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

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ABSTRACT

The kinetics of chlorination of hematite by $Cl_2 + O_2$ have been investigated in the temperature range from 600 to 1025 °C by using thermogravimetric analysis (TGA). The effects of Cl_2/O_2 ratio, gas velocity, temperature and partial pressure of reactive gases on the reaction rate were determined.

The reaction rate of Fe_2O_3 chlorination increased steadily with Cl_2/O_2 ratio reaching the maximum for the chlorination in absence of oxygen. The hematite chlorination process by $Cl_2 + O_2$ was characterized by an apparent activation energy of about 148 kJ/mol in the whole temperature range studied. The apparent reaction orders with respect to $Cl_2 + O_2$, Cl_2 and O_2 at 750 °C were about 0.71, 1.44, and −0.61, respectively. Almost the same values of reaction orders were obtained at 950 °C.

1. Introduction

The literature review reported previously [1] showed that the chlorination of hematite in the presence of oxygen has been very little studied. One may mention the work of Daradimos and Kuxmann [2] which proposed that the chlorination of hematite with a mixture of $Cl_2 + N_2$ and $Cl_2 + O_2$ was progressing with the volatilization of $FeCl_3$. They reported that the reaction order with respect to chlorine changed from 0.85 to 2.75 when the diluting gas changes from nitrogen to oxygen. Titi-Manyaka and Iwasaki [3] investigated the chlorination of the iron oxides in Cl_2, $Cl_2 + O_2$ and HCl by using thermogravimetric analysis ‘TGA’ up to about 800 °C. Regarding to the chlorination of these oxides by $Cl_2 + O_2$, the authors noted that the oxygen pressure had little effect on the reaction rate for oxygen contents varying from 0 to 40%.

The chlorination in presence of oxygen was often seen as a selective process to separate one group of elements from others during the treatment of their bearing oxides. This selectivity is based on the thermodynamic consideration. Works devoted to the chlorination of chromite [4–6] showed that chlorination with $Cl_2 + O_2$ led to the transformation of chromium oxide into chromium oxychloride ($Cr^{VI}O_2Cl_2$) which is in gaseous state at room temperature. Kinetics parameters studied [7] on the oxychlorination of chromium trioxide ($Cr^{III}{}_2O_3$) suggested that the reaction of Cr_2O_3 with chlorine and oxygen could be described by Eq. (1). For instance, as it is shown by Fig. 1, the maximum reaction rate of Cr_2O_3 oxychlorination was obtained by using a gaseous mixture of $Cl_2 + O_2$ having a Cl_2/O_2 molar ratio of 4 which is consistent with Eq. (1). Accordingly, chromium (III) oxide was oxidized into chromium (VI) oxychloride.

$$(1/2)Cr_2O_3 + Cl_2 + (1/4)O_2 \rightarrow CrO_2Cl_2 \qquad (1)$$

Reactions of iron (II) and (III) oxides with different chlorination gas mixtures are summarized previously [1]. The most probable reaction of hematite with chlorine could be described by Eq. (2). The formation of iron oxychloride (FeOCl) was not envisaged, as it is not stable in the temperature range of this study. Besides, the presence of iron (II) chloride is unlikely due to high oxidative ability of chlorine. Compounds known as ferrates and containing iron at higher oxidation states, especially hexavalent iron (Fe^{VI}), were also synthesized by using chlorine as oxidant [8,9]. However, ferrates could be achieved only in the presence of a high alkali medium and they were decomposed at temperature higher than 200°C.

$$(1/3)Fe_2O_3 + Cl_2 \rightarrow (2/3)FeCl_3 + (1/2)O_2 \qquad (2)$$

With these evidences and assumptions, this work deals with a kinetic investigation of the reaction of hematite with chlorine as described by Eq. (2). From a thermodynamic point of view, the presence of oxygen will shift Reaction (2) from the right side to the left. Whilst, the quantitative data concerning the effects of Cl_2/O_2 ratio, gas velocity, temperature as well as the partial pressure of reactive gases on the reaction rate of hematite with chlorine in presence of oxygen were revealed from this experimental study within temperatures ranging from 600 to 1025 °C.

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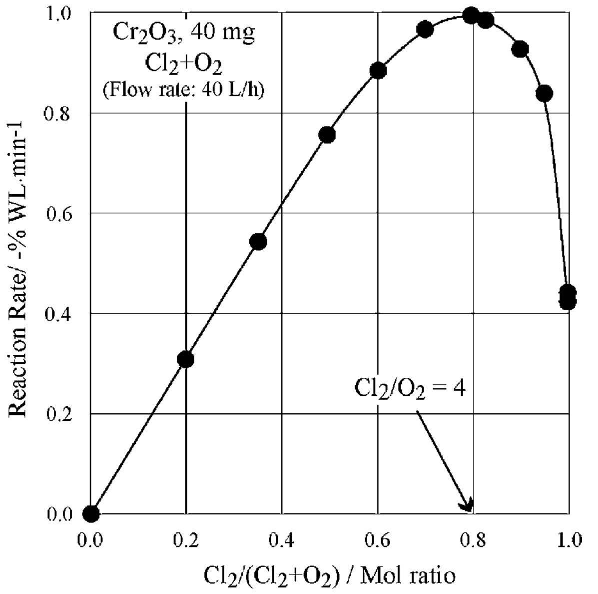

Fig. 1. Effect of $Cl_2/(Cl_2 + O_2)$ molar ratio on the reaction rate of Cr_2O_3 oxychlorination at 800 °C.

2. Materials and experimental procedures

The hematite sample of 99 pct purity used in this study was obtained from Merck Chemicals (Eurolab, France). The elemental composition and structure of the Fe_2O_3 sample were checked in the scanning electron microscopy by EDXS (electron dispersive X-ray spectroscopy) and X-ray diffraction 'XRD' analyses, respectively. The chlorination of the hematite sample was measured by a thermogravimetric analysis technique described previously [10]. 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 was hooked to the balance by a quartz chain. For all isothermal runs, the sample was first heated by an electrical furnace up to a given temperature, under nitrogen atmosphere, before introducing the reactive gases ($Cl_2 + O_2$, $Cl_2 + O_2 + N_2$, Cl_2). The data obtained was plotted as evolution of the percent (%) weight change as a function of the temperature. It is important to note that negative values of the sample weight change represent percent weight losses (% WL).

As the considered reaction product ($FeCl_3$) is volatile at temperature higher than 300 °C, the sample chlorination extent 'X' is directly deduced from the percent weight losses of the sample. Unless specified otherwise, the average reaction rate is calculated for the reaction extent ($0.05 \leq X \leq 0.40$) assuming that this part of the TGA curves are almost linear. Since, the reaction rate is expressed as $-\%WL\,min^{-1}$.

3. Results

3.1. Effect of $Cl_2/(Cl_2 + O_2)$ ratio

To determine this effect two series of isothermal tests were performed at 750 and 950 °C by using an oxychlorinating gas mixture of $Cl_2 + O_2$ with a total flow rate of 60 L per hour (L/h) and varying the molar chlorine content from 10 to 100%. Results of several isothermal experiments were plotted in Fig. 2 as evolution of the weight change as a function of reaction time. As shown by Fig. 2(a), less than 20% of hematite sample reacted at 750 °C during 250 min of treatment when the chlorine content in $Cl_2 + O_2$ is 30%. Whilst, about 75 min are sufficient to reach a reaction extent of 0.8 during the chlorination of hematite in pure chlorine. Almost similar trends were observed during the chlorination of hematite at 950 °C (Fig. 2(b)). Data of Fig. 2 was used to follow the chlorination reaction rate of hematite as a function of the $Cl_2/(Cl_2 + O_2)$ ratio and the result is plotted in Fig. 3.

As shown by Fig. 3(a), the chlorination rate of Fe_2O_3 increases almost following a parabolic law as a function of the $Cl_2/(Cl_2 + O_2)$ molar ratio and it reaches a maximum for the chlorination in absence of oxygen. Data depicted in Fig. 3(b) represents a similar dependency of reaction rate as a function of the $Cl_2/(Cl_2 + O_2)$ ratio in the oxychlorinating atmosphere. This is in agreement with Eq. (2) representing the chlorination of Fe_2O_3 by chlorine. One may underline that the average reaction rate of hematite in pure chlorine at 950 °C is about 90 times higher than that obtained during its chlorination with a ($Cl_2 + O_2$) mixture containing 10% Cl_2.

The investigation regarding the effects of the gas flow rate, temperature and partial pressure of $Cl_2 + O_2$ on the chlorination of hematite is developed in the next sections and was done by using gaseous mixtures characterized by a $Cl_2/(Cl_2 + O_2)$ ratio equal to 0.8 (i.e. $Cl_2/O_2 = 4$). This ratio was kept constant as it is considered suitable for the beneficiation of chromite by oxychlorination [4–6].

3.2. Effect of chlorine flow rate

In order to determine the intrinsic parameters of the gas–solid reactions, it is appropriate to minimize the effect of the external mass transfer phenomena. This can be achieved by using a sufficient flow rate of reactive gases. The effect of $Cl_2 + O_2$ gas flow rate on the chlorination reaction rate of hematite is studied at 750 and 950 °C.

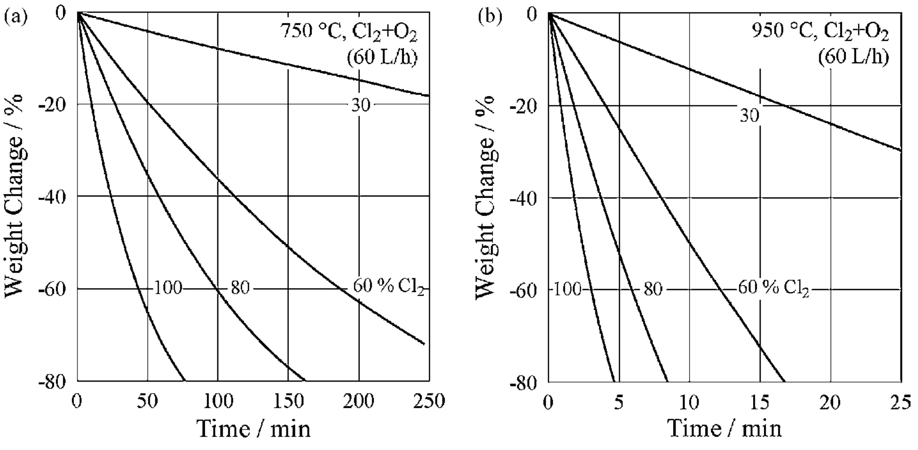

Fig. 2. Isotherms of Fe_2O_3 chlorination with $Cl_2 + O_2$ gas mixture of various chlorine contents.

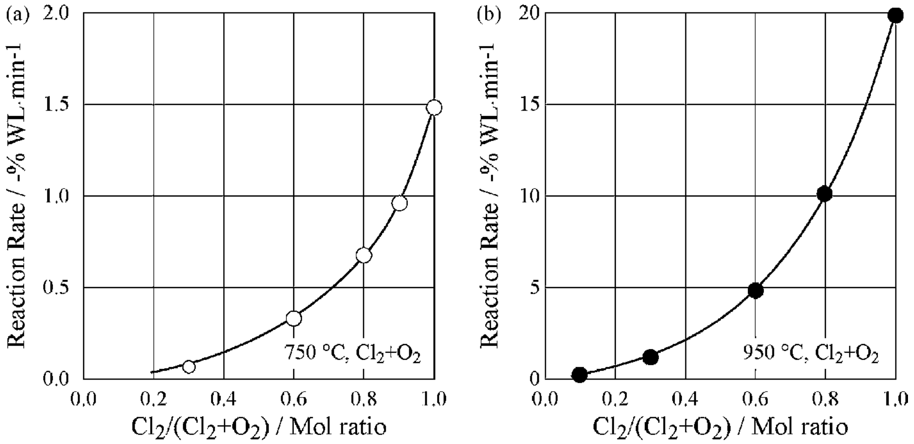

Fig. 3. Effect of $Cl_2/(Cl_2+O_2)$ molar ratio on the reaction rate of Fe_2O_3 chlorination at 750 and 950 °C.

The gas flow rate of chlorine was varied from 10 to 75 L/h and the initial sample weight was 40 mg.

Fig. 4(a) and (b) give a typical example of evolution of weight change (right ordinate) of the sample as a function of time during the chlorination of hematite at 750 °C at 10 and 70 L/h of Cl_2+O_2. Both figures contain also the reaction rate evolution (left ordinate) versus time for the two chosen flow rates of Cl_2+O_2. The reaction rate is calculated as $-\mathrm{d}WL/\mathrm{d}t$ and expressed as $-\%\mathrm{WL\,min}^{-1}$. Less than 48% of sample has reacted for a reaction time of 150 min when a Cl_2+O_2 flow rate of 10 L/h was used (Fig. 4(a)), whilst about 80% of the reaction were observed for the same time at 75 L/h (Fig. 4(b)). As also shown by Fig. 4(a), the reaction rate remains almost constant versus time when a low flow rate of gas was used, as illustrated by the linear aspect of the weight change curve. This is a typical example of an overall reaction governed by external mass transfer.

Values of Cl_2+O_2 flow rates were converted into Cl_2+O_2 linear velocity 'V_g' taking into account the cross section area of the reactor and the obtained values are expressed as $\mathrm{cm\,min}^{-1}$. An average reaction rate is calculated for a reaction extent 'X': $0.05 \le X \le 0.40$ for all isothermal data obtained at 750 and 950 °C.

Fig. 5 summarizes the results of reaction rate evolution as a function of Cl_2+O_2 velocity for both temperatures. As shown by Fig. 5(a),

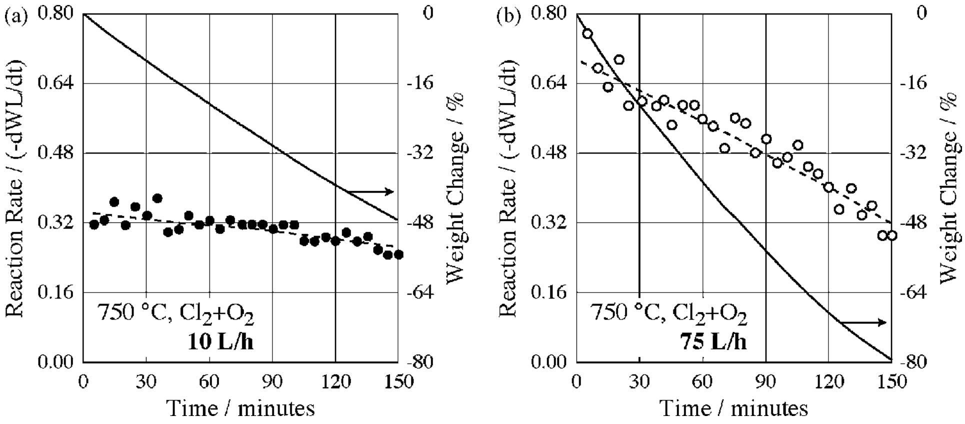

Fig. 4. Isothermal chlorination of hematite by Cl_2+O_2 at 750 °C at 10 and 75 L/h.

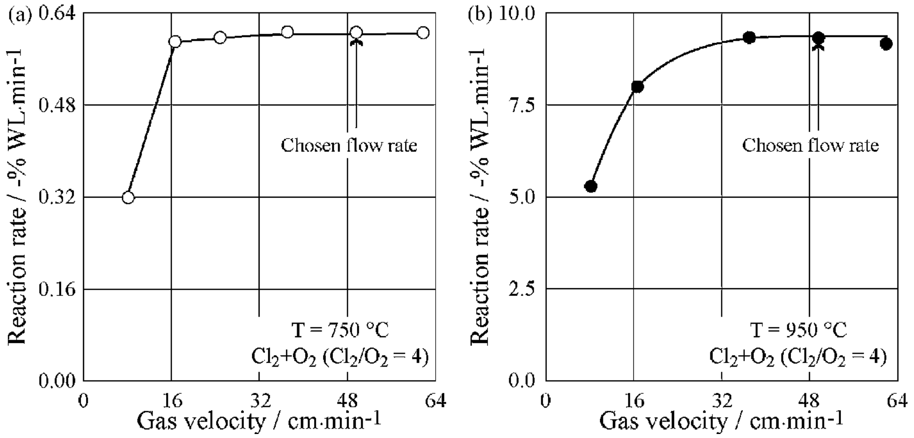

Fig. 5. Effect of Cl_2+O_2 velocity on the reaction of Fe_2O_3 chlorination at 750 and 950 °C.

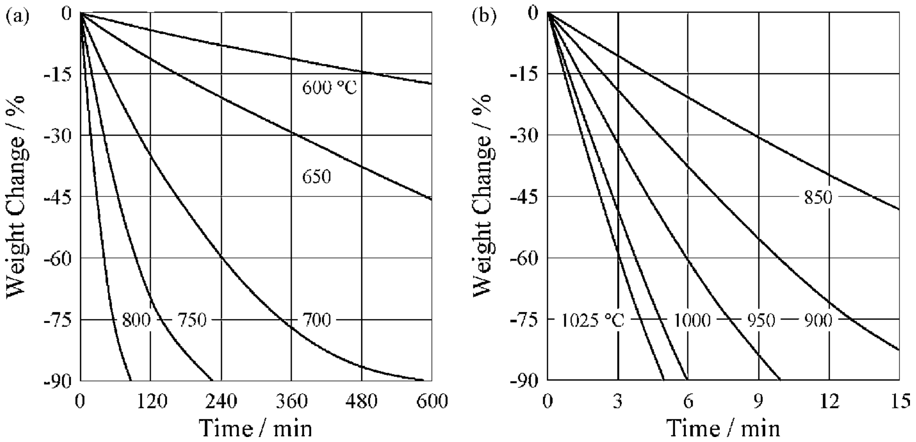

Fig. 6. Isotherms of Fe_2O_3 chlorination by Cl_2+O_2 between 600 and 1025 °C.

the reaction rate at 750 °C is almost independent from the chlorine linear velocity at values higher than about 16 cm/min. As it could be expected, at 950 °C, the chlorination rate of hematite is more dependent on the chlorine velocity (Fig. 5b). A chlorine velocity higher than 40 cm/min will be required to minimize the effect of mass transfer phenomena in the reaction. However, gaseous mixtures with a V_g of 50 cm/min are used to investigate the effect of all other parameters on the chlorination of hematite in presence of oxygen.

3.3. *Effect of temperature*

Series of isothermal tests were carried out at different temperatures ranging from 600 to 1025 °C using $Cl_2 + O_2$. Fig. 6(a) and (b) shows the % WL 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 20%. The reaction rate increases steadily with the temperature rise between 600 and 1025 °C. It reaches 90 pct at 1000 °C for a reaction time of about 6 min.

After calculating the average reaction rate for each isotherm, the data was plotted according to the Arrhenius' law and traced in Fig. 7. The apparent activation energy 'E_a' is 148 ± 3 kJ/mol over the whole temperature range. Although the value of the apparent activation energy is relatively high it is difficult to attribute this value to a pure chemical reaction as slowest step of the hematite chlorination with $Cl_2 + O_2$. A work performed by Gennari and Pasquevich [11] for the chlorination of hematite indicated that the process at temperatures higher than 750 °C is in a mixed regime strongly affected by convective mass transfer.

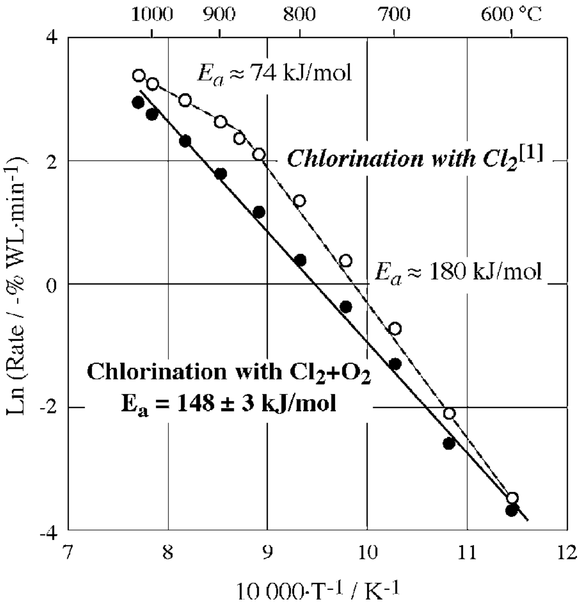

Fig. 7. Arrhenius diagram of Fe_2O_3 chlorination with $Cl_2 + O_2$ and Cl_2 between 600 and 1025 °C.

The temperature dependency of the hematite chlorination by Cl_2 [1] is also given for comparison with that of chlorination with $Cl_2 + O_2$. It was noted previously [1] that the decrease of the E_a value at temperature higher than 875 °C, during hematite chlorination with chlorine, is due to use of the chlorine flow rates lower than that of optimal Cl_2 velocity. This provoked a depletion of the chlorine in the reaction zone leading to an apparent predominance of the mass transfer phenomena on the overall reaction rate of the chlorination.

Fig. 7 clearly shows that the chlorination rate of hematite in pure chlorine is higher than its chlorination with $Cl_2 + O_2$ at all temperatures between 600 and 1025 °C. However, this difference is more pronounced at moderate temperatures, i.e. around 850 °C. Whilst, the difference between the reaction rates of the two types of hematite treatments became less significant at low and high temperatures.

It was observed during the chlorination of hematite in presence of oxygen, that the curves representing the reaction progress with time have different shapes at various temperatures. Typical examples of isotherms are shown in Fig. 8 displaying the evolution of the weight changes (right ordinate) and reaction rates (left ordinate) as a function of the reaction time. Fig. 8(a) shows that the weight change curve versus time follows mostly a one-third-power 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 70 pct. As a contrast, plots of data obtained at 1000 °C show a nearly linear dependency of weight change versus time with an almost constant reaction rate during the first 5 min of chlorination. Although a nominal flow rate of the reactive gases was used, it is possible that diffusion of chlorine through the gaseous phases affected the chlorination of hematite by $Cl_2 + O_2$ especially at high temperatures leading to the shape change of the %WL curves versus reaction time.

3.4. *Effect of $Cl_2 + O_2$ partial pressure*

Experiments to determine the effect of $Cl_2 + O_2$ partial pressure on the reaction rate of hematite chlorination were carried out by using a $Cl_2 + O_2 + N_2$ gas mixture having a Cl_2/O_2 molar ratio constant and equal to 4. The partial pressure of $Cl_2 + O_2$ was varied from 0.25 to 1.00 atm and the results are grouped in Fig. 9 for two cho-

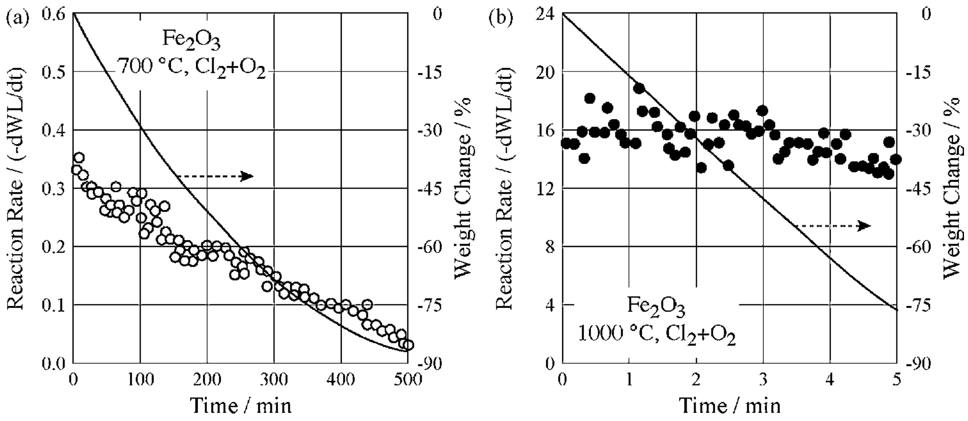

Fig. 8. Reaction rate evolution versus time during hematite chlorination at 700 and 1000 °C.

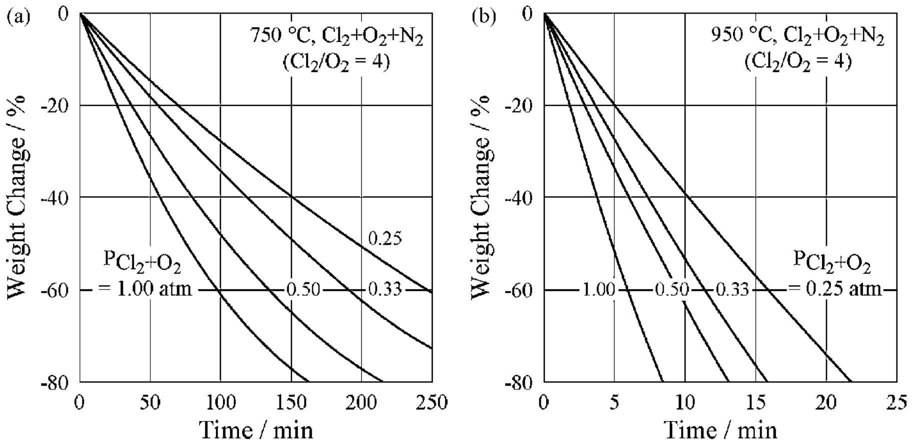

Fig. 9. Isotherms of Fe_2O_3 chlorination using various $Cl_2 + O_2$ pressures at 750 and 950 °C.

sen temperatures of chlorination. As it is shown by Fig. 9(a), the time required to reach a given reaction extent at 750 °C decreased with the rise of partial pressure of $Cl_2 + O_2$. Similar observations are obvious during the chlorination of hematite at 950 °C.

The dependency of the reaction rate from $P(Cl_2 + O_2)$ during the chlorination of hematite at 750 and 950 °C is represented in Fig. 10 using a natural logarithm scale. An apparent reaction order with respect to $Cl_2 + O_2$ of about 0.70, for both treatment temperatures, was deduced from this chart.

3.5. *Effect of Cl_2 partial pressure*

Two series of experimental tests were performed at 750 and 950 °C by using a $Cl_2 + O_2 + N_2$ gas mixture with a constant partial pressure of oxygen equal to 0.33 atm. The data obtained is traced as evolution of pct weight change as a function of time and the resulting curves are shown in Fig. 11. Less than 40% of sample has reacted for about 500 min at 750 °C when the partial pressure of chlorine was 0.20 atm. Use of a gas mixture containing 67% chlorine lowered the reaction time to about 85 min (Fig. 11(a)). Analogous trends are obvious during hematite chlorination at 950 °C and at a constant partial pressure of oxygen.

Data of Fig. 11 is processed and traced in Fig. 12 showing the evolution of the reaction rate as a function of the chlorine partial pressure in natural logarithm scale. An apparent reaction order with respect to chlorine of about 1.44 at 750 °C was deduced from this chart. At 950 °C, the chlorine partial pressure has almost a similar impact on the reaction rate, as nCl_2 was about 1.39.

3.6. *Effect of O_2 partial pressure*

As in the previous case, the effect of the oxygen partial pressure was examined at 750 and 950 °C. The partial pressure of chlorine of the $Cl_2 + O_2 + N_2$ gas mixture was kept constant and

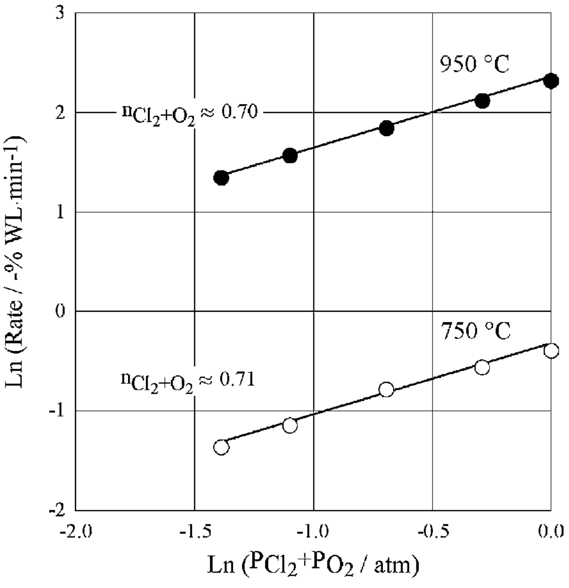

Fig. 10. Apparent reaction order with respect to $Cl_2 + O_2$ for Fe_2O_3 chlorination with $Cl_2 + O_2 + N_2$.

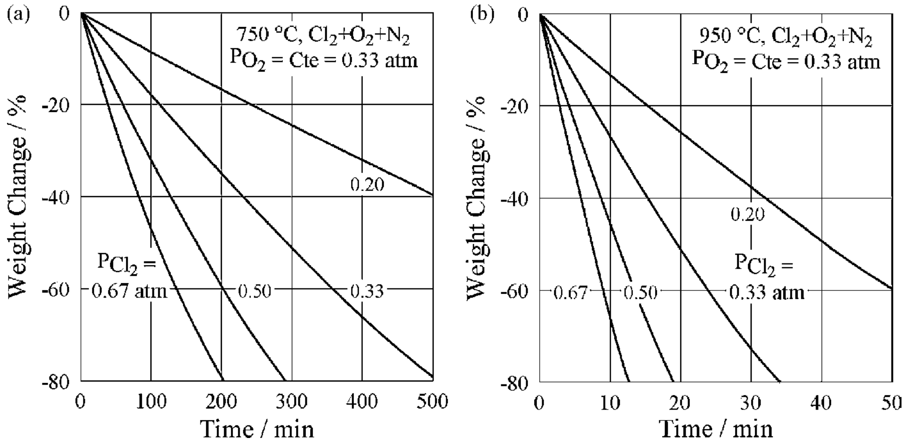

Fig. 11. Isotherms of Fe_2O_3 chlorination using various Cl_2 partial pressures at 750 and 950 °C.

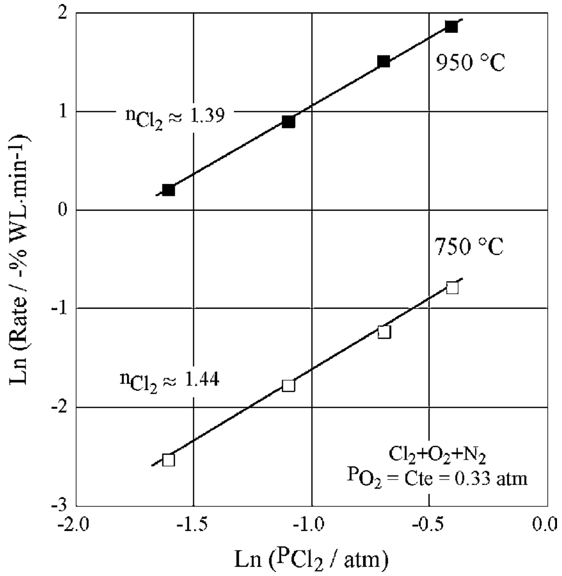

Fig. 12. Apparent reaction order with respect to Cl_2 for Fe_2O_3 chlorination with $Cl_2 + O_2 + N_2$.

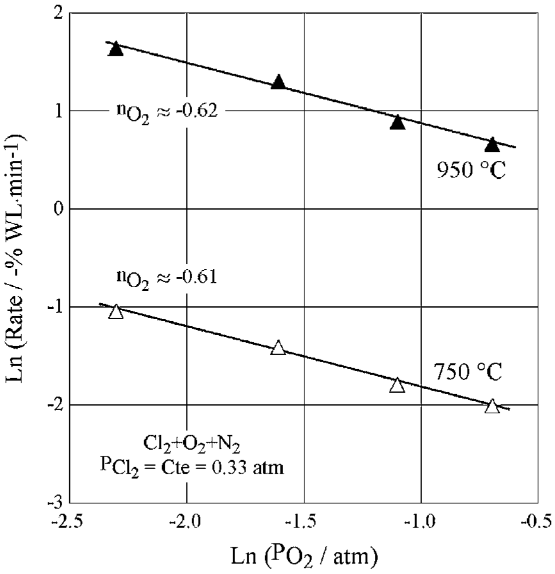

Fig. 14. Apparent reaction order with respect to O_2 for Fe_2O_3 chlorination with $Cl_2 + O_2 + N_2$.

equal to 0.33 atm, when the oxygen content was varied from 10 to 50%. Results of the experimental trials are traced in Fig. 13. For both temperatures studied, the increase of the oxygen partial pressure led to less solid chlorinated at a fixed reaction time. In order to give an insight about the apparent reaction order with respect to oxygen, the initial reaction rate of isotherms presented in Fig. 13 is traced in Fig. 14 as function of the partial pressure of oxygen. The slopes of the straight lines are about −0.61 indicat-

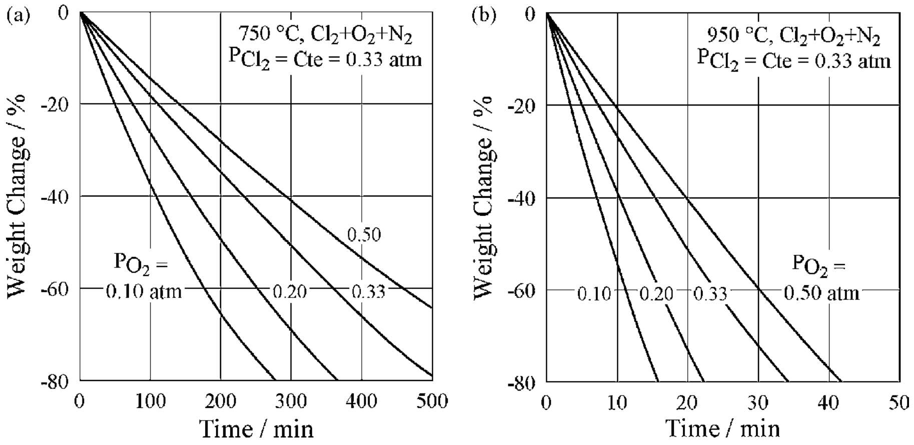

Fig. 13. Isotherms of Fe_2O_3 chlorination using various O_2 partial pressures at 750 and 950 °C.

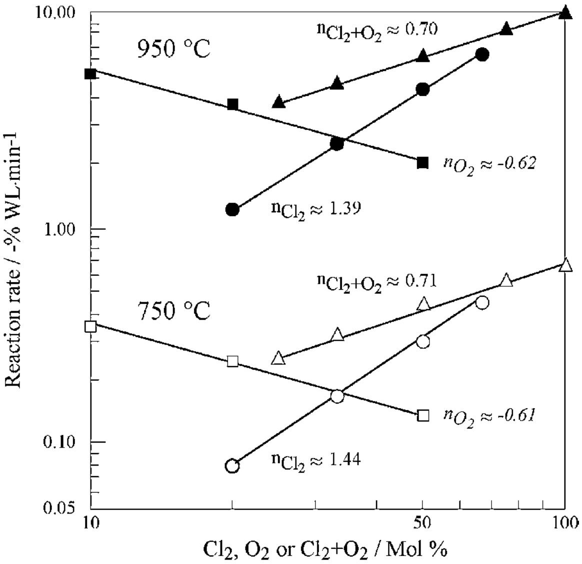

Fig. 15. Effect of gas composition on the reaction rate of Fe_2O_3 chlorination at 750 and 950 °C.

ing that oxygen has a negative effect on the chlorination rate of hematite.

Finally, effects of the reactive gases on the reaction rate of hematite at 750 and 950 °C are summarized in Fig. 15. At both temperatures, the higher impact is attributable to the chlorine. As it could be expected and in accordance with Eq. (2), the reaction rate decreased with the increase of the oxygen content. In both cases, the apparent global reaction order is almost equal to the algebraic sum of the partial orders: $n(Cl_2 + O_2) \approx nCl_2 + nO_2$.

4. Conclusions

1. Reaction rate of the hematite with chlorine depended on the oxygen content of the $Cl_2 + O_2$ gaseous mixture reaching a maximum during chlorination in the absence of oxygen.
2. Hematite reacts with the $Cl_2 + O_2$ gaseous mixture from at least 600 °C and the reaction rate became significant at temperatures approaching 1025 °C. The hematite chlorination proceeded with an average value of the apparent activation energy of about 148 kJ/mol in the temperatures range studied.
3. The partial pressure of $Cl_2 + O_2$ with a Cl_2/O_2 molar ratio of 4 has a weak impact on the chlorination of hematite with an apparent reaction order of about 0.7.
4. The apparent reaction order with respect to oxygen had a negative value in agreement with the envisaged chlorination reaction that involved oxygen. Similarly, the high positive impact of chlorine derived from this work is consistent with the hematite chlorination reaction.
5. For both temperatures (750 and 950 °C), the apparent global order is almost equal to the algebraic sum of the partial orders: $n(Cl_2 + O_2) \approx nCl_2 + nO_2$. This information combined with the E_a value suggests that the rate controlling step of the overall process of hematite chlorination in presence of oxygen remained unchanged between 600 and 1025 °C and within the studied interval of gas compositions.

Acknowledgments

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