Spouted Bed Reactor for kinetic measurements of reduction of Fe$_2$O$_3$ in a CO$_2$/CO atmosphere Part I: atmospheric pressure measurements and equipment commissioning.

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Highlights:

- A pressurised spouted bed reactor is commissioned for study of gas-solid kinetics.
- Accurate kinetic measurements can be made using the reactor.
- A comprehensive method for extracting intrinsic kinetics is proposed.
- Consistent intrinsic kinetics are obtained for reduction of Fe₂O₃ with CO.
- The work provides a solid basis for further modelling of reaction dynamics.
Abstract

A high pressure and high temperature spouted bed reactor, operating in fluidisation mode, has been designed and validated at low pressure for the study of gas-solid reaction kinetics. Measurements suggested the bed exhibited a fast rate of gas interchange between the bubble and particulate phases. Pressurised injection of the particles to the bottom of the bed allowed the introduction of solid reactants in a simple and controlled manner. The suitability of the reactor for the purpose of kinetic studies was demonstrated by investigation of the intrinsic kinetics of the initial stage of the reduction of Fe₂O₃ with CO over multiple cycles for chemical looping.

Changes of pore structure over the initial cycles were found to affect the observed kinetics of the reduction. The initial intrinsic rate constant of the reduction reaction \( k_i \) was measured by using a kinetic model which incorporated an effectiveness factor. The uncertainty arising from the measurement of particle porosity in the model was compensated for by the tortuosity factor. The average activation energy obtained for cycles three to five was 61 ± 8 kJ/mol, which is comparable with previous studies using both fluidised beds and thermogravimetry.

Keywords: Spouted bed reactor, Fluidisation, intrinsic kinetics, chemical looping, iron oxides.

1 Introduction

In light of the need for mitigation of climate change, the concept of chemical looping combustion (CLC), a term first used by Ishida et al. (1987), which offers an exegetically efficient method of power generation with inherent sequestration of CO₂ (Boot-Handford et al., 2014), has received increasing attention. CLC utilises the redox reactions of metal oxides (also referred to as oxygen carriers) to deliver oxygen from air to a carbonaceous fuel. The resulting combustion products, mainly comprising CO₂, are inherently separated from other flue gas components, i.e. depleted air, and thus no additional separation steps are required.
Recently, growing interest in CLC and its derived applications in fuel conversion have been evident because of its potential to significantly reduce the economic costs for the chemical and utility industries as they move towards a low carbon future (Bhavsar et al., 2014; Fan et al., 2012; Fan et al., 2015). Chemical looping technologies applying to areas such as combustion, gasification and reforming of carbonaceous fuels have been well summarised in the literature (Adanez et al., 2012; Fennell and Anthony, 2015). Their commercial feasibility, especially for CLC with gaseous fuels, has also been demonstrated with extended pilot-scale tests using different oxygen carriers (Fan et al., 2015; Lyngfelt, 2011).

Among typical candidates of metal oxides for chemical looping, iron oxides have attracted particular attention owing to their low cost (especially in the case of iron ore), minimal toxicity and various oxidation states for different applications of chemical looping (Boot-Handford et al., 2014; Luo et al., 2015; Lyngfelt, 2014). For combustion purposes, the reduction of Fe$_2$O$_3$ is likely to be limited to Fe$_3$O$_4$ because further reduction requires a high $P_{CO}/P_{CO_2}$ (0.6 at 1173 K) which only occurs during incomplete combustion. When CO is used as the fuel gas, the reduction and oxidation of iron oxide for chemical looping combustion are Reactions 1 and 2, respectively:

$$3Fe_2O_3 + CO \leftrightarrow 2Fe_3O_4 + CO_2 \quad \Delta H^{1023K}_{1023K} = -44.3 \text{ kJ mol}^{-1} \quad \text{Reaction 1}$$

$$2Fe_3O_4 + \frac{1}{2}O_2 \leftrightarrow 3Fe_2O_3 \quad \Delta H^{1023K}_{1023K} = -238.4 \text{ kJ mol}^{-1} \quad \text{Reaction 2}$$

Reaction 1 is a classical gas-solid reaction that is important for iron based CLC processes. In the case of CLC with solid fuel, gasification was proposed to be a necessary step before the product (CO and H$_2$) could effectively react with the oxygen carrier (Brown et al., 2010; Dennis et al., 2006; Jin and Ishida, 2004; Leion et al., 2007; Scott et al., 2006). The rate of solid-solid reactions between the char and metal oxide are also believed to be extremely slow (Brown et al., 2010; Leion et al., 2007). It was found, for example, the gasification rate was accelerated in the presence of iron oxide, which improved the mass transfer of syngas (CO and H$_2$) leaving the surface of solid fuel (Saucedo et al., 2014). Thus a better understanding of the intrinsic kinetics of the reduction reaction, especially over repeated cycles, will assist system modelling and optimisation of the processes in the fuel reactor.
Early interest in the kinetics of iron oxide reduction came from the iron and steel industry in an effort to better understand the processes through which iron oxide was reduced to elemental iron by CO and/or H$_2$ in the blast furnace (Szekely et al., 1976). While comprehensive kinetic models have been developed based on a shrinking core for this purpose (McKewan, 1962; Spitzer et al., 1966a, b) , there are very few cases where the intrinsic kinetics of the reduction reactions have been explored (Trushenski et al., 1974). Most studies employed thermogravimetric analysis and considered that the reduction reaction occurred with a sharp interface moving towards the centre of the iron oxide pellet as the reduction proceeded, which is generally applicable in the steel making process where the reaction is significantly limited by intra-particle diffusion, but may not be true in all situations.

To enable rapid reaction and reasonable reactor sizes, the chemical looping process will most likely use relatively small, and porous, iron oxide particles. In contrast to the aforementioned shrinking core models, the reduction reaction interfaces become diffuse and, with increasing particle porosity, may eventually become indistinguishable owing to much improved intra-particle diffusivity. Although the observed kinetics in such a chemical reaction may still be slowed by inter- and intra-particle diffusion, they are more influenced by the intrinsic kinetics of the reaction.

Gas-solid reactions with a diffuse reaction interface in porous particles can be satisfactorily described by models formulated based on grain geometry (Szekely and Evans, 1970, 1971), reaction zone (Trushenski et al., 1974) or pore structure (random pore model (Bhatia and Perlmutter, 1980)). However, intrinsic kinetics are difficult to obtain by directly fitting those models to experimental data influenced by mass transfer and intra-particle diffusion. This difficulty is compounded by the existence of the intermediate reducing step of Fe(II) (Abad et al., 2007). Careful experimental design can not only avoid the need for the use of mathematically complex models, but can also avoid the effects of the response time of the measurement and effects of mass and heat transfer limitation that shield the intrinsic kinetics. Bohn et al. (2010) provided an example of studying the initial intrinsic kinetics of Fe$_2$O$_3$. The study was carried out in a fluidised bed reactor over repeated reduction and oxidation cycles at various temperatures in the 723–973 K temperature range. By calculating the effectiveness factor of the reaction, the authors concluded that reactions of particles
with radii under 300 µm were limited by intrinsic kinetics rather than intra-particle diffusion. A basic physical model was applied to the gas solid reactions. The choice of lower temperatures, compared to those normally applicable to CLC, was owing to the limitations of intra-particle diffusion and response time of the measurement systems at higher temperatures; however, (and similar to this study) model validation based on basic physical models does allow reasonable extrapolation to higher temperatures, and the use of a large enough system to allow recovery of particles post-reaction allows insight into physical changes within particles over multiple cycles.

As demonstrated by Bohn et al. (2010), the use of a fluidised bed under certain conditions can greatly simplify the study of intrinsic kinetics of gas-solid reactions. This study uses a spouted fluidised bed to experimentally obtain intrinsic kinetics for gas-solid reactions at high temperature in a strictly controlled environment. In a fluidised bed the method for introducing of solid reactant is often limited to either feeding from the top or the side of the bed. Those feeding methods increase the complexity of the reactor, especially for pressurised operation. Furthermore, by using these feeding methods, some types of solid particle (such as coal, limestone, metal oxides etc.) may experience chemical or physical changes in the freeboard even before they enter the fluidised bed. Errors in kinetic analysis may arise since the temperature and residence time of the particles in the freeboard and dispersion of them in the bed cannot be easily controlled and depend on experimental conditions such as the gas flow rate. The reactor utilised here minimises the effects of such issues.

Conventional spouted beds are two-phase reactors consisting of a central lean solid phase (spout) where solid particles entrain in a fluid jet penetrating the bed from below, and a downward-moving dense solid phase (annulus) which creates a counter-current flow between the solid and gas. A recent review of this type of reactor is provided by Epstein and Grace (1997). Konduri et al. (1999) suggested that fluidisation of spouted beds occurs due to two mechanisms: bubbles forming in the annulus, and bubbles forming at the spout inlet, with the former mechanism playing a dominant role. Figure 1 describes these mechanisms schematically. At the bottom of the annular phase, the solids move downwards around the spout while the upward-moving gas velocity ($U_a$) in the annular phase is less than $U_{mf}$. As the axial distance in
the bed increases, $U_a$ increases owing to gas cross-flow from the spout phase to the annular phase across the axis of the bed. At a critical height, $U_a$ equals $U_{mf}$. Additional cross-flow from the spout phase above the critical height will travel in the form of bubbles in the annular phase. The global solid circulation in the bed is facilitated by the gulf streaming (which is observed experimentally under cold modelling) as a result of radially non-uniform bubble flow, causing solid material close to the wall to move downwards to the bottom of the annular phase, where it is entrained into the spout. Then, at a certain height when the spout jet breaks down, the material is released to join the bubbling bed above the spout.

![Diagram](image)

**Figure 1** Illustration of the behaviour of the bubbling spouted bed reactor.

The objective of this investigation is to demonstrate and validate the use of a spouted bed operating in bubbling fluidised mode for accurate measurement of solid-gas reaction kinetics under strictly reaction-controlled conditions. The big advantage of this reactor is that it reduces the complexity of the system (by allowing samples to be pneumatically fed to the bed). The particular initial intrinsic kinetics of iron oxide reduction by a CO/CO$_2$ mixture have been investigated. The aim was to elucidate the detailed reaction mechanism and to allow subsequent development of an intrinsic kinetic model over the course of reaction.
2 Equipment and Experiment

2.1 Design of equipment

The system consists of five parts: the spouted bed reactor; the solids feeding and gas transport apparatus; the gas filters; the control system; and the data acquisition system.

Spouted bed reactor. A schematic diagram of the high pressure spouted bed reactor is shown in Figure 2. It was designed based upon a pressurised spouted bed reactor previously intended for investigation of gasification of coal and char (Spiegl et al., 2010), but with significantly improved control systems for kinetic measurements (pressurised dosing of solid reactant, automated multi-gas switching and faster response to the variation of bed temperature). The reactor shell (504 mm long, 48 mm o.d., 7 mm wall thickness) was constructed from Incoloy® Alloy 800HT, acting both as a pressure vessel and an electrical resistance-based heater (Cousins et al., 2008). The reactor body was sealed completely without any welding (a pressure test was also conducted). The designed maximum temperature and pressure of the reactor were 1273K and 3 MPa, respectively. The fluidised bed was contained within a quartz reactor body placed within the reactor shell, which comprised a cylindrical section (i.d. 30 mm) attached to a conical frustum at the bottom. The quartz liner sat tightly on a supporting ring. The gas inlet tube (spout line, 6 mm i.d.) was designed to protrude a short length (3.6 mm) into the quartz liner, and the angle of the conical frustum $\theta_c$ was chosen to be 60° to facilitate the circulation of the bed.
Figure 2 Schematic diagram of the spouted bed reactor

Gas transport system. Rotameters and needle valves were used to control the volumetric flow rate of individual gases, at ambient temperature. A pressure gauge was installed on each gas line before the flow meter to monitor the pressure at which each rotameter measured the volumetric flow rate, which was set to 1 bar. Burkert solenoid switch valves were attached to the downstream of the Rotameters. This enabled automatic, immediate starting and stopping of flow in the various gas lines, simulating a step function of gas mixtures.

Gas filters. After leaving the reactor, the gas stream passed through a series of filtration traps which separated elutriated fine solid material and water (if necessary) from the product gas stream. The gas from the outlet of the reactor was first passed
through a ½ inch inner tube to the bottom of a vertical 1 inch outer tube, which was immersed in a circulating salted ice-water bath. The outer tube acted as a heat exchanger, and the gas stream was cooled to ambient temperature as it travelled up through the inner tube. Water vapour (if any) was condensed and trapped in the tube during the cooling process, and was collected afterwards. Another horizontally-held 1 inch tube, packed with glass fibre, was fitted after the vertical cooling trap to collect fines generated by solids attrition. An extra moisture filter, filled with CaCl₂ and plugged at both ends with glass fibre, was placed before the gas analyser (with a similar but smaller moisture trap) when performing long cycling experiments (> 2.5 h) to prevent any moisture or dust from contaminating the equipment. The moisture filter was removed when conducting experiments involving the measurement of kinetics (as opposed to reaction extent) in order to reduce the response time of the system.

The process control system. Online process control was achieved by using a purpose-built controller through an operator interface written in Agilent VEE™. The program allowed PID (proportional-integral-derivative) control of the bed temperature by controlling the current passing through the reactor shell. The program also controlled the solenoid valves mentioned in the gas transport system section.

Data measurement and acquisition (DMA). The DMA system was integrated with the same purpose-built controller as the process control system. The exhausted gas in the sampling line contained the major components CO and CO₂ alongside N₂ as a balance gas. Most of the flue gas was directed to the venting line, where any combustible gases were burned by passing the gas stream through a propane burner. A small, controlled amount of the product gases was passed to a gas analyser train for sampling and then re-joined the venting line before the propane burner. An ADC MGA 3000 infrared multi-gas analyser was used to detect the concentrations of CO and CO₂. Its measurement range and rated accuracy were 0–50 vol. % and ± 1 % of the measured value. A multi-point calibration for the concentration of CO and CO₂ was conducted each month using certified calibration gas mixtures (BOC). A single-point calibration was conducted prior to each experiment using the same gas mixtures to check that the calibration was still valid.
2.2 Material
Iron (III) oxide particles were prepared from Fe$_2$O$_3$ powder (5 µm, Sigma-Aldrich > 99.9 wt. %) by a wet granulation method. Deionised water (0.125 gram per gram of Fe$_2$O$_3$) was slowly sprayed on to the powder while it was vigorously mixed in a high shear food mixer (Kenwood Chef). Fe$_2$O$_3$ agglomerates were formed during the process, these were then sieved gently into different size fractions (212–300 µm, 300–425 µm, 425–500 µm, 500–710 µm) before being transferred into 20 ml alumina crucibles. The crucibles were then placed in a muffle furnace (Carbolite), where the particles were heated up for 1 hour to 900 °C and then calcined for 3 hours. The resultant particles were cooled down to ambient temperature under air and sieved again to the desired size fractions. Fe$_2$O$_3$ particles in the size fraction of 300–425 µm (3960 kg/m$^3$) were used in all of this study unless otherwise stated.

2.3 Experimental procedure
40 g of G60 white silica sand ($d_{sand} = 500–700$ µm, $\rho_{sand} = 2600$ kg/m$^3$, purity >98 %, David Ball Co. plc) was used as an inert bed material (un-fluidised height: 70 mm) in the reactor. The particular size fraction was chosen so that the Fe$_2$O$_3$ particles could easily be separated from the bed material after an experiment by sieving, yet both the particles and the inert bed would fluidise and fully mix. The experiments were conducted in the temperature range of 723–973K. The sand bed was added into the reactor when the temperature stabilised at the set point, and was fluidised with a N$_2$ flow of 50 ml/s as measured at laboratory temperature and pressure (0.1 MPa). At 723K and 773K larger amounts of Fe$_2$O$_3$ (0.700 g and 0.600 g respectively) were used to reduce experimental error by ensuring the concentration changes of CO and CO$_2$ were significantly larger than the resolution of the analysers. This was necessary because of the slow reaction rates at these temperatures. At 823K and above only 0.500 g of Fe$_2$O$_3$ was required for kinetic analysis, though experiments were also conducted with larger or smaller masses to measure the cross-flow factor of the bed and to ensure that inter-phase mass transfer was not an issue.

Prior to experiments 0.300–2.000 g iron oxide particles were weighed and fed in to a 50 ml double-ended stainless steel sample cylinder from Swagelok®, which was connected via a ball valve to an independent N$_2$ cylinder with a pressure 0.05 MPa higher than that of the spouted bed system. The other end of the sample cylinder was attached to the reactor gas inlet line via another ball valve. The solid was then rapidly
pressure-injected into the spouted bed by opening the ball valve between the bottom of the reactor and the cylinder. The sample cylinder was weighed before and after an experiment to verify the amount of sample injected. Tests demonstrated that the particles were injected as a single pulse.

The Fe$_2$O$_3$ particles were injected into the bed only after successful completion of the one-point calibration for CO and CO$_2$ and two reduction and oxidation cycles with the inert sand bed to ensure that the cycling system exhibited no side reactions and had a repeatable baseline. When the temperature had stabilised at the set point, the time-dependent gas-switching program was initiated to effect pre-programmed reduction and oxidation cycles. The gas mixture in reduction cycles was supplied by an oxygen-free nitrogen cylinder (99.998 %, BOC), a CO$_2$ cylinder (99.9 %, BOC) and 10.12 % CO with nitrogen balance calibration cylinder (BOC). In oxidation cycles, the nitrogen cylinder and an air cylinder (99.9 %, BOC) were used. During all reduction cycles, the fluidising gas was first switched to mixtures of 85 % N$_2$ and 15 % CO$_2$ for 120 seconds until the concentration stabilised. This was then instantaneously changed to mixtures of 84–80 % N$_2$, 1–5 % CO and 15 % CO$_2$ using a solenoid valve. The reducing gas mixture was fed for 180 seconds to ensure that no further reduction was observed (CO and CO$_2$ concentrations returned to baseline). The ratio of partial pressure of CO and CO$_2$ in the reduction gas mixture, $P_{CO_2}/P_{CO}$, was at least equal or higher than 3 so that the product of Fe$_2$O$_3$ reduction was restricted to only Fe$_3$O$_4$ (the equilibrium constants ($P_{CO_2}/P_{CO}$) for further reduction of Fe$_3$O$_4$ within the temperature range of study is at most 1.6). X-ray Diffraction was also carried out on the sample retrieved after 5th reduction, which suggested Fe$_3$O$_4$ was the only phase present (Figure S2). In all oxidation cycles mixtures of nitrogen and air (96.2% N$_2$, 3.8% O$_2$) were used to oxidise the Fe$_3$O$_4$ back to Fe$_2$O$_3$. Each oxidation cycle lasted 240 seconds to ensure complete oxidation of Fe$_3$O$_4$. Between the reduction and oxidation stages the whole system was purged with nitrogen for 120 seconds to remove the possibility of gas mixing between reduction and oxidation stage. The total flow rate for both reduction and oxidation was kept at $U/U_{mf} \approx 2.5$ ($U_{mf}=0.147$m/s at 823K, calculated for the inert sand bed which dictated the fluidisation regime) as calculated from the correlation of Wen and Yu (1966). The response time (space time) of the reactor, together with those of the drying and measurement chambers for the
infrared analyser, was characterised using a published method developed by Fennell et al. (2009).

2.4 Theory for derivation of initial intrinsic kinetics

The initial intrinsic kinetics of the reaction are the primary focus of this work; a subsequent publication will model in detail the subsequent stages of the work by integrating the random pore model and Wagner theory for solid-state diffusion (Zhang et al., in preparation(Unpublished)). A few assumptions were made in order to simplify the analysis of reaction rate: a) the iron oxide particles were spherical; b) the particles were at the same (measured) temperature as the sand; c) the gas concentrations within the particles were pseudo-steady state; and d) the kinetics were first order and irreversible (an assumption which will be verified experimentally later in section 3.2, Figure 5) due to the large equilibrium constants (10^4-10^5, based on thermodynamic calculation in Factsage™ (Bale et al., 2009)) over the temperature range of the investigation.

Considering a spherical Fe₂O₃ particle, a mass balance for CO on a spherical shell with differential thickness dr gives (Bird et al., 2007)

\[ D_{e,CO} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dc_{CO}}{dr} \right) = k_i c_{CO} \]

Equation 1

\( D_{e,CO} \), the effective diffusivity of CO, is used to describe the diffusion of the reactant within the particle and is assumed to be constant; \( c_{CO} \) is the concentration of reactant CO contained within the pores; and \( k_i \) is the intrinsic rate constant for the forward reaction of Error! Reference source not found..

The extent to which the rate of reaction is lowered due to intra-particle diffusional resistance is measured by the effectiveness factor, \( \eta_{CO} \), which is defined as the percentage of the intrinsic rate of reaction that is obtained by the actual mean reaction rate within the pores. For spherical particles of radius \( R \), it is given as

\[ \eta_{CO} = \left( \frac{W_{CO,R}}{W_{CO,0}} \right) = \frac{4\pi RD_{e,CO}c_{CO,R}(1 - \sqrt{\frac{k_i}{D_{e,CO}}R \coth \sqrt{\frac{k_i}{D_{e,CO}}R}})}{\frac{4}{3}\pi R^3(-k_i c_{CO,R})} \]

Equation 2

\[ = \frac{3}{\phi^2} (\phi \coth \phi - 1) \]
$W_{CO,R}$ is the molar flux of reactant CO at the particle surface when considering the intra-particle diffusional resistance and $W_{CO,O}$ is the molar flux of reactant CO when all active surfaces of the reacting particle are exposed to reactant CO of concentration $c_{CO,R}$ and diffusional resistance is negligible. $\phi$ is the Thiele modulus, and it is given as

$$\phi = \sqrt[3]{\frac{k_i}{k_{e,CO}}} \ R \quad \text{Equation 3}$$

The mean reaction rate within pores can now conveniently expressed as $\eta_{CO} k_i$. It can be combined with the external mass transfer coefficient of CO, $k_{g,CO}$, and the observed rate of reaction, $r'$, in mol g$^{-1}$ s$^{-1}$, to determine the overall rate constant, $k_0$, in s$^{-1}$, for the irreversible chemical reaction:

$$r' = \frac{k_0}{\rho_{Fe_2O_3}} c_{CO,P} \quad \text{Equation 4}$$

$$\frac{1}{k_0} = \frac{R}{3k_{g,CO}} + \frac{1}{\eta_{CO} k_i} \quad \text{Equation 5}$$

$\rho_{Fe_2O_3}$ is the envelope density of Fe$_2$O$_3$ and $c_{CO,P}$ is the CO concentration of the particular phase. Assuming the bed as a whole is completely mixed (so it can be treated as an ideally mixed fluidised bed where the outlet concentration of the bed is equal to the concentration at the outlet of bubble phase, which is the same as that of a well-mixed particulate phase, an assumption checked later in section 3.1), the CO concentration in the particulate phase of the reactor (which is equal to the concentration at the outlet of the reactor) is related to the measured CO concentration at the analyser as:

$$c_{CO,P} = c_{CO,m} + \tau_{mix,CO} \frac{dc_{CO,m}}{dt} \quad \text{Equation 6}$$

$c_{CO,m}$ is the measured concentration of CO. Equation 6 has been used to deconvolute $c_{CO,m}$ to obtain $c_{CO,P}$. The overall response time of the reactor, drying tube and analyser were measured via the introduction of step impulses to be $\tau_{mix,CO_2} = 2.0$ s and $\tau_{mix,CO} = 2.8$ s. By assuming a two CSTR in series model, the response time of the bed was experimentally determined to be $\tau_{mix,CO_2} = \tau_{mix,CO} = 0.7$ s. Deconvolutions of the CO and CO$_2$ signals were carried out to estimate the transient
concentration in the particulate phase of the bed, but considering the overall response
time was at least an order of magnitude lower than the duration of the reactions, and
the addition of a CSTRs-in-series model made a negligible difference to the maximum
reaction rate ($\leq 18\%$), the likely errors caused by the somewhat simple response time
model on the measured rate of reaction are insignificant.

The external mass transfer coefficient and intra-particle diffusivities were estimated
using the equations listed in Table 1. $k_{g,CO}$ in Equation 5 was estimated using the
definition of the Sherwood number, $Sh = k_g d_p/D_b$. A semi-empirical correlation
was used to estimate the Sherwood number in the particulate phase in a fluidised bed
(Equation 7). The Reynolds number of the particulate phase was suggested by two-
phase theory, $Re_p = \rho_g d_{s,avg} U_{mf}/(\mu e_{mf})$, with the voidage of the bed at minimum
fluidisation $e_{mf} = 0.42$ and $Sc = \mu/(\rho_g D_b)$. The bulk diffusivity of the CO – N$_2$
system was estimated by using Equation 8, based on Chapman-Enskog kinetic theory
and the Lennard-Jones potential function for intermolecular forces. Here, $T$ is the
absolute temperature in K, $M$ is the molecular weight of the gaseous species in g mol$^{-1}$; $P$ is pressure in atmospheres; $\Omega^{(1,1)}$ is the “collision integral”, which is a function
of dimensionless temperature $\kappa T/\varepsilon_{AB}$; and $\sigma_{AB}$ and $\varepsilon_{AB}$ are force constants in the
Lennard-Jones potential function. The Knudsen diffusivity of gases in a straight round
pore is expressed in Equation 9, where $r_e$ is the equivalent pore radius in m, $\varepsilon_{Fe_2O_3}$ is
the porosity of the Fe$_2$O$_3$ particles, $S_x$ in m$^2$ g$^{-1}$ is their specific total surface area, and
$\rho_{Fe_2O_3}$ in g m$^{-3}$ is the density of the particles. Diffusion in the Knudsen regime was
likely to co-exist with the bulk diffusion as 33% of the total pore volume (based on
cut-off of pore sizes of 10µm, Table S1) of the iron oxide particle were equal or
smaller than the mean free path of a CO molecule ($2.1 \times 10^{-7}$ m at 973K atmospheric
pressure), calculated based on kinetic theory (Hirschfelder et al., 1954).

The effective diffusivity was evaluated using Equation 10, where $\tau$ is a fitted
tortuosity. The initial, estimated value of $\tau$ was 4, as recommended by Satterfield
(1980) for commercial catalysts. The initial intrinsic rate constant, $k_i$, which corrected
the mass transfer effect in $k_0$, was calculated iteratively. First, an effectiveness factor
of $\eta_{CO} = 1$ was assumed in Equation 5 to calculate a $k_i$ value, which was then
substituted into Equation 3 to obtain a value for the Thiele modulus, $\phi$. The value of $\phi$
was used in Equation 2 to obtain another value of $\eta_{CO}$. The process was then repeated until the value of $\eta_{CO}$ converged.

The final value of $D_e$, and therefore the final $k_i$ value, depends on the final $\tau$ value, that was determined experimentally by adjusting its value until $k_i$ calculated from different particle radii converged. In this way, the theoretical prediction of the effectiveness factor and the experimental results converged. The final values calculated for $\tau$ in cases assuming different porosities are listed in Table 2. The method of comparing the intrinsic rate of particles of different sizes has been previously used for determining $\tau$ in the Knudsen diffusion regime, and it was deemed that the method could be used to calculate the tortuosity and effective diffusivity (Satterfield, 1970).

Table 1 Equations for estimating mass transfer coefficient and diffusivities

| Parameter to be Estimated | Equation | Reference |
|---------------------------|----------|-----------|
| $k_g$                     | $Sh = (2\varepsilon_{mf} + 0.95Re_p^{0.5}Sc^{0.3})$ | Equation 7 Turnerill and Davidson (1984) |
| $D_b$                     | $D_b = 0.001858$ | Hirschfelder et al. (1954) |
|                           | $D_b = \sqrt[4]{\frac{T^3(\frac{1}{M_1} + \frac{1}{M_2})^{1/2}}{P\sigma_1^2\Omega^{(1,1)*}}}$ | Klein and Smith (1968) |
| $D_K$                     | $D_K = 97r_e \sqrt{\frac{T}{M}} = 194 \frac{\varepsilon_{Fe_2O_3}}{S_gP_{Fe_2O_3}} \sqrt{\frac{T}{M}}$ | Satterfield (1980) |
| $D_e$                     | $\frac{1}{D_e} = \frac{\varepsilon_{Fe_2O_3}}{\tau} \left(\frac{1}{D_K} + \frac{1}{D_b}\right)$ | Equation 10 Satterfield (1980) |
3 Results and discussion

3.1 Gas interchange between gas and particulate phase

A dimensionless ratio, $X_f$, is used here to characterise the gas exchange efficiency between the bubble phase (the bubbles passing through the bed) and the particulate phase (the fluidised sand) in the fluidised bed. The theoretical value of $X_f$ was estimated using the model of Kunii and Levenspiel (1990). The estimated value of $X_f$ obtained is 13.7, which indicates very efficient gas exchange between the two phases.

Further examination of $X_f$ has been carried out experimentally using a two-phase model for a first order reaction in a bubbling fluidised bed proposed by Davidson and Harrison (1963). The model is obtained by assuming perfect mixing in the particulate phase. A relationship between the ratio of $c_{\text{CO, out}}/c_{\text{CO, in}}$ (outlet to inlet concentration of the bed) and $X_f$ could be found by using this model as shown in Equation 11:

$$
c_{\text{CO, out}}/c_{\text{CO, in}} = \beta e^{-x_f} + \frac{(1 - \beta e^{-x_f})^2}{k_o W q \rho_{\text{Fe}_2\text{O}_3} C_1 q \rho_{\text{Fe}_2\text{O}_3} + (1 - \beta e^{-x_f})} \quad \text{Equation 11}
$$

Where

$$
\beta = 1 - \frac{U_{mf}}{U}, \quad \text{Equation 12}
$$

$$
C_1 = \frac{W}{(\rho_{\text{Fe}_2\text{O}_3} H_{mf} A_r)}
$$

$W$ is the weight of $\text{Fe}_2\text{O}_3$ added into the bed in g; $k_o$ is the observed rate constant including mass transfer effects in s$^{-1}$; $q$ is the volumetric flow rate of total gas through the bed when fluidising in m$^3$ s$^{-1}$; $\rho_{\text{Fe}_2\text{O}_3}$ is the particle density in g m$^{-3}$; and $C_1$ is the volume of particles per unit volume of the particulate phase.

By assuming that iron oxide particles were evenly distributed in the particulate phase ($C_1$ is constant), and that $k_o$ is not significantly influenced by the addition of the $\text{Fe}_2\text{O}_3$ particles to the bed, $X_f$ was determined by performing a least square fit of $c_{\text{CO, out}}/c_{\text{CO, in}}$ versus $W$ (see Supporting Info., S1). The value of $X_f$ was found to be greater than 14.5, which is comparable with the theoretical calculation from Kunii and Levenspiel (1990), validating the assumption of rapid interchange between the particulate and bubble phases.
3.2 Validation

The outlet mole fractions of CO and CO$_2$ of a typical reduction cycle of Fe$_2$O$_3$ to Fe$_3$O$_4$ detected by the analyser, along with the corresponding temperature profile, are shown in Figure 3. The time-dependent gas switching program for the reduction cycle is also illustrated (on the top of Figure 3). The reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$ (Reaction 1) started once the reducing gas was switched on. Compared with the inert cycle, the CO mole fraction decreased as the mole fraction of CO$_2$ increased, indicating that Fe$_2$O$_3$ oxidised CO to form CO$_2$ during the reduction stage. It can be seen that the reaction finished approximately 50 seconds after the reducing gas was first fed as the mole fractions of CO and CO$_2$ returned to the input value.

Figure 3 Mole fraction of outlet CO$_2$ and CO with respect to time for a typical cycle of reduction of 0.5g Fe$_2$O$_3$ to Fe$_3$O$_4$ at 823K in the spouted bed. Superimposed on the line is the mole fraction of CO$_2$ and CO with time for a cycle with only inert bed of sand before Fe$_2$O$_3$ was injected. (The concentration is here plotted every 5 seconds, but was measured every second)

The mole fractions of CO and CO$_2$ were de-convoluted with respect to time. The resulting mole fractions of CO and CO$_2$ were taken as the instantaneous mole fractions of the gas components in the particulate phase of the reactor. Figure 4(a) shows the de-convoluted mole fractions of CO and CO$_2$ during the reaction stage of a typical cycle and those during the same stage of an inert cycle (i.e. before any active Fe$_2$O$_3$ particles were added). The rates of reaction at a specific time, $r'$, in mol s$^{-1}$ g$^{-1}$. 

![Figure 3](image-url)
were obtained by multiplying the instantaneous difference in mole fraction between the reaction and inert curves of CO or CO$_2$ in Figure 4(a) by the total molar flow rate and dividing by the total sample mass. Note that the total molar flow rate did not change during the reaction because the number of moles of gaseous product is equal to that of the reactant according to the stoichiometry of Error! Reference source not found.. The conversion, $X$, was defined as the ratio between accumulated molar flow rate of consumed CO or generated CO$_2$ until a specific time, to the theoretical maximum consumption or generation values derived from the moles of Fe$_2$O$_3$ added to the bed, and the reaction stoichiometry. The quantity of consumed CO or generated CO$_2$ was calculated by integrating the difference between the reaction and inert curves in Figure 4(a) with respect to time. Figure 4(b) demonstrates that the rate measured by the CO signal ($\circ$) agreed very well with that measured by the CO$_2$ signal ($\bullet$). It was obvious that, however, full conversion of Fe$_2$O$_3$ was not achieved. The rate of the reduction diminished at $X>0.86$. This may be because the diffusion resistance of the ionic species increased significantly at the later stage of the reaction, which will be discussed in a following publication (Zhang et al., in preparation (Unpublished)). For consistency, the CO$_2$ signal was used to determine the rate because it provided a less variable baseline (Figure 4(a), $c_{CO_2,In}$) compared to that of CO (Figure 4(a), $c_{CO,In}$). This means that the overall error for response time correction in the rate calculation is relatively small. The slight oscillation of the CO$_2$ rate could not be attributed to noise, but in fact is probably a real reflection of the slight temperature oscillation of the bed due to the PID control.
Figure 4 a) Mole fraction of CO and CO$_2$ in the particulate phase during a typical reduction reaction stage within a typical cycle of reduction 0.5 g Fe$_2$O$_3$ to Fe$_3$O$_4$ at 823 K (unfilled symbols), superimposed on that during the same stage of an inert cycle of the experiment (filled symbols). b) Variation of the rate of reaction with conversion of Fe$_2$O$_3$ estimated from [CO] and [CO$_2$] in Figure 4(a), respectively.

The maximum rate of reaction ($r' = 7.7 \times 10^{-5}$ mol s$^{-1}$ g$^{-1}$) in Figure 4 was assumed to correspond to the rate per initial unit mass (hereafter referred to as the maximum rate method). It may be worth noting that the maximum rate was reached at $X$ of about 0.2, even after de-convolution. This was potentially because the CO input was not an ideal step function and that the reaction surface area, which was also proportional to the
reaction rates, would inevitably increase to a maximum before decreasing during reaction according to the random pore model (Bhatia and Perlmutter, 1980). Another method of estimating the initial rate of the reduction reaction, hereafter referred to as the linear fit method, involved taking the intercept of a linear fit of $r'$ versus $X$ in the interval $0.1 < X < 0.7$ as the initial rate. A detailed description of this method is available elsewhere (Bohn et al., 2010).

It was assumed in the theory section that the reaction was first order with respect to [CO], i.e. $r' \propto c_{CO,P}$ (See Equation 4). Considering the fact that the differential term $\tau_{mix,CO} \frac{dc_{CO,m}}{dt}$ in Equation 6 is small, it is reasonable to assume that the effect of convolution is minimal, and therefore it is acceptable to replace $c_{CO,P}$ with $c_{CO,m}$, and assume $r' \propto c_{CO,\text{out}}$. A material balance on CO yields:

\[ r' = \frac{Q}{W} (c_{CO,m} - c_{CO,\text{in}}) \quad \text{Equation 13} \]

$Q$ is the total volumetric flow rate ($m^3 s^{-1}$) and $W$ is the total mass of Fe$_2$O$_3$ introduced into the bed (g). Then if the relationship $r' \propto c_{CO,m}$ holds, using Equation 13, it follows that $r' \propto c_{CO,\text{in}}$. It is convenient to use this linear relationship to test the first order assumption since the inlet concentration of CO could be used as a controlled variable in experiments. A more detailed model of the bed and reaction, which integrates the random pore model with a detailed numerical treatment of the fluidised bed, together with a detailed discussion of intra-particle and solid-state diffusion has also been produced (though that paper does not discuss the experimental setup in detail)(Zhang et al., in preparation(Unpublished)). The detailed numerical model validates the assumption that a simple fluidised bed model, assuming a well-mixed reactor is sufficiently good that a more complex model does not significantly affect the findings concerning the initial order of reaction before significant diffusion effects occur. The high cross-flow factor (supporting information S1), combined with the low consumption of gases across the bed (see Figure 4) also support a simple model.

The first order assumption was tested by varying the inlet CO mole fraction from 0 to 5 % at 823 K whilst keeping the inlet mole fraction of CO$_2$ constant at 15 %. Figure 5(a) demonstrates the initial rate estimated by the different methods against the inlet mole fraction of CO in the fourth cycle. It can be seen that for both methods used to
estimate the initial reaction rate, the linear relationship between $r'$ and [CO] is strong within the range of inlet mole fractions of CO investigated. The initial rates determined from both the maximum rate method and the linear fit method agreed with the initial rate measured in a fluidised bed reactor of smaller scale but in similar conditions (Bohn et al., 2010), especially at the lower inlet mole fractions of CO. Interestingly, initial rates determined from the linear fit method only started to deviate from first order kinetics at higher concentrations of CO (4–5 %). It was confirmed in Figure 5(b) that the first order dependence of $r'$ on [CO] remains unchanged over repeated cycles, and the initial rate obtained at each inlet mole fraction of CO remains relatively constant from the 3rd cycles onwards ($r'$ stabilised after the first two cycles). Thus, Figure 5(a) and (b) verified the first order assumption made in the theory section.
Figure 5(a) Dependence of initial rate of a typical reduction cycle estimated by two methods on the inlet mole fraction of CO at 823 K: when the initial rate is taken from the maximum rate in rate versus conversion graph (○); when the initial rate is calculated from the linear fit of the rate versus conversion graph using the linear fit method (□); and the initial rate as measured by Bohn et al. (2010) using the linear fit method (△). The straight line is a linear least-squares fit with zero intercept to the initial rate data estimated by the maximum rate method ($R^2 = 0.998$). (b) Dependence of the initial rate, $r'$, on the inlet mole fraction of CO at 823 K. The straight line is a least-squares fit to the average rates of three cycles at each measured mole fraction of CO. The inlet mole fraction of CO$_2$ was fixed at 15 % and the balance was N$_2$. 

(r'(10$^{-6}$ mol/(g*s)) vs. Inlet mole fraction CO (vol. %))
3.3 Different behaviour between cycles

As mentioned previously, all the rates and rate constants shown hereafter were derived from deconvoluted measurements. Significantly different behaviour was observed during the first cycle of reduction compared to other cycles (Figure 6). The reaction for the first cycle took about twice the time to complete compared to other cycles. The rates in the first cycle did not demonstrate such a pronounced maximum value with time in comparison to the other cycles, but rather reached a plateau; this plateau was of a lower rate than the maximum exhibited during other cycles.

Figure 6 Change of the rate of the reduction reaction over time for different reduction cycles at 823 K, 3 vol. % CO, 15 vol. % CO₂, balance N₂.

The observed rate constants, \( k \), versus conversion plot enables insight into the difference in behaviour between cycles (Figure 7). Here \( k \), which is independent of CO concentration, was obtained by dividing \( r' \) by the concentration driving force of CO and multiplying by the envelope density of Fe₂O₃ (Equation 4). The rate constants for all cycles other than the first reached a maximum at very low conversion (\( X \leq 0.03 \)), and remained relatively stable (regime 1) until a certain conversion was attained before decreasing again (regime 2). The distinctive behaviour of the first cycle may be due to denser particles; i.e., the porous structure was not fully developed, leading to a diffusion-limited reaction. The development of porosity may be attributed to varying of the porous structures during the redox cycles via four major mechanisms: (1) mechanical stress (Park and Levenspiel, 1975), (2) change of molar volume, (3)
thermal sintering (Lange and Kellett*, 1989) and (4) solid phase ionic diffusion (Sun et al., 2012). As is shown in the particle characterisation (Supporting info S2, Table S1), the porosity of the particle increased upon cycling, which is likely the reason for the improved initial rate constant observed after the first cycle. Similar rate constants were observed from cycle three to five, suggesting that the porosity and distribution of pores stabilises after two cycles. This also highlights the importance of investigating kinetics of the reduction over repeated cycles.

Figure 7 Observed rate constants versus conversion for different reduction cycles at 823 K, 3 vol. % CO, 15 vol. % CO₂, balance N₂.

### 3.4 Effective diffusivity, porosity and tortuosity

To verify the change of pore structure after first cycle of reaction, the porosity and pore size distribution of the Fe₂O₃ particles before and after the cycling experiments were measured using mercury porosimetry (Micromeritics Autopore IV) (Supporting Info., Figure S2). This is a key advantage of the method used (as opposed to TGA analysis) – sufficient material can be produced to allow subsequent pore-size distribution analysis. It was found that for porosity determined by pores with diameters less than 10 μm (most likely to be the ‘true’ porosity of the particles) the reacted particle displayed an increase of porosity of around 40% (Supporting Info., S2). The differences in porosity would result in significant discrepancy between the effective diffusivities of the reacted and fresh particles. Table 2 lists the typical values of the mass transfer coefficient and diffusivities estimated under the specific
conditions (marked in bold) for calculating the intrinsic rate constant. Porosity after 5 cycles of reduction and oxidation was used to estimate these coefficients for the second cycle onwards since the porosity is believed to increase after the first cycle, as discussed earlier. Two porosities, $\varepsilon_{\text{Fe}_2\text{O}_3} = 0.31$ and $\varepsilon_{\text{Fe}_2\text{O}_3} = 0.57$ were tested for the first and subsequent cycles, respectively, which represented different cut-off of pore sizes of 10 and 180 $\mu$m. The estimates of bulk and Knudsen diffusivities for the larger porosity were relatively comparable with those given by Bohn et al. (2010), where the resistance of Knudsen diffusion was determined to be relatively low compared to the bulk diffusion; the overall diffusion was controlled by bulk diffusion in this case. The Knudsen diffusivities calculated for the smaller porosity, which is considered to be the porosity for the particles at the conservative end, were only around one third of those calculated for the larger pores because the mean pore diameter, $r_e$, reduced significantly. Such considerations increase the importance of the Knudsen diffusion process, and overall diffusion is likely to be in the transition region between Knudsen diffusion and bulk diffusion.

Table 2 Parameters used for determining the intrinsic rate constant, $k_1$, for reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$.

| $P$ (atm) | $W$ (g) | $d_{\text{sand}}$ (m) | $\varepsilon_{\text{mf}}$ | $S_g$ ($m^2 g^{-1}$) |
|-----------|---------|------------------------|--------------------------|---------------------|
| 1         | 0.5     | 5.96E-04               | 0.42                     | 0.8                 |

$\varepsilon_{\text{Fe}_2\text{O}_3} = 0.31, \tau = 0.5$

| $T$ (K) | $U_{\text{mf}}$ (m s$^{-1}$) | $D_{\text{b,CO}}$ (10$^{-5}$ m$^2$ s$^{-1}$) | $D_{\text{k,CO}}$ (10$^{-5}$ m$^2$ s$^{-1}$) | $D_{\text{a,CO}}$ (10$^{-5}$ m$^2$ s$^{-1}$) | $k_{\text{g,CO}}$ (m s$^{-1}$) |
|---------|-----------------------------|---------------------------------|---------------------------------|---------------------------------|------------------|
| 723     | 0.16                        | 9.29                            | 10.42                           | 3.05                            | 0.51              |
| 773     | 0.153                       | 10.40                           | 10.78                           | 3.28                            | 0.55              |
| 823     | 0.147                       | 11.55                           | 11.12                           | 3.52                            | 0.59              |
| 873     | 0.142                       | 12.75                           | 11.45                           | 3.74                            | 0.62              |
| 923     | 0.137                       | 13.99                           | 11.78                           | 3.97                            | 0.66              |
| 973     | 0.133                       | 15.28                           | 12.09                           | 4.19                            | 0.70              |

$\varepsilon_{\text{Fe}_2\text{O}_3} = 0.57, \tau = 4$

| $T$ (K) | $U_{\text{mf}}$ (m s$^{-1}$) | $D_{\text{b,CO}}$ (10$^{-5}$ m$^2$ s$^{-1}$) | $D_{\text{k,CO}}$ (10$^{-5}$ m$^2$ s$^{-1}$) | $D_{\text{a,CO}}$ (10$^{-5}$ m$^2$ s$^{-1}$) | $k_{\text{g,CO}}$ (m s$^{-1}$) |
|---------|-----------------------------|---------------------------------|---------------------------------|---------------------------------|------------------|
| 723     | 0.16                        | 9.29                            | 30.90                           | 1.02                            | 0.51              |
| 773     | 0.153                       | 10.40                           | 31.95                           | 1.12                            | 0.55              |
| 823     | 0.147                       | 11.55                           | 32.96                           | 1.22                            | 0.59              |
| 873     | 0.142                       | 12.75                           | 33.95                           | 1.32                            | 0.62              |
The effect of particle size on the initial observed rate constant, \(k_o\), was investigated at 823 K, with 3% CO and 15% CO\(_2\) (Figure 8, Figure 9). Figure 8 plots the initial observed rate constant, \(k_o\), against the average particle radius \(R\) of 180–300 μm. Here the envelope density of Fe\(_2\)O\(_3\) used was 2 180 kg m\(^{-3}\) since the particle porosity was assumed to be 0.57. As expected, \(k_o\) decreases with increasing \(R\) because the diffusional resistance increased with larger particle sizes. The value of \(k_o\) is slightly lower than that reported by Bohn et al. (2010) especially at higher particle radii. \(k_i\) was recovered for different particle radii for cycle 5, also see Figure 8. As discussed previously, the value of \(k_o\) for each radius was corrected to a constant \(k_i\), which is close to the average \(k_i = 557\) s\(^{-1}\) that was calculated for 823 K. The effectiveness factors, \(\eta_{co}\), were 0.92, 0.87 and 0.80 for average particle radii of 178 μm, 230 μm and 298 μm respectively. Despite an initially lower \(k_o\) measured in this study, the values of \(k_i\) were 14% higher than those reported in the literature. The difference in \(k_i\), although relatively small, was mainly due to the fact that Bohn et al. used the porosity and surface area of fresh particles while in this study the porosity and surface area after five cycles of redox reaction was used, as this is the point at which both of these properties are believed to have stabilised (the initial observed rate constant becomes stable after about two cycles).
Figure 8 Initially observed rate constants, $k_o$, and intrinsic rate constants, $k_i$, for average radii of particles. $k_i$ was calculated assuming a particle porosity of 0.57. The reference (filled black circle) was from Bohn et al. (2010), who reported a particle porosity of 0.6 and density of 2 060 kg/m³. The black dashed line represents the average intrinsic rate constant at 823 K. The dotted line is the average intrinsic rate constant at 823 K reported by Bohn et al. (2010).

In Figure 9, $k_o$ and $k_i$ for varying particle radii was calculated assuming a different porosity of Fe₂O₃, i.e., $\varepsilon_{Fe₂O₃} = 0.31$. Here, $k_o$ was higher than in the previous case ($\varepsilon_{Fe₂O₃} = 0.57$) because the envelope density in Equation 4 increased when a smaller $\varepsilon_{Fe₂O₃}$ was used. The same method was used for determining $k_i$ and $\tau$ as previously. $\tau = 0.5$ was chosen in this case. The value of fitted $\tau$ here is below its theoretical minimum ($\tau = 1$), which has lost its physical meaning and illustrates the error of using a mean pore diameter for calculating $D_K$ in Equation 10, resulted in a $\tau < 1$, in order to bring the experiment and theory together. Particles of all radii generated the same $k_i$ value, equal to the average value of 900 s⁻¹ at 823 K. The effectiveness factor, $\eta_{co}$, was 0.95, 0.92 and 0.88 for particle radii of 178 µm, 230 µm and 298 µm respectively, which are only slightly higher the previous case when a larger porosity was assumed. This suggested the errors in porosity measurement were most likely
compensated for by $\tau$ in the calculation of effectiveness factor. The overall high effectiveness factors within the size range of interest (average radius of 178 $\mu$m) suggest that the diffusion effects are insignificant compared to the effect of chemical reaction. Since it was experimentally observed that any particles with radii less than 100 $\mu$m were easily elutriated during cycles (judging from the weight of Fe$_2$O$_3$ recovered after an experiment), the intrinsic kinetics in the following sections used particles with an average $R$ of 178 $\mu$m (particle sizes: 300–425 $\mu$m).

Figure 9 Initially observed rate constants, $k_0$, and intrinsic rate constants, $k_i$, with average radii of particles. $k_i$ was calculated assuming a particle porosity of 0.31. The black dashed line represents the average intrinsic rate constant at 823 K.

### 3.5 Pseudo-intrinsic kinetics

The analysis in section 3.4 showed in analysis based on two extreme porosities (0.31 and 0.57) that the uncertainty in porosity measurement may be compensated for by $\tau$ in the calculation of effectiveness factor. If it was true, the recovered intrinsic kinetics subjected to the uncertainty may still represent the ‘true’ kinetics of chemical reaction. The assumption was numerically validated by evaluating the effect of intermediate value of porosity on the final results of intrinsic kinetics using a looped non-linear optimisation routine written based on Matlab® fmincon function (Supporting Info., Figure S3).
The results of the sensitivity analysis are shown in Figure 10 and Figure 11. It can be seen that \( \tau \) increased exponentially to compensate the increase of assumed porosities (Figure 10) in order to recover the same intrinsic rate constants for all particle sizes. As a result, \( \eta \) for different particle sizes only decreased slightly and linearly as the assumed porosity increased. This proved that \( \eta \) was bounded by the boundary values calculated at porosities of 0.31 and 0.57. On the other hand, \( k_i \) (in s\(^{-1}\)) did change significantly as different porosities were assumed (Figure 11). This uncertainty, however, was introduced because the rate constants were per volume of the particles (the volume of the particles depended on the envelop density that requires accurate knowledge of the porosity). Hence when \( k_i \) was normalised by \((1 - \varepsilon)\), \( k_i \) calculated using the model based on absolute volume of the particles did not show dependency on the change of assumed porosity, suggesting the model was not sensitive to the uncertainty in porosity measurement, and the intrinsic rate constants estimated at any assumed porosity remains the same. Overall, it was shown pseudo-intrinsic parameters such as intrinsic rate constants and effectiveness factor can be derived on the basis that the uncertainty in porosity measurement only presented marginal effect on the model prediction.

![Figure 10](image)

Figure 10 Numerical results of \( \tau \) and \( \eta \) at different particle sizes when assuming different porosities between 0.31 and 0.57 at 823K.
Figure 11 Numerical results of $k_i$ and $k_i/(1-\varepsilon)$ when assuming different porosities between 0.31 and 0.57 at 823K.

Based on the analysis, the effectiveness factor, $\eta_{co}$, for each cycle was calculated based on a particle porosity of 0.31, and it was found to be reduced but remain high with increasing temperature (Figure 12), suggesting a fast intra-particle diffusion across the range of temperature. Understandably $\eta_{co}$ approached unity at lower temperatures, e.g., $\eta_{co} = 0.97$, $\phi = 0.65$ at $T = 773$ K for cycle five. $\eta_{co}$ decreased to 0.87 when $\phi$ was increased to 1.50 for cycle five at the maximum temperature of 973 K.
Figure 12 Plot of $\eta_{\text{co}}$ for each cycle as a function of $10^3/(RT)$ for every 50 K from 723 K to 923 K.

![Arrhenius plot](image)

Figure 13 The activation energy for the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$ shown by the slope of the Arrhenius plot. The activation energy, $E$, was determined based on $k_i$ recovered from $k_0$ for cycles two to five, for the particle size range of 300–425 μm at the temperature range of 773–973 K. The solid line is a least-squares fit of the data.

The temperature dependence of each of these terms in Equation 3 may be expressed in simple Arrhenius form, i.e., $k_i = A e^{-E/RT}$, where $E$ (kJ mol$^{-1}$) is activation energy and $A$ (s$^{-1}$) is pre-exponential factor for the reduction reaction. The value of $k_i$ was recovered from the $k_0$ measured at each temperature by applying the effectiveness factors in Figure 12. From the slope of Figure 13, the activation energy ($E$) for $k_i$ can be estimated for each cycle. A 95% confidence interval for $E$ was derived using the Student $t$ statistic with ($n$–2) degrees of freedom, where $n$ is the number of experimental data points. The activation energy for the reduction reaction is tabulated Table 3, and it is relatively constant for cycles three to five, with an average value of 61 ± 8 kJ mol$^{-1}$. The values of $E$ overlapped with those measured by Bohn et al. (2010), who reported an average activation energy of 75 ± 11 kJ mol$^{-1}$ for cycles two to nine. Trushenski et al. (1974) reported activation energies of 100 kJ mol$^{-1}$ and 69 kJ mol$^{-1}$ for the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$ when they performed the single step
reduction and multi-step reduction to FeO in a thermo-gravimetric furnace at 1023–1073 K, respectively. However, significant mass transfer effects may have inherently existed in their furnace. The average value for the natural logarithm of the pre-exponential factor of cycles three to five is 15.7 ± 0.3 (the logarithm was taken to be normally distributed), which is equal to a pre-exponential factor of 6.52 × 10^6. Again, the pre-exponential factor was found to be around one third that measured by Bohn et al. (2010), who gave a pre-exponential factor of 2.4 × 10^7. The discrepancy is mainly due to the difference in the envelope density used when assuming different porosities. The Arrhenius form for average initial intrinsic rate constant \( k_i \) is expressed as

\[
k_i = 6.52 \times 10^6 \exp\left(\frac{-61 \text{kJ mol}^{-1}}{RT}\right) \text{s}^{-1}
\]

Equation 14

Table 3: Activation energies (\( E \)) and pre-exponential factors (\( A \)) determined based on calculated \( k_i \) values, and their respective lower and upper bounds at a confidence interval (or prediction range) of 95%, estimated based on the samples collected.

| Cycle No. | \( E \) (723–973 K) (kJ mol\(^{-1}\)) | \( \ln A \) (723–973 K) (s\(^{-1}\)) |
|-----------|-----------------------------------|-----------------------------------|
| Cycle 2   | 52 ± 10                           | 14.4 ± 0.4                        |
| Cycle 3   | 65 ± 8                            | 16.1 ± 0.3                        |
| Cycle 4   | 59 ± 7                            | 15.4 ± 0.3                        |
| Cycle 5   | 60 ± 8                            | 15.5 ± 0.3                        |

4 Conclusions

The study demonstrated the design and development of a spouted bed reactor for the study of gas-solid kinetics at high temperature and (potentially) pressurised conditions. The design demonstrates direct injection of solids of interest into the reactor, which is of particular utility during future pressurised operation. The solid reactant was introduced as a sharp pulse by pressurised injection of the particles to the bottom of the bed, which facilitated kinetic analysis of gas-solid reactions. It was demonstrated both experimentally and theoretically that the bed can be characterised as a fluidised bed with very fast rate of gas interchange between bubble and particulate phase providing that a small mass of the solid reactant is used.
The spouted bed was employed to study the intrinsic kinetics of the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$ in a CO$_2$/CO mixture over multiple cycles. The measured initial rates and the order of the reaction from the second cycle onwards were similar to those reported in literature where a small fluidised bed was used. The observed kinetics of the reduction improved over the first few cycles, which was revealed for the first time to be due to the development of a porous structure within the particles during cycling. This highlights the importance of studying the reduction kinetics over multiple cycles for chemical looping application, and the importance of particle morphology.

The initial intrinsic rate constant, $k_i$, was recovered by using a kinetics model incorporating an effectiveness factor. By using a similar standard for porosity as the literature, comparable values of $k_i$ can be recovered with relatively small discrepancy (less than 15 %) with those from the literature. It was also demonstrated that the model was not sensitive to the uncertainty in porosity measurement owing to the mathematical combination with the (fitted) tortuosity factor. The activation energy and pre-exponential factor were calculated for values of $k_i$ in the temperature range of 723–973 K. High effectiveness factors were obtained for the particle across the temperature range. The calculated value of the activation energy overlapped with the literature values. The Arrhenius form for average initial intrinsic rate constant $k_i$ is expressed as $k_i = 6.52 \times 10^6 \exp \left( \frac{-61 \text{kJ mol}^{-1}}{RT} \right)$.

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Supporting Information

S1 Experimental verification of cross flow factor

The measured ratio $c_{\text{CO, out}}/c_{\text{CO, in}}$ is plotted against increasing masses of Fe$_2$O$_3$ added to the bed at 823 K in Figure S1. The apparent deviation from the fit at masses higher than 1.5 g is probably a result of deviation from the assumptions made above, implying the leaking of the iron oxide into the gas phase or the changing of $k$ due to external mass transfer limitations.
Figure S1 The ratios of outlet to inlet concentration for different cycles, $C_{out}/C_{in}$, plotted against the weights of Fe$_2$O$_3$ added into the bed, $W$, at 823 K with 3 vol. % CO, 15 vol. % CO$_2$, with N$_2$ balance. The solid line is a least-squares fit of the data in cycle 4.

S2 Particle characterization

X-ray diffraction (XRD) for reduced Fe$_2$O$_3$

XRD analysis of reduced Fe$_2$O$_3$ particles retrieved after 5$^{th}$ reduction cycle of a typical cycling experiment was carried out using a XRD diffractometer (X’Pert Pro PANalytical, CuK$\alpha$, 40kV and 40mA, Figure S2). The Fe$_3$O$_4$ sample was protected from aerial oxidation using N$_2$ during cooling down, and was immediately recovered and sealed afterwards. The samples used for the analysis were ground into a fine powder. It is shown that the XRD pattern of the reduced sample confirmed the presence of Fe$_3$O$_4$, with no Fe$_2$O$_3$ or other further-reduced forms of Fe$_2$O$_3$ were detected.
Figure S2 XRD patterns for reduced iron oxide samples retrieved after the 5th reduction cycle in 3% CO, 15% CO$_2$ at 823K. The standard reference pattern for Fe$_2$O$_3$ (JCPDS, 2005a) and Fe$_3$O$_4$ (JCPDS, 2005b) are also plotted for comparison.

**Density and pore size distribution**

A contact angle of 130º and surface tension of 0.485 N m$^{-1}$ was assumed for the mercury (Giesche, 2006). The pore size distribution of the fresh Fe$_2$O$_3$ particle was bimodal, with one narrow peak at 0.15 μm and another much wider peak at 90 μm. Upon cycling it was observed that some of the fine pores of the fresh particles had been lost. The narrow peak originally at 0.15 μm was smoothed and transformed into a much wider distribution of pores spanning an order of magnitude (from 0.1–1 μm). It is also interesting to note the growth of a porous network between 1 μm and 10 μm, which may have linked the fine pores with the particle surface. These results provide evidence of a porous network that upon cycling provided routes for larger CO fluxes to flow through. Brown (2010) also observed the same effect of a shift of the pore size distribution to larger pores for reduced Fe$_2$O$_3$ over 11 reduction cycles, suggesting that the overall effect of reduction and oxidation favours the development of such a pore network.
Figure S3 Pore size distribution of $\text{Fe}_2\text{O}_3$ before and after 5 cycles of reduction and oxidation at 823 K. Reduction gas: 3 vol. % CO, 15 vol. % $\text{CO}_2$, balance $\text{N}_2$.

The porosity of the $\text{Fe}_2\text{O}_3$ particles before and after cycling is shown in Table S1. Care should be taken, however, when interpreting the results provided. Considering the particle size of the sample was 300–425 $\mu$m, a fraction or all of the macro pores that are larger than 10 $\mu$m in Figure S2 may actually be the inter-particle voids. Porosity was estimated here by pores with a mean pore diameter between 10 nm and 180 $\mu$m and between 10 nm and 10 $\mu$m. Here, two extreme cut-offs for the porosity were used rather than an arbitrary one in the middle. The former range resulted in the maximum porosity possible for the particles (inter-particle voids were included), comparable to the value of the porosity with similar work (Bohn et al., 2010), which used the same range. The latter range is believed to be the envelope porosity (ASTM Standard D3766, 2013) of the particles at the conservative side, judging from Figure S2. For porosity determined by pores with diameters less than 10 $\mu$m the reacted particle displayed an increase of porosity of around 40 %. The absolute density measured by a pycnometer (Micrometritics, AccuPyc 1330) was 5 079 kg $\text{m}^3$. The envelope density before and after reaction were calculated by multiplying the absolute density by $(1 - \varepsilon_{\text{Fe}_2\text{O}_3})$, where $\varepsilon_{\text{Fe}_2\text{O}_3}$ is the porosity calculated in the 10 nm to 10 $\mu$m range. It was observed that the envelope density decreased after reaction. The BET surface areas of the particles that were measured are also listed in Table S1 (Micrometritics, Tristar 3000).
Table S1 Summary of the results of porosity, envelope density and surface area for the Fe$_2$O$_3$ particles before and after 5 cycles of reduction of oxidation at 823 K with 3 vol. % CO, 15 vol. % CO$_2$, balance N$_2$.

| Sample                                      | Porosity $\varepsilon_{\text{Fe}_2\text{O}_3}$ | Envelope density $\rho_{\text{Fe}_2\text{O}_3}$ (kg m$^{-3}$) | Surface area $S_g$ (m$^2$ g$^{-1}$) |
|---------------------------------------------|-----------------------------------------------|---------------------------------------------------------------|-------------------------------------|
| Fresh Fe$_2$O$_3$ particle (300-425 μm)     | 0.52                                          | 0.22                                                          | 3 962                               |
| Fe$_2$O$_3$ particle after 5 reduction and oxidation cycles (300-425 μm) | 0.57                                          | 0.31                                                          | 3 510                               |

S3 Sensitivity of the effectiveness factor model to assumed porosities

Here, following the methodology described in section Error! Reference source not found., a looped non-linear optimisation routine were developed based on Matlab® fmincon function using Interior-Point Algorithm for estimating $\tau$ at each intermediate value of porosity between 0.31 and 0.57 with a step size of 0.01(Figure S3). It is worth noted that $\tau$ was converted to a logarithmic scale when converging the $k_i$ calculated from different particle radii in order to obtained a global minimum.
Figure S4  Looped non-linear optimization routine for sensitivity analysis.

**Notations**

**Roman Letters**

- \( A \) Pre-exponential factor for the Arrhenius equation \( (s^{-1}) \)
- \( A_r \) Cross-sectional area of reaction vessel \( (m^2) \)
- \( c_{CO} \) Concentration of reactant CO contained within particle pores \( (mol \ m^{-3}) \)
- \( c_{CO,R} \) Concentration of reactant CO at the particle surface \( (mol \ m^{-3}) \)
- \( c_{CO,P} \) Concentration of reactant CO in particulate phase \( (mol \ m^{-3}) \)
- \( c_{CO,in} \) Concentration of reactant CO at reactor inlet \( (mol \ m^{-3}) \)
- \( c_{CO,m} \) Measured concentration of reactant CO at analyser \( (mol \ m^{-3}) \)
\(c_{\text{CO,out}}\) Concentration of reactant CO at reactor outlet (mol m\(^{-3}\))

\(c_{\text{CO,s}}\) Concentration of CO at the surface of the particle (mol m\(^{-3}\))

\(d_p\) Particle diameter (m)

\(D_b\) Bulk diffusivity (m\(^2\) s\(^{-1}\))

\(D_e, D_{e,co}\) Effective diffusivity within porous particle (m\(^2\) s\(^{-1}\))

\(D_K\) Knudsen diffusivity within porous particle (m\(^2\) s\(^{-1}\))

\(E\) Activation energy (J mol\(^{-1}\))

\(E_D\) Temperature coefficient of effective diffusivity (J mol\(^{-1}\))

\(E_{\text{obs}}\) Apparent activation energy (J mol\(^{-1}\))

\(H\) Height of the bed (m)

\(k_o\) Observed rate constant, including mass transfer effects (s\(^{-1}\))

\(k_{g}, k_{g,CO}\) External mass transfer coefficient for a particle (m s\(^{-1}\))

\(k_i\) Forward intrinsic rate constant, chemical rate-controlled, given by:

\[k_{i,i} = k_i K_p\] (s\(^{-1}\))

\(k'\) Reaction rate constants (m\(^3\) g s\(^{-1}\))

\[k' = r'/c_{\text{CO,s}}\]

\(L_0\) Initial total length of the cylindrical pores (m\(^2\))

\(Q\) Cross flow rate between bubble and particulate phase (m\(^3\) s\(^{-1}\))

\(q\) Total volumetric flow rate of gas through the bed when fluidising (m\(^3\) s\(^{-1}\))

\(r\) Radial position within particle (m)
Rate of reaction per unit mass of particle as Fe$_2$O$_3$ (mol s$^{-1}$ g$^{-1}$)

Particle radius (m)

Ideal gas constant (J mol$^{-1}$ K$^{-1}$)

Reaction rate of CO or CO$_2$ (mol s$^{-1}$)

Reynolds number of gas flow in a tube, given by:

$$Re_b = \frac{\rho Q D_h}{\mu A}$$

Reynolds number of the particle in particular phase suggested by two-phase theory, -

$$Re_p = \rho g d_{sand} U_{mf}/(\mu e_{mf})$$

Reynolds number at the minimum fluidisation condition -

Schmidt number Sc = $\mu/\rho g D_b$ -

Sherwood number, Sh = $k_g d/D_b$ -

t-statistic with (n–2) degrees -

Absolute temperature (K)

Superficial velocity of fluidising gas (m s$^{-1}$)

Superficial gas velocity in the annular phase (m s$^{-1}$)

Value of $U$ at incipient fluidisation (m s$^{-1}$)

Value of $U$ at minimum spouting conditions (m s$^{-1}$)

Total mass of particles of Fe$_2$O$_3$ added to reactor (kg)

Molar flux of reactant CO at the particle surface when accounting for the intra-particle diffusional resistance. (mol s$^{-1}$)
Molar flux of reactant CO when all active surfaces of the reacting particle are exposed to reactant CO: $W_{CO,0}$ (mol s$^{-1}$)

Fractional conversion of particle: $X$

Cross-flow factor: $X_f$

Greek Letters

Porosity of the Fe$_2$O$_3$ particles: $\varepsilon_{Fe_2O_3}$

Voidage of the bed at minimum fluidisation velocity: $\varepsilon_{mf}$

Force constant in in Lennard-Jones potential: $\varepsilon_{AB}/\kappa$ (K)

Effectiveness factor for spherical particles, $\eta = \frac{3}{\phi^2} (\phi \coth \phi - 1)$

Angle of the conical frustum of the quartz liner: $\theta_c$ (degrees)

Dynamic viscosity of gas mixture: $\mu$ (Pa·s)

Envelope density of Fe$_2$O$_3$: $\rho_{Fe_2O_3}$ (kg m$^{-3}$)

Gas density: $\rho_g$ (kg m$^{-3}$)

Molar density of gas: $\rho_m$ (mol m$^{-3}$)

Force constant in Lennard-Jones potential: $\sigma$ (Ångstrom)

Tortuosity: $\tau$

Response time (space time) of CO or CO$_2$ for the free board and downstream before sampling point: $\tau_{mix}$ (s)

Thiele modulus for irreversible reactions, given by:

$$\phi = \frac{k_i}{\sqrt{D_{e,CO}}R}$$
Reference:

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