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**Recovery and Purification of Titanium Dioxide and Aluminium
Compounds from Corundum By-product of the TiPro Process**

A thesis
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of the requirements for the degree
of

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Abstract

The TiPro process developed at the University of Waikato utilises an aluminothermic reaction to create titanium rich intermetallic alloys or alloy powders by solid-liquid separation. The product is then reduced with calcium vapour or calcium hydride to lower the oxygen content. This process involves intimately mixing titanium oxide powder with stoichiometric quantities of aluminium powder and heating the mixture to initiate a thermite reaction that transfers oxygen from the titanium oxide to the aluminium to produce titanium aluminide alloy and aluminium oxide. The liquid alloy is drained off from the by-product, called corundum, before going on to further processing. The corundum is left behind and contains significant quantities of valuable titanium alloy and aluminium and titanium oxides which must be recovered to increase the efficiency and lower the cost of the process.

This thesis describes and explains *proof-of-concept* wet chemistry methods of processing the corundum by-product to recover and separate the valuable metal oxides. Using acid-base equilibria, over 90% of the titanium was recovered from the corundum phase as impure titanium oxide. Aluminium was recovered as aluminium hydroxide and aluminium oxide, both of which can be processed into feedstock for fresh aluminium smelting and hence represent a potential revenue stream. The products were characterised using SEM-EDX and XRD to determine their composition and structure. The proposed treatment produces no waste other than environmentally benign neutral salt water.

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CHAPTER ONE

INTRODUCTION



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Chapter 1: Introduction

1.1 Historical Materials

Throughout human history culture and technological status have been defined by the main material of choice for construction, tool use and generic material of ubiquity. First, the people of the Stone Age utilised simple shaped rocks and wood, with a few rare instances of native metal found naturally such as gold, silver and copper. The discovery of the much better hardness and durability of the alloying of copper and tin led to the start of the Bronze Age around 3300BCE (Bienkowski & Millard, 2010). Bronze's superior properties to other metals made it ubiquitous for weapons, tools, polished mirrors and other devices.



Figure 1: Bronze billets from continuous casting (Shutter Stock Images, 2013)

Technological advance is an inherently iterative process; crude tools are used to fashion better tools and these better tools are used to fashion more precise tools and so on. As technology progressed, eventually the production of iron (which is far more difficult to smelt and manufacture than bronze) began to emerge. The earliest known iron object is a dagger from a tomb dated at 2500BCE (Cowen, 1999). As iron technology advanced, steel came to the fore although without the associated understanding of atomic theory and the chemical elements the ancient smiths did not know exactly why certain ‘irons’ displayed better properties, only that treating iron in a certain way produced better results. In the early 1700s, Abraham Darby the First developed iron and steel making on an industrial scale in England (Raistrick, 1989) and kick-started the Industrial Revolution with mass quantities of high quality iron and steel. Steel is a very strong material with excellent mechanical properties but is dense and heavy which makes it a poor choice for applications that demand low weight as well as high strength. This was seen during the First World War when the first air combat took place using primitive aircraft. The engines were made of steel but the framework of the aeroplanes were made of light wood and covered with stretched, lacquered canvas (Bruce, 1982) in a rather bizarre mixture of ancient and modern materials.

The demand for high strength and low weight lead to the widespread use of aluminium; its low atomic weight and high strength when alloyed made it ideal. Aluminium is the most abundant metallic element in the Earth’s crust and the 3rd overall most abundant element after silicon and oxygen (Greenwood & Earnshaw, 1997) but its’ extremely high affinity for oxygen made it more expensive than gold or silver until the late 1890s when the development of the Hall-Hérout process made it available in quantities larger than a few kilograms. The pure metal

is soft and has poor mechanical qualities but when alloyed and tempered with a few weight percentage of elements like copper, zinc, magnesium, manganese and silicon it displays greatly improved hardness, stiffness and strength (Lyle, Granger, & Sanders, 2005).



Figure 2: Aluminium die-castings (Shutter Stock Images, 2013)

Aluminium has some drawbacks however; its relatively low melting point of the pure metal at 660°C and tendency to experience severely reduced mechanical properties when heated makes it undesirable for high temperature applications such as aerospace. Aluminium alloys are also subject to corrosion at high or low pH as well as being attacked by organic liquids such as phenols and methanol (Davis, 1999).

1.2 The Role of Titanium

The constant demand for better performance lead to the development of titanium production processes as titanium has a number of useful attributes; it displays excellent corrosion resistance and the highest strength-to-weight ratio of any metal (Donachie, 1988). The pure metal has comparable strength to some steels but nearly half the weight. Titanium is 60% denser than aluminium but has more than double the tensile strength. (Barksdale, 1968) Like steels, titanium alloys also have a fatigue limit which ensures longevity in certain applications where repeat stresses are involved (Stwertka, 1998). Titanium is the 9th most abundant element in the Earth's crust and the 7th most abundant metal and found only in oxide form in any significant quantities due its high chemical activity. The metal was not produced in mass quantities until 1932 with the invention of the Kroll Process by William Justin Kroll who reacted titanium tetrachloride with calcium to deposit pure titanium metal. This was perfected later on by replacing calcium with magnesium (Greenwood & Earnshaw, 1997).

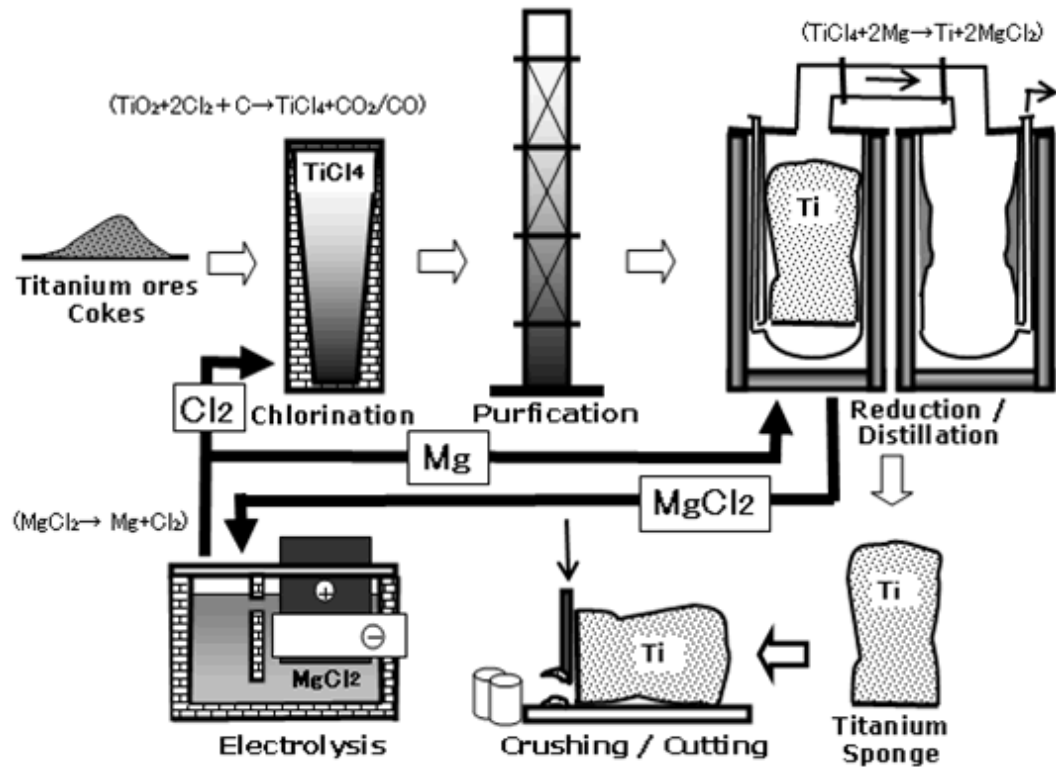


Figure 3: The Kroll Process

The Kroll process has not been superseded to the present day, although new processes like the FCC Cambridge process and the TiPro method have the potential to do so.

Titanium remains a very expensive metal to produce as high value magnesium is sacrificed in order to produce the metal in a cumbersome and expensive batch process. Titanium is chemically very reactive and the usual methods of producing a metal from its oxide by reacting the oxide with carbon at high temperature fails as the titanium forms titanium carbide rather than titanium metal (Stwertka, 1998). Titanium metal also has the annoying property of burning in air before reaching its melting point due to the reaction of titanium with nitrogen at 800°C to form titanium nitride. This means the metal cannot be melted and cast under normal conditions, further complicating processing of the material;

raw titanium metal sponge from the Kroll process must be re-melted and cast into ingots in a vacuum arc furnace.



Figure 4: High Purity titanium-crystal bar (Shutter Stock Images, 2013)

Despite these difficulties it remains in high demand due to its peerless properties for aerospace, automobile, marine and industrial engineering.

Titanium, like most metals, is rarely used in its pure elemental form but is alloyed with other elements to improve properties such as strength, fatigue limit, hardness and creep resistance. Of interest to this paper is alloying with large quantities of aluminium to form titanium aluminide, an alloy which displays excellent high temperature corrosion and creep resistance which makes it ideal for replacing heavy, dense nickel superalloys in these applications.

Ti-Al Phase Diagram

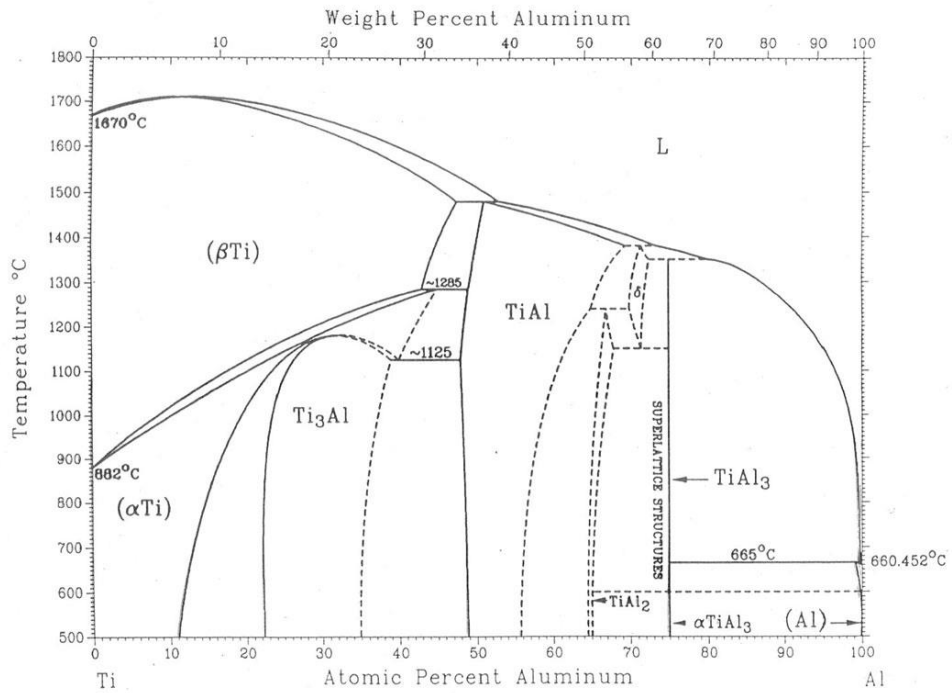


Figure 5: Titanium Aluminide Phase Diagram (Warnes, 2011)

Titanium aluminide has three major intermetallic compounds: gamma TiAl, alpha 2-Ti₃Al and TiAl₃ as shown in Figure 5. Out of these three the gamma TiAl has garnered the most commercial attention due to the aforementioned mechanical and corrosion resistant properties at temperatures over 600°C (Collings, 1994); economical production of gamma-TiAl would be highly lucrative.

1.3 The TiPro Method

The TiPro method is a novel approach to directly form TiAl alloys from titanium oxide powder and aluminium powder, obviating the expense of producing titanium metal beforehand; a great cost saving. By sealing the reactants in a reaction vessel and heating them until an aluminothermic reaction occurs, molten titanium and aluminium metal combine directly and intimately to form the titanium aluminide intermetallic alloy. Under an inert atmosphere the liquid alloy can be drained off leaving behind a ceramic phase consisting mainly of aluminium oxide mixed with trapped alloy and mixed oxides of titanium and aluminium. This 'corundum' phase is the by-product of the reaction and contains large quantities of valuable titanium and aluminium which need to be recovered in order to improve the economics of the process. This thesis details a cheap and straight forward effort to treat, separate and refine the metal species in the by-product and turn a waste product into recyclable or sellable material.

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CHAPTER TWO

LITERATURE

REVIEW



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Chapter 2: Literature Review

To fully understand the chemical nature of the problem and possible solutions it is necessary to investigate the chemical nature of the component materials and elements contained within the by-product of the TiPro method of preparing titanium aluminide alloys. Analysis of the material shows that it consists of aluminium oxides, titanium oxides and residual titanium aluminide alloy. Physical separation of these substances is not possible due to how intimately bound the components are; thus treating the by-product as a whole would seem to be the most logical way of approaching the problem. As the metals and oxides are ionic species when separated, an aqueous, or ‘wet chemical’ approach involving acids and bases is the most straight forward and well known process.

Examining the literature involving the chemical nature and wet chemistry of titanium, aluminium and their respective oxides as well as the metal alloy should suggest a method of applying wet chemical techniques to separating, isolating and refining the desired species to acceptable purities at minimal cost, if it is indeed possible to do so without resorting to obscure or expensive methods or reagents.

The main purpose of this work is to investigate whether or not titanium dioxide can be recovered at all using mild conditions and simple readily available chemicals. It is very much an exploratory proof-of-concept endeavour.

2.1 Review of Titanium Chemistry

2.1.1 Aqueous Titanium Chemistry

Titanium does not have a particularly rich aqueous chemistry which is to be somewhat expected from an element that is close to the left side of the periodic table. Titanium has three main oxidation states, +2, +3 and +4 corresponding to the number of outer electrons it possesses; 2 *d* electrons and 2 *s* electrons. No stable +1 state has been documented (Lyle, Granger, & Sanders, 2005).

In most cases, the +4 state and the metallic (0) state dominate the usual applications of titanium. The +2 oxidation state is a powerful reducing agent and is highly unstable, reacting instantly with water to form hydrogen. It also reacts strongly with oxygen to become oxidised to +3 and +4 and so is unknown in aqueous solution. That is not to say that it cannot be encountered; titanium (II) oxide (TiO) is formed by combining titanium (IV) oxide (TiO₂) and titanium metal under an inert atmosphere at 1500°C. It displays some interesting electrical and magnetic properties and has some niche applications (Banus, 1972). Acid solutions of TiO are stable for a brief period before decomposing into hydrogen and Ti⁴⁺ (Holleman & Wiberg, 2001).

Titanium's +3 oxidation state is more stable but is still susceptible to oxidation by atmospheric oxygen. As it possesses a lone *d* electron it can display quantum excitation of the electron to higher energy levels and quantum orbitals within compounds and complexes. The most (literally) visible outcome of this is that compounds and solutions of Ti³⁺ ions are coloured as shown in Figure 6

below. The colour is not as intense when compared to other electronic transitions as it is forbidden by the Laporte quantum selection rule (Shriver & Atkins, 2009).



Figure 6: The deep purple colour of Ti^{3+} ions in solution

Most compounds and solutions of titanium in its +3 oxidation state are unstable as atmospheric or dissolved oxygen oxidises the metal centre to the +4 state. Such compounds must be handled in air-free environments to avoid erratic or outright incorrect results when attempting to use the compounds (Fleming & McMurry, 1981). While this knowledge may not appear to be of much relevance to the matter at hand, during the experimentation phase of this investigation, seeing colours appear and disappear will allow progress of the reactions to be tracked and explained.

2.1.2 Titanium Oxides

Titanium is only found bound to other elements in nature; its very high reactivity in chemical terms ensures that it is never found in elemental, metallic form (Barksdale, 1968). Titanium oxide can exist in a number of forms; TiO_2 , Ti_2O_3 and TiO (in order of oxidation). Of these, only the TiO_2 form is found in nature, mainly as the minerals rutile, anatase and brookite. Chemically speaking, all of the oxides show much the same physical properties when exposed to acids and bases; they react with strong, oxidising acids and show little reaction to all but the most concentrated and powerful bases. They are all insoluble in water alone or organic solvents. Ti_2O_3 has the corundum crystal structure, which it shares with Al_2O_3 , TiO_2 has the rutile crystal structure (named after the principle ore of TiO_2) (Greenwood & Earnshaw, Chemistry of the Elements (2nd ed.) p217, 1997). All three show distinct physical appearances: pure TiO forms bronze crystals, pure Ti_2O_3 is a violet-black solid and pure TiO_2 is a brilliant white solid (see Figures 7 and 8 below).



Figure 7: Ti_2O_3 pellets (Shutter Stock Images, 2013)



Figure 8: Titanium Dioxide powder (Shutter Stock Images, 2013)

Ideally the pure white powder of titanium dioxide is the target material to be recovered from the reprocessing of the corundum by-product as it is the feedstock material for the TiPro process and has an economic value of approximately USD\$2000 - USD\$3000 depending on purity and crystal phase (Alibaba Global Marketplace, 2013). Merely discarding the by-product would be a waste of material as well as costly to dump and likely make the entire process uneconomic.

Any deviation from the characteristic pure white colour of titanium dioxide or, when studied under X-ray Dispersion, any defect in the crystal lattice is indicative of contamination of the final product. While there is no ‘goal’ of purity in this work, every effort will be made to acquire as pure a product as possible; ideally >80% purity would be acceptable as a starting point for further iterative refining of the procedure.

2.2 Review of Aluminium Chemistry

2.2.1 Aqueous Aluminium Chemistry

Like titanium, aluminium does not possess a particularly rich aqueous chemistry; indeed it has even less variety than titanium. Positioned in Group 3 of the periodic table, aluminium has 3 electrons in its outer quantum orbital to engage in bonding, 2 *s* electrons and 1 *p* electron. All three electrons are active for bonding and in aqueous solutions the Al^{3+} ion is the only stable ion that can exist. Al^+ and Al^{2+} ions have been characterised only existing in the gas phase at extremely high energies, often in the aftermath of explosions by aluminium containing compounds or in stellar supernovae (Greenwood & Earnshaw, Chemistry of the Elements (2nd ed.) p217, 1997).

Aluminium has the rare property of being amphoteric, due to its electron configuration. This means it can react as both an acid and a base in chemical reactions; more practically speaking the metal and many of its compounds will dissolve in both acidic and alkaline conditions. This can be demonstrated by placing aluminium metal in strong acid or strong alkali and it will dissolve in both, although the kinetics of the reactions differ (Shriver & Atkins, 2009). Much like titanium, aluminium is protected by a strongly adhering oxide layer that forms rapidly on exposed metal, protecting it from chemical and physical attack, making it highly corrosion resistant. To attack the metal, the passivating layer must be removed to access the metal beneath. Sheer pH is no indicator of effectiveness of corrosion of this surface layer as the diagram in Figure 9 beneath shows:

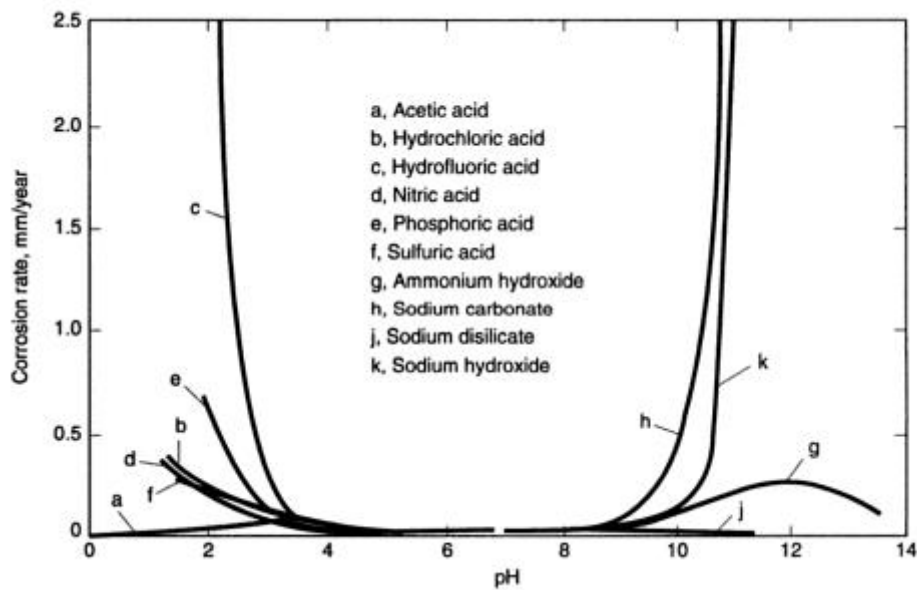
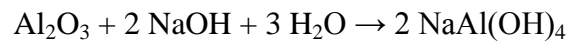


Figure 9: Rates of corrosion of aluminium by different acids and bases (Craig & Anderson, 1995).

As the figure shows, the effective rate of corrosion varies wildly with chemical species rather than pH. This demonstrates that it is the activity of the counter-ion of the dissolved salt rather than the concentration of protonated hydronium ions (Craig & Anderson, 1995). With this in mind, selection of the chemical with the fastest corrosion rate becomes clear. The counter-ion selection only matters for the attack of the titanium aluminide alloy trapped in the corundum phase, it has little effect on the corrosion and dissolution of aluminium oxide and titanium oxide as those reactions proceed via a different mechanistic route than attack of the metal (Kirk & Othmer, 1997). Strong acids such as sulphuric, phosphoric, nitric, hydrochloric and hydrofluoric and bases like sodium hydroxide and sodium disilicate show the most activity towards aluminium oxide.

2.2.2 Review of Aluminium Oxide and Hydroxide Chemistry

As has been noted in the previous sub-section, aluminium oxide (alumina) only occurs in any appreciable amounts with the chemical formula Al_2O_3 . This oxide has the corundum crystal structure and is the principle source of aluminium for metal production in the world. In the Bayer Process, raw oxide is mixed with dilute sodium hydroxide (~30%) at 275°C under very high pressure for several hours. This process relies on aluminium's amphoteric nature to selectively be dissolved while leaving impurities, principally iron oxides, undissolved. The solubilised aluminium forms sodium aluminate according to the following equation (Habashi, 2005):



The hot, saturated liquor is cooled and aluminium hydroxide crystallises out of the solution as a fluffy white solid according to the equation below:



The solid is filtered out and the liquor is returned to the leaching stage for reheating. The final stage to the process is heating the precipitated aluminium hydroxide to 980°C in order to drive off water from the molecule to leave pure Al_2O_3 (calcining). The pure alumina is then sent for smelting in the Hall-Héroult Process.

Aluminium is soluble in both acid and alkali but the principle reason for crystallising out the hydroxide from a saturated solution is due to the difficulty of

treating aluminium hydroxide that is precipitated from non-saturated solutions. When this occurs the precipitate is sticky, gelatinous and retains a very high water content, making it difficult to filter and hard to dry. During this work it was not possible to replicate on a bench scale the harsh conditions that occur in the Bayer Process so this difficulty was simply worked around. However on larger scale more attention will have to be paid to this point as it may force the acid leaching to be done under similar conditions to the Bayer Process. This would be cumbersome but the high pressure and temperatures would greatly accelerate the leaching time.

The aluminium hydroxide created in this paper will be filtered and calcined under similar conditions to the Bayer process calcination and then be subjected to elemental analysis for purity appraisal and XRD to determine the crystal structure of the product. Potentially, recovered alumina or aluminium hydroxide can be resold to aluminium smelters as feedstock. Calcining the hydroxide to remove water will reduce its volume by 30-50%, making it much more cost effective to transport and having a higher value. This is contingent of course on it having a sufficient purity for it to be acceptable to buyers.

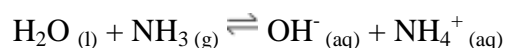
2.3 Review of Acids and Alkalis

The corundum phase contains aluminium oxides, titanium oxide and titanium aluminide. Attempting to dissolve the whole lot will require an agent that can attack all chemical species present. While sodium hydroxide would seem to be an easy and effective agent for dissolving aluminium and its oxides, it does not attack titanium oxide or titanium metal and thus will not be effective at leaching the titanium compounds into solution. Thus a solution of a strong acid, seemingly hydrogen fluoride (HF) would suffice. Hydrogen fluoride however is a dangerous, highly toxic and hard to store compound and its acid, hydrofluoric acid, attacks most metals and even glass, making it difficult to use in industrial processes, as well as giving off poisonous hydrogen fluoride gas due to HF being a weak acid (Greenwood & Earnshaw, Chemistry of the Elements (2nd ed.) p217, 1997).

An easier method is to generate active fluoride ions *in situ* during the reaction by adding a source of fluoride to an acid solution, such as sulphuric or hydrochloric acid. Nitric acid should be avoided as it can engage in unpredictable side reactions that generate toxic and corrosive nitrogen dioxide gas (Dean, 1992). Adding catalytic quantities of a fluoride salt, such as sodium fluoride or calcium fluoride, should greatly accelerate the reaction without the need to engage in handling of bulk hydrofluoric acid. The effect of dissolved fluoride will be investigated as part of this work.

The acid used in the leaching phase will need to be neutralised and the pH made very high (> pH 10) in order for the precipitated aluminium hydroxide to re-dissolve and leave behind the titanium oxide to be filtered out of the solution. Neutralising with sodium hydroxide is cheap but might introduce large amounts of sodium which could become trapped in the forming crystal structure of the titanium dioxide. Moreover, the positively charged sodium ions would attract the fluoride ions present and incorporate them into the crystal lattice too (Churan, 2011). This would present a major purity problem for the product and would need a work around solution. Using ammonia to neutralise the acid solution to a pH of 9 would prevent major contamination by sodium. Aluminium hydroxide will not dissolve in ammonia as the pH is not high enough so a small amount of sodium hydroxide (or other strong base) will need to be added to increase the pH to sufficient levels to re-dissolve the aluminium hydroxide (Barksdale, 1968).

Ammonia should not become a major contaminant of the product as ammonia is a weak alkaline gas and is subject to the following equilibrium reaction:



As the product titanium oxide or aluminium hydroxide dries, the water in the equation is removed. This forces (by Le Chatelier's Principle) the equilibrium to the left, converting ammonium and hydroxide ions into ammonia gas and water, which boil away. This process continues until there is no ammonia left; thus the product 'self-cleans' itself of ammonia contamination. The only issue is that freshly precipitated product should be dried in well ventilated ovens until the ammonia has evaporated and dispersed.

In selecting an acid for the acid leaching stage, several variables must be taken into account:

- *The counter ion* – The solubility coefficient of the counter ion (anion) in solution when in the presence of aluminium and titanium ions, as well as impurity vanadium (which is often present in titanium due to its chemical similarity). If the anion is insoluble in water or in low pH aqueous environments then this would complicate the process as part of the leach liquor will precipitate out of solution prematurely. Tables 1 and 2 below show the solubility of relevant titanium and aluminium compounds formed from the action of common acids under consideration for experimentation.

<u>Acid</u>	<u>Anion</u>	<u>Titanium Compound</u>	<u>Soluble in Water</u>	<u>Soluble in Acid</u>
Sulphuric	Sulphate (SO ₄ ²⁻)	Ti(SO ₄) ₂	Soluble	Highly Soluble
Nitric	Nitrate (NO ₃ ⁻)	Ti(NO ₃) ₄	Highly Soluble	Highly Soluble
Hydrochloric	Chloride (Cl ⁻)	TiCl ₄	Violently reacts	Soluble
Hydrofluoric	Fluoride (F ⁻)	TiF ₄	Violently reacts	Soluble

Table 1: Behaviour of titanium salts in acid and neutral aqueous solutions (American Element Inc., 2013).

<u>Acid</u>	<u>Anion</u>	<u>Aluminium Compound</u>	<u>Soluble in Water</u>	<u>Soluble in Acid</u>
Sulphuric	Sulphate (SO ₄ ²⁻)	Al ₂ (SO ₄) ₂	Soluble	Highly Soluble
Nitric	Nitrate (NO ₃ ⁻)	Al(NO ₃) ₃	Highly Soluble	Highly soluble
Hydrochloric	Chloride (Cl ⁻)	AlCl ₃	Reacts	Soluble
Hydrofluoric	Fluoride (F ⁻)	AlF ₃	Sparingly soluble	Soluble

Table 2: Behaviour of aluminium salts in acid and neutral aqueous solutions (American Element Inc., 2013).

- Safety and Toxicity* - As has been noted above, nitric acid has the potential for side reactions that release toxic nitrogen dioxide. Hydrofluoric acid is dangerous to handle, store and use. These complications make it difficult to use these two acids in this work.
- Contamination* - Inclusion of anions from the acid have the potential to disrupt the crystal structure of the precipitated product and reduce its purity. This is more prevalent when the ions are small and charge dense. The fluoride ion and chloride ion would likely be ions that would be included in the precipitated products. Large, more charge diffuse anions are unlikely to be trapped in the crystal structure as they are more soluble due to being less strongly attracted to the small, charge dense metal ions. This can be seen in the tables above as the sulphate and nitrate salts of aluminium and titanium are more soluble than halide salts.

- *Dilution* – The dilution of the acid selected must be sufficient to ensure solubility of the dissolved species as well as a rapid reaction rate but not so concentrated as to cost excessive amounts in feedstock costs. As the acid must be neutralised at a later point, excessive amounts of acid will necessarily incur excessive amounts of alkali. This will have the knock-on effect of increasing the levels of dissolved salts that can potentially contaminate the products.

After review of the different factors as well as the cost of bulk quantities of acid, sulphuric acid was chosen as the acid of choice for the leaching stage and sodium hydroxide chosen as the strong base for neutralisation for the precipitation step. Ammonia was selected for investigation as well due to its ability to neutralise acid without contamination of the end product. Catalytic quantities of a fluoride salt will be added to accelerate the reaction.

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CHAPTER THREE

EXPERIMENTAL

PROCEDURES



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Chapter 3: Experimental Procedures

This chapter details the procedures used in the laboratory to carry out the research into separating the aluminium compounds from the titanium ones and the steps in purification. The procedures draw heavily on inorganic chemical techniques and should be readily repeatable by people skilled in handling and processing in a chemical laboratory. All experiments were carried out in the Geochemistry laboratory on the 3rd floor of F block rather than in the Large Scale Laboratory as this lab has dedicated delicate balances of four decimal places, capable of fine measurements and are regularly tested and calibrated. This laboratory also had the requisite glassware and equipment required for the experiments.

3.1 Sample Characteristics

A sample of the material of interest, the composite phase by-product of the TiPro reaction was obtained from Kenneth Sichone, PhD candidate at the University of Waikato Engineering department. The material was milled to an average particle size of $105\mu\text{m}$ using a disc mill in the Large Scale Laboratory. The sample presents as a fine grey-black metallic looking powder as seen below in Figure 10.

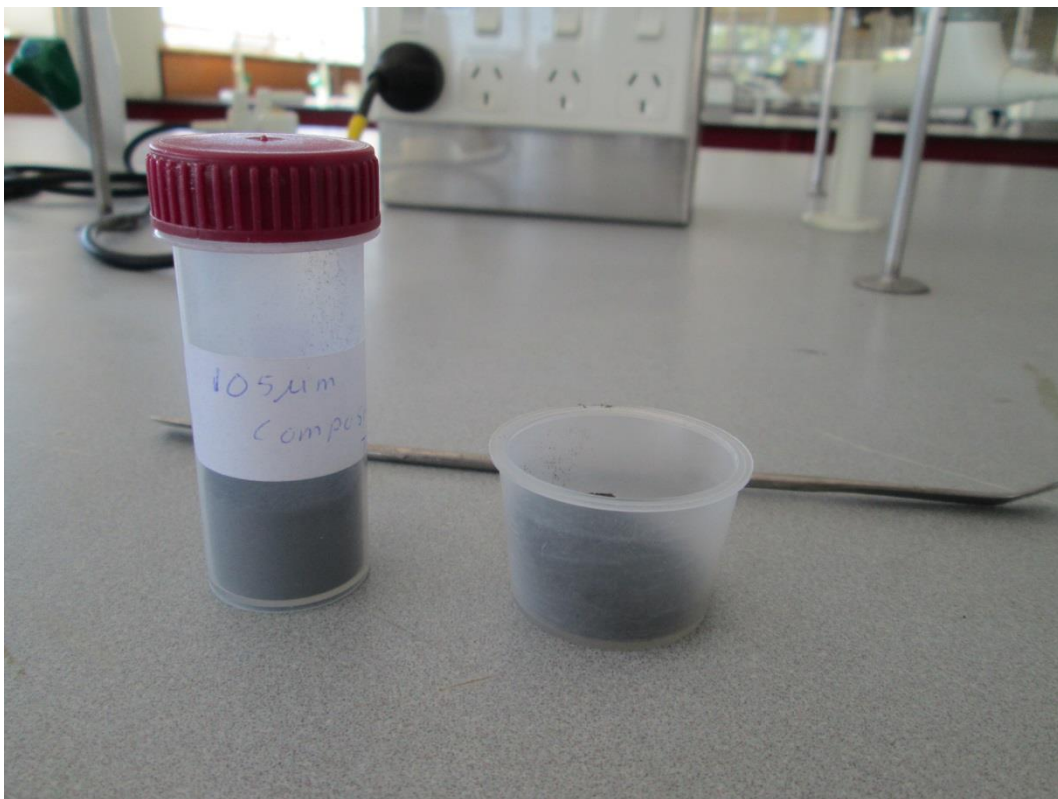


Figure 10: The composite corundum sample used in the experiments.

The material is dense and heavy which is to be expected as it contains significant quantities of titanium aluminide. The small particle size gives it a very large surface area for reaction.

The by-product was characterised via XRD, SEM and EDX. When seen under an electron microscope as shown below in Figure 11 it is a porous solid with dark spots that are rich in titanium aluminide embedded in a matrix of aluminium oxide.

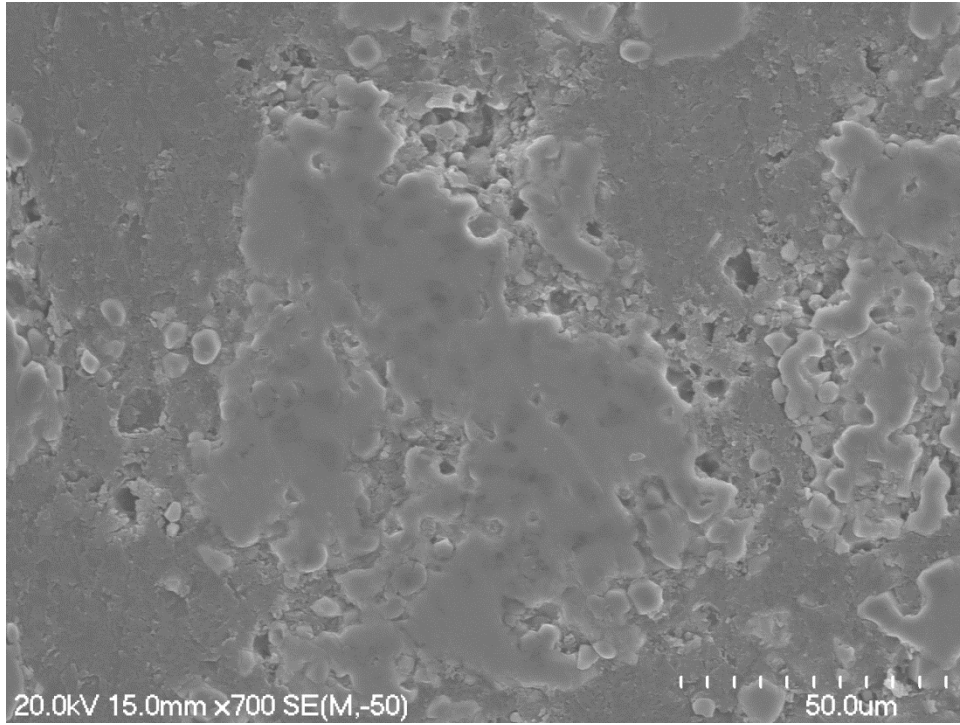


Figure 11: SEM image of the starting material.

The material was also characterised by EDX for elemental analysis and thus accurate knowledge of the starting composition was obtained as shown in the table below.

Element	Atom %	Error ±%	Weight %	Error ±%
Oxygen	43.94	0.94	27.20	0.58
Aluminium	39.64	0.27	43.28	0.28
Titanium	15.48	0.22	28.39	0.40
Vanadium	0.12	0.08	0.24	0.16
Silicon	0.81	0.15	0.89	0.16

Table 3: Elemental Analysis of corundum by-product from the TiPro process.

3.2 Acid Leaching

A 10 gram sample of composite material was weighed out with an accurate balance in a measuring cup as shown in Figure 11.



Figure 11: Accurate weighing of a sample of composite material

The sample was then transferred to a conical flask with a magnetic stirrer bar and placed on a hot plate. The experimental setup was confined to a fume cupboard as the reaction of acid with metal generates hydrogen gas which is intensely flammable. There was also the risk of fumes of hydrogen fluoride from the acid. To minimise any danger of fire or explosion the initial leaching with acid was thus done in a fume hood. A 20% w/w concentration of sulphuric acid was prepared by carefully adding 20 grams of concentrated (98%) sulphuric acid to 80mls of cold water. The flask this was prepared in was cooled with cold water by

running the flask under a tap as the dilution of concentrated sulphuric acid with water is intensely exothermic and can rapidly boil the water leading to a spray of caustic acid if done carelessly. Acid was added to water rather than other way around to maximise the heat capacity of the water to enable a safe buffer for temperature.

Once the solution of acid was cooled it was transferred to the fume hood for the reaction. A beaker of ice was on standby to quench the reaction if there was any indication of thermal runaway occurring. The generation of hydrogen in the reaction will create turbulence and could conceivably bubble over the top of the flask if the reaction becomes too vigorous; ice will both cool and dilute the reaction solution if this occurs. The experimental setup is shown below in Figure 12:



Figure 12: The experimental equipment prior to adding acid to the corundum.

The final reagent to be prepared was sodium fluoride. This highly toxic chemical's purpose is to be a catalytic source of fluoride ions to generate *in situ* hydrofluoric acid. It was not added at the start of the reaction so as to observe the behaviour of the corundum when exposed to acid without the presence of fluoride. 0.5 grams of fluoride was measured out into a cup; it presents as a white powder as shown in Figure 13.

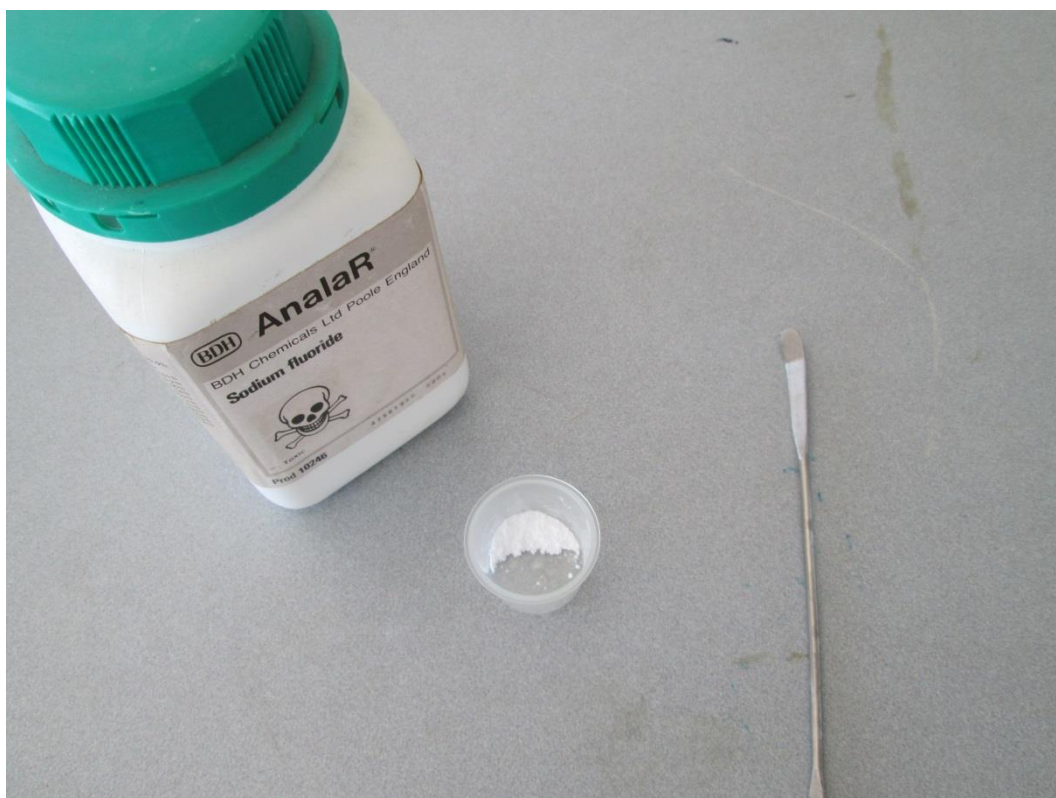


Figure 13: Sodium Fluoride measured out for the reaction.

Once the reagents and sample were weighed out and prepared, the experiment was ready to start. The flask was on a hotplate the heating element was not turned on to start with. This was done in case of a vigorous reaction occurring in the initial stages of the experiment; having the mixture hot at the start would make a thermal runaway event much more likely.

The flask containing the by-product was charged with the acid and the magnetic stirrer activated to thoroughly mix the powder and acid. The flask was observed carefully for ten minutes before the stirring was stopped and the powder allowed to settle in order to observe the evolution of gas bubbles that would indicate a reaction occurring. Figure 14 below is a photograph of the flask at that time.

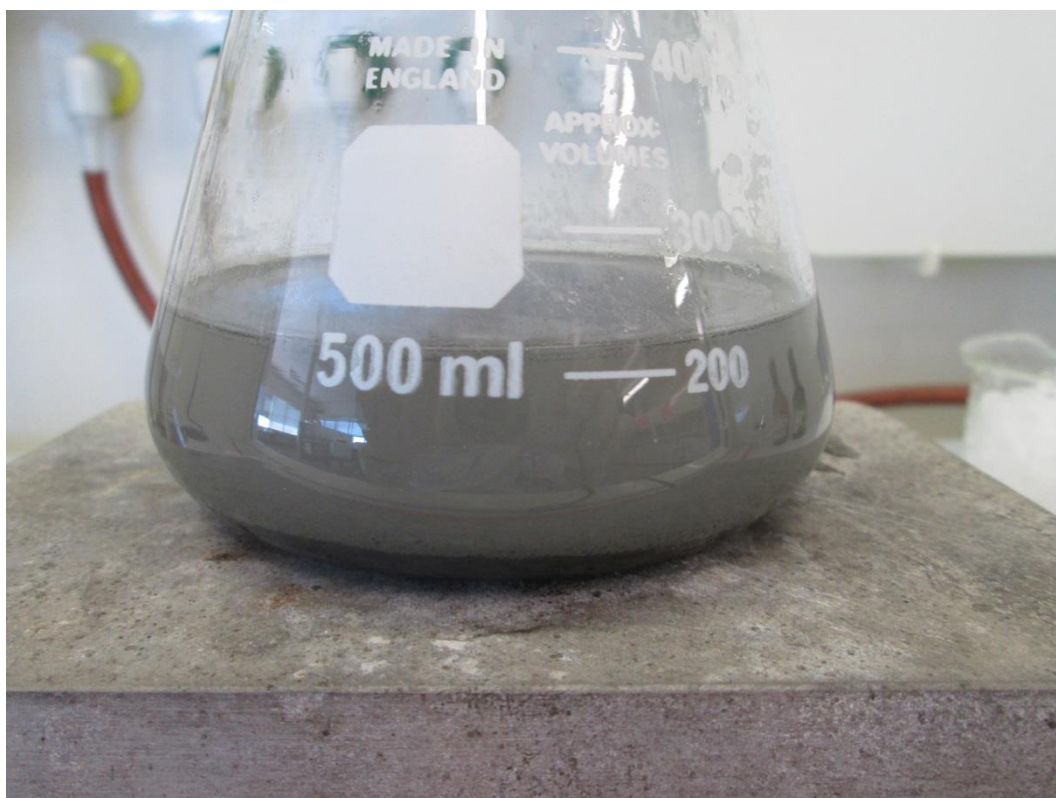


Figure 14: State of the reaction at 10 minutes.

As can be seen, there was little indication of a reaction occurring. Some slight frothing was observed but the reaction of metal with acid would be expected to be more vigorous. The explanation for this is that the passivating oxide layer on the surface of the titanium aluminide alloy is preventing reaction with the underlying metal. This eventuality was hypothesised before the work started and planned for with the addition of sodium fluoride to generate

hydrofluoric acid. The pre-prepared 0.5 grams of the fluoride was carefully added to the flask and immediately, without stirring needed, the reaction greatly accelerated as shown in Figure 15.

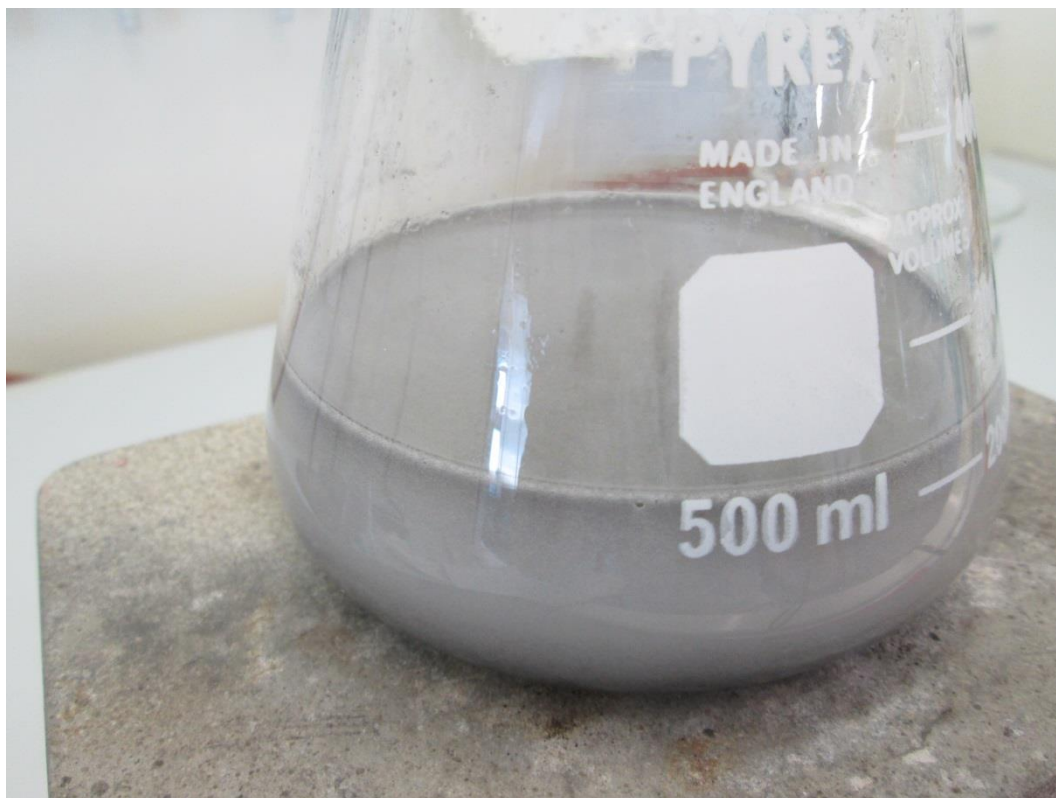


Figure 15: State of reaction immediately after fluoride addition.

Prolific gas generation was observed within seconds of the sodium fluoride catalyst being added. Confirmation of the gas's identity was confirmed by holding a test tube over the neck of the flask for 10 seconds and then applying a flame to the tube. A popping sound and a flash of flame confirmed the presence of hydrogen gas; this indicates that the hydrogen fluoride rapidly attacked and removed the oxide layer on the surface of the metal allowing acid to directly attack the metal and generate hydrogen. Stirring was restarted and continued for an hour while the gas generation and temperature of the sample was monitored.

The acid temperature rose from 26°C to 33°C within 15 minutes of the fluoride addition and slowly decreased back to 28°C after 40 minutes and then held steady.

After one hour the hot plate heating element was switched on and the temperature slowly increased to 70°C. The rate of gas generation increased but remained stable and did not become violent. After one and a half hours the rate of effervescence was observed to be declining and the liquor had a noticeably purple colouration as shown below in Figure 16.

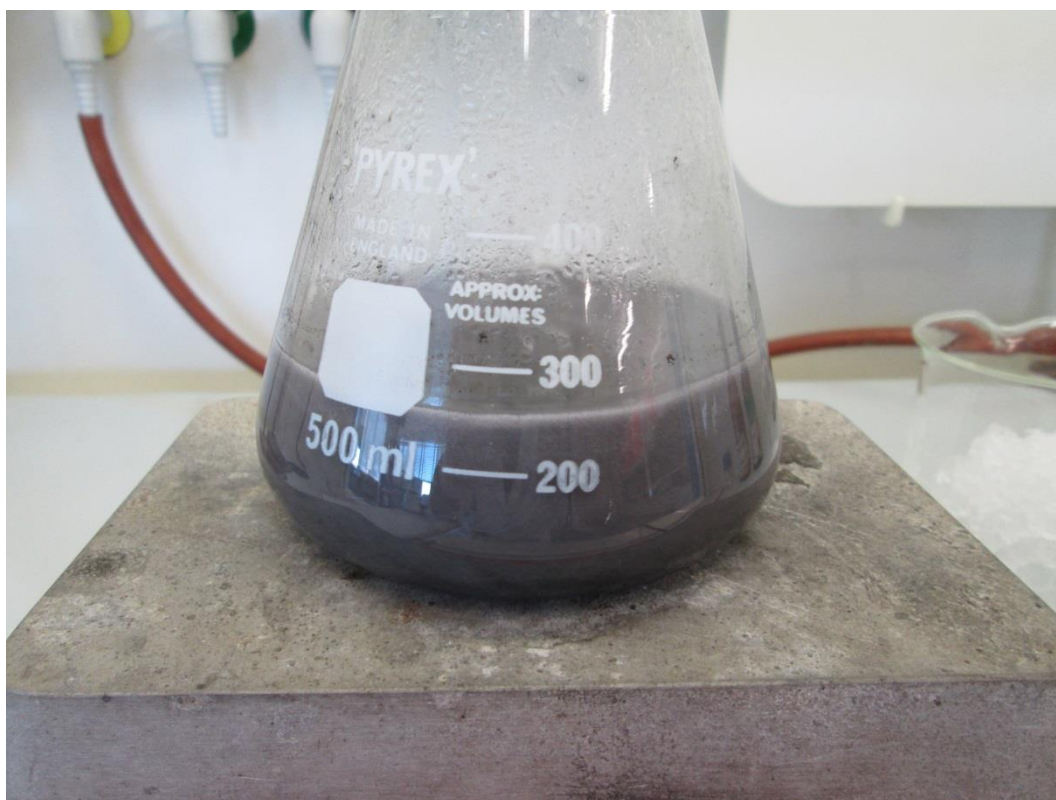


Figure 16: State of the flask after 1.5 hours of reaction.

Heating was increased to raise the temperature of the reaction mixture to 90°C to maximise the rate of reaction and ensure full reaction. A watch-glass was placed on the top of the flask to condense vapour and prevent excessive evaporative losses disturbing the acid concentration. Stirring and heat were

maintained for a further hour and a half, although gas generation appeared to have ceased after two hours reaction time.

After three hours reaction time the flask was removed from the hotplate and stirrer and transferred to cold water bath to cool the reaction mixture to allow safe handling. There was a distinct residue of unreacted powder in the bottom of the flask and the liquid was an intense violet colour. The residue was separated from the liquid phase by simple filtration with filter paper as pictured in Figure 17.

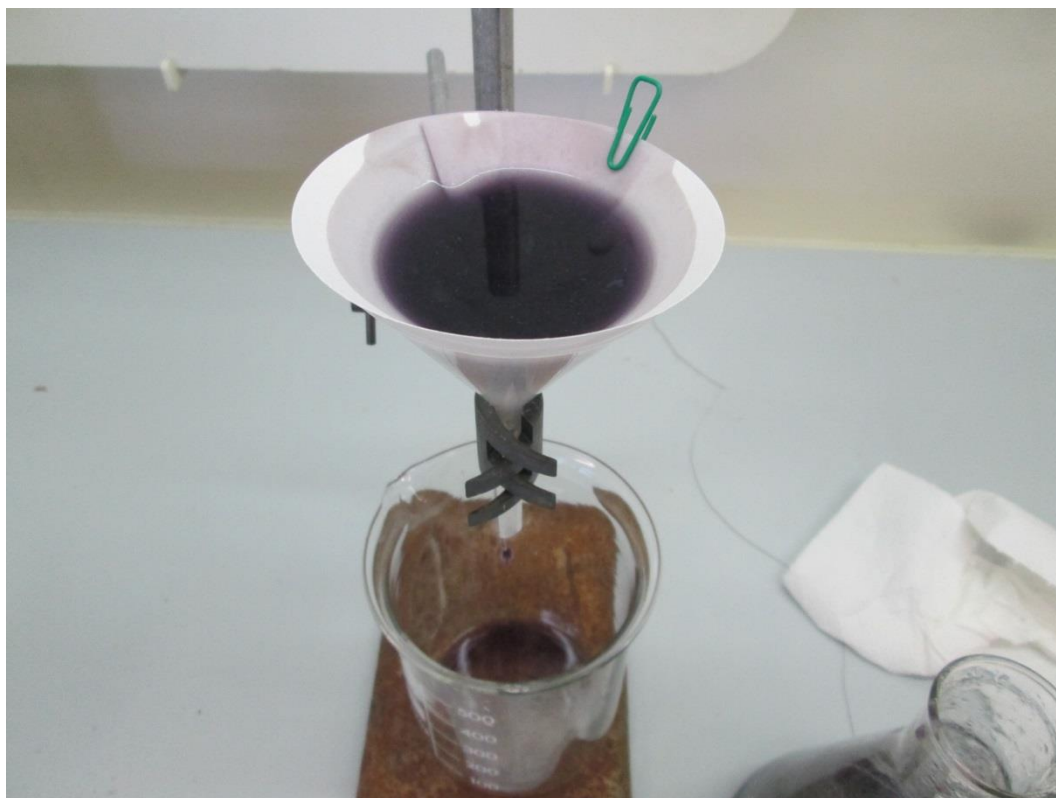


Figure 17: Filtration of the acidic liquor from the residue.

The residue was washed with dilute sulphuric acid and then cold water, with the washings added to the leachate to ensure as little loss as possible of the

liquor. The residue was then transferred to a drying oven at 100°C overnight. When dried the residue presented as a fine, crumbly, light grey powder.

After filtration the leachate presented as clear, deep violet solution, very similar to solutions of Ti^{3+} ions seen in textbooks. The clarity of the solution can be seen in Figure 18; the lack of any cloudiness is indicative of good filtration and no unforeseen precipitation.

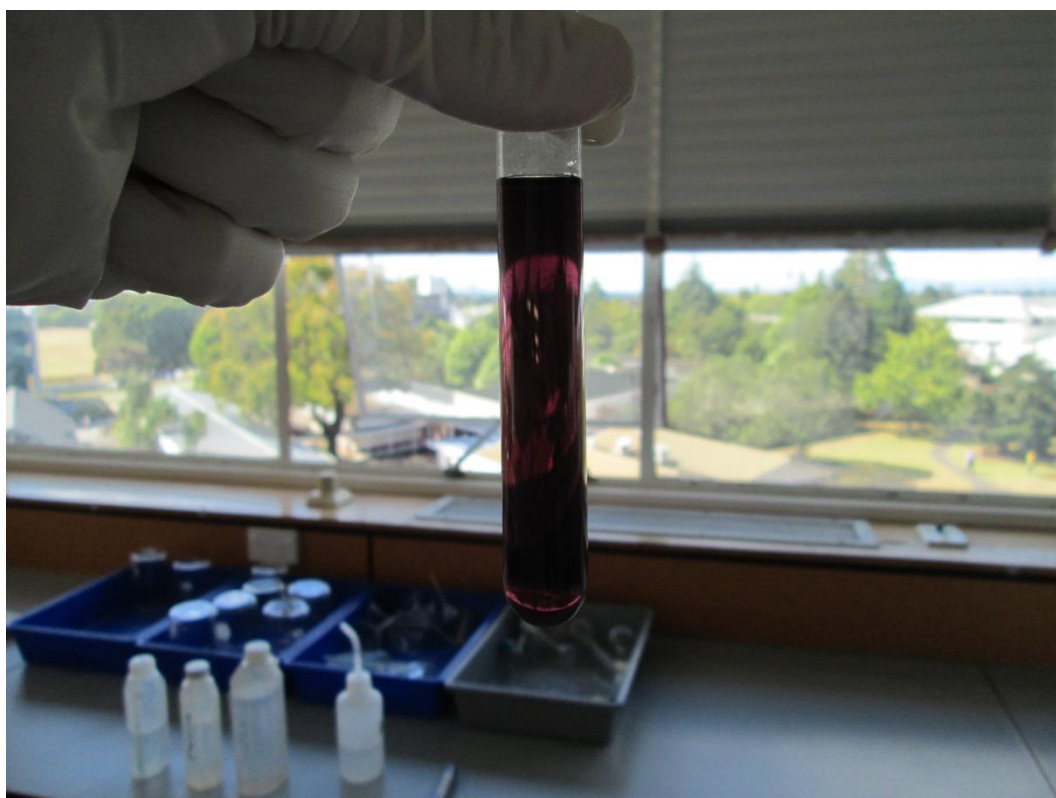


Figure 18: Clarity and colour of the leachate solution.

3.3 Precipitation of Titanium Oxide and Aluminium Hydroxide

The liquor and washings combined were approximately 200mls of dark violet solution. To neutralise the acid, 200mls of 25% ammonia stock solution was poured into a beaker and the leachate slowly added to the ammonia. Addition was gradual to avoid sudden heat generation caused by the neutralisation of the acid and alkali.

Ammonia was chosen instead of a strong alkali like sodium hydroxide to avoid excessive amounts of sodium ions being trapped in the precipitated product (as noted in the literature review). Prior qualitative work by the student (pictures in Section 3.4) showed that precipitation with strong alkali produced unacceptable levels of contamination in the product. This manifested as a dark green colouration in the precipitate which should otherwise have been white. Repeated steps of re-dissolution and re-precipitation reduced the contamination but it was arduous and wasteful of acids and alkalis, as well as adding unnecessary complexity to the process. To counter this, precipitation with ammonia was utilised instead. Upon adding the leachate to the ammonia a dark brown precipitate immediately formed as seen in Figure 19. This is the formation of titanium complex ions with ammonia; these ions are not energetically stable however and are only transitory until the titanium ions become fully oxidised.

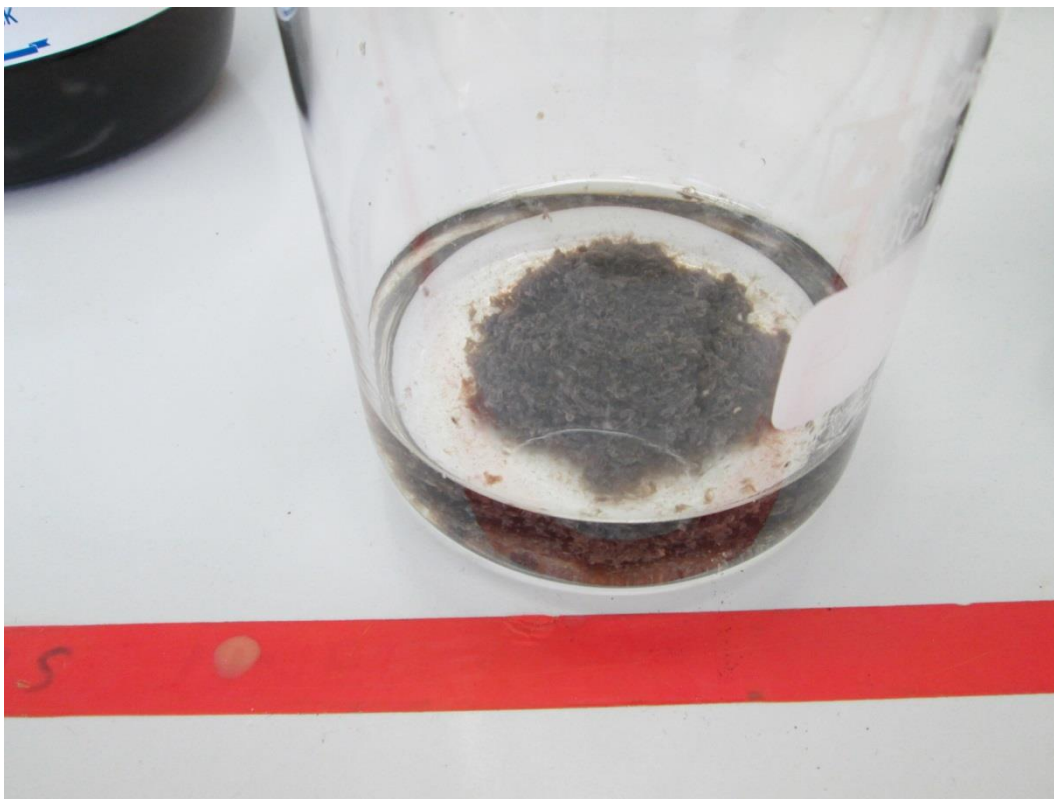


Figure 19: Precipitation of titanium and aluminium in ammonia solution.

With stirring the precipitate breaks up into a fine, dense mass that rapidly settles to the bottom of the beaker. After approximately fifteen minutes the colour changed to a deep blue, possibly indicative of the $\text{Ti}(\text{NH}_3)_6^{3+}$ complex ion although this is difficult to establish definitively due to the presence of other dissolved species. The precipitate was allowed to settle for 3 hours before being examined again. The precipitate was observed to be slowly decolourising in a ‘wave’ from the top of the beaker to the bottom, seen in Figure 20. This phenomenon is due to the dissolved oxygen in the solution slowly oxidising the blue Ti^{3+} complex ions to colourless Ti^{4+} . As the dissolved oxygen is used up in the water more oxygen must dissolve and diffuse into the solution from the atmosphere which explains the reason the ‘wavefront’ of oxidation is seen travelling from the top to the bottom of the precipitate. Left untouched, this

process is extremely slow as oxygen can only dissolve up to 8mg/litre at room temperature in water. The precipitate was then left overnight for a period of approximately 18 hours (Figure 21) to observe any changes.

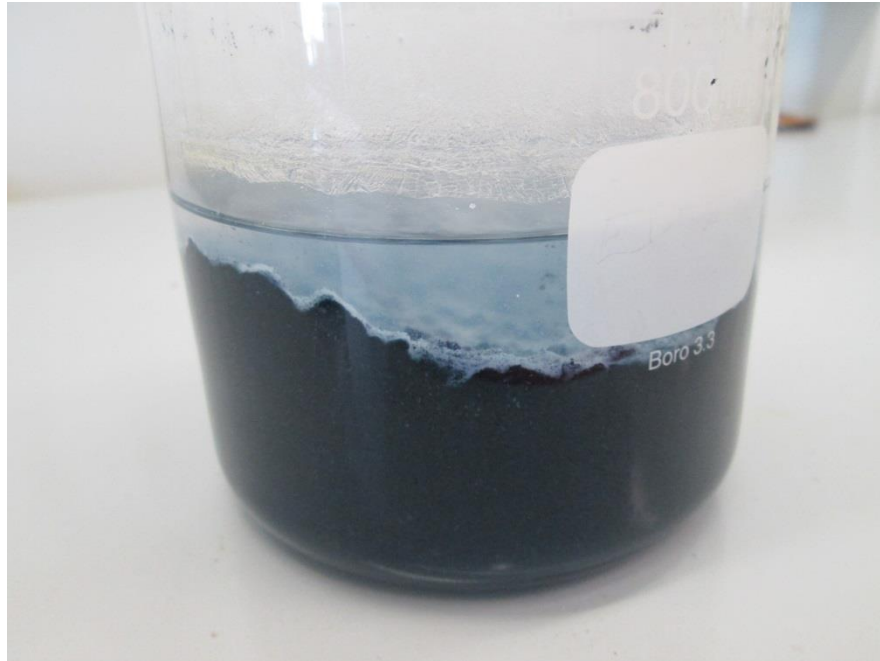


Figure 20: Oxidation of the precipitate after 3 hours.

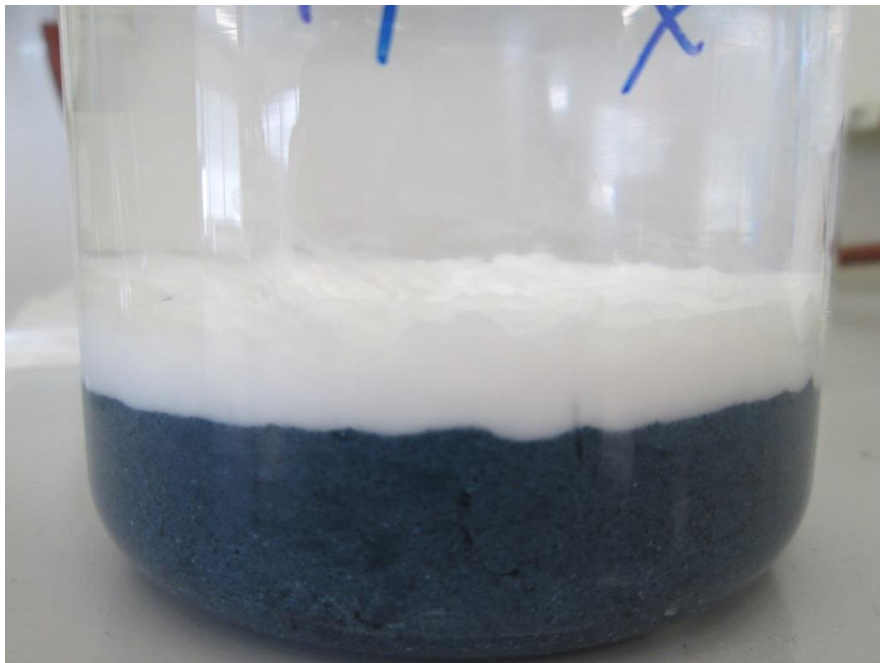


Figure 21: Oxidation of the precipitate after being left overnight (~18 hours).

Obviously this method of oxidising the titanium in the solution is very inefficient and slow. A chemical method of speeding this process up would be to add an oxidising agent (such as hydrogen peroxide) to the precipitate but this would incur unnecessary expense when atmospheric oxygen will be just as effective. To accelerate the process, the precipitate was placed back on the magnetic stirrer and mixed at high speed to ‘beat’ air into the solution and oxidise the titanium as shown in Figure 22. Bubbling air into the beaker would also greatly increase the level of dissolved oxygen.



Figure 22: Rapid stirring of the precipitate to encourage oxidation.

After one hour of stirring the colouration of the precipitate had dissipated and the solution was a pure white milky colour. The stirring was stopped and the magnetic rod removed to allow the precipitate to settle again to form the dense, pure white precipitate seen in Figure 23:

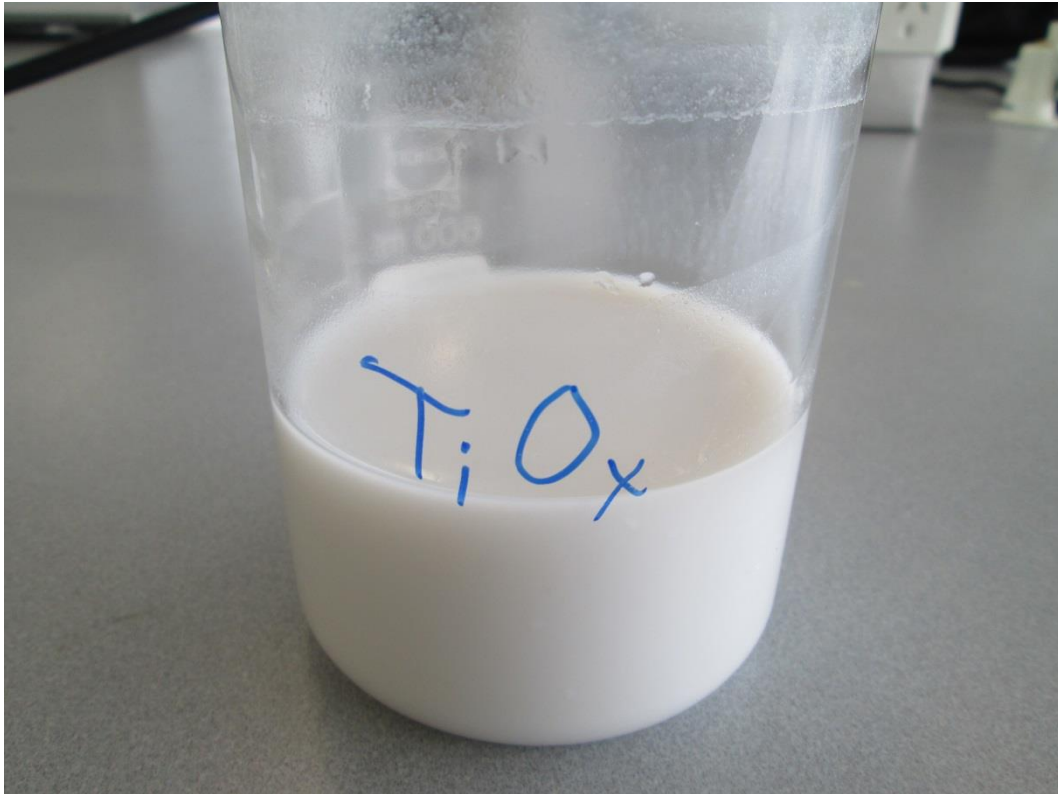


Figure 23: Fully oxidised precipitate appearance.

3.3 Separation and Purification of TiO_2

At this point, the precipitate was a mixture of aluminium hydroxide and titanium dioxide. In order to separate the aluminium compound from the target titanium compound, further acid-base equilibria was exploited. As aluminium hydroxide is soluble in solutions of a pH above 11, the precipitate needed to be washed with strong alkali to remove the aluminium without contaminating the titanium oxide to any great degree.

This was achieved by first filtering the precipitate from the ammonia solution using a Buchner funnel and vacuum system. The precipitate was washed with several aliquots of hot water to ensure as much ammonia was removed as possible before being removed to the oven and dried overnight. After the precipitate was dried it was ground using a pestle and mortar to a fine powder. A 5% solution of sodium hydroxide was prepared by adding 2.5 grams of sodium hydroxide granules to 50mls of water. This solution was heated to 80°C and then poured into a beaker; the precipitate was then added and stirred vigorously for 15 minutes. The resulting suspension of titanium dioxide was then filtered again and washed several times with hot water to ensure no sodium hydroxide remained as shown in Figure 24. It was theorised by the student that since the titanium dioxide was already formed, the sodium hydroxide would be unlikely to contaminate it at this stage.

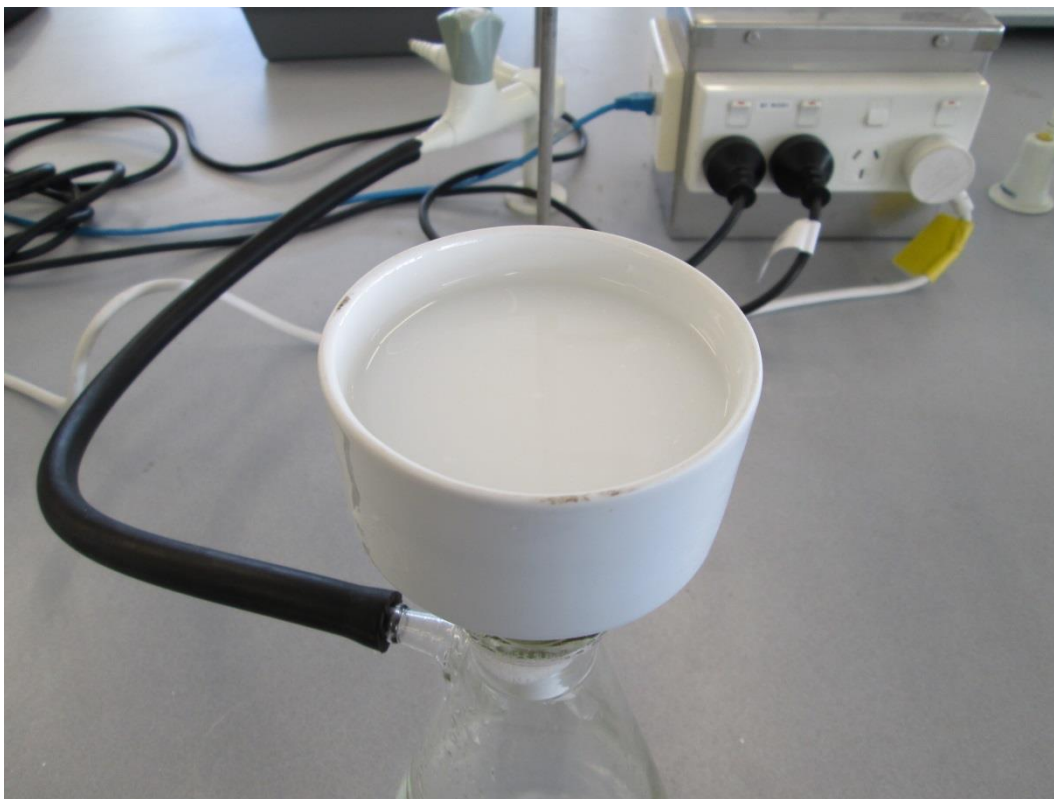


Figure 24: Filtration and washing of the TiO₂ with sodium hydroxide and hot water.

The cleaned titanium dioxide was then collected and placed in the oven to dry. The wash water and sodium hydroxide solution were combined and neutralised to pH 7 with dilute acid; a sticky gelatinous precipitate of aluminium hydroxide rapidly formed as depicted in Figure 25. This precipitate was filtered, washed and also transferred to the oven for drying.

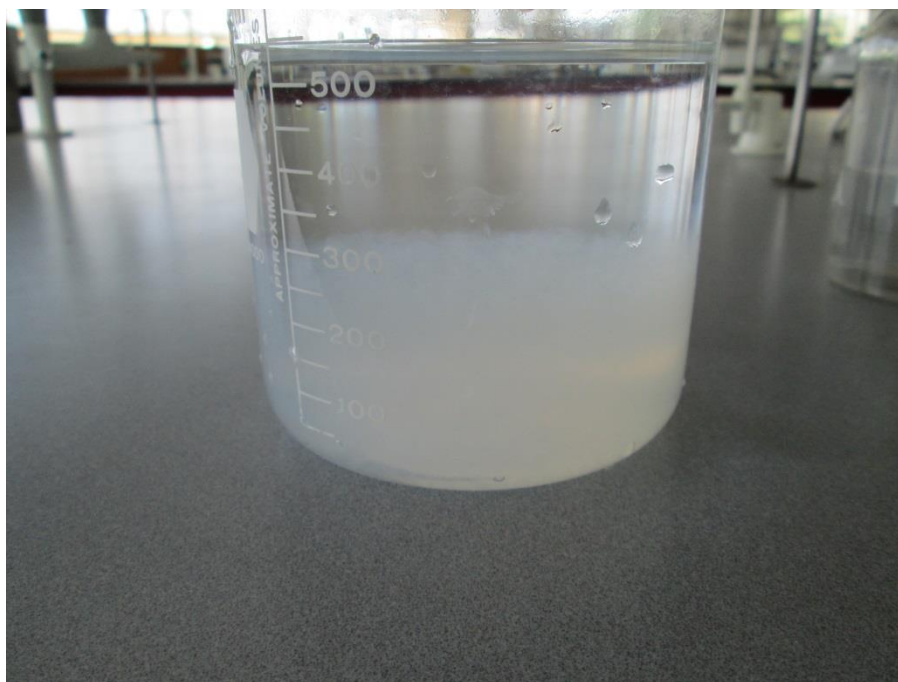


Figure 25: Gelatinous precipitate of aluminium hydroxide.

After drying overnight, the aluminium hydroxide was ground to the clean, white powder shown in Figure 26 below:



Figure 26: Dry aluminium hydroxide

The precipitated aluminium hydroxide has a large amount of water bound chemically into the structure. This is inefficient for transporting this material as a lot of the weight of the compound is unwanted water rather than the valuable aluminium oxide. To determine how much water could be easily removed, the aluminium hydroxide was split roughly into two small crucibles and heated for five hours in a furnace at 950°C. After cooling the samples were removed from the crucibles, seen in Figure 27, and weighed again to determine the mass loss. This ‘calcining’ step also serves to transform the aluminium hydroxide into aluminium oxide and is analogous to the Bayer Process for production of aluminium oxide.



Figure 27: Calcined aluminium hydroxide.

The previously soft, crumbly hydroxide was transformed into hard, crystalline material that was much more difficult to grind into powder than before the calcining step.

The cleaned and purified titanium dioxide was removed from the oven and a small amount taken for EDX. The rest was washed twice more with hot dilute sodium hydroxide and then dried in the oven overnight. The following morning it was removed, cooled and then crushed into a pure white, dense, free-flowing powder seen below in Figure 28.

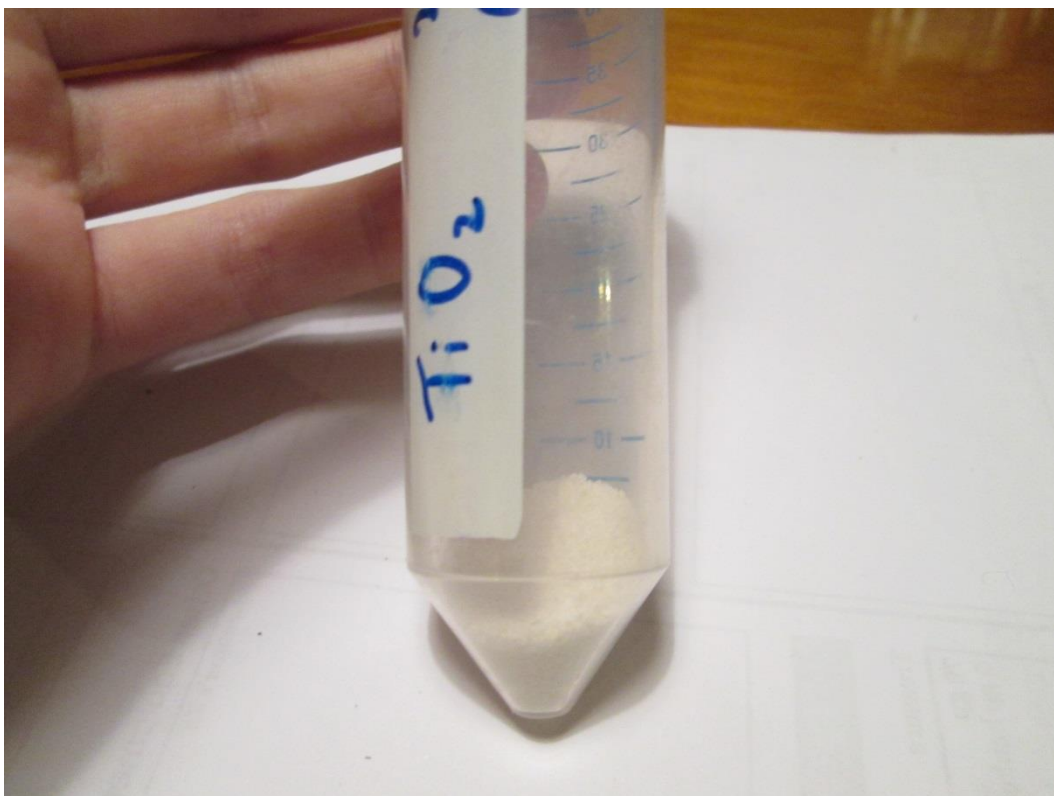


Figure 28: Purified titanium dioxide product.

Samples of all the products were set in resin, polished and prepared for SEM and EDX analysis. The residue, titanium dioxide and calcined aluminium hydroxide were also prepared for XRD analysis to investigate the crystal phase of the material.

3.4 Experimental Variant

Precipitation of the titanium dioxide from the acid leachate can be done with a weak base such as ammonia which will precipitate both aluminium and titanium at the same time or by adding a strong base such as sodium hydroxide. The advantage of using sodium hydroxide is that the precipitated aluminium will re-dissolve almost immediately and the product will not need to be cleaned of aluminium hydroxide. However a large amount of sodium hydroxide will be needed to neutralise the acid and the precipitated titanium oxide will contain large numbers of sodium ions trapped in the forming crystal structure, which is a major contaminant. This appears to manifest itself as a dark green colouration of the precipitate as seen in Figure 29:



Figure 29: Sodium contaminated precipitated titanium dioxide.

The precipitated product can be re-dissolved in acid if it is kept wet after filtering. Dissolving in the minimum amount of strongly diluted acid (~1% w/w concentration is enough to swing the pH very low) and then re-precipitating with the minimum required ammonia to bring it to a pH of 9 greatly reduces the contamination as shown in Figure 30.

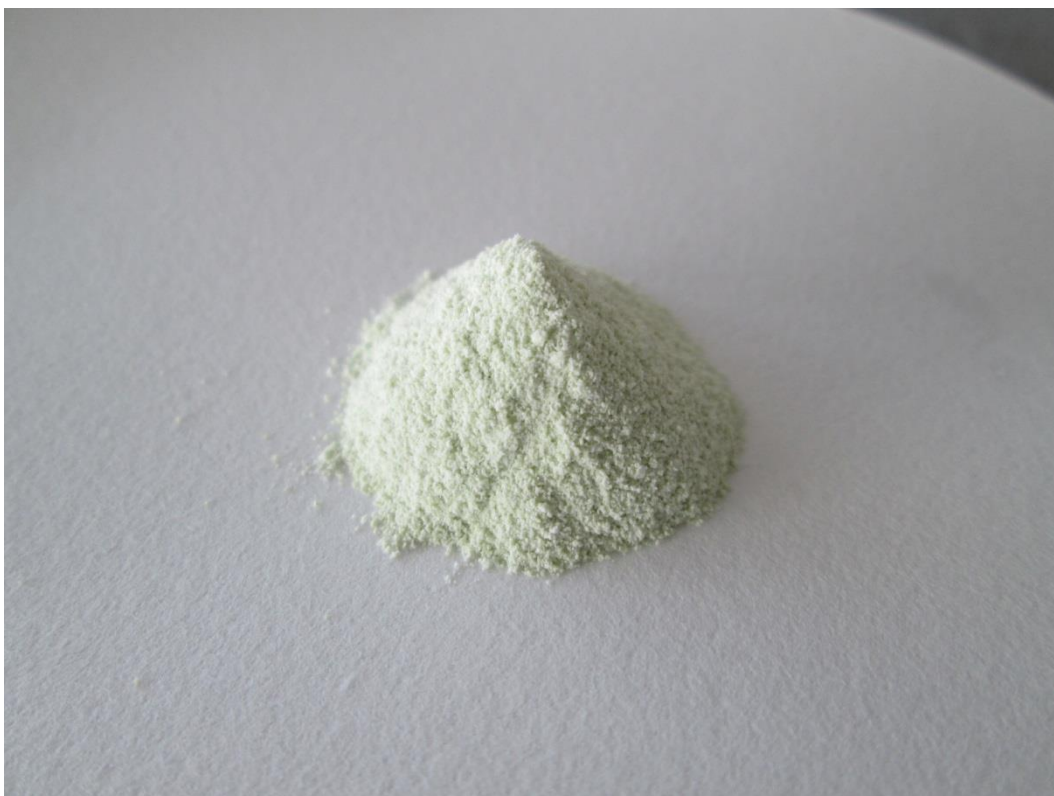


Figure 30: Titanium dioxide after being re-dissolved and re-precipitated.

The green colour is still present although much less pronounced after only a single cleaning step. Repetition of this step reduces the colour even further, though with diminishing returns.

It appears a choice must be made: do the initial precipitation with ammonia and then clean the product of aluminium hydroxide or precipitate with a strong base like sodium hydroxide and clean the product of sodium ions.

CHAPTER FOUR

RESULTS AND DISCUSSION



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Chapter 4: Results and Discussion

In order to properly ascertain the effectiveness of the chemical treatment process of the by-product the yield of titanium dioxide and aluminium compounds must be calculated. The purity of the products must also be determined in order to gauge whether the experimental method is effective in separating the compounds from each other.

Scanning Electron Microscopy allows great magnification of samples and inspection of the physical structure of the material. While in the electron microscope, Energy Dispersive X-ray spectroscopy can also be carried out. This method allows extremely accurate determination of the chemical elements present in both weight and atom percentage, very useful for identifying the purity of a sample and also for detecting contaminants even if they are present at very low levels. Although EDX allows for chemical analysis it does not reveal the structure of a material or its crystal phase to be determined. The titanium dioxide, calcined aluminium oxide and leaching residue will also be subjected to X-ray Diffraction to ascertain the structural phase that the samples possess.

4.1 Analysis of Aluminium Compounds

Although the principle goal of the research was to recover titanium dioxide from the waste by-product of the TiPro process, a significant proportion of the material is aluminium oxide and if this can be recovered at low cost or even as a side effect of recovering the titanium without undue difficulty then this is a valuable additional bonus to the treatment process.

4.1.1 Aluminium Oxide

The precipitated and calcined aluminium oxide was set in epoxy resin and polished to give a smooth surface for SEM/EDX. An image of the physical structure is shown below in Figure 31:

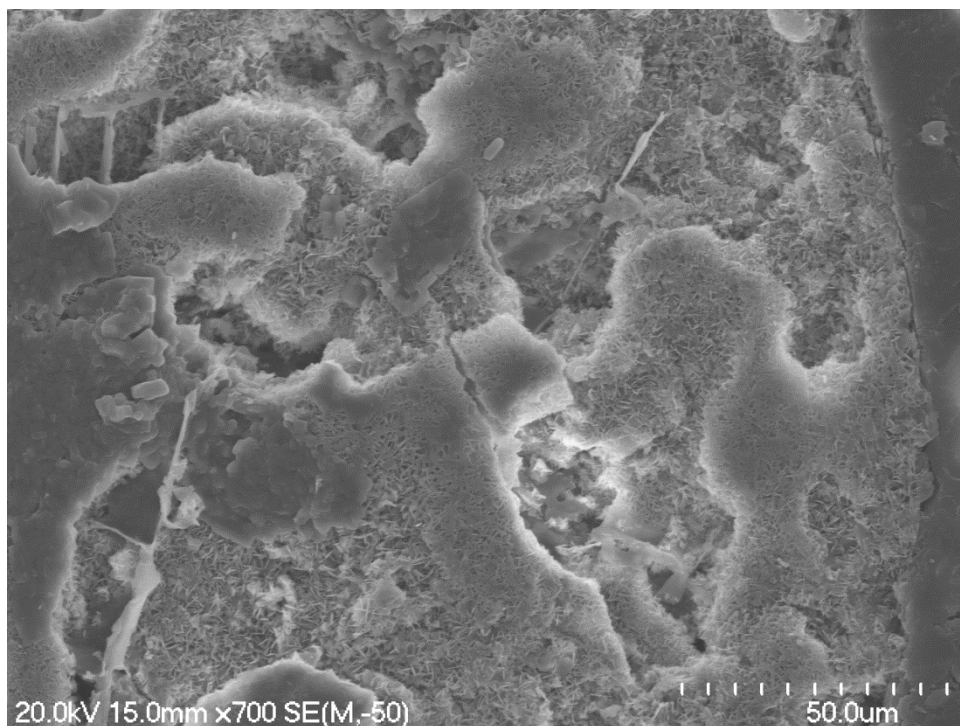


Figure 31: SEM image of aluminium oxide.

The SEM image shows elongated needle-shaped crystals of material randomly orientated making up the bulk of the sample. The crystal shape is likely an artefact of the strong heating the material was subjected to in the drying process.

The EDX elemental analysis results were encouraging and they are tabulated below in Table 3 as well as the raw spectrum obtained shown in Figure 32.

Element	Weight %	Error $\pm\%$	Atomic %	Error $\pm\%$	Cumulative Weight %	Cumulative Atom %
Aluminium	45.26	0.35	35.94	0.28	45.26	35.94
Oxygen	39.25	0.71	52.55	0.96	84.51	88.49
Chlorine	7.45	0.26	4.50	0.16	91.96	92.99
Sodium	5.41	0.15	5.04	0.14	97.37	98.03
Silicon	2.27	0.24	1.73	0.19	99.64	99.76
Sulphur	0.36	0.36	0.24	0.07	100.00	100.00

Table 3: Elemental analysis of the aluminium oxide

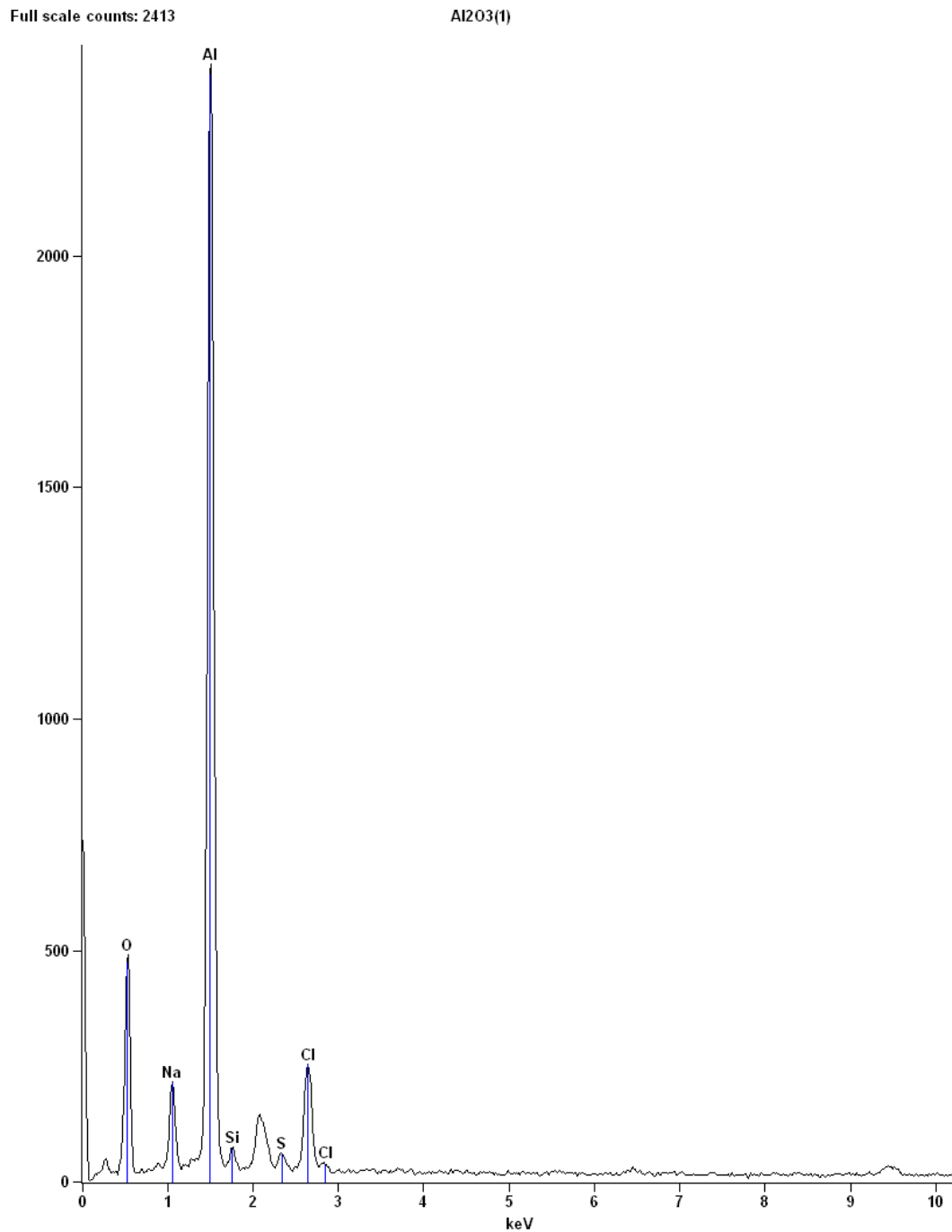


Figure 32: EDX spectrum of the aluminium oxide

The results show that the calcined Al₂O₃ was 84.51% pure by weight and 88.49% pure by atom in the desired aluminium oxide. The principle contaminants are sodium and chlorine, likely introduced during the re-precipitation step as hydrochloric acid and sodium hydroxide were used to swing the pH. The other

main contaminant is silicon which could possibly have come from the action of hydrofluoric acid attacking the glassware that the acid leaching was carried out in. This is an important point and can be easily solved by using plastic beakers and flasks to prevent this from happening. The last detected element is sulphur, probably from the sulphuric acid used in the leaching stage.

The XRD analysis of the Al_2O_3 was carried out soon after the SEM/EDX and the trace spectrum is shown below in Figure 33:

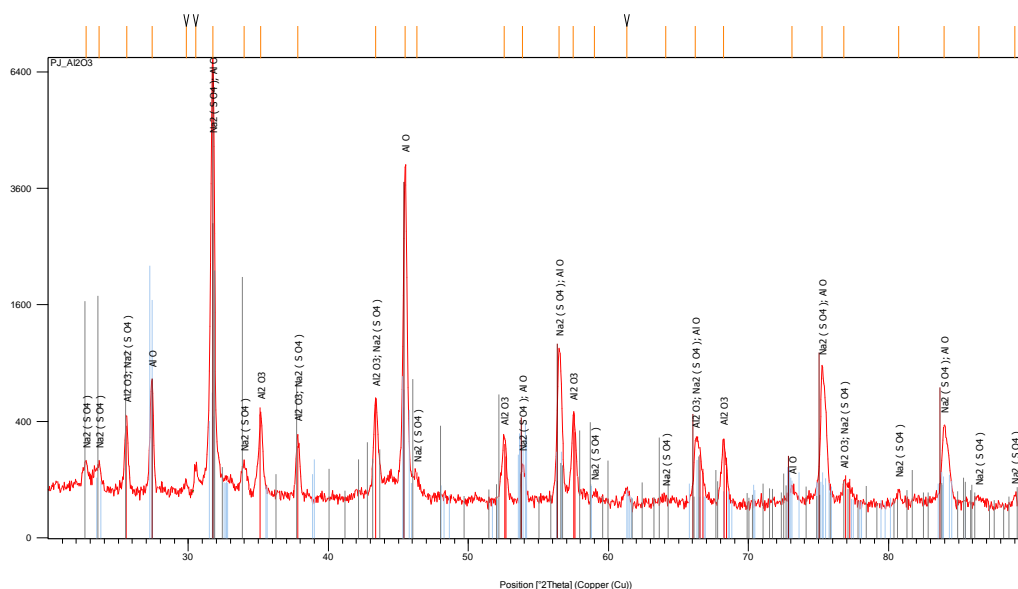


Figure 33: XRD spectrum of the aluminium oxide

The XRD software identified likely materials present by matching the obtained spectrum against a library of spectra of known materials. It identified the presence of AlO , Al_2O_3 and possibly NaSO_4 . Judging from this it is likely that the contaminants disrupted the crystal structure of the forming Al_2O_3 by substituting themselves and led to the somewhat confused spectrum. It is highly unlikely that AlO (aluminium II oxide) is present as it is very unstable at room temperatures.

4.1.2 Residue

After the acid leaching stage there was a considerable amount of fine, grey powder remaining undissolved in the flask. Initially there was some confusion about the nature of this substance as theoretically everything in the TiPro by-product should be soluble in acid, especially hydrofluoric acid. Its appearance and texture was a fine, crumbly, grey powder shown below in Figure 34.



Figure 34: Residue powder after leaching.

Analysis by SEM revealed the composition of the material to be mainly aluminium and oxygen with small amounts of titanium and silicon. The weight composition and EDX results are shown below in Table 4 and Figure 35.

Element	Weight %	±% Error	Atom %	±% Error
Aluminium	54.88	0.48	43.46	0.38
Titanium	1.88	0.23	0.84	0.10
Oxygen	39.68	0.76	52.99	1.02
Silicon	3.56	0.43	2.70	0.32

Table 4: Elemental analysis of residue.

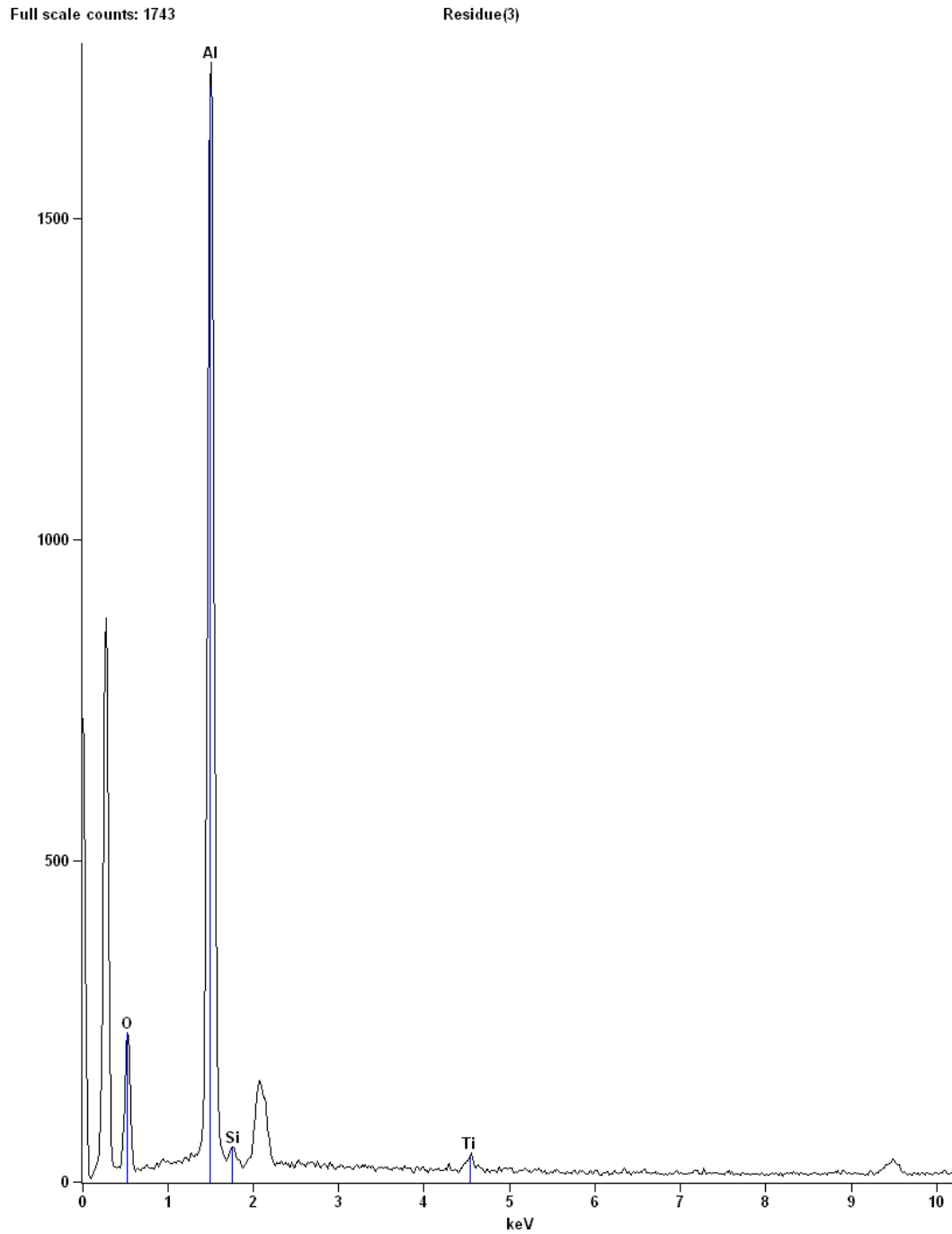


Figure 35: EDX spectrum of residue.

This result suggests that the material is aluminium oxide; the correct weight ratio of aluminium to oxygen in pure aluminium oxide is approximately **53% Al : 47% O**, a close match to the recorded values from the EDX. However alumina should dissolve in hot hydrofluoric acid and this did not. To resolve this, the substance was examined by XRD and the result is shown below in Figure 36.

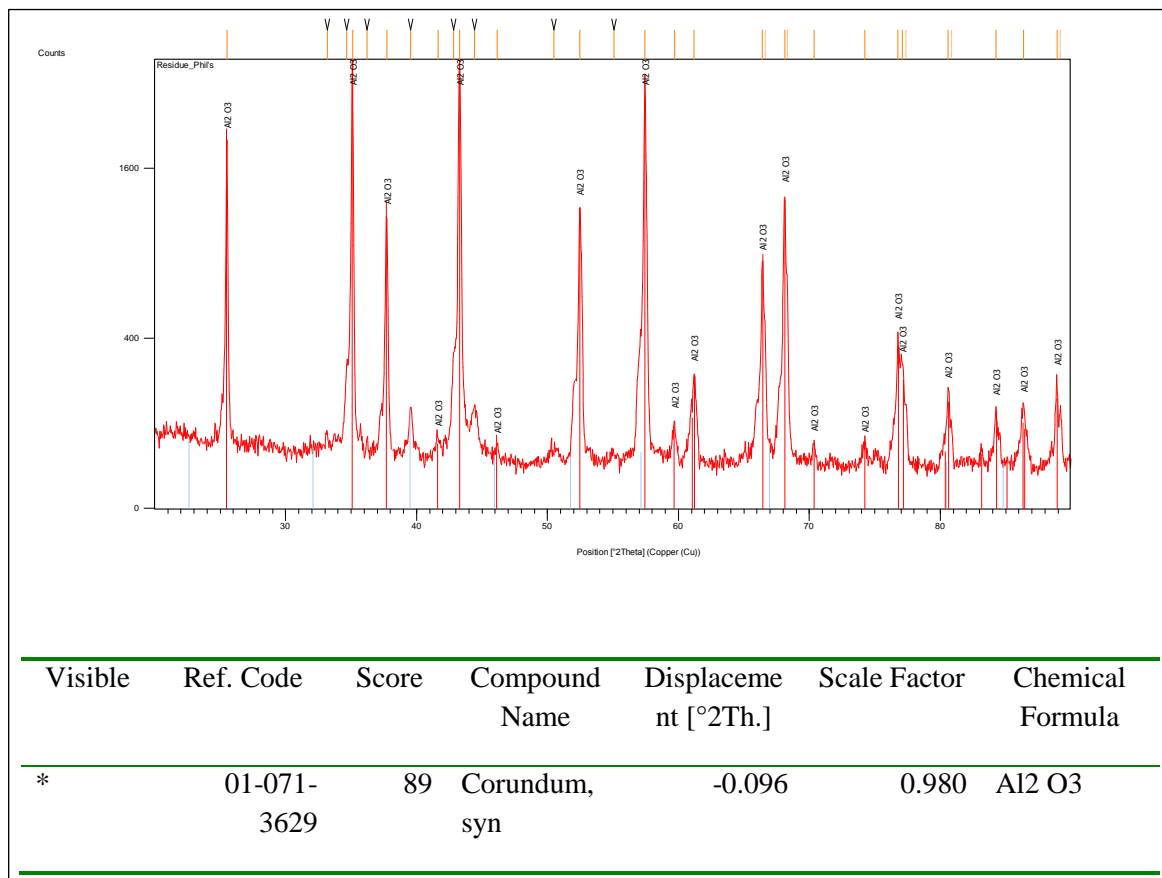


Figure 36: Spectrum and results of XRD of residue.

The XRD identified the material as corundum phase alumina which is known to be extremely slow to chemically interact with anything other than concentrated, hot acids and very high temperature strong, dilute alkali. While interesting, it has little bearing on the utility of the material as it is very low in titanium.

Any titanium present is likely to have been trapped within the crystal structure and only revealed when cut and polished for the EDX; any surface titanium will have been dissolved by the acid leaching. Small amounts of silicon in the material are likely again to have been caused by the interaction of hydrofluoric acid with the glassware used during the experiment.

4.2 Analysis of the Titanium Product

The target of the process was the recovery of titanium in dioxide form of sufficient purity to at least be a good proof of concept. In this regard a recovery of 85% or more would be desirable and contamination would have to be below 5% in order to be reused in the TiPro method, an improbably optimistic outcome. A more likely result would be up to 10-20% of the product would be impurity compounds that resist further purification under the mild reaction conditions used. Tweaking of the recovery process in later studies would perhaps achieve higher purities but short of actually carrying out the Sulfate or Chloride processes which actually produce commercial grade titanium dioxide this work would likely not achieve such purities.

In the end the results from the elemental analysis are encouraging and are shown below in Table 5 and Figure 37:

Element	Weight %	±% Error	Atom %	±% Error
Aluminium	14.09	0.17	13.35	0.16
Titanium	43.64	0.54	23.30	0.29
Oxygen	36.84	1.27	58.90	2.03
Silicon	1.65	0.20	1.50	0.18
Vanadium	0.27	0.22	0.15	0.11
Sulphur	3.51	0.13	2.80	0.10

Table 5: Elemental analysis of recovered titanium dioxide.

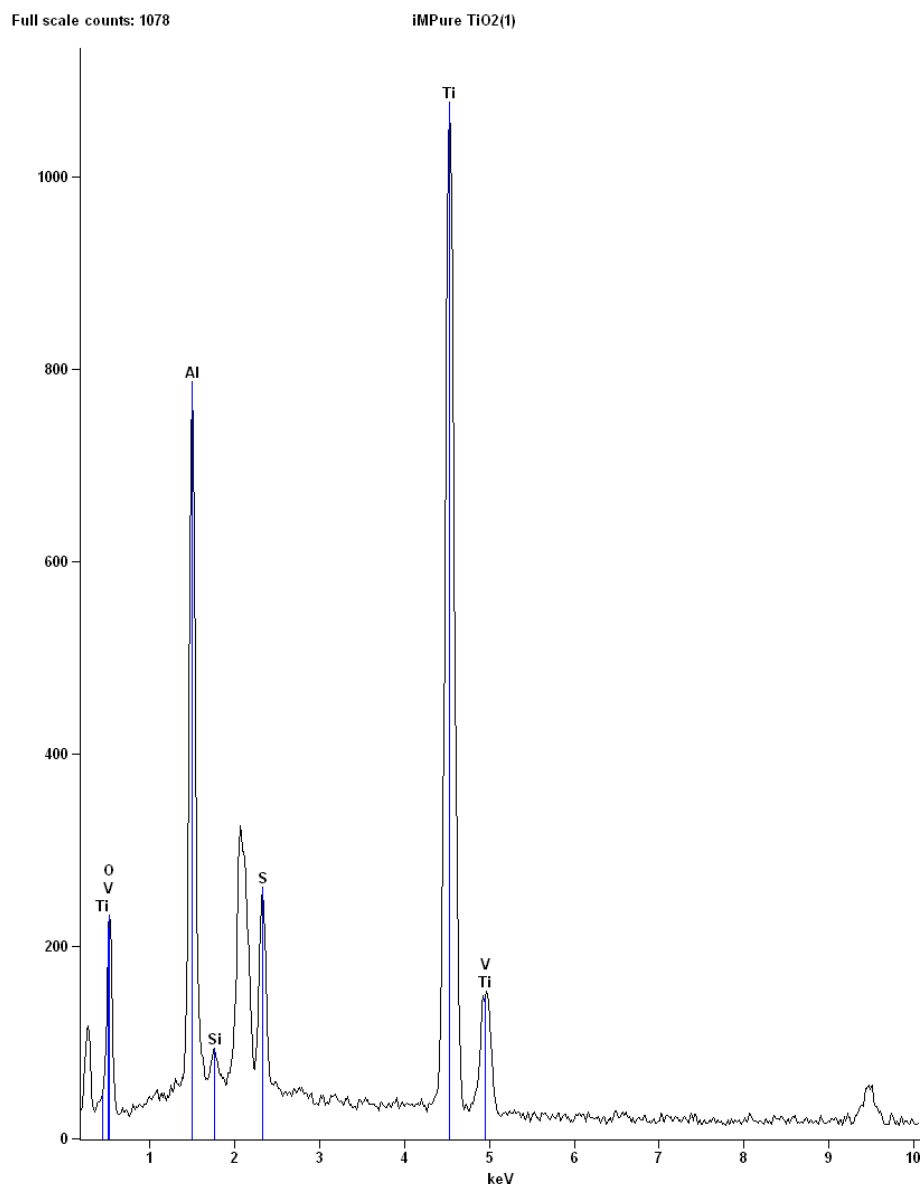


Figure 37: EDX spectrum of recovered titanium dioxide.

Pure titanium dioxide is 60% by weight titanium and the balance oxygen; the recovered product is calculated at 72.7% 'pure' as a measure of deviation from the pure substance. The main impurity is aluminium as expected, likely trapped inside the titanium dioxide grains and thus shielded from being dissolved by the sodium hydroxide washes that would have dissolved it. An SEM image of the physical appearance is shown in Figure 38.

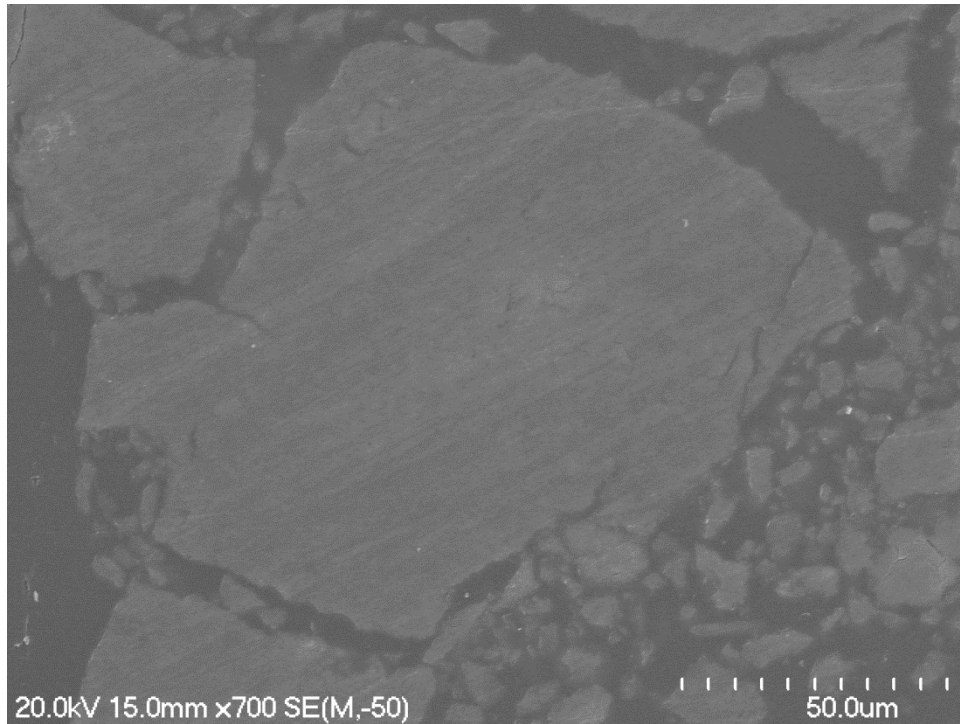


Figure 38: SEM image of recovered titanium dioxide grain.

The SEM shows a fairly uniform, amorphous appearance of the titanium dioxide product which confirms the intimate nature of the aluminium hydroxide mixed in with the titanium dioxide. It is likely in hydroxide form as the product was not calcined, it is also likely that the product therefore contains chemically bound water which also lowers its apparent purity and probably disrupts XRD analysis.

A follow-up XRD study of the sample produced a confused, messy spectrum due to the mixing of aluminium with the titanium; the product was not sufficiently pure and crystalline for the XRD to properly identify the phases present in the sample and inclusion of chemically bound water molecules would also not help. Repeating the XRD of the sample to confirm produced the same results. However the spectrum obtained is shown in Figure 39.

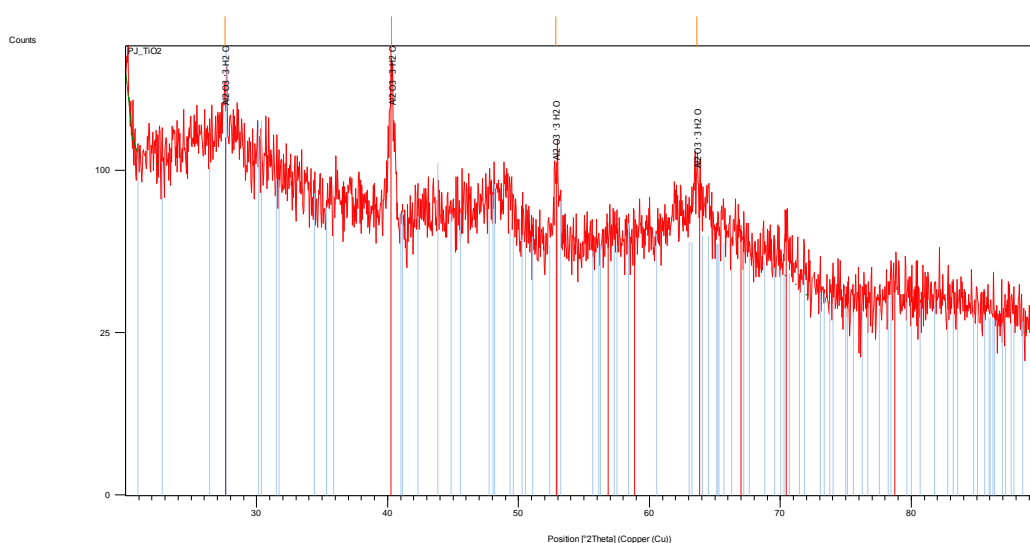


Figure 39: XRD result of aluminium contaminated titanium dioxide product.

The XRD identified a few peaks associated with aluminium hydroxide but peaks associated with titanium oxide were not sufficiently distinguishable to be certain that the software could identify them.

4.3 Quantitative Analysis

The masses of the products and the starting material need to be tabulated and the individual elements tracked in order to determine yields. Only the aluminium and titanium is of importance as oxygen atoms generally make the balance as both the oxide of the products and the impurities as shown in Table 6. The overall mass of the products exceeds that of the starting material due to oxidation of the titanium and introduction of impurities.

Corundum starting material – 10 grams

	Ti	O	Al	Impurities
Weight %	28.39	27.20	43.28	1.130
Mass (g)	2.839	2.720	4.328	0.113

Residue – 3.51 grams

	Ti	O	Al	Impurities
Weight %	1.89	39.68	54.88	3.55
Mass (g)	0.07	1.43	1.97	0.13

Aluminium Oxide - 4.70 grams starting, 2.91 grams after calcining

	Ti	O	Al	Impurities
Weight %	0.00	39.25	45.26	15.49
Mass (g)	0.00	1.14	1.31	0.45

Titanium dioxide product – 6.01 grams

	Ti	O	Al	Impurities
Weight %	43.64	36.84	14.09	5.43
Mass (g)	2.62	2.21	0.84	0.21

Table 6: Mass accounting of titanium, oxygen and aluminium.

4.3.1 Aluminium

	<u>Weight (g)</u>	<u>Cumulative weight (g)</u>
Residue	1.97	1.97
Aluminium oxide product	1.31	3.28
Titanium oxide product	0.84	4.12

Table 7: Aluminium mass accounting.

Out of a total starting mass of 4.328 grams of aluminium, 3.28 grams were recovered in desired products, the aluminium oxide and the residue. This gives a ‘recovery’ of **75.8%**. A further 0.84 grams of aluminium was in the titanium dioxide product as an impurity, giving a total account of aluminium of 4.12 grams; **95.2%** of the starting mass of aluminium.

The material experienced a **38.1%** mass loss during calcining, indicating the very high water content of the aluminium hydroxide prior to this step.

4.3.2 Titanium

	<u>Weight (g)</u>	<u>Cumulative weight (g)</u>
Residue	0.07	0.07
Aluminium oxide product	0.00	0.07
Titanium oxide product	2.62	2.69

Table 8: Titanium mass accounting.

The initial starting mass of titanium was 2.839 grams and of this initial mass 2.62 grams was recovered in the desired product, giving a recovery yield of **92.3%**. A small amount, 0.07g was present in the residue giving a total mass account of the titanium of **94.7%** of the initial starting mass of titanium.

The missing material from the results, small quantities of aluminium and titanium, are unaccounted for as some losses occur during the processing in the form of 'lab losses'. This is caused by small amounts of material being left in the bottom of flasks, on spatulas or retained on filter papers. 5%-10% loss is not unusual and can be even higher when working with small amounts of material. 0.1g of a product retained on a filter paper is, in percentage terms, a larger loss when dealing with 1g of material (10%) than when working with 10g of material (1%).

On a larger scale, especially with continuous processes rather than batch operations, losses become smaller still and with sufficient attention to detail and care can become negligible.

4.3.3 Waste

The waste water from the treatment contained sulphate ions, ammonium ions and/or ammonia, sodium ions and small amounts of fluoride ions. When pH corrected to neutral this waste water is highly dilute and contains no toxic metals, no organic compounds or harmful chemical species and thus can be disposed of with minimal difficulty.

CHAPTER FIVE

CONCLUSIONS AND FURTHER STUDIES



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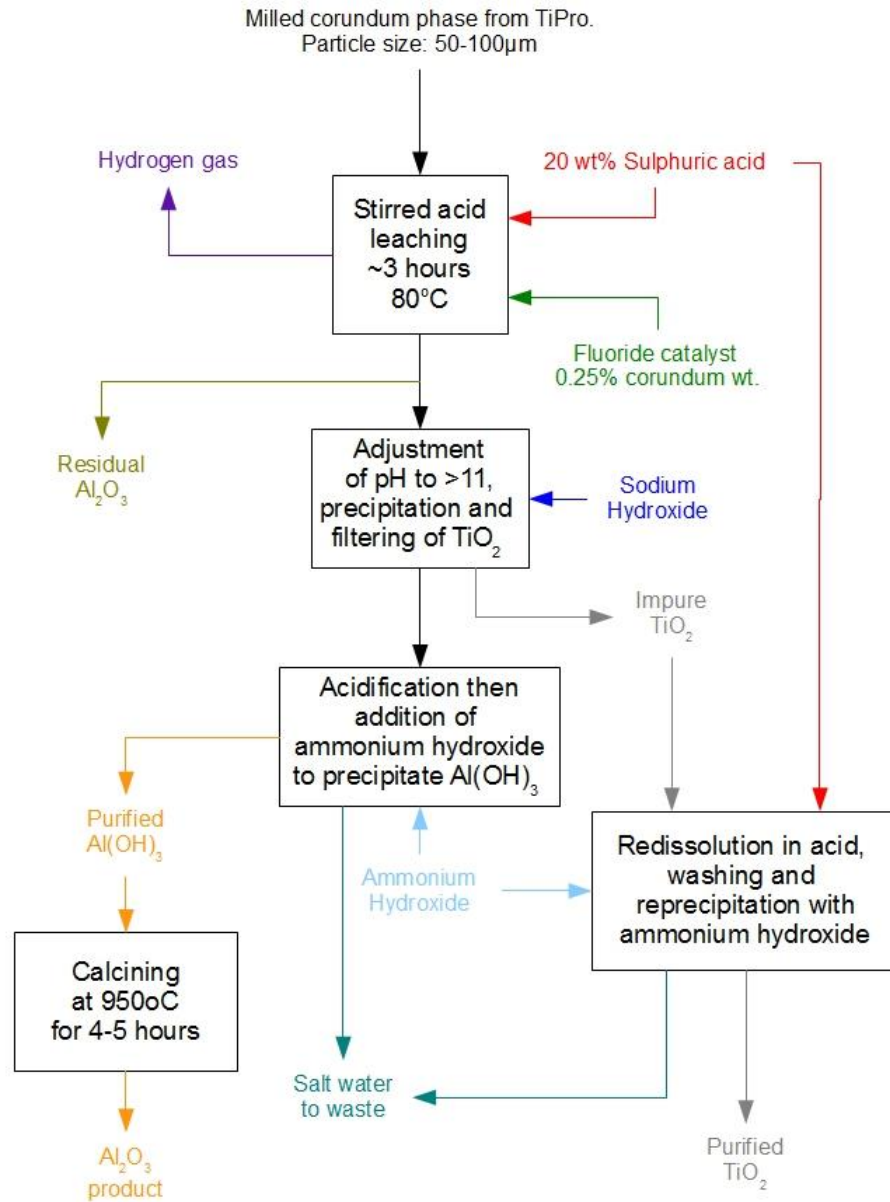
Chapter 5: Conclusions and Further Studies

5.1 Conclusions

The purpose of this proof-of-concept research was to ascertain whether or not the by-product from the aluminothermic reaction of the TiPro method of producing titanium aluminide alloys could be treated to produce titanium dioxide of sufficient purity with simple chemicals and mild conditions such that it could be recycled. While this was not achieved the research showed that it is at least possible in theory and the general approach shows promise sufficient to warrant further investigation. A process flow diagram of the overall procedure is shown in Figure 40. The general conclusions drawn from this work are as follows:

- The by-product was treated using simple chemicals that are readily available in bulk to ‘upgrade’ the titanium content of the material from 28.39% w/w to 43.64% w/w, an relative increase of 53.7% with excellent efficiency and yields.
- Separation of aluminium compounds from titanium compounds was largely achieved. The aluminium oxide containing products totalled 6.42g of material with only 0.07g of titanium present, only 1.1% w/w.
- Predicted chemical behaviour of the by-product was largely accurate with the exception of the formation of corundum phase alumina residue.
- Over 90% of the mass of metals under investigation was accounted for and little was lost due to processing.

- The waste stream comprised environmentally benign chemical species that were heavily diluted.



Corundum treatment and titanium dioxide recovery process flow diagram

Philip Jennings 2013

Figure 40: Process flow diagram of the treatment carried out.

5.2 Further Studies

- One possibility is to subject the corundum by-product of the TiPro process to Bayer conditions (30% sodium hydroxide aqueous solution, 275°C and 130atm of pressure) in order to remove the aluminium oxide compounds directly in a single step. Theoretically speaking, the aluminium oxide present should dissolve (even the corundum phase aluminium oxide that was resistant to the acid leaching) and leave behind the titanium compounds as titanium oxide. TiO_2 is not soluble in dilute alkali but under such extreme conditions its behaviour may not be so easily predicted. This suggestion is made as in the normal Bayer process, bauxite is separated from the principle contaminant (iron) by exploiting this relationship. The ‘red mud’ waste of the Bayer process is principally iron oxide. Titanium should display similar behaviour. Equipment to test this idea was not available to the student during this investigation.
- Using less concentrated acid at the leaching phase would reduce the needed amounts of alkali and so limit the impurities introduced. Using an organic base, such as piperidine or other amines, may also neutralise the acid without introducing soluble ions. The organic compounds may be reused after neutralisation.
- Treating larger quantities of by-product may reduce the levels of contamination due to the lower impact of percentage based effects such as lab losses.