Thermochimica Acta 497 (2010) 52–59

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Kinetics of hematite chlorination with Cl_2 and $Cl_2 + O_2$: Part I. Chlorination with Cl_2

N. Kanari[a,*], D. Mishra[a], L. Filippov[a], F. Diot[a], J. Mochón[b], E. Allain[a]

[a] Laboratoire Environnement et Minéralurgie, UMR 7569 CNRS, Nancy-University, ENSG, BP 40, 54501 Vandoeuvre-lès-Nancy Cedex, France
[b] CENIM-CSIC, Av. Gregorio del Amo 8, Madrid 28040, Spain

ARTICLE INFO

Article history:
Received 24 May 2009
Received in revised form 19 August 2009
Accepted 25 August 2009
Available online 31 August 2009

Keywords:
Hematite
Thermogravimetric analysis
Chlorination
Kinetics

ABSTRACT

Preliminary tests of the chlorination of two iron oxides (wüstite and hematite) in various chlorinating gas mixtures were performed by thermogravimetric analysis (TGA) under non-isothermal conditions. Wüstite started to react with chlorine from about 200 °C generating ferric chloride and hematite as the final reaction products. The presence of a reducing and oxidizing agent in the chlorinating gas mixtures influenced the chlorination reactions of both iron oxides, during non-isothermal treatment, only at temperatures higher than 500 °C.

The chlorination kinetics of hematite with Cl_2 have been studied in details between 600 and 1025 °C under isothermal chlorination. The values of the apparent activation energy (E_a) were about 180 and 75 kJ/mol in the temperature ranges of 600–875 and 875–1025 °C, respectively. The apparent reaction order with respect to Cl_2 was found to be 0.67 at 750 °C. Mathematical model fitting of the kinetics data was carried out to determine the most probable reaction mechanisms.

1. Introduction

Chlorine technology is proved to be an efficient method for the extraction of several non-common metals such as Zr, Hf, Nb, Ta, Ti, rare-earth elements, the treatment of solid wastes, and the upgrading of lean ores and minerals. The attractiveness of chlorine metallurgy is essentially based on:

(i) high reactivity of chlorine towards almost all metals, many metal oxides and sulphides, etc.,
(ii) appreciable differences in the boiling points of metal chlorides and/or oxychlorides for a good number of metals, and
(iii) low boiling points of metal chlorides and/or oxychlorides, etc.

An overview concerning several chlorination methods developed by our laboratory in the past two decades was presented recently [1]. Besides, various industrial practices of chlorine metallurgy for several non-common metals, can be found from the review work of Korshunov [2].

Iron is the fourth most abundant element, constituting about 5.0% by weight of the earth crust [3]. It is found naturally in the form of oxides or sulphides and it also constitutes an important part of the primary ores of several valuable metals such as Cu, Zn, Cr, Pb, Ti, Nb and Ta and of metallurgical wastes containing some of these metals. The extraction of these metals and/or upgrading of their ores by chlorination process depends on the amount and nature of the iron compounds content. In some cases, such as from laterites [4], jarosites [5], steel making waste dusts [6], and slags from tin metallurgy [7], selective separation of nonferrous metals are desirable, whilst in other cases, for example in the upgrading of chromite [8], bauxite [9], ilmenite [10], etc., removal of Fe as volatile chlorides has been proved to be highly beneficial. Selectivity in the processes, as mentioned above, is greatly dependent on the nature of interaction between iron oxides and different chlorinating agents.

The thermodynamic of Fe–O–Cl system are well known. Furthermore, this item becomes easily available thanks to thermochemical databases such as ‘HSC Chemistry’ [11] designed for many different kinds of chemical reactions and equilibria calculations. Whilst, the kinetics parameters are derived from experimental studies. A literature survey on the chlorination of iron oxides (wüstite, magnetite and hematite) in various chlorination mediums was given in an early work [12]. Thus, only a summary of the chlorination kinetics of hematite using the most usual chlorination agents found in the literature is shown in Table 1.

The literature survey indicated that several reports are available for the chlorination kinetics of hematite with Cl_2, but little information is available for the oxychlorination behavior of hematite. The values of the apparent activation energy of hematite chlorina-

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* Corresponding author at: Laboratoire Environnement et Minéralurgie, UMR 7569 CNRS, Nancy-University, ENSG, Institut National Polytechnique de Lorraine, Rue du Doyen Marcel Roubault, BP 40, 54501 Vandoeuvre-lès-Nancy Cedex, France. Tel.: +33 383 596 343; fax: +33 383 596 339.
E-mail address: ndue.kanari@ensg.inpl-nancy.fr (N. Kanari).

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doi:10.1016/j.tca.2009.08.007

Table 1
Works devoted to the chlorination of hematite by different chlorinating agents.

Chlorinating agent	Temperature range[a] (°C)	Observations	Reference
$C + Cl_2$	25–800	Formation of $FeCl_2$ which volatilized as $FeCl_3$.	[13]
$CO + Cl_2$	27–727	Reaction started at $T > 577\,^\circ C$ with formation of Fe_2Cl_6.	[14]
$CO + Cl_2$	27–927	$E_a{}^{b} = 84$ kJ/mol between 327 and 527 °C.	[15]
$COCl_2$	27–727	Reaction started at $T > 427\,^\circ C$ with formation of Fe_2Cl_6.	[14]
$COCl_2$	27–927	$E_a = 88$ kJ/mol between 237 and 297 °C, $E_a = 60$ kJ/mol between 297 and 447 °C.	[15]
CCl_4	27–927	$E_a = 125$ kJ/mol between 397 and 597 °C, $n^{c}CCl_4 = 0.5$ at 527 °C.	[16]
CCl_4	27–927	$E_a = 130$ kJ/mol between 452 and 552 °C.	[15]
Cl_2	25–800	Reaction started at 700 °C generating $FeCl_3$ and O_2.	[13]
Cl_2	700–900	$E_a = 136.8$ kJ/mol, $^{n}Cl_2 = 0.85$.	[17]
Cl_2	25–900	$E_a \approx 96$ kJ/mol between 700 and 900 °C.	[18]
Cl_2	597 to >777	$E_a = 188$–191 kJ/mol between 597 and 777 °C, $E_a = 100$ kJ/mol at $T > 777\,^\circ C$.	[19]
Cl_2	27–927	$E_a = 188$ kJ/mol between 597 and 777 °C, $E_a = 100$ kJ/mol between 777 and 807 °C.	[15]
Cl_2	800–1200	$E_a = 167$ kJ/mol, $^{n}Cl_2 = 1$.	[20]
Cl_2	600–950	$E_a = 200$ kJ/mol between 600 and 750 °C, $E_a = 125$ kJ/mol between 750 °C and 950 °C	[21]
$Cl_2 + O_2$	700–900	$^{n}Cl_2 = 2.75$.	[17]
$Cl_2 + O_2$	25–900	Oxygen had little effect from 0 to 40%.	[18]
HCl	25–900	Formation of FeOCl decomposing from 300 to 400 °C.	[18]
HCl	800–1000	$E_a = 34$ kJ/mol, $^{n}HCl = 1$.	[17]
HCl	25–750	Formation of FeOCl, $E_a = 5.9$ kJ/mol.	[20]

[a] When treatment starts from room temperature, non-isothermal conditions were also used.

[b] Apparent activation energy.

[c] Apparent reaction order.

tion varied from about 6–200 kJ/mol depending on the chlorinating agent used and on the temperature range explored. Moreover, the kinetics parameters obtained are generally dependent on the investigation methodology. For instance, research works regarding the use of nominal flow rate of gases in order to minimize the starvation phenomena and mass transfers through the boundary layer around the sample were seldom performed.

The objective of the present study is to explore the chlorination and oxychlorination kinetics of hematite and to understand the reaction mechanisms occurring between chlorine and iron oxides. In this part, results of non-isothermal chlorination of wüstite and hematite obtained under different atmospheres followed by the isothermal kinetics of hematite chlorination between 600 and 1025 °C are revealed and discussed.

2. Materials and experimental procedures

The hematite sample of 99 pct purity used in this study was obtained from Merck Chemicals (Eurolab, France). A sample of wüstite was also used for some experimental tests. It was prepared by hematite reduction using a controlled H_2–H_2O atmosphere. The elemental composition and structure of both samples were checked by scanning electron microscopy 'SEM' and X-ray diffraction 'XRD' analyses, respectively. The chlorination of iron oxides was measured by a thermogravimetric analysis (TGA) technique described previously [22]. Its main unit is a CAHN 1000 microbalance having a sensitivity of 10 μg. A sample of about 40 mg was uniformly distributed in a quartz crucible having a section of about 0.5 cm^2. This crucible is suspended to the balance by a quartz chain. During the non-isothermal treatment, the sample was directly heated in the chlorinating gas mixture by an electrical furnace. Data obtained was plotted as evolution of % weight change as a function of temperature. One may emphasize that all negative values represent % weight losses (% WL), whilst positive ones express % weight gains.

For the isothermal runs, the sample was first heated in nitrogen atmosphere up to a given temperature before introducing the reactive gases (Cl_2, or $Cl_2 + N_2$). The sample chlorination extent is deduced from the percent weight change of the sample as a function of time.

3. Results

3.1. Non-isothermal chlorination tests of iron oxides

Three experimental tests of wüstite sample chlorination were performed under isothermal condition from 25 to 1000 °C in $Cl_2 + CO$, $Cl_2 + N_2$ and Cl_2+ air gas mixtures having an equimolar proportion of their constituents. The heating rate of the furnace was about 25 °C/min. The experimental results are grouped in Fig. 1 as weight change (%) as function of temperature.

A rough analysis of these plots suggests that the reaction of wüstite with the three chlorinating gas mixtures started at temperatures as low than below 250 °C and a maximum weight gain is reached at about 325 °C. Since then, only losses of sample weight were observed up to temperatures approaching 500 °C. The effect of oxygen on the reaction of wüstite with chlorine seems to be lim-

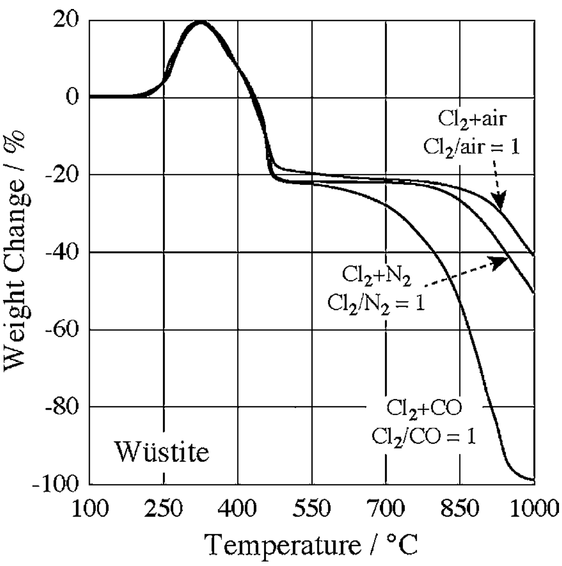

Fig. 1. Non-isothermal treatment of wüstite in different chlorinating gas mixtures.

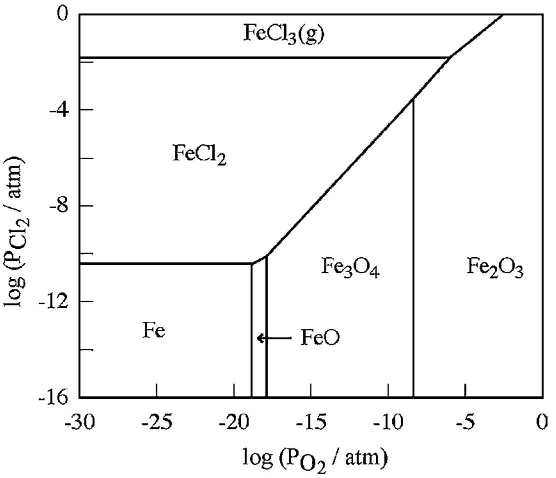

Fig. 2. Phase stability diagram of the Fe–O–Cl system at 800 °C.

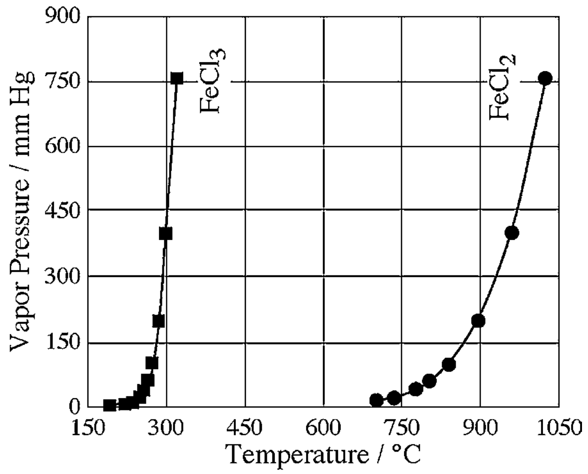

Fig. 3. Vapor pressure evolution as a function of the temperature for ferrous and ferric chlorides.

ited as the three curves almost overlap at temperatures lower than 500 °C. During the chlorination with $Cl_2 + CO$, an additional continuous weight loss was observed from 550 °C and the full sample had reacted at $T < 1000$ °C. Whilst, a plateau in weight change was observed up to about 750 °C during chlorination with $Cl_2 + N_2$ and Cl_2 + air, and about 50 and 42% WL of samples were observed at 1000 °C, respectively.

Tests of the chlorinating of wüstite for all chlorinating gas mixtures were stopped at 550 °C and the partially reacted samples were subjected to XRD analysis. Only hematite (Fe_2O_3) was identified as crystallized phase whichever was the chlorinating gas mixture indicating the oxidation of Fe^{2+} into Fe^{3+} during chlorination.

The reactions of ferrous oxide with Cl_2 and $Cl_2 + CO$ to be considered are shown by Eqs. (1)–(8), respectively. From a thermodynamic point of view, all these envisaged reactions are favorable up to 1000 °C [11]:

$$FeO + Cl_2 \rightarrow FeCl_2 + 1/2\,O_2 \tag{1}$$

$$2/3\,FeO + Cl_2 \rightarrow 2/3\,FeCl_3 + 1/3\,O_2 \tag{2}$$

$$8/3\,FeO + Cl_2 \rightarrow 2/3\,FeCl_3 + 2/3\,Fe_3O_4 \tag{3}$$

$$2\,FeO + Cl_2 \rightarrow 2/3\,FeCl_3 + 2/3\,Fe_2O_3 \tag{4}$$

$$FeO + Cl_2 + CO \rightarrow FeCl_2 + 2/3\,CO_2 \tag{5}$$

$$2/3\,FeO + Cl_2 + 2/3\,CO \rightarrow 2/3\,FeCl_3 + 2/3\,CO_2 \tag{6}$$

$$5/3\,FeO + Cl_2 + 1/3\,CO \rightarrow 2/3\,FeCl_3 + 1/3\,Fe_3O_4 + 1/3\,CO_2 \tag{7}$$

$$4/3\,FeO + Cl_2 + 1/3\,CO \rightarrow 2/3\,FeCl_3 + 1/3\,Fe_2O_3 + 1/3\,CO_2 \tag{8}$$

The phase stability diagram of the system Fe–O–Cl [11] is given in Fig. 2. It suggests that at high chlorine partial pressure and low partial pressure of oxygen the predominant stable phase is ferric chloride. The ferrous chloride becomes a predominant specie only at low partial pressure of chlorine. The evolution of vapor pressure of ferrous and ferric chloride as a function of the temperature is shown in Fig. 3 [23]. It is clear from this figure that $FeCl_3$ possesses a high vapor pressure at temperatures close to 300 °C. One may mention that ferric chloride is volatilized as a dimer (Fe_2Cl_6) at low temperature and as a monomer ($FeCl_3$) at high temperature. Ferrous chloride is in solid state up to about 700 °C and it has a vapor pressure nearing 1 atm only at 726 °C.

These thermodynamic considerations seem to be in good agreement with the results of Fig. 1. In other words, wüstite reacted with chlorine resulting to hematite and volatile ferric chloride as final reaction products. The weight loss observed in Fig. 1 was shifted towards higher temperatures due to the heating rate (25 °C/min) of the furnace which was somewhat higher. If ferrous chloride is formed (Eqs. (1) and (5)), it is probably transformed to ferric chloride because of the high partial pressure of chlorine. Few boat experimental tests performed earlier [12] about the chlorination of wüstite in $Cl_2 + CO$ at 2 h showed that full reaction and volatilization of the reaction products were achieved at 550 °C indicating that $FeCl_3$ is the final chlorinated compound.

This study shows that the overall reaction of wüstite with chlorine can be described by Eqs. (4) and (8). It seems that carbon monoxide has little effect on the chlorination of wüstite at low temperatures during non-isothermal treatment. Similar results were reported in other investigations [14,15].

An hematite sample was also subjected to non-isothermal treatments under conditions identical to those described above for wüstite. Results obtained for the chlorination of wüstite allow to assume Eqs. (9) and (10) for the reaction of Fe_2O_3 with Cl_2 and $Cl_2 + CO$, respectively. Data obtained for the non-isothermal chlorination of hematite is charted in Fig. 4. Hematite seems to be inert in chlorinating atmospheres up to about 550 °C in spite of the presence of carbon monoxide. However, full carbochlorination ($Cl_2 + CO$) of the sample was achieved at about 1000 °C.

$$1/3\,Fe_2O_3 + Cl_2 \rightarrow 2/3\,FeCl_3 + 1/2\,O_2 \tag{9}$$

$$1/3\,Fe_2O_3 + Cl_2 + CO \rightarrow 2/3\,FeCl_3 + CO_2 \tag{10}$$

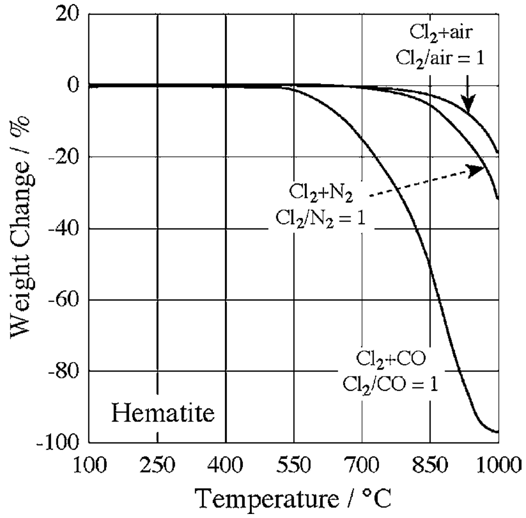

Fig. 4. Non-isothermal treatment of hematite in different chlorinating gas mixtures.

Hematite starts to react with $Cl_2 + N_2$ from 700 °C and only 30% of sample had reacted at 1000 °C. Similarly, the reaction of Fe_2O_3 with Cl_2 + air is obvious at high temperature and the reaction extent at 1000 °C is somewhat lower than with $Cl_2 + N_2$. This result may be explained by the presence of oxygen shifting the reaction of hematite chlorination (Eq. (9)) from the right to the left side of the equation.

An examination of Figs. 1 and 4 indicates that the curves of the chlorination of wüstite and hematite have same trend and shape for a selected chlorinating gas mixture at temperatures higher than 550 °C. This is an indirect confirmation of Fe_2O_3 formation during the treatment of wüstite at low temperatures. Another information from these non-isothermal tests is the formation of volatile ferric chloride during the chlorination of iron oxides. With this assumption, the isothermal chlorination of hematite at temperatures equal to and higher than 600 °C leads to a complete gasification of the reaction product. Consequently, the % WL of sample is directly related to the reaction extent of hematite with chlorine.

3.2. Effect of chlorine flow rate

In order to determine the intrinsic parameters of the gas–solid reactions, it is suitable to minimize the effect of the external mass transfer phenomena. This could be achieved by using a sufficient flow rate of reactive gases. The effect of Cl_2 gas flow rate on the chlorination reaction rate of hematite is studied at 750 and 950 °C. The gas flow rate of chlorine was varied from 5 to 70 liter per hour (L/h).

Fig. 5 gives a typical example of evolution of weight change (right ordinate) of the sample as a function of time during hematite chlorination at 750 °C at 5 and 70 L/h of chlorine. This figure contains also the reaction rate evolution (left ordinate) versus time for the two chosen flow rates of chlorine. The reaction rate is calculated as $-dWL/dt$ and expressed as −% WL/min. More than 80% of sample has reacted for a reaction time of 80 min when a Cl_2 flow rate of 70 L/h was used, whilst less than 48% of the reaction were observed for the same time at 5 L/h of chlorine. As also shown by Fig. 5, the reaction rate remains almost constant versus time when a low flow rate was used, as illustrated by the linear aspect of the weight change curve. This is a typical example of a reaction governed by external mass transfer.

Chlorine flow rates data were converted into chlorine linear velocity ones 'V_g' taking into account the cross-section area of the reactor and the obtained values are expressed as cm min^{-1}. An average reaction rate is calculated for a reaction extent 'X': $0.05 \leq X \leq 0.40$ for all isothermal data obtained at 750 and 950 °C.

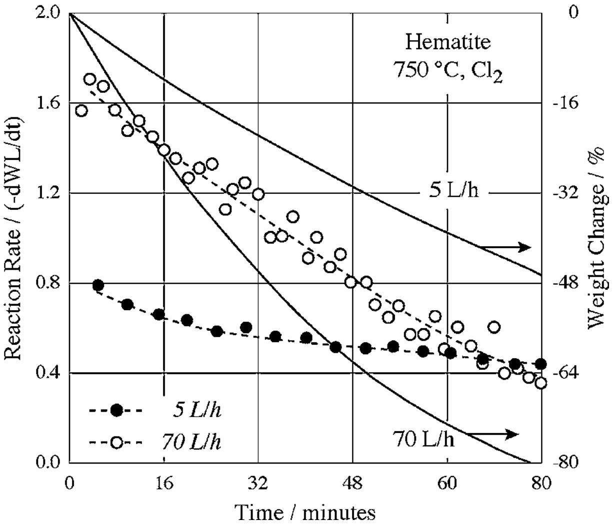

Fig. 5. Isothermal treatment of hematite at 750 °C for two chosen flow rates and evolution of the reaction rate as a function of the reaction time.

Fig. 6 summarizes the results of reaction rate evolution as a function of chlorine velocity for both temperatures. As shown by Fig. 6(a), the reaction rate at 750 °C is almost independent from the chlorine linear velocity at values higher than about 30 cm/min. As it could be expected, at 950 °C, the chlorination rate of hematite is more dependent on the chlorine velocity (Fig. 6(b)). A chlorine velocity higher than 50 cm/min will be required to minimize the effect of mass transfer phenomena in the reaction. However, chlorine with a V_g of 50 cm/min is used to investigate the effect of other parameters on the chlorination of hematite.

3.3. Effect of temperature

Series of isothermal tests were carried out at different temperatures ranging from 600 to 1025 °C using Cl_2 at a constant chlorine velocity of 50 cm/min. Fig. 7(a) and (b) shows the % weight change versus time curves obtained by the chlorination of Fe_2O_3. At 600 °C and a reaction time of 10 h, the weight loss is less than 25%. The reaction rate increases steadily as the temperature rises between 600 and 1025 °C and about 90 pct of sample are chlorinated at 950 °C for a reaction time of about 6 min.

The average reaction rate of the obtained isotherms is calculated using the initial almost linear stage for a reaction extent 'X'

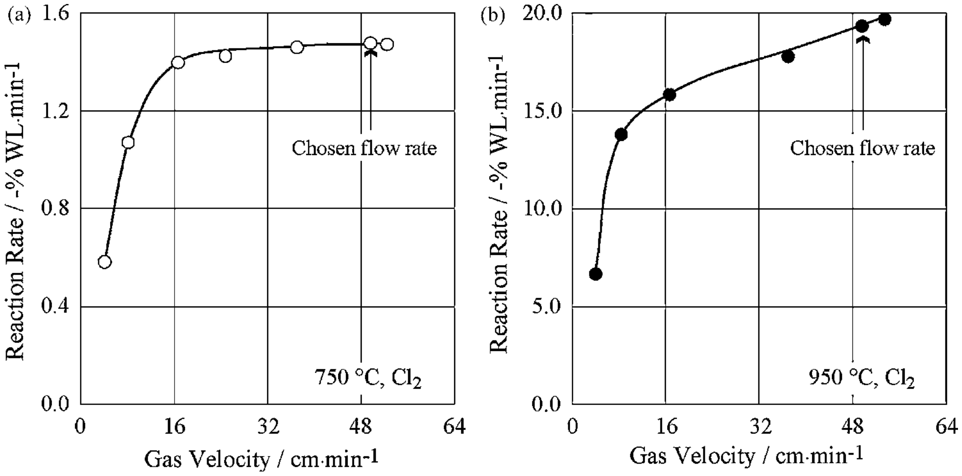

Fig. 6. Effect of chlorine velocity on the reaction rate of Fe_2O_3 chlorination at 750 and 950 °C.

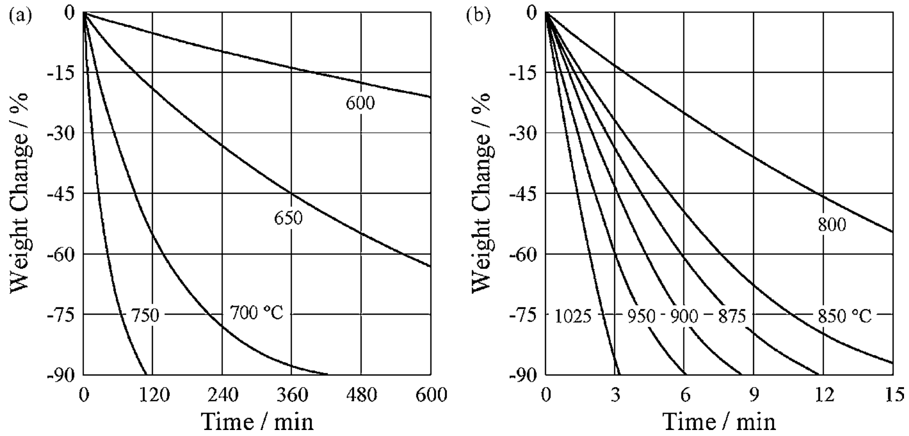

Fig. 7. Isotherms of Fe_2O_3 chlorination between 600 and 1025 °C.

($0.05 < X < 0.40$). The Arrhenius plot is given in Fig. 8. The apparent activation energy 'E_a' is 180 ± 4 kJ/mol for the temperature range of 600–875 °C. Such a high value suggests that the chlorination mechanism of Fe_2O_3 is controlled by the chemical reaction in this temperature range. As indicated by Fig. 8, the chlorination of Fe_2O_3 beyond 875 °C proceeds with an E_a value of about 74 kJ/mol. Similar values of E_a, although in different temperature intervals, are also reported in the literature. Bertoti et al. [15] found an apparent activation energy of about 188 and 100 kJ/mol in the temperature ranges of 597–777 and 777–807 °C during the chlorination of hematite by chlorine.

To correlate these activation energy values with a change of reaction mechanism, a mathematical formulation of the experimental data is attempted using the following equations [24]:

$$1-(1-X)^{1/\mathrm{Fp}} = kt \tag{11}$$

$$X = kt \quad (\text{for Fp} = 1) \tag{12}$$

$$1-(1-X)^{1/2} = kt \quad (\text{for Fp} = 2) \tag{13}$$

$$1-(1-X)^{1/3} = kt \quad (\text{for Fp} = 3) \tag{14}$$

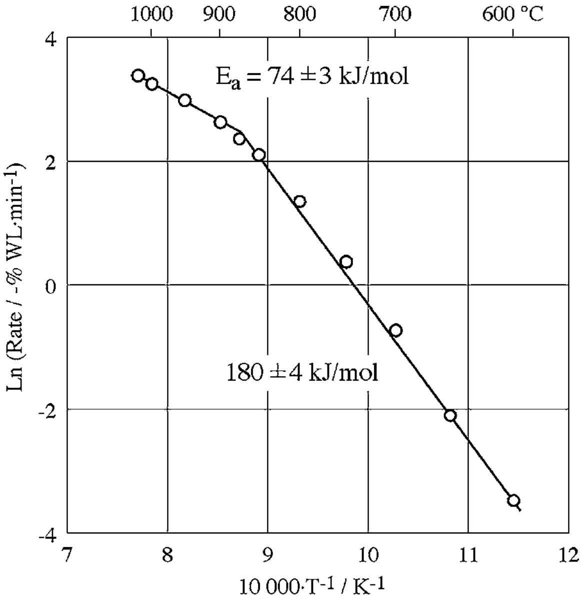

Fig. 8. Arrhenius diagram of Fe_2O_3 chlorination between 600 and 1025 °C.

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

Eq. (11) 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. It also applies for a mechanism affected by pore diffusion in the case of complete gasification of porous solids. One may underline that the chlorination of hematite at the explored temperature range belongs to the reactions of complete gasification of solids. As mentioned in Section 3.1, iron tri-oxide (Fe_2O_3) is converted to iron tri-chloride ($FeCl_3$) which is volatile at temperatures higher than 300 °C.

Fig. 9(a) and (b) shows the mathematical fitting of the experimental data obtained during the chlorination of hematite between 600 and 875 °C by using Eq. (14). The correlation coefficient of the data linearization is close to unity. This supports the hypothesis that the chlorination reaction of Fe_2O_3 particles is controlled by the chemical reaction according to the shrinking sphere model described by Eq. (14). Whilst, the best fitting data for temperatures higher than or equal to 900 °C (Fig. 9(c)) is obtained by using Eq. (12). This result combined with the value of $E_a \approx 74$ kJ/mol suggests that the chlorination of hematite is probably diffusion controlled in this temperature range. As mentioned in Section 3.2, the chlorine velocity maintained at this temperature is lower than the optimum one required for minimizing the mass transfer phenomena (see Fig. 6(b)).

Typical examples of isotherms in two distinguished temperature regions are shown in Fig. 10 displaying the evolution of the weight changes (right ordinate) and reaction rates (left ordinate) as a function of the reaction time. Fig. 10(a) shows that the weight change curve versus time follows mostly a one-third-power law function for the chlorination of hematite at 700 °C. The deduced reaction rate decreased rapidly with time, at least, for a weight loss up to 75 pct. As a contrast, plots of data obtained at 1000 °C show a linear dependency of weight change versus time with an almost constant reaction rate during the first 3 min of chlorination. Again, these parameters' variation at 1000 °C must be indicative trends only for a reaction controlled by a diffusion step.

3.4. Effect of partial pressure of chlorine

To determine this effect, a series of experimental tests was carried out at 750 °C. Nitrogen was used as diluting gas and a total gas velocity was kept at 50 cm/min. The chlorine partial pressure

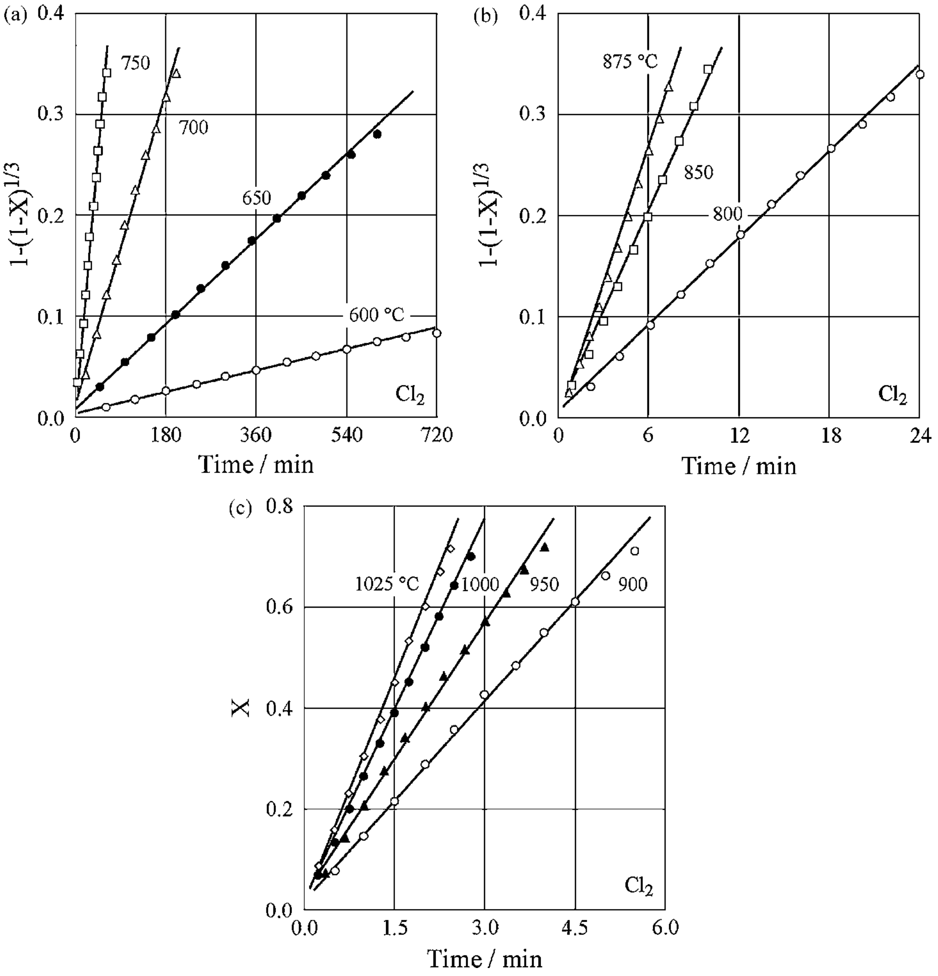

Fig. 9. Mathematical fitting of data for the chlorination at: (a) and (b) $T \leq 875\,^\circ C$ using Eq. (14) and (c) $T \geq 900\,^\circ C$ using Eq. (12).

was varied from 0.20 to 1.00 atm. Fig. 11(a) gives the evolution of % weight change as a function of time for different chlorine partial pressures. As it could be expected, the chlorination extent, for a given reaction time, increased with partial pressure of chlorine in the $Cl_2 + N_2$ gaseous mixtures. The evolution of reaction rate as a function of Cl_2 partial pressure is shown in Fig. 11(b) in natural logarithm scale. The apparent reaction order with respect to chlorine '$^nCl_2$' derived from this figure is about 0.67. It appears difficult to hypothesize about the paths of the hematite chlorination by chlorine. However, such value of '$^nCl_2$' seems to indicate that the molecular chlorine could be dissociated before reacting with hematite. Mathematical formulation of the experimental data for different partial pressure of chlorine was established using Eqs. (11)–(14). This data, shown by Fig. 12, matches Eq. (14) well with an average correlation coefficient of 0.999 confirming that the rate of the chemical reaction remains the rate controlling step of the overall process of chlorination for partial pressures of chlorine ranging from 0.20 to 1.00 atm.

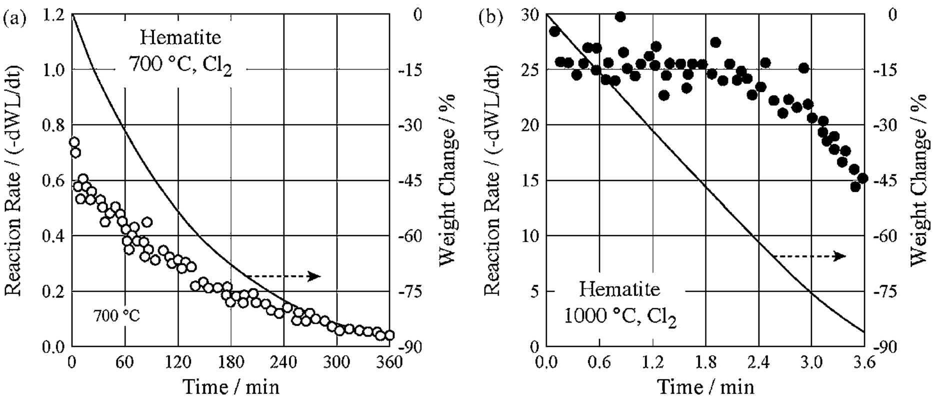

Fig. 10. Reaction rate evolution versus time during hematite chlorination at 700 and 1000 °C.

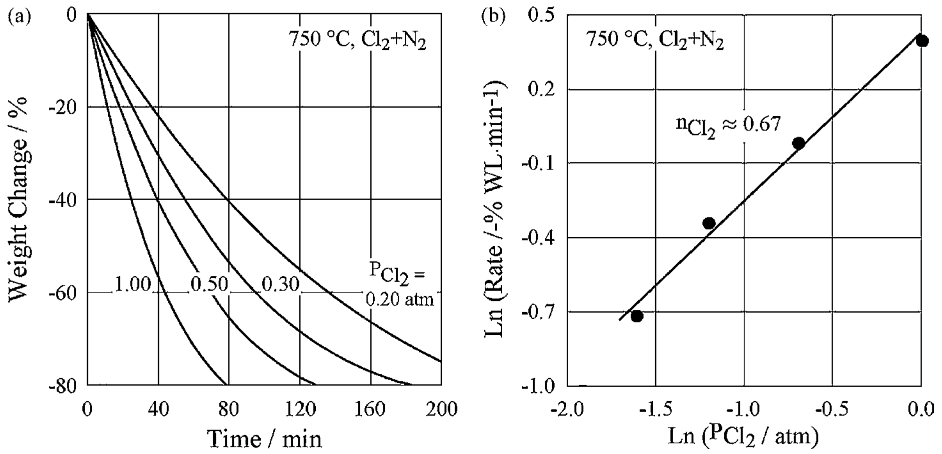

Fig. 11. Effect of chlorine partial pressure on the Fe_2O_3 chlorination at 750 °C.

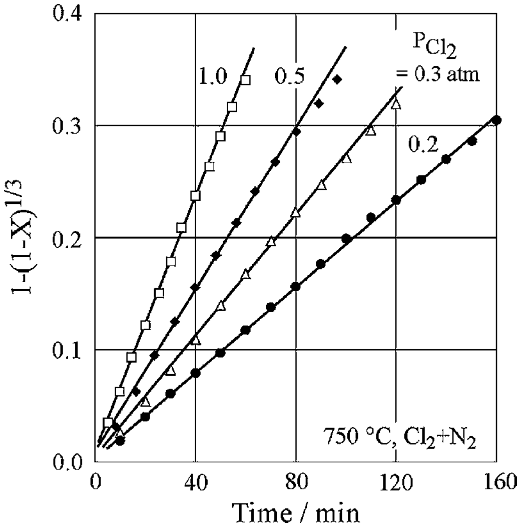

Fig. 12. Mathematical fitting of experimental data of Fig. 11(a).

4. Conclusions

1. Wüstite reacted with chlorine at low temperatures generating hematite and ferric chloride as final reaction products. The presence of carbon monoxide affected the chlorination rate for hematite chlorination especially at high temperatures during non-isothermal conditions.
2. Under isothermal conditions, hematite started to react with chlorine from at least 600 °C and the reaction becomes very fast at temperatures approaching 1025 °C.
3. Two temperature regions have been distinguished for the chlorination of hematite. The first one is comprised between 600 and 875 °C and is characterized by an apparent activation energy of about 180 kJ/mol. Mathematical fitting of experimental data indicates that the shrinking sphere model is the most adequate to describe the reaction of hematite chlorination in this temperature range. Beyond this temperature, there is a second temperature dependency for which the overall reaction is mostly controlled by diffusion phenomena with a value of E_a of about 74 kJ/mol.
4. Chlorination of hematite at 750 °C depended slightly on the partial pressure of chlorine resulting to an apparent reaction order of 0.67. Decreasing the Cl_2 partial pressure in the chlorinating gas mixture from 1.00 to 0.20 atm does not affect the rate controlling step of hematite chlorination.

Acknowledgments

This work was performed in the frame of contract No. BRE2-CT92-0173. Thanks to the financial support of the European Union (DG-XII).

References

[1] N. Kanari, E. Allain, R. Joussemet, J. Mochón, I. Ruiz-Bustinza, I. Gaballah, An overview study of chlorination reactions applied to the primary extraction and recycling of metals and to the synthesis of new reagents, Thermochim. Acta (2009), in press.

[2] B.G. Korshunov, Applications and potential use of chlorination methods in metallurgy of non-common metals, Metall. Rev. 8 (2) (1992) 1–33.

[3] F.W. Clarke, The Relative Abundance of the Chemical Elements, vol. 11, Bull. Phil. Soc., Washington, 1889, 131 pp.

[4] S.B. Kanungo, S.K. Mishra, Kinetics of chloridization of nickel bearing lateritic iron ore by hydrogen chloride gas, Metall. Mater. Trans. B 28B (1997) 389–399.

[5] N. Kanari, A. Bonazebi, E. Allain, I. Gaballah, Decontamination of jarosite through thermal treatment, in: Proceeding of the International Conference: Recycling and Waste Treatment in Mineral and Metal Processing: Technical and Economic Aspects, vol. 1, Luleå, Sweden, June, 2002, pp. 909–918.

[6] L. Komorova, I. Imris, I. Novak, Chlorinating roasting of steel making waste dusts, Zbornik Vedeckych Prac (Vysokej Skoly Technickej V. Kosiciach) 110 (1979) 97–109.

[7] I. Gaballah, E. Allain, M. Djona, Extraction of tantalum and niobium compounds from tin slags by chlorination and carbochlorination of pure oxides and concentrates, Metall. Mater. Trans. B 28B (1997) 359–369.

[8] N. Kanari, I. Gaballah, E. Allain, Use of chlorination for chromite upgrading, Thermochim. Acta 351 (1–2) (2000) 109–117.

[9] I. Szabo, A. Ujhidy, R. Jelinko, I. Vassanyi, Decrease of iron content of bauxite through high temperature chlorination, Hung. J. Ind. Chem. 17 (4) (1989) 465–475.

[10] F.C. Gennari, A.E. Bohe, D.M. Pasquevich, Effect of reaction temperature on the chlorination of a Fe_2O_3–TiO_2–C mixture, Thermochim. Acta 302 (1997) 53–61.

[11] A. Roine, Outokumpu HSC Chemistry for Windows Version 3.0, Outokumpu Research, Pori, Finland, 1997.

[12] N. Kanari, Extraction des métaux de valeur des concentrés de chalcopyrite et de chromite par chloruration, Ph.D. Thesis, Institut National Polythechnique de Lorraine, Laboratoire Environnement et Mineralurgie, Nancy, France, November 1995, 209 pp.

[13] Y. Okahara, I. Iwasaki, Chlorination of manganiferous iron ores, Trans. Soc. Mining Eng. AIME 247 (1970) 73–80.

[14] I.S. Pap, I. Bertoti, T. Szekely, I.Z. Babievskaya, L. Bottyan, TG studies on the reactions of hematite, magnetite and wüstite with $COCl_2$ and CO + Cl_2, Thermochim. Acta 92 (1985) 587–590.

[15] I. Bertoti, I.S. Pap, T. Szekely, I.Z. Babievskaya, Comparative thermogravimetric study of chlorinations of hematite and wustite, J. Therm. Anal. 32 (1) (1987) 281–292.

[16] I. Bertoti, I.S. Pap, T. Szekely, I.Z. Babievskaya, L. Bottyan, TG studies on the reactions of hematite, magnetite and wüstite with CCl_4, Thermochim. Acta 85 (1985) 87–90.

[17] G. Daradimos, U. Kuxmann, Chlorination of SnO_2 and Fe_2O_3 with chlorine gas in the temperature range from 700 to 1050 °C, Erzmetall 24 (4) (1971) 163–172.

[18] R. Titi-Manyaka, I. Iwasaki, Thermogravimetric investigation of the chlorination behaviors of some common metals and their oxides, Trans. Soc. Mining Eng. AIME 252 (1972) 307–313.

[19] V.I. Evdokimov, I.Z. Babievskaya, N.F. Drobot, I. Bertoti, I. Pap, T. Szekely, The reaction of iron oxides with chlorine, Zh. Neorg. Khim. 30 (6) (1985) 1507–1512.

[20] R.J. Fruehan, L.J. Martonik, Rate of chlorination of metals and oxides. Part III. Rate of chlorination of Fe_2O_3 and NiO in Cl_2 and HCl, Met. Trans. 4 (12) (1973) 2793–2797.

[21] F.C. Gennari, D.M. Pasquevich, Kinetics of chlorination of hematite, Thermochim. Acta 284 (1996) 325–339.

[22] N. Kanari, I. Gaballah, Reactivity of magnesium oxide in different chlorination gas mixtures, in: B. Mishra (Ed.), Paper presented at the 127th TMS Annual Meeting 'EPD Congress 1998', TMS, San Antonio, TX, 1998, pp. 595–609.

[23] D.R. Lide, Ed., Handbook of Chemistry and Physics, 74th edition, CRC Press, Boca Raton, New York, London, Tokyo, 1993–1994, 6–68 to 6–70.

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