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Thermochimica Acta 351 (2000) 109–117

thermochimica acta

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Use of chlorination for chromite upgrading

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Received 26 July 1999; accepted 26 January 2000

Abstract

The chlorination of a chromite concentrate was studied between 600 and 1000°C. The reaction products were analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD), and chemical analyses. Chlorination of a chromite concentrate at about 700°C allowed the extraction of about 50% of the iron, thus doubling the Cr/Fe ratio in the treated concentrate. Aluminum chloride was tested as a chlorinating agent in the presence of a reducing atmosphere.

The effect of temperature on the kinetics of chromite chlorination was studied between 900 and 1040°C using thermogravimetric analysis (TGA). Temperature effects changed significantly with reaction extent. The initial stage of the chlorination was characterized by an apparent activation energy of about 112 kJ/mol, while a value of about of 269 kJ/mol was found for reaction extents greater than 0.4. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Chlorination; Chromite upgrading; Aluminum chloride

1. Introduction

The high reactivity of chlorine towards various compounds at moderate temperatures makes chlorine technology a competitive alternative for the extraction of several valuable metals. Further, the periodic imbalance between the world consumption of NaOH and Cl_2 generates troubles for the producers, as storage of chlorine gas is costly and dangerous. Besides, in certain cases, chlorine technology can replace other processes and lead to a better environmental plan. For example, the production of titanium oxide from the carbochlorination of titanium-bearing materials is more advantageous from an environmental point of view than the sulphate process [1].

Recently, Gaballah et al. [2] used chlorination for the recovery of valuable metals (Pb, Zn, and Cu) contained in Jarosite. The resulting residues contained essentially iron oxides that are environmentally acceptable. Allain et al. [3,4] investigated the chlorination and the carbochlorination of Ta and Nb in tin slags at temperatures up to 1000°C to recover these refractory metals. The chlorination technique was also used successfully for the recovery of Co, Ni, Mo, and V from spent hydrorefining catalysts [5].

Different applications using chromite concentrates and ores require a high Cr/Fe ratio [6]. The increase in this ratio by physical means seems to be limited

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PII: S0040-6031(00)00423-8

because most of the iron is included in the spinel structure of chromite (MN_2O_4: M=Fe^{2+}, Mg; N=Fe^{3+}, Cr, Al). For this reason, chlorination of chromite concentrates has been tested at various partial pressures of oxygen (Cl_2+O_2, Cl_2, and Cl_2+CO). It was suggested that this technique would be appropriate for improving poor chromite concentrates and/or ores [7–10].

The literature concerning the thermodynamic and kinetic aspects of the chlorination of simple oxides contained in the chromite (FeO, Fe_2O_3, Cr_2O_3, MgO, Al_2O_3, and SiO_2) using different chlorinating agents is vast. Results of this bibliographic survey have been summarized in [7–10]. This literature review includes few papers concerning the chlorination of chromium-bearing materials at low temperatures. However, no publications have been devoted to the chlorination of chromite ores and concentrates in the absence of a reducing atmosphere.

This paper focuses on the chlorination of chromite concentrates to selectively remove iron as $FeCl_3$. In addition, the use of aluminum chloride as a chlorinating agent has been reported. The effect of temperature on the reaction of chromite mineral with Cl_2 has also been studied by using the thermogravimetric analysis (TGA) technique.

2. Materials and experimental procedure

The sample of chromite concentrate was obtained from an Albanian mine. Scanning electron microscopy (SEM), X-ray diffraction (XRD), microprobe and chemical analyses were used in the physical characterization of this concentrate. Table 1 gives the results of the chemical and microprobe analysis of five major elements contained in the chromite concentrate. This concentrate consists of about 48% Cr_2O_3 and was of metallurgical grade. It was characterized by a Cr/Fe ratio close to 3.2. The distribution of these oxides in the chromite and the gangue was revealed by microprobe analysis. Results of this analysis showed (Table 1) that the chromite was composed of Cr, Fe, Mg, and Al oxides. Calculations using data obtained from the microprobe analysis indicated the following formula for the chromite mineral: $(Fe^{2+}_{0.30}, Mg_{0.70})(Cr_{1.56}, Al_{0.37}, Fe^{3+}_{0.07})O_4$. This formula can also be expressed as simple 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. These different spinels have the same crystalline structure and lattice parameters, making their identification by XRD almost impossible. A similar chromite ore composition has been reported by [11,12].

Table 1
Composition of chromite concentrate (wt.%)

Chemical analyses		Microprobe	
Oxide	Average	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

The gangue is essentially composed of magnesium and silicon oxides along with iron and aluminum oxides (Table 1). Results of microprobe and XRD analyses indicate that olivine and serpentine were the main phases present in the gangue. The combination of the results of both chemical and microprobe analyses showed that the chromite represented about 80 wt.% of the concentrate.

The chlorination tests were performed using several grams of chromite concentrates. The horizontal experimental setup shown schematically in Fig. 1 was used to perform chlorination tests of chromite concentrate. This setup is composed of a gas metering unit followed by a gas purification unit and an electrical horizontal furnace. When using aluminum chloride as a chlorinating agent, an additional furnace heated at 130°C was used for the volatilization of $AlCl_3$ (Fig. 1). The gaseous reaction products are recovered through condensors and the outlet gases are treated before their release into the atmosphere. The reaction products were examined by XRD, SEM, and conventional chemical analyses.

The sample used to investigate the temperature effect on chlorination was the chromite mineral contained in the concentrate mentioned earlier. It was separated from the gangue by a series of successive treatments using heavy media. The chlorination tests were carried out on 40 mg of chromite sample and using the experimental setup described in [8].

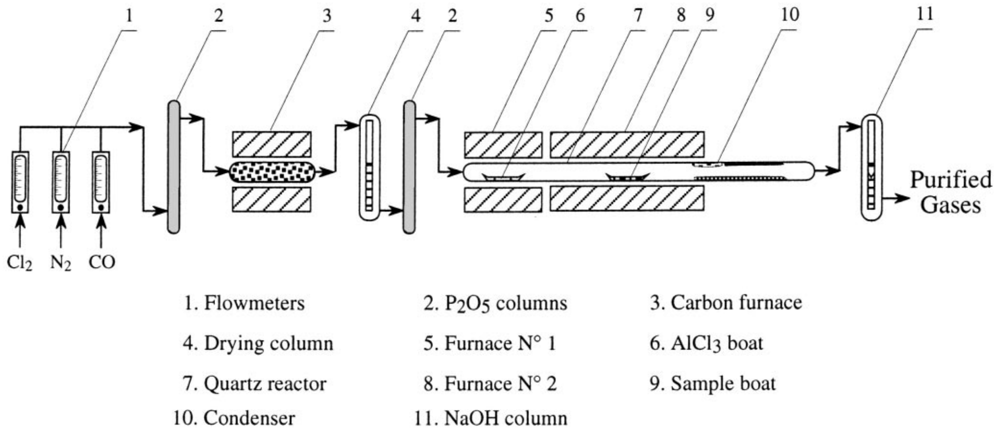

Fig. 1. Horizontal experimental setup.

3. Results

3.1. *Chlorination of chromite concentrate using the horizontal experimental setup*

3.1.1. *Chlorination with chlorine*

The chromite concentrate was treated using a gas mixture of chlorine and nitrogen having a Cl_2/N_2 ratio equal to 1. The investigated temperature range was 600–1000°C and the reaction time was 2 h. Fig. 2(a) shows the percentage weight loss (% WL) of the sample as a function of temperature. The interaction of the chromite concentrate with chlorine starts at about 600°C. About 25% of the sample is chlorinated at temperatures close to 1000°C. The chlorination residues were analyzed to determine their iron content. The curve of iron extraction as a function of temperature is given in Fig. 2(b). For a reaction time of 2 h, about 20 and 90% of the iron contained in the chromite was extracted at 600 and 1000°C, respectively. However, the weight loss obtained at 1000°C indicates that other oxides, besides iron, had partially reacted with the chlorine. A calculation based on the chemical composition of the chromite suggests that the majority of iron chromite ($FeCr_2O_4$) had reacted at 1000°C.

Table 2 lists the results of SEM analysis of the several residues and condensates produced by the

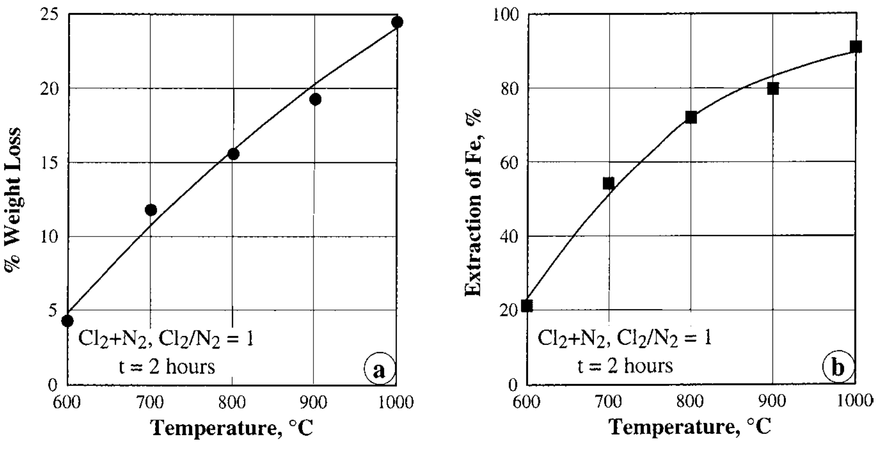

Fig. 2. Evolution of % WL of sample (a) and % iron extraction (b) as a function of temperature during the chlorination of chromite concentrate for 2 h.

Table 2
XRD analyses of the products obtained at different temperatures during the chlorination of chromite concentrate[a]

T (°C)	Residues	Condensates	
		C_1	C_2
Raw sample	Cr, Mg, Si, Fe, Al		
600	Cr, Si, Mg, Fe, Cl, Al	Cl, Fe	NC
800	Cr, Si, Mg, Al, Fe	Cl, Fe, Cr	Cl, Fe, Cr
1000	Cr, Si, Mg, Al, εFe	Cl, Mg	Cl, Mg, Fe, Cr

[a] C_1 and C_2: condensate nos. 1 and 2 recovered at different temperatures of the condenser, ($T_{C_1} > T_{C_2}$); NC: no condensate; ε: traces.

chlorination of chromite concentrate in the experimental conditions mentioned above. Chromium remained a major element even in the residue obtained at 1000°C. However, the presence of chromium in the condensates at temperatures higher than 800°C suggests that the chromium compounds had partially reacted with chlorine. A similar observation can be made for the magnesium compounds at 1000°C. Although iron was detected in all the residues obtained, its content decreased as the chlorination temperature increased. XRD results indicate that the spinel (Fe, Mg)(Cr, Al)$_2$O$_4$ was the predominant phase in all the chlorination residues. The condensates were only slightly crystallized. Finally, the chromium chloride was identified in the condensate obtained at 1000°C.

Another series of chlorination experiments of chromite concentrate was carried out at 1000°C. Pure chlorine and a gas mixture containing Cl_2+N_2 ($Cl_2/N_2=1$) were used, while the reaction time was varied from 0.5 to 8 h. Chromium and iron contents of the residues were determined by chemical analysis. Fig. 3(a) plots the evolution of the % WL of the chromite concentrate versus reaction time. It is obvious from Fig. 3(a) that about 20% of the sample was chlorinated during the first half-hour of the treatment. A longer reaction time of 8 h led to a weight loss between 40 and 50%, depending on the composition of the chlorinating gas mixture.

Extraction of iron and chromium as a function of the reaction time is illustrated in Fig. 3(b). About 80% of the iron is removed within 30 min of chlorination with both gas mixtures. Extraction of chromium was about 19 and 13% for chlorination by Cl_2 and Cl_2+N_2, respectively. For a reaction time of 30 min, the Cr/Fe weight ratios of the chlorination residues were equal to about 18 and 14 using Cl_2 and Cl_2+N_2, respectively. Beyond 2 h of treatment, the extraction of chromium increased gradually with time and about 50% of the chromium was extracted after a reaction time of 8 h.

One may note that shorter chlorination times will only lead to partial removal of iron and lower extraction extents of chromium. Thus, the chlorination of chromite ores or low grade concentrates using a gas mixture of chlorine and nitrogen at about 1000°C generates a residue having a high Cr/Fe ratio and meeting the standard requirements for the metallurgical production of ferro-chromium.

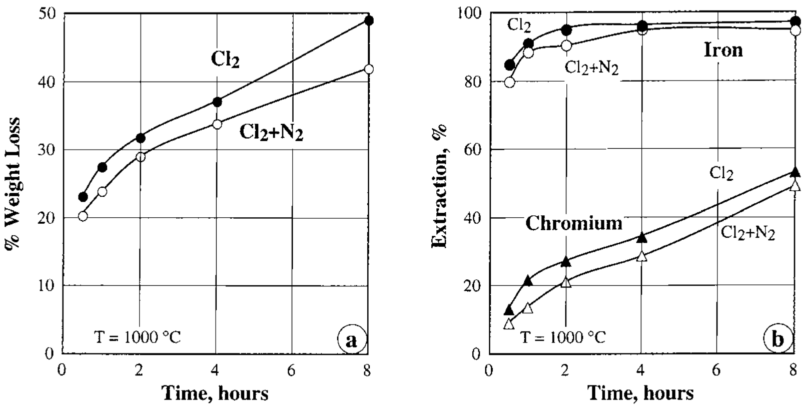

Fig. 3. Evolution of % WL of sample (a) and % Fe and % Cr extraction (b) as a function of time during the chlorination of chromite concentrate using Cl_2 and Cl_2+N_2 at 1000°C.

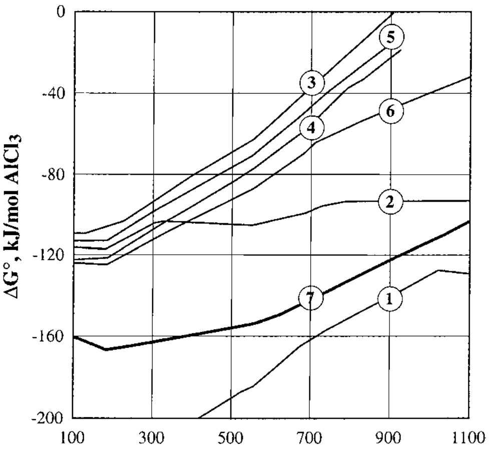

Fig. 4. Evolution of the free-energy changes (ΔG^0) as a function of temperature for the chlorination with $AlCl_3$ of several compounds contained in the chromite [13,14].

3.1.2. Chlorination in the presence of aluminum chloride

From the thermodynamic point of view, aluminum chloride appears to be a good chlorinating agent. The evolution of the free-energy changes (ΔG^0) as a function of temperature for the reactions of $AlCl_3$ with the main oxides of chromite (Eqs. (1)–(6)) is traced in Fig. 4. All envisaged reactions are thermodynamically feasible up to at least 900°C. However, the chlorination reactions of iron oxides (Eqs. (1) and (2)) seem to be the most favorable at temperatures higher than 400°C:

$$\tfrac{3}{2}FeO + AlCl_3 \rightarrow \tfrac{3}{2}FeCl_2 + \tfrac{1}{2}Al_2O_3 \qquad (1)$$

$$\tfrac{1}{2}Fe_2O_3 + AlCl_3 \rightarrow FeCl_3 + \tfrac{1}{2}Al_2O_3 \qquad (2)$$

$$\tfrac{1}{2}Cr_2O_3 + AlCl_3 \rightarrow CrCl_3 + \tfrac{1}{2}Al_2O_3 \qquad (3)$$

$$\tfrac{3}{8}FeCr_2O_4 + AlCl_3 \rightarrow \tfrac{3}{8}FeCl_2 + \tfrac{3}{4}CrCl_3 + \tfrac{1}{2}Al_2O_3 \qquad (4)$$

$$\tfrac{3}{8}MgCr_2O_4 + AlCl_3 \rightarrow \tfrac{3}{8}MgCl_2 + \tfrac{3}{4}CrCl_3 + \tfrac{1}{2}Al_2O_3 \qquad (5)$$

$$\tfrac{3}{2}MgAl_2O_4 + AlCl_3 \rightarrow \tfrac{3}{2}MgCl_2 + 2Al_2O_3 \qquad (6)$$

$$\tfrac{3}{4}O_2 + AlCl_3 \rightarrow \tfrac{3}{2}Cl_2 + \tfrac{1}{2}Al_2O_3 \qquad (7)$$

Results of the chlorination of chromite concentrate with Cl_2+AlCl_3 at 1000°C are given in Fig. 5. The evolution of % WL of the sample versus time during the chlorination with Cl_2+AlCl_3 is traced in Fig. 5(a). Comparison of the results of Figs. 3(a) and 5(a) indicates that the presence of aluminum chloride did not increase the % WL of the sample. Identical figures were obtained for the extraction of iron and chromium during the chlorination with Cl_2+AlCl_3 (Fig. 5(b)) and chlorine alone (Fig. 3(b)).

While the chlorination reactions of chromite compounds with $AlCl_3$ are thermodynamically more favorable than those of its chlorination by chlorine [8], experimental results do not agree with

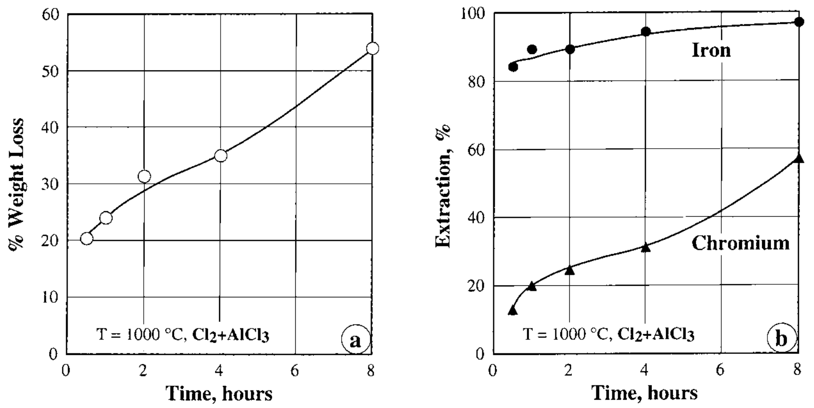

Fig. 5. Evolution of % WL of sample (a) and % Fe and % Cr extraction (b) as a function of time during the chlorination of chromite concentrate using Cl_2+AlCl_3 at 1000°C.

this result. This could be attributed to the applied experimental conditions that do not enhance the role of aluminum chloride significantly during the chlorination of chromite concentrate due to the following reasons:

1. The partial vapor pressure of aluminum chloride in Cl_2+$AlCl_3$ gas mixture was lower than that of chlorine.
2. The diffusion of $AlCl_3$ towards non-reacted core is expected to be lower than that of Cl_2.
3. The oxygen partial pressure in the reactor allows partial oxidation of gaseous $AlCl_3$, generating Al_2O_3 that is thermodynamically favorable (Eq. (7) and Fig. 4).
4. The Al_2O_3 generated can act as a diffusion barrier for further interaction of the chlorinating gas mixture with the chromite.

To avoid some of these disadvantages, another series of experiments were conducted between 800 and 1000°C, using CO as a reducing agent. A gaseous mixture of $AlCl_3$+CO+N_2 (CO/N_2=1) was used for the chlorination of the chromite concentrate. The majority of iron was chlorinated and extracted from this concentrate at 800°C. XRD analysis revealed the presence of $FeCl_2$ in the condensates. This observation indicates that the chlorination of iron chromite ($FeCr_2O_4$) occurred according to Eq. (4). About 40% of the chromium was extracted using such treatment.

3.2. TGA of the chlorination of chromite

3.2.1. Non-isothermal tests

The non-isothermal chlorination test of chromite mineral was investigated from room temperature to 1000°C using TGA. Fig. 6 gives the % WL of the sample versus temperature between 500 and 1000°C. The chromite started to react with chlorine at temperatures higher than 600°C and a final weight loss of about 43% was obtained at 1000°C. About 35% of the sample was chlorinated and volatilized at a temperature close to 950°C. The derivative of the % WL traced in Fig. 6 showed clearly a maximum in the reaction rate at about 725°C. At higher temperatures, the reaction rate slowed down and increased again at temperatures higher than 975°C.

3.2.2. Isothermal tests

To determine the effect of temperature, isothermal tests of chromite chlorination were performed between 900 and 1040°C. Results are given in Fig. 7 as % WL versus time. At 1000°C, about 10 min were needed to chlorinate 35% of the sample and more than 120 min were necessary to obtain a % WL of about 70. It is clear from Fig. 7(b) that the slope of % WL versus time changes after the chlorination of 35% of chromite.

Different kinetic equations [15] can be used to describe mathematically the evolution of the reaction extent as a function of time between $X \leq 0.35$ and $X \geq 0.40$. Eq. (8) seems to be the most appropriate

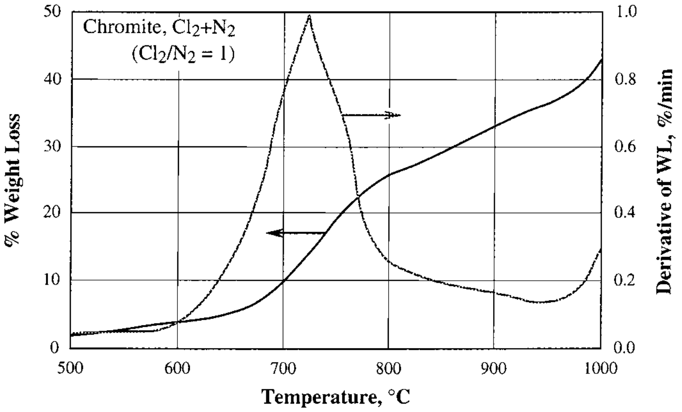

Fig. 6. Evolution of % WL of the sample and derivative of WL vs. temperature during non-isothermal chlorination of chromite.

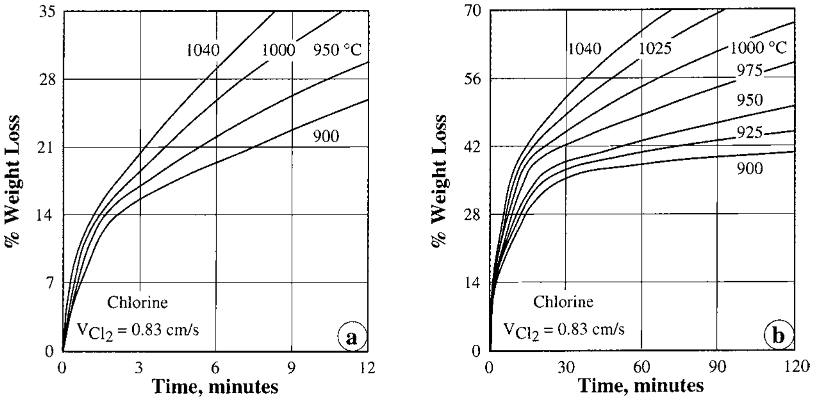

Fig. 7. TGA results of chromite chlorination using chlorine between 900 and 1040°C for (a) 35% WL and (b) for 70% WL.

to describe the evolution of reaction extent as a function of time in the investigated temperature range. Results are represented in Fig. 8(a) and (b). The average correlation coefficient for data fitting was about 0.999.

Eq. (8) describes pore diffusion control of a reaction of porous or non-porous solids with a porous product layer applied to spheres:

$$1 - 3(1 - X)^{2/3} + 2(1 - X) = kt \qquad (8)$$

where k is the rate constant and t is the chlorination time.

Nevertheless, the kinetics of the chromite chlorination is complex due to the simultaneity of several phenomena as follows:

1. Chromite contains several elements having different reactivities towards chlorine.
2. Chlorination of iron and to some extent of chromium (≈35% WL) probably generates porous chromite grains.
3. Formation of a layer of magnesium chloride can act as a barrier for further reaction.
4. Iron chloride enhances the vapor pressure of other produced chlorides due to the formation of gaseous binary chlorides [16] etc.

However, the effect of temperature on the chlorination and the volatilization of products was estimated by constructing an Arrhenius diagram. Fig. 9 gives an example of the Arrhenius plots for % WL lower than 35% and higher than 40%. An Arrhenius diagram was

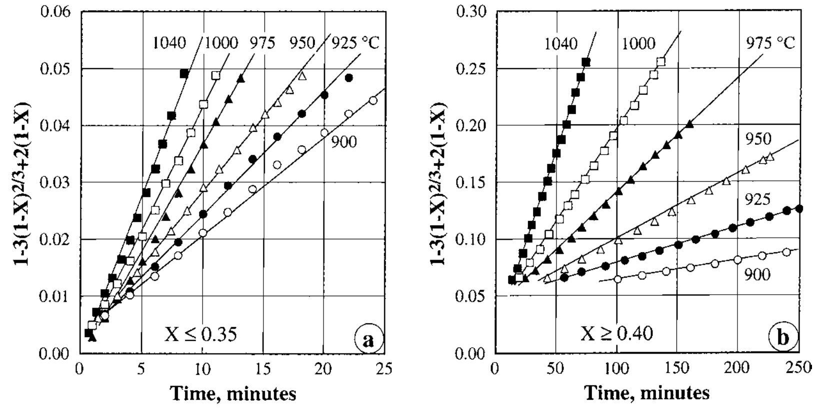

Fig. 8. Mathematical fitting of the chlorination data using Eq. (8) for the reaction extents: (a) $X \leq 0.35$ and (b) $X \geq 0.40$.

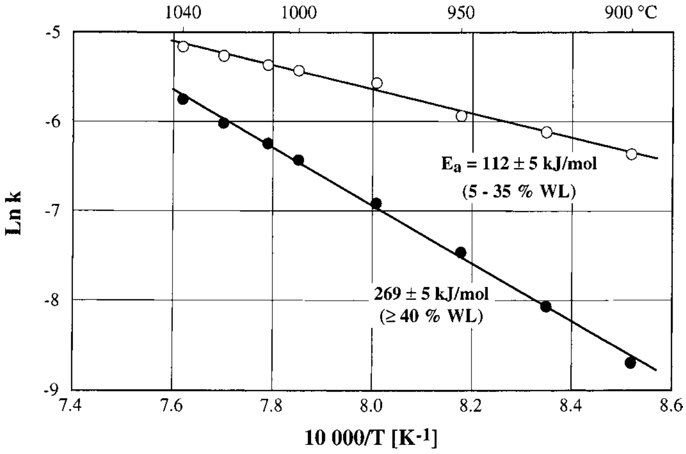

Fig. 9. Arrhenius diagram of chromite chlorination between 900 and 1040°C.

calculated using the value of the chlorination rate constant, *k*, from the linear relationship of data represented in Fig. 8(a) and (b). The value of the apparent activation energies changes with the reaction extent. An apparent activation energy, E_a, of about 112 kJ/mol, was calculated for the chlorination of chromite up to 35% WL. This value probably corresponds to the chlorination of $FeCr_2O_4$. A higher value of E_a of about 269 kJ/mol characterizes the chlorination process at higher reaction extents and probably describes the chlorination of $MgCr_2O_4$.

These results confirm that upgrading of the chromite concentrate, at a temperature lower than 900°C, will operate mainly through the selective extraction of iron allowing the increase in Cr/Fe without significant loss of chromium.

4. Conclusions

The chlorination of chromite at 800°C could be employed to upgrade chromium concentrates. At this temperature and for a reaction time of 2 h, more than 60% of the iron was removed during the treatment of a chromite concentrate. The chlorination at 1000°C using diluted chlorine for short times (<30 min) leads to a selective removal of iron and low extraction extents of chromium. The Cr/Fe ratio could be increased easily to the required level.

Aluminum chloride can be used as a chlorinating agent for the chromite at temperatures of about 800°C. However, special caution to control the partial pressure of oxygen in the chlorination reactor is needed.

Between 900 and 1040°C, the temperature coefficient of the reaction of chromite mineral with Cl_2 changes with the extent of reaction. The average value of the apparent activation energy was about 112 kJ/mol for reaction extents up to 0.35. The chlorination process for a reaction extent higher than 0.4 proceeded with a value of E_a of about 269 kJ/mol.

Acknowledgements

This work was performed in the frame of the contract N° BRE2-CT92-0173 thanks to the financial support of the European Union (DG-XII). The authors thank Dr. H.L. Schmidt for discussion, suggestion and help.

They also would like to thank Dr. J.C. Mugica, Dr. R. Solozabal (INASMET, San Sebastian, Spain) and Dr. M. Coelho (INETI, Lisbon, Portugal) for technical discussions. Authors are indebted to Dr. A. Bonazébi, Dr. M. Djona, Dr. S. Ivanaj, Dr. N. Menad, Dr. N. Mirghaffari for discussions and help on different subjects and to Mrs. C. Richard for technical and administrative support.

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