Techno-economic evaluation of demilitarized $TiCl_4$ recycling processes

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ABSTRACT

Demilitarization has become a critical field of study in South Africa over the last decade. With the focus of reusing or recycling all components with potential values, hazardous environmental impacts can be drastically reduced or even eliminated. The aim of this study was to analyse potential recycling solutions of demilitarized titanium tetrachloride ($TiCl_4$), which had been obtained by the preceding demilitarization of smoke mortars. The demilitarized $TiCl_4$ was quantified to be approximately 42 ton, distributed into smaller batches and processed over a period of six years. This analysis was performed by means of a detailed techno-economic evaluation. The three main potential recycling considerations were titanium (Ti) sponge production, titanium dioxide (TiO_2) pigment production and a vaporization process to obtain $TiCl_4$ that can be reused in the manufacturing of new smoke mortars.

Prior to process configuration, received samples of demilitarized $TiCl_4$ were analysed to identify and quantify common impurities and determine initial feed quality from the demilitarization stock. These processes were then simulated on Aspen Plus^{TM} as part of the technical assessment. Ti sponge was produced by implementation of the Kroll process while TiO_2 pigment was produced through the chloride process and reusable $TiCl_4$ was obtained by a two-step boiling process of demilitarized $TiCl_4$. Simulation results indicate that all three processes are technically executable and correspond with independent theoretical calculations. Verification of both sets of results with existing stipulations indicates that produced sponge and pigment conform to the American Society of Testing and Materials (ASTM) standards and recovered $TiCl_4$ complies with industrial requirements for mortar manufacturing applications.

Simulation results were then implemented to construct an economic model of the pre-treatment and production part of each option. The various potential incomes based on applicable product values and quantities were integrated into this part of the assessment. Present costs of operating units were determined using applicable design equations that incorporated specific process values. These resulting values were then used to calculate capital expenditure (CAPEX), while operating expenditure (OPEX) was based on relevant feed material and utility costs. Final profitability was indicated by subsequent payback period (PBP), internal rate of return (IRR) and return on investment (ROI) values.

Results show that Ti sponge production offers the largest operating profits but becomes entirely unfeasible due to the substantial initial capital investment required. A similar conclusion is deduced for TiO_2 pigment. Both these processes had PBP's that far exceeded the six-year focus period. The financial unfeasibility of these options are highlighted by the negative IRR and ROI values. In contrast, the third considered process of reusing 99% pure $TiCl_4$ in new smoke mortars, proves to be superior with regard to comparison results. Furthermore, profitability determinations return positive values.

This option was firstly analysed for a general perspective that was based on common product values. For the second perspective, this model was constructed based on South African market values at the time of this study. The value of $TiCl_4$ is significantly higher in local markets. Results of both outlooks display PBP's of less than half the focus period and IRR and ROI percentages that are expected to be favourable in any market. Based on these results, it is viable to conclude that this process serves as an appropriate solution to the supplied problem statement.

Improved operating parameters of the identified solution were established by performing sensitivity analyses. These improvements can aid in plant designs and development of this process in future studies and applications. An additional comparison of findings with options that are not deemed to be recycling processes reaffirm the favourable profitability of the deduced solution.

Demilitarized $TiCl_4$ can therefore effectively be recycled and reused in new smoke mortars at a financial gain. Implementation of this solution additionally provides an alternative to harmful environmental impacts of disposal, incineration or destruction.

Keywords: Demilitarize, titanium tetrachloride, $TiCl_4$, techno-economic, smoke mortar, titanium

OPSOMMING

Demilitarisering het ŉ kritiese studieveld geword in Suid-Afrika oor die afgelope dekade. Met die fokus om alle komponente wat moontlik van waarde mag wees te hergebruik of te herwin, kan nadelige gevolge op die omgewing verminder of selfs uitgeskakel word. Die doel van hierdie studie was om potensiële herwinningsoplossings van gedemilitariseerde titaantetrachloried ($TiCl_4$) te analiseer. Hierdie chemikalieë is verkry deur die voorafgaande demilitarisering van rookmortiere. Die hoeveelheid gedemilitariseerde $TiCl_4$ is gekwantifiseer as ongeveer 42 ton, wat in kleiner hoeveelhede verdeel is en oor ŉ tydperk van ses jaar geprosesseer word. Hierdie analise is uitgevoer deur middel van ŉ sorgvuldige tegno-ekonomiese evaluering. Die drie oorhoofse herwinningsoorwegings is titaanspons (Ti) produsering, titaandioksied-pigement (TiO_2) produsering en ŉ verdampingsproses om $TiCl_4$ te verkry wat hergebruik kan word in die vervaardiging van nuwe rookmortiere.

Voordat prosesse uiteengesit kon word, is monsters van gedemilitariseerde $TiCl_4$ eers ontleed om die teenwoordigheid van algemene onsuiwerhede in die gedemilitariseerde voorraad te identifiseer en te kwantifiseer. Daarmee saam is die $TiCl_4$ komposisie ook bepaal. Hierdie prosesse is gevolglik gesimuleer op Aspen Plus^{TM} as deel van die tegniese beoordeling. Ti-spons is deur die Kroll-proses geproduseer terwyl TiO_2-pigment deur middel van die chloriedproses vervaardig word. Herbruikbare $TiCl_4$ is verkry deur gedemilitariseerde $TiCl_4$ te kook deur middel van twee opeenvolgende stappe. Simuleringsresultate dui daarop dat al drie prosesse tegnies uitvoerbaar is. Verder stem hierdie resultate ook ooreen met onafhanklike teoretiese berekeninge van hierdie drie oorwegings. Verifiëring van beide stelle resultate bevestig dat geproduseerde Ti-spons en TiO_2-pigment ooreenstem met standaarde van die Amerikaanse Vereniging vir Toetsing en Materiale, terwyl herbruikbare $TiCl_4$ voldoen aan industriële mortiervervaardiging-vereistes.

ŉ Ekonomiese model is daarna ontwikkel met betrekking tot die voorbereiding- en produksiestappe van elke proses. Data is gebaseer op simulasie-resultate. Potensiële inkomstes is bereken vir die relevante materiaalwaardes en hoeveelhede. Huidige kostes van elke proses-eenheid is bereken deur middel van verwante ontwerpsvergelykings wat spesifieke prosesveranderlikes as insetwaardes ontvang. Berekende resultate is gebruik om kapitaaluitgawes en bedryfsuitgawes te bepaal. Die winsgewendheid van elke oplossing word gevolglik aangedui deur individuele terugbetalingstydperke, interne opbrengskoerse en opbrengste op beleggings.

Resultate dui daarop dat die opsie om Ti-spons te produseer die voordeligste bedryfswinste lewer, maar met die inagneming van aanvanklike kapitaalvereistes word hierdie proses as nielewensvatbaar beskou. Soortgelyke bevindings is ook van toepassing op die proses waarvolgens TiO_2-pigment geproduseer word. Beide moontlikhede het terugbetalingstydperke wat die begrotingsperiode van ses jaar ver oorskry. Finansiële ontoepaslikheid van hierdie opsies word verder beklemtoon deur die negatiewe waardes vir interne opbrengskoerse en opbrengste op beleggings. Daarteenoor toon vergelykte resultate van die derde proses-oorweging om $TiCl_4$ te hergebruik in nuwe rookmortiere dat hierdie proses beslis die beste opsie is. Tesame met oortreffende vergelykingsresultate van proses-winsgewendheid, is hierdie berekende bepalings ook positief van aard.

Hierdie opsie is eerstens oorweeg en weergegee in die konteks van algemene markte en produkwaardes. Die tweede oorweging het meer gefokus op die toepaslikheid van hierdie proses op die Suid-Afrikaanse mark gedurende die tydperk van hierdie studie. Die markwaarde van $TiCl_4$ is aansienlik hoër in die plaaslike industrie. Resultate van beide perspektiewe toon positiewe interne opbrengskoerse en opbrengste op beleggings wat as gunstig beskou sal word in talle oorwegings. Verder is die terugbetalingstydperke in beide gevalle minder as die helfte van die begrotingsperiode. Dit is dus geldig om die gevolgtrekking te maak dat hierdie proses as ŉ gepaste oplossing tot die probleemstelling beskou kan word.

Meer voordelige bedryfstoestande vir hierdie oplossing is bepaal deur middel van sensitiwiteitsanalises. Hierdie verbeterige sal gunstig bydra tot proses-ontwerpe en -ontwikkelinge in toekomstige projekte. Ter wille van ŉ volledige finansiële assessering is bevindings vergelyk met alternatiewe moontlikhede wat nie as herwinningsprosesse geklassifiseer is nie. Hierdie resultate het die gunstige lewensvatbaarheid van die aangewysde oplossing bevestig.

Hergebruik van gedemilitariseerde $TiCl_4$ in nuwe rook mortiere is dus ŉ doeltreffende herwinningsmetode wat ook as ŉ waardevolle aanwins dien. Uitvoering van hierdie proses bied gevolglik ŉ uitkoms wat die negatiewe omgewingsimpakte van wegdoening, verbranding en vernietiging verhoed.

Sleutelterme: Demilitariseer, titaantetrachloried, $TiCl_4$, tegno-ekonomies, rookmortier, titaan

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS

AEGL:	Acute exposure guideline level
ASME:	American Society of Mechanical Engineers
ASTM:	American Society for Testing and Materials
AUD:	Australian Dollar
CAPEX:	Capital expenditure
CAS:	Chemical Abstracts Service
CEPCI:	Chemical Engineering Plant Cost Index
CP:	Commercially pure
CSIR:	Council for Scientific and Industrial Research
EPA:	Environmental Protection Agency
FCI:	Fixed-capital investment
HE:	High explosive
HETP:	Height equivalent to a theoretical plate
INR:	Indian Rupee
IRR:	Internal rate of return
KMML:	The Kerala Mineral & Metals Ltd.
N/A:	Not applicable
NR:	Not recommended
OPEX:	Operating expenditure
PBP:	Payback period
PFR:	Plug flow reactor
ROI:	Return on investment
WMO:	White mineral oil
U.S.:	United States
USD:	United States Dollar
ZAR:	South African Rand

NOMENCLATURE

Al:	Chemical element – Aluminium
$AlCl_3$:	Chemical compound – Aluminium chloride
Al_2O_3:	Chemical compound – Aluminium oxide
$AsCl_3$:	Chemical compound – Arsenic trichloride
$SbCl_3$:	Chemical compound – Antimony trichloride
C:	Chemical element – Carbon
CCl_4:	Chemical compound – Carbon tetrachloride
$C_{15}H_{16}O_2 \cdot C_3H_5ClO$:	Chemical compound – Bisphenol A-epichlorohydrin
$C_{10}H_{18}O_4$:	Chemical compound – 1,4-butanediol diglycidyl ether
Cl_2:	Chemical compound – Chlorine
Cu:	Chemical element – Copper
CuCl:	Chemical compound – Copper(I) chloride
$CuCl_2$:	Chemical compound – Copper(II) chloride
$Cu_2Cl(OH)_3$:	Chemical compound – Copper oxychloride
CuO:	Chemical compound – Copper(II) oxide
$Cu(OH)_2$:	Chemical compound – Copper(II) hydroxide
Fe:	Chemical element – Iron
$FeCl_2$:	Chemical compound –Iron(II) chloride
$FeCl_3$:	Chemical compound – Iron(III) chloride
HCl:	Chemical compound – Hydrochloric acid
H_2O:	Chemical compound – Water
H_2S:	Chemical compound – Hydrogen sulphide
H_2SO_4:	Chemical compound – Sulphuric acid
$K_2Cr_2O_7$:	Chemical compound – Potassium dichromate
Mg:	Chemical element – Magnesium
$MgCl_2$:	Chemical compound – Magnesium chloride

NaCl:	Chemical compound – Sodium chloride
NaOH:	Chemical compound – Sodium hydroxide
NH_4Cl:	Chemical compound – Ammonium chloride
NH_4VO_3:	Chemical compound – Ammonium metavanadate
O_2:	Chemical compound – Oxygen
$SiCl_4$:	Chemical compound – Silicon tetrachloride
Sn:	Chemical element – Tin
$SnCl_4$:	Chemical compound – Tin(IV) chloride
SO_4:	Chemical ion – Sulphate
Ti:	Chemical element – Titanium
$TiCl_4$:	Chemical compound – Titanium tetrachloride
TiO_2:	Chemical compound – Titanium dioxide
$TiO(OH)_2$:	Chemical compound – Metatitanic acid
V:	Chemical element – Vanadium
VCl_2:	Chemical compound – Vanadium(II) chloride
VCl_3:	Chemical compound – Vanadium(III) chloride
VCl_4:	Chemical compound – Vanadium tetrachloride
V_2O_5:	Chemical compound – Vanadium(V) oxide
VOCl:	Chemical compound – Vanadium oxide-chloride
$VOCl_2$:	Chemical compound – Vanadyl dichloride
$VOCl_3$:	Chemical compound – Vanadium oxytrichloride
ΔH:	Symbol – Change in enthalpy [kJ]
M_x:	Symbol – Molecular weight of component x [g/mol]
Btu:	Unit – British thermal unit
°C:	Unit – Degrees Celsius
cm:	Unit – Centimetre
gpm:	Unit – Gallons per minute (Imperial)

ft:	Unit – Feet
hr:	Unit – Hour
Hp:	Unit – Horsepower
K:	Unit – Kelvin
kg:	Unit – Kilogram
kJ:	Unit – Kilojoule
kW:	Unit – Kilowatt
kWh:	Unit – Kilowatt hour
L:	Unit – Litre
lbs:	Unit – Pound
m:	Unit – Metre
M:	Unit – Molar [mol/L]
µm:	Unit – Micrometre
mg:	Unit – Milligram
min:	Unit – Minute
mm:	Unit – Millimetre
mol:	Unit – Mole
mol%:	Unit – Mole percentage
MW:	Unit – Megawatt
ppm:	Unit – Parts per million
ton:	Unit – Tonne
tpa:	Unit – Tonnes per annum
wt%:	Unit – Weight percentage

CHAPTER 1: INTRODUCTION

1.1 Background

From the start of the 20th century chemical and technological advancements can be observed in just about every aspect of society. These advancements are almost always to increase profitability, enhance comfortability or improve the safety of the involved party. An example of the latter is the development of smoke mortars, which dates back to the First World War. These mortars were used during military operations to create a temporary smoke screen (see Figure 1-1) that obstructs the view of an enemy and hide the movements of troops or vehicles.

Figure 1-1: Smoke screen produced by smoke mortars

War is a very unpredictable phenomenon that every country's defence force has to be prepared for. It is thus essential for countries to have full arsenals of weapons and ammunition available in anticipation and defence from any external or internal attacks. A problem, however, is that ammunition and energetic material can become unreliable and unstable over time. Most manufacturers and producers of ammunition recommend a safe usage period to the ammunition that they supply. After this period, it is recommended not to use the ammunition for military applications and it is thus stored in magazines in various depots across the country. Ammunition that is declared unstable or unsafe are incinerated, destroyed or disposed of, depending on the chemical nature of each material and the environmental influence it holds. A new solution that is being developed and implemented is demilitarization of ammunition that exceeds its safe usage period. This entails the breaking down of ammunition into its various raw components.

The necessity to demilitarize old ammunition is not unique to a certain party or country. It was also not just applicable at the time this study was conducted, but can be implemented in the foreseeable future.

When the focus is placed on recent military activities on a global scale, it can be seen that of the 163 countries in the world, 138 countries have not been directly involved in a full-scale war since the start of the 21st century. Ray (2017) states that there have been eight major wars in this time, with 25 countries directly involved (see Table 1-1).

Table 1-1: Wars of the 21st century and the countries involved (Ray, 2017)

War	Countries involved
Second Congo War	Democratic Republic of the Congo, Angola, Namibia, Chad, Sudan, Zimbabwe, Burundi, Rwanda and Uganda
Syrian Civil War	Syria, Iraq, USA, Russia
Darfur Conflict	Sudan
Iraq War	Iraq, USA
Afghanistan War	Afghanistan, Pakistan, USA
The War against Boko Haram	Nigeria, Cameroon, Chad, Benin and Niger
Yemeni Civil War	Yemen, Saudi Arabia
Ukraine Conflict	Ukraine, Russia (unofficially)

South Africa has also not been at war since the conclusion of the South African Border War in 1989. The recommended safe usage period for the ammunition used by this country is only 10 to 20 years. The implication of the current situation is that some ammunition is stored longer than the recommended safe usage period and is thus ineffective or unreliable by the time of this study.

Various demilitarization processes have been researched, developed and implemented by the time of this study, but areas still occur where solutions and alternatives are required. As revealed in the first paragraph of this chapter, specific focus was placed on smoke mortars. Smoke mortars have an identical shell to High Explosive (HE) mortars, but are filled with titanium tetrachloride ($TiCl_4$) and have a light green shell for identification purposes (see Figure 1-2). $TiCl_4$ is a clear liquid and is contained in the area indicated by the white solid in Figure 1-2.

Figure 1-2: Colour of smoke mortars and $TiCl_4$ position

Upon impact the mortar would explode, resulting in the formation of a smoke burst. The smoke that forms is produced by the reaction of titanium tetrachloride with humid air according to Equation 1-1 (Kapias & Griffiths, 2005).

$$TiCl_4(l) + 3H_2O(v) \rightarrow TiO_2 \cdot H_2O \cdot 3HCl(s) + HCl(g) + \Delta H \qquad [1\text{-}1]$$

The opaque clouds of titanium-complex particles ($TiO_2 \cdot H_2O \cdot 3HCl$) and hydrochloric acid (HCl) are heavier than air and thus work effectively as smoke screens due to its tendency to remain at ground level.

A problem with smoke mortars, however, is that over time mortars will start to corrode on the inner walls due to small amounts of HCl that formed. This increases the risk of accidents and leakages during handling and firing procedures. As previously stated, energetic material in the primer also becomes unstable over time and increases the risks of using these mortars even further. Appropriate solutions are thus required, as the economic and environmental impacts of incineration, destruction and disposal are simply not sustainable.

Safe disassembly procedures for smoke mortars are being finalised by other studies, but a main issue that has not yet been addressed is the need to find a solution of what to do with $TiCl_4$ that is extracted from the demilitarized smoke mortars. It is currently considered as an economic and environmental waste and the need thus exists for it to be converted to an asset.

1.1.1 Demilitarized $TiCl_4$

$TiCl_4$ is removed during the demilitarization of smoke mortars. At the time of this study, no procedures have been implemented to recycle or reuse the demilitarized $TiCl_4$. Possible uses and recycling processes are stated in Section 1.1.2.

The main criteria for each recycling process are as follow:

- It must fall within environmental regulations
- It be as economically beneficial as possible
- The retained product must be of an acceptable quality.

An adequate technique to determine the best solution for such a scenario is to perform a techno-economic evaluation. The results of such an evaluation will indicate the most profitable and practical process, which is fundamental to the end user who will be implementing the process.

In order for recycling processes to operate on a continuous or uniform cycle, it is important that the quality and composition of the demilitarized $TiCl_4$ tend to be constant, as separation and purification processes are quite sensitive to these properties. Industrial grade $TiCl_4$ is used to fill the mortars during production and it thus creates the requirement to establish the quality and uniformity of the $TiCl_4$ after demilitarization

1.1.2 Possible uses of demilitarized $TiCl_4$

Various uses exist for $TiCl_4$ in the industry. However, the amounts required in these industrial processes ranges from minute to infinite volumes. All these respective processes are stated and discussed in the Literature Survey (Chapter 2).

For this study, large quantities of demilitarized $TiCl_4$ were available, but due to the intended purposes of mortars, future availabilities of demilitarized $TiCl_4$ are quite precarious. Because of these two factors, the focus of the study was narrowed down to processes that don't necessarily require fixed amounts of $TiCl_4$, but rather where production is directly proportional to the amount of unprocessed materials available. Three possible recycling processes were identified.

1.1.2.1 Titanium metal production

The first process to be considered was the use of demilitarized $TiCl_4$ in the production of pure titanium metal. $TiCl_4$ is a feed material in the original titanium metallurgical process. If the demilitarized $TiCl_4$ is of high enough quality, it should be possible to extract titanium metal without substantial purification expenses.

1.1.2.2 Titanium dioxide (TiO_2) pigment production

Secondly, demilitarized $TiCl_4$ can be used in the production of pigment titanium dioxide (TiO_2). TiO_2 has numerous uses in various fields of society. Due to its distinctive white natural colour, it is a common pigment in paint, food colouring and household items such as toothpaste and sun screen. Swiler (2005) states that pure TiO_2 is produced by oxidising titanium tetrachloride according to Equation 1-2. It should thus be possible to obtain the same result with demilitarized $TiCl_4$.

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2 \qquad [1\text{-}2]$$

1.1.2.3 Smoke mortars for military applications

The third possibility that was critically assessed was to remove any impurities in the demilitarized $TiCl_4$ and possibly reuse it in the production of new smoke mortars.

In order for recycling processes to operate on a continuous or uniform cycle, it is important that the quality and composition of the demilitarized $TiCl_4$ tend to be constant, as separation and purification processes are quite sensitive to these properties. It was thus necessary to establish the quality and uniformity of the $TiCl_4$ after demilitarization to determine if additional processes were required to deliver a more uniform feed material.

1.1.3 Background

During the time of this study, large quantities of smoke mortars were already stored away and needed to be demilitarized. The estimated amounts are given in Table 1-2.

Table 1-2: Smoke mortars to be demilitarized.

	60 mm Mortars	**81 mm Mortars**
Quantities	± 63 000	± 37 000
Amount of $TiCl_4$	255 – 275 g	640 – 660 g
Production Period	1964 - 1998	1970 - 1993

From Table 1-2 it can be calculated that for the current situation more than 40 ton $TiCl_4$ need to be demilitarized, with the average life span being far greater than 20 years. In circumstances where mortars are not used for other purposes than training and demonstrations, mortars requiring demilitarization will also be added annually.

1.2 Problem statement

About 100 000 mortars have exceeded their safe usage period and are no longer safe or effective for operation. These mortars are currently taking up storage space in depots and need to be demilitarized as soon as possible. Within the ± 100 000 mortars are more than 40 ton $TiCl_4$ that need to be recycled. Under current circumstances, it is predicted that an additional 1000 mortars that require demilitarization will be added annually, contributing an estimated mass of 400 kg $TiCl_4$. The focus of this study is to determine the most effective $TiCl_4$ recycling process with the best economic feasibility.

1.3 Objectives

The aim of this study is to analyse the possible recycling processes of demilitarized $TiCl_4$. To successfully complete this project, the following objectives had to be met:

- Determine the composition and uniformity of demilitarized $TiCl_4$.
- Conduct a technical evaluation by developing theoretical mass balances of identified processes and constructing flow sheets on Aspen Plus^{TM} simulation package.
- Confirm the consistency between these sets of values and verify that results conform to industrial standards.
- Calculate the capital expenditure (CAPEX) for each process.
- Calculate the operating expenditure (OPEX) for each process.
- Construct economic models to determine the profitability of each process. Relevant expenses avoided by the implementation of a process should be included to give an accurate representation of the financial implications.
- Perform sensitivity analyses on solutions that were identified to be profitable or potentially profitable in order to establish financially beneficial process conditions.
- Determine the most beneficial demilitarized $TiCl_4$ recycling process based on techno-economic evaluation results.

1.4 Method of investigation

A techno-economic evaluation of demilitarized $TiCl_4$ recycling processes consists of two individual evaluations (technical and economic) followed by a modelling process to relate the two evaluations.

The research methodology that was followed was to start by doing a critical literature survey on the processes that used $TiCl_4$ at the time of the study. The literature study was essential to establish previous work that had been done and to get a better perception of the limitations within this field. Processes that would be studied and evaluated were then identified. For the technical evaluation, information on technical evaluations done on these processes was collected. Areas that were focused on included process enhancements and new developments, existing product stipulations and design features and operating parameters of each process. For the economical evaluation, relevant information was garnered from economic evaluations that had been done on the identified processes. This included capital expenses (CAPEX), operating expenses (OPEX), feed material costs, *etc*.

After the literature study was concluded and all the necessary information was collected, the processes were firstly modelled theoretically, followed by simulations. This was done by constructing a flow sheet on the simulation package, Aspen Plus^{TM}. This simulation software can be used to determine the production rates of the processes at various operational conditions.

Secondly, an economic model was developed in Microsoft Excel©. The CAPEX and OPEX values of the processes were incorporated into the economic model.

Corresponding CAPEX and OPEX values for each process's operating conditions were obtained from relevant design equations and simulation results. Input and output values were determined from the simulations at the corresponding conditions. These values were then used in the economic results model to determine the most effective and economically feasible process. To conclude this project, process results from the economic evaluation and models were compared and the appropriate recycling solution was identified.

1.5 Limitations of the study

The limitations to this project are listed below:

- The actual demilitarization process of smoke mortars was not covered and the feed material for the recycling processes are thus $TiCl_4$ after demilitarization;
- The techno-economic evaluation was only done on the processes identified from the literature survey;
- Results from the economic model are highly dependent on unit prices, transportation costs, importation costs and market demands, which vary globally;
- Actual construction and physical testing of the proposed processes were not done for this project. However, a technical and economic evaluation was sufficient, less time-consuming and inexpensive to verify and validate the proposed recycling processes.

These limitations did not limit the quality and accuracy of the project.

1.6 Contributions of this study

The contributions of this project are listed below:

- Recycling demilitarized $TiCl_4$ (and demilitarization) will give a practical solution that prevents the environmental effects of disposal, incineration or destruction of these materials and chemicals;
- Results of this study will have advantageous economic and ethical implications to demilitarization studies and practices, as it determines how a financial and environmental waste can be converted into an asset.

These two contributions were the main incentives for this project as the environmental impacts of destruction, incineration and disposal cannot be condoned in modern times.

1.7 Summary

This chapter gave a general idea of what to expect in the content of this study and how this study can be implemented in practical scenarios. One can also see the extensive need on a global level for a solution to this project and the great benefits it holds for companies and the environment as a whole. Industrial processes that exist as possible recycling solutions are elaborated on more extensively in the following chapter.

CHAPTER 2: LITERATURE SURVEY

2.1 Introduction

The main focus of this chapter is an in-depth study on the various demilitarized titanium tetrachloride ($TiCl_4$) recycling processes to be considered. The chemical and physical properties of $TiCl_4$ are firstly studied to obtain a clear understanding of this compound. Numerous applications of $TiCl_4$ exist and several processes have been developed to deliver the required product for each application. These methods and its applicability to this study are discussed. Due to the reactive nature of $TiCl_4$ and the fact that it exists in conjunction with other elements in titanium-bearing ore, it is quite probable that impurities are present in the liquid $TiCl_4$. This is also expected for demilitarized $TiCl_4$, since it is imaginable that contaminants could have entered the liquid. Relevant $TiCl_4$ purification procedures that could be applicable in various circumstances are discussed and compared to some extent.

2.1.1 Structure of this study

The structure that was used in this study is graphically depicted in Figure 2-1. When decisions had to be made, attention was firstly given to the broad situation and then narrowed down to where an option was selected that was relevant to this particular study and its scope.

The initial focus was firstly placed on the diverse possible solutions to recycling demilitarized $TiCl_4$. After appropriate applications were identified, their various process alternatives were considered. The applicable production techniques or operating methods of each application were selected. These selections were then compared using a techno-economic evaluation to determine the most feasible option.

The initiative to initially focus on the broad possibilities and then narrow it down to a selection that was applicable to this process was firstly to ensure that a potentially optimal solution was not overlooked. The second reason was to enhance this study’s relevance to the demilitarization, recycling and $TiCl_4$ fields by informing the reader of the possible options, supplying a guideline to how a solution can be obtained and to enable the reader to identify an applicable process, even if it was not selected in this study. Nonetheless, the primary focus of this study was to evaluate the possible solutions that were applicable to the problem statement of this study.

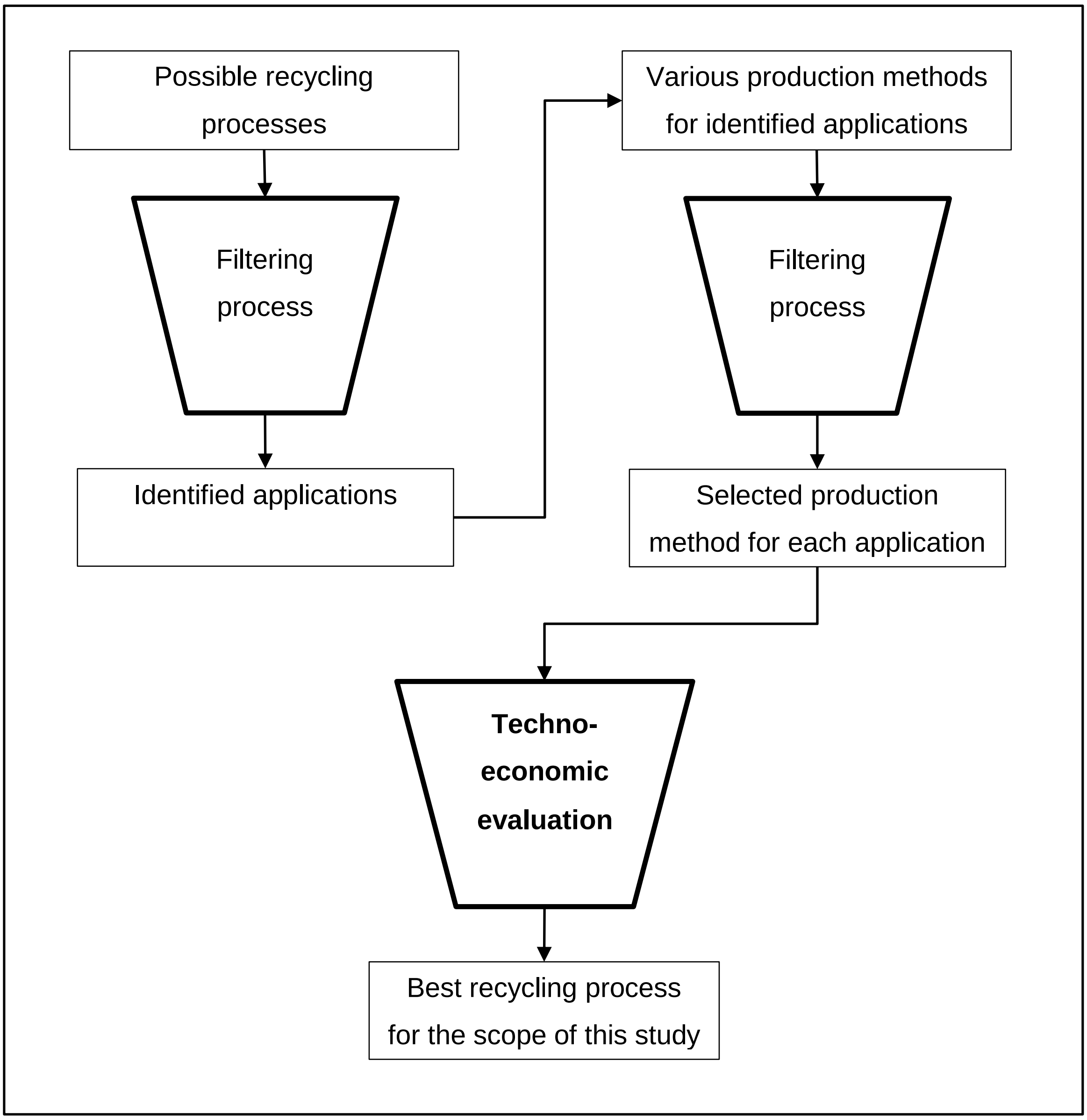

Figure 2-1: Structure of this study

2.2 Titanium tetrachloride ($TiCl_4$)

Titanium tetrachloride does not occur naturally and is predominantly produced from titanium bearing deposits, such as anatase, brookite, rutile and ilmenite (Jones & Egerton, 2012). It is a colourless liquid with a penetrating acrid odour (U.S. EPA, 2007). Titanium tetrachloride is most commonly found as an intermediate product in various chemical processes where the required volumes vary from millilitres to kilolitres. It is highly unconventional for $TiCl_4$ to be used in any practical applications other than smoke formation in military operations. This is due to the fact that $TiCl_4$ is extremely reactive towards moisture in air to form opaque clouds of a chemical complex that primarily consists of titanium dioxide (TiO_2) and hydrochloric acid (HCl) (see Equation 1-1). The chemical properties of titanium tetrachloride are listed in Table 2-1. It can be seen that $TiCl_4$ is a liquid at room temperature with a higher density than water.

Table 2-1: Chemical properties of titanium tetrachloride

Property (unit)	Value	Reference
CAS Number	7550-45-0	
Molecular weight (g/mol)	189.68	Green and Perry (2008)
Specific gravity	1.726	Green and Perry (2008)
Melting point (°C)	-30	Green and Perry (2008)
Boiling point (°C)	136.4	Green and Perry (2008)
Conversion factor	1 ppm = 7.75 mg/m^3	U.S. EPA (2007)

Titanium tetrachloride is particularly corrosive and toxic and has induced numerous medical conditions in the past. Although it is not a common occurrence, exposures where this chemical is in excess can have devastating medical conditions and various studies have been conducted on this matter. To give an indication of the risks involved with exposure to various concentrations of this chemical, Acute Exposure Guideline Levels (AEGLs) are established. The National Academies of Sciences, Engineering, and Medicine (2017) states that these guidelines are based on once-off exposures and are determined for five different time intervals (10min, 20min, 1hr, 4h and 8h). AEGLs consist of three levels, with AEGL-1 giving an indication of the exposed concentration which will lead to non-disabling, temporary and reversible effects. Examples of these conditions include irritation, notable discomfort and asymptomatic non-sensory effects. AEGL-2 gives a guideline of the concentration above which irreversible or serious long-lasting adverse health effects could be experienced. The concentrations above which life-threatening health effects or death could occur are given by AEGL-3. The United States Environmental Protection Agency (U.S. EPA) published a report in 2007, where the AEGLs of titanium tetrachloride where determined by various case studies of previous incidents and by evaluating the influence of exposure to $TiCl_4$ on numerous laboratory animals. An AEGL-1 could not be determined as these effects are difficult to detect on animals and reports of incidents where people were exposed to $TiCl_4$ lacks the necessary information. The AEGL-1 of titanium tetrachloride are thus reported as not recommended (NR). The AEGLs are given in Table 2-2 with $TiCl_4$ concentrations in parts per million (ppm) and milligram per square meter (mg/m^3).

Table 2-2: Summary of proposed AEGL Values for Titanium Tetrachloride from U.S. EPA (2007) [ppm (mg/m3)].

Classification	10 minutes	30 minutes	1 hour	4 hours	8 hours
AEGL-1 (Non-disabling)	NR	NR	NR	NR	NR
AEGL-2 (Disabling)	7.6 (59)	2.2 (17)	1.0 (7.8)	0.21 (1.6)	0.094 (0.73)
AEGL-3 (Lethal)	38 (290)	13 (100)	5.7 (44)	2.0 (16)	0.91 (7.1)

The European Union has implemented the use of risk phrases (R Phrases), which is being used globally. These risk phrases are assigned to chemicals to give an indication of its behaviour and repercussions that will follow should one be exposed to the chemical. Risk phrases is defined in Annex III of European Union Directive 2001/59/EC. Titanium tetrachloride is classified by the risk phrases R14 and R34, which are respectively defined as “reacts violently with water” and “causes burns” (Vince, 2008). Instances where unwanted exposure to titanium tetrachloride were experienced reflect these two risks. One of many applicable examples is given by Park *et al.* (1984), where it is stated how a chemical engineer was exposed to titanium tetrachloride after a glass pipe containing the chemical broke and sprayed his back, neck, chest and his head. This exposure caused second and third degree burns on the affected areas and also resulted in immense damages to the man’s respiratory system.

Two reported cases of lethal exposure were found. In the first case a worker inhaled an unestablished amount of titanium tetrachloride (U.S. EPA, 2007). The symptoms that followed the exposure was a high temperature, increasing respiratory and pulse rates and mottled densities in the upper half of his lungs. The man passed away four days after the exposure due to a complete respiratory failure, which was the aftermath of the severe damage done by the titanium tetrachloride and the hydrolysis reactions that occurred on the surfaces of his respiratory system. In the second case a worker accidentally splashed his whole body with titanium tetrachloride. The exposure caused severe burns on his skin and extensive damage to his eyes. The greatest damage, however, was also inflicted on his respiratory system and the man died 14 days later from critical pulmonary injuries (Murray & Llados, 1997).

Fayerweather *et al.* (1992) discussed how studies were conducted to establish the carcinogenicity of titanium tetrachloride. Results indicated that no association can be made between exposure to titanium tetrachloride and being diagnosed with lung cancer.

Another risk related to titanium tetrachloride is being exposed to hydrochloric acid (HCl), which is a by-product that forms when $TiCl_4$ reacts with moisture. Hydrochloric acid is an extremely corrosive and toxic compound and exposure may cause irritation and inflammation to the respiratory system and have corrosive effects on the human ingestion system (U.S. EPA, 2000). The National Research Council (1998) compiled a toxicology report for hydrochloric acid. This report concluded that exposure to high concentrations of HCl causes closure of the glottis and constriction of the larynx and bronchi. It is also extremely irritating to eyes and mucosal surfaces of the respiratory tract and prolonged exposures at higher concentrations may cause severe damage. Hydrochloric acid is not classified as carcinogenetic by the Environmental Protection Agency (U.S. EPA, 2000).

The results and conclusions from these studies highlight the importance of preventing exposure to these chemicals and thus to determine and implement environmentally friendly recycling solutions.

2.3 Uses of $TiCl_4$

Several uses exist for titanium tetrachloride, with the required quantities ranging from minute amounts up to levels large enough to use the liquid as feed for an industrial process. The diverse applications of $TiCl_4$ are discussed in this section, along with preceding specifications.

The possible quantities of demilitarized $TiCl_4$ that could be obtained for this study were estimated at about 40 ton with the contents of 1000 mortars being added annually (as stated in Section 1.2). Seeing that the available volumes of $TiCl_4$ were quite significant, emphasis was placed on processes that were able to utilize those quantities. These processes were studied thoroughly before being considered in the techno-economic evaluation. Other miscellaneous systems that make use of less significant levels are also stated.

2.3.1 Titanium metal production

Titanium metal can be formed by processing $TiCl_4$. Although this application only contributes to 4-5% of titanium-bearing ore consumption, metal production is globally the second largest industrial application of this mineral (Kotzé *et al.*, 2006). Metallic titanium is an extremely valuable and versatile element and is particularly useful in technological advancements. This can predominantly be ascribed to the remarkable strength-to-weight ratio of the metal and how the surface film of titanium oxidises to form a coating that completely impedes further corrosion of the metal (Imam *et al.*, 2010). The versatility of titanium is deduced from its ability to be exposed to high temperatures without creeping and its crack propagation resistance when free of impurities. Therefore titanium serves as a viable choice for electronic applications (Inagaki *et al.*, 2014). Furthermore, its tensile strength to density ratio is exceptionally greater than that of iron and aluminium, which makes it ideal for aerospace applications, where it is of utmost importance for a metal to be able to withstand drag resistance while still being light enough to be elevated by these forces (Inagaki *et al.*, 2014). Other uses include in marine applications and units in chemical plant, while it is also utilized in the production of spectacles, golf clubs, *etc.* (Bordbar *et al.*, 2017). Titanium is the ninth most abundant element in the earth's crust, but the metal's substantial production costs contribute to its hefty price (Zhang *et al.*, 2011).

2.3.1.1 The Kroll process

A multitude of methods exist to produce titanium metal. The current industrial process, namely the Kroll process, was firstly focused on to establish a framework for this section. This process was developed by Wilhelm Kroll and patented in 1940 (Kroll, 1940). The crux of this process is that it produces metallic titanium that are free from oxides, carbides and nitrates. The presence of these compounds causes the metal to be hard and brittle and is detrimental to the invaluable strength-to-weight ratio and corrosion resistance of titanium. It is thus crucial to obtain a metal that is not degraded by the mentioned impurities.

Industrial Kroll processes use titanium-bearing ores such as rutile and ilmenite as the feed material. A basic flow diagram of the process is depicted in Figure 2-2. Rutile has a high percentage of titanium dioxide (about 95%), opposed to ilmenite (40-65%) that contains excessive levels of iron (Zhang *et al.*, 2011; Gambogi & Gerdemann, 1999). It is thus first required to beneficiate the ilmenite to synthetic rutile (or titania slag) in order for it to be of acceptable purity for utilization. Gambogi and Gerdemann (1999) state that synthetic rutile is obtained by oxidation and reduction of the ilmenite ($FeTiO_3$), followed by acid leaching to separate iron oxides from the

TiO_2 product. Bordbar *et al.* (2017) explain how titania slag, on the other hand, is obtained by thermal reduction in a smelting furnace, with titania slag removed from the top of the reaction furnace while pig iron is recovered from the bottom.

The TiO_2-rich material is then fed to a fluidized bed reactor where it is chlorinated in a carbon-saturated atmosphere to form $TiCl_4$, according to Equation 2-1 (Bordbar *et al.*, 2017).

$$TiO_2 + 2Cl_2 + C \rightarrow TiCl_4 + CO_2 \qquad [2\text{-}1]$$

The titanium tetrachloride is purified to prevent metal-, chloride- and oxychloride impurities from contaminating the titanium and degrading the metal. Various purification processes exist and are implemented based on the impurities present and the required quality of $TiCl_4$ (as discussed in Section 2.3).

The following step is metal reduction of the $TiCl_4$ with alkali or alkaline earth metal. The choice of reducing agent serves as the differentiating factor for many of the processes in the titanium industry. For the Kroll process it is stipulated that magnesium (Mg) should be used to deliver titanium metal from the metal halide feed (Equation 2-2).

$$TiCl_{4\,(l)} + 2Mg_{(l)} \rightarrow Ti_{(s)} + 2MgCl_{2\,(l)} \qquad [2\text{-}2]$$

To deliver a final product of high purity, the reduced titanium sponge is fed through a stripper followed by a vacuum distillation where most impurities are separated from the metal. Common impurities are removed at this stage includes chlorides of the metal reducing agent, titanium subchlorides, oxides, nitrates and carbides (Van Tonder, 2010). An alternative purification method is to leach the reduced product with an acid (usually HCl) to capture and remove impurities that is entrapped in the sponge (Nagesh *et al.*, 2008; Roskill Information Services, 2007).

The metal sponge produced by the Kroll process can either be sold, melted into titanium ingots or shipped to titanium mills for refinement and treatment. A market exists for titanium powder, which can easily be obtained by grinding titanium sponge. This is economically beneficial since the large cost of melting the metal into ingots will not to be incorporated into the selling price.

The $MgCl_2$ that is separated and removed from the sponge can be dissociated into Mg and Cl_2 by fused salt electrolysis (Nagesh *et al.*, 2008). The Mg can be used again as reduction agent, while chlorine gas is recycled back to feed the chlorination process in Kroll process.

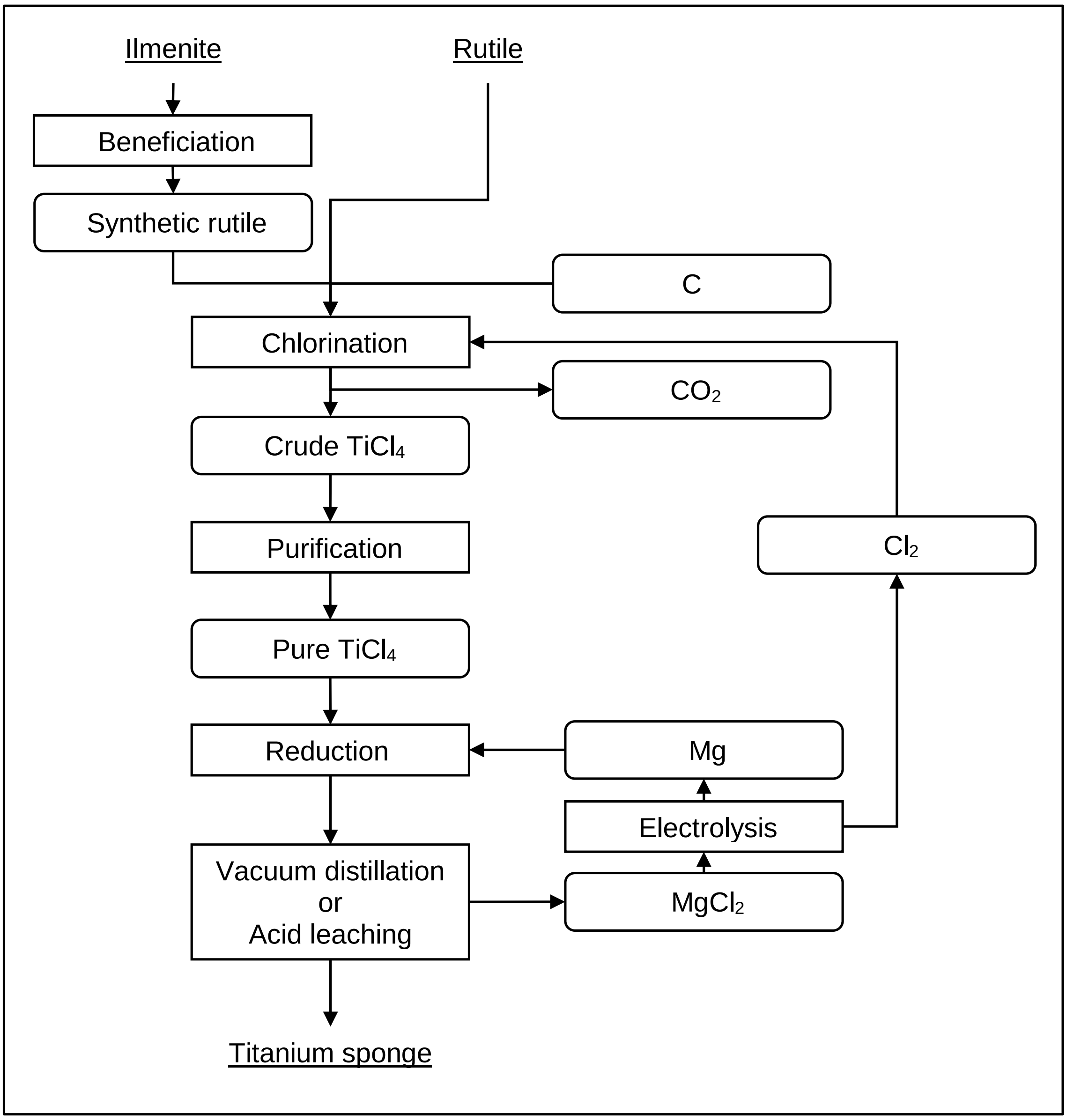

Figure 2-2: Simple process flow diagram of the Kroll process

The proposition to be considered for this study is to produce titanium metal from the purified demilitarized $TiCl_4$. Since this particular metal halide is an intermediate product in the Kroll process, it could be possible to initiate the process from the metal reduction step. If the purification of $TiCl_4$ is sufficient, this suggestion should be practicable. An initial investigation of the material balance reveals that chemicals are added and removed at certain process steps to deliver an intermediate or the final product. The material streams that are referred to in particular are the recycling streams of Mg and Cl_2. If the process is initiated from the reduction step for this study, Cl_2 will form as by-product and will require treatment or handling and could be sold, since it is not required in any other processes on the plant. Considering that the Mg cycle occurs within the part of the process that is focused on, it does not hold any obstacles to the material balance. Before a method can be identified as the adequate solution, it is first necessary to determine if processes exist that are more optimal and whose implementation will be more beneficial than the Kroll process.

Careful considerations of the contributing factors should be made to assess this theory before a valid conclusion can be derived. The tools that could be used is mass balances based on findings from literature, along with simulations based on chemical properties of the reactions and finally by performing energy balances on the identified processes. Since these techniques form part of the scope of this techno-economic evaluation, they are covered in the following chapters. In this section, only the findings from literature are taken into consideration to identify an applicable process and discuss the relevant process conditions.

2.3.1.2 Comparison between the Kroll and Hunter processes

The Kroll process is by a large extent the most popular process for producing metallic titanium from rutile and ilmenite, with the only other process that has been implemented globally on an industrial scale being the Hunter process. The major difference between the Kroll and the Hunter process is that the latter uses sodium (Na) to accomplish the reduction of $TiCl_4$. Due to continuous developments and enhancements to the Kroll process, it has almost completely replaced its counterpart, the Hunter process. This is mainly due to the fact that sodium is more challenging to handle and implement on an industrial scale than magnesium (Van Tonder, 2010). Notwithstanding this factor, other features also played a role in replacing the Hunter process with the Kroll process. Van Tonder (2010) compiled a comparison between the Kroll and Hunter processes, based on the findings of Roskill Information Services (2007) and Turner *at al.* (2001). This comparison is conveyed in Table 2-3. It is evident from the table that some specifications of the Kroll process seem favourable, while it’s contrariwise for other aspects of the Hunter process.

Another major advantage of the Kroll process is that its process units are available in larger capacities and improved operating techniques, which is ascribed to the substantial research and development that have been conducted to improve this process. This means that greater quantities of titanium can be produced between uneconomical downtime steps (Roskill Information Services, 2007).

Table 2-3: Comparison between the Kroll and Hunter processes

Kroll process	**Hunter process**
Operated on a batch scale	Operated on a batch scale OR Continuous step followed by a batch step
15% - 50 % excess Mg should be fed to retort	Small excess of $TiCl_4$ should be fed to retort
Doesn't receive many fines	Receives up to 10% fines
Sponge is hard to grind	Sponge can easily be grinded
Retort walls causes considerable iron contamination in the sponge	Retort walls causes minimal iron contamination in the sponge
Sponge product requires leaching or vacuum distillation to remove impurities	Sponge product requires leaching to remove impurities
Retort is predominantly filled with titanium	Retort content comprises of 4 moles NaCl for every mole of titanium formed
$MgCl_2$ is dissociated by electrolysis and Mg can be used again	NaCl is discarded and new Na is required for every run
Requires a third of the energy for magnesium recovery as opposed to that for sodium	Requires a three times the amount of energy for sodium recovery

At first glance it may seem that both the Kroll and Hunter processes have its respective benefits and disadvantages. However, after careful consideration of the excelling attributes of the Kroll process, it becomes evident that almost all the advantages is financially beneficial to the production costs. Thus, when the main objective is to deliver large quantities of pure titanium at the lowest possible price, the Kroll process appears as the superior process between the two considerations.

2.3.1.3 Challenges of the Kroll process

Despite its broad application, the original Kroll process is not considered to be the optimal method to produce titanium metal for the foreseeable future. Numerous studies have been conducted to improve the process or even to develop alternative techniques for obtaining titanium. This tendency is due to certain drawbacks of the Kroll process, which researchers strive to improve. Some of these drawbacks are listed by Van Tonder (2010) as follow:

1. The production cost for titanium is extremely high, which gives rise to the costliness of the metal.
2. The process is performed on a batch scale and requires excessive downtimes between executions. These periods where the manufacturing plant is unproductive, are unprofitable to a manufacturer and negatively influence the product cost.
3. The process exhibits slow reaction kinetics because of the inefficient contact that occurs between reactants.
4. The formation and use of $TiCl_4$ are somewhat undesired due to its corrosiveness and corresponding health and safety risks (handling and treatment of this chemical are inevitable for this study though).
5. Only expensive rutile or beneficiated ilmenite can be used as feed for the process.
6. The $MgCl_2$ that is removed from the sponge requires electrolysis to be dissociated to Mg and Cl_2. This procedure accounts for approximately 6% of the sponge’s final cost.
7. To deliver a final product with low oxygen and iron compositions, a vacuum distillation or acid leaching step is implemented. These steps are complex and expensive and contribute to 30% of the end product’s cost.

2.3.1.4 Alternative titanium production processes

Some of the various attempts to develop an improved process for producing metallic titanium are now considered. Van Tonder (2010) categorized the existing processes into four main disciplines, namely titanium halide reduction, plasma thermal reduction, electrochemical production and electrolytic production, with all the methods possessing their own associated challenges. These four disciplines are briefly discussed to generate a clear understanding of the main chemical techniques that can be utilized to produce titanium metal. After this discussion, the focus is narrowed down on the specific processes and how they compare when evaluated against a certain criteria. A final major factor that is discussed is each process’ applicability to this study.

In a titanium halide reduction system, a vast amount of impurities coexist with the titanium product. Complex and expensive procedures are required to remove these contaminants and deliver a product of high quality. An additional disadvantage of these steps is that it decreases the obtained titanium yield.

Plasma thermal reduction of titanium is a complex process to administer as it operates at a temperature of around 4000°C. Since this process is immensely energy sensitive, accurate process steps and plant units are required. The capital and production costs of this method is thus quite substantial.

Electrochemical production of titanium is a relatively simple process to execute. This process entails the deposition of solid titanium particles onto a suitable electrode through electron transfer protocols. The challenging part of the process is to collect or strip the metal particles from the electrode, which is an exceptionally labour intensive action. The reaction is performed in molten salt, which requires a large energy input to maintain the process at the appropriate process conditions. The labour and energy costs of this technique are consequently abnormally steep.

Electrolytic production of metallic titanium is quite an intricate method. Due to the high melting point of titanium metal (1660°C), this process is operated with the titanium cells being in a solid state. This complicates the functionality of this method and possible solutions to this problem should be considered. Titanium is a complex metal to produce by means of an electrolytic setup, since multiple valence states exist where the element is stable. Ions could therefore easily move between the electrodes, which would severely decrease the process efficiency. One of the major challenges of this process, which hinders its applicability for industrial implementation is that the titanium that is deposited onto the electrode is in the solid state. The deposit has a crystalline morphology that consists of large surface areas, but has a low bulk density.

Van Tonder (2010) and Van Vuuren (2009) conducted studies to evaluate and rank these proposed improved production methods to identify processes that could potentially replace the Kroll process. The main areas that were focused on were suggestions to reduce capital and production costs, decrease labour and downtime requirements and enhance production rates and quantities. The purpose of this study was not to determine the optimal titanium production process, but it was essential to identify an applicable process that would benefit this project, as this falls within the scope of a techno-economic evaluation. Potentially feasible processes that were established through the evaluations by Van Tonder (2010) and Van Vuuren (2009) are stated and each process's viability is discussed. Since this study focused on the implementation of demilitarized $TiCl_4$ to produce titanium metal, procedures that do not utilize $TiCl_4$ are not considered.

The order in which the processes are discussed is based on the rankings of Van Tonder (2010) and Van Vuuren (2009). These selections and rankings were compiled by the method's potential to reduce associated production and capital costs for titanium production. The first filtering stage was based on each method's financial attributes and how it compares to the current Kroll process (Van Vuuren, 2009). Options that had no potential to excel past the financial barriers of the Kroll process were dismissed. The second filtering stage considered several factors with regard to the identified process, with each criteria carrying a justifiable weight. These factors are: research conducted and academic coverage; readiness to be implemented commercially; process alternatives complexity and results of a sensitivity analysis (Van Tonder, 2010).

2.3.1.4.1 Armstrong/ITP

The highest ranked process for titanium metal production from $TiCl_4$ is the Armstrong/ITP process, which was developed by International Titanium Powder (ITP) and is conveyed by Armstrong *et al.* (1998), Armstrong *et al.* (1999) and Armstrong *et al.* (2002). It should be noted that this is the only method that falls within the specifications that is ranked above the Kroll process. In this approach titanium metal powder is obtained by reducing $TiCl_4$ with sodium (Na), similar to the Hunter process and given by Equation 2-3.

$$TiCl_{4_{(g)}} + 4Na_{(l)} \rightarrow Ti_{(s)} + 4NaCl_{(s)} \qquad [2\text{-}3]$$

Molten sodium acts as the carrying stream, with $TiCl_4$ vapour slowly introduced to the liquid by means of injection to directly form titanium powder. Due to the exothermic nature of the reaction, it is important to maintain a low enough temperature to prevent sintering of the formed powder, which occurs at about 1000°C. Slow $TiCl_4$ introduction and quenching of the titanium containing stream is fundamental in maintaining an adequate temperature. After the reaction between the two materials, separation of the different components in the stream is achieved by feeding the stream to either conventional cyclones or particulate filters.

Anderson *et al.* (2004) improved this process by implementing the use of excess $TiCl_4$, while applying chloride in a superheated state and ensuring that the products are in particulate form. These advancements implies that separation and purification of the product can be conducted by sweeping the reaction product with an inert gas followed by a water wash. These simple processes replace the complicated vacuum distillation step, while still removing all vapour impurities and metal particulates from the titanium powder.

At the time when the critical analyses and rankings of the various processes were completed by Van Tonder (2010) and Van Vuuren (2009), the Armstrong process had not been implemented in the industry. In 2008 ITP was bought and renamed to Cristal Metals. Cristal Metals has since developed and commenced the full-scale production of titanium powder through the Armstrong process (Cristal Metals, 2018).

This process is performed on a continuous scale and is an incredible advancement in the titanium metal production industry. Due to the mode of operation and the complexity of the process to treat the intermediate and recycled chemicals, numerous plant units are required. This greatly increases the capital cost of the plant, but it is justifiable by the increase in production rates over a batch process. It is thus important to take into consideration that high production rates and large production volumes should be maintained to deliver sufficient quantities of titanium on a scale that makes the process is profitable.

When this is put into perspective with the scope and problem statement of this study (Section 1.2), it is clear that an initial mass of 40 ton $TiCl_4$ and an estimated annual addition of 400 kg demilitarized $TiCl_4$ will not sufficiently feed a plant of this magnitude to an extent that the produced quantity of titanium can justify the capital investment that is required. It will thus not be sensible to implement a process with a required capital investment that is unsatisfactory by the maximum potential product quantities. The accurate conditions and optimized process techniques are not published at the time of this study and are purposely being withheld due to trademark rights. The implementation of the Armstrong process cannot be carried out successfully before additional tests and analyses are completed or if the intricate process details are obtained. Development and analysis of an optimized chemical process do not fall within the scope of this project however, since the main aim is to determine the best option from identified recycling methods and not development of possible alternatives. A process can thus not be considered without sufficient information to successfully apply the method as a possible solution to the identified problem.

2.3.1.4.2 Kroll

As previously mentioned, the Kroll process was ranked second on the list of titanium production processes that uses $TiCl_4$ as a feed. Despite the numerous studies that have been conducted to develop improved methods for titanium production, the Kroll process along with the Hunter process was until very recently the only two processes that has been implemented globally on an industrial scale. Though this method is regarded as ancient by some studies and industries, it is greatly benefited by its substantial academic coverage and process readiness in the applied criteria's structure.

2.3.1.4.3 Hunter

The third process is the Hunter process. Similar to the Kroll process, its major advantages are academic coverage and process readiness, since it has been implemented successfully to produce metallic titanium on an industrial scale.

2.3.1.4.4 Ginatta

The method that was ranked after the Hunter process is the Ginatta process. The process was developed by an Italian company named Ginatta Tecnologie Titanio (GTT) and patented by Ginatta and Orsello (1987). This technique covers the formation of liquid titanium from $TiCl_4$ by means of an electrowinning cell at a temperature in excess of 1700°C. Superheated $TiCl_4$ is introduced and absorbed into calcium-containing electrolyte. The molten titanium cathode is separated from the electrolyte by means of a multilayer cathodic interphase. This interphase contains ions of calcium, chlorine, fluorine, potassium and titanium. Titanium metal is produced at the bottom layer of the setup and can be removed from the bottom of the vessel.

Important stipulations that should be considered in this process is that contact between the reaction components and atmospheric gases should be prevented to hinder contamination. The reaction should thus occur under inert conditions. Furthermore attention should be paid to how the titanium metal is formed, since it can be challenging to deliver a product with a satisfactory crystalline morphology. Complications that still needs to be addressed include the determination between operating on a batch or continuous scale, start up and shut down procedures as well as finer details on the complex reactor (Van Vuuren, 2009; EHK Technologies, 2004).

A pilot plant that implements the Ginatta process was developed to produce liquid titanium. The molten titanium is then casted into ingots (EHK Technologies, 2004). The particulate details of this process is not supplied and the process has not yet been applied on an industrial scale. Intricate information still needs to be determined or obtained before the issues of this process are resolved and before this process can be considered for implementation on industrial scale.

2.3.1.4.5 TiRO

The process that was ranked fifth for the current criteria was the TiRO process, which was developed by The Commonwealth Scientific and Industrial Research Organisation (CSIRO). This process is predominantly similar to the Kroll process, with only two notable differences. The first is that titanium is produced in a powder form opposed to sponge, while the second is the possibility of implementing the process on a continuous scale (Hogan *et al.*, 2008).

The technique that is used for this process is to perform the magnesiothermic reduction reaction (similar to Equation 2-2 for the Kroll process) in a fluidized bed reactor to continuously produce titanium powder. The fluidized bed consists of solid particles than are suspended in a gas to act as the fluid (CSIRO, 2016). It is also stated that favourable kinetics can be observed for this reaction inside the fluidised bed reactor and that a high conversion is obtained on a singular pass. This process is characterised by a high product yield and is benefitted by a remarkable decrease in material losses at the retort walls and to subhalides compared to the Kroll process (Froes, 2012).This is primarily a result of the titanium product forming as a powder as opposed to sponge. This technique can also be implemented in such a way that with the appropriate steps and process conditions the necessity to perform a vacuum distillation will be negligible.

This process has not yet been fully developed to the level of being ready for industrial applications. Analysis, simulations and models have determined that the required capital investment and production costs could be quite low for this process. Additionally, the complexities regarding start-up and shut-down procedures along with altering production capacities will be relatively simple to control (CSIRO, 2016). Laboratory scale plants have been developed with mixed results and it was recommended that a pilot plant with a higher capacity will deliver more meaningful results to enable a more accurate evaluation of the process (Doblin, 2012; Froes, 2012). CSIRO (2016) started development of a pilot plant in 2016, but does not have new findings available at the time of this study.

Since this process is not ready for industrial implementation, it does not qualify as a valid option for the techno-economic analysis and was not considered. It is however clear that if the process conditions and parameters can be determined to the extent that industrial application is possible, the ranking of this process could improve tremendously.

2.3.1.4.6 ITT

Idaho Titanium Technologies (ITT) developed a process to produce titanium hydride powder from TiCl4 using a plasma reactor, followed by a rapid quenching step (Cordes & Donaldson, 2000). The reaction that occurs during the plasma process is given by Equation 2-4 (EHK Technologies, 2004). A highlight of this innovation is the efficiency of the heat transfer in the reactor. Temperatures above 4500°C can be achieved quite rapidly to ensure short residence times for the reactor and in return avert corrosion of the reactor or the electrodes (Cordes & Donaldson, 2000). This is even relevant to corrosive elements such as chlorine.

$$TiCl_{4(g)} \xrightarrow[Plasma]{} Ti + 4Cl \tag{2-4}$$

EHK Technologies (2004) states that the quenching step transpires directly after the plasma process. Along with the addition of hydrogen, the reaction in Equation 2-5 occurs. Detering *et al.* (1998) discuss the development of a reactor that is equipped with a Delaval nozzle to rapidly cool down the reactants. The importance of the swift decrease in temperature is that it impedes any back-reactions of the material and enables the retention of products that are usually unstable.

$$Ti + 4Cl + 3H_2 \xrightarrow[Quench]{} TiH_{2(s)} + 4HCl_{(g)} \tag{2-5}$$

ITT has made substantial efforts to resolve and improve any issues that were associated with the design or operation performances of the process steps (Cordes & Donaldson, 2000). These steps include the operation of the plasma torch reactor, the quenching system and the technique used to collect the powder products. Pilot plants of the invention has been developed and are in operation, but the process has not yet been implemented on an industrial scale though.

A major factor to consider with this process is that it produces titanium hydride powder and not pure titanium. Applications of this powder is quite limited, but it has a greater resistance to oxidation than pure titanium powder (Senkov *et al.*, 1996). Senkov *et al.* (1996) further state that the presence of hydrogen in the metal alloy causes an increase in ductility, but decrease in strength of metal at high temperatures. Pure titanium powder can be obtained by heating the powder to above 400°C to remove the hydrogen from the alloy (Cordes & Donaldson, 2000).

Should this process be considered, it will be important to analyse the market to determine the need for titanium hydride powder or to factor in the cost for producing pure titanium powder. The fact that the necessary information for implementing this process has not been published yet, necessitates the need to first develop or obtain these parameters before this process can be considered.

2.3.1.4.7 SRI

SRI International has developed a method to produce titanium powder from $TiCl_4$ in a fluidized bed and by using hydrogen as the reduction agent (Sanjurjo *et al.*, 2005). This is accomplished by first feeding the metal halide to a reaction zone that is operated between 900°C and 1200°C to pass through titanium sponge and dissociate into titanium subhalides (see Equation 2-6 and Equation 2-7).

$$3TiCl_{4(g)} + Ti_{(s)} \rightarrow 4TiCl_{3(g)} \qquad [2\text{-}6]$$

$$TiCl_{4(g)} + Ti_{(s)} \rightarrow 2TiCl_{2(g)} \qquad [2\text{-}7]$$

These intermediate products are then fed to a second separate reaction zone along with an inert carrier gas (usually argon) and reduction agent (which is hydrogen). This zone is maintained at a temperature greater than 1200°C, with the occurring reaction given by Equation 2-8, to produce pure titanium powder.

$$2TiCl_{x(g)} + xH_{2(g)} \rightarrow 2Ti_{(s)} + 2xHCl_{(g)} \qquad [2\text{-}8]$$

This process implements a fluidized bed chemical vapour deposition (FB-CVD) reactor, which operates at atmospheric pressure to obtain significant metal deposition efficiencies.

Sanjurjo *et al.* (2005) state that an advantage of this process over other alternatives is that the titanium powder product does not require further purification after its formation in the second reaction zone. This is essentially due to the absence of a mixture between the titanium product and a halide-rich intermediate material, which is the case in numerous alternative methods. Carbon and nitrogen compounds should easily be moved through the carrier gas, although the presence of oxygen could potentially be problematic since it reacts with titanium to form $TiOCl_2$. It should thus be removed from the feed mixture prior to commencement of this process or additional technique could be developed and incorporated into the process to prevent the occurrence of $TiOCl_2$ in the product.

This method does seem capable of improving the implemented Kroll process. Adequate information for successful implementation is still lacking though and additional research are being conducted to develop a fully operational pilot plant that incorporates this technique (Heydorn & Lantman, 2014; Klausner & Perez, 2013; Sanjurjo *et al.*, 2005). Without the necessary results and information, this process cannot be presented as a potential solution to this study and was thus not considered. This process does have the potential to be adequate for industrial scale application and should definitely be considered once the appropriate details are determined or obtained.

2.3.1.5 Selection of applicable process

Most of these processes cover the necessary steps to convert $TiCl_4$ into titanium sponge or powder. This metal is not always sold in sponge or powder form however. Most of the titanium in the metallic industry, especially for aerospace applications, are acquired in ingot form. Further refinement and smelting processes are thus necessary to obtain this metal in the required form. Since these treatment steps are complex and require a substantial capital investment (Roskill Information Services, 2007), it did not fall within the scope of this project as it was not part of the objectives of this study and the available quantities of $TiCl_4$ that were treated cannot justify the investment of the required capital costs. The final product for this study was thus purified titanium sponge or powder, depending on the identified process.

Methods like the Armstrong process, TiRO process and SRI process certainly have enormous potential to replace the Kroll process globally and should be considered in future applications when the necessary information and details have been developed or obtained. The Armstrong process has been fully developed and implemented for industrial scale operation, but since the necessary information is not yet available at this time, it could not be applied as a solution to this study. Based on the findings on these processes, the Kroll and Hunter processes seem like the preferable choices to select as solutions since adequate information is available on these processes and because both methods have been tried and tested on industrial level. The findings from Section 2.4.1.2 additionally indicate that the Kroll process is more favourable than the Hunter process, resulting in the Kroll process being selected as the ideal titanium production process at the time of this study.

2.3.2 Titanium dioxide (TiO_2) pigment production

The largest application of titanium-bearing materials is found in the production of titanium dioxide pigment. This is the case by a substantial margin, since Bordbar *et al.* (2017) state that this implementation makes up about 95% of the global usage of titanium minerals each year. Diverse uses and different production methods exist for titanium dioxide pigment and are discussed in this section.

Titanium dioxide (TiO_2) functions exceptionally well as a pigment, since it contributes to complete opacity of a product when an adequate quantity is added. It has a refractive index of between 2.49 and 2.73, depending on whether the TiO_2 crystals are in rutile, anatase or brookite form. Pure TiO_2 pigment is perfectly white and one of the most opaque materials available, making it the preferable pigment option for providing a white opaque property to materials (Swiler, 2005).

2.3.2.1 Uses

The need for such a product exists on an extensive scale, which is evident by the diverse field that this pigment is implemented in. This ranges from coatings and paints, plastics, food colourings, paper, rubber, glass, cosmetics, stationary and numerous other uses. It is also the preferable compound to use as a basis in colouring substances since it enables the colourant to completely block out wavelengths of other colours in the spectrum. The global annual usage of titanium dioxide pigment was estimated to be approximately 4.5 million ton in 2007 (McNulty, 2008).

2.3.2.2 Miscellaneous properties of TiO_2 pigments

The degree of whiteness and opacity of the pigment is related to the purity of the TiO_2. It is however difficult and costly to produce TiO_2 of high quality since $TiCl_4$ of extreme purity needs to be obtained. This contributes to an increase in the price of the pigment. Since pigment of absolute purity is not always required or affordable, different grades of pigment are available. Distinction between these pigments is generally based on diverging purities, while different properties are also given to each pigment. Swiler (2005) listed the main properties as follow: composition; crystal structure; particle size; surface area; colour; infrared reflection; pigment opacity and hiding power; tinting strength; colour matching; lightfastness and weathering; heat stability; chemical resistance and finally surface treatments.

A major differentiating factor of these pigments is its mentioned crystal structure. Three TiO_2 crystals exist, namely rutile, anatase and brookite. Between these three, only rutile and anatase have acceptable pigmentary properties, which is contributed by its crystallization in the tetragonal system, as opposed to the rhombic system of brookite. This means that rutile and anatase have remarkable refraction indices, a property that is essential for pigmentary applications. Between these two crystals anatase is the softest and has an inferior refraction index of 2.49 to the 2.73 of rutile (Swiler, 2005). It is also less weatherable and is primarily used in applications where lower abrasion is important, such as paper and fibre industries. Anatase will however transform to rutile above 700°C. Due to its superior stability and weathering capabilities, rutile is the favoured crystal structure for coatings and plastics. Another beneficial factor of rutile over anatase is its resistance to ultraviolet (UV) degradation (Gázquez *et al.*, 2014).

A multitude of pigments with diverse properties exist in the industry and are used in the various stated applications. The Kerala Mineral & Metals Ltd. (KMML) is a company located in India that produces various grades of titanium pigment for industrial applications. These pigments, along with their respective properties, have been listed in Table 2-4. The applications for each type of pigment are listed in Table 2-5, along with the references to the information in Table 2-4 and 2-5. These pigments are mentioned and discussed to indicate the various types of pigments available from a single company and how the difference in properties is beneficial in respective applications.

An interesting observation is that these pigments with different properties and applications are sold for the same price by KMML, which is around R 42 000 per metric ton (The Kerala Minerals & Metals, 2008h). The alumina, silica and zirconia treatments occur after TiO_2 production and form part of the finishing steps, along with the milling procedures. KMML also produces nano-sized pigments of the same grades. From The Kerala Minerals & Metals (2008h) it can be seen that the price for these pigments increases more than threefold for the finer particles.

The principal factor to consider when developing a finishing procedure, is the application where the product is required since the various pigments are sold for the same price. The other aspect that should be evaluated is the size that the product should be milled to, since the required capital for these operating units contributes immensely tot the total capital required. An appropriate milling process should thus be identified that is financially beneficial based on the quantities of pigment that will be produced.

The various finishing steps are discussed in Section 2.3.2.3.2.

Table 2-4: Variety of pigments produced by KMML.

	KEMOX RC 800	KEMOX RC 813	KEMOX RC 802	KEMOX RC 808	KEMOX RC 822	KEMOX RC 800 PG
TiO_2 %	95.4	85.6	92.5	92.8	91.5	95.6
Rutile %	99+	99+	99	99+	99+	99+
Specific gravity	4.1	3.73	4	4	4	4.1
Bulk density (g/cc)	0.88	0.55	0.82	0.85	0.87	0.87
Treatment	Al	Al, Si	Al, Si	Al, Zr, Si	Al, Si	Al
Oil absorption / 100g pigment	18g	35g	21g	20g	19.7g	17.5g
pH	6.0	7.1	7.4	7.3	7.1	6.0
Volatile matter % @ 105 c	0.5	1.0	0.6	0.5	0.6	0.3
Average particle size µ	0.32	0.38	0.33	0.33	0.33	0.31
Chalk resistance	-	High	Medium	High	High	-
Grit (325 mesh) %	< 0.2	< 0.5	< 0.2	< 0.2	< 0.2	< 0.2
ISO 591 Clause	R2	R3	R2	R2	R2	R2

Table 2-5: **Applications of pigments produced by KMML.**

	Applications	Reference
KEMOX RC 800	Printing inks; high gloss coatings; industrial coatings.	The Kerala Minerals & Metals (2008a)
KEMOX RC 813	Interior and exterior low gloss and flat paints and coatings; maintenance paints; chemical coating.	The Kerala Minerals & Metals (2008b)
KEMOX RC 802	Architectural and industrial paints for interior and exterior applications.	The Kerala Minerals & Metals (2008c)
KEMOX RC 808	Automotive, industrial and architectural finishes; oil coating; emulsion paint systems powder coating; printing inks.	The Kerala Minerals & Metals (2008d)
KEMOX RC 822	Interior and exterior enamels and lacquers for architectural and industrial applications.	The Kerala Minerals & Metals (2008e)
KEMOX RC 800 PG	Plastic with high dispersion TiO_2; powder coating; polyethylene films and vinyl sheets; plastic / rubber floors.	The Kerala Minerals & Metals (2008f)

2.3.2.3 Production methods

Two methods are implemented for producing titanium dioxide pigment in the industry. Alternative processes exist, but have not yet been developed to an extent where it can be applied on an industrial scale (Kang & Okabe, 2014; Gázquez *et al.*, 2014). The first of the two operational methods is the sulphate process, which accounts for about 40% of global TiO_2 production (Gázquez *et al.*, 2014). For this production sequence sulphuric acid is utilized to react with titanium-bearing ores to form titanyl sulphate ($TiOSO_4$). The intermediate products are then hydrolysed to titanium dioxide hydrated and treated to produce and obtain TiO_2 pigment (Speight, 2002). These reactions are given by Equations 2-9 to 2-11, with n being a balancing integer.

$$FeTiO_3 + 2H_2SO_4 \rightarrow TiOSO_4 + FeSO_4 + H_2O \qquad [2\text{-}9]$$

$$TiOSO_4 + H_2O \rightarrow TiO_2n.H_2O + H_2SO_4 \qquad [2\text{-}10]$$

$$TiO_2n.H_2O \rightarrow TiO_2 + nH_2O \qquad [2\text{-}11]$$

Preferential properties of the sulphate process over the chloride process are that the implemented technologies are less complex, while it is also not as essential to feed the process with high grade ilmenite. Burger *et al.* (2009) and Borowiec *et al.* (2003) state that cheaper titanium-bearing minerals with moderate TiO_2 content, such as sand ilmenite or slag from rock ilmenite, can sufficiently be used as feedstock to the sulphate process. Due to the depletion of high-quality ilmenite deposits, it is also increasingly common for pigment production facilities to use ilmenite of lesser quality (lower TiO_2 content) to feed this process (Gázquez *et al.*, 2014). These pigments from the sulphate process are favoured in the paper, ceramics and ink production industries due to its cost reduction benefits. The opposing drawbacks of the sulphate process are the limitations in the quality of the product that is produced by it. Furthermore, the excessive quantities of waste iron sulphate that are introduced into the system through the ilmenite are also problematic and solutions need to be implemented to remove and treat this undesired by-product.

The remaining 60% of titanium dioxide pigment production are conducted using the chloride process (Gázquez *et al.*, 2014).

2.3.2.3.1 The chloride process

This process was introduced in the commercial pigment production industry by DuPont in 1951 (DuPont, 2014). It has since been the dominant option in the titanium dioxide pigment production industry, because of its favourable production properties over that of the sulphate process. These attributes include enhanced product qualities, lower production costs and superior waste management techniques (Gázquez *et al.*, 2014).

As illustrated by Figure 2-3, the chloride process starts off through the chlorination of a titanium-bearing ore with a high TiO_2 composition (90% - 95%) to form titanium tetrachloride. The chlorination is performed in a fluidised bed reactor in the presence of coke (which acts as the reducing agent) and is operated at a temperature of 900°C - 1000°C (McNulty, 2008). Equation 2-12 illustrates this reaction, along with the intermediate products that are formed.

$$2TiO_2 + 3C + 4Cl_2 \rightarrow 2TiCl_4 + 2CO + CO_2 \qquad [2\text{-}12]$$

Additionally, metal impurities in the feedstock convert to metal chlorides in unison with the titanium tetrachloride and oxides of carbon. It is thus crucial to select ores with low impurity levels to use as feedstock for this process, since all these impurities have to be removed from the $TiCl_4$. McNulty (2008) further states that the required volume of gaseous chlorine is directly proportional to the amount of impurities in the feedstock (especially to the iron content of the ilmenite). Ores that possess a high constitution of TiO_2 and low impurities will therefore avert supplementary expenses associated with acquiring chemical additives. Metal chloride impurities that entered the process by means of the titanium-bearing ores are removed in the solid phase from the $TiCl_4$ at various process steps. The only exception is $SiCl_4$ that is removed by fractional distillation.

After purification of the $TiCl_4$, it is heated and fed to an oxidation reactor than is operated at temperatures between 950 and 1500°C (Allen & Evers, 1993). These temperatures are achieved either by a toluene-fired furnace or by means of a plasma arc furnace (Gázquez *et al.*, 2014). From this reactor titanium dioxide is produced, along with the substituted chlorine that was replaced by oxygen in the titanium compound. The chemical reaction for this step is given by Equation 2-13.

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2 \qquad [2\text{-}13]$$

The gaseous chlorine is then removed by aqueous hydrolysis or filtration and recycled to the chlorination step of this process. Water (as superheated steam) is also added to the pigment particles to form a slurry with the pure TiO_2. The produced slurry is then fed to the finishing section.

Swiler (2005) states that deviations and alterations to the operating conditions affect the quality of the obtained pigment. The conditions that have been proven to have this influence is mixing procedures in the reactor; excess of oxygen; reaction temperature; water addition and introduction of other reactants into the reactor. An example of the latter is $AlCl_3$ that is sometimes added to the system to promote rutile formation. These conditions could contribute or have detrimental effects to the purity of the product. It is thus important to identify the properties of the desired pigment and alter the conditions to meet the determined specifications.

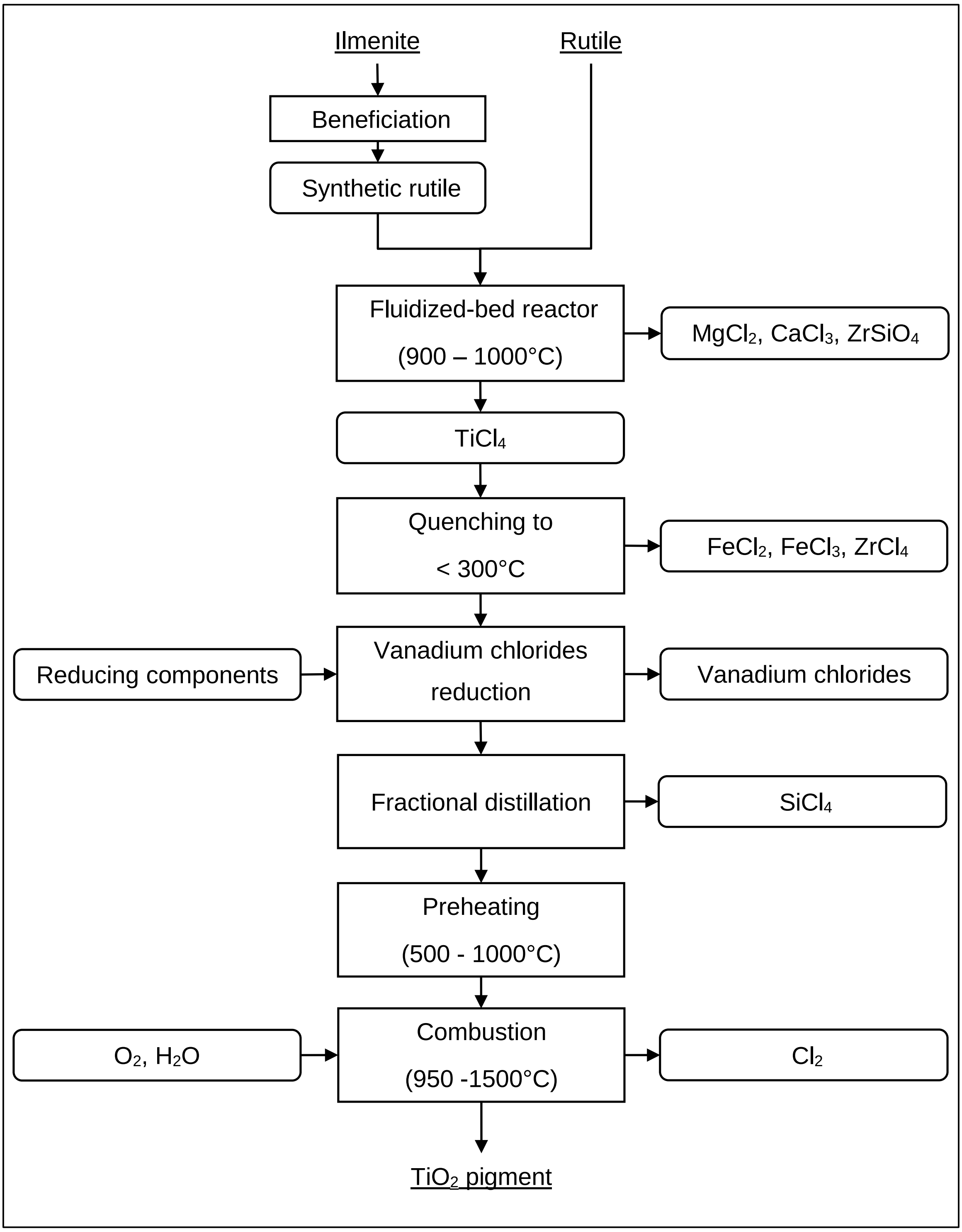

Figure 2-3: Flow diagram of the chloride process (adapted from Swiler (2005) and The Kerala Minerals & Metals (2008g)).

As previously discussed, the chloride process requires a feedstock with a high TiO_2 composition. It is thus not desirable to feed ores such as ilmenite with high calcium and magnesium compositions to this process (Burger *et al.*, 2009); Borowiec *et al.*, 2003). Since natural rutile is not as commonly found as ilmenite it is more expensive and not available in quantities that are able to meet the global annual demand for titanium dioxide pigments. Because ilmenite is the more predominant titanium-bearing mineral, methods have been developed to enhance these ores for implementation in the chloride process. This is achieved by similar processes to those that are used in the titanium metal production industry to produce upgraded titania slag or synthetic rutile (mentioned in Section 2.4.1.1).

Methods for manufacturing upgraded titania slag mainly consist of thermal treatment steps and HCl leaching at high pressures (Borowiec *et al.*, 2003; Borowiec *et al.*, 1998). The obtained upgraded titania slag has a TiO_2 composition of 95% and considerably lower levels of calcium and magnesium.

Synthetic rutile is primarily produced by either the Becher or the Benilite process (Zhang *et al.*, 2011). Both processes utilize reduction and acid leaching steps to enhance the ilmenite feedstock to products that contain 90% - 96% TiO_2. The synthetic rutile can then successfully be used as feedstock for the chloride process to produce titanium dioxide feedstock.

Supplementary to the enhanced product qualities, lower production costs and superior waste management systems, the chloride process also has advantageous product control features and is less labour intensive while it is considered to be safer to the environment (Gázquez *et al.*, 2014).

2.3.2.3.2 Finishing

After TiO_2 production and removal of residual chlorine, the titanium dioxide could be fed through several beneficiation treatments to improve the quality of the pigment, add properties and to ensure that it conforms to the expected standards. These steps include but are not limited to milling processes, classifications, chemical treatments, filtration and drying, micronizing and packaging (The Kerala Minerals & Metals, 2008g). The main pigment properties that are influenced by these steps are: particle sizes; surface areas; colour; infrared reflection; pigment opacity and hiding power; tinting strength; colour matching; lightfastness and weathering; heat stability and chemical resistance.

Milling systems are imposed to firstly break down any clusters or lumps in the TiO_2 product, secondly to ensure that all particles are below a specified particle size and thirdly to prepare the surfaces of the particles for chemical treatments (The Kerala Minerals & Metals, 2008g; Swiler, 2005). Milling can be conducted on a wet or dry basis.

During classification processes the pigment is assessed against the specified standards and particles that are larger than the prescribed size; off-coloured or impure are rejected and removed from the process stream.

The prepared pigment particles are then subjected to surface coatings and other forms of chemical treatments. The most common substances used for chemical treatment is alumina and silica, while zirconia is required in some cases. These coatings impart most of the enriched properties to the pigments and avert any contact between pigment and the associated medium. One of the major contributions by these coatings to the pigment is enhanced chemical and thermal resistance (Swiler, 2005).

The main function of filtration and drying procedures is to wash the particles and to retrieve dried pigment by removing the water from the pigment slurry. Common filters to be used are rotary drum filters and pressure filters. After filtration the pigment is dried to compositions of less than 1% moisture (The Kerala Minerals & Metals, 2008g).

The final process step before packaging of the pigment occurs is again a particle size reduction procedure. In this step the pigment is micronized to below the stipulated diameters from the client, usually to less than 0.5 µ and optimally to between 0.2 and 0.3 µ for rutile crystals (Swiler, 2005). The desired particle sizes ranges from micro to nano measurements and the process units for achieving these sizes are quite costly.

Finally, the pigment is packed or stored and is ready to be transferred to the consumer.

2.3.2.4 Process selection

When comparing the findings of this section to the scope of the product, it is evident that the sulphate process cannot be considered for manufacturing titanium dioxide pigment, since it does not incorporate $TiCl_4$ into its process steps. $TiCl_4$ does occur as an intermediate in the chloride process and the initiative is to commence this process from before the final oxidation step, where purified $TiCl_4$ are fed to the reactor. The specifications, properties and required finishing steps of the pigment is determined by financial feasibility studies and thus largely depend on market demands and capital and production costs.

2.3.3 Other uses of $TiCl_4$

Titanium dioxide pigment production and titanium metal production processes are the principal applications of titanium-bearing minerals, with these processes respectively utilizing 95% and 4-5% of the global ore production. Numerous other uses exist for titanium compounds and more specifically for $TiCl_4$. This section states some of these options and discuss its applicability to this study.

2.3.3.1 Smoke screens and military application

One of the alternative uses of $TiCl_4$ that should be emphasized is the utilization of $TiCl_4$ in smoke mortars for military applications (Murray, & Llados, 1997; Zaytsev & Kuznetsov, 1970). Due to the dense opaque clouds that form when $TiCl_4$ reacts with moist air (reaction given by Equation 1-1), the resulting cloud blocks any vision between parties on opposite sides of the smoke (United States. Department of the Army, 2017; Evans, 2003).

$$TiCl_4(l) + 3H_2O(v) \rightarrow TiO_2 \cdot H_2O \cdot 3HCl(s) + HCl(g) + \Delta H \qquad [1\text{-}1]$$

These clouds that consist of titanium-complex particles ($TiO_2 \bullet H_2O \bullet 3HCl$) are heavier than air and will thus remain at ground level until it disperses completely (Kapias & Griffiths, 2005).

For this application, mortars are filled with liquid titanium tetrachloride with a relatively high purity of about 99% (Rheinmetall Denel Munition, 2017). There are no restraints with regard to the composition of specific impurities in the liquid (as is the case with metallic titanium and TiO_2 pigment production) since the impurities will not affect the smoke formation to a great extent. The only constraint that are implemented by the production company is the $TiCl_4$ purity. This aspect is beneficial to the required capital and operating expenses since complicated procedures and units will not be required, but it also implies that the product value will be low.

The option of purifying the demilitarized $TiCl_4$ to conform to the required specifications for application in smoke mortars was considered for this study. A major contribution to the applicability of this application is the fact that the received $TiCl_4$ is obtained from demilitarizing smoke mortars. It should thus be viable to purify this liquid from corrosion, unsteady chemicals and contaminants that entered the liquid and prepare it for filling new mortars.

Because of the replication of its initial application, it can be assumed that the potential volume of $TiCl_4$ that will be produced within the scope of this study will sufficiently feed this process. Due to the difference in process expenses and product value between the identified recycling methods, a techno-economic evaluation is required to determine the best option.

2.3.3.2 Diverse uses not to be included in evaluation

As previously mentioned, a multitude of processes exist that use or require titanium tetrachloride. However, in most of the cases this chemical is only required in minute amounts. The remaining fundamental uses of $TiCl_4$ that have not yet been mentioned are discussed in this section and its potential applicability to this study is determined.

2.3.3.2.1 Ziegler-Natta catalyst

The Ziegler-Natta catalyst was discovered by Karl Ziegler and Giulio Natta and is an extremely valuable catalyst for the polymerization of olefins. This $TiCl_4$-based catalyst accelerates the polymerization reaction and reduces the activation energy to the extent that polymerization can occur under mild conditions (Bordbar *et al.*, 2017). This catalyst promoted the development of polymers and production of polyolefins in the modern world.

The production of the Ziegler-Natta catalyst is somewhat complex and consists of various chemicals that are added to the $TiCl_4$ (Abbas-Abadi, 2017). Furthermore, tri- or diethyl aluminium is added as co-catalyst to the polymerization reactions that are catalysed by the Ziegler-Natta catalyst (Bordbar *et al.*, 2017). Abbas-Abadi (2017) also states that the dosages of catalyst used during polymerization are somewhat diminutive.

2.3.3.2.2 Catalyst to diverse reaction

Additional to the Ziegler-Natta catalyst, $TiCl_4$ also operates as a solitary catalyst or cooperatively with another standalone compound in a range of diverse reactions. Examples include esterification of carboxylic acids (Shang *et al.*, 2007), conversion of aldehydes to nitriles (Leggio *et al.*, 2017), reaction of ketones with benzaldehyde (Tao *et al.*, 2005), *etc.*

The quantities utilized by the latter two reactions range from almost negligible volumes to dosages of around 10 mol%, which are rather small amounts with regard to this study.

2.3.3.2.3 Coagulant

Titanium tetrachloride can successfully be implemented as a coagulant in purification or recovery treatments. The first example of this application is the determination by Galloux *et al.* (2015) that

$TiCl_4$ sufficiently removes inorganic compounds (aluminium, copper, zinc) from coal mining wastewater by means of coagulation. During that analysis it displayed exceptional turbidity, while also removing dissolved organic carbons to some extent. Galloux *et al.* (2015) further state that titanium-based coagulants is beneficial over some coagulants, since the sludge can be recycled to produce titanium dioxide photocatalyst. $TiCl_4$ coagulants also successfully recovered sludge during real water treatment (Zhao, Gao, Zhang, Qi *et al.*, 2014) and fulvic acid from test water (Zhao, Gao, Zhang, Phuntsho *et al.*, 2014).

Optimal dosages of these $TiCl_4$ coagulants were extremely small though, ranging between 10 and 80 mg/L for the three applications.

2.3.3.2.4 Reactant to wood coating processes

Pori *et al.* (2016) determined that $TiCl_4$ can be utilized to apply rutile particles onto wood by means of hydrothermal deposition. These particles will then form a TiO_2 coating on the surface of the wood to protect the wood from degradation.

The aqueous solution of $TiCl_4$ that were used to treat the wood had a concentration of 0.5 mol/L, which is a rather small quantity of $TiCl_4$.

2.3.3.2.5 Treatment of nanoporous films

Lee and Lee (2015) studied the possibility of enhancing the refractive index of nanoporous TiO_2 films by treating it with $TiCl_4$. Nanoparticulate TiO_2 films are applied to glass surfaces to act as opaque filters that absorb or reflect light to a certain extent. The results from the study indicated that the refractive index of the film was successfully increased by subjecting the TiO_2 to two separate treatments of $TiCl_4$ with respective concentrations of 0.08 M and 0.04 M.

2.3.3.2.6 Process considerations

It became quite clear from the discussed processes that these applications could present several challenges for the successful implementation of $TiCl_4$. Most options seems practically viable, but the utilized volumes and dosages will not satisfy the amount of demilitarized $TiCl_4$ that is available for the study. In addition, these processes are not that common and it is unlikely that scenarios will exist that requires the supplied quantities of reactant. The fundamental challenge is thus to identify a sustainable process that is financially feasible, while utilizing the volumes of $TiCl_4$ supplied in the problem statement.

A possible solution that was considered in the techno-economic evaluation is to firstly beneficiate the demilitarized $TiCl_4$ by means of purification and secondly supply this $TiCl_4$ to consumers that are willing to purchase the product. The titanium tetrachloride can then still be implemented in any of these diverse processes by an already established consumer in the appropriate quantities.

Since all the identified processes commence with a purification step, combinations of these options are also possible. For example, the $TiCl_4$ can be purified and used to fill new smoke mortars. Excessive volumes that are not required could then be sold to consumers. All these options were measured and tested during the techno-economic evaluation. Various methods for producing high purity titanium tetrachloride are discussed in the subsequent section.

2.4 $TiCl_4$ purification

Crude titanium tetrachloride may contain numerous impurities of elements that were present along with titanium in the titanium bearing deposits. Due to the chlorination step of $TiCl_4$ production, these elements most commonly exist as metal chlorides in the mixture. It is thus expected that demilitarized titanium tetrachloride from smoke mortars may contain impurities, as it is contained in metal shells for periods exceeding 20 years and the titanium tetrachloride that was used at the time of production may have been of lesser quality. The impurity composition and purity of the demilitarized titanium tetrachloride that needs to be recycled are determined in Chapter 3. A broader study will therefore be conducted in this section to cover various processes from literature that will be adequate in removing a significant range of impurities. This is also fitting when it is considered that the need for this project exists on a global scale and the composition of the feed material used in the smoke mortars may vary slightly or contain other impurities altogether. This necessitates the need to develop appropriate processes to remove relevant impurities. The different purification processes that will be considered may, however, deliver different product purities, which is another factor that will be taken into consideration.

It should be mentioned that it is fundamental to remove these impurities as its presence causes a great reduction in efficiency of the $TiCl_4$ and the processes it is implemented in. When the focus is placed on the three identified processes for this study it can be stated that titanium tetrachloride with a high impurity content will produce less smoke in mortar applications as there are less $TiCl_4$ present to react. Some impurities can even act preferentially with the moisture in air to inhibit the smoke formation reaction. The required purity of $TiCl_4$ in pigment production processes are extremely high, as impurities (especially vanadium) generally appear as coloured spots and drastically reduces the quality and value of the pigment (Lynch, 2002; Boyd, 1966). In titanium metal production processes, impurities in the $TiCl_4$ feedstock will also negatively influence the ductility and rigidity of titanium sponge (Xiong *et al.*, 2012; Boyd, 1966). Another effect of impurities in the $TiCl_4$ feed is contamination of process units, which reduces efficiencies or in worst cases, alters the formed product altogether. These effects are especially evident in the pigment and metal production industries where further reactions and heat treatments are required. Examples include chemical corrosion to refractory brinks in the chlorinator by ferrous and ferric chlorides or accumulation of silica and zirconia in the chlorinator bed, which can lead to a deviation in bed composition (Kale & Bisaka, 2016). The issue of contaminated process units is not sustainable and will have great financial consequences to rectify or replace. It is thus essential to prevent these impurities from entering the system.

2.4.1 Required $TiCl_4$ purities

As mentioned in Section 2.3, various grades of TiO_2 pigments exist. Similarly, metallic titanium can also be graded based on its impurity levels and properties. The purity of the obtained end-product is highly dependent on the purity of the feedstock, which is the demilitarized $TiCl_4$ in this scenario. Clear specifications for all three processes exist and are implemented in the relevant industries. The required purities of $TiCl_4$ for these processes are studied and obtained from industry or other literature sources.

Required specifications for $TiCl_4$ that is to be used in the production of metallic titanium and TiO_2 pigment are listed in Table 2-6. These values were obtained from the stipulations that are in place at industrial $TiCl_4$ production companies (Toho Titanium, 2016; OSAKA Titanium Technologies, 2013) and correspond with the academic findings of Sibum *et al.* (2005). The Hazen colour scale that is referred to in the table is a system used by American Public Health Association (APHA) to determine the extent of colouring of a specified liquid. The scale ranges from 0 (for clear distilled water) to 500 (for dark and polluted liquids). A Hazen number of 20 is consequently quite clear and transparent.

Table 2-6: Required $TiCl_4$ composition for Ti metal and TiO_2 pigment production

	$TiCl_4$ % (min)	Fe ppm (max)	V ppm (max)	Si ppm (max)	Sn ppm (max)	Hazen colour no. (max)
Composition	99.9	10	10	10	30	20

The specification for $TiCl_4$ that is used in smoke mortars for military applications is less stringent than that for the former metallurgic uses. Since low concentrations of impurities wouldn't affect the desired smoke formation it is not necessary the limit individual impurity levels. The only specification that should be adhered to is an overall $TiCl_4$ quality, to ensure that satisfactory volumes and densities of smoke emerges when the mortars are employed.

The required purity of $TiCl_4$ for this application varies between manufacturers and information on this specification is difficult to obtain and share, since it is regarded as an extremely confidential industry. The prescribed purity that was used in this study for smoke mortar applications is discussed in Section 3.4 along with the stipulations of the other two produced products.

The specified purities are quite high and it is expected that demilitarized $TiCl_4$ with production dates of more than 20 years ago could be contaminated to such degrees that it does not conform to the requirements. If this is the case, purification of the liquid is required by either selectively removing the $TiCl_4$ from the mixture or by identifying and separating each impure element's compounds. Available purification processes were identified and researched to determine applicable and relevant methods.

2.4.2 $TiCl_4$ purification processes

Hockaday and Kale (2016) have listed the common impurities that are associated with titanium tetrachloride and have stated that the most common way to remove the majority of these impurities is by means of distillation. Impurities along with their respective boiling points, taken from Green and Perry (2008), are listed in Table 2-7.

When it is taken into consideration that titanium tetrachloride has a boiling point of 136°C, it can be deduced that some of the impurities with similar boiling points will exit with the purified product in the distillate. Impurities that are commonly known for not being removed by the distillation process are $AlCl_3$, $AsCl_3$, $SnCl_4$, VCl_4 and $VOCl_3$ due to their boiling points being in the same region as that of titanium tetrachloride. Ferric chloride ($FeCl_3$) is an impurity that is often present in crude titanium tetrachloride. Although it has a much higher boiling point than $TiCl_4$, it tends to react with other components in the system when it is present in large quantities. This usually results in the formation of low-boiling complexes that escape the distillation column in the overhead product (Hockaday & Kale, 2016).

Table 2-7: **Common impurities in $TiCl_4$ (adapted from Hockaday and Kale (2016))**

Chemical name	Chemical formula	Boiling point (°C)
Aluminium chloride	$AlCl_3$	183
Antimony pentachloride	$SbCl_5$	Decomposes at 140°C
Antimony trichloride	$SbCl_3$	220
Arsenic trichloride	$AsCl_3$	130
Calcium chloride	$CaCl_2$	1935
Copper chloride	$CuCl_2$	993
Ferric chloride	$FeCl_3$	315
Ferrous chloride	$FeCl_2$	1023
Magnesium chloride	$MgCl_2$	1412
Nantokite	Cu_2Cl_2	1366
Silicon tetrachloride	$SiCl_4$	58
Tin tetrachloride	$SnCl_4$	114
Titanium trichloride	$TiCl_3$	Decomposes at 440°C
Vanadium dichloride	VCl_2	1506
Vanadium oxychloride	$VOCl_3$	127
Vanadium tetrachloride	VCl_4	149
Vanadium trichloride	VCl_3	Decomposes at 300°C

2.4.2.1 Additional purification methods and treatment agents

To deal with the problem of impurities that contaminate the distillate, a diverse range of reagents can be used to react with the impurities and prevent it from escaping the liquid residue in the distillation column. Another possibility is to treat the impure titanium tetrachloride prior to or after distillation. Various purification processes and the specific impurities that it specialises in removing were studied and are discussed in this section.

A good area to initiate this topic is to look at the various registered patents on purifying titanium tetrachloride. A multitude of patents exist. Some are small variations or improved methods on existing patents, while others are for removing different impurities all together. A summary of a diverse range of patents are listed in Table 2-8. The applicability of each patent is thus highly dependent on the impurities present and the required purity of the end product.

Most of the listed patents in Table 2-8 are historically older than 30 years, but this could primarily be due to the fact that patents are registered upon first development, while improvements and adjustments by companies that implement these processes are not always registered as new patents. The diversity in the solutions to purification is also notable. While popular methods for removing vanadium compounds are treatment with organic agents or hydrogen sulphides, it can be seen than the most recent development is adsorption of impurities onto alumino-silicate materials. This is a new process altogether that has not really been implemented and assessed over long periods of time. It thus greatly complimented this study to also look at other sources that discuss processes that are being used and developed in the industry before a final conclusion can be formulated.

2.4.2.1.1 Copper powder / particles

Wang *et al.* (2009) state that common low-boiling impurities ($SiCl_4$, Cl_2 and HCl) can effectively be separated by means of rectification, while distillation is used for separating impurities such as $FeCl_3$ and $AlCl_3$. Impurities with similar boiling points to $TiCl_4$, such as vanadium compounds, are successfully removed from crude titanium tetrachloride by the addition of treatment agents such as hydrogen sulphide (H_2S), organic matter, aluminium powder and copper wire. According to Wang *et al.* (2009), the preferred purification method in China is treatment with copper wires. This entails the reduction of $VOCl_3$ to $VOCl_2$, while CuCl forms as a by-product (Equation 2-14).

$$VOCl_3(l) + Cu(s) \rightarrow VOCl_2(s) + CuCl(s) \qquad [2\text{-}14]$$

Table 2-8: Patents on titanium tetrachloride purification processes

Treatment agent / method	Impurities	Reference
Adsorption with alumino-silicate materials	Metal chlorides	Derecskei *et al.* (2017)
Copper powder	Arsenic, antimony, niobium, tin and vanadium	Goddard and Litwin (2002)
Catalytic metals (Cu, Fe, or Cu & Fe alloys)	Oxychlorides	Ishizuka (1988)
Chlorination with high-surface-area carbon	Vanadium compounds	Bonsack and Shneider (1982)
Titanium trichloride - aluminium trichloride ($TiCl_3 \cdot 1/3AlCl_3$)	Vanadium compounds	Winter (1975)
Hydrogen sulphide gas (H_2S)	Vanadium compounds	Sironi *et al.* (1971)
Organic treating agent (*e.g.* soaps)	Vanadium compounds	Clark and Kolb (1970)
Titanium trichloride ($TiCl_3$) and white mineral oil	Vanadium compounds	Boyd (1966)
Mineral oils (especially with high molecular weights) and inert gas purge	Carbon or oxygen compounds; Metals chlorides and oxychlorides	Fahnoe and Sturm (1964)
Reactive sulphides (*e.g.* H_2S)	Chlorine, aluminium chloride, silicon chloride, phosgene and vanadium compounds	Guthrie (1956)

Table 2-8 (Continued): Patents on titanium tetrachloride purification processes

Treatment agent / method	Impurities	Reference
Hydrogen sulphide (H_2S) with heavy metal soaps (*e.g.* ferric stearate)	Liquid metal halides; iron and vanadium compounds	Meyers (1946)

These copper and vanadium compounds will then precipitate from the mixture and can therefore easily be separated from $TiCl_4$. Wang *et al.* (2009) and Wang *et al.* (2011) explain how $VOCl_2$ and CuCl molecules accumulate on the surface of the copper wire as the reaction progresses, which will hinder the rate at which $VOCl_3$ is reduced after a period of time. This prompted the necessity to regularly rinse the copper wire particles to wash off collected impurities. When these impurities contact the water, disproportionation of Cu^+ into Cu and Cu^{2+} takes place, while formed TiO_2, HCl and $VOCl_2$ dissolve into the water.

Wang *et al.* (2009) and Wang *et al.* (2011) further conducted studies on how to extract the impurities in order for wash water to be recycled and to recover vanadium and copper elements from the precipitate. The first treatment step is oxidation of the wash water. This step is followed by neutralization to form a precipitate with a composition of $xCuO \cdot yV_2O_5 \cdot zH_2O$, where x, y and z represent the ratios of the respective molecules (Zhang *et al.*, 2008).

The more time-consuming method, which also gives a greater vanadium recovery from the wash water (95.7%), is by stacking the precipitate in air for a period of one month for natural oxidation to occur. This results in more than 90% of the metallic copper to be converted into $CuCl_2 \cdot 2H_2O$ and $Cu_2Cl(OH)_3$. Sodium hydroxide (NaOH) is added to convert the copper oxychlorides to $Cu(OH)_2$. By lowering the pH, copper can selectively be leached into solution leaving an acid leach residue that contains iron, titanium and vanadium oxides. After evaporation and condensation of the solution, $CuSO_4 \cdot 5H_2O$ with a purity of 99.7% can be obtained as a product. The filter cake that remains is roasted to form calcine, which is then leached with water. NH_4Cl is added to precipitate NH_4VO_3. This compound undergoes calcination to form high purity (98.6%) V_2O_5 (Wang *et al.*, 2009)

The second method of vanadium recovery is a lot less time-consuming, but in returns gives a lower vanadium recovery from the precipitate (79.5%). The process starts of by leaching the precipitate with a NaOH solution, which can reach a vanadium leaching of 81.5% under optimum conditions. The second step is an ion-exchange procedure which consists of adsorption of vanadium in the leach liquor by weak-base anion exchange resin D314 and elution of the loaded resin by NaOH. NH_4Cl is added to precipitate NH_4VO_3, which is calcined to form V_2O_5 powder (Wang *et al.*, 2011). Although this method takes less time than the process that was discussed in the previous paragraph, it will present a problem when recycling and reusing the wash water and copper particles as 20.5% of the vanadium is not removed. Possible solutions that could be considered should this process be implemented is an additional recovery process or safe disposal and dilution practices.

2.4.2.1.2 Mixture of Al powder and WMO

Another captivating method for removing vanadium impurities that are tough to separate is by treating the titanium tetrachloride with a mixture of aluminium powder and white mineral oil (WMO) (Xiong *et al.*, 2012). It should be stressed however that this method was developed for purification of crude $TiCl_4$ with a high vanadium content. Various patents were incorporated to develop this method of $TiCl_4$ purification and determine which reactions would actively transform impurities into separable compounds. Treatment with Al powder results in the formation of a titanium trichloride - aluminium trichloride ($TiCl_3$•1/3$AlCl_3$) complex, as shown in Equation 2-15. This complex is also the treatment agent of the patent developed by Winter (1975).

$$Al(s) + 3TiCl_4(l) \rightarrow 3TiCl_3(l) + AlCl_3(l) \qquad [2\text{-}15]$$

$TiCl_3$ in its turn reacts with $VOCl_3$ impurities to precipitate as $VOCl_2$ (Equation 2-16).

$$TiCl_3(l) + VOCl_3(l) \rightarrow TiCl_4(l) + VOCl_2(s) \qquad [2\text{-}16]$$

The patent invented by Boyd (1966) stated that vanadium impurities can be removed from $TiCl_4$ by treatment with $TiCl_3$ and WMO, while Fahnoe and Sturm (1964) revealed that mineral oils can be used as treatment agent. Xiong *et al.* (2012) suggested possible reactions that are most likely to occur by addition of WMO, based on Gibbs free energy calculations. The mechanism of this technique is described through Equations 2-17 to 2-19.

$$WMO \rightarrow C\ (active\ carbon) \qquad [2\text{-}17]$$

$$C(s) + 2VOCl_3(l) \rightarrow 2VCl_3(s) + CO_2(g) \qquad [2\text{-}18]$$

$$C(s) + 2VOCl_3(l) \rightarrow VCl_4(g) + VCl_2(g) + CO_2(g) \qquad [2\text{-}19]$$

The mineral oil is a feedstock for producing active carbon through pyrolytic cracking. The theory of applying active carbon to remove vanadium and ferric impurities coincides with the patent registered by Bonsack and Shneider (1982). Another function of WMO for this specific process is to act as activating agent for aluminium powder due to its moderate acidity, which eliminates Al powder's exterior oxidation film and accelerate its reaction kinetics. Verification of the reactions in Equation 2-18 and 2-19 with the phase stability diagram of vanadium, chloride and oxygen at the reaction temperature (138°C) confirmed that VCl_3 is a stable product and will probably precipitate. VCl_4, however, is unstable and is thus not likely to form (Xiong *et al.*, 2012; Bonsack & Shneider, 1982). The observed precipitates of vanadium compounds are thus expected to be solid $VOCl_2$ and VCl_3, in accordance with Equation 2-16 and 2-18, respectively.

The initiative for this process is that Al powder is an expensive agent when one considers the required solitary amount that should be used to obtain the required purity. WMO, on the contrary, is an inexpensive alternative, but cannot be used excessively as large volumes WMO will produce residues that are difficult to control and lower heat transfer efficiencies in boilers. Xiong *et al.* (2012) state that a general quality standard for purified titanium tetrachloride is a vanadium content of ≤0.0012 wt%. In cases where the vanadium content in the feedstock is ≥0.3 wt%, WMO will not be able to successfully purify the $TiCl_4$ to the given standard without formation of unwanted residues occurring. By conducting experimental procedures, it was further determined that the Al and WMO mixture where capable of lowering the vanadium content in the TiCl4 to a minimum of 0.00049 wt%, while Al powder or WMO alone could only purify TiCl4 to a 0.0007 wt% of vanadium. The Al and WMO mixture also achieved this purity in only 40 minutes, which is 55.5% and 66.7% shorter that the respective process times of Al powder or WMO. A mixture of Al powder and WMO is thus an excellent treating agent for purifying titanium tetrachloride with high levels of impurities (especially vanadium). Since it can successfully remove the vanadium content in $TiCl_4$ to minute levels, it can be considered as a treating agent regardless of the liquid being contaminated with high or low levels of impurities. Its consideration will thus mainly be dependent on the required purity and comparable process costs.

2.4.2.1.3 WMO

From the previous paragraph and listed patents it is observed that white mineral oil (WMO) on its own can also act as a viable treatment agent for removing impurities with similar boiling points to that of titanium tetrachloride. The only requisite for its applicability is that a small dosage should be utilized to treat the contaminated liquid, otherwise formation of unwanted residues will transpire. It is thus not able to remove excessive amounts of impurities. Although WMO on its own delivers a lower $TiCl_4$ purity than a mixture of the oil and aluminium powder, it removes unwanted elements to levels that are still well below expected impurity composition levels. Major advantages of WMO are firstly its low costs in comparison to metal treatment agents and secondly, due to its addition in the liquid phase it can also react more thoroughly than solid treatment agents. This can engender a decrease in the dosages being required for effective impurity removal, which is conducive to the financial advantages that are observed with its usage in comparison to that of solid treating agents. Hockaday and Kale (2016) conducted a study where modern industrial $TiCl_4$ purification processes was reviewed. Four treatment agents that are widely used in the industry were identified and the financial viability and performance of these agents were compared. The first three additives were oleic acid, sodium oleate and potassium oleate, which are all white mineral oils, while the fourth agent was copper particles.

The main impurities that the review by Hockaday and Kale (2016) focused on were iron and vanadium compounds. Possible reactions were first evaluated using the FactSage© thermodynamic simulation software. This program calculates changes in Gibbs free energy, enthalpy and entropy to determine the preferred reactions that can be expected. A major drawback of this evaluation, however, is that the necessary data for some of the vanadium oxychlorides (VOCl and $VOCl_2$) was not available and could not be included in the results. Be that as it may, the program output is still adequate to determine whether certain reactions will occur spontaneously or not.

It was found that active carbon, formed by cracking of WMO, will react with vanadium oxychloride to form solid vanadium trichloride and carbon dioxide gas (identical to the reaction given in Equation 2-18). The obtained results further indicated that any vanadium tetrachloride will react preferentially with active carbon to reduce to vanadium trichloride with carbon tetrachloride forming as by-product (Equation 2-20). This corresponds with the findings of Xiong *et al.* (2012) about the instability of VCl_4. WMO thus seems to be a good treatment agent for removing vanadium impurities from $TiCl_4$.

$$VCl_4 + \frac{1}{2}C \rightarrow VCl_3 + \frac{1}{2}CCl_4 \qquad [2\text{-}20]$$

The reaction between active carbon and ferric chloride to form ferrous chloride and carbon tetrachloride (Equation 2-21) has a positive change in Gibbs free energy within the process temperature range and would thus not occur spontaneously (see Figure 2-4(a)).

$$FeCl_3 + \frac{1}{4}C \rightarrow FeCl_2 + \frac{1}{4}CCl_4 \qquad [2\text{-}21]$$

By extrapolation of the graph of change in Gibbs free energy for Equation 2-21 in Figure 2-4(b), it can be seen that the value does decrease to a negative value at high temperatures (about 425°C) and the reaction could thus be carried out by the addition of heat. For this conclusion it is assumed that the change in Gibbs free energy for Equation 2-21 remains linear up to the determined temperature. This interpretation is thus not scientifically proven and further studies or simulations should be conducted before decisions can be based on these findings.

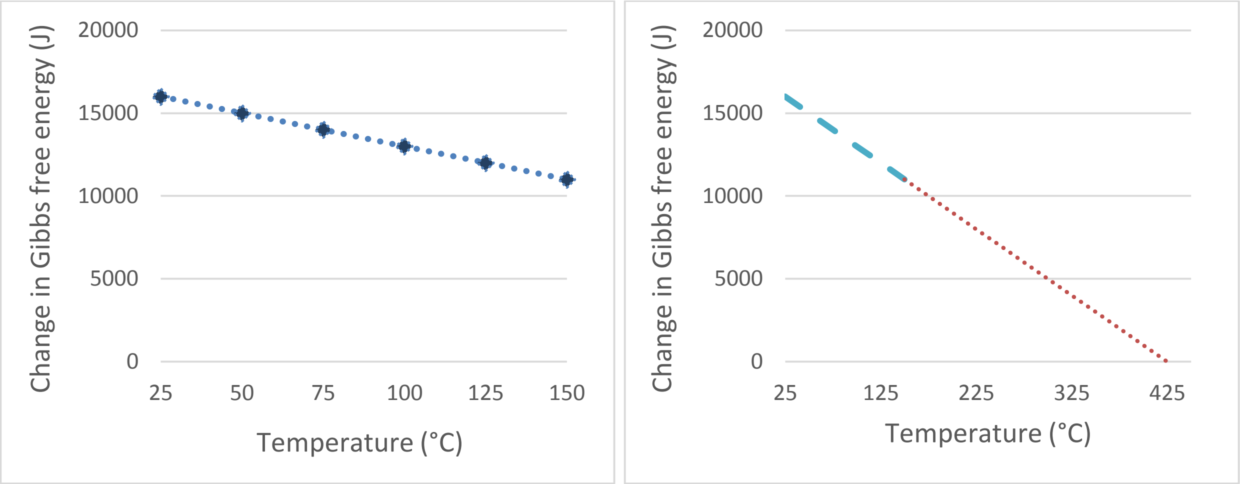

Figure 2-4: (a) Change in Gibbs free energy for Equation 2-21 (amended from Hockaday and Kale (2016)); (b) extrapolation of change in Gibbs free energy for Equation 2-21

From this calculation it can be suggested that other treating agents might be more optimal for removing ferric chloride, but WMO will still be sufficient to obtain the desired purity. Further economic impacts of its implementation and the increase in process temperature should be considered though.

Copper is a highly reactive metal and the FactSage© thermodynamic simulation software indicated that various reactions between the metal particles and impurities had negative Gibbs free energy changes.

When vanadium tetrachloride is present, it will react preferentially with copper to form copper chloride and vanadium trichloride (Equation 2-22).

$$Cu + VCl_4 \rightarrow CuCl + VCl_3 \qquad [2\text{-}22]$$

Problematic ferric chloride impurities will also react spontaneously with copper particles to form ferrous chloride and cuprous chloride (Equation 2-23).

$$FeCl_3 + Cu \rightarrow FeCl_2 + CuCl \qquad [2\text{-}23]$$

Copper particles will thus successfully remove vanadium and iron impurities. Although spontaneous reduction of vanadium oxychloride by treatment with copper could not be evaluated by the thermodynamic software, Wang *et al.* (2009) and Wang *et al.* (2011) stated that it is the only treatment agent that are being used for $TiCl_4$ purification in China. For this process $VOCl_3$ reacts with copper to form $VOCl_2$ and CuCl (see Equation 2-14). Its successful and preferential implementation in the Chinese industry serves as proof that it is a viable additive for removing metal impurities from $TiCl_4$. Patents by Goddard and Litwin (2002) and Ishizuka (1988) also describe how copper can be used for treating $TiCl_4$ to respectively remove vanadium compounds and oxychlorides.

For the experimental procedure of Hockaday and Kale (2016), four samples of crude $TiCl_4$ were respectively treated with oleic acid, potassium oleate, sodium oleate and copper particles. The experimental operating conditions that were maintained for each treating agent are tabulated in Table 2-9. Dosages of the WMO treatment agents were determined by Hockaday and Kale (2016), while the copper particles dosage was specified by Goddard and Litwin (2002).

Table 2-9: Experimental operating conditions (amended from Hockaday and Kale (2016))

	Treatment agent	**Dosage (wt%)**	**Reflux T (°C)**	**Time (min)**
Trial 1	Oleic acid	0.15	136	30
Trial 2	Potassium oleate	0.25	136	30
Trial 3	Sodium oleate	0.25	136	30
Trial 4	Copper particles	1	136	30

The impurities that were tested for were any compounds of aluminium, iron and vanadium. Initial impurity compositions in the crude sample are given in Table 2-10. After addition of the treatment agents, each sample were distilled and the distillate was analysed to determine the obtained impurity levels. These values can be observed in Table 2-10.

Table 2-10: Impurity compositions of the treated $TiCl_4$ (adapted from Hockaday and Kale (2016))

Treatment agent	Al (ppm)	Fe (ppm)	V (ppm)
Initial	4	20	726
Oleic acid	5.7	<2	<2
Potassium oleate	5.1	<2	<2
Sodium oleate	5.3	<2	<2
Copper particles	5.3	<2	<2

It is thus evident that all four treatment agents will effectively purify titanium tetrachloride from iron and vanadium compounds. However, in cases where high levels of aluminium impurities are present, it will not be adequate treatment agents. Aluminium impurities are not as ordinarily found in $TiCl_4$ as iron and vanadium compounds. These four treating agents will thus be appropriate in most purification processes. Should aluminium compounds be present in the mixture, alternative treatment agents and processes should be considered.

With this result it is possible to reflect back on a previous paragraph in this section that discussed the capability of active carbon to remove ferric chlorides. It was not determined whether the iron impurities in the aforementioned experiment were ferric chlorides, ferrous chlorides or other iron compounds, but since the former two chlorides are inclined to form during chlorination of rutile, it is highly possible for it to exist in the crude $TiCl_4$. Hockaday and Kale (2016) performed the distillation with a fixed boiler temperature of 200°C which is substantially lower than the 425°C that was required for reaction of ferric chloride (Equation 2-21), as determined from extrapolation of the graph of change in Gibbs free energy. It is thus conceivable to suggest that this reaction occurs below 200°C and that WMO is an appropriate treatment agent for removing ferric chlorides or the alternative conclusion is that relatively low levels of ferric chloride will not form low-boiling complexes as initially suggested. It is then viable to consider the fact that $TiCl_4$ (boiling at 136°C) could be easily separated from ferric chloride (with a boiling point of 315°C) by a normal distillation.

Pivotal factors for identifying a suitable treatment agent are cost and availability. Oleic acid, potassium oleate, sodium oleate and copper particles are readily available and should not be troublesome to acquire. Prices of these materials vary greatly though and due to the difference in dosages, production costs differ even further. Selling prices for the treatment agents were requested from an international chemicals supplier. These prices excludes shipment costs and are only for comparative purposes. It was decided that high purity substances should be used to prevent addition of impurities to an existing purification system. Oleic acid is purchased in the liquid state, while the prices of potassium oleate and sodium oleate are for the powder of those compounds. The size of the copper particles are 1 µm. The relevant purities, selling prices and implementation costs for each agent are listed in Table 2-11.

Table 2-11: Purities, selling prices and implementation costs of treatment agents

Treatment agent	Purity	Price (USD $/kg)	Dosage (wt%)	Cost ($/t $TiCl_4$)	Reference of price
Oleic acid	99.5%	6.70	0.15	10	Alibaba (2018b)
Potassium oleate	99.0%	10.50	0.25	26	Alibaba (2018c)
Sodium oleate	99.0%	9.50	0.25	24	Alibaba (2018d)
Copper particles	99.9%	78.00	1	780	Alibaba (2018a)

The utilization of copper powder as a treatment agent is thus substantially more expensive than WMO alternatives. The process costs are further increased by associated washing expenses. Washing of the copper particles is required to remove accumulated impurities, as described by the processes of Wang *et al.* (2009) and Wang *et al.* (2011). The cleaned copper should be available to be used again, which will have financial benefits to the economic variables of that process. On the contrary, the price of WMO treatment agents are considerably lower and lesser dosages than that of copper are applied. Oleic acid comes across as being the best option when one only considers the economic aspects of its acquisition. Hockaday and Kale (2016) stated that after distilling the $TiCl_4$ that were respectively treated with oleic acid, potassium oleate and sodium oleate, sludge residues remained in the reboiler. These residues were very hard to remove from the surface and could not successfully be rinsed off or dissolved in water. In cases where the treatment agent and impurities escape the distillation column through the distillate, the sludge could have detrimental effects to downstream units and heat transfer efficiencies, starting with the condenser. This will necessitate the implementation of regular shutdown and cleaning or maintenance operations, which negatively affects production and thus carry disadvantageous economic implications. This phenomenon corresponds with the findings of Stoddard and Pietz (1947), where it is stated that the oil decomposes thermally in the still boiler at temperatures higher than 170°C. These temperatures are often obtained during the latter part of the distillation when smaller amounts of liquid is still present in the column. The decomposition products that form are particularly difficult to remove from the distillate. A distillation column that is heated by steam and operates between 5 and 8 bar is recommended to aid in the prevention of superheating the treatment agent. Hockaday and Kale (2016) proposed a possible alternative. The consideration is to use carbonaceous reagents that are less likely to polymerize, as it is suggested that the fouling are caused by polymerization of the WMO. Emphasis was placed on the possibility of using alkanes, alcohols or esters to prevent polymerization.

2.4.2.1.4 Alkanes, alcohols or esters

Based on that recommendation, soya oil was identified as a possible treatment agent that could be used for removing metal chloride impurities from titanium tetrachloride. Soya oil is found in the soya bean and is mainly composed of glycerol. Glycerol consists of esters, but also alkene containing fatty acids. The alkenes could serve to be a problem as it is inclined to polymerize. Crane (2014) completed a thesis on the chemical mechanisms behind the use of soya oil to separate $VOCl_3$ from $TiCl_4$. He found that soya oil sufficiently purified titanium tetrachloride as the $TiCl_4$ coordinated with the ligands without actually disrupting it, while $VOCl_3$ reacted with the ligand by sacrificing a chlorine atom. It is based on the difference in reactivity that a separation mechanism can be implemented. Nuclear magnetic resonance (NMR) spectroscopy was used to analyse the soya oil and it was found that oleic acid is a major constituent, along with linoleic acid, α-linoleic acid and stearic acid. These results thus correlate with the findings of Hockaday and Kale (2016) on the applicability of some of these acids. The purification process that was studied are being implemented at Huntsman Pigments, which is an American multinational pigment company (Crane, 2014). In this process the metal chlorides (iron, aluminium and vanadium) were removed before the distillation step to produce $TiCl_4$ of high purity for pigment production. Crane (2014) still found that fouling was a critical problem in downstream heat exchangers. Figure 2-5 was taken at Huntsman Pigments' titanium dioxide pigment plant. This could be due to polymers forming in the solution from the alkene-containing fatty acids or due to soya oil and other organic compounds escaping the distillation column through the distillate.

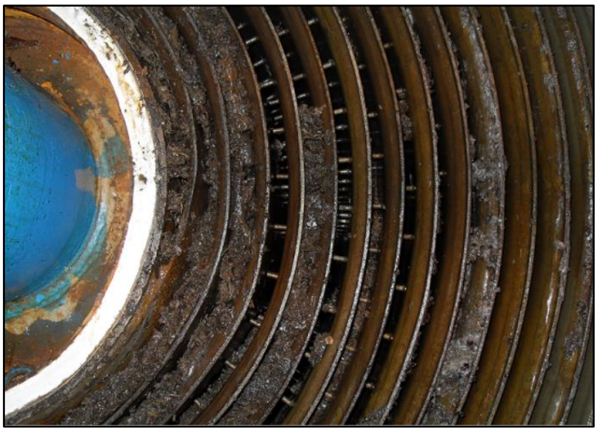

Figure 2-5: Fouling in heat exchanger at Huntsman Pigments' TiO_2 plant (taken from Crane (2014))

In summary, it is thus evident that these oils serve as an acceptable treatment agent for removing metal chloride impurities from $TiCl_4$, but cause excessive fouling in downstream units. This in turn has severe impacts on plant efficiencies and requires regular downtime for cleaning and maintenance operation. Downtime has adverse effects on production costs, but should not be neglected as it is essential for production and safety requirements. The necessity for downtime should thus be minimized. The applicability of using esters as treatment agents to avoid polymer residues could not be accurately determined as alkenes were also present in the soya oil. Copper is a suitable alternative for producing high purity $TiCl_4$ and does not cause fouling in process units, but is between 30 and 80 times the cost of WMO alternatives (see Table 2-11). Low-cost treatment agents that won't cause fouling have not been implemented and a need exists for the determination or development of such a product. Further studies on the applicability of alkanes, alcohols and esters are being conducted by Hockaday and Kale (2016) at the time of this study and should definitely be considered in future applications.

Patents that are listed in Table 2-8 that have not been discussed yet include adsorption of impurities with alumino-silicate materials and using hydrogen sulphide as a treating agent.

2.4.2.1.5 Alumino-silicate materials

Adsorption with alumino-silicate materials is a patent developed by Derecskei *et al.* (2017) and it is registered as an effective method for removing numerous impurities from titanium tetrachloride.

The list of impurities includes compounds of carbonyl sulphide, sulphur dioxide, phosgene, hydrogen sulphide and carbon disulphide. Furthermore, it also includes chlorides and oxychlorides of post transition metals, metalloids, zirconium, hafnium, iron, chromium, copper, carbon, manganese, vanadium, nickel and combinations of these stated compounds. Alumino-silicates are minerals that consists of aluminium, silicon and oxygen, along with counter-cations that enable ion exchange mechanisms (Walkley *et al.*, 2016). The crux of this concept is that the choice of alumina-silica adsorbent is determined by the impurities that are present and is thus dependant on the properties and geometries of the chemical contaminants. In this manner, the relevant impurities can be removed from the $TiCl_4$ by bringing the liquid in contact with the appropriate alumino-silica material. Impurities will adsorb onto the alumino-silicates and purified $TiCl_4$ will exit the contacting vessel as the product stream. The adsorbent can be regenerated and impurities washed off in order for it to be used again. A favourable factor of this purification method is that it also effectively removes tin (Sb) chlorides, which is not the case for active carbon according to Derecskei *et al.* (2017). Tin impurities are not commonly found in $TiCl_4$ and a decision should not be based solely on this factor, but it should be noted in cases where tin compounds could be present.

Although the concept of this invention seems sensible, it is still relatively new and the applicability and financial feasibility has not yet been fully determined through comprehensive studies. This is definitely a possible purification method for $TiCl_4$, but as an in-depth study on its applicability did not fall within the scope of this project, it was not considered as the main solution at the time of the study.

2.4.2.1.6 H_2S

The final treatment agent that is discussed which has been used in various patents is hydrogen sulphide (H_2S) gas (Sironi *et al.*, 1971; Guthrie, 1956; Meyers, 1946). For this method, vapour $TiCl_4$ should be cooled down in a spray-quencher evaporator. During this step, H_2S should be added. Purification is obtained by the formation of solid particles when the metal compounds bind with H_2S, while purified $TiCl_4$ will leave the column in the vapour phase. This technique is able to remove a vast range of metal chloride or oxychloride impurities from the titanium tetrachloride. It also does this to great extent, since Sironi *et al.* (1971) state that it will deliver $TiCl_4$ with a vanadium content of lower than 1 ppm.

The drawback of utilizing H_2S as a treatment agent is that it is an extremely toxic substance (Beauchamp *et al.*, 2008). The use of such a chemical has considerable effects on the safety protocols that need to be implemented for usage, handling and transportation of the compound. Environmental regulations are also strict with regard to storing and disposal of H_2S. The norm in recent years is to avoid risks with regard to poisonous materials and rather use alternative methods and substances, should it be available. Since numerous other purification procedures exist, H_2S treatment was not considered.

2.4.2.2 Distillation

After addition of the necessary treatment agent or completion of the determined dosing method, distillation of the titanium tetrachloride is carried out in a distillation column. Effective separation of the $TiCl_4$ from the determined impurities can be obtained by performing the distillation at the correct process conditions in a conforming vessel.

2.4.2.2.1 Pressure

For this procedure it is consequential that contact between the $TiCl_4$ liquid and moist air is averted at any stage in the process. Xiong *et al.* (2012) achieved this by performing a vacuum distillation to first remove any moist air from the system before $TiCl_4$ is introduced. Consequently, no or minimal corrosive acidic mist will develop in the airtight system as the formation of hydrochloric acid is inhibited.

2.4.2.2.2 Temperature

In the distillation performed by Xiong *et al.* (2012), the liquid in the bottom of the column was superheated to 148°C in order for saturated $TiCl_4$ vapour to leave the column through the distillate. The negative pressure at which the column operates is not mentioned and the altered boiling point of $TiCl_4$ could therefore not be determined.

For the batch distillation that was conducted by Hockaday and Kale (2016), the bottom of the column was heated from room temperature up to a set value of 200°C while no pressure alteration was implemented.

The method of separation and purification of $TiCl_4$ from ferric chloride ($FeCl_3$) through distillation was first developed by Ignace Joseph Krchma in 1946 and patented in 1949 (Krchma, 1949). In this patent, the $TiCl_4$ and $FeCl_3$ are subjected to a heat of ideally between 180°C and 300°C in order to obtain proper vaporization of titanium tetrachloride. $TiCl_4$ that leaves the vessel will initially exit as a saturated vapour at 136°C, but as the temperature of the liquid increases and the $TiCl_4$

concentration in the mixture decreases, the temperature of the vapour will rise to superheated conditions. Special care should be given to regulate heat addition to the vessel in order for the exit temperature of the vapour to remain between 140°C and 160°C. This will ensure minimal vaporization of ferric chloride and prevent excessive energy expenditures.

The operating temperatures and pressures of the column is highly dependent on the impurities present in the $TiCl_4$. Most references recommend some degree of superheating to the discharging vapour. This is obtained by superheating the liquid in the bottom of the vessel to a larger extent. In this matter, careful considerations should be made to take into account that boiling points of some impurities fall within or are close to proposed temperature ranges. From Table 2-7 it is evident that $AsCl_3$ (130°C), $AlCl_3$ (183°C) or even $SbCl_3$ (220°C) would also vaporize if present in the liquid. Another factor that promotes mindful temperature considerations is the phenomenon of oil that decomposes in the vessel above 170°C (Stoddard & Pietz, 1947). As discussed in the previous subsection, white mineral oils are often used in the pre-treatment of $TiCl_4$ to prevent vanadium impurities from escaping in the distillate.

2.4.2.2.3 Fractional distillation

For instances when impurities with lower boiling points than $TiCl_4$ exist in the liquid, such as $SiCl_4$ (58°C) or $SnCl_4$ (114°C), it would be a viable option to conduct a fractional distillation to obtain uncontaminated $TiCl_4$. This type of column operates on the basis of removing constituents with different boiling points from the distillation column at various temperature levels along the column. In this manner the mixture inside the column can be separated into pure fractions of the original composition. This is the optimal method of separation to use when pure fractions of multiple compounds in the feed need to be obtained. It is also used in general when the boiling points of the composing chemicals lie within 25°C of each other (Fair & Kister, 2018).

Turner *et al.* (2001) do however state that with careful monitoring of the reaction temperature during rutile chlorination, it is possible to prevent the chlorination of silica in order for it to remain in the chlorinator residue. The existence of $SiCl_4$ impurities in $TiCl_4$ is thus improbable in recent times, but since this project focuses on demilitarized $TiCl_4$, it is in most cases undisclosed how the $TiCl_4$ was produced or what impurities were present in the acquired $TiCl_4$ that was used to fill the mortars. It is therefore recommended to implement a fractional distillation process to remove high- and low-boiling point compounds from the $TiCl_4$ in cases where both these types of impurities are present.

2.4.2.2.4 Two-step distillation

It should be noted that the use of a fractional distillation column is not mandatory for removing a single pure substance from mixtures that contains both impurities with higher and lower boiling points than that of the desired product. India’s Defence Research & Development Organisation (2018) achieves $TiCl_4$ purification by conducting a two-stage distillation. This technique entails the use of the first distillation column to boil off all impurities with lower boiling points than $TiCl_4$ from the liquid. $TiCl_4$, along with high-boiling impurities, are transferred in the liquid phase to a second column where an additional distillation is carried out to separate the $TiCl_4$ through the distillate. Seader *et al.* (2011) also discussed this technique and state that the holdup for a single fractionating column is much less than the holdup in two distillation columns. Holdup refers to the material that remains inside the column that cannot be extracted completely during a distillation. This includes liquid on the trays or on the packing or even droplets on the inner wall of the vessel. These volumes are thus lost and these losses carry financial burdens which should be managed. It can be concluded that careful consideration should be given to procurement and operating costs of these different type of processes to determine which option would be optimal for the applicable scenario of this study.

2.4.2.2.5 Distillation followed by partial condensation

A third possibility of purification trough distillation is to remove the vapour product along with other low-boiling compounds through the distillate and only cool it in the condenser to an extent that the saturated vapour product is condensed to a saturated liquid. When this stream is carried to a drum the product can be collected as a liquid at the bottom of the vessel while the low-boiling impurities is removed at the top of the drum as a vapour. With that being said, this technique does deliver a much lower degree of separation since it fosters contact between the pure $TiCl_4$ and vapour impurities after the distillation is completed (Seader *et al.*, 2011).

2.4.2.2.6 Packing versus trays

Turner *et al.* (2001) comment on the significance of theoretical stages in the distillation column and how a higher number of trays gives rise to obtaining a product of higher purity. Trays enhance contact between the vapour and liquid inside the column. More contact between the vapour and the liquid implicates that more opportunities are being created for the high-boiling compounds in the vapour to release heat and condensate to the liquid form. This energy then aids in vaporizing low-boiling compounds from the liquid to rise up in the column. The end result is a greater degree of separation. Stoddard and Pietz (1947) alternatively suggested the use of random packing in the distillation column to optimise heat transfer and maximize the purity of the obtained product. Packed bed distillation columns is also implemented in the two-stage distillation process for obtaining pure $TiCl_4$ in India's titanium sponge production plant (Defence Research & Development Organisation, 2018). Fair and Kister (2018) explains how trays are more suited for certain processes, while packing is ideal for other processes. These processes vary mainly in terms of operating pressures, column design and chemical characteristics of the mixture to be fractionated. It is thus not possible to conclude beforehand that one technique is more advanced than the other and the optimal technique for this study was based on the attributes of the distillation process.

2.4.2.2.7 Batch versus continuous operation

Another major factor to consider in the distillation column design is whether the distillation is conducted as a batch or as a continuous process. In a batch process the column is filled with a fixed volume of the feed mixture and the distillation is conducted on the contents of the column. Product are being removed from the distillate and / or bottom of the column, but no additional feed mixture is added during the distillation. On a continuous scale the column is operated at steady state where feed mixture is constantly added to the column, usually in equal amounts to the aggregate quantity that is being removed (Fair & Kister, 2018). Batch processes hold numerous advantages over continuous distillation, but these are accompanied by the challenges associated with this type of processes. Most of the advantages are based on the flexibility of a batch unit. It can easily incorporate alterations in the feed mixture of different batches to still deliver a product that complies with defined specifications. This makes it favourable for recycling or recovery processes where feed compositions are not uniform (Costello, 2016; Hasebe *et al.*, 1995). Because of the flexibility of a batch process, it is also easy to make adjustments to the setup or operating conditions in circumstances where product requirements vary. This feature is particularly auspicious for purification or recovery processes where certain environmental regulations have to be met, since these specifications are amended from time to time or are adapted based on location (Hasebe *et al.*, 1995). Costello (2016) and Klingberg (2000) state that another factor to take into account in these considerations is the higher product purity that can be obtained in a batch distillation. Cases exist where a continuous steady state process will be optimal over a batch distillation. The major drawback of batch distillation units is its substantial energy consumption compared to continuous setups. Thus, although operation of a continuous distillation system may be more complicated and have higher unit costs than batch systems, it is more profitable in the long run when accounting for production costs (Klingberg, 2000). Another emphasized distinction between these two operation modes is that batch distillation is more suitable for processing smaller quantities, opposed to continuous setups that are ideal for large-scale industrial processes. This is contributed by the fact that capacities of a continuous distillation process are not limited by the size of the still pot in the column, which is the case for batch systems. This makes batch distillations an exemplary option for demilitarization practices, since the obtained feed volumes are inconsistent and could be relatively small in same cases.

Different recommendations from literature are based on different scenarios with dissimilar process inputs and variations in product requirement. An example of this is how the goal of the studies by Hockaday and Kale (2016) and Xiong *et al.* (2012) was to remove vanadium impurities, while the focus of Turner *et al.* (2001) was to purify $TiCl_4$ from $SnCl_4$, $SiCl_4$, $FeCl_3$ and $AlCl_3$. Stoddard and Pietz's (1947) primary focus was only placed on separating $TiCl_4$ from $SiCl_4$ when Krchma (1949) on the other hand, mentions metal halides in general, but only considered iron chlorides in his study. The most applicable distillation process that was implemented in this study, along with its operating parameters, was determined in the technical analysis section (Chapter 3).

2.5 Processes to be evaluated

The identified applications and purification processes that were evaluated in the techno-economic evaluation are:

1. Reduction of purified $TiCl_4$ to Ti sponge using magnesium;
2. Oxidation of purified $TiCl_4$ to form TiO_2 pigment;
3. Processing demilitarized $TiCl_4$ to prepare $TiCl_4$ of adequate quality that can be re-used in smoke mortars.

It should be noted that the Ti sponge and TiO_2 pigment production processes require a preceding purification process of the demilitarized $TiCl_4$ feed.

Other options exist for treating or handling demilitarizes $TiCl_4$, which includes:

- Neutralization with NaOH (Shon *et al.*, 2009);
- Disposal by a chemical waste disposal company;
- Possibility of supplying to future consumers.

These options are not considered as recycling processes though and do not meet the aim of this project. The necessity for finding a suitable recycling project is attributed to the aim of demilitarization in general, which reads “zero wastes – only by-products”.

The option of supplying the obtained chemical to future consumers does not exist currently, since no local processes or applications that make use of this volume of $TiCl_4$ as feed or intermediate product is operational. A future project is currently being developed though, which entails the construction of a TiO_2 pigment plant in Richards Bay, South Africa (Mining Online, 2017). Production of this plant is scheduled to start in 2020. Reputable information that deemed this development to be on track could not be obtained. It was also not possible to confirm this business as a potential demilitarized $TiCl_4$ consumer. Once these two aspects can be guaranteed, this option should be considered as a viable option in evaluations to determine if it is an improved solution.

The determined process from the techno-economic evaluation are compared with these options in Chapter 5 to give a general indication of the financial feasibility of the established solution.

2.6 Conclusion

This chapter initially discussed the chemical properties of titanium tetrachloride. It can be concluded from this chapter that titanium tetrachloride is highly reactive towards moisture and is a particularly corrosive and toxic compound. Both titanium tetrachloride and hydrochloric acid, which is a by-product of the $TiCl_4$ hydrolysis reaction, provoke major discomfort and irritation to living entities and high concentrations can cause severe damage to the respiratory and ocular systems. It should thus be regarded as an indisputable importance to prevent these chemicals from entering the atmosphere and find environmentally friendly recycling processes.

Attention was then turned to the importance of obtaining titanium tetrachloride of a high purity and the relevant purification methods that could be implemented are discussed. A normal distillation at an operating temperature near the boiling point of $TiCl_4$ will separate most impurities from the liquid. However, some metal chlorides and oxychlorides possess boiling points quite close to that of $TiCl_4$ and additional purification processes or treatment agents should be applied. Hydrogen sulphide has been dismissed as treating agent due to its toxicity and the hazards involved with its usage, while copper particles has been identified as a clean but extremely expensive solution. White mineral oils have been proven from literature to be feasible treatment agents for removing impurities that cannot be separated simply by a distillation, but prompted the requirement for regular downtime due to fouling that occurs in downstream units. It was suggested that excessive fouling was a result of polymerization reactions from the WMO. Future studies can thus focus on determining a treatment agent that consist of alkanes, alcohols or esters, since these groups are less likely to polymerize. An alternative purification method emerged, which is the adsorption of impurities onto an alumina-silicate material. What makes this technique effective is that the choice of alumino-silicate are determined by the properties and molecular geometries of the contaminants. Any metal compounds could thus be separated from the liquid. This technology is still relatively new though and it's financial and practical applicability have not yet been determined. This purification process was thus not regarded as the primary method, but should definitely be considered in future applications. The deduction was made that the appropriate treatment agent and its necessity will be determined by the impurities present in the $TiCl_4$, the prerequisites of the relevant processes and the cost of implementing these treatment agents.

After relevant pre-treatment methods or dosing of treatment agents were conducted to prepare the $TiCl_4$ for purification, a distillation is performed on the liquid to separate pure $TiCl_4$ from dissolved and insoluble impurities. Many factors have to be accounted for in the distillation to determine the most fitting mode of operation at the correct operating conditions. This includes operating pressures, temperature profiles, heat transfers techniques, distillation column designs, batch or continuous systems, *etc*. Since these specifications are mainly dependent on the extent of the separation that is required to purify the $TiCl_4$, they have to be determined once the initial purity is established and contaminants in the feed are identified.

The current industrial process for titanium production, which is the Kroll process, was studied and discussed. The major challenges of this process are its slow production rates and high production costs. This greatly contributes to the cost of the metal. The Kroll process was compared to the Hunter process, which is another method for titanium production in the industry. With its associated challenges, the Kroll process still seemed to be the best option between the two existing methods. This was predominantly due to the favourable production and capital costs of the Kroll process as opposed to that of the Hunter process.

Various alternative processes exist for producing pure titanium from $TiCl_4$. These processes were stated and discussed in accordance with a ranking that were determined from Van Vuuren (2009) and Van Tonder (2010). The evaluation criteria for their studies were based on production and capital costs, research conducted and academic coverage, process readiness for commercial application and the complexity of process alternatives. The Armstrong, TiRO and SRI processes were identified as potential improvements over the existing industrial Kroll process. Adequate information and process details of these methods are still required before it can be considered as possible solutions to this study though. Of these three processes, only the Armstrong process has been implemented for industrial titanium production, but due to trademark rights the particulars of this process have not been published and it could thus not be simulated or modelled accurately. Once the necessary information on these processes has been developed or obtained, it should definitely be considered as possible solutions for future evaluations that are similar to this study.

The Kroll process was selected as the preferable choice for titanium production from $TiCl_4$ for this study. This process is therefore applied as one of the options for recycling demilitarized $TiCl_4$ in the techno-economic evaluation.

The second process to be identified as a possible solution for recycling demilitarized $TiCl_4$ was the production of titanium dioxide pigment through the chloride process. For this process high quality titanium-bearing ores are chlorinated to produce $TiCl_4$. The titanium tetrachloride is purified and oxidized at extremely high temperatures to produce TiO_2. The titanium dioxide is then fed through finishing steps to ensure that the pigment conforms to the necessary standards (size, quality, *etc.*) and is chemically treated to impart the necessary properties (lightfastness, thermal and chemical resistance, colour, pigment opacity, *etc.*).

The physical end chemical properties of the pigment contribute greatly to the applications that the pigment are implemented in. The difference in chemical properties does not significantly influence the selling price of the various grades of pigments, but a remarkable increase in selling price are observed when the particle sizes of the pigments are reduced beyond the micro scale to nano measurements. The applicable physical end chemical properties that are required for the pigment produced in this study were identified by determining parameters that are financially beneficial. These values are predominantly determined by the demands of the market, as well as the required capital costs and prospective operating costs.

The third application that is considered in the techno-economic evaluation is purification of the demilitarized $TiCl_4$ and reimplementation of the liquid in the filling of new smoke mortars. It was assumed that the quantities of titanium tetrachloride available would satisfy the quantities required since the source of the chemicals is related to the future application in the sense that old mortars are demilitarized and new mortars will be acquired. The objective of the purification steps is to remove any corrosion products, contaminants or unstable chemicals that could have entered the $TiCl_4$.

Other diverse uses of $TiCl_4$ include implementation as a catalyst, coagulant, coating and treatment agent, *etc.* The challenge of this study is that an option has to be identified that is sustainable, financially feasible and that utilizes the supplied quantity of $TiCl_4$ from the problem statement. The final possibility to consider is to beneficiate the demilitarized $TiCl_4$ and supply it to consumers.

The appropriate process (or combinations thereof) is determined by the techno-economic evaluation in the upcoming chapters.

CHAPTER 3: TECHNICAL ANALYSIS

3.1 Introduction

The chapter covers the technical analysis of the study. Information and process details from the literature survey are used to analyse the selected processes to determine each option's practicality. The main analysing method is a dynamic simulation with a preceding theoretical mass balance.

The prerequisites of these methods are firstly a quantification of the composition and quality of the available $TiCl_4$, followed by a determination of the feedstock and product stipulations for each process.

3.2 Sampling

To analyse the liquid from the demilitarized smoke mortars, samples of $TiCl_4$ have to be taken. Due to military confidentiality and the purpose of these mortars, undisclosed quantities is stored in unpublicised locations. It would thus require a substantial amount of administrative permissions and confidentiality agreements before it is possible to determine the sample population that is relevant to this study and its problem statement. It is therefore challenging to utilize a statistical sampling approach to determine what samples would best represent the available population. Other complications could include the safety measures for handling and sampling, transport arrangements for dangerous chemicals, costs of analyses, *etc.*

A possible alternative that emerged was to analyse a small number of samples with various production dates. From the results of these analyses it could be possible to determine the probability of variations in the compositions of different mortars. The objective is thus to determine from the initial samples if extensive deviations exist in the compositions of the demilitarized $TiCl_4$ and use those results to conclude if a complex statistical approach is required. Four batches of smoke mortars that require demilitarization were available to be sampled from. One set of mortars from each batch were supplied to be sampled and analysed for this study. Three of these batches consisted of 60 mm mortars, with the other batch containing 81 mm mortars. A single 60 mm mortar contains 255 – 275 g $TiCl_4$, while an 81 mm mortar is filled with 640 – 660 g $TiCl_4$. Additionally, an unused sample of the $TiCl_4$ that were to be used to fill new mortars was also obtained. The $TiCl_4$ from this sample was produced in 2016. The production dates, sizes and amounts of samples from each batch are listed in Table 3-1.

Table 3-1: Samples obtained for analyses

Production date	Size of mortars	Amount of samples
1975	60 mm	3
1980	60 mm	4
1981	81 mm	3
1983	60 mm	4
2016	N/A	1

The components that are mentioned during the sampling process are shown in Figure 3-1 to give a clear explanation of how the samples were obtained. Sampling was performed by trained staff who had the necessary training and implemented the required safety measures. The steps that were taken are listed as follow:

1. Before any investigations or assessments commenced the mortars were first made safe by removing the fuse, propellant charges and ignition cartridge from each mortar.
2. The secondary explosive was removed from inside the mortar and the area that contained the explosive was washed with a chemical solvent.
3. A hole was pierced by a sharp object in the inner shell that separated the secondary explosive from the $TiCl_4$.
4. The mortar was turned over and the liquid $TiCl_4$ poured out into a glass container. This step occurred in a fume hood.
5. The container was tightly sealed off and covered by layers of black paper.
6. The sample containers were packed in a travel-safe box and the mortar shell (with the attached tail) were removed by a third party for further processing.

It should be noted that this is not the optimal sampling method and that demilitarization processes have been designed to safely and cleanly remove the $TiCl_4$ from the mortar. These process have not been implemented at the time of this study though. By piercing the hole with a sharp object, some metal shavings and paint particles may have entered the liquid and are now present as insoluble solids in the sample. Handling of the $TiCl_4$ occurred in a fume hood to prevent exposure to the titanium-complex particles and HCl gas that formed when $TiCl_4$ came in contact with moist air. A glass container was preferred over a plastic or metal container, since the latter two materials are more likely to contaminate the liquid sample. By finally covering the glass containers with thick layers of black paper it was possible to block off any UV rays from entering the container, since exposure to this light will cause a breakdown in the molecular structure of $TiCl_4$ to yield $TiCl_3$ and chlorine (Diem & Kennedy, 1978).

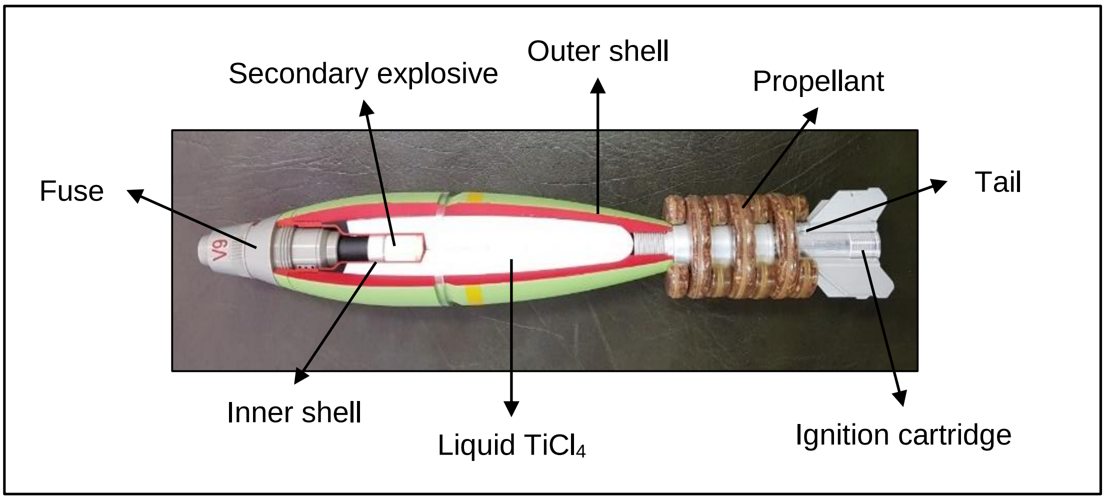

Figure 3-1: Breakdown of a mortar

Samples that were to be analysed were left for a month before the analysis occurred. During this time the insoluble metal and paint particles settled to the bottom of the container. These containers were then moved as little as possible when the required volume of liquid was extracted from each sample to prevent the sediment from rising and being present in the analysis.

Due to confidentiality reasons, no images of the sampling procedure are available.

3.3 Sample analyses

3.3.1 Identification and quantification of common impurities in $TiCl_4$

The first objective was to determine the impurity compositions of the $TiCl_4$. Since these samples are more than 20 years old, it is expected that soluble contaminants could have entered or dissolved in the liquid. Documentation and specifications of the $TiCl_4$ that was used to fill the mortars are not available from the supplier. The company that manufactured these mortars currently has a stipulated purity of 99% for the $TiCl_4$ that is used to fill new smoke mortars (Rheinmetall Denel Munition, 2017). It is however not known when this specification was introduced, but it is expected that $TiCl_4$ within the same quality range was used over the last 40 to 50 years since it does not require extreme technological advancements to obtain a $TiCl_4$ purity of 99%. This expectation is backed up by the company that imports $TiCl_4$ and supplies it to the manufacturer of these smoke mortars. In a personal interview this supplier stated that it has delivered $TiCl_4$ to the applicable company for more than 25 years at a fixed quality specification of 99% or higher (Wagner, 2018). It is thus improbable to find substantial levels of impurities in the demilitarized $TiCl_4$.

To determine the composition of high-purity substances, it is preferential to use an analysing method that does not measure the concentration of the main compound. This promotes detection and quantification of minute volumes of impurities, as the scale of the analysis is not expanded by the substantial presence of the main compound. Developing or finding existing methods that are able to omit the detection of the main material, but still accurately quantify the presence of all other impurities, is quite a challenging issue though.

Additionally, $TiCl_4$ is an extremely challenging compound to handle, since any exposure of the liquid to moist air will result in hydrolysis of the $TiCl_4$ and cause smoke formation. Hockaday and Kale (2016) also state that this will cause the formation of oxygen compounds and dissolved HCl in the mixture, which will give a yellow colour to the initially clear liquid. Great care has to be applied in conjunction with sufficient knowledge to effectively handle, prepare and analyse $TiCl_4$ samples.

Various possible options were explored to find an analysis that will identify and quantify the impurities in the system, while disregarding the titanium tetrachloride. An optimal analysing method could not be identified. However, an external company that has ample experience in handling and examining $TiCl_4$ samples was distinguished from the possible solutions. This analytical service division make use of inductively coupled plasma optical emission spectrometry (ICP-OES) to determine and measure the impurities that are present in the $TiCl_4$. ICP-OES is a popular method of elemental analysis since it is less complex, less expensive and less time-consuming than many other analytical methods. Furthermore, it can adequately quantify the concentrations of most constituents that are above the detection limit, which is usually about 2 ppm for most elements (Boss & Fredeen, 2004; Hou & Jones, 2000). This method can easily detect numerous elements, with the exceptions being radioactive components, elements from the halogen group and contaminants that are present in the utilized gas (Hou & Jones, 2000). Additional measures or treatments are required before these elements can be identified.

Relevant steps to prepare the samples for ICP-OES analysis are given in Annexure A.1.

Since the cost of analysis greatly increases with each element's concentration that needs to be quantified, the company's spectrometer was only calibrated and set to detect the most common impurities in crude $TiCl_4$. These elements are aluminium, copper, iron and vanadium. The results from the ICP-OES analysis are given in Table 3-2.

Table 3-2: Concentration of metal impurities in each sample (ppm)

Sample No.	Al	Cu	Fe	V
1975 (1)	<1	<2	15.6	<2
1975 (2)	<1	<2	4.71	<2
1975 (3)	2.57	<2	7.74	<2
1980 (1)	<1	<2	3.81	<2
1980 (2)	<1	<2	<2	<2
1980 (3)	<1	<2	12.5	4.69
1980 (4)	<1	<2	<2	<2
1981 (1)	<1	<2	<2	2.3
1981 (2)	<1	<2	<2	<2
1981 (3)	<1	<2	<2	<2
1983 (1)	<1	<2	<2	<2
1983 (2)	<1	<2	<2	<2
1983 (3)	<1	<2	<2	3.75
1983 (4)	<1	<2	<2	<2
2016 (1)	<1	<2	<2	<2

It is evident from the table that most of these impurities have concentrations below the detection limit, which is 1 ppm for aluminium and 2 ppm for copper, iron and vanadium. Based on the results the samples can be considered free from copper and aluminium compounds. Since aluminium is only detected in one sample and on a level that is almost negligibly small, it was treated as an outlier. It is further recommended to perform secondary analyses or analyse additional samples prior to making any conclusions based on this single detection or before any measures are taken to attempt the removal of this element's compounds. Vanadium was detected in three of the samples, with each sample from a different batch. The concentrations of this metal is also very small and can be deemed quite insignificant. Iron compounds were detected in some of the samples, especially in the two older batches. Since the material of construction of these mortars is mild steel, a notable extent of contamination of iron compounds is expected in the liquid. However, to inhibit corrosion of the metal body of the mortar by $TiCl_4$ and HCl, the inner wall is coated with red oxide primer. From the obtained results it seems to be an adequate method for preventing iron impurities from dissolving in the liquid. As discussed in the Section 2.4, ferric chloride is only deemed problematic if it is present in large quantities. This corresponds with the findings of Kale (2018), who is a chief engineer at Mintek and has extensive experience with titanium compounds. He states that low concentrations of iron impurities can easily be removed from $TiCl_4$ by a distillation process and would not require further treatments.

Other elemental compounds may be and probably are present in the demilitarized $TiCl_4$, but were not tested for by the ICP analysis. These impurities are however not a major concern, seeing that it was indicated in Section 2.3 ($TiCl_4$ purification) that the most troublesome impurities to remove from $TiCl_4$ are vanadium and excessive levels of iron compounds. The other impurities could easily be removed by a distillation step, with only a few exceptions (aluminium, tin, *etc.*). Aluminium compounds evidently are not present in the liquid, while the probability of tin compounds existing in the $TiCl_4$ is highly unlikely as it is not commonly detected in titanium-bearing ores. However, if it is suspected that these or any other compounds are present in the liquid or if it is commonly found near the titanium-bearing sources of the $TiCl_4$, it could be detected and quantified by further analyses. The required methods or standards do entail additional funds though.

3.3.2 Determination of $TiCl_4$ purity

Since only the concentrations of the common impurities in $TiCl_4$ was measured by the ICP-OES analysis, it is still not clear what purities of $TiCl_4$ each sample possesses. A dedicated method of determining the composition of $TiCl_4$ in a liquid was not available. A possible solution that was identified was to quantify the chloride in the solution by means of analytical chemistry and relate this answer to the quality of the $TiCl_4$ sample.

Some of the preparation and analytical steps that were taken for this analysis are stated in Annexure A.2, along with the calculations that were performed. $TiCl_4$ purities that were calculated by determining the chloride in solution of each sample are given in Table 3-3.

Table 3-3: $TiCl_4$ purities of samples

Sample No.	Purity
1975 (1)	97.0%
1975 (2)	96.6%
1975 (3)	97.7%
1980 (1)	97.7%
1980 (2)	98.5%
1980 (3)	98.5%
1980 (4)	96.2%
1981 (1)	96.6%
1981 (2)	97.3%
1981 (3)	97.3%
1983 (1)	97.3%
1983 (2)	98.1%
1983 (3)	98.1%
1983 (4)	97.3%
2016 (1)	98.1%

The prescribed purity of $TiCl_4$ to be used in smoke mortars is specified to be 99% or higher (Rheinmetall Denel Munition, 2017). The values in Table 3-3 is quite high and rather close to the prescribed $TiCl_4$ purity of 99%. It should be noted that the accuracy of calculated $TiCl_4$ purities from the chloride in solution concentrations can be influenced by the presence of other metal chlorides. However, results from the ICP-OES indicated that the common metal impurities are essentially absent from most of the samples.

A factor that should be discussed is the calculated purity of the newly produced $TiCl_4$ sample from 2016, which is 98.1%. This batch of $TiCl_4$ was supplied to the mortar manufacturer above the specified purity of 99% and was accompanied with corresponding results from an external quality analysis that deemed the actual $TiCl_4$ purity to be 99.99% (Rheinmetall Denel Munition, 2017).

A possible limitation or potential inaccuracy of this analytical method that could influence the calculated results is the substantial dilution that is required before a meaningful result can be obtained. As stated in Annexure A.2, the $TiCl_4$ was analysed by titration with silver nitrate ($AgNO_3$). Only after the $TiCl_4$ concentration was lowered considerably, a titration could be performed that didn’t give immediate discolouration with the first drop being added to liquid. A dilution factor of 4000 was used in the calculations, which gives an indication of the extent of dilution that was required. It is highly possible that this negatively influenced the calculated results and can be ascribed as a reason for the difference between the supplied and analysed purity. By studying the volumes of $AgNO_3$ required for each titration (listed in Table A-1) it is evident that an error of 0.1 ml will only cause a deviation of 0.3 to 0.4% in the resulting purity. Due to the accuracy of the analytical techniques and instruments that were utilized in the titration, it is improbable that an error large enough was repeatedly made to cause a deviation of 1% in the calculated purity. The techniques and instrumentation that were utilized could thus not cause the deviated between obtained and expected results and could only contribute to it on minute levels.

Another potential contributing factor could be contamination that occurred during sampling procedures. Although measures were taken to hinder hydrolysis of $TiCl_4$, notable clouds of smoke were still visible when the liquid were transferred from the sample volume to a cooled solution by means of a pipette. It is thus reasonable to assume that minor levels of contamination occurred during the sampling and analysing methods.

Both the dilution and sampling techniques could cause deviations between the actual sample purity and the determined purity. Since these methods were repeated for all samples, the actual

$TiCl_4$ purities of the demilitarized samples might be marginally higher than the calculated purities. This won't affect the process selections or considered operating units though.

It should be mentioned that the samples were protected from UV light and that sampling, preparation and analysing procedures occurred in fume hoods at lowered temperatures, but there were still spells when the $TiCl_4$ was exposed to air. This possibly led to hydration of the reactive $TiCl_4$ by moist air to form titanium complexes with HCl and other oxygen-based contaminants in the liquid. It is definitely recommended to perform these steps in an inert environment in the future.

All the samples have purities of between 96% and 98.5%, which indicate that there are contaminants in the liquid. It would however be extremely expensive to attempt identification and quantification of all these impurities from the countless possibilities. The possible impurities and sample compositions are further discussed in the following sections.

Since these are the only two analytical techniques implemented to analyse the samples, a conclusion on the necessity to implement a complex statistical approach for sampling and analysing the entire population should be based on these results. It is clear that extensive deviations are not observed between the impurity concentrations and $TiCl_4$ purities of the various samples or batches. The same purification techniques are required to obtain $TiCl_4$ of adequate quality from a sample with a purity of 96% and that of 98.5%. Furthermore, since iron levels of all samples are relatively low and vanadium concentrations are below 5 ppm, no samples require additional purification techniques or unique treatments methods that differentiate it from the population. A complex statistical approach to determine sample selection and sample requirements is thus deemed not to be necessary.

3.3.3 Visual analysis

It became clear from the previous subsections that impurities are present in the demilitarized $TiCl_4$. To confirm these findings, focus is also placed on the visual aspects of the samples. Literature states that pure $TiCl_4$ is a clear transparent liquid. Images of the samples that were extracted from the smoke mortars are shown in Figure 3-2.

When the colour and clarity of these samples are inspected it can be seen that none of the samples are clear, while some samples aren't even transparent. Various colours can also be observed between samples in the batches from 1975, 1980 and 1983.

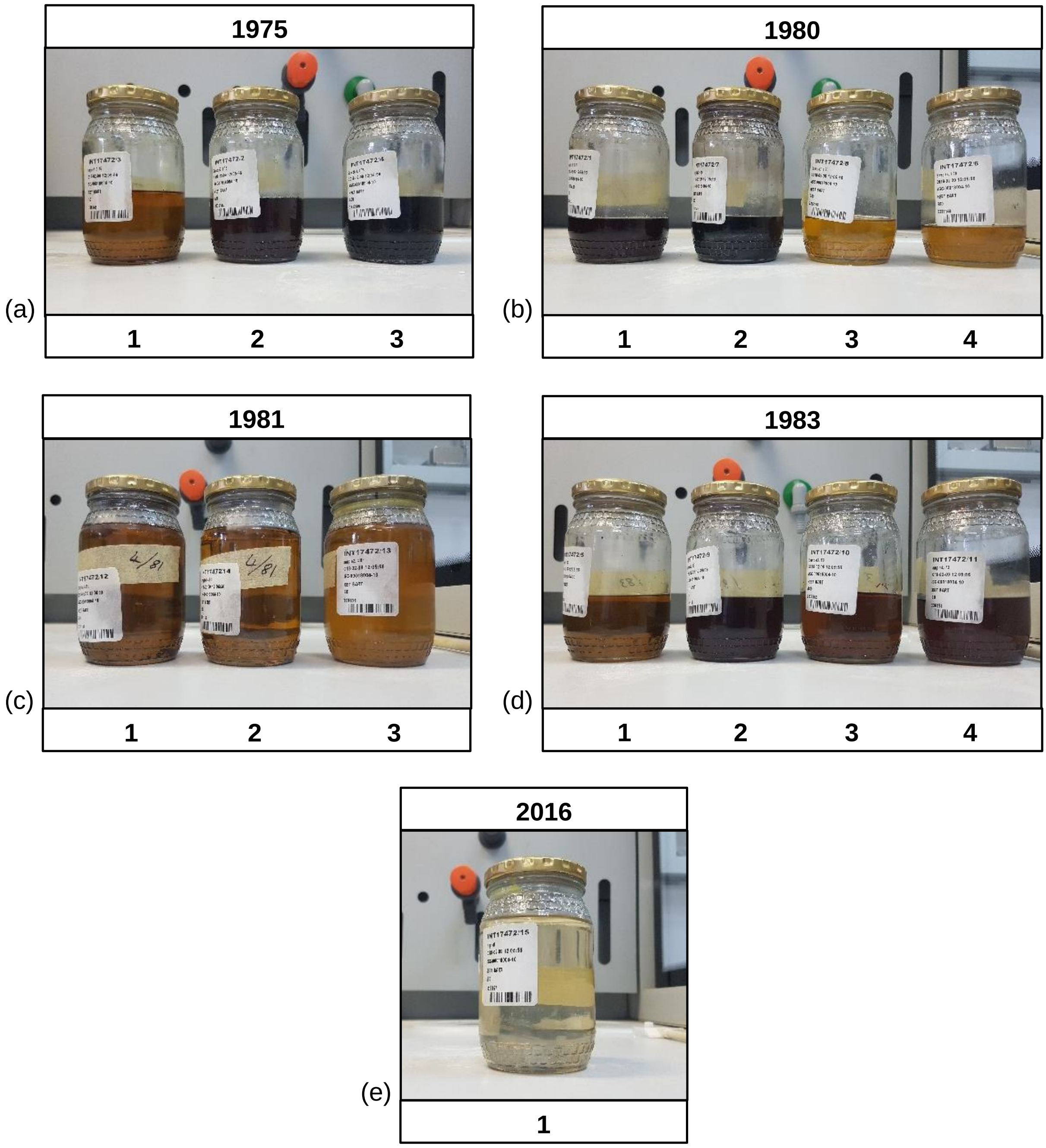

Figure 3-2: **Images of $TiCl_4$ samples that were produced in (a) 1975, (b) 1980, (c) 1981, (d) 1983 and (e) 2016**

A comparison between these images and the previous two analyses doesn't indicate any definite correlations to the impurities present or the $TICl_4$ purities and the colour of the liquid. The only batch where some consistency can be observed is that of 1981, which has an average purity of around 97% and impurity levels close to or below the detection limits.

One thing these images do emphasize is that there are impurities present in the liquid.

Several factors need to be considered and discussed to determine the possible causes that could induce the observed colours, since the liquid is expected to be transparent and clear. No cameras were allowed at the location where the samples were taken and the immediate colours that were observed directly after sampling could not be captured. All the above images were taken at the analytical laboratory after the necessary volumes of $TiCl_4$ were withdrawn from the sample. It is thus likely that oxidation, hydrolysis and decomposition by UV light occurred during the sampling, transport and sample preparation procedures. These occurrences would promote contamination of the liquid by oxide complexes, dissolved HCl and subchlorides of titanium. The sample with the least possible contamination is the $TiCl_4$ that was produced in 2016. As previously stated, this liquid has not yet been used in smoke mortars and has been obtained directly from the vessel that it was stored in by the supplier. Although this sample is transparent, it has a slight yellow colour and is evidently not clear. It is believed that this sample was colourless at the time when sampling was conducted, but no visual evidence are available to prove this suggestion. It is nonetheless known that formation of oxides, dissolved HCl and metal chloride impurities could result in the observed colouring of the liquid sample. Metal chloride impurities are expected to form between metal impurities that are present in the liquid and free chlorine ions that are released during decomposition of $TiCl_4$ when subjected to UV light. The presence of the mentioned contaminants is thus expected.

Several third parties from industry that have extensive experience with $TiCl_4$ were consulted about the dark and almost black colours that are evident in some of the samples. The uniform opinion was that $TiCl_4$ that was initially clear will not turn black over time and this appearance will only be prompted by external factors or contaminants.

A logical cause or contribution to the observed colours of the demilitarized samples is possible contamination between the liquid and the mortar body. As the results from the ICP analysis were discussed, it was determined that only low levels of iron are present in the earlier samples and these values decrease to below the lower detection limit in the later samples. It is also improbable that the $TiCl_4$ was contaminated by the red oxide primer used on the inside of the mortar, since this primer was specifically selected to prevent corrosion by $TiCl_4$ and contamination of the liquid. If some particles were dissolved in the liquid a red colour would also be expected, contrary to the yellow and black tones that are observed. It is thus assumed that negligible to no degree of contamination occurred between the $TiCl_4$ and the inside of the mortar.

A topic that needs to be addressed is the difference in colours of samples from the same batch. It is unexpected, since similar mortars were uniformly treated and filled by $TiCl_4$ from the same batch according to a consistent technique. The only potential possibility where a variation in the extent of contamination could occur, is where human labour or influences is being utilized. After a comprehensive study of the mortar production process and careful consideration of any possible substances that could enter the $TiCl_4$, a possible source was identified. After the mortars are filled with $TiCl_4$ an epoxy resin is applied to the thread of the mortar to completely seal the mortar and prevent any leakages into or from the mortar. This chemical is applied by hand and it is thus highly possible that generous volumes are applied to some mortars, which will cause the epoxy resin to run down the threads into the $TiCl_4$. In other instances, adequate or deficient quantities are used, which would result in no contamination of $TiCl_4$ by the sealant. Based on this perspective, it is valid to consider it is a possible explanation to the evident variation in colours between the different samples. The adhesive that was used in the production and assembly of these mortars were Araldite Rapid resin. It is a two component epoxy based adhesive where the two respective additives predominantly consist of bisphenol A-epichlorohydrin epoxy resin and 1,4-butanediol diglycidyl ether. It is unclear whether contamination by these components will cause a reaction with $TiCl_4$ to effect the evident dark or black tones, but it seems to be the only logical explanation at the time of this study.

A final phenomenon to be included in this consideration is the observed consistency in the colours of the samples that were produced in 1981. As mentioned in Section 3.2, these samples were taken from 81 mm mortars, which contain almost three times more $TiCl_4$ than 60 mm mortars. When this fact is taken into consideration with the discussed suspicion from the previous paragraph, it is viable to suggest that the greater volumes of $TiCl_4$ caused dilution of the Araldite adhesive to such an extent that it did not affect the observed colours of the samples.

Although these speculative explanations seem reasonable, further investigations and tests are required before this hypotheses can be proofed with concrete evidence.

3.4 Product stipulations

It is evident from all the previously discussed variables and requirements that these factors will influence the final properties and quality of the product of each application. It is also obvious that some stipulations require additional or more complex treatment processes to successfully obtain an acceptable product. These processes and conditions usually increase the production cost of the product. The problem is that sometimes products of lesser quality will still be acceptable for certain applications. Since adequate products of the lowest possible cost are requested, it is deemed redundant to apply unnecessary processes or conditions that are not required to produce the desired product. This reason, along with limitations in the titanium-bearing sources, resulted in different qualities of products being produced by the moderate commercial producers of metallic titanium, TiO_2 pigment and purified $TiCl_4$. To promote uniformity of these products in the industry, grades and standards were developed to classify these commodities and supply the relevant specifications that it should conform to.

3.4.1 Metallic titanium

The compositions and qualities of various companies' titanium sponge differ on noteworthy to negligible levels, with each having its own distinctive naming and classification system for the metal that it produces. However, uniform regulations were found and standards were developed by the American Society for Testing and Materials (ASTM), along with American Society of Mechanical Engineers (ASME), based on these determinations. Standard B 299 was established to specify the maximum levels of impurities in titanium sponge (ASTM International, 2002). This standard creates a distinction between three groups of magnesium reduced sponge, which are general purpose (GP) grade titanium; sponge that is purified by leaching or inert gas sweep or sponge that are purified by vacuum distillation. The compositional percentages supplied by this standard are given in Table 3-4.

Table 3-4: ASTM standard B 299 for compositional percentages of titanium sponge (adapted from ASTM International (2002))

	N (max)	C (max)	Mg (max)	Al (max)	Cl (max)	Fe (max)	Si (max)	H (max)	H_2O (max)	O (max)	Ti (min)
GP	0.02	0.03	0.50	0.05	0.20	0.15	0.04	0.03	0.02	0.15	Bal.
ML	0.015	0.02	0.50	0.05	0.20	0.15	0.04	0.03	0.02	0.10	Bal.
MD	0.015	0.02	0.50	-	0.12	0.12	0.04	0.01	0.02	0.10	Bal.

With GP: General purpose grade, magnesium reduced and finished by leaching or inert gas sweep, or both:
ML: Magnesium reduced, purified by leaching or inert gas sweep;
MD: Magnesium reduced, purified by vacuum distillation.

An additional classification system exists, which is based on four grades of unalloyed metallic titanium and is referred to as commercially pure (CP) titanium grades. This is functional for consumers, since they can obtain metals for a specific application from various producers or batches and be ensured that it will conform to the applicable requirements. Produced titanium of the producers' classes thus has to adhere to the stipulations and specifications of these standards in order for a certificate of conformance to be issued. Relevant requirements were established with the intention of the metal being favourable to certain applications. Prescribed compositions CP grades 1 to 4 are given in Table 3-5. These values were obtained from Fort Wayne Metals (2018) and Hangzhou King Titanium (2009).

Table 3-5: Required compositions of unalloyed CP grades of titanium (adapted from Fort Wayne Metals (2018) and Hangzhou King Titanium (2009))

	N % (max)	**C % (max)**	**H % (max)**	**Fe % (max)**	**O % (max)**	**Ti % (min)**
CP Grade 1	0.03	0.08	0.015	0.20	0.18	Balance
CP Grade 2	0.03	0.08	0.015	0.30	0.25	Balance
CP Grade 3	0.05	0.08	0.015	0.30	0.35	Balance
CP Grade 4	0.05	0.08	0.015	0.50	0.40	Balance

It is thus essential that sponge conforming to these compositions is obtained as a product from the purification process (*i.e.* either vacuum distillation or acid leaching) that succeeds the reduction of titanium in the Kroll reactor. The sponge will then be treated further or processed into the desired form, which is normally powder or ingots. CP grades furthermore dictate the main mechanical properties of the produced metal. The major differentiating aspects between the four grades are the titanium's tensile strength, yield strength and elongation. These values are listed in Table 3-6.

CP grade 1 titanium, which is the purest of the four unalloyed grades, is evidently the softest and most ductile form of the metal. As the concentrations of impurities increase, an increase in the hardness and advertently the strength of the metal is also observed, while the ductility decreases. All four grades of metals have exceptional corrosion resistance, which is not influenced to a notable extent by the trivial presence of impurities.

Table 3-6: Minimum mechanical properties of unalloyed CP grades of titanium (adapted from Fort Wayne Metals (2018))

	Tensile strength (MPa)	Yield strength, 0.2% offset (MPa)	Elongation (%)
CP Grade 1	240	170	24
CP Grade 2	345	275	20
CP Grade 3	450	380	18
CP Grade 4	550	483	15

As previously stated, the principal reason for the variations between the given standards is advanced suitability of different properties to different uses. CP grade 1 titanium clearly performs favourably in applications which require a metal with good cold forming properties and possesses high impact toughness, while titanium from the fourth CP grade is more ideal for aerospace, industrial, medical and other applications that demand a greater strength. The predominant applications of titanium from the four CP grades were obtained from Continental Steel & Tube Company (2018) and are given in Table 3-7.

Numerous alloying options exist for titanium and a multitude of different grades of titanium and alloys thereof are covered by the standards from ASTM and ASME. Obtained $TiCl_4$ samples do not contain levels of metal impurities even close to the requirements for alloying and demands already exist for CP grades of titanium based on the listed applications. Production of alloying alternatives was thus not considered in the techno-economic evaluation and falls outside the scope of this study, which is more on the processing of $TiCl_4$.

It should be mentioned that demands for more pure metallic titanium than that of CP grade 1 exist. Examples include 4N, 4N5 and 5N titanium that have respective purities of 99.99%, 99.995% and 99.999%, which are required in electronic applications. The applicable capital and operating costs necessary to produce these products are substantial, with feed and process requirements also being quite stringent. Due to limitations on the feed and divergent focus of the scope of this study, these complex processes were not included in the techno-economic evaluation.

Table 3-7: Typical applications of unalloyed metallic titanium from CP grades (adapted from Continental Steel & Tube Company (2018))

	Applications
CP Grade 1	Automotive desalination, construction, dimensional stable anodes, medical, marine, processing & chlorate manufacturing
CP Grade 2	Aerospace, automotive, chemical processing & chlorate manufacturing, desalination, architecture, hydro carbon processing, marine, medical, power generation
CP Grade 3	Aerospace, automotive, chemical processing & chlorate manufacturing, construction, desalination, hydro carbon processing, marine, medical, power generation
CP Grade 4	Aerospace, chemical process, industrial, marine, medical

3.4.2 Titanium dioxide pigment

The subject of various pigment grades and examples of its diverse applications have already been touched on in Section 2.3.2. The aim of this section is to focus more on the requirements on these pigments, which are determined from the supplied standards by ASTM and ASME. Standard D 476 covers the required qualities and properties of seven types of TiO_2 pigments, as well as its typical end use applications (ASTM International, 2000). This information can be seen in Table 3-8 and 3-9.

Several treatment, drying and size reduction processes are required to manufacture pigments that conform to these standards. These steps are conducted after oxidation of $TiCl_4$ is completed and TiO_2 is obtained.

Table 3-8: Specified qualities and properties of TiO_2 pigments (adapted from ASTM International, 2000)

	Crystal type	TiO_2, % (min)	Specific resistance, Ω (min)	Moisture content, % (min)	Specific gravity	45-μm screen residue, %
Type I	anatase	94	5000	0.7	3.8-4.0	0.1
Type II	rutile	92	5000	0.7	4.0-4.3	0.1
Type III	rutile	80	3000	1.5	3.6-4.3	0.1
Type IV	rutile	80	3000	1.5	3.6-4.3	0.1
Type V	rutile	90	3000	1	3.6-4.3	0.1
Type VI	rutile	90	5000	0.7	3.6-4.3	0.1
Type VII	rutile	92	5000	0.7	4.0-4.3	0.1

It is evident from the pigments produced by Kerala Minerals and Metals that are listed in Table 2-4 (in Section 2.3.2) that additional processes and treatments can be conducted on these pigments to add additional attributes and promote it in the commercial market, as long as it conforms to the supplied standard.

Table 3-9: Chalking resistance and applications of TiO_2 pigments (adapted from ASTM International, 2000)

Class	Chalking resistance	Applications
Type I	free chalking	White exterior house paint and interior uses
Type II	low-medium	Low-medium % PVC
Type III	medium	High % PVC
Type IV	high	Exterior coatings requiring excellent durability
Type V	high	Exterior coatings requiring great durability with high gloss
Type VI	medium-high	Interior and exterior coatings; medium-high % PVC
Type VII	medium-high	Interior and exterior coatings; low-high % PVC

3.4.3 Titanium tetrachloride in smoke mortars for military application

The specified purity of $TiCl_4$ that is used in smoke mortars is lower than the required purity for metal and pigment production, while less focus is also placed on limitations to the elemental compositions of the liquid. The complete specification for this compound is given in Table 3-10.

Table 3-10: Specification of $TiCl_4$ to be used in smoke mortars

Constituent	Composition
$TiCl_4$ % (min)	99.0
SO_4 % (max)	0.01
Heavy metals % (max)	0.006

Smaller extents of separations or purification will generally requires less complex process units and procedures, which are beneficial in lowering capital and operating expenses. This does decrease the potential selling price of the compound though.

3.5 Process configuration and mass balances

Before the actual development of a process begins, it is first recommended to do an economic potential analysis between the potential product values and the cost of the raw material. This determination will indicate if a potential profit is possible purely based on the component values. A detailed economic potential of these processes were conducted and all were deemed to be potential solution with beneficiated products being formed. Although this analysis was conducted during the initiation of these process developments, it seemed fitting to only provide these calculations in the economic evaluation chapter (Chapter 4).

Theoretical mass or mole balances are effective techniques to validate results obtained from simulation software or actual analytical tests. The objective of this section is to perform mass balances on all three processes before the actual simulations are performed and discussed in the following section.

3.5.1 Assumptions

Some information required for completing the applicable mass balances is simply not available and some observations can’t be explained entirely, but need to be accounted for. Some assumptions are thus required to be able to construct these balances and the succeeding simulations. Assumptions in this study are only made when absolutely necessary, since it can be detrimental to the accuracy of obtained results.

3.5.1.1 Initial $TiCl_4$ composition

In order to determine the composition of demilitarized $TiCl_4$ that can be obtained from the smoke mortars, it is recommended to first establish the composition of the $TiCl_4$ that was initially used to fill these mortars. The importer of $TiCl_4$ that supplies this chemical to the local mortar manufacturer states that it has been supplying $TiCl_4$ to this company for the past 25 years or longer. This company also supplied a compositional breakdown of the current $TiCl_4$ that it delivers, which can be seen in Table 3-11 (Crescent Chemicals, 2018).

Table 3-11: Composition of new $TiCl_4$

Constituent	Composition
$TiCl_4$ %	99.99
SO_4 %	0.005
Heavy metals %	0.006
$FeCl_3$ %	0.0002
$SiCl_4$ %	0.002
$VOCl_3$ %	0.0012
$K_2Cr_2O_7$ mg/L	5

It was further stated by the supplier (without proof of relevant documentation) that the quality and composition of delivered $TiCl_4$ have remained constant and above specification since they started supplying this titanium halide to the relevant mortar manufacturer.

Since no documentation or knowledge could be obtained to contradict this statement and since no knowledge or information are available on the possibility of using other $TiCl_4$ suppliers prior to the current company, it was assumed that the initial $TiCl_4$ composition in Table 3-11 was constant for all the smoke mortars that were filled.

3.5.1.2 Demilitarized $TiCl_4$ composition

A prerequisite to an accurate mass balance or process simulation is a detailed composition of the process feed. Since it is valid to consider the filled and stored away smoke mortars as a relatively closed system, it is possible to identify any possible impurities that could enter the liquid and amend the current composition accordingly.

From previous paragraphs and sections it became clear that the only impurities that could be expected to contaminate the $TiCl_4$ are minute amounts of iron from the storage vessel and mortar body, formed TiO_2, water and HCl complexes from hydrolysis reactions and dissolved adhesive that was applied abundantly to seal the mortars.

In order to establish the demilitarized $TiCl_4$ feed composition, it is imperative to incorporate results of the various analyses with the initial composition while also taking the appearances of the samples into considerations. The approach that was chosen was to construct an overall composition using the lowest $TiCl_4$ purity value along with the highest impurity levels. With this approach it can then be guaranteed that demilitarized smoke mortars with $TiCl_4$ compositions similar to any of the sampled mortars could be sufficiently purified and be used to feed any of the considered processes. Although vanadium levels from the initial $TiCl_4$ values were 12 ppm, results from the ICP analysis have shown that this element is mostly absent from samples. In cases where compounds of vanadium were present it still had an elemental concentration of less than 5 ppm. Since a value of 12 ppm is above the tolerable limit of 10 ppm, it will require additional treatment steps and agents which will influence economic calculations. It was opted to rather use a value of 10 ppm and reconsider the necessity for vanadium removal procedures if quantities greater than 10 ppm are detected.

The other 'heavy metals' than are referred to in Table 3-11 could not be identified, but are not of great importance since the literature states that other metal compounds than those already mentioned can easily be removed through a distillation procedure. SO_4 compounds are assumed to be H_2SO_4.

Contamination by the $TiO_2 \cdot H_2O \cdot HCl$ complex was determined from the 2016 sample of unused $TiCl_4$. According to accompanying documentation, this liquid had a tested $TiCl_4$ purity of 99.99%, but analysis deemed it only to be 98.2%. It can thus be seen that undesired hydrolysis reactions during sampling and analyses resulted in the formation of 1.8% contaminants. For greater flexibility, this value was assumed as 1.99%.

Araldite epoxy resin consists mainly of bisphenol A-epichlorohydrin for the first component of the adhesive (Bostik, 2013). The supplied composition of this compound in the first component is 60-100% percent. The second part of the adhesive consists of 5-10% of 1,4-butanediol diglycidyl ether, yet no other chemicals are revealed (Bostik, 2013). Since no other constituents for either component are listed, the maximum percentages were assumed as the composition. It is further assumed that these contaminants are primarily responsible for the observed decrease in $TiCl_4$ quality to 96.2% and makes up 2% of the demilitarized $TiCl_4$. Seeing that the two components are applied in equal quantities, respective constitutions of 1.8% bisphenol A-epichlorohydrin and 0.2% 1,4-butanediol diglycidyl ether are assumed.

The resulting composition that was used in balances and simulations can be seen in Table 3-12. All percentage values are mass-based.

Table 3-12: Composition of demilitarized $TiCl_4$

Constituent	Composition
$TiCl_4$ %	96
H_2SO_4 %	0.0050
$SiCl_4$ %	0.0020
$FeCl_3$ %	0.0015
$VOCl_3$ %	0.0010
$K_2Cr_2O_7$ %	0.0005
$TiO_2 \cdot H_2O \cdot 3HCl$ %	1.99
Bisphenol A-epichlorohydrin %	1.8
1,4-butanediol diglycidyl ether %	0.2

3.5.1.3 $TiCl_4$ purification

The various analyses that were performed on the obtained samples indicated that impurities were present in the demilitarized $TiCl_4$, with the purity determination and visual analysis emphasizing that these samples do not conform to the relevant specifications in Section 2.4.1.

Based on the elaborate studies and discussions in Section 2.4 on $TiCl_4$ purification, it can be concluded that an adequate distillation procedure will be able to sufficiently purify $TiCl_4$ to conform to required specifications. Several literature sources indicated that the most problematic constituents are vanadium compounds and high concentrations of iron chlorides and that additional treatment steps are required to successfully remove it from the liquid. Since these elemental compounds were not present in the initial $TiCl_4$ and did not enter the liquid, pre-treatment or additional purifications steps are deemed not to be necessary.

The distillation was conducted as a two-step process. Initially, a low temperature was utilized to only vaporize H_2O and HCl molecules from the $TiO_2 \cdot H_2O \cdot 3HCl$ complex in the liquid. It was believed that $SiCl_4$ would also leave the system at this temperature. These vaporized impurities were removed directly from the distillation column without running it through the distillate and reflux sections to prevent subsequent contaminations. Thereafter the temperature was increased to remove $TiCl_4$ from column through the distillate.

The other aspect that needed to be considered was the clarity of the $TiCl_4$, since a specification exist for the Ti metal and TiO_2 pigment production processes to use $TiCl_4$ with a Hazen colour number of 20. As mentioned, this number refers to a quite clear transparent liquid. Since the extremely dark colours of some of the $TiCl_4$ samples had not yet been encountered by industries that were approached during this study and since relevant literature sources that covered this topic were not found, the source of these observations could not be identified. It is therefore not yet possible to prove that a distillation will be adequate in delivering titanium tetrachloride of acceptable colour. It is evident from the study by Hockaday and Kale (2016) that crude $TiCl_4$ with a foul colour could be purified to a clear liquid though (see Figure 3-3).

Figure 3-3: Crude $TiCl_4$ (left) and four samples of clear $TiCl_4$ (right) obtained from distillation (taken from Hockaday and Kale (2016))

It is thus viable to suggest that clear $TiCl_4$ could similarly be produced for this study as well. Role-players in the $TiCl_4$ industry also believe that a single distillation step will deliver $TiCl_4$ of acceptable colour and clarity (Kale, 2018).

Based on these opinions it is assumed that colouring of the liquid is caused by the stated impurities and that purification of $TiCl_4$ from these contaminants will deliver a clear liquid of acceptable colour. It is recommended to perform additional tests in future studies to determine the accuracy of this assumption though.

3.5.1.4 Separation of organic compounds

The larger than normal quantity of organic compounds in the assumed demilitarized $TiCl_4$ composition is expected to be problematic. It was however stated in literature that white mineral oils were used with long carbon chains to remove metal chlorides and that these chemicals could easily be removed from the $TiCl_4$ due to its high boiling points. Since it is not known how bisphenol A-epichlorohydrin and 1,4-butanediol diglycidyl ether from the Araldite epoxy resin will react with this mixture, no clear decisions could be made on its activity with regard to other constituents. However, seeing that it is also classified as organic compounds with many carbon atoms in each molecule, it is assumed that these two compounds will to large extents be separated from the $TiCl_4$ distillate. Reference is made in the design section of the distillation column to the overall separation efficiency. It was assumed that this value for these organic compounds would be higher than the overall value.

3.5.1.5 Processing steps that are focused on

The desired approach for the study was to consider the entire production process and required chemical plant for each option. This basis would have promoted precise and accurate comparisons between the three considered outcomes. However, limited to no information is available on the process design, operating units and piping and instrumentation (P&ID) diagrams of these processes.

Several local and international companies were contacted or visited and the main issue for each party was that these are very competitive industries since there are only a few producers and suppliers, hence confidential information was not shared. Another challenging factor is that at the time of this study there aren’t any local commercial producers of either pure $TiCl_4$, metallic titanium or TiO_2 pigment. These products are being imported and international companies are not willing to run the risk of exposing valuable information that enables external parties to oppose them in the market.

The only viable option that could be considered to still obtain relatively meaningful results and applicable conclusions, is to focus on the principal step of each process and perform simulations based on the segment of information that could be obtained from various literature sources.

Only the following sections were accordingly considered in the mass balance and simulation of each process:

1. $TiCl_4$ purification: purification via a distillation column
2. Metallic titanium production: Kroll reactor where Ti sponge is produced from $TiCl_4$
3. TiO_2 pigment production: Furnace where $TiCl_4$ is oxidised to TiO_2
4. $TiCl_4$ recovery for use in smoke mortar: recovery via a separation unit

Heat added and removed from these systems will be incorporated in the simulations, but it is not possible to include accurate determinations of the required valves, pressure changers, heat exchangers, piping, and other capital sections of the entire process.

3.5.1.6 Reactivity of chemicals

An extremely difficult phenomenon to predict or explain in a system with multiple compounds is how these species will react with adjacent species and molecules and what consequence it will have on composition, temperature, pressure, state, colour, *etc.* Since it is almost virtually impossible to account for these occurrences without modelling, simulation or actual testing and since no literature data is available on this unique set of chemicals, it is assumed that the influences of reactions between system constituents are negligible.

3.5.1.7 Pressure drop over heat exchangers

It will be quite challenging to mathematically determine pressure drops over heat exchangers from general engineering equations. The limited data available on this mixture and its constituents will cause unknown parameters which should be determined before pressure alterations can be modelled. Development and derivations of models for the various unknown variables will not contribute to the results of this evaluation and are therefore not within the scope of this study. Raza (2013) states that pressure over shell-and-tube heat exchangers should not exceed 0.5 bar over the shell side and 0.7 bar over the tube side. Due to the relatively low volumes and flow rates of each process, a moderate pressure drop of 0.2 bar is assumed over all heaters and heat exchangers unless it is stated otherwise.

3.5.2 Purification of $TiCl_4$ for metallic Ti and TiO_2 pigment production

Since the desired specifications for $TiCl_4$ to be used in metal and pigment production processes are identical, it was covered prior to the two actual processes. Although the third option of obtaining $TiCl_4$ of adequate quality also involves purification of the demilitarized $TiCl_4$, it is of a lesser extent than the former two processes and was therefore considered independently.

Following on from the discussions in Section 2.4.2.2, various design parameters and operating conditions need to be selected for the distillation unit of these process. The applicable properties are stated in the subsequent paragraphs.

3.5.2.1 Design features and operating parameters

Batch versus continuous operation

A batch distillation was identified as the optimal operating system, since in is more flexible with regard to input qualities, batch sizes, required product qualities and because the less complex setup is more ideal for smaller operations such as this study.

Size of batches

Required quantities of purified $TiCl_4$ is quite varied and the approach that was followed was to distil batches consisting of 1000 kg demilitarized $TiCl_4$. This aided in calculations since it could easily be multiplied to additional sizes, should it be required.

Boiler temperature

The first set temperature of the boiler at the bottom of the distillation column was 125°C. Once the liquid ceases to boil and when there aren’t any vapour visible at the top of the column, the temperature was increased to the second setting. The final set temperature of the boiler was 200°C.

Distillate temperature

The expected temperature of the distillate leaving the column is 136°C.

Operating pressure

A positive pressure was selected to prevent air (especially moist air) from leaking through and contaminating the system. The column operated at a slight positive gauge pressure of about 0.3 bar, based in the general recommendations by Lieberman & Lieberman (2014).

Inert gas

The column was filled with inert argon gas prior to distillation to flush out all air from the system to prevent additional contamination of the $TiCl_4$.

Theoretical stages

The preferred method for designing a distillation column and determining appropriate parameters is explained by Seader *et al.* (2011). These methods advise that McCabe-Thiele diagrams of a specie's relative volatility with regard to the other components are utilized to determine the required amount of theoretical stages. Once this value has been obtained, reflux ratios, duties, column dimensions, *etc.* can be calculated by mathematical equations for specific product requirements. Although this method aids in obtaining accurate results, it can become extremely challenging to construct McCabe-Thiele diagrams of species in a complex mixture such as the one in this study. These diagrams could not be generated or obtained from literature and an alternative strategy is required for determining column parameters.

The required theoretical stages of the column were determined during simulation of this process.

Reflux ratio

The liquid in the reflux drum was partially removed as the distillate, while a larger fraction was refluxed back to the column. It was decided to operate this column to give a constant distillate quality by varying the reflux ratio. Reflux ratio was thus a function of $TiCl_4$ product still remaining in the pot and increased over time.

Since the methods and mathematical equations from Seader *et al.* (2011) could not be used, it was needed to determine actual reflux ratios from accurate simulations or actual testing and product analysis.

Packing versus trays

Packing has been selected as the appropriate contacting agents for inducing better contact between the vapour and liquid of the system. Packing is also more flexible than trays in batch distillations where the fluid volume in the column decreases over time.

Packing material

Random packing was selected over structured packing. The packing material that was used in this column is glass Raschig rings. Although modern packing material display advanced efficiencies, it is not constructed of glass. Glass is a favourable material of construction over metal and ceramic materials in corrosive systems (ChemAlone, 2016; Mendes 2011).

Condenser

The appropriate operation of the condenser that were identified for this application is a partial condenser for the first step, which operates at the dew point of the first distillate. A reflux drum was installed to collect the liquefied fluids from the condenser, while vapours can also be removed at this point. It was expected that the vapour consisted of inert argon gas, HCl and $SiCl_4$, which are present in extremely small volumes. The condenser can be set to completely condense column vapour in the second step, since $TiCl_4$ is easier to handle in liquid phase. Clean argon can be recycled back to the column to maintain a positive pressure.

Column dimensions

The column consists of a pot, which is responsible for heating the contents of the column and a packed-bed, where the actual separation of constituents occur by facilitating contact between vapour and liquid phases. These sections have different dimensions, which could prove to be quite challenging to determine. The dimensions of the pot are relative to the expected processing capacity, while the packed-bed height is dependent on the amount of theoretical stages required and the height equivalent to a theoretical plate (HETP) of the packing.

ChemAlone (2016) advises that the packed-bed diameter for Raschig rings should be greater than ten times the packing size. Lieberman and Lieberman (2014) state that the typical dimensions of Raschig rings is a length of 1 inch with inner and outer diameters of 0.75 and 1 inch. The diameter of the packed-bed should therefore exceed 10 inch (25.4 cm).

Sinnott *et al.* (2013) state that an HETP value of between 0.4 and 0.5 m can be used for 1 in. Raschig rings. The requisite for using this value is that a pressure drop of at least 42 mm liquid per m of packing height is maintained. A value of 0.45 m is selected for the HETP of the packed-bed and was implemented by ensuring a pressure drop of more than 42 mm liquid per m packing were observed.

Options of existing batch distillation column can be selected in the Aspen Plus^{TM} simulation software and were used to determine the pot dimensions in the simulation section (Section 3.6). Seeing that the required amount of theoretical stages was determined by the simulation, the bed height were also established in that section.

Pressure drop over column

The recommended pressure drop of a distillation column that contains random packing and operates at atmospheric or moderate pressure ranges between 40 and 80 mm water per m packing (Sinnott *et al.*, 2013). In the book by Lieberman and Lieberman (2014), a general pressure drop of 1.2 inch water per foot of packing was suggested for 1 in. Raschig rings beds. This is an equivalent of 100 mm water per foot of packing. For the initial consideration, a value towards the upper limit of the suggested range was used. Hence, a pressure drop of 75 mm liquid per m packing was assumed over the column.

The pressure drop of a batch column is not constant though and can be extremely challenging to predict for a dynamic system.

Material of construction

The column was constructed of normal carbon steel with an inner glass lining to impede any contact between the chemicals and the metal walls.

3.5.2.2 Separation efficiency

Minimum separation efficiencies of 99.7% for the organic compounds and 99% for the remaining constituents are required for producing $TiCl_4$ with a quality of 99.9% or better that conforms to elemental restrictions. The required extent of separation of the organic compounds is that much greater due to the strict regulations for carbon and hydrogen atoms in titanium sponge. These high values contribute immensely to large reflux ratios and required amounts of theoretical stages.

It is expected that noteworthy quantities of $TiCl_4$ will be lost through the first distillate, since the boiling point of this chemical is quite close to the operating temperature range. The column is designed and parameters are selected with the intention of minimizing $TiCl_4$ without incurring excessive additional costs. Complete recovery of the remaining $TiCl_4$ in the column is expected in the second distillate, since all heavier components have vastly higher boiling points and is not expected to be detrimental to the quality of the removed distillate.

3.5.2.3 Expected input-output quantities

In order to gain a better perspective of the expected separation from the distillation columns, it is necessary to first study the boiling points of the respective compounds. All temperature values are at atmospheric pressure and were obtained from Green and Perry (2008), except those of 1,4-butanediol diglycidyl ether and bisphenol A-epichlorohydrin, which was from Electron Microscopy Sciences (2016) and Møller *et al.* (2012). These temperatures can be found in Table 3-13.

It is predicted that HCl will dissolve in water to form a solution, but it’s not essential to take it into consideration since these species will concurrently be removed from the $TiCl_4$. Green and Perry (2008) states that H_2SO_4 will dissolve in water to form a molecular complex with relatively close to that of $TiCl_4$. It is known that organic polymers have relatively high boiling points, which is also observable in this scenario. The molecules in these polymers are connected by strong secondary bonds, which inhibit decomposition of these polymers below its boiling point. The TiO_2 from the $HCl{\cdot}H_2O{\cdot}TiO_2$ complex that formed from the $TiCl_4$ hydrolysis reaction is expected to break free from the complex during distillation and remain in the liquid residue.

It is clear that a two-step distillation at 125°C and 200°C will deliver a first distillate that consists predominantly of HCl, $SiCl_4$ and H_2O. The second distillate product will contain the desired $TiCl_4$ along with $VOCl_3$ and $H_2SO_4{\cdot}2H_2O$ while the majority of remaining compounds will be entrapped in the liquid residue of the column.

The expected input and output for a 1000 kg batch are given in Table 3-14. No liquid was extracted from the column as a bottoms product during distillation and each procedure will ultimately reach its conclusion when no vapour is formed in the column. Remaining liquid, sludge or crystallized residues were removed after completion of each run. Minute quantities are included in these estimations due to the intricate degree of separation required and stringent product stipulations that exist.

Table 3-13: Boiling points of compounds in the demilitarized $TiCl_4$

	Boiling point (°C)
HCl	-85
$SiCl_4$	58
H_2O	100
$VOCl_3$	127
$TiCl_4$	136
$H_2SO_4 \cdot 2H_2O$	167
1,4-butanediol diglycidyl ether	266
$FeCl_3$	315
Bisphenol A-epichlorohydrin	320
$K_2Cr_2O_7$	500
TiO_2	<3000

The required separation efficiency that was stated in Subsection 3.5.2.2 of 99.5% for the organic species and 99% overall was applied to all compounds in the mixture. It should be noted that greater extents of separation are expected between $TiCl_4$ and impurities with vastly different boiling points (*e.g.* TiO_2) to the point where no trace of those chemicals are found in the distillate product. However, since the initiative is that this column should sufficiently purify demilitarized $TiCl_4$ of even the lowest qualities to the supplied specifications, it was decided to account for all possible impurities.

Table 3-14: Mass of each compound for the various input and product volumes of the purification process

	Input (kg)	Distillate 1 (kg)	Distillate 2 (kg)	Residue (kg)
$TiCl_4$	960	10	950	
$H_2SO_4 \cdot 2H_2O$	0.050	0.001	0.049	
$SiCl_4$	0.020	0.019	0.001	
$FeCl_3$	0.015		0.001	0.014
$VOCl_3$	0.010	0.001	0.009	
$K_2Cr_2O_7 \cdot 2H_2O$	0.005		0.001	0.004
Bisphenol A-epichlorohydrin	18		0.054	17.95
1,4-butanediol diglycidyl ether	2		0.006	1.99
$TiO_2 \cdot H_2O \cdot 3HCl$	19.9			
H_2O	(1.73)	1.713	0.017	
HCl	(10.5)	10.395	0.105	
TiO_2	(7.67)		0.077	7.593
TOTAL	**1000**	**22**	**951**	**27**

Operating parameters were manipulated to ensure that $TiCl_4$ was removed from the column in the second distillate to the extent that remaining quantities were negligible. Other factors that also contribute to this expectation are the high temperature of the boiler (200°C) and an implemented operating specification, which states that process completion is only achieved once vapour formation has stopped.

A verification of theoretical calculations with stated stipulations indicates that the purified $TiCl_4$ obtained from the column will conform to the predetermined specifications. These values are seen in Table 3-15. The obtained $TiCl_4$ is of much greater purity than required, but extent of separation is dependent on elemental specifications of the Ti sponge, which requires adequate removal of those elemental compounds from the $TiCl_4$ feed. The elemental compounds that are referred to are carbon and chlorine containing molecules.

Table 3-15: Specified and theoretical percentages of elemental compositions in purified $TiCl_4$

	$TiCl_4$ % (min)	**Fe ppm (max)**	**V ppm (max)**	**Si ppm (max)**	**Sn ppm (max)**	**Hazen colour no. (max)**
Stipulation	99.9	10	10	10	30	20
Theoretical	99.97	1	9	1	-*	20 (Literature)

*Sn values were not measured and are unaccounted for

The purified $TiCl_4$ is thus of adequate quality to be used as feed to the Kroll and chloride processes.

3.5.3 Titanium metal production by Kroll process

Detailed design properties and parameters are required to deliver titanium sponge that conforms to the stipulated ASTM standards or CP grades. By accurately following these regulations, sponge of a satisfactory quality can be produced at acceptable efficiencies.

The principal chemical reaction of this process were given by Equation 2-2.

$$TiCl_{4_{(l)}} + 2Mg_{(l)} \rightarrow Ti_{(s)} + 2MgCl_{2_{(l)}} \qquad [2\text{-}2]$$

The physical reactor consists of a retort which contains a crucible. Titanium is formed in the crucible and it can be removed from the retort after completion of the process to aid in metal extraction. Metal production is achieved by filling the crucible in the reactor with an excess quantity of magnesium. Pure $TiCl_4$ is then slowly added to the Mg, which reacts to form Ti sponge and $MgCl_2$ at high temperatures. The $MgCl_2$ was drained from the reactor at certain intervals.

Identifying and selecting correct values and sequences could be quite challenging for this process.

Nagesh *et al.* (2004) and Subramanyam and Rao (1986) both developed and constructed a prototype Kroll reactor that produced batches of titanium sponge. Due to the limited information available in literature on the actual implementation of the Kroll process, these references were incorporated into several design aspects of this study.

3.5.3.1 Design features and operating parameters

Batch versus continuous operation

The Kroll process is a batch process. Although enhancements have been made to this process to produce titanium powder in semi-batch systems, these values have not yet been published and could not be obtained for implementation in this study. Titanium sponge will therefore be produced along the original Kroll process.

Size of batches

The prototype Kroll reactor produced 2000 kg titanium sponge per cycle. The required $TiCl_4$ feed for producing 2000 kg sponge is approximately 8000 kg. It will not be feasible to enlarge the scale of this process, since it was stated in the problem statement that only 40 ton $TiCl_4$ are available with an additional 400 kg added annually.

It is important to note that industrial titanium plants produce more than 20 000 tons of metallic titanium per annum (Fazluddin, 2018). This factor was considered and discussed more elaborately in following sections.

Reactor temperature

The reactor was operated at 900°C.

Operating pressure

A slight positive gauge pressure of 0.3 bar was implemented. $TiCl_4$ and inert gas will continuously be added to the reactor. This will cause a constant increase in pressure, which necessitates regular bleed-off procedures by means of a bleeder valve on the retort lid to maintain a constant gauge pressure.

Required quantity of pure $TiCl_4$

As stated, the required quantity of pure $TiCl_4$ is rounded to 8000 kg per batch.

Flow rate of $TiCl_4$

The $TiCl_4$ was added to the molten Mg at 138 kg/h.

Excess magnesium used

An excess of about 40% Mg are required. Stoichiometrically, this equals a rounded value of 2900 kg Mg that the crucible in the reactor was filled with when the process commences.

Intervals of $MgCl_2$ removal

$MgCl_2$ was tapped off from the reactor once 2000 kg $TiCl_4$ has been added (after 14.5 hours for this scenario) and thereafter at intervals of every 500 kg $TiCl_4$ injected into the reactor (2 hours and 40 minute intervals).

Inert gas

Argon was used as the inert gas in the reactor.

Flow rate of inert gas

The reactor will initially be filled with argon and added during the reaction at an implemented flow rate of 0.2 L/min.

Indication of process completion

Initially bleed-offs will occur once every few hours to maintain a low pressure. An indication of process completion is when the frequency of bleed-offs suddenly shortens to once every 30-40 minutes.

Reaction time

The expected time required for this process to reach completion is 53 h.

Retort dimensions

The retort was 3500 mm high with an internal diameter of 1360 mm and a wall thickness of 25 mm.

Crucible dimensions

The crucible will have a height of 3050 mm, an internal diameter of 1210 mm and a wall thickness of 25 mm.

Material of construction

The retort was constructed of stainless steel, while a carbon steel crucible was used.

3.5.3.2 Conversion of $TiCl_4$

Due to the excess Mg that are supplied to the reactor (41% to be precise), complete conversion of $TiCl_4$ is expected at the conclusion of this process.

3.5.3.3 Possible downstream purification

Literature explains how obtained titanium sponge can be purified from residual $MgCl_2$ salts and unreacted magnesium through acid leaching, vacuum distillation or an inert gas sweep. Of these three techniques, vacuum distillation is the most popular in industry as it is more beneficial with regard to product purities and properties.

Shibata *et al.* (2002) found that approximately 200 kg excess Mg and 80 kg $MgCl_2$ are entrapped per m^3 Ti sponge prior to purification. Vacuum distillations are performed in a heat resistant stainless steel retort at room temperature under a pressure of about 1.3×10^{-6} bar. Thereafter the temperature of the retort is increased to 1000°C to remove remaining $MgCl_2$ and excess Mg from the sponge. The minimum separation efficiency that is required for this process is 99.4% to ensure that chloride levels are below that of the ASTM standards. It is logical to expect additional chemical activity of the other impurities that are still present in the system, but since no information is available on these possibilities, it is directly carried over into the metal.

Findings by Kosemura *et al.* (2002) indicate that the time required for completion of the vacuum distillation step is similar to that of the reduction process, which is 53 hours in this case. Based on the study by Kosemura *et al.* (2002), it is also valid to assume a similar time will be required for the heated sponge to be cooled to room temperature.

3.5.3.4 Possible electrolysis of $MgCl_2$

$MgCl_2$ that is removed from the Kroll reactor and downstream purification units, can be separated into magnesium metal and chlorine gas. Obtained magnesium could be recycled back to the Kroll reactor while chlorine could potentially be sold. For the calculations performed in this study, complete decomposition of $MgCl_2$ and separation of ions are assumed.

Mg and Cl ions are separated by electrolysis to obtain metallic magnesium at the iron cathode with chlorine gas being removed at the graphite anode (Kosemura *et al.*, 2002). This process is conducted at 700°C in a $MgCl_2$/NaCl/KCl electrolyte. Demirci and Karakaya (2016) developed a technique to rapidly remove chlorine gas from the anode to enhance magnesium production. Determined energy consumption from the performed experiment was 7.0 kWh/kg Mg with an anodic current density of 0.68 A/cm^2.

The electric power consumption of this electrolysis substantially contributes to the total consumption of the titanium production process however. Kosemura *et al.* (2002) stated that this process step accounted for about 60 to 70% of the entire process's power usage before implementation of technological advancements. With new improvements this value has decreased to about 40%, which is still a significant quantity.

3.5.3.5 Expected input-output quantities

By means of a theoretical design and calculations of the discussed production techniques and process units, it was possible to quantify the expected masses and compositions of each input and output volume. These values are given in Table 3-16.

As mentioned, these values are theoretical estimates and it is possible that deviations in results will be observed should experimental procedures be performed. A comparison of the calculated values with ASTM standard values for titanium sponge indicates that theoretically, these values should conform to stipulations. Both sets of values are listed in Table 3-17. It has been mentioned in this section that a study of this process will only cover sponge production and additional treatment and melting procedures were not incorporated into calculations. There will thus only be focussed on the ASTM standards for titanium sponge and not for titanium ingots.

Table 3-16: Mass of each compound for the various input and product volumes of the Kroll process

	Kroll input (kg)	Kroll output (kg)	Kroll discharge (kg)	VD output (kg)	VD discharge (kg)	Elec output (kg)
$TiCl_4$	8000					
H_2SO_4	0.413	0.413		0.413		
$SiCl_4$	0.008	0.008		0.008		
$FeCl_3$	0.008	0.008		0.008		
$VOCl_3$	0.076	0.075		0.075		
$K_2Cr_2O_7$	0.008	0.008		0.008		
$C_{15}H_{16}O_2 \cdot C_3H_5ClO$	0.455	0.455		0.455		
$C_{10}H_{18}O_4$	0.051	0.051		0.051		
H_2O	0.146	0.146		0.146		
HCl	0.884	0.884		0.884		
TiO_2	0.646	0.646		0.646		
Mg	2900	850		5.099	845	2894
Cl_2						5980
$MgCl_2$		280	7752	1.678	278	
Ti		2019		2019		
TOTAL	**10903**	**3151**	**7752**	**2028**	**1123**	**8874**

With Kroll: reactor where reduction of $TiCl_4$ with Mg is performed
VD: vacuum distillation where residual Mg and $MgCl_2$ is removed from sponge
Elec: electrolysis where $MgCl_2$ is decomposed to Mg and Cl_2

Table 3-17: Specified and theoretical percentages of elemental compositions in titanium sponge

	N (max)	C (max)	Mg (max)	Al (max)	Cl (max)	Fe (max)	Si (max)	H (max)	H_2O (max)	O (max)	Ti (min)
Spec	0.015	0.02	0.5	-	0.12	0.12	0.04	0.01	0.02	0.10	Bal.
T	-	0.017	0.27	-	0.11	<0.01	<0.01	0.003	0.007	0.03	99.5

With Spec: specified maximum values
T: theoretically calculated value

Nitrogen (N) was not tested for and negligible levels of aluminium (Al) were present in the $TiCl_4$. The expected actual value of iron (Fe) compounds in the sponge is substantially higher than the theoretical value, since numerous sources stated that iron contamination of the sponge occurs at the carbon steel walls of the crucible. A uniform iron composition will thus not be obtained, with high-purity sponge being found in the centre of the crucible, furthest away from the walls, while levels of iron compounds increase towards the sides. In practice, the sponge of different purities are utilized in different CP grades. Since it will be extremely difficult to accurately determine the quality of the titanium at various locations within the sponge without an actual test being conducted, these deviations were not considered in this study, but present possibilities for future research.

3.5.4 Titanium dioxide pigment production by chloride process

Only a few manufacturers of TiO_2 pigment exist globally, of which DuPont and Cristal is arguably the largest. DuPont initialized the chloride process for TiO_2 pigment production in the early 1950s, which is currently being utilized in 60% of global TiO_2 pigment production plants to produce approximately 2.7 million ton per annum.

Limited information is available on the actual quantities, ratios, parameters and operating techniques used in this application of $TiCl_4$. Without definite information it will be extremely challenging to construct a conclusive design of the actual process. It is therefore understandable that none of the companies that were approached during this study were willing to supply confidential intelligence. West (2008) developed an in-depth kinetic model of this process and compared obtained information with findings from other studies and meagre available data from the industry. The study by West (2008), along with the registered patents by Allen and Evers

(1993), Lewis and Braun (1965), Schaumann (1954), Krchma and Schaumann (1951) and Schaumann (1949) were used to determine parameters and variables of this process, unless otherwise stated.

Purified $TiCl_4$ is oxidized at extremely high temperatures to form TiO_2 and Cl_2 (Equation 2-13).

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2 \qquad [2\text{-}13]$$

Water, a catalyst and a spacing gas could also be fed to the system together with the required O_2 to administer formation of particles that conform to desired properties.

3.5.4.1 Design features and operating parameters

Batch versus continuous operation

This process is operated on a continuous cycle at a constant feed of reactants.

Type of reactor

This process is conducted in a plasma arc furnace, with plug flow being assumed inside the reactor (West, 2008). A horizontal plug flow reactor, heated by a plasma arc, has therefore been selected.

Operating pressure

The gauge pressure inside the reactor was regulated at 3 bar.

Reactor temperature

The operating temperature of the reactor is directly proportional to the particle sizes of the produced pigment. A moderate temperature within the proposed range of 950 - 1500°C by Allen and Evers (1993) has been identified. West (2008), along with various other sources suggest an approximate value of 1500 K. This reactor will accordingly be operated at 1250°C.

Preheating of reactants

A study from Jones *et al.*, (1993) was conducted on the developments in plasma furnace technologies, which stated that preheating of reactants is required for effective reaction and temperature maintenance in a plasma arc reactor.

Both streams of reactants will therefore be preheated to 850°C before being introduced into the plasma arc furnace.

Residence time

West (2008) concluded that an average residence time of 10 milliseconds are required to achieve thermodynamic equilibrium in an equimolar system and that 90% of $TiCl_4$ were already consumed within the first 0.4 ms from inception. The referenced patents also recommends a residence time of between 1 and 16 ms in the mixing zone. 'Mixing zone' refers to volume on reactor where reactants are introduced.

Rigorous control of the residence time should be executed, since an increase in this value will cause an increase in particle sizes of the produced pigments. Too large residence time will thus result in particle diameters above the stipulated values.

A residence time of 10 milliseconds will consequently be implemented in the mixing zone to sufficiently convert $TiCl_4$ to TiO_2.

Feed rate of $TiCl_4$

Since no references to pilot plants or laboratory-scale experiments of this process were found, it was decided to feed this process with one batch of $TiCl_4$ from the purification sections over a period of one hour. Due to the scope of this study it is not feasible to design a process with larger feed rates, since a limited volume of $TiCl_4$ is available. The resulting feed rate will thus be 950 kg/h pure $TiCl_4$.

It should again be noted that the general production of industrial TiO_2 pigment plants are more than 20 000 tons per annum (Fazluddin, 2018) at a rate of five or more ton TiO_2 per hour (Allen & Evers, 1993). This production rate requires an approximate feed rate of 12 ton $TiCl_4$ per hour. This factor will also be considered and discussed more elaborately in following sections.

Feed rate of O_2

$TiCl_4$ is regarded as the limiting reagent for this process and excess oxygen is thus fed to ensure complete conversion of $TiCl_4$. Schaumann (1954) proposed an excess of 10 mol%. Addition of larger quantities of than 10% excess are not advisable, seeing that the oxygen will contaminate formed chlorine gas, rendering it unsuitable for reuse. Tronox (2013) has been actively trying to reduce the required volume of oxygen down to stoichiometric values to deliver a Cl_2 by-product of higher quality. Performed developments and research enabled them to lower oxygen consumption in the chloride process by 5% between 2013 and 2007. These developments aren't available in general literature, but are mentioned to indicate that improvements are possible.

For an excess of 10 mol% and purity of 99.5%, a flow rate of 179 kg/h O_2 was added.

Quality of oxygen

High-purity oxygen should be used to avoid contamination of the white pigment, which would decrease its value. Impure air can therefore not be used. The prescribed purity of O_2 to be used in this process is 99.5%.

H_2O addition

Water vapour is added together with the oxygen gas to aid in the formation of smaller rounder particles. It is critical not to add excessive quantities of water, since the hydrolysis reaction competes with the oxidation reaction and forms larger aggregates of undesired anatase crystals (West, 2008). At high temperatures the oxidation reaction is favoured, but not to the extent that hydrolysis would not take place. This occurrence is countered by the addition of a chemical catalyst.

A moisture content not exceeding 3 wt% in the final product was proposed for the TiO_2 pigment (Allen & Evers, 1993; Schaumann, 1949). A H_2O vapour flow rate of 16 kg/h was selected, which would deliver a water content of 2.7 wt% in the pigment particles.

Catalyst used

$AlCl_3$ has been identified as the applicable catalyst to use in this study as it induces the TiO_2 to form as rutile crystals rather than anatase (West, 2008). This is essential when water vapour is added along with reactants.

Flow rate of catalyst

West (2008) and Krchma and Schaumann (1951) suggest using a ratio of $AlCl_3$ that will equate to an Al_2O_3 product composition of between 0.5 and 2 wt%, while patents by Allen and Evers (1993) and Lewis and Braun (1965) recommends quantities of between 0.1-10 wt% of the amount of $TiCl_4$ added.

A flow rate of 20 kg/h $AlCl_3$ was added, which is about 2 wt% of the $TiCl_4$ feed, to deliver a final product composition of 1.7 wt% Al_2O_3. This chemical reaction is displayed in Equation 3-1.

$$2AlCl_3 + 3H_2O \rightarrow Al_2O_3 + 6HCl \qquad [3\text{-}1]$$

Spacing gas

A spacing gas can be added in conjunction with reactant gases to carry formed particles through the reactor and prevent deposition of solid particles on the reactant inlets and reactor walls. An additional function of spacing gases can be to control operating temperatures. An inert gas should be used, with Cl_2, CO_2, N_2 or noble gases being suggested by Allen and Evers (1993).

To prevent contamination or discoloration of pigment particles, argon has been selected as a suitable option.

Flow rate of spacing gas

Allen and Evers (1993) further stated a preferable volume of spacing gas to be between 5 and 25 mol%, based the $TiCl_4$ and O_2 added. A flow rate proportional to 15 mol% has been selected, which is achieved by adding 73 kg/h argon.

Reactor dimensions

It is not possible to determine the reactor layout and dimensional measurements from this theoretical study. These values are either provided by the simulation software or applicable empirical data from an external source.

Materials of construction

Steveson (2000) recommends a steel tube with an inner glass lining to prevent contamination between the reactor wall and system components.

3.5.4.2 Conversion of $TiCl_4$

Due to the excess O_2 being fed, it is assumed that complete conversion of $TiCl_4$ to TiO_2 is achieved.

3.5.4.3 Temperature profile along reactor

A study by West (2008) on industrial reactors indicated that a plug flow reactor with a constant pressure of 3 bar and initial temperature of 1500 K (± 1227°C), maintains that temperature for the first 100 ms in the reactor, after which it linearly cools to 1000 K (± 727°C) over the next 100 ms.

3.5.4.4 Particle sizes of produced pigment

West (2008) further approximated expected particle sizes after the initial 200 ms to have a diameter of around 45 nm. These pigment particles are further cooled in a plug flow cooler for a period of 10 seconds to obtain an average particle diameter of 250 nm.

3.5.4.5 Possible downstream purification

Steveson (2000) recommends using either a cyclone or bag filter to remove residual Cl_2, HCl and excess O_2 gases from the pigment particles. Gázquez *et al.* (2014) suggest that it can also be performed by aqueous hydrolysis of the collected product from the reactor. An overall separation efficiency of 98% is required to deliver a TiO_2 pigment of adequate purity.

3.5.4.6 Finishing steps

Obtained pigment particles are mixed with water to form a slurry, which aids in finishing, sizing and further processing. Possible finishing and treatments steps were stated in Section 2.3.2 and are selected based on application and the ASTM standard type that it should conform to.

DuPont, a leading producer of TiO_2 pigments, comprehensively discusses various properties and attributes that can be altered and added by finishing and treatment procedures (DuPont, 2007). However, since the pigment from this study is not produced for specific applications or markets, it is not possible to identify which treatment or sizing processes should be implemented. This is also backed up by the assumption from Section 3.5.1 that only the actual chemical production steps would be considered for this process.

3.5.4.7 Expected input-output quantities

Stated process selections and design parameters were used to perform stoichiometric calculations and construct a theoretical model of overall inputs and outputs for the chemical production units. These values are listed in Table 3-18.

Table 3-18: Mass of each compound for the various input and product volumes of the chloride process

	Chloride input (kg)	Chloride output (kg)	Purification output (kg)	Purification discharge (kg)
$TiCl_4$	950			
H_2SO_4	0.049	0.049	0.049	
$SiCl_4$	0.001	0.001	0.001	
$FeCl_3$	0.001	0.001	0.001	
$VOCl_3$	0.009	0.009	0.009	
$K_2Cr_2O_7$	0.001	0.001	0.001	
$C_{15}H_{16}O_2 \cdot C_3H_5ClO$	0.090	0.090	0.090	
$C_{10}H_{18}O_4$	0.010	0.010	0.010	
H_2O	16	12	12	
HCl	0.105	17	0.330	16
TiO_2	0.077	400	400	
O_2	179	17	0.373	18
Cl_2		711	14	697
$AlCl_3$	20			
Al_2O_3		8	8	
TOTAL	**1166**	**1166**	**435**	**731**

A comparison with production stipulations of provided ASTM standards indicated that these pigments conform to Type II to Type VII specifications with regard to crystal structure and TiO_2 content. Rutile crystals are formed in the presence of $AlCl_3$. The stipulated and theoretical values are given in Table 3-19.

Table 3-19: Theoretical and specified qualities and crystal structures of TiO_2 pigments

	Theoretical	Type I	Type II	Type III	Type IV	Type V	Type VI	Type VII
TiO_2 content	92.04%	94%	92%	80%	80%	90%	90%	92%
Crystal structure	Rutile	Anatase	Rutile	Rutile	Rutile	Rutile	Rutile	Rutile

Remaining fields are dependent on implemented treatment, drying, milling / grinding and other possible finishing steps and can therefore not be determined from these calculations.

3.5.5 Titanium tetrachloride in smoke mortars for military application

An evaluation of the available demilitarized $TiCl_4$ with the applicable specifications for $TiCl_4$ in smoke mortar manufacturing indicates that purification is required. A similar separation unit to the one in Section 3.5.2 for purification of $TiCl_4$ for the metal and pigment production processes was considered. Nevertheless, the specifications for this process are not as stringent and a simpler (and less expensive) separation unit was sufficient.

The design parameters for such a column are again be listed in this section, with the only notable deviations occurring in the column dimensions, reflux ratio and amount of theoretical stages.

3.5.5.1 Design features and operating parameters

Batch versus continuous operation

The distillation column was operated on a batch scale.

Size of batches

A quantity of 1000 kg demilitarized $TiCl_4$ was processed per batch.

Boiler temperature

A two-step separation was implemented again, with the initial boiler temperature being set at 108°C. The second setting of the boiler temperature was 240°C.

Distillate temperature

The temperature of the first distillate is expected at around 100°C, while the expected distillate temperature of the second step is 136°C.

Operating pressure

The operating gauge pressure of the column was 0.3 bar.

Inert gas

Argon gas was used to fill the column prior to distillation to flush out all air from the system.

Theoretical stages

The amount of theoretical stages was determined in Aspen Plus^{TM}.

Reflux ratio

It is expected that the column was operated on a constant distillate quality basis by varying reflux ratio, should it have been required.

This parameter was therefore determined in Aspen Plus^{TM}.

Packing versus trays

Packing were to be utilized as theoretical stages, should it have been required.

Packing material

Glass Raschig rings would have been used as packing material.

Condenser

The condenser was set as a total condenser for the second phase.

Pressure drop over column

This parameter was negligible for this process.

Column dimensions

The dimensions is highly dependent on the separation unit being used and its selected parameters. Since these values were obtained from the simulation software, the design dimensions are also discussed in that section.

Material of construction

A normal carbon steel column with an inner glass lining was used.

3.5.5.2 Separation efficiency

A minimum separation efficiency of 77% is required for adequate purification of the $TiCl_4$. This value gives a comprehensible indication of the lesser extent of separation that is required over the former applications. A simpler separation unit will thus be implemented.

The moderate degree of separation of the first distillate implicates that perceptible quantities of $TiCl_4$ was lost through this stream. Minimizing $TiCl_4$ losses was attempted through the selection of appropriate operation parameters. A fine balance do exist between the losses incurred due to the inability to recover some $TiCl_4$ against the increased costs of developing a more complex separation unit. Complete recovery of remaining $TiCl_4$ though the second distillate is expected, since soiling points of heavier components are higher than that of $TiCl_4$ by quite a large margin.

3.5.5.3 Expected input-output quantities

Although a separation efficiency of only 77% is required, care has to be taken to ensure low volumes of $TiCl_4$ escape from the column in the first distillate, otherwise it could hamper the feasibility of the process. A greater recovery is generally achieved by manipulation of the reflux ratio of by installing additional stages in the column. To obtain a final $TiCl_4$ purity above 99% while removing 77% of impurities, a $TiCl_4$ recovery of 96% should be maintained.

The expected input and output quantities and individual compound masses are tabulated in Table 3-20.

Table 3-20: Mass of each compound for the various input and product volumes of the distillation process

	Input (kg)	Distillate 1 (kg)	Distillate 2 (kg)	Residue (kg)
$TiCl_4$	960	38	922	
$H_2SO_4 \cdot 2H_2O$	0.050	0.011	0.030	0.009
$SiCl_4$	0.020	0.015	0.005	
$FeCl_3$	0.015		0.003	0.012
$VOCl_3$	0.010	0.002	0.008	
$K_2Cr_2O_7$	0.005		0.001	0.004
$TiO_2 \cdot H_2O \cdot 3HCl$	20			
Bisphenol A-epichlorohydrin	18		4.1	13.9
1,4-butanediol diglycidyl ether	2		0.5	1.5
H_2O	(1.73)	1.33	0.40	
HCl	(10.5)	8.1	2.4	
TiO_2	(7.67)		1.76	5.91
TOTAL	**1000**	**48**	**931**	**21**

The focus of this design and calculations was to obtain conforming $TiCl_4$ by the simplest (or cheapest) possible developed column. From Table 3-20 it can be seen that a rather large quantity of $TiCl_4$ leaves through the first distillate, which is inadvertently lost. A possible cost analysis could be conducted to attempt determination of the most feasible ratio between product recovery and column enhancements.

The distillation was carried out until negligible quantities of $TiCl_4$ remain in the column.

The expected values are compared with the supplied specifications to ensure conformance of the obtained product. Both sets of values are given in Table 3-21.

Table 3-21: Specified and theoretical percentages of elemental compositions in $TiCl_4$ for smoke mortar manufacturing

	$TiCl_4$ % (min)	SO_4 % (max)	Heavy metals % (max)
Specification	99.0	0.01	0.006
Theoretical	99.01	0.005	0.004

It is thus evident that this process delivers $TiCl_4$ of acceptable quality for utilization in smoke mortar manufacturing.

3.6 Simulation

A simulation is required to determine the technical possibility of operation of the identified options. The results from this evaluation is required to verify that products conforming to the discussed stipulations can be obtained, while it will also aid in assessment of the preceding theoretical calculations. The subsequent economic analysis of the feasible processes will also be conducted based in the simulations' results.

Aspen Plus^{TM} software was available to conduct the necessary simulations for this study. It is an accurate program with comprehensive capabilities, but as it is generally the case, accuracy of supplied results is principally dependent on quality of the input data.

3.6.1 Thermodynamic property package

By following the property method selection guidelines in the Aspen Plus^{TM} software, NRTL, Wilson, UNIQUAC and UNIFAC models were identified as primary thermodynamic property method options to be selected for modelling the relevant processes. The NRTL, Wilson and UNIQUAC models utilize the ideal gas and Henry's law for modelling vapour and liquid behaviour in the system, along with the respective components' activity coefficients and binary interaction parameters with regard to the other compounds. UNIFAC makes use of Redlich-Kwong equation of state and Henry's law.

Aspen Plus^{TM} software has built-in default parameters to use in activity coefficient models to determine how species interact with one another. These parameters are then used to calculate new values for the NRTL, Wilson and UNIQUAC models that are applicable to the relevant system or make accurate estimations with the UNIFAC model when these values can't be calculated.

An obstacle to this study and required simulations was that no default parameters for activity coefficient models were available for $TiCl_4$. Default values for $TiCl_4$ in the intricate and unique mixture of this study could also not be found in literature and since it is one of the principal compounds, it was not possible to only focus on the remaining components. The result was that neither of these four recommended models could be used to accurately model these processes. The only possible option that remained was to select the 'ideal' thermodynamic property package, which uses Raoult's law and Henry's law to model the $TiCl_4$ and all impurities and products. By using this property package, it is thus assumed that these vapours and liquids can be characterized by the applicable assumptions for these two ideal phases. Although these assumptions will hamper the accuracy of obtained results, it was the only remaining solution to successfully perform simulations. It was also decided to not attempt estimations of the required values, since this could contribute to a greater error of results, but rather use a constant model and enable future studies to improve or start from a set and known basis.

The supplied Aspen Plus^{TM} template for pyrometallurgy was potentially beneficial for simulation of the metallic Ti and TiO_2 pigment production processes. However, its default thermodynamic method also required activity coefficient and solid handling parameters that needed to be supplied, but could not be obtained externally. By modelling these processes as ideal substances, accuracy of results will deviate from empirical results obtained in industry.

It is important to note that Aspen Plus^{TM} is well suited for simulating hydrocarbons and organic material, but is not regarded as the optimal simulation software for heavy metal production and treatment simulations. A possible solution that industries and institutions implement is incorporation of the FactSage© database into component parameters of Aspen Plus^{TM}, which supplies the necessary values for accurate simulations. Product licenses for this database are extremely expensive however and data can't be accessed without acquisition of the relevant product key. This option was thus not available and Aspen Plus^{TM} was the only simulation software available for usage at the time of this study.

3.6.2 Purification of $TiCl_4$ for metallic Ti and TiO_2 pigment production

The purification of demilitarized $TiCl_4$ for application in metallic Ti and TiO_2 pigment production processes are discussed first again, but it should be noted that this step should be included in relevant considerations of each process.

3.6.2.1 Components

The objective was to simulate a process with a feed similar to the theoretical composition of demilitarized $TiCl_4$ that was deduced from applicable analysis results and assumptions. Some of these components were not available for selection in the Aspen Plus^{TM} simulation software and alternative options were selected to account for these chemicals. It is expected that this will cause a slight deviation in accuracy of the obtained results and could be considered for improvement in future studies.

These challenges and limitations are discussed in Annexure B.1 along with the selected input alternatives.

3.6.2.2 Flow sheet

The desired method was to simulate a batch distillation column and consequently model this procedure as a dynamic process with changing column compositions and reflux ratios over time. A fatal obstacle to this approach was again missing property parameters in the Aspen Plus^{TM} database. Additionally, this software also considers $FeCl_3$ as a nonconventional chemical while the rest of the compounds are regarded as conventional. An error was generated during the attempted execution of this simulation, which stated that it was not possible to consider a mixture of conventional and nonconventional chemicals in a dynamic simulation. Due to the fact that the removal of $FeCl_3$ is one of the major objectives of this purification step, it was decided to develop a simulation which incorporated separation of this compound.

A continuous steady state process was therefore modelled with the selected flow rate being equivalent to the size of one batch over a period of one hour. The technique that was used to determine relevant column parameters was to first simulate this two-step process as two DSTWU columns in series to determine approximate reflux ratios and theoretical stages needed to obtain $TiCl_4$ of desired quality. The input stream was then fed to two DISTL columns in series which provided respective condenser and reboiler duties. The obtained results from the DSTWU and DISTL columns were used as initial values in two RADFRAC columns that were also connected in series to resemble the two steps of the distillation process. Design specifications of the RADFRAC columns were then adjusted until it delivered $TiCl_4$ suitable for use in the metallic and pigment processes.

The utilized flow sheet and all input and output values of this technique are found in Annexure B.1.

It is further not good practice to feed a mixture to a distillation column that is outside the operating temperature range of the column. It does not have such major influence in batch operations, but it was decided to preheat this liquid feed to a temperature close or equal to the bubble point of the predominant constituent in the first distillate, which is water. The heating efficiency of a heat exchanger is generally greater than that of the pot in a batch distillation column. This will also further aid in speeding up the distillation process.

The resulting flow sheet of preheated demilitarized $TiCl_4$ feed and a two-step RADFRAC distillation is seen in Figure 3-4.

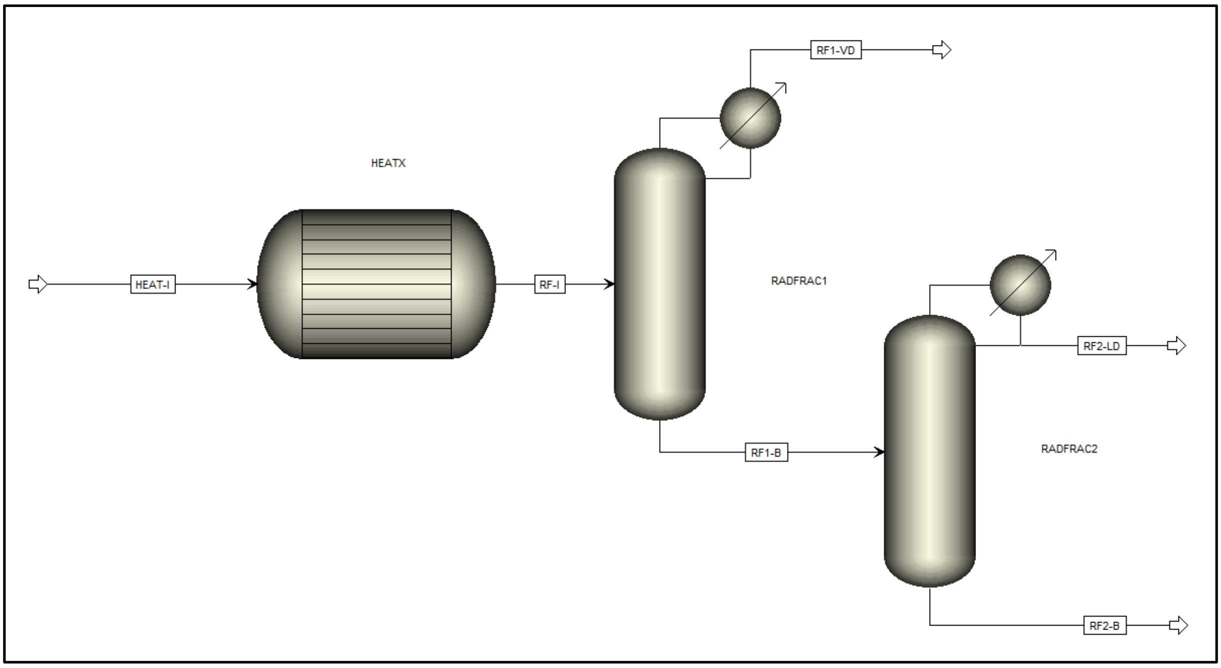

Figure 3-4: **Simulation flow sheet for $TiCl_4$ purification by means of a two-step distillation**

3.6.2.3 Column dimensions

Batch distillation columns with respective operating capacities of 630, 1000, 1600, 2000 and 2500 litres were some of the available options to select in the Aspen Plus^{TM} simulation software. The density of demilitarized $TiCl_4$ with a liquid fraction of 1 was obtained from the simulation and was determined to be 1.66 kg/dm^3. The approximate volume of a single 1000 kg batch feed can then be calculated to be around 600 L. Since Seader *et al.* (2011) state that the fluid volume inside the column should not exceed two thirds of the overall capacity, a 1000 L column is adequate for implementation in this project. Design properties for this column were obtained in Aspen Plus^{TM} for the De Dietrich DIN Reactor AE 1000 and are listed in Table 3-22.

Since it was determined that the column's packed-bed diameter should exceed 25.4 cm, a value of 28 cm was selected.

From the simulation it was determined that a column with 13 theoretical stages will be able to deliver the desired separation and product purification. The initial reflux ratio of the first step is set as 14, while the second step will have a ratio of 2. The actual value of the second step is 1.54, but using reflux ratios below 2 is not ideal and should first be tested before implementation. This ratio can then be altered during the batch process to deliver a product of uniform quality.

Table 3-22: Design properties of the pot in the batch distillation column

	Value
Capacity (L)	1000
Internal diameter (m)	1.2
Straight side (m)	0.485
Top and bottom	2:1 elliptical heads
Surface area (m^2)	4.6
Lining thickness (mm)	1.5
Wall thickness (mm)	20
Vessel mass (kg)	2230

The height of the packed bed is calculated by the HETP times the required stages. For 12 theoretical stages (condenser accounts for the first stage) and an HETP of 0.45, the height of the packed-bed is 5.4 m.

Okutani (2018) provided Equation 3-2 to quantify the amount of packing required in the packed bed.

$$n = C/D^3 \qquad [3\text{-}2]$$

with

n: quantity of rings in 1 m^3

C: constant for random packing = 0.77

D: diameter = 0.0254 m

The amount of Raschig rings that was used to fill the packing section is calculated to be 15 650.

These design properties and parameters are summarized in Table 3-23.

Table 3-23: Design properties of the packed section of the batch distillation column

	Value
Capacity (L)	333
Internal diameter (m)	0.28
Height (m)	5.4
Lining thickness (mm)	1.5
Wall thickness (mm)	20
Vessel mass (kg)	136
Raschig rings required	15 650

The observed pressure drop of 75 mm liquid per m packing will then equal an overall decrease of 0.04 bar over the column.

A graphical representation of the column layout is illustrated in Figure 3-5.

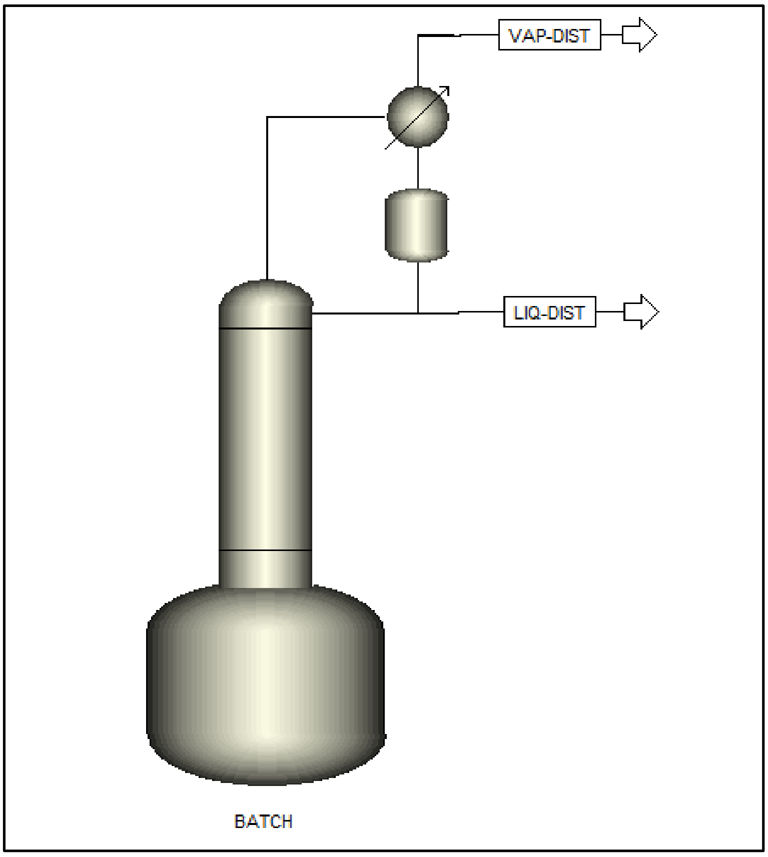

Figure 3-5: Graphical representation of batch distillation column design (obtained from Aspen Plus^{TM})

3.6.2.4 Units and utilities

Gravity is used to supply demilitarized $TiCl_4$ from a storage tank at a gauge pressure of 0.1 bar. A pump is then implemented to increase the pressure to 0.5 barg before it is preheated. The 'ideal' thermodynamic property package calculated the liquid fraction of the process feed to be less than one. The pump could therefore not be modelled in this simulation and the required duty was determined separately by simulating this pressure increase in a similar stream with a liquid fraction of one.

The selected method of preheating was by means of a heat exchanger that implemented low-pressure steam to heat the $TiCl_4$ from room temperature to 100°C. The steam will flow in a counter-current direction with regard to the liquid feed and a pressure drop of 0.2 bar is observed over the heat exchanger.

The input values and results of all process units (including the separate pump) are illustrated in Annexure B1. The required duties of the pump, heat exchanger and reboilers and condensers of each distillation step can be found in Table 3-24.

Table 3-24: Required duty of each process unit

	Duties (kW)
Pump	0.02
Heat exchanger	18.6
Reboiler of first step	39.9
Condenser of first step	29.4
Reboiler of second step	122.9
Condenser of second step	120.5

These duties are supplied by various utilities with different efficiencies and costs. A standard electrical pump was used to increase the pressure of the stored $TiCl_4$. As mentioned, low-pressure steam was used to preheat the liquid feed, while vapour from the first step was cooled in the condenser by cooling water. For the second distillation step low-pressure steam was generated in the condenser from boiler-feed water. The produced steam volumes can be fed to the rest of the plant for utilization in downstream or external units.

Low-pressure steam enters the initial heat exchanger at 125°C with a vapour faction of one and leaves the unit at 124°C with a liquid fraction of one. These input and output specifications is reversed for the steam generation of the second step. The cooling water in the simulation enters the condenser at 20°C and has an exit temperature of 25°C. An electrically powered pot was installed as the reboiler to heat the liquid in the column. A list of the utilities is supplied in Table 3-25.

Table 3-25: Required utilities for each process unit

	Electricity (kW)	LP steam (kg)	C water (kg)	BFW (kg)
Pump	0.02			
Heat exchanger		30.5		
Reboiler of first step	39.9			
Condenser of first step			5068	
Reboiler of second step	122.9			
Condenser of second step				198

With LP: low-pressure
C: cooling
BFW: boiler-feed water

3.6.2.5 Stream results

A summary of the feed, first distillate, second distillate and remaining liquid volumes is listed in Table 3-26.

Due to the vast differences in boiling temperatures between some of the components in the mixture and that of $TiCl_4$, the simulation proved that species were removed from the $TiCl_4$ to a much greater extent. This is also contributed by the simplifying calculations and assumptions of the ‘ideal’ property method, which could influence the accuracy of relative volatilities of each chemical.

A distillate product with a $TiCl_4$ purity of 99.99% are obtained from the second step of the process. This is substantially greater than the desired 99.9%. It was considered to simply the column design to, which will reduce the required costs. After a careful investigation into this matter it was determined that water is actually the limiting factor of this purification process. Thorough removal of this compound is required in the first distillate, which will reduce the remaining quantity in the second distillate product. Although no specification exists for water composition in the $TiCl_4$, a composition greater than 0.004% will cause a violation of the ASTM specification on the amount of water molecules in titanium sponge. It should be mentioned that the stated percentage is unique for this specific scenario and is influenced by overall liquid composition. The current H_2O percentage based on simulation results is 0.003%.

Table 3-26: Summary of the input and product streams of the purification process from the Aspen Plus^{TM} simulation

	Units	INPUT	RF1-VD	RF2-LD	RF2-B
Temperature	°C	25	89	145	319
Gauge pressure	barg	0.1	0.26	0.26	0.3
Mass flow rates					
$TiCl_4$	kg/h	960	10	950	
H_2SO_4	kg/h	0.050			0.050
$SiCl_4$	kg/h	0.020	0.020		
$FeCl_3$	kg/h	0.015			0.015
$VOCl_2$	kg/h	0.010			0.010
$K_2Cr_2O_7$	kg/h	0.005			0.005
TiO_2	kg/h	7.67			7.67
H_2O	kg/h	1.73	1.69	0.04	
HCl	kg/h	10.5	10.5		
Bisphenol A	kg/h	18			18
1,4-butanediol	kg/h	2		0.02	1.98
Total mass flow	kg/h	1000	22	950	28

Although no restrictions on H_2O particles exist for TiO_2 pigment production that process still demands a $TiCl_4$ feed of great purity, since impurities causes pigment discoloration. The purified $TiCl_4$ will therefore adequately feed both processes.

The cooled distillate product was then transferred to a storage container for application in subsequent processes while impure volumes were treated further or correctly disposed.

3.6.2.6 Verification of simulation results

Verification of the simulation results with stated specifications indicated that the purified $TiCl_4$ conforms to elemental and purity specifications. Both sets of values are given in Table 3-27.

Table 3-27: Verification that simulation results of purified $TiCl_4$ conforms to product stipulations

	$TiCl_4$ % (min)	Fe ppm (max)	V ppm (max)	Si ppm (max)	Sn ppm (max)	Hazen colour no. (max)
Stipulation	99.9	10	10	10	30	20
Simulation	99.99	<1	<1	<1	-*	

*Sn values and colours were not measured and are unaccounted for

The colour of resulting product could not be obtained from simulation. It is further expected that by inclusion of $VOCl_3$ instead of $VOCl_2$ in the process model, elevated levels of vanadium would have been detected in the $TiCl_4$.

3.6.3 Titanium metal production by Kroll process

It should be noted early in this section that severe errors were encountered during the attempted simulation of this process.

These errors, along with other challenges, limitations and respective solutions are discussed in Annexure B.2.

The erroneous output still aids in providing a general indication of the expected products and proportion of utilities required to conduct this process successfully once the correct input has been acquired. The intention was that it could aid in future developments and considerations that are based on this study. A critical discussion of the practicality of this process as solution to this study can be found in Section 3.7.

3.6.3.1 Components

The components that were fed to the reactor are $TiCl_4$, H_2O and 1,4-butanediol from the purification process, along with Mg metal reactant. The formed products are Ti sponge and $MgCl_2$.

3.6.3.2 Flow sheet

The initiative was to simulate this batch process in a batch reactor. The major obstacle to this approach was that no kinetic rate equations of the Kroll process were found in literature and it is expected that this can be an extremely difficult process to model since it occurs over such a large time period and is highly dependent on process parameters and operation techniques.

The batch reactor in the simulation could not operate without the applicable kinetic values and it was therefore decided to utilize a GIBBS reactor, which determined products by minimizing Gibbs free energies and entropies. The GIBBS reactor operates on a continuous steady state basis and a constant feed should therefore be supplied to the reactor to perform this simulation.

This alteration causes another deviation between the simulated and actual processes. With that said, the focus of this chapter is to evaluate the technical feasibility of this process and not to develop a simulation of absolute accuracy with regard to empirical determinations.

The flow sheet that were developed consists of a pump to increase the pressure of the liquid $TiCl_4$ feed, followed by preheating of the reactants. Each reactant stream was heated separately before introduction to the reactor. The $TiCl_4$ stream was heated to 700°C before introduction to the reactor with an observed pressure drop of 0.2 bar over the heater. The Mg metal was technically heated in its solid phase to 600°C and can either be manually or mechanically transferred to the reactor for melting. Accordingly, no pressure readings or adjustments are observed. The flow sheet can be seen in Figure 3-6.

Input and output values of each unit can be found in Annexure B.2.

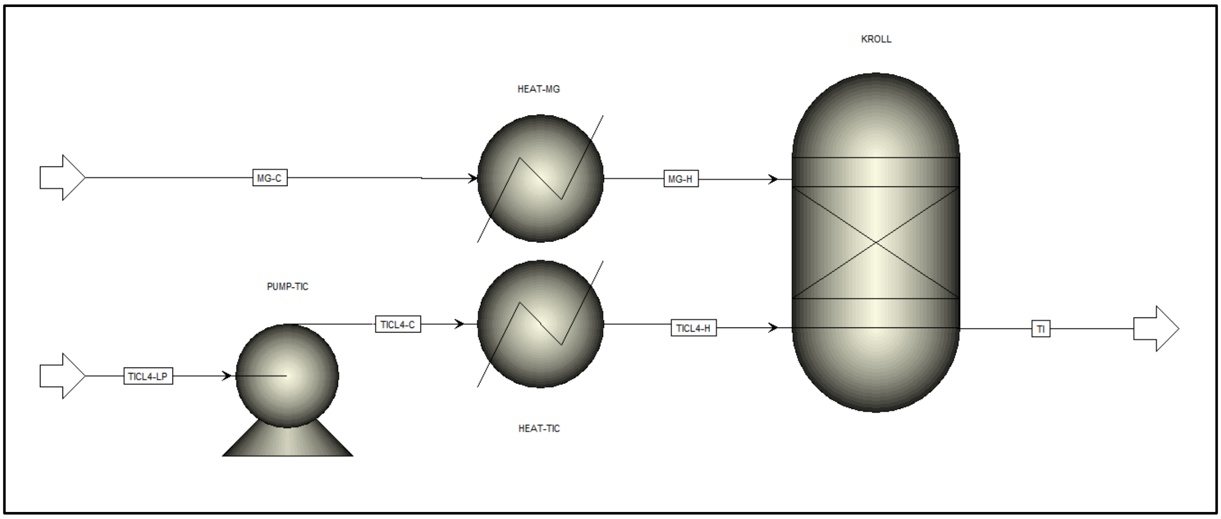

Figure 3-6: **Flow sheet of the simulated Kroll process**

3.6.3.3 Reactor dimensions

Recommended reactor dimensions for this process could not be calculated in the GIBBS reactor of the simulation software. The best remaining option is to implement empirical data from literature that is applicable for this process capacity and conditions. A suitable option is the pilot plant reactor by Nagesh *et al.* (2004), which the theoretical calculations of this study were based on. Dimensions of the crucible and the retort are similar to the values stated in the process configuration section and can be seen in Table 3-28.

3.6.3.4 Units and utilities

The pump was operated on electrical power to apply the required feed pressure. The two heaters and reactor will heated by burning natural gas. This latter utility was not an available option in the simulation software and is accordingly not included in this results. A list of the required duties of each unit is given in Table 3-29.

The ‘ideal’ thermodynamic method used to determine reaction conditions in the GIBBS reactor is set to only consider vapour and liquid phases. Products in the solid phase, especially titanium sponge, are therefore not modelled flawlessly, which will have an influence on resulting unit duties. This is also regarded as a potential improvement for future studies.

Table 3-28: Dimensions of retort and crucible of the reactor

	Value
Retort:	
Internal diameter (m)	1.36
Straight side (m)	2.77
Wall thickness (m)	0.025
Top and bottom	Elliptical head
Crucible:	
Internal diameter (m)	1.21
Straight side (m)	3.05
Wall thickness (m)	0.025
Top and bottom	Open

Table 3-29: Required duty of each process unit

	Duties (kW)
Pump	0.2
Mg heater	1362
$TiCl_4$ heater	1283
Kroll reactor	14792

3.6.3.5 Stream results

The GIBBS reactor includes various products in its free energy and entropy calculations to determine the probable reaction results. It can either be set to consider all components included in the simulation as possible products or expected products can be manually selected in the software interface. It was first attempted to simulate the process by considering all components as products, but a minuscule extent of reaction for the Ti production was observed. This can be largely contributed by the software's inability to successfully simulate solids with the missing parameters and selected thermodynamic method. However, a purpose of this technical evaluation was obtain estimated values for the utility usage of this process and to identify required process units and their respective sizes for further implemented in economic evaluations.

In order to adequately simulate this process as it is expected to occur in practice, anticipated products of the reactor were selected. These products were Ti sponge, water and 1,4-butanediol from the feed, excess Mg and residual $MgCl_2$.

The conditions and compositions of the overall input and output streams for this process are given in Table 3-30.

The produced titanium sponge can then be transferred to an applicable purification process for the removal of residual Mg and $MgCl_2$. The removed Mg and $MgCl_2$ mixture can then in its turn be separated in Mg and Cl_2 through electrolysis.

3.6.3.6 Verification of simulation results

In order to effectively evaluate the sponge composition, sufficient separation of Mg and $MgCl_2$ during vacuum distillation is required. The separation efficiency of 99.4% from the theoretical calculations is used in this simulation, which makes it important to note that an adequate vacuum distillation process should be implemented to deliver the prescribed separation. Verification of the simulation results with values from ASTM standards then indicates that produced sponge conforms to the applicable stipulations. Both sets of values are given in Table 3-31.

Table 3-30: Summary of the input and product streams of the Kroll process from the Aspen Plus^{TM} simulation

	Units	MG-C	TICL4-LP	TI
Temperature	°C	25	25	900
Pressure	barg	0	0.1	0.2
Mass flow rates				
Ti	kg/h			2019
$TiCl_4$	kg/h		8000	
Mg	kg/h	2900		850
$MgCl_2$	kg/h			8031
H_2O	kg/h		0.9	0.9
1,4-butanediol	kg/h		0.2	0.2
Total mass flow	kg/h	2900	8001	10901

Table 3-31: Verification that elemental compositions of simulation results in titanium sponge conform to specified standards

	N (max)	C (max)	Mg (max)	Al (max)	Cl (max)	Fe (max)	Si (max)	H (max)	H_2O (max)	O (max)	Ti (min)
Spec	0.015	0.02	0.5	-	0.12	0.12	0.04	0.01	0.02	0.10	Bal.
Sim	-	0.005	0.3	-	0.06	<0.01	<0.01	0.001	0.017	0.003	99.6

With Spec: specified maximum values
Sim: results obtained from simulation

3.6.4 Titanium dioxide pigment production by chloride process

Similar issues to the simulation of the Kroll process were encountered for this process.

Challenges and obtained simulation errors of this process are discussed in Annexure B.3.

The effect of these occurrences on the overall result of this study is discussed in Section 3.7. Results obtained from this section will aid in indicating the required units and utilities that are to be considered in economic evaluations.

3.6.4.1 Components

The components that were included in this simulation are $TiCl_4$, H_2O and 1,4-butanediol from the feed, along with O_2 and additional water. Chemicals formed from the main reaction are TiO_2 and Cl_2.

3.6.4.2 Flow sheet

TiO_2 pigment production by the chloride process is a continuous process and will therefore be modelled as such.

Gravity is used to supply $TiCl_4$ to a pump to increase the pressure to 0.5 barg. It is anticipated that a pump is not required for the second feed stream, since acquired O_2 is already stored in a pressurized vessel and can be applied to the water (and catalyst) at pressures that will transfer it through the heater. Both streams were separately heated to 850°C in similar heating units with a pressure drop of 0.2 bar over each unit. Both streams were then compressed to 3 barg before being introduced in the reactor.

Since the plasma arc reactor of this process is considered to be a plug flow reactor (PFR), the initial approach was to simulate this process by a PFR on Aspen Plus^{TM}. A kinetic equation for this reaction rate was obtained from West (2008) and is given by Equation 3-3. The reaction rate, *r*, is a first order equation with regard to the concentration of $TiCl_4$ in the reactor.

$$r = k_{total}[TiCl_4] \qquad [3\text{-}3]$$

The rate coefficient k_{total} is calculated by the Arrhenius expression (Equation 3-4)

$$k_{total} = A\, exp\left(\frac{-E_a}{RT}\right) \qquad [3\text{-}4]$$

with

A: pre-exponential factor = 8.26×10^4 s^{-1}

E_a: activation energy = 88 800 J / mol

R: molar gas constant = 8.314 J / (mol·K)

T: reaction temperature (K)

This rate equation was developed for a reaction between 700 and 1000°C since it is extremely challenging to take accurate measurements at the temperature range of the industrial process. It is therefore advised to be cautious in extrapolating this equation for use at industrial conditions of the chloride process.

It was decided to see what effect this kinetic rate equation will have on this simulation of this process. A PFR was selected in the simulation software and all relevant input was entered. However, after the expected reaction and its kinetic values were specified the simulation deemed that no reaction will take place. Reactor parameters (temperature, diameter and length) were varied separately and concurrently, but even at the maximum values of these properties, the product formation was still determined to be null.

The objective of the thesis by West (2008) was to develop a kinetic model of greater accuracy for this process. In his study he modelled 67 elementary reactions which occur during the formation of TiO_2 from $TiCl_4$. His conclusion was that the developed model enhanced the accuracy of the kinetic model for TiO_2 formation, but it is not flawless and still had areas which could be improved. Inclusion of that model was considered, but was deemed to fall outside the current scope since using computational software to model an extremely complex set of reactions is not the primary focus of this study. Another factor to consider is that modelling of this system in software such as MATLAB® will cause difficulties in comparison of the results from the other process, which are simulated in Aspen Plus™. Furthermore, the extent by which this model improved the accuracy of the process results was not stated by West (2008) and could therefore not be accounted for. Obtaining and modelling intricate reaction systems of the other processes in conjunction with this model will certainly aid in improving the accuracy of each process and could be considered in future studies.

The best remaining option was to simulate this process in a GIBBS reactor.

The constructed flow sheet for the chloride process can be seen in Figure 3-7 while each unit's input and output values are displayed in Annexure B.3.

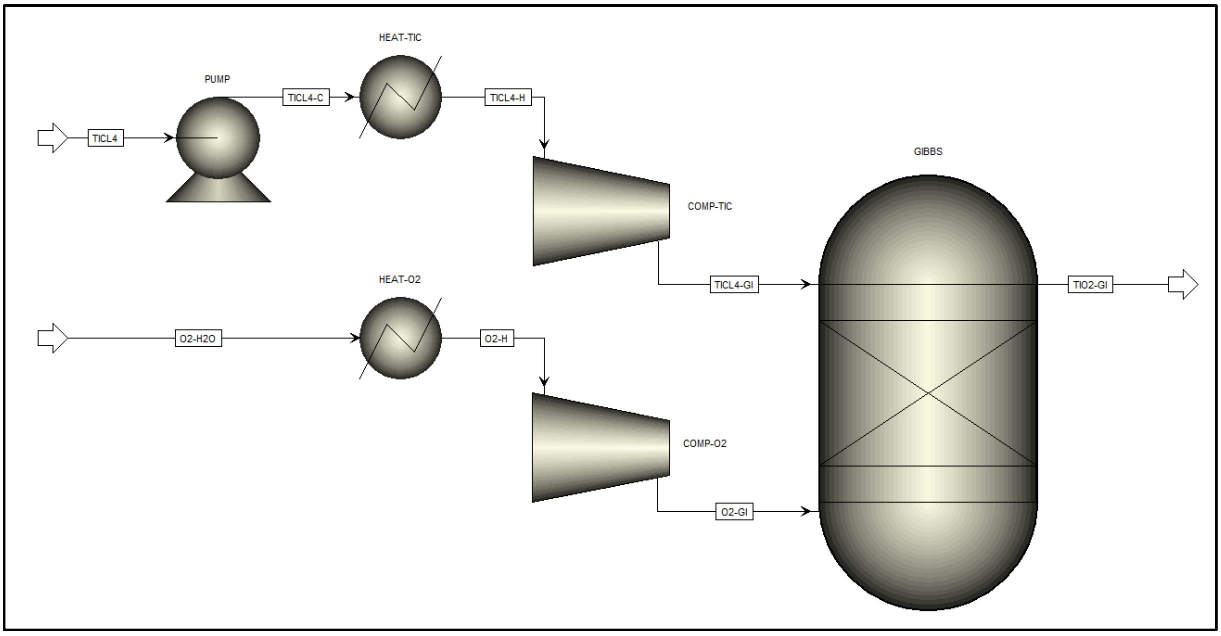

Figure 3-7: **Flow sheet of the simulated chloride process**

3.6.4.3 Reactor dimensions

A successful model of the kinetic TiO_2 formation reactions is required to determine the dimensions of this reactor in Aspen Plus^{TM}. Since it was not possible to develop this model, alternative options should be identified to determine the applicable dimensions.

A possible solution that was recognized was to find a suitable plasma arc furnace from literature with similar processing capacities. The general layout of a typical plasma arc furnace for TiO_2 pigment production was obtained from Nel *et al.* (2010) and can be seen in Figure 3-8.

The calculated reactor duty from the simulation software was 652 kW. It was not possible to obtain reactor dimensions for this plasma arc furnace, but a similar reactor to the one in Figure 3-8 was selected based on its relevant duty. The available furnace that was identified had a duty of 1 MW and was modelled accordingly in the economic evaluation.

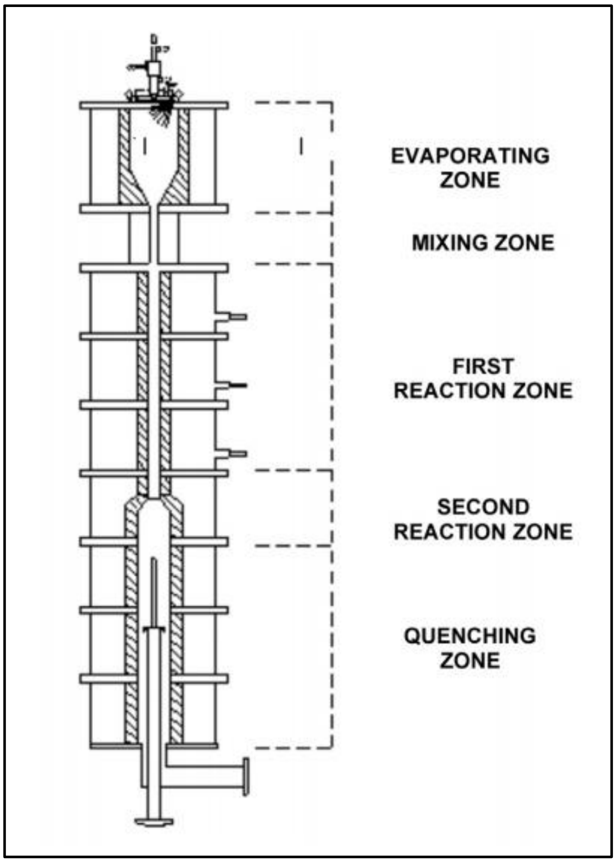

Figure 3-8: Schematic of a plasma arc furnace for TiO_2 pigment production (taken from Nel *et al.* (2010))

3.6.4.4 Units and utilities

All used pressure manipulators during the pre-treatment of the reactant streams are electrically powered. The heaters feed stream heaters and the plasma arc furnace are operated on natural gas to supply the necessary heat. No viable option was available in Aspen Plus^{TM} to effectively simulate the heat generation in the units. The best available alternative for simulation purposes was to supply heat addition to the heaters and reactor by using electrical power. The factors are considered and amended for economic calculations in the following chapter.

Duties for each process unit are given in Table 3-32.

It should be noted that the duty of the furnace was influenced by the fact that only vapour and liquid phases were considered. The accuracy of obtained results will be improved by also modelling solid compounds, which could be included in future studies.

Table 3-32: Required duty of each process unit

	Duties (kW)
$TiCl_4$ pump	0.02
$TiCl_4$ heater	175
O_2 heater	59
$TiCl_4$ compressor	21
O_2 compressor	30
Plasma arc furnace	652

3.6.4.5 Stream results

An identical problem to that of the Kroll process were found with the Gibbs reactor and expected products were specified to obtain an appropriate simulation of the service. The identified products were 1,4-butanediol from the feed, along with H_2O, excess O_2, formed TiO_2 and the by-product Cl_2.

A summary of the overall input and output streams are given in Table 3-33.

The produced TiO_2 pigment particles are then purified and water is added to transfer the formed slurry through various treatment and sizing steps before the pigment is finally dried.

3.6.4.6 Verification of simulation results

It is assumed that 98% of the remaining O_2 and formed Cl_2 can be removed from the pigment during purification. By comparing the stipulations and simulation results in Table 3-34 it is then possible to successfully verify that produced TiO_2 pigment complies with ASTM standards. The other specifications from the standards are more dependent on utilized finishing procedures.

Table 3-33: Summary of the input and product streams of the chloride process from the Aspen Plus™ simulation

	Units	TICL4	O2-H2O	TIO2-GI
Temperature	°C	25	25	1250
Pressure	barg	0.1	0.1	3
Mass flow rates				
TiO_2	kg/h			400
$TiCl_4$	kg/h	950		
O_2	kg/h		179	18.7
Cl_2	kg/h			710
H_2O	kg/h	0.1	15.9	16
1,4-butanediol	kg/h	0.02		0.02
Total mass flow	kg/h	950	195	1145

Table 3-34: Verification that TiO_2 content of pigment from simulation conforms to supplied standards

	Simulation	Type I	Type II	Type III	Type IV	Type V	Type VI	Type VII
TiO_2 content	92.9%	94%	92%	80%	80%	90%	90%	92%
Crystal structure	-	Anatase	Rutile	Rutile	Rutile	Rutile	Rutile	Rutile

The observed TiO_2 content of simulation results is greater than the required purities. However, notable decrease to 92.06% is observed when the mass of catalyst is included in calculations.

Since it was already determined that $AlCl_3$ can be used as catalyst in the actual process even though it was not included in the simulation, it can be deduced that the crystal structure of the pigment will consist of rutile crystals.

3.6.5 Titanium tetrachloride in smoke mortars for military application

The requirements on $TiCl_4$ for use in smoke mortars more lenient than those of the $TiCl_4$ that is used for feeding the metal and pigment production processes. A less complex separation unit is thus required.

Because of the low required purity, the possibility of performing only a single step distillation was examined. The large volumes of $SiCl_4$, HCl and H_2O in the demilitarized $TiCl_4$ meant that this will deliver a product with a maximum purity of below 98%. Hence, a two-step process is still required to remove the lighter impurities.

A similar approach to that in Section 3.6.2 was used to design a distillation column by first modelling DSTWU columns followed by DISTL columns to obtain initial values for RADFRAC columns. The resulting parameters indicated that a column with only two stages and meagre reflux ratios will adequately purify the $TiCl_4$ for use in smoke mortars.

Due to the simplicity of the determined parameters, it was further suspected that the theoretical stages and refluxing procedures could be redundant for this particular separation unit. The subsequent process that was tested was consisted of a vessel with a boiler unit and no stages or reflux returning to the column. A two-step process was still conducted to promote separation of the lighter components. The resulting simulation proved that this setup could deliver $TiCl_4$ of satisfactory quality with an acceptable overall product recovery.

3.6.5.1 Components

Identical issues to those of the purification process in Section 3.6.2 and Annexure B.1 played a role in this simulation. Similarly, the major changes in input components are the $VOCl_3$, bisphenol A-epichlorohydrin and 1,4-butanediol diglycidyl ether species that will respectively be modelled as $VOCl_2$, bisphenol A and 1,4-butanediol.

3.6.5.2 Flow sheet

The two-step process of the batch vaporization unit was simulated by two flash units in series. Due to the challenges with relevant property parameters and the thermodynamic method, it is required to model this batch process as a continuous steady state operation in this simulation software.

Demilitarized $TiCl_4$ was supplied by means of gravity to a pump that will increase the pressure to 0.5 barg. This pump was simulated separately for an identical stream with a liquid fraction of one. The temperature of the feed is then increased in a heat exchanger to 107°C. A pressure drop of 0.2 bar occurs over the heat exchanger. This exit temperature of the feed was selected based on the bubble point of water, which is between 107 and 108°C at 0.3 barg. The heated volume is then transferred to the vaporization unit where the first boiling step was conducted at an operating temperature of 108°C. Most of HCl and $SiCl_4$ were removed in this step.

The second step (represented by the second flash unit in the simulation) was conducted at 240°C to deliver a maximum recovery of $TiCl_4$ at a purity above 99%.

This vapour product is then condensed to below its bubble point.

The constructed flow sheet is illustrated in Figure 3-9. Input and output values of each unit are provided in Annexure B.4.

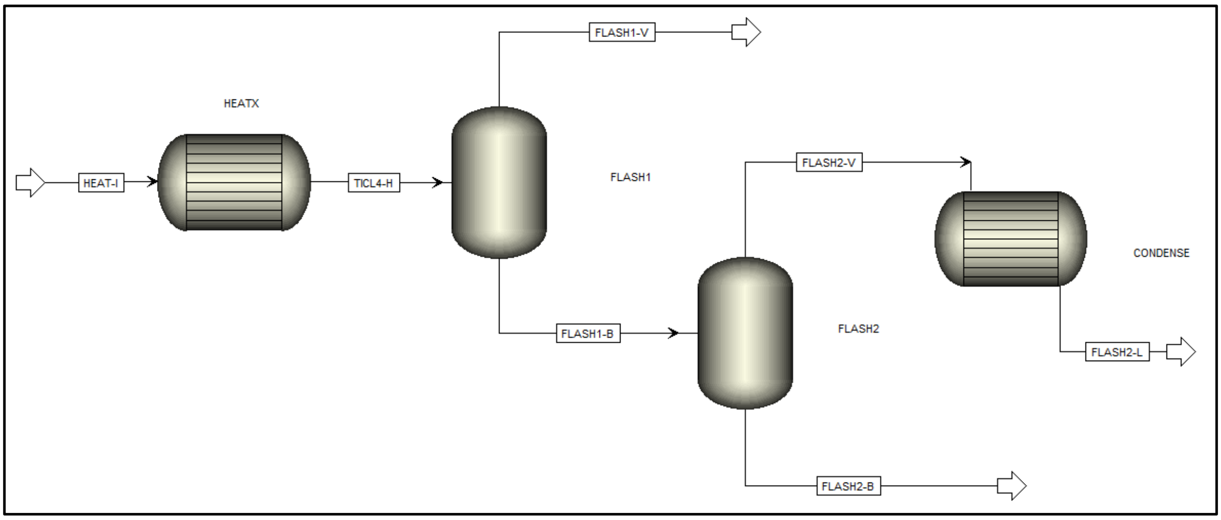

Figure 3-9: Simulation flow sheet for obtaining $TiCl_4$ by means of a two-step vaporization process

3.6.5.3 Vessel dimensions

A similar vessel to the pot of the distillation column in Section 3.6.2 is used for the two-step vaporization process.

3.6.5.4 Units and utilities

The duty of each process step, or process unit in the case of the simulation, is given in Table 3-35.

Table 3-35: Required duty of each process unit

	Duties (kW)
Pump	0.02
Heat exchanger	20.5
First boiling step	0.3
Second boiling step	70.2
Condenser of second vapour product	64.9

The pump and flash units are powered with electricity, while the initial heat exchanger utilizes low-pressure steam to affect the desired temperature increase in the cold stream. This steam is fed at a temperature of 125°C with a vapour fraction of one and exits the heat exchanger at 124°C with a liquid fraction of one. The heat exchanger that cools the second vapour product removes quite a substantial amount of energy from the $TiCl_4$. The selected utility for this unit is boiler-feed water which is converted to low-pressure steam. A water stream with a liquid fraction of one enters the exchanger and is removed in the vapour phase at 125°C. Only latent heat of vaporization are considered in steam generation calculations (Seider *et al.*, 2010).

The generated steam can be supplied to the rest of the chemical plant for external applications.

The quantity of each utility for each procedure is listed in Table 3-36.

Table 3-36: Utilities for each process unit

	Electricity (kW)	LP steam (kg)	BFW (kg)
Pump	0.02		
Heat exchanger		33.7	
First boiling step	0.3		
Second boiling step	70.2		
Condensing second vapour product			106.5

With LP: low-pressure
BFW: boiler-feed water

3.6.5.5 Stream results

Each streams composition and physical conditions are given in Table 3-37.

An operation temperature slightly above the bubble point of water was selected for the first step to remove most of the HCl and $SiCl_4$ from the liquid volume while the water will just start to boil. Due to only a slight margin between the boiling points of water and $TiCl_4$, it was expected that a notable quantity of product was lost along with the water. After completion of the first boiling step, a high temperature was selected for the second step to enhance product recovery, while monitoring $TiCl_4$ composition. The $TiCl_4$ in the second vapour product showed an almost negligible increase when the temperature exceeded 240°C and the relevant purity dropped below 99% at 250°C.

3.6.5.6 Verification of simulation results

With the intention of minimizing unit costs and maximizing product recovery it can become quite challenging to find a balance between these two objectives. An overall $TiCl_4$ recovery of 96% is achieved, which is acceptable for the current scenario. Verification of the resulting products conformance to stated stipulations showed that a product of adequate quality is obtained. These two sets of values are listed in Table 3-38.

Table 3-37: Summary of the input and product streams of the two-step vaporization process from the Aspen Plus^{TM} simulation

	Units	INPUT	FLASH1-V	FLASH2-L	FLASH2-B
Temperature	°C	25	108	125	240
Pressure	barg	0.1	0.3	0.1	0.3
Mass flow rates					
$TiCl_4$	kg/h	960	27	928	5
H_2SO_4	kg/h	0.050		0.042	0.008
$SiCl_4$	kg/h	0.020	0.004	0.016	
$FeCl_3$	kg/h	0.015		0.012	0.003
$VOCl_2$	kg/h	0.010			0.010
$K_2Cr_2O_7$	kg/h	0.005			0.005
TiO_2	kg/h	7.67			7.67
H_2O	kg/h	1.73	0.13	1.60	
HCl	kg/h	10.5	9.8	0.7	
Bisphenol A	kg/h	18		4	14
1,4-butanediol	kg/h	2		1.9	0.1
Total mass flow	kg/h	1000	37	936	27

Table 3-38: Verification that obtained $TiCl_4$ from the simulation conforms to product stipulations

	$TiCl_4$ % (min)	SO_4 % (max)	Heavy metals % (max)
Specification	99.0	0.01	0.006
Simulation	99.1	0.004	0.003

By accounting for $VOCl_3$ in the $TiCl_4$ product instead of the removed $VOCl_2$, the heavy metal composition will only increase to 0.004%, which still falls within prescribed regulations.

3.7 Considerations for metallic Ti and TiO_2 pigment production

During the study of the Ti metal and TiO_2 pigment production processes in the literature survey, it became evident that capacities of existing industrial plants is substantially greater than the maximum possible production of this study. No minimum operating capacities were found from literature and it was thought best to still include these two processes in the evaluation and to use obtained results to determine if plants with capacities that are applicable to this study, are feasible.

Several industrial companies and research divisions that focus on titanium have been consulted during the technical evaluation of these processes. The main aim of each visit or discussion was to obtain relevant process information to improve the accuracy of this study. One factor that repeatedly came up was that the capacities of these two processes for this study were far below the required volumes for the production plant to be feasible.

The average industrial capacities or production rates of these two processes were mentioned in the relevant design sections. In order to produce 20 000 tpa of each product, respective $TiCl_4$ feeds of ± 80 000 tpa is required for the Kroll process and ± 50 000 tpa for the chloride process. These values are incomparable to the available quantities of this process.

The conclusion that was made based on their respective opinions was that it can be expected that these two processes won’t be identified as the best recycling processes from the results of the techno-economic evaluation. The technical evaluation determined that all considered processes were practical and possible but it is expected that the CAPEX and OPEX values of the metal and pigment production processes far outweigh the possible revenues.

For an improved flexibility of this study, these options are still be analysed in the economical evaluation and minimum capacities could be identified, which can be useful to third parties that have similar problems, but larger scopes.

3.8 Conclusion

The focus of this chapter was to perform a technical evaluation on the processes that were selected based on the findings on the literature survey.

In order to determine the required pre-treatment steps and to accurately model the chemical process, it was necessary to determine the composition of the demilitarized $TiCl_4$. Fifteen samples of five different batches were obtained and were analysed by an ICP-OES to determine impurity concentrations and by a chloride in solution test to calculate $TiCl_4$ purities. No problematic levels of impurities that were tested for were present in the liquid. Purities did range between 96 and 99% however and a visual analysis showed that the expected clear and transparent liquid was actually completely discoloured to dark yellow or in some cases black.

After various considerations and queries to members of the $TiCl_4$ industry, it was assumed that a contribution to the observed discolorations was contamination by Araldite epoxy resin that is used to seal smoke mortars. Based on this assumption and the various results from analysis, a low quality demilitarized $TiCl_4$ composition was assumed, which was to be used in calculations and simulations.

The focus was then shifted towards the desired products and relevant standards and stipulations that exist in industry. Specification that the output of each process should conform to was identified.

Hereafter, the theoretical process designs and calculations were performed. Process units and applicable parameters were determined from literature and required efficiencies were stated. These values were also used to give a general expectation of possible results from the succeeding simulations.

The methods for purification of $TiCl_4$ for use in metallic Ti and TiO_2 pigment production processes, the actual manufacturing steps of these two products and the preparation of $TiCl_4$ to fill smoke mortars, were all simulated on the Aspen Plus^{TM} software. Several challenges and discrepancies emerged that hampered the accuracy of the simulations when compared to empirical results. The main issue was the choice of thermodynamic property method to use for chemical and energy calculations. The ‘ideal’ property package was selected, since all other options required parameters that were missing for intricate set of chemicals.

Results were obtained and all products conform to the relevant standards or stipulations. These values were used to perform the economical evaluation in Chapter 4.

A final issue that was discussed was the contrast between the available capacities of the metal and pigment production processes of this study and that found in industry. This gives an expectation that results of this study will be dismissive towards these two processes. The decision was made to still evaluate these processes for greater flexibility of this study.

CHAPTER 4: ECONOMIC ANALYSIS

4.1 Introduction

The identified recycling processes from the literature survey was technically evaluated in Chapter 3 to determine the expected product formation of each process at relevant operating conditions and parameters. An economic analysis of each process based on its simulation data is conducted in this chapter.

The economic potential of these processes is determined initially, followed by the relevant CAPEX and OPEX calculations. Certain assumptions were required to complete this economic model. These assumptions are stated clearly.

The required purification process for obtaining $TiCl_4$ of acceptable quality to feed the metallic Ti and TiO_2 pigment production processes is again modelled separately in this chapter. These calculated results are then carried over to the production processes to be included in its calculations.

4.2 Assumptions for process calculations

The initiative was to try not to make assumptions which will cause accuracy deviations between the obtained results and industrial values. Most of these assumptions were made to set the scope of the study or to establish which factors are omitted and should be considered in further developments.

4.2.1 Budget period

The focus period of this study for which a budget was constructed is six years.

This period length was selected based on the fact that the smoke mortars that require demilitarization are not stored at the same location and it will be a timely process to transport these mortars (or mobile process units) to the location where demilitarization of $TiCl_4$ will take place. Furthermore, the demilitarization process itself is quite a time consuming process. The final factor that played a role was the annual consumption of 99% pure $TiCl_4$ for use in filling new smoke mortars. This annual manufacturing rate has a $TiCl_4$ uptake just below 7 tpa, which makes it somewhat undesirable to deliver values above this volume.

The total demilitarized $TiCl_4$ feed then consists of the initial 40 ton in the first year, with an additional 2 ton added over the next five years (at 400 kg pa) to give a total value of 42 ton. This available quantity of feed is deemed as the limiting factor to the study.

4.2.2 Consumption rate of feed

This study focused on gradually consuming the 42 ton of $TiCl_4$ feed over the six years. The selected option was therefore not be operated continuously, but rather on a sporadic basis.

4.2.3 Exchange rate

An exchange rate of ZAR 14.00 for USD 1 are used for conversions between South African Rand and United States Dollar (August 2018).

Prices from The Kerala Minerals & Metals (2008h) are given in Indian Rupees. A conversion rate of INR 70.00 for USD 1 is used to convert these prices to United States Dollar (August 2018).

4.2.4 Transport, import and export fees

Costs of transporting and importing / exporting of process units and inputs were not included in calculations. It is recommended that an in-depth study is dedicated towards this matter to select the most cost effective option from the various existing alternatives.

All stated values can therefore be considered as free on board (FOB) prices.

4.2.5 Disregard of inflation

The focus of this study is more on how these processes compare to one another and not to deliver design values of absolute accuracy over the focus period of six years. Since inflation will influence all processes to nearly the same extent, it was not regarded as influential for this budget period.

4.2.6 Cost of inert gas

It is evident from the process configuration section (Section 3.5) that all processes incorporate the use of an inert gas. Argon has been selected as the applicable gas, but the cost of this entity was not included in economic potential calculations. This decision was based on the fact that the use of an inert gas is rather considered to be a utility than an input our output material. It is also expected that somewhat similar quantities of gas were used in each process with the result that it will have little effect on process comparisons.

4.2.7 Efficiencies of process units

Both the Aspen Plus^{TM} simulation software and the financial modelling equations by Seider *et al.* (2010) consider built-in default efficiencies of process units in delivered results. Consequently, no additional unit efficiencies were considered or accounted for in calculations.

4.2.8 Impact of chemical waste

Another important factor to include in process designs and financial considerations is the production of chemical wastes that have little to no potential of being supplied as a by-product. However, the chemical wastes of each process in this comparative study is almost similar in magnitude and composition. This is visible when the first vapour product and vessel residue of the two-step vaporization process is compared with the first distillate and column residue of the purification step which precedes the production processes. Consideration of the waste treatment utility will have negligible effects on the final comparisons and are therefore not included in utility costs.

4.3 Economic potential

Douglas (1988) recommends to initiate each potential process by first determining its economic potential. This method of analysis indicates whether the value of the product is actually increased by the process and if a potential income can therefore be generated.

The economic potential at level 1 (Equation 4-1) is used for a simple input-output process with a single desired product.

$$EP_1 = Product\ value - Raw\ material\ cost \tag{4-1}$$

A positive EP value is thus desired.

When a secondary by-product is formed during the reaction, the economic potential changes to Equation 4-2.

$$EP_2 = Product\ value + By\ product\ \ - Raw\ material\ cost \tag{4-2}$$

For a process that contains a recycle stream, the economic potential should be duly adapted to account for the recycled volume.

The stated values were obtained from major chemical companies that supply a large range of products in substantial quantities. The objective was to obtain prices for the various compounds from the same supplier to ensure a degree of standardization between calculation results. Most of these large suppliers are situated outside of Africa. The obtained prices will therefore differ to some extent when compared to costs that are relevant to the current South African market. This will not have a remarkable influence on the outcome however, since the focus of this economic potential analysis is more on comparisons between the product and input values and not the actual differences.

4.3.1 Purification of $TiCl_4$ for metallic Ti and TiO_2 pigment production

The relevant quantities of this process over six years is given in Table 4-1. Only components that are present in significant volumes were accounted for. Values are rounded for ease of calculations.

Table 4-1: Summary of components with noteworthy volumes in the $TiCl_4$ purification process

	Input (kg)	**Distillate 1 (kg)**	**Distillate 2 (kg)**	**Residue (kg)**
$TiCl_4$	40 300	400	39 900	
Bisphenol A-epichlorohydrin	760			760
1,4-butanediol diglycidyl ether	80			80
H_2O	70	70		
HCl	440	440		
TiO_2	320			320
TOTAL	**42 000**	**900**	**39 900**	**1 200**

No previous studies or data were found on the actual implementation of demilitarized $TiCl_4$ in industrial processes which meant that actual values for this feed could not be obtained from literature. It was decided to use the price for crude $TiCl_4$, since it is treated and purified by similar process units and techniques. Crude $TiCl_4$ is not a common commodity in industrial markets and no supplier of this item was found. Kale (2018) did however provide useful information on this matter by stating that the average price increase between crude and purified $TiCl_4$ is between 20 and 30%. This information is then used to reverse calculate this price from the selling price of the purified product, which is assumed to be beneficiated by 25%.

The price of purified $TiCl_4$ (99% purity) from The Kerala Minerals & Metals (2008h) is $ 1440 per ton. Crude $TiCl_4$ would therefore cost about $ 1150 per ton.

The selling price of $TiCl_4$ with a purity of 99.99% is obtained from Alibaba (2018e) and is approximately $ 1700 per ton.

Chemical mixtures of the first distillate and column residue have an almost negligible worth and since these volumes are somewhat insignificant, it is not feasible to separate it as by-products.

The economic potential is then calculated by Equation 4-3 to give a positive value of $ 19 530 over the six years.

$$EP_1 = Distillate\ 2 - Demilitarized\ TiCl_4\ feed \qquad [4\text{-}3]$$

Hence, it is noted that this process could potentially be beneficial and should be modelled further.

4.3.2 Titanium metal production by Kroll process

Significant values of the Kroll process can be seen in Table 4-2. These values are rounded.

Economic potential of the isolated Kroll reactor is calculated by Equation 4-4.

$$EP_2 = Kroll\ output + Kroll\ discharge\ - Metal\ grade\ TiCl_4\ feed - Mg\ feed \qquad [4\text{-}4]$$

The price for high purity $TiCl_4$ (99.99%) was taken from Alibaba (2018e) and equals $ 1 700 per ton.

Magnesium is priced at $ 2 300 per ton by Alibaba (2018f).

Table 4-2: Summary of components with noteworthy volumes in the Kroll process

	Kroll input (kg)	Kroll output (kg)	Kroll discharge (kg)	VD output (kg)	VD discharge (kg)	Elec output (kg)
$TiCl_4$	39 900					
$MgCl_2$		1 400	38 700		1 400	
Mg	14 500	4 200			4 200	14 500
Cl_2						29 800
Ti		10 100		10 100		
TOTAL	54 400	15 700	38 700	10 100	5 600	44 300

With Kroll: reactor where reduction of $TiCl_4$ with Mg is performed
VD: vacuum distillation where residual Mg and $MgCl_2$ is removed from sponge
Elec: electrolysis where $MgCl_2$ is desynthesized to Mg and Cl_2

Various prices for Ti sponge are supplied by The Kerala Minerals & Metals (2008h) and since it is difficult to determine what percentage of sponge will conform to each category it was decided to use the price for uncut bottom parts of the titanium sponge. This option was chosen since its value is more or less in the centre of the observable price range. It should be considered that $TiCl_4$ of exceptional quality is used to feed the process and the obtained sponge will therefore consist of high levels of pure Ti, but residual $MgCl_2$ and Mg should still be removed through purification. The selected value for Ti sponge from the reactor equates to $ 8 570 per ton.

The Kerala Minerals & Metals (2008h) sells $MgCl_2$ by-product from the Kroll process at a price of $ 110 per ton.

The economic potential at level 2 for an input of 39.9 ton purified $TiCl_4$ is calculated to give a result of $ 37 630.

When the focus is expanded towards the scope of this study which concentrates on recycling demilitarized $TiCl_4$, the economic potential of the applicable $TiCl_4$ purification and sponge formation processes is calculated by Equation 4-5.

$$EP_2 = Kroll\ output + Kroll\ discharge\ - Demilitarized\ TiCl_4\ feed - Mg\ feed \qquad [4\text{-}5]$$

The resulting economic potential at level 2 increases to \$ 57 160. It is viable to conclude that this positive value implies the process could serve as a feasible solution.

By broadening the focus outside of the current scope towards the inclusion of additional product treatment steps, it is possible to construct Equation 4-6. This equation is used to determine the economic potential of the overall Kroll process at level 2. The vacuum distillation and electrolysis steps ensure that almost all Mg is recycled and Cl_2 is removed.

$$EP_2 = Pure\ Ti\ sponge\ + Cl_2 - Demilitarized\ TiCl_4\ feed \qquad [4\text{-}6]$$

The centre half of the purified high-quality Ti sponge can be used for aerodynamic applications and sells for about \$ 18 020 per ton while the remaining 50% purified sponge has a market price of \$ 11 430 (The Kerala Minerals & Metals, 2008h).

Additionally, the price for 1 ton of Cl_2 is \$ 600 (Alibaba, 2018g) to give a calculated EP_2 value of \$ 118 300.

The overall Kroll process is clearly financially beneficial and will increase in profitability as process volumes increase.

4.3.3 Titanium dioxide pigment production by chloride process

Rounded values of the notable components of the chloride process are found in Table 4-3.

The EP_2 value for the general chloride process is formulated in Equation 4-7.

$$EP_2 = TiO_2\ pigment + Cl_2/HCl/O_2\ - Purified\ TiCl_4\ feed - O_2/H_2O\ feed - AlCl_3 \qquad [4\text{-}7]$$

This calculation incorporate the price of sellable TiO_2 pigment that has already undergone the necessary sizing, drying and treatment steps. Although these steps are not considered in the conducted models of this study, it is not possible to omit it from this calculation since no price was found for unfinished pigment particles. The price of all TiO_2 pigments from The Kerala Minerals & Metals (2008h) is \$ 3 070 per ton.

Impure Cl_2 is removed and sold for \$ 250 per ton (Alibaba, 2018h). This gas has a purity of about 95% due to the presence of HCl and O_2 contaminants.

Table 4-3: Summary of components with noteworthy volumes in the chloride process

	Chloride input (kg)	Chloride output (kg)	Purification output (kg)	Purification discharge (kg)
$TiCl_4$	39 900			
H_2O	700	500	500	
HCl		700		700
TiO_2		16 800	16 800	
O_2	7 500	800		800
Cl_2		29 800	600	29 200
$AlCl_3$	800			
Al_2O_3		300	300	
TOTAL	48 900	48 900	18 200	30 700

The added O_2 and $AlCl_3$ catalyst have respective prices of $ 1 230 (Alibaba, 2018i) and $ 1 150 (Alibaba, 2018j) per ton.

The cost of 700 litre water is negligible in comparison to the other components.

The calculated economic potential at level 2 for the general chloride process is a negative value of -$ 14 430.

When the focus is placed on the current scenario of recycling demilitarized $TiCl_4$, the EP_2 equation is adapted to Equation 4-8.

$$EP_2 = TiO_2\ pigment + Cl_2/HCl/O_2\ - Demilitarized\ TiCl_4\ feed - O_2/H_2O\ feed - AlCl_3 \quad [4\text{-}8]$$

The resulting economic potential at level 2 is then $ 5 100.

Hence, it is evident that the chloride route for pigment production is only profitable when cheap $TiCl_4$ is used. This will again require additional purification step, which increase CAPEX and OPEX values.

4.3.4 Titanium tetrachloride in smoke mortars for military application

Compounds with large enough volumes to influence the economic potential are listed in Table 4-4. All these values are rounded.

Table 4-4: Summary of components with noteworthy volumes in the two-step boiling of $TiCl_4$

	Input (kg)	Product 1 (kg)	Product 2 (kg)	Residue (kg)
$TiCl_4$	40 300	1 100	39 000	200
Bisphenol A-epichlorohydrin	800		200	600
1,4-butanediol diglycidyl ether	100		100	
H_2O	100		100	
HCl	400	400		
TiO_2	300			300
TOTAL	**42 000**	**1 500**	**39 400**	**1 100**

This option is probably the most basic option out of the four processes. By using values that were determined during discussions of the previous three processes, the EP_1 is calculated with Equation 4-9.

$$EP_1 = Flash\ product\ 2 - Demilitarized\ TiCl_4\ feed \tag{4-9}$$

No remarkable worth could be added to the vapour product of the first step or the remaining residue after the second step.

The economic potential at level 1 of this two-step vaporization process to obtain $TiCl_4$ with a purity of 99% is calculated as $ 8 440.

Since the use of $TiCl_4$ in smoke mortars is the only existing application in the current South African industry, it is possible to establish an additional consideration. Extensive $TiCl_4$ purification, Ti sponge reduction and TiO_2 pigment production are not conducted on industrial scales on the current local market. These products are therefore mostly imported.

The consequence of this is that raw products and process units will have to be acquired and imported of it is not available locally. Should demilitarized $TiCl_4$ be purified and reused in smoke mortars, it was not necessary for the mortar production company to import this material. The selling price of 99% $TiCl_4$ in South Africa at the time of this study is R 103.50 per kg or $ 7 390 per ton, which is inclusive of 15% VAT, transport and importation costs (Crescent Chemicals, 2018).

If this price is used for the product value in the EP_1 calculation, it gives an economic potential of $ 242 900 for this process.

4.4 CAPEX

The capital expenditure (CAPEX) of a system refers to the investment that needs to be made to acquire, construct and initiate the desired process plant. Several factors are accounted for in the required capital for a chemical plant. A detailed layout of the various categories that contribute to the overall capital investment is given in Peters *et al.* (2003). These categories can be classified as either direct or indirect costs. A summary of the breakdown of fixed-capital investment (FCI) for process plant is given in Table 4-5. Each component's relative percentage range of the overall FCI is also supplied in this table.

Whether the actual value falls within the higher or lower percentages of the stated ranges is somewhat dependent on the type of processes that will be conducted in the plant. Peters *et al.* (2003) explain how this breakdown and percentage ranges can be used to determine values of each category if the cost and percentage of one of the categories are known. The applicable high or low percentages (or mid-range if it is unknown) can be normalized to a value of 100%, after which the fractions can be calculated. These values have an expected accuracy of ±30%.

Table 4-5: Summary of the breakdown of a plant's FCI along with relative percentage ranges (adapted from Peters *et al.* (2003))

Component	Range of FCI, %
Direct costs	
1. Purchase equipment	15-40
2. Purchased-equipment installation	6-14
3. Instrumentation and controls	2-12
4. Piping	4-17
5. Electrical systems	2-10
6. Buildings	2-18
7. Yard improvements	2-5
8. Service facilities	8-30
9. Land	1-2
Indirect costs	
1. Engineering and supervision	4-20
2. Legal expenses	4-17
3. Construction expenses	1-3
4. Contractor’s fee	2-6
5. Contingency	5-15

Only the ‘purchase equipment’ (first) category was compared in this study, since the focus is exclusively placed on the actual formation process and not on downstream treatment or finishing steps. The costs of only the process units on each simulated flow sheet (Section 3.6) are stated and compared. Since this is the largest margin of the processes' FCI, its comparison results will give a good indication on the relative performance of each process.

It is desired to include all definite process units in the CAPEX calculations, but this was not possible since a majority of the costs are dependent on external factors. These factors are unique to the plant where this solution is implemented or simply not possible to determine at this stage of the design process.

The method of Peters *et al.* (2003) can be used to obtain estimated values of each FCI expense for the determined solution in future developments.

The process units in this section are priced based on the design equations and graph readings that are found in Seider *et al.* (2010). These prices are based on a Chemical Engineering Plant Cost Index (CEPCI) of 500. The CEPCI of 2017 was obtained from Chemical Engineering (2018) as 567.5. This number is used to convert the obtained prices to current values along Equation 4-10.

$$New\ price = Old\ price\ \left(\frac{New\ CECPI}{Old\ CECPI}\right) \qquad [4\text{-}10]$$

Stated values in this section were determined from equations, correlations and recommendations from Seider *et al.* (2010) with obtained input data from the simulations.

4.4.1 Purification of $TiCl_4$ for metallic Ti and TiO_2 pigment production

4.4.1.1 Pump

The size factor, S, is determined from Equation 4-11 and is required for calculating the cost of a pump with Equation 4-12 (Seider *et al.*, 2010).

$$S = Q(H)^{0.5} \qquad [4\text{-}11]$$

$$C_p = \exp\{9.7171 - 0.6019[\ln(S)] + 0.0519[\ln(S)]^2\} \qquad [4\text{-}12]$$

with

Q: flow rate through pump = 2.2 gpm

H: pump head = 8.1 ft

The sizing factor is then calculated as 6.3 gpm·ft$^{0.5}$. This is below the minimum applicable value of 400 for the graph. Since this logarithmic graph is quadratic, it was not possible to extrapolate this data beyond the stated range. An S value of 400 gpm·ft$^{0.5}$ is therefore selected.

For a sizing factor of 400 gpm·ft$^{0.5}$ and a CEPCI of 500, the unit cost is \$ 2 900. This cost is relatively low and the inaccuracy is not expected to have an influence on the results of this study.

This price is for a single-stage centrifugal pump which operates at 3 600 rpm and has a vertical split case (VSC) that is constructed of cast iron.

4.4.1.2 Heat exchanger

A double-pipe heat exchanger is recommended over a shell-and-tube heat exchanger for applications under 41 barg and required surface areas between 0.2 and 37 m^2. The cost of this heat exchanger, C_P, can be calculated with Equation 4-14, which was obtained from Seider *et al.* (2010). The base cost is determined from Equation 4-13.

$$C_B = \exp\{7.1460 + 0.16[\ln(A)]\} \quad [4\text{-}13]$$

$$C_P = F_M C_B \quad [4\text{-}14]$$

with

A: exchanger surface area = 4.4 ft^2

F_M: material factor = 2.0 for outer pipe of carbon steel and inner pipe of stainless steel

C_B: base cost = \$ 1 610

Stainless steel is the preferable material of construction for heat transfer units that is in direct contact with $TiCl_4$, since the corrosiveness of this chemical and minute volumes HCl will severely shorten the life span of carbon steel.

The corresponding purchase cost of this double-pipe heat exchanger at a CEPCI of 500 is determined as \$ 3 220.

4.4.1.3 Batch distillation column

It was decided to calculate the costs of the pot and the packing section of the distillation column separately, since these dimensions differ.

The equations and graphs in Seider *et al.* (2010) are only developed for vessels that have shell weights heavier than 1 900 kg and distillation towers with a shell mass exceeding 4 100 kg. The trend line on the logarithmic graph for distillation towers is very close to linear and it was decided to determine the applicable price by extrapolation of this data.

The cost of a vertical vessel, C_V, is calculated with Equation 4-15 and the platforms and ladders costs with Equation 4-16. The overall purchase cost of the pot, C_P, is determined with Equation 4-17.

$$C_V = \exp\{7.0132 + 018255[\ln(W)] + 0.02297[\ln(W)]^2\} \tag{4-15}$$

$$C_{PL} = 361.8\,(D_i)^{0.73960}(L)^{0.70684} \tag{4-16}$$

$$C_P = F_M C_V + C_{PL} \tag{4-17}$$

with

W: weight of vessel shell = 1470 lbs

C_V = $ 14 280

D_i: inside diameter = 3.9 ft

L: tangent-to-tangent length = 1.6 ft

F_M: vessel material-of-construction factor = 1.0 for carbon steel

C_{PL}: cost of platforms and ladders = $ 1 380

Similarly, the column’s packing section dimensions do not coincide with the conditional diameter range (1 – 7 m) and length range (8 – 52 m) of the equations for estimating platform and ladder costs. These equations will also be used for measurements outside of the specified ranges.

The cost of glass is slightly higher than carbon steel but less expensive than stainless steel. The value of carbon steel Raschig rings is used in the calculations.

Equation 4-18 is solved along with Equations 4-15 to 4-17 to calculate the purchase cost, C_P, of the packing section of the distillation column.

$$C_P = F_M C_V + C_{PL} + V_P C_{PK} + C_{DR} \qquad [4\text{-}18]$$

with

$F_M = 1.0$

W = 301 lbs

C_V: cost of a vertical tower = $ 8 640

$D_i = 0.92$ ft

L = 17.7 ft

C_{PL} = $ 2 160

V_P: volume of packing = 11.7 ft^3

C_{PK}: installed cost of packing = $ 54 / ft^3

C_{DR}: installed cost of distributors and redistributors = $ 80

These values were obtained using the equations, correlations and recommendations in Seider *et al.* (2010).

The resulting unit price at a CEPCI of 500 is then $ 15 680 for the pot and $ 11 510 for the packing section.

4.4.1.4 Condenser

The required tube surface area according to the simulation results is 56 ft^2. A double pipe heat exchanger with pricing equations similar to Equation 4-13 and 4-14 are used to calculate the overall unit cost. Since the $TiCl_4$ product is in contact with both pipes in this unit, the inner and outer pipe should be constructed of stainless steel. The material factor in the calculations is therefore 3.0.

The unit cost is calculated to be \$ 7 250 at a CEPCI of 500.

4.4.1.5 Total

The unit prices at a CEPCI of 567.5 are given and summed in Table 4-6.

Table 4-6: Unit costs of the $TiCl_4$ purification process (CEPCI of 567.5)

	Price
Pump	\$ 3 300
Heat exchanger	\$ 3 650
Distillation column	\$ 30 860
Condenser	\$ 8 230
Total	\$ 46 040

4.4.2 Titanium metal production by Kroll process

4.4.2.1 Pump

By using Equation 4-11, with a volumetric flow rate of 2.0 gpm and a pump head of 7.9 ft, the size factor is calculated to be 5.6 gpm·ft$^{0.5}$. This is again below the minimum value of 400.

A pump with a size factor of 400 gpm·ft$^{0.5}$ and cost of \$ 2 900 at a CEPCI of 500 is selected.

4.4.2.2 Heaters

Fired heaters or furnaces are the preferred units for heating reactant volumes beyond steam temperatures. Prices of these units are calculated by Equations 4-19 and 4-20, which depend mostly on heat duties of the unit.

$$C_B = \exp\{0.32325 + 0.766[\ln(Q)]\} \qquad [4\text{-}19]$$

$$C_P = F_M C_B \quad [4\text{-}20]$$

with

Q: heat duty in Btu/h

C_B: base cost

F_M: material factor = 1.0 for carbon steel and 1.7 for stainless steel tubes

The heater used for increasing the temperature of magnesium is constructed of carbon steel and has a heat duty of 4.65 million Btu/h. The price is then calculated as $ 176 800 (CEPCI of 500).

The continuous process from the simulation of this process had a $TiCl_4$ flow rate of 8000 kg/h while in actual fact, this feed volume was added to the batch reactor at 138 kg/h. To avoid unbalanced and inaccurate economic modelling, this unit is developed for a feed stream of 138 kg/h $TiCl_4$. The $TiCl_4$ heater with stainless steel tubes has a duty of 75 600 Btu/h. For a CEPCI of 500, the unit price is calculated as $ 12 810.

4.4.2.3 Batch reactor

The retort and the crucible were modelled as pressurised empty vessels. Equations 4-15 to 4-17 can therefore be used to calculate the cost of these two units based on its weight. No ladders and platforms are required for the crucible since it fits inside the retort.

The calculated values for the retort is then $ 32 100 for the vertical vessel and $ 5 200 for ladders and platforms, while a cost factor of 1.7 is used for stainless steel 304. The smaller crucible has a vessel cost of $ 28 200 and a carbon steel cost factor of 1.0.

The cost of these units at a CEPCI of 500 is calculated as $ 59 800 for the retort and $ 28 200 for the crucible.

As previously mentioned, errors were encountered while simulating the chemical and thermal behaviour of $MgCl_2$ in this process. This could result in potential inaccuracies of utilized design and utility values. It is therefore recommended to test or confirm these figures before practical implementation of this process commences.

4.4.2.4 Total

The cost of demilitarized $TiCl_4$ purification is included in the overall production cost. The total cost of these Ti sponge production units at a CEPCI of 567.5 are provided in Table 4-7.

Table 4-7: Unit costs of the Ti sponge production process (CEPCI of 567.5)

	Price
$TiCl_4$ purification	$ 46 040
Pump	$ 3 300
Mg heater	$ 200 670
$TiCl_4$ heater	$ 14 540
Reactor	$ 101 460
Total	$ 366 000

4.4.3 Titanium dioxide pigment production by chloride process

4.4.3.1 Pump

The sizing factor of this unit is smaller than the stipulated range and a pump with a size factor of 400 $\text{gpm}\cdot\text{ft}^{0.5}$ and cost of $ 2 900 at a CEPCI of 500 is selected.

4.4.3.2 Heaters

The prices of the fired heaters / furnaces of this process can be calculated at a CEPCI of 500 using Equations 4-19 and 4-20.

The $TiCl_4$ heater has a heat duty of 595 900 Btu/h and since the tubes are constructed of stainless steel, the purchase cost at a CEPCI of 500 is calculated to be $ 62 320.

The O_2-H_2O stream is heated in a carbon steel heater with an applied duty of 201 200 Btu/h. The resulting price is $ 15 960.

4.4.3.3 Compressors

Seider *et al.* (2010) recommend using screw compressors for moderate flow rates and output pressures. The base cost, C_B, of a screw compressor is determined with Equation 4-20 with P_C in horsepower. Equation 4-21 is used to calculate the purchase cost, C_P, of a compressor with an electric motor.

$$C_B = \exp\{8.1238 + 0.7243[\ln(P_C)]\} \qquad [4\text{-}21]$$

$$C_P = F_M C_B \qquad [4\text{-}22]$$

with

F_M: material factor = 1.0 for carbon steel

Compression of the $TiCl_4$ stream requires a screw compressor which operates at 28 Hp and has a calculated cost of $ 37 960.

The O_2-H_2O compressor is also constructed of carbon steel and operates at 40 Hp to deliver the required pressure of 3 barg. The purchase cost of this compressor is calculated to be $ 48 590. Both prices are for carbon steel units and a CEPCI of 500.

4.4.3.4 Plasma arc furnace

No modelling equations or correlations were supplied to determine the unit cost of a plasma arc furnace. As previously stated, dimensions of this reactor were also not supplied by the simulation software. The decision that was taken was to enquire about the price of a reactor with similar functions from industry.

The production of 400 kg/h TiO_2 pigment requires a supplied duty of 652 kW. The price for a 1 MW plasma arc furnace was obtained from Hayman (2018), who has extensive personal experience in this field. This unit has a base purchase price of $ 1 430 000 in the current South African market. With inclusion of accessories required for feeding, extraction and general operating procedure this cost can increase up to $ 7 000 000 for a single reactor. The base cost of the reactor is used in CAPEX calculations to determine the produced TiO_2 quantity that should be exceeded for this process to be feasible.

4.4.3.5 *Total*

By also accounting for the purification costs of demilitarized $TiCl_4$, the unit values of this process at a CEPCI of 567.5 are given in Table 4-8.

Table 4-8: Unit costs of the TiO_2 pigment production process (CEPCI of 567.5)

	Price
$TiCl_4$ purification	$ 46 040
Pump	$ 3 300
$TiCl_4$ heater	$ 70 730
O_2-H_2O heater	$ 18 110
$TiCl_4$ compressor	$ 43 090
O_2-H_2O compressor	$ 55 150
Plasma arc furnace	$ 1 430 000
Total	$ 1 666 000

4.4.4 Titanium tetrachloride in smoke mortars for military application

4.4.4.1 *Pump*

This unit's size factor does not meet the prescribed value, hence a pump with a size factor of 400 gpm·ft$^{0.5}$ and cost of $ 2 900 is selected for a CEPCI of 500.

4.4.4.2 *Heat exchanger*

By using Equations 4-13 and 4-14, the cost of a heat-exchanger with a stainless steel inner pipe and outer surface area of 5.5 ft^2 is calculated to be $ 3 330.

4.4.4.3 Boiler unit

As stated in the design and simulation sections of this study, this process utilizes an identical vertical vessel to the pot of the distillation column of the purification process. Hence, this unit also has a cost of $ 15 680 at a CEPCI of 500.

4.4.4.4 Condenser

Equations 4-13 and 4-14 are used to determine the base cost of this unit. The inner and outer pipes are constructed of carbon steel while the required surface area equals 38 ft^2. The resulting price is calculated to be $ 6 800.

4.4.4.5 Total

The values of each plant unit for this process is given in Table 4-9. Values are for the 2017 CEPCI of 567.5.

Table 4-9: Unit costs of the two-step vaporization process (CEPCI of 567.5)

	Price
Pump	$ 3 300
Heat exchanger	$ 3 780
Boiler unit	$ 17 800
Condenser	$ 7 720
Total	$ 32 600

4.5 OPEX

The operating expenditure (OPEX) of a process is mostly dependent on the actual production of a plant. Plainly put, it is the expenses that need to be paid for plant operation to take place and for a product to be obtained. Prime examples include production utilities, packing material, raw materials, *etc.*

Certain costs do exist that still need to be settled irrespective of the quantity of product delivered. Examples of these fixed costs include labour fees, admin fees, permits, marketing, research costs, *etc.*

Since the main purpose of this study and these determinations is to thoroughly compare and evaluate the proposed recycling solution, it will have little benefit to determine fixed costs that are identical for all processes. The realization was that the most deviations will be observed between the raw material expenses and costs of each process's utilities. The focus of this section will therefore only be on these two categories.

Prices of raw materials are provided in the economic potential analysis (Section 4.3) and will only be listed in this section.

The price of each utility was obtained from Seider *et al.* (2010) and is tabulated in Table 4-10.

Table 4-10: Cost of each utility

Utility	**Cost**
Electricity ($ /kWh)	0.06
Low-pressure steam ($ /1000 kg)	6.60
Cooling water ($ /1000 kg)	0.02
Boiler-feed water ($ /1000 kg)	0.50
Natural gas ($ /m^3)	0.136

Seider *et al.* (2010) state that the financial benefit of steam production in the condenser has already been accounted for in the price of the boiler-feed water. It is critical that demineralized water is used to avoid foiling in heat exchangers. The demineralization process is quite costly, which contributes to the cost of the water. Generated steam can consequently be used in other areas of the chemical plant. Since it is only formed in the studied batch processes, the steam can't be used to heat the feed in the earlier steps.

The natural gas in Table 4-10 has a propane content of 90% and higher heating value (HHV) of 39 121 kJ/m^3. Seider *et al.* (2010) recommend using a thermal efficiency of between 50 and 80% in calculations for fired heaters. A value of 70% is used throughout this section.

Similarly to the economic potential calculations, these OPEX values are for the entire scope of the process which entails the recycling of 42 ton demilitarized $TiCl_4$ over six years.

4.5.1 Purification of $TiCl_4$ for metallic Ti and TiO_2 pigment production

The main utilities and accompanying expenses that contribute to the OPEX of the distillation process are given and summed in Table 4-11.

Table 4-11: Utility costs of the $TiCl_4$ purification process

	Electricity (kWh)	LP steam (kg)	C water (kg)	BFW (kg)	Cost ($)
Pump	0.8				Neg.
Heat exchanger		1 281			8
Reboiler of 1st step	1 676				101
Condenser of 1st step			212 856		4
Reboiler of 2nd step	5 162				310
Condenser of 2nd step				8 316	4
Total					$ 430

With LP: low-pressure
C: cooling
BFW: boiler-feed water
Neg.: negligible

4.5.2 Titanium metal production by Kroll process

Raw material as well as quantities and costs of utilized electricity and natural gas for the Kroll process are supplied in Table 4-12. Preceding $TiCl_4$ purification costs are also included.

Table 4-12: Raw material and utility costs of the Kroll process

	Electricity (kWh)	Natural gas (m^3)	Reactant mass (kg)	Cost ($)
$TiCl_4$ purification				430
Mg metal			14 500	33 350
Pump	0.8			Negligible
Mg heater		893		121
$TiCl_4$ heater		590		80
Kroll reactor		9 700		1 320
Total				$ 35 300

4.5.3 Titanium dioxide pigment production by chloride process

The required process costs for purification of demilitarized $TiCl_4$, added raw materials, applied electrical power and consumed natural gas are listed in Table 4-13.

4.5.4 Titanium tetrachloride in smoke mortars for military application

Required electricity, low-pressure steam and boiler-feed water costs to operate this process are given in Table 4-14.

Table 4-13: Raw material and utility costs of the chloride process

	Duties (kW)	**Natural gas (m^3)**	**Reactant mass (kg)**	**Cost ($)**
$TiCl_4$ purification				430
O_2 gas			7 500	9 230
$AlCl_3$ catalyst			800	920
$TiCl_4$ pump	0.8			Negligible
$TiCl_4$ heater		966		131
O_2 heater		326		44
$TiCl_4$ compressor	882			53
O_2 compressor	1 260			76
Plasma arc furnace		3 600		490
Total				$ 11 370

Table 4-14: Utility costs of the two-step vaporization process

	Electricity (kW)	LP steam (kg)	BFW (kg)	Cost ($)
Pump	0.8			Neg.
Heat exchanger		1 415		9
1st boiling step	12.6			1
2nd boiling step	2 948			177
Condensing 2nd vapour product			4 473	2
Total				$ 190

With LP: low-pressure
BFW: boiler-feed water
Neg.: negligible

4.6 Investment considerations

More focus is placed on the financial feasibility of each process in this section. This is done by determining the corresponding payback period (PBP), internal rate of return (IRR) and return on investment (ROI) of each process. Calculated values from economic potential analyses, CAPEX and OPEX are used in these equations.

It is noted that this section and furnished calculations are for the production sections of each potential solution and not for the process in its entirety. The main focus of this study is on processing 42 ton demilitarized $TiCl_4$ over six years. Sustainability of this project after this period is difficult to predict, since obtained $TiCl_4$ volumes is dependent on numerous external factors.

Firstly, the PBP of each process is calculated using Equation 4-23 to determine the time period required to redeem capital expenses from generated incomes for each process. This will also serve as a good determination of whether the initial investment can be recovered for each process or the duration required to achieve this.

$$PBP = \frac{Fixed\ capital\ investment}{Annual\ cash\ flow} \qquad [4\text{-}23]$$

In order to perform this calculation, it is assumed that six equal batches of 7 ton demilitarized $TiCl_4$ are processed each year. The fixed capital investment consists of the relevant CAPEX values. Annual cash flow is calculated by subtracting annual reactant and utility costs from product values.

A good indication of a process's profitability is by determination of its IRR percentage. This value is obtained by setting the net present value (NPV) value equal to zero and solving for r in Equation 4-24.

$$NPV = \sum_{t=1}^{T} \frac{C_t}{(1+r)^t} - C_0$$

[4-24]

with

C_0: initial investment cost

C_t: net cash flow during period t

r: discount rate

t: number of time periods

The general conclusion on IRR values are that higher percentages are indicative of greater profitability.

The ROI is used to determine the extent to which a process is profitable. Certain stipulated ROI ranges exist for different processes. This value is a common indication of whether a sufficient income is generated based on the supplied funds, or if a greater income can be obtained through external investments. Equation 4-25 is implemented to perform this calculation.

$$ROI = \frac{Gain\ from\ investment - Cost\ of\ investment}{Cost\ of\ investment} \qquad [4\text{-}25]$$

It became evident from economic potential calculations that the limited local market and availability of this chemical have a considerable effect on potential incomes and more specifically on reducing the cost of raw materials. The specific process that is being referred to is the two-step vaporization of $TiCl_4$ to obtain a 99% pure product which can be used to manufacture new smoke mortars. Therefore calculation of each process's financial parameters that are based on general industrial values of products and reactants are given initially. Thereafter, these calculations are performed on this process that will serve as an improvement on the existing application of mortar manufacturing in the current local market.

The cost of demilitarized $TiCl_4$ is not considered as a raw material expense and was not accounted for in the annual cash flow, since it does not have to be acquired for this specific scenario. Corresponding annual cash flow values for PBP calculations are $ 17 251 (Ti sponge), $ 8 697 (TiO_2 pigment) and $ 9 424 ($TiCl_4$ for smoke mortars).

A summary of financial determinations of each of the three considered applications is given in Table 4-15.

Table 4-15: Financial indicators of each considered process

	PBP (years)	**IRR (%)**	**ROI (%)**
Ti sponge production	21	(27%)	(72%)
TiO_2 production	192	(54%)	(97%)
$TiCl_4$ for smoke mortars	3.5	18%	73%

Strong indications of the performance and feasibility of each process have started to become visible from the report of these values. Comprehensive discussions on normalized data can be found in Chapter 5.

When the perspective is switched from the physical value of each product towards existing agreements and current transactions, it becomes possible to consider a decrease in feed costs as a financial benefit. With focus then being placed on the sums of money that are being saved due to the implementation of this process, it can be added to the value of this product to aid in relative comparisons.

With the focus placed on the possible advantages of this study in the current local market, the values in Table 4-16 are obtained for the possibility of manufacturing smoke mortars with recycled $TiCl_4$. The relevant financial benefit to annual cash flow is calculated as $ 48 496.

Table 4-16: Financial parameters relative to current markets for using demilitarized $TiCl_4$ in new smoke mortars

	PBP	IRR (%)	ROI (%)
$TiCl_4$ for smoke mortars in local market	8 months	148%	793%

4.7 Alternative options

Supplementary to observed deviations between product values and market prices, it is advisable to also evaluate how these results compare with low-cost solutions that may not be classified as recycling processes.

It is stated in the process selection section (Section 2.5) that the identified process from this evaluation is compared with other available options. These options are not recycling processes and do not serve as potential solutions to demilitarization, which has a general objective of producing zero waste, only by-products. Some mentioned alternatives do have potential to be financially beneficial though. These options and their relevant incomes, expenses and net profits/losses for the entire scope are listed in Table 4-17.

Table 4-17: Financial considerations of alternative processes

	Incomes	Expenses	Net profit/loss
Neutralizing $TiCl_4$ with NaOH		$ 14 400	($ 14 400)
Chemical disposal		$ 10 500	($ 10 500)
Selling demilitarized $TiCl_4$	$ 48 300		$ 48 300
Selling purified $TiCl_4$ (99.99%)	$ 67 830		$ 67 830

The calculation for neutralizing $TiCl_4$ with NaOH is based on a NaOH price of $ 400 per ton (Alibaba, 2018k) and an added quantity that is slightly above stoichiometric levels (36 ton). This will prompt the reaction in Equation 4-26 to occur.

$$TiCl_4 + 4NaOH = TiO(OH)_2 + 4\,NaCl + \,H_2O \qquad [4\text{-}26]$$

The safe disposal can be performed by a chemical waste disposal company at a fee of $ 250 per ton (Marsden Jacob Associates, 2014). An exchange rate of AUD 1.35 for USD 1 was used for this calculation. This value includes treatment, transport and regulating costs.

As mentioned, the local demand for demilitarized (similar to crude) $TiCl_4$ is an extremely limited market with potential consumers mostly being research facilities. The potential solution of supplying this contaminated chemical to the planned TiO_2 pigment plant do exist. These developments have not been confirmed at the time of this study though.

No additional applications of purified $TiCl_4$ were found in the local markets. Research facilities (*e.g.* CSIR) do produce titanium powder from $TiCl_4$ but not in levels that support the available quantity. In contrast, the exportation of this compound is not feasible for the finite available volumes.

These two options are therefore disqualified as potential solutions in the local industrial market.

4.8 Conclusion

The three main processes that were simulated and discussed in Chapter 3 were further evaluated based on economic benefits. This chapter contains initial economic potential analyses at level 1 or level 2 that were performed to confirm the potential feasibility of each process. Obtained results indicated that product beneficiation occurred in all three considered options.

A comprehensive list of capital investment costs and its recommended fraction of the overall CAPEX values was supplied. A method for determining other capital components from prescribed ranges was also discussed. The major difference between each consideration's capital investments is expected to exist between unit costs. The general expectation was that deviations in other costs and variables were negligible compared to this factor and these fields were omitted from calculations.

The next section covered the capital costs of each production sequence. These values were calculated using the process parameter that were obtained from the Aspen Plus^{TM} simulation software and design equations from Peters *et al.* (2003). Values and quantities were converted to imperial inputs for supplied calculations, but final reports are in SI units.

The wide range of factors that contribute to the OPEX of a process was mentioned. The potential categories where major deviations between these processes are expected were the costs of raw materials and utilities of each process. Other factors are anticipated to be quite similar or negligible in magnitude. The breakdown of each process's OPEX values was listed and summed.

Calculated values of products, CAPEX and OPEX values were used to determine PBP, IRR and ROI parameters. These results are compared and discussed in Chapter 5 in order to conclude this study in Chapter 6.

For a more complete economic perspective, subsidiary solutions that are not regarded as recycling processes were stated and their financial and market feasibility were discussed.

CHAPTER 5: EVALUATION OF RESULTS AND DISCUSSIONS

5.1 Introduction

Several production factors, financial parameters and process considerations were determined or calculated in the technical and economic evaluations of this study. It is evident that some areas exist where substantial deviations occur between each recycling solution. The results from Chapters 3 and 4 are compared and discussed in this chapter.

It has become evident that two separate scenarios can be considered for this study. The first consideration is to compare the general results of each process's economic model. These values are based on the general market and increase the flexibility of this study, since it could also be of meaning to external independent parties. The second situation is more applicable towards the current South African market and aids in the evaluation and determination of an appropriate solution to this study's problem statement. These evaluations and discussions therefore consist of two parts.

It is stated a few times in this report that the focus of this study was more on a comparison between possible recycling solutions than on process values itself. The decision was therefore taken to normalize these values, which would aid in comparisons by indicating the extent to which a process differs. The process that would serve as the best basis for normalization of this data is determined by an initial overview of produced results. It became clear that the general process of reusing obtained $TiCl_4$ with a purity of 99% in the manufacture of new smoke mortars has the smallest parameter values in several calculations. This process is therefore selected.

For the second consideration, the general application of $TiCl_4$ in new smoke mortars is substituted by this same process but with market values that are relevant to the current South African market. It was decided to still use the basis of the first scenario in these comparisons for ease of interpretation.

Production volumes and process results from the technical evaluation (Chapter 3) are not addressed and compared directly in this chapter. This decision was based on the fact that all simulation results and process parameters were included in the economic evaluation (Chapter 4), which provided a more appropriate basis for assessment.

5.2 Accuracy of models and obtained results

Peters *et al.* (2003) state that capital estimations made on different degrees of detail have diverse levels of accuracy. The economic results of the unit cost determinations are categorized as 'order-of-magnitude' estimations with probable accuracies above ±30%. This is based on the fact that only the main production units were considered and included in this study. It was deemed that a model of these units would be sufficient for obtaining relevant and definite results. Error bars of ±30% of each specific value were therefore added to all graphs where results are reported.

5.3 General results

5.3.1 Evaluation of economic values for process operations

For this section that studies the performance of the three selected processes in general, it was decided to first compare operating values and resulting operational profits or losses. The normalized potential incomes, expected OPEX values and generated profits or losses of each process are given in Figure 5-1.

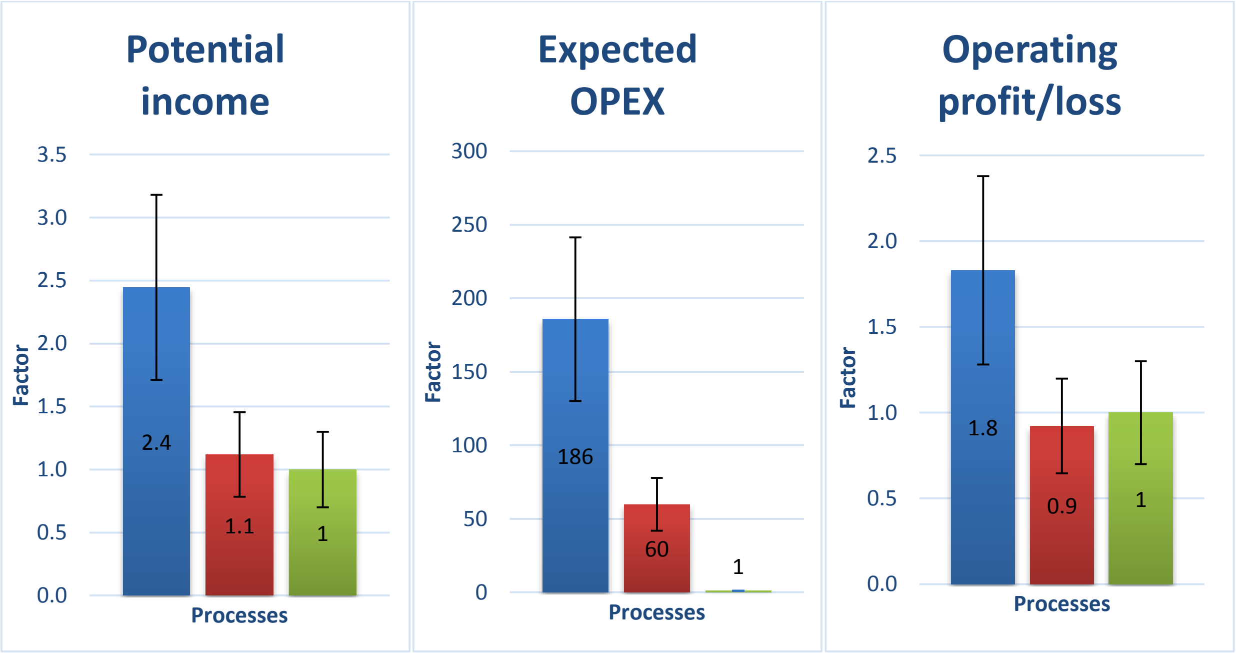

Figure 5-1: Column charts of normalized (a) potential income, (b) expected OPEX and (c) operating profit/loss values for the (i) Ti sponge production, (ii) TiO_2 pigment production and (iii) preparation of $TiCl_4$ for smoke mortar manufacturing processes

From Figure 5-1(a) it is evident that Ti sponge production has a greater expected income than the other two processes and although it also has a substantially higher OPEX value, it still displays favourable operating profits over the other two options. The high OPEX value of TiO_2 pigment production prompted the operation of this process be slightly less profitable than the two-step vaporization process of obtaining $TiCl_4$ of adequate quality for smoke mortar manufacturing.

5.3.2 Evaluation of economic values for process investments

It is required that the generated profits from plant operations are large enough to sufficiently cover the capital investments that were made to develop and construct these processes. Additional to breaking even, it also desirable to obtain a return on this investment after the payback period. Graphs charts of the CAPEX values and investment profits/losses are seen in Figure 5-2. The values in Figure 5-2(b) are calculated by subtracting required capital costs from operating profits that are obtained from processing 42 ton $TiCl_4$.

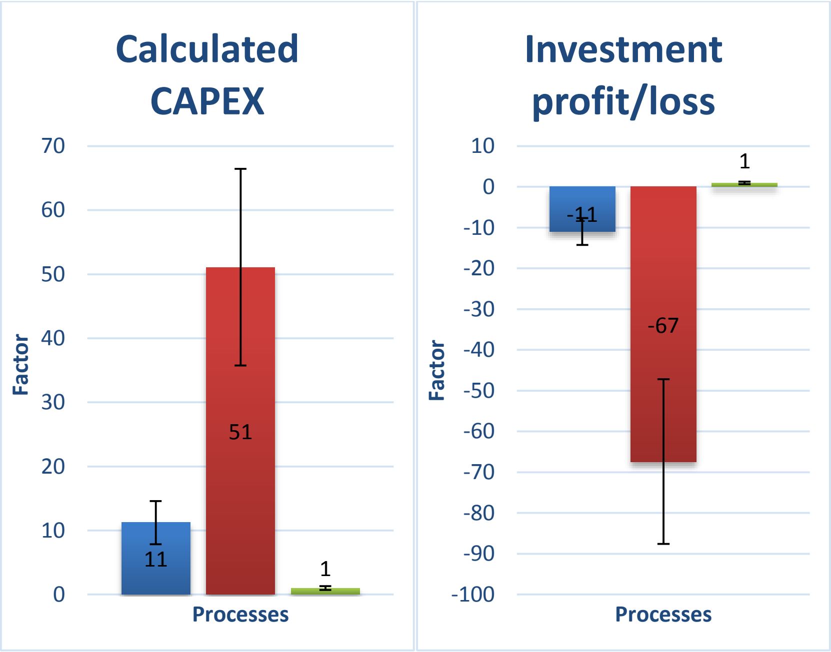

Figure 5-2: Graph charts of normalized (a) calculated CAPEX and (b) investment profit/loss values for the (i) Ti sponge production, (ii) TiO_2 pigment production and (iii) preparation of $TiCl_4$ for smoke mortar manufacturing processes

The capital required for TiO_2 pigment production is enormous in comparison to the other two applications. This high value is predominantly due to the price of a 1 MW plasma arc furnace. The

CAPEX value of sponge production is also larger than that of the two-step vaporization process by eleven factors. When extensive capital is required, it is vital that processes deliver an appreciable operating profit.

By comparing the graphs in Figure 5-2(b) it is evident that a processed $TiCl_4$ volume of 42 ton will not sufficiently cover the capital investment required to establish either the sponge or pigment production processes. Reusing demilitarized $TiCl_4$ does produce a profit after settling capital costs though.

5.3.3 Evaluation of economic parameters

These values can be properly evaluated or put into perspective by implementation of existing financial parameters. The payback period (PBP), internal rate of return (IRR) and return on investment (ROI) of each studied process are given in Section 4.6. These values are normalized and compared by graph charts in Figure 5-3.

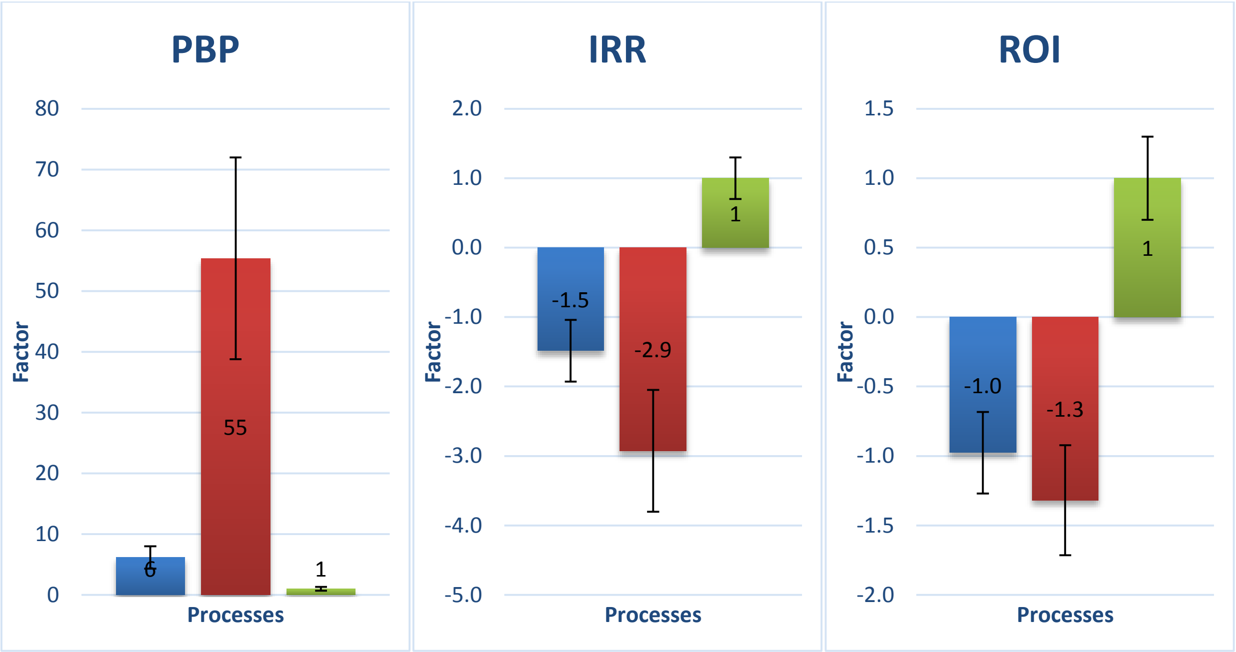

Figure 5-3: Graph charts of normalized (a) PBP, (b) IRR and (c) ROI parameters for the (i) Ti sponge production, (ii) TiO_2 pigment production and (iii) preparation of $TiCl_4$ for smoke mortar manufacturing processes

As it was stated in Section 4.7, the PBP value is an appropriate indication of whether a process can be deemed financially feasible over a certain time period while the IRR value is an acceptable parameter to use when the profitability of various processes were to be compared. Finally, the

ROI is used to determine if the expected financial returns from an application are more profitable than external investment options.

When considering these explanations and by studying the displayed results of these three charts, it becomes clear that the extent at which the sponge and pigment production processes differ from the normalized process is quite substantial. These deviations are definitely problematic towards the considered implementation of these processes as recycling solutions. PBP values are substantially longer than that of the third process. Furthermore, since supplied values of 21 years ± 7 years (Ti sponge) and 190 years ± 60 years (TiO_2) for the parameter are greater than six years, it also implies than the available demilitarized $TiCl_4$ feed is completely insufficient for this processes to be profitable. This is further emphasized by the negative IRR and ROI values which is an indication in both cases that a profit is not generated over the six years for a 42 ton demilitarized feed. With a PBP of 3 years ± 1 year, an IRR of 18% ± 6% and a ROI of 70% ± 30%, the two-step vaporization process for obtaining 99% pure $TiCl_4$ is a strong indication that this option serves as a possible solution The performance of this process is therefore also superior in comparison to the other two options, as evident from the normalized values in the supplied figure.

It can be stated with certainty that the estimated process inaccuracies of ±30% has no effects on derived results from this study, since none of the error bars from the best solution in each graph chart overlapped with the bars of the other two options.

5.4 Results applicable to the current local market

This evaluation consists of similar categories and considerations, but applicability is set on the current South African market. Similar estimations are thus made and deviations of above ±30% can again be expected. These inaccuracies will also be accounted for by the inclusion of error bars in graph charts.

Results of the Ti sponge and TiO_2 pigment production processes are not discussed in this section, but are included to aid in ease of comparison.

5.4.1 Evaluation of economic values for process operations

Normalized potential incomes, expected OPEX values and operating profits or losses are depicted in Figure 5-4.

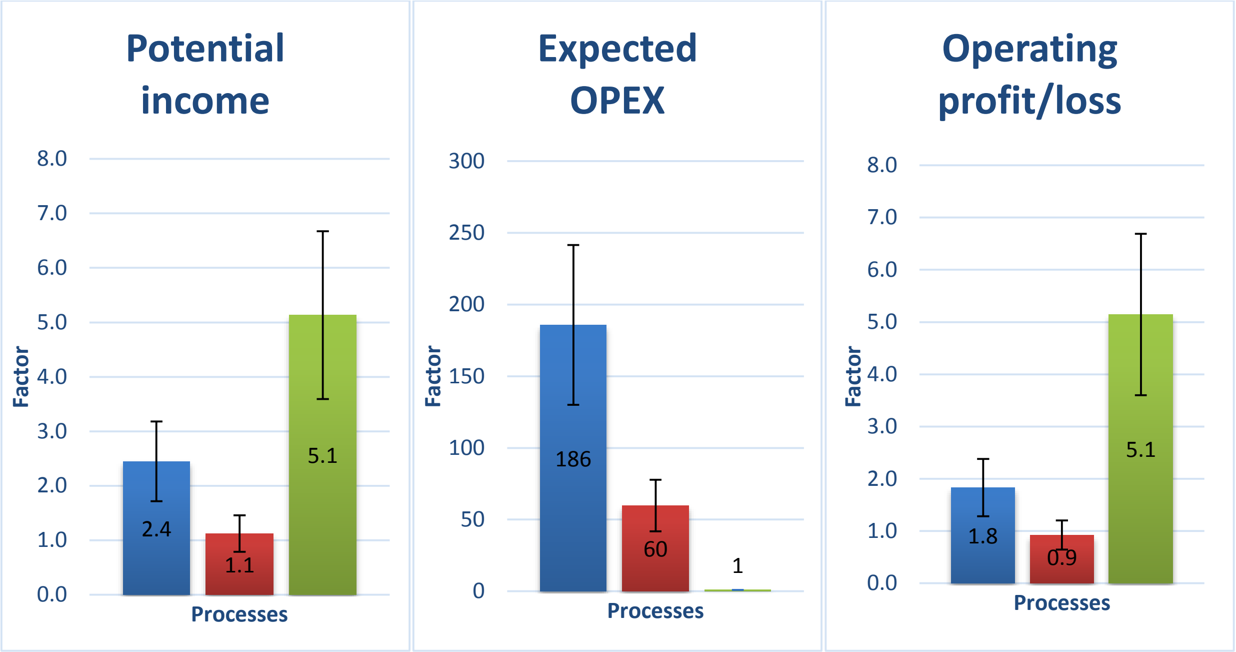

Figure 5-4: Column charts of normalized (a) potential income, (b) expected OPEX and (c) operating profit/loss values for the (i) Ti sponge production, (ii) TiO_2 pigment production and (iii) local market $TiCl_4$ preparation for smoke mortar manufacturing processes

Although the process and operating parameters have remained constant, the cost averted by implementation of the two-step vaporization process far surpasses the actual value of the delivered $TiCl_4$. This enables local smoke mortar manufacturers to regard this decrease in raw material cost as an economic benefit that is financially superior to the sponge and pigment production processes. This can be seen in Figure 5-4(a, c) by the increased income and operating profit over the other two options.

5.4.2 Evaluation of economic values for process investments

Capital requirements and investment profits or losses over six years are compared in Figure 5-5.

The capital required for implementing the third process in the local market is identical to that of general industries. However, the attained profit is vastly increased by the avoided expenses that are regarded as additions to the product value. The superiority of this option’s profit on capital investment is observed in Figure 5-5(b).

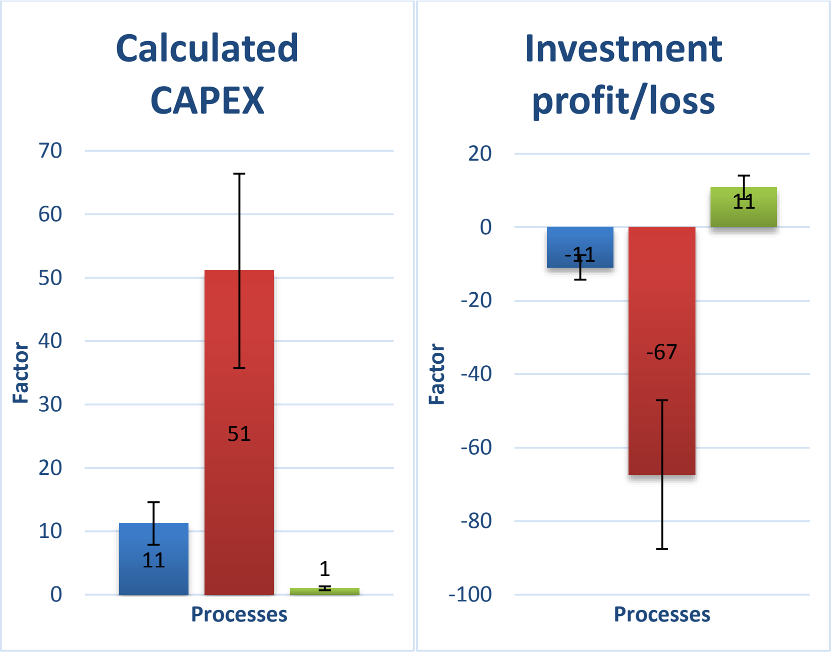

Figure 5-5: Graph charts of normalized (a) calculated CAPEX and (b) investment profit/loss values for the (i) Ti sponge production, (ii) TiO_2 pigment production and (iii) local market $TiCl_4$ preparation for smoke mortar manufacturing processes

5.4.3 Evaluation of economic parameters

Normalized PBP, IRR and ROI values are depicted in Figure 5-6.

The two-step vaporization process to obtain $TiCl_4$ for use in smoke mortar manufacturing proves to be dominant in financial feasibility. Values from Figure 5-6 for this solution in the local market take even greater precedence with relevance to the current South African titanium industry. The distinctive calculated parameters of this potential application bode quite well with regard to process feasibility in general and the attributed PBP of 8 months ± 3 months, IRR of 150% ± 50% and ROI of 800% ± 300% are desirable in almost any process.

By studying the error bars of each graph it is viable to conclude that the estimated inaccuracies of ±30% which were included in these comparisons do not influence the portrayed results.

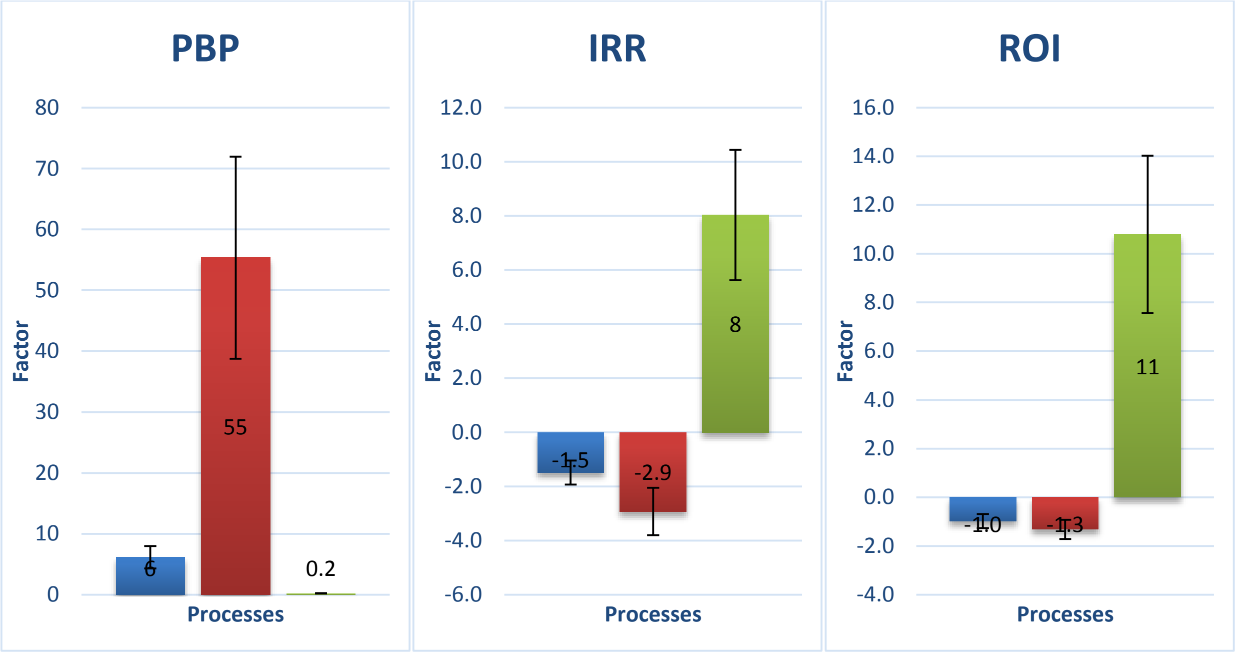

Figure 5-6: Column charts of normalized (a) potential income, (b) expected OPEX and (c) operating profit/loss values for the (i) Ti sponge production, (ii) TiO_2 pigment production and (iii) local market $TiCl_4$ preparation for smoke mortar manufacturing processes

5.5 Available quantities required before processes break even

It has been established that the Ti sponge and especially the TiO_2 pigment production processes are not feasible solutions for processing $TiCl_4$ quantities similar to the magnitude available for this study. Although these processes operate on a profitable income, the required capital investment far surpasses the possible financial gain.

A substantial volume of $TiCl_4$ is therefore required to produce a large enough quantity of TiO_2 pigment in order for this process to be profitable. In the study by Nel *et al.* (2010) it was found that an annual production of 100 000 ton pigment would be sufficient for obtaining a favourable IRR and ROI. That process produced nano-titania, which has a smaller particle size than regular pigments and is sold at a higher price. It is therefore expected that even greater production rates of normal TiO_2 pigments are required for this process to be financially beneficial.

The supplied demilitarized $TiCl_4$ feed quantities that should be exceeded for each process to become profitable are supplied in Table 5-1. Values were determined by solving for the quantities of $TiCl_4$ required for the sum of operating profits to equal the relevant capital investments. It was decided to include these values to broaden the applicability of portrayed results.

Table 5-1: Feed quantities that should be exceeded before processes can become profitable

	$TiCl_4$ required (kg)
Ti sponge production	149 000
TiO_2 production	1 340 000
$TiCl_4$ for smoke mortars	24 000
$TiCl_4$ for smoke mortars in local market	5 000

For quantities greater than each value stated in the table, that applicable process can be considered.

5.6 Evaluation of non-recycling options

Mentioned alternative treatment solutions that could potentially possess superior financial possibilities are discussed in this section.

The fact that one of the considered recycling solutions displays positive IRR and ROI values implicates that alternative considerations with negative overall financial implications were not viable choices. It is therefore fair to eliminate both the options of neutralizing $TiCl_4$ with NaOH and disposal of the recovered demilitarized liquid through a chemical waste disposal agency, since these processes entail incurred expenses without potential incomes.

The options of selling either crude or purified $TiCl_4$ boast potential financial implications. These applications are completely market relevant though and a demand for these products should exist before this option can be considered. Furthermore, the industrial demand will contribute immensely to obtainable selling prices of this chemical. The possible vending of demilitarized $TiCl_4$ could therefore be more profitable than purifying and selling $TiCl_4$. However, since these possibilities are completely dependent on industrial markets and regions, a definite verdict could not be compiled on its performance in general. Accordingly, these alternatives should definitely be considered and analysed along with the selected recycling option.

It is possible though to finalize that these options are not viable for the current local market, since there is not a great enough demand for crude or purified $TiCl_4$ to consume the available quantities. A potential future option has been discussed in this study, but since there is no certainty yet of whether it could serve as a possible solution, it cannot have an influence on attained results.

A final concern that should be discussed is that the validity of reusing obtained $TiCl_4$ to manufacture new smoke mortars is somewhat dependent on whether this manufacturer could consume a demilitarized $TiCl_4$ sum of 42 ton. If some fraction of this quantity is deemed as redundant, the possibility of supplying this compound to local consumers could again be revisited. As determined in the literature survey, several other uses exist for $TiCl_4$ but with minute processing capacities. The consumption of this metal halide thus exists in the local market, but for extremely limited volumes.

Utilized volumes during smoke mortar manufacturing could not be quantified with certainty due to the confidential nature of this industry and no propositions could therefore be made on supplied volumes and frequencies to provide noteworthy opportunities of selling this material. It can then be concluded that remaining $TiCl_4$ could be supplied to these consumers, but this proposal should be finalized by preceding negotiations. Hence, this possibility is not incorporated in conclusions of this study.

5.7 Sensitivity analysis

A sensitivity analysis is included in this study to determine the effect that some selections which were made during process development, have on reported results.

Based on the results of the economic analysis, it is viable to deduce that input and operating values do not have a meaningful influence of the feasibilities of the sponge and pigment production processes. These applications are dependent on extensive capital costs of process units and more specifically the relevant reactors. None of the available features can be varied to the extent that it changes the overall results of these options.

A sensitivity analysis of these two processes would therefore not produce meaningful results and only the two-step vaporization process is considered.

5.7.1 Titanium tetrachloride in smoke mortars for military application

During the development of this process it was evident that an operating condition which had a major influence on product properties was the temperature of both the first and second boiling steps. This factor also has an impact on the utilized utilities, but since the influence of utility costs on the overall economic performance is almost negligible, its effect on OPEX values is not included. Along with the unit's temperature, the impacts of varying operating pressures and alternative demilitarized $TiCl_4$ qualities will also be analysed.

During the commencement of this sensitivity analysis it became clear that the operating temperatures of both boiling steps could be decreased and $TiCl_4$ of appropriate quality will still be obtained. These lowered temperatures further delivered greater recovered quantities. It was expected that the selected temperatures during process development may not be the optimal operating temperatures, since the setting of the first step was based on the bubble point of water and not by optimization studies. The second step temperature was selected to obtain a maximum recovery based on the first step temperature though. The influence of each step's temperature is depicted in Figure 5-7.

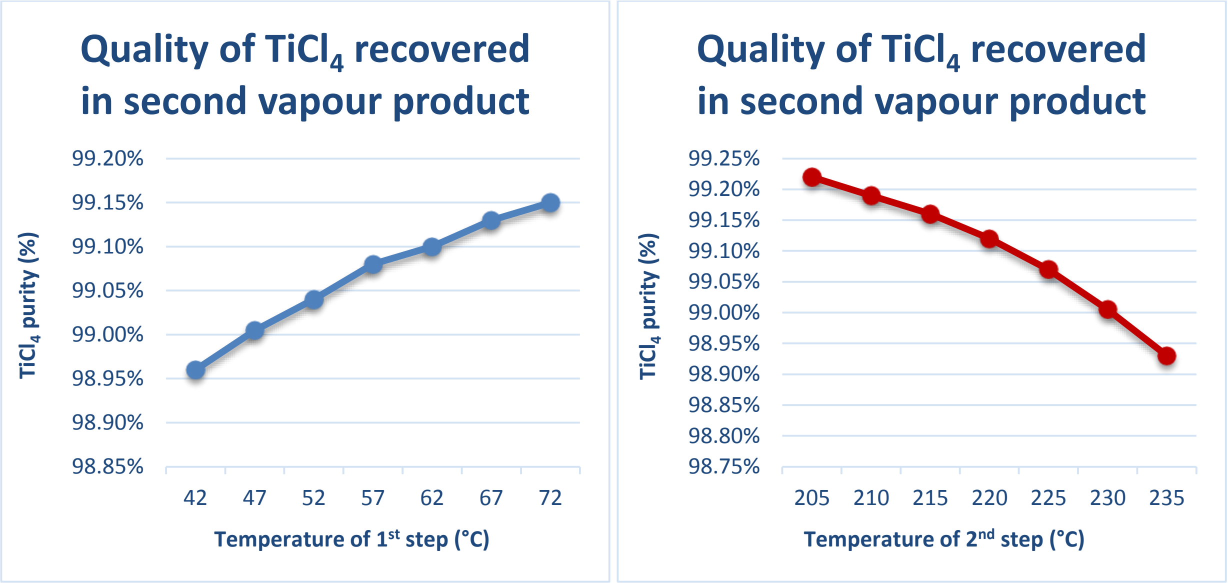

Figure 5-7: **Graph of the variation in obtained $TiCl_4$ quality as a function of the (a) temperature of the first boiling step and (b) temperature of the second boiling step**

By manually decreasing both temperatures in the simulation software until it started to decrease the recovery efficiency of this unit it was possible to determine that a temperature of 47°C for the first step and 230°C for the second would still deliver 952 kg $TiCl_4$ with a purity of 99.01% from the initial 1000 kg batch. The temperature of the first step was then varied by increments of 5°C while the second step was kept constant at 230°C (Figure 5-7(a)). Thereafter, the first temperature of 47°C was fixed with the variations occurring in the second temperature (Figure 5-7(b)). It can be deduced that the product quality is quite sensitive to both temperature steps. Based on these results it is recommended to implement a slight margin for errors by selecting operating temperatures of approximately 5°C from the established value. Based on the results of this sensitivity analysis it can be presumed that respective operating temperatures of 52°C and 225°C are suitable parameters for this process. The resulting $TiCl_4$ recovery from Aspen Plus^{TM} is 950 kg at a quality of 99.1%.

These lowered parameters will also cause a decrease in utility costs and heat exchanger sizes. This will benefit the operating and investment profits that were calculated for this process. Since these recommended alterations does not affect the comparison result of this study, but only confirm the discussed observations, it won't serve a meaningful purposes to amend the relevant input values. It is recommended to use these corrected temperature values for implementations of this process though. Additional advice is to confirm these results analytically to ensure that these lowered temperatures still deliver adequate $TiCl_4$, since it can be influenced by deviations from the assumed feed compositions.

The recovery of $TiCl_4$ has already been partially discussed, but its sensitivity analyses as a function of first and second step temperatures are given in Figure 5-8.

It can be concluded that these quantities are also relatively sensitive to the selected parameters. Seeing that no stipulations for the recovery of this compound exists, the objective is to maximize this value without impairing product qualities. The identified operating values from the discussion on Figure 5-7 was therefore made in conjunction with the observed results from Figure 5-8.

The influence of operating pressures on product properties are illustrated in Figure 5-9.

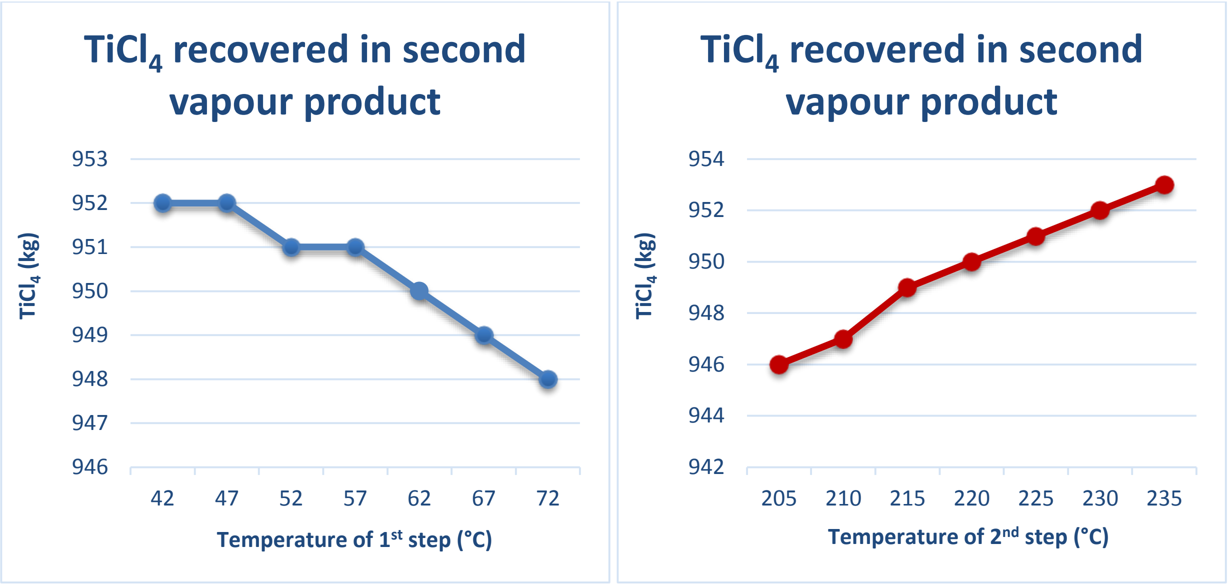

Figure 5-8: **Graph of the recovered $TiCl_4$ quantity as a function of the (a) temperature of the first boiling step and (b) temperature of the second boiling step**

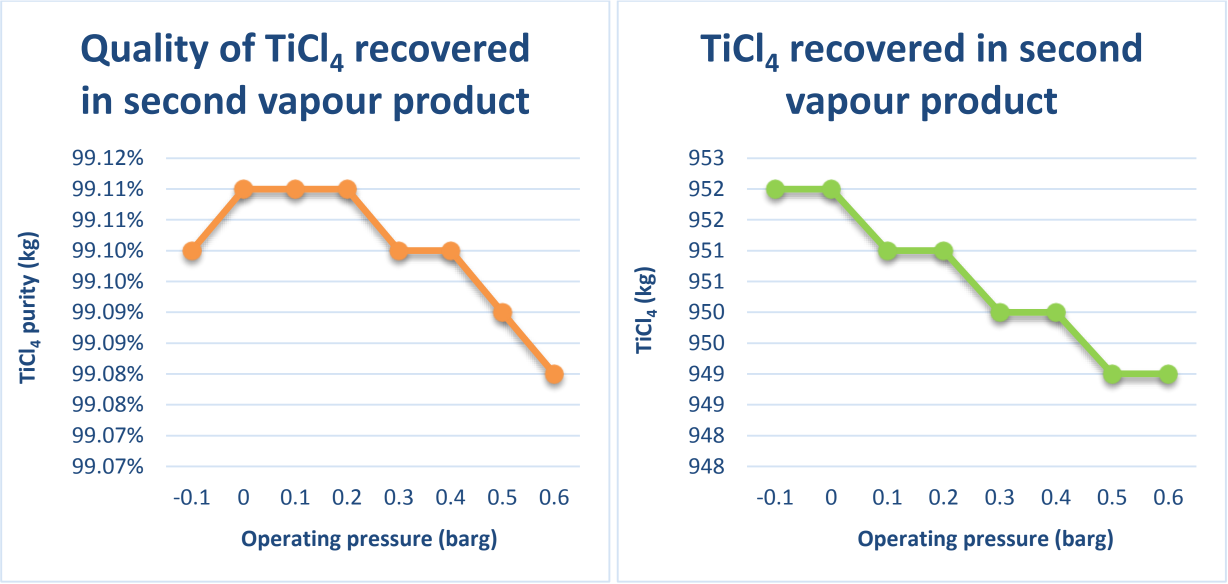

Figure 5-9: **Graph of the (a) observed $TiCl_4$ qualities and (b) obtained $TiCl_4$ recoveries as a function of operating pressure**

By altering the pressure of the boiler unit on the simulation software it became clear that this parameter does not have a substantial impact on obtained purities and slight variations of this condition would not alter the properties of delivered $TiCl_4$. The slight decrease observed in product qualities at increased pressures does not significantly influence the current choice of this operating condition. In Figure 5-9(b) a decrease in product recovery is observed with an increase in pressure. Lower pressures are therefore more desirable, but this parameter should still be operated at a positive gauge pressure to prevent contamination from external gas or vapours. Operating pressures between 0.1 and 0.2 barg will therefore produce the most favourable results, while values between 0.2 and 0.4 barg would still be acceptable

The obtainable $TiCl_4$ purity as a function of demilitarized $TiCl_4$ quality is depicted in Figure 5-10.

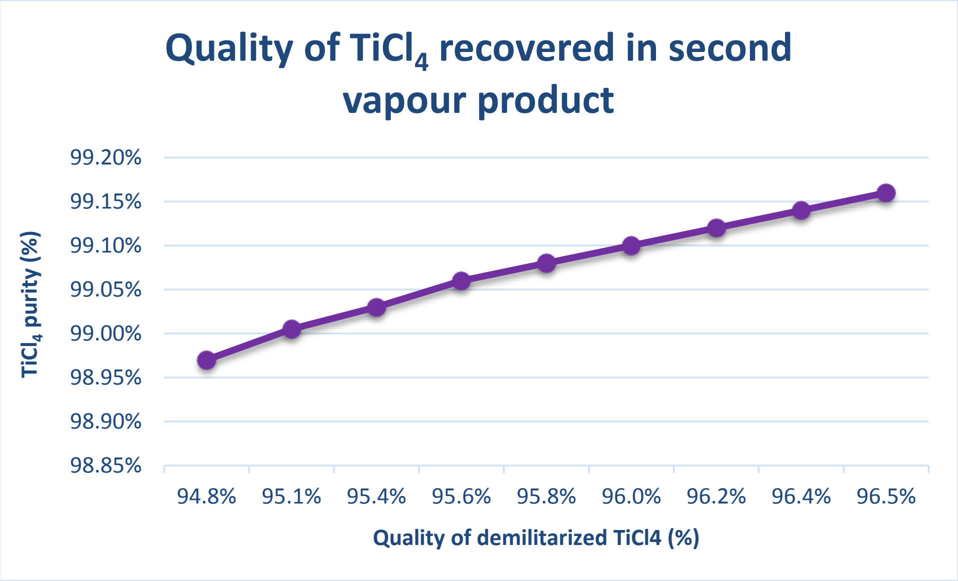

Figure 5-10: **Graph of obtained $TiCl_4$ purities as a function of the $TiCl_4$ composition in the demilitarized feed**

The results depicted in Figure 5-10 were obtained by implementing a temperature of 52°C for the first boiling step and 225°C for the second at an operating pressure of 0.3 barg. It is viable to conclude from Figure 5-10 that the implemented margins for error in the operating parameters enable this unit to deliver $TiCl_4$ of adequate purity even when a demilitarized feed with a quality of 95% is processes. Furthermore, the observable proportionality of these two properties were expected.

The cost of the boiler unit is the largest contributor to the CAPEX of the vessel. However, since this is a very simplified unit there aren’t many factors that can be varied to study its influence on investment costs. It is obvious that the cost of this particular unit is proportional to the size of the vessel, but variation of this property will have no function to towards the conclusions of this study since its capacity was made equal to the other processes for comparative reasons.

5.8 Conclusion

The resulting values and parameters from the techno-economic evaluation were normalized and compared in this chapter. The expected errors of these estimations were quantified by Peters *et al.* (2003) as more than ±30%. These inaccuracies were taken into consideration and were included in reported results.

The comparison was separated into two separate considerations. The first of these was for results that are based on the general values of the applicable products. The normalized data indicated that the Ti sponge production process had the best potential operating profit. From the CAPEX and investment comparisons it became clear that the sponge and TiO_2 pigment production options cannot be profitable for processing a limited quantity of 42 ton demilitarized $TiCl_4$. The third recycling solution entailed the use of a two-step vaporization unit to obtain $TiCl_4$ with a purity of 99% that can be reused in the production of new smoke mortars. This option displayed quite contrasting results though, by delivering both favourable operating and overall investment profits. These observations were confirmed by the corresponding PBP, IRR and ROI values. The PBP's of both the sponge and pigment production processes exceeded the scope period of six years for this study by quite a large margin, while the IRR and ROI parameters were negative. The third option possessed better parameter values in comparison to the former two processes and the IRR and ROI of the studied section boasted to be quite positive with regard to general market values for these parameters.

The second consideration is relevant to the current South African market. The operation of all three processes remained constant while the economic models of the sponge and pigment production options were unchanged. Comments on the feasibility of these two options are therefore still applicable. For this comparison, the local cost of $TiCl_4$ was used to account for fees that did not need to be spent in the manufacturing of new smoke mortars. This outlook was based on the fact that $TiCl_4$ can be reused to avoid the acquirement of new raw materials. This chemical is more expensive in South Africa, since it has to be imported and transported which add to the relevant market cost. Consequently, this considered solution proved to be even more favourable and the calculated PBP, IRR and ROI values for the studied section were extremely positive in relation to market figures.

Since the obtained results from the sponge and pigment production processes indicated that both these option are unfeasible, it was decided to provide the fewest volumes of processed feed that need to be exceeded before these sections could breakeven. It is evident from supplied results that significantly larger quantities are required before these potential solution can be deemed viable. In contrast, the values of the $TiCl_4$ recovery step for smoke mortar manufacturing were well below 42 ton for both scenarios.

Other diverse process alternatives which were mentioned in the literature study were evaluated against the observed results of the discussed comparisons. Naturalization and chemical disposal considerations were disqualified based on the fact these processes operate at a financial loss while solutions exist that have the potentially earn or save large sums of money. The option of supplying crude or purified $TiCl_4$ to external consumers is completely market dependent and this factor should first be analysed for the region where implementation is considered. It was deemed to be an unfeasible solution for the local market, since demands for both these processes are extremely limited.

The final objective of this section was to conduct a sensitivity analysis to determine how deviations in input values affect the process outcome and also to identify operating parameters which can be altered in order to obtain a better outcome. Based on the disqualification of several considered options in this chapter, it was valid to determine that the third option of reusing $TiCl_4$ in smoke mortars had the largest relevance towards this study. Improvements to this process could potentially benefit its financial model. Decreasing the temperatures of both flash steps to respective values of 52°C and 225°C will still deliver a product of similar quality, while recovery rates are increased. The implemented margin for error in these values allow the quality of the $TiCl_4$ to decrease to 95% and still conform to stipulations. This process was not very sensitive to the operating pressure and a lowered positive gauge pressure was proven to be an adequate selection. Although these improved process parameters did not affect the outcome of this study, it will decrease the design and utility costs of operating units and enhance the profitable of this solution. It is accordingly recommended to incorporate the stated values in process implementation or future developments.

Final conclusions and recommendations based on discussed results are provided in Chapter 6.

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

6.1 Introduction

The focus of this chapter is to take all findings, results and discussions into consideration to supply a relevant and accurate conclusion. Since it was determined in the economic evaluation that the markets of components in this study differ to a substantial extent, it was deemed appropriate to derive conclusions for both the general and local markets.

It should be noted that separate conclusions of the developments, findings and relevant content of each chapter are not included in these sections, since they were rigorously summarized at the end of the applicable chapter.

Obtained conclusions from the subsequent sections are used to reflect on the aim and objectives of this study. Results and identified limitations throughout the progression of conducted work are then considered to compile recommendations for future work.

6.2 Identification of general solution

The developed conclusions of this general solution are from a perspective that purely focuses on industrial values for all components. Limitations to product demands or difficulties to acquire necessary operating units and chemicals are thus not accounted for.

Based on this perspective, it is possible to conclude which recycling process is deemed to be the most feasible option. Out of the three considered processes that were assessed by this techno-economic evaluation, the option of reusing $TiCl_4$ to manufacture new smoke mortars displays the best economic results and is therefore the appropriate option. This $TiCl_4$ with a purity of 99% is obtained from a two-step vaporization process. Operating conditions for this unit has been improved by a sensitivity analysis to the extent that $TiCl_4$ with a purity of 99.1% can be obtained with product losses that are close to the minimum amount. This can be achieved by operating temperatures below those selected in the technical model of Chapter 3, which will result in a decrease in utility and unit costs. This will further improve the favourable results of this option.

The alternative two options that were considered (Ti sponge and TiO_2 pigment production) were determined to be technically possible, but applicable economic parameters eliminated these options as viable considerations under the current conditions. This was based on their unfeasible

PBP, IRR and ROI values that indicated a substantially greater feed than 42 ton $TiCl_4$ is required before these processes should be reconsidered.

Available quantities of $TiCl_4$ feed that should be exceeded before these processes can be considered were determined to be 150 ton ± 50 ton for sponge production and 1 300 ton ± 400 ton for pigment production. It is critical to note that these are not the masses required for each process to become profitable, but only to cover the cost of the studied production section. Several cost factors and downstream processes are omitted from the techno-economic evaluation, since it would not have made a difference in the comparison of results.

Similarly, it can be reported that the selected solution displayed extremely positive PBP, IRR and ROI values which compares well with other industrial processes. However, these are not the final parameter values seeing that secondary costs and cost factors are omitted. It would therefore not serve a purpose to provide calculated results in this section, but only to comment on the comparison results. It can be stated though that the positive extent of these financial parameters implicates that this process should still be feasible when all costs are accounted for.

A final option that seems viable in general markets is to sell the demilitarized or purified $TiCl_4$ to external consumers at a profit. This solution is extremely market dependent though, since the demand and price of these components vary considerably between regions and when no market exists, this alternative is basically eliminated. No solid conclusions can therefore be made on the feasibility of this solution with regard to this study, but it is recommended that this option is taken into consideration for future applications.

6.3 Identification of applicable solution to the current local market

For this conclusion, the focus is directed towards the feasibility of these solutions in the current South African market. This also serves as the more specific solution to this study and supplied problem statement. Technical production methods and performances of each of the three studied solutions have not changed, but deviations are observed in the market value of $TiCl_4$. These observations are prompted by the fact that $TiCl_4$ needs to be imported for the manufacturing of smoke mortars. The market price after adding corresponding transport, importation and tax fees is considerably higher than the general product value.

This raw material expense which is averted by the implementation of this solution is regarded as the obtained product value, seeing that it represents an equivalent positive consequence to operating profits. With the economic models of the sponge and pigment production processes remaining unfeasible for this scope, the comparison results are further reinforced for this scenario. Consequently, the two-step vaporization process for delivering $TiCl_4$ that can be reused in smoke mortars is identified as the best possible recycling solution. The difference between the general value of 99% pure $TiCl_4$ ($ 1440 per ton) and the local price of imported $TiCl_4$ ($ 7390 per ton) is just below $ 6000 per ton. This difference in product value increases the profitability of this process even further and substantial increases in IRR and ROI percentages are observed.

Options for selling 42 ton crude or pure $TiCl_4$ do not currently exist in the local market and can therefore not be considered as possible independent solutions. Minute applications of $TiCl_4$ are present but utilized volumes are extremely limited. A possible combination can potentially be initiated where purified $TiCl_4$ is used to manufacture smoke mortars while surplus volumes are supplied to small-scale consumers in industry. This option is largely dependent on the actual volumes of $TiCl_4$ that are being consumed by the smoke mortar manufacturer and can consequently not be finalised in this study.

By observing the enormous financial potential and profitability of this process, it is viable to ask the question of why this has not been done before. A relevant answer would be that the requirement for demilitarizing smoke mortars and recycling obtained components has not been actively focused on for more than a few years, since this is quite a modern problem. It is mentioned in the background to this study that smoke mortars should be demilitarized once they are older than 20 years. With the conflicted history of South Africa, this problem has only surfaced a couple of years ago.

An aspect that largely contributes to the feasibility of this process is the fact that $TiCl_4$ is already in possession and does not contribute to raw material costs. Recycling demilitarized $TiCl_4$ is furthermore not a common problem and could be why this solution has not yet been studied or developed. With that said, it is possible that this process or other solutions have already been implemented by other ammunition manufacturers, but were not published due to the extreme confidentially of this field of knowledge.

6.4 Fulfilment of objectives

The aim of analysing possible recycling processes of demilitarized $TiCl_4$ is revisited. This chemical is obtained after the demilitarization of smoke mortars had been conducted, which is a thoroughly developed process and does not fall within the scope of this project.

The commencing step of this study was to perform a critical literature survey on the considered solutions amongst other things. Raw demilitarized $TiCl_4$ was then analysed to identify and quantify impurities and determine feed quality. The technical analysis of each process was conducted by construction of a theoretical mass balance and simulated flow sheet. The theoretical mass balance was based on empirical and industrial data while the flow sheet was simulated on Aspen Plus^{TM} using the 'Ideal' property method. No substantial differences were found between resulting quantities of the major chemical components. Verification of these results proved that products of all three processes conform to ASTM standards or industrial stipulations.

Results from the simulation software were consequently used to determine the CAPEX and OPEX of each process. Corresponding economic models were constructed to determine the financial feasibility of these solutions. Profitable or potentially profitable options were identified, which was only one of the three processes for this scenario. The improved operating conditions of this process was then established through sensitivity analyses to determine where operating and unit costs could be reduced. The appropriate solution for recycling demilitarized $TiCl_4$ was determined accordingly from the results of this techno-economic evaluation.

Obtained results of this study therefore enable relevant parties to recycle this material at a financial gain. This option is also applicable to $TiCl_4$ that is obtained from nonconforming mortars which are now being demilitarized as opposed to past recourses where this chemical was disposed, detonated or destructed along with the ammunition. From an environmental perspective, it is consequently viable to conclude that this solution offers an immense improvement to current practices while being financially beneficial.

6.5 Verification and validation

Verification of each product's conformance to ASTM standards or industrial stipulations is performed in the same section where these products are reported. Verification was executed for both the theoretical (Section 3.5) and simulation results (Section 3.6).

When the focus is placed on the final result of this study, it can successfully be verified that the simulation and theoretical results indicate that the $TiCl_4$ obtained from the two-step boiler unit has a purity above 99%, contains less than 0.01% SO_4 and less than 0.006% heavy metals. The actual values of these respective fields for the obtained product are 99.01%, 0.005% and 0.004% from the calculated results and 99.1%, 0.004% and 0.003% from the simulation results. Differences between these values are considered to be negligible.

A definite form of validation occurs at the end of the literature survey in Section 2.5 where the potential solutions are identified. It is understood that the validation required for this study is to affirm that proposed solutions are indeed valid in the sense that it actually solve the problem and satisfy industrial and client expectations. In the mentioned section processes were selected based on their ability to comply with the general demilitarization aim of “zero wastes – only by-products”. Although it may not be possible to literally have no wastes it all, the focus should be to reuse or recycle any components with potential value. Based in the stated criteria, all three processes are deemed to be valid solutions since it covers the process of beneficiating a demilitarized material.

A second step of validation is the techno-economic evaluation itself. This statement is based on the fact that the technical assessment is used to confirm that processes are practical, but feasibility with regard to this study is validated by the economic evaluation. From this perspective it can be established whether the proposed process is feasible and therefore valid, or unfeasible and as a result not valid.

More specifically, the identified solution of reusing $TiCl_4$ to manufacture new smoke mortars can firstly be validated by affirming that it meets the requirement of recycling demilitarized $TiCl_4$. Secondly, it is confirmed by the positive IRR and ROI values from its economic model and evaluation that this is a profitable process and accordingly a feasible solution.

6.6 Recommendations for future studies

Several areas that bear potential for future research and development were identified throughout this study. Some of the topics would benefit this study and its implementation in future scenarios, while other would make a meaningful contribution in conjunction with this study to demilitarization, recycling and titanium industries. These recommended fields are listed next.

- It became evident from market values in the economic model that titanium sponge or powder is quite a valuable commodity and also has the highest operating profits. The profitability of this process is mainly diminished by costs of operating units which contributes to the substantial capital investment requirement. It would therefore be beneficial to develop and implement improved processes that utilize $TiCl_4$ to produce titanium. Several existing developments that offer improvements to the selected Kroll process are discussed in the literature survey. Methods that potentially require smaller capital investments and could yield a larger net profit were the Armstrong, TiRO and SRI processes. Once sufficient information on these processes is available and accessible, it could be reconsidered as an appropriate solution for $TiCl_4$ recycling.

- Certain limitations to the Aspen Plus^{TM} simulation software were identified which could potentially be improved for further process developments. A major aspect was the missing property parameters for some of the major chemical components. This hindered the choice of an applicable thermodynamic property method with the result that the ‘Ideal’ property package had to be selected. This is not the optimal choice for a complex chemical system that includes solids, aqueous solutions, vapours and batch units. The recommendation is to obtain these parameters by the FactSage© database or a similar source to attempt a more a more accurate simulation of each process. Although it can be stated with great confidence that these limitations have not negatively influenced the resulting solution of this study, it would immensely contribute towards the accurate development and future implementations of this process.

- After identification of this appropriate recycling solution, subsequent steps would include the development of a detailed process design. A recommended method of determining initial costs for overall and individual cost factors were mentioned in Section 4.4 and can be estimated using the categories and ranges stated in Table 4-5. The identified process design should also incorporate a more detailed consideration of the necessary transportation, handling and exposure controls of the applicable chemicals, since these factors are crucial in the actual business case. The identified solution can then be implemented to resolve the relevant problem statement.

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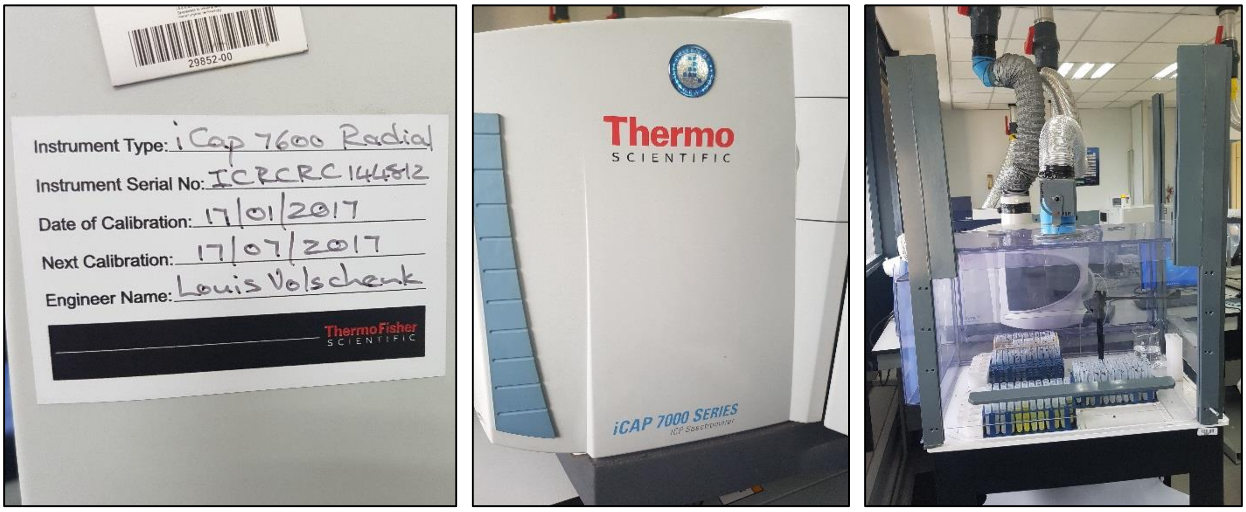
ANNEXURE A

A.1 ICP-OES analyses of demilitarized $TiCl_4$ samples

Each obtained sample of demilitarized $TiCl_4$ was treated and analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) according to the following steps:

1. A 100 ml beaker containing 10 ml 1:1 hydrochloric acid (HCl) was cooled in an ice batch.
2. 5 ml of the demilitarized $TiCl_4$ was withdrawn from the glass container by means of a pipette. This liquid was then added drop wise to the cold HCl while swirling the beaker.
3. 2.5 ml of 0.2 g/L Sc solution was added to a 50 ml flask.
4. The contents of the beaker was then quantitatively added to this 50 ml flask.
5. The flask was filled with distilled water up to the mark.
6. Sample tubes was filled with the aqueous solution from the flask.
7. Contents of each sample tube was analysed in the ICP spectrometer.

The instrument that was used for analysis was an iCap 7600 Radial ICP Spectrometer (See Figure A-1).

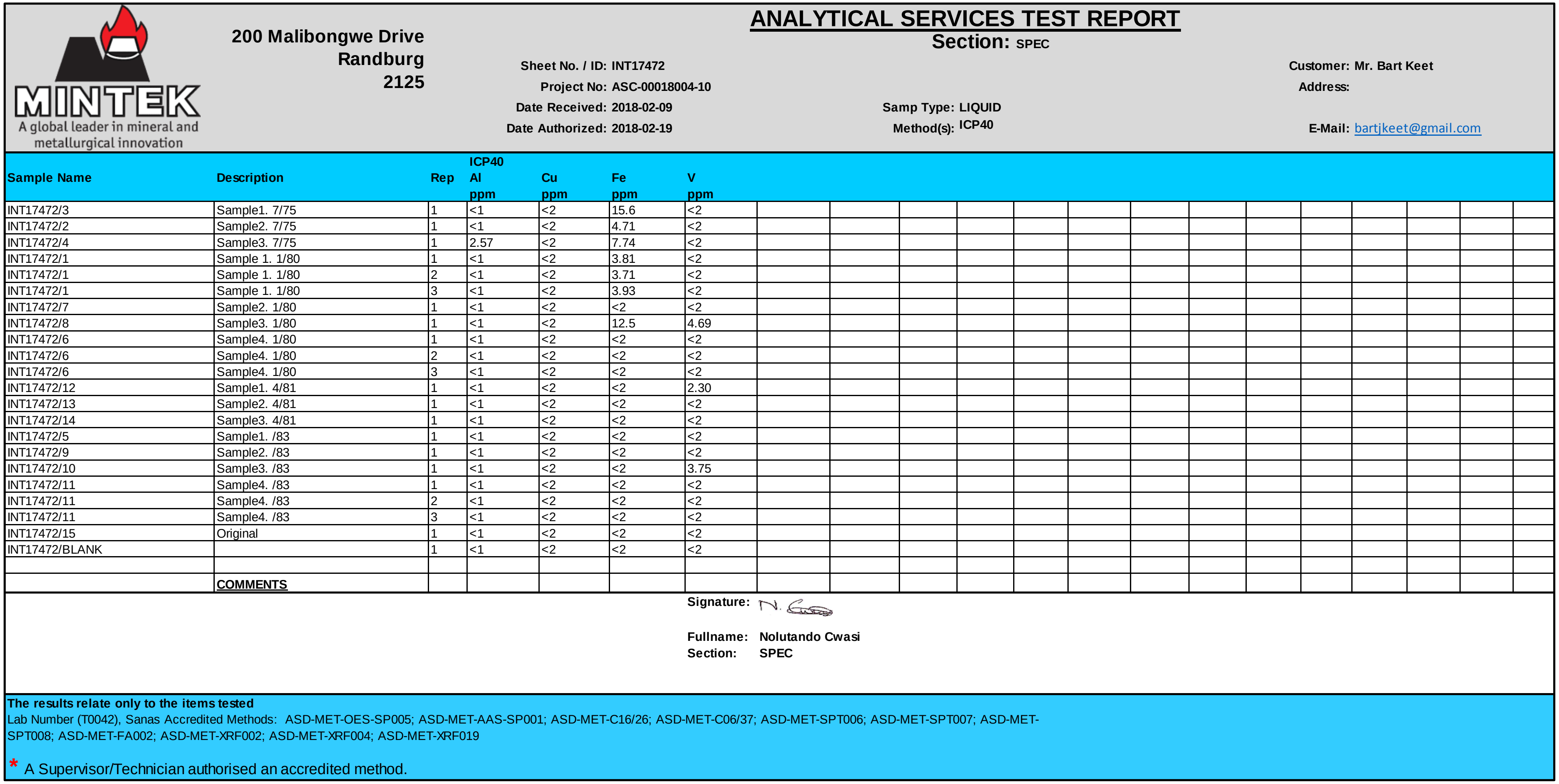


Instrument Type: iCap 7600 Radial
Instrument Serial No: ICRCRC144812
Date of Calibration: 17/01/2017
Next Calibration: 17/07/2017
Engineer Name: Louis Volschenk

Figure A-1: iCap 7600 Radial ICP spectrometer

Five standards and two quality control samples were analysed prior to the $TiCl_4$ samples to validate that the machine is correctly calibrated and produces accurate results. Duplicate and triplicate volumes of selected samples were prepared and analysed to confirm the consistency of the final results.

A depiction of the results that were obtained from the ICP-OES analysis are given in Figure A-2.



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ANALYTICAL SERVICES TEST REPORT

Section: SPEC

Sheet No. / ID: INT17472
Project No: ASC-00018004-10
Date Received: 2018-02-09
Date Authorized: 2018-02-19

Samp Type: LIQUID
Method(s): ICP40

Customer: Mr. Bart Keet
Address:
E-Mail: bartjkeet@gmail.com

Sample Name	Description	Rep	ICP40 Al ppm	Cu ppm	Fe ppm	V ppm
INT17472/3	Sample1. 7/75	1	<1	<2	15.6	<2
INT17472/2	Sample2. 7/75	1	<1	<2	4.71	<2
INT17472/4	Sample3. 7/75	1	2.57	<2	7.74	<2
INT17472/1	Sample 1. 1/80	1	<1	<2	3.81	<2
INT17472/1	Sample 1. 1/80	2	<1	<2	3.71	<2
INT17472/1	Sample 1. 1/80	3	<1	<2	3.93	<2
INT17472/7	Sample2. 1/80	1	<1	<2	<2	<2
INT17472/8	Sample3. 1/80	1	<1	<2	12.5	4.69
INT17472/6	Sample4. 1/80	1	<1	<2	<2	<2
INT17472/6	Sample4. 1/80	2	<1	<2	<2	<2
INT17472/6	Sample4. 1/80	3	<1	<2	<2	<2
INT17472/12	Sample1. 4/81	1	<1	<2	<2	2.30
INT17472/13	Sample2. 4/81	1	<1	<2	<2	<2
INT17472/14	Sample3. 4/81	1	<1	<2	<2	<2
INT17472/5	Sample1. /83	1	<1	<2	<2	<2
INT17472/9	Sample2. /83	1	<1	<2	<2	<2
INT17472/10	Sample3. /83	1	<1	<2	<2	3.75
INT17472/11	Sample4. /83	1	<1	<2	<2	<2
INT17472/11	Sample4. /83	2	<1	<2	<2	<2
INT17472/11	Sample4. /83	3	<1	<2	<2	<2
INT17472/15	Original	1	<1	<2	<2	<2
INT17472/BLANK		1	<1	<2	<2	<2
	COMMENTS					

Signature:

Fullname: Nolutando Cwasi
Section: SPEC

The results relate only to the items tested
Lab Number (T0042), Sanas Accredited Methods: ASD-MET-OES-SP005; ASD-MET-AAS-SP001; ASD-MET-C16/26; ASD-MET-C06/37; ASD-MET-SPT006; ASD-MET-SPT007; ASD-MET-SPT008; ASD-MET-FA002; ASD-MET-XRF002; ASD-MET-XRF004; ASD-MET-XRF019

* A Supervisor/Technician authorised an accredited method.

Figure A-2: Results obtained from ICP-OES

A.2 Determining chloride in solution to calculate $TiCl_4$ purity

As mentioned in Chapter 3, the basis of this analysis is to quantify the chloride in solution of each sample and use these results to calculate the $TiCl_4$ purity in each sample. The presence of other metal chlorides in solution will cause a deviation in the accuracy of the calculated results though. It is thus imperative to identify and quantify impurities in the liquid to warrant the results obtained from this analysis.

The steps that were taken to measure the amount of chloride in solution of each sample are as follow:

1. A beaker with an undisclosed volume of 0.2 mol/L nitric acid (HNO_3) was cooled in an ice bath.
2. A volume of 1 ml demilitarized $TiCl_4$ was withdrawn from the glass container with a pipette. This liquid was then added drop wise to the cold HNO_3 while swirling the beaker.
3. Distilled water was added to the mixture to make up a sample of the prescribed volume and dilution.
4. The sample was titrated with silver nitrate ($AgNO_3$), which caused silver chloride to precipitate. Potassium dichromate was used as indicator. The titration was complete when the initial orange-yellow colour of the liquid turned rusty-brown.
5. The volume of $AgNO_3$ required for a successful titration of each sample was used to determine the chloride in solution and calculate its $TiCl_4$ purity.

It is shown in Equation A-1 how the concentrations of chloride in solution was determined from the titration values.

$$ppm\ Chloride = \frac{AgNO_3\ required\ \ (L) \times 35.45\ g/mol \times N\ mol/L \times dilution\ factor}{sample\ volume\ (L)} \qquad [A\text{-}1]$$

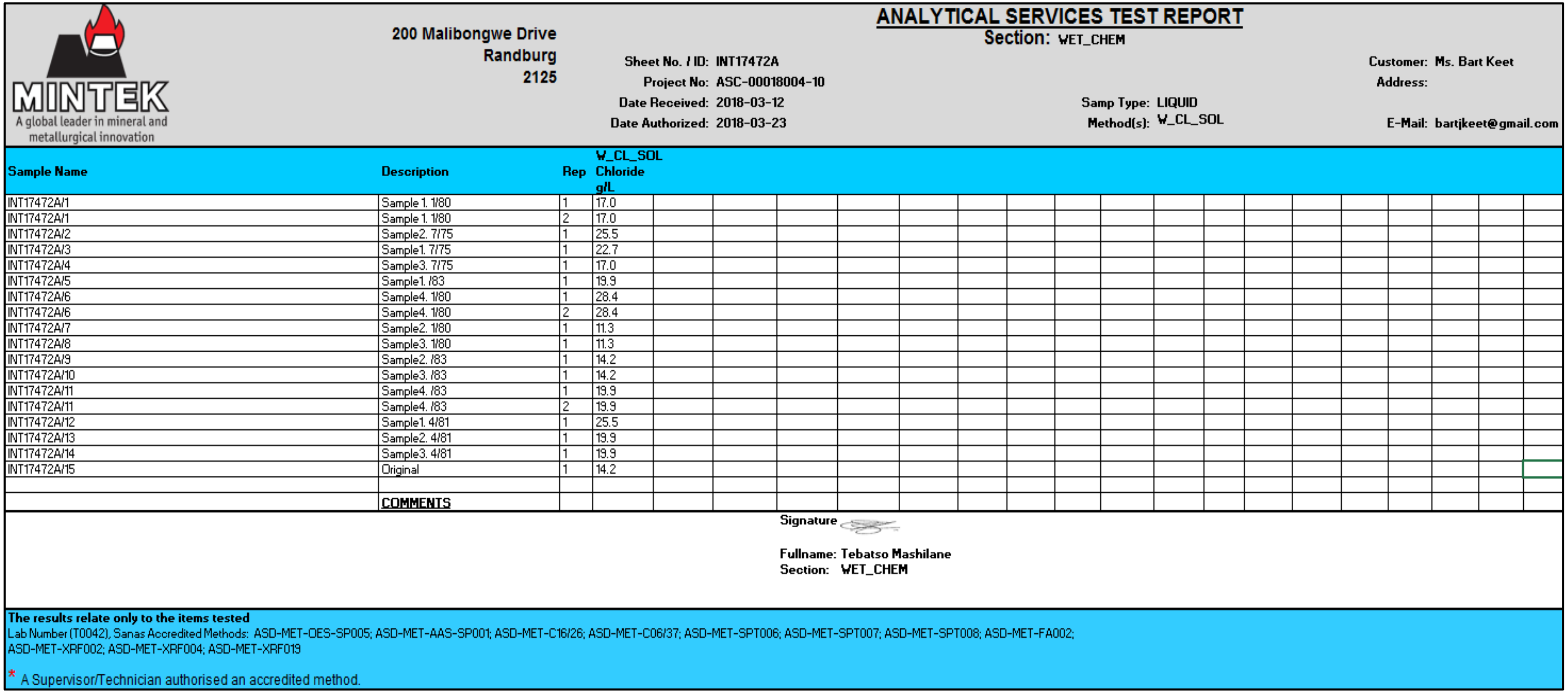
with:

N = 0.2 mol/L

Dilution factor = 4000

Sample volume = 0.001 L

The obtained results from the chloride in solution analysis are given in Figure A-3 while the volumes of $AgNO_3$ required for successful titration of each sample are given in Table A-1.



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ANALYTICAL SERVICES TEST REPORT

Section: WET_CHEM

Sheet No. / ID: INT17472A
Project No: ASC-00018004-10
Date Received: 2018-03-12
Date Authorized: 2018-03-23

Samp Type: LIQUID
Method(s): W_CL_SOL

Customer: Ms. Bart Keet
Address:

E-Mail: bartjkeet@gmail.com

Sample Name	Description	Rep	W_CL_SOL Chloride g/L
INT17472A/1	Sample 1. 1/80	1	17.0
INT17472A/1	Sample 1. 1/80	2	17.0
INT17472A/2	Sample2. 7/75	1	25.5
INT17472A/3	Sample1. 7/75	1	22.7
INT17472A/4	Sample3. 7/75	1	17.0
INT17472A/5	Sample1. /83	1	19.9
INT17472A/6	Sample4. 1/80	1	28.4
INT17472A/6	Sample4. 1/80	2	28.4
INT17472A/7	Sample2. 1/80	1	11.3
INT17472A/8	Sample3. 1/80	1	11.3
INT17472A/9	Sample2. /83	1	14.2
INT17472A/10	Sample3. /83	1	14.2
INT17472A/11	Sample4. /83	1	19.9
INT17472A/11	Sample4. /83	2	19.9
INT17472A/12	Sample1. 4/81	1	25.5
INT17472A/13	Sample2. 4/81	1	19.9
INT17472A/14	Sample3. 4/81	1	19.9
INT17472A/15	Original	1	14.2
	COMMENTS		

Signature

Fullname: Tebatso Mashilane
Section: WET_CHEM

The results relate only to the items tested
Lab Number (T0042), Sanas Accredited Methods: ASD-MET-OES-SP005; ASD-MET-AAS-SP001; ASD-MET-C16/26; ASD-MET-C06/37; ASD-MET-SPT006; ASD-MET-SPT007; ASD-MET-SPT008; ASD-MET-FA002; ASD-MET-XRF002; ASD-MET-XRF004; ASD-MET-XRF019

* A Supervisor/Technician authorised an accredited method.

Figure A-3: Obtained results from the chloride in solution analysis

Each sample's $TiCl_4$ purity was calculated by comparing the concentration of chloride in solution to that of pure $TiCl_4$.

The mass percentage of chloride in pure $TiCl_4$ was determined by calculating the mass fraction of the four chloride atoms (4 x 35.45 g/mol) to a $TiCl_4$ molecule (189.7 g/mol) (see Equation A-2).

$$mass\%\ Cl_4\ of\ pure\ TiCl_4 = \frac{4 \times M_{Cl}}{M_{TiCl_4}} = \frac{4 \times 35.45\ g/mol}{189.7\ g/mol} = 74.8\ \% \qquad [A\text{-}2]$$

The mass% of chloride in solution was then subtracted from the mass% Cl_4 of pure $TiCl_4$ to determine the mass% Cl_4 in the sample (Equation A-3).

$$mass\%\ Cl_4\ of\ sample = mass\%\ Cl_4\ of\ pure\ TiCl_4 - \frac{ppm\ chloride}{1\ 000\ 000} \qquad [A\text{-}3]$$

Sample purities were determined with Equation A-4 by calculating the ratio of mass% Cl_4 in the sample to mass% Cl_4 of pure $TiCl_4$.

$$TiCl_4\ purity\ of\ sample = \frac{mass\%\ Cl_4\ of\ sample}{mass\%\ Cl_4\ of\ pure\ TiCl_4} \qquad [A\text{-}4]$$

The results of these calculations are given in Table A-1.

Table A-1: Titration and calculations results

	$AgNO_3$ required* (L)	ppm chloride	mass% Cl_4	$TiCl_4$ purity
1975 (1)	0.0008	22 688	72.5%	97.0%
1975 (2)	0.0009	25 524	72.2%	96.6%
1975 (3)	0.0006	17 016	73.1%	97.7%
1980 (1)	0.0006	17 016	73.1%	97.7%
1980 (2)	0.0004	11 344	73.6%	98.5%
1980 (3)	0.0004	11 344	73.6%	98.5%
1980 (4)	0.0010	28 360	71.9%	96.2%
1981 (1)	0.0009	25 524	72.2%	96.6%
1981 (2)	0.0007	19 852	72.8%	97.3%
1981 (3)	0.0007	19 852	72.8%	97.3%
1983 (1)	0.0007	19 852	72.8%	97.3%
1983 (2)	0.0005	14 180	73.4%	98.1%
1983 (3)	0.0005	14 180	73.4%	98.1%
1983 (4)	0.0007	19 852	72.8%	97.3%
2016 (1)	0.0005	14 180	73.4%	98.1%

*Volumes of $AgNO_3$ required for titration of each sample were received upon request.

ANNEXURE B

B.1 Purification of $TiCl_4$ for metallic Ti and TiO_2 pigment production

B.1.1 Challenges and limitations of available input components

Vanadium oxytrichloride ($VOCl_3$) was not on the available components list and $VOCl_2$ was selected to account for the presence of vanadium compounds in the liquid. $VOCl_3$ has a boiling point of 127°C and is expected to vaporize along with $TiCl_4$ while $VOCl_2$ in contrast will precipitate as a solid at low temperatures or decompose into $VOCl_3$ at higher temperatures. The approach that was considered in this simulation is similar to the theoretical calculations in Section 3.5. Hence, it is assumed that a small quantity of $VOCl_3$ will be extracted in the first distillation step, while the remaining volume will escape with $TiCl_4$ through the distillate in the second step.

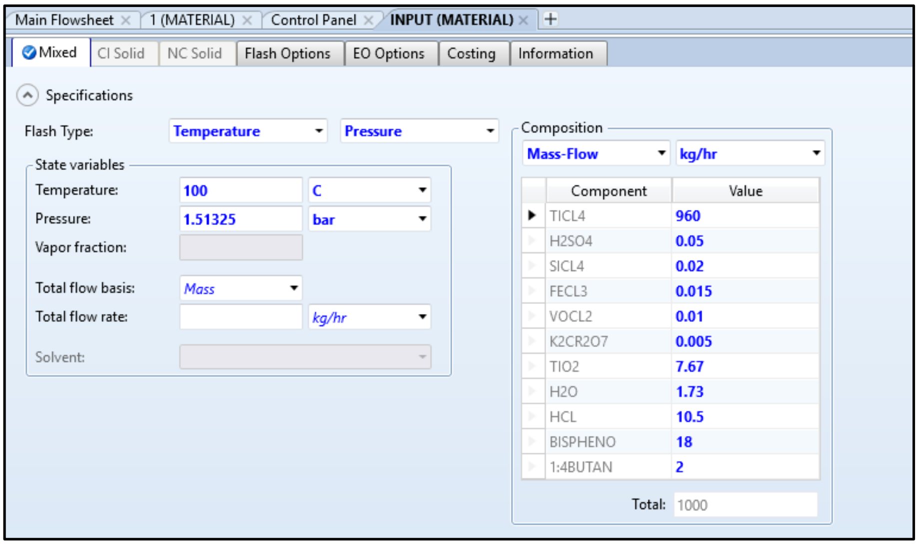
Both the complex polymers, bisphenol A-epichlorohydrin and 1,4-butanediol diglycidyl ether, which were assumed to contaminate the liquid during smoke mortar manufacturing are not included in the Aspen Plus^{TM} software. The base molecule of each compound (*i.e.* bisphenol A and 1,4-butanediol) was therefore selected for consideration in simulation of this process. The differences in boiling points are not detrimental to accuracy of obtained results since it is larger than that of $TiCl_4$ by quite a substantial margin. The boiling points of these four chemicals are listed in Table B-1.

Table B-1: Boiling points of complex and base molecules considered in simulation

	Boiling point (°C)
bisphenol A	220
1,4-butanediol	230
1,4-butanediol diglycidyl ether	266
bisphenol A-epichlorohydrin	320

B.1.2 Simulation development and results

The comprehensive simulation procedure that was followed to design an adequate distillation column is given in this section by means of screenshots of the input values and obtained results.



Flash Type: Temperature | Pressure

State variables

Temperature: 100 C

Pressure: 1.51325 bar

Vapor fraction:

Total flow basis: Mass

Total flow rate: kg/hr

Solvent:

Composition: Mass-Flow | kg/hr

Component	Value
TICL4	960
H2SO4	0.05
SICL4	0.02
FECL3	0.015
VOCL2	0.01
K2CR2O7	0.005
TIO2	7.67
H2O	1.73
HCL	10.5
BISPHENO	18
1:4BUTAN	2

Total: 1000

Figure B-1: Demilitarized $TiCl_4$ feed to distillation process

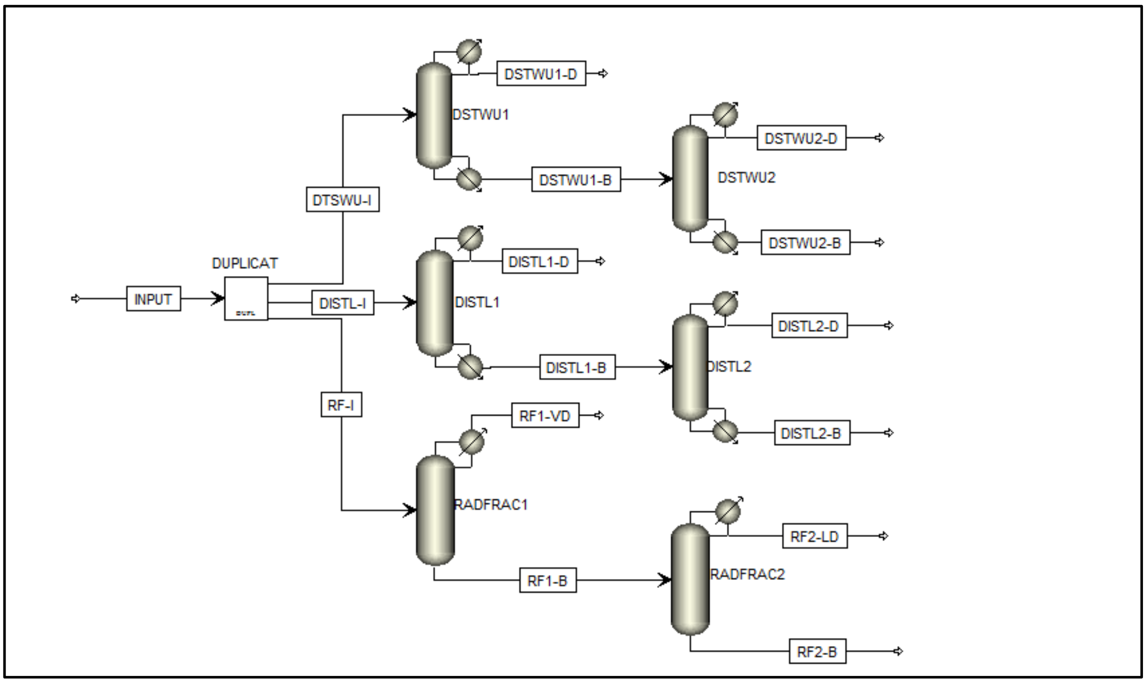
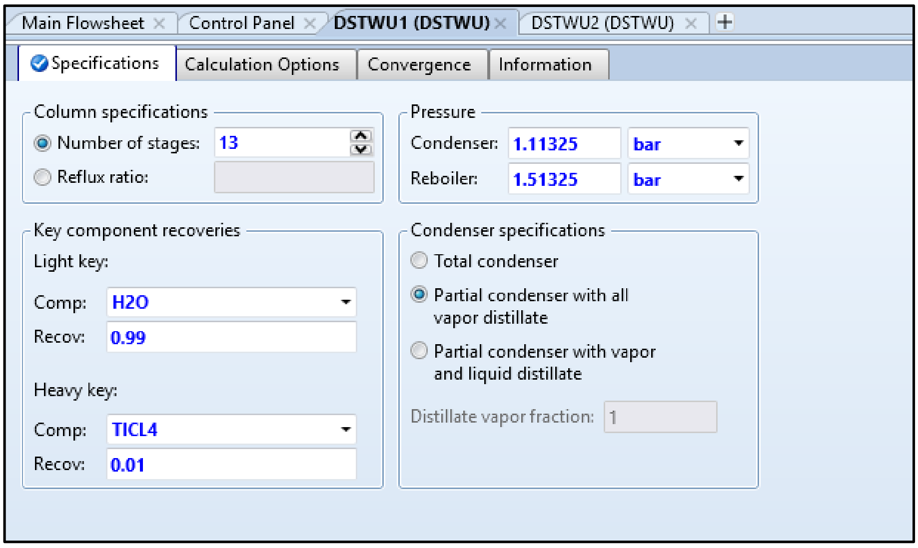


Figure B-2: Flow sheet used for developing column parameters



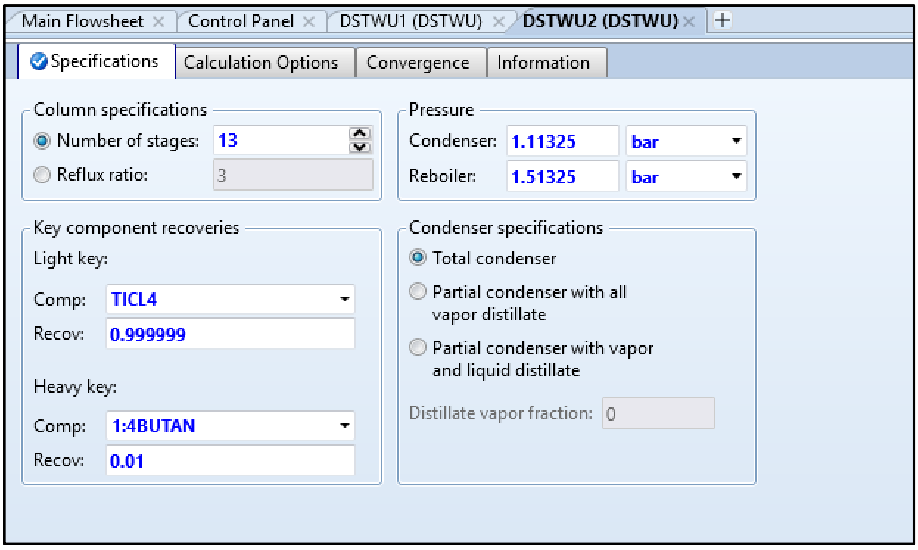
Column specifications
● Number of stages: 13
○ Reflux ratio:

Pressure
Condenser: 1.11325 bar
Reboiler: 1.51325 bar

Key component recoveries
Light key:
Comp: H2O
Recov: 0.99
Heavy key:
Comp: TICL4
Recov: 0.01

Condenser specifications
○ Total condenser
● Partial condenser with all vapor distillate
○ Partial condenser with vapor and liquid distillate
Distillate vapor fraction: 1

Figure B-3: **Input of column DSTWU1**



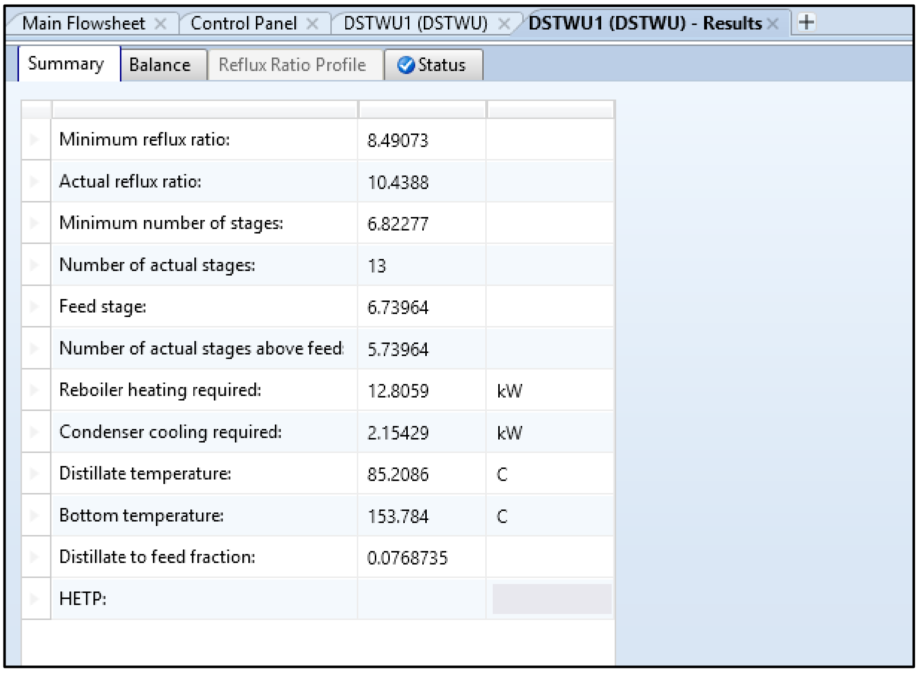
Column specifications
● Number of stages: 13
○ Reflux ratio: 3

Pressure
Condenser: 1.11325 bar
Reboiler: 1.51325 bar

Key component recoveries
Light key:
Comp: TICL4
Recov: 0.999999
Heavy key:
Comp: 1:4BUTAN
Recov: 0.01

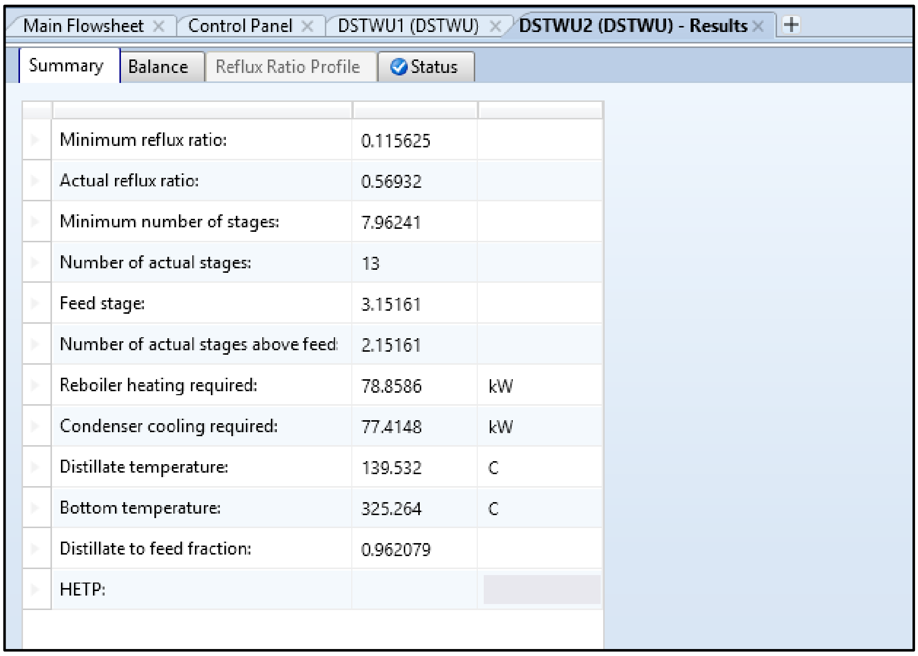
Condenser specifications
● Total condenser
○ Partial condenser with all vapor distillate
○ Partial condenser with vapor and liquid distillate
Distillate vapor fraction: 0

Figure B-4: **Input of column DSTWU2**



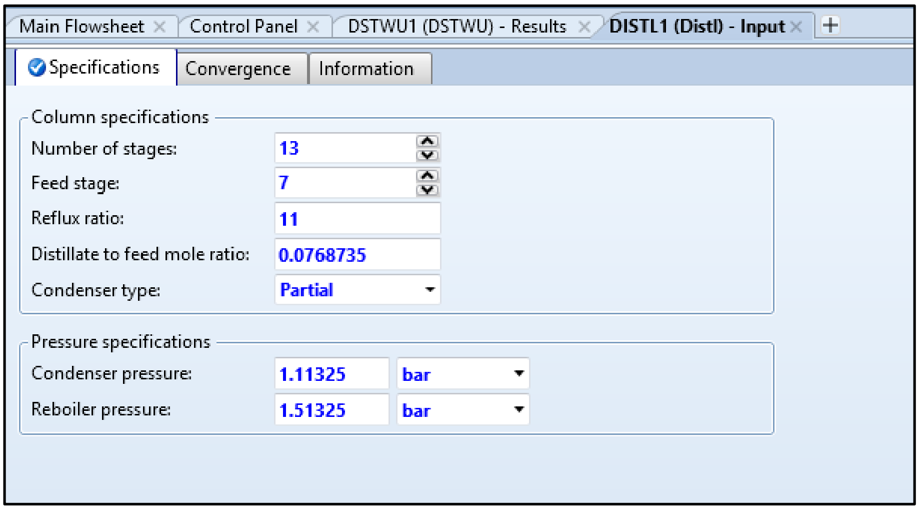
Minimum reflux ratio:	8.49073	
Actual reflux ratio:	10.4388	
Minimum number of stages:	6.82277	
Number of actual stages:	13	
Feed stage:	6.73964	
Number of actual stages above feed:	5.73964	
Reboiler heating required:	12.8059	kW
Condenser cooling required:	2.15429	kW
Distillate temperature:	85.2086	C
Bottom temperature:	153.784	C
Distillate to feed fraction:	0.0768735	
HETP:		

Figure B-5: Results of DTSWU1



Minimum reflux ratio:	0.115625	
Actual reflux ratio:	0.56932	
Minimum number of stages:	7.96241	
Number of actual stages:	13	
Feed stage:	3.15161	
Number of actual stages above feed:	2.15161	
Reboiler heating required:	78.8586	kW
Condenser cooling required:	77.4148	kW
Distillate temperature:	139.532	C
Bottom temperature:	325.264	C
Distillate to feed fraction:	0.962079	
HETP:		

Figure B-6: Results of DSTWU2



Column specifications

Number of stages: 13

Feed stage: 7

Reflux ratio: 11

Distillate to feed mole ratio: 0.0768735

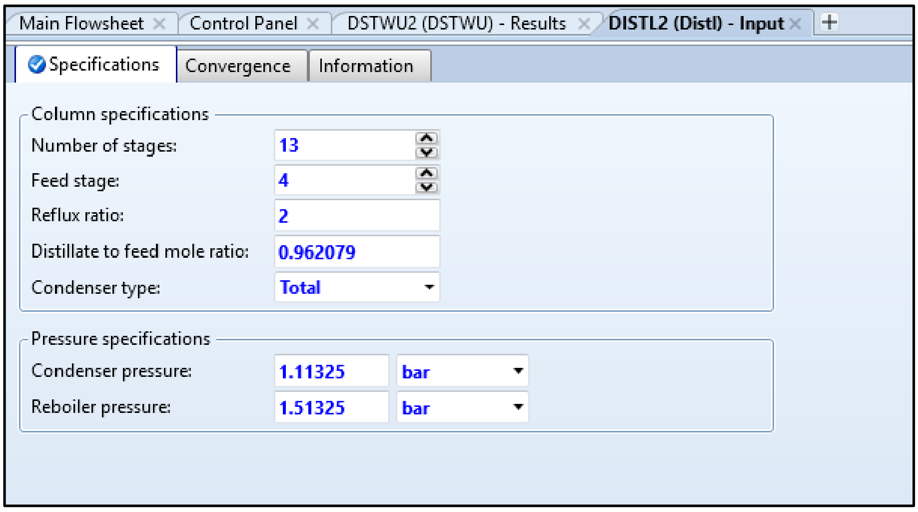
Condenser type: Partial

Pressure specifications

Condenser pressure: 1.11325 bar

Reboiler pressure: 1.51325 bar

Figure B-7: Input of column DISTL1



Column specifications

Number of stages: 13

Feed stage: 4

Reflux ratio: 2

Distillate to feed mole ratio: 0.962079

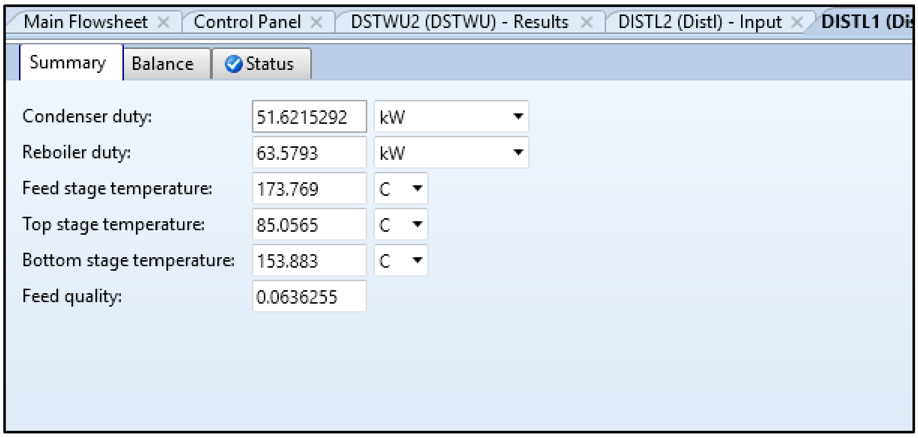
Condenser type: Total

Pressure specifications

Condenser pressure: 1.11325 bar

Reboiler pressure: 1.51325 bar

Figure B-8: Input of column DISTL2



Condenser duty: 51.6215292 kW

Reboiler duty: 63.5793 kW

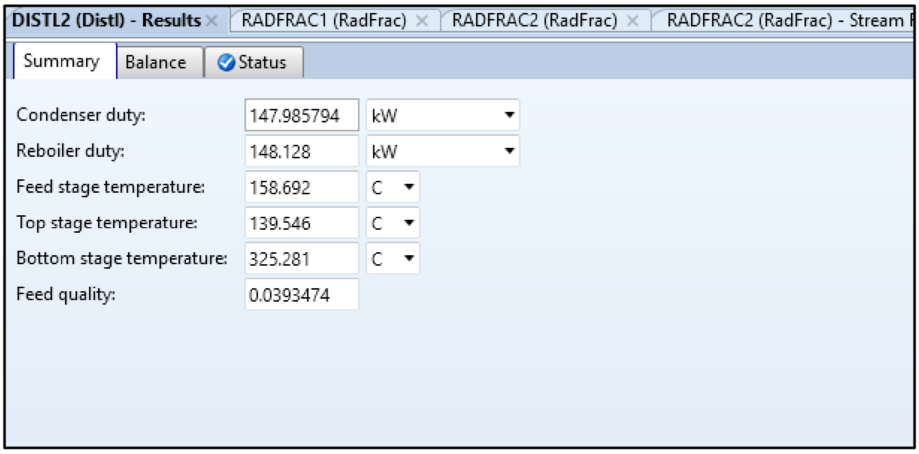
Feed stage temperature: 173.769 C

Top stage temperature: 85.0565 C

Bottom stage temperature: 153.883 C

Feed quality: 0.0636255

Figure B-9: Results of DISTL1



Condenser duty: 147.985794 kW

Reboiler duty: 148.128 kW

Feed stage temperature: 158.692 C

Top stage temperature: 139.546 C

Bottom stage temperature: 325.281 C

Feed quality: 0.0393474

Figure B-10: Results of DISTL2

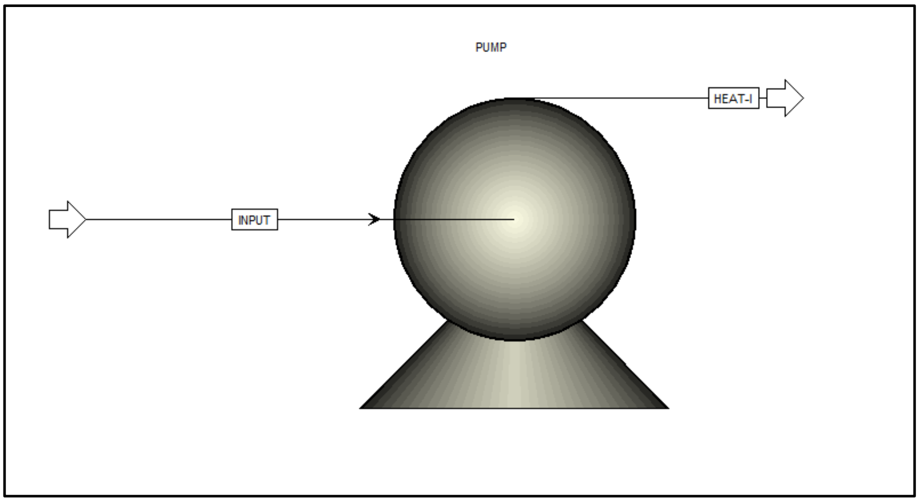
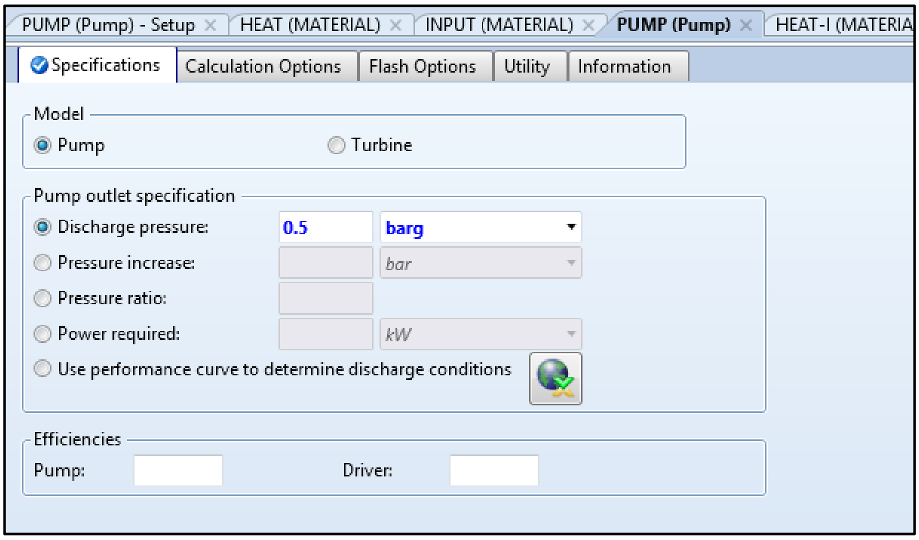


Figure B-11: **Flow sheet of the pump used for feeding demilitarized $TiCl_4$**



Model

● Pump ○ Turbine

Pump outlet specification

● Discharge pressure: 0.5 barg

○ Pressure increase: bar

○ Pressure ratio:

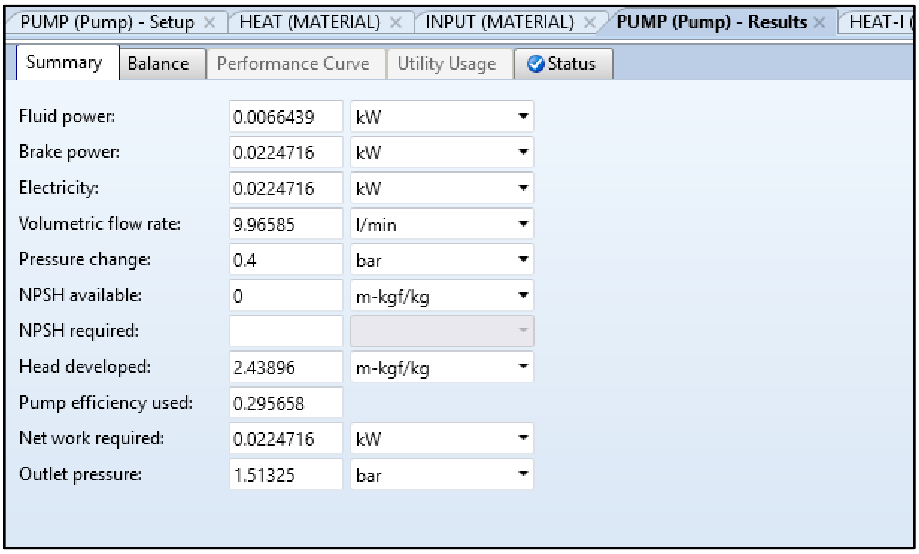
○ Power required: kW

○ Use performance curve to determine discharge conditions

Efficiencies

Pump: Driver:

Figure B-12: **Input of PUMP**



Fluid power:	0.0066439	kW
Brake power:	0.0224716	kW
Electricity:	0.0224716	kW
Volumetric flow rate:	9.96585	l/min
Pressure change:	0.4	bar
NPSH available:	0	m-kgf/kg
NPSH required:		
Head developed:	2.43896	m-kgf/kg
Pump efficiency used:	0.295658	
Net work required:	0.0224716	kW
Outlet pressure:	1.51325	bar

Figure B-13: Results of PUMP

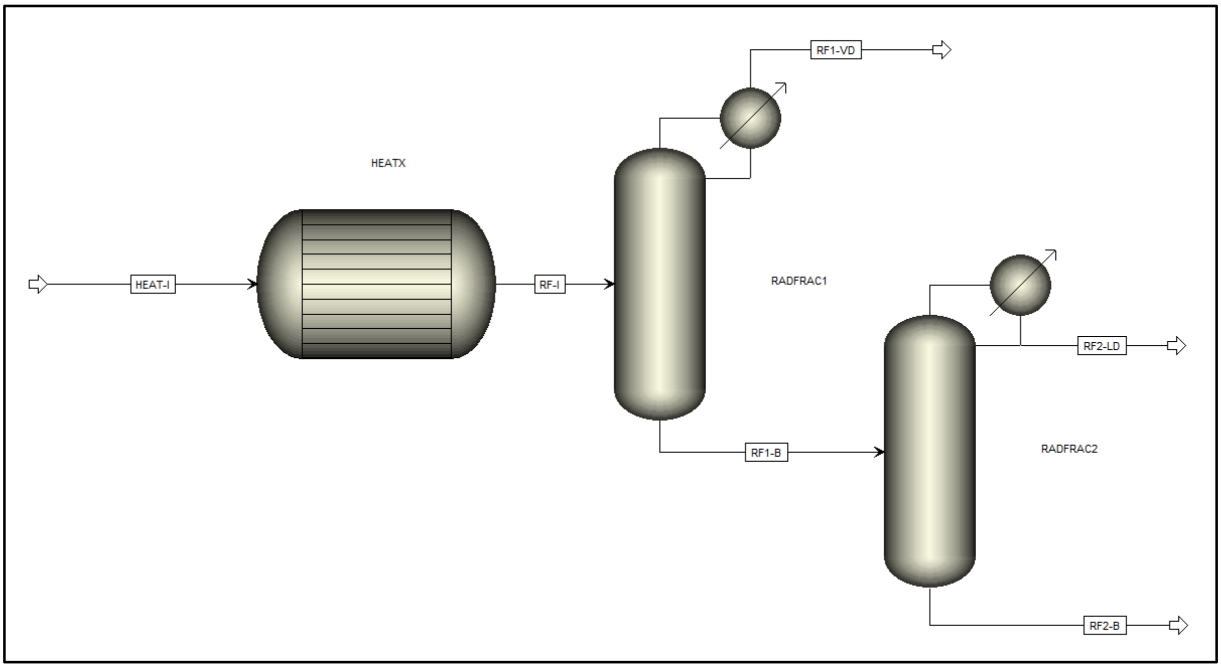
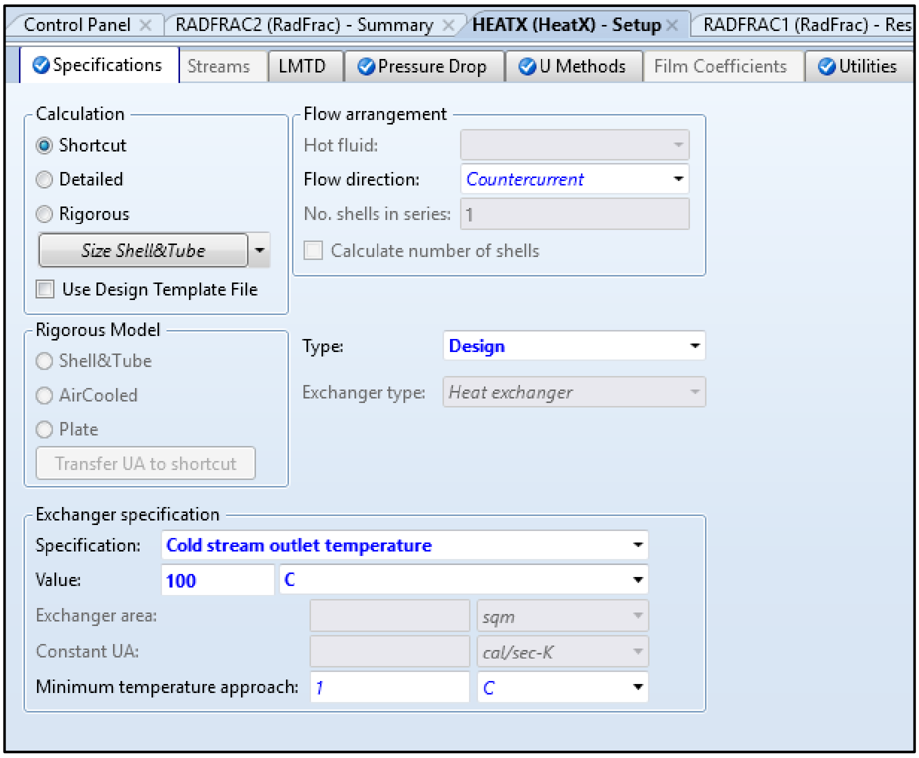


Figure B-14: Flow sheet of $TiCl_4$ purification process



Calculation
● Shortcut
○ Detailed
○ Rigorous
☐ Use Design Template File

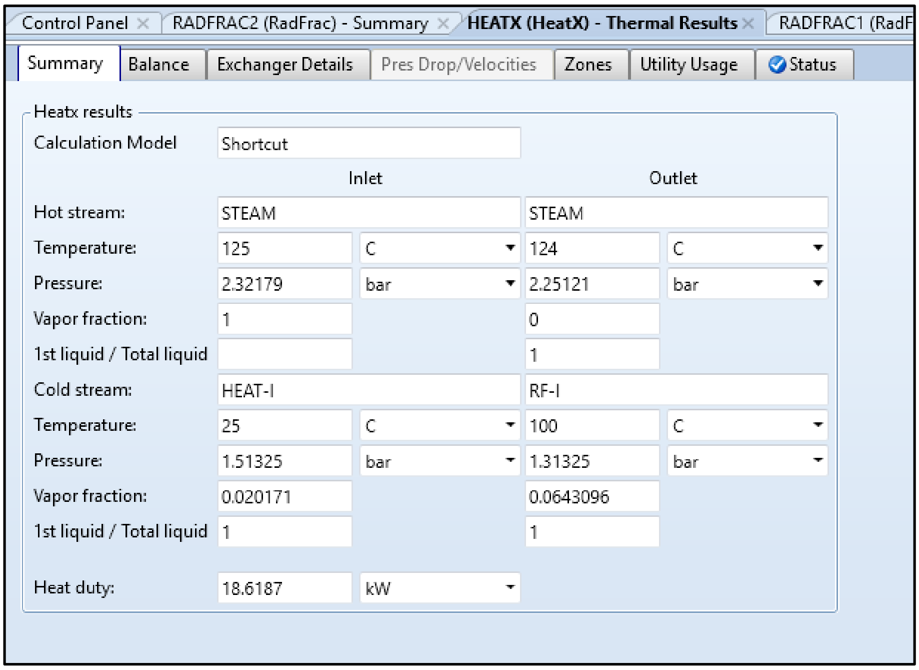
Flow arrangement
Hot fluid:
Flow direction: Countercurrent
No. shells in series: 1
☐ Calculate number of shells

Rigorous Model
○ Shell&Tube
○ AirCooled
○ Plate

Type: Design
Exchanger type: Heat exchanger

Exchanger specification
Specification: Cold stream outlet temperature
Value: 100 C
Exchanger area: sqm
Constant UA: cal/sec-K
Minimum temperature approach: 1 C

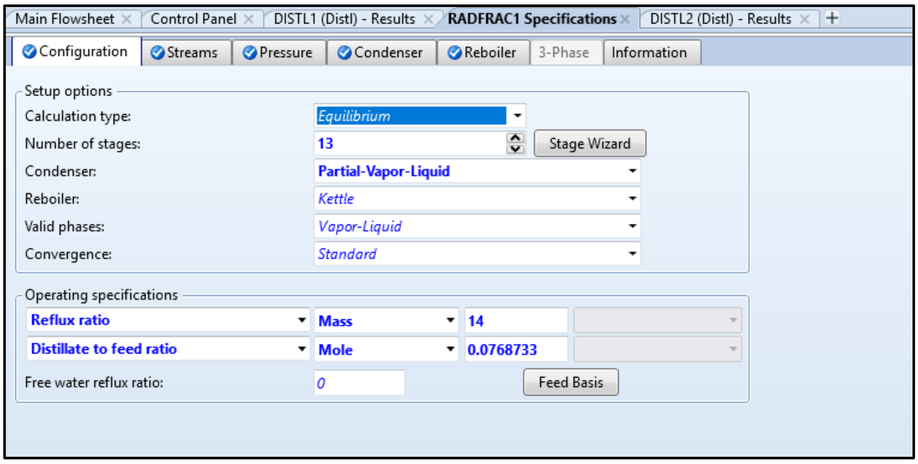
Figure B-15: **Input of heat exchanger HEATX**



Heatx results
Calculation Model: Shortcut

	Inlet		Outlet	
Hot stream:	STEAM		STEAM	
Temperature:	125	C	124	C
Pressure:	2.32179	bar	2.25121	bar
Vapor fraction:	1		0	
1st liquid / Total liquid			1	
Cold stream:	HEAT-I		RF-I	
Temperature:	25	C	100	C
Pressure:	1.51325	bar	1.31325	bar
Vapor fraction:	0.020171		0.0643096	
1st liquid / Total liquid	1		1	
Heat duty:	18.6187	kW		

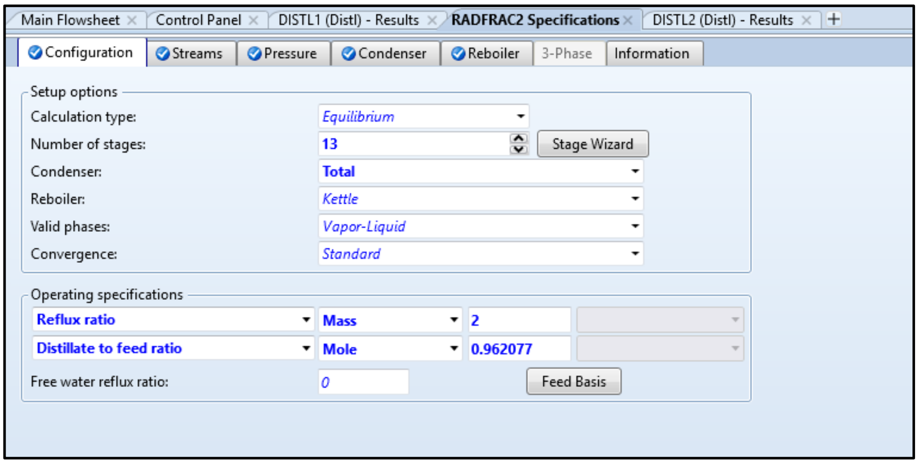
Figure B-16: **Results of HEATX**



Setup options
Calculation type: Equilibrium
Number of stages: 13
Condenser: Partial-Vapor-Liquid
Reboiler: Kettle
Valid phases: Vapor-Liquid
Convergence: Standard

Operating specifications
Reflux ratio | Mass | 14
Distillate to feed ratio | Mole | 0.0768733
Free water reflux ratio: 0

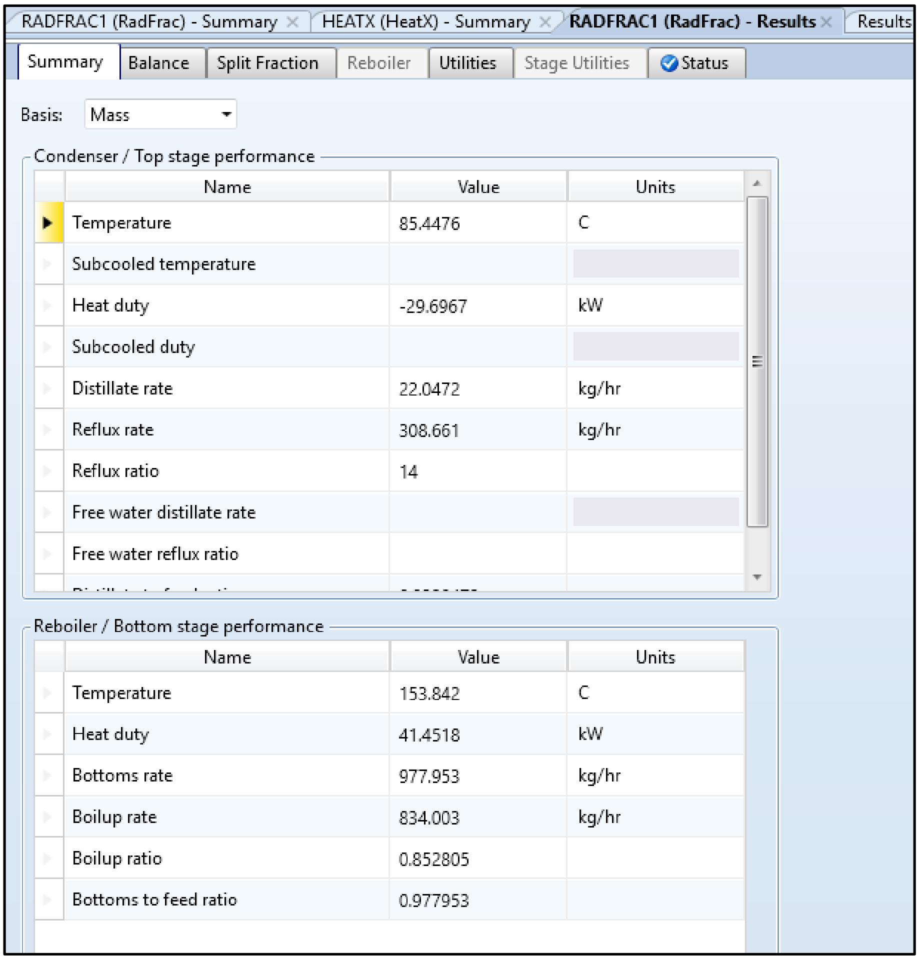
Figure B-17: Input of column RADFRAC1



Setup options
Calculation type: Equilibrium
Number of stages: 13
Condenser: Total
Reboiler: Kettle
Valid phases: Vapor-Liquid
Convergence: Standard

Operating specifications
Reflux ratio | Mass | 2
Distillate to feed ratio | Mole | 0.962077
Free water reflux ratio: 0

Figure B-18: Input of column RADFRAC2



Basis: Mass

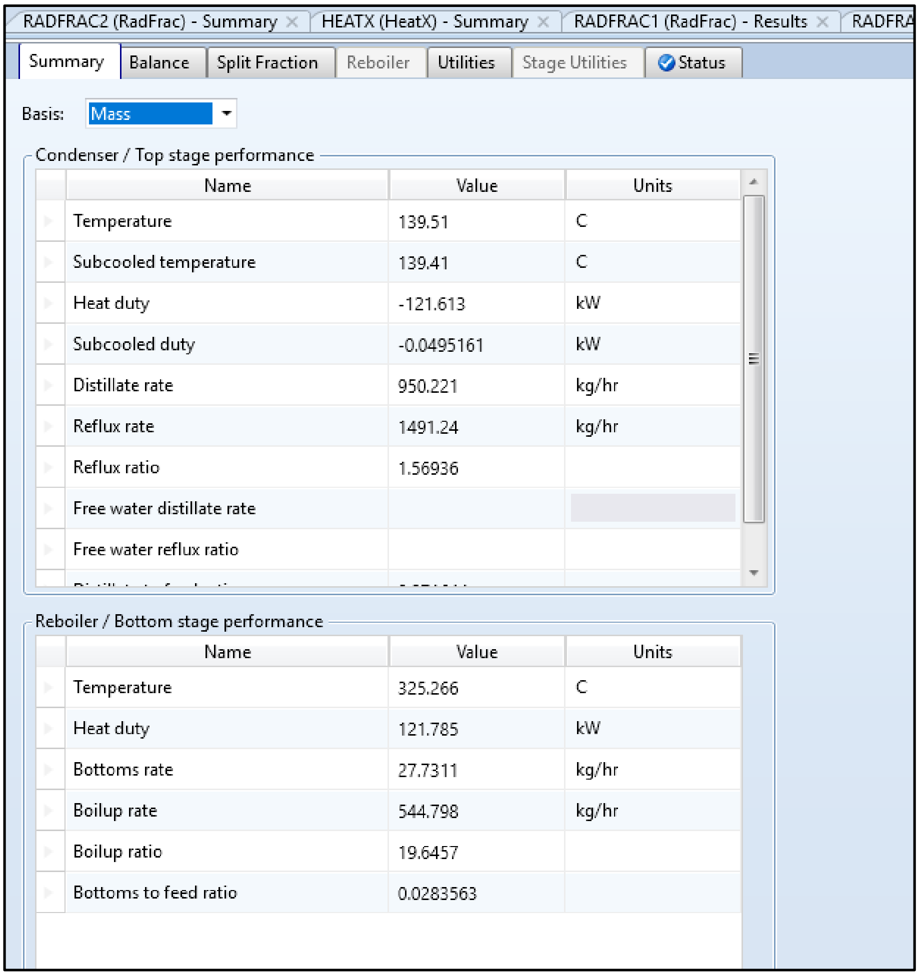
Condenser / Top stage performance

Name	Value	Units
Temperature	85.4476	C
Subcooled temperature		
Heat duty	-29.6967	kW
Subcooled duty		
Distillate rate	22.0472	kg/hr
Reflux rate	308.661	kg/hr
Reflux ratio	14	
Free water distillate rate		
Free water reflux ratio		

Reboiler / Bottom stage performance

Name	Value	Units
Temperature	153.842	C
Heat duty	41.4518	kW
Bottoms rate	977.953	kg/hr
Boilup rate	834.003	kg/hr
Boilup ratio	0.852805	
Bottoms to feed ratio	0.977953	

Figure B-19: Results of RADFRAC1



Basis: Mass

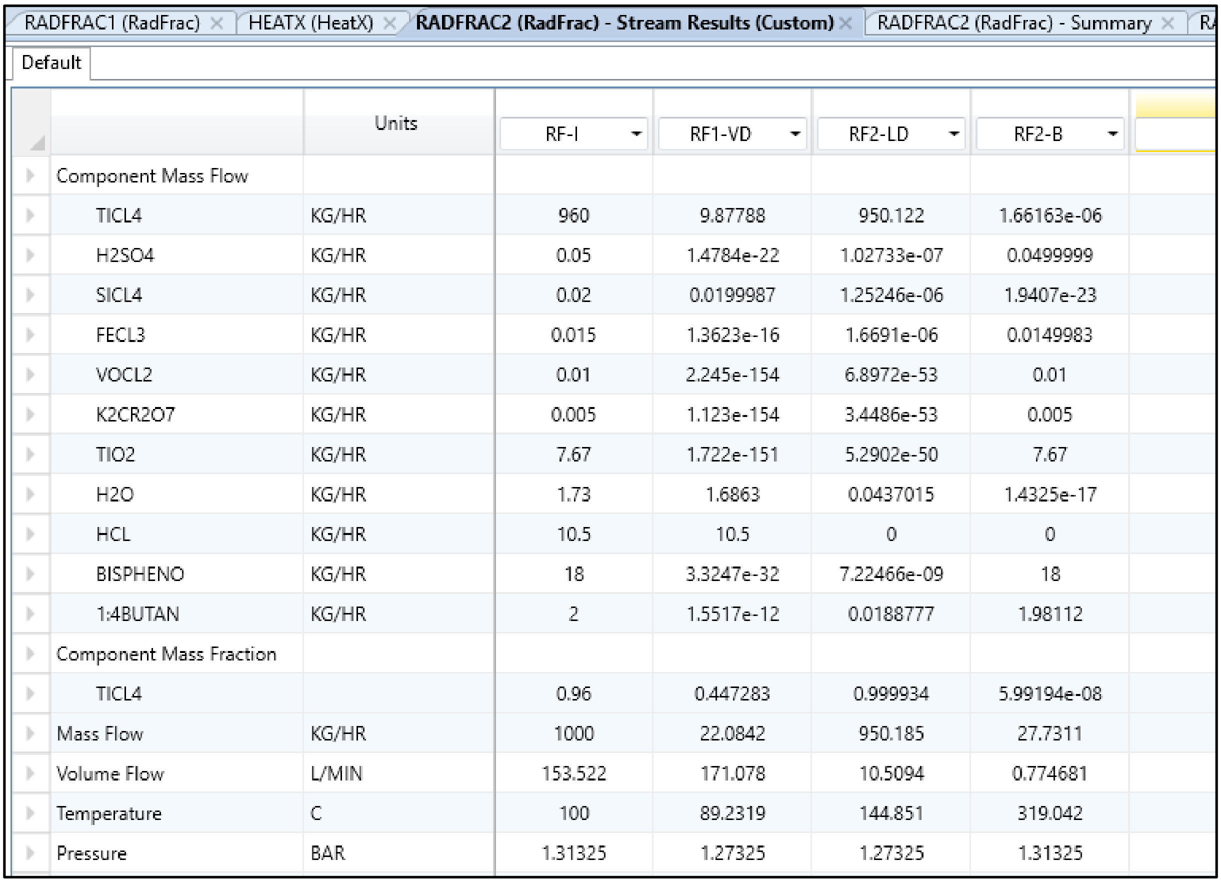
Condenser / Top stage performance

Name	Value	Units
Temperature	139.51	C
Subcooled temperature	139.41	C
Heat duty	-121.613	kW
Subcooled duty	-0.0495161	kW
Distillate rate	950.221	kg/hr
Reflux rate	1491.24	kg/hr
Reflux ratio	1.56936	
Free water distillate rate		
Free water reflux ratio		

Reboiler / Bottom stage performance

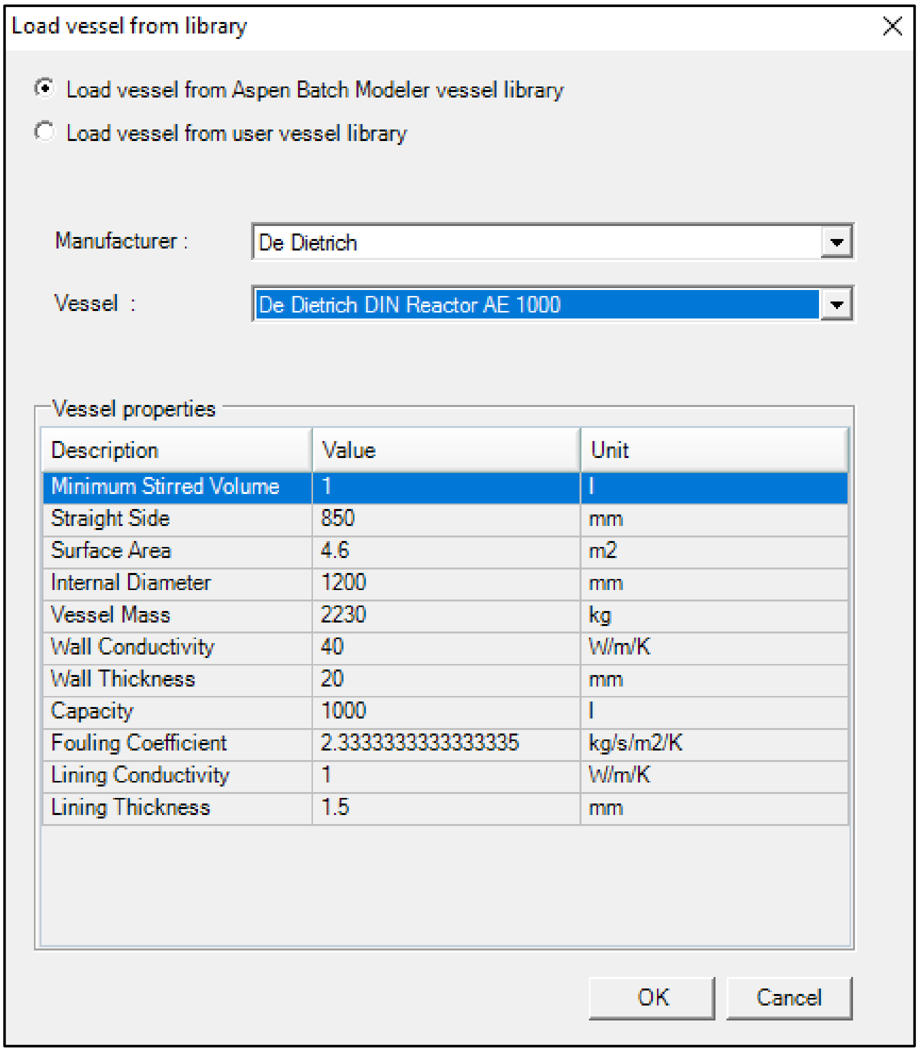
Name	Value	Units
Temperature	325.266	C
Heat duty	121.785	kW
Bottoms rate	27.7311	kg/hr
Boilup rate	544.798	kg/hr
Boilup ratio	19.6457	
Bottoms to feed ratio	0.0283563	

Figure B-20: Results of RADFRAC2



	Units	RF-I	RF1-VD	RF2-LD	RF2-B
Component Mass Flow					
TICL4	KG/HR	960	9.87788	950.122	1.66163e-06
H2SO4	KG/HR	0.05	1.4784e-22	1.02733e-07	0.0499999
SICL4	KG/HR	0.02	0.0199987	1.25246e-06	1.9407e-23
FECL3	KG/HR	0.015	1.3623e-16	1.6691e-06	0.0149983
VOCL2	KG/HR	0.01	2.245e-154	6.8972e-53	0.01
K2CR2O7	KG/HR	0.005	1.123e-154	3.4486e-53	0.005
TIO2	KG/HR	7.67	1.722e-151	5.2902e-50	7.67
H2O	KG/HR	1.73	1.6863	0.0437015	1.4325e-17
HCL	KG/HR	10.5	10.5	0	0
BISPHENO	KG/HR	18	3.3247e-32	7.22466e-09	18
1:4BUTAN	KG/HR	2	1.5517e-12	0.0188777	1.98112
Component Mass Fraction					
TICL4		0.96	0.447283	0.999934	5.99194e-08
Mass Flow	KG/HR	1000	22.0842	950.185	27.7311
Volume Flow	L/MIN	153.522	171.078	10.5094	0.774681
Temperature	C	100	89.2319	144.851	319.042
Pressure	BAR	1.31325	1.27325	1.27325	1.31325

Figure B-21: Overall stream results of RADFRAC1 and RADFRAC2


Load vessel from library

● Load vessel from Aspen Batch Modeler vessel library

○ Load vessel from user vessel library

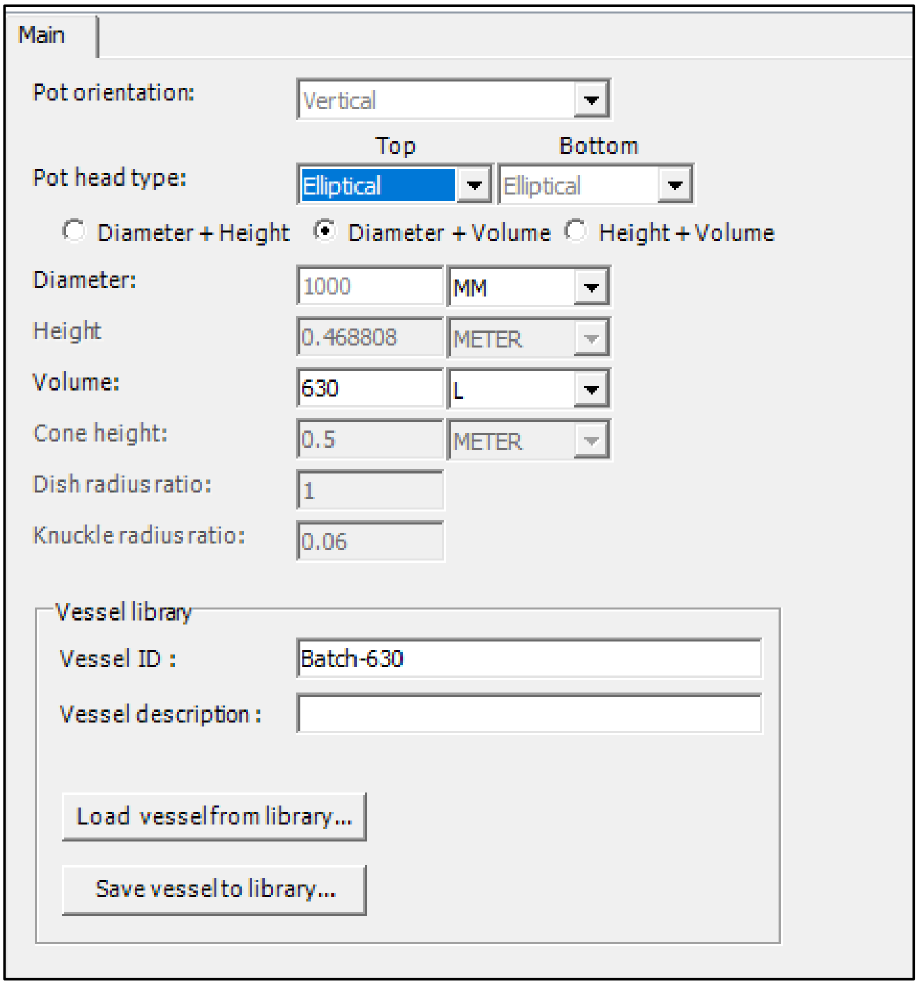
Manufacturer : De Dietrich

Vessel : De Dietrich DIN Reactor AE 1000

Vessel properties

Description	Value	Unit
Minimum Stirred Volume	1	l
Straight Side	850	mm
Surface Area	4.6	m2
Internal Diameter	1200	mm
Vessel Mass	2230	kg
Wall Conductivity	40	W/m/K
Wall Thickness	20	mm
Capacity	1000	l
Fouling Coefficient	2.3333333333333335	kg/s/m2/K
Lining Conductivity	1	W/m/K
Lining Thickness	1.5	mm

Figure B-22: **Properties of pot used in batch distillation column**



Pot orientation: Vertical

Pot head type: Top: Elliptical; Bottom: Elliptical

○ Diameter + Height ● Diameter + Volume ○ Height + Volume

Diameter: 1000 MM

Height 0.468808 METER

Volume: 630 L

Cone height: 0.5 METER

Dish radius ratio: 1

Knuckle radius ratio: 0.06

Vessel ID : Batch-630

Vessel description :

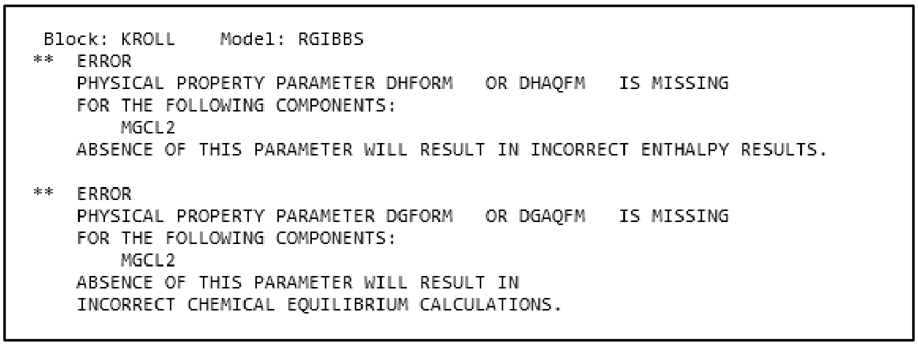
Figure B-23: Dimensions of pot used in distillation column

B.2 Titanium metal production by Kroll process

B.2.1 Challenges and limitations of available input components

Encountered errors in this simulation were firstly due to the missing property parameters of some of the components, while implementation of the ‘ideal’ thermodynamic method also had difficulties with chemical and enthalpy calculations. This is especially the case in the software’s inability to account for solid metal production under the selected property methods and input values. Inclusion of the FactSage© database will again aid in conducting a more accurate simulation to obtain results that are closer to empirical values.

The compound that required major property parameters for this simulation was the by-product $MgCl_2$ from the titanium metal production reaction. The resulting error message from Aspen Plus^{TM} is observable in Figure B-24.



```
 Block: KROLL    Model: RGIBBS
**  ERROR
    PHYSICAL PROPERTY PARAMETER DHFORM   OR DHAQFM   IS MISSING
    FOR THE FOLLOWING COMPONENTS:
        MGCL2
    ABSENCE OF THIS PARAMETER WILL RESULT IN INCORRECT ENTHALPY RESULTS.

**  ERROR
    PHYSICAL PROPERTY PARAMETER DGFORM   OR DGAQFM   IS MISSING
    FOR THE FOLLOWING COMPONENTS:
        MGCL2
    ABSENCE OF THIS PARAMETER WILL RESULT IN
    INCORRECT CHEMICAL EQUILIBRIUM CALCULATIONS.
```

Figure B-24: Generated error message by Aspen Plus^{TM} for missing parameters of $MgCl_2$

No other simulation software was available for this study and since it was not possible to construct a prototype reactor or laboratory scale experiment of this process, it was decided to use obtained results from the simulation but clearly note the errors that were encountered and how it can be corrected.

B.2.2 Simulation development and results

The comprehensive simulation procedure that was followed to design the Kroll process is given in this section by means of screenshots of the input values and obtained results.

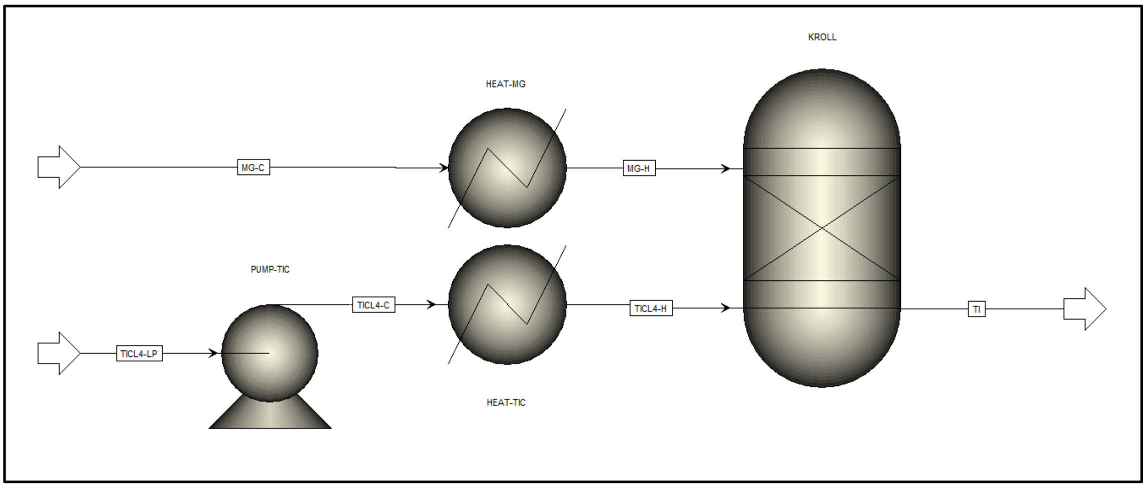
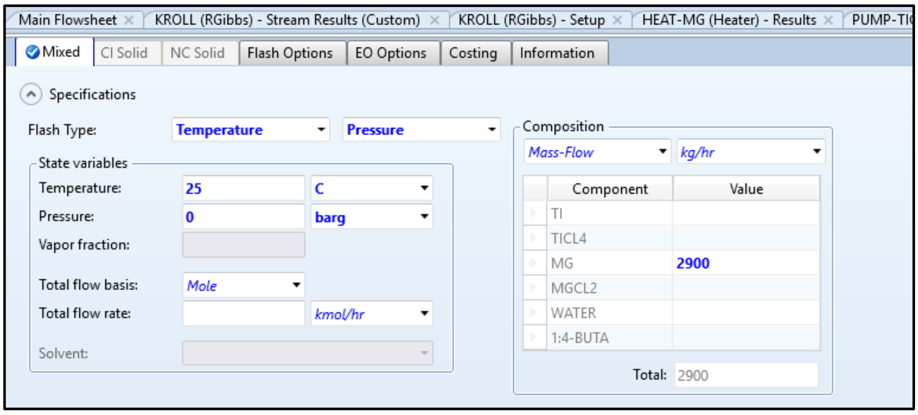


Figure B-25: Flow sheet of the Kroll process



Flash Type: Temperature Pressure

State variables

Temperature: 25 C

Pressure: 0 barg

Vapor fraction:

Total flow basis: Mole

Total flow rate: kmol/hr

Solvent:

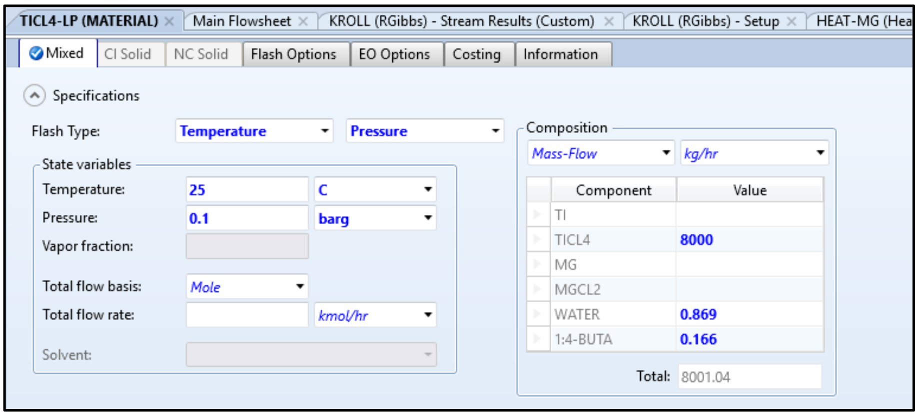
Composition

Mass-Flow kg/hr

Component	Value
TI	
TICL4	
MG	2900
MGCL2	
WATER	
1:4-BUTA	

Total: 2900

Figure B-26: Magnesium feed to the process



Flash Type: Temperature Pressure

State variables

Temperature: 25 C

Pressure: 0.1 barg

Vapor fraction:

Total flow basis: Mole

Total flow rate: kmol/hr

Solvent:

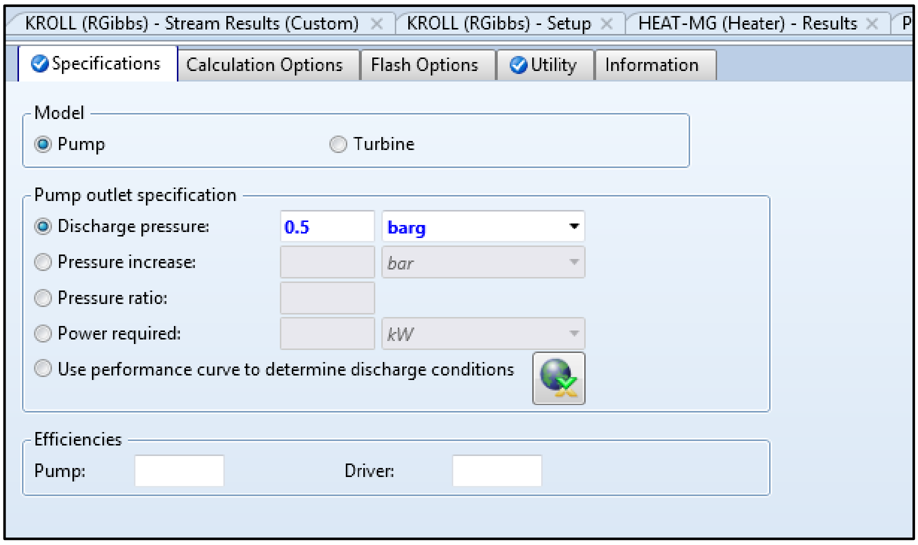
Composition

Mass-Flow kg/hr

Component	Value
TI	
TICL4	8000
MG	
MGCL2	
WATER	0.869
1:4-BUTA	0.166

Total: 8001.04

Figure B-27: Purified $TiCl_4$ feed to the process



Model

● Pump ○ Turbine

Pump outlet specification

● Discharge pressure: 0.5 barg

○ Pressure increase: bar

○ Pressure ratio:

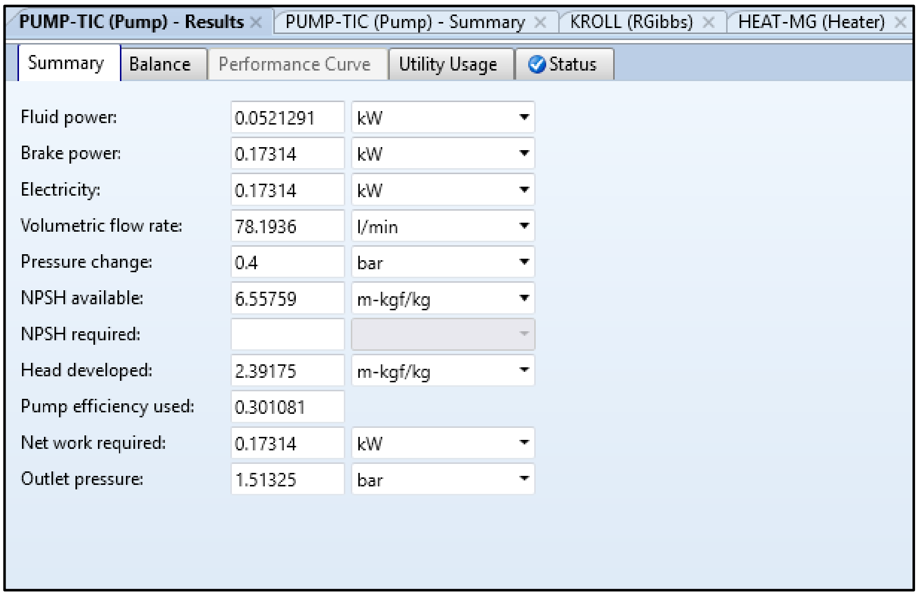
○ Power required: kW

○ Use performance curve to determine discharge conditions

Efficiencies

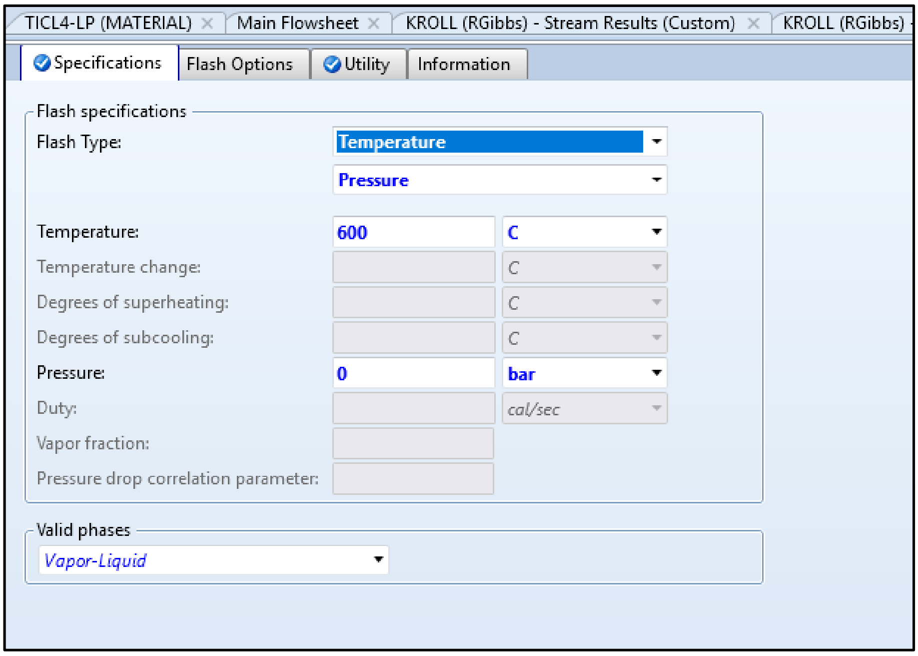
Pump: Driver:

Figure B-28: Input of $TiCl_4$ pump



Fluid power:	0.0521291	kW
Brake power:	0.17314	kW
Electricity:	0.17314	kW
Volumetric flow rate:	78.1936	l/min
Pressure change:	0.4	bar
NPSH available:	6.55759	m-kgf/kg
NPSH required:		
Head developed:	2.39175	m-kgf/kg
Pump efficiency used:	0.301081	
Net work required:	0.17314	kW
Outlet pressure:	1.51325	bar

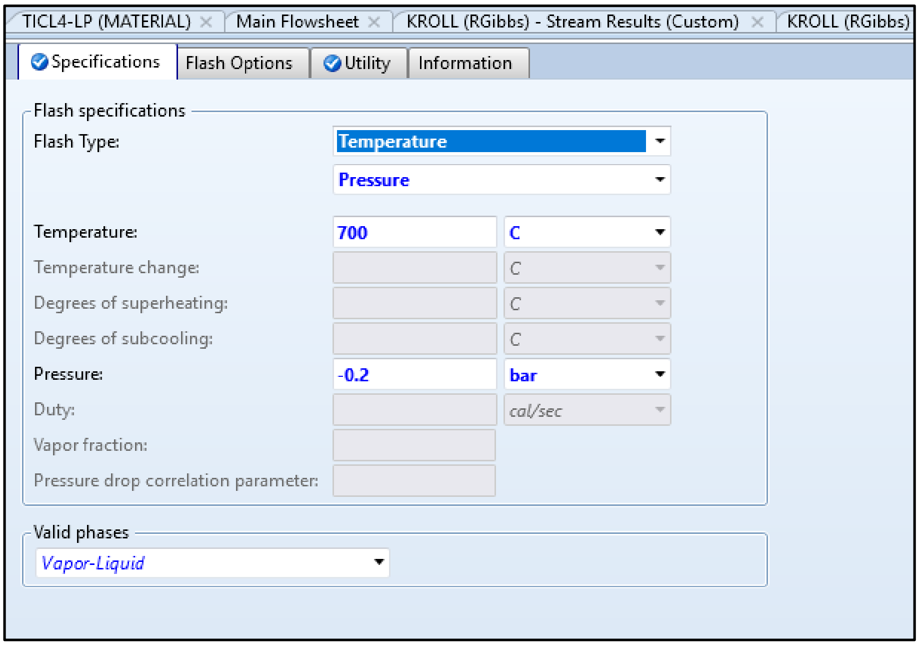
Figure B-29: Results of $TiCl_4$ pump



Flash specifications
Flash Type: Temperature
Pressure
Temperature: 600 C
Temperature change: C
Degrees of superheating: C
Degrees of subcooling: C
Pressure: 0 bar
Duty: cal/sec
Vapor fraction:
Pressure drop correlation parameter:

Valid phases
Vapor-Liquid

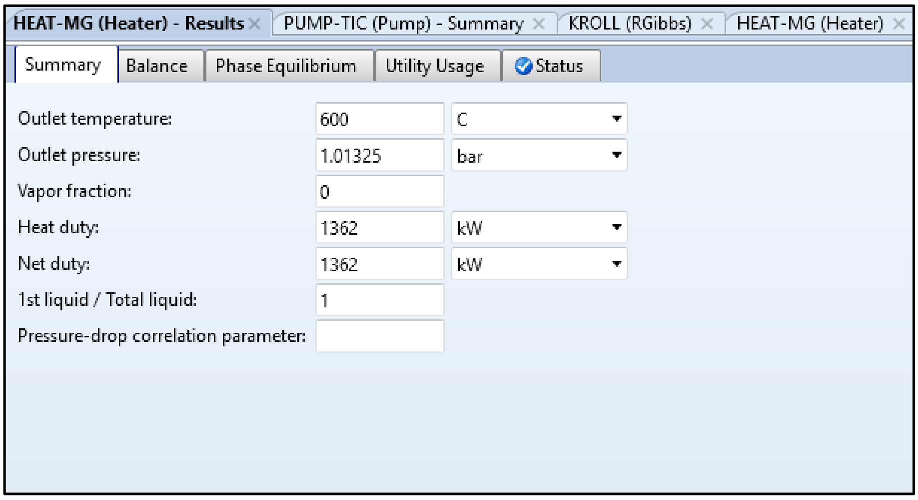
Figure B-30: Input of magnesium heater HEAT-MG



Flash specifications
Flash Type: Temperature
Pressure
Temperature: 700 C
Temperature change: C
Degrees of superheating: C
Degrees of subcooling: C
Pressure: -0.2 bar
Duty: cal/sec
Vapor fraction:
Pressure drop correlation parameter:

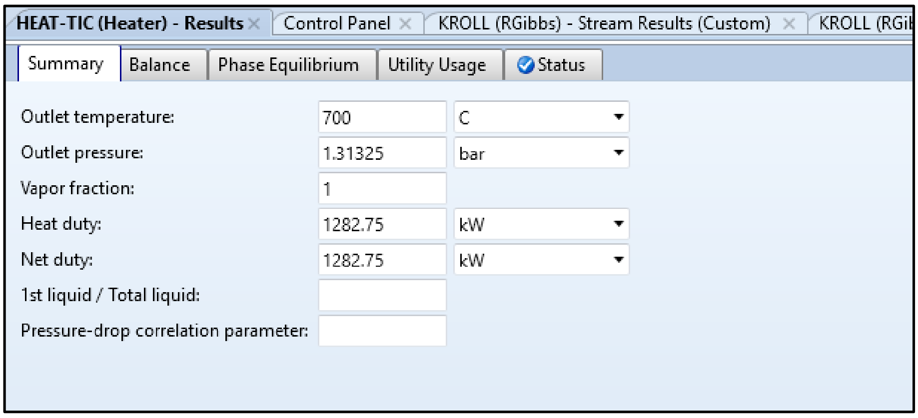
Valid phases
Vapor-Liquid

Figure B-31: Input of $TiCl_4$ heater HEAT-TIC



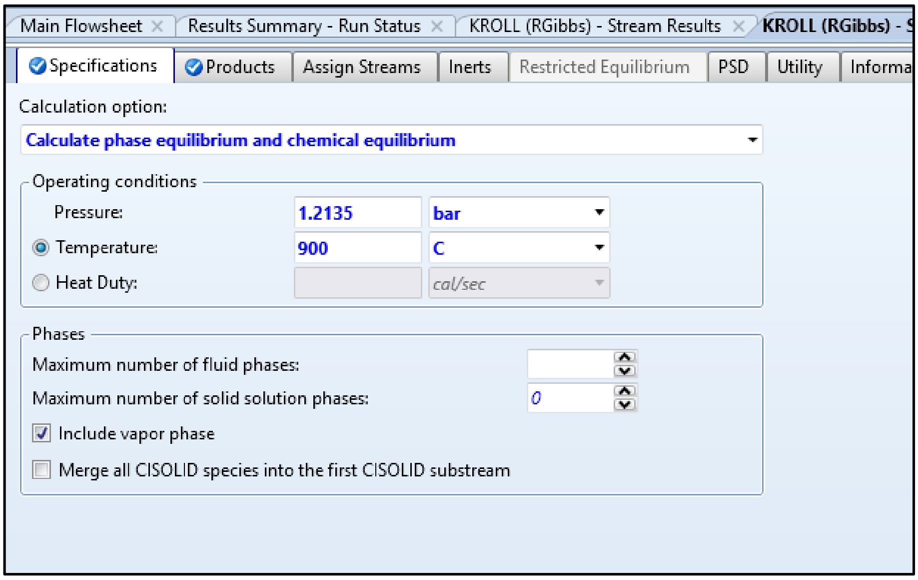
Outlet temperature: 600 C
Outlet pressure: 1.01325 bar
Vapor fraction: 0
Heat duty: 1362 kW
Net duty: 1362 kW
1st liquid / Total liquid: 1
Pressure-drop correlation parameter:

Figure B-32: Results of HEAT-MG



Outlet temperature: 700 C
Outlet pressure: 1.31325 bar
Vapor fraction: 1
Heat duty: 1282.75 kW
Net duty: 1282.75 kW
1st liquid / Total liquid:
Pressure-drop correlation parameter:

Figure B-33: Results of HEAT-TIC

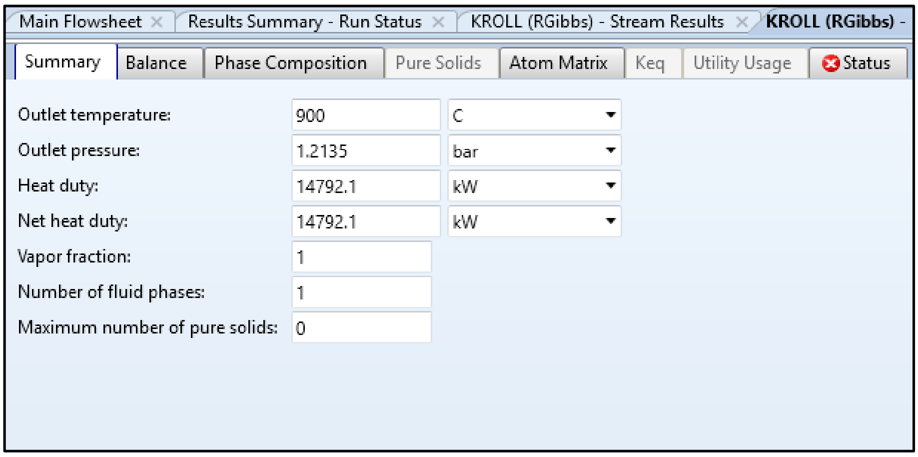


Calculation option:
Calculate phase equilibrium and chemical equilibrium

Operating conditions
Pressure: 1.2135 bar
● Temperature: 900 C
○ Heat Duty: cal/sec

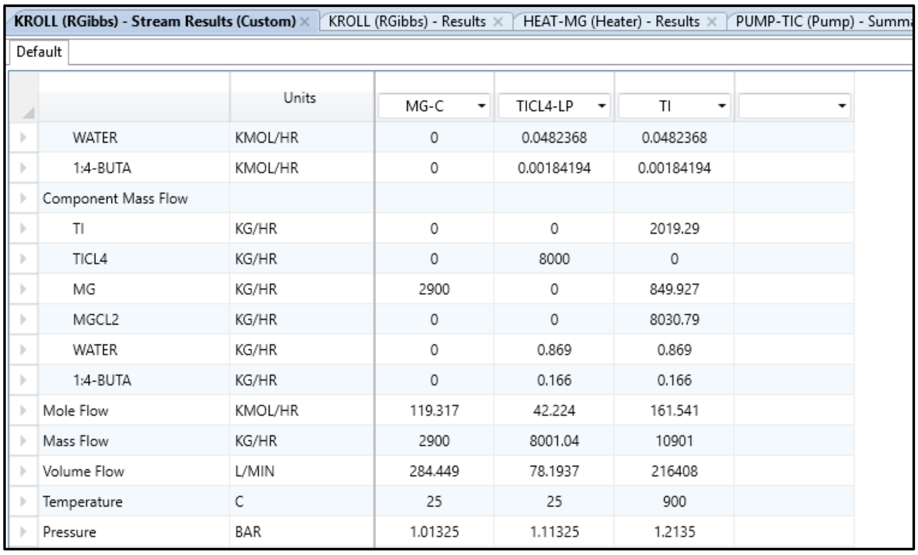
Phases
Maximum number of fluid phases:
Maximum number of solid solution phases: 0
☑ Include vapor phase
☐ Merge all CISOLID species into the first CISOLID substream

Figure B-34: Input of GIBBS reactor KROLL



Outlet temperature: 900 C
Outlet pressure: 1.2135 bar
Heat duty: 14792.1 kW
Net heat duty: 14792.1 kW
Vapor fraction: 1
Number of fluid phases: 1
Maximum number of pure solids: 0

Figure B-35: Results of KROLL



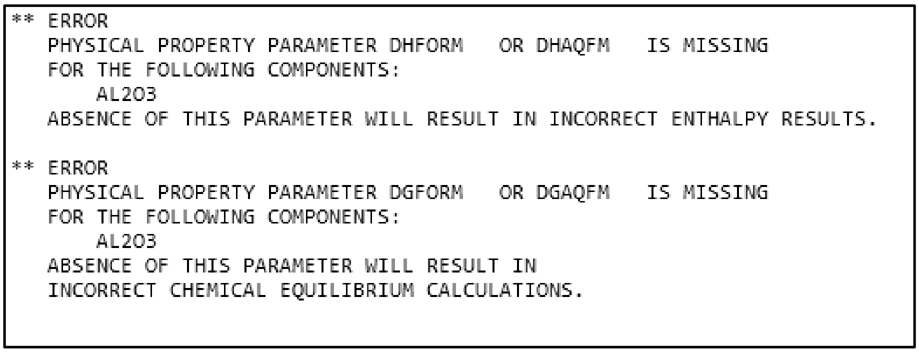
	Units	MG-C	TICL4-LP	TI	
WATER	KMOL/HR	0	0.0482368	0.0482368	
1:4-BUTA	KMOL/HR	0	0.00184194	0.00184194	
Component Mass Flow					
TI	KG/HR	0	0	2019.29	
TICL4	KG/HR	0	8000	0	
MG	KG/HR	2900	0	849.927	
MGCL2	KG/HR	0	0	8030.79	
WATER	KG/HR	0	0.869	0.869	
1:4-BUTA	KG/HR	0	0.166	0.166	
Mole Flow	KMOL/HR	119.317	42.224	161.541	
Mass Flow	KG/HR	2900	8001.04	10901	
Volume Flow	L/MIN	284.449	78.1937	216408	
Temperature	C	25	25	900	
Pressure	BAR	1.01325	1.11325	1.2135	

Figure B-36: Stream results of KROLL

B.3 Titanium dioxide pigment production by chloride process

B.3.1 Challenges and limitations of available input components

Al_2O_3, produced by reaction of the catalyst $AlCl_3$ with water, has missing property parameters. This impedes successful simulation of the chemical and energy calculations of the process units. The resulting error message are portrayed in Figure B-37.



```
** ERROR
   PHYSICAL PROPERTY PARAMETER DHFORM   OR DHAQFM   IS MISSING
   FOR THE FOLLOWING COMPONENTS:
       AL2O3
   ABSENCE OF THIS PARAMETER WILL RESULT IN INCORRECT ENTHALPY RESULTS.

** ERROR
   PHYSICAL PROPERTY PARAMETER DGFORM   OR DGAQFM   IS MISSING
   FOR THE FOLLOWING COMPONENTS:
       AL2O3
   ABSENCE OF THIS PARAMETER WILL RESULT IN
   INCORRECT CHEMICAL EQUILIBRIUM CALCULATIONS.
```

Figure B-37: Generated error message by Aspen Plus^{TM} for missing parameters of Al_2O_3

The resulting decision was to not consider the presence of the catalyst $AlCl_3$ for this process by removing it from the simulation. The reader is reminded that $AlCl_3$ is only included to ensure the formation of rutile crystals and does not actively participate in the main reaction. The catalyst is included in economic considerations though.

Additional obstacles were further encountered during the simulation of the reactor of this process. This is due to software's inability to accurate simulate a plasma arc furnace based on existing parameters and available inputs.

B.3.2 Simulation development and results

The comprehensive simulation procedure that was followed to design the chloride process is given in this section by means of screenshots of the input values and obtained results.

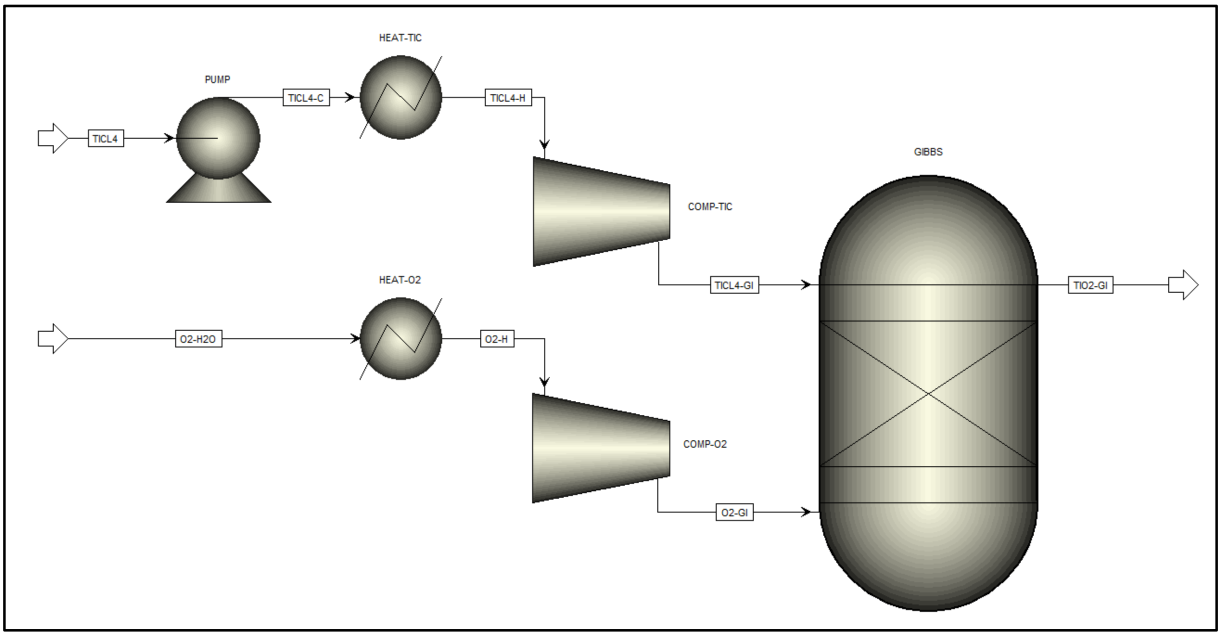
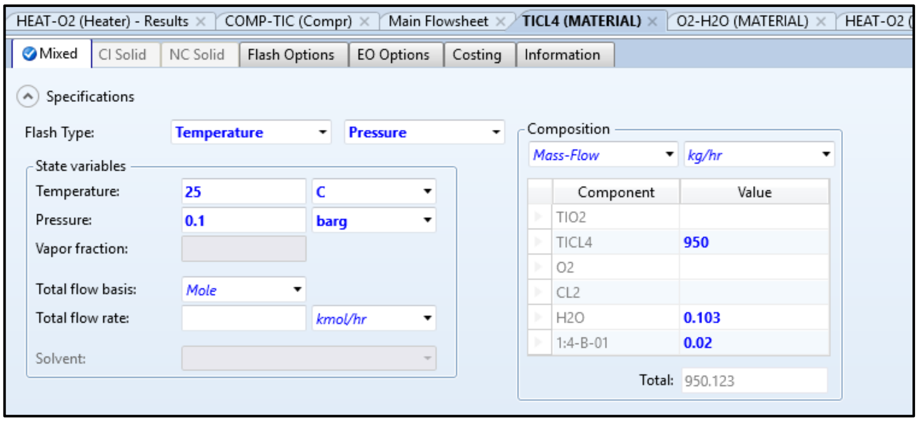


Figure B-38: Flow sheet of the chloride process



Flash Type: Temperature Pressure

Temperature: 25 C

Pressure: 0.1 barg

Vapor fraction:

Total flow basis: Mole

Total flow rate: kmol/hr

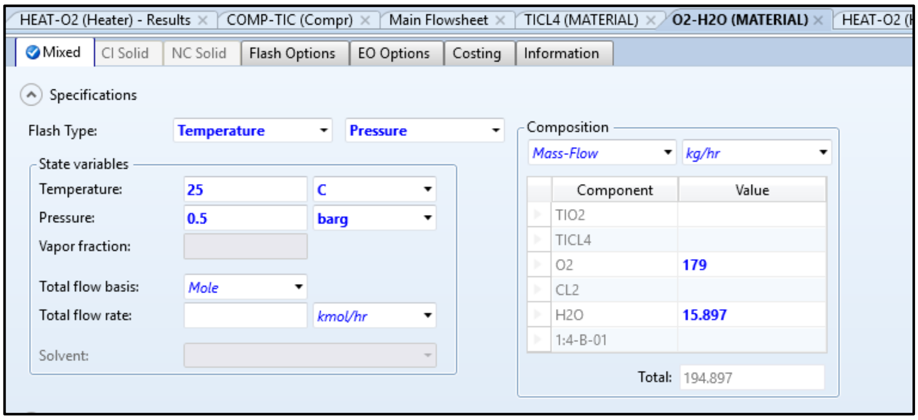
Solvent:

Mass-Flow kg/hr

Component	Value
TIO2	
TICL4	950
O2	
CL2	
H2O	0.103
1:4-B-01	0.02

Total: 950.123

Figure B-39: Purified $TiCl_4$ feed to the process



Flash Type: Temperature Pressure

Temperature: 25 C

Pressure: 0.5 barg

Vapor fraction:

Total flow basis: Mole

Total flow rate: kmol/hr

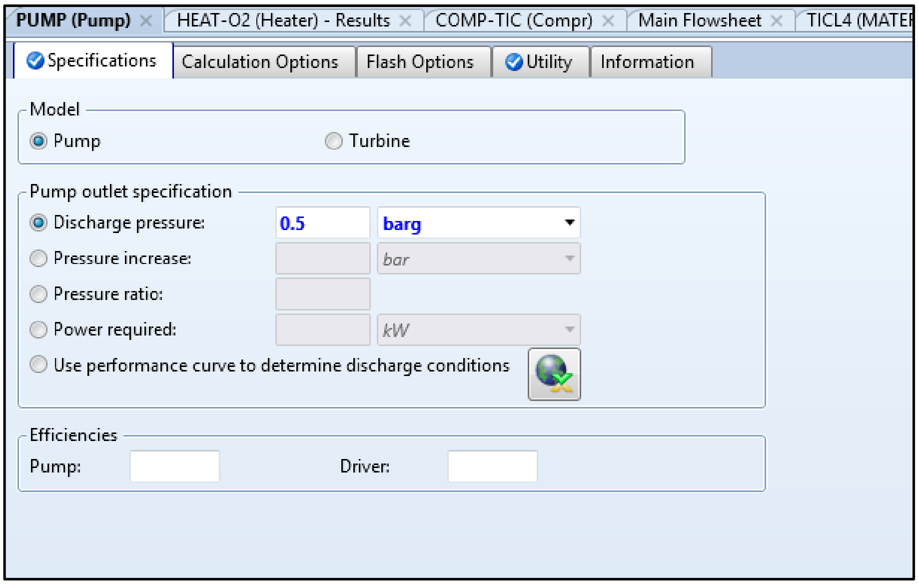
Solvent:

Mass-Flow kg/hr

Component	Value
TIO2	
TICL4	
O2	179
CL2	
H2O	15.897
1:4-B-01	

Total: 194.897

Figure B-40: Mixture O_2 and H_2O feed to the process



Model

● Pump ○ Turbine

Pump outlet specification

● Discharge pressure: 0.5 barg

○ Pressure increase: bar

○ Pressure ratio:

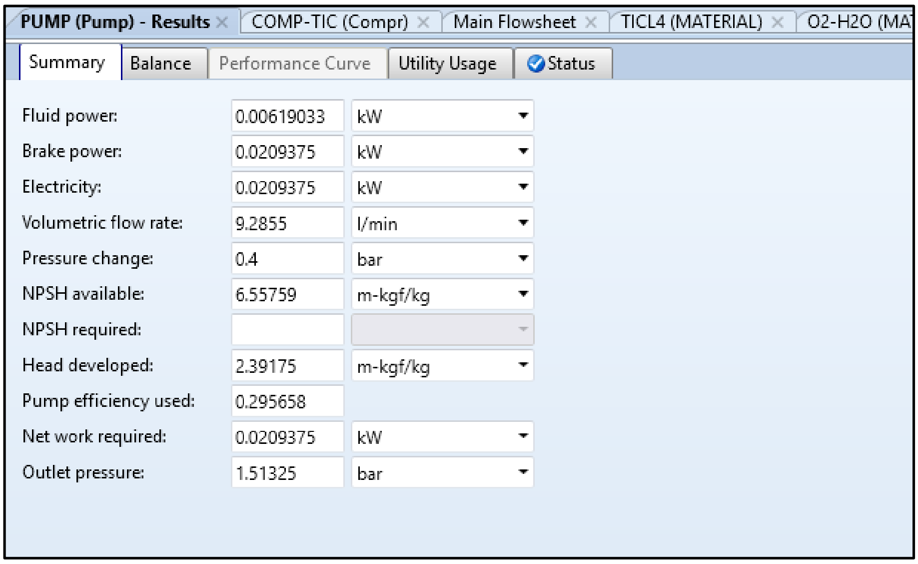
○ Power required: kW

○ Use performance curve to determine discharge conditions

Efficiencies

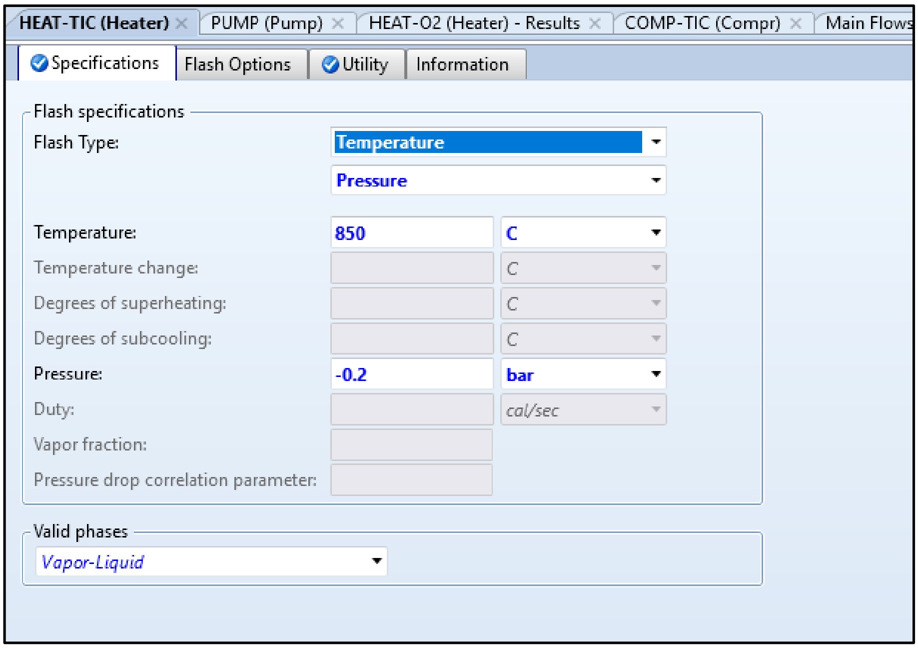
Pump: Driver:

Figure B-41: Input of TiCl$_4$ PUMP



Fluid power:	0.00619033	kW
Brake power:	0.0209375	kW
Electricity:	0.0209375	kW
Volumetric flow rate:	9.2855	l/min
Pressure change:	0.4	bar
NPSH available:	6.55759	m-kgf/kg
NPSH required:		
Head developed:	2.39175	m-kgf/kg
Pump efficiency used:	0.295658	
Net work required:	0.0209375	kW
Outlet pressure:	1.51325	bar

Figure B-42: Results of PUMP



Flash specifications

Flash Type: Temperature
Pressure

Temperature: 850 C

Temperature change: C

Degrees of superheating: C

Degrees of subcooling: C

Pressure: -0.2 bar

Duty: cal/sec

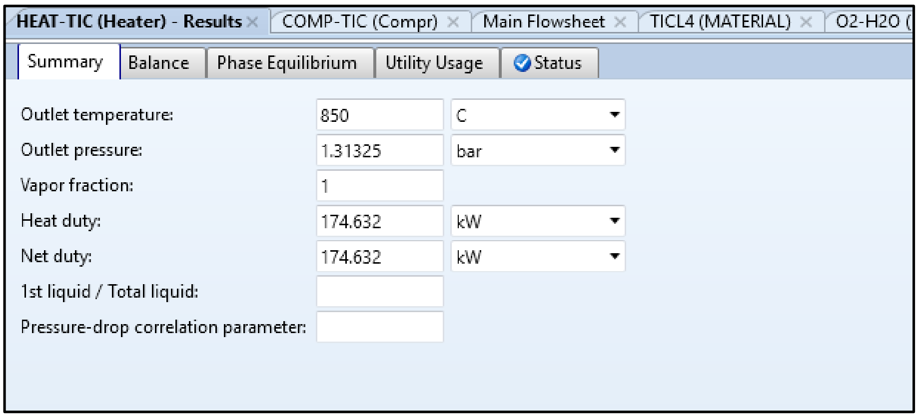
Vapor fraction:

Pressure drop correlation parameter:

Valid phases

Vapor-Liquid

Figure B-43: **Input of both the $TiCl_4$ heater HEAT-TIC and O_2 heater HEAT-O2**



Outlet temperature: 850 C

Outlet pressure: 1.31325 bar

Vapor fraction: 1

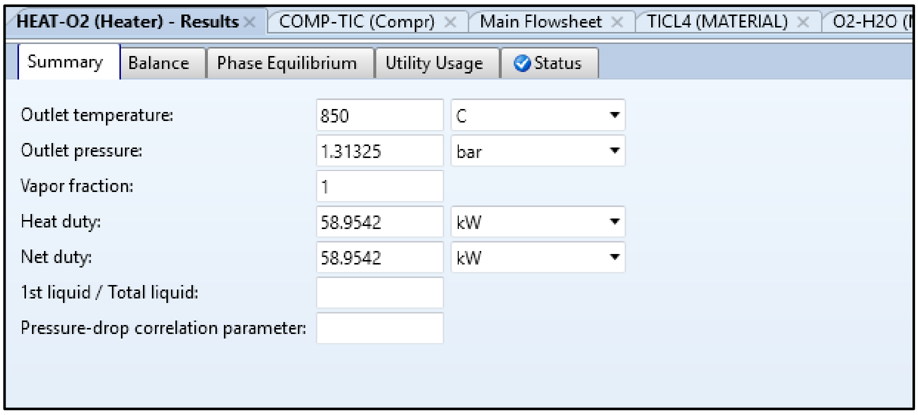
Heat duty: 174.632 kW

Net duty: 174.632 kW

1st liquid / Total liquid:

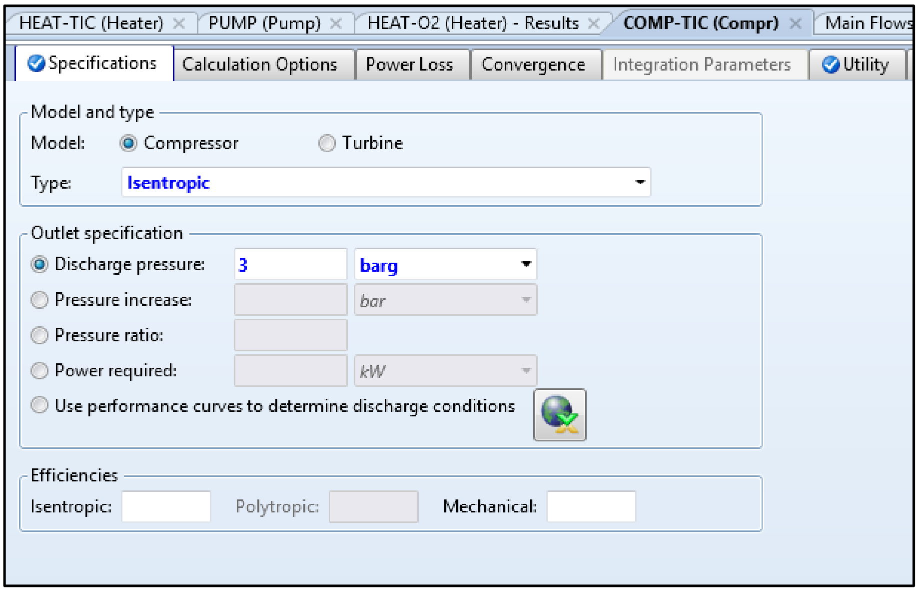
Pressure-drop correlation parameter:

Figure B-44: **Results of HEAT-TIC**



Outlet temperature: 850 C
Outlet pressure: 1.31325 bar
Vapor fraction: 1
Heat duty: 58.9542 kW
Net duty: 58.9542 kW
1st liquid / Total liquid:
Pressure-drop correlation parameter:

Figure B-45: Results of HEAT-O2

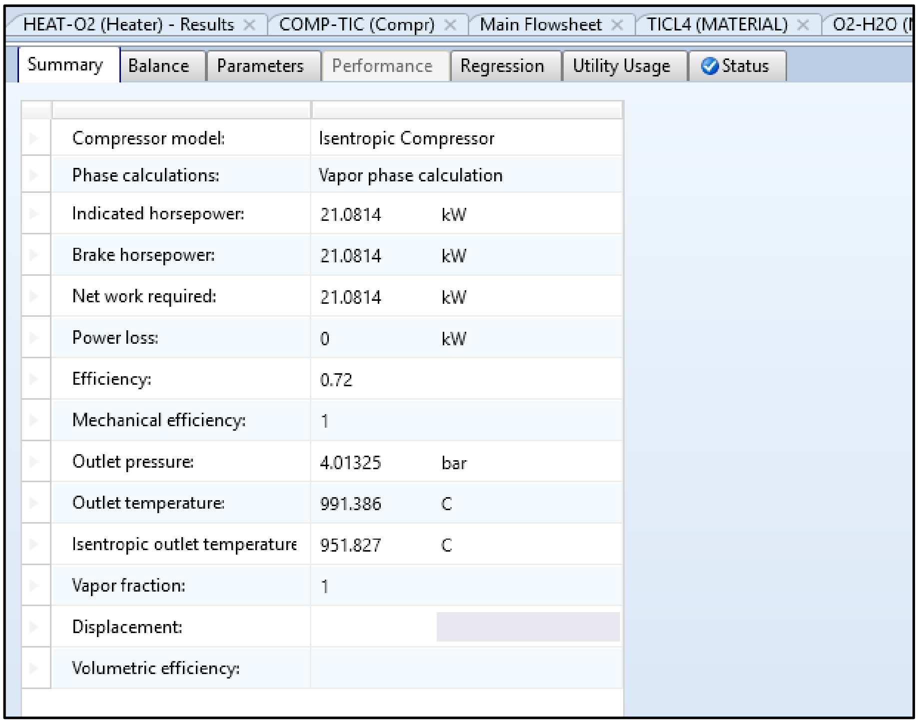


Model and type
Model: ● Compressor ○ Turbine
Type: Isentropic

Outlet specification
● Discharge pressure: 3 barg
○ Pressure increase: bar
○ Pressure ratio:
○ Power required: kW
○ Use performance curves to determine discharge conditions

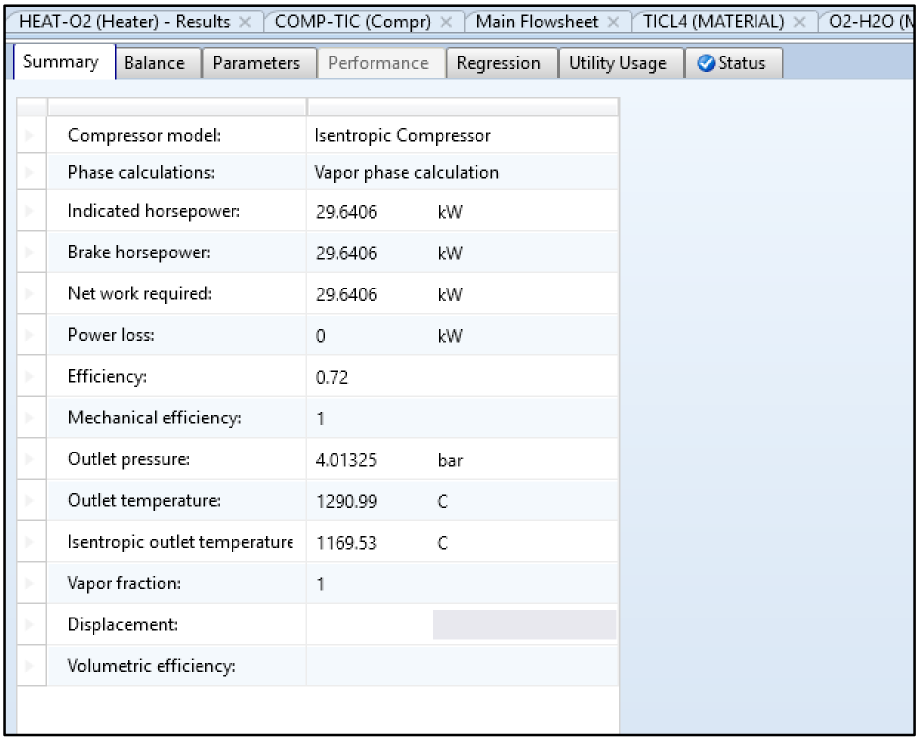
Efficiencies
Isentropic: Polytropic: Mechanical:

Figure B-46: Input of both the $TiCl_4$ compressor COMP-TIC and O_2 compressor COMP-O2



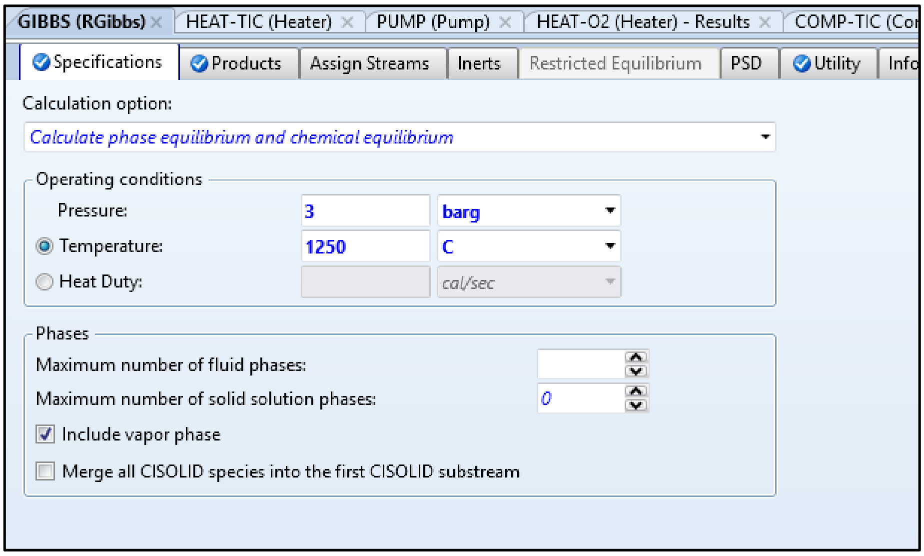
Compressor model:	Isentropic Compressor	
Phase calculations:	Vapor phase calculation	
Indicated horsepower:	21.0814	kW
Brake horsepower:	21.0814	kW
Net work required:	21.0814	kW
Power loss:	0	kW
Efficiency:	0.72	
Mechanical efficiency:	1	
Outlet pressure:	4.01325	bar
Outlet temperature:	991.386	C
Isentropic outlet temperature	951.827	C
Vapor fraction:	1	
Displacement:		
Volumetric efficiency:		

Figure B-47: Results of COMP-TIC



Compressor model:	Isentropic Compressor	
Phase calculations:	Vapor phase calculation	
Indicated horsepower:	29.6406	kW
Brake horsepower:	29.6406	kW
Net work required:	29.6406	kW
Power loss:	0	kW
Efficiency:	0.72	
Mechanical efficiency:	1	
Outlet pressure:	4.01325	bar
Outlet temperature:	1290.99	C
Isentropic outlet temperature	1169.53	C
Vapor fraction:	1	
Displacement:		
Volumetric efficiency:		

Figure B-48: Results of COMP-O2

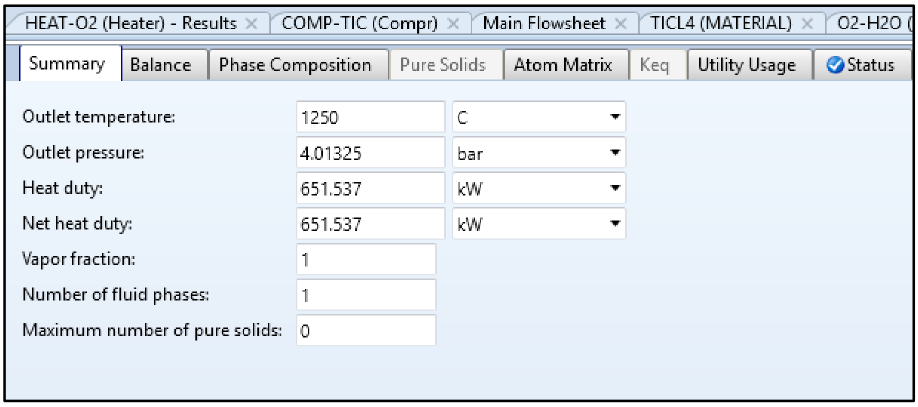


Calculation option:
Calculate phase equilibrium and chemical equilibrium

Operating conditions
Pressure: 3 barg
● Temperature: 1250 C
○ Heat Duty: cal/sec

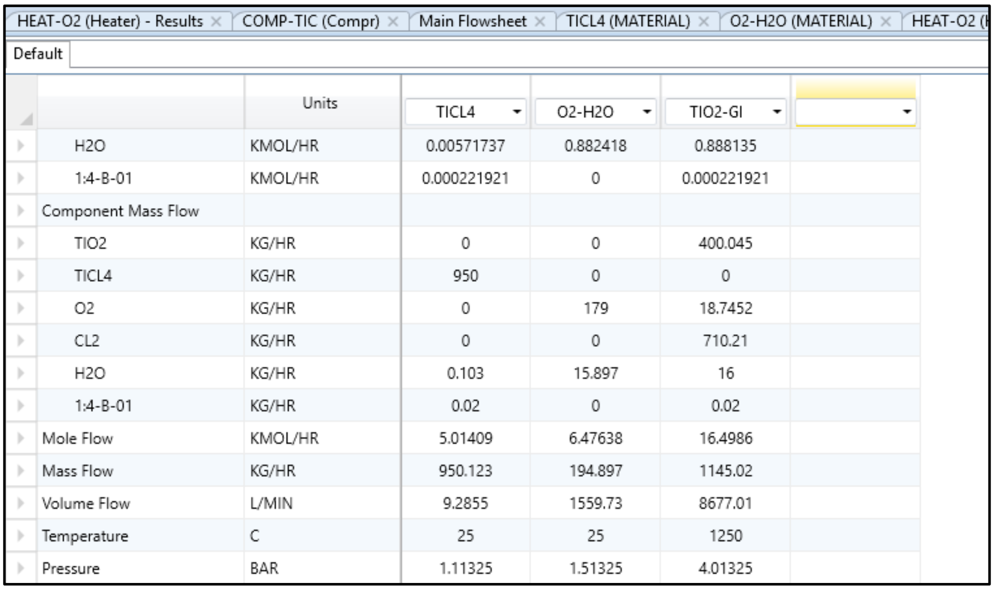
Phases
Maximum number of fluid phases:
Maximum number of solid solution phases: 0
☑ Include vapor phase
☐ Merge all CISOLID species into the first CISOLID substream

Figure B-49: Input of GIBBS reactor



Outlet temperature:	1250	C
Outlet pressure:	4.01325	bar
Heat duty:	651.537	kW
Net heat duty:	651.537	kW
Vapor fraction:	1	
Number of fluid phases:	1	
Maximum number of pure solids:	0	

Figure B-50: Results of GIBBS



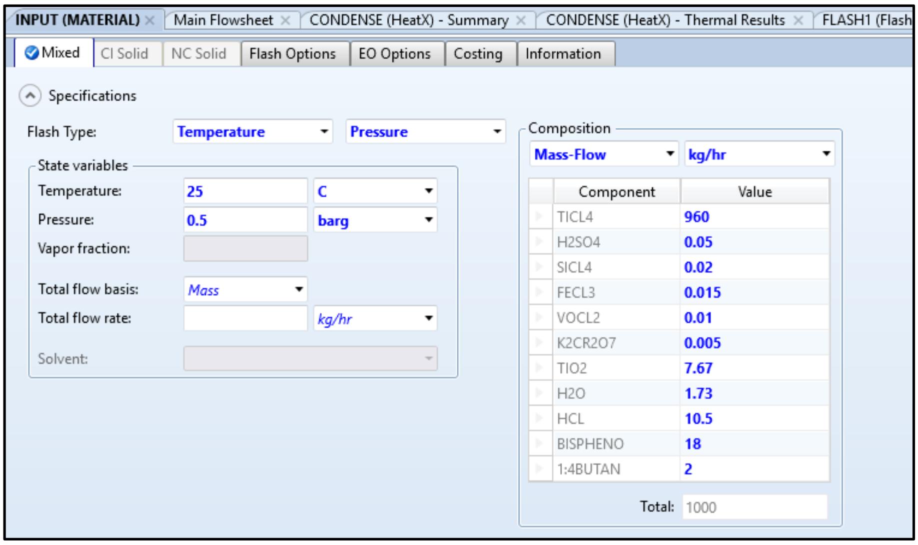
	Units	TICL4	O2-H2O	TIO2-GI	
H2O	KMOL/HR	0.00571737	0.882418	0.888135	
1:4-B-01	KMOL/HR	0.000221921	0	0.000221921	
Component Mass Flow					
TIO2	KG/HR	0	0	400.045	
TICL4	KG/HR	950	0	0	
O2	KG/HR	0	179	18.7452	
CL2	KG/HR	0	0	710.21	
H2O	KG/HR	0.103	15.897	16	
1:4-B-01	KG/HR	0.02	0	0.02	
Mole Flow	KMOL/HR	5.01409	6.47638	16.4986	
Mass Flow	KG/HR	950.123	194.897	1145.02	
Volume Flow	L/MIN	9.2855	1559.73	8677.01	
Temperature	C	25	25	1250	
Pressure	BAR	1.11325	1.51325	4.01325	

Figure B-51: Stream results of GIBBS

B.4 Titanium tetrachloride in smoke mortars for military application

B.4.1 Simulation development and results

The comprehensive simulation procedure that was followed to obtain $TiCl_4$ for use in smoke mortars is given in this section by means of screenshots of the input values and delivered results.



Flash Type: Temperature Pressure

State variables

Temperature: 25 C

Pressure: 0.5 barg

Vapor fraction:

Total flow basis: Mass

Total flow rate: kg/hr

Solvent:

Composition

Mass-Flow kg/hr

Component	Value
TICL4	960
H2SO4	0.05
SICL4	0.02
FECL3	0.015
VOCL2	0.01
K2CR2O7	0.005
TIO2	7.67
H2O	1.73
HCL	10.5
BISPHENO	18
1:4BUTAN	2

Total: 1000

Figure B-52: Demilitarized $TiCl_4$ feed to the process

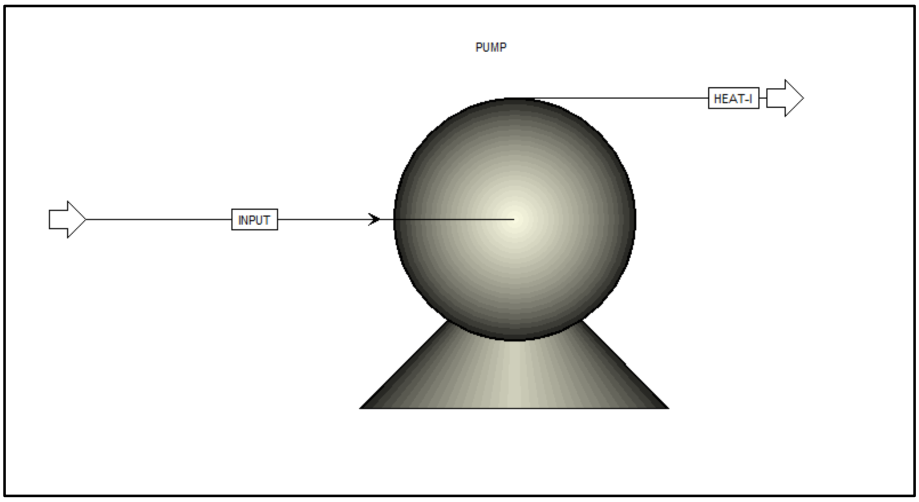
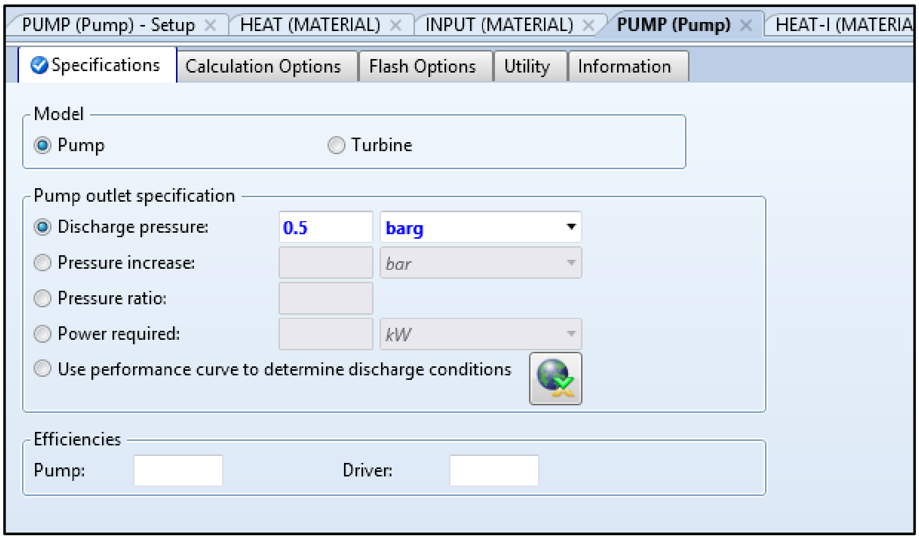


Figure B-53: Flow sheet of the pump used for supplying demilitarized $TiCl_4$



Model

● Pump ○ Turbine

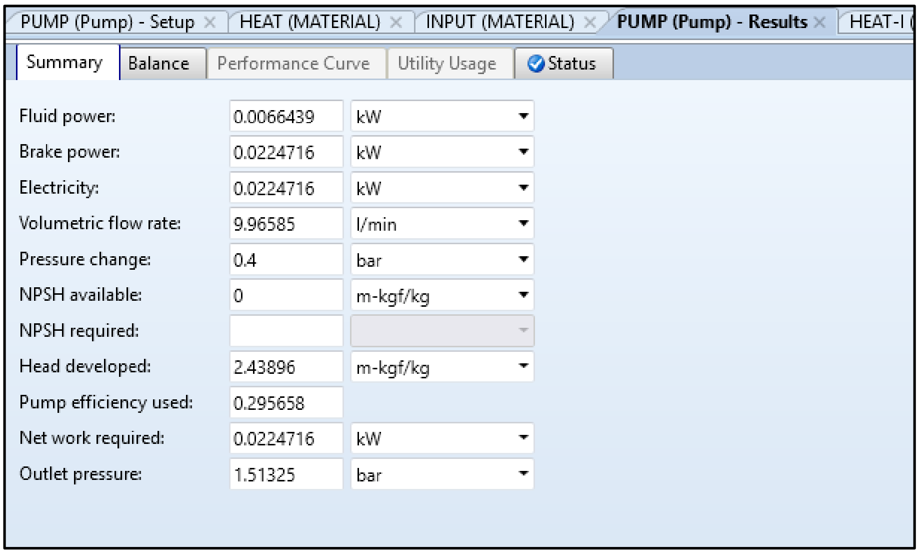
Pump outlet specification

● Discharge pressure: 0.5 barg
○ Pressure increase: bar
○ Pressure ratio:
○ Power required: kW
○ Use performance curve to determine discharge conditions

Efficiencies

Pump:
Driver:

Figure B-54: Input of PUMP



Fluid power: 0.0066439 kW
Brake power: 0.0224716 kW
Electricity: 0.0224716 kW
Volumetric flow rate: 9.96585 l/min
Pressure change: 0.4 bar
NPSH available: 0 m-kgf/kg
NPSH required:
Head developed: 2.43896 m-kgf/kg
Pump efficiency used: 0.295658
Net work required: 0.0224716 kW
Outlet pressure: 1.51325 bar

Figure B-55: Results of PUMP

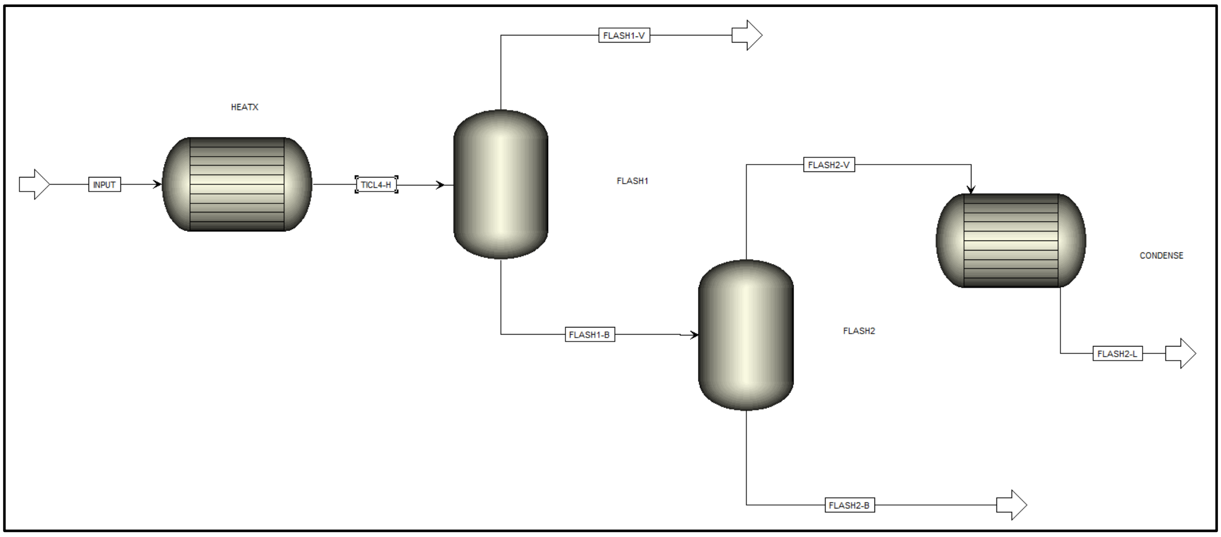
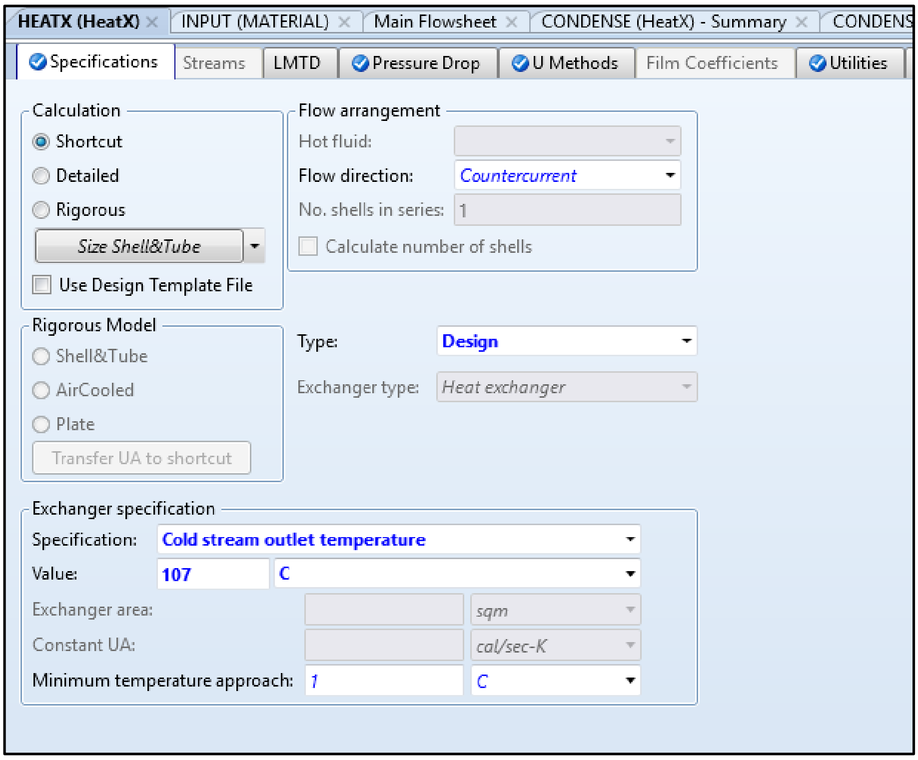


Figure B-56: Flow sheet of two-step vaporization process



Calculation
● Shortcut
○ Detailed
○ Rigorous
Size Shell&Tube
☐ Use Design Template File

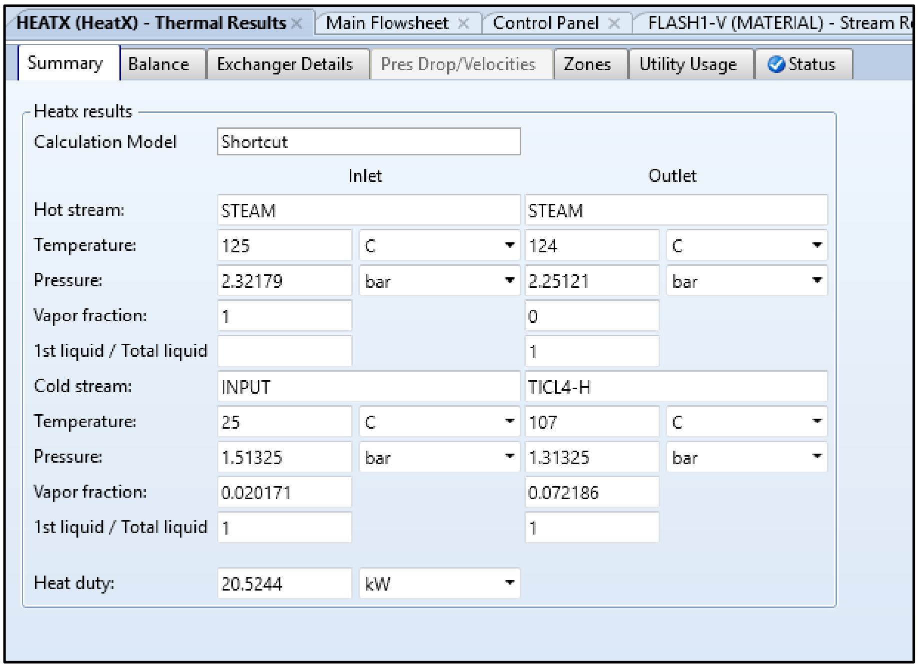
Flow arrangement
Hot fluid:
Flow direction: Countercurrent
No. shells in series: 1
☐ Calculate number of shells

Rigorous Model
○ Shell&Tube
○ AirCooled
○ Plate
Transfer UA to shortcut

Type: Design
Exchanger type: Heat exchanger

Exchanger specification
Specification: Cold stream outlet temperature
Value: 107 C
Exchanger area: sqm
Constant UA: cal/sec-K
Minimum temperature approach: 1 C

Figure B-57: Input of heat exchanger HEATX

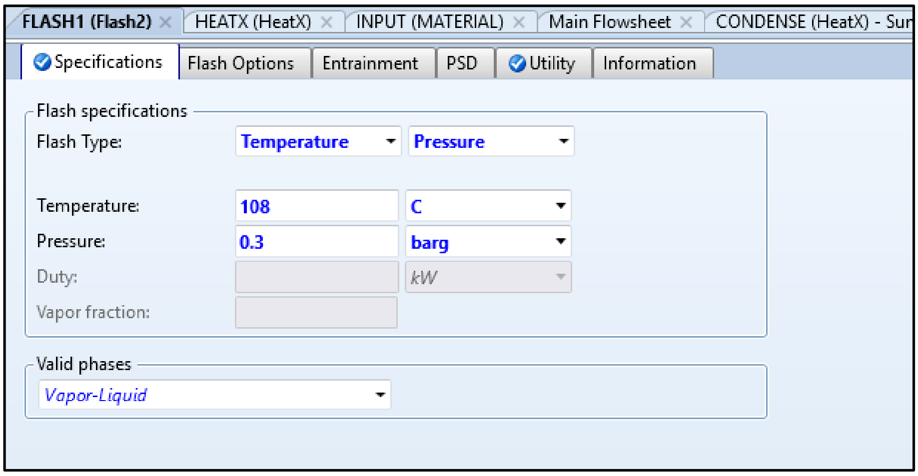


Heatx results

Calculation Model: Shortcut

	Inlet		Outlet	
Hot stream:	STEAM		STEAM	
Temperature:	125	C	124	C
Pressure:	2.32179	bar	2.25121	bar
Vapor fraction:	1		0	
1st liquid / Total liquid			1	
Cold stream:	INPUT		TICL4-H	
Temperature:	25	C	107	C
Pressure:	1.51325	bar	1.31325	bar
Vapor fraction:	0.020171		0.072186	
1st liquid / Total liquid	1		1	
Heat duty:	20.5244	kW		

Figure B-58: Results of HEATX



Flash specifications

Flash Type: Temperature, Pressure

Temperature: 108 C

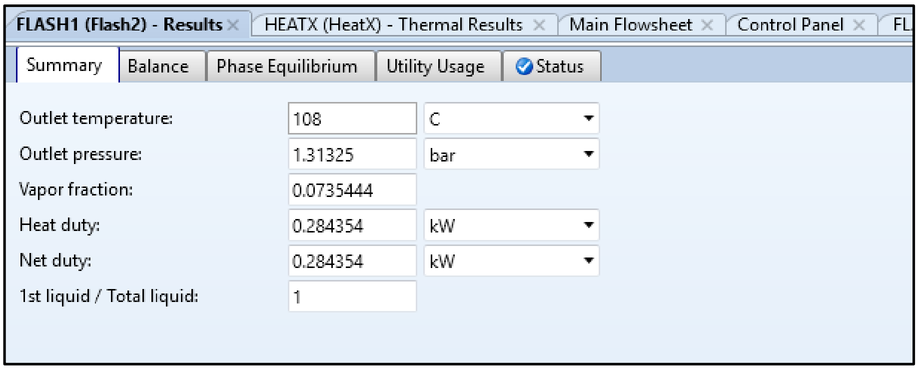
Pressure: 0.3 barg

Duty: kW

Vapor fraction:

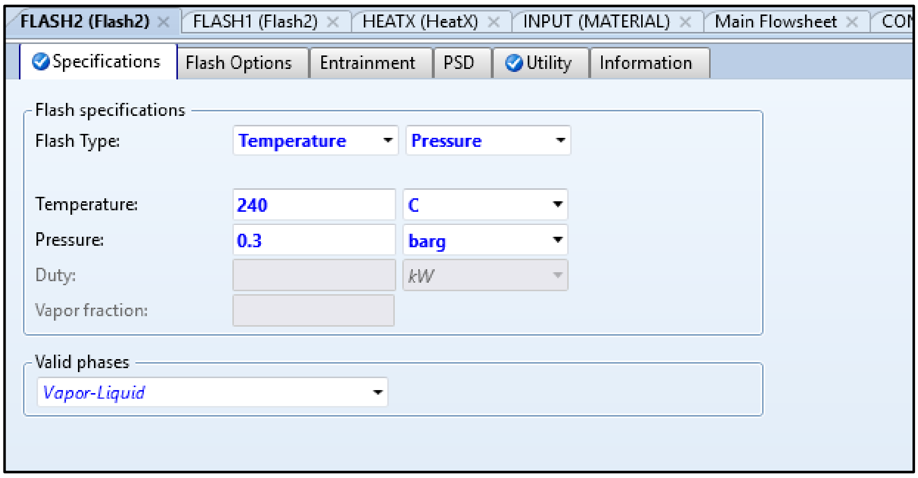
Valid phases: Vapor-Liquid

Figure B-59: Input of unit FLASH1



Outlet temperature: 108 C
Outlet pressure: 1.31325 bar
Vapor fraction: 0.0735444
Heat duty: 0.284354 kW
Net duty: 0.284354 kW
1st liquid / Total liquid: 1

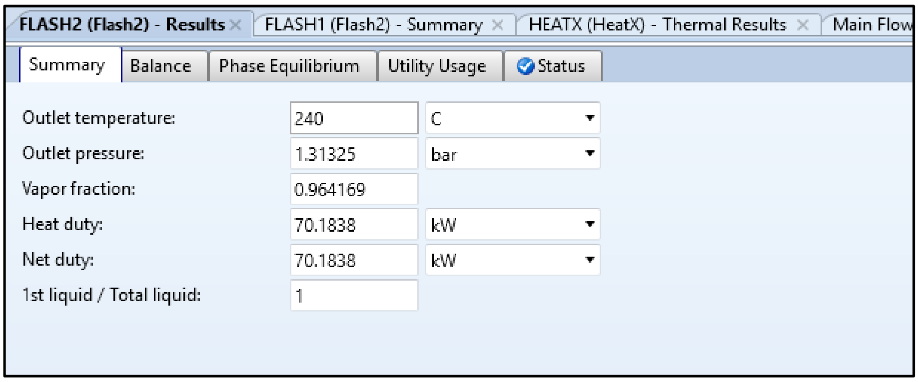
Figure B-60: Results of FLASH1



Flash specifications
Flash Type: Temperature Pressure
Temperature: 240 C
Pressure: 0.3 barg
Duty: kW
Vapor fraction:

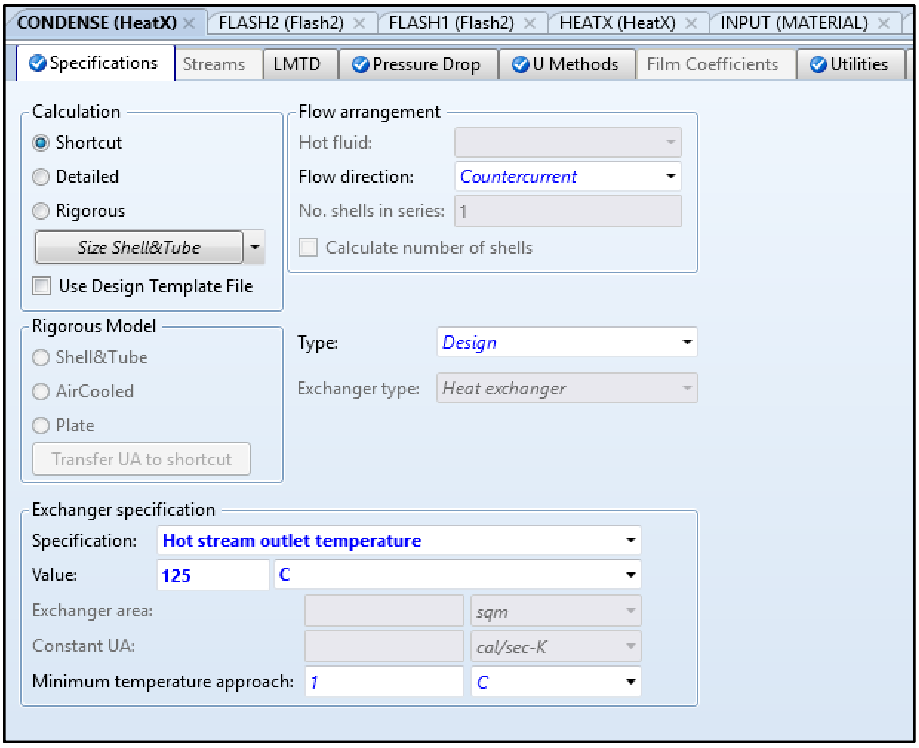
Valid phases
Vapor-Liquid

Figure B-61: Input of unit FLASH2



Outlet temperature: 240 C
Outlet pressure: 1.31325 bar
Vapor fraction: 0.964169
Heat duty: 70.1838 kW
Net duty: 70.1838 kW
1st liquid / Total liquid: 1

Figure B-62: Results of FLASH2



Calculation
● Shortcut
○ Detailed
○ Rigorous
☐ Use Design Template File

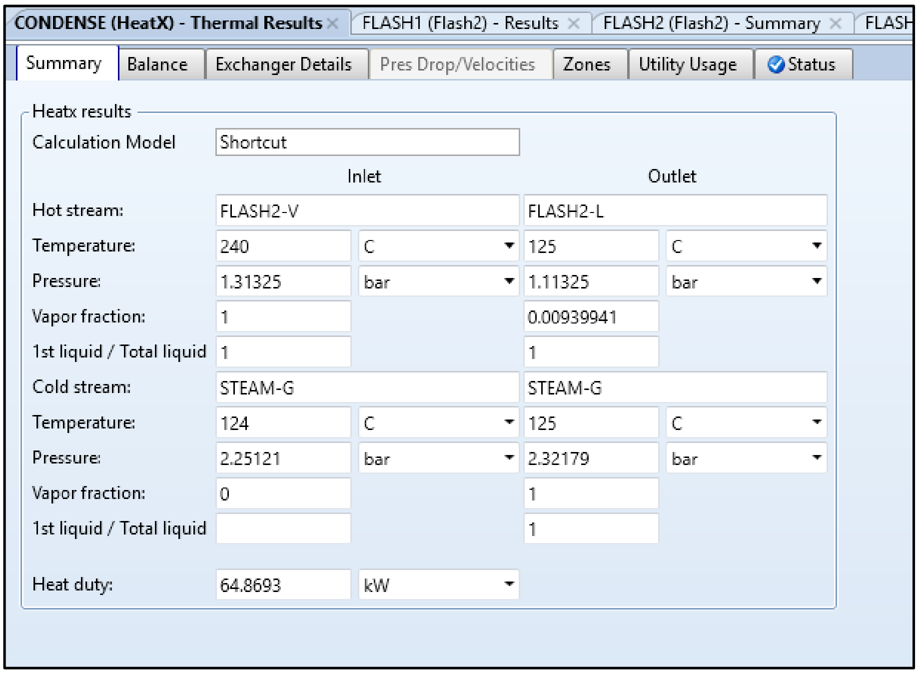
Flow arrangement
Hot fluid:
Flow direction: Countercurrent
No. shells in series: 1
☐ Calculate number of shells

Rigorous Model
○ Shell&Tube
○ AirCooled
○ Plate

Type: Design
Exchanger type: Heat exchanger

Exchanger specification
Specification: Hot stream outlet temperature
Value: 125 C
Exchanger area: sqm
Constant UA: cal/sec-K
Minimum temperature approach: 1 C

Figure B-63: Input of heat exchanger CONDENSE

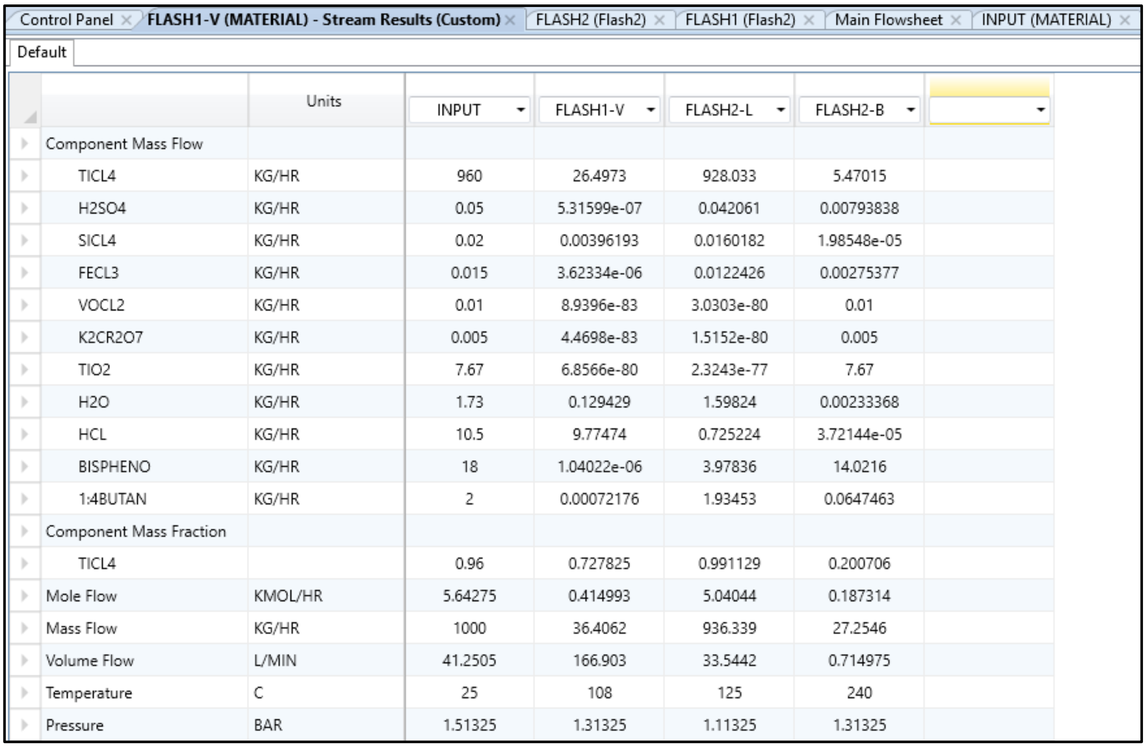


Heatx results

Calculation Model: Shortcut

	Inlet		Outlet	
Hot stream:	FLASH2-V		FLASH2-L	
Temperature:	240	C	125	C
Pressure:	1.31325	bar	1.11325	bar
Vapor fraction:	1		0.00939941	
1st liquid / Total liquid	1		1	
Cold stream:	STEAM-G		STEAM-G	
Temperature:	124	C	125	C
Pressure:	2.25121	bar	2.32179	bar
Vapor fraction:	0		1	
1st liquid / Total liquid			1	
Heat duty:	64.8693	kW		

Figure B-64: Results of CONDENSE



	Units	INPUT	FLASH1-V	FLASH2-L	FLASH2-B
Component Mass Flow					
TICL4	KG/HR	960	26.4973	928.033	5.47015
H2SO4	KG/HR	0.05	5.31599e-07	0.042061	0.00793838
SICL4	KG/HR	0.02	0.00396193	0.0160182	1.98548e-05
FECL3	KG/HR	0.015	3.62334e-06	0.0122426	0.00275377
VOCL2	KG/HR	0.01	8.9396e-83	3.0303e-80	0.01
K2CR2O7	KG/HR	0.005	4.4698e-83	1.5152e-80	0.005
TIO2	KG/HR	7.67	6.8566e-80	2.3243e-77	7.67
H2O	KG/HR	1.73	0.129429	1.59824	0.00233368
HCL	KG/HR	10.5	9.77474	0.725224	3.72144e-05
BISPHENO	KG/HR	18	1.04022e-06	3.97836	14.0216
1:4BUTAN	KG/HR	2	0.00072176	1.93453	0.0647463
Component Mass Fraction					
TICL4		0.96	0.727825	0.991129	0.200706
Mole Flow	KMOL/HR	5.64275	0.414993	5.04044	0.187314
Mass Flow	KG/HR	1000	36.4062	936.339	27.2546
Volume Flow	L/MIN	41.2505	166.903	33.5442	0.714975
Temperature	C	25	108	125	240
Pressure	BAR	1.51325	1.31325	1.11325	1.31325

Figure B-65: **Stream results of the two-step vaporization process**