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First Version

CHLORINATION AND CARBOCHLORINATION OF MAGNESIUM OXIDE

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Abstract

Thermogravimetric technique and boat experiments were used to study the chlorination of MgO and its reactivity with respect to Cl_2+air, Cl_2+N_2 and Cl_2+CO gas mixtures at temperatures lower than 1000 °C. Oxychlorination of MgO occurs at temperatures higher than that of its carbochlorination. Effects of experimental parameters such as : gas flow rate, temperature and partial pressure of the carbochlorinating gas mixture on the reaction rate were examined.

At 550 °C, the apparent reaction orders with respect to Cl_2+CO, Cl_2 and CO, were 2.37, 1.47 and 0.89, respectively. At this temperature, the maximum reaction rate was obtained using a Cl_2+CO gas mixture having a Cl_2/CO molar ratio equal to about 0.6. The apparent activation energy of carbochlorination of MgO was calculated as 49 kJ/ mol between 425 °C and 600 °C.

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INTRODUCTION

Magnesium is the eighth most abundant element in the earth's crust (2.3 pct) and is one of the most plentiful elements in sea water[1, 2]. Magnesium carbonate $MgCO_3$, magnesia-rich brines and dolomite (Ca, Mg) CO_3 are the main sources for magnesium.

Magnesium metal is produced mainly either by the electrolysis of purified $MgCl_2$ from natural brine or by silicothermy. The repartition of the consumption of magnesia in USA is detailed in Table I. 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.

Table I : Repartition of USA Consumption of Magnesium [3].

Utilization	Percentage
Aluminum industry	51
Casting and wrought magnesium products	24
Desulfurization of iron and steel	13
Cathodic protection	5
Reducing agent in nonferrous metals	2
Others	5

Few publications are devoted to the study of chlorination of MgO. Ishii et al.[4] investigated the chlorination of FeO, Fe_2O_3, SiO_2, MgO as well as olivine, protoenstatite and talc 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 is negligible at 640 °C in absence of reducing agents. Two peaks were detected during the chlorination of MgO in the presence of carbon. The first is exothermic, observed at 500 °C, attributed to the formation of $MgCl_2$ and shifts to lower temperatures with increasing the mounts of carbon. The second peak is endothermic, detected at 700 °C, that corresponds to the fusion of magnesium chloride. The reaction rate is rapid at the beginning then proceeds slowly and stops completely at about 55 pct of MgO conversion. The authors suggested that the layer of $MgCl_2$ formed on the surface of the MgO particle acts as a barrier for further reaction.

Ishii et al.[5] also investigated the chlorination of MgO between 25 °C and 970 °C using DTA under isothermal conditions. At 970 °C, they indicated that the amount of $MgCl_2$ formed, during the MgO chlorination with Cl_2, is small. The presence of carbon enhances the conversion of MgO to $MgCl_2$ up to 49 pct. Exothermic peaks are observed at 530 °C, 485 °C and 475 °C during MgO treatment by $C+Cl_2$ for molar ratios of C/MgO equal to 1, 2 and 3, respectively. Equation 1 describes the assumed role of carbon in the reaction. The activation energy obtained between 450 °C and 500 °C are 182.4, 191.6 and 260 kJ/ mol for the C/MgO ratios equal to 0.5, 1 and 2, respectively. Finally, Jander' equation fits the experimental data of isothermal carbochlorination.

$$MgO + C + Cl_2 \rightarrow [MgCl_2 \cdot O] + C \rightarrow MgCl_2 + CO \qquad [1]$$

Smith[6] confirmed the low conversion of MgO into $MgCl_2$ at 650 °C in absence of a reducing atmosphere. He indicated that the chlorination of porous pellets of magnesium oxide starts by a high reaction rate that slows down after a conversion of ≈ 15 pct of MgO. The low reactivity of MgO towards chlorine was used by LeRoy[7] for its purification. He eliminated impurities such as CaO and Fe_2O_3 by selective chlorination of natural calcined magnesite between 500 °C and 800 °C. Generated ferric chloride volatilized and calcium chloride was removed by water washing of the chlorination's residue. According to this author, the MgO losses vary from 0.09 to 6.28 pct.

The kinetics of chlorination of Fe_2O_3 and MgO contained in a chromite concentrate was studied by Vil'nyanskii and Martirossyan[8] using HCl + C between 1000 °C and 1200 °C. 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.

Stupina et al[9] studied the chlorination of MgO by HCl in a KCl melt between 850 °C and 940 °C . They proposed that the rate-controlling step of the MgO chlorination is the diffusion of HCl to MgO surface through the $MgCl_2$ layer. This phenomenon was later confirmed by the same authors[10] during the chlorination of MgO by HCl in fused KCl and NaCl between 780 °C and 1000 °C.

Thermodynamic Considerations

Thermodynamic calculations were made to study the possibility of chlorination of magnesium oxide with different chlorinating gas mixtures using data of references 11 and 12. Calculations were also done for the chlorination of common major impurities contained in magnesium oxide such as Ca, Fe and Si oxides. Equations 2 to 9 describe the carbochlorination (Cl_2+CO) and chlorination (Cl_2) of these oxides. Figure 1 summarizes the evolution of the standard free energy changes ‘ΔG°’ as a function of temperature for the carbochlorination and chlorination of the four oxides. It indicates that carbochlorination of the four metal oxides is possible in the explored temperature range. The most probable reaction is that of CaO and the least probable one is that of SiO_2. Figure 1 also shows that the chlorination of Ca, Fe and Mg oxides is thermodynamically feasible and thus gives allowance to the selective chlorination of Ca and Fe oxides present in MgO as impurities.

Figure 2 shows the phase stability diagrams for the (Mg, Fe, Ca, Si)-O-Cl systems at 800 °C. These diagrams are established using data of reference [12]. The estimated experimental partial pressures of Cl_2 and O_2 are indicated in these diagrams for different chlorinating atmospheres. According to these diagrams, oxides of the four elements will react with Cl_2 in presence of CO at 800 °C. While using Cl_2+N_2 gas mixture, only oxides of Mg, Ca and Fe could be chlorinated. The thermodynamic probability of chlorinating these oxides decreases as the oxygen partial pressure increases.

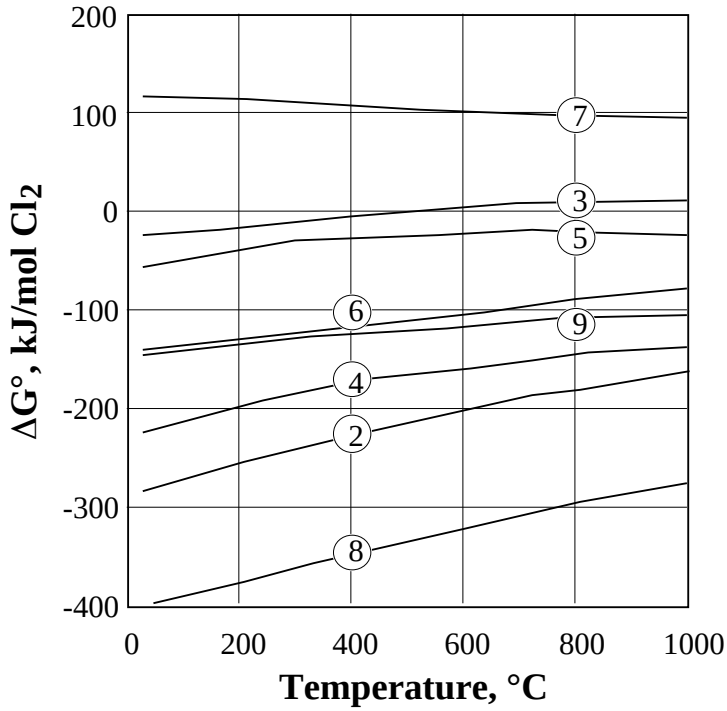


Figure 1 : Standard free energy changes of chlorination and carbo-chlorination reactions as a function of temperature[11,12].

	MgO	+	Cl_2	+		CO	→		$MgCl_2$	+		CO_2	[2]
	MgO	+	Cl_2				→		$MgCl_2$	+	1/2	O_2	[3]
2/3	FeO	+	Cl_2	+	2/3	CO	→	2/3	$FeCl_3$	+	2/3	CO_2	[4]
2/3	FeO	+	Cl_2				→	2/3	$FeCl_3$	+	1/3	O_2	[5]
1/2	SiO_2	+	Cl_2	+		CO	→	1/2	$SiCl_4$	+		CO_2	[6]
1/2	SiO_2	+	Cl_2				→	1/2	$SiCl_4$	+	1/2	O_2	[7]
	CaO	+	Cl_2	+		CO	→		$CaCl_2$	+		CO_2	[8]
	CaO	+	Cl_2				→		$CaCl_2$	+	1/2	O_2	[9]

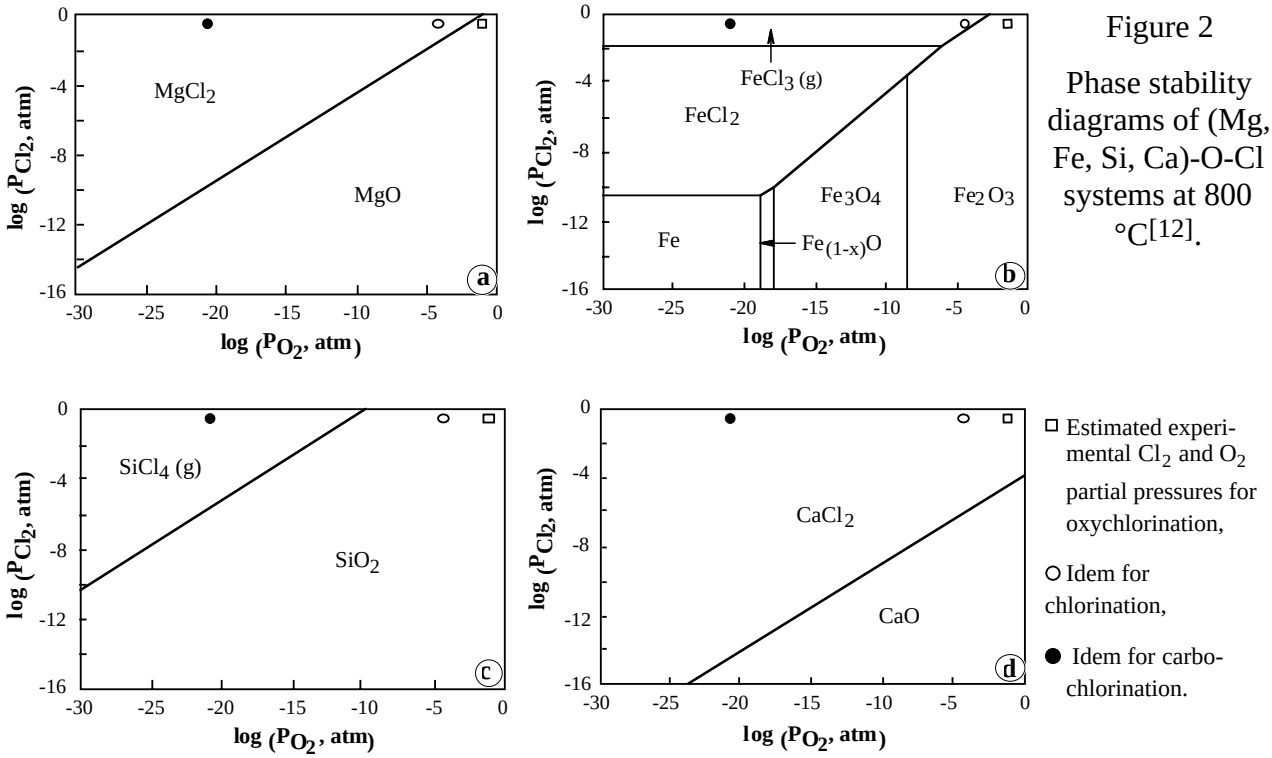


Figure 2

Phase stability diagrams of (Mg, Fe, Si, Ca)-O-Cl systems at 800 °C[12].

EXPERIMENTAL

The sample used in this study was MgO powder with a purity of 98 pct and supplied by PROLABO (Paris, France). It is obtained by calcination of $MgCO_3$. The remaining 2 pct is attributed essentially to the presence of carbonate and/ or oxide of calcium, iron and silicon. Results of Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD) analyses of the magnesium oxide sample indicate that the only identified phase is MgO. Impurites were not detected because of their feeble contents.

The thermogravimetric (TG) chlorination tests were performed with 40 to 100 mg of sample, using the experimental set shown in Figure 3. Its main component is a CAHN 1000 microbalance having a sensitivity of 10 µg. The chlorinating gas mixtures are composed of Cl_2+air, Cl_2+N_2 or Cl_2+CO dried by H_2SO_4 and $CaCl_2$ prior to their introduction in the reaction chamber. The sample was uniformly distributed in a quartz crucible having a section of about 0.5 cm^2. The crucible suspended from the balance by a quartz chain. Non-isothermal tests were carried out by heating the sample in the chlorinating gas mixture by an electrical furnace at a heating rate of about 25 °C/min. Such tests allow a rapid evaluation of the sample's reactivity towards the different chlorinating gas mixtures. The change in the sample's weight and temperature was recorded automatically. The exhaust gases were purified before their release to the atmosphere. For the TG isothermal runs, the sample was heated in nitrogen atmosphere to a given temperature before the introduction of the chlorinating gas mixture in the reaction chamber.

The horizontal experimental set-up, Figure 4, was used to perform few tests to carbochlorinate MgO. This set is composed of a gas metering unit followed by a gas purification unit and a horizontal furnace. In the case of carbochlorination, a carbon furnace was added to eliminate any traces of oxygen. The gaseous reaction products were recovered through condensers and the outlet gases were purified before their release to the atmosphere. The reaction products were examined by SEM and XRD.

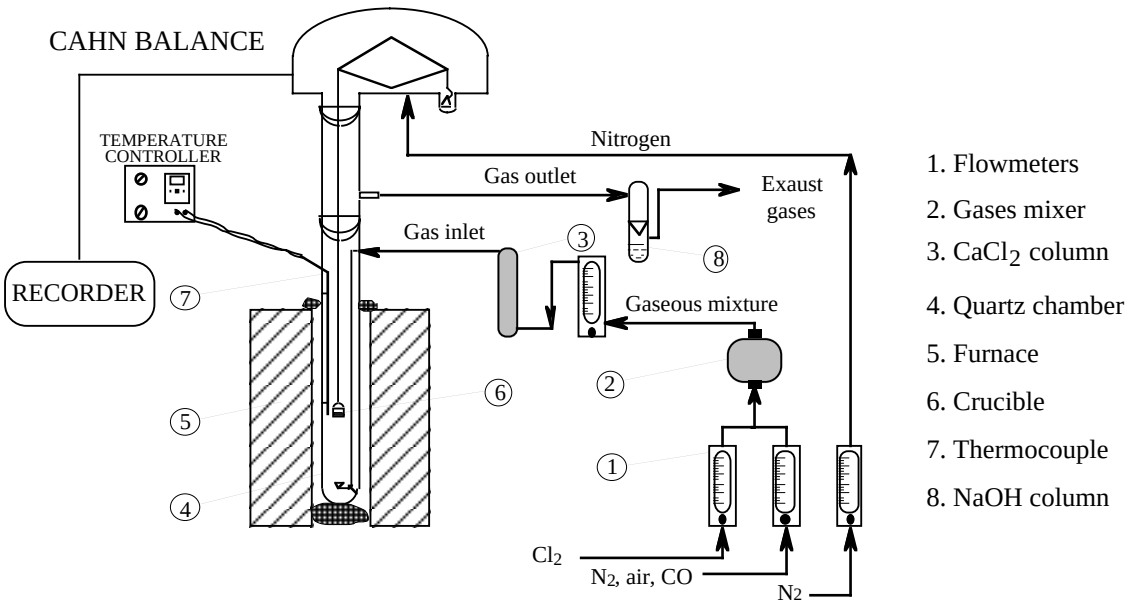
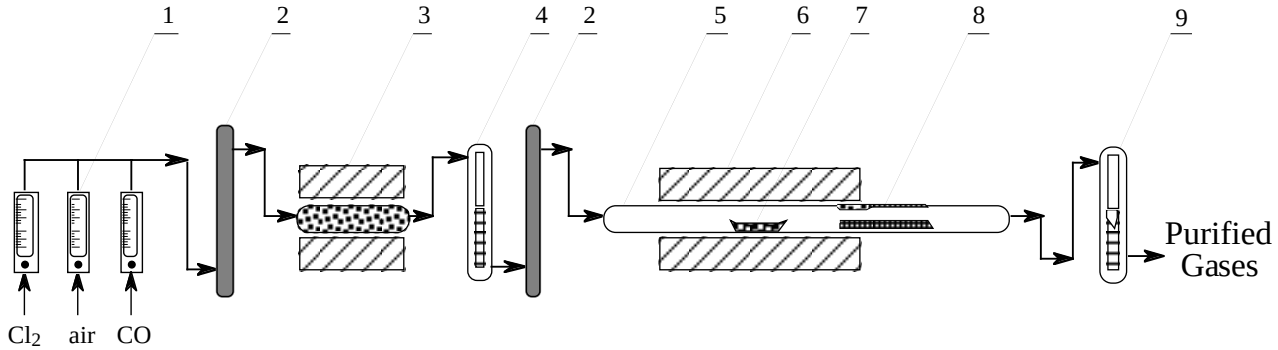


Figure 3 : Thermogravimetric experimental set-up.



1. Flowmeters
2. P_2O_5 columns
3. Carbon furnace
4. Drying column
5. Quartz chamber
6. Furnace
7. Sample boat
8. Condenser
9. NaOH column

Figure 4 : Horizontal experimental set-up.

RESULTS AND DISCUSSION

Nonisothermal TG Measurements

Figure 5 traces the percentage weight loss of MgO *versus* temperature during its treatment in Cl_2+air, Cl_2+N_2 and Cl_2+CO gas mixtures. The chlorination of magnesium oxide started at temperatures higher than 600 °C. The oxychlorination rate of MgO was limited to 3 pct when the sample reacted with the Cl_2+air gas mixture till 1000 °C. The main chlorination product identified by XRD was $MgCl_2$. In the case of chlorination using the Cl_2+N_2 or Cl_2+CO gas mixtures, the continuous increase of the sample's weight, at temperatures higher than 550 °C and 900 °C, respectively, could be explained by the important difference between the formation and volatilization rates of $MgCl_2$. One may underline that boiling point of $MgCl_2$ is 1412 °C[13].

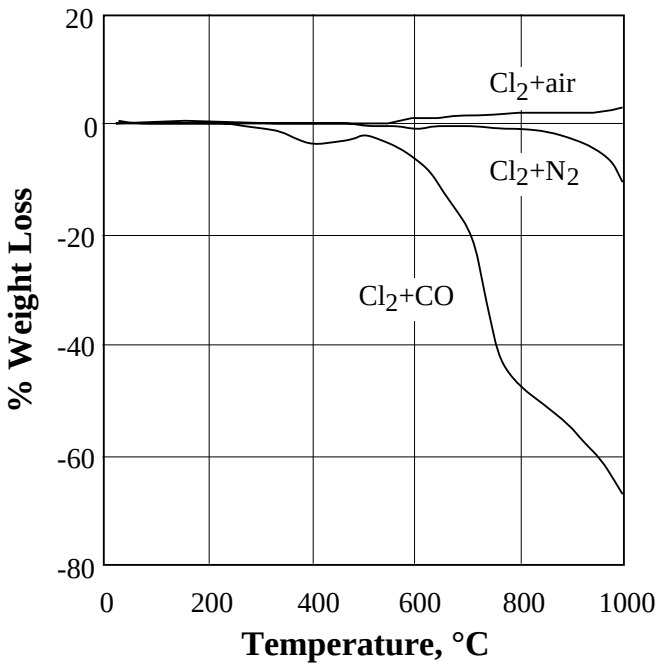


Figure 5 : TG analysis of MgO chlorination in different gas mixtures.

Magnesium oxide reacted with Cl_2+CO at temperatures higher than 500 °C. The reaction rate increased with temperature up to 750 °C. Beyond this temperature, the reaction rate decreased probably due to the fusion of $MgCl_2$ that acts as a diffusion barrier for the carbochlorinating gas mixture. As shown by Figure 5, the increase of the sample's weight is due to a formation rate of $MgCl_2$ that is higher than its volatilization one. The reaction is incomplete at 1000 °C as confirmed by the presence of MgO and $MgCl_2$ phases identified by XRD in the carbochlorination residue.

Isothermal Treatment in the Horizontal Experimental Set

Preliminary data on the reactivity of MgO, obtained in nonisothermal conditions, was completed by a series of experiments performed under isothermal conditions between 500 °C and 1000 °C for a reaction time of two hours. Results of isothermal experiments on the carbochlorination of MgO are grouped in Figure6. Treated residues were lixiviated by water to dissolve the formed $MgCl_2$ for the measurement of the carbochlorination rate of MgO. Besides, the reaction rate was also calculated from the weight losses up to about 700 °C. The obtained reaction rates, by the two methods, are almost equal. This similarity may be attributed to the feeble vapor pressure of $MgCl_2$ that is only 1 mm Hg at 778 °C[13].

The measured and calculated carbochlorination rates of MgO are represented in Figure 6, which shows that about 67 pct of MgO was chlorinated at 500 °C. It also indicates that the reaction rate increased with temperature reaching 82 pct at 675 °C. Afterwards, the reaction rate dropped and only 35 pct of the sample was chlorinated at 700 °C. This result 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

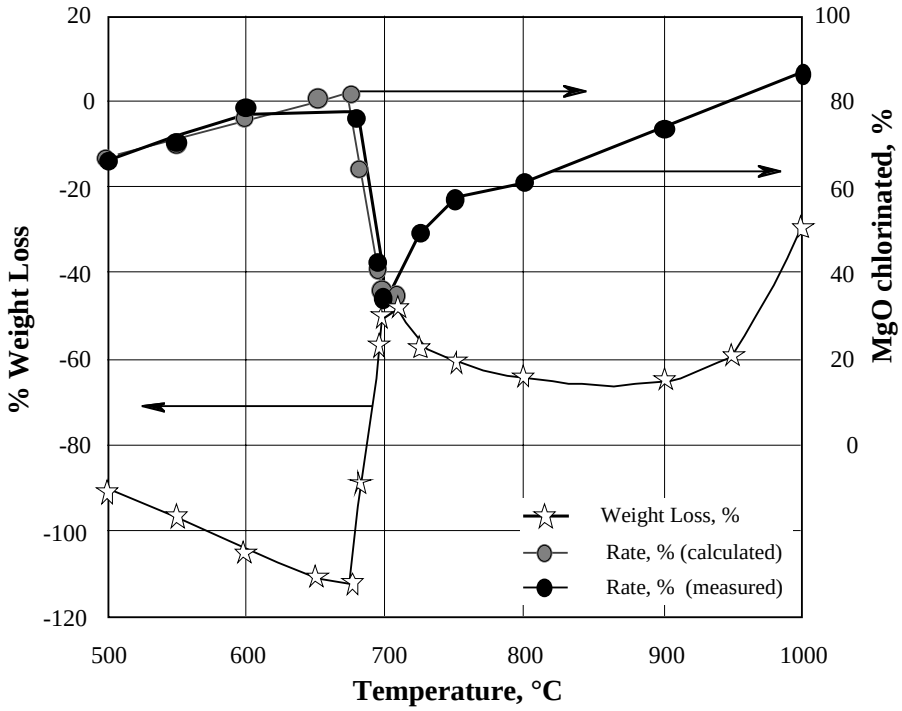


Figure 6 : Carbochlorination of MgO in the horizontal set-up for two hours, showing the measured and calculated rates.

the carbochlorinating gas mixture. A temperature higher than 900 °C is 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 pct of MgO is chlorinated during a reaction time of two hours and $MgCl_2$ and MgO were identified, by XRD, in the residues. This confirms that chlorination of MgO is incomplete even at 1000 °C. On the other hand, the presence of $MgCl_2$ in the treated residues suggests that the carbochlorination rate of MgO is higher than the volatilization rate of $MgCl_2$.

Kinetics of Carbochlorination of MgO by Cl_2+CO

Effect of gas flow rate

The effect of Cl_2+CO gas velocity on the carbochlorination reaction rate was performed to determine the optimum gas velocity. Use of this gas velocity will avoid starvation and will minimize the mass transfers' phenomena. A series of isothermal tests was carried out at 600 °C employing a total gas flow rate of 8 to 60 L/h and keeping the Cl_2/CO molar ratio equal to 1. Figure 7 (a) illustrates the extent of MgO reaction against time as a function of the gas mixture velocity. As mentioned above, the volatilization of magnesium chloride is negligible at temperatures lower than 778 °C. For this reason, the percentage of weight loss could be used to calculate the reaction extent 'X' (X = weight ratio of reacted MgO to its initial weight). Figure 7 (b) traces the reaction rate as a function of the gas velocity ($0.05 \leq X \leq 0.40$). This figure shows that reaction rate increases as the gas flow rate augments up to 40 L/h (linear velocity : 'V_g' = 33 cm/min). For higher gas velocities, the chlorination rate is independent of the gas flow rate. Consequently, a gas flow rate of 48 L/h ($V_g \approx 40$ cm/min) is used for further experimentation concerning the carbochlorination of MgO.

Effect of temperature

The effect of temperature was studied in the range of 425 °C to 715 °C and the corresponding isotherms are grouped in Figure 8. This figure shows that a reaction extent of about 75 pct requires about 120 and 20 minutes at 425 °C and 600 °C, respectively. Figure 8 also reveals that the conversion of MgO to $MgCl_2$ attains a maximum of about 85 pct. This limitation has been also observed by other investigators[4,5]. They suggested that $MgCl_2$ formed on the surface of the MgO particle acts as a barrier against further progress of the reaction. Smith[6] attributed the low conversion of magnesium oxide pellets into magnesium chloride to the differences between the molar volume of these two substances. According to this author, the molar volumes of MgO and $MgCl_2$ are 11.26 and 41.04 cm^3/mol. Thus, the bulky magnesium chloride could cause the clogging of the pellet's pores and hence decrease the mass transfer with the chlorinating gas mixture thus ceasing the chlorination of MgO.

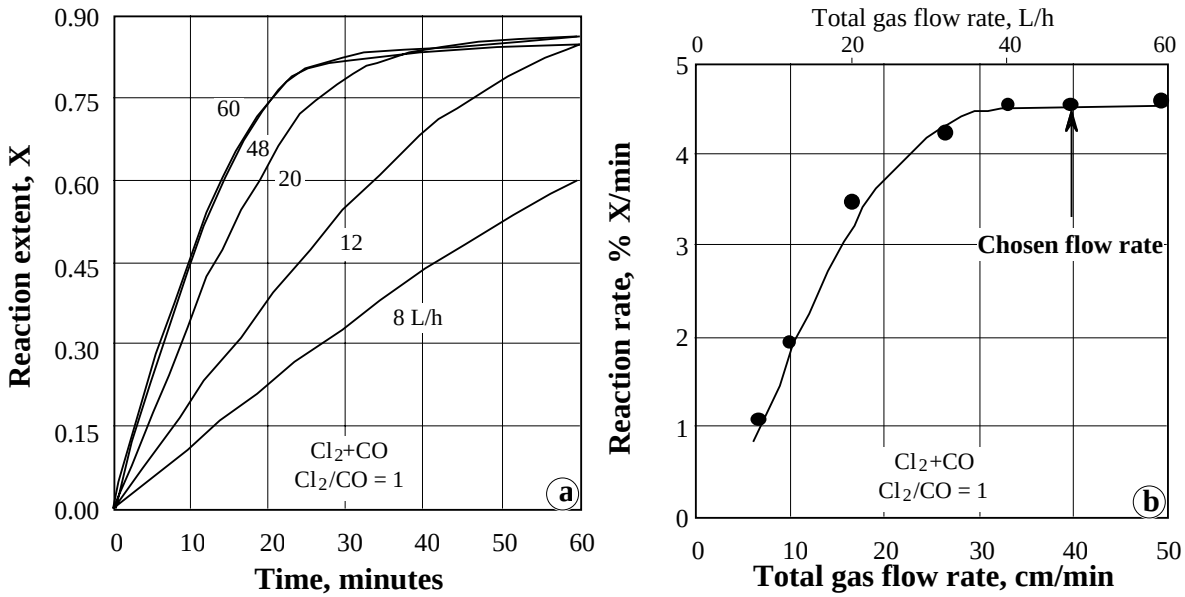


Figure 7 : Effect of gas flow rate on the carbochlorination of MgO at 600 °C.

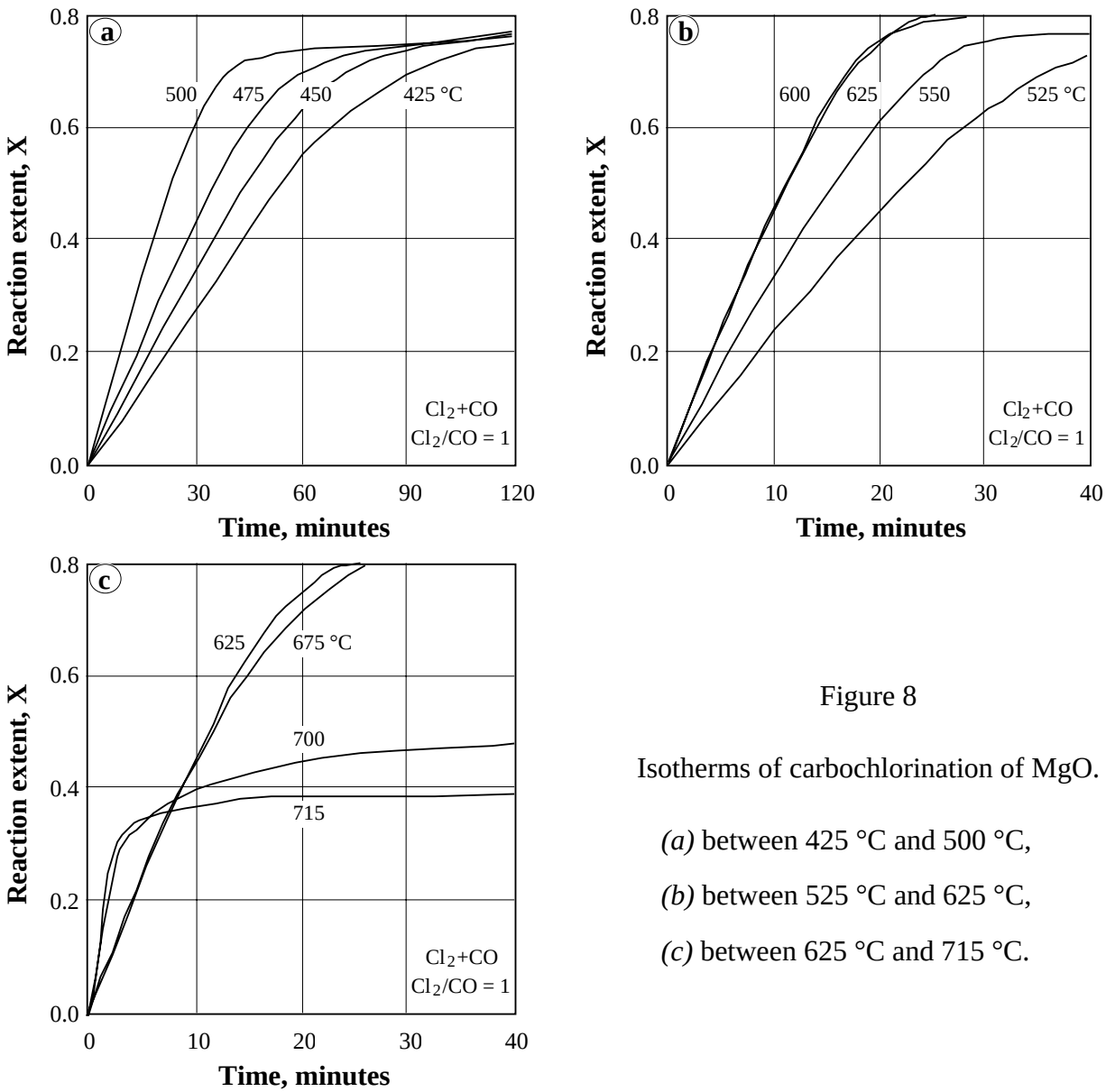


Figure 8

Isotherms of carbochlorination of MgO.

(a) between 425 °C and 500 °C,

(b) between 525 °C and 625 °C,

(c) between 625 °C and 715 °C.

For a reaction time of 20 minutes, the reaction extent decreases as the temperature increases from 625 °C to 715 °C as shown in Figure 8 (c). This behavior is probably due to the fusion of $MgCl_2$[13]. At temperatures lower or equal to 700 °C, the exothermic nature of the carbochlorination reaction of MgO could locally increase the temperature leading to the melting of magnesium chloride. An increase of temperature of about 52 °C is observed by Ishii et al.[5] during the carbochlorination of MgO by Cl_2+C at 600 °C for a reaction time of 10 minutes. At 600 °C, the carbochlorination of MgO, according to equations 1 and 2, is characterized by a ΔH° value of about -144 and -316 kJ, respectively. The effect of fusion of $MgCl_2$ on the extent of the carbochlorination of MgO is clearly manifested at 700 and 715 °C (Figure 8 c) where only 48 and 39 pct of the samples were chlorinated, respectively. This phenomenon is also observed during the carbochlorination of MgO in the horizontal experimental set (Figure 6).

The Arrhenius plot of the carbochlorination of MgO ($0.05 \leq X \leq 0.40$) is given in Figure 9. The apparent activation energy was found at 49 ± 2 kJ/mol between 425 °C and 600 °C. This value suggests that the kinetics of MgO carbochlorination is affected by diffusion. Beyond 600 °C, the reaction rate is almost independent of 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 mass exchange with the chlorinating gas mixture. Due to the hygroscopic nature of $MgCl_2$, it is difficult to examine the carbochlorination residues by SEM. $MgCl_2 \cdot 6H_2O$ formed has a molar volume of 129.5 cm^3/mol[6] that is about 3.2 and 11.5 times that of $MgCl_2$ and MgO, respectively. The formation of $MgCl_2 \cdot 6H_2O$ was confirmed by XRD analysis.

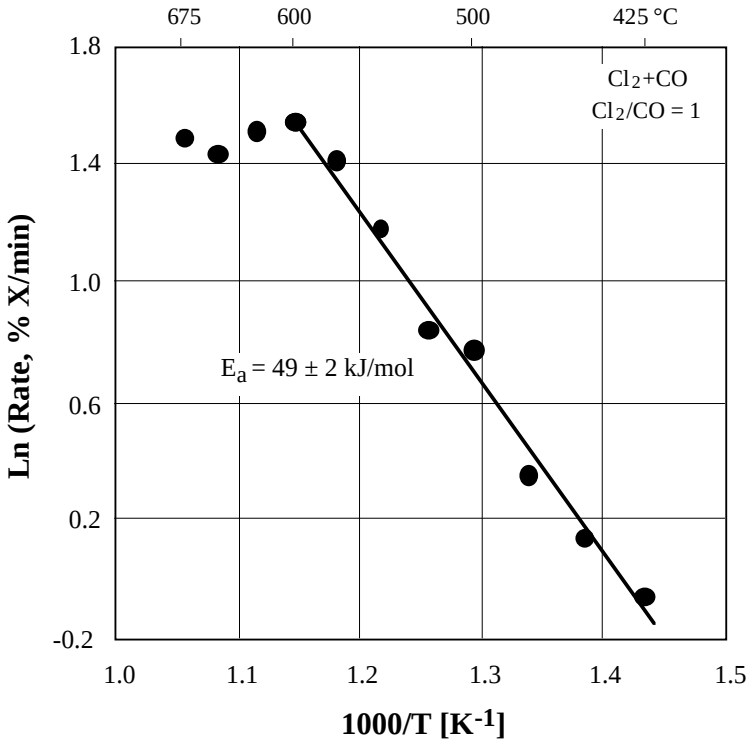


Figure 9 : Arrhenius plot of carbochlorination of MgO by Cl_2+CO.

Effect of (Cl_2+CO) partial pressure

It was examined at 550 °C during the carbochlorination of MgO using the Cl_2+CO+N_2 gas mixture with a gas velocity of 40 cm/min. The Cl_2/CO molar ratio was kept constant and equal to 1, while the partial pressure of Cl_2+CO varied from 0.25 to 1 atm. Figure 10 (a) groups the isotherms as a function of reaction extent *versus* time. At 550 °C, about 580 and 25 minutes are required for the carbochlorination of 70 pct of MgO samples using a gas mixture having 25 and 100 pct Cl_2+CO, respectively. The slow down of MgO chlorination, $X \geq 0.80$, is almost independent of the partial pressure of the reactive gases.

The correlation between the reaction rate ($0.05 \leq X \leq 0.40$) and the partial pressure of the reactive gases is given in Figure 10 (b). The apparent reaction order with respect to Cl_2+CO is 2.37 ± 0.04 as calculated using data of Figure 10 (a). This high and fractional value suggests that the carbochlorination of MgO passes probably through intermediate steps and is dependent of the two reactive gases. The reaction of Cl_2 with CO to form $COCl_2$ could be one of these intermediate steps. The thermodynamic calculations showed that the value of ΔG° and the equilibrium constant at 550 °C for its formation, according to equation 10, are about 3.2 kJ/mol and 0.63, respectively[11].

$$Cl_2 + CO \rightarrow COCl_2 \qquad [10]$$

Effect of Cl_2 partial pressure

This effect was examined at 550 °C. A series of tests was carried out using Cl_2+CO+N_2 with a total flow rate of 40 cm/min. The CO partial pressure was kept constant and equal to 0.33 atm, while the Cl_2 partial pressure was varied from about 0.17 to 0.67 atm. Figure 11 (a) traces the

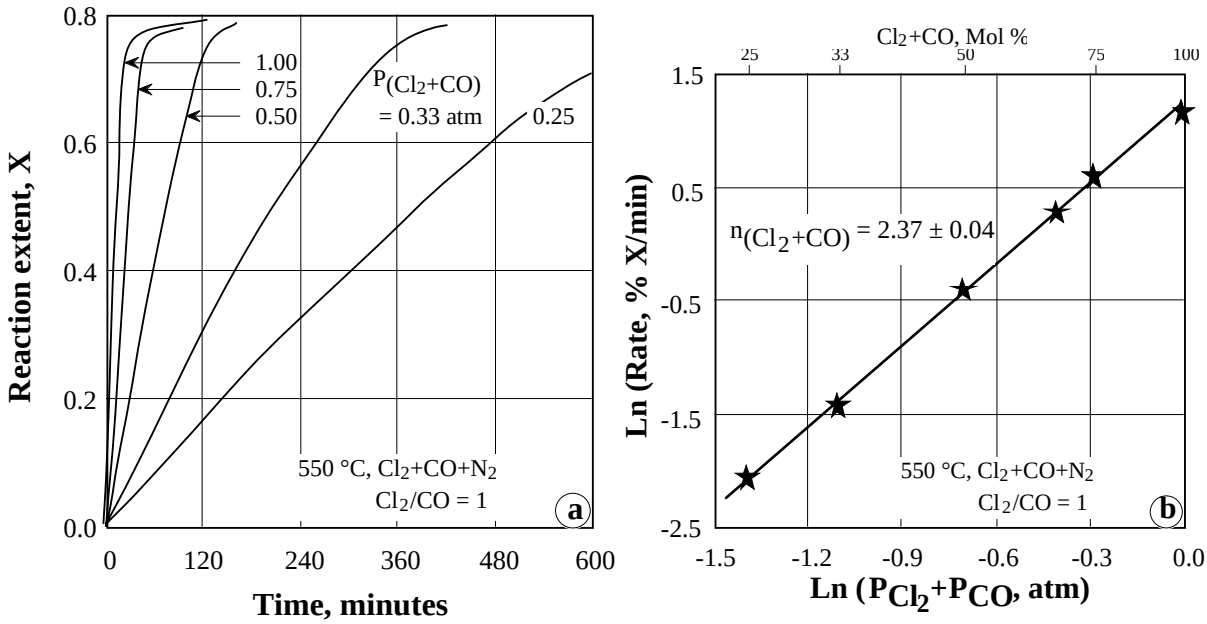


Figure 10 : Isotherms of carbochlorination of MgO *(a)* at various Cl_2+CO partial pressures and *(b)* apparent reaction order with respect to Cl_2+CO.

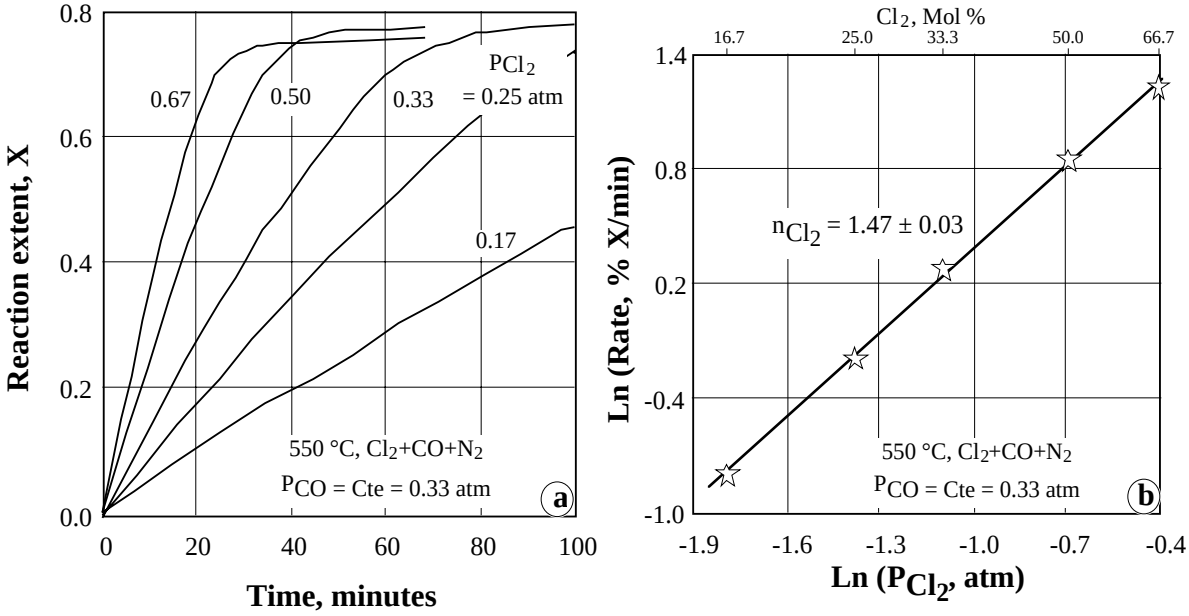


Figure 11 : Isotherms of carbochlorination of MgO *(a)* at various Cl_2 partial pressures and *(b)* apparent reaction order with respect to Cl_2.

evolution of reaction extent as a function of time for different chlorine partial pressures. The apparent reaction order with respect to Cl_2 was deduced from Figure 11 (b) representing the reaction rate ($0.05 \leq X \leq 0.40$) as a function of chlorine partial pressure. The value of $n_{Cl_2} = 1.47 \pm 0.03$ was obtained indicating that the carbochlorination of magnesium oxide is highly dependent on the chlorine partial pressure at 550 °C. Again, the fraction value of reaction order suggests that the carbochlorination of MgO could proceed through the intermediate steps. However, no direct experimental evidence is available to confirm this hypothesis.

Effect of CO partial pressure

Figure 12 (a) groups the isotherms obtained at 550 °C showing the role of CO partial pressure during the carbochlorination of MgO at constant chlorine pressure. The partial pressure of CO, in the Cl_2+CO+N_2 gas mixture, was varied from 0.17 to 0.67 atm. The reaction order was deduced from the slope of the curve relating the evolution of reaction rate ($0.05 \leq X \leq 0.40$) with the partial pressures of CO. The apparent reaction order with respect to carbon monoxide is $n_{CO} = 0.89 \pm 0.04$. This value indicates that the contribution of CO to the carbochlorination of MgO is lower than that of Cl_2 (Figure 11 b) at 550 °C. This result could be due to the dismutation of CO into C and CO_2 according to Eq. 11. The value of $\Delta G°$ and that of the equilibrium constant for this reaction at 550 °C are -26.4 kJ/mol and 4.6, respectively[11]. The carbon formed from CO could affect the carbochlorination of MgO.

$$2\ CO \rightarrow C + CO_2 \qquad [11]$$

The effects of Cl_2+CO, Cl_2 and CO partial pressures on the carbochlorination rate of MgO at 550 °C are compared in Figure 13. The apparent reaction orders, follow the sequence : $n_{(Cl_2+CO)} > n_{Cl_2} > n_{CO}$, and the global apparent reaction order is the algebraic sum of n_{Cl_2} and n_{CO}.

Effect of $Cl_2/(Cl_2+CO)$ ratio

To confirm the asymmetrical effect of Cl_2 and CO on the carbochlorination of MgO another series of experiments was conducted at 550 °C using a Cl_2+CO gas mixture having a $Cl_2/(Cl_2+CO)$ molar ratio that varies from 0.13 to 0.94. The reaction rate is calculated for a reaction extent of 0.05 to 0.40. Some of the isotherms obtained are shown by Figure 14.

As shown in Figure 14 (a), the reaction rate increases with the chlorine content in the gas mixture up to about 58 pct Cl_2. Further, the reaction rate decreases with rise of chlorine content in the gas mixture. Again, as in the previous cases, the reaction was slowed down after a reaction extent of about 0.80. This result is independent of the $Cl_2/(Cl_2+CO)$ ratio in the investigated range.

Figure 15 depicts the reaction rate as a function of the $Cl_2/(Cl_2+CO)$ molar ratio. The maximum reaction rate is obtained for a carbochlorination gas mixture having a $Cl_2/(Cl_2+CO)$ molar ratio equal to 0.58. This value shows the prevailing role of chlorine over that of CO during the carbochlorination of MgO in spite of Eq. 2. These observations conform some of the hypothesis previously discussed that the MgO carbochlorination probably passes through intermediate steps such as [$MgCl_2$·O] as suggested by Ishii et al.[5]. Consequently, the vapor pressure of this compound, in the explored temperature range, is low. In such case, the magnesium chloride will systematically cover the surface of the MgO either by a solid or a liquid layer.

The mathematical fitting of the experimental data was performed using equation 12 developed by Szekely[14].

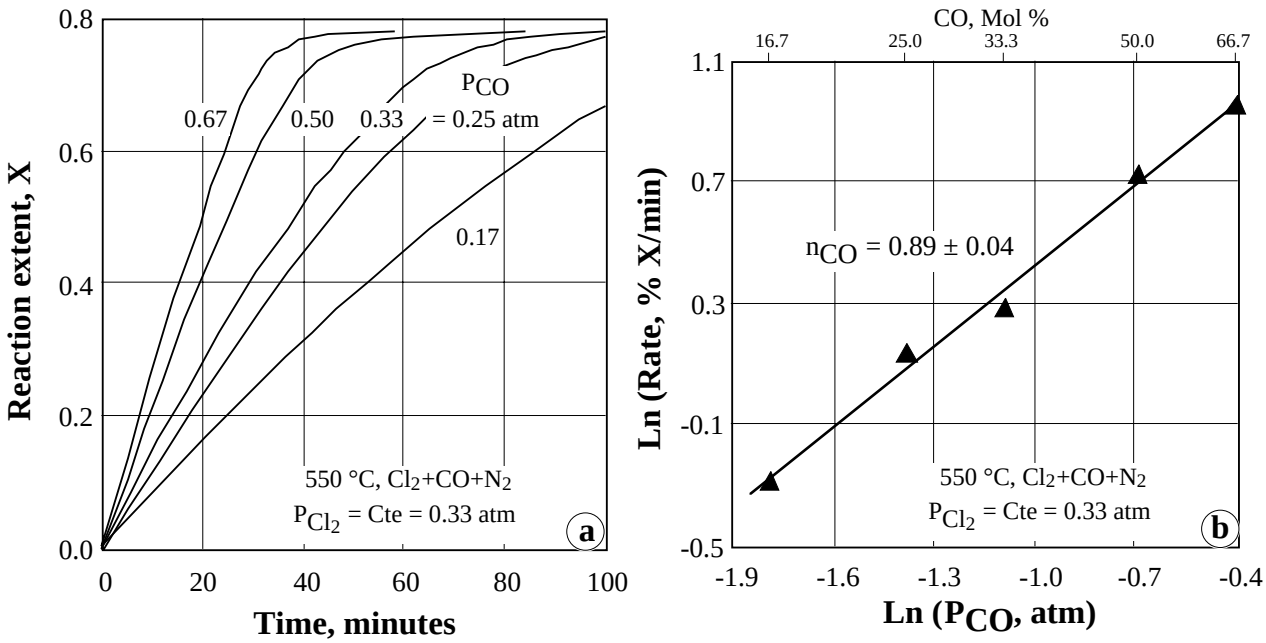


Figure 12 : Isotherms of carbochlorination of MgO *(a)* at various partial pressures of CO and *(b)* apparent reaction order with respect to CO.

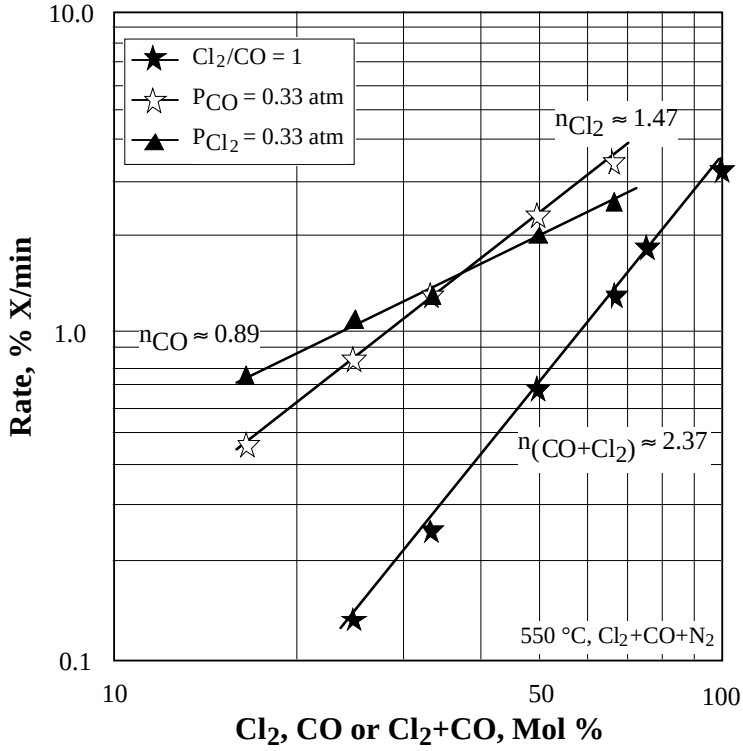


Figure 13 : Effect of gas composition on the reaction rate of carbochlorination of MgO.

$$1-(1-X)^{1/F_p} = kt \qquad [12]$$

Where X is the reaction extent (ratio of weight of the reacted fraction to initial weight),
F_p = particle shape factor (1 for infinite slabs, 2 for long cylinders and 3 for spheres),
k = constant and t = chlorination time.

The best correlation coefficient was obtained using equation 12 with a particle shape factor equal to two. This result combined to the value of the apparent activation energy suggests that the chlorination rate of MgO is ruled by a mixed control process which is both chemical and diffusion controlled.

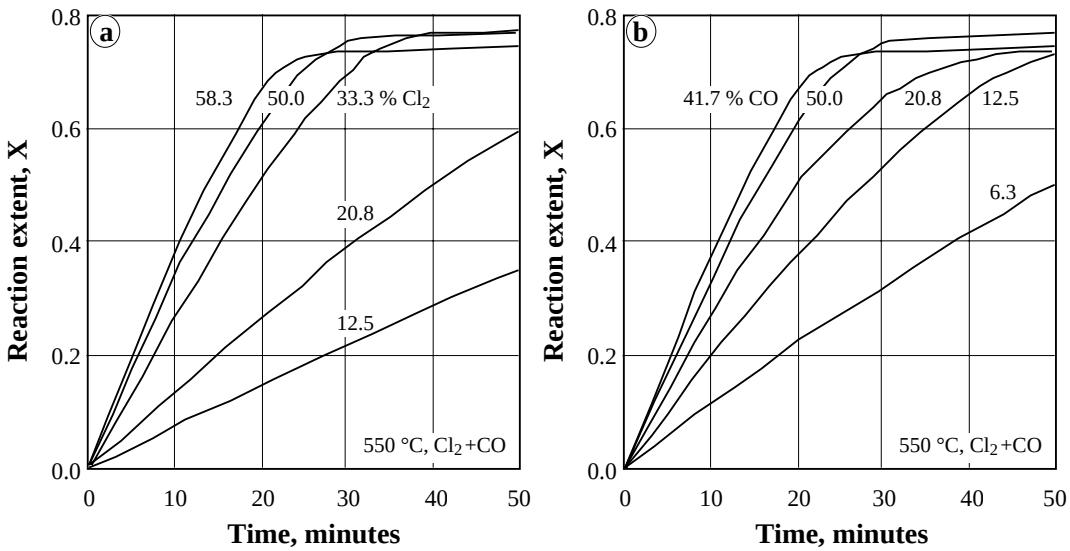


Fig. 14 : Isotherms of reaction of MgO with Cl_2+CO gasmixture having various Cl_2 and CO content.

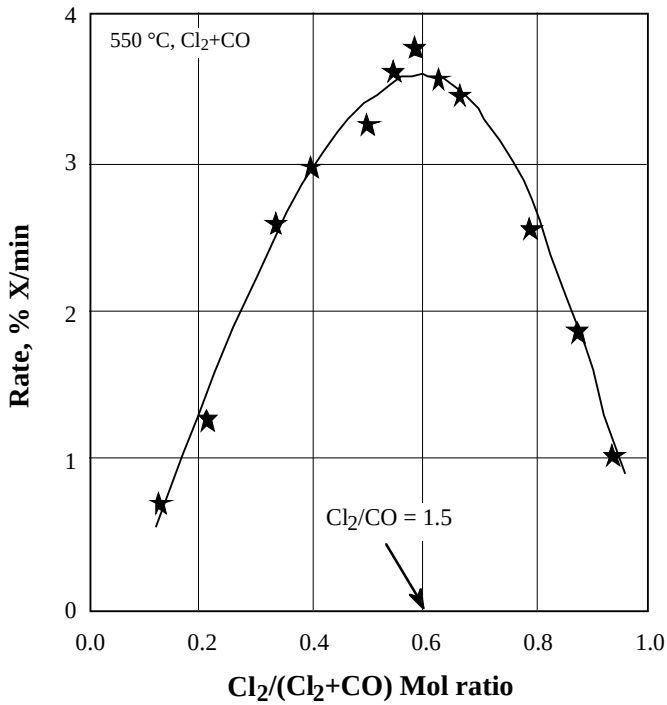


Fig. 15 : Effect of $Cl_2/(Cl_2+CO)$ molar ratio on the reaction rate of MgO carbochlorination.

CONCLUSIONS

In non isothermal conditions, chlorination and carbochlorination of MgO, generating $MgCl_2$, started at temperatures higher than 700 °C and 500 °C, respectively. In both cases, the volatilization rate of $MgCl_2$ was lower than the chlorination rate of MgO. The carbochlorination rate of MgO decreases sharply at about 700 °C due to the fusion of magnesium chloride and the reaction was incomplete at 1000 °C in a reaction time of two hours. The carbochlorination extent of MgO, with Cl_2+CO,was less or equal to 85 pct probably due to the formation of a layer composed of magnesium chloride. Between 425 °C and 600 °C, the apparent activation energy of the carbochlorination of MgO was about 49 kJ/mol. However, the reaction rate was independent of the temperature between 600 °C and 675 °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. At this temperature, the maximum reaction rate is obtained using a Cl_2+CO gas mixture having a Cl_2/CO molar ratio equal to about 0.6.

The data analysis combined to the value of the apparent activation energy suggests that the chlorination rate is controlled by a mixed regime of diffusion and chemical process.

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FIGURE CAPTIONS

Figure 1 : Standard free energy changes of carbochlorination and chlorination reactions as a function of temperature[11,12].

Figure 2 : Phase stability diagrams of (Mg, Fe, Si, Ca)-O-Cl systems at 800 °C[12].

Figure 3 : TG experimental set-up.

Figure 4 : Horizontal experimental set-up.

Figure 5 : TG analysis of MgO chlorination in different gas mixtures.

Figure 6 : Carbochlorination of MgO in the horizontal set-up for two hours, showing the measured and calculated rates.

Figure 7 : Effect of gas flow rate on the carbochlorination of MgO at 600 °C.

Figure 8 : Isotherms of carbochlorination of MgO.

(a) between 425 °C and 500 °C,

(b) between 525 °C and 625 °C,

(c) between 625 °C and 715 °C.

Figure 9 : Arrhenius plot of carbochlorination of MgO by Cl_2+CO.

Figure 10 : Isotherms of carbochlorination of MgO *(a)* at various Cl_2+CO partial pressures and *(b)* apparent reaction order with respect to Cl_2+CO.

Figure 11 : Isotherms of carbochlorination of MgO *(a)* at various Cl_2 partial pressures and *(b)* apparent reaction order with respect to Cl_2.

Figure 12 : Isotherms of carbochlorination of MgO *(a)* at various partial pressures of CO and *(b)* apparent reaction order with respect to CO.

Figure 13 : Effect of gas composition on the reaction rate of carbochlorination of MgO.

Figure 14 : Isotherms of reaction of MgO with Cl_2+CO gas mixture having various Cl_2 and CO content.

Figure 15 : Effect of Cl_2/(Cl_2+CO) molar ratio on the reaction rate of MgO carbochlorination.

TABLE CAPTIONS

Table I : Repartition of USA consumption of magnesium [3].