Chlorination of manganese oxides

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ABSTRACT

In this work the reaction between several manganese oxides and chlorine is investigated. The reaction path for the chlorination of the oxides is established, which involves recrystallization of high valence manganese oxides: Mn_3O_4 and Mn_2O_3 during the chlorination of MnO, and Mn_2O_3 during the chlorination of Mn_3O_4 and Mn_2O_3. The starting temperature for the reaction of the oxides is determined by non-isothermal thermogravimetric measurements. Analysis of the samples at different reaction degrees reveals that three simultaneous processes are taking place during the whole reaction: chlorination, volatilization of manganese chloride and recrystallization of manganese oxides. The effect of temperature in the reaction rate is analyzed. The activation energies obtained for the reaction of the three oxides with chlorine, which are in accordance with the vaporization enthalpy of $MnCl_2$, suggest that although during the mass loss three processes occur (chlorination, recrystallization and volatilization), volatilization of manganese chloride has a strong influence in the rate observed.

1. Introduction

Many oxide ores which have manganese in their composition undergo chlorination processes during the extraction of refractory metals such as Ti, Hf and Nb. For this reason, when these types of minerals are subject to chlorination, also manganese oxides may be involved in the reaction. To establish the importance of manganese elimination process in the chlorination of these minerals, it is necessary to study the chlorination of manganese oxides. The present study arises from a previous one from Fouga [1] which is about the chlorination of an ilmenite from Venezuela with the following composition: $Fe_{0.96}Mn_{0.04}TiO_3$.

Dry chlorination processes can also be applied for recovering and recycling of valuable metals [2–5]. Recently, a method has been proposed that involves the addition of chloride that comes from an undesired waste formed during cement production, to separate and recuperate metals from bottom ashes by formation of volatile metal chlorides [6]. In order to develop this kind of process it is necessary to study the reaction of metal oxides with chlorine. Murthy and Reddy [7] applied chlorination for the extraction of Cu, Ni, Co, and Mn from manganese nodules from the Indian Ocean. Their results indicate the possibility of preferential chlorination of Cu, Ni, Co and Mn with respect to iron.

The basic advantage of the chlorination process is that the selective extraction of metals could be affected by exploiting the difference either in the reactivity of the metal oxides with chlorine or taking advantage of differences in the volatilization and/or condensation temperatures of their chlorides.

Regarding recuperation of manganese, the results of this study could also be applied in the development of methods for recuperation of manganese from spent dry-cell batteries.

A few works related with chlorination of manganese oxides were reported, and there is no information about the kinetics or mechanism of the manganese oxide chlorination reactions.

Okahara and Iwasaki [8] investigated the chlorination of MnO, Mn_3O_4, Mn_2O_3 and MnO_2, they obtained the non-isothermal thermogravimetric curves, the starting temperature for the chlorination of MnO, Mn_3O_4 and Mn_2O_3 were determined at 200, 350 and 450 °C, respectively. For the chlorination of Mn_3O_4 and Mn_2O_3 they postulated the following reactions:

$$2Mn_2O_3 + Cl_2 \rightarrow MnCl_2 + 3MnO_2 \tag{1}$$

$$Mn_3O_4 + Cl_2 \rightarrow MnCl_2 + 2MnO_2 \tag{2}$$
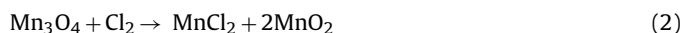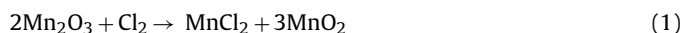
For the initial state of MnO chlorination they proposed:

$$MnO + Cl_2 \rightarrow MnCl_2 + Mn_xO_y \tag{3}$$

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Ivashentsev and Simkina [9] determined that the chlorination of MnO by Cl_2 begins at 130 °C and occurs up to 310 °C according to:

$$MnO + Cl_2 \rightarrow MnCl_2 + (1/2)O_2 \tag{4}$$

Between 310 and 400 °C, Mn_2O_3 was detected in the products and it also reacts with Cl_2 according to:

$$2Mn_2O_3 + 4Cl_2 \rightarrow 4MnCl_2 + 3O_2 \tag{5}$$
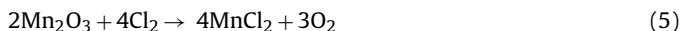
They found that formation of $MnCl_2$ starts at 300 °C for Mn_3O_4 and at 430 °C for Mn_2O_3.

In the present work the starting temperatures for the chlorination of manganese oxides were obtained, since there is no good agreement in the values reported as mentioned before. The reactions occurring during manganese oxide chlorination were identified and formation of high valence manganese oxide was determined.

2. Experimental

The gases used were Cl_2 99.8% purity (Indupa, Argentina) and Ar 99.99% purity (AGA, Argentina). The solids were MnO powder (reagent grade, Alfa Aesar Company), and Mn_3O_4 and Mn_2O_3 which were obtained from MnO by thermal treatments in air for 24 h at 950 and 600 °C, respectively.
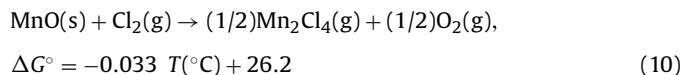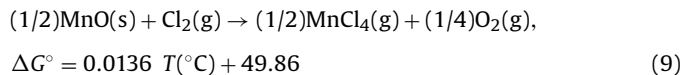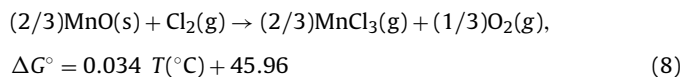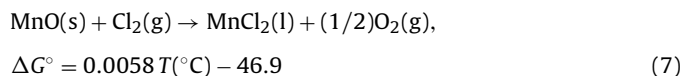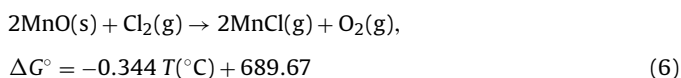
The powder samples of each oxide were characterized by scanning electron microscopy (SEM 515, Philips Electronics Instruments) and X-ray diffraction (XRD). XRD patterns obtained (Fig. 1a–c), are in good agreement with the corresponding reference patterns for the oxides [10] also shown in the figure. No other phases were detected in each pattern.

Fig. 1d and e shows the morphology of MnO, it consists of intergrowth crystals of different sizes ranging between 20 and 80 μm. Micron-order pores were observed in the crystal surface by SEM (Fig. 1e). A BET area [11] of 0.53 m^2/g was determined with N_2 (Digisorb 2600, Micrometrics Ins. Corp.) for the initial MnO powder. The morphology of the Mn_3O_4 and Mn_2O_3 samples (Fig. 1f–i) is similar to that of MnO. The high valence oxides are formed by well-shaped crystal agglomerates greater than 100 μm in size. Also a decrease in the surface porosity was observed.

Isothermal and non-isothermal chlorination reactions were carried out in a thermogravimetric analyzer (TGA), which is extensively described elsewhere [12]. This thermogravimetric analyzer consists of an electrobalance (Model 2000, Cahn Instruments, Inc.) suitable for working with corrosive atmospheres, a gas line and an acquisition system. This experimental set-up has a sensitivity of ±5 μg while operating at 950 °C under a flow of 8 l/h. Samples of 20 mg were placed in a quartz crucible inside the reactor in an argon flow of 1.3 l/h. To begin the non-isothermal reactions, a chlorine flow of 0.8 l/h was introduced and, at the same time, the heating started with a ramp of 100 C/h. For the isothermal reactions, the solids were heated until they reached the desirable temperature before chlorine injection. The partial pressure of chlorine in the Ar–Cl_2 mixture was 35.5 kPa.

3. Thermodynamical analysis

Several manganese chlorides are reported, MnCl, $MnCl_2$, $MnCl_3$, $MnCl_4$ and Mn_2Cl_4. The values of $\Delta G°$ (kJ/mol of Cl_2) as a function of temperature, corresponding to formation of these chlorides are presented in Eqs. (6)–(10) by mol of chlorine for temperatures between 650 and 950 °C:

$$2MnO(s) + Cl_2(g) \rightarrow 2MnCl(g) + O_2(g),$$
$$\Delta G° = -0.344\, T(°C) + 689.67 \tag{6}$$

$$MnO(s) + Cl_2(g) \rightarrow MnCl_2(l) + (1/2)O_2(g),$$
$$\Delta G° = 0.0058\, T(°C) - 46.9 \tag{7}$$

$$(2/3)MnO(s) + Cl_2(g) \rightarrow (2/3)MnCl_3(g) + (1/3)O_2(g),$$
$$\Delta G° = 0.034\, T(°C) + 45.96 \tag{8}$$

$$(1/2)MnO(s) + Cl_2(g) \rightarrow (1/2)MnCl_4(g) + (1/4)O_2(g),$$
$$\Delta G° = 0.0136\, T(°C) + 49.86 \tag{9}$$

$$MnO(s) + Cl_2(g) \rightarrow (1/2)Mn_2Cl_4(g) + (1/2)O_2(g),$$
$$\Delta G° = -0.033\, T(°C) + 26.2 \tag{10}$$

Among these, formation of $MnCl_2$ and Mn_2Cl_4 are the only ones that have negative $\Delta G°$ values in the range of temperatures considered. The dimerization reaction (Eq. (11)) is thermodynamically feasible below 870 °C.

$$2MnCl_2(g) \rightarrow Mn_2Cl_4(g), \qquad \Delta G° = 0.14\, T(°C) - 122.17 \tag{11}$$

The experimental set-up used allows continuous evacuation of the reaction products (i.e. O_2, $MnCl_2$), leading to low partial pressures of these species, whereas partial pressure of Cl_2, which is given by the incoming chlorine stream, will remain constant at 35.5 kPa. For this reason, the values of ΔG will be lower than the values of $\Delta G°$, and even with a $\Delta G° > 0$ a reaction could occur.

On the other hand, an opposite situation can be held locally at certain places. Although the chlorinating gas is a mixture of Cl_2–Ar, in the sample surroundings O_2 is being generated and Cl_2 is being exhausted by the reaction, for that reason the partial pressure of O_2 is expected to be high. Moreover, the residence time of O_2 in the sample is long due to the low gaseous flow (2.1 l/h) and because the O_2 formed may have to diffuse through a $MnCl_2$ layer before reaching the gaseous phase. A Kellog-diagram [13] (Fig. 2) of the Mn–Cl–O system at 800 °C shows the stability areas of manganese containing substances as a function of Cl_2(g)- and O_2(g)-pressures in the atmosphere at that temperature. It shows that for partial pressures of Cl_2 close to zero value, as expected at the reaction surface, partial pressures of O_2 lower than 101.3 kPa (1 bar) are high enough to allow formation of high valence manganese oxides such as Mn_3O_4 and Mn_2O_3.

Finally, no information is available regarding manganese oxychlorides, with the only exception of the existence of gaseous $MnClO_3$ that has been reported [13].

4. Results and discussion

4.1. Reactivity

The initial reaction temperature which is associated with the system reactivity was determined by non-isothermal thermogravimetric measurements. The chlorination curves for MnO, Mn_3O_4 and Mn_2O_3 are shown in Fig. 3. This figure shows the ratio between the mass change and the initial mass of the sample ($\Delta M/M_i$) as a function of temperature. The starting temperatures for the chlorination of MnO, Mn_3O_4 and Mn_2O_3 are 270, 380 and 520 °C, respectively.

The TG curves start with a slow mass gain which corresponds to formation of condensed $MnCl_2$, and high valence oxides, as will be discussed later. When temperature reaches about 650 °C ($MnCl_2$ melting point) there is an increase in the reaction rate, this behavior may be due to the melting of the chloride layer formed that allows chlorine to easily reach fresh oxide. The mass gain observed in the maximum of the curves for the three systems are lower than
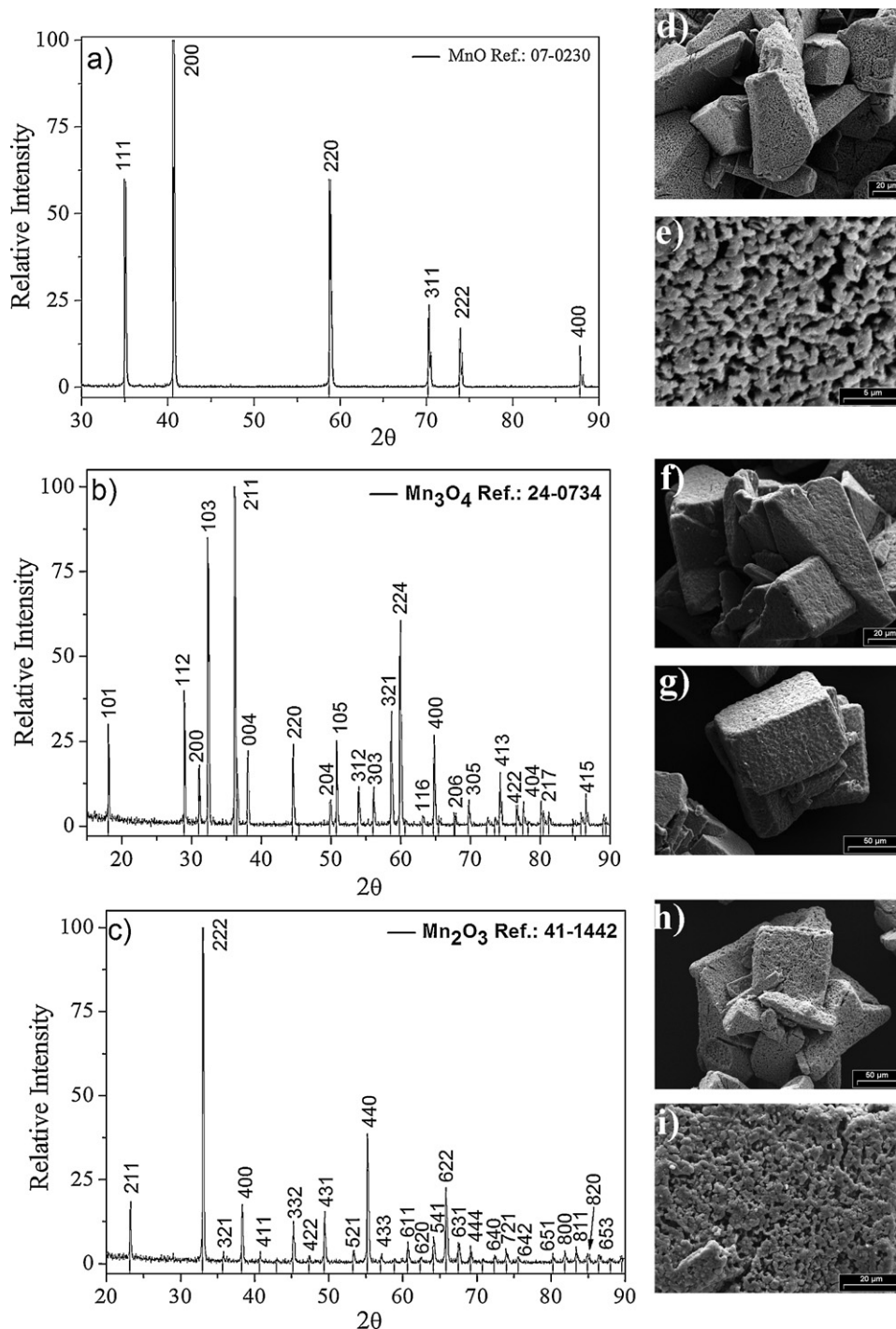
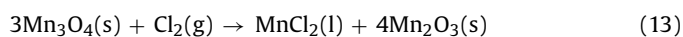**Fig. 1.** XRD patterns, SEM photographs of the initial samples of MnO, Mn_3O_4 and Mn_2O_3.
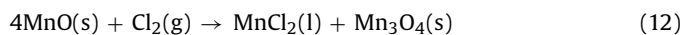
that needed for complete reaction to form $MnCl_2$ which indicates that also volatilization of the chloride formed is taking place. This is expectable since the partial pressure of manganese chloride (also shown in Fig. 3) reaches a value of 10^{-2} kPa at 640 °C [13], which suggests that the mass change due to volatilization will be significant above that temperature [14]. For temperatures above 730 °C the mass continuously decreases until complete volatilization.

4.2. Isothermal chlorination of manganese oxides

The TG curve for the chlorination of MnO at 800 °C is shown in Fig. 4. The reaction starts with a mass gain followed by a mass loss until complete volatilization.

In order to understand how the chlorination reaction occurs, the chlorinations were interrupted at different reaction degrees (as shown by symbols in Fig. 4). Samples were analyzed by SEM and XRD. SEM photographs and phases detected by XRD are shown in Fig. 4. In the maximum of the curve, after the mass gain, there is $MnCl_2$, Mn_3O_4 and Mn_2O_3. The occurrence of Mn_3O_4 and Mn_2O_3 indicates that MnO is being chlorinated according to:

$$4MnO(s) + Cl_2(g) \rightarrow MnCl_2(l) + Mn_3O_4(s) \tag{12}$$

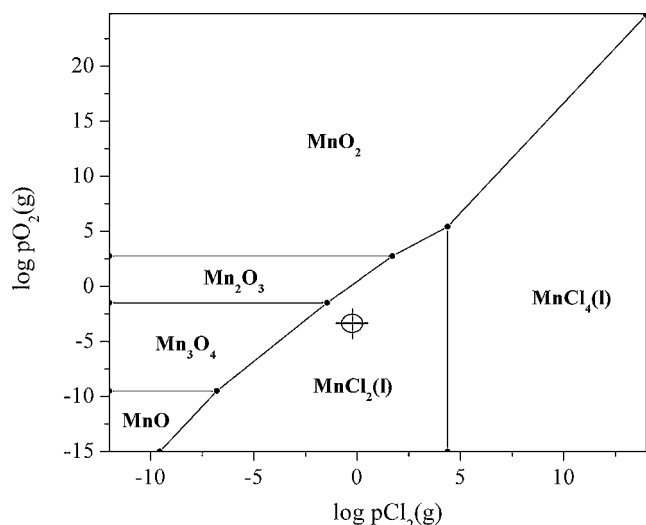$$3Mn_3O_4(s) + Cl_2(g) \rightarrow MnCl_2(l) + 4Mn_2O_3(s) \tag{13}$$

Fig. 2. Predominance diagram for Mn–Cl–O system at 800 °C (partial pressures expressed in bar units). The average reaction conditions during chlorinations are indicated by ⊕.

Fig. 3. Non-isothermal chlorination reactions of MnO, Mn_3O_4 and Mn_2O_3.

The high ratio of mass gain obtained in the maximum of the curve, 0.29 which is higher than the one expected taking into account Eq. (12) (i.e. 0.26), is in accordance with the reactions proposed.

SEM examination shows that while manganese chloride forms agglomerates of small grains (Fig. 4a), manganese oxides growth as well defined crystals (Fig. 4b). The morphology of the oxides indicates that they are being formed from an isotropic media, two possible processes can lead to formation of these crystals: a gaseous phase reaction taking place in the boundary layer between manganese chloride and oxygen which is thermodynamically feasible, or a reaction occurring in the liquid phase formed by liquid manganese chloride saturated with dissolved oxygen.

An advanced stage of the reaction was analyzed by interrupting a chlorination during the mass loss (also shown in Fig. 4.) $MnCl_2$ and Mn_2O_3 were detected by XRD the corresponding morphologies are shown in Fig. 4d and e. These results are also in accordance with reaction (13).
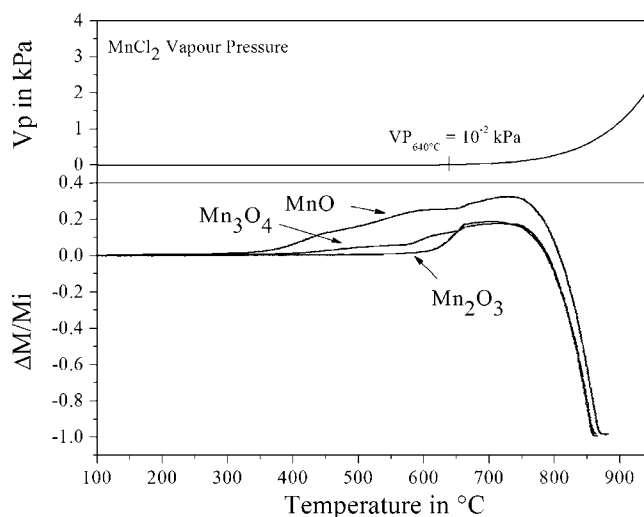
To check the occurrence of the reactions proposed, chlorinations of Mn_3O_4 and Mn_2O_3 at 800 °C were performed, and interrupted reaction samples were analyzed. The corresponding TG curves are shown in Fig. 5. Both reactions were interrupted during the mass loss near the maximum, and Mn_2O_3 and $MnCl_2$ were detected by XRD. Regarding Mn_2O_3 chlorination, an interrupted reaction shows that the sample consists of $MnCl_2$ and Mn_2O_3.

Formation of $MnCl_2$ during the chlorination of manganese tri-oxide in a highly oxidizing atmosphere can be understood considering the Kellog-diagram (Fig. 2). With a simple calculation based on the moles of oxygen lost during the chlorination of Mn_2O_3 it is possible to estimate the average partial pressure of O_2 under the experimental conditions, the value is in the order of 0.1 kPa (10^{-3} bar). The partial pressure of Cl_2 is given by the incoming chlorine stream (35.5 kPa = 0.355 bar). A symbol was included in Fig. 2 which indicates these conditions, it can be seen that the stability diagram predicts formation of $MnCl_2$.

These results confirm that chlorination of Mn_3O_4 occurs through formation of Mn_2O_3 (Eq. (13)) and chlorination of Mn_2O_3 according to Eq. (14) with formation of manganese chloride and oxygen
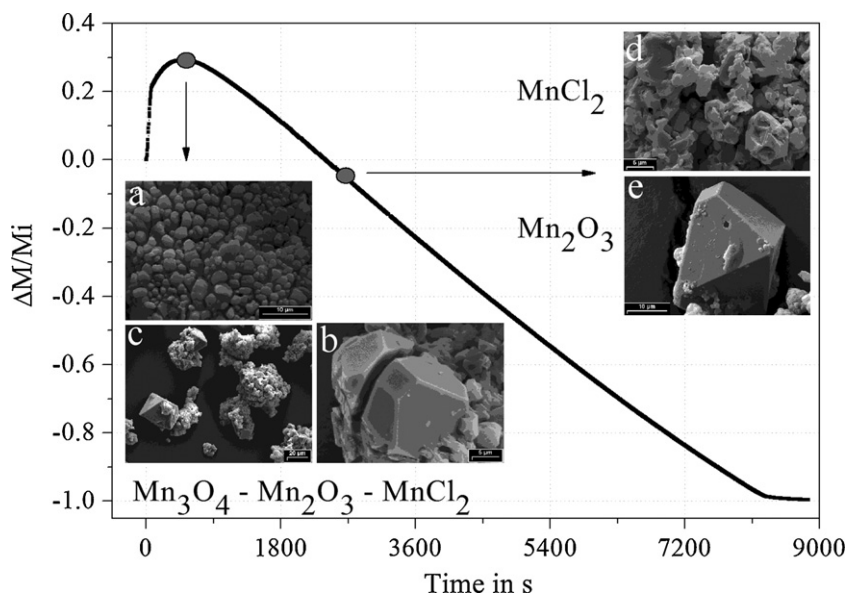

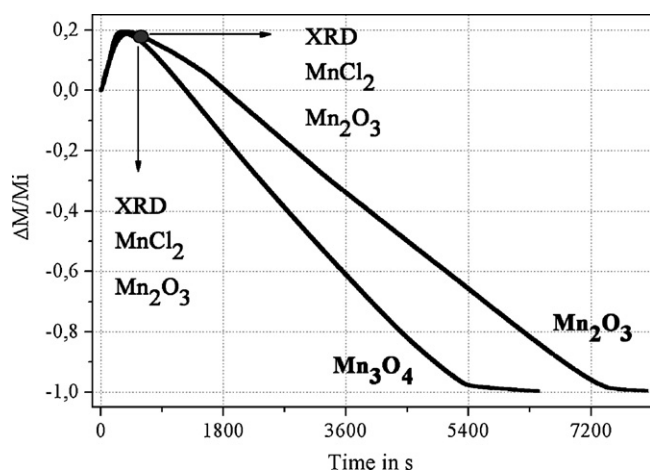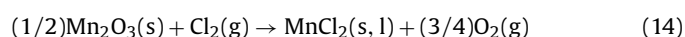**Fig. 4.** Chlorination of MnO at 800 °C.

Fig. 5. Chlorination of Mn_3O_4 and Mn_2O_3 at 800 °C.

release:

$$(1/2)Mn_2O_3(s) + Cl_2(g) \rightarrow MnCl_2(s, l) + (3/4)O_2(g) \qquad (14)$$

To sum up, the following reaction mechanism for the chlorination of MnO can be proposed: chlorination of manganese oxide with formation of manganese chloride and manganese tetra oxide according to Eq. (12), chlorination of manganese tetra-oxide with formation of manganese chloride and manganese tri-oxide according to Eq. (13) and chlorination of manganese tri-oxide according to Eq. (14).

Consequently, during the chlorination of manganese oxides at least three different processes can influence the rate observed: chlorination, volatilization and recrystallization.

4.3. Influence of temperature in the chlorination of manganese oxides

Isothermal chlorinations of the different oxides in the range between 650 and 950 °C and chlorine partial pressure of 35.5 kPa were performed. The influence of temperature on the chlorination reactions can be observed in Fig. 6a–c, where the TG curves for the chlorination of MnO, Mn_3O_4 and Mn_2O_3 are presented.

These curves show two different regions, an initial mass gain where the rate of formation of condensed manganese chloride and high valance manganese oxides is higher than the rate of volatilization, and a region of mass loss where the rate of volatilization of the chloride formed predominates. At high temperatures only weight losses were observed although the conversion of the oxides into $MnCl_2$ is characterized by a significant weight gain, this is because the rate of volatilization is so enhanced by temperature that the amount of mass loss due to volatilization is higher that the amount of mass gain due to formation of manganese chloride leading to an overall mass loss.

The initial rate of the mass gain is independent of temperature and the rate order, 10^{-6} moles of Cl_2/s, reveals that the chlorination reaction is very fast and diffusion of chlorine through the bound-
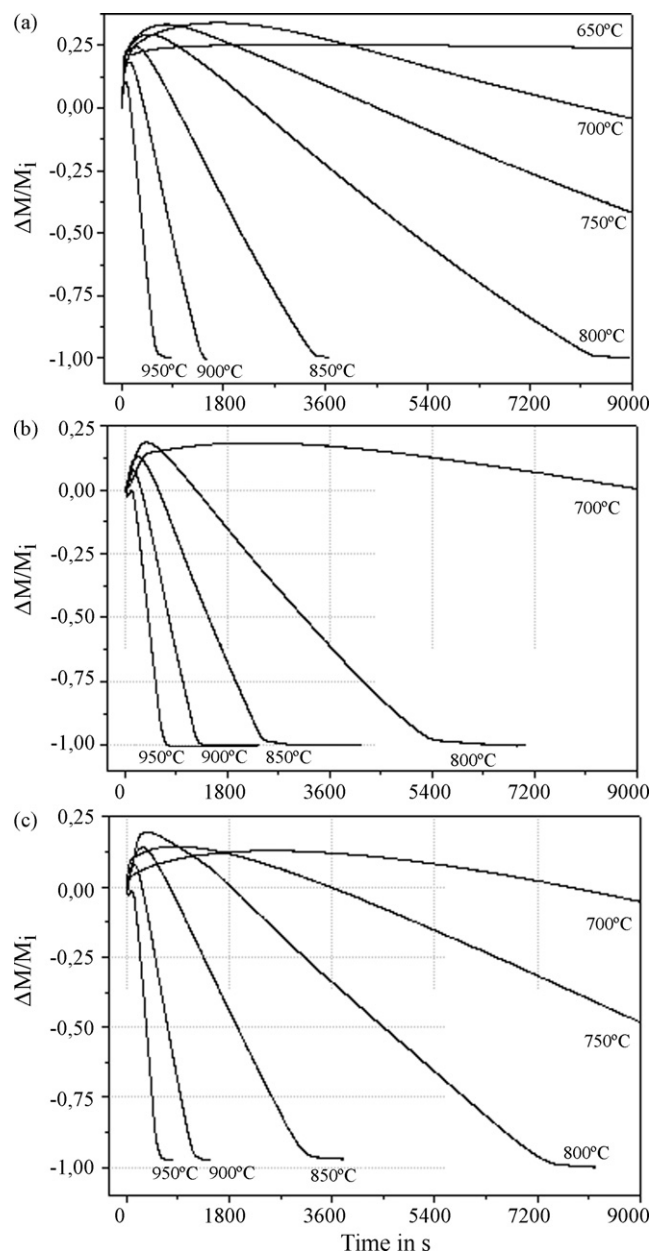

Fig. 6. Influence of temperature in the chlorination of manganese oxides.

ary layer controls the reaction rate as demonstrated by previous publication [15].

The rate of mass loss increases with temperature, the values obtained for the different oxides are shown in Table 1.

These values are lower than the aforementioned values (10^{-6} moles of Cl_2/s i.e. 7×10^{-2} mg/s), which indicates that for temperatures below 950 °C, the rate is not controlled by diffusion of the incoming chlorine through the boundary layer. The constant values obtained for the different oxides suggest that the rate is controlled

Table 1
Rate of mass loss in mg/s during manganese oxide chlorination.

Oxide	Temperature in °C					
	700	750	800	850	900	950
MnO	1.2×10^{-3}	2×10^{-3}	3.9×10^{-3}	9.5×10^{-3}	2.2×10^{-2}	4.6×10^{-2}
Mn_3O_4	8.3×10^{-4}	–	4.9×10^{-3}	1.1×10^{-2}	2.2×10^{-2}	4.2×10^{-2}
Mn_2O_3	8.8×10^{-4}	2×10^{-3}	3.6×10^{-3}	8.4×10^{-3}	2.2×10^{-2}	4.9×10^{-2}

by volatilization of $MnCl_2$. Activation energies of 171 ± 9 kJ/mol, 148 ± 3 kJ/mol and 173 ± 8 kJ/mol were calculated for the reactions of MnO, Mn_3O_4, and Mn_2O_3 with Cl_2, respectively, with the Flynn method [16] from the slope of the curve of $\ln t$ versus $1/T$ during the mass loss. These values are similar to the average value of the vaporization enthalpy of manganese chloride between 750 and 950 °C, 162 kJ/mol [13], which also suggests that volatilization of $MnCl_2$ has a strong influence in the rate of reaction during the mass loss. However, a detailed kinetic study is beyond the scope of the present work.

5. Conclusions

The starting temperatures for the chlorination of selected manganese oxides were established. Volatilization of manganese chlorides at temperatures above 700 °C was observed, this is in accordance with manganese chloride partial pressure at that temperature (10^{-2} kPa). Three stages were identified during chlorination of MnO: the first one leads to formation of $MnCl_2$ and Mn_3O_4, in the second step Mn_3O_4 is chlorinated forming $MnCl_2$ and Mn_2O_3. Finally, volatilization of $MnCl_2$ takes place. Chlorination of Mn_3O_4 and Mn_2O_3 confirmed the reaction path proposed for the chlorination of MnO. Formation of well-defined crystals of high valence manganese oxides was observed during chlorination. This evidences that a recrystallization reaction from an isotropic media takes place during the whole reaction, the rates observed correspond to three coupled processes: chlorination, recrystallization and volatilization. The value of the activation energy obtained is in well accordance with the enthalpy of vaporization of $MnCl_2$ which suggest that volatilization of $MnCl_2$ could be the rate determining step.

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