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Fixed bed reduction of hematite under alternating reduction and oxidation cycles

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HIGHLIGHTS

- Data cannot be fit to a single process but occurs with 2; grain surface and core.
- One process consumes all available the oxygen close to the grain surface.
- The other process is controlled by the diffusion of oxygen to the grain surface.
- The thickness of the surface layer is on the order of 8 unit crystals.
- The surface layer accounts for about 25% of the conversion for a 10 min cycle.

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ABSTRACT

The rate of the reduction reaction of a low cost natural hematite oxygen carrier for chemical looping combustion was investigated in a fixed bed reactor where hematite samples of about 1 kg were exposed to a flowing stream of methane and argon. The investigation aims to develop understanding of the factors that govern the rate of reduction with in larger reactors as compared to mostly TGA investigations in the literature. A comparison of the experimental data with a model indicated that reaction between the methane and the iron oxide shows multi-step reactions. The analysis also shows that the conversion occurs with a process that likely consumes all the oxygen close to the surface of the hematite particles and another process that is likely controlled by the diffusion of oxygen to the surface of the particles. Additional analysis shows that the thickness of the fast layer is on the order of 8 unit crystals. This is only about 0.4% of the hematite; however, it comprises about 20–25% of the conversion for the 10 min reduction cycle.

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1. Introduction

Over the past couple of decades, anthropogenic CO_2 has been proposed as the reason for climate changes. Whether or not these CO_2 increases have led to climate change or are the result of climate change, it is important to investigate technology options that can reduce and control CO_2 emissions. The U.S. Department of Energy has set goals for carbon capture systems at 90% carbon dioxide (CO_2) capture with less than a 35% increase in cost of electricity [1]. There are four main categories of these technologies that can achieve these goals: pre-combustion, post-combustion, oxy-fuel and chemical looping [2]. The work presented in this paper looks into the reduction performance of a fixed bed chemical looping system.

Chemical looping is a new name to a relatively old concept that was utilized in the early 1900s for the coal gasification technology called the Steam-Iron Process and again in the late 1960s and 1970s for another gasification technology which was called the CO_2 Acceptor Process [3]. The terminology, chemical looping, was introduced in the 1990s to refer to a cyclic process in which an oxygen rich solid was contacted with a fuel such as natural gas to reduce the oxygen rich solid to form carbon dioxide and water (combustion products). The reduced solid could then be transferred to another vessel and re-oxidized. The cycling of the oxygen carrier between the reducer vessel and the oxidizer vessel is now termed chemical looping combustion. A conceptual process diagram is shown in Fig. 1. In this figure, a bed of the oxygen carrying solid particles is fluidized with a recycle stream of CO_2 and steam. Fuel (methane) is introduced to this reactor to produce CO_2 and water according to the chemical reaction noted below:

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Nomenclature

b	the stoichiometric coefficient in Abad model
C_i	the reacting gas concentration in Abad model where i – denotes gas species CH_4, CO or H_2
k	rate constant in current work
k_1	rate constant for the first mechanism in Monazam et al. model
k_2	rate constant for the first mechanism (min_1^{-n}) in Monazam et al. model
k_{si}	the reaction rate in Abad model
n	solids reaction order
r_g	the grain radius in Abad model
Re	Reynolds Number
R_T	overall reaction rate in current work
R_f	rate of the fact reaction in current work
R_s	rate of the slow reaction in current work
S_A	the particle surface area in current work
Sh	Sherwood Number
t	time
T	the temperature (K) in Monazam et al. model and in current work
u	gas velocity in current work
w_1	weight factor for the first mechanism in Monazam et al. model
w_2	weight factor for the second mechanism in Monazam et al. model
X	conversion of Fe_2O_3 in Abad model and current work
X_1	conversion of Fe_2O_3 by R_1 at any time t in Monazam et al. model
X_2	conversion of Fe_2O_3 by R_2 at any time t in Monazam et al. model
X_∞	equilibrium conversion in Monazam et al. model
τ_i	time for complete conversion in Abad model
ρ_m	the molar density of Fe_2O_3 in Abad model
y_{CH_4}	the methane mole fraction in Monazam et al. model
y_g	gas mole fraction in current work

$$CH_4 + 4\,MO \rightarrow CO_2 + 2\,H_2O + 4M \quad (1)$$

where MO represents the oxygen rich solid, usually a metal oxide and M represents the reduced carrier. The combustion products exit the process as shown while the reduced carrier is conveyed to the oxidizer through a loop seal to keep the gases apart. The reduced carrier is re-oxidized according to the chemical reaction

$$4\,M + 2\,O_2 \rightarrow 4\,MO \quad (2)$$

In the concept loop shown in Fig. 1, the re-oxidized carrier is separated from the oxygen depleted air (vitiated air) in the cyclone, passed through a loop seal and fed back to the reducer to complete the "loop".

Chemical looping combustion is under investigation around the world for power production because the technology allows for fuel conversion with easy CO_2 separation [4–6]. The current investigation is aimed at evaluating hematite, a naturally occurring Fe_2O_3 mineral, as an oxygen carrier for natural gas fuels applications. Fe_2O_3 has been cited as a potential carrier in numerous research publications [7–24] with many of these focusing on the development of required kinetics from TGA experimental investigations for scale-up of this technology.

In an effort to jump start the chemical looping combustion technology, the Office of Research and Development at the US Department of Energy's National Energy Technology Laboratory is focused on a two pronged (experimental and modeling) approach to introduce and develop chemical looping combustion.

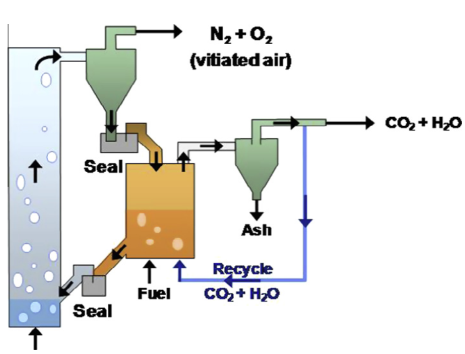

Fig. 1. Chemical looping concept configuration.

In one aspect of this work, NETL-ORD has been investigating natural gas chemical looping with hematite. The work presented herein has two purposes. The first is to provide model validation data such that large reactors can be designed using modern CFD approaches that NETL is pioneering. The second is to provide possible operational assessment on small batch systems for early technology adoption. In this second objective, it has been thought that in the current unconstrained carbon world that early adopters might be found for industrial applications that can utilize both the carbon dioxide and the process heat. One such application that has been considered is for a small cyclic batch unit at a green house, where the CO_2 can be used to accelerate the plant growth. Therefore, to accomplish both of these objectives, small scale cyclic tests were carried out in a batch unit. The experimental results are discussed below.

2. Literature review of Fe_2O_3 reduction

Numerous researchers are investigating various naturally occurring and manufactured iron oxide based carriers for reduction with methane [5–24]. These are summarized in Table 1. Of particular interest is the work of Abad et al. [9], as they have put forward the most advanced and complete model for the reduction of ilmenite. Ilmenite is a naturally occurring iron and titanium mineral in the form of $FeTiO_3$. The actual material tests by Abad et al. [9] consisted of 94.3% ilmenite with the balance being rutile (TiO_2) and hematite (Fe_2O_3). The material had an Fe to Ti ratio of approximately 1. Abad et al. [9] found the reactions of ilmenite with methane to follow the reaction scheme noted below:

Reduction with methane

$$(Fe_2O_3 \cdot TiO_2) + TiO_2 + CH_4 \rightarrow CO + 2\,H_2 + 2\,FeTiO_3 \quad (3)$$

$$3\,Fe_2O_3 + CH_4 \rightarrow CO + 2\,H_2 + 2\,Fe_3O_4 \quad (4)$$

Reduction with carbon monoxide

$$(Fe_2O_3 \cdot TiO_2) + TiO_2 + CO \rightarrow CO_2 + 2\,FeTiO_3 \quad (5)$$

$$3\,Fe_2O_3 + CO \rightarrow CO_2 + 2\,Fe_3O_4 \quad (6)$$

Reduction with hydrogen

$$(Fe_2O_3 \cdot TiO_2) + TiO_2 + H_2 \rightarrow H_2O + 2\,FeTiO_3 \quad (7)$$