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Kinetics of oxychlorination of chromite
Part II. Effect of reactive gases

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Abstract

The effects of Cl_2/O_2 ratio, $P_{(Cl_2+O_2)}$, P_{Cl_2}, and P_{O_2} on the oxychlorination rate of the chromite mineral were determined between 750 and 1000°C using isothermal TGA measurements. The effect of the gases' composition on the oxychlorination rate of chromite were compared with those resulting from the oxychlorination of simple oxides of the chromite (Cr_2O_3, Fe_2O_3 and MgO). The apparent reaction orders with respect to $Cl_2 + O_2$, Cl_2, and 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 as the reaction progressed.

Boat experiments were carried out to oxychlorinate a chromite concentrate between 600 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 (CrO_2Cl_2). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Oxychlorination; Chromite; Reactive gases; Apparent reactor orders

1. Introduction

In Part I [1] of this paper, experimental results concerning the effect of temperature on the oxychlorination of chromite between 600 and 1050°C have been reported. It was observed that the temperature effect changed with the progress of the reaction, the investigated temperature range and to some extent with the Cl_2/O_2 ratio in the oxychlorinating gas mixture.

Reactions of the two main chromite constituents ($FeCr_2O_4$ and $MgCr_2O_4$) with chlorine could be represented by Eqs. (1) and (2) indicating that chromium oxychloride is the bearing chromium product. However, it was observed previously [2] that chromium trichloride ($CrCl_3$) was generated along with 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

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simple constituents of the chromite (Fe, Cr and Mg oxides).

$$\tfrac{2}{7}FeCr_2O_4 + Cl_2 \rightarrow \tfrac{2}{7}FeCl_3 + \tfrac{4}{7}CrO_2Cl_2 \quad (1)$$

$$\tfrac{1}{3}MgCr_2O_4 + Cl_2 \rightarrow \tfrac{1}{3}MgCl_2 + \tfrac{2}{3}CrO_2Cl_2 \quad (2)$$

The oxychlorination of chromium (III) oxide is given by Eq. (3), and, as could be expected, the presence of oxygen is necessary for the formation of chromium oxychloride (CrO_2Cl_2). The chlorination of iron and magnesium oxides producing their respective chlorides (Eqs. (4) and (5)) releases some oxygen and consequently low oxygen partial pressures are necessary to achieve the chlorination of these oxides.

$$\tfrac{1}{2}Cr_2O_3 + Cl_2 + \tfrac{1}{4}O_2 \rightarrow CrO_2Cl_2 \quad (3)$$

$$\tfrac{1}{3}Fe_2O_3 + Cl_2 \rightarrow \tfrac{2}{3}FeCl_3 + \tfrac{1}{2}O_2 \quad (4)$$

$$MgO + Cl_2 \rightarrow MgCl_2 + \tfrac{1}{2}O_2 \quad (5)$$

However, these hypotheses are only a simple theoretical approach. To explain how the composition of the reactive gases ($Cl_2 + O_2$) affects the oxychlorination of chromite, the effects of Cl_2/O_2 ratio, $P_{(Cl_2+O_2)}$, P_{Cl_2} and P_{O_2} on the reaction rate at different temperatures and reaction extents of the chromite oxychlorination were investigated. Results were compared with those obtained previously for Cr_2O_3 [3], MgO [4], and Fe_2O_3 [5] 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 contained in the chromite concentrate. This approach leads to a high chromium-to-iron ratio of the treated chromite and consequently, it will be benefit for the ferro-chromium production.

The materials used and the experimental procedures are those described in Part I [1]. The effects of the above mentioned parameters were studied using the oxychlorination gaseous mixtures with the optimal linear velocity (V_g) equal to 49.6 cm/min. The experimental tests were carried out using TGA measurements under isothermal conditions. Boat experiments were performed to oxychlorinate a chromite concentrate by Cl_2 + air gaseous mixture between 600 and 1000°C. The evolution of Cr/Fe ratio of the treated concentrate was determined by classical chemical analysis.

2. Results and discussion

2.1. TGA studies of the gas composition on the oxychlorination of the chromite mineral

As mentioned previously [1], two kinetics regions were distinguished for the oxychlorination of chromite for 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 reaction extents higher than 0.35 was characterized by a slow reaction rate at temperatures lower than 900°C. For these raisons, the effects of the gas composition on the reaction rates of the chromite with $Cl_2 + O_2$ were studied at 750 and 1000°C.

2.1.1. Oxychlorination of chromite at 750°C

2.1.1.1. Effect of $Cl_2/(Cl_2 + O_2)$ ratio. A series of isothermal tests was conducted with $Cl_2 + O_2$ gas mixtures having chlorine content of 0–100%. As could be expected, no reaction of oxygen with chromite was observed. The isothermal data for the oxychlorination of chromite with $Cl_2 + O_2$ containing 40–100% chlorine and for $X \leq 0.30$ are given in Fig. 1(a). It shows that the time required to reach a given percent weight loss (%WL) of the sample decreases with increase of the chlorine content in the $Cl_2 + O_2$. Fig. 1(b) traces the evolution of the average reaction rate as a function of the $Cl_2/(Cl_2 + O_2)$ molar ratio for $X \leq 0.25$. Clearly, the reaction rate increases as the $Cl_2/(Cl_2 + O_2)$ ratio augments. However, this increase of the reaction rate is less dependent on $Cl_2/(Cl_2 + O_2)$ ratio for reaction extents higher than 0.20 [2]. The dependency of the reaction rate of Cr_2O_3 [3] and Fe_2O_3 [5] oxychlorination on the $Cl_2/(Cl_2 + O_2)$ molar ratio is illustrated in Fig. 2. A maximum reaction rate of Cr_2O_3 oxychlorination was obtained using a Cl_2/O_2 ratio of 4. This ratio satisfies the stoichiometry of reaction [3] for the formation of CrO_2Cl_2. As in the case of chromite oxychlorination, the reaction rate of Fe_2O_3 with $Cl_2 + O_2$ increases with the $Cl_2/(Cl_2 + O_2)$ ratio. These results as well as those obtained for the temperature effect [1] suggest that the overall reaction rate of chromite oxychlorination at low temperatures

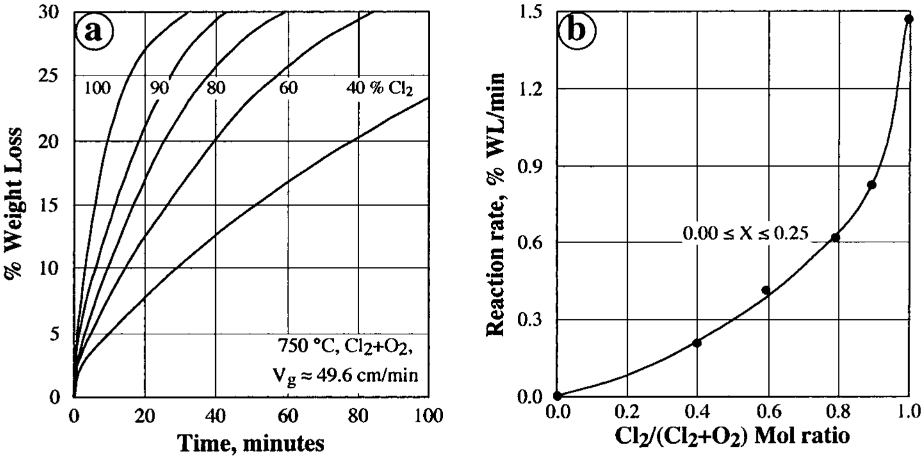


Fig. 1. Isotherms of oxychlorination of chromite at 750°C : (a) using different chlorine contents and (b) effect of Cl_2/O_2 ratio on the reaction rate.

depends essentially on the oxychlori-nation of iron oxides contained in the chromite.

2.1.1.2. Effect of $Cl_2 + O_2$ partial pressure. Experiments to determine the effect of $Cl_2 + O_2$ partial pressure on the reaction rate of chromite oxychlorination were carried out by using a $Cl_2 + O_2 + N_2$ gas mixture having a Cl_2/O_2 molar ratio constant and equal to 4. The partial pressure of $Cl_2 + O_2$ was varied from 0.25 to 1.00 atm and the results are given in Fig. 3(a) as evolution of the %WL versus time. Fig. 3(b) gives the evolution of the reaction rate as function of ln $Cl_2 + O_2$ partial pressure for $X \leq 0.25$. Fig. 3(b) indicates that the apparent reaction order of chromite, with respect to $Cl_2 + O_2$, is about 0.94.

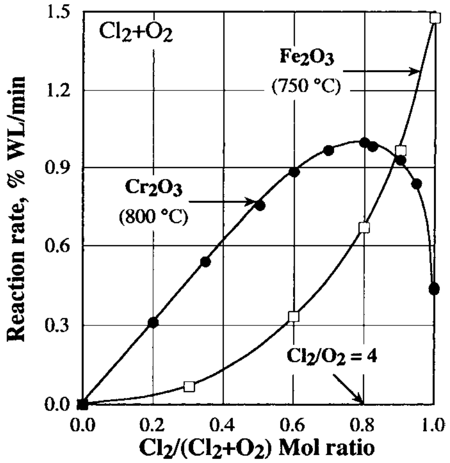


Fig. 2. Effect of $Cl_2/(Cl_2 + O_2)$ ratio on the oxychlorination rate of Cr_2O_3 and Fe_2O_3.

2.1.1.3. Effect of Cl_2 and O_2 partial pressures. Two series of tests were carried out using $Cl_2 + O_2 + N_2$ with a V_g equal to 49.6 cm/min. The first one 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.

Fig. 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 $X \leq 0.25$. Similarly, Fig. 5(a) and (b) describe the effect of the oxygen partial pressure on the oxychlorination. As shown by Fig. 5(b) the oxygen had a negative effect on the oxychlorination reaction rater of chromite, since the apparent reaction order is about −30.

The effects of $Cl_2 + O_2$, Cl_2 and O_2 on the reaction rates of Cr_2O_3, Fe_2O_3, and chromite $(0.00 \leq X \leq 0.25)$ with the $Cl_2 + O_2$ gas mixtures are summarized

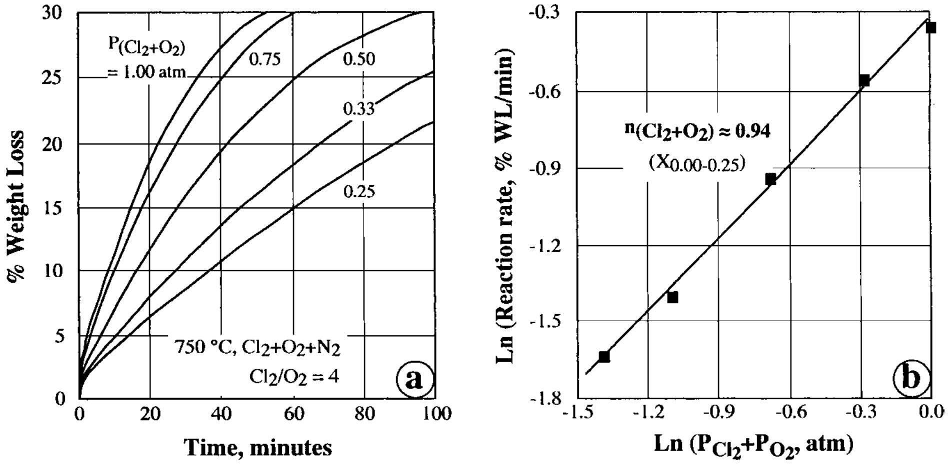


Fig. 3. Isotherms of oxychlorination of chromite at 750°C using (a) different $Cl_2 + O_2$ partial pressures and (b) apparent reaction order with respect to $Cl_2 + O_2$.

in Table 1. The comparison of these data indicates that the chromite oxychlorination is characterized by the values of $^{n}(Cl_2 + O_2)$, $^{n}Cl_2$, and $^{n}O_2$, that are near to those of Fe_2O_3 oxychlorination.

2.1.2. Oxychlorination of chromite at 1000 °C

2.1.2.1. Effect of $Cl_2/(Cl_2 + O_2)$ ratio. Tests to determine this effect were carried out at different chlorine contents in the oxychlorinating gas mixture. Fig. 6(a) traces the experimental data obtained using gas mixture having a chlorine content of 33.3–100% and for reaction extents lower or equal to 0.35. The reaction rate increases as the chlorine content in the gas mixture augments. However the time required to reach 35% WL of sample with 100% Cl_2, is higher than that obtained using a gas mixture containing 80% Cl_2. This is probably due to lack of oxygen for the formation of chromium oxychloride. The change of the slope of the percent weight loss curves at about 15% seems to correspond to the chlorination of iron oxides ($L_1{}^{Fe}$ of

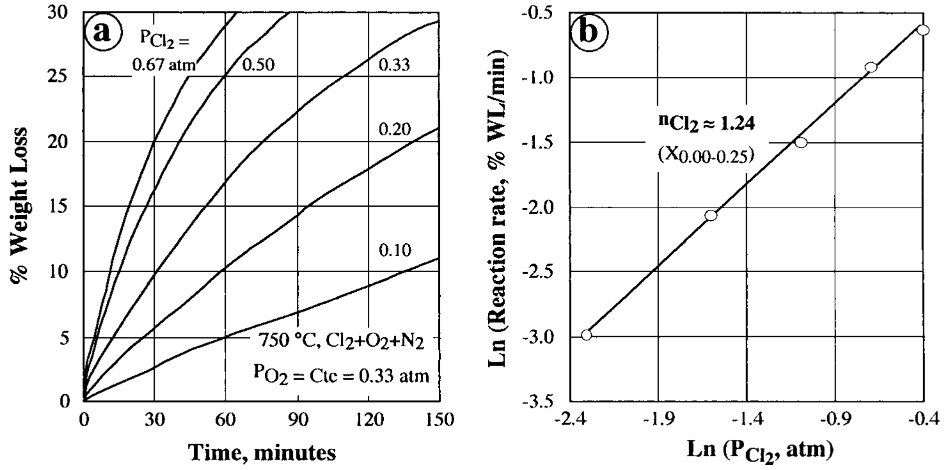


Fig. 4. Isotherms of oxychlorination of chromite at 750°C using (a) different Cl_2 partial pressures and (b) apparent reaction order with respect to Cl_2.

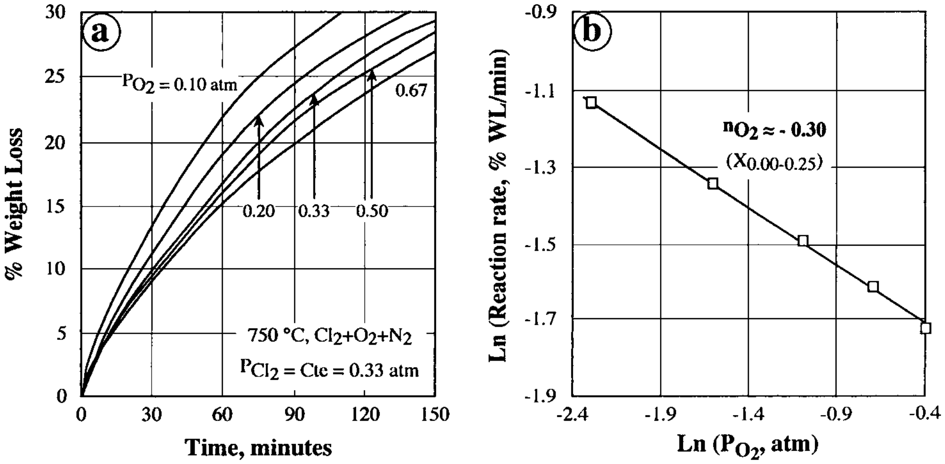


Fig. 5. Isotherms of oxychlorination of chromite at 750°C using (a) different O_2 partial pressures and (b) apparent reaction order with respect to O_2.

Table 1
Comparison of reaction orders with respect to reactive gases of different solids' oxychlorination

Solids	T (°C)	$^{n}(Cl_2 + O_2)$	$^{n}Cl_2$	$^{n}O_2$
Cr_2O_3 [3]	800	1.29	1.08	0.23
Fe_2O_3 [5]	750	0.71	1.44	−0.61
Chromite ($0.00 \leq X \leq 0.25$)	750	0.94	1.24	−0.30

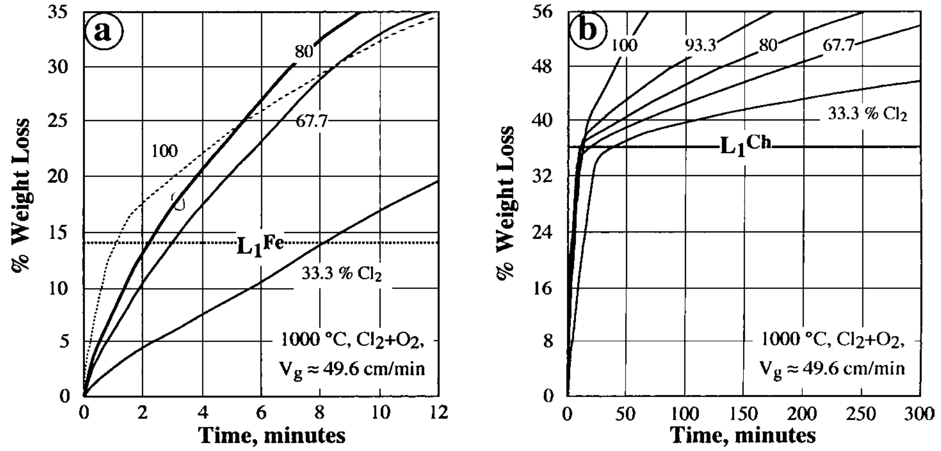


Fig. 6. Isotherms of oxychlorination of chromite at 1000°C using different chlorine contents for (a) $X \leq 0.35$ and (b) $X \leq 0.56$.

Fig. 6(a)) where L_1^{Fe} is the calculated %WL for the iron oxides' extraction. The oxychlorination results of chromite at different chlorine contents and for sample weight losses up to 56% are given in Fig. 6(b). The drop of the reaction rate beyond 35% WL is obvious regardless of 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% WL corresponds essentially to the reaction of $Mg(Cr, Al)_2O_4$ [1] with $Cl_2 + O_2$.

The evolution of the reaction rate versus $Cl_2/(Cl_2 + O_2)$ ratio was calculated for different reaction extents. Fig. 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 $Cl_2/(Cl_2 + O_2)$ ratio. While for $0.1 \leq X \leq 0.3$, the reaction rate passes by a maximum corresponding to $Cl_2/(Cl_2 + O_2)$ ratio of about 0.8. This observation reminds the reaction of chromium (III) oxide oxychlorination according to Fig. 2 and Eq. (3). Fig. 7(b) illustrates results for X comprised between 0.4 and 0.5. The reaction rate increases with chlorine content in the oxychlorinating gas. Comparable behavior was acquired for the oxychlorination of MgO.

2.1.2.2. Effect of $Cl_2 + O_2$ partial pressure. The experimental procedure to study the effect of $Cl_2 + O_2$ partial pressure on the oxychlorination of chromite at 1000°C was the same as that applied at 750°C. Results obtained are given in Fig. 8(a) as evolution of percent weight loss versus time. As in the previous case, the reaction rate droped after 35% WL whatever the $Cl_2 + O_2$ partial pressure used. A mathematical treatment of the experimental data of Fig. 8(a) was performed to relate the evolution of the reaction rate of chromite oxychlorination with gas mixtures having different partial pressures of $Cl_2 + O_2$ for various reaction extents. Results are represented in Fig. 8(b) in natural logarithm scale. The apparent reaction orders with respect to $Cl_2 + O_2$ 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 $^{n_1}(Cl_2 + O_2)$, $^{n'_1}(Cl_2 + O_2)$, and $^{n_2}(Cl_2 + O_2)$, respectively. The beginning of the chromite oxychlorination is characterized by a reaction order of 1.04 that increases to 1.23 for X equal to 0.2–0.3. For reaction extent ≥ 0.4, the reaction order of chromite is 0.43 as shown by Fig. 8(b).

2.1.2.3. Effect of Cl_2 and O_2 partial pressures. Tests to determine the effect of chlorine partial pressure on the oxychlorination rate of chromite were performed with $Cl_2 + O_2 + N_2$ at constant oxygen partial pressure (0.33 atm) with a constant gas velocity of 49.6 cm/min. Plots of obtained experimental data are given in Fig. 9(a) for 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

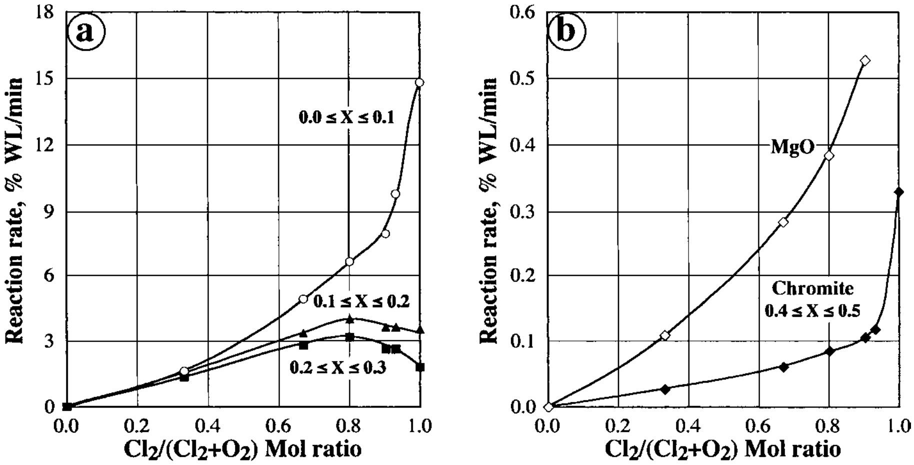


Fig. 7. Evolution of the reaction rates versus $Cl_2/(Cl_2 + O_2)$ ratio for the oxychlorination of chromite at (a) $X \leq 0.3$ and (b) at $0.4 \leq X \leq 0.5$ compared with that of MgO.

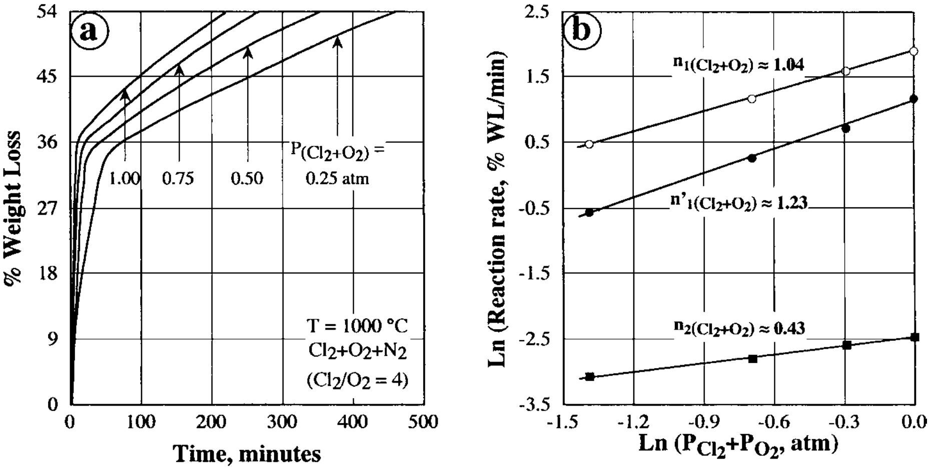


Fig. 8. Isotherms of oxychlorination of chromite at 1000°C using (a) different $Cl_2 + O_2$ partial pressures and (b) apparent reaction orders with respect to $Cl_2 + O_2$.

to Cl_2 for different values of X are deduced from the data of Fig. 9(b).

Effect of oxygen on the reaction rate of chromite oxychlorination was studied at constant partial pressure of chlorine (0.33 atm) while the partial pressure of oxygen in the $Cl_2 + O_2 + N_2$ was varied from about 0.07 to 0.67 atm. Typical plots representing the evolution of the percent weight loss versus time for several isotherms are given in Fig. 10(a). These plots show that the oxychlorination of chromite is slightly dependent on the partial pressure of oxygen in the investigated range. The apparent reaction orders with respect to oxygen (Fig. 10(b)) are ${}^{n_1}(O_2) \approx -0.24$, ${}^{n_1'}(O_2) \approx 0.16$, and ${}^{n_2}(O_2) \approx -0.25$ 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.

The apparent reaction orders with respect to $Cl_2 + O_2$, Cl_2, and O_2 for the reactions of chromite and oxides of chromium, iron, and magnesium with

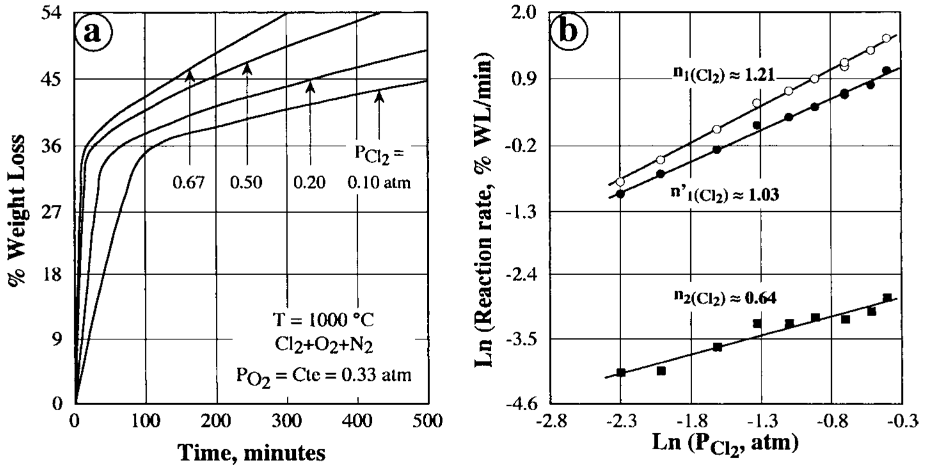


Fig. 9. Isotherms of oxychlorination of chromite at 1000°C using (a) different Cl_2 partial pressures and (b) apparent reaction orders with respect to Cl_2.

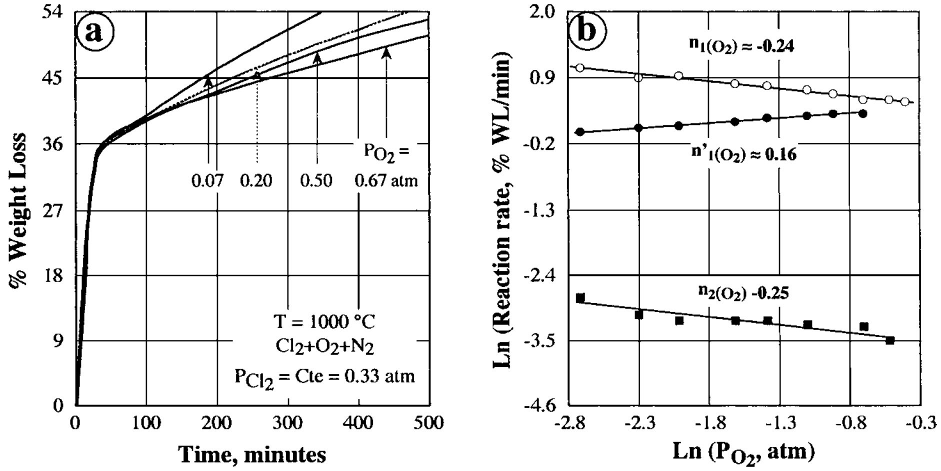


Fig. 10. Isotherms of oxychlorination of chromite at 1000°C using (a) different O_2 partial pressures and (b) apparent reaction orders with respect to O_2.

$Cl_2 + O_2$ are summarized in Table 2. Although the temperatures for the determination of the apparent reaction orders of simple oxides are lower than that of the chromite one, it seems that values of the apparent reaction orders is slightly different as temperature increases. For example, the apparent reaction orders for the oxychlorination of Fe_2O_3 at 750 and 950°C are almost equivalent (see Tables 1 and 2) and the effect of temperature, for Fe_2O_3 oxychlorination, remained constant up to 1025°C [1].

The following observations could be deduced from the data of Table 2:

1. Apparent reaction order with respect to 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 Fe_2O_3 oxychlorination. Thus, one may suggest that the initial stage of chromite oxychlorination is affected by the oxychlorination reactions of iron oxides,
2. Oxygen has a positive effect on the chromite oxychlorination for 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 $Cl_2 + O_2$ may affect the overall oxychlorination reaction of chromite,
3. Chromite oxychlorination is slightly dependent on the partial pressures of reactive gases for the $X \geq 0.4$. The values of the apparent reaction orders are close to those obtained for the MgO oxychlorination.

Table 2
Comparison of reaction orders with respect to reactive gases of different solids' oxychlorination

Solids	T (°C)	$^n(Cl_2 + O_2)$	$^nCl_2$	$^nO_2$
Cr_2O_3 [3]	800	1.29	1.08	0.23
Fe_2O_3 [5]	950	0.70	1.39	−0.62
MgO [4]	950	0.65	0.98	−0.37
Chromite				
$0.0 \leq X \leq 0.1$	1000	1.04	1.21	−0.24
$0.2 \leq X \leq 0.3$	1000	1.23	1.03	0.16
$0.4 \leq X \leq 0.5$	1000	0.43	0.64	−0.25

The values of the reaction orders, with respect to different reactive gases, for the oxychlorination of chromite and those of its simple oxides suggest that the overall reaction rate of chromite be controlled by the slowest step during the oxychlorination of the chromite constituents.

The effect of the gas composition on the oxychlorination rate of iron chromite (i.e., $X \leq 0.25$) at 750 and 1000°C are compared in Fig. 11. This figure gives some advisability data for the partial pressures range of the reactive gases and temperature in order to obtain

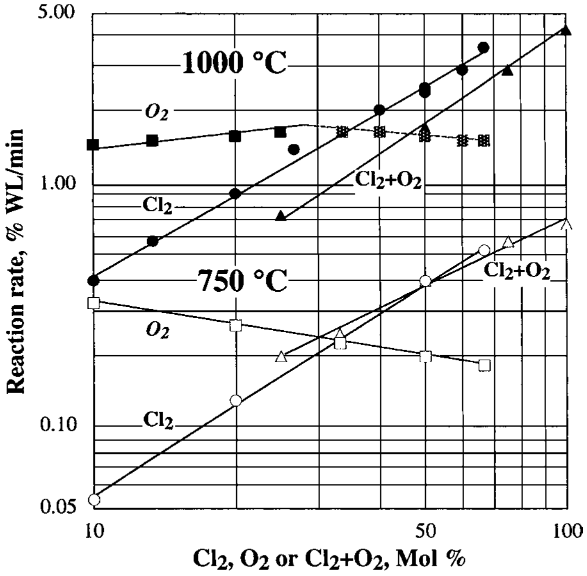


Fig. 11. Effect of gas composition on the reaction rate of chromite oxychlorination at 750 and 1000°C for $X \leq 0.25$.

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.

The oxychlorination rate of the chromite with $Cl_2 + O_2$ for $X \geq 0.35$ is slow regardless the partial pressure of the reactive gases and the reaction temperature [1] within the investigated range. Consequently, the recovery of chromium compounds from magnesium chromite ($MgCr_2O_4$) is difficult through oxychlorination at temperatures of 1000°C. However, full reaction of chromite can be achieved, with relatively high reaction rate, by its chlorination in presence of a reducing atmosphere such as carbon monoxide [6]. A comparison of the reaction rates of the chromite reaction with $Cl_2 + O_2$, Cl_2, and $Cl_2 + CO$ $(0.4 \leq X \leq 0.5)$ for X comprised between 0.4 and 0.5 is given in Fig. 12. The reaction rate of the magnesium chromite chlorination with $Cl_2 + CO$ is about two order of magnitudes with respect to that of chromite chlorination with $Cl_2 + O_2$ and/or Cl_2. For example, at 950°C, the reaction rate of the chromite carbochlorination is about 500 and 90 times that of the oxychlorination and chlorination, respectively. One may underline that the carbochlorination of chromite at about 1000°C will lead to the full removal of the chromite elements (Cr, Fe, Mg, Al) 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 [1,2]. This selectivity could be used for the selective removal of iron from a chromite concentrate. The experimental results are represented in the following section.

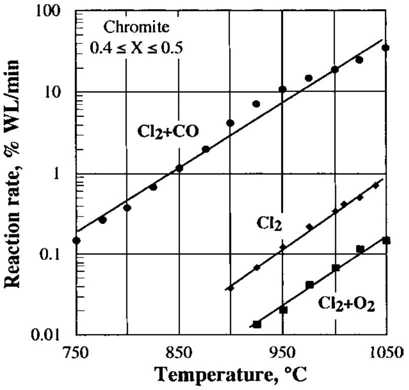


Fig. 12. Comparison of the reaction rates of the chromite with different chlorinating gas mixtures for the reaction extent between 0.4 and 0.5.

2.2. Oxychlorination of the chromite concentrate using boat experiments

The above mentioned results, concerning the oxychlorination of chromite, indicate that only iron chromite ($FeCr_2O_4$) could react with the $Cl_2 + O_2$ at a relatively fast reaction rate for temperature lower or equal to 1000°C. To investigate the possibility of selective 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 and 1000°C.

The chemical and microprobe analyses of the used chromite concentrate indicate the presence of 80% chromite and 20% gangue (Table 3). Based on the microprobe analysis data [6], the general formula of the chromite mineral could be the following:

$$(Fe_{0.30}{}^{2+}, Mg_{0.70})(Cr_{1.56}, Al_{0.37}, Fe_{0.07}{}^{3+})O_4$$

This solid can also be formulated as: 30.9% $FeCr_2O_4$, 51.0% $MgCr_2O_4$, 13.7% $MgAl_2O_4$ and 4.4% Fe_3O_4. One may underline that these spinels have the same

Table 3
Composition of chromite concentrate (wt.%) [6]

Oxide	Chemical analyses (average)	Microprobe	
		Chromite	Gangue
Cr_2O_3	47.7	59.4	0.7
FeO	13.4	13.9	3.7
MgO	17.8	14.2	42.0
Al_2O_3	8.8	9.5	1.4
SiO_2	7.1	0.1	39.7

Table 4
Evolution of Cr/Fe ratio of the oxychlorination residues of chromite concentrate as a function of temperature

T (°C)	%WL	Cr (wt.%)	Fe (wt.%)	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

crystalline structure and lattice parameters making their identification, by XRD, almost impossible.

A gas mixture composed of Cl_2 + air (Cl_2/air = 1) was used for the oxychlorination of chromite for a reaction time of 2 h. The exhausted gases were successively cooled to room temperature and to −35°C so as to condense the generated metal chlorides.

Fig. 13(a) traces the evolution of the percent weight loss of the sample versus temperature. As could be expected, the %WL increases as the temperature augments. About 25% 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 Fig. 13(b) and Table 4. The extraction rate of iron is higher than that of chromium for all the explored temperature range. About 90 and 25% for iron and chromium, respectively, are extracted at 1000°C. As shown by Table 4, 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 did not exceed 15%.

Residues and condensates were analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Fig. 14 shows the morphological evolution of chromite as the oxychlorination reaction extent progress from 0.4 to 0.88. One may underline that the major change of the chromite concentrate is the chlorination of iron and chromium contained in the chromite itself as shown in Fig. 14(a)–(c). As mentioned previously [1], it is difficult to trace the evolution of the treatments' residues by XRD analysis due to very slight change of the crystal lattice's dimensions during the oxychlorination of the spinels.

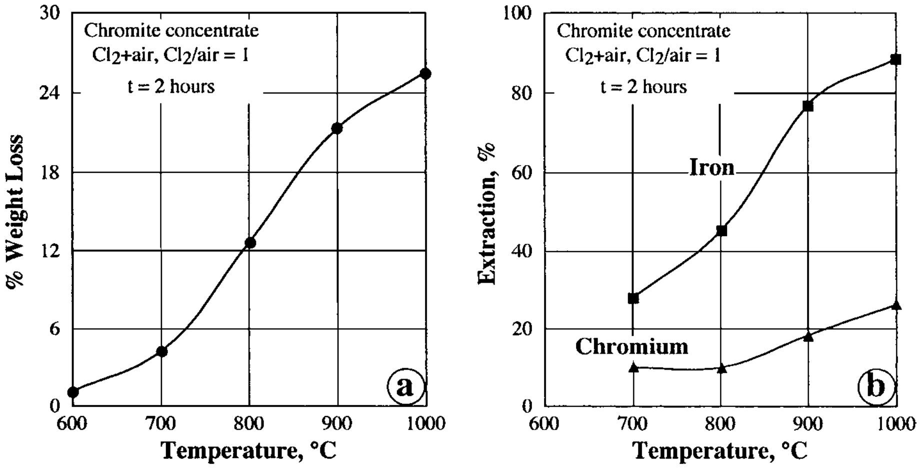
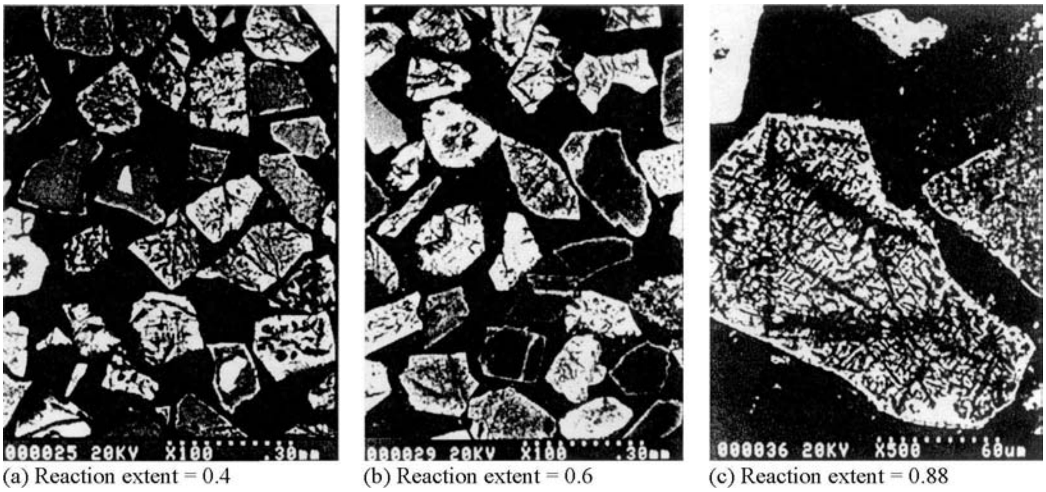


Fig. 13. Evolution of %WL of the sample (a) and extraction extent of Cr and Fe (b), as a function of temperature, during oxychlorination of the chromite concentrate for 2 h.



(a) Reaction extent = 0.4 (b) Reaction extent = 0.6 (c) Reaction extent = 0.88

Fig. 14. Morphological aspects of the chromite oxychlorination for reaction extent equal to 0.4 (a), 0.6 (b) and 0.88 (c).

Solid condensates obtained by cooling the outlet gases 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 experimental conditions. Although a part of chromium contained in the concentrate was removed (refer to Fig. 13(b)), it was not detected in the solid condensate obtained by cooling the outlet gases to room temperature. However, cooling these gases 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 CrO_2Cl_2 [3,8]. The absence of chromium in the solid condensates obtained at 25°C is explained by the fact that melting and boiling points of CrO_2Cl_2 are −96.5 and 117°C [7], respectively.

These results suggest that it is possible to use the oxychlorination of chromite concentrate to increase its Cr/Fe ratio and to recover the extracted chromium as chromium oxychloride.

3. Conclusions

Oxychlorination of a chromite mineral at 750°C by $Cl_2 + O_2 + N_2$ lead, essentially, to the selective removal of iron chromite ($FeCr_2O_4$). The reaction rate augments with the increase of Cl_2/O_2 ratio in the chlorinating gas mixture. The apparent reaction orders with respect to $Cl_2 + O_2$, Cl_2, and 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 of the composition of the oxychlorinating gas mixtures in the studied range. The first stage corresponds to the oxychlorination of iron chromite and second one to the reaction of magnesium chromite ($MgCr_2O_4$) with the oxychlorinating gas mixture.

At 1000°C and for a reaction extent ≤ 0.3, results of the effect of variation of the composition of the chlorinating gas mixture (Cl_2/O_2 ratio, $P_{(Cl_2+O_2)}$, P_{Cl_2}, and P_{O_2}), suggest that the oxychlorination of iron and chromium oxides contained in $FeCr_2O_4$, affects successively the overall reaction of chromite.

The apparent reaction orders with respect to $Cl_2 + O_2$, Cl_2, and 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 slightly dependent on the composition of the reactive gases. In addition, the similarity of the kinetics parameters between $MgCr_2O_4$ and MgO oxychlorination implies that the oxychlorination process of the chromite is slightly affected by the rate of MgO reaction with $Cl_2 + O_2$.

Oxychlorination of poor chromite concentrates and/or ores at moderate temperatures could be used for their upgrading. Iron is advantageously removed selectively while the chromium had reacted partially and it was recovered as CrO_2Cl_2.

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