RB698

RESEARCH FOR INDUSTRY

THE AUSTRALIAN MINERAL DEVELOPMENT LABORATORIES

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Please quote this reference in your reply:

1/1/12

30th August, 1963

The Director,
Department of Mines,
169 Rundle Street,
ADELAIDE.

Dear Sir,

We are transmitting to you ten copies of AMDL Report 268 entitled "The Chlorination of Ilmenite – Reaction Kinetics and Reactor Design", dated August, 1963.

The report is complementary to the first report on this project, AMDL Report 243. It describes experimental work and considerations of the results and their implications as they affect the design of the chlorination reactor.

As a result of these considerations we have recommended that further investigation of the project should be suspended. It appears at this stage that there is no method of design which would meet both the practical and economic requirements for the process. It is possible that new materials, new techniques or a change in the economic climate could justify reopening the investigation at a future date, as all of the experimental work has demonstrated that the chemistry of the process is well founded.

Yours faithfully,

L. Wallace Coffer

L. Wallace Coffer
Director.

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AMDL Report 268
August, 1963
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CHLORINATION OF ILMENITE
Reaction Kinetics and Reactor Design

by

I. B. Ketteridge

to

SOUTH AUSTRALIAN GOVERNMENT
DEPARTMENT OF MINES

Investigated by: Industrial Chemistry Section
Officer in Charge: F.R. Hartley

THE AUSTRALIAN MINERAL DEVELOPMENT LABORATORIES
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ABSTRACT

This report is an account of work carried out as part of an investigation of a process for extracting titanium dioxide from ilmenite sands.

The process makes use of reaction between chlorine and oxidised ilmenite to produce ferric oxide and titanium dioxide as separate products of high purity.

Details are given of experiments carried out to measure rates at which chlorine reacts with oxidised ilmenite and of the application of the data to the preliminary design of a large scale chlorination reactor.

1. INTRODUCTION

The process which was the subject of this investigation comprised a sequence of three chemical reactions.

Ilmenite is first oxidised with air at high temperature to convert ferrous oxide to ferric oxide according to reaction (1)

$$4FeO.TiO_2 + O_2 \rightleftharpoons 2Fe_2O_3.TiO_2 + 2TiO_2 \quad \ldots\ldots\ldots\ldots \quad (1)$$

The oxidised ilmenite is treated with chlorine to remove the iron as volatile ferric chloride and leave a solid titanium dioxide residue.

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

The ferric chloride and oxygen produced in the chlorination reaction are cooled to a suitable temperature, whereby ferric oxide is deposited and chlorine is released for return to the chlorination stage.

$$4FeCl_3 + 3O_2 \rightleftharpoons 2Fe_2O_3 + 6\,Cl_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Fluidised bed reactors were selected for both the oxidation and chlorination reactions. The main considerations which led to this choice were:

i. the particle size distribution of beach sand ilmenites was suitable for fluidisation,

ii. the particles did not appear to break up during either reaction,

iii. good contact could be obtained between reacting solids and gases, and

iv. fluidised bed reactors, having no moving parts, might fairly readily be constructed in suitable heat and corrosion resistant materials.

For the successful operation of the process, both the oxidation of ilmenite and the chlorination of oxidised ilmenite must be substantially complete.

Oxidation of ilmenite must approach completion to reduce the addition of pure oxygen to the cyclic system to an economic minimum. At this stage the optimum grade of product from the oxidation reaction cannot be predicted.

Chlorination must be sufficiently complete to reduce the ferric oxide content of oxidised ilmenite from about 50 per cent to below 0.5 per cent which is the market specification for mineral rutile. The titania product must therefore be at least 99.5 per cent reacted.

Fluidised bed reactors are extensively used in the petroleum industry for catalytic vapour phase reactions and they are in limited use in various chemical industries for drying, roasting and calcining operations (Anon.[1] 1954, Anon[2] 1958, Anon[3] 1962, Kite and Roberts 1947, Labine 1960 White and Kinsella 1952)(a).

(a) All references are listed in Section 10 "Literature References".

Fluidised bed reactors have not until now been used to produce the degree of reaction in the solid products required in this process. A survey of available literature has disclosed no suitable method of reactor design. Consequently a mathematical analysis of fluidised bed reactor systems has been undertaken and a scheme for reactor design has been devised and has been reported elsewhere (Ketteridge, 1962).

Experimental work, subsequently carried out to determine the rate at which the chlorination reaction proceeds, forms the subject of this report. Reaction rate data have been correlated with significant variables and the resulting relationships used in preliminary designs for large scale fluidised bed chlorination reactors.

2. SUMMARY

The possibility of chlorinating oxidised ilmenite in a fluidised bed reactor has been demonstrated.

Precautions were necessary to prevent the fluidised bed from sintering and to prevent entrainment in the gas stream of rutile produced during chlorination.

It was found that 1100°C was a suitable chlorination temperature and that chlorine gas flows of between 8 and 12 times the minimum fluidising velocity at this temperature prevented sintering without causing significant losses by entrainment.

At 1100°C, the maximum conversion of chlorine to ferric chloride to be expected in a continuously fed system was shown to be about 40 per cent. At higher temperatures this value would be greater, but the tendency to sinter also would increase. The maximum temperature was therefore limited to 1100°C.

Chlorination experiments with different chlorine flow rates and different bed depths showed that an increased gas velocity increased the rate of reaction but reduced the chlorine conversion. However, longer contact time between chlorination gas and fluidised solids in deeper beds increased chlorine conversion. Both reaction rate and chlorine conversion could be increased by using higher chlorine flow rates, up to the limit of 12 times the minimum fluidising velocity, and by using deep fluidised beds to compensate for the high flow rates of chlorine.

A series of tests was performed which showed that, within the size range of the ilmenite tested, the influence of particle size upon the rate of chlorination was not great. The error introduced by assuming that the feed was composed of uniform average sized particles was not significant.

Chlorination experiments conducted with mixtures of oxidised ilmenite and chlorinated product have shown that the reaction rate increased as the proportion of ilmenite in the charge decreased, but this effect was accompanied by a decline in the percentage of chlorine utilized.

The data from these experiments have been correlated on an empirical basis. The correlation has been used to predict both the extent of reaction in small, continuously fed, fluidised bed reactors and also the resulting chlorine conversion.

Experiments were then conducted with a 2-stage, fluidised bed reactor, the bottom stage of which was fed continuously with oxidised ilmenite and chlorine while the top stage contained a batch charge of oxidised ilmenite which was treated with the gaseous chlorination products from the bottom stage. The influence of chlorination gas composition on the rate of reaction was thereby studied.

The chlorine conversions predicted for various flow rates in the bottom stage were confirmed. The variability in the composition of these gaseous products in the early stages of continuous chlorination tests is discussed and the necessity for ensuring a steady value for chlorine conversion in the lower stage has been demonstrated.

Finally, data from the chlorination tests with variable chlorination gas compositions have been correlated. An approximate correlation has been accepted in order to simplify the relationship and so reduce the magnitude of subsequent design calculations.

On the basis of data gained in small scale fluidised bed experiments, preliminary design calculations for industrial scale reactors have been performed.

These calculations showed that the hold-up of oxidised ilmenite in a fluidised bed reactor could be markedly reduced by increasing the number of stages from 1 to 3.

Multiple stage reactors have been considered with the stages arranged horizontally or vertically.

In order to retain a practicable depth of fluidised bed, no more than two stages were shown to be necessary in the chlorination reactor. The best arrangement appeared to be a horizontally arranged 2-stage reactor with the first stage about 20 times larger than the second.

Finally the necessary rates of heat transfer to the reactor to supply the heat consumed by the endothermic chlorination reaction have been calculated.

Two methods of supplying the heat have been considered.

The first has been the construction of a fluidised bed reactor with a combustion chamber around the outside. In view of the high reaction temperature and of the corrosive nature of the chlorination gases, construction of a suitable impervious reactor would be difficult. The temperature differential necessary to transfer sufficient heat through the walls of such a reactor is so great that the system is not practicable.

The alternative method considered was to withdraw solids from the fluidised bed continuously, superheat the stream of partially reacted material and return it to the chlorination reactor. Withdrawal of material from and return of superheated material to the chlorination reactor, at the temperatures required through gas-tight seals, would not be simple. The recirculating load necessary to transfer sufficient heat by this means would be of the order of 10 times the feed rate.

The conclusion was that there is no practical method of supplying heat to a chlorinator of significantly large capacity.

Further chlorination experiments with large scale equipment are therefore not justified.

3. MATERIAL EXAMINED

The ilmenite came from dune deposits on Stradbroke Island, Queensland. The sample as received, was contaminated with silicates and was cleaned by magnetic separation with a cross-belt magnetic separator. The concentrate produced had the following chemical composition and particle size distribution:

Chemical Analysis

	%
Ferrous oxide	31.6
Ferric oxide	14.4
Titanium dioxide	50.1
Chromic oxide	0.18

Screen Analysis

Mesh BSS	%
+ 52	0.7
- 52 + 72	2.2
- 72 + 100	23.9
- 100 + 150	53.4
- 150 + 200	18.8
- 200	1.0
	100.0

Specific Gravity

Material	4.7
Bulk	2.5

4. ANCILLARY MATERIALS

The chlorine used in these experiments was commercial grade liquid chlorine purchased in steel cylinders. The commercial gas was reported to contain in excess of 99.9 per cent chlorine on a volumetric basis.

5. EQUIPMENT

Two types of fluidised bed reactor were used for this work. Both were constructed from lengths of 3-inch nominal bore silica tubing.

One was a single stage reactor used for chlorination of batch charges of oxidised ilmenite. The other was a 2-stage reactor in which oxidised ilmenite in the bottom stage was continuously fed and discharged while a batch charge was treated in the top.

The reactors are illustrated diagrammatically in Figures A-1 and A-2 of Appendix A.

A gas fired cylindrical furnace was used to heat the single stage reactors. Two oil fired furnaces, one above the other, were used for heating the 2-stage reactors.

The reactors, the gas and oil fired furnaces and such ancillary equipment as chlorine supply and metering equipment, screw feeders, rotary pressure seals and reactor discharging equipment have been described in detail by Nordin (1961).

6. EXPERIMENTAL PROCEDURES AND RESULTS

The techniques used in these experiments have also been described in detail by Nordin (1961) and only a brief outline is reported here.

Oxidised ilmenite was prepared by fluidising ilmenite with air at 1000°C. Charges of 1000 grams were fluidised in a 3-inch diameter reactor with an air flow of 0.019 grams per square inch of cross section per second for periods in excess of 2 hours, under which conditions the ilmenite was completely oxidised.

Chlorination tests were conducted with oxidised ilmenite. Weighed charges were fluidised with air and brought up to temperature before changing the fluidising gas to chlorine and commencing the tests.

Small samples were drawn from the fluidised bed at timed intervals and assayed for iron content, thereby providing a means of following the course of the chlorination reaction.

The degree of reaction of a charge of oxidised ilmenite, used as a measure of the progress of the reaction, is defined as the mass of iron oxide which has been removed by reaction with chlorine expressed as a fraction of the iron oxide content of the original charge.

This factor was calculated taking into account the loss in weight of the charge as the test proceeded.

let a = initial concentration Fe_2O_3 (a)
b = initial concentration TiO_2 (b)
at = concentration of Fe_2O_3 at time "t"
x = mass of Fe_2O_3 per unit mass of original charge chlorinated in time "t"

Chlorination of unit mass (a + b = 1) of charge for time "t" leaves a residue containing

Fe_2O_3	a - x
FeO_2	b
Sum	1 - x

(a) Concentration is expressed as mass fraction.

(b) For the purpose of this calculation, the concentration of TiO_2 is taken to include all materials other than Fe_2O_3.

Concentration of ferric oxide at time "t" is therefore

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

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 reaction (2) from the mass flow of chlorine, the mass of charge, the initial concentration of ferric oxide and the degree of reaction.

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

The results of chlorination tests carried out by this procedure are given in Appendix B, Tables B-1 to B-20 and Figures B-1 to B-20.

In order to examine the influence of chlorination gas composition on the rate of chlorination, a short series of tests was carried out with the 2-stage fluidised bed chlorination reactor illustrated in Appendix A Figure A-2. The bottom stage of the reactor was continuously fed at controlled flow rates with oxidised ilmenite and the chlorinated product was continuously removed. Chlorine gas was fed to the bottom stage and the chlorination gases produced passed upwards to fluidise and react with a batch charge of oxidised ilmenite in the upper stage. By regulating the rate at which oxidised ilmenite was fed to the bottom stage, and maintaining the chlorine flow rate at a constant level, the composition of the chlorination gases produced in the bottom stage could be controlled. Details of the techniques adopted in these experiments have been described by Nordin (1961).

The degree of reaction of the solids in the bottom stage was determined by comparing the chemical analysis of the oxidised ilmenite feed with that of the chlorinated product. The composition of the chlorination gases produced in the bottom stage was then calculated in accordance with reaction (2) from the feed rates of chlorine and of oxidised ilmenite and from the extent of reaction of the oxidised ilmenite.

The degree of reaction in the top stage was calculated in the same manner as previously for experiments with the single stage reactor.

The results for these experiments are presented in Tables B-21 to B-24 and in Figures B-21 to B-24 in Appendix B.

7. DISCUSSION OF RESULTS

Experiment had shown that a rising air velocity of about 1.3 inches per second was necessary at room temperature to fluidise the ilmenite sands used in this work.

Leva et al (1951) obtained an expression for calculating the minimum gas velocity necessary to fluidise a granular solid. For a particular granular solid, this expression may be reduced to the following proportional relationship.

$G_{mf} \; : \; d/u$

where G_{mf} = minimum mass flow of gas for fluidisation

d = gas density

u = gas viscosity

Values for the density and viscosity of air at room temperature are available from Hinselrath et al (1955) and similar data for chlorine are available from Perry (1950). The minimum fluidising velocity of room temperature for chlorine can therefore be calculated.

To estimate the minimum fluidising velocity at high temperatures, the density for chlorine has been calculated assuming that chlorine behaves as a perfect gas and the viscosity has been calculated with a value for the Sutherland constant taken from Perry (1950).

The following expression was obtained:

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

where T = degrees Kelvin

Fluidised beds of oxidised ilmenite tended to sinter at high temperatures. For this reason the minimum fluidising gas velocity could not be measured at high temperatures in order to check the above expression.

The tendency for oxidised ilmenite to sinter at high temperatures was most noticeable at the beginning of a chlorination test and decreased as the test proceeded. Fully chlorinated material did not sinter. However, as chlorination proceeded, removal of iron oxide, which comprised about 50 per cent of the material, caused a reduction in the density of the solid particles. The susceptibility to breakage by attritioning and to consequent dust formation therefore increased. Increased losses by entrainment in the gas stream then followed.

A chlorine flow rate of between 8 and 12 times the minimum fluidising gas flow rate calculated by the above formula was a suitable fluidising gas flow. This gas flow rate effectively prevented sintering without causing excessive dust losses.

A series of five chlorination tests was performed to determine the influence of temperature on the rate of chlorination.

Temperatures ranged from 1000°C to 1175°C. All five tests were carried out in $2\frac{3}{4}$-inch diameter fluidised bed reactors with 725 gram charges of oxidised ilmenite to give a unit ratio of bed depth to bed diameter. Chlorine flow rates were maintained at 0.043 gram per square inch per second, about eight times the calculated minimum fluidising mass 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 85 per cent complete. In the initial stages of the test, chlorine utilization was about 15 per cent, and 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 270 minutes. In this test the characteristic decrease in the reaction rate as the test proceeded was more apparent than with the first test. Chlorine conversion was initially about 22 per cent and decreased to about 11 per cent when the reaction approached completion.

Test No. 3 at 1100°C showed an even faster reaction rate, reaching 99.8 per cent reaction in 180 minutes. The initial and final conversions of chlorine were approximately 29 and 16 per cent.

Test No. 4 at 1150°C had a greater reaction rate, reacting to 99.8 per cent in 120 minutes. The initial chlorine utilization was about 40 per cent and decreased to approximately 25 per cent on completion.

Repeated attempts to conduct chlorination tests at temperatures higher than 1150°C were unsuccessful. Test No. 5 at 1175°C commenced with a rapid reaction rate and high chlorine utilization. However the fluidised bed sintered into a solid mass after 40 minutes and the test could not be continued. Other attempts at 1175°C and 1200°C ended in the same way.

In general the higher the chlorination temperature the greater the utilization of chlorine. However the maximum temperature at which chlorination was practicable in a fluidised bed was limited by the tendency of the material to sinter. It was also desirable from the viewpoint of heat economy and of finding suitable materials of construction to operate the reactor at as low a temperature as possible.

Assessment of all the factors influencing the selection of a suitable chlorination temperature is not possible at this stage, so that 1100°C has been tentatively selected as the most suitable temperature.

Further chlorination tests were then conducted at 1100°C to determine the influence of chlorine flow rate upon the rate of reaction.

Test No. 6 was carried out under similar conditions to Test No. 3 except that the chlorine flow rate was increased to 0.0620 grams per square inch per second or about 12 times the calculated minimum fluidising velocity. This rate was approximately the limit beyond which gas flow could not be increased without causing excessive entrainment loss.

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

Chlorine conversion was about the same in the initial stages of both tests, but it decreased a little more rapidly with the high chlorine flow rate, being about 14 per cent at completion compared with 16 per cent for Test No. 3.

The chlorine flow could not be reduced much below the level of Test No. 3 without at least 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 a fluidising gas consisting of a mixture of chlorine and nitrogen.

The chlorine flow was reduced to about 40 per cent and the nitrogen flow was about 50 per cent of the chlorine flow for Test No. 3.

The gaseous volume change which accompanied the chlorination reaction was small so that dilution of chlorine with an inert gas had relatively little effect on the equilibrium composition of the gaseous chlorination mixture.

The reaction rate was slow, some 330 minutes being required for reaction compared to 180 minutes for Test No. 3. Initially chlorine conversion was high, 35 per cent, and decreased to 21 per cent at completion compared with 28 per cent and 16 per cent respectively for Test No. 3.

A further test, No. 8, was carried out under conditions similar to Test No. 3 but with 1450 grams, twice the charge of oxidised ilmenite. 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, 28 per cent, but did not decrease as rapidly. At completion of the reaction, the conversion of chlorine had fallen to 19.4 per cent compared to 16.4 per cent for Test No. 3.

Results of Test No. 8 are not strictly comparable with those of Tests 3 and 6 as the charge of oxidised ilmenite had been doubled and the chlorine flow had remained unaltered. However, the type of fluidisation would not have been much affected by the increased bed depth. Although the gas bubbles rising through the bed might have been larger in this case, the chlorination was probably unaffected.

The conclusions from these tests were that an increase of the gas velocity increased the rate of reaction but reduced the chlorine utilization slightly. However, longer contact time between gas and solids with deeper beds increased the chlorine utilization. Reaction rate and chlorine utilization were both increased by using higher gas flows and deeper beds.

The extent to which gas flow could be increased was limited by the accompanying increase in entrainment losses.

The extent to which bed depth can be increased and improve reaction rate and chlorine utilization is not known. There is a limit on how far this can profitably be carried because increased depth increases the pressure loss incurred by the fluidising gas in passing through the bed.

Further tests were performed to examine the influence of particle size on the rate of chlorination.

Tests were conducted in 3-inch diameter fluidised bed reactors, in place of the previous 2¾-inch reactors, and with 1000 gram charges to maintain the ratio of unity between bed depth and diameter.

Two chlorination tests, 9 and 10, were carried out with charges of unsized oxidised ilmenite to provide a basis of comparison for subsequent tests. Both were conducted with chlorine flows of 0.0344 grams per square inch per second. The results for these tests, Tables B-9 and B-10 and Figures B-9 and B-10, are very similar.

Test No. 11 was carried out under similar conditions except that the charge of oxidised ilmenite was a screen fraction of the size range minus 52- plus 72-mesh (BSS). The result was a slightly lower rate of chlorination and a correspondingly lower chlorine utilization at completion. Initially the chlorine utilization was the same as for Tests 9 and 10, but it decreased more rapidly, presumably as a result of the lower surface area of the charge and correspondingly greater thickness of reacted product formed on the surface as the test proceeded.

Chlorination Test No. 12 was similar except that the size fraction minus 150- plus 200-mesh (BSS) was used. The fluidised bed sintered after 80 minutes and no significant results were obtained.

Test No. 13 was similar to No. 12 excepting that the chlorine flow was increased to 0.0383 grams per square inch per second, an increase of about 10 per cent. This charge also sintered after 80 minutes.

The most probable explanation of this phenomenon was that aggregates of fine material, formed during fluidisation, sintered into solid particles, commencing a process which did not cease until the whole bed was sintered. Presumably with unsized ilmenite coarse particles are present in sufficient quantity to prevent or limit the extent of this sintering.

A different technique was therefore tried in an attempt to elucidate the effect of particle size. One kilogram charges of oxidised ilmenite were chlorinated under similar conditions for varying periods of time, the chlorinated products were screened and the various size fractions assayed for iron content. The chlorine flow was held at 0.0441 grams per square inch per second when chlorinating each of six samples, and the chlorination times were chosen to allow samples to be taken at suitable time intervals over a 3-hour period. Results are presented in Table B-14 and Figure B-14. The initial chlorination rate was approximately the same for all size fractions, but the rate fell off more rapidly toward completion of the reaction with coarse particles than with fine. However, no great difference was discernable and no significant error was introduced by ignoring this effect and treating the oxidised ilmenite as if it were composed of uniform size particles.

A series of tests was performed to measure the influence of dilution of ilmenite with chlorinated product upon the chlorination rate.

Firstly two tests were carried out with 1000 gram charges of oxidised ilmenite in a 3-inch diameter reactor with a chlorine flow rate of 0.434 grams per square inch per second. Results for these tests are reported in Tables B-15 and B-16 and Figures B-15 and B-16. In each case 180 minutes was required for 99.5 per cent reaction. Chlorine utilization was initially about 33 per cent and gradually decreased to about 19 per cent at completion.

Chlorination Test No. 17 was then carried out with a charge comprising 75 per cent by volume of oxidised ilmenite and 25 per cent of chlorinated product from a previous test. The weight of the mixed charge was 910 grams, giving a bed depth equal to the diameter.

Reaction was complete in about 120 minutes. Chlorine utilization commenced at about 35 per cent and decreased to 21.5 per cent at completion.

Chlorination Test No. 18 was similar to No. 17 except that the proportion of ilmenite in the charge was reduced to 50 per cent by volume. Reaction was complete in about 100 minutes but chlorine utilizations were lower than with the previous test.

For Tests 19 and 20 charges containing respectively 25 per cent and 12.5 per cent by volume of oxidised ilmenite were used. The periods required for chlorination were successively less and chlorine conversions successively lower, than for previous tests in the series.

No reduction in chlorine conversion occurred when the ilmenite content of the charge was reduced from 100 per cent to 75 per cent by volume. The reaction therefore proceeded at a correspondingly faster rate.

With a charge containing 50 per cent of oxidised ilmenite, the reaction proceeded at a faster rate than for 75 per cent but the chlorine conversion was lower. Further dilution of the charge further reduced the reaction time and also reduced the chlorine conversion.

The final series of tests was conducted in a 2-stage fluidised bed reactor. Chlorine was fed to the bottom stage at the rate of 0.0443 grams per square inch per second. Oxidised ilmenite was continuously fed to the bottom stage and chlorinated product continuously removed at rates which gave chlorine conversions in the bottom stage of approximately 5, 10, 15 and 20 per cent respectively. Charges of 1000 grams of oxidised ilmenite were treated in the top stage with the reaction gases from the bottom stage.

The method by which the feed rates of oxidised ilmenite to the bottom reactor stage were determined in order to produce chlorination gases of the desired compositions is dealt with in a later stage of this report.

Results for the first chlorination test, No. 21, with 5 per cent chlorine conversion in the bottom stage, were very little different from Tests 15 and 16 which were conducted with pure chlorine under comparable conditions. The reaction rate was similar and the overall chlorine conversion was about 5 per cent greater than in the previous tests.

Test 22 with 11 per cent conversion of chlorine in the bottom stage was somewhat slower. Initially the rate of reaction was much the same as for Tests 15, 16 and 21, chlorine conversion being about 33 per cent. However, the rate decreased more rapidly than had previously been the case so that, at completion of the reaction, chlorine conversion had fallen to 14.3 per cent. The total chlorine conversion was about the same as for Test 21.

Test 23 was performed with about 16 per cent conversion in the bottom stage. The reaction rate was markedly slower, 405 minutes being required for 99.5 per cent reaction. Chlorine conversions were lower than previously and reduced to 8 per cent at completion of the reaction. Total chlorine utilization was about the same as for Tests 21 and 22.

Test 24 with 21 per cent conversion in the lower stage was slower still. In 480 minutes reaction was only 85 per cent complete. Gross chlorine conversion was initially about the same as for previous tests in the series but, as the reaction proceeded, decreased to a greater extent than had occurred with the previous tests.

From the results of these tests, it appeared that chlorination with a gaseous mixture, in which about 5 per cent of the chlorine had been converted to ferric chloride with the release of an equivalent quantity of oxygen, proceeded as rapidly as with pure chlorine, at least in fluidised beds of this size. As conversion of chlorine in the bottom stage increased, reaction rate in the upper stage decreased, although the total chlorine conversion remained high. With up to 16 per cent conversion of chlorine in the bottom stage, total chlorine conversion was greater than was obtained when chlorinating with pure chlorine in a single stage. With 20 per cent conversion in the lower stage, total chlorine conversion was greater in the initial stages of reaction than was the case when chlorinating with pure chlorine, but indications were that it might have been less at the completion of the reaction.

Three further chlorination tests were conducted.

A charge comprising 1000 grams of oxidised ilmenite and an equal volume of chlorinated ilmenite from a previous test was chlorinated under conditions similar to those under which 1000 gram charges were treated in Tests 15 and 16. Results are presented in Table B-25 and Figure B-25.

The chlorination rate was faster than for Tests 15 and 16, reaction going to 99.5 per cent completion in 150 minutes compared with 180 minutes, and chlorine conversion was correspondingly higher.

Test 26 was conducted under similar conditions with a 2000 gram charge of oxidised ilmenite. Reaction time was 240 minutes for 99.7 per cent reaction and chlorine conversion was high, being 26.4 per cent at completion. This was about the same as the overall chlorine conversion previously obtained in the 2-stage reactor with 5, 10 and 15 per cent conversion in the bottom stage.

Comparison of the results for Tests 3 and 8 has shown that an increase in bed depth increased chlorine utilization. This is confirmed by comparison of the results of Tests 15 and 16 with Test 3, where a small increase in bed depth with a larger charge of ilmenite resulted in increased chlorine efficiency and no increase in reaction time. Comparison of results for Tests 25 and 26 with Tests 15 and 16 have shown similar effects.

Comparison of the results of Tests 18 and 25 show that this effect was still evident when oxidised ilmenite was diluted with reacted product.

Finally Test 27 was conducted with 1000 gram charge of oxidised ilmenite as for Tests 15 and 16, but with the chlorine flow increased by about 17 per cent to 0.0508 gram per square inch per second. The rate of reaction was faster than Tests 15 and 16, reaction being complete in 150 minutes instead of 180 with no decrease in chlorine utilization.

The comparison between these tests can now be considered in relation to the comparison previously drawn between the results of Tests 6 and 3. In that case an increase of 45 per cent in the chlorine flow caused a reduction in reaction time from 180 minutes to somewhat less than 120 minutes. Chlorine conversion was reduced from 16.4 per cent to 13.7 per cent.

Apparently, for fluidised beds with a depth of 3 inches, chlorine flow can be increased to a value between 0.0508 gram per square inch per second and 0.062 gram per square inch per second resulting in an increase in the reaction rate without significant loss of chlorine efficiency.

The results of these tests are now briefly summarized. 1100°C has tentatively been selected as the chlorination temperature.

At this temperature the optimum chlorine flow rate was between 0.05 and 0.06 gram per square inch per second when treating oxidised ilmenite in fluidised beds 3 inches in depth. The flow rate could not be increased very much faster even if a deeper bed were used as the utilization of chlorine is approximately the equilibrium value. Little error was caused by disregarding the effect of particle size distribution on the rate of reaction and assuming that the oxidised ilmenite was composed of uniform size particles.

Dilution of the ilmenite charge with reacted product increased reaction rate but decreased chlorine efficiency.

The effect of treating ilmenite with chlorine diluted with ferric chloride and oxygen was to reduce the reaction rate although the overall chlorine conversion was little affected.

Increasing the depth of the fluidised bed and so providing longer contact time between chlorine and oxidised ilmenite increased chlorine efficiency.

These points summarise quantitatively the conclusions which may be drawn from the data. They exemplify the complicated nature of the fluidisation - chlorination process. No detailed analysis of the results is reported here. Arbitrary correlations of the data have been obtained and used for designing some of these experiments and, in the preliminary design of large scale fluidised bed reactors, for the purpose of assessing the feasibility of operating the process on an industrial scale. These correlations and their applications are reported in the following section.

8. CORRELATIONS

The derivation of a method for designing multiple stage fluidised bed reactors has been reported elsewhere (Ketteridge 1962). Reaction rates are classified according to the magnitude of the exponent "p" in the equation.

$$d_x/d_t = k\,(a - x)^p$$

where a = initial concentration of reactant in the solid expressed as a mass fraction.

x = change in concentration during time t.

t = time elapsed since commencement of reaction

k = reaction "rate" constant

p = reaction "order" constant

An integrated form of this equation is

$$\frac{a - x}{a} = \left(1 - \frac{kqt}{a^q}\right)^{1/q} \qquad o \leqslant t \leqslant \frac{a^q}{kq}$$

where $q = 1 - p$

Plots of the experimental data for the chlorination tests can be fitted with this type of curve and a good fit is obtained in most cases if the value of p is taken as 0.5. The significance of this fact is discussed in a later section of this report.

When p = 0.5 the expression for the fraction of unreacted material remaining in the charge after time t becomes

$$\frac{a-x}{a} = \left(1 - \frac{kt}{2a^{0.5}}\right)^2, \qquad o \geqslant t \geqslant \frac{2a^{0.5}}{k}$$

Then for p = 0.5 the cumulative conversion of chlorine, C, is given by

$$C = \frac{M}{fst_c} \left(2 - \frac{t}{t_c}\right)$$

where M = mass of charge
f = chlorine flow rate
s = stoicheiometric constant
t_c = $2\,(a)^{0.5}\;(k)^{-1}$

The chlorine conversion therefore decreases linearly from a value at the commencement of reaction of

$$C_{t=o} = \frac{2M}{f_s t_c}$$

to half this value at the instant the last trace of ferric oxide is removed from the charge.

A good fit of the data was obtained when curves of this type with p = 0.5 were fitted to the results for Tests 15 to 20, the series with varying fractions of oxidised ilmenite in the charge. The experimental data and matching curves are shown in Appendix C Figures C-1 to C-6. The following values for the rate constant k have been found from these figures:

Test	i	k
15	1	0.00762
16	1	0.00806
17	0.75	0.0106
18	0.5	0.0146
19	0.25	0.0249
20	0.125	0.0264

where i = volumetric fraction of oxidised ilmenite in the charge.

These data are shown as a plot of rate constant against fraction of oxidised ilmenite in Figure C-7, Appendix C.

It is interesting to observe that extrapolation of the curve to i = o gives a value for k of 0.0266. This can be interpreted as the rate constant at which a single average size particle of oxidised ilmenite reacts in a stream of pure chlorine. The time taken for complete reaction corresponding to this rate constant is 51.5 minutes.

The relationship between the fraction of oxidised ilmenite in the charge and the rate constant was used in calculation of feed rates of oxidised ilmenite to the bottom stage of the 2-stage chlorination reactor to produce various percentages of chlorine conversion in the bottom stage. Tests 21 to 24 were conducted on the basis of these calculations which are reported here.

The extent of reaction occurring in a continuously fed single stage fluidised bed reactor in which a reaction of type (3) with p = 0.5 is taking place, is given by the following equation (Ketteridge 1962)

$$Fu_1 = 1 - \frac{Vk}{va^{0.5}} + \frac{1}{2}\left(\frac{Vk}{va^{0.5}}\right)^2\left(1 - e^{-\frac{2Va^{0.5}}{Vk}}\right)$$

where Fu_1 = fraction of unreacted material in the effluent from a single stage reactor.

V = single stage reactor capacity

v = rate of throughput

Trial and error type calculation can now be used to determine the feed rate necessary to product a desired degree of chlorine conversion in the bottom stage.

A chlorine flow of 0.0434 grams per square inch per second in a 3-inch diameter reactor was assumed and it was also assumed that oxidised ilmenite contained 47 per cent of ferric oxide, i.e., = 0.47. The rate at which oxidised ilmenite is consumed by reaction for a given conversion of chlorine can be calculated from stoicheiometric proportions.

Chlorine Conversion %	Ilmenite Consumed g/min
5	1.47
10	2.93
15	4.40
20	5.87

With 5 per cent conversion of chlorine, the fraction of unreacted ilmenite in the solid product is therefore

$$Fu_1 = \frac{v - 1.47}{v}$$

An expression for Fu_1 in terms of v, V, a and k has already been given, so the following relationship has been obtained

$$\frac{1.47}{v} = \frac{Vk}{va^{0.5}} + \frac{1}{2}\left(\frac{Vk}{va^{0.5}}\right)^2\left(1 - e^{-\frac{2va^{0.5}}{Vk}}\right)$$

Providing values can be assigned to a, V and k, the value of v can be obtained from this expression.

A value for "a" has already been taken as 0.47.

A precise value cannot be fixed for V. Discharge from the reactor was by means of an overflow system with the overflow level 3 inches above the gas distributor. The capacity of the bed then depends on the degree of expansion which accompanies fluidisation and is therefore variable. The value taken for "V" was tentatively fixed on the basis of a simple experiment at 850 grams of oxidised ilmenite. This value will be reconsidered later.

It now remains to fix a value for "k".

With low conversion of chlorine, the fraction of unreacted material in the product will be low. When the fraction of oxidised ilmenite in the reactor is low the rate constant is correspondingly high.

At the time this calculation was performed, the only data on which a correlation between "i" and "k" could be based were the results of Tests 15, 18 and 19.

The times required for complete reaction were taken as 180, 90 and 60 minutes respectively and corresponding values for "k" were calculated.

Test	i	k
15	1.0	0.0076
18	0.5	0.0152
19	0.25	0.0228

The following relationship between "i" and "k" then holds:

$$k = 0.0329 + 0.0456\ i + 0.0203\ i^2$$

This is illustrated in Figure C-8, Appendix C.

To fix a value for "k", it was assumed initially that $i = 0.1$, in which case $k = 0.0285$, so that the time required for complete reaction is 48 minutes.

Substitution of this value for "k" in the expression for "Fu_1" gives the following relation:

$$\frac{1.47}{v} = \frac{850 \times 0.0285}{v\,(0.47)^{0.5}} + \frac{1}{2}\left(\frac{850 \times 0.0285}{v\,(0.48)^{0.5}}\right)^2 \left(1 + e^{-\frac{2v\,(0.47)^{0.5}}{850 \times 0.0285}}\right)$$

The solution of this equation is: $v = 1.5$

so that $Fu_1 = \dfrac{1.5 - 1.47}{1.5} = 0.02$

The original estimate of 10 per cent of unreacted ilmenite in the charge was high, so that the assumed rate constant was low. Substituting a value of $i = 0.02$ in the expression for "k" yields a value $k = 0.0320$.

This value is greater than the assumed value on which the calculation was based. Since both values are based on extrapolation beyond the limit of experimental measurement, the original and more conservative value for "k" was accepted and the corresponding value "v" of 1.5.

Fortunately subsequent experiments, particularly chlorination Test 20, have shown that the value of "k" chosen was very near the true value.

The effect can now be considered of variable bed volume on the degree of chlorine conversion in the lower reactor stage.

When the reactor being used for this work was fluidised with air at room temperature and fed with 7.9 grams of oxidised ilmenite per minute, the reactor retained 850 grams in the fluidised bed. If the ilmenite feed was cut off and the air flow rate maintained constant, the reactor capacity fell to 700 grams.

The previous calculation was based on a fluidised bed capacity of 850 grams. It was repeated with $V = 700$, and again the solution was $v = 1.5$ grams per minute. A change in reactor capacity of this magnitude is apparently not significant.

The problem of obtaining a fluidised bed of suitable composition at the start of reaction can now be considered.

The only materials available for making up the initial charge were oxidised ilmenite and chlorinated product, whereas under steady stage operation the bed would contain material varying in composition from oxidised ilmenite to fully chlorinated product. The problem was therefore to obtain a mixture of oxidised ilmenite and chlorinated product in such proportion that the degree of chlorine conversion would remain as close to 5 per cent as possible during the initial period until a fluidised bed of the correct composition was established.

The time required for complete reaction of oxidised ilmenite at the prevailing reaction rate was 48 minutes, so the initial period during which bed composition varies was somewhat less than 48 minutes.

This initial "settling down" period has been divided into four 12 minute periods and the average chlorine conversion calculated for each.

Firstly the charge of oxidised ilmenite initially added to the bed was chosen so that the initial reaction rate was sufficient to give 5 per cent conversion of chlorine.

Reaction rate is given by:

$$dx/dt = k\,(a-x)^p$$

Therefore the initial rate of consumption of oxidised ilmenite is

$$\frac{d\left(x/a\right)}{dt} = 0.0285\ (0.47)^{-0.5} \times W \quad \text{grams per minute}$$

where W = weight of oxidised ilmenite in the charge.

To produce 5 per cent conversion of chlorine requires a consumption of 1.47 grams of oxidised ilmenite per minute.

Therefore $W = 35.2$ grams

We can now consider the case where we start with a fluidised bed reactor having a total capacity of 850 grams of oxidised ilmenite containing 35.2 grams of oxidised ilmenite and the remaining volume filled with chlorinated product. The chlorinated product required would therefore be

$$(850 - 35.2) \times 0.53 = 432 \text{ grams}$$

The reactor is therefore charged with 35.2 grams of oxidised ilmenite and 432 grams of chlorinated product and brought up to the chlorination temperature. Chlorine is then admitted and oxidised ilmenite fed at the rate of 1.5 grams per minute.

At the instant chlorine is admitted to the charge, consumption of oxidised ilmenite will be at the rate of 1.47 grams per minute and chlorine conversion will be 5 per cent.

After the first 12 minute period, part of the original 35.2 grams of oxidised ilmenite will have passed out of the system. The remainder will amount to (see Ketteridge, 1962)

$$35.2 \times e^{-\frac{1.5 \times 12}{850}} = 34.5 \text{ grams}$$

The grade is reduced to

$$a - x = 0.47 \left(1 - {}^{12}/_{48}\right)^2$$
$$= 0.264$$

The reaction rate expressed as consumption of oxidesed ilmenite is

$$\frac{d(x/a)}{dt} = 0.0285 \times (0.264)^{0.5} \times (0.47)^{-1} \times 34.5$$
$$= 1.08 \text{ grams per minute}$$

During this 12 minute period, oxidised ilmenite has been added at the rate of 1.5 grams per minute. Part of this will also have overflowed so that of this there is left approximately

$$12 \times 1.5 \times e^{-\frac{1.5 \times 6}{850}} = 17.8 \text{ grams}$$

The mean grade of this is approximately

$$a - x = 0.47 \left(1 - {}^{6}/48\right)^2$$
$$= 0.766$$

The mean reaction rate is approximately

$$\frac{d(x/a)}{dt} = 0.0285 (0.766)^{0.5} \times (0.47)^{-1} \times 17.8$$
$$= 0.66 \text{ grams per minute}$$

The total rate of consumption of oxidised ilmenite at the end of the first 12 minute period is therefore:

$$1.08 + 0.66 = 1.74 \text{ grams per minute}$$

This corresponds to a chlorine conversion of

$$\frac{5.0 \times 1.74}{1.47} = 5.9 \text{ per cent}$$

Similar calculations have been carried out for the second and third 12 minute periods. After 48 minutes, chlorine conversion will be 5 per cent. The results of these calculations are summarised in the following tabulation.

Time min	Chlorine Conversion %
0	5.0
12	5.9
24	7.0
36	6.2
48	5.0

A better approximation to a constant chlorine conversion of 5 per cent would obviously be obtained with a smaller amount of oxidised ilmenite in the initial charge. The calculation was therefore repeated for a charge of 25 grams of oxidised ilmenite and the balance rutile. The results were:

Time min	Chlorine Conversion %
0	3.6
12	4.85
24	5.6
36	5.75
48	5.0

For 20 grams of oxidised ilmenite in the initial charge, the chlorine conversion was calculated to be:

Time min	Chlorine Conversion %
0	2.9
12	4.3
24	5.25
36	5.55
48	5.0

and for 23 grams of oxidised ilmenite in the initial charge:

Time min	Chlorine Conversion %
0	3.2
12	4.55
24	5.4
36	5.6
48	5.0

The results for all these calculations are compared in Figure C-9. It can be seen that any mixture made in this way gives a chlorination gas whose composition varies considerably from the desired 5 per cent during the initial stages of chlorination. The only way in which a steady 5 per cent conversion can be obtained is to use a bed containing correct proportions of oxidised ilmenite and partially and fully chlorinated ilmenite. The time required under the prevailing conditions for complete reaction of oxidised ilmenite is 48 minutes. A bed of correct composition is therefore obtained after chlorination under steady state conditions for longer than this period of time. The following technique was used to obtain a fluidised bed of the correct composition and so ensure steady conversion of chlorine in the lower stage during a chlorination test.

A charge comprising 23 grams of oxidised ilmenite and 438 grams of chlorinated product was fluidised with air and brought up to temperature. It was then chlorinated with a continuous addition of 1.5 grams of oxidised ilmenite per minute for about an hour. The fluidising gas was changed back to air and the feed of oxidised ilmenite stopped until a charge of 1000 grams of oxidised ilmenite had been placed in the top stage and brought up to temperature. Chlorination of the bottom stage was then resumed and the chlorination gases produced were used to treat the charge in the top stage.

For chlorination Test 21 it was found that a feed rate of 1.55 grams of oxidised ilmenite per minute to the bottom stage gave a chlorine conversion of 5.15 per cent.

The feed rates necessary to give 10, 15 and 20 per cent conversion of chlorine in the bottom stage were calculated in a similar manner to that for 5 per cent conversion. The results of these calculations are:

Chlorine Conversion	Feed Rate of Oxidised Ilmenite	
%	V = 850 g	V = 700 g
5	1.5	1.5
10	3.1	3.15
15	4.7	4.9
20	6.7	6.9

The test with 5 per cent conversion of chlorine in the lower stage was carried out first and those with 10, 15 and 20 per cent conversion were subsequently carried out in ascending order.

The way in which a fluidised bed of correct composition was obtained for the test with 5 per cent conversion has already been described. For the three subsequent tests the bed from the preceeding test was used as starting material. Otherwise the technique was the same as for the first test. The bottom fluidised bed was brought up to temperature with air as the fluidising medium. Then, without any charge in the top stage, oxidised ilmenite was fed at the necessary rate to the bottom stage and chlorine admitted. After 1 hour the fluidising gas was changed back to air and the feed of oxidised ilmenite stopped. The charge of oxidised ilmenite was added to the top stage and brought up to temperature. Continuous chlorination and continuous addition of feed to the bottom stage was resumed and the gaseous mixture produced used for fluidising and chlorinating the charge in the top stage.

For each of the four chlorination tests, from the rate constant for the bottom stage, the time required for complete reaction of an individual particle of ilmenite was calculated to be less than 1 hour. Therefore preliminary chlorination of the bottom stage under steady state conditions for this period would give a fluidised bed of the correct composition and would ensure the subsequent steady conversion of chlorine during the actual chlorination test.

Experimental results for the four chlorination tests were:

Test	Feed Rate gpm	Chlorine Conversion %
21	1.55	5.15
22	3.3	11.0
23	4.9	15.8
24	7.0	20.7

The data for chlorination of oxidised ilmenite in the upper stage of the 2-stage reactor with varying degrees of chlorine conversion in the lower stage, Tests 21 to 24, have been fitted to curves for reactions having a value of $p = 0.5$. These curves are shown in Figures C-10 to C-13, Appendix C. The value of $p = 0.5$ does not give a good fit to the experimental data for Tests 22, 23 and 24 and the reasons for selecting this value of p are discussed later.

The rate constants for Tests 21 to 24 determined from these fitted curves, together with those for Tests 15 and 16, are tabulated:

Test	c	k
15	0	0.00762
16	0	0.00806
21	0.0515	0.00762
22	0.110	0.00571
23	0.158	0.00339
24	0.207	0.00196

where c = lower stage chlorine conversion expressed as a fraction of total chlorine flow.

These data have been extrapolated to give zero rate of reaction when conversion of chlorine in the bottom stage equals 40 per cent and the resulting relationship between c and k is illustrated in Appendix C Figure C-14.

A previous report (Ketteridge and Wilmshurst, 1963) showed that the maximum, i.e., equilibrium, conversion of chlorine to ferric chloride when reacted with oxidised ilmenite is 44 per cent. Throughout this work 40 per cent was the value taken as the maximum conversion that can be obtained in a continuous system. This was the reason for extrapolating the data for the "c" series tests to zero rate constant at 40 per cent conversion.

The influence of dilution of ilmenite with reacted product on the rate constant when the order of reaction was taken as $p = 0.5$ has already been discussed and is illustrated in Figure C-7.

The effect of gas composition on reaction rate has been assumed to be independent of dilution of oxidised ilmenite with chlorinated product, and the effect of simultaneous dilution of oxidised ilmenite with chlorinated product and of chlorine gas with gaseous chlorination products determined by simple proportion.

These data, which show the dependance of "k" on "i" and "c" for a value of the order of reaction of $p = 0.5$, are illustrated in Figure C-15.

To summarise this work, it can be stated that an approximate relationship between "k" and the independant variables "i" and "c" has been obtained by assuming a constant value of $p = 0.5$. This relationship can be used to perform preliminary design calculations for multiple stage fluidised bed reactors and the practicability of continuous operation of the process can be assessed. The approximations used in obtaining Figure C-15 depicting the dependance of "k" on "i" and "c" are now discussed.

The first approximation was that the "c" series tests, Tests 15, 16 and 21 to 24, have been correlated on the basis that $p = 0.5$. This value for p provided curves which gave a good fit of the data for Tests 15, 16 and 21. However, Tests 22, 23 and 24 could be fitted better with curves for higher values for p. From figures C-11, C-12 and C-13 a good fit of the data was obtained with values for p of $^2/_3$, $^3/_4$ and 2 for Tests 22, 23 and 24 respectively. At the particle surfaces the reaction rate should decrease as the available surface decreases. If the rate varied linearly with the exterior surface of unreacted material, the reaction should, from geometric considerations, be of the type having $p = {}^2/_3$.

For chlorination experiments with pure chlorine, the data was well fitted by curves having $p = 0.5$. A possible explanation is that the surface area available for reaction was greater than the exterior surfaces of the particles. This was confirmed by microscopic examination of partially chlorinated material which showed attack along grain boundaries within the particles as well as at exterior surface. The subsequent reduction in chlorination rates was in excess of that which can be explained by simple geometric considerations and was assumed to be caused by titanium doixide formed on the reacting surface presenting a continually increasing barrier to gas diffusion.

For the experiments in which mixed chlorine, oxygen and ferric chloride were used as chlorination gases and higher values of p are found, lower partial pressures of chlorine were considered to extend the diffusion controlled region to earlier stages of the reaction, thereby causing higher values of p.

A study of the tabulated values for chlorine consumed by reaction confirmed this consideration. For example the chlorination Test 24 with 20.7 per cent conversion of chlorine in the lower stage, the chlorine consumed at 85 per cent reaction is 5.8 per cent. This consumption is 0.3 times the value when reaction is only 30 per cent complete (17.8 per cent). Comparable ratios for tests with smaller chlorine conversions in the lower stage increase successively from 0.7 to 0.8, that is to say that chlorine conversion remains more nearly constant throughout the tests. This fact indicates that reaction products on the particle surfaces form less of a diffusion barrier with high partial pressures of chlorine in the chlorination gas.

No attempt was made here to confirm these postulates rigorously nor to measure resulting effects quantitatively. The experimental data were correlated on an arbitrary basis alone.

Taking a value of p = 0.5 for Tests 22, 23 and 24 introduced an error by reducing the reaction rate in the initial stages of reaction and accelerating it toward the end of reaction. However, by taking a constant value for p throughout all the tests, the number of reaction rate variables involved in design calculations for multiple stage fluidised bed reactors was reduced from four to three.

Design calculations for multiple stage reactors were lengthy, even with three such variables. With four, recourse to calculation by a computer would have been necessary. Since the purpose of the calculation was to provide an approximate design for assessing the practicability of operating the process, the simplification of taking a constant value for p was justified.

The second approximation was that of assuming the effects of gas composition and of dilution of ilmenite with chlorinated product upon the reaction rate were independant and estimating the simultaneous effect of both by simple proportion.

To measure the simultaneous effects of these two variables would have involved further chlorination experiments with the two stage experimental equipment. The immediate purpose of this project did not justify the time and expense involved in such experiments.

The third approximation was that data determined in fluidised bed equipment only 3 inches in diameter were used for preliminary design calculations for large scale reactors. Again there was no justification at this stage for performing further experiments with larger scale equipment. If the results of these calculations showed that the operation of this process on an industrial scale was likely to be practicable, then further measurements of reaction rates under various conditions would have to be made with larger scale equipment.

9. REACTOR DESIGN

Five types of fluidised bed reactors were considered. These were a single stage reactor, a 2-stage reactor having both stages on the same horizontal level and a common gas distributor, 2-stages with one set above the other so that chlorination gases from the lower bed pass through the upper, a 3-stage reactor with the stages arranged vertically so the gases pass successively through each stage and a 3-stage reactor with the first stage arranged vertically above the second and third stages, these 2-stages being on the same (horizontal) plane. These reactors are illustrated in Appendix D Figures D-1 to D-5 respectively.

Design calculations were based on the daily treatment of 106.4 tons of oxidised ilmenite containing 50 tons of ferric oxide.

In order to produce marketable grade titanium dioxide containing less than 0.5 per cent ferric oxide, the chlorination reaction has to proceed to 99.43 per cent completion.

The permissible fraction of unreacted material in the product was therefore taken as 0.0057.

Single Stage Reactor

(refer Appendix D, Figure D-1)

For a reaction of the type having p = 0.5, the fraction of unreacted material in the effluent from a single stage reactor is given by:

$$Fu_1 = 1 - \frac{Vk}{va^{0.5}} + 0.5\left(\frac{Vk}{va^{0.5}}\right)^2\left(1 - e^{-\frac{2va^{0.5}}{Vk}}\right)$$

When $\frac{Vk}{va^{0.5}} = 100$

$Fu_1 = 0.005$

A value for the rate constant k could be determined provided values for c and i were known. The reactant gas was pure chlorine so c = 0. The fraction of unreacted material in the effluent was 0.005 so i = 0.005.

A value for k corresponding to this value for i from Figure C-7 Appendix C was k = 0.0266.

The feed rate v was equal to 0.0736 tons of oxidised ilmenite per minute.

The feed material contained 47 per cent of ferric oxide so a = 0.47.

Substitution of these values in the previous expression yielded a value for the reactor capacity of V = 190 tons of oxidised ilmenite.

The amount of chlorine which could be converted to ferric chloride under equilibrium conditions for the chlorination reaction at 1100°C was 44 per cent (Ketteridge and Wilmshurst 1963). In most of the chlorination results reported there, the chlorine conversion was much less than this value. However, in some instances, the initial chlorine conversions were close to 40 per cent.

A fluidised bed reactor with a capacity of 190 tons of oxidised ilmenite must necessarily have a much greater depth of bed than the 3 inch fluidised beds used for these experiments. Chlorine gas rising through the bed will therefore remain in contact with the charge for a longer period and conversion of chlorine will be greater although this could not exceed equilibrium.

The increase in chlorine conversion could not be determined without measurements made with larger scale equipment, so a value of 40 per cent conversion was assumed.

2-Stage Reactor - Horizontal Arrangement

(refer Appendix D, Figure D-2)

For a fluidised bed reactor with 2 equal size stages in which a reaction of the type having $p = 0.5$ is taking place with the same rate constant in each stage, the author has shown (Ketteridge 1962):

$$Fu_2 = 1 - \frac{Vk}{va^{0.5}}\left(2 + e^{-\frac{2va^{0.5}}{Vk}}\right) + \left(\frac{3}{2}\;\frac{Vk}{va^{0.5}}\right)^2\left(1 - e^{-\frac{2va^{0.5}}{Vk}}\right)$$

with $\frac{Vk}{va^{0.5}} = 8$

$$Fu_2 = 0.0047$$

For the first stage of this reactor alone

$Fu_1 = 0.0784$

The chlorinating gas entering both stages was pure chlorine therefore, as with the single stage reactor stage $i = 0.0784$ therefore from Figure C-7 Appendix C, $k = 0.0265$. For the second stage $i = 0.0047$ so $k = 0.0266$ was taken for both stages and the small error so introduced, was disregarded.

As with the calculation for a single stage reactor, $v = 0.0736$ tons of oxidised ilmenite per minute and $a = 0.47$.

Substitution of these values yielded a value for the capacity of each stage of $V = 15.2$ tons of oxidised ilmenite and a total reactor capacity of 30.4 tons.

As previously, the assumption was now made that a chlorine conversion of 40 per cent could be obtained in the first stage of the 2-stage reactor.

The calculated extent of reaction in the first stage amounted to 92.16 per cent and in the second to 7.37 per cent.

Since the two stages were considered of equal size and on the same horizontal level, the chlorine flow to each was considered to be the same. Conversion of chlorine in the second stage was therefore calculated to be:

$$40 \times \frac{7.37}{92.16} = 3.20 \text{ per cent}$$

The overall conversion of chlorine in both stages was therefore assessed as 21.6 per cent.

A greater value for the overall conversion of chlorine could be obtained with a 2-stage reactor if the capacities of the 2-stages differed.

For a 2-stage reactor with the first stage having a capacity V_1 and the second V_2;

$$Fu_2 = \frac{V_1}{V_1 - V_2} \left(1 - \frac{V_1 k}{va^{0\cdot 5}} + \frac{1}{2}\left(\frac{V_1 k}{va^{0\cdot 5}}\right)^2 \left(1 - e^{-\frac{2va^{0\cdot 5}}{V_1}}\right)\right)$$

$$- \frac{V_2}{V_1 - V_2} \left(1 - \frac{V_2 k}{va^{0\cdot 5}} + \frac{1}{2}\left(\frac{V_2 k}{va^{0\cdot 5}}\right)^2 \left(1 - e^{-\frac{2va^{0\cdot 5}}{V_2 k}}\right)\right)$$

The case of a reactor having stage capacities in the ratio $V_1 : V_2 = 20:1$ were then considered.

Substitution of a value of

$$\frac{V_1 k}{va^{0\cdot 5}} = 40$$

in the previous expression yielded a value of 0.0038 for the fraction of unreated material in the product. The fraction of unreacted material in the first stage was by calculation 0.0168.

Therefore for stage 1

$$c = 0 \quad \text{and } i = 0.0168$$

and for stage 2

$$c = 0 \quad \text{and } i = \underline{0.0038}$$

From Figure C-7 and Appendix C, a value for k of 0.0266 was obtained for both stages.

With values for v and a as before, values for V_1 and V_2 of 75.9 tons and 3.8 tons respectively were obtained, giving a calculated total reactor capacity of 79.7 tons.

Values calculated for the fraction of unreacted material in effluent from stage 1 and stage 2 were 0.0168 and 0.0038 respectively. The extent of reaction in each of the two stages was therefore assessed as 98.32 per cent and 1.30 per cent.

If the two stages were so arranged that they had the same depth of bed, then the chlorine flow to each would be in the proportion of 20:1. If 40 per cent conversion of chlorine was achieved in the first stage, then the conversion in the second stage would be:

$$\frac{20 \times 40 \times 1.30}{98.32} = 10.58 \text{ per cent}$$

Chlorine conversion for the reactor as a whole was therefore calculated:

$$\frac{20 \times 40 + 10.58}{21} = 38.60 \text{ per cent}$$

The reactor capacity in this case was greater than with two equal size stages, being 79.7 tons compared with 30.4 tons. This figure is considerably less than the 190 tons required for a single stage reactor. However, this reduction in the reactor size was achieved at the expense of reducing the chlorine conversion from 40 per cent to 38.6 per cent.

If the ratio of $V_1 : V_2$ was increased to 200:1, with a value for

$$\frac{V_1 k}{va^{0.5}} = 75$$

the fraction of unreacted material in the product was calculated to be 0.0052.

In this case $V_1 = 142.4$ tons and $V_2 = 0.71$ tons, giving a total capacity of 143.1 tons. Overall chlorine conversion was assessed as 39.94 per cent. The reactor capacity was therefore reduced from the 190 tons required for a single stage reactor to 143 tons with negligible loss in chlorine conversion.

The values of 20:1 and 200:1 for the ratios of stage capacities were chosen arbitrarily to illustrate the effect of different size stages. Obviously reduction of reactor capacity would have to be balanced against maintaining chlorine conversion at as high a value as possible.

Two Stage Reactor - Vertical Arrangement

(refer Appendix D, Figure D-3)

The rearrangement of the 2-stage fluidised bed reactor with equal size stages with one stage above the other was then considered.

The reactor under consideration has two stages, each with a capacity of 15.2 tons of oxidised ilmenite, arranged vertically so that chlorination gases from the bottom stage enter the top stage.

The gas entering the bottom stage would be pure chlorine so for this stage $c = 0$. Assuming that the grade of product leaving the reactor was the same as for the horizontal arrangement of stages, then for the bottom stage $i = 0.0047$. The reaction rate constant was therefore the same as for the horizontal arrangement of stages, $k = 0.0266$.

If the further assumption was made that the extent of reaction in the first stage was the same as with the horizontal arrangement of stages, then the extent of reaction in the second will be the same as with the horizontal arrangement.

Chlorine conversion in the bottom stage will be 3.20 per cent, so that for the top stage $c = 0.032$, and as before for the first stage, $i = 0.0784$.

From Figure C-15 Appendix C, the rate constant in this stage would be $k = 0.0262$.

The difference between this value for k and the value of 0.0266 used in the calculation for the horizontal arrangement of stages was small and does not invalidate the assumption that the extent of reaction in the vertical arrangement of stages was the same as for the horizontal arrangement.

A reactor having two stages, each with a capacity of 15.2 tons of oxidised ilmenite, arranged vertically would therefore produce a satisfactory grade of product with an overall chlorine conversion of 40 per cent.

Three Stage Reactor – Vertical Arrangement

(refer Appendix D, Figure D-4)

For a three stage reactor in which V, k and p are the same for each stage:

$$Fu_3 = \sum_{n=1}^{\infty} \frac{(-1)^{n+1}\left(\sum_{a=1}^{n} a\right)\left(\frac{va^{q}}{Vkq}\right)^{n+2}}{\prod_{m=1}^{n+2}\left(\frac{1}{q} + m\right)}$$

Since results for the chlorination experiments have been based on a value of $p = 0.5$, the substitution of

$$q = 1-p = 0.5$$

can be made.

Substitution of a value for

$$\frac{va^{0.5}}{Vk} = 0.4$$

yielded a value for

$$\begin{aligned} Fu_3 &= 0.005770 \quad -0.000,017 \\ &= 0.0058 \end{aligned}$$

For the first two stages of this reactor

$$Fu_2 = 0.0392$$

For the first stage alone

$$Fu_1 = 0.2208$$

The overall extent of reaction was therefore calculated to be 99.42 per cent. The extent calculated to occur in the bottom stage alone was 3.34 per cent and in stages 2 and 3 combined was 21.5 per cent.

$$\begin{aligned} i &= 0.0058 \\ c &= 0 \end{aligned}$$

so that from Figure C-7 Appendix C, $k = 0.0266$

For stage 2 the fraction of unreacted material in the bed

$$i = 0.0322$$

Assuming an overall chlorine conversion of 40 per cent, reaction in the bottom stage would give a value for c in the second stage of:

$$c = \frac{0.40 \times 0.0334}{0.9942} = 0.001344$$

From Figure C-15 Appendix C, for the second stage

$$k = 0.0266.$$

For the first stage the calculated fraction of unreacted material in the bed was 0.2208 so that for this stage

$$i = 0.2208.$$

The extent of reaction in the second and third stages was such that for the first stage

$$c = \frac{0.40 \times 0.215}{0.9942} = 0.0865$$

Therefore from Figure C-15 Appendix C,

$$k = 0.0219$$

This value was less by some 18 per cent than the value for stages 2 and 3. Therefore a common velocity constant and size of stage could not be assumed for all three stages of the reactor.

For all three stages:

$$\frac{va^{0.5}}{Vk} = 0.4$$

For stages 2 and 3, $k = 0.0266$. Substitution of the values previously determined for a and v yielded a value for V of 4.74 tons for each of these stages.

For the first stage

$$k = 0.0219 \text{ so that } V_1 = 5.76.$$

The total reactor capacity would therefore be 15.2 tons.

Three Stage Reactor - Vertical and Horizontal Arrangement

(refer Appendix D, Figure D-5)

An alternative arrangement of the three stage reactor was then considered.

The extent of reaction in the bottom stage was shown to be small and the amount of chlorine converted to ferric chloride not sufficient to influence the reaction rate constant in the second stage. The rate constant in both second and third stages was 0.0266, the same value as would result if pure chlorine were fed to each.

The second and third stages could therefore be arranged on the same horizontal plane with a common gas distributor without altering the rate or extent of reaction in either. The first stage would remain vertically above these stages.

With the three stages one above the other, the extent of reaction in the bottom two stages was shown to result in 8.65 per cent chlorine conversion. With these stages arranged horizontally the chlorine conversion would be 4.325 per cent so that for the first stage

$$c = 0.04325$$

For the first stage in the vertical arrangement of stages calculations have shown:

$$i = 0.2208$$

A corresponding value for k was obtained from Appendix C Figure C-15.

$$k = 0.0250$$

It has been shown for the vertical arrangement of stages that

$$\frac{va^{0.5}}{Vk} = 0.4$$

Therefore for the first stage of the combined vertical and horizontal arrangement

$$v = 5.04 \text{ tons}$$

The second and third stages would be the same as for the vertical arrangement of stages, 4.7 tons, therefore the total reactor capacity would be 14.5 tons of oxidised ilmenite.

The results of these calculations are now summarised.

To treat 106.4 tons of oxidised ilmenite per day and produce a product containing less than 0.5 per cent ferric oxide required a single stage fluidised bed reactor of the type shown in Appendix D Figure D-1 having a capacity of 190 tons of oxidised ilmenite. Chlorine conversion was assumed to be 40 per cent.

If a fluidised bed reactor was partitioned to give two equal size stages on the same plane as in Figure D-2, the total reactor capacity required was reduced to 30.4 tons. However chlorine conversion was calculated to be reduced from 40 per cent to 21.6 per cent.

However, if the stages were made with different capacities, chlorine conversion could be increased while the total reactor capacity would remain less than a single stage reactor but greater than one with two equal size stages.

As an example, a reactor having the first stage 20 times the capacity of the second required a total reactor capacity of 80 tons and resulted in a calculated overall chlorine conversion of 38.6 per cent. If the ratio of the size of stages was increased to 200:1, the total reactor capacity required was 143 tons and the chlorine conversion was 39.94 per cent.

For a reactor with two equal size stages one above the other (Figure D-3), a total reactor capacity of only 30.4 tons has shown to be necessary to produce an acceptable grade of product and maintain chlorine conversion at 40 per cent.

A three stage vertical reactor (Figure D-4) having a first stage with a capacity of 5.8 tons and the second and third stages each 4.7 tons, i.e., a total capacity of 15.2 tons, was calculated to produce a suitable grade of product with 40 per cent conversion of chlorine.

Finally if the three stage reactor was rearranged with the second and third stages on the same horizontal plane and the first stage vertically above (Figure D-5), the first stage could be reduced to 5.0 tons to give a total reactor capacity of 14.5 tons.

The results from considerations of the various reactor designs are now summarised.

The simplest, a single stage, requires a reactor having a capacity of 190 tons of oxidised ilmenite or an average hold up time of 43 hours to produce a suitable grade of product.

For a suitably arranged 2-stage reactor a capacity of 30 tons or an average retention time of 6.5 hours is required.

For a 3-stage reactor a total capacity of 15 tons or an average retention time of 3.3 hours is sufficient.

Chlorine Flow. Reactor design calculations have been based on the treatment of 106.4 tons of oxidised ilmenite per day requiring the removal of 50 tons of ferric oxide per day. The chlorine consumed would be, by stoicheiometric proportion,

$$50 \times \frac{213}{159.7} = 66.7 \text{ tons per day}$$

In chlorination experiments carried out in small scale fluidised bed equipment, a chlorine flow sufficient to maintain the bed in a well fluidised condition but insufficient to casue significant loss of solids by entrainment, was found to be

$$0.05 \text{ g } (\text{in})^{-2} \ (\text{sec})^{-1}$$

This value was taken as a suitable flow-rate for industrial scale equipment. Conversion to more convenient units yielded

$$0.612 \text{ tons } (\text{ft})^{-2} \ (\text{day})^{-1}$$

The bulk specific gravity of oxidised ilmenite is 2.5 so 1 ton occupies 14.35 cubic feet. Allowing 20 per cent expansion on fluidisation, 1 ton in the fluidised state occupies 17.2 cubic feet.

On the basis of these values for specific gravity and fluidised bed expansion, the gas pressure loss through 1 foot of fluidised bed was calculated to be 0.90 psi.

However, fully chlorinated product has a specific gravity of only 1.25 so that gas pressure loss through 1 foot of fluidised bed would be in this case 0.45 psi.

Consider the single stage fluidised bed reactor.

A value of 40 per cent has been taken as the probable extent of chlorine conversion for the single stage fluidised bed reactor, and the size of bed necessary has been estimated at 190 tons of oxidised ilmenite.

The chlorine flow required would be

$$66.7 \times 2.5 = 167 \text{ tons per day.}$$

The cross-sectional area required to give a suitable linear chlorine gas velocity would be

$$\frac{167}{0.612} = 273 \ (\text{ft})^2$$

Assuming a circular construction, a reactor having a diameter of 18.5 ft, cross-section area 269 square feet, would be suitable.

The volume of the expanded fluidised bed would be

$$190 \times 17.2 = 3270 \text{ (ft)}^3$$

and the expanded bed height

$$\frac{3270}{269} = 12.2 \text{ ft}$$

The fluidised bed would contain almost completely reacted product so the gas pressure loss through the bed would be

$$12.2 \times 0.45 = 5.5 \text{ psi.}$$

The single stage fluidised bed reactor would therefore have a diameter of 18.5 feet and the depth of the fluidised bed would be 12.2 feet. This would cause a fluidising gas pressure loss through the bed of 5.8 psi.

For a reactor with two equal size stages arranged on the same horizontal plane, a total reactor capacity of 30.4 tons of oxidised ilmenite was shown to be necessary and the overall chlorine conversion should be 21.6 per cent. In order to give a suitable linear velocity of chlorine through the fluidised bed, a reactor 25.5 feet in diameter partitioned in the centre would be necessary. The depth of the expanded fluidised bed necessary would then be 1.0 foot and the corresponding chlorine pressure loss 0.5 psi.

A 2-stage reactor having the first stage 20 times the volume of the second required a total reactor capacity of 79.7 tons of oxidised ilmenite and was calculated to give 38.6 per cent conversion of chlorine. In order to give a suitable velocity of chlorine through this reactor, a diameter of 19 feet would be required with a partition placed to give a second stage having an area in cross section of 14 square feet. The depth of bed in this reactor would be 4.8 feet and gas pressure loss 2.2 psi.

If the ratio of sizes was increased to 200:1, the necessary total reactor capacity increased to 143.1 tons and the chlorine conversion to 40 per cent. The area requirement in this case was the same as for a single stage reactor,so a diameter of 18.5 feet would be necessary with a partition so placed that the second stage would have a cross section of 1.4 square feet. The depth of the fluidised bed would be 9.2 feet giving a gas pressure loss of 4.1 psi.

With a vertical arrangement of two equal size stages, a total reactor capacity of 30.4 tons of oxidised ilmenite was necessary and chlorine conversion would be 40 per cent. Therefore a reactor of 18.5 feet diameter would again be necessary. The depth of bed in each stage would be 1.0 foot and the pressure loss in each 0.44 psi giving a total pressure loss through the fluidised beds of 0.88 psi.

For the vertically arranged 3-stage reactor, the anticipated chlorine conversion was 40 per cent so that an 18.5 feet diameter reactor would be required. The capacity of the first stage has been calculated at 5.76 tons of oxidised ilmenite, so the fluidised bed depth necessary would be 0.37 feet. This stage contains 22.1 per cent ilmenite so the average specific gravity would be 1.53. The gas pressure loss through this stage would therefore be 0.20 psi.

The capacities of the second and third stages are each 4.74 tons of oxidised ilmenite. The depth of bed in each would be 0.30 feet. Both beds would contain almost completely chlorinated product so the pressure loss through each would be 0.14 psi and pressure loss through the three fluidised beds will be 0.48 psi.

If the stages were rearranged with the second and third stages on the same horizontal plane, an 18.5 feet diameter reactor would still be necessary. The capacity of the top stage in this case was calculated to be 5.04 tons so the bed depth would be 0.32 feet and the gas pressure loss 0.18 psi.

The capacity of each of the bottom stages was calculated at 4.74 tons so the depth of bed in each would be 0.61 feet and the gas pressure loss 0.27 psi. Total pressure loss through the fluidised beds would be 0.45 psi.

In all cases therefore bed depth would be shallow, say 1 foot or less, the distributors would have to have a pressure drop of the order of 1.0 psi in order to prevent channelling.

These calculations may now be summarised.

To carry out the chlorination reaction in a single fluidised bed would require a reactor 18.5 feet in diameter containing a fluidised bed 12.2 feet in depth.

If a reactor comprising two equal size stages on the same horizontal plane were used, chlorine conversion would be less than with a single stage fluidised bed so a larger diameter (25.5 feet) reactor would be necessary. Hold up of solids in a 2-stage reactor would be less and this effect, together with the larger diameter,would result in a much smaller depth of bed, 1.0 foot, rather shallow for this diameter.

With a 3-stage reactor, the diameter would remain the same as for a single stage reactor, but hold up would be further reduced and extremely shallow beds result. There would be little difference whether all three stages were arranged vertically or whether the second and third stages were on the same horizontal plane.

The calculated depth of bed would be, of course, a minimum depth and deeper beds would be possible. However this would counter the advantage of using three stages in place of two, in order to reduce hold up of solids.

Further discussion is confined to reactors with less than three stages.

Hold up in a 2-stage reactor would be least when the stages were the same size.

With two equal size stages on the same horizontal plane, chlorine conversion was shown to be inordinately low, requiring a large diameter reactor and a shallow fluidised bed. If the two stages were arranged vertically, chlorine conversion would be high and the necessary bed diameter reduced to the same as for a single stage reactor. However, the two fluidised beds would still be very shallow.

Fluidised beds deeper than the calculated minimum could be used, but the operation of two stages one above the other would be more difficult than if both were on the same plane. Apart from difficulties in minimising gas pressure fluctuations, entrainment of solids frequently tends to seal gas distribution in the upper stage and restrictions would be necessary in the gas distributors in order to produce a positive pressure drop to control any tendency to channel.

The possibility of using two vertical stages should not be overlooked, but two horizontally arranged stages, correctly proportioned, would appear to offer the best solution.

Only two reactors having two differently sized stages have been considered here, the ratios of the stages being 20:1 and 200:1.

The former would be the better, requiring a reactor 19 feet in diameter and a fluidised bed 4.8 feet deep. Conversion of chlorine should be 38.6 per cent.

This compared favourably with a single stage reactor and, while the ratio of the sizes of the stages should be the subject of further study, a reactor consisting of two horizontally arranged stages was selected for the present as the most suitable compromise.

Heat Requirement. The heat of reaction for reaction (2) has been determined by Ketteridge and Wilmshurst (1963).

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

$$\Delta H_{1100^\circ C} = 173{,}000 \text{ calories}$$

The heat consumed when treating 106.4 tons of oxidised ilmenite per day containing 50 tons of ferric oxide would amount to:

$$4.55 \times 10^6 \quad \text{BTU (hr)}^{-1}$$

or, converting to other units

$$1{,}330 \text{ kw}$$

This is the heat consumed by reaction alone. Preheating of reactants to the reaction temperature of 1100°C was assumed and no allowance was made for heat losses. Therefore in practice the heat requirement would be significantly greater than this value.

The first method to be considered for supplying this heat was external heating of the fluidised bed reactor.

For a 2-stage reactor with the first stage 20 times larger than the second and with both stages on the same horizontal plane, a 19 foot diameter reactor was required containing a fluidised bed 4.8 feet deep.

If the external surface available for heating was 4.5 feet high at this diameter, the available area would be

$$269 \text{ (ft)}^2$$

The necessary heat transfer rate through this area would then be

$$\frac{4.55 \times 10^6}{269} = 16{,}900 \text{ BTU (ft)}^{-2} \text{ (hr)}^{-1}$$

Experience has shown that siliceous or aluminous refractories are inert to attack by chlorine under the conditions prevailing in the chlorination reactor. Construction of a gas-tight fluidised bed reactor of these dimensions would be possible if a steel shell could be built around the outside.

However no steel shell could be used if the reactor were to be externally heated.

A reactor would be difficult to construct without this impervious shell. However, assuming that this were possible, and the overall heat transfer coefficient through the reactor wall to be

$$20 \text{ BTU } (\text{ft})^{-2} \quad (\text{hr})^{-1} \quad (^0\text{C})^{-1}$$

(probably excessive), the necessary temperature differential between the heating medium on the outside and the fluidised bed on the inside would become

$$\frac{16900}{20} = 850^0\text{C}$$

The temperature of reaction is 1100°C so that the external temperature would be 1950°C which is plainly not practicable.

Even if we consider a single stage fluidised bed reactor which, being larger, has a greater available heating surface, the temperature differential would be large. In this case the heating surface would be a 12 foot length of 18.5 feet diameter reactor or 697 square feet. The temperature differential would then be 326°C.

This is a conservative estimate of the temperature differential and, as before, would require the construction of a large fluidised bed reactor impervious to chlorine in siliceous or aluminous refractories.

The difficulties involved in the use of high temperatures and this form of construction are such that this method of heating the reactor does not seem practicable.

An alternative means of heating the reactor would involve continuously drawing off portion of the solids, superheating, and returning the superheated material to the chlorination reactor.

For the 2-stage reactor with the first stage 20 times greater than the second, the fraction of unreacted material in the first stage would be 0.017 and in the second 0.004. Therefore, for the purposes of heat content calculations, the material withdrawn from the fluidised bed could be regarded as pure titanium dioxide.

If we assumed that rutile could be superheated to 1400°C, as for example by direct flame heating in an entrained state, then the useful heat which could be transported in 4 mols of titanium dioxide would be

$$\begin{aligned} H_{1673^0\text{K}} - H_{1373^0\text{K}} \ (4\text{TiO}_2) &= 4\ (23,910 - 18,330) \\ &= 23,300 \text{ calories} \end{aligned}$$

(data from Kelley, 1960)

The necessary recirculating load would therefore be

$$\frac{173,000}{22,300} = 775 \text{ per cent}$$

This calculation has been based on the minimum possible heat requirement and, in practice, a greater circulating load would be required, probably in excess of 1000 per cent.

The problems involved in withdrawing such a large proportion of the solids from the chlorination reactor without loss of chlorine and of returning the superheated solids without serious contamination of the chlorination gases with nitrogen and gaseous products of combustion appear formidable.

It appears that the major obstacle to be overcome in designing a practicable chlorination reactor would be to provide means of introducing sufficient heat for the reaction to proceed. The heat requirement is so large that there appears to be no practicable way of doing this.

10. CONCLUSIONS AND RECOMMENDATIONS

Fluidised bed reactors have been selected as the most suitable type for conducting the chlorination reaction.

Preliminary design calculations for industrial scale reactors have been carried out based on empirical correlations of data obtained from experiments in small scale equipment.

Approximate correlations of the data have been accepted in order to simplify subsequent calculations. The correlations, being empirical, are themselves questionable when applied to calculations for reactors substantially different in size from those in which the data were measured. These shortcomings are discussed later in the light of the results obtained.

The design calculations have demonstrated that hold up times can be markedly reduced by increasing the number of stages in the chlorination reactor from one to three.

The cross-section area of the reactor is determined by the velocity of chlorine flowing through the system.

For a 3-stage reactor, the hold up of solids is so reduced that fluidised beds of only a few inches in depth are required, while the cross section area required is such that a reactor of the order of 20 feet in diameter is necessary. This is plainly not practicable so there is nothing to be gained by having more than two reactor stages.

It has been shown that, when two equal size stages are arranged side by side in a single reactor, conversion of chlorine is very low.

By arranging one stage vertically above the other, chlorine conversion is restored to the value obtainable in a single stage reactor which, of necessity, will have a much greater hold up. However, the operation of a reactor with two vertical stages could be much more difficult than if the two stages were arranged on the same horizontal plane.

It has been shown that the simplicity of operation of a single stage reactor and the reduced hold up of a 2-stage reactor can be achieved at small expense in chlorine conversion by making two stages of different capacity. By varying the ratio of the two sizes, hold up and chlorine conversion can be varied between the limits obtained with a single stage reactor on one hand and with a horizontal arrangement of two equal size stages on the other.

A suitable compromise appears to be a reactor having the first stage about 20 times the size of the second. This arrangement appears to be close to the optimum for number and size of stages.

However, the heat requirement of the highly endothermic chlorination reaction is of such magnitude that it is not practicable to supply sufficient heat from an outside source to maintain the reaction temperature.

Fuel cannot be burnt in the chlorination reactor without radically altering the process by interfering with the chlorination reaction and by requiring the continuous separation and removal of gaseous products of combustion from the chlorination gas stream.

The preliminary calculations demonstrate the impracticability of designing and constructing an industrial scale reactor for the chlorination reaction.

The empirical correlation of experimental data and the extrapolation of data from small scale experiments are sources of error in the design calculations. However, the supply of sufficient heat to the chlorination reactor is a problem of such magnitude that further chlorination experiments in larger scale equipment to obtain more accurate data for industrial scale design calculations are not justified.

No further work should be done on this project.

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12. NOTATION

a = initial concentration of reactant in the solid expressed as mass fraction

t = time since commencement of reaction

a_t = concentration of reactant is the solid at time t

b = inert constituent of the solid

x = mass of solid reactant consumed per unit mass of original charge

G_{mf} = critical fluid mass velocity

d = fluid density

u = fluid viscosity

T = temperature in degrees Kelvin

k = reaction "rate" constant

p = reaction "order" constant

q = $1 - p$

M = mass of charge

F = chlorine flow rate

s = stoicheiometric constant

t_c = $2\,(a)^{0.5}.(k)^{-1}$

i = fraction of oxidised ilmenite initially in the charge

Fu = fraction of unreacted material in the solid

V = capacity of reactor stage

v = solids flow rate

e = base of natural logarithms

W = weight of oxidised ilmenite initially in the charge

c = chlorine conversion expressed as a fraction of total chlorine flow

APPENDIX A

FIGURE A-1: SINGLE STAGE FLUIDISED BED REACTOR
Silica tube: bore 3", length 30", with
thermocouple entering from top.

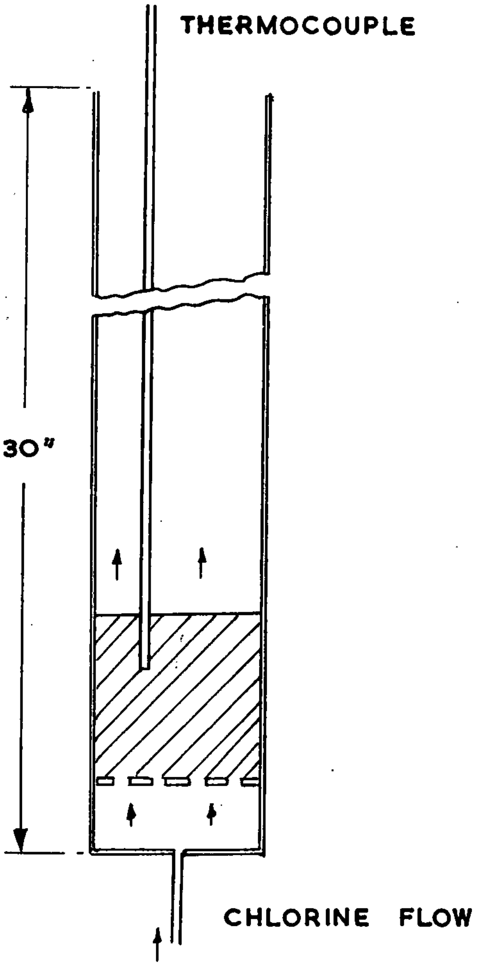
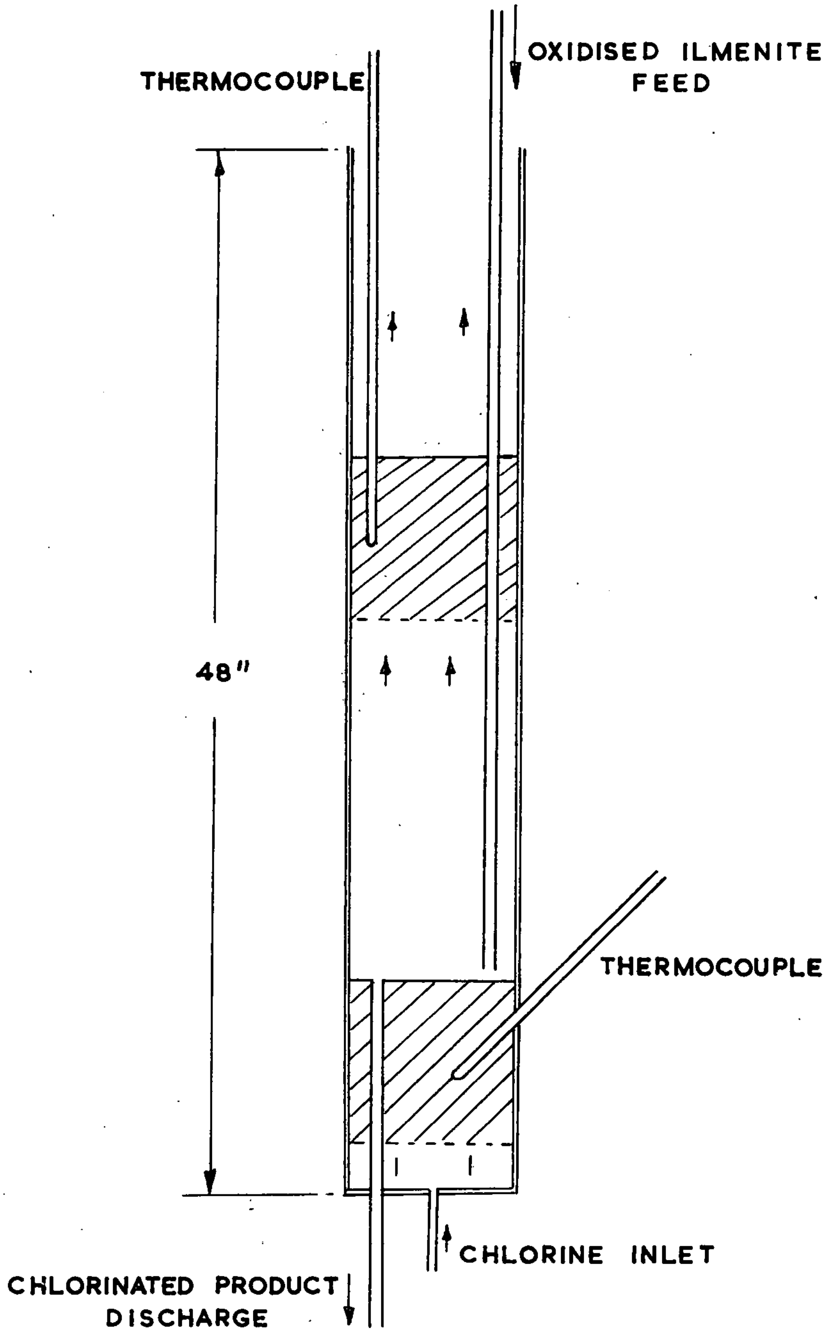


FIGURE A-2: TWO STAGE FLUIDISED BED REACTOR
Bottom stage fed and discharged continuously
with batch charge in top stage.



APPENDIX B

TABLE B-1: CHLORINATION TEST 1
Material: Oxidised Stradbroke Island Ilmenite
Charge: 725 g (L/D = 1 D = 2.75 in.)
Gas composition: 100 % chlorine
Flow: 0.0436 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1000°C

Time Min.	FeO %	Fe_2O_3 %	Reaction %	Cl_2 used %
0	nd[a]	46.6	nd	nd
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	4.3
300	-	11.8	84.7	8.2

(a) nd - not determined.

FIGURE B-1: CHLORINATION TEST 1
Material: Oxidised Stradbroke Island Ilmenite
Charge: 725 g (L/D = 1 D = 2.75 in.)
Gas Composition: Chlorine (pure)
Gas flow: 0.0436 g $(\text{in.})^{-2}$ $(\text{sec})^{-1}$
Temperature: 1000°C

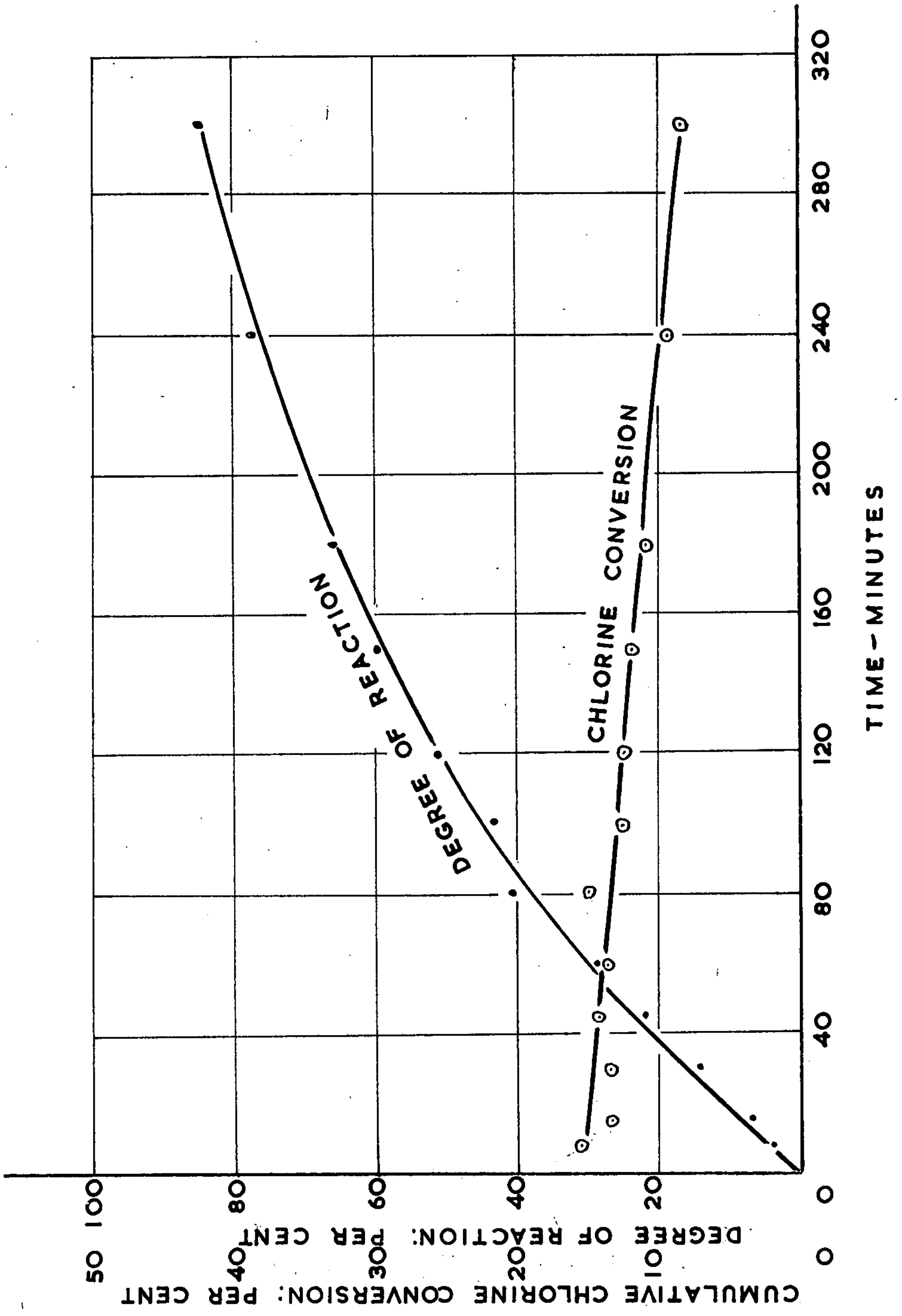


TABLE B-2: CHLORINATION TEST 2
Material: Oxidised Stradbroke Island Ilmenite
Charge: 725 g (L/D = 1 D = 2.75 in.)
Gas composition: 100 % chlorine
Flow: 0.0429 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1050°C

Time Min.	FeO %	Fe_2O_3 %	Reacted %	Cl_2 used %
0	nd[a]	46.8	nd	nd
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	93.39	13.2
240	-	2.2	97.44	12.01
270	-	0.10	99.89	10.96

(a) nd - not determined.

FIGURE B-2: CHLORINATION TEST 2
Material: Oxidised Stradbroke Island Ilmenite
Charge: 725 g (L/D = 1 D = 2.75 in.)
Gas composition: Chlorine (pure)
Gas flow: 0.0429 g $(\text{in.})^{-2}$ $(\text{sec})^{-1}$
Temperature: 1050°C

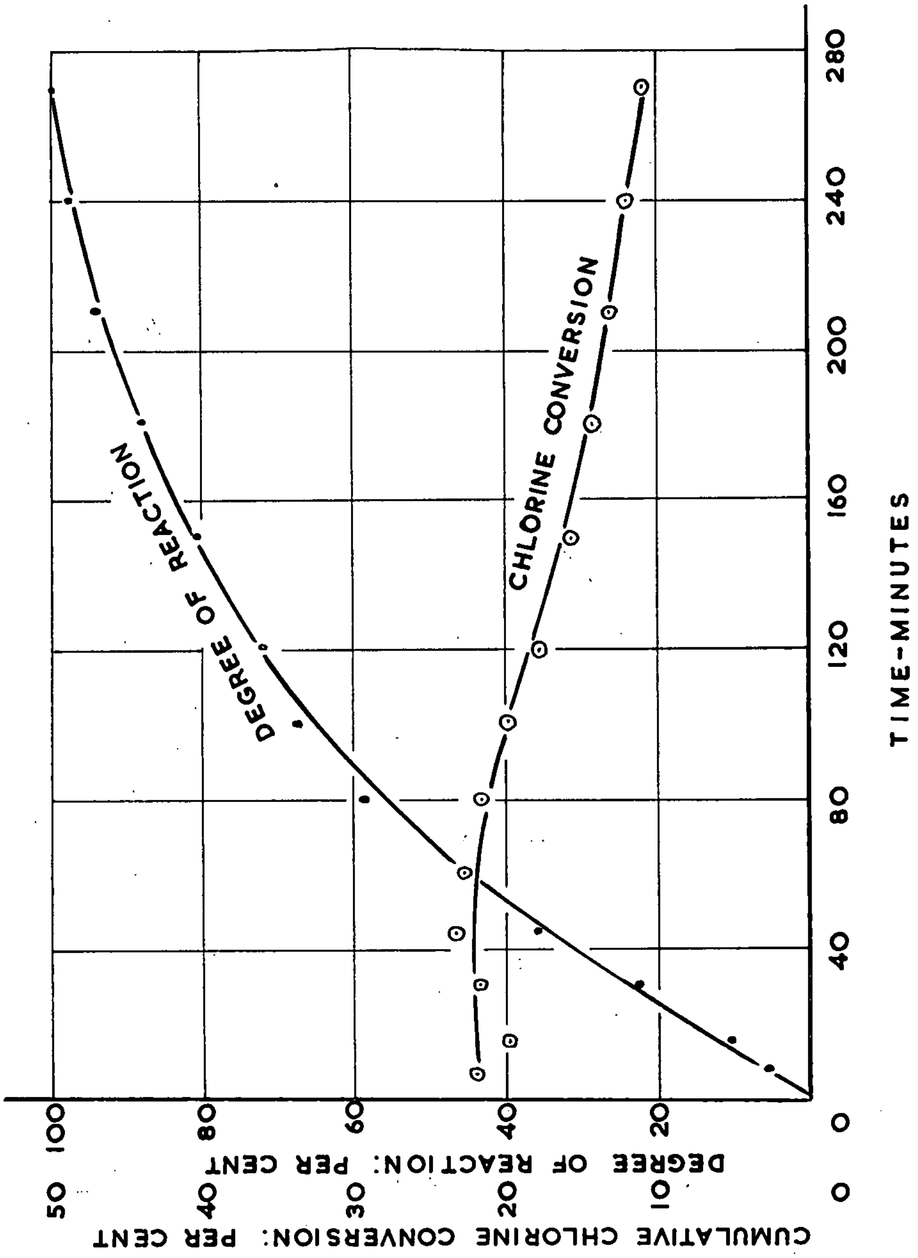


TABLE B-3: CHLORINATION TEST 3
Material: Oxidised Stradbroke Island Ilmenite
Charge: 725 g (L/D = 1 D = 2.75 in.)
Gas composition: 100% chlorine
Gas flow: 0.0429 g $(\text{in.})^{-2}$ $(\text{sec})^{-1}$
Temperature: 1100°C

Time Min.	FeO %	Fe_2O_3 %	Reaction %	Cl_2 used %
0	nd[a]	46.7	nd	nd
7.5	-	44.9	7.1	27.95
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	99.78	16.4
210	-	0.03	99.97	14.05
240	-	0.02	99.98	12.3
300	-	0.01	99.99	9.8

(a) nd - not determined.

FIGURE B-3 CHLORINATION TEST 3

Material: Oxidised Stradbroke Island Ilmenite
Charge: 725 g (L/D = 1 D = 2.75 in.)
Gas composition: 100% chlorine
Gas flow: 0.0429 g $(\text{in.})^{-2}$ $(\text{sec})^{-1}$
Temperature: 1100°C

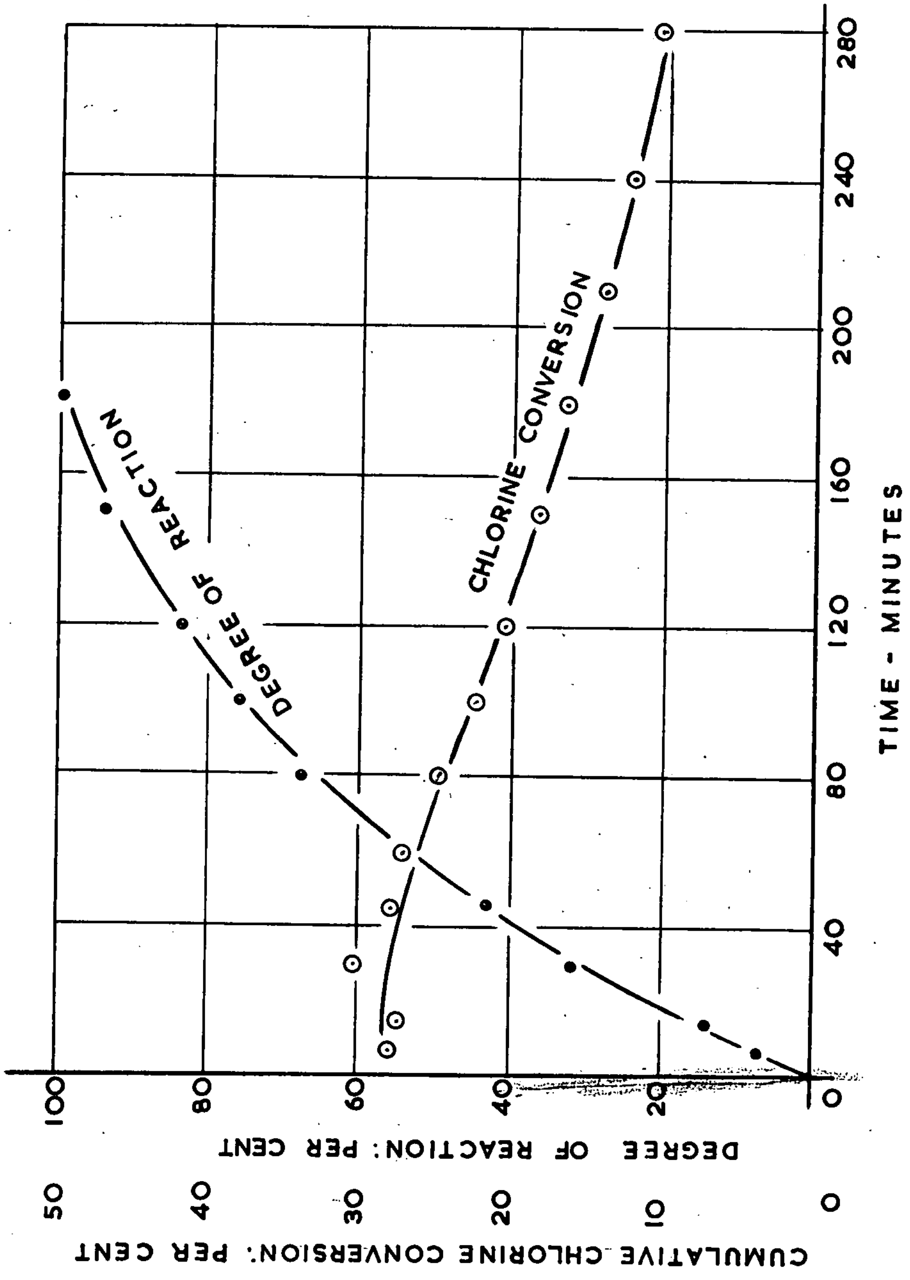


TABLE B-4: CHLORINATION TEST 4
Material: Oxidised Stradbroke Island Ilmenite
Charge: 725 g (L/D = 1, D = 2.75 in.)
Gas composition: 100% chlorine
Gas flow: 0.0429 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1150°C

Time Min.	FeO %	Fe_2O_3 %	Reaction %	Cl_2 used %
0	11.35	46.7	nd	nd
7.5	nd(a)	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
120	-	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

(a) nd - not determined.

FIGURE B-4: CHLORINATION TEST 4
Material: Oxidised Stradbroke Island Ilmenite
Charge: 725 g (L/D = 1, D = 2.75 in.)
Gas composition: 100% chlorine
Gas flow: 0.0429 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1150^{0}C

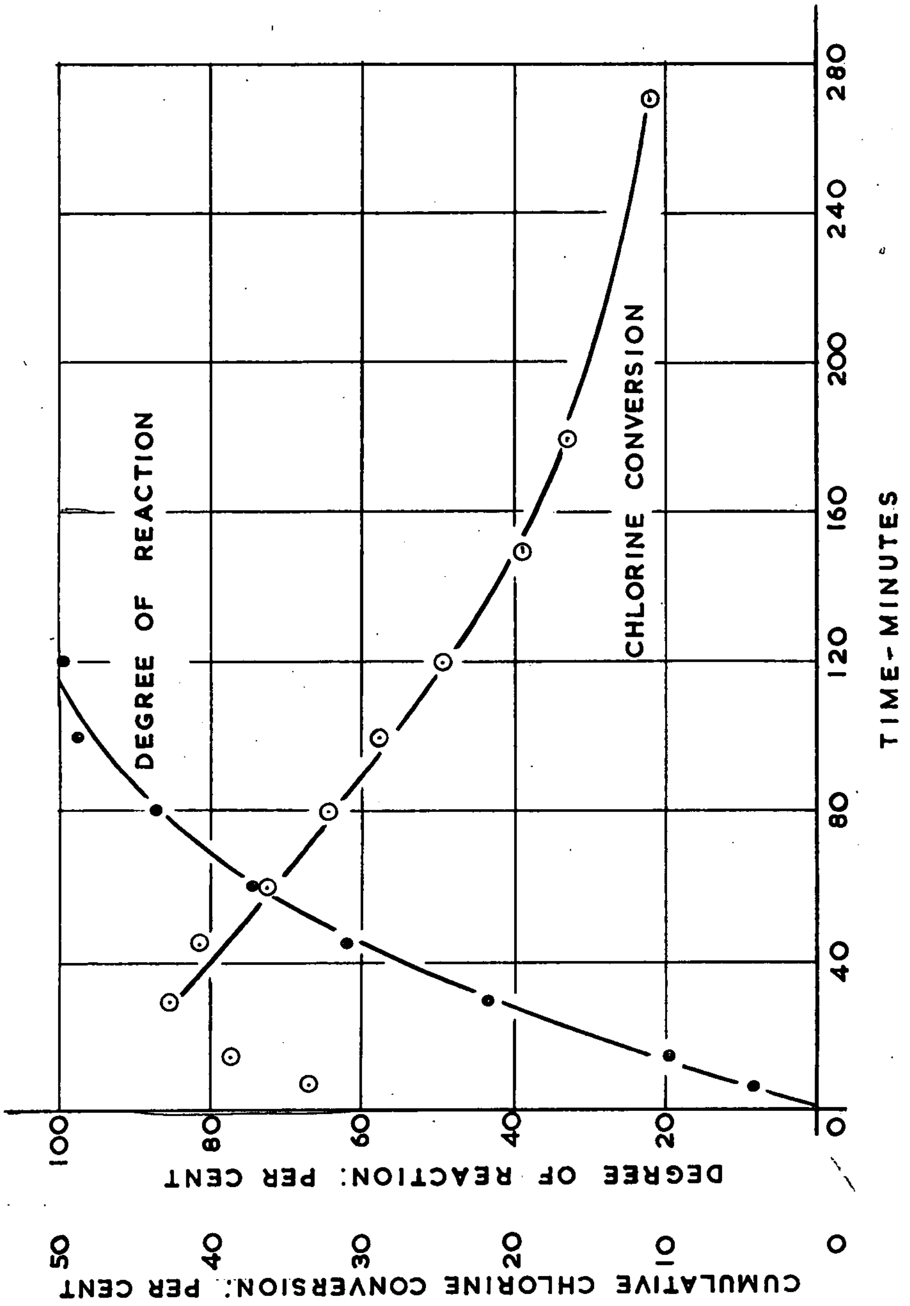


TABLE B-5: CHLORINATION TEST 5
Material: Oxidised Stradbroke Island Ilmenite
Charge: 725 g (L/D = 1, D = 2.75 in.)
Gas composition: 100% chlorine
Gas flow: 0.0427 g $(in.)^{-2}$ $(sec)^{-1}$
Temperature: 1175°C

Time Min.	Fe_2O_3 %	Reacted %	Cl_2 used %
0.	46.7	nd[(a)]	nd
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

(a) nd - not determined.

FIGURE B-5: CHLORINATION TEST 5
Material: Oxidised Stradbroke Island Ilmenite
Charge: 725 g (L/D = 1, D = 2.75 in.)
Gas composition: 100% chlorine
Gas flow: 0.0427 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1175°C

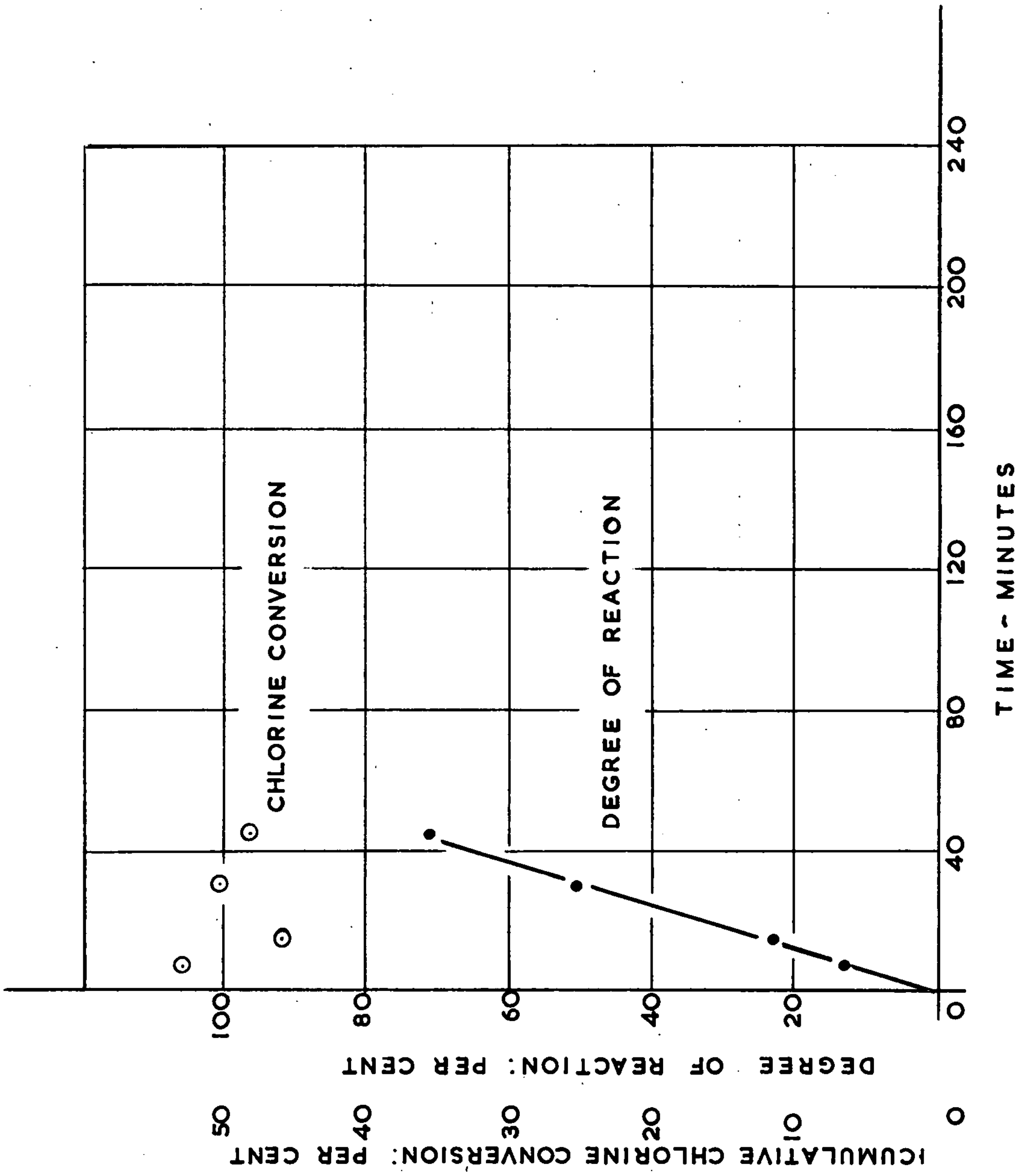


TABLE B-6: CHLORINATION TEST 6
Material: Oxidised Stradbroke Island Ilmenite
Charge: 725 g (L/D = 1, D = 2.75 in.)
Gas composition: 100% chlorine
Gas flow: 0.0620 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

Time Min.	Fe_2O_3 %	Reaction %	Ol_2 used %
0	47.0	nd(a)	nd
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	91.25	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

FIGURE B-6: CHLORINATION TEST 6
Material: Oxidised Stradbroke Island Ilmenite
Charge: 725 g (L/D = 1, D = 2.75 in.)
Gas composition: 100% chlorine
Gas flow: 0.0620 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

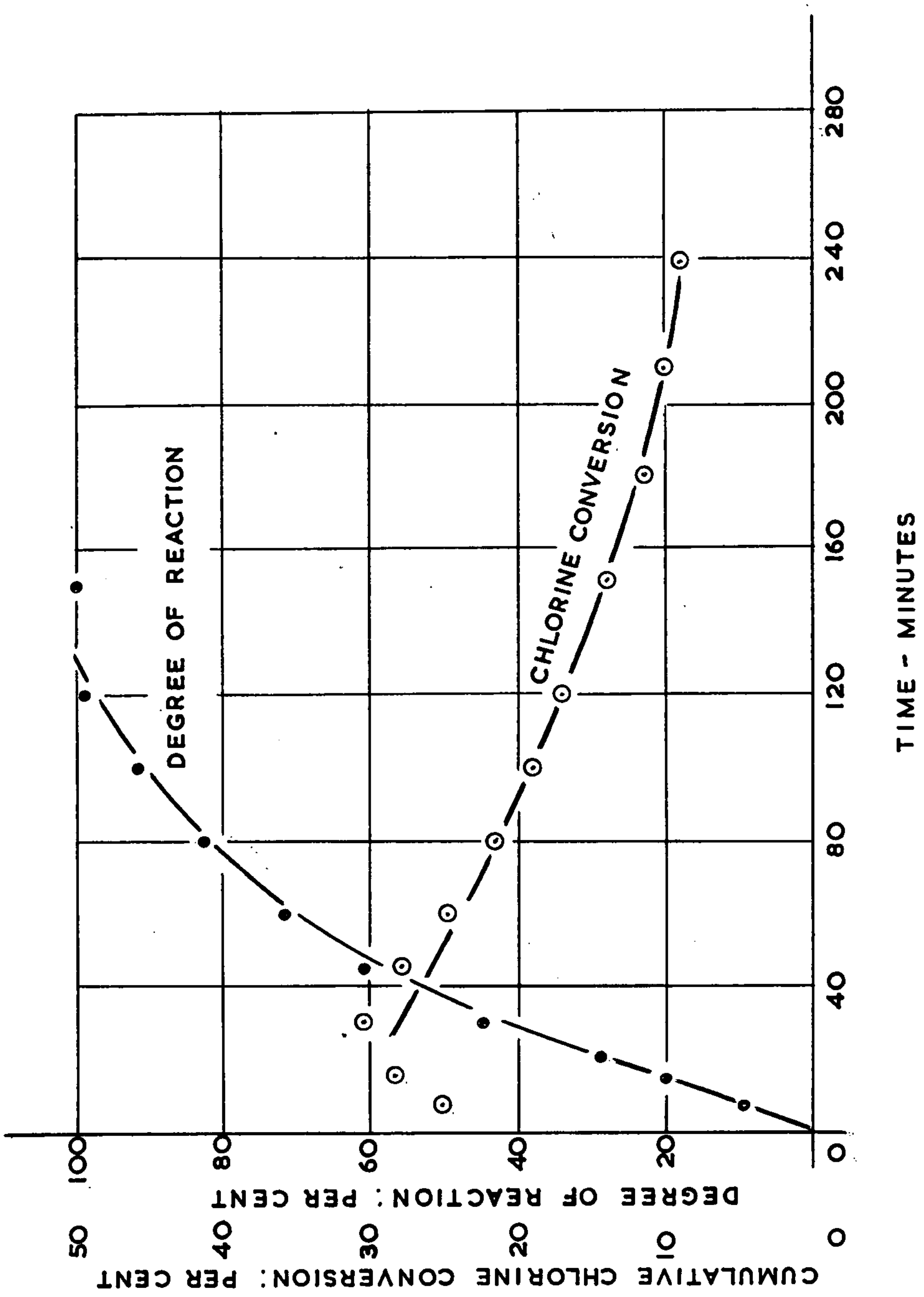


TABLE B-7: CHLORINATION TEST 7
Material: Oxidised Stradbroke Island Ilmenite
Charge: 725 g (L/D = 1, D = 2.75 in.)
Gas composition: 48% chlorine,
52% nitrogen by volume
Gas flow: 0.0185 g (in.)$^{-2}$ (sec)$^{-1}$ Cl_2,
0.0088 g (in.)$^{-2}$ (sec)$^{-1}$ N_2
Temperature: 1100°C

Time Min.	Fe_2O_3 %	Reaction %	Cl_2 used %
0	46.8	nd(a)	nd
15	45.3	5.8	26.5
30	42.7	15.3	34.9
45	40.6	22.3	34.0
60	37.6	31.5	36.0
80	33.4	43.2	37.0
100	29.9	51.5	35.3
120	25.0	60.3	34.4
150	21.0	69.8	31.9
180	16.2	78.1	29.8
240	10.1	87.3	24.9
285	4.8	94.32	22.7
330	0.67	99.24	20.6

(a) nd - not determined.

FIGURE B-7: CHLORINATION TEST 7
Material: Oxidised Stradbroke Island Ilmenite
Charge: 725 g (L/D = 1, D = 2.75 in.)
Gas composition: 48% chlorine,
52% nitrogen by volume.
Gas flow: 0.0185 g $(\text{in.})^{-2}$ $(\text{sec})^{-1}$ Cl_2,
0.0088 g $(\text{in.})^{-2}$ $(\text{sec})^{-1}$ N_2
Temperature: 1100°C

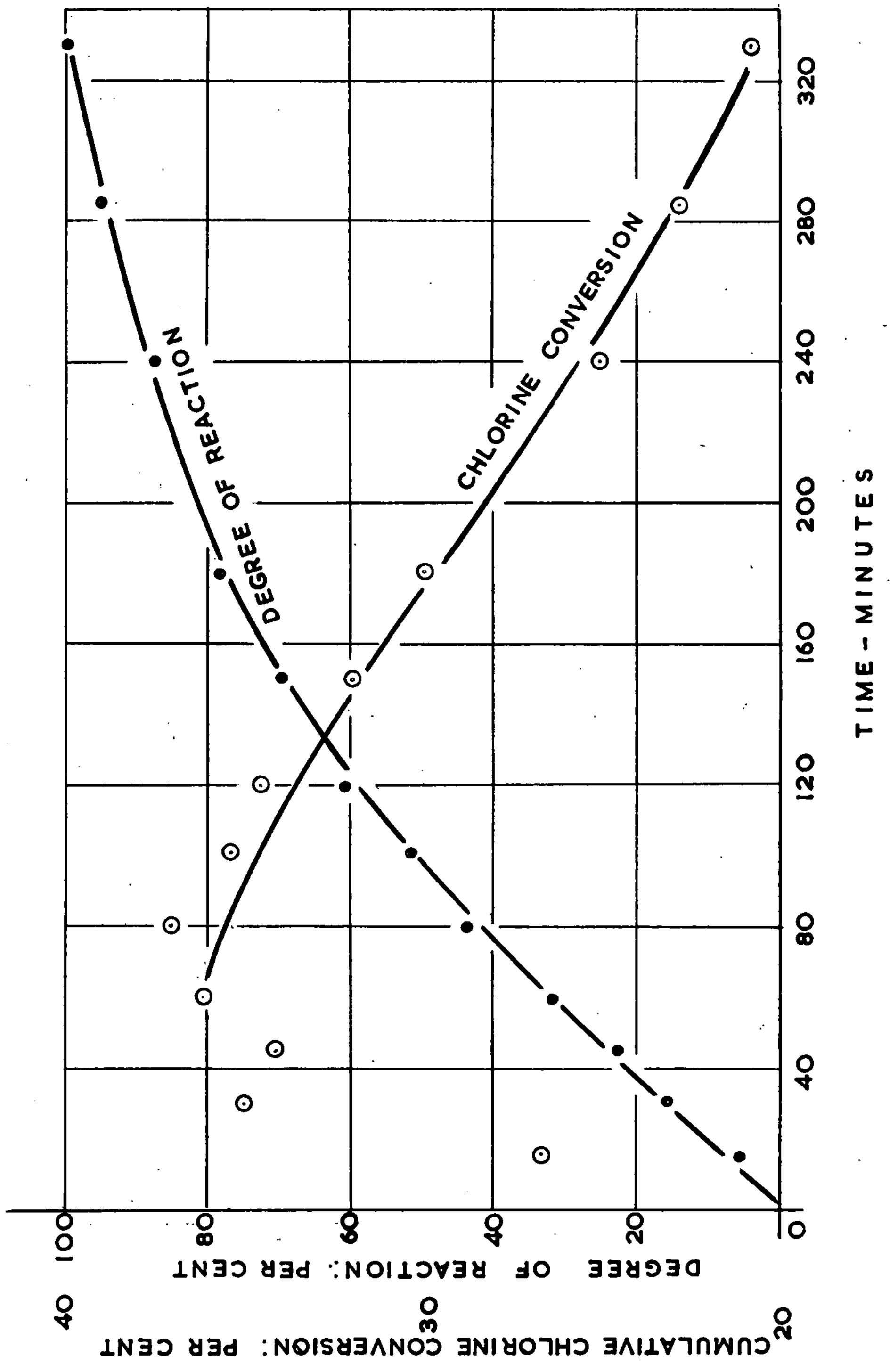


TABLE B-8: CHLORINATION TEST 8
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1450 g (L/D = 2, D = 2.75 in.)
Gas composition: 100% chlorine
Gas flow: 0.0434 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

Time Min.	Fe_2O_3 %	Reacted %	Cl_2 used %
0	46.9	nd[(a)]	nd
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	92.13	22.4
270	3.7	95.65	20.8
300	0.73	99.17	19.3

(a) nd - not determined.

FIGURE B-8: CHLORINATION TEST 8
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1450 g (L/D = 2, D = 2.75 in.)
Gas composition: 100% chlorine
Gas flow: 0.0434 g $(in.)^{-2}$ $(sec)^{-1}$
Temperature: 1100°C

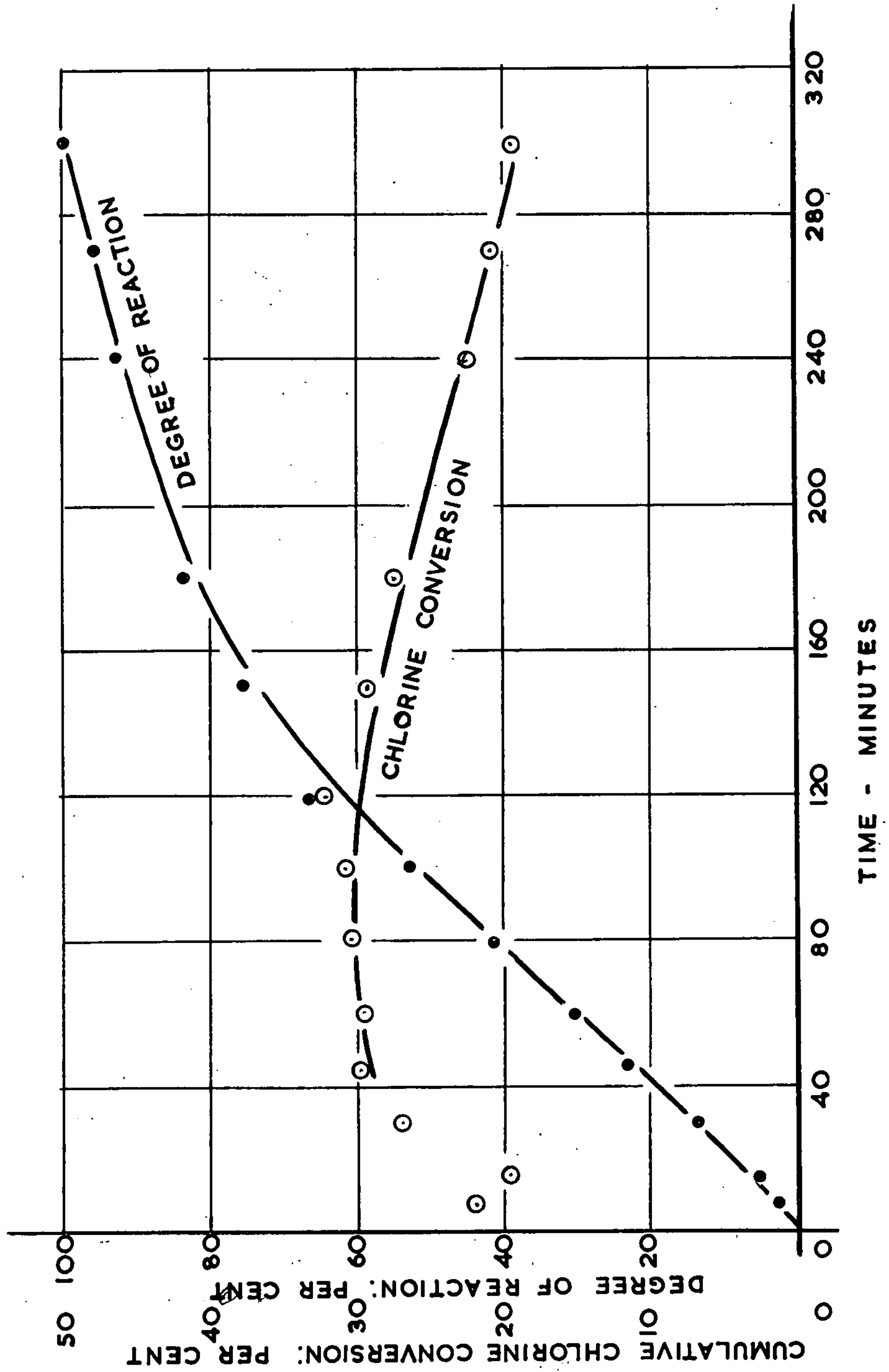


TABLE B-9: CHLORINATION TEST 9
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine (100%)
Gas flow: 0.0344 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

Time Min.	Fe_2O_3 %	Reaction %	Chlorine Utilization Cum. %
0	45.9	nd(a)	nd
7.5	44.9	4.0	22.4
15	43.0	11.1	31.0
30	39.3	23.7	33.1
45	34.0	39.3	36.6
60	27.3	55.7	39.0
80	20.7	69.2	36.3
100	14.2	80.5	33.8
120	8.75	88.7	31.0
150	3.75	95.4	26.7
180	0.15	99.8	23.3
210	nd	nd	20.0

(a) nd - not determined.

FIGURE B-9: CHLORINATION TEST 9
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine (100%)
Gas flow: 0.344 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

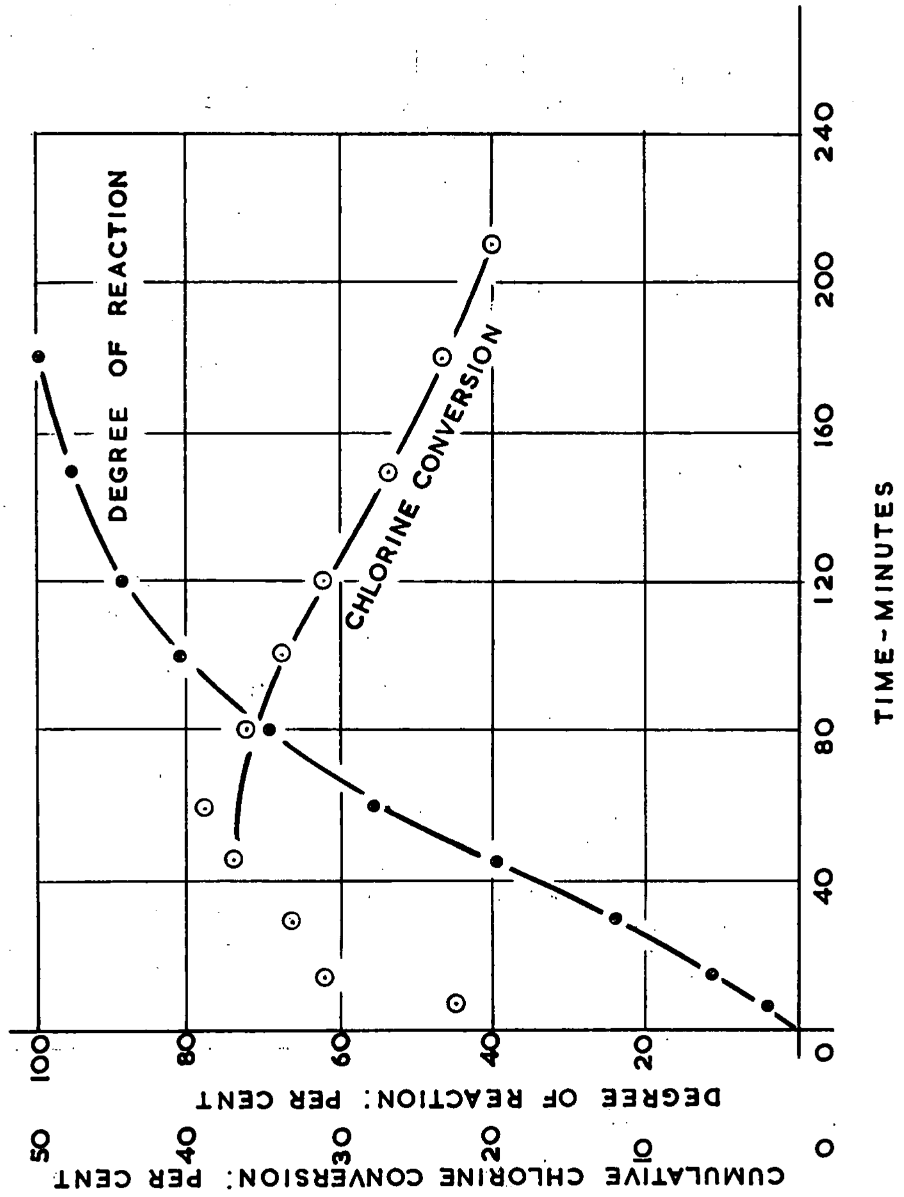


TABLE B-10: CHLORINATION TEST 10
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: chlorine (100%)
Gas flow: 0.0343 g $(in.)^{-2}$ $(sec)^{-1}$
Temperature: 1100°C

Time Min.	Fe_2O_3 %	Reaction %	Chlorine used %
0	46.7	nd[a]	nd
7.5	45.6	4.3	24.6
15	44.0	10.3	29.4
30	40.7	21.7	31.0
45	35.6	36.9	35.1
60	29.0	53.4	38.1
80	20.7	70.2	37.6
100	14.6	80.5	34.5
120	10.0	87.3	31.2
150	3.80	95.5	27.3
180	0.090	99.9	23.8
210	0.052	99.9	20.4
240	0.041	99.9	17.8
270	0.050	99.9	15.9

(a) nd - not determined.

FIGURE B-10: CHLORINATION TEST 10
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: chlorine (100%)
Gas flow: 0.0343 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

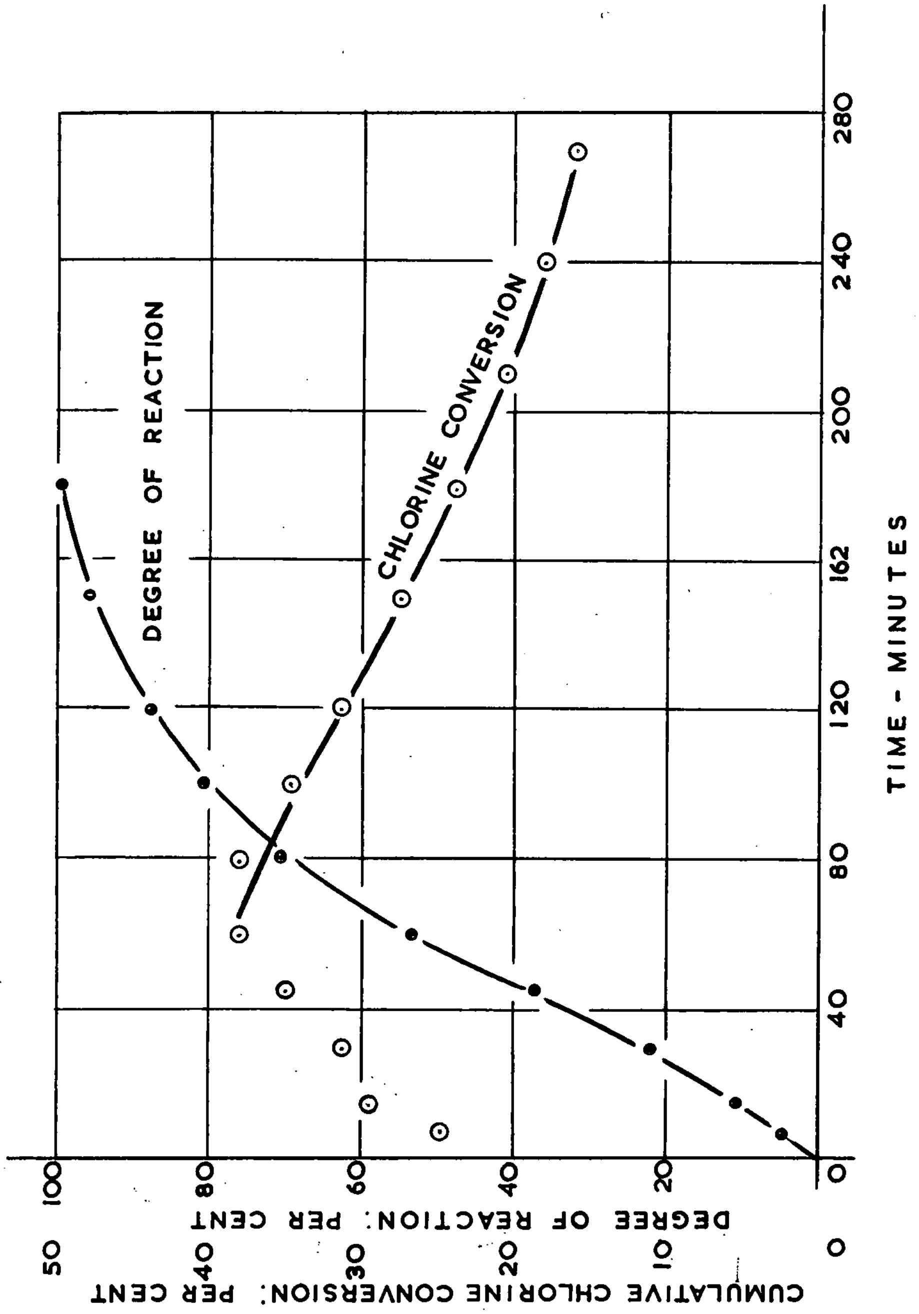


TABLE B-11: CHLORINATION TEST 11
Material: Oxidised Stradbroke Island Ilmenite $^{-52}/_{+72}$ mesh
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine (pure)
Gas flow: 0.0344 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

Time Min.	Fe_2O_3 %	Reaction %	Chlorine used %
0	49.4	nd[a]	nd
8.5	47.7	6.6	35.1
15	46.4	11.3	34.0
30	43.2	22.1	33.3
45	39.4	33.3	33.4
60	34.5	46.0	34.6
80	29.3	57.5	32.5
100	23.6	68.3	30.8
120	21.4	72.1	27.1
150	15.4	81.3	24.5
180	1.58	98.3	24.7
210	0.032	99.9	21.5
240	0.014	100.0	18.8
270	0.013	100.0	16.7

(a) nd - not determined.

FIGURE B-11: CHLORINATION TEST 11
Material: Oxidised Stradbroke Island Ilmenite $^{-52}/_{+72}$ mesh
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine (pure)
Gas flow: 0.0344 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

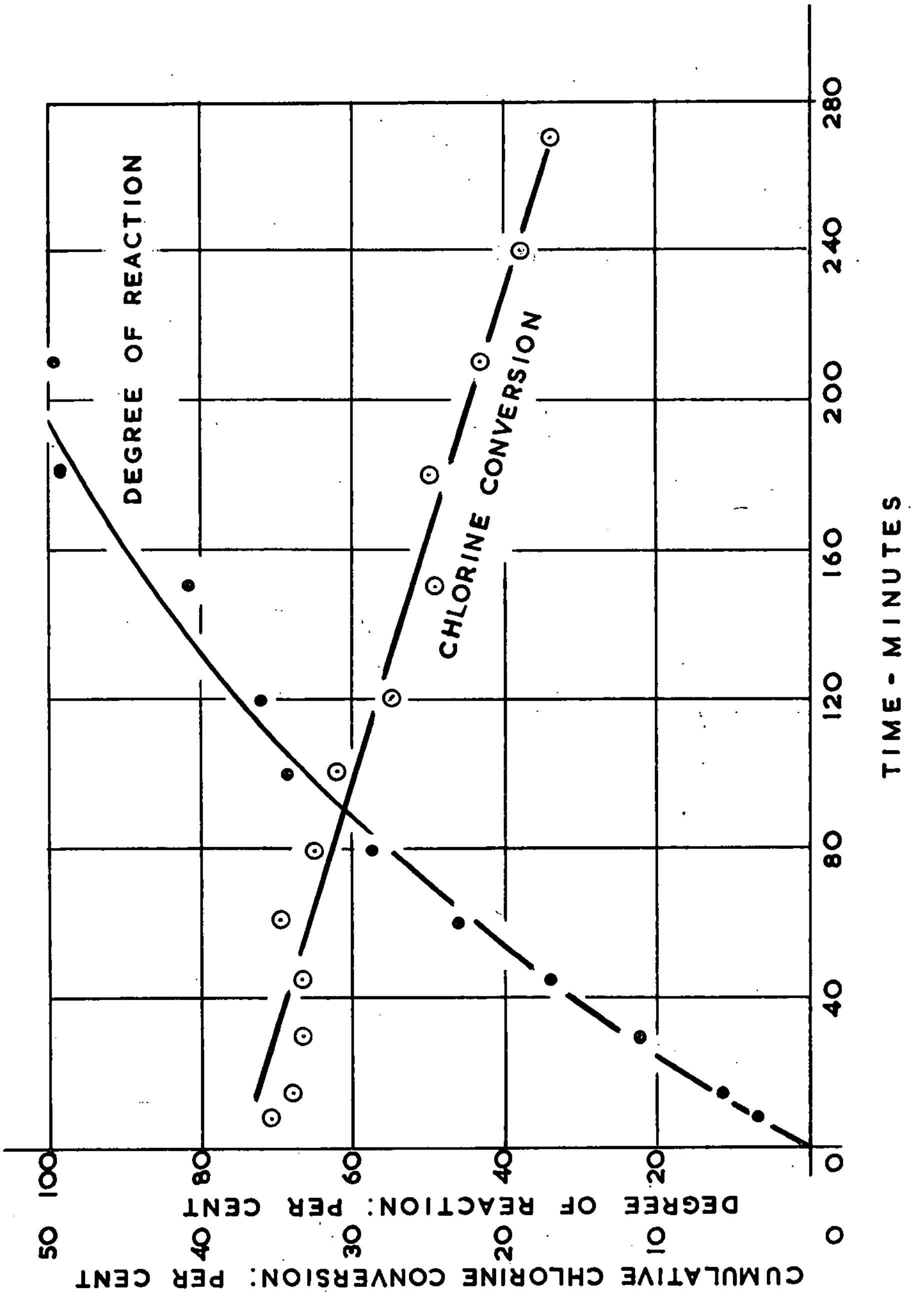


TABLE B-12: CHLORINATION TEST 12
Material: Oxidised Stradbroke Island Ilmenite, $^{-150}/_{+200}$ mesh
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine (100%)
Gas flow: 0.0342 g $(in.)^{-2}$ $(sec)^{-1}$
Temperature: 1100°C

Time Min.	Fe_2O_3 %	Reaction %	Chlorine used %
0	47.8	nd(a)	nd
7.5	47.2	2.4	14.0
15	45.6	8.5	24.9
25	42.6	19.0	33.4
40	36.6	37.0	36.1
60	31.7	49.3	36.1
80	25.2	63.2	34.7

(a) nd - not determined.

FIGURE B-12: CHLORINATION TEST 12
Material: Oxidised Stradbroke Island Ilmenite, $-150/+200$ mesh
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine (100%)
Gas flow: 0.0342 g $(\text{in.})^{-2}$ $(\text{sec})^{-1}$
Temperature: 1100°C

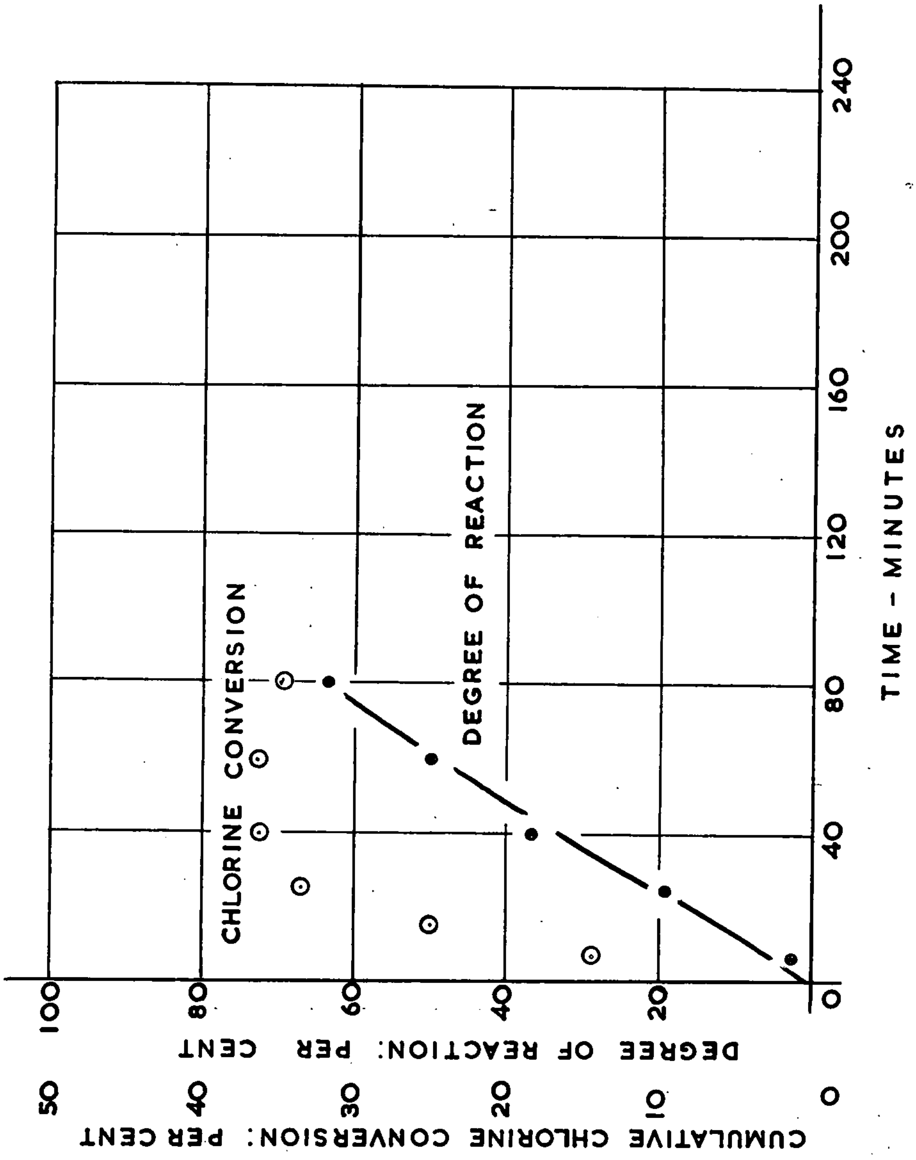


TABLE B-13: CHLORINATION TEST 13
Material: Oxidised Stradbroke Island Ilmenite
-150/+200-mesh
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine (100%)
Gas flow: 0.0383 g $(\text{in.})^{-2}$ $(\text{sec})^{-1}$
Temperature, 1100°C

Time Min.	Fe_2O_3 %	Reaction %	Chlorine used %
0	47.8	nd(a)	nd
7.5	46.5	5.1	26.6
15	44.6	12.1	31.6
30	40.4	26.0	33.9
45	34.8	41.7	36.3
60	30.9	51.2	33.4
80	23.7	66.1	32.3

FIGURE B-13: CHLORINATION TEST 13
Material: Oxidised Stradbroke Island Ilmenite
-150/+200-mesh
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine (100%)
Gas flow: 0.0383 g $(\text{in.})^{-2}$ $(\text{sec})^{-1}$
Temperature: 1100°C

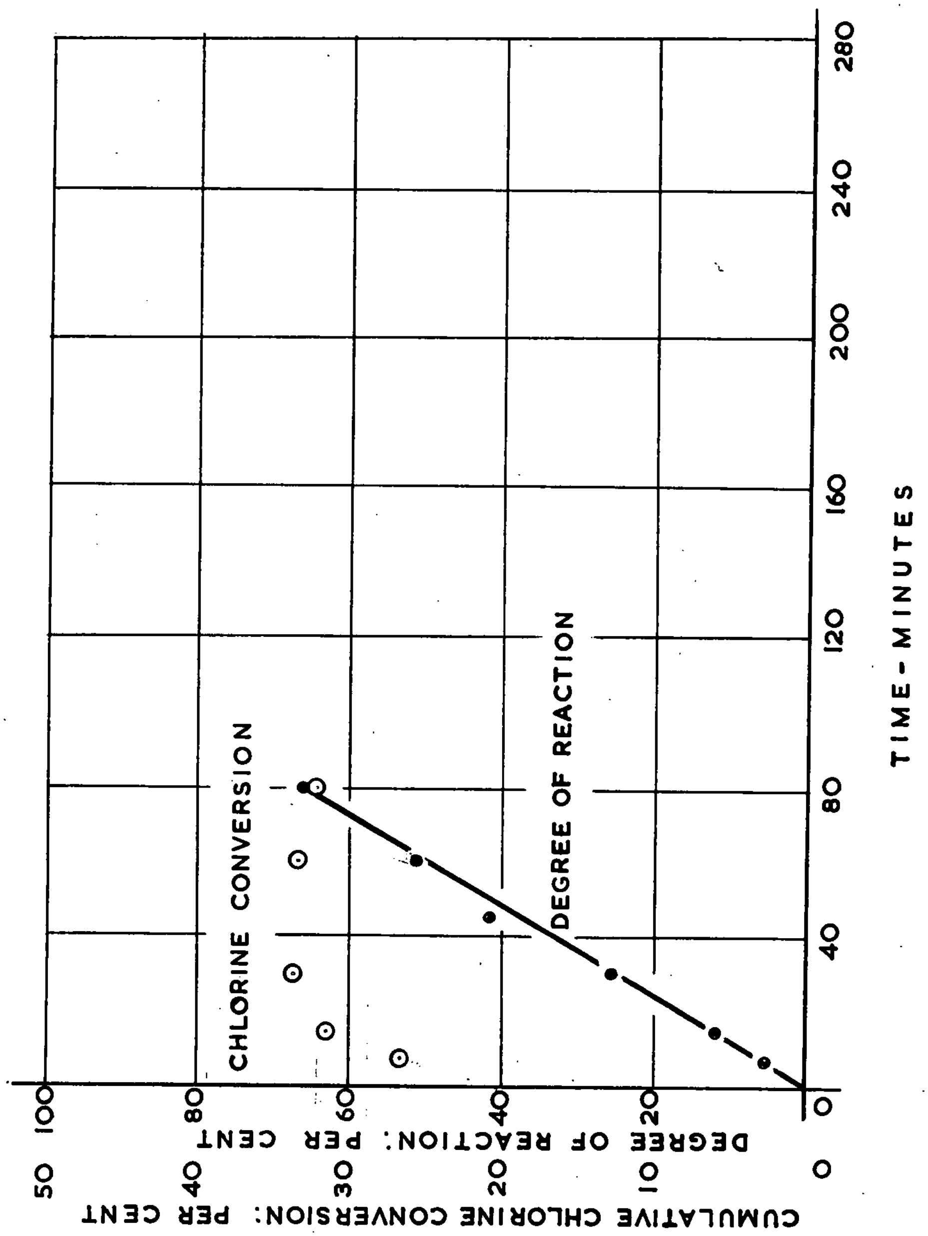


TABLE B-14: CHLORINATION TEST 14
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine (100%)
Gas flow: 0.0441 g (in.)$^{-2}$ sec)$^{-1}$
Temperature: 1100°C

	Screen Fraction				Unsized
	-52/+72	+100	+150	+200	
Head sample:					
Screen analysis %	7.9	23.3	40.1	28.6	
Fe_2O_3 %	48.4	47.7	45.5	47.1	46.6
Chlorination time - min.	Grade - Fe_2O_3 %				
20	43.4	43.7	41.3	41.6	42.1
40	35.6	37.5	33.9	34.3	35.0
60	27.5	27.4	25.1	25.6	25.9
90	18.0	19.7	16.2	14.1	16.5
120	11.4	11.3	7.3	5.8	8.1
180	1.39	0.63	0.21	0.24	0.41
Chlorination time - min.	Degree of Reaction %				
20	18.25	14.9	15.7	20.0	16.7
40	41.0	34.2	38.6	41.4	38.3
60	59.6	58.6	59.9	61.3	59.9
90	76.6	73.1	76.8	81.6	77.4
120	86.3	86.0	90.6	93.1	89.9
180	98.5	99.3	99.7	99.7	99.5
Chlorination time - min.	Chlorine used %				
20	2.5	5.9	10.2	9.6	27.7
40	2.8	6.8	12.5	9.9	31.8
60	2.7	7.7	6.4	5.7	33.2
90	2.3	6.4	11.1	9.8	28.6
120	2.0	5.7	9.8	7.4	24.9
180	1.5	4.4	7.2	5.3	18.4

FIGURE B-14: CHLORINATION TEST 14
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine (100%)
Gas flow: 0.0441 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

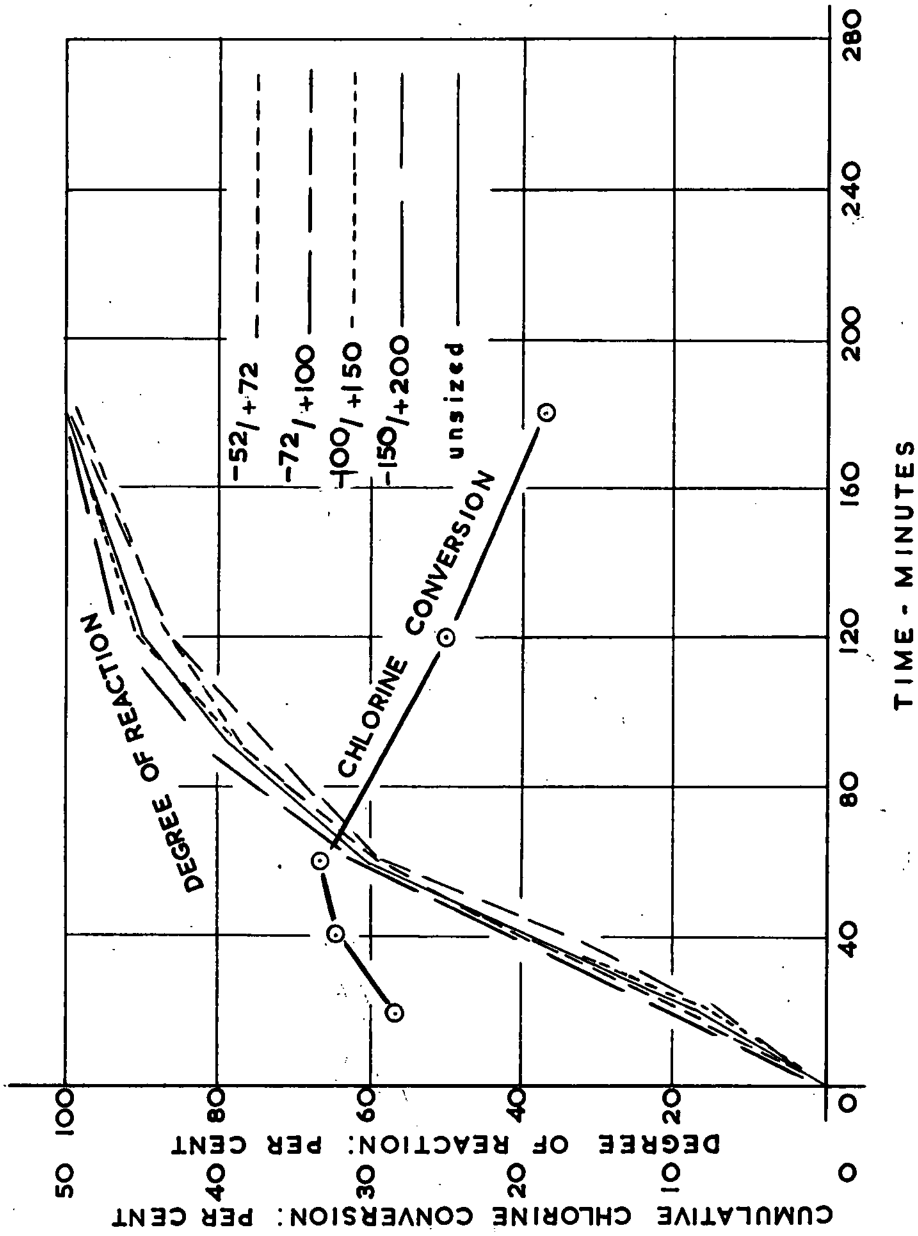


TABLE B-15: CHLORINATION TEST 15
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine (100%)
Gas flow: 0.0434 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

Time Min.	Fe_2O_3 %	Reaction %	Chlorine used %
0	46.8	nd[a]	nd
7.5	44.9	7.4	33.4
15	43.4	12.8	28.9
30	38.8	27.9	31.5
45	33.1	43.7	32.9
60	27.5	56.9	32.1
80	23.2	65.6	29.6
100	13.2	82.7	28.0
120	8.4	89.5	25.3
150	3.6	95.7	21.6
180	0.02	99.9	18.8
210	0.02	99.9	16.1
240	0.02	99.9	14.1

(a) nd - not determined.

FIGURE B-15: CHLORINATION TEST 15
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine (100 %)
Gas flow: 0.0434 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

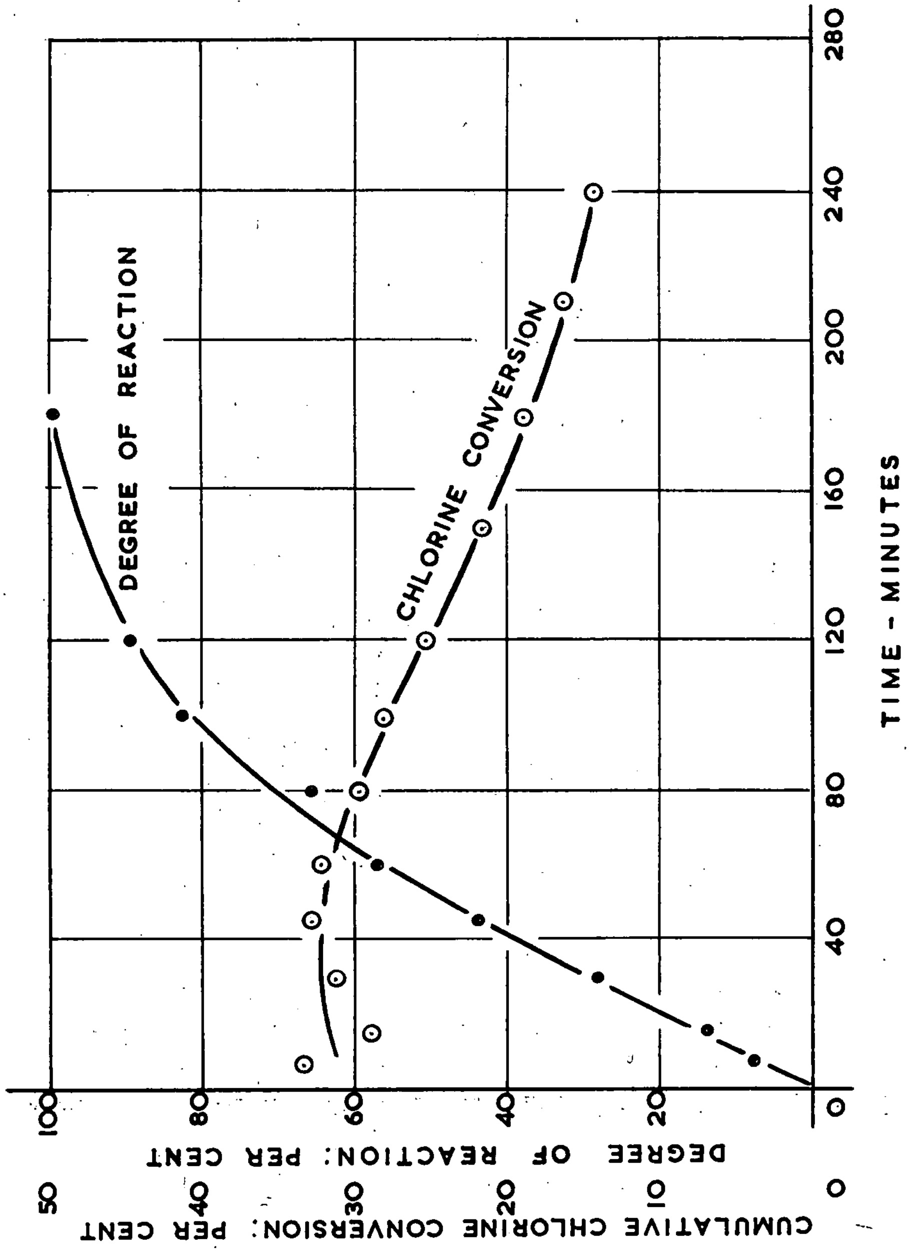


TABLE B-16: CHLORINATION TEST 16
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine (100%)
Gas flow: 0.0437 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

Time Min	Fe_2O_3 %	Reaction %	Chlorine used %
0	46.4	nd[(a)]	nd
7.5	45.0	5.49	24.5
15	42.7	13.9	31.0
30	37.9	29.5	32.9
45	32.7	43.9	32.6
60	27.1	57.1	31.8
80	19.6	71.8	30.0
100	14.0	81.2	27.2
120	10.5	87.2	24.3
150	5.6	93.1	20.8
180	0.28	99.68	18.5
210	0.017	99.98	15.9
240	0.016	99.98	13.9

(a) nd - not determined.

FIGURE B-16: CHLORINATION TEST 16
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine (100%)
Temperature: 1100°C

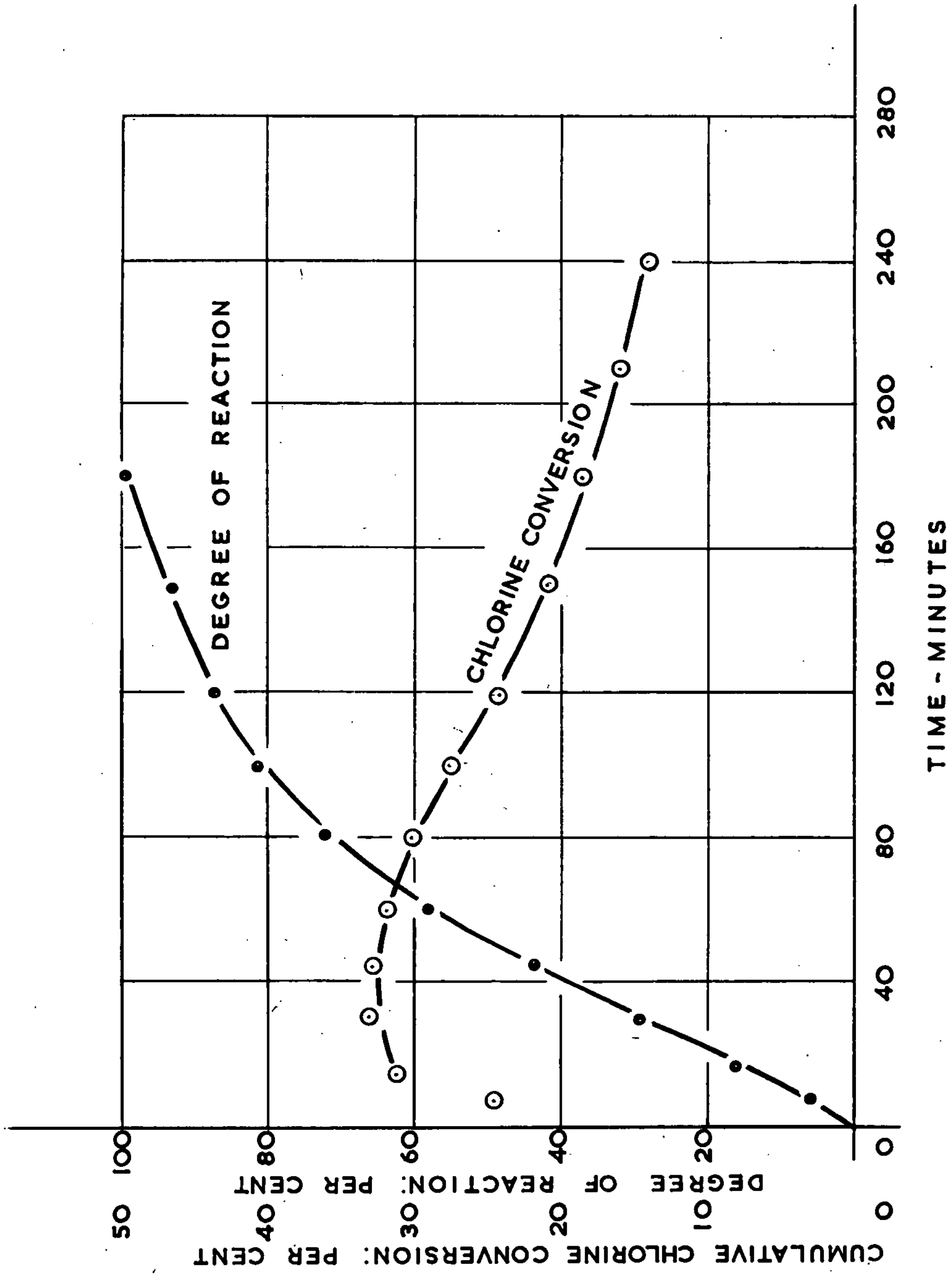


TABLE B-17: CHLORINATION TEST 17

Material: Oxidised Stradbroke Island Ilmenite and rutile residue ex oxidised Stradbroke Is. ilmenite, mixture 75/25 by volume

Charge: 777 g oxidised ilmenite (bulk density 2.70 g/ml)
133 g rutile (bulk density 1.38 g/ml)
910 g mixture (L/D = 1, D = 3 in.)

Gas composition: Chlorine (100%)

Gas flow: 0.0442 g $(\text{in.})^{-2}$ $(\text{sec})^{-1}$

Temperature: 1100°C

Time Min.	Fe_2O_3 %	Reaction %	Chlorine used %
0	39.8	nd[(a)]	nd
7.5	37.8	8.1	27.9
15	35.1	18.2	31.3
30	27.5	42.6	36.6
45	19.9	62.4	34.9
60	13.8	75.8	32.6
90	5.55	91.1	26.1
120	0.15	99.8	21.5
150	0.039	99.94	17.2

(a) nd - not determined.

FIGURE B-17: CHLORINATION TEST 17

Material: Oxidised Stradbroke Island Ilmenite and Rutile Residue ex Oxidised Stradbroke Island Ilmenite, mixture 75/25 by volume

Charge:
777 g oxidised ilmenite (bulk density 2.70 g/ml)
133 g rutile (bulk density 13.8 g/ml)
910 g mixture (L/D = 1, D = 3 in.)

Gas composition: Chlorine (100%)

Gas flow: $0.0442\ g\ (in.)^{-2}\ (sec)^{-1}$

Temperature: 1100°C

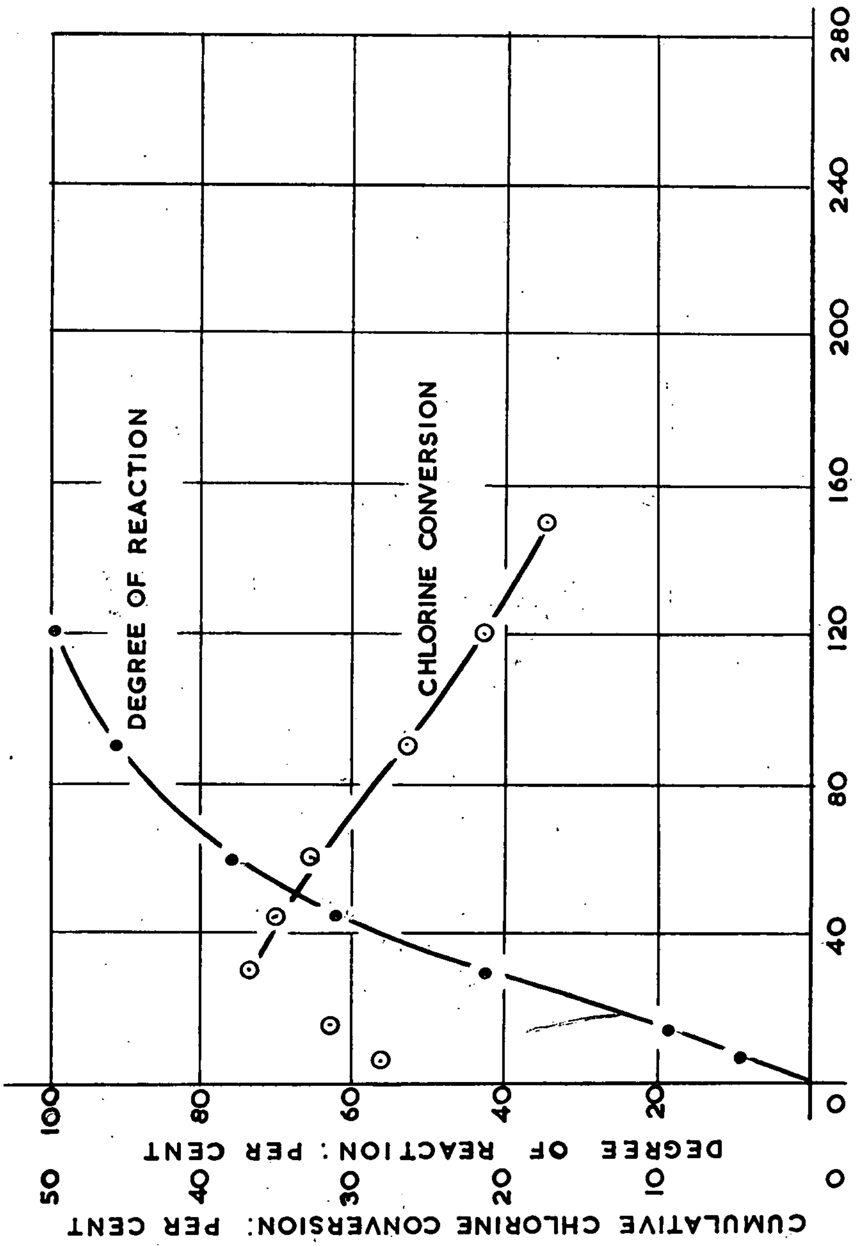


TABLE B-18: CHLORINATION TEST 18

Material: Oxidised Stradbroke Island Ilmenite and Rutile Residue ex Oxidised Stradbroke Island Ilmenite.
Mixture 50/50 by volume.

Charge:
500 g ilmenite (bulk density 2.70 g/ml)
255 g residue (bulk density 1.38 g/ml)
755 g mixture (L/D - 1, D - 3 in.)

Gas composition: Chlorine (100%)
Gas flow: 0.0435 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

Time Min.	FeO %	Fe_2O_3 %	Reaction %	Chlorine used %
0	0.62	31.3	nd[(a)]	nd
7.5	-	28.5	12.5	28.5
15	-	24.7	28.0	31.9
30	-	15.2	60.6	34.5
45	-	10.4	74.5	28.3
60	-	5.75	86.6	24.7
80	-	0.66	98.5	21.0
100	-	0.38	99.1	16.9
120	-	0.12	99.7	14.2
150	-	0.005	100.0	11.4
180	-	* 0.005	-	-

* Less than.
(a) nd - not determined.

FIGURE B-18: CHLORINATION TEST 18

Material: Oxidised Stradbroke Island Ilmenite and Rutile Residue ex Oxidised Stradbroke Island Ilmenite
Mixture 50/50 by volume.
Charge: 500 g ilmenite (bulk density 2.70 g/ml)
255 g residue (bulk density 1.38 g/ml)
755 g mixture (L/D = 1, D = 3 in.)
Gas composition: Chlorine (100%)
Gas flow: 0.0435 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

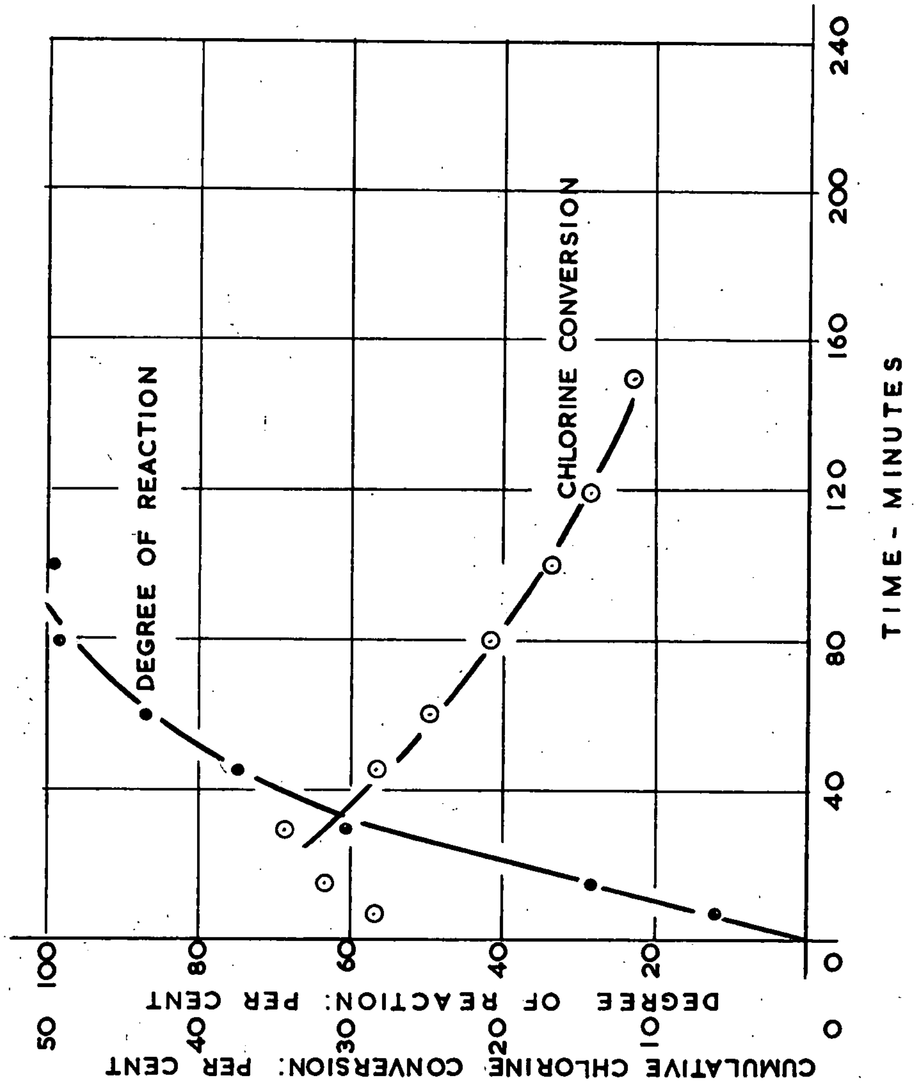


TABLE B-19: CHLORINATION TEST 19

Material: Oxidised Stradbroke Island Ilmenite and Rutile Residue ex Oxidised Stradbroke Is. Ilmenite, mixture 25/75 by volume

Charge:	250 g	ilmenite	(bulk density 2.70 g/ml)
	382 g	residue	(bulk density 1.38 g/ml)
	632 g	mixture	(L/D = 1, D = 3 in.)

Gas composition: Chlorine (100%)

Gas flow: 0.0435 g (in.)$^{-2}$ (sec)$^{-1}$

Temperature: 1100°C

Time Min.	Fe_2O_3 %	Reaction %	Chlorine used %
0	18.0	nd[(a)]	nd
7.5	13.4	29.5	32.3
15	10.4	47.1	25.8
30	4.4	79.0	21.7
45	0.51	97.7	17.9
60	0.018	99.9	13.7
80	0.012	99.9	10.3
100	0.005	100.0	8.2
120	0.006	-	-

(a) nd - not determined.

FIGURE B-19: CHLORINATION TEST 19

Material:	Oxidised Stradbroke Island Ilmenite and Rutile Residue ex Oxidised Stradbroke Is. Ilmenite, mixture 25/75 by volume.		
Charge:	250 g	ilmenite	(bulk density 2.70 g/ml)
	382 g	residue	(bulk density 1.38 g/ml)
	632 g	mixture	(L/D = 1, D = 3 in.)

Gas composition: Chlorine (100%)
Gas flow: 0.0435 g $(\text{in.})^{-2}$ $(\text{sec})^{-1}$
Temperature: 1100°C

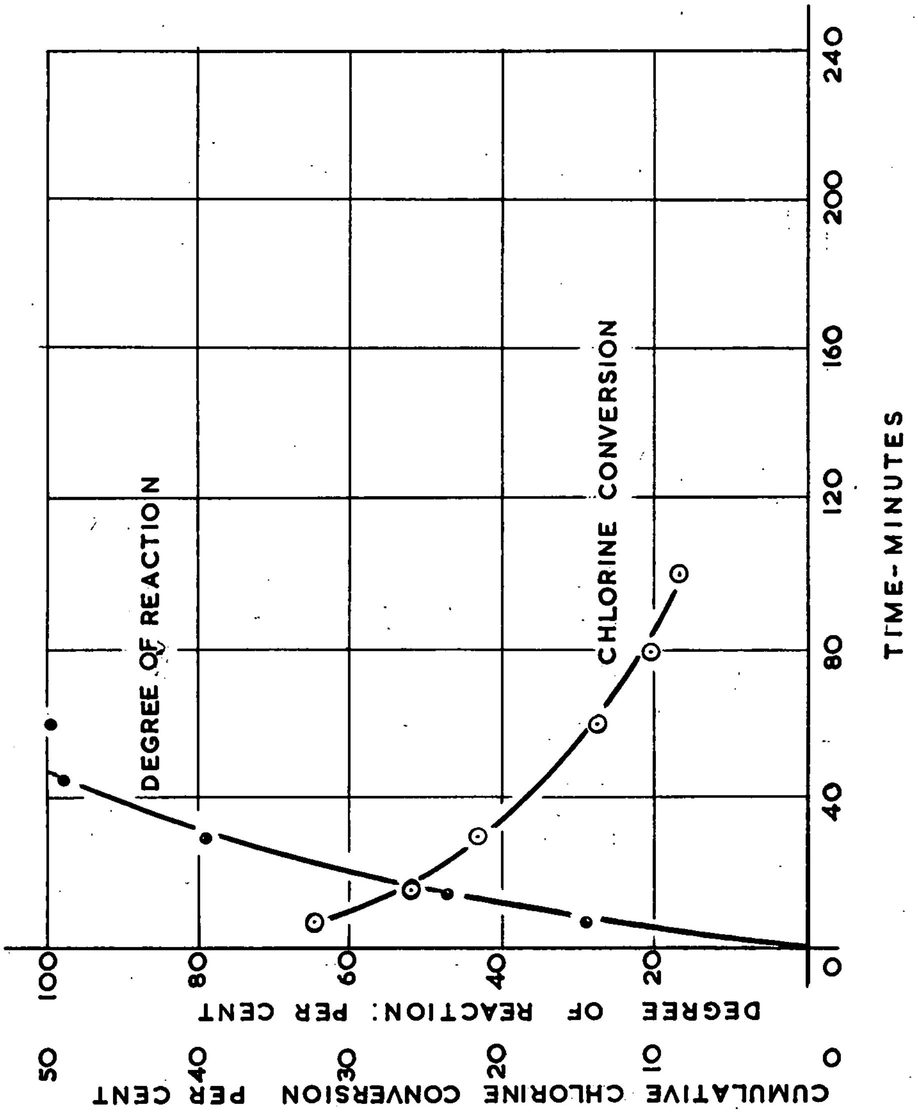


TABLE B-20: CHLORINATION TEST 20

Material: Oxidised Stradbroke Island Ilmenite and Rutile Residue ex Oxidised Stradbroke Is. Ilmenite, mixture 12.5/87.5 by volume

Charge:	125 g	ilmenite	(bulk density 2.70 g/ml)
	447 g	rutile	(bulk density 1.38 g/ml)
	572 g	mixture	(L/D = 1, D = 3 in.)

Gas composition: Chlorine (100%)

Gas flow: 0.0433 g (in.)$^{-2}$ (sec)$^{-1}$

Temperature: 1100°C

Time Min.	Fe_2O_3 %	Reaction %	Chlorine used %
0	12.5	nd[(a)]	nd
6	10.3	19.6	17.0
10	8.35	36.2	18.8
16	7.05	46.9	15.2
20	6.05	54.9	14.3
25	4.60	66.2	13.8
30	3.10	77.6	13.4
35	2.00	85.7	12.7
40	0.84	94.1	12.2
45	0.27	98.1	11.3
50	0.064	99.55	10.3
60	0.026	99.82	8.64
70	0.029	99.80	7.41
100	0.016	99.89	5.19

(a) nd - not determined.

FIGURE B-20: CHLORINATION TEST 20
Material: Oxidised Stradbroke Island Ilmenite and
Rutile Residue ex Oxidised Stradbroke Is.
Ilmenite, mixture 12.5/87.5 by volume.
Charge: 125 g ilmenite (bulk density 2.70 g/ml)
447 g rutile (bulk density 1.38 g/ml)
572 g mixture (L/D = 1, D = 3 in.)
Gas composition: Chlorine (100%)
Gas flow: 0.0433 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

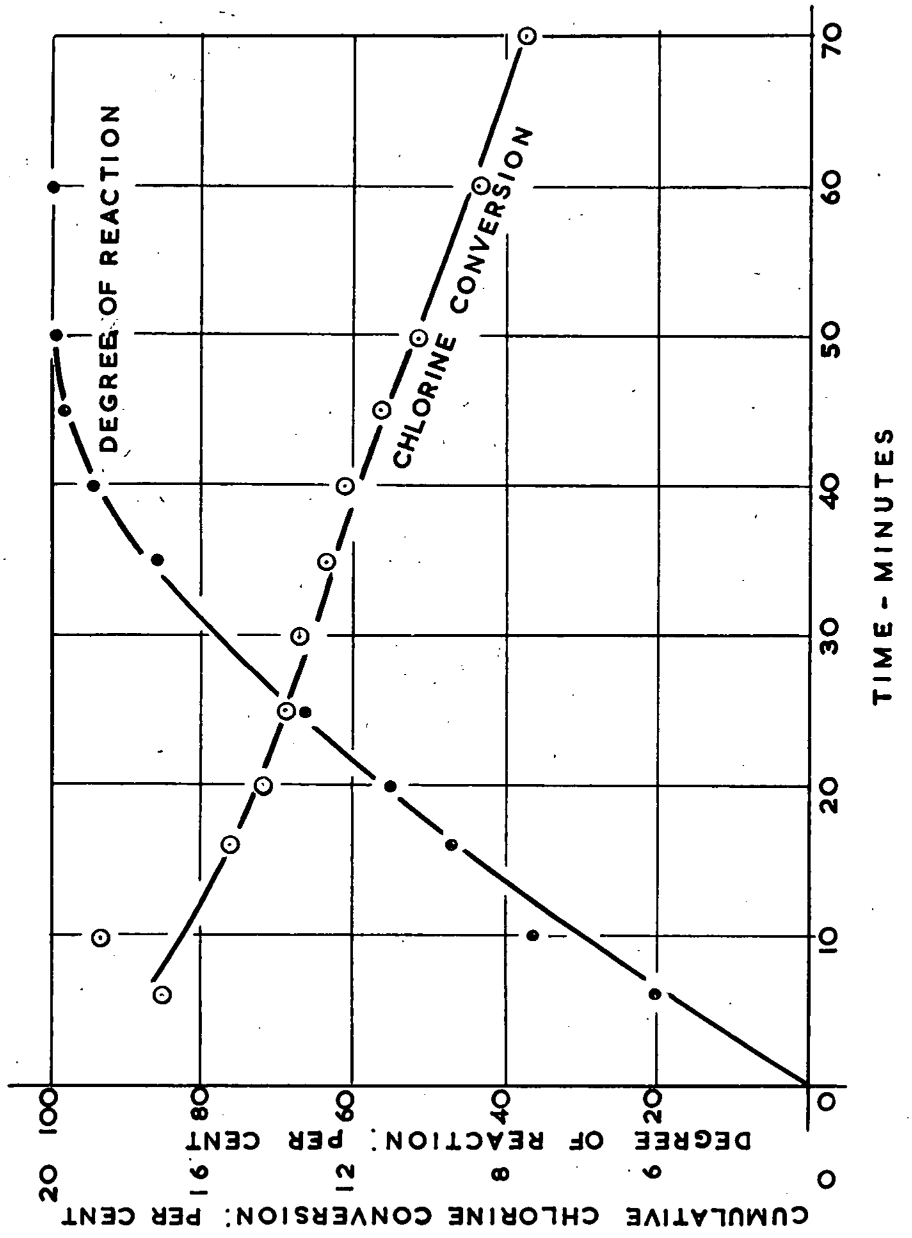


TABLE B-21: CHLORINATION TEST 21
Chlorination with partially reacted gas in the two stage reactor.
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine at 5.15% utilization
Gas flow: 0.0446 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

Lower Stage

Fed at 1.55 g/min of oxidised ilmenite at 47.3% Fe_2O_3
Produced 0.693 g/min of chlorinated ilmenite at 0.419% Fe_2O_3
Degree of reaction in lower stage = 99.53%

Chlorine utilization = 5.15 %
i = 0.00886

Upper stage

Time Min.	Fe_2O_3 %	Reaction %	Chlorine used cum. %	Total Chlorine used %
0	47.3	nd(a)	nd	nd
7.5	46.2	4.32	19.2	24.4
15	44.3	11.4	25.4	30.5
30	38.6	30.0	33.3	38.5
45	33.1	44.9	33.3	38.4
60	27.3	58.2	32.4	37.5
90	15.3	79.9	29.6	34.8
120	8.15	90.1	25.1	30.2
150	3.85	95.5	21.3	26.4
180	0.24	99.7	18.5	23.7
210	0.063	99.93	15.9	21.0
240	0.043	99.95	13.9	19.0
270	0.059	-	-	-

FIGURE B-21: CHLORINATION TEST 21
Chlorination with partially reacted gas in the two stage reactor.
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine at 5.15% utilization
Gas flow: 0.0446 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

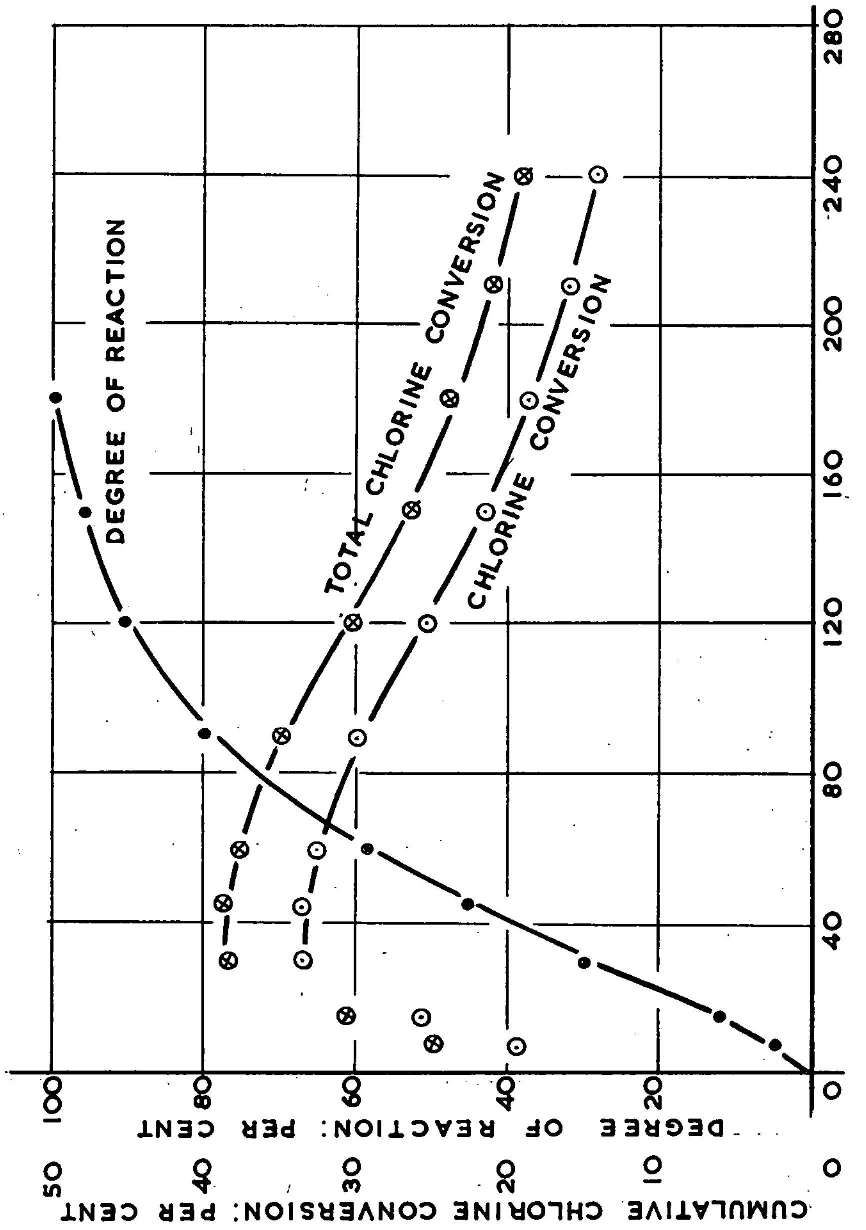


TABLE B-22: CHLORINATION TEST 22
Chlorination with partly reacted gas in a two stage reactor.
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine at 11.0% utilization
Gas flow: 0.0441 g $(in.)^{-2}$ $(sec)^{-1}$
Temperature: 1100°C

Lower Stage

Fed at 3.3 g/min of oxidised ilmenite at - 48.07% Fe_2O_3
Produced 1.63 g/min of chlorinated ilmenite at an average 2.35% Fe_2O_3
Degree of reaction in lower stage averages 97.40%

Chlorine utilization = 11.0%
i = 0.0489

Upper Stage

Time Min.	Fe_2O_3 %	Reaction %	Chlorine used cum %	Total Chlorine used %
0	48.07	nd[a]	nd	nd
7.5	47.78	1.16	5.30	16.3
15	44.44	13.6	31.1	42.1
30	38.87	31.3	35.8	46.8
45	34.40	43.35	33.0	44.0
60	27.91	58.2	33.2	44.2
90	18.11	76.1	29.0	40.0
120	11.08	86.5	24.7	35.7
150	6.36	92.7	21.2	32.2
180	3.13	96.5	18.4	29.4
210	0.92	99.0	16.2	27.2
240	0.20	99.8	14.3	25.3
270	0.16	99.8	12.7	23.7
300	0.16	99.8	11.4	22.4

Note: from 3½ hours onward, there was a large amount Fe_2O_3 around the top of the furnace, and that the last samples are high is possibly due to knocking oxide into the furnace.

FIGURE B-22: CHLORINATION TEST 22

Chlorination with partly reacted gas in a two stage reactor.

Material: Oxidised Stradbroke Island Ilmenite

Charge: 1000 g (L/D = 1, D = 3 in.)

Gas composition: Chlorine at 11.0% utilization

Gas flow: 0.0441 g $(in.)^{-2}$ $(sec)^{-1}$

Temperature: 1100°C

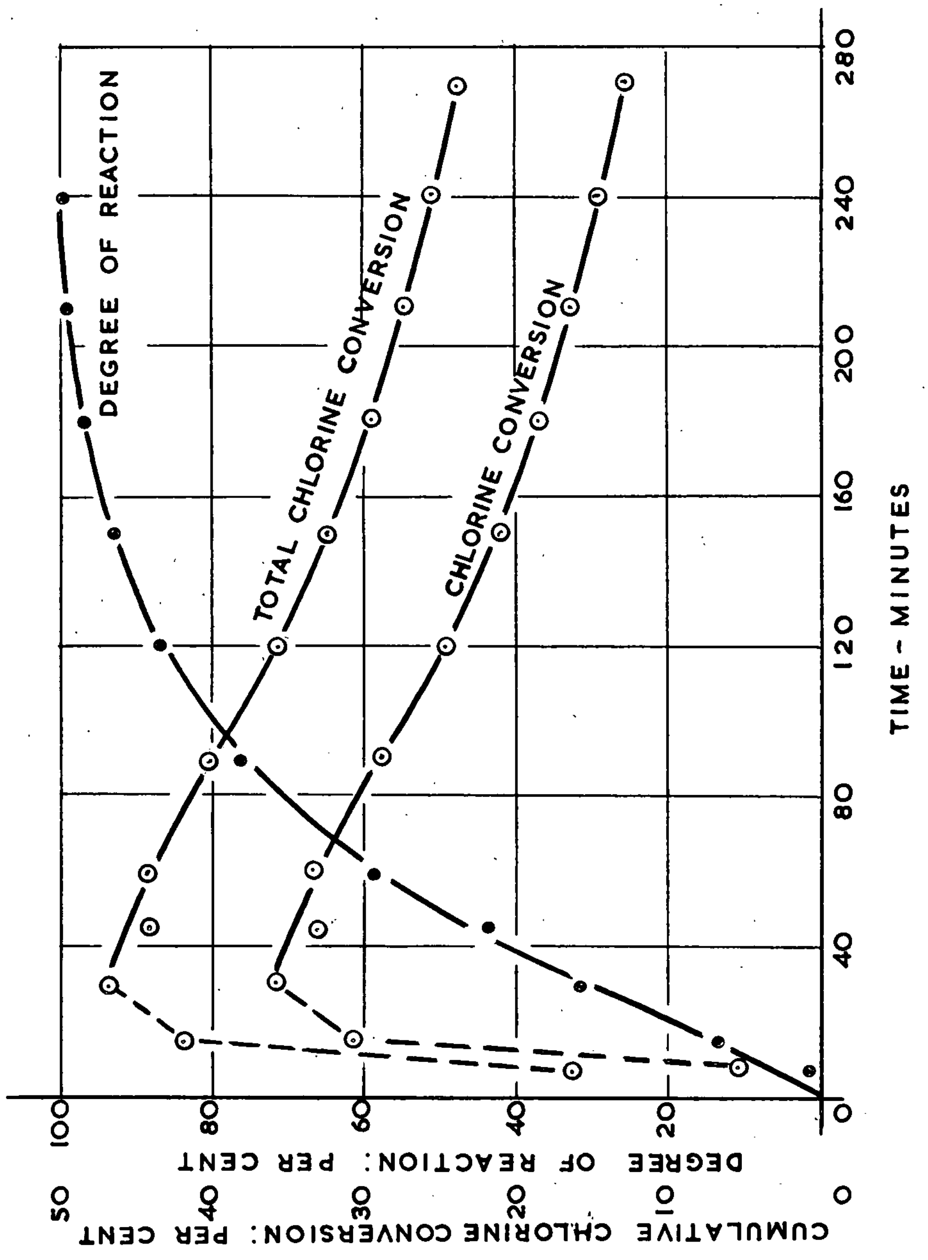


TABLE B-23: CHLORINATION TEST 23

Chlorination with partially reacted gas in two stage reactor.
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine at 15.8% utilization
Gas flow: 0.0443 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

Lower Stage

Fed at 4.9 g/min of oxidised ilmenite at - 47.7% Fe_2O_3
Produced 2.45 g/min of chlorinated ilmenite at an average rate 2.45 Fe_2O_3
Degree of reaction in lower stage = 95.3%
Chlorine utilization = 15.8%
i = 0.0870

Upper Stage

Time Min.	Fe_2O_3 %	Reaction %	Chlorine used cum %	Total Chlorine used %
0	47.7	nd(a)	nd	nd
7.5	46.6	4.3	19.4	35.2
15	45.1	9.9	22.4	38.2
30	42.0	20.6	23.3	39.1
45	37.0	35.6	26.8	42.6
60	32.4	47.4	26.8	42.6
80	27.2	59.0	25.0	40.8
100	22.4	68.4	23.2	39.0
120	18.6	74.9	21.2	37.0
150	14.2	81.9	18.5	34.3
180	10.0	87.8	16.5	32.3
210	8.2	90.2	14.7	30.4
240	7.0	91.7	12.9	28.7
270	5.25	93.9	11.8	27.6
300	4.0	95.4	10.8	26.6
330	2.9	96.7	9.9	25.7
360	1.6	98.2	9.2	25.0
390	0.9	99.0	8.6	24.4
405	0.42	99.5	8.3	24.1

FIGURE B-23: CHLORINATION TEST 23
Chlorination with partially reacted gas in a two stage reactor.
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine at 15.8% utilization
Gas flow: 0.0443 g $(\text{in.})^{-2}$ $(\text{sec})^{-1}$
Temperature: 1100°C

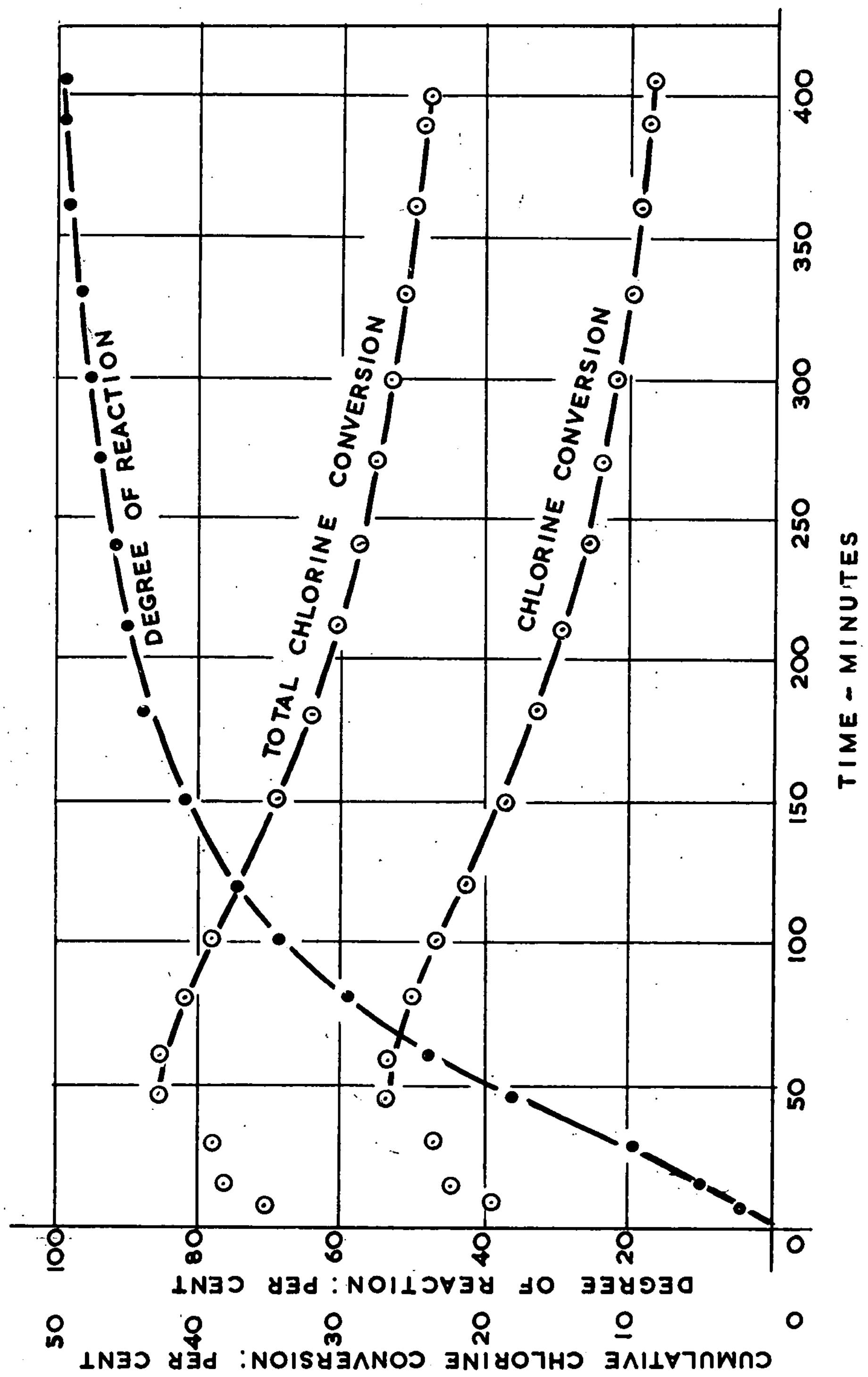


TABLE B-24: CHLORINATION TEST 24
Chlorination with partially reacted gas in a two stage reactor
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D - 1, D - 3 in.)
Gas composition: Chlorine at 20.7% utilization
Gas flow: 0.0442 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100^{0}C

Lower Stage

Fed at 7.0 g/min of oxidised ilmenite at 46.3% Fe_2O_3
Produced (average rate 3.80 g/min) chlorinated ilmenite, at an average of 8.27% Fe_2O_3

Degree of reaction in lower stage = 89.55 %
Chlorine utilization - 20.67 %
i = 0.1786

Upper Stage

Time Min.	Fe_2O_3 %	Reaction %	Chlorine used cum %	Total Chlorine used %
0	45.7	nd[(a)]	nd	nd
7.5	45.6	0.402	1.74	22.4
15	45.1	2.39	5.19	25.9
30	42.0	14.0	15.2	35.9
60	36.1	32.9	17.8	38.5
90	30.2	48.6	17.6	38.3
120	24.7	61.0	16.5	37.2
150	22.3	65.9	14.3	35.0
180	19.4	71.4	12.9	33.6
210	17.5	74.8	11.6	32.3
240	16.1	77.2	10.5	31.2
270	15.9	77.5	9.34	30.0
300	14.4	80.0	8.65	29.4
360	14.2	80.3	7.26	28.0
420	11.9	84.0	6.51	27.2
480	11.2	85.0	5.76	26.5

(a) nd - not determined.

FIGURE B-24: CHLORINATION TEST 24
Chlorination with partially reacted gas in a two stage reactor
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine at 20.7% utilization
Gas flow: 0.0442 g $(in.)^{-2}$ $(sec)^{-1}$
Temperature: 1100°C

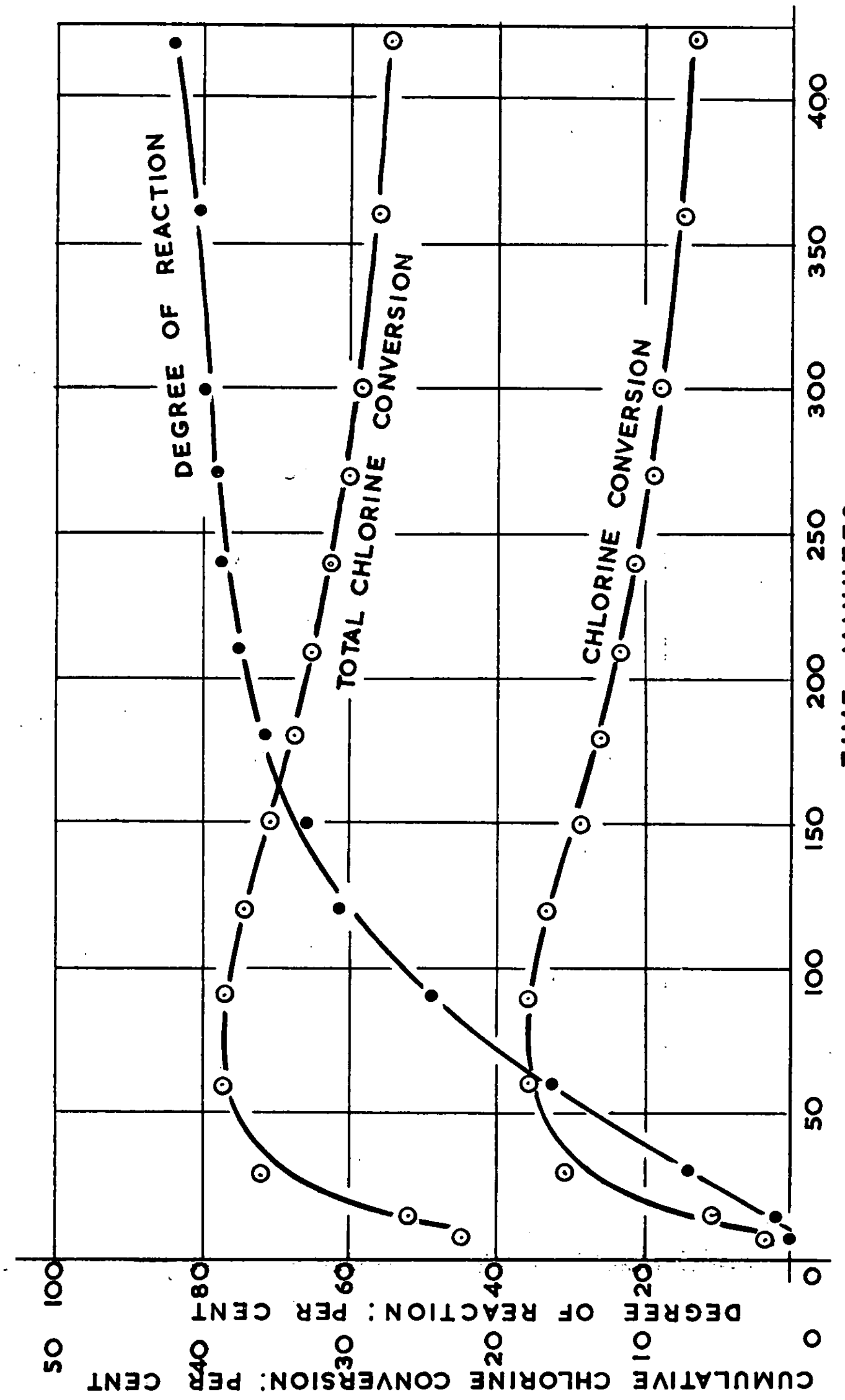


TABLE B-25: CHLORINATION TEST 25

Material: Oxidised Stradbroke Island Ilmenite and rutile residue ex oxidised Stradbroke Is. ilmenite mixture 50/50 by volume

Charge: 1037 g oxidised ilmenite (bulk density 2.70 g/ml)
530 g rutile (bulk density 1.38 g/ml)
1567 g mixture (L/D = 2, D = 3 in.)

Gas composition: Chlorine (100%)

Gas flow: 0.0440 g (in.)$^{-2}$ (sec)$^{-1}$

Temperature: 1100°C

Time Min.	Fe_2O_3 %	Reaction %	Chlorine used %
0	32.1	nd[(a)]	nd
7.5	30.2	8.5	40.6
15	28.6	15.3	36.7
30	25.3	28.4	25.1
45	21.8	41.0	32.7
60	15.7	60.6	36.3
90	8.05	81.5	32.5
120	3.35	92.7	27.8
150	0.22	99.5	23.8
180	0.044	99.90	19.9
210	0.031	99.94	17.1

(a) nd - not determined.

FIGURE B-25: CHLORINATION TEST 25

Material: Oxidised Stradbroke Island Ilmenite and rutile residue ex oxidised Stradbroke Is. ilmenite mixture 50/50 by volume.

Charge:
1037 g oxidised ilmenite (bulk density 2.70 g/ml)
530 g rutile (bulk density 1.38 g/ml)
1567 g mixture (L/D = 2, D = 3 in.)

Gas composition: Chlorine (100%)

Gas flow: 0.0440 g (in.)$^{-2}$ (sec)$^{-1}$

Temperature: 1100°C

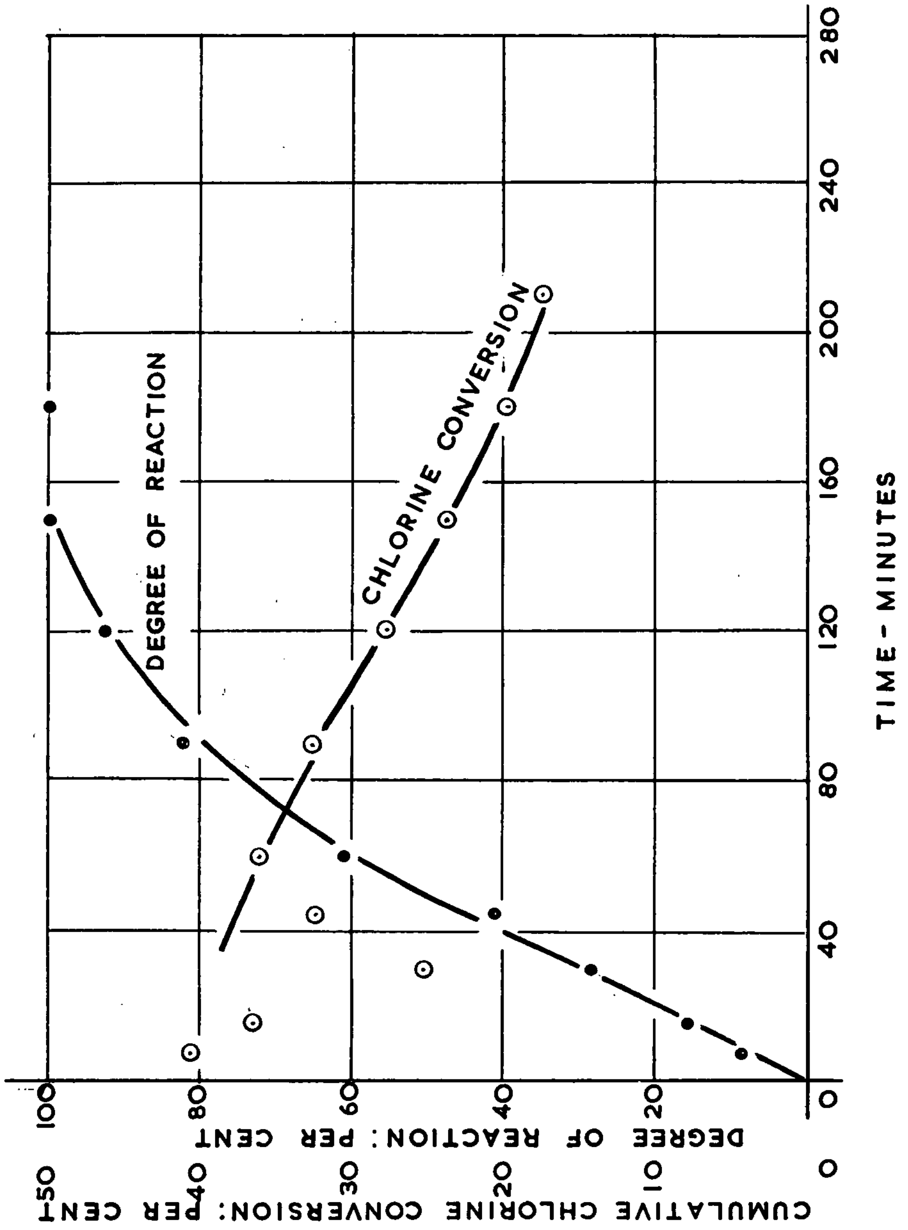


TABLE B-26: CHLORINATION TEST 26
Material: Oxidised Stradbroke Island Ilmenite
Charge: 2000 g)L/D = 2, D = 3 in.)
Gas composition: Chlorine (100%)
Gas flow: 0.0450 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

Time Min.	Fe_2O_3 %	Reaction %	Chlorine used %
0	45.5	nd(a)	nd
7.5	45.3	0.8	6.8
15	45.0	2.0	8.4
30	41.5	15.0	31.8
45	38.2	26.0	36.8
60	33.6	39.4	41.8
90	25.6	57.8	40.8
123	16.9	75.6	39.2
150	10.9	85.3	36.2
180	4.85	93.9	33.2
210	1.95	97.6	29.6
240	0.24	99.7	26.4
270	0.16	99.8	23.6

(a) nd - not determined.

FIGURE B-26: CHLORINATION TEST 26
Material: Oxidised Stradbroke Island Ilmenite
Charge: 2000 g (L/D = 2, D = 3 in.)
Gas composition: Chlorine (100%)
Gas flow: 0.0450 g $(in.)^{-2}$ $(sec)^{-1}$
Temperature: 1100°C

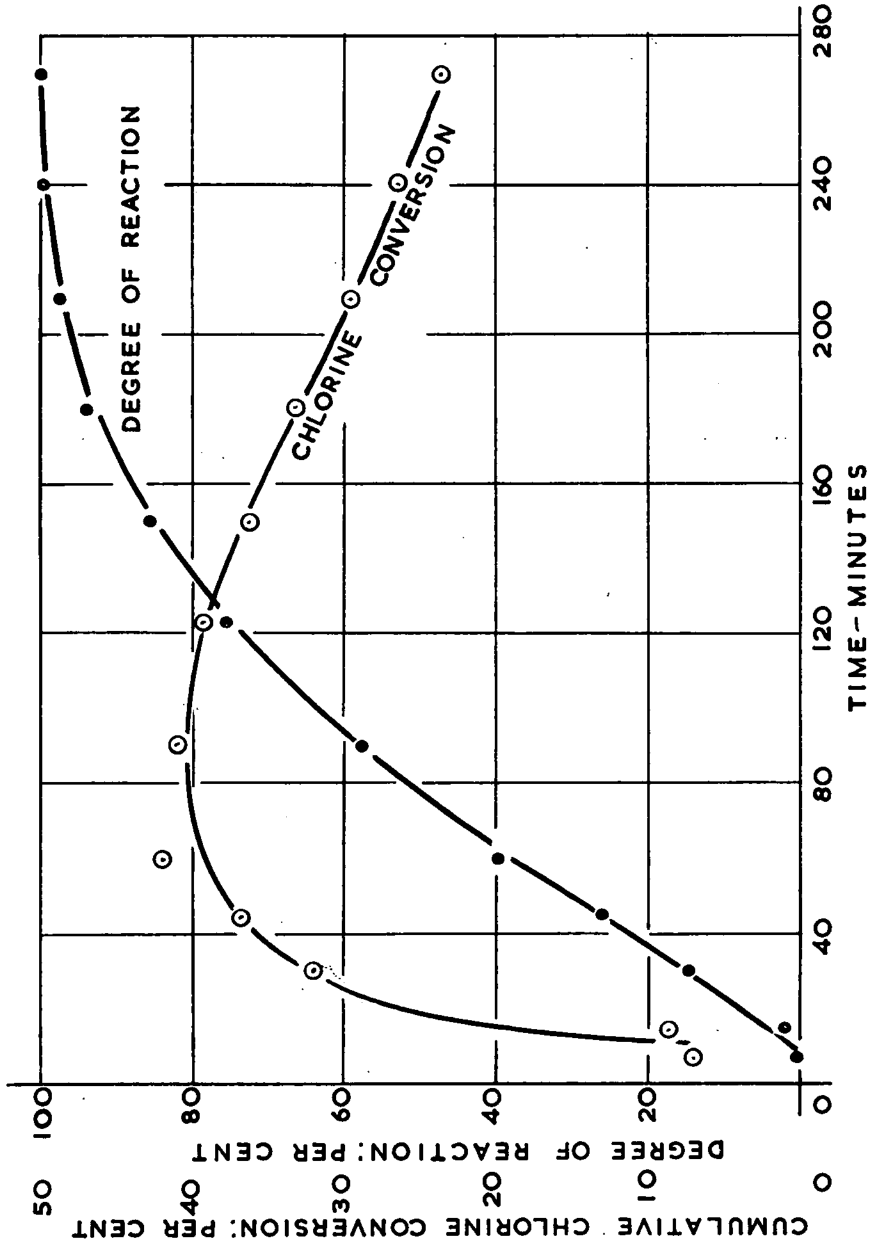
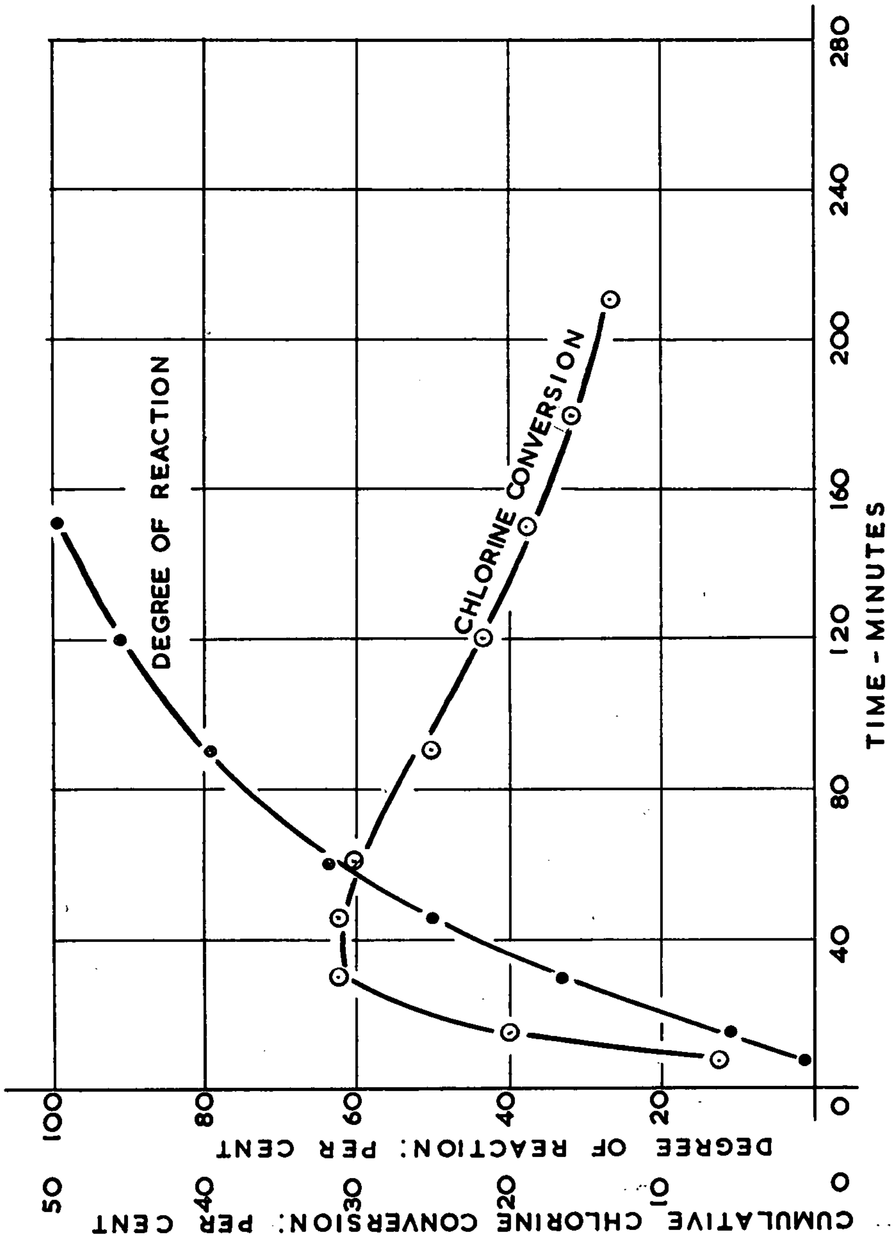


TABLE B-27: CHLORINATION TEST 27
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine (100%)
Gas flow: 0.0508 g $(in.)^{-2}$ $(sec)^{-1}$
Temperature: 1100°C

Time Min.	Fe_2O_3 %	Reaction %	Chlorine used %
0	45.9	nd[a]	nd
7.5	45.5	1.6	6.06
15	43.1	10.7	20.3
30	36.3	32.8	31.1
45	30.0	49.5	31.3
60	23.5	63.8	30.2
90	15.0	79.2	25.0
120	6.9	91.3	21.6
151	0.38	99.6	18.7
180	0.029	99.98	15.8
210	0.021	99.99	13.5

(a) nd - not determined.

FIGURE B-27: CHLORINATION TEST 27
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine (100%)
Gas flow: 0.0508 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C



APPENDIX C

FIGURE C-1: CHLORINATION TEST 15

Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine (100%)
Gas flow: 0.0434 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

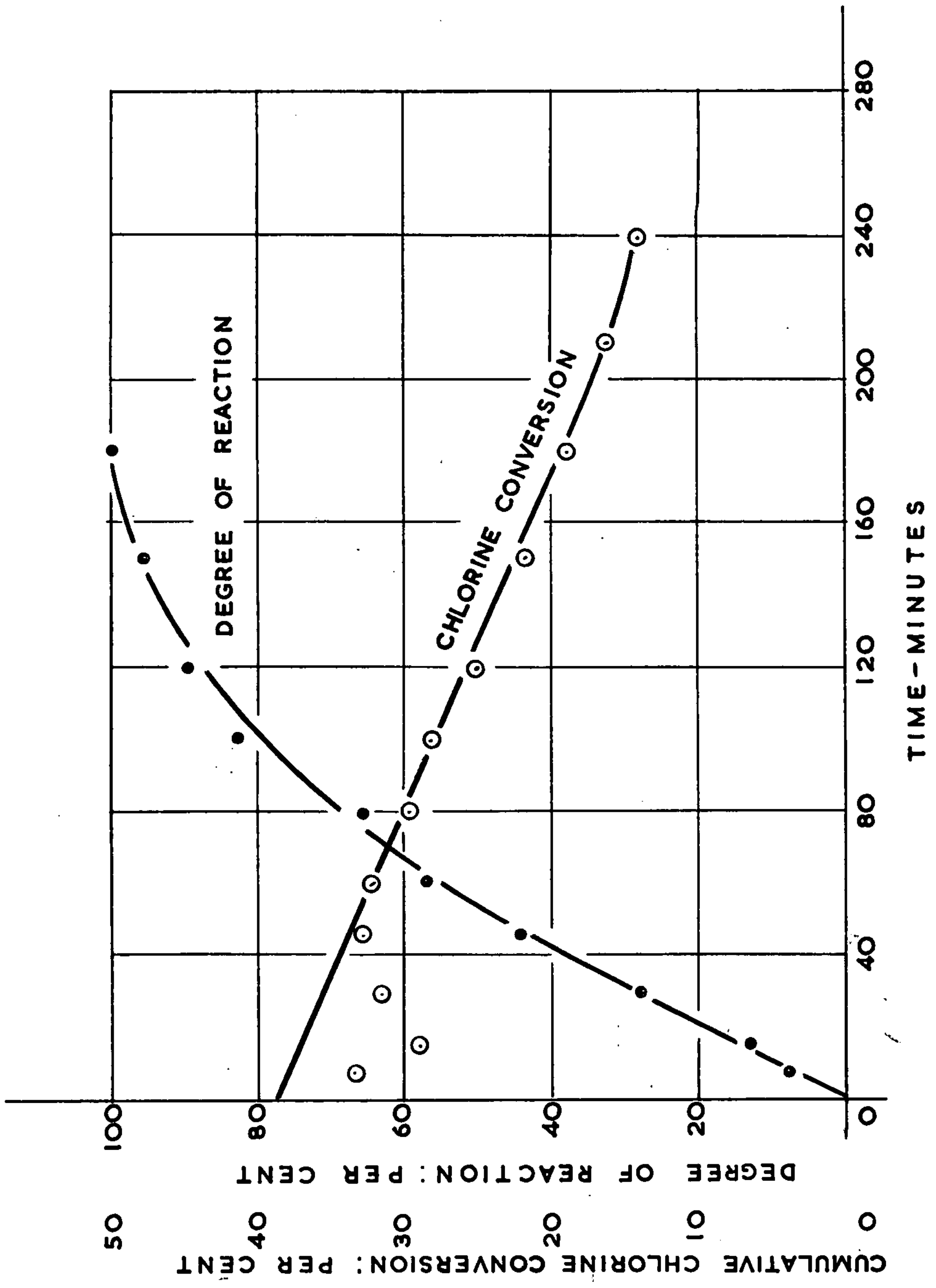


FIGURE C-2: CHLORINATION TEST 16
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine (100%)
Gas flow: 0.0437 g $(\text{in.})^{-2}$ $(\text{sec})^{-1}$
Temperature: 1100°C

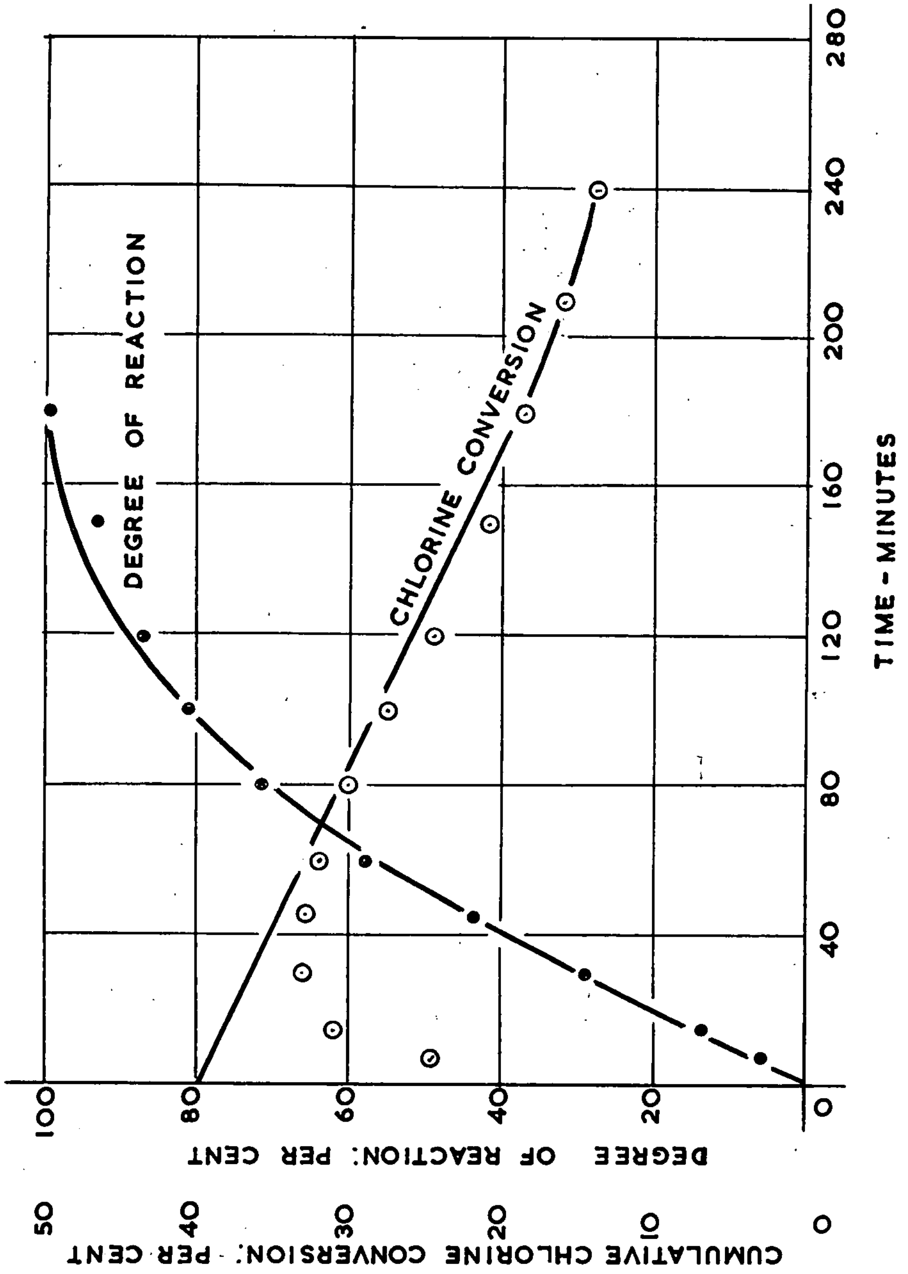


FIGURE C-3: CHLORINATION TEST 17

Material: Oxidised Stradbroke Island Ilmenite and rutile residue ex oxidised Stradbroke Is. ilmenite, mixture 75/25 by volume.

Charge: 777 g oxidised ilmenite (bulk density 2.70 g/ml)
133 g rutile (bulk density 13.8 g/ml)
910 g mixture (L/D = 1, D = 3 in.)

Gas composition: Chlorine (100%)

Gas flow: 0.0442 g (in.)$^{-2}$ (sec)$^{-1}$

Temperature: 1100°C

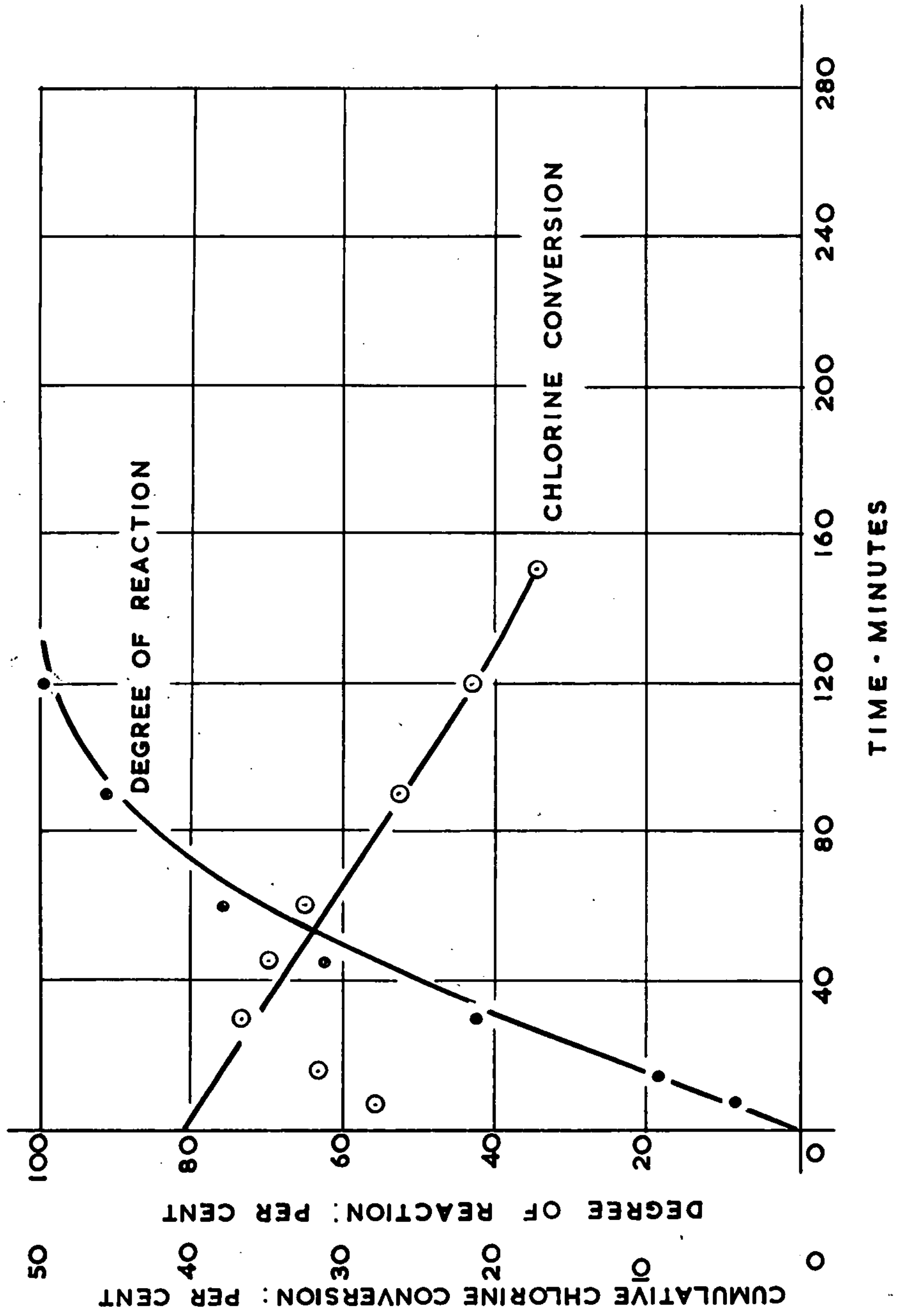


FIGURE C-4: CHLORINATION TEST 18:

Material: Oxidised Stradbroke Island Ilmenite and rutile residue ex oxidised Stradbroke Is. ilmenite.
Mixture 50/50 by volume

Charge: 500 g ilmenite (bulk density 2.70 g/ml)
255 g residue (bulk density 1.38 g/ml)
755 g mixture (L/D = 1, D = 3 in.)

Gas composition: Chlorine (100%)

Gas flow: 0.0435 g $(\mathrm{in.})^{-2}$ $(\mathrm{sec})^{-1}$

Temperature: 1100°C

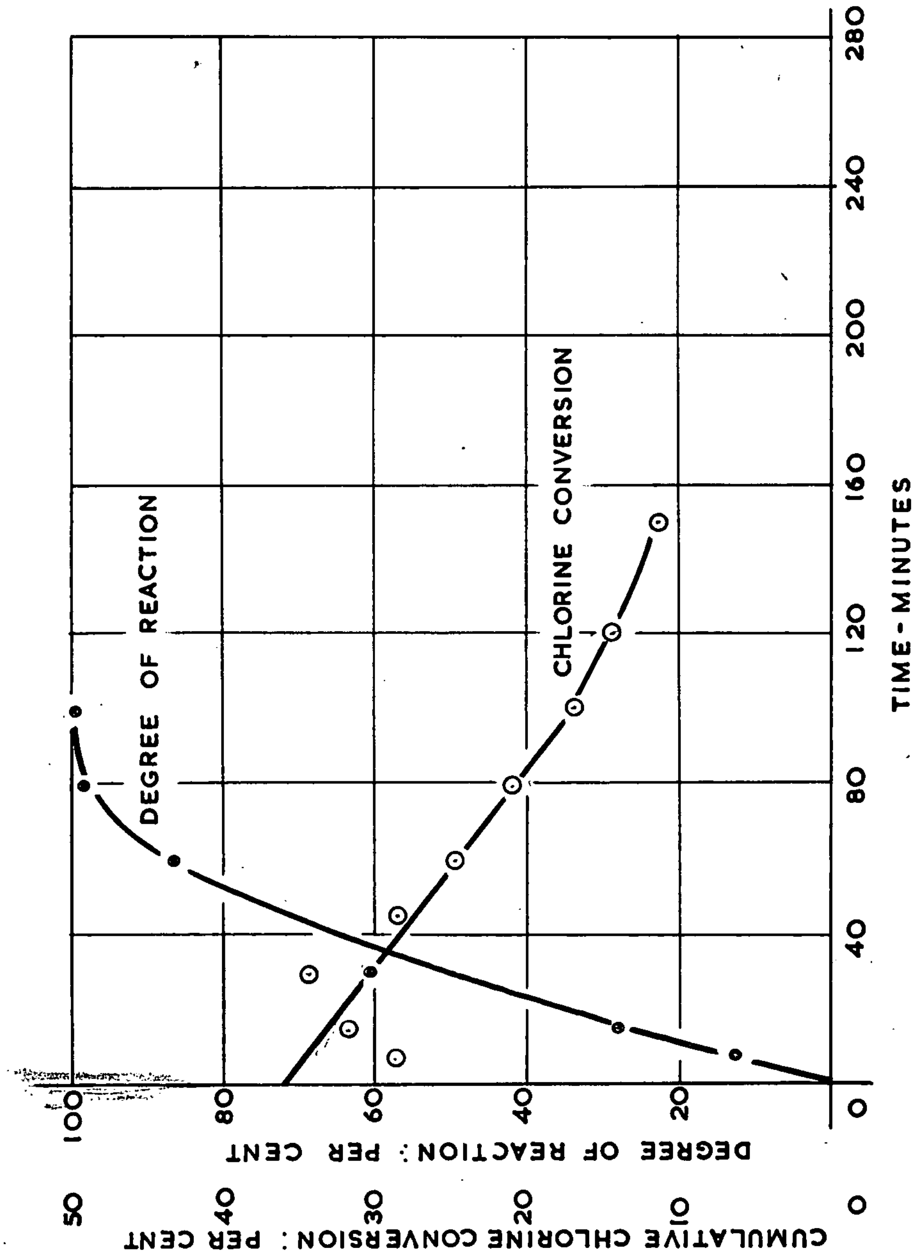


FIGURE C-5: CHLORINATION TEST 19
Material: Oxidised Stradbroke Island Ilmenite and rutile residue ex oxidised Stradbroke Is. ilmenite.
Mixture 25/75 by volume.
Charge: 250 g ilmenite (bulk density 2.70 g/ml)
382 g residue (bulk density 1.38 g/ml)
632 g mixture (L/D = 1, D = 3 in.)
Gas composition: Chlorine (100%)
Gas flow: 0.0435 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

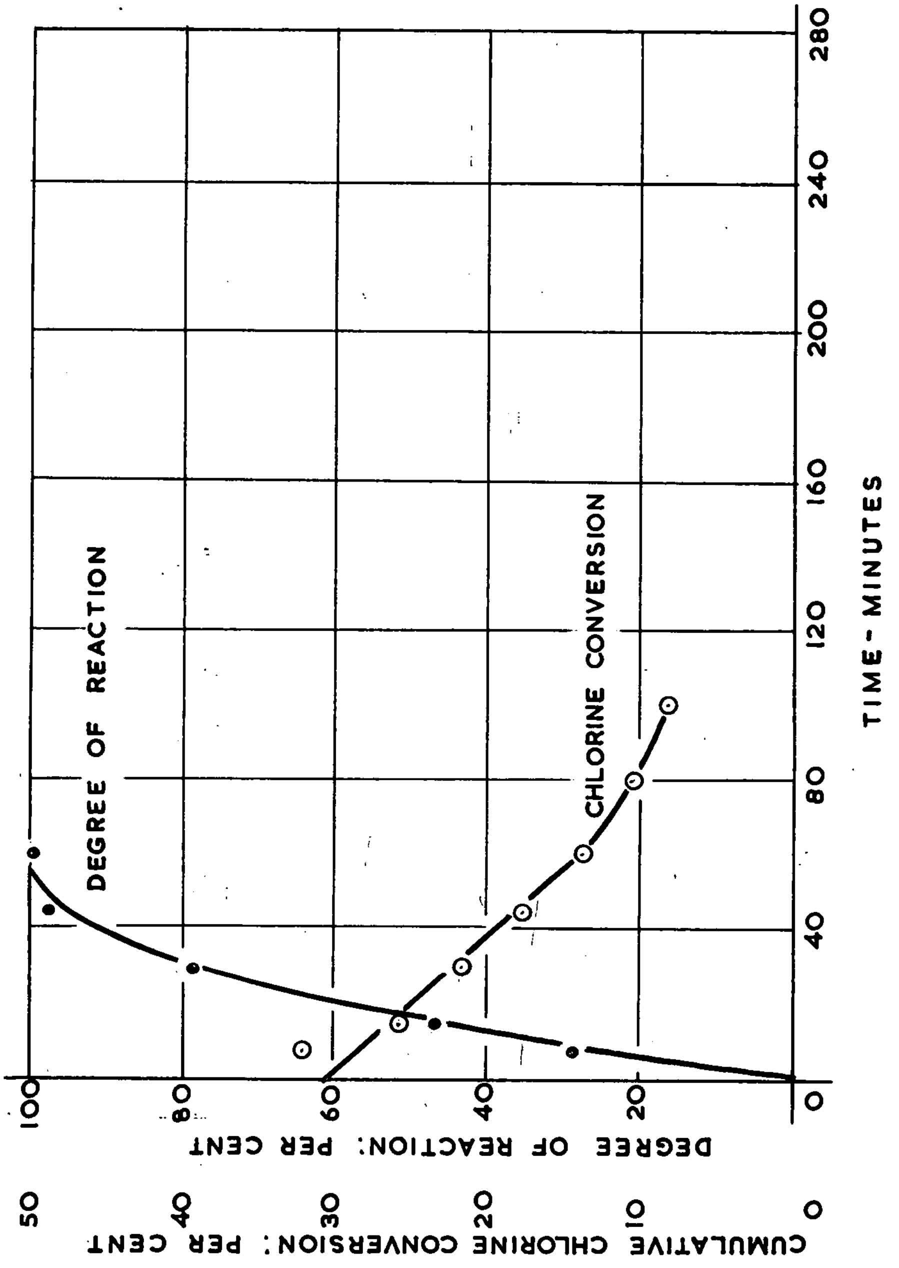


FIGURE C-6: CHLORINATION TEST 20

Material: Oxidised Stradbroke Island Ilmenite and rutile residue ex oxidised Stradbroke Is. ilmenite.
Mixture 12.5/87.5 by volume

Charge:
125 g ilmenite (bulk density 2.70 g/ml)
447 g rutile (bulk density 1.38 g/ml)
572 g mixture (L/D = 1, D = 3 in.)

Gas composition: Chlorine (100%)

Gas flow: 0.0433 g (in.)$^{-2}$ (sec)$^{-1}$

Temperature: 1100°C

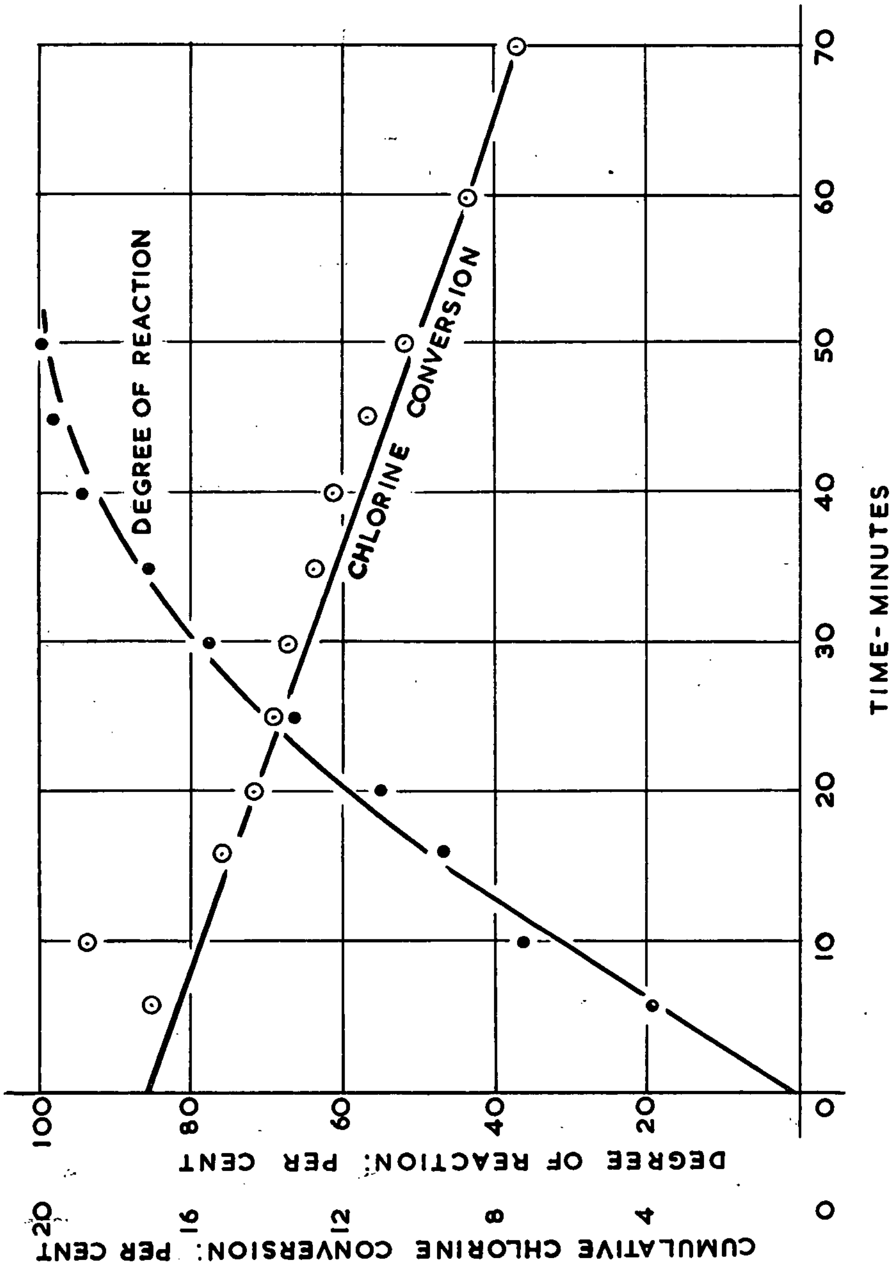


FIGURE C-7: RELATION BETWEEN "k" AND "i"
Obtained by correlating the results for Chlorination Tests 15 to 20 on the basis that "P" = 0.5

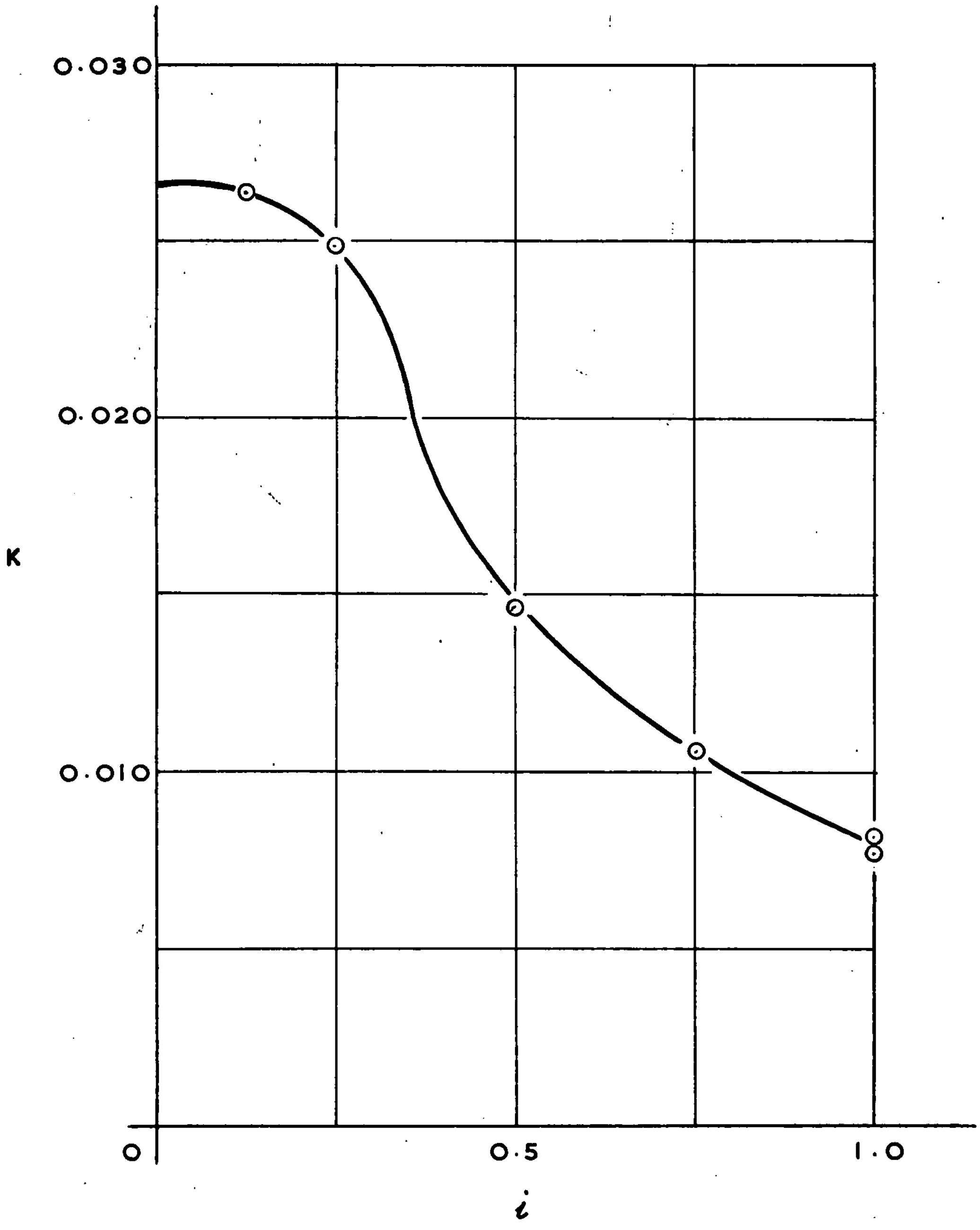


FIGURE C-8: DEPENDENCE OF "k" ON "i"
$k = 0.0329 + 0.0456\, i + 0.0203\, i^2$
This expression was obtained by correlating the results of Chlorination Tests 15, 18, and 19 on basis that "P" = 0.5

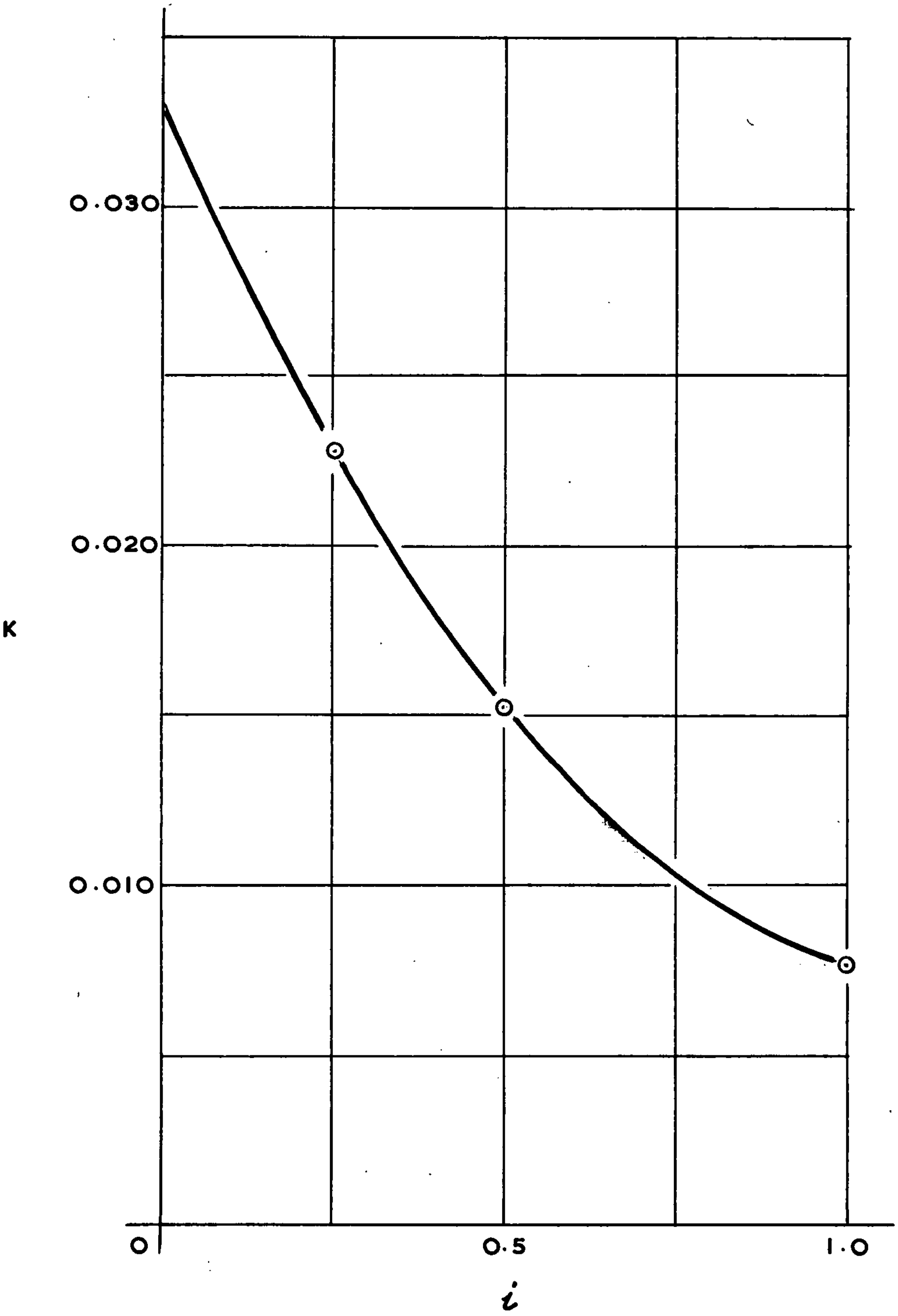
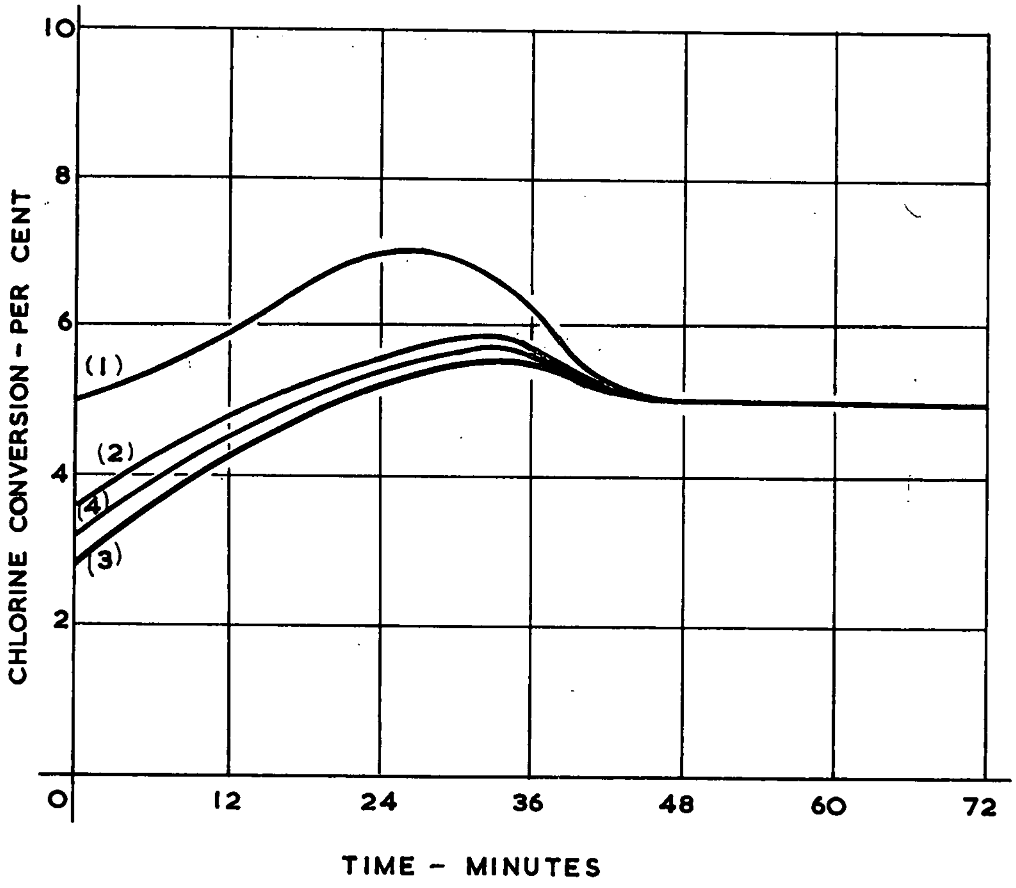


FIGURE C-9: VARIATION OF CHLORINE CONVERSION WITH TIME FOR VARIOUS AMOUNTS OF OXIDISED ILMENITE IN THE INITIAL CHARGE



INITIAL CHARGE CONTAINS

(1)	35.2 g	OXIDISED	ILMENITE
(2)	25 g	"	"
(3)	20 g	"	"
(4)	23 g	"	"

FIGURE C-10: CHLORINATION TEST 21
Chlorination with partially reacted gas in the two stage reactor.
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine at 5.15% utilization
Gas flow: 0.0446 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

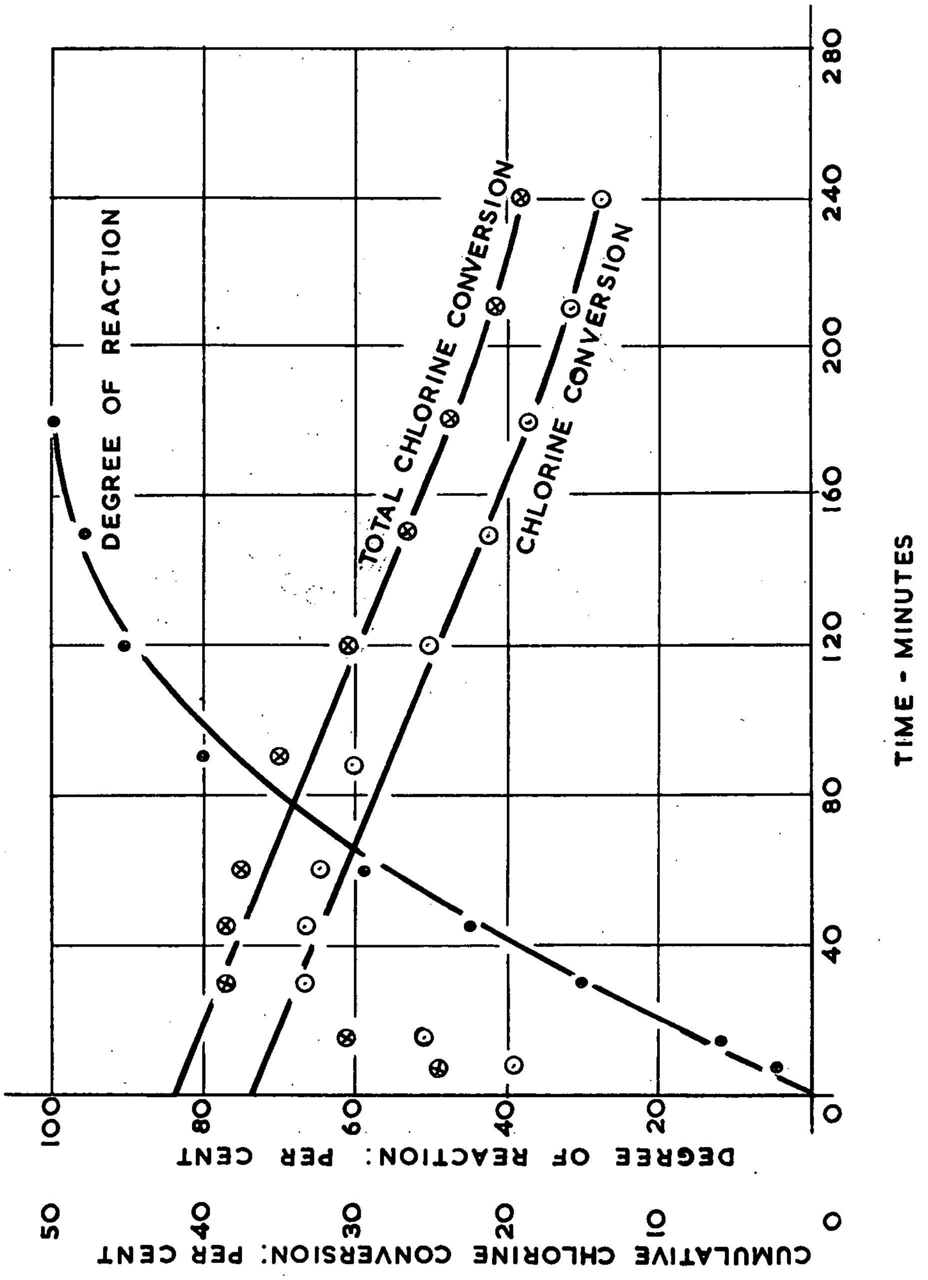


FIGURE C-11: CHLORINATION TEST 22
Chlorination with partly reacted gas in a two stage reactor.
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine at 11.0% utilization
Gas flow: 0.0441 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

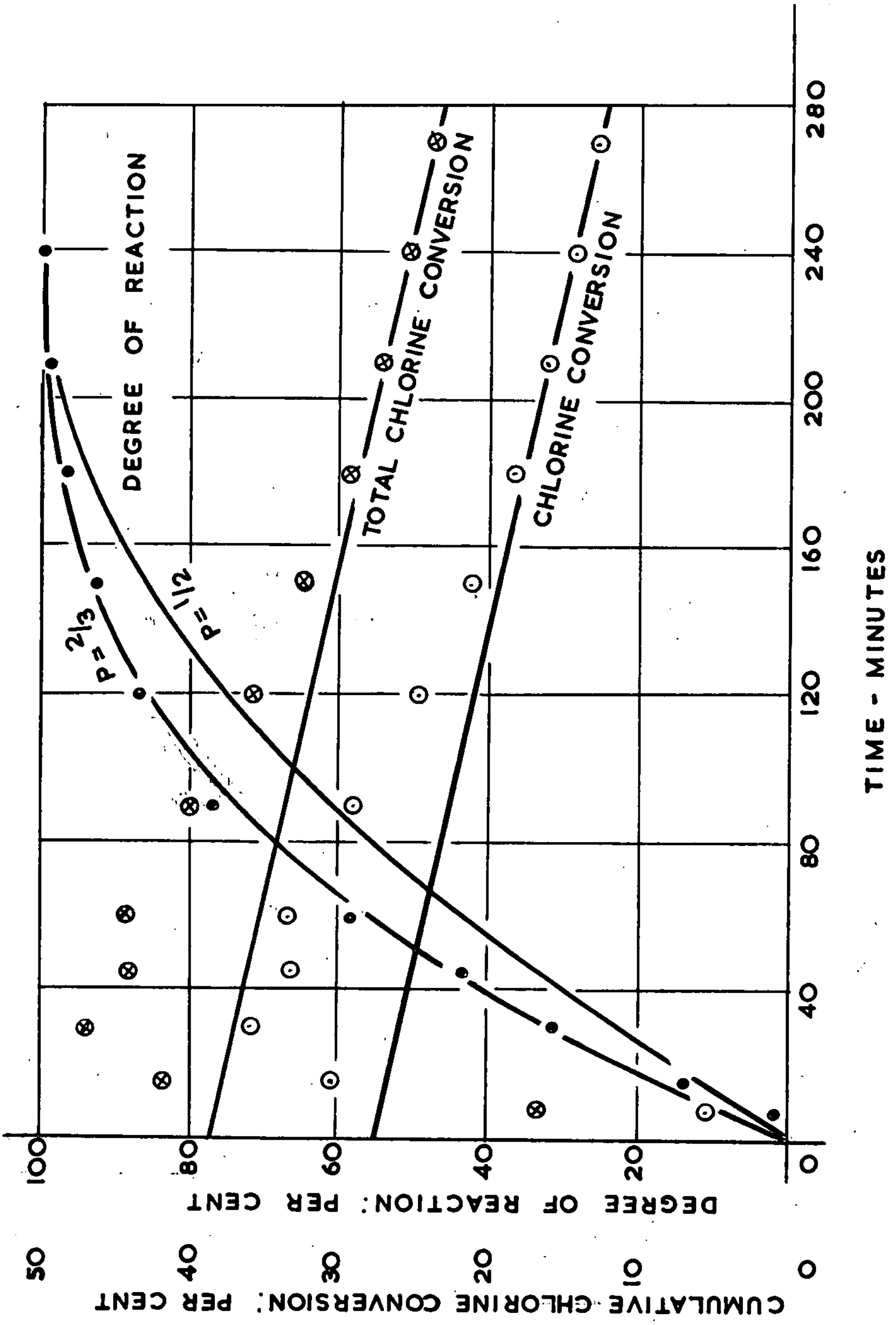


FIGURE C-12: CHLORINATION TEST 23
Chlorination with partially reacted gas in a two stage reactor
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine at 15.8% utilization
Gas flow: 0.0443 g (in.)$^{-2}$ (sec)$^{-1}$
Temperature: 1100°C

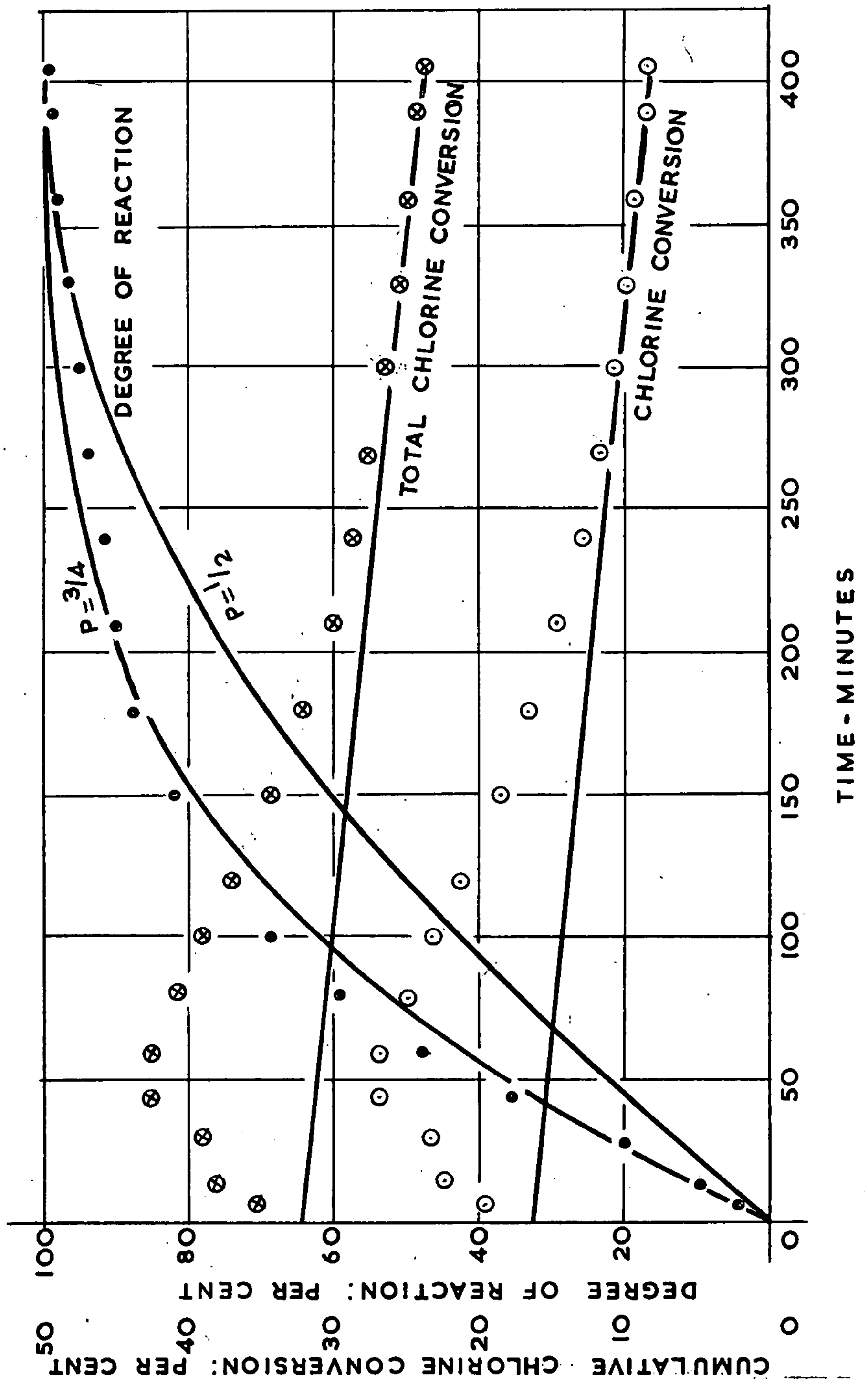


FIGURE C-13: CHLORINATION TEST 24
Chlorination with partially reacted gas in a two stage reactor
Material: Oxidised Stradbroke Island Ilmenite
Charge: 1000 g (L/D = 1, D = 3 in.)
Gas composition: Chlorine at 20.7% utilization
Gas flow: 0.0442 g $(\text{in.})^{-2}$ $(\text{sec})^{-1}$
Temperature: 1100°C

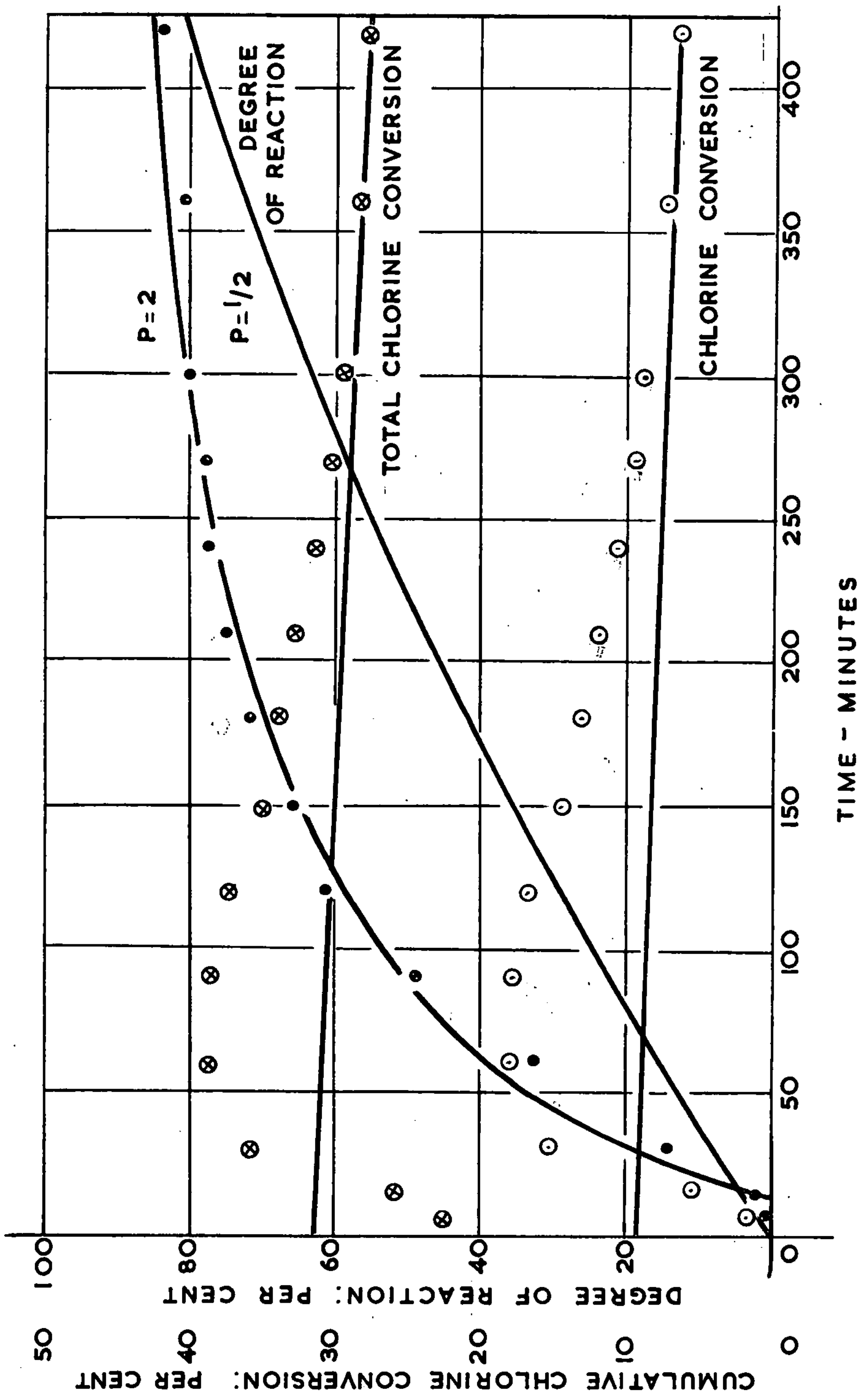


FIGURE C-14: RELATION BETWEEN "k" AND "c"
Obtained by correlating the results for Chlorination Tests 15 and 16 and 21 to 24 on the basis that P = $\frac{1}{2}$

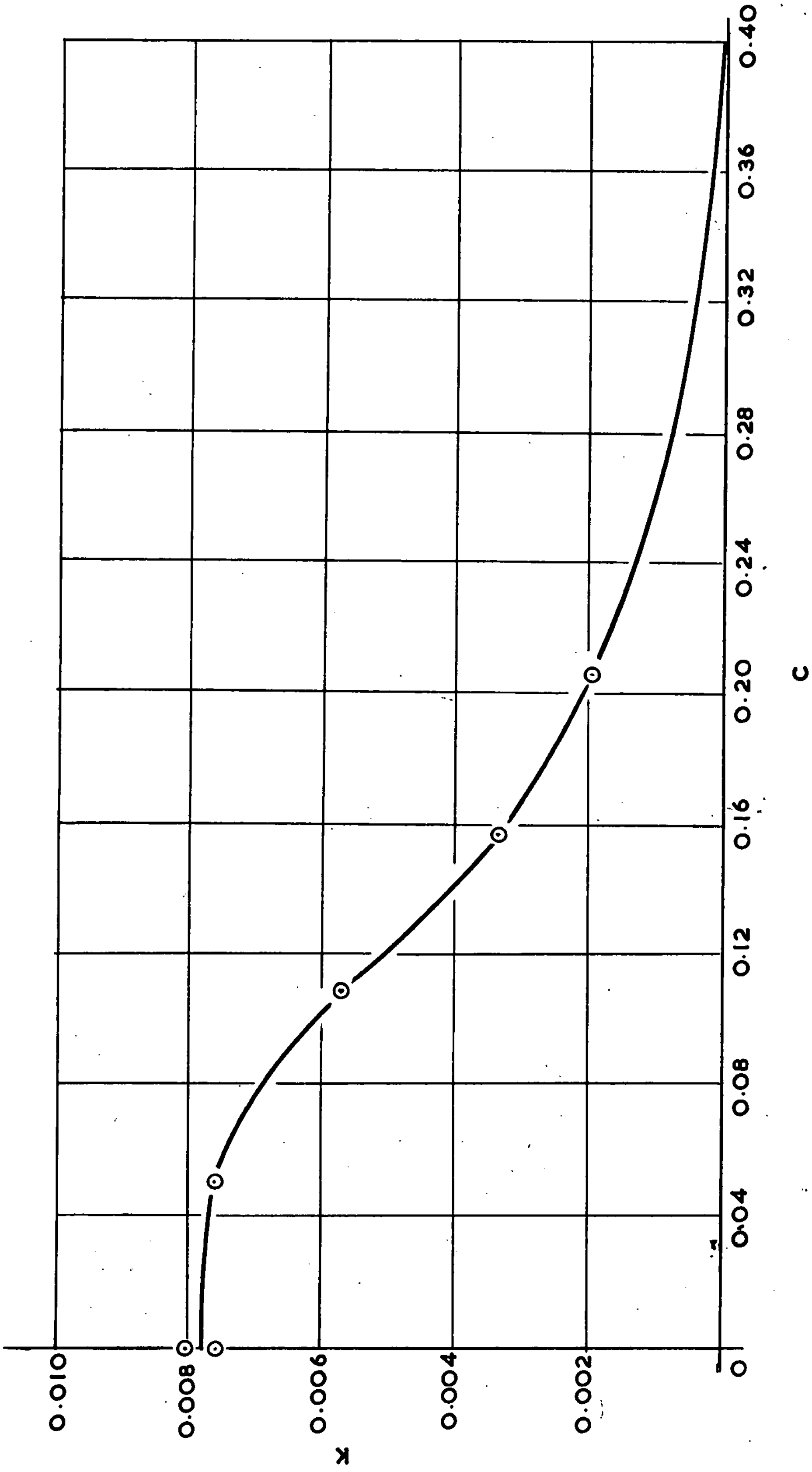
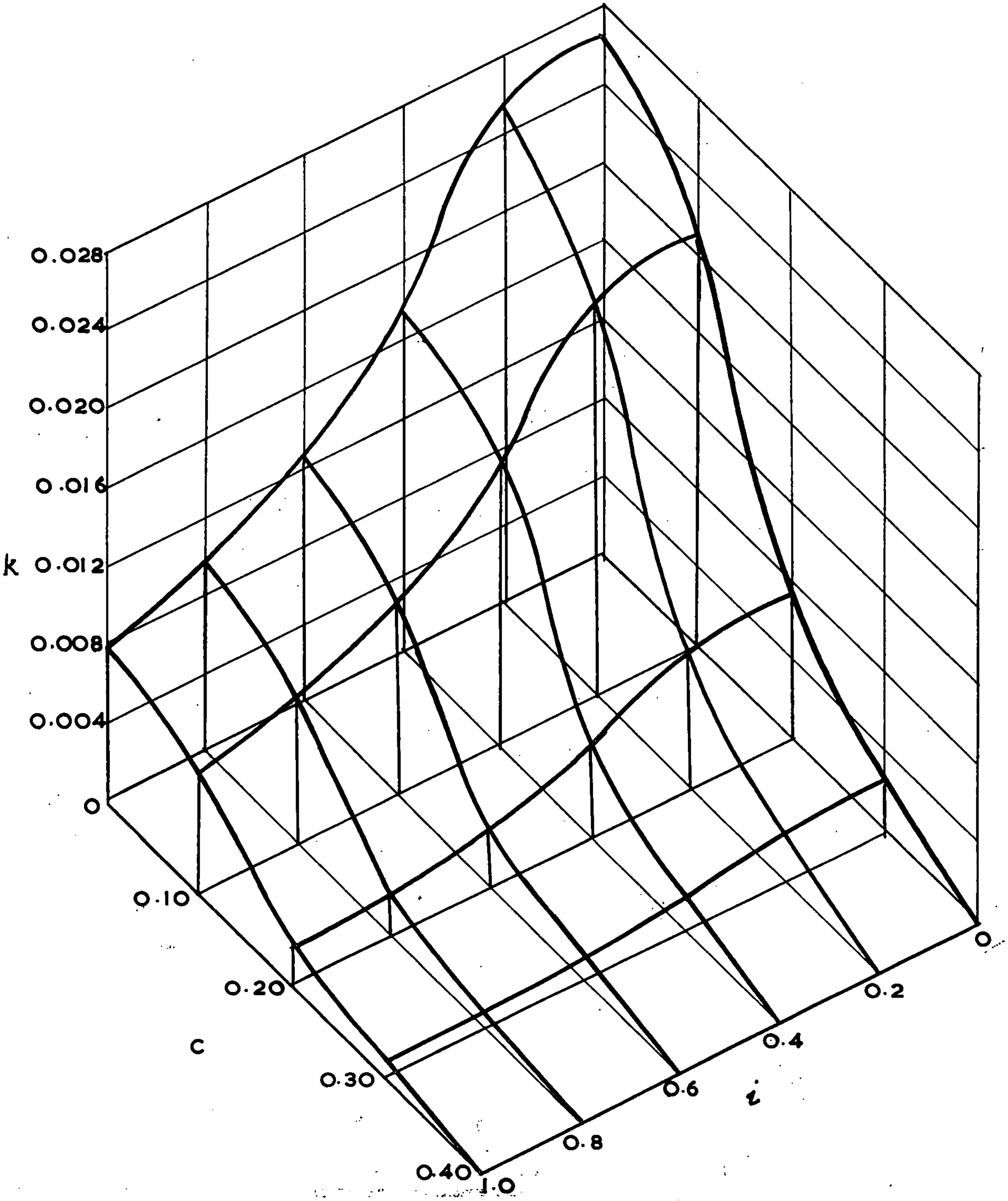


FIGURE C-15: RELATION BETWEEN "k" ON "i" AND "c"
Obtained by correlating the results for Chlorination
Tests 15 to 24 on the basis that "P" = 0.5



APPENDIX D

FIGURE D-1: SINGLE STAGE CONTINUOUS FLUIDISED BED REACTOR

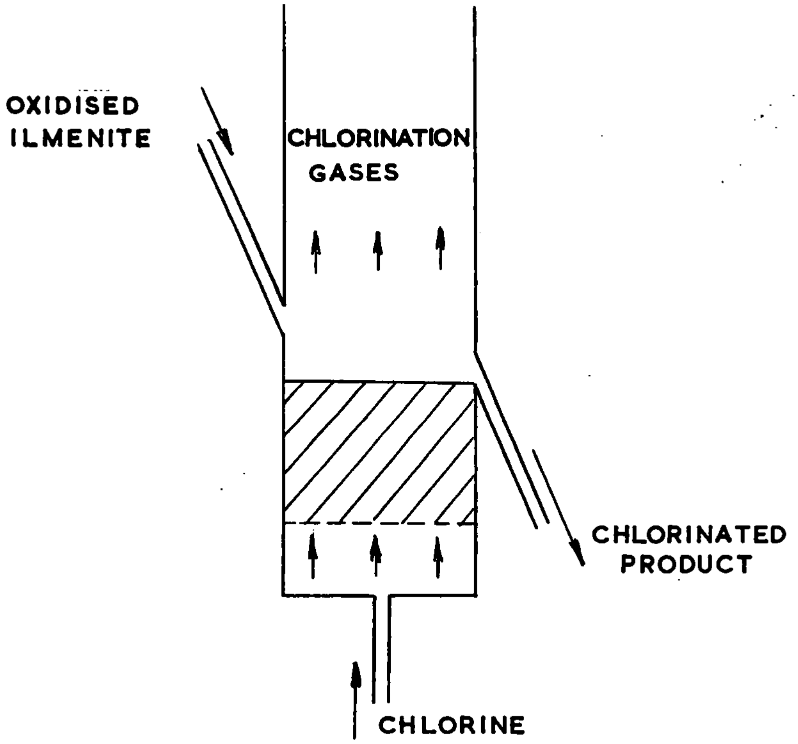


FIGURE D-2: TWO STAGE CONTINUOUS FLUIDISED BED REACTOR
Horizontal Arrangement

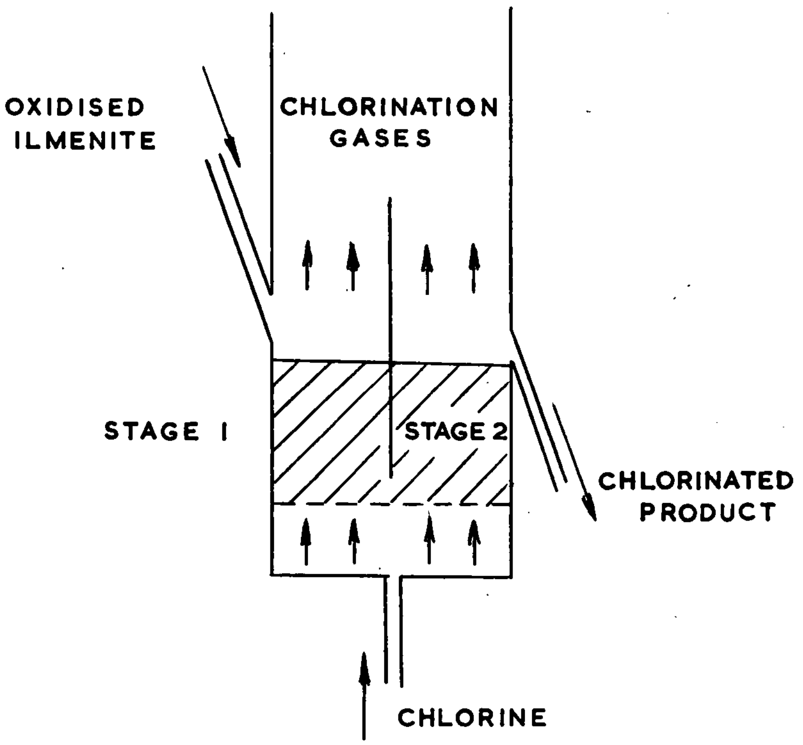


FIGURE D-3: TWO STAGE CONTINUOUS FLUIDISED BED REACTOR
Vertical Arrangement

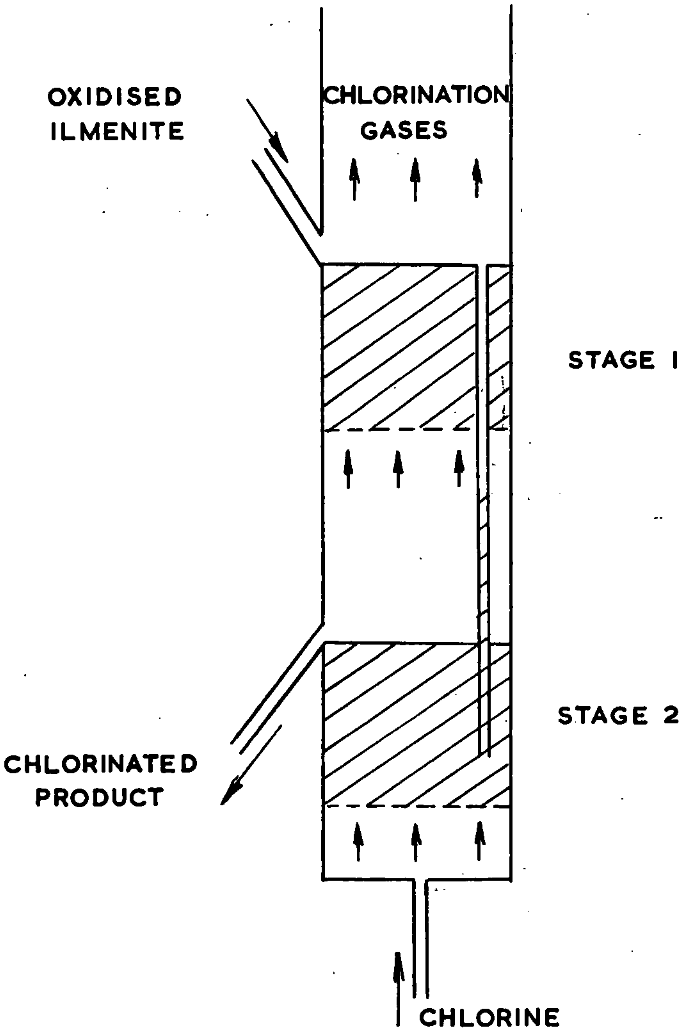


FIGURE D-4: THREE STAGE CONTINUOUS FLUIDISED BED REACTOR
Vertical Arrangement

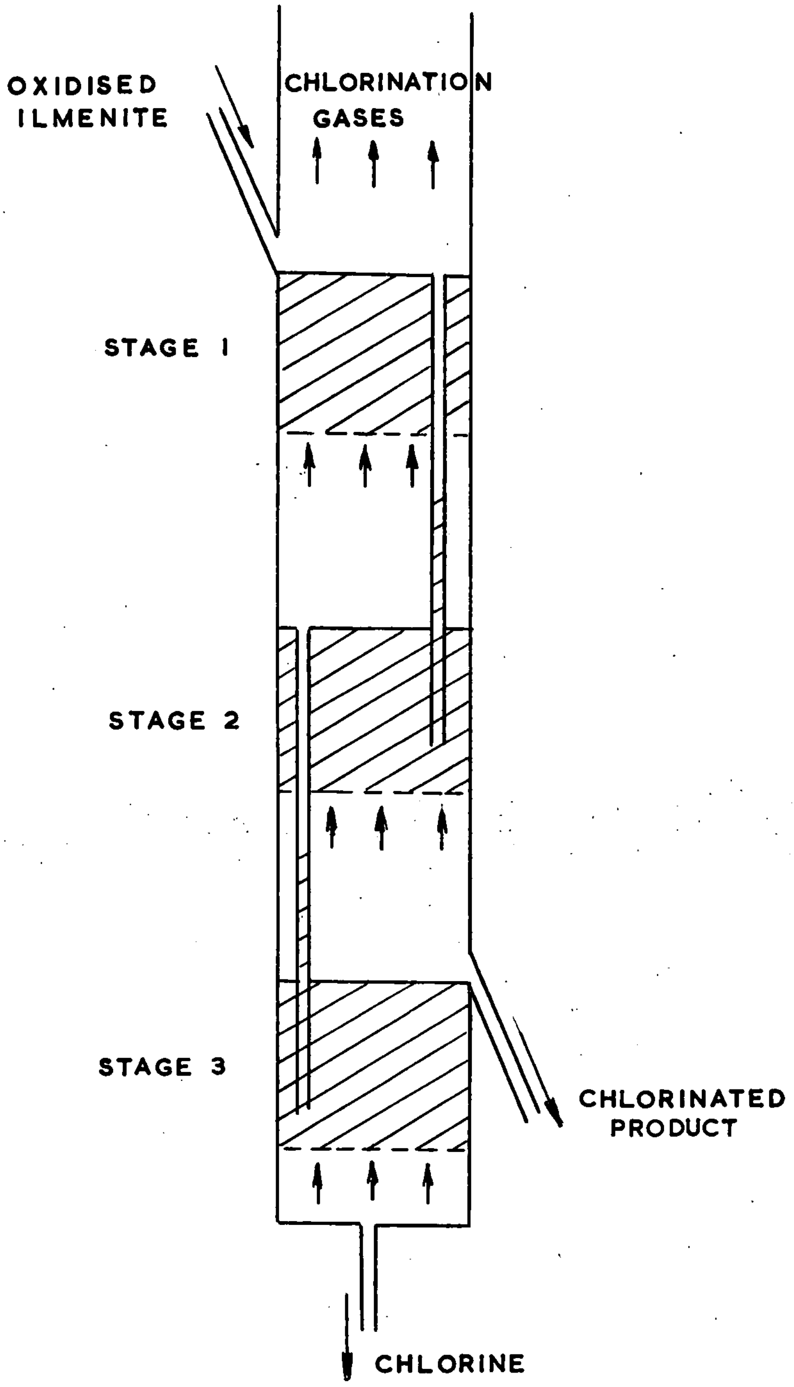


FIGURE D-5: THREE STAGE CONTINUOUS FEED FLUIDISED BED REACTOR
Vertical and Horizontal arrangement.