

Crude TiCl₄ purification: a review of the current state of the art and future opportunities

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Raw titanium tetrachloride (TiCl₄) is produced by chlorination of titania feedstock. Prior to its utilization in the manufacture of titanium dioxide pigment or titanium metal, the TiCl₄ is purified by adding reagents that react with the impurities in the crude TiCl₄, followed by distillation of the mixture. The current state of the art in purification of crude TiCl₄ was surveyed. Tests were conducted at the laboratory scale to assess the efficiency of various additives used in the purification process to minimize the vanadium content in the distillate. The effects of various reagents, namely oleic acid, sodium oleate, potassium oleate, and copper on the purification of crude TiCl₄ were compared. The purified TiCl₄ was water-clear in aspect and analysed < 2 ppm vanadium for all reagents tested. Possible reactions between the impurities in the crude TiCl₄ and the reagents are investigated thermodynamically with the FactSage program.

INTRODUCTION

Titanium tetrachloride (TiCl₄) is obtained by the chlorination of a titanium-bearing mineral such as ilmenite and rutile, as well as from titanium slag. The chlorination process usually takes place in a fluidized bed in the presence of chlorine gas and a reducing agent such as petroleum coke, resulting in crude titanium tetrachloride. TiCl₄ is an intermediate product in the production of titanium dioxide (TiO₂) pigment and titanium metal. The pure form of titanium dioxide is used in the pigment industry for paints, food colouring *etc.*, and titanium metal is widely used in the aerospace, medicine, sport, and semiconductor production industries. The crude TiCl₄ has many impurities, most of which can be removed through distillation; however, some are difficult to remove *e.g.* vanadium oxychloride (VOCl₃). This impurity has a boiling point close to that of the desired product, making separation by distillation ineffective. The removal of impurities is especially important as their presence in TiO₂ pigment and titanium sponge reduces the quality of pigment and increases the hardness of the metal respectively (Xiong *et al.*, 2012).

A chemical treatment is often used to precipitate such impurities or to convert them into high-boiling impurities, ensuring that separation by distillation is effective. Various substances can be used as chemical treatment agents, such as metal powders (iron, aluminium, copper *etc.*), petroleum fractions, alkali metal hydroxides, inorganic gases, and vegetable or animal oils and their derivatives.

The aim of this work was to produce TiCl₄ of high purity, containing significantly low levels of vanadium and suitable for use in the TiO₂ pigment and Ti metal industries, utilizing Mintek's laboratory-scale set-up. Various purification experiments were conducted using both organic and inorganic treatment agents to purify crude TiCl₄. The agents were compared in terms of their effects and economic viability.

From Table I, it can be seen that Air Products and TOHO high grade have stringent restrictions on vanadium content, at 1 ppb and 1 ppm respectively. Air Products uses the TiCl_4 for production of titanium metal and TOHO high grade supplies the semiconductor industry. For use in the pigment industry, the vanadium content must be below 10 ppm and preferably below 5 ppm. The vanadium content in crude TiCl_4 is typically between 200 and 500 ppm. Judging from the commercial specifications, purification of TiCl_4 is essential. Table I shows some commercial specifications by various industries.

Table I. Commercial specifications of TiCl_4 .

	TiCl_4 (%)	V (ppm)	Fe (ppm)	Al (ppm)	Sn (ppm)	Si (ppm)	Sb (ppm)	As (ppm)
Air products (Koiro, 2013)	>99.7	<0.001	<0.003	<0.002	<0.001	-	<0.001	<0.002
TLT -1 (TOHO Titanium, 2016)	>99.9	<10	<10	-	<30	<5	-	-
High grade (TOHO Titanium, 2016)	-	1	1	1	1	2	0.1	0.1
Osaka Titanium Technologies (, 2013)	99.9	1	1	-	-	1	-	-

LITERATURE REVIEW

Literature sources were reviewed in order to gain a better understanding of the crude TiCl_4 purification process. Various reagents, namely alkali metal hydroxides, metal powders (Fe, Zn, Sn, Cu, Sb, Na, Mg, Ti or Al), $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$, the salts of stearic, myristic, palmitic, oleic, and lauric acids, oleic acid, animal fat, vegetable oil, petroleum fractions, hydrocarbon polymers, soap, dichlorobenzene, chlorotoluene, hydrogenated naphthenic oil, white mineral oil (WMO), and chloronaphtholene have been used as treatment agents, alone or in combination, to bind impurities before purified TiCl_4 is distilled off. The treatment agents, operating conditions and results are summarized in Table II. Some unique processes are discussed separately as they did not conform to the common procedure of refluxing followed by distillation.

In a paper on the preparation of high-purity TiCl_4 , Clabaugh, Leslie, and Gilchrist (1955) claim that most metal impurities except V and Sn can be removed by distillation without any treatment agents. They also describe the removal of organic impurities by the addition of Cl_2 , aluminium chloride hexahydrate ($\text{AlCl}(\text{OH})_6$), and water or by the addition of Br; the use of Cu to remove V is also described.

A patent entitled 'Process for the purification of titanium tetrachloride' (Sironi *et al.*, 1971) describes a method of producing titanium tetrachloride with a vanadium content of less than 1 ppm, using hydrogen sulphide gas (H_2S) to achieve the desired purity levels through precipitation of vanadium impurities. According to the invention, the crude TiCl_4 from the chlorination process is passed through a spray quencher where it is injected with the liquid TiCl_4 and at the same time treated with H_2S in order to cool the vapour stream from high temperatures to 130–180°C, to remove the vanadium and other low-boiling impurities in the vapour phase.

Winter (1975) proposes the purification of vanadium-containing TiCl_4 by heating with $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$. The reaction between the reagent and impurities in the TiCl_4 has very fast kinetics, and the reaction products are filterable from liquid TiCl_4 .

Bonsack (1978) added water to crude TiCl_4 to remove impurities of niobium pentachloride and tantalum pentachloride. Water reacts preferentially with the niobium and tantalum compounds to form insoluble hydrates.

Table II. Experimental conditions and results from some reviewed articles.

Reference	Treatment agent	Addition of treatment agent	Initial vanadium content	Final vanadium content	Operating temperature (°C)	Refluxing time
Cole and Meister, 1946	Alkali metal hydroxide	-	-	-	136	1-6 h
Meyers, 1946	Alkali salts of fatty acids	0.1 to 1% wt% crude TiCl_4	-	<10 ppm	No heating	No reflux
Stambaugh, 1956	Alkali metal hydroxide + metal	0.15-0.3 wt% crude TiCl_4	2500-3500 ppm	1-3 ppm	134-138	1-2 h
Hansley and Schott, 1960	Fine salt and powdered metal	0.5-0.6 wt% metal to crude TiCl_4	-	<10 ppm	136	90 min
Clark and Kolb, 1970	Any organic soap (e.g. potassium oleate)	0.05-5 wt% crude TiCl_4	200-4000 ppm	5 ppm	90-136	15-50 s in scrubber set-up
Sironi <i>et al.</i> , 1971	Hydrogen sulphide	3 mol H_2S /1 mol V	2200 ppm	1 ppm	145	15-50 s
Goddard and Litwin, 2002	Copper	1-2 wt% crude TiCl_4	0.1 ppm	0.03 ppm	136	30 min
Xiong <i>et al.</i> , 2012	Aluminium powder + WMO	1.6 g/g VOCl_3	2860 ppm	4.9 ppm	136	40 min

Bonsack and Schneider (1982) claim that vanadium chlorinated with high-surface-area carbon forms VCl_3 , rather than VOCl_3 or VCl_4 , which can readily be separated as it remains in solid form below 450°C. This alternative process allows the separation of vanadium impurities before TiCl_4 condensation.

Ishizuka (1988) removed impurities from crude TiCl_4 by heating over a catalytic metal (Cu, Fe, or Cu and Fe alloys) above 300°C to reduce oxygen impurities to substances less volatile than TiCl_4 , which can then be removed from gaseous TiCl_4 or in the subsequent distillation. Lowering the oxygen content in TiCl_4 used for metal production improves the ductility of the titanium metal produced.

According to the literature, the problem is clearly not to find a treatment agent, since many has been described, but rather to find a reagent that achieves the desired TiCl_4 purity in a cost-effective way with minimal adverse impact on the production process.

THERMODYNAMIC DATA

Table III shows the boiling points of metal chlorides often associated with titanium tetrachloride in the crude mixture. It can be seen that AlCl_3 , AsCl_3 , VOCl_3 , VCl_4 , and SnCl_4 have boiling points close to that of titanium tetrachloride (136°C), making it difficult to separate them from one another using physical processes such as distillation. Although ferric chloride, which is a very common impurity in titaniferous materials, has a boiling point significantly higher than 136°C , it is known to react with other components in the system to form lower-boiling complexes/compounds that can contaminate the titanium tetrachloride. Antimony chlorides, ferrous chloride, and calcium and magnesium chlorides are high-boiling compounds and do not pose any problems during the distillation process.

Table III. Boiling points of common crude TiCl_4 constituents and possible reaction products (Perry and Green, 1997).

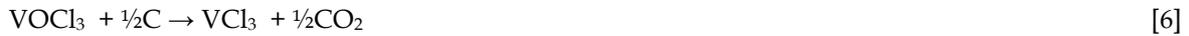
Chemical name	Chemical formula	Boiling point ($^\circ\text{C}$)
Titanium tetrachloride	TiCl_4	136
Titanium trichloride	TiCl_3	Decomposes at 440°C
Vanadium oxychloride	VOCl_3 , yellow	127
Vanadium tetrachloride	VCl_4 , red	149
Vanadium trichloride	VCl_3 , pink or violet	Decomposes at 300°C
Vanadium dichloride	VCl_2 , green	1506
Antimony pentachloride	SbCl_5	Decomposes at 140°C
Antimony trichloride	SbCl_3	220
Ferric chloride	FeCl_3	315
Tin tetrachloride	SnCl_4	114
Arsenic trichloride	AsCl_3	130
Silicon tetrachloride	SiCl_4	58
Aluminium chloride	AlCl_3	183
Ferrous chloride	FeCl_2	1023
Copper chloride, Nantokite	CuCl_2 , brown-yellow Cu_2Cl_2 , white	993 1366
Calcium chloride	CaCl_2	1935
Magnesium chloride	MgCl_2	1412

Evaluation of reactions

The crude titanium tetrachloride contains a lot of impurities as a result a number of chemical reactions that can occur between TiCl_4 and other metal chlorides present in the crude mixture upon addition of either an organic or an inorganic treating agent. Some chemical reactions between the treatment agent and various chlorides/oxychlorides of vanadium and iron have been thermodynamically evaluated and the results are discussed in the following sections. These reactions are by no means the only reactions that can take place; for instance, no data was available for reactions with VOCl and VOCl_2 as

products, and these reactions were not investigated. Vanadium is the most detrimental impurity in TiCl_4 , and iron chlorides are often present in higher concentrations than desirable.

The thermodynamic properties of the reactions, such as changes in Gibbs free energy, enthalpy, and entropy, can be calculated using the FactSage thermodynamic simulation software. This requires an input of possible reactants and products, operating temperature, and pressure.



Solubility data for the iron chlorides and vanadium oxychlorides in TiCl_4 was not available.

The thermodynamic evaluation shows that copper may indeed react with vanadium and iron chlorides, producing chlorides with much higher boiling points than TiCl_4 and thus ensuring that purified TiCl_4 is obtained through distillation.

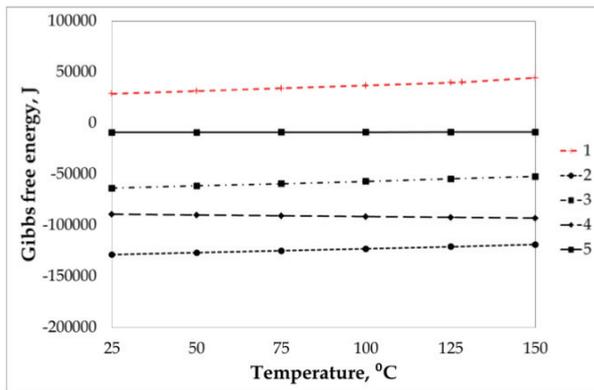


Figure 1. Gibbs free energy evaluation for reactions [1] to [5].

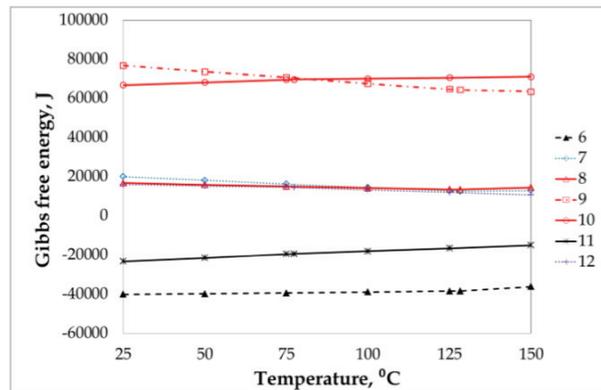


Figure 3. Gibbs free energy evaluation for reactions [6] to [12].

Xiong *et al.* (2012) proposed that VOCl_3 was converted to VOCl_2 (solid phase) by TiCl_3 formed through the reduction of TiCl_4 using aluminium powder and carbon, which was obtained from the pyrolytic

cracking of WMO. Although pyrolytic cracking of the white mineral oil to carbon seems unlikely at such low temperatures and is contra-indicated by the fouling caused by the polymerized organic residue in industry, thermodynamic investigation confirms that carbon might be an effective treatment agent to pacify vanadium and iron impurities.

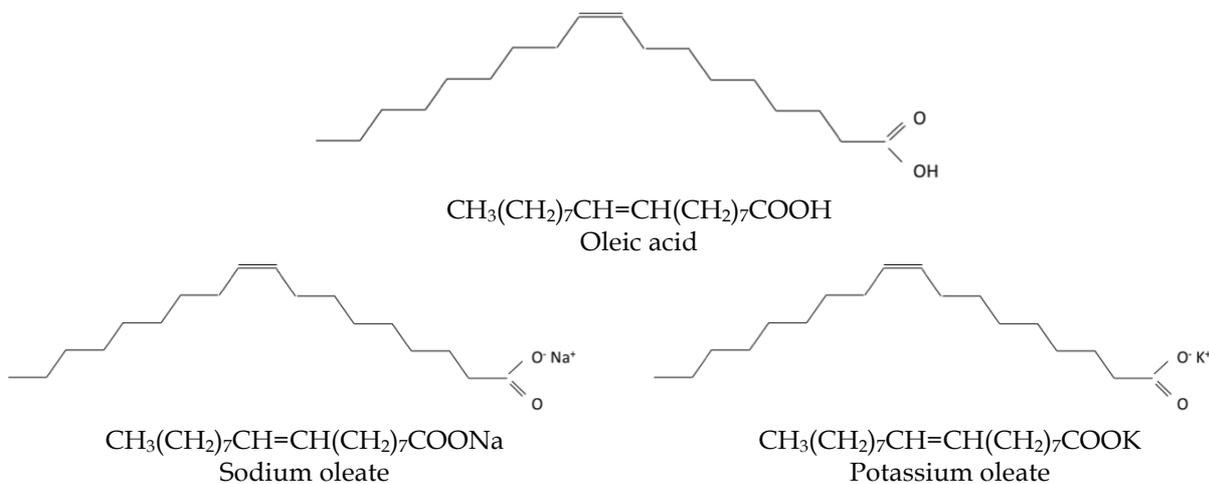


Figure 2. Line structure, chemical formulae, and common names for oleic acid and its salts.

Oleic acid ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$) is an unsaturated organic carboxylic acid and therefore likely to undergo the typical reactions of both alkenes and carboxylic acids. These reactions include addition and polymerization of the alkene bond and nucleophilic substitution reactions of the carboxylic acid bonds (McMurry, 1996). In Figure 2 the line bond structures of the organic treatment agents are compared.

Sodium oleate and potassium oleate share the same structural form as oleic acid, with the alkali metals replacing the hydrogen of the $-\text{OH}$ group. For ease of discussion we replace $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}$ with placeholder R. We can then write oleic acid as ROH and its salts as RNa and ROK.

VOCl_3 reacts with alcohols, especially in the presence of a proton acceptor, to give alkoxides (McMurry, 1996). Writing these reactions for our organic reagents gives:



Vanadium oxytrichloride (VOCl_3) is also strongly Lewis acidic (Wikipedia, 2016) and is used as a catalyst in alkene polymerization. It would therefore promote polymerization of the alkene bond in the carboxylic acid and its salts, leading to the organic residue that fouls reactors in industry. TiCl_3 is also known to act as a catalyst for polymerization of alkenes (McMurry, 1996).

EXPERIMENTAL PROCEDURES

Titanium tetrachloride is a highly insoluble, thermally stable metal halide that is liquid at room temperature. It is a clear colourless liquid in pure form, but crude titanium tetrachloride may be yellow or reddish-brown in appearance. It has low melting and boiling temperatures, namely -24.1°C

and 136.4°C respectively. TiCl_4 is extremely moisture-sensitive and reacts violently with water/air to form toxic HCl gas and titanium dioxide/oxychloride.

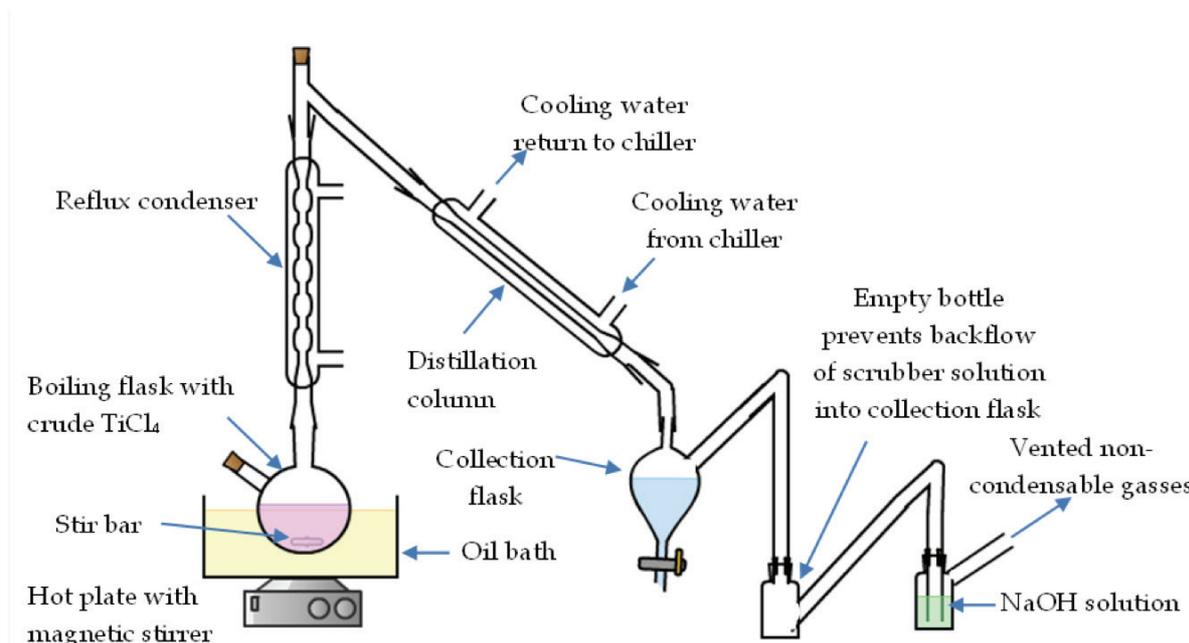


Figure 3. Experimental set-up of reflux column and condenser.

Figure 3 depicts the set-up used for investigation of the chemical treatment and distillation of the crude mixture of TiCl_4 using various additives. The set-up consists of a round-bottom flask containing a mixture of crude TiCl_4 and treatment agents agitated with a magnetic stir bar; the flask is immersed in a beaker containing heating oil. The oil should be stable at high temperatures as it is heated to up to 200°C to enable distillation. The beaker is placed on a hot plate with a magnetic stirrer. During the experiment, the vapours from the heated crude mixture enter the reflux condenser where they are condensed back into the liquid phase and return to the flask; this process is called refluxing. The distillation column is connected to the reflux column in an inclined position. The collection flask is connected to the bottom of the distillation column. After the crude mixture has undergone chemical pre-treatment, a heating mantle/heating oil bath can be used to provide increased energy to the mixture in the round-bottom flask, causing the vapour to reach the distillation column, condense, and collect in the collection flask. The non-condensable gases from the distillation column are vented after being bubbled through NaOH solution. The distillation column may be cooled with cold water from a chiller. In the present configuration, the cooling water to the distillation column was at room temperature and no cooling was needed on the reflux column. A data logger connected to a B-type thermocouple was used to monitor the temperature of the oil bath around the feed flask.

Table IV. Operating conditions of the purification trials.

	Refluxing agent	Dosage (wt%)	Refluxing T (°C)	Time (min)
Trial 1	Oleic acid	0.15	136	30
Trial 2	Sodium oleate	0.25	136	30
Trial 3	Potassium oleate	0.25	136	30
Trial 4	Copper metal powder	1	136	30

Table IV shows the details of each purification trial, including the type and dosage of the treatment agent and the refluxing time. The dosages selected for the tests were estimated from the literature.

The crude and purified batches of titanium tetrachloride were analysed for metals such as Fe, Al, Cu, and V using inductively coupled plasma-optical emission spectrometry.

RESULTS

Trials for the purification of TiCl_4 with oleic acid were successfully executed. The measured oil bath temperatures are given in Figure 4 to Figure 7. The oil bath temperature proved a reliable indicator of the reflux and distillation zones and temperature measurements inside the reflux column were unnecessary. A sticky organic residue formed in the boiling flask. This residue proved impossible to decant and was scrubbed out of the reactor with soapy water. A sticky organic residue also formed in the boiling flask in the trials with sodium oleate and potassium oleate. Although similar in colour to the residue produced by treatment with oleic acid, the residues from sodium oleate and potassium oleate appeared to the eye less stringy and more particulate in nature. This is, however, subjective and would need to be confirmed by analysis before decisions are based on this observation. The residues from the trial purification with Cu appeared much like crude TiCl_4 with copper shavings in it. After standing overnight in a sealed bottle, the residue appeared to solidify and turn white. This may be explained by oxidation of residual chlorides in contact with air.

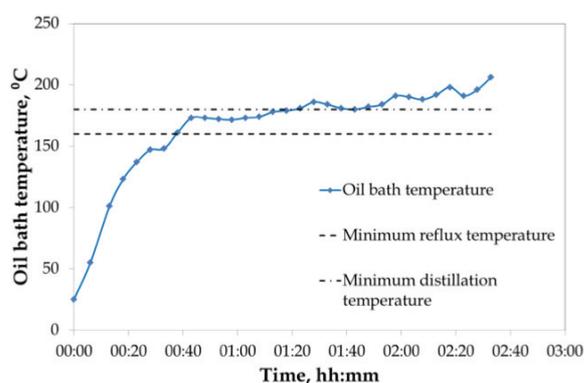


Figure 1. Oil bath temperature for purification of TiCl_4 with oleic acid.

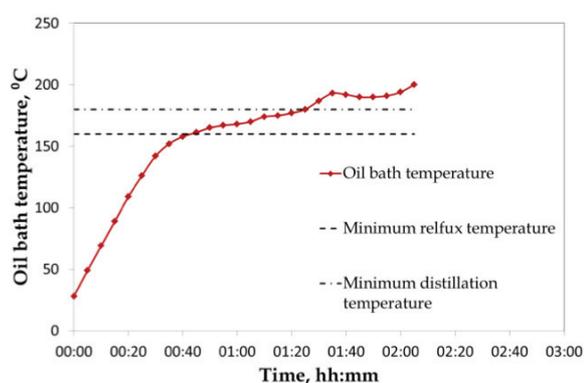


Figure 2. Oil bath temperature for purification of TiCl_4 with sodium oleate.

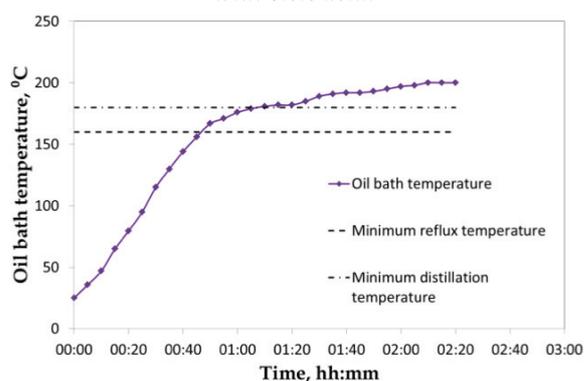


Figure 3. Oil bath temperature for purification of TiCl_4 with potassium oleate.

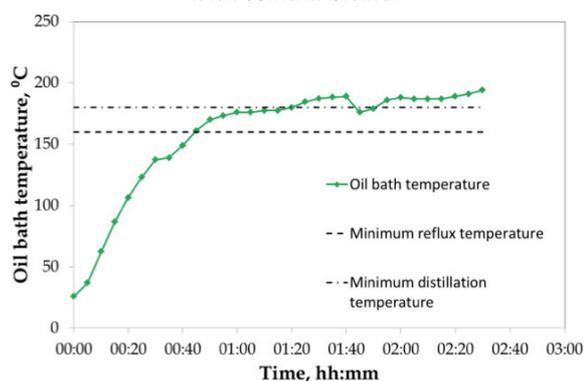


Figure 4. Oil bath temperature for purification of TiCl_4 with copper.

When cleaning the boiling flask, the addition of water to residues remaining in the flask produced a mixture purple in colour. Copper reacts with some of the titanium tetrachloride to produce a lavender material that renders some impurities non-volatile. It is believed that the lavender material is probably $\text{CuCl}\cdot\text{TiCl}_3$ or involves the reduction of some of the titanium tetrachloride to a trivalent titanium chloride compound.



Figure 5. Purple colour on cleaning boiling flask used for copper trial.



Figure 6. Crude TiCl_4 (left) and purified TiCl_4 (four product bottles on right).

Product analysis

The crude TiCl_4 used in the experiments was produced in Mintek's pilot plant chlorination facility using rutile as a titanium feedstock. For all the reagents tested, clear TiCl_4 were produced, as shown in Figure 9. The product analyses for impurities are given Table V. Typical V contents in crude TiCl_4 in industry are around 200–500 ppm; Al is in the range of 50–200 ppm and Fe below 50 ppm. Our test uses a V level of around 700 ppm. This is much higher than the typical value of 200–500 ppm V in crude TiCl_4 .

Table V. Analysis of crude and purified TiCl_4 .

Purified Product	Mass, g	337	304	307	322		
	Crude TiCl_4					Ref. actual	Ref. result
Reagent	None	Oleic acid	Sodium oleate	Potassium oleate	Copper	References	
V ppm	726	<2	<2	<2	<2	15	16
Al ppm	4	5.7	5.3	5.1	5.3	15	15
Fe ppm	20	<2	<2	<2	<2	15	14

Analysis by Mintek's Analytical Science Division (ASD)

The analytical method is challenging, as TiCl_4 is very reactive with any moisture and the resulting TiO_2 particles and HCl vapour cause blockages in the instruments and interfere with the readings.

Between 88 and 97 wt% of the crude TiCl_4 was recovered as purified product.

Economic evaluation

In Table VI the high cost of copper compared to the organic reagents can be seen. Various grades of mineral oils are currently used in the commercial production of TiCl_4 . The use of metal powders is not favoured due to economic reasons. The use of mineral oil entails some operational challenges as it forms sludge that causes fouling in the condensers.

Table VI. Economic comparison of reagents used in experiments (R15.71 per US dollar).

Reagent	Source	Price US\$/t	Dosage wt% of crude TiCl ₄	Price R/t crude TiCl ₄
Copper	InvestMine, 2016	4776	1.00	750.31
Oleic acid	Alibaba, 2016a	1200	0.15	28.28
Sodium oleate	Alibaba, 2016b	2000	0.25	78.55
Potassium oleate	Alibaba, 2016c	2000	0.25	78.55

DISCUSSION

The use of various treatment agents for the purification of raw TiCl₄ by distillation was investigated. The purity of raw and distilled TiCl₄ samples was measured by the amount of impurities present. However, impurity levels below 10 ppm were difficult to detect and required extreme precision in the make-up of reference and control solutions.

The use of organic materials as treatment agents often results in the introduction of organic contaminants into the system and requires an additional step for their removal. Regular shutdowns and maintenance are required in order to clean the equipment, as the residue formed by the organic contaminants reduces the heat transfer efficiencies. If these contaminants are formed by polymerization of the treatment agents, an agent that does not polymerize easily, such as saturated alkanes or alcohols, should produce less fouling. Such treatment reagents would need to be tested in practise to ensure that they provide the same or better efficiency than those currently used.

The use of inorganic treatment agents such as copper results in chlorides that are non-volatile and do not interfere with heat transfer; however, metals and their powders are expensive and furthermore their recovery from waste before disposal could prove problematic.

According to the literature H₂S is effective in the removal of vanadium impurities, but since it is a poisonous gas its use would be very limited because of the associated safety, transportation, and environmental issues.

CONCLUSION

Experimental trials confirmed the effectiveness of copper and oleic acid and its alkali salts as reagents to bind impurities in crude TiCl₄, enabling the distillation of purified TiCl₄ suitable for use in the TiO₂ pigment industry.

The literature survey and thermodynamic studies illustrated possible reactions taking place between impurities and reagents. Additional work is planned to confirm the reaction mechanism for carbonaceous reagents by comparing the effectiveness of carbon, and saturated hydrocarbons such as alkanes, alcohols, and esters, with the known carboxylic acids as treatment agents in order to identify a cost-effective non-fouling reagent suitable for industrial use.

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After obtaining her masters of science in engineering degree at the University of Stellenbosch, Lina joined Mintek's Pyrometallurgy Division in 2002 and gained experience in DC arc furnace technology and extractive metallurgy including the recovery of PGMs to iron alloys, ferrochrome smelting and the production of titanium metal in a Kroll reactor. In 2011 she resigned to be a full time mother, but re-joined Mintek in 2015. She is currently involved in $TiCl_4$ production and purification research, as well as research into the application of concentrated solar thermal energy in the minerals processing industry.