Chlorination of High-titania Slag in Fluidized Beds

By M. A. Doheim, A. Abdel Raaouf and S. A. Rassoul

The chlorination of high-titania slag to give titanium tetra-chloride is of growing importance. The present work was done to study the effect of some factors on the chlorination process in presence of solid carbon as a reducing agent. The factors involve the temperature, flow rate, and particle size. A synthetic slag near in composition to the natural slag obtained from reduction smelting of titaniferous ores was chlorinated in a fluidized bed silica reactor. A pre-chlorination step was necessary to get rid of the non-volatile chlorides causing the sticking and agglomeration of fluidized slag particles.

It was found that the temperature and flow rate of Cl₂ greatly affect the chlorination rate with points of maximum effect. Different particle sizes give distinctly different conversion curves with the smaller size giving higher conversion. The energy of activation was obtained from the Arrhenius plot as 19400 cal/mol.

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I. Introduction

The formation of volatile chlorides is an important step in the production and refining of certain metals and the Kroll(1) process for the production of titanium is an example. Different titanium-bearing minerals may be chlorinated for such a purpose e.g. ilmenite, rutile, and high-titania slag. The high-titania slag is preferred for the following two reasons: shortage in rutile supplies and economic recovery(2) of iron from titaniferous ores through its reduction smelting to produce the slag.

Many investigations were carried out on the chlorination of the slag to titanium tetrachloride but a little was done on fluidized bed chlorination(3)-(4). Fluidized beds offer many established merits for processes to be carried out. With respect to the Egyptian high-titania slag, many studies(5)-(6) were carried out on its investigation, but the present investigation is believed to be the first using fluidized beds.

A difficulty in fluidized bed chlorination is the sticking and agglomeration of solid particles due to the formation of non-volatile chlorides. This necessitates a pre-chlorination step and leaching away of these chlorides, as will be explained latter. The paper reports and discusses the results obtained from studying the effect of temperature, particle size, and gas flow rate on the chlorination process of high-titania slag.

II. Thermodynamic Considerations

In the chlorination of titanium-bearing minerals, e.g. high-titania slag, a reducing agent may or may not be used. In the latter case the standard free energy change, ΔG°, of the chlorination reactions for TiO₂, SiO₂, Al₂O₃ and other oxides have positive values in the temperature range 200−1200°C as can be seen from Fig. 1. Therefore the direct chlorination with Cl₂ without using any reducing agent does not take place spontaneously within this temperature range. In case of using a reducing agent, such as CO or C, the chlorination reactions have negative values of ΔG° as can be seen from Fig. 2 for CO and Figs. 3 and 4 for C.

Fig. 1 Effect of temperature on ΔG° of the chlorination reactions using Cl₂ only.
1: 3/2SiO₂ + 3Cl₂ = 3/2SiCl₄ + 3/2O₂
2: Al₂O₃ + 3Cl₂ = 2AlCl₃ + 3/2O₂
3: 3/2TiO₂ + 3Cl₂ = 3/2TiCl₄ + 3/2O₂
4: 3MgO + 3Cl₂ = 3MgCl₂ + 3/2O₂
5: 3FeO + 3Cl₂ = 3FeCl₃ + 3/2O₂
6: Fe₂O₃ + 3Cl₂ = 2FeCl₃ + 3/2O₂
7: 3MnO + 3Cl₂ = 3MnCl₂ + 3/2O₂
8: 3CaO + 3Cl₂ = 3CaCl₂ + 3/2O₂

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and thus the reactions may occur spontaneously. The
values shown in the figures were calculated using the
thermodynamic data compiled by Kubaschewski and
Evans(7).

The chlorination reactions using solid C as a re-
ducing agent have more negative $\Delta G^\circ$ values than
when using CO above 700°C and thus more thermo-
dynamically feasible, as can be seen from Figs. 2, 3 and
4. It was also found by Bergholm(8) and others(9)~(11)
that the chlorination using CO as a reducing agent is
much slower than when using solid C in the tempera-
ture range below 1000°C. Accordingly it was decided
to use solid corbon as a reducing agent in the chlorina-
tion process.

The main reactions which may occur in the chlorina-
tion of TiO$_2$ in slag are:

$\text{TiO}_2 + 2\text{Cl}_2 + \text{C} \rightarrow \text{TiCl}_4 + \text{CO}_2$
$\text{TiO}_2 + 2\text{Cl}_2 + 2\text{C} \rightarrow 2\text{TiCl}_4 + 2\text{CO}_2$
$\text{CO}_2 + \text{C} \rightarrow 2\text{CO}_2$

Most of the high-titania slag constituents (Fe
oxides, MnO, CaO and MgO) are chlorinated prefer-
ably before and others (Al$_2$O$_3$ and SiO$_2$) are chlori-
nated during the chlorination of TiO$_2$.

III. Experimental

1. Materials

The used material for chlorination was a high

(9) A. V. Pamfilov, and M. G. Chikher: J. Gen. Chem.
U.S.S.R., 7 (69) (1937), 2760.
U.S.S.R., 7 (69) (1937), 258.
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Table 1 The chemical analysis of coke and slag.

<table>
<thead>
<tr>
<th>Material</th>
<th>Component (%)</th>
<th>Volatile matter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TiO₂</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Slag</td>
<td>90.0</td>
<td>2.3</td>
</tr>
<tr>
<td>Coke Ash of coke</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

titania synthetic slag prepared from rutile and other oxides present usually in the slag produced from the smelting of titaniferous ores (ilmenite). In preparing the slag, its constituents were proportioned to give a slag of composition approximately similar to that produced from the reduction smelting of Egyptian ilmenite\(^{(12)}\). The mixture of oxides was melted in a Tammann furnace at a temperature of about 1600°C in a graphite crucible. The prepared slag was crushed, ground, and screen analysed. The size fractions -200 +160 and -160 +125 were used in the present investigation. The chemical analysis of a representative sample of the slag is given in Table 1. The density of the slag was determined and found to be 247 lb/ft³ (3.95 g/cm³). The coke used is common metallurgical coke and its assay is given in Table 1, and its density 1.4 g/cm³. Cl₂ supplied in cylinders was used as fluidizing and chlorinating gas.

In order to minimize particle segregation in beds of coke and slag, due to the density difference, the particle size of coke was taken as being two times greater than that of slag. The minimum fluidization velocities of solids under different conditions were determined using the correlation of Leva et al.\(^{(13)}\). This was due to difficulties in measuring the velocities experimentally in the different conditions.

2. Apparatus

A schematic representation of the apparatus used in chlorination of slag is shown in Fig. 5. The used gases, N₂ and Cl₂, were dried by passing through CaCl₂ columns, and measured by an orifice-meter. The fluidized bed reactor shown in Fig. 6 consists of a silica column with an enlarged section at the top to remove the entrained solids from the gases and to decrease the amount of elutriated fines. The reactor is preceded with a pre-heater filled with broken silica. The used gas distributor is made of silica bars, 1.5 mm diameter, welded to the column. The heating was conducted electrically by using kanthal resistance wire wound on the outside walls. The temperature was measured by a Pt/Pt·Rh thermocouple. The details of the TiCl₄ condensation system are shown in the apparatus sketch. The exhaust gases were passed through an absorption system to absorb Cl₂.

3. Procedure

The general procedure consists of fluidizing the charge (slag + coke) with nitrogen while heating until a temperature is reached which is about 60°C-75°C.
below the desired temperature. Then the nitrogen stream was diverted and the Cl₂ stream was allowed at the desired flow rate. The exothermic heat of the chlorination reactions of impurities, most of which are preferably chlorinated at the beginning, was found to be enough to raise the temperature to the desired one.

The time from the start of Cl₂ flow is recorded against the volume of TiCl₄ collected in the graduated cylinders through the condensing system. At the end of reaction period the Cl₂ stream is diverted and the N₂ is allowed to insure complete recovery of any residual chlorides. Finally everything was off and the residue in the reactor was weighed.

Sticking and agglomeration of the fluidized charge was noticed and was attributed to the presence of non-volatile chlorides such as CaCl₂, MnCl₂, and MgCl₂. To get rid of this phenomenon, which is highly undesirable in fluidized beds, pre-chlorination step was necessary. The pre-chlorination was found to remove most of the non-volatile chlorides. The pre-chlorination was carried out at 400 °C for a period of about 15 min, after which the bed residue was leached (for removal of chlorides) with water, filtered, dried, and weighted. The amount of TiCl₄ formed during the pre-chlorination stage was recorded. After that the leached residue was further chlorinated.

IV. Results

The agglomeration of fluidized solids was noticed during preliminary runs carried out on the chlorination of titanium slag. This phenomenon of sticking and agglomeration was also noticed by others\(^{14}\), and attributed to the formation of non-volatile chlorides such as MnCl₂, CaCl₂, and MgCl₂. The agglomeration effect was reflected on the conversion levels obtained as being low, and this effect was severe at lower temperatures below 800 °C. Following the pre-chlorination step, the leached residue was chlorinated. The TiCl₄ collected in the pre-chlorination (averaging 25%) and chlorination steps was used in calculating the conversion. Time-conversion curves were obtained at the different conditions.

The effect of temperature on the chlorination process within the range 625 – 925 °C is shown in Fig. 7. The time-conversion curves for two beds of different particles sizes are shown in Figs. 7 and 8. The work on the two different sizes was carried out at different temperatures. The results of changing Cl₂ flow rate are plotted and shown in Fig. 9.

A kinetic model was applied to the data at different temperatures to determine the energy of activation of the chlorination reaction. The chlorination reaction is considered an irreversible first order heterogeneous non-catalytic reaction which is temperature dependent as indicated by the results. The particle size affects the conversion and the unreacted core model\(^{15}\) was adopted for the conversion reaction of TiO₂ to TiCl₄. The particles are assumed spherical. The reaction rate is given by:

\[
\frac{dN_g}{4\pi r_e^2} \frac{dt}{dt} = -b \frac{dN_g}{4\pi r_e^2} \frac{dt}{dt} = b k C.
\]


From which we can get the following after (rearranging) and integrating\(^{15}\):

\[
t = \frac{\rho}{bkC} \cdot R_p \left(1 - (1 - X)^3\right)
\]

where the meaning of symbols is given in the nomenclature. Equation (2) was used to calculate the reaction velocity constant \(k\). According to the Arrhenius equation

\[
k = Ae^{-E/RT},
\]

the Arrhenius plot (log \(k\) vs 1/T) is given in Fig. 10, from which the energy of activation \(E\) was obtained as 19400 cal.

**V. Discussion**

The chlorination process is strongly affected by the temperature involved, as can be seen from Figs. 7 and 8, and the increase of the reaction rate with temperature passes through a maximum at about 840°C. This behaviour was observed in the investigation involving slag\(^{16}\) and other Ti-bearing minerals\(^{8}(11)\). Three factors may be related to this behaviour; (1) the formation of CO and its amount increase (Boudward reaction) with temperature rise, (2) the tendency of solids to stick and agglomerate at high temperatures, and (3) the decrease in amount of Cl\(_2\) entering the reactor as the temperature rises so as to keep the fluidization velocity constant, i.e., a constant volumetric flow rate at different temperatures. With respect to the activation energy, similar values were obtained by Dunn\(^{17}\).

The effect of Cl\(_2\) flow rate in increasing the chlorination rate is evident from Fig. 9. The percent conversion after 1 hr is plotted against \(U_f/U_{mf}\) in Fig. 11. There are two factors affecting in such a case. The first is a kinetic one and shows itself through the increase in amount of Cl\(_2\) available for a reaction by an increase of the flow rate. The second is a hydrodynamic one with its consequences. The increase in flow rate through fluidized solids increases the bubble formation and size, intensifies the mixing of solids and gas, improves heat and mass transfer, and increases bypassing and back-mixing. Due to these various effects, the conversion to TiCl\(_4\) may increase or decrease. All these aspects have complicated effects, but the net effect is that shown in the given curves. The general behaviour was observed by other investigators\(^{18}\).

Regarding the chlorination of different slag particle sizes, a plot showing this effect clearly at different temperatures is given in Fig. 12. The smaller particle size gives a higher conversion level than the larger one. Similar behaviour was observed by other workers\(^{19}(20)\). This supports the shrinking core (unreacted core) model, used in data interpretation, with surface reaction control.

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VI. Conclusions

(1) The chlorination of high-titania slag, in presence of solid C as a reducing agent, depends strongly on temperature and the effect passes through a maximum at about 840°C. The non-reacting core kinetic model for first-order reactions was applied to determine the data, and the energy of activation was evaluated from the Arrhenius plot to be 19400 cal/mol.

(2) The conversion to TiCl₄ increases with the flow rate of Cl₂ and up to $U_f/U_{mf}$ equals 4 the hydrodynamic condition of the bed did not adversely affect the obtained conversion.

(3) Different particle sizes give clearly different conversion curves at different temperatures, with the result that the smaller size gives the higher conversion.

Nomenclature

- $A$: Constant of Arrhenius equation.
- $b$: Stoichiometric coefficient and equals $\frac{1}{2}$ in the present case.
- $C$: Concentration of fluid reactant, moles Cl₂/cm³.
- $E$: Energy of activation (cal/mol).
- $k$: Reaction velocity constant based on unit surface (cm/min).
- $N_s$, $N_g$: Number of moles of solid and gaseous reactant respectively.
- $r_c$: Radius of unreacted core (cm).
- $R_p$: Radius of solid particles (cm).
- $t$: Time (min).
- $T$: Absolute temperature (°K).
- $U_{mf}$: Minimum fluidization velocity (cm/min).
- $U_f$: Fluidizing velocity (cm/min).
- $X_s$: Fractional conversion of TiO₂.
- $\rho$: Molar density of solid reactant, moles TiO₂ per unit volume of solid.