TECHNICAL PAPER

# Controlling Conditions of Fluidized Bed Chlorination of Upgraded Titania Slag

**M. H. El-Sadek**[1] · **O. A. Fouad**[1] · **M. B. Morsi**[1] · **K. El-Barawy**[1]

**Abstract** Titanium tetrachloride with 98% purity was successively synthesized by chlorination of upgraded titania slag (88% $TiO_2$, 2.9% $Fe_2O_3$) using chlorine gas in the presence of activated charcoal at 1173–1373 K in a fluidized bed chlorinator. The different parameters affecting the chlorination processes such as carbon source, carbon amount, temperature and time of chlorination were studied. Moreover, kinetics of chlorination of upgraded titania slag was studied. The results showed that the chlorination of upgraded titania slag was mainly controlled by diffusion of chlorine gas with calculated apparent activation energy of 11.9 kJ/mole.

**Keywords** Titania slag · Chlorination · Fluidized bed · Activated charcoal · Kinetic · Activation energy

## 1 Introduction

In recent years almost 95% of titanium sources has been used in the production of white $TiO_2$ pigment, which is subsequently used in paint, plastic and paper industries. Owing to its unique characteristics, titanium dioxide also has high potential applications in environmental purification, gas sensors, and in photovoltaic cells. Titanium tetrachloride ($TiCl_4$) is an intermediate, which is used in the production of $TiO_2$ pigment and titanium sponge [1].

Commercial $TiCl_4$ is produced by fluidized bed chlorination of rutile or titanium feedstock using carbon as a reducing agent in the temperature range from 1073 to 1373 K where the impurities present are also chlorinated [2–4].

Bergholm [5] studied the chlorination of titania feedstock with carbon and CO and found that the presence of carbon significantly improved the reaction rate. The chlorination of rutile with carbon and carbon monoxide was studied [6], and it was reported that small amounts of CO did not affect the reaction rate significantly. However, CO in large amounts tended to have a sharp negative effect on the reaction kinetics. Moreover, chlorination of pure titanium dioxide in the presence of coke was studied [7], it was concluded that chlorination rate of $TiO_2$ with $TiO_2$–C contact was 40–50 times faster than that in the absence of carbon.

Bonsack and Schneider [8] chlorinated a low-grade titaniferous slag over the temperature range of 823–1373 K and prepared titanium tetrachloride. It was found that carbon reactivity employed for the chlorination process had a strong effect on the chlorination rates. Sohn and Zhou [9] studied the chlorination kinetics of titania slag with chlorine gas and petroleum coke at 1223–1393 K. A rate equation was established in which the effects of temperature, chlorination partial pressure and initial particle size were accounted for and the calculated activation energy value was 29 kJ mol$^{-1}$.

The aim of this study is to synthesize $TiCl_4$ from local upgraded titanium-rich slag and investigate the parameters affecting the chlorination process and also determine the kinetic parameters of chlorination process.

✉ M. H. El-Sadek
mohamedhussien2002@hotmail.com

1 Minerals Technology Division, Pyrometallurgy Department, Central Metallurgical R&D Institute (CMRDI), P. O Box 87, Cairo, Egypt

## 2 Experimental

### 2.1 Materials

The starting materials used in this study were as follows:

- Upgraded titania slag used in the present study with mean particle size of 75 μm was produced locally from Abu Ghalaga ilmenite concentrate. The chemical analysis of titania-rich slag was examined by XRF (AXIOS-Advanced, PANalytical, 4 kW), and the results are tabulated in Table 1.
- The phase composition of upgraded titania-rich slag was investigated by XRD (Bruker axs D8 Advance, with Cu kα radiation). Figure 1 represents the XRD pattern of upgraded titania-rich slag. It is noticed that the main crystalline phases in upgraded titania-rich slag are rutile ($TiO_2$, JCPDS: 73-1765), perovskite ($CaTiO_5$, JCPDS: 72-1192) and pseudobrookite ($Fe_2TiO_5$, JCPDS: 73-1256).
- Two types of carbon sources (anthracite and activated charcoal) were used as reducing agents. Table 2 shows the chemical analysis of both types of carbon.

### 2.2 Charge Preparation

Upgraded titania slag was mixed thoroughly with excess carbon (C/O molar ratio of 1.5) to provide sufficient carbon to ensure complete formation of metal chloride according to the following equations:

**Table 1** Chemical analysis of upgraded titania-rich slag

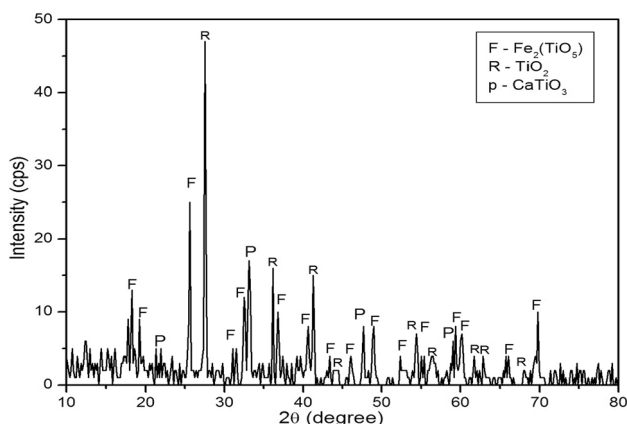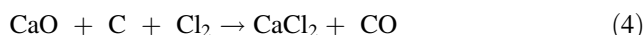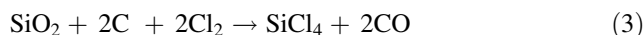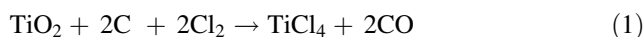| Element | TiO$_2$ | Fe$_2$O$_3$ | SiO$_2$ | CaO | Al$_2$O$_3$ | MgO | K$_2$O |
|---------|---------|-------------|---------|-----|-------------|-----|--------|
| wt% | 88 | 2.9 | 5.3 | 2.2 | 0.34 | 0.22 | 0.11 |



**Fig. 1** XRD patterns of upgraded titania-rich slag

**Table 2** Chemical analysis of the main components of anthracite and active charcoal

| Component | Anthracite (%) | Activated charcoal (%) |
|-----------|----------------|------------------------|
| Fixed carbon (C) | 99.9 | 86 |
| Sulphur (S) | 0.02 | – |
| Moisture | – | 10 |
| Ash | 0.08 | 4 |

$$TiO_2 + 2C + 2Cl_2 \rightarrow TiCl_4 + 2CO \qquad (1)$$

$$Fe_2O_3 + 3C + 3Cl_2 \rightarrow 2FeCl_3 + 3CO \qquad (2)$$

$$SiO_2 + 2C + 2Cl_2 \rightarrow SiCl_4 + 2CO \qquad (3)$$

$$CaO + C + Cl_2 \rightarrow CaCl_2 + CO \qquad (4)$$

A suitable binder (4% molasses) was added during mixing. The obtained homogeneous mixture was pelletized and dried overnight at 383 K.

### 2.3 Chlorination System

A laboratory-scale fluidized bed reactor consists of quartz tube with a perforated disc divided it into two parts and placed in a vertical tube furnace where the perforated disc is in the middle of the hot zone of the furnace. Chlorine gas and high-purity (99.9%) argon gas were used during chlorination process. Chlorine gas was used as active gas to form the corresponding metal chlorides through the reaction with metal oxides in upgraded titania slag in the presence of carbon. Argon gas was used as a carrier gas and was passed through silica gel and soda lime bubblers to remove moisture and $CO_2$ prior to its introduction into the reactor.

Pellets in the size range of $-4 + 2.3$ mm were introduced into a quartz reactor and placed over a perforated disc in the middle of the hot zone of the furnace. Pure argon gas (diluent gas) with a flow rate of 1 l/min was passed over the pellets at a constant rate. The furnace was heated up to the chlorination temperature (1173–1373 K). When the required temperature was reached, chlorine gas with a flow rate of 0.25 l/min was passed over the sample for a certain time, till complete chlorination. The gaseous titanium tetrachloride produced in the fluidized bed reactor was part of a gas stream also containing other chloride products. The gas stream was usually cooled as it left the fluidized bed reactor and was then condensed. Separation of $TiCl_4$ produced from the other chloride products was possible due to differences in boiling points of the various chloride products. The produced $TiCl_4$ was collected in a standard measuring cylinder. The chlorination extent was calculated according to the following equation:

Chlorination extent $=$ Volume of collected $TiCl_4$
/Initial volume of $TiCl_4$

where initial volume of $TiCl_4$ was calculated from the weight of $TiCl_4$ equivalent to $TiO_2$ in used slag divided by the density of $TiCl_4$ (1.73 g/cm$^3$).

At the end of each run, the bed materials were allowed to cool down under argon atmosphere.

# 3 Results and Discussion

## 3.1 Effect of Carbon Source

Two types of carbon sources have been used as reducing agents in chlorination process of upgraded titania slag samples. Figure 2 shows the variation of chlorination extent of titania in the presence of anthracite and active charcoal at 1273 K. Although higher fixed carbon content is present in the anthracite than that in the active charcoal, the chlorination extent and rate are lower. About 90% chlorination extent is achieved for the sample containing active charcoal sample compared with 56% chlorination extent for the sample containing anthracite as a reducing agent. This may be attributed to the reactivity of charcoal surface which initiates the activation of chlorine gas and enhances transfer of activated chlorine through upgraded titania slag/carbon interface. Activated chlorine species are formed on the carbon and desorbed into the gas phase where $TiO_2$ reach the surface and react to form $TiCl_4$ and $O_2$. The chlorination reaction can be considered a multi-step reaction where the following mechanism can be suggested:
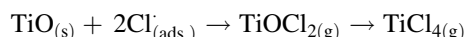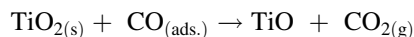
1. Dissociation of chlorine gas and adsorption on carbon surface

$$Cl_{2(g)} \rightarrow 2Cl^{\cdot}_{(ads.)}$$
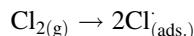
2. Oxidation of carbon surface to carbon monoxide by adsorbed moisture (10%)

$$C_{(s)} + 1/2\ O_{2(g)} \rightarrow CO_{(ads.)}$$
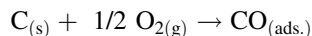
3. The adsorbed chlorine and carbon monoxide gases diffuse through rutile/carbon interface to form lower oxide of titanium; oxychloride and then titanium chloride

$$TiO_{2(s)} + CO_{(ads.)} \rightarrow TiO + CO_{2(g)}$$

$$TiO_{(s)} + 2Cl^{\cdot}_{(ads.)} \rightarrow TiOCl_{2(g)} \rightarrow TiCl_{4(g)}$$

The overall reaction is given by Eq. (1).

## 3.2 Effect of Carbon Stoichiometry

Figure 3 shows the variation of the chlorination extent of upgraded titania-rich slag at different carbon ratios (1X and 1.5X, where X represents the theoretical amount of carbon). It is clear that the chlorination extent achieved at 1X is about 85.42%, while the chlorination extent increases up to 92.23% with increasing carbon ratio up to 1.5X. This increase in chlorination extent can be attributed to high amount of active chlorine gas generated from carbon surface.

## 3.3 Effect of Chlorination Time and Temperature

Chlorination temperature has been studied in the range from 1173 to 1373 K using 1.5X active charcoal as a reducing agent. Figure 4 represents the variation of
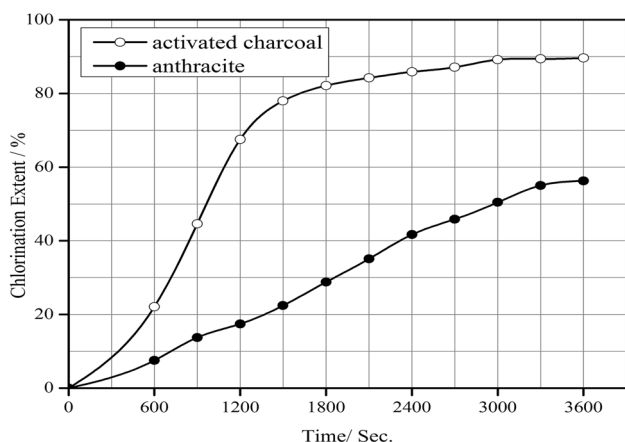


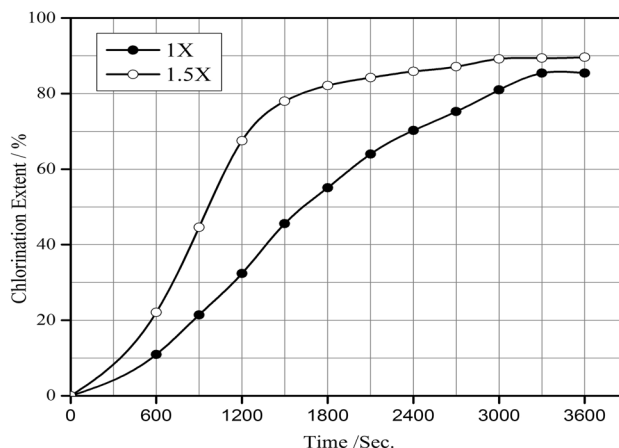**Fig. 2** Effect of different carbon sources on chlorination extent at 1273 K for 3600 s



**Fig. 3** Effect of activated charcoal stoichiometry on chlorination extent at 1273 K for 3600 s
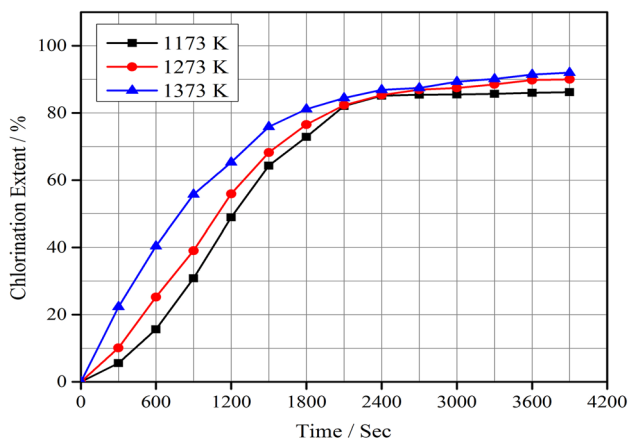
Fig. 4 Effect of chlorination temperature on chlorination extent at various chlorination time periods
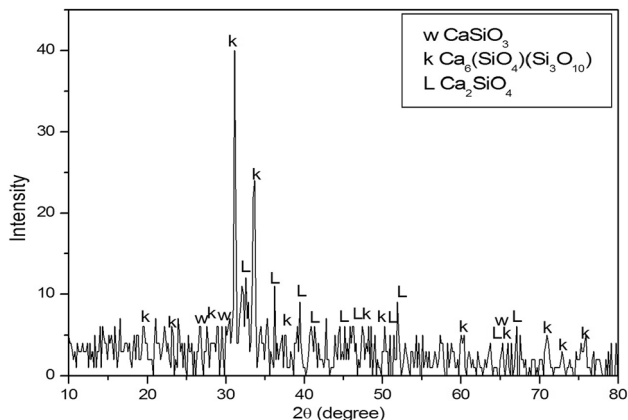


Fig. 5 XRD patterns of chlorination residue at 1173 K

chlorination extent at different temperatures for different times. The results indicate that the variation of the chlorination extent of upgraded slag samples at different slag temperatures for 3600 s are about 86, 90 and 92% for samples chlorinated at 1173, 1273 and 1373 K, respectively. It is observed that the chlorination extent steadily increases with increasing temperature up to 2400 s after which a slight increase is observed. Also, the effect of chlorination time becomes less pronounced at temperature higher than 1173 K, when the process is carried out for time longer than 3600 s.

Residue after chlorination of upgraded titanium slag sample at 1173 K has been investigated with XRD (Fig. 5). It is clear that the residue is composed of mainly non-volatile calcia and silica in the form of different calcium silicate phases. Also, the volatile titanium chloride is condensed and is collected for characterization. The chemical composition of collected $TiCl_4$ is shown in Table 3.

**Table 3** Chemical analysis of collected $TiCl_4$

| Element | Free $Cl_2$ | Fe | Si |
|---------|-------------|-------|------|
| wt% | 1.29 | 0.018 | 0.09 |

It is obvious that the produced $TiCl_4$ has a purity of about 98.08% which is in agreement with the commercial grade.

### 3.4 Kinetics of Chlorination Process

In the light of previous studies [9–12] on chlorination of different titanium sources and regarding the kinetic equations governing the fluidized bed chlorination, the change of chlorination extent of upgraded titania slag in the presence of active charcoal with time (Fig. 4) can be expected to follow diffusion Jander equation:

$$1 - (1 - X)^{1/3} = K_{app}t \qquad (5)$$

where $X$ is fractional conversion, $K_{app}$ is the overall rate constant, $s^{-1}$, and $t$ is the time in seconds.

It is shown from the diffusion model that the overall rate ($K_{app}$) is determined by diffusion of chlorine gas through the outer shell of oxide at 1173–1373 K. The rate constant of interfacial reaction can be obtained from slopes of Fig. 6 based on Eq. (5). The calculated results of the kinetic parameters are listed in Table 4.
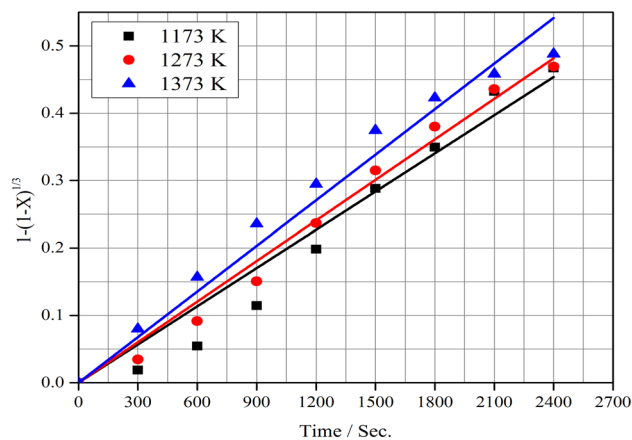


Fig. 6 Effect of the chlorination temperature on the chlorination rate using Jander equation

**Table 4** Kinetic parameters of chlorination of upgraded titania slag

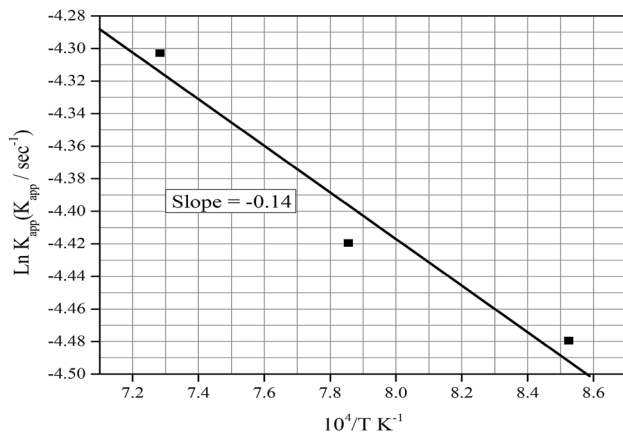| Temperature (K) | $K_{app}$ ($s^{-1}$) | $R^2$ |
|-----------------|----------------------|-------|
| 1173 | 0.00019 | 0.98 |
| 1273 | 0.00020 | 0.99 |
| 1373 | 0.00022 | 0.99 |

**Fig. 7** Arrhenius plot of the rate constants (from the data of Fig. 6)

According to the Arrhenius equation, the apparent activation energy ($E_{app}$) can be calculated in the chlorination process (Fig. 7). The calculated value of apparent activation energy is 11.7 kJ/mol, showing that the reaction rate is mainly controlled by the diffusion control.

## 4 Conclusion

- Titanium tetrachloride (98%) was produced by chlorination of upgraded titania slag (88% $TiO_2$) using 1.5$X$ activated charcoal as a reducing agent.

- The results showed that the chlorination of upgraded titania slag was mainly controlled by diffusion of chlorine gas with calculated apparent activation energy of 11.9 kJ/mole.

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