



# Hematite to magnetite reduction monitored by Mössbauer spectroscopy and X-ray diffraction

J.P. Gaviria<sup>a,\*</sup>, A. Bohé<sup>a,b</sup>, A. Pasquevich<sup>c</sup>, D.M. Pasquevich<sup>a</sup>

<sup>a</sup>Centro Atómico Bariloche-CNEA, CONICET, Argentina

<sup>b</sup>CRUB-University Nac. del Comahue, Argentina

<sup>c</sup>CICPBA, Depto. de Física, Fac. Ciencias Exactas, UNLP, Argentina

## Abstract

The aim of the present research is to determine the kinetics of the transformation from hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) to magnetite (Fe<sub>3</sub>O<sub>4</sub>). The procedure consisted of an isothermal heating in a flow of a H<sub>2</sub>-Ar mixture at temperatures between 260 and 360 °C. The phase evolution at a given temperature, as a function of the thermal treatment time, was monitored by using room temperature Mössbauer spectroscopy and X-ray diffraction analysis (XRD). In the range of temperatures and times studied the only iron oxide that was formed was magnetite.

In order to optimize equipment requirements for the quantification of the reaction products a calibration curve was constructed. This allows to estimate the conversion degree (measured as the percentage of magnetite produced) with a short-run XRD pattern. We calculate an apparent activation energy of  $98 \pm 4$  kJ/mol from reaction grade-time curves at each temperature.

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## 1. Introduction

The Fe<sub>3</sub>O<sub>4</sub> system has become of long-standing interest due to its rich variety of applications in the industry as pigment or precursor for magnetic fluids [1]. It is of great interest to study alternative methods of synthesis to reduce costs of preparation and improve the rate and quality (purity, stoichiometry and crystallinity) of the final products. Several chemical methods have been proposed to synthesize magnetite [1]. The direct reduction of ferric oxide by gaseous reductants is an industrially important reaction. The reaction proceeds through the formation of Fe<sub>3</sub>O<sub>4</sub> if the temperature is below 575 °C since the wustite phase is unstable under these conditions [2].

Many researchers have studied the gaseous reduction of iron oxide [3–5]. The data reported can be summarized by stating that the consecutive reduction of iron oxides should

be viewed as a complex series of heterogeneous reactions whose rates are influenced both by chemical kinetics factors and mass (and/or heat) transfer factors.

Betancur et al. [6] studied the dynamics of transformation from hematite to magnetite by following two solid-state methods. One of the procedures consisted of a thermal treatment under a 20% H<sub>2</sub> and 80% N<sub>2</sub> atmosphere at 375 °C, whereas the second method involved a planetary ball mill to induce the transformation. The results of the first procedure evidenced a well-behaved structural transformation for which highly stoichiometric Fe<sub>3</sub>O<sub>4</sub> as a single phase was obtained for treatment above 12.5 min. In contrast, a less stoichiometric magnetite in the case of the ball milled samples was obtained.

Wiltowski et al. [7] and Piotrowski et al. [8] investigated the kinetics of Fe<sub>2</sub>O<sub>3</sub> to FeO reduction using the thermogravimetric data in the temperature range of 700–900 °C. They used a reducing atmosphere of composition 90% N<sub>2</sub> + (10-x)% CO + x% H<sub>2</sub> (0 < x < 1) and the reducing mixture flow rate was 30 ml/min. They found that

\*Corresponding author. Fax: + 54 02944 44 52 93.

E-mail address: [gaviriaj@cab.cnea.gov.ar](mailto:gaviriaj@cab.cnea.gov.ar) (J.P. Gaviria).

initially the reduction of hematite is a surface-controlled process. However, once a thin layer of iron oxides with lower oxidation state (magnetite, wustite) is formed on the surface, it changes to diffusion control. The values of activation energies obtained were  $\Delta E_a = 104$  and  $\Delta E_a = 24$  kJ/mol for the reducing gas mixtures of  $N_2 + CO$  and  $N_2 + H_2$ , respectively.

In this work, we study the kinetics of the reduction of hematite to magnetite under a 5%  $H_2$ –95% Ar flow at temperatures between 260 and 360 °C.

## 2. Experimental

### 2.1. Materials

The material used was an hematite powder (analytical reagent, Mallinckrodt). Particles were well characterized by scanning electron microscopy (SEM). The powder is formed by non-porous crystalline grains of approximately 0.7  $\mu\text{m}$  in size, which in turn form porous agglomerates from several microns to 100  $\mu\text{m}$  in size. The gaseous reductant was a 5%  $H_2$ –95% Ar mixture provided by AGA.

### 2.2. Equipment

The reactants and products were examined by Mössbauer spectroscopy (MS), SEM (Philips 515), and by a Philips PW 1310/01 diffractometer using Ni-filtered  $\text{CuK}\alpha$ . The MS studies were carried out at room temperature using a  $^{57}\text{Co}/\text{Rh}$  source in a constant-acceleration transmission spectrometer. The spectrometer was calibrated using a standard  $\alpha\text{-Fe}$  foil and the reported isomer shifts (IS) are relative to the center of the  $\alpha\text{-Fe}$  spectrum. The spectra were least squares fitted with Lorentzian line shapes.

### 2.3. Procedure

The sample was placed in a quartz reactor outside the furnace at room temperature in a 5%  $H_2$ –95% Ar flow of 100 ml/min (furnace temperature was previously set up at the experimental temperature), during 20 min to purge the system. Subsequently, the flow rate was adjusted to 50 ml/min and the sample was introduced into the furnace. The zero time of the reaction was taken at this moment. The 5%  $H_2$ –95% Ar flow rate was measured at the outlet with a soap film flow meter and regulated with a needle-valve Gilmont flow meter.

### 2.4. Data handling

The hematite to magnetite reduction is not conveniently followed by gravimetry due to the fact that the total loss of mass is very small (3.34%). Hence, we used the following methodology to characterize the products and estimate the amount of magnetite produced in the reactions:

- 1) *Mössbauer spectroscopy (MS)*. With the areas of the fitted patterns and considering that 1 mol of  $\text{Fe}_3\text{O}_4$  has three iron atoms and 1 mol of  $\text{Fe}_2\text{O}_3$  has two iron atoms (since fitting give the iron amount present in each phase).
- 2) *X-ray diffraction patterns*. In order to optimize equipment requirements for the quantification of the reaction products a calibration curve (CC) was constructed. This allowed to estimate the conversion degree (measured as the percentage of magnetite produced) with a short-run XRD pattern. This curve was obtained analyzing several samples by MS to obtain the amount of hematite and magnetite, and by XRD to obtain the area ratio of two characteristic peaks. The characteristic peaks for each phase were  $2\theta = 30.1^\circ$  for magnetite (220) and  $2\theta = 33.2^\circ$  for hematite (104). The patterns were taken from  $2\theta = 20^\circ$  to  $50^\circ$ .
- 3) *Reference samples*. Two mixtures were prepared by weighting known quantities of hematite and magnetite in order to compare with the amount obtained by MS and by the CC measurements.

## 3. Results and discussion

### 3.1. Reduction at 320 °C

The reductions were carried out with a hematite mass of 90 mg and a flow rate of 50 ml/min. Figs. 1 and 2 show the reaction time evolution of the room temperature MS and XRD pattern. The reduction of hematite to magnetite is complete for times above 40 min. XRD and Mössbauer results showed that the magnetite obtained has a high

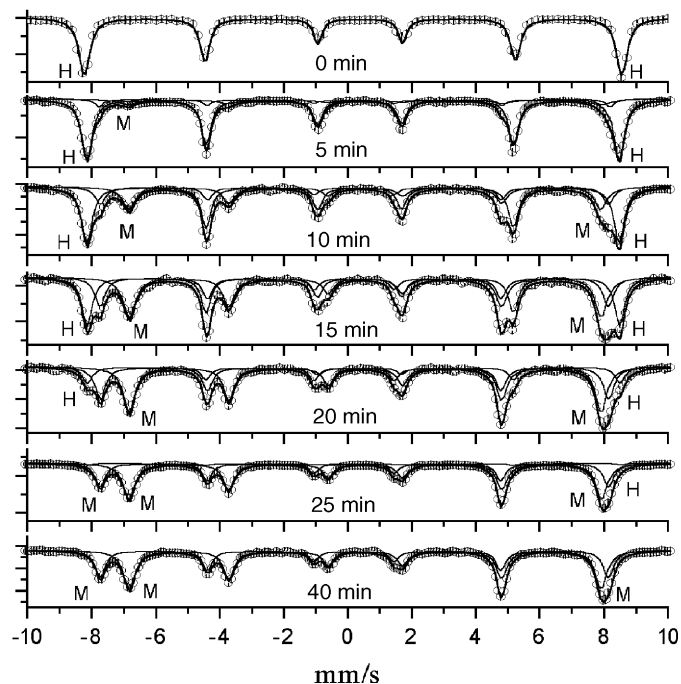


Fig. 1. Room temperature Mössbauer spectra for the hematite samples treated at 320 °C.

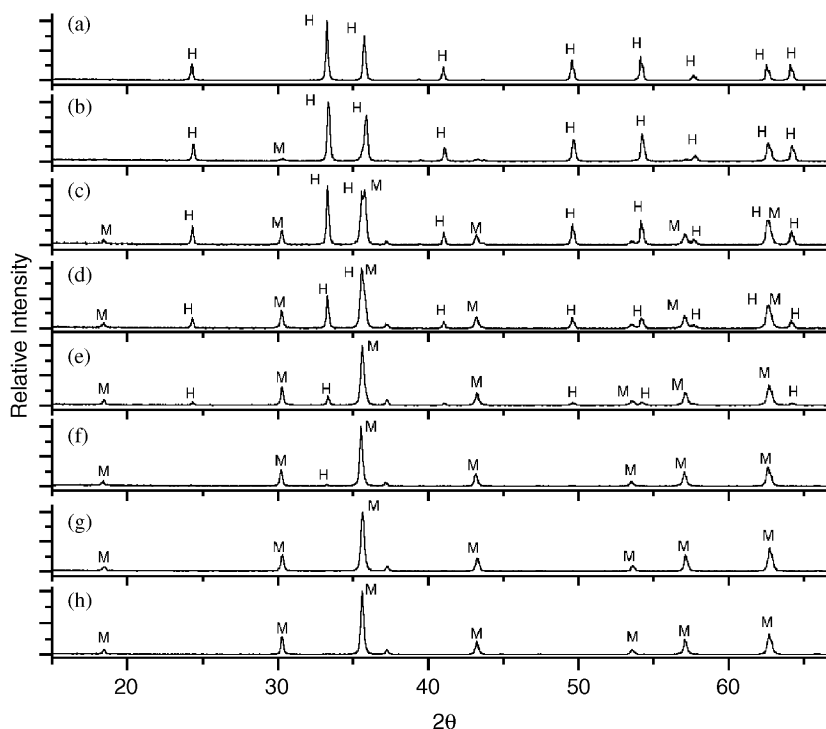


Fig. 2. XRD patterns for the treatment at 320 °C at different reaction times. (a) Original hematite, (b) 5 min, (c) 10 min, (d) 15 min, (e) 20 min, (f) 25 min, (g) 40 min, and (h) 50 min.

Table 1  
Fitted hyperfine parameters and calculated areas from the Mössbauer spectra

	Reaction time (min)						
	0	5	10	15	20	25	40
$B_{\text{hf}}$ (T) $\alpha\text{-Fe}_2\text{O}_3$	51.8	51.6	51.5	51.5	51.5	51.6	—
$B_{\text{hf}}$ (T) $\text{Fe}^{+3}$	—	49.2	49	49.1	49.2	49.3	49.2
$B_{\text{hf}}$ (T) $\text{Fe}^{+2.5}$	—	45.9	45.8	45.8	45.8	45.8	45.8
IS(Fe) (mm/s) $\alpha\text{-Fe}_2\text{O}_3$	0.37	0.37	0.37	0.38	0.41	0.39	—
IS(Fe) (mm/s) $\text{Fe}^{+3}$	—	0.36	0.29	0.29	0.3	0.3	0.3
IS(Fe) (mm/s) $\text{Fe}^{+3}$	—	0.62	0.64	0.54	0.54	0.65	0.65
A( $\text{Fe}_2\text{O}_3$ ) (%)	100	85	59	50	16	2	—
A( $\text{Fe}_3\text{O}_4$ ) (%)	—	15	41	50	84	98	100

Three sextets were used corresponding to hematite and magnetite ( $\text{Fe}^{+3}$  and  $\text{Fe}^{+2.5}$  sites).

crystallinity and this is the only phase that is present after the treatments.

The global reaction may be represented by the following chemical equation:

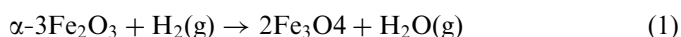


Table 1 summarizes the hyperfine parameters of the three sextets employed in the Mössbauer fitting process corresponding to the presence of hematite and magnetite. These values are in good agreement with those reported in the literature [9].

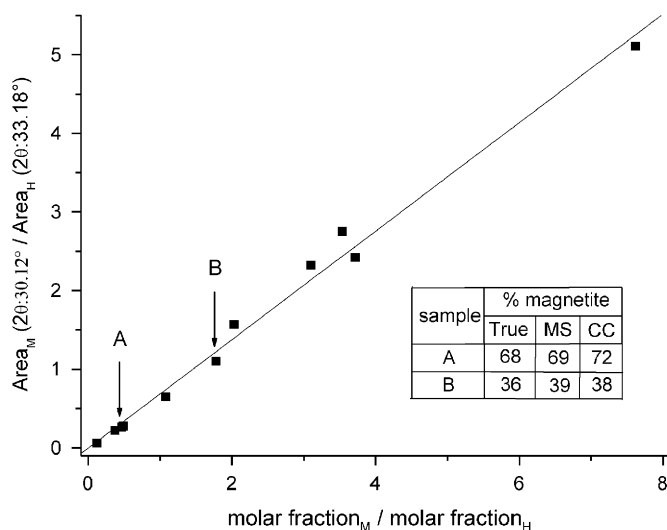


Fig. 3. Calibration curve constructed to estimate the amount of magnetite produced with a short-run XRD pattern. The table shows the results of the quantification of two prepared samples with known quantities of hematite and magnetite.

### 3.2. Calibration curve

Fig. 3 shows the CC used to determine the amount of magnetite produced. The vertical axis corresponds to the ratio of the XRD peaks' area of magnetite and hematite, and the horizontal axis is the molar fraction ratio of magnetite and hematite calculated by MS. The samples used were those obtained from partial reduction at 320 °C.

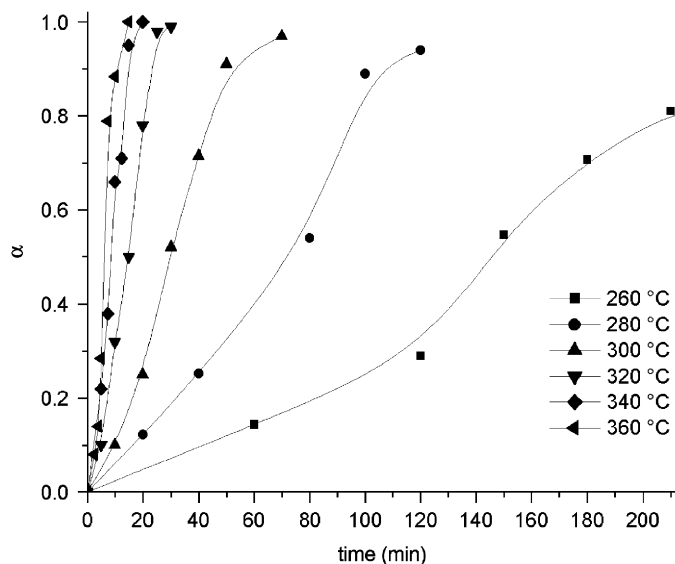


Fig. 4.  $\alpha$  vs. time curves for the reduction of hematite to magnetite with a 5%  $H_2$ –95% Ar flow.

In order to test this curve and the Mössbauer quantification, two reference samples (A and B) with well-known quantities of hematite (H) and magnetite (M) were prepared. The table in Fig. 3 shows the results of the quantification of these samples using MS and the CC. The results show that these methods are good to estimate the amount of magnetite produced with an error less than 4%.

### 3.3. Temperature dependence

Fig. 4 shows the reaction degree ( $\alpha$ ) vs. reaction time curves at temperatures between 260 and 360 °C ( $\alpha$  is defined as the molar fraction of magnetite). The  $\alpha$  values

corresponding to 320 °C were obtained by MS and those corresponding to the other temperatures were calculated from the CC. The curves show that it is possible to obtain pure magnetite in a wide range of temperatures, and that the kinetics of this reaction is strongly dependent on temperature. The activation energy of the reaction was calculated by Flynn's method [10] and an average value of  $98 \pm 4$  kJ/mol was obtained. This value is in good agreement with the data reported in literature [11].

### 4. Conclusions

- The CC allowed us to estimate the amount of hematite and magnetite in each sample.
- A value of activation energy of  $98 \pm 4$  kJ/mol was calculated for this reduction reaction carried out with a gaseous mixture of 5% of  $H_2$ .

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