Kinetics of oxychlorination of chromite
Part I. Effect of temperature

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Abstract

Nonisothermal thermogravimetric (TG) analysis was used to evaluate the reactivity of a chromite mineral [$(Fe^{2+}, Mg)(Cr, Al, Fe^{3+})_2O_4$] towards $Cl_2 + CO$, $Cl_2 + N_2$ and $Cl_2 + O_2$ gaseous mixtures up to $1000°C$. Full chlorination and volatilization of reaction products were achieved at about $975°C$ using $Cl_2 + CO$, while only about 40% of the sample have reacted at $1000°C$ using $Cl_2 + N_2$ and $Cl_2 + O_2$.

The effect of the temperature on the oxychlorination with $Cl_2 + O_2$ of the chromite mineral was studied between 600 and $1050°C$ using isothermal TG measurements. The results show that the oxychlorination of chromite occurs in two stages. The initial stage of the oxychlorination was characterized by average values of apparent activation energy of about 151 and 57 kJ/mol for the temperatures lower and higher than $825°C$, respectively. While a value of about 262 kJ/mol was found for the second stage of the oxychlorination process between 925 and $1050°C$. The effects of temperature on the oxychlorination of the simple chromite constituents (Cr_2O_3, Fe_2O_3 and MgO) were also studied. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: TG analysis; Oxychlorination of chromite; Apparent activation energy

1. Introduction

Chlorine technology is used for the recovery of several metals such as Ti, Zr, Hf, Nb, Ta, rare-earth elements, etc., from their bearing materials. Korshunov [1] described, in a recent overview, the theoretical aspects of chlorination, the methodology and the apparatus used as well as the industrial application of the chlorine technology. As the majority of the above-mentioned elements are present in the earth crust as oxides, a reducing agent (C, CO) was employed in the chlorination process to increase its efficiency.

However, chlorination in presence of oxygen (oxychlorination) was applied to separate selectively a group of elements from other ones. In certain cases, the presence of oxygen in the system modifies the thermodynamic feasibility of specific oxychlorination reactions. Recently, Gaballah and Djona [2] extracted Co, Ni, Mo, and V chlorinated compounds from spent hydrodesulfurization catalysts using $Cl_2 + air$ gas mixtures without chlorinating the catalyst support (Al_2O_3). In previous investigations [3–6], oxychlori-

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nation was employed to upgrade the chromite concentrates as well as the partial recovery of chromium as chromium oxychloride (CrO_2Cl_2).

This paper is devoted to the study of temperature effect on the oxychlorination of chromite mineral using experimental conditions that minimize the effect of mass transfer phenomenon. To our knowledge, no studies concerning the oxychlorination of chromite were reported in the literature.

2. Materials and experimental procedure

The sample used in this study is a chromite mineral obtained from its concentrate described in detail previously [7]. Microprobe analyses revealed the following weight composition of this mineral reported as simple oxides: 59.4% Cr_2O_3, 13.9% FeO, 14.2% MgO, 9.5% Al_2O_3, and 0.1% SiO_2. The first four oxides are part of the spinel structure of chromite. Based on the microprobe data, the general formula of the chromite sample could be given as: $(Fe_{0.30}^{2+},$ $Mg_{0.70})(Cr_{1.56},$ $Al_{0.37},$ $Fe_{0.07}^{3+})O_4$. On the other hand, it could be represented as spinels having the following weight composition: 30.9% $FeCr_2O_4$, 51.0% $MgCr_2O_4$, 13.7% $MgAl_2O_4$ and 4.4% Fe_3O_4.

The thermogravimetric (TG) chlorination tests were performed using 40 mg of the sample and the experimental setup described earlier [7]. Some oxychlorination tests, using several grams of sample, were carried

out in a horizontal experimental setup described also in [7].

3. Results and discussion

3.1. Nonisothermal TGA treatment in various chlorinating atmospheres

This study was started by nonisothermal TGA treatment of the chromite mineral in $Cl_2 + CO$ ($Cl_2/CO = 1$), $Cl_2 + N_2$ ($Cl_2/N_2 = 1$), and $Cl_2 + O_2$ ($Cl_2/O_2 = 4$) gaseous mixtures to evaluate its reactivity towards these chlorinating gaseous mixtures between 25 and 1000°C. The sample's heating rate was about 7°C/min. Fig. 1(a) shows the evolution of the percent weight loss (%WL) of chromite sample as a function of temperature for the chosen gaseous mixtures. At 1000°C, about 40% of the sample were chlorinated in $Cl_2 + N_2$ and/or $Cl_2 + O_2$ gas mixtures indicating a relatively low reactivity of chromite towards these chlorinating gaseous mixtures. While full chlorination of the chromite was possible, at 975°C, using $Cl_2 + CO$ gas mixture.

The derivative of weight loss versus temperature is reported in Fig. 1(b). Two maximums of reaction rate at about 655 and 890°C are observed during the carbochlorination of the sample. The chlorination and the oxychlorination of chromite sample proceed with the maximal reaction rates at about 725 and
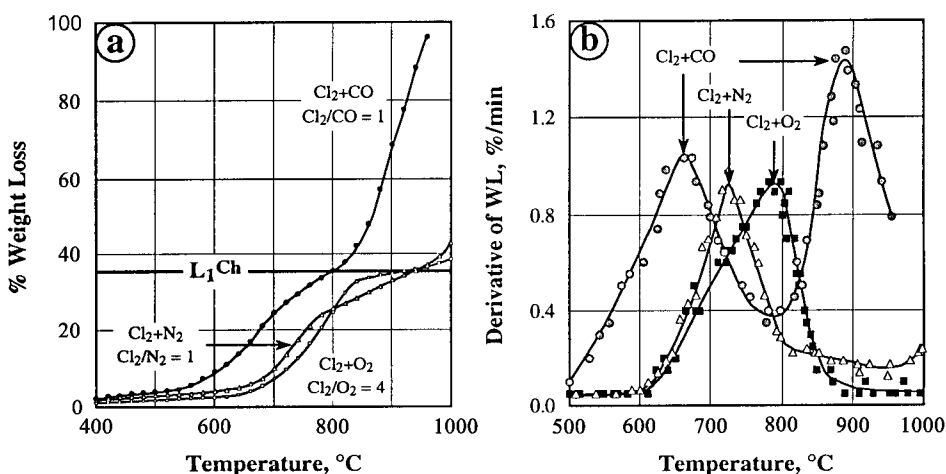

Fig. 1. TG analysis of chromite: (a) in different chlorinating gas mixtures; (b) derivative of weight losses versus temperature.

785°C, respectively. Beyond these temperatures, the reaction rate decreases sharply with temperature increase. Examination of Fig. 1(a) and (b) revealed that, at least, two different constituents of chromite possess different reactivities towards the three chlorinating gas mixtures. As first approximation, it seems that Fe_3O_4 and $FeCr_2O_4$ were the first to react with reactive gases. The calculated weight loss for the chlorination of these compounds (L_1^{Ch} in Fig. 1(a)) agrees with the data obtained experimentally at $\approx 900°C$ during the reaction of $Cl_2 + N_2$ and $Cl_2 + O_2$ gas mixtures with chromite. $MgCr_2O_4$ and $MgAl_2O_4$ appear to be less reactive to chlorine in absence of a reducing agent. This is in good agreement with thermodynamic predictions [4]. In the case of carbochlorination, $CrCl_3$, $FeCl_2$ or $FeCl_3$, $MgCl_2$, $AlCl_3$ are the most probable reaction products of chromite with $Cl_2 + CO$. Details concerning the kinetic aspects of the chromite carbochlorination are given in previous paper [7].

The main products of the chromite oxychlorination are expected to be CrO_2Cl_2, $FeCl_3$, and $MgCl_2$. The evolution of the vapor pressure of chlorides as a function of temperature is given in Fig. 2 [8,9]. This figure suggests that the chromium oxychloride is volatile at low temperatures and ferric chloride possesses a vapor pressure of about 1 atm at temperatures approaching 300°C. On the other hand, using a $Cl_2 + O_2$ with a Cl_2/O_2 molar ratio equal to 4 led to a volatilization rate of $MgCl_2$ higher than its rate of formation [10]. Thus, the rate of the chlorides' volatilization will be higher than that of their formation during the oxychlorination of chromite and consequently the measured weight loss is directly related to the oxychlorination rate of the sample.

3.2. Isothermal TGA treatment in $Cl_2 + O_2$

3.2.1. Oxychlorination of chromite at 1050°C

To get an insight about the effect of grain size on the chromite oxychlorination, isothermal treatment with $Cl_2 + O_2$ gas mixture using ground chromite samples having a particle size of <10 and 125–180 μm was conducted at 1050°C. The evolution of the sample %WL versus time is traced in Fig. 3. The time scale is graduated in minutes up to 30 min and the rest of chlorination time is given in hours. About 35% of sample are chlorinated and volatilized for a reaction time of about 15 min. Then, the reaction rate falls sharply and about 12 h are required to reach 88%WL whereas the weight loss is stabilized. In both cases, the reaction rate is slightly affected by the particles' size.

The oxychlorination residues corresponding to the extent of reaction 'X' (weight ratio of the reacted fraction to its initial weight) equal to 0.40, 0.60, 0.80 and 0.88 (points a, b, c and d of Fig. 3) were analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The SEM spectrums of these residues, as well as that of the raw sample, are grouped in Fig. 4. The residue of point 'a' ($X = 0.40$) is free of
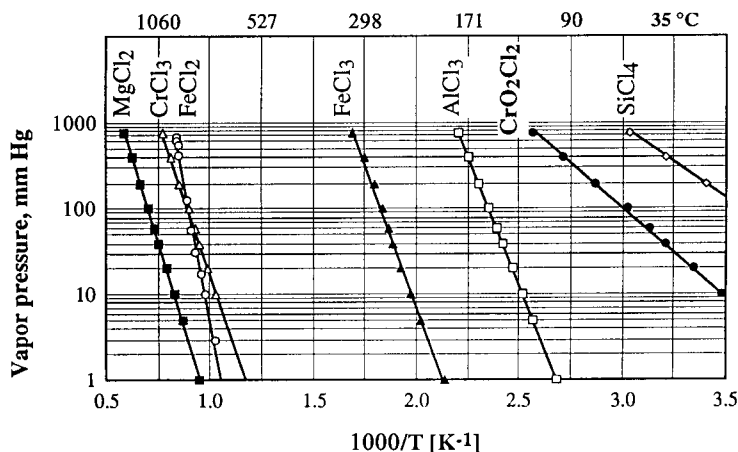

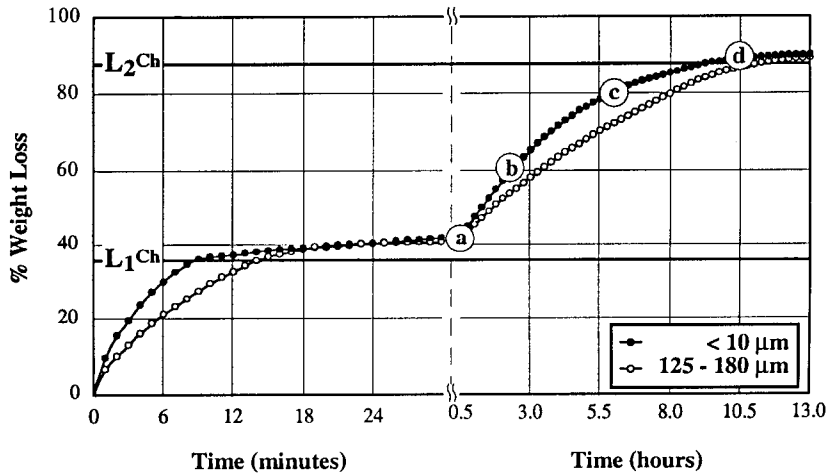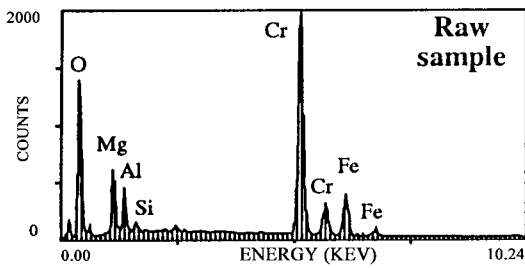Fig. 2. Evolution of vapor pressure of several chlorides as a function of temperature [8,9].

Fig. 3. Isothermal oxychlorination with $Cl_2 + O_2$ of two grain sizes of chromite at 1050°C.
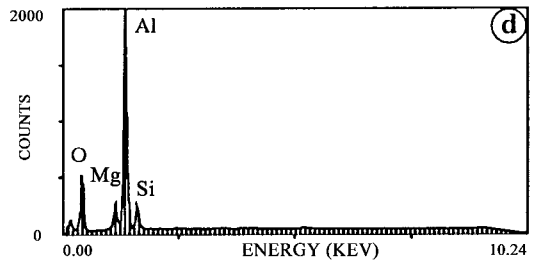
a : X = 0.40,

b : X = 0.60,

c : X = 0.80,

d : X = 0.88.
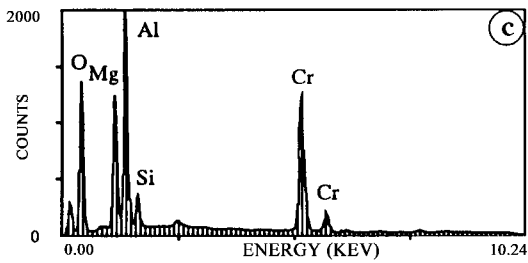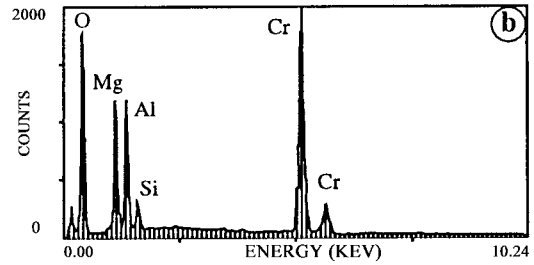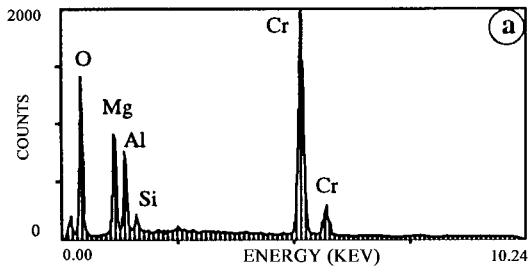
Fig. 4. SEM results of oxychlorination residues of chromite at 1050°C for different reaction extents.

iron. However, full elimination of iron oxides cannot justify a reaction extent of 0.40 as the iron oxides' content of the chromite is about 14%. Only the chlorination of both $FeCr_2O_4$ and Fe_3O_4 is in good agreement with an extent of reaction of 0.40 (refer to L_1^{Ch} in Fig. 3). The SEM spectrums of points 'b' and 'c' show the decrease of Cr peak intensity and the increase of Mg and Al ones. Finally, the SEM spectrum of points 'd' is essentially composed of Al and Mg without Cr. The evolution of elemental composition of residues from 'b' to 'd' indicates that $MgCr_2O_4$ was chlorinated leaving $MgAl_2O_4$ that is least reactive compound of chromite towards $Cl_2 + O_2$ gas mixture. The %WL calculated (refer to L_2^{Ch} in Fig. 3) for the chlorination of $(FeCr_2O_4 + Fe_3O_4 + MgCr_2O_4)$ were in fair agreement with the observations of Figs. 3 and 4. It is important to note that chlorine was not detected in the chlorination residues. This confirmed the hypothesis that the reaction rate of chromite with $Cl_2 + O_2$ was lower than the rate of volatilization of generated products.

XRD diagrams of the residues corresponding to points 'a' to 'd' were almost identical. This is probably due to the fact that the different spinels ($FeCr_2O_4$, Fe_3O_4, $MgCr_2O_4$, $MgAl_2O_4$) have the same lattice parameters making their identification almost impossible. Moreover, the simultaneous removal of divalent (Fe^{2+}, Mg) and trivalent (Fe^{3+}, Cr) elements from the chromite structure seems to compensate the ionic radii effects on the lattice parameters.

3.2.2. Effect of gas flow rate

The effect of the gas flow rate on the reaction rate was measured to determine the experimental conditions that minimize the effect of mass transfer phenomena. A series of experiments was performed at 1000°C using $Cl_2 + O_2$ gas mixtures with a Cl_2/O_2 molar ratio equal to 4. The total gas flow rate was varied from 15 to 75 l/h. Fig. 5(a) traces the evolution of the %WL versus temperature. After about 35%WL, a dramatic decrease of the sample's reactivity was observed. This decrease is almost independent of the gas flow rate. The evolution of the reaction rate as a function of the gas flow rate was determined for reaction extents $0.10 \leq X \leq 0.25$ and $0.40 \leq X \leq 0.50$ as shown in Fig. 5(b). The gas flow rate has almost no effect on the oxychlorination reaction rate for a gas velocity (V_g) higher than 40 cm/min. For this reason, determination of the temperature effect on the chromite oxychlorination was performed using a chlorinating gas mixture having a $V_g \approx 49.6$ cm/min.

3.2.3. Isothermal oxychlorination of chromite at different temperatures

A series of TGA experiments was carried out in the temperature range 600–1050°C. As the reaction rate was low for $X > 0.35$, the experiments carried out up to 900°C are stopped when the reaction extent of 0.35 is approached. Fig. 6(a) and (b) trace the evolution of the %WL of the chromite sample versus time for
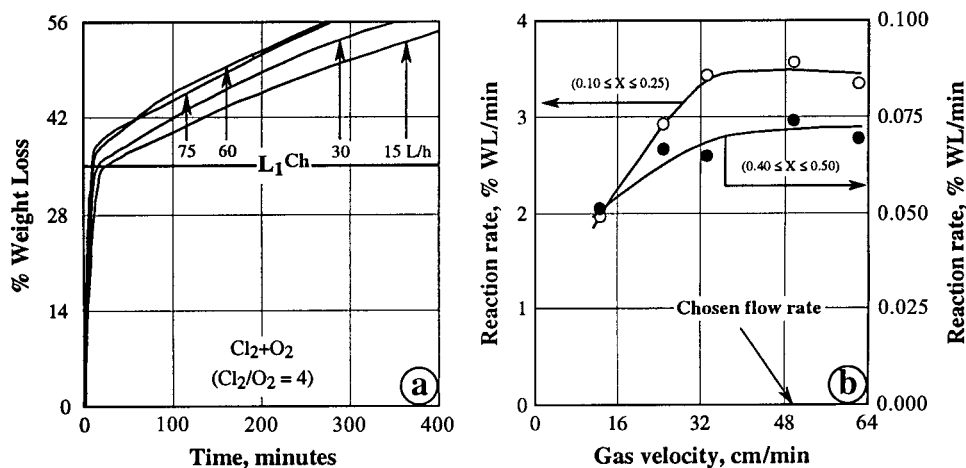

Fig. 5. Isotherms of the chromite oxychlorination using: (a) different gas flow rate; (b) its effect on the reaction rate.
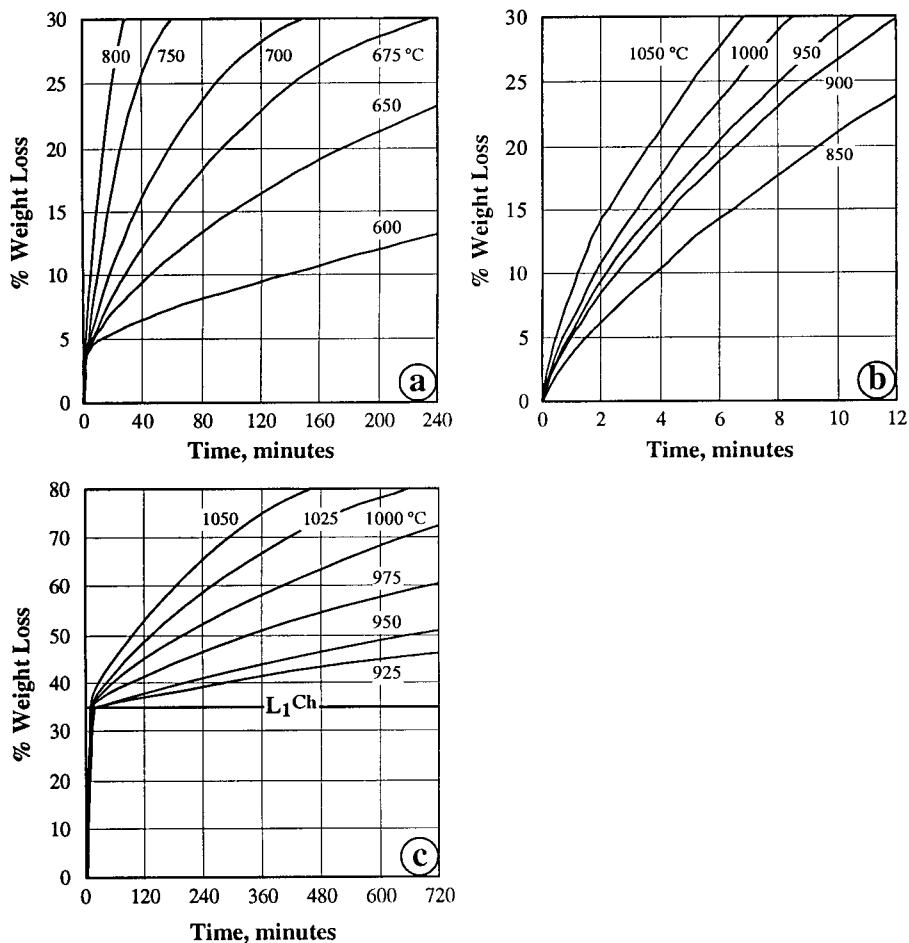
Fig. 6. Isotherms of the chromite oxychlorination with $Cl_2 + O_2$ between: (a) 600 and 800°C ($X \leq 0.30$); (b) 850 and 1050°C ($X \leq 0.30$); (c) 925 and 1050°C ($X \leq 0.80$).

several isotherms performed for reaction extents lower than 0.35. It is clear from these figures that the time required to reach a given reaction extent decreases with the temperature increase. Data of the isothermal oxychlorination of the chromite at temperatures higher than 900°C and for reaction extent ≤ 0.80 are displayed in Fig. 6(c). After a rapid weight loss at the beginning of the reaction, the reaction rate decreases sharply. At 950°C and for a reaction extent higher than 0.35, the reaction rate drops by two order of magnitudes.

The temperature dependency of the reaction rate was determined according to Arrhenius diagram. It was interesting to follow the evolution of apparent activation energy (E_a) as a function of reaction extent. The variation of E_a values versus the reaction extent is shown in Fig. 7 between 925 and 1050°C. The beginning of the reaction is characterized by an E_a of about 80 kJ/mol and decreases slightly with the progress of reaction up to $X \leq 0.25$. An important increase of E_a is observed for $X > 0.35$ and the average value of activation energy is about 265 kJ/mol for $0.40 < X < 0.70$. It should be pointed out that the important change of the apparent activation energy coincides roughly with the chlorination of iron chromite : $FeCr_2O_4$ (refer to $L_1{}^{Ch}$ in Fig. 6(c)). An example of Arrhenius diagram for the oxychlorination of chromite sample is shown in Fig. 8. The apparent activation energy is calculated for $0.00 \leq X \leq 0.25$ between 600 and 1050°C and for $0.40 \leq X \leq 0.50$ between 925 and
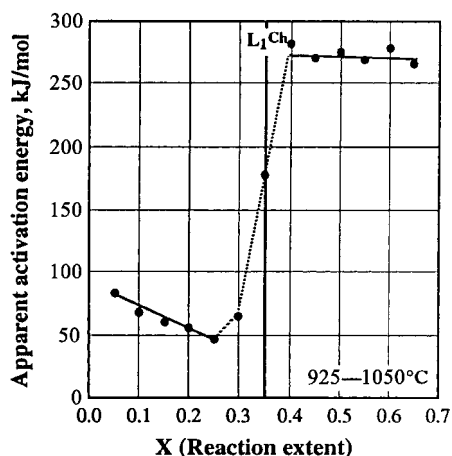
Fig. 7. Evolution of the activation energy as a function of the reaction extent.

1050°C. The oxychlorination of chromite for $X \leq 0.25$ is characterized by an E_a value of about 151 and 57 kJ/mol for temperatures lower and higher than 825°C, respectively. As shown by Fig. 8, the apparent activation energy for $0.40 \leq X \leq 0.50$ is about 262 kJ/mol. This high value of E_a indicates that the oxychlorination of magnesium chromite is strongly dependent on temperature probably due to solid state diffusion.

Mathematical fitting of experimental data of isothermal oxychlorination of chromite was performed. Different kinetics equations [11] were used to describe
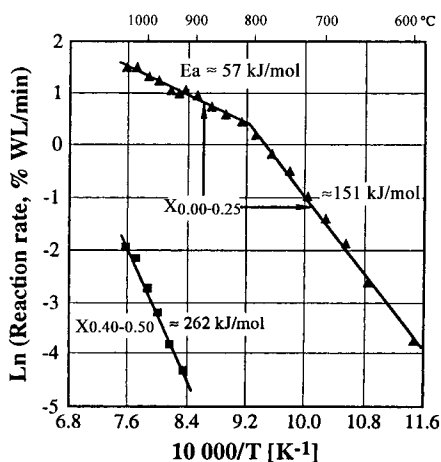

Fig. 8. Example of Arrhenius plot of the chromite oxychlorination.

the evolution of the reaction extent as a function of time for the reaction extents lower and higher than 0.30. Eq. (1) seems to be the most appropriate to describe the evolution of the reaction extent ($X \leq 0.30$) as a function of time for the oxychlorination of chromite between 600 and 800°C. While, Eq. (2) matches well the oxychlorination data ($X \leq 0.30$) for the temperature ranges from 825 to 1050°C (Fig. 9(b)). Similarly, Fig. 9(c) gives the data linearization by using Eq. (2) of the chromite oxychlorination isotherms for $X \leq 0.30$ between 925 and 1050°C.

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

$$X + (1 - X)\ln(1 - X) = kt \qquad (2)$$

where k is the constant and t the chlorination time.

Eqs. (1) and (2) describe pore diffusion control for spherical and cylindrical pores' shape, respectively, if either the initial solid or the reaction product are porous. Microscopic examination of the chromite samples at 1000°C, for different reaction extents, showed that the particles become porous with the progress of the reaction. On the other hand, the small dependency of the reaction rate on the particles' size of the sample (Fig. 3) is probably due to the pore formation inside the particles, due to gradual extraction of iron and chromium from the chromite. This is also supported by the fact that the particles' size decreased slightly as the reaction progress for reaction extents of about 0.80.

However, it is difficult to clarify the kinetics of the chromite oxychlorination due to complex composition and structure of the chromite. Thus, a mixed regime of pore diffusion and chemical reaction could control the oxychlorination. Further clarification of the kinetics phenomena of the oxychlorination was performed by initiating another series of TGA tests of chromite oxychlorination between 700 and 1040°C using a $Cl_2 + O_2$ gas mixture with a Cl_2/O_2 molar ratio equal to 0.5. In other words, the partial pressure of chlorine was decreased, leading probably to a decrease of reactivity of the chlorinating gaseous mixtures and limiting the pore diffusion phenomena.

Fig. 10(a) and (b) group the experimental data obtained for the oxychlorination of chromite with $Cl_2 + O_2$ ($Cl_2/O_2 = 0.5$) for $X \leq 0.30$. In these conditions, the effect of the temperature on the chromite
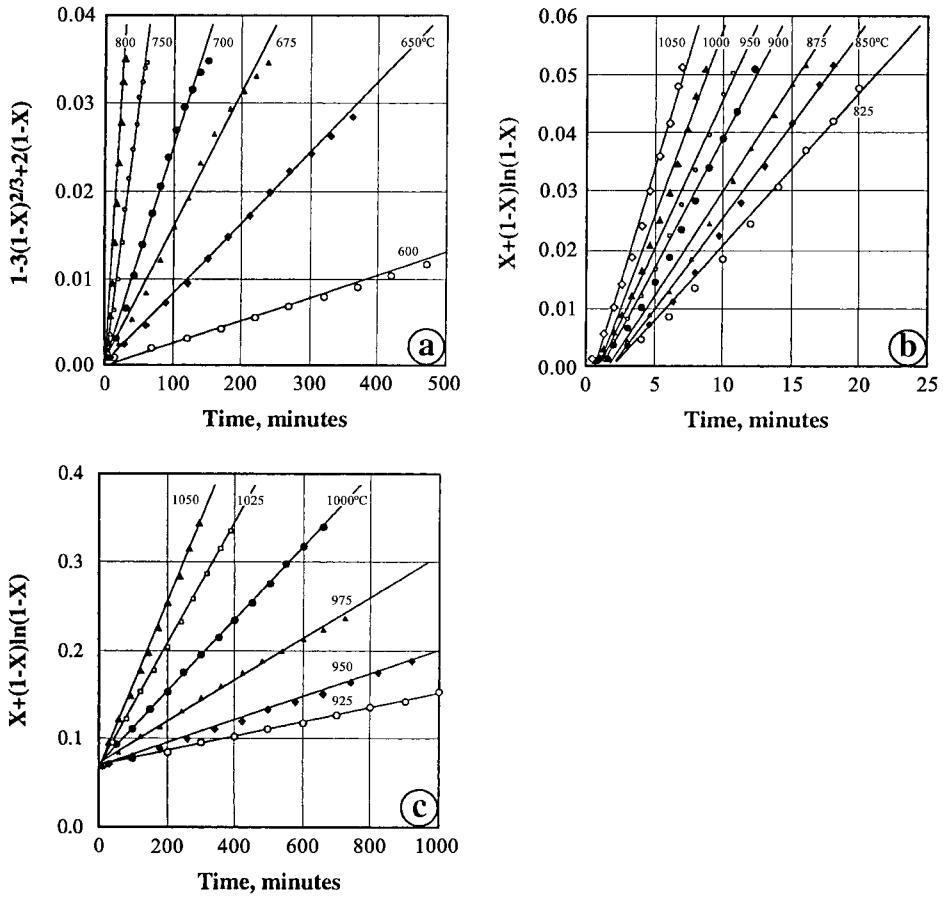
Fig. 9. Mathematical fitting of the data of the chromite oxychlorination for: (a) $T \leq 800°C$, $X \leq 0.30$ using Eq. (1); (b) $T \geq 825°C$, $X \leq 0.30$ using Eq. (2); (c) $T \geq 925°C$, $X \geq 0.35$ using Eq. (2).
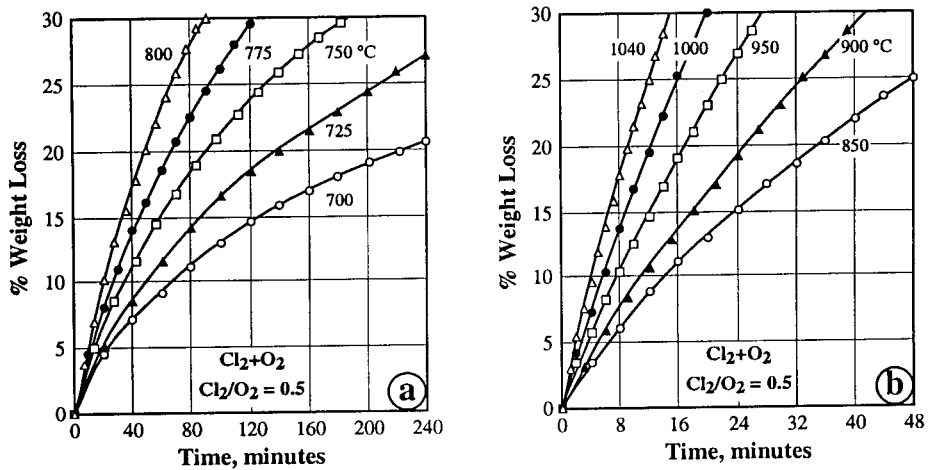

Fig. 10. Isotherms of the chromite oxychlorination with $Cl_2 + O_2$ having a Cl_2/O_2 molar ratio equal to 0.5 for: (a) $T \leq 800°C$; (b) $T \geq 850°C$.
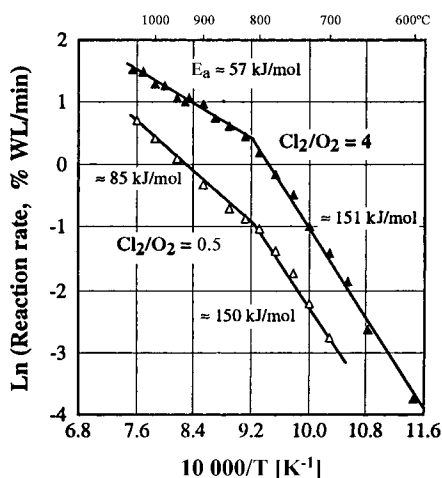
Fig. 11. Comparison of Arrhenius plots of the chromite oxychlorination with $Cl_2 + O_2$ gaseous mixtures having different Cl_2/O_2 molar ratios.

oxychlorination was determined by the Arrhenius diagram.

The Arrhenius diagrams of the oxychlorination of chromite $(X \leq 0.25)$ for both oxychlorination gas mixtures are compared in Fig. 11. As could be expected, the reaction rate using $Cl_2 + O_2$ with $Cl_2/O_2 = 4$ is higher than that obtained using $Cl_2 + O_2$ with $Cl_2/O_2 = 0.5$ in the explored temperature range. The values of the apparent activation energy at temperatures lower than $825°C$ are equivalent in both cases. However, at temperatures higher

than $825°C$, the value of the E_a obtained using $Cl_2 + O_2$ with $Cl_2/O_2 = 0.5$ is higher (85 kJ/mol) than that deduced when Cl_2/O_2 ratio in the gas mixture was 4. The increase in the value of E_a could be related to a mixed regime controlling the reaction mechanism.

The mathematical fitting of experimental data for the chromite oxychlorination with $Cl_2 + O_2$ $(Cl_2/O_2 = 0.5)$ is represented in Fig. 12. As shown by Fig. 12(a), experimental data are linearized using Eq. (1) for reaction temperatures lower or equal to $800°C$. Fig. 12(b) gives the evolution of the reaction extent versus time related by Eq. (3) for the oxychlorination of chromite at temperatures equal or higher than $850°C$. This result combined to the decrease of E_a value from 150 to 85 kJ/mol confirm that the oxychlorination reaction rate of chromite is controlled by a mixed regime when using $Cl_2 + O_2$ $(Cl_2/O_2 = 0.5)$ at temperatures higher than $800°C$.

$$1 - (1 - X)^{1/2} = kt \tag{3}$$

where k is the constant and t the chlorination time.

3.2.4. Effect of temperature on the oxychlorination of the simple chromite oxides

Although the simple oxides of chromite mineral are combined in the spinel structure $(Fe^{2+}, Mg)(Cr, Al, Fe^{3+})_2O_4$, it is worthwhile to study the effect of temperature on the oxychlorination of simple oxides: Cr_2O_3, $Fe_{(1-x)}O$, Fe_2O_3, MgO and Al_2O_3. Their composition and structures were determined by SEM and XRD analysis [4]. The tests were carried out in boat

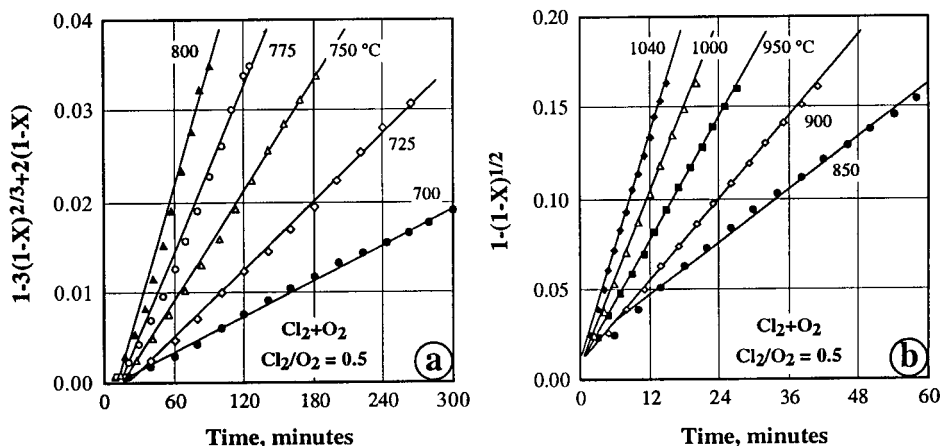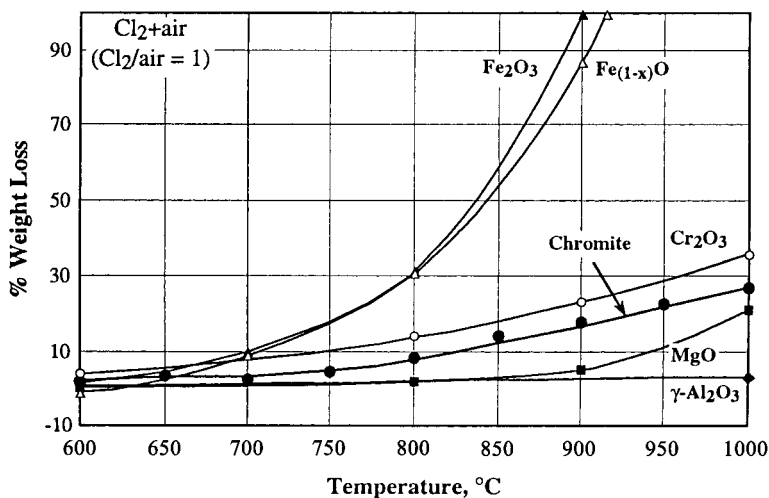Fig. 12. Mathematical fitting of the oxychlorination data at: (a) $T \leq 800°C$; (b) $T \geq 850°C$ using Eqs. (1) and (3), respectively.

Fig. 13. Oxychlorination of chromite and its simple oxides with Cl_2 + air between 600 and 1000°C for 2 h using boat experiments.

experiments using the horizontal setup. Several grams were used for each test. An oxychlorinating gas mixture composed of Cl_2 + air with a Cl_2/air molar ratio equal to 1 was used and the oxychlorination time was 2 h. The results are given in Fig. 13 as evolution of %WL versus time. This figure contains also the results of the oxychlorination of chromite in the same experimental conditions as those used in the case of simple oxides.

Details concerning the behavior of these oxides in the oxychlorinating gas mixture were given previously [4]. Iron oxides are the most reactive towards the oxychlorinating gas mixture and almost full reaction was obtained at about 900°C. The reaction product was identified as $FeCl_3$. The reactivity of Cr_2O_3 is lower than that of iron oxides especially at high temperatures and the reaction product was chromium oxychloride (CrO_2Cl_2). Magnesium oxide seems to be inert up to about 850°C and only 20% of sample had reacted at 1000°C generating magnesium chloride. No reaction of Al_2O_3 with the oxychlorinating gas mixture was observed even at 1000°C. Chromite started to react with Cl_2 + air at about 600°C and less than 30% of the sample had reacted at 1000°C during 2 h. This series of experiments revealed roughly the reactivity of these oxides towards oxychlorinating gas mixtures as well as the main reaction products.

More consist information was obtained during the treatment of these oxides using TG measurements

while minimizing the mass transfer phenomena. Wüstite ($Fe_{(1-x)}O$) was not tested because it is oxidized rapidly into hematite (Fe_2O_3) during its chlorination. Aluminum oxide was not taken into consideration due to its refractive nature towards Cl_2 in absence of a reducing atmosphere [4].

The other oxides (Cr_2O_3, Fe_2O_3, and MgO) were oxychlorinated with Cl_2 + O_2 gas mixture with Cl_2/O_2 molar ratio equal to 4. Kinetic aspects of the oxychlorination Cr_2O_3 and MgO were reported in [12] and [10], respectively. Fig. 14 compares the temperature effects on the oxychlorination of the chromite and its simple oxides. The following observations could be deduced from this figure:

1. Concerning the oxychlorination of chromite (first stage), Cr_2O_3, and Fe_2O_3:
    1.1. chromite oxychlorination is characterized by an apparent activation energy of about 151 kJ/mol between 600 and 825°C. The same value of the E_a ($\approx$148 kJ/mol) was obtained for the hematite oxychlorination. Chromium (III) oxide oxychlorination proceeds with an E_a value of about 46 kJ/mol [12] at temperatures higher than 700°C. The reaction rate of chromite and that of hematite with Cl_2 + O_2 at temperatures lower or equal to 800°C are of the same order of magnitude. This suggest that the first stage of the

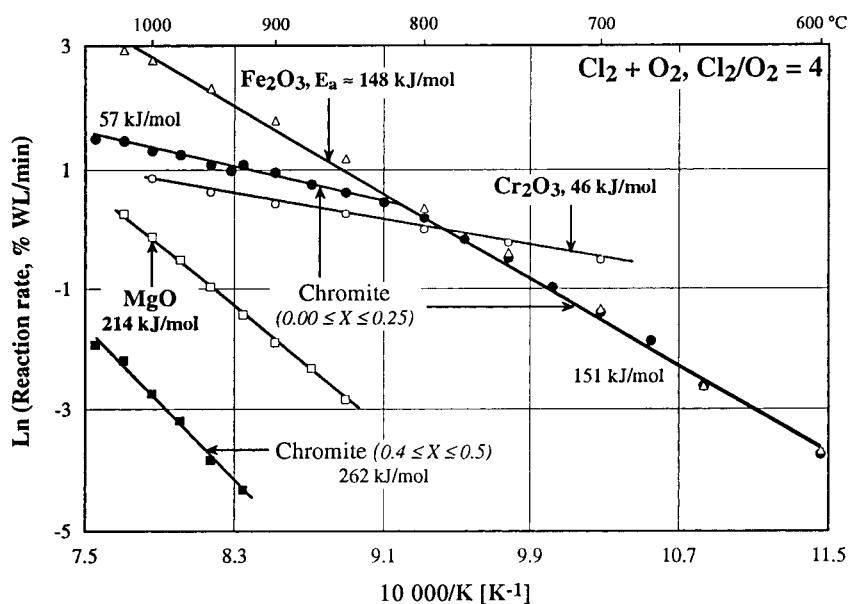Fig. 14. Comparison of Arrhenius plots of the oxychlorination of chromite, Fe_2O_3, Cr_2O_3, and MgO.

chromite ($FeCr_2O_4$) reaction with $Cl_2 + O_2$ at temperatures $\leq 800°C$ depend on the oxychlorination rate of iron oxides;

1.2. at temperatures higher than 825°C, the oxychlorination of chromite and that of Cr_2O_3 were characterized by approximately the same values of the E_a and the reaction rates. It seems that the global reaction rate of chromite, in this temperature range, is affected by the oxychlorination rate of Cr_2O_3.

2. Concerning the oxychlorination of chromite ($MgCr_2O_4$), Cr_2O_3, and MgO: the value of E_a deduced from the data of chromite ($X \geq 0.4$), Cr_2O_3, and MgO oxychlorination are about 262, 46 [12] and 214 kJ/mol [10], respectively. The reaction rate of Cr_2O_3 is much higher than that of chromite. Thus, it suggests that the oxychlorination of chromite for $X \geq 0.4$ ($MgCr_2O_4$) depends more on MgO reaction rate than that of Cr_2O_3.

While similarities of the chromite oxychlorination with the reactions of its simple oxides with $Cl_2 + O_2$ exists, one may underline that other phenomena such as the chemical bonds between the simple oxides in the chromite spinel structure, the interaction between

the reaction products and chromite, the formation of the lacunaire spinels, etc., affect the chromite oxychlorination.

4. Conclusions

The presence of a reducing atmosphere was necessary to achieve a complete reaction of the chromite mineral with chlorine. Only iron chromite ($FeCr_2O_4$) could be oxychlorinated at temperatures lower than 1000°C using nonisothermal conditions.

The oxychlorination of the chromite occurred in two stages characterized by widely different reactivities of chromite towards $Cl_2 + O_2$ gaseous mixture. Similarly, the effect of the temperature changed significantly with the progress of the reaction. Iron chromite seems to be more reactive than magnesium chromite in the oxychlorinating gases.

The oxychlorination of chromite with $Cl_2 + O_2$ ($Cl_2/O_2 = 4$), for reaction extents up to 0.30, proceeded with an apparent activation energy of about 151 and 57 kJ/mol between 600–825°C and 825–1050°C, respectively. Oxychlorination with a $Cl_2 + O_2$ mixture, having a Cl_2/O_2 ratio of 0.5, at temperatures lower than 825°C lead to similar tem-

perature effect on the reaction rate. While, a value of E_a of about 85 kJ/mol was obtained for the oxychlorination at temperatures higher than 825°C. The oxychlorination rate using $Cl_2 + O_2$ with $Cl_2/O_2 = 4$ is systematically higher than that obtained using a $Cl_2 + O_2$ with $Cl_2/O_2 = 0.5$. The second stage of the chromite oxychlorination $(X > 0.35)$ is strongly dependent on the reaction temperature and was characterized by E_a value of ≈ 262 kJ/mol between 925 and 1050°C. The effect of temperature on the chromite oxychlorination may be roughly explained by that of its simple constituents.

Acknowledgements

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