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Kinetics of Oxychlorination of Magnesium Oxide

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The kinetics of oxychlorination of MgO by Cl₂+O₂ were studied in the temperature range of 850 °C to 1025 °C, using thermogravimetric analysis. The effects of Cl₂/O₂ ratio, gas velocity, temperature and partial pressure of reactive gases on the reaction rate were investigated. The oxychlorination process was characterized by an apparent activation energy of about 214 kJ/mol. The reaction orders with respect to O₂, Cl₂ and Cl₂+O₂ at 950 °C were about -0.37, 0.98, and 0.65, respectively.

Data concerning oxychlorination of MgO, Cr₂O₃ and MgCr₂O₄ contained in chromite were compared. Effectiveness of using oxychlorination to extract iron oxides contained in magnesia was demonstrated.

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I. INTRODUCTION

Magnesium is a major element of the chromite ores. It is present in the spinel structure of chromite having the general formula $(\text{Fe}^{2+}, \text{Mg})(\text{Cr}, \text{Al}, \text{Fe}^{3+})_2\text{O}_4$ and also in the gangue of chromite concentrates that is essentially composed of magnesium silicates such as olivine and serpentine.^[1] Recently, chlorination was studied as a potential method to improve the quality of poor chromite concentrates and for the recovery of specific elements (Cr, Fe, ...) from chromite concentrates^[1-3]. The oxychlorination of chromite concentrates by Cl_2+O_2 at about 900 °C allowed almost full extraction of iron and partial recovery of chromium as chromium oxychloride (CrO_2Cl_2). It was found^[4] that the kinetics parameters of the chromite oxychlorination such as activation energies and reaction orders changed with the reaction extents.

Magnesium metal is produced mainly either by the electrolysis of purified MgCl_2 from natural brine or by silicothermy. The use of light weight alloys of magnesium by the transport industry allows the production of lighter weight vehicles and consequently reduces the fuel consumption and CO_2 emissions^[5]. Moreover, magnesium oxide is employed in some applications, such as rubber processing, pharmaceuticals, and electrical insulator uses, which require a high-purity MgO ^[6]. The common impurities contained in MgO are Fe, Si, Ca ... oxides.

For these reasons, kinetic studies of the reactions of MgO , Cr_2O_3 , Fe_2O_3 with Cl_2+O_2 were undertaken. This paper focused on the oxychlorination kinetics of magnesium oxide in isothermal conditions using thermogravimetric analysis 'TGA'.

No studies concerning the oxychlorination of magnesium oxide were found in the literature. Most of investigations were devoted to the thermodynamical and kinetics aspects of the reactions of MgO with Cl_2 , Cl_2+C , HCl , and $\text{HCl}+\text{C}$ and they were summarized in Reference [7].

II. MATERIALS AND EXPERIMENTAL PROCEDURE

The sample used in this study was MgO powder having a purity of 98 pct and supplied by PROLABO (Paris, France). Results of Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD) analyses of the magnesium oxide sample are showed in Figure 1. The main identified phase was MgO .

The TGA tests for the oxychlorination of MgO were performed using 40 mg of sample in a vertical experimental set-up schematized previously^[7]. Its main unit was a CAHN 1000 microbalance having a sensitivity of 10 μg . The oxychlorination gas mixture composed of Cl_2+O_2 was purified through H_2SO_4 and CaCl_2 columns before its introduction in the reactor. The sample was homogeneously distributed in the quartz crucible having a section of about 0.5 cm^2 . This crucible was hooked to the balance using quartz rods. The sample was preheated in nitrogen atmosphere up to the desired temperature before the introduction of the chlorinating gas mixture. Exhaust gases were purified from chlorine excess by NaOH solution before their release to the atmosphere.

III. RESULTS

A. Effect of $Cl_2/(Cl_2+O_2)$ ratio on the oxychlorination of MgO.

The chlorination of MgO by Cl_2 can be represented by Eq. [1]. The melting and boiling points of produced magnesium chloride are 714 °C and 1412 °C, respectively^[8]. As the TGA technique was used to measure the reaction rate, it was mandatory to insure that the rate of $MgCl_2$ volatilization was higher than that of its formation. One possible way to decrease the reaction rate of MgO with chlorine is to increase the partial pressure of oxygen in the system. Thus, a series of experiments was performed at 950 °C, using a Cl_2+O_2 gas mixture having a molar ratio of $Cl_2/(Cl_2+O_2)$ varying from 0.33 to 1.00. Figure 2 shows the evolution of the percentage weight loss (pct WL) of magnesium oxide versus time during its oxychlorination using the conditions mentioned above. Only weight losses were observed when using gas mixtures containing less than 90 pct of Cl_2 . A weight gain followed by a weight loss was recorded when the chlorine content in the gas mixture was higher than 90 pct. This last result indicates that the volatilization rate of magnesium chloride was lower than that of MgO chlorination and consequently the overall reaction rate was probably controlled by the $MgCl_2$ volatilization rate. For this reason, the kinetics parameters of MgO oxychlorination were studied using the Cl_2+O_2 gas mixtures having a chlorine content lower or equal to 80 pct. In these conditions the observed weight loss was a direct measure of the extent of the overall oxychlorination reaction.



B. Effect of gas flow rate

In order to determine the intrinsic parameters of the gas-solid reactions, it was necessary to minimize the effect of external mass transfer phenomena^[9]. This can be achieved by using a high gas velocity of reactive gases that don't affect the reaction rate. To determine the optimum gas velocity on the oxychlorination rate of MgO, isothermal tests were conducted at 950 °C, using gas mixtures having a linear velocity ' V_g ' ranging from 12 to 62 cm/min. Figure 3 gives the evolution of the oxychlorination rate as a function of the gas velocity. The reaction rate increases with the gas velocity up to $V_g \approx 40$ cm/min. Beyond this value, the rate of oxychlorination was independent of the gas velocity. Therefore, the gas velocity was kept constant and equal to 50 cm/min to study the effect of the other parameters on the oxychlorination rate of MgO.

C. Effect of temperature

The temperature effect on MgO oxychlorination was studied between 850 °C and 1025 °C, using isothermal conditions. An oxychlorinating gas mixture of Cl_2+O_2 having a molar ratio $Cl_2/O_2 = 4$ was used. Figure 4 gives the evolution of pct WL as a function of time for different temperatures. At 850 °C, more than 24 hours were required to reach a reaction extent X^* of about 0.8, while the same reaction extent was achieved at 1025 °C for a reaction time of about 1 hour.

* $X = \text{weight of the reacted fraction} / \text{initial weight}$

The data of Figure 4 were used to determine the effect of temperature on the reaction rate for a reaction extent between 0.05 and 0.40. Figure 5 gives the results in an Arrhenius plot. The apparent activation energy 'E_a' of MgO oxychlorination was about 214 kJ/mol. On the other hand, it was observed that the value of the apparent activation energy remained almost constant for reaction extents equal to or lower than 0.70. Such a high value suggests that the overall rate of MgO oxychlorination could be controlled by the rate of the chemical reaction.

Different mathematical equations^[9, 10] were tested to fit the experimental data obtained at different temperatures. Best fitting was obtained using Eq. [2] to describe the evolution of X *versus* time for data of Figure 4. Figure 6 gives curves obtained by fitting the chlorination data (0 ≤ X ≤ 0.7) of MgO using this equation for temperatures between 850 °C and 1025 °C. The correlation coefficient of linearized data was higher than 0.998.

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

where k is a constant and t is chlorination time.

D. Effect of partial pressures of the reactive gases

The effects of partial pressure of Cl₂+O₂, Cl₂ and O₂ were determined in isothermal conditions in order to evaluate the apparent reaction orders with respect to these gases. The partial orders with respect to the reagents could be equal to the stoichiometric coefficients of the reaction only in the case of elemental reactions. For complex reactions the reaction orders differ from these stoichiometric coefficients. They are obtained experimentally and they may be integer, improper fraction, nil, positive or negative numbers^[11].

1. Effect of partial pressure of Cl₂+O₂ gas mixture

The effect of partial pressure of Cl₂+O₂ ranging from 0.25 to 1.00 atm was studied at 950 °C using a Cl₂+O₂+N₂ gas mixture having a constant Cl₂/O₂ ratio equal to 4. This ratio was chosen because it was the optimum value for the selective oxychlorination of the chromite concentrate^[1-3]. Its use in this case facilitates the comparison of kinetic data of MgO oxychlorination with those of chromite concentrate. Figure 7 (a) shows the evolution of pct WL as a function of time whilst the relationship between the reaction rate (0.05 ≤ X ≤ 0.40) and P(Cl₂+O₂) is illustrated in Figure 7 (b). An apparent reaction order with respect to Cl₂+O₂ of about 0.65 was deduced from this plot.

2. Effect of partial pressure of chlorine

This effect was also studied at 950 °C keeping the oxygen partial pressure constant and equal to 0.33 atm while varying the chlorine partial pressure from 0.20 to 0.67 atm. Nitrogen was used as a dilution gas and the total gas velocity was about 50 cm/min. The obtained isotherms were plotted in Figure 8 (a), showing the evolution of pct WL *versus* time. Figure 8 (b) indicates that the reaction rate was almost proportional to PCl₂ since the apparent reaction order with respect to chlorine is close to one. On the other hand, nCl₂ was higher than n(Cl₂+O₂) (Figure 7 b and 8 b).

3. Effect of partial pressure of oxygen

Having determined the effects of Cl_2+O_2 and Cl_2 partial pressures on the reaction rate it was worthwhile to examine the influence of oxygen partial pressure. The tests were carried out at constant chlorine partial pressure (0.33 atm) while the partial pressure of O_2 was varied from 0.20 to 0.67 atm. Figure 9 (a) traces the evolution of pct WL *versus* time during the oxychlorination of MgO at 950 °C. This figure clearly shows that the time required to reach a given reaction extent increases with the augmentation of the partial pressure of O_2 in the gas mixture. The evolution of the reaction rate as a function of the oxygen partial pressure is illustrated in Figure 9 (b). The apparent reaction order with respect to oxygen was about -0.37 indicating that the oxygen had a negative effect on the chlorination rate of MgO. This result was expected and agrees with Eq. 1.

The effects of (Cl_2+O_2) , Cl_2 and O_2 partial pressures on the oxychlorination rate of MgO at 950 °C were compared in Figure 10. The significance of the effects of reactive gases partial pressures, expressed as apparent reaction orders, clearly follows the following sequence : $n_{\text{Cl}_2} > n_{(\text{Cl}_2+\text{O}_2)} > n_{\text{O}_2}$. The apparent reaction order of $n_{(\text{Cl}_2+\text{O}_2)}$ was almost equal to the algebraic sum of those of n_{Cl_2} and n_{O_2} .

IV. DISCUSSION

As mentioned previously, this study was performed to explain the kinetics of chromite oxychlorination. More details concerning the reaction kinetics of chromite with Cl_2+O_2 are available in References 1 through 4. However, some typical curves of chromite oxychlorination were displayed in Figure 11. It was noticed that the chlorination of chromite was characterized by a rapid reaction rate followed by slow one for reaction extents higher than 0.35. As an example at 1000 °C, 35 pct of the sample reacted after a reaction time of 15 minutes, while about 12 hours were necessary to reach a reaction extent of 70 pct. This phenomenon was explained by a different reactivity of the two main components of the chromite, FeCr_2O_4 and MgCr_2O_4 , towards oxychlorination gas mixture. The apparent activation energy for reaction extents higher than 0.40 was calculated and corresponds to the oxychlorination of MgCr_2O_4 ^[4].

Figure 12 shows the Arrhenius plots for the oxychlorination of MgO, Cr_2O_3 and MgCr_2O_4 contained in the chromite. The values of E_a were about 214, 46 and 262 kJ/mol for oxychlorination of MgO, Cr_2O_3 , and MgCr_2O_4 , respectively. The oxychlorination apparent activation energy of MgCr_2O_4 is comparable to that of MgO oxychlorination.

To confirm that the kinetics parameters of MgCr_2O_4 oxychlorination are controlled by the MgO oxychlorination ones, the effects of the partial pressure of the reactive gases on the reaction rate for the oxychlorination of MgO, Cr_2O_3 ^[12] and MgCr_2O_4 ^[4] are compared in Table I. The

reaction order with respect of oxygen had a positive value only for the oxychlorination of Cr_2O_3 because it favors the formation of CrO_2Cl_2 according to Eq. 3. The apparent reaction orders with respect to Cl_2+O_2 , Cl_2 and O_2 for the oxychlorination of MgO and MgCr_2O_4 contained in chromite were closer, compared with those of Cr_2O_3 . This suggests that the oxychlorination kinetics of MgCr_2O_4 is mostly controlled by the oxychlorination rate of MgO .



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

Solids	$n(\text{Cl}_2+\text{O}_2)$	$n\text{Cl}_2$	$n\text{O}_2$	$n\text{Cl}_2+n\text{O}_2$
Cr_2O_3 ^[12]	1.29	1.08	0.23	1.31
MgO	0.65	0.98	-0.37	0.61
MgCr_2O_4 ^[4]	0.43	0.64	-0.25	0.39

LeRoy ^[6] used the low reactivity of magnesium oxide towards chlorine in order to produce high-purity MgO by selective chlorination of natural calcined magnesite at temperatures ranging from 500 °C to 800 °C. The impurities such as CaO and Fe_2O_3 , contained in the MgO , were converted to chlorides. Ferric chloride was volatilized and calcium chloride was separated by water washing of the residue. The MgO losses ranged from 0.09 to 6.28 pct according to this author. The following paragraphs describe the possibility to remove iron oxides from MgO by oxychlorination.

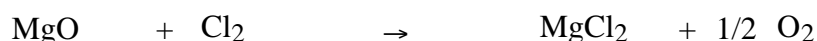
Figure 13 shows the TGA plots of pct WL *versus* temperature for the MgO and Fe_2O_3 during their treatment in Cl_2+O_2 using non isothermal conditions. This figure clearly shows that the reactivity of Fe_2O_3 towards an oxychlorinating gas mixture was higher than that of MgO . Almost full chlorination of hematite and volatilization of reaction products were achieved at about 825 °C while the loss of magnesium oxide was negligible.

More consistent information was obtained during the reaction of these solids with Cl_2+O_2 using isothermal tests. These oxides were chlorinated at 850 °C and 950 °C. Figure 14 illustrates the evolution of pct WL as a function of time. Hematite sample was almost fully chlorinated for a reaction time of about 50 and 10 minutes, at 850 and 950 °C, respectively. Using the same conditions, the weight losses of MgO were less than 5 pct. In our experimental conditions, CaO could be chlorinated even in presence of high oxygen partial pressure in the oxychlorinating gas mixture^[7] thus leading to the purification of MgO from its main impurities.

V. CONCLUSIONS

Different kinetics parameters of the MgO oxychlorination were investigated using the TGA technique. Results indicate that the oxychlorination of magnesium oxide between 850 °C and 1025 °C was characterized by an apparent activation energy of about 214 kJ/mol indicating that the overall rate of the process was probably controlled by the rate of the chemical reaction.

The reaction rate of MgO oxychlorination at 950 °C was almost proportional to the partial pressure of chlorine. The reaction orders, at this temperature, with respect to Cl₂+O₂ and O₂ were 0.65 and -0.37, respectively. Negative value of ⁿO₂ is consistent with the nature of the following reaction :



Experimental results also demonstrated that the oxychlorination could be used as an efficient method to purify MgO from iron oxides. Almost full extraction of iron can be achieved between 850 °C and 950 °C with MgO losses less than 5 pct.

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Figure Captions

Figure 1 : Results of (a) SEM and (b) XRD of the magnesium oxide sample.

Figure 2 : Effect of $\text{Cl}_2/(\text{Cl}_2+\text{O}_2)$ molar ratio on the MgO weight loss.

Figure 3 : Effect of gas velocity on the oxychlorination rate of MgO at 950 °C.

Figure 4 : Isotherms of oxychlorination of magnesium oxide for (a) $T \leq 925$ °C and (b) $T \geq 950$ °C.

Figure 5 : Arrhenius plot of oxychlorination of MgO by Cl_2+O_2 .

Figure 6 : Fitting of oxychlorination data of MgO using Eq. [2] for (a) $T \leq 925$ °C
and (b) $T \geq 950$ °C.

Figure 7 : Isotherms of oxychlorination of MgO (a), using various Cl_2+O_2 partial pressures and (b) apparent reaction order with respect to Cl_2+O_2 .

Figure 8 : Isotherms of oxychlorination of MgO (a), using various Cl_2 partial pressures and (b) apparent reaction order with respect to Cl_2 .

Figure 9 : Isotherms of oxychlorination of MgO (a), using various O_2 partial pressures and (b) apparent reaction order with respect to O_2 .

Figure 10 : Effect of gases composition on the reaction rate of oxychlorination of MgO.

Figure 11 : Typical isotherm plots for the oxychlorination of chromite.

Figure 12 : Arrhenius plots of MgO, Cr_2O_3 ^[12] and MgCr_2O_4 ^[4] oxychlorination.

Figure 13 : Non isothermal chlorination of MgO and Fe_2O_3 using Cl_2+O_2 .

Figure 14 : Oxychlorination of MgO and Fe_2O_3 at 850 °C and 950 °C.

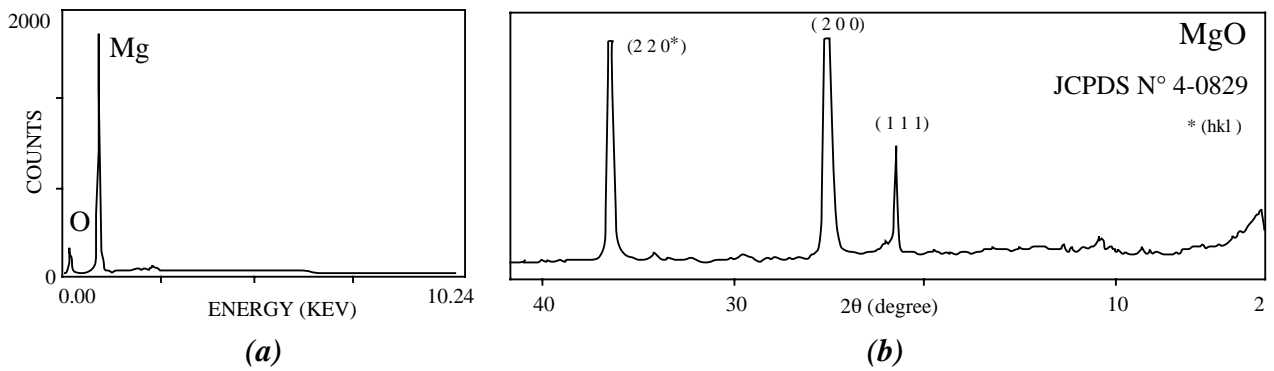


Fig. 1 : Results of (a) SEM and (b) XRD of the magnesium oxide sample.

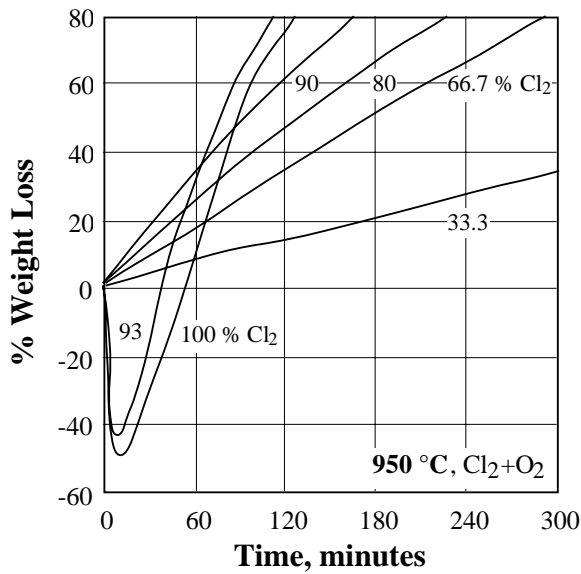


Fig. 2 : Effect of Cl₂/(Cl₂+O₂) molar ratio on the MgO weight loss.

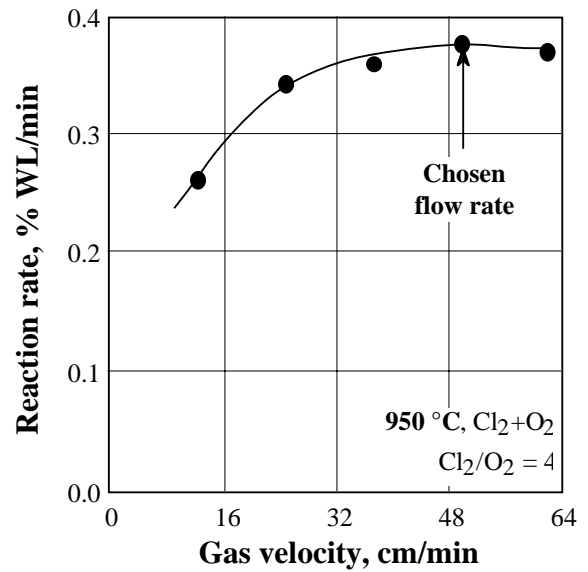


Fig. 3 : Effect of gas velocity on the oxy-chlorination rate of MgO at 950 °C

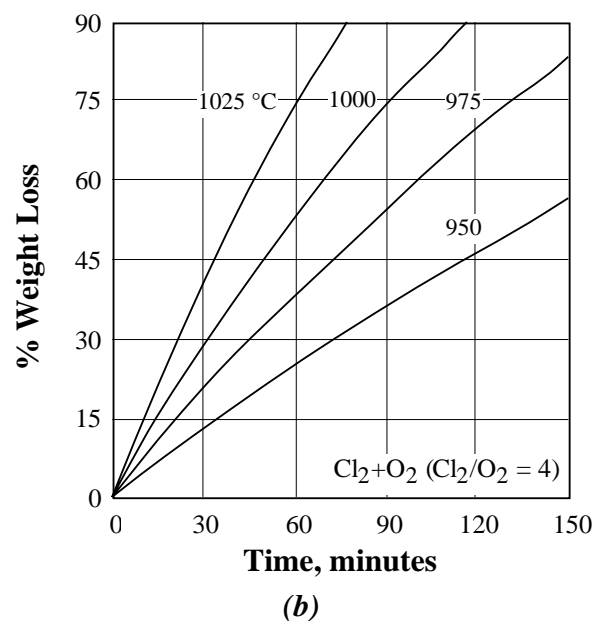
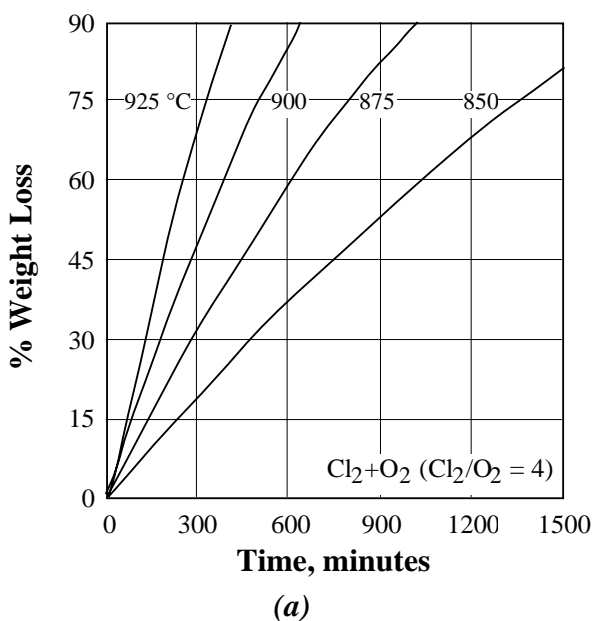


Fig. 4 : Isotherms of oxychlorination of magnesium oxide for (a) $T \leq 925$ °C and (b) $T \geq 950$ °C.

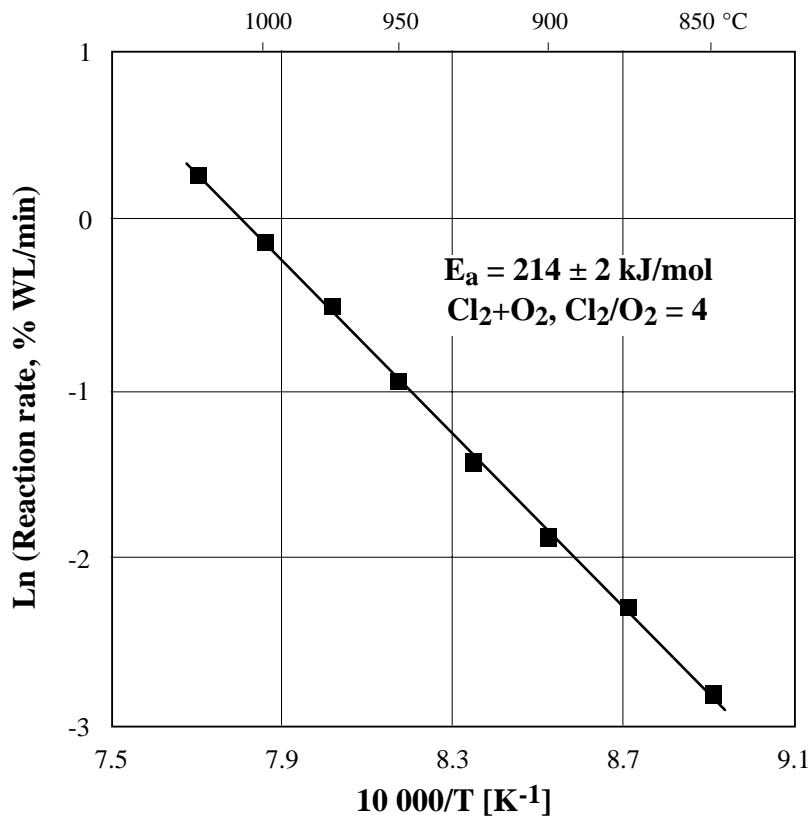
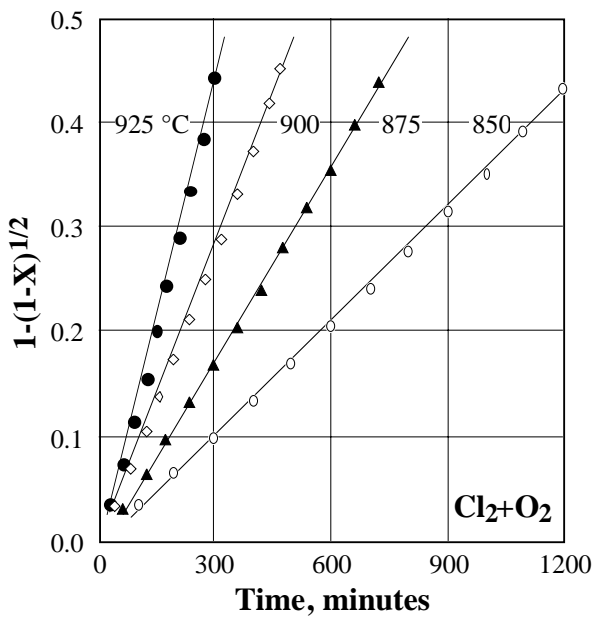
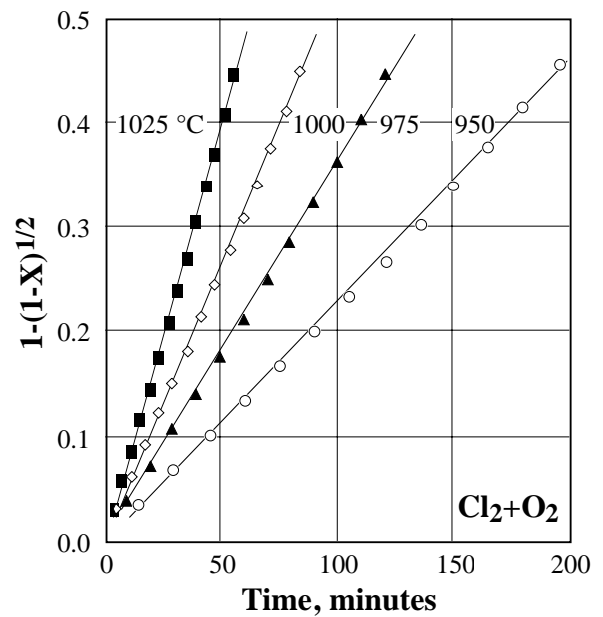


Fig. 5 : Arrhenius plot of oxychlorination of MgO by $\text{Cl}_2 + \text{O}_2$.

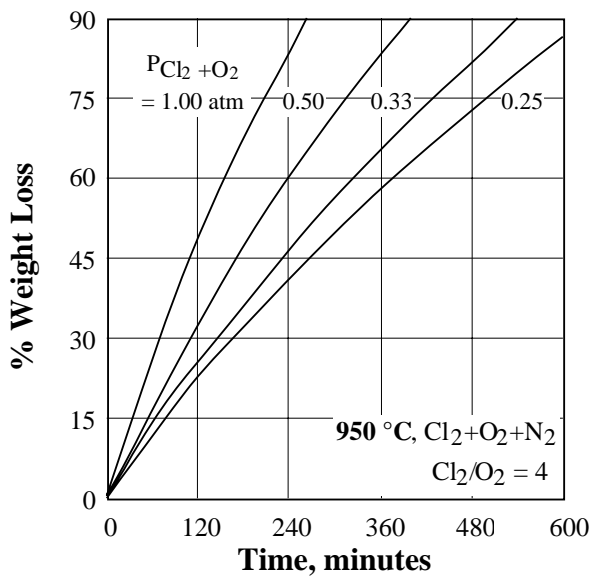


(a)

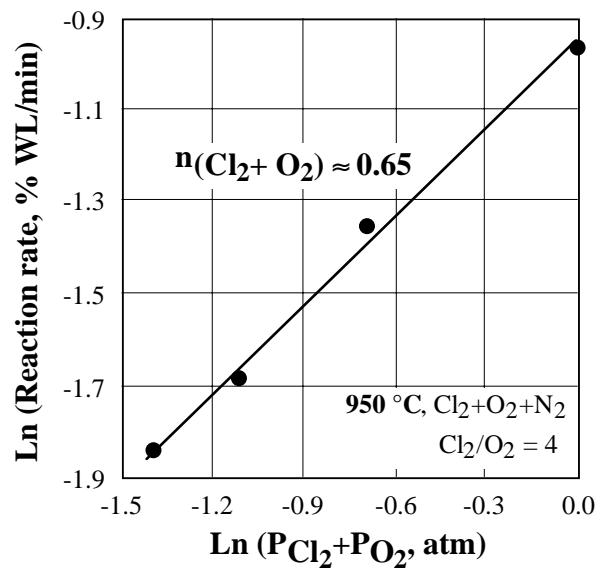


(b)

Fig. 6 : Fitting of oxychlorination data of MgO using Eq. [2] for (a) $T \leq 925 \text{ }^\circ\text{C}$ and (b) $T \geq 950 \text{ }^\circ\text{C}$.

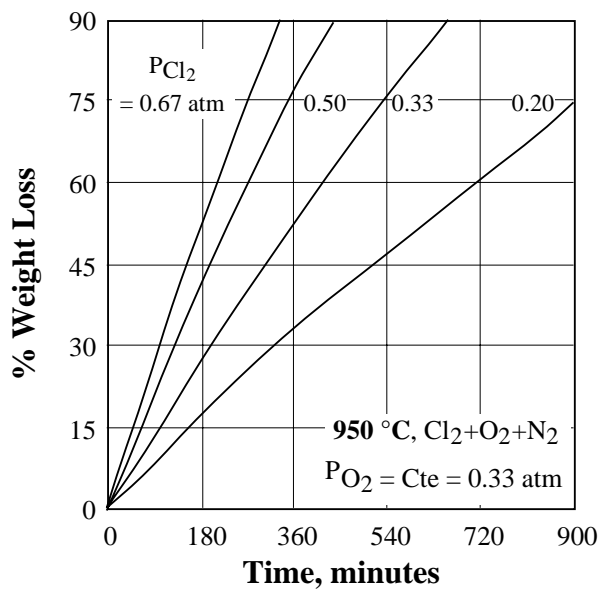


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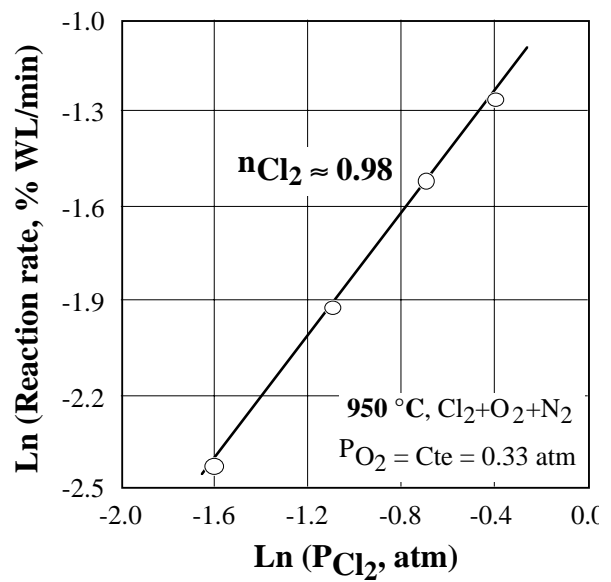


(b)

Fig. 7. Isotherms of oxychlorination of MgO (a), using various $\text{Cl}_2 + \text{O}_2$ partial pressures and (b) apparent reaction order with respect to $\text{Cl}_2 + \text{O}_2$.



(a)



(b)

Fig. 8 : Isotherms of oxychlorination of MgO (a), using various Cl_2 partial pressures and (b) apparent reaction order with respect to Cl_2 .

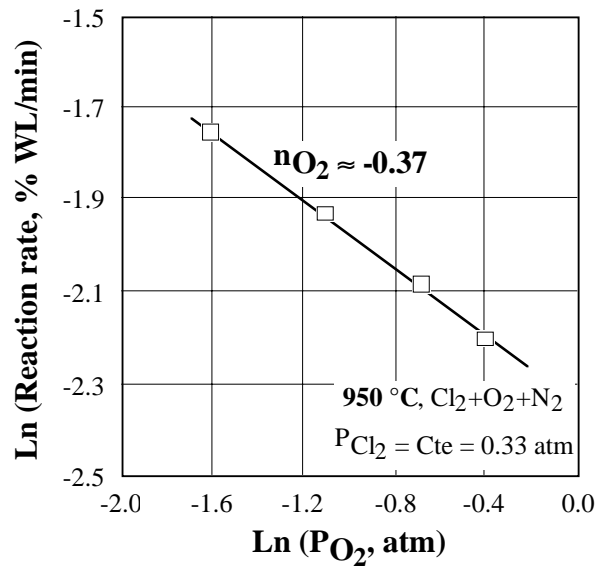
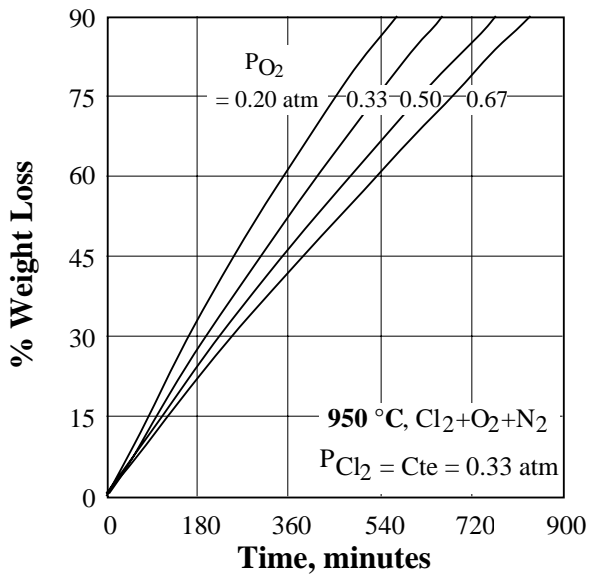


Fig. 9 : Isotherms of oxychlorination of MgO (a), using various O₂ partial pressures and (b) apparent reaction order with respect to O₂.

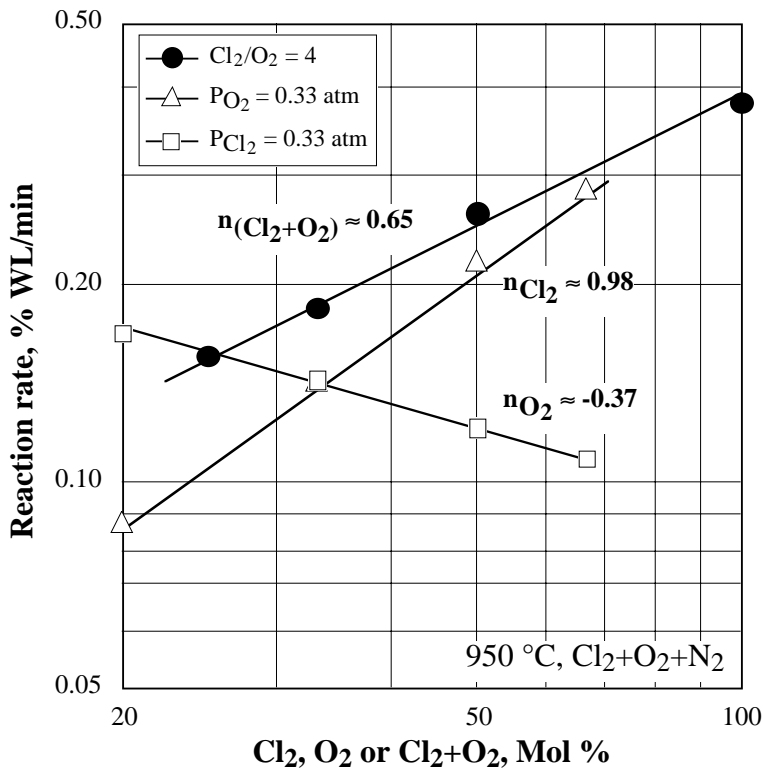


Fig. 10 : Effect of gases composition on the reaction rate of oxychlorination of MgO.

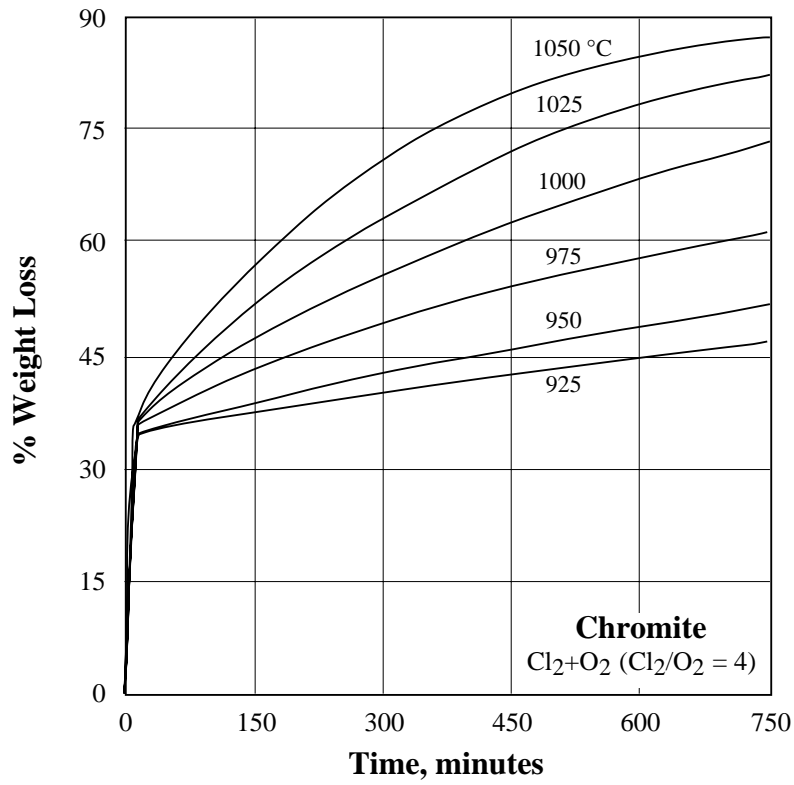


Fig. 11 : Typical isotherm plots for the oxychlorination of chromite.

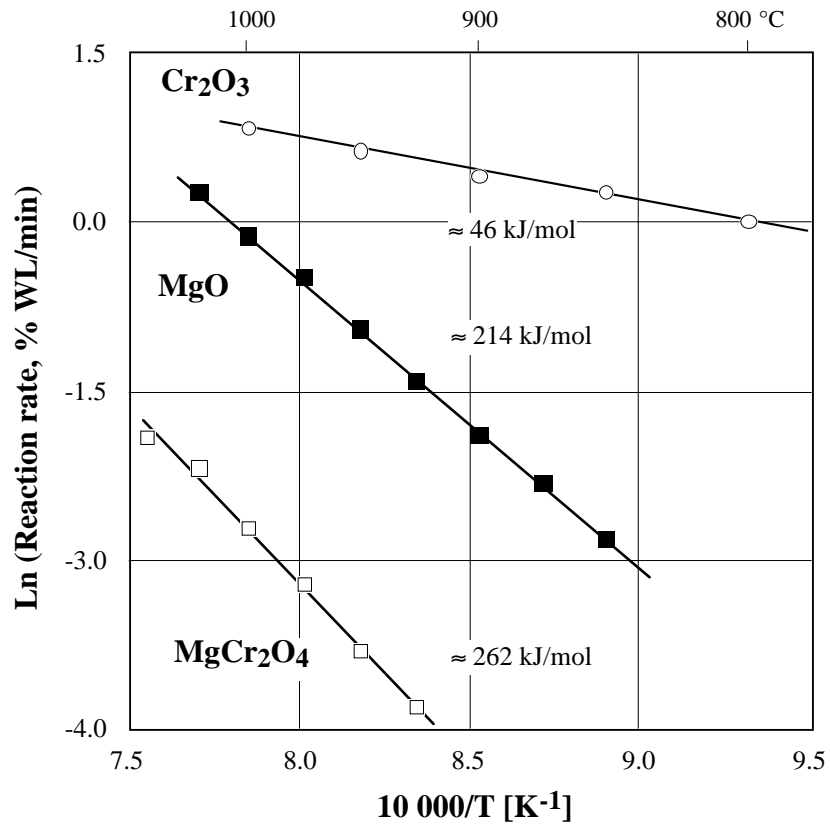


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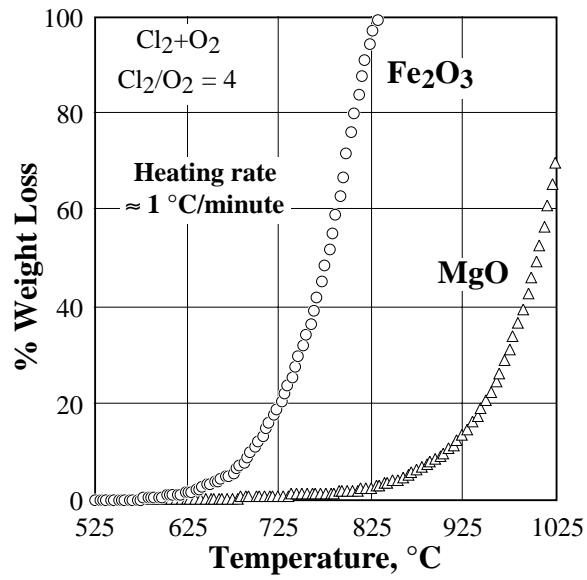


Fig. 13 : Non isothermal chlorination of MgO and Fe₂O₃ using Cl₂+O₂.

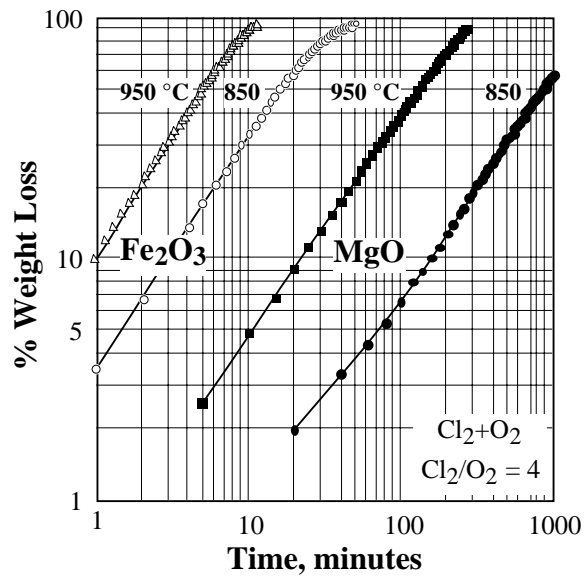


Fig. 14 : Oxychlorination of MgO and Fe₂O₃ at 850 °C and 950 °C.