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Fluidized Coke-Bed Chlorination of Ilmenites

By H. M. Harris, A. W. Henderson, and T. T. Campbell
Albany Metallurgy Research Center, Albany, Oreg.

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FLUIDIZED COKE-BED CHLORINATION OF ILMENITES

by

H. M. Harris,[1] A. W. Henderson,[2] and T. T. Campbell[3]

ABSTRACT

The Bureau of Mines investigated chlorination of domestic ilmenites in a fluidized coke bed at temperatures of 950° to 1,150° C. Objectives were to develop an effective process for producing $TiCl_4$ suitable for TiO_2 pigment and to reduce pollution by collecting and treating waste byproduct chlorides. The reactor for these tests was a 10.2-cm-diam quartz tube heated externally by electrical resistance heaters. It contained coke beds of from 35.6 to 82.5 cm in depth that were fluidized by 13 to 25 l/min of chlorine. Ilmenite concentrate powders were introduced at the bottom of the fluid-bed reactor, using the chlorine gas stream as a carrier. Test results showed that greater than 90 pct of the ilmenite reacted at optimum conditions and recovery of $TiCl_4$ ranged from 95 to 99 pct of stoichiometric. A temperature-controlled cyclone was used to remove high-boiling-point chlorides such as $MnCl_2$, $MgCl_2$, and $FeCl_2$, and also collected fine unreacted ilmenite and coke dust. Impure $TiCl_4$ and $FeCl_3$ were separated by collecting the iron chloride in a condenser controlled at 200° C. Titanium tetrachloride vapor was cleaned by passage through a salt-column filter followed by condensation in water-cooled and refrigerated condensers. Liquid $TiCl_4$ was purified further by well-known industrial methods to meet specifications for pigment-grade chloride. Integrated tests were conducted in which chlorine, produced by dechlorination of $FeCl_3$ with oxygen, was recycled and used directly in a fluidized-bed chlorinator.

INTRODUCTION

An effective economic process is needed to make titanium dioxide pigment from ilmenite ($FeTiO_3$) because of a pending worldwide shortage of rutile (TiO_2), and also because of the pollution and waste generated from current industrial processes. Production of titania pigment from ilmenite by the sulfuric acid process generates waste sulfuric acid containing iron and other sulfates, which causes a water pollution problem when disposed of on land or in the sea (8-10).[4] Waste iron chlorides must be disposed of when titania

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[1] Supervisory ceramic research engineer.

[2] Metallurgist.

[3] Supervisory chemical research engineer.

[4] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

pigment is produced by the chlorination process. Processes that make rutile substitutes are of interest for resources far distant from a market and for the supply of existing chlorination plants (3, 7, 11-12, 15). These methods add to costs and may not eliminate pollution problems. A direct conversion process for ilmenite to pigment is needed that recovers and recycles the major chemical reagents with little soluble waste and with usable byproducts.

Previous research showed the feasibility of dechlorinating iron chlorides at 500° C using a fluidized bed treated with a NaCl catalyst to recover chlorine for recycling and to generate a nonpolluting iron oxide byproduct (6), thus enhancing the economics of the direct chlorination of ilmenites where iron chlorides are a major waste byproduct. In the United States, where supplies of ilmenite are available close to markets, the direct chlorination of ilmenite should provide an economic process for producing TiO_2 pigment when coupled with recycling Cl_2 from iron chlorides. Existing methods used to convert rutile to TiO_2 pigment are probably not usable with the more complex ilmenite minerals (10, 23). A variety of methods have been used to chlorinate ilmenite, but none of these methods have been fully evaluated (1, 14-15, 17, 21-22). Data on kinetics (4) and thermodynamics of reactions involved in ilmenite chlorination indicate that the use of C and Cl_2 together is an effective means for converting oxides to chlorides (13, 20). Industrial success with use of C and Cl_2 for chlorination of rutile (10, 23) fortifies this conclusion, as does the production of pigment-grade TiO_2 from enriched ilmenite by E. I. du Pont de Nemours & Co. as disclosed in various patents (25). The Du Pont process is economic because it produces a significant portion of the TiO_2 pigment consumed even though it is an incomplete process without recovery of chlorine from iron chloride wastes. A pilot plant dechlorinator is reportedly under construction in Tennessee (2, 16, 24).

Fluidized-bed chlorination of ilmenite is difficult because the high-boiling-point chlorides produced from iron and impurities tend to clog reactor systems. Equation 1 is a general formula for the chlorination of ilmenite. The indefinite moles of C and Cl_2 denoted by (x) and (y) result from the wide differences in ilmenite ore compositions (33 to 66 pct TiO_2), and variations in $FeCl_3$-$FeCl_2$ and CO-CO_2 ratios with process conditions.

$$FeO \cdot TiO_2 + (x)\ Cl_2 + (y)\ C \longrightarrow FeCl_3/FeCl_2 + CO/CO_2 + TiCl_4. \qquad (1)$$

Most ilmenite ores differ from the idealized mineral formula, and table 1 gives melting and boiling points of most of the compounds formed during chlorination. Most of the chlorine used for chlorination of rutile or enriched ilmenite is recovered for recycling by oxidation of $TiCl_4$ to form titania pigment as shown in equation 2.

$$TiCl_4 + O_2 \rightleftarrows TiO_2 + 2\ Cl_2. \qquad (2)$$

TABLE 1. - Properties of product and impurity chlorides[1]

Class	Chloride	Melting point, ° C	Boiling point, ° C
Products....................	$TiCl_4$	-25	136.4
	$FeCl_3$	306	315
	$FeCl_2$	674	1,025
High boiling point impurities	$MnCl_2$	650	1,190
	$MgCl_2$	708	1,412
	$CaCl_2$	772	>1,600
Low boiling point impurities.	$AlCl_3$	190	182.7
	$SiCl_4$	-70	57.6
	VCl_4	-28±2	148.5

[1] Chemical Rubber Co. Handbook of Chemistry and Physics. Cleveland, Ohio, 52d ed., 1971-72, pp. B63-B152.

When chlorinating ilmenite, recovery of chlorine for recycling from iron chloride and other impurities as well as $TiCl_4$ is an economic and ecological necessity (10). A possible method for Cl_2 recycling, investigated by Henderson (6) and Paige (19) in related Bureau of Mines research, involved the dechlorination of $FeCl_3$ in a heated fluidized bed as shown in reaction 3.

$$2\ FeCl_3 + 3/2\ O_2 \rightleftarrows Fe_2O_3 + 3\ Cl_2. \tag{3}$$

Reaction 1 was evaluated by estimating the mole-fractions of products at conditions of interest. Equilibrium calculations based on thermodynamic and phase data were made for the reaction as a function of reaction temperature. Results for two ilmenite-chlorine ratios are shown in figures 1 and 2. A carbon-ilmenite mole ratio of 3.8 was used to provide carbon in excess of that needed for all possible reactions in a coke-bed reactor. The moles of carbon remaining are not shown. Although equilibrium was not reached in the fluidized-bed chlorinator, it was closely approached when finely powdered ilmenite and coke were reacted with chlorine at high temperatures. Operation with the higher ilmenite-Cl_2 ratio of 0.7

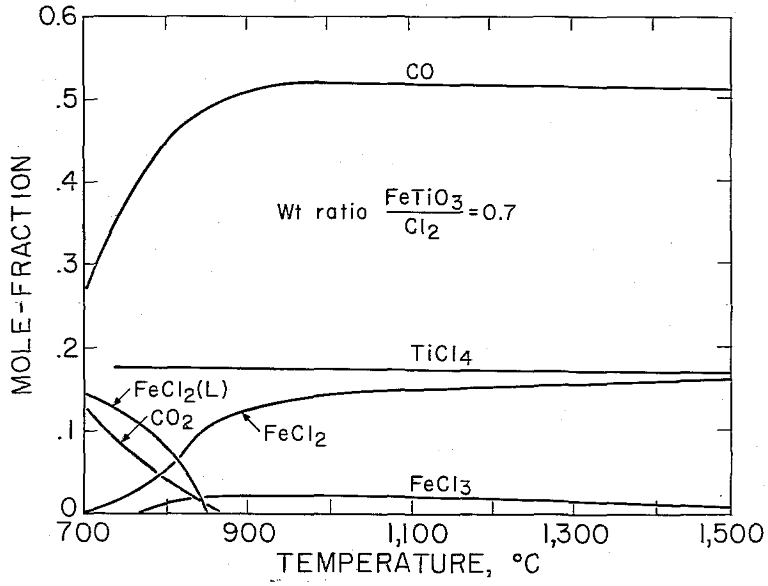

FIGURE 1. - Mole-fractions of products versus temperature, ilmenite-chlorine ratio of 0.7.

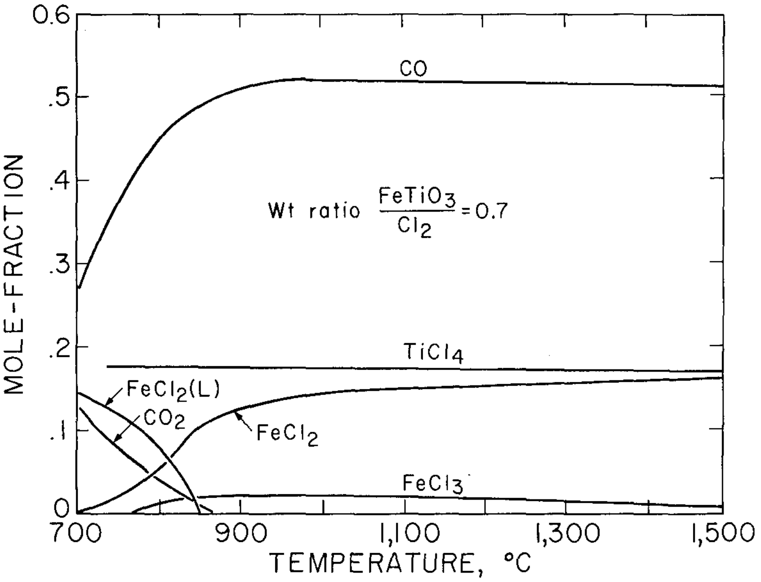

FIGURE 2. - Mole-fractions of products versus temperature, ilmenite-chlorine ratio of 0.6.

as shown in figure 1 would impose the problem of freezing the bed with liquid ferrous chloride $FeCl_{2(l)}$ or condensed solids (1,025° C boiling point) unless very high offgas temperatures and gas velocities were maintained. High-boiling-point chloride impurities also add to these difficulties. Operation at the lower ilmenite-chlorine ratio of 0.6 as shown in figure 2 is preferable with some excess Cl_2 in the offgas because this would produce a high concentration of $FeCl_3$, which has a higher vapor pressure (boiling point 315° C) than $FeCl_2$. Also important is the high concentration of carbon monoxide reductant present in the temperature range of operation (900° to 1,100° C). Carbon monoxide allows rapid gas-solid reduction rather than the slower solid-solid reaction of carbon and ilmenite.

Stoichiometric calculations for converting rutile and domestic ilmenites to $TiCl_4$ and $FeCl_3$ are shown in table 2. These data illustrate the increased chlorine required for ilmenite chlorination. The low cost of ilmenite compared with that of rutile (approximately 1 to 10) is a favorable economic factor for the direct chlorination process.

TABLE 2. - Ore and reagents required to produce 1 kilogram of TiO_2 pigment and byproducts from rutile and ilmenites[1]

Type	Reactants, kg			Byproducts, kg	
	Ore	Cl_2	Coke[2]	$FeCl_3$	Cl_2 in $FeCl_3$
Rutile................	1.1	1.9	0.25	0.04	0.02
Ilmenites............	1.7-3.2	2.7-4.9	.3 -0.6	1.00-3.9	.70-2.6

[1] With stoichiometric reaction of all elements in the ore to form chlorides and of all iron to form $FeCl_3$ from Idaho, Florida, New York, and New Jersey ilmenites and Australian rutile.

[2] Coke reacted for an offgas of equal CO and CO_2 (volume-percent).

A flowsheet of the coke-bed chlorination process being investigated by the Bureau of Mines is given in figure 3. As shown, the main products are Fe_2O_3 and TiO_2 pigment with nearly complete recycling of chlorine from iron and titanium chlorides. Features of the new process (5) that provide ease of operation and clean byproducts are conditions that limit troublesome buildup of ilmenite or chlorides in the bed; for example, controlled feed of reactive finely ground ilmenite, and use of gas velocities that carry high-boiling-point

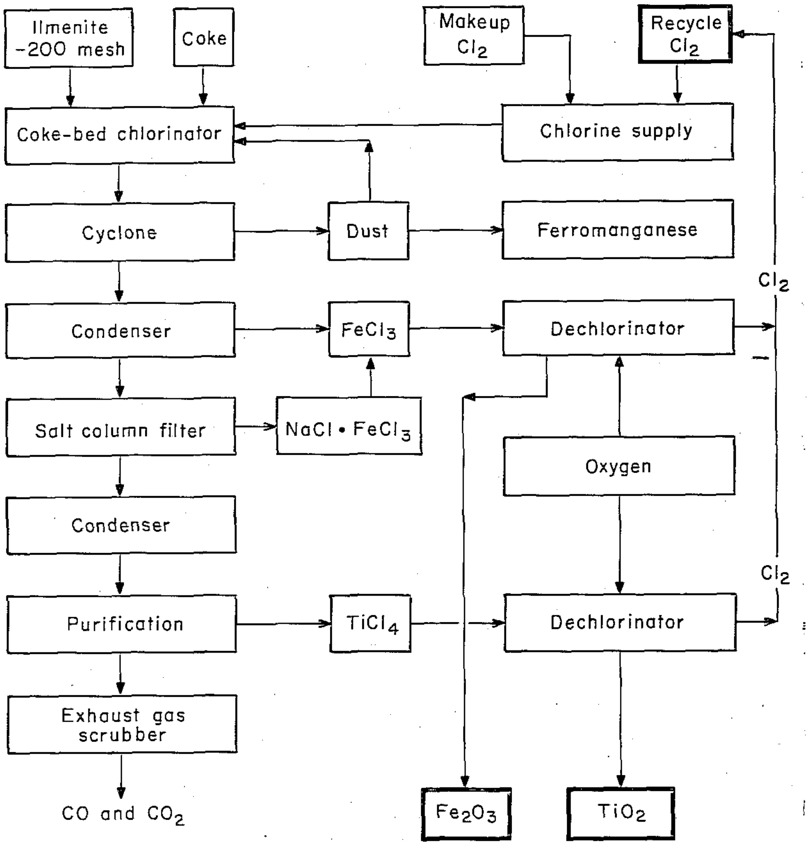

FIGURE 3. - Flowsheet of ilmenite chlorination process.

chloride dusts out of the bed into a collecting cyclone. Maintaining a clean bed is aided by using self-cleaning coke particles (18) rather than ore, and the cyclone cleans the chloride vapors before condensation. A ferromanganese byproduct, ilmenite, and coke for recycling might be recovered by further treatment of the cyclone dusts. Other chlorination methods were considered, but they lacked the advantages of simplicity, ease of control, and superior reaction afforded by a bottom-fed, fluidized coke bed. Research on the dechlorination of iron chlorides is covered in previous reports (6, 19) and is not included here except for the discussion of integrated chlorination-dechlorination tests.

Some advantages of a bottom-fed, fluidized coke bed were shown by the ease of operation and the high product recoveries at 950° C in previous chlorination tests in a 5.1-cm reactor (5). Other advantages are maximum reduction efficiency and accurate control of the ilmenite-chlorine ratio, and therefore of the $FeCl_3$-$FeCl_2$ ratio. This is not always possible with bed mixtures containing ilmenite in excess of reaction needs. The use of finely ground ilmenite and continuous monitoring of chlorine is necessary to prevent overfeeding and loss of control of the $FeCl_3$-$FeCl_2$ ratio. Also, finely ground ilmenite should provide finely divided high-boiling-point chlorides or oxides that carry over into cyclones, thus preventing clogging of the bed or crossover. Research reported herein was done to determine results in a larger reactor system, at temperatures higher than 950° C, and with cyclones to clean chloride vapors.

ACKNOWLEDGMENT

Professor John R. Riter of the University of Denver, Denver, Colo., under a cooperative program, determined the equilibrium products for the reaction of ilmenite, chlorine, and carbon. A computer program was used to determine equilibrium values based on thermodynamic calculations and phase equilibria.

Contributions of James E. Mauser, chemist, Albany Metallurgy Research Center, Albany, Oreg., in sampling and making qualitative analyses of byproducts are appreciated. Also, contributions of Darrell G. Burt, chemical engineering technician, Albany Metallurgy Research Center, Albany, Oreg., in perfecting new devices and in the construction and operation of the chlorinator are acknowledged.

EQUIPMENT, PROCEDURE, AND ORES

Equipment

A schematic drawing of the unit used for chlorination of ilmenite is given in figure 4. It does not include the reactors used to dechlorinate titanium tetrachloride or iron chlorides that are indicated on the flowsheet in figure 3. Commercial-grade chlorine, oxygen, and nitrogen were used in most chlorination tests. In the chlorination unit, measured amounts of chlorine and powdered ilmenite were reacted in a heated fluidized coke bed, and the products were separated by the removal of dust in a cyclone and fractional condensation of iron chloride powder and $TiCl_4$ liquid.

The chlorination reactor was a 10.2-cm-ID vitreous silica tube 107 cm long. A flared ground flange at the top and a reduced inlet with a tapered ground joint were used to connect the reactor tube to the feeder and condensing sections of the system. A removable 1.7-cm-OD Vycor[5] feed loop and distributor that extended 2 cm into the bed was fitted into the bottom of the reactor and was connected to the ilmenite feed screw and chlorine inlet. This permitted chlorine-entrained feeding of ilmenite powders. An external electric furnace heated the reactor tube to temperatures up to 1,150° C.

An Acrison hollow-helix screw feeder (model 105-XA) was used to feed ilmemite or ilmenite-coke mixtures into the feed loop inlet. Weights of material fed were measured using a scale equipped with a jack mounted beneath the feeder.

The reactor was sealed at the top to a water-cooled, refractory-lined, Inconel housing with a Buna-N flat gasket. The housing was lined with A. P. Green castable Greencast number 12, with an inner coating of cured Fiberfrax putty, also used for metal-to-graphite junctions. Three flexible Inconel connectors, somewhat protected by inner Vycor tubes, were used in the system. All tube junctions had four-way crosses. The extra inlets were used for insertion of thermocouples and immersion heaters, which were used to prevent clogging.

The 10.2-cm-ID Inconel cyclone used to collect ilmenite and coke dusts was heated with an outer, insulated Nichrome element to temperatures of 500° to 700° C. This allowed condensation of high-boiling-point chlorides and passage of $FeCl_3$ and $TiCl_4$, which have lower boiling points. Iron chlorides were then condensed in a 45-cm-ID by 92-cm-deep metal condenser that was

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[5] Reference to specific materials or equipment is made for identification only and does not imply endorsement by the Bureau of Mines.

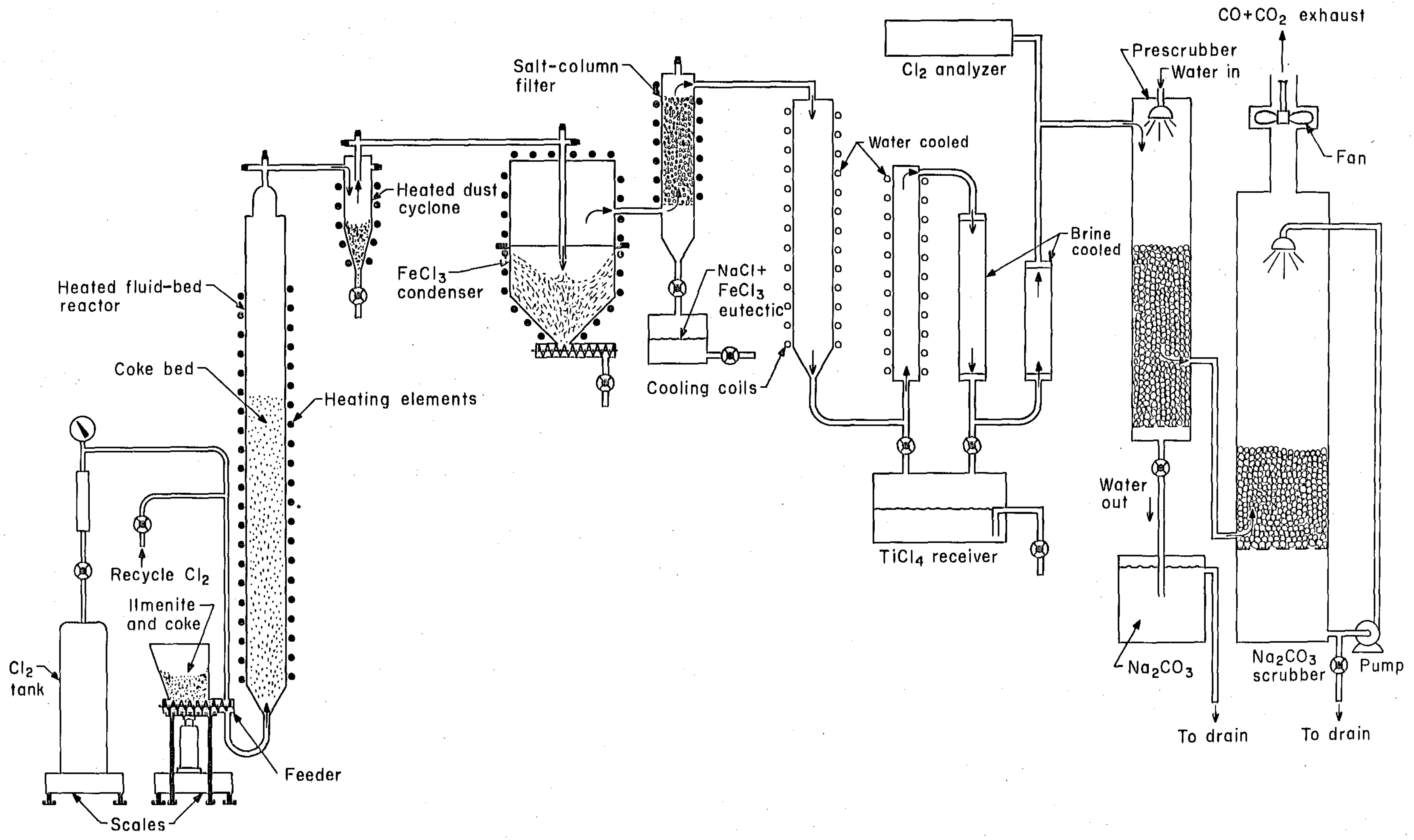

FIGURE 4. - Unit for chlorinating ilmenite in a fluidized bed.

heated by an external, insulated Nichrome element to temperatures of 100° to 250° C.

Offgases and $TiCl_4$ vapor were cleaned in a bed of heated salt pellets at 200° to 400° C, and the liquid NaCl-$FeCl_3$ eutectic that formed was collected. Some of this minor byproduct may furnish the NaCl catalyst used in the dechlorination of iron chloride powders. Most of the salt-column filter and $TiCl_4$-condensing system was constructed from pyrex double-tough glass tubing and fittings.

In the primary $TiCl_4$ condenser (15.2-cm-ID), vapors were cooled by an internal hollow plate with fins and with an externally wound coil, both cooled with tapwater. Secondary condensers of the tube-and-shell type were cooled to minus 11° C by circulated brine from an ice-salt mixture. Liquid $TiCl_4$ was collected in graduated tubes and then discharged into preweighed storage containers.

Vapor and gas mixtures leaving the final $TiCl_4$ condenser were scrubbed with tapwater in a countercurrent packed column to collect soluble chlorides to evaluate condensation. The resulting solution was neutralized with sodium carbonate before disposal. Final scrubbing of gases was done with sodium carbonate solution sprayed into the top of a countercurrent packed column. The clean CO-CO_2 offgas could be recycled and burned to heat systems in pilot or industrial plants. Elements heating the reactor, cyclone, and iron chloride condensers were controlled by thermocouples and Wheelco controllers, with a second thermocouple and controller to guard against override. Other heaters were manually controlled using powerstats with ammeters. A six-point recorder was used to continuously record temperatures in the fluidized bed, crossarms, cyclone, iron chloride condenser, and salt column.

During chlorination tests, a continuous sample of offgas was aspirated through a calibrated automatic chlorine analyzer. A photocell in this analyzer sensed the preferential adsorption of utltraviolet light by chlorine in the offgas. The output was amplified and recorded on a Leeds and Northrup strip chart recorder. This allowed ease in sensing suitable ilmenite-chlorine ratios and facilitated maintenance of positive but low chlorine concentration (>5 vol-pct) in the system. Fairly high chlorination efficiency was attained, but it also insured that most of the iron would form $FeCl_3$ rather than the high-boiling-point $FeCl_2$. Samples of the offgases were also analyzed periodically by Orsat methods for Cl_2, CO, CO_2, O_2, and $COCl_2$.

Procedure

Most chlorination tests were performed at close-to-steady-state conditions to obtain material balance data and to permit valid comparison of the effect of operating variables. Most of the tests were conducted for 3- to 5-hr periods, and operating conditions of temperature (±10° C), chlorine flow (±1 l/min), and ilmenite feed rate (±2 g/min) were maintained as constant as possible. Chlorine flows and ilmenite feed rates tested were from 15 to 25 l/min and 25 to 54.8 g/min, respectively.

Ilmenite and coke used in all tests were predried at 110° C. Generally the chlorinator system was preheated; then 4,000 g of coke was loaded into the reactor and heated to the selected operating temperature using a fluidizing flow of nitrogen. Upon initiating the chlorine flow, the nitrogen flow was turned off and the ilmenite feed was started. Initial weights of the chlorine tank and ilmenite feeder were recorded. In the majority of tests, the ilmenite fed contained no coke to simplify material balances. Preliminary bed-height tests, and other tests using 15 to 20 pct coke in the ilmenite fed, showed no appreciable differences in processing results with bed depths from 30 to 76 cm, the range encountered in a 5-hr test without a coke feed.

However, in some tests, mixtures of coke and ilmenite were used to compensate for the coke used up to maintain a constant bed height. Temperatures were adjusted to those desired for the reactor, cyclone, $FeCl_3$ condenser, and salt-column filter. Flow of water and brine coolants was started during the preheating stage.

Chlorine flow and ilmenite feed rates were set using calibration charts. Final adjustments were made depending on the chlorine content in the offgas as indicated by the continuous analyzer and on rates calculated from periodic weights of chlorine and ilmenite supplied. Ilmenite feed rates were generally slightly less than for stoichiometric reaction to produce $TiCl_4$ and $FeCl_3$, thus insuring the presence of chlorine (2 to 5 pct) in the offgas.

Records were kept of all operating conditions and of the volume of liquid $TiCl_4$ collected versus time. When tests were terminated, all systems except cooling lines were shut off, and a small flow of nitrogen was started to carry residual chloride vapors to the condensers. When the system was cooled to room temperature, weights of collected $TiCl_4$ and byproducts were recorded.

Samples of the $TiCl_4$ and byproducts were analyzed, and the water-soluble, insoluble, and ignited insoluble materials in the byproducts were determined. Soluble materials were itemized as chlorides; ignited insoluble materials, as unreacted ilmenite; and loss on ignition of the insoluble portion, as coke. Spectrographic and chemical methods were used to determine chemical content of the as-collected samples and soluble and insoluble portions of samples. Soluble chlorides were generally dissolved in distilled water, and then precipitated with NH_4OH; the precipitate was ignited at 800° C. This simplified qualitative spectrographic analysis and gave impurity results in terms of the end-product oxides (TiO_2 and Fe_2O_3) rather than chlorides. Periodic analyses showed that solutions remaining after filtering hydroxides had insignificant amounts of soluble chlorides.

The ilmenite reacted in each test was calculated from the ilmenite fed less the weight of ignited insoluble material in the bed residue, cyclone, and iron chloride byproducts. Recovery of $TiCl_4$ was calculated in percent of stoichiometric recovery based on the ilmenite reacted rather than on the ilmenite fed. This is reasonable because it gives recoveries more representative of continuous operation in which most of the unreacted ilmenite collected in cyclones would be recycled, thereby increasing $TiCl_4$ recovery.

Also, this procedure facilitated material balances because the ore left in the bed and cyclone was eliminated.

Chemical Analyses and Particle Size of Ores

Table 3 shows the chemical analyses of the domestic ilmenites and one slag that were tested. Significant features are the lower TiO_2 and higher FeO content of New York ilmenite compared with the other ores. Appreciable amounts of Al, Mg, Mn, and Si impurities are found in all of the ilmenites. High-boiling-point chlorides form from Mn, Mg, Ca, and Cr impurities. Vanadium and silicon form low-boiling-point chlorides that may condense with the $TiCl_4$. Part of the loss on ignition (LOI) shown is accounted for by the water, C, and S contents indicated. Some may result from flotation reagents used to prepare these ore concentrates from the original ores.

TABLE 3. - Chemical analyses of ilmenites tested, wt-pct

Oxide	Titania ore sources				Tennessee slag[1]
	Florida	New Jersey	New York	Tennessee	
TiO_2	63.0	61.4	45.2	66.0	85.1
FeO	3.5	2.1	37.5	-	7.5
Fe_2O_3	26.7	28.3	7.1	26.7	-
Al_2O_3	1.63	.99	2.06	.05	1.97
MnO_2	1.22	.88	.36	.68	1.88
MgO	.48	.35	2.65	.05	.48
SiO_2	.46	1.12	3.74	2.40	1.98
CaO	.06	.02	.12	.05	.33
V_2O_5	.18	.16	.14	.08	.09
Cr_2O_3	.15	.03	.06	.09	.09
ZrO_2	.14	.01	.22	.07	.50
LOI	2.2	3.2	[2]+3.60	1.7	[2]+4.7
C	.26	.11	.08	.28	.01
S	.04	.03	.41	.01	.03
H_2O	.36	.44	.10	.29	0

[1] Slag made from Tennessee ilmenite. Also contains 0.16 pct Cb and 0.05 pct K_2O.

[2] Gained weight on ignition.

Ilmenites used for the majority of tests were ground to 90 pct finer than 325 mesh for rapid reaction, thus allowing close control of the ilmenite-chlorine reaction ratio and, therefore, of the $FeCl_3$-$FeCl_2$ ratio. Coarser ores might accumulate in the bed allowing preferential iron removal and would produce too much $FeCl_2$, which would adversely affect subsequent processing. Wet screen analyses are given in table 4 for the ores tested. As shown, coarser sizes of New York ilmenite, Tennessee ilmenite, and slag were tested also. A calcined grade of petroleum coke, 98.6 pct of which was minus 20- plus 100-mesh screen size, served as the fluidized-bed material and as the reductant.

TABLE 4. - Particle size distribution of ilmenites wt-pct retained[1]

Mesh	Source and type of ore					Tennessee slag
	Florida	New Jersey	New York-1	New York-2	Tennessee[2]	
Minus 20 plus 48	0	0	0	0	0	0.1
Minus 48 plus 65	.1	0	0	0	0	.1
Minus 65 plus 100...........	.1	0	0	.4	0	.1
Minus 100 plus 200...........	.2	0	.2	32.8	7.0	9.7
Minus 200 plus 325...........	2.6	.1	.2	29.6	32.4	24.1
Minus 325.......	97.0	99.9	99.6	37.2	60.6	65.9

[1] Wet sieve analyses.

[2] A finer ground ore (83 pct minus 325 mesh) was also tested.

RESULTS

Florida Ilmenite

The effect on results of coke-bed temperatures during chlorination of Florida ilmenite is given in the top three lines of table 5. As shown, both the ilmenite reacted and the $TiCl_4$ recovered were greater in tests at higher temperatures in the range of 1,050° to 1,150° C. Recovery of up to 97.4 pct of the $TiCl_4$ from the ilmenite reacted indicates the effectiveness of the processing. These results are for close to optimum conditions of chlorine flow and ilmenite feed rate. Based on the ore fed, maximum $TiCl_4$ recovery was 93 pct. Fluidized-bed height at the start of the tests was 75.2 to 82.5 cm. Ilmenite reacted was 89.1 to 95.3 pct of the ilmenite fed into the reactor. Most of the unreacted ilmenite, 2.7 to 7.1 pct of that fed, was collected in the cyclone and would be recycled in industrial processing, thereby increasing ore conversion and $TiCl_4$ recovery.

TABLE 5. - Results of chlorination tests of Florida ilmenite: ore reacted and $TiCl_4$ recovery

Temperature, ° C	Cl_2 flow, l/min	Ore feed rate, g/min	Ore[1] reacted, pct	$TiCl_4$[2] recovered, pct	Cyclone[3] ore, pct
950..........	18.2	31.5	89.1	89.7	6.2
1,050.........	18.4	35.2	89.0	95.6	7.1
1,150.........	18.0	30.0	95.3	97.4	2.7
1,050.........	21.6	39.7	89.6	85.0	6.0
1,050.........	25.0	54.8	77.6	82.3	16.9

[1] Ore reacted in percent of ore fed.

[2] $TiCl_4$ recovered in percent of stoichiometric from the ore reacted.

[3] Ignited insoluble (unreacted ore) in cyclone collected dusts in percent of ore fed.

Results of chlorinating Florida ilmenite at 1,050° C with chlorine flow rates ranging from 18.4 to 25.0 l/min also are shown in table 5. At the lowest chlorine flow shown (18.4 l/min), approximately 89 pct of the ilmenite fed reacted, and recovery of $TiCl_4$ from the ore reacted was 95.6 pct. As shown, reaction of ilmenite and recovery of $TiCl_4$ were lower in tests with chlorine flows greater than 18.4 l/min. The chlorine flow rates shown in table 5 correspond to superficial linear velocities of 15 to 23 cm/sec. At chlorine flow rates above 18.4 l/min, the increased gas velocity would result in shorter residence times for the reactants with reduced yields. This assumption is supported by the fact that greater amounts of ilmenite are carried over into the cyclone and into the $FeCl_3$ byproduct at the higher chlorine flow rates. Lower velocities promote higher recoveries and are within the range used in industrial reactors. With chlorine flows lower than 18 l/min, recovery was higher but output was less than optimum. A mixed feed of ilmenite-20 pct coke was used without problems in the test at 1,050° C and a chlorine flow of 21.6 l/min.

Cyclone Byproduct

Amounts of unreacted ore in the cyclone and analyses of byproducts such as bed residue and material collected in the cyclone are given in table 6. Higher dust carryover is evident at lower temperatures or higher Cl_2 flow rates. Care must be used in considering the results because they reflect the effects of varied conditions of temperature, chlorine flow rate, and ilmenite feed rate. These and other data indicate that the optimum conditions for processing Florida ilmenite (a compromise between output and recovery) are reaction temperatures of 1,050° to 1,150° C and a chlorine flow rate of approximately 18 l/min. The water-insoluble portion of the cyclone byproduct is a mixture of coke and ilmenite, which could be recycled to industrial reactors when neutralized and dried. The partially reacted ilmenite is enriched in TiO_2 and has reduced iron content. Water-soluble chlorides removed from the cyclone product were approximately one-half $MnCl_2$, one-fourth $MgCl_2$, and one-fourth $FeCl_2$. Preliminary tests indicate that a manganese oxide-iron oxide byproduct or separate iron and manganese oxide byproducts can be recovered by controlled precipitation and calcination of the chloride solutions.

TABLE 6. - Results of chlorination tests of Florida ilmenite: analyses of byproducts

Temperature, ° C	Cyclone dust, pct		Iron chloride, pct		Bed residue, pct	
	Soluble	Ore	Ore	Coke	Soluble	Ore
950................	13.7	58.0	3.6	3.8	1.6	4.2
1,050................	13.1	65.7	2.6	0	1.5	7.2
1,150................	19.8	42.3	1.2	1.6	-	-
1,050................	6.0	38.8	3.7	.1	.8	1.0
1,050................	7.2	84.7	4.0	.8	3.1	12.2

Iron Chloride and Bed Residue

The percentages of ignited insolubles and coke material in the iron chloride byproduct are also given in table 6. Amounts of ignited insolubles found in the iron chlorides indicate the need for improved processing or filtering to lower ilmenite dust in the iron chloride. Operating conditions necessary to minimize carryover of titania into the iron chloride are indicated. An iron chloride byproduct with a titanium content of less than 1 pct is needed to produce Fe_2O_3 byproduct acceptable for use in the manufacture of iron or steel in the United States. In the test at 1,050° C with 18.4 l/min of chlorine and an ilmenite feed rate of 96 pct of stoichiometric, the data on insoluble content in the iron chloride or cyclone are considered to be the most significant. Coke contents of the iron chloride were from zero to 3.8 pct of the total sample but are not objectionable because coke is needed for heating the dechlorinator. Data for the bed residues cannot be directly related to continuous, industrial, fluidized-bed operation but do show that the coke bed remains very clean and therefore free flowing during short-term tests, except at the highest feed rates used.

Chemical Analyses

The as-condensed $TiCl_4$ products (converted to TiO_2) contained the following impurities: Fe, 0.02 to 0.06 pct; V, 0.12 to 0.15 pct; and Si, 0.11 to 0.14 pct. Crude $TiCl_4$ was purified by the customarily used oleic acid oil treatment followed by fractional distillation, which separates impurities from the refined $TiCl_4$ (<u>11</u>). This treatment gave a $TiCl_4$ product that contained less than 5 ppm Fe and V, and less than 0.1 pct Si, thus meeting specifications for pigment-grade $TiCl_4$.

Chemical impurities in the Fe_2O_3 made from the soluble portions of the iron chloride byproduct are given in table 7 for tests at 950° and 1,050° C. Ratios of $FeCl_3$-$FeCl_2$ from 70 to 420 were found with all ilmenites tested when ilmenite feed rates were less than stoichiometric for producing $TiCl_4$ and $FeCl_3$.

TABLE 7. - Chemical analyses of iron chloride byproducts[1]

Temperature, ° C	Main soluble impurities, pct[2]					Coke, pct	Total Ti, pct	Ore, pct
	Al	Mg	Mn	Ti	Si			
950..................	0.74	0.27	1.09	0.45	0.07	3.8	1.69	3.6
1,050................	.84	.26	.77	.24	.10	0	1.61	2.6

[1] Insoluble contents were 7.4 and 2.6 pct, respectively, including both ilmenite and coke.

[2] Analyses are for Fe_2O_3 made by precipitation of chloride solutions with NH_4OH, followed by drying and ignition.

Analyses of the ignited insoluble portions of the cyclone dusts, bed residue, and iron chlorides showed the major elements present were titanium at 39.6 to 47.1 pct (66 to 78.6 pct TiO_2) and iron in amounts of 4.0 to 13.7 pct. The Florida ilmenite processed contained 63 pct TiO_2 and 21.4 pct iron.

Some minor byproducts from the salt-column filter and water scrubber were analyzed. For example, about 4 pct of the total $TiCl_4$ made was collected in a water scrubber in the aforementioned test at 1,050° C. This amount of $TiCl_4$ was not recovered in the condensers and it also was not included in the recoveries reported. An ignited precipitate of the wash contained 50.2 pct Ti (84 pct TiO_2), 3.3 pct Si (5.9 pct SiO_2), and minor amounts of V and Fe.

Eutectic collected from the salt-column filter in the aforementioned test contained 15 pct of the $FeCl_3$ byproduct; this is higher than found in later tests. An improved condenser installed reduced the amount of iron chloride reporting to the filter to <5 pct.

Other Ores

Results of chlorination tests with ores from Tennessee, New York, and New Jersey are summarized in tables 8-9. The Tennessee ilmenite was less reactive than the other ores, possibly because of its coarser particle size and high silica content (tables 3-4). Also, the ore feed rate was somewhat higher than normal at 105 to 110 pct of stoichiometric in these two tests. This ilmenite, when ground to 83 pct finer than 325 mesh and chlorinated at 1,050° C, was slightly more reactive than the coarser size (60.6 pct minus 325 mesh) used in the other tests, but was less reactive than other ores. Of the ores tested, that from New York was the most reactive: 93 to 96 pct of the ilmenite reacted in a series of tests at temperatures from 950° to 1,050° C. Coarser New York ore that was only 37.2 pct minus 325 mesh (table 4) was 96 pct reacted at 1,050° C, with 96-pct recovery of $TiCl_4$. The test series with the low-grade, rock-type New York ore and others indicated that reactivity of the ores depends considerably on the chlorine flow rate, temperature, and ore feed rate. Small increases in chlorine flow above approximately 17 l/min and ilmenite feed rates above 30 g/min decrease the amount reacted and increase the ilmenite dust content of the iron chloride byproduct. Increasing the reaction temperature within the limits of 950° to 1,150° C increased ore reactivity and decreased the dust content of the iron chloride byproduct. Highest recovery of $TiCl_4$ (99 pct) from the ore reacted was obtained in tests of the New York and New Jersey ilmenites, probably because of higher condenser efficiency. Further research is needed to determine more fully the effect of particle size of ores on reactivity and $TiCl_4$ recovery. Ore with a 15-pct addition of coke was used in the first and last tests listed in tables 8-9.

As shown in table 8, the ore carryover (ignited insoluble) collected in the cyclone ranged from 1.8 to 14.4 pct of the total fed. Analyses of the cyclone byproducts given in table 9 showed considerable variation in the amounts of coke, ilmenite, and soluble materials collected, depending on the particular ore and test conditions. As with the Florida ilmenite, the major elements in the soluble portion were Mn, Mg, and Fe. The silicon in the ignited insoluble portion was generally higher than in the ore tested. Some of the variations in cyclone byproducts result from the differences in constituents of the various ores as well as the test conditions used. The remainder of the cyclone dust, not shown, is coke.

TABLE 8. - Chlorination tests of domestic ores

Temperature, ° C	Cl_2 flow, l/min	Ore feed rate, g/min	Ore size, mesh	Ore[1] reacted, pct	$TiCl_4$[2] recovery, pct	Cyclone[3] ore, pct
TENNESSEE SLAG						
1,000..........	19.0	28.6	-200	90	95	8.0
TENNESSEE ILMENITE						
1,050..........	18.7	32.2	-200	84	93	14.4
950..........	17.8	37.7	-100	75	87	18.9
1,050..........	18.0	39.0	-100	82	95	8.6
NEW YORK ILMENITE						
950..........	16.6	27.6	-325	96	99	2.8
1,000..........	17.6	32.6	-325	93	[4]90	5.7
1,050..........	18.0	22.3	-325	93	94	2.9
1,050..........	18.5	32.4	-100	96	96	1.8
NEW JERSEY ILMENITE						
950..........	17.7	31.2	-325	89	99	9.1
1,050..........	18.0	31.6	-325	90	99	8.2
950..........	13.0	14.0	-325	91	[4]84	6.2

[1] Ore reacted in pct of ore fed.

[2] $TiCl_4$ recovery in pct of stoichiometric for ore reacted.

[3] Ore in cyclone dust in pct of ore fed.

[4] Condensers were not operating at full efficiency.

TABLE 9. - Analyses of byproducts

Temperature, ° C	Cyclone dust, pct		Iron chloride, pct		Bed residue, pct	
	Soluble	Ore[1]	Ore[1]	Coke[2]	Soluble	Ore[1]
TENNESSEE SLAG						
1,000................	17.8	72.3	3.3	1.5	1.6	4.3
TENNESSEE ILMENITE						
1,050................	4.1	90.7	3.8	1.0	0.7	1.2
950................	3.0	90.7	11.2	1.4	1.8	4.3
1,050................	14.7	80.8	18.2	2.8	2.0	8.6
NEW YORK ILMENITE						
950................	43.7	35.4	0.4	0.2	-	-
1,000................	27.3	66.0	1.6	.1	0.7	1.0
1,050................	46.7	44.0	.6	.1	0	3.6
1,050................	48.2	42.1	.2	.2	1.6	5.3
NEW JERSEY ILMENITE						
950................	12.0	82.6	4.4	1.1	0.9	1.0
1,050................	32.2	59.1	3.0	.3	.7	1.4
950................	6.5	47.6	2.9	2.0	0	1.3

[1] Ignited insoluble content of dust (unreacted ore).

[2] Loss on ignition of insoluble portion of dusts (coke).

Iron chloride byproducts are quite similar for the different ores except for that made from the coarser Tennessee ilmenite, which contained a greater-than-usual amount of ilmenite dust. Ilmenite and coke contents in the iron chlorides were lowest when chlorine flows were less than 17 l/min and when ore feed rates slightly lower than stoichiometric were used at temperatures of 1,050° to 1,150° C, except for the Tennessee ilmenite. A compromise probably will be necessary between conditions for maximum output and those for the cleanest iron chloride unless an improved cyclone and filter system (scheduled for testing) reduces dust carryover into the iron chlorides.

Integrated Tests

Results are given for one of the integrated chlorination-dechlorination tests, the last listed in tables 8-9. Except for the limited chlorine flow, which was the maximum possible with the compressor used, the results were similar to those for other tests. Offgas containing 85 wt-pct Cl_2 and 15 wt-pct O_2, made by dechlorination of commercial-grade $FeCl_3$, was filtered and pumped to the chlorinator where New Jersey ilmenite was chlorinated under the conditions indicated. Although the reaction was satisfactory, recovery of $TiCl_4$ was lower because of ineffective operation of the last two condensers. Byproducts did not differ much from those for regular tests except for a higher coke content in the cyclone byproduct. Byproduct iron chlorides collected were reacted with oxygen at 500° C in a fluidized bed of Fe_2O_3 to produce chlorine-rich gases and Fe_2O_3 (19).

Chemical Analyses

Products and byproducts made from Tennessee, New Jersey, and New York ores had analyses similar to those discussed for the Florida ilmenite with a few exceptions. The unrefined $TiCl_4$ from the New Jersey ilmenite had a lower content of impurities than that from other ores, as shown in table 10. The soluble chloride content of the cyclone dusts was highest for the New York ore, as expected because of its higher content of iron and impurities. Iron chloride byproducts contained 0.2 to 4.4 pct ignited insoluble material except for that made from the coarser Tennessee ilmenite. With close control of chlorine flow, ilmenite feed rate, and use of high temperatures (>1,050° C), an iron chloride byproduct with less than 1 pct ignited insoluble content should be possible except with the Tennessee ore. Low insoluble contents were especially notable in the series of tests with New York ore when chlorine flows were less than 18 l/min at temperatures of 1,000° C or higher. In future tests an improved cyclone and filtering system will be used to reduce dust content of the iron chloride.

TABLE 10. - Chemical analyses of TiO_2 made from unrefined $TiCl_4$[1]

Type of ore	Chemical content, pct			
	Fe	V	Si	Al
Florida	0.06	0.12	0.11	0.15
New Jersey	.05	.01	.01	0
New York	.08	.17	.17	.13
Tennessee	.43	.15	.15	0
Tennessee slag	.01	.12	.12	0

[1] Chlorination tests made at 1,050° C.

DISCUSSION AND CONCLUSIONS

Direct chlorination of domestic ilmenites in a fluidized coke bed at reaction temperatures from 950° to 1,150° C gave high recovery of $TiCl_4$. As condensed, the $TiCl_4$ had minor amounts of V, Fe, and Si chlorides that were removed by treatment with oleic acid oil followed by distillation. This gave a refined $TiCl_4$ product acceptable for use in manufacturing TiO_2 pigment or for further refining for Ti metal production. When finely ground to minus 325 mesh, all the domestic ilmenites tested had adequate reactivity to allow high conversion of the TiO_2 content to $TiCl_4$. Also, close control of important variables was demonstrated such as the $FeCl_3$-$FeCl_2$ ratio, low accumulation of ilmenite and soluble chlorides in the fluidized coke bed, and a minimum amount of cyclone collected dusts requiring recycle. The $FeCl_3$ byproduct, with other chloride impurities, had a fairly low insoluble (ilmenite) content and was reacted with O_2 in another unit to make Fe_2O_3 and Cl_2 for recycling to the chlorinator, thus eliminating the majority of soluble waste generated during chlorination of ilmenite. A manganese byproduct was made from the soluble portion of the cyclone dusts; the insoluble portion, mainly ilmenite and coke dusts, may be recycled to the process to increase recovery of $TiCl_4$. Additional research is being conducted to reduce the tendency toward clogging of the reactor outlet and crossover encountered when processing some ores and to effect more complete dust removal in cyclones and filters prior to condensing the iron chloride. This should give an Fe_2O_3 with a much lower Ti content, which could be used in the iron and steel industry.

Results of tests in a 10.2-cm reactor were similar to those in a 5.1-cm reactor (5) except that higher reaction temperatures were possible with a vitreous silica rather than Vycor reactor. Output of the larger reactor was approximately six times that of the smaller reactor for an area ratio increase of 4, but higher reaction temperatures were used.

No serious problems were encountered with structural materials used in the chlorinator system. The heated Inconel cyclone (600° C) and nickel-stainless steel iron chloride condenser (200° C) are still in service after 2 years of testing. The vitreous silica (clear quartz) reactor used was not appreciably eroded. However, results with these materials cannot be projected for design of larger systems because construction and heat requirements of industrial-sized systems are completely different. Large chlorinators for enriched ilmenite and rutile ores are presently operated safely and economically at conditions comparable with those used in the laboratory testing.

The favorable results obtained in laboratory-sized systems indicate that further investigation of the chlorination-dechlorination process in a larger, fully integrated pilot plant is warranted.

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