January 2015

Attrition Rate Of Oxygen Carriers In Chemical Looping Combustion Systems

Harry Martin Feilen

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ATTRITION RATE OF OXYGEN CARRIERS
IN CHEMICAL LOOPING COMBUSTION SYSTEMS

by

Harry Martin Feilen
Bachelor of Science, University of North Dakota, 2014

A Thesis
Submitted to the Graduate Faculty

of the

University of North Dakota

in partial fulfillment of the requirements
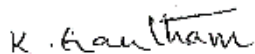

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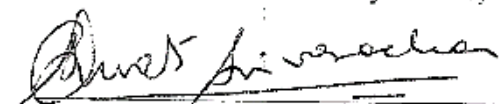
Master of Science

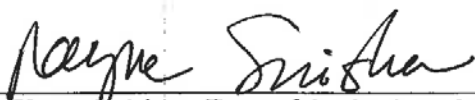Grand Forks, North Dakota
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This thesis, submitted by Harry Martin Feilen in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done and is hereby approved.
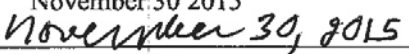
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This thesis meets the standards for appearance, conforms to the style and format requirements of the Graduate School of the University of North Dakota, and is hereby approved.

Wayne Swisher
Dr. Wayne Swisher   (Dean of the Graduate School)

November 30 2015
November 30, 2015
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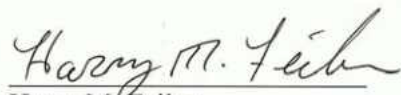
Title   Attrition Rate of Oxygen Carriers in Chemical Looping Combustion Systems

Department   Mechanical Engineering

Degree   Master of Science

Signature   *Harry M. Feilen*
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Date   November   30,   2015

TABLE OF CONTENTS

LIST OF FIGURES

ACKNOWLEDGEMENTS

I would also like to thank Mr. Robert R. Jensen from UNDs Energy & Environmental Research Canter (EERC) for assisting me with programming the LabView software which is the main control and data acquisition system for this project. Finally, I would like to thank all other people who have contributed directly or indirectly to my research that I am unable to thank individually.

ABSTRACT

This project developed an evaluation methodology for determining, accurately and rapidly, the attrition resistance of oxygen carrier materials used in chemical looping technologies. Existing test protocols, to evaluate attrition resistance of granular materials, are conducted under non-reactive and ambient temperature conditions. They do not accurately reflect the actual behavior under the unique process conditions of chemical looping, including high temperatures and cyclic operation between oxidizing and reducing atmospheres. This project developed a test method and equipment that represented a significant improvement over existing protocols.

Experimental results obtained from this project have shown that hematite exhibits different modes of attrition, including both due to mechanical stresses and due to structural changes in the particles due to chemical reaction at high temperature. The test methodology has also proven effective in providing reactivity changes of the material with continued use, a property, which in addition to attrition, determines material life. Consumption/replacement cost due to attrition or loss of reactivity is a critical factor in the economic application of the chemical looping technology.

This test method will allow rapid evaluation of a wide range of materials that are best suited for this this technology. The most important anticipated public benefit of this project is the acceleration of the development of chemical looping technology for lowering greenhouse gas emissions from fossil fuel combustion.

CHAPTER I

INTRODUCTION

There has been a significant amount of information redacted from this report to protect confidentiality and proprietary rights. This may leave the reader with some questions which cannot be disclosed at this time.

The Problem

Due to dependency on fossil fuels for energy production, the global atmospheric concentration of CO_2 has increased strongly from a pre-industrial value of about 280 to 390 ppm in 2010 [1]. Concentration values around 450 ppm are considered as a limit to minimize catastrophic climate change, a level that is only 15 percent over today's value. A reduction in emissions of greenhouse gases, particularly CO_2, is necessary as soon as possible.

Several strategies are being considered and deployed to reduce CO_2 emissions, including reducing energy consumption, increasing energy efficiency, switching to less carbon-intensive fuels (natural gas instead of coal), increasing renewable energy sources, and use of nuclear energy. However, no single technology option is likely to provide a majority of emissions reduction. In this context, CO_2 capture and storage (CCS) appears as a necessary additional option. According to some recent studies [2,3], CCS could

account for about 20 percent of the total CO_2 emission reductions needed to stabilize climate change impacts.

The purpose of CCS technology is to produce a pure stream of CO_2 from industrial operations, transport it to a suitable storage location, and sequester it from the atmosphere. Three main approaches are being considered for CO_2 capture from fossil Fuel combustion: post-combustion capture, oxy-fuel combustion, and pre-combustion capture. In post-combustion capture, a solvent, sorbent or membrane is used to separate the CO_2. In pre-combustion capture, CO_2 is separated from a gasification process stream. Oxy-fuel combustion, rather than combustion in air, results in a very concentrated CO_2 stream, and presents an opportunity to simplify CO_2 capture. Oxy-combustion power production requires oxygen separated from air using a cryogenic air separation unit (ASU). However, energy, capital, and operating costs for oxygen separation add a significant economic penalty.

Chemical-looping combustion (CLC) has emerged as an attractive alternative for CO_2 capture, where a near-pure CO_2 stream is produced from fossil fuel combustion without the use of oxygen obtained from air separation. In this type of system, a solid carrier is used to bring oxygen to the fuel gas, so that it can be subsequently released as a pure CO_2 stream. The solid is then regenerated using air. The technology effectively achieves oxygen separation from air without the use of a cryogenic process or membrane technology. The concept of chemical looping can be applied to both fuel combustion and gasification.

The key advantage of chemical looping is there is no requirement for an expensive ASU, and CO_2 separation takes place within the process. It also has many

challenges, including the need for reliable solids transport systems, efficient heat integration, efficient ash separation, high capacity and attrition-resistant oxygen carrier materials. In particular, oxygen carriers represent a significant cost element and their loss due to attrition must be minimized to make chemical looping technology economically viable.

Chemical Looping Combustion Process
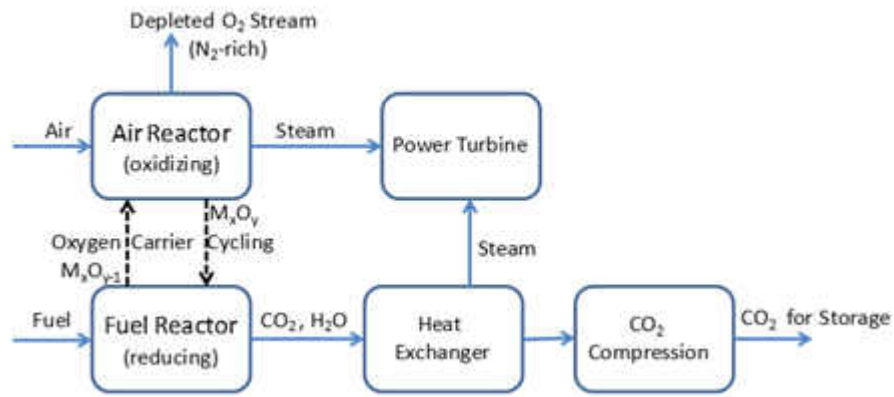
Figure 1. Process Schematic for Chemical Looping Combustion

Figure 1 presents a simplified process schematic for chemical looping combustion. Fuel combustion is split between separate oxidation and reduction reactors. The oxygen carrier is usually a solid, metal-based compound with chemical composition of M_xO_{y-1}. In the fuel reactor, the oxidized carrier material reacts with the fuel to release the oxygen and oxidize the fuel. The fuel reactor typically operates at an elevated temperature (700-900°C). The reaction in the fuel reactor can be exothermic or endothermic depending on the type of oxygen carrier. Heat is extracted from the gases leaving the fuel reactor and transferred into the power cycle. In this manner, the products of fuel oxidation (CO_2 and H_2O) are kept separate from the rest of the flue gases/nitrogen, resulting in a concentrated CO_2 stream and simplifying CO_2 capture. After reaction in

the fuel reactor, the oxygen carrier, now in its' reduced form, is cycled to the air reactor (typically 800–1000ºC), where it is oxidized, to produce a compound (M_xO_y) and nitrogen-rich hot flue gas. The hot flue gas is then used to produce steam, drive a turbine, and generate power.

The oxygen carrier may be in the form of a single metal oxide, such as a CuO, NiO, Fe_2O_3, Mn_2O_3 or a metal oxide supported on a high-surface-area substrate (e.g., alumina or silica) which does not take part in the reactions. Using a supported metal oxide carrier allows independent optimization of oxygen-carrying capacity and mechanical strength. The overall chemical reactions in the two reactors, shown for a Ni/NiO carrier, can be expressed as:

Oxidizer: $Ni + \frac{1}{2} O_2 \rightarrow NiO$

Reducer: $CnH_2m + (2n+m) NiO \rightarrow n CO_2 + m H_2O + (2n+m) Ni$

Net reaction: $CnH_2m + \frac{1}{2} (2n+m) O_2 \rightarrow n CO_2 + m H_2O + heat$
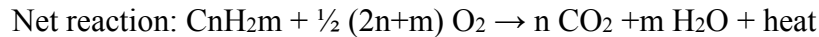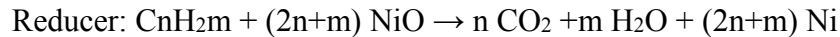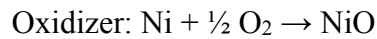
Chemical Looping Combustion Process Equipment
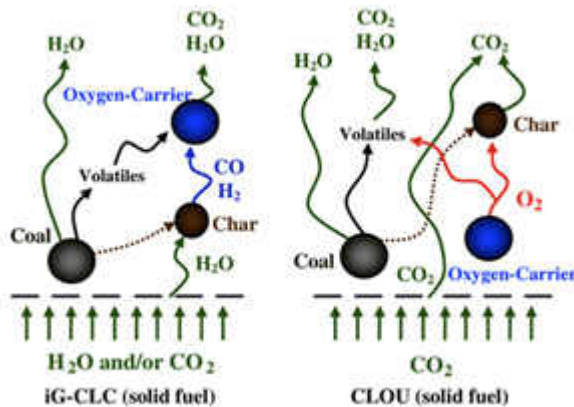
Figure 2. Chemical Looping Combustion for Solid Fuels – iG-CLC and CLOU [4]

The majority of the CLC test units worldwide use the configuration of two interconnected fluidized bed reactors, one being the fuel-reactor and the other being the

air- reactor. Interconnected fluidized bed systems can provide the necessary residence time and good solids/gas contacting for oxygen uptake and release, as well as enable efficient segregation of the solids from the gas streams using cyclones. One option (iG-CLC), identified [4] for solid fuel chemical looping combustion is integrated gasification of the solid fuel and the oxidation of the volatiles, CO and H_2 (Figure 2).
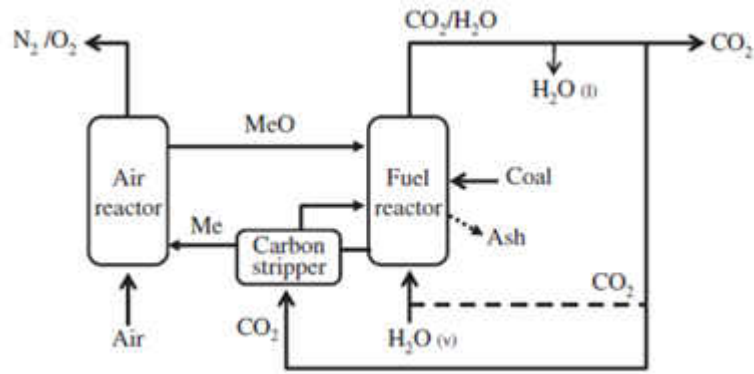
Figure 3. iG-CLC: Chemical Looping Combustion for Solid Fuels [4]

Figure 3 shows a configuration of iG-CLC with two connected fluidized beds. With solid fuels, additional issues need to be considered, including incomplete conversion of volatiles and CO to CO_2 in the fuel reactor, incomplete gasification of char in the fuel reactor and the buildup of ash.

Researchers have proposed methods to address these issues, including recycling a portion of the exit stream from the fuel reactor and use of a char/carbon stripper for the solids (oxygen carrier-char mixture). It is important to understand the process conditions that the oxygen carrier is subject to. For example, to achieve adequate conversion of solid fuel in the fuel reactor, typical operating temperatures are around 1000°C for most oxygen carriers and solid fuel types, and the fluidizing gas used is typically steam.

5

Lower temperatures of around 850°C are relevant when Cu-based oxygen carriers are used, as well as when reactive fuels such as lignite or biomass are used. To overcome the low reactivity of the char gasification step in the iG-CLC process, another mode that is seeing increasing attention is termed chemical looping oxygen uncoupled (CLOU) - Figure 2. The CLOU process is based on the use of an oxygen-carrier that releases O_2 in the fuel-reactor, thereby allowing the solid fuel to burn with gas-phase O_2. In this way, the slow solid gasification step is avoided, giving a much faster solid conversion. Of the metal oxide systems identified so far for the CLOU process, CuO/Cu_2O and Mn_2O_3/Mn_3O_4 pairs have the most favorable characteristics. A more detailed discussion of the oxygen carriers with these pairs is provided in a later section.

Oxygen Carriers (OC)

The oxygen carrier is the most important component of a CLC system. The role of an OC is to transfer O_2 between air and fuel efficiently. Suitable oxygen-carriers for solid fuels in the CLC process must have selectivity to form CO_2 and H_2O, enough oxygen transport capacity, high reactivity, high mechanical strength, attrition resistance, and negligible agglomeration tendency. Besides these, the OC must also be abundantly available, environmentally benign and inexpensive. Each of the different types of oxygen carriers are discussed further below, with their particular suitability for use with solid fuels.

Cu-based Materials

Cu-based materials have shown to be very reactive, with full combustion of gasification products at a mass ratio of OC/solid fuel of only 10:1 at 850°C [5]. Cu-based oxygen carriers are especially suited for the CLOU process, where oxygen is released

from the carrier in the fuel reactor. Cu-oxygen carriers prepared by impregnation on SiO_2, TiO_2, γ-alumina or co-precipitation with alumina [6] have excellent chemical stability and mechanical strength after multi-cycle testing. Other supports have shown unacceptable levels of attrition. The main concern with Cu-based oxygen carriers is agglomeration due to melting. A content of less than 20% CuO was required to avoid agglomeration issues. Forero et al. [7] analyzed the behavior of a Cu-based oxygen-carrier with γ-Al_2O_3. Stable operation for more than 60 h was only feasible below 800°C in the fuel reactor and 900°C in the air reactor.

Adánez et al. [8] prepared stable bimetallic Cu-Ni/Al_2O_3 particles and observed that the presence of NiO in the oxygen carrier stabilized the CuO phase. Long-term tests in a CLC unit under continuous operation showed high metal oxide utilization, and low and stable attrition rate after 67 h of operation at high temperature. This was the first time that a Cu-based oxygen-carrier, prepared by a commercial manufacturing method, exhibited good behavior at these temperatures.

The required inventory of Cu-oxygen carrier is significantly lower (120-200 kg/MWth) compared to other OCs (e.g. Fe-based OC-2000 kg/MWth). Even with lower inventory requirement, the significantly higher cost implies that it needs to have high particle lifetimes and excellent attrition resistance.

Fe-based Materials

Iron-based materials represent an abundant, low cost, environmentally benign alternative for OC material, but have much lower reactivity and consequently a high OC to solid fuel ratio (50-100:1). At Ohio State University [9], the iron-based OC developed incorporates inert support materials, increasing the reactivity and recyclability. A 200-

hour test performed in a 25 kWth chemical looping facility with lignite and sub-bituminous coal was presented by Bayham et al. [10], and showed minimal $CH_4/CO/H_2$ slippage through the fuel reactor. Particle size of the oxygen carrier was around 1.5-5 mm, the fuel reactor was operated as a moving bed and the air reactor as a fluidized bed. Other researchers have used Fe-based carriers, including Leion et al [11]. An OC of 60 wt% Fe_2O_3 and $MgAl_2O_4$ as inert was used with petroleum coke as the fuel. High reactivity was found with the gasification products (H_2 and CO) of coke with steam. Shen et al [12] used a biomass fuel in a continuous 10 kWth CLC system and accomplished a 30 h test. The fuel reactor temperature was varied between 740 and 920°C and CO_2 was used as a gasification medium. Low reactivity of the oxygen carrier was observed due to sintering.

The use of cheap natural minerals such as ilmenite (iron titanate) represents another promising OC candidate. Berguerand and Lyngfelt [13,14] operated a 10 kWth unit using coal and petroleum coke; combustion efficiencies of 85-95% were obtained. The results also showed a low tendency for attrition and agglomeration for this material and its low market price makes it a promising option for use as an oxygen carrier.

Ca-based Materials

$CaSO_4$ has been widely analyzed as an oxygen carrier in the iG-CLC process [15]. The general reactions for the $CaSO_4$ reduction in the fuel-reactor are the following:

$CaSO_4 + 4H_2 \rightarrow CaS + 4H_2O$; $CaSO_4 + 4CO \rightarrow CaS + 4CO_2$; $CaSO_4 + CH_4 \rightarrow CaS + CO_2 + 2H_2O$
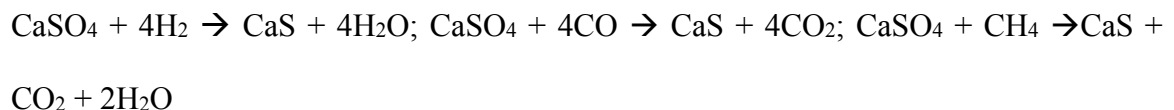
Other Oxygen Carrier Candidates

Ni-based OCs

Ni-based OCs have all the desirable characteristics for CLC mainly because they can operate at high temperatures (> 900ºC) and have good methane conversion rates. Examples of support materials include Yttria stabilized-zirconia (YSZ), Al_2O_3, $NiAl_2O_4$, $MgAl_2O_4$, and oxides of Si, Ti, Zr. Ash rejection that is necessary with the use of solid fuels implies that some of the Ni-based OC's would also have to be disposed and this is environmentally hazardous, and for this reason, this type of OC is not likely to be used in conjunction with solids fuels.

Mn-based OCs

Although a promising metal oxide, Mn-based oxygen carriers have not been widely tested so far. The disadvantage of manganese oxides is their incompatibility with common support materials like Al_2O_3 and SiO_2. Mn-based OC supported on ZrO_2 stabilized with MgO has shown good reactivity with syngas components [17], but lower reactivity has been found for CH_4 [18]. These particles have also been tested in a continuously operated 300Wth CLC unit [19]. Absence of agglomeration and low attrition rate were observed. Very high efficiencies (>99.9 %) were obtained at temperatures in the range 800-950ºC for syngas combustion.

Others

Mixed metal oxides are novel materials that aim to avoid the disadvantages and combine the advantages of individual metal oxides. For example, though CuO cannot operate at high temperatures and NiO leads to the formation of CO and H_2 in the products, the combination of CuO and NiO can be operated at high temperatures without

CO formation. Mixed metal oxides have potential to become efficient oxygen carriers for CLC. Perovskites are materials in which metal oxides are combined in a non-stoichiometric ratio, thereby introducing structural and electronic defects that can be used to enhance reactivity. While some perovskites (e.g. La0.8Sr0.2Co0.2Fe0.2O3-δ) have been tested, their use is still in an exploratory stage.

Methods of Preparation

Several methods can be used for preparing OCs, including mechanical mixing, incipient wet impregnation, mechanical alloying, and spray drying followed by sintering. The method must be scalable and inexpensive to implement. The preparation method is most critical in determining the reactivity, strength, and attrition resistance of the OC.

Attrition Characteristics and Their Importance

The attrition behavior of OCs is a very important characteristic for their use in full-scale systems. Standard tests for attrition behavior of fluidizable solids give a preliminary, but not a fully relevant indication, because conditions are different for industrial operation [20]. It is necessary to consider the chemical stress due to reduction reactions present together with physical attrition effects. Thus attrition behavior obtained during multicycle redox reactions in a batch-fluidized bed or in a continuously operated CLC unit is a good indicator of the expected behavior in a CLC system.

Lifetime of oxygen-carriers is an important parameter to be evaluated at full scale. The lifetime of the oxygen-carriers can be defined as the mean time that a particle must be under reaction (reduction or oxidation) in the system without any reactivity loss or without suffering the attrition/fragmentation processes that produce particle elutriation out of the system. Normally, loss of fines is defined as the loss of particles smaller than

45 μm [21]. The economical cost of the makeup stream of solids to replace loss of fines will depend on the lifetime of particles (attrition rates) and on the cost of the oxygen-carrier, which is mainly affected by the metal used and its content in the solid.

Modes of Attrition
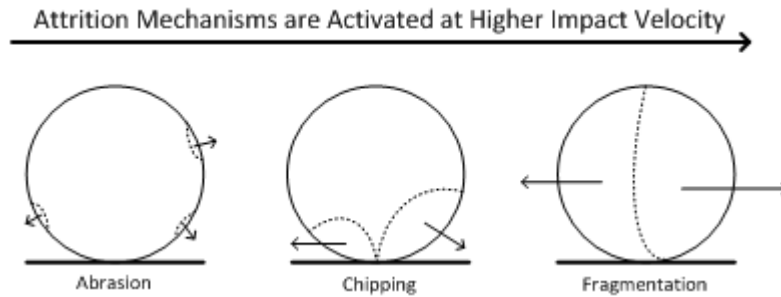
Figure 4. Attrition mechanisms as a function of system velocity [22]

In addition to the chemical degradation, mechanical degradation due to attrition of solids, caused by the motion and collisions of the particles occurs. Several mechanisms of attrition can occur, chiefly related to impacts, abrasion, thermal stresses, and stresses caused by internal generation of gases. Bemrose and Bridgwate [23] identified the regions of fluidized beds where attrition is most likely to occur. Within the bed, attrition originates from bubbling, grid jets and splashing of ejected particles. The degree of attrition depends on the flow regime, with attrition increasing as the superficial gas velocity increases. The presence of baffles and internals may also cause increased attrition.

Standard Method of Attrition Determination

The standard attrition test that would be the basis for the evaluation of the oxygen carrier materials would be the ASTM D5757 [20] test method for determining the attrition characteristics of powdered catalysts by air jets. This apparatus is designed for attrition to be tested at ambient temperatures and in a non-reactive environment. In a

properly constructed jet system, the interaction between particles is dominant. This test determines the relative attrition characteristics of powders by means of gas jets to provide information about the ability of powders to resist particle size reduction in a fluidized bed environment.

The ASTM D5757 gas jet attrition system consists of (i) a stainless steel, 710-mm-long attrition tube of inside diameter 35 mm; (ii) 3 nozzles of diameter 0.381 mm at the bottom of the attrition tube; (iii) a settling chamber, a 300-mm-long cylinder of inner diameter 110 mm with conical ends assembled on top of the attrition tube; and (iv) fines collection assembly, downstream of the settling chamber. When the gas velocity in the settling chamber exceeds the terminal velocity for a given particle size, the particles are transported to the fines collector. This is set to allow particles less than 45 μm to be transported to the downstream filter. The Air Jet Index (AJI) is defined as the percentage by mass of fines produced in a period of 5 h.

Shortcomings of ASTM Standard

The ASTM air-jet test method has important advantages and disadvantages that should be discussed to give context to the proposed experimental changes and to provide suggestions for improving the standard. The test requires about 50 g of sample per test run. For industrially common (e.g. FCC) or inexpensive (e.g. limestone, dolomite) materials, 50 g is a low requirement. However, for synthetic or novel materials, it would be beneficial to reduce this amount while still keeping the test representative.

The ASTM test is designed to be operated at less than ambient temperature (0°C) in a non-reactive environment. However, these conditions are not representative of chemical looping systems. To accurately gauge the attrition of OCs, it will be necessary

12

to operate the attrition test at realistic operating temperatures and in continuously cycled oxidation/reduction atmospheres.

In the ASTM test, the requirement for 10 L/min of gas flow is demanding, if cylinder gas is required. The high flow rate was likely chosen to provide sonic velocities through the distributor orifices, to allow for rapid attrition and therefore reduce the duration of the required test cycle. However, a short test cycle also causes issues with simply accounting for initial attrition effects without properly measuring long-term attrition. It is important to note that any changes to the standard would make the new results technically incomparable to previous results. Nevertheless, suggesting the modifications, and with a dialogue about the current standard with potential end users and researchers, will allow additional concerns and suggestions to be incorporated and evaluated.

The Solution

After considering the advantages and disadvantages of the current standard attrition testing method, a new methodology is proposed. The overall focus of the proposed changes to the test method is to make the testing unit compact, easier to load/unload material, require less material, and make it easier to heat for high temperature tests and vary the gas composition to enable cycling between conditions of the fuel reactor and the air reactor.

As discussed above, the initial mass of sample required will be decreased to ease the evaluation of specialized or novel materials produced in small quantities in the laboratory. Reducing the sample size will also allow the size of the equipment to be decreased, making the system less expensive, easier to heat to the required temperatures,

and easier to operate. However, a smaller equipment size requires a lower gas flow rate in order to maintain the same gas velocities. The flow rate will be scaled down accordingly, which also has the added benefit of being able to use gas cylinders which will be required to supply the gas compositions representative of the air and fuel reactors of CL systems. Further, the temperature of the test will be elevated to a range that is typical of the reaction mechanism and process conditions for the material being tested. In addition, the gas composition will be cycled between the fuel and air reactor conditions. Finally, depending on the number and size of jets used, the length of time required to reach a certain attrition level may increase. However, a longer test period will give a more accurate representation of the long-term attrition rate, reducing the effect of high initial attrition rates.

In addition to the above proposed modifications, the plan is to utilize a sequence of test series in order to differentiate the relative contributions of each of the modes of attrition. By identifying the relative contributions, the oxygen carrier manufacturer can focus on specific aspects of the OC material design in increasing its attrition resistance. The sequence can be summarized as follows:

1.   Ambient temperature with inert fluidization gas – this test will give an indication of the mechanical strength of the material.

2.   Elevated temperature with inert fluidization gas – this test will give an indication of the mechanical strength of the material at temperatures typical of CL systems.

3.   Elevated temperature with oxidation/reduction cycling – this test will give an indication of both the mechanical and chemical stability of the material under realistic operating conditions.

Project Scope of Work

To implement the above solution we developed equipment and methodologies required to evaluate the attrition characteristics of OCs. The scope of work included developing relationships and initiating communications with prominent CL technology developers to gain a better understanding of the needs of these parties in regards to evaluating their materials. Using the information gathered, a test system was designed and constructed based on modifications to the ASTM air-jet apparatus. Detailed procedures and methodologies were developed to evaluate a wide range of OCs. A single type of OC was selected for evaluation to validate the test equipment and methodologies. In addition, ways to increase automation of the test system was identified so that multiple continuous cycles and long duration tests can be accomplished with minimal operator supervision.

Project Technical Objectives

This project targeted the development of equipment, procedures and methodologies for the evaluation of attrition characteristics of oxygen carriers for coal-based chemical looping technology. The work was accomplished in the following tasks.

• Task 1 – Identification of Areas for Improvement and Specific Needs - Prominent chemical looping technology developers, specifically oxygen carrier manufacturers and designers were identified. Communications were initiated in order to identify the current need of these parties in regards to evaluation of oxygen carriers for attrition characteristics.

• Task 2 – Design and Construction of an Attrition Evaluation Test System - Designed and constructed an attrition evaluation system capable of operating over the

range of conditions identified during Task 1 and with multiple types of materials. The initial test system design was based on the current ASTM D5757 method, but with modifications to accommodate the evaluation of chemical looping oxygen carriers.

• Task 3 – Development of Attrition Evaluation Procedures and Methodologies - Developed a broad and encompassing set of procedures and methodologies for the evaluation of the attrition characteristics of chemical looping oxygen carriers utilizing the test equipment constructed during Task 2.

• Task 4 – Validation of Equipment and Attrition Evaluation Methodologies - One oxygen carrier material type was identified for evaluation using the equipment and methods developed during Tasks 2 and 3. The full sequence of tests, material sampling and data reduction methodologies was completed.

Questions answered in this project

The questions answered during this project included: 1) How can existing attrition test methods be improved and retrofitted for chemical looping technologies? 2) What is the equipment design and test methodology that will produce the most useful, repeatable and comparable results? 3) How should the test equipment be automated for continuous operation and minimal operator supervision?

Project Background / Technical Approach

The current standard for attrition evaluation is the ASTM air-jet method (D5757). While it can be a useful method for many types of materials and processes, it does not adequately capture the true conditions unique to coal-based chemical looping systems. In this project, the approach is to modify the air-jet method to better accommodate CL

oxygen carriers utilization. Key modifications to the ASTM air-jet method (D5757) are listed below:

1.   Ability to run the test at elevated temperatures found in CL systems.

2.   Ability to distinguish between the modes of attrition – mechanical (abrasion, fragmentation) and chemical.

3.   Utilize multiple fluidization gas compositions representative of the air and fuel reactors in CL systems.

4.   Use smaller sample size due to difficulty in manufacturing large quantities of specialized materials in the laboratory. Smaller size also decreases equipment cost and simplifies operation.

In addition, the current ASTM standard does not provide sufficient data that encompasses the entire range of attrition characterization. The standard only addresses the amount of fines that are generated, while not looking at the entire particle size range and how it changes with time. The equipment and methodologies developed in the proposed work will aim to better characterize the attrition characteristics, as listed below:

1.   The modes of mechanical attrition – fragmentation and abrasion – can be quantified by examining particle size distribution (intermediate sizes for fragmentation and fines from abrasion) and the particle's surface morphology using scanning electron microscopy.

2.   Chemical degradation: quantified by analyzing the composition of the fines and the rest of the sample. This will determine the extent to which the active component and/or the support material are enriched or depleted in various particle size ranges.

3.	The overall attrition rate as well as the rate attributable to mechanical attrition, high temperatures and chemical attrition will be quantified, allowing the OC material designer to focus their efforts effectively.

CHAPTER II

EXPERIMENTAL

This project targeted the development of equipment, procedures, and methodologies for the evaluation of attrition characteristics of oxygen carriers for coal-based chemical looping technology. The experimental setup work was accomplished in Tasks 1 and 2 during this project.

Task 1 – Identification of Areas for Improvement and Specific Needs

Prominent chemical looping technology developers, specifically oxygen carrier manufacturers and designers were identified. Communication with the above parties was made and identified their current need in regards to evaluation of oxygen carriers for attrition characteristics. The oxygen carrier hematite was obtained from the U.S. Department of Energy. Results from testing with hematite are presented as part of this project.

This task also allowed the necessary information to be gathered to design the test system, with the following key parameters:

• OC physical characteristics – particle size, density, composition

• Temperature range of operation

• Gas composition during reduction

• Typical gas flows or U_0/U_{mf} (bed velocity/minimum fluidization velocity) ratios of operation.

Task 2 – Design & Construction of Attrition Evaluation Test System

An attrition evaluation system was designed and constructed that is capable of operating over the range of conditions (temperature up to 900ºC and with cyclic oxidizing and reducing conditions) identified during Task 1 and with multiple types of materials. The test system was based on modifications to the ASTM D5757 method, with the ability to accommodate the evaluation of chemical looping oxygen carriers at the high temperature and reacting conditions. In conjunction with the test equipment construction, software was implemented for data collection and for control and automation of the test equipment operation.

With the information from CLC technology developers, we designed the test system to be as robust and flexible as possible, so as to cover a broad range of possible test conditions and employ multiple types of materials. The key components of the test system include:

- Gas supply – High pressure gas cylinders, pressure regulators and mass flow controllers

- Preheating system – For high temperature operation, a clamshell-type preheater, high temperature heat tracing, and reactor furnace are installed. The OC bed is located in the reactor furnace, and thus the inlet gases have additional heated zone prior to introduction to the OC. Further, a bed of zirconia beads is located below the jet plate and assists in heating of the gas.

- Attrition bed – The bed is located within a high temperature clamshell-type furnace. A distributor plate with several small diameter holes provides high jet velocities in the OC material bed. The bed height was sized in order to dissipate

energy sufficiently to keep the desired particle size range within the bed and to only allow small particles to escape.

- Settling chamber – A chamber with conical ends is located on top of the attrition bed. Here, any oversized particles which escape the main attrition bed are exposed to a lower velocity and can drop back into the bed. A feed port is placed on top of this section so that the OC material can be introduced after the reactor has reached the desired set point temperature. In these tests (700-850°C)

- Fines collection – Two filters are placed in parallel as close to the exit of the settling chamber as possible. A three way valve is installed to switch between the parallel filters such that filters can be replaced without having to stop gas flow or interrupt the test.

- Gas analysis – An 8-gas Laser Gas Analyzer (LGA) (O_2, N_2, CO_2, CO, H_2, H_2S, H_2O, CH_4) is installed to monitor the composition of the gas leaving the system.

- Data acquisition and control – A National Instrument LabVIEW program was written and installed to control the components of the system and to record and monitor data in real time. A high degree of automation is provided with this program, such as automatic cyclic operation, valve actuation, temperature control and flow control.
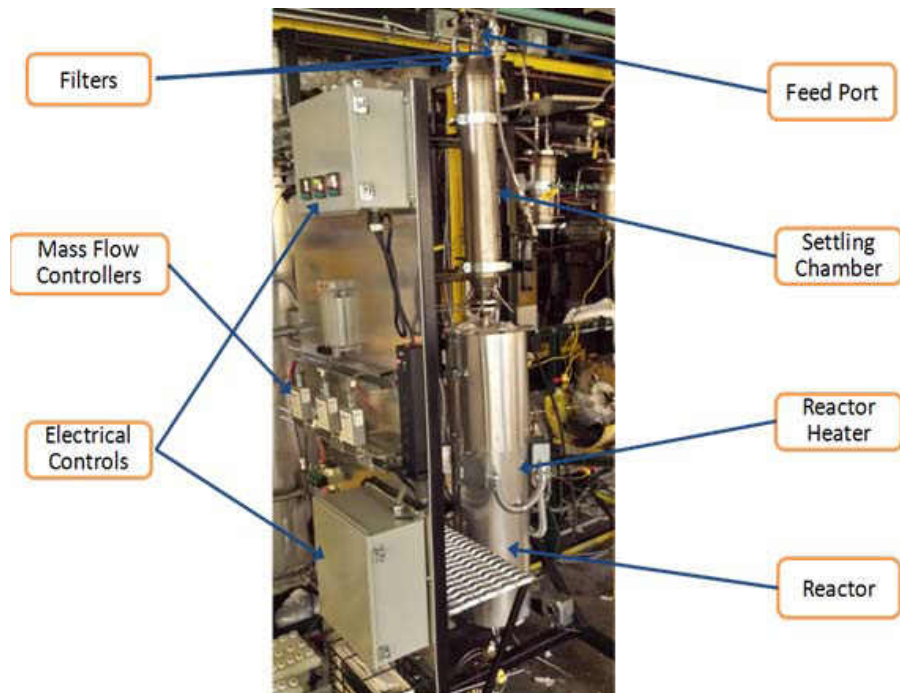
Figure 5. Picture of the Assembled Attrition Evaluation Test system

Figure 5 is a photograph of the completed test system. The system was constructed as a mobile unit that is built around a structure that has wheels so that it can easily be moved if necessary.

Chapter III

RESULTS & DISCUSSIONS

Results from Tasks 3, which included the development of the attrition evaluation procedures and methodologies and from Task 4, validation of the methodology with data presented for a selected oxygen carrier are discussed in this section.

Development of Attrition Evaluation Procedures and Methodologies

The test system was designed to operate in three modes in order to gather information about the attrition mechanisms which are present in CLC systems. These are: (1) ambient temperature with inert gas; (2) high temperature (~800°C) with inert gas; and (3) high temperature with cyclic oxidizing/reducing atmospheres. With this sequence of tests we can distinguish the relative effects due to mechanical, thermal and chemical stresses. Additionally, operating procedures were developed to gather as much information as possible from a given test. The following summarizes the key components of the methodology:

- Collect/determine mass of attrited (elutriated) particles as a function of time

- Maintain attrition energy input to be similar for different modes of operation

- Use exit gas composition to establish cycle time of oxidation/reduction step

- Particle characterization – morphology, size, composition (SEM/x-ray microanalysis, cross-section, cascade impactor), density

- Reactivity of material as a function of time.

Prior to implementation of the above test methodology, some preliminary data was needed to ensure proper operation of the system.
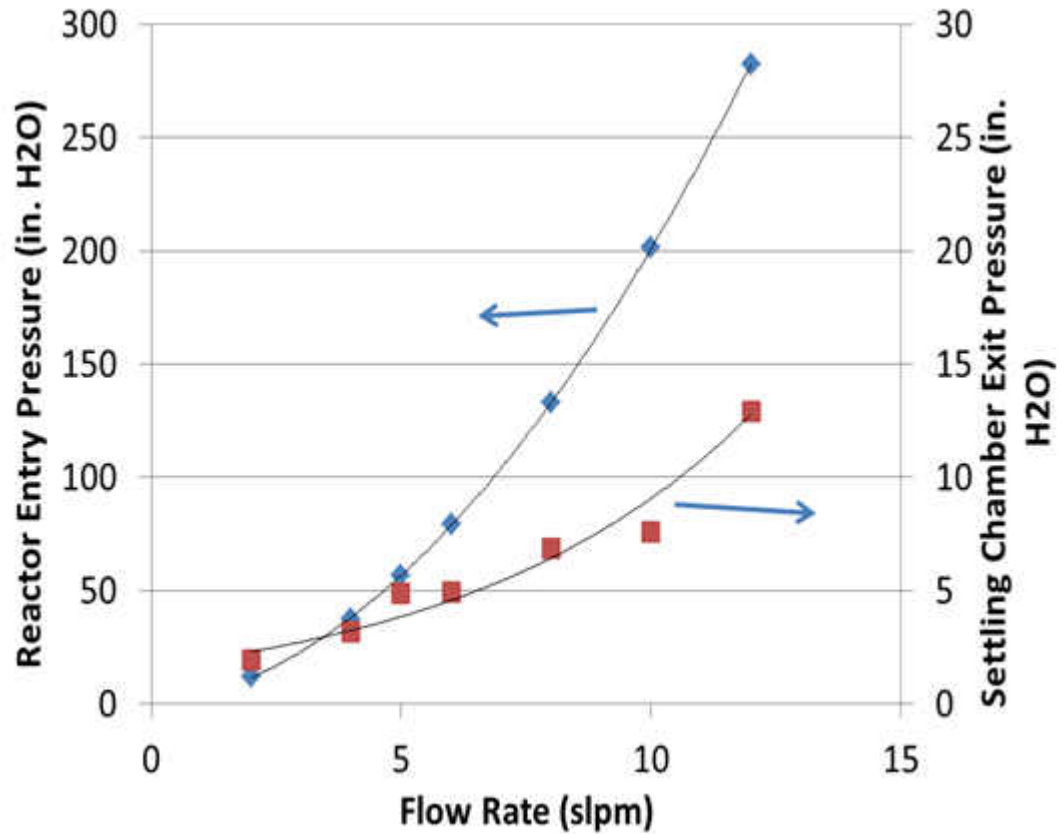
Figure 6. Test methodology validation–cold and hot flow conditions without reaction

Figure 6 displays the pressure drops in the system as a function of the flow rate. As is shown in the figure, the largest pressure drop in the system occurs in the distributor plate that provides the high jet velocity in the OC bed. Additional pressure drop occurs due to restriction in the downstream particulate filter. This data provided system pressures in order to calculate velocity within the bed for a given flowrate. In order to ensure that the appropriate "cut size" is achieved for the elutriated particles during a test,

some preliminary calculations were completed which determined particle terminal velocity as a function of particle size and flow rate.

**Terminal Velocity vs Particle Size and Pipe Size
Hematite at Density of 2551 kg/m^3**
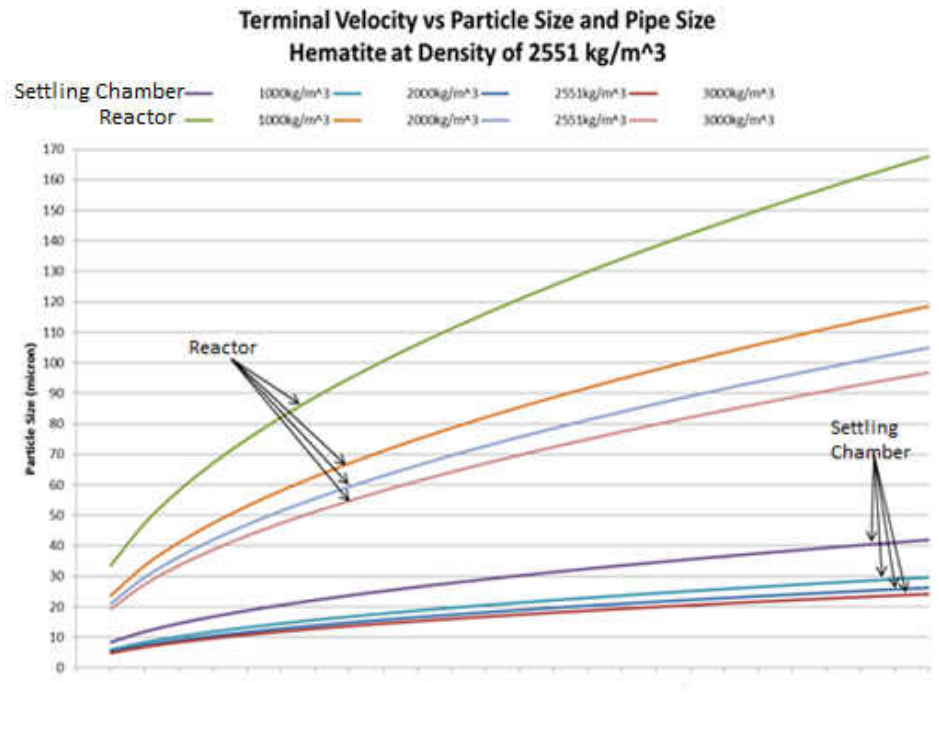
Figure 7. Terminal Velocity vs Particle Size Chart

Figure 7 is a chart which was developed to establish the cut size vs flow rates. The X axis was deleted to protect confidentiality and proprietary rights. This data is for particles with multiple densities and for the settling chamber and the main attrition bed. For the hematite material, the cut size for particles that are elutriated and collected in the particulate filters is approximately 25 microns.

Validation of Equipment and Attrition Evaluation Methodologies

Below is a list of "Mode of operation" and the "Method of operation" which was developed during the testing of the equipment. This list confirms the information in section 3.1 was achieved during the actual running and testing of the equipment and that the equipment is capable of operation under similar conditions found in CLC systems.

25

- • "Mode of operation"

- − Ambient temperature

- − High temperature (700-850°C)

- − Cyclic operation (700-850°C; Oxidizing – 10% O_2 /Reducing – ~5% H_2)

- • "Method of operation"

- − Collect/determine mass of attrited particles as a function of time

- − Maintain attrition energy input to be similar for different modes of operation

- − Use exit gas composition to establish cycle time of oxidation/reduction step

- − Particle characterization – morphology, size, composition (SEM/EDAX, cross-section, cascade impactor), density.

Results from Hematite Oxygen Carrier Testing

A sample of an iron-based oxygen carrier – hematite – was acquired from DOE NETL and served as the base material for validation of the test equipment and methodologies. This material was evaluated in each of the modes of operation and the full test methodology was completed which included data reduction, sample collection, and particle characterization.

Attrition Rate Results and Structural Integrity
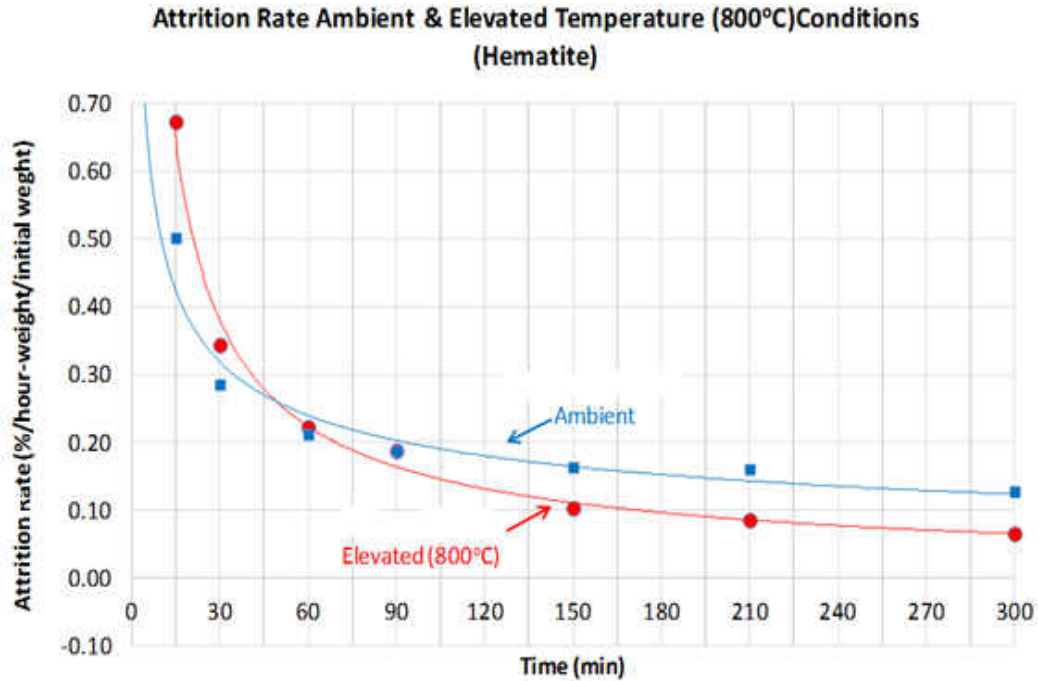
Figure 8. Attrition rates of Hematite over 300 minutes

Figure 8 displays the measured attrition rate for the first two test modes, ambient and high temperature operation for hematite. The high temperature test was conducted at 800°C. In both cases, attrition rates are somewhat high initially and subsequently decrease to relatively low plateau at long times. This behavior may reflect the abrasion of "corners and edges" initially, with the particles becoming smoother and more resistive to abrasion at longer times. The attrition rate is less for the high temperature test and for times longer than 60 minutes, most likely due to sintering of the material during this test. Sintering is the melting, by heat and/or pressure, without liquefying, of a material causing it form a solid mass. Due to the presents of other materials contained in our sample batch of hematite, like Si, which may facilitate agglomerations, and the sintering effects with

27

the hematite itself, agglomerations may form and cause the attrition rate to decrease as these particles become larger causing less fluidization or not fluidize at all in the reactor during the test. If the agglomerated material does not fluidize it has less forces acting on it to cause attrition. Depending on the size of the agglomeration mass or the number of agglomerations formed this will affect the attrition rate dramatically. This agglomeration process and how it can be controlled, will be studied further in future work.
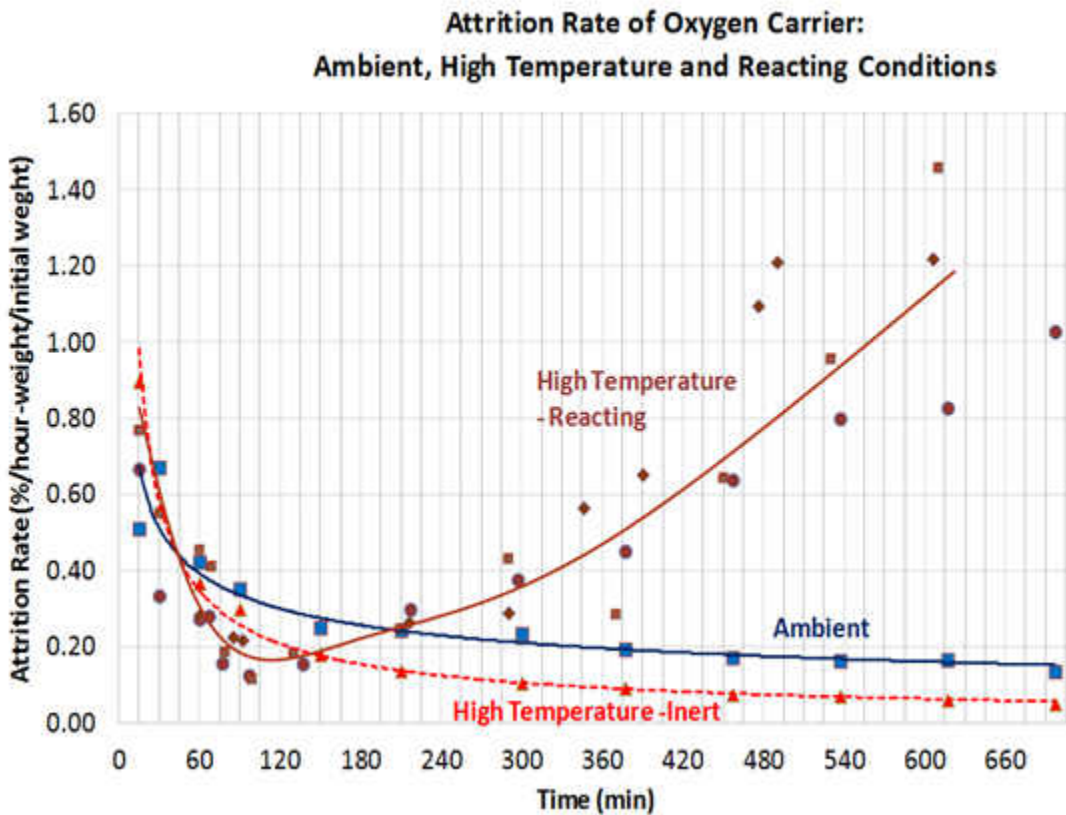
Figure 9. Attrition rates for hematite during all three modes of operation

Figure 9 displays the measured attrition rate for the high temperature-reacting mode along with the other two modes of operation for hematite. For both of the non-reacting modes the attrition rates start out relatively high initially (~1%/hr), and then drop to somewhat constant low levels (~0.1%/hr) over a longer duration. Interestingly, however the attrition rate observed for the high temperature inert case was lower than that

of the ambient inert case. This was presumably due to some sintering of the hematite particles that occurred at the high temperature condition that increased their strength, which reconfirms the data in figure 9. With only the information from the inert tests available, one may make the conclusion that the hematite has excellent attrition resistance and might be a good candidate for CLC. However, when looking at the high temperature reacting case with cycling between oxidizing and reducing conditions, there is a stark contrast in the attrition behavior of the material. Again, the attrition rate starts out high and drops to a low level over time when only N_2 gas is used during the first 75 to 100 minutes, but immediately upon introducing oxidation / reduction cycling, the attrition rate begins to increase rapidly, even exponentially. After a 600-700 minute duration, the attrition rate with reaction cycling is about one order of magnitude higher than the material in the inert cases. This is in addition to the fact that the rate is trending upwards quickly for the reacting case, while it is steady or slightly decreasing for the inert cases. This is a profound observation because it indicates that the chemical reactions that occur during CLC operation can have a substantial impact on the overall attrition rate of the material, and thus, this aspect must be taken into account when evaluating oxygen carriers.
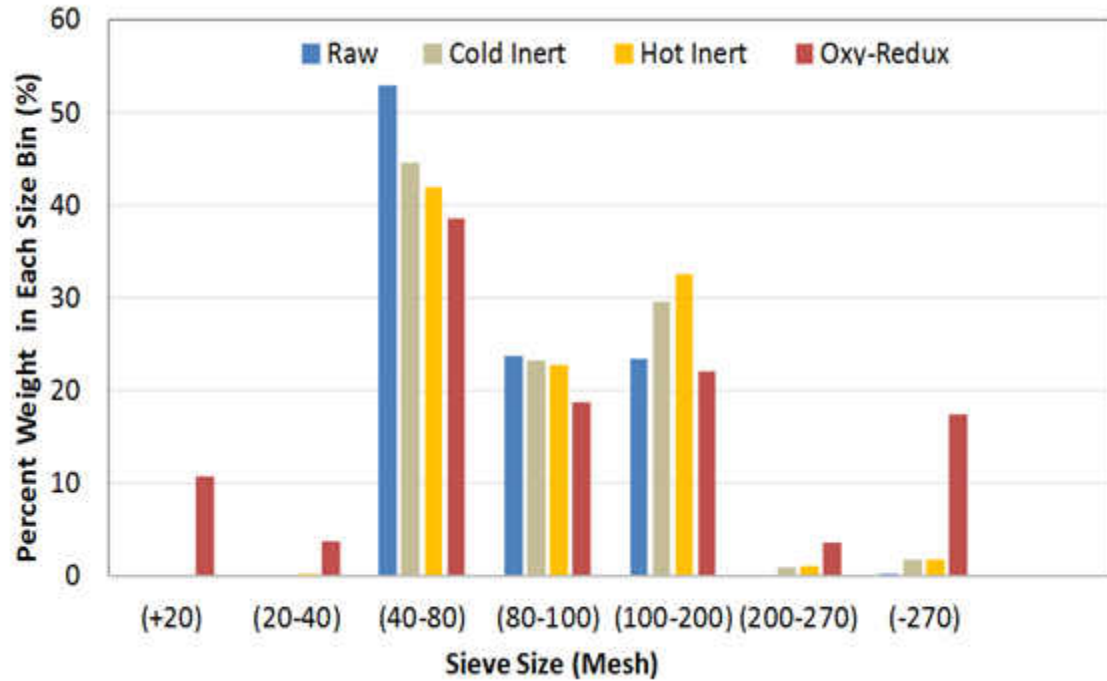
Figure 10. Size distributions of bed (retained) material for hematite testing

Figure 10 displays the size distribution of the raw material before testing and the remaining particles in the bed after testing in each mode of operation. For the inert cases there appears to be a slight increase in the amount of fines, but for the reacting case, there is a significant (even dramatic) increase in the generation of fine particles, again suggesting a much higher attrition rate occurs due to the chemical reactions. Interestingly, however, there is also an increase in large particles during the reacting case. This is attributed to particle agglomerates presumably formed due to softening/plasticization of the hematite particles, and which is described later when we characterized the material using microscopy.

Gas Composition Results and Reactivity

Figures 11-12 display the exit gas compositions during the high temperature reacting case for the hematite. This is another important observation from this work.

Because of the capability to continuously monitor the inlet and outlet gas compositions during testing, the ability to assess some of the reactivity characteristics of the hematite material, or any other material, is possible.
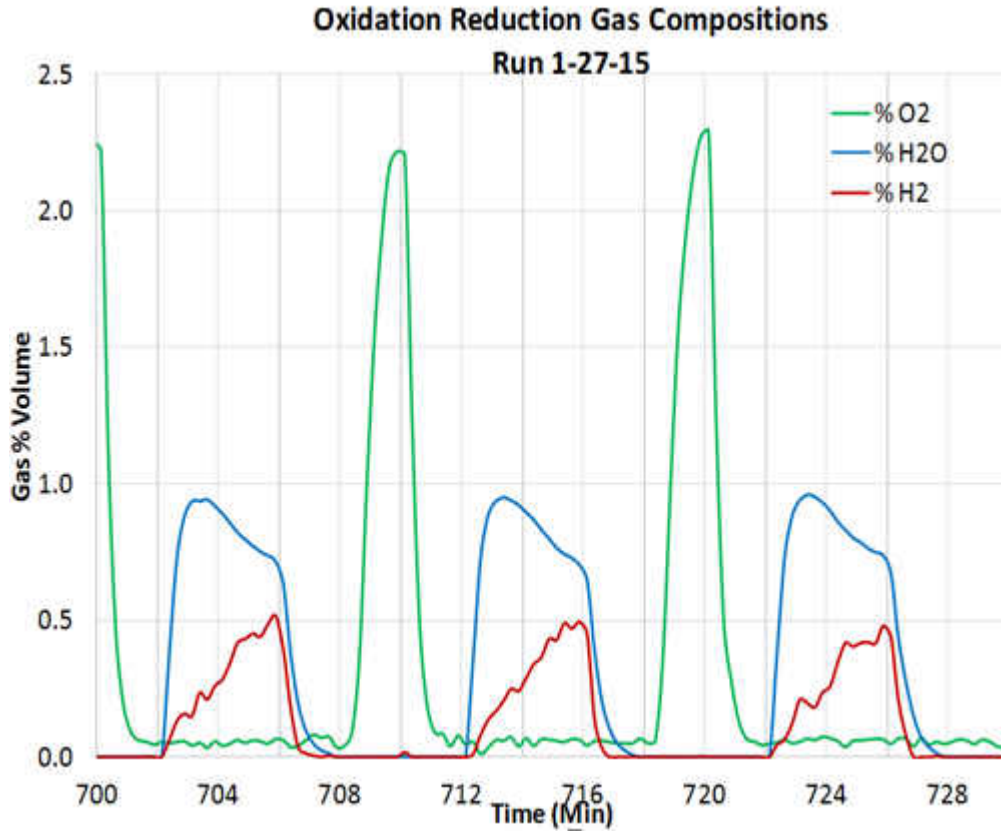
Figure 11. Snapshot of real-time exit gas composition measurements

In Figure 11, a snapshot view of a three-cycle period is shown. The oxygen curve increases to complete breakthrough as the oxygen carrier is oxidized (e.g. around the 710 minute mark), which is followed by a N_2 purge period, where all concentrations go to low values (e.g. around the 712 minute mark). At this point, the reduction step begins. The water vapor is initially increasing due to reaction of the H_2 with the OC. As the reaction proceeds, the water vapor decreases and the H_2 increases until breakthrough is established when the OC becomes significantly reduced (e.g. around the 716 minute

31

mark). By integrating these curves, the fraction of gas that was reacted with the OC during each step can be calculated.
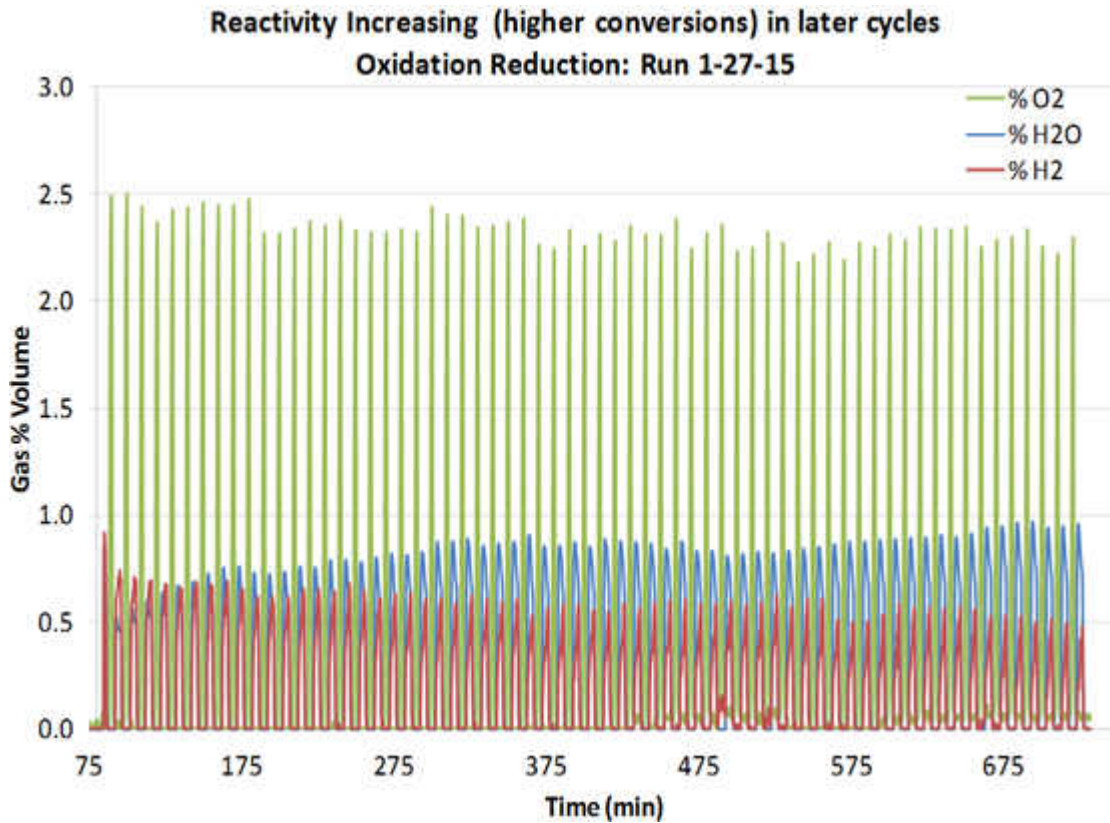
Figure 12. Real-time exit gas composition measurements

Figure 12, displays the same data, but over a larger number of cycles. In this figure, we can see that the reactivity of the material is actually continuously increasing as a function of time – H_2 (reactant) decreasing at exit and H_2O (product) increasing at exit. This is an important observation because there are really two pieces in determining the "lifetime" of the OC – attrition and reactivity maintenance. For the case of hematite, the data indicates that attrition appears to be the dominant governing factor; attrition rate significantly increases with time, while reactivity also increases with time.

Particle Structure and Composition Evolution

To characterize the hematite attrition and reactivity characteristics further, scanning electron microscopy with energy dispersive x-ray microanalysis (SEM/EDAX) was used to study the morphology of the hematite particles before and after testing.
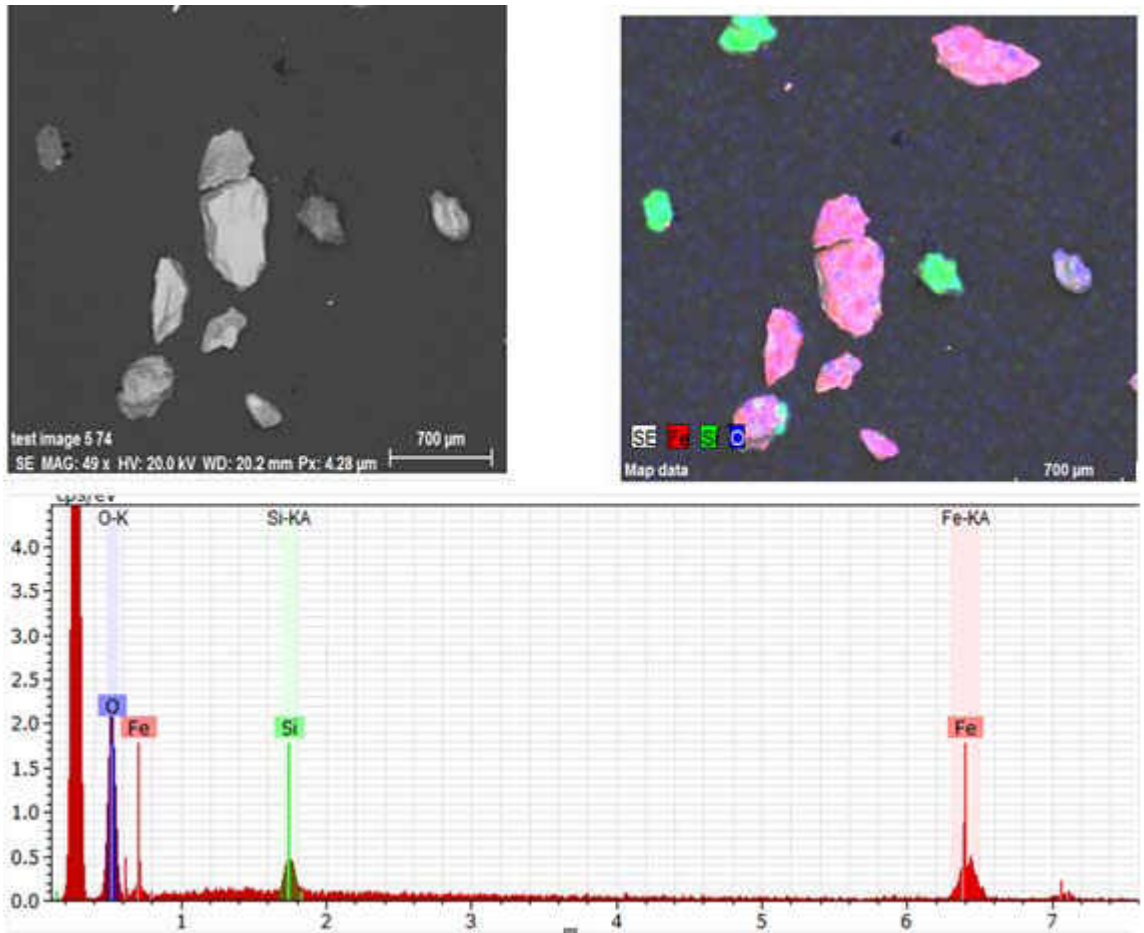
Figure 13. SEM/EDAX analysis of hematite material (raw).

Figure 13 displays the raw hematite materials before testing. The images show the particles are angular and have no distinguishable porosity. There was also some silica particles mixed in with the hematite

33
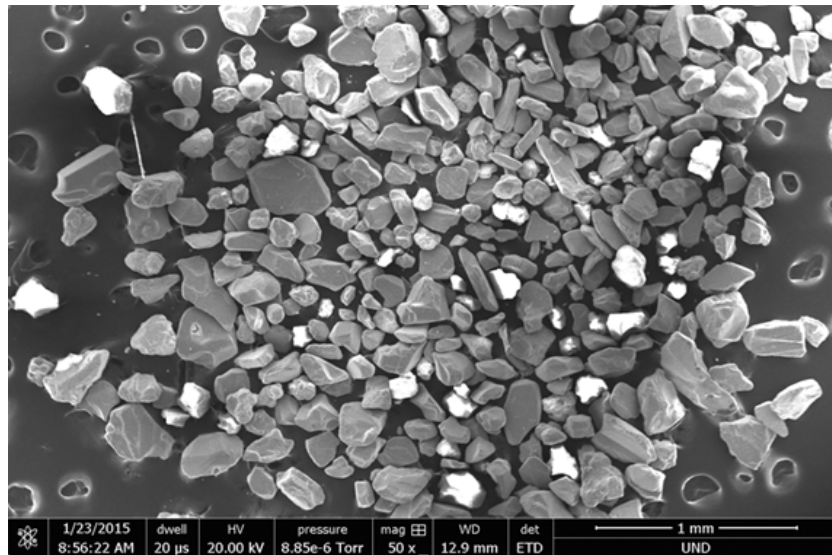
Figure 14. SEM analysis of hematite material after ambient temperature attrition test.
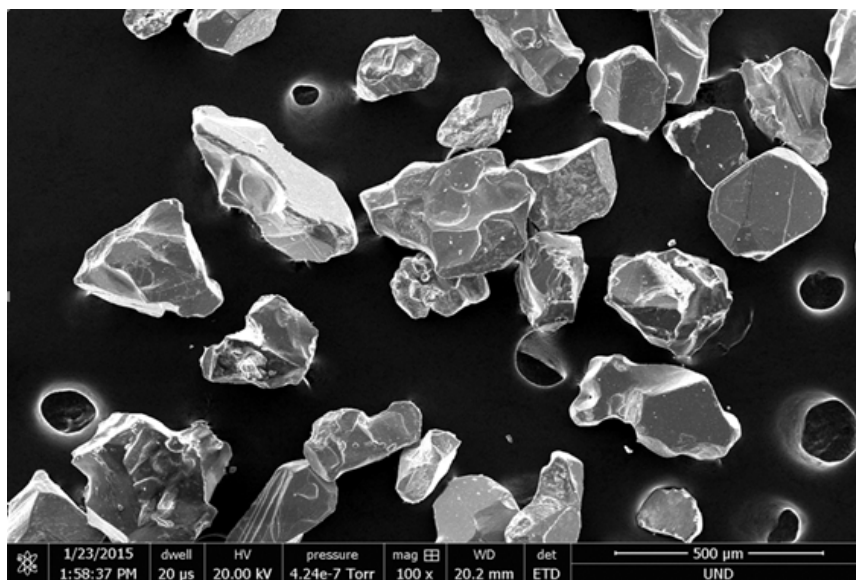
Figure 15. SEM analysis of hematite material after high temperature attrition test.

Figures 14 and 15 display the micrographs for the hematite particles after the ambient temperature and high temperature inert runs. In these images, the angularity of the particles is still evident and overall, the particles look very similar to the raw material. This would agree with the measurement of very little attrition during these runs.
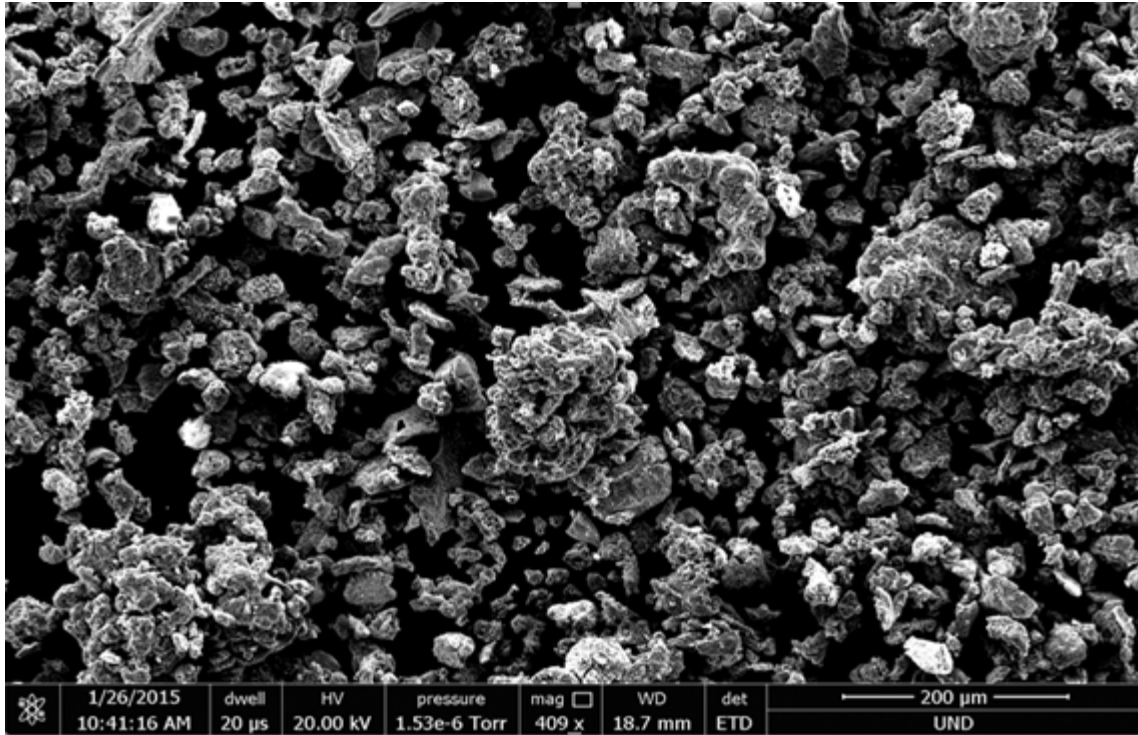
Figure 16. SEM of hematite after high temperature cyclic oxidation/reduction test.

Figure 16 is SEM photomicrographs of the particles after oxidation/reduction cycling. In this figure, the particles have gained significant porosity and have substantially softer edges with evidence of plasticization. Overall, there is clear indication of dramatic morphological changes due to the reacting conditions. It is likely that the increase in porosity reduced the strength of the particle and caused high attrition rates, but that the increase in porosity also made additional surface area available for reaction and resulted in the increasing reactivity that was observed.
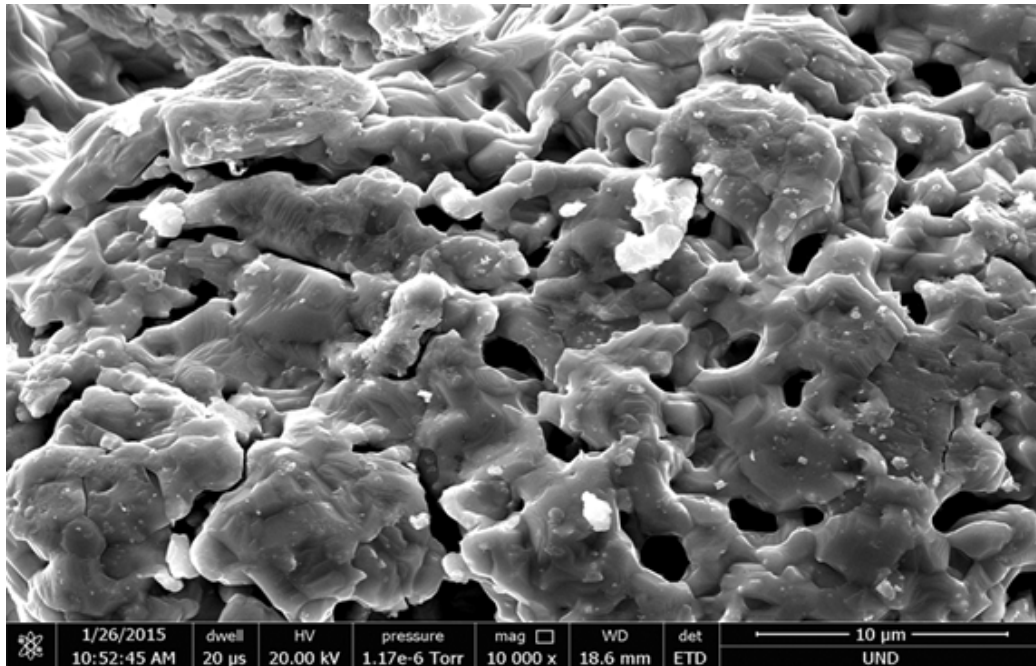
Figure 17. Expanded view of hematite particle after reaction

Figure 17 displays a 10,000 times magnification view of the surface of the oxygen carrier material. This was after high temperature, oxidation/reduction reaction testing. The expanded pore structure is very obvious in this figure.
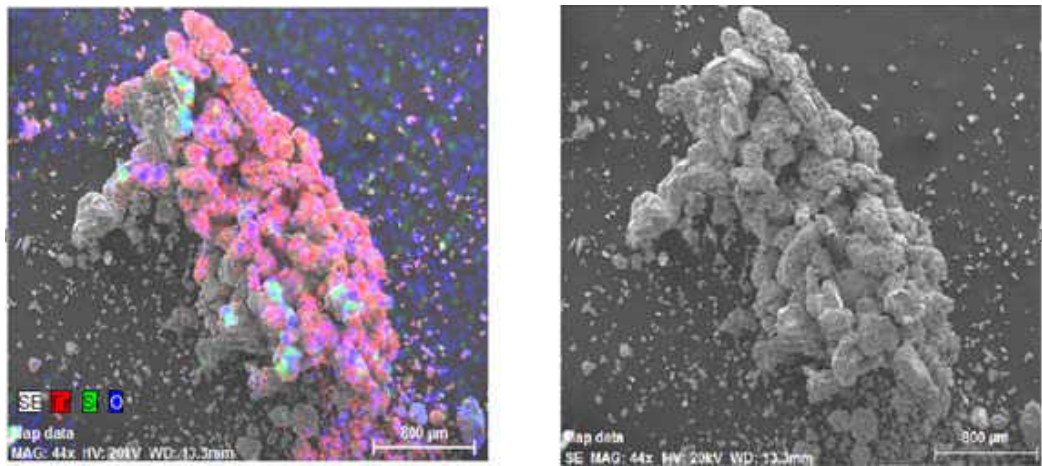
Figure 18. View of iron oxide agglomerate

Other images of particles in the reacted sample showed some additional features. Some particles looked like agglomerates comprising smaller primary particles. The

particles were porous but it looked as if, due to the particle softening, smaller particles agglomerated (Figure 18). These pictures are consistent with larger than "original" particles noted in Figure 10, which indicated some sort of an agglomeration phenomenon.

In summary, attrition evaluation of the hematite oxygen carrier under reacting and non-reacting conditions showed that the hematite material exhibited excellent attrition resistance during non-reacting testing at both ambient and high temperatures, but had an order of magnitude higher rate during the continuously cycling oxidizing/reducing test. This observation alone demonstrates the necessity of incorporation of reacting conditions during attrition testing. The data was further verified by examination of the particle size distribution that showed a significant increase in the formation of fine particles during the reacting test as compared to the inert tests. The hematite reactivity was characterized and showed an increasing trend over time. Further, SEM/EDAX analysis showed that dramatic physical transformations occurred to the hematite particles during the reacting test. It is assumed the increasing porosity likely led to a weakening of the particle and subsequently higher attrition rates. However, added surface area was the likely cause of the increasing reactivity. Particle softening was also evident, which explains the particle agglomerates that were present after testing. Overall, the lifetime of this hematite OC in a CLC process is likely to be governed by its attrition rate.

CHAPTER IV

CONCLUSION

With regard to oxygen carrier (OC) testing the attrition evaluation test equipment has proven to be a powerful tool to assist in determining the life expectancy of the OC during different operating conditions. From the tests conducted during this project and the results obtained, our test equipment and methodology has proven to be robust and reliable to provide valuable information to technology development community and is a stepping stone for evaluation of additional materials and process conditions.

We measured attrition rate for each of the three modes of operation for hematite as an oxygen carrier. For both of the non-reacting modes (ambient and high-temperature operation) the attrition rates start out high initially (~1 %/hour), and then drop to relatively constant low levels (~0.1 %/hour) over a longer duration. Interestingly, the attrition rate observed for the high temperature inert case was lower than that of the ambient inert case, presumably due to an increase in strength from particle sintering.

Based only on the inert tests, one may make the conclusion that hematite has excellent attrition resistance and might be a good candidate for chemical looping combustion. However, when looking at the high temperature reacting case with cycling between oxidizing and reducing conditions, there was a stark contrast in the attrition behavior of the material. Immediately upon introducing oxidation/reduction cycling, the attrition rate began to increase rapidly, and at the end of the test, the attrition rate with reaction cycling was about one order of magnitude higher than the inert tests. In addition,

the rate was trending upwards quickly for the reacting case (greater than 1%/hour), while it was slightly decreasing for the inert cases. This is a profound observation, showing that chemical reactions that occur during CLC operation can dramatically impact the overall attrition rate of OCs.

The attrition rate test equipment developed in this project has proven to be a valuable piece of equipment which could be implemented into a separate testing facility for a small business, which was one of the goals of this project.

CHAPTER V

FUTURE WORK

Oxygen Carrier Characterization Planned Work

In moving forward, several additional oxygen carriers will be tested. Selected materials will undergo several additional tests under many different reducing conditions such as different types of reducing gases. Other modes of attrition will be evaluated. For example, in a chemical looping combustion process, impaction of particles in a cyclone and duct bends can lead to attrition. This mode has different characteristics than jet-based attrition. The equipment can be modified to include impaction-based (cyclone) attrition. Additional changes may include incorporation of extra safety features to allow extended testing without supervision by an operator.

Limestone Planned Work

The attrition test methodology developed in this work has the potential for other applications beyond chemical looping. For example, this methodology is currently being used for limestone characterization, particularly their suitability for sulfur capture in circulating fluidized bed combustors. The methodology can provide information on the propensity of the limestone material to be retained in the fluid bed and provide sulfur capture, as well as what fraction of the limestone-derived particles would be entrained and leave the main reactor system, which would have deleterious effect in downstream heat exchangers and potentially pose challenges in particulate capture equipment.

Other Uses for the Test Equipment

There are several other ongoing projects for which the attrition behavior of materials is important. For example, this test equipment has potential application for evaluating the attrition resistance for CO_2-capture sorbents in post-combustion capture processes. We are conducting tests with our equipment for these other projects as well to establish attrition rates for candidate materials.

APPENDIX

Error Analysis

The errors in the recorded data within this report includes a time error, and a weight error. The time error would be the response time of the operator. When the filter change time is recorded it is within 1 second of the full minute. Therefore the largest error associated with time is 1 second and the largest error amount for the runs are as follows:

Cold Ambient Runs------------- 0.000037g/s * 1s = (+/-) 0.000037 grams
Hot Inert Runs------------------ 0.000035g/s * 1s = (+/-) 0.000035 grams
Oxidation / Reduction Runs--- 0.000062g/s * 1s = (+/-) 0.000062 grams

The standard deviation and confidence intervals are calculated for two runs of each condition: cold ambient conditions, hot inert conditions, and oxidation and reduction conditions. The confidence interval was calculated at 95% and this calculation was conducted within the Microsoft Excel program. The largest standard deviation for the runs are:

Cold Ambient Runs------------- 0.0007
Hot Inert Runs------------------ 0.0008
Oxidation / Reduction Runs--- 0.0095

The largest confidence interval for the runs are:

Cold Ambient Runs------------- 0.0009
Hot Inert Runs------------------ 0.0011
Oxidation / Reduction Runs--- 0.0132

Therefore, it is with good confidence that I can say the error within the recorded data is very small and does not have much of an influence on the results reported within this report. This is further affirmed by the following data. The most probable error (y_p) equation is:

$$y_p(\dot{W}) = 100 * \sqrt{\left(\frac{\Delta w}{w}\right)^2 + \left(\frac{\Delta t}{t}\right)^2}$$

The maximum error (y_{max}) equation is:

$$y_{max}(\dot{W}) = 100 * \left(\frac{\Delta w}{w} + \frac{\Delta t}{t}\right)$$

Where:
$y_p(\dot{W})$ & $y_{max}(\dot{W})$ is the error rates of time and weight combined
Δw is the error rate for the balance (0.0002 grams)
w is the weight of the filter post run
Δt is the error rate of time (1 second)
t is the time interval of the filter change

Cold Ambient Runs

Δt (s)	$y_p(\dot{W})$ (%)	$y_{max}(\dot{W})$ (%)
900	0.5434	0.6430
1800	0.6314	0.6845
3600	0.4091	0.4359

Hot Inert Runs

Δt (s)	$y_p(\dot{W})$ (%)	$y_{max}(\dot{W})$ (%)
900	0.4271	0.5235
1800	0.6255	0.6786
3600	0.6607	0.6878

Oxidation / Reduction runs

Δt (s)	$y_p(\dot{W})$ (%)	$y_{max}(\dot{W})$ (%)
900	0.3640	0.4577
1800	0.2985	0.3488
4800	0.0401	0.0551

The largest error amount is (+/-) 0.7 % over all of the runs. Therefore the error included within this report is very small and has no significant influence on the data.

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