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Processing of magnesium bearing materials by dry chlorination - An overview of kinetic aspects

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Abstract. This paper is focused on the reactivity of Cl_2 towards MgO in presence of a reducing (CO) and oxidizing (O_2) agent at temperatures up to 1025°C . Kinetics parameters are determined by thermogravimetry under isothermal conditions. The overviewed results showed that the carbochlorination (Cl_2+CO) occurred at temperatures lower than oxychlorination (Cl_2+O_2). The reaction of MgO with Cl_2+CO from 425°C to 600°C proceeds with an activation energy (E_a) of about 49 kJ/mol , while the reaction rate does not longer depend on the temperature between 600 and 675°C . The reaction of MgO with Cl_2+O_2 at 850 - 1025°C was characterized by a value of E_a of 214 kJ/mol indicating that the overall rate of the process is controlled by the rate of chemical reaction. Oxychlorination can also be used for removing the impurities contained in the industrial magnesium raw materials. Further, the behavior of the MgO in chlorine atmosphere leads to give an insight about the reaction mechanisms useful for the selective chlorination of complex ores and concentrates containing magnesium oxide.

1. Introduction

Although magnesium is abundant in the earth crust, its natural resources for a commercial purpose include only a few number of minerals (magnesite, dolomite, brucite, carnallite, olivine,...) as well as salt pits, magnesia-rich brine and seawater. Reduction of magnesia and electrolysis of molten magnesium chloride are two principal routes for the production of magnesium [1, 2]. The thermal processes (mostly silicothermic and carbothermic reductions) are performed at high temperature and under a reduced pressure to promote the vaporization of the obtained magnesium. Concerning the anhydrous chloride route, the magnesium chloride is generated during chlorination by Cl_2+C of MgO bearing materials and/or from brine dehydration. Therefore, the electrolysis of molten MgCl_2 producing liquid MgCl_2 is performed at 700 - 800°C and as it could be expected, chlorine (Cl_2) is generated at the anode from the oxidation of chloride ion (Cl^-).

Use of the dry chlorination process for the transformation of magnesium oxide and more complex magnesium substances into magnesium chloride seems to be a good alternative route due to the high reactivity of chlorine and to the fact that chlorine can be recycled during metallic magnesium recovery. A literature review showed that several studies [3-9] are devoted to the chlorination of materials containing magnesium compounds by using various chlorinating agents. One may mention the work by Ishii et al. [3] that studied the chlorination of MgO , olivine (Mg_2SiO_4), protoenstatite (MgSiO_3) and talc [$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$] as well as FeO , Fe_2O_3 and SiO_2 between 25°C and 1000°C using differential thermal and thermogravimetric analysis (DTA and TGA). According to these authors, the reactivity of MgO towards chlorine, in absence of carbon, is negligible at 640°C . Two peaks were perceived during the chlorination of MgO in presence of carbon. The first is exothermic and observed at 500°C corresponding to the formation of MgCl_2 . The second peak is endothermic and



detected at about 700 °C. It is attributed to the fusion of MgCl_2 . The reaction rate is fast at the beginning of the reaction that afterwards proceeds slowly and is stopped completely at 55 % of MgO conversion. The authors suggested that MgCl_2 formed on the surface of the MgO particle acts as a barrier for further chlorination. The kinetics parameters of chlorination of MgO and Fe_2O_3 contained in a chromite concentrate using $\text{HCl}+\text{C}$ between 1000 °C and 1200 °C are given by Vil'nyanskii and Martirossyan [4]. The apparent activation energy of the MgO chlorination is about 118 kJ/mol and the apparent reaction orders with respect to HCl are 0.98, 0.99 and 0.99 at 1000 °C, 1100 °C and 1200 °C, respectively. The chlorination of MgO by HCl in a potassium chloride melt between 850 °C and 940 °C has been studied by Stupina et al. [5], they proposed that the rate-controlling step of the MgO chlorination is the diffusion of HCl to MgO surface. The same phenomenon was also underlined by the same authors [6] during the chlorination of MgO by HCl in fused KCl and NaCl between 780 °C and 1000 °C. Further literature details regarding to the chlorination of magnesium oxide were summarized earlier [7, 8]. Recently, Cecchi et al. [9] examined the production of MgCl_2 from raw chrysotile tailings. They concluded that temperature is the determining factor for both the recovery of Mg (85%) and for limiting impurities.

This paper gives a summary of our kinetics results obtained during dry chlorination of the magnesium oxide under a reducing (CO) and oxidizing (O_2) atmosphere.

2. Materials and methods

The sample used for the experimental tests was a magnesium oxide powder with a purity of 98 pct. X-ray diffraction (XRD) analysis revealed the presence of MgO as the only crystallized phase in the sample. The thermogravimetric (TG) chlorination tests were realized with 40 to 100 mg of sample, using the experimental setups described in [7]. Its main device is a CAHN 1000 microbalance with a sensitivity of 10 μg . The results are mostly expressed as the evolution of the reaction extent as a function of the chosen experimental conditions and the methodology applied for the kinetic study [10] consists of the following items:

- thermogravimetric analysis (TGA) using non isothermal conditions,
- comparison of the reaction rate with that of the volatilization of the reaction products,
- determination of adequate gaseous mixture flow rate,
- effect of the proportions of the reactive gases on the reaction rate,
- determination of the apparent reaction orders with respect to the reactive gases,
- evaluation of the apparent activation energy of the process (effect of temperature),
- data processing of the experimental data to define the geometry of the reaction interface (shape factor),
- analysis of the solid products (SEM, microprobe, XRD, specific surface area, etc.),
- indication of the possible rate controlling step.

Only some typical data will be described here illustrating the steps for the chlorination of MgO. Detailed results can be found in our previously published papers [7, 8, 10].

3. Results

3.1. Kinetics of the carbochlorination of MgO

The first isothermal tests for this kinetics study were performed in order to check the effect of Cl_2+CO gas velocity on the carbochlorination rate. Using this gas velocity will avoid starvation and will minimize the mass transfer phenomena. A series of isothermal tests was carried out at 600 °C using total gas flow rates of 8 to 60 L/h and keeping the Cl_2/CO molar ratio equal to 1. Figure 1 (a) illustrates the evolution of MgO reaction extent "X" as a function of reaction time. Figure 1 (b) traces the evolution of the reaction rate (expressed as % X/min) as a function of the gas velocity ($0.05 \leq X \leq 0.40$). This figure shows that the reaction rate increases as the gas flow rate augments up to 40 L/h (linear velocity of gases: $V_g = 33 \text{ cm/min}$). For higher gas velocities, the chlorination rate does not depend on the gas flow rate. Consequently, a gas flow rate of 48 L/h ($V_g \approx 40 \text{ cm/min}$) was used for further tests of the MgO carbochlorination with Cl_2+CO .

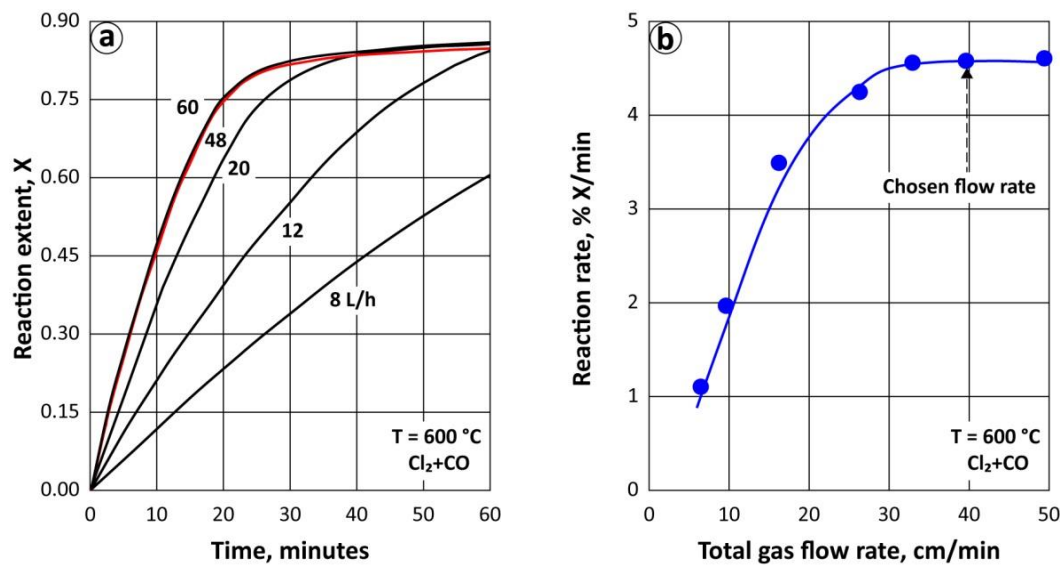


Figure 1. (a) Isotherms of the MgO carbochlorination at 600 °C at various gas flow rates; (b) evolution of the reaction rate as a function of the linear gas velocity.

A careful examination of figure 1 (a) shows that the maximum conversion of MgO into MgCl_2 tends to an asymptote of about $X = 0.85$ indicating that the reaction of $\text{Cl}_2 + \text{CO}$ with MgO is almost stopped. To give an insight about this phenomenon, several boat isothermal tests were performed for a reaction time of two hours and the results are grouped in figure 2. Treated residues were water-leached to dissolve formed MgCl_2 in order to measure the carbochlorination degree of MgO. Besides, the reaction rate is also calculated from the mass losses up to about 700 °C. The reaction extents obtained by these two methods are almost equal (figure 2).

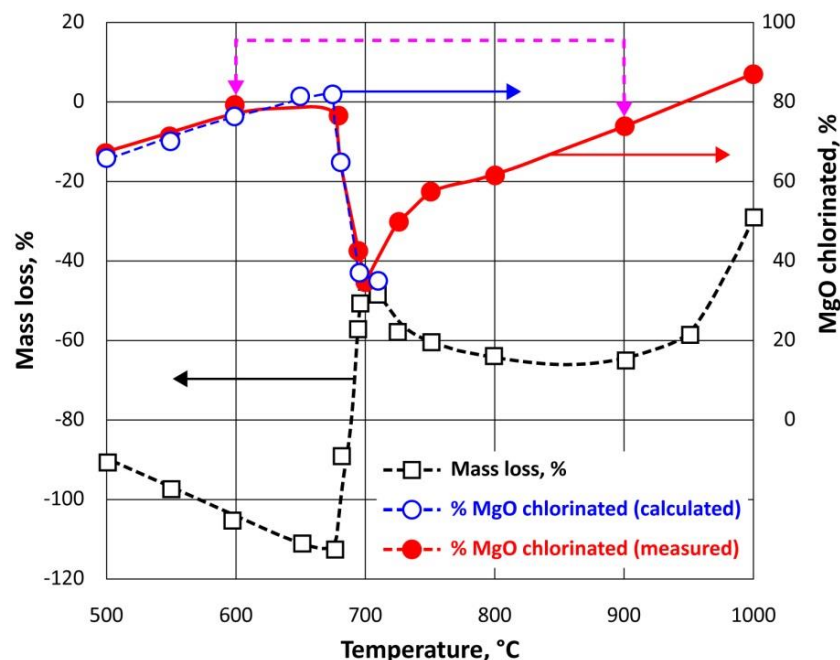


Figure 2. Carbochlorination of MgO in the horizontal set-up during 2 hours.

This figure shows that about 67 % of MgO are chlorinated at 500 °C and reaction extent increases with temperature and reaches 82% at 675 °C. Therefore, the reaction rate drops and only 35 % of the sample are chlorinated at 700 °C. This is probably due to the fusion of MgCl_2 leading to the formation

of a liquid layer that decreases the mass transfer between MgO and the carbochlorinating gas mixture. Temperatures as higher as 900 °C are required to achieve the same rate obtained at 675 °C. Beyond 900 °C, magnesium chloride is sufficiently volatile and is recovered by cooling the gas phase. At 1000 °C, about 85 % of MgO are chlorinated with a reaction time of two hours and MgCl₂ and MgO are identified by XRD in the obtained residues. This confirms that chlorination of MgO is incomplete even at 1000 °C. Moreover, the presence of MgCl₂ in the treated residues suggests that the carbochlorination rate of MgO is higher than the volatilization rate of MgCl₂.

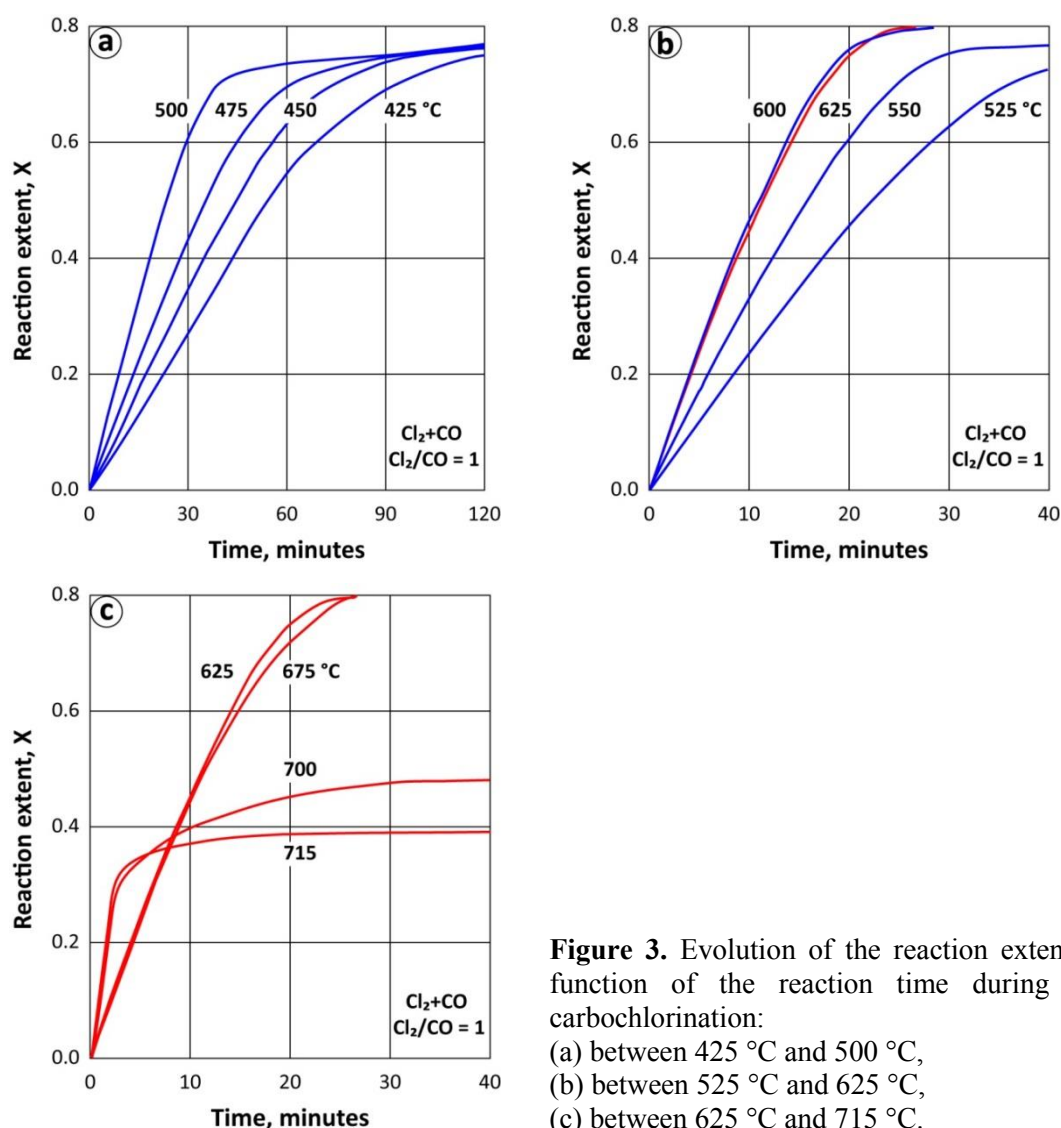


Figure 3. Evolution of the reaction extent as a function of the reaction time during MgO carbochlorination:

- (a) between 425 °C and 500 °C,
- (b) between 525 °C and 625 °C,
- (c) between 625 °C and 715 °C.

The effect of temperature on the carbochlorination of MgO was investigated from 425 °C to 715 °C by thermogravimetry and the obtained isotherms are grouped in figures 3. This figure shows that a reaction extent of about 75 % requires about 120 and 20 minutes at 425 °C and 600 °C, respectively. As in previous case, figure 3 also reveals that the conversion of MgO into MgCl₂ reaches a maximum of about 85 %. One may speculate that the MgCl₂ formed on the surface of the MgO particle acts as a barrier against further progress of the reaction. Note that the molar volume of MgCl₂ (41.04 cm³/mol) is much higher than that of MgO (11.26 cm³/mol).

As obviously demonstrated in figure 3 (c), for a reaction time of 20 minutes, the reaction extent decreases as the temperature increases from 675 °C to 715 °C which is provoked by the fusion of MgCl₂ (M.p. = 714 °C). Note also that the high exothermic nature of the carbochlorination reactions will increase the temperature in the reaction zone allowing the fusion of the generated MgCl₂.

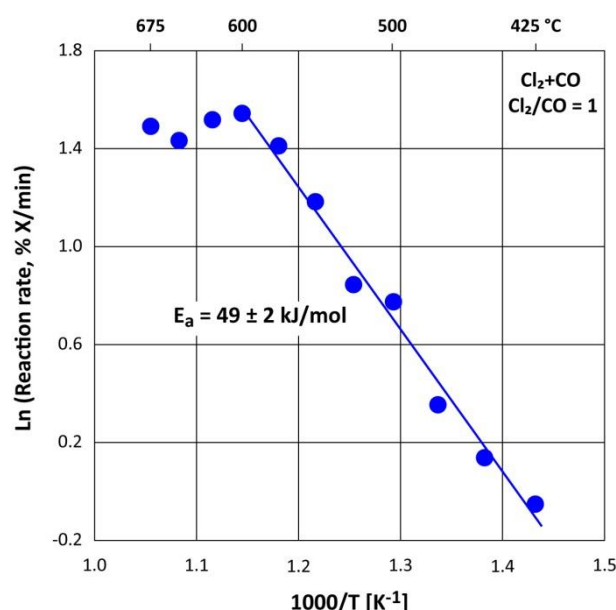


Figure 4. Arrhenius plot for the carbochlorination of MgO by $\text{Cl}_2 + \text{CO}$.

The Arrhenius plot of MgO carbochlorination ($0.05 \leq X \leq 0.40$) is given in figure 4. The apparent activation energy is $49 \pm 2 \text{ kJ/mol}$ between 425 $^\circ\text{C}$ and 600 $^\circ\text{C}$. This value suggests that the kinetics of MgO carbochlorination is affected by diffusion. Beyond 600 $^\circ\text{C}$, the reaction rate does not depend on the temperature. As mentioned above, the exothermic nature of carbochlorination reaction could lead to the partial fusion of MgCl_2 , consequently leading to a layer formation surrounding the MgO particles and thereby decreasing the mass exchange with the chlorinating gas mixture. Due to the hygroscopic nature of MgCl_2 , it was difficult to examine the carbochlorination residues by microscopy, while the XRD confirmed the formation of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

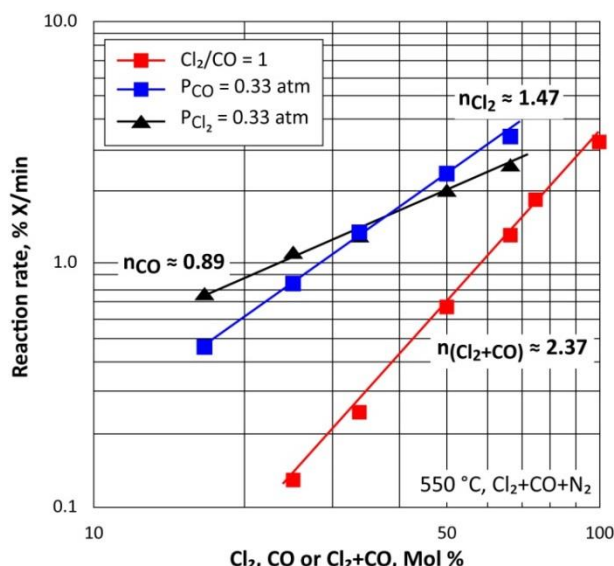


Figure 5. Effect of gases composition on the carbochlorination rate of MgO at 550 $^\circ\text{C}$.

The effects of $\text{Cl}_2 + \text{CO}$, Cl_2 and CO partial pressures on the carbochlorination rate of MgO at 550 $^\circ\text{C}$ are compared in figure 5. The apparent reaction orders with respect to $\text{Cl}_2 + \text{CO}$, Cl_2 and CO are about 2.37, 1.47 and 0.89, respectively. Obviously, the effects of reactive gases follow the sequence: $n(\text{Cl}_2 + \text{CO}) > n_{\text{Cl}_2} > n_{\text{CO}}$ and these reaction orders satisfy the relation: $n(\text{Cl}_2 + \text{CO}) \approx n_{\text{Cl}_2} + n_{\text{CO}}$.

3.2. Kinetics of the oxychlorination of MgO

The chlorination of MgO by chlorine produces magnesium chloride which is characterized by its melting and boiling points of 714 °C and 1412 °C, respectively. As the TGA technique is used to measure the reaction rate, it was mandatory to insure that the rate of MgCl₂ volatilization is 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. The impact of the oxygen potential on the reaction rates during the chlorination of the iron oxides was also investigated earlier [11-13].

To check this effect on the MgO interaction with chlorine, a series of experiments was performed at 950 °C, using a Cl₂+O₂ gas mixture with a molar ratio of Cl₂/(Cl₂+O₂) from 0.33 to 1.00. Only mass losses of sample were observed during the oxychlorination using a Cl₂+O₂ mixture containing less than 90 % Cl₂ suggesting that the observed mass loss is a direct measure of the extent of the overall oxychlorination reaction. For this reason, the kinetics parameters of MgO oxychlorination were studied using the Cl₂+O₂ gas mixtures having chlorine content lower or equal to 80 %.

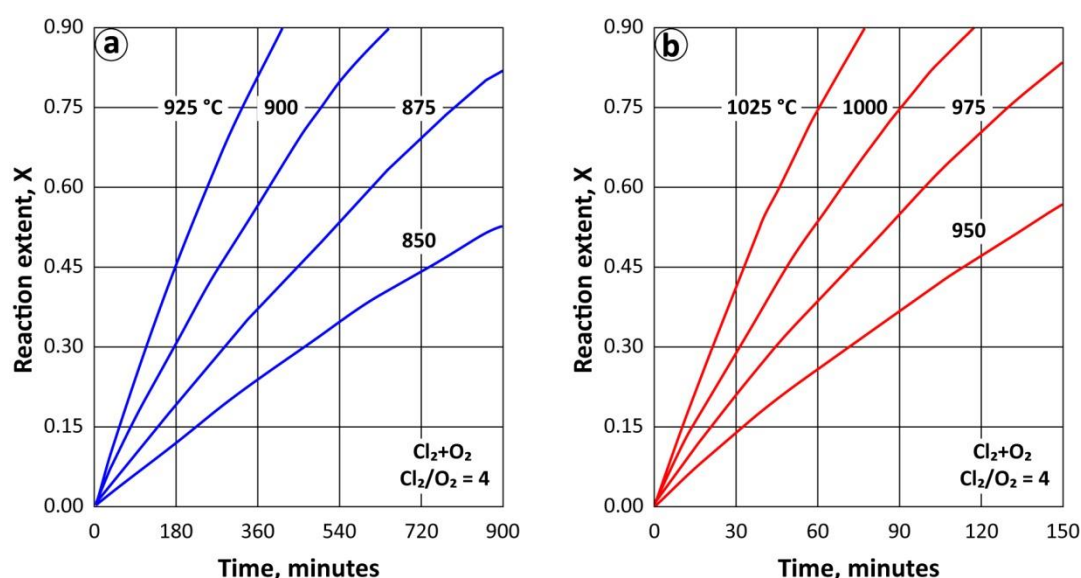


Figure 6. Isotherms of oxychlorination of magnesium oxide for: (a) $T \leq 925^\circ\text{C}$ and (b) $T \geq 950^\circ\text{C}$.

The temperature effect on MgO oxychlorination was studied in isothermal conditions between 850 °C and 1025 °C. An oxychlorinating gas mixture of Cl₂+O₂ with a molar ratio $\text{Cl}_2/\text{O}_2 = 4$ was used. Figure 6 gives the evolution of the reaction extent 'X' as a function of time for different isotherms. More than 24 hours were required to reach a value of X of about 0.80 during the experiment at 850 °C, while the same reaction extent at 1025 °C was obtained for a reaction time of about 1 hour.

The data of figure 6 were used to determine the effect of the temperature on the reaction rate for a reaction extent between 0.05 and 0.40. Figure 7 gives the results in the Arrhenius plot. A value of the apparent activation energy of MgO oxychlorination close to 214 kJ/mol was deduced from this plot. Such a high value suggests that overall rate of MgO oxychlorination is mostly controlled by the rate of the chemical reaction.

The effect of the partial pressures of the reactive gases on the oxychlorination of MgO is studied at 950 °C using a Cl₂+O₂+N₂ gas mixture with the optimal gas flow rate. For the Cl₂+O₂ impact, the (Cl₂+O₂) partial pressure is varied from 0.25 to 1.00 atm by keeping the Cl₂/O₂ molar ratio constant and equal to 4. To follow the influence of the p_{Cl_2} , the oxygen partial pressure is kept as a constant and equal to 0.33 atm, while chlorine partial pressure is varied from 0.20 to 0.67 atm. Similarly, the influence of the O₂ in the reaction rate is measured at $p_{\text{Cl}_2} = 0.33$ atm by changing the oxygen content between 20 % and 67 % in the Cl₂+O₂+N₂ gas mixtures. Obtained results are summarized in figure 8 as the evolution of the reaction rate versus reactive gas content using a natural logarithm scale.

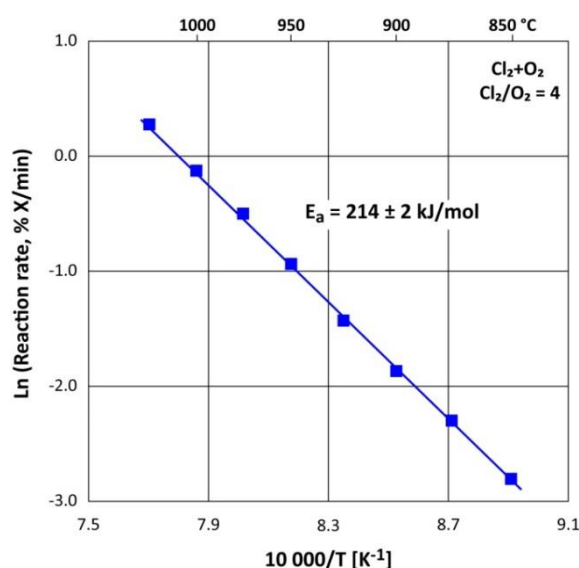


Figure 7. Arrhenius plot for the oxychlorination of MgO by Cl_2+O_2 .

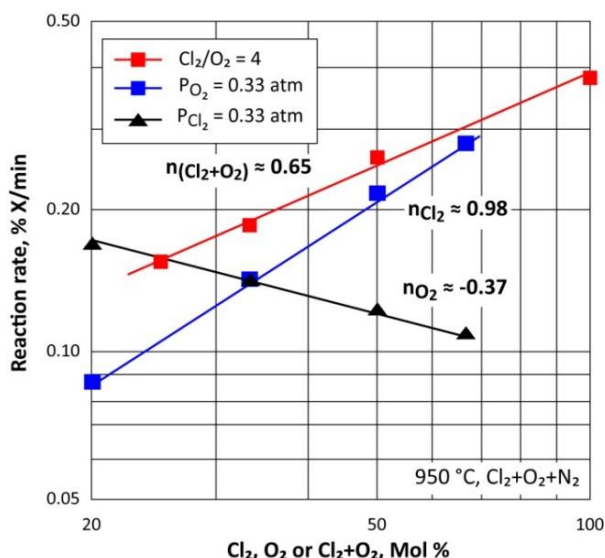


Figure 8. Effect of gases composition on the oxychlorination rate of MgO at 950 °C.

Examination of figure 8 shows that the reaction rate of MgO oxychlorination is almost proportional to the $p\text{Cl}_2$ since the apparent reaction order with respect to chlorine is close to one. The apparent reaction order with respect to O_2 is about -0.37 indicating that the oxygen has a negative effect on the chlorination of MgO. The significance of the effects of reactive gases, expressed as apparent reaction orders, follows the sequence: $n\text{Cl}_2 > n(\text{Cl}_2+\text{O}_2) > n\text{O}_2$ and the apparent reaction orders are related by the following relationship: $n(\text{Cl}_2+\text{O}_2) \approx n\text{Cl}_2 + n\text{O}_2$.

The low reactivity of Cl_2+O_2 towards MgO can be applied for the removal of impurities such as iron oxides from the magnesium bearing materials. These results are also used [14, 15] to understand the oxychlorination mechanisms of chromite $[(\text{Fe}^{2+}, \text{Mg})(\text{Cr}, \text{Al}, \text{Fe}^{3+})_2\text{O}_4]$ in order to separate selectively its main constituents.

As reported recently [16, 17], the selective removal of the iron from chromite, resulting to Cr/Fe increase, is achieved by chlorination and the selectivity is enhanced by adding sodium chloride at temperatures lower than or equal to 720 °C. Other investigations used chlorination for the purification of talcs [18, 19] at about 900 °C allowing an important extraction of iron without magnesium loss.

4. Conclusions

Kinetics of the MgO reaction with Cl_2+CO was studied under isothermal conditions. The carbochlorination process from 425 °C to 600 °C proceeded with an activation energy of about 49 kJ/mol, while the initial reaction rate does not longer depended on the temperature between 600 °C and 675 °C. The carbochlorination rate is dropped down at about 700 °C due to the fusion of the generated magnesium chloride and the reaction is not complete for two hours at 1000 °C. The apparent reaction orders with respect to Cl_2+CO , Cl_2 and CO at 550 °C are about 2.37, 1.47 and 0.89, respectively.

The oxychlorination of MgO with Cl_2+O_2 starts at temperatures higher than 800 °C and the reaction rate is lower than that of the MgCl_2 volatilization. The reaction of magnesium oxide with Cl_2+O_2 ($\text{Cl}_2/\text{O}_2 = 4$) between 850 °C to 1025 °C was characterized by an apparent activation energy of about 214 kJ/mol indicating that the overall rate of the process is probably controlled by rate of chemical reaction. The reaction rate of MgO oxychlorination at 950 °C had an almost linear relationship with the partial pressure of chlorine. The reaction orders, at this temperature, with respect to Cl_2+O_2 and O_2 were 0.65 and -0.37, respectively.

This kinetic study was explored to explain the observed phenomena during the chlorination of raw materials such as chromite concentrate. Thermodynamic studies were also performed to complement the kinetic studies to achieve a selective separation of valuable metals (Cr, Mg, Fe, Al) contained in these complex materials.

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