Dechlorination of Ferric Chloride With Oxygen

A. W. HENDERSON, T. T. CAMPBELL, AND F. E. BLOCK

Because of increasing ecological concern, the Bureau of Mines is investigating the use of chlorination technology in extractive metallurgy. A key problem is the fact that ferric chloride is commonly generated during processing of a wide variety of ores and minerals. This paper describes small laboratory-scale studies designed to effect dechlorination of ferric chloride by oxygen in a fluidized bed reactor to produce a viable, nonpolluting iron oxide product and chlorine gas, which could be recycled in a chlorination process. These studies demonstrated that close to 100 pct conversions of ferric chloride to ferric oxide and chlorine can be effected by reaction with oxygen at temperatures ranging from 500° to 650°C. The off-gas from the single-stage reactor contained up to 95 pct chlorine. The study also demonstrated that the presence of a small amount of NaCl in the reactor catalyzed the reaction between ferric chloride and oxygen and permitted high conversions at temperatures as low as 500°C.

BECAUSE of pending world-wide shortages of rutile, there has been intensified interest in methods of utilizing ilmenite as a source of titania either for pigment or for metal production. Although ilmenite can be treated by sulfuric acid attack, undesirable quantities of ferrous sulfate are generated that constitute a water pollution problem. Other approaches being studied include pyrometallurgical practices to produce high-titania slags, synthetic rutile, or titanium carbide.[1] These upgraded materials can be chlorinated to produce titanium tetrachloride and a small amount of iron chloride, which is readily removed by fractional condensation and distillation. After final purification the resulting titanium tetrachloride can be used for metal production or converted to pigment-grade TiO_2.

An alternate approach for recovering titania from ilmenite involves direct chlorination; however, in this case, excessive quantities of ferrous or ferric chloride are generated which constitute a loss of chlorine and pose a serious pollution problem. The application of chlorine in metallurgical processing is seriously hampered from both an economic and an ecological standpoint by the generation of iron chlorides.

Although we have emphasized the generation of ferric chloride during ilmenite processing, it should be recognized that the use of chlorination practice in processing a wide variety of ores and concentrates depends upon the successful development of a method for dechlorinating ferric chloride. Accordingly, this study was undertaken to develop an economical method for dechlorinating ferric chloride to produce a nonpolluting iron oxide product and chlorine for recycle.

In general, there is only limited information in the literature dealing with dechlorination of ferric chloride. The information that is available is mostly restricted to patents, which disclose the displacement of chlorine by oxygen. These patentable disclosures differ primarily in the method used to introduce ferric chloride into a reactor for combustion with oxygen according to the following equation:

$$2\,FeCl_3 + \tfrac{3}{2}O_2 = Fe_2O_3 + 3\,Cl_2$$
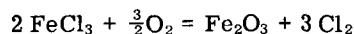
The patents indicate that the above reaction occurs at temperatures ranging from 500° to 1000°C. Dunn[2] describes the use of a sodium chloride-iron chloride eutectic salt in a moving bed reactor. The eutectic salt is dispersed as a liquid film on inert spheres (alumina) which are introduced at the top of a vertical reactor. The coated spheres move downward through the reactor countercurrent to a flow of oxygen. As the coated spheres move downward, iron oxide and Cl_2 are produced. Another method reported involves the direct combustion of ferric chloride vapor with oxygen.[3] Carbon or carbon monoxide was introduced near the outlet of the reactor to inactivate oxygen. This inactivation procedure is reported to prevent a crust of iron oxide forming which would otherwise cause plugs. The use of a fluidized-bed reactor was also reported.[4,5] Particles of iron oxide are maintained in a state of fluidization to provide a large number of surfaces for ferric chloride vapor to react with oxygen. The fluidized particles of iron oxide are reported to catalyze the formation of iron oxide and chlorine.

After a preliminary investigation of these patentable disclosures, the combustion of $FeCl_3$ in a fluidized bed of iron oxide was chosen for more extensive study. Attractive features of a fluidization process include excellent heat transfer, high throughput, good control of process streams, and continuous operation.

Preliminary studies on the dechlorination of $FeCl_3$ quickly indicated that a critical feeding problem is associated with the physical and chemical characteristics of this compound and its reaction products with oxygen. At temperatures ranging from 100° to about 320°C, stable compounds including Fe_2O_3, $FeCl_2$, and $FeOCl$ form on the $FeCl_3$ feed inlet lines leading into the fluidized-bed reactor, causing plugging and disrupting operation.

EXPERIMENTAL PROCEDURES AND RESULTS

Prior to conducting research in a fluidized bed reactor, studies were undertaken in a closed system to obtain a better understanding of the $FeCl_3$-O_2 system.

| Table I. Physical Properties of Iron Chlorides[7]			
Chloride	Melting Point, °C	Boiling Point, °C	Thermal Decomposition Reactions[6]
$FeCl_3$	304	319	$FeCl_3 = FeCl_2 + \frac{1}{2}Cl_2$
$FeCl_2$	677	1,026	None
FeOCl	Decomposes above 200°C	Decomposes above 200°C	$3FeOCl = Fe_2O_3 + FeCl_3$

Selected physical properties of these iron chloride compounds are given in Table I.

Reaction rates were determined by pressure differences as a function of time and temperatures. Studies were conducted at 1 to 2 atm pressure and temperatures ranging from 50° to 300°C. Results show two simultaneous, first-order reactions, neither of which went to completion, probably because of interference by a product layer on the unreacted chloride. Grinding the reacting solid increased the amount of $FeCl_3$ reacted, but the reaction was still not complete, and the reaction gases had a low chlorine content.

Low-temperature (below 300°C) reaction of oxygen with ferric chloride has been characterized by three general temperature regions. Below 100°C no substantial reaction occurs. Between 100° and 200°C the reaction

$$2\,FeCl_3 = 2\,FeCl_2 + Cl_2 \qquad [1]$$

occurs, along with some oxidation to FeOCl according to the reaction:

$$2\,FeCl_2 + O_2 = 2\,FeOCl\ and\ Cl_2 \qquad [2]$$
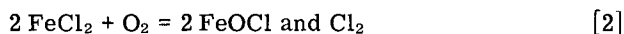
At temperatures greater than 200°C FeOCl decomposes as shown in Eq. [3]

$$3\,FeOCl = FeCl_3 + Fe_2O_3 \qquad [3]$$

$$2\,FeCl_3 + \tfrac{3}{2}\,O_2 = Fe_2O_3 + 3\,Cl_2 \qquad [4]$$
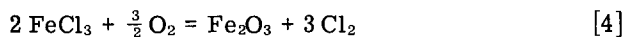
and further reaction with oxygen occurs slowly. The rate of reaction between $FeCl_3$ and O_2 to form Fe_2O_3 and Cl_2 is somewhat slow at 300°C but is almost instantaneous at 600°C.

Equipment

Several fluidized-bed reactor designs were tested for the dechlorination of $FeCl_3$. The major problem encountered was that caused by plugging of feed inlet lines by $FeCl_2$, FeOCl, and $FeCl_3$. This problem was largely overcome by passing both cold fluidizing gas and $FeCl_3$ through a U-shaped feed tube. Ferric oxide bed particles oscillated in the feed tube owing to pressure fluctuations and tended to scour the feed inlet. The combined effects of using a cold fluidizing gas and the scouring action of the bed material tended to keep the line open and prevented premature reaction in the feed inlet to the reactor. The reactor shown in Fig. 1 proved effective and allowed attainment of steady-state conditions in a few minutes of operation with only infrequent plugging of feed lines. Major features of the apparatus include a feed mechanism, fluid-bed reactor, condenser, dust trap, and Cl_2 analysis unit. Heat to the fluidized bed was supplied by a 2 in. diam, 24 in. long, two-zone resistance-heated tube furnace. The 2 in. diam reactor was constructed of Vycor.* The condenser and dust

traps were constructed of 2 in. diam double-tough Pyrex pipe followed by two saturated NaCl bubblers which incorporated the gas sampling unit and a continuous ultraviolet Cl_2 analyzer.

Iron compounds ($FeCl_3$, Fe_2O_3), NaCl, and O_2 were technical-grade materials purchased from commercial suppliers and used as received. It was found necessary to pretreat the Fe_2O_3 because of its extremely fine particle size. The method adapted for preparing a suitable bed of Fe_2O_3 for fluidization involved blending Fe_2O_3 with anhydrous $FeCl_3$ in a 10 to 1 ratio, followed by adding water, baking, and ignition at 600°C. A suitable particle size was obtained by screening this material through a standard 20-mesh Tyler screen. The $FeCl_3$ was also screened to minus 20 mesh; however, care was exercised to prevent excessive pickup of moisture by the highly hygroscopic chloride salt.

The $FeCl_3$ was contained in a mild steel hopper and screw-fed into a U-shaped Pyrex tube. Oxygen was introduced along with the $FeCl_3$ to assist transport of the chloride salt into the base of the fluidized bed. The U-shaped feed tube was kept free of plugs by the scouring action of Fe_2O_3 particles which oscillated up and down, along with $FeCl_3$, at the base of the fluidized bed. The base of the tapered fluidized bed was joined to a water-cooled 12-mm Pyrex feed assembly by a ball joint connection. A short length of piano wire was inserted into the U-shaped feed line which extended into the fluidized bed. Occasional rotation of this wire caused a flicking motion which was particularly effective in maintaining a smooth flow of reactants and also helped prevent crust formation at the base of the FluoSolids reactor.

Chlorine was continuously analyzed by splitting the off-gas stream, and passing the O_2 and Cl_2 mixture through a system of filters and then into a chlorine analysis unit. The chlorine analysis unit incorporates an ultraviolet light source and photocell. Absorption of ultraviolet light by chlorine permits determination of chlorine concentration. Light which passes through a special filter falls upon a photoelectric cell which converts the light energy into a microamp current. This current is then relayed to a continuous recording instrument for readout. Increased chlorine content of
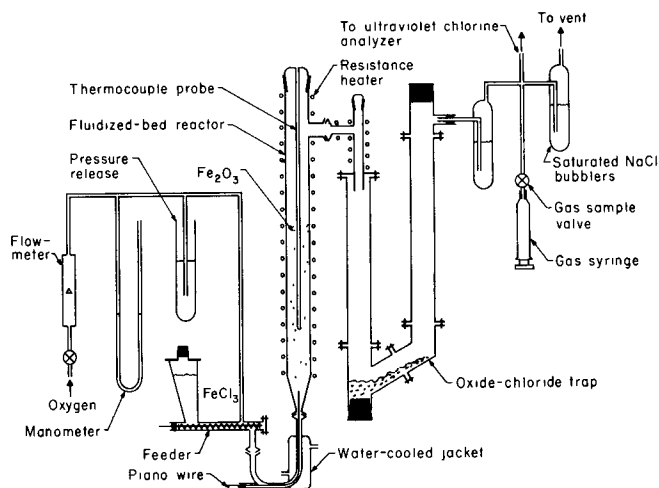

Fig. 1—Fluidized bed for conversion of $FeCl_3$ to Fe_2O_3 and Cl_2.

Fluidized Bed			Oxygen Flow Rate*		Pressure Drop Across Bed
Fe_2O_3, Wt, g	Bed Height, cm	Cross Section, cm^2	cc/Min	cc/cm^2-Min	mm/Hg
800	33 to 38	18	1950 ± 50	108 ± 2.8	60 to 80

*By stoichiometry this amount of O_2 reacts with 18.15 ± 0.47 g/min of $FeCl_3$ (1.01 ± 0.126 g/cm^2-min).

the gas stream decreases the microamp reading because chlorine gas is a strong absorber of light with wave lengths between 280 and 390 mμ. Calibrating and monitoring this gas analysis unit involved the use of a standard Orsat gas analysis apparatus. The gas analysis method involved measuring a volume of gas before and after passing through a solution of potassium hydroxide.

Operating Procedure

Start-up of the fluidized bed reactor was accomplished by charging 800 g of Fe_2O_3 into the reactor, introducing O_2 for fluidization, and then bringing the bed up to the desired operating temperature which ranged from 400° to 650°C. When the Fe_2O_3 bed reached operating temperature, a slow feed (0.25 g/cm^2-min)*

*(g/cm^2-min) refers to grams of $FeCl_3$ per cm^2 of reactor cross section per minute.

of $FeCl_3$ was introduced into the reactor for 5 min, after which O_2 at a flow rate of 108 cc/cm^2-min* was

*(cc/cm^2-min) refers to cm^3 of O_2 per cm^2 of reactor cross section per minute.

passed through the bed for 5 min. This procedure tended to remove fines from the bed, promoted particle size growth of Fe_2O_3 particles, and stabilized the bed, which promoted smooth operation. After this bed conditioning step, final temperature adjustments were made and $FeCl_3$ feeding was resumed. Ferric chloride feed rates were varied by use of a variable speed motor which drove the feed screw. Bed weight, bed height, O_2 flow rate, and pressure were essentially held constant during experimental runs. The magnitude of these parameters is shown in Table II. The amount of $FeCl_3$ converted to Fe_2O_3 and Cl_2 was calculated from the known oxygen flow rate and the percent Cl_2 in the product gas stream, Reaction [4]. Continuous analysis of the percent Cl_2 in the product gas allowed determination of steady-state operation which was indicated by constant Cl_2 gas composition. The percent conversion of $FeCl_3$ to Fe_2O_3 was also calculated from the $FeCl_3$ feed rate, and the amount of unreacted $FeCl_3$ in the system condenser and dust collector.

The percent chlorine in the off-gas as a function of time at several different feed rates is shown in Fig. 2. Inspection of Fig. 2 indicates that steady-state conditions were established in from 5 to 10 min. Wide fluctuations in the percent chlorine were detected immediately and indicated deviations from steady-state operation. These deviations were caused by channeling, bed slugging, and plugs forming either at the inlet or at some point downstream.

Major objectives of experiments were to maximize the conversion of $FeCl_3$ to Fe_2O_3 and Cl_2, and to produce an off-gas containing a high (>90 pct) chlorine content, which would be suitable for recycle as a chlor-
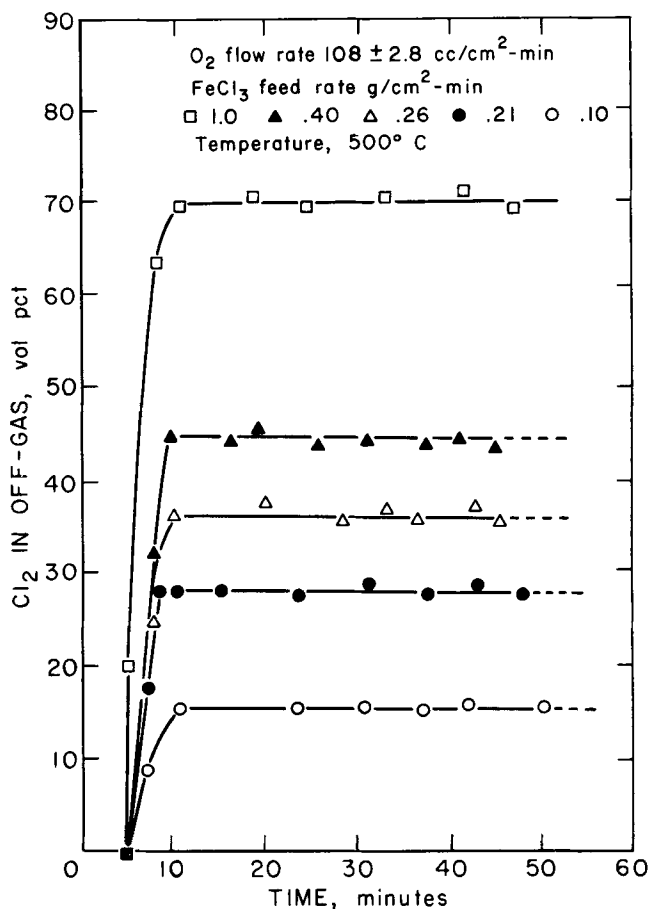

Fig. 2—Percent Cl_2 in off-gas as a function of time.

inating agent. Variables studied during this investigation included temperature, ferric chloride feed rates, and the catalytic effect of NaCl.

Effects of Temperature

A series of tests was performed at temperatures ranging from 400° to 650°C. These tests were conducted in Fe_2O_3 beds which contained no NaCl. Tests were conducted at a $FeCl_3$ feed rate of 1.0 g/cm^2-min and an oxygen flow rate of 108 cm^3/cm^2-min.* Inspection of

*Theoretically an O_2 flow of 108 cc/cm^2-min should convert 1.0 g/cm^2-min of $FeCl_3$.

Fig. 3 shows that conversion of $FeCl_3$ to Fe_2O_3 and Cl_2 is temperature dependent and is very low at temperatures below 500°C. High chlorine concentrations (>90 pct) and high conversions (>90 pct) of $FeCl_3$ to Fe_2O_3 were not effected at temperatures below 600°C.

Effects of Varying $FeCl_3$ Feed Rates

After establishing the necessity of conducting operations at or above 600°C, a series of tests was conducted to determine the effect of varying $FeCl_3$ feed rate on the percent conversion of $FeCl_3$ and the percent chlorine in the off-gas. These tests were conducted at 600°C with an O_2 flow of 108 cc/cm^2-min and without NaCl in the fluidized Fe_2O_3 bed. The results of these tests are shown in Fig. 4.

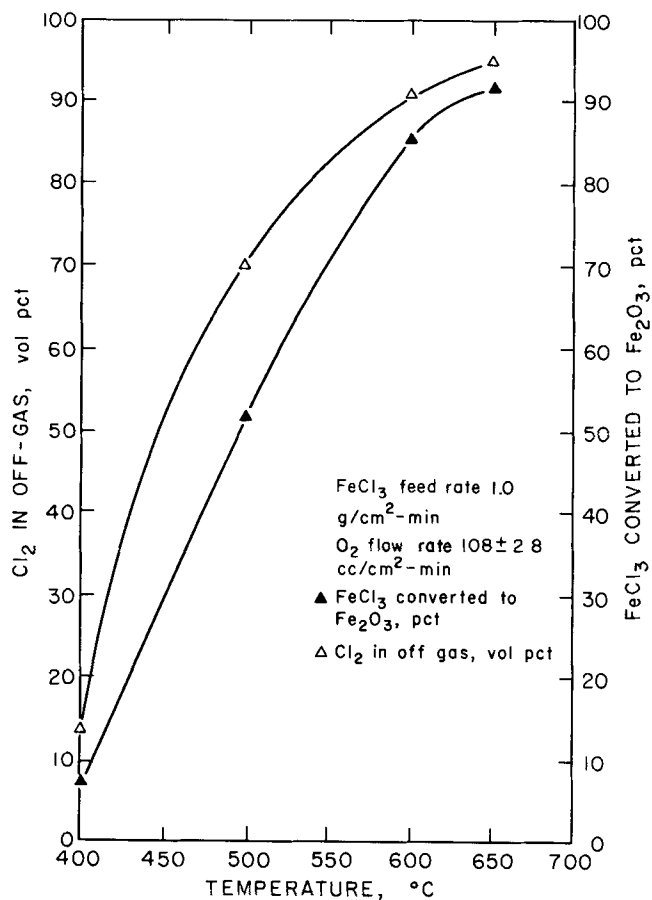Inspection of Fig. 4 indicates that optimum results from the standpoint of both percent conversion and per-

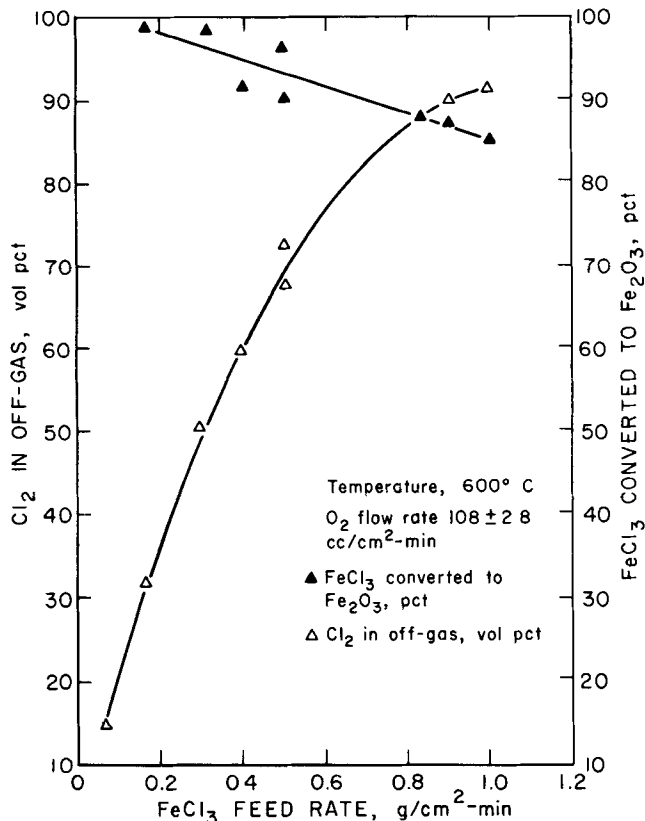Fig. 3—Conversion of FeCl₃ and percent Cl₂ in off-gas as a function of temperature.

cent chlorine in the off-gas was obtained at a feed rate of 0.83 g $FeCl_3/cm^2$-min. This feed rate gave an off-gas containing 87 pct Cl_2 and an 87 pct conversion of $FeCl_3$. Fig. 4 also shows that high conversions of $FeCl_3$ are readily effected but only at the expense of having a low concentration of Cl_2 in the off-gas. It should also be observed that Cl_2 concentration and $FeCl_3$ conversions above 90 pct were obtained at high $FeCl_3$ feed rates or at temperatures above 600°C, as shown in Figs. 3 and 4. An adverse factor associated with operating at temperatures of 600°C or above is due to the corrosive nature of both $FeCl_3$ and Cl_2 at elevated temperature. Accordingly, studies were initiated to determine if the presence of NaCl in the Fe_2O_3
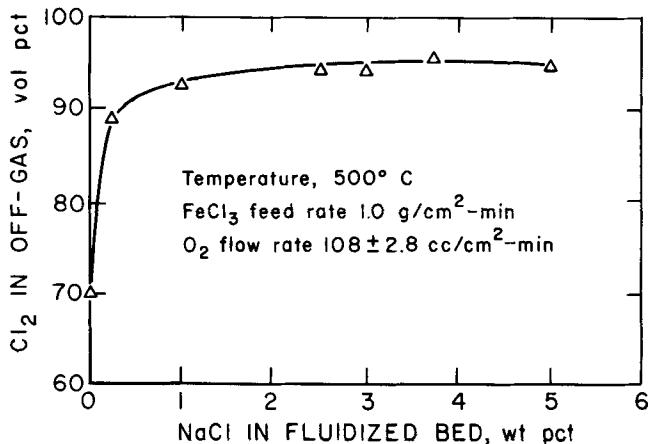

Fig. 5—Percent Cl₂ in off-gas as a function of percent NaCl in Fe₂O₃ bed.

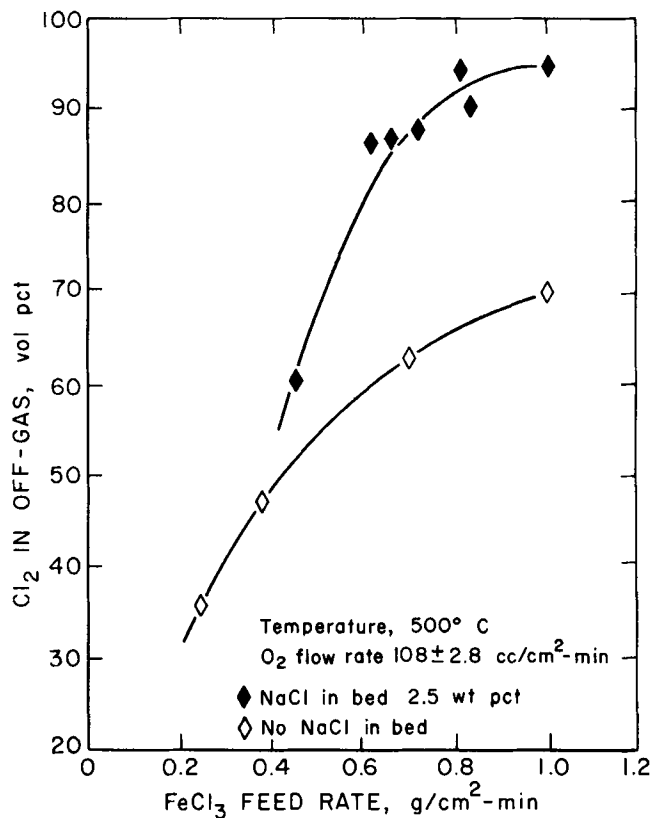Fig. 4—Conversion of FeCl₃ and percent Cl₂ in off-gas as a function of FeCl₃ feed rate.

Fig. 6—Percent Cl₂ in off-gas as a function of FeCl₃ feed rate and bed composition.
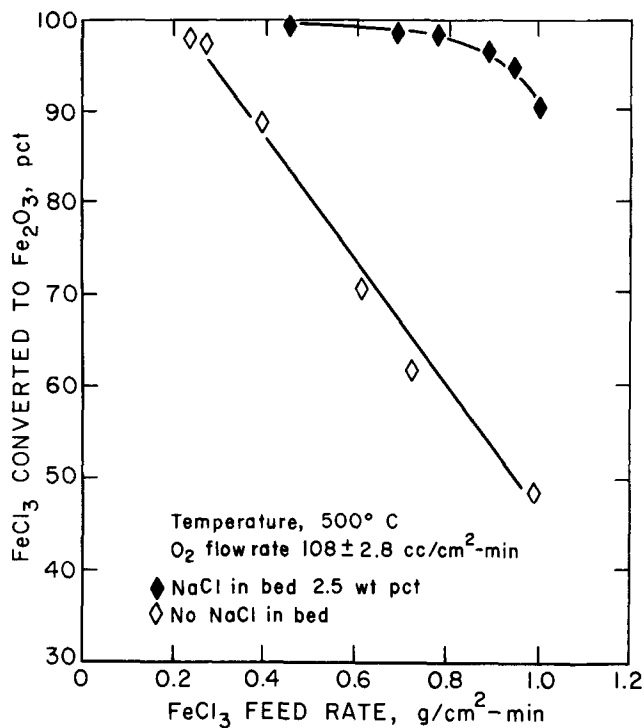
Fig. 7—Percent conversion of FeCl$_3$ as a function of FeCl$_3$ feed rate and bed composition.

would permit operation at lower temperatures. A lower temperature would be desirable because it would reduce corrosion and possibly permit the use of nickel or Inconel as materials of construction.

Effects of NaCl Additions

During an earlier study involving NaCl-FeCl$_3$ salt mixtures,[8] it was observed that the vapor pressure of FeCl$_3$ is significantly reduced by the presence of even small amounts of NaCl and that oxidation of FeCl$_3$ is catalyzed by NaCl. Accordingly, a series of tests was made in which NaCl additions were made to the Fe$_2$O$_3$ bed in amounts ranging from 0 to 5 pct of the bed weight. These tests were all conducted at 500°C, a feed rate of 1.0 g FeCl$_3$/cm^2-min, and a gas flow of 108 cc/cm^2-min. The percent Cl$_2$ in the off-gas is plotted vs the wt pct NaCl in Fig. 5. Inspection of Fig. 5 shows that Cl$_2$ concentrations ranged from 89 to 95 pct and

that as little as 0.2 wt pct NaCl effectively catalyzed the reaction between FeCl$_3$ and O$_2$.

An additional series of tests was conducted under the same conditions but with the wt pct NaCl in the bed held constant. The results of these tests are shown in Fig. 6 along with data from a series of tests conducted at 500°C but without NaCl in the bed. The effectiveness of NaCl as a catalyst can be readily seen by inspection of Fig. 6. The percent FeCl$_3$ conversion is shown in Fig. 7. Results obtained in similar tests but without NaCl are shown for comparison. These results show that FeCl$_3$ conversions above 95 pct and an off-gas containing over 90 pct Cl$_2$ are obtainable at 500°C when NaCl is used to catalyze the dechlorination of FeCl$_3$ by O$_2$.

Reference to Fig. 3 shows that comparable results required a temperature of 650°C in the absence of NaCl.

CONCLUSIONS

This study has shown that FeCl$_3$ can be fed into a fluidized bed of Fe$_2$O$_3$ and can be dechlorinated by reaction with O$_2$ to produce an off-gas containing over 90 pct Cl$_2$ and with conversions of FeCl$_3$ above 95 pct. These results can be achieved at 500°C when NaCl is added to the bed as a catalyst. In the absence of NaCl, a temperature of 650°C is required to achieve comparable results. The work also showed that as little as 0.2 wt pct NaCl in the bed effectively catalyzed reaction between FeCl$_3$ and O$_2$.

ACKNOWLEDGMENT

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