

Magnetic roasting of some Egyptian ferruginous manganese ores

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FOR production of standard grade ferro-manganese the iron content in manganese ores should not exceed certain limits. Vast reserves of ferruginous manganese ores exist in several locations in U. A. R., which do not find good markets on account of their high iron content. Preliminary work showed that the iron content could be successfully reduced by magnetic roasting followed by magnetic separation. As reduction to the magnetic stage takes place readily in the fluidized state¹, it was decided to use the fluidization technique in the present study.

Experimental

Mineralogy and chemical analysis

The three samples investigated were collected from Sinai (U. A. R.). Polished sections showed the presence of pyrolusite, manganite and gangue minerals. The typical colloform-texture of psilomelane is common in the sections. The manganese minerals are in the form of well developed crystals in some sections, while in the others, they are in the form of colloidal aggregates.

The chemical analysis of the three samples is given in Table I.

Apparatus

The apparatus used for reduction is shown in Fig. 1. It consists mainly of two-gas trains, one for hydrogen and the other for nitrogen, meeting at the entrance of a transparent silica reduction tube. The trains include essentially the appropriate gas purification units, flow meters and flow regulators.

The fluidized bed reactor is 70 cm long and 3.5 cm inner diameter silica tube with a sintered silica disc fixed 40 cm from its bottom to support the solid charge.

Arrangements to determine the pressure drop through the fluidized bed are provided. The reactor is externally heated by a tube furnace of which the constant temperature zone extends 5 cm below and above the

SYNOPSIS

Representative samples of ferruginous manganese ore of different grades were subjected to magnetic roasting, as a means of beneficiation, for the subsequent concentration and production of ferro-manganese.

Reduction was carried out with hydrogen using the fluo-solid technique. Different factors affecting the process, namely, temperature, time of reduction, particle size of feed and rate of hydrogen flow, were investigated.

The extent of magnetic roasting was followed by the Davis-tube tester, and the different phases were identified by X-ray analysis.

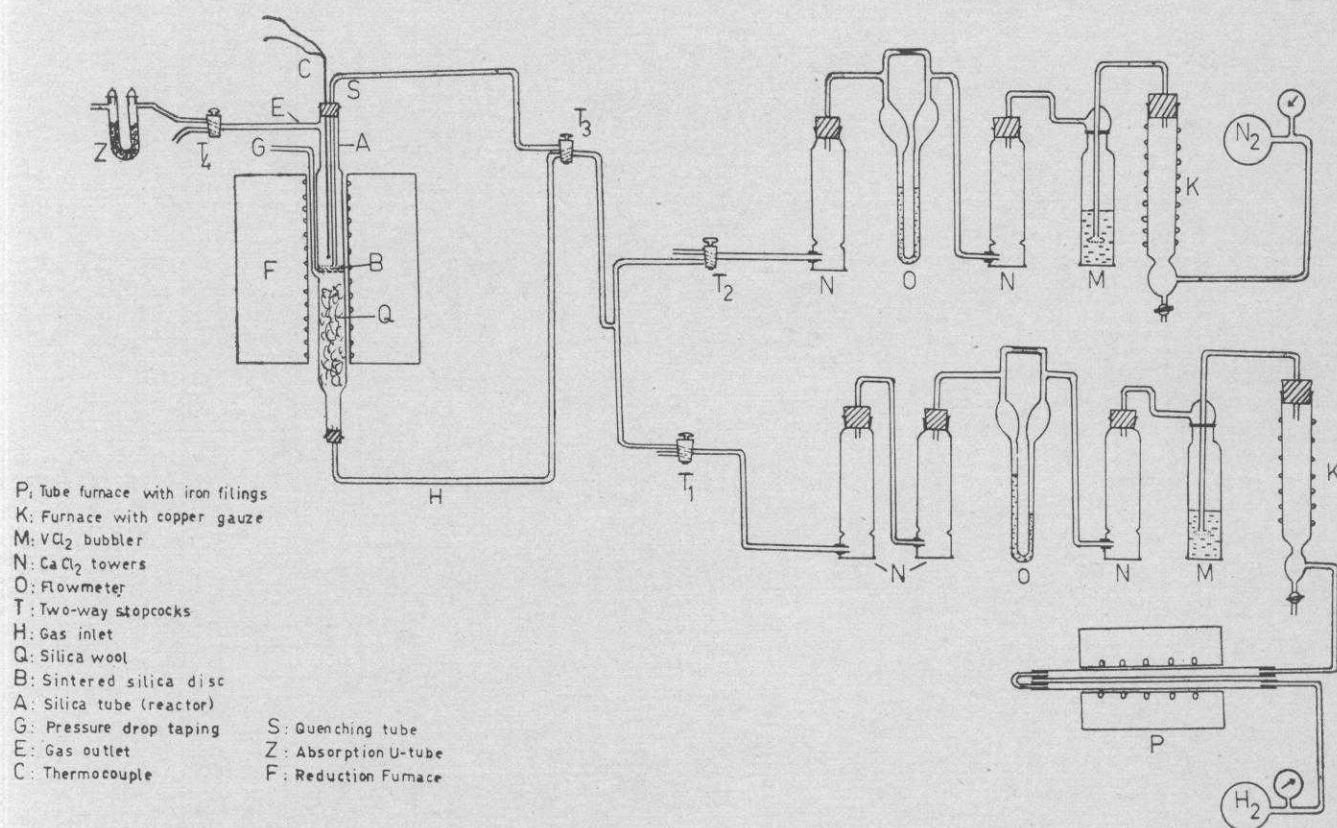
TABLE I Chemical composition of the ore samples

Constituents %	Sample I	Sample II	Sample III
Mn	19.95	13.92	10.38
MnO ₂ *	26.87	16.43	13.20
Fe	40.71	48.48	50.20
Fe ₂ O ₃	58.21	69.31	72.85
MgO	0.67	0.62	0.44
CaO	1.20	1.36	2.63
Al ₂ O ₃	2.48	2.80	3.14
SiO ₂	5.80	3.50	1.80
P	0.076	0.073	0.097
Insoluble**	7.75	4.65	4.50
Moisture	1.39	1.98	0.80

*The value of MnO₂ represented is the one found experimentally. As theoretically calculated from Mn content, it should be 31.58, 22.03, and 16.43 for samples I, II and III respectively, the balance being manganite.

**Acid insoluble matter.

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1 Sketch for reduction apparatus

fluidized bed. The temperature is measured inside the fluidized bed by a Pt/Pt 13% Rh thermocouple. The lower part of the silica tube is filled with silica wool to help in pre-heating the gas.

Anhydrous calcium chloride U-tubes were used for collecting water vapour produced from the reaction and care was taken to prevent any condensation in the upper part of the reduction tube and in the tubes leading to U-tubes by heating with infra-red lamps.

Inside the reactor, just above the sintered disc is a tube for blowing a high current of cold hydrogen to quench the reduced mass and thus stop the reaction.

Reduction procedure

Runs were conducted on 50 gm ore charges at temperatures ranging between 300 and 500°C. The particle sizes, worked on, are: $-1.0+0.5$, $-0.5+0.25$, $-0.25+0.125$ and $-0.125+0.062$ mm and the flow rate used with respect to all sizes is $1.5 \text{ G}_{\text{mf}}$. Other flow rates, namely, $1.0 \text{ G}_{\text{mf}}$, $2.0 \text{ G}_{\text{mf}}$ and $3.0 \text{ G}_{\text{mf}}$ were also used for the particle size $-0.5+0.25$ mm which correspond to 2, 4 and 6 l/min. at N.T.P. respectively.

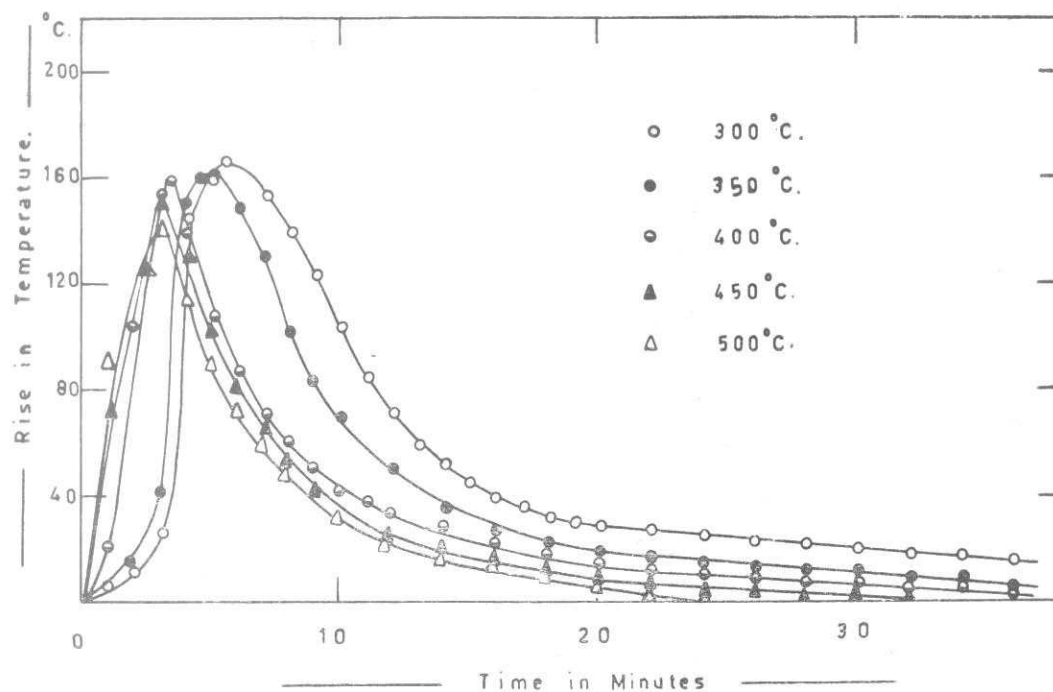
After switching on the furnace, nitrogen was allowed

to pass through the apparatus until the required temperature in the reactor is obtained and fixed to within $\pm 2^\circ\text{C}$. By the passage of hydrogen, the thermocouple reading reflects the type of reaction taking place: whether exothermic or endothermic.

The progress of reduction was followed by changing the absorption U-tube at the pre-determined time intervals and the cumulative percentage reduction-time curves were plotted. At the end of experiment, the reduction was stopped by passing a high flow rate of hydrogen through tube S (see Fig. 1). The cold reduced mass was discharged into acetone to prevent re-oxidation by air, then ground and the size fraction $-0.125+0.057$ mm was collected to be used for magnetic testing.

Magnetic separation

Magnetic testing was carried out by a Davis-tube tester² after determining its optimum conditions for separation which are: 230 stroke/min., current 1 amp., rate of water 0.3 l/min., time of agitation 5 minutes. Cleaning was carried out for the non-magnetic fraction using the same conditions, but the time of agitation was only 3 minutes.



2a Heat effects during reduction at different temperatures

Determination of the minimum fluidizing gas velocity

The minimum fluidizing gas velocity was determined by Leva's formula.³

$$G_{mf} = 688 D_p^{1.82} \frac{[\rho_s(\rho_s - \rho_f)]^{0.94}}{\mu^{0.88}}$$

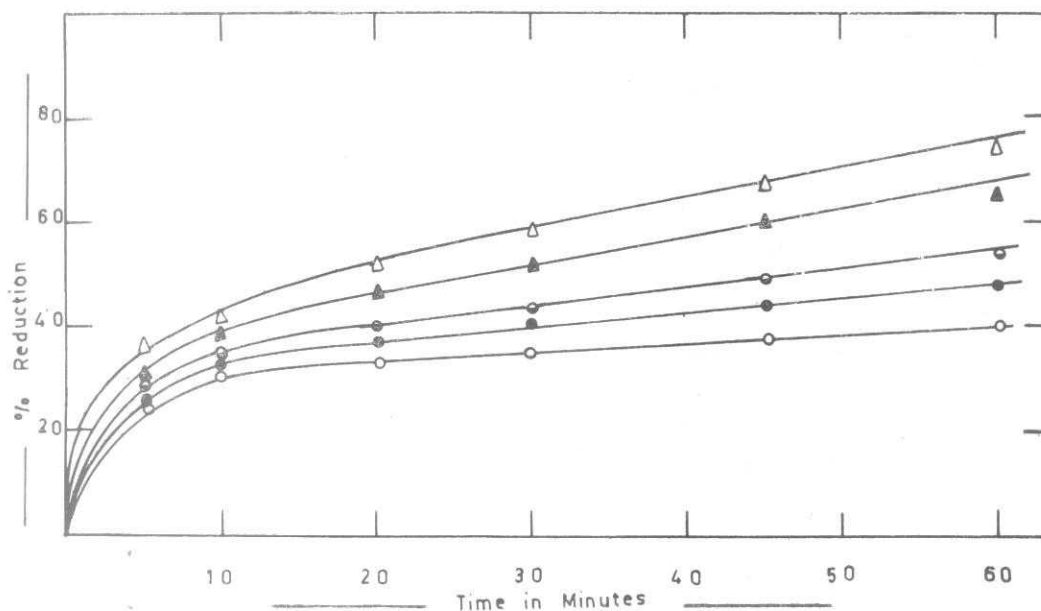
where

G_{mf} = fluid mass velocity for the onset of fluidization (lbs/hr/sq. ft.).

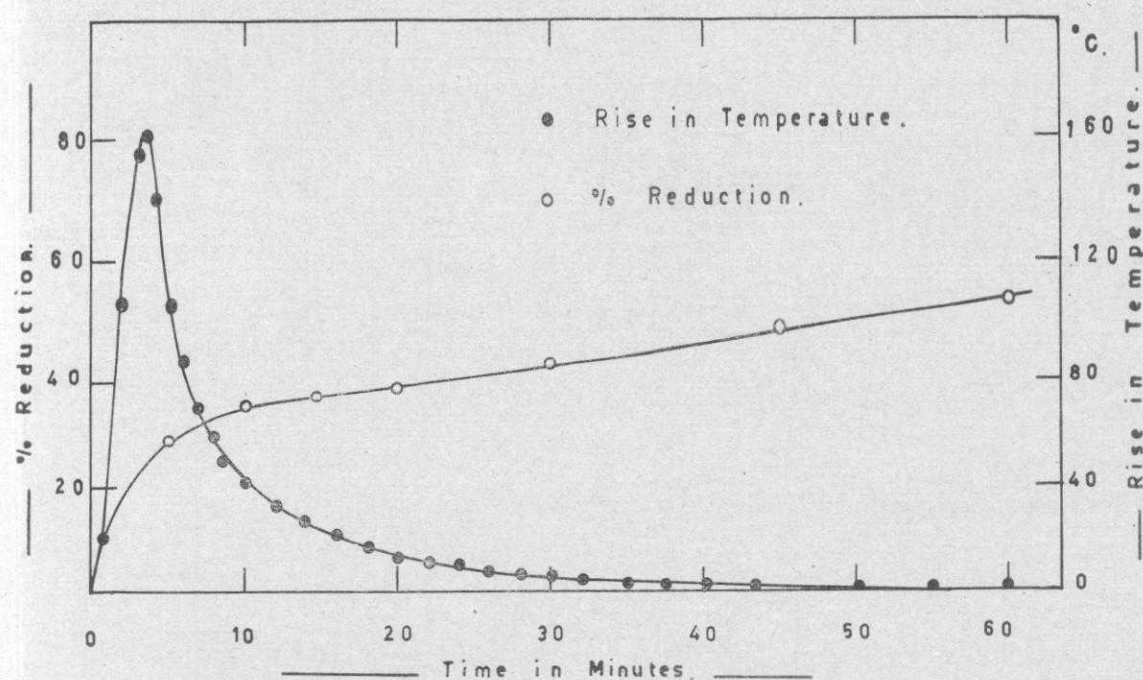
D_p = particle size (inches).

ρ_s, ρ_f = solid and fluid densities (lbs/cub. ft.)

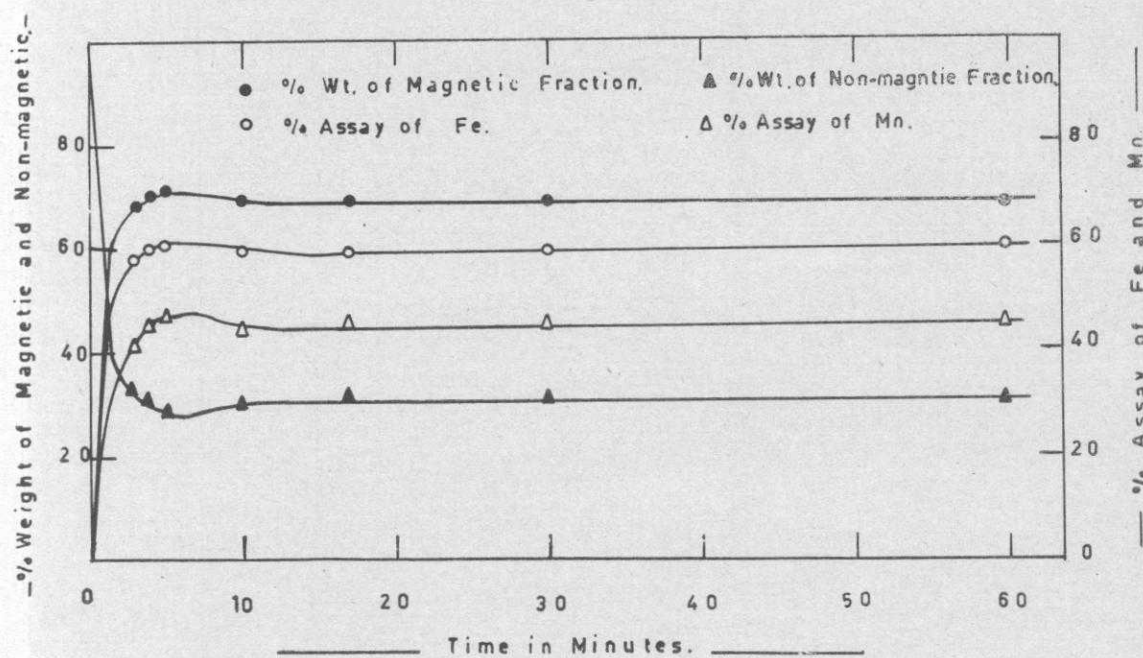
μ = fluid viscosity (centipoise).



2b Effect of temperature on the rate of reduction (particle size 0.5+0.25 mm and hydrogen flow 3.0 l/min.)



3a



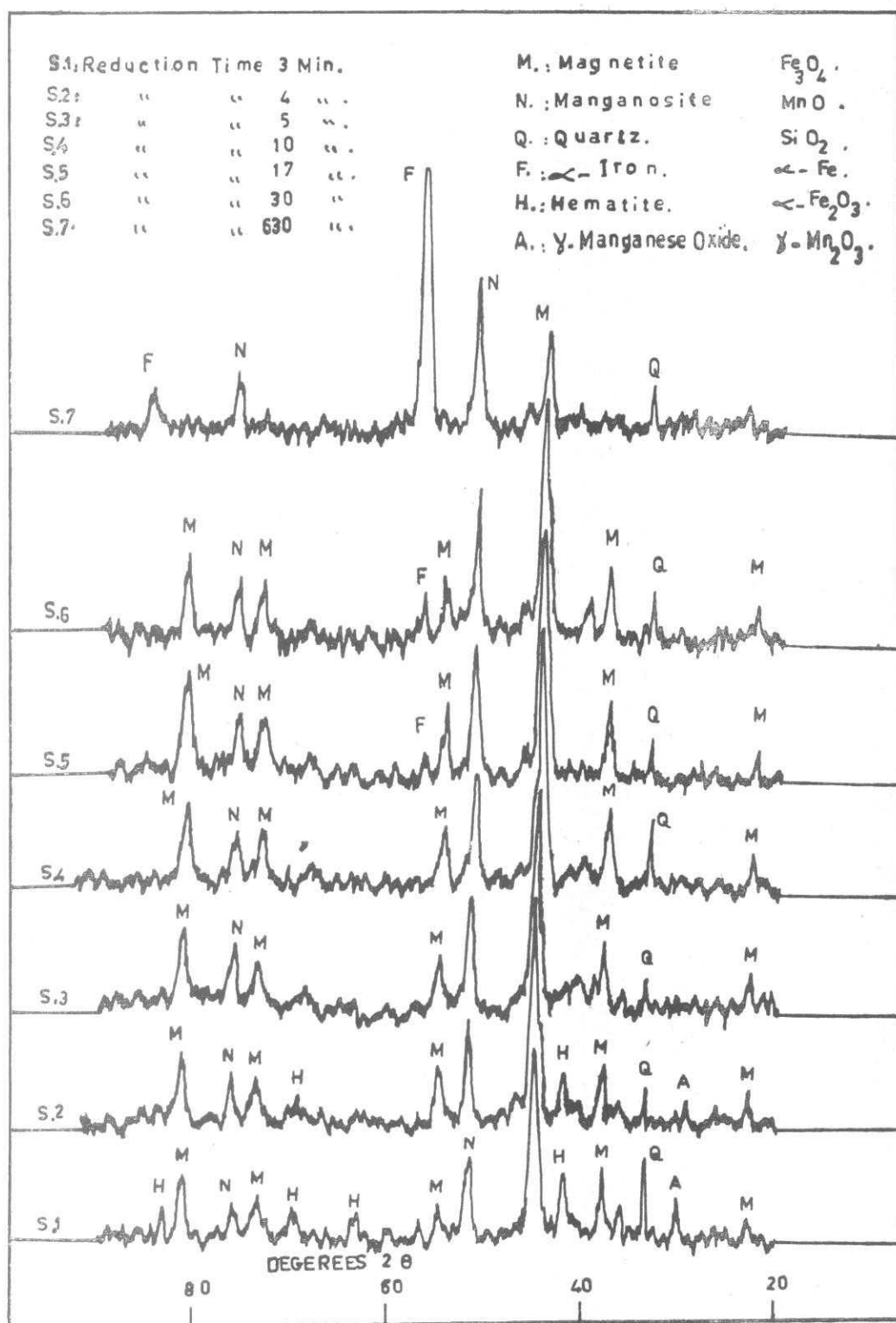
3b

3 Effect of the extent of reduction on magnetic separation at 400°C (particle size $0.5+0.25$ mm, hydrogen flow 3.0 l/min.)

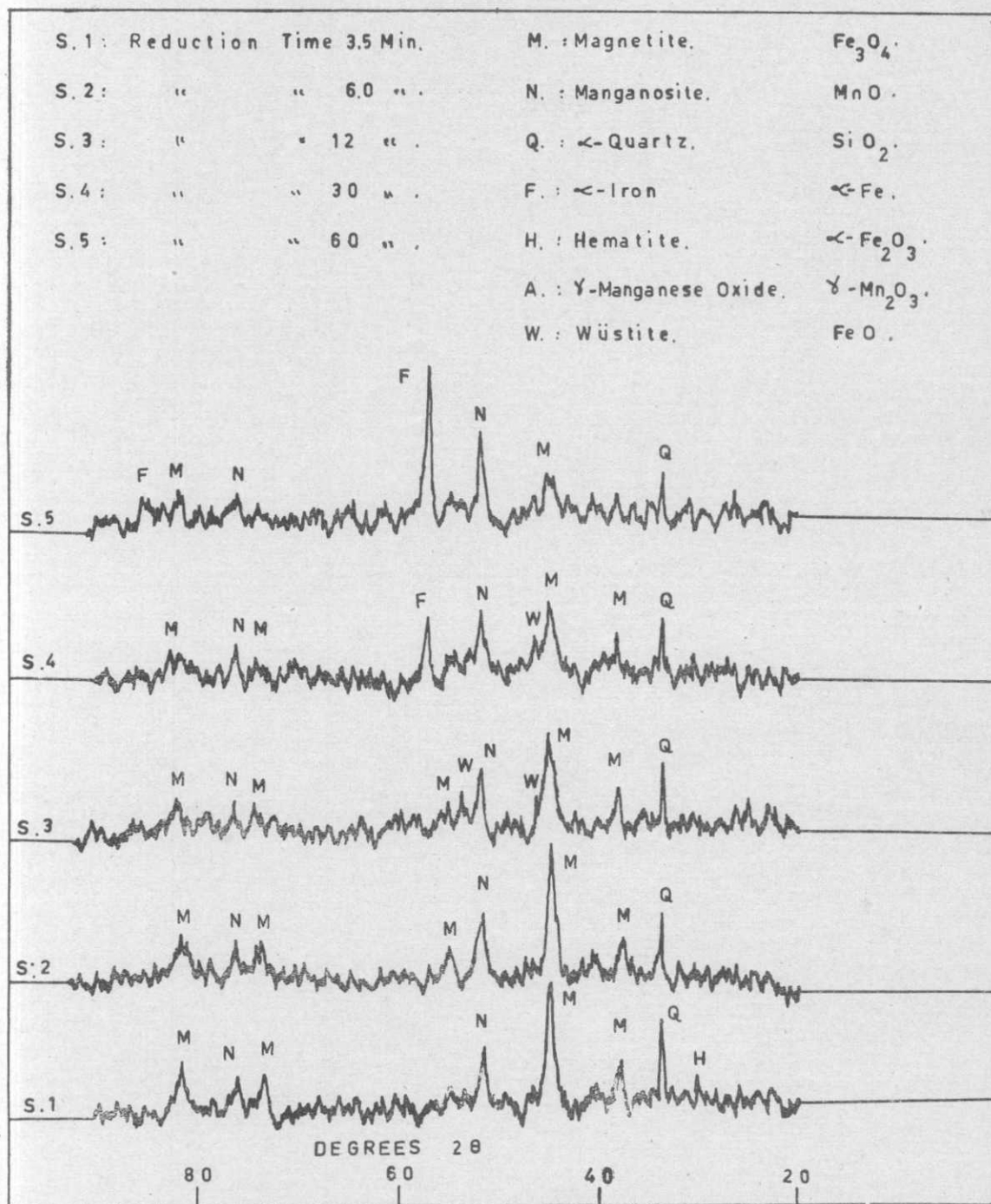
The density and viscosity of the fluidizing gas were determined for the working temperatures.

The value of G_{mf} calculated by this formula was used only as an indicative value to know approximately the minimum fluidizing gas velocity. This was determined experimentally for each run by gradually, but quickly,

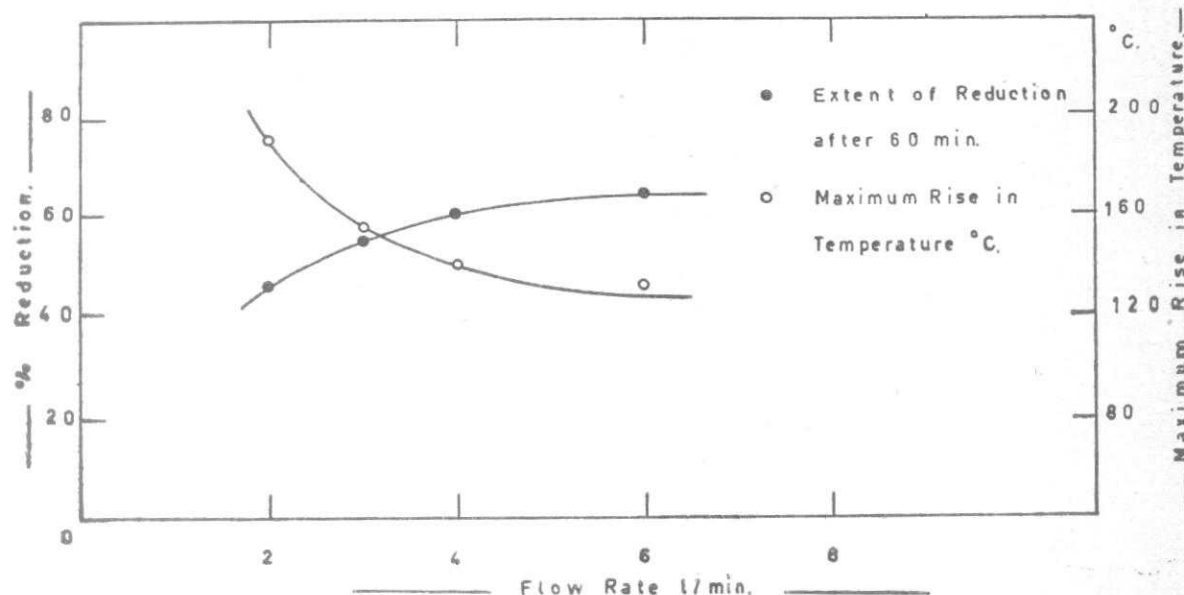
increasing the gas flow rate and plotting the pressure drop through the bed against it. The flow at which the pressure drop becomes constant determines the minimum fluidizing gas velocity. The actual fluidizing gas velocity used was some multiple of this value as will be seen later.



4 X-Ray diffraction patterns for reduced samples at 400°C



5 X-Ray diffraction patterns for reduced samples at 500°C



6 Effect of hydrogen flow rate on reduction at 400°C

Results and discussion

Effect of temperature on reduction

This was studied by using particle size fraction $-0.5 + 0.25$ mm of sample I and a hydrogen flow rate of 3.0 l/min. ($1.5 G_{mf}$ at 400°C). Figs. (2a) and (2b) represent the heat changes taking place during reduction at different temperatures used. Fig. (2a) indicates a starting great increase in temperature due to the starting exothermic reactions of the reduction stages $Fe_2O_3 \rightarrow Fe_3O_4$; and $MnO_2 \rightarrow MnO$; followed by a gradual decrease in temperature due to the following endothermic reactions. The peaks of the rise in temperature differ with time. The first being for the highest temperature used where the reaction is quickest, and as the reduction temperature decreases, the reaction becomes slower and the peak is attained at a longer time. The rates of reduction curves in Fig. (2b) endorse this. The smaller rise in temperature with the increase in reduction temperature is attributed to the higher heat losses.

The increase in reduction rate with temperature (Fig. 2b) is natural, since the reduction rate is controlled by gaseous and solid diffusion, and by the dynamic potential of the reaction, which is related to the fundamental driving energy of the reaction, the free energy, and both factors (diffusion and free energy) increase with temperature.⁴

Determination of the optimum extent of reduction for magnetic roasting

Fig. (3a) shows the reduction rate and rise in temperature with time for size fraction $-0.5 + 0.25$ mm at 400°C using a hydrogen flow rate of $1.5 G_{mf}$ (3.0 l/min.).

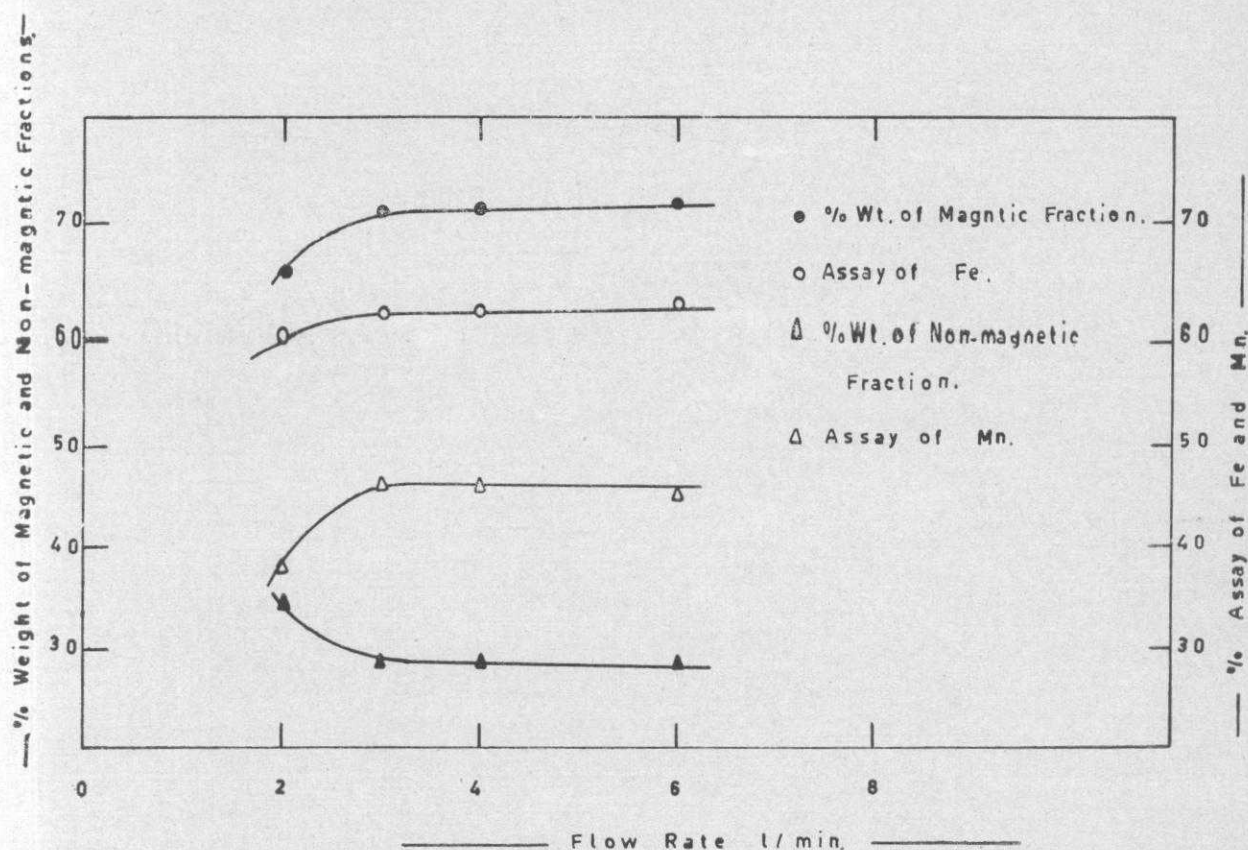
By stopping the reaction at different times according to the rise in temperature curve, and determining the magnetic and non-magnetic fractions in the partially reduced mass by the Davis tester, as well as the iron content of the magnetic fraction and manganese content of the non-magnetic one, the curves shown in Fig. (3b) could be traced.

It can be seen from Fig. 3 that the highest extent of separation and the maximum assays of iron and manganese in the magnetic and non-magnetic fractions respectively are attained for samples reduced for about 5 minutes (i.e.) just after the transformation of Fe_2O_3 to Fe_3O_4 as indicated by the rise in temperature peak; which is confirmed by X-ray analysis (Fig. 4). After the optima, a slight decrease is observed in the magnetic curves, which is attributed to the metallic iron formation (due to difference in molecular weights, although metallic iron is more strongly magnetic than magnetite).

Table II compares the values obtained at 400°C and 500°C for the magnetic separation after 5 minutes reduction, using the same gas flow and particle size. It is evident that on increasing the temperature

TABLE II Magnetic separation at 400°C and 500°C

Temp. °C	Magnetic		Non-magnetic	
	Wt. %	Fe %	Wt. %	Mn %
400	71.00	60.40	29.00	47.32
500	70.42	62.97	29.58	46.13



7 Effect of hydrogen flow rate on magnetic concentration (Reduction for 5 min. at 400°C)

from 400°C to 500°C the weight per cent of the magnetic product decreases and the iron assay increases. It can be seen from Fig. 2(a) that during reduction at 500°C a rise in temperature of 140°C took place i.e. the actual reduction temperature during the first stages of reduction was higher than the quadruple point (570°C) which should result in the formation of wustite, which is a non-magnetic compound, as an intermediate product.⁴ This is confirmed by X-ray analysis (Fig. 5).

For temperatures below 400°C the same results as those obtained at 400°C were attained but at longer times due to slower rates of reduction. At 450°C, the results are intermediate between those of 400°C and 500°C. Thus, it can be concluded that the best temperature for magnetic roasting is 400°C since it gives the highest extent of magnetic separation at minimum reduction time.

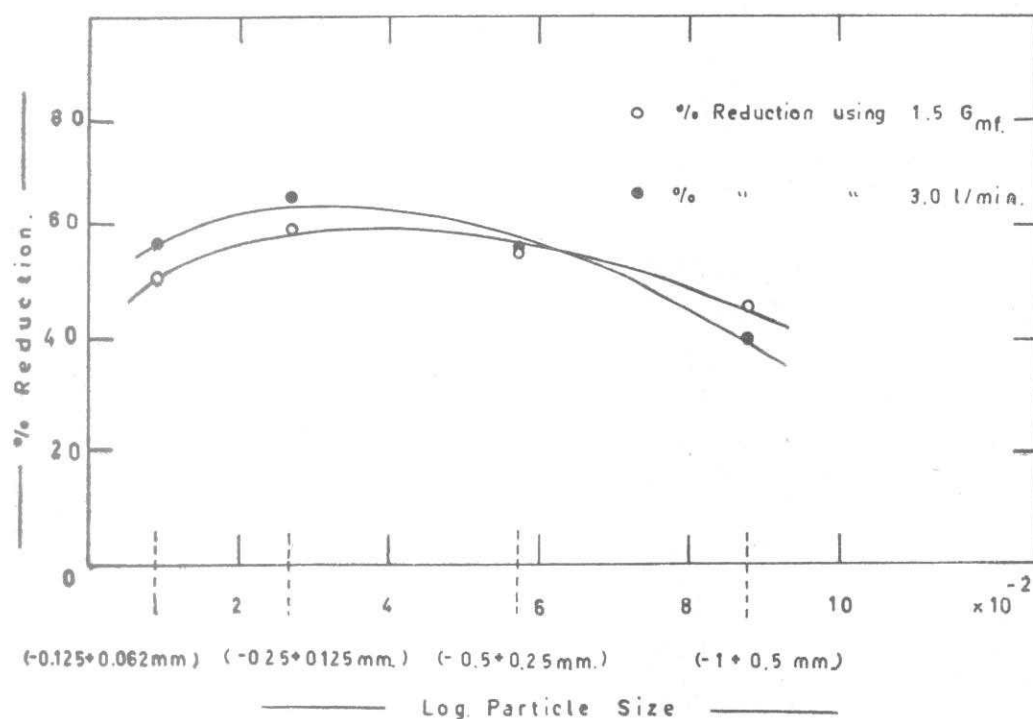
Effect of rate of hydrogen flow

Beside the effect of temperature, the rate of reduction in the fluidized state is mainly controlled by the rate of flow of reducing gas, because of the intimate contact between gas and ore which makes the gaseous product (water vapour) formation appreciable.

Fig. 6 shows the variation in the extent of reduction after one hour and in the maximum rise in temperature with change of hydrogen flow rate at 400°C for particle size $-0.5+0.25$ mm. The change in the rise in temperature is due to the cooling effect of higher flow rates. The effect of gas:ore ratio (rate of hydrogen flow) is understandable in terms of the low mass action since increasing the gas flow rate means an increase in the reactions concentration.^{4,5}

The first stages of reduction $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ and $\text{MnO}_2 \rightarrow \text{MnO}$ take place readily even with low concentration of the reducing gas in the ambient atmosphere. Accordingly, little or no effect of hydrogen flow rate of these stages should be expected. This was the case as can be seen from Fig. 7 since no effect of hydrogen flow on magnetic concentration for samples reduced for 5 minutes could be detected except for low flow rates where the water vapour fugacity will be high in the ambient gas. It is expected, naturally, that if the reduction period increases beyond 5 minutes for a certain time, the magnetic roasting stage will be complete for all the flow rates used and accordingly flow rate would appear to be of no effect at all.

However, since the flow rate of $1.5G_{mf}$ (3.0 l/min.) represents the minimum flow rate that can achieve good fluidization, it is considered as the optimum flow



8 Effect of particle size on the extent of reduction (Reduction for 60 min. at 400°C)

rate for magnetic roasting since, apart from the fact that no advantage can be gained from using higher flow rates, in an industrial magnetic roasting unit only a part of the reducing gas is engaged in reduction and the remainder is recirculated and the higher the flow rate, the larger this circulated portion which renders the process more expensive.

Effect of particle size

The extent of reduction was determined for the different size fractions $-1.0 + 0.5$, $-0.5 + 0.25$, $-0.25 + 0.125$ and $-0.125 + 0.062$ mm at 400°C using 1.5 G_{mf.} hydrogen flow rate with respect to the different sizes and also using a constant flow rate of 3.0 l/min. for all the sizes.

The first increase in the reduction rate with the decrease in particle size shown in Fig. 8 is quite normal due to the smaller diffusion path in the smaller particles and the bigger external surface area exposed to the reducing gas action. However, this increase is followed by a decline on dealing with the finer size ($-0.125 + 0.062$ mm). This is mainly due to channelling effect which is an abnormality in fluidization that occurs when particles are too fine or do not contain sufficient proportion of coarse particles. This channelling results in most of the gas passing through channels developed in the bed and not surrounding all the particles.⁵

The change between the two curves corresponding to the 1.5 G_{mf.} and 3.0 l/min. flows is due to changes in the flow rates for each particle size, the higher point corresponding to the higher flow rate.

Table III represents the data obtained by the Davis magnetic tester for the reduced products after 5 minutes at 400°C and hydrogen flow rate 1.5 G_{mf.} for the different size fractions used, except for the finer size. It is apparent that magnetic roasting is more efficient as the particle size decreases although the assay of iron and manganese decrease which may be due to their lower contents for the smaller size fractions of the original samples.

However, it can be concluded that if the ore is crushed to -1.0 mm, magnetic roasting will be efficient in producing good concentrates for both iron and manganese, the weight per cent and assay lying within the margins in Table III.

TABLE III Effect of particle size on magnetic separation

Size in mm.	Original analysis		Magnetic		Non-magnetic	
	Fe%	Mn%	Wt%	Fe%	Wt%	Mn%
$-1.0 + 0.5$	36.09	22.01	66.86	63.10	33.32	53.58
$-0.5 + 0.25$	36.62	20.29	71.00	62.34	29.00	47.32
$-0.25 + 0.125$	38.57	18.32	73.50	58.20	26.50	44.20

Tests on samples II and III showed that these two samples behave exactly the same as sample I.

Conclusion

Egyptian manganese ores can be magnetically roasted efficiently with hydrogen using the fluo-solid technique. The optimum reduction temperature is 400°C and the optimum hydrogen flow rate is 1.5 G_{mf}; the ores being crushed to -1.0 mm and the stay period in a continuous process being about 5 minutes.

Acknowledgement

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