

Analysis of hematite re-oxidation in the chemical looping process



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HIGHLIGHTS

- Re-oxidation of Fe₂O₃ CLC carrier is examined to assess O₂ and temperature.
- A two process step model has been developed – grain surface and grain core.
- Grain surface oxidizes which transports oxygen to the core by vacancy diffusion.
- The surface model is 1st order with a tendency toward nucleation with 1-D growth.
- The model for the core corresponds to nucleation with 2-dimensional growth.

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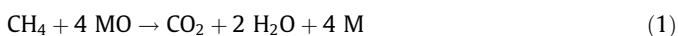
ABSTRACT

Very little attention has been dedicated to the carrier re-oxidation in chemical looping systems. The work presented in this paper is for the re-oxidation of partially reduced hematite from a cyclic chemical looping fixed bed process. The underlying purpose of this work is to develop engineering rates and mechanisms for the re-oxidation of partially reduced hematite that can be included in CFD models for a chemical looping process. To this end, experiments were run using nominally 1000 g of hematite material in a fixed bed reactor cycling between reduction and re-oxidation. The cyclic processing began with the reduction step then proceeded to the oxidation step repeating this analysis for several cycles ranging from 5 to 10. The re-oxidation process was conducted at temperatures ranging from 745 °C to 825 °C and oxygen concentrations ranging between 9% and 11%. The reduction was carried out at the same temperature as the re-oxidation step at various CH₄ concentrations from 5% to 9%. In this paper, cyclic induced variations in performance are presented as well as the kinetic parameters for the first cycle. The re-oxidation of the depleted hematite occurs through a 2 step parallel process in which oxygen reacts to fill the surface of each grain within the particles and then migrates through oxygen vacancy diffusion to the depleted cores of each grain.

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1. Introduction

In the wake of the global warming debate, several technologies to reduce CO₂ emissions are in various levels of development [1]. Chemical Looping Combustion (CLC) is a promising in-situ CO₂ capture technology that is being developed. In the CLC process, a fuel source (say CH₄) is fed to an oxygen carrier reduction reactor, in which the carrier (hematite for example) undergoes the chemical reaction seen below:



where “MO” stands for the carrier in its oxide form and “M” represents the oxygen depleted carrier. The depleted carrier then flows to a second reactor where it is re-oxidized according to the chemical reaction:



This concept is pictured in Fig. 1 for a fluidized bed configuration. It shows a two reactor loop system where the carrier is transferred between the reducer (fuel reactor) and the oxidizer (air reactor). In this configuration, the oxygen depleted (vitiating) air at the top of the oxidizer riser reactor is separated from the oxidized carrier via a cyclone. The carrier is then fed into the reducer through a loop seal to ensure separation of the fuel and the gaseous oxygen in the air where it is reduced according to Eq. (1). The oxygen depleted (reduced) carrier is fed to the air reactor through another loop seal to re-oxidize it.

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Nomenclature

A	is the Arrhenius pre-exponential (g/s)	w_s	is the weight factor for the surface mechanism (-)
E	is the activation energy (kJ/mole)	X_{O_2}	is the mass fraction of oxygen (-)
k	is the rate constant (g/s)		
n_c	is the shape parameter for the core mechanism (-)	Greek Symbols	
n_s	is the shape parameter for the surface mechanism (-)	α_s	is the nucleation rate constant for the surface (-)
R	is the gas constant (kJ/mole T)	α_c	is the nucleation rate constant for the core mechanism (-)
S_A	is the Langmuir area (m ² /g)	β	is the reaction order (-)
t	is the time (s)	γ	is the exponent of the power for the term accounting for the reduction time (-)
t_R	is the time of reduction process (s)		
T	is the Temperature of oxidation in (°K or °C)		
w_c	is the weight factor the core mechanism (-)		

Chemical looping combustion is a relatively new technology that has significant potential to be the lowest cost commercial technology for simultaneous energy production and CO₂ separation [2–4]. Alstom reports [2,3] that chemical looping combustion and gasification are the two lowest cost technologies in a CO₂ constrained world. The work at NETL [4] reports that chemical looping combustion of natural gas has a lower cost than conventional natural gas combustion with CO₂ control but that carrier durability is a potential issue. Over the past 20–25 years there has been a plethora of research that has been conducted on this technology looking at the reduction of many such potential oxygen carriers and summarized by Fan [5]. One particular carrier that has shown considerable commercial interest is hematite (Fe₂O₃) due primarily to its wide availability and cost. Numerous researchers have looked at using Fe₂O₃ in a chemical looping system fueled by methane [6–25] as shown in Table 1. Looking at Table 1, it can be seen that most researchers neglect investigating the re-oxidation of the reduced Fe₂O₃. Only Abad et al. [6,7], Adanez et al. [8], Cho et al. [10] and Go et al. [12] comment on the re-oxidation and then barely discussing it. Abad et al. [6,7] presents a rate model and kinetic parameters but omits any detailed discussion about the process. Adanez et al. [8] states that the re-oxidation is first order but provides no kinetic data for the process. Cho et al. [10] notes that the rate of re-oxidation is limited by the O₂ feed rate. Finally, Go et al. [12] states that the re-oxidation is diffusion controlled.

In addition to the above work, Monazam et al. [26] report on the re-oxidation of Fe₂O₃ starting from Fe₃O₄ when reduction was carried out with carbon monoxide. They report that the re-oxidation is a multistep process in which the rate for one of the processes is a

nucleation process with one dimensional growth and the other is diffusion controlled. In summary, the researchers that even discuss the re-oxidation process find vastly different results. Abad et al. [6,7] and Adanez et al. [8] report that the process is single first order step, Go et al. [12] reports that the process is diffusion controlled and Monazam et al. [26] reports that the re-oxidation is a multistep process controlled by nucleation with one dimensional growth and diffusion controlled.

Given the vast research effort into the development of chemical looping there still remains a paucity of investigations on the re-oxidation of these carriers with mixed and conflicting mechanisms for that limited body of work [6–8,12,26]. It is supposed that this topic has been neglected since the re-oxidation in many carriers is faster than the reduction, especially in synthetic carriers [7]. This is not necessarily the case when using iron based ores as the carriers.

These ores have a number of advantages over the synthetic carriers that make them the likely commercial choice as they are generally low in cost, non-toxic and have the potential of increasing the spent carrier value over that of the initial ore. The rapid commercialization and deployment of chemical looping technology using ores necessitates the need for engineering models for the reduction and re-oxidation steps that can be used in CFD simulations being done at the Department of Energy. These models for the reduction step were developed and can be found in the work by Breault and Monazam [27]. Therefore, in light of these findings, the objective of this work was to conduct a detailed analysis of the carrier re-oxidation process to develop an engineering kinetic model for the re-oxidation of reduced hematite. Furthermore, in the work by Breault and Monazam [27] they show that heat liberated in the particle during the first reduction cycle significantly changes the particle morphology in the fixed bed work and not in fluidized beds due to the higher heat transfer rates. Therefore, the kinetic analysis is done only on the first cycle from each test series.

2. Experimental facility and test procedure

Experiments were conducted in NETL's Modular Integrated Reactor (MIR) unit in which approximately 1.0 kg of hematite was added (see Fig. 2). The MIR test unit can be operated in the packed or fluidized modes. In this investigation it was operated as a packed bed. The Hematite is reacted, first with methane (CH₄) for the reduction half-cycle and then with air for the oxidation half cycle. Argon was supplied to the unit between half cycles to keep the methane from contacting the oxygen in the air. The unit has a diameter of 6.0 cm and a height of 62.3 cm. Gas concentrations leaving the reactor were measured with a mass spectrophotometer.

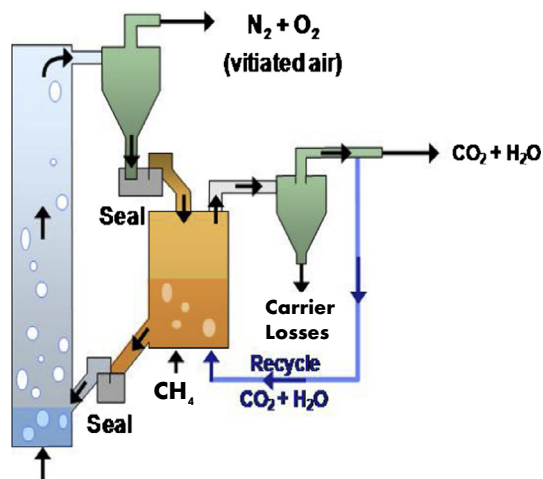


Fig. 1. Chemical looping concept configuration.

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