ELSEVIER

Thermochimica Acta 351 (2000) 131–137

thermochimica acta

www.elsevier.com/locate/tca

# Determination of temperature effect of oxychlorination of $Cr_2O_3$ and MgO using non-isothermal conditions

N. Kanari[a,1], I. Gaballah[a,*], E. Allain[b]

[a]Mineral Processing and Environmental Engineering team, LEM, CNRS, UMR 7569, ENSG, INPL, BP 40, 54501 Vandoeuvre, France
[b]University of Missouri-Rolla, School of Mines and Metallurgy, Center for Pyrometallurgy, 210 Fulton Hall, 65401 Rolla, MO, USA

Received 1 August 1999; accepted 1 February 2000

---

## Abstract

The effect of temperature on the oxychlorination of $Cr_2O_3$ and MgO using $Cl_2+O_2$ was evaluated using non-isothermal conditions. A mathematical treatment of the experimental data was performed. Results were compared with those obtained using isothermal conditions.

The oxychlorination of $Cr_2O_3$ up to 650°C was characterized by an apparent activation energy '$E_a$' of ca. 83 kJ/mol. Beyond 650°C, the reaction proceeded with an $E_a$ of ca. 51 kJ/mol. Between 850 and 1025°C, the reaction of MgO with $Cl_2+O_2$ was strongly dependent on temperature and its $E_a$ was equal to ca. 215 kJ/mol.

The values of the apparent activation energies, found for the oxychlorination of both oxides using non-isothermal conditions, were comparable to those obtained during isothermal treatment.

*Keywords:* Thermogravimetric analysis; Oxychlorination; Chromium(III) oxide; Magnesium oxide; Non-isothermal conditions; Apparent activation energy

---

## 1. Introduction

The activation energy of a specific reaction is an important engineering data. It will condition the reactor size and the optimum temperature for any industrial application of this specific reaction. Generally, the effects of temperature on the gas–solid reactions are determined using isothermal conditions. Thus, solids are first heated at a predetermined temperature under an inert atmosphere and when a steady state is reached the reactive gases are introduced to react with the solid isothermally. The dependency of the reactions on the temperature is evaluated by Arrhenius plot. This method was recently used by Djona et al. [1], Gaballah et al. [2], Allain et al. [3], and Kanari et al. [4] for the determination of the kinetics parameters of the chlorination and carbochlorination of some refractory metals oxides.

The literature survey revealed that some research works were devoted earlier to the determination of the temperature effect on the gas–solid reactions using

---

[*] Corresponding author. Tel.: +33-383-596-336; fax: +33-383-569-585.
*E-mail address*: gaballah@ensg.u-nancy-fr (I. Gaballah)

[1] LEM, *L*aboratoire *E*nvironnement et *M*inéralurgie, rue du Doyen M. Roubault, BP 40, 54501 Vandoeuvre Cedex, France; CNRS, *C*entre *N*ational de la *R*echerche *S*cientifique, 3 rue Michel-Ange, 75794 Paris Cedex, France; ENSG, *E*cole *N*ationale *S*upérieure de *G*éologie, rue du Doyen M. Roubault, BP 40, 54501 Vandoeuvre Cedex, France; INPL, *I*nstitut *N*ational *P*olytechnique de *L*orraine, 2 rue de la Forêt de Haye, 54501 Vandoeuvre Cedex, France.

0040-6031/00/$ – see front matter
PII: S0040-6031(00)00430-5

one single non-isothermal experiment. Chaubal and Sohn [5] developed a theoretical approach to define the rate-controlling step of the chalcopyrite oxidation up to 877°C using non-isothermal conditions. Similarly, Wang et al. [6] investigated the kinetics of the oxidation of cobaltite between 300 and 900°C using the non-isothermal technique. Bustens et al. [7] obtained consistent kinetics results testing isothermal and non-isothermal reduction of molybdenum and tungsten oxides by hydrogen.

The advantage of using one single non-isothermal test, to determine the temperature effect on gas–solid reactions, is time and material saving. However, if the gas reactivity towards the solid is high and the heating rate of furnace is low, the temperature effect will be defined only in a small temperature range. On the other hand, higher furnace heating rates will lead to a large difference of temperature between the sample and the bulk of reactive gas mixture. To avoid such disadvantage in determining the value of the apparent activation energy, at least two non-isothermal tests using different furnace heating rates are required. The determination of the temperature effect by the non-isothermal technique will be especially appreciated when the solids undergo various thermal phenomena such as: decomposition; sublimation; volatilization; dehydration, etc.

This paper is focused on the determination of temperature effect of the oxychlorination rate of $Cr_2O_3$ and MgO using non-isothermal conditions. The results were compared with those obtained for the isothermal oxychlorination of the same oxides.

## 2. Theoretical approach

The following paragraphs describe the theoretical approach [5] for the determination of the activation energy of a gas–solid reaction under non-isothermal conditions.

The reaction rate of a process can be expressed as follow:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = kf_1(p_\mathrm{A})f_2(X)f_3(d) \tag{1}$$

where $X$ is the reaction extent (defined to be the weight of the reacted fraction to the initial solid weight ratio), $p_\mathrm{A}$ the partial pressure of the reactive gas(es) and $d$ the mean particle size.

The effects of partial pressure of the reactive gases, reaction extent and particle size on the reaction rate are described by $f_1(p_\mathrm{A})$, $f_2(X)$ and $f_3(d)$, respectively.

Arrhenius law gives the temperature effect on the reaction rate:

$$k = k_0 \exp\left(\frac{-E_\mathrm{a}}{RT}\right) \tag{2}$$

Integration of Eq. (1) in isothermal conditions gives:

$$\int_0^X \frac{\mathrm{d}X}{f_2(X)} = g(X) = \int_0^t kf_1(p_\mathrm{A})f_3(d)\mathrm{d}t \tag{3}$$

The conversion function $g(X)$ generally depends on the geometric change appearing in the solid as the reaction proceeds. The different types of $g(X)$ were summarized earlier by Szekely et al. [10].

If the temperature is raised linearly with respect to time the temperature evolution may be given by Eq. (4):

$$T = \phi t \tag{4}$$

or

$$\mathrm{d}T = \phi\,\mathrm{d}t \tag{5}$$

Substituting Equations (2) and (4) in Eq. (1) and rearranging the resulting equation, it was obtained:

$$\ln\left[\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)g'(X)\right] = \ln\left[\frac{k_0 f_1(p_\mathrm{A})f_3(d)}{\phi}\right] - \frac{E_\mathrm{a}}{RT} \tag{6}$$

In the above equation, $g'(X)$ is the derivative of $g(X)$ with respect to $X$. The activation energy can be determined from the slope of data fitted by Eq. (6) when the appropriate type of $g(X)$ is determined.

## 3. Materials and experimental procedure

The samples of chromium (III) oxide and magnesium oxide used for this study were of pure analytical grade. Results of physico-chemical analysis of these two samples were given earlier [8,9]. They confirmed the purity of both those oxides.

The thermogravimetric analysis (TGA) of oxychlorination was investigated using 40 mg of sample. The experimental set described in Ref. [9] was employed in this study. Its main unit was a CAHN 1000 micro-balance having a sensitivity of 10 μg. The oxychlorination gas mixture composed of $Cl_2+O_2$ was purified using $H_2SO_4$ and $CaCl_2$ columns before its introduction in the reactor. The sample was homogeneously distributed in a quartz crucible having a section of ca. 0.5 $cm^2$. This crucible was hooked to the balance using quartz rods. For TGA isothermal runs, the sample was preheated in nitrogen atmosphere up to the desired temperature before the introduction of the chlorinating gas mixture. In the case of non-isothermal TGA runs, using a linear heating rate, the sample was directly heated in the chlorinating atmosphere.

## 4. Results

### 4.1. Oxychlorination of $Cr_2O_3$

An oxychlorinating gas mixture of $Cl_2+O_2$ having a linear velocity of ca. 33 cm/min and a molar ratio $Cl_2/O_2=4$ was used for the non-isothermal oxychlorination test of $Cr_2O_3$. This gas composition was chosen to allow the formation of chromium oxychloride according to Eq. (7). Taking into account the reactivity of $Cr_2O_3$ towards the oxychlorinating gas [8], the heating rate of the sample ($\phi=dT/dt$) was kept constant at ca. 2°C/min.

$$\tfrac{1}{2}Cr_2O_3 + Cl_2 + \tfrac{1}{4}O_2 \rightarrow CrO_2Cl_2 \qquad (7)$$

Fig. 1 shows the evolution of the percent weight loss (pct WL) of the $Cr_2O_3$ sample as function of the temperature using the conditions given above. Chromium trioxide starts to react with the oxychlorinating gas mixture at temperatures higher than 500°C and ca. 80% of the sample were oxychlorinated at 850°C. A higher heating rate of furnace would be necessary to get a lower reaction rate at lower temperatures. However, as mentioned in the introduction, higher furnace heating-rates would have led to a large temperature gradient between the sample and the gas bulk.The data obtained during the isothermal oxychlorination of $Cr_2O_3$ with $Cl_2+O_2$ ($Cl_2/O_2=4$) are available in Ref. [8] and grouped in Fig. 2a and b. It must be reported that the evolution of the reaction extent as function of time could be described by Eqs. (8) and (9) at temperatures lower and higher

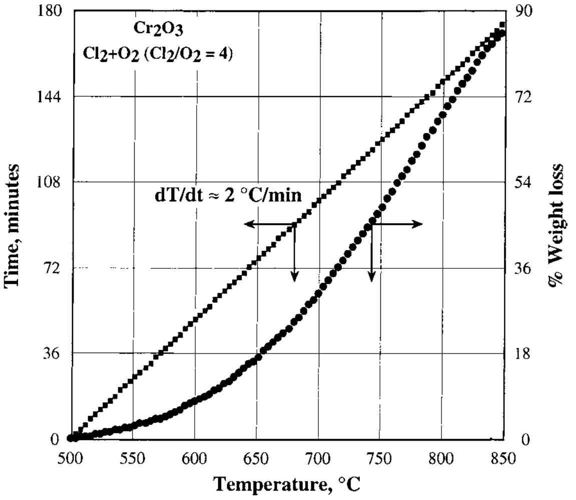

Fig. 1. TGA of $Cr_2O_3$ oxychlorination using linear temperature raise.

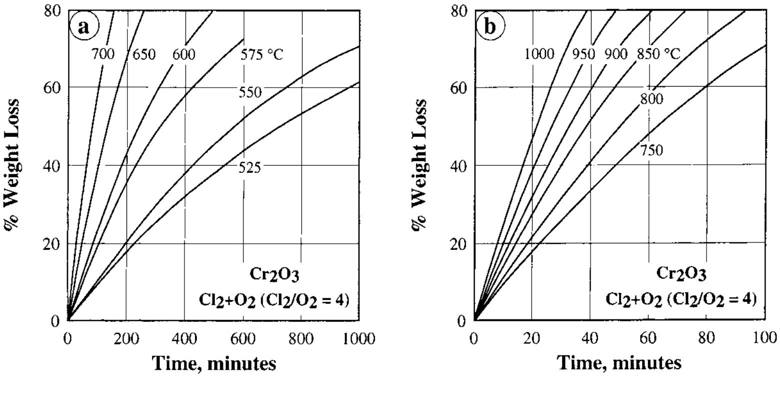

Fig. 2. Isotherms of oxychlorination of $Cr_2O_3$ for (a) $T\leq700°C$ and (b) $T\geq750°C$.

Table 1
Kinetics data obtained during the isothermal oxychlorination of $Cr_2O_3$ between 525 and 650°C

| Temperature (°C) | Value of $C_c$[a] of the data fitted by: $1-(1-X)^{1/3}=kt$ | Value of the rate constant, '$k$' |
|---|---|---|
| 525 | 0.998 | $2.61\times10^{-4}$ |
| 550 | 0.997 | $3.44\times10^{-4}$ |
| 575 | 0.995 | $5.93\times10^{-4}$ |
| 600 | 1.000 | $8.49\times10^{-4}$ |
| 625 | 0.999 | $1.26\times10^{-3}$ |
| 650 | 0.998 | $1.61\times10^{-3}$ |

[a] Correlation coefficient.

than 650°C, respectively.

$$1-(1-X)^{1/3}=kt \tag{8}$$

$$1-(1-X)^{1/2}=kt \tag{9}$$

where $X$ is reaction extent, $k$ a constant and $t$ a chlorination time.

Table 1 gives the fitting curves obtained using Eq. (8) (for $X$=0.8) and concerning the isothermal oxychlorination of $Cr_2O_3$ between 525 and 650°C. Fig. 3a shows the Arrhenius diagram of the $Cr_2O_3$ isothermal oxychlorination, plotted as the evolution of the rate constant as function of temperature. A value of apparent activation energy '$E_a$' of ca. 94 kJ/mol was obtained for the isothermal oxychlorination of $Cr_2O_3$ up to 650°C. A similar value of $E_a$ was reported earlier [8] for the initial reaction rate of $Cr_2O_3$ with $Cl_2+O_2$.

Data of Fig. 1, concerning the non-isothermal oxychlorination of $Cr_2O_3$, were processed using Eq. (6) and trying different possible formulations given by Szekely et al. [10] concerning the conversion function $g(X)$ at temperatures up to 650°C. The expression given by Eq. (8) was the best fitting for the linearilization of ln [(d$X$/d$T$)$g'(X)$] as function of 1/$T$. The result is given in Fig. 3b. A value of $E_a$ of ca. 83 kJ/mol was obtained for the non-isothermal oxychlorination of $Cr_2O_3$ up to 650°C. This value is in fairly good agreement with the value obtained from isothermal treatment tests.

Table 2
Kinetics data obtained during the isothermal oxychlorination of $Cr_2O_3$ between 680 and 1000°C

| Temperature (°C) | Value of $C_c$[a] of the data fitted by: $1-(1-X)^{1/2}=kt$ | Value of the rate constant, '$k$' |
|---|---|---|
| 680 | 1.000 | $3.11\times10^{-3}$ |
| 700 | 1.000 | $3.56\times10^{-3}$ |
| 750 | 1.000 | $4.59\times10^{-3}$ |
| 800 | 1.000 | $5.96\times10^{-3}$ |
| 850 | 1.000 | $7.71\times10^{-3}$ |
| 900 | 1.000 | $9.15\times10^{-3}$ |
| 950 | 0.999 | $1.15\times10^{-2}$ |
| 1000 | 0.999 | $1.45\times10^{-2}$ |

[a] Correlation coefficient.

The kinetics data concerning the isothermal oxychlorination of $Cr_2O_3$ between 680 and 1000°C for $X$=0.8 are given in Table 2. While Fig. 4a traces the evolution of the rate constant as function of temperature in Arrhenius ordinates. The value of $E_a$ deduced from Fig. 4a is ca. 48 kJ/mol. The decrease of the value of the apparent activation energy at temperatures

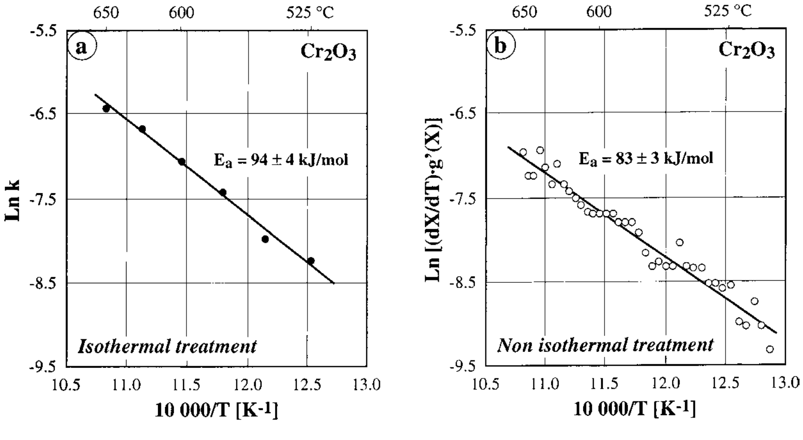

Fig. 3. Effect of temperature on the oxychlorination of $Cr_2O_3$ up to 650°C using isothermal (a) and non-isothermal (b) conditions.

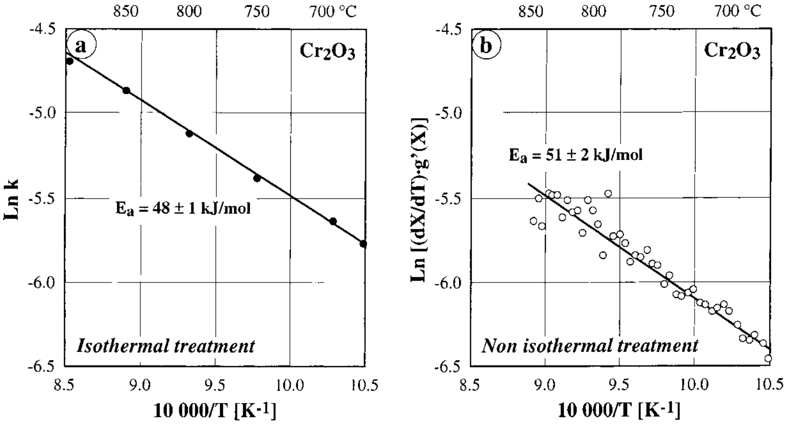

Fig. 4. Effect of temperature on the oxychlorination of $Cr_2O_3$ at temperatures higher than 650°C using isothermal (a) and non-isothermal (b) conditions.

higher than 650°C (Fig. 3a and Fig. 4a) is due to the decrease of the sample specific surface area with the raise of temperature [8].

Non-isothermal data of $Cr_2O_3$ oxychlorination represented in Fig. 1a for the temperatures higher than 650°C were also tried to be fitted by Eq. (6) for different types of the function $g(X)$. The appropriateness of the fitting was determined by calculating the coefficient correlation. As for the isothermal test case, the best correlation was found using Eq. (9). Fig. 4b represents the plot of Eq. (6) for non-isothermal treatment of $Cr_2O_3$ with $Cl_2+O_2$. A value of $E_a$ of ca. 51 kJ/mol was calculated from the slope of this plot. The comparison of the results exhibited in Fig. 4a and b shows that the values of the apparent activation energy within the experimental error.

### 4.2. *Oxychlorination of MgO*

Isothermal oxychlorination of MgO with $Cl_2+O_2$ between 850 and 1025°C was described in details in Ref. [11] and summarized by Fig. 5a and b. The chlorination of MgO by chlorine can be represented by Eq. (10). The generated magnesium chloride is characterized by its melting and boiling points of 714 and 1412°C, respectively [12]. To insure that the rate of $MgCl_2$ volatilization was higher than that of its formation, it was suggested to increase the partial pressure of oxygen in the system to decrease the rate of the chlorination of MgO by chlorine. Thus, the chlorination of MgO was achieved using an oxychlorinating gas mixture $Cl_2+O_2$ having a molar ratio $Cl_2/O_2=4$.

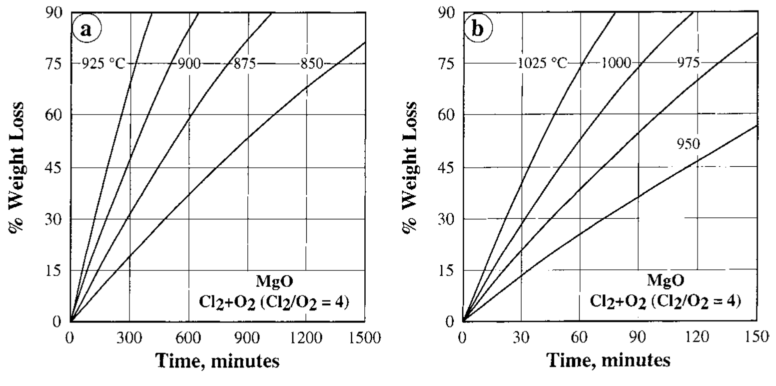

Fig. 5. Isotherms of oxychlorination of MgO for (a) $T\leq 925°C$ and (b) $T\geq 950°C$.

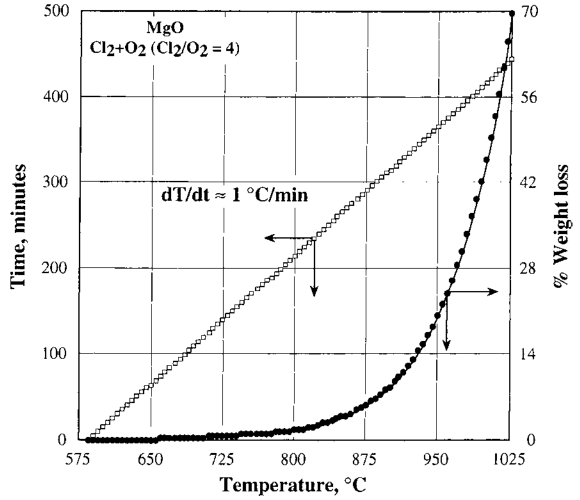

Fig. 6. TGA of MgO oxychlorination using linear temperature raise.

To determine the effect of temperature on the oxychlorination rate of MgO one single non-isothermal test under $Cl_2$+$O_2$ ($Cl_2/O_2$=4) was carried out from ca. 575 to 1025°C. As the reactivity of MgO towards oxychlorinating gas mixture was relatively low [11], the heating rate of the sample was chosen to be ca. 1°C/min. This heating rate generates accurate data as the temperature gradient between the sample and the gas bulk is small. The evolution of the temperature and pct WL of the sample as a function of time are shown in Fig. 6. Magnesium oxide started to react with the oxychlorinating gas mixture at temperatures higher than 750°C and ca. 70% of the sample had reacted at 1025°C.

$$MgO + Cl_2 \rightarrow MgCl_2 + \tfrac{1}{2}O_2 \qquad (10)$$

The main kinetics data obtained during the isothermal treatment of MgO in $Cl_2$+$O_2$ ($Cl_2/O_2$=4) are given in Table 3. The evolution of the reaction extent ($X$=0.7) as function of time for all isotherms was appropriately described by Eq. (9). The Arrhenius plot of Fig. 7a reveals the temperature effect of the MgO isothermal oxychlorination. An apparent activation energy of ca. 213 kJ/mol was deduced from this Arrhenius diagram.

Using Eq. (6), it is clear that the activation energy could be determined only after finding the appropriate

Table 3
Kinetics data obtained during the isothermal oxychlorination of MgO between 850 and 1025°C

| Temperature (°C) | Value of $C_c$[a] of the data fitted by: $1-(1-X)^{1/2}=kt$ | Value of the rate constant, '$k$' |
|---|---|---|
| 850 | 0.999 | $3.65\times10^{-4}$ |
| 875 | 0.999 | $6.18\times10^{-4}$ |
| 900 | 0.997 | $9.72\times10^{-4}$ |
| 925 | 0.997 | $1.50\times10^{-3}$ |
| 950 | 0.999 | $2.33\times10^{-3}$ |
| 975 | 0.999 | $3.69\times10^{-3}$ |
| 1000 | 0.999 | $5.32\times10^{-3}$ |
| 1025 | 0.998 | $7.98\times10^{-3}$ |

[a] Correlation coefficient.

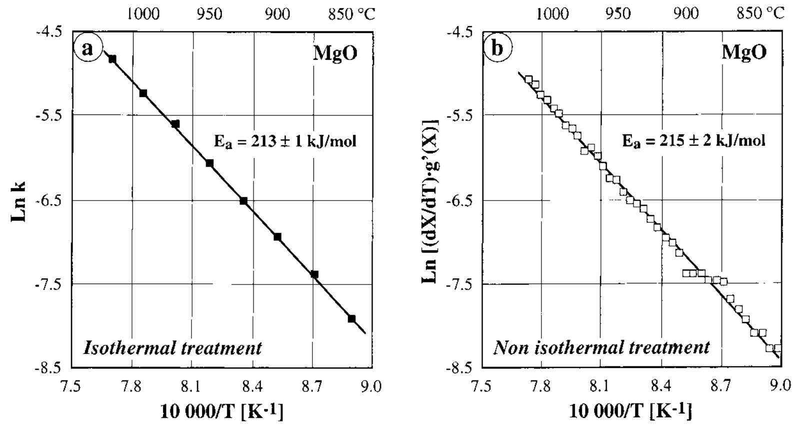

Fig. 7. Effect of temperature on the oxychlorination of MgO between 850 and 1025°C using isothermal (a) and non-isothermal (b) conditions.

form of $g(X)$. As for the isothermal tests, different models of the conversion function $g(X)$ were tried and the best data fitting was obtained using Eq. (9). The data were plotted in Fig. 7b using Eq. (6). A value of $E_a$ of ca. 215 kJ/mol was deduced for the non-isothermal oxychlorination of MgO, between 850 and 1025°C, for a reaction extent up to 0.7. Fig. 7 indicates that the activation energy values calculated using the two sets of data, for MgO oxychlorination, were within the experimental error (213 and 215 kJ/mol). This result confirms once again the validity of the non-isothermal measurements to determine the activation energy of a reaction.

## 5. Conclusions

The non-isothermal technique was found to be suitable for studying the effect of temperature on the oxychlorination of chromium and magnesium oxide. Results were in good agreement with those obtained during isothermal treatment.

Oxychlorination of chromium (III) oxide was characterized by an apparent activation energy values of ca. 83 and 51 kJ/mol for temperatures lower and higher than 650°C, respectively.

The oxychlorination of magnesium oxide between 850 to 1025°C was strongly depended on the temperature with an apparent activation energy of ca. 215 kJ/mol.

## Acknowledgements

This work was performed in the frame of contract No. 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 Drs. J.C. Mugica, R. Solozabal (INASMET, San Sebastian, Spain) and M. Coelho (INETI, Lisbon, Portugal) for technical discussions. Authors are indebted to Drs. A. Bonazébi, M. Djona, S. Ivanaj, N. Menad, N. Mirghaffari for discussions and help on different topics and to Mrs. C. Richard for technical and administrative support.

## References

[1] M. Djona, E. Allain, I. Gaballah, Metall. Mater. Trans. B 26B (1995) 703–710.

[2] I. Gaballah, M. Djona, E. Allain, Metall. Mater. Trans. B 26B (1995) 711–718.

[3] E. Allain, M. Djona, I. Gaballah, Metall. Mater. Trans. B 28B (1997) 223–233.

[4] N. Kanari, B.R. Reddy, I. Gaballah, Metall. Mater. Trans. B 29B (1998) 729–737.

[5] P.C. Chaubal, H.Y. Sohn, Metall. Trans. B 17B (1986) 51–60.

[6] G.X. Wang, D. Chandra, M.C. Fuerstenau, Metall. Mater. Trans. B. 26B (1995) 523–527.

[7] J.A. Bustnes, Du Sichen, S. Seetharaman: Paper presented at Proc. of the TMS Annual Meeting, San Francisco, California, 27 February–3 March 1993, EPD Congress 1994, G. Warren (Ed.), Published by TMS, pp. 581–600.

[8] I. Gaballah, S. Ivanaj, N. Kanari, Metall. Mater. Trans. A 29A (1998) 1299–1308.

[9] N. Kanari, I. Gaballah: Paper presented at Proc. of the TMS Annual Meeting, San Antonio, Texas, 15–19 February 1998, EPD Congress 1998, B. Mishra (Ed.), Published by TMS, pp. 595–609.

[10] J. Szekely, J.W. Evans, H.Y. Sohn, in Gas–Solid Reactions, Academic Press, New York, NY, 1976, 68–70, 73–88, 109–131 and 232–235.

[11] N. Kanari, E. Allain, I. Gaballah: Paper presented at Proc. of the TMS Annual Meeting, San Diego, California, 28 February–4 March 1999, EPD Congress 1999, B. Mishra (Ed.), Published by TMS, pp. 29–37.

[12] D.R. Lide, Editor-in-Chief, Handbook of Chemistry and Physics, 74th Edition (CRC Press, Florida, USA, 1993–1994), pp. 4–71 and 6–69.