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## Kinetics of hydrogen reduction of magnetite ore fines

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### ARTICLE INFO

#### Article history:

Received 29 December 2015

Received in revised form

8 April 2016

Accepted 12 April 2016

Available online xxx

#### Keywords:

Magnetite ore fines

Hydrogen

Iron making

TGA

Activation energy

Reduction kinetics

### ABSTRACT

The current work deals with the production of iron by the hydrogen reduction of magnetite ore fines in a thermogravimetric analyzer (TGA). The variables studied were time (0–30 min), temperature (973–1273 K), hydrogen flow rate (0.1–0.5 L min<sup>-1</sup>), hydrogen partial pressure (0.25–1 atm), sample bed height (0.25–0.75 cm) and particle size (75–180 μm). Phase identification, chemical analysis and elemental analysis were carried out by X-ray diffraction (XRD), X-ray fluorescence (XRF) analysis and energy-dispersive X-ray spectroscopy (EDS) of the scanning electron microscopic (SEM) images, respectively. The governing rate equations for the gas–solid reaction in a cylindrical/rectangular powder bed system with reacting gas flowing over the solid were used. Consistent with the thermodynamic prediction, the experimental results showed that the reduction of magnetite fines took place in two stages: Fe<sub>3</sub>O<sub>4</sub> to FeO and FeO to Fe. Each stage was controlled by pore diffusion kinetics. The activation energies in the two stages were found to be 42 kJ mol<sup>-1</sup> and 55 kJ mol<sup>-1</sup>, respectively. The fractional reduction of magnetite in the ore went up to 1.0. In addition to the kinetic study, the thermodynamics of the hydrogen reduction of magnetite (Fe<sub>3</sub>O<sub>4</sub>) is discussed briefly, giving the theoretical efficiency of hydrogen utilization in the reduction.

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### Introduction

In view of the emission of carbon dioxide during the carbothermic reduction of iron ore, as in the blast furnace iron making, the problem of global warming poses a challenge to the continuation of this industrially important process as extensively as has been practiced so far. Ironically, to achieve a greater utilization efficiency of the input carbon, a greater proportion of CO<sub>2</sub> in the blast furnace exit gas (containing CO, CO<sub>2</sub>, and N<sub>2</sub>) is required. Thus, while reducing a given mass of iron ore, a cut down on the coke rate, which is a favorable

factor from the viewpoint of fuel consumption, is accompanied by a greater CO<sub>2</sub>/CO ratio in the produced gas leading to the undesirable greenhouse effect. In an effort to explore an alternative, viable reducing agent for iron ores, the use of hydrogen, either alone or in combination with CO, has been considered for a pollution-free reduction process [1–9]. In this context, it may be argued that hydrogen is primarily produced by the steam reforming of fossil fuels (say, natural gas) during which a considerable quantity of carbon dioxide is generated as well. However, it should be noted that since the production is concentrated in one facility, it is possible to separate the CO<sub>2</sub> and dispose of it without atmospheric release, for example by

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<http://dx.doi.org/10.1016/j.ijhydene.2016.04.075>

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injecting it in an oil or gas reservoir. The high cost of hydrogen can be partially offset by using hydrogen mixed with a diluent such as nitrogen or argon. In such a case, the effect of hydrogen partial pressure on the reduction kinetics requires to be studied to examine the suitability of this dilution.

In addition, hematite ( $\text{Fe}_2\text{O}_3$ ) ore has been considered as the chief iron ore for the blast furnace reduction. Consequently, a large reserve of magnetite ( $\text{Fe}_3\text{O}_4$ ) ore has been lying unutilized over the years. For instance, in the Indian context, out of 28.52 billion tons of total iron ore, 17.88 billion tons is hematite and the rest is magnetite. This magnetite reserves has remained almost untapped. The main difficulty of directly using magnetite ore in the blast furnace is its high density and lack of permeability, which hinders easy penetration of the reducing gas. On the other hand, the magnetite obtained in transit during the stagewise reduction of hematite ( $\text{Fe}_2\text{O}_3$ )  $\rightarrow$  magnetite ( $\text{Fe}_3\text{O}_4$ )  $\rightarrow$  wustite ( $\text{FeO}$ )  $\rightarrow$  iron ( $\text{Fe}$ ) is a porous substance that facilitates gas–solid reduction in the blast furnace stack. The hexagonal hematite undergoes volume expansion when it converts into the cubic magnetite and, consequently, develops cracks and pores, which make the reduction of the resulting magnetite kinetically favorable [10,11]. To use magnetite directly as the starting material is rather challenging, which has attracted the interest of researchers in the recent days [12–18]. Wang and Sohn [12] studied the kinetics of the flash reduction of magnetite concentrate particles by hydrogen in the temperature range of 1423–1673 K. Bahgat and Khedr [13] investigated hydrogen reduction of magnetite at 1173–1373 K. They reported an activation energy of about 99 kJ mol<sup>-1</sup>. Kim et al. [14] reduced pure cylindrical compacts of magnetite isothermally at 773–1273 K with pure  $\text{H}_2$  or  $\text{H}_2$ – $\text{H}_2\text{O}$  mixtures. The initial reduction rates increased with temperature and partial pressures of  $\text{H}_2$ . With the progress of reduction, a dense iron layer formed around the wustite grains, which significantly reduced the rate. Al-Kahtany and Rao [15] investigated the reduction of magnetite by pure hydrogen and mixtures of hydrogen and inert gas ( $\text{He}$ ,  $\text{N}_2$ , and  $\text{Ar}$ ) in the temperature range 507–893 K.

In the current work, the reduction of magnetite ore fines, instead of pure magnetite which has been used in most previous studies, by hydrogen was considered. This would make the study more practical and industrially important. It is to be noted that in the abovementioned study of Wang and Sohn [12] with magnetite concentrate, experiments were conducted at high temperatures in the range 1423–1673 K. Reduction at a lower temperature would be more economical and worth studying. The main objective of the present work was to study the kinetics of hydrogen reduction of a magnetite ore. The variables studied for this purpose were as follows: time (0–30 min), temperature (973–1273 K), hydrogen flow rate (0.1–0.5 L min<sup>-1</sup>), hydrogen partial pressure (0.25–1 atm), sample bed height (0.25–0.75 cm), and particle size (75–180  $\mu\text{m}$ ). It is to be noted here that the results of some initial experiments carried out by the current authors have been published in a conference paper [19], which considered only a few of the currently studied six variables with no detailed analysis of the results.

A thermodynamic discussion of the hydrogen reduction of pure magnetite ( $\text{Fe}_3\text{O}_4$ ) is presented in Appendix 1. This will

compare the utilization efficiencies of  $\text{H}_2$  and  $\text{CO}$  in the reduction of  $\text{Fe}_3\text{O}_4$  to  $\text{Fe}$ .

## Materials and methods

### Raw materials

An Indian magnetite ore from Pokphur in the Kiphre district of Nagaland was collected and prepared in proper fineness by crushing and grinding, followed by sieve analysis. The ore fines were made in three particle sizes ( $-106 + 75 \mu\text{m}$ ,  $-125 + 106 \mu\text{m}$ , and  $-180 + 125 \mu\text{m}$ ). The oxygen content of the ore was measured by energy dispersive X-ray spectroscopy (EDS) (make: Oxford Instrument, model: 7582 with INCA software), based on a scanning electron microscopic (SEM) image. For this purpose, the magnetite ore fines were subjected to scanning electron microscopy (JEOL JSM 8360 microscope) with the lowest possible magnification so that an extended surface area of the fines was covered in the micrograph. This analysis was repeated on a number of locations of the ore fines and the average value was taken. This measurement was crosschecked with the oxygen analysis obtained from an Oxygen Determinator (make: Leco, model: TC600) and the chemical analysis by X-ray fluorescence (XRF) (make: Bruker, model: S8 TIGER).

### Gases

Hydrogen gas supplied by the Indian Refrigeration Stores, Kolkata, with the purity of 99.9%, was used as the reducing gas. Argon gas, from the same supplier and with the same purity, was employed for the purging purpose before and after the reduction. In addition, argon was mixed with hydrogen in different proportions to produce different partial pressures of hydrogen.

### Thermogravimetric study

The reduction of the magnetite ore fines was carried out in a thermogravimetric analyzer (TGA) apparatus (make: Bysakh, model: Okay), which was comprised of a furnace with a Pt–Rh heating element, an impervious reaction tube (internal diameter, 25 mm) made of alumina, a balance (accuracy: 0.1 mg), and an alumina crucible, with 10 mm height and 8 mm internal diameter, for holding the sample. The temperature was controlled within  $\pm 2$  K by a Pt-13%Rh/Pt (R type) thermocouple. About 0.2 g of the magnetite ore fines was taken inside the alumina crucible, which formed a shallow bed inside the crucible. The crucible was placed in the TGA at room temperature and its initial mass was recorded by the in-built balance. Next, the temperature of the furnace was raised at a rate of 10 K per minute to the selected reduction temperature in an argon atmosphere. When the temperature was attained, argon was stopped and hydrogen gas was started passing at the selected flow rate, recorded by a flowmeter (rotameter). Gases were made free from oxygen, carbon dioxide, and moisture by passing through an alkaline pyrogallol solution and through the columns of silica gel and molecular sieve, respectively. The gas left the furnace continuously

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