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Kinetics of Carbochlorination of Chromium (III) Oxide

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Kinetics of the carbochlorination of Cr_2O_3 has been studied with Cl_2+CO gas mixtures between 500 °C to 900 °C using thermogravimetric analysis. The apparent activation energy is about 100 kJ/mol. Mathematical fitting of the experimental data suggests that the shrinking sphere model is the most adequate to describe the carbochlorination mechanism of chromium oxide and that is controlled by the chemical reaction.

In the temperature range of 550 °C to 800 °C, the reaction order is about 1.34 and is independent of temperature. Changing the Cl_2+CO content from 15 pct to 100 pct increase the reaction rate and does not affect the reaction mechanism. Similarly, changing the ratio of $\text{Cl}_2/(\text{Cl}_2+\text{CO})$ from 0.125 to 0.857 do not modify the carbochlorination mechanism of Cr_2O_3 . In these conditions, the reaction rate passes through a maximum when using a chlorinating gas mixture having a $\text{Cl}_2/(\text{Cl}_2+\text{CO})$ ratio of about 0.5.

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I. INTRODUCTION

More than 75 pct of the world chromium consumption is used for the production of the ferro-chromium alloys [1]. About 25 pct is used for chemical, refractory and foundry applications. Chromium oxide and its compounds are utilized mainly as pigment, catalyst and as a raw material for the synthesis of chemicals used in the tanning, textile coloring, ...

A survey of literature concerning the chromium oxide and related materials indicate that most of the research work relates to the conversion of oxide to chlorides/or oxychlorides depending on the oxygen partial pressure in Cr-Cl-O system. Kinetics information concerning carbochlorination of Cr_2O_3 is limited.

Saeki et al. [2] investigated chlorination of Cr_2O_3 by Cl_2 using samples obtained by heating a hydrated chromium oxide either at 440 °C or 1000 °C. These solids were chlorinated with chlorine to CrO_2Cl_2 at 500 °C and 590 °C, respectively. These authors also investigated the chlorination of the same samples of Cr_2O_3 by Cl_2+C mixture. The carbochlorination of these solids to CrCl_3 start at 200 °C and 225 °C, respectively. The conversion extents of Cr_2O_3 were 38 and 98 pct at 600 °C and 850 °C, respectively.

Hussein et al. [3] reported the chlorination of pure FeO, MgO, Fe_2O_3 , Cr_2O_3 and Al_2O_3 , their mixture and synthetically prepared compounds having spinel general formula $\text{Me}^{2+}\text{Me}_2^{3+}\text{O}_4$. They concluded that chlorination can be achieved in the presence of carbon for all the oxides. They emphasized that for a reaction time of one hour, temperatures higher than 800 °C, a chlorine flow rate of about 3 L/g/h and three times the stoichiometric amount of carbon are necessary for the chlorination of the above mentioned oxides. However, without carbon the reaction is very slow and proceeds with the formation of oxychlorides. Morozov and Fefelova [4] in their study on chlorination of Cr_2O_3 with Cl_2 in the temperature range of 700 °C to 1000 °C reported the formation of Cr^{+2} , Cr^{+3} and Cr^{+4} chlorides and the non existence of oxychlorides in this temperature range.

Sano and Belton [5] investigated the chlorination of Cr_2O_3 with $\text{Cl}_2\text{-O}_2\text{-Ar}$ atmosphere using transpiration technique in the temperature range of 627 °C to 977 °C. They observed that the reaction product is gaseous CrO_2Cl_2 . Maximum reaction rate was obtained for a Cl_2/O_2 molar ratio equal to 4. The formation of chromium oxychloride had been confirmed by Jacobson

et al. [6] using the mass spectrometric observation of chlorinated products issued from the oxychlorination of Cr_2O_3 - forming alloys. On the other hand, Kuffa et al. [7] confirmed the formation of CrO_2Cl_2 during the oxychlorination of Cr_2O_3 briquettes using thermogravimetric analysis 'TGA'.

This paper is a part of a research program concerning the chlorination kinetics of refractory metals oxides such as V_2O_5 [8], MoO_3 [9], Nb_2O_5 and Ta_2O_5 [10] as well as eventual application to the extraction of these metals from spent catalysts [11] or tin slag [12]. It deals with the study of the carbochlorination kinetics' of chromium (III) oxide with Cl_2+CO and $\text{Cl}_2+\text{CO}+\text{N}_2$ gas mixtures.

II. EXPERIMENTAL

A. Raw Materials

The sample used in this study is Cr_2O_3 powder supplied by LABORATOIRES STANDA having a purity higher than 99 pct. Spectra of EPMA - SEM (electron probe microanalysis of the scanning electron microscope) and that of XRD (X-rays diffraction) of the sample indicate only the presence of Cr_2O_3 phase (Fig. 1). The specific surface area of the sample was about $3.8 \text{ m}^2/\text{g}$. The gases (Cl_2 , CO , N_2) used were of high pure quality. Chemicals employed in this study were analytical grade.

B. Equipment

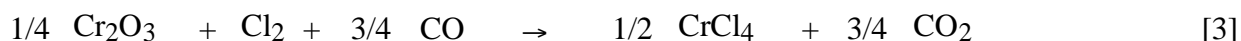
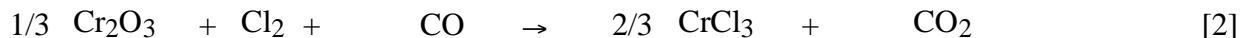
Chlorination experiments were carried out using TGA including the CAHN D100 microbalance with a direct data acquisition described previously [8]. The XRD was done with a PHILIPS diffractometer equipped with a Co or Cu anti-cathode and a monochromator. The scanning electron microscope used in this study was a CAMBRIDGE STEREO - SCAN 250 equipped with a microprobe PGT-III that permits a qualitative or a semi-qualitative elementary analysis of elements having an atomic number higher than 5. Specific surface area measurements were done using the analyzer Beta 4201 of Beta Scientific Corporation, Albertson, New York.

C. Experimental procedure

A sample of about 40 mg placed in a boat was introduced into the furnace. The furnace heating rate was maintained at about 7 °C/min for non-isothermal tests. In this case, the sample was heated directly in the chlorinating gas mixture. For isothermal experiments, the sample was heated to the desired temperatures under nitrogen atmosphere. As soon as the furnace attains the experimental temperature, N₂ flow was replaced by the chlorinating gas mixture and maintained during the reaction time. The exhaust gases were purified using NaOH solution before their release to the atmosphere.

III. THERMODYNAMIC STUDY

The possible carbochlorination reactions and the corresponding metal chlorides that are generated during the reaction of Cr₂O₃ with Cl₂+CO gas mixtures are as follow.



The standard Gibbs energy changes of the reactions 1 to 3 as a function of temperature [13] are given in Figure 2. It can be seen that the carbochlorination reactions of chromium oxide are thermodynamically feasible in the explored temperature range. CrCl₂ and CrCl₃ are the probable reaction products at temperatures lower and higher than 650 °C, respectively. The formation of CrCl₄ is the least favored from the thermodynamic point of view.

Figure 3 shows the phase stability diagrams of Cr-O-Cl system at 600 °C and 800 °C. Based on the gases purity, the estimated P_{Cl₂} and P_{O₂} of the gas mixtures used in this study for these temperatures are indicated by a black and white circles, respectively. This figure indicates that the carbochlorination of Cr₂O₃, in our experimental conditions, will only produce CrCl₃.

IV. RESULTS AND DISCUSSION

A. Non-isothermal chlorination of Cr_2O_3

To define the reactivity of Cr_2O_3 with respect to the Cl_2+CO gas mixture, carbochlorination of chromium oxide under continuous rising temperature conditions was carried out up to 900 °C. The total gas flow rate was maintained at 80 L/h. The pct weight loss observed as a function of temperature is shown in Figure 4. It can be seen that the reaction of Cl_2+CO with Cr_2O_3 starts at about 500 °C and is complete at about 900 °C. This figure also gives the pct weight loss of CrCl_3 treated in the same conditions. Clearly, the rate of CrCl_3 volatilization is higher than that of its formation during the carbochlorination of Cr_2O_3 in the explored temperature range. In such case, the measurement of pct weight loss as a function of time will probably represent the reaction rate of the Cr_2O_3 with Cl_2+CO gas mixture.

B. Kinetics of the carbochlorination of Cr_2O_3

1. Effect of gas flow rate

The effect of Cl_2+CO gas velocity on the chlorination reaction rate was studied to determine the conditions where gas starvation and mass transfer limitations could be minimized. As the carbochlorination of chromium oxide is almost complete at 900 °C, tests to define the critical gas flow rate is determined at this temperature (Fig. 4). Figure 5 summarizes the results of reaction rate evolution as a function of total gas flow rate ranging from 7 - 100 cm/ min that corresponds to 8 to 120 L/ h. The effect of gas velocity on reaction rate can be considered negligible beyond 50 cm/ min. A gas flow rate of 80 L/ h eliminate the gas starvation and minimize the mass transfer effects [14].

2. Effect of temperature

A series of isothermal tests was carried out at different temperatures ranging from 500 °C to 900 °C using Cl_2+CO ($\text{Cl}_2/\text{CO} = 1$) and $\text{Cl}_2+\text{CO}+\text{N}_2$ gas mixtures ($\text{N}_2/\text{Cl}_2/\text{CO} = 1$) at a constant total flow rate of 80 L/ h. Figures 6(a) and 6(b) show the pct weight loss *versus* time curves obtained by the carbochlorination of Cr_2O_3 with Cl_2+CO .

At 500 °C and a reaction time of 4 hours, the weight loss is less than 15 pct. The reaction rate increases steadily with the temperature rise between 500 °C and 900 °C. It reaches 90 pct at 900 °C for a reaction time of about 6 min. The nature of the TG curves for the chlorination of Cr₂O₃ obtained by using Cl₂+CO+N₂ or Cl₂+CO gas mixtures is similar. The only difference is lower reaction rates, for gas mixtures containing N₂, than those obtained with Cl₂+CO gas mixture for a given temperature and reaction time. For example, the pct weight loss with Cl₂+CO at 900 °C and a reaction time of 4 minutes was 66 pct while that for Cl₂+CO+N₂ gas was 46 pct.

The reaction rate was calculated using the initial linear stage for a reaction extent 'X' (0.05 < X < 0.4). The Arrhenius plot is given in Figure 7. The apparent activation energy is about 100 kJ/mol. Such a value tends to indicate that the carbochlorination mechanism of Cr₂O₃ powder is controlled by the chemical reaction in the explored temperature range.

To examine this hypothesis, the mathematical formulation of the experimental data was attempted using the following equations [14].

$$1 - (1 - X)^{1/F_p} = kt \quad [4]$$

$$X = kt \quad (\text{For } F_p = 1) \quad [5]$$

$$1 - (1 - X)^{1/2} = kt \quad (\text{For } F_p = 2) \quad [6]$$

$$1 - (1 - X)^{1/3} = kt \quad (\text{For } F_p = 3) \quad [7]$$

where k = constant,

t = chlorination time,

X = extent of reaction (ratio of weight of the reacted fraction to initial weight),

F_p = particle shape factor (1 for infinite slabs, 2 for long cylinders and 3 for spheres).

Equation 4 is considered to describe a reaction controlled by the chemical reaction in the case of shrinking nonporous particles (with or without a solid porous product) and porous particles with unchanged overall sizes. It also applies for a mechanism affected by pore diffusion in the case of complete gasification of porous solids.

Figure 8 shows the mathematical fitting (using equations 5 to 10) of experimental data of carbochlorination of Cr₂O₃ with Cl₂+CO at 700 °C for 0 ≤ X ≤ 0.8. The best mathematical fitting for these experimental data was obtained using equation 7 with a correlation coefficient equal to 1.

Figure 9 shows the mathematical fitting of the experimental data obtained during the carbochlorination of chromium oxide between 550 °C and 900 °C by using equation 7. The average correlation coefficient is 0.998. This supports the hypothesis that the carbochlorination reaction of Cr₂O₃ particles is controlled by the chemical reaction according to the shrinking sphere model described by equation 7. The similar values of activation energy are reported for the carbochlorination of V₂O₅^[8] and Ta₂O₅^[10].

3. Comparison between the rate of CrCl₃ formation and volatilization during the isothermal carbochlorination of Cr₂O₃

Figure 10 groups the evolution of the carbochlorination reaction rate of Cr₂O₃ and that of CrCl₃ volatilization as a function of temperature. It can be noticed that the volatilization rate of CrCl₃ is systematically higher than that of Cr₂O₃ chlorination in the explored temperature range. This observation agrees well with the results obtained in non-isothermal run (Fig. 4). XRD of the reaction product indicates the presence of chromium trichloride for the whole investigated temperature range. Chromium dichloride had not been detected in reaction products obtained at temperature lower than 650 °C. This is probably due to the presence of chlorine excess in the gas mixture.

4. Effect of Cl₂/(Cl₂+CO) molar ratio

The effect of this molar ratio on the reaction rate was studied at 800 °C. The chlorine content in the Cl₂+CO gas mixture was varied from 0 to 100 pct that corresponds to a Cl₂/(Cl₂+CO) ratio of 0 to 1, while the total gas flow rate was kept constant at 80 L/h. Figure 11 groups the evolution of the pct weight loss as a function of time. These curves clearly indicate that the reaction extent is maximum when using a chlorine concentration of about 50 pct in the Cl₂+CO gas mixture. Increasing or decreasing the chlorine content beyond this value leads to lower reaction extent.

Figure 12 gives the evolution of initial reaction rate ($0.05 \leq X \leq 0.40$) as a function of Cl₂/(Cl₂+CO) molar ratio. The reaction rate of Cr₂O₃ with 100 pct CO is almost equal to zero and rises with increasing the chlorine content in the gas mixture. It reaches a maximum value for

a $\text{Cl}_2/(\text{Cl}_2+\text{CO})$ molar ratio equal to about 0.5. Beyond this ratio, the reaction extent decreases as the chlorine content increases and reaches a minimum value with 100 pct Cl_2 . The observed maximum reaction rate at $\text{Cl}_2/(\text{Cl}_2+\text{CO})$ molar ratio of 0.5 clearly suggests that the carbochlorination of Cr_2O_3 with Cl_2+CO gas mixture follows equation 2. The XRD and SEM spectra of condensate, obtained from a boat experiment under similar conditions, confirm the presence of CrCl_3 .

To check the eventual effect of the composition of the chlorinating gas mixture on the reaction mechanism, mathematical formulation of the experimental data was examined. Figure 13 shows the transforms of data of Figure 11 using equation 7. The plots are straight lines with a correlation coefficient close to unity. This observation seems to indicate that the mechanism of carbochlorination of Cr_2O_3 remains the same for chlorine contents varied from 12.5 to 85.7 pct in the gas mixture.

5. Effect of Cl_2+CO partial pressure

To determine the effect of diluting the carbochlorinating gas mixture with nitrogen on the reaction rate, a series of experiments was performed at 550 °C, 650 °C and 800 °C with gas mixture having a Cl_2+CO content that varied from 15 pct to 100 pct. During these experiments, the Cl_2/CO molar ratio was kept constant and equal to 1. Figure 14 summarizes the pct weight loss as a function of reaction time for different contents of reactive gases at 550 °C and 800 °C. The results indicate that the reaction rate increases with rise of the partial pressure of Cl_2+CO at any given time and temperature.

Figure 15 gives the evolution of the natural logarithm of the initial reaction rate ($X = 0.05$ to 0.40) as a function of the partial pressure of Cl_2+CO at different temperatures. The apparent reaction order ' n_T ' is about 1.34 and is independent of the reaction temperatures between 550 °C and 800 °C. It seems that the carbochlorination mechanism is again independent of the partial pressure of reactive gases in the chlorinating gas mixture. To check this possibility, mathematical formulation of the experimental data was made using equations 5 to 10.

Best results are grouped in Figure 16. The data matches equation 7 well with an average correlation coefficient of 0.999. This confirms that the carbochlorination mechanism of Cr_2O_3 follows a chemical controlled reaction.

V. CONCLUSIONS

The thermodynamic study suggests that the reaction products of the carbochlorination of Cr_2O_3 will be CrCl_2 and CrCl_3 at temperatures lower and higher than 650 °C. Chromium (III) oxide starts to react with Cl_2+CO gas mixture at about 500 °C generating chromium trichloride. In our experimental conditions, chromium dichloride had not been detected in the reaction product.

During the carbochlorination of Cr_2O_3 , the rate of formation of chromium trichloride was systematically lower than its rate of volatilization between 500 °C and 900 °C. Consequently, the experimental data obtained from the TGA can be used for the kinetic study.

The apparent activation energy of the carbochlorination of Cr_2O_3 is about 100 kJ/ mole. This value is near to that obtained for the carbochlorination of V_2O_5 ^[8] and Ta_2O_5 ^[10]. This suggests that the carbochlorination rate of chromium oxide is controlled by the chemical reaction. Mathematical fitting of experimental data indicates that the shrinking sphere model is the most adequate to describe the reaction mechanism. The overall reaction proceeds through the formation of chromium trichloride.

Increasing the Cl_2+CO content in the chlorinating gas mixture from 15 pct to 100 pct does not affect the carbochlorination mechanism of Cr_2O_3 . Same conclusion is obtained when varying the $\text{Cl}_2/(\text{Cl}_2+\text{CO})$ ratio from 0.125 to 0.857.

Maximum reaction rate is obtained with a carbochlorinating gas mixture having a $\text{Cl}_2/(\text{Cl}_2+\text{CO})$ ratio of 0.5. The reaction order is about 1.34 with respect to the Cl_2+CO content in the gas mixture. It is independent of temperature between 550 °C and 800 °C.

Results obtained in this study had been extrapolated for upgrading of lean chromite concentrate. This material is essentially composed of spinel having the general formula : $[(\text{Fe}^{2+}, \text{Mg})(\text{Cr}, \text{Al}, \text{Fe}^{3+})_2\text{O}_4]$. Carbochlorination at low temperatures of the chromite concentrate allows the selective removal of iron leading to higher chromium content and Cr/Fe ratio. Such treatment can not be achieved by classical mineral processing methods.

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FIGURE CAPTIONS

- Figure 1 : Results of (a) SEM and (b) XRD analysis of Cr_2O_3 sample.
- Figure 2 : Standard free energy change of Cr_2O_3 carbochlorination reactions.
- Figure 3 : Phase stability diagram of Cr-O-Cl system at 600 °C and 800 °C.
- Figure 4 : Thermogravimetric analysis of Cr_2O_3 in Cl_2+CO gas mixture.
- Figure 5 : Effect of gas flow rate on the chlorination rate of Cr_2O_3 with Cl_2+CO .
- Figure 6 : Comparison of rate of CrCl_3 volatilization and Cr_2O_3 reaction with Cl_2+CO .
- Figure 7 : Isotherms of carbochlorination of Cr_2O_3 with Cl_2+CO gas mixture for (a) $T \leq 700$ °C and (b) $T \geq 725$ °C.
- Figure 8 : Arrhenius plot of carbochlorination of Cr_2O_3 by Cl_2+CO .
- Figure 9 : Mathematical fitting of carbochlorination data of Cr_2O_3 at 700 °C for different model equations.
- Figure 10 : Mathematical fitting of carbochlorination data of Cr_2O_3 with Cl_2+CO for (a) $T \leq 700$ °C and (b) $T \geq 725$ °C using equation 7.
- Figure 11 : Isotherms of carbochlorination of Cr_2O_3 at 800 °C with Cl_2+CO for (a) $12.5 \leq \text{Cl}_2 \leq 50.0$ pct and (b) $55.0 \leq \text{Cl}_2 \leq 100.0$ pct.
- Figure 12 : Effect of $\text{Cl}_2/(\text{Cl}_2+\text{CO})$ ratio on the Cr_2O_3 carbochlorination rate at 800 °C.
- Figure 13 : Mathematical fitting of experimental data of Figure 11.
- Figure 14 : Effect of Cl_2+CO ($\text{Cl}_2/\text{CO} = 1$) partial pressure on Cr_2O_3 carbochlorination at (a) 550 °C and (b) 800 °C.
- Figure 15 : Apparent reaction order with respect to Cl_2+CO .
- Figure 16 : Mathematical fitting of the carbochlorination data for different partial pressures of Cl_2+CO at (a) 650 and (b) 800 °C using equation [7].

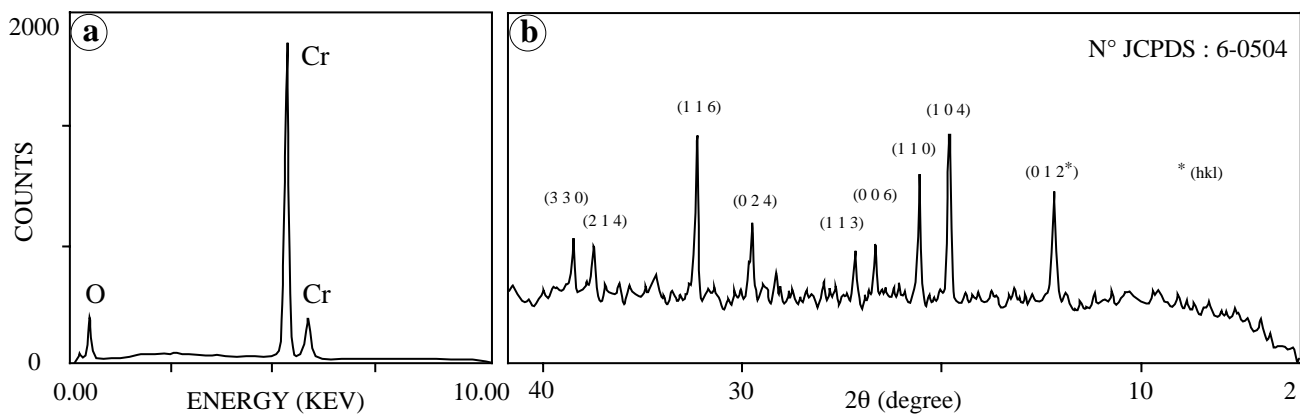


Fig. 1- Results of (a) SEM and (b) XRD analysis of Cr_2O_3 sample.

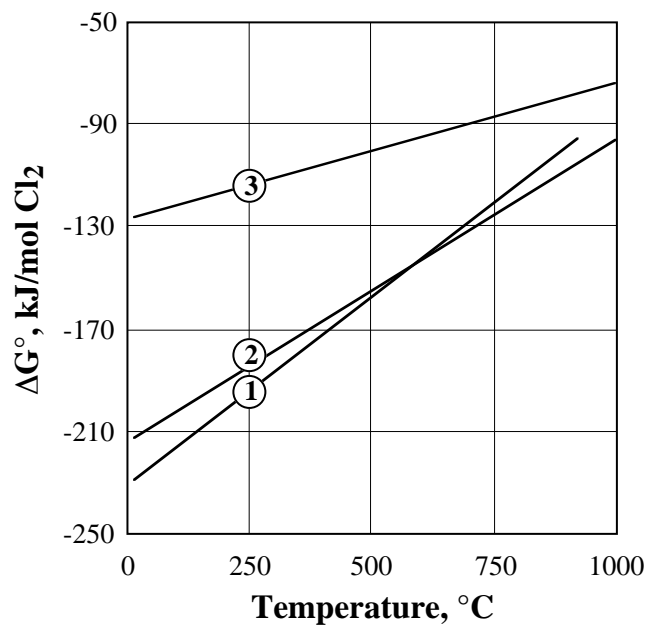
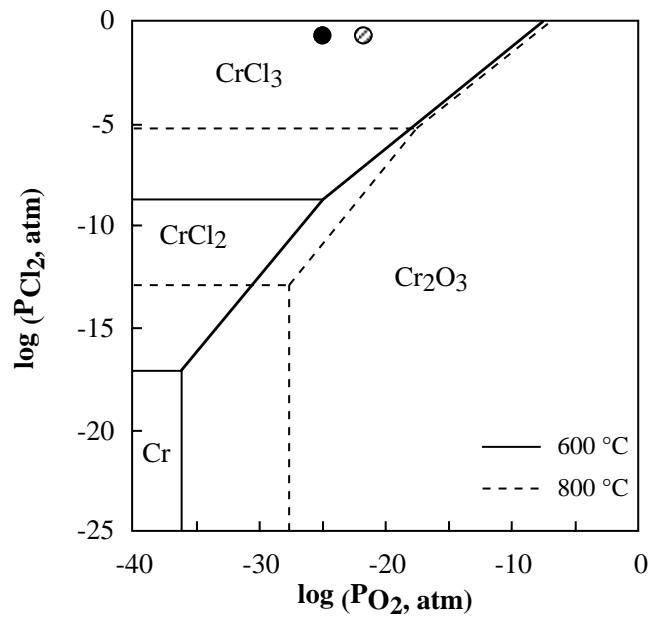


Fig. 2 - Standard free energy change of Cr_2O_3 carbochlorination reactions.



Estimated P_{Cl_2} and P_{O_2} at 600 (●) and 800 °C (⊙)

Fig. 3 - Phase stability diagram of Cr-O-Cl system at 600 °C and 800 °C.

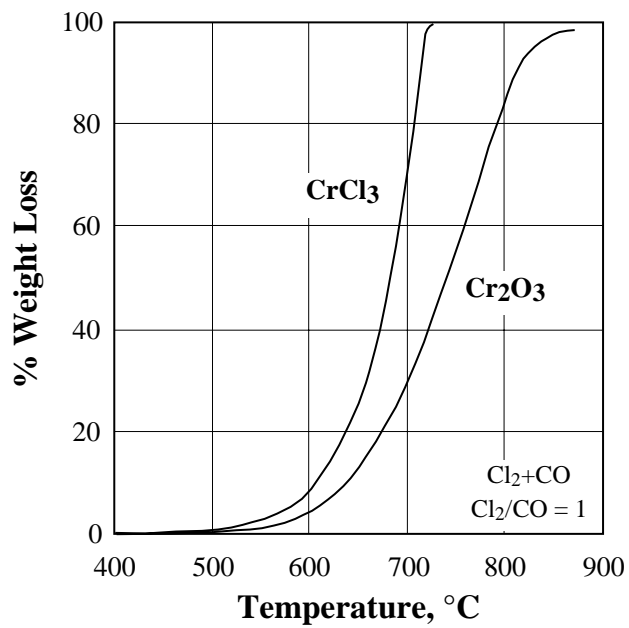


Fig. 4 - Thermogravimetric analysis of Cr_2O_3 in $\text{Cl}_2 + \text{CO}$ gas mixture.

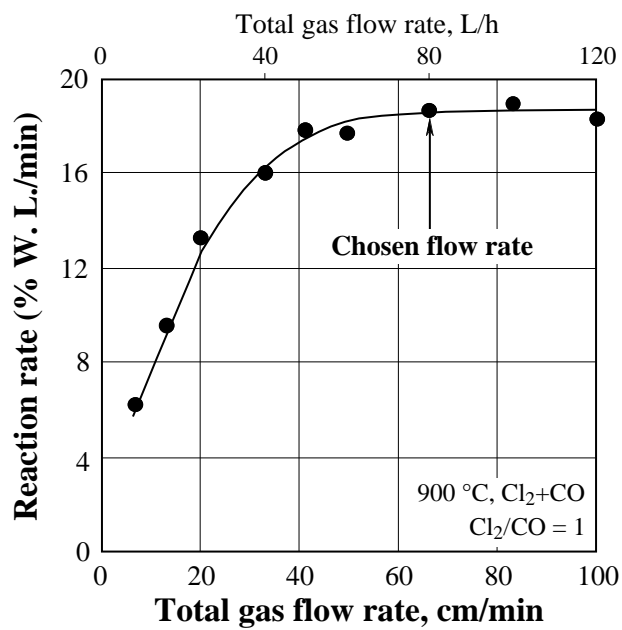


Fig. 5- Effect of gas flow rate on the chlorination rate of Cr₂O₃ with Cl₂+CO.

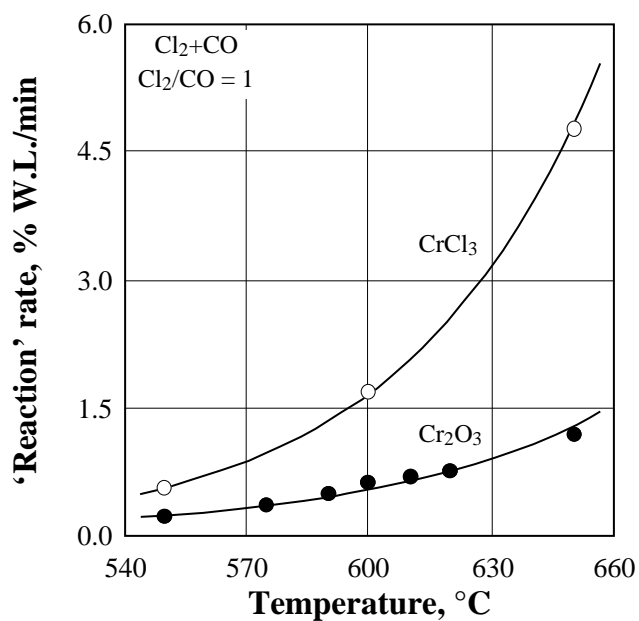


Fig. 6- Comparison of rate of CrCl₃ volatilization and Cr₂O₃ reaction with Cl₂+CO.

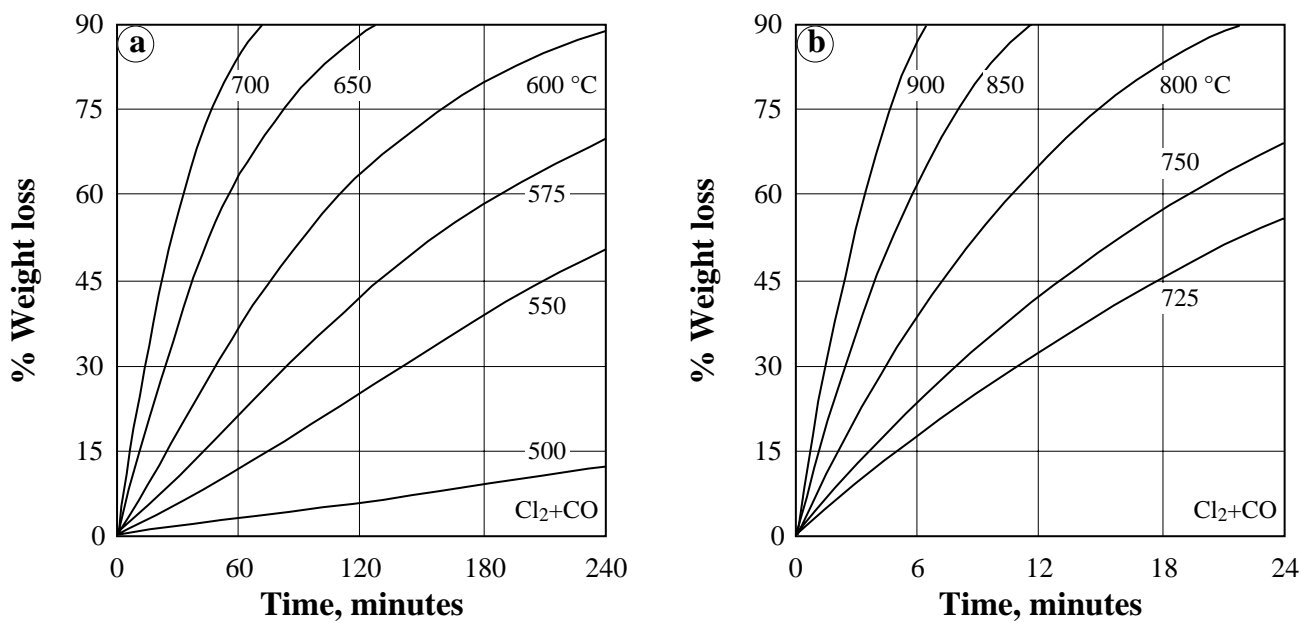


Fig. 7- Isotherms of carbochlorination of Cr_2O_3 with Cl_2+CO for (a) $T \leq 700^\circ\text{C}$ and (b) $T \geq 725^\circ\text{C}$.

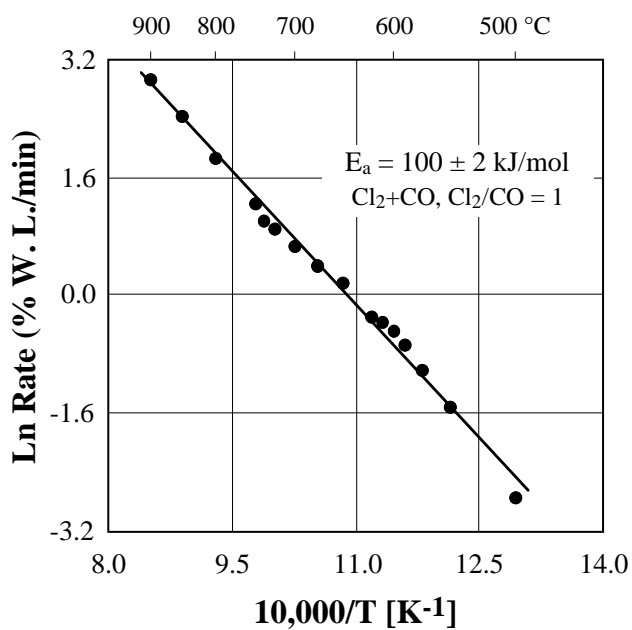


Fig. 8- Arrhenius plot of carbochlorination of Cr_2O_3 by Cl_2+CO .

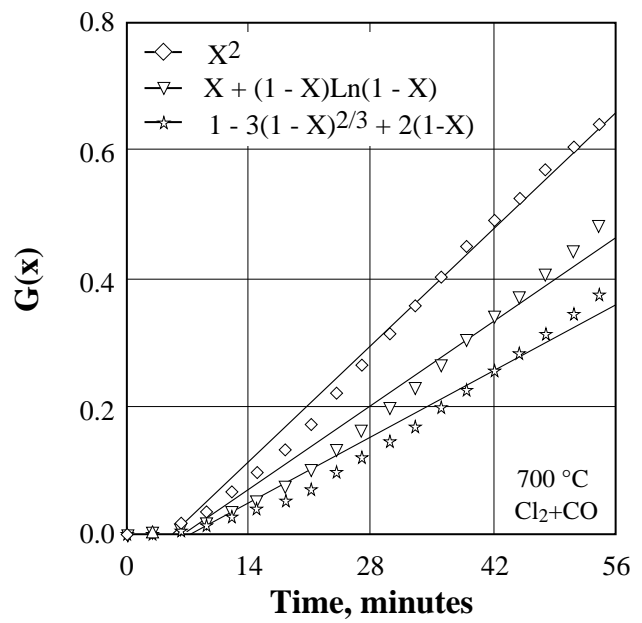
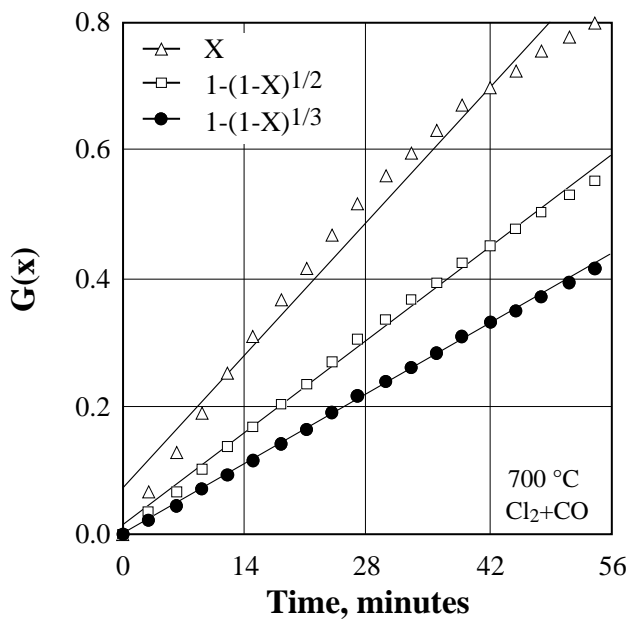


Fig. 9- Mathematical fitting of carbochlorination data of Cr_2O_3 at $700\text{ }^\circ\text{C}$ for different model equations.

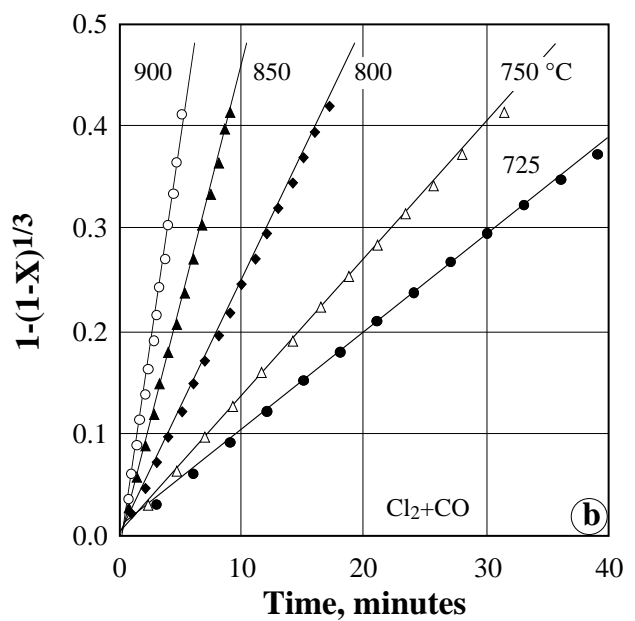
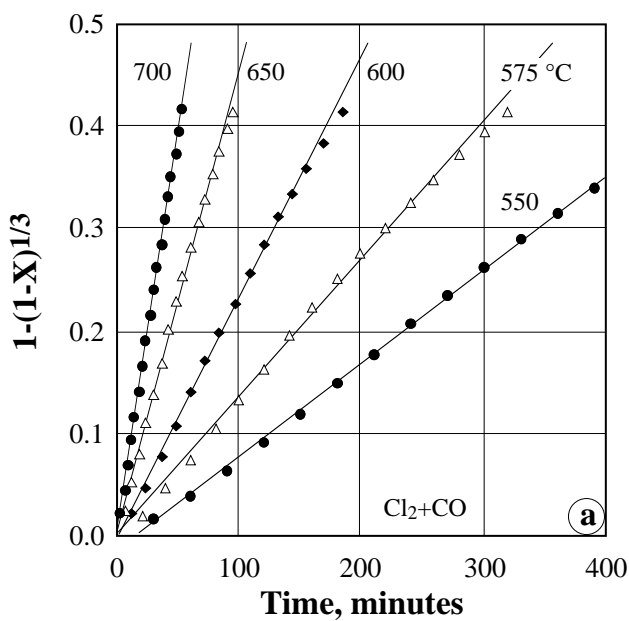


Fig. 10- Mathematical fitting of carbochlorination data of Cr_2O_3 with Cl_2+CO for (a) $T \leq 700\text{ }^\circ\text{C}$ and (b) $T \geq 725\text{ }^\circ\text{C}$ using equation 7.

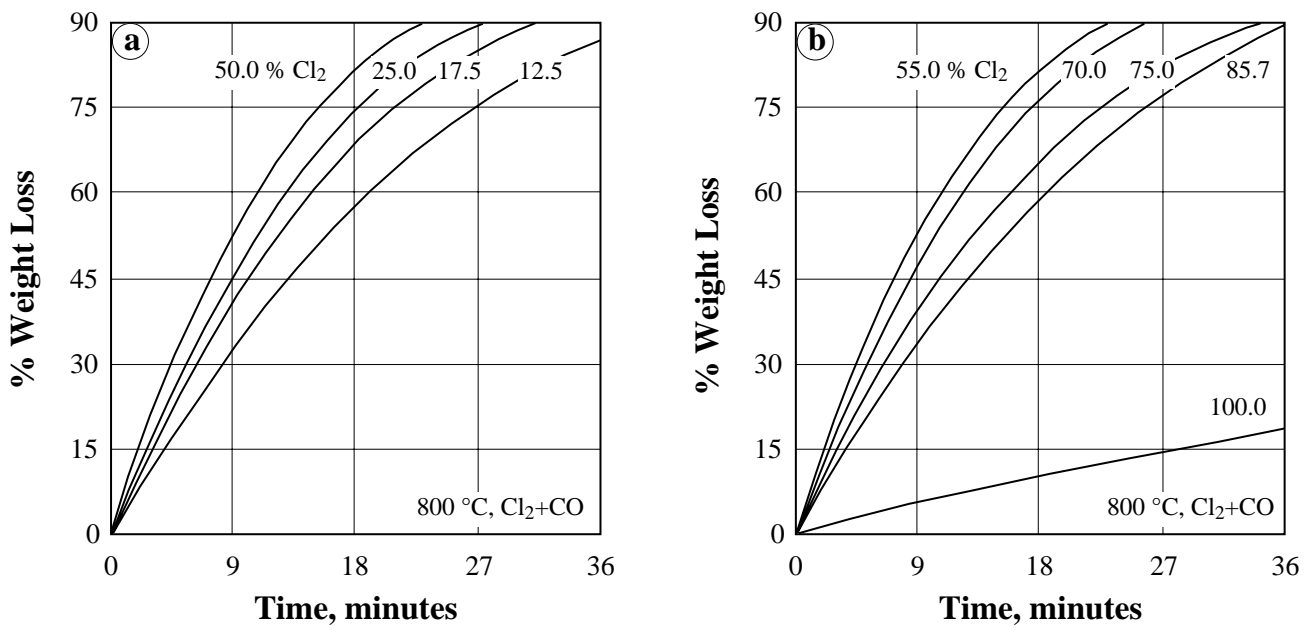


Fig. 11- Isotherms of carbochlorination of Cr₂O₃ at 800 °C with Cl₂+CO for (a) 12.5 ≤ Cl₂ ≤ 50.0 pct and (b) 55.0 ≤ Cl₂ ≤ 100.0 pct.

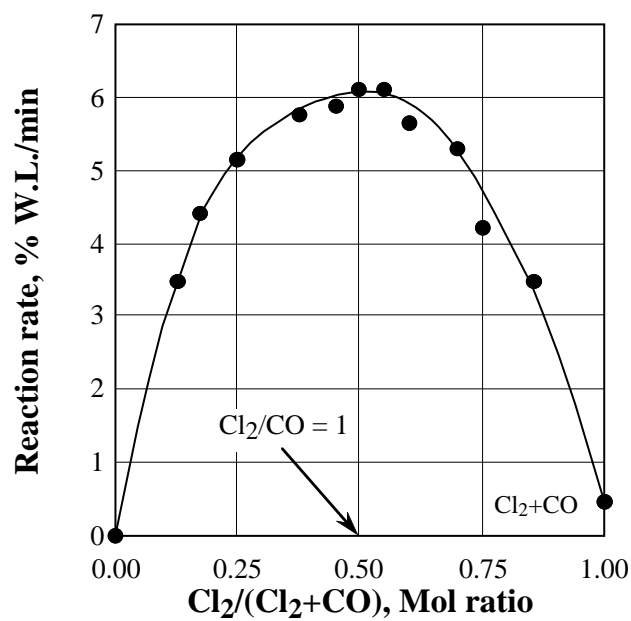


Fig. 12- Effect of Cl₂/(Cl₂+CO) ratio on the Cr₂O₃ carbochlorination rate at 800 °C.

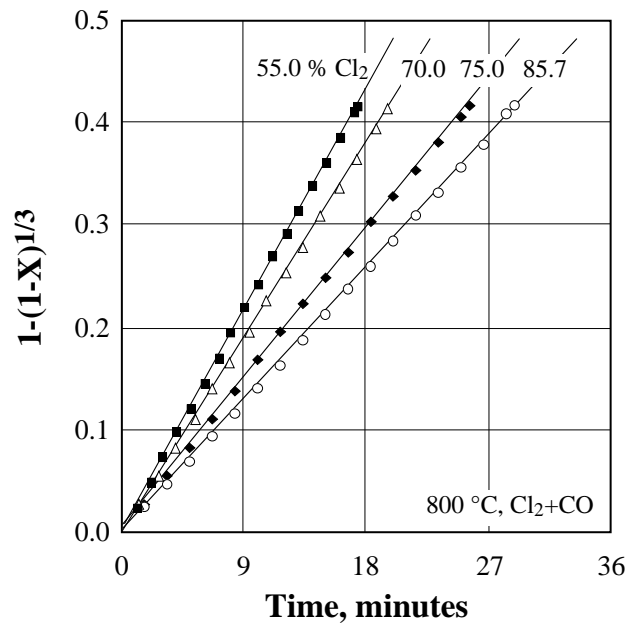
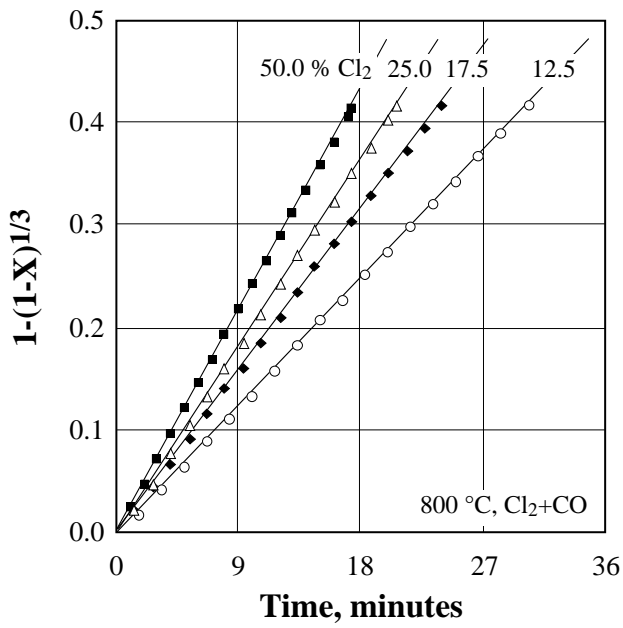


Fig. 13- Mathematical fitting of experimental data of Figure 11.

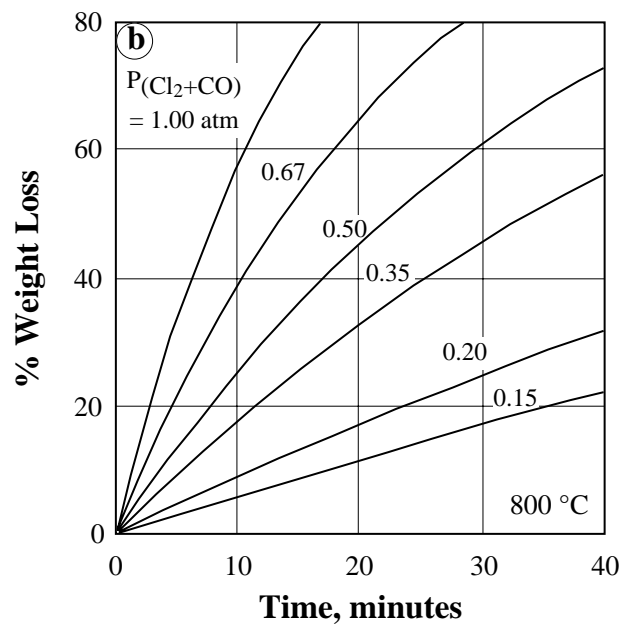
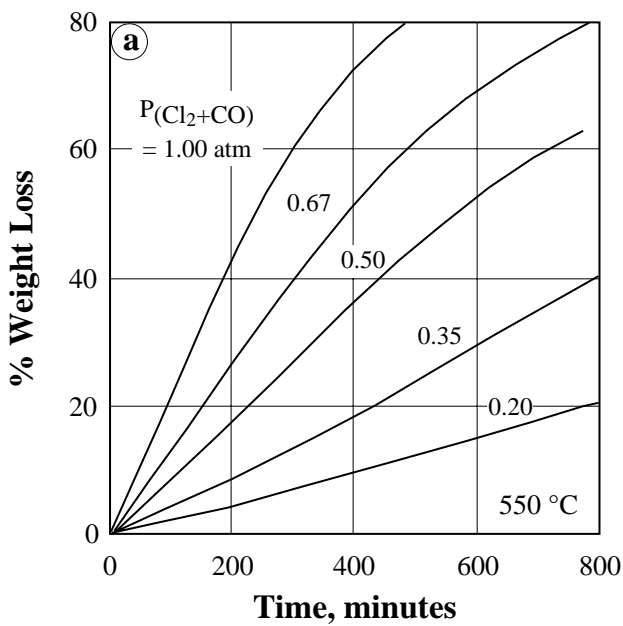


Fig. 14- Effect of Cl_2+CO ($\text{Cl}_2/\text{CO} = 1$) partial pressure on Cr_2O_3 carbochlorination at (a) 550°C and (b) 800°C .

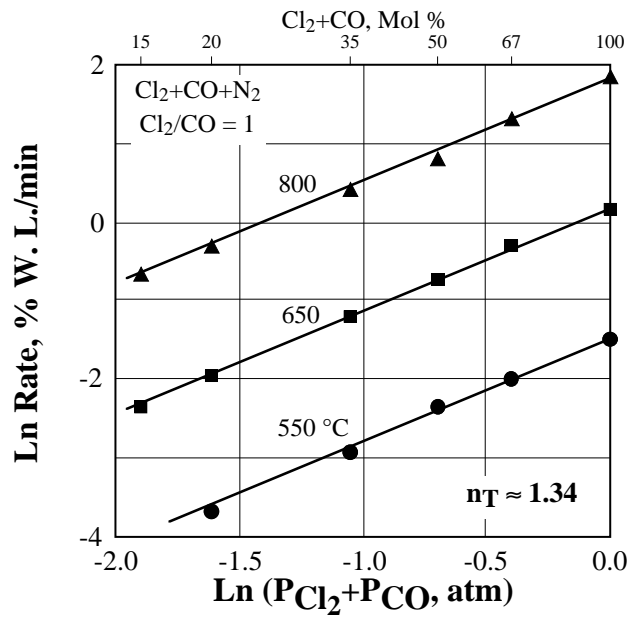


Fig. 15- Apparent reaction order with respect to Cl_2+CO .

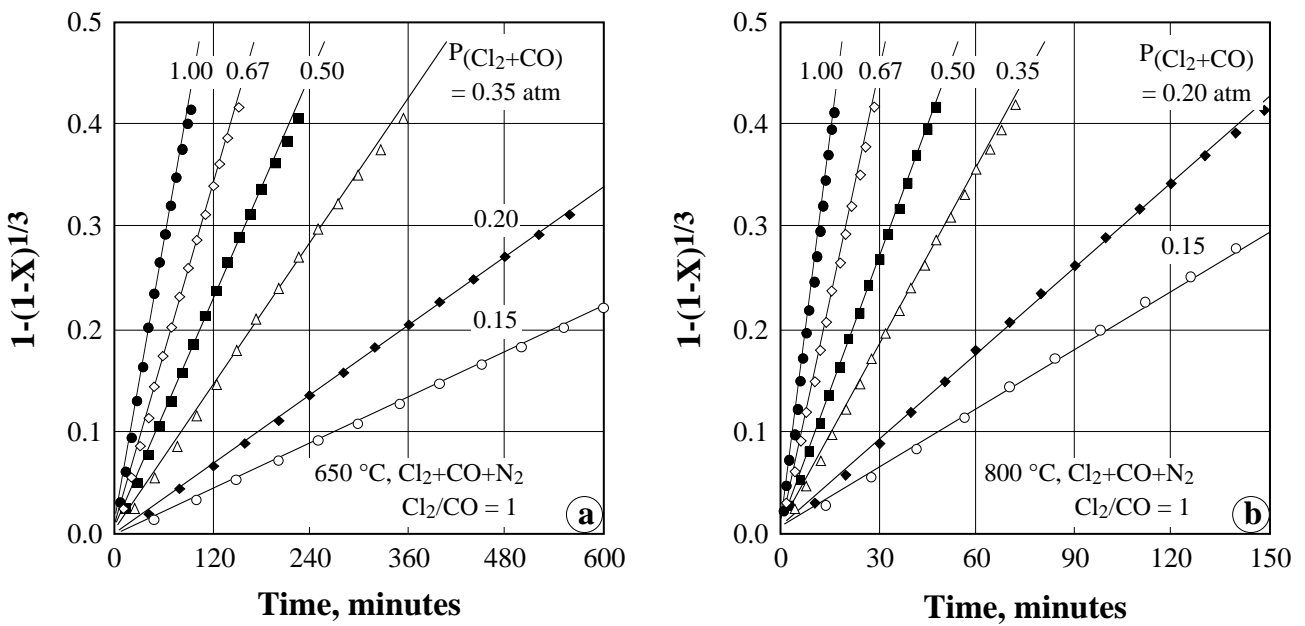


Fig. 16- Mathematical fitting of the carbochlorination data for different partial pressures of Cl_2+CO at (a) 650 and (b) 800 °C using equation [7].