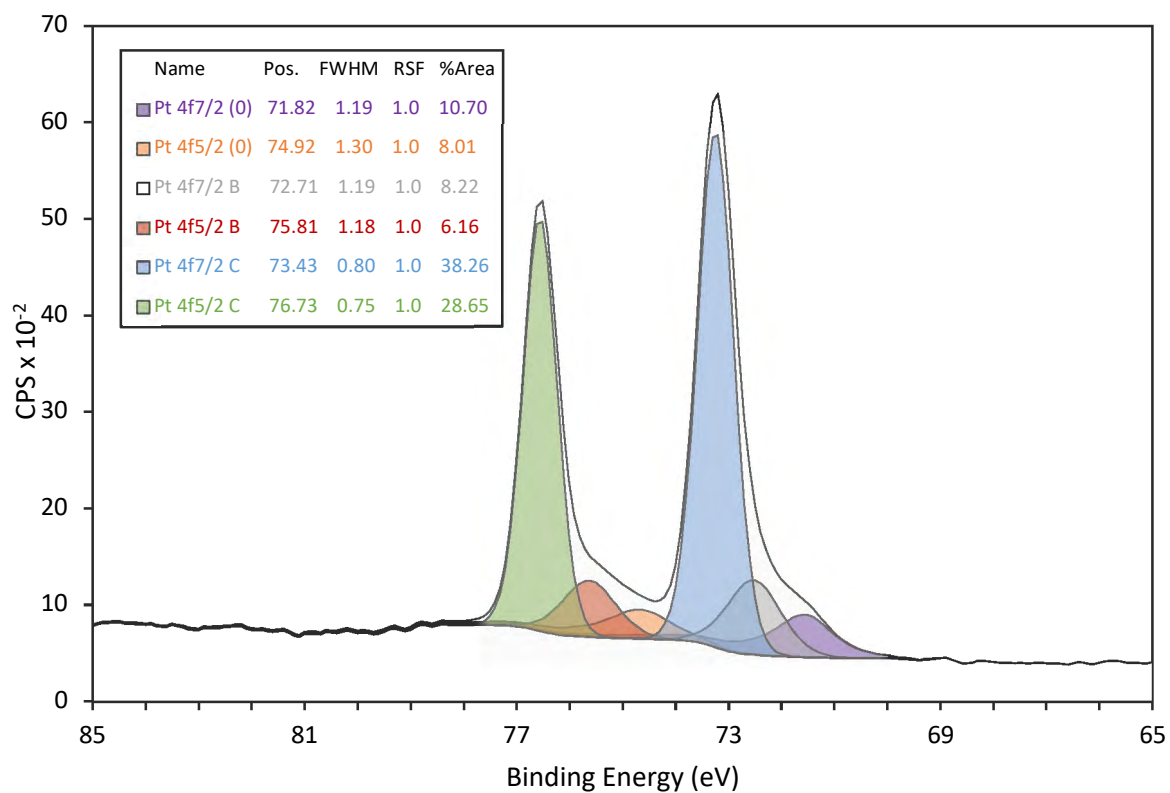


Figure C.17: Pt 4f XPS spectra from sperrylite conditioned at pH 3 with 5×10^{-4} M PAX

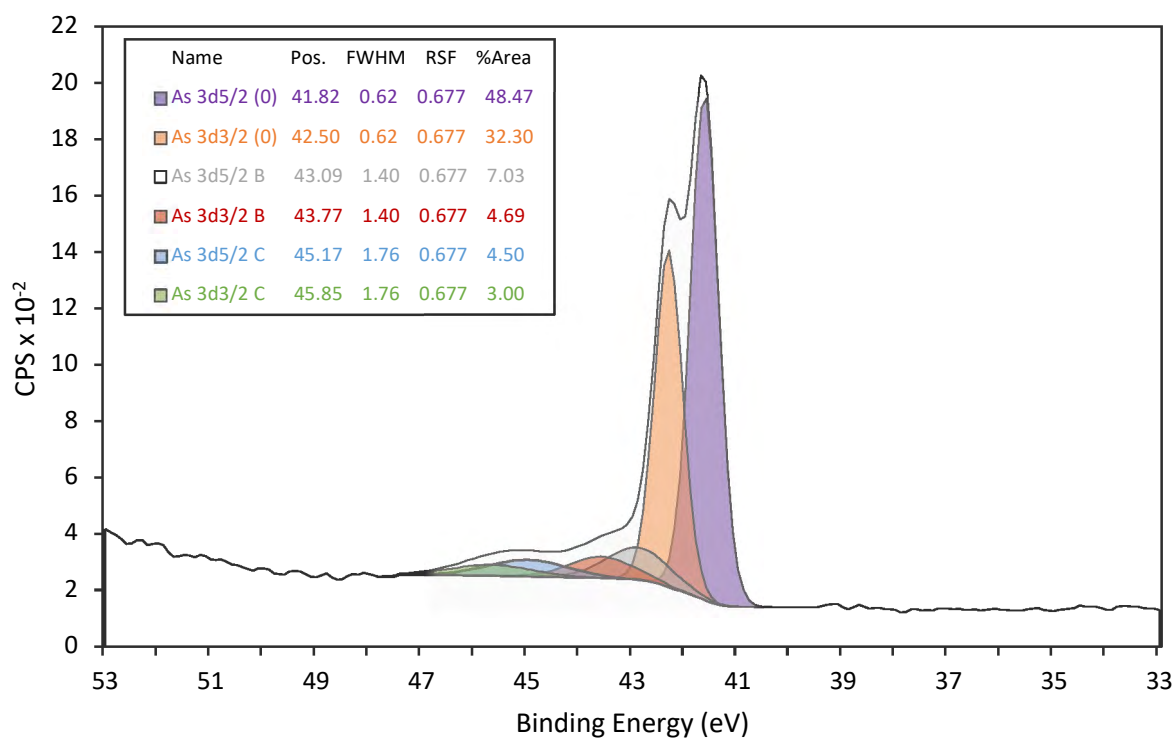


Figure C.18: As 3d XPS spectra from sperrylite conditioned at pH 3 with 5×10^{-4} M PAX

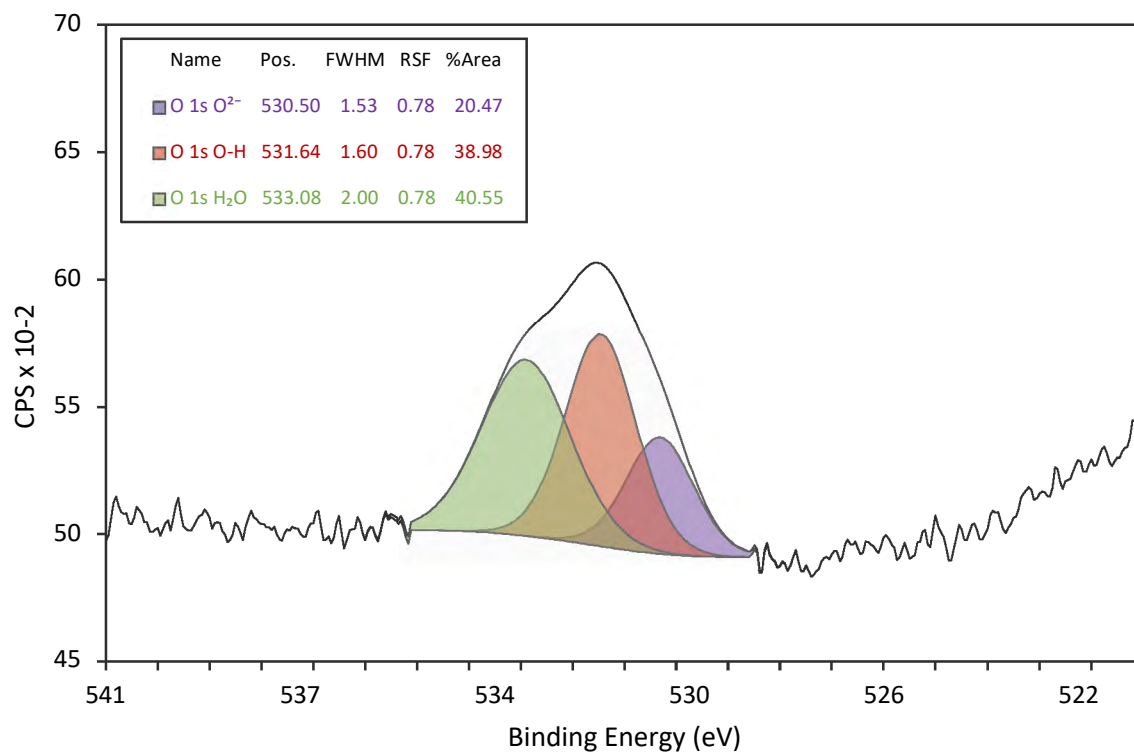


Figure C.19: O 1s XPS spectra from sperrylite conditioned at pH 3 with 5×10^{-4} M PAX

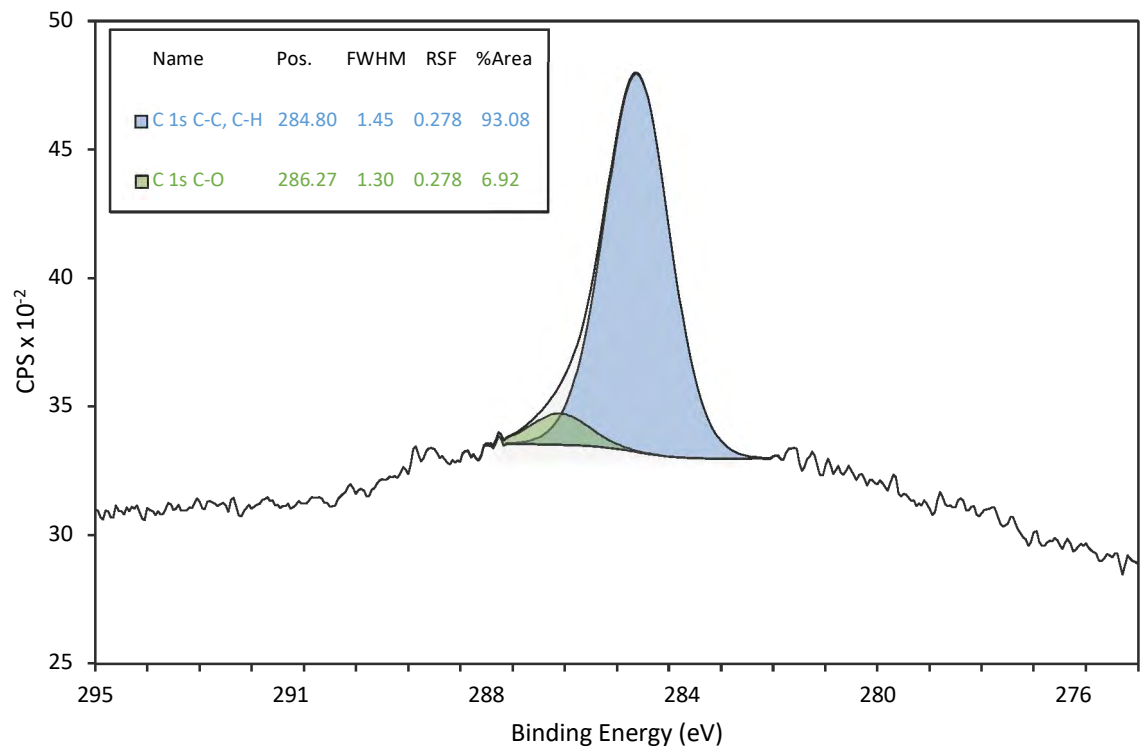


Figure C.20: C 1s XPS spectra from sperrylite conditioned at pH 3 with 5x10⁻⁰⁴ M PAX

D. APPENDIX D: Rest potential measurement profiles

The results presented in CHAPTER 6: Comparisons of floatability of PGE arsenides and tellurides showed the full rest potential profiles for only pH 3 and 9. The full rest potential profiles for the rest of the tested pH conditions, i.e. pH 5 and 7, are shown in this Appendix. The rest potentials at pH 5 and 7 are shown in Figure D.1 and Figure D.2, respectively.

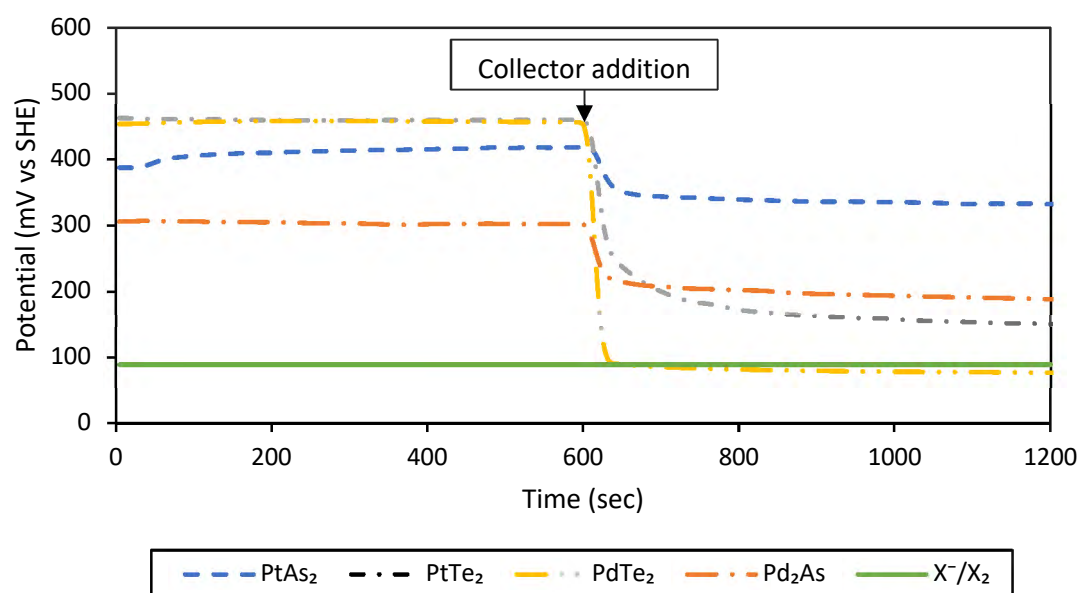


Figure D.1: Rest potential profiles of PtAs_2 , PtTe_2 , Pd_2As and PdTe_2 at pH 5; 6.24×10^{-4} M PAX added at 600 seconds

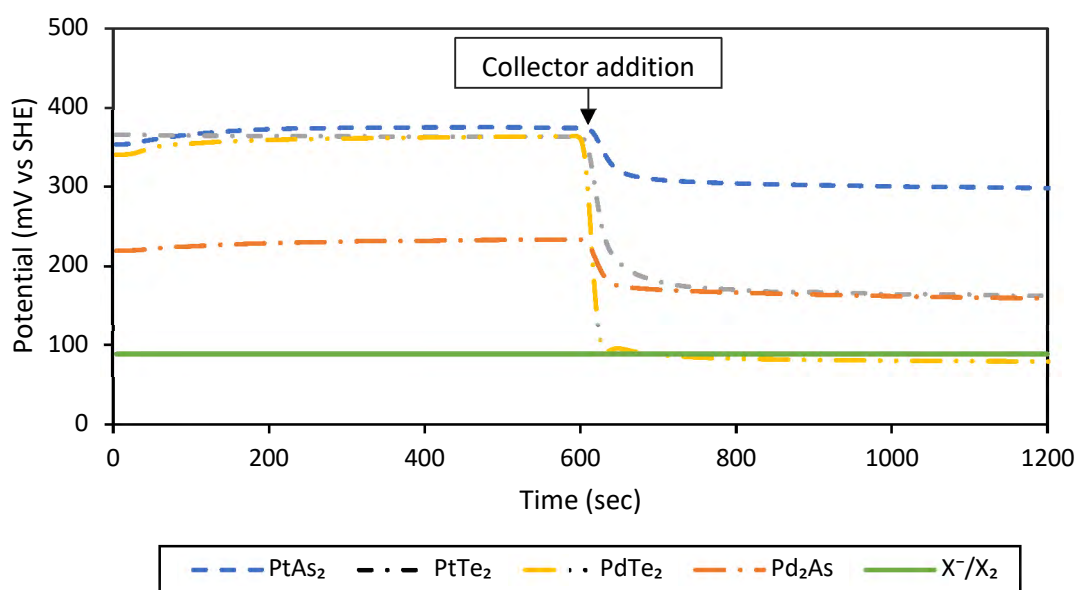


Figure D.2: Rest potential profiles of PtAs_2 , PtTe_2 , Pd_2As and PdTe_2 at pH 7; 6.24×10^{-4} M PAX added at 600 seconds

E. APPENDIX E: Batch flotation

In **Chapter 6**, the flotation kinetics of Pt, Pd, As and Te were reported. The flotation recoveries as a function of time that were used to determine the flotation kinetics are presented in this Appendix. The Klimpel model described by equation E-1 was used to the flotation rate constant:

$$R = R_{inf}(1 - e^{-kt}) \quad \text{E-1}$$

where:

- R - Recovery at time t (%)
- R_{inf} - Maximum possible recovery (%)
- k - first-order rate constant (min^{-1})
- t - time (min)

This model was fitted on the experimental Recovery-Time data using the least squares method, where R_{inf} and k were used as the fitted parameters. The Recovery-Time data is shown in Figure E.1 (Pt), Figure E.2 (Pd), Figure E.3 (As) and Figure E.4 (Te).

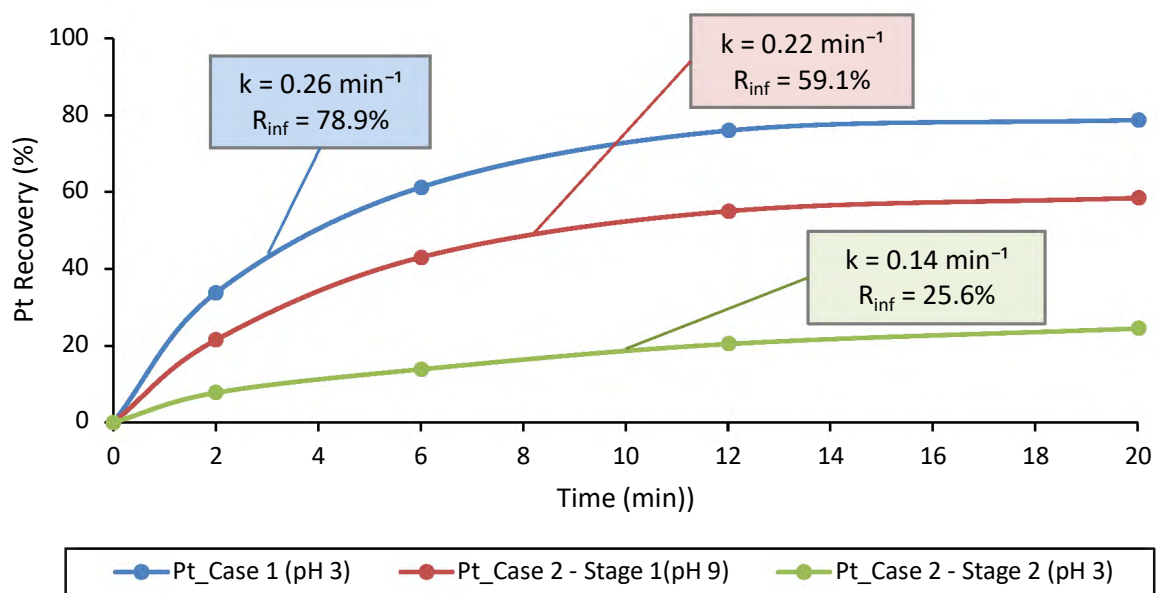


Figure E.1: Recovery of Pt as a function of time for the different batch flotations tests conducted

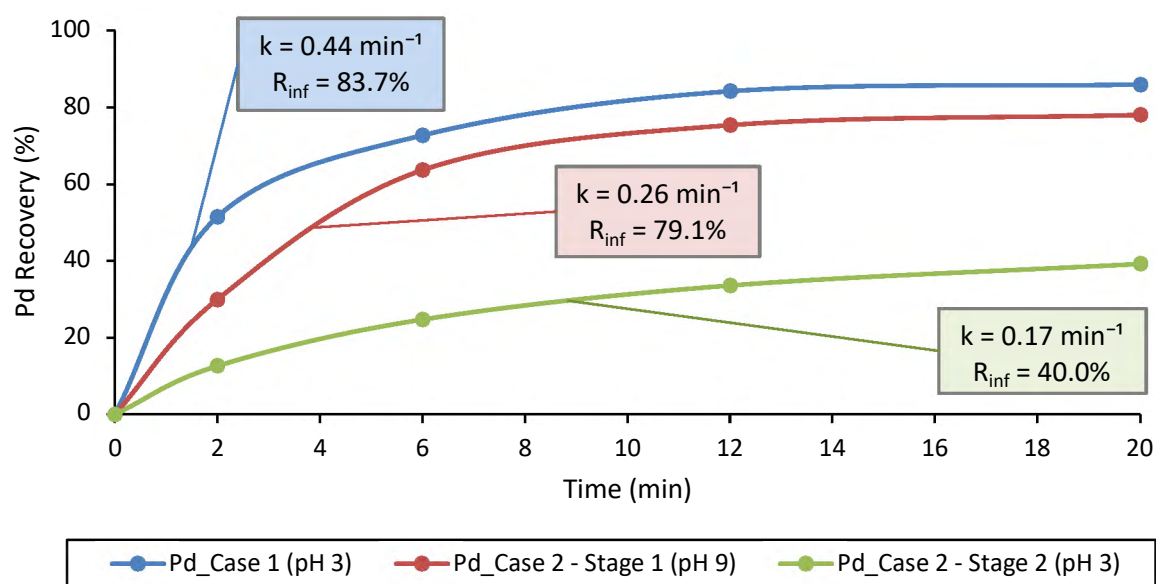


Figure E.2: Recovery of Pd as a function of time for the different batch flotation tests conducted

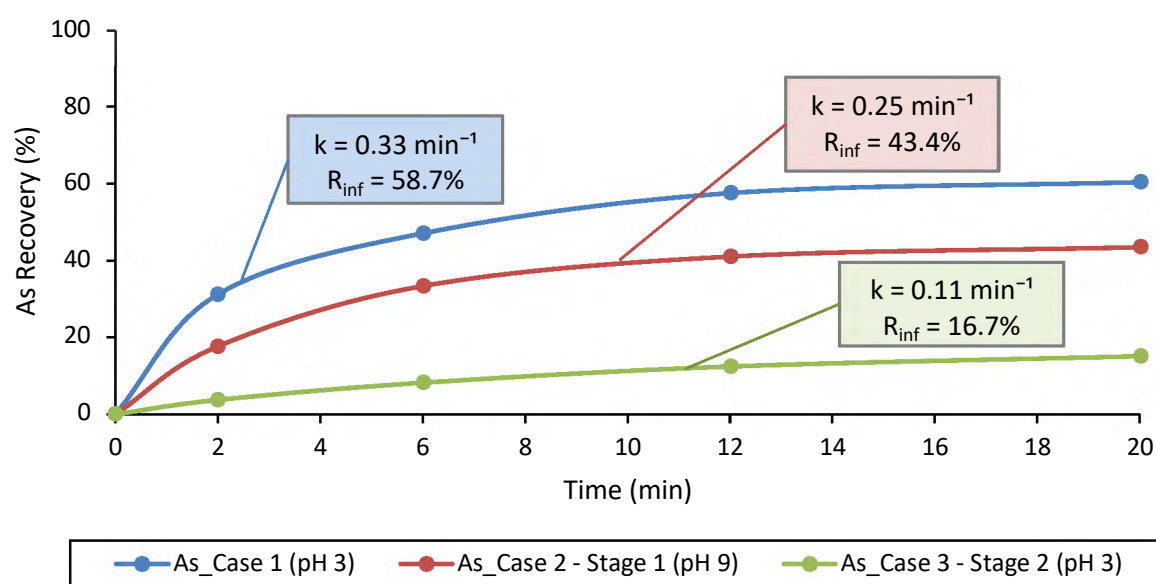


Figure E.3: Recovery of As as a function of time for the different batch flotation tests conducted

Chapter 9: Appendices

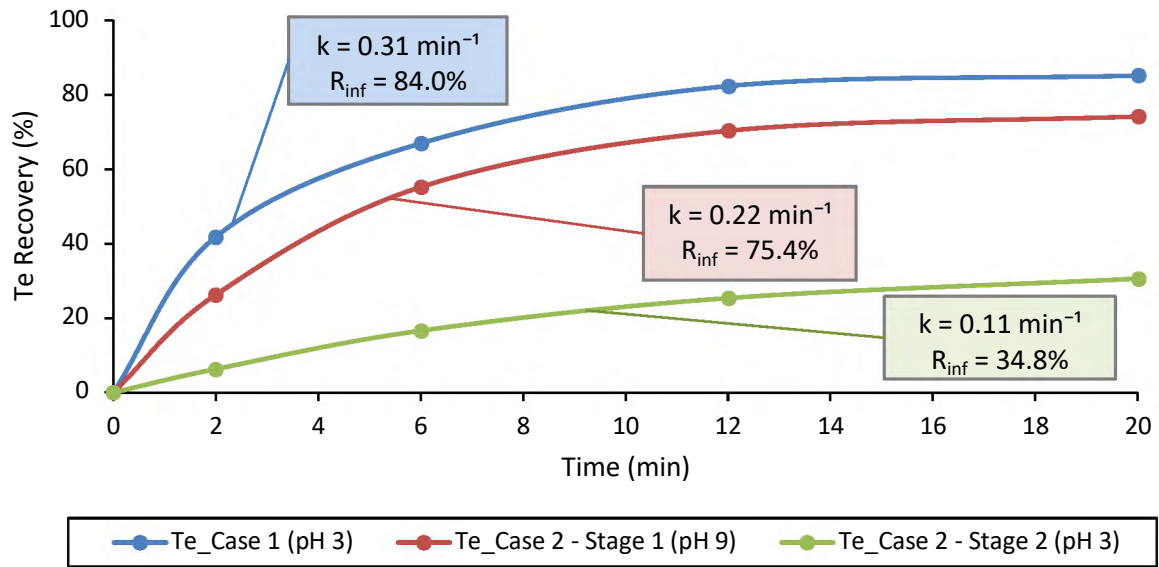


Figure E.4: Recovery of Te as a function of time for the different batch flotations tests conducted