Development and Particle Scale Modeling of Metal Oxide Oxygen Carriers in Chemical Looping Applications

Jarrett A Riley

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Development and Particle Scale Modeling of Metal Oxide Oxygen Carriers in Chemical Looping Applications

Jarrett A. Riley

Dissertation submitted
to the College of Engineering and Mineral Resources
at West Virginia University

in partial satisfaction of the requirements for the degree of
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in Chemical Engineering

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Abstract

Development and Particle Scale modeling of Oxygen Carriers for Chemical Looping Applications

Jarrett Riley

Greenhouse gas (GHG) effects and environmental warming due to CO₂ emissions have been considered as the main drivers for climate change. Development of near-term reactor and process engineering solutions by combining fossil fuel based energy production with cost effective and energy-efficient carbon capture are of significant importance to address the challenge of environmental protection and energy sustainability. An Advanced combustion concept called Chemical Looping Combustion (CLC) arose as a bridging technology for clean fuel combustion in energy production with inherent CO₂ capture, while standing out as prospective cost-effective and efficient alternative. CLC relies on the use of an oxygen carrier (OC) to transfer oxygen to the fuel source. The choice of OC is often crucial to the application, making the carrier an essential component in the success of the technology. Herein, a protocol is presented to determine oxygen carrier viability in CLC systems that utilize circulating fluidized bed designs. Key physical and reaction properties are discussed for a designed OC candidate. CuFeAlO₄, copper-ferri-aluminate, was shown to be viable for advancement to pilot scale testing and a promising candidate that could withstand the harsh conditions of CLC.

Following viability verification, a series of kinetic analyses for reduction with common coal related syngas components in gas phase fueled chemical looping combustion applications were used to augment the development and implementation of suitable particle scale representative models for the CuFeAlO₄ oxygen carrier. The work examines the oxygen transfer mechanisms that occur between gaseous fuels and the solid oxide OCs in addition to using a wide array of characterization techniques to provide a thorough understanding of the material as reduction occurs. Reduction occurs in a multistep process that was successfully emulated using a two interface Grainy pellet model. A multi-interface Grainy pellet model was devised to accommodate primary reduced phases and the associated reaction equilibria. The research effort advances knowledge of the application of model descriptions by devising a description that was able to accommodate key aspects based on the reaction phenomena, thermodynamics, solid-state chemistry, oxygen carrier construct morphology, and prevailing rate limiting resistances. Solid-state chemistry changes due to depletion of the lattice oxygen from the cubic spinel structure were quantified to aid in modeling approaches. It was found that as oxygen ions were removed from the lattice in a manner that a secondary cubic spinel structure was generated that ultimately reduced to base components:

\[ \text{CuFeAlO}_4 \xrightarrow{-o^{2-}} \text{Cu} + \text{FeAl}_2\text{O}_4 \xrightarrow{-o^{2-}} \text{Cu} + \text{Fe} + \text{Al}_2\text{O}_3. \]

The research effort advances modelling approaches in Chemical looping applications by accommodating reaction equilibria with key product gases, which provides additional mechanisms for control in CL systems. It was found that FeAl₂O₄ and its reduction products were susceptible to oxidation by soft oxidant products of CO₂ and H₂O. Intrinsic reaction rates with the product gases were orders of magnitude greater than that of the lattice oxygen ion stripping mechanism from the reduction gases. The overall reduction model was shown to be viable for multiple gas
components through a preliminary examination of reduction processes with CH$_4$ and has potential for applicability among a wide range of OCs with similar design and rate limiting conditions.

A secondary research effort was initiated that examined a novel topic concerning the kinetics of oxygen transfer between a group 2 ferrite OC, CaFe$_2$O$_4$, and solid pretreated fuels for Chemical Looping Gasification applications. The research effort advances modelling approaches by representing direct solid-solid interactions between an oxygen carrier and a solid fuel source, a topic that has only recently peaked interest in the scientific community. The work provided particle scale representation for both solid OCs and char based fuel sources that would be used CLG based processes. Accurate and descriptive model representations are pivotal to the advancement of Chemical Looping process concepts as they are essential tools needed for rational reactor design, process scale-up and optimization strategies making the research efforts of this work important to the field of study.
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Chapter 1 Introduction

Greenhouse gas (GHG) effects and environmental changes due to CO\textsubscript{2} emissions have been considered the main drivers for climate change. Emissions from energy production are one of the main contributions to GHGs, accounting for 44\% of the total CO\textsubscript{2} emissions to the atmosphere [1]. Development of near-term reactor and process engineering solutions by combining fossil fuel based energy production with cost effective and energy-efficient carbon capture are of significant importance to address the challenge of environmental protection and energy sustainability. Advanced combustion concepts such as Chemical Looping Combustion (CLC) arose as a bridging technology for clean fuel combustion in energy production with inherent CO\textsubscript{2} capture, while standing out as a cost-effective and efficient alternative [2]. Chemical-looping combustion (CLC) is a novel combustion technology [3-9] that utilizes an oxygen carrier, such as a metal oxide, to transport oxygen from the air to the fuel, inherently avoiding direct contact between fuel and air. The significant advantage of CLC over conventional combustion is a sequestration-ready carbon dioxide (CO\textsubscript{2}) stream can be generated, making this technology advantageous for the reduction of CO\textsubscript{2} emissions without major energy penalties. CLC is divided in to two spatially separated reaction steps, often referred to as reduction (depletion of oxygen from the carrier with a fuel source to form gaseous products and a reduced OC, occurring in the fuel reactor) and oxidation (regeneration of the oxygen deficient carrier with air or other oxidizing media, occurring in the oxidizer), shown in Figure 1-1. The oxygen carrier serves as a medium to selectively transport oxygen from the air reactor to the fuel reactor, while also thermally coupling the reaction half steps. The key advantage of CLC over conventional combustion is the fact that CLC ideally produces a pure mixture of CO\textsubscript{2} and H\textsubscript{2}O as combustion effluent, from which highly concentrated high-pressure (i.e. sequestration-ready) CO\textsubscript{2}-streams can be produced after removal of steam via
simple condensation and compression. CLC avoids the fundamental issues of conventional oxyfuel combustion such as expensive pre-combustion air separation, without the cost and energy penalty of post-combustion CO₂ capture. The technology provides significant promise as an alternative to conventional power generation and CO₂ separation and sequestration [2].

![Chemical Looping Conceptual Schematic](image)

**Figure 1-1: Chemical Looping Conceptual Schematic**

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction</td>
<td>((2n + m)Me_xO_y + C_nH_2m \rightarrow (2n + m)Me_xO_{y-1} + nCO_2 + mH_2O) (E1-1)</td>
</tr>
<tr>
<td>Gasification/Partial Oxidation</td>
<td>(nMe_xO_y + C_nH_2m \rightarrow nMe_xO_{y-1} + nCO + mH_2) (E1-2)</td>
</tr>
<tr>
<td>Fuel-Steam Gasification</td>
<td>(C_nH_2m + H_2O \rightarrow nCO + mH_2) (E1-3)</td>
</tr>
<tr>
<td>Fuel-CO₂ Gasification</td>
<td>(C_nH_2m + CO_2 \rightarrow nCO + mH_2) (E1-4)</td>
</tr>
<tr>
<td>Boudouard</td>
<td>(2CO \leftrightarrow CO_2 + C) (E1-5)</td>
</tr>
<tr>
<td>OC Regeneration: Oxidation</td>
<td>(Me_xO_{y-1} + (0.5)O_2 \rightarrow Me_xO_y) (E1-6)</td>
</tr>
</tbody>
</table>

With the increase in demand for cleaner approaches to generate energy, environmentally friendly and efficient fuel conversion technologies have become exceedingly desirable. Coal is an abundant and relatively inexpensive fuel source [3] so a resurgence in its use as a fuel in Chemical
Looping strategies has been of paramount interest to many researchers [4] [5] [6]. The primary reactions that have been identified for these solid fuel based systems are fuel gasification followed by syngas oxidation to combustion products as shown through Reactions depicted in (E1-1)-(E1-6) [7]. Kinetics for coal gasification and particle scale modeling have been presented due to their necessity in the development of the conventional coal gasification technologies [8]. As the deeper oxidation of coal derived syngas proceeds via interactions with oxygen carriers in CLC, it is important to understand the interaction between the syngas components with the solid oxygen carrier system in order to form a more complete mechanistic profile for implementation of CLC process modeling and optimization/techno-economic assessments. Accurate and descriptive model representations are necessary to the advancement of CLC process concepts as they are pivotal tools needed for rational reactor design, process scale-up and optimization strategies [1].

In addition to exploring topics of CLC, kinetics for a novel coal gasification concept was explored. Coal gasification is an important technology because of its multifaceted nature as an energy producer and the useful chemical products that can be derived from the processing technique [9]. Synthesis gas generated from coal gasification can be used for several purposes ranging from energy generation and hydrogen production [10] to MTH (methanol-to-hydrocarbon) processes [11] [12]. Conventional coal gasification techniques are often plagued with parasitic energy inefficiencies and additional capital expenses because either pure oxygen feed stocks or subsequent nitrogen separation due to product dilution. Alternative technologies that eliminate the need for intensive effluent separations or pure oxygen feed stocks are desirable [13], comparable to the driving force for CLC implementation. Similarly, with the increase in shale gas availability the need for efficient conversion technologies has sparked interest in the utilization of Chemical looping concepts for partial oxidation applications [14]. A resurgence of interest in the use of solid
fuels such as coal, biomass, and derived cokes for the generation of synthesis gas have occurred due to the emergence of novel technologies such as Chemical Looping Gasification (CLG) [9][13-16]. Technologies such as CLG arose from parent process concepts, Chemical Looping Combustion (CLC). Researchers have sought to achieve gasification of solid fuels with this technology through the use of Nickel-based ferrites [15], Calcium sulfates [9], Calcium oxide decorated Iron oxide [13]. Ba-Ferrites and Ca-Ferrites have also shown favorability for this application [16]. CaFe$_2$O$_4$ and BaFe$_2$O$_4$ have high reactivity with coal to produce syngas but have limited and slow reactivity with gas phase components such as CO and H$_2$, making them desirable oxygen carrier candidates for CLG processes. Reactions proceed via solid-mediated interactions and understanding the interactions between the solid chars with these unique metal ferrites is necessary to be able to predict their behavior for the scaling up and advancement of the process concept.

This research effort focuses on topics of both Chemical Looping Combustion and gasification with primary focus on the complete oxidative processes. CLC and related processes rely on the use of an oxygen carrier (OC) to transfer oxygen to the fuel source. The choice of OC is often crucial to the application, making the carrier an essential component in the success of the technologies for their intended purpose. In this work, the oxygen transfer mechanisms that occur between solid and gaseous fuels for CLC and related applications were examined. The ultimate outcome of these evaluations were kinetic model descriptions for the observed behaviors and a thorough understanding of the materials utilized. It was also intended that the techniques developed provide a platform for future researchers in this and related fields to apply for comparative purposes. This platform is developed due to the vast array of descriptions in the literature and the lack of agreement among authors on the use of fundamentally derived models.
and applicable phenomena. A unified approach, that improves particle scale model descriptions, is applied that couples experimental characterization techniques and modeling approaches to answer key questions about oxygen carrier material behavior in these systems.

Explanation of dissertation format

The alternate dissertation format used in this work is designed to incorporate research papers that have been submitted for publication in refereed journals, and co-authored reports that have been written primarily by the first listed author. Consequently, this dissertation presents: (1) a general screening protocol was developed to determine oxygen carrier viability in Chemical Looping Combustion systems. (2) A general overview of significant current literature on particle scale modeling efforts followed by (3) two co-authored research papers that have been submitted to various journals. One of the research works is an experimentally driven study that examines particle scale modeling approaches of a OC candidate deemed viable by the carrier screening protocol. This research work feeds into two other works that are presented in this dissertation. The last abridged peer-reviewed study is a novel work that examines the kinetics of solid mediated interactions for a CLG oxygen carrier. All results are based solely on the author’s work, and represent a contribution to the field of oxygen carrier development and modeling approaches.
Chapter 2  **Oxygen Carrier Viability and Practical screening protocol**

Development of efficient oxygen carriers is essential to successful CLC systems. Oxygen carriers composed of CuO, Fe$_2$O$_3$, and Al$_2$O$_3$ have shown great promise as viable candidates for commercial scale CLC plants through sub-pilot scale (50kW$_{th}$) auto thermal demonstrations [17] [18]. This is due to the synergistic nature resulting in improved reactivity, increased thermal stability and exothermic behavior in both reduction and oxidation environments. The ratio of Cu, Fe, and Al cations can play a significant role in this synergistic response [19] [20]. Oxygen carriers for CLC applications must contain certain desirable properties in order to be considered viable for the application. These desirable properties are high oxygen transfer capacity (OTC), stable reactivity performance, low attrition index (AI), low unit cost and should be considered environmentally benign. These factors have been touched on in a previous work [18] showing that the oxygen carrier that is being examined in this work is viable for pilot scale operation, of which is a monumental step for synthetic oxygen carrier development. In this section, a developed screening method is discussed with a synthetically derived oxygen carrier, stemming from precursor oxides of CuO, Fe$_2$O$_3$, and Al$_2$O$_3$, to show promise of commercial viability.

The assessment method provides a series of standard procedures for which the candidate oxygen carrier is ranked and evaluated based on performance and effectiveness. Ultimately, the goal of the screening process is to display favorable potential for a candidate material use in pilot to a commercial scale CLR unit (Chemical Looping Reactor). Section 2.1 outlines a method for the assessment and evaluation of candidate oxygen carrier materials. The method includes assessment criteria such as oxygen transfer capacity, cycle stability, attrition index, fluidization characteristics, methane conversion, etc.
2.1 Material Screening Protocol:

Screening methods begin with the selection of metal oxide materials that have inherent properties suitable to the application of chemical looping combustion. These materials mostly begin as the by-product of mining industries and/or precursors for metallurgical industries. In cases where these materials are being designed, the individual constituents stem from the aforementioned industries and are manufactured in a manner to provide a cost-effective product. Figure 2-1 displays a logic flow diagram outlining the material screening method after the selection of an oxygen carrier or the creation of a synthetic blend in anticipation of enhanced material properties specific to the application of CLC. In this section a synthetic oxygen carrier derived from precursor oxides of CuO, Fe₂O₃, and Al₂O₃ is evaluated through the protocol and shown to be viable for further evaluation.

2.1.1 Synthesis, Material Structure, Prospective Oxygen Carrier cost:

A rotary drum mixer was used to mix water and dry metal oxide powder precursors (CuO, Fe₂O₃, Al₂O₃) into a spherical pelletized form. When the powders reach an optimal saturation point agglomeration into particles occurred and tumbling was continued until the desired particle size was achieved (200-600µm). After agglomeration, particles were sintered above 1000°C to achieve the desired mechanical properties and phase formation. Combination of the three metal oxide components and calcining above 1000°C allows for the formation of Cu(Fe₂−ₓAlₓ)O₄ (0 ≤ x ≤ 2) spinel structures in which Cu, Fe and Al cations can be substituted into both the tetrahedral A sites and octahedral B sites of the base formula \((A_{1−δ}B_{δ})[A_{δ}B_{2−δ}]O_4\) [21], with an example of this structure displayed in Figure 2-2 with tetrahedral A sites and octahedral B sites denoted by the parenthesis and brackets respectively in the base formula. Fe and Al cations tend to occupy
Figure 2-1: Logic Flow Diagram outlining the screening method of new oxygen carrier materials for CLC applications
the octahedral A and B sites with more favorability than the tetrahedral positions, while Cu
cations tends to only favor the tetrahedral positions due to the cation charge distributions [22] [23].
Based on the ratios of metal cations input into the system and the associated XRD diffraction pattern,
(Figure 2-2, b) a normal cubic spinel structure of CuFeAlO₄ was obtained.

A mixing-tumbling wet granulation method (pelletization) was employed due to the necessity for a commercially acceptable production method. This method has been employed by the iron oxide manufacturing industry for the past 40 years [24]. Shown in Figure 2-3 is a flow diagram of iron ore pellet production from taconite ore deposits. The processing of enriched taconite ore to iron oxide pellets shares many similarities with the production method used to make CuO-Fe₂O₃-Al₂O₃ oxygen carrier. In the iron oxide pelletization process, Fe-concentrate (which is primarily magnetite, Fe₃O₄) is blended with approximately 10wt% bentonite for binding and the mixture is pelletized via a wet agglomeration method in balling drums. The green pellets are sieved between a range of 1-5mm. Undersized pellets are returned to the balling drums for additional growth while oversized pellets are sent to crushing mills for re-use. These are all avenues to increase the desired pellet size yield. After screening, the pellets undergo a process called induration, or pellet hardening.

Figure 2-2: (a) Crystal Structure of Cu(Feₓ-Alₓ)O₄ (0 ≤ x ≤ 2) spinel in cubic phase [102] (b) XRD of CuFeAlO₄ (x=1) material under evaluation

Figure 2-2: (a) Crystal Structure of Cu(Feₓ-Alₓ)O₄ (0 ≤ x ≤ 2) spinel in cubic phase [102] (b) XRD of CuFeAlO₄ (x=1) material under evaluation
This process is accomplished by heating the pellets to the incipient fusion temperature (IFT) for time ranging between 10 minutes to 3 hours. Heating the pellets to IFT allows for the desired strength properties to be attained. The IFT is a phenomenon that occurs when the material at the grain boundaries begins to melt prior to the rest of the material [27]. This melting allows bonds to form between individual grains and increases the strength of the material, additionally new phase formation can occur. These temperatures can vary widely depending upon the composition of the material. Table 2-1 compares the depicted pelletization process with the one employed to produce the CuFeAlO₄ OC.
Table 2-1: Comparison of Industrial Iron Ore Pelletization to current Oxygen carrier production method

<table>
<thead>
<tr>
<th>Property</th>
<th>Iron Oxide Pellets</th>
<th>CuO-Fe₂O₃-Al₂O₃ Pellets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production Method</td>
<td>Tumbling</td>
<td>Tumbling</td>
</tr>
<tr>
<td>Desired Particle Size Range</td>
<td>1-5 mm</td>
<td>200-600 μm</td>
</tr>
<tr>
<td>Induration Temperature</td>
<td>1200-1400°C</td>
<td>1000-1200°C</td>
</tr>
<tr>
<td>Induration Time</td>
<td>360-720 min</td>
<td>360-720 min</td>
</tr>
<tr>
<td>Type of process</td>
<td>Semi-Batch</td>
<td>Batch</td>
</tr>
</tbody>
</table>

The production methods are comparable with the only minor differences being the extent of the induration process and the desired pellet size range, both of which are adaptable process parameters. The major difference between iron oxide pellet manufacturing and the proposed oxygen carrier is apparent with the feed stocks used to generate the materials. Noting this, iron oxide pellet production can serve as a benchmark process to gain an idea for the cost to produce oxygen carriers on a much larger scale by applying additional costs associated with raw material feedstocks. To establish a benchmark for production costs associated with pelletization, the market price for iron oxide pellets and Enriched Iron oxide fines are examined. Shown in Figure 2-4 are the market prices, in 2017 USD, for both components and the mean difference between the two products. From the mean difference, a production cost estimate can be derived which can be applied to the oxygen carrier production method. Production cost average at $23.9±5 per ton of
material. This value is similar to quantities, ($34.3 per ton in 2001) reported by Heller and Yang et al [24]. Market prices of the precursor oxide feedstocks are presented in Figure 2-5.

Figure 2-5: Market Price Analysis of Raw materials for CuO-Fe₂O₃-Al₂O₃ production (a) CuO market price based on Cu content, (b) Al₂O₃ and Iron ore fines market price based in 2017 USD [103]
The market price of CuO can vary and does not have a definitive trackable price as a commodity item like Alumina and iron ore. To provide an estimate of the market price, the market price of CuO is determined based on its Cu content, which is approximately 79.9 wt.%. This allows for the use of Cu market price which can be scaled by the Cu content in CuO. Market prices for CuO average $3800/ton and Al₂O₃ averages $294/ton. Table 2-2 combines the market values and estimated conservative production cost to show a derived production cost for the oxygen carrier material.

Table 2-2: Estimated production cost of CuFeAlO₄ Oxygen Carrier based on market analysis and comparable production method

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>3800</td>
<td>30</td>
<td>1140</td>
<td>Cumulative Estimated material cost</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>58</td>
<td>30</td>
<td>17.4</td>
<td>Manufacturing Costs</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>294</td>
<td>40</td>
<td>117.6</td>
<td>Total</td>
</tr>
</tbody>
</table>

Based on this simplified analysis, production costs are estimated to be around $1.5/kg, making it an acceptable candidate for further screening.

2.1.2 Particle size selection:

An initial size selection is done to refine the distribution to a range that is applicable for direct use with the CLR unit. In the logic flow diagram, a size range of 200-600 µm is displayed and this corresponds to the development of pelletized synthetic oxygen carriers for use in NETL’s 50kWth Chemical Looping reactor (CLR) unit. This criterion can be modulated based on the material properties and particle size limitations set by the design of the CLR unit.
2.1.3 Initial Reduction (20% CH₄ Balanced by inert carrier gas) and Oxidation (Air) Reactivity (TGA methods):

The starting point for determining a material’s reactive potential, in terms of its ability to transfer oxygen to a fuel source and then return to a stable state after accepting oxygen from a gaseous source, is quantified using Thermogravimetric Analysis (TGA). Oxygen carriers (OC) are cycled in a manner to reflect their movements between the fuel and air reactors of the CLR under isothermal conditions at 800°C. This temperature is chosen because it is the nominal temperature used for the CLR unit [28]. Oxygen carriers are subjected to ten Reduction/Oxidation Cycle tests where the material is initially heated to 800°C at 10 °C/min and held isothermally at this temperature for the remainder of the experiment. During the isothermal hold, the OC is subjected to a reduction and oxidation segment to complete a full cycle. During the reduction segment, materials are exposed to 20%CH₄ balanced by Argon. Flow set points are equipment specific and often dependent upon the sample mass chosen. For consistency among samples, a 60-mg sample mass is used as well as flow set points of 20 ml/min from the balance chamber and 80 ml/min from the sample port. Reduction and oxidation segments are both limited to ten minutes to provide consistent sampling conditions for comparative purposes. Thermo-gravimetric analyses are conducted with a TA model 2050 (Q50) coupled with a mass spectrometer (Pfeiffer thermostat D-35614) to examine effluent compositions [29].

There are five major criteria extrapolated from the cyclic testing carried out using thermogravimetric analysis. These include oxygen transfer capacity, rate of reduction, coking potential, rate of oxidation, and overall cycle stability.

The oxygen transfer capacity is defined as the total mass of oxygen that the oxygen carrier can exchange with a fuel source during a given time period and is depicted in (E2-1).
Development and Particle Scale Modeling of Metal Oxide Oxygen Carriers for CL applications

\[ OTC \, (\%) = \frac{m_i - m_f}{m_i} \quad (E2-1) \]

Where \( m_i \) is the initial mass of the sample prior to introduction of a reducing gas (20% CH\(_4\) Bal Argon) and \( m_f \) is the final weight of the sample after the reduction segment has ended. Rate of reduction and rate of oxidation are quantified as the instantaneous change in the mass of the material at any given time point during the reduction or oxidation segment, depending upon the segment of interest. Rate of reduction and oxidation are defined in (E2-2) and (E2-3) respectively.

\[ R_{\text{reduction}} = \frac{dm_{\text{reduction}}}{dt} = \frac{m_r - m_{r+\delta}}{t_r - t_{r+\delta}}, \delta \to 0 \quad (E2-2) \]

\[ R_{\text{oxidation}} = \frac{dm_{\text{oxidation}}}{dt} = \frac{m_o - m_{o+\delta}}{t_o - t_{o+\delta}}, \delta \to 0 \quad (E2-3) \]

Rates associated with reduction and oxidation can shed light on how quickly a material can achieve the overall oxygen transfer capacity and return to the original oxidized state.

Coking may occur when methane begins to decompose on exposed metal active sites on the surface of the oxygen carrier during reduction. This phenomenon typically occurs near the end of reduction segments where the material has surface partial-reduced metal phase that can promote the decomposition of methane. The onset of this behavior is denoted by slowing of the reduction rate during weight loss followed by weight gains associated with carbon deposition on the surface. The identification of the extent of coking and the time frame by which it occurs can shed light on the maximum residence times for the application of the material types in the CLR when natural gas is used as a fuel source. Coking potential is quantified by examining the time frame by which it
begins to occur in the reduction segment and the extent of mass gain due to carbon deposition, (E2-4).

\[ t = n \text{ minutes, } \text{Coking (\%)} = \frac{m_{f,c} - m_{i,c}}{m_{f,c}} \]  

(E2-4)

Where \( m_{f,c} \) is the final mass of the sample at the end of the reduction segment in instances with coking and \( m_{i,c} \) is the initial weight of the sample recorded after the onset of carbon deposition. To explore all these criteria in detail, a 10-cycle test of a pelletized CuFeAlO\(_4\) oxygen carrier shown in Figure 2-6 and examined in Figure 2-7-Figure 2-8.

*Figure 2-6: 10 Cycle Experiment with Pelletized CuFeAlO\(_4\) Oxygen Carrier 213-582 \( \mu \)m*
Figure 2-6 displays a typical 10 cycle TGA test. It can be observed that there are modulations in the oxygen transfer capacity, due to an initial period of activation followed by stabilization. There are also subtle changes including an oxygen uncoupling response during the segments prior to reduction, minor changes in reduction and oxidation rate, and some segments where carbon deposition occurs in the later portion of the reduction segment. Figure 2-7 displays an example where the oxygen transfer capacity is determined for cycles 1 and 2.

Cycling stability is quantified by examining the standard deviation and the skewness from the mean oxygen transfer capacity over the course of the 10-cycle test. For this particular experiment, the mean OTC falls in the range of 11% with a standard deviation of 0.38%. If this value falls within 2.5% then it can be noted that a steady state will likely be achieved. In the event that a period of activation or deactivation would occur with a standard deviation greater than 2.5%, then a cycling experiment of 25-50 cycles should be explored to examine the extent of activation/deactivation and the OTC associated with the steady state achieved to see if this falls within the minimum criterion rating (OTC > 5%, in the case of deactivation) to move forward with the oxygen carrier screening. Cycle stability is also quantified in terms of rate. Figure 2-8 displays the instantaneous rates for both the reduction and oxidation segments of the first 5 cycles for the same experiment.
Figure 2-8: Rate of Reduction and Oxidation Example - Cycles 1-5 of 10 Cycle test with 213-582 micron pelletized CuFeAlO₄ OC

The criterion limits for reduction and oxidation rates are similar to those used for OTC. If there is low amount of variation in the distribution of rates and the skewness appears to be relatively small, then it can be anticipated that there is minimal likelihood for material deactivation and that the material will return to its initial oxidized state. A statistical analysis of the 10-cycle test is shown in Table A-A1, Appendix A. The material meets criterion specifications for OTC and cycle stability.

2.1.4 Fresh Attrition Evaluation:

If a material meets the criterion specifications for OTC and cycle stability, then the next step is to evaluate the attrition index over a 5-hour test period. Attrition index evaluations are done with guidance from ASTM D5757-11: Standard test method for the determination of attrition of FCC
catalyst by air jets [30]. Refer to ASTM D5757-11 for the design specifications of the attrition index evaluation unit and detailed test methods. Oxygen carriers of the desired size range are compared to a FCC standard, as these are the standard materials for circulating fluidized bed systems. Attrition indices provide a benchmark for material losses due to wearing and ejection of fine constituents during harsh fluidization conditions over extended time periods. The attrition indices for the sample during these time segments are calculated in accordance with (E2-5 through (E2-7). The recovery percentage can also be quantified using (E2-8).

\[
\text{Attrition Index, } 1^{st} \text{ hour} \ (\%) = \left( \frac{m_1 - m_0}{m_s} \right) \times 100 \tag{E2-5}
\]

\[
\text{Attrition Index, } 3^{rd} \text{ hour} \ (\%) = \left( \frac{m_1 - m_0 + m_3 - m_0'}{m_s} \right) \times 100 \tag{E2-6}
\]

\[
\text{Attrition Index, } 5^{th} \text{ hour} \ (\%) = \left( \frac{m_1 - m_0 + m_3 - m_0' + m_5 - m_0''}{m_s} \right) \times 100 \tag{E2-7}
\]

\[
\text{Recovery} \ (\%) = \left( \frac{m_r + m_1 - m_0 + m_3 - m_0' + m_5 - m_0''}{m_s} \right) \times 100 \tag{E2-8}
\]

Where \( m_0 \) is mass of the first empty fines collection assembly (filter), \( m_1 \) is the mass of the first fines collection assembly (filter) at 1 hour, and \( m_s \) is the mass of the mass of the sample charged to the apparatus (nominally 50g). For sampling during the third and fifth hour segments, \( m_0' \) is mass of the second empty fines collection assembly (filter), \( m_3 \) is the mass of the second fines collection assembly (filter) at 3 hours, \( m_0'' \) is mass of the third empty fines collection assembly (filter), \( m_5 \) is the mass of the third fines collection assembly (filter) at 5 hours, and \( m_r \) is the mass of the sample recovered from the attrition tube and settling chamber.
To satisfy the attrition index criterion when evaluating a fresh sample, the attrition indices must be less than that of the FCC standard over the 5-hour test period. This provides a benchmark until an oxygen carrier of suitable performance is established as a standard test material. Figure 2-9 displays an example of the results of a 5-hour attrition evaluation with 213-582 micron pelletized CuFeAlO₄ oxygen carrier.

Figure 2-9: Attrition Index Evaluation Example - Comparison of Fresh Pelletized CuFeAlO₄ OC with FCC standard

It can be observed that the material loss due to attrition are less than the FCC standard so the material can move to the next test criterion in the screening protocol.

2.1.5 Material Ambient Minimum Fluidization Velocity Characterization:

If a material meets the passing criterion for fresh attrition indices, then it is subjected to granular/powder material characterizations. These characterizations consist of a concise size and shape analysis, helium pycnometry to determine skeletal density, and bench scale minimum fluidization experiments [31].
i. **Size and Shape Analysis:**

Particle size distributions, Sauter mean diameter, aspect ratio, and sphericity are obtained using a SympaTEC – QICPIC Particle Analyzer following ASTM standards B822 [32] and E2651 [33] and ISO Standard 13322-2 [34]. For detailed discussion of the sampling method refer to Tucker et al [31]. Figure 2-10 displays the particle size distribution and sphericity determined from this type of analysis for CuFeAlO₄ pelletized oxygen carrier.

![Graph showing particle size distribution and sphericity](image)

**Figure 2-10:** Particle Size distribution and sphericity determination of CuFeAlO₄ 213-582µm

ii. **Skeletal density:**

Skeletal densities of particles are obtained using a Micrometrics – AccuPyc 1330 Helium Pycnometer. Skeletal Densities are determined using methodology derived from ISO standard 12154 [35] and ASTM B923 [36]. For detailed discussion of the sampling method refer to Tucker et al [31].

iii. **Bulk/Packed Densities and Minimum Fluidization at Room Temperature:**

Minimum fluidization velocity measurements are conducted in accordance with methods
developed by Tucker et al [31] as an adaption to industrially accepted practices and in accordance with ASTM D7743 [37]. The measurement procedures for minimum fluidization, void fraction and packed/fluffed densities of the materials have been well-established. As an example of the culmination of these test methods, the minimum fluidization velocity as well as void fraction are presented in Figure 2-11 for pelletized CuFeAlO$_4$ OC.

**Figure 2-11: Minimum Fluidization Velocity and Void fraction determination for CuFeAlO$_4$ 213-582 µm**

### 2.1.6 Minimum Fluidization Velocity Experiments at 800 °C – SFBR:

Minimum fluidization experiments are also conducted in the Bench scale FBR unit at 800°C. These procedures are performed to verify any changes in fluidization properties at operating temperatures. This test serves as a verification associated with the ambient temperature experiments therefore, properties such as the packed/fluffed density and void fraction are held constant in agreement with the ambient temperature experiments. A similar test methodology to the ambient temperature experiments is used to quantify the minimum fluidization velocities at operating temperature regimes. Materials are subjected to a sinusoidal ramping flow rate with a period of 600 seconds, where the maximum chosen flow rate is approached at 300 seconds and the remaining segment is associated with the de-fluidization of the material. The maximum chosen
flow rate is typically 2-3 times what would be necessary to fluidize the material based on ambient temperature experiments. The Pressure drop across the bed ($\Delta P_{\text{bed}}$) is measured throughout the ramp. When the material begins to fluidize the $\Delta P_{\text{bed}}$ approaches a constant value. The flow rate associated with onset of constant $\Delta P_{\text{bed}}$ is used to determine the minimum fluidization velocity. Velocities determined from the ramp segments are averaged in accordance with common practice, as there may be some hysteresis associated with the fluidization segments. Defluidization segments typically lack hysteresis. Minimum fluidization velocities determined at operating temperature are applied when a material is subjected to 25 cycle testing in the FBR as outlined in section 2.1.7.

### 2.1.7 25 Cycle Red-Ox Experiments with 20% CH₄ at 800°C and 1.2 XUMF – Fluidized Bed Reactor:

The next stage in the screening of the oxygen carrier material was to evaluate the performance in fluidizing and emulative reacting conditions over a 25-cycle period at 800°C, mimicking fluidization regimes in the fuel reactor of the CLR. A description of the experimental setup is shown in Figure 2-12.

![Figure 2-12: Bench Scale Fluidized Bed Reactor Setup](image)
A number of mass flow controllers are used to control the reaction environment as well as the degree of fluidization. The setup is discussed in more detail by Bayham et al. [38] in their work for the evaluation of Hematite reactivity with methane and steam.

Run procedures for a 25 cycle test series consist of a number of segments that create a full reduction and oxidation cycle:

1. **Heat up segment**
2. **Reduction segment**
3. **Purge Segment**
4. **Oxidation Segment**
5. **Purge segment**
6. **Repeat steps 2-5 for another 24 cycles**

In the heat up segment, the unit is heated to 800 °C at a ramp rate of 10°C/min after 1000g of OC materials have been loaded and the system leak checked. In the reduction segment of the first cycle, 20% methane is introduced for a predetermined time based on total methane throughput. This establishes a comparative baseline. Following the reduction segment, a purge of 25L with an inert gas is used to flush out the remaining gases in preparation for the oxidation segment. In the oxidation segment, air is introduced into the reactor to oxidize the depleted carrier. After oxidation, the reactor is purged with an inert gas 25L. This procedure is repeated for a total of 25 cycles. During all segments the necessary flow rates to establish 1.2xUMF are maintained following the constraints outlined in the previous section.

*Note about reduction and oxidation segments:* Reduction segment times are determined based on a set amount of methane introduced to the oxygen carrier (**1.0 mole**) and the flow rates necessary to achieve 1.2xUMF. This value is chosen to establish a benchmark for comparative purposes.
The total number of moles of methane are estimated by converting the volumetric flow rate to a molar flow rate by assuming that the gas obeys the idea gas law. Segment time is established by solving for the time necessary to introduce the benchmark molar quantity of methane. Oxidation times are determined based on oxygen breakthrough and are extended to 10 minutes past oxygen breakthrough to ensure that oxygen carrier has sufficient time to re-oxidize. The FBR unit has several filter loops connected the effluent. Flows are switched to an adjacent filter assembly and the contents of the filter examined after every 5th oxidation cycle.

Four major criteria are examined over the course of the 25-cycle test period. These include methane conversion, oxygen transfer, cycle stability, and in-situ filter collection. Methane conversion is extrapolated based on the measurements of the effluent concentrations and defined in (E2-9).

\[
\text{Methane Conversion (\%)} = \left( \frac{CH_{4,\text{fed}} - CH_{4,\text{breakthrough}}}{CH_{4,\text{fed}}} \right) \times 100 \quad \text{(E2-9)}
\]

Where \(CH_{4,\text{fed}}\) is the total amount of methane fed into the reactor for the reduction segment and \(CH_{4,\text{breakthrough}}\) is the total amount of methane that bypassed the oxygen carrier and were not converted to \(CO_2\) and \(H_2O\).

Oxygen transfer during the reduction segment is estimated through the use of the effluent concentration of \(CO_2\). The total number of moles of \(CO_2\) are determined for the reduction cycle through integration of the constituent’s molar flow profile. This is considered an estimate because the number of moles of \(H_2O\) cannot be directly measured in the setup, therefore it is estimated that for every mole of \(CO_2\) generated 2 moles of \(H_2O\) are formed in accordance with combustion stoichiometry. The quantity of molecular oxygen exchanged to the carbon source can then be
extrapolated and correlated to the quantity that is present in the OC loaded in the reactor, OTC, shown in (E2-10).

\[
OTC(\%) = \left( \frac{\text{Moles of Molecular Oxygen determined from effluent products}}{\text{Moles of molecular oxygen available in loaded OC sample}} \right) \times 100 \quad (E2-10)
\]

Carbon balances can also be evaluated through the extrapolation of the number of moles of carbon from measured CO$_2$ and CH$_4$ quantities over the course of the reduction cycle. The quantity of carbon entering the reactor can be determined based on the methane feed and total reduction time. The carbon exiting the reactor is assumed to only be in the form of product CO$_2$ or CH$_4$ that has bypassed the carrier.

Cycle stability is also examined in a similar manner to techniques used in the examination of TGA data. In this case, the methane conversion for each cycle is compared to the mean methane conversion and the variance/skewness quantified based on the deviation from the mean. Standard deviation limits on methane conversion over the course of the test series can extend to values of ±10% as long as the lower conversion limit remains above 75%. Figure 2-13 displays an example of a typical reduction segment in the FBR, corresponding to the 5th reduction segment and the trends in conversion with respect to cycle number.

It can be observed that methane conversion maintains above 90% with minor deviation from the mean over the course of the 25-cycle test period, attributing a standard deviation in conversion of 1.7%. Figure 2-14 displays the OTC based on the evaluation of the effluent products and cumulative attrition via filter collection over the course of the test. The material satisfies the criterion for methane conversion & OTC, cycle stability and attrition resistance, showing high stable reactivity with maintained material strength.
Figure 2-13: (a) 5th Reduction Segment in SFBR & (b) methane conversion with respect to cycle number for 25 Cycle test series with CuFeAlO$_4$ 213-582 µm pelletized OC.

Figure 2-14: (a) Oxygen transfer based on the production of CO$_2$ for 25 Cycle test series with CuFeAlO$_4$ 213-582 µm pelletized OC (b) In-situ filter collection
2.1.8 **Attrition Index Evaluation Post 25 Cycle FBR Test:**

In order to satisfy the post cycling attrition index criterion, the reacted sample must have attrition indices that are less than or equal to the FCC standard over the 5-hour test period. Establishing this upper limit provides a benchmark for a safe range of operation.

Figure 2-15 displays the results of a 5-hour attrition evaluation with reacted 213-582 micron pelletized CuFeAlO$_4$ oxygen carrier. It can be observed that the material’s attrition indices lie below that of the FCC standard, so the criterion is within acceptable limits and the material is feasible for trial use in the CLR.
The attrition evaluation represents an extreme case where materials are subjected to superficial jetting velocities $\geq 400$ m/s. These superficial velocities would be about 20x what would be seen in the harshest sections of a CLR unit [28].

Following a successful material screening, a viable candidate, in this case, the CuFeAlO$_4$ oxygen carrier is worth further evaluation. These areas include pilot scale testing to get real operational data for feasibility assessments, kinetic analyses for the development of predictive particle scale models, and particulate attrition modeling to understand OC lifetime/replacement rates in the CLR system. The focus of this work is on the experimental techniques and modeling approaches needed to determine feasible particle scale models for viable oxygen carrier candidates. The subsequent sections will discuss these methods for the CuFeAlO$_4$ oxygen carrier. In addition, a supplementary chapter has been added for kinetic analysis of solid mediated interaction between
Development and Particle Scale Modeling of Metal Oxide Oxygen Carriers for CL applications

a Calcium ferrite oxygen carrier and coal char due to the novelty of the work. This supplementary section is for an alternate Chemical Looping application called CLG.

2.2 Prospective Kinetic and Particle Scale Modeling of viable OC candidates

There is a vast array of approaches to modeling of oxygen carriers in the literature. In this section, a rational overview with key criteria is presented to provide an idea of what should be considered when approaching the kinetics and particle scale modeling of oxygen carriers. Figure 2-16 displays a flow diagram for an overview of critical areas in kinetic analysis and particle scale modeling of oxygen carrier materials for Chemical Looping Applications. The kinetics associated with reduction and oxidation for metal oxide carrier materials have four major aspects that feed into particle scale model selection. These include reaction phenomena, solid state chemistry, oxygen carrier morphology, and interconnected are the thermodynamics associated with the reacting system. Each aspect has key variables that impact the ultimate selection of a model and drives the experimental approaches to make sure that all the critical variables and their functionality are included.

Key operational variables in the Chemical looping system including temperature, reactive and product gas concentration and pressure. All of these variables impact how oxygen is removed or returned to the carrier depending upon where the material is located in the circulating system. Reaction phenomena influence parameters such as the activation energy, reaction order, and can shed light on phenomena such as equilibrium; of which is inherently linked to the thermodynamics of the system. The response of the material to these variables will influence the model chosen to emulate the appropriate behavior. With this noted, model or models chosen should include these key variables if found to be of significant importance.
Solid state chemistry plays a major role in the selection of a model. This aspect sheds light on the crystal structure of the material and how it changes as oxygen is depleted or added depending upon location in the system. Analysis of crystal structure as a function of oxygen depletion/addition allows for a reduction/oxidation pathway to be developed. The pathway denotes the initial and final states as well as any intermediates that emerge to accommodate changes in the lattice structure. The reduction/oxidation pathway is a critical aspect of the modeling because it denotes how many steps are in the coupled reaction mechanism [39] [40]. It also denotes whether the reaction mechanism is sequential or parallel if multistep. This aspect becomes exceedingly important when dealing with non-standard metal oxides with unknown reduction/oxidation pathways. Materials such as Fe2O3, CuO, and Mn2O3 have well characterized pathways due to their links in metallurgy and are considered standard metal oxides. However, with non-standard metal oxides these pathways cannot be inferred based on the precursor oxides used to make the complex materials such as CuFeAlO4, the main subject of this work. Experimental approaches are necessary to deduce these pathways and these methods will be discussed in later chapters.

Macroscopic and microscopic morphology of the material directly influence the derivation of the model used to emulate changes due to reaction. For instance, with the case of the CuFeAlO4 OC a tumbling agglomeration method is used to synthesize a spherical pellet (pelletization). It is likely that a model with spherical geometry will be best suited for use and this will be discussed in later chapters. Other material properties such as surface area and porosity can impact the movement of gaseous species internally in the material construct. Knowing how prominent these variables are will influence whether a certain controlling regime should be considered. Controlling regimes are denoted by the magnitude of a certain rate
controlling factor that influences the solid-state chemistry changes in the material construct. These regimes are split up into 4 main categories.

(1) External mass transfer controlled, often referred to as Film Diffusion.
(2) Reaction controlled
(3) Internal Mass Transfer Controlled, often referred to as Product Layer Diffusion
(4) Solid-State Diffusion Controlled

There exist situations where the magnitude of these rate controlling factors can be equivalent and in those cases a combinatory regime would be used. The presence of a controlling regime impacts the derivation of the representative particle scale model as it directly impacts the boundary conditions and assumptions used to derive an analytical expression. This will be discussed in Chapter Chapter 3.

When a depictive model is developed and optimized to best represent the material and its associated reaction phenomena, solid state chemistry, and morphology, a series techno-economic assessments can be conducted [2], allowing for rational reactor design and the implementation of scale up strategies. In-addition, higher fidelity simulations such as those conducted in computational fluid dynamics [41] can be employed by applying models derived using the methods in this work, making them directly applicable for further utilization.
Development and Particle Scale Modeling of Metal Oxide Oxygen Carriers for CL applications

Figure 2-16: Logic Flow diagram for the kinetic and particle scale modeling of viable candidate oxygen carriers
Chapter 3 Conceptual Kinetic Particle Scale Models for Oxygen Transfer in Chemical Looping Applications:

The reduction of oxygen carriers in a fuel reactor and oxidation in the air reactor have a significant influence on the conversion and thermal efficiency of chemical looping system [7]. Historically the reduction process has been treated as a network of gas–solid reactions as discussed in Chapter Chapter 1. Numerous kinetic models have been proposed to explain the influence of reactor conditions on the kinetic rate of oxygen transfer both to and from the solid with the ultimate outcome to predict transient solid conversion responses. Oxygen carriers primarily consist of metal oxides, so the reduction reaction is inherently accompanied by the consumption of surface and lattice oxygen as a result of mass transfer between the solid particles and gas atmospheres [42].

Typical kinetic models employed to describe these transfer mechanisms are the shrinking core model (SCM), the pellet model (PM), and the nucleation and nuclei growth model (NNGM). In this section, these models are discussed, and their limitations and assumptions are examined. Some less commonly used models are also reviewed including models for solid-solid reactions.

3.1 Shrinking Core Model (SCM):

The unreacted shrinking core model was first developed by Yagi and Kunii [43] refined by others [44] and used for CL applications [45] [46] [47]. The derivation is based on differential shell balances on a reacting sphere of which three characteristic resistances were considered for the generalized gas-solid reaction as displayed in (E3-1. The shrinking core model links the change of reduction/oxidation degree of the solid with the change in radius of an unreacted core of a sphere.
\[ aA(g) + bB(s) \rightarrow cC(g) + dD(s) \]  

These resistances include film (external) mass transfer, product layer diffusion (internal mass transfer) and reaction (kinetic) control as depicted in a rate based form in (E3-2):

\[
- \frac{dr_c}{dt} = \frac{b C_A / \rho_B}{\frac{R_i^2 k_g}{f_{ilm}}} + \frac{(R_i - r_c) r_c}{R_i D_e} + \frac{1}{k'''_{\text{reaction}}} 
\]

where \( r_c \) is the core radius of the OC, \( R_i \) is the radius of the OC, \( b \) is OC stoichiometric coefficient, \( C_A \) is the concentration of A in the gas phase, \( \rho_B \) is the density of the OC, \( k_g \) is the mass transfer coefficient of the gaseous reactant, \( D_e \) is the effective diffusion coefficient in the product layer, \( k'' \) is the specific reaction rate constant of the unreacted core of a single particle. The rate of the advancing core front can be expressed in terms of the overall solid conversion, \( X_p \), by application of the relation outline in (E3-3 resulting in (E3-4):

\[
1 - X_p = (\gamma)^3 \text{, where } \gamma = \frac{r_c}{R_i} 
\]

\[
\frac{dX_p}{dt} = \frac{b \frac{3}{R_i} C_A / \rho_B}{\frac{1}{\gamma^2 k_g f_{ilm}}} + \frac{(R_i) \left( \frac{1}{(1 - X_p)^3} \right) - 1}{D_e (1 - X_p)^3} + \frac{1}{(1 - X_p)^{2/3} k'''_{\text{reaction}}} 
\]

This description is derived based on the following assumptions: (a) the oxygen carrier is considered non-porous, (b) the particle is considered spherical, (c) crystallite size/volume is constant during the reaction, (d) the reaction is isothermal, (e) the reaction is first order with respect to the concentration of A, (f) the quasi-steady state approximation is applicable. The quasi-steady
state approximation assumes that the concentration gradient of A in the product layer is not a function of time but solely a function of the core position, \( r_c \) and intern this assumes a constant flux of A into the reacting particle. This model can be applied for a number of aspects where \( R_i \) is considered as the individual grain size in the spherical particle and the particle reacts uniformly with respect to the consumption of its individual grains. It can also be considered for overall particle conversion. Further simplifications can be made to the SCM model based on the rate limiting step. External mass transfer limitations can be evaluated by examining the relative magnitudes of the specific reaction rate with respect to the radial flux of the reaction gas. Internal mass transfer limitations can be evaluated through examination of the Weitz parameter criterion. For a detailed discussion and example of this evaluation see reference [48]. If the aforementioned limitations are found to be negligible resistances, then the SCM is considered under reaction control and can be expressed in a simplified form as shown in (E3-5) and (E3-6. Conversely, if internal diffusional resistances are found to be rate controlling then the SCM can be simplified to (E3-7).

\[
\frac{dX_p}{dt} = \frac{b}{R_i} \frac{3}{1} \frac{C_A}{\rho_B} \left( \frac{1}{1 - X_p} \right)^{2/3} \frac{k^e}{k^o} \tag{E3-5}
\]

\[
\frac{t}{\tau_R} = 1 - \left( 1 - X_p \right)^{1/3}, \quad \tau_R = \frac{\rho_B R_i}{b k^o C_A} \tag{E3-6}
\]

\[
\frac{t}{\tau_D} = 1 - 3 \left( 1 - X_p \right)^2 + 2(1 - X_p), \quad \tau_D = \frac{\rho_B R_i^2}{6 b D_e C_A} \tag{E3-7}
\]
3.2 Pellet Model (PM):

Other authors [49] [44] have proposed variations for the SCM for irregularly shaped particles that include both reaction and internal diffusional resistances as rate controlling aspects.

\[
\frac{dX_p}{dt} = \frac{1}{g_{F_p} \rho_B} \frac{bk^* \left( \frac{1}{R_i} \right) C_A}{1 - \frac{k' R_i}{2(2 - F_p) D_e g_{F_p}^t} P_{F_p}'}
\]

Where \( P_{F_p}' \) and \( g_{F_p}' \) are conversion function derivatives for internal diffusion and chemical reaction control for the particle and grain respectively, as displayed in (E3-9 & E3-10).

\[
P_{F_p}' = -\frac{2}{F_p} \left[ V_{pt} + (1 - V_{pt}) \left( 1 - X_p \right) \right]^{2-F_p}_{F_p} + \frac{2}{F_p} \left( 1 - X_p \right)^{2-F_p}_{F_p}
\]

\[
g_{F_p}' = \frac{1}{F_p} (1 - X_p)^{1-F_p}_{F_p - 1}
\]

With \( F_p \) describing the shape factor of the particle or grain and \( V_{pt} \) describing the volume of product formed per unit volume of reactant if significant volume changes occur during solid consumption, refer to [49] for detailed explanations of the later. When \( F_p \) is equal to 3 the characteristic expression for the SCM is obtained. There also exist permutations where \( F_p \) can be different for both grain and pellet geometry.

3.3 Unsteady State Diffusion Model (USSDM):

Sarshar [50] and others [51] [52] proposed the use of unsteady state oxygen ion diffusion models for the reduction of perovskite based OCs assuming that the rate limiting process was the bulk diffusion of \( O^{2-} \) to the material’s surface. The unsteady state diffusion profile within a spherical solid assuming that the external surface concentration \( C_o \) of the diffusing species is constant with time is displayed in (E3-11 and associated particle conversion in (E3-12).
\[
\frac{C_1 - C}{C_1 - C_0} = 1 - \frac{2a}{\pi r_p} \sin \left( \frac{\pi r_p}{a} \right) \exp \left( -\frac{D_{O_2} - \pi^2 t}{a^2} \right) \quad (E3-11)
\]

\[
X_p = \frac{1}{a} \int_0^a \left[ 1 - \frac{2a}{\pi r_p} \sin \left( \frac{\pi r_p}{a} \right) \exp \left( -\frac{D_{O_2} - \pi^2 t}{a^2} \right) \right] \, dr_p \quad (E3-12)
\]

3.4 Continuous Model (CM):

Melchiori and Canu [45] performed a critical analysis on the SCM and its fundamental assumptions used for the derivation depicted in (E3-4. From this analysis, several limitations were discussed and a simplified version of a continuous model (CM) proposed for use. The governing assumptions used to generate the expression are (a) the gas mixture is only composed of A and C, (b) the MW of solid species B and D are almost the same, as well as their intrinsic densities considering the porosity is constant. (c) The system is isothermal and isobaric. (d) The external mass transfer is fast, concentration at the particle surface is the same as the bulk. (e) The reaction is equimolar in A = C. Under the specified assumptions for gas reactant A and solid B and expression can be defined.

\[
\varepsilon \frac{\partial C_A}{\partial t} = D_{AC} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_A}{\partial r} \right) - bk(1 - X)^a C_A \quad (E3-13)
\]

\[
\frac{\partial C_B}{\partial t} = -ak(1 - X)^a C_A \quad (E3-14)
\]

With the boundary conditions are:

\[
r = 0 \quad \frac{\partial C_A}{\partial r} = 0 \quad (E3-15)
\]

\[
r = r_0 \quad C_A = C_{A, Bulk} \quad (E3-16)
\]
\[ t = 0 \quad C_A = C_A^0 \quad C_B = C_B^0 \]  
\text{(E3-17)}

E3-13 & (E3-14) can be nondimensionalized through the application of non-dimensional variables and numbers:

\[ \theta = \frac{t}{t^*}, \quad \lambda = \frac{r}{r_0}, \quad Y = \frac{C_A}{C_{A,\text{Bulk}}}, \quad X = 1 - \frac{C_B}{C_B^0} \]  
\text{(E3-18)}

\[ \Phi^2 = \frac{kr_0^2}{D_{AC}}, \quad \beta = \frac{ɛr_0^2}{t^* D_{AC}}, \quad \Gamma = k t^* \frac{C_{A,\text{Bulk}} C_B^0}{C_B^0} \]  
\text{(E3-19)}

Resulting in (E3-20) and (E3-21):

\[ \beta \frac{\partial Y}{\partial \theta} = \frac{1}{\Gamma^2} \frac{\partial}{\partial \Gamma} \left( \Gamma^2 \frac{\partial C_A}{\partial r} \right) - b \Phi^2 (1 - X)^a Y \]  
\text{(E3-20)}

\[ \frac{\partial X}{\partial \theta} = -a \Gamma (1 - X)^a Y \]  
\text{(E3-21)}

Where \( t^* \) is the characteristic time for full conversion of the particle. \( \Phi^2 \) is the Thiele modulus, quantifying the ratio between the kinetic and diffusive resistances. For a detailed CM derivation where multicomponent species are examined see references [45] [53] [51], as this may need to be considered for the overall reduction reaction with methane.

### 3.5 Nucleation and Nuclei Growth Model (NNGM) & Other Solid-State Reaction Models:

Generally, the rate of the decomposition of a solid can be expressed in terms of a generalized expression for a single step mechanism [54], shown in (E3-22)

\[ \frac{dx_p}{dt} = k(T) f(X_p) \]  
\text{(E3-22)}
The temperature dependence of the rate constant is assumed to follow the Arrhenius equation in kinetically controlled reactions and is shown in (E3-23).

\[ k(T) = A e^{\left(\frac{-E_a}{RT}\right)} \]  

(E3-23)

However, for the models in which the diffusion of oxygen ions out of the metal oxide through the reduced metal/metal oxide lattice framework becomes a controlling aspect of the mechanism, the rate constant must be expressed in terms of a temperature dependent diffusion coefficient, shown in E3-24.

\[ \tau(T) = \frac{D_{O2-}(T)}{R_p^2} = \frac{D_l}{R_p^2} e^{\left(\frac{-E_{a^*}}{k_B T}\right)} \]  

(E3-24)

where \( D_{O2-} \) is the oxygen ion diffusion coefficient, \( D_l \) is the jump frequency constant, \( E_{a^*} \) is the activation energy on a per atom basis, and \( k_B \) is the Boltzmann constant. The jump frequency constant reflects the tendency for the ion of interest to move from one vacancy to the next.

The \( f(X_p) \) term is representative of the reaction model. For reactions that proceed under isothermal conditions, (E3-22) can be integrated to yield (E3-25).

\[ g(X) = \int_0^X \frac{d(X)}{f(X)} = k(T)t \]  

(E3-25)

where \( g(X) \) is the integral form of the reaction model and often \( X_p \) can be explicitly solved in terms of the independent variable of time \( t \). Representations of NNGM, Order of reaction, and some numerical diffusion approximations are displayed in Table 3-1.
### Table 3-1: Additional kinetic models for solid state reactions following the generalized rate expression

<table>
<thead>
<tr>
<th>Kinetic Model</th>
<th>Mechanism</th>
<th>(f(x))</th>
<th>(g(x))</th>
<th>(X = h(t))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Order of Reaction</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1st Order</td>
<td>((1 - X))</td>
<td>(-\ln(1 - X))</td>
<td>(1 - e^{(-k(T)t)})</td>
<td></td>
</tr>
<tr>
<td>2nd Order</td>
<td>((1 - X)^2)</td>
<td>((1 - X)^{-1} - 1)</td>
<td>(1 - (k(T)t + 1)^{-1})</td>
<td></td>
</tr>
<tr>
<td>3rd Order</td>
<td>((1 - X)^3)</td>
<td>((1 - X)^{-2} - 1)</td>
<td>(1 - (k(T)t + 1)^{-1/2})</td>
<td></td>
</tr>
<tr>
<td>nth Order</td>
<td>((1 - X)^n)</td>
<td>((1 - X)^{-(n-1)} - 1)</td>
<td>(1 - (k(T)t + 1)^{-1/(n-1)})</td>
<td></td>
</tr>
<tr>
<td><strong>Diffusion</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-D</td>
<td>(\frac{1}{2}X)</td>
<td>(X^2)</td>
<td>(-k(T)t)^{1/2})</td>
<td></td>
</tr>
<tr>
<td>3-D (SCM PD)</td>
<td>(\frac{3}{2} (1 - X)^{\frac{3}{2}} \left[ 1 - (1 - X)^{\frac{1}{2}} \right] )</td>
<td>((1 - X)^{\frac{1}{2}})</td>
<td>((1 - (\tau(T)x)^{\frac{1}{2}})^{2})</td>
<td></td>
</tr>
<tr>
<td><strong>NNGM</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nth Order</td>
<td>(n(1 - X)(-\ln(1 - X))^{(1 - \frac{1}{n})})</td>
<td>([-\ln(1 - X)]^\frac{1}{n})</td>
<td>(1 - e^{(-k(T)t)^n})</td>
<td></td>
</tr>
<tr>
<td>(n = 1)</td>
<td>-</td>
<td>([-\ln(1 - X)])</td>
<td>(1 - e^{(-k(T)t)^1})</td>
<td></td>
</tr>
<tr>
<td>(n = 2)</td>
<td>-</td>
<td>([-\ln(1 - X)]^\frac{1}{2})</td>
<td>(1 - e^{(-k(T)t)^2})</td>
<td></td>
</tr>
<tr>
<td>(n = 3)</td>
<td>-</td>
<td>([-\ln(1 - X)]^\frac{1}{3})</td>
<td>(1 - e^{(-k(T)t)^3})</td>
<td></td>
</tr>
</tbody>
</table>

The Nucleation and Nuclei growth model was refined by Avrami [55] [56] [57] to depict the crystalline phase changes that occurred during the solidification of austenite in various doped steels. This model is developed from the basis of a differential volume change with respect to time in association with a new phase formation. The model is based on three fundamental assumptions about nucleation in a particle: (1) All nuclei are randomly distributed. (2) All nuclei are either present at t=0 or are created at a steady state. (3) The nucleation boundary moves outward at a
constant rate and with time, boundaries can coalesce. The model examines two types of changes associated with phase change (1) the consumption of germ nuclei and initiation of nuclei growth (2) the statistical probability of one growth nuclei overlapping with one another (i.e., Assumption 3), often referred to as the dimensional aspects associated with nuclei growth. This can be further explained by examining the NNGM rate based function shown in (E3-26) & outlined in Table 3-2.

\[
\frac{dx_p}{dt} = k(T) n(1 - X_p)(-\ln(1 - X_p))^{(1 - \frac{1}{n})} 
\]

(E3-26)

Where \( k(T) \) is the rate constant associated with growth of nuclei, which contains energy threshold barriers for the initial consumption of germ nuclei. The dimensional growth term \( n \) delineates two aspects: (1) the dimensional growth of nuclei and (2) the presence of germ nuclei or their formation rate with descriptions of this displayed in Table 3-2.

**Table 3-2: Dimensional growth of nuclei and the impact of germ nuclei on the dimensional growth term**

<table>
<thead>
<tr>
<th></th>
<th>One dimensional growth of product nuclei (needle like)</th>
<th>2- dimensional growth of product nuclei (flat-plate)</th>
<th>3-dimensional growth (spherical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All nuclei are present at start</td>
<td>( n = 1 )</td>
<td>( n = 2 )</td>
<td>( n = 3 )</td>
</tr>
<tr>
<td>Nuclei are formed at a steady rate</td>
<td>( n = 2 )</td>
<td>( n = 3 )</td>
<td>( n = 4 )</td>
</tr>
</tbody>
</table>
The steady state formation of nuclei can have an immense impact on the order of dimensional growth. Hossain and de Lasa [58] and others [29] [59] [50] have employed the use of NNGM to explain the kinetics associated with reduction of transition series metal cation predominated oxygen carriers (Co-Ni/Al2O3, Fe2O3, CuFe2O4, and perovskites). It is suggested that the formation of germ nuclei often occurs in a period of induction consistent with reaction initiation. The length of the induction period is often dependent upon the gas-solid system and the reaction temperature. After initiation and the activation of germ nuclei sites, the reaction continues to progress with further nucleation accompanied by dimensional growth. Nuclei growth occurs due to the overlapping of nuclei or ingestion of nuclei sites, with a depiction of this process outlined in Figure 3-1.

![Figure 3-1:Activation, Formation and growth of nuclei during the reduction and oxidation reactions for oxygen carriers in chemical looping applications, adapted from [58]](image)

The overall conversion of the particle is controlled by the relative rate of nucleation including the dimensional growth and germ nuclei sites (potential nucleus forming sites). Monozam [29] [59] discussed the link between dimensional growth and phase change for metal oxides such as Fe2O3 and CuFe2O4, in which the reduction mechanisms involved multiple parallel steps. NNGM application has shown much success in multistep parallel solid transitions based on the randomized distribution of nucleation and reaction initiation sites. This allows for the use of linearly expressed rate models to explain the consumption of multiple phases with respect to time, making the use of these expressions attractive for kinetic representation of complex metal oxides. The only drawback
to the use of these models for gas phase reactions is the indirect connection between nucleation and nuclei growth interfaces to the reaction atmosphere. As can be seen from (E3-22) the conversion of the particle must be expressed in terms of a generalized rate function, in which most authors introduce a reaction atmosphere concentration term to link it to the expression. However, it can be observed from derivations of the SCM and its more complicated permutations that these terms for reaction, and diffusion based control are built into the fundamental derivations and boundary conditions making them more attractive for use.

Table 3-1 outlined another permutation of the shrinking core model (SCM). The 3D diffusion model proposed by Jander is a simplification of the SCM with product layer diffusion control [44]. This form of the SCM is based on the derivation of product diffusion control with a uniform reactive boundary. In this case, the description of the oxygen ion flux is applied in a parabolic manner assuming planar movement of ions. It is estimated that the quasi-steady state approximation still holds for the derivation of a description of this kind, when considering the flux of a single component out of the metal oxide and if metal cation migration does not occur in a magnitude greater than oxygen ion outward migration [60].

Reaction order based models have also been proposed for use with gas-solid and solid-solid reactions and these have correlation with the quasi-steady state approximation of the SCM. For instance, a reaction order of n = 2/3 corresponds to the SCM with reaction control, and an n value of 1 is consistent with one dimensional nuclei growth consistent with the NNGM representation. Although some reaction orders correlate to other derivations, for the conversion of solids the reaction order is not always a simplifying concept, and does not always particularly clarify the mechanism of solid conversion [43].
Chapter 4 Experimental and Kinetic Analysis for particle scale modeling of a CuFeAlO$_4$ oxygen carrier during reduction with H$_2$ in Chemical Looping combustion applications

Chapter Chapter 4 Preface:

A kinetic analysis of the H$_2$ reduction of a Copper-Ferri-Aluminate oxygen carrier for gas phase fueled chemical looping combustion of synthesis gas was utilized to derive particle scale representation. An experimentally driven study was carried out to provide an array of operational data sets for modelling approaches. The impact of key operational variables on the kinetics of the novel oxygen carrier were examined, with emphasis on the application of reliable phenomena driven particle scale models to describe the reduction behavior. Due to the novel nature of the material, a series of experimental studies were carried out to provide a fundamental understanding of how the material changed as oxygen was depleted from the structure due to reduction with H$_2$. H$_2$ acts a model reductant with minimal side reactions. This makes it one of the only feasible starting points for developing particle scale models for OC’s in CLC. This includes quantification of the complex mixed metal oxide phase and changes due to lattice oxygen depletion.

Recalling from Chapter 2.1.1, a normal cubic spinel structure of CuFeAlO$_4$ was obtained for the manufactured OC that was shown to be viable for use in pilot scale operation [28] [17] and is the subject of this kinetic evaluation. This structure is unique to the application of CLC with limited knowledge on how the material changes with extent of reduction. Understanding the effects of reduction on the material was a key component to applying kinetic and particle scale model descriptions to accompany the behavior. Three key questions arose when approaching the problem and include: (1) How does the phase, chemical and physical properties of the oxygen
carrier change with extent of solid conversion? (2) How do reactants and products impact reaction phenomena? (3) Can certain physical properties be considered constant validating the use of certain conventional models? (4) What types of interfaces exist for oxygen transfer and what is their impact on the transfer rate? All of these questions arise from criteria in the kinetic analysis flow diagram previously presented in Figure 2-16, section 2.2. Each criterion is explored with the intent of answering these main questions.

4.1 Experimental Techniques and Methods:

4.1.1 Experimental Apparatus

Simultaneous Thermogravimetric Analyzer and Differential Scanning Calorimeter (TGA-DSC): A TA Q600 SDT (simultaneous differential thermogravimetric analyzer was used to measure the weight changes and enthalpic changes due to reaction with H$_2$. A description of the experimental setup can be found in a previous work [61] and displayed in Figure 4-1. Experiments were conducted isothermally at reactions temperature 700-900°C, in 100°C

![Figure 4-1: Q600 SDT (simultaneous differential thermogravimetric analyzer) experimental setup.](image)
increments with 20 vol% H₂ in U.H.P Ar introduced for 80 minutes. R denotes an interchangeable reduction gas, (H₂, CO, or CH₄). The reduction segment was followed by an inert purge for 30 minutes to insure the reaction chamber was free of combustible gases prior to the introduction of Air for the oxidation step (20 minutes). A second set of isothermal experiments were conducted using the auxiliary vapor generator (VG) to introduce H₂O after reduction. The set-up is also equipped with an auxiliary gas header where CO₂ was connected for experiments in Chapter 5. All experiments were conducted with 100 ml/min volumetric flow rates.

Thermogravimetric Analyzer (TGA) and Mass Spectrometer (MS): The cyclic reduction and oxidation of CuFeAlO₄ OC was performed in a thermogravimetric analyzer (TGA, TA Instruments model Discovery) equipped with an online mass spectrometer (MS, Pfeiffer Vacuum).

Figure 4-2: Experimental setup for TA Discovery TGA-MS reaction chamber and evolved gas analysis
Omnistar GSD-320) [40] and displayed in Figure 4-2. A gas distribution module (GDM) provided flexibility for the introduction of critical gas components in an integrated form. Additionally reduction gases \( R \) (H\(_2\), CO, or CH\(_4\) blended in Ar) were introduced through an auxiliary mass flow controller into the TGA setup. When reduction gases were not in use the MFC and inlet line were purged with Ar to maintain a clean, dry and oxygen free environment in the ambient pressure line. An auxiliary vapor generator was also available for the introduction of a maximum of 2vol%H\(_2\)O into the reaction chamber. All flows were held constant at a total of 100 ml/min (the maximum possible for the unit).

A brief overview of the experimental test matrices associated with target operational variables can be found in

**Table 4-1.**

<table>
<thead>
<tr>
<th>Operational Variable</th>
<th>Range</th>
<th>Increment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>500-900°C</td>
<td>50°C</td>
</tr>
<tr>
<td>Concentration (vol%)</td>
<td>5-40 vol% H(_2)</td>
<td>5 vol % H(_2)</td>
</tr>
<tr>
<td>Pellet Size</td>
<td>213-582 (\mu)m</td>
<td>~100(\mu)m</td>
</tr>
</tbody>
</table>

**Table 4-1: Major Operational Variables**
A TGA apparatus was chosen because it provides a controlled environment in which reactive gas concentration and external temperature can be controlled accurately. The complex effects of gas mixing and particle movement can be excluded, allowing for the decoupling of these complex effects associated with fluidization ensuring that only the reaction contributions were being evaluated.

4.1.2 OTHER EXPERIMENTAL APPARATUS AND SPECTROSCOPIC TECHNIQUES

X-ray Diffraction and other spectroscopic analysis:

XRD analyses were carried out using a Panalytical PW 3040 X-Pert Pro XRD system equipped with a 60 kV PW 3373/00 Cu LFF high power ceramic tube with a Cu anode and a PW 3011/20 detector. Phase identification was done through the use of Panalytical X-Pert Pro Plus Diffraction analysis software coupled with PDF4-2016 database. Stoichiometry and weight fractions for multiphase scans were determined through Rietveld refinement. SEM analyses were conducted with a JEOL-840A Scanning Electron Microscope. The X-ray Microanalysis system consisted of a JEOL-840A Scanning Electron Microscope (SEM) interfaced to a Noran NS-6 X-ray microanalysis system. The JEOL-840A is equipped with an annular backscatter detector (BSED), an ET type secondary electron detector (SED), and a Noran Ultra-Dry Energy Dispersive Spectrometer (EDS); EDS detector was calibrated utilizing the Cu Kα = 8.041 kV. The JEOL 840A SEM was routinely operated in a pressure range of 10⁻⁶-10⁻⁵ Torr (1.3x10⁻⁵ to 1.3x10⁻⁶ Pa; 1 Torr ≈ 1.3224 Pa).
Physical Properties:

Particle size analyses were carried out using a Sympatec QICPIC with GRADIS-VIBRI/L. Surface area and micropore analysis were conducted using a Micromeritics ASAP 2920. Skeletal densities were measured using a Micromeritics AccuPyc II Helium pycnometer.

4.1.3 Mathematical fitting of reaction models:

All fitting approaches for reaction model analysis were implemented using the curve fitting application in MATLAB 2017a. A non-linear least squares regression fit was implemented in the software to minimize the differences between the experimentally derived conversion versus time curves at a desired isothermal temperature with those derived by a model description for each contribution. Model selection was based on the principle of parsimony in which the most rational and feasible model was applied for fitting approaches. Goodness of fit was evaluated based on the correlation coefficient between the experimental and theoretically derived curves. Estimated confidence interval bounds were extrapolated from the software to provide an estimate of ranges on the determined coefficients. These were derived based on a spread of data generated from at least 3 repeat experiments. In addition a propagated error analysis was conducted to add an additional spread of data when considering the inherent error associated with the experimental setup, see appendix B for further details. Fitting was conducted on 5th reduction cycle, as to represent the material after reaching a steady state.

4.2 Results and Discussion

4.2.1 Determining the oxygen carrier reduction pathway:
The CuFeAlO$_4$ OC has a unique structure and a reduction pathway with H$_2$ corresponding to this structure has not been reported previously. In order to address this, a series of experiments were
performed to determine the CuFeAlO$_4$ OC reduction pathway during exposure with H$_2$.

Samplings of material (100mg, ±1mg) were reduced for incremental time intervals isothermally, then rapidly quenched (500°C/min) to room temperature (Figure 4-3a). Subsequent scans using ambient temperature XRD were conducted to determine the phases present associated with exposure time and oxygen depletion. Figure 4-3b displays XRD of the quenched samplings, corresponding to various reduction times, depicting the reduction pathway for the CuFeAlO$_4$ OC during exposure to 20 vol% H$_2$ at 800°C.

Figure 4-3: Controlled exposure to 20 vol% H$_2$ at 800°C. (a) Weight data and sampling points during controlled exposure conducted in TG apparatus and (b) resultant ambient temperature XRD scans of controlled exposure samplings.
From the thermogravimetric weight loss profile, it can be observed that an initial fast reaction stage is followed by a slower reacting stage. XRD scans of the partially reduced quench samplings shed light on the chemical changes due to the depletion of oxygen from the metal oxide lattice associated with these stages. During the initial fast stage of reduction, oxygen ions bound to Cu$^{2+}$ cations in the tetrahedral positions are removed more readily than those associated with Fe and Al bonds. This is confirmed due to the presence of metallic copper leaving solid solution prior to other components. As the Cu cations are removed out of the lattice structure due to tetrahedral bound oxygen depletion, lattice reorientation takes place causing the formation of Fe-Aluminate (hercynite) and unbound metallic Cu. Finally, during the slower reaction segment, oxygen is depleted further from hercynite until base metal/metal oxide components of Fe & Al$_2$O$_3$ remain, as shown in E4-1.

\[
\text{CuFeAlO}_4 \rightarrow \text{Cu} + \text{FeAl}_2\text{O}_4 \rightarrow \text{Cu} + \text{Fe} + \text{Al}_2\text{O}_3 \quad \text{E4-1}
\]

Hercynite was identified as a solid reduction product of Fe$_2$O$_3$-Al$_2$O$_3$ mixture by Cabello et al and was considered a relatively inactive material with reduction gases such as H$_2$, CO, and CH$_4$ [46] due the slow reactivity. Minowa et al also discussed the reduction of Hercynite in H$_2$ stating that at temperature ranges between 700-900°C, partial reduction was possible in time intervals up to 120 minutes [62]. The reduction times (50 min @ 800°C, 20vol% H$_2$) depicted in Figure 4-3a suggest that the metallic copper component adds to the synergy of reduction, allowing hercynite to transfer oxygen and reduce to base components in an accelerated manner in comparison to Minowa and Cabello et al findings when the phase was absent of metallic Cu.
4.2.2 **Thermodynamic Considerations:**

Another consideration that must be examined are the enthalpic contributions from reduction. Common materials such as Fe$_2$O$_3$ and CuO both have known thermodynamic properties that allow for the prediction of enthalpies due to reaction, whether this be H$_2$ reduction or Air oxidation. Due to the novel nature of CuFeAlO$_4$, these properties are not readily available and enthalpic contributions were directly measured. Figure 4-4 displays the TGA-DSC profiles for a single reduction-oxidation cycle where reduction was conducted with 20 vol% H$_2$ and oxidation with 80 vol% Air with both gas mixtures balanced by U.H.P. Ar. The test was carried out isothermally at 800°C, with the $\Delta H_{rxn}$ for CuFeAlO$_4$ being compared with standard materials of Fe$_2$O$_3$ and CuO. Measured values were also compared with those computed by FactSage 7.1 software for the standard materials Fe$_2$O$_3$ and CuO, and are shown in Figure 4-4b. Measured values
were extracted by integrating the weight normalized heat flow for the time periods associated with either reduction or oxidation then converting to a per mole basis through application of the component’s molecular weight. Full reductions were carried out, where Fe$_2$O$_3$ and CuO were reduced to base metal components (Fe, Cu respectively). In general, measured values for $\Delta H_{\text{reduction}}$ were lower (~25-30%) than those computed theoretically but show closer agreement with values presented by Abad et al for the two common metal oxides [63].

$\Delta H_{\text{oxidation}}$ were more consistent with values predicted theoretically showing variances of less than 1%, in cases when full re-oxidation was possible (Fe→Fe$_2$O$_3$). Deviations from the theoretical values are likely due to experimental limitations with the measurement apparatus. The rate at which energy is released or consumed will dictate the measurement accuracy due to velocity distributional differences above and below the sample crucible [64] as these can impact the convective heat losses. Lower energy generators, that occur with slower reaction rates are likely to be impacted the most by convective heat losses. These convective heat losses are thought to be due to the loss of heat to the environment rather than solely raising the temperature of the measurement device. With this noted, measured values provide realistic, qualitative and conservative estimates of the enthalpic contributions from reduction and oxidation. From the TGA-DSC analysis, it can be deduced that the reduction of CuFeAlO$_4$ in H$_2$ is highly exothermic with values (54kJ/mole) nearly matching those measured for pure CuO. The oxidation of the material is also quite exothermic with values of 230 kJ/mol.
4.2.3 **Effect of reduction with H$_2$ on the overall pellet size surface area, micro porosity, skeletal and bulk density of the pellet:**

To address the effect reduction with H$_2$ on the pellet morphology, a series of controlled reduction and cycling experiments were conducted to determine if material properties such as pellet size, density, surface area, and porosity changed with reduction and the magnitude of these changes were quantified. Figure 4-5 displays the results of these experiments showing the changes in these physical properties.

![Image](image.png)

**Figure 4-5:** Effect of extent of reduction on the pellet surface area and pore distribution (a,b), pellet size distribution (c), and skeletal and bulk densities (d).

To examine the effects of reduction on pellet size, materials were refined to the mean pellet size range of 300-450 µm. Fresh, fully reduced and re-oxidized (10 cycles) samples were analyzed with a Sympatec QICPIC to determine the apparent particle size of the materials. Insignificant changes are observed in the reduced sampling (+3µm), with this value being within the error limits.
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of sampling; subsequently particle size was considered constant with extent of reduction. These same samplings were also analyzed for surface area and micropore distribution. Low incremental dosing (0.010 cm³/g STP) was used to increase the accuracy of the measurement of the low surface area material and obtain information of the micropore distribution. Surface area of the material increases with the initial reduction of 0.16 m²/g →1.6 m²/g; the material surface area maintained a constant value following further reduction cycles. This suggests that the material has a low surface area that can be considered relatively constant after the material has undergone a few redox cycles to achieve a steady state (period of activation, in the case of this material typically around 3 cycles). N₂ adsorption can only shed light on the pore size ranges from 4-1000Å, so the majority of the macroporous distribution (0.1-100µm) must be examined through alternative techniques including SEM and Mercury Intrusion porosymetry. Combination of the microporous-mesoporous distribution and surface area make it clear that the grains of the pellets are relatively non-porous. The grains do gain porosity in this range due to reduction, however these porosity gains are not appreciable enough to alter the global size of the grain and pellet, making the assumption of constant grain size viable. It should be noted that the presence of microporous regions can impose diffusion limiting regimes if they act as the major thorough-fare for mass transport, this aspect is discussed further in section 4.2.8. Based on skeletal and bulk density determination (Figure 4-5d), bulk density can also be considered constant.

Figure 4-6 displays images from the cross sections of the fresh and reacted materials. Reacted material sampling Q7 (60 min, 800°C with 20vol% H₂), refer to Section 4.2.1, was cross sectioned and imaged to examine apparent grain size and macropore size differences from the fresh unreacted material. In general, non-porous component apparent sizes range from 4-20 µm
(RGY) with macropores (B, Carbon species from mounting epoxy resin) ranging 1-22 µm. Indicating that the large pore size in the material will not contribute to diffusion limitations.

Elemental mapping shows that components are evenly distributed throughout individual grains with some localizations of unbound Al₂O₃, also confirmed by XRD. Cross sections were analyzed to give a general estimate of the non-porous component size for model application, with an average diameter of 10 µm chosen for further use.

Figure 4-6: SEM-EDS Analysis of particle cross sections (a,c) Fresh unreacted material and (b,d) material reduced for 60 minutes at 800°C with 20 vol% H₂. Color Scheme: Red – Fe, Green – Cu, Yellow – Al, Blue – Carbon (Carbon sources from mounting epoxy resin)
4.2.4 Impact of Particle Size on the reduction characteristics

The effect of spherical pellet size on the oxygen depletion and reduction rate was evaluated to determine if particle size could impose internal diffusional effects on the reduction of the oxygen carrier, shown in Figure 4-7. Minimal changes occur between the 1100µm range (±2%), suggesting that internal pellet diffusional effects were not appreciable. De Bruijn et al have also noted this behavior for Manganese oxides in which they take note that the non-porous grains form a conglomerate pellet with microporous nature [65], much like the structure observed for the OC under evaluation. This observation leads to a key assumption that the grains within the pellet can uniformly convert simultaneously. Suggesting that within this size range (25-1100µm) there would be minimal concentration gradients within the pellet and is attributed to the macroporous network that exists in the pellet structure.

4.2.5 Effect of reactive gas concentration on the reduction behavior:

A major operational variable for CLC units is the fuel gas concentration as this can dictate the thermal output of the unit [28]. In addition, H₂ concentrations can vary widely
depending upon the input fuel source. Therefore, the effect of concentration on the extent of reduction was examined to determine its significance in OC conversion. The impact of H₂ reducing gas concentration on the oxygen depletion from the CuFeAlO₄ oxygen carrier is shown in Figure 4-8. A range of 5-40 vol% H₂ was utilized at 800°C to provide a wide range of the operation variable. It was determined that the concentration of the reductant H₂ plays a major role in the extent of reduction and the time to complete full conversion, with concentration playing a significant role in both fast and slow reaction segments. At high H₂ concentrations (20-40 vol%) full depletion of lattice oxygen in the OC occurred in ~1000 secs, while concentrations on the low end of the range (5 vol%) took upwards of 5000 secs to fully deplete transferable oxygen in the OC. These results indicate that fuel gas concentration is a critical variable and must be accounted for in the particle scale model description to appropriately provide full functionality and predictive potential.

Figure 4-8: Effect of reducing gas concentration on CuFeAlO₄ reduction behavior with 5-40 vol% H₂ at 800°C
4.2.6 Effect of temperature on reduction behavior and the application of model free isoconversional methods for the initial determination of activation energy

The degree of conversion of a particle, $X_p$, was obtained from experimental TGA data. The degree of conversion represents a normalization of solid state transitions with respect to the recorded weight changes associated and is described by E4-2,

$$X_p(t) = \frac{m_{0,OC} - m(t)}{m_{0,OC} - m_{f,OC}}$$ \hspace{1cm} (E4-2)

where $m_{0,OC}$ is the initial weight of the sample, $m(t)$ is the instantaneous weight of the solid material during reduction corresponding to oxygen loss from the metal oxide and $m_{f,OC}$ is the theoretical weight associated with the final reduced states of the starting metal oxide. $X_p(t)$ is a normalized function, and is therefore on a scale of 0-1. The application E4-2 allows thermogravimetric data to be converted to a form suitable for comparative purposes, and in addition conversion allows the application of iso-conversional methods. Through the application of iso-conversional model free methods, values of the activation energy for the process can be estimated using E4-3 which is a rearranged form of the generalized conversion function [29], with the derivation presented in a previous work [40].

$$\ln(t) = \left(-lnA + \ln\int_{0}^{X} \frac{dX}{f(x)}\right) + \frac{E_a}{RT}$$ \hspace{1cm} (E4-3)

By plotting ln(t) with respect to 1/T, the activation energy can be obtained for a given value of $X_p$ from the slope of the regression line if at least three isothermal temperatures are explored. Model-free iso-conversional techniques have typically been used in the past when determining the kinetic rate parameters from thermal analysis techniques [66] [67]. In this work, model-free iso-conversional techniques were used to evaluate the kinetic parameter of overall activation energy associated with the reduction of the metal oxide with H$_2$. This technique provides a non-biased
approach to determining the reduction activation energy without the assumption of an underlying model and results of the analysis are shown in Figure 4-9.

From the analysis, a clear shift in activation energy is observed around $X_p = 0.6$, were a mean shift from 13kJ/mol to ~75kJ/mol is observed. This shift in conversion happens consistently with the oxygen depletion quantities necessary for the formation of hercynite and supports the hypothesis that the formation of another phase is predominantly contributing to the transfer of oxygen to the gas phase reductant at $X_p = 0.6$. The analysis also provides insight on the magnitude

Figure 4-9: Effect of Temperature on $X_p$ (a,b) and (c,d) determination of Activation Energy with respect to conversion based on model free iso-conversional methods (Expts. conducted with 20 vol% H$_2$)
of the operational variable of temperature, where it can be observed that temperature plays a major role in the extent of reduction. This is found to be particularly true for the less active phase of hercynite which requires increased energy inputs to allow for the transfer of oxygen. It is interesting to note that the CuFeAlO$_4$ material is still partially active at 500-600°C, with the ability to transfer 7-8wt% lattice oxygen. As these values are below the oxygen transfer quantities needed to form hercynite, it can be concluded that the FeAl$_2$O$_4$ phase is inactive at temperatures below 700°C. Subsequently, viable temperature ranges for a model description will be confined to 700-900°C where the primary (CuFeAlO$_4$) and secondary (FeAl$_2$O$_4$) phases are actively participating in oxygen transfer with H$_2$. Temperatures below this range would require a separate description as the reduction mechanism and pathway are different (only approaching partial completion).

4.2.7 Effect of product gas concentration and the implication of reversibility in reaction equilibria:  
Product gas contributions can potentially play a significant role in the kinetics of reduction if a material has the ability to uptake molecular oxygen from soft oxidants such as the product gas H$_2$O. In this section, the product gas, H$_2$O, concentration is explored to determine if any of the primary reduced phases are able to utilize this oxygen containing molecule as an oxygen donor. Two experimental configurations, Q600 SDT and TGA-MS, were used to determine if this effect was possible with the current OC. X-ray diffraction was used to examine the predominant phases before and after reaction. Figure 4-10a displays the TGA-DSC profile for the reduction of CuFeAlO$_4$ OC and subsequent exposure to 2 vol% H$_2$O at 800°C. Figure 4-10b displays the primary phase determinations before and after H$_2$O exposure. The fully reduced material is able to utilize oxygen from H$_2$O to re-form the cubic spinel FeAl$_2$O$_4$ phase and observed weight percentages correspond with this observation.
Figure 4-10: (a) TGA-DSC profile for the reduction of CuFeAlO$_4$ OC and subsequent exposure to 2 vol% H$_2$O at 800°C (b) primary phase determinations from XRD before and after H$_2$O exposure.

Figure 4-11: (a) TGA exposures for 800-900°C with 2vol% H$_2$O after full reduction with H$_2$ (b) conversion profiles for exposure segments (c) & (d) isoconversionally determined $E_a$. 
The metallic Cu component remains isolated and does not reincorporate into the structure. This allows for the deduction that the reaction progression with the second phase is reversible whereas the first can be considered irreversible. It also can be noted that oxygen uptake to form FeAl₂O₄ is mildly exothermic, with ΔH ≈ 10.9 kJ/mol. Due to the apparent reversibility for the second phase progression, iso-conversional methods were applied to provide an estimate of the activation energy associated with the reverse reaction, shown in Figure 4-11. There were minor differences in the conversion progression as temperature was increased from 800-900°C in 50°C segments, insinuating that the activation energy for the reaction should be relatively small in magnitude. The activation energy, determined from iso-conversional methods, for the uptake of molecular oxygen from H₂O (often referred to as water splitting) is 7x less than that of the forward reaction in which oxygen is removed from FeAl₂O₄ crystal structure by H₂ (9.85kJ/mole vs. 75kJ/mole, respectively)

4.2.8 Examination of film convective mass and heat transfer coefficients:

External film convective heat and mass transfer coefficients are examined to determine if film resistances in the current experimental setup could potentially play a role in the reduction behavior. The Nusselt number and Sherwood number are examined based on the TGA reactor operating conditions and configuration to determine the pellet external convective heat transfer coefficient, \( h'_{g} \), and mass transfer coefficient, \( k'_{g} \), respectively. The Nusselt correlation for heat transfer from a sphere [68] and the Sherwood correlation for mass transfer from a sphere [69] are shown in E4-4 and E4-5 respectively.
\[ N_{Nu} = \frac{h'_{g}D_p}{k_{e,f}} = 2 + 0.552N_{Re}^{0.5}N_{Sc}^{1/3} \quad \text{where} \quad N_{Re} = \frac{D_p \nu \rho}{\mu}, \quad N_{Pr} = \frac{C_p \mu}{k_{e,f}} \quad \text{E4-4} \]

\[ N_{Sh} = \frac{k'_{g}D_p}{D_{AB}} = 2 + 0.552N_{Re}^{0.5}N_{Sc}^{1/3} \quad \text{where} \quad N_{Sc} = \frac{\mu}{\rho D_{AB}} \quad \text{E4-5} \]

The Nusselt and Sherwood correlations are dependent upon the fluid properties \((\mu: \text{viscosity}, C_p: \text{Heat capacity}, \rho: \text{density}, k_{e,f}: \text{effective thermal conductivity})\), with these properties being estimated by considering the mole fraction of the component multiplied by the property of the pure component, with all individual components summed to arrive at the mixture property. Tabulated properties and temperature dependent correlations of the pure gases were used when determining the mixture properties [70]. Heat capacities of the pure components were calculated using the Shomate equation with coefficients provided and tabulated by NIST [71]. Thermal conductivity, \(k_e\), of the primary gases in the reactive gas mixture were estimated using correlations. Thermal conductivity of hydrogen was estimated through correlations developed by Saxena et al [72] and alternatively determined for Argon through correlations developed by Faubert et al [73]. Binary diffusivities, \(D_{AB}\), were estimated through the application of E4-6 [74].

\[ \frac{\rho D_{AB}}{(\rho_{CA}\rho_{CB})^{1/3}(T_{cA}T_{cB})^{1/5}(\frac{1}{M_A} + \frac{1}{M_B})^{1/2}} = a \left( \frac{T}{(T_{cA}T_{cB})} \right)^b \quad \text{E4-6} \]

Binary diffusivities, \(D_{AB}\), were estimated through correlation with critical properties of the components in the binary mixture, mixture density, and component molecular weight. See nomenclature (Chapter 9) for individual details. Table 4-2 depicts the convective film heat and mass transfer coefficients for the mean pellet size over the range of 500-900°C (773-1173K).
The relatively high magnitude of the film mass transfer coefficients suggests that it is not a controlling resistance over the operational range, recalling that it is associated with the fluid properties, TGA reactor configuration and other experimental parameters. Heat transfer coefficients for the external film are low in magnitude and suggest that internal pellet heating is possible. Internal pellet heating is examined in further detail in section 4.4.5. Internal diffusional limitations within the particle can be neglected based on findings reported in section 4.2.4 and grain based internal diffusion limitations are expected to be small with effective diffusivities on the range of 2-3 cm²/s. In addition to this observation, the Weitz-Prater criterion ($C_{WP}$) was examined from a heuristic standpoint to provide guidance and estimate if internal diffusion limitations were possible, displayed in E4-7. For a detailed discussion and example of this evaluation see references [48] [75].

$$C_{WP} = \frac{-r_{H2}\rho_B R_p^2}{D_e C_A} \quad \text{E4-7}$$

In the above equation E4-7, $-r_{H2}$ is the apparent rate of H₂ consumption, $\rho_B$ is the bulk density, $R_p$ is the particle radius, $D_e$ is the effective diffusivity, and $C_A$ is the concentration of reductant (H₂). In this work, the value of $C_{WP}$ was on the order of $1 \times 10^6$, similar to values Sedor
et al [48] reported in their work on the reduction kinetics of a Ni-Alumina OC. The relative magnitude suggests that diffusion limitations should be negligible within the grain.

4.3 Review of Conceptual Kinetic Particle Scale Models used for Oxygen Transfer in Chemical Looping Applications and Applicability to the CuFeAlO$_4$ OC system:

The material under evaluation has characteristics that would limit the sole use of many of the conventional models presented in section Chapter 3. These limitations include the multiple phases associated with reduction and the instance of equilibria in the second phase with the products generated from reduction. In this section, these limitations are discussed with the models presented by other authors and an alternate description proposed.

The reduction behavior of oxygen carriers in a fuel reactor and oxidation behavior in the air reactor have a significant influence on the conversion and thermal efficiency of chemical looping system [7]. Historically the reduction process has been treated as a network of gas–solid reactions as discussed in section Chapter 3. Numerous kinetic models have been proposed to explain the influence of reactor conditions on the kinetic rate of oxygen transfer both to and from the solid with the ultimate outcome to predict transient solid conversion responses. Conceptual particle scale models that have been used to describe oxygen transfer in CLC applications fall into two categories: (1) Transport phenomena based and (2) Nucleation and Growth based. Typical transport based models employed to describe these transfer mechanisms are the shrinking core model (SCM) and its many derivations based on controlling resistances and underlying derivation assumptions that lead to a gambit of different models and descriptions. In this section, these models are discussed briefly with emphasis on their application to CLC.
Abad et al have reported the use of the conventional pseudo-steady state approximation (P.S.S.A) derived SCM with reaction based control for the reduction of Cu-, Fe-, and Ni-based oxygen carriers [63]. Cabello et al also employed the use of the SCM with both reaction and diffusional resistances to describe the reduction of a Fe₂O₃ impregnated alumina oxygen carrier [46]. Chen et al [49] proposed variations for the SCM for irregularly shaped particles that include both reaction and internal diffusional resistances as rate controlling aspects. This added further utility to the SCM model by allowing for the accommodation of irregular shaped particles, but added to the question of what certain shape factors can be related too. Sarshar [50] proposed the use of unsteady state oxygen ion diffusion models for the reduction of perovskite based OCs assuming that the rate limiting process was the bulk diffusion of O²⁻ to the material’s surface. Melchiori and Canu [45] performed a critical analysis on the SCM and its assumptions used for the fundamental derivation. From this analysis, several limitations were discussed including the use of the pseudo-steady state approximation for diffusion based rate limitations. A simplified version of a continuous model (CM) proposed for use in scenarios where reaction and diffusion based resistances could present rate limiting control was derived by the Melchiori and Canu.

Hossain and de Lasas [58] and others [29] [59] [50] have employed the use of NNGM to explain the kinetics associated with reduction of transition series metal cation predominated oxygen carriers (Co-Ni/Al₂O₃, Fe₂O₃, CuFe₂O₄, and perovskites). It is suggested that the formation of germ nuclei often occurs in a period of induction consistent with reaction initiation. The length of the induction period is often dependent upon the gas-solid system and the reaction temperature. After initiation and the activation of germ nuclei sites, the reaction continues to progress with further nucleation accompanied by dimensional growth. Nuclei growth occurs due to the overlapping of nuclei or ingestion of nuclei sites. The overall conversion of the particle is
controlled by the relative rate of nucleation including the dimensional growth and germ nuclei sites (potential nucleus forming sites). Monazam [29] [59] discussed the link between dimensional growth and phase change for metal oxides such as Fe$_2$O$_3$ and CuFe$_2$O$_4$, in which the reduction mechanisms of which involve multiple parallel steps. This provided a means of describing multistep reactions in a convient manner.

All of the aforementioned models lack complete detail to describe the reduction of CuFeAlO$_4$. Particularly, the SCM based models presented previously in the literature for oxygen carriers focus on a single step mechanism and lack the incorporation of equilibria for instances where product gases can be utilized by the carrier. Mutli-step mechanisms have been emulated by NNGM based models, however these models lack direct derivation with the key operational variable of gas concentration. Additionally, NNGM based models cannot currently accommodate equilibria due to this limitation. In this work, particle scale modeling for the OC is approached from a new standpoint by applying a multi interface SCM called the multi-zone Grainy pellet model to describe the multiphase reduction mechanism associated with the removal of oxygen from CuFeAlO$_4$ structure. This model is chosen based on its applicability to multicomponent systems as well as the derivations direct association with key operational variables including the reactive gas concentration, which has been shown (section 4.2.5) to play a critical role in the rate, extent of reduction with respect to exposure time, and equilibria. The model can also be linked to rate controlling phenomena. It is also chosen based on the need to depict the reduction of the individual non-porous grain components that comprise the conglomerate pellet structure. The individual grain components act as the solid reacting species the comprise the pellet macrostructure.
4.4 Application of the Grainy Pellet Two interface model for the Gas Phase Reaction Mechanisms between CuFeAlO$_4$ Oxygen Carrier with H$_2$.

In this section, the application of the GPM two interface model is presented to describe the reduction mechanism of the CuFeAlO$_4$ OC material with H$_2$. Key findings derived from the experimental study are restated and correlated to the particle scale model. The range of applicability is defined as well as model limitations.

4.4.1 Summary of assumptions based on experimental data for the application of the model:

The experimental studies conducted in section 4.2 provided answers regarding the physical and chemical properties of the CuFeAlO$_4$ oxygen carrier, specifically with respect to H$_2$ reduction. These properties include the material’s reduction pathway, determination of intermediate reduced phases, and the route to final reduced solid products (Figure 4-3), with two distinct reaction phases, CuFeAlO$_4$ and FeAl$_2$O$_4$, being identified. The grains of the material comprise the non-porous reactive components (Figure 4-5), with the grains being considered spherical to simplify the model description. The bulk density is considered constant. The spherical pellets were found to not swell or shrink with extent of reduction, indicating that particle size can be considered constant. Additional assumptions are discussed as the model description is developed in subsequent sections.

4.4.2 Proposed Scheme and Representations:

Multi-interface grainy pellet models have been proposed and utilized by a number of researchers to describe fluid-solid reactions in which secondary phases in the product layer can further react with gas species [76] [77] [65]. Tsay et al have used these approaches to model the reduction of Hematite to iron through the use of a three-interface model accounting for secondary and tertiary reduced phases [77] and De Bruijn et al have used similar approaches for the reduction of
Manganese oxides [65]. These approaches are based on the prevailing principles derived from the unreacted shrinking core model first developed by Yagi and Kunii [43] and further refined and described by Szekely [44], Sohn [78], Ishida and Wen [79]. The model links the gas-solid reactions determined through experiments in section 4.2 and as displayed in (E4-8 & E4-9) to continuity balances in a spherical particle.

\[
3H_2(g) + 2CuFeAlO_4(s) + Al_2O_3(s) \xrightarrow{k_{c1}} 2Cu(s) + 2FeAl_2O_4(s) + 3H_2O
\]

\[
aA(g) + bB(s) + l(s) \rightarrow eE(s) + cC(s) + dD(g)
\]  

\[
H_2(g) + FeAl_2O_4(s) \xrightarrow{k_{c2}} Fe(s) + Al_2O_3(s) + H_2O
\]

\[
aA(g) + cC(s) \leftrightarrow fF(s) + l(s) + dD(g)
\]

CuFeAlO_4 reduction, E4-8, is considered to be irreversible with no observed interaction with the product gas. FeAl_2O_4 reduction, E4-9, is considered reversible and showing strong prevalence for interaction with the product gas of the reaction.

The grainy pellet model links the change in degree of reduction of the solid with the change in radius of an unreacted core of a spherical grain. A schematic of the two-interface grainy pellet model is shown in Figure 4-12. The individual grains non-porous grain components accompanied by the pellets macroprosity make up the conglomerate pellet structure. The non-porous grains components act as the solid reacting species in the pellet construct while the macropores act as a network for gas transport of reactive gases to the reacting grains and an exit point for product gases produced from the reactions.
As depicted in Figure 4-12, $L_1$ is the portion of the grain associated with the primary initial phases of $CuFeAlO_4$ & $Al_2O_3$ with $r_{c}^{B-C}$ and $\rho_{1}^{B-C}$ attributing to the reacting core interface and associated bulk density. $L_2$ is the portion of the grain associated with the secondary product layer reactive phases of $FeAl_2O_4$ & $Cu$ with $r_{c}^{C-F}$ and $\rho_{2}^{C-F}$ attributing to the secondary reacting core interface and associated bulk density. $L_3$ is the portion of the grain associated with the unreactive oxygen depleted product layer phases of $Cu,Fe$ & $Al_2O_3$ with $\rho_{p}^{E-F}$ as the associated bulk density of the product layer mixed phase.

Expressions for the advancement of the reacting core interface can be derived from continuity with the gas phase reactant as show in E4-10,

$$\frac{\partial C_{i}}{\partial t} + \nabla N_{i} = \vec{R}_{i}$$  \hspace{1cm} E4-10
where $C_i = \text{conc. of } i\text{th component}, N_i = \text{molar flux of } i\text{th component}, \bar{R}_i = \text{molar rate of production per unit vol } i\text{th comp.}$ If the pseudo steady state approximation (PSSA) is applied, $\frac{\partial C_i}{\partial t} = 0$ (a reasonable approximation for gas-solid systems [80]), then the expression can be simplified to E4-11.

$$R_{g,o} > r > r_c^{t-s}, \quad \frac{d}{dr} \left( (r_c^{t-s})^2 \frac{dC_A}{dr} \right) = 0 \quad \text{E4-11}$$

where $t - s = B - C, C - F$ accounting for the radius associated with reacting zones $L_1$, and $L_2$ respectively. Application of boundary conditions defined in E4-12 through E4-14 allows for the introduction of resistances to front progression.

$$D_e \left( \frac{dC_A}{dr} \right)_{r_c^{t-s}} = k_{Cl} C_A^{n_i}, i = 1,2 \quad \text{E4-12}$$

$$D_e \left( \frac{dC_A}{dr} \right) = k_g \cdot (C_{Ab} - C_{As}) \quad \text{E4-13}$$

$$\frac{\rho_i^{t-s}}{b} \left( \frac{dr_c^{t-s}}{dt} \right) = k_{Cl} (C_A^{n_i} - \frac{C_D^{n_i}}{K_{ei}^r}), \quad r_c^{t-s}|_{t=0} = R_{g,o} \quad \text{E4-14}$$

Internal diffusional resistances are introduced through the effective diffusivity $D_e$. External mass transfer resistances are introduced through the convective mass transfer term, $k_g$. Reaction controlling resistances are introduced through the application of the intrinsic reaction rate based term, $k_{Cl}^r$ where $i$ denotes different interfaces where rates can be different with presence of secondary and tertiary reduced phases. The equilibrium constant, $K_{ei}^r$, is the ratio of the forward rate to the reverse rate, shown in E4-15. In instances where $k_{Cl,R}^r \to 0, K_{ei}^r \to \infty$ making the
contribution from the second term negligible and the expression consistent with an irreversible reaction.

$$K_{ei}^* = \frac{k_{ci}^*}{k_{CI,R}}$$  \hspace{1cm} \text{E4-15}

Application of the boundary conditions allows for a general expression, E4-16, to be developed relating the reacting sphere-core interface with the three characteristic resistances, including film (external) mass transfer, product layer diffusion (internal mass transfer) and reaction (kinetic) control, with $k_{-ci}^* \rightarrow 0, K_{ei}^* \rightarrow \infty$.

$$-\frac{dr_c}{dt} = \frac{b C_{A}^{n_i}}{\rho_i^{t-s}} + \frac{r_c^2}{R_{g,0}^2 k_g} + \frac{(R_{g,0} - r_c) r_c}{R_{g,0} D_e} + \frac{1}{k_{CI}^*}$$  \hspace{1cm} \text{E4-16}

where $r_c$ is the reacting core radius of the OC grain, $R_0$ is the radius of the OC grain, $v$ is stoichiometric coefficient, $C_A$ is the concentration of A in the gas phase, $\rho_i^{t-s}$ is the density of the OC in the appropriate zone, $k_g$ is the mass transfer coefficient of the gaseous reactant, $D_e$ is the effective diffusion coefficient in the product layer, $k_{CI}^*$ is the intrinsic reaction rate constant of the unreacted core of a single grain for the specified $i^{th}$ zone.

The rate of the advancing core front can be expressed in terms of the overall solid conversion, $X_{Li}$, by application of the relation outlined in E4-17 resulting in E4-18:

$$1 - X_{Li} = (\gamma)^3, \text{where } \gamma = \frac{r_c}{R_{g,0}}$$  \hspace{1cm} \text{E4-17}
\[
\frac{dX_{Li}}{dt} = \frac{b}{R_{g,0}} \frac{3 C_A^{ni}}{\rho_i^{r-s}} + \frac{1}{\gamma^2 k_g \text{film}} \left( \frac{1}{D_e} \left( \frac{1}{(1 - X_B)^{1/3}} - 1 \right) \right) + \frac{1}{(1 - X_B)^{2/3}} k_{Ci}^{\text{reaction}}
\]

This description is derived based on the following assumptions: (a) the oxygen carrier grain is considered non-porous, (b) the grain is considered spherical, (c) crystallite size/volume is constant during the reaction, (d) the reaction is isothermal, (f) the pseudo-steady state approximation is applicable. The pseudo-steady state approximation assumes that the concentration gradient of A in the product layer is not a function of time but solely a function of the core position, \( r_c \), in which a constant flux of A into the reacting particle is assumed. This assumes that bulk concentration, \( C_{A,0} \), is equal to the concentration at the surface of the reaction controlled front. This model can be applied for a number of applications where \( R_0 \) is considered as the individual grain size in the spherical particle and the particle reacts uniformly with respect to the consumption of its individual grains; it can also be considered for overall particle conversion. Further simplifications can be made to the model based on the rate limiting step. As was shown in section 4.2.6-4.2.8, internal diffusional limitations within the particle and grain can be neglected and external mass transfer limitations can be neglected based on the relative magnitudes with respect to the radial flux of the reaction gas. Internal mass transfer limitations can be neglected through examination of the Weitz parameter criterion. Based on these assumptions, the GPM is considered to occur under reaction control and the rate of conversion of an individual grain can be expressed in a simplified form as shown in E4-19 with the integrated expression defined in E4-21 for the initial reacting core interface associated with the reduction of phases present in E4-8. E4-20 defines the intrinsic reaction rate constant in terms of an Arrhenius form.
\[
\frac{dX_{Li}}{dt} = \frac{b(C_A^{ni} - C_D^{ni})}{1 + \frac{1}{(1 - X_{Li})^{2/3} k_{Cl}^*}} 
\]

E4-19

\[
k_{Cl}^* = A_{Cl} e^{\frac{E_{Al}}{RT}} 
\]

E4-20

\[
\frac{t}{\tau_{R1}} = 1 - (1 - X_{L1})^{1/3}, \quad \tau_{R1} = \frac{\rho_1^{p-c} R_{g,0}}{b k_{Cl}^* (C_A^{ni} - C_D^{ni})} 
\]

E4-21

Since \(FeAl_2O_4\) is not present at the initiation of reaction an initial condition must be introduced that links the initiation of the 2\textsuperscript{nd} zone reaction front to that of the first, with this condition identified in E4-22 & E4-23 and the modified expression for 2\textsuperscript{nd} zone advance displayed in E4-24

\[
t_c = \tau_{R1} (1 - (1 - X_{LC})^{1/3}) 
\]

E4-22

\[
X_{LC} = 1 - \left(\frac{r_{LC}}{R_{g,0}}\right)^3, \quad r_{LC} = R_{g,0} (1 - \left(\frac{t}{\tau_{R1}}\right)) 
\]

E4-23

\[
\frac{t - \tau_{R1} (1 - (1 - X_{LC})^{1/3})}{\tau_{R2}} = 1 - (1 - X_{L2})^{1/3}, \quad \tau_{R2} = \frac{\rho_1^{c-f} R_{g,0}}{b k_{Cl}^* (C_A^{ni} - C_D^{ni})} 
\]

E4-24

where \(r_{LC}\) is the critical radius associated with the advance of 1\textsuperscript{st} reaction zone, \(L_1\), in which the first signs of \(FeAl_2O_4\) are possible and was determined experimentally (section 4.2.1).

Expression E4-22 through E4-24 allows for this term to be linked to the core advance of the 1\textsuperscript{st} zone. The fractional reduction of the overall \(CuFeAlO_4\) grain, \(F_g\), can be expressed in terms of
effective interface radii at any time instant as shown in E4-25 and described in terms of individual conversion in E4-26.

$$F_g = \frac{1}{R_{g,0}^3} \left[ \phi^{C-F}(R_{g,0}^3 - (r_{c}^{C-F})^3) \right] + \left[ \phi^{B-C}(R_{g,0}^3 - (r_{c}^{B-C})^3) \right]$$  \hspace{1cm} \text{E4-25}$$

$$F_g = \left[ \phi^{C-F}(X_{L2}) \right] + \left[ \phi^{B-C}(X_{L1}) \right]$$  \hspace{1cm} \text{E4-26}$$

$F_g$ is defined as the weight fraction of available oxygen originally present with respect to the amount which is removed due to reduction. The advance of the individual zone radii is associated with the oxygen density change $\phi^{t-s}$ from one predominant phase to the next [77], see nomenclature for details (Chapter 9). Generally if the grains of the material do not change uniformly with time then the overall global pellet conversion is expressed as shown in E4-27 [81] [82] [65] [83].

$$F_p = \frac{\int_{0}^{R_p} r^2 F_g(r_c,t) \, dr}{\int_{0}^{R_p} r \, dr} = \frac{3}{R_p^3} \int_{0}^{R_p} r^2 F_g(r_c,t) \, dr$$  \hspace{1cm} \text{E4-27}$$

The application of E4-27 is only necessary if the grains in the center of the particle initiate reaction at separate times from those on the pellet’s surface. This is applicable if a porous pellet has internal diffusional resistances and there exists a concentration gradient across the pellet radius. It has been shown in section 4.2.4 that diffusional resistances are not internally present in the pellet due to the macro-porous nature and relatively small particle size (25-1100µm). The only components that exhibit controlling resistances are the individual grains that cohesively make-up the spherical pellet. Taking this into consideration the overall pellet conversion can be approximated by E4-28.
\[ F_p = F_{p, \text{uniform conversion}} \]

This is consistent with descriptions in which uniform conversion of the grains occur simultaneously, independent of the grain position with respect to the pellet radius [82].

4.4.3 **Application of the GPM model for the Reversible reaction phase**

The reversible reaction front corresponding to reaction depicted in E4-9, FeAl\(_2\)O\(_4\) interaction with H\(_2\) and reduced species (Fe + Al\(_2\)O\(_3\)) interactions with product gas of H\(_2\)O, is a feasible starting point for approaching the use of the GPM. The singular primary phase contribution allows for a direct determination of appropriate kinetic parameters within the model, over an explored range of operational variables for the particular step, in the absence of other contributions. It is known from experimentation that phases of metallic Fe and Al\(_2\)O\(_3\) in the OC will reorient upon donation of molecular oxygen from H\(_2\)O to form the cubic spinel phase of FeAl\(_2\)O\(_4\). It was also shown that preliminary determinations for the energy barriers, from iso-conversional methods, for this reaction were nearly an order of magnitude less than that of mechanism for stripping of oxygen from the spinel structure. These parameters are optimized in this section and linked to the progression of the reaction front. The analysis is initiated by a discussion on the appropriate use of available data in the experimental evaluation system.

*Importance of Applying data driven concentration profiles for model emulation and kinetic parameter determination:*

In addition to using thermogravimetric derived weight data for developing an experimental conversion profile \((X_p(t), E44)\), mass spectra profiles are also available for all species of interest (H\(_2\)O, H\(_2\)) in this case. Appropriate use of these concentration profiles allows for an accurate determination of the kinetic parameters due to imposed experimental system effects. E4-29
shows how the measured concentration, $[j]$, is converted to the appropriate form ($C_{j,g}$) for use in the model.

$$C_{j,g} \left[ \frac{g}{cm^3} \right] = \left( \frac{P}{RT_{STP}} \right) \left( \frac{273.15}{T_b} \right) \left( \frac{[j, (vol \%)]}{100} \right) (MW_j)$$ E4-29

The gas is assumed to follow the ideal gas law, where $\left( \frac{P}{RT_{STP}} \right)$ is the molar density at standard temperature and operating pressure, $T_b$ is the temperature of the bulk gas phase (isothermal reaction temperature) and $MW_j$ is the molecular weight of component $j$. This form allows for operating pressure and temperature to be accommodated into the component concentration as these factors impact the molar density of the gas. In this form, experimentally measured values can be directly input into the model. Figure 4-13 displays a comparison of model descriptions when experimental concentration is used versus a constant maximal value. Figure 4-14 displays the Arrhenius and reaction order dependence plots for the refined representation.

The use of experimentally measured concentration profiles in the model aids in the accuracy of the kinetic parameters determined for that step. It also allows for certain effects to be accommodated by the model that authors typically deem as induction periods and tend to neglect in the analysis [65]. Conventionally, the concentration of the reactant is considered constant as was shown in Figure 4-13b, however in real systems including the thermogravimetric systems in use, it takes time for the concentration of the reactant gas to approach the intended set point value. The time frame being on the order of a few seconds depending upon the chosen set point (larger concentrations are realized in shorter times due to increased flow rates of the intended reaction gas, and the effects are less noticeable).
Figure 4-13: Implication of the use of real concentration versus estimated maximum value (Data for 900°C exposure with ~2vol% H₂O).
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![Arrhenius plot for $k_{C2,R}$ for 800-900°C and (b) rate order dependence for 5000ppm-2vol% H$_2$O]

Figure 4-14: (a) Arrhenius plot for $k_{C2,R}$ for 800-900°C and (b) rate order dependence for 5000ppm-2vol% H$_2$O

The time that it takes for the gas to reach the desired set-point impacts the induction period of the material ($F_{C2,H2O} < 0.1$). A greater contribution to the impact of the conversion profile is an effect called product-feed dilution, in which the generated product gas concentration displaces that of the reactant gas in the reaction chamber. In Figure 4-13a, it can be observed that H$_2$ from water splitting occupies up to 1 vol% during the main portion of the reaction. This dilution effect causes the observed rate of conversion to slow due to a lower reactant concentration than the
intended maximal value. As the reaction approaches completion, the maximal intended value is obtained as the product gas elutriates and production halts. Conventionally, in these flow systems these effects were attributed to mass transfer limitations [84]. Based on calculations of $N_{sh}$, it is known that mass transfer limitations would be minimal due to the two orders of magnitude difference between the mass transfer coefficient, $k'_g$, and the experimentally determined reaction rate constant, $k''_{c2,R}$. What this eludes to, is that the only feasible way of determining the kinetic rate parameters accurately for these materials in experimental systems of the kind used are to apply the experimentally measured concentration profiles into the coupled particle scale model. This can be done even though the PSSA approximation had been applied to the derivation. The PSSA assumes that the particles does not impose a time dependent gradient of the concentration of the reactant gas making the concentration at the surface of the reaction front only a function of radial position. In this case the concentration at the surface is assumed to be that of the bulk gas phase in the chamber due to the elimination of any internal diffusion limitations. This allows for the bulk measured concentration to be input directly into the model to aid in kinetic parameter determination.

Table 4-3 summarizes the kinetic parameters determined for the reverse reaction of the L₂ front from experiments used to generate plots in Figure 4-14. The low activation energy determined for this process is within the bounds determined by iso-conversional methods and suggest that reaction will proceed readily with small effects of temperature over the evaluated range consistent with what was observed in Figure 4-11b. The reaction order is first order with respect to the concentration of H₂O and suggests that the reaction is elementary as the order follows stoichiometry.
Table 4-3: Kinetic Parameters for reverse reaction of the L2 front

<table>
<thead>
<tr>
<th>Interface</th>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
<th>95% Confidence Interval Bounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_{2,R}$</td>
<td>$A_{C2,R}$</td>
<td>$cm/s$</td>
<td>1.95</td>
<td>±0.2</td>
</tr>
<tr>
<td>$L_{2,R}$</td>
<td>$E_{A2,R}$</td>
<td>$kJ/mole$</td>
<td>11.85</td>
<td>±0.95</td>
</tr>
<tr>
<td>$L_{2,R}$</td>
<td>$\rho_{2-C}^{C-F}$</td>
<td>$g/cm^3$</td>
<td>2.9</td>
<td>±0</td>
</tr>
<tr>
<td>$L_{2,R}$</td>
<td>$n_2$</td>
<td>unitless</td>
<td>1</td>
<td>±0</td>
</tr>
</tbody>
</table>

4.4.4 **Application of the GPM two interface model to reduction of CuFeAlO₄ with H₂**

The application of the model to the reacting system as well as the distribution of predicted phases are shown in Figure 4-15. The depiction in Figure 4-15 is shown for a single temperature of 900°C and with 35 vol% H₂, balance Ar. At this temperature and reductant concentration the model prediction for the grain oxygen consumption shows agreement with the experimentally derived data. Through application of the model representation, a description of the phase changes can be shown with respect to time by applying the fractional conversions of each reacting front and linking it to the component molar balances and reaction stoichiometry shown in E4-30-E4-35 [65] [85].
<table>
<thead>
<tr>
<th>Species</th>
<th>Symbol</th>
<th>Mole Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CuFeAlO_4$</td>
<td>$B$</td>
<td>$N_{Bo}(1 - X_{L2})$</td>
</tr>
<tr>
<td>$Al_2O_3$</td>
<td>$I$</td>
<td>$N_{Io} - \left( \frac{1}{2} N_{Bo} X_{L1} \right) + (N_{Bo}X_{L2})$</td>
</tr>
<tr>
<td>$FeAl_2O_4$</td>
<td>$C$</td>
<td>$N_{Bo} (X_{L1} - X_{L2})$</td>
</tr>
<tr>
<td>$Cu$</td>
<td>$E$</td>
<td>$N_{Bo} (X_{L1})$</td>
</tr>
<tr>
<td>$Fe$</td>
<td>$F$</td>
<td>$N_{Bo} (X_{L2})$</td>
</tr>
<tr>
<td>$O^{2-}$</td>
<td>$G$</td>
<td>$\frac{3}{2} N_{Bo} X_{L1} + (N_{Bo}X_{L2})$</td>
</tr>
</tbody>
</table>

Figure 4-15b displays the component balances on the amount of $CuFeAlO_4$ loaded into the sample pan plus unincorporated residual $Al_2O_3$ as a basis. As can be observed, $CuFeAlO_4$ consumption occurs rapidly within the first 60 seconds of reduction attributing to the donation of lattice oxygen to the gas phase reductant ($H_2$) and the formation of metallic Cu accompanied by hercynite ($FeAl_2O_4$). Hercynite formation occurs due to the presence of residual $Al_2O_3$, which is partially consumed to form the intermediate. Hercynite then continues to transfer oxygen to the gas phase reductant ultimately forming reduced phases of Fe and $Al_2O_3$ in equimolar quantities. The ability of the model to ascribe to the prediction of these intermediate phases and experimental phenomena with fair agreement at 900°C and at a single $H_2$ concentration indicates its potential usefulness in application and utility.
Figure 4-15: Application of the two zone GPM to reduction of CuFeAlO4 with 20% H2 @ 850°C: (a) Comparison of experimental conversion with $F_p$ and the individual interface fractional conversions. (b) Component mole balances showing new phase formation due to reduction and oxygen transferred to gas phase.
To further validate the usefulness of the GPM, predictive reliability studies over the range of operational variables were carried out. A comparison of the experimentally derived conversion with respect to the model predictions for operating temperature range 750-900°C and gas phase reductant concentration 5-40 vol% H₂ are shown in Figure 4-16.

![Figure 4-16: Examination of GPM reliability over operational parameter range: (a) Temperature range 750-900°C, (b) Hydrogen concentration range of 5-40 vol%](image)

The model predicts well with respect to concentration changes, by emulating the experimental behavior over a substantial change in H₂ concentration. At lower concentrations, the model slightly over-predicts (maximum, +3%SE) for the L₁ reaction front while undergoing slight under-predictions for the (maximum, -4%SE) L₂ reaction front. Other concentrations perform similarly through-out the range. All trends fall within the standard error (SE) bounds generated by a propagated error analysis on the experimental setup. In addition to concentration changes in H₂, the model was also able to effectively emulate substantial changes over the temperature range 700-900°C,
suggesting reliability of the application of the model. As previously stated, at temperatures below this range (700-900°C) CuFeAlO₄ is only partially active with Hercynite being almost entirely inactive making the described model overpredict reduction behavior in the temperature regime below 700 °C due to its inability to account for material inactivity.

Some uncertainty arises from the simplifying assumptions of the model, including the primarily shape factors and the application of a mean grain size when there is likely a distribution of grain sizes. Models have been presented in the literature to handle grain size distributions but add an additional layer of complexity by relying on integration of statistical grain size distribution functions [86]. Further refinement and the addition of layers of complexity would improve this outcome but at a cost of increased computational time. Potential avenues to improve model fidelity include the incorporation of statistically grain size distribution functions as well as real grain shape. These represent an area of future research as the implementation of these two features would require high fidelity model simulation techniques in the form of computational fluid dynamics. Strictly speaking, it is known that the assumptions for the model constitute an oversimplification of the system, of which an assessment has been done aposteriori by comparing the predictions based on the model with the experimentally collected measurements. Given the outlined assumptions and the prediction comparisons with experimental data, the model description and applicability to the variables that directly influence behavior show good reliability over the outlined ranges of interest. The ultimate objective was the development of a practical model for representing a OC particle in the CLC reducing reactor and the outlined model captures key aspects and transport phenomena without increased layers of
complexity. Key model parameters for the derived GPM two interface model for CuFeAlO$_4$ reduction with H$_2$ are shown in

Table 4-4.

**Table 4-4: Properties of CuFeAlO$_4$ system for 2-interface GPM Reduction with H$_2$**

<table>
<thead>
<tr>
<th>Interface</th>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
<th>95% Confidence Interval Bounds</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Overall Pellet</strong></td>
<td>$R_p$</td>
<td>cm</td>
<td>0.02</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>$R_{g,0}$</td>
<td>cm</td>
<td>0.0005</td>
<td>NA</td>
</tr>
<tr>
<td><strong>$L_1$</strong></td>
<td>$A_{C1}$</td>
<td>cm/s</td>
<td>17</td>
<td>±2.54</td>
</tr>
<tr>
<td></td>
<td>$E_{A1}$</td>
<td>kJ/mole</td>
<td>13.4</td>
<td>±3.45</td>
</tr>
<tr>
<td></td>
<td>$\rho^A_{1-c}$</td>
<td>g/cm$^3$</td>
<td>2.9</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>$n_1$</td>
<td>unitless</td>
<td>0.8</td>
<td>±0.02</td>
</tr>
<tr>
<td></td>
<td>$M_B$</td>
<td>g/mole</td>
<td>210.37</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>$\Phi^A_{7-c}$</td>
<td>mole O$^{2-}$ transferable mole O$^{2-}$ in MeO</td>
<td>0.6</td>
<td>±0.03</td>
</tr>
<tr>
<td><strong>$L_2$</strong></td>
<td>$A_{C2}$</td>
<td>cm/s</td>
<td>90</td>
<td>±6.05</td>
</tr>
<tr>
<td></td>
<td>$E_{A2}$</td>
<td>kJ/mole</td>
<td>85.88</td>
<td>±3.65</td>
</tr>
<tr>
<td></td>
<td>$\rho^C_{2-F}$</td>
<td>g/cm$^3$</td>
<td>2.9</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>$n_2$</td>
<td>unitless</td>
<td>0.8</td>
<td>±0.04</td>
</tr>
<tr>
<td></td>
<td>$M_C$</td>
<td>g/mole</td>
<td>173.81</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>$\Phi^C_{7-F}$</td>
<td>mole O$^{2-}$ transferable mole O$^{2-}$ in MeO</td>
<td>0.4</td>
<td>±0.03</td>
</tr>
<tr>
<td></td>
<td>$t_C$</td>
<td>sec, critical time before FeAl$_2$O$_4$ emergence</td>
<td>0</td>
<td>NA</td>
</tr>
</tbody>
</table>
Activation energy values for both interfaces show agreement with the iso-conversionally determined values presented in section 4.2.6, and were reverified using conventional approaches such as those employed by Tsay et al [77]. Gas phase concentration power terms, $n_i$, were determined using similar methods and show agreement with those reported by other authors for metal oxide reduction with $H_2$ [63]. The critical time for $FeAl_2O_4$ emergence, $t_C$, is set at zero due to the implication of product gas impact on the phase reducibility. This functionality would be necessary in instances where equilibrium was not an important factor. Activation energy for $CuFeAlO_4$ reduction to hercynite is lower than those reported for supported $CuO$ (20-33kJ/mol) [63] and $Fe_2O_3$ (24-50kJ/mol) [63] [29]. Confidence interval bounds were based on estimations provided by model fits generated in MATLAB 2017a software for the population of conditions examined. In addition, linearity coefficients associated with refinement of Arrhenius parameters and reaction order dependence were also applied to these individual coefficients. $\phi^{t-s}$ is given some flexibility due to potential for minor compositional variations with the initial starting mass ratios of $CuFeAlO_4$ and $Al_2O_3$. All other components, denoted by NA were considered constant in fitting approaches.

4.4.5 Examination of the non-isothermal correction for the proposed model to reduction of $CuFeAlO_4$ with $H_2$

To examine whether the isothermal assumption is valid, the non-isothermal correction for the GPM model was employed to determine and correlate the changes in the pellet temperature with changes in extent of reduction. Utilizing energy balances on the spherical grain system, changes in temperature in the reacting grain can be described by E4-36,

$$r_0 > r > r_c, \quad p_B C_p \frac{\partial T}{\partial t} = k_{e,\text{solid}} \left( \frac{\partial^2 T}{\partial r^2} + \frac{2 \partial T}{r \partial r} \right) \tag{E4-36}$$
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with boundary conditions described by E4-37 and E4-38:

\[
\frac{\partial T}{\partial r} = h_g (T_s - T_b) + h_r (T_s^4 - T_b^4) \quad \text{E4-37}
\]

\[
r = r_c, \quad p_b C_p \frac{\partial T_c}{\partial t} = k_c' (T_c) * C_Ac (-\Delta H_{rxn}) + \left( \frac{\partial T}{\partial r} \right)_{r=r_c} \quad \text{E4-38}
\]

Assuming the pseudo steady state approximation for a material with low heat capacity E4-36 - E4-38 can be simplified to E4-39 - E4-41.

\[
r_o > r > r_c, \quad k_{e,\text{solid}} \left( \frac{\partial^2 T}{\partial r^2} + \frac{2 \partial T}{r \partial r} \right) = 0 \quad \text{E4-39}
\]

With boundary conditions described by E4-40 and E4-41:

\[
r = r_o, \quad k_{e,\text{solid}} \left( \frac{\partial T}{\partial r} \right)_{r=r_p} = h'_g (T_s - T_b) \quad \text{E4-40}
\]

\[
r = r_c, \quad -k_{e,\text{solid}} \left( \frac{\partial T}{\partial r} \right)_{r=r_c} = k_c' (T_c) * C_Ac (-\Delta H_{rxn}) \quad \text{E4-41}
\]

where the radiative and convective heat transfer coefficients have been lumped into \( h'_g \). An analytical solution to the pseudo-steady state correction has been presented by Yake [87], Calvelo et al [88], and Szekely et al [89] and is displayed in E4-42.

\[
\frac{1}{k_{e,\text{solid}} \left( \frac{1}{r_{ci}} - \frac{1}{R_{g,0}} \right)} + \frac{1}{R_{g,0}^2 h'_g} = \frac{C_{A,B}^{ni} (-\Delta H_{rxn})}{1 \frac{1}{D_A (r_{ci} - \frac{1}{R_{g,0}})} \frac{1}{R_{g,0}^2 k_g (T_b)} \left( \frac{T_c}{T_b} \right) \frac{T_c/T_b}{r_{ci} k_g \left( \frac{T_c}{T_b} \right)}} \text{E4-42}
\]
The left-hand side of the E4-42 is equal to the heat loss of the grain while the right is equal to the heat generated due to reaction. Simplifications can be further made when certain resistances can be considered negligible. In the case established in the previous sections, 4.4.2-4.4.3, external and internal mass transfer resistances are negligible allowing for the further simplification to solely reaction (kinetically) controlled. Through application of the non-isothermal correction, the temperature of the reacting core interface, $T_c$, in the grain of the oxygen carrier can be calculated based on predetermined values of $k_{Cl}^\prime$, known values of $h_g$ from the Nusselt correlation, and estimated values of the solid thermal conductivity, $k_{e,solid}$. The thermal conductivity of the solid was estimated to be close to that of Al$_2$O$_3$ from tabulated values at the temperature range (700-1000°C), due to the lack of available information on CuFeAlO$_4$. The pseudo steady state approximation assumes that the temperature of the particle changes uniformly throughout the advance of the reaction front, so the reaction front temperature, $T_c$, is indicative of the grain temperature at the time associated with the front advance to the core. Figure 4-17 displays the calculated grain temperature based on the non-isothermal correction with parameter values used from the correction depicted in Table 4-5. The temperature in the first 100 seconds of reaction is depicted as this is related to the exothermic reduction of CuFeAlO$_4$ to hercynite and Cu. The subsequent step is not evaluated due to the endothermic nature.

Based on the energy generated due to the transfer of lattice oxygen to the gas phase fuel source and the convective heat transfer coefficient in the external film, the grain’s temperature was estimated to rise upwards of +7°C. This is not a significant increase given the magnitude of the film convective heat transfer coefficient. These findings suggest a small temperature rise, which
would impact temperature dependent functions such as the kinetic rate constant in a minimal manner, indicating that the isothermal assumption was appropriate in this case. Exothermic reactions, such as those associated with oxidation, which show order of magnitude increases in the exothermic $\Delta H_{rxn}$ as compared to this reduction reaction could favor larger temperature jumps in comparison to those reported in this section. Convective film heat transfer coefficients are also a strong function of the component fluid properties and should be considered for alternative reducing gases. This evaluation was done to ensure the accuracy of the kinetic rate constants determined from the experimental data derived in the previously described TGA-setup, recalling that these coefficients would increase for a fluidized bed system due to the higher Reynolds numbers around the particles.

![Figure 4-17: Application of the non-isothermal correction on the reduction of CuFeAlO4 with H2 (Experimental conditions: $T_b = 800^\circ$C, 20 vol% H2)](image)

### Table 4-5: Parameters used for application of non-isothermal correction

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{g,0}$</td>
<td>cm</td>
<td>0.0005</td>
</tr>
<tr>
<td>$A_{C1}$</td>
<td>cm/s</td>
<td>17</td>
</tr>
<tr>
<td>$E_{A1}$</td>
<td>kJ/mol</td>
<td>13.4</td>
</tr>
<tr>
<td>$\Delta H_{rxn}$</td>
<td>J/gH2</td>
<td>3.21E+04</td>
</tr>
<tr>
<td>$n_1$</td>
<td>cm/s</td>
<td>0.8</td>
</tr>
<tr>
<td>$T_0$</td>
<td>K</td>
<td>1073.15</td>
</tr>
<tr>
<td>$h_{g}'$</td>
<td>[J/s * cm$^2$ * K]</td>
<td>0.046</td>
</tr>
<tr>
<td>$k_{e,solid}$</td>
<td>[J/s * cm * K]</td>
<td>0.0711</td>
</tr>
</tbody>
</table>

---
4.5 Section Summary

A detailed experimental study was carried out to determine the impact of key operational variables on the kinetics of a novel CuFeAlO$_4$ oxygen carrier, with emphasis on the application of a reliable phenomenon driven particle scale model to describe the reduction behavior with H$_2$. Due to the novel nature of the material, several areas were explored experimentally to provide a fundamental understanding of how the material changed as oxygen was depleted from the structure due to reduction with H$_2$. These areas include chemical phenomena such as phase transition (defined as the reduction pathway), physical properties, resistances to oxygen transfer, reaction equilibria all of which are key aspects in the decision-making process for model selection and application. It is found that reduction occurs in a multistep process where CuFeAlO$_4$ → Cu$^{0+}$ + FeAl$_2$O$_4$ → Cu$^{0+}$ + Fe$^{0+}$ + Al$_2$O$_3$ as oxygen is depleted from the structure. The multistep process was successfully emulated through the use of a two interface Grainy pellet model in which reaction (kinetic) control is the main rate limiting step. This approach was validated through the examination of other potential rate limiting resistances. The model emulates changes in key operation variables with good accuracy, ensuring reliability for further use. This work is the first to present the multi-interface GPM for CLC applications, in addition another first to consider the implication of phase dependent reversibility and its influence on reduction. As part of this work, care was taken to examine the implication of non-isothermality on the determination of kinetic rate parameters for the exothermic portions of reduction. It was shown that minor increases in temperature from the bulk fluid temperature would be encountered and suggests the examination of this assumption for other reaction atmospheres, due to $h'_g$ strong functionality of fluid mixture properties, and case specific $\Delta H_{rxn}$. 
Chapter 5 Experimental and Kinetic Analysis for particle scale modeling of a CuFeAlO$_4$ oxygen carrier during reduction with CO in Chemical Looping combustion applications

Chapter Chapter 5 Preface:

In this section the kinetics and particle scale modeling of gas phase reduction of CuFeAlO$_4$ OC with a second major syngas component, CO, are examined as an effort to provide representation for coal fueled CLC. A detailed examination of the influence of key operation variables on reduction of the oxygen carrier material was conducted. In this analysis, product gas reversibility was also examined to understand reaction equilibria. In addition, the influence of the Boudouard reaction was examined and predictive models developed to emulated experimentally observed behavior due to the catalytically driven reaction.

Understanding the effects of reduction on the OC material is a key component to applying kinetic and particle scale model descriptions to accompany the behavior. Once again key questions are revisited and include: (1) How does the phase, chemical and physical properties of the oxygen carrier change with extent of solid conversion? (2) Can certain physical properties be considered constant validating the use of certain conventional models? (3) What types of interfaces exist for oxygen transfer and what is their impact on the transfer rate? (4) Can equilibria impact reduction? Some of these questions were already answered in the previous section. The physical properties of the solid will be considered constant due to the findings with H$_2$ reduction. However, key criterion such as the reduction pathway, potential resistances to mass transfer, and equilibria are examined as these can be impacted by the properties of the reduction gas. These criteria additionally require verification so a similar model description can be used. In
addition to the aforementioned criterion, catalytic coking effects are examined and linked to the predictive model.

5.1 Results and Discussion

5.1.1 Determining the oxygen carrier reduction pathway with CO:
The CuFeAlO$_4$ OC has a unique structure and a reduction pathway with CO corresponding to this structure has not been reported previously. In order to address this, a series of experiments were performed to determine the CuFeAlO$_4$ OC reduction pathway during exposure with CO. Samplings of material (100mg, ±1mg) were reduced for incremental time intervals isothermally, then rapidly quenched (500°C/min) to room temperature (Figure 5-1a) using the same method used in section 4.2.1. Subsequent scans using ambient temperature XRD were conducted to determine the phases present associated with exposure time and oxygen depletion. Figure 5-1b displays XRD of the quenched samplings, corresponding to various reduction times, depicting the reduction pathway for the CuFeAlO$_4$ OC during exposure to 20 vol% CO at 800°C.

From the thermogravimetric weight loss profile, it can be observed that an initial fast reaction stage is followed by a slower reacting stage. Near the end of the slow reaction stage weight increases begin to occur due to the deposition of carbon. XRD scans of the partially reduced quench samplings shed light on the chemical changes due to the depletion of oxygen from the metal oxide lattice associated with these stages. During the initial fast stage of reduction, oxygen ions bound to Cu$^{2+}$ cations in the tetrahedral positions are removed more readily than those associated with Fe and Al bonds. This is confirmed due to the presence of metallic copper leaving solid solution prior to other components. As the Cu cations are removed out of the lattice structure due to tetrahedral bound oxygen depletion, lattice reorientation takes place causing the formation of Fe-Aluminate
Development and Particle Scale Modeling of Metal Oxide Oxygen Carriers for CL applications

(hercynite) and unbound metallic Cu. Finally, during the slower reaction segment, oxygen is depleted further from FeAl$_2$O$_4$ until base metal/metal oxide components of Fe & Al$_2$O$_3$ remain, as was shown previously in E4-1. Metallic Iron, Fe, presence initiates carbon deposition to occur.

\[
\text{C}u\text{FeAlO}_4 \rightarrow O^{2-} \rightarrow \text{Cu} + \text{FeAl}_2\text{O}_4 \rightarrow O^{2-} \rightarrow \text{Cu} + \text{Fe} + \text{Al}_2\text{O}_3 \quad \text{E4-1}
\]

\[
2\text{CO} \rightarrow \text{Fe} \rightarrow \text{C} + \text{CO}_2 \quad \text{E5-1}
\]

E5-1 depicts the Boudouard reaction catalyzed by the reduced metallic iron species. Once again, it is observed that FeAl$_2$O$_4$ has increased reductive potential when in the presence of Cu recalling...
that the phase was identified as a solid reduction product of Fe$_2$O$_3$-Al$_2$O$_3$ mixture by Cabello et al and was considered a relatively inactive material with reduction gases of CO [46]. These experiments provide two major findings: (1) The reduction pathway is the same regardless of the whether the reduction gas is H$_2$ or CO. (2) Increased complexities occur due to iron’s ability to catalyze the Boudouard reaction. No characteristic peaks for carbon are seen in the XRD analysis which suggests that the phase was amorphous.

5.1.2 Thermodynamic Considerations:
Another consideration that must be examined are the enthalpic contributions from reduction. Due to the novel nature of CuFeAlO$_4$, these properties are not readily available and enthalpic contributions were directly measured. Figure 5-2 displays the TGA-DSC profiles for a single reduction cycle where reduction was conducted with 20 vol% CO and compared with reduction reactions conducted with 20 vol% H$_2$ at the same isothermal temperature of 800°C. $\Delta H_{\text{rxn}}$ determined for CuFeAlO$_4$ was compared with measured values determined for H$_2$ and are shown.

Figure 5-2: TGA-DSC profiles for the reduction of CuFeAlO$_4$ OC with 20 vol% R @ 800°C. (a) comparison of redox profiles in when R = CO & H$_2$. (b) Comparison of experimentally determined values for $\Delta H_{\text{rxn}}$ when R=CO & H$_2$. 
in Figure 5-2b. Measured values were extracted by integrating the weight normalized heat flow for the time periods associated with the reduction reaction and then converting to a per mole basis through application of the component’s molecular weight.

Full reductions were carried out, where the complex cubic spinel was reduced to base metal components (Cu, Fe, & Al₂O₃). In general, values for $\Delta H_{\text{reduction}}$ with CO were slightly lower than those measured with H₂, approximately 7 kJ/mol-OC less. In addition, the reaction progression is slower for the same vol% of reactive gas when comparing CO with H₂. These values are mainly for the primary exothermic reaction where oxygen is removed from Cu²⁺ cations bound in the tetrahedral position of the crystal structure. FeAl₂O₄ reduction does not contribute greatly to changes in heat flow suggesting that its enthalpic contribution is neutral. In these sets of experiments the enthalpic contribution from the Boudouard reaction is not examined as it happens only when metallic Fe is present for extended periods of time.

This comparison of experiments provided three major findings: (1) The enthalpic contribution, $\Delta H_{\text{reduction}}$, with the reduction gas of H₂ or CO are similar. Values are generally 7 kJ/mol-OC lower with the higher molecular weight reduction gas. (2) Enthalpic contribution cannot be readily predicted for the complex spinel so knowledge of these measurable quantities are critical for model assumption verification and further use in techno-economic assessments. Since the enthalpies of reaction are nearly equivalent for the two reduction gases it can be assumed that the isothermal assumption in the model description is valid based on the observation from section 4.4.5. The non-isothermal correction will likely not provide significant increased internal temperatures in the exothermic reaction segments based on the relations observed with H₂. The film heat transfer coefficients are evaluated in section 5.1.2 to further verify the model assumption.
5.1.3 Impact of Particle Size on the reduction characteristics

Experiments were conducted to determine if spherical pellet size could impact the oxygen depletion rate. These experiments were conducted to determine if particle size could impose internal diffusional effects on the reduction of the oxygen carrier. Experiments were conducted at 900°C to minimalize the effects of carbon deposition due to the Boudouard reaction at later stages of reduction. Minimal changes occur between the 1000µm range (±2%), as shown in Figure 5-3, suggesting that internal pellet diffusional effects were not appreciable over the size range of interest. The same phenomenon was observed for experiments in which H₂ was used as a reduction gas. This observation leads to a key assumption that the grains within the pellet can uniformly convert simultaneously. Suggesting that within this size range (25-1100µm) there would be minimal concentration gradients within the pellet and this phenomenon is attributed to the macroporous network that exists in the pellet structure, as shown in section 4.2.3.

5.1.4 Effect of reactive gas concentration and temperature on the reduction behavior:

A major operational variable for CLC units is the fuel gas concentration as this can dictate the thermal output of the unit [28]. In addition, depending upon the fuel source CO concentrations...
can vary widely in the system. Therefore, the effect of concentration on the extent of reduction was examined to determine its significance in OC conversion. The impact of CO reducing gas concentration on the oxygen depletion from the CuFeAlO$_4$ oxygen carrier is shown in Figure 5-4. A range of 5-30 vol% CO was utilized at 800°C to provide a wide range of the operation variable. It was determined that the concentration of the reductant CO plays a major role in the extent of reduction and the time to complete full conversion, with concentration playing a significant role in both fast and slow reaction segments. At high CO concentrations (30 vol%) full depletion of lattice oxygen in the OC occurred in ~1200 secs, while concentrations on the low end of the range (5 vol%) took upwards of 7000 secs to fully deplete the OC,

![Figure 5-4: Effect of reducing gas concentration (a) 5-30 vol% CO at 900°C and temperature (b) 700-900°C on CuFeAlO$_4$ reduction behavior](image)

similarly to observations when H$_2$ was used as a reduction gas. These results indicate that CO gas concentration is a critical variable and must be accounted for in the particle scale model description to appropriately provide full functionality.

A second aspect that is critical to chemical looping combustion systems is carbon capture efficiency. The idea behind the system is to minimalize the need for energy intensive carbon
dioxide separation techniques by eliminating the need to separate CO$_2$ from Air [90]. With that noted, any carbon formation on the surface of the reduced carrier that is transferred to the Air reactor will reduce the carbon capture efficiency of the system. Understanding when coking can occur and the extent of carbon deposition is a critical aspect for maintaining a system with a high carbon capture efficiency. In Figure 5-4b, the effects of temperature show a clear picture of the extent of coking that can occur due to the Boudouard reaction when CO is part of the fuel source being converted to higher oxidation products. The Boudouard reaction is exothermic and equilibrium based, so higher concentrations of CO and lower temperatures will drive the reaction in the forward direction promoting surface carbon formation [91]. Over the temperature range 850-900°C, minimal carbon deposition was observed suggesting that above 900°C the forward reaction is thermodynamically unfavorable. The effects of this reaction are discussed further in section 5.2.4

5.1.5 The application of model free isoconversional methods for the initial determination of activation energy

In section 4.2.6, a technique for converting thermogravimetric weight profiles into a normalized conversion function $X_p$, was presented. The normalized conversion function can be used for a number of comparative purposes, one being model-free isoconversional methods. Recalling E4-3, by plotting $\ln(t)$ with respect to $1/T$, the activation energy can be obtained for a given value of $X_p$ from the slope of the regression line if at least three isothermal temperatures are explored. Model-free iso-conversional techniques have conventionally been used in the past when determining the kinetic rate parameters from thermal analysis techniques [66] [67]. In this work, model-free iso-conversional techniques were used to evaluate the kinetic parameter of the overall activation energy associated with the reduction of the metal oxide with CO. This technique provides a non-
biased approach to determining the reduction activation energy without the assumption of an underlying model and results of the analysis are shown in Figure 5-5.

From the analysis, a clear shift in activation energy is observed around $X_p = 0.5-0.6$, were a mean shift from 25kJ/mol to ~75kJ/mol is observed. This shift in conversion happens consistently with the oxygen depletion quantities necessary for the formation of hercynite and supports the hypothesis that the formation of another phase is predominantly contributing to the transfer of
oxygen to the gas phase reductant at that conversion level. The analysis also provides insight on the magnitude of the operational variable of temperature, where it can be seen that temperature plays a major role in the extent of reduction. This is found to be particularly true for the less active phase of hercynite which requires increased energy inputs to allow for the transfer of oxygen. It is interesting to note that the CuFeAlO$_4$ material is still partially active at 500-600°C, with the ability to transfer 3-7wt% lattice oxygen. As these values are below the oxygen transfer quantities needed to form hercynite, it can be concluded that this phase is inactive at these temperatures. Subsequently, viable temperature ranges for the model description will be confined to 700-900°C where the primary (CuFeAlO$_4$) and secondary (FeAl$_2$O$_4$) phases are actively participating in oxygen transfer with CO. These are the same as findings from analysis conducted with H$_2$, showing consistency among the gases. The only major difference being that the primary reaction phase of CuFeAlO$_4$ has an activation energy of +10kJ/mol higher when CO is the reduction gas.

### 5.1.1 Effect of product gas concentration and the implication of reversibility in reaction equilibria:

Product gas contributions can potentially play a major role in the kinetics of reduction if a material has the ability to uptake molecular oxygen from soft oxidants such as the product gas CO$_2$. In this section, the product gas (CO$_2$) concentration is explored to determine if any of the primary reduced phases are able to utilize this oxygen containing molecule as an oxygen donor. Two experimental configurations, Q600 SDT and TGA-MS, are used to determine if this effect is possible with the current OC. X-ray diffraction is used to examine the predominant phases before and after reaction. Figure 5-6a displays the TGA-DSC profile for the reduction of CuFeAlO$_4$ OC and subsequent exposure to 20 vol% CO$_2$ at 800°C.
Figure 5-6: (a) TGA-DSC profile for the reduction of CuFeAlO4 OC and subsequent exposure to 20 vol% CO₂ at 800°C (b) primary phase determinations from XRD before and after CO₂ exposure.

Figure 5-7: (a) TGA exposures for 700-900°C with 10vol% CO₂ after full reduction with H₂ (b) conversion profiles for exposure segments (c) & (d) isoconversionally determined Eₐ.
Figure 5-6b displays the primary phase determinations before and after CO\textsubscript{2} exposure. The fully reduced material was able to utilize oxygen from CO\textsubscript{2} to re-form the cubic spinel FeAl\textsubscript{2}O\textsubscript{4} phase and observed weight percentages correspond with this observation.

The metallic Cu component remains isolated and does not reincorporate into the structure after the initial exposure of 20 vol\% CO\textsubscript{2}. At extended periods of time during the CO\textsubscript{2} exposure, weight gains begin to occur suggesting that some Cu becomes incorporated at a very slow rate. This allows for the deduction that the reaction progression with the second phase is reversible whereas the first can be considered relatively irreversible. For the sake of model simplicity, the second step will be considered irreversible due to the very slow nature of progression. It also can be noted that oxygen uptake to form FeAl\textsubscript{2}O\textsubscript{4} is mildly exothermic, with ΔH ≈ 9.68 kJ/mol of which is less exothermic than with H\textsubscript{2}O. Due to the apparent reversibility for the second phase progression, iso-conversional methods were applied to provide an estimate of the activation energy associated with the reverse reaction, shown in Figure 5-7. There were minor differences in the conversion progression as temperature was increased from 700-900°C, insinuating that the activation energy for the reaction was small in magnitude. The activation energy, determined from iso-conversional methods, for the uptake of molecular oxygen from CO\textsubscript{2} (referred to as Carbon dioxide splitting) is 2x less than that of the forward reaction in which oxygen is removed from FeAl\textsubscript{2}O\textsubscript{4} crystal structure by CO. Two major findings were deduced from this set of experiments: (1) The reverse reaction with CO\textsubscript{2} was a very prominent step and should be included in the model description. (2) Moderate concentrations of CO\textsubscript{2} can potentially hinder the forward reaction from progressing, this is discussed further in the model application section, 5.2.
5.1.2 **Examination of film convective mass and heat transfer coefficients:**
External film convective heat and mass transfer coefficients are examined to determine if film resistances in the current experimental setup could possible play a role in the reduction behavior with the reduction gas of interest (CO). The Nusselt number and Sherwood number are examined based on the TGA reactor operating conditions to determine the pellet external convective heat transfer coefficient, \( h'_g \), and mass transfer coefficient, \( k'_g \), respectively. The Nusselt correlation for heat transfer from a sphere [68] and the Sherwood correlation for mass transfer from a sphere [69] were shown previously in E4-4 and E4-5 respectively in section 4.2.8.

The Nusselt and Sherwood correlations are dependent upon the fluid properties with these properties being estimated by considering the mole fraction of the component multiplied by the property of the pure component, with all individual components summed to arrive at the mixture property. Tabulated properties and temperature dependent correlations of the pure gases were used when determining the mixture properties [70]. Heat capacities of the pure components were calculated using the Shomate equation with coefficients provided and tabulated by NIST [71]. Thermal conductivity, \( k_e \), of the primary gases in the reactive gas mixture were estimated using correlations. Thermal conductivity of Carbon monoxide was estimated through correlations developed by Barua et al [92] and alternatively determined for Argon through correlations developed by Faubert et al [73]. Binary diffusivities, \( D_{AB} \), were estimated through the application of E4-6 [74].

Binary diffusivities, \( D_{AB} \) were estimated through correlation with critical properties of the components in the binary mixture, mixture density, and component molecular weight. Table 5-1 depicts the convective film heat and mass transfer coefficients for the mean pellet size over the range of 500-900°C (773-1173K).
Table 5-1: Calculated Convective heat, mass transfer coefficients, and Weitz-Prater criterion for 20% CO-Ar mixture over operating temperature range

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>773</th>
<th>873</th>
<th>973</th>
<th>1023</th>
<th>1073</th>
<th>1123</th>
<th>1173</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h_g'$ $[J_{s} \cdot cm^2 \cdot K]$</td>
<td>0.054</td>
<td>0.062</td>
<td>0.068</td>
<td>0.071</td>
<td>0.074</td>
<td>0.077</td>
<td>0.080</td>
</tr>
<tr>
<td>$k_g'$ $[cm/s]$</td>
<td>19.8</td>
<td>26.3</td>
<td>33.9</td>
<td>38.1</td>
<td>42.6</td>
<td>47.3</td>
<td>52.4</td>
</tr>
<tr>
<td>$C_{WP}$ ($*10^{-4}$)</td>
<td>5.94</td>
<td>6.70</td>
<td>8.67</td>
<td>8.64</td>
<td>8.01</td>
<td>7.32</td>
<td>6.84</td>
</tr>
</tbody>
</table>

The relatively high magnitude of the film mass transfer coefficients suggests that it is not a controlling resistance over the operational range. It should be noted that the reduction gas properties significantly impact this coefficient due to the near order of magnitude reduction in comparison with those calculated for H$_2$. With this noted, the coefficient values are large enough in magnitude to the conventionally obtained values for the reaction front progression that the effects would be negligible. This is further verified in the model application section to ensure that all limiting resistances are properly accounted. Heat transfer coefficients for the external film are low in magnitude but larger than those determined for H$_2$. Based on this observation and the lower reaction enthalpy, internal pellet heating will not play a major role in the determination of kinetic parameters when applying the model description. Therefore, the isothermal assumption is valid in this case. Internal diffusional limitations within the particle can be neglected based on findings reported in section 5.1.3 and grain based internal diffusion limitations are expected to be minimal with effective diffusivities on the range of 1-2 cm$^2$/s. In addition to this observation, the Weitz-Prater criterion ($C_{WP}$) was examined from a heuristic standpoint to provide guidance and estimate if internal diffusion limitations were possible. The low relative magnitude of values reported in Table 5-1 ($1x10^{-4}$) suggests that diffusion limitations should be negligible within the grain.
5.2 Application of the Grainy Pellet Two interface model for the Gas Phase Reaction Mechanisms between CuFeAlO\textsubscript{4} Oxygen Carrier with CO.

In this section, the application of the GPM two interface model is presented to describe the reduction mechanism of the CuFeAlO\textsubscript{4} OC material with CO. Key findings derived from the experimental study are restated and correlated to the particle scale model. The range of applicability is defined as well as model limitations.

5.2.1 Summary of assumptions based on experimental data for the application of the model:

The experimental studies provided answers regarding the physical and chemical properties of the CuFeAlO\textsubscript{4} oxygen carrier. These properties include the material’s reduction pathway, determination of intermediate reduced phases, and the route to final reduced solid products with three distinct reaction phases, CuFeAlO\textsubscript{4}, FeAl\textsubscript{2}O\textsubscript{4}, and Fe being identified. The grains of the material comprise the non-porous reactive components with the grains being considered spherical to simplify the model description. The bulk density is considered constant. Particle size is considered constant. Additional assumptions are discussed as the model description is developed in subsequent sections.

5.2.2 Proposed Scheme and Representations:

A Multi-interface grainy pellet model was utilized in section 4.4 to describe the reduction kinetics of H\textsubscript{2} with the CuFeAlO\textsubscript{4} oxygen carrier. Based on experimental observations, the same model description can be applied for this scenario with CO as the reacting gas. The model links the gas-solid reactions determined through experiments in section 5.1 (E5-2 - E5-4) to continuity balances in a spherical particle.
3CO(g) + 2CuFeAlO₄(s) + Al₂O₃(s) ⇌ 2Cu(s) + 2FeAl₂O₄(s) + 3CO₂ \hspace{3cm} \text{E5-2}

CO(g) + FeAl₂O₄(s) \underset{k_{c2,R}}{\overset{k_{c2,F}}{\rightleftharpoons}} Fe(s) + Al₂O₃(s) + CO₂ \hspace{3cm} \text{E5-3}

CO(g) + Fe(s) \overset{k_c}{\rightleftharpoons} Fe(s) + C + CO₂ \hspace{3cm} \text{E5-4}

The grainy pellet model links the change in degree of reduction of the solid with the change in radius of an unreacted core of a spherical grain. A schematic of the two-interface grainy pellet model was shown in Figure 4-12, section 4.4.2. L₁ is the portion of the grain associated with the primary initial phases of CuFeAlO₄ & Al₂O₃ with \( r_c^{B-C} \) and \( \rho_1^{B-C} \) attributing to the reacting core interface and associated bulk density. L₂ is the portion of the grain associated with the secondary product layer reactive phases of FeAl₂O₄ & Cu with \( r_c^{C-F} \) and \( \rho_2^{C-F} \) attributing to the secondary reacting core interface and associated bulk density. L₃ is the portion of the grain associated with the unreactive oxygen depleted product layer phases of Cu, Fe & Al₂O₃ with \( \rho_P^{E-F} \) as the associated bulk density of the product layer mixed phase. The only major difference with applying the model to CO exposure is the addition of the catalytic Boudouard reaction (E5-4) in the outermost layer with available Fe species. With this noted, the derivation is equivalent and will not be rederived. Differences arise to establish a connection between the 2 interface GPM and the catalytic reaction leading to carbon deposition and this is explored in further detail. The application section is presented in the following manner: (1) Model representation for the reverse reaction of E5-3 is addressed as this allows for the examination of a single unconvoluted step. (2) Equilibrium for E5-4 is examined and the appropriate model representation for the Boudouard
reaction is derived. (3) All the steps are brought together to provide a complete model description and the benefits/limitations are discussed.

5.2.3 Application of the GPM model for the Reversible reaction phase

The reversible reaction front corresponding to reaction depicted in E5-3 in which reduced species (Fe + Al₂O₃) interact with product gas of CO₂ to form FeAl₂O₄, is a feasible starting point for approaching the use of the GPM. The singular primary phase contribution allows for a direct determination of appropriate kinetic parameters within the model, in the absence of other contributions. It is known from experimentation that phases of metallic Fe and Al₂O₃ in the OC will reorient upon donation of molecular oxygen from CO₂ to form the cubic spinel phase of FeAl₂O₄. It was also shown that preliminary determinations for the energy barriers, from isoconvensional methods, for this reaction were nearly 2 times less than that of mechanism for stripping of oxygen from the spinel structure. These parameters are optimized in this section and linked to the progression of the reaction front. Figure 5-8 displays the model representation for the spherical pellet, $F_{C₂, CO₂}$, for the reverse reaction front progression in which Fe & Al₂O₃ utilizes molecular oxygen from CO₂ to form FeAl₂O₄ and product gas of CO. In this case a simplified expression is taken to determine $k_{C₂,R}$, of which can be used in the equilibrium constant, $K_{e₂}$, for the second reaction front.

$$\frac{t}{\tau_{R2,R}} = 1 - \left(1 - X_{L2,R}\right)^{\frac{1}{3}}, \quad \tau_{R2,R} = \frac{E_{C₂,R} - C_{CO₂,n}}{b k_{C₂,R} C_{CO₂}} X_{L2,R} = F_{C₂, CO₂}$$  \hspace{1cm} E5-5

In this case and as was presented in earlier sections, the grain conversion, $X_{L2,R}$, is representative of the conversion of all grains over the entire spherical pellet, $F_{C₂, CO₂}$. Application of the model shows good agreement with the experimental data and well within relative error of the
measurement. In these fitting approaches the experimentally measured concentration profile is input into the model description to ensure accuracy of the derived kinetic parameters. There are some minor effects of product dilution that occur in the first 150 seconds of CO$_2$ introduction.

Product gas of CO is formed during the entire reaction segment following agreement with the identified reaction mechanism. Model agreement with experimentally determined data allows for refinement of kinetic parameters.

Figure 5-8: Model Representation, $F_{CL, CO_2}$, for the reverse reaction front progression in which Fe + Al$_2$O$_3$ + CO$_2$ → FeAl$_2$O$_4$ + CO (Data shown for 900°C exposure with ~11vol%CO$_2$).
Figure 5-9 displays the Arrhenius and reaction order dependence plots for the refined representation. The Arrhenius plot (\( \ln k^*_{CZ,R} \)) vs. \( 1/T \) shows linearity over the explored temperature range suggesting that the single activation energy and preexponential factor are suitable for the temperature window explored.

![Arrhenius plot and reaction order dependence](image)

Table 5-2 summarizes the kinetic parameters determined for the reverse reaction of the L\(_2\) front from experiments used to generate plots in Figure 5-9. The low activation energy determined for
this process is within the bounds determined by iso-conversional methods and suggests that the reaction will proceed readily with small effects of temperature over the evaluated range. The reaction order was first order with respect to the concentration of CO\(_2\) and insinuates that the reaction is elementary as the order follows stoichiometry.

Table 5-2: Kinetic Parameters for reverse reaction of the L\(_2\) front

<table>
<thead>
<tr>
<th>Interface</th>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
<th>95% Confidence Interval Bounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L_{2,R})</td>
<td>(A_{C2,R})</td>
<td>(cm/s)</td>
<td>0.442</td>
<td>±0.05</td>
</tr>
<tr>
<td>(E_{A2,R})</td>
<td></td>
<td>(kJ/mole)</td>
<td>20.95</td>
<td>±1.95</td>
</tr>
<tr>
<td>(\rho_{2}^{\Sigma-F})</td>
<td></td>
<td>(g/cm^3)</td>
<td>2.9</td>
<td>±0</td>
</tr>
<tr>
<td>(n_{2})</td>
<td></td>
<td>unitless</td>
<td>1</td>
<td>±0</td>
</tr>
</tbody>
</table>

The activation energy \(E_{A2,R,CO2} > E_{A2,R,H2O}\) and pre-exponeontial factor \(A_{C2,R,CO2} < A_{C2,R,H2O}\).

These observations shed light on the magnitude of the intrinsic rate constant \(k_{c2,R,i}^{\ast}\) for the individual gas components. In general, H\(_2\)O has a faster intrinsic reaction rate than CO\(_2\) and is not impacted as significantly by temperature, making H\(_2\)O have a more prominent impact on reducibility of FeAl\(_2\)O\(_4\). Small continuous concentrations (≥2vol%) of either of the soft oxidants (H\(_2\)O, CO\(_2\)) at operating temperatures will hinder the reduction of FeAl\(_2\)O\(_4\) to base metallic and oxide components.
5.2.4 **Examining equilibria and deriving the model representation for the Boudouard reaction with Reduced Iron species.**

Carbon deposition via the Boudouard reaction is a catalytic process that is dependent upon the concentration of free available Fe in the reduced outer layer OC grains. Brown et al have noted the catalytic effects of Fe and its prevalence to drive the Boudouard reaction forward to generate carbon species [93]. This is well known in the field of refractory ceramics because small amounts of available Fe in ceramic refractories can lead to carbon induced disintegration of the ceramic constructs. It is important that the mechanism incorporate the available concentration of Fe as this changes with extent of reduction. The concentration of Fe is defined in E5-6.

\[
[Fe](\text{g/cm}^3) = \frac{\gamma_{Fe}N_{0,\text{FeAl}_{2}O_{4}}X_{L2}MW_{Fe}}{V_{g}n_{g}}
\]

The available concentration of Fe is linked to the progression of the fractional conversion of FeAl$_2$O$_4$, $X_{L2}$, the initial number of moles of FeAl$_2$O$_4$ ($N_{0,\text{FeAl}_{2}O_{4}}$), the stoichiometric coefficient $\gamma_{Fe}$, the volume of the grain $V_{g}$, and the estimated number of grains, $n_{g}$, in the sample based on the total sample weight. Since the Boudouard reaction is dependent on the Fe concentration as well as the other species, this must be included in the rate expression. Langmuir-Hinshelwood kinetics are used to derive a mechanism for the reaction.

\[
\begin{align*}
2\text{CO} + 2\text{Fe} & \overset{k_{\text{Ads}}}{\leftrightarrow} 2\text{CO} - \text{Fe} \quad \text{E5-7} \\
2\text{CO} - \text{Fe} & \overset{k_{\text{rx}}}{\leftrightarrow} \text{CO}_2 - \text{Fe} + \text{C} - \text{Fe} : \text{RLS} \quad \text{E5-8} \\
\text{CO}_2 - \text{Fe} & \overset{k_{\text{Des}}}{\leftrightarrow} \text{CO}_2 + \text{Fe} \\
\text{C} - \text{Fe} & \overset{k_{\text{decomposition}}}{\rightarrow} \text{C} + \text{Fe} \quad \text{E5-10}
\end{align*}
\]

It is assumed that the reaction between the adsorbed CO species is the rate limiting step. Therefore, the rate expression can be defined as a function of the species in E5-8 as shown in E5-11.
Development and Particle Scale Modeling of Metal Oxide Oxygen Carriers for CL applications

\[
\frac{d}{dt} = k_f \left[ [CO - Fe]^2 - \frac{[CO_2][C]}{K_c} \right] \tag{E5-11}
\]

Examination of equilibrium can allow for the determination of the unhindered forward reaction rate as well as the prevalence of the forward reaction with respect to temperature and CO concentration. It is observed from experimental results that the amount of carbon deposition decreases with increases in temperature, shown previously in Figure 5-4b. The only way to address this phenomenon is to introduce an equilibrium constant based on the enthalpy associated with the reaction, shown in E5-12.

\[
K_c = K_c(T_{ref}) e^{\frac{\Delta H_{rxn}}{R} \left( \frac{1}{T_{ref}} - \frac{1}{T} \right)} \tag{E5-12}
\]

Naturally, \( K_c \) will decrease in magnitude with temperature for exothermic reactions as displayed in Figure 5-10.

\[\text{Figure 5-10: Estimation of } K_c \text{ for the Boudouard Reaction based on estimation of Enthalpy from FactSage 7.1}\]

At 500°C the forward reaction rate is ~500x that of the reverse and at 600°C around 200x that of the reverse. This means that the forward rate can be evaluated free of major contributions from
the reverse in this temperature range. The oxygen carrier was fully reduced with H₂ to expose all the available Fe so the maximum carbon deposition rate could be determined, as well as the activation energy and associated Arrhenius rate constants, shown in Figure 5-11 & 5-12, with the expression for carbon production delineated in E5-13.

\[
[C](\frac{g}{cm^3}) = k_f[2[CO][Fe]]t \tag{E5-13}
\]

By applying \(V_gn_g\) to the carbon production density a mass quantity can be obtained. With the kinetic parameters known for the forward reaction rate leading to carbon deposition, an expression can be developed for the production of carbon on the surface of the material that couples the intrinsic reaction rate with equilibria and gas concentrations shown in E5-14.

Figure 5-11: Carbon deposition experiments for \(k_f\) (Boudouard) in the unhindered forward reaction regime
Figure 5-12: Kinetic parameters determination for $k_f$ (Boudouard) in the unhindered forward reaction regime

$$
\ln[k_f'' \text{[cm}^3\text{g}^{-1}\text{sec}] = \text{y} = -4341.5x + 3.7421 \quad R^2 = 1
$$

Conventionally, the solid active site is removed from the expression by performing a total site balance. Additionally, coking due to a carbonous species adsorption is treated using an alpha decay term in which the detailed expressions are lumped into a single term to describe how a catalysts’ activity decays with coking [94] [95]. These types of expressions are not suitable in this case due to the need for predicting the amount of carbon that is deposited as this impacts the carbon capture efficiency of the CLC system. Few authors have set out to devise kinetic expression for determining the quantity of carbon deposited and an appropriate coke formation rate equation. Annaland et al presented a Langmuir-Hinshelwood type mechanism to describe the coking during propylene cracking [96] and the work was used as an inspiration for the mechanism and model presented in E5-7 - E5-15. In this case, the quantity of Fe in the solid is known because the extent of conversion

$$
[C] \left( \frac{g}{cm^3} \right) \approx Kc k_f [CO][Fe * \theta]t - \frac{k_f}{K_c} [CO_2][Fe * \theta]t
$$

$$
[\theta] = \theta_1 e^{(-\theta_2 t)}
$$
from the L2 front can be used to correlate the amount of Fe that has come out of solid solution due to oxygen depletion from the FeAl$_2$O$_4$ structure. An Fe active site availability term, $\theta$, is introduced into the expression to scale the quantity of available Fe. This is done to accommodate for iron that has come out of phase but is not readily available for participation in the reaction. Carbon quantities that are determined from the coupling of available Fe and Boudouard reaction model can be used to derive a carbon corrected overall pellet conversion shown in E5-16 -

\[
E5-16.
\]

\[
m_{OC}(t)_{predicted} = m_{o,OC} - F_p(m_{o,OC} - m_{f,OC})
\]

\[
F_{p,carbon \ corrected} = \frac{(m_{o,OC} - m_{OC}(t)_{predicted} + m_{Carbon}(t)_{predicted})}{(m_{o,OC} - m_{f,OC})}
\]

A predictive mass loss profile was obtained by using the model predictive conversion function, $F_p$ and initial, $m_{o,OC}$, and final, $m_{f,OC}$, weights of the OC. This format being similar to how the experimental conversion was defined, refer to section 4.2.6 for further detail.

$F_{p,carbon \ corrected}$ is accomplished by adding the predictive mass loss profile with the mass of carbon generated with respect to the initial and final OC weights.

5.2.5 Application of the GPM two interface model to reduction of CuFeAlO$_4$ with CO

The application of the GPM to the reacting system involves the coupling of the multiple interfaces. In addition, catalytic effects of carbon deposition are accounted for through model coupling of the equilibrium driving Boudouard reaction. In this section, three cases of the model are presented and the limitations discussed. Three different temperatures 900, 800, 750°C are presented as the effects of carbon deposition are different among the range due to the impact of
the equilibrium driven Boudouard reaction. Figure 5-13 displays a comparison between experimental and predictive conversion profiles for 900°C with ~27vol% CO exposure. At this temperature and reductant concentration the model prediction for the grain oxygen consumption shows agreement with the experimentally derived data. The correlation coefficient for the predictive fit is within acceptable bounds. At 900°C, the equilibrium constant $K_c$ for the Boudouard reaction, was approximately 1.0002. This means that carbon deposition cannot occur at this temperature because the forward and reverse rates are approximately equal. Any carbon that is formed is quickly converted back to CO by the product CO$_2$ formation. Examination of Figure 5-13b further supports this by showing no appreciable carbon deposition in the molar quantity phase distribution profiles. A description of the phase changes is shown with respect to time by applying the fractional conversions of each reacting front and linking it to the component molar balances and reaction stoichiometry, see section 4.4.4 for details. Figure 5-13b displays the component balances on the CuFeAlO$_4$ OC plus unincorporated residual Al$_2$O$_3$. The basis for this calculation is a typical quantity loaded in the TGA apparatus. As can be observed, CuFeAlO$_4$ consumption occurs rapidly within the first 90 seconds of reduction attributing to the donation of lattice oxygen to the gas phase reductant (CO) and the formation of metallic Cu accompanied by hercynite (FeAl$_2$O$_4$). FeAl$_2$O$_4$ formation occurs due to the presence of residual Al$_2$O$_3$, which is partially consumed to form the intermediate. FeAl$_2$O$_4$ then continues to transfer oxygen to the gas phase reductant ultimately forming reduced phases of Fe and Al$_2$O$_3$ in equimolar quantities. Figure 5-14 displays a comparison between experimental and predictive conversion profiles at 800°C with ~27vol% CO exposure. At this temperature, the equilibrium constant $K_c$ for the Boudouard reaction, was approximately 5.07 making the potential for carbon
Figure 5-13: Application of the two zone GPM to reduction of CuFeAlO$_4$ with 27 vol% CO @ 900°C: (a) Comparison of experimental conversion with $F_P$ and the individual interface fractional conversions. (b) Component mole balances showing new phase formation due to reduction and oxygen transferred to gas phase.
Figure 5-14: Application of the two zone GPM to reduction of CuFeAlO$_4$ with 27vol% CO @ 800°C: (a) Comparison of experimental conversion with $F_p$ and the individual interface fractional conversions. (b) Component mole balances showing new phase formation due to reduction and oxygen transferred to gas phase with carbon deposition.
deposition possible. It can be seen from the correlation coefficient that the predictive model suitably matches experimentally acquired data. FeAl$_2$O$_4$ reduction initiation does not occur until reactor CO$_2$ levels drop below 1 vol%. This highlights the magnitude of reversibility on reaction E4-42. Once FeAl$_2$O$_4$ begins to reduce to base metal components of Fe and Al$_2$O$_3$, carbon deposition begins to occur due to the catalytic effects of E5-1. At 750 seconds, small amounts of carbon begin to accumulate on to the surface of the OC and cause the experimentally observed conversion rate to slow and eventually changes directional magnitude at 1500 seconds of exposure time where the rate of carbon deposition exceeds the rate of oxygen depletion from the FeAl$_2$O$_4$ phase with gas phase CO. After 1500 seconds, carbon accumulates with a linear rate as the majority of available Fe is present for participation in the catalytic reaction. Figure 5-15 displays a comparison between the experimentally determined conversion profiles with those predicted from the model description at 750°C. At 750°C, the equilibrium constant $K_c$ for the Boudouard reaction was approximately 12.9, making the impact of coking even more prevalent then higher temperatures. It is important to note that the only way of accommodating this type of behavior (carbon deposition effects increase with decreasing temperature) was to include considerations of equilibrium and the thermodynamics of the reaction. At temperatures below 800°C, the effects of carbon deposition are more challenging to predict as can be seen in Figure 5-15. Carbon deposition effects are under predicted by the model to some extent. This suggests that the simplified model for carbon deposition does not capture the effects entirely and may need a separate description for cases of lower temperature. This represents an area of future research for model fidelity improvement. In the present case, it is unlikely that CLC systems will operate at temperature ranges below 800°C, so the description provided is suitable in this case [2].
Figure 5-15: Application of the two zone GPM to reduction of CuFeAlO$_4$ with 27% CO @ 700°C:
(a) Comparison of experimental conversion with $F_p$ and the individual interface fractional conversions. (b) Component mole balances showing new phase formation due to reduction and oxygen transferred to gas phase.
Figure 5-16 displays the Arrhenius and reaction order dependence plots for both the L₁ and L₂ reaction fronts. These plots are used to derive intrinsic rate constants for both fronts as well as the reaction order dependence with respect to CO. The linearity of the fits over the temperature range explored also sheds light on the reliability over a wide range of temperature (750-900°C).

![Arrhenius and reaction order dependence plots](image)

Figure 5-16: Examination of GPM reliability over operational parameter range: (a) Arrhenius Plot over 750-900°C, (b) Reaction order dependence for CO concentration range of 5-30 vol%.
and reactive gas concentration (5-30 vol% CO) as the correlation coefficients are on the order of unity.

Given the outlined assumptions, the model description and applicability to the variables that directly influence behavior show good reliability over the ranges of interest. Further refinement and the addition of layers of complexity would improve this outcome but at a cost of increased computational time as was discussed in section 4.4.4. The addition of increased complexity represents an area of future research. Key model parameters for the derived GPM two interface model for CuFeAlO$_4$ reduction with CO are shown in Table 5-3. Table 5-4 displays the model parameter values for the Boudouard reaction.

**Table 5-3: Properties of CuFeAlO$_4$ system for 2-interface GPM Reduction with CO**

<table>
<thead>
<tr>
<th>Interface</th>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
<th>95% Confidence Interval Bounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall</td>
<td>$R_p$</td>
<td>cm</td>
<td>0.02</td>
<td>NA</td>
</tr>
<tr>
<td>Pellet</td>
<td>$R_g,0$</td>
<td>cm</td>
<td>0.0005</td>
<td>NA</td>
</tr>
<tr>
<td>$L_1$</td>
<td>$A_{C1}$</td>
<td>cm/s</td>
<td>2.93</td>
<td>±0.23</td>
</tr>
<tr>
<td></td>
<td>$E_{A1}$</td>
<td>kJ/mole</td>
<td>22.49</td>
<td>±2.25</td>
</tr>
<tr>
<td></td>
<td>$\rho_{1}^{B-C}$</td>
<td>g/cm$^3$</td>
<td>2.9</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>$n_1$</td>
<td>unitless</td>
<td>1</td>
<td>±0</td>
</tr>
<tr>
<td></td>
<td>$M_B$</td>
<td>g/mole</td>
<td>210.37</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>$\phi_{1}^{B-C}$</td>
<td>mole O$^{2-}$ transferable mole O$^{2-}$ in MeO</td>
<td>0.60</td>
<td>±0.05</td>
</tr>
<tr>
<td>$L_2$</td>
<td>$A_{C2}$</td>
<td>cm/s</td>
<td>0.828</td>
<td>±0.07</td>
</tr>
<tr>
<td></td>
<td>$E_{A2}$</td>
<td>kJ/mole</td>
<td>43.45</td>
<td>±3.65</td>
</tr>
<tr>
<td></td>
<td>$\rho_{2}^{C-F}$</td>
<td>g/cm$^3$</td>
<td>2.9</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>$n_2$</td>
<td>unitless</td>
<td>1</td>
<td>±0</td>
</tr>
<tr>
<td></td>
<td>$M_C$</td>
<td>g/mole</td>
<td>173.81</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>$\phi_{2}^{C-F}$</td>
<td>mole O$^{2-}$ transferable mole O$^{2-}$ in MeO</td>
<td>0.40</td>
<td>±0.05</td>
</tr>
<tr>
<td></td>
<td>$t_C$</td>
<td>sec, critical time before FeAl$_2$O$_4$ emergence</td>
<td>0</td>
<td>NA</td>
</tr>
</tbody>
</table>

*NA = Not applicable*
### Table 5-4: Model parameters for Carbon deposition via the Boudouard Reaction

<table>
<thead>
<tr>
<th>Interface</th>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
<th>95% Confidence Interval Bounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boudouard Reaction</td>
<td>$\Delta H_{rxn}(T_{ref})$</td>
<td>$kJ/mol$</td>
<td>-170 (exothermic)</td>
<td>±30.2</td>
</tr>
<tr>
<td></td>
<td>$T_{ref}$</td>
<td>°C</td>
<td>900</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>$K_C(T_{ref})$</td>
<td>unitless</td>
<td>1.0002</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>$k_f$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$A_f$</td>
<td>$cm^3/g*sec$</td>
<td>14.7</td>
<td>±2.65</td>
</tr>
<tr>
<td></td>
<td>$E_f$</td>
<td>$kJ/mol$</td>
<td>35</td>
<td>±5.13</td>
</tr>
<tr>
<td></td>
<td>$\theta_1$</td>
<td>unitless</td>
<td>1</td>
<td>±0</td>
</tr>
<tr>
<td></td>
<td>$\theta_2$</td>
<td>1/sec</td>
<td>800</td>
<td>±10.1</td>
</tr>
</tbody>
</table>

#### 5.2.6 A note on the impact of TGA reactor loading on derived kinetic parameters:

This section serves to delineate the effects of TGA reactor loading on determined kinetic parameters. The dynamic range of the TGA balance was explored by using 5, 60, and 100mg sample loadings. Figure 5-17 displays a comparison between 5 and 100 mg loadings with Table 5-5 summarizing the difference in kinetic parameters. The kinetic study presented in earlier sections utilized 60 mg loadings with flow rates at the maximum attainable for the TGA reactor system (100ml/min), so these values are compared with the lower (5mg) and upper (100mg) limits. In Figure 5-17, the effects a product dilution are more prominent in higher loadings, i.e. the bolus of CO$_2$ that is generated reduces the bulk gas phase concentration of CO for a longer duration of time. This effect impacts the determination of frequency factors for the intrinsic rate constant.
Table 5-5: Comparison of Intrinsic Rate constant values for GPM model determined for TGA weight loading range

<table>
<thead>
<tr>
<th>Interface</th>
<th>Parameter</th>
<th>Units</th>
<th>Value. 5mg</th>
<th>Value. 60mg</th>
<th>Value. 100mg</th>
<th>95% Confidence Interval Bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall Pellet</td>
<td>$R_p$</td>
<td>cm</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>$R_{g,0}$</td>
<td>cm</td>
<td>0.0005</td>
<td>0.0005</td>
<td>0.0005</td>
<td>NA</td>
</tr>
<tr>
<td>$L_1$</td>
<td>$A_{c1}$</td>
<td>cm/s</td>
<td>3.1</td>
<td>2.93</td>
<td>2.73</td>
<td>±0.23</td>
</tr>
<tr>
<td></td>
<td>$E_{A1}$</td>
<td>kJ/mole</td>
<td>22.49</td>
<td>22.49</td>
<td>22.49</td>
<td>±2.25</td>
</tr>
<tr>
<td></td>
<td>$\rho_{E-C}$</td>
<td>g/cm$^3$</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>$n_1$</td>
<td>unitless</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>±0</td>
</tr>
<tr>
<td></td>
<td>$M_B$</td>
<td>g/mole</td>
<td>210.37</td>
<td>210.37</td>
<td>210.37</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>$\phi^{B-C}$</td>
<td></td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
<td>±0.05</td>
</tr>
<tr>
<td>$L_2$</td>
<td>$A_{C2}$</td>
<td>cm/s</td>
<td>1.01</td>
<td>0.828</td>
<td>0.818</td>
<td>±0.07</td>
</tr>
<tr>
<td></td>
<td>$E_{A2}$</td>
<td>kJ/mole</td>
<td>43.45</td>
<td>43.45</td>
<td>43.45</td>
<td>±3.65</td>
</tr>
<tr>
<td></td>
<td>$\rho_{C-F}$</td>
<td>g/cm$^3$</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>$n_2$</td>
<td>unitless</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>±0</td>
</tr>
<tr>
<td></td>
<td>$M_C$</td>
<td>g/mole</td>
<td>173.81</td>
<td>173.81</td>
<td>173.81</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>$\phi^{C-F}$</td>
<td></td>
<td>0.40</td>
<td>0.40</td>
<td>0.40</td>
<td>±0.05</td>
</tr>
</tbody>
</table>

Figure 5-17: Comparison of TGA loading on the conversion output and predictive model representation (a) 5mg loading (b) 100mg loading
This effect causes a slight reduction in the frequency factor, \( A_{c1} \), determined for the L1 reaction front. These differences are minor with values at the lower limit being +0.17 cm/sec and at the higher limit of -0.23 cm/sec, within the determined confidence intervals. What this eludes to, is that there are not significant gains in reducing the sample mass nearly 55mg and kinetic rate constant values determined in subsequent sections are valid and can be considered intrinsic, as it has been shown that external and internal mass transfer effects do not play a significant role in the evaluation of the parameters. The main controlling factor in these cases is the experimentally observed concentration profiles. Less significant effects are observed for the determination of the L2 reaction front kinetic rate constant. This is due to the presence of CO\(_2\) gas residuals that are generated when FeAl\(_2\)O\(_4\) reduces to base metal and oxide components. With larger loadings, and increased baseline reactor concentration of CO\(_2\) causes equilibrium to shift and the forward rate of conversion to slow. There is no significant difference in the determined intrinsic reaction rates but the observed conversion rate is slower due to the effects of increased CO\(_2\) concentration in the reaction chamber. These observations point to some key effects that have not been discussed thoroughly in the literature. (1) A thorough understanding of the reacting system can help delineate observed effects from one another. In this case, it has been shown that rate slowing that may have been attributed to as external or internal mass transfer limitation is actually a product of material reversibility and experimentally observed concentration profiles in the evaluation system. (2) In the absence of the analytical tools used in these studies, it would be impossible to deduce these effects and this significantly points towards the importance of considering all external variables that could potentially impact the system. As was shown previously in section 4.4.3, simply knowing and applying the experimentally determined concentration profiles in
model fitting approaches can drastically impact the outcome of model fits and should henceforth be considered in all other studies of the like.

5.3 **Section Summary**
A detailed experimental study was carried out to determine the impact of key operational variables on the kinetics of a novel CuFeAlO$_4$ oxygen carrier, with emphasis on the application of a reliable phenomenon driven particle scale model to describe the reduction behavior with CO (a second major gas phase component in coal derived synthesis gas). Due to the novel nature of the material, several areas were explored experimentally to provide a fundamental understanding of how the material changed as oxygen was depleted from the structure due to reduction with CO. These areas include chemical phenomena such as phase transition (defined as the reduction pathway), resistances to oxygen transfer, and reaction equilibria all of which are key aspects in the decision-making process for model selection and application. It is found that reduction occurs in a multistep process consistent with the reduction pathway observed with H$_2$. The multistep process was successfully emulated through the use of a two interface Grainy pellet model in which reaction (kinetic) control is the main rate limiting step. This approach was validated through the examination of other potential rate limiting resistances. The model emulates changes in key operation variables with good accuracy, ensuring reliability for further use. As part of this work, care was taken to emulate the effects of the Boudouard reaction on the reduced OC due to the stringent requirements for carbon capture efficiency of a CLC system. The proposed catalytic carbon deposition model was linked to the fractional conversion of FeAl$_2$O$_4$ as the catalytic reaction was dependent upon the amount of available Fe in the reduced OC. The coupling of these two different model types adds to the novelty of the work and has not been attempted previously in the reviewed literature for CL applications.
Chapter 6 Preliminary investigation into the application of the multi-interface GPM for a CuFeAlO4 oxygen carrier during reduction with CH4 in Chemical Looping combustion applications:

Chapter 6 Preface:
In this section an initial assessment was conducted for the use of the multi-interface GPM with a more complex reduction gas of CH4. Although this component is potentially a minor aspect in coal based CLC, current rise in localized natural gas reserves pose the feedstock as a potentially feasible fuel source for Natural Gas Fired CLC. As methane is a major component (>90%) in Marcellus based reserves [97], understanding the fuel source is of significant importance as its potential use is foreseeable.

6.1.1 Proposed Scheme and Representation:
The Multi-interface grainy pellet model utilized in section 4.4 and 5.2 to describe the reduction kinetics of H2 and CO respectively with the CuFeAlO4 oxygen carrier was applied for use with methane, CH4, as a fuel source. The model links the gas-solid reactions displayed in E6-1 - E6-3 to continuity balances in a spherical grain within a macroscopic particle.

\[ 3CH_4(g) + 8CuFeAlO_4(s) + 4Al_2O_3(s) \xrightarrow{k_{r1}} 8Cu(s) + 8FeAl_2O_4(s) + 3CO_2 + 6H_2O \]  
\[ E6-1 \]

\[ CH_4(g) + FeAl_2O_4(s) \xrightarrow{k_{r2}} Fe(s) + Al_2O_3(s) + CO + H_2 \]  
\[ E6-2 \]

\[ CH_4(g) + Fe(s) \xleftrightarrow{k_f} Fe(s) + C + 2H_2 \]  
\[ E6-3 \]

The grainy pellet model links the change in degree of reduction of the solid with the change in radius of an unreacted core of a spherical grain. There are two major differences with applying the model to CH4. (1) The addition of the catalytic methane decomposition reaction (E6-3)
in the outermost layer with available Fe species must be accounted for to accommodate changes due to carbon deposition. (2) The products of the primary reduction steps are not the same. In E6-1, \( \text{CH}_4 \) reacts directly with \( \text{CuFeAlO}_4 \) to form complete combustion products. Where as in E6-2, \( \text{FeAl}_2\text{O}_4 \) only partially oxidizes \( \text{CH}_4 \) to form incomplete oxidation products. (3) The second reaction front associated with \( \text{FeAl}_2\text{O}_4 \) is still susceptible to equilibrium based reactions with products of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \), as was outlined in sections 4.2.7 and 5.1.1. With this noted, the derivation is more expansive than those that were previously presented and is derived in E6-4-E6-8 for each of the interfaces associated with the primary reacting phases.

\[
\frac{t}{\tau_{R_{1,\text{overall}}}} = 1 - (1 - X_{L1})^{\frac{1}{3}}, \quad \tau_{R_{1,\text{overall}}} = \frac{\rho_1^{R_{1,\text{overall}}}}{b_{\text{CH}_4} k_{CL}^* (C_{\text{CH}_4})^{n_1}}
\]

\[
\frac{t}{\tau_{R_{2,\text{overall}}}} = 1 - (1 - X_{L2})^{\frac{1}{3}}, \quad \tau_{R_{2,\text{overall}}} = \frac{\rho_1^{R_{2,\text{overall}}}}{b_{\text{CH}_4} k_{CL}^* (C_{\text{CH}_4})^{n_1} + b_{H_2O} k_{CLH_2}^* (C_{H_2O})^{n_2} + b_{CO} k_{CLCO}^* (C_{CO})^{n_1} - \frac{C_{CO_2}^{n_2}}{K_{e_2,CO_2}}}
\]

\[
k_{CL}^* = A_{CL} e^{\left(\frac{E_{AI}}{RT}\right)}
\]

\[
K_{e_{CL}}^* = \frac{k_{CL}^*}{K_{CLR}^*}
\]

\[
[C] \left(\frac{g}{cm^3}\right) = k_f \left[ [\text{CH}_4][\text{Fe}]t \right]
\]

Due to the product formation route with methane and the primary phase, \( \text{FeAl}_2\text{O}_4 \), susceptibility to reversibility with the product gases of E6-1 and continued reduction with product gases from E6-3, the functionality must be included in the model description. The individual intrinsic reaction rate expressions are coupled into the characteristic time constant, \( \tau_{R_{I,\text{overall}}} \), for each prevailing reaction. The characteristic time constant for L1 reaction front only includes the terms
for CH₄ conversion to direct combustion products as the primary phase associated with reduction, CuFeAlO₄, reacts in an expedited manner which facilitates this assumption. Additionally, it was found in previous sections that this phase is not easily susceptible to oxidation from soft oxidants such as CO₂ and H₂O, therefore including equilibrium expressions is unnecessary in the description of this step. The characteristic time constant for the L2 reaction front includes all of the necessary contributions due to FeAl₂O₄ susceptibility to oxidation by product CO₂ and H₂O with addition reducibility to product gases formed from methane decomposition on the interface. The use of \( \tau_{R_{total}} \) provides a convenient way to couple multiple reacting gas phase species to a single reaction front. The terms only contribute to the overall constant when the gas concentrations are present that influence each individualized rate expression. This further points at the importance of using experimentally measured concentration profiles when approaching model fitting and optimization. Without the inclusion of these pivotal data sets it would be impossible to accurately capture the effects of CH₄ reduction.

### 6.1.2 Application of the GPM model with CH₄

Figure 6-1 displays the application of the multi-interface GPM model to reduction of CuFeAlO₄ OC with 5 vol%CH₄ at 800°C. This serves as a proof of concept that the coupling of reaction contributing resistances into a singular characteristic time constant, \( \tau_{R_{total}} \), gives the model the ability to accommodate phenomena observed with the individual gases. In Figure 6-1a, the gas concentration profiles are also presented. The initial reduction phase is predominated by CO₂ and H₂O as anticipated. Small amounts of unconverted H₂ and CO are generated during this phase but peak after its completion and the reduction of FeAl₂O₄ begins. During this phase of the
Figure 6-1: Application of the two zone GPM to reduction of CuFeAlO$_4$ with 5vol% CH$_4$ @ 800°C:
(a) Comparison of experimental conversion with $F_P$ and the individual interface fractional conversions with volumetric concentration profiles. (b) Component mole balances showing new phase formation due to reduction and oxygen transferred to gas phase.
reaction mechanism the major products are \(H_2\) and \(CO\). The model captures the equilibrium aspects of \(\text{FeAl}_2\text{O}_4\) by hinder forward rate progression until reactor concentrations of \(H_2\text{O}\) and \(CO_2\) lower to below 1 vol%. Effects of coking are minimal at such a low concentration of \(\text{CH}_4\), so this phenomena is not readily apparent in the data set shown in Figure 6-1 and represents an area of further research. Table 6-1 compares the determined kinetic rate constants for \(\text{CH}_4\) to those determined for other gas types. From this preliminary comparison, it can be seen that \(\text{CH}_4\) has a slightly higher intrinsic rate than \(\text{CO}\) but less than \(H_2\).

<table>
<thead>
<tr>
<th>Interface</th>
<th>Parameter</th>
<th>Units</th>
<th>Value. (\text{CH}_4)</th>
<th>Value. (\text{H}_2)</th>
<th>Value. (\text{CO})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall Pellet</td>
<td>(R_p)</td>
<td>(cm)</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>(R_{g,0})</td>
<td>(cm)</td>
<td>0.0005</td>
<td>0.0005</td>
<td>0.0005</td>
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<tr>
<td>(L_1)</td>
<td>(A_{C1})</td>
<td>(cm/\text{s})</td>
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<td>17.00</td>
<td>2.93</td>
</tr>
<tr>
<td></td>
<td>(E_{A1})</td>
<td>(kJ/\text{mole})</td>
<td>20*</td>
<td>13.5</td>
<td>22.49</td>
</tr>
<tr>
<td></td>
<td>(\rho_1^{B-C})</td>
<td>(g/cm^3)</td>
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<td>2.9</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>(n_1)</td>
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<td>0.8</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>(b_1)</td>
<td>stochiometric coeff</td>
<td>8/3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>(\phi^{B-C})</td>
<td>mole (O^{2-}) transferable mole (O^{2-}) in (\text{MeO})</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
</tr>
<tr>
<td>(L_2)</td>
<td>(A_{C2})</td>
<td>(cm/\text{s})</td>
<td>70*</td>
<td>90</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>(E_{A2})</td>
<td>(kJ/\text{mole})</td>
<td>60*</td>
<td>70</td>
<td>43.45</td>
</tr>
<tr>
<td></td>
<td>(\rho_2^{C-F})</td>
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<tr>
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<tr>
<td></td>
<td>(b_2)</td>
<td>stochiometric coeff</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>(\phi^{C-F})</td>
<td>mole (O^{2-}) transferable mole (O^{2-}) in (\text{MeO})</td>
<td>0.40</td>
<td>0.40</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>(t_C)</td>
<td>s, critical time before (\text{FeAl}_2\text{O}_4) emergence</td>
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</tr>
</tbody>
</table>

Table 6-1: Comparison of Parameters determined for the Multi-Interface GPM model for reduction gases of \(\text{CH}_4\), \(\text{H}_2\), and \(\text{CO}\)
Chapter 7  An additional novel topic: An abridged Kinetic Analysis of Solid Mediated Interactions between CaFe$_2$O$_4$ and Solid Carbon Fuels

In this section, a novel topic was examined concerning the kinetics of oxygen transfer between a group 2 ferrite OC, CaFe$_2$O$_4$, and solid pretreated fuels. This study was one of the first to attempt to represent direct solid-solid interactions between an oxygen carrier and a solid fuel source. Details of the materials are discussed and the modes of oxygen transfer examined to explain the calcium ferrites’ use for partial oxidation applications and the link between oxygen transfer rates and product outcomes. This analysis also provides a unique scenario where the carbon-OC reaction interface is fixed. With any particle scale modeling approach, key questions arose that needed to be answered before a thorough kinetic analysis was performed: (1) How does the oxygen carrier change with extent of solid conversion, (with primary concerns of phase transitions)? (2) What are the product distributions and how do they refine the understanding of the kinetic models? (3) What types of interfaces exist for oxygen transfer and what is their impact on the transfer rate? These same questions arose in the previous gas phase studies and similar techniques are used to address the criterion. Currently there are no pilot scale CLG systems and the implementation of validative screening protocols has not been established. Due to the novelty of the material and the discovery that product distributions could be selective towards syngas products [16] made the task for development of particle scale models for the system an attractive research goal. This section provides an abridged version of the published research work, see reference [40] for the complete analysis.
7.1 Experimental:

7.1.1 CaFe₂O₄ Oxygen Carrier: Synthesis and Characterization

Calcium ferrites were prepared through direct decomposition of calcium and iron nitrate precursors. Nitrate precursors (calcium nitrate hexahydrate (GHS Chemicals) and Iron (III) nitrate (non-hydrate, Fisher Scientific)), were mixed evenly in stoichiometric ratios for the formation of the CaFe₂O₄ phase after calcination [17] [18] (as shown in Figure 7-1). Mixtures were then subjected to a two-step calcination: (1) 500 °C at 4 °C/min and held isothermally for 6 hours, (2) mixtures were then ground once more and subjected to 1000 °C induration at a ramping rate of 4 °C/min and held isothermally for 6 hours. The phase of the metal oxide was verified using X-ray diffraction. CaFe₂O₄ samples were then separated through sonic sieving into 4 size ranges: 43–53μm, 53–125μm, 125–177μm, and 177–354μm for subsequent testing. BET surface area of the metal oxide ranged from 0.2–1.5 m²/g between the size ranges, suggesting the materials have minimal porosity.

7.1.2 Experimental Apparatus

Thermogravimetric Analyzer (TGA) and Mass Spectrometer (MS):

The reduction of CaFe₂O₄ and selective oxidation of coal chars were performed in a thermogravimetric analyzer (TGA, TA Instruments model Discovery) equipped with an online
mass spectrometer (MS, Pfeiffer Vacuum Omnistar GSD-320) shown in Figure 4-2. Samples were prepared by physical mixing of 24 mg of CaFe$_2$O$_4$ with 6 mg of desired coal char. This ratio was chosen based on the equivalent molar quantities of available carbon in the char and available transferable oxygen in the lattice of the metal ferrite for gasification. For a typical test, 30 mg (MeO-Char) of sample was placed into a 100µl platinum crucible. Samples were equilibrated at 50 °C for 45 min with 200 ml/min flow of U.H.P Argon to ensure an inert oxygen-free atmosphere at the initiation of the experiment. Gas flow rates were then set to 20 ml/min U.H.P Argon from the balance chamber and 45 ml/min U.H.P Argon from the sample gas delivery port. Samples were then heated at 200 °C/min and held isothermally at 850 °C, 900 °C, and 950 °C for 240 minutes then oxidized in air for 60 minutes to regenerate the metal ferrite material. All experiments were repeated three times to establish standard error between samplings. The concentrations of H$_2$, CH$_4$, H$_2$O, CO, O$_2$, Ar, and CO$_2$ from the effluent stream of the reactor were analyzed continuously using the online mass spectrometer. Concentrations were calibrated using various gas blends to ensure accuracy. The mass spectrometer sampling capillary was located 10mm away from the sample pan, which allowed for limited delay and increased accuracy in the measurement of out-gassed products from the reactions between the coal char and metal ferrite. Figure 7-2 displays a typical TG-MS profile for the aforementioned system and materials used.
X-ray Diffraction and other spectroscopic analysis:

XRD analyses were carried out using a Panalytical PW 3040 X-Pert Pro XRD system equipped with a 60 kv PW 3373/00 Cu LFF high power ceramic tube with a Cu anode and a PW 3011/20 detector. SEM analyses were conducted with a JEOL 7600 FESEM system interfaced with a Thermo-Electron system 7 microanalysis system. The Thermo-electron microanalysis system is equipped with a Thermo-electron Ultra dry Energy dispersive spectrometer (EDS) and an EDAX Electron backscatter diffraction system.

7.2 Results and Discussion

7.2.1 Kinetic Model Representation Approach:

Model-free iso-conversional techniques have typically been used in the past when determining the kinetic rate parameters from thermal analysis techniques [66] [67]. In this work, model-free iso-conversional techniques are primarily used to evaluate the kinetic parameter of the overall activation energy associated with the selective oxidation of char carbon and the energy barriers associated with the movement of oxygen from the metal ferrite to the char reaction interface. Once the activation energy was determined, a model fitting process was performed to determine the solid-state decomposition models that describe the process and the solid-state chemistry necessary to facilitate the oxygen transfer to the carbon available in the char. Empirical model-based approaches have been developed over the past century coupled with thermal analysis methods to describe solid state reactions [98]. Before examining kinetic model based methods, the reaction network is outlined for a process of this nature. The selective oxidation of coal char and ultimate reduction of Ca-ferrite can be expressed by the following reactions:
The selective oxidation of bound carbon ($C^*$) in the coal char occurs via two pathways. E7-1 is the desired reaction of the selective oxidation of carbon to carbon monoxide. E7-2 is the undesired reaction of the oxidation of carbon monoxide to carbon dioxide. Here the production of H$_2$ is not examined due to the low relative content in char and the exclusion aids in the isolation of the reaction. E7-3 is the reduction of CaFe$_2$O$_4$ to its base metal and metal-oxide components and serves as the oxygen ion donation for reactions depicted in E7-1 & E7-2 to take place. E7-3 can be split into several steps depending upon the prevalence of stable intermediate reduced states. One of these stable intermediate phases is Ca$_2$Fe$_2$O$_5$. These reduced states are examined in detail through XRD patterns of sampling reacted material at different time points during reduction and are discussed in detail in section 7.2.2.

The rate of the decomposition of a solid can be expressed in terms of a generalized expression for a single step mechanism [54], shown previously in E3-22 section 3.5. $X_p$, the normalized degree of conversion of a particle is obtained from experimental data. The degree of conversion represents a normalization of solid state transitions with respect to the recorded weight changes associated and is described by E7-4

$$X_p(t) = \frac{m_0 - m(t)}{m_0 - m_f} \quad \text{E7-4}$$

where $m_0$ is the initial weight of the sample, $m(t)$ is the instantaneous weight of the solid materials during reduction corresponding to oxygen loss from the metal ferrite and carbon losses from coal char via the formation of CO and other products, and $m_f$ is the theoretical weight associated with
the final reduced state of the starting metal oxide and complete consumption of carbon in the char. $X_p(t)$ being a normalized function, and is therefore on a scale of 0-1.

Through the application of iso-conversional model free methods, values of the Activation energy for the process can be estimated using E7-5, see reference [29] for a detailed derivation.

$$ln(t) = (-lnA + ln \int_0^X f(x) \, dx) + \frac{E_a}{RT} \quad \text{E7-5}$$

By plotting ln(t) with respect to 1/T, the activation energy can be obtained for a given value of $X_p$ from the slope of the regression line if at least three isothermal temperatures are explored. The application of this approach provides a means of estimating the overall activation energy associated with the process [99].

All model fitting approaches were implemented using the curve fitting application in MATLAB 2016a. A non-linear least squares regression fit was implemented in the software to minimize the differences between the experimentally derived conversion versus time curves at a desired isothermal temperature with those derived by the empirical-mechanistic model description for each contribution. Goodness of fit was evaluated based on the correlation coefficient between the experimental and theoretically derived curves. Model expression fits attaining values equating to a minimum $R^2 = 0.99$ were considered.

### 7.2.2 Char-OC Conversion Deconvolution, Determining the OC Reduction Pathway of CaFe$_2$O$_4$ and impact on kinetic representation:

In this approach, it becomes necessary to examine the individual components of the reaction network. The overall conversion must be de-convoluted based on its individual steps outlined in reaction network. Unfortunately, the thermogravimetric weight loss data alone does not provide suitable information to accurately de-convolute the contributions of carbon consumption to major
products such as CO and CO₂. Evolved gas analysis (EGA) via mass spectrometry is used to examine the reaction schemes and derive the relationship of carbon consumption and mono-atomic oxygen ion release based on the two-major measurable gas phase components (CO, CO₂). The conversion of effluent concentration percentages to molar flow rates are described in a previous work [16] and displayed in E115,

\[ n_{i,t} = \dot{V}_{\text{Total,e}} \left( \frac{C_i}{100} \right) \left( \frac{P_o}{RT_o} \right) \]  

E7-6

where, \( n_{i,t} \) is the \( i^{th} \) component molar flow rate at any time \( t \), \( R \) is the ideal gas constant, \( P_o \) (kPa) and \( T_o \) (K) are the ambient pressure and temperature of the gas at the inlet of the MS detector, and \( C_i \) is the concentration percentage of the effluent measured gas component. Individual component molar flow rates \( n_{i,t} \) are the product of the total effluent volumetric flow rate, \( \dot{V}_{\text{Total,e}} \), and the concentration percentage of the individual component recorded by the MS at a given time during the experiment. The total effluent volumetric flow rate, \( \dot{V}_{\text{Total,e}} \), was calculated by dividing the known inert flow rate into the system with the outlet inert concentration. The incremental mass of the \( i^{th} \) component, \( m_{i,t} \), can be calculated by integrating \( n_{i,t} \) with respect to incremental time lapsed and multiplying by the molecular weight of the \( i^{th} \) component (\( m_{w_i} \)), shown in E116.

\[ m_i(t) = \left( \int_{t = t_1 \text{ sec}}^{t = t_2 \text{ sec}} n_{i,t} \, dt \right) \ast m_{w_i} \]  

E7-7

Molar flow rates of the components were integrated with respect to individual time intervals (~1 second) to form a cumulative molar distribution of each component with respect to time during the experiment. Cumulative mass quantities of carbon and monoatomic oxygen (MO) were then further derived from the molar distributions of CO and CO₂, depicted in Figure 7-3b.
The individual de-convoluted donations to the overall conversion are scaled based on the mass losses associated with the decompositions of the carbon in the char and the oxygen (MO) loss from the metal oxide, shown in E7-8 and E7-9 respectively. The char types evaluated could contain up to 20% ash by weight and considering the initial loading (6.0 mg, char), carbon loadings could range from 4.8–5.4 mg ($m_{0,\text{carbon}}$) depending on the char type. When considering the oxygen carrier, a mass loss associated with oxygen release of 22.5% of the initial weight corresponds to the complete reduction from CaFe$_2$O$_4$ to CaO and Fe$^0$. With an initial loading of 24 mg ($m_{0,\text{MO}}$), this change corresponds to a weight loss of 5.4 mg to a final weight of 18.6 mg ($m_{f,\text{MO}}$). E7-10 and E7-11 display the oxygen carrier and char conversions in terms of the overall conversion scale:

\textit{Figure 7-3: Deconvolution(a) of the $X_{AD,\text{overall conversion}}$ of Wyodak char and CaFe$_2$O$_4$ using mass spectra analysis coupled with TGA (Final isothermal temperature, 950 °C). (b) Component concentration percentages with respect to MS derived carbon and mono-atomic oxygen outputs from EGA (Truncated at 50 min for visual clarity).}
The contributions from char conversion \( (X_{\text{char}, \, MS}) \) and oxygen carrier reduction \( (X_{\text{oxygen carrier}, \, MS}) \) are combined to attain a cumulative conversion \( (X_{AD (overall conversion), \, MS}) \) of the overall process and this is intern compared to the those derived from the recorded thermal gravimetric weight loss \( (X_{AD (overall conversion), \, TGA}) \), as shown in Figure 7-3a for CaFe\(_2\)O\(_4\) and Wyodak char. Curves derived from evolved gas analysis show minor deviation from those derived from recorded weight loss, with a maximum standard deviation (STDEV±3.2\%) occurring during the initiation of the secondary reaction phase. A series of experiments were performed to examine the distinct reduced phases during the reduction of CaFe\(_2\)O\(_4\) with Wyodak char to gain an understanding of the reduction pathway. In this series of experiments, mixtures of Wyodak char and CaFe\(_2\)O\(_4\) were heated at a ramp rate of 200 °C/min to 850 °C and held for pre-specified isothermal hold times (30, 90, 180, 240 minutes) depicted in Figure 7-4.
The isothermal temperature of 850 °C was chosen based on the slower rate of reactivity which allowed for a more controlled sampling. Upon reaching the specified hold time, samples were rapidly cooled to room temperature at a ramp rate of 500 °C/min. Equivalent loadings of 20 mg of...
the reacted samples were examined using XRD to determine predominate reduced phases present, shown in Figure 7-4a.

Upon examination of the first sampling interval (Q1—30 min), an immediate phase change occurs in the bulk of the material after the initial reduction, as shown in Figure 7-4a. Enough oxygen has been depleted from the lattice for a rearrangement to occur, showing the reduction of orthorhombic CaFe$_2$O$_4$ to brownmillerite type Ca$_2$Fe$_2$O$_5$ and the rise of FeO. The creation of surface oxygen vacancies results in a lattice rearrangement. This reorientation starts from vacancies that are induced on the surface and occurs rapidly so models developed by Avrami [55] and others (NNGM) can provide useful information on the initial changes resulting from the reduction process. The rapid nature suggests that the reorientation is not limited by diffusional or mass transfer constraints but rather in kinetically (reaction) controlling regimes [43]. As oxygen continuously migrates from the bulk phase to the reaction interface due to the increase in deficiencies, both Ca$_2$Fe$_2$O$_5$ and FeO get further reduced giving rise to phases of Fe$^0$ and CaO. The variation of sampling quantities was below ±0.1 mg in order to validly compare spectral intensity. The intensities associated with the (110) and (200) planes in Fe$^0$ and CaO respectively increase with 120–240-minute sampling times, whereas the intensity associated with the (141) plane predominant in Ca$_2$Fe$_2$O$_5$ decreased in intensity. The slower progression of the reduction to Fe$^0$ and CaO suggested that the slow oxygen ion movement into the reduced solid layers could present as a rate-determining factor. Also, as the reduced layer increases in size, the distance for oxygen ion movement inherently increases, which can decrease the rate of ion transfer at the OC-char interface. From these controlled reduction experiments, the overall reduction reaction can be expanded in to two primary steps with an associated secondary intermediary phase, as shown in Reactions depicted by E7-12 through E7-14:

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Development and Particle Scale Modeling of Metal Oxide Oxygen Carriers for CL applications

\[ 2CaFe_2O_4 \x (k_c) \x Ca_2Fe_2O_5 + 2FeO + O^{2-} \quad E7-12 \]
\[ Ca_2Fe_2O_5 \x (k_{D,1}) \x 2CaO + 2Fe^0 + 3O^{2-} \quad E7-13 \]
\[ 2FeO \x (k_{D,2}) \x 2Fe^0 + 2O^{2-} \quad E7-14 \]

CaFe_2O_4 initially was reduced to a mixture of Ca_2Fe_2O_5 and FeO, which ultimately gets reduced to CaO and Fe^0 in a parallel manner. Phase reorientation occur due to the redistribution of charge after oxygen vacancy induction. Based on these findings, the reduction process can be driven by the movement of oxygen ions through the bulk to the char/metal ferrite reaction interface. The rational for this hypothesis is due to the position of the carbon reaction interface in proximity with the OC, realizing that the only feasible route for oxygen transfer from zones of higher concentration is through the bulk and outer lying reduced layers.

This is depicted further in Figure 7-5 where the interfaces are examined and some metrics for model representation are identified. As the OC transfers oxygen with the reactable carbon in the char, an oxygen depleted layer forms at the OC-char reaction interface. For further oxygen transfer to occur, lattice oxygen (O^{2-}) must move from the bulk through the depleated layer (Core-Product layer interface) to the OC-char reaction interface. As the OC becomes more oxygen delpeated the distance for O^{2-} migration increases. This eludes that the oxygen ion diffusion is ultimately a function of the OC-char contact radius. With this noted, model representation should account for ion diffusion controlling regimes as influence will increase with a higher OC-Char contact radius.

Considering the impact on kinetic model representation further, based on the reduction pathway findings and product distributions, multistep dependence occurs [29] [100]. Char oxidation
proceeds via two pathways and metal oxide reduction proceeds through at least two primary pathways (E121 & E122) including an intermediary reduced phase (E123). The progression of the overall conversion $X_{AD}$ can be expressed as the linear combination of multistep reactions, as depicted in E7-15

$$X_{AD} = \sum_i w_i X_i, \quad X_{AD} = w_A X_A + w_B X_B + w_C X_C + w_D X_D$$  \hspace{1cm} \text{E7-15}$$

where $X_A$ is the conversion associated with the loss of carbon and oxygen to generate CO, $X_B$ is the conversion associated with the loss of carbon and oxygen to generate CO$_2$, $X_C$ is the conversion associated with the donation of oxygen ions and reduction of CaFe$_2$O$_4$, and $X_D$ is the conversion associated with the donation of oxygen ions and reduction of Ca$_2$Fe$_2$O$_5$. The $w_A, w_B, w_C, w_D$ are weight fractions that contribute to a portion of the overall conversion, as depicted in E7-16:

$$\sum_i w_i \leq 1, \quad w_A + w_B + w_C + w_D \leq 1$$  \hspace{1cm} \text{E7-16}$$

Other authors have also proposed this type of scheme when considering the reduction of metal oxides such as Fe$_2$O$_3$ and CuFe$_2$O$_4$ [29] [59] [101]. Each of the individual reaction steps are weighted and limited based on their individual contributions to the overall conversion.

If one reaction is contributed by more than one prevailing mechanism, the individual step is split into its prevailing components. For example, the formation of CO was contributed by both a kinetically controlled mechanism and an underlying diffusion controlled mechanism, the portion could be split into the contributing components as shown in E7-17:

$$w_A X_A = W_{A,1} X_{A,1} + W_{A,2} X_{A,2}$$  \hspace{1cm} \text{E7-17}$$

This examination is necessary when individual components of the reduction mechanism have prevailingly different kinetic controls. It is also necessary when reactions approach partial completion limits. A detailed examination of this kind can be referred to as a combinatory kinetic analysis where discrete reactions are separated based on analytic techniques and brought together
to explain the entirety of reaction progression in the network. These techniques show validity when reactions occur in parallel and when there are limited time shifts between when the reactions initiate [29].

### 7.2.3 Kinetic Representation and the importance of lattice oxygen ion diffusion on CO formation:

Oxygen carrier reduction is assumed to proceed through two parallel steps: (1) kinetically controlled based on readily available surface oxygen ions—adequate char contact and (2) reduction controlled by the diffusion of oxygen ions through the reduced surface layer to the char with oxygen ion diffusion a function of the mean OC-char contact radius. Char oxidation proceeds in two parallel steps: (1) kinetically controlled oxidation to CO$_2$ in an ideal case when the char ash content is low and (2) kinetically controlled oxidation to CO when the size constraints do not impose impacts on the movement of ions to the reactive carbon sites. Shown in E7-18 through E7-26 are derived rate expressions based on the experimental findings and model fitting approaches for OC conversion. Complementary expressions for char oxidation are not shown due to their similarity in form. Details of the kinetic rate constants can be found in Table 7-1. Complementary experimental model fits and graphical representation are outlined in Figure 7-6 to visually examine the oxygen transfer mechanism.

\[
X_{OC} = w_3X_{CaFe204} + w_4AX_{Ca2Fe205} + w_2BX_{Ca2Fe205} \quad \text{E7-18}
\]

\[
X_{OC} = w_3(1 - e^{\frac{-E_{A3}}{RT}t}) + w_4A(1 - e^{\frac{-E_{A4A}}{RT}t}) + w_4B(1 - (1 - (\tau_2(T)\tau)^{\frac{1}{2}})^3) \quad \text{E7-19}
\]
Development and Particle Scale Modeling of Metal Oxide Oxygen Carriers for CL applications

\[ X_{OC}^* = \frac{w_3}{f_{OC}} \left(1 - e^{-\left(\frac{E_{a3}}{RT}t\right)}\right) + \frac{w_{AA}}{f_{OC}} \left(1 - e^{-\left(\frac{E_{a4A}}{RT}t\right)}\right) + \frac{w_{AB}}{f_{OC}} \left(1 - (1 - (\tau_2(T)t)^{\frac{3}{2}})\right) \]  

E7-20

\[ \frac{w_3}{f_{OC}} + \frac{w_A}{f_{OC}} = 1 \text{, } \frac{w_{AA}}{f_{OC}} + \frac{w_{AB}}{f_{OC}} = \frac{w_A}{f_{OC}} \]  

E7-21

\[ \tau_2(T) = D_{G2-}^2 / (R_{OC})^2 \]  

E7-22

\[ D_{G2-}^2 = D_{4B} e^{\left(-\frac{E_{aA}}{RT}\right)} \]  

E7-23

\[ D_{4A} = D_{4B} e^{(-7.5+\theta)} \]  

E7-24

\[ \theta = (1 - \frac{R_{char,initial} + R_{OC}}{2R_{max}}) \]  

E7-25

\[ f_{OC} = 1 - f_{char} \]

\[ f_{char} = \frac{m_{0,carbon}}{(m_{0,carbon} + m_{0,MO}) - (m_{f,carbon} + m_{f,MO})} \]

\[ \frac{dX_{OC}^*}{dt} = \frac{w_3}{f_{OC}} k_3(T) \left(e^{\left(k_3(T)t\right)}\right) + \frac{w_{AA}}{f_{OC}} k_{AA}(T) \left(e^{\left(k_{AA}(T)t\right)}\right) + \frac{w_{AB}}{f_{OC}} 3 \tau_2(T) \left(1 - \left((\tau_2(T)t)^{\frac{3}{2}}\right)\right) \]

E7-26

Solid contact zones act as the sites of initial reaction nucleation, inducing oxygen vacancies on the surface of the metal ferrite and propagating the transfer of oxygen ions from the core of the solid towards the char reaction interface. The observed production of CO\(_2\) occurs rapidly at the beginning of the reaction due to the increased flux of surplus oxygen ions to the surface of the char. After the initial surplus of oxygen ions are depleted, the production of CO\(_2\) halts and CO production continues in the secondary reaction phase where it is hypothesized that ion movement...
is controlled by the resistances in the reduced layer and driven by the vacancy concentration induced from the slow char carbon-oxygen uptake, as shown in Figure 7-6a-c.

Component molar balances linked to the fractional conversions are depicted in Table 7-2.

Figure 7-6: Comparison of the experimental (a) Char (43-53µm) oxidation and (b) CaFe₂O₄ (43-53µm) reduction to the proposed model representation to the multistep reaction mechanism with Wyodak char. (c) Proposed reaction scheme schematic based on kinetic analysis
Table 7-1: Kinetic Parameters for Wyodak Char-CaFe$_2$O$_4$

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$i$</th>
<th>$w_i$</th>
<th>$Ea_i$ (kJ mol$^{-1}$)</th>
<th>$A_i$ (sec$^{-1}$)</th>
<th>$D_i$ ($cm^2$ sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>1.67E+05</td>
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<td>NA</td>
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<td>8.89E+00</td>
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<td>NA</td>
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<td>2B</td>
<td>$f(w_{2A})$</td>
<td>200</td>
<td>NA</td>
<td>2.50E+00</td>
<td>NA</td>
</tr>
<tr>
<td>3</td>
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<td>170</td>
<td>1.24E+05</td>
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<td>NA</td>
</tr>
<tr>
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<td>9.69E+00</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>4B</td>
<td>$f(w_{4A})$</td>
<td>205</td>
<td>NA</td>
<td>4.05E+00</td>
<td>NA</td>
</tr>
</tbody>
</table>

Table 7-2: Component molar balances for CaFe$_2$O$_4$-Char System

\[
N_{CO}^T(t) = N_{CO}^0(t) + N_{CO}^B(t) \tag{E136}
\]

\[
N_{CO}^T(t) = \frac{1}{\int_{Char} a} \int_{0}^{t} N_{CO}^0 - \left[ w_{2A}(1 - e^{(k_{2A}(T))^T}) + \frac{1}{2}(1 - (\tau_1(T))^T)^3 \right] + N_{CO}^0 \tag{E137}
\]

\[
N_{CO_2}^T(t) = \frac{1}{\int_{Char} a} \int_{0}^{t} N_{CO_2}^0 - \left[ w_{1}(1 - e^{(k_{1}(T))^T}) \right] + N_{CO_2}^0 \tag{E138}
\]

\[
N_{C}^T(t) = N_{C}^0 - (N_{CO}^T(t) + N_{CO_2}^T(t)) \tag{E139}
\]

\[
N_{O_2}^T(t) = N_{O_2}^0 - \left( N_{CO}^T(t) + \frac{1}{2}N_{CO_2}^T(t) \right) \tag{E140}
\]
Chapter 8 Summary and Conclusions:

The research effort conducted for this work represents a contribution to the field of oxygen carrier development and modeling approaches. In this work development strategies were discussed for a manufactured pelletized oxygen carrier, CuFeAlO$_4$, for Chemical Looping Combustion applications. The viability of the novel CuFeAlO$_4$ oxygen carrier was discussed and a generalized screening protocol presented, that can potentially serve as a benchmark protocol for other researchers to compare viable OC candidates. Through partnership with NETL researchers the developed OC was implemented in sub-pilot scale Chemical Looping reactor and represented a major achievement in the advancement of Chemical Looping concepts. The main topic of the research efforts was to advance the use of representative particle scale models for the viable OC candidates in Chemical looping systems. An experimentally driven method was devised to examine key modeling criterion with the viable CuFeAlO$_4$ oxygen carrier.

- A multi-interface Grainy pellet model was devised to accommodate primary reduced phases and the associated reaction equilibria. The research effort advances knowledge of the application of model descriptions by devising a description that was able to accommodate key aspects based on the reaction phenomena, thermodynamics, solid-state chemistry, oxygen carrier construct morphology, and prevailing rate limiting resistances.

- Detailed experimentally driven analyses were conducted for primary gas phase components in Coal fueled CLC, H$_2$ and CO. Solid-state chemistry changes due to depletion of the lattice oxygen from the cubic spinel structure were quantified to aid in modeling approaches. It was found that as oxygen ions were removed from the lattice a sequential based mechanism for both gas components:
\[ CuFeAlO_4 \xrightarrow{-\ce{O^{2-}}} Cu + FeAl_2O_4 \xrightarrow{-\ce{O^{2-}}} Cu + Fe + Al_2O_3 \].

During the initial fast stage of reduction, oxygen ions bound to Cu\(^{2+}\) cations in the tetrahedral positions are removed more readily than those associated with Fe and Al bonds. This is confirmed due to the presence of metallic copper leaving solid solution prior to other components. As the Cu cations are removed out of the lattice structure due to tetrahedral bound oxygen depletion, lattice reorientation takes place causing the formation of Fe-Aluminate and unbound metallic Cu. Finally, during the slower reaction segment, oxygen is depleted further from FeAl\(_2\)O\(_4\) until base components of Fe & Al\(_2\)O\(_3\) remained. This lead to the deduction that a singular model representation could describe the reduction process for each gas component with the unique OC.

- Key physical properties were evaluated to determine their impact on model derivation. It was found that mature materials did not have appreciable changes in surface area, density, and size with respect to reduction making the standard assumptions used for the SCM applicable to model derivation.

- The research effort advances modelling approaches in Chemical looping applications by accommodating reaction equilibria with key product gases, which provides additional handles for control in CL systems. It was found that FeAl\(_2\)O\(_4\) and its reduction products were susceptible to oxidation by soft oxidant products of CO\(_2\) and H\(_2\)O. Intrinsic reaction rates with the product gases were orders of magnitude greater than that of the lattice oxygen ion stripping mechanism from the reduction gases. This suggests that high continuous levels of CO\(_2\)/H\(_2\)O in a Chemical looping system can potentially prevent the reduction of this primary phase. Consequently, there is a trade off when considering reactive gas concentration and the impact on overall reaction rate. Extremely high
concentrations of reduction gases could potentially counteract the effects product reversibility. The model and rate parameters provided in this work allow for such an examination to be conducted.

- Catalytic carbon deposition effects due to the Boudouard reaction are coupled to the reaction model by linking the available solid active site, Fe, to a model for carbon deposition that links thermodynamic properties and reaction equilibria to capture the exothermic nature of the carbon deposition mechanism. The proposed model behaves well in a confined range of 800-900°C, predicting the increase in carbon deposition as temperature was reduced as was observed experimentally.

- A proof of concept investigation showed that multi-interface GPM was suitable for describing a more complex reduction gas of CH4. This investigation also showed that intrinsic reaction rate expressions for individual gases and associated equilibrium could be coupled into a single model representation for each primary phase that contributed to a reacting front. This finding allows for a convenient way to express model representation in system with multiple gas components.

- A novel topic was examined concerning the kinetics of oxygen transfer between a group 2 ferrite OC, CaFe2O4, and solid pretreated fuels. The research effort advances modelling approaches in Chemical looping applications by representing direct solid-solid interactions between an oxygen carrier and a solid fuel source, a topic that has only recently peaked interest in the scientific community. The work provided particle scale representation for both solid OCs and char based fuel sources that would be used CLG based processes. The work is a successor to a preliminary study in which the oxygen carrier material was discovered for CLG applications.
Chapter 9 **NOMENCLATURE OF KEY VARIABLES FOR CHAPTERS 2-6:**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition (units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_p(t)$</td>
<td>Experimentally derived overall solid conversion</td>
</tr>
<tr>
<td>$m_0$</td>
<td>Measured initial weight (mg)</td>
</tr>
<tr>
<td>$m(t)$</td>
<td>Measured instantaneous weight (mg)</td>
</tr>
<tr>
<td>$m_f$</td>
<td>Theoretically determined final weight (mg)</td>
</tr>
<tr>
<td>$R_{g,o}$</td>
<td>Grain radius (cm)</td>
</tr>
<tr>
<td>$r_c^{gs}$</td>
<td>Radius of the advancing reaction front (cm)</td>
</tr>
<tr>
<td>$C_i$</td>
<td>Concentration of ith component in the gas phase (g/cm$^3$)</td>
</tr>
<tr>
<td>$n_i$</td>
<td>Reaction order coefficient (unitless)</td>
</tr>
<tr>
<td>$\rho_i^{fs}$</td>
<td>Bulk density of solid (g/cm$^3$)</td>
</tr>
<tr>
<td>$t - s$</td>
<td>Solid phase $t - s$, $t = B, C$ $s = C, F$</td>
</tr>
<tr>
<td>$D_e$</td>
<td>Effective diffusion coefficient</td>
</tr>
<tr>
<td>$k_g$</td>
<td>Film Mass transfer coefficient of the gaseous reactant (cm/s)</td>
</tr>
<tr>
<td>$k_{ci}^{*}$</td>
<td>Intrinsic reaction rate constant if the ith interface (cm/s)</td>
</tr>
<tr>
<td>$E_{Al}$</td>
<td>Activation Energy for the reduction of components in the ith interface (kJ/mole)</td>
</tr>
<tr>
<td>$A_{ci}$</td>
<td>Arrhenius Frequency Factor for ith interface (cm/s)</td>
</tr>
<tr>
<td>$\tau_{Ri}$</td>
<td>Reaction Characteristic Time (s)</td>
</tr>
<tr>
<td>$L_i$</td>
<td>Ith reaction zone/interface</td>
</tr>
<tr>
<td>$i$</td>
<td>$i = 1, 2$ interface</td>
</tr>
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<td>$X_i$</td>
<td>Fractional conversion of $L_i$</td>
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<tr>
<td>$\Phi^{fs}$</td>
<td>Oxygen density change from t-s $\text{mole O}_2^{\text{transferable}}/\text{mole O}_2^{\text{in MeO}}$</td>
</tr>
<tr>
<td>$F_g$</td>
<td>Overall grain conversion</td>
</tr>
<tr>
<td>$F_p$</td>
<td>Overall Pellet conversion</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Specific Heat Capacity $[J/g \cdot K]$</td>
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<tr>
<td>$k_{e,\text{solid}}$</td>
<td>Solid effective thermal conductivity $[W/cm \cdot K]$</td>
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<td>$T_c$</td>
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<td>$T_b$</td>
<td>Bulk fluid temperature (K)</td>
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<td>$h_g^{*}$</td>
<td>Lumped film heat transfer coefficient $[W/m^2 \cdot K]$</td>
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<td>$K_{eq}$</td>
<td>Equilibrium rate constant</td>
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<td>Enthalpy of reaction (J/mol)</td>
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**Species**

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<td>C</td>
<td>$FeAl_3O_6$</td>
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<td>D</td>
<td>$H_2O, CO_2$</td>
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<td>E</td>
<td>$Cu$</td>
</tr>
<tr>
<td>F</td>
<td>$Fe$</td>
</tr>
<tr>
<td>I</td>
<td>$Al_2O_3$</td>
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</table>
References


[21] L. M. Plyasovaa, T. P. Minyukovaa, T. M. Yurievaa, I. A. Bobrikovb and A. M. Balagurovb, "Cation Distribution in Cu(Cr2 – xAlx)O4 and Cu(Fe2 – xAlx)O4


Appendix A : Statistical Analysis Evaluation Protocol

The tabulated data set depicted in Table A-A1 provides an analysis of Cycling stability by examining the standard deviation and the skewness from the mean oxygen transfer capacity and reaction rates over the course of the 10-cycle test.

<table>
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<th>Cycle</th>
<th>OTC</th>
<th>Deviation From Mean</th>
<th>Cycle</th>
<th>Reduction Rate</th>
<th>Deviation From Mean</th>
<th>Oxidation Rate</th>
<th>Deviation From Mean</th>
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Appendix B: Propogated Error Analysis

There is inherent error with any experimental setup. Therefore, a statistical propagation of error analysis was performed to determine the accuracy of the calculated results and provide upper/lower limits on confidence intervals obtained through the curve fitting application in MatLab 2017a. The experimental setup refers to the TGA-MS displayed in 4.1.1. This was applied after an initial fit of the system model was achieved with the experimental data spread from at least three repeat runs. Once a model was known then all the key variables that can potentially impact the experimental results can be explored. These include the probability of reactive gas concentration deviation due to mass flow deviations, concentration deviations, temperature deviations, and potential weight deviations due to measurement accuracy. These variables are outlined in Table A-B1 with the inherent error ranges.

<table>
<thead>
<tr>
<th>Component</th>
<th>Type</th>
<th>Range</th>
<th>Error (%) ±</th>
<th>Value</th>
</tr>
</thead>
<tbody>
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<td>Sample Ar MFC</td>
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<td>2 ml/min</td>
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<tr>
<td></td>
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<tr>
<td></td>
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<tr>
<td></td>
<td>H₂O Generator</td>
<td>0-3 ml/min</td>
<td>1% of Full Scale</td>
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<td>Pfieffer GSD 320</td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Temperature</td>
<td>Platinell</td>
<td>0-1500°C</td>
<td>-</td>
<td>2°C</td>
</tr>
<tr>
<td>Balance</td>
<td>Discovery TGA</td>
<td>0-100 mg</td>
<td>0.01% of Full scale</td>
<td>10µg</td>
</tr>
</tbody>
</table>

The case applied for H₂O oxidation of Fe + Al₂O₃ → FeAl₂O₄ is shown as an example since it is a single reaction step in which a singular model description was used. For this case, error associated with the Balance MFC, Sample Ar MFC, H₂O generator, MS, and temperature are introduced to show the potential for the propagation of error through the calculation of Oxygen.
carrier conversion ($F_p$). Error associated with balance noise was considered to be negligible when considering the resolution with respect the anticipated weight changes (~6000µg, resolution ~10µg). The two major variables that can potentially impact error propagation included reactive gas concentration and temperature. These variables are linked to the model expression as shown with the following equations:

\[
C_{j,g} \left[ \frac{g}{cm^3} \right] = \left( \frac{P}{RT_{STP}} \right) \left( \frac{273.15}{T_b} \right) \left( \frac{[j, (vol\%)]}{100} \right) (MW_j)
\]

\[
k_{CI}^* = A_{CI} e^{\frac{E_{A_i}}{RT_b}}
\]

\[
\frac{t}{\tau_R} = 1 - (1 - X_{LI})^{\frac{1}{3}}, \quad \tau_R = \frac{p_1^{B-C} R_{g,0}}{b k_{CI} C_{j,g}^{n_f}} \quad X_{LI} = F_p
\]

Concentration of the reactive gas, $[j, (vol\%)]$, is a function of the cumulative flow rate and the potential for deviation from the setpoint based on inherent error with the flow controllers.

\[
[j, (vol\%)] \pm e_j = \frac{\dot{V}_{H2O,g} \pm e_{H2O,g}}{\dot{V}_{Ar,Balance} \pm e_{Ar,Balance} + \dot{V}_{Ar,Sample} \pm e_{Ar,Sample} + \dot{V}_{H2O,g} \pm e_{H2O,g}}
\]

Where $\dot{V}_i$ is the volumetric flow rate associated with the component and $e_i$ is the reported standard error associated with the device that controls the components flow. Concentration, $C_{j,g} \left[ \frac{g}{cm^3} \right]$, and intrinsic reaction rate constant $k_{CI}^*$ are both functions of temperature, so deviations in this variable can impact the anticipated outputs. Inherent error in temperature, although minor, propagates in both functions and ultimately the calculation of particle conversion.
An upper and lower limit analysis was conducted to examine the maximum deviations that could potentially occur due to the inherent error in the system. Table A-B2 shows deviations in the reactive gas concentration and intrinsic rate parameters based on the maximum error limits.

Table A-B2: Experimental Error Propagation in Reactive gas concentration and intrinsic rate constants

<table>
<thead>
<tr>
<th>Concentration Deviation</th>
<th>Vol%</th>
<th>2% MS Error Added</th>
<th>Cag (g/cm³)</th>
<th>Temperature (°C)</th>
<th>Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.292</td>
<td>2.338</td>
<td>0.00048</td>
<td>802</td>
<td>Upper</td>
</tr>
<tr>
<td></td>
<td>2.100</td>
<td>2.100</td>
<td>0.00043</td>
<td>800</td>
<td>Target</td>
</tr>
<tr>
<td></td>
<td>1.825</td>
<td>1.789</td>
<td>0.00037</td>
<td>798</td>
<td>Lower</td>
</tr>
<tr>
<td></td>
<td>0.192</td>
<td>0.238</td>
<td>0.00005</td>
<td>2</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>0.275</td>
<td>0.311</td>
<td>0.00006</td>
<td>2</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Kc1 Deviation</th>
<th>A1</th>
<th>Ea (kJ/mol)</th>
<th>Temperature (°C)</th>
<th>Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.574</td>
<td>1.944</td>
<td>10.91000</td>
<td>802</td>
<td>Upper</td>
</tr>
<tr>
<td>0.514</td>
<td>1.944</td>
<td>11.86000</td>
<td>800</td>
<td>Target</td>
</tr>
<tr>
<td>0.461</td>
<td>1.944</td>
<td>12.81000</td>
<td>798</td>
<td>Lower</td>
</tr>
<tr>
<td>0.059</td>
<td>0.000</td>
<td>-0.95000</td>
<td>2</td>
<td>+</td>
</tr>
<tr>
<td>0.053</td>
<td>0.000</td>
<td>0.95000</td>
<td>2</td>
<td>-</td>
</tr>
</tbody>
</table>

The values reported in Table A-B2 represent the maximum deviations for the target variables. Figure A-B1 displays the application of these bounds in the predictive expression and shows the spread of the distribution that can be obtained based on the instance of error introduction into the system. The limits range from 3-5% deviation from the target data set, with lower bounds showing the greatest amount of deviation. These bounds can be added to the data spread and a secondary regression conducted. This often results in an increased spread of the distribution and a widening of values for the 95% Confidence interval range. It is noted that these upper and lower bounds represent a maximum amount of deviation noting that other permutations would fall within the residual limits that the two bounds define. The confidence intervals of the prediction
are an output of the Matlab software suit and represent the range of the variables in which a potential solution was found based on the data distribution.

![Figure A-B1: Upper and Lower bound residual distributions generated from propagated error analysis for the calculation of \( F_p \).](image)

The confidence intervals or bounds for fitted coefficients are denoted by the following equation

\[
C = b \pm t\sqrt{S}
\]

Where \( b \) are the coefficients produced by the regression, \( t \) depends on the confidence level (in this case 95%) and is computed using the \( t \) cumulative distribution function and \( S \) is a vector of the diagonal elements from the estimated covariance matrix. A more detailed discussion of this can be found in the Matlab software suit.