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CHLORINATION OF ILMENITE

Review of Project and Economic Assessment

by

R. E. Wilmshurst

Investigated by: Industrial Chemistry Section

Officer in Charge: F. R. Hartley

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L. Wallace Coffer. Director

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1. INTRODUCTION

The most widely used titanium compound is the white pigment oxide, TiO_2, used in large quantities in paints, lacquers, plastics, and in paper products. Current production of this material in U.S.A. is about 500,000 tons per year and is expected to rise to 700,000 tons by 1970.[1] The free world capacity at present is about 1 million tons, and considerable expansion is being undertaken. The pigment market is quite stable with prices unchanged for the last 3-4 years.

Pigment titanium oxide is a high purity product with carefully controlled physical properties, and is normally prepared by wet methods. Ilmenite is digested with sulphuric acid and the solution is purified and hydrolysed to precipitate pure hydrated titania, which is ignited to rutile or anatase type pigment. In this process the iron which is the other major metallic constituent of ilmenite is rejected as ferrous sulphate, and sulphuric acid consumption is thus high. Pigment is made at Burnie in Tasmania by this process.

A competitive pigment process, developed in U.S.A. by du Pont, and in England by La Porte[13], uses titanium tetrachloride as raw material. This is oxidised at high temperature in burners of special design to give an oxide which is regarded[7,13] as being at least as good as the sulphate process product.

Titanium tetrachloride is the raw material also for manufacture of metallic titanium, and various other titanium compounds. It is prepared by chlorination of rutile in the presence of carbon, giving a crude chloride which requires purification before use. Chlorination of ilmenite in the presence of carbon, gives a mixture of titanium and ferric chlorides. Separation of the titanium is more difficult in this case, and recovery of chlorine from the waste ferric chloride is a further complication. A number of patents have been taken out for methods of recovery of chlorine from ferric chloride, but as far as is known, none of these processes has been used on a large scale.

Rutile is this the preferred titanium source, and would be consumed in much larger quantities if supplies were available. Australia currently produces rutile at the rate of about 100,000 tons annually[4], about 90 per cent of the world production.[5,6] This material is not available in sufficient quantity to enable expanded production, and is unlikely to supply more than about 20 per cent of the world titanium demand in the foreseeable future.

The current improvement in titanium mineral markets is based on expansion of the pigment industry and the introduction of the new process. Natural rutile prices have increased from between £21 and £22 and to £27 per ton in the past 3 months, with some long term contracts being let at £34.[2,3] This is a much sounder basis than the earlier rutile boom caused by demant for titanium metal. Although prices cannot be expected to rise as sharply as they did previously, there should be a good market for titanium minerals for some years to come. The contract price of £34/ton is a good indication of the expected trend.

Current prices for ilmenite and rutile are £4 and £27 per ton respectively, or on the basis of contained TiO_2, about £8 and £29. There is a substantial margin here, and an opening for a process to produce from ilmenite a material comparable with natural rutile. Further, there may be some advantage in producing a titanium oxide intermediate material of better quality than natural rutile, and if this could be sold for little more than the £27 quoted for rutile, a ready market would be assured.

Since this oxide intermediate would ultimately be chlorinated to tetrachloride, which could in turn be used for either metal or pigment manufacture, a process to give the tetrachloride from ilmenite without the troublesome $TiCl_4$-$FeCl_3$ separation would be useful. If the chloride is regarded as the end product, large amounts of chlorine would be required.

The aluminium industry is at present undergoing rapid development in Australia. The need for large quantities of sodium hydroxide for Bayer process alumina plants could well bring a large amount of by-product chlorine on to the local market. This chlorine could become an embarrassment to a large producer, since it would present a major disposal problem.

There are large deposits of beach sand ilmenite in Western Australia, and on the East Coast of Australia. If chlorine were also available, a process for manufacture of titanium tetrachloride from ilmenite should offer excellent prospects and it seems reasonable to suppose that this would be a most convenient method of disposal of chlorine.

This report discusses the economic and technological aspects of the cyclic chlorination process for rutile production from ilmenite, with particular reference to a plant producing 50 tons daily. The modification of this basic process to give a partially cyclic system producing titanium tetrachloride from ilmenite is also examined.

2. SUMMARY

Following a slump in rutile prices over the past few years, a result of the reduced demand for titanium metal, world rutile prices are rising. This is attributed to the increasing use of rutile as a raw material for pigment manufacture by oxidation of titanium tetrachloride. There should be an opening for a process to produce rutile (selling at ca. £29/ton contained TiO_2) from ilmenite (selling at £8/ton TiO_2).

The cyclic chlorination process is suitable for application to ilmenites, so long as these contain less than about 2 per cent of chromium and manganous oxides, since these consume chlorine irreversibly under the process conditions.

Use of multistage fluid bed reactors is impracticable because of pumping difficulties arising from the high pressure drop across each bed of ilmenite. The high reaction rate in a fluid bed is highly desirable, and a system of batch reactors is proposed. Chlorine utilisation is estimated to be 25 per cent, compared with 40 per cent in a 3-stage continuous fluid bed.

Heating of the fluid bed is difficult as the chlorination is strongly endothermic, and use of reactors intermittently, with internal heating (cf. water gas producer practice) is suggested. Other engineering problems remain to be solved, but none are regarded as insoluble.

A plant to remove 50 tons of ferric oxide daily from ilmenite requires an estimated capital investment of £500,000 and should produce rutile containing less than 0.01 per cent Fe_2O_3 for £24.3/ton at Stradbroke Island or for £21.6/ton at Capel. This compares with a current price of £27/ton, and further development of the process is recommended.

The possibility of obtaining cheap by-product chlorine from the aluminium industry may enable production of titanium tetrachloride which could be marketed in New York at an estimated 13 cents per pound, using natural rutile. The latest available tetrachloride price in New York is 26½ cents per pound.

It is suggested that a 4-stage program of development should be followed -

(1) Firstly, to absorb chlorine as it becomes available, natural rutile could be shipped to the source of chlorine and used for manufacture of tetrachloride.

(2) When market conditions are suitable, the chlorination of ilmenite could be introduced but without re-cycling, using natural rutile also.

(3) If rutile prices continue to rise, the use of natural rutile could be discontinued and the process made partially cyclic by re-cycling the chlorine not required for the second stage chlorination.

(4) Ultimately chlorinating ilmenite by a fully cyclic process to produce rutile for sale, using surplus chlorine and some of the product rutile to make tetrachloride.

As this presupposes the existence of surplus chlorine, large aluminium or chlorine producers should be regarded as potential sponsors for this development.

Application of the cyclic chlorination process to iron ores is most unlikely to be economic, as the hematite product would probably cost at least £20 per ton.

3. THE BASIC PROCESS

The process which has been studied by the Research and Development Branch of the South Australian Government Department of Mines, and latterly by Australian Mineral Development Laboratories under the sponsorship of the South Australian Government, has been described by Ketteridge and Nordin[8]. In its simplest form there are three major steps:-

A. The oxidation of beach sand ilmenite with air, giving a mixture of pseudo-brookite and rutile.

B. The chlorination of the oxidised material, leaving a residue of rutile, and removing the iron as ferric chloride vapour.

C. Regeneration of chlorine for re-use by simply changing the temperature of the gas stream from stage B, when ferric oxide is deposited.

3.1 Oxidation of Ilmenite

The existence of large deposits of beach sand ilmenite in Australia made the use of this material the logical starting point. To carry out the reaction of ilmenite with gas, fluid bed reactors were used almost exclusively. The convenient and uniform particle size, ideal for fluidisation, and the high reaction rates associated with this technique, made the alternative packed bed much less attractive.

After initial difficulty with sintering, it was found possible to oxidise ilmenite with air or a nitrogen plus 10 per cent oxygen mixture at 1000°C in a fluid bed. The reaction was 95 per cent complete in about 30 minutes. The product, not much different in appearance from the raw ilmenite, was a mixture of pseudobrookite and rutile -

$$2FeO.\ TiO_2 + \tfrac{1}{2}O_2 \rightleftharpoons Fe_2O_3.\ TiO_2 + TiO_2 \qquad (1)$$

The heat of reaction was found to be minus 63,000 calories at 1300°K.

3.2 Chlorination of Oxidised Ilmenite

This process has also been studied in fluid bed reactors. A large amount of experimental data shows that the reaction -

$$6Cl_2 + 2Fe_2O_3 . TiO_2 + 2TiO_2 \rightleftharpoons 4FeCl_3 + 3O_2 + 4TiO_2 \qquad (2)$$

proceeds readily at high temperature. A temperature of 1100°C has been selected as most suitable, and equilibrium tests have shown that at this temperature about 44 per cent of the chlorine can be converted to ferric chloride. Rutile is attacked by chlorine to a smaller but still significant extent at this temperature. The resultant titanium tetrachloride is expected to attack pseudo-brookite fairly readily, reverting to ferric chloride and titania, so little tetrachloride should be produced in a multistage countercurrent reactor.

The heat of reaction for reaction (2) above was found to be plus 173,000 calories at 1300°K. The chlorination is quite selective between iron and titanium, and high grade titania products have been produced repeatedly. The oxide in these products is in the rutile form, but is not suitable for use as a pigment, as the particle size and shape are governed largely by the starting material and are quite different from those required.

Experimentally the chlorination rate, using pure chlorine gas was limited at first by the supply of chlorine, but decreased as the reaction proceeded. From a batch of ilmenite 99.5 per cent of the iron was removed in approximately 3 hours at 1100°C using the fluid bed.

3.3 Recovery of Chlorine

The extent of chlorination of pseudo-brookite according to equation (2) is fairly strongly temperature-dependent, as is the corresponding chlorination of ferric oxide

$$2Fe_2O_3 + 6Cl_2 \rightleftharpoons 4FeCl_3 + 3O_2 \qquad (3a)$$

$$4FeCl_3 + 3O_2 \rightleftharpoons 2Fe_2O_3 + 6Cl_2 \qquad (3b)$$

The fraction of chlorine which reacts by reaction (2) is less at any given temperature than by reaction (3a), and as the oxide products of (2) are solid and are not carried over in the gas stream, any reversion at lower temperatures will take place according to the reverse of equation (3a), i.e. by equation (3b).

There will however, be a small temperature range through which an equilibrium gas mixture from reaction (2) can be cooled before reaction (3b) will proceed. On further cooling the reaction will proceed, with deposition of ferric oxide. The extent of this reaction has been determined experimentally down to ca 800°C, at which temperature about 10 per cent of the chlorine remains combined as ferric chloride. The chloride which has been oxidised gives a deposit of a micaceous form of hematite. Over the range 800°C - 1100°C the heat of reaction (3b) is minus 160,000 calories.

At lower temperatures rather less chlorine remains in the gaseous phase as ferric chloride, but no experimental data is available and published results are conflicting. It is expected that no more than 0.1 per cent will remain combined at 500°C. On reducing the temperature still further there will probably be little effect until the ferric chloride begins to condense at about 300°C.

From the point of view of a cyclic process, with two reactors at different temperatures, the amount of iron carried by the gas stream depends on the difference between the combined chloride at the two temperatures. At 1100°C and 800°C this will be(44 minus 10)- 34 per cent, and at 1100°C and 500°C approximately 44 per cent, assuming that equilibrium is attained in each reactor. There would be no advantage in using a temperature lower than 500°C unless pumping of the regenerated hot chlorine is too difficult, in which case further cooling would be required. In any case the regenerated chlorine, containing only small amounts of ferric chloride and oxygen, is suitable for recycle to the chlorination stage.

Experimental difficulty has been experienced in carrying out the "reverse reaction", i.e. (3b), continuously. The gases, when being cooled, deposit hematite on any available surface. Use of a conventional heat exchanger is impossible as the surfaces would be fouled by deposits in a very short time. Attempts to introduce the gas into a fluid bed, baffled to give incomplete mixing and therefore maintain a temperature gradient, failed because the deposited oxide cemented the bed particles together. A method which may be suitable is to introduce cool, finely divided solid into the gas stream. This solid should serve the dual function of cooling the gases (absorbing both sensible heat and heat of reaction) and providing a large surface for deposition of oxide. The method has not yet been investigated experimentally.

3.4 Side Reactions

The beach sand ilmenite contains some metals other than titanium and iron. Although these are present in small amounts, they can have an appreciable effect on the overall process, particularly the chlorine requirement.

In a study of the thermodynamics of the chlorination process, Madigan[9] concluded that the following oxides could be chlorinated:-

CaO, CoO, FeO, Fe_2O_3, Fe_3O_4, Li_2O, MnO_2, Na_2O,

NiO, PbO, Ta_2O_5, TiO and ZnO.

Of these, FeO, Fe_3O_4, MnO_2 and TiO are unlikely to be present in an oxidised ilmenite. Experimental results, in general agreement with Madigan's calculations, indicate that iron, manganese, lead, tin and molybdenum are removed from the titanium by batch chlorination. Magnesium, zinc, chromium and nickel are reduced but not eliminated entirely - this may be a rate effect, these elements forming chlorides more slowly than the others.

In the presence of large amounts of ferric oxide and ferric chloride these other chlorides may not form so readily. The results mentioned are from batch tests in which most of the iron was removed in the early stages. This effect has been observed with titania, which chlorinates slightly at 1100°C -

$$TiO_2 + 2Cl_2 \longrightarrow TiCl_4 + O_2$$

but in the presence of ferric oxide the further reaction

$$3TiCl_4 + 2Fe_2O_3 \longrightarrow 4FeCl_3 + 3TiO_2$$

also proceeds and practically no titanium tetrachloride leaves the system.

Experimentally, small amounts of chromic chloride and manganous chloride have been observed as solid deposits in products collected in the back reactor. The chlorine in these compounds is effectively lost from the cyclic system. Thus manganous oxide reacts as follows with chlorine -

$$\underset{71}{MnO} + \underset{71}{Cl_2} \longrightarrow MnCl_2 + \tfrac{1}{2}O_2$$

and each ton of manganous oxide in the ilmenite would cause loss of a ton of chlorine, so the amount of manganese which can be tolerated in the raw material may be quite small.

A similar situation applies to chromium. There has also been evidence in some back reactors of deposits of ferrous chloride, $FeCl_2$. This compound is apparently formed by the decomposition of ferric chloride.

$$FeCl_3 \rightleftharpoons FeCl_2 + \tfrac{1}{2}Cl_2$$

It is difficult to imagine that this compound could form in sufficient quantity to exceed its vapour pressure when both chlorine and oxygen are present in large amounts, but a small amount has been observed repeatedly.

Any of these chlorides which condense appear in the back reaction product and could be recovered by leaching the ferric oxide but this procedure would probably be uneconomic. They also reduce the value of the oxide and complicate its handling by their hygroscopic nature which could lead to severe corrosion of plant by formation of HCl.

4. PROCESS FLOWSHEET

To enable a proper assessment of the process to be made, a flowsheet has been prepared for a plant to produce an arbitrary 50 tons of rutile product daily. The ferric oxide specification was fixed at 0.50 per cent, comparable with a good quality natural rutile. With continuous operation the plant would produce 17,500 tons per year, which is approximately the capacity of the larger beach sand plants.

The raw ilmenite was assumed to have the composition shown in Table 1.

TABLE 1: COMPOSITION OF ILMENITE

	per cent
TiO_2	50
FeO	35
Fe_2O_3	10

This is an arbitrary composition but similar to the material used in experimental work. The production of 50 tons of rutile daily therefore requires 100 tons of raw ilmenite.

The ilmenite is first heated to 1000°C and oxidised by air. To heat the ilmenite from ambient temperature to 1000°C requires 78×10^6 BTU per day. The reaction is exothermic to the extent of about 60×10^6 BTU per day, leaving the net heat requirement at 18×10^6 BTU daily.

The pseudo-brookite-rutile mixture now contains approximately 47 per cent each of TiO_2 and Fe_2O_3. A total of 106 tons per day is chlorinated at 1100°C. The chlorination reaction is endothermic, with an estimated heat requirement of 109×10^6 BTU per day, and in addition the solid feed has to be heated from 1000°C to 1100°C, requiring another 8×10^6 BTU.

The gas stream from the chlorinator, a mixture of chlorine, oxygen and ferric chloride, passes to the "back reactor" where it is cooled to 500°C. Ferric oxide is formed and chlorine regenerated, passing to the compressor at ca. 500°C. It is then reheated to 1100°C in the chlorine reheater.

The ferric oxide from the reverse reactor is cooled by air in a unit similar to that used for cooling the rutile product. The heat is rejected at about 400°C, too low for use in power generation. Part of the cool oxide - 50 tons daily -is withdrawn to storage.

Loss of oxygen is assumed to be small, as the oxygen content of the gas streams is low. As the oxidation of ilmenite in the first process stage has been assumed to be only 95 per cent complete, extra oxygen has to be supplied to keep the ferric chloride: oxygen ratio stable. The 5 per cent deficiency represents 0.30 ton daily, to be supplied as commercial oxygen, and this is 7,800 ft^3 at standard conditions. To assist in the back reaction the oxygen make-up goes to the back reactor, the chlorine make-up goes to the chlorine re-heater.

5. EQUIPMENT SPECIFICATION

Operation of the process outlined in the previous section calls for many items of equipment which are far from standard. The specification and design of these units is discussed in detail.

5.1 Chlorination Reactor

Because experimental data were available, fluid bed contacting was assumed in the first instance. Production of rutile containing 0.50 per cent ferric oxide requires a 3-stage countercurrent reactor operating at 1100°C, with a solids retention time estimated to be 4.7 hours per stage. For a throughput of 100 tons of oxidised ilmenite daily, the expanded or working bed volume for each stage is 300 cubic feet.

Choice of height: diameter ratio is governed by the chlorine mass flow rate, i.e. the velocity required to maintain fluidisation. In the small scale equipment it was found necessary to use a chlorine rate equivalent to 5.3 tons per square foot of reactor cross-section per day. Higher rates caused entrainment of solids, while the lower limit to maintain satisfactory fluidised conditions in the beds was about 2.9 tons/ft^2 day.

With the ilmenite feed rate fixed, the amount of Fe_2O_3 to be removed is known. The fractions of combined chlorine from the chlorination and reverse reactors were assumed to be 40 per cent and 3 per cent giving a differential of 37 per cent. This is slightly less than the equilibrium value given in 3.3 above. To remove 50 tons of ferric oxide is found to require 180 tons of chlorine, and this becomes the daily mass throughput. The bed cross-section is fixed at $\frac{180}{53}$ = 34 square feet, or 6.6 ft diameter.

For a 3-stage fluid bed reactor the required retention time of 4.7 hours per stage requires a stage working volume of 300 cubic feet, and the bed depth is then $\frac{300}{34}$ = 8.8 feet per stage. Pressure drop over 3-stages becomes 39.6 psi which exceeds the practical value for such an operation.

By reducing the mass flow to its lower limit of 2.9 tons/day, the diameter can be increased to 8 ft and the pressure drop is then 27 psi, still much too high. Recalculation of the retention times on the basis of 2-solid stages, with the lower one baffled to reduce back-mixing, may reduce this to 18 - 20 psi but no further. Thus the use of multiple fluid bed contacting is rendered quite impracticable by the high pressure drops involved.

The use of packed beds is not attractive as the process relies on achieving a close approach to equilibrium in the chlorination stage and this requires extremely low flow rates in other than fluid beds. The very large cross-section required for this arrangement complicates the problem of heating the interior of the bed.

The most critical stage of a fluid bed contactor, from the point of view of chlorine utilisation, is the first solid stage. This suggests the possibility of using only a single fluid bed to give good chlorine utilisation, subsequent stages being replaced by some alternative arrangement such as a rotary kiln, in which the solids retention time could be quite high.

The types of compressors likely to be suitable for handling chlorine at 500°C include turbo-blowers (multi-stage), Roots Blowers or similar rotary designs, and Nash Hytor pumps. In the latter case a liquid seal is required and a fused salt mixture may serve. For any of these machines the operating pressure is limited to about 10 psi.

A single fluid bed 6.6 ft diameter and 8.8 ft deep still has a rather high pressure requirement and can be modified to 8 ft diameter and 6 ft deep as discussed above. Pressure drop of 9 psi is then within the limits imposed by the compressor.

With these dimensions the area of reactor wall around the bed is 151 sq ft. For the first stage, requiring a heat input of 80 x 10^6 BTU daily, and allowing a temperature differential across the reactor wall of 300°C (540°F), an overall heat transfer coefficient of 41 BTU/ft^2 hr °F is required. With forced convection gas heating on the exterior of the reactor an outer film coefficient of perhaps 10 BTU/ft^2 hr °F may be realised so the simple arrangement is quite inadequate. A film coefficient of 100 BTU/ft^2 hr °F can be obtained between a fluid bed and its containing vessel, so transfer from one bed to another via a wall of high conductivity would give ca 50 BTU/ft^2 hr °F. The refractory wall may be of alumina brick or silicon carbide, and coefficients for 4-inch thicknesses of these materials are about 6 and 20 respectively. External heating of a simple cylindrical reactor is thus not practicable, even when the added complication of a metal gas-tight shell is neglected, and the chances of maintaining a leak free brickwork system without a metal casing are remote. The situation could be improved somewhat by using an annular reactor, with heating from fluid beds both internally and externally, but the arrangement becomes cumbersome.

The use of a metal shell at high temperature introduces material problems as few metals will withstand continuous operation at 1300°C, and heat transfer from shell to refractory is likely to be poor - differential expansion will almost certainly leave appreciable gaps in the conduction paths. Heat could be introduced through tubes passing through the bed, but it is difficult to pack more transfer surface into the bed than is available at the wall, and plumbing is again difficult.

Alternatively the bed could be heated by circulating the solids through an external heater. Assuming that the solids could be heated to 1300°C without sintering, a circulation rate of 440 tons/day is required to introduce 80 x 10^6 BTU. This introduces the problem of solids handling through a chlorine seal at 1300°C, an operation which may be quite difficult.

By using a number of smaller reactors a greater heating surface can be obtained and the use of a thinner walled silicon carbide monolith becomes possible. With a 3-inch thickness of carbide and no metal shell (assuming the walls to be impervious) an overall heat transfer coefficient of perhaps 20 BTU/ft^2 hr °F may be achieved with fluid beds on each side. Allowing a temperature differential of 300°C (540°F) this leads to four reactors just under 4 ft in diameter and 6 ft deep, operating with parallel gas flows. If silicon carbide is found to be unsuitable, alumina bricks could be used, but the likely overall coefficient of ca 6 BTU requires use of much smaller reactors - 1.2 ft diameter if the depth is left at 6 ft. To process 50 tons of rutile daily would then require about 50 reactors.

Electrical heating, estimated to be at least twice as expensive as oil, has also been considered. Resistive heating, using silicon carbide heaters, depends on stability of the carbide to chlorine, and as this is in doubt at 1100°C, it is even more so at 1300°C or above, at which temperature the heaters would operate. Graphite is also unsuitable as it would be attacked. Self-resistance of the bed could possibly be used but voltages of the order of 1000 volts/meter of path length are required, and as most electrical insulators likely to be resistant to chlorine become conducting at the required operating temperature, high voltages are best avoided. Radiant heating from panels set in the reactor walls and radiating on to the bed surface is also impractical because of the expected high absorption of ferric chloride vapour in the infra-red - the gas would be heated rather than the bed. Inductive heating suffers from the same disadvantages as direct heating in that the heat would be generated in the metal shell and would transfer into the bed by conduction only.

Use of one or more multistage fluid bed reactors is therefore excluded by two separate considerations - the high pressure drop in the gas stream, and the difficulty of heating the beds.

All the above considerations apply to continuous operation, but it may be possible to operate a reactor intermittently. In this case - cf gas producer practice - the bed, fluidised with air, could be heated by direct injection of fuel oil to a temperature of perhaps 1200-1300°C. The gas stream would then be changed and chlorine introduced. The temperature would fall slowly as the reaction proceeded. When the bed cooled to 1100°C, the gas stream would again be changed to air, and the cycle repeated. It is estimated that reaction times of 1 hr would require heating at 1300°C in the top bed, and this should not be impossible provided that suitable plumbing can be devised. Two reactors would be necessary to keep the remainder of the plant operating continuously. Normal aluminous refractories would be suitable, and these are resistant to chlorine.

For the remaining stages of the chlorination a rotary kiln is suggested as this can be operated continuously. Indirect firing is required, and the kiln is required to operate under pressure. This is unorthodox, but there seems no valid reason why such a system could not be operated successfully.

Another possibility is the use of a number of batch fluid beds in parallel. Each bed of ilmenite would then be oxidised and chlorinated in situ, and the difficulties of gas sealing in solids handling would be avoided. Chlorine utilisation would fall as the reaction proceeded, but in the later stages of chlorination the quality of fluidisation and the chlorine flow could be reduced as the solids would not then sinter. Operation of a number of units in parallel would reduce the dilution effect of those in which the reaction was well advanced.

These units could be externally heated as discussed earlier. The initial reaction rate in a batch bed is higher than in a continuous bed, and larger heat inputs are required in the early stages. This reduces the maximum diameter, with 2-inch silicon carbide walls, to 2.8 ft. If the depth is left at 6 ft, 12 reactors are required to give the 50 tons/day output.

Each of these reactors requires a separate heating bed, although two or at most three could perhaps be built into a unit. The oxidation would be carried out in the same reactors at 1000°C, so all vessels of a unit must operate at the same temperature, and to the same time cycle. The heating bed would be held at perhaps 1050°C during oxidation, then at 1300°C, falling gradually to 1100°C, during chlorination, controlled to maintain the temperature constant in the inner bed. Higher temperatures in the chlorination should be avoided, as these would increase loss of rutile as titanium tetrachloride. The average overall chlorine utilisation in small scale batch tests has been 20-25 per cent. The upper limit should be at least equalled and probably exceeded in larger equipment. In a single bed the utilisation is over 40 per cent initially and falls to zero at completion of the reaction. Staggering of the cycles of multiple reactors should eliminate most of the fluctuation and give a gas stream to the reverse reactor containing at least 25 per cent combined chlorine.

This batch operation is based on external heating through silicon carbide walls. As mentioned previously, there is some doubt as to whether this material is sufficiently resistant to chlorine under operating conditions. Madigan (loc cit) chlorinated some powdered carbide and found 30 per cent loss in weight over several hours. A specimen exposed in a 3-inch fluid bed reactor during a chlorination experiment showed some signs of attack, but insufficient to cause rejection as unsuitable. Full experimental evaluation of the material is urgently required.

If silicon carbide is found to be unsuitable, indirect heating of a reasonable size of reactor is virtually impossible. The direct firing, intermittent operation described previously is one way of avoiding the heat transfer problem, but the use of a kiln to complete the reaction is not without drawbacks for engineering reasons. This leads to the idea of reactors operated batch-wise to completion of chlorination, with internal heating cycles as required during the run, i.e. a combination of the other two possibilities. In this case the restrictions on the size of reactor no longer apply, and any suitable refractory can be used, regardless of its thermal conductivity. Solids handling is reduced to a minimum, although the gas handling is rather more complicated. To permit continuous operation of the back reactor, use of perhaps 4 chlorinators, with staggered cycles, would be required. Chlorine utilisation should be 25 per cent or better. It is suggested that this method offers the best compromise between engineering simplicity and operational efficiency.

One other advantage of batch operation is the low residual iron content in the product. This should be of the order of 0.01 per cent Fe_2O_3, compared with 0.5 per cent from the 3-stage continuous reactor mentioned earlier. This may give the product a significant market advantage over natural rutile, and may even sustain a useful price differential.

5.2 Preheater - Oxidiser

Experimentally the oxidation has been carried out in a fluid bed reactor, and on the larger scale this could be done, but once again the high pressure drop required for multi-stage operation becomes a problem. With the chlorination system described above, preheating and oxidation can be carried out in the chlorination reactor, and no extra equipment is required.

5.3 Product Cooler

The solid product from the chlorinator emerges at 1100°C and offers a good source of waste heat - about 40 x 10^6 BTU daily - if this is required. Use of a fluid bed outside of boiler tubes to generate steam may be somewhat unconventional but quite efficient. Alternatively the air for the heating cycle of the chlorinators could be preheated by contact with the rutile in a shallow bed cooler, e.g. a Link-Belt Fluid-Flo cooler or similar device with a low gas pressure drop.

5.4 Back Reactor

The back reaction has been found to be difficult to control on the small scale, but should be considerably easier in larger equipment. This is in direct contrast to the chlorination, which is more difficult on the plant scale.

The general problem is to remove some 215 x 10^6 BTU daily from the gas stream. Of this total slightly more than half is sensible heat, while the remainder is generated by the exothermic reaction. These two sources of heat cannot be separated, and any removal of heat (below the "saturation" or equilibrium temperature) will cause deposition of ferric oxide. In a normal tubular heat exchanger, or in a brickwork recuperator or similar device, this deposit would rapidly render the system inoperative.

The heat can only be removed by direct contact with a cool mass, and in principle this could be solid, liquid, or gaseous. These possibilities are discussed in turn.

5.4.1 Cooling with Solid

Introduction of cold solid into the gas stream in controlled amounts should be a fairly simple operation. The solid, in being heated, would provide also the nuclei on which the reaction product could deposit. The obvious choice is ferric oxide, recycled from earlier contact, probably through a ball mill to reduce the tendency for continued increase in particle size. Removal of heat from the solids should not present any difficulty. Contact time between solid and gas in a chamber of practical size could be of the order of 10 seconds and this should be ample time for the reaction to go almost to equilibrium[16].

To remove 215 x 10^6 BTU daily requires a circulating load of 700 tons per day of ferric oxide, with heating over an interval of 400°C.

5.4.2 Cooling with Liquid

The mechanism of cooling with a liquid would be similar to that of the solid - gas system, but the droplets of liquid may not be such good nuclei for solid growth as the hematite particles. Contact time would be of the same order as before.

Choice of a suitable liquid is restricted. No organic liquids are known which are completely resistant to chlorine or to temperatures of 500°C. Inorganic materials most likely to be suitable are molten chlorides, and these usually have high melting points. Low melting eutectics can be used but only over a restricted temperature range. The eutectic ferric chloride - sodium chloride, melting at 158°C, may be suitable. Circulating load here would be about 800 tons/day or 60 gallons/minute. The oxide would have to be removed from the salts by filtration and this may be difficult as the particle size could be quite small. Pumping of the salt mixture should not be difficult. Cooling should also be fairly straightforward, although some care would be necessary to prevent freezing of the material on the heat exchange surfaces.

5.4.3 Cooling with Gas

By mixing the hot gas stream with a cool one, the required temperature could be achieved. The cooling gas could only be chlorine, as other gases would require subsequent separation. Dilution of the incoming gases with chlorine would tend to slow the reaction somewhat, but as the oxidation of the ferric chloride should go virtually to completion no displacement of the equilibrium would be encountered. Contact times to reach equilibrium may be significant, but mixing of the gases is most likely to control the rate.

The mechanism of the reaction is not known and a cloud of fine ferric oxide may be produced, which could be very difficult to handle. If a surface could be provided, e. g. by introduction of the gases into a fluid bed, the product would probably deposit in a better form. The bed material would again be ferric oxide, and circulation through a mill would be necessary to control the particle size.

To remove the 215 x 10^6 BTU daily requires a circulation of 1130 tons of chlorine, with heating over 400°C - this represents about 12,000 cfm at 100°C. Cooling of this gas must be carried out indirectly and large surfaces would be required.

Contact time between the gases and the fluid bed would be much shorter than in the two other cases - about 0.1 second - and this may not be sufficient to establish equilibrium.

5.4.4 Discussion

In examining the heat transfer in the systems, it becomes apparent that the gas system is least favourable, as large surfaces would be required for rejection of the heat. The best is the solid - gas system, since the solid could be cooled by direct contact with air.

The respective residence times are probably important also, as the short contact in the fluid bed of the gas - gas system may be insufficient to approach equilibrium, leading to deposition of solid in other parts of the system. This could be overcome by cooling in stages, with a considerable increase in complexity of the system.

In the absence of any experimental information, the solid cooling system appears most likely to succeed. A preliminary design can be carried out from first principles with reasonable certainty, and for estimating purposes this arrangement is assumed. The reactor is a large chamber, 15 ft diameter and 25 ft high into which the gas stream and solids are introduced at the top. The solid collects in a fluid bed at the bottom of the chamber. The gases pass upward through an annular disengagement zone to the chlorine compressor.

5.5 Oxide Cooler

The heat from the back reactor would be rejected in the oxide at 500°C, and would not be worth recovering at this temperature. For simplest cooling of the oxide, water sprays could be used but any chlorides would then give HCl which may cause corrosion troubles. In the absence of HCl a useful amount of process steam could be generated. Alternatively the oxide could be cooled by air - a fluid bed may be useful here, or a combination pneumatic cooler-conveyor.

5.6 Chlorine Compressor

This unit has been mentioned previously. Use of a Roots or similar blower would not be sound practice because of the possibility of corrosion and the need to maintain small working clearances in the casing. A turbo-blower would be more practical, as the clearances could be larger, but the high rotational speeds would require materials with exceptionally good high temperature strength. Resistance to chlorine would also be required, and the only metals suitable are the noble metals and a few nickel alloys - the latter may be most appropriate. The Nash compressor with molten salt sealing, offers an interesting possibility but no specific information on the application is available and the manufacturers would have to be approached.

5.7 Contamination of Gas Stream

With intermittent operation of the chlorination reactors, some air would be introduced into the chlorine circuit. To keep dilution within reasonable limits it would be necessary to bleed off a portion of the circulating gas continuously. In a system operating in a non-cyclic or partially cyclic manner, this would not be necessary, but in fully cyclic operation it is essential.

The bleed would be taken from the lowest temperature part of the cycle, i.e. after the gas leaves the back reactor, and to facilitate handling it may be taken from the high pressure side of the chlorine compressor. The gas would consist mostly of chlorine, with minor amounts of ferric chloride, oxygen, nitrogen, hydrogen chloride and oxides of carbon. Only the chlorine would be worth recovering, and this could be achieved by compression and cooling to condense liquid chlorine. The need to carry out this operation is a good argument against a fully cyclic process.

While contamination of the gas stream is one problem, another associated problem is the converse, i.e. loss of chlorine from the circuit. In properly maintained equipment mechanical losses must be quite small, for leaks large enough to be significant in relation to the gas load would quickly render the plant area uninhabitable.

Chlorine loss could occur in two other ways:-

(a) losses by fixation, as discussed in section 3.3 above, and

(b) mechanical losses associated with the intermittent operation of the chlorinators.

The volume of each batch chlorinator is about 750 ft^3. If it is assumed that this amount is lost at the end of each cycling operation, with a cycle time of 1-hour, the average loss is 12.5 cfm or a quarter of 1 per cent of the gas load. For estimating purposes a loss of 1 per cent is assumed and this should be ample to cover losses except with a feed material grossly contaminated with manganese or chromium.

6. PRODUCT COST

To enable preparation of a cost estimate, a full flowsheet with material and energy balances has been prepared. A capital estimate is given in Appendix A. Other cost factors are examined in the following sections.

In calculating the material and energy balances for the flowsheet, the ilmenite composition was assumed to be as shown in Table 2, and although this is typical of the material used experimentally, it is not a particularly good ilmenite. It is a magnetic concentrate prepared from crude Stradbroke Island ilmenite, and is regarded as almost worthless because of its high chromium content, about 0.2 per cent Cr_2O_3. Some samples of this material have contained up to 1.6 per cent of manganous oxide, and allowance is made for loss of chlorine in formation of manganous chloride.

The plant is essentially one for removal of ferric oxide from the feed material, and if this contains a lower proportion of iron, the output of titania can be increased to keep the ferric oxide transfer constant. In estimation of costs, this is taken into account and where ilmenite from Capel is used, the composition is that shown in Table 2.

TABLE 2: COMPOSITION OF CAPEL ILMENITE
per cent

FeO	13
Fe_2O_3	30
TiO_2	55

6.1 Raw Material

When handling low cost materials such as ilmenite, freight costs become a large proportion of the total at any place remote from the mineral deposit. For this reason the location of a plant consuming the material has a large effect on product cost. In the following estimate, plants located at the following sites are considered: -

1. Adelaide, for comparison purposes.
2. Stradbroke Island, Queensland, because of the availability there of otherwise worthless ilmenite.
3. Capel, Western Australia, where high quality ilmenite is produced.
4. Invercargill, New Zealand, where chlorine may be available as a by-product of sodium hydroxide production, and
5. Geelong, for the same reason.

Material costs at these places are considered in turn.

6.1.1 Adelaide

Current price for ilmenite at Capel[2] is £4/ton. Cartage to the nearest port, Bunbury, together with wharfage charges there are estimated at 30/- per ton. Adelaide Steamship Co. have estimated £5/ton freight for 5000 ton cargoes from Bunbury to Osborne, with bulk handling at each end. Handling from Osborne to a plant at e.g. Birkenhead at 10/- ton makes the cost of ilmenite £11/ton.

Fuel oil is estimated to cost £11.5 per ton, and oxygen £3-2-6 per 1000 ft^3 (Commonwealth Industrial Gases Pty. Ltd.).

Chlorine from Imperial Chemical Industries is quoted at £76-6-0 per ton fob Melbourne, with freight, including return of empty cylinders, costing £19/ton, making £95.3/ton

These figures are shown in Table 3, calculated on the basis of 50 tons of Fe_2O_3 removed daily - for Capel ilmenite this corresponds to 61.8 tons TiO_2 product from 112 tons raw ilmenite.

TABLE 3: RAW MATERIAL COST - ADELAIDE

Material	Quantity/day		Price	Cost per ton TiO_2
Ilmenite	112	tons	£11/ton	£19.9
Fuel oil	13.5	tons	£11.5	2.5
Oxygen	7,800	ft^3	£ 3.2.6	0.4
Chlorine	2.22	tons	£95.3	3.4
			Total	£26.2

6.1.2 Capel

Fuel oil and oxygen prices are assumed to be 10 per cent higher than in Adelaide. Chlorine is available in Western Australia at Kwinana[1] and freight to Capel is estimated at £3/ton. If the Kwinana price is assumed to be the same as the I.C.I. Melbourne figure the Capel cost becomes £79.3/ton. On this basis the raw material costs are shown in Table 4.

TABLE 4: RAW MATERIAL COST - CAPEL

Material	Quantity/day		Price		Cost per ton TiO_2
Ilmenite	112	tons	£ 4/ton		£ 7.3
Fuel oil	13.5	tons	£12.7		2.8
Oxygen	7,800	ft^3	£ 3.44		0.4
Chlorine	2.22	tons	£79.3		2.8
				Total	£13.3

6.1.3 Stradbroke Island

Ilmenite, unsuitable for normal use, is available in dumps on the island. With a magnetic separation a product suitable for the present purpose is obtainable at about 60 per cent recovery and an estimated cost of £1-5-0 per ton.

Chlorine from Sydney at £76.3/ton, plus freight, calculated from the Adelaide figure, £27.3/ton, costs £103.6 per ton.

Oil and oxygen are estimated at the same rate as at Capel. Using the composition shown in Table 1 gives, - with 50 tons each of ferric oxide and titania daily - the raw material costs shown in Table 5.

TABLE 5: RAW MATERIAL COST - STRADBROKE ISLAND

Material	Quantity/day		Price		Cost per ton TiO_2
Ilmenite	100	tons	£ 1.25		£ 2.5
Fuel oil	13.5	tons	£ 12.7		3.4
Oxygen	7,800	ft^3	£ 3.44		0.5
Chlorine	3.84	tons	£103.6		7.9
				Total	£14.3

6.1.4 Invercargill

Fuel oil and oxygen prices are 20 per cent above those at Adelaide. Chlorine is assumed to cost £A30/ton, available locally as by-product of hydroxide manufacture.

It is assumed that ilmenite from the Westport region of New Zealand is available, comparable in quality with the Stradbroke Island material, although this may be optimistic[10]. Freight from Westport to Invercargill is estimated at three pence per ton mile for 460 miles. Ilmenite then costs £9.25 at Invercargill if the Westport price is £4/ton.

TABLE 6: RAW MATERIAL COST - INVERCARGILL

Material	Quantity/day		Price	Cost per ton TiO_2
Ilmenite	100	tons	£A 9.25	£18.5
Fuel oil	13.5	tons	£A13.8	3.7
Oxygen	7,800	ft^3	£A 3.75	0.6
Chlorine	3.84	tons	£A30	2.3
			Total	£25.1

6.1.5 Geelong

Two cases are considered here. Ilmenite as in Table 1 from Stradbroke Island at £1-5-0 per ton plus an estimated £4/ton freight is used in Table 7. Alternatively Table 8 is based on Capel ilmenite at £4 per ton plus an estimated £6 freight. Oil and oxygen are the same as in Adelaide, and chlorine is assumed available at £30 as a local by-product, since this is the only justification for the site.

TABLE 7: RAW MATERIAL COST - GEELONG
Stradbroke Island Ilmenite

Material	Quantity/day		Price	Cost per ton TiO_2
Ilmenite	100	tons	£ 5.25	£10.5
Fuel oil	13.5	tons	£11.5	3.1
Oxygen	7,800	ft^3	£ 3.125	0.5
Chlorine	3.84	tons	£30	2.3
			Total	£16.4

TABLE 8: RAW MATERIAL COST - GEELONG
Capel Ilmenite

Material	Quantity/day		Price		Cost per ton TiO_2
Ilmenite	112	tons	£10		£18.1
Fuel oil	13.5	tons	£11.5		2.5
Oxygen	7,800	ft^3	£ 3.125		0.5
	2.22	tons	£30		1.1
				Total	£22.1

6.2 Labour Costs

For four shift operation, with three operators and a leading hand per shift, three maintenance man and one clerk, with a superintendent, Ketteridge and Nordin[11] estimate the wage bill as £400 weekly. Adding 50 per cent for long service, annual and sick leave, and overtime etc., makes £600 weekly. This is taken as the Adelaide figure and for other sites is adjusted in proportion to the local basic wage. For New Zealand the Adelaide figure is used. Based on the same ilmenite as in the raw material estimates the labour costs are given in Table 9.

TABLE 9: LABOUR COSTS

Location	Cost per ton TiO_2
Adelaide	£1.39
Capel	1.43
Stradbroke Island	1.72
Invercargill	£A1.71
Geelong - Stradbroke Island	£1.74
Geelong - Capel	1.41

6.3 Power Costs

The installed horsepower is 642. Putting both load factor and efficiency at 80 per cent, and using power at 1.5 pence per unit in Adelaide, Capel and Stradbroke Island, 1.0 pence at Geelong and 0.5 pence in New Zealand, power costs are as shown in Table 10.

TABLE 10: POWER COSTS

Location	Cost per ton TiO_2
Adelaide	£1.2
Capel	1.2
Stradbroke Island	1.5
Invercargill	£A0.5
Geelong - Stradbroke Island	£1.0
Geelong - Capel	0.8

6.4 Depreciation and Maintenance

These are taken as 15 per cent and 10 per cent of the fixed capital annually. The capital requirements are increased by 5 per cent for Capel and 10 per cent for Invercargill.

6.5 Miscellaneous Costs

To cover interest,rates and taxes, plus minor items, this is put at 10 per cent of the total capital.

6.6 Summary

The figures for the various cost items are collected in Table 11.

From the totals can be deducted allowances for the sale of ferric oxide and waste heat. If the oxide could be sold e. g. to Japanese buyers as a source of iron, it may bring £1 per ton, reducing the rutile cost by £1 when using Stradbroke Island ilmenite or £0. 8 when using the Capel material. Recovery of waste heat is possible and credits are allowed for this at Adelaide, Stradbroke Island and Capel only - waste heat is probably worthless in New Zealand and little better at Geelong in competition with the cheap thermal power probably available for aluminium reduction.

6.7 Discussion

The current market price[2] for natural rutile is £27/ton so clearly the process is uneconomic at present anywhere other than at Capel or on Stradbroke Island, although it may be regarded as marginal at Geelong. The cost figures bring out a number of points: -

(a) The best site for a plant of this nature is at the source of the ilmenite. More of this material is consumed than any other, and freight costs are prohibitive away from the sand deposits.

(b) A worthwhile reduction in cost can be achieved by using a high quality ilmenite, as in the case of Capel, and use of the Stradbroke Island product can only be justified by its low first cost. The high chromium content which makes this material worthless for wet methods of pigment manufacture is not expected to detract from its value in the present context, but the high manganese content causes high chlorine consumption.

(c) Availability of low cost chlorine at either Stradbroke Island or Capel would reduce the product cost appreciably to a figure much below current rutile costs.

There remains the possibility that the rutile product on which the estimates are based may command a higher price than the less pure natural rutile, but no information is available at present on this aspect.

With the reservations made previously about the practicability of the process, there is every indication that rutile could be produced from Capel ilmenite at a price up to 20 per cent, and from Stradbroke Island material at about 10 per cent below current markets quotations.

7. MODIFICATIONS TO THE PROCESS

A modified version of the process, with complete ferric chloride removal from the gas stream before re-cycling was also considered. The circulating gas load can be reduced slightly but this is more than offset by the increased pumping costs in the recovery circuit and the product cost is estimated to be £0.2/ton higher.

Use of mechanical compressors for chlorine could be eliminated by using a jet pumping system, with fused salts as the working fluid. This is a distinct possibility and the design should not be unduly difficult.

The pumping problem is then changed to one of handling large amounts of fused chlorides at 500°C. This too, is possible, but pumps for this duty, e.g. electromagnetic pumps, are notoriously inefficient and power costs would increase perhaps by a factor of four or five. The chlorine pumping power is only about a third of the total, so at worst the total power cost would be about double the estimated figure, and this could not be regarded as prohibitive if the process were satisfactory from all other aspects.

Changes in the product specification with respect to iron would not alter the design of the chlorination reactors and the overall effect on cost would be quite small. The cost is governed primarily by the amount of ferric oxide removed, as this fixes the gas load, back reactor specification and energy requirements.

From the opposite view-point, the chlorination can be regarded as a means of upgrading ferric oxide, and should be applicable to low grade iron ores. This has been examined experimentally and within the limits imposed by chlorination of other oxide impurities, found to be quite effective. Cost-wise, using the figures derived for ilmenite, the ferric oxide would be a most expensive product, (ca £25/ton) and although it would be a first quality hematite, it is most unlikely to be saleable at this price.

Chlorine is normally purchased as liquid and has a high vapour pressure - 5 atmospheres at 10°C. This suggests that pumping could be eliminated by using the vapour pressure to force the gases through the process. The pumping energy is then supplied as heat. No recycling is possible in this case except by liquefaction of the chlorine in the effluent gas stream. The chlorine cannot be discarded, because of its cost and also because of its toxicity, and a once-through process could only succeed if the gas could be fixed in some other product. Titanium tetrachloride is one such product.

As shown in the flow-sheet, to remove the iron from 100 tons of ilmenite requires 296 tons of chlorine at 25 per cent utilisation. After passage through a back reactor and other purifying stages if required, this chlorine is available for re-use. To chlorinate the 50 tons of rutile product daily, in the presence of carbon, requires 90 tons of chlorine, leaving a surplus of 206 tons still to be used. This would chlorinate a further 115 tons of natural rutile. Thus a plant could be designed to use ilmenite, rutile and chlorine in the proportion 1:1.15:2.06, producing titanium tetrachloride and leaving a ferric oxide by-product.

Such a plant would be smaller than the one discussed previously, as 296 tons of chlorine daily is not available in Australia at present, and is unlikely to be available at any one place in this area in the foreseeable future. The proposal is discussed in detail in the following section.

TABLE 11: COST OF PRODUCT RUTILE

Item	Adelaide	Capel	Stradbroke I	Invercargill	Geelong	
					Stradbroke I.	Capel
Ilmenite	£19.9	£ 7.3	£ 2.5	£A18.5	£10.5	£18.1
Fuel oil	2.5	2.8	3.4	3.7	3.1	2.5
Oxygen	0.4	0.4	0.5	0.6	0.5	0.4
Chlorine	3.4	2.8	7.9	2.3	2.3	1.1
Labour	1.4	1.4	1.7	1.7	1.7	1.4
Power	1.2	1.2	1.5	0.5	1.0	0.8
Depreciation	4.3	4.5	5.3	5.8	5.3	4.3
Miscellaneous	2.5	2.5	3.0	3.3	3.0	2.5
Total	35.6	22.9	25.8	36.4	27.4	31.1
Credits: Oxide	0.8	0.8	1.0	1.0	1.0	0.8
Waste heat	0.5	0.5	0.5	-	-	-
Final Cost	£34.3	£21.6	£24.3	£A35.4	£26.4	£30.3

8. PRODUCTION OF TITANIUM TETRACHLORIDE

For the present purpose it is assumed that 50 tons of chlorine per day is available in the Invercargill area of New Zealand. From published information on the Bayer Process and the activities of Comalco, this is a reasonable estimate of the amount of by-product chlorine to be produced. A similar amount is assumed to be available at Geelong.

At the 25 per cent chlorine utilisation used in previous calculations, the 50 tons should be sufficient to remove all the iron from 17 tons of the Stradbroke Island ilmenite, leaving 8.5 tons of rutile. The 50 tons of chlorine, after recovery, is sufficient to chlorinate 28 tons of titanium oxide, so an additional 19.5 tons of natural rutile could be treated to produce in all 63 tons of tetrachloride. To make each ton of titanium tetra-chloride then requires 0.33 tons of natural rutile, 0.27 tons of ilmenite and 0.79 tons of chlorine. Reagent costs at various locations are estimated below.

8.1 Stradbroke Island

Using chlorine from Invercargill at £30/ton plus six pence per ton mile to allow for return of cylinders, gas cost at Stradbroke Island is £66/ton. This is used to amend the previous estimate for "synthetic" rutile, which now becomes £21.5/ton. Because of the reduced scale of operation this is increased by 20 per cent to £25.8/ton. Reagent costs are shown in Table 12. Additional minor reagents include coke 0.1 ton, metallic zinc 0.01 ton and sodium hydroxide 0.005 ton per ton of product - these last two items could be replaced by fuel oil or metallic copper with little change in cost.

TABLE 12: REAGENT COST - STRADBROKE ISLAND

Material	Price	Cost/ton $TiCl_4$
Chlorine	£66	£52.1
Natural Rutile	£27	9.0
Product Rutile	£25.8	3.5
Minor	-	2.8
	Total	£67.4

8.2 Invercargill

Here natural rutile is assumed to come from Stradbroke Island and to cost £27/ton plus freight at three pence per ton mile, making £45.1/ton. Rutile from ilmenite is taken as £35.4 + 20 per cent = £42.5/ton. The detailed reagent costs are shown in Table 13.

TABLE 13: REAGENT COST - INVERCARGILL

Material	Price	Cost/ton $TiCl_4$
Chlorine	£30	£23.7
Natural Rutile	£45.1	15.0
Product Rutile	£42.7	5.8
Minor	-	2.8
	Total	£A47.3

8.3 Geelong

Ilmenite from Stradbroke Island is treated to give rutile at £26.4 + 20 per cent = £31.7/ton. East Coast rutile at £27 is taken to cost £31 at the plant. Detailed costs are shown in Table 14.

TABLE 14: REAGENT COST - GEELONG

Material	Price	Cost/ton $TiCl_4$
Chlorine	£30	£23.7
Natural Rutile	£31	10.3
Product Rutile	£31.8	4.2
Minor	-	2.8
	Total	£41.0

8.4 Discussion

Costs of rutile from ilmenite have been taken as 20 per cent higher than the estimates of Table 11 because of the smaller scale of operation. This may be a rather higher margin than is justifiable, since elimination of re-cycling should introduce significant economies.

Under present conditions there is little justification for use of the prepared rutile in preference to natural rutile, unless the higher purity is a significant advantage. The figures in Tables 12, 13 and 14 show that the cost advantage is very slight. If the market price of rutile continues to rise, the advantage may be come significant. As natural rutile reserves are known to be limited, and as the demand is increasing, a rising market can be expected for some years, and the once-through process should be a worthwhile proposition. With cheap chlorine available the manufacture of titanium tetrachloride offers a useful outlet and it is suggested that development of such a project could be carried out in four stages :-

(1) Firstly, to absorb chlorine as it becomes available, natural rutile could be shipped to the source of chlorine and used for manufacture of tetrachloride.

(2) When market conditions are suitable, the chlorination of ilmenite could be introduced but without recycling and using natural rutile to absorb the chlorine as described earlier.

(3) If the rutile prices continue to rise, the use of natural rutile could be discontinued and the process made partially cyclic, recycling the chlorine not required for the production of titanium tetrachloride.

(4) Ultimately, chlorinating ilmenite by a fully cyclic process to produce rutile for sale, using surplus chlorine and some of the product rutile to make tetrachloride.

Ideally stages (1), (2) and (3), should be located at the chlorine supply, while stage (4) would require operation at two sites - the source of ilmenite and chlorine. New Zealand is at a disadvantage here, as supplies of ilmenite of suitable quality may not be available locally, and it would be uneconomic to ship both rutile and ilmenite from Australia - rutile alone would be preferable.

As a further indication of the value of item (1) outlined above, estimates of the cost of tetrachloride have been prepared. The capital cost of the plant is estimated in Appendix B. The plant is taken to require 50 tons of chlorine and 28 tons of rutile daily to produce 67 tons of tetrachloride. Coke breeze, 10 tons daily, is also required. Costs per ton of product are shown in Table 15, calculated f.o.b. New York for a plant located at Invercargill. For a Geelong site the reagent cost would be less by perhaps £8 and containers by a similar amount, but this may be at least partly offset by an increase in freight. The £50/ton freight cost is based on a recent quotation for thorium oxide from New York to Melbourne.

TABLE 15: COST OF TITANIUM TETRACHLORIDE

Chlorine,	0.75 ton	at	£30	£ 22.5
Rutile,	0.42 ton	at	£45	18.9
Coke,	0.15 ton	at	£20	3.0
Hydroxide, metallic zinc				1.2
Labour, estimated				0.6
Power, small				0.1
Depreciation, maintenance				1.8
Miscellaneous				5.8
Containers 3 x 44 gallon heavy drums		at	£ 8	24.0
Freight to New York,	1.1 tons	at	£50	55.0
			Total	£A132.9

The £133/ton corresponds to 13 cents per pound, appreciably less than the 26½ cents quoted in recent market reports.[15]

The effect on the market of an addition 67 tons daily of tetrachloride is difficult to assess without first hand knowledge of the titanium market. In terms of oxide pigment, for which most of the chloride would be used, the production is rather less than 10,000 tons per year which is quite small in proportion to the 500,000 tons produced annually. Most of this larger amount is produced by wet methods and the 10,000 tons becomes significant compared with present production by the dry process.

The estimated profit margin of $13\frac{1}{2}$ cents per pound or £135/ton is large enough to justify careful examination of the proposal as an outlet for surplus chlorine.

9. RECOMMENDATIONS

The discussion and cost estimates indicate that the process has a good chance of becoming a commercial proposition, and further development is recommended.

The expansion of aluminium production in Australia will probably be accompanied by an expansion of local sodium hydroxide manufacture, and by-product chlorine may be available. Any producer of large tonnages of hydroxide should thus be regarded as a potential sponsor for the chlorination process, since this could consume substantial amounts of chlorine. As the aluminium projects are presently in the advanced planning stages, it is recommended that any approach for sponsorship of the present project should be made as soon as possible.

Further experimental work is required on two aspects of the process -

(a) The use of silicon carbide for construction of chlorination equipment.

(b) The development of a technique for control of the reverse reaction.

This should be regarded as urgent.

To enable more accurate assessment of the process economics, a survey of likely markets for synthetic rutile and for titanium tetrachloride should be undertaken. It is suggested that the Commonwealth Department of Trade be approached to undertake this investigation.

10 ACKNOWLEDGMENT

The thermodynamic data on the several reactions in the process and information on the use of multistage chlorination reactors were supplied by I. B. Ketteridge.

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APPENDIX A

CAPITAL ESTIMATE, CYCLIC PROCESS

In preparing this estimate many items of equipment were found to be far from standard, and no reliable prices were available. Where-ever possible detailed estimates were made for manufacture of these items. The cost data of Aries and Newton[12] has been used freely, applying the appropriate exchange rates.

		Cost £	Horsepower
1.	Ilmenite elevator, 100 tons per hour, 50 ft lift	900	10
2.	Ilmenite bins, 2 x 200 tons, 14 ft dia. x 20 ft	6000	
3.	Solids feeder, (Weightometer) with elevator	1180	5
4.	Fluid bed chlorinators (4) I.D. 8 ft, bed 6 ft deep, height 15 ft Steel casing 10 ft x 18 ft Refractory brickwork Refractory concrete Insulation Gas nozzles	21,600	
5.	Rutile cooler, single fluid bed unit	1610	10
6.	Blower, air, 6000 cfn at 6 psi	6000	150
7.	Air lock feeder, rutile, cold	300	3
8.	Rutile bins, similar to item 2, with elevator	6900	10
9.	Back Reactor, steel shell, brickwork, insulation	16,500	
10.	Gas lock feeder, hematite, 500^0	600	3
11.	Oxide cooler, single fluid bed unit	1610	10
12.	Fan air, 8000 cfm (for 11)	400	25
13.	Solids feeder, weightometer as 3	1180	3
14.	Ball mill, 5 ft x 4 ft	3500	50
15.	Gas lock feeder, cold hematite	300	3

		Cost £	Horsepower
16.	Compressor, chlorine, 500^0, 6000 cfm to 10 psi	10,000	300
17.	Chlorine reheater, firebrick, steel shell, 5000 ft^2	20,800	-
18.	Chlorine bleed and recovery system, 5% of gas stream = 11 tons daily Compressor 300 cfm to 100 psi Condensor 75 ft^2 Evaporator 150 ft^2	3,450	60
19.	Instruments 7 Recording-controlling pyrometers 6 Recording pyrometers 1 Chlorine flow controller 2 Oxygen analysers 1 Chlorine - ferric chloride - oxygen analyser	11,310	-
		114,140	642 HP

Following the procedure of Aries and Newton, Method I.

		£
Cost of plant items		114,140
Installation 30%) Piping 15%) Building 40%)	85%	97,000
Physical Plant Cost		211,140
Engineering and construction 30%		63,340
Direct Plant Cost		274,480
Contractor's Fee 6%		16,500
		290,980
Contingency 20%		58,200
Fixed Capital		349,180
Working Capital		150,000
Total Capital		499,180

APPENDIX B

CAPITAL ESTIMATE - TETRACHLORIDE PLANT

			£
1.	Fluid bed reactor, Hastelloy B, 12 ft dia x 15 ft		15,000
	Plus insulation, cooling		2,000
2.	Cyclone		2,000
3.	Condenser, 120 ft^2		1,500
4.	Filter, Stainless steel		3,000
5.	Batch still, 2000 gallons, 2 required		16,000
6.	Condensers for same, 2, 240 ft^2 each		4,000
7.	Surge tanks, 2 required, 10,000 gallons		4,000
8.	Drum filling station		5,000
9.	Instruments Controlling pyrometer		650
	Controlling chlorine flow-meter		350
	Controlling water flow-meter, cooling 3 required at £300		900
	Cycle timer		200
10.	Solids feeders, 3 required at £1000		3,000
11.	Air lock feeder		500
			58,100
	Installation	30 %	17,400
			75,500
	Piping and building,	55%	41,500
			117,000
	Engineering	30%	152,100
	Contractors Fee	6%	9,100
			161,200
	Contingency	20%	32,200
	Fixed Capital		193,400
	Working capital, 3 months production - 67 x 90 = 6030 tons at £200		1,206,000
	Total Capital		1,399,400