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The non-existence of iron-rich magnetites

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While magnetite is known to be iron deficient at high temperature, five publications have independently claimed that iron-rich magnetites $Fe_{3+x}O_4$ have been observed in the range 250 to 620° C. The related experiments are based upon reduction of magnetite, goethite, maghemite, hematite or iron ore, and for the one of them, upon ferrous hydroxide decomposition. Another article reports an unsuccessful attempt to produce the iron-rich magnetites through hematite reduction at 535° C, but this temperature is considerably higher than almost all of the reduction temperatures used where iron-rich magnetite has been detected. We have therefore carried out an extensive series of experiments in order to prepare iron-rich magnetite through reductions as near as possible to the published experimental conditions. Through thermogravimetric analysis, chemical analysis, Mössbauer spectrometry and magnetic measurements, we have shown that no excess iron magnetite has been obtained. A possible explanation could be, in some cases at least, the fact that OH groups remain in the material due to preparation from solutions and annealing at moderate temperatures.

1. Introduction

Since the basic work of Darken and Gurry [1], magnetite has been known to be non-stoichiometric at high temperatures with some iron deficiency due to cationic vacancies. More recently, Dieckmann and Schmalzried [2] have shown that in the same high-temperature range some interstitial iron may exist at low oxygen pressure; this has been confirmed by Halloran and Bowen [3].

The present authors have noted that five publications have pointed out that an iron-rich magnetite has been observed at temperatures below 600° C.

On the other hand, another publication reported negative results when trying to prepare an iron-rich magnetite, but we shall see that the experimental conditions of this work were not well chosen.

It was thus tempting to prompt a research programme in order to obtain iron-rich magnetites which could be of much interest when considering the large amount of work carried out by physicists and chemists on pure and oxygen-rich magnetites. It was expected that many, if not all the properties of magnetite would be altered by excess iron which, according to some of the five above mentioned publications, could be as large as 10%.

2. Literature survey

2.1. Reduction of precipitated magnetite

In 1967, Columbo, Gazzarini and Lanzavecchia [4], investigating the mechanism of iron oxide reduction with hydrogen, pointed out that in the thermogravimetric analysis (TGA) curves, when reducing magnetite prepared by precipitation and annealing at 400° C, there was a plateau corresponding to the composition $Fe_{3.06}O_4$.

The quenched material was pure spinel, from X-ray diffraction (XRD) measurements, with a cell parameter greater than that of the pure magnetite. From a series of different iron-rich magnetites, they showed that the parameter was a linear function of composition, which extrapolated to Fe_3O_4 (0.8402 nm) and Fe_2O_3 (0.835 nm).

2.2. Ferrous hydroxide decomposition

In 1971, Pritchard, Haddon and Walson [5] com-

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pared the Mössbauer spectra of the decomposition products obtained in hydrothermal experiments at different temperatures and pH, from ferrous hydroxide prepared through the action of soda on iron–ammonium sulphate.

In some circumstances, they observed a third sextuplet pattern which they interpreted as an abnormal magnetite with a composition around $Fe_{3.23}O_4$. However, it must be noted that the cell parameter was the same as for pure magnetite.

2.3. Hematite reduction at 535° C

In 1975, Graham, Channing, Swallow and Jones [6], aware of the results of Colombo *et al.*, investigated hematite reduction with thermogravimetric analysis (TGA) and Mössbauer spectrometry, and observed only stoichiometric magnetite.

However, it is clear from the experimental data of other workers presented in Table I that most reports of iron-rich magnetite have resulted from reduction experiments carried out at much lower temperatures than 535° C.

Indeed, the reason why they chose such a high temperature is that they wanted, at the same time, to check the results of Romanov *et al.* [7] concerning the formation of transient wustite, just under the eutectoid temperature (570° C).

Thus, even if Colombo *et al.* claimed that no iron could be detected through annealing the iron-rich magnetite at 550° C, it seems that the experimental conditions chosen by Graham *et al.* were not ideal for the detection of non-stoichiometric magnetites.

2.4. Reduction of goethite

In 1976, Garcia-Gonzales *et al.* [8] observed a plateau in the TGA curve recording reduction, at 290° C, of hematite coming from in situ dehydration of goethite.

This plateau was between $Fe_{3.3}O_4$ and $Fe_{3.5}O_4$ according to the experimental conditions, and the first material, $Fe_{3.3}O_4$, when checked through XRD, appeared to be a pure spinel (without, however, any indication of the cell parameter).

2.5. Reduction of magnetite

In 1976, Gaballah [9] mentioned a plateau at $Fe_{3.1}O_4$ in the reduction, through carbon monoxide, of magnetite, prepared from hematite, with reduction by hydrogen at 600° C.

It must be noted that such a result is not obtained with hydrogen nor with magnetite prepared at 1200° C instead of 600° C.

2.6. Reduction of an iron-rich ore

In 1977, Dubois, Le Caër and Offroy [10] dealt with reduction of iron-ore pellets by a gaseous mixture ($CO + CO_2 + H_2 + H_2O$) in a counter current shaft furnace.

The part of the iron-core pellets which was reduced at a temperature slightly higher than the eutectoid temperature (570° C) displayed a Mössbauer spectrum which they interpreted as being due to a $Fe_{3.3}O_4$ magnetite (although it was different from the spectrum obtained by Prichard *et al.* [5]).

They considered that such a magnetite could result from slow wustite disproportionation.

2.7. Conclusion

The above mentioned results are summarized in Table I, and it is striking to find that the only experiment designed in order to prepare an iron-rich magnetite failed, while five others, aiming at something else, succeeded.

However, it appears rather conclusively from the Table I that the temperature of Graham *et al.*, chosen for another reason, was not appropriate, and that the best temperature range is under 400° C (the experiment of Dubois *et al.* conducted at around 600° C, being an exception).

So it seemed to us that a research programme to determine the conditions for obtaining iron-rich magnetites was worthwhile, and it will be described hereafter.

3. Experiments and discussion

It appears from the above literature survey, that the simplest way to obtain iron-rich magnetite is to reduce iron oxide (magnetite or hematite) at temperatures below 400° C. This obviously requires an iron oxide reactive enough to react in these conditions. Thus, we have prepared different oxides through procedures known to provide materials with high reactivity, mainly through treatments carried out at temperatures as low as possible.

We have made considerable use of TGA in order to observe the behaviour during the reduction and to stop the process whenever desired. However, as TGA provides overall information which could be characteristic of a mixture, we have complimented it with XRD, Mössbauer spectrometry and chemical analysis. It must be emphasized that the classical chemical determination of the Fe^{total}/Fe^{II} ratio is a sensitive method for compositions

TABLE I Literature data

Starting material	Experimental conditions	Results				Reference
		x	Δa	Nuclear γ resonance	Remarks	
Fe_3O_4 prepared at 400° C	H_2 at 245° C H_2 at 264° C H_2/He at 264° C	0.06 0.05 0.05	+0.01 Å		Annealing 1000 h at 550° C no iron	[4]
$3Fe(OH)_2 = Fe_3O_4 + H_2 + 2H_2O$	230° C at pH 13	0.23	0	$\Delta H = -3$ (T) IS = 0.9 mm sec^{-1} †	Decrease of the octa pattern	[5]
Fe_2O_3 obtained through iron oxidation	H_2 at 535° C and 1 torr	0				[6]
α-goethite, FeOOH, from Bayer	H_2 at 290° C	0.3–0.5	–	–		[8]
Fe_3O_4 (reduction of Fe_2O_3 at 600° C)	CO at 370° C	0.10				[9]
Malmberget-rich ore	$H_2 + CO + H_2O$ at $T < 750$° C	< 0.3		Increase of octa lines		[10]

* ΔH is the decrease of the hyperfine field of the third sextruplet as referred to the other sextuplets (in tesla).

† IS is the isomer shift of the third sextuplet, referred to iron.

TABLE II

Composition $Fe_{3+x}O_4$	Fe^{II} $1+3x$	Fe^{III} $2-2x$	Fe^{tot} $3+x$	Fe^{tot}/Fe^{II} $3+x/1+3x$
$Fe_{2.95}O_4$	0.85	2.10	2.95	3.47
$Fe_{3.00}O_4$	1.00	2.00	3.00	3.00
$Fe_{3.05}O_4$	1.15	1.90	3.05	2.65
$Fe_{3.10}O_4$	1.30	1.80	3.10	2.38

around Fe_3O_4 as shown by Table II, which means that departures from stoichiometry as low as $Fe_{3.02}O_4$ or $Fe_{2.98}O_4$ may be firmly stated from simple chemical analysis (provided that dissolution does not introduce any error).

3.1. Reduction of goethite

It seemed, from the above literature survey, that this was the best method, providing large x-values in $Fe_{3+x}O_4$.

We used the same goethite as Garcia-Gonzales *et al.* (supplied by Bayer, labelled 910), and varied the experimental parameters as follows: $275°C < T < 340°C$ (instead of 290° C only in [8]); H_2 or $H_2 + N_2$ (with $N_2/H_2 = 9$ or 19); static or dynamic method (steady gas or flowing gas).

The dehydration, carried out at 300° C with a residual pressure around 10^{-5} torr, is fast (around 5 min) and gives a plateau with a weight-loss slightly greater than expected for Fe_2O_3 (this is probably due to some excess water in goethite, which moreover captures some water vapour inside the reactor before dehydration, as shown by a small peak in the thermograms; this is related to the large surface of the sample: around $22\,m^2\,g^{-1}$).

The reduction, when carried out in a dynamic way (flowing gas), never gives a plateau with pure H_2, yields a strong slowing down, not far from a horizontal plateau, with the H_2–N_2 mixtures at 275° C (see A in Fig. 1). The materials obtained here, between Fe_3O_4 and Fe on the weight-loss scale, indeed appeared, from X-ray diffraction, as a mixture of iron and normal magnetite ($a = 0.8395$ nm).

On the other hand, reduction carried out in a static way (steady gas) exhibits a nearly horizontal plateau (see B in Fig. 1) located at a composition around $Fe_{3.1}O_4$ with, however, some scattering near this value. However, from XRD, as well as from chemical analysis, it appeared that the material corresponding to the plateau is pure magnetite. The explanation is as follows:

(a) the wrong composition deduced from TGA comes from the fact that the first stage, namely geothite dehydration, may be incomplete; but, as goethite is microcrystalline (0.5 μm length, 0.05 μm in diameter), its X-ray intensities are very weak, and it is difficult to determine small contents. Moreover, heating to 600° C, after this stage, brings about a weight-loss of around 1.5% showing that dehydration was not complete.

(b) the plateau arises from a local increase of H_2O pressure (p_{H_2O}) as a consequence of the hematite reduction, as proved by the fact that pumping and renewing of the gas provokes further reduction. Such an observation of similar behaviour has also been reported by Graham *et al.* [6]

(c) a sample extracted from the plateau stage, was investigated through Mössbauer spectroscopy at room temperature. There are two hyperfine six-

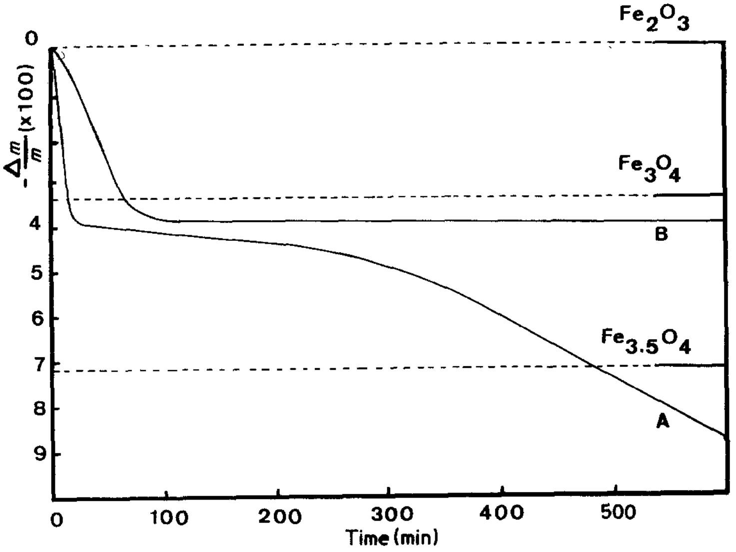

Figure 1 Reduction of goethite with H_2–N_2 ($H_2/N_2 = 9$) at 275° C. A: dynamic method. B: static method.

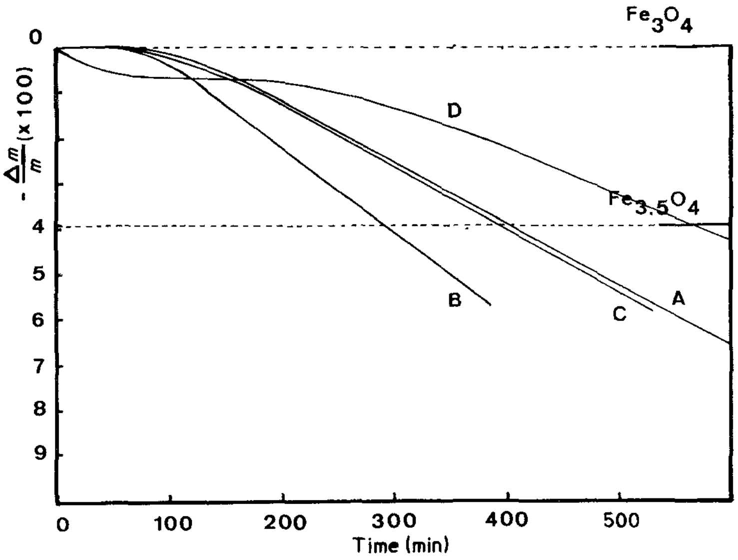

Figure 2 Reduction of magnetite with H_2–N_2 ($H_2/N_2 = 9$). A and B: 249° C dynamic method (the difference between these two curves reflects the experimental scattering). C: 320° C static method. D: from Colombo *et al.* [4], 264° C mixture H_2–He (H_2/He = 1).

line patterns (and not three as in Pritchard's results), the parameters of which are given in Table III (Sample G), where they may be compared with pure magnetite parameters, obtained in this laboratory in good agreement with other publications [15–17]; the f_R ratio of B and A site recoilless fractions equal to 0.92 has been taken from [17], a value that we applied to the experimental intensity ratios. For Sample G decrease of the I_B/I_A ratio and a broadening of the lines is seen. The magnetization of the samples at room temperature was also recorded. The results, given in Table III show that Sample G displays a lower value than that of pure magnetite. We shall discuss this point further.

Thus, it may be safely concluded that in the above experimental conditions, no iron-rich magnetite is produced.

3.2. Reduction of magnetite

Reactive samples of magnetite have been prepared as follows: reduction of hematite (Merck) in an H_2–H_2O mixture at 450° C (this is the minimum temperature above which magnetite immediately oxidizes in air).

The reduction, carried out with H_2–N_2 at 240° C (dynamic) or 320° C (static) shows the behaviour depicted in Fig. 2. An inductory period is followed by a regular nearly linear reduction. This is also the trend reported by previous authors studying magnetitie reduction below 570° C [4, 12–14]. However, it must be pointed out that Colombo *et al.* [4] are the only authors who observed an intermediate stage corresponding to $Fe_{3+x}O_4$. All the same, some samples in our experiments on compositions around $Fe_{3.1}O_4$ have been examined by XRD and appeared to be mixtures of iron and normal magnetite.

3.3. Reduction of maghemite

As γFe_2O_3 already has the spinel lattice, it was interesting to test its reducibility at low temperatures, as previously investigated by Colombo *et al.*

It was prepared as follows: precipitation from a solution of Fe^{II} and Fe^{III} salts (chlorides or sulphates) by soda, and annealing at 200° C in air. The product obtained, checked by magnetic and XRD methods, is indeed Fe_2O_3 (ferrimagnetic, $a = 0.833$ nm). It was reduced at 220° C with H_2–N_2, in both static and dynamic methods.

Fig. 3 shows that only the static method provides a plateau, but the related materials display the analytical and crystallographic features of stoichiometric magnetite. This directly contradicts the results of Colombo *et al.* who report a plateau of several hours at 261° C in a stream of pure hydrogen.

On the other hand, heating the product obtained at this plateau in vacuum to 600° C a weight-loss of about 1.5% was obtained.

A sample obtained at this plateau was checked with Mössbauer spectroscopy. The recorded parameters are given in Table III, along with the room-temperature magnetization. Nearly the same trends are observed as in Sample G.

3.4. Reduction of iron ore pellets

The same iron ore (origin Malmberget) as used by

TABLE III

Sample	IS_A	IS_B	H_A	H_B	ϵ_A	ϵ_B	I_B/I_A	b_A	b_B	σ
Fe_3O_4	0.25	0.68	39.2	36.8	−0.013	0.004	1.81	0.27	0.34	3.98
G	0.26	0.68	39.4	37.0	−0.007	−0.001	1.55	0.33	0.46	3.30
M	0.27	0.66	39.0	36.8	−0.016	0.005	1.64	0.33	0.55	3.11
D	0.27	0.69	39.6	37.1	−0.006	−0.002	1.83	0.27	0.42	–

G: Sample from goethite reduction.
M: Sample from maghemite reduction.
D: Sample obtained according to the procedure of Dubois *et al.*
IS_A and IS_B: Isomer shifts for A and B sites (octa-tetrahedral), respectively (mm sec^{-1} referred to iron).
H_A and H_B: Hyperfine fields (T).
ϵ_A and ϵ_B: Quadrupole shifts (mm sec^{-1}).
I_B/I_A: Ratio of the A and B line intensities (from the 2 strongest lines) (× 0.92).
b_A and b_B: Breadths of the strongest lines (mm sec^{-1}).
σ: magnetization at 1.5 T (μ_B mol^{-1}).

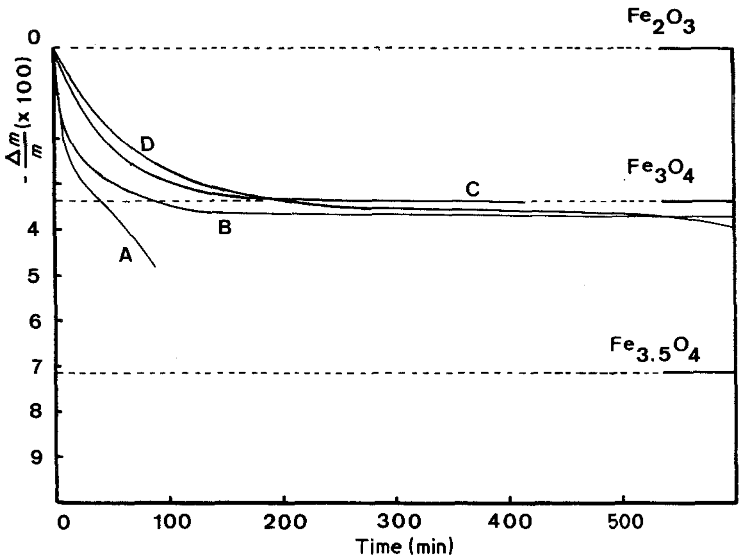

Figure 3 Reduction of maghemite with H_2–N_2 ($H_2/N_2 = 9$) at 220° C. A: dynamic method. B and C: static method. D: from Colombo *et al.* [4], 261° C, dry H_2.

Dubois *et al.* [10] was crushed and reduced at 620° C with H_2–N_2 dynamically. The process was stopped for a 10% reduction degree and then the sample was annealed for 15 h in vacuum at approximately 500° C and then the cooling down, over an hour, to room temperature was monitored.

Fig. 4 shows the isotherms obtained. XRD reveals that, for $Fe_{3+x}O_4$ compositions, the material is a mixture of wustite, magnetite (normal) and iron. The results are the same below 570° C (without wustite), where, however, we did not apply the annealing process needed for the wustite decomposition.

The material obtained at 620° C was investigated through Mössbauer spectroscopy. Its parameters are given in Table III (Line D): there are no significant changes from pure magnetite, except a broadening of the line showing some local disorder. These results agree with the XRD data.

4. Discussion

Although it is often difficult to reproduce the experimental conditions described by previous authors, it must be concluded here that the existence of an iron-rich magnetite remains to be proved, except perhaps as regards the procedure of Pritchard *et al.* [5] which was not attempted in the present work.

A possible explanation of some results, including those of Pritchard *et al.* [5], is the following. It is obvious that in order to insure good reactivity at low temperatures, many procedures are carried out

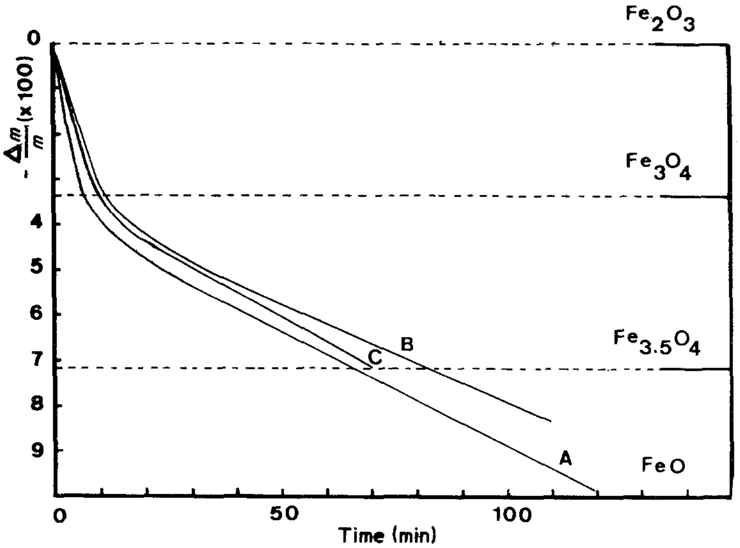

Figure 4 Reduction of iron-ore pellets with H_2–N_2 ($H_2/N_2 = 9$) at 620° C. A, B and C: dynamic method.

using aqueous solution, providing solid materials which are annealed at low or moderate temperatures, so that some hydroxyl ions may be retained changing to varying degrees the supposed composition.

Such a hypothesis is supported by the following observations: Sample M (Table III) has the lowest magnetization; assuming the presence of some $(\mathrm{OH})^-$ ions, we can write the following composition:

$$\mathrm{Fe}^{\mathrm{III}}_{1}[\mathrm{Fe}^{\mathrm{III}}_{1}\mathrm{Fe}^{\mathrm{II}}_{1-x/2}\square_{x/2}]\,\mathrm{O}_{4-x}(\mathrm{OH})_x$$

putting, as usual, the octahedral population between brackets. Classical Néel antiferromagnetic coupling between A and B sites allows calculation of the magnetic moment as a function of x, so that:

$$4\left(1-\frac{x}{2}\right)\bigg/4 = 75/96 \qquad (1)$$

for a comparison with pure magnetite; from which $x = 0.44$.

This value is consistent with

(a) The Mössbauer ratio, $I_\mathrm{B}/I_\mathrm{A}$, since

$$I_\mathrm{B}/I_\mathrm{A} = \left(2-\frac{x}{2}\right)f_\mathrm{R} = 1.64, \qquad (2)$$

is exactly the measured value (Table III)

(b) The weight-loss through heating to 600° C, calculated as follows:

$$\mathrm{Fe}_{3-x/2}\mathrm{O}_{4-x}(\mathrm{OH})_x = \frac{x}{2}\mathrm{H_2O} + \mathrm{Fe}_{3-x/2}\mathrm{O}_{4-x/2}, \qquad (3)$$

for $x = 0.44$ and $\Delta m/m = 1.8\%$, to compare with the experimental value of 1.5%.

The above formulation of the reduced oxide is thus satisfactory. It may also explain some features of the Mössbauer spectra: the unpaired $\mathrm{Fe}^{\mathrm{III}}$ in the octahedral population generates an additional six-lines pattern and thence decreases the $I_\mathrm{B}/I_\mathrm{A}$ ratio in the manner suggested by Daniels and Rosencwaig [15]; this is actually observed in the data from Samples G and M.

The persistence of water in solids prepared from hydroxides at moderate temperature is not uncommon. For instance XPS studies have shown OH groups in oxides of Co, Ni, Fe or Zn, even outgassed in an ultra-high vacuum at 500° C [18]. Thus, it could be the case for some the above prepared "magnetites", including that of Pritchard *et al.*, which is obtained from iron hydroxide.

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