A Study of Chromite Carbochlorination Kinetics

N. KANARI, I. GABALLAH, and E. ALLAIN

The carbochlorination of a chromite concentrate was studied between 500 °C and 1000 °C using boat experiments. The reaction products were analyzed by scanning electron microscopy (SEM), x-ray diffraction (XRD), and chemical analysis. The carbochlorination of a chromite concentrate at about 600 °C led to the partial selective elimination of iron, thus increasing the Cr/Fe ratio in the treated concentrate. Total carbochlorination of the chromite concentrates and volatilization of the reaction products was achieved at temperatures higher than 800 °C. The kinetics of the chromite carbochlorination was studied between 750 °C and 1050 °C using thermogravimetric analysis (TGA). The results were discussed in terms of the effects of gas flow rate, temperature, partial pressure of Cl_2 + CO, and Cl_2/CO ratio on the carbochlorination process. It was observed that the temperature effect changed significantly with the progress of the reaction. The initial stage of the carbochlorination was characterized by an apparent activation energy of about 135 and 74 kJ/mol below and above 925 °C, respectively, while a value of about of 195 kJ/mol was found for the remainder of the carbochlorination process.

I. INTRODUCTION

ALTHOUGH chromium is found in a variety of minerals[1] (crocoite $PbCrO_4$, vauquelinite $Pb_2Cu[CrO_4][PO_4]$, uvarovite $Ca_3Cr_2[SiO_4]_3$, merumite 4 $(Cr, Al)_2O_3$ 3 H_2O, *etc.*), the main ore of chromium is the chromite mineral, which is a spinel with the simple formula $FeCr_2O_4$. Chromite belongs to the spinel group, and its space group is *Fd*3*m*.[2] However, naturally occurring chromite ore is characterized by the substitution of Fe^{2+} by Mg^{2+} and that of Cr^{3+} by Al^{3+} and Fe^{3+}, with the following general formula: $(Mg, Fe^{2+})(Cr, Al, Fe)_2^{3+}O_4$. Figure 1 shows the chromite structure, where the iron and magnesium occupy the tetrahedral sites while the chromium, aluminum, and iron fill the octahedral ones.[3] The gangue is essentially composed of orthopyroxene, olivine, and plagioclase, as well as hydrous alteration products such as serpentine, chlorite, and talc.

About 75 pct of chromite is used for ferrochromium production. Moreover, chromite is used for chemical, refractory, and foundry applications. Natural characteristics such as the chromium-to-iron ratio, the chromite grain size, and the SiO_2, Al_2O_3, MgO, and P contents can be as important as the Cr_2O_3 content in determining the suitability of a chromite product for various end uses, as well as its market price. Table I[4] represents some chromite specifications for different uses. Thus, the metallurgical chromite is characterized by its high chromium content and a Cr/Fe ratio higher than 2. Conventional mineral processing cannot modify the composition of chromite. This composition can be modified only by using chemical or thermal methods. Chlorination appeared to be a potential approach for beneficiation of poor-chromite concentrates and/or ores.[5–8] This article deals with the carbochlorination of chromite concentrate to increase its Cr/Fe ratio through selective chlorination of iron compounds. The effect of several parameters on the reaction of the chromite mineral with Cl_2 + CO was studied by using thermogravimetric measurements.

The literature is rich with respect to the thermodynamic and kinetic aspects of chlorination of simple oxides contained in chromite (FeO, Fe_2O_3, Cr_2O_3, MgO, Al_2O_3, and SiO_2), using different chlorinating agents. Results of this bibliographic study are summarized in References 5 through 8. However, few articles were devoted to the chlorination of chromite ores and concentrates.

Athawale and Altekar[9] investigated the selective chlorination of iron oxides contained in a chromite concentrate, by using HCl in a fluidized bed. The authors suggested that selective chlorination could be carried out effectively between 900 °C and 950 °C, producing a residue with a high Cr/Fe ratio, which is useful to the steel industry.

The chlorination of a chromite ore (38.2 wt pct Cr_2O_3) and its concentrate (51.1 wt pct Cr_2O_3) with Cl_2 + C between 600 °C and 1000 °C was carried out by Hussein and El-Barawi.[10] Between 800 °C and 1000 °C, they found that the amount of carbon necessary to achieve almost-full chlorination and volatilization of products, for the chromite ore or its concentrate, was 4 and 5 times that of the stoichiometric amounts, respectively.

The decrease in reaction rate at temperatures higher than 800 °C was explained by the possible decomposition of $COCl_2$ formed *in situ*. The chlorination rate of iron was higher than that of chromium and is attributed to favorable thermodynamic data. Finally, the authors suggested that it is possible to make products with Cr/Fe ratios suitable for ferrochromium production by using short-term carbochlorination of chromite ores at 600 °C or even at lower temperatures.

Hussein *et al.*[11] studied the chlorination of Cr_2O_3, Al_2O_3, MgO, FeO, and Fe_2O_3 of their mixtures and of synthetic compounds with the formula $Me^{2+}Me_2^{3+}O_4$ (M = metal), by using Cl_2 + C. The behavior of a chromite ore and its concentrate was also tested using the same chlorination conditions; it was found to be in fair agreement with the results obtained from synthetic compounds.

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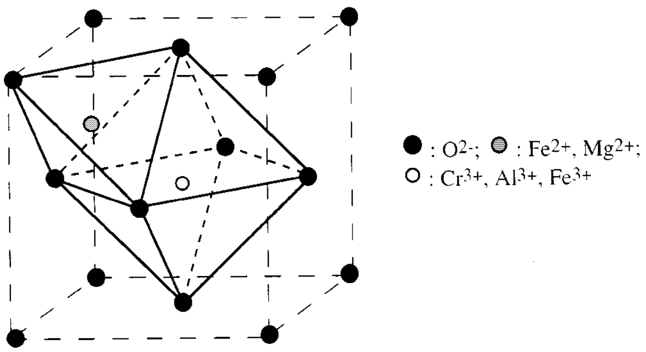


Fig. 1—Spinel chromite structure.[3]

Table I. Chromite Specifications by Use (Weight Percent)[4]

	Metallurgical	Chemical	Refractory	Foundry
Cr_2O_3	>46	>44	30 to 40	>44
Cr/Fe	>2	>1.5	2 to 2.5	2
SiO_2	<10	<3.5	6	<4
Al_2O_3	—	—	25 to 30	—
CaO	—	—	—	<0.5

The European patent 0 096 241[12] described the chlorination of oxidized materials by using C + Cl_2 in a fluidized bed at temperatures higher than 800 °C, in order to produce the metal chlorides. The chlorination of chromite was performed between 1000 °C and 1100 °C. The charge was composed of 20.25 kg of upgraded chromite ore and 7.75 kg of coke. A gas mixture of $Cl_2 + N_2$, at a flow rate of 3 m^3/h and containing 30 pct Cl_2, was used. About 95 pct of all the oxides contained in the chromite were chlorinated and volatilized, and the chlorides ($CrCl_3$, $FeCl_{2/3}$, $AlCl_3$, and $MgCl_2$) were recovered in cyclones, while the dusts were composed of chromium and aluminum oxides.

II. MATERIALS AND EXPERIMENTAL PROCEDURE

The sample of chromite concentrate was obtained from an Albanian plant (Bulqiza, Peshkopi). Scanning electron microscopy (SEM), X-ray diffraction (XRD), microprobe, and chemical analyses were used to determine the composition of this concentrate. Figure 2 gives some aspects of the chromite concentrate as revealed by the SEM and microprobe analyses. Results of the chemical and microprobe analyses concerning five major oxides of the chromite concentrate were grouped in Table II. This concentrate contained about 48 pct Cr_2O_3 and was of a metallurgical grade, characterized by a Cr/Fe ratio close to 3.2. As is shown in Figure 2 and Table II, the microprobe analysis suggested the presence of two different bodies in the concentrate. The chromite is essentially composed of chromium, iron, magnesium, and aluminum oxides, and the gangue contained the oxides of magnesium and silicon along with small amounts of iron and aluminum oxide.

Combining the results of chemical and microprobe analysis, it was found that chromite constituted about 80 pct of the concentrate. Based on the microprobe analysis data, the general formula of the chromite mineral could be the following: $(Fe^{2+}_{0.30}, Mg_{0.70})(Cr_{1.56}, Al_{0.37}, Fe^{3+}_{0.07})O_4$. This solid can also be formulated as 30.9 pct $FeCr_2O_4$, 51.0 pct $MgCr_2O_4$, 13.7 pct $MgAl_2O_4$, and 4.4 pct Fe_3O_4. One may underline that these spinels have the same crystalline structure and lattice parameters, making their identification by XRD almost impossible. References 11 and 13 also mentioned the presence of these compounds in the chromite ores.

Carbochlorination of chromite concentrate was performed using the horizontal experimental setup schematized in Figure 3. This apparatus is composed of a gas-metering unit followed by a gas-purification one and a horizontal furnace. A carbon furnace was added to eliminate any traces of oxygen contained in the gaseous mixture. The gaseous reaction products were recovered, in the condensers, by cooling, and the spent gases were purified before their release to the atmosphere. The reaction products were examined by XRD and SEM and were analyzed using conventional chemical methods.

The kinetic study was performed using samples of chromite mineral contained in the concentrate mentioned previously. It was separated from the gangue by successive treatments using dense liquors. The kinetics of the carbochlorination of chromite with $Cl_2 + CO$ was determined by the thermogravimetric analysis (TGA) technique schematized in Figure 4. Its main unit is a CAHN 1000 microbalance with a sensitivity of 10 μg. The carbochlorinating gas mixture was dried by H_2SO_4 and $CaCl_2$ before its introduction into the reactor. About 40 mg of chromite mineral was used for every test. The sample was uniformly distributed in a quartz crucible with a cross section of about 0.5 cm^2. This crucible was hooked to the balance by quartz rods. It was heated in the carbochlorinating gas mixture by an electrical furnace, with a heating rate of about 7 °C/min. The evolution of the sample weight and temperature was continuously recorded. For the TGA isothermal runs, the sample was heated in nitrogen to the desired temperature before the introduction of the carbochlorination gas mixture into the reactor.

III. THERMODYNAMIC CONSIDERATIONS

The evolution of free standard-energy changes ($\Delta G°$) as a function of temperature, for the carbochlorination reactions (Eqs. [1] through [16]) of major compounds contained in the chromite concentrate, was calculated. The data of References 14 and 15 were used for these calculations. Figure 5 traces the evolution of $\Delta G°$ *vs* temperature for the considered reactions. All the considered reactions were thermodynamically feasible in the explored temperature range. However, the carbochlorination reactions of the iron oxides (Eqs. [7] through [9]) were more favorable than those of the chromium compounds (Eqs. [1] through [3]) at temperatures higher than 500 °C.

$$1/3Cr_2O_3 + Cl_2 + CO \rightarrow 2/3CrCl_3 + CO_2 \qquad [1]$$

$$2/9FeCr_2O_4 + Cl_2 + 8/9CO \rightarrow 2/9FeCl_3 + 4/9CrCl_3 + 8/9CO_2 \qquad [2]$$

$$1/4MgCr_2O_4 + Cl_2 + CO \rightarrow 1/4MgCl_2 + 1/2CrCl_3 + CO_2 \qquad [3]$$

$$1/3Al_2O_3 + Cl_2 + CO \rightarrow 2/3AlCl_3 + CO_2 \qquad [4]$$

$$2/9FeAl_2O_4 + Cl_2 + 8/9CO \rightarrow 2/9FeCl_3 + 4/9AlCl_3 + 8/9CO_2 \qquad [5]$$

$$1/4MgAl_2O_4 + Cl_2 + CO \rightarrow 1/4MgCl_2 + 1/2AlCl_3 + CO_2 \qquad [6]$$

$$2/3FeO + Cl_2 + 2/3CO \rightarrow 2/3FeCl_3 + 2/3CO_2 \qquad [7]$$

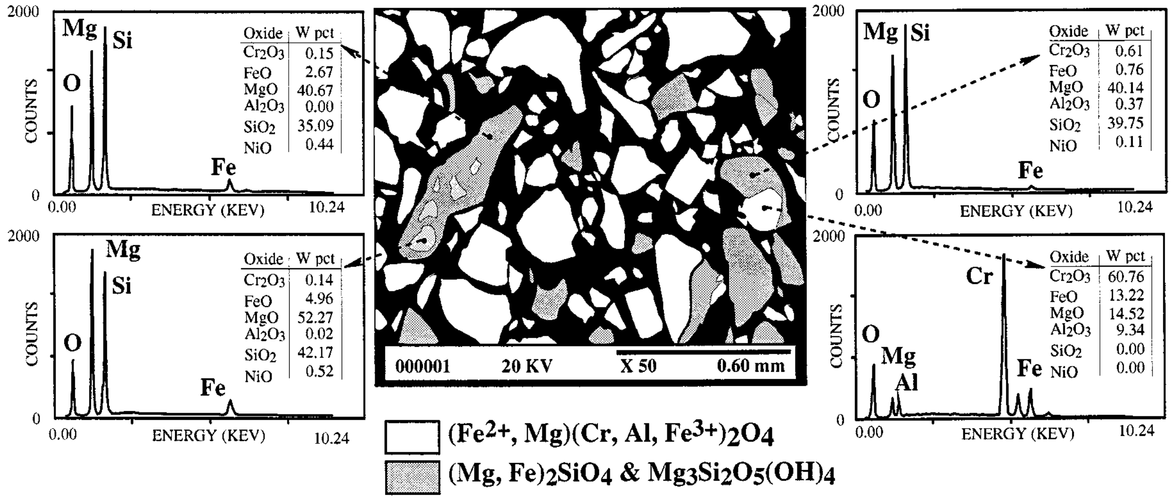


Fig. 2—Results of microprobe and SEM analyses of chromite concentrate.

Table II. Composition of Chromite Concentrate (Weight Percent)

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

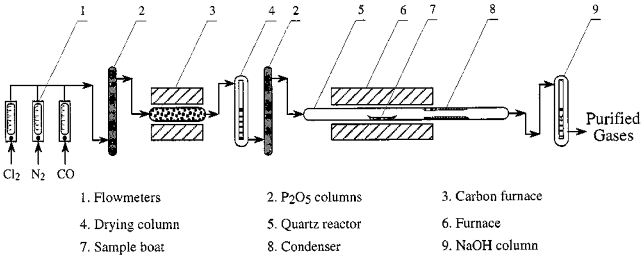


Fig. 3—Horizontal experimental setup.

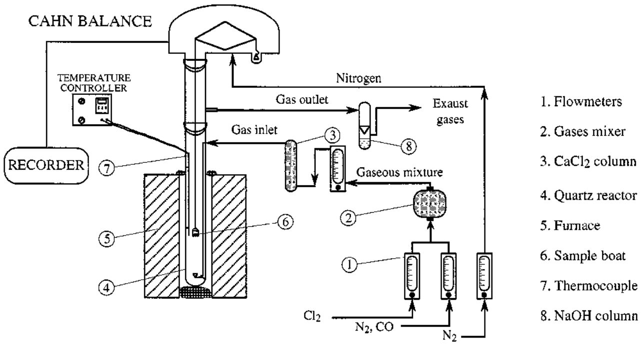


Fig. 4—Thermogravimetric experimental setup.

$$2/9Fe_3O_4 + Cl_2 + 8/9CO \rightarrow 2/3FeCl_3 + 8/9CO_2 \quad [8]$$

$$1/3Fe_2O_3 + Cl_2 + CO \rightarrow 2/3FeCl_3 + CO_2 \quad [9]$$

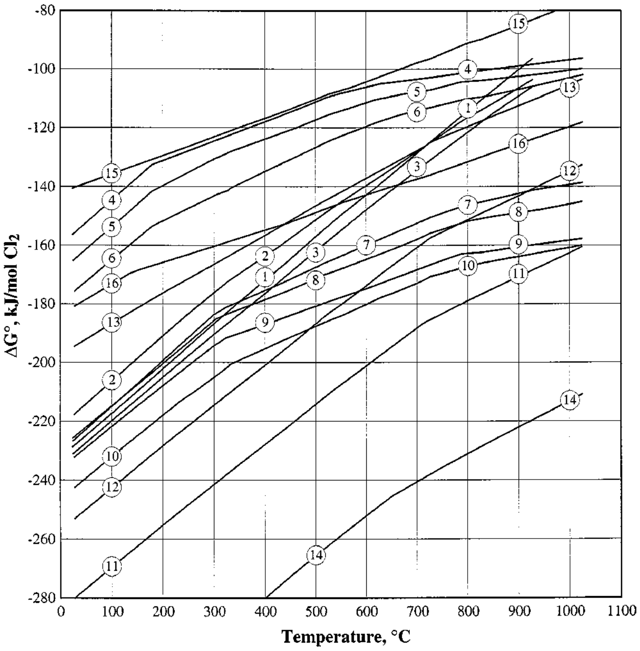


Fig. 5—Evolution of standard free-energy changes as a function of temperature for the carbochlorination of compounds of chromite concentrate.[14,15]

$$1/4MgFe_2O_4 + Cl_2 + CO \rightarrow 1/4MgCl_2 + 1/2FeCl_3 + CO_2 \quad [10]$$

$$MgO + Cl_2 + CO \rightarrow MgCl_2 + CO_2 \quad [11]$$

$$Mg_2SiO_4 + Cl_2 + CO \rightarrow MgSiO_3 + MgCl_2 + CO_2 \quad [12]$$

$$1/4Mg_2SiO_4 + Cl_2 + CO \rightarrow 1/2MgCl_2 + 1/4SiCl_4 + CO_2 \quad [13]$$

$$MnO + Cl_2 + CO \rightarrow MnCl_2 + CO_2 \quad [14]$$

$$1/2SiO_2 + Cl_2 + CO \rightarrow 1/2SiCl_4 + CO_2 \quad [15]$$

$$1/2TiO_2 + Cl_2 + CO \rightarrow 1/2TiCl_4 + CO_2 \quad [16]$$

The phase-stability diagrams of (Cr, Fe, Mg, Al, Si)-O-Cl systems[5,6] suggested that the chlorides were the stable phases during the chlorination of oxides in the presence of a reducing atmosphere. Using carbon monoxide as reducing

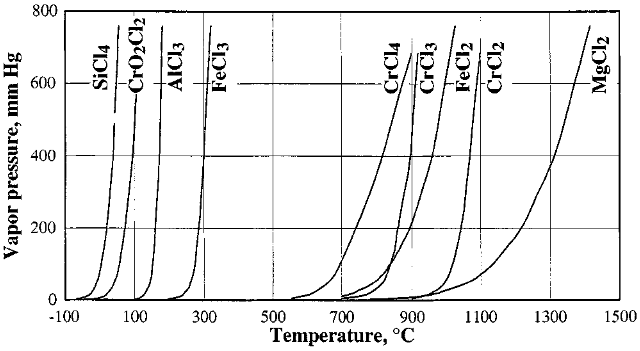


Fig. 6—Evolution of vapor pressure of several chlorides.[1,17]

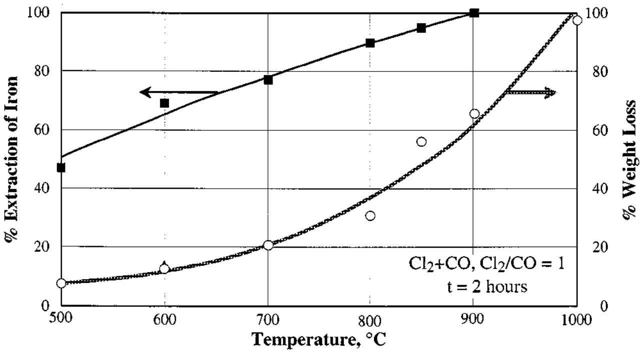


Fig. 7—Evolution of PWL and extraction of iron as a function of temperature during carbochlorination of chromite concentrates for 2 h.

agent, the main products of the carbochlorination of chromium, iron, aluminum, magnesium, and silicon oxides are expected to be $CrCl_3$, $FeCl_3$, $AlCl_3$, $MgCl_2$, and $SiCl_4$,[5,6] respectively. The chromium oxychloride (CrO_2Cl_2) is formed using a chlorinating gas mixture with a high partial pressure of oxygen.[16]

Figure 6 shows the evolution of the vapor pressure of the chlorides of major elements contained in chromite as a function of the temperature.[1,17] As shown by this figure, these chlorides are characterized by a wide difference in vapor pressures at a given temperature. Silicon, aluminum, and ferric chlorides possess a high vapor pressure at temperatures lower than or equal to 300 °C. This suggests that the carbochlorination of chromite compounds at temperatures close to 500 °C permits the volatilization of these chlorides, leading to a residue rich in chromium compounds.

IV. RESULTS

A. *Carbochlorination of Chromite Concentrate in the Horizontal Experimental Setup*

Several grams of the chromite-concentrate sample were treated in $Cl_2 + CO$ ($Cl_2/CO = 1$) between 500 °C and 1000 °C for a reaction time of 2 hours. Figure 7 gives the evolution of the percent weight loss (PWL) of the sample *vs* temperature. The chromite concentrate starts to react with the carbochlorination gas mixture at 500 °C. However, temperatures close to 1000 °C were required to achieve a complete reaction of the sample and volatilization of the reaction products. The residues were analyzed in order to determine their iron content. The extraction curve of iron as function of the temperature is also traced in Figure 7. Clearly, more than 45 pct of the iron contained in the chromite was extracted at 500 °C for a reaction time of 2 hours. At higher temperatures, the extraction of iron increased almost linearly, while the PWL was augmented exponentially.

Another series of carbochlorination experiments on the chromite concentrate was carried out between 500 °C and 850 °C for reaction times of 2 and 8 hours. The chromium and iron contents of the residues were determined by chemical analysis. In addition, the residues and condensates were characterized by XRD and SEM analyses. Figure 8(a) traces PWL of the chromite concentrate *vs* temperature for the two residence times. A small difference in PWL was observed at temperatures lower than 700 °C when the reaction time was increased from 2 to 8 hours. The effects of temperature and reaction time on the extraction of iron and chromium are given in Figure 8(b). Results suggested that the increase in reaction time had only a slight effect on the extraction of iron in the entire temperature range examined. The extraction of chromium at temperatures lower than or equal to 650 °C did not exceed 15 pct and was also slightly dependent on the reaction time. However, the extraction of chromium at temperatures higher than 700 °C depended strongly on the temperature and reaction time. These results suggested that low temperatures and short reaction times might allow the selective extraction of iron with limited losses of chromium.

Table III gives the results of SEM and XRD analyses of several carbochlorination residues and condensates obtained at different reaction times and temperatures. Spinel ((Fe, Mg)(Cr, Al)$_2$O$_4$) was identified to be the main phase in the residue up to 800 °C. As mentioned earlier, it was difficult to detect the evolution of the spinels by XRD. Moreover, the lattice parameters are almost independent of the simultaneous removal of divalent (Fe^{2+} and Mg) and trivalent (Fe^{3+}, Cr, and Al) elements. On the other hand, the lacunaire spinels could be generated, but the current experimental tools do not allow their detection. Chromium trichloride ($CrCl_3$) was identified in the condensate at temperatures higher than or equal to 600 °C. As shown by Table III, magnesium was detected in the condensates at 800 °C, and it was identified as $MgCl_2 \cdot 6H_2O$ due to the hygroscopic nature of $MgCl_2$. These results confirm the possibility of the selective separation of chlorides of Mg and Cr from those of Fe and Al by a careful selective cooling of the gas phase.

Spectra of the SEM analyses of the carbochlorination residues of chromite, along with the semiquantitative analysis, are shown in Figure 9. These results agree with those obtained by chemical analysis. Almost all the iron was removed at temperatures higher than 600 °C. Total extraction of chromium was achieved at 800 °C for a reaction time of 8 hours, and the residue was essentially composed of Cl, Mg, Si, and O. These results indicate that magnesium chloride (Table III) was only partially volatilized due to its low vapor pressure at 800 °C (Figure 6). Moreover, the presence of silicon in this residue suggests than the magnesium silicates were less reactive toward the $Cl_2 + CO$ gas mixture.[6] Water leaching of this residue allows the separation of magnesium chloride from magnesium silicates.

Table IV summarizes the results obtained during the carbochlorination of chromite concentrate between 500 °C and

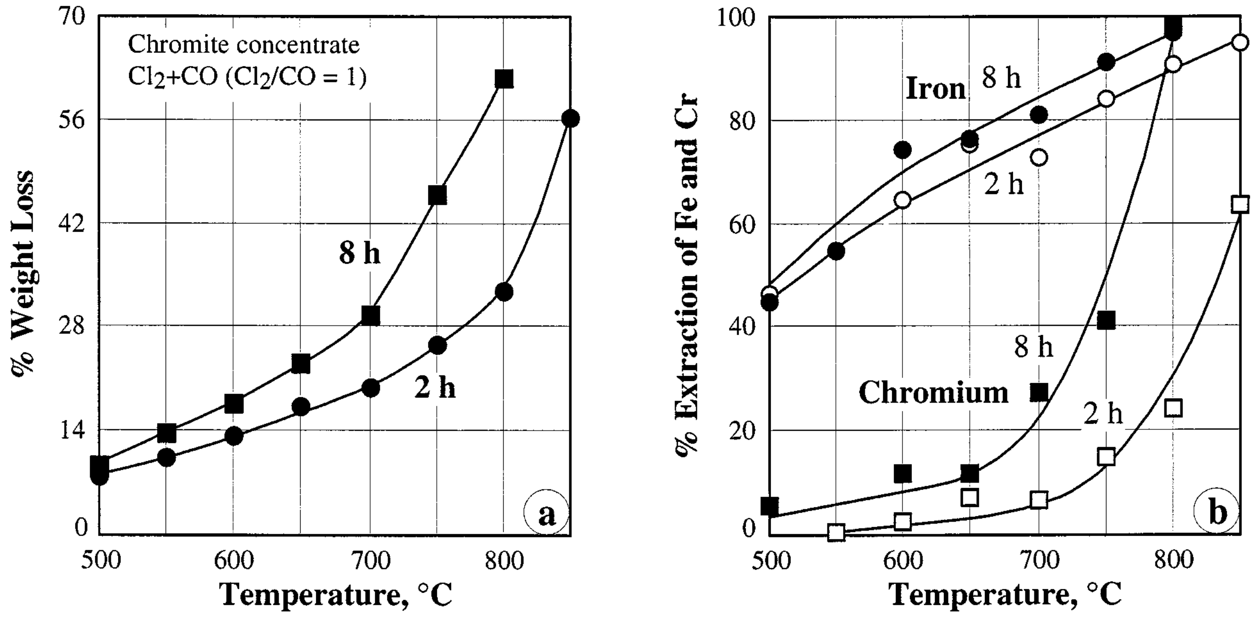


Fig. 8—(*a*) Evolution of PWL and (*b*) extraction of Cr and Fe as a function of temperature and reaction time during carbochlorination of chromite.

Table III. SEM and XRD Results of Carbochlorination Products of Chromite Concentrate for Different Temperatures and Reaction Times

				Condensates			
		Residues		C_1*			
T (°C)	t (h)	SEM	XRD	SEM	XRD	C_2 (SEM)	C_3 (SEM)
500	2	Cr, Mg, Si, Al, Fe, Cl	(Fe, Mg)(Cr, Al)$_2$O$_4$	Cl, Fe, ε Cr			
	8	Cr, Mg, Si, Al, Cl, Fe		Cl, Fe, ε Cr			
600	2	Cr, Si, Mg, Al, Cl, Fe	(Fe, Mg)(Cr, Al)$_2$O$_4$	Cl, Fe, Cr	CrCl$_3$	Cl, Fe, Cr	
	8	Cr, Si, Mg, Al, Cl, Fe		Cl, Fe, Cr, Al		Cl, Fe, Cr, Al	
700	2	Cr, Si, Mg, Cl, Al, Fe	(Fe, Mg)(Cr, Al)$_2$O$_4$	Cl, Fe, Cr	CrCl$_3$	Cl, Fe, Cr, Al	Cl, Cr, Fe
	8	Cl, Cr, Mg, Si, Al, Ca, Fe		Cl, Cr, Fe, Al		Cl, Cr, Fe, Al	Cl, Cr, Al, Fe
800	2	Cl, Cr, Mg, Si, Al, Ca	(Fe, Mg)(Cr, Al)$_2$O$_4$	Cl, Mg	MgCl$_2$	Cl, Cr, Fe, Al, Mg	Cl, Cr, Al
	8	Cl, Mg, Si, Ca	MgCl$_2$**	Cl, Mg		Cl, Cr, Al, Fe	Cl, Cr, Al

*Condensates 1 through 3 were recovered at different temperatures of the condenser.
**Magnesium chloride was identified as $MgCl_2 \cdot 6H_2O$.

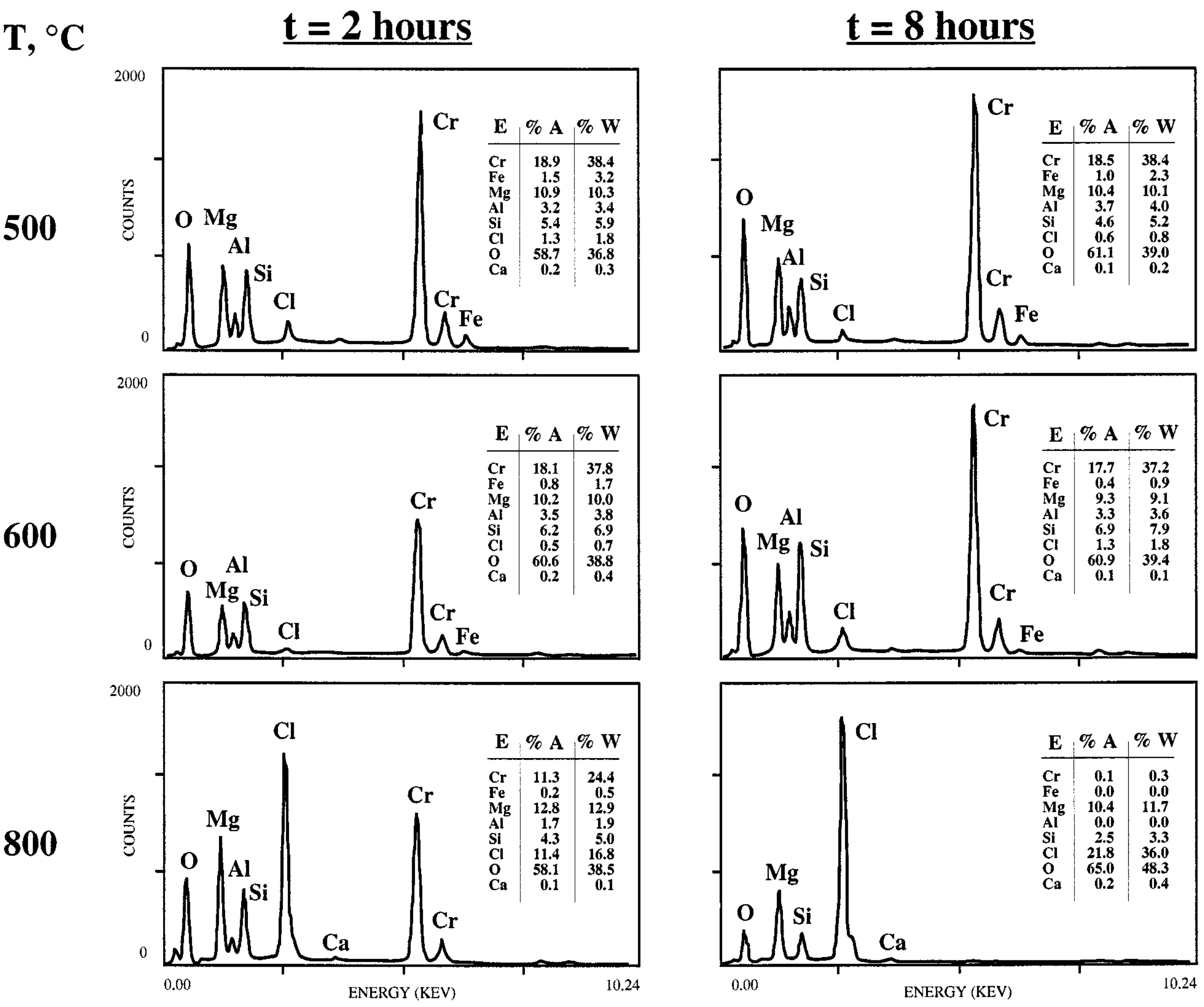
800 °C. As shown in this table, the initial Cr/Fe ratio is close to 3.2. This ratio increases as the carbochlorination temperature and time is increased. It was doubled during the carbochlorination of the chromite concentrate at 500 °C, with limited losses of chromium. This suggests that the carbochlorination of a chromite ore and/or a concentrate with a low Cr/Fe ratio, around 500 °C, will lead to the increase of this ratio to a satisfactory level for the ferrochromium production specifications. The selective chlorination of iron could be also advantageous for chromite concentrates used for other applications.

In order to obtain an insight into the reaction mechanism of this complex solid, it was worthwhile to carry out a kinetic study of the carbochlorination of the chromite by a Cl_2 + CO gaseous mixture, using TGA at a relatively high temperature. The following paragraphs describe these kinetic parameters as determined by TGA.

B. *Kinetics of Carbochlorination of a Chromite Mineral*

1. *Nonisothermal TGA*

The nonisothermal carbochlorination of a chromite mineral was investigated from room temperature to about 975 °C, using the apparatus described in Figure 4. Figure 10 gives PWL as a function of temperature, at temperatures higher than 400 °C. The chromite started to react with the carbochlorinating gas mixtures at about 500 °C. Total reaction of the chromite with Cl_2 + CO and volatilization of

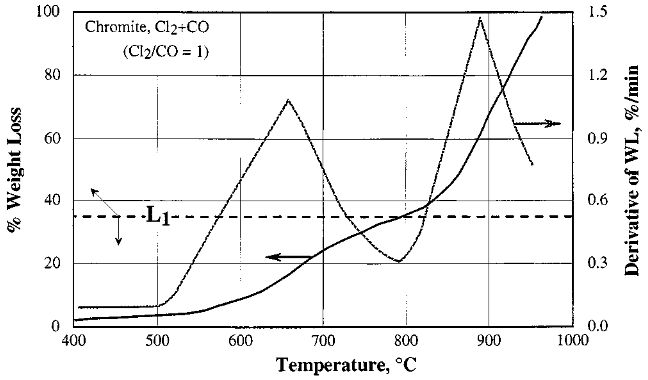


E : Element, % A : Atomic pct, % W : Weight pct.

Fig. 9—Semiquantitative analyses of the carbochlorination residues of chromite concentrate at different temperatures for a reaction time of 2 and 8 h.

Table IV. Evolution of Cr/Fe Ratio in the Carbochlorination Residues of Chromite Concentrate as a Function of the Treatment's Conditions

T, °C	Time, h	Cr, Wt Pct	Fe, Wt Pct	Cr/Fe
Raw sample	—	34.2	10.8	3.2
500	2	40.9	6.3	6.5
	8	35.7	6.6	5.4
600	2	38.5	4.4	8.8
	8	36.7	3.4	10.8
700	2	39.9	3.7	10.8
	8	35.2	2.9	12.1
800	2	38.7	1.5	25.8



L_1 : Weight loss calculated for the carbochlorination of ($FeCr_2O_4$+Fe_3O_4).

Fig. 10—Evolution of PWL of the sample and derivative of WL *vs* temperature during nonisothermal carbochlorination of chromite.

the reaction products were achieved at about 975 °C. The PWL curve had a plateau of weight loss (≈35 PWL) observed at about 775 °C prior to a sharp increase of PWL at temperatures higher than 825 °C. The derivative of the PWL traced in Figure 10 shows clearly the existence of two regions of distinct kinetics. The PWL observed corresponds roughly to the calculated weight loss for the carbochlorination of Fe_3O_4 and $FeCr_2O_4$ (refer to L_1 in Figure 10), both contained in the chromite. This could not be attributed to

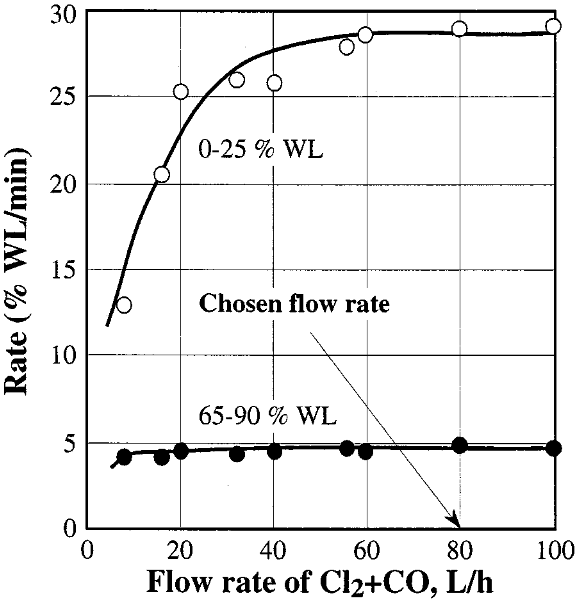


Fig. 11—Effect of gas flow rate on the carbochlorination of chromite at 1000 °C.

the difference between the rate of $MgCl_2$ formation and that of its volatilization. Moreover, the slowdown of the reaction rate at about 35 PWL was also observed during the oxychlorination of chromite by $Cl_2 + O_2$, where the volatilization rate of $MgCl_2$ was higher than that of its formation.[6,8]

2. *Effect of gas flow rate*

The effect of gas flow rate was studied at 1000 °C during the carbochlorination of chromite with a gas mixture which had an equimolar content of carbon monoxide and chlorine. The total flow rate of Cl_2 + CO was varied from 8 to 100 L/h. It was interesting to follow the evolution of the reaction rate as function of gas flow rate at different PWL levels of the sample. Figure 11 gives a typical example of the reaction-rate evolution *vs* flow rate for the WL range up to 25 pct and between 65 and 90 pct. For a gas flow rate higher than 20 L/h, the initial reaction rate was at least 5 times faster than that obtained for a WL higher than 65 pct. On the other hand, the reaction rate seems to be almost independent of the gas flow rate for values higher than 60 L/h, regardless of the PWL chosen. A gas flow rate of 80 L/h (linear gas velocity (V_g) of 1.1 cm/s) was used to study the effect of other parameters on the carbochlorination of chromite.

3. *Effect of temperature*

The effect of temperature during the isothermal carbochlorination tests of a chromite sample was studied between 750 °C and 1050 °C. Results are given in Figure 12 as PWL *vs* time. About 400 minutes were required to carbochlorinate 90 pct of the sample at 775 °C, while only 5 minutes were necessary to reach the same PWL at 1050 °C. On the other hand, the reaction rate up to 35 PWL was rapid in the investigated temperature range.

Different kinetics equations[18] were used to fit the experimental data concerning the evolution of the reaction extent (ratio of weight of the reacted fraction to initial weight) as a function of time. The best mathematical fitting of the experimental data was obtained using Eqs. [17] and [18]. As mentioned before, the chlorination of $(Fe, Mg)(Cr, Al)_2O_4$ proceeds in two steps. The first is up to 35 pct of weight loss, which corresponds roughly to the chlorination of $FeCr_2O_4$ characterized by a high reaction rate. The second step is that of the chlorination of $Mg(Cr, Al)_2O_4$, with a weight loss of 35 to 100 pct and characterized by a relatively slow rate of reaction.

Figure 13 shows the mathematical fitting of experimental data for a reaction extent of 5 to 35 PWL. Up to 850 °C, the reaction progresses according to Eq. [17], with a correlation coefficient of 0.971. Equation [17] represents the pore diffusion control in the reaction of porous or nonporous solids with a porous product layer of spheres. This suggests that

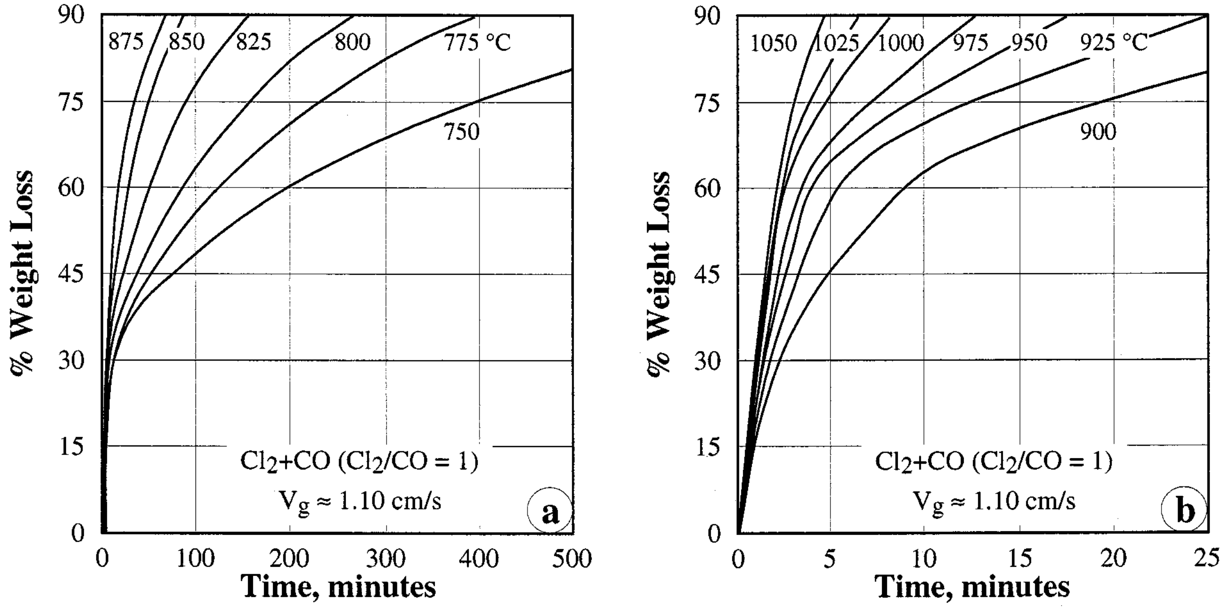


Fig. 12—Isotherms of carbochlorination of chromite from (*a*) 750 °C to 875 °C and (*b*) 900 °C to 1050 °C.

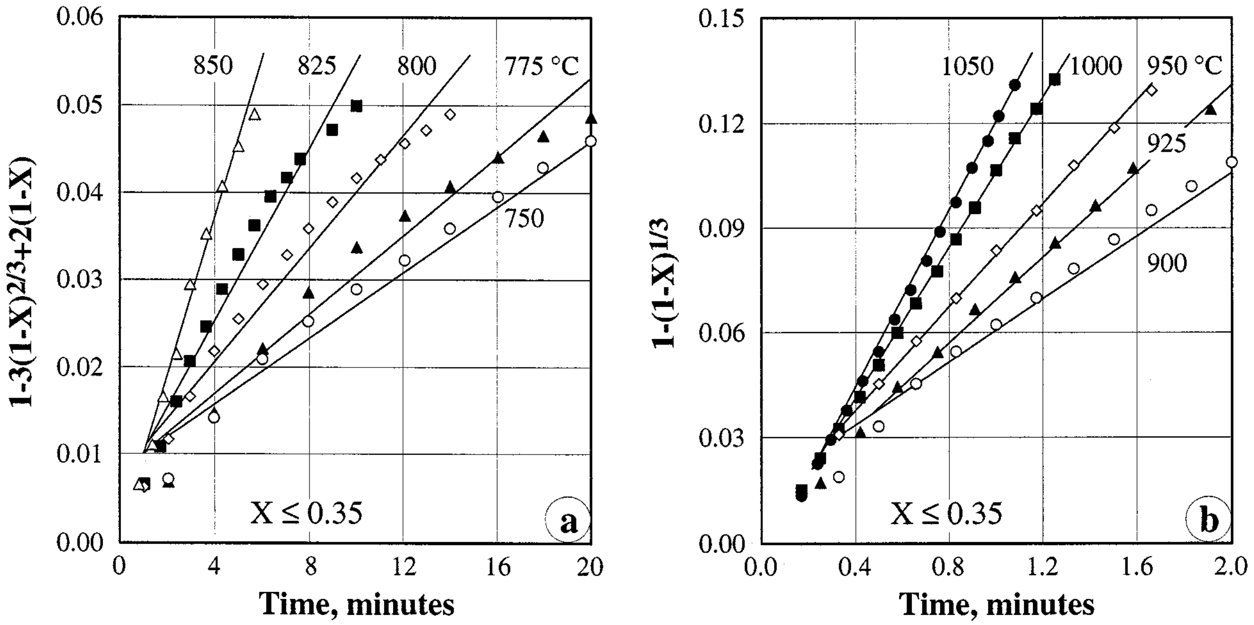


Fig. 13—(*a*) and (*b*) mathematical fitting of the carbochlorination data ($X \leq 0.35$) using Eq. [17] and [18].

the diffusion of iron and chromium in the spinel could be the slowest step during the chlorination of the chromite. At temperatures higher than 925 °C, Figure 13(b) suggests that the experimental data fit Eq. [18], with a correlation coefficient of 0.991. Equation [18] is considered to describe a reaction controlled by the chemical reaction in the case of shrinking nonporous particles (with or without a solid porous product) and porous particles with unchanged overall sizes. This suggests that the chlorination of chromite is controlled by the chemical reaction. This change may be attributed to the presence of nonvolatilized $CrCl_3$ (Figure 6) and/or molten magnesium chloride, which offers a privileged access for the chlorination of the unreacted portion of chromite.[6] Such an hypothesis is partially confirmed by the change of the apparent activation energy from 135 to 74 kJ/mol around 925 °C.

For the chlorination of $Mg(Cr, Al)_2O_4$ and the rest of the sample, Eq. [17] seem to be the most appropriate to describe the evolution of the reaction extent as function of time for the temperature range from 750 °C to 1050 °C, with a correlation coefficient of 0.996 (Figures 14(a) and (b)).

$$1 - 3(1 - X)^{2/3} + 2(1 - X) = kt \qquad [17]$$

$$1 - (1 - X)^{1/3} = kt \qquad [18]$$

where k = constant and t = chlorination time.

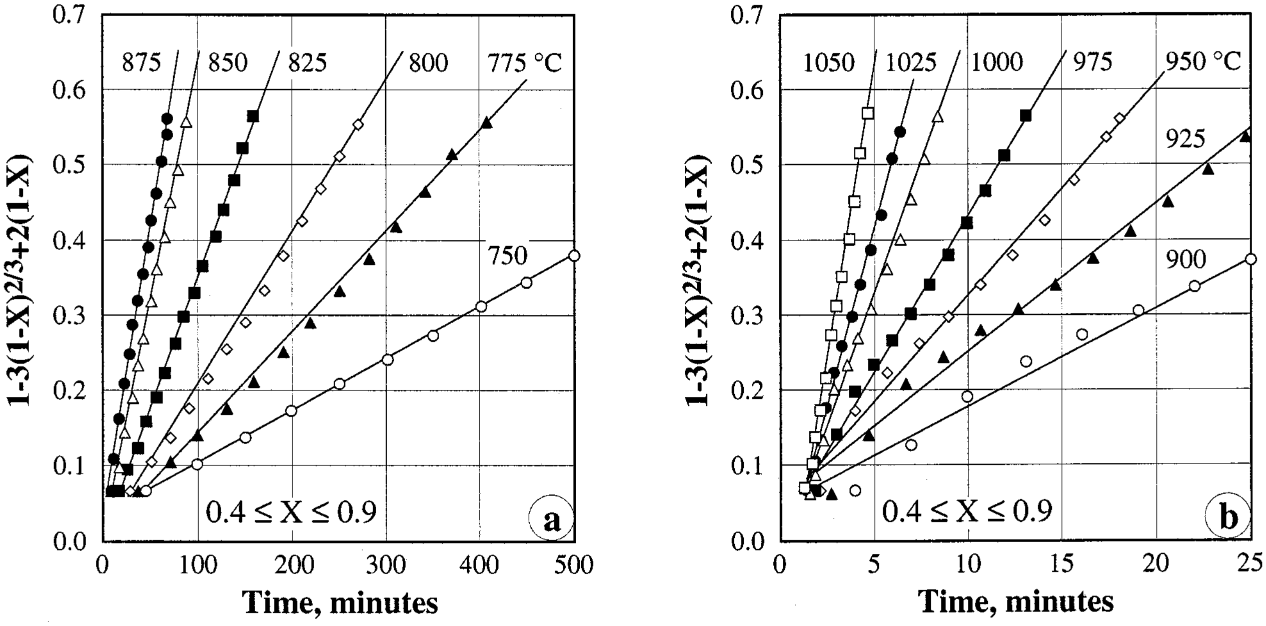


Fig. 14—(*a*) and (*b*) mathematical fitting of the carbochlorination data ($0.4 \leq X \leq 0.9$) using Eq. [17].

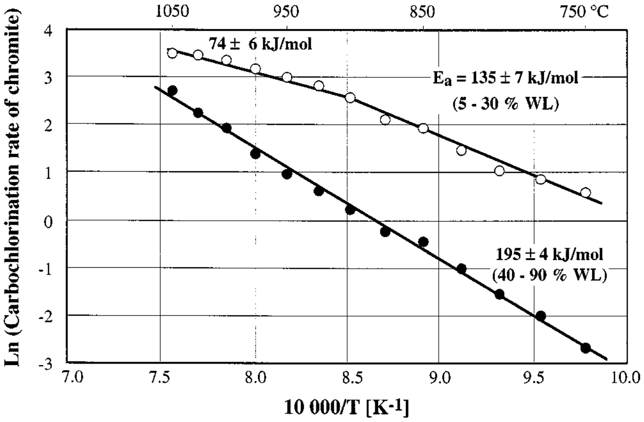


Fig. 15—Arrhenius diagrams of the chromite carbochlorination.

The effect of temperature on the carbochlorination was estimated thanks to the Arrhenius diagram. Figure 15 gives plots for PWL ranging from 5 to 30 pct and from 40 to 90 pct. The apparent activation energies of about 135 and 74 kJ/mol were calculated for the carbochlorination of chromite, up to 30 PWL, below and above 925 °C. A higher value of E_a of about 195 kJ/mol characterizes the carbochlorination process between 40 and 90 PWL.

4. *Effect of (Cl_2 + CO) partial pressure*

To determine this effect, a series of isothermal tests was carried out at 1000 °C. A gas mixture of $Cl_2 + CO + N_2$, with a linear velocity of 1.10 cm/s, was used. The Cl_2/CO molar ratio was kept constant and equal to 1, while the (Cl_2 + CO) content was varied from 15 to 100 pct. Figure 16a represents the obtained data plotted as PWL *vs* time. Results show that the time required to obtain a given PWL decreased with the raise of the percent Cl_2 + CO in the gas mixtures. The evolution of the reaction rate as a function of the partial pressure of Cl_2 + CO for the 2 PWL ranges is traced in Figure 16(b). The apparent reaction orders obtained were 1.30 and 1.40 for $5 \leq \text{PWL} \leq 30$ and $40 \leq \text{PWL} \leq 60$, respectively. These noninteger values may reflect a complex mechanism, probably involving several intermediate steps.

5. *Effect of $Cl_2/(Cl_2 + CO)$ ratio*

The effect of the $Cl_2/(Cl_2 + CO)$ molar ratio was also studied at 1000 °C using a Cl_2 + CO gas mixture with V_g of 1.10 cm/s. The chlorine content was varied from 10 to 90 pct. Figures 17(a) and (b) show the data plotted as PWL *vs* time. About 9 minutes were required to obtain 80 PWL of the sample using a gas mixture containing 10 or 90 pct Cl_2. The evolution of the reaction rate as function of $Cl_2/(Cl_2 + CO)$, for $5 \leq \text{PWL} \leq 30$ and $40 \leq \text{PWL} \leq 60$, is illustrated in Figure 17(c). It indicates that the maximum reaction rate was obtained for a gas mixture with an almost equimolar Cl_2 and CO content.

V. CONCLUSIONS

The carbochlorination of chromite at about 600 °C could be used for upgrading the chromium concentrates and ores. More than 60 pct of iron was extracted during the treatment of a chromite concentrate at this temperature during 2 hours, with a chromium extraction of less than 5 pct. Consequently, the Cr/Fe ratio was at least doubled. The reaction time and temperature had only a slight effect on the kinetics of iron removal. However, total extraction of chromium was achieved at temperatures higher than 750 °C and it depended on the temperature and reaction duration.

The partial removal of magnesium as $MgCl_2$ occurred at temperatures higher than 800 °C. Carbochlorination of the chromite concentrates at these temperatures, followed by a controlled cooling of the gas phase, allows selective separation of chlorides of major elements contained in the chromite.

The effect of temperature on the reaction of the chromite mineral with Cl_2 + CO, between 750 °C and 1050 °C, changes with the reaction progress. The average value of

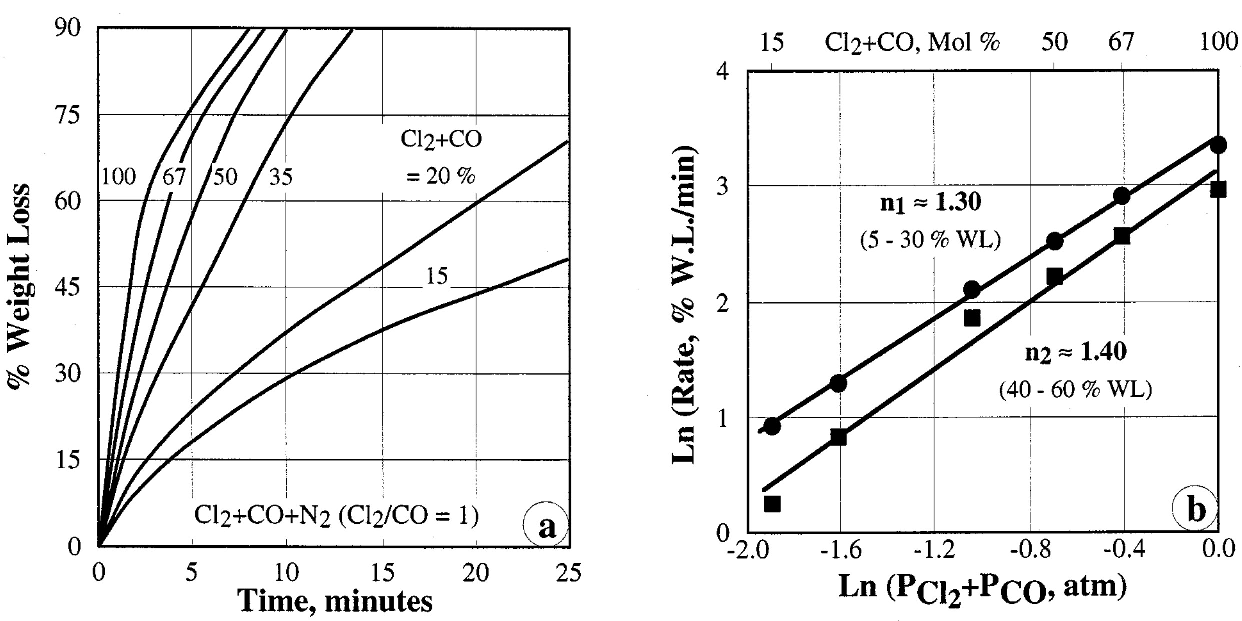


Fig. 16—Isotherms of carbochlorination of chromite at 1000 °C (*a*) using various Cl_2 + CO contents and (*b*) apparent reaction orders with respect to Cl_2 + CO.

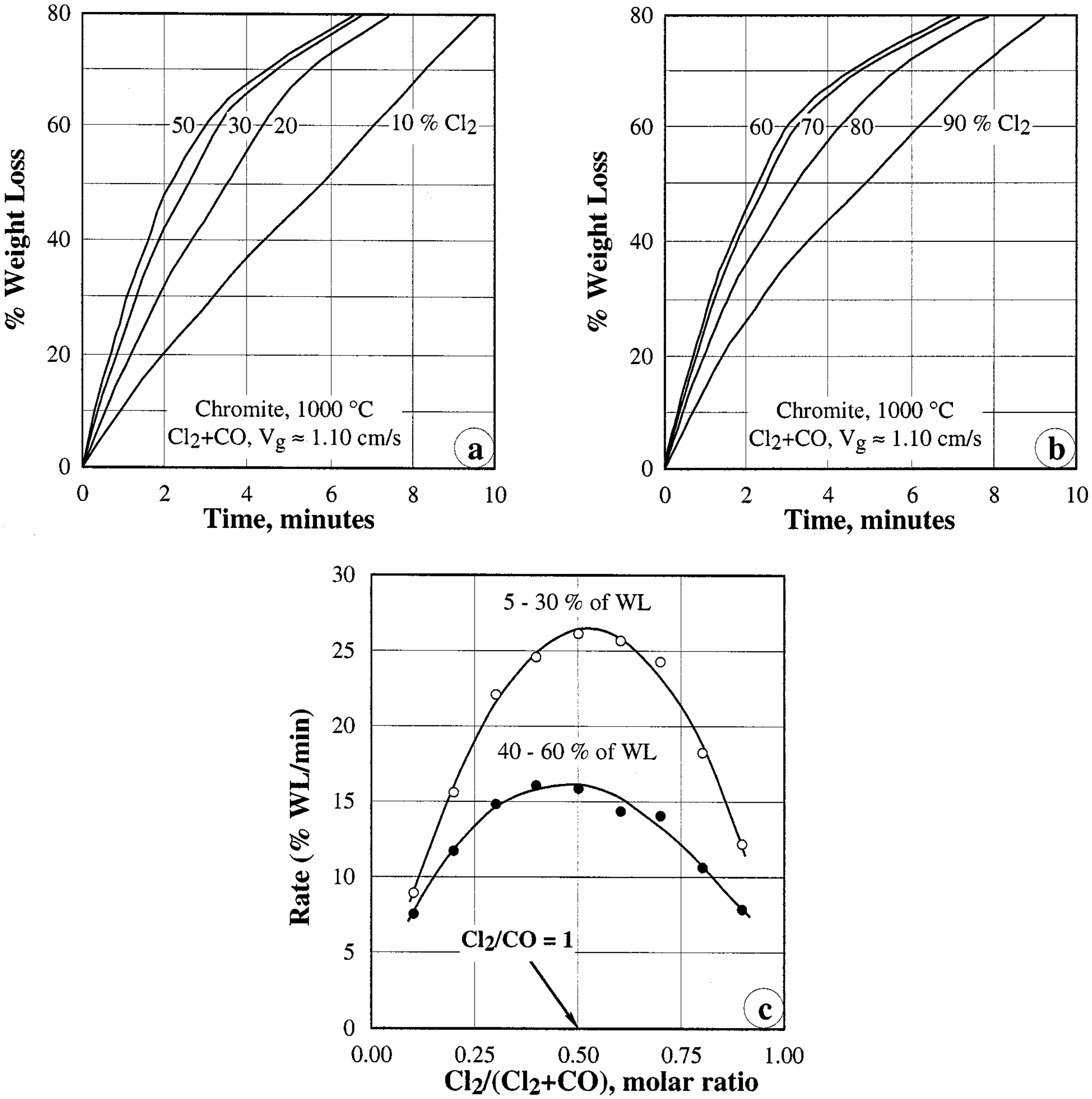


Fig. 17—Carbochlorination of chromite at 1000 °C: (*a*) and (*b*) PWL *vs* temperature for different Cl_2 contents in Cl_2 + CO gas mixture; and (*c*) reaction rate against $Cl_2/(Cl_2 + CO)$ molar ratio.

the apparent activation energy was about 135 and 74 kJ/mol for reaction extents up to 0.35, at temperatures lower than and higher than 925 °C, respectively. The carbochlorination process for a reaction extent higher than 0.4 proceeded with an E_a value of of about 195 kJ/mol.

The mean apparent reaction order of the chromite carbochlorination was about 1.35 with respect to Cl_2 + CO at 1000 °C. At this temperature, a maximum reaction rate was obtained with a carbochlorinating gas mixture which had a $Cl_2/(Cl_2 + CO)$ ratio of 0.5.

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