

Niobium and tantalum beneficiation using gas-phase fluorination

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Executive Summary

Keywords: tantalum, niobium, separation, purification, gas-phase fluorination

The processing of minerals containing tantalum and niobium is a challenge that has most modern researchers focused on optimising the processes that have already reached scientific maturity. Ore digestion in aqueous mixtures of sulfuric and hydrofluoric acid, followed by selective liquid-liquid extraction, is the method of choice for recovery of tantalum and niobium from the parent minerals. As this method has significant environmental and practical drawbacks, there is a need for a new process to beneficiate these minerals.

The Advanced Metals Initiative (AMI) programme of the Department of Science and Technology (DST) proposes that no tantalum or niobium values should leave South Africa without some degree of local beneficiation. A significant strategic advantage may be gained from developing a process which is economically viable and more environmentally friendly.

This thesis proposes a technology which would circumvent many of the drawbacks of wet chemical systems. The proposed technology would use anhydrous fluorinating gases ($\text{HF}_{(g)}$ and F_2) to convert the oxidic minerals to oxyfluorides and/or fluorides, followed by thermal separation.

Since little is known about the reaction between the fluorinating agents mentioned and the ores containing Ta/Nb, a detailed study of these reactions and possible products for the current concept is realised.

Oxyfluorides are the most probable intermediates during the fluorination process. As part of the research, the most likely oxyfluoride intermediates were synthesised. The details of their spectral and crystallographic properties are discussed. Their thermal properties were investigated; this showed that oxyfluorides can be used to develop a thermal separation process in either the high

temperature (600-900 °C) or low temperature region (150-200 °C). Thermogravimetric analysis also suggests a difference in the decomposition pathways for niobium and tantalum oxyfluorides.

Dioxyfluoride is the most stable of the oxyfluorides and is a necessary byproduct, regardless of which other oxyfluoride is synthesised, and may occur even during the synthesis of the pentafluorides. It was therefore considered imperative to understand the decomposition kinetics of the dioxyfluoride compounds, to calculate the decomposition activation energies, and to construct physical decomposition models for these compounds. By means of mechanistic methods, it is shown that the decomposition of the oxyfluorides occurs *via* Avrami-Erofeev A2 or A3 models and that for this process the activation energy for TaO₂F (320 kJ.mol⁻¹) is roughly double that for NbO₂F (156 kJ.mol⁻¹).

Once the characterisation of the possible reaction intermediates had been completed, the reaction and interaction of F₂ and anhydrous HF with pure metal oxides of Ta and Nb were investigated. To this end, both thermogravimetric and differential scanning calorimetry were employed. Thermodynamic calculations indicated that for both these fluorinating agents, the corresponding pentafluorides were the preferred (indeed the only) reaction products, though the experimental results showed that a whole range of oxyfluorides form. The data collected showed no evidence of a two-step mechanism, as has been observed for Nb₂O₅, for the fluorination of Ta₂O₅ with elemental fluorine. However, in both cases the rate-limiting step is governed by the contracting volume (R3) mechanistic. The activation energy for the Ta₂O₅ + F₂ reaction is 63-67 kJ.mol⁻¹, and leads to the formation of the pentafluoride without detectable oxyfluoride formation.

A single ore containing tantalum and niobium was selected for study and characterised prior to evaluating its reaction with the chosen fluorinating gases. As the reaction products have a substantially more complex matrix, they were shown to be far less self-evident than in the studies conducted on the pure oxides. Nevertheless, it is shown that separation using this methodology is indeed feasible. Aided by techniques such as SEM and ICP-OES, it could be shown that physical and chemical changes occur in the mineral during the fluorination reaction.

The concluding chapter considers the information assimilated during this study and provides likely scenarios for a process based on the selective volatilisation of tantalum and niobium

fluorides and oxyfluorides. Two likely processes are postulated, the first one involving partial fluorination and sublimation, the second one complete fluorination to the pentafluoride.

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Conferences and publications

Patent

- Wagener, J.B., Pienaar, A.D., Carstens, P.A.B., Treatment of tantalum- and/or niobium-containing compounds and recovery of these compounds, WO 2011121573.

Peer-reviewed publications

- Pienaar, A.D., Vilakazi, B., (2012). “Gas-phase fluorination kinetics of Ta₂O₅ with elemental fluorine”, *The Journal of the Southern African Institute of Mining and Metallurgy*, 7a: 545.
- Pienaar, A.D., Crouse, P.L., Wagener, J.B., (2012). “Niobium and tantalum separation by gas-phase fluorination”, *International Journal of Mineral Processing*, **114**: 7.

Non-peer-reviewed publications

- Pienaar, A.D., (2012). “Separation of Ta and Nb using a dry process”, *Innovate*, 70.

Conference contributions

- Pienaar, A.D., (2010). *Reaction of fluorinating gasses with tantalum and niobium pentoxide*, Light Metals Conference, Misty Hills, Johannesburg.
- Lekgoathi, M. D. S., Pienaar, A.D., (2010). *Spectroscopic study of tantalum and niobium oxyfluorides*, The South Africa Institute of Mining and Metallurgy, Light Metals Conference, Misty Hills Conference Centre.
- Pienaar, A.D., Wagener, J.B., (2011). *Formation of oxyfluorides of niobium and tantalum using solid-gas reactions*, SACI, Wits University, Johannesburg.
- Pienaar, A.D., Wagener, J.B., Crouse, P.L., (2011). *Niobium and tantalum separation using gas-phase fluorination*, 11th International Conference on Frontiers of Polymers and Advanced Materials, University of Pretoria, Pretoria.
- Pienaar, A.D., Kock, L.D., (2011). *Characteristic investigation of niobium and tantalum dioxyfluoride*, ZrTa2011, Mount Grace, Magaliesburg.

- Pienaar, A.D., (2013). *Perspectives on dry fluoride based separation of Tantalum and Niobium*, The South African Institute of Mining and Metallurgy, PMDN Conference, President Hotel, Cape Town.

Contents

LIST OF FIGURES	xi
CHAPTER 1	1
1.1 Background	1
1.2 Current and historical research processes	3
1.2.1 The Marignac process	4
1.2.2 Nitrofluor	5
1.2.3 Liquid-liquid extraction	5
1.3 Dry separation	7
1.4 Patent analysis.....	9
1.5 Aims and objectives	10
1.6 References.....	11
CHAPTER 2	14
OXYFLUORIDES OF TANTALUM AND NIOBIUM	14
2.1 Introduction.....	14
2.2 Experimental	15
2.2.1 Preparation of MO_2F	15
2.2.2 Preparation of MOF_3	16
2.2.3 Characterisation of oxyfluorides	17
2.3 Results and discussion	17
2.3.1 Dioxyfluorides	17
2.3.2 Characterisation	17
2.3.3 Thermal decomposition	23
2.4 Higher fluorinated oxyfluorides ($\text{O:F} < 2$).....	25
2.5 Conclusion	30

2.6	References.....	31
CHAPTER 3		34
DECOMPOSITION KINETICS OF MO_2F		34
3.1	Introduction.....	34
3.2	Theoretical background	35
3.3	Experimental	38
3.3.1	Samples	38
3.3.2	Thermal decomposition experiments	38
3.4	Results and discussion	38
3.4.1	Niobium dioxyfluoride (NbO_2F)	38
3.4.2	Tantalum dioxyfluoride (TaO_2F).....	44
3.5	Conclusion	49
3.6	References.....	49
CHAPTER 4		51
FLUORINATION OF Nb_2O_5 AND Ta_2O_5		51
4.1	Introduction.....	51
4.2	Experimental	52
4.2.1	F_2 fluorination of $\text{Ta}_2\text{O}_{5(\text{g})}$	52
4.2.2	$\text{HF}_{(\text{g})}$ fluorination in DSC	53
4.3	Theory behind experimental runs	53
4.3.1	Fluorination of Ta_2O_5 with F_2	53
4.3.2	$\text{HF}_{(\text{g})}$ fluorination	55
4.4	Results and discussion	55
4.4.1	$\text{F}_{2(\text{g})}$ fluorination of Ta_2O_5	55
4.4.2	$\text{HF}_{(\text{g})}$ fluorination of Nb_2O_5 and Ta_2O_5	61

4.4.2.1	Thermodynamic calculations.....	61
4.4.2.2	DSC study of the $\text{Nb}_2\text{O}_5 + \text{HF(g)}$ reaction	65
4.4.2.3	DSC study of the $\text{Ta}_2\text{O}_5 + \text{HF(g)}$ reaction	68
4.5	Conclusion	69
4.6	References.....	70
CHAPTER 5		71
SEPARATION OF Nb_2O_5 AND Ta_2O_5		71
5.1	Introduction.....	71
5.2	Experimental	71
5.2.1	Fluorination reactions.....	71
5.2.2	Preparation of model compounds	72
5.3	Results and discussion	73
5.3.1	Single-component reactions	73
5.3.2	Reaction of mixtures	78
5.4	Conclusion	79
5.5	References.....	79
CHAPTER 6		80
FLUORINATION OF TANTALITE ORE CONCENTRATE.....		80
6.1	Introduction.....	80
6.2	Experimental	81
6.2.1	Instrumentation	81
6.2.2	Fluorination reactions.....	81
6.2.3	Characterisation of ore concentrate.....	81
6.2.3.1	Milling	81
6.2.3.2	ICP-OES/XRF analyses.....	83

6.2.3.3 SEM/EDS analyses	84
6.3 Reaction of ore concentrate with $F_{2(g)}$	85
6.4 Reaction with $HF_{(g)}$	88
6.5 Separation using $HF_{(g)}$	94
6.6 References.....	97
CHAPTER 7	99
PROCESS FLOW DIAGRAMS	99
7.1 Discussion of possible processes	99
7.2 Partial fluorination and sublimation.....	99
7.3 Complete fluorination and sublimation	100
7.4 Concluding remarks	101
7.5 References.....	102
APPENDIX A.....	103
INSTRUMENTATION.....	103
A. C80 Calorimeter.....	103
B. SDT Q600 TG/DSC.....	105
C. Corrosive TG	106

LIST OF FIGURES

Figure 1: Percentage of globally mined tantalum of the main tantalum-producing countries.	2
Figure 2: Schematic diagram of industrially practiced niobium and tantalum production (Zhu and Cheng).	6
Figure 3: Background subtracted powder diffraction pattern of prepared sample overlaid with stick patterns of the proposed niobium dioxyfluoride (NbO_2F) phase and the corresponding Miller indices.	18
Figure 4: Powder diffraction pattern of prepared TaO_2F overlaid with a stick pattern of database XRD pattern of TaO_2F	19

Figure 5: FTIR spectrum for prepared NbO ₂ F and TaO ₂ F.	21
Figure 6: Deconvoluted Raman spectrum of prepared NbO ₂ F.	21
Figure 7: Deconvoluted Raman spectrum of TaO ₂ F.	22
Figure 8: Decomposition analysis of prepared NbO ₂ F.	24
Figure 9: TG for prepared TaO ₂ F.	25
Figure 10: XRD pattern for the reaction product of niobium pentafluoride and niobium dioxyluoride overlaid with stick patterns for NbOF ₃ . This pattern clearly shows unreacted NbO ₂ F.	26
Figure 11: XRD pattern of the reaction product of tantalum pentafluoride and tantalum dioxyluoride overlaid with stick patterns for TaOF ₃ . This pattern clearly shows unreacted TaO ₂ F.	26
Figure 12b: FTIR spectrum of synthesised TaOF ₃	28
Figure 13: Raman spectrum of synthesised NbOF ₃	28
Figure 14: Raman spectrum of synthesised TaOF ₃	29
Figure 15: TG of synthesised TaOF ₃	29
Figure 16: TG of synthesised NbOF ₃	30
Figure 17: TG curves for the decomposition of NbO ₂ F at different heating rates.	39
Figure 18: E_a values for the decomposition of NbO ₂ F according to the Starink method.	40
Figure 19: The da/dT curves for the decomposition of NbO ₂ F at different heating rates.	42
Figure 20: Coats-Redfern plot for the decomposition of NbO ₂ F.	43
Figure 21: Fit of calculated to experimental data for the decomposition of NbO ₂ F.	44
Figure 22: TG curves for the decomposition of TaO ₂ F at different heating rates.	45
Figure 23: E_a values for the decomposition of TaO ₂ F according to the Starink method.	46
Figure 24: Coats-Redfern linearity plot for the decomposition of TaO ₂ F. With A2 fitted.	47
Figure 25: Fit of calculated to experimental data for the decomposition of TaO ₂ F.	48
Figure 26: Simulated Avrami-Erofeev data for n=2 and n=3 plotted with experimental data. ...	48
Figure 27: Data set for Ta ₂ O ₅ + F ₂ at 325 °C. At T > 90 °C the product TaF ₅ is gaseous and volatilised from the TG crucible.	54
Figure 28: Fluorination results of niobium (Pienaar and Wagener, 2011) and tantalum oxide treated with elemental fluorine.	56
Figure 29: Graph constructed from collected data runs for the fluorination of Ta ₂ O ₅	57

Figure 30: Conversion at different fluorination temperatures.	58
Figure 31: $g(\alpha)$ vs. t plot for the fluorination of Ta_2O_5 with F_2 assuming the R3 model.	60
Figure 32: A plot of $\ln(k)$ against $1/T$ for the considered reaction models.	61
Figure 33: Gibbs free energy plots (calculated from HSC Chemistry®) for the reaction between $HF_{(g)}$ and pentoxide forms of niobium and tantalum.	62
Figure 34: Gibbs free energy plots for oxyfluoride formation during the reaction between $HF_{(g)}$ and pentoxides of niobium and tantalum.	62
Figure 35: Gibbs free energy plots for product interactions from the Nb_2O_5 and $HF_{(g)}$ reaction.	63
Figure 36: Free energy calculation for the conversion of $NbOF_3$ to gas phase. This graph shows that it becomes thermodynamically possible at 140 °C.	63
Figure 37: Gibbs free energy plots for solid-solid reaction products of tantalum oxyfluorides (no information for $TaOF_{3(s)}$).	64
Figure 38: Heat evolved during the reaction between $HF_{(g)}$ and Nb_2O_5 at different isothermal temperatures.	66
Figure 39: TG profile for Nb-A, the product of Nb_2O_5 and $HF_{(g)}$ at 30 °C.	66
Figure 40: TG profile for Nb-A, the product of Nb_2O_5 and $HF_{(g)}$ at 50 °C.	67
Figure 41: TG profile for Nb-B, the product of Nb_2O_5 and $HF_{(g)}$ at 60 °C.	67
Figure 42: Heat evolved during the reaction between $HF_{(g)}$ and Ta_2O_5 at different isothermal temperatures.	68
Figure 43: TG of products for 50 °C runs (runs 2 and 3).	69
Figure 44: Energy profiles for single-component reactions ($M_2O_5 + HF$). (solid line: $M = Nb$, dashed line: $M = Ta$)	74
Figure 45: TG profiles for experimental fluorination products of Nb_2O_5 and Ta_2O_5	76
Figure 46: First derivative for (normalised) TG data for oxyfluoride species (dotted line for $M = Nb$ and solid line for $M = Ta$).	77
Figure 47: Energy profile observed for the reaction of $HF_{(g)}$ with mixtures of Ta_2O_5 and Nb_2O_5	78
Figure 48: Particle size distribution using the sieve and shaker method.	83
Figure 49: Elements measured using EDS.	85
Figure 50: TG/DSC analysis of the untreated tantalite.	86

Figure 51: Reaction of $F_{2(g)}$ with tantalite ore concentrate during a dynamic temperature curve from 20 to 500 °C.....	87
Figure 52: First derivative (smoothed) of the TG curve presented in Figure 51.	88
Figure 53: Heat flow observed during the $HF_{(g)}$ treatment of tantalite at different temperatures.	89
Figure 54: TG graphs of tantalite and $HF_{(g)}$ reaction products at different temperatures.	90
Figure 55: Free energy of formation for the fluorides of different metals during the reaction between their oxides and $HF_{(g)}$	90
Figure 56: SEM image of tantalite ore concentrate at different magnifications.....	91
Figure 57: BSE (back-scattering) mode of SEM image.	92
Figure 58: SEM image of product at 200 °C.	92
Figure 59: SEM back-scattering image of product at 200 °C.	93
Figure 60: SEM images of product at 1000 °C.	93
Figure 61: SEM BSE image of product at 1000 °C.	94
Figure 62: Changes in Nb:Ta ratio for samples heated to different temperatures post-fluorination.....	96
Figure 63: Process block diagram for partial fluorination and sublimation.	100
Figure 64: Process block diagram for complete fluorination and sublimation.....	101
Figure 65: C80 sample vessel.	104
Figure 66: PID for the gas handling of Setaram C80.	105
Figure 67: Image of the SDT Q600.	106
Figure 68: Schematic diagram of the modified TG instrument	107

LIST OF TABLES

Table 1: Common minerals used as sources for niobium and tantalite (Agulyansky, 2004).	3
Table 2: Owners of tantalum and niobium patents filed during the past 10 years.....	9
Table 3: Top ranking patents according to Formula 5.	10
Table 4: Characterisation completed on niobium and tantalum oxyfluoride species by other researchers.....	16
Table 5: Comparison of unit cell data found in the literature to the data calculated from this experimental work. All angles are 90 °.	18

Table 6: Miller indices for NbO ₂ F and TaO ₂ F according to the Treor algorithm.....	20
Table 7: Values obtained for Starink's method.	40
Table 8: Mechanistic models that give an upward convex shape for a plot of (d α /dt) vs. α	41
Table 9: E _a and ln(A) according to the Coates-Redfern method for NbO ₂ F.....	42
Table 10: Refined A2 kinetic parameters for NbO ₂ F.	44
Table 11: Values obtained using Starink's method.	45
Table 12: The value of E _a for the decomposition of TaO ₂ F during three stages of conversion .	46
Table 13: E _a and ln(A) according to the Coates-Redfern method for TaO ₂ F.	47
Table 14: Optimised kinetic parameters from a gridsearch for TaO ₂ F.	49
Table 15: Conversion values (α) for the experiment at different temperature and exposure times.	57
Table 16: Values of k determined by calculating the slope of a plot of g(α) against time.	60
Table 17: Experimental conditions for Ta ₂ O ₅ fluorination runs.	68
Table 18: Mixtures of tantalum and niobium pentoxide prepared for separation.....	72
Table 19: Operating parameters for fluorination experiments.....	72
Table 20: Experimental volatilisation temperatures of prepared oxyfluoride species and pentafluorides.....	73
Table 21: Products identified using the 2007-PDF-2 database for the reaction between M ₂ O ₅ and HF _(g)	75
Table 22: Mass ratio of Nb:Ta according to ICP-OES results before heating to 165 °C and after.	78
Table 23: Particle size distribution using the sieve and shaker method.....	82
Table 24: Comparative metal analysis of milled tantalite ore (main fraction).	84
Table 25: Elements identified with EDS.....	85
Table 26: Heat treatment temperature for each experiment.....	95
Table 27: ICP results for selected metal values.	95
Table 28: Nb/Ta ratio for different post fluorination heat treatments.	96
Table 29: Preferred Ta/Nb separation pairs.	99
Table 30: Technical specifications for TA SDT Q600.	105

CHAPTER 1

INTRODUCTION

1.1 Background

As tantalum is needed for the production of electronic components in devices such as cell phones, DVD players and mobile gaming stations (Agulyansky, 2004), the volume of tantalum consumed by world markets has increased significantly in recent years. In particular, the beneficiation of tantalum from tantalite ore is lucrative as the value increases from US\$132 /kg for the ore concentrate to US\$660 /kg for the capacitor grade tantalum powder (Kabangu and Crouse, 2012). Many tantalum consumers have accumulated significant stockpiles of tantalum, which has made mining less profitable. In 2008 several tantalum mines suspended their mining operations for this reason.

Though the predominating beneficiators of tantalum are located in Australia and Brazil, there are significant deposits on the African continent*, notably in countries such as Rwanda, Mozambique and the Democratic Republic of Congo (Enghag, 2000; Survey, 2011). In fact, in the period from 2005 to 2010, African countries collectively became the greatest source of tantalite ore (Figure 1). Pegmatites are the main source of tantalum in South Africa and are usually mined as by-products of commodities such as mica and feldspar.

Up to 200 tonnes/month of unprocessed ore may reach the South African borders, and considering the tantalum value chain, the economic value of processing these ores is self-evident. The AMI (Advanced Metals Initiative) is a resource beneficiation programme of the Department of Science and Technology (DST) of the South African government. As part of this department's vision, it is suggested that Ta and Nb ore should not be allowed to pass unprocessed through South Africa's borders. To this end, a new anhydrous fluoride route is envisaged for the beneficiation of niobium and tantalum minerals. The research into this dry fluorination process in which niobium and tantalum ores are processed, is potentially unique to South Africa and would give the country a unique competitive advantage. This research

*Official reports from the Department of Minerals and Energy state that about 19% of tantalum ores occur in Africa, but a presentation by the President of the international Tantalum/Niobium Study Center in 2011 gives the occurrence as being closer to 10%.

may also result in several opportunities for patents and strengthen the country's intellectual property position.

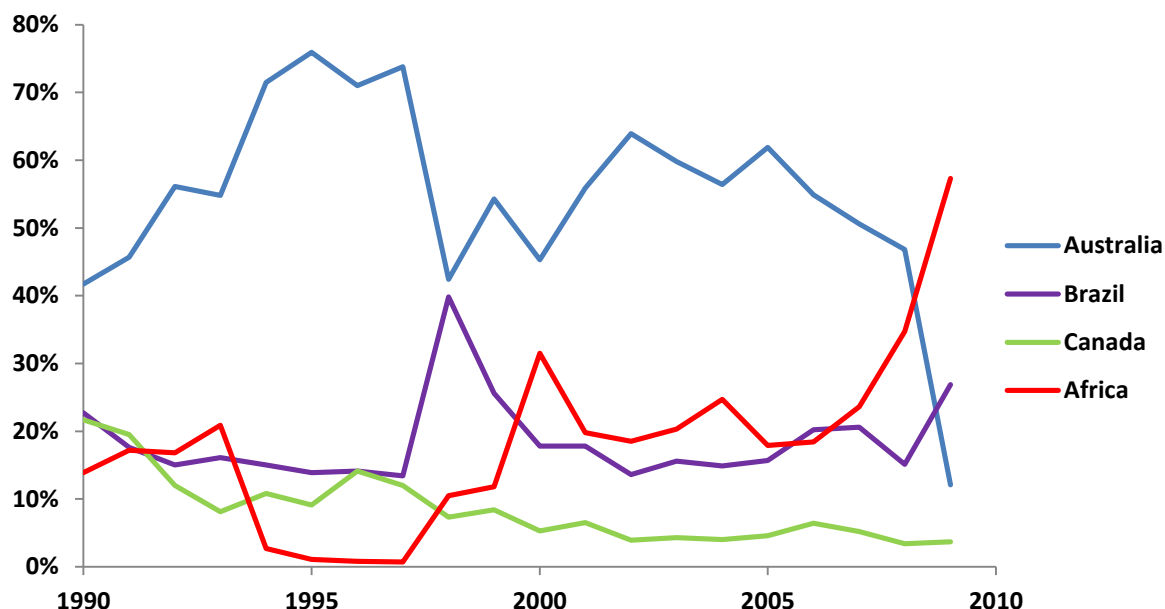


Figure 1: Percentage of globally mined tantalum of the main tantalum-producing countries.

This research will also dovetail with the Fluorochemical Expansion Initiative (FEI) and may provide an additional take-off for the fluorine market. Currently the niobium and tantalum values are recovered from mineral ores by liquid-liquid extraction.

This thesis investigates the possibility of using anhydrous HF to convert these metals to oxyfluorides and separate them by selective sublimation. This work also addresses several academic questions as will be outlined in the aims and objectives.

The lack of knowledge about the oxyfluorides of tantalum and niobium is surprising, given their perennial appearance in research where both oxygenated and fluorinated species are present. Workers in previous decades have spent some time on the characterisation of the oxyfluorides of tantalum and niobium, but even the few bits of data they collected were obtained by using outdated techniques and equipment.

In addition, the reaction of anhydrous fluorinating agents such as $\text{HF}_{(g)}$ and F_2 with tantalum and niobium compounds is not well documented and therefore poorly understood, a failing which is addressed in the present study.

Subsequent chapters analyse the work that has already been completed, and improves and extends the body of knowledge in a way that could make it scientifically and commercially useful. Chapter 2 is devoted to the synthesis and characterisation of oxyfluorides which are likely to form during the reaction with anhydrous fluorinating agents, whereas Chapter 3 contains work regarding the decomposition kinetics of the most stable of these compounds. Chapter 4 considers the anhydrous fluorination reactions of tantalum and niobium oxide. Chapters 5 to 7 discuss the development of a separation protocol for tantalum and niobium metal values from mineral ores.

1.2 Current and historical research processes

Tantalum and niobium occur in a variety of minerals (Table 1), sometimes collectively – but inaccurately – referred to as columbite (Enghag, 2000). Other sources of tantalum include tin slags and tantalum scrap, or secondary tantalum (Agulyansky, 2004).

These metals are industrially important materials due to their use in the fields of electronics, optics and nuclear energy (Moller, 1986). The main consumer of tantalum is the capacitor industry which has defined the industry standard for high-purity tantalum production. By contrast, niobium, found predominantly in pyrochlore deposits in Brazil and Canada (Selig *et al.*, 1968), has its main application in the manufacture of high-grade structural steel and super alloys (Papp, 2006).

Table 1: Common minerals used as sources for niobium and tantalite (Agulyansky, 2004).

Mineral	Composition	Ta_2O_5 /Wt%	Nb_2O_5 /Wt%
Columbite	$(\text{Fe, Mn})(\text{Nb, Ta})_2\text{O}_6$	5-30	55.5-78
Tantalite	$(\text{Fe, Mn})(\text{Nb, Ta})_2\text{O}_6$	42-84	2-40
Pyrochlore	$(\text{Ce,Ca,Y})_2(\text{Nb,Ta})_2\text{O}_6(\text{OH,F})$	0-6	37-66
Microlite	$(\text{Na,Ca})_2\text{Ta}_2\text{O}_6(\text{O,OH,F})$	68-77	0-7
Loparite	$(\text{Ce,Na,Ca})_2(\text{Ti,Nb})_2\text{O}_6$	0.5-3	5-20

There is an uncanny chemical similarity between these two metals, which can be attributed to their virtually identical ionic sizes, resulting from lanthanide contraction. This similarity, combined with their simultaneous occurrence in metal ores, makes the refinement and separation of these metals troublesome and justifies the combined study of Nb(V) and Ta(V) compounds (Bhattacharyya and Ganguly, 1986; Sadoway and Flengas, 1980).

A new anhydrous fluoride route is envisaged for the beneficiation of niobium and tantalum minerals. This beneficiation process for niobium and tantalum ores promises to be a more environmentally friendly method than the present acid digestion methods. Furthermore, it is potentially unique to South Africa and would give the country a competitive advantage.

Currently several technologies are available for the separation of niobium and tantalum. These technologies include steps such as chromatography (Burstall *et al.*, 1952; Monroy-Guzman *et al.*, 2002), distillation, reversed-phase chromatography (Wilk *et al.*, 2007), the nitrofluor process (Kigoshi *et al.*, 1972; Sato and Kigoshi, 1982), the Marignac process (Agulyansky, 2004; Miller, 1962), ion exchange (Barney and Kent, 1968; Fritz and Dahmer, 1965; Tereshatov *et al.*, 2008), liquid-liquid extraction (Maiorov and Nikolaev, 2002; Maiorov *et al.*, 2001; Stevenson and Hicks, 1953), and capillary electrophoresis (Liu *et al.*, 2001). Liquid-liquid extraction is the industry standard among these wet separation techniques.

With the exception of the Marignac, Nitrofluor and liquid-liquid extraction (LLE) methods, the extraction/purification methods mentioned above have never been practised commercially.

1.2.1 The Marignac process

For many years, the accepted method of facilitating the separation of tantalum from niobium has been the Marignac process – and derivations of it – involving batch crystallisation from dilute hydrofluoric acid solutions (Agulyansky *et al.*, 2004).

According to this method, niobium and tantalum are dissolved in aqueous hydrofluoric acid. A stoichiometric quantity of KF is added to the HF-metal reaction mixture and the less soluble K_2TaF_7 is precipitated, while the more soluble niobium analogue remains in solution.

This process has significant drawbacks owing to the concentration of impurities in the aqueous phase (Fritz and Dahmer, 1965; Sadoway and Flengas, 1980; Werning *et al.*, 1954).

1.2.2 Nitrofluor

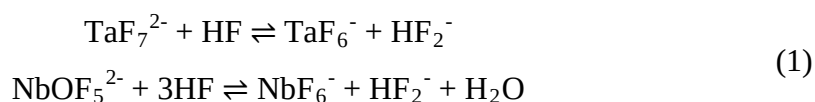
Another “wet” process used for recovering niobium and tantalum from columbite ores is the Nitrofluor process (Kigoshi, *et al.*, 1972; Sato and Kigoshi, 1982). The Nitrofluor process uses a solvent comprising NO₂ and anhydrous HF. The mineral is disintegrated at room temperature by using HF solutions of N₂O₃, N₂O₄ or NOF. Metal values are complexed with NO, and then separated according to their sublimation temperatures.

1.2.3 Liquid-liquid extraction

Tantalum and niobium are both resistant to most acids, though HNO₃-HF and pure HF can be used to dissolve them (Kwon *et al.*, 2002). Even though tantalum and niobium may be present in several oxidation states, namely +5, +4, +3, +2 and +1, only the +5 state is stable in solution (Zhu and Cheng., 2011). Niobium compounds are more soluble in aqueous media and it therefore follows that, based on polarity, more tantalum may be extracted into an organic phase during solvent extraction.

By the late 1960s the extraction of tantalum by using organic and aqueous solvents was already a well-known process (Alexander, 1969). This process is multifaceted (Figure 2) and comprises the isolation and separation of major and minor elements, and control of the aqueous solution composition, the organic extractant volume, the number of extraction steps and wash-back conditions (Nikolaev and Maiorov, 2007).

The choice of organic solvent is also a function of more than merely efficiency, since chemical toxicity, physical characteristics and flammability also have to be considered (Maiorov and Nikolaev, 2002). The heart of this process is control of the chemical equilibrium:



In non-acidic aqueous solution, the complexes on the left are stable, and a solution of low acidity is therefore used to strip the salts from an organic phase into aqueous solution.

Since niobium complexes are stronger Lewis acids than tantalum complexes, higher acid concentrations are required to shift the niobium equilibrium towards the hexafluoride than for

the corresponding tantalum. Accordingly, the selective extraction of tantalum can be achieved by controlling the pH. NMR ^{19}F spectroscopy also confirms that the HTaF_6 and HNBf_6 forms of the metals are extracted into organic media (Yu *et al.*, 2001).

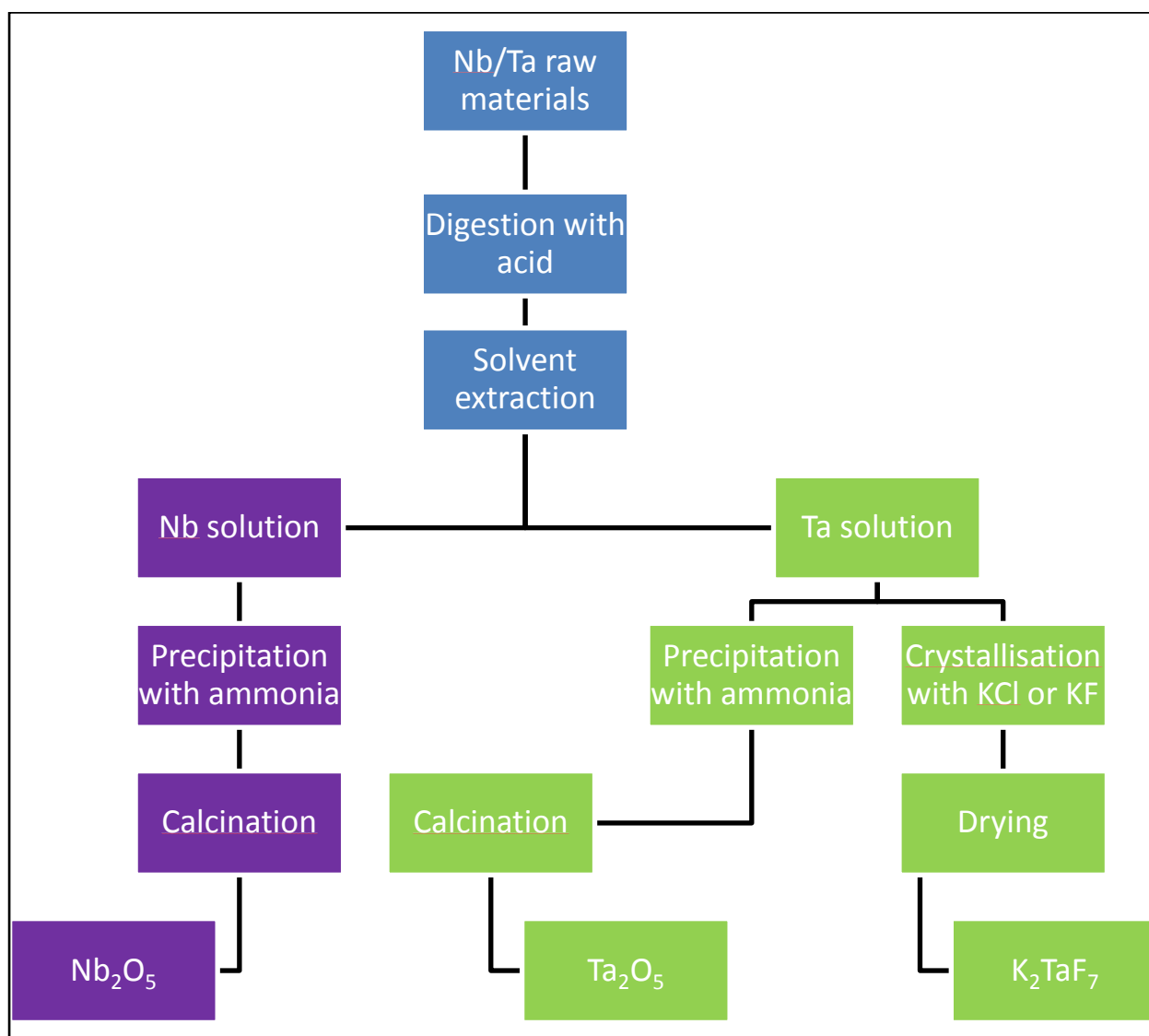


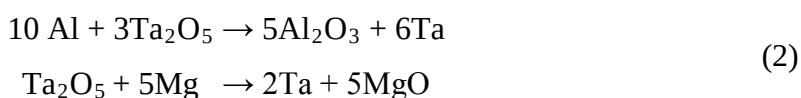
Figure 2: Schematic diagram of industrially practiced niobium and tantalum production (Zhu and Cheng).

Niobium and tantalum are far more soluble in fluoride solutions than in other aqueous acids (Nikolaev *et al.*, 2009). Since the solubility of the less acidic species (TaF_6^-) is lower in organic media than that of H_2TaF_7 the equilibrium should be shifted to the right as the HF concentration increases. Moreover, niobium forms more stable anionic complexes with

fluoride, making extraction into the organic phase less likely (Bhattacharyya and Ganguly, 1986).

A variety of extracting solvents may be used during the liquid-liquid extraction of tantalum and niobium; popular solvents include tributyl phosphate (TBP), cyclohexanone, octanols and methyl isobutyl ketone (MIBK) (Agulyansky *et al.*, 2004; Maiorov and Nikolaev, 2002; Nikolaev and Maiorov, 2007). Even though tantalum and niobium may both be extracted from acidic solutions using ketones, the equilibrium distribution favours the extraction of tantalum, and more acidic conditions are needed to make the extraction of niobium favourable. All the commercialised solvent extraction processes operate in the presence of fluoride ions (Zhu and Cheng, 2011), which inhibits the formation of polymeric species in solution (Seleznez *et al.*, 1971).

After the oxide has been isolated, it can be reduced to the metal value using sodium (Boča *et al.*, 2007), aluminium (Emeleus and Gutmann, 1950), magnesium or calcium (Welham, 2001):



Potassium tantalum fluoride, produced by the Marignac process, is reduced by using metallic sodium (Nel *et al.*, 2011).

1.3 Dry separation

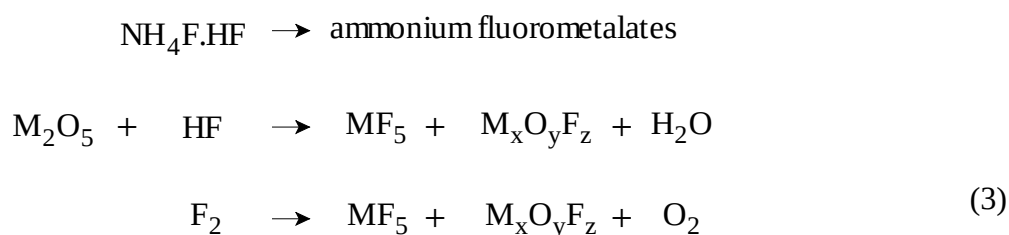
The oxide forms of tantalum and niobium can be converted to pentafluorides (MF_5) by fluorination with $\text{F}_{2(g)}$. These compounds may then in theory be separated by using sublimation, since they sublime at relatively low temperatures which are not identical (Pienaar *et al.*, 2012). Tantalum pentafluoride (TaF_5) melts with evaporation at 90 °C, but this occurs at a lower temperature of 80 °C in the case of niobium pentafluoride (NbF_5) (Priest, 1950). Separation, although possible in the laboratory, is not feasible as a commercial process. A greater window of separation is opened by converting them to oxy-fluoride values instead.

The present study investigates the reaction of tantalum or niobium oxides to a dry fluorine source such as $\text{HF}_{(g)}$ or $\text{F}_{2(g)}$, so as to prepare metal fluorides or oxy-fluorides in non-aqueous media. From a perusal of the literature on fluorination, these dry processes are expected to have many advantages over wet processes as regards to reaction kinetics and production of secondary waste material (Kwon *et al.*, 2002).

Though the use of $\text{NH}_4\text{F}\cdot\text{HF}$ as dry fluorinating agent is not unknown (Tikhomirova *et al.*, 2008), relevant literature is less abundant than that available for the aqueous routes. $\text{NH}_4\text{F}\cdot\text{HF}$ reacts with Nb_2O_5 to form $(\text{NH}_4)_3\text{NbOF}_6$, which decomposes to NbOF_3 and NbO_2F at 375 – 420 °C (Buslaev *et al.*, 1971).

The experimental results that Rakov (1971) obtained, allowed them to infer that niobium may be thermally separated from uranium when a mixture of uranium and niobium oxide is treated with fluorine.

When processing tantalum or niobium oxides with a fluorinating agent, oxyfluorides of the form $\text{M}_x\text{O}_y\text{F}_z$ are the probable reaction products, as in reaction 3.



Metal oxides may be formed from the hydrolysis reaction with steam, for NbO_2F (Nikolaev *et al.*, 2009):



There are only a few literature reports about these oxyfluorides, specifically for $\text{M} = \text{Ta}$, so a considerable part of this research report is devoted to elucidating their properties and exploring the possibility of designing a separation route for them.

1.4 Patent analysis

A patent search of several free patent databases[†] using the Boolean search string “(**tantalum OR niobium**) AND (**recovery OR separation**)” showed more than 300 patents were filed within the past 10 years. Upon closer scrutiny, however, only 80 were considered relevant to this study.

The results of this analysis show that the majority of these patents were filed in the People’s Republic of China (Table 2), and that the Guangzhou Research Institute of Non-Ferrous Metals, which specialises in the utilisation of new materials, is the most prolific filer.

Table 2: Owners of tantalum and niobium patents filed during the past 10 years.

Company	Country	Number of Patents
Guangzhou Research Institute of Non-ferrous Metals	Peoples Republic of China	4
Nanchang University	Peoples Republic of China	4
Dowa Eco System Co Ltd	Japan	3
Jianxi University of Science and Technology	Peoples Republic of China	3
King Tan Tantalum Industry Ltd	Peoples Republic of China	3
Mitsui Mining & Smelting Company Ltd	Japan	3
China Nerin Engineering Company Ltd	Peoples Republic of China	2
Crystal Technology Inc.	USA	2
Eramet	France	2

To gauge the importance of the filed patents, the patents were weighted according to publication year, combined with the number of times the specific patent was cited by other patents (equation 5). A list of the top ranking patents is given in Table 3.

$$\text{Patent Strength} = 10 - (\text{Current Year} - \text{Publication Year}) + \text{Number of Citations} \quad (5)$$

It is clear from the patent list that most of the commercial research has focused on the recovery of Ta/Nb from sources other than the ores. Indeed, because of the well-established and proven technology seen in liquid-liquid extraction, research has focused on the optimisation of this technique instead of on the development of new techniques.

[†] European Patent Office, <http://ep.espacenet.com/> and Freepatentsonline, <http://www.freepatentsonline.com/>

Table 3: Top ranking patents according to Formula 5.

Strength	Name
10	Method of pressure leaching niobium from red mud using sulfuric acid
10	Process for upgrading tantalum and niobium ores and concentrates with the recovery of manganese and rare-earth oxides
10	Method for beneficiating fine-grained tantalum-niobium ore
10	Apparatus for washing hydroxides of tantalum and niobium
10	Device with cooler and method for magnesium reduction of tantalum powder for reducing oxygen content [Machine Translation].
10	Excavation production method of soft magnetic material based on completely spacing method
9	Method for recovering tantalum
9	Method for preparation of battery grade lithium carbonate using Ta-Nb tailing lepidolite
9	Process for production of high-quality feldspar from tantalum-niobium ore tailing
9	Recovery of niobium from capacitors
9	Recovery of rare earth metals from tin slags generated in tin refining
9	Dissolution and recovery of Nb or Ta and rare earth elements from ores by roasting and calcination
9	Method for producing and isolation-purifying niobium
9	Method for recycling associated rare elements from ion adsorption type rare earth tailings
9	Method and apparatus for preparing metallurgic powder from spent Ta-Nb capacitors
9	Recovery method of tantalum from motherboards or capacitors
9	Method for comprehensive recovery of RE, Nb, Ta and Fe from RE metal ore
9	Method for producing and isolation-purifying niobium
9	Tantalum recovery method from tantalum-containing scraps
9	Dissolution and recovery of Nb or Ta and U or rare earth elements from ores and concentrate
9	Method for selective separation and recovery of metal solutes from solution by the use of membrane based solvent extraction.
9	Process for recycling fine tantalum-niobium concentrate from tantalum-niobium ore

1.5 Aims and objectives

The broad aims of this research study were to explore the viability of a dry mineral processing route by using $\text{HF}_{(g)}$ or $\text{F}_{2(g)}$ as a fluorinating agent to fluorinate minerals containing Ta/Nb and separating them on the basis of their thermal properties.

The objectives of this research study were to generate the physical property and reaction data, and to develop a conceptual industrial process for the separation and purification of tantalum.

Specifically, in addition to the literature review presented in this chapter, the final product includes the following specific research outcomes:

- Detailed experimental results concerning synthesis and characterisation of products as well as intermediates that may result from the treatment of minerals containing tantalum and niobium with fluorinating agents, such as anhydrous HF and F₂. It was assumed that the relevant metal values occurred in pentoxide form.
- Dioxyfluorides of tantalum and niobium are stable and likely products during the fluorination of the oxidic species. These oxyfluorides decompose to form other intermediate products. A study on the decomposition kinetics should provide valuable information for the development of thermal separation processes. By employing several established kinetic methods, the study provided the likely kinetic parameters for the decomposition reaction.
- Experimental work would provide the reactions between HF_(g) and F₂ with the metal pentoxides. These reactions were followed by thermal analysis techniques such as TG and DSC. By using the data obtained from model compounds, product characterisation would be provided.
- Molecular modelling of the most prevalent intermediates and products would be guided by the collected experimental properties. The data generated by using several software packages, including Materials Design, provides an increased understanding of the thermodynamic properties of the subject matter.
- Proof of concept for a separation route using anhydrous HF followed by thermal separation is provided by using this technique on model mixtures of tantalum and niobium oxides.
- A specific ore concentrate, rich in tantalum and niobium, was chosen and characterised. This concentrate was then treated in a similar fashion to the model mixtures and comparative results are provided in this study.

1.6 References

- Agulyansky, A., (2004). "The Chemistry of Tantalum and Niobium Fluoride Compounds". Elsevier, London.
- Agulyansky, A., Agulyanski, L. and Travkin, V.F., (2004). "Liquid-liquid extraction of tantalum with 2-octanol". *Chem. Eng. Proc.*, **43**: 1231-1237.
- Alexander, G.B., (1969). "Tantalum recovery by liquid-liquid extraction". *J. Chem. Ed.*, **46**: 157-159.
- Barney, D.L. and Kent, C.E., (1968). "Ion exchange separation processes for niobium and tantalum". *Ind. Eng. Chem. Proc. Des. Dev.*, **7**: 1-5.

- Bhattacharyya, S.N., Ganguly B., (1986). "Solvent extraction separation of tantalum from niobium on macro scale using di(2-ethylhexyl) phosphoric acid as extractant". *J. Rad. Nucl. Chem.*, **98/2**: 247-253.
- Boča, M., Danielik, V., Izanová, Z., Mikšiková, E. and Kubiková, B., (2007). "Phase diagrams of the $\text{KF-K}_2\text{TaF}_7$ and $\text{KF-Ta}_2\text{O}_5$ systems". *J. Therm. Anal. Cal.*, **90**: 159-165.
- Burstall, F.H., P. Swain, P., Williams, A.F. and Wood, G.A., (1952). "Inorganic chromatography on cellulose. Part XI. A study on the separation of tantalum from niobium and its application to quantitative analysis". *J. Chem. Soc.*, **77**: 1497.
- Buslaev, J., Yu, A., Ilyin, E.G., Kopanov, V.D. and Gavrish, O.G., (1971). *Isv. Akad. Nauk. SSSR, Ser. Chim.*, 1139
- Emeleus, H.J. and Gutmann, V., (1950). "The fluorides of niobium, tantalum, tungsten and rhenium". *J. Chem. Soc.*, 2115-2118.
- Enghag, P., (2000). "Encyclopedia of the elements". Wiley-VCH, Stockholm.
- Fritz, J.S. and Dahmer, L.H., (1965). "Cation exchange separation of molybdenum, tungsten, niobium and tantalum from other metal ions". *Anal. Chem.*, **37**: 1272-1274.
- Kabangu, M.J. and Crouse, P.L., (2012). "Separation of niobium and tantalum from Mozambican tantalite by ammonium bifluoride digestion and octanol solvent extraction". *Hydrometallurgy*, **129-130**: 151-155.
- Kigoshi, A., Okada, K. and Ohmi, M., (1972). "The Extraction of Niobium and Tantalum from Columbite by the Nitrofluor Process", Tohoku University, Sr. A. Physics, Chemistry and Metallurgy.
- Kwon, S.W., Kim, E.H., Ahn, B.G., Yoo, J.H. and Ahn, G., (2002). "Fluorination of metals and Metal Oxides by Gas-Solid Reaction" *Ind. Eng. Chem.*, **8**: 477-482.
- Liu, E.B., Liu, Y.-M. and Cheng, J.-K., (2001). "Separation of niobium(V) and tantalum(V) by capillary electrophoresis with chemiluminescence detection" *Anal. Chem. Acta*: 101-105.
- Maierov, V.G. and Nikolaev, A.I., (2002). "Tantalum(V) and niobium(V) extraction by octanols" *Hydrometallurgy*, **66**: 77-83.
- Maierov, V.G., Nikolaev, A.I., Sklokin, L.I. and Baklanova, I.V., (2001). "Extractive recovery of tantalum(V) and niobium(V) with octanol from hydrofluoric acid solutions containing large amounts of titanium(IV)." *Russ. J. Appl. Chem.*: 945-949.
- Miller, G.L., (1962). "Purification of tantalum and niobium" *The Industrial Chemist*, **38**: 406-410.
- Moller, P., (1986). "Lanthanides, Tantalum and Niobium, Verlag". Special Publication No. 7 of the Society for Geology Applied to Mineral Deposits. P1. Springer, Berlin.
- Monroy-Guzman, F., Trubert, D. and Naour, C.L., (2002). "Adsorption behavior of Zr, Hf, Nb, Ta and Pa on macroporous anion exchanger in $\text{NH}_4\text{SCN}/\text{HClO}_4$ and $\text{NH}_4\text{SCN}/\text{HF}$ media". *J. Rad. Nucl. Chem*, **254**: 431-437.
- Nel, J.T., Du Plessis, W., Crouse, P. L., Le Roux, J.P, Retief, W.L.N., (2011). "Treatment of minerals", Patent: WO2011030301.
- Nikolaev, A.I., Kirichenko, N.V. and Maierov, V.G. (2009). "Niobium, tantalum and titanium Fluoride solutions". *Russ. J. Inorg. Chem.*, **54**: 505-511.
- Nikolaev, A.I. and Maierov, V.G., (2007). "New Approaches to Niobium and Tantalum extraction technology". *Doklady Chemistry*, **46**: 644-652.
- Papp, J.F. (2006). Mineral Commodity Summaries, Columbium (Niobium), U.S. Department of the Interior, U.S. Geological Survey
- Pienaar, A.D., Wagener, J.B. and Crouse, P.L., (2012). "Niobium and tantalum separation by gas-phase fluorination". *Intl. J. Min. Proc.*, **114-117**: 7-10.
- Priest, H.F., (1950). "Anhydrous Metal Fluorides". Inorganic Syntheses, 3. McGraw-Hill, New York.
- Rakov, E.G., Kopchikhin, D.S., Sudarikov, B.N. and Gromov, B.V., (1971). "Fluorination kinetics of Nb_2O_5 ". *Atomnaya Energiya*, **31**: 137-138.
- Sadoway, R.D. and Flengas, S.N., (1980). "A new process for the separation of tantalum from niobium". *Metal. Trans. B*, **11**: 57-62.
- Sato, N. and Kigoshi, A., (1982). "Extraction of niobium, tantalum and titanium from columbite". *AIChE Journal*, **28**: 522-524.
- Seleznev, V.P., Rakov, E.G. and Mikulenok, V.V., (1971). "Thermodynamic properties of niobium and tantalum pentafluorides". *Zhurnal Fizicheskoi Khimii*, **45**: 2941.

- Selig, H., Reis, A. and Gasner, E.L., (1968). "Raman spectra of liquid NbF₅ and TaF₅". *J. Inorg. Nucl. Chem.*, **30**: 2087-2090.
- Stevenson, P.C. and Hicks, H.G., (1953). "Separation of tantalum and niobium by solvent extraction". *Anal. Chem.*: 1517-1519.
- Survey (2011). "Mineral commodity summaries 2011". US Government Printing Office, Washington.
- Tereshatov, E.E., Bruchertseifer, H., Bozhikov, G.A., Aksenov, N.V., Starodub, G.Y., Vostokin, G.K., Belov, A.G., Shiskin, S.V., Dmitriev, S.N., Gäggeler, H.W., Eichler, R. and Schumann, D., (2008). "Cation-Exchange Separation of Group V Elements: Model Experiments on Isolation and Chemical Identification of Db". *Radiochemistry*, **50**: 290.
- Tikhomirova, E.L., Makarov, D.V. and Kalinnikov, V.T., (2008). "Reaction of niobium pentoxide with ammonium hydrodifluoride". *Russ. J. Inorg. Chem.*, **53**: 988-992.
- Welham, N.J., (2001). "Enhanced dissolution of tantalite/columbite following milling". *Intl. J. Min. Proc.*, **61**: 145-154.
- Werning, J.R., Higbie, K.B., Grace, J.T., Speece, B.F. and Gilbert, H.L., (1954). "Separation of tantalum and niobium by liquid-liquid extraction". *Ind. Eng. Chem.*, **46**: 644-652.
- Wilk, P.A., Landrum, J.H., Shaughnessy, D.A., Kenneally, J.M., Stoyer, N.J., Stoyer, M.A., Moody, K.J., Aksenov, N.V., Bozhikov, G.A., Tereshatov, E.E., Vostokin, G.K., Shiskin, S.V. and Dmitriev, S.N., (2007). "Separation of group five elements by reversed-phase chromatography". *J. Radioanal.Nucl. Chem.*, **3**: 651-657.
- Yu, M.G., Travkin, V.F., Ilyin, E.G., Karamushko, E.V. and Koralev, V.V., (2001). *Zvetnay Metallurgiy*, 10: 23-27.
- Zhu, Z., Cheng, C. Y.,(2011). "Solvent extraction technology for the separation and purification of niobium and tantalum: A review", *Hydrometallurgy*: **107**, 1-12

CHAPTER 2

OXYFLUORIDES OF TANTALUM AND NIOBIUM

2.1 Introduction

By preparing and characterising several of the intermediate oxyfluorides that may arise during the reaction between niobium or tantalum oxide with anhydrous hydrofluoric acid, the goal is to generate sufficient data to characterise the actual reaction pattern. Knowledge of this reaction is integral to the study of tantalum/niobium ore fluorination since these metals are in oxide form and likely to form oxyfluorides when exposed to fluorinating agents.

This chapter presents the results of the preparation and characterisation of the dioxyfluoride as well as the oxytrifluorides of tantalum and niobium. Throughout this chapter other oxyfluorides that may arise during the experimental steps may be mentioned, such as $\text{Nb}_3\text{O}_5\text{F}_5$, but no detailed attention to their physical properties will be given.

Pentafluorides of niobium and tantalum can be readily prepared by the reaction between elemental fluorine (F_2) and the respective metal oxides at temperatures greater than 300 °C (Hiskey and Batik, 1953), whereas the dioxyfluoride (MO_2F) forms of tantalum and niobium can be prepared by dissolving the pentoxide (M_2O_5) in aqueous hydrofluoric acid (Köhler *et al.*, 2002). Nikolaev *et al.* (2009) has shown that the calcination temperatures of the oxides have a significant effect on their ability to dissolve in $\text{HF}_{(\text{aq})}$, though some forms remain insoluble even after prolonged periods of digestion. This was postulated as being due to changes in the crystal structure of the oxide.

After the preparation of the dioxyfluoride, the oxytrifluoride (MOF_3) is prepared by heating it with the pentafluoride in stoichiometric quantities (Cordier *et al.*, 2004; Köhler *et al.*, 2002).



The dioxyfluorides and oxytrifluorides may also occur when the pentafluoride is exposed to trace amounts of moisture (Adetunji *et al.*, 2005; Andersson and Astrom, 1965; Cordier *et al.*, 2004), and produce a mixture of these compounds. Nieder-Vahrenholz and Schäfer (1987) showed that the oxytrifluorides (MOF_3) also hydrolyse immediately in the presence of water. The hygroscopicity of the oxyfluorides is expected to decrease as the fluorine content decreases (Cordier *et al.*, 2004).

Conversely, oxygen rich species such as the pentoxides may undergo fluorination in the presence of fluorine rich species. It is therefore often found that a mixture of different oxyfluorides results when preparing a specific oxyfluoride.

Köhler *et al.* (2002) collected XRD patterns and infrared spectra for both the dioxyfluoride and oxytrifluoride and Raman spectra for the dioxyfluoride. In the cited paper, they show that the niobium and tantalum oxytrifluoride crystallise isostructurally with SnF_4 in spacegroup $I 4/mmm$. The dioxyfluorides of these metals are isostructural with ReO_3 and crystallise in the $\text{Pm}3m$ spacegroup. The authors show that from the calculations performed, niobium and tantalum also have nearly identical unit cell constants for the analogous oxyfluorides, which is not unexpected given the similar ionic sizes of the metal centres.

Since XRD equipment is not always readily available, an alternative reliable identification of oxyfluoride phases is required. This study is built on the data collected by previous workers (Table 4), and extends the characterisation of the oxyfluorides to spectroscopic and thermogravimetric data.

2.2 Experimental

2.2.1 Preparation of MO_2F

Niobium dioxyfluoride (NbO_2F) was prepared according to the technique described by Andersson and Åström (1965), namely by dissolving niobium pentoxide powder (0.50 g, Nb_2O_5 , 99.5% Sigma Aldrich) in 20 ml, 40% HF (Protea Chemicals) in a microwave (CEM Mars 5) digester. A large excess of HF was used since the $\text{HF}_{(\text{aq})}$ acts as both reagent and solvent. The temperature was set at 200 °C for 30 min. The samples were dried in N_2 atmosphere at 350 °C.

Table 4: Characterisation completed on niobium and tantalum oxyfluoride species by other researchers.

Decomposition Studies	XRD	FTIR	Raman	Thermodynamics
<i>Niobium Species</i>				
NbF ₅		(Yu <i>et al.</i> , 2001)	(Ayanda and Adekola, 2011; Rai <i>et al.</i> , 2009)	(Greenberg <i>et al.</i> , 1965; Hiskey and Batik, 1953; Seleznez <i>et al.</i> , 1971)
NbOF ₃	(Nieder-Vahrenholz and Schafer, 1987)	(Köhler <i>et al.</i> , 2002; Mulja, <i>et al.</i> 1996)	(Cordier <i>et al.</i> , 2004; Köhler, <i>et al.</i> , 2002)	
NbO ₂ F	(Åström, 1967; Kodama and Goto, 1975; Wilkinson <i>et al.</i> , 2014)	(Frevel and Rinn, 1956)	(Cordier, <i>et al.</i> , 2004)	(McConnell <i>et al.</i> , 1975)
Nb ₃ O ₅ F ₅		(Cordier <i>et al.</i> , 2004)	(Cordier <i>et al.</i> , 2004)	
Nb ₃ O ₇ F		(Okamoto, 1992)		
Nb ₂ O ₅		(Seleznez <i>et al.</i> , 1971)		
<i>Tantalum Species</i>				
TaF ₅		(Pienaar and Vilakazi, 2012)	(Ayanda and Adekola, 2011)	(Greenberg <i>et al.</i> , 1965; Seleznez <i>et al.</i> , 1971)
TaOF ₃	(Nieder-Vahrenholz and Schafer, 1987)	(Köhler <i>et al.</i> , 2002; Mulja, <i>et al.</i> , 1996)	(Köhler <i>et al.</i> , 2002)	(Zmbov and Margrave, 1968)
TaO ₂ F	(Frevel and Rinn, 1956)	(Frevel and Rinn, 1956)	(Kamali <i>et al.</i> , 2014)	
Ta ₂ O ₅				(Buslaev <i>et al.</i> , 1971)

2.2.2 Preparation of MOF₃

These compounds were prepared according to the method mentioned in section 2.1. The solid-solid reaction was done by adding a slight excess of MF₅ (Alfa Aeser, 99.5% with M = Ta/Nb respectively) to the prepared MO₂F in a stainless steel autoclave reactor.

The solids were mechanically mixed by means of an agate mortar and pestle. The mixing and loading of the reactor were performed in a nitrogen glove box. After having been loaded, the reactor was sealed and heated to 200 °C for 2h. The reaction proceeded according to Equation 6.

2.2.3 Characterisation of oxyfluorides

Infrared spectra were collected on a Bruker Tensor FTIR fitted with a HarrickTM diamond ATR cell. The spectral resolution was set at 4 cm⁻¹ with an acquisition time of between 3 and 5 min. Raman spectra were acquired with a Model T64000 Dilor Raman triple stage spectrometer fitted with a water-cooled CCD detector. An Ar⁺ laser provided the 514.5 nm wavelength exciting radiation and the integration times were typically 100 s with one to two accumulations in each spectral window and a resolution of 2 cm⁻¹. XRD patterns were recorded on a D8 advance diffractometer with the following measurement parameters: target tube Cu; 2θ recording range 10° to 135°; step size 0.02°; counting time 1 s.

Decomposition and sublimation behaviour was recorded on a TA Instruments SDT Q600 TG/DSC with heating programs specified on each curve and a constant 100 ml.min⁻¹ nitrogen purge.

2.3 Results and discussion

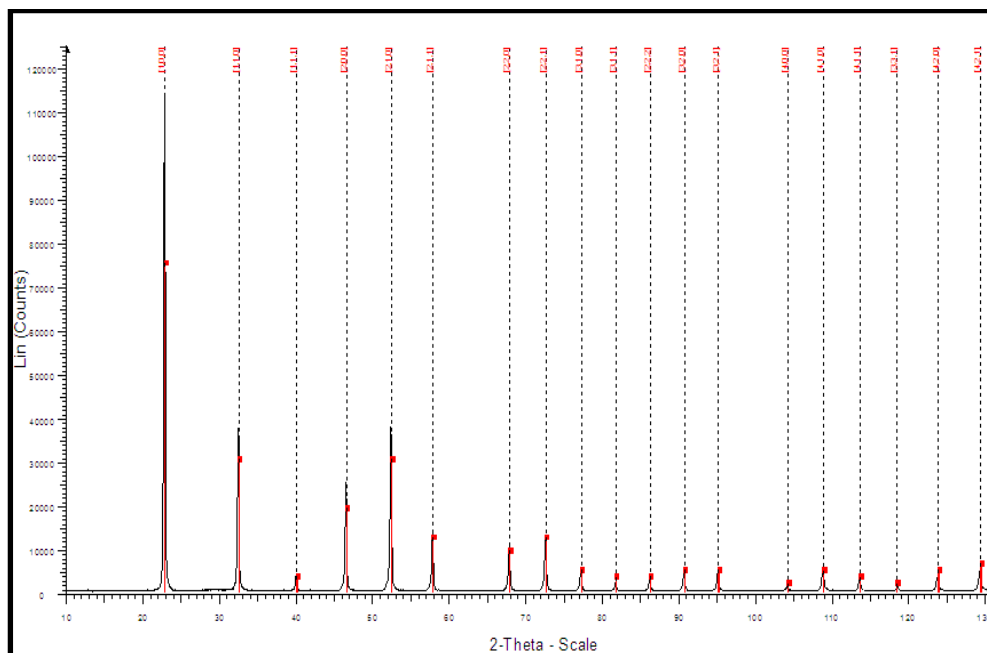
2.3.1 Dioxyfluorides

Though single crystal diffraction has not been done on these compounds, other structural investigations have been reported. Electron diffraction studies show that O:F have distinct ordering in NbO₂F (Brink *et al.*, 2002), though there is no evidence of order for the oxytrifluoride analogues. The cited report does indicate, however, that the lack of order may be a kinetic artefact of the synthesis. Cordier *et al.* (2004) state that the structural dimensionality of the Nb-O-F system is directly correlated to the (O,F)/Nb mol ratio, and that an increase in this ratio must lead to non-bridging anions within the structure.

2.3.2 Characterisation

Figures 3 and 4 show the XRD patterns collected for the prepared NbO₂F and TaO₂F respectively. These figures are overlaid with the stick patterns for these compounds, as recorded in the PDF-2007 database. The most relevant result from this is that all diffraction lines were

assigned, which confirms not only the synthesis, but also the purity of the product. The bands seen in Raman and infrared spectra recorded for this product can therefore be unambiguously assigned to the properties of the dioxyfluoride, not any other impurities which may be present.



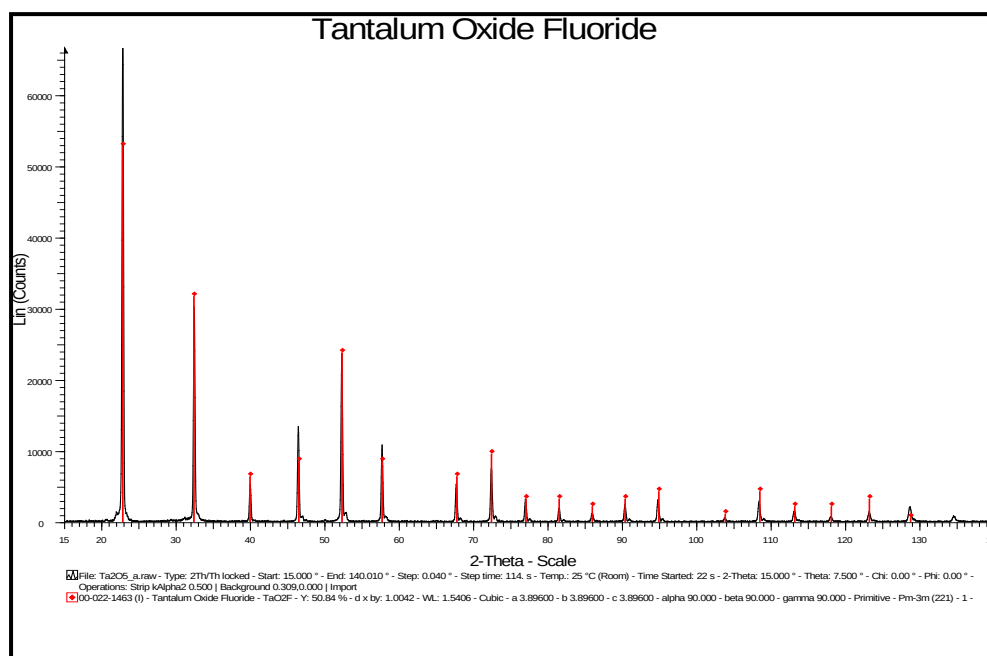


Figure 4: Powder diffraction pattern of prepared TaO₂F overlaid with a stick pattern of database XRD pattern of TaO₂F.

The structural and physical chemistry of tantalum oxyfluorides, specifically TaO₂F, have not been as well studied as similar compounds of niobium, which has been characterised by both XRD and spectroscopic investigations (McConnell *et al.*, 1975). The present study used the chemical similarities of tantalum and niobium (Cooper *et al.*, 1999; Kalinnikov and Agulyansky, 1985; Nagiev, 2004; Zhang, 1982) to assist with the interpretation of the spectroscopic results.

Infrared absorption spectra of niobium oxyfluoride have been reported (Barner *et al.*, 1991; Cordier *et al.*, 2003; Cordier *et al.*, 2004; Köhler *et al.*, 2002) and it has been suggested that niobium oxyfluoride is built up from one crystallographically independent Nb(O,F)₆ octahedron that does not contain non-bridging anions (Cordier *et al.* 2004). Raman spectroscopy studies for this compound have also been reported (McConnell *et al.*, 1976), evidence of a cubic crystal has been identified, and the consistency of these results has been established by electron diffraction studies (Brink *et al.*, 2002). Based on the electron diffraction results, some authors propose that

the most probable local octahedral stoichiometry around the niobium ion is O_4F_2 (Brink *et al.*, 2002).

Table 6: Miller indices for NbO_2F and TaO_2F according to the Treor algorithm.

NbO_2F					TaO_2F				
2θ	h	k	l	$h^2+k^2+l^2$	2θ	h	k	l	$h^2+k^2+l^2$
22.69	1	0	0	1	22.67	0	1	0	1
32.35	1	1	0	2	32.29	1	0	1	2
39.91	1	1	1	3	39.9	1	1	1	3
46.43	2	0	0	4	46.33	0	0	2	4
52.31	2	1	0	5	52.15	1	0	2	5
57.75	2	1	1	6	57.65	1	1	2	6
67.79	2	2	0	8	67.68	2	0	2	8
72.54	3	0	0	9	72.22	0	0	3	9
77.17	3	1	0	10	76.85	1	0	3	10
81.71	3	1	1	11	81.43	1	1	3	11

According to solid state theory, a molecule should have $3N-3$ vibrations, where N is the degrees of freedom, or the number of symmetrically different atoms in the unit cell. Characteristic infrared peaks (Figure 5) for niobium dioxyfluoride were observed at 877, 690, 584 and 455 cm^{-1} and for tantalum dioxyfluoride at 903, 685, 634 and 439 cm^{-1} .

Raman spectra show broad bands similar to those observed by Kamali *et al.*(2014) and were deconvoluted using the Origin Pro 8 software package (Figures 6 and 7). The absorptions between 650 and 730 are probably due to M-O-M bridging stretches (Laptash *et al.*, 2013) and are visible in both the Raman and infrared spectra.

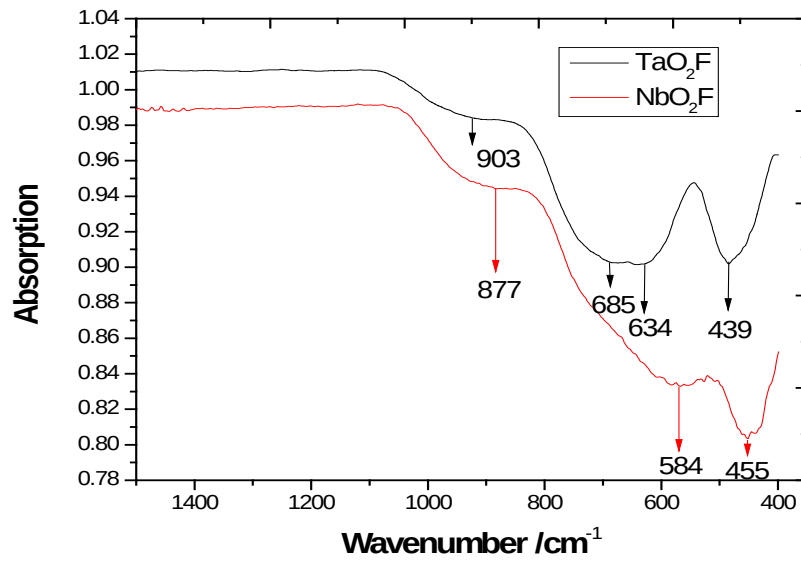


Figure 5: FTIR spectrum for prepared NbO_2F and TaO_2F .

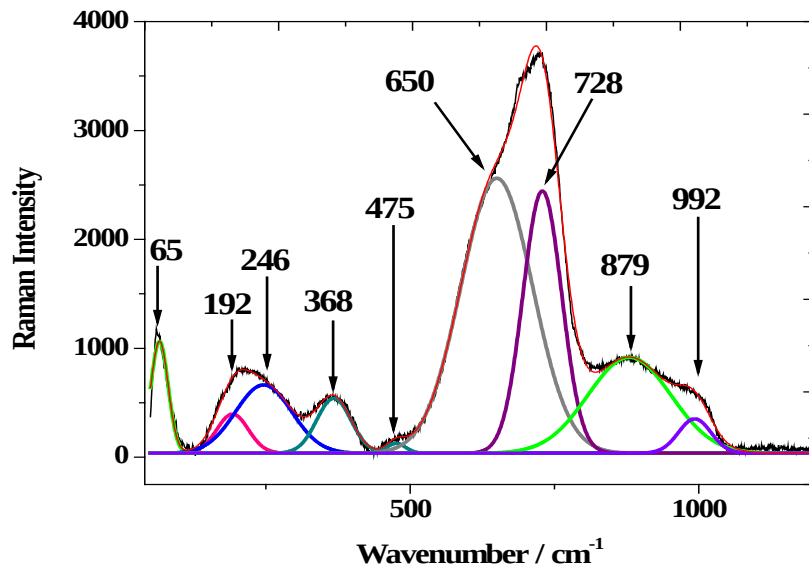


Figure 6: Deconvoluted Raman spectrum of prepared NbO_2F .

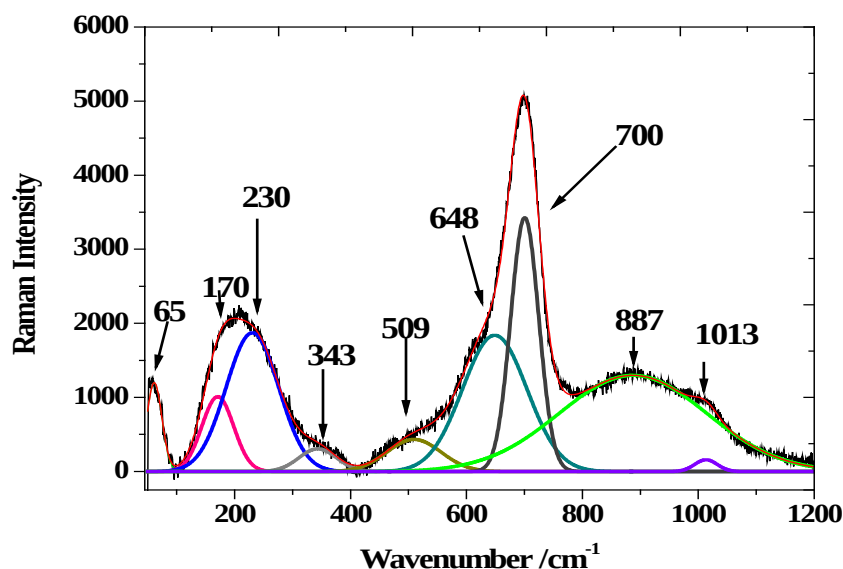


Figure 7: Deconvoluted Raman spectrum of TaO₂F.

For terminal M-F bonds, a prominent stretch at about 755 cm⁻¹ is expected for both tantalum and niobium (Lassner and Schubert, 1999), as well as a band at 530 cm⁻¹ in the IR spectrum (Kent and Margrave, 1965). From the spectra collected in the present study, it can therefore be inferred that all M-F bonds are bridging for these compounds. The bands at ~880-1000 cm⁻¹ are assigned to terminal M-O stretches, with multiple bond character (Köhler *et al.*, 2002; Laptash *et al.*, 2013; Levason *et al.*, 2013). Another possibility for the appearance of these bands, may be a result of asymmetrical Ta-X-Ta bridges (Morelock, *et al.*, 2013).

Though the bigger size of the Ta atom compared to the Nb atom will cause decreases in stretching frequencies (Haendler *et al.*, 1954), each vibrational band in the TaO₂F spectrum corresponds to a band in the NbO₂F system.

The corner-connected octahedral (M(O/F)₆) units that have been described for niobium oxyfluoride (Ignat'eva *et al.*, 2006) are known to possess inherent rotational flexibility, resulting in low frequency modes (Dove, 1997; Glazer, 1972; Hammonds *et al.*, 1996). Specifically, electron diffraction studies of niobium dioxyfluoride show the coexistence of transverse polarised <1/2, 1/2, ξ>* type diffuse scattering, implying the simultaneous co-existence of Rigid

Unit Modes (RUM) (Brink *et al.*, 2002). The Raman band that appears at 65 cm^{-1} in the NbO_2F and TaO_2F spectra is consistent with this description. The mode observed here is also independent of the mass located at the centre of the octahedral structure from niobium to tantalum, in line with the description given by Brink *et al.* (2002).

With the exception of the RUM mode at 65 cm^{-1} , the highest wavenumber bands (992 and 1013 cm^{-1} in the Nb and Ta Raman spectra) and the M-F-M Raman bands (475 and 509 cm^{-1}), we observe small but noticeable red shifts in the frequency of the Raman bands from niobium to tantalum dioxyfluoride (Figures 6 and 7). It is known that halides of tantalum have larger force constants than their niobium analogues for their M-X (M = Nb, Ta and X = F, Cl, Br) stretching modes (Dove *et al.*, 2000; Mehta and Avasthi, 1972; So, 1973). It is therefore expected that the Nb-F stretching modes will be observed at higher frequencies than the Ta-F stretching modes.

Due to the higher sensitivity of the Raman instrument used in this study, the highest Raman band of NbO_2F was observed at 992 cm^{-1} as opposed to the 725 cm^{-1} previously determined. The highest Raman band for TaO_2F was observed at 1013 cm^{-1} .

2.3.3 Thermal decomposition

The thermal-decomposition products that form are not only of theoretical interest, but also of interest in technological applications (Muraleedharan *et al.*, 2010; Yun *et al.*, 2008). Despite this, the thermal properties of oxyfluorides of tantalum and niobium have received little attention, even though they may be of great benefit for scaling up the beneficiation processes.

Andersson and Åström (Andersson and Åström, 1965; Åström, 1967) determined that the decomposition reaction for niobium oxyfluoride proceeds according to the equation:



While more recently Wilkinson *et al.* (2014) reported that 26% mass decrease during decomposition indicates formation of $\text{NbF}_{5(g)}$, 38% formation of NbOF_3 and an 8% mass decrease indicates pyrohydrolysis with formation of Nb_2O_5 . Further, they suggested that when synthesising NbO_2F via aqueous HF, a more accurate formulation of the product would be

$\text{Nb}_{1-\delta}\text{O}_\delta(\text{O}, \text{OH}, \text{F})$ which allows inclusion of water or hydroxyl groups into the structure upon heating.

The TG analysis of both the tantalum and niobium oxyfluorides shows that a weight loss of less than 5% occurs below 400 °C and that another weight loss event occurs at 651 °C for niobium dioxyfluoride and at 754 °C for tantalum dioxyfluoride.

The decomposition curve shown in Figure 8 indicates about 3.5% of the mass is lost prior to the decomposition of NbO_2F at 651 °C. This is probably due to a small quantity of oxyfluorides with a higher $\text{F} > \text{O}$ mol ratio than NbO_2F (e.g. NbOF_3). If the fraction that decomposes at 651 °C is normalised to 96.5, the total mass decrease is 22.3%.

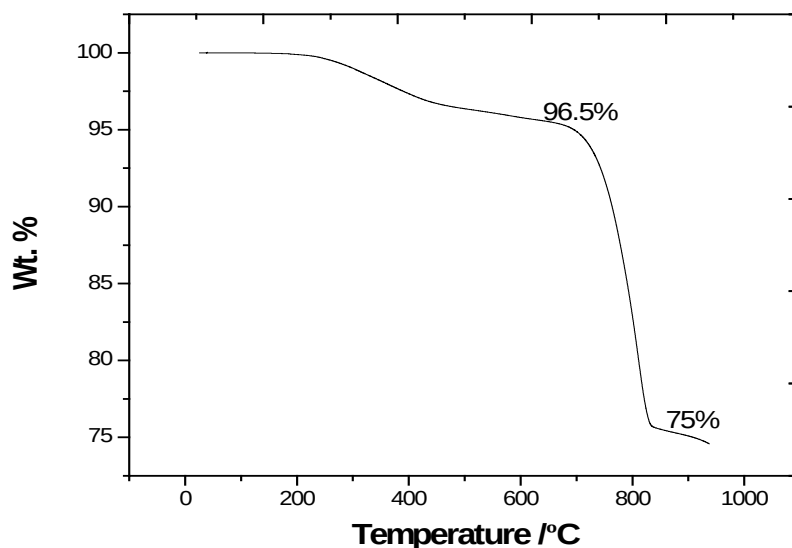


Figure 8: Decomposition analysis of prepared NbO_2F .

This value is what is expected for formation of $\text{Nb}_3\text{O}_7\text{F}_{(s)}$ with evaporation of NbOF_3 (equation 7).

Since pure TaO_2F was obtained according to the XRD and spectroscopic determinations in the present study, molar masses may be related to the weight loss. The two most likely solid decomposition products are Ta_2O_5 and $\text{Ta}_3\text{O}_7\text{F}$ as seen for the niobium analogue. Considering

the mass percent change (7%) observed on figure 9, no plausible set of decomposition steps was found for an anhydrous environment. If, however, we assume that some moisture was available either due to incomplete purging of the TG furnace, or trapped in the sample as allowed by Wilkinson *et al.*(2014)'s formulation of the niobium analogue, the decomposition can be postulated to proceed according to Equation 8.

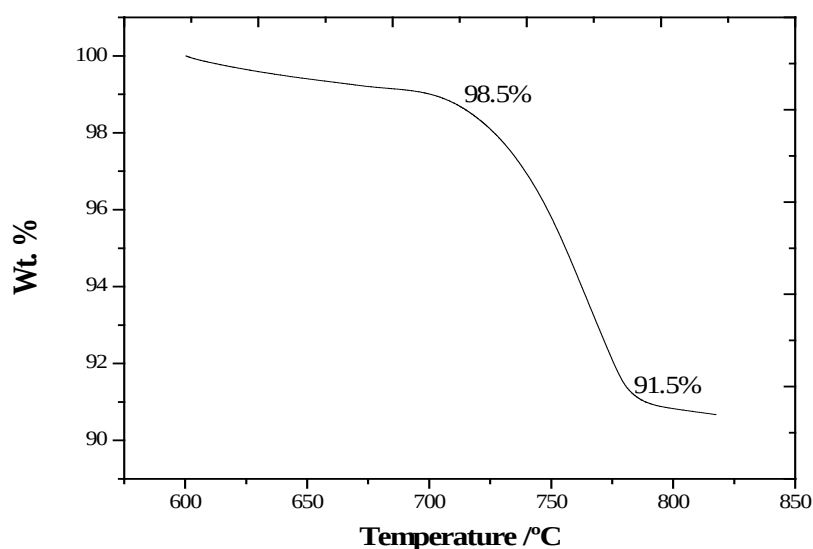
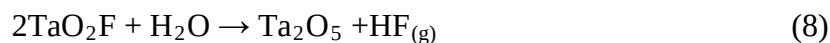


Figure 9: TG for prepared TaO₂F.

2.4 Higher fluorinated oxyfluorides (O:F < 2)

The fluorination of the dioxyfluorides of both tantalum and niobium leads to more highly fluorinated compounds such as MOF₃. To study these compounds, a slight excess of MF₅ was reacted with MO₂F as described by Equation 6. The reaction was completed in a stainless steel autoclave, flushed with N₂, at 200 °C. Two hours reaction time was given.

The presence of unreacted dioxyfluorides was confirmed by XRD analysis (Figures 10 and 11).

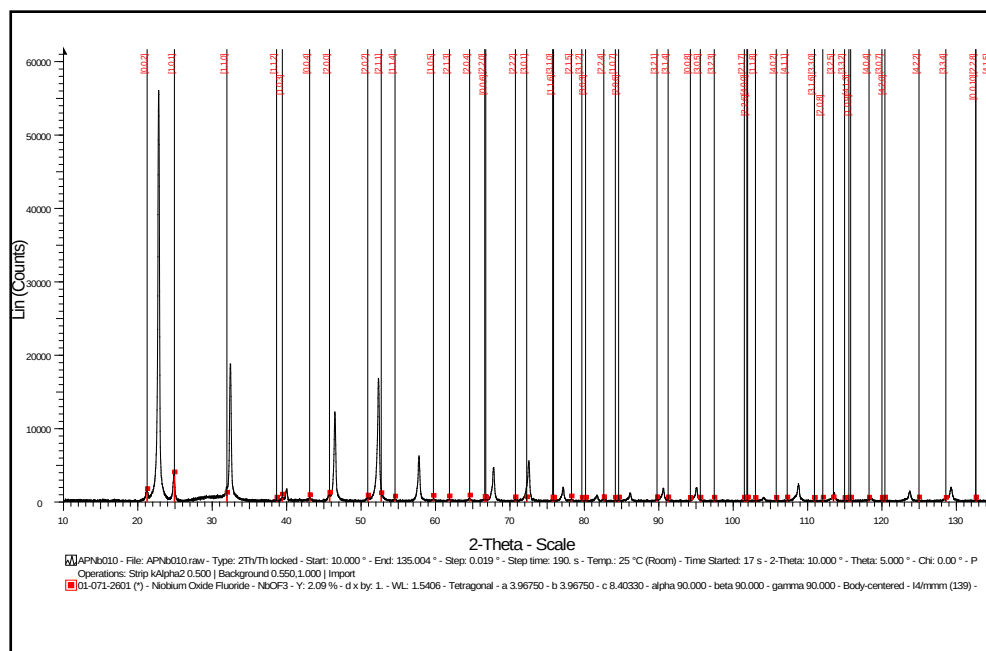


Figure 10: XRD pattern of the reaction product of niobium pentafluoride and niobium dioxyfluoride overlaid with stick patterns for NbOF_3 . This pattern clearly shows unreacted NbO_2F .

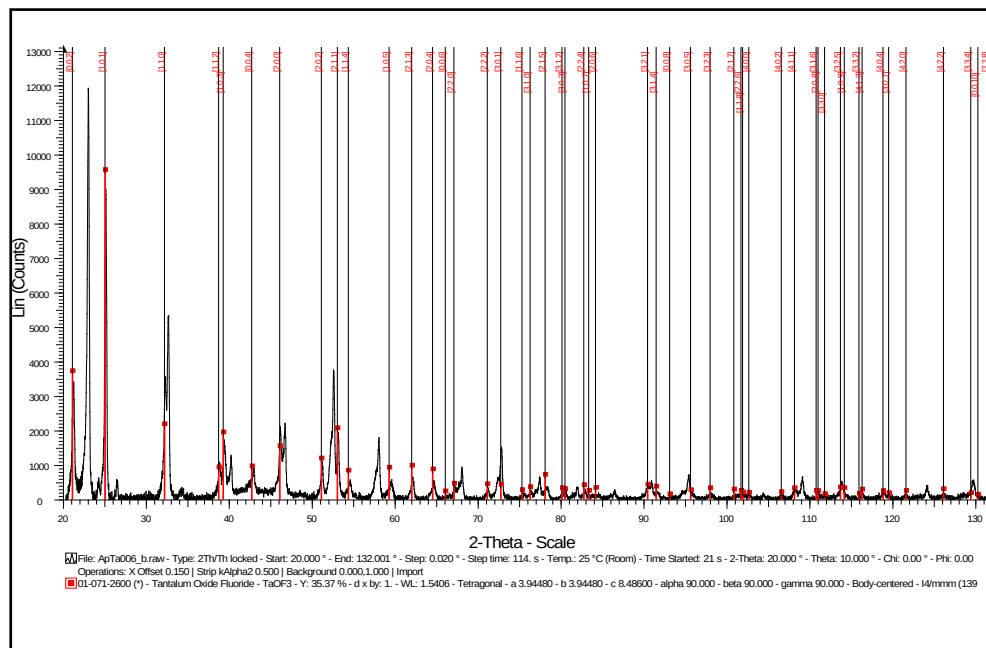


Figure 11: XRD pattern for the reaction product of tantalum pentafluoride and tantalum dioxyfluoride overlaid with stick patterns for TaOF_3 . This pattern clearly shows unreacted TaO_2F .

The prepared products have IR absorption spectra shown in Figure 12a and b, and Raman absorptions shown in Figures 13 and 14. The Raman spectra are not consistent with the infrared counterpart and makes their accuracy questionable, this may in part be due to instability of the compounds in the Raman laser. In their work, Köhler *et al.*(2002) did not obtain Raman spectra for these compounds either.

Unfortunately, the presence of unreacted dioxyfluoride values precludes unambiguous assignment of these absorption bands.

In addition to the bands already attributed to TaO₂F, there were absorptions at 1 000 and 944 cm⁻¹ that correspond to terminal metal oxygen (M=O) vibrations.

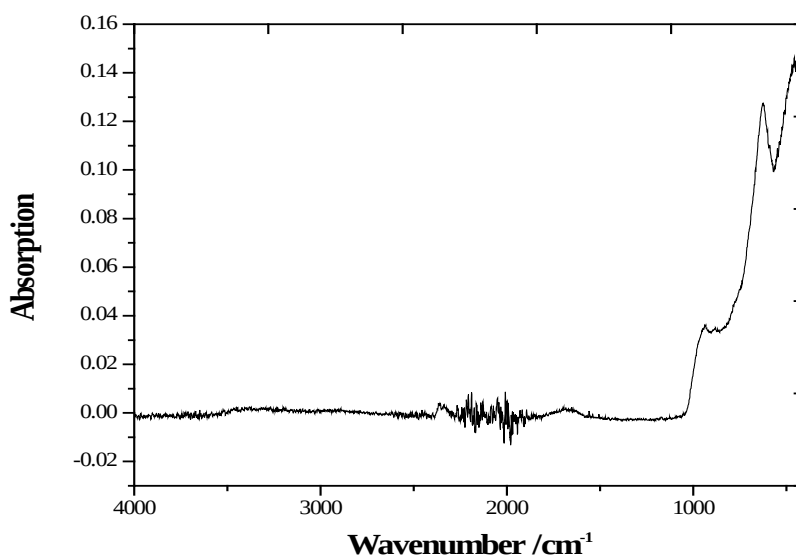


Figure 12a: FTIR spectrum of synthesised NbOF₃

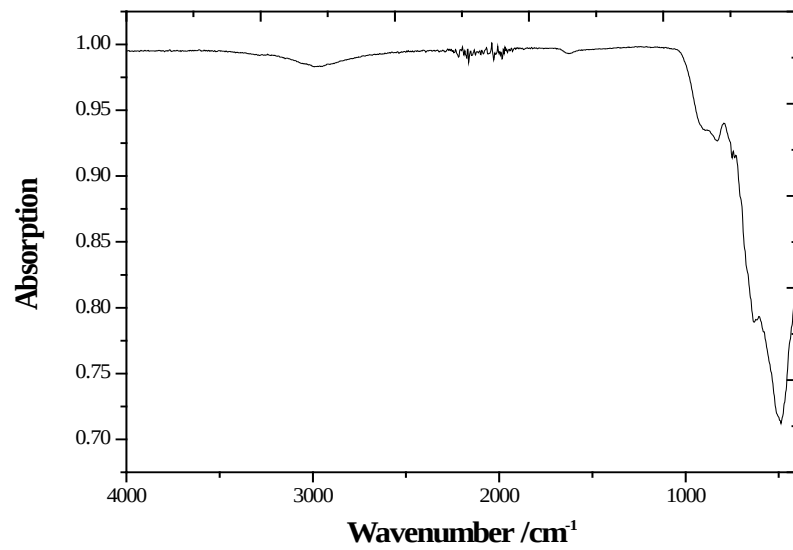


Figure 12b: FTIR spectrum of synthesised TaOF₃.

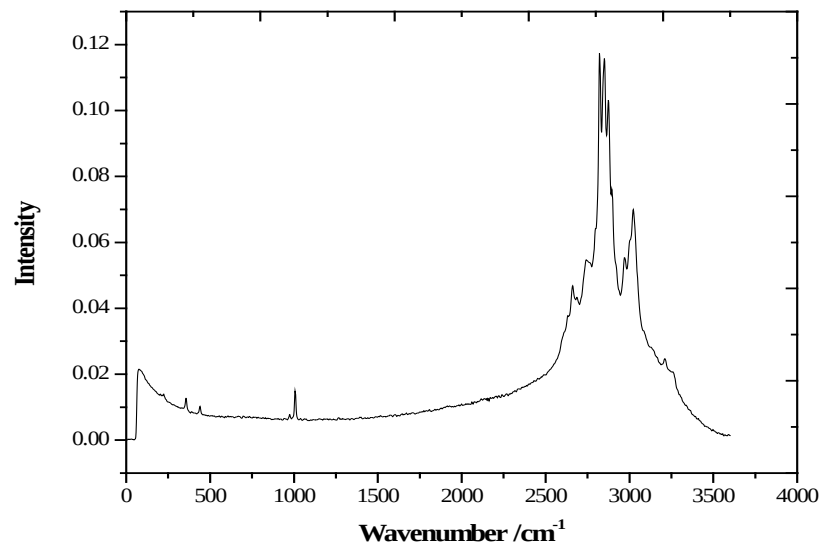


Figure 13: Raman spectrum of synthesised NbOF₃.

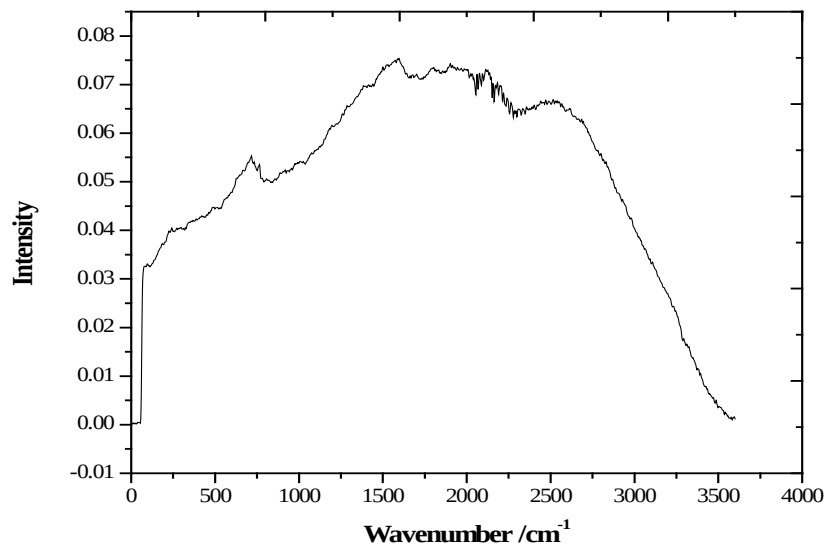


Figure 14: Raman spectrum of synthesised TaOF₃.

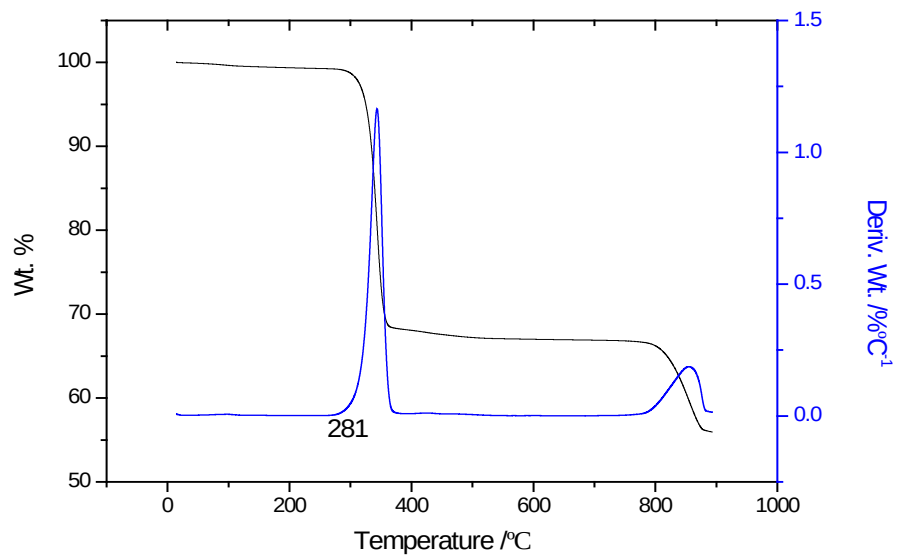


Figure 15: TG of synthesised TaOF₃, with some unreacted TaO₂F.

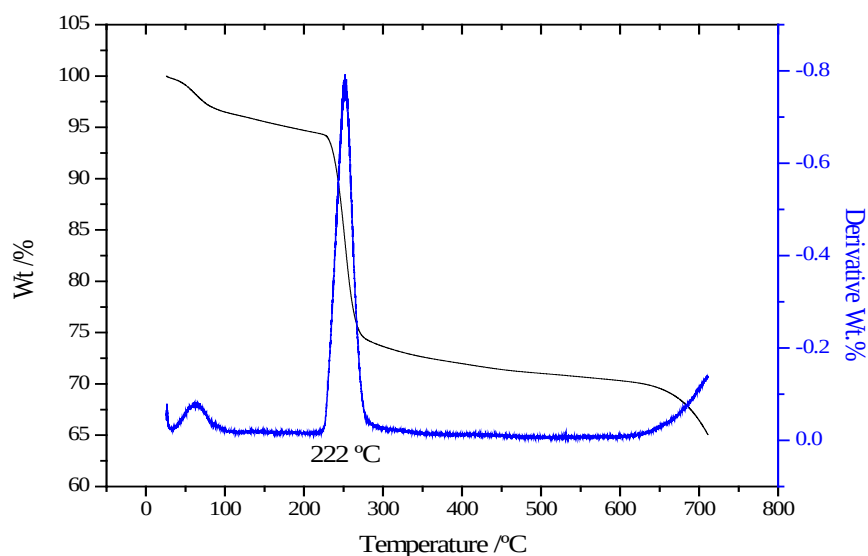


Figure 16: TG of synthesised NbOF_3 , with some unreacted NbO_2F .

Nieder-Vahrenholz *et al.* (1987) state that the decomposition temperatures of NbOF_3 and TaOF_3 are 280 and 400 °C respectively, but judging from the experiments conducted in the present study (Figures 15 and 16). The values determined from our measurements indicate significantly lower values at 222 °C and 281 °C respectively. Though the presence of unreacted reagent may influence the values that were determined, it's not expected to be significantly different from the real value since it involves sublimation of the product from the reaction mixture.

2.5 Conclusion

The work in this chapter comprises the preparation and characterisation of the dioxyfluorides (MO_2F) and oxytrifluorides (MOF_3) of niobium and tantalum. It is shown from the collected data that XRD cannot be used to discriminate between these two compounds and that even Raman/IR spectral properties are too similar to make a confident distinction. Systematic assignment of the vibrational spectra led to the conclusion that the dioxyfluorides of tantalum and niobium are structurally and functionally identical. Despite being the heavier atom, by calculating unit cell parameters from XRD data, it can be concluded that tantalum dioxyfluorides are almost identical in size to the niobium analogues.

The only aspect in which the oxyfluorides of tantalum and niobium show a remarkable difference is their thermal properties. The decomposition temperature is 50-100 °C lower for NbO₂F than for TaO₂F, and 60 °C lower for NbOF₃ than for TaOF₃. There is strong evidence from the TG pattern of the dioxyfluorides that the decomposition of TaO₂F does not proceed along the same pattern as that of NbO₂F.

2.6 References

- Adetunji, A.R., Siyanbola, W.O., Funtua, I.I., Olsunle, S.O.O., Afonja, A.A. and Adewoye, O.O., (2005). "Assessment of beneficiation routes of tantalite ores from key locations in Nigeria". *J.Min.Mat.Char.Eng.*, **4**: 67-73.
- Andersson, S. and Åström, A., (1965). "The thermal decomposition of NbO₂F". *Acta Chem.Scand.*, **19**: 2136-2138.
- Åström, A., (1967). "Vapour pressure studies on the thermal decomposition of NbO₂F". *Acta Chem. Scand.*, **21**: 915-919.
- Ayanda, O.S. and Adekola, F.A., (2011). "A review of niobium-tantalum separation in hydrometallurgy". *J.Min.Mat.Char.Eng.*, **10**: 245-256.
- Barner, J.H.v., Christensen, E., Bjerrum, N.J. and Gilbert, B., (1991). "Vibrational Spectra of Nb(V) Fluoro and Oxofluoro Complexes Formed in Alkali-Metal Fluoride Melts". *Inorg. Chem.*, **30**: 561.
- Brink, F.J., Withers, R.L. and Noren, L., (2002). "An electron diffraction and crystal chemical investigation of oxygen/fluorine ordering in niobium oxyfluoride, NbO₂F". *J. Solid State Chem.*, **166**: 73-78.
- Buslaev, Yu. A., Ilyin, E.G., Kopanev, V.D. and Gavrish, O.G. , (1971). "Synthesis and properties of complex ammonium fluorides of niobium and tantalum". *Isv. Akad. Nauk. SSSR, Ser. Chim.*, 1139
- Cooper, M.A., Hawthorne, F.C. and Cerny, P., (1999). "Ta-Nb order in the crystal structure of niobium-rich calcionate". *Can. Mineral.*, **37**: 1289.
- Cordier, S., Hernandez, O., Thepot, J.Y., Shames, A.I. and Perrin, C., (2003)., "Synthesis, crystal structure, and characterization of the first Nb(3) triangular cluster compound bonded to fluorine ligands: association of Nb(3)I(i)F(i)(3)F(a)(8)L(a) units and Nb(IV)L(6) Octahedra with L=O and F", *Inorg. Chem.*, **42**: 1101.
- Cordier, S., Roisnel, T. and Poulain, M., (2004). "Synthesis and characterization of the novel Nb₃O₅F₅ niobium oxyfluoride: the term n = 3 of the Nb_nO_{2n-1}F_{n+2} series ". *J. Solid State* , **177**: 3119-3126.
- De Wolff, P. M., (1972), "The definition of the indexing figure of merit M20", *J. Appl. Cryst.*, **5**, 243
- Dove, M., (1997). "Theory of displacive phase transitions in minerals", *Am. Miner.*, **82**: 213-244.
- Dove, M., Pryde, A.K.A. and Keen, D.A., (2000). "Phase transitions in tridymite studied using 'Rigid Unit Mode' theory, Reverse Monte Carlo methods and molecular dynamics simulations", *Miner. Maga.*, **64**: 267-283.
- Frevel, L.K. and Rinn, H.W., (1956). "The crystal structure of NbO₂F and TaO₂F", *Acta. Cryst.*, **9**: 626 - 627.
- Glazer, A.M., (1972). "Classification of tilted octahedra in perovskites", *Acta. Cryst.*, **28**: 3384.
- Greenberg, E., Natke, C.A. and Hubbard, W.N., (1965). "Fluorine bomb calorimetry. X. The enthalpies of formation of niobium and tantalum pentafluoride". *J. Phys. Chem.*, **69**: 2089-2093.
- Haendler, H.M., Bartram, S.F., Becker, R.S., Bernard, W.J. and Bukata, S.W., (1954). "The reaction of fluorine with titanium, zirconium and the oxides of titanium(IV), zirconium(IV) and vanadium(V)". *J. Am. Chem. Soc.*, **76**: 2177.

- Hammonds, K.D., Dove, M., Giddy, A.P., Heine, V. and Winkle, B., (1996). "Rigid-unit phonon modes and structural phase transitions in framework silicates", *Am. Miner.*, **81**: 1057.
- Hiskey, C.F. and Batik, A.L., (1953). "Analytical chemistry of niobium and tantalum". *Anal. Chem.*, **25**: 823-825.
- Hoppe, R., Dähne, W. and Klemm, W., (1961). "Mangantetrafluorid, MnF_4 ". *Naturwissenschaften* **48**: 429.
- Ignat'eva, L.N., Atokhina, T.F., Merkulov, E.B., Polishchuk, S.A., Savchenko, N.N., Plotnichenko, V.G., Koltashev, V.V. and Buznik, V.M., (2006)., "Structure and properties of oxofluoroniobate glasses based on $MnNbOF_5$ ", *Zhurnal Neorganicheskoi Khimii* , **51**: 1532.
- Kalinnikov, V.T. and Agulyansky, A.I., (1985). "Preparation and some properties of Nb(Ta) complex fluorides and oxyfluorides ". *J. Fluor. Chem.*, **29**: 61.
- Kamali, K, Ravindran, T. R., Sairam, T. N., (2014). "High pressure Raman spectroscopic study of phase transformation in TaO_2F ". *Vib. Spec.*, **71**:12-17
- Kent, R. and Margrave, J.L., (1965). "Mass spectrometric at high temperatures. VIII. The sublimation pressure of iron(II) fluoride". *J. Am. Chem. Soc.*, **87**: 4754-4756.
- Kodama, H. and Goto, M., (1975). "The thermal decomposition of Nb_3O_7Cl and NbO_2F ". *Z. Anorg. Allg. Chem.*, **415**: 185.
- Köhler, J., Simon, A., Wüllen, L.V., Cordier, S., Roisnel, T., Poulain, M. and Somer, M., (2002). "Structure and properties of $NbOF_3$ and $TaOF_3$ – with a remark to the O/F ordering in the SnF_4 type structure", *Z. Anorg. Allg. Chem.*, **628**: 2683.
- Laptash, N. M., Maslennikova, I. G., Slobodyuk, A. B., Kavun, V. Ya., Goncharuk, V. K., (2013). "Bonding and structure of oxofluoroniobate-based glasses", *Inorg. Chem.*, **52**: 5722-5728
- Lassner, E. and Schubert, W.D., (1999). "Tungsten – Properties, Chemistry, Technology of the Element, Alloys, and Chemical Compounds". Springer, New York.
- Levason, W., Reid, G., Trayer, J., Zhang, W., (2014), "Synthesis, properties and structures of $NbOF_3$ complexes and comparisons with $NbOCl_3$ analogues". *Dalton Trans.*, **43**:3649-3659
- McConnell, A.A., Anderson, J.S. and Rao, C.N.R., (1976). "Raman spectra of niobium oxides". *Spect. Acta*, **32A**: 1067.
- Mehta, M.L. and Avasthi, M.N., (1972). "Normal coordinate analysis of tantalum(I) and niobium(I) hexahalide anions". *J. Cryst. Mol. Struct.*, **2**: 299-302
- Morelock, C.R., Greve, B.K., Cetinkol, M., Chapman, K.W., Chupas, P.J., Wilkinson, A.P., (2013). "Role of Anion Site Disorder in the Near Zero Thermal Expansion of Tantalum Oxyfluoride". *Chem. Mater.*, **25**: 1900-1904
- Mulja, T., Williams-Jones, A.E., Martin, R.F. and Wood, S.A., (1996). "Compositional variation and structural state of columbite-tantalite in rare-element granitic pegmatites of the Preissac-Lacorne batholith, Quebec, Canada". *American Mineralogist*, **81**: 146-157.
- Muraleedharan, K., Mujeeb, V.M.A., Aneesh, M.H., Gangadevi, T. and Kannan, M.P., (2010). "Effect of pre-treatment on isothermal decomposition kinetics of potassium metaperiodate". *Thermochim. Acta*, **510**: 160-167.
- Nagiev, K.D., (2004). "Spectrophotometric determination of simultaneously present niobium and tantalum". *J. Anal. Chem.*, **59**: 930.
- Nieder-Vahrenholz, H., Schäfer, H., (1987), "Die oxidfluoride de niobs und tantals". *Z. Annorg. Allg. Chem.*, **544**, 122-126
- Nikolaev, A.I., Kirichenko, N.V. and Maiorov, V.G., (2009). "Niobium, tantalum and titanium fluoride solutions". *Russ. J. Inorg. Chem.*, **54**: 505-511.
- Okamoto, H., (1992). *J. Phase Eq.*, **13**: 109.
- Osin, S.B., Davlyathsin, D.I. and Ogden, J.S., (2001). "The infrared spectra of products of tantalum and ruthenium reaction with fluorine isolated in solid argon". *Russ. J. Phys. Chem.*, **75**: 1312.
- Pienaar, A.D. and Vilakazi, B., (2012). "Gas-phase fluorination kinetics of Ta_2O_5 with elemental fluorine", *J. S.A. Inst Min. Metal.*, **112**: 545-549.

- Priest, H.F., (1950). "Anhydrous Metal Fluorides". Inorganic Syntheses, 3. McGraw-Hill, New York.
- Rai, A.K., Raju, S., Jeyagenesh, B., Mohandas, E., Sudha, R. and Ganesan, V., (2009). "Effect of heating and cooling rate on the kinetics of allotropic phase changes in uranium: A differential scanning calorimetry study". *J. Nucl. Mat.*, **383**: 215-225.
- Rau, J.V., Albertini, V.R., Chilingarov, N.S., Colonna, S. and Tamburini, U.A., (2001). "In situ time-resolved X-ray diffraction study of manganese trifluoride thermal decomposition". *J. Fluor. Chem.*, **108**: 253-256.
- Ruff, O., Eisner, F. and Heller, W., (1907), "On the properties of hexavalent tungsten", *Z. Anorg. Allg. Chem.*, **52**, 256
- Seleznov, V.P., Rakov, E.G. and Mikulenev, V.V., (1971). "Thermodynamic properties of niobium and tantalum pentafluorides". *Zhurnal Fizicheskoi Khimii*, **45**: 2941.
- So, S.P., (1973). "Normal coordinate analysis and thermodynamic functions of niobium and tantalum pentahalides", *J. Mol. Struct.*, **16**: 311-320.
- Werner, P. E., Eriksson, L., Westdahl, M., (1985). "TREOR, a semi-exhaustive trial-and-error powder indexing program for all symmetries", *J. Appl. Cryst.*, **18**: 367-370
- Wilkinson, A. P., Josefberg, R. E., Gallington, L. C., Morelock, C. R., Monaco, C. M., (2014). "History dependent thermal expansion in NbO₂F", *J. Sol. State Chem.*, **213**: 38-42
- Yu, M.G., Travkin, V.F., Ilyin, E.G., Karamushko, E.V. and Koralev, V.V., (2001). *Zvetnay Metallurgiy*, 10: 23-27.
- Yun, D., Li, J., Yang, X., Hu, L., Wang, Z., Liu, Y. and Wang, C., (2008). "Kinetic analysis on the non-isothermal dehydration by integral master-plots method and TG-FTIR study of zinc acetate dihydrate". *J. Anal. Appl. Pyrolysis*, **83**: 1-6.
- Zhang, Y., (1982), "Electronegativities of elements in valence states and their applications. 1. Electronegativities of elements in valence states", *Inorg. Chem.*, **21**: 3886-3889.
- Zmbov, K.F. and Margrave, J.L., (1968). "Mass spectrometric studies at high temperatures. XXII. The stabilities of tantalum pentafluorides and tantalum oxytrifluoride". *J. Phys. Chem.*, **72**: 1099-1101.

CHAPTER 3

DECOMPOSITION KINETICS OF MO_2F

3.1 Introduction

As described in the previous chapter, there is a definite need to study the decomposition reactions of the oxyfluorides of niobium and tantalum (Muraleedharan *et al.*, 2010; Yun *et al.*, 2008). Despite this, the oxyfluorides of tantalum and niobium have received little attention as regards to their physicochemical properties, even though an understanding of their nature would be of great benefit for scaling up the beneficiation process.

Though Andersson and Åström (1965; Åström, 1967) determined that, close to 700 °C (Tikhomirova *et al.*, 2008), they neglected to calculate the kinetic parameters and did not consider the effect of crystal water (Wilkinson, 2014) on the decomposition. From the literature search conducted for this thesis it seems that no other attempt has been made to obtain kinetic parameters for the decomposition reaction of either niobium or tantalum dioxyfluoride. In fact, no information at all has been published about the thermal decomposition of tantalum dioxyfluoride.

It is clear from a perusal of the literature that the correct method for determining the “true” values of the kinetic rate parameters during thermal decomposition is no simple matter and has been the subject of debate for several decades. Broadly it may be argued that there are three schools of thought regarding this matter, namely isothermal, non-isothermal and controlled-rate techniques. These categories can be further subdivided, and the results produced by each respective technique may differ significantly from the rest. Ultimately the value of the kinetic parameters lies in their ability to predict the decomposition, as well as the energies involved, accurately at different temperatures.

In the present study, several methods were used to analyse the thermal decomposition reaction data of the dioxyfluorides of tantalum and niobium to determine the previously unknown activation energies during the transformation. The experimental decomposition data were

obtained by means of thermogravimetric analysis and the data analysis techniques were based on the methods developed for thermal analysis data.

3.2 Theoretical background

Early attempts to determine the activation energy (E_a) and pre-exponential factor (A), using non-isothermal methods, without the inclusion of the conversion model, were pioneered by Kissinger (Budrugaec and Segal, 2007; Kissinger, 1956; 1957).

Though Sewry and Brown (2002) state that it is imperative to determine the values for the full kinetic triplet, E_a , A and the reaction model $f(\alpha)$, a good estimate of E_a and A may be obtained by taking the model-free approach. The model-free approach is also recommended by Vyazokin and Wight (1999) due to its ability to obtain “reliable and accurate” kinetic information. Reading *et al.* (1984) suggest several ways to obtain more meaningful kinetic data, specifically referring to sample preparation and experimental conditions.

By taking an approach similar to that followed by Kissinger, Ozawa (1965) and Wall and Flynn (1966) employed a method for the determination of E_a and A for the decomposition reactions, without any knowledge of the reaction model. This method included Doyle’s (1961) approximation, however, which leads to numerical inaccuracies (Vyazovkin *et al.*, 2011).

The more accurate Kissinger method was later generalised by Akahira and Sunose (1971) and further improved by Starink (2003). Starink’s method is recommended as the preferred method by ICTAC (Vyazovkin, *et al.*, 2011) when doing a model-free analysis. If an alternative methodology is considered, such as controlled-rate methods, the rate-jump method can be applied to the determination of these same kinetic parameters. This is difficult, however, when using a thermal analysis instrument with a large furnace since the method may require the furnace to be cooled to keep the reaction rate constant. If the assumption is that the reaction rate can be controlled by merely keeping the furnace at a constant temperature (true for certain reaction models), then the results obtained may be verified by using the more classical thermal analysis kinetic techniques.

Since minimal additional work is required when applying more than one technique for determining the kinetic constants, it is prudent to apply more than one technique as this not only increases accuracy but also provides a sanity check for the results.

The transformation rate during a reaction is assumed to obey the equation:

$$\frac{d\alpha}{dt} = f(\alpha)k(T) \quad (9)$$

where α signifies the degree of conversion. In most cases, the dependence of the reaction constant, k , on temperature (T) may be assumed to obey the Arrhenius (sometimes referred to as the kinetic) equation:

$$k = Ae^{-\frac{E_a}{RT}} \quad (10)$$

while $f(\alpha)$ is one of the several idealised reaction models that have been derived.

The generalised Kissinger equation (also called the Kissinger-Akahira-Sunose method) includes the heating rate, β , and combines Equations 10 and 11, which after integration leads to:

$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = -\frac{E_a}{RT_\alpha} + C \quad (11)$$

By means of this equation, E_a can be determined by plotting $\ln\left(\frac{\beta}{T_\alpha^2}\right)$ against $1/T$ at different heating rates but identical values of α . This method requires no assumption of the function $f(\alpha)$, but does require an approximation of the temperature integral (Starink, 2003). Starink (Qiu *et al.*, 2012; Starink, 2003) improved the approximation of this integral to arrive at his equation for the determination of E_a .

$$\ln \frac{\beta}{T_{\alpha}^{1.92}} = -1.0008 \frac{E_a}{RT_{\alpha}} + C \quad (12)$$

According to the Starink method, activation energy is determined from a plot of $\ln (\beta/T^{1.92})$ against $1/T$, where C is the integration constant, R the universal gas constant, β the heating rate, and T_{α} the temperature at transformation α .

Since the activation energy may depend significantly on the progress of the transformation, the shape of the graph of E_a should be plotted accordingly as a function of the extent of the reaction and may give additional insight into the reaction (Tribelhorn and Brown, 1995; Vyazovkin, *et al.* 2011). This is an example of an isoconversional approach.

Redfern and Coats (1964) introduced the heating rate, β , into the kinetic equation by multiplying both sides of the rate equation by $(\frac{1}{\beta} = \frac{dt}{dT})$. The activation energy is then calculated by using the slope of $\ln \left[\frac{g(\alpha)}{T^2} \right]$ vs $1/T$ according to the equation:

$$\ln \left[\frac{g(\alpha)}{T^2} \right] = \ln \left(\frac{AR}{\beta E_a} \right) \left(1 - \frac{2RT}{E_a} \right) - \frac{E_a}{RT} \quad (13)$$

Here $g(\alpha)$ is the integral form of the kinetic model $f(\alpha)$.

When using this technique, it is assumed that the term $\ln \left(\frac{AR}{\beta E_a} \right) \left(1 - \frac{2RT}{E_a} \right)$ remains constant over the temperature range, which is valid when $E_a \gg RT$. Recently some researchers have shown that deviations from linearity may occur when more complex kinetics are involved (Nikolaev *et al.*, 2009). Nevertheless, this technique is still often used in the current research (Boča *et al.*, 2007; Su *et al.*, 2009) and gives an accurate indication of the reaction model.

This chapter evaluates a series of well-known reaction models (Maitra *et al.*, 2007; Vlaev *et al.*, 2008) associated with decomposition to determine the activation energy of the decomposition

transformation of the dioxyfluorides of tantalum and niobium. After getting an indication of the kinetic parameters E_a and A using Starink's method, the technique of Redfern and Coats is used to determine the reaction model.

Further refinement of kinetic parameters E_a and A is then performed by using a grid search, varying these two variables and minimising the error between the experimental and theoretical decomposition curves.

3.3 Experimental

3.3.1 Samples

The preparation and identification of niobium dioxyfluoride (NbO_2F) and tantalum dioxyfluoride (TaO_2F) are described in Chapter 2, and analyses were performed without prior “drying” of the sample.

3.3.2 Thermal decomposition experiments

Between 5 and 10 mg of the sample was weighed, placed in an alumina crucible and analysed with a TA Instruments SDT Q600 analyser.

Samples were heated at ramp rates between 2 and 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$ in the range 500 to 900 $^{\circ}\text{C}$ (Figures 17 and 18) and the mass signal was recorded. All runs were performed in triplicate under a 100 $\text{ml}\cdot\text{min}^{-1}$ N_2 flow.

3.4 Results and discussion

3.4.1 Niobium dioxyfluoride (NbO_2F)

A conversion (α) plot can be made by converting the change in weight fraction shown in Figure 17, to conversion by using the formula:

$$\alpha = \frac{m_t - m_i}{m_t} \quad (14)$$

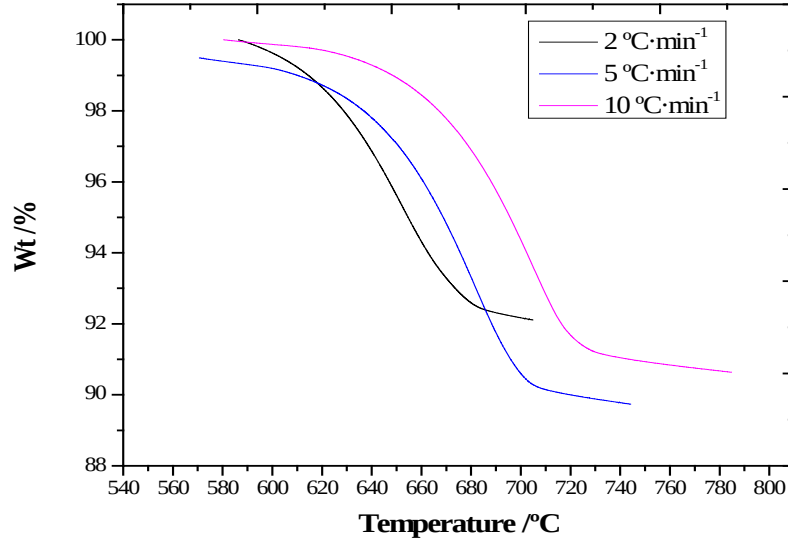


Figure 17: TG curves for the decomposition: $2\text{NbO}_2\text{F} \cdot x\text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{Nb}_2\text{O}_5$ at different heating rates.

where m_t is the total mass (absolute or percentage) at the start of the transformation, and m_i the instantaneous mass at a given temperature.

According to Starink's method, $\ln(\beta/T^{1.92})$ has to be plotted against $1/T$. Solving Starink's equation for E_a then leads to the data shown in Table 7, graphically presented in Figure 18.

The monotonic decrease seen in E_a with conversion is not an unknown phenomenon (Malecka *et al.*, 2003) and is in fact quite common (Vyazovkin *et al.*, 2011). A dependence of E_a on α where E_a decreases as α increases and is concave is usually indicative of a reversible stage process such as that seen during dehydration (Ball, 1995).

Table 7: Values obtained for Starink's method.

α	$\ln(\beta/T^{1.92})$			$E_a / \text{J.mol}^{-1}$
	2	5	10	
	$/ ^\circ\text{C} \cdot \text{min}^{-1}$			
0.10	-12.37	-11.52	-10.91	149483.5
0.20	-12.41	-11.56	-10.95	148469.3
0.30	-12.43	-11.58	-10.97	147162.3
0.40	-12.44	-11.60	-10.99	145856.8
0.50	-12.46	-11.61	-11.00	144912.0
0.60	-12.47	-11.63	-11.02	144156.8
0.70	-12.48	-11.64	-11.03	143820.2
0.80	-12.49	-11.65	-11.04	143514.4
0.90	-12.50	-11.66	-11.05	143514.4

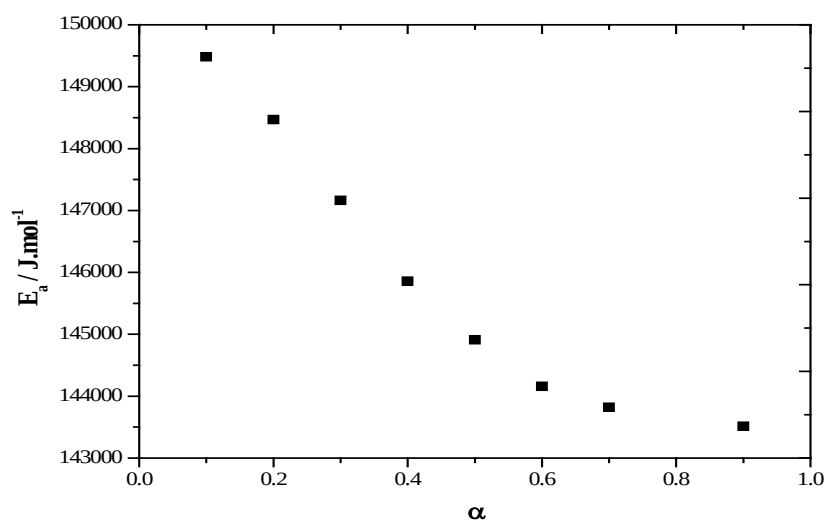


Figure 18: E_a values for the decomposition of NbO_2F according to the Starink method.

Literature in the field of thermal analysis suggests (Vyazovkin *et al.*, 2011) that E_a should be determined for $0.05 < \alpha < 0.95$. The average E_a value in this region is $145.4 \text{ kJ} \cdot \text{mol}^{-1}$ for NbO_2F .

If the correct function (Table 8), $f(\alpha)$, can be determined, the Starink and Coates-Redfern method should yield similar values for E_a . By using this as an additional criterion, some of the ambiguity that may arise from a linearity evaluation between $\ln \left[\frac{g(\alpha)}{T^2} \right]$ against $1/T$ can thus be removed.

Decomposition reactions usually obey one of the following kinetic mechanisms: nucleation; random nucleation; contracting disk, cylinder or sphere; or diffusion control. A plot of $d\alpha/dT$ against α gives a first indication of the kinetic model that may be governing the transformation.

According to the figures published by Khawam and Flanagan(2006), a plot of $(d\alpha/dt)$ vs. α gives an upward convex shape for the diffusion, shrinking-core, or Avrami-Erofeev models (Table 10). This correlates to the plot shown in Figure 21, suggesting that one of these models apply.

Table 8: Mechanistic models that give an upward convex shape for a plot of $(d\alpha/dt)$ vs. α

Symbol	Model description	$f(\alpha)$
A2	Avrami-Erofeev	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$
A3	Avrami-Erofeev	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$
A4	Avrami-Erofeev	$4(1-\alpha)[- \ln(1-\alpha)]^{3/4}$
R2	Contracting area	$2(1-\alpha)^{1/2}$
R3	Contracting volume	$3(1-\alpha)^{2/3}$
D1	1-D diffusion	$1/(2\alpha)$
D2	2-D diffusion	$-[1/\ln(1-\alpha)]$
D3	3-D diffusion-Jander	$[3(1-\alpha)^{2/3}]/[2(1-(1-\alpha)^{1/3})]$

It is evident from the $d\alpha/dT$ vs α data (Figure 19) that at a heating rate of $2\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ there is a shoulder in the derivative curve of the transformation. At lower values of α the transformation proceeds at a faster rate than when higher temperature ramps are used. This provides evidence that, at this heating rate at least, more than a single reaction model is in play. At higher values of α , the transformation rate is similar for all ramp rates.

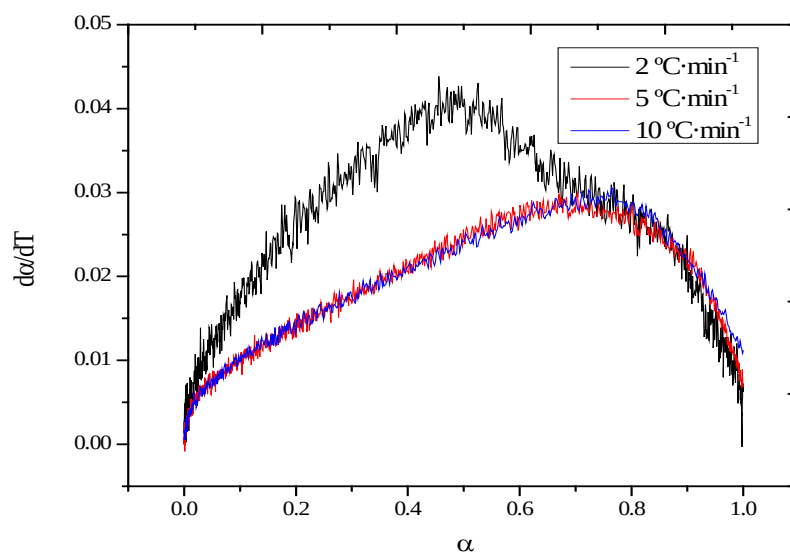


Figure 19: The $d\alpha/dT$ curves for the decomposition of NbO_2F at different heating rates.

The data presented in Figure 20 shows how the A2 model correlates linearly across the temperature ramps used. Even though a good correlation coefficient arises for the full conversion range studied, deviations from linearity are visually evident at conversions higher than $\alpha = 0.74$. This may indicate deviations from the idealised models, or an artefact of the assumptions of Redfern and Coats (1964). Further evidence that the A2 model has been correctly chosen can be garnered from the good agreement between the E_a value determined by using Starink's method and the E_a corresponding to A2 that is shown in Table 9.

Table 9: E_a and $\ln(A)$ according to the Coates-Redfern method for NbO_2F .

Heating rate (β) / $^{\circ}\text{C}\cdot\text{min}^{-1}$	E_a / $\text{kJ}\cdot\text{mol}^{-1}$	$\ln(A)$	R^2
2	179.6	22.8	0.996
3	176.2	25.3	0.999
5	156.9	20.1	0.999
7	147.4	19.1	0.997
10	162.9	21.2	0.999

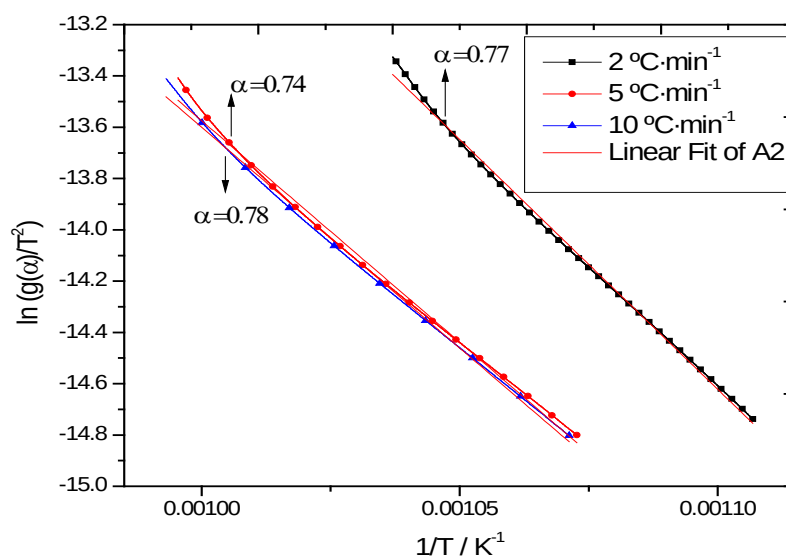


Figure 20: Coats-Redfern plot for the decomposition of NbO₂F.

The kinetic parameters were refined further by minimising the absolute value of the difference between the experimental conversion values and the values predicted by the integration of the rate law. Integration was done by using Euler's method, and minimisation was done by making a direct grid search, using the parameter values in Table 9 as a guide to establish the search bounds.

The sum of the difference between the calculated and experimental values ($\alpha_{\text{calc}} - \alpha_{\text{exp}}$) is then minimised by varying E_a and A until the best fit between the experimental and calculated values is obtained.

The activation energy (E_a) was varied between 120 and 200 kJ using step sizes of 1 kJ, whereas A was varied between 0 and 1.5×10^8 for each value of E_a using step sizes of 1×10^4 . The refined kinetic parameters obtained in this way are listed in Table 10, with the fitted data shown on Figure 21.

For completeness, and to double-check the Coats-Redfern results, n was also varied between 2 and 4 to include all the Avrami-Erofeev models. The best fit was obtained for $n = 2$ in each case. The results of each temperature ramp were fitted individually.

Table 10: Refined A2 kinetic parameters for NbO_2F .

Heating rate (β) / $^{\circ}\text{C}\cdot\text{min}^{-1}$	E_a / $\text{kJ}\cdot\text{mol}^{-1}$	$\ln(A)$
2	147	16.0
3	156	17.5
5	145	16.2
7	140	15.8
10	141	16.1

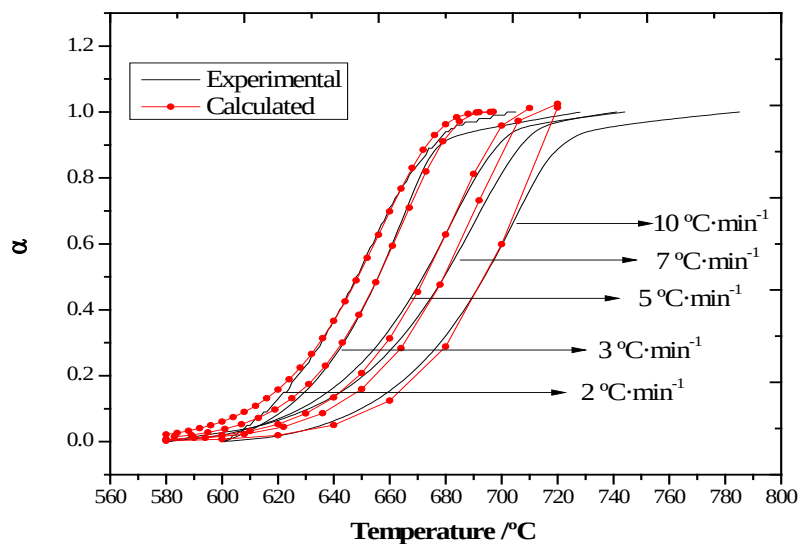


Figure 21: Fit of calculated to experimental data for the decomposition of NbO_2F .

3.4.2 Tantalum dioxyfluoride (TaO_2F)

An approach identical to that followed in section 3.4.1 was followed to obtain the kinetic parameters for the decomposition of TaO_2F . Figure 22 shows the TG curves for the decomposition of TaO_2F , with Table 12 and Figure 23 showing values for the Starink method.

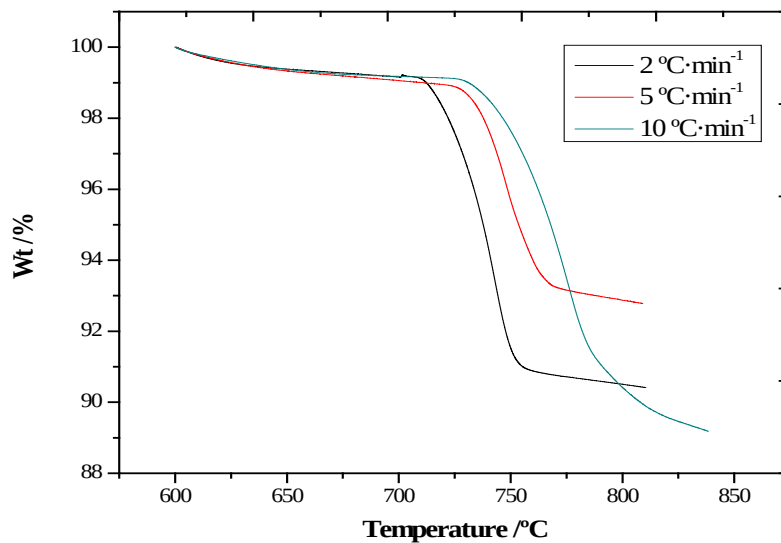


Figure 22: TG curves for the decomposition of TaO₂F at different heating rates.

Table 11: Values obtained using Starink's method.

α	$\ln(\beta/T^{1.92})$			$E_a / \text{J.mol}^{-1}$
	2	5	10	
	/ °C·min ⁻¹			
0.10	-12.37	-11.52	-10.91	409613.9
0.20	-12.41	-11.56	-10.95	377572.9
0.30	-12.43	-11.58	-10.97	355868.2
0.40	-12.44	-11.60	-10.99	337416.8
0.50	-12.46	-11.61	-11.00	321694.1
0.60	-12.47	-11.63	-11.02	308735.5
0.70	-12.48	-11.64	-11.03	298683.3
0.80	-12.49	-11.65	-11.04	290920.5
0.90	-12.50	-11.66	-11.05	282924.2

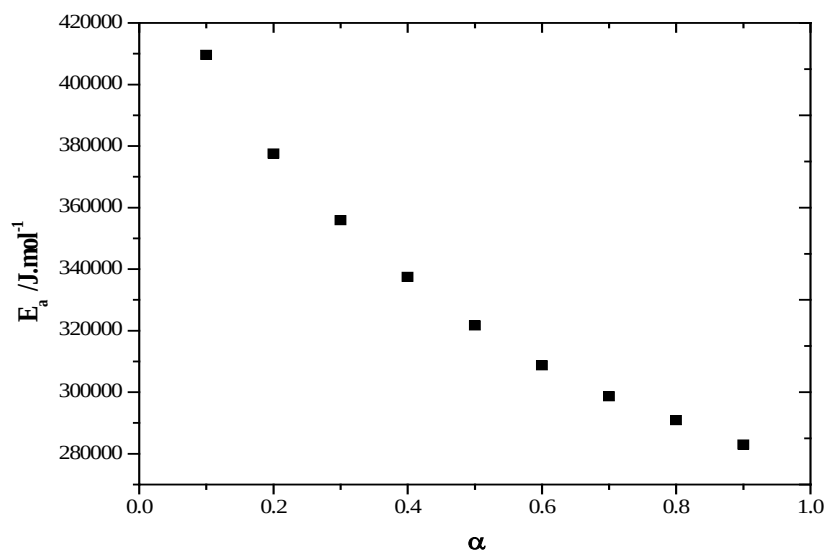


Figure 23: E_a values for the decomposition of TaO_2F according to the Starink method.

Unlike NbO_2F , the E_a of decomposition for TaO_2F varies from the start towards the end of the transformation. It may be more informative to report the E_a values in three distinct regions (Table 12).

Table 12: The value of E_a for the decomposition of TaO_2F during three stages of conversion

conversion range	E_a /J·mol ⁻¹	Standard deviation /J·mol ⁻¹
$0.1 < \alpha < 0.2$	393 593	22 600 (5.7%)
$0.2 < \alpha < 0.6$	330 928	20 346 (6.5%)
$0.6 < \alpha < 0.9$	290 842	7879 (2.7%)

For the decomposition of TaO_2F (Figure 24), a very good correlation with linearity is seen over the full conversion range studied, namely $0.1 < \alpha < 0.9$, for $\beta = 5$ and $10^\circ\text{C}\cdot\text{min}^{-1}$. For $\beta = 2^\circ\text{C}\cdot\text{min}^{-1}$ a marked deviation from linearity occurs $\alpha < 0.3$. The correlation coefficient or this ramp rate is significantly lower, $R^2 = 0.985$, than for $\beta = 5$ and $10^\circ\text{C}\cdot\text{min}^{-1}$. If the conversion range is limited to $0.3 < \alpha < 0.9$, however, the correlation improves to $R^2 = 0.998$.

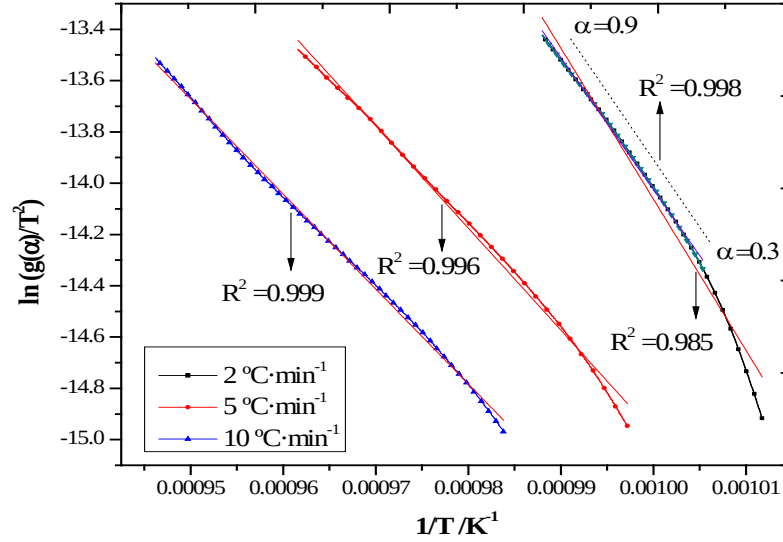


Figure 24: Redfern-Coats linearity plot for the decomposition of TaO₂F. With A2 fitted.

Table 13: E_a and ln(A) according to the Coates-Redfern method for TaO₂F.

Heating rate (β) /°C·min ⁻¹	E _a /kJ·mol ⁻¹	ln (A)	R ²
2	389.74	56.52	0.985
3			
5	330.72	37.00	0.996
7			
10	307.95	34.34	0.999

Using the Redfern-Coats values for the decomposition of TaO₂F (Table 13) as guide, E_a was varied between 200 and 400 kJ, using step sizes of 5 kJ, whereas A was simultaneously varied between 0 and 5 × 10⁷, using step sizes of 1 × 10⁴.

The resultant calculated data is plotted along with the experimental data in Figure 25 .

For n=2, the worst fit using this method was achieved for β = 2 °C·min⁻¹. When the grid search was expanded to optimise for order n in the Avrami-Erofeev equation as well, a surprising result was that there was a better fit to the experimental values for β = 2 °C·min⁻¹, when n=3 (Figure 26). Different values of the constant n in the equation may be interpreted as the differences in nucleation and nucleation growth. Optimised kinetic parameters are listed in Table 14.

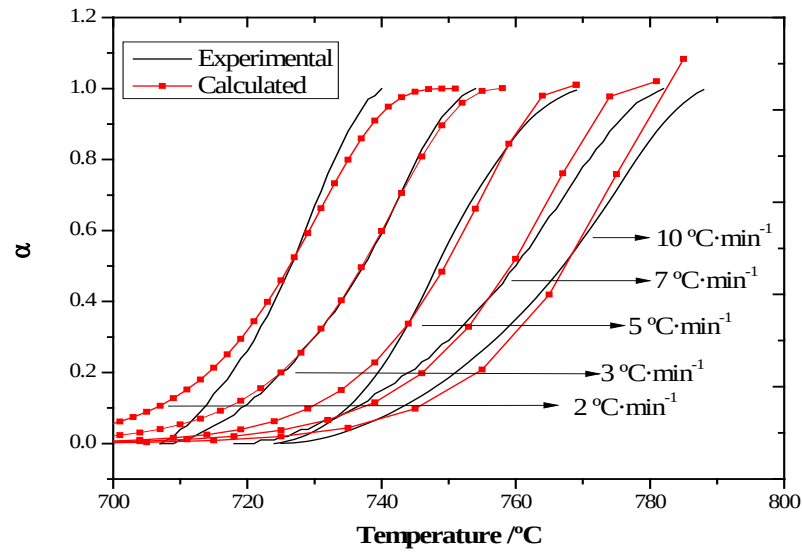


Figure 25: Fit of calculated to experimental data for the decomposition of TaO_2F .

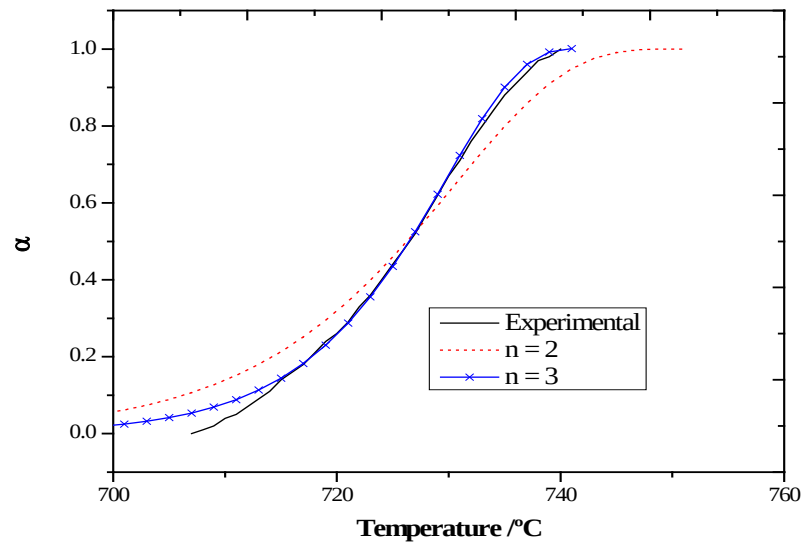


Figure 26: Simulated Avrami-Erofeev data for $n=2$ and $n=3$ plotted with experimental data.

Table 14: Optimised kinetic parameters from a grid search for TaO₂F.

β /°C·min ⁻¹	n	E_a /kJ·mol ⁻¹	ln (A)
2	2	359	40.7
2	3	327	36.8
3	2	359	40.6
5	2	336	37.9
7	2	327	36.8
10	2	320	36.1

3.5 Conclusion

The most likely set of kinetic parameters for the decomposition of (undried) NbO₂F as well as TaO₂F was determined from the data reported here. By using model-dependent and model-independent isoconversional kinetic analysis, an E_a value of 145-149 kJ·mol⁻¹ and A2 kinetic model were determined for niobium dioxynfluoride.

For TaO₂F, the E_a value for the decomposition is roughly double that for NbO₂F. Although the A3 kinetic model fits the decomposition best at a heating rate of 2 °C·min⁻¹, the best general fit is still the A2 model.

By using a grid search while varying the parameters, n , E_a and A , calculated data was fitted directly to the experimental data and an improved E_a value of 156 kJ·mol⁻¹ was obtained for NbO₂F and between 320 and 350 kJ·mol⁻¹ for TaO₂F, depending on the ramp rate.

3.6 References

- Akahira, T. and Sunose, T., (1971). "Method for determining activation deterioration constant of electrical insulating materials". *Research Report Chiba Institute Technology (Sci. Technol)*, **16**, 22-31.
- Andersson, S. and Astrom, A., (1965). "The thermal decomposition of NbO₂F". *Acta Chem. Scan.*, **19**: 2136-2138.
- Åström, A., (1967). "Vapour pressure studies on the thermal decomposition of NbO₂F". *Acta Chem. Scan.*, **21**: 915-919.
- Ball, M.C., (1995). "The thermal dehydration of solid ammonium copper(II) sulphate hexahydrate". *Thermochim.Acta*, **257**: 139-147.
- Boča, M., Danielik, V., Izanová, Z., Mikšiková, E. and Kubiková, B., (2007). "Phase diagrams of the KF-K₂TaF₇ and KF-Ta₂O₅ systems". *J. Therm. Anal. Cal.*, **90**: 159-165.

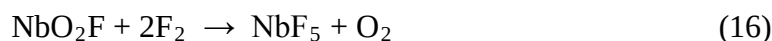
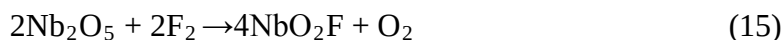
- Budrugaec, P. and Segal, E., (2007). "Applicability of the Kissinger equation in thermal analysis: revisited". *J. Therm. Anal. Cal.*, **88**: 703-707.
- Doyle, C.D., (1961). "Kinetic analysis of thermogravimetric data". *J. Appl. Polymer Sci.*, **5**: 285-292.
- Khawam, A. and Flanagan, D.R., (2006). "Solid-state kinetic models: Basics and mathematical fundamentals". *J. Phys. Chem. B*, **110**: 17315-17328.
- Kissinger, H.E., (1956). "Variation of peak temperature with heating rate in differential thermal analysis". *J. Res. Natl. Bur. Std.*, **57**: 217-221.
- Kissinger, H.E., (1957). "Reaction kinetics in differential thermal analysis". *Anal. Chem.*, **29**: 1702-1706.
- Maitra, S., Pal, A.J., Bandyopadhyay, N., Das, S. and Pal, J., (2007). "Use of genetic algorithm to determine the kinetic model of solid-state reactions". *J. Am. Ceram. Soc.*, **90**: 1611-1614.
- Malecka, B., Drożdż-Cieśla, E. and Olszewski, P.K., (2003). "Kinetics of thermal decomposition of manganese(II) oxalate". *J. Therm. Anal. Cal.*, **74**: 485-490.
- Muraleedharan, K., Mujeeb, V.M.A., Aneesh, M.H., Gangadevi, T. and Kannan, M.P., (2010). "Effect of pre-treatment on isothermal decomposition kinetics of potassium metaperiodate". *Thermochim. Acta*, **510**: 160-167.
- Nikolaev, A.I., Kirichenko, N.V. and Maiorov, V.G., (2009). "Niobium, tantalum and titanium fluoride solutions". *Russ. J. Inorg. Chem.*, **54**: 505-511.
- Ozawa, T., (1965). "A new method of analyzing thermogravimetric data". *Bull. Chem. Soc. Jpn.*, **38**: 1881-1886.
- Qiu, N.Y., Qiang; Miao, Yu-long, (2012). "Experimental study on relationship between thermal decomposition of SF₆ and overheat temperature". *Gaoya Dianqi*, **48**: 27-30.
- Reading, M., Dolimore, D., Rouquerol, J. and Rouquerol, F., (1984). "The measurement of meaningful activation energies". *J. Therm. Anal.*, **29**: 775-785.
- Redfern, J.P. and Coats, A.W., (1964). "Kinetic parameters from thermogravimetric data". *Nature*, **201**: 68-69.
- Sewry, J.D. and Brown, M.E., (2002). "'Model-free' kinetic analysis?", *Thermochim. Acta*, **390**: 217-225.
- Starink, M.J., (2003). "The determination of activation energy from linear heating rate experiments: a comparison of the accuracy of isoconversion methods". *Thermochim. Acta*, **404**: 163-176.
- Su, T.T., Zhai, Y.C., Jiang, H. and Gonh, H., (2009). "Studies on the thermal decomposition kinetics and mechanism of ammonium niobium oxalate". *J. Therm. Anal. Cal.*, **98**: 449-455.
- Tikhomirova, E.L., Makarov, D.V. and Kalinnikov, V.T., (2008). "Reaction of Niobium Pentoxide with ammonium hydrodifluoride". *Russ. J. Inorg. Chem.*, **53**: 988-992.
- Tribelhorn, M.J. and Brown, M.E., (1995). "Thermal decomposition of barium and strontium peroxides". *Thermochim. Acta*, **225**: 143-154.
- Vlaev, L., Nedelchev, N., Gyurova, K. and Zagorcheva, M., (2008). "A comparative study of non-isothermal kinetics of decomposition of calcium oxalate monohydrate". *J. Anal. Appl. Pyrolysis*, **81**: 253-262.
- Vyazovkin, S., Burnham, A.K., Criado, J.M., Pérez-Maqueda, L.A., Popescu, C. and Sbirrazzuoli, N., (2011). "ICTAC Kinetics Committee recommendation for performing kinetic computations on thermal analysis data". *Thermochim. Acta*, **520**: 1-19.
- Vyazovkin, S. and Wight, C.A., (1999). "'Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data". *Thermochim. Acta*, **340/341**: 53-68.
- Wall, L.A. and Flynn, J.H., (1966). "A quick direct method for the determination of activation energy from thermogravimetry data". *J. Polym. Sci. B*, **4**: 323-328.
- Wilkinson, A. P., Josefberg, R. E., Gallington, L. C., Morelock, C. R., Monaco, C. M., (2014). "History dependent thermal expansion in NbO₂F", *J. Sol. State Chem.*, **213**:38-42
- Yun, D., Li, J., Yang, X., Hu, L., Wang, Z., Liu, Y. and Wang, C., (2008). "Kinetic analysis on the non-isothermal dehydration by integral master-plots method and TG-FTIR study of zinc acetate dihydrate". *J. Anal. Appl. Pyrolysis*, **83**: 1-6.

CHAPTER 4

FLUORINATION OF Nb₂O₅ AND Ta₂O₅

4.1 Introduction

Elemental fluorine is a harsh fluorinating agent, which is expected to convert transition metal oxides to fluorides when the fluorination is performed in an anaerobic and dry environment. Rakov (Rakov *et al.*, 1971) demonstrated with the aid of x-ray phase analysis that, during the fluorination of Nb₂O₅ with F₂, two consecutive reactions take place:



and that the rate of the first reaction is much faster than the rate of the second. Rakov also completed a kinetic study and described the kinetics of the complete reaction with the equation:

$$1 - (1 - \alpha)^{\frac{1}{3}} = K_1 e^{\frac{-E_a}{RT}} p^n \tau \quad (17)$$

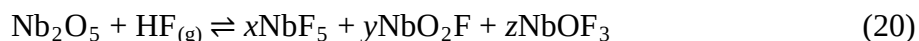
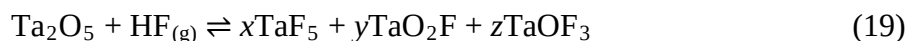
where α is the degree of the reaction response to the time τ ; $E_a = 109.5 \text{ kJ.mol}^{-1}$ (apparent activation energy); $n = 0.97 \pm 0.08$ is the order of the reaction; p the pressure in atm and $K_1 = 5 \times 10^7 \text{ min}^{-1}.\text{atm}^{-1}$. Furthermore he showed that the fluorination rate at 350 °C is closest to the theoretically predicted fluorination rate when the reaction is limited by fluorine adsorption or when the process is governed by a monomolecular reaction between the oxide (or oxyfluoride) and fluorine.

In a recent publication, Scheele *et al.* (Scheele, 2012) considered the use of NF_{3(g)} for the fluorination of Nb₂O₅. This route is less harsh than that of elemental fluorine. These authors report in their study that fluorination occurs above 200 °C and results in the formation of at least

one volatile (possibly NbF_5) and one non-volatile oxyfluoride species. Due to the chemical similarities between Ta_2O_5 and Nb_2O_5 , it is expected that Ta_2O_5 will behave similarly during fluorination, but no reference could be found in the current literature to any study concerning Ta_2O_5 fluorination. Similarly no literature on the use of anhydrous $\text{HF}_{(g)}$ for the fluorination of either of these compounds was found.

Differential scanning calorimetry and thermogravimetry are both useful when following the mentioned reactions. The mass changes seen on a TG thermogram may be related to F/O substitution as well as to the volatilisation and decomposition of oxyfluoride products. By contrast, isothermal DSC may be used to obtain an indication of the exothermic/endothermic heat flow that occurs during the fluorination reaction as well as when the reaction is complete. An advantage of using DSC to follow the reaction, is that it does not depend on mass changes occurring, which might be slight if no volatile products form.

In this chapter the investigation of the following three (unbalanced) reactions are reported:



Since the kinetics have already been determined, the qualitative results for $\text{Nb}_2\text{O}_5 + \text{F}_2 \rightleftharpoons \text{NbF}_5$ are reported without the calculation of the kinetic data.

4.2 Experimental

Commercially available Ta_2O_5 and Nb_2O_5 (>99.5%, Sigma Aldrich, Alfa Aesar) were used for all the experiments in the current study.

4.2.1 F_2 fluorination of $\text{Ta}_2\text{O}_{5(g)}$

A Perkin Elmer TGS2 TGA modified for use with corrosive gases was used in these experiments. More details of this experimental set-up appear in Appendix A. The complete

experimental set-up was located in an inert atmosphere (N_2) glove box. Samples of between 10 and 15 mg were loaded into nickel TG sample crucibles.

The initial reaction data for Ta_2O_5 and Nb_2O_5 was obtained by ramping the temperature from ambient to 500 °C at 10 °C·min⁻¹ under constant F_2 (10% F_2 in N_2) flow.

For subsequent Ta_2O_5 runs, the temperature was equilibrated at 315, 325, 335 and 345 °C before introducing $F_{2(g)}$. Several runs were completed at each temperature, exposing the sample to $F_{2(g)}$ for 5, 10, 20, 60 and 120 min respectively.

4.2.2 $HF_{(g)}$ fluorination in DSC

A Setaram C80 DSC (a description of this instrument appears in Appendix A) was connected to a stainless steel gas manifold system. The manifold system was equipped with a $N_{2(g)}$ mass flow controller for the purge gas, as well as a separate mass flow controller for the reactive gas.

A dilute HF/N_2 reactive gas mixture was prepared by loading a cylinder with 0.6 bar of $HF_{(g)}$ followed by $N_{2(g)}$ up to 6 bars. This yielded an HF/N_2 mixture of approximately 10 vol%.

Once the respective oxides had been loaded into the sample chamber of the C80 and heat-flow equilibrium reached, the purge gas flow was reduced to 10 ml·min⁻¹ and the reactive gas mixture introduced at 100 ml·min⁻¹. The reactive gas passed through both the sample and reference chamber so that only the reaction heat generated from the sample chamber was registered.

4.3 Theory behind experimental runs

4.3.1 Fluorination of Ta_2O_5 with F_2

Though kinetic parameters may be calculated by using a single TG run, it is accepted in modern thermal analysis that the determination of kinetic parameters from a single TG program should be avoided (Vyazovkin *et al.*, 2011). It is also accepted that when employing the scientific method, a minimum of 3 to 5 repetitions for every data point is required to ensure the reproducibility of reported results.

Accordingly, it would take 40 h to complete 5 runs at 4 temperatures for a 2 h reaction, excluding the time for preparing the samples and cooling down the instruments. For the

experimental programme designed for the present study, the reaction time was reduced to 14 h, as explained below.

During a TGA run the conversion value, α , is defined as:

$$\alpha = \frac{m_t - m_i}{m_t - m_\infty} \quad (21)$$

where m_t is the initial, m_i the instantaneous and m_∞ the final mass after reaction.

If it is assumed that at a set temperature the reaction proceeds along the same pathway, the 5 runs at each temperature can be combined into a single data set with the α value at 5 min for each run being equal to the conversion at the end of the 5 min run, and so forth. For example, Figure 27 shows the five runs conducted at 325 °C. During the first run, the F_2 exposure time was five minutes for point A, the second run was 10 minutes for point B, etc. Since all the graphs are superimposed it is therefore safe to construct Figure 29 from the collected points.

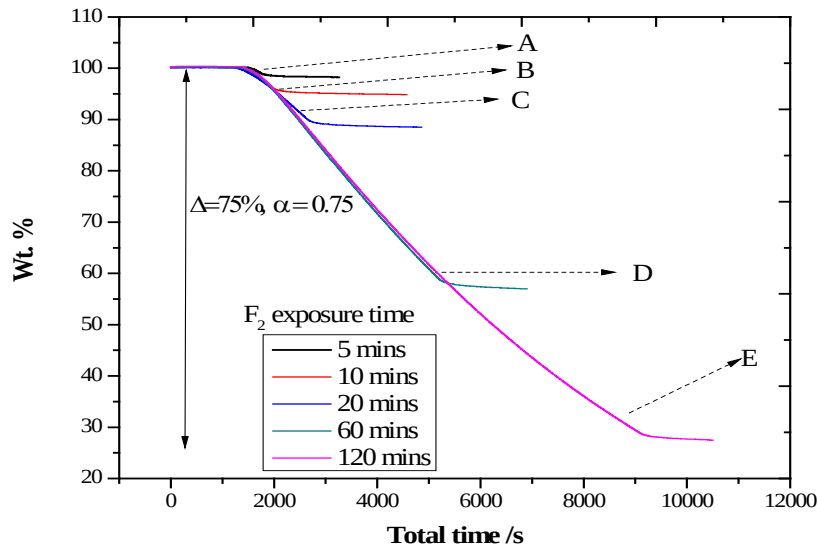


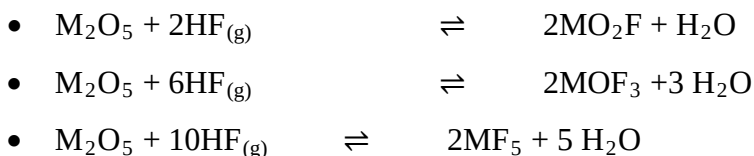
Figure 27: Data set for $Ta_2O_5 + F_2$ at 325 °C. At $T > 90$ °C the product TaF_5 is gaseous and volatilised from the TG crucible.

There are unique conditions at the extremes of the reaction (inception and termination), therefore all points were collected at $\alpha = 0.90$ to avoid deviations.

This method not only saves time but the 5-fold repetition also becomes inherent in the data set. Any spurious data points can immediately be identified by comparing the slopes of the TG curves. This procedure was followed for each of the four temperatures studied, and a single conversion curve at each temperature was generated.

4.3.2 HF_(g) fluorination

By using the HSC software package, it is possible to predict the possible reaction products from known thermodynamic values. For the reaction between HF_(g) and the pentoxides of niobium and tantalum, the following reactions have to be considered:

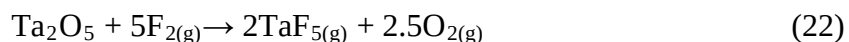


Additional reactions between products, as well as between products and the oxide, are also important.

4.4 Results and discussion

4.4.1 F_{2(g)} fluorination of Ta₂O₅

The reaction of Ta₂O₅ and F_{2(g)} is described by the equation:



which should result in 100% mass loss if complete conversion to TaF₅, which is gaseous at $T > 90^\circ C$, is achieved. It is necessary to evaluate further the physical aspects of the reaction.

During the fluorination of the tantalum oxide species, two possibilities could occur at the reaction interface.

The first possibility involves the formation of a solid intermediate, possibly an oxyfluoride, that covers the reaction surface. If this scenario occurs, the F_2 gas would have to diffuse through the solid layer to reach the unreacted core. This process has been reported for the fluorination of UO_2 (Homma *et al.*, 2008) as well as CeO_2 (Takashima *et al.*, 1992) with elemental fluorine. A D-type mechanism is expected to occur during such a process.

There is a second one-step possibility for the fluorination reaction. If fluorination occurs in a single step, no intermediate is formed and therefore the diffusion of the gas will not limit rate of the reaction. This may even be feasible if the lifetime of the intermediate is too short to create a significant effect.

The referenced fluorination of UO_2 and CeO_2 in both cases showed an initial increase in mass at the start of the fluorination reaction, corresponding to the formation of an oxyfluoride intermediate. This increase was also observed in the fluorination experiments with niobium oxide (Figure 28), but not in the experiments on tantalum oxide, which supports the second possibility.

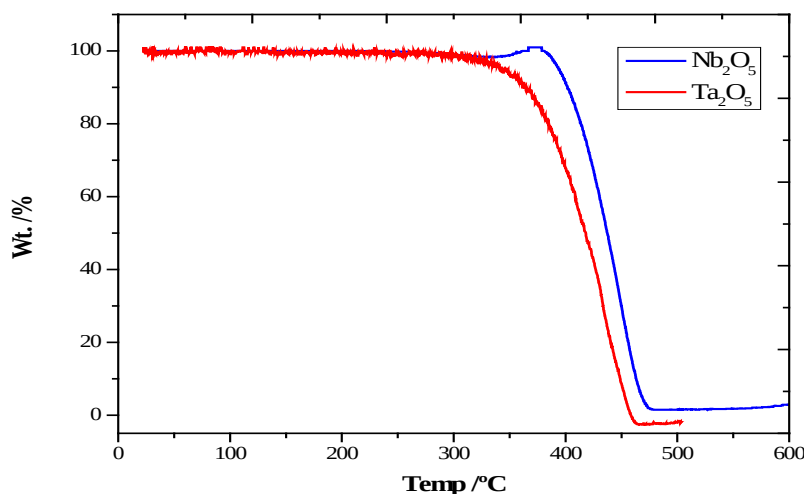


Figure 28: Fluorination results of niobium (Pienaar and Wagener, 2011) and tantalum oxide treated with elemental fluorine.

Figure 29 was obtained by using the method described in the theory section. Table 15 contains a complete list of the conversion values at different temperatures for this curve. By plotting these values as a function of reaction time (Figure 30), it is shown that the data is consistent with the expectation of a faster reaction rate at higher reaction temperatures.

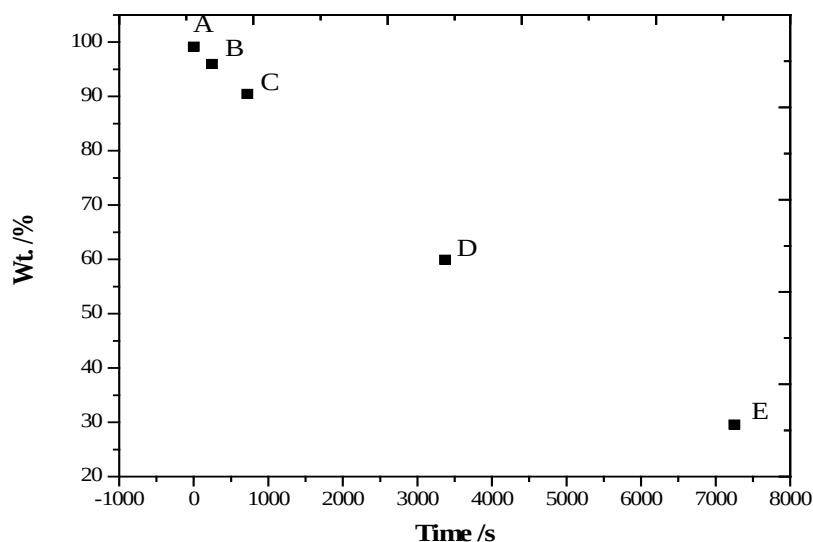


Figure 29: Graph constructed from collected data runs for the fluorination of Ta_2O_5 .

Table 15: Conversion values (α) for the experiment at different temperature and exposure times.

Point	Time (mins)	Temperature /°C			
		315	325	335	345
A	5	0.02	0.02	0.03	0.06
B	10	0.04	0.05	0.11	0.13
C	20	0.11	0.12	0.22	0.26
D	60	0.3	0.43	0.62	0.61
E	120	0.55	0.73	0.84	0.94

According to the kinetic equation, conversion is a function of the rate constant k , the kinetic model $f(\alpha)$ and pressure $h(P)$. It will be assumed for this study that the effect of pressure is negligible, as recommended by ICTAC (Vyazovkin, 2011).

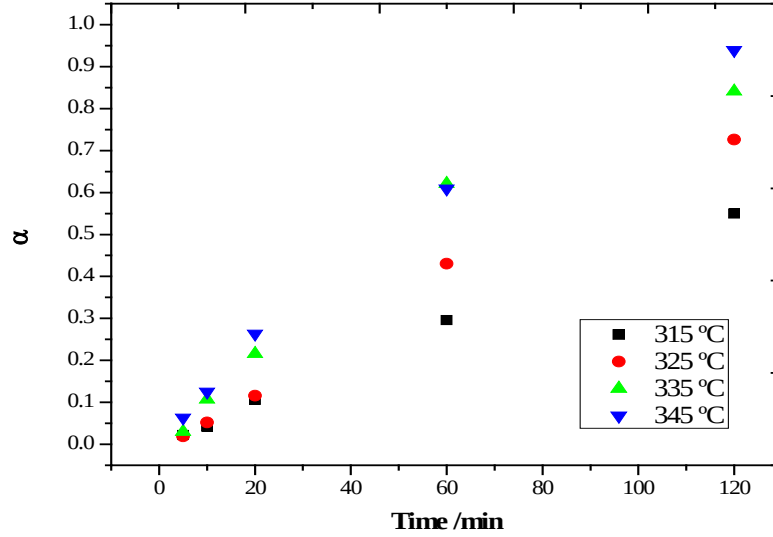


Figure 30: Conversion at different fluorination temperatures.

$$\frac{d\alpha}{dt} = k(T)f(\alpha)h(P) \quad (23)$$

Mathematical expressions for $f(\alpha)$ are well known (Maitra *et al.*, 2007; Vlaev *et al.*, 2008) and are only cursorily discussed here. The stability of the integral function of $f(\alpha)$, $g(\alpha)$, across different temperatures is an additional requirement for selecting the correct reaction model (Brown, 2001).

$$g(\alpha) = \int_0^\alpha [f(\alpha)]^{-1} d\alpha = kt \quad (24)$$

$$\ln(k) = \ln(A) - \frac{E_a}{RT} \quad (25)$$

One of the quickest ways to determine the kinetic model for the reaction is by determining the linearity of a plot of $g(\alpha)$, the integral form of $f(\alpha)$ against time (Ptáček *et al.*, 2010), since according to Equation 25, $g(\alpha)$ has to equal kt .

The stability of $g(\alpha)$ across different temperatures is an additional requirement for selecting the correct reaction model (Brown, 2001), because these experiments are best satisfied by the F2 and R3, D6 and D7 mechanisms. To determine the validity of each model across the different temperature ranges, the following Boolean argument was used:

$$\text{IF } (v_1 \text{ AND } v_2 \text{ AND } v_3 \text{ AND } v_4) > x \text{ then Fit} = \text{TRUE}$$

with v_{1-4} the values of the correlation coefficient (R^2) at 315, 325, 335 and 345 °C respectively, and the value of x is set at 0.98 as limiting. Accordingly, F2 and R3 best match the criteria, though D6 and D7 are reasonable fits as well.

Unfortunately it is often the case that several kinetic models fit a set of data, at which point some interpretation is needed. Specific consideration should be given to what type of reaction is being studied and the physical processes involved.

Though the F2 model is the only one that satisfies the criterion $x > 0.98$, this model indicates a second-order chemical reaction. A second-order kinetic reaction is intrinsically linked to the concentration of the reactants at any time. With $F_{2(g)}$ in excess at all times, at least pseudo first-order kinetics would be expected, and with the reaction rate independent of the F_2 exposure time (as suggested by coinciding TG curves), the $F_{2(g)}$ model is considered unlikely.

The R3 model describes a phase boundary-controlled reaction based on a contracting sphere model. During a reaction following this mechanism, the rate is determined by the movement of a reaction interface at a constant velocity inward (Sharp *et al.*, 1966).

Diffusion-controlled mechanisms are shown by the symbol D, and as the name suggests, the reaction is governed by diffusion. Three-dimensional diffusion is considered in both the D6 and D7 models.

For the three models that displayed the best correlation coefficient to linearity, k was calculated by plotting $g(\alpha)$ against time (Figure 31) and determining the slope (Table 16).

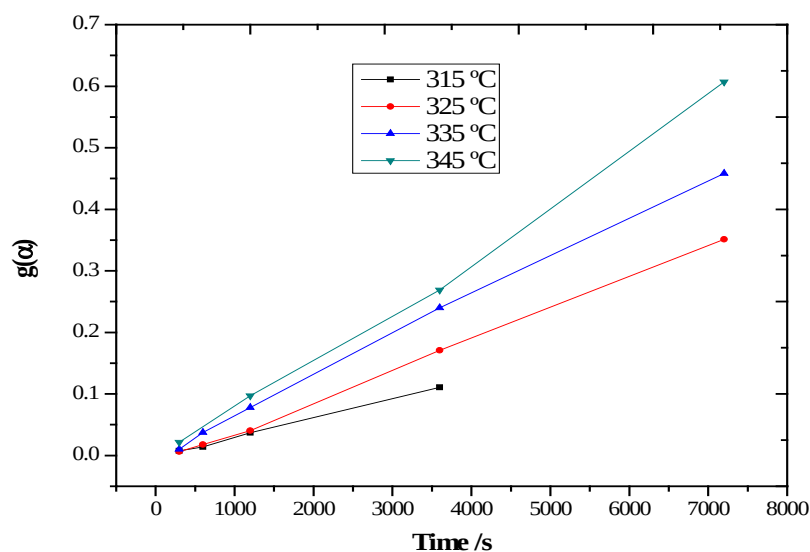


Figure 31: $g(\alpha)$ vs. t plot for the fluorination of Ta_2O_5 with $F_{2(g)}$ assuming the R3 model.

Table 16: Values of k determined by calculating the slope of a plot of $g(\alpha)$ against time.

Temp /°C	R3	D6	D7
315	0.0394	0.00305	0.0032
325	5.058×10^5	5.925×10^6	6.700×10^6
335	6.567×10^5	7.703×10^6	8.860×10^6
345	8.431×10^5	8.899×10^6	1.039×10^5

According to equation 26, the slope of $\ln(k)$ against $1/T$ (Figure 32) is multiplied by $-R$ ($-8.314 \text{ J} \cdot \text{K}^{-1}$) and results in E_a values of $78.5 \text{ kJ} \cdot \text{mol}^{-1}$ for the R3 model, $62.6 \text{ kJ} \cdot \text{mol}^{-1}$ for the D6 model and $67.5 \text{ kJ} \cdot \text{mol}^{-1}$ for the D7 model.

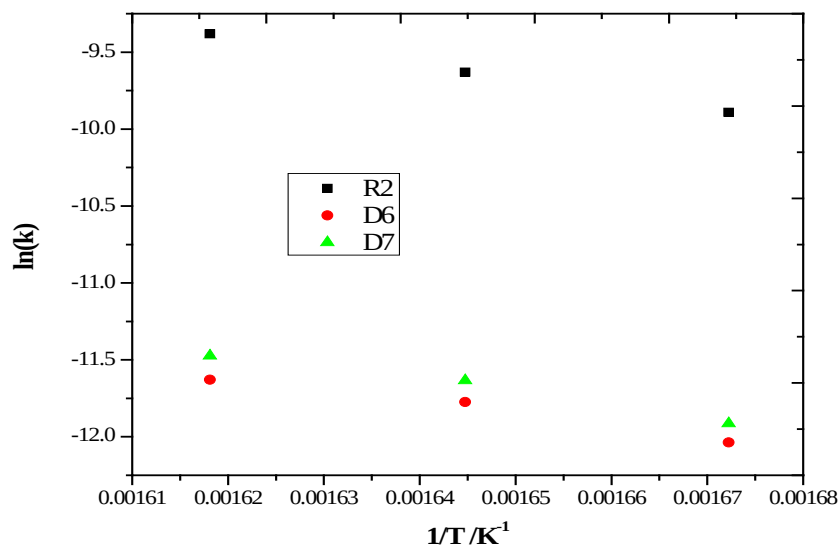


Figure 32: A plot of $\ln(k)$ against $1/T$ for the considered reaction models.

4.4.2 $\text{HF}_{(g)}$ fluorination of Nb_2O_5 and Ta_2O_5

4.4.2.1 Thermodynamic calculations

Several interesting conclusions can be drawn from the thermodynamic calculations completed using HSC (Figures 33-37). Referring to Figure 33, pentafluorides are only expected to form at lower temperatures; specifically, niobium pentafluoride should only form below 80 °C and tantalum pentafluoride below 120 °C.

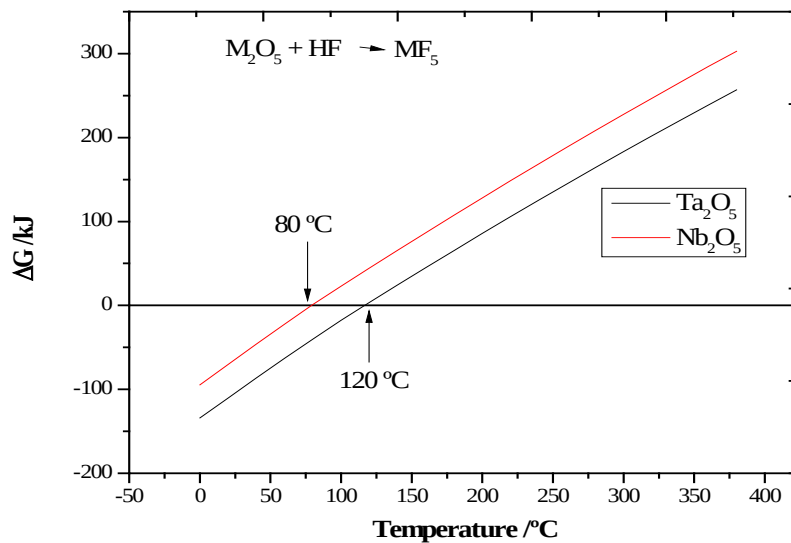


Figure 33: Gibbs free energy plots (calculated from HSC Chemistry®) for the reaction between $\text{HF}_{(\text{g})}$ and pentoxide forms of niobium and tantalum.

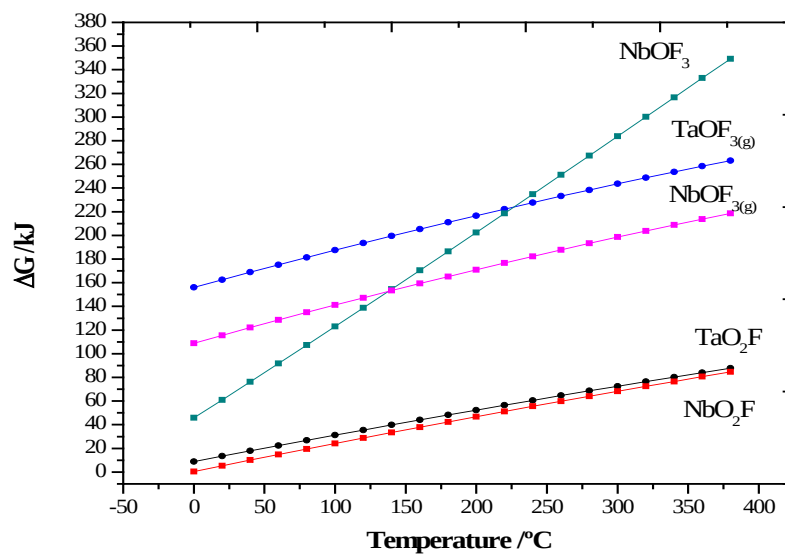


Figure 34: Gibbs free energy plots for oxyfluoride formation during the reaction between $\text{HF}_{(\text{g})}$ and pentoxides of niobium and tantalum.

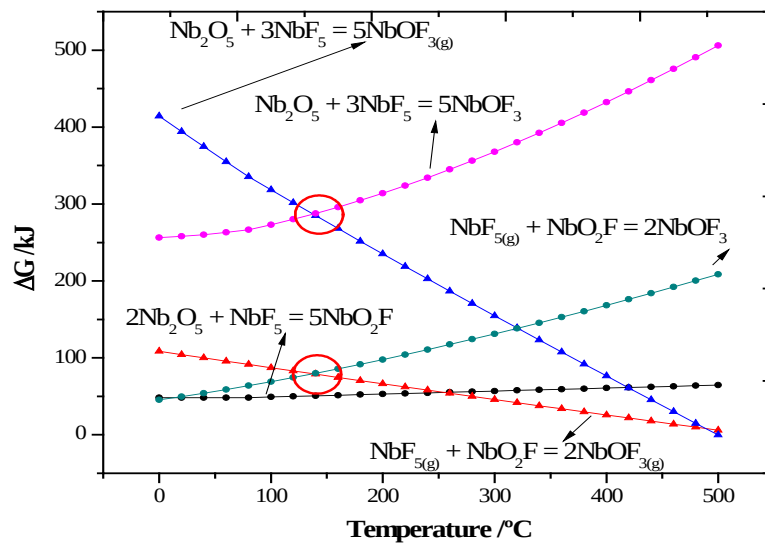


Figure 35: Gibbs free energy plots for product interactions from the Nb_2O_5 and $\text{HF}_{(\text{g})}$ reaction.

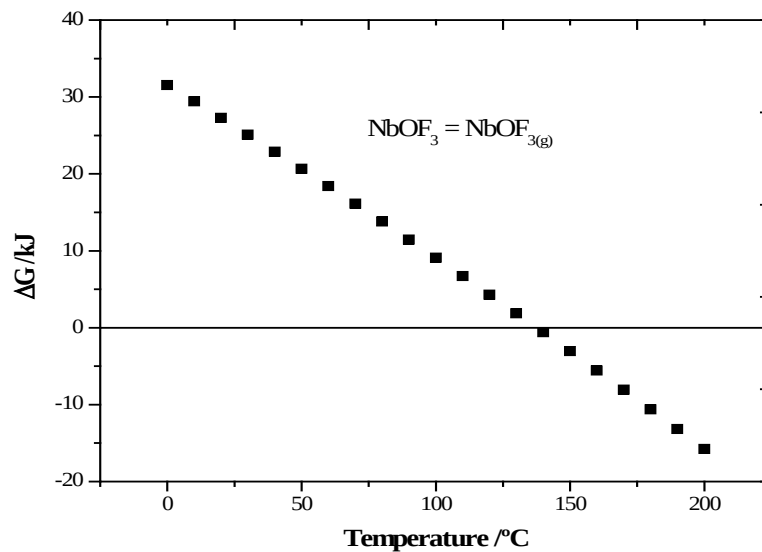


Figure 36: Free energy calculation for the conversion of NbOF_3 to gas phase. This graph shows that it becomes thermodynamically possible at 140 $^{\circ}\text{C}$.

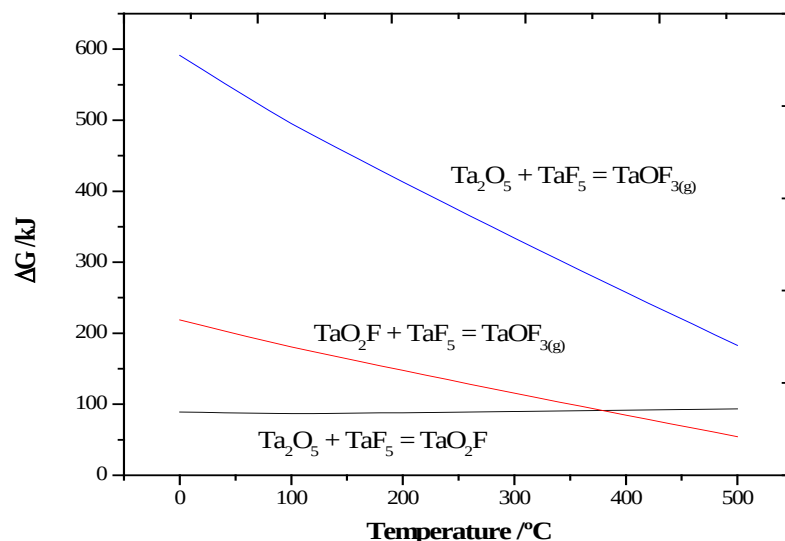


Figure 37: Gibbs free energy plots for solid-solid reaction products of tantalum oxyfluorides (no information for $\text{TaOF}_{3(s)}$).

This leaves a temperature bracket of 40 °C between 80 and 120 °C where only tantalum pentafluoride should be produced. The dilemma for this temperature bracket, however, is that NbF_5 and TaF_5 start sublimation/evaporation at 80 and 95 °C respectively. If a simultaneous reaction is performed on both niobium and tantalum oxide in this temperature range, care should be taken regarding the gaseous products that may form. Working below 80 °C ensures that only solid products are possible, but both oxides will react.

Figure 34 shows Gibbs free energy calculations for the reaction between Nb_2O_5 and $\text{HF}_{(g)}$ as well as Ta_2O_5 and $\text{HF}_{(g)}$ respectively. According to these calculations, the likelihood of oxyfluoride formation decreases as the temperature increases, and is not thermodynamically possible even at room temperature.

Figure 35 displays plots for the Gibbs free energy calculations for niobium oxyfluoride interactions with Nb_2O_5 , NbF_5 and $\text{NbF}_{5(g)}$. Since, in this temperature range, none of the energies calculated is negative, it is not thermodynamically possible for the oxyfluorides to form. The exceptions are $\text{NbOF}_{3(g)}$ which can form via reaction of NbF_5 with either Nb_2O_5 or NbO_2F ,

but only at temperatures higher than 480 °C. The points marked with red circles coincide with the temperature where the vapour pressure of NbOF_3 becomes significant (Figure 36)

Unfortunately no thermodynamic data is available for $\text{TaOF}_{3(s)}$. Figure 37 indicates that the formation of $\text{TaOF}_{3(g)}$ from these reactions below 500 °C is not thermodynamically allowed. Similarly, the formation of TaO_2F from the reaction between Ta_2O_5 and TaF_5 is forbidden.

4.4.2.2 DSC study of the $\text{Nb}_2\text{O}_5 + \text{HF}(g)$ reaction

During chemical reactions, heat is evolved and can be followed using DSC. Figure 38 shows the heat evolved during the reaction between $\text{HF}(g)$ and Nb_2O_5 at different temperatures. One run was repeated (50 °C), to confirm reproducibility. At least 3 peaks are visible at each temperature. If a sample is taken at the first peak, TG analysis shows that all mass losses occur below 150 °C, suggesting that the first peak correlates to the adsorption of HF onto the metal oxide. The second peak becomes less convoluted as the reaction temperature increases.

The TG thermograms (Figure 39 and Figure 40) of product Nb-A show a decrease in mass at 80 °C corresponding to the formation of NbF_5 . From the TG profile, and oxyfluoride characterisation completed, the decomposition of NbO_2F can be identified. Also seen is an additional oxyfluoride that sublimates at 140 °C; this is much lower than expected from the model NbOF_3 synthesised (Figure 16), but matches the thermodynamic data perfectly. The discrepancy may be due to the inability to synthesise a pure NbOF_3 sample. The product Nb-B (Figure 41), shows a similar trend, but without the formation of NbF_5 .

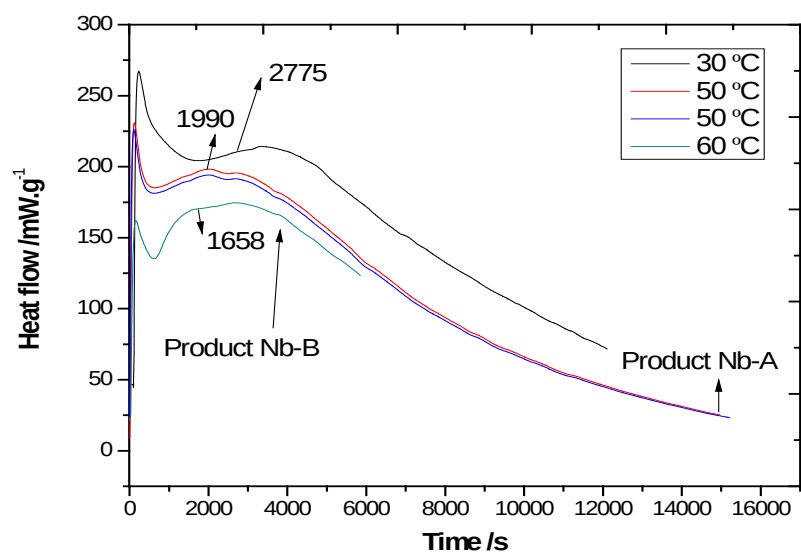


Figure 38: Heat evolved during the reaction between HF_(g) and Nb₂O₅ at different isothermal temperatures.

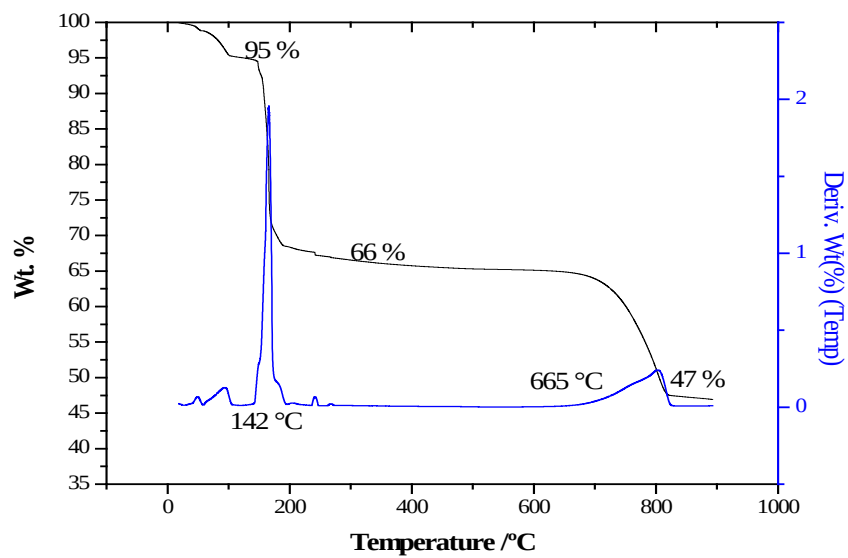


Figure 39: TG profile for Nb-A, the product of Nb₂O₅ and HF_(g) at 30 °C.

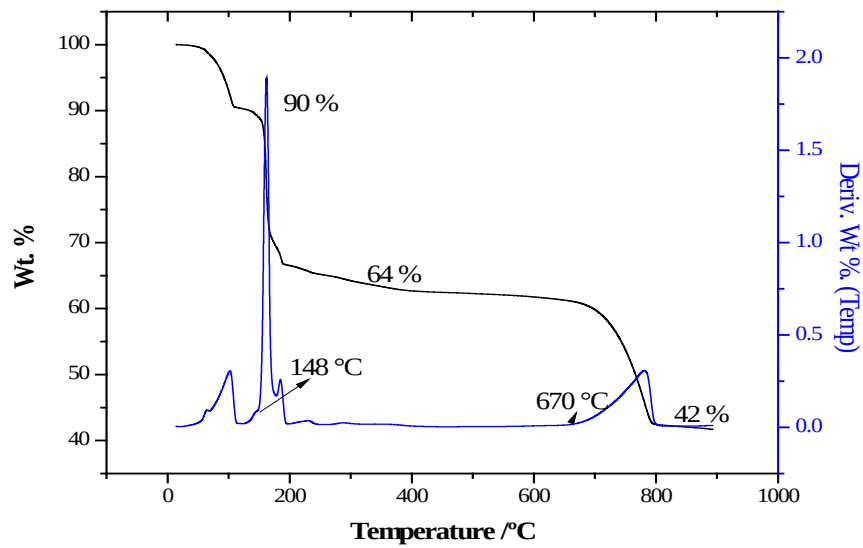


Figure 40: TG profile for Nb-A, the product of Nb_2O_5 and $\text{HF}_{(\text{g})}$ at 50 °C.

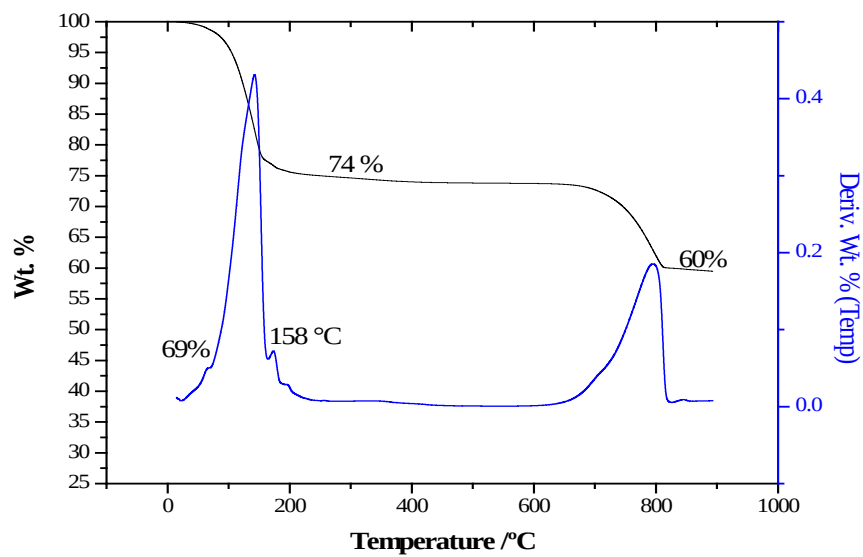


Figure 41: TG profile for Nb-B, the product of Nb_2O_5 and $\text{HF}_{(\text{g})}$ at 60 °C.

4.4.2.3 DSC study of the $\text{Ta}_2\text{O}_5 + \text{HF}_{(\text{g})}$ reaction

Similarly to the experiments completed for Nb_2O_5 , Ta_2O_5 was also treated with $\text{HF}_{(\text{g})}$ (Figure 42, Table 17). The only difference for these runs was that the 40 °C and 50 °C runs were done consecutively on the same day with only a few minutes of N_2 purge between runs. The first immediate result was the absence of the first exotherm for the 50 °C run. It was considered possible that the first exotherm would then be due to the adsorption of HF on the reaction vessel walls for the 40 °C run, which had then already been “passivated” for the next run done at 50 °C.

Table 17: Experimental conditions for Ta_2O_5 fluorination runs.

Run	Temp /°C	Δt	ΔH
1	40	7239	-412.57
2	50	9543	-617.89
3	50	10757	-635.67
4	60	12171	-793.91

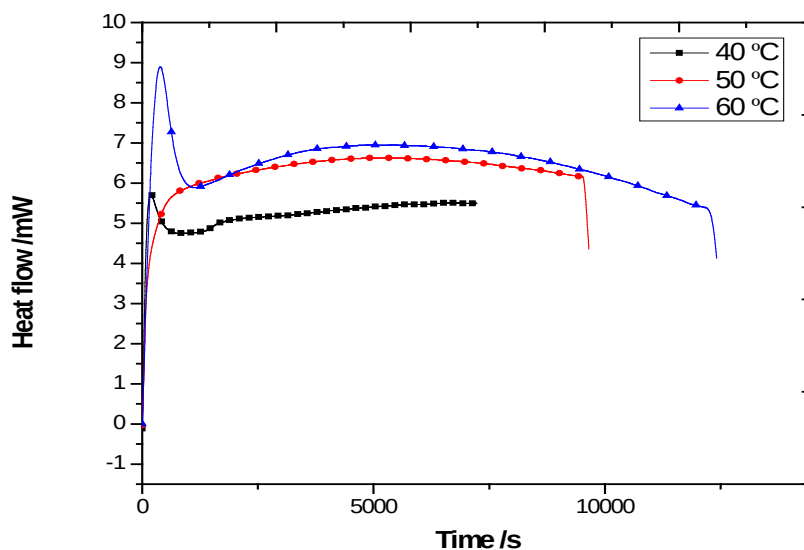


Figure 42: Heat evolved during the reaction between $\text{HF}_{(\text{g})}$ and Ta_2O_5 at different isothermal temperatures.

To confirm this, the 50 °C run was repeated the following day after an overnight N_2 purge. No difference in the reaction heat profile was observed for the two runs.

When the TG decomposition profile is examined for the product of the 50 °C reaction (Figure 43), it can be seen that the amount of volatiles (oxyfluorides and pentafluorides) below 100 °C and the amount of dioxyfluoride increased. This is expected owing to the longer exposure to $\text{HF}_{(g)}$. In this case the mass decrease at 290 °C matches the experimental data for TaOF_3 very well (Figure 15).

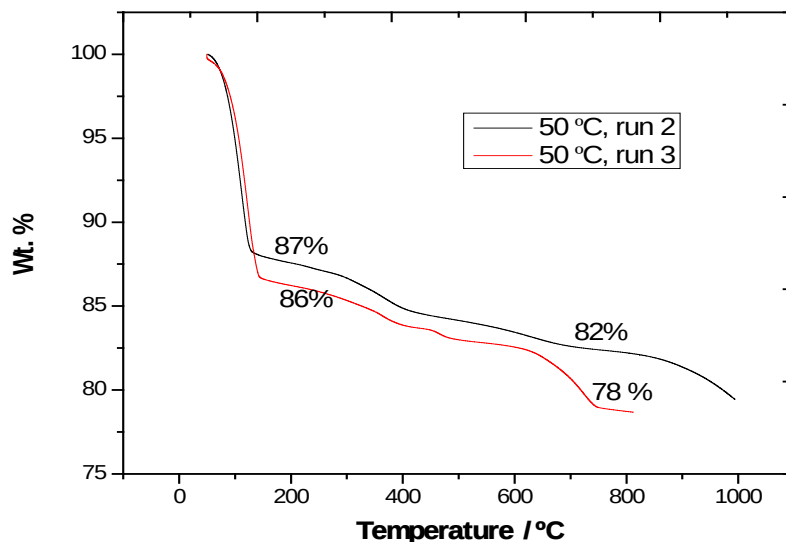


Figure 43: TG of products for 50 °C runs (runs 2 and 3).

4.5 Conclusion

The experiments completed for this chapter did not give definitive evidence of a two-step reaction mechanism as suggested by Rakov (Rakov *et al.*, 1971) for the $\text{Nb}_2\text{O}_5 + \text{F}_2$ reaction. Similar to the assertion that R3 governs the fluorination of Nb_2O_5 , the results of the present study indicate that the same mechanism fits Ta_2O_5 fluorination, although it may be argued that the reaction is diffusion controlled instead.

It is therefore proposed that if the reaction pathway for $\text{Ta}_2\text{O}_5 + \text{F}_{2(g)}$ proceeds along R3 pathway, it has an activation energy of $78.5 \text{ kJ}\cdot\text{mol}^{-1}$. However, if the D6 or D7 model governs the reaction, the activation energy is $62.6 \text{ kJ}\cdot\text{mol}^{-1}$ or $67.5 \text{ kJ}\cdot\text{mol}^{-1}$ for the respective models.

By using the methodology employed for the $F_{2(g)}$ reaction, a significant amount of time was saved, without compromising the accuracy of the results. Moreover there was no evidence of side products to the pentafluoride that formed from this reaction.

It is known that at least two oxyfluorides of both tantalum and niobium form from the $HF_{(g)}$ fluorination reactions. This is in stark contrast to the thermodynamic calculations that predict only the formation of the pentafluoride under these conditions.

4.6 References

- Brown, M.E., (2001). "Introduction to Thermal Analysis". Kluwer Academic Publishers, Dordrecht.
- Homma, S., Uoi, Y., Braun, A., Koga, J. and Matsumoto, S., (2008). "Reaction model for fluorination of uranium dioxide using improved unreacted shrinking core model for expanding spherical particles". *J. Nucl. Sci. Tech.*, **45**: 823-827.
- Maitra, S., Pal, A.J., Bandyopadhyay, N., Das, S. and Pal, J., (2007). "Use of genetic algorithm to determine the kinetic model of solid-state reactions". *J. Am. Ceram. Soc.*, **90**: 1611-1614.
- Pienaar, A.D. and Wagener, J.B., (2011), "Formation of oxyfluorides of niobium and tantalum using solid-gas reactions", 40th SACI Convention, Johannesburg, South Africa.
- Ptáček, P., Kubátová, D., Havlica, J. and Brandštetr, J., (2010). "Isothermal kinetic analysis of the thermal decomposition of kaolinite: The thermogravimetric study". *Thermochim. Acta*, **501**: 24-29.
- Rakov, E.G., Kopchikhin, D.S., Sudarikov, B.N. and Gromov, B.V., (1971). "Fluorination kinetics of Nb_2O_5 ". *Atomnaya Energiya*, **31**: 137-138.
- Scheele, R., McNamara, B., Casella, A.M. and Kozelisky, A., (2012). "On the use of thermal NF_3 as the fluorination and oxidation agent in treatment of used nuclear fuels". *J. Nucl. Mat.*, **424**: 224-236.
- Sharp, J.H., Brindley, G.W. and Achar, B.N.N., (1966). "Numerical data for some commonly used solid state reaction equations". *J. Am. Ceram. Soc.*, **49**: 379-381.
- Takashima, M., Fukami, S., Nosaka, Y. and Unishi, T., (1992). "Reaction between rare earth oxides and elemental fluorine. II. Kinetics of the fluorination of cerium dioxide". *J. Fluor. Chem.*, **57**: 131-138.
- Vlaev, L., Nedelchev, N., Gyurova, K. and Zagorcheva, M., (2008). "A comparative study of non-isothermal kinetics of decomposition of calcium oxalate monohydrate". *J. Anal. Appl. Pyrolysis*, **81**: 253-262.
- Vyazovkin, S., Burnham, A.K., Criado, J.M., Pérez-Maqueda, L.A., Popescu, C. and Sbirrazzuoli, N., (2011). "ICTAC Kinetics Committee recommendation for performing kinetic computations on thermal analysis data". *Thermochim. Acta*, **520**: 1-19.

CHAPTER 5

SEPARATION OF Nb_2O_5 AND Ta_2O_5

5.1 Introduction

Separation using liquid-liquid extraction has significant drawbacks since it involves the use of aqueous hydrofluoric acid as well as several organic solvents. The procedure generates a large quantity of hazardous liquid waste that is difficult and expensive to store and process.

Naturally occurring tantalum and niobium are found in a pentoxide form in mineral ores (Kent and Margrave, 1965). The fluorination of niobium and tantalum oxide were respectively described in the previous chapter; in the present chapter the possibility of separating these oxides when they are fluorinated in concert is investigated. The metal pentoxides were converted to a mixture of dioxyfluorides and more highly fluorinated species. The differences in the thermal decomposition/sublimation (using volatilisation when decomposition or sublimation is undefined) temperatures of these compounds allow thermal separation.

5.2 Experimental

5.2.1 Fluorination reactions

Dilute $\text{HF}_{(\text{g})}$ was prepared by loading a cylinder with 0.6 bars of $\text{HF}_{(\text{g})}$ followed by N_2 up to 6 bar. This yielded an HF/N_2 mixture of approximately 10 vol%. A Setaram C80 calorimeter with Hastalloy sample holders, used as fluorination reaction vessels, was employed to monitor the reaction heat flow. All experiments were conducted under constant nitrogen purge and the $\text{HF}_{(\text{g})}$ mixture was introduced into the purge gas at $95 \text{ std ml} \cdot \text{min}^{-1}$ once thermal equilibrium had been achieved.

For single component experiments, both Ta_2O_5 (Alfa Aesar, 99.9 %) and Nb_2O_5 (Alfa Aesar, 99.9 %) were first treated with $\text{HF}_{(\text{g})}$ at 30°C , to get an indication of their reaction products. The effect of temperature on the fluorination reaction in mixtures of these oxides was then studied by

varying the temperature from 30 to 60 °C in several separate experiments. The flow rate of the purge gas was also varied between 30 and 100 ml·min⁻¹. The compositions used for the experiments using oxide mixtures are shown in Table 18, and the operating parameters for the fluorination and the separation steps in Table 19.

Table 18: Mixtures of tantalum and niobium pentoxide prepared for separation.

Mixture	Ta ₂ O ₅ /g	Nb ₂ O ₅ /g
1	1.356	1.188
2	0.366	0.343

Table 19: Operating parameters for fluorination experiments.

Experiment	Mixture	N ₂ Flow /ml.min ⁻¹	Fluorinating Temp /°C
1	1	100	40
2	1	100	40
3	1	50	40
4	2	50	60
5	2	50	30

Product distributions were determined by the selective sublimation and decomposition of the product at selected temperatures, using a TA Instruments QDT 600 simultaneous TG/DSC. The metal content of each product was determined by ICP-OES analysis.

5.2.2 Preparation of model compounds

The oxyfluorides (MO₂F and MOF₃) of both niobium and tantalum were prepared according to the procedure used by Köhler (Köhler *et al.*, 2002). The metal pentoxide was dissolved in 40% HF_(aq) aided by microwave digestion. After filtration and precipitation of the dioxyfluoride from solution, a powdery white product was obtained and dried at 150 °C overnight. XRD analysis indicated that MO₂F was the only crystalline phase present for both the niobium and tantalum products when using this technique.

The oxytrifluorides (MOF_3) were subsequently prepared by the reaction of MF_5 with the MO_2F species, as described by the following reaction equations:



These reactions were completed in sealed Hastalloy C80 sample vessels by adding a mechanically mixed excess (*ca.* 20%) of MF_5 to MO_2F and heating the vessel to 200 °C. After two hours at this temperature, the vessel was cooled and the XRD patterns were collected. The only crystalline phases that could be identified from these diffractograms were MO_2F and MOF_3 . Thermogravimetric measurements were performed on a TA Instruments SDT Q600. The experimentally determined volatilisation temperatures of these four species, along with the sublimation temperature of the commercially available pentafluorides, are given in Table 21.

Table 20: Experimental volatilisation temperatures of prepared oxyfluoride species and pentafluorides.

	M = Nb /°C	M = Ta /°C
MO_2F	651	720
MOF_3	223	272
MF_5 [*] (Alfa Aeser)	80	96

^{*}Though these are the melting temperatures of the pentafluorides, they have significant vapour pressure which allows volatilisation.

5.3 Results and discussion

In practice, the preparation of a single oxyfluoride is problematic since the higher fluorinated species are prone to hydrolysis (Cordier *et al.*, 2004) and the oxygen-rich species may in turn be fluorinated by the fluorine-rich ones. As a consequence, the preparation of a single species often results in a mixture of different oxyfluorides.

5.3.1 Single-component reactions

The reactions between $\text{HF}_{(\text{g})}$ and niobium and tantalum pentoxide are characterised by two consecutive exothermic events (Figure 44). For the reaction between tantalum pentoxide and $\text{HF}_{(\text{g})}$, the second exotherm is less intense, but broader than that observed for niobium pentoxide.

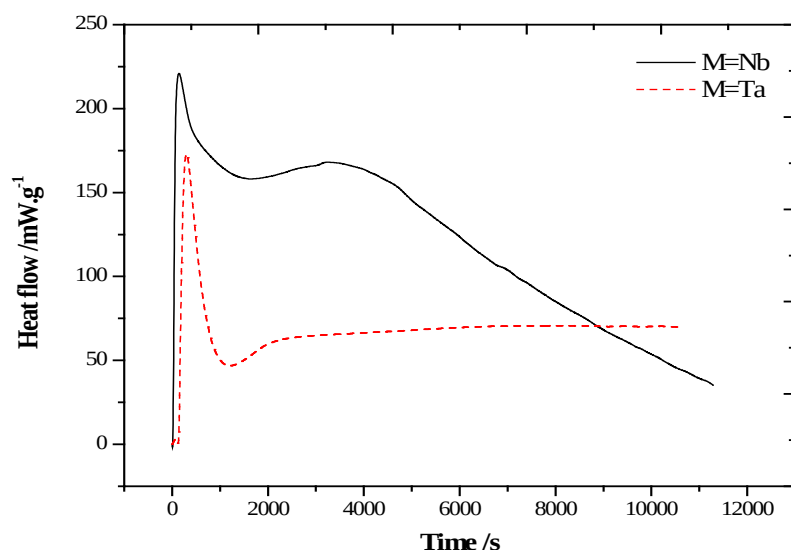
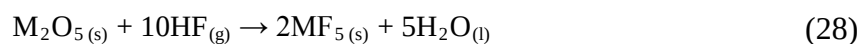


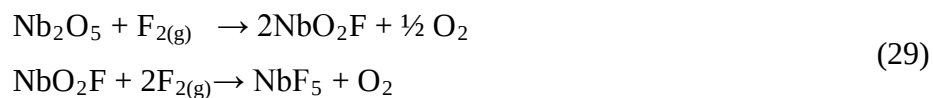
Figure 44: Energy profiles for single-component reactions ($M_2O_5 + HF$).

Thermodynamically the metal pentafluorides are the stable products for the reactions between the metal pentoxides and anhydrous HF at relatively low temperatures, that is for the substitution reactions:



For Ta and Nb the values for the change in standard Gibbs energy at room temperature are -101.5 and $-64.2 \text{ kJ}\cdot\text{mol}^{-1}$ respectively, calculated from the database in Outotec Research HSC Chemistry v6.0. Clearly, however, there is a kinetic barrier to achieving full fluorination in each case, as discussed below.

A two-step reaction, with oxyfluoride intermediates, is similarly observed when elemental fluorine is used as the fluorinating agent (Rakov *et al.*, 1971):

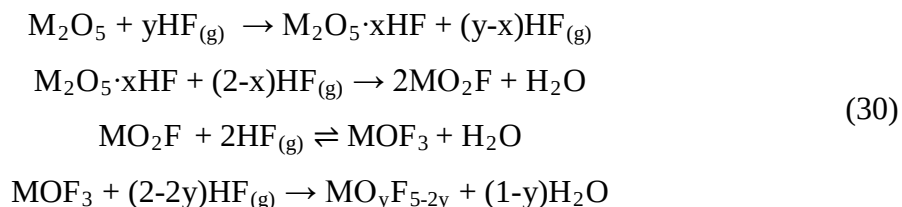


Using the TG data collected for the prepared model compounds and the comparison of XRD data in the PDF-2007 database, the species noted in Table 21 were identified after HF treatment at 30 °C.

Table 21: Products identified using the 2007-PDF-2 database for the reaction between M_2O_5 and $\text{HF}_{(g)}$.

M=Nb	M=Ta
NbO_2F	TaO_2F
NbOF_3	TaOF_3
Nb_2O_5	$\text{Ta}_3\text{O}_7\text{F}$
	Ta_2O_5

During the thermogravimetric study of the fluorination reaction products (Figure 45), different species volatilise at different temperatures. Below 120 °C, the removal of any adsorbed HF and any possible pentafluorides, occurs. Next, at >148 °C, the volatilisation of a niobium species occurs. This oxyfluoride could not be identified from the collected XRD or TG data. After that, $\text{TaOF}_{3(g)}$ sublimates at 272 °C, and the decomposition of niobium dioxyfluoride (NbO_2F) and tantalum dioxyfluoride (TaO_2F) follow at >651 and >720 °C respectively. Varying the time that the pentoxides are exposed to HF and comparing the resulting products allowed the following reaction steps to be postulated:



With $0 \leq y \leq 1$. The formation of species that are more fluorinated than MO_2F occurs slowly and accounts for the slow decrease in heat flow seen in Figure 44; an elegant explanation for the deviation of Gaussian symmetry for the second reaction peak. Once the reaction is complete, a mixture of the dioxyfluoride, oxytrifluoride, and more fluorinated compounds results.

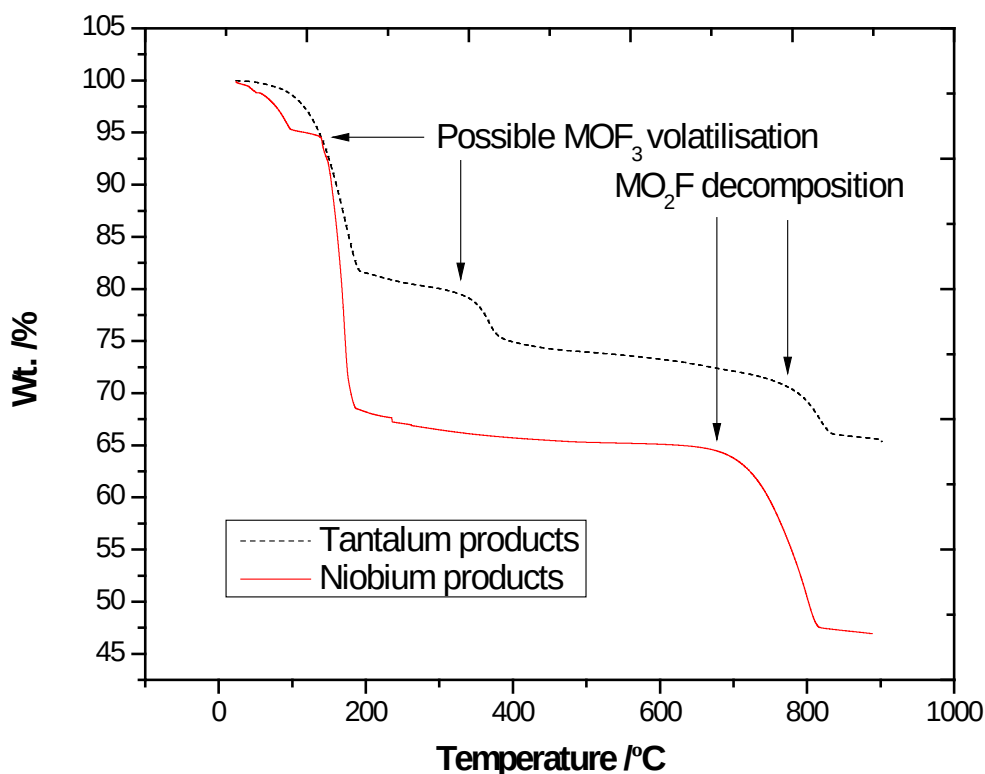
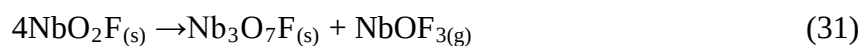


Figure 45: TG profiles for experimental fluorination products of Nb_2O_5 and Ta_2O_5 .

Figure 46, the first derivative of TG data, summarises the recorded sublimation/decomposition temperatures of the identified $\text{HF}_{(g)}$ fluorination products as well as the commercial pentafluoride samples. The most fluorinated of the compounds, the pentafluorides, start volatilising below 100°C , followed by the volatilisation of MOF_3 and finally, the dioxyfluoride species decomposing at $>655^\circ\text{C}$ ($\text{M}=\text{Nb}$) and $>720^\circ\text{C}$ ($\text{M}=\text{Ta}$). Kodama and Goto(1975) determined that the decomposition reaction for NbO_2F proceeds according to the reaction:



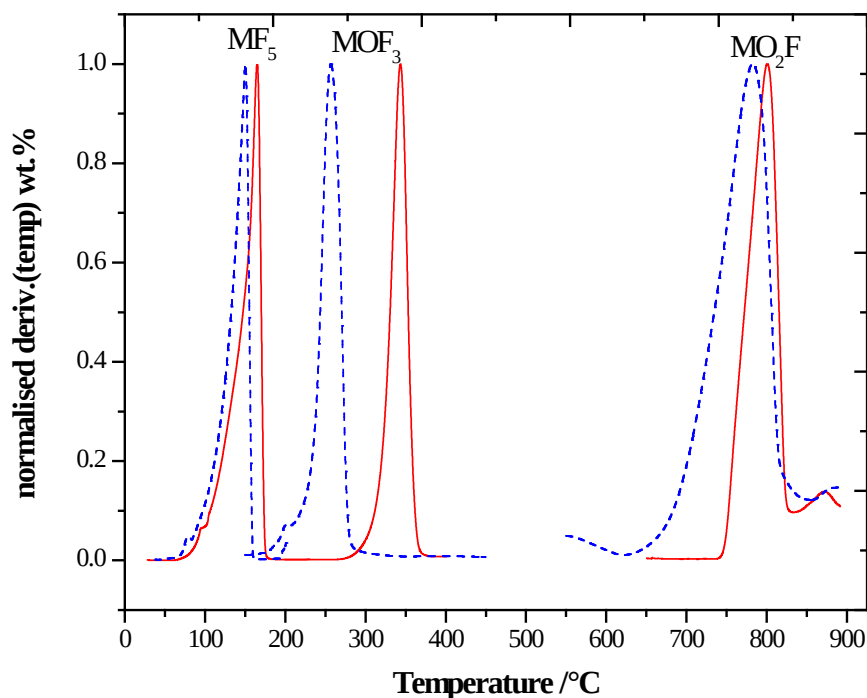


Figure 46: First derivative for (normalised) TG data for oxyfluoride species (dotted line for M = Nb and solid line for M = Ta).

According to the literature, and the experiments conducted in the present study, the sublimation temperatures of niobium pentafluoride (80 °C) and tantalum pentafluoride (96.8 °C) are 15 °C apart and could in theory be used for separation, by means of a thermal process.

It can be seen from the data presented in Figure 46 that this is not feasible since significant overlapping occurs (onset temperature) and near-perfect temperature control would be required – especially for larger samples. If the dioxyfluorides were targeted, however, separation might be possible, but the high temperature above 650 °C would have a substantial effect on the cost of the process. The most favourable set of oxyfluorides to target would be therefore be TaOF₃/NbOF₃, for which the niobium species sublimates at about 148 °C and the tantalum analogue only at >272 °C. Alternatively, if both compounds could be converted to oxy-trifluorides, a separation via this set might also be possible.

5.3.2 Reaction of mixtures

The $\text{HF}_{(\text{g})}$ fluorination of mixtures of Nb_2O_5 and Ta_2O_5 showed similar heat-flow profiles to those observed for single component experiments (Figure 47). The products of these runs were heated to 165 °C where the temperature was maintained for 30 minutes. At this temperature, after the evolution of volatiles, only NbOF_3 was expected to sublime, leaving the majority of the tantalum values in the solid phase (Table 22).

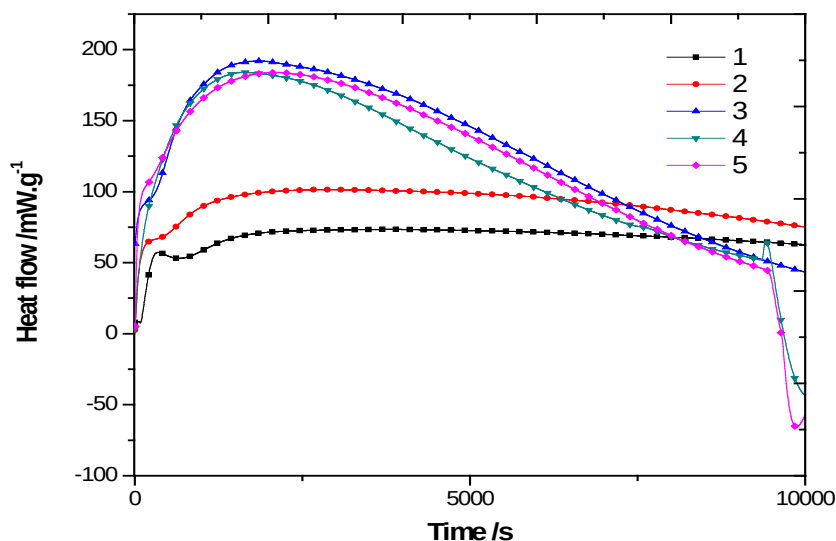


Figure 47: Energy profile observed for the reaction of $\text{HF}_{(\text{g})}$ with mixtures of Ta_2O_5 and Nb_2O_5 .

Table 22: Mass ratio of Nb:Ta according to ICP-OES results before heating to 165 °C and after.

Experiment	Nb:Ta Ratio	
	Before	After
1	0.74	0.56
2	0.74	0.59
3	0.85	0.74
4	0.99	0.77
5	0.99	0.80

5.4 Conclusion

A mixture of oxyfluoride compounds was created by treating mixtures of tantalum and niobium pentoxide with $\text{HF}_{(\text{g})}$. Though the thermal behaviour of the pentoxides and pentafluorides of tantalum and niobium was similar, the oxyfluorides had substantially different sublimation and decomposition temperatures. This difference allowed a separation process that did not involve the use of aqueous HF or organic solvents. Indeed, the present study has shown that such a separation is possible at 165 °C. Even though the change in metal ratio is relatively small, it should be noted that this is only first pass separation to prove the concept.

Further work may include optimising the experimental parameters to produce the desired oxyfluoride species, which may make an even more efficient process possible. Since both tantalum and niobium occur in nature in pentoxide form, this process could be extended to recover metal values from minerals. A patent application for this process has been filed (Wagener *et al.*, 2011).

5.5 References

- Cordier, S., Roisnel, T. and Poulain, M., (2004). "Synthesis and characterization of the novel $\text{Nb}_3\text{O}_5\text{F}_5$ niobium oxyfluoride: the term $n = 3$ of the $\text{Nb}_n\text{O}_{2n-1}\text{F}_{n+2}$ series ". *J. Sol. State Chem.*, **177**: 3119-3126.
- Kent, R. and Margrave, J.L., (1965). "Mass spectrometric at high temperatures. VIII. The sublimation Pressure of iron(II) fluoride". *J. Am. Chem. Soc.*, **87**: 4754-4756.
- Kodama, H. and Goto, M., (1975). "The thermal decomposition of $\text{Nb}_3\text{O}_7\text{Cl}$ and NbO_2F ". *Z. Anorg. Allg. Chem.*, **415**: 185-189.
- Köhler, J., Simon, A., Wüllen, L.V., Cordier, S., Roisnel, T., Poulain, M. and Somer, M., (2002)., "Structures and properties of NbOF_3 and TaOF_3 – with a remark of the O/F ordering in the SnF_4 type structure", *Z. Anorg. Allg. Chem.*, **628**: 2683-2690.
- Rakov, E.G., Kopchikhin, D.S., Sudarikov, B.N. and Gromov, B.V., (1971). "Fluorination kinetics of Nb_2O_5 ". *Atomnaya Energiya*, **31**: 137.
- Wagener, J. B., Pienaar, A.D, Carstens, P.A.B., "Treatment of tantalum- and/or niobium-containing compounds and recovery of these compounds", WO 2011121573.

CHAPTER 6

FLUORINATION OF TANTALITE ORE CONCENTRATE

6.1 Introduction

As described in the introductory chapter, the term “tantalite” is used to describe a family of minerals containing tantalum and niobium, usually with a higher tantalum concentration than that of niobium. The mineral may be described as having the general formula $(\text{Fe,Mn})(\text{Ta,Nb})_2\text{O}_6$ (Mulja *et al.*, 1996), though specific metal values for ores sourced from different locations may vary greatly.

The processing of this mineral may involve several steps. Primary concentrates may be broken down via several processes (Ayanda and Adekola, 2011):

- Aluminothermic reduction – oxides are reduced to a metallic state by the addition of aluminium. The reduction is feasible at room temperature.
- Carbothermic reduction – similar to aluminothermic reduction, but is feasible only at high temperatures with carbides as unwanted by-products.
- Chlorination – chlorinated values show increased volatility and solubility which aid in downstream processing.
- Alkaline fusion – alkaline fluxes such as caustic soda are used to break down the mineral, which, followed by acid leaching, allows the processing of metal values.
- Direct leaching/Extraction – the required metal values are dissolved from the solid phases.

It has been suggested that conventional methods require the combined mass percentages of Ta_2O_5 and Nb_2O_5 to be at least 50% before an ore is considered for further processing (Adetunji *et al.*, 2005).

In the current study, ore concentrate sourced from Mozambique was used to investigate the effect of $\text{HF}_{(g)}$ and $\text{F}_{2(g)}$ on the mineral matrix, with specific attention to the transformation of the tantalum and niobium values.

6.2 Experimental

6.2.1 Instrumentation

ICP-OES analyses were completed on a Spectro Arcos ICP-OES, using a mixture of HNO_3/HF to facilitate sample digestion.

Scanning Electron Microscopy (SEM) analyses were completed on an EDS-enabled FEI Quanta 200.

TG/DSC analyses were performed on a TA Instruments QDT 600 simultaneous TG/DSC, with a temperature ramp of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and $100\text{ ml}\cdot\text{min}^{-1}$ N_2 unless specified otherwise.

6.2.2 Fluorination reactions

F_2 fluorination was facilitated on a Perkin Elmer TG which had been modified to handle corrosive gases such as elemental fluorine (see Appendix A). A constant flow-rate of $100\text{ ml}\cdot\text{min}^{-1}$ 10% F_2/N_2 was maintained during the analyses, with a temperature ramp of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$.

A Setaram C80 microcalorimeter fitted with Hastalloy sample vessels was used to follow and facilitate the reaction of $\text{HF}_{(\text{g})}$ with the ore samples. The reaction was kept at isothermal values of 40, 50 and $60\text{ }^\circ\text{C}$. Temperature equilibration was achieved (DSC heat flow $< 2\text{ mW}$) before a 10 vol% mixture of HF/N_2 was introduced.

6.2.3 Characterisation of ore concentrate

6.2.3.1 Milling

Since tantalite has a hardness of 6 on the Mohs' scale, a Retsch mixer mill fitted with tungsten carbide ($>8.5\text{ Moh}$) crushing cell was used for milling the ore concentrate. Ore was milled for 2 h and particle size distribution determined by using the sieve and shaker method.

It is clear from the results listed in Table 23 (presented in Figure 48) that the majority of particles are within the 150-250 μm diameter range.

Table 23: Particle size distribution using the sieve and shaker method.

Batch 1	Sieve no	Sieve mass (cumulative)	Sieve mass	Fraction + sieve	Fraction	%
	600	5132.01	498.33	503.75	5.42	0.50
	300	4633.68	474.93	544.76	69.83	6.48
	250	4158.75	476.05	624.80	148.75	13.80
	150	3682.7	476.28	1082.42	606.14	56.24
	90	3206.42	473.27	598.53	125.26	11.62
	75	2733.15	463.66	500.12	36.46	3.38
	63	2269.49	478.74	530.88	52.14	4.83
	53	1790.75	456.29	468.24	11.95	1.11
	38	1334.46	449.73	462.00	12.27	1.14
	25	884.73	451.83	459.03	7.20	0.67
	20	432.90	432.9	435.14	2.24	0.21

Batch 2	Sieve no	Sieve mass (cumulative)	Sieve mass	Fraction + sieve	Fraction	%
	600	5132.01	498.33	502.32	3.99	0.37
	300	4633.68	474.93	527.96	53.03	4.97
	250	4158.75	476.05	515.90	39.85	3.74
	150	3682.70	476.28	999.93	523.65	49.11
	90	3206.42	473.27	702.37	229.10	21.48
	75	2733.15	463.66	506.93	43.27	4.06
	63	2269.49	478.74	557.05	78.31	7.34
	53	1790.75	456.29	475.95	19.66	1.84
	38	1334.46	449.73	502.47	52.74	4.95
	25	884.73	451.83	468.05	16.22	1.52
	20	432.90	432.90	439.44	6.54	0.61

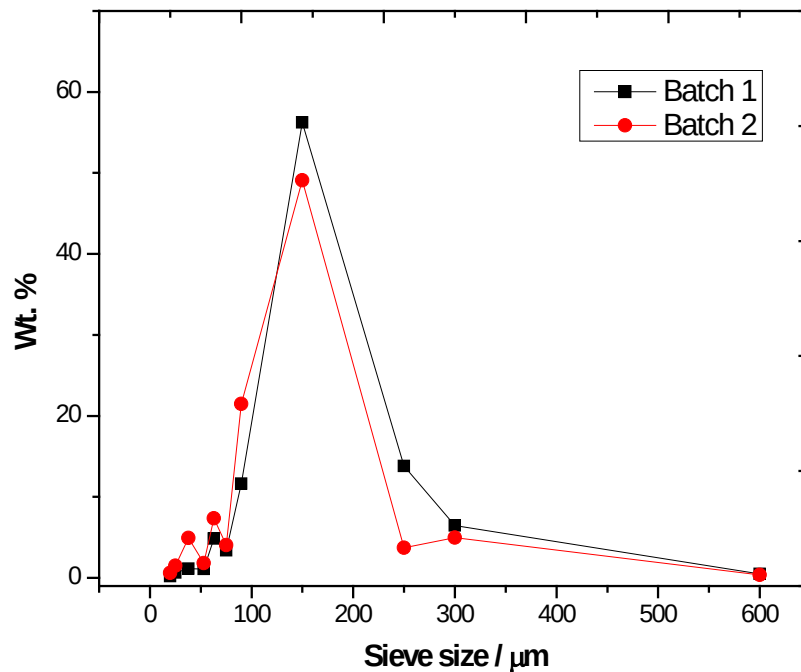


Figure 48: Particle size distribution using the sieve and shaker method.

6.2.3.2 ICP-OES/XRF analyses

ICP-OES analyses of solid samples are routinely done by dissolving the sample in a strong mineral acid or a mixture of mineral acids (HF and HNO_3). It was found that a mixture of acids dissolved the untreated tantalite ore concentrate best.

After the fluorination and heat-treatment of the ore, however, the samples became progressively less soluble. Without going into a long-term solubility experimental programme, it was found that the best solubility was achieved using 40% HF as the solvent.

Even when using this solvent, a microwave digester operating at 200 °C, with pressure-proof vessels, was required to obtain good dissolution. Depending on the sample, between 5% and 10% did not dissolve.

Table 24 shows the metal concentrations for the analysed tantalite ore according to the ICP-OES and XRF results.

Table 24: Comparative metal analysis of milled tantalite ore (main fraction).

Element	Symbol	ICP-OES	XRF
		/mass %	/mass %
Aluminium	Al	0.7	0.7
Iron	Fe	4.6	4.3
Manganese	Mn	6.1	5.9
Niobium	Nb	23.1	17.8
Tantalum	Ta	23.7	21.3
Tin	Sn	0.6	1.1
Titanium	Ti	1.4	1.3
Tungsten	W	0.9	1.2
Uranium	U	2	2.5
Yttrium	Y	0.9	1.7

According to the ICP-OES/XRF analyses, the ore concentrate contains 18-23% niobium and 21-24% tantalum. If it is assumed that this is the minimum amount and that the metals are in pentoxide form as the literature reports, then:

for 1 g of ore the niobium oxide content is: $(18/92.906) \times 265.8 = 51\%$;

and the tantalum oxide content is: $(21/180.95) \times 441.9 = 51\%$.

Naturally, a Ta/Nb oxide value of 102% is impossible, which means either the metal values are over-estimated or some of the metal value is not in pentoxide form.

6.2.3.3 SEM/EDS analyses

Using a SEM, images of the tantalite ore were captured (shown in Section 6.4) during which the EDS values were also measured (Figure 49).

The elements identified with EDS (Table 25) are similar to those measured using ICP-OES/XRF – with the notable exception of uranium, which according to the ICP/XRF values is present in quantities greater than 2%, but not seen at all during EDS analysis.

Table 25: Elements identified with EDS.

Symbol	Element
O	Oxygen
Al	Aluminium
Ti	Titanium
Fe	Iron
Nb	Niobium
Nd	Neodymium
Ce	Cerium
Ta	Tantalum
K	Potassium
Mn	Manganese

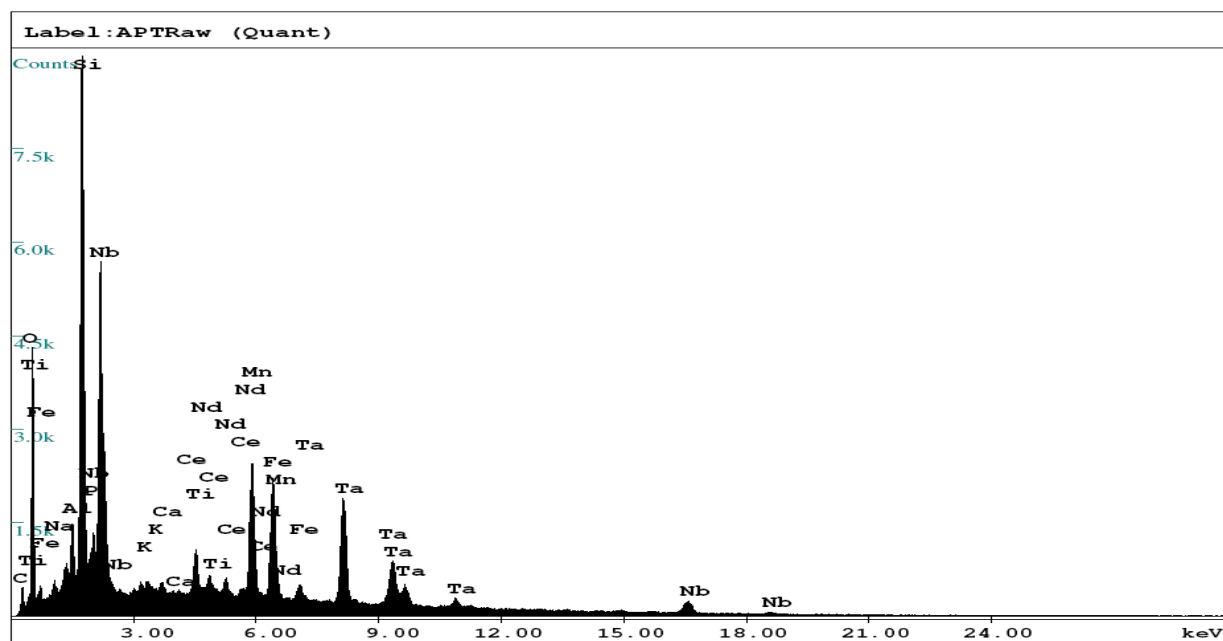


Figure 49: Elements identified using EDS.

6.3 Reaction of ore concentrate with $F_{2(g)}$

The TG/DSC analysis of the untreated tantalite (Figure 50) shows that the untreated ore concentrate contains no volatiles for the 20 – 1000 °C thermal region. In the area from 500 – 700 °C, there are a few small (< 2 Wt%) but sharp decreases, which are probably due to the fracture of crystallites which are then expelled from the sample holder.

When treated with F_2 , the TG curve (Figure 51) shows that at temperatures above 350 °C, up to 90% of the ore volatilises, which is similar to the result observed for the tantalum and niobium pentoxide species. This high level of volatilisation is not unexpected, owing to the metal content given in Table 24.

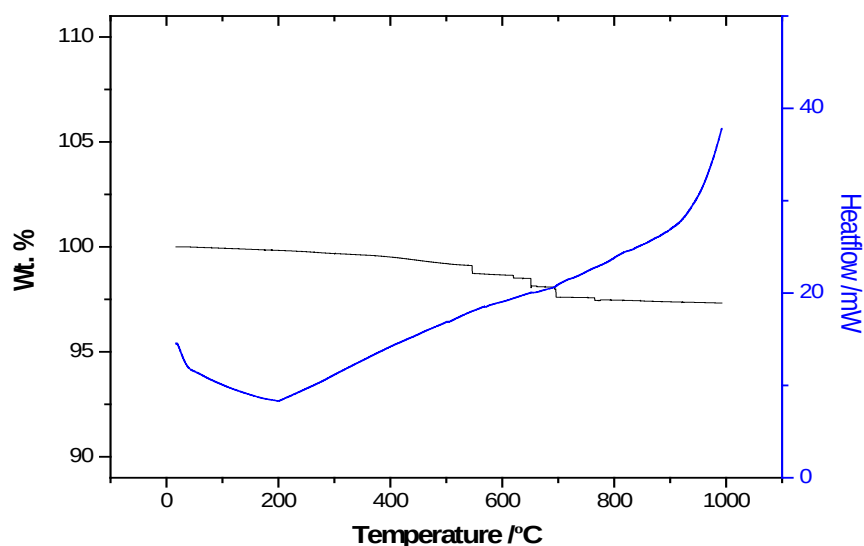


Figure 50: TG/DSC analysis of the untreated tantalite.

When F_2 reacts with tantalum and niobium pentoxide, the metal values are converted to pentafluorides (Pienaar and Wagener, 2011) which are volatile at temperatures above 90 °C. When the ore concentrate is reacted with $F_{2(g)4+00}$ at least 85% of the ore is volatilised at 350 °C. This is a large value, but not unexpected since 20% (mass percentage) of both tantalum and niobium would equate to about 100% if all Ta/Nb were in pentoxide form. Without extensive analytical phase studies, it is impossible to say conclusively how much of the metal value is present as pentoxide, but from a perusal of the literature, it is safe to assume that it is a very large fraction.

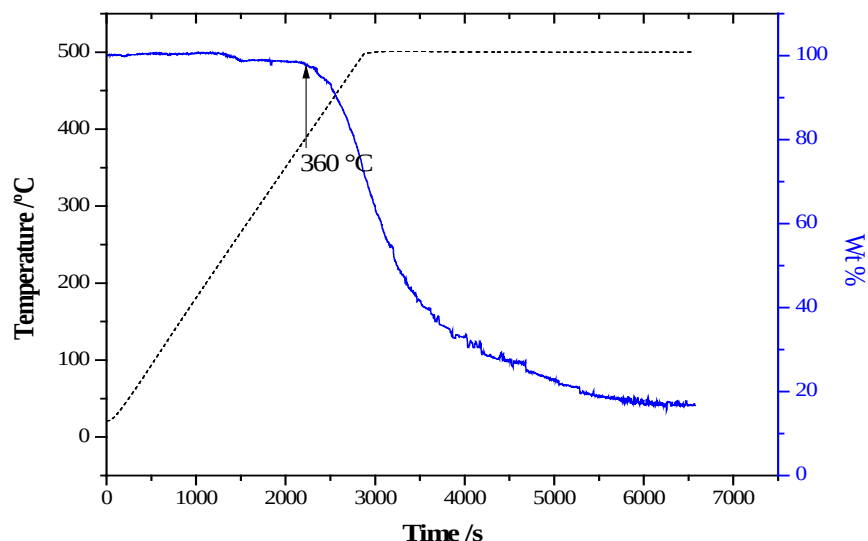


Figure 51: Reaction of $F_{2(g)}$ with tantalite ore concentrate during a dynamic temperature curve from 20 to 500 °C.

Volatiles are not expected for the metals Fe and Mn. Iron fluorides are volatile only for $T > 1\,000\text{ °C}$ (Hargittai *et al.*, 1990; Kent and Margrave, 1965) and therefore cannot contribute to any mass losses observed. Manganese difluoride may be volatile at 70 °C (Hoppe *et al.*, 1961) but is not expected to form below 507 °C (Rakov *et al.*, 1997). MnF_3 and MnF_4 are solids below 614 °C (Kent *et al.*, 1964; Rau *et al.*, 2001).

Ti reacts with $F_{2(g)}$ above 250 °C (Haendler *et al.*, 1954) to form TiF_4 , which is volatile at this temperature. WF_6 , which is usually formed by direct fluorination of $W_{(s)}$ with $F_{2(g)}$, is likely to form and is volatile at 20 °C (Lassner and Schubert, 1999). These two metals, Ti and W, are present at low concentrations (<1%) in the ore. If they do appear in the final product, they can easily be separated from the Ta/Nb values by fluorination.

The first derivative of the TGA curve for the reaction between F_2 and tantalite ore concentrate (Figure 52) show three distinct thermal events below 500 °C. When compared to the mass losses observed in this region (Figure 51), it is seen that these events (which are not related to Ta/Nb fluorination) correlate with less than 1% to the total change in mass that is observed, so should not prove a significant source of contamination if an $F_{2(g)}$ process is used.

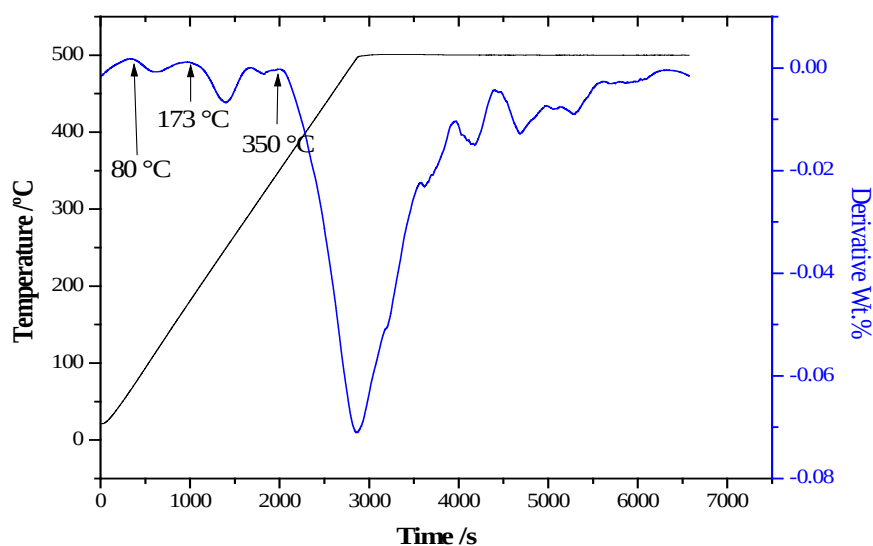


Figure 52: First derivative (smoothed) of the TG curve presented in Figure 51.

6.4 Reaction with HF_(g)

According to the reactions discussed in Chapter 4, the area of interest for the reaction between HF_(g) and tantalite lies below 100 °C. The heat flow observed during the reaction between HF_(g) and the tantalite ore concentrate is displayed in Figure 53. It is clear that there is a systematic decrease in exothermicity as the reaction temperatures increase; this mirrors both the thermodynamic calculation of the pure oxides and the experimental results reported for this temperature bracket. The TG curves for the products of these reactions are shown in Figure 54.

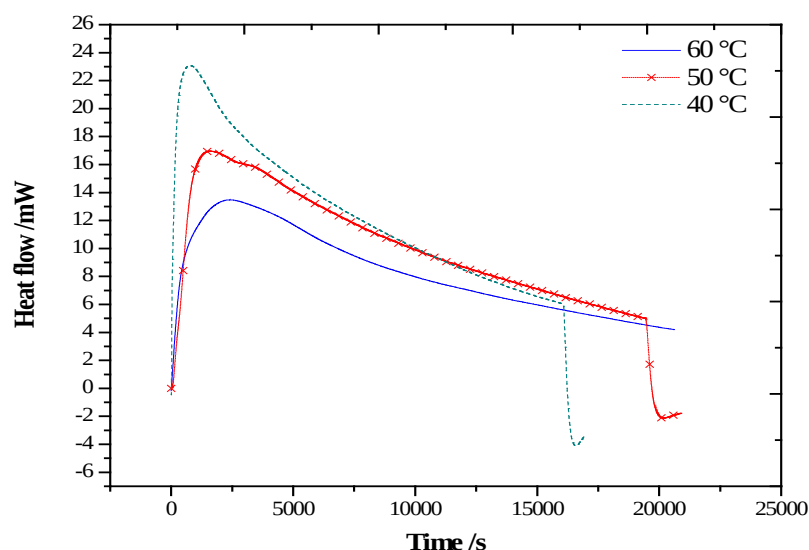


Figure 53: Heat flow observed during the $\text{HF}_{(g)}$ treatment of tantalite at different temperatures.

The products of the reactions at all three temperatures have components that are volatile below 100 °C, which are probably the pentafluorides of tantalum and niobium, tungsten hexafluoride and water.

For the minority metals (Ti, W, Mn) with volatile fluorides, the formation of the said fluorides, via reaction with $\text{HF}_{(g)}$, are not expected from the thermodynamic calculations (Figure 55). Even though the presence of these compounds cannot be excluded on this basis alone, no indication on the TG curve of the HF-fluorinated (Figure 54) tantalite suggests their presence either.

The mass change (shown in Figure 54) between 450 and 500 °C has not been observed for any of the model compounds considered, and may be due to a reaction with another element in the matrix.

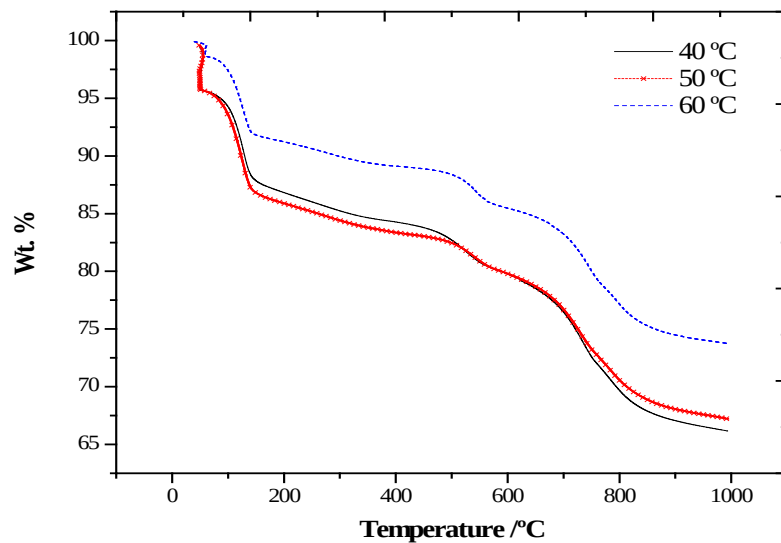


Figure 54: TG graphs of tantalite and $\text{HF}_{(g)}$ reaction products at different temperatures.

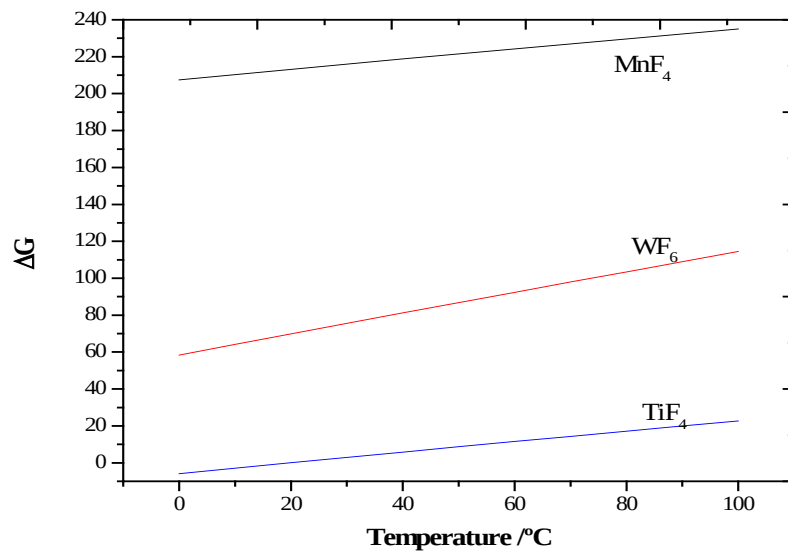


Figure 55: Free energy of formation for the fluorides of different metals during the reaction between their oxides and $\text{HF}_{(g)}$.

It is clear from examining the TG curves of the treated samples that there are only marginal differences between the ore treated at 40 and 50 °C. At 60 °C, however, far less of the initial volatile pentafluoride forms.

Valuable insights into the physical changes in the ore may be gained by using SEM. SEM images of the ore were taken before the $\text{HF}_{(g)}$ and thermal treatment as well as during different stages of the thermal decomposition process.

The images show that particles are irregular in shape, but have smooth surface areas (Figures 56-57). These images may be compared to those of the 200 °C decomposition product (Figures 58-59) where it can be seen that the smooth surface has been destroyed and there is a combination of pockets and regularly shaped crystallites (visually orthorhombic). This result suggests that some values have been volatilised from the mineral whereas others have formed crystallites.

At 1 000 °C (Figures 60-61) the situation is different. Two distinct morphologies are now visible, a porous (sponge) bulk as well as an area where crystalline threads/structures protrude in clusters from the surface. The heavier elements show up lighter in colour in the back-scattering mode (Figure 61), and in view of the bulk elemental analysis, the protruding structures probably contain niobium or tantalum.

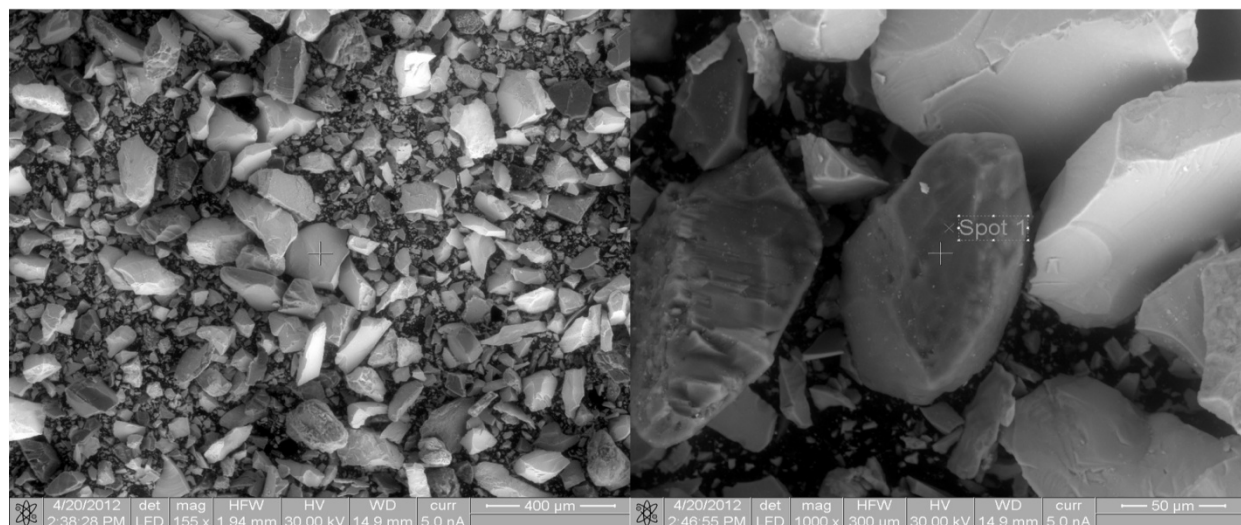


Figure 56: SEM image of tantalite ore concentrate at different magnifications.

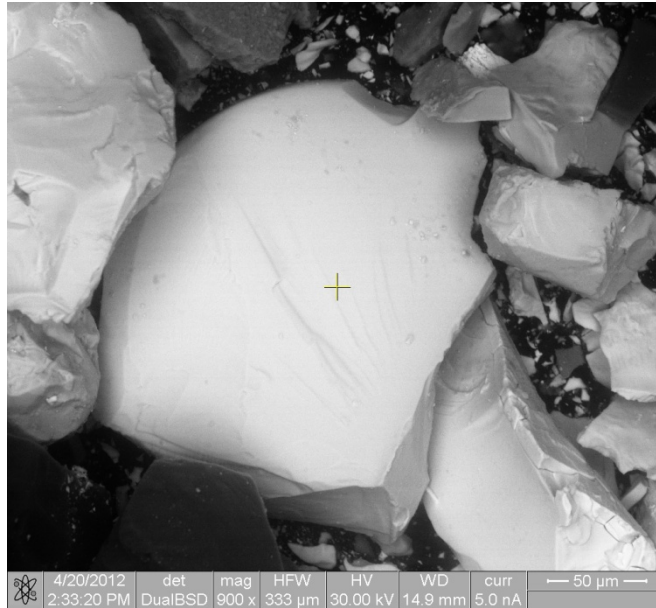


Figure 57: BSE (back-scattering) mode of SEM image.

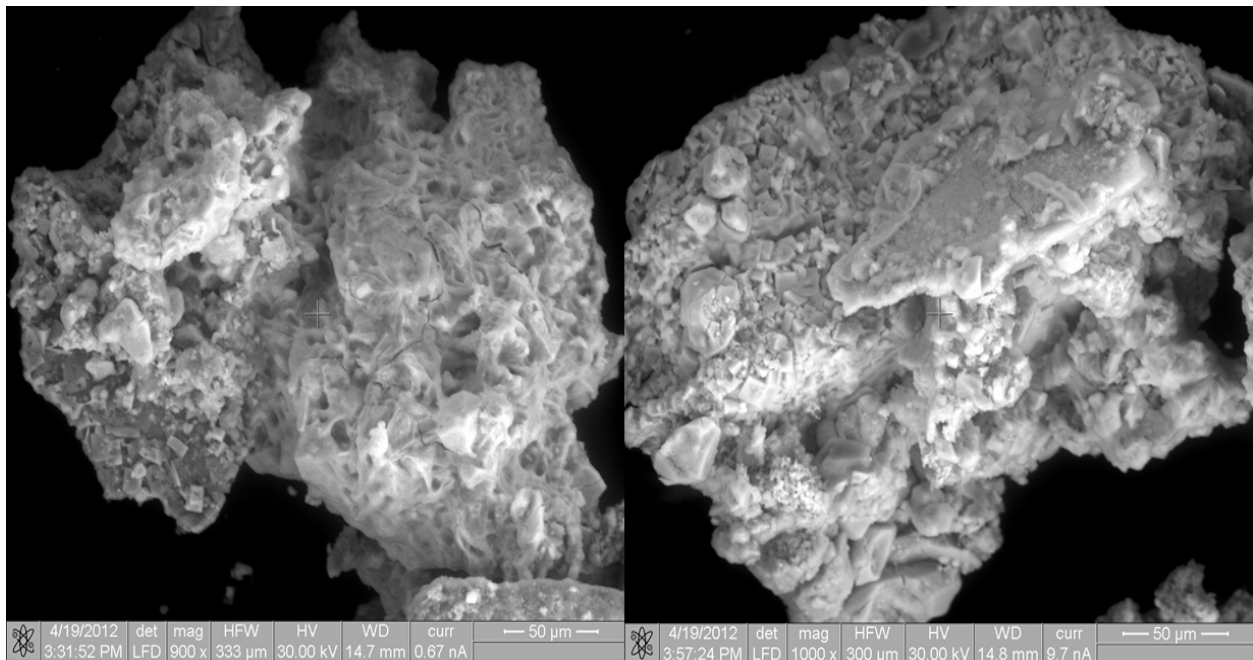


Figure 58: SEM image of product at 200 °C.

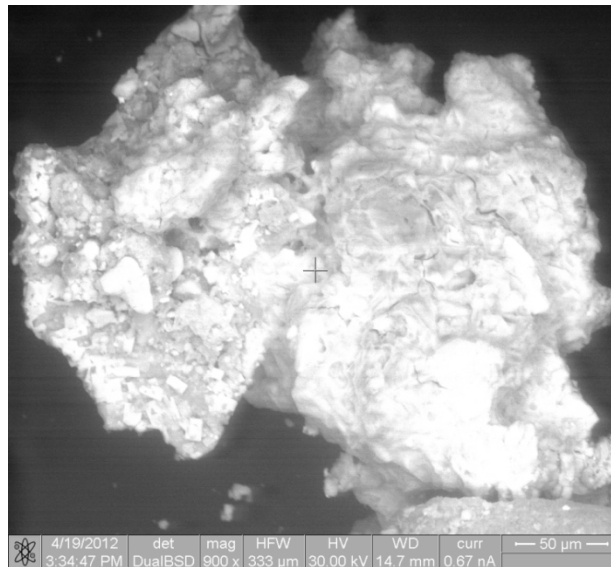


Figure 59: SEM back-scattering image of product at 200 °C.

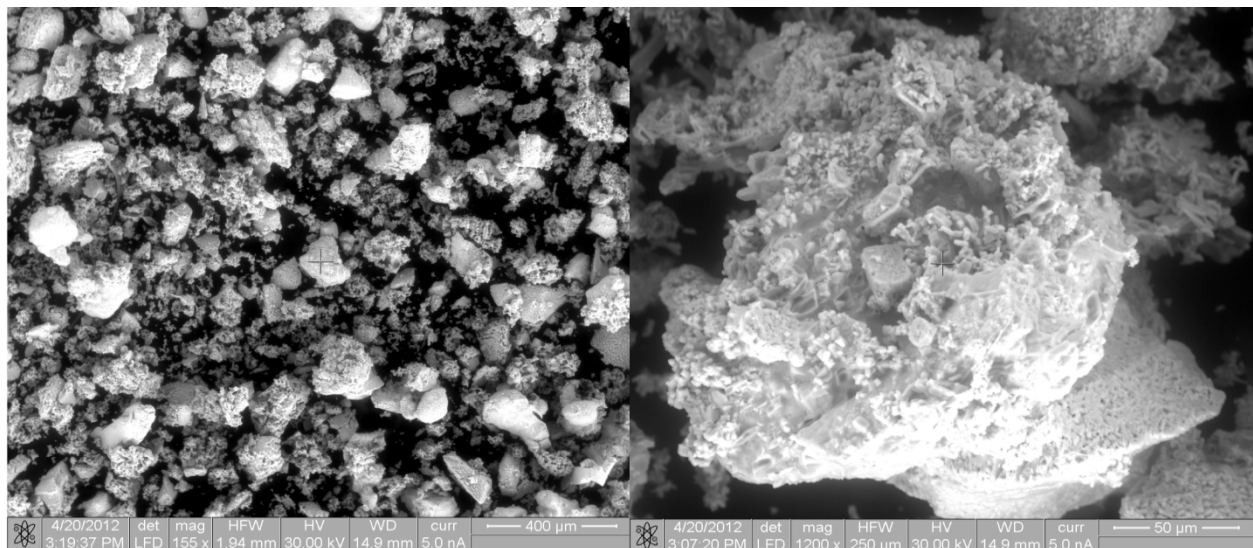


Figure 60: SEM images of product at 1000 °C.

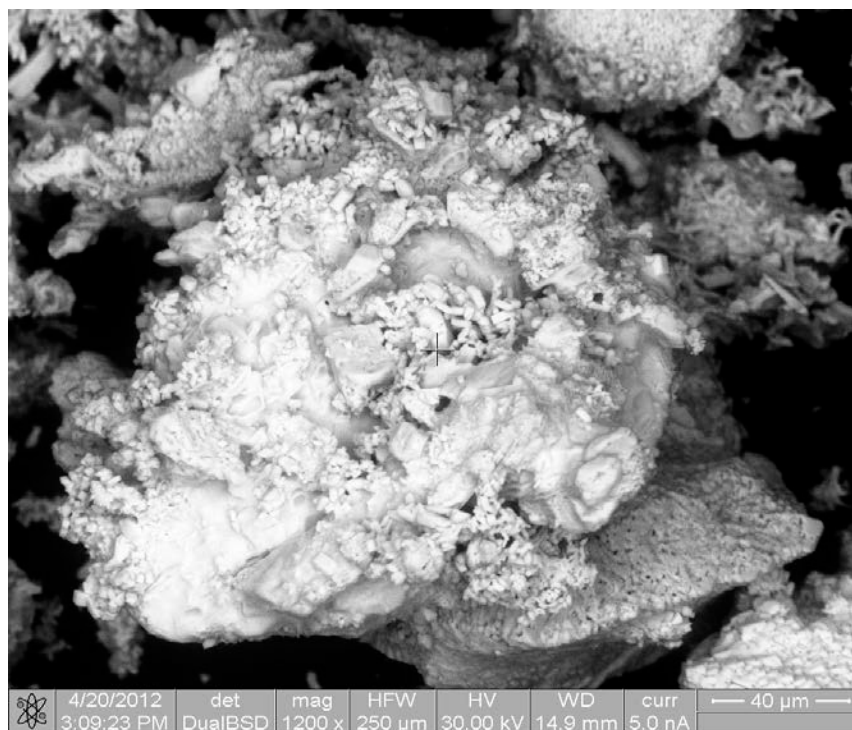


Figure 61: SEM BSE image of product at 1000 °C.

6.5 Separation using $\text{HF}_{(g)}$

Both tantalum and niobium are converted to the pentafluoride using $\text{F}_{2(g)}$ as fluorinating agent. Separation of these pentafluorides were not attempted for this work, and separation using $\text{HF}_{(g)}$ as fluorinating agent will be discussed instead.

There are different ways to interpret the analytical results in order to evaluate the efficiency of separation in these ores. One can look either at the Ta/Nb ratios before and after treatment, or at the absolute difference between the metal concentration (ΔTa and ΔNb). Initially it was decided absolute concentrations be used, but difficulties in the dissolution of samples (see experimental section) for ICP-OES analysis made this approach impractical. It was assumed that the fraction that did dissolve was homogenous with the ore, and Nb/Ta ratios were calculated.

The temperature to which each sample was heated after fluorination is given in Table 26, and the corresponding ICP results in Table 27. (The experiments are listed in the order they were completed).

Table 26: Heat treatment temperature for each experiment.

Exp	Temp /°C	Exp	Temp /°C	Exp	Temp /°C
1	0	11	200	21	180
2	180	12	0	22	950
3	950	13	950	23	0
4	0	14	0	24	200
5	0	15	950	25	950
6	170	16	200		
7	950	17	0		
8	950	18	200		
9	200	19	950		
10	950	20	0		

Table 27: ICP results for selected metal values.

Exp	Mn mg/L	Fe mg/L	Nb mg/L	Ta mg/L	U mg/L	Exp	Mn mg/L	Fe mg/L	Nb mg/L	Ta mg/L	U mg/L
1	4.40	4.50	13.40	15.70	1.60	14	0.65	0.67	2.46	2.73	0.23
2	4.10	4.60	14.80	15.30	1.50	15	0.49	0.46	1.49	1.89	0.16
3	1.33	1.71	4.15	5.70	0.54	16	0.41	0.39	1.47	1.71	0.19
4	0.97	1.02	3.40	4.20	6.50	17	0.83	0.78	3.59	4.32	0.29
5	0.83	1.31	3.40	3.80	13.90	18	0.36	0.36	1.36	1.53	0.20
6	4.44	5.10	15.06	16.98	2.17	19	0.46	0.45	1.29	1.74	0.13
7	2.35	2.23	7.40	7.36	0.55	20	0.97	0.95	3.54	4.26	0.14
8	2.50	2.05	5.79	8.25	0.86	21	0.28	0.30	1.22	1.43	0.15
9	5.34	4.39	18.67	20.88	1.71	22	0.29	0.32	0.85	1.16	0.14
10	1.58	3.39	18.03	16.43	1.88	23	0.71	0.70	2.61	2.96	0.11
11	3.51	6.50	29.61	35.33	5.28	24	0.43	0.42	1.63	1.87	0.17
12	0.96	1.09	2.75	3.64	0.26	25	0.27	0.28	0.76	1.11	0.17
13	0.55	0.57	2.03	2.28	0.24						

Nb/Ta ratios are shown in Table 28. These values were grouped according to the different post-fluorination treatments and are shown on Figure 62 with the solid line indicating the average ratio for the samples not heated after fluorination and the dotted line indicating the error margin. It can easily be seen from these figures how the different heat treatments affected the mineral ore concentrates that were treated with HF(g).

Table 28 Nb/Ta ratio for different post fluorination heat treatments.

	Temperature /°C		
	N/A	180	950
	0.854	0.967	0.728
	0.810	0.887	0.702
	0.895	0.894	0.685
	0.755	0.838	0.890
	0.901	0.860	0.788
	0.831	0.889	0.741
	0.83	0.853	0.733
	0.88	0.872	

When heated to 180-200 °C, there the Nb/Ta concentration does not significantly change (Figure 62) from the unheated samples. When the treated ore is heated above 950 °C, however, the Nb/Ta value decreases.

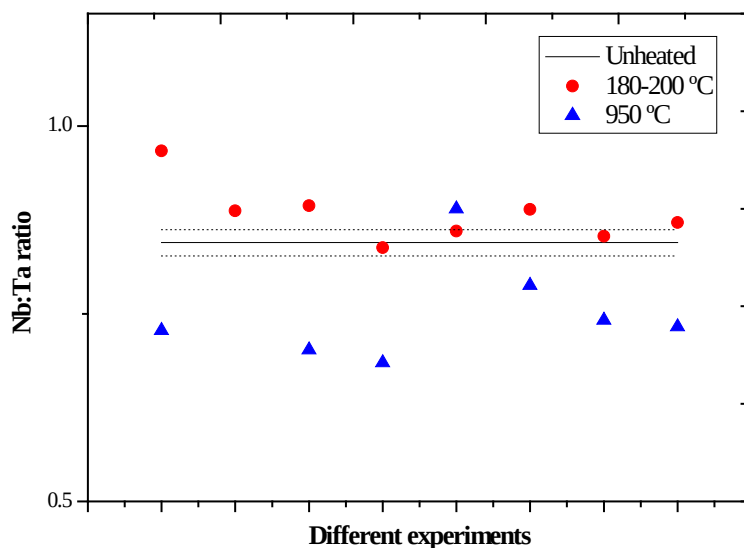


Figure 62: Changes in Nb:Ta ratio for samples heated to different temperatures post-fluorination.

By comparing this result to the known volatilities of the oxyfluoride species discussed in Chapter 3, it would appear that under the selected conditions the more volatile oxyfluoride (NbOF_3) does

not form, and higher separation temperatures would be required. At these higher temperatures, it is unfortunately likely that a mixture of Ta/Nb oxyfluorides would sublime.

Though this result is different from that of the model oxides, it opens up interesting possibilities. The present study determined that both tantalum and niobium can form volatile species directly from the mineral matrix. This means that they may either be jointly lifted from the mineral (as is the case with F₂ fluorination), or possibly targeted to form mostly volatile niobium species.

It is also obvious from the incremental changes observed, that the process is far from ideal at this stage. Reproducibility may be increased by having a more consistent HF(g) delivery system and improving the sample dissolution techniques. The overall fluorination could be improved by addressing the issues of mass and heat transfer:

- Mass and heat transfer may be improved by means of several techniques:
- HF_(g)/N₂ concentration may be increased
- mineral particle size decreased, by increasing the mill time.
- reactor design could be improved.

Several reactor designs have been developed for gas-solid interaction, such as floating or even packed beds. The limitations of the C80 system for this type of reaction are discussed in Appendix A.

6.6 References

- Adetunji, A.R., Siyanbola, W.O., Funtua, I.I., Olsunle, S.O.O., Afonja, A.A. and Adewoye, O.O., (2005). "Assessment of beneficiation routes of tantalite ores from key locations in Nigeria". *J. Min. Mat. Char. Eng.*, **4**: 67-73.
- Ayanda, O.S. and Adekola, F.A., (2011). "A review of niobium-tantalum separation in hydrometallurgy". *J. Min. Mat. Char. Eng.*, **10**: 245-256.
- Haendler, H.M., Bartram, S.F., Becker, R.S., Bernard, W.J. and Bukata, S.W., (1954). "The reaction of fluorine with titanium, zirconium and the oxides of titanium(IV), zirconium(IV) and vanadium(V)". *J. Am. Chem. Soc.*, **76**: 2177.
- Hargittai, M., Kolonits, M., Tremmel, J., Fourquet, J.-L. and Ferey, G., (1990). "The molecular geometry of iron trifluoride from electron diffraction and a reinvestigation of aluminum trifluoride". *Struct. Chem.*, **1**: 75-78.
- Hoppe, R., Dähne, W. and Klemm, W., (1961). "Mangantetrafluorid, MnF₄". *Naturwissenschaften* **48**: 429.
- Kent, R. and Margrave, J.L., (1965). "Mass spectrometric at high temperatures. VIII. The sublimation pressure of iron(II) fluoride". *J. Am. Chem. Soc.*, **87**: 4754-4756.

- Kent, R.A., Ehlert, T.C. and Margrave, J.L., (1964). "Mass spectrometric at high temperatures. V. The sublimation pressure of manganese(II) fluoride and the dissociation energy of manganese(I) fluoride". *J. Am. Chem. Soc.*, **23**: 5090-5093.
- Lassner, E. and Schubert, W.D., (1999). "Tungsten – Properties, Chemistry, Technology of the Element, Alloys, and Chemical Compounds". Kluwer Academic, New York
- Mulja, T., Williams-Jones, A.E., Martin, R.F. and Wood, S.A., (1996). "Compositional variation and structural state of columbite-tantalite in rare-element granitic pegmatites of the Preissac-Lacorne batholith, Quebec, Canada". *Am. Min.*, **81**: 146-157.
- Pienaar, A.D. and Wagener, J.B., (2011). Formation of oxyfluorides of niobium and tantalum using solid-gas reactions, 40th SACI Convention, Johannesburg, South Africa.
- Rakov, E.G., Ostropikov, V.V. and Khaustov, S.V., (1997). "Kinetics of fluorination of manganese compounds with fluorine gas". *Zhurnal Neorganicheskoi Khimii*, **42**: 199-203.
- Rau, J.V., Albertini, V.R., Chilingarov, N.S., Colonna, S. and Tamburini, U.A., (2001). "In situ time-resolved X-ray diffraction study of manganese trifluoride thermal decomposition". *J. Fluor. Chem.*, **108**: 253-256.

CHAPTER 7

PROCESS FLOW DIAGRAMS

7.1 Discussion of possible processes

The aim of this project was to generate sufficient data to propose probable separation processes using a dry fluorination route. Separation by sublimation/decomposition occurs by producing a specific set of Ta and Nb oxyfluoride pairs (Table 29), these pairs are then separated using a sublimation/decomposition process. From the results collected and cited publications, three likely separation/purification scenarios may be suggested. The final step in all of the processes discussed involves hydrolyses and pyrolysis of the intermediates to the oxides.

Table 29: Preferred Ta/Nb separation pairs.

Tantalum Species	Niobium Species
TaF ₅	Nb ₂ O ₅ , NbO ₂ F, NbOF ₃ (g)
TaOF ₃	Nb ₂ O ₅ , NbO ₂ F (NbF ₅ not likely to form)
TaO ₂ F	Nb ₂ O ₅ , NbO ₂ F
TaO ₂ F, TaOF ₃ (TaF ₅ not likely to form)	NbF ₅

7.2 Partial fluorination and sublimation

In this incarnation of the process (Figure 63), tantalite ore concentrates are treated with HF_(g) and converted to oxyfluoride values. During this process, the tantalum and niobium pentoxide values are converted to oxyfluorides. Ideally the temperature and other operating parameters should be chosen preferentially to form the more volatile species of one (possibly tantalum) of these metals. Preferred pairs of oxyfluorides for separation are given in Table 29.

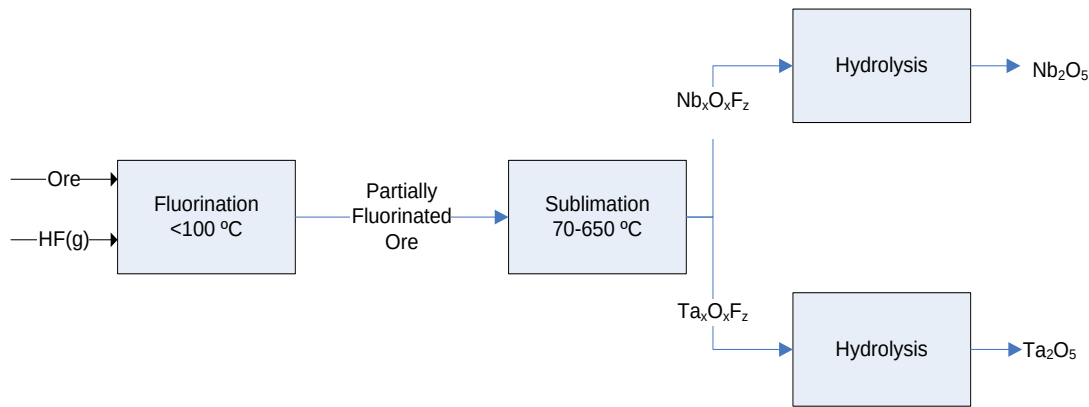


Figure 63: Process block diagram for partial fluorination and sublimation.

7.3 Complete fluorination and sublimation

When the ore is treated with elemental fluorine or anhydrous $\text{HF}_{(g)}$ (Figure 64), complete fluorination is possible if the appropriate temperature has been chosen and enough time is allowed. As mentioned in the experimental section, the pentafluoride values of tantalum and niobium may then be removed from the ore at a relatively low ($<100\text{ }^{\circ}\text{C}$) temperature. When the pentafluorides are hydrolysed (Adetunji *et al.*, 2005; Andersson and Astrom, 1965; Cordier *et al.*, 2004), the dioxyfluoride (MO_2F ; $\text{M} = \text{Ta/Nb}$) forms. It is possible to separate these oxyfluorides with sublimation since their sublimation temperatures are about $100\text{ }^{\circ}\text{C}$ apart, but at a rather high process temperature ($650\text{ }^{\circ}\text{C}$). By introducing an additional – but optional – $\text{HF}_{(g)}$ fluorination step (shown in the red block), the dioxyfluorides may be converted to oxyfluorides that sublime at lower temperatures.

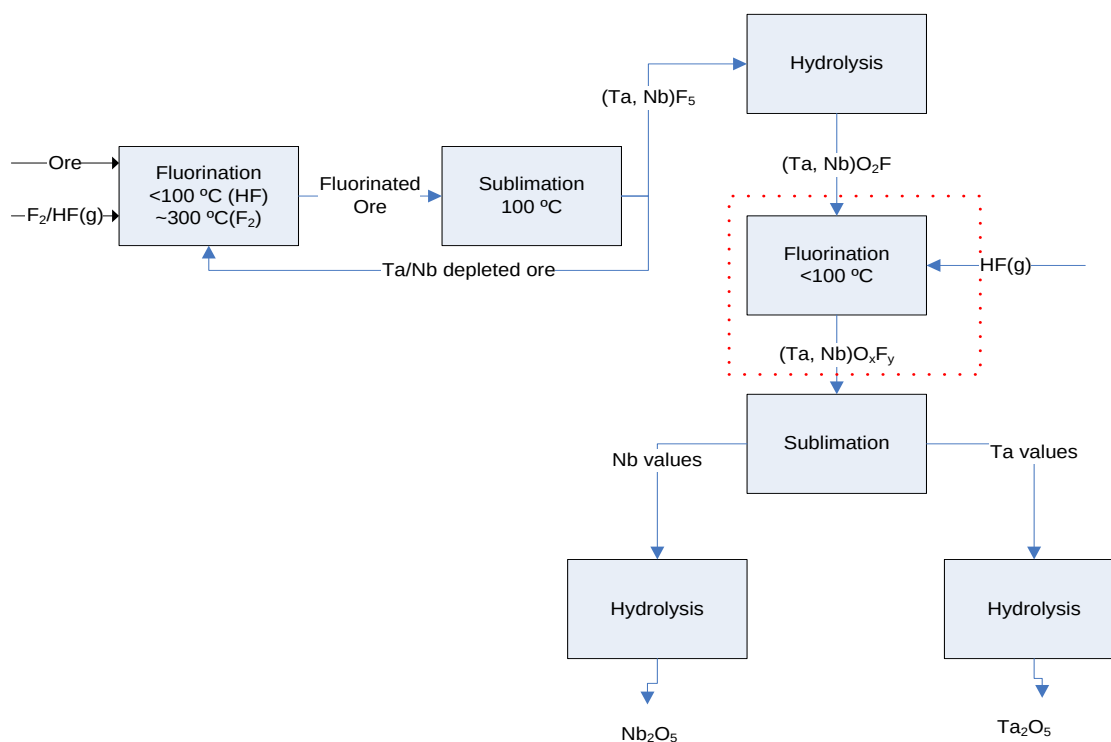


Figure 64: Process block diagram for complete fluorination and sublimation.

7.4 Concluding remarks

The work presented considers the possibility of a dry fluorination and sublimation process for the separation of Ta/Nb. Many unknown properties of tantalum and niobium oxyfluorides have been recorded and studied, including their thermal, spectroscopic and crystallographic features. When examining the reactions of elemental fluorine (F_2) and anhydrous hydrofluoric acid ($HF_{(g)}$) with the oxide forms of tantalum and niobium, both the kinetics and the reaction products were determined.

The characterisation of tantalite also made it possible to confirm the usefulness of $HF_{(g)}$ as a fluorination agent to induce physical and chemical changes in the mineral matrix, which could facilitate additional separation on the basis of a sublimation process.

The experimental data collected supports this as a viable process which would eliminate many of the disadvantages of the industry standard system of liquid-liquid extraction. Though laboratory-scale studies have allowed the definition of the three concept processes, reactor and pilot scale

work would be needed to determine whether larger-scale reactor systems would be viable. In addition, the phase diagrams of the TaF_5 and NbF_5 species should be determined, which might prove an interesting project on its own.

7.5 References

- Adetunji, A.R., Siyanbola, W.O., Funtua, I.I., Olsunle, S.O.O., Afonja, A.A. and Adewoye, O.O., (2005). "Assessment of beneficiation routes of tantalite ores from key locations in Nigeria". *J. Min. Mat. Char. Eng.*, **4**: 67-73.
- Andersson, S. and Astrom, A., (1965). "The Thermal Decomposition of NbO_2F ". *Acta Chem. Scan.*, **19**: 2136-2138.
- Cordier, S., Roisnel, T. and Poulain, M., (2004). "Synthesis and characterization of the novel $\text{Nb}_3\text{O}_5\text{F}_5$ niobium oxyfluoride: the term $n = 3$ of the $\text{Nb}_n\text{O}_{2n-1}\text{F}_{n+2}$ series ". *J. Sol. State Chem.*, **177**: 3119-3126.

APPENDIX A

INSTRUMENTATION

A. C80 Calorimeter

Similar to other differential scanning calorimeters, the C80 compares the heat flow in a sample vessel to the heat flow in a reference vessel. Both reference and sample cells are inserted into the measurement compartments at the top of the instrument.

This instrument is particularly suitable for this type of measurement owing to the dimensions of the sample vessel. Figure 65 shows a schematic diagram of the C80 sample vessel. Identical hastalloy vessels were used in both the sample and reference compartments of the instrument.

An array of thermocouples surrounds both a sample and a reference chamber and therefore all heat flow to and from the sample compartment is captured and measured. Since the instrument takes a differential measurement between the sample and reference vessels, any deviations in baseline from zero are due to the heat capacity of the loaded sample. By choosing an accurate baseline during integration, no further compensation for heat capacity is required.



Figure 65: C80 sample vessel.

The modifications to the calorimeter set-up include a gas manifold and handling system that allow the introduction of a reagent gas as well as inert carrier gases during measurements. A simple PID for the system is shown in Figure 66.

All gases are routed through the manifold which is located in the fume hood, off gases are passed through an Al_2O_3 scrubber before being released into the fume hood.

Unfortunately, the gasflow through the sample vessel severely limits the gas-solid interaction and mass transfer is a significant effect, which makes the calculation of kinetics impossible. The reaction speed is slowed tremendously for the same reason.

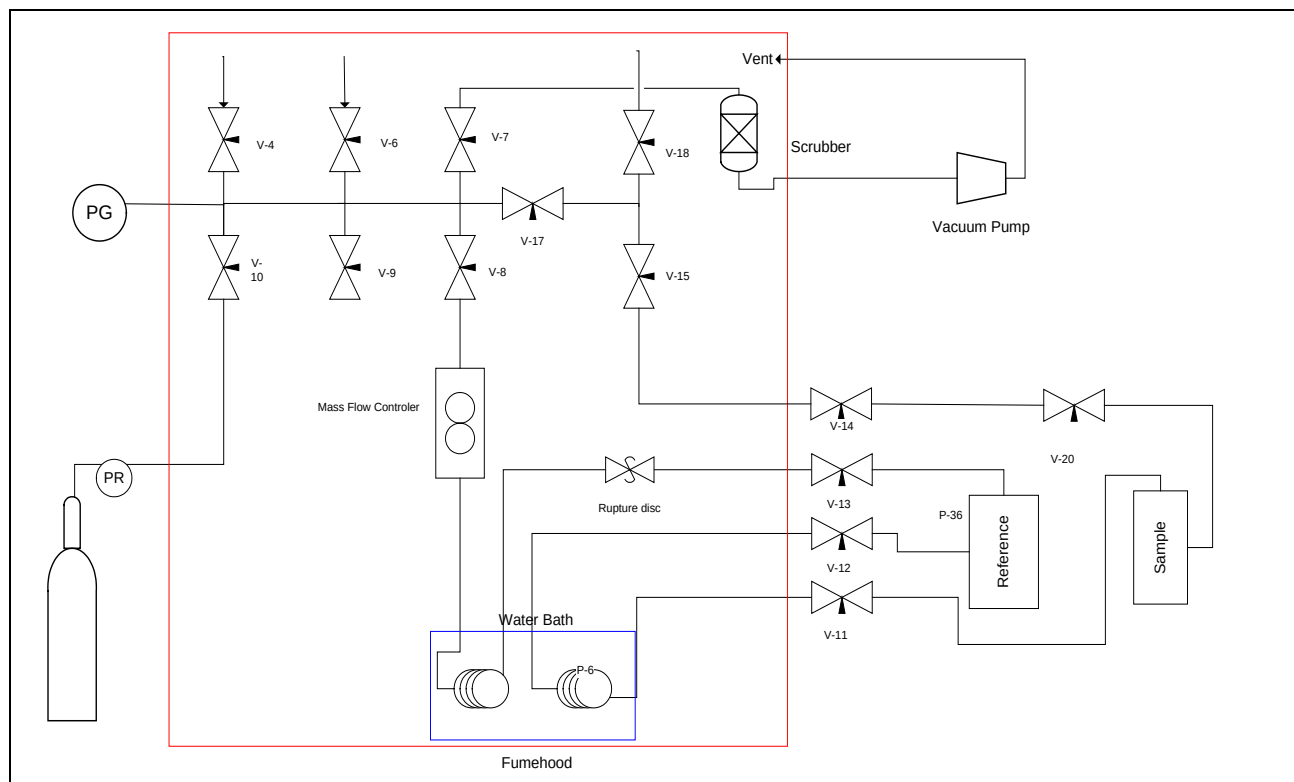


Figure 66: PID for the gas handling of Setaram C80.

B. SDT Q600 TG/DSC

Thermogravimetry is a technique that measures changes in the weight of a sample as a function of temperature. The TA Instruments SDT Q600 TG/DSC (Figure 67) is a horizontal balance instrument that allows the measurement of DSC (heat flow to and from the sample) simultaneously with the thermogravimetric measurement. The technical specifications are listed in Table 30.

Table 30: Technical specifications for TA SDT Q600.

Furnace Type:	Horizontal, Bifilar Wound
Temperature Range:	Ambient to 1500 °C
Heating Rate – Ambient to 1 000 °C:	0.1 to 100 °C/min
Heating Rate – Ambient to 1 500 °C:	0.1 to 25 °C/min
Thermocouples:	Platinum/Platinum-Rhodium (Type R)
Furnace Cooling:	Forced Air (1500 to 50°C in < 30 min)

Sample Capacity:	200 mg (350 mg including sample holder)
Balance Design:	Dual Beam Horizontal
Balance Sensitivity:	0.1 μg
Calorimetric Accuracy / Precision:	$\pm 2\%$ (based on metal standards)
DTA Sensitivity:	0.001 $^{\circ}\text{C}$
Vacuum:	to 7 Pa (0.05 ton)
Sample Pans:	40 μL , 110 μL Alumina: 40 μL



Figure 67: Image of the SDT Q600.

C. Corrosive TG

A Perkin Elmer TG with a high-precision hanging wire balance mechanism was used for corrosive measurements. A schematic diagram of the instrument is given in Figure 68 below. Normally an inert gas is passed over the sample to allow the purging of the volatiles that are released as the sample is heated. However, reactive gases can also be introduced – for instance H_2 can be used for reduction experiments. For the experiments in the current study, F_2 was used as the fluorinating agent.

Flow regulators maintained the net gas flow rate, irrespective of the type of gas in the purge stream. All gas tubing was changed to stainless steel to prevent corrosion, and the outlet connected to a fume hood.

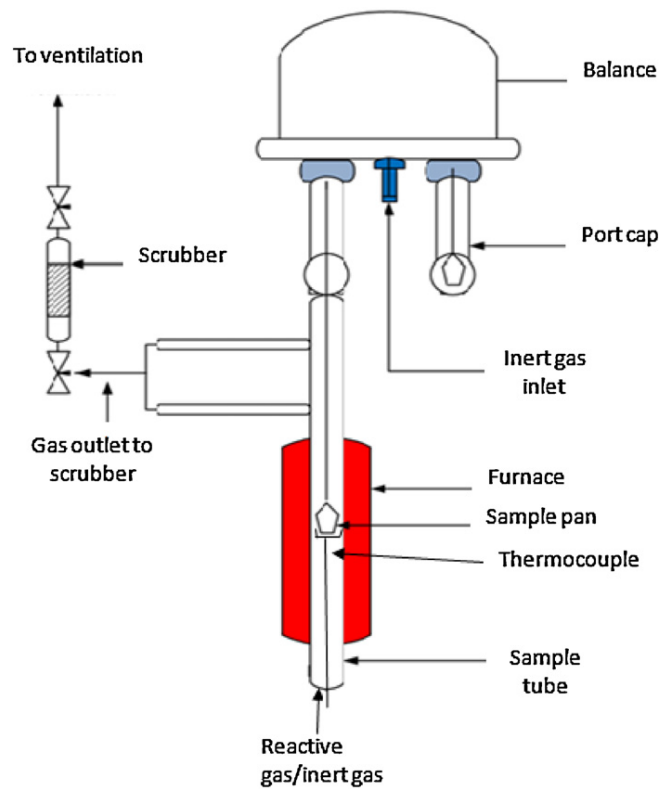


Figure 68: Schematic diagram of the modified TG instrument