# REDUCTION KINETICS OF MAGNETITE CONCENTRATE PARTICLES WITH HYDROGEN AT 1150 – 1600 ºC RELEVANT TO A NOVEL FLASH IRONMAKING PROCESS

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Keywords: Reduction Kinetics, Magnetite Concentrate, Hydrogen Reduction, Ironmaking, Flash Reduction

## Abstract

A novel ironmaking process is under development at the University of Utah aimed at producing iron directly from iron oxide concentrate in a flash reactor. This process will reduce hazardous emissions and save energy. The kinetics of magnetite reduction with hydrogen was previously investigated in our laboratory in the temperature range 1150 to 1400 ºC at large temperature increments (~100 ºC increments). Due to the significant melting that occurs above 1350 ºC, the reduction kinetics was measured and analyzed in two distinct temperature ranges of 1150 to 1350 ºC and 1350 to 1600 ºC (~50 ºC increments). Experiments were performed using magnetite concentrate particles of different sizes under various hydrogen partial pressures and residence times. Reduction degrees of more than 90 % were achieved in a few seconds at temperatures as low as 1250 ºC. Different rate expressions were needed to obtain reliable agreement with experimental data.

## Introduction

Ironmaking by the blast furnace (BF) is a multi-step process which consumes energy and produces hazardous emissions during its steps as sintering/pelletization, coke-making, etc. The novel ironmaking process being developed at the University of Utah [1-10] aims at producing iron directly from iron oxides concentrate particles in a gas-solid flash reaction utilizing hydrogen gas or natural gas as the reductant and fuel within temperature range 1200-1600 ºC. Without the need of pelletization, sintering or coke, this process significantly saves energy and cuts $CO_2$ emissions. For designing flash reactors, it is important to determine the reduction rate equations. Natural gas will be used in this process by partial oxidation with oxygen in a flame where $H_2$ and CO gas are produced as a results of this in situ reforming. Although in general the reduction kinetics by $H_2$ is much faster than that by CO, it is necessary to study the reduction kinetics of each gas separately in order to analyze the complex kinetics of magnetite reduction by $H_2$ + CO mixtures.

The kinetics of magnetite reduction by hydrogen gas was studied in this project previously [11]. In that work, the kinetics model formulated using various runs at temperatures 1150, 1200, 1300,

and 1400 ºC. Due to their gangue content, the concentrate particles melt at temperatures higher than 1350 ºC, which will change the reduction mechanism. It is important to study the reduction kinetics in the temperature range lower than 1350 ºC separately from that at higher temperatures using smaller temperature increments (50 ºC). In this work, two rate equations were formulated for two temperature ranges: 1150-1350 ºC and 1400-1600 ºC.

## Experimental Work

Magnetite concentrate particles were used in this work with 3 size fractions: 20-25, 32-38 and 45-53 µm. The concentrate particles are irregularly shaped and angular. As the concentrate particles experience melting at temperature higher than 1350 ºC, the mechanism of reduction is expected to change together with the reduction kinetics. Therefore, the temperature range was divided into 1150-1350 ºC and 1400-1600 ºC. For each temperature range, a reduction rate equation was formulated including the effect of particle size, reducing gas partial pressure, and temperature.

Two drop tube reactors (DTR) were used for measuring reduction rate of concentrate particles. Both reactors had a dilute particles-gas conveyed system in which the fine particles fall in the tube with the reducing gas. The reactor system consists of a vertical tubular furnace housing an alumina tube, a pneumatic powder feeder, gas delivery lines, a powder cooling and collecting system, and an off-gas outlet.

For nominal particle residence time calculation, temperature profile is performed before each temperature set in order to define the reaction zone inside the reactor as ($T_s \pm 30$ ºC) where $T_s$ is the set temperature. A honeycomb was placed at the beginning of the reaction zone in order to straighten the flow inside the reactor. Concentrate was fed through a water-cooled tube at the beginning of the reaction zone directly. The reaction zone was corrected according to the method described by Chen et al. [9, 10].

During heating up the reactor, nitrogen gas was flowed until the target temperature was reached then the reducing gas was introduced according to the experiment conditions. Nitrogen gas was added to adjust the partial pressure of the hydrogen and the nominal particle residence time. Gases flow rates were controlled using rotameter flow meters.

Once all the gases are introduced and the reactor temperature is stable, magnetite concentrate is fed into the reactor at the specified feeding rate. All the experimental conditions are designed to maintain the excess hydrogen gas of more than 500% to ensure that the gaseous reactant concentration remains essentially unchanged over the entire reactor length for accurate quantification of the effect of partial pressure. The reduced powder was collected in the collection bin after the experiment. The collection bin was kept hot during the experiment to prevent any water condensation in the sample collection bin then after the experiment, the collection bin was cooled in water under $N_2$ atmosphere to avoid any re-oxidation of the product.

Samples collected were analyzed by ICP-OES to determine the iron fraction which was used to calculate the reduction degree. SEM analysis was employed to study morphology of the reduced samples.

The relevant equations for calculating the nominal particles residence time, %excess hydrogen, excess driving force (EDF), and reduction degree (RD%) was described elsewhere [9].

Reproducibility of the experiments was confirmed by the consistency of the results of repeated experiments under the same conditions including the reproducibility of the analysis method. The experimental precision was within ± 5%.

## Results

Reduction Kinetics at Temperature Range 1150-1350 °C

The samples produced by the reduction experiments were analyzed using ICP-OES. Then, the reduction degree (%) change with nominal particle residence time (s), an example is shown in Figure 1. More than 90% reduction degree was achieved at 1250 °C with $H_2$ partial pressure 0.3 atm and particle residence time 3.6 s. The kinetics of hydrogen reduction of hematite concentrate particles was studied previously by Chen et al. [9] and the nucleation and growth kinetics model was found to best describe the reduction kinetics. Based on their studies, the nucleation and growth kinetics expression given by the following equation was tested and was found to describe the reduction rate of magnetite concentrate particles:

$$(-Ln(1-X))^{1/n} = k_{app}t \tag{1}$$

$$(-Ln(1-X))^{1/n} = k' \times e^{\frac{E_a}{RT}} \times f(p_{H_2}) \times h(D_p) \times t \tag{2}$$

where $X$ is the iron fraction, $n$ is the Avrami parameter, $k_{app}$ is the apparent rate constant, $k'$ is the pre-exponential factor, $E_a$ is the activation energy for the reaction, $f(p_{H_2})$ is the function for the hydrogen partial pressure dependence, $h(D_p)$ is the particles size dependence function and $t$ is the nominal particle residence time.
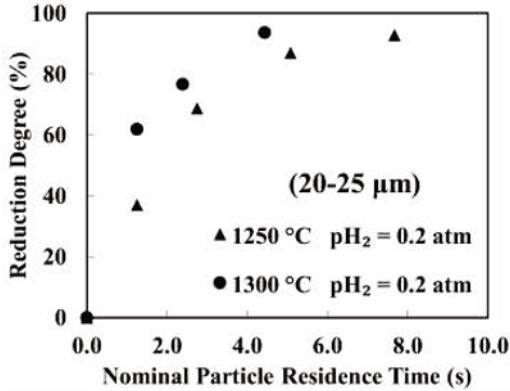


**Figure 1.** Change of reduction degree (%) with the nominal particle residence time at different conditions using particles size (20-25 microns).

The nucleation and growth mechanism was evident as seen in the SEM micrographs, Figure 2, where nuclei were formed on active sites on the particles. Avrami parameter, n, was obtained by plotting $Ln(-Ln(1-X))$ with $Ln(t)$ and found to be 1, as shown in Figure 3. The reduction kinetics had a first-order dependence on the hydrogen partial pressure, as shown in Figure 4. When

studying the particle size effect, it was found that there is no noticeable effect on the reduction kinetics. The activation energy was calculated according to the Arrhenius equation to be 190 kJ/mol, as shown in Figure 5. As shown by XRD and SEM previously [9], a combination of different iron oxides and iron metal is present at any given moment during the reduction process. Therefore, the rate of reduction in this work was represented by the overall fraction of oxygen removed without distinguishing the formation of different iron oxide phases. In this global equation, the rate of oxygen removal from the iron oxide without specifying a reduction reaction for an oxide phase. The complete rate equation was:

$$(-Ln(1-X)) = 6.41 \times 10^6 \times e^{(\frac{-190,000}{RT})} \times [(p_{H_2}) - (\frac{p_{H_2O}}{K_{eq}})]_{lm} \times t \qquad (3)$$

where $R$ is 8.314 J/mol K, $T$ is in K, $p$ is in atm, and $t$ is in seconds. It was found that Eq. (3) can satisfactorily predict the reduction degree as shown in Figure 6.
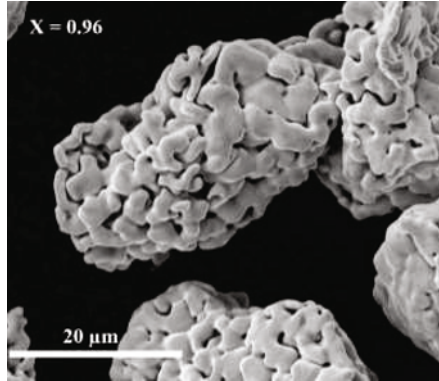


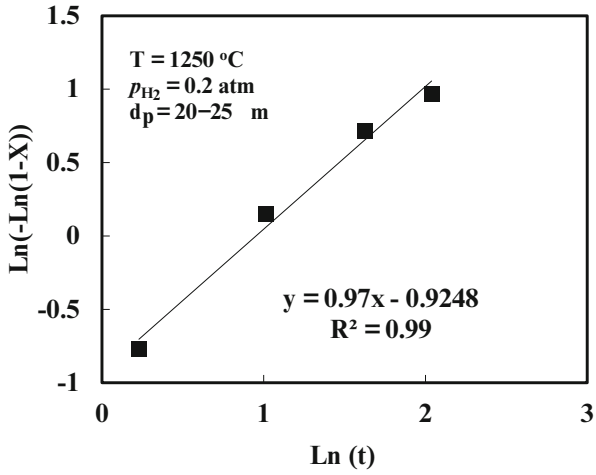**Figure 2.** SEM micrograph for the reduced magnetite particles at 1250 °C and X = 0.96.

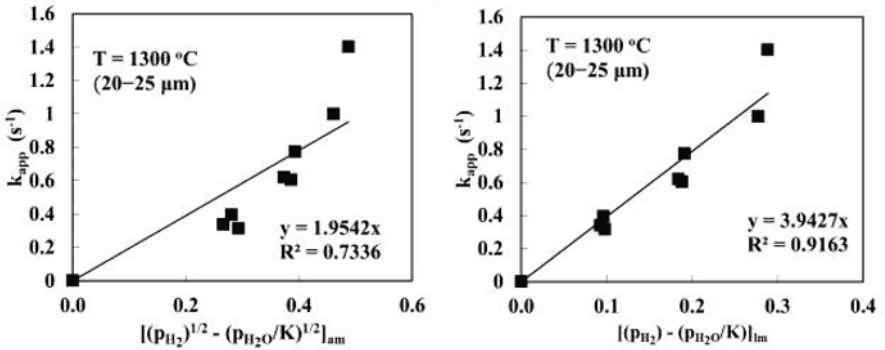**Figure 3.** Determination of the Avrami parameter.



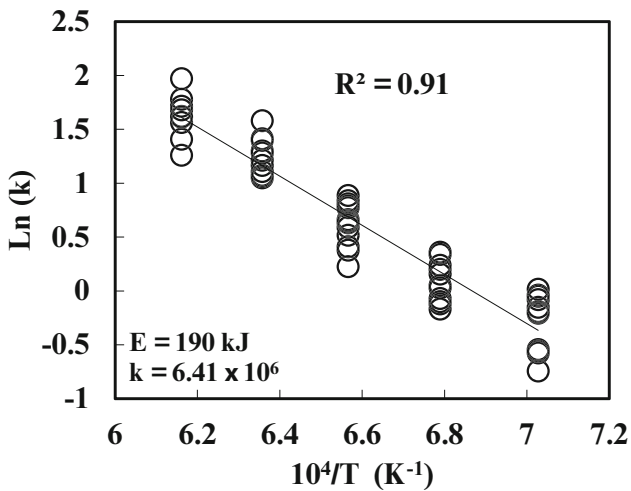**Figure 4.** Obtaining the $pH_2$ dependence.

**Figure 5.** The Arrhenius plot for obtaining the activation energy and the rate constant for the reaction.
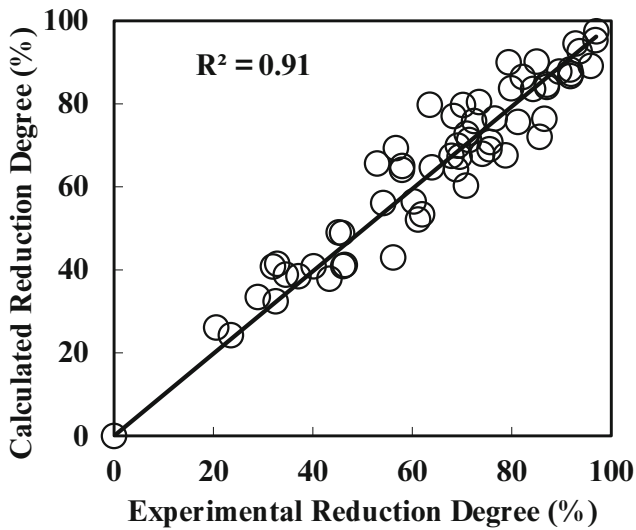


**Figure 6.** Calculated reduction degree (%) compared to the experimental reduction degree (%).

Reduction Kinetics at Temperature Range 1400-1600 °C

At 1400 °C, reduction degree of 95% was achieved at $H_2$ partial pressure 0.15 and particles residence time 1.8 s, as shown in Figure 7. Nucleation and growth kinetics expression was tested and found to describe the reduction kinetics in this temperature range, with an Avrami parameter n = 1. The reducing gas partial dependence was found to be of the first order. The particle size dependence was determined and the activation energy was found to be 182 kJ. The complete rate equation is:

$$(-Ln(1-X)) = 6.31 \times 10^7\ e^{\left(\frac{-182000}{RT}\right)}\ (D_p)^{-1}\ [(p_{H_2}) - (\frac{p_{H_2O}}{K_{eq}})]_{lm}\ t \qquad (4)$$

where R is 8.314 J/mol K, T is in K, p is in atm, and t is in seconds. The calculated versus the experimental results are shown in Figure 8 with a good agreement.

Although the activation energy in the two temperature ranges were close, the pre-exponential factors were an order of magnitude different. In addition the effect of particle size in the temperature range 1400-1600 °C was observed, perhaps because of the melting of the particles which removes any cracks and porosity.
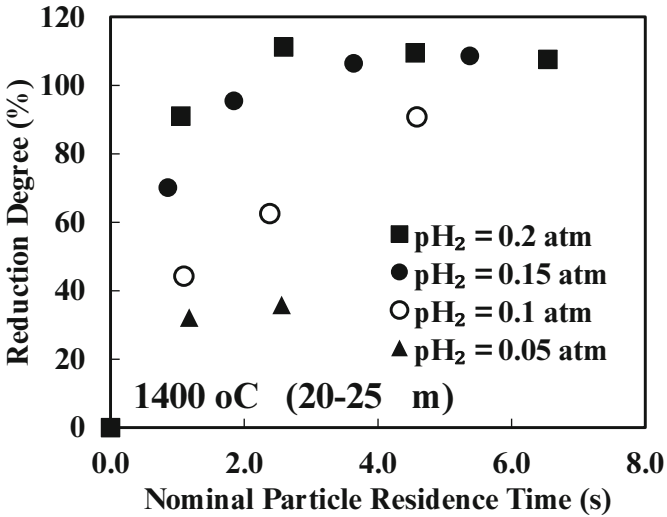


**Figure 7.** Change of reduction degree (%) with the nominal particle residence time at 1400 °C and different $H_2$ partial pressures using particles size (20-25 microns).
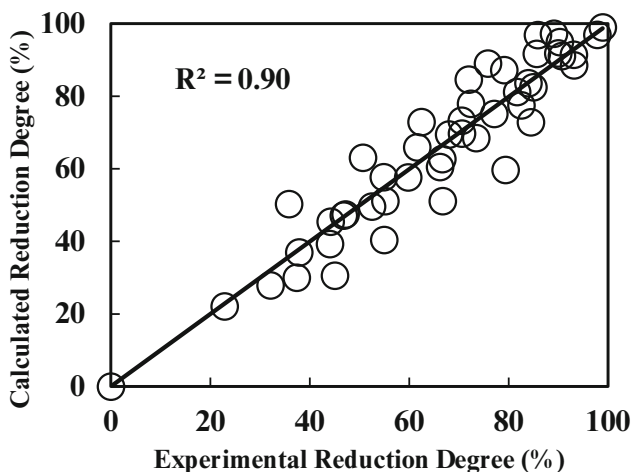
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**Figure 8.** Calculated reduction degree (%) compared to the experimental reduction degree (%).

## Conclusions

The kinetics of magnetite concentrate reduction with hydrogen gas was studied in the temperature ranges 1150-1350 °C and 1400-1600 °C. It was found that magnetite particles can be reduced to more than 90% in a few seconds available in the gas-solid flash reactor at temperature as low as 1250 °C. It was found that the nucleation and growth kinetics describe the reduction in the two temperature ranges. In both temperature ranges, an Avrami parameter n = 1 and 1st-order reduction rate dependence on the partial pressure of hydrogen were observed. In the temperature range 1150-1350 °C, an activation energy value of 190 kJ/mol was determined whereas in the temperature range 1400-1600 °C, 182 kJ/mol was obtained. In addition, effect of particle size was present in the temperature range 1400-1600 °C. Two complete rate equations were obtained representing the reaction rates at each temperature range. The rate equations showed good agreement with the experimental results with magnetite concentrate particles.

## Acknowledgments

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