EXTRACTION OF TITANIA FROM ILMENITE

by

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This work commenced in the Research and Development Branch of the South Australian Government Department of Mines. It continued under the sponsorship of the Mines Department after the Research and Development Branch had been reconstituted as the Australian Mineral Development Laboratories.

Permission of the Director of Mines to write this thesis is gratefully acknowledged.

CONTENTS

SUMMARY

This thesis is an account of an investigation of a process for separating titanium dioxide from ilmenite.

The process makes use of three chemical reactions, all conducted at high temperatures. Ilmenite is first oxidised with air, the oxidised ilmenite is then treated with chlorine, and finally the ferric chloride and oxygen produced by the action of chlorine upon oxidised ilmenite are reacted to release chlorine for further use in the process.

The application of this process to the treatment of ilmenite from beach sand deposits is the subject of this investigation.

The work reported in this thesis covers three aspects of the application of the process to the treatment of ilmenite sands and the thesis is accordingly divided into three sections.

Ilmenite from beach sand deposits is physically well suited to treatment in fluidised beds. The first section of this thesis is an account of a study of the fluidising characteristics of ilmenite sands and of their amenability to treatment at high temperatures with air and

chlorine in fluidised beds.

The second section of this thesis is a report of a study of the thermodynamics of the three chemical reactions involved in the process. Not all the data necessary for this study are available from the literature and some thermo-chemical quantities have been determined from measurements of equilibrium states.

The third section of this thesis is an account of preliminary studies of the rates at which ilmenite sands react at high temperatures with air and chlorine when in a fluidised state.

The progress of the investigation is then reviewed and future work is outlined.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any University and, to the best of the candidate's knowledge and belief, this thesis contains no material previously published or written by another person, except when due reference is made in the text of the thesis.

I.B. Ketteridge.

1.   INTRODUCTION.

This project commenced in the Research and
Development Branch of the South Australian Government
Department of Mines and continued under State
Government sponsorship after the Research and
Development Branch had been reconstituted as the
Australian Mineral Development Laboratories.

The project originated in the Chemical
Research Section of the Research and Development
Branch. Free energy data, using estimates where
published data were not available, were compiled
for the reactions:

$$FeO + 3/2Cl_2 = FeCl_3 + 1/2O_2 \qquad (1)$$
$$Fe_2O_3 + 3Cl_2 = 2FeCl_3 + 3/2O_2 \qquad (2)$$
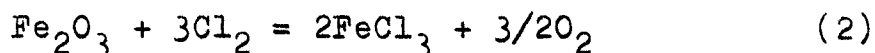
These data (Madigan, unpublished data 1956)
indicated that reaction (1) would proceed in a
forward direction at all temperatures between $500^{o}K$
and $1500^{o}K$, and that reaction (2) was reversible,
having a positive free energy change for the reaction
as written at $500^{o}K$ and negative free energy changes
at $1000^{o}K$ and $1500^{o}K$.

Similar calculations showed that titanium
dioxide should not react with chlorine at the
temperatures being considered.

It was therefore proposed to chlorinate

ilmenite (FeO.TiO$_2$) at a high temperature, separate the iron as gaseous chloride, and leave titanium dioxide residue according to the reaction:
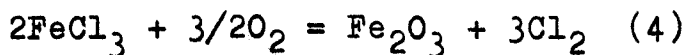
$$FeO.TiO_2 + 3/2Cl_2 = FeCl_3 + 1/2O_2 + TiO_2 \quad (3)$$
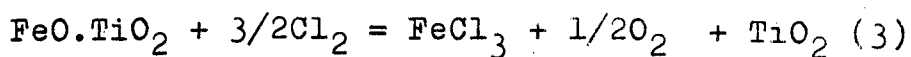
Chlorine could be recovered and recycled by adding pure oxygen in sufficient amount to the gaseous reaction products and lowering the temperature, where the following reaction would take place:

$$2FeCl_3 + 3/2O_2 = Fe_2O_3 + 3Cl_2 \quad (4)$$

It was proposed to operate the process in a closed cyclic system with a continual addition of oxygen. The oxygen would therefore need to be of high purity to prevent an accumulation of gaseous impurities in the system.

Experimental confirmation of the reactions was obtained by heating small weighed samples of ilmenite and rutile (TiO$_2$) to about 1000°C in a stream of chlorine, and by heating solid ferric chloride to about 240°C in a stream of oxygen.

Heating ilmenite for four hours in a stream of chlorine resulted in a loss of weight corresponding to removal of the iron oxide content and left a residue containing 99.7 per cent. titanium dioxide.

Similar treatment of rutile left the sample substantially unaffected.

Heating ferric chloride for about an hour in

a stream of oxygen left a residue consisting mostly
of ferric oxide.

The project was reviewed at this stage.
It appeared that the process was feasible and
warranted further investigation.

Further chlorination tests were carried out
with unground ilmenites from beach sand deposits,
the previous tests having been conducted with a
finely crushed sample of massive ilmenite. The
iron oxide content of the beach sand ilmenites were
reduced to about 0.4 per cent in about 30 minutes.
X-ray analysis showed that the mineral form of the
residue was rutile, and microscopic examination
showed the material to be essentially unchanged in
particle size and shape.

At this stage the project passed from the
Chemical Research Section to the Chemical Engineer-
ing Section, and the author became responsible for
the further conduct of the project.

A survey of the available literature (Dunn
and Morgan 1955, 1956; Gardner 1955; Bradford 1957;
Jaffe 1957; Anon. (1) 1956, 1957; Anon. (2) 1957)
showed that mineral rutile, the largest reserves of
which occur in Australia, is the principal raw
material used for titanium metal production, and
known reserves are insufficient to supply world

requirements for very long. Other possible sources of titanium are the known large deposits of ilmenite and titaniferous iron ores. However if these materials are to be used as raw materials for the existing titanium metal manufacturing process, preliminary treatment for separating high grade titania is necessary. As recently as August 1959, W.J. Kroll, who was largely responsible for the development of the present titanium metal manufacturing process, stated that "The ore basis of the large titanium industry of the future can only be ilmenite" and that "separation of iron from the ore will be necessary".

Ilmenite is used chiefly for the manufacture of titania white pigments. The conventional process is expensive and for this reason titania pigments cannot be considered as raw material for titanium metal production.

Ilmenite is being smelted at Sorel in Canada to produce pig iron and a slag containing about 75 per cent titania (Knoeri 1952; Merriman 1953; Gray and Carter 1958; Elliot 1959). The slag is used for pigment manufacture (Anon. (3) 1958) but due to the presence of lime and magnesia, can be chlorinated and used for titanium metal production only with difficulty (Gray and Carter 1958). A pilot plant

was built at Shawinigan Falls, Canada, for this
purpose but operated for a short time only (Janes 1957).
An improvement has been reported (Gray and Carter 1958)
in that slags containing 90 per cent titania have
been produced and chlorinated in Japan. No details
of the Japanese process are available.

Dunn and Morgan (1957) have estimated the
cost of using slags to be equivalent to rutile at
£65 to £70 (Australian) per ton. This is about twice
the current price for rutile, hence smelting, as a
prior step in the use of ilmenite for titanium metal
manufacture does not appear promising, at least in
the immediate future.

Several other schemes have been considered
as means of utilizing ilmenite and titaniferous
iron ores for their titania content. It has been
proposed (Weil 1958) to chlorinate titanium iron
oxide ores, separate anhydrous ferric chloride and
electrolyse the ferric chloride in fused salt and
recover the chlorine as hydrochloric acid. Another
proposal (Cunningham 1958) has been to reduce the
iron oxide content to metallic iron and leach it
from the ore with ferric chloride solution, leaving
a titania residue. It was proposed to reactivate
and recycle the leach solution by electrolysis.

It has also been proposed (Anon. (4) 1957) to

dissolve ilmenite in sulphuric acid and separate the iron by crystallisation. The titania content could then be precipitated as potassium chlorotitanate which decomposes on heating to produce titanium tetrachloride. The economics of this process which depend "mainly on discarding the iron as sulphate instead of chloride seems rather dubious" (Gray and Carter 1958).

A process has been patented (Gaskin and Ringwood 1957) for converting ilmenite to rutile by sulphiding the iron of the ilmenite to iron sulphide and subjecting the resulting mixture to the action of water and oxygen at high pressure and temperature. Conventional mineral dressing methods can then be used to separate rutile from the mixture of rutile, sulphur, and iron oxide so formed.

At present there is no proven satisfactory method for producing high grade titania from ilmenite. The scheme proposed by the Chemical Research Section seemed promising and further investigation of the project was therefore justified.

A further search of the literature showed that both the selective chlorination of iron in ilmenite and the reaction of ferric chloride with oxygen as a means of recovering chlorine from ferric chloride have been considered before. Both have been the subjects of patents (Saklawalla, 1928;

Millar 1929; Murphree 1942; Pye and Joseph 1947; Sawyer 1948; Fry 1957).

In addition, the operation of a small pilot plant for the manufacture of sulphur from pyrites in which ferric chloride is burnt with air to recover chlorine is described, unfortunately with little detail, by Rowe (1938).

Roberson and Banning (1955) propose chlorination of ilmenite in the presence of carbon to produce titanium tetrachloride and ferric chloride, separation of the two chlorides and oxidation of the ferric chloride to recover chlorine.

On the other hand Rowe and Opie (1955) state that direct oxidation of ferric chloride for recovering chlorine would be difficult "owing to its tendency to dissociate into the difficulty oxidisable ferrous chloride." No authority or experimental evidence is given for this statement.

Kroll (1956) in a discussion of the oxidation of ferric chloride as a means of recovering chlorine states that "formation of solid accretions of magnetite in the furnace seem difficult to avoid." No further information is given.

Gray and Carter (1958) in a review of titanium metal production methods discuss the use of ilmenite as raw material. They state that "the recovery of

chlorine and ferric chloride by combustion with oxygen presents many technical problems that still await solution."

It would appear that the proposed process for chlorination of ilmenite has been considered by a number of authors but has not been the subject of experimental investigation. This survey produced no quantitative data for either the chlorination reaction or the reaction for recovering chlorine. However two papers (Galmiche 1955; Smullin 1957) which were subsequently found did not include experimental measurements of the equilibrium between ferric oxide and gaseous ferric chloride, chlorine, and oxygen at various temperatures. These papers are discussed in detail in Section 3 of this thesis.

Beach sand deposits of ilmenite occur in the Bunbury area of Western Australia and are at present being worked to produce raw material for the titania pigment industry.

Other deposits of ilmenite, associated with rutile, monazite and zircon, occur on the eastern coasts of Australia. These deposits are being worked principally for the recovery of rutile, but also for monazite and zircon. The ilmenite is unsaleable as it contains a few per cent of chromite which cannot readily be separated and which makes it unsuitable

for pigment manufacture. Large dumps of this material have accumulated and for this reason it was decided to use this ilmenite as the subject of this investigation. A ten ton parcel from Stradbroke Island, Queensland, was therefore obtained.

On arrival it was found that this sample contained an appreciable proportion of silicates and was not suitable for direct chlorination. Magnetic concentration with a cross-belt magnetic separator produced a concentrate containing less than one per cent silicates and reduced the chromic oxide content from 2.7 to 0.18 per cent. Subsequent chlorination to remove the iron reduces the chromium content to less than 10 parts per million, so the chromium content has, up to the present time, been of no further significance in this investigation.

This ilmenite was not immediately available for test work and initial experiments, which were mainly dependent on the physical properties of the test material rather than chemical composition, were conducted with a sample of beach sand ilmenite from Capel, near Bunbury in Western Australia. This material is similar to Stradbroke Island ilmenite in size distribution and bulk and material densities but differs slightly in chemical composition, having a lower ferrous iron to ferric iron ratio.

It was found by experiment that ilmenite could be oxidised fairly readily to pseudobrookite ($Fe_2O_3 \cdot TiO_2$) and rutile by heating to about $1000^\circ C$ in a stream of air.

The reaction is :

$$2FeO.TiO_2 + 1/2O_2 = Fe_2O_3.TiO_2 + TiO_2 \qquad (5)$$
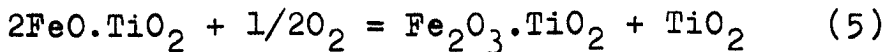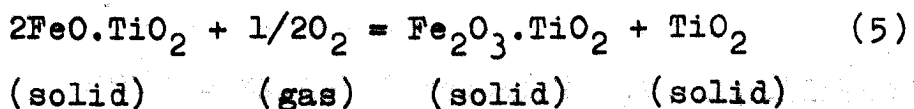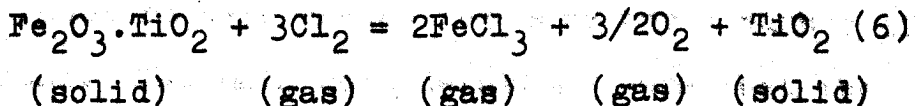
The process suggested by the Chemical Research Section was therefore modified to include a prior oxidation stage with air as oxidant, thereby avoiding the need for adding high purity oxygen to the chlorine recovery stage.

The reactions on which the process depend are

Oxidation :

$$2FeO.TiO_2 + 1/2O_2 = Fe_2O_3.TiO_2 + TiO_2 \qquad (5)$$
$$\text{(solid)} \qquad \text{(gas)} \qquad \text{(solid)} \qquad \text{(solid)}$$

Chlorination :

$$Fe_2O_3.TiO_2 + 3Cl_2 = 2FeCl_3 + 3/2O_2 + TiO_2 \quad (6)$$
$$\text{(solid)} \qquad \text{(gas)} \qquad \text{(gas)} \qquad \text{(gas)} \quad \text{(solid)}$$

Regeneration :

$$2FeCl_3 + 3/2O_2 = Fe_2O_3 + 3Cl_2 \qquad (4)$$
$$\text{(gas)} \qquad \text{(gas)} \quad \text{(solid)} \quad \text{(gas)}$$
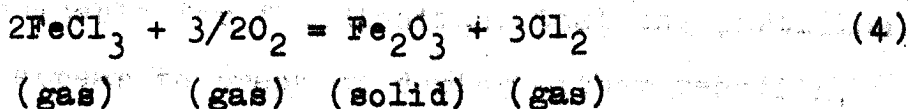
The process comprises the oxidation of ilmenite with air at high temperature and transfer of the oxidised product to a chlorination reactor. In this reactor the iron oxide content is converted to gaseous ferric chloride, leaving pure rutile.

The gaseous chlorination products are transferred
to another reactor and cooled where reaction in
the reverse direction proceeds, producing solid
ferric oxide and recovering chlorine. The ferric
oxide is separated and the chlorine enriched gases
are reheated and returned to the chlorination
reactor. It is proposed to operate the process in
a continuous cyclic system.

For reasons which are established in later
sections of this thesis, it appears that a
temperature of $1000^{\circ}C$ would be suitable for the
oxidation reaction, $1100^{\circ}C$ for chlorination and
about $500^{\circ}C$ for regeneration.

Various types of reactors were considered
for the oxidation and chlorination reactions. Fluid
bed reactors were chosen for both for a number of
reasons. The main considerations were that the
particle size distribution of beach sand ilmenite
is suitable for fluidisation, that the particles do
not appear to break up during either reaction,
that good contact can be obtained between reacting
solids and gases, and that fluid bed reactors can
fairly readily be constructed in suitable heat and
corrosion resistant materials.

For the successful continuous operation of
the process, both the oxidation of ilmenite and the

chlorination of pseudobrookite must be substantially complete. Oxidation of the ilmenite must approach completion to reduce the addition of pure oxygen to the cyclic system to an absolute minimum. Chlorination must be sufficiently complete to reduce the ferric oxide content from about 50 per cent. to below the market specification for rutile viz. 0.5 per cent. Process requirements are therefore that the solid products from both the oxidation and chlorination reactions should be in excess of 99.5 per cent. reacted.

Fluidised bed reactors are extensively employed in the petroleum industry for catalytic vapour phase reactions and they are in limited use in various chemical industries, mainly for roasting and calcining operations (Anon. (5) 1954, Anon. (6) 1958, Kite and Roberts 1947, White and Kinsella 1952, Labine 1960).

The use of fluidised bed reactors to produce the degree of reaction in the solid products required in this process is not known. A survey of the literature has disclosed no suitable method of reactor design.

It is therefore necessary to devise a scheme for reactor design if extensive and expensive pilot plant testing of an empirical nature is to be avoided.

Experimental determination of various factors influencing fluidised bed reactor performance, mathematical analysis of fluidised bed reactor systems, and the application of such analyses to the design of fluidised bed reactors for the oxidation and chlorination of ilmenite therefore form a major part of this project.

This thesis is a report of an investigation to determine the suitability of fluidised bed reactors for the oxidation and chlorination reactions and, as the first step in the development of a mathematical analysis of fluidised bed reactor systems, measurement of the degree of mixing of solids in fluidised beds.

Experimental determination of the equilibrium conditions of the chlorination reaction at various temperatures, determination of the extent to which the oxidation, chlorination, and regeneration reactions proceed and the heats of reaction involved are also reported.

Finally preliminary tests to determine rates of oxidation and chlorination of ilmenite in fluidised beds are reported.

2.   FLUIDISATION.

If the velocity of a stream of fluid rising
through a loosely packed bed of solid particles
steadily increases, the difference in pressure
between the fluid entering and the fluid leaving the
bed increases linearly with increasing fluid flow.
The pressure drop rises until it reaches a point of
equilibrium, known as the point of incipient
fluidisation, where it equals the weight per unit
area of the bed of solid particles. At this point
the solid particles become individually supported
in the fluid stream and further increase in fluid
velocity causes no further increase in pressure
drop through the bed.

If the fluid is a liquid, continuous uniform
expansion of the bed, termed particulate fluidisation
(Wilhelm and Kwauk 1948) usually occurs with
increasing fluid velocity beyond the point of
incipient fluidisation. Ultimately, when the fluid
velocity exceeds the terminal velocity of the
particles falling through the fluid, the surface of
the fluid disappears. The fluid and solids then
form a dispersed suspension in which solids are
transported with the fluid.

If the fluid is a gas, little further expansion
usually occurs beyond the point of incipient

fluidisation. Increasing gas velocity results in proportion of the gas accumulating in bubbles, which rise through the more or less uniform suspension of solids and gas which form the bed. The appearance of the bed may vary widely depending on the number and size of gas bubbles relative to the size of the bed. If the gas velocity exceeds the terminal velocity of the particles falling through the gas, then as with liquids, fluid transport occurs.

This type of fluidisation is termed aggregative fluidisation (Wilhelm and Kwauk 1948). It is with this type only that we are concerned in this project.

2.1 Literature Review

The fundamental observations that the pressure drop through a loosely packed bed of solid particles increases with fliud flow until the bed is fluidised and that for a fluidised bed the pressure drop remains essentially constant and equal to the weight per unit area of the bed have been reported by several authors (Parent et al. 1947; Wilhelm and Kwauk 1948; Leva et al. 1951). Lewis et al. (1949) have reported pressure drops in excess of the weight of solids per unit area. However these were reported for fluid beds which

were tall in relation to their diameters i.e. with high aspect (length/diameter) ratios, and the excessive pressure drops were attributed to frictional drag on the walls of the containing vessels. For practical purposes the pressure drop through a fluidised bed can be regarded as being that necessary to support the weight of the bed.

Leva and co-workers (1951) made use of the relation between pressure drop and weight of bed to derive an expression for the mass velocity of fluid necessary to initiate fluidisation. An expression for the pressure drop through the expanded bed, based on the Kozeny (1927) and Carman (1937) correlation for pressure drop through packed beds, was equated to the weight per unit area of the bed. An expression for fluid mass velocity in terms of fluid and particle densities, fluid viscosity, particle diameter, particle shape factor, and voidage of the bed resulted.

Similar expressions have been obtained by Van Heerden et al. (1951), Miller and Logwinuk (1951), Cathala (1953) and by Pinchbeck and Popper (1956).

These expressions are considered in the assessment of experimental measurements of gas velocities necessary for fluidisation.

A nomenclature has been proposed (Anon.(8),

1949) to describe the various types of fluidisation observed in aggregatively fluidised beds.

A quiescent fluidised bed is a dense fluidised bed in which little mixing of the solid particles occurs.

A turbulent fluidised bed is one in which mixing of the mass of solids does occur. The degree of turbulence, which ranges from the lower limit of quiescent bed conditions to violent mixing, is dependant mainly on fluid velocity.

Channelling is the establishment of flow paths in a bed of solid particles through which a disproportionately large quantity of the fluid flows. It usually occurs in beds which have a low aspect ratio.

Slugging is a condition in which bubbles of fluid extend across the diameter of the containing vessel and the mass of particles supported above the bubbles moves upward in a piston-like fashion. This usually occurs in small beds with high aspect ratios.

Quality of fluidisation has been defined by Morse (1949) as the uniformity of particle dispersion and gas velocity in a turbulent fluidised bed. The need for a quantitive measure of the quality of fluidisation has been discussed by Bakhtiar (1956)

and by Leva (1957). Various physical properties
of fluidised beds have been measured in endeavours
to find a direct quantitative measure.

The frequency and intensity of impacts on a
microphone inserted in the bed have been measured
by Gerald (1951).

The frequency and amplitude of pressure
fluctuations on a diaphragm were measured by
Shuster and Kisliak (1952).

The variation in intensity of light trans-
mitted through a fluid bed has been measured by
Gopichand and co-workers (1957).

X-ray absorption and Y-ray absorption were
measured by Ghrose (1955) and by Bartholomew and
Casagrande (1957) respectively. The measurement
of Y-ray absorption has also been reported by
Baumgarten and Pigford (1960).

The torque required to rotate vanes within
a fluid bed, analogous to liquid viscosity measure-
ment, has been measured by Matheson et al. (1948)
and by Kramers (1951).

The variation in capacitance of fixed plate
condensers with fluidised solids between the plates
was first measured by Dotson et al. (1949).
Capacitance measurements have since been reported
by Morse and Ballou (1951), James (1953), Bakker

and Heertjes (1958, 1959), Dotson (1959) and Lanneau (1959).

On the basis of their work with capacitance probes, Morse and Ballou (1951) proposed a uniformity of fluidisation index, defined in terms of the amplitude and frequency of capacitance fluctuations, to replace the quality of fluidisation previously defined by Morse (1949).

This index could be used to determine the reproducibility of fluidising conditions but it is not in itself a measure of optimum process conditions. It is therefore necessary to determine optimum fluidising conditions for the oxidation and chlorination of beach sand ilmenites in fluidised bed reactors by direct measurement of the rate and extent of the respective chemical reactions.

Hammond (1958) states that optimum process conditions are usually obtained when the gas passes up through the bed in small bubbles with the solids circulating uniformly. Gas velocities from two to five times the minimum required for fluidisation usually produce such conditions.

The overall extent of reaction of the solid product from a fluid bed reactor will of course depend on the degree of reaction of the individual particles which comprise the product. This may vary

from particle to particle. In general, for heterogenous reactions invloving solid particles carried out in continuous multiple stage reactors, the extent to which an individual solid particle reacts depends on the time that particular particle is retained in each stage of the reactor. The distribution of particle retention times lepends in turn on the degree of mixing of the solids in each reactor stage.

Mixing in fluid bed reactors has been the subject of a number of investigations. Gilliland and Mason (1949) have reported measurements of heat transfer in small fluid beds which demonstrate a high degree of solids mixing.

Radioactive tracer techniques have been used by Singer, Todd, and Guinn (1957) to study retention times in a number of large commercial fluid bed installations. High rates of mixing in turbulent fluid beds are reported. May, (1959), using similar techniques in smaller scale equipment has reported extremely rapid mixing. In one instance 50 gms of radioactive catalyst were mixed in 15 tons of fluidised inert catalyst in less than one minute.

Hull and Rosenberg (1960) have also reported the use of radio-tracer techniques to demonstrate high degrees of solids mixing in pilot scale eqiupment.

It would appear that the degree of solids mixing in fluid beds is usually high, and that retention times can be calculated on this basis.

Expressions for retention times in continuous flow stirred vessels were first derived by Ham and Coe (1918). A short table was compiled by means of which it is possible to determine the distribution of retention times in the outflowing material for reactor systems with up to seven equal sized stages.

McMullin and Weber (1935) in a paper discussing short circuiting in continuous flow mixing vessels and reaction kinetics in such systems, derive similar equations for retention time distribution. They separately consider the distribution of retention times for material retained within the reactor systems (original contents) and for material flowing from the reactor (incoming flow). Short tables were compiled for each.

Although they claim to present clearer derivations than Ham and Coe, their derivation of retention time functions for outflowing material is cumbersome, and they separately and needlessly derived expressions for retention times of reactor contents when these follow directly from expressions for outflowing material. Their treatment is more

complete than that of Ham and Coe, although this paper also considers only reactor systems with equal size stages.

Dankwerts (1953) gives a treatment of retention times in incompletely mixed reactors, defines segregation as the departure from perfect mixing and presents a graphical experimental method for its determination. This paper is confined to comparing retention times in reactor systems with those obtained in perfectly mixed single stage reactors, although the basis taken for comparison could readily be extended to perfectly mixed multiple stage reactors. Alternatively the degree of segregation could be determined separately for each stage of a multiple stage reactor.

Further work with incompletely mixed single stage reactors has been reported by Zwietering (1959) and by Cholette and Cloutier (1959).

2.2 Experimental

The various expressions given for determining minimum fluidising velocities, Leva et al (1951), Van Heerden et al. (1951), Miller and Logwinuk (1951), Cathala (1953), and Finchbeck and Popper (1956), all invlove mean effective particle diameters and particle shape factors, neither of which can be measured precisely for beach sand

ilmenties.   It was therefore necessary to determine

minimum fluidising gas velocities experimentally.

It was also considered necessary to determine ex-

perimentally whether the degree of solids mixing in

the small beds being considered for oxidation and

chlorination tests with ilmenite would be as high

as has been reported for larger units.

　　　　With these ends in view a model of the

proposed multistage fluid bed reactors was construct-

ed in a transparent plastic material and operated

at room temperature with air as the fluidising

medium.

　　　　The model (see Appendix 1, Figure 1) is made

in flanged interchangeable sections from $2\frac{3}{4}$ inch

internal diameter "perspex" tubing.   An air inlet

is set at the bottom and a settling chamber at

the top to collect any solids which may be carried

over.   Air distribution plates were made from $\frac{1}{4}$ inch

perspex sheet drilled with 1/32 inch diameter holes

at 1/8 inch centres and countersunk with a 1/8 inch

drill.   Air flows were measured at the inlet with

a rotameter and small perspex tubes were cemented into

the sides of each section for manometer connections

to measure pressure losses.   Half inch outside

diameter perspex tubes were cemented in place in the

air distribution plates so that solids could be

continuously fed from stage to stage through the
model and collected in a sealed glass jar at the
bottom. The apparatus can be set up as a single
stage batch fluid bed or as a continuous flow fluid
bed reactor with up to five stages.

The model was first set up as a single stage
batch fluid bed reactor and air flow-pressure loss
plots recorded for fluid beds with various aspect
ratios.

The materials used for these tests were
ilmenite from beach sand deposits at Capel, Western
Australia, and quartz sand from Moana Beach, South
Australia. Capel ilmenite was the only beach sand
ilmenite available at the time. The quartz sand
was a tailing produced from the gravity concentration
of beach sands from Moana. This material was used
because it was roughly the same particle size
distribution as the ilmenite but has about half the
material density. It therefore resembles, at least
for the purpose of fluidising tests, the granular
rutile produced by chlorinating ilmenite. The
physical properties of both materials are presented
in Appendix 11, Tables 1 and 2. Physical properties
for granular rutile are reported for comparison with
those of quartz sand in Appendix 11 Table 5.

Before commencing mixing tests in the perspex

model fluid bed, a short series of tests was carried out to see if any segregation, either as a result of differences in particle densities or particle size, would occur in a fluid bed. Segregation of different materials in fluid beds under special conditions has been reported by Leva et al. (1951)and by Richardson and Bakhtiar (1958). Segregation of fine and coarse particles has been reported by Parent et al. (1947), Leva et al. (1951), Osberg and Charlesworth (1951), Hall and Crumley (1952), Morse (1959) and Thomas et al. (1961).

The model was set up as a single stage batch fluid bed and charged with a mixture of equal volumes of Capel ilmenite and quartz sand. Tests were carried out with beds having aspect ratios ranging from 0.25 to 4.0. The tests comprised setting the air flow at various levels and maintaining the flow rate constant for periods of fifteen minutes. The beds were inspected for evidence of segregation.

Although a wide range of conditions were tried, no visible segregation either of quartz and ilmenite or of coarse and fine particles, was observed. It was concluded that the range of particle sizes and the differences in particle densities were insufficient to cause visible

segregation and it seemed that a fairly high degree of mixing took place in the small perspex model. More specific mixing tests were then carried out.

For the first test, the perspex model was set up as a single stage continuous feed fluid bed with unit aspect ratio, i.e. the overflow was set at a height of one bed diameter above the air distribution plate. Air flow was set at 25 litres per minute, about three times the minimum required for fluidisation. This level was sufficient to keep the bed in a turbulent fluidised condition and was maintained throughout the test.

The test comprised setting up the model with a steady flow of quartz sand through it and then changing to ilmenite at the same volumetric flow rate. The change in composition of the outflowing material with time was determined by collecting samples of the product at regular intervals and magnetically separating the samples into their constitutents with a "Franz Isodynamic Separator". A measure of the degree of mixing was thus provided.

A similar test was conducted with the model set up as a five stage reactor with the stages all at unit aspect ratio. This test was repeated for reasons which are discussed in the following section, with magnetic and non magnetic sands having similar

densities. The two materials used were produced
by the magnetic separation of a sample of impure
ilmenite obtained from Stradbroke Island, Queensland.
Screen sizings and densities for these materials are
given in Appendix 11, Tables 3 and 4.

For fluid bed tests at high temperature, a
single stage reactor was made from a 30 inch length
of $2\frac{3}{4}$ inch internal diameter silica tube (see
Appendix 1, Figure 2). A gas distrubutor plate was
made from 3/16 inch silica plate cemented into the·
tube, with nine $\frac{1}{4}$ inch holes drilled through it.
Into each hole a short length of silica tube was
cemented. These tubes were sealed at one end and
had three approximately 0.030 inch holes blown
in the sealed end. The lower end of the reactor
was sealed with another silica plate also cemented
in place. This plate had an 18 inch length of 6 m.m.
bore silica tube fused into a hole drilled in the
centre for the gas inlet.

A vertical tubular gas fired furnace (shown
Appendix 1, Figure 3) was constructed to heat the
silica reactor. This comprised two welded steel
moulds into which a shell of refractory material
(Nonporite "Pyrocrete S") was cast. One half of the
shell could be removed to allow access to the
reactor which was held in the centre of the furnace.

Four gas "tunnel" burners were set along the length of the fixed half of the shell firing tangentially into the inner cylindrical combustion chamber.

Compressed air for the gas burners was fed through an air aspirator and reduced to a suitable pressure. Gas was fed through a proportional mixing set, mixed with the air, and then to four 15/32 inch tunnel burners having a maximum total capacity of 400 cubic feet of gas per hour. The burners were controlled by regulation of the air pressure admitted to the air aspirator.

Fluidising gas flow rates were measured before the gases were admitted to the reactor, air, oxygen, and nitrogen with rotameters and chlorine with a laboratory orifice type flowmeter. The chlorine flowmeter was used mainly to maintain the chlorine flow at a constant level, average flow rates during test runs being determined by weighing the chlorine cylinder before and after test.

Temperatures were measured with a chromel-alumel thermocouple in a silica sheath entering the bed from the top of the reactor.

Samples of solids were drawn from the fluid bed during the course of reaction by dipping a silica tube with a small pocket blown in one end, into the bed. Chemical analyses of all samples were

carried out by the Analytical Section.

For fluid bed oxidation tests, the waste reaction gases were discharged to atmosphere. Waste gases from chlorination tests were absorbed in soda ash solution. For this purpose an aspirator was made in one inch and two inch water pipe (see Appendix 1, Figure 4). A three inch Thompson centrifugal pump was used to pump 15 per cent. soda ash solution from a storage tank having a capacity of approximately 250 gallons of solution, through the aspirator, and back to the tank. Waste gases from the top of the fluid bed reactor were drawn through one inch pipe to the aspirator and mixed with the solution, giving virtually complete absorption of chlorine in the solution. The unabsorbed gases could then safely be discharged to atmosphere.

2.3 Results and Calculations.

2.3.1 Fluidisation

Air flow-pressure loss plots for fluid beds of ilmenite and quartz sands are presented in Appendix 111, Figures 1 and 2. Pressure losses measured across the air distribution plate were small in comparison to those measured across the fluid beds and consequently were not taken into account.

It can be seen that for both the ilmenite and quartz sands, fluidisation commences with a superficial air velocity i.e. air velocity in the open tube, of about 1.3 inches per second. Pressure losses for fluidised beds are proportional to the weight of bed, i.e. pressure losses for tests with the same material are proportional to the bed heights and corresponding tests for the two different materials are roughly in the proportion of the two bulk densities, viz. 1.7.

The behaviour of the fluid bed was noted during the tests and areas are shown on the plots where channelling, turbulent fluidisation and slugging occur. The region most suitable for oxidation and chlorination is probably the turbulent fluidised zone, the limiting conditions for which can be obtained from the plots.

The critical fluid mass velocity has been defined as the fluid velocity necessary to initiate fluidisation. In Section 2.1 it has been stated that Leva et al. (1951) developed an expression for the critical fluid mass velocity, G_{mf}, in terms of:

fluid density ρ

fluid velocity μ

particle density ρ_s

mean effective particle diameter D

particle shape factor λ

bed voidage at minimum fluidisation δ

The expression is

$$G_{mf} = \frac{0.005\ D^2.g.\rho(\rho_s - \rho).\delta^3}{\mu.\lambda^2(1 - \delta)}$$

where g is a gravitational constant.

The mean effective particle diameter is
defined as

$$D = \sum_{z=1}^{z}(X.d)$$

where X is the weight fraction, $\sum_{z=1}^{z}(X) = 1$,

and d is the equivalent spherical particle daimeter.

The expression for critical mass velocity may,
for a given particulate solid, be reduced to

$$G_{mf} \propto \frac{\rho(\rho_s - \rho)}{\mu}$$

or $G_{mf} \propto \frac{\rho}{\mu}$

Expressions for critical mass velocity develop-
ed independently by Van Heerden et el. (1951) and
by Cathala (1953) both reduce to the above proport-
ional relation.

The superficial air velocity necessary to
fluidise a bed of ilmenite at room temperature has
been experimentally determined as 1.3 inches per
second. Hence the critical mass velocity is

$$G_{mf} = 0.025 \quad (g).(sq.in).(sec)^{-1}$$

The critical mass velocity for air at high
temperatures can therefore be obtained from
equation (2) using published data for the density
and viscosity of air at high temperatures. Such
data is given by Hilsenrath et al. (1955).
This involves the assumption that the effect of
pressure on both density and viscosity can be
neglected. Pressure losses through the experimental
fluid beds were of the order of a few inches water
gauge, so the error introduced by this assumption
is negligible.

The critical mass velocity for chlorine at
room temperature, calculated from equation (2)
with values for densities and viscosities of air
and chlorine taken from Perry (1950) and Hodgman
(1955), is 3.4 times as great as that for air at
room temperature.

Published values for the density and
viscosity of chlorine at high temperature are not
available. Densities can be estimated by assuming
that chlorine behaves as a perfect gas. Licht
and Stechert (1944) have shown that the Sutherland
function for variation of viscosity with temperature
is generally accurate to within one per cent.

Sutherland constants for air and chlorine have been taken from Perry (1950) and by assuming that both gases behave as perfect gases, the following expressions for variation of critical mass velocities with temperature were obatined.

For ilmenite sand having the same particle size distribution as the sample tested, when fluidised with air at temperature T (degrees Kelvin),

$$G_{mf} \text{ (air)} = \frac{114 + T}{16320} \left(\frac{298}{T}\right)^{5/2} \text{ (g).(sq.in).(sec)}^{-1}$$

For chlorine

$$G_{mf} \text{ (Cl}_2\text{)} = \frac{325 + T}{7281} \left(\frac{298}{T}\right)^{5/2} \text{ (g).(sq.in).(sec)}^{-1}$$

The results of oxidation and chlorination tests carried out with the high temperature reactor are given in Appendices VI and VII respectively, and will be discussed in detail in a later section. Experimental measurement of critical fluidising mass velocities at high temperatures was not possible because it was found that at high temperatures granular ilmenite readily sinters into a solid mass.

Microscopic examination of sintered ilmenite by the Petrology Section (Whittle, unpublished data 1957) has shown that sintering is due to crystallisation of pseudobrookite across particle

boundries where particles are in contact, locking
the particles together. This is illustrated in a
sketch of a microphotograph, Appendix 111, Figure 3,
which shows particles composed of crystals of
rutile in a matrix of pseudobrookite, with pseudo-
brookite extending from one particle to the next.

Sintering can be prevented by maintaining
the bed in a turbulent fluidised condition.
However the tendency to sinter effectively prevents
direct experimental measurement of critical
fluidising mass velocities at high temperatures.

The minimum air velocity necessary to prevent
sintering during oxidation at $1000^{\circ}C$ was found to
be about four times the critical mass velocity
calculated for that temperature by means of the
equation developed previously (0.0023 g./sq.in./sec.).
Oxidation tests have been conducted at $1000^{\circ}C$
with air flows up to 18 times the critical mass
velocity. However at this velocity the amount of
solids carried from the bed in the air stream
tends to become excessive. Air flows of about
nine times the calculated critical mass velocity
were found to be a suitable intermediate level.

When chlorinating oxidised ilmenite it was
found that the tendency to sinter decreases as the
reaction proceeds and that fully chlorinated rutile

residue does not sinter. As with oxidation at 1000°C, chlorine flows of the order of nine times the critical mass velocity, calculated with the equation developed for chlorine (0.0051 g./sq.in./sec) were found suitable for chlorinating at 1000°C. However with chlorine flows of only 13 times the critical mass velocity, dust losses were noticeably large.

Microscopic examination of chlorinated ilmenite has shown the grains to be composed of a porous mass of rutile crystals ranging in size from about one micron to about 13. High dust losses have therefore been attributed partly to the low particle density of chlorinated ilmenite reducing the terminal velocity of the particles, and partly to attritioning from violent fluidisation at high gas velocities causing the grains to break down at a comparatively fast rate to fine particles which are carried away in the gas stream.

2.3.2 Mixing

The results of the mixing tests carried out in the perepex model can be assessed by comparing the experimental data with results predicted on the assumption of complete mixing in each stage of the reactor, complete mixing being defined as the instantaneous dispersion of incoming feed

throughout the reactor stage. It has been stated
in Section 2.1 that expressions for retention
times in stirred reactors have been derived by
Ham and Coe (1918) and by McMullin and Weber (1935).
However both these papers had shortcomings and an
original and more concise derivation is presented
here.

Frequency and distribution functions for
particle residence times in multiple stage fluidised
bed reactors have been derived on the assumption
of complete mixing. Multiple stage reactor systems
having equal size stages are considered. Residence
time frequency and distribution functions for the
effluent from such reactor systems are derived.

2.3.2.1 Residence Time Distributions.

Consider a single reactor of capacity V
being fed at a constant flow rate v and assume
complete mixing within the reactor. Let $f_1(t)$
represent thefraction of reactor effluent which
has been retained in the reactor for longer than
time t, i.e. let $f_1(t)$ represent the frequency
distribution function of the effluent. Then $f_1(t)$
will necessarily also represent the frequency
distribution function of the reactor contents.

Since it is assumed that mixing within the

reactor is complete, then

$$\frac{d\, f_1(t)}{d\,t} = \frac{v}{V} \cdot f_1(t), \qquad 0 < t < \infty$$

Integrating and applying the boundary conditions:

$$t = 0, \quad f_1(t) = 1,$$

$$f_1(t) = e^{-\frac{vt}{V}}$$

The frequency function, $\emptyset_1(t)$, can be found from the relation:

$$f_1(t) = \int_t^\infty \emptyset_1(t)\, dt$$

$$\emptyset_1(t) = \frac{v}{V} e^{-\frac{vt}{V}}$$

Now consider a two stage reactor with the capacity of each stage equal to V. The fraction of throughput material retained in the first stage for the time between t' and t'+ dt is

$$\frac{v}{V} e^{-\frac{vt'}{V}}$$

Of this material, the fraction retained in the second stage for the time between t − t' and t − t'+ dt, where t is the total time retained in the reactor, is

$$\frac{v}{V} e^{-\frac{v(t-t')}{V}}$$

Then the fraction of reactor effluent which has been retained in the first stage for time t' and in the reactor for time t is

$$\frac{v}{V} e^{-\frac{vt}{V}} \cdot \frac{v}{V} e^{-\frac{v(t-t')}{V}} = \left(\frac{v}{V}\right)^2 e^{-\frac{vt}{V}}$$

Hence the frequency function for the effluent from a two stage reactor is

$$\phi_2(t) = \int_0^t \left(\frac{v}{V}\right)^2 t\, e^{-\frac{vt}{V}}\, dt'$$

$$= \left(\frac{v}{V}\right)^2 t\, e^{-\frac{vt}{V}}$$

and the distribution function is

$$f_2(t) = \int_t^\infty \phi_2(t)\, dt$$

$$= \frac{vt}{V} e^{-\frac{vt}{V}} + f_1(t)$$

By similar arguments it can be shown that for a three stage reactor:

$$\phi_3(t) = \frac{1}{2} \left(\frac{v}{V}\right)^3 t^2 e^{-\frac{vt}{V}}$$

$$f_3(t) = \frac{1}{2} \left(\frac{vt}{V}\right)^2 e^{-\frac{vt}{V}} + f_2(t)$$

For a four stage reactor :

$$\phi_4(t) = \frac{1}{3!} \left(\frac{v}{V}\right)^4 t^3 e^{-\frac{vt}{V}}$$

$$f_4(t) = \frac{1}{3!} \left(\frac{vt}{V}\right)^3 e^{-\frac{vt}{V}} + f_3(t)$$

It can be shown by induction that for a reactor with n stages that :

$$\phi_n(t) = \frac{1}{(n-1)!} \left(\frac{v}{V}\right)^n t^{n-1} e^{-\frac{vt}{V}}$$

$$f_n(t) = e^{-\frac{vt}{V}} \sum_{i=o}^{n-1} \frac{1}{i!}\left(\frac{vt}{V}\right)^i$$

2.3.2.2   Test Results.

Before proceeding with experimental mixing tests, the number of grains per unit weight of ilmenite sand was estimated from the screen analysis reported in Appendix II, Table 1. The number was conservatively estimated at 120,000 grains per gram. The number of grains in a fluidised bed containing of the order of a kilogram of ilmenite is therefore very large, sufficiently so to justify the assumption that the bed contains an infinite number of particles.

This assumption is implicit in the setting

up in Section 2.3.2.1 of the equation :

$$\frac{\partial f_1(t)}{\partial t} = \frac{v}{V} f_1(t) \; ; \qquad 0 < t < \infty$$

The derivation of functions for particle retention times is based on this equation.

Mixing tests were conducted with a fluidising air flow of 4.25 inches per second. It can be seen from results reported in Appendix III Figures 1 and 2 that this air flow produces turbulent fluidisation in beds of both ilmenite and silica sands having unit aspect ratio.

The first test comprised setting up the perspex model fluidised bed reactor as a single stage continuous flow reactor with the overflow level set at a height of one bed diameter above the air distributor. The reactor was set up with a continuous flow of silica sand passing through it. The feed was changed to ilmenite sand and the subsequent change in composition of the outcoming material with time determined by sampling the product at half minute intervals. The proportions by weight of the two materials were determined by magnetic separation of the samples. These data were converted to volumetric proportions on the

basis of the densities of the two materials.

The silica and ilmenite sands were each fed at a volumetric flow rate of 35 mils per minute. By weighing the contents of the fluidised bed reactor, nominal retention time was determined at 6.2 minutes when feeding quartz sand.

It has been shown that the distribution function for particle residence times in single stage reactors is given by :

$$f_1(t) = e^{-\frac{vt}{V}} \qquad 0 < t < \infty$$

$$\text{hence} \quad \frac{vt}{V} = \ln (f_1(t))^{-1}$$

If the logarithm of the volume fraction of silica in the outcoming mixture is plotted against time, a straight line should result, the gradient of which will be a measure of the space velocity. Results are shown in Appendix IV Figure 1.

The plot approximates a straight line showing that departures from the assumptions on which the above relation was established are not great. The stepped section in the latter stages of the test result from assay results being reported to the nearest whole per cent. When the product contains only a few per cent. of quartz, a logarithmic plot results in these exaggerated steps.

It can be seen that the plotted points fall
on a gradual curve instead of a straight line.
This is attributed to variation of the nominal
retention time, $\frac{V}{v}$, as the test proceeds. With
a fixed overflow level the capacity of a continious
reactor is dependant upon the expansion of the bed
which accompanies fluidisation. An air flow of
4.25 inches per second causes expansion in beds of
this size of about 25 per cent. for silica sand
and about 15 per cent for ilmenite, presumably as
a result of differing material densities. There is
therefore an increase in the nominal retention
time as the test proceeds.

From the gradient of a straight line drawn
through the experimental points, the mean space
velocity, $\frac{V}{v}$, is found to be 0.15, which is in
reasonable agreement with the $\frac{1}{6.2}$= 0.16 previously
determined for silica sand.

The test was repeated with the perspex
model set up as a five stage fluidised bed reactor,
each stage being the same size as the single stage
used in the previous test. To reduce the error
introduced by change in material density, the test
was limited to 20 minutes duration, during which
time the amount of ilmenite charged to the system
amounted to about 2/3 of the reactor contents.

The distribution function for a five stage reactor has been established as :

$$f_5(t) = e^{-\frac{vt}{V}} \sum_{i=1}^{5} \frac{1}{(i-1)!} \left(\frac{vt}{V}\right)^{i-1}$$

hence

$$\frac{vt}{V} = \ln \left(\frac{\sum_{i=1}^{5} \frac{1}{(i-1)!} \left(\frac{vt}{V}\right)^{i-1}}{f_5(t)} \right)$$

A plot of $\ln \left(\dfrac{\sum_{i=1}^{5} \frac{1}{(i-1)!} \left(\frac{vt}{V}\right)^{i-1}}{\text{vol. fraction silica}} \right)$

against time is shown in Appendix IV Figure 2.

The experimental plots fall on a straight line drawn to a gradient representing a space velocity of 0.16, the value previously determined for silica sand.

A further test was conducted with the five stage fluidised bed model using magnetic and non magnetic fractions separated from an impure sample of ilmenite sand from Stradbroke Island. These products, which are described in Appendix 11, Tables 3 and 4, have reasonably similar densities and there should not be much variation in the nominal retention time changing from one to the other during the test.

The space velocity was determined experiment-
ally at 0.184 prior to the test. Test results are
shown in Appendix 1V, Figure 3.

The straight line drawn through the
experimental points has a gradient equivalent to
a space velocity of 0.185, which is close to the
previously determined value of 0.184.

The most notable feature of the result is
the variation from the straight line of the points
determined after 60 minutes. The non magnetic
content of the product at 60 minutes was reported
as 1.8 per cent. The position of the points for the
last few per cent could not be determined precisely
through limitations of the method of magnetic
separation. The points are plotted on a logarithmic
scale so deviations from the straight line are
magnified. This irregularity is not regarded
as significant.

The three mixing tests were necessarily
approximate, mainly because of the small size of
the reactor model, but also because of differences
in densities of the materials used and inaccuracies
in analytical methods. Nevertheless experimental
results are sufficiently close to those predicted
on the assumption of complete mixing to indicate

that in a well fluidised bed, rapid and thorough mixing does occur. The results were reasonably conclusive and it was considered that further tests were not warranted.

3. CHEMICAL EQUILIBRIA.

It has been stated in Section I that this project originated as a result of free energy calculations for the reactions :

$$FeO + 3/2Cl_2 = FeCl_3 + 1/2O_2 \qquad (1)$$

$$Fe_2O_3 + 3Cl_2 = 2FeCl_3 + 3/2O_2 \qquad (2)$$
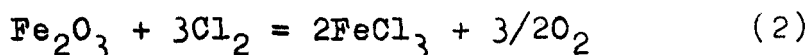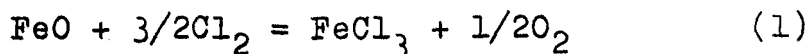
Free energy changes were calculated for these reactions at temperatures of $500^{\circ}K$, $1000^{\circ}K$ and $1500^{\circ}K$ (Madigan, unpublished data 1956). Published thermodynamic values were insufficient for calculation of the free energy changes so where necessary data were estimated.

The free energy values so obtained indicated that Reaction (1) would proceed in a forward direction at temperatures between $500^{\circ}K$ and $1500^{\circ}K$ and that Reaction (2) would proceed in a forward direction at $1000^{\circ}K$ and $1500^{\circ}K$ and in the reverse direction at $500^{\circ}K$.

Similar calculations showed that titanium dioxide should not react with chlorine in the temperature range $500^{\circ}K$ to $1500^{\circ}K$.

It was on the basis of these calculations that the original cyclic chlorination process for treating ilmenite originated.
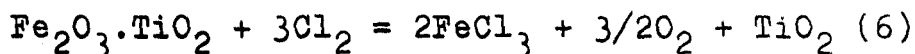
This process was subsequently modified to include prior oxidation of ilmenite to pseudobrookite and rutile, the pseudobrookite being treated by a cyclic chlorination process without the need for substantial addition of pure oxygen.

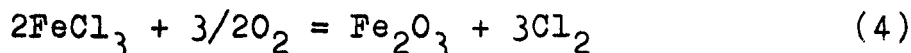The three reactions on which this process is based are :

Oxidation at 100C^{o}C :

$$2FeO.TiO_2 + 1/2O_2 = Fe_2O_3.TiO_2 + TiO_2 \qquad (5)$$

Chlorination at 1100°C :

$$Fe_2O_3.TiO_2 + 3Cl_2 = 2FeCl_3 + 3/2O_2 + TiO_2 \quad (6)$$

Regeneration at 500°C :

$$2FeCl_3 + 3/2O_2 = Fe_2O_3 + 3Cl_2 \qquad (4)$$
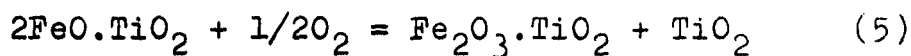
A search of available literature was made for reports of measurements of the extent to which these reactions proceed at various temperatures.

3.1   Literature Review.

It was first confirmed that titanium dioxide will not react with chlorine according to the following reaction to any great extent in the temperature interval 298°K to 1500°K.

$$TiO_2 + 2Cl_2 = TiCl_4 + O_2 \qquad (7)$$
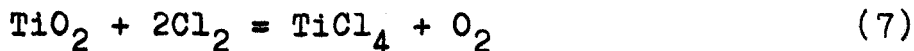
High temperature heat content and entropy data were taken from Kelley (1960). Heats of formation at $298^{\circ}K$ and standard entropy values were taken from Kubaschewski and Evans (1958). These data yielded free energy changes for Reaction (7) at $298^{\circ}K$ and at $1373^{\circ}K$ of +39.2 and +24.7 kilocalories respectively.

From the relation

$$\Delta G = -R.T.\ln Kp$$

it can be shown on the basis of these free energy changes that the percentages of chlorine converted to titaniun tetrachloride under equilibrium conditions are 8×10^{-13} and 2.1 at $298^{\circ}K$ and $1373^{\circ}K$ respectively.

For convenience it is assumed that the extent of this reaction is not significant and that the titania content of oxidised ilmenite does not react with chlorine in this temperature range. This assumption is reconsidered in a later section of this thesis.

An extensive search of the literature yielded little information on the high temperature oxidation of ilmenite with air. No report of the chlorination of oxidised ilmenite was found.
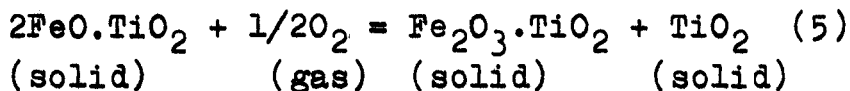
Japanese workers, Yoskida and Takei (1957)

and Hirakoso et al (1959) have reported finding
only one compound, pseudobrookite ($Fe_2O_3 \cdot TiO_2$) in
the binary ferric oxide - titanium dioxide system.
This is confirmed by the findings of Schmahl and
Meyer (1959). Hirakoso et al report that during
the roasting of ilmenite the following reaction
occurs:

$$4FeO \cdot TiO_2 + O_2 = 2Fe_2O_3 \cdot TiO_2 + 2TiO_2 \quad (8)$$
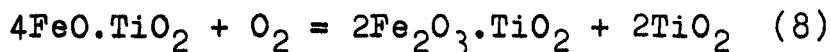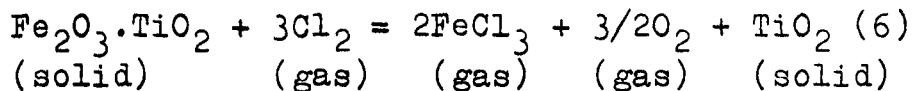
No quantitative measures of the oxidation
and chlorination reactions are available. An
extensive literature search yielded insufficient
thermodynamic data to calculate free energy changes
for either reaction.

For the oxidation reaction

$$2FeO \cdot TiO_2 + 1/2O_2 = Fe_2O_3 \cdot TiO_2 + TiO_2 \quad (5)$$
$$\text{(solid)} \quad \text{(gas)} \quad \text{(solid)} \quad \text{(solid)}$$

high temperature heat content and entropy data
for reactants and products have been published by
Kelley (1960). Standard entropies for the three
solid compounds and for gaseous oxygen have been
published by Kubaschewski and Evans (1958). Heats
of formation at $298^{\circ}K$ for ilmenite and for rutile
are available from the same source, but no value
for ferric titanate has been reported. Free energy
values therefore cannot be calculated.

For the chlorination reaction.

$$Fe_2O_3 \cdot TiO_2 + 3Cl_2 = 2FeCl_3 + 3/2O_2 + TiO_2 \quad (6)$$
$$\text{(solid)} \qquad \text{(gas)} \quad \text{(gas)} \quad \text{(gas)} \quad \text{(solid)}$$

in addition to the ferric titanate, oxygen and
rutile involved in reaction (5), data for chlorine
and ferric chloride are required. Adequate data
for chlorine are available from Kelley (1960) and
Kubaschewski and Evans (1958), however the data
available for ferric chloride are insufficient.

Anhydrous ferric chloride melts at $307^{\circ}C$ and
boils at $319^{\circ}C$ (Kubaschewski and Evans, 1958).
Ringwald (1949), surveying earlier investigations
of the properties of ferric chloride, found that
all previous workers reported that below $500^{\circ}C$ the
vapour density is in agreement with the formula
Fe_2Cl_6. At higher temperatures it was reported
that the dimeric form increasingly dissociates to
the monomer according to equation (9)

$$Fe_2Cl_6 = 2FeCl_3 \quad (9)$$
$$\text{(gas)} \qquad \text{(gas)}$$
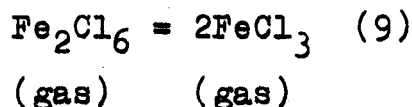
Ringwald further states that most of these
investigators observed the dissociation of gaseous
ferric chloride to ferrous chloride and chlorine
according to the reaction

$$Fe_2Cl_6 = 2FeCl_2 + Cl_2 \quad (10)$$
$$\text{(gas)} \qquad \text{(solid)} \ \text{(gas)}$$
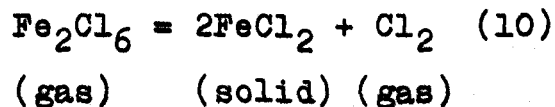
Stirneman (1925) reported that with gaseous mixtures

at 500°C the partial pressure of chlorine was 0.1
atmospheres when the vapour pressure of ferric
chloride was 10 atmospheres.

Partington (1937) gives vapour density
measurements for ferric chloride at intervals over
the temperature range 450° to 1300°C. According to
these data the vapour density corresponds to the
formula Fe_2Cl_6 at 444°C and to $FeCl_3$ at 750°C.
The degree of dissociation to ferrous chloride and
chlorine increases with temperature but does not
appear to be large at temperatures less than 1300°C.

It appears that at the chlorinating temperat-
ure of 1100°C, ferric chloride exists mostly as
the monomer and that the degree of dissociation to
ferrous chloride and chlorine is not very great.

Kubaschewski and Evans (1958) give the data
of Schäfer and Oehler (1953) for the reaction

$$2FeCl_3 = Fe_2Cl_6 \qquad (11)$$
$$(gas) \qquad (gas)$$
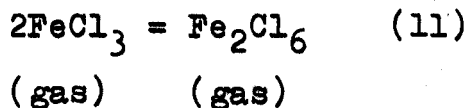
Over the temperature range 778° to 978°K,
the free energy change is given as

$$\Delta G \text{ (calories)} = -32,550 + 31.65T \pm 1000.$$

By extrapolation, the free energy change at
1373°K (1100°C) for equation (11) is 10.9 kilocalories.
The equilibrium constant can then be calculated by
means of the relation:

$$\Delta G_T = -RT.\ln K_p$$

If x is the fraction of monomeric ferric chloride converted to the dimeric form, then

$$K_p = \left(\frac{x/2}{1 - x/2}\right)\left(\frac{1 - x/2}{1 - x}\right)^2$$

$$= \frac{x(2 - x)}{4(1 - x)^2}$$

The value of 10.9 kilocalories for the free energy change at 1100°C yields a value of 3.5 per cent for the fraction of monomeric chloride converted to the dimeric form.

If it is assumed that monomeric and dimeric ferric chloride, ferrous chloride, and chlorine have densities in accordance with the formula Fe_2Cl_3, Fe_2Cl_6, $FeCl_2$ and Cl_2 respectively, and that at 1100°C 3.5 per cent of monomeric ferric chloride associates to the dimer, then according to the vapour densities reported by Partington (1937) about 14 per cent of monomeric ferric chloride dissociates to ferrous chloride and chlorine.

It appears that at the chlorination temperature of 1100°C a significant proportion of ferric chloride dissociates to ferrous chloride.

The accuracy of the data is questionable, so for the present ferric chloride is regarded as

existing only in monomeric form in the temperature range 700° to 1100°C. This assumption is reconsidered later.

While no work on the chlorination of oxidised ilmenite has been reported, several reports of investigations into the ferric oxide-chlorine-ferric chloride-oxygen system are available. The most important of these is that of Galmiche (1948) on the chlorination of ferric oxide.

Galmiche measured the amount of chlorine converted to ferric chloride when chlorine was passed over a sample of ferric oxide at various temperatures. A series of tests with different chlorine flow rates was carried out at each temperature and the chlorine utilized in the formation of ferric chloride extrapolated to the equilibrium condition of zero chlorine flow.

Equilibrium constants were calculated for the reaction :

$$2Fe_2O_3 + 6Cl_2 = 4FeCl_3 + 3O_2 \qquad (12)$$
$$\text{(solid)} \quad \text{(gas)} \quad \text{(gas)} \quad \text{(gas)}$$
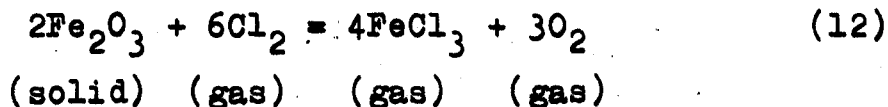
If x is the fraction of chlorine utilized in the formation of ferric chloride, then the equilibrium constant is given by the expression :

$$K_p = \frac{\left(\frac{2/3x}{1 + x/6}\right)^4 \left(\frac{x/2}{1 + x/6}\right)^3}{\left(\frac{1 - x}{1 + x/6}\right)^6}$$

$$= \frac{2x^7}{81(1 - x)^6(1 + x/6)}$$

Tests were conducted over a temperature range of from 700°C, below which the formation of dimeric ferric chloride becomes appreciable, to 1100°C. Chlorine utilizations and corresponding equilibrium constants are given in Table 1, Appendix V.

This method of determining equilibrium compositions is dependent on the nature of the ferric oxide surface. It has been demonstrated by Giauque (1949) that the surface energy of finely powdered solids can significantly influence the results with a method such as that used by Galmiche. The ferric oxide used by Galmiche was prepared by calcination of ferric nitrate and prior treatment with chlorine.

Subsequent to Galmiche's work, Smullin (1952) approached the equilibrium for reaction (12) from the other direction. Steady flowing streams of ferric chloride, chlorine and oxygen were mixed at controlled temperatures and the rate of deposition of ferric

oxide measured. The flow rate of ferric chloride was varied from test to test with flow rates for oxygen and chlorine and the temperature being held constant. The rates of formation of ferric oxide were then plotted against the flow of ferric chloride and were extrapolated to obtain conditions for zero rate of formation. Equilibrium compositions were determined by this means for temperatures between $704^{\circ}C$ and $982^{\circ}C$.

Equilibrium constants were then calculated from the relation :

$$K_p = \frac{\left(\dfrac{M_{FeCl_3} \cdot P}{M}\right)^4 \left(\dfrac{M_{O_2} \cdot P}{M}\right)^3}{\left(\dfrac{M_{Cl_2} \cdot P}{M}\right)^6}$$

$$= \frac{\left(M_{FeCl_3}\right)^4 \left(M_{O_2}\right)^3}{\left(M_{Cl_2}\right)^6} \cdot \frac{P}{M}$$

where M = mols of substance

P = absolute pressure in atmospheres

Results are presented in Table 2, Appendix V.

The results of Galmiche and Smullin are not

directly comparable and the nearest approach to
direct comparison is afforded through the calculated
equilibrium constants.   These are compared in
Figure 1 Appendix V.

That the difference between the results is
significant can be seen by calculating the equilib-
rium composition corresponding to Galmiche's
method using equilibrium constants determined by
Smullin.

Galmiche found that under equilibrium
conditions at $1000^{o}C$, 32.4 per cent of chlorine was
utilized in the formation of ferric chloride,
yielding a value for ln Kp of -9.29.

On the other hand Smullin found that at $982^{o}C$
the equilibrium flow rates for ferric chloride,
oxygen and chlorine were 0.000124, 0.00244 and
0.00549 mols per minute respectively.   This yielded
a value for ln Kp of -18.0.   Calculating the chlorine
utilization according to Galmiche's method which
corresponds to this value of the equilibrium
constant yields a value of 11.4 per cent, approx-
imately one third of that measured by Galmiche.

Insufficient detail is reported by Smullin
for a thorough assessment of his experimental
method, but it would seem that accurate measurement
of the rate of formation of ferric oxide according

to his method would be difficult. Smullin's results are much more inconsistent within themselves than are those of Galmiche.

In view of the different results reported by Galmiche and Smullin, measurements of equilibrium conditions for this system have been made by Wilmshurst (unpublished data 1959) working in the same laboratories as the author. Chlorine utilizations after the method of Galmiche were measured using pelletized rouge powder of 99.8 per cent purity as ferric oxide.

Experimental results and corresponding equilibrium constants are given in Table 3, Appendix V. Results of Wilmshurst and Galmiche are compared in Figure 2, Appendix V.

Finally one further quantitative measurement of the equilibrium between ferric oxide, chlorine, and ferric chloride has been reported in the literature. Kangro (1957) has stated that at $530^{\circ}C$ in the presence of the stoichiometric proportion of oxygen, about 96 per cent of ferric chloride converts to finely powered ferric oxide and free chlorine.

It appears that $500^{\circ}C$ would be a suitable temperature at which to conduct the regeneration reaction and reclaim chlorine for further chlorinat-

ion. This will be discussed later.

3.2 Experimental

Measurements of the fraction of chlorine
utilized in the formation of ferric chloride by
reaction with ferric titanate were made following
the method of Galmiche (1948) and Wilmshurst (1959).

The material used for the tests was oxisised
Stradbroke Island ilmenite. This was prepared by
oxidising 1000 gm charges of ilmenite in the three
inch diamete: high temperature fluidised bed
reactor described in Section 2.

The charge was fluidised with an air flow rate
of 8.9 gms per minute and held at 1000°C for two
hours. Composition of the oxidised material was
reported as:

Ferric oxide	46.8 per cent
Ferrous oxide	nil
Titanium dioxide	49.0 per cent.

For each test a charge of about 100 gms of
oxidised ilmenite was held in a 1-inch diameter
aluminous porcelain tube with plugs of silica wool
at either end. The tube was held vertically inside
a resistance furnace. The temperature of the charge
was measured with a chromel-alumel thermocouple
and was regulated by manual adjustment of a stepless
auto-transformer controlling the resistance winding
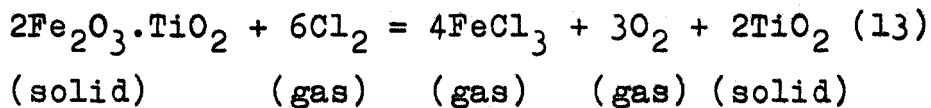
of the furnace.

Chlorine at metered flow rates was passed upward through the charge for periods of up to three hours, depending on the rate of chlorine flow. The extent of reaction was determined by the loss in weight of the charge.

3. 3 Results and Calculations

The first tests were carried out at a temperature of $1100^{o}C$ with chlorine flow rates of 0.30, 0.15 and 0.075 gms per minute. The results at different flow rates did not appear to be significantly different. In addition, while the ilmenite in the bottom of the charges was subject to considerable attack, there was no visible evidence of attack at the top of the charge.

It was therefore concluded that the gases leaving the bed were in equilibrium with the solid charge at all three flow rates. Subsequent tests at different temperatures were carried out at chlorine flow rates of 0.30 and 0.15 gms per minute only.

The results, together with equilibrium constants calculated for the reaction:

$$2Fe_2O_3 \cdot TiO_2 + 6Cl_2 = 4FeCl_3 + 3O_2 + 2TiO_2 \quad (13)$$
$$\text{(solid)} \quad \text{(gas)} \quad \text{(gas)} \quad \text{(gas)} \quad \text{(solid)}$$

are reported in Table 4, Appendix V and in Figures

3 and 4, Appendix V. Equilibrium constants were
calculated on the same basis as has previously
been done with the data of Galmiche (1948) for
the chlorination of hematite. If x is the fraction
of chlorine utilized in the formation of ferric
chloride, then

$$K_p = \frac{2x^7}{81(1-x)^6(1+x/6)}$$

It is usual with data of this type to obtain
a straight line relationship between ln Kp and 1/T.
The slope of this line is used to obtain a measure
of the heat of reaction. The temperature range
over which a straight line relationship can be
assumed without introducing excessive error is
about 150°C (Kubaschewski and Evans, 1958).

The plot, Figure 4, Appendix V, of -ln Kp
against reciprocal temperature shows that although
the span is only 200°C, experimental points do not
fall on a straight line but could better be fitted
by a smooth curve. Accordingly both linear and
curvelinear regressions were considered before
selecting the linear regression as providing the
most suitable algebraic expression for the data.

To obtain a curvelinear relationship, a
curve of the form

$$\ln Kp = A + B(T^{-1}) + C(T)$$

was fitted to the data.

Then the heat of reaction may be found from the relationship

$$\Delta H = R T^2 \cdot \frac{d \ln Kp}{d T}$$

$$= -R B + R C T^2$$

The free energy charge is given by

$$\Delta G = -R T \ln Kp$$

$$= -R B - R A T - R C T^2$$

The entropy change for the reaction is

$$\Delta S = \frac{\Delta G - \Delta H}{T}$$

$$= R A + R C T$$

The change in the heat capacity is obtained from the relation

$$\Delta H_T = \int_{298}^{T} \Delta Cp \; dT + \Delta H_{298}$$

Hence $\Delta Cp = 2 R C T$

and $\Delta H_{298} = -R B$

A least squares fit of the data gave values for the coefficients in the equation

$$\ln Kp = A + B(T^{-1}) + C(T)$$

of

$$A = -494$$

$$B = 290,000$$

$$C = 0.201$$

This curve is shown in Figure 4, Appendix V. Values for ΔCp calculated from these data range from 1020 calories per **degree** at $1000^{\circ}C$ to 1180 at $1200^{\circ}C$.

Heat capacity values are available for all substances participating in the reaction with the exception of gaseous monomeric ferric chloride. Following the data of Kelly (1960), for equation(13),

$$\Delta Cp = 4 \ (Cp \ (FeCl_3) - 87.74$$
$$- 7.92x \ 10^{-3} \ T + 9.00x \ 10^5 \ T^{-2} \ \text{calories}$$

per degree

This function yields values for ΔCp as follows:

at $1000^{\circ}C$ $\quad \Delta Cp = 4(Cp \ (FeCl_3)) - 97.3$

at $1200^{\circ}C$ $\quad \Delta Cp = 4(Cp \ (FeCl_3)) - 99.0$

Equating these values to those obtained experimentally yield the following values for the heat capacity of monomeric gaseous ferric chloride:

at $1000^{\circ}C$ $\qquad Cp \ (FeCl_3) = 280$ calories per degree

at $1200^{\circ}C$ $\qquad Cp \ (FeCl_3) = 320$ calories per degree

The heat capacity of ferric chloride may be

estimated after the method outlined by Kubaschewski and Evans (1958) from the interatomic linkages in the molecule. This method yields a value of 18 calories per degree. The values obtained from the experimentally determined relationship

$$\ln Kp = A + B(T^{-1}) + C(T)$$

are therefore grossly in error.

Fitting a curve of this type to the data results in coefficients B and C having a dependence of large magnitude on the amount of curvature in the experimental plot. Small errors in determining the curvature therefore produce extreme errors in the values of B and C with consequent variation in such derived quantities as ΔCp.

For this reason a linear relationship between ln Kp and reciprocal temperature was established.

The relationship was of the form

$$\ln Kp = A + B(T^{-1})$$

Hence $\quad \Delta H = -RB$

$$\Delta G = -RB - R A T$$

$$\Delta S = RA$$

$$\Delta Cp = 0$$

Values of coefficients determined by a least fit were

$$A = 57.7$$

$$B = -87,100$$

This line is shown in Figure 4, Appendix V.

These values for A and B yield a value for ΔH over the temperature range $1000^{\circ}C$ to $1200^{\circ}C$ of +173,000 calories and for ΔS a value of 115 calories per degree.

Free energy changes calculated from these values of A and B are:

T	ΔG
$1000^{\circ}C$	27,100 calories
$1027^{\circ}C$	24,000
$1050^{\circ}C$	21,400
$1100^{\circ}C$	15,600
$1150^{\circ}C$	9,900
$1200^{\circ}C$	4,200

Equilibrium compositions corresponding to these free energy values were then calculated and are represented by the line of accepted values in Figure 3 Appendix V.

T	Chlorine utilization
$1000^{\circ}C$	27.9 per cent
$1100^{\circ}C$	45.2 per cent
$1200^{\circ}C$	61.7 percent

It is implicit in assuming a linear relationship between ln Kp and 1/T that $\Delta Cp = 0$ over the temperature range being considered.

It has been shown previously that

at $1000^{\circ}C$ $\triangle Cp = 4(Cp(FeCl_3)) - 97.3$

and at $1200^{\circ}C$ $\triangle Cp = 4(Cp(FeCl_3)) - 99.0$

The average value for $Cp(FeCl_3)$ over the temperature range $1000^{\circ}C$ to $1200^{\circ}C$ is therefore 24.5 calories per degree. This exceeds the value of 18 calories per degree estimated from the inter-atomic linkages, but as the molecular weight of ferric chloride is relatively high, and the temperature is high (Kubaschewsli and Evans, 1958) this value is acceptable.

Similar treatment of the data of Wilmshurst (unpublished data 1959) for the chlorination of hematite according to equation (12) yields values for the coefficients of

$A' = 56.0$

$B' = -80,600$

These yield values for $\triangle H$ and $\triangle S$ of $+ 160,000$ calories and 111 calories per degree respectively over the temperature range $865^{\circ}C$ to $1100^{\circ}C$.

Calculated free energy changes are:

T	$\triangle G$
$900^{\circ}C$	29,600 calories
$950^{\circ}C$	24,100
$1000^{\circ}C$	18,500

T	ΔG
$1027^\circ C$	15,500 Calories
$1050^\circ C$	12,900
$1100^\circ C$	7,400

Equilibrium compositions corresponding to these free energy values were then calculated and are shown as the line of accepted values in Figure 2 Appendix V.

T	Chlorine utilization
$900^\circ C$	22.3 per cent
$1000^\circ C$	39.3 per cent
$1027^\circ C$	43.8 per cent
$1100^\circ C$	56.8 per cent

Since a linear relationship between ln Kp and 1/T is assumed, ΔCp for reaction (12) will be zero. With heat capacity values for ferric oxide, chlorine, and oxygen from Kelley (1960) the following values for ΔCp are obtained:

$$\Delta Cp \; 900^\circ C = 4 \; (Cp(FeCl_3)) - 96.57$$

$$\Delta Cp \; 1100^\circ C = 4 \; (Cp(FeCl_3)) - 96.92$$

The average value for the heat capacity of ferric chloride is therefore 24.2 calories per degree. This figure is very close to that obtained previously from chlorinating oxidised ilmenite.

As a result of this work, values of

thermodynamic properties are available over the temperature range $1000^{\circ}C$ to $1100^{\circ}C$ for reactions (12) and (13).

$$2Fe_2O_3 + 6Cl_2 = 4FeCl_3 + 3O_2 \quad (12)$$

$$2Fe_2O_3 \cdot TiO_2 + 6Cl_2 = 4FeCl_3 + 3O_2 + 2TiO_2 \quad (13)$$
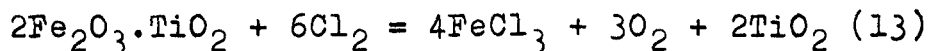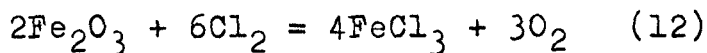
Corresponding thermodynamic values can therefore be obtained by subtraction for reaction (14)

$$2Fe_2O_3 + 2TiO_2 = 2Fe_2O_3 \cdot TiO_2 \quad (14)$$
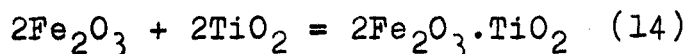
Heat reaction, ΔH, between $1000^{\circ}C$ and $1100^{\circ}C$ is therefore $-12,900$ calories and ΔS is -2.4 calories per degree.

The free energy is

T	ΔG
$1000^{\circ}C$	-8600 calories
$1027^{\circ}C$	-8500
$1050^{\circ}C$	-8400
$1100^{\circ}C$	-8300

Published data are available from which the entropy change for reaction (14) may be calculated. The standard entropy at $298^{\circ}K$ for pseudobrookite is available from Kubaschewski and Evans (1958) and the high temperature entropy from Kelley (1960).

$$S_{1300^{\circ}K} \ (Fe_2O_3 \cdot TiO_2) = 106.63 \text{ calories}$$

per degree.

The same source provide data for hematite.

$S_{1300\ ^{O}K}$ $(Fe_2O_3) = 70.01$ calories per degree.

Kelley and Mah (1959) give a value for the entropy of rutile at $1300^{O}K$.

$S_{1300^{O}K}$ $(TiO_2) = 36.39$ calories per degree.

The entropy change for reaction(14) is obtained by difference

$$\Delta S_{1300^{O}K} = 213.26 - 140.02 - 72.78$$
$$= 0.46 \text{ calories per degree}$$

This may be compared with the value previously obtained by subtraction of the experimentally determined entropy change for reaction (13) from reaction (12).

$$\Delta S_{1300^{O}K} = 112.2 - 114.6$$
$$= -2.4 \text{ calories per degree}$$

Since both values are obtained by differences between comparatively large numbers, the difference between the two values for the entropy change is not regarded as significant.

With data for high temperature heat from Kelley (1960), it is now possible to calculate ΔH_{298} for reaction (15)

$$Fe_2O_3 + TiO_2 = Fe_2O_3 \cdot TiO_2 \quad (15)$$
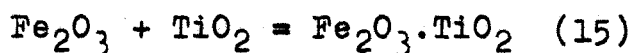
$$\Delta H_{298} = -3800 \text{ Calories}$$

With a value for the heat of formation at

$298^\circ K$ for rutile from Kelley and Mah (1959) and for hematite from Kubaschewski and Evans (1958), it becomes possible to calculate the standard heat of formation of pseudobrookite.

$$\Delta H_{f298^\circ K} (Fe_2O_3 \cdot TiO_2) = -426,000 \text{ calories}$$

With values for the heats of formation for ilmenite and rutile at $298^\circ K$, Kelley and Mah (1959), it is possible to calculate the heat of reaction (5)

$$2FeO \cdot TiO_2 + 1/2O_2 = Fe_2O_3 \cdot TiO_2 + TiO_2 \quad (5)$$

$$\Delta H_{298} = -60,000 \text{ calories}$$

With values for high temperature heat contents from Kelley (1960) it becomes possible to calculate the heat reaction at $1300^\circ K$ for reaction (5)

$$\Delta H_{1300^\circ K} = -59,000 \text{ calories}$$

With high temperature entropy values from Kelley (1960) and with the heat reaction at $1300^\circ K$ previously calculated reaction (8) it is now possible to calculate the free energy change at $1300^\circ K$ for this reaction.

$$4FeO \cdot TiO_2 + O_2 = 2Fe_2O_3 \cdot TiO_2 + 2TiO_2 \quad (8)$$
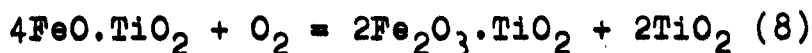
$$\Delta G_{1300} = \Delta H_{1300} - T \Delta S_{1300}$$

$$= -57,000 \text{ calories}$$

The equilibrium pressure for oxygen may be found from the relation

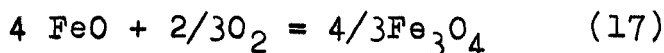$$\Delta G = - R T \ln K_p$$
$$= R T \ln (P(O_2))$$

The equilibrium oxygen pressure at $1300^{\circ}K$ is

$P(O_2) = 2 \times 10^{-10}$ atmospheres

The dissociation pressure at $298^{\circ}K$, calculated in a similar manner, is 3×10^{-78} atmospheres.
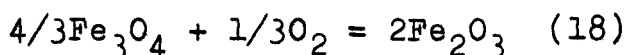
Alternatively the free energy change for reaction (8) may be calculated from the free energy data, available from Kubaschewski and Evans (1958), for the reactions:
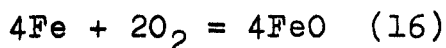
$$4Fe + 2O_2 = 4FeO \quad (16)$$
$$\Delta G_{1300} = -170,500 \text{ calories}$$

$$4 FeO + 2/3O_2 = 4/3Fe_3O_4 \quad (17)$$
$$\Delta G_{1300} = -47,700 \text{ calories}$$

$$4/3Fe_3O_4 + 1/3O_2 = 2Fe_2O_3 \quad (18)$$
$$\Delta G_{1300} = -10,600 \text{ calories}$$

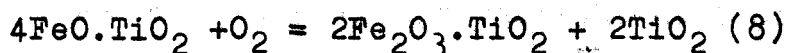$$4FeO.TiO_2 = 4Fe + 2O_2 + TiO_2 \quad (19)$$
$$\Delta G_{1300} = 191,200 \text{ calories}$$

These data may be combined with the free energy change at $1300^{\circ}K$ previously calculated for reaction (14)
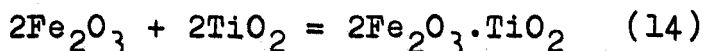
$$2Fe_2O_3 + 2TiO_2 = 2Fe_2O_3.TiO_2 \quad (14)$$
$$\Delta G_{1300} = -8500 \text{ calories}$$

The free energy change reaction (8) is obtained by summation.

$$4FeO.TiO_2 + O_2 = 2Fe_2O_3.TiO_2 + 2TiO_2 \quad (8)$$

$$\Delta G_{1300} = -46,000 \text{ calories}$$

The oxygen pressure corresponding to this free energy is 2×10^{-8} atmospheres.

The free energy changes for reaction (8) at $1300°K$ calculated by the two methods differ by some 10,000 calories. This difference appears to result from drawing data from different sources for the two calculations.

The difference is of no practical significance as the corresponding oxygen dissociation pressures are both extremely small. These data indicate that it should be possible to oxidise ilmenite completely to pseudobrookite with comparatively low partial pressures of oxygen. For example it should be possible to burn carbonaceous fuels with an excess of air and use the resulting heated gas mixture containing a few per cent of oxygen to oxidise ilmenite. The rate of oxidation under any given conditions could only be determined by experiment.

The free energy changes involved in the oxidation of ilmenite and the formation of pseudobrookite can now be examined with a view to determining the process involved in the natural weathering of ilmenite.

It has been established that the heat of reaction at $298°K$ for reaction (15) is -3750 calories.

$$Fe_2O_3 + TiO_2 = Fe_2O_3 \cdot TiO_2 \quad (15)$$
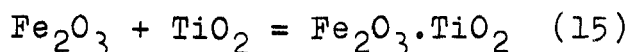
With entropy values at $298^{\circ}K$ for pseudo-brookite and hematite from Kubaschewski and Evans (1958), and for rutile from Kelley and Mah (1959), it is possible to calculate the free energy change at $298^{\circ}K$ for reaction (15).

$$\Delta G_{298} = -4900 \quad \text{calories}$$

It has already been established that for reaction (15)

$$\Delta G_{1300} = -4300 \text{ calories}$$

Oxidation of ilmenite in the temperature range $298^{\circ}K$ to $1300^{\circ}K$ should therefore yield pseudobrookite and rutile and not hematite and rutile. The free energy changes for the formation of both mixtures have been calculated for comparison.

The free energy change at $298^{\circ}K$ has been calculated for reaction (5) as follows:

$$2FeO \cdot TiO_2 + 1/2O_2 = Fe_2O_3 \cdot TiO_2 + TiO_2 \quad (5)$$
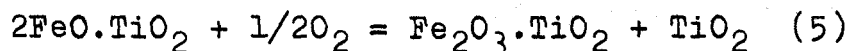
The heat of reaction at $298^{\circ}K$ has been determined as $- 60,000$ calories. Values for the entropy at $298^{\circ}K$ for ilmenite and oxygen are available from Kelley and Mah (1959), which together with the data used in the previous calculation yield a value for the free energy change at $298^{\circ}K$ for reaction (5).

$$\Delta G_{298} = -52,800 \text{ calories}$$

It has already been determined that for reaction (5)

$$\Delta G_{1300} = -28,700 \text{ calories}$$

Subtracting the values for reaction (15) from those for reaction (5) yield values for the free energy changes at $298^{\circ}K$ and $1300^{\circ}K$ for reaction (20)

$$2FeO.TiO_2 + 1/2O_2 = Fe_2O_3 + 2TiO_2 \qquad (20)$$
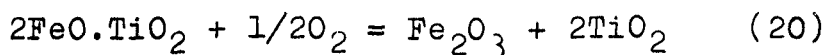
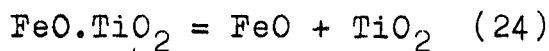$$\Delta G_{298} = -47,900 \text{ calories}$$

$$\Delta G_{1300} = -24,000 \text{ calories}$$

The free energy changes involved in the oxidation of ilmenite to pseudobrookite and rutile, equation (5), is greater than that for oxidation to hematite and rutile equation (20), so that only pseudobrookite and rutile should be formed.

The free energy changes for these reactions at $298^{\circ}K$ and $1300^{\circ}K$ have accordingly been calculated.
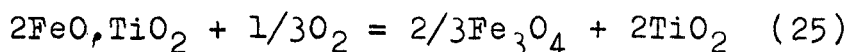
The free energy of formation at $298^{\circ}K$ and at $1300^{\circ}K$ for wüstite, magnetite and hematite can be determined from the standard heats of formation at $298^{\circ}K$ of the three oxides and from entropy values for iron, oxygen and the iron oxides given by Kubaschewski and Evans (1958) and from high temperature heat contents and entropies given by Kelley (1960). With values for the free energy

of formation at $298^{\circ}K$ and $1300^{\circ}K$ for ilmenite and rutile from Kelley and Mah (1959) the free energy changes for the following reactions may be calculated:
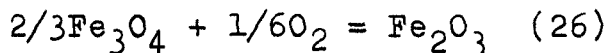
$$FeO.TiO_2 = FeO + TiO_2 \quad (24)$$

$\Delta G_{298} = 6400$ calories

$\Delta G_{1300} = 5100$ calories

$$2FeO.TiO_2 + 1/3O_2 = 2/3Fe_3O_4 + 2TiO_2 \quad (25)$$

$\Delta G_{298} = -32,800$ calories

$\Delta G_{1300} = -18,200$ calories

$$2/3Fe_3O_4 + 1/6O_2 = Fe_2O_3 \quad (26)$$

$\Delta G_{298} = -15,100$ calories

$\Delta G_{1300} = -3,800$ calories

It has formerly been shown that for reaction (15) the free energy changes at $298^{\circ}K$ and $1300^{\circ}K$ are:

$$Fe_2O_3 + TiO_2 = Fe_2O_3.TiO_2 \quad (15)$$
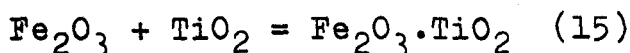
$\Delta G_{298^{\circ}K} = -4900$ calories

$\Delta G_{1300^{\circ}K} = -4300$ calories

These free energy changes show that the sequence of reactions is possible.

It is evident from the positive free energy change for reaction (24) that ilmenite will not spontaneously dissociate to ferrous oxide and titania.

It is also apparent from the high favourable

free energy change for reaction (25) that ilmenite could be oxidised to magnetite and rutile. No compounds of magnetite and rutile having the form $(Fe_3O_4)_x \cdot (TiO_2)_y$ have been identified and reported in the literature so it appears that such compounds do not exist.

It is evident from the free energy change for reaction (26) that magnetite could be oxidised to hematite which could then combine with rutile to form pseudobrookite.

It is possible that natural weathering of ilmenite produces magnetite and eventually hematite but that the hematite is not favourably situated for recombination with rutile and is transformed into limonite instead.
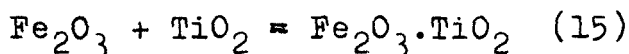
This is possibly the explanation of why ilmenite beach sands almost invariably contain rutile, magnetite and limonite in association with ilmenite but very rarely contain pseudobrookite.

The cyclic chlorination process as a whole involves three separate chemical reactions, the oxidation of ilmenite to pseudobrookite and rutile, chlorination of pseudobrookite to produce ferric chloride, oxygen and rutile, and regeneration of chlorine for further use by reaction of the ferric chloride and oxygen to produce ferric oxide and
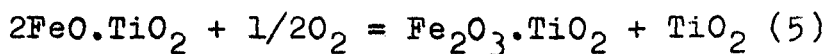
chlorine. The overall process may be summarised by equation (20)

$$2FeO.TiO_2 + 1/2O_2 = Fe_2O_3 + 2TiO_2 \quad (20)$$
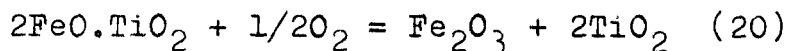
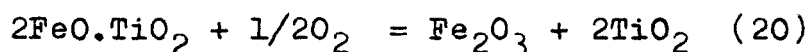The heat of reaction for reaction (20) may be obtained from the heats of reaction for reactions (15) and (5).

$$Fe_2O_3 + TiO_2 = Fe_2O_3.TiO_2 \quad (15)$$

$$\Delta H_{298} = -3,800 \text{ calories}$$

$$2FeO.TiO_2 + 1/2O_2 = Fe_2O_3.TiO_2 + TiO_2 \quad (5)$$

$$\Delta H_{298} = -60,000 \text{ calories}$$

By summation

$$2FeO.TiO_2 + 1/2O_2 = Fe_2O_3 + 2TiO_2 \quad (20)$$

$$\Delta H_{298} = -57,000 \text{ calories.}$$

The overall process is therefore exothermic, releasing 28,000 calories per gram-molecular weight of ilmenite treated.

It has been stated previously on the basis of thermodynamic data published by Kubaschewski and Evans (1958) and Kelley (1960), that at $1373^{\circ}K$ 2.1 per cent of chlorine is converted to titanium tetrachloride when reacted with rutile according to equation (21)

$$3TiO_2 + 6Cl_2 = 3TiCl_4 + 3O_2 \quad (21)$$
(solid) (gas) (gas) (gas)
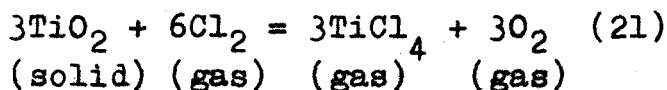
Calculation of the experimental data for

chlorination of pseudobrookite according to equation (13) has been based on the assumption that no reaction occurs between the titania content of the oxidised ilmenite and chlorine.
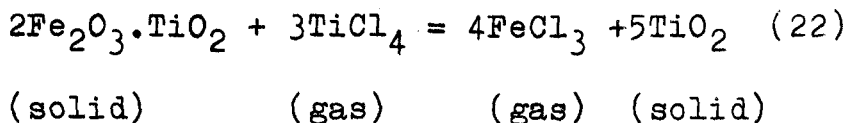
$$2Fe_2O_3.TiO_2 + 6Cl_2 = 4FeCl_3 + 3O_2 + 2TiO_2 \quad (13)$$
$$\text{(solid)} \qquad \text{(gas)} \quad \text{(gas)} \quad \text{(gas) (solid)}$$
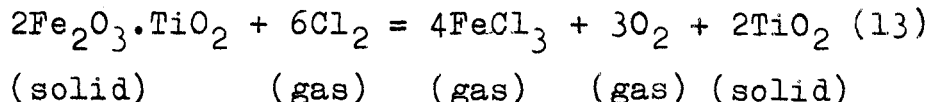
It is necessary to reconsider this assumption.

Subtraction of the free energy change for reaction (21) from that of reaction (13) yields the free energy change for reaction (22).

$$2Fe_2O_3.TiO_2 + 3TiCl_4 = 4FeCl_3 + 5TiO_2 \quad (22)$$
$$\text{(solid)} \qquad \text{(gas)} \qquad \text{(gas) (solid)}$$

The free energy change for reaction (22) at $1000°C$ is $-51,000$ calories and that at $1200°C$ is $-66,000$ calories.

If y is the fraction of titanium tetrachloride consumed by reaction (22) then

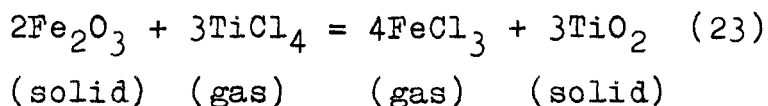$$Kp = \frac{4y/3}{1 + y/3}^4 \; \frac{1 + y/3}{1 - y}^3$$
$$= \frac{9.48y^4}{(3 + y)(1 - y)^3}$$

Values for y calculated from the relation

$$\Delta G = -RT \ln Kp$$

range from 99.92 per cent at $1000°C$ to 99.93 per cent at $1200°C$.

It is interesting to compare these values with corresponding values for the chlorination of hematite with titanium tetrachloride according to reaction (23)

$$2Fe_2O_3 + 3TiCl_4 = 4FeCl_3 + 3TiO_2 \quad (23)$$
$$\text{(solid)} \quad \text{(gas)} \qquad \text{(gas)} \quad \text{(solid)}$$

Subtracting the free energy change for reaction (21) from that for the chlorination of hematite according to reaction (12) yields the free energy change for reaction (23).

$$2Fe_2O_3 + 6Cl_2 = 4FeCl_3 + 3O_2 \quad (12)$$
$$\text{(solid)} \quad \text{(gas)} \qquad \text{(gas)} \quad \text{(gas)}$$
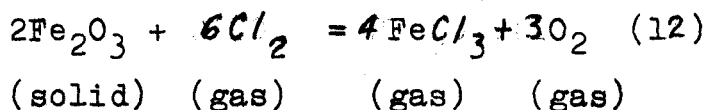
The free energy change at $900^{\circ}C$ is $-52,000$ calories, and at $1100^{\circ}C$ is $-67,000$ calories. Corresponding values for the percentages of titanium tetrachloride consumed by reaction (23) at $900^{\circ}C$ and $1100^{\circ}C$ are 99.93 and 99.96 per cent respectively.
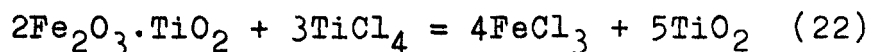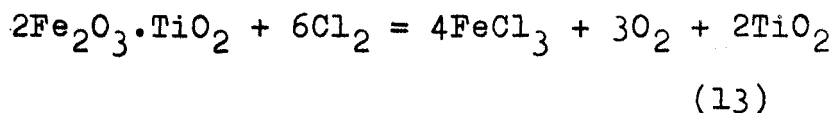
It appears therefore that no significant amount of titanium tetrachloride is formed during the chlorination of pseudobrookite until all the ferric oxide is removed. However this may be determined more precisely by considering the reactions which take place in a multiple stage chlorination reactor with substantially pure rutile in the bottom stage and oxidised ilmenite in the upper stages.

Reaction between chlorine and rutile occurs in the bottom stage according to equation (21).

$$3TiO_2 + 6Cl_2 = 3TiCl_4 + 3O_2 \quad (21)$$
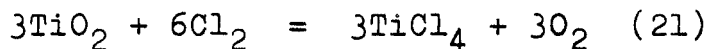
If x represents the mols of chlorine consumed by this reaction per mol of chlorine passing through the bottom stage, then the gas entering the upper stages will be depleted by x mols of chlorine and will contain $x/2$ mols of titanium tetrachloride and $x/2$ mols of oxygen.

This gaseous mixture then reacts in the upper stages according to reactions (13) and (22).

$$2Fe_2O_3 \cdot TiO_2 + 6Cl_2 = 4FeCl_3 + 3O_2 + 2TiO_2$$
$$(13)$$

$$2Fe_2O_3 \cdot TiO_2 + 3TiCl_4 = 4FeCl_3 + 5TiO_2 \quad (22)$$

If a further y mols of chlorine are consumed by reaction (13) and z mols of titanium tetrachloride are consumed by reaction (22), then the resulting gaseous mixture contains:

Cl_2	$1 - x - y$ mols
$TiCl_4$	$x/2 - z$ mols
$FeCl_3$	$2y/3 + 4z/3$ mols
O_2	$x/2 + y/2$ mols
	$1 + y/2 + z/3$
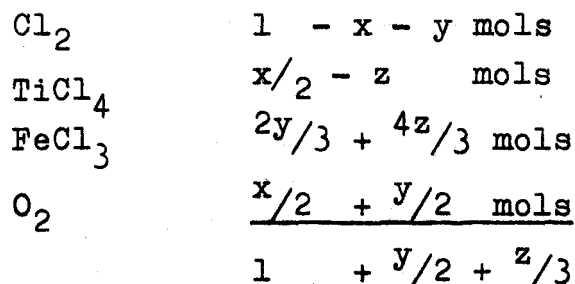
It has already been established that at $1373^{\circ}K$ 2.1 per cent of chlorine is consumed by reaction (21) i.e. $x = 0.021$.

Equilibrium constants at $1373^\circ K$ for reactions (13) and (22) are known so it is possible to find values for y and z at $1373^\circ K$ from the relations:

Reaction (13)

$$Kp = \frac{6912 \left(\frac{y}{6} + \frac{z}{3}\right)^4 \left(\frac{x}{6} + \frac{y}{6}\right)^3}{\left(1 + \frac{y}{6} + \frac{z}{3}\right) \left(1 - x - y\right)^6}$$

Reaction (22)

$$Kp = \frac{256 \left(\frac{y}{6} + \frac{z}{3}\right)^4}{\left(1 + \frac{y}{6} + \frac{z}{3}\right) \left(\frac{x}{2} - z\right)^3}$$

Hence y = 0.431

z = 0.0103

The gaseous mixture leaving the bottom stage therefore contains:

Cl_2	0.979	mols
$TiCl_4$	0.0105	mols
O_2	0.0105	mols

The gaseous mixture leaving the top stage contains:

Cl_2	0.548	mols
$TiCl_4$	0.00015	mols
O_2	0.226	mols
$FeCl_3$	0.301	mols

Under equilibrium conditions the chlorine converted to titanium tetrachloride in the bottom stage of a multiple stage fluidised bed reactor amounts to 2.1 per cent of the total chlorine.

Of the titanium tetrachloride so formed, 98.6 per cent is reconverted to titanium dioxide in the upper stages so that 0.03 per cent of the chlorine fed to the reactor leaves as titanium tetrachloride. This compares with 45.2 per cent leaving in the form of ferric chloride.

Substantially all of the titanium tetrachloride formed in the bottom stage should react with ferric oxide in the upper stages. The removal of titanium from the reactor as titanium tetrachloride should not be significant but there would be some titanium circulating between the bottom few stages.

Since at most 2.1 per cent of the chlorine passing through the reactor would be involved in this transport reaction, the amount of titanium recirculating is not likely to be of any consequence. However, it would be desirable to measure experimentally the amount of titanium deposited as oxide from the tetrachloride as the rate of reaction may be sufficiently slow to influence the extent to which deposition of the oxide proceeds. However, this is not likely to be significant. One would expect rapid reaction between titanium tetrachloride vapour and oxygen released by reaction of chlorine with pseudobrookite. An investigation into this

aspect lies outside the scope of the present work.

The equilibrium composition of the gaseous
mixture leaving the top stage of a multiple stage
reactor, which has been determined, is the same
as the equilibrium composition of the chlorination
gases leaving a single stage reactor containing
oxid sed ilmenite.

Therefore the assumption that no signific-
ant reaction occurs between the titania content of
the oxidised ilmenite and chlorine, on which
calculation of the experimental data for the
chlorination of pseudobrookite has been based, is
justified.

It has been assumed in the calculation of
chlorination test results that the only iron
chlorine compound formed has been monomeric ferric
chloride. Extrapolation of data from Kubaschewski
and Evans (1958) has yielded a figure of 3.5
per cent for the proportion of monomer which
associates to the dimeric form at $1100^{o}C$. This
data is extrapolated well outside the rage over
which it was determined and consequently the result
cannot be regarded as accurate. It is probable
that the degree of association is less than that
obtained by linear extrapolation of the data. In
any case the extent is small so that assuming

association does not take place at all does not introduce any great error.

It has been shown on the basis of data reported by Partington (1937) that about 14 per cent of monomeric ferric chloride dissociates at $1100^{o}C$ to ferrous chloride and chlorine. This has been disregarded up to the present and should now be reconsidered.

Data is available (Kubaschewski and Evans, 1958) from which it is possible to calculate the free energy of formation of gaseous ferrous chloride from its elements over the temperature range $1300^{o}K$ to $1812^{o}K$.

$$Fe + Cl_2 = FeCl_2 \qquad (27)$$
$$(\delta) \quad (gas) \quad (gas)$$
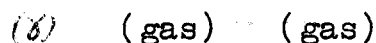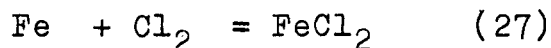
$$\Delta G_{f1373^{o}K} \ (FeCl_2) = -49,300 \ \text{calories}$$

This data, together with the experimental data of Wilmshurst (unpublished data 1959), for reaction (12) affords a means of calculating the degree of dissociation in the temperature range of interest.

$$2Fe_2O_3 + 6Cl_2 = 4FeCl_3 + 3O_2 \quad (12)$$
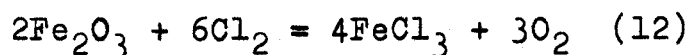
$$\Delta G_{1373^{o}K} = +7,400 \ \text{calories}$$

The free energy of formation at $1373^{o}K$ of ferric oxide may be calculated from the heat of

formation at 298°K of ferric oxide and the standard entropies at 298°K for ferric oxide, iron, and oxygen from Kubaschewski and Evans (1958), and the high temperature heat contents and entropies for ferric oxide, iron, and oxygen from Kelley (1960).

These data yield a value for the free energy of formation of ferric oxide of

$$G_{1373^{\circ}K} \ (Fe_2O_3) \ = \ -112,200 \text{ calories}$$

The free energy of formation of gaseous monomeric ferric chloride can then be determined approximately from the free energy change for reaction (12)

$$G_{1373^{\circ}K} \ (FeCl_3) \ = \ -54,200 \text{ calories}$$

Combining this data with the free energy of formation of ferrous chloride yields the free energy change for reaction (28)

$$FeCl_3 \ = \ FeCl_2 \ + \ 1/2Cl_2$$

(gas)　　(gas)　　(gas)
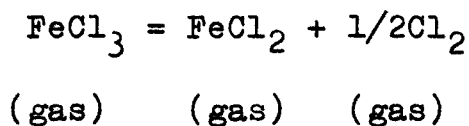
$$G_{1373^{\circ}K} \ = \ 5,000 \text{ calories}$$

The equilibrium constant may then be evaluated from the relationship.

$$G \ = \ -RT \ \ln K_p.$$

If x is the amount of monomeric ferric chloride dissociating to ferrous chloride and

chlorine then

$$Kp = \frac{(x)}{(1-x)} \cdot \frac{(x/2)^{\frac{1}{2}}}{(1+x/2)^{\frac{1}{2}}}$$

This expression yields a value of 30.6 per cent for the fraction of ferric chloride which dissociates to ferrous chloride and chlorine at $1100^{\circ}C$.

This figure is approximate since it is based on the original assumption on which the assessment of Wilmshurst's experimental data was made, namely that in the reaction between ferric oxide and chlorine only monomeric ferric chloride and oxygen are formed. A more accurate result could be obtained only by an extremely lengthy iterative type calculation which in this instance is not justified. The result of the present calculation, although approximate, does indicate that at $1100^{\circ}C$ the degree of dissociation is considerable.

It is therefore necessary to calculate the amount of ferrous chloride which is formed in the chlorination of hematite. Again this is performed by an approximate method to avoid excessively lengthy calculations.
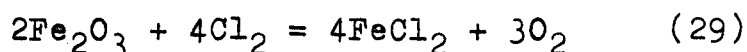
On the basis of experimental results

(Wilmshurst, unpublished data 1959) the free energy change for reaction (12) at 1100°C is:

$$2Fe_2O_3 + 6Cl_2 = 4FeCl_3 + 3O_2 \quad (12)$$
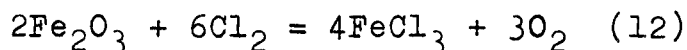
$$\Delta G_{1373^\circ K} = 7,400 \text{ calories}$$

From previously determined free energies of formation for ferric oxide and ferrous chloride, the free energy change for reaction (29) can be calculated.

$$2Fe_2O_3 + 4Cl_2 = 4FeCl_2 + 3O_2 \quad (29)$$

$$\Delta G_{1373^\circ K} = 27,300 \text{ calories}$$

Equilibrium constants at 1100°C for reactions (12) and (29) corresponding to these free energy changes are 6.7×10^{-2} and 4.5×10^{-5} respectively.

The relative amounts of ferric and ferrous chlorides formed in the chlorination of hematite at 1100°C has been obtained in the following manner.

If x is the mol fraction of chlorine converted to ferric chloride according to equation (12) per mol of chlorine supplied and y is the mol fraction converted to ferrous chloride according to reaction (29), then the chlorination gases contain:

$$Cl_2 \qquad 1-x-y \qquad mols$$

$$FeCl_3 \qquad 2x/3 \qquad mols$$

$$FeCl_2 \qquad y \qquad mols$$

$$O_2 \qquad \frac{x/2 + 3y/4}{1 + x/6 + 3y/4}$$

The equilibrium constant for reaction (12) is therefore:

$$Kp_{1373^\circ K} = \frac{(2x/3)^4 \; (x/2 + 3y/4)^3}{(1 + x/6 + 3y/4) \cdot (1-x-y)^6}$$

$$= 6.7 \times 10^{-2}$$

For reaction (29) the equilibrium constant is:

$$Kp_{1373^\circ K} = \frac{(y)}{(1-x-y)} \cdot \frac{(x/2 + 3y/4)^3}{(1 + x/6 + 3y/4)}$$

$$= 4.5 \times 10^{-5}$$

The solution for these two simultaneous equations is

$$x = 0.50$$

$$y = 0.09$$

In the calculation of experimental results for reaction (12) it was assumed that only ferric chloride was formed and the amount formed was calculated from the weight loss of ferric oxide:

$$2Fe_2O_3 + 6Cl_2 = 4FeCl_3 + 3O_2 \quad (12)$$

At 1100°C the chlorine utilized was 56.9 per cent, so 6 mols of chlorine removed $0.569 \times 319.4 = 181.6$ gms. of ferric oxide, 319.4 being twice the molecular weight of ferric oxide.

In fact only part of the ferric oxide was converted to ferric chloride and part was converted to ferrous chloride. It is assumed that the relative proportions of chlorine converted to ferric and ferrous chlorides is the same as the ratio of the calculated values for x and y, 0.50 : 0.09.

If z is the number of mols of chlorine converted to ferric chloride when 6 mols of chlorine are passed through the charge of ferric oxide, then 0.18z is the number of mols converted to ferrous chloride. The quantity of ferric oxide removed as ferric chloride is therefore

$$z \times \frac{319.4}{6} = 53.2z \text{ gms.}$$

That removed as ferrous chloride is

$$0.18z \times \frac{319.4}{4} = 14.4z \text{ gms.}$$

The total ferric oxide removed is

$$53.2z + 14.4z = 67.6z \text{ gms.}$$

It has been calculated that the amount removed was 181.6 gms so that

$$z = \frac{181.6}{67.6} = 2.69 \text{ mols}$$

$$0.18z = 0.48 \text{ mols}$$

The value of z has been calculated on the basis of passing 6 mols of chlorine through the system, so that

$$z = \frac{2.96}{6} = 44.8 \text{ per cent}$$

$$0.18z = \frac{0.48}{6} = 8.0 \text{ per cent}$$

In the chlorination of hematite at $1100^{\circ}C$, about 44.8 per cent of chlorine is converted to ferric chloride and 8.0 per cent to ferrous chloride, giving a total utilization of 52.8 per cent. This compares with 56.8 percent calculated on the basis that only monomeric ferric chloride is formed.

A similar calculation has been carried out for $1300^{\circ}K$, the result being that 37.6 percent of chlorine is converted to ferric chloride and 3.9 per cent to ferrous chloride. The total utilization is 41.5 per cent compared to 43.8 per cent calculated previously for the formation of ferric chloride alone.

Data is not available for the formation of gaseous ferrous chloride at $900^{\circ}C$, the lower limit of the temperature range for which experimental data for the chlorination of hematite are available.

In fact ferrous chloride vapour liquifies when cooled below 1012°C. However the vapour pressure at 900°C is quite high, namely 250 m.m. of mercury (Kubaschewski and Evans, 1958). The data for the free energy of formation of ferrous chloride vapour has therefore been extrapolated to 1173°K and the amount of ferrous chloride formed in the chlorination of hematite has been calculated in the same way as for higher temperatures.

At 1173°K, 21.1 per cent of chlorine is converted to ferric chloride and 0.8 percent to ferrous chloride. Total chlorine utilization is 21.9 per cent compared to 22.3 per cent calculated on the basis of forming only ferric chloride.

These results are presented graphically in Figure 5 Appendix V.

It has been stated previously that if x represents the mols of chlorine converted to ferric chloride per mol of chlorine reacted with ferric oxide and y represents the mols of chlorine converted to ferrous chloride, then the chlorination gases contain:

Cl_2	$1-x-y$	mols
$FeCl_3$	$2x/3$	mols
$FeCl_2$	y	mols
O_2	$x/2 + 3y/4$	mols

$$\text{Sum} \quad = \quad 1 + {}^x/_6 + {}^{3y}/_4$$

The partial pressure of ferrous chloride in a system under a total pressure of P is therefore

$$\frac{y}{1 + {}^x/_6 + {}^{3y}/_4} \cdot P$$

The partial pressure of ferrous chloride in the gases produced by reacting chlorine with hematite has been calculated according to this expression from the chlorination gas compositions calculated for temperatures of 900°C, 1027°C and 1100°C.

Assuming a total pressure of one atmosphere, the partial pressures of ferrous chloride are 6.1, 27 and 54 m.m. of mercury respectively.

The vapour pressure of ferrous chloride over the temperature interval from the melting point to the boiling point is given by the expression (Kubaschewski and Evans 1959).

Log pressure (m.m. of mercury)

$$= 26.53 - \frac{9475}{T} - 5.23 \log T$$

where T is the temperature in degrees Kelvin.

The vapour pressure of ferrous chloride according to this expression, together with the partial pressure of ferrous chloride in gases

produced by the chlorination of hematite are
presented in Appendix V Fig. 6.

At temperatures below the boiling point of
ferrous chloride the partial pressure of ferrous
chloride in the chlorination gases is much less
than the vapour pressure over liquid.   It can be
seen from the figure that the partial pressure
decreases as the temperature is lowered, resulting
from reaction of ferrous chloride vapour with
free chlorine. It is apparent that if the gases
produced by the chlorination of ferric oxide at a
temperature of say $1100^{o}C$ were cooled under such
conditions that the gases remain in equilibrium,
no liquid ferrous chloride would be deposited.
Since the gases contain a small amount of ferrous
chloride and an excess of free chlorine, and
since the temperature range being considered is
sufficiently high for reaction rates to be extreme-
ly fast, it is not likely that the gases could be
quenched with sufficient speed to inhibit the
reaction between ferrous chloride and chlorine
and so precipitate liquid ferrous chloride.

The reaction between chlorine and oxidised
ilmenite has now been considered. The amount of
ferrous chloride formed during the chlorination
of oxidised ilmenite has been calculated by the

method previously used for the chlorination of hematite.

The free energy change for the reaction of chlorine with oxidised ilmenite at $1100^{\circ}C$ according to reaction (13) has been calculated previously from experimental data.

$$2Fe_2O_3.TiO_2 + 6Cl_2 = 4FeCl_3 + 3O_2 + 2TiO_2$$

$$(13)$$
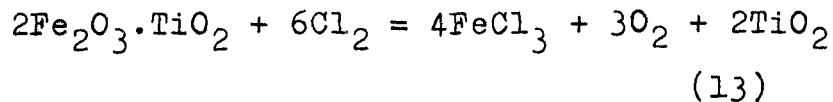
$$\Delta G_{1373^{\circ}K} = 15,645 \text{ calories}$$

The free energy of formation of monomeric ferric chloride at $1100^{\circ}C$ has been calculated previously from the experimental data of Wilmshurst.

$$\Delta G_{f1373^{\circ}K} (FeCl_3) = -54,200 \text{ calories}$$

The free energy of formation of ferrous chloride at $1100^{\circ}C$ has previously been calculated with data from Kubaschewski and Evans (1959).

The free energy change for the reaction of chlorine with oxidised ilmenite to form ferrous chloride according to equation (30) can therefore be obtained.

$$2Fe_2O_3.TiO_2 + 4Cl_2 = 4FeCl_2 + 3O_2 + 2TiO_2 \quad (30)$$
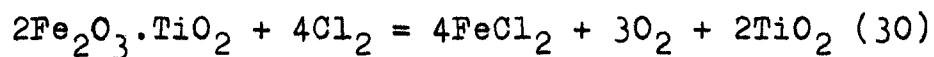
$$\Delta G_{1373^{\circ}K} = 35,600 \text{ calories}$$

It has been calculated previously that at $1100^{\circ}C$ 45.2 percent of chlorine reacts with oxidised ilmenite, assuming only ferric chloride

is formed. With this value for the chlorine
utilization and with free energy values calculated
for equations (13) and (30) the same type of
calculation of the amount of ferrous chloride
formed during chlorination of oxidised ilmenite can
be made as was previously carried out for the
chlorination of hematite. This results in a value
of 36.6 per cent of chlorine forming ferric
chloride and 5.7 per cent forming ferrous chloride
when reacted with oxidised ilmenite at $1100^{\circ}C$.
Total chlorine utilization is then 42.3 per cent
compared with 45.2 per cent calculated previously
on the basis of forming ferric chloride alone.

The partial pressure of ferrous chloride in
the chlorination gases, calculated in the same way
as was done for the chlorination of hematite is
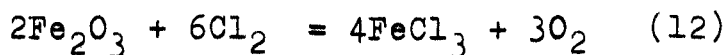39 mm. of mercury.

The composition of the gases produced by
chlorinating oxidised ilmenite will now be
compared with those produced by chlorinating
hematite.

Expressions for equilibrium constants based
on experimental data have been obtained for the
chlorination of oxidised ilmenite according to
equation (13) and for hematite according to
equation (12).

$$2Fe_2O_3 \cdot TiO_2 + 6Cl_2 = 4FeCl_3 + 3O_2 + 2TiO_2$$
$$(13)$$
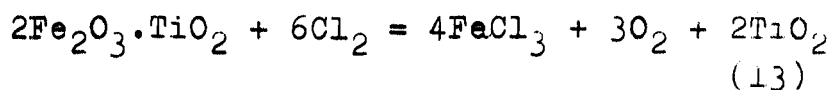
$$\ln K_p = 57.7 - \frac{87180}{T}$$

range 1273° to $1473^\circ K$

$$2Fe_2O_3 + 6Cl_2 = 4FeCl_3 + 3O_2 \quad (12)$$

$$\ln K_p = 56.0 - \frac{80,600}{T}$$

range 1173° to $1373^\circ K$

The temperatures, T_h to which the gases produced by chlorinating oxidised ilmenite at temperature T_i can be cooled without precipitating hematite is obtained by equating the expressions for the equilibrium constant.

$$57.7 - \frac{87180}{T_i} = 56.0 - \frac{80600}{T_h}$$

$$T_h = \frac{80,600}{87,100 - 1.7T_i}$$

Therefore if oxidised ilmenite is chlorinated at $1373^\circ K$, the chlorination gases can be cooled to $1305^\circ K$ without precipitating ferric oxide. This does not mean that the gases produced by chlorinating oxidised ilmenite at $1373^\circ K$ have the same composition as those produced by chlorinating hematite at $1305^\circ K$. Dissociation of ferric chloride to ferrous chloride increases with temperature so that the partial pressure of ferrous

chloride in the gases produced by chlorirating ilmenite at $1373^{O}K$, previously determined as 39mm. of mercury, is greater than that produced by chlorinating hematite at $1305^{O}K$. As the gases are cooled, ferrous chloride reacts witl free chlorine until at $1305^{O}K$ the composition is the same as that produced by chlorinating hematite at that temperature. Further cooling results in reaction between ferric chloride and oxygen and the deposition of ferric oxide as well as further reduction in the partial pressure of ferrous chloride.

The partial pressure of ferrous chloride in the gases produced by chlorinating hematite under equilibrium conditions at $1300^{O}K$ has been determined at 27 mm. of mercury so that the 39 mm. of mercury partial pressure of ferrous chloride in the gases produced in chlorinating ilmenite at $1373^{O}K$ is reduced on cooling to a little greater than 27 mm. at $1305^{O}K$.

These data are illustrated in Figure 5 Appendix V.

It has previously been shown (Appendix V Figure 6) that during the cooling of the chlorination gases, the partial pressure of ferrous chloride is always well below the vapour pressure.

Therefore although an appreciable amount of ferrous chloride is formed in the chlorination of oxidised ilmenite, liquid ferrous chloride is not precipitated during the cooling of the chlorination gases.

Had this been so this could have seriously affected the gaseous transport system. The deposition of liquid ferrous chloride would mean a constant removal of iron and chlorine from the cyclic gaseous system and a continually increasing unbalance in the residual gas mixture. Frequent corrective addition of components could have been necessary to restore the gaseous mixture to stoichiomertic proportions. Also liquid chloride, if deposited in a fluidised bed could cause sintering.

However the formation of ferrous chloride during the chlorination reaction is of no significance in the operation of the cyclic process and may be disregarded. The reactions which occur during cooling of the chlorination gases are now considered.

It has been shown that the ferrous chloride formed during chlorination is of no significance and may be disregarded. However as monomeric ferric chloride is cooled from the chlorination temperature of $1100^{\circ}C$, association to dimeric ferric

chloride becomes important.

Data for the association of ferric chloride over the temperature range $778^{\circ}K$ to $978^{\circ}K$ is recorded by Kubaschewski and Evans (1958)

$$2FeCl_3 = Fe_2Cl_6 \qquad (11)$$
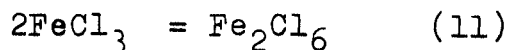
$$\Delta G(\text{calories}) = -32,550 + 31.65T$$

The free energy changes for reaction (11) at $778^{\circ}K$ and $975^{\circ}K$ are $-7,900$ and $-1,600$ calories respectively. Corresponding equilibrium constants are 169 and 2.3.

If x represents the fraction monomer which associates, then

$$Kp = \frac{x(2-x)}{4(1-x)^2}$$

The fraction of monomer which associates at $778^{\circ}K$ is therefore 96.2 per cent and at $978^{\circ}K$ is 68.5 per cent.

It has previously been stated that on the basis of the reported 96 per cent conversion of ferric chloride to ferric oxide at $530^{\circ}C$ (Kangro 1957), $500^{\circ}C$ would be a suitable temperature to conduct the regeneration reaction.

The lower limit of the temperature range for which data for the association of monomeric ferric chloride is available is $778^{\circ}K = 505^{\circ}C$.

Accordingly 505°C will be taken as the temperature at which the reverse reaction is conducted.

It has been shown that at 505°C, 96.2 per cent of ferric chloride associates to the dimer.

For the purpose of calculation it will be assumed that ferric chloride is wholly converted to the dimeric form at 505°C.

The free energy of formation of ferric oxide at 505°C can be calculated from the heat of formation at 298°K from Kubaschewski and Evans (1958), from the entropies at 298°K for ferric oxide, iron and oxygen from the same source, and from the high temperature heat contents and entropies from Kelley (1960). These data yield a value of:

$$\Delta G_{f\ 778°K}(Fe_2O_3) = -147,000 \text{ calories}$$

The free energy of formation of gaseous dimeric ferric chloride at 778°K is available from the data of Kelley and Mah (1959).

$$\Delta G_{f\ 778°K}(Fe_2Cl_6) = -116,000 \text{ calories}$$

The free energy change for reaction (31) can therefore be calculated.

$$2Fe_2O_3 + 6Cl_2 = 2Fe_2Cl_6 + 3O_2 \quad (31)$$
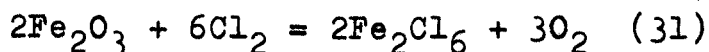
$$\Delta G_{778°K} = 61,600 \text{ calories}$$

The corresponding equilibrium constant is

therefore

$$Kp = 4.8 \times 10^{-18}$$

If x represents the fraction of chlorine which reacts with ferric oxide according to equation (31) then the equilibrium constant is given by

$$Kp = \frac{x^5(1 - {}^x/6)}{72(1 - x)^6} = 4.8 \times 10^{-18}$$

Solution of this equation yields a value of 0.09 per cent for the fraction of chlorine which remains as ferric chloride at 505°C. It appears therefore that the regeneration reaction should proceed almost to completion.

This was the last step required to show that at least on the basis of thermodynamic data, the cyclic chlorination process is quite feasible.

It has been shown that the oxidation of ilmenite should proceed at 1000°C with almost complete utilization of oxygen, that chlorination of oxidised ilmenite at 1100°C should result in conversion of 45.2 per cent of chlorine to ferric chloride and that on cooling the chlorination gases to 505°C substantially all of the chlorine should be recovered for further chlorination. In effect 45.2 per cent of the chlorine circulating

in the system is usefully employed in the removal
of iron from oxidised ilmenite.

It has also been shown that although gaseous
ferrous chloride is formed during the chlorination
reaction, it is present only in small amounts
when the temperature of the chlorination gases is
lowered below the boiling point of ferrous chloride.
At no stage in the cooling operation will liquid
ferrous chloride be precipitated and interfere
with the gaseous transport system.

It has also been shown that monomeric ferric
chloride formed during the chlorination reaction
tends to associate to the dimeric form during the
cooling operation. This also is of no significance
in the operation of the gaseous transport system.

It remains to consider the heats of reaction
involved in each stage of the process.

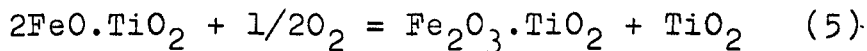The heat required to preheat the reactants
for the oxidation of ilmenite at $1000^{o}C$ according
to equation (8) has been calculated with data
taken from Kelley (1960).

$$4FeO.TiO_2 + O_2 = 2Fe_2O_3.TiO_2 + 2TiO_2 \quad (8)$$
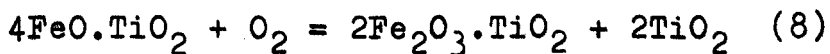
$$H_{1273^{o}K} - H_{298^{o}K}(reactants) = 125,000 \text{ calories.}$$

The heat of reaction for the oxidation of
ilmenite at $1300^{o}K$ according to equation (5) has

already been determined.

$$2FeO.TiO_2 + 1/2O_2 = Fe_2O_3.TiO_2 + TiO_2 \quad (5)$$

$$\Delta H_{1300^\circ K} = -59,000 \text{ calories.}$$

The heat of reaction for oxidation at $1000^\circ C$ according to equation (8) is therefore :

$$\Delta H_{1273^\circ K}(\text{Oxidation}) = -118,000 \text{ calories}$$

The heat required to superheat the oxidised ilmenite from $1000^\circ C$ to $1100^\circ C$ has been calculated with data from Kelley (1960).

$$H_{1373^\circ K} - H_{1273^\circ K} \quad (\text{Oxidised Ilmenite})$$
$$= 14,200 \text{ calories.}$$

It has been determined experimentally that 45 per cent of chlorine is converted to ferric chloride in the chlorination reaction. The heat required to raise the temperature of the recirculated chlorine, including the unused excess, from the regeneration reaction temperature of $505^\circ C$ to the chlorination temperature of $1100^\circ C$ has been calculated from data compiled by Kelley(1960).

$$H_{1373^\circ K} - H_{778^\circ K} (\text{Recycled Chlorine})$$
$$= 77,900 \text{ calories.}$$

The heat of reaction between chlorine and oxidised ilmenite at $1100^\circ C$ in accordance with equation (32) has already been determined from experimental data.

$$2Fe_2O_3 \cdot TiO_2 + 2TiO_2 + 6Cl_2$$

$$= 4FeCl_3 + 3O_2 + 4TiO_2 \quad (32)$$
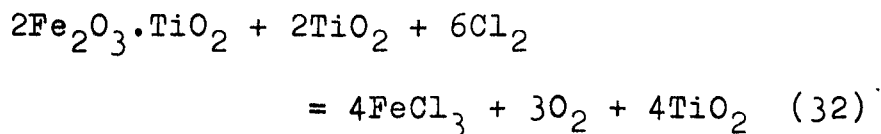
$$\Delta H_{1373^oK}(chlorination) = 173,000 \text{ calories.}$$

The heat which can be recovered from the titania produced by the chlorination of oxidised ilmenite has been calculated from data compiled by Kelley (1960).

$$H_{1373^oK} - H_{298^oK}(titania) = -73,700 \text{ calories}$$

The chlorination gases comprise excess chlorine, oxygen, and monomeric ferric chloride. The heat which can be recovered while cooling chlorine and oxygen from the chlorination temperature to the regeneration temperature can be calculated with data from Kelley (1960). However no published data is available for monomeric ferric chloride. An average value for the heat capacity of monomeric ferric chloride of 24.5 calories per mol per degree over the temperature range 1000^oC to 1200^oC has been determined previously from the results of chlorination tests with oxidised ilmenite. With this figure it is possible to calculate the heat released while cooling the chlorination gases.

$$H_{1373^oK} - H_{778^oK}(chlorination \ gases)$$

$$= 114,900 \text{ calories}$$

Before the heat of reaction for the association

of monomeric ferric chloride to the dimeric form
at $505^{O}C$ can be calculated it is necessary to
calculate the heat of formation at $298^{O}K$ for
gaseous monomeric ferric chloride.

The heat of reaction for the chlorination
of oxidised ilmenite at $1100^{O}C$ according to
equation (32) has been determined from experimental
results.

$$2Fe_2O_3 \cdot TiO_2 + 2TiO_2 + 6Cl_2$$
$$= 4FeCl_3 + 3O_2 + 4TiO_2 \quad (32)$$
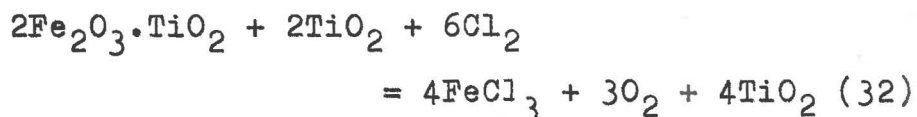
$\Delta H_{1373^{O}K} = 173,000$ calories

High temperature heat capacities for all
substances excepting monomeric ferric chloride
have been published by Kelley (1960). These data
together with the value 24.5 calories per mol per
degree previously determined for monomeric ferric
chloride, make it possible to calculate the heat
of reaction for equation (32) at room temperature

$\Delta H_{298^{O}K}$ (reaction (32)) = 168,000 calories.

The heat of formation of rutile at $298^{O}K$
is available from Kelley and Mah (1959), that for
ferric titanate has been determined previously from
chlorination test results, so the heat of formation
at $298^{O}K$ for gaseous monomeric ferric chloride can
be obtained by difference.

$\Delta H_{f\ 298}$ (FeCl$_3$ vapour) = -57,900 calories.

A value for the heat of formation at 298°K for dimeric ferric chloride vapour has been published by Kelley and Mah (1959), so it is possible to calculate the heat of reaction at 298°K for the association of monomeric ferric chloride vapour according to equation (33).
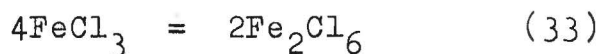
$$4FeCl_3 = 2Fe_2Cl_6 \qquad (33)$$
$$\Delta H_{298^{\circ}K} = -65,200 \text{ calories.}$$

With the heat capacity of monomeric ferric chloride vapour taken as 24.5 calories per mol per degree as before, and with the high temperature heat content of dimeric ferric chloride vapour taken from Kelley and Mah (1959), it is possible to calculate the heat of reaction for equation (33) at 505 $^{\circ}$C.

$$\Delta H_{778^{\circ}K} \text{ (Reaction (33))} = -79,400 \text{ calories.}$$

Alternatively Kubaschewski and Evans (1958) give the data of Schafer and Oehler (1953) for the free energy of association over the temperature range 505°C to 705°C according to equation (9).
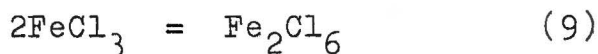
$$2FeCl_3 = Fe_2Cl_6 \qquad (9)$$
$$\Delta G_t = -32,550 + 31.65\ T$$

If it is assumed that the heat of reaction remains constant over the 200°C temperature range,

then the heat of reaction at $505^\circ C$ according to equation (33) becomes $-65,100$ calories compared to the previously calculated $-79,400$ calories.

The heat of reaction at $505^\circ C$ for the regeneration reaction according to equation (34) can be calculated from heats of formation at $298^\circ K$ for ferric oxide and for dimeric ferr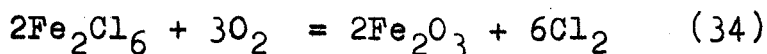ic chloride from Kubaschewski and Evans (1958) and Kelley and Mah (1959) respectively, together with high temperature heat contents from Kelley (1960).

$$2Fe_2Cl_6 + 3O_2 = 2Fe_2O_3 + 6Cl_2 \qquad (34)$$

$$\Delta H_{778^\circ K} = -82,300 \text{ calories}$$

The heats of reaction at $505^\circ C$ for reactions (33) and (34) can now be summed to give the heat of reaction for the regeneration reaction according to equation (35)

$$4FeCl_3 + 3O_2 = 2Fe_2O_3 + 6Cl_2 \qquad (35)$$
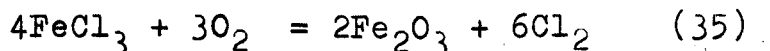
$$\Delta H_{778^\circ K} = -162,000 \text{ calories}$$

The sensible heat of the ferric oxide product can be obtained from Kelley (1960).

$$H_{778^\circ K} - H_{298^\circ K} \text{ (ferric oxide)}$$
$$= -30,600.$$

The heats involved in the various stages of the process according to the following sequence of reactions have been summarised:

Oxidation (1000°C)

$$4FeO.TiO_2 + O_2 = 2Fe_2O_3.TiO_2 + 2TiO_2 \quad (8)$$

Chlorination (1100°C)

$$2Fe_2O_3.TiO_2 + 2TiO_2 + 6Cl_2$$
$$= 4FeCl_3 + 3O_2 + 4TiO_2 \quad (32)$$

Regeneration (505°C)

$$4FeCl_3 + 3O_2 = 2Fe_2O_3 + 6Cl_2 \quad (35)$$

Overall Process (25°C)

$$4FeO.TiO_2 + O_2 = 2Fe_2O_3 + 4TiO_2 \quad (36)$$
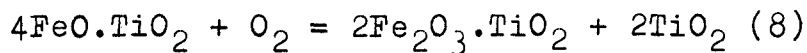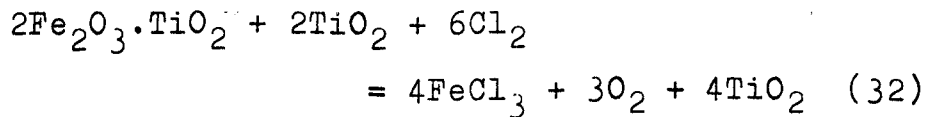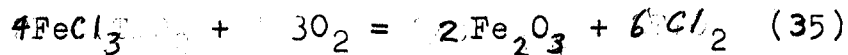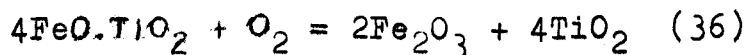
The sensible heats and heats of reaction are:

Preheating Oxidation Reactants

$$H_{1273°K} - H_{298°K} \qquad = \qquad 125,000 \text{ calories}$$

Oxidation Reaction

$$\Delta H_{1273°K} \qquad = \qquad -118,000 \text{ "}$$

Superheating Oxidised Ilmenite

$$H_{1373°K} - H_{1273°K} \qquad = \qquad 14,200 \text{ "}$$

Superheating Recycled Chlorine

$$H_{1373°K} - H_{778°K} \qquad = \qquad 73,900 \text{ "}$$

Chlorination Reaction

$$\Delta H_{1373°K} \qquad = \qquad 173,000 \text{ "}$$

Heat from Titania Product

$$H_{1373°K} - H_{298°K} \qquad = \qquad -73,000 \text{ "}$$

Heat from Chlorination Gases

$$H_{1373°K} - H_{778°K} \qquad = \qquad -115,000 \text{ "}$$

Regeneration Reaction

$$\Delta H_{778^\circ K} \quad = \quad -162,000 \text{ Calories}$$

Heat from Hematite Produce

$$H_{778^\circ K} - H_{298^\circ K} \quad = \quad -30,600 \quad "$$

Overall Process

$$\text{Nett } \Delta H_{298^\circ K} \quad = \quad \underline{-113,000} \text{ calories}$$

The nett overall heat of reaction at $298^\circ K$ according to equation (36) is in agreement with that calculated previously from the heats of formation at $298^\circ K$.

It can be seen from the summary that little heat is consumed by the oxidation reaction, the heat required to preheat the reactants being only a little greater than the heat released by the reaction.

The heat required for the chlorination reaction is considerable, being of the order of 260 kilocalories for four mols of ilmenite. Not only is the reaction endothermic but since only about 45 per cent of the chlorine present is utilized in this reaction, excess chlorine has to be heated to the reaction temperature along with the reactants. Furthermore the heat has to be supplied at the high temperature of $1100^\circ C$.

The regeneration reaction is quite highly exothermic, which together with the sensible heat of the chlorination gases means that a large quantity of heat is recoverable at this stage in the process. However, the heat is recovered at the relatively low temperature of $505^{\circ}C$.

The overall process involves high heat consumption at $1100^{\circ}C$, and the release of an even greater amount of heat at $500^{\circ}C$.

It appears that in the operation of the process on an industrial scale, a large installation of ancillary equipment for the recovery of waste heat will be necessary.

The regeneration temperature has been chosen rather arbitrarily, and it is possible that the most economic temperature for conducting the regeneration reaction is much higher, even at the expense of recirculating some unreacted ferric chloride to the chlorination reactor. Evaluation of all the factors influencing selection of the optimum temperature for this reaction and determination of the optimum temperature will be a major part of the development of this process.

4.   REACTION RATES.

In this section of the thesis, measurements
of the rate of oxidation of ilmenite and of the
rate of chlorination of oxidised ilmenite are
reported when these reactions are carried out in
small fluidised bed reactors. The work described
is of an introductory nature and the basis for a
more comprehensive examination of the factors
influencing the rates of reaction is established.

4.1   Literature Review.

A search of available literature produced
no reports of experimental measurement of the rate
of oxidation of ilmenite or of the rate of chlor-
ination of oxidised ilmenite.

One paper, Dunn (1960), describes the chlor-
ination of ilmenite with chlorine - carbon monoxide
mixtures. Another, Daubenspeck and McNeil (1956),
report the chlorination with chlorine of partially
reduced titaniferous iron ores. A third, Dauben-
speck and Toomey (1954) reports the chlorination
of oxidised titanium iron ores with titanium
tetrachloride. A fourth, Kangro (1957), describes
the chlorination of iron ores with chlorine.
None of these papers are relevant to the present
work.

4.2 Experimental

Fluidised bed oxidation and chlorination
tests were conducted with fluidised bed reactors
made from three inch bore fused silica tubing.
The reactors were externally heated with a gas
fired furnace constructed for this purpose. The
fluidised bed reactors, the heating furnace,
ancillary chlorine supply apparatus and waste
chlorine absorption equipment have been described
in detail in Section 2 of this thesis.

Two series of tests are reported for the
oxidation of ilmenite.

It has been reported in Section 2 that a
fluidising gas velocity about nine times greater
than the critical fluidising velocity was a
suitable intermediate level, providing sufficient
turbulence in the fluidised bed to prevent sinter-
ing and yet not causing substantial solids loss
by entrainment in the gas stream. A series of
oxidation tests were carried out at different
temperatures with an air flow about nine times the
critical fluidising velocity. A second series
was carried out with air flows varying from the
minimum air flow which would prevent sintering,
about four times the critical velocity, to the
maximum beyond which entrainment losses become

excessive, about 17 times the critical velocity.

Two similar series of tests were carried out for the chlorination of oxidised ilmenite.

Results were assessed on the basis of the time required for 99.5 per cent completion of both oxidation and chlorination reactions. This level has previously been established as the minimum requirement for both reactions.

4.3 Results and calculations.

4.3.1 Oxidation tests.

The technique by which the samples were drawm from a fluidised bed at timed intervals during a test run has been decribed in Section 2 of this thesis. These samples were assayed for ferrous iron and the degree of oxidation of the charge at the time the sample was drawn was calculated taking into account the increased oxygen content of the sample.

Let a = initial concentration FeO

b = " " Fe_2O_3

c = " " TiO_2

a_t = concentration of FeO at time "t".

x = mass of FeO per unit mass of original charge oxidised in time "t".

The mass of ferric oxide produced in time "t" can be obtained from the ratio of molecular weights of ferrous and ferric oxides.

$$\text{Fe}_2\text{O}_3 \text{ produced } = \frac{159.7x}{143.7}$$

$$= \frac{10x}{9}$$

At time "t", unit mass of original charge contains :

$$
\begin{array}{ll}
\text{FeO} & a - x \\
\text{Fe}_2\text{O}_3 & b + \dfrac{10x}{9} \\
\text{TiO}_2 & c \\
\hline
& 1 + \dfrac{x}{9}
\end{array}
$$

$$a_t = \frac{a - x}{1 + x/9}$$

Therefore the degree of oxidation,

$$\frac{x}{a} = \frac{9(a - a_t)}{a(9 + a_t)}$$

The fraction of oxygen in the air which passes through the charge utilised in the oxidation of ferrous iron in accordance with equation (8) was then calculated from the mass of air flow, the mass of ilmenite charge, the initial concentration of ferrous oxide in the charge, and the conversion $\dfrac{a_t}{a}$.

$$4FeO.TiO_2 + O_2 = 2Fe_2O_3.TiO_2 + 2TiO_2 \qquad (8)$$
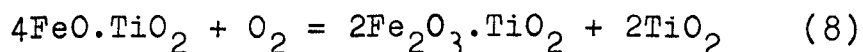
The results of the two series of oxidation tests are presented in Tables 1 to 5, Appendix VI and graphically in Figures 1 to 5, Appendix VI. The figures are plots of percentage oxidation and percentage oxygen utilization with time.

Figures 1, 2, and 3, Appendix VI, present the results of comparative tests carried out at different temperatures. All three tests were conducted in three inch diameter reactors with 1000 gm. charges of Stradbroke Island ilmenite and with fluidising air flows of 0.0191 gms per square inch per second.

From Figure 1 it can be seen that under these conditions about 70 minutes is required for 99.5 per cent oxidation at $900^\circ C$. At $1000^\circ C$ this time is reduced to about 55 minutes. At $1100^\circ C$ the initial reaction rate is faster but the reaction rate reduces markedly as the reaction goes beyond about 97.5 percent. It appears that at $1100^\circ C$ the inner core of ferrous oxide is less accessible to the action of oxygen than at $900^\circ C$ or $1000^\circ C$. This presumably results from the formation of ferric oxide in a form that is impervious to diffusion of oxygen.

The oxygen utilizations reported for the early stages of tests 1 and 3 are excessively high and are obviously erroneous.

These high values are attributed to air oxidation of the assay samples as they were withdrawn from the furnace. Test No.2 was carried out after tests 1 and 3 and precautions were taken to prevent this oxidation. It was not considered necessary to repeat tests 1 and 3 at this stage.

It has been established in Section 3 of this thesis that the partial pressure of oxygen in equilibrium with ilmenite is very small in the temperature range 900° to $1100^{\circ}C$.

Oxygen utilization of 100 per cent for the initial stages of fluidised bed oxidation tests are not inconsistent with this finding.

Oxidation at $900^{\circ}C$ is obviously significantly slower than at $1000^{\circ}C$, and at $1100^{\circ}C$ the reaction becomes very slow during the latter stages of oxidation. It appears that $1000^{\circ}C$ is about the optimum.

Figures 4, 2, and 5, Appendix V1, show the effect of different air flow rates on the rate of oxidation at $1000^{\circ}C$.

Oxygen utilization in the early stages of test No. 4 is obviously erroneous. This again

is attributed to the oxidation of assay samples as they were drawn from the reactor. Test No. 5 was one of the tests carried out at a later date taking precautions to prevent oxidation of the assay samples. It was not considered necessary to repeat test No. 4 as the error introduced by oxidation of the assay samples is significant only in the early stages of the test and it is with the latter stages that we are mostly concerned.

It can be seen that for test No. 4, conducted with an air flow of 0.0191 gms. per square inch per second, the time required to achieve 99.5 per cent reaction is about 65 minutes. Oxygen utilization at this point is about 35 per cent.

With test No. 2, air flow rate 0.0191 gms. per square inch per second, the time required for 99.5 per cent oxidation is about 55 minutes, corresponding oxygen utilization being about 31 per cent.

For test No. 5 with an air flow rate of 0.0380 gms. per square inch per second, the time for 99.5 per cent reaction is about the same as for test No. 2, so the corresponding oxygen utilization is half that of test No. 2.

It is apparent that during the initial stages of all five tests reported here, utilization of

oxygen passing through the bed is 100 per cent and so reaction rates are initially controlled exclusively by the supply of oxygen.

As the tests proceeded reaction rates decreased. Presumably diffusion of oxygen into the grains limits the rate of reaction. This becomes significent at the earliest stage of reaction in test No. 1 at $900^{\circ}C$ and at the latest stage of reaction in test No. 3 at $1100^{\circ}C$. However as discussed previously, a barrier more impervious to diffusion of oxygen is formed during the test at $1100^{\circ}C$ than in any other test, so that the required 99.5 per cent reaction is not achieved at all at $1100^{\circ}C$.

With test No. 4 with a low air flow rate, high oxygen utilization apparently persists until the charge is about 95 per cent oxidised. The diffusion controlled stage then lasts for a further 35 minutes before 99.5 per cent reaction is attained.

With tests 2 and 5 the points of departure from the lines representing complete utilization occur at about 60 per cent reaction in both cases. In test No. 5 the departure is more marked so both test conditions require about 55 minutes for

99.5 per cent reaction.

It appears on the basis of these tests that for fluidised bed oxidation at $1000^\circ C$, there is little to be gained by increasing the air flow beyond 0.0191 per square inch per second.

These tests were all conducted in a three inch bore reactor with 1000 gm. charge, giving an aspect ratio for the fluidised bed $L/D = 1/1$. It is probable that increasing the depth of bed could influence the optimum air flow level.

To summarise the results of these tests it appears that $1000^\circ C$ is close to the optimum temperature for the fluidised bed oxidation of ilmenite. It also appears that the optimum air flow rate is about 0.020 gms. per square inch per second.

The influence of the depth of the fluidised bed, and of dilution of ilmenite with partially and fully oxidised material as would occur in a continuously fed system, remain to be elucidated. These could affect the selection of the optimum air flow rate but probably not the optimum temperature.

4.3.2 Chlorination Tests.

Two series of tests are reported. One series of tests shows the influence of temperature on the

fluidised bed chlorination of oxidised ilmenite.
The other was carried out to examine the influence
of chlorine gas flow on the rate of chlorination.

As with the oxidation tests, the degree of
chlorination was determined by chemical analysis
of samples drawn from the fluidised charge during
a test. The degree of reaction was calculated taking
into account the loss in weight of the charge as
the test proceeds.

$$\text{Let} \quad a = \text{initial concentration } Fe_2O_3$$

$$b = \quad " \quad\quad " \quad\quad TiO_2$$

$$a_t = \text{concentration of } Fe_2O_3 \text{ at time "t".}$$

$$x = \text{Mass of } Fe_2O_3 \text{ per unit mass of original charge chlorinated in time "t".}$$

Chlorination of unit mass of charge for time
"t" leaves a residue containing :

$$
\begin{array}{ll}
Fe_2O_3 & a - x \\
TiO_2 & \dfrac{b}{a - x + b}
\end{array}
$$

Therefore concentration of ferric oxide at time "t"

$$a_t = \frac{a - x}{a - x + b}$$

$$= \frac{a - x}{1 - x}$$

Degree of reaction

$$\frac{x}{a} = \frac{a - a_t}{a(1 - a_t)}$$

The fraction of chlorine passing through the charge utilized in the production of ferric chloride was then calculated in accordance with equation (13) from the mass flow of chlorine, the mass of the charge, the initial concentration of ferric oxide and the degree of reaction.

$$2Fe_2O_3 \cdot TiO_2 + 6Cl_2 = 4FeCl_3 + 3O_2 + 2TiO_2 \quad (13)$$
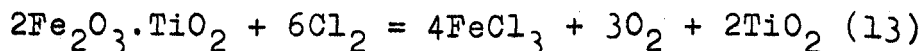
The results of the two series of tests are presented in Tables 1 to 7 Appendix Vll and graphically in Figures 1 to 7, Appendix Vll. The figures are plots of the degree of reaction and the chlorine utilization, both expressed as percentages, with time.

Five tests were carried out at temperatures ranging from $1000^{\circ}C$ to $1175^{\circ}C$. All the tests were carried out in $2\frac{3}{4}$ inch diameter reactors with 725 gm. charges of oxidised Stradbroke Island ilmenite, giving an aspect ratio of $L/D = 1/1$. Chlorine flows were maintained at 0.047 gms. per square inch per second, about nine times the critical fluidising velocity.

Test No. 1 was carried out at the lowest

temperature, 1000°C, and resulted in the slowest
rate of reaction. After 300 minutes the reaction
was only 85 per cent complete. Chlorine utilization
is about 14 per cent, approximately 50 per cent
of the equilibrium value established for this
temperature in Section 3 of this thesis. The
utilization steadily decreased as the test
progressed. Test No. 2 at 1050°C was considerably
faster, 99.5 per cent of the iron being removed
from the charge in about 280 minutes. In this
test the characteristic decrease in the reaction
rate as the test proceeds become more apparent than
with the first test. Chlorine utilization is
initially about 22 percent, about 60 per cent of
the equilibrium value, and this decreases to about
11 percent utilization or 30 percent of the equil-
ibrium value when the reaction approaches
completion.

Test No 3 at 1100°C shows an even faster
reaction rate, reaching 99.5 percent reaction in
180 minutes. The initial chlorine utilization of
about 29 percent is 65 percent of the equilibrium
value. This decreases gradually to 16.4 percent,
36 percent of the equilibrium value, when reaction
is complete.

Test No. 4 at 1150°C has a greater reaction rate, reacting to 99.5 percent in 120 minutes. The initial chlorine utilization is about 40 percent or about 75 percent of the equilibrium value, and decreases to about 25 percent utilization or 47 percent of the equilibrium value at 99.5 percent reaction.

Test No. 5 at 1175°C commenced with a rapid reaction rate and high chlorine utilization. However the bed sintered into a solid mass after 40 minutes and the test could not be continued. Other attempts to chlorinate at 1175°C or 1200°C also ended with sintered beds and the tests were abandoned. It is interesting to note that the initial chlorine utilization of about 49 per cent is 85 per cent of the equilibrium value at 1175°C.

On the basis of these tests, 1100°C was selected as the most suitable temperature for fluidised bed chlorination.

In general, the higher the chlorination temperature the faster the rate of reaction and the greater the utilization of chlorine. Not only is the chlorine utilization greater in absolute terms, but the utilization is higher in proportion to the equilibrium value as the

temperature is increased.

To achieve maximum chlorine utilization it is therefore advantageous to chlorinate at the highest temperature. However the maximum temperature at which it is practicable to chlorinate in a fluidised bed is limited by the tendency for the material to sinter at high temperature. It is also desirable from other practical considerations to operate the reactor at as low a temperature as possible.

For these reasons $1100^{\circ}C$ was selected as the temperature most suitable for chlorination.

A second series of tests was then conducted at $1100^{\circ}C$ to examine the influence of the rate of chlorine flow upon the rate of reaction.

Test No. 6 was carried out under similar conditions to Test No. 3 excepting that the chlorine flow was increased to 0.0676 gms. per square inch per second or 13.2 times the critical fluidising velocity. This was about the limit beyond which gas flow could not be increased without causing excessive entrainment loss.

The reaction rate was somewhat faster with the high flow rate, 150 minutes being required to produce an acceptable grade of product compared with 180 minutes for test No. 3

with a gas flow rate of 0.0468 gms. per square inch per second.

Chlorine utilization was about the same in the initial stages for both tests, but it fell off more rapidly with the high chlorine flow rate, being about 13.7 per cent at complete reaction compared with 16.4 per cent for test No. 3.

It was not possible to reduce the chlorine flow much below the level of test No. 3 without partial sintering of the fluidised bed occurring. To examine the effect of reduced chlorine flow in relation to the ilmenite charge, test No. 7 was carried out under similar conditions to test No. 3 but with twice the charge of oxidised ilmenite, 1450 gms.

The rate of reaction was much slower for this test than for test No. 3, about 300 minutes being taken for complete reaction. The initial chlorine utilization was about the same or a little higher than for test No. 3 but the utilization remained relatively constant for about 75 per cent of the reaction. At completion of the reaction the chlorine utilization had fallen to 19.4 per cent, compared to 16.4 per cent for test No. 3 and 13.7 per cent for test No. 6.

This test is not strictly comparable with tests 3 and 6 as the aspect ratio and not the chlorine flow has been altered. However the type of fluidisation would not be much affected by the increased bed depth although the gas bubbles rising through the bed might be larger in this case. It is probable that this does not affect the chlorination in any way.

The conclusions that can be drawn from these three tests are that increased gas velocity increases the rate of reaction while reducing the chlorine utilization slightly. However longer contact time between gas and solids increases the chlorine utilization.

It is apparent that reaction rate and chlorine utilization can be increased by using higher gas flows and deeper beds.

Further experimental work is needed to determine how far the gas flow and bed depth could be increased without causing excessive entrainment losses or excessive gas pressure loss through the bed.

Further work is also necessary to determine the effect on the reaction rate of dilution of chlorine with ferric chloride and oxygen and also of dilution of the oxidised ilmenite with

chlorinated residue. Both these situation

would be encountered in continuous multiple stage

fluidised bed chlorination.

5. DISCUSSION OF RESULTS

The results of experiments which have shown that the fluidised bed technique is suitable for conducting the oxidation and chlorination reactions are reported in Section 2 of this thesis.

It has been shown that beach sand ilmenite as it is received from concentrating plants can readily be fluidised at room temperature. Neither grinding nor sizing is necessary.

It has also been shown that while a tendency to sinter exists at high temperatures, sintering can be prevented by keeping ilmenite sands in a well fluidised condition. Both the oxidation and chlorination reactions can be carried out at high temperatures in fluidised beds.

The use of fluidised beds for these reactions is important from two aspects. Intimate contact is obtained between gases and solids, and, as the reactors contain no moving parts, they can readily be constructed in corrosion resistant refractory materials.

It has been established that segregation of materials on the basis of difference in densities does not occur to a significant degree in fluidised beds. It is therefore not possible to separate low density chlorinated ilmenite from

unreacted ilmenite in a fluidised bed.

It has also been demonstrated that the mixing of solids which occurs in fluidised beds is both rapid and complete. Feed to a fluidised bed is almost immediately dispersed through the bed. Consequently when a finite period of retention in the bed is required for an individual particle to react, some completely unreacted and some partially unreacted material will leave the reactor with the reacted product.

It is therefore desirable to have a number of fluidised beds in series in a single reactor to limit the extent of by-passing and so reduce the total hold up of material in the reactor if a solid product having a high degree of reaction is required. Algebraic functions have been derived which express retention times for solid particles in fluidised bed reactors in terms of throughput, stage capacity, and the number of reactor stages.

Having established that fluidised bed reactors are practicable for conducting the oxidation and chlorination reactions, the thermodynamics of the reactions involved in the process were studied more closely than had been done previously by other workers. The purpose of this work, which is reported in Section 3 of this thesis, was to

determine the extent to which the reactions proceed at various temperatures and the heats of reaction involved.

For the chlorination reaction experiments were carried out to determine the equilibrium of the gaseous mixtures produced when chlorine reacts with oxidised ilmenite.

The results of this work, in conjunction with the results of similar work by Wilmshurst on the reaction between chlorine and hematite, has provided most of the data required for the thermodynamic study.

It has been shown that ilmenite can be oxidised at $1000^{\circ}C$ with air with complete utilization of the oxygen in the air. It has been established that the oxidation reaction is exothermic to an extent where the heat released is almost sufficient to supply the sensible heat of the reactants.

The extent to which the chlorination reaction proceeds has been determined experimentally at intervals over the temperature range $1000^{\circ}C$ to $1200^{\circ}C$ by measuring the amount of iron oxide converted to ferric chloride. This was done by reacting a known amount of chlorine with a known amount of oxidised ilmenite and

measuring the weight loss of the oxidised ilmenite.
At 1100°C, 45 per cent of chlorine is consumed
by reaction with oxidised ilmenite and converted
to ferric chloride under equilibrium conditions.

With these data it has been shown that the
chlorination reaction is endothermic and the
heat of reaction has been determined.

It has also been shown that chlorine reacts
with titanium dioxide to a small but measurable
extent in the temperature range 1000°C to 1200°C.
However titanium tetrachloride readily reacts
with the iron content of oxidised ilmenite,
depositing titanium dioxide and forming gaseous
ferric chloride.

The result in a multiple stage counter-
current fluidised bed reactor being used for the
chlorination of oxidised ilmenite would be to
have some titania removed from the bottom stage
as gaseous titanium tetrachloride. This would
react with oxygen or oxidised ilmenite in the
upper stages and deposit the titanium content as
titanium dioxide. The overall process in the
reactor would be one of selective chlorination of
iron with no detectable amount of titanium
leaving the reactor as titanium tetrachloride in
the chlorination gas stream. Some of the

titanium would however circulate around the
bottom few stages of the reactor.

It has also been shown that some ferrous
chloride is formed during the chlorination of
oxidised ilmenite. However the amount formed is
small and as the temperature of the gaseous
reaction products is lowered to the temperature
at which the regeneration reaction is carried
out, the ferrous chloride reacts with free chlorine
to form ferric chloride.

At no temperature is the partial pressure
of ferrous chloride sufficiently high to pre-
cipitate liquid ferrous chloride. This is
fortunate as continuous deposition of liquid
ferrous chloride in a cyclic chlorination system
would lead to the accumulation of excess oxygen
in the circulating gas stream and a reduction
in the efficiency of the process.

The heat involved in the chlorination reaction
has been calculated directly from experimental
results. The results themselves were calculated
on the basis of forming monomeric ferric chloride
alone, whereas some ferrous chloride is also
formed.

Without extremely lengthy and tedious
repetitive calculation it is not possible to

determine precisely how much ferrous chloride is formed and it is probable that the accuracy of the experimentally determined data does not warrant the time and labour involved in precise calculation.

The heat of reaction for the chlorination reaction has been determined from the gradient of the logarithm of the equilibrium constant with respect to temperature. It has been assumed that the gradient and so the heat of reaction is constant over the temperature interval $1000^{\circ}C$ to $1200^{\circ}C$.

Two errors are thereby introduced.

Firstly the equilibrium constant calculated for the formation of ferrous chloride will differ from that calculated for the formation of ferric chloride.

Secondly while no great error is introduced by assuming the heat of reaction for a single reaction is constant over a limited temperature range, a greater error may be introduced by assuming that the sum of two heats of reaction is constant when the relative proportions of the two reactions differ over the temperature range.

This method seemed the only practicable method of calculating the heat of reaction for the

chlorination reaction and in spite of the errors involved is probably as accurate as the experimental data warrants.

Sufficient published thermodynamic data has recently become available for evaluation of the reverse reaction in the temperature range $500^{\circ}C$ to $700^{\circ}C$.

With this data it has been shown that at $500^{\circ}C$ gaseous ferric chloride exists almost entirely in the dimeric form. At $700^{\circ}C$ dissociation to monomeric ferric chloride is appreciable.

It has also been shown that at $500^{\circ}C$ dimeric ferric chloride reacts with oxygen to the extent that virtually all of the chlorine is recovered for re-use in the chlorination reaction.

Therefore, since recovery of chlorine is virtually complete, if the chlorination reaction is conducted at $1100^{\circ}C$ under such conditions that the chlorination gases leaving the reactor are in equilibrium with oxidised ilmenite, then 45 per cent of the chlorine circulating in the cyclic system is used in the transport of iron as chloride. The remaining 55 per cent circulates continuously without participating in the chlorination and regeneration reactions.

The heats of reaction for both the association of monomeric ferric chloride to dimeric ferric chloride and the reaction of dimeric ferric chloride with oxygen at $500^{\circ}C$, both exotherimc reactions, have been calculated.

These data together with sensible heats for the various reactants and products have enabled the tabulation of the heat absorbed or released at each stage of the oxidation and cyclic chlorination and regeneration process.

It can be seen from the tabulation of the heat requirements for each stage that the overall process, that is the oxidation of ilmenite and separation of the oxidised product to ferric oxide and titanium dioxide, is exothermic. However, while the oxidation reaction is almost thermally neutral when sensible heats of reaction are considered, the chlorination reaction is endothermic and the regeneration is exothermic.

The chlorination reaction is carried out at high temperature, $1100^{\circ}C$ has been established as the optimum, while the regeneration reaction is carried out at a much lower temperature, about $500^{\circ}C$. Heat must therefore be supplied to the process at high temperature and recovered at low temperature.

The design of auxiliary heating and heat recovery equipment will therefor be very important in the operation of the process on an industrial scale.

In Section 4 of this thesis, the results of experiments undertaken to examine factors influencing the rates of oxidation and of chlorination in fluidised beds are reported.

Suitable gas flow rates for both reactions have been determined, being sufficiently high to maintain adequate fluidisation and so prevent sintering, yet not so high that solids are swept from the bed by entrainment in the gas stream.

A temperature of $1000^{\circ}C$ has been established as the optimum for the oxidation reaction. At lower temperatures the rate of reaction is relatively slow while at higher temperatures oxidation does not proceed to completion.

A temperature of $1100^{\circ}C$ has been established as the optimum for the chlorination reaction.

The higher the chlorination temperature the greater the rate of reaction and the greater the utilization of chlorine. However at temperatures much above $1100^{\circ}C$, it is very difficult to prevent fluidised beds of oxidised ilmenite from sintering.

For this reason, $1100^{\circ}C$ has been selected as the optimum temperature for chlorination.

This summarises the progress of the project at this stage.

6.   CONCLUSIONS AND RECOMMENDATIONS.

It has been demonstrated that fluidised
bed reactors are suitable for conducting the
oxidation and chlorination reactions, that products
of suitable grade can be produced by both react-
ions, and that utilization of gaseous reactants
is sufficiently high in both cases for the
chlorination process to be practicable.

That reaction rates for both the oxidation
and chlorination reactions are sufficiently rapid
for the process to be practicable has also been
demonstrated.

It has been shown on the basis of thermo-
dynamic calculations that complete recovery of
chlorine from ferric chloride for recycling for
further use in the process should be practicable.
In addition, heat requirements for the process have
been calculated.

The need for multiple stage fluidised bed
reactors, as opposed to single stage reactors, to
reduce bypassing of solids for both the oxidation
and chlorination reactions has been discussed.
Expressions for retention times in single and
multiple stage reactors have been derived.

It therefore remains to correlate solids
retention times with data for reaction rates to

predict the performance of single or multiple stage fluidised reactors. The optimum number and size of stages can then be selected.

Before this can be done a thorough investigation of reaction rates in fluidised beds for both oxidation and chlorination reactions is necessary. Quantitative data are needed on the influence of bed depth, bed composition, gas velocity and gas composition on the rate of reaction at the selected temperatures of $1000^{\circ}C$ for oxidation and $1100^{\circ}C$ for chlorination.

These data have then to be correlated and reaction rates expressed in convenient algebraic form and combined with the derived expressions for solids retention times for the prediction of reactor performance.

For the regeneration reaction, the rate of reaction and the extent of reaction at various temperatures will have to be determined by experiment. In this work the physical nature of the iron oxide deposit will have to be considered.

It is anticipated that iron oxide of high purity will be produced by this process. However some metal chlorides deriving from impurities in the ore may cause contamination. In spite of this it may be possible by control of the physical

conditions under which the regeneration reaction
is carried out to deposit iron oxide in a physical
form suitable for special applications, such as,
for example, polishing powers.

The cumulative effect on the cyclic chlorinat-
ion system of minor impurities in the ilmenite
will also need close examination.

It may be necessary to condense out chlorides
so formed from part or all of the circulating
gas stream.

To prevent the accumulation of inert diluents
such as nitrogen in the circulating gas stream,
it will almost certainly be necessary to bleed off
portion of the gas stream, either continuously or
intermittently. This could be either replaced with
fresh chlorine or treated for chlorine recovery
by compression and condensation and chlorine so
recovered returned to the gas atream.

The optimum temperature for regeneration will
have to be determined taking into consideration
rate of reaction, extent of reaction, the nature of
the iron oxide deposit, the removal of impurities,
particularly chlorides, and the heat requirements
of the process.

Possibly the greatest difficulty with the
process will be in supplying the large high

temperature heat requirements of the chlorination
reaction and recovering the heat released by the
low temperature regeneration reaction.

Practical difficulties and the high capital
cost of equipment to do this may make the process
either unworkable or uneconomic.

Future work should therefore cover the
correlation of various variables influencing
reaction rates for the oxidation and chlorination
reactions. The development of a suitable scheme
for reactor design correlating reaction rates and
retention times and its application in preliminary
designs for industrial scale reactors for the
oxidation and chlorination reactors should follow.

Experimental investigation of the rate and
extent of the reverse reaction to the point where
preliminary design of industrial scale equipment
is possible should be the next step.

This should be followed by a careful economic
assessment of the process having available
approximate designs for large scale equipment
based on experimental work for all three reactions.

Further work would depend on the outcome of
the economic assessment.

The major outstanding problem would then
be in maintaining the circulating gas stream

relatively free of impurities and with the ferric chloride and oxygen content in stoichiometric proportion.

To do this the development of a suitable method for the analysis of mixtures of ferric chloride, oxygen and chlorine gases would be necessary.

In conclusion it can be said that there are many technical problems associated with the operation of this process on an industrial scale. However there appear to be no insurmountable difficulties.

It is not possible to make a detailed economic assessment of the process at this stage and it is possible that the process may ultimately prove uneconomic.

However the project should be continued until a thorough economic assessment is possible.

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EQUATIONS.

(1) $FeO + 3/2Cl_2 = FeCl_3 + 1/2O_2$

(2) $Fe_2O_3 + 3Cl_2 = 2FeCl_3 + 3/2O_2$

(3) $FeO.TiO_2 + 3/2Cl_2 = FeCl_3 + 1/2O_2 + TiO_2$

(4) $2FeCl_3 + 3/2O_2 = Fe_2O_3 + 3Cl_2$

(5) $2FeO.TiO_2 + 1/2O_2 = Fe_2O_3.TiO_2 + TiO_2$

(6) $Fe_2O_3.TiO_2 + 3Cl_2 = 2FeCl_3 + 3/2O_2 + TiO_2$

(7) $TiO_2 + 2Cl_2 = TiCl_4 + O_2$

(8) $4FeO.TiO_2 + O_2 = 2Fe_2O_3.TiO_2 + 2TiO_2$

(9) $Fe_2Cl_6 = 2FeCl_3$

(10) $Fe_2Cl_6 = 2FeCl_2 + Cl_2$

(11) $2FeCl_3 = Fe_2Cl_6$

(12) $2Fe_2O_3 + 6Cl_2 = 4FeCl_3 + 3O_2$

(13) $2Fe_2O_3.TiO_2 + 6Cl_2 = 4FeCl_3 + 3O_2 + 2TiO_2$

(14) $2Fe_2O_3 + 2TiO_2 = 2Fe_2O_3.TiO_2$

(15) $Fe_2O_3 + TiO_2 = Fe_2O_3.TiO_2$

(16) $4Fe + 2O_2 = 4FeO$

(17) $4FeO + 2/3O_2 = 4/3Fe_3O_4$

(18) $4/3Fe_3O_4 + 1/3O_2 = 2Fe_2O_3$

(19) $4FeO.TiO_2 = 4Fe + 2O_2 + TiO_2$

(20) $2FeO.TiO_2 + 1/2O_2 = Fe_2O_3 + 2TiO_2$

(21) $2TiO_2 + 6Cl_2 = 3TiCl_4 + 3O_2$

(22) $2Fe_2O_3.TiO_2 + 3TiCl_4 = 4FeCl_3 + 5TiO_2$

(23) $2Fe_2O_3 + 3TiCl_4 = 4FeCl_3 + 3TiO_2$

(24) $FeO.TiO_2 = FeO + TiO_2$

(25) $2FeO.TiO_2 + 1/3O_2 = 2/3Fe_3O_4 + 2TiO_2$

(26) $2/3Fe_3O_4 + 1/6O_2 = Fe_2O_3$

(27) $Fe + Cl_2 = FeCl_2$

(28) $FeCl_3 = FeCl_2 + 1/2Cl_2$

(29) $2Fe_2O_3 + 4Cl_2 = 4FeCl_2 + 3O_2$

(30) $2Fe_2O_3.TiO_2 + 4Cl_2 = 4FeCl_2 + 3O_2 + 2TiO_2$

(31) $2Fe_2O_3 + 6Cl_2 = 2Fe_2Cl_6 + 3O_2$

(32) $2Fe_2O_3.TiO_2 + 2TiO_2 + 6Cl_2$
$$= 4FeCl_3 + 3O_2 + 4TiO_2$$

(33) $4FeCl_3 = 2Fe_2Cl_6$

(34) $2Fe_2Cl_6 + 3O_2 = 2Fe_2O_3 + 6Cl_2$

(35) $4FeCl_3 + 3O_2 = 2Fe_2O_3 + 6Cl_2$

(36) $4FeO.TiO_2 + O_2 = 2Fe_2O_3 + 4TiO_2$

NOTATION.

G_{mf} = Critical fluid mass velocity.

ρ = Fluid density.

ρ_s = Particle density.

μ = Fluid viscosity.

D = Mean effective particle diameter.

λ = Particle shape factor.

δ = Bed voidage at mininum fluidisation.

X = Weight fraction.

d = Equivalent spherical particle diameter.

T = Temperature, degrees Kelvin.

v = Flow rate of particulate solids.

V = Stage capacity.

n = Number of stages.

t = Time.

$\emptyset(t)$ = Frequency function for reactor effluent.

$f(t)$ = Distribution function for reactor effluent.

log = Logarithm to base 10.

ln = Logarithm to base "e".

K_p = Equilibrium constant in terms of partial pressures.

C_p = Heat capicity at constant pressure.

ΔC_p = Heat capacity of products of reaction less heat capacity of reactants.

ΔH = Heat of reaction.

ΔH_f = Heat of formation from the elements in standard states.

S = Entropy.

ΔS = Entropy change for reaction.

ΔG = Free energy change for reaction.

ΔG_f = Free energy of formation from elements in standard states.

a = Initial concentration of reactant in the solid.

a_t = Concentration of reactant in the solid at time "t".

b = Inert constituent of solid.

c = Inert constituent of solid.

x = Mass of solid reactant consumed per unit mass of original charge.

x = Mass of gaseous reactant consumed per unit mass of gas flowing through the solid charge.

M_x = Mols of substance "x".

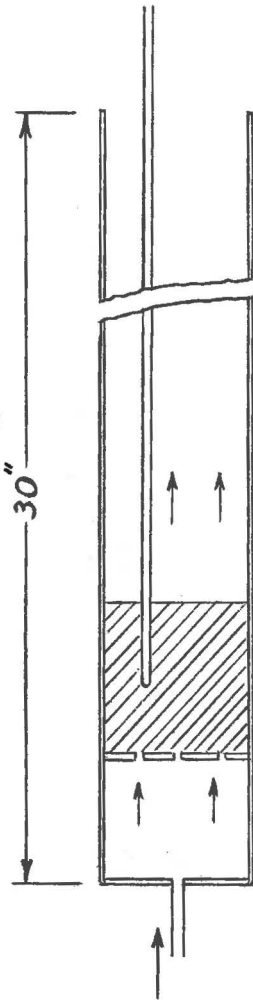P = Absloute pressure in atmospheres.

APPENDIX I   Figure 1.
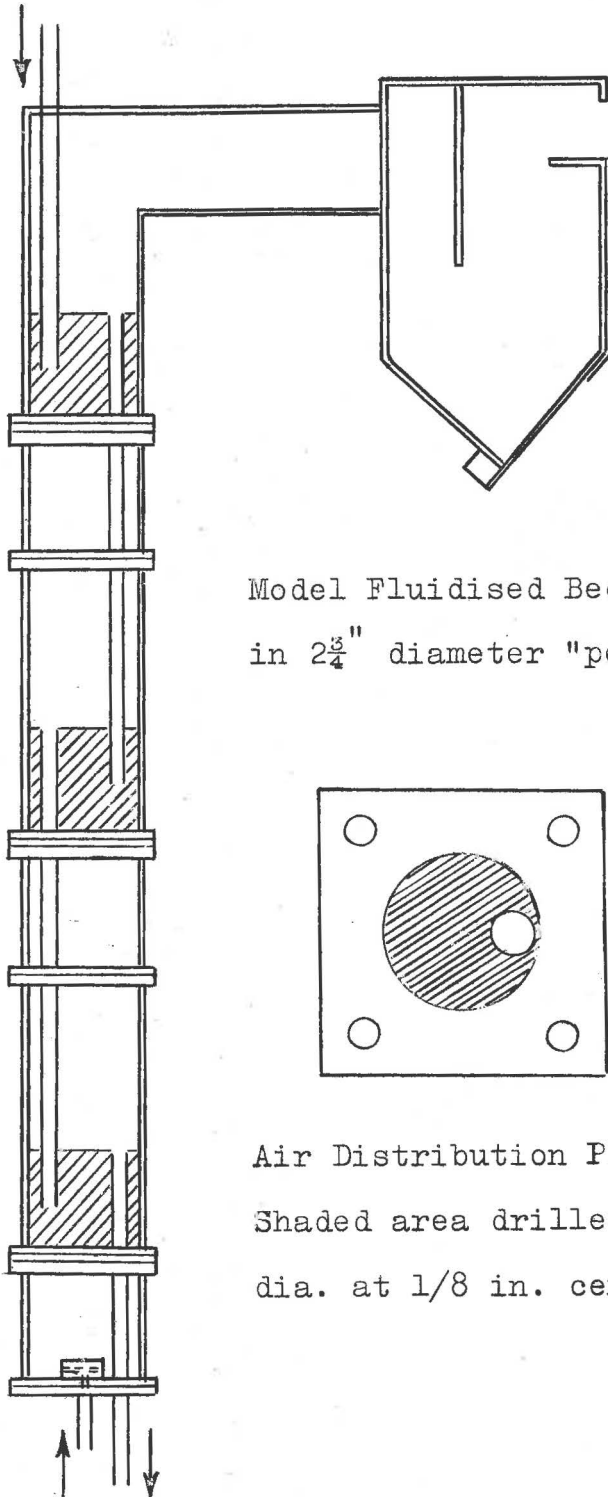
Model Fluidised Bed Reactor

in $2\frac{3}{4}$" diameter "perspex".

Air Distribution Plate.

Shaded area drilled 1/32 in.

dia. at 1/8 in. centres.

APPENDIX I Figure 2.

Fluidised Bed Reactor

in silica tubing, bore 3 ins.,

length 30 ins.

Silica bubble cap.

Length $\frac{3}{8}$ in., made from $\frac{1}{4}$ in.

tube with 3 x 0.012 in. holes

set around top end.

Caps are set in air distribution

plate with 3 o 1 in. P.C.D.

and with 6 on 2 in. P.C.D.
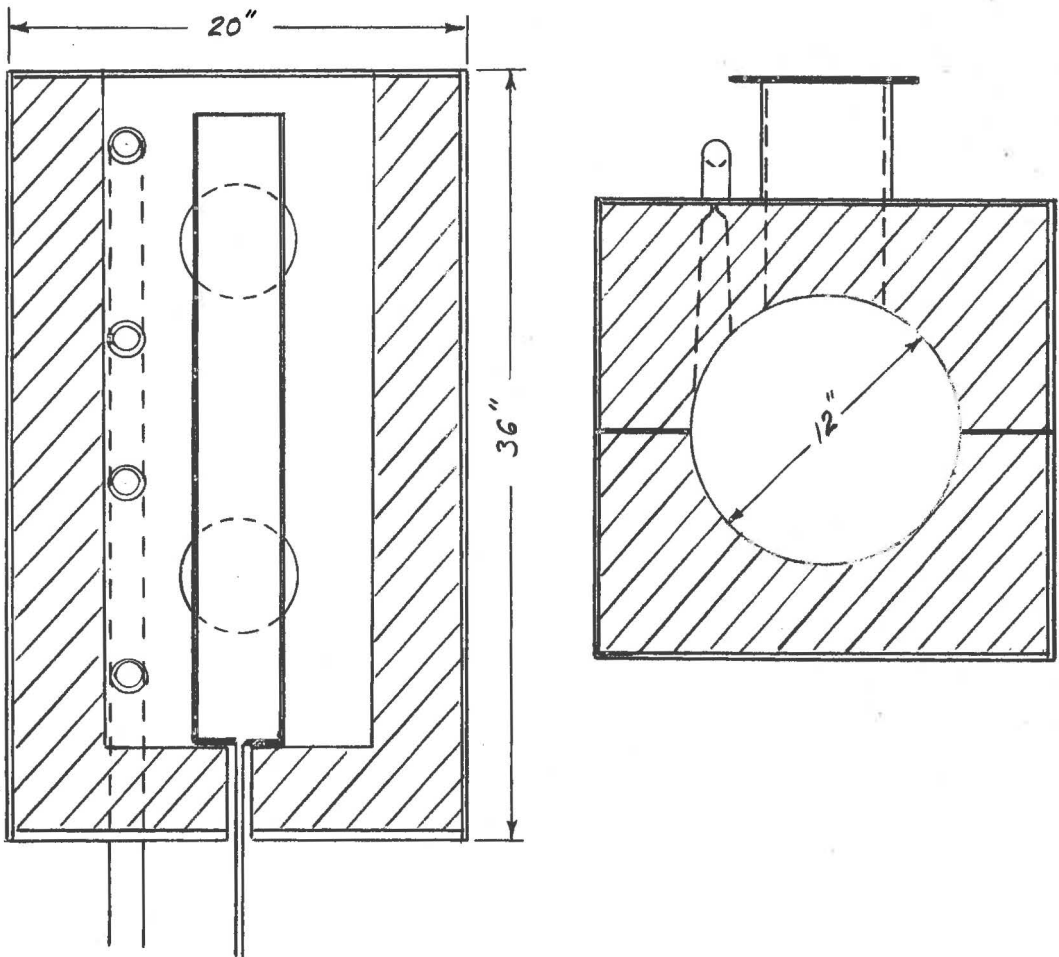
30"

158.

APPENDIX I   Figure 3.

Gas fired furnace with :
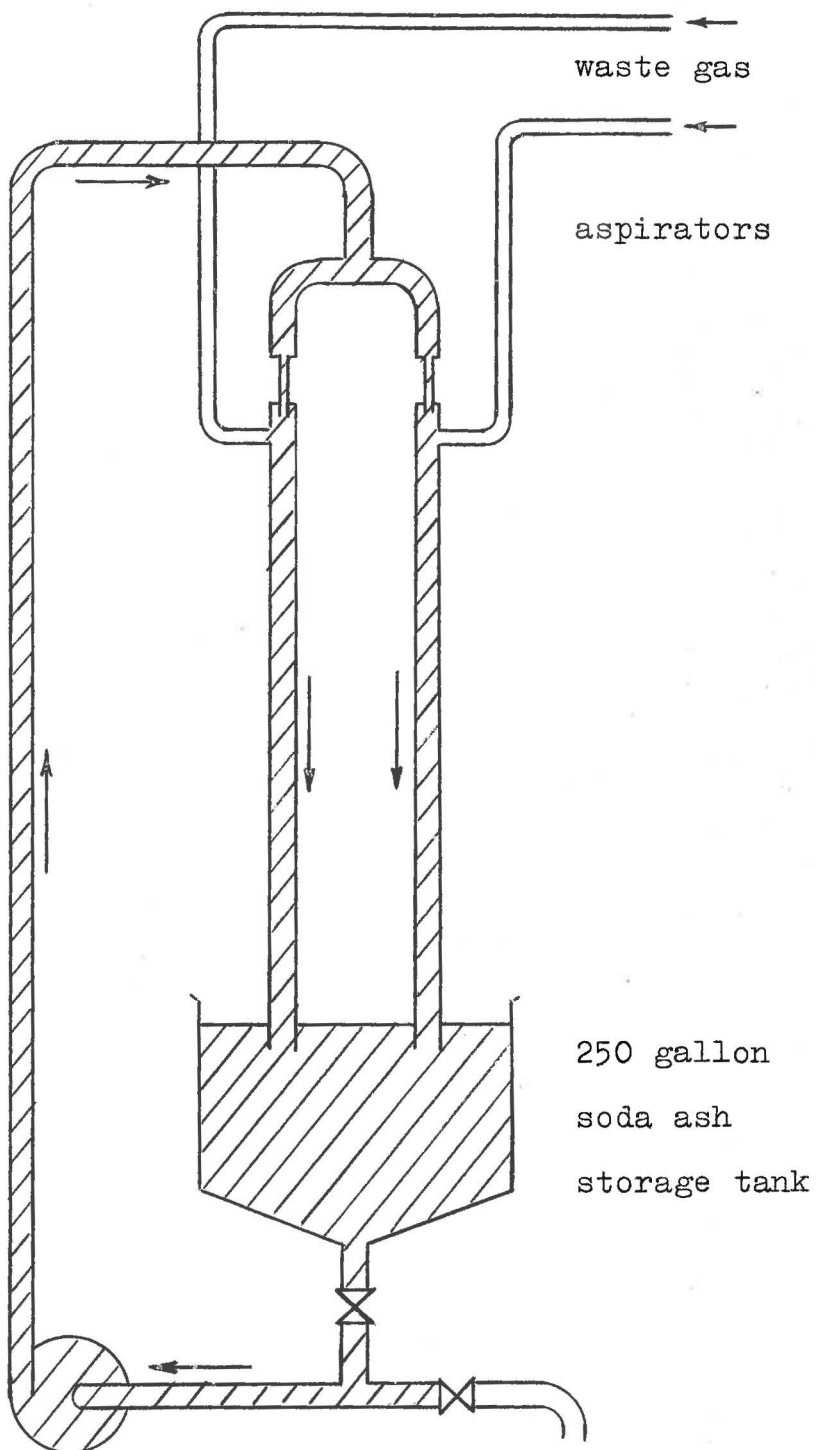
fluidised bed reactor

moveable half section

four gas burners

two 4 in. diameter flues.

APPENDIX I   Figure 4.

Waste Chlorine Absorption System.

waste gas

aspirators

250 gallon
soda ash
storage tank

APPENDIX   11   Table 1.

Capel Ilmenite.

Chemical Composition.	Weight Percent.
Ferrous Oxide (FeO)	13.5
Ferric Oxide (Fe_2O_3)	29.1
Titanium Dioxide (TiO_2)	54.9
Insoluble	2.5
	100.0

Screen Analysis.	Weight Percent.
+52 mesh (B.S.S.)	0.5
−52 / +72	10.8
−72 / +100	58.8
−100 / +150	27.5
−150 / +200	2.1
−200 mesh	0.3
	100.0

Specific Gravity.	
Material	4.5
Bulk	2.5

APPENDIX 11   Table 2

Moana Quartz Sand.

Screen Alysis.	Weight Percent.
+52 mesh	5.1
-52 / +72	42.0
-72 / +100	39.1
-100 / +150	11.1
-150 / +200	1.5
-200 mesh	1.2
	100.0

Specific Gravity.

Material	2.6
Bulk	1.5

APPENDIX   11 Table 3.

Stradbroke Island Ilmenite.

Chemical Composition.	Weight Percent.
Ferrous Oxide (FeO)	31.6
Ferric Oxide Fe_2O_3)	14.4
Titanium Dioxide (TiO_2)	50.1
Chromic Oxide (Cr_2O_3)	0.18
Insoluble	0.85

Screen Analysis.	Weight Percent.
+52 mesh (B.S.S.)	0.7
-52 / +72	2.2
-72 / +100	23.9
-100 / +150	53.4
-150 / +200	18.8
-200 mesh	1.0
	100.0

Specific Gravity.	
Material	4.7
Bulk	2.5

APPENDIX 11 Table 4.

Stradbroke Island Non-Magnetic.

Screen Analysis.	Weight Percent.
+52 mesh (B.S.S.)	0.1
-52 / +72	0.5
-72 / +100	12.0
-100 / +150	65.0
-150 / +200	20.2
-200 mesh	2.2
	100.0

Specific Gravity.	
Material	4.5
Bulk	2.5

APPENDIX 11 Table 5.

Rutile Product.

(ex Stradbroke Island Ilmenite).

Chemical Composition.	Weight Percent.
Ferric Oxide (Fe_2O_3)	0.01
Titanium Dioxide (TiO_2)	99.0
Chromic Oxide (Cr_2O_3)	0.001

Screen Analysis.	Weight Percent.
+52 mesh (B.S.S.)	0.4
-52 / +72	4.5
-72 / +100	20.9
-100 / +150	63.6
-150 / +200	8.1
-200 mesh	2.5
	100.0

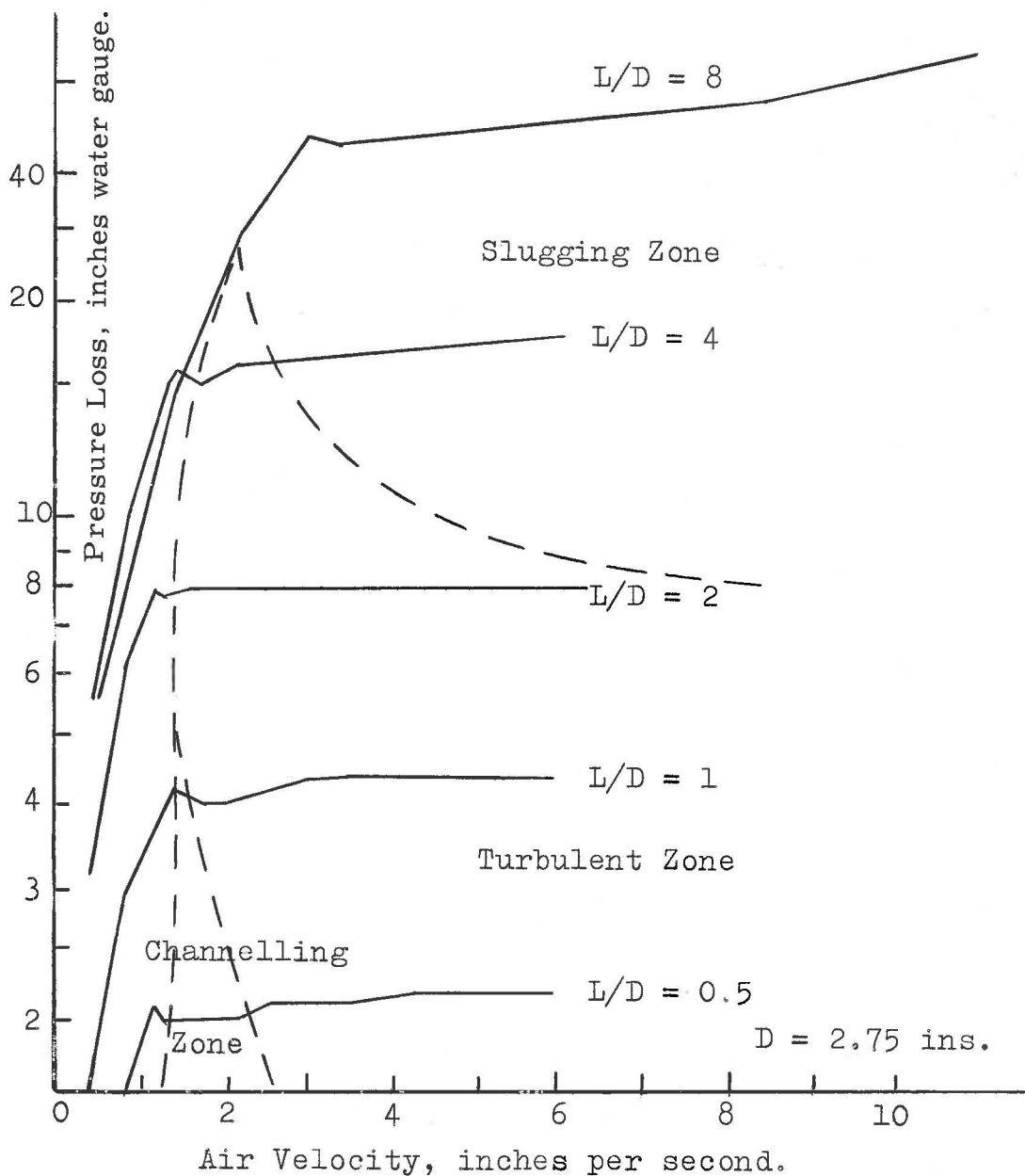| Specific Gravity.	
Bulk	1.3

APPENDIX III   Figure 1.

Pressure Loss Curves for Fluidised Capel Ilmenite.
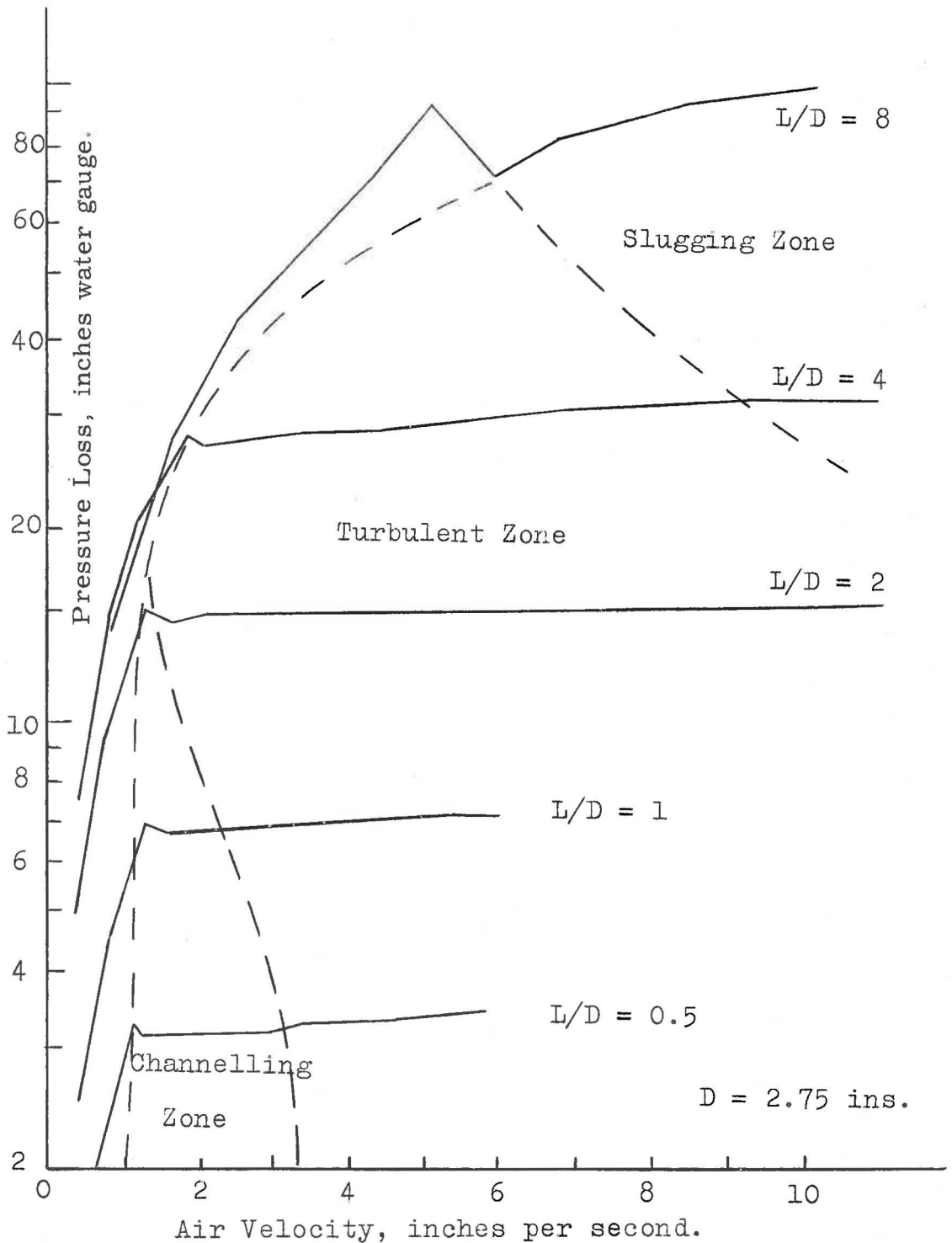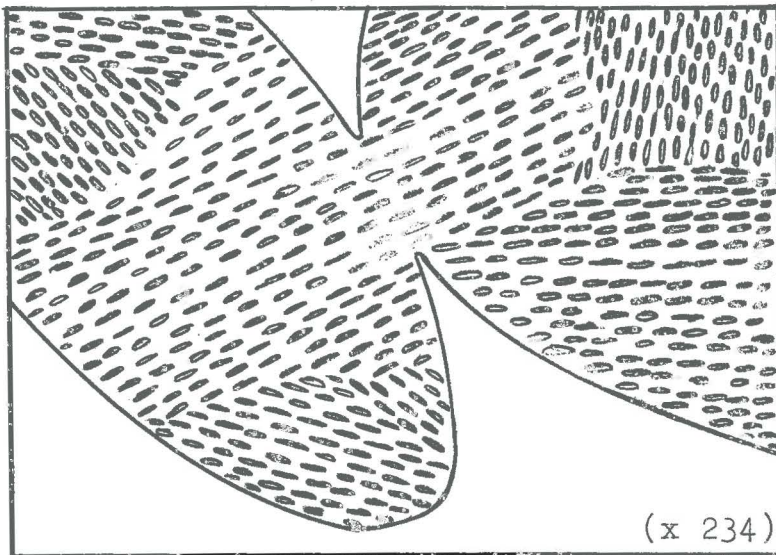
APPENDIX III   Figure 2.

Pressure Loss Curves for Fluidised Quartz Sand.

APPENDIX III   Figure 3.

Sintered Oxidised Ilmenite.

(x 234)

"The individual grains of ilmenite are
converted to a fine grained granular aggregate of
pseudobrookite crystals, all of which contain very
fine parallel oriented intergroxths of rutile
usually less than 10 microns in size.

Bonding between individual grains to form
the sinter lumps is due to crystallisation across
the contact between individual grains. The cryst-
allisation involves the formation of pseudobrook-
ite crystals continuous across the contact. The
illustrations indicate this structure quite
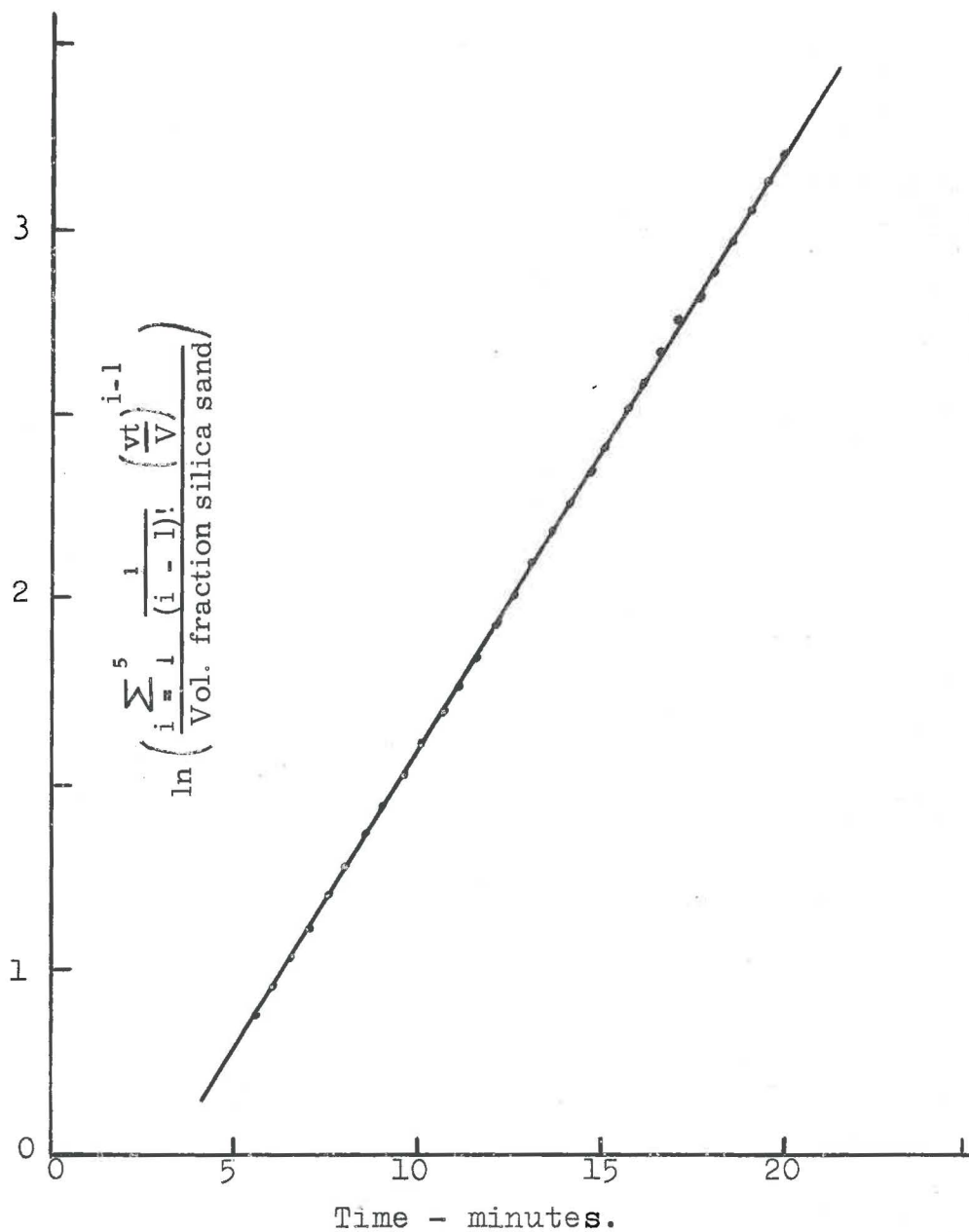clearly."

(Whittle, unpublished data 1957.)

APPENDIX IV   Figure 1.

Single Stage Mixing Test :

Ilmenite and Quartz Sands.

Time - minutes.
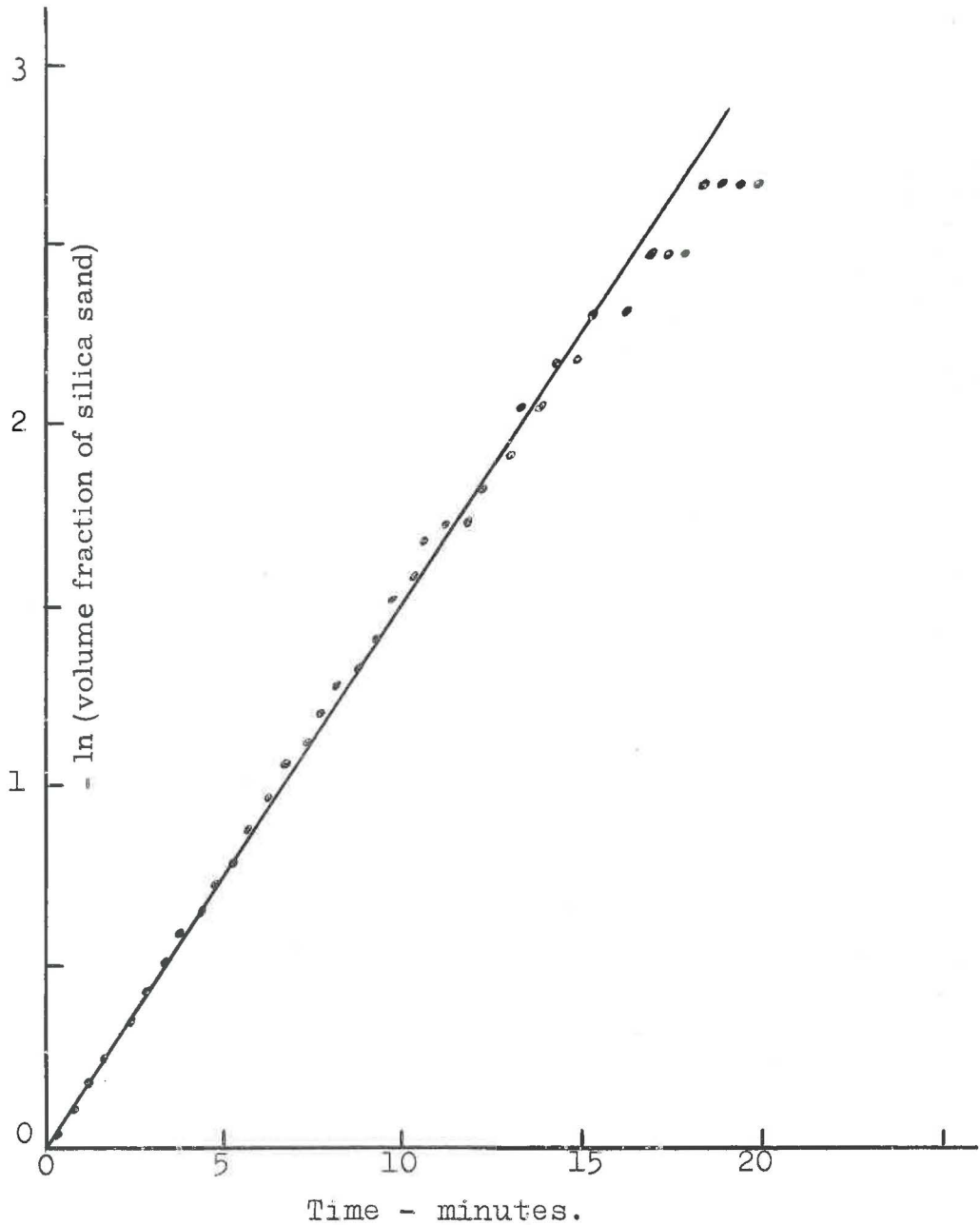
APPENDIX IV   Figure 2.

Five Stage Mixing Test :

Ilmenite and Quartz Sands.

The y-axis is labelled $\ln\left(\dfrac{\sum\limits_{i=1}^{5} \dfrac{1}{(i-1)!}\left(\dfrac{vt}{V}\right)^{i-1}}{\text{Vol. fraction silica sand}}\right)$ with gridline values 0, 1, 2, 3. The x-axis is labelled Time — minutes, with values 0, 5, 10, 15, 20.
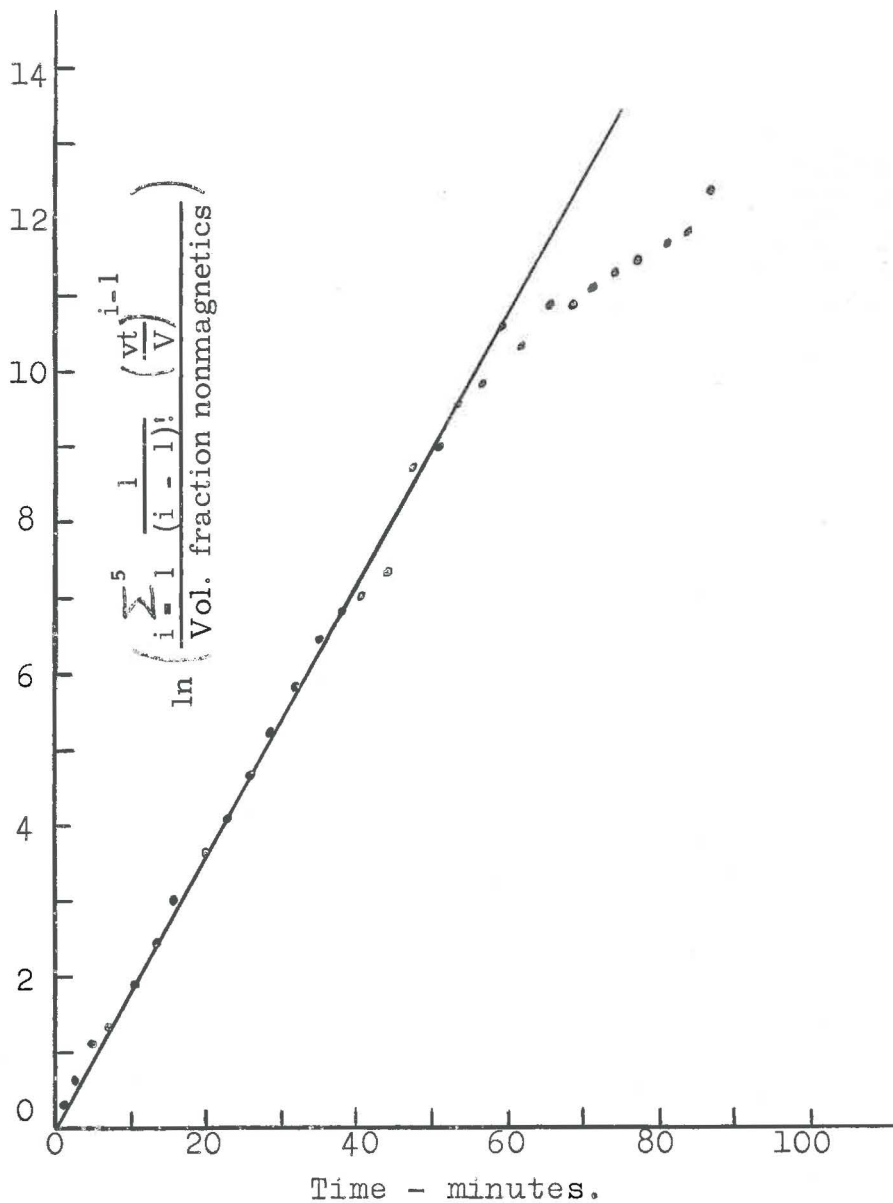
APPENDIX IV   Figure 3.

Five Stage Mixing Test :

Ilmenite and High Density Nonmagnetic Sands.

Time — minutes.

APPENDIX V   Table 1.

Chlorination of Ferric Oxide.

(After Galmiche, 1948).

$$2Fe_2O_3 + 6Cl_2 = 4FeCl_3 + 3O_2$$

Temperature	Chlorine Utilization	$\ln K_p$
$700^\circ C$	3.8 percent	−26.38
$800^\circ C$	9.8	−19.30
$900^\circ C$	19.6	−13.93
$1000^\circ C$	32.4	−9.29
$1100^\circ C$	57.0	−5.25

APPENDIX V Table 2.

Equilibrium Constants for the Chlorination

of Ferric Oxide.

(After Smullin, 1952).

$$2Fe_2O_3 + 6Cl_2 = 4FeCl_3 + 3O_2$$

Temperature	$\ln K_p$
$704\,^{\circ}C$	-23.24
$760\,^{\circ}C$	-24.26
$816\,^{\circ}C$	-22.57
$816\,^{\circ}C$	-23.80
$871\,^{\circ}C$	-22.22
$927\,^{\circ}C$	-18.76
$982\,^{\circ}C$	-17.97

APPENDIX V   Figure 1.

Equilibrium constants for the ferric oxide –

chlorine – ferric chloride – oxygen system.

$- \ln K_p$

(Temperature)$^{-1}$ x 10^{4} ($^{\circ}$Kelvin)

● = Galmiche (1948).

▣ = Smullin (1952).
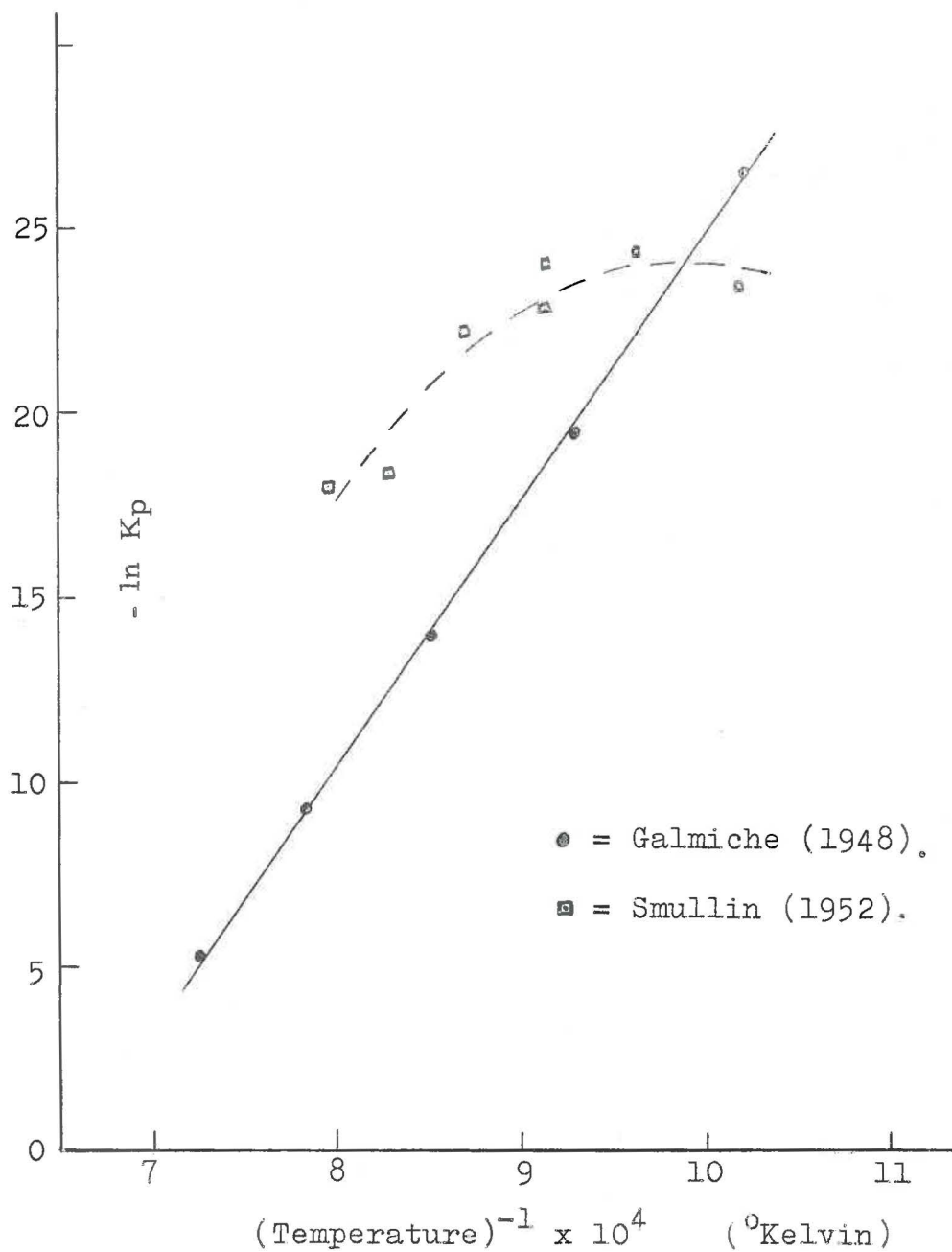
APPENDIX V   Table 3.

Chlorination of Ferric Oxide

(After Wilmshurst, 1959).

$$2Fe_2O_3 + 6Cl_2 = 4FeCl_3 + 3O_2$$

Temperature	Chlorine Utilization	$\ln K_p$
$865^{\circ}C$	18.0 percent	-14.54
$920^{\circ}C$	23.5	-12.27
$956^{\circ}C$	31.0	-9.72
$1000^{\circ}C$	36.0	-8.23
$1028^{\circ}C$	43.8	-6.09
$1060^{\circ}C$	46.6	-5.36
$1060^{\circ}C$	54.0	-3.44
$1100^{\circ}C$	56.0	-2.92

APPENDIX V Figure 2.

Chlorination of ferric oxide.

$$4Fe_2O_3 + 6Cl_2 = 4FeCl_3 + 3O_2$$

accepted best
values for
Wilmshurst.

Chlorine conversion, percent

Temperature - Centigrade.

$\oplus$ = Galmiche (1948).

$\triangle$ = Wilmshurst (1959).
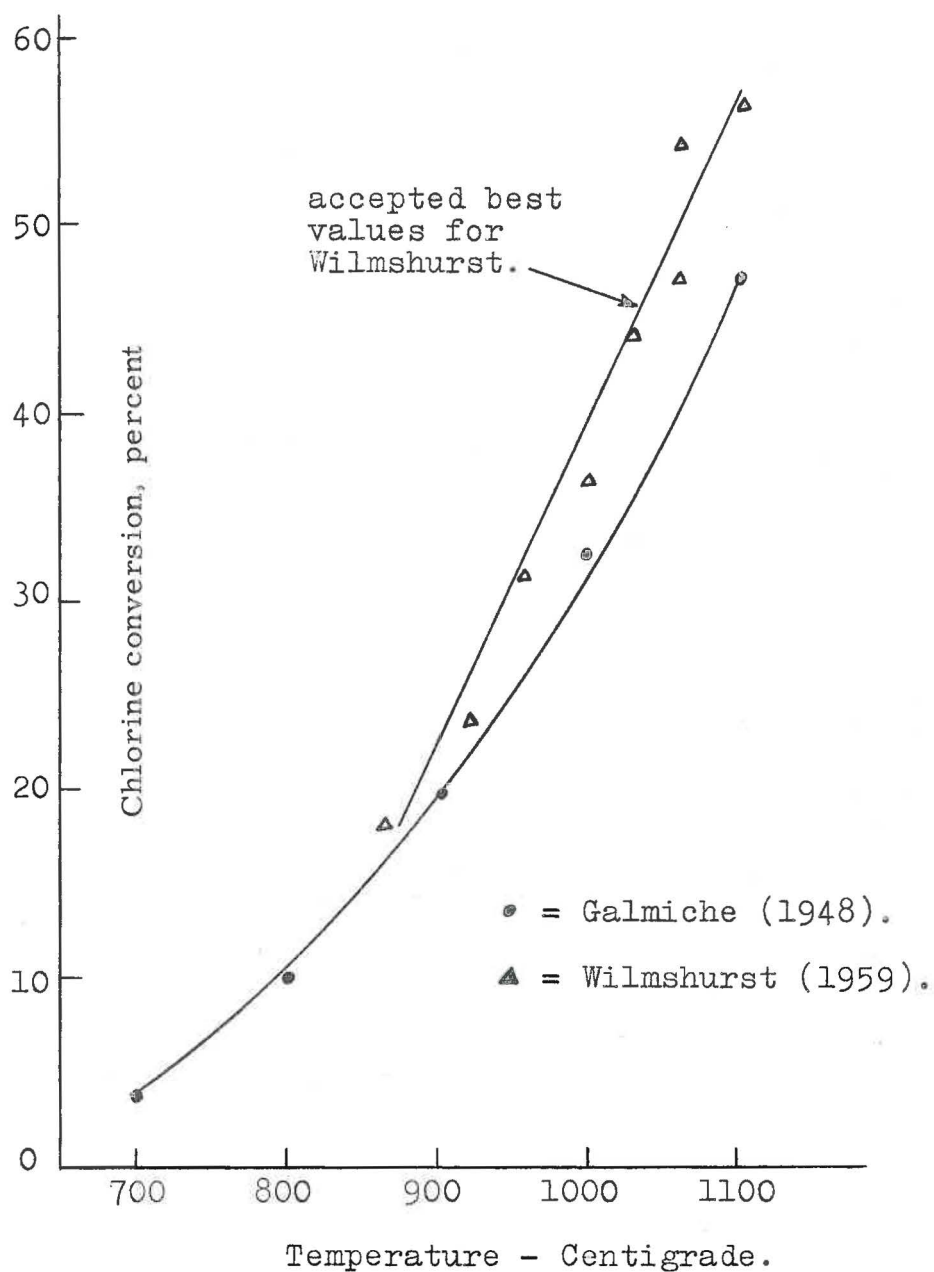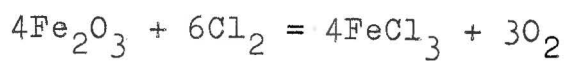
APPENDIX V   Table 4.

Chlorination of Oxidised Ilmenite.

$2 Fe_2O.TiO_2 + 6Cl_2 = 4FeCl_3 + 3O_2 + 2TiO_2$
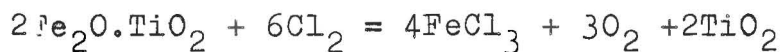
Temperature	Chlorine Flow (gm. / minute)	Chlorine Utilization	$\ln K_p$
1000°C	0.30	30.2	-9.94
	0.15	30.3	
1050°C	0.30	35.7	-8.29
	0.15	35.9	
1100°C	0.30	41.7	
	0.30	43.6	-6.44
	0.15	42.2	
	0.075	42.4	
1150°C	0.30	52.1	
	0.15	52.9	-3.75
	0.15	53.3	
1200°C	0.30	64.5	-0.52
	0.15	65.4	

APPENDIX V   Figure 3.

Chlorination of Oxidised Ilmenite.

$$4Fe_2O_3.TiO_2 + 6Cl_2 = 4FeCl_3 + 3O_2 + 2TiO_2$$
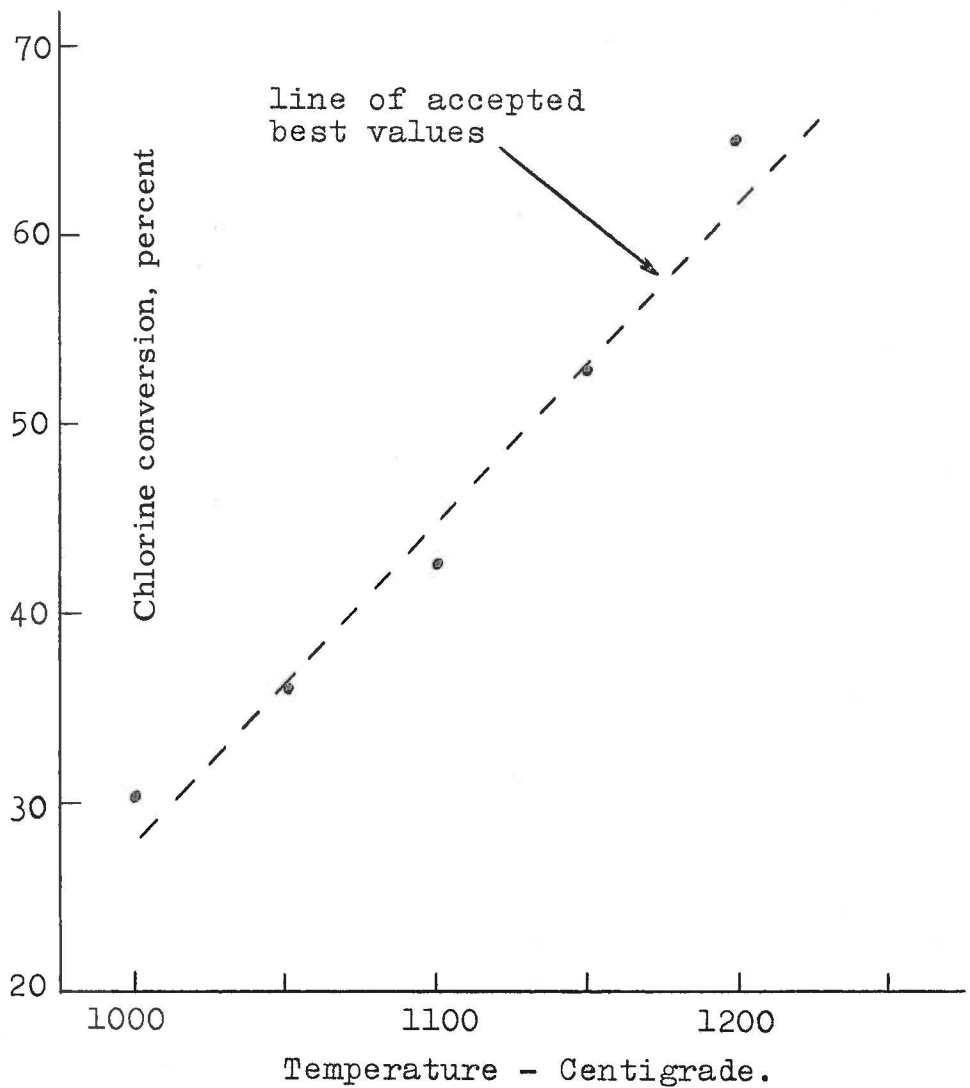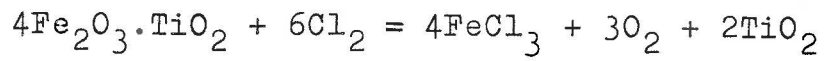
APPENDIX V   Figure 4.

Chlorination of Oxidised Ilmenite.

$$4Fe_2O_3.TiO_2 + 6Cl_2 = 4FeCl_3 + 3O_2 + 2TiO_2$$

- - - - = linear regression
——— = curvelinear regression

$- \ln Kp$

$(Temperature)^{-1} \times 10^4$ $(^{\circ}Kelvin)$
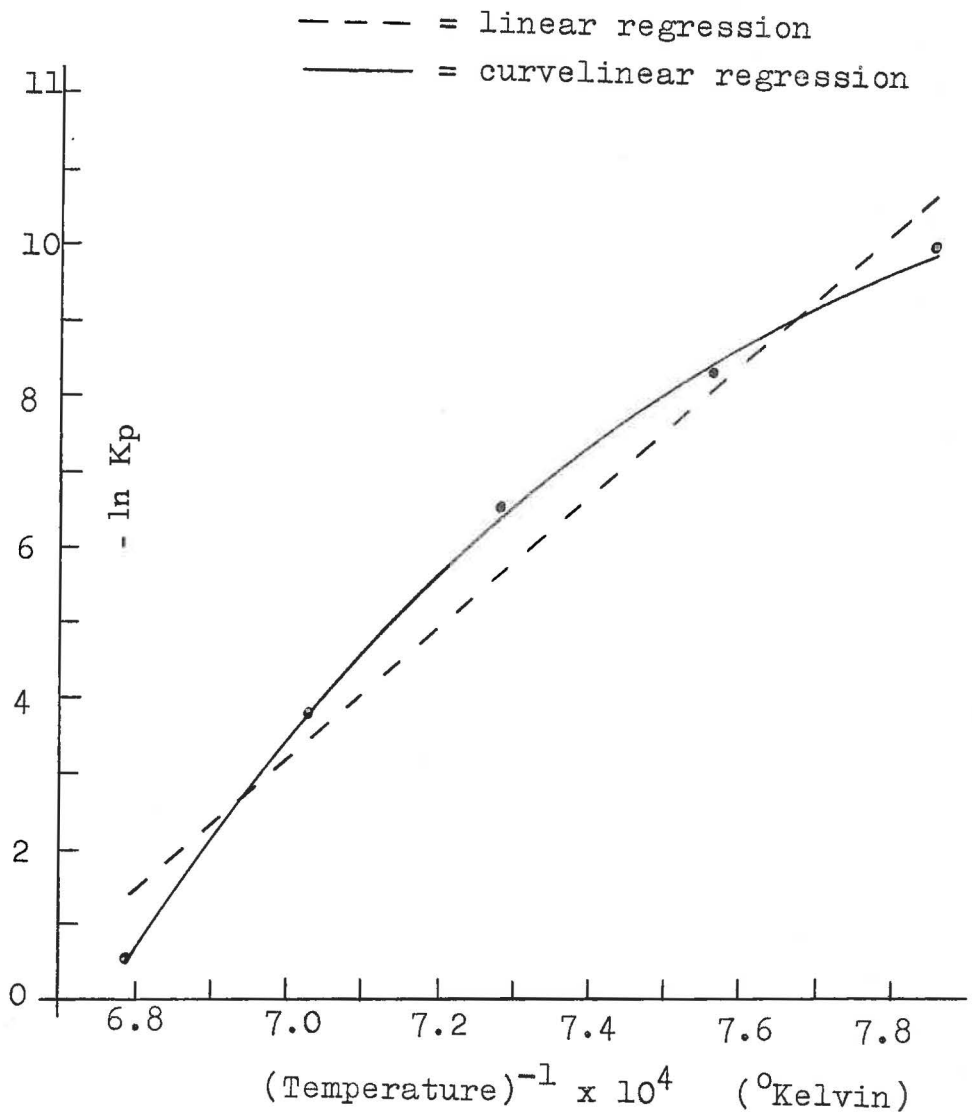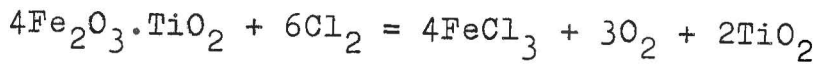
APPENDIX V   Figure 5.

Chlorination of Hematite :

   based on data of Wilmshurst.

$$4Fe_2O_3 + 6Cl_2 = 4FeCl_3 + 3O_2$$

$$4Fe_2O_3 + 4Cl_2 = 4FeCl_2 + 3O_2$$

Chlorine conversion on basis of formation of $FeCl_3$ only.

Chlorine converted to $FeCl_2$

Chlorine converted to $FeCl_3$

Chlorine conversion, percent

Temperature - Centigrade.
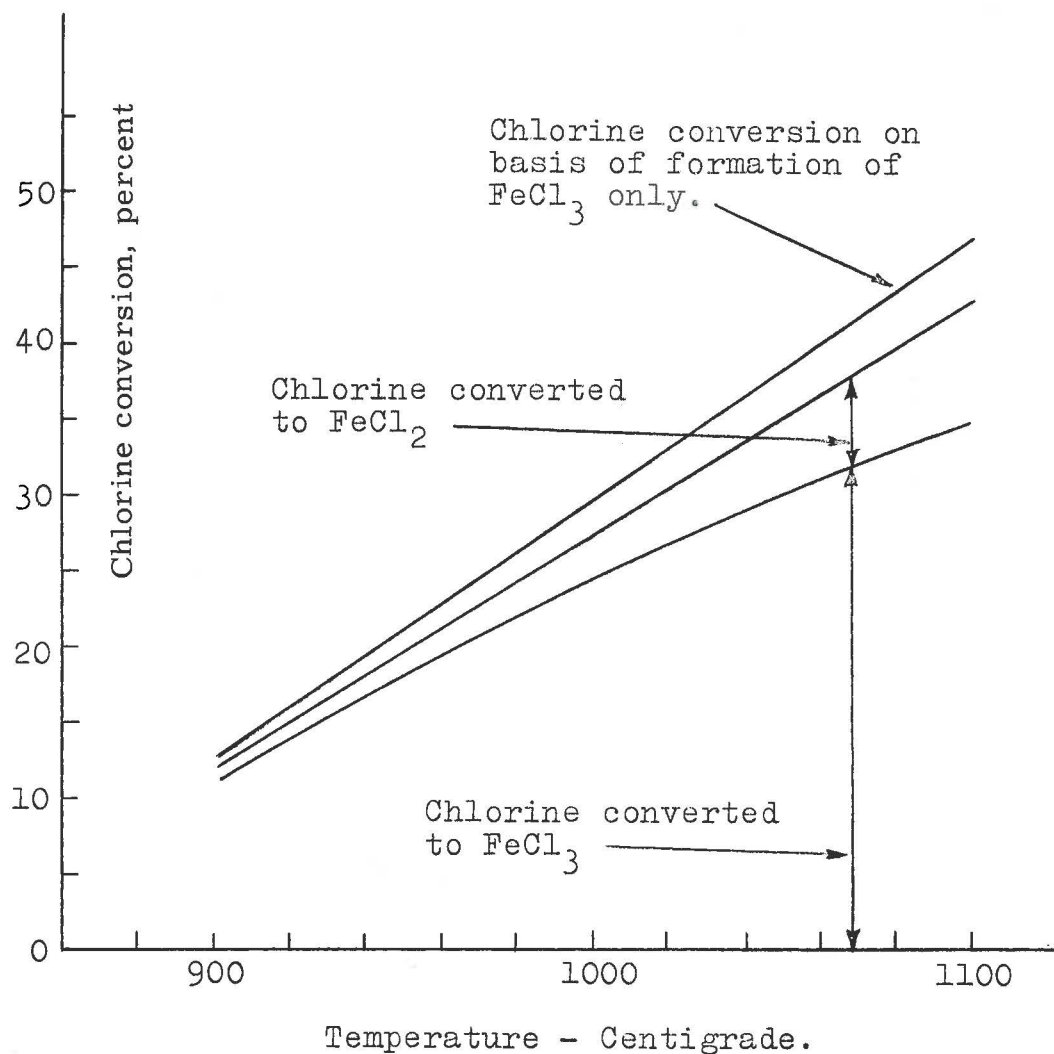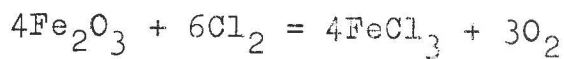
APPENDIX V   Figure 6.

Vapour Pressure of Ferrous Chloride.

$\bullet$ = partial pressure of $FeCl_2$ in
the gases formed by chlorination
of oxidised ilmenite with chlorine
at $1100^{\circ}C$.
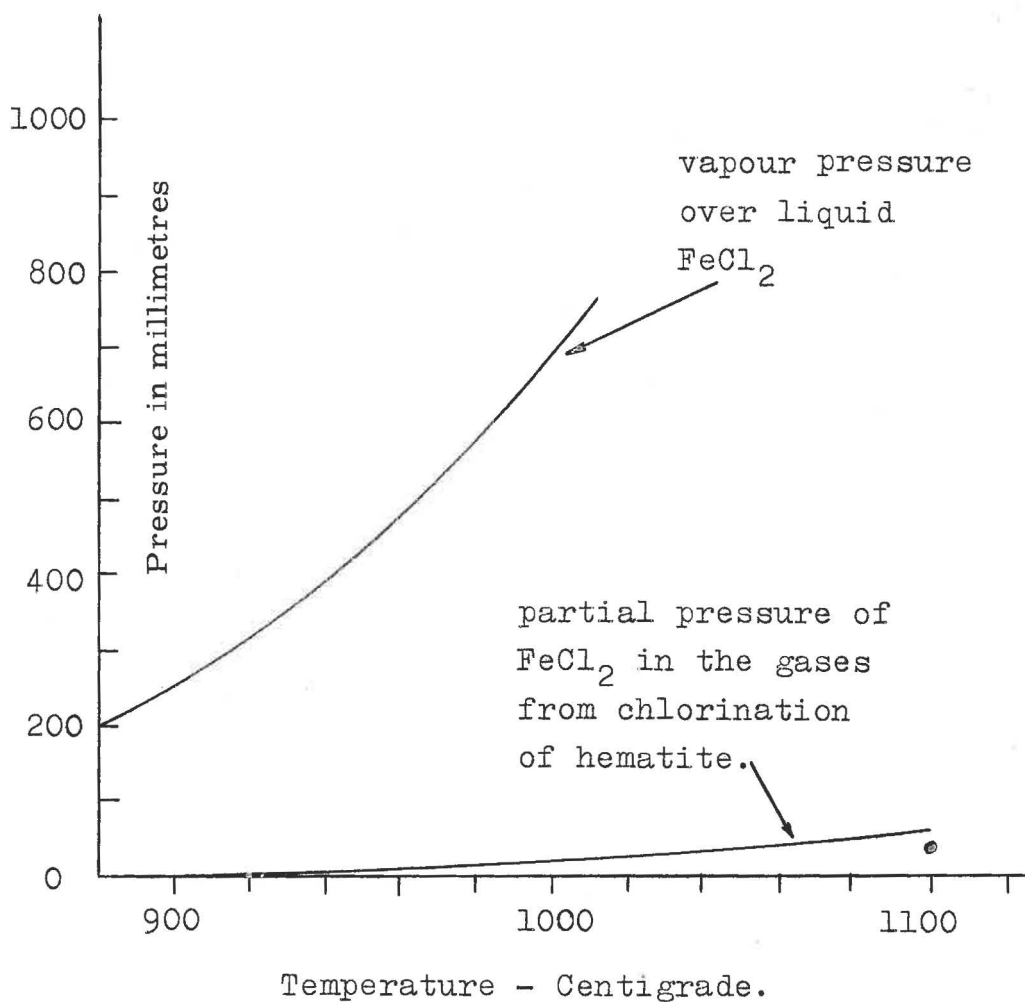

vapour pressure
over liquid
$FeCl_2$

partial pressure of
$FeCl_2$ in the gases
from chlorination
of hematite.

Temperature – Centigrade.

APPENDIX VI   Table 1.

Fluidised Bed Oxidation Test No. 1.

Material: Stradbroke Island Ilmenite.

Charge: 1000 gms. (L/D = 1, D = 3").

Air Flow: 0.0191 gms./sq. in./sec.

Temperature: 900°C

Time minutes	FeO percent	Reaction percent	Oxygen used percent
0	27.2	–	–
5	15.8	41.2	132.6
10	9.4	64.8	104.3
15	6.4	75.9	81.4
20	4.85	81.7	65.7
30	2.70	89.8	48.2
45	1.15	95.6	34.2
60	0.40	98.5	26.4
75	nil	100.0	21.5

APPENDIX VI   Figure 1.

Fluidised Bed Oxidation Test No. 1.

APPENDIX VI   Table 2.
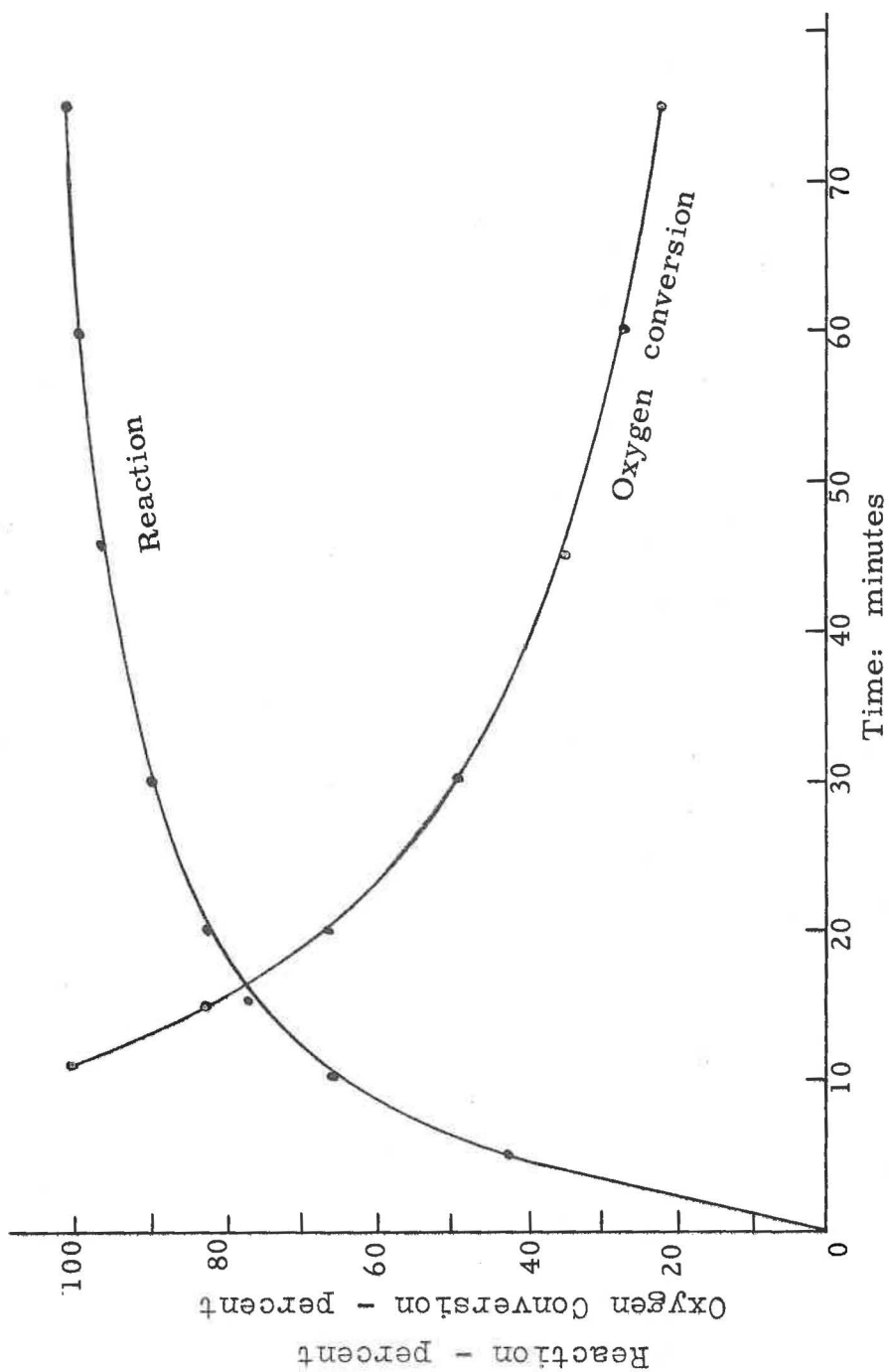
Fluidised Bed Oxidation Test No. 2.

Material: Stradbroke Island Ilmenite.

Charge: 1000 gms. (L/D = 1, D = 3").

Air Flow: 0.0191 gms./sq. in./sec.

Temperature: $1000^{\circ}C$

Time minutes	FeO percent	Reaction percent	Oxygen Used percent
0	28.8	–	–
5	20.1	29.5	100.5
10	12.2	57.2	97.5
15	5.5	80.4	91.3
20	3.0	89.3	76.1
25	2.1	92.5	63.0
30	1.05	96.2	54.6
40	0.51	98.2	41.8
50	0.23	99.2	33.8
60	0.07	99.7	28.3
75	nil	100.0	22.7

APPENDIX VI   Figure 2.

Fluidised Bed Oxidation Test No. 2.
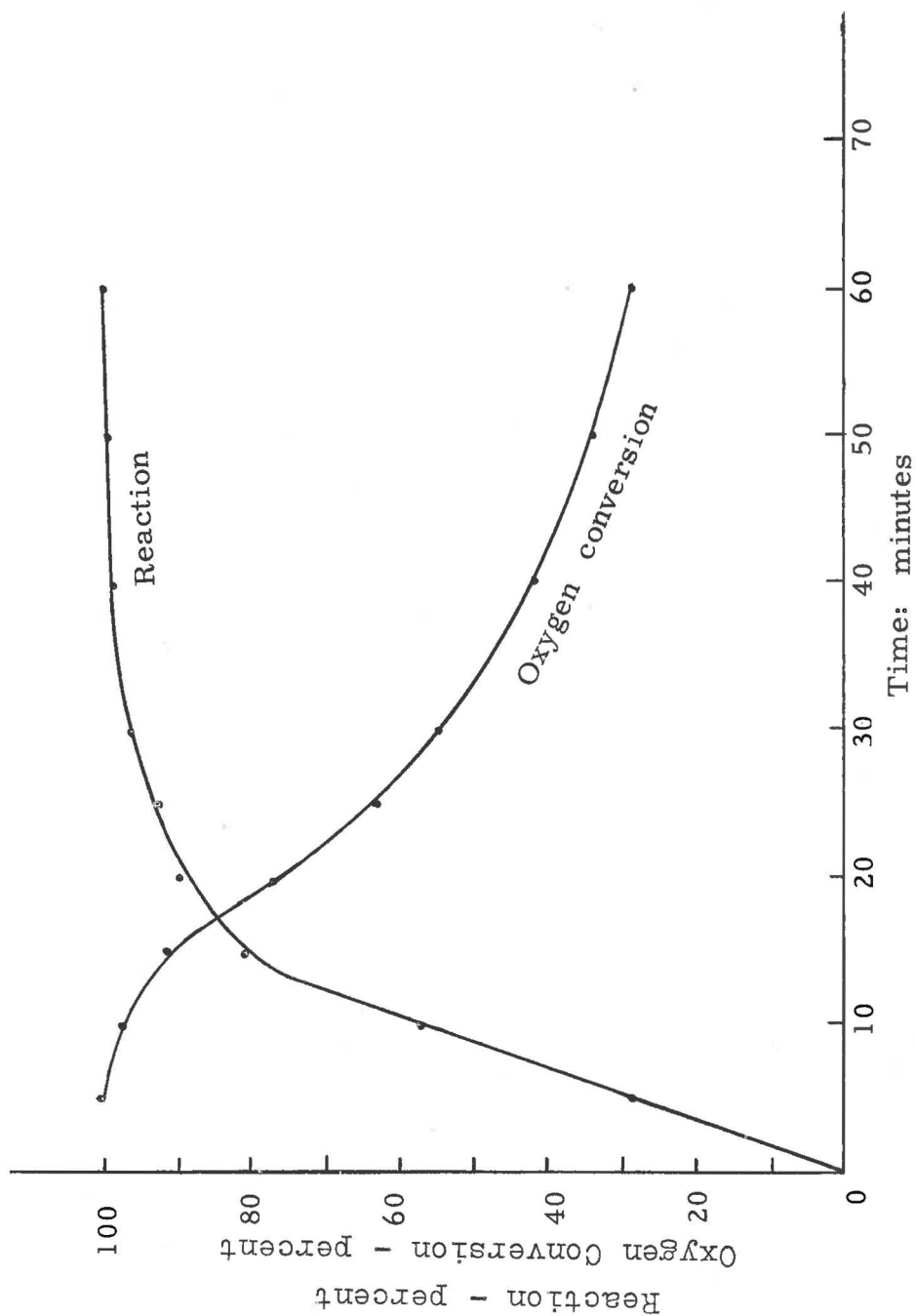
APPENDIX VI   Table 3.

Fluidised Bed Oxidation Test No. 3.

Material: Stradbroke Island Ilmenite.

Charge: 1000 gms. (L/D = 1, D = 3").

Air Flow: 0.0191 gms./sq. in./sec.

Temperature: 1100°C

Time minutes	FeO percent	Reaction percent	Oxygen Used percent
0	29.1	—	—
5	17.8	38.1	131.1
10	6.05	78.7	135.5
15	1.46	94.8	108.8
20	0.77	97.3	83.8
25	0.75	97.3	67.0
30	0.73	97.4	55.9
40	0.68	97.6	42.0

APPENDIX VI   Figure 3.

Fluidised Bed Oxidation Test No. 3.
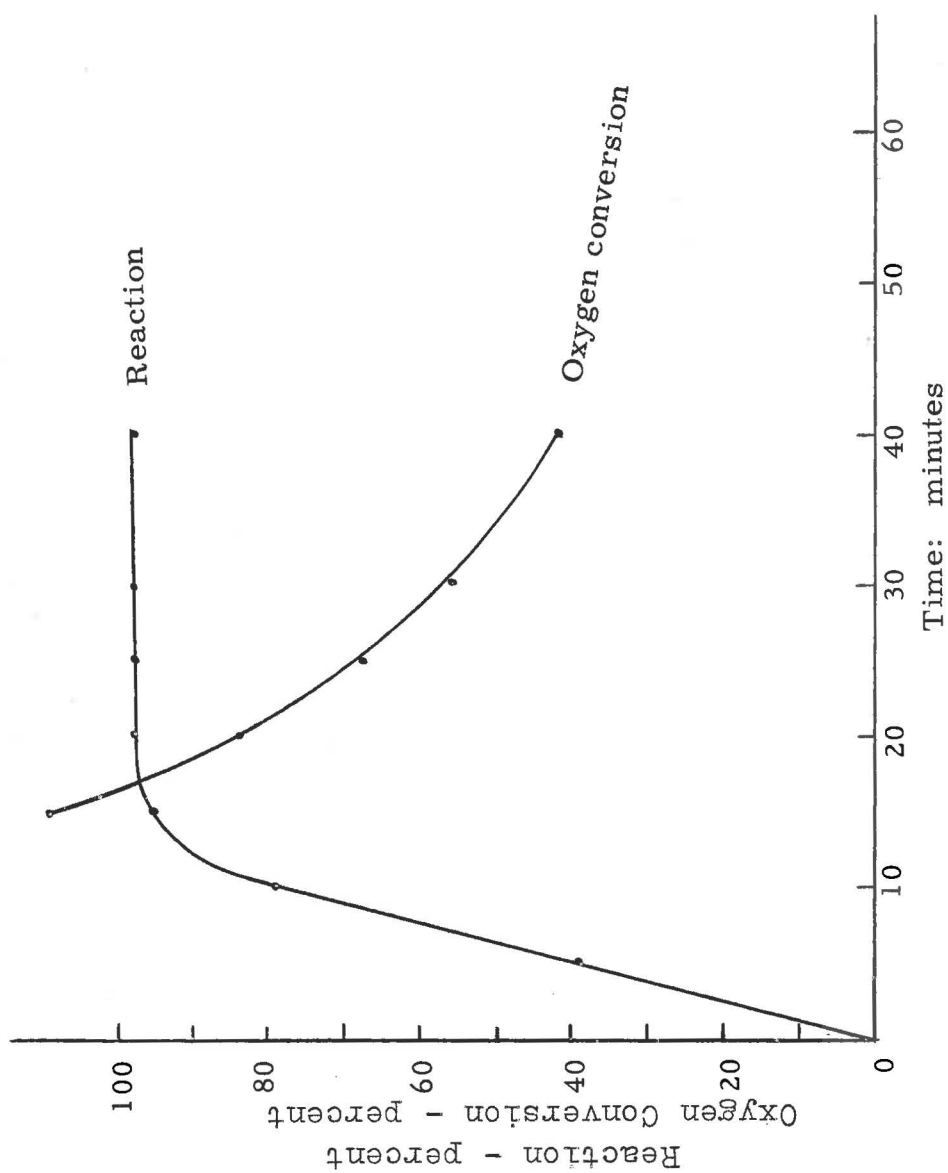
APPENDIX VI   Table 4.

Fluidised Bed Oxidation Test No. 4.

Material: Stradbroke Island Ilmenite.

Charge: 1000 gms. (L/D = 1, D = 3").

Air Flow: 0.0095 gms./sq. in./sec.

Temperarure: $1000^{\circ}C$.

Time minutes	FeO percent	Reaction percent	Oxygen Used percent
0	29.7	—	—
5	23.2	21.3	149.7
10	16.6	43.3	152.2
20	4.75	83.6	146.9
30	1.81	93.7	109.8
45	0.42	98.5	76.9
60	0.19	99.3	58.2
75	0.06	99.8	46.8
90	nil	100.0	39.1

APPENDIX VI   Figure 4.

Fluidised Bed Oxidation Test No. 4.

APPENDIX VI   Table 5.
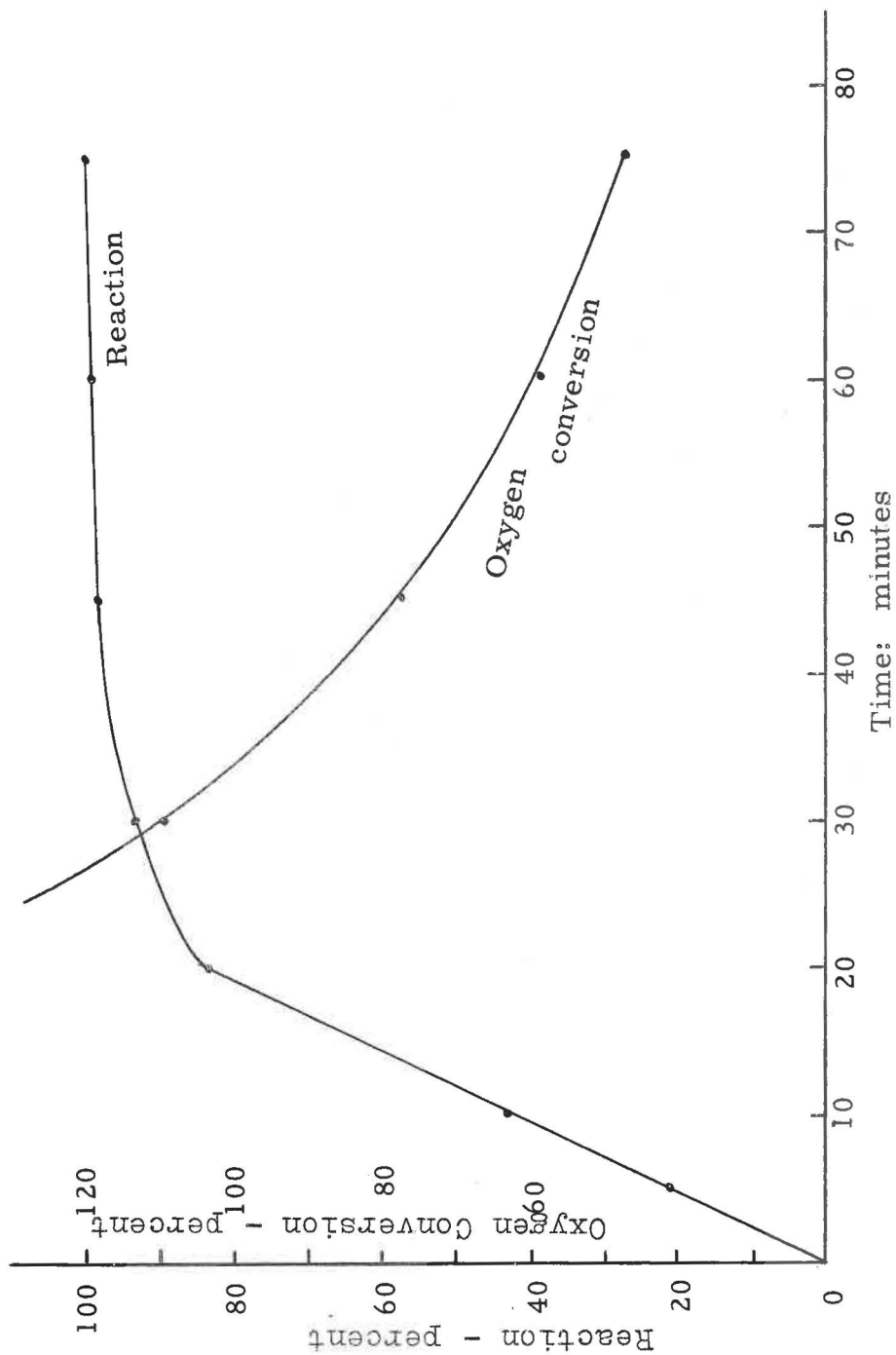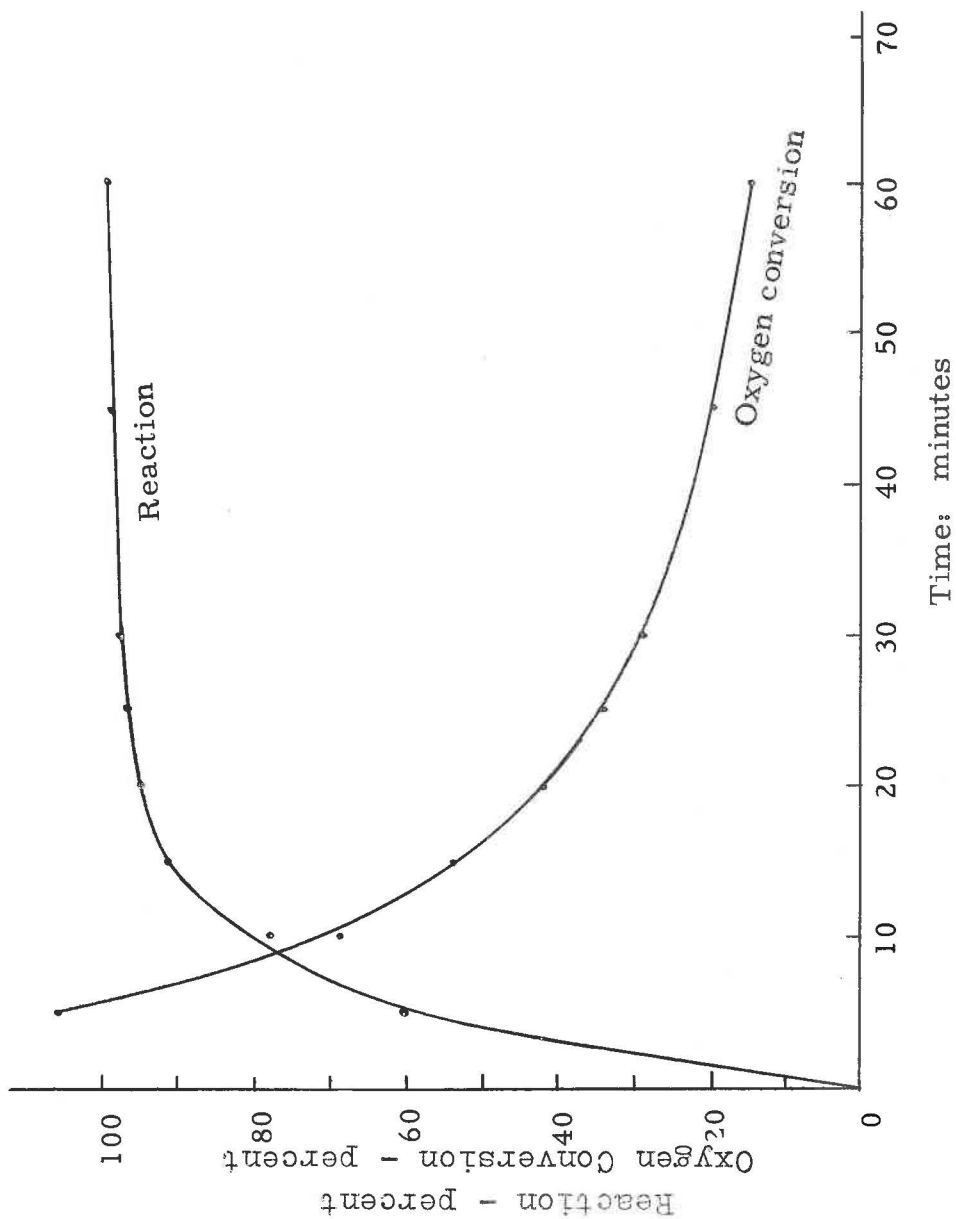
Fluidised Bed Oxidation Test No. 5.

Material: Stradbroke Island Ilmenite.
Charge: 1000 gms. (L/D = 1, D = 3").
Air Flow: 0.0382 gms./sq. in./sec.
Temperature: 1000°C.

Time minutes	FeO percent	Reaction percent	Oxygen Used percent
0	29.8	—	—
5	11.7	60.0	105.8
10	6.55	77.5	68.3
15	2.60	91.0	53.5
20	1.61	94.4	41.6
25	1.14	96.1	33.9
30	0.63	97.8	28.7
45	0.39	98.6	19.3
60	0.11	99.6	14.6

APPENDIX VI   Figure 5.

Fluidised Bed Oxidation Test No. 5.

APPENDIX VII Table 1.

Fluidised Bed Chlorination Test No. 1.

Material: Oxidised Stradbroke Island Ilmenite.

Charge: 725 gms. (L/D = 1, D = 2.75").

Chlorine Flow: 0.0475 gms./sq. in./sec.

Temperature: $1000^{o}C.$

Time minutes	Fe_2O_3 percent	Reaction percent	Chlorine Used percent
0	46.6	–	–
7.5	45.6	4.0	15.5
15	44.8	6.9	13.4
30	42.9	14.0	13.5
45	40.5	22.0	14.2
60	38.4	28.5	13.8
80	34.2	40.5	14.7
100	32.8	43.0	12.5
120	29.9	51.1	12.4
150	26.1	59.6	11.6
180	22.9	66.0	10.7
240	16.6	77.2	9.3
300	11.8	84.7	8.2

APPENDIX VII   Figure 1.

Fluidised Bed Chlorination Test No. 1.
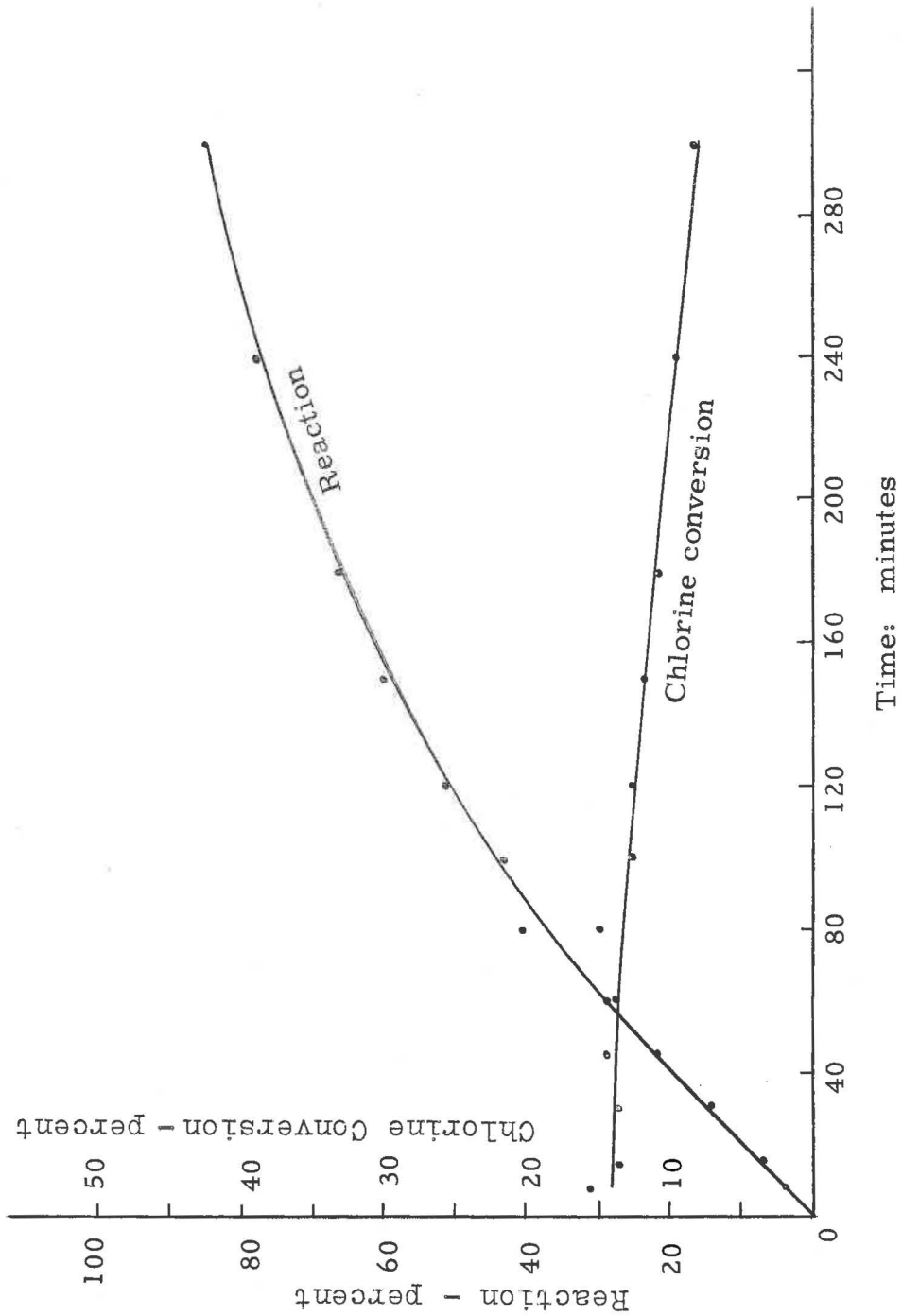
APPENDIX VII   Table 2.

Fluidised Bed Chlorination Test No. 2.

Material: Oxidised Stradbroke Island Ilmenite.

Charge: 725 gms. (L/D = 1, D = 2.75").

Chlorine Flow: 0.0468 gms./sq. in./sec.

Temperature: $1050^{O}C$.

Time minutes	Fe_2O_3 percent	Reaction percent	Chlorine Used percent
0	46.8	–	–
7.5	45.4	5.6	22.1
15	44.2	10.0	19.7
30	40.6	22.2	21.9
45	36.2	35.5	23.3
60	32.3	45.8	22.6
80	26.7	58.6	21.7
100	22.4	67.3	19.9
120	19.8	72.0	17.7
150	14.6	80.6	15.9
180	9.7	87.8	14.4
210	5.5	93.4	13.2
240	2.2	97.4	12.0
270	0.10	99.9	11.0

APPENDIX VII Figure 2.

Fluidised Bed Chlorination Test No. 2.

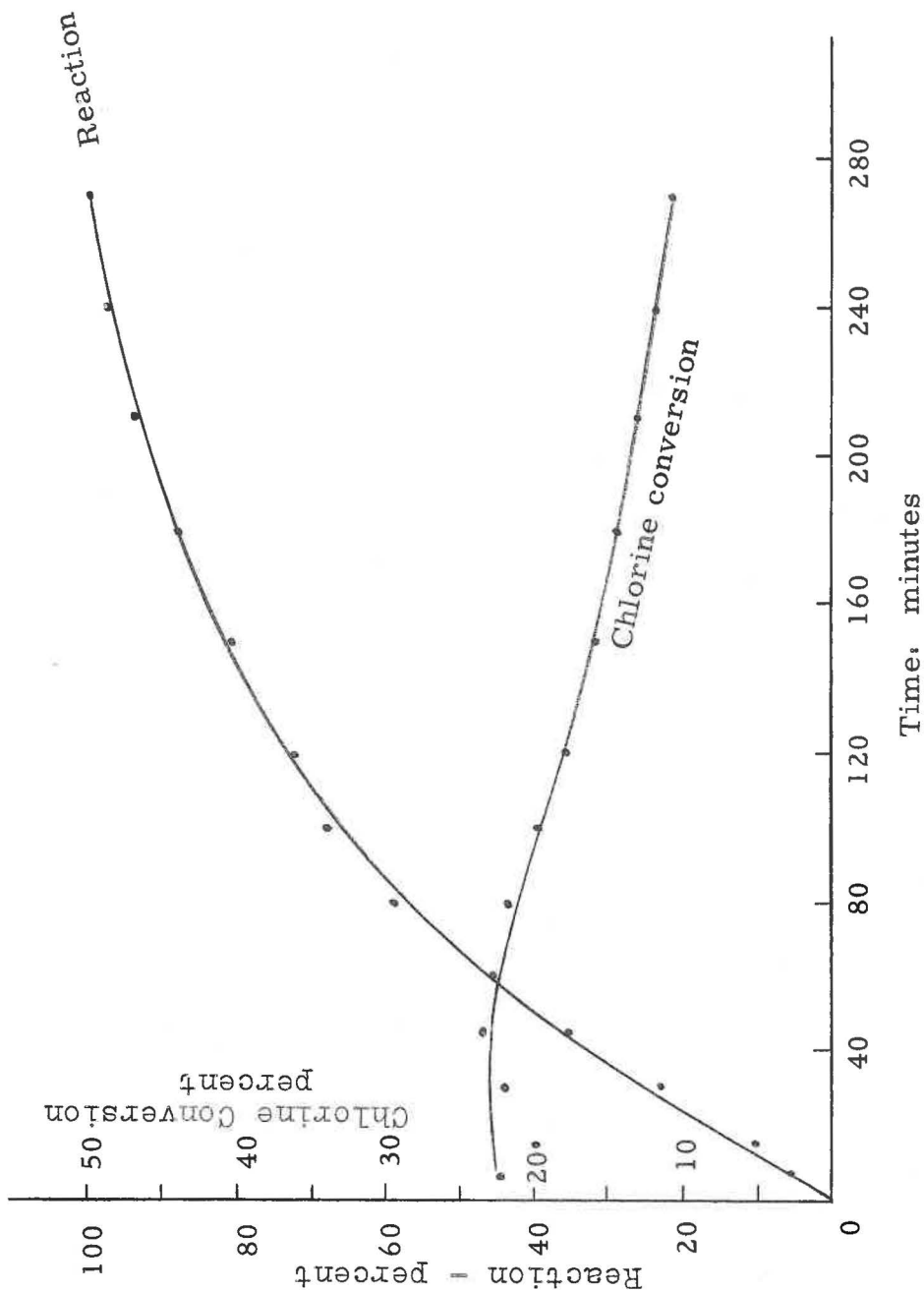## APPENDIX Vll Table 3.

Fluidised Bed Chlorination Test No. 3.

Material: Oxidised Stradbroke Island Ilmenite.

Charge: 725 gms. (L/D = 1, D = 2.75").

Chlorine Flow: 0.0468 gms./sq. in./sec.

Temperature: 1100°C.

Time minutes	Fe_2O_3 percent	Reaction percent	Chlorine Used percent
0	46.7		
7.5	44.9	7.1	27.9
15	43.0	14.0	27.5
30	37.7	30.9	30.4
45	33.4	42.8	28.0
60	28.3	54.9	27.0
80	22.1	67.6	24.9
100	17.4	75.9	22.4
120	12.7	83.3	20.5
150	5.4	93.5	18.4
180	0.19	99.8	16.4
210	0.03	99.97	14.0
240	0.02	99.98	12.3
300	0.01	99.99	9.8

APPENDIX VII   Figure 3.

Fluidised Bed Chlorination Test No. 3.

APPENDIX Vll Table 4.

Fluidised Bed Chlorination Test No. 4.

Material: Oxidised Stradbroke Island Ilmenite.
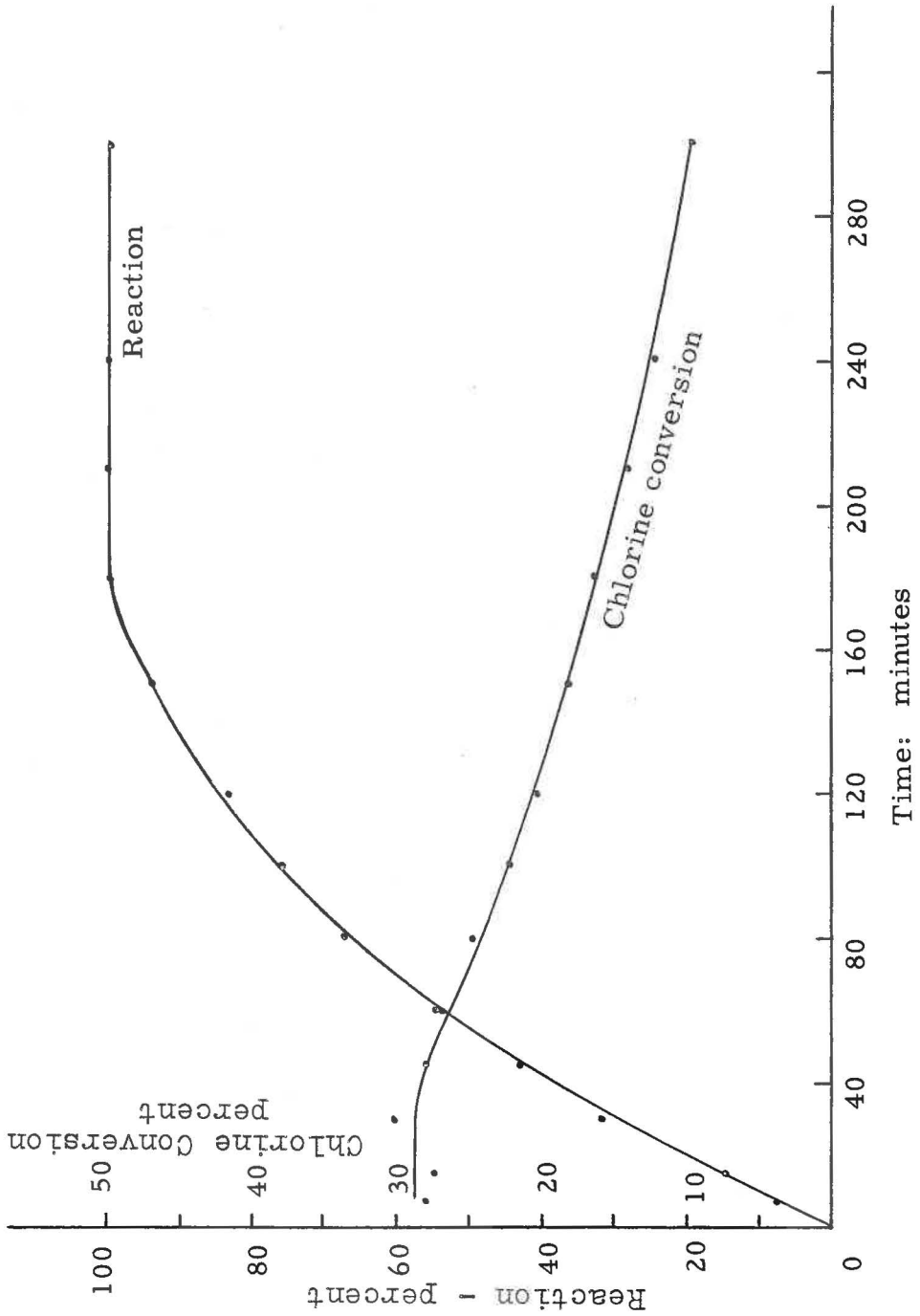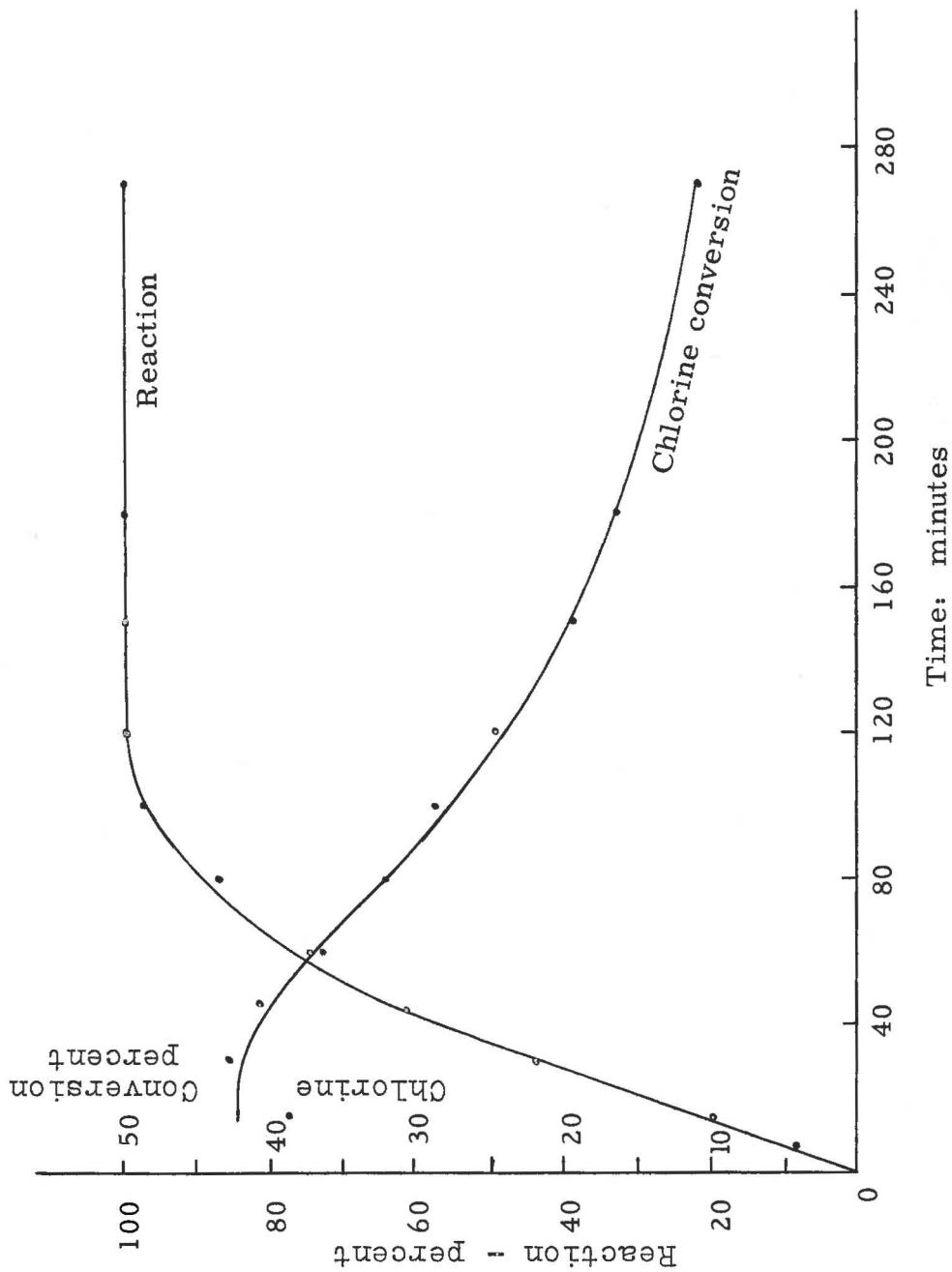
Charge: 725 gms. (L/D = 1, D = 2.75").

Chlorine Flow: 0.0468 Gms./sq. in./sec.

Temperature: 1150°C.

Time minutes	Fe_2O_3 percent	Reaction percent	Chlorine Used percent
0	46.7		
7.5	44.5	8.5	33.4
15	41.3	19.7	38.7
30	33.1	43.5	42.8
45	25.0	62.0	40.6
60	18.4	74.3	36.7
80	10.2	87.0	32.1
100	2.4	97.2	28.7
120	0.2	99.8	24.6
150	0.03	99.97	19.7
180	0.01	99.99	16.4
270	0.01	99.99	10.9

APPENDIX VII   Figure 4.

Fluidised Bed Chlorination Test No. 4.

APPENDIX Vll Table 5.

Fluidised Bed Chlorination Test No. 5.

Material:	Oxidised Stradbroke Island Ilmenite.
Charge:	725 gms. (L/D = 1, D = 2.75").
Chlorine Flow:	0.0465 gms./sq. in./sec.
Temperature:	1175°C.

Time minutes	Fe_2O_3 percent	Reaction percent	Chlorine Used percent
0	46.7		
7.5	43.2	13.4	53.0
15	40.3	23.0	45.5
30	30.2	50.7	50.2
44	20.2	71.1	48.0

APPENDIX VII   Figure 5.

Fluidised Bed Chlorination Test No. 5.
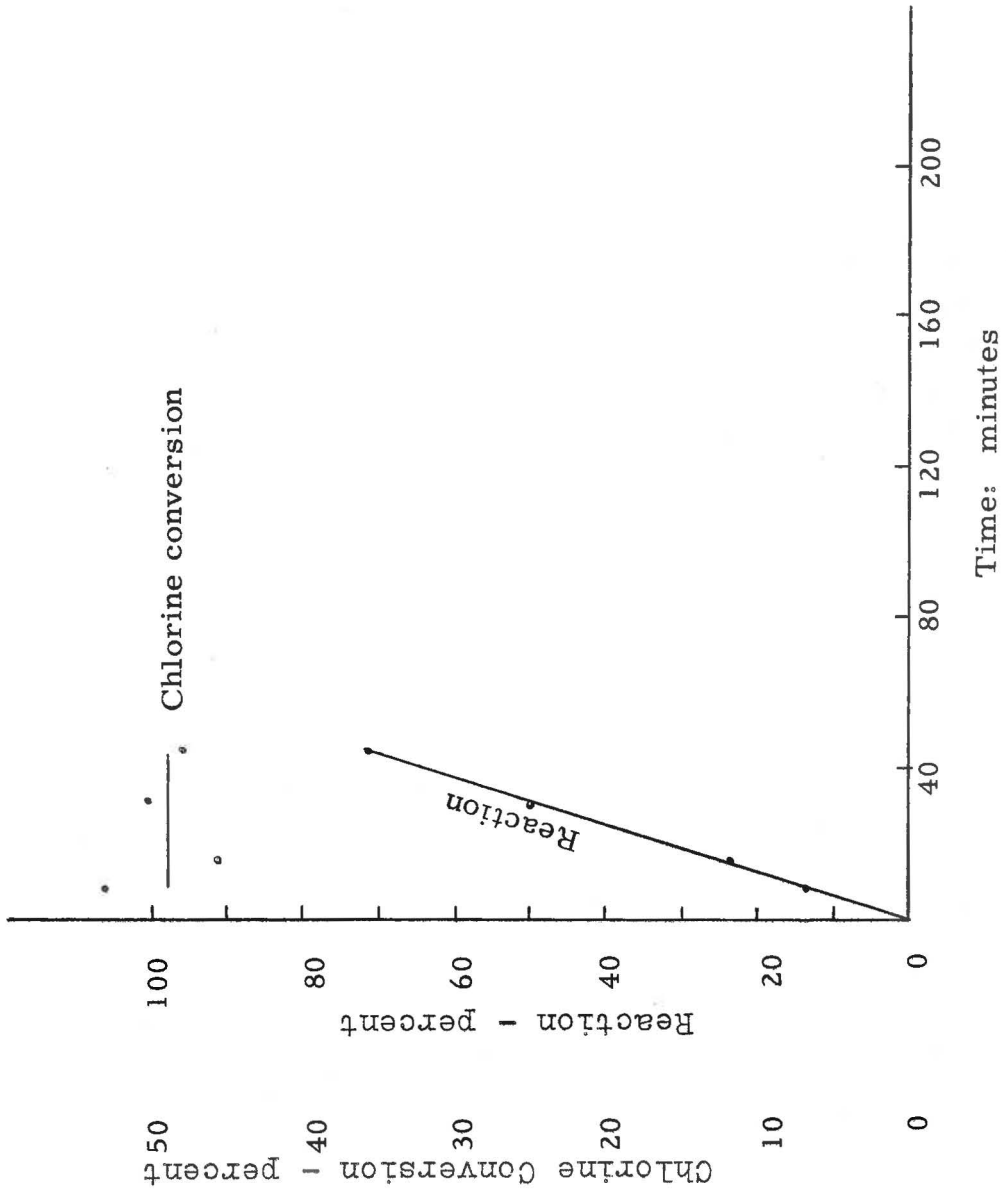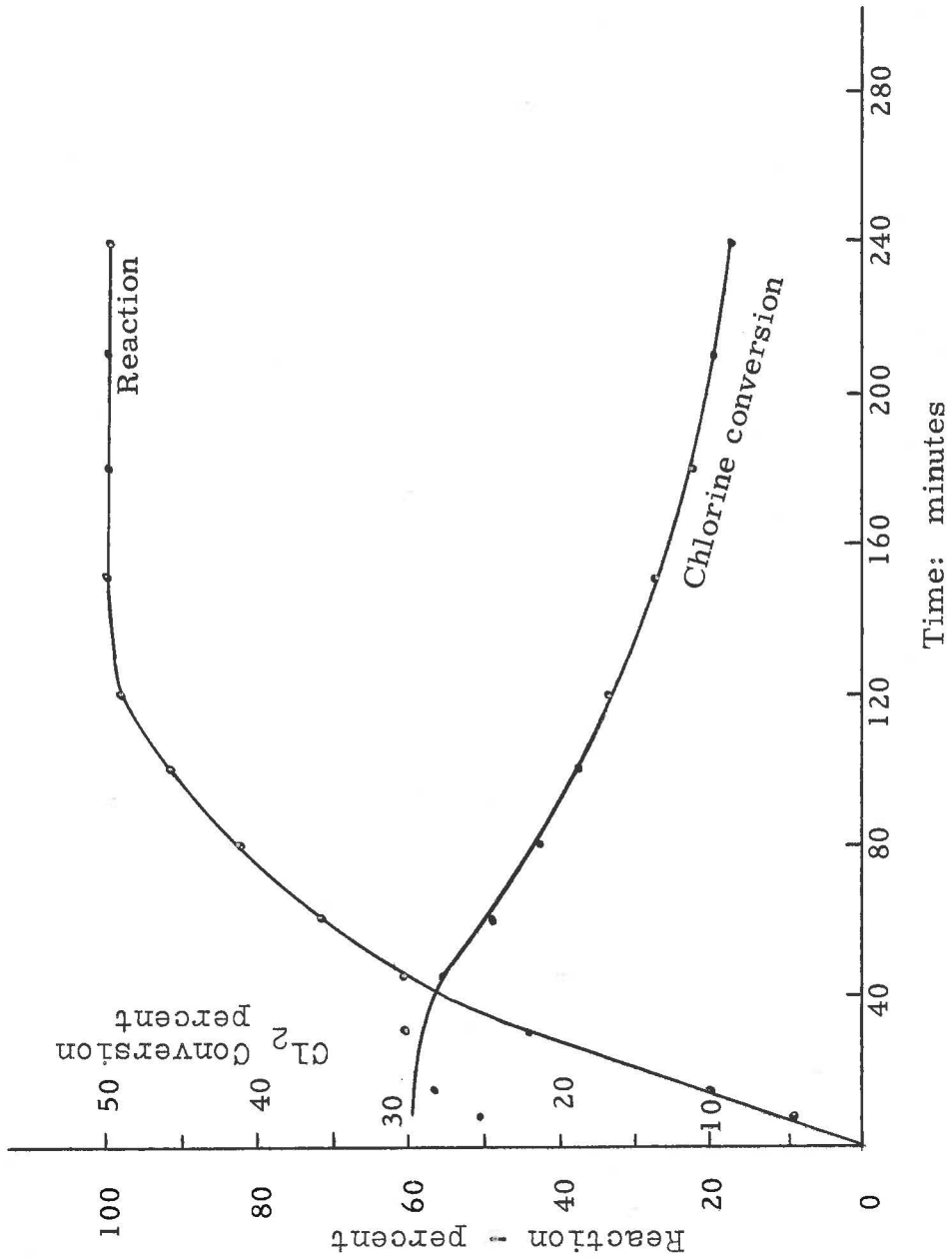
201.

APPENDIX V11 Table 6.

Fluidised Bed Chlorination Test No. 6.

Material: Oxidised Stradbroke Island Ilmenite.

Charge: 725 gms. (L/D = 1, D = 2.75).

Chlorine Flow: 0.0676 Gms./sq. in./sec.

Temperature: $1100^{o}C$.

Time minutes	Fe_2O_3 percent	Reaction percent	Chlorine Used. percent
0	47.0		
7.5	44.6	9.2	25.3
15	41.3	20.6	28.3
30	33.1	44.2	30.3
45	25.8	60.7	27.8
60	20.2	71.5	24.6
80	13.3	82.7	21.3
100	7.2	91.2	18.8
120	1.4	98.4	16.9
150	0.06	99.93	13.7
180	0.04	99.95	11.4
210	0.04	99.95	9.8
240	0.03	99.97	8.6

APPENDIX VII   Figure 6.

Fluidised Bed Chlorination Test No. 6.

APPENDIX Vll Table 7.

Fluidised Bed Chlorination Test No. 7.

Material: Oxidised Stradbroke Island Ilmenite.

Charge: 1450 gms. (L/D = 2, D = 2.75").

Chlorine Flow: 0.0473 gms./sq. in./sec.

Temperature: 1100°C.

Time	Fe_2O_3	Reaction	Chlorine Used.
minutes	percent	percent	percent
0	46.9		
7.5	46.2	2.8	21.8
15	45.6	5.0	19.5
30	43.2	13.9	27.1
45	40.5	22.8	29.7
60	38.1	30.4	29.7
80	34.1	41.3	30.2
100	29.4	52.8	30.9
120	22.9	66.4	32.3
150	17.9	75.3	29.4
180	12.6	83.7	27.2
240	6.5	92.1	22.4
270	3.7	95.6	20.8
300	0.73	99.2	19.3

APPENDIX VII   Figure 7.

Fluidised Bed Chlorination Test No. 7.