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## **Kinetics of Oxychlorination of Chromite : Part II. Effect of Reactive Gases**

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The effects of  $\text{Cl}_2/\text{O}_2$  ratio,  $P_{(\text{Cl}_2+\text{O}_2)}$ ,  $P_{\text{Cl}_2}$ , and  $P_{\text{O}_2}$  on the oxychlorination rate of the chromite mineral were determined at 750 °C and 1000 °C using isothermal TGA measurements. The effects of the gases' composition on the oxychlorination rate of chromite were compared with those one resulting from the oxychlorination of simple oxides of the chromite ( $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{MgO}$ ). The apparent reaction orders with respect to  $\text{Cl}_2+\text{O}_2$ ,  $\text{Cl}_2$ , and  $\text{O}_2$  for the chromite oxychlorination at 750 °C were about 0.94, 1.24, and -0.30, respectively. At 1000 °C, apparent reaction orders with respect to the reactive gases changed significantly with the reaction progress.

Boat experiments were carried out to oxychlorinate a chromite concentrate between 600 °C and 1000 °C. The reaction products were analyzed by SEM, XRD and chemical analysis. The oxychlorination of a chromite concentrate at about 800 °C led to the partial elimination of iron increasing the Cr/Fe ratio in the treated concentrate. A part of chromium was also oxychlorinated and it was recovered as chromium oxychloride ( $\text{CrO}_2\text{Cl}_2$ ).

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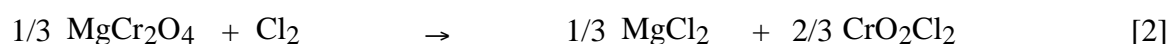
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## I. INTRODUCTION

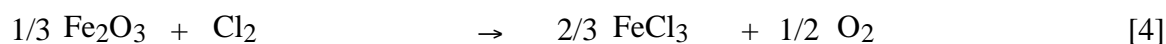
In Part I<sup>[1]</sup> of this series, experimental results concerning the effect of temperature on the oxychlorination of chromite between 600 °C and 1050 °C have been reported. It was observed that the temperature effect changed with the progress of the reaction, temperature interval studied and to some extent with the Cl<sub>2</sub>/O<sub>2</sub> ratio in the oxychlorinating gas mixture.

Reactions of two main chromite constituents (FeCr<sub>2</sub>O<sub>4</sub> and MgCr<sub>2</sub>O<sub>4</sub>) with chlorine could be represented by Eqs. [1] and [2] indicating that chromium oxychloride is the bearing chromium product. However, it was observed previously<sup>[2]</sup> that chromium trichloride (CrCl<sub>3</sub>) was generated besides chromium oxychloride when the chromite was treated in chlorine in absence of oxygen. This may be explained by the removal, preferentially, step-by-step of the simple constituents of the chromite (Fe, Cr and Mg oxides).



The oxychlorination of chromium (III) oxide is given by Eq. [3], and, as could be expected, the presence of oxygen is necessary to lead to the chromium oxychloride (CrO<sub>2</sub>Cl<sub>2</sub>) formation. The chlorination of iron and magnesium oxides producing their respective chlorides (Eq. [4] and [5]) releases some oxygen and consequently low oxygen partial pressures are required to ameliorate the chlorination of these oxides.

However, these hypotheses are only a simple theoretical approach. In order to explain how the composition of the reactive gases (Cl<sub>2</sub>+O<sub>2</sub>) affects the oxychlorination of chromite, the effects of Cl<sub>2</sub>/O<sub>2</sub> ratio, P<sub>(Cl<sub>2</sub>+O<sub>2</sub>)</sub>, P<sub>Cl<sub>2</sub></sub> and P<sub>O<sub>2</sub></sub> on the reaction rate at different temperatures and at different reaction extents of the chromite oxychlorination were investigated. Results were compared with those obtained previously for Cr<sub>2</sub>O<sub>3</sub><sup>[3]</sup>, MgO<sup>[4]</sup>, and Fe<sub>2</sub>O<sub>3</sub><sup>[5]</sup> oxychlorination.



The purpose of this study is to determine the adequate partial pressures of the reactive gases and temperature to remove selectively iron oxides and to prevent the chlorination of chromium. With this approach, the treated chromite was be characterized by a high chromium-to-iron ratio, consequently, it will be befitting for the ferro-chromium production.

The materials used and the experimental procedures are those described in Part I<sup>[1]</sup>. The effects of the mentioned above parameters were studied by using the oxychlorination gaseous mixtures with the optimal linear velocity ( $V_g$ ) equal to 49.6 cm/min and the experimental tests were carried out using TGA measurements under isothermal conditions. Boat experiments were performed to oxychlorinate by  $\text{Cl}_2$ +air gaseous mixture a chromite concentrate between 600 °C and 1000 °C. The evolution of Cr/Fe ratio of the treated concentrate was determined by classical chemical analysis.

## II. RESULTS AND DISCUSSION

### A. TGA Studies of the Gas Composition on the Oxychlorination of the Chromite Mineral

As mentioned previously<sup>[1]</sup>, two kinetics regions were distinguished for the oxychlorination ( $\text{Cl}_2+\text{O}_2$ ) of chromite for the reaction extents 'X' (ratio of weight of the reacted fraction to initial weight) up to 0.35 and this change was observed at about 825 °C. On the other hand, the oxychlorination of chromite for the reaction extents higher than 0.35 was characterized by a slowly reaction rate at temperatures lower than 900 °C. For these reasons, the effects of the gas composition on the reaction rates of the chromite with  $\text{Cl}_2+\text{O}_2$  were studied at 750 °C and 1000 °C.

#### 1. Study at 750 °C

##### 1.1. Effect of $\text{Cl}_2/(\text{Cl}_2+\text{O}_2)$ ratio

A series of isothermal tests was conducted with  $\text{Cl}_2+\text{O}_2$  gas mixtures and the chlorine content in the gas mixture was varied from 0 to 100 pct. As could be expected, non reaction of oxygen with chromite was observed. The isothermal data for the oxychlorination of chromite with  $\text{Cl}_2+\text{O}_2$  containing 40 to 100 pct chlorine and for  $X \leq 0.30$  are given in Figure 1 (a). As shown by this figure, the time required to reach a given percent weight loss (PWL) of the sample decreases with the increase of the chlorine content in the  $\text{Cl}_2+\text{O}_2$ . Figure 1 (b) traces the evolution of the average reaction rate as a function of the  $\text{Cl}_2/(\text{Cl}_2+\text{O}_2)$  molar ratio for  $X \leq 0.25$ . Clearly, the reaction rate increased with the  $\text{Cl}_2/(\text{Cl}_2+\text{O}_2)$  ratio. However, this increase in the reaction rate was less dependent on  $\text{Cl}_2/(\text{Cl}_2+\text{O}_2)$  ratio for the reaction extents higher than 0.20<sup>[2]</sup>. Dependency of the reaction rate of the  $\text{Cr}_2\text{O}_3$ <sup>[3]</sup> and  $\text{Fe}_2\text{O}_3$ <sup>[5]</sup> oxychlorination from  $\text{Cl}_2/(\text{Cl}_2+\text{O}_2)$  molar ratio is illustrated in Figure 2. A maximum reaction rate of the  $\text{Cr}_2\text{O}_3$  oxychlorination was obtained when the  $\text{Cl}_2/\text{O}_2$  ratio was 4, that satisfies the stoichiometry of the reaction [3] for the  $\text{CrO}_2\text{Cl}_2$  formation. Like in the case of chromite oxychlorination, the reaction rate of the  $\text{Fe}_2\text{O}_3$  with  $\text{Cl}_2+\text{O}_2$  increases with the  $\text{Cl}_2/(\text{Cl}_2+\text{O}_2)$  ratio. These results as well as those obtained for the temperature effect<sup>[1]</sup> seem indicate that the overall reaction rate of the chromite oxychlorination at lower temperatures depends essentially on the oxychlorination of iron oxides contained in the chromite.

### 1.2. Effect of Cl<sub>2</sub>+O<sub>2</sub> partial pressure

Experiments to determine the effect of Cl<sub>2</sub>+O<sub>2</sub> partial pressure on the reaction rate of chromite oxychlorination were carried out by using a Cl<sub>2</sub>+O<sub>2</sub>+N<sub>2</sub> gas mixture and keeping the Cl<sub>2</sub>/O<sub>2</sub> molar ratio constant equal to 4. The partial pressure of Cl<sub>2</sub>+O<sub>2</sub> was varied from 0.25 to 1.00 atm and the results are given in Figure 3 (a) as evolution of the PWL *versus* time. Figure 3 (b) gives the evolution of the reaction rate as function of the Cl<sub>2</sub>+O<sub>2</sub> partial pressure for X ≤ 0.25. An apparent reaction order with respect to Cl<sub>2</sub>+O<sub>2</sub> of about 0.94 was deduced from the data linearisation of Figure 3 (b).

### 1.3. Effect of Cl<sub>2</sub> and O<sub>2</sub> partial pressures

Two series of tests were carried out using Cl<sub>2</sub>+O<sub>2</sub>+N<sub>2</sub> with a V<sub>g</sub> equal to 49.6 cm/min. The first series of the tests was performed by keeping the oxygen partial pressure constant (0.33 atm) and varying the chlorine partial pressure from 0.10 to 0.67 atm. The second one was conducted using a constant chlorine partial pressure (0.33 atm) and varying the oxygen partial pressure from 0.10 to 0.67 atm.

Figures 4 (a) and (b) compile the experimental data concerning the oxychlorination of chromite at constant partial pressure of oxygen. The apparent reaction order with respect to chlorine is about 1.24 for X ≤ 0.25. Similarly, Figures 5 (a) and (b) describe the effect of the oxygen partial pressure on the oxychlorination. As shown by Figure 5 (b) the oxygen had a negative effect on the reaction rate, since the apparent reaction order is about -0.30.

Table I. Comparison of Reaction Orders with Respect to Reactive Gases of Different Solids' Oxychlorination.

Solids	T, °C	<sup>n</sup> (Cl <sub>2</sub> +O <sub>2</sub> )	<sup>n</sup> Cl <sub>2</sub>	<sup>n</sup> O <sub>2</sub>
Cr <sub>2</sub> O <sub>3</sub> <sup>[3]</sup>	800	1.29	1.08	0.23
Fe <sub>2</sub> O <sub>3</sub> <sup>[5]</sup>	750	0.71	1.44	-0.61
Chromite (0.00 ≤ X ≤ 0.25)	750	0.94	1.24	-0.30

The effects of Cl<sub>2</sub>+O<sub>2</sub>, Cl<sub>2</sub> and O<sub>2</sub> on the reaction rates of Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and chromite (0.00 ≤ X ≤ 0.25) with the Cl<sub>2</sub>+O<sub>2</sub> gas mixtures are summarized in Table I. The comparison of these data indicates that the chromite oxychlorination was characterized by the values of <sup>n</sup>(Cl<sub>2</sub>+O<sub>2</sub>), <sup>n</sup>Cl<sub>2</sub>, and <sup>n</sup>O<sub>2</sub> that are nearest of those of the Fe<sub>2</sub>O<sub>3</sub> oxychlorination.

## 2. Study at 1000 °C

### 2.1. Effect of $\text{Cl}_2/(\text{Cl}_2+\text{O}_2)$ ratio

Tests to determine this effect were carried out at different chlorine contents in the  $\text{Cl}_2+\text{O}_2$  gas mixture. Figure 6 (a) gives some compilations of the experimental data for the chlorine contents between 33.3 and 100 pct and for reaction extents lower or equal to 0.35. The beginning of the reaction is as faster as the chlorine content in the gas increases. However the time required to reach 35 PWL of the sample when chlorine alone was used, is higher than that when  $\text{Cl}_2+\text{O}_2$  containing 80 pct  $\text{Cl}_2$  was used. The change of the slope of the PWL curves at about 15 PWL of the sample seems to correspond to the chlorination of iron oxides (refer to  $L_1^{\text{Fe}}$  of Figure 6 (a)). The oxychlorination results of the chromite at different chlorine contents and for the sample weight losses up to 56 pct are given in Figure 6 (b). The slow down of the reaction rate beyond 35 PWL is obvious regardless the chlorine content in the oxychlorinating gaseous mixture. Calculations based on the chemical and mineralogical composition of the chromite suggested that the oxychlorination of chromite after 35 PWL corresponds essentially to the reaction of  $\text{Mg}(\text{Cr}, \text{Al})_2\text{O}_4^{[1]}$  with  $\text{Cl}_2+\text{O}_2$ .

The evolution of the reaction rate *versus*  $\text{Cl}_2/(\text{Cl}_2+\text{O}_2)$  ratio was calculated for different reaction extents. Figure 7 (a) is an example concerning the reaction extents up to 0.30. Only for  $X \leq 0.1$ , the reaction rate increases significantly with  $\text{Cl}_2/(\text{Cl}_2+\text{O}_2)$  ratio. While for  $0.1 \leq X \leq 0.3$ , the reaction rate passes by a soft maximum corresponding to  $\text{Cl}_2/(\text{Cl}_2+\text{O}_2)$  ratio of about 0.8. This observation reminds the reaction of chromium (III) oxide oxychlorination according to Eq. [3]. Figure 7 (b) gives similar results displayed in Figure 7 (a) for  $X$  comprised between 0.4 and 0.5. The reaction rate rises with chlorine content in the oxychlorinating gas. Comparable behavior was acquired for the oxychlorination of  $\text{MgO}$ .

### 2.2. Effect of $\text{Cl}_2+\text{O}_2$ partial pressure

The experimental procedure to study the effect of  $\text{Cl}_2+\text{O}_2$  partial pressure on the oxychlorination of chromite at 1000 °C was the same one applied for the study at 750 °C. Results obtained were given in Figure 8 (a) as evolution of PWL *versus* time. Like in the previous case, the reaction rate drooped after 35 PWL whichever the  $\text{Cl}_2+\text{O}_2$  partial pressure was used. A mathematical treatment of the experimental data of Figure 8 (a) was performed to relate the evolution of the reaction rate of the chromite oxychlorination with the  $\text{Cl}_2+\text{O}_2$  partial pressure for different reaction extents. Results are represented in Figure 8 (b) in natural logarithm scale. The apparent reaction orders with respect to  $\text{Cl}_2+\text{O}_2$  for the reaction extents comprised between 0.0 to 0.1, 0.2 to 0.3 and 0.4 to 0.5 are designated as  $n_1(\text{Cl}_2+\text{O}_2)$ ,  $n_1'(\text{Cl}_2+\text{O}_2)$ , and  $n_2(\text{Cl}_2+\text{O}_2)$ , respectively. The beginning of the chromite oxychlorination is almost proportional to the  $\text{Cl}_2+\text{O}_2$  partial pressure and increased slightly for  $X$  between 0.2 and 0.3. While, small effect of  $\text{Cl}_2+\text{O}_2$  on the oxychlorination rate of chromite was observed for reaction extent higher than 0.4, since a value of  $n_2(\text{Cl}_2+\text{O}_2)$  of about 0.43 is deduced from the data of Figure 8 (b).

### 2.3. Effect of Cl<sub>2</sub> and O<sub>2</sub> partial pressures

Tests to determine the effect of Cl<sub>2</sub> on the oxychlorination rate of chromite were performed with Cl<sub>2</sub>+O<sub>2</sub>+N<sub>2</sub> at constant partial pressure (0.33 atm) of oxygen when the total gas velocity was kept constant at 49.6 cm/min. Plots of the experimental data are given in Figure 9 (a) for the reaction extents up to 0.54. As in the previous cases, the effect of chlorine on the reaction rate was calculated for different reaction extents. The apparent reaction orders with respect to Cl<sub>2</sub> for different values of X are deduced from the data linearisation of Figure 9 (b). Comparison of the results obtained from Figures 8 (b) and 9 (b) indicates that  $n_{\text{Cl}_2} > n_{\text{Cl}_2+\text{O}_2}$  for the reaction extents lower than 0.1 and higher than 0.4. While,  $n_{\text{Cl}_2} < n_{\text{Cl}_2+\text{O}_2}$  for X comprised between 0.2 and 0.3.

Effect of the oxygen on the reaction rate was studied at constant partial pressure of chlorine (0.33 atm) while the partial pressure of chlorine in the Cl<sub>2</sub>+O<sub>2</sub>+N<sub>2</sub> was varied from about 0.07 to 0.67 atm. Typical plots representing the evolution of the PWL *versus* time for several performed isotherms are given in Figure 10 (a). These plots show that the oxychlorination of chromite is little dependent on the partial pressure of oxygen in the  $P_{\text{O}_2}$  interval investigated. The apparent reaction orders with respect to oxygen (Figure 10 (b)) are  $n_{1(\text{O}_2)} \approx -0.24$ ,  $n'_{1(\text{O}_2)} \approx 0.16$ , and  $n_{2(\text{O}_2)} \approx -0.25$  for the reaction extents of 0.0-0.1, 0.2-0.3, and 0.4-0.5, respectively. It is important to note that the oxygen has a positive effect for X comprised between 0.2 and 0.3 and for oxygen partial pressures lower or equal to 0.5 atm.

Table II. Comparison of Reaction Orders with Respect to Reactive Gases of Different Solids' Oxychlorination.

Solids	T, °C	$n_{\text{Cl}_2+\text{O}_2}$	$n_{\text{Cl}_2}$	$n_{\text{O}_2}$
Cr <sub>2</sub> O <sub>3</sub> <sup>[3]</sup>	800	1.29	1.08	0.23
Fe <sub>2</sub> O <sub>3</sub> <sup>[5]</sup>	950	0.70	1.39	-0.62
MgO <sup>[4]</sup>	950	0.65	0.98	-0.37
Chromite (0.0 ≤ X ≤ 0.1)		1.04	1.21	-0.24
(0.2 ≤ X ≤ 0.3)	1000	1.23	1.03	0.16
(0.4 ≤ X ≤ 0.5)		0.43	0.64	-0.25

The apparent reaction orders with respect to Cl<sub>2</sub>+O<sub>2</sub>, Cl<sub>2</sub>, and O<sub>2</sub> for the reactions of chromite and oxides of chromium, iron, and magnesium with Cl<sub>2</sub>+O<sub>2</sub> are summarized in Table II. Although the chosen temperatures for the study of the apparent reaction orders for the simple

oxides are lower than that of the chromite one, it appears that values of the apparent reaction orders do not change significantly with the temperature in the temperature range when the apparent activation energy is constant. For example, the apparent reaction orders for the oxychlorination of  $\text{Fe}_2\text{O}_3$  at 750 °C and 950 °C are similar (refer to Tables I and II) and the effect of temperatures for  $\text{Fe}_2\text{O}_3$  oxychlorination remained constant up to 1025 °C<sup>[1]</sup>.

The following observations could be deduced from the data of Table II :

- a. the apparent reaction order with respect to  $\text{O}_2$  for the oxychlorination of chromite at  $X \leq 0.1$  has a negative value (-0.24). Similarly, negative effect was observed for the  $\text{Fe}_2\text{O}_3$  oxychlorination. Thus, it may be supposed that the initial stage of oxychlorination of the chromite is affected by the oxychlorination reactions of iron oxides,
- b. the oxygen has a positive effect, although small, on the chromite oxychlorination for the reaction extents higher than 0.1. Only the oxychlorination of chromium (III) oxide generating chromium oxychloride can explain this phenomenon indicating that the chromium oxide reaction with  $\text{Cl}_2+\text{O}_2$  may affect the overall oxychlorination reactions,
- c. the chromite oxychlorination is little dependent on the partial pressures of the reactive gases for the  $X \geq 0.4$  and the values of the apparent reaction orders are near to those obtained for the  $\text{MgO}$  oxychlorination.

These roughly similarities between the kinetics parameters of the chromite oxychlorination and those of its simple oxides may suggest the hypothesis that the overall reaction rate of the chromite with  $\text{Cl}_2+\text{O}_2$  is controlled by the slowest step of the oxychlorination of the chromite constituents.

The effects of the gas composition on the oxychlorination rate of iron chromite (first stage of the chromite oxychlorination, i. e.,  $X \leq 0.25$ ) at 750 °C and 1000 °C were compared in Figure 11. This figure gives some advisability data for the the partial pressures range of the reactive gases and temperature in order to obtain a desired reaction extent of the iron chromite oxychlorination. One may stress that the first stage of the oxychlorination of chromite takes place at an appreciable rate even at 750 °C.

While the oxychlorination rate of the chromite with  $\text{Cl}_2+\text{O}_2$  for  $X \geq 0.35$  is slow regardless the partial pressure of the reactive gases and the temperature<sup>[1]</sup> within whole chosen intervals for this study. Consequently, the recovery of chromium from magnesium chromite ( $\text{MgCr}_2\text{O}_4$ ) seems to be difficult by using oxychlorination at temperatures near to 1000 °C. A possibility to achieve the full chlorination of chromite wit a high reaction rate will be the chlorination in the presence of a



reducing atmosphere such as carbon monoxide<sup>[6]</sup>. A comparison of the reaction rates of the chromite reaction with  $\text{Cl}_2+\text{O}_2$ ,  $\text{Cl}_2$ , and  $\text{Cl}_2+\text{CO}$  ( $0.4 \leq X \leq 0.5$ ) for X comprised between 0.4 and 0.5 is given in Figure 12. The reaction rate of the magnesium chromite chlorination with  $\text{Cl}_2+\text{CO}$  is too much higher than that of the chlorination with  $\text{Cl}_2+\text{O}_2$  and/or  $\text{Cl}_2$ . For example, at 950 °C, the reaction rate of the chromite carbochlorination is more than 500 and 90 times higher than that of the oxychlorination and chlorination, respectively. However, the carbochlorination at temperature approaching 1000 °C could be used for the full removal of the chromite elements (Cr, Fe, Mg, Al, Si) recovered as respective chlorides. Oxychlorination seems to be more selective than carbochlorination thanks to large difference in the reactivity of chromite constituents towards chlorine in presence of oxygen<sup>[1,2]</sup>. This selectivity was used for the preferential removal of iron from a chromite concentrate. The experimental results are represented in the following section.

### B. Oxychlorination of the Chromite Concentrate using Boat Experiments

The aforementioned results concerning the oxychlorination of the chromite indicated that only iron chromite ( $\text{FeCr}_2\text{O}_4$ ) could react with the  $\text{Cl}_2+\text{O}_2$  at a relatively fast reaction rate for the temperature lower or equal to 1000 °C. In order to investigate the possibility of preferentially removal of iron oxides from the chromite ores and/or concentrates a series of boat experiments using several grams of sample was performed between 600 °C and 1000 °C. The used sample was a chromite concentrate containing about 80 pct chromite and 20 pct gangue. The physico-chemical characteristics of this chromite concentrate were described in details early<sup>[6]</sup>. A gas mixture composed of  $\text{Cl}_2+\text{air}$  ( $\text{Cl}_2/\text{air} = 1$ ) was used for the oxychlorination and the reaction time was fixed at 2 hours. The exhausted gases were successively cooled to room temperature and to -35 °C.

Figure 13 (a) traces the evolution of the PWL of the sample as a function of temperature. As could be expected, the PWL increases with the temperature and about 25 pct of the sample have reacted at 1000 °C. The iron and chromium contents of the obtained residues were determined by chemical analysis and the results are grouped in Figure 13 (b) and Table III. The extraction rate of iron is higher than that of chromium for all the explored temperature range. About 90 and 25 pct for iron and chromium, respectively, are extracted at 1000 °C. As shown by Table III, the Cr/Fe ratio of the treated concentrate increases with the treatment temperature from 3.9 at 700 °C to 19.8 at 1000 °C. These results suggest that the oxychlorination of chromite at about 800 °C will lead to a residue with a high chromium-to-iron ratio and the chromium extraction didn't exceed 15 pct.

Residues and condensates were analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Chromium remained main element of all residues, while iron become minor element at high treatment temperature. As mentioned previously<sup>[1]</sup>, it was difficult to follow the

evolution of the residue by XRD analysis due to similar structure of the chromite spinels.

Table III. Evolution of Cr/Fe Ratio of the Oxychlorination Residues of Chromite Concentrate as a Function of Temperature.

T, °C	PWL	Cr, Wt pct	Fe, Wt pct	Cr/Fe ratio
Raw sample	—	34.2	10.8	3.2
700	4.2	31.7	8.1	3.9
800	12.7	35.5	6.8	5.2
900	21.4	35.6	3.2	11.1
1000	25.4	33.7	1.7	19.8

Solid condensates obtained by cooling of gas phase at 25 °C are essentially composed of Fe and Cl for the oxychlorination temperatures lower than 800 °C and of Fe, Mg, Cl at higher temperatures. Aluminum was not detected indicating the refractory nature of aluminum oxide in the oxychlorinating gas mixture. Although a part of chromium contained in the concentrate was removed (refer to Figure 13 (b)), it was not detected in the solid condensate obtained by cooling the gas phase to room temperature. However, cooling the gas phase to - 35 °C led to the formation of a red liquid. The physicochemical properties of the obtained liquid are in good agreement with those given previously for the  $\text{CrO}_2\text{Cl}_2$ <sup>[3, 8]</sup>. The absence of chromium in the solid condensates obtained at 25 °C is explained by the fact that melting and boiling points of  $\text{CrO}_2\text{Cl}_2$  are -96.5 and 117 °C<sup>[7]</sup>, respectively. These results show that it is possible to use the oxychlorination for the increase of Cr/Fe ratio of the chromite concentrates and to recover the extracted chromium as chromium oxychloride.

### III. CONCLUSIONS

Oxychlorination of the chosen chromite mineral at 750 °C by  $\text{Cl}_2+\text{O}_2+\text{N}_2$  lead, essentially, to the selective removal of iron chromite ( $\text{FeCr}_2\text{O}_4$ ). The reaction rate increases with the rise of  $\text{Cl}_2/\text{O}_2$  ratio in the gas mixture. The apparent reaction orders with respect to  $\text{Cl}_2+\text{O}_2$ ,  $\text{Cl}_2$ , and  $\text{O}_2$  are about 0.94, 1.24 and -0.30, respectively. The overall reaction rate seems to be affected by the chlorination rate of iron oxide.

At least, two stages of the oxychlorination of the chromite are distinguished at 1000 °C regardless the composition of the oxychlorinating gas mixtures in whole interval studied. The first

stage corresponds to the oxychlorination of iron chromite and second one to the reaction of magnesium chromite ( $\text{MgCr}_2\text{O}_4$ ) with the oxychlorinating gas mixture.

The effect of gases' composition ( $\text{Cl}_2/\text{O}_2$  ratio,  $P_{(\text{Cl}_2+\text{O}_2)}$ ,  $P_{\text{Cl}_2}$ , and  $P_{\text{O}_2}$ ), for the reaction extent up to 0.30 at 1000 °C, changes with the reaction progress suggesting that the oxychlorination of iron and chromium oxides contained in  $\text{FeCr}_2\text{O}_4$  affects successively the overall reaction.

The apparent reaction orders with respect to  $\text{Cl}_2+\text{O}_2$ ,  $\text{Cl}_2$ , and  $\text{O}_2$  for the second stage of oxychlorination of chromite at 1000 °C are about 0.43, 0.64 and -0.25, respectively, indicating that the oxychlorination of magnesium chromite is little dependent on the composition of the reactive gases. In addition, the similarity of the kinetics parameters between  $\text{MgCr}_2\text{O}_4$  and  $\text{MgO}$  oxychlorination advances the hypothesis that the oxychlorination process of the chromite is somewhat affected by the rate of  $\text{MgO}$  reaction with  $\text{Cl}_2+\text{O}_2$ .

Oxychlorination of poor chromite concentrates and/or ores at moderate temperatures could be used for their upgrading. Iron is advantageously removed while the chromium had reacted partially and it was recovered as  $\text{CrO}_2\text{Cl}_2$ .

## **ACKNOWLEDGMENTS**

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# Kinetics of Oxychlorination of Chromite : Part II. Effect of Reactive Gases

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## FIGURE CAPTIONS

- Figure 1 : Isotherms of oxychlorination of chromite at 750 °C (*a*) using different chlorine contents and (*b*) effect of  $\text{Cl}_2/\text{O}_2$  ratio on the reaction rate.
- Figure 2 : Effect of  $\text{Cl}_2/(\text{Cl}_2+\text{O}_2)$  ratio on the oxychlorination rate of  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ .
- Figure 3 : Isotherms of oxychlorination of chromite at 750 °C using (*a*) different  $\text{Cl}_2+\text{O}_2$  partial pressures and (*b*) apparent reaction order with respect to  $\text{Cl}_2+\text{O}_2$ .
- Figure 4 : Isotherms of oxychlorination of chromite at 750 °C using (*a*) different  $\text{Cl}_2$  partial pressures and (*b*) apparent reaction order with respect to  $\text{Cl}_2$ .
- Figure 5 : Isotherms of oxychlorination of chromite at 750 °C using (*a*) different  $\text{O}_2$  partial pressures and (*b*) apparent reaction order with respect to  $\text{O}_2$ .
- Figure 6 : Isotherms of oxychlorination of chromite at 1000 °C using different chlorine contents for (*a*)  $X \leq 0.35$  and (*b*)  $X \leq 0.56$ .
- Figure 7 : Evolution of the reaction rates versus  $\text{Cl}_2/(\text{Cl}_2+\text{O}_2)$  ratio for the oxychlorination of chromite at (*a*)  $X \leq 0.3$  and (*b*) at  $0.4 \leq X \leq 0.5$  compared with that of  $\text{MgO}$ .
- Figure 8 : Isotherms of oxychlorination of chromite at 1000 °C using (*a*) different  $\text{Cl}_2+\text{O}_2$  partial pressures and (*b*) apparent reaction orders with respect to  $\text{Cl}_2+\text{O}_2$ .
- Figure 9 : Isotherms of oxychlorination of chromite at 1000 °C using (*a*) different  $\text{Cl}_2$  partial pressures and (*b*) apparent reaction orders with respect to  $\text{Cl}_2$ .
- Figure 10 : Isotherms of oxychlorination of chromite at 1000 °C using (*a*) different  $\text{O}_2$  partial pressures and (*b*) apparent reaction orders with respect to  $\text{O}_2$ .
- Figure 11 : Effect of gas composition on the reaction rate of chromite oxychlorination at 750 °C and 1000 °C for  $X \leq 0.25$ .
- Figure 12 : Comparison of the reaction rates of the chromite with different chlorinating gas mixtures for the reaction extent between 0.4 and 0.5.
- Figure 13 : Evolution of PWL of the sample (*a*) and extraction extent of Cr and Fe (*b*), as a function of temperature, during oxychlorination of the chromite concentrate for two hours.

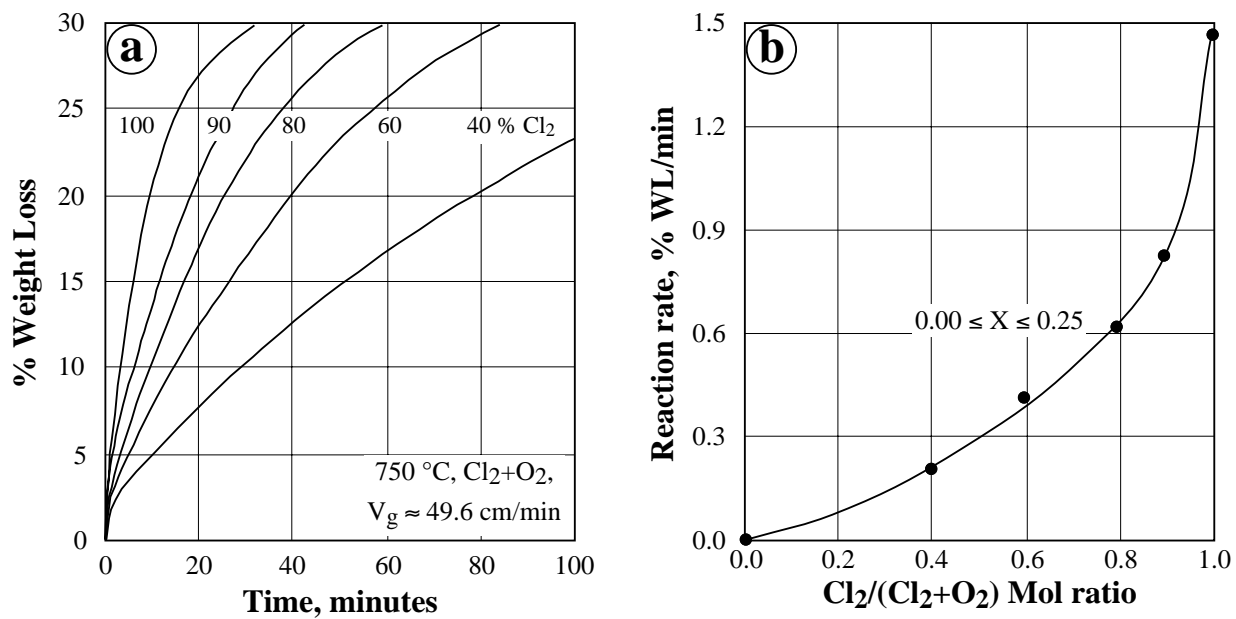


Figure 1 : Isotherms of oxychlorination of chromite at 750 °C (a) using different chlorine contents and (b) effect of Cl<sub>2</sub>/O<sub>2</sub> ratio on the reaction rate.

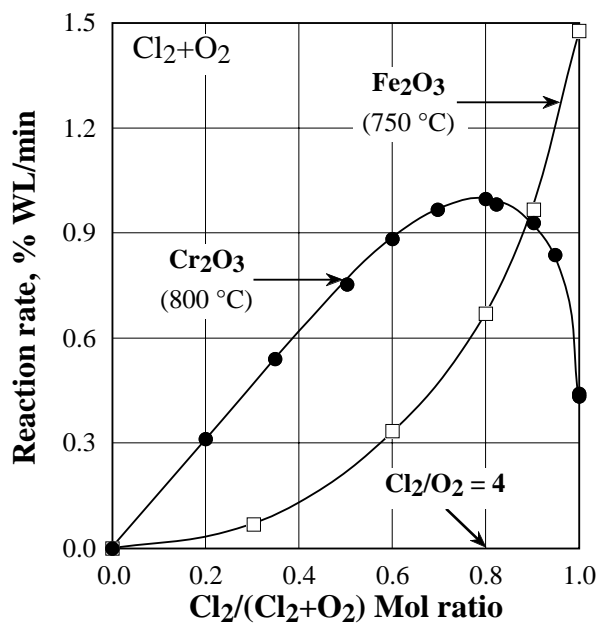


Figure 2 : Effect of Cl<sub>2</sub>/(Cl<sub>2</sub>+O<sub>2</sub>) ratio on the oxychlorination rate of Cr<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>.

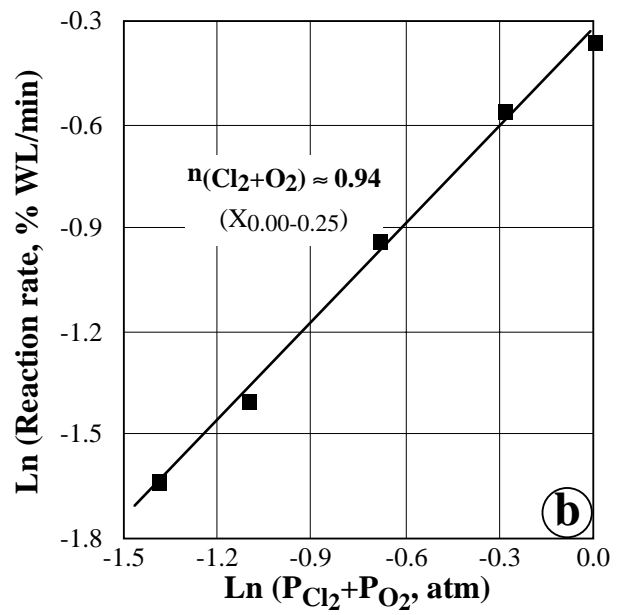
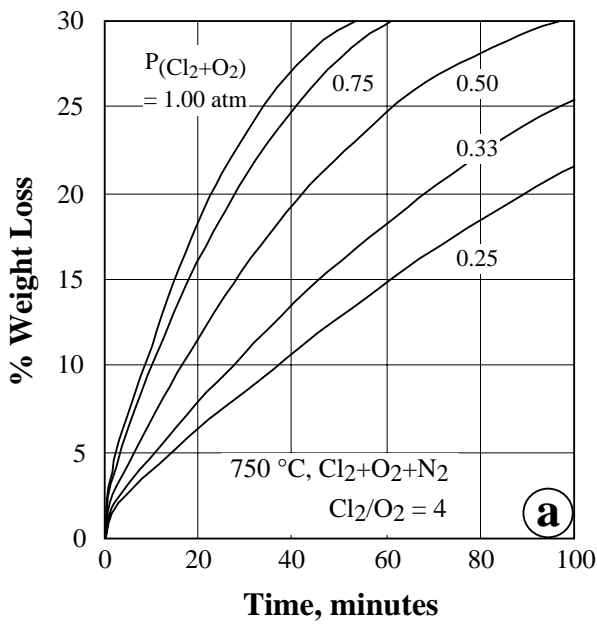


Figure 3 : Isotherms of oxychlorination of chromite at 750 °C using (a) different  $\text{Cl}_2+\text{O}_2$  partial pressures and (b) apparent reaction order with respect to  $\text{Cl}_2+\text{O}_2$ .

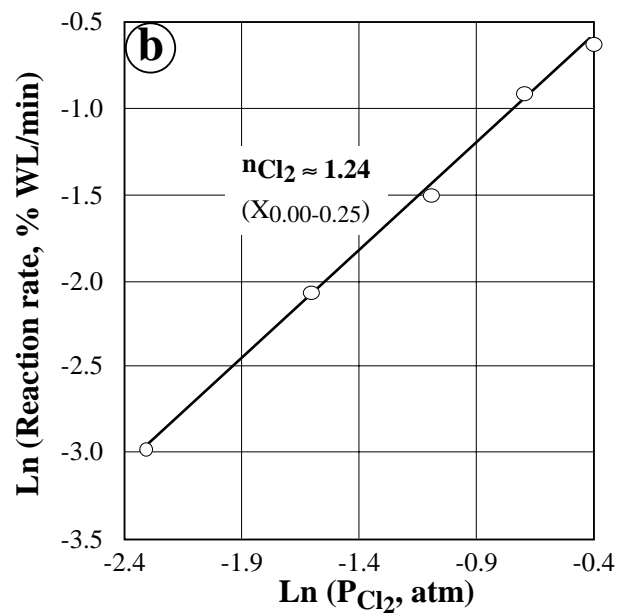
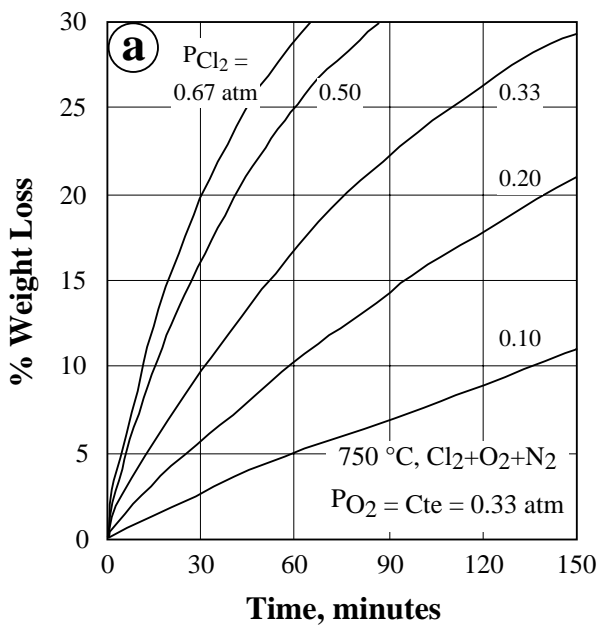


Figure 4 : Isotherms of oxychlorination of chromite at 750 °C using (a) different  $\text{Cl}_2$  partial pressures and (b) apparent reaction order with respect to  $\text{Cl}_2$ .

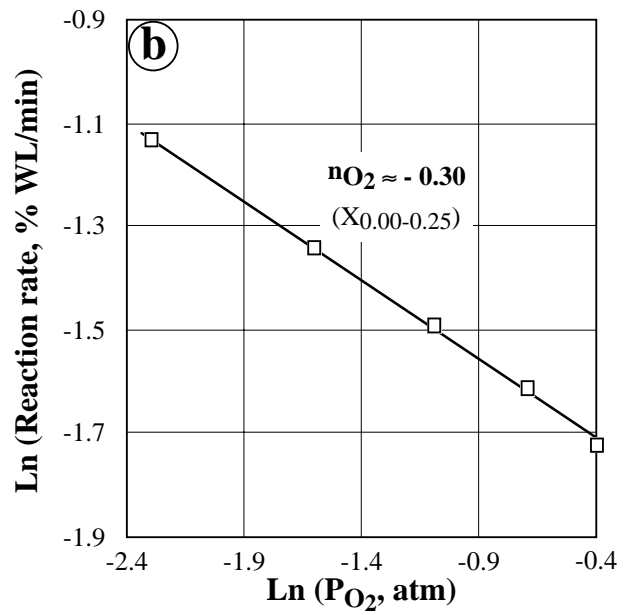
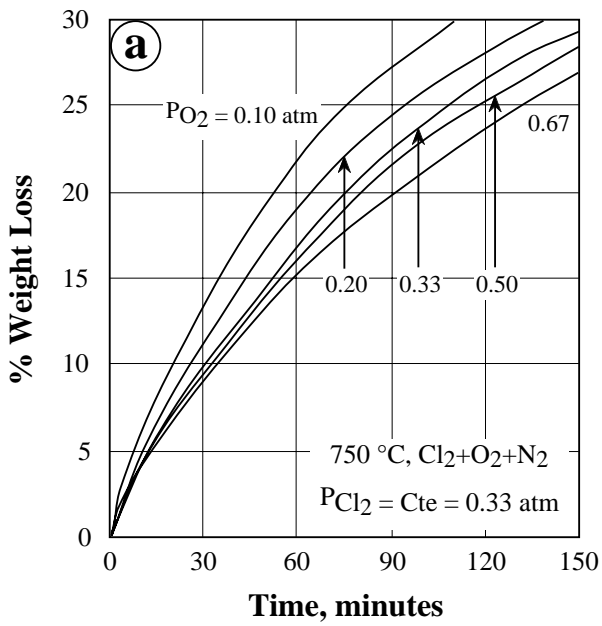


Figure 5 : Isotherms of oxychlorination of chromite at 750 °C using (a) different O<sub>2</sub> partial pressures and (b) apparent reaction order with respect to O<sub>2</sub>.

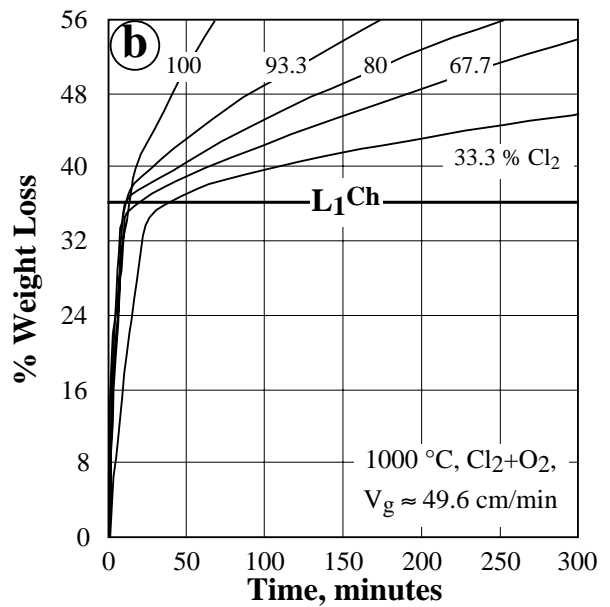
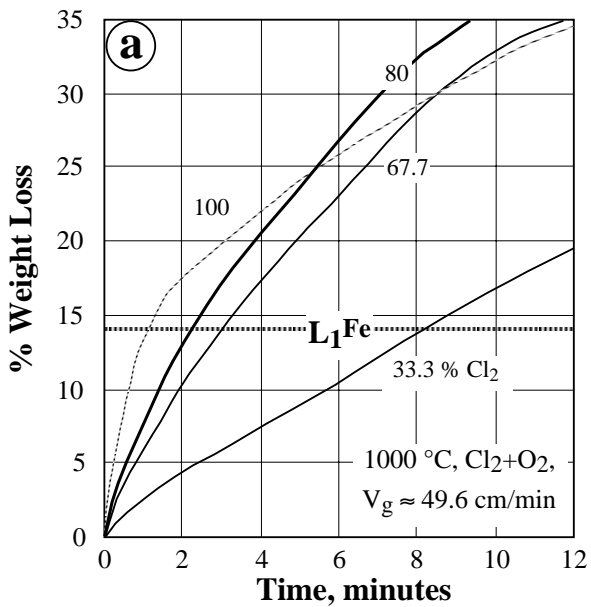


Figure 6 : Isotherms of oxychlorination of chromite at 1000 °C using different chlorine contents for (a)  $X \leq 0.35$  and (b)  $X \leq 0.56$ .



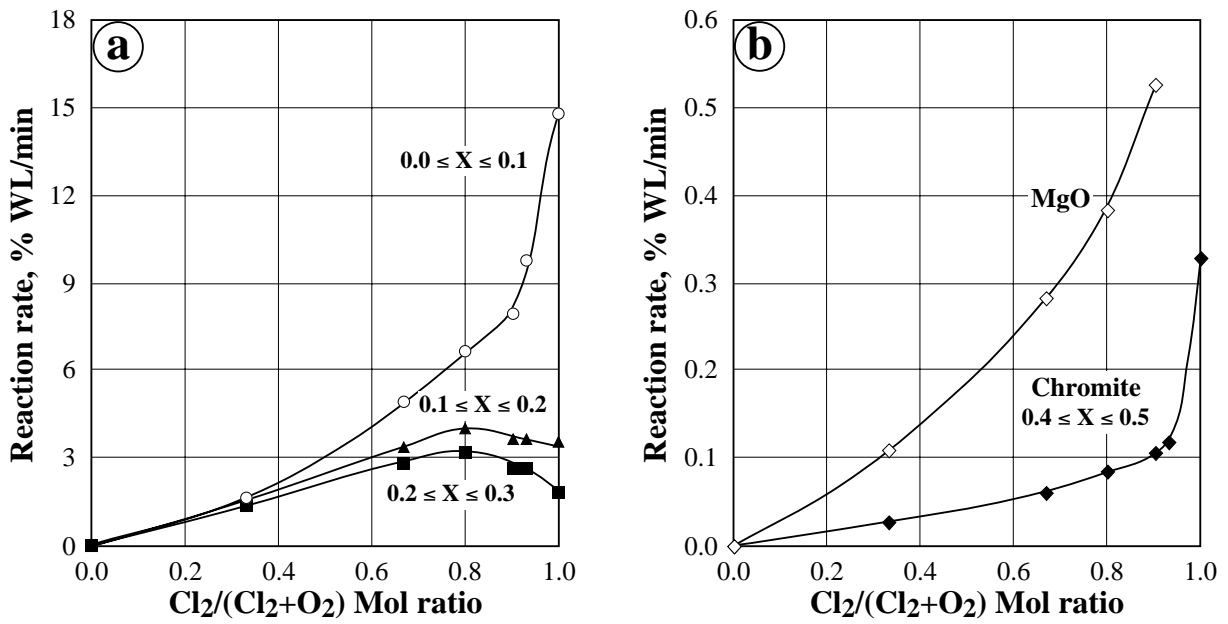


Figure 7 : Evolution of the reaction rates *versus*  $\text{Cl}_2/(\text{Cl}_2+\text{O}_2)$  ratio for the oxychlorination of chromite at (a)  $X \leq 0.3$  and (b) at  $0.4 \leq X \leq 0.5$  compared with that of MgO.

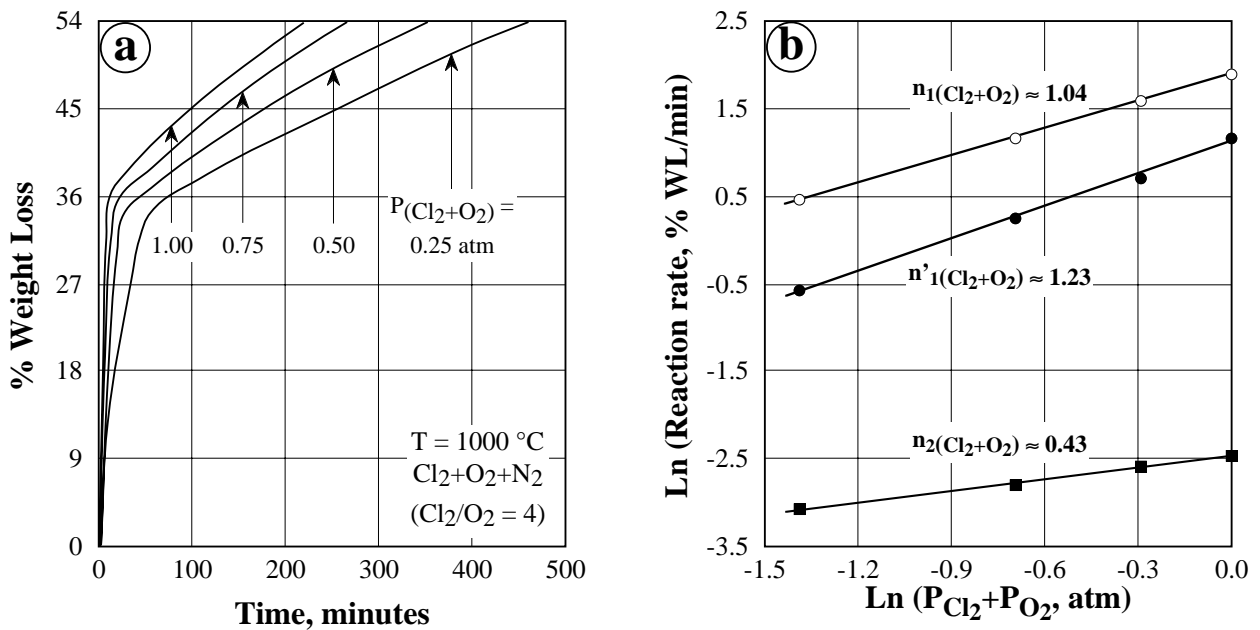


Figure 8 : Isotherms of oxychlorination of chromite at 1000 °C using (a) different  $\text{Cl}_2+\text{O}_2$  partial pressures and (b) apparent reaction orders with respect to  $\text{Cl}_2+\text{O}_2$ .

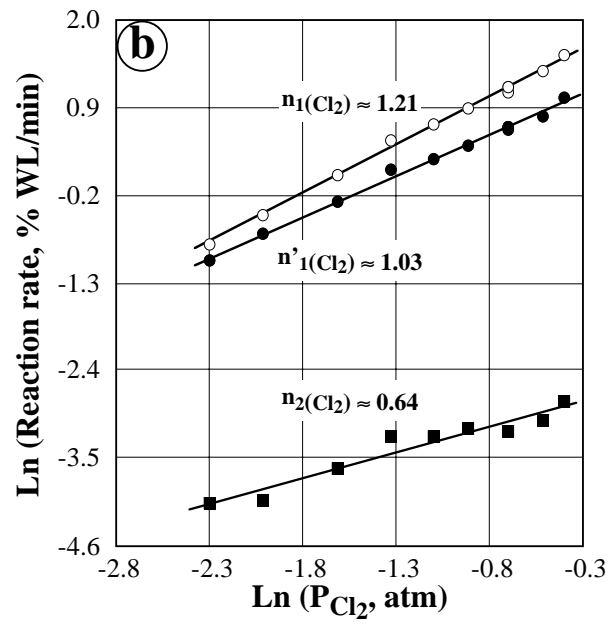
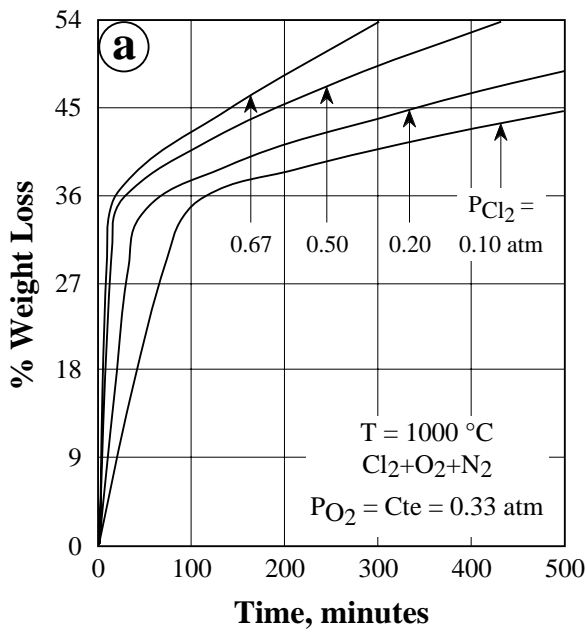


Figure 9 : Isotherms of oxychlorination of chromite at 1000 °C using (a) different Cl<sub>2</sub> partial pressures and (b) apparent reaction orders with respect to Cl<sub>2</sub>.

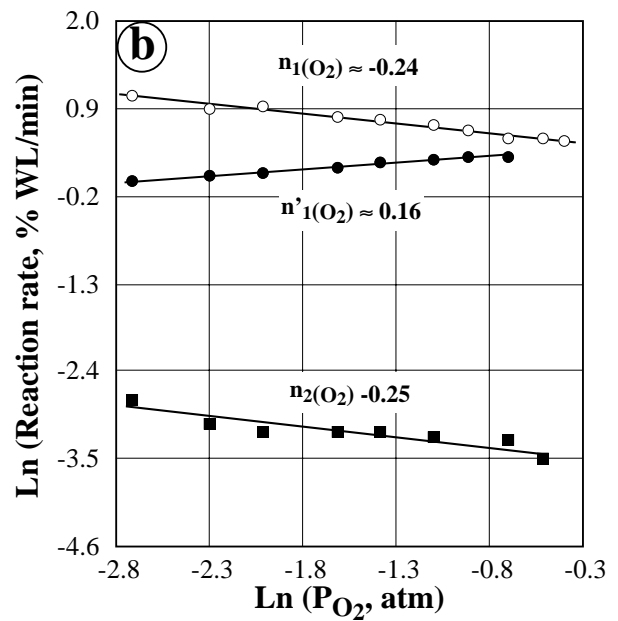
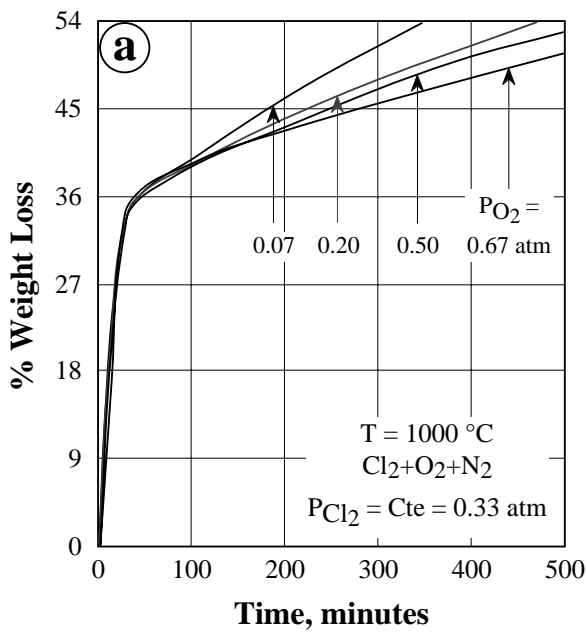


Figure 10 : Isotherms of oxychlorination of chromite at 1000 °C using (a) different O<sub>2</sub> partial pressures and (b) apparent reaction orders with respect to O<sub>2</sub>.

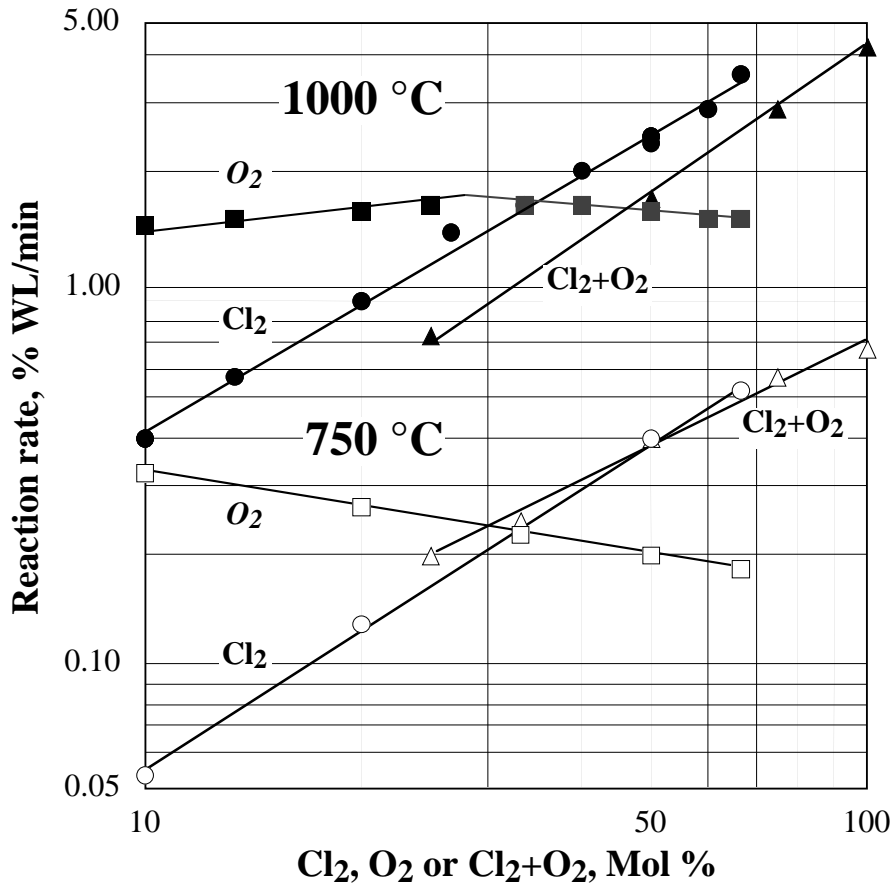


Figure 11 : Effect of gas composition on the reaction rate of chromite oxychlorination at 750 °C and 1000 °C for  $X \leq 0.25$ .

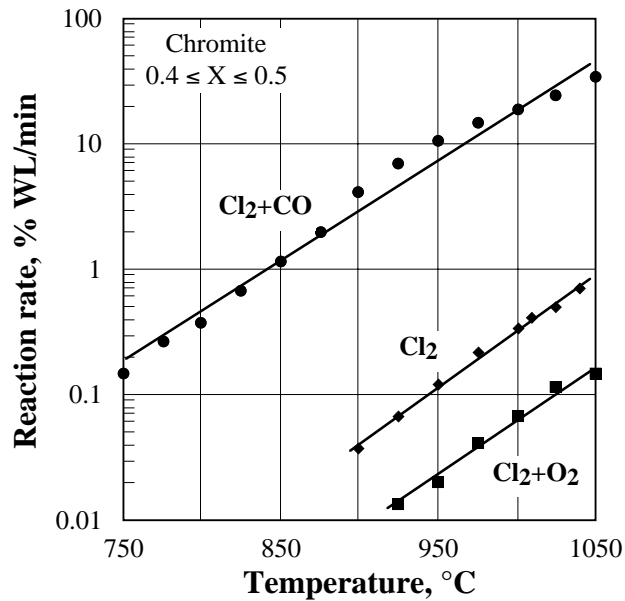


Figure 12 : Comparison of the reaction rates of the chromite with different chlorinating gas mixtures for the reaction extent between 0.4 and 0.5.

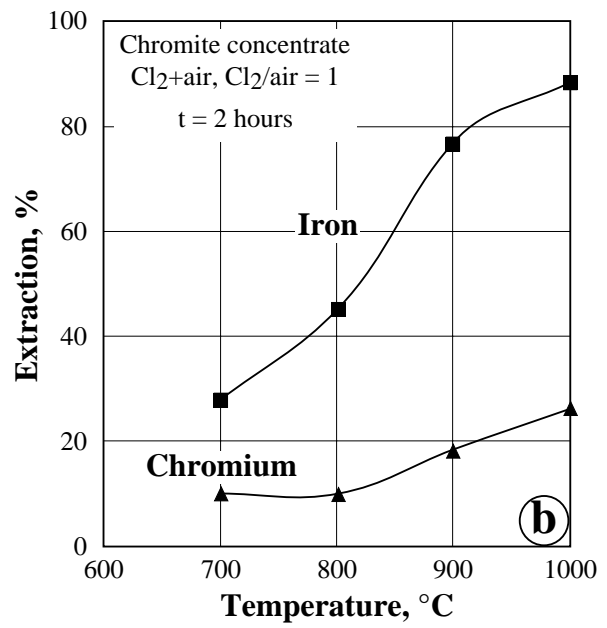
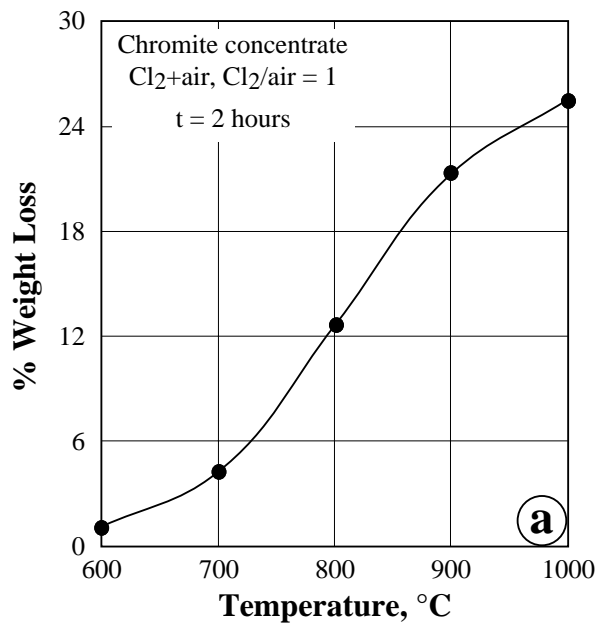


Figure 13 : Evolution of PWL of the sample (a) and extraction extent of Cr and Fe (b) as a function of temperature during oxychlorination of the chromite concentrate for two hours.