ABSTRACT

The chemical looping combustion (CLC) strategy, which involves indirect combustion of carbonaceous fuels such as coal or natural gas via the redox reactions of pure or mixed metal oxides, offers a potentially viable approach to convert coal in a more efficient and less carbon-intensive manner. A CLC approach that is of particular relevance to coal conversion is the so-called chemical looping with oxygen uncoupling (CLOU). Since the CLOU process utilizes oxygen carriers with relatively high equilibrium oxygen partial pressures (PO\textsubscript{2}), the reactions between the metal oxide and the fuel proceed through metal oxide decomposition – solid fuel combustion pathway, resulting in fast reaction kinetics. Although single component metal oxides such as oxides of Cu or Mn are frequently investigated as the active oxygen carrier for CLOU, recent experimental studies have indicated that many mixed metal oxides can possess more desirable redox properties. The inclusion of mixed metal oxides significantly expands the material design space for CLOU oxygen carriers, thereby enhancing the likelihood of finding improved oxygen carriers in terms of activity, recyclability, mechanical strength, and cost. Of these materials CaMnO\textsubscript{3} has been extensively studied due to its low cost and suitable CLOU properties. CaMnO\textsubscript{3} begins to release oxygen under low oxygen partial pressures at around 850°C. However, CaMnO\textsubscript{3} has also been shown to decompose into Ruddlesden-Popper (Ca\textsubscript{2}MnO\textsubscript{4}) and spinel (CaMn\textsubscript{2}O\textsubscript{4}) phases under cyclic redox conditions. Both Sr and Ba are explored as potential A-site dopants at various concentrations. Phase segregations are observed with the addition of Ba dopant even at relatively low concentrations (5% A-site doping). In contrast, stable solid solutions are formed with Sr dopant at a wide range of doping level. Sr doping is found to effectively stabilize the perovskite structure. \textit{In-situ} XRD studies indicate that the Sr doped CaMnO\textsubscript{3} maintains a stable orthorhombic perovskite structure under an inert environment (tested up to 1,200 °C). The same oxygen carrier sample exhibited high recyclability over 100 redox cycles at 850 °C. Besides being highly recyclable, Sr doped CaMnO\textsubscript{3} is found to be capable of releasing its lattice oxygen at a temperature significantly lower than that for CaMnO\textsubscript{3}, rendering it a potentially effective oxygen carrier for solid fuel, e.g. bituminous Illinois coal, combustion and carbon dioxide capture.
EXECUTIVE SUMMARY

The objective of this research was to develop “perovskite based oxygen carriers for enhanced conversion of Illinois coal.” The developed oxygen carriers will be able to convert coal char effectively while being recyclable, attrition resistant, phase stable, and having increased sulfur/ash resistance.

Of the various carbon capture technologies under development, chemical looping combustion (CLC) has emerged as a potentially promising option. The CLC processes utilize a solid oxygen carrier to transfer oxygen from the air to the fuel. While oxygen carriers exhibit fast reaction kinetics for gaseous fuels, solid fuel conversion can be slow. Two ways to mitigate the slow kinetics is by (1) gasification of the solid fuel into gaseous products which in turn can react with the solid oxygen carriers or (2) use a modified version of CLC known as chemical looping with oxygen uncoupling (CLOU). In CLOU, the oxygen carrier is able to release its stored oxygen as gaseous oxygen due to an oxygen partial pressure difference. The released oxygen leads to greatly improved reaction kinetics. Due to the highly oxidative nature of these types of oxygen carriers, it is possible to minimize the effects of sulfur commonly found in coal.

Oxygen carrier design for CLOU has been extensively studied with materials comprised of Cu, Co, and Mn oxides. Typical issues with current developed oxygen carriers include high cost (CuO), difficulty in regeneration (Mn₂O₃), and/or low oxygen carrying capacity (perovskite) and strength (Fe₂Mn₂₋ₓO₃). Due to the increased tailoring of properties, perovskite based oxides offer highly tunable and desirable properties for CLOU. Of the available perovskites, CaMnO₃ has been the most extensively studied perovskite oxygen carrier. The low cost of the perovskite due to increased availability makes it promising. However, CaMnO₃ has large disadvantages which include low strength, negative sulfur interactions, and can be difficult to regenerate.

This project proposes to improve the perovskite based oxides CLOU properties while improving the structural integrity of the oxygen carrier. Several oxides based on the CaMnO₃ were prepared using metals to replace some of the A (Ca) and B-sites (Mn) with a third metal. For the A-site, Sr and Ba are chosen, while Fe, Co, Ni, Al, and V are chosen as possible dopants. Besides their CLOU properties, oxygen carriers will be tested for their long term recyclability, ability to convert coal, and attrition resistance.
OBJECTIVE
The objective of this research was to develop perovskite based oxygen carriers for enhanced conversion of Illinois coal. Specific objectives outlined in the proposal include:

Task 1. Oxygen carrier synthesis and characterization
Task 2. Oxygen carrier reactivity, recyclability, and phase stability testing
Task 3. Oxygen carrier-coal reactions in fluidized bed
Task 4. Attrition studies and long term testing

INTRODUCTION AND BACKGROUND
Climate change caused by anthropogenic carbon dioxide emissions along with the ever increasing demand for energy requires new power generation processes with lower carbon footprints. Of the various carbon capture technologies under development, chemical looping combustion (CLC) has emerged as a potentially promising option. (Figueroa et al.; Hansen and Sato) The CLC processes utilize a solid oxygen carrier to transfer oxygen from the air to the fuel. This is achieved using interconnected fluidized bed or moving bed reactors. (Adanez et al.; Fan and Li; Fan; Lyngfelt; Sorgenfrei and Tsatsaronis; Tong et al.) In the first reactor, commonly termed the reducer/fuel reactor, the oxidized form of the oxygen carrier is reacted with the fuel to form carbon dioxide and water vapor. The oxygen depleted carrier is then transported to a second reactor referred to as the oxidizer/air reactor. Here, air is used to regenerate the oxygen depleted carrier while producing heat for power generation.

While most oxygen carriers are effective for gaseous fuel combustion, they tend to be less active in converting solid fuels such as biomass or coal due to mass transfer and kinetic limitations. To enhance the combustion rate for solid fuels, two methods are typically used. In the first method, solid fuel is gasified into syngas by steam, carbon dioxide, or oxygen. The resulting syngas is then reacted with the oxygen carrier at a faster rate than direct solid-solid interactions. (Lyngfelt; Sorgenfrei and Tsatsaronis; Tong et al.; Scott et al.; Henrik Leion, Mattisson, and Lyngfelt; Luo et al.) A variety of oxygen carriers including Fe (Tong et al.; Henrik Leion, Mattisson, and Lyngfelt; Cuadrat et al.; Linderholm et al.; H Leion, Mattisson, and Lyngfelt), Mn (Linderholm et al.; Arjmand, Leion, et al.), and Ni (Shen, Wu, and Xiao; Shen et al.) based oxides have been used in the conversion of solid fuels via such an in-situ gasification approach. An even faster approach to combust solids fuel is the so-called chemical looping with oxygen uncoupling (CLOU). (Adanez et al.; Mattisson, Lyngfelt, and Leion; Mattisson) The CLOU process takes the advantage of oxygen carriers with high equilibrium oxygen partial pressure ($P_{O2}$). As a result, solid fuels are combusted with gaseous oxygen released from the oxygen carrier, resulting in significantly improved reaction kinetics. Typical oxygen carriers that exhibit CLOU properties include oxides and mixed oxides containing Cu, Mn, and/or Co. (Mattisson, Lyngfelt, and Leion; Mattisson; Imtiaz, Hosseini, and Müller; Azimi, Leion, Mattisson, et al.; Azimi, Leion, Rydén, et al.; Shafieifarhood, Stewart, and Li; Shulman et al., “Manganese/Iron, Manganese/Nickel, and

Despite possessing excellent oxygen uncoupling properties, copper oxides face challenges including a low melting point of the reduced Cu phase which can lead to agglomeration and defluidization. Supports, such as MgAl$_2$O$_4$, SiO$_2$, and Al$_2$O$_3$, have been shown to help prevent sintering and defluidization while maintaining the oxygen uncoupling properties of the copper oxide. (Mattisson; Arjmand, Azad, et al.; Arjmand, Keller, et al.; Gayán et al.) Nevertheless, the relatively high cost of copper oxide may limit its applications. Cobalt oxides, while potentially feasible, are typically avoided due to their low decomposition temperature, toxicity, and negative environmental impact. (Mattisson, Lyngfelt, and Leion; Shafiefarhood, Stewart, and Li) Manganese oxides hold advantages over copper oxides in terms of high availability and low cost. However, pure manganese oxide is difficult to regenerate with air due to its high equilibrium P$_{O2}$. Formation of mixed oxide phases through the addition of secondary metal oxides such as Fe, Ni, Mg, and Ca to manganese oxides has been shown as an effective approach to improve the regenerability and structural stability of Mn based oxygen carriers. (Arjmand, Leion, et al.; Mattisson; Azimi, Leion, Mattisson, et al.; Azimi, Leion, Rydén, et al.; Shafiefarhood, Stewart, and Li; Shulman et al., “Manganese/Iron, Manganese/Nickel, and Manganese/Silicon Oxides Used in Chemical-Looping With Oxygen Uncoupling (CLOU) for Combustion of Methane”; Shulman et al., “Chemical – Looping with Oxygen Uncoupling Using Mn/Mg-Based Oxygen Carriers – Oxygen Release and Reactivity with Methane”; Arjmand, Hedayati, et al.; Arjmand, Kooiman, et al.; Hallberg, Jing, et al.; Leion et al.; Rydén, Lyngfelt, and Mattisson; Sundqvist et al.)

More recently, perovskite structured oxygen carriers have received increasing attentions as oxygen carriers for redox applications. (Shafiefarhood, Stewart, and Li; Arjmand, Hedayati, et al.; Hallberg, Jing, et al.; Leion et al.; Rydén, Lyngfelt, and Mattisson; Sundqvist et al.; Källén et al.; Pishahang et al.; Moldenhauer et al.; Dai et al.; Fang He et al.; Mihai, Chen, and Holmen, “Chemical Looping Methane Partial Oxidation”; Murugan, Thursfield, and Metcalfe; Readman et al.; Rydén, Lyngfelt, et al.; Sarshar et al.; Zhao et al.; Sarshar, Kleitz, and Kaliaguine; Noorman et al.; Chen et al.; Galinsky, Huang, et al.; Shafiefarhood et al.; Neal, Shafiefarhood, and Li; Galinsky, Shafiefarhood, et al.) Typical perovskite takes the form of ABO$_{3-\delta}$, where A is a large cation of either the alkali earth or rare earth metal and B is a smaller transition metal cation. As a support, mixed ionic and electronic conductive (MIEC) perovskites such as La$_1-x$Sr$_x$FeO$_3$ (LSF) have shown to enhance the redox activity of iron oxides by nearly two orders of magnitude. (Galinsky, Huang, et al.; Shafiefarhood et al.; Neal, Shafiefarhood, and Li; Galinsky, Shafiefarhood, et al.) Perovskite and perovskite supported iron oxide have also been explored as redox catalysts for syngas generation and water-splitting. (Feng He et al.; Mihai, Chen, and Holmen, “Chemical Looping Methane Partial Oxidation”) In terms of CLOU applications, La containing perovskite supports are reported to be effective to enhance the oxygen donation properties of mixed Mn-Fe and
Co-Fe oxides. (Shafiefarhood, Stewart, and Li) Up to 8.8% decrease in initial decomposition temperature was reported for perovskite supported mixed metal oxides. As a standalone oxygen carrier, perovskites of the CaMnO$_3$ family are extensively studied for CLOU and CLC applications. (Imtiaz, Hosseini, and Müller; Pour et al.; Arjmand, Hedayati, et al.; Hallberg, Jing, et al.; Leon et al.; Rydén, Lyngfelt, and Mattisson; Källén et al.; Jing et al.; Bakken, Norby, and Stolen; Arjmand, Kooiman, et al.; Cabello et al.; Fossdal et al.; Hallberg, Källén, et al.; Moldenhauer et al.; Noorman et al.; Pishahang et al.; Rydén, Leion, et al.; Sundqvist et al.) While its oxygen uncoupling capacity is smaller than copper oxides, CaMnO$_3$, which can be synthesized from abundantly available manganese ores and Ca precursors (Pour et al.; Fossdal et al.) has been reported to be active for solid fuel conversions. (Arjmand, Hedayati, et al.; Pour et al.; Leion et al.; Sundqvist et al.) A challenge to CaMnO$_3$ is its lack of long term stability and activity with fuels. Undoped CaMnO$_3$ has been reported to undergo irreversible phase change to CaMn$_2$O$_4$ and Ca$_2$MnO$_4$ phases, leading to eventual deactivation of the oxygen carrier. (Bakken, Norby, and Stolen; Imtiaz, Hosseini, and Müller; Mattisson; Arjmand, Kooiman, et al.; Cabello et al.) In addition, CaMnO$_3$ has been shown to deactivate in the presence of sulfur, a common constituent of coal, through formation of CaSO$_4$. (Arjmand, Kooiman, et al.; Cabello et al.; Sundqvist et al.) Prevention of irreversible phase transition has been investigated by doping secondary metals into the A and B-sites of the CaMnO$_3$ parent material. The dopants can also be used to increase the activity of the oxygen carrier. The most common elements used to stabilize the structure are Ti and Mg.

Pishahang et al. investigated Ca$_{1-y}$Mn$_{1-x}$Ti$_x$O$_{3-δ}$ oxygen carriers under fixed bed conditions using syngas as the fuel. (Pishahang et al.) The authors reported that adding Ti and decreasing the Ca content increased stability of the oxygen carrier. 95% conversion of the syngas was achieved with no observable coke formation. Rydén et al. studied a CaMn$_{0.875}$Ti$_{0.125}$O$_{3-δ}$ oxygen carrier for CLOU. (Rydén, Lyngfelt, and Mattisson) The oxygen carrier exhibited oxygen uncoupling at temperature above 720°C in a fluidized bed with a maximum oxygen uncoupling rate of 0.03 L/min at 950°C. The maximum oxygen concentration was 4 vol. %. Besides the good uncoupling properties, the oxygen carrier exhibited good redox activity and stability for methane conversion. Kallen et al. used Mg doped CaMnO$_3$ and tested the oxygen carrier in a 10kWth gas-fired CLC unit. (Källén et al.) The synthesized oxygen carrier released oxygen at above 700°C. The oxygen carrier did not agglomerate for 120 hrs. at hot conditions (including 55hrs. of reaction) and formation of fines (<45 µm.) was below 0.01%, indicating possible longevity in the particle’s lifetime. Another study using Mg, Ti, and Fe dopants conducted by Hallberg et al. shows good activity with methane and syngas while releasing 0.3-0.5% by weight gaseous oxygen at 900°C. (Hallberg, Jing, et al.) A maximum oxygen release of ~1 w.t.% was reported at 1,000°C. The authors noted CaMn$_2$O$_4$ spinel formation after testing the oxygen carrier’s CLOU properties in three cycles and activity for methane conversion in a single cycle. Hallberg et al. also investigated the addition of both Ti and Mg in a 300W fluidized bed system using natural gas as the fuel. (Hallberg, Källén, et al.) The designed oxygen carriers showed higher conversion of the fuel than Ni oxides while showing little attrition, however, it was determined that the spent particles contained a noticeable amount of the spinel CaMn$_2$O$_4$.
phase. Pour et. al. examined different oxygen carriers created by combining cheap manganese ores with Ca(OH)$_2$. (Pour et al.) While the primary phase was CaMnO$_{3.5}$, the manganese ores also contained Al, Fe, K, Ti, Mg, etc. in small quantities. In reaction with methane, ores containing high concentrations of Al showed poor performance due to spinel formation between Al and Mn. The best performing oxygen carrier made from a South African manganese ore, which was mainly composed of Fe, Si, Ca, Mg, and Mn, had an oxygen capacity of 1.5 w.t. % in methane. Oxygen uncoupling capacity was between 0.37-0.68 w.t.% for the various oxygen carriers investigated.

Although extensive studies on B-site dopants were performed, limited studies using A-site dopants have been conducted. Arjmand et. al. investigated Ca$_x$La$_{1-x}$Mn$_{y}$M$_{1-y}$O$_{3-δ}$ (M=Mg, Ti, Fe, or Cu) oxygen carriers for CLOU properties between 900-1,000°C in a laboratory scale fluidized bed. (Arjmand, Hedayati, et al.) The authors characterized the oxygen carriers’ capability to release oxygen by measuring oxygen concentration in the product gas stream during the uncoupling step. It was determined that pure CaMnO$_3$ had the highest oxygen release capability (~0.7% after 360 s). La-doped CaMnO$_3$ had a lower oxygen concentration of ~0.5% after 360 s. Doping of both A and B-sites caused even further decrease in oxygen release except for copper doping which exhibited higher oxygen concentration than CaMnO$_3$. However, copper caused the perovskite materials to defluidize when fuel was added. The authors did detect small amounts of spinel CaMn$_2$O$_4$ although its effect on the oxygen carrier performance was not documented. To summarize, further studies on the effect of A-site substitution using low cost alkali earth metals are desired in order to obtain a more informed strategy to develop oxygen carriers with lower cost and improved CLOU performance.

This project investigates the effect of A and B-site dopants on CaMnO$_3$ based oxygen carriers for CLOU applications. Both Sr and Ba are explored as potential A-site dopants at various concentrations. Fe, Co, Ni, V, and Al. Focus on the research are on A-site effects due to the readily investigated B-site dopants. The impacts of A-site dopants on phase stability, oxygen release properties, redox stability, and reactivity of the Ca$_{1-x}$A$_x$MnO$_3$ (A= Sr and Ba) based oxygen carriers are investigated using an in-situ X-ray diffraction (XRD) instrument, a thermogravimetric analyzer (TGA), and a fluidized bed reactor. It is determined that Sr dopant can enhance the stability of the perovskite structure while providing facile oxygen release for solid fuel conversions.

**EXPERIMENTAL PROCEDURES**

**Oxygen carrier synthesis**

Several doped and undoped-CaMnO$_3$ oxygen carriers were synthesized using the sol-gel method. All samples are listed in Table 1.

<table>
<thead>
<tr>
<th>Perovskite</th>
<th>Synthesis</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaMnO$_3$</td>
<td>Sol-gel</td>
<td>CM</td>
</tr>
<tr>
<td>Ca$_{1-x}$Sr$_x$MnO$_3$</td>
<td>Sol-gel</td>
<td>CSM</td>
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</table>
The sol-gel method (or modified Pechini method) used is to achieve a better distribution of metal ions and thus a better phase purity. The sol-gel method takes nitrate salt precursors and dissolves them in distilled water. Citric acid (CA) is used as a chelating agent and ethylene glycol is used to help promote gel formation. Water is slowly vaporized until almost all the water is removed; at this time, the liquid solution solidifies into a gel. The gel is then dried at slightly above water boiling temperature overnight. The resulting solid mixture is then annealed at moderate temperatures to ensure correct phase formations. For example, the CaMn$_{0.8}$Fe$_{0.2}$O$_3$ oxygen carrier, precursors of Ca(NO$_3$)$_2$∙4H$_2$O (99%, Sigma-Aldrich), Mn(NO$_3$)$_2$∙4H$_2$O (≥97%, Sigma-Aldrich), and Fe(NO$_3$)$_3$∙9H$_2$O (98+%, Sigma-Aldrich) are dissolved in 50mL of deionized water. The resulting solution is mixed at room temperature for 30 minutes at 600 rpm to ensure full dissociation of nitrate salts. Citric acid is added to the solution in a ratio of about 2.5:1 molar ratio between CA and metal ions. The temperature is raised to 50°C for 30 minutes. Afterwards, 1.5:1 molar ratio of ethylene glycol to CA is used to promote gel formation. The temperature is finally raised to 80°C to slowly evaporate water. Once most of the water is removed, a gel will begin to form after slow cooling. The gel is dried at 120°C for 12 hours and the resulting solid is then annealed at 1000-1200°C for 8 hours.

### Oxygen carrier characterizations

Phase identification of the oxygen carriers is conducted using X-ray powder diffraction. Powdered samples are prepared and tested using a Rigaku SmartLab X-ray diffractometer with Cu-Kα (λ=0.1542nm) radiation operating at 40kV and 44mA. A scanning range of 20-80° (2θ) with a step size of 0.1° holding for 3.5 seconds at each step is used to generate the XRD patterns. To examine phase properties during temperature programmable desorption (TPD) experiments, *in-situ* X-ray diffraction was conducted using an Empyrean PANalytical XRD using a similar Cu-Kα radiation operating at 45kV and 40mA. A 2θ range of 20-80 is used at a ramp rate of 0.1° holding each step for 0.1s. A TPD experiment is conducted in the *in-situ* XRD by heating the sample at 5°C/min in pure argon. XRD scans are conducted the entire length of the ramp to 1,200°C.

### Oxygen uncoupling testing

Initial oxygen uncoupling properties of the oxygen carriers are characterized in a thermogravimetric analyzer (TGA). Two primary experiments are conducted in the TGA:
(1) temperature programmable desorption TPD experiments using inert helium (5.0, Airgas) up to 1,000°C at a ramp of 20°C/min and (2) isothermal experiments between 650-950°C. Isothermal experiments are conducted at various temperatures to determine the oxygen uncoupling capabilities at low to high temperatures. At each temperature, 5 cycles of switching between pure inert and 10% O₂ (Extra Dry, Airgas) balanced with a mixture of argon (5.0, Airgas) and helium are conducted for short term recyclability of the oxygen carrier. Best performing oxygen carriers are also tested for 100 cycles at 850°C to demonstrate the oxygen uncoupling performance of the perovskite oxygen carriers over the long term.

**Fluidized bed tests**

A laboratory-scale fluidized-bed reactor is used for solid fuel conversion experiment. The quartz fluidized-bed reactor has an outer diameter of 25.4 mm. The reactor is heated through external heating from a tube furnace (MTI OTF-1200X-S-VT). Temperature is measured inside the reactor with an Inconel (Type K) thermocouple to set the temperature of the reactor to 850°C. A 3.75mm ID stainless steel tube is used for solid fuel injection into the reactor. A gas mixing panel is used to send the desired ratio of gases from both the bottom of the reactor for fluidization and through the smaller stainless steel tube for solid fuel injection. For maintaining fluidization, flow rates of 1,080 and 1,200 mL/min (at S.T.P) are used for solid fuel conversion (inert environment) and oxidation cycles, respectively. The flow rates correspond to 6-7 times the calculated minimum fluidization velocity, \( U_{mf} \), of the synthesized oxygen carrier. Prior to experiments, the reactor bed is loaded with 16 mesh silicon carbide (Kramer Industries) at the bottom of the reactor. The SiC particles act as a gas preheater and distributor. The SiC layer also supports the oxygen carrier bed. After the SiC layer is placed, approximately 15 grams of the oxygen carrier is placed into the reactor.

For redox reactions of solid fuel, bituminous coal (Asbury Inc.) is converted into devolatilized coal char through heating in the reactor at 800°C in a N₂ environment. Injection of the coal is conducted in a pulse mode by loading from the top of the reactor through the small stainless steel tube and is pulsed into the bottom of the oxygen carrier layer of the reactor bed using N₂. 10 redox cycles are tested using the fluidized bed reactor conducting two experiments in those 10 cycles. During cycles 1, 3, 5, and 10 solid fuel conversion is tested. Cycles 2, 4, and 6-9 are examining the oxygen uncoupling properties. Exhaust gas concentrations are measured using a quadrupole mass spectrometer (MKS Cirrus 2) and a near-IR based gas analyzer (Emerson X-Stream).

**RESULTS AND DISCUSSION**

**Thermal stability of CaMnO₃**

Although previous studies revealed irreversible decomposition of CaMnO₃ to Ruddlesden-Popper and spinel phases, the decomposition was observed under extended redox cycles at relatively low temperatures (<1,000 °C).(Arjmand, Hedayati, et al.) An alternative approach that can conveniently quantify phase stability of perovskites without
undergoing extended redox cycles would be desirable for efficient screening of perovskite based oxygen carriers. In the current study, temperature programmed desorption (TPD) and in-situ XRD are used to determine the stability of perovskites as well as their initial oxygen uncoupling temperature and rate of oxygen uncoupling. Figure 1 shows the TPD and in-situ XRD results. The sample weight loss profile in TPD indicates an initial decomposition temperature at approximately 800°C followed with significant release of lattice oxygen. This is corroborated by the in-situ XRD spectra, which exhibit significant increase in lattice parameter (decreasing 2θ angles) at above 800 °C. When heated above 1,000°C, the CaMnO₃ phase decomposes into undesired Ca₂MnO₄ and CaMn₂O₄ structures as evidenced by the peaks formed at or near 29.5, 33, 34.5, 37.7, 39, 40.4, 43.2, and etc. 2θ angles.

![Figure 1](image1.png)

Figure 1- (a) TPD of the pure CaMnO₃ at 5°C/min to 1,000°C in pure helium environment. Sample weight: 20 mg; Gas flow rate: 100mL/min. He (Grade 5.0). (b) In-situ XRD of the same oxygen carrier at 5°C/min to 1,200°C in argon. Gas flow rate: 50mL/min Ar (Grade 5.0)

**Oxygen carrier screening (B-site effects)**

Initial characterizations and screening of the oxygen carriers include testing the oxygen carriers in a TGA/differential bed to monitor initial oxygen capacity under inert helium environment. Figure 2 compares the oxygen uncoupling capacity of various as-prepared oxygen carriers over 5 cycles. As seen, pure CaMnO₃ has the highest oxygen capacity by nearly 2 times the doped samples. However, it is well known that pure CaMnO₃ when reduced with fuel often forms very difficult to oxidize phases of Ca₂MnO₄ and CaMn₂O₄.
The doped materials, which have between 1.5 and 2.2 % oxygen uncoupling capacity, can help stabilize the oxygen carrier and provide better selectivity during redox experiments.

Of the doped samples, Ni, Co, and V have the highest oxygen uncoupling capacity. However, Fe doped in the B-site exhibited the most stability in oxygen capacity over the 5 cycles. Adding Ba had a negative effect on the oxygen capacity of the A-doped samples. To elucidate more over the effect of the A-site addition additional Ba-doped only samples were synthesized. However, these samples have yet to be characterized. It is important to characterize the phase properties of the oxygen carriers of the as-prepared and after experiments. Since Mn oxides are known to uncouple oxygen, it is important to ensure the Mn is incorporated into the perovskite. Figure 3 illustrates the typical XRD pattern seen for the synthesized oxygen carriers.

Phase fitting is completed using High Score Plus© software to help fit the peaks to the limited database. The dopant containing perovskites are not all available in the software’s database. The sharpness of the peaks and lack of unidentified peaks is a good indication that the dopant may have been incorporated. If Fe is incorporating some of the previous Mn-sites in the perovskite phase it is expected that the volume of the cell should decrease. Through lattice parameter refinement, experimental values for the lattice
parameters and volume of the unit cell can be calculated. As table 2 shows, compared to the database values the unit cell volume decreases.

Table 2- Lattice parameter comparison of the CaMnO$_{2.98}$ phase found of the fresh CMF perovskite sample.

<table>
<thead>
<tr>
<th>Lattice Parameters</th>
<th>Database</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>5.2715</td>
<td>5.17</td>
</tr>
<tr>
<td>b (Å)</td>
<td>7.4619</td>
<td>7.49</td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.2859</td>
<td>5.30</td>
</tr>
<tr>
<td>V ($10^6$ pm$^3$)</td>
<td>207.92</td>
<td>205.1764</td>
</tr>
</tbody>
</table>

When characterizing the other oxygen carriers, it was apparent that there were often peaks that were unidentified by the software, and the broadening of the peaks occurred more often. This is indicative of impurity phases. These can be seen in Figure 3. From the database, the likelihood of unidentified peaks could be pure oxides of the various dopants of Ni, V, and Co. When Ba is doped, it was often seen to contain a BaMnO$_3$ phase.

![XRD patterns of the (a) CMV and (b) CBMV fresh perovskite oxygen carriers.](image)

While it is likely that the impurities won’t majorly affect operating performance, it may be worthwhile to test phase pure samples after initial screenings of samples. Due to lack of phase purity and extensive studies on B-site dopants, focus of the work was shifted to A-site dopants.

**Oxygen carrier screening (A-site dopants)**

Since perovskites can accommodate significant amount of oxygen vacancies, the decomposition would occur in two steps. In the first step, manganese undergoes reduction from a 4+ valence state (CaMnO$_3$) to 3+ (CaMnO$_{2.5}$) with the perovskite structure maintained. Further reduction of Mn will result in the formation of new phases:

$$6\text{CaMnO}_{2.5} \leftrightarrow 2\text{CaMn}_2\text{O}_{4.8} + 2\text{Ca}_2\text{Mn}_4 + (6-0.5)\text{O}_2$$

Reaction 1

One potential approach to avoid such an undesired transition is to add dopants that enhance the stability of the perovskite phase. By inspection of the Goldschmidt or bond-valence model (BVM) tolerance factor, it is possible to project dopant effect on the
structural stability of perovskites semi-empirically. The Goldschmidt tolerance factor is defined in equation 1 (Bhalla, Guo, and Roy):

\[ t = \frac{r_A + r_O}{\sqrt{2(r_B + r_O)}} \]  

(Eq. 1)

Where \( r_A \), \( r_B \), and \( r_O \) are the ionic radii of the A-site ion, B-site ion, and oxygen ion. BVM tolerance factor replaces the summations of effective ionic radii in Equation 1 with ideal A-O and B-O bond distances. (Lufaso and Woodward) Based on the report by Dabrowski et. al., (Dabrowski et al.) CaMnO\(_3\) has a tolerance factor of 0.985. While this value is within the suitable range to form stable cubic perovskites (0.9≤t<1), further increase of the tolerance factor towards an ideal value of 1 for cubic perovskite can potentially enhance the stability of the oxygen vacant Ca\(_{1-x}\)A\(_x\)MnO\(_{2.5}\) perovskite. It is apparent from Equation 1 that larger A-site dopants such as Ba and Sr should render such an effect. It is also noted that the ionic radius of Ba\(^{2+}\) (1.61 angstrom) is significantly larger than Mn\(^{3+}\) (0.58 angstrom under low spin) and Ca\(^{2+}\) (1.34 angstrom). Therefore, significant doping of Ba will lead to a tolerance factor larger than 1, resulting in a hexagonal perovskite structure.

Figure 4- Normalized differential thermal gravimetric (DTG) curves of (a) Ba-doped and (b) Sr-doped CaMnO\(_3\) ramped to 1,000°C at a rate of 20°C/min in a pure helium atmosphere. Sample weight: 20mg; Gas flow rate: 100mL/min. He (5.0 Grade).

Perovskite samples with various dopant amounts are tested using TPD to observe initial oxygen release temperature and total amount of oxygen released. Differential thermal gravimetry (DTG) curves of selected samples are shown in Figure 4. The area under the DTG curves is the total weight loss exhibited by the oxygen carriers. As can be seen, CaMnO\(_3\) exhibits a significant decomposition peak at around 800°C. A similar feature is also observed for Ca\(_{0.95}\)Ba\(_{0.05}\)MnO\(_3\). Both Sr and Ba dopant affect the initial decomposition temperature, oxygen release rate, and total oxygen release of Ca\(_{1-x}\)A\(_x\)MnO\(_3\). Both pure SrMnO\(_3\) and BaMnO\(_3\) are more stable than CaMnO\(_3\) and, as a result, release less total oxygen. BaMnO\(_3\) offers about 7 times less total oxygen release and SrMnO\(_3\) offers about 3.5 times less oxygen compared to pure CaMnO\(_3\). When Sr and Ba are doped to the A-site, properties of both oxides can be observed. Ba and Sr doped samples tend to decompose at significantly lower temperatures (<700°C) than Ca based perovskites. When Ba is doped, the trend is apparent to shift between pure CaMnO\(_3\) and pure BaMnO\(_3\). While 0.05 Ba doping does not significantly affect the properties of oxygen uncoupling, increasing the dopant amount to 0.25 can shift the initial reduction
temperature by approximately 200°C. Total oxygen release for Ca\textsubscript{0.75}Ba\textsubscript{0.25}MnO\textsubscript{3} is 3 w.t.% during the TPD experiment. This is only slightly lower than the 3.7 w.t.% oxygen release by pure CaMnO\textsubscript{3}. The rate of oxygen release in the high temperature ranges (>750°C), however, is significantly slower for Ca\textsubscript{0.75}Ba\textsubscript{0.25}MnO\textsubscript{3}. Another intriguing property is the significant weight loss observed at low temperatures (<600°C) in which almost 0.5 w.t.% of the sample is released in the form of oxygen (Figure 4a). Further doping of Ba onto the perovskite follows a trend to reduce total oxygen release and oxygen donation rate in the high temperature range. Sr-doped samples follow a trend similar to that exhibited by the Ba-doped samples. Rates of oxygen release at high temperatures are slightly faster than the Ba-doped samples, although still slower than pure CaMnO\textsubscript{3}. Doping up to 0.25 Sr does not significantly affect the total oxygen released. Initial temperature for oxygen release; on the other hand, is lowered. For instance, Ca\textsubscript{0.75}Sr\textsubscript{0.25}MnO\textsubscript{3} exhibits significant weight loss in two distinct temperature regions, i.e. 300 – 450 °C and > 600 °C. The low temperature oxygen release could be associated with chemisorbed oxygen in the lattice structure. Figure 5 summarizes the total oxygen release and initial decomposition temperature for several representative perovskite samples.

![Graph showing total oxygen release and initial decomposition temperature comparison between CaMnO\textsubscript{3} and Sr- and Ba-doped synthesized oxygen carriers. Sample weight: 20 mg; Gas flow rate: 100mL/min. He (5.0 Grade).](image)

**Characterizations of A-site dopants**

Effectiveness of dopant addition largely relies on the compatibility of the dopant and its parent structure. Ideally, dopant should be fully incorporated into the host structure to form a homogeneous solid state solution. Figure 6 illustrates the XRD patterns for the oxygen carriers for Ba and Sr doped CaMnO\textsubscript{3} at a range of x=0 to x=1. As can be seen, Ba cannot be fully incorporated into the CaMnO\textsubscript{3} structure in most cases. Even at small dopant levels (x<0.1), a secondary hexagonal BaMnO\textsubscript{3} phase can be identified. When doped further, ternary phases, such as Mn oxides, are observed until A-site is fully occupied by Ba. Sr-doped CaMnO\textsubscript{3}, on the other hand, forms a relatively homogenous solid-solution. Sr doping up to x=0.25 exhibits complete incorporation of Sr into CaMnO\textsubscript{3} while shifting the structure from cubic to orthorhombic. At x=0.5, co-existence
of SrMnO$_3$ and CaMnO$_3$ structures are observed. At higher doping levels (>0.5), a single orthorhombic SrMnO$_3$ phase is observed.

Figure 6- XRD of various doped CaMnO$_3$ with (a) Sr doping and (b) Ba doping. Phases: (●) SrMnO$_3$, (x) CaMnO$_3$, (▲) BaMnO$_3$, and (★) Mn$_3$O$_4$.

The primary motivation for dopant addition is to stabilize the CaMnO$_3$ structure and prevent the formation of stable spinel phases at high temperatures. Figure 7 investigates the in-situ XRD of the Sr- and Ba-doped CaMnO$_3$. For the Sr-doped sample, the structure of the perovskite phase is maintained even at a high temperature of 1,200 °C. To compare, CaMnO$_3$ is decomposed at 1,000 °C. Significant shift of 2θ angles, which are indicative of oxygen release, begins at approximately 600°C. This is consistent with TPD observations. Ca$_{1-x}$Ba$_x$MnO$_3$ sample with a low dopant level (x=0.05) was chosen for in-situ XRD due to the difficulty to incorporate Ba into the CaMnO$_3$ host structure. As shown in Figure 7, the Ba-doped sample, similar to CaMnO$_3$, exhibited phase decomposition at 1,000°C. It is therefore concluded that Sr is likely to be a more suitable dopant for CaMnO$_3$, since it readily incorporates into the host structure and helps to enhance the stability of the perovskite phase. Ba-doped samples, on the other hand, do not exhibit the desired CLOU properties. This may have resulted from the significant differences in ionic sizes between Ba$^{2+}$ and Ca$^{2+}$, which can lead to large lattice distortions and stresses.
Figure 7- *In-situ* XRD of the (a) Ca$_{0.75}$Sr$_{0.25}$MnO$_3$ and (b) Ca$_{0.95}$Ba$_{0.05}$MnO$_3$ in argon at a ramping rate of 5°C/min to 1,200°C. Gas flow rate: 50mL/min Ar (Grade 5.0).

**Redox testing**

CLOU performance of an oxygen carrier can be characterized by its oxygen donation properties under cyclic redox conditions. In order to determine the oxygen donation properties of the reference (CaMnO$_3$) and Sr doped (Ca$_{0.75}$Sr$_{0.25}$MnO$_3$) oxygen carrier samples, short-term isothermal redox experiments are carried out at 650°C, 750°C, 850°C, and 950°C. The results are summarized in Figure 8.

As can be seen, undoped CaMnO$_3$ does not observe any noticeable weight loss at 650°C. Once the temperature reaches 850°C, significant oxygen release is observed. When the temperature is increased even further, the oxygen carrier exhibits even higher oxygen donation.
When doping Sr and Ba into CaMnO$_3$, different phenomena are observed. When Ba is doped, there is no indication that the material is being reoxidized to any extent at any temperature using 10% O$_2$. From XRD of the reduced sample, the formation of spinel CaMn$_2$O$_4$ phase is observed. This may indicate that Ba could be distorting the structure to promote the decomposition of the cubic CaMnO$_3$ phase. *In-situ* XRD (Figure 7b) also corroborates the formation of spinel and reduced perovskite phases at a lower temperature than pure CaMnO$_3$. When Sr is doped into the CaMnO$_3$ structure, it promotes oxygen donation at a much lower temperature while still being able to reoxidize. While at 650°C, ~0.1 w.t.% oxygen release is observed. Once the material is heated to 850 and 950°C, total oxygen release becomes more significant. In pure CaMnO$_3$, near complete oxidation using 10% oxygen is achieved. However, Sr-doped CaMnO$_3$ is only able to restore roughly 99% of the initial weight. Each sample was cycled 5 times at each temperature and no change in performance was observed.

In chemical looping schemes, long term cycling is important due to the need to replenish the solid oxygen carriers over time. Figure 9 examines the Sr-doped perovskite at 850°C for 100 uncoupling cycles. Over 100 cycles, the material has no observable deactivation and is very stable throughout all 100 cycles. After 100 cycles are performed, oxygen release is still observed at lower temperatures 650°C and 750°C. The oxygen capacity and rate of oxygen release at these lower temperatures are comparable to what was observed in Figure 8. XRD analysis shows a small amount of SrMnO$_3$ appearing after the 100 cycles. However, no spinel or Ruddlesden-Popper phases were identified.

![Figure 9](image)

**Figure 9-** 100 cycles at 850°C Ca$_{0.75}$Sr$_{0.25}$MnO$_3$ oxygen carrier. Sample weight: 50mg. Gas flow rates: Reduction step: 30mL/min He (5.0 grade) and 60mL/min Ar (5.0 grade). Oxidation step: additional 10mL/min O$_2$ (Extra Dry grade) added to aforementioned inert gas.

**Coal conversion and attrition testing**

Initial coal char reactions were conducted in a TGA. Coal char was well mixed with the oxygen carrier and placed in the TGA and heated to 250°C to remove any moisture. The TGA is then heated to 950°C in helium and the reaction is allowed to proceed to completion. Figure 10 examines the results of pure CaMnO$_3$ versus a Sr-doped sample.
The Sr-doped oxygen carrier has an initial reaction temperature of approximately 100°C lower compared to the undoped CaMnO$_3$ oxygen carrier. Besides the lower reaction temperature, the Sr-doped has a higher activity in reaching full conversion of solid char. Due to the inhomogeneity of coal char-oxygen carrier mixture, the results were repeated three times with similar results.

Figure 10- Char combustion using TGA of pure and Sr-doped CaMnO$_3$. Heating in inert to 250°C for drying, then heated at a rate of 20°C/min. in helium to 950°C. Sample weight: 20mg for the oxygen carrier and 0.2mg of coal char. Gas flow rates: 100mL/min He (5.0 Grade).

Due to the improved CLOU and initial char oxidation studies, the Sr-doped samples are further tested in a laboratory sized fluidized bed. A schematic of the reactor is shown in Figure 11.

Figure 11- Fluidized bed reactor design that is used for solid fuel redox cycles in the present work.
Fluidized bed results are shown in Figure 12. Examination of the solid char cycles of the Ca$_{0.75}$Sr$_{0.25}$MnO$_3$ reveals nearly 100% conversion of the coal char in every cycle. This is confirmed through no observable CO$_2$ during the oxidation step (see Figure 13). Further comparison of the CO$_2$ to CO selectivity reveals around 90% selectivity during every cycle. The fluidized bed results confirm the viability of the Ca$_{0.75}$Sr$_{0.25}$MnO$_3$ oxygen carrier in CLOU applications.

Figure 12- Char conversion and CO$_2$ selectivity of the Ca$_{0.75}$Sr$_{0.25}$MnO$_3$ oxygen carrier in a fluidized bed reactor. Sample weight: 17 gms. Ca$_{0.75}$Sr$_{0.25}$MnO$_3$ and 10mg of char Temperature: 850°C Gas Flow Rates: nitrogen: 800mL/min (Grade 5.0) and helium (Grade 5.0): 280mL/min (Char Reduction) and oxygen (Extra dry grade): 120mL/min (during oxidation only).

Figure 13- (a) CO$_2$ and (b) CO concentration profiles during the fluidized bed experiments. Temperature: 850°C Flow rates: 1080 mL/min during char injection and 1200mL/min during oxidation (10% O2 balanced with inert).
After fluidized bed testing, attrition results are calculated from horizontal zone leading out of the top of the reactor and from a filter to catch smaller particulates before the gas analyzing equipment. The Ca$_{0.75}$Sr$_{0.25}$MnO$_3$ oxygen carrier suffers from some attrition with about 5w.t.% particles in the horizontal zone after 10 cycles. These particles are larger (>90 microns). These particles are elutriated due to the design limitation of the current fluidized bed reactor which does not a adequate free board region with lower superficial gas velocity. The amount of fine particulates (<45 microns) captured on the filter is determined to be small, which amounts to about 1w.t.% of particles. Post experimental analysis also indicates small degree of agglomeration for oxygen carriers in the reactor. This could be a potential issue in long term operations for large scale CLOU reactors. It is noted that a similar issue has been observed with CaMnO$_3$. A potential solution of this issue is to add Ti or Mg in the B-site to improve structural properties of the oxygen carrier. Such a strategy will be attempted in follow up studies.

CONCLUSIONS AND RECOMMENDATIONS

The present study investigates the redox properties of A and B-site doped CaMnO$_3$ as oxygen carriers for CLOU processes. B-site dopants such as Fe, Ni, Co, V, and Al are chosen for their CLOU properties. Ni, Co, and V dopants showed the highest oxygen uncoupling capacity. However, each of these dopants showed noticeable decrease in oxygen uncoupling capacity. Fe doped CaMnO$_3$ exhibited the most stability of the B-site dopants with 20% less oxygen uncoupling capacity compared to Ni, Co, and V doped samples. Phase analysis of the perovskites showed singular phases, but due to the limited database exact compositions were difficult to determine. Some of the B-site dopants also observed undesired secondary phases. The effects of A-site substitution are investigated in more depth. Sr and Ba dopants are used to test structural stability, oxygen carrying capacity, and oxygen donation temperature of the oxygen carriers. Ba addition to the CaMnO$_3$ structure is found to be ineffective due to the inability of Ba to incorporate into the CaMnO$_3$ structure. Sr, on the other hand, is found to form homogeneous solid solutions with the CaMnO$_3$ host structure. Sr-doped samples are also found to be effective in preventing irreversible decomposition of the parent perovskite structure to the Ruddlesden-Popper (Ca$_2$MnO$_4$) and spinel (CaMn$_2$O$_4$) phases. Excellent stability is observed for Sr doped sample (Ca$_{0.75}$Sr$_{0.25}$MnO$_3$) through various conditions including heating to 1,200°C, 100 isothermal redox cycles, and reaction with solid fuels. Besides the increased stability of the structure, Sr-doped oxygen carriers exhibit noticeable oxygen release at significantly lower temperature than that observed for pure CaMnO$_3$. Due to its various advantages compared to undoped CaMnO$_3$, Sr-doped CaMnO$_3$ oxygen carrier offers a potentially viable option for solid fuel conversion in CLC schemes.

More studies would need to be investigated for full utilization of these oxygen carriers for chemical looping conversion of coal. Further improved structural stability of the oxygen carriers through addition of materials like Ti or Mg would be suggested for use in long term applications of fluidized bed operations. Another issue for coal conversion is the effect of sulfur on the oxygen carrier. CaMnO$_3$ oxygen carriers have been shown to have negative effects when sulfur is introduced. This is due to the formation of CaSO$_4$ which is very stable even in high P$_{O2}$. The idea of A-site dopants further can help with coal conversion by providing increased resistance to sulfur contamination by reducing the
formation of CaSO₄. Economic evaluations of using perovskite oxygen carriers with CLOU capabilities over common high performing oxygen carriers like CuO would need to be investigated.

The milestones of the project related to the tasks were achieved and future work has been presented:

A. Oxygen carriers (OC) synthesized and 6 OC samples chosen- 7 dopants including both A-site (Sr and Ba) and B-site (Fe, Ni, Co, V, and Al) were chosen to dope into the CaMnO₃ structure. Sr and Ba were chosen as a focus as low oxygen uncoupling temperatures and unique redox properties were found in these materials.

B. TGA tests completed: Sr and Ba doped at various ratios were tested in TGA using 2 primary experiments (1) temperature programmable desorption (TPD) for understanding temperatures oxygen uncoupling occurred and (2) isothermal redox cycles to determine short and long term recyclability at various temperatures. Sr-doped samples were determined to be highly active at lower temperatures with longer stability and chosen for fluidized bed tests.

C. Fluidized bed tests concluded: Sr-doped CaMnO₃ were tested with bituminous coal in a fluidized bed reactor at 850°C. Results show repeatable conversion and selectivity towards CO₂ over 10 cycles.

D. Attrition resistance quantified: Sr-doped samples showed a little over 5w.t.% of attrition in particle range of >90µm and 1 w.t.% (<45µm). Slight agglomeration of the particles was observed after the reaction which could pose problems for long term applications. Recommendations for addition of Ti or Mg to the perovskite structure could improve strength of oxygen carriers.

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