Perovskite Sorbent Oxygen Separation Modeling with MFiX

2 February 2022
Disclaimer

This project was funded by the United States Department of Energy, National Energy Technology Laboratory, in part, through a site support contract. Neither the United States Government nor any agency thereof, nor any of their employees, nor the support contractor, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Cover Illustration: A three-dimensional (3D) slice of the prototype mid-scale model showing the variation of solid phase oxygen mass fraction and temperatures during absorption (within the two tubes - initially blue) and desorption (outside of the two tubes - initially red).


An electronic version of this report can be found at:
https://netl.doe.gov/energy-analysis/search
Perovskite Sorbent Oxygen Separation Modeling with MFiX

Deepthi Chandramouli\textsuperscript{1,2}, MaryAnn Clarke\textsuperscript{1,2}

\textsuperscript{1} U.S. Department of Energy, National Energy Technology Laboratory, 3610 Collins Ferry Road, Morgantown, WV 26507, USA
\textsuperscript{2} NETL Support Contractor, 3610 Collins Ferry Road, Morgantown, WV 26507, USA

DOE/NETL-2022/3727

2 February 2022

NETL Contacts:
William A. Rogers, Principal Investigator
Jonathan Lekse, Technical Portfolio Lead
Bryan Morreale, Executive Director, Research & Innovation Center
This page intentionally left blank.
# Table of Contents

EXECUTIVE SUMMARY ........................................................................................................ 1

1. INTRODUCTION ........................................................................................................... 2

2. DERIVING KINETIC RATES ......................................................................................... 4
   2.1 TGA DATA ............................................................................................................... 4
   2.2 METHODS OF HE .................................................................................................... 4
   2.3 METHODS OF BULFIN .......................................................................................... 8

3. CFD RESULTS ................................................................................................................ 15
   3.1 MATERIAL PROPERTIES ......................................................................................... 15
   3.2 CFD SET-UP USING THE METHODS OF HE ......................................................... 15
   3.3 CFD SET-UP USING THE METHODS OF BULFIN .............................................. 19

4. CONCLUSIONS AND FUTURE WORK ......................................................................... 26

5. REFERENCES .................................................................................................................. 27
This page intentionally left blank.
List of Figures

Figure 1: Idealized perovskite body centered cubic lattice for ABX₃
Figure 2: O₂ release rates over temperature as a function of x in Sr₁ₓCaₓFeO₃
Figure 3: TGA data as a function of x and temperature for Sr₁ₓCaₓFeO₃₅
Figure 4: (Left): Oxygen absorption kinetic curve for Ba₁₋ₓSrₓCo₀.₈Fe₀.₂O₅₋₅ at various x values, 500°C in mmol/g; (Right): Typical oxygen absorption kinetic curve for Sr₁₋ₓFeO₃ at x = 0.30, 450°C in kgO₂/kgperov
Figure 5: Mole fractions of oxygen in the effluent gas measured during TGA experiment for Ba₁₋ₓSrₓCo₀.₈Fe₀.₂O₅₋₅ at various x values, 500°C
Figure 6: Data from Figure 4 recast to a form similar to Equation 4 in order to capture 2nd order kinetic rate constants: (Left): Ba₁₋ₓSrₓCo₀.₈Fe₀.₂O₅₋₅ at various x values, 500°C in min⁻¹ gperov/mmolO₂; (Right): Typical oxygen absorption linear force model kinetic curve for Sr₁₋ₓFeO₃ at x = 0.30, 450°C in s⁻¹ kgperov/kgO₂
Figure 7: Initial slope (dm/dt; t=0) plotted against oxygen concentration at 523 K (n = 0.71) and 573 K (n = 0.68)
Figure 8: Plots of (dX/dt) vs. (1−X) with log-log scale showing fitting of m at different temperatures
Figure 9: (a) Conversion extent versus time at temperatures between 453–553 K in 10 K increments; (b) Capturing the value for activation energy and rate constant using lines of constant conversion extent
Figure 10: Relative non-stoichiometry, Δδ(t), is plotted against oxygen partial pressure for a range of temperatures (623 K–803 K)
Figure 11: Basic CFD set-up for small-scale PSA simulations
Figure 12: (Left) Matching experimental isothermal (723 K) absorption curve with no heat of reaction for Sr₀.₇₅Ca₀.₂₅FeO₃₋₅ using MFiX-DEM and MFiX-TFM; (Right) Matching experimental isothermal (723 K) desorption curve for Sr₀.₇₅Ca₀.₂₅FeO₃₋₅ using MFiX-DEM and MFiX-TFM
Figure 13: Gas enters from top and moves downward. (Left) Solid phase oxygen composition, (Right) Gas phase oxygen composition: Stages of visualization: (a) time = 0 s, Absorption swing begins (no O₂ in solid phase or gas phase); (b) time = 30 s, O₂ appears in both solid and gas phases; (c) time = 390 s, perovskite has absorbed as much O₂ as it can; (d) time = 400 s, desorption swing begins; (e) time = 430 s, O₂ has been released from solid phase; (f) t = 600 s, desorption complete
Figure 14: Gas enters from top and moves downward. (Left) Solid phase temperature (K), (Right) Gas phase temperature (K); Stages of visualization: (a) time = 0 s, Absorption swing begins (no O₂ in solid phase or gas phase); (b) time = 30 s, O₂ appears in both solid and gas phases; (c) time = 390 s, perovskite has absorbed as much O₂ as it can; (d) time = 400 s, desorption swing begins; (e) time = 430 s, O₂ has been released from solid phase; (f) t = 600 s, desorption complete
Figure 15: Oxygen content for SrFeO₃₋₅ and Sr₀.₇₅Ca₀.₂₅FeO₃₋₅ samples at 550°C as a function of ambient oxygen concentration
Figure 18: (Left) Matching experimental isothermal (723 K) absorption curve with no heat of reaction for Sr₀.₇₅Ca₀.₂₅FeO₃₋₅ using unit-test MFiX-TFM; (Right) Matching experimental isothermal (723 K) desorption curve for Sr₀.₇₅Ca₀.₂₅FeO₃₋₅ using unit-test MFiX-TFM
List of Figures (cont.)

Figure 19: Visualization of mid-scale MFiX-TFM perovskite PSA unit geometry with square tubes. ...........................................................................................................................................................................21
Figure 20: Visualization of mid-scale MFiX-TFM perovskite PSA unit with square tubes in counterflow: (Top Row) O₂ in solids fraction; (Bottom Row) solids temperature in unit ...22
Figure 21: Visualization of mid-scale MFiX-TFM perovskite PSA unit with square tubes in counterflow: (Top Row) O₂ in solids fraction; (Bottom Row) solids temperature in unit ...22
Figure 22: Visualization of mid-scale MFiX-TFM perovskite PSA unit in counterflow (Top Row) solids temperature in unit; (Bottom Row) O₂ in solids fraction square tubes only; ...23
Figure 23: Visualization of mid-scale MFiX-TFM perovskite PSA unit geometry with stair-stepped tubes. ...........................................................................................................................................................................24

List of Tables

Table 1: Kinetic Constants and Model Input Derived using the Methods of He for NETL Perovskite at Isothermal Temperatures ....................................................................................................................... 7
Table 2: Kinetic Constants Derived from the Methods of Bulfin for SrFeO₃₋δ ...................... 14
### Acronyms, Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>BCC</td>
<td>Body-centered cubic crystal</td>
</tr>
<tr>
<td>CFD</td>
<td>Computational Fluid Dynamics</td>
</tr>
<tr>
<td>DEM</td>
<td>Discrete Element Method</td>
</tr>
<tr>
<td>DOE</td>
<td>Department of Energy</td>
</tr>
<tr>
<td>MFiX</td>
<td>Multiphase Flow with interphase eXchanges</td>
</tr>
<tr>
<td>NETL</td>
<td>National Energy Technology Laboratory</td>
</tr>
<tr>
<td>TFM</td>
<td>Two Fluid Method</td>
</tr>
<tr>
<td>TGA</td>
<td>ThermoGravimetric Analysis</td>
</tr>
<tr>
<td>( \delta )</td>
<td>Non-stoichiometry co-efficient</td>
</tr>
<tr>
<td>( Sr_{1-x}Ca_xFeO_{3-\delta} )</td>
<td>Strontium Calcium Ferrous Oxide with variable ( x ) ((0 &lt; x \leq 0.3) ) and ( \delta ) (partially reduced)</td>
</tr>
<tr>
<td>( Sr_{1-x}Ca_xFeO_3 )</td>
<td>Strontium Calcium Ferrous Oxide with variable ( x ) ((0 &lt; x \leq 0.3) ) (oxygenated)</td>
</tr>
</tbody>
</table>
Acknowledgments

This work was performed in support of the U.S. Department of Energy’s (DOE) Fossil Energy Crosscutting Technology Research Program. The research was executed through the National Energy Technology Laboratory’s (NETL) Research and Innovation Center’s Advanced Reaction Systems Field Work Proposal.

The authors wish to acknowledge Mehrdad Shahnam, Ph.D. and Jeff Dietiker, Ph.D., whose programming assistance was instrumental in successful computational implementation. The authors also wish to acknowledge Sittichai Natesakhawat, Ph.D. and Eric Popczun, Ph.D., whose experimental lab work undergirded the proper formulation of the Bulfin model for NETL’s Sr$_{0.25}$Ca$_{0.75}$FeO$_3$$_{\delta}$ perovskite material.
EXECUTIVE SUMMARY

This document chronicles the development and implementation of computational kinetic rate models that capture absorption and desorption characteristics of the National Energy Technology Laboratory (NETL) developed perovskite, $\text{Sr}_{1-x}\text{Ca}_x\text{FeO}_{3-\delta}$.

Two paths to create accurate kinetic rates were followed: (1) an isothermal rate approach where thermogravimetric (TGA) data are recast as oxygen capacities through a pseudo-second order Lagergren equation (He et al., 2009); and (2) a more traditional Arrhenius approach where experimental data are fit with a power law model to derive associate activation energies (Bulfin et al., 2020a). For reference, the mathematics and associate experimental strategies that support these derivations are included in this report.

In addition, computational fluid dynamics (CFD) models were developed to utilize both kinetic rate formulations and applied to simulate oxygen uptake and release in small scale scenarios. The program Multiphase Flow with interphase eXchanges (MFiX) was used to create: (1) discrete element method (DEM) simulations of a single tube of granular perovskite experiencing isothermal $\text{O}_2$-absorption; and desorption and (2) two-fluid-model (TFM) non-isothermal simulations of perovskite $\text{O}_2$-absorption and desorption tubes that share a wall. Conjugate heat transfer between steel walled tubes and the perovskite bed were managed with user-defined functions.

As the project moves to simulating larger scale devices that will require more robust conjugate heat transfer methods, developed kinetic rates and associate methodologies have been recast for use in the ANSYS Fluent CFD program.
1. INTRODUCTION

Kinetic rate equations for chemical reactions often are published in chemical literature and used by computational modelers to advance simulations that include multiple chemical species that interact with each other to create new chemical compounds. Rates are usually published with a litany of values, including Arrhenius constants and activation energies that govern the reactions. A newer material, such as National Energy Technology Laboratory’s (NETL) perovskite, $Sr_{1-x}Ca_xFeO_3$, may not have published kinetic rates, and as such, rates must be derived from experimental data.

In addition, the kinetic rates associated with perovskite materials are somewhat unique from other kinetic rates as the process of interest (absorption and desorption of $O_2$) is not a chemical change per se, but a mechanistic structural change of the perovskite lattice that either holds or releases oxygen. Figure 1 illustrates an idealized perovskite body-centered cubic crystal (BCC) structure. Red spheres represent oxygen anions that are trapped in a BCC lattice of green (Sr or selectively, Ca) and blue (Fe) cations.

![Figure 1: Idealized perovskite body centered cubic lattice for ABX₃ (Wikipedia, 2020).](image)

When $O_2$ absorbs or desorbs, the amount is governed by a $\delta$-limit, whose value is sensitive to the local values of temperature ($T$) and partial pressure of oxygen ($p_{O_2}$) in any surrounding gas, as illustrated in Equation 1 (Popczun et al., 2019).

\[
Sr_{1-x}Ca_xFeO_3 \xrightleftharpoons{\delta(T,p_{O_2})} Sr_{1-x}Ca_xFeO_{3-\delta} + \frac{\delta}{2}O_2
\]  

(1)
NETL laboratory scientists have confirmed that the mechanism of Equation 1 is fully reversible without hysteretic effects, for values of $0 \leq x \leq 0.3$ (Popczun et al., 2019). The mechanism moving left to right is desorption of oxygen and moving right to left is absorption of oxygen. The value of $x$ does, however, influence the speed of O$_2$ release at varying temperatures. Figure 2 exhibits how O$_2$ release rate is dependent on the value of $x$ and temperature.

![Figure 2: O$_2$ release rates over temperature as a function of $x$ in Sr$_{1-x}$Ca$_x$FeO$_3$ (Popczun et al., 2019).](image)

Kinetic rate equations were created following two distinct paths. The first kinetic rate equation set was derived through isothermal methods described by He et al. (2009), whereby NETL’s thermogravimetric data for the perovskite material, Sr$_{1-x}$Ca$_x$FeO$_{3-\delta}$, were used. These rates successfully captured oxidation and reduction at constant temperatures, 450°C and 500°C, and fixed levels of O$_2$ in sweep gas.

The second kinetic rate equation set was derived through methods described by Bulfin et al. (2020). Additional physical experimentation to capture rate constants specific to Sr$_{1-x}$Ca$_x$FeO$_{3-\delta}$ are ongoing at the time of this report, but the model has been demonstrated successfully with published data for SrFeO$_{3-\delta}$. 
2. DERIVING KINETIC RATES

2.1 TGA DATA

Experimental thermogravimetric (TGA) data is used to characterize how perovskite absorbs and desorbs oxygen. Typically, a small quantity of perovskite is held at an isothermal condition while a gas stream of constant and known chemical composition is exposed to the material. As the material interacts with the gas stream, mass of the perovskite is monitored. When mass increases, the perovskite experiences O\textsubscript{2}-absorption. When mass decreases, the perovskite experiences O\textsubscript{2}-desorption. When mass plateaus, the perovskite is either saturated with as much O\textsubscript{2} as it can absorb or desaturated with as much O\textsubscript{2} as it can expend. The levels of saturation and desaturation are very dependent on temperature and O\textsubscript{2} concentration in the gas stream.

TGA data was collected for \( \text{Sr}_{1-x}\text{Ca}_x\text{FeO}_3-\delta \) at NETL laboratories and a selection of that data is given in Figure 3.

![Figure 3: TGA data as a function of \( x \) and temperature for \( \text{Sr}_{1-x}\text{Ca}_x\text{FeO}_3-\delta \) (Popczun et al., 2019).](image)

Figure 3 particularly shows data associated with 400°C, 450°C, and 500°C, the temperature range most expected for an industrial application. From these data, NETL has further concluded that \( \text{Sr}_{0.7}\text{Ca}_0.3\text{FeO}_3 \) or \( \text{Sr}_{0.75}\text{Ca}_0.25\text{FeO}_3 \) (more likely the latter) would be material candidates for industrial use based on material stability through absorption/desorption cycling and quantity of O\textsubscript{2} absorbed/desorbed in this temperature range.

Using these data, kinetic constants following the methods of He et al. (2009) and Bulfin et al. (2020a) were derived and examined within the context of computational fluid dynamics (CFD) simulations.

2.2 METHODS OF HE

A two-step approach for extracting kinetic reaction rates for perovskite from TGA data is described below. The methodology is adopted from a pressure swing adsorption process applied to a fixed bed of \( B\text{a}_{1-x}\text{Sr}_x\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3-\delta \) perovskite (He et al., 2009). In He’s example,
isothermal TGA data was collected at discrete temperature points in the range of 300–600°C, where synthesized air and pure nitrogen were used as experimental purge gases. Absorption was observed when applying synthesized air, and desorption was observed when applying nitrogen. Throughout this section, data and graphs from He et al. (2009) will be interleaved with data derived for NETL’s perovskite, $S_{r1-x}Ca_xFeO_{3-d}$.

Typically, TGA data is presented in terms of percent change in mass (or weight) from some initial condition. For perovskite, this change in mass is directly related to the absorption or desorption of oxygen. Consequently, TGA data can be recast in terms of how much oxygen exchange has occurred on a per gram sample-basis. In the context of absorption, this exchange is termed oxygen absorption capacity ($q_{abs}$).

Note that NETL data is collected in kg$O_2$/kg$_{perov}$ instead of mmol$O_2$/kg$_{perov}$ to better support unit conversion in simulation efforts. This choice does not influence the veracity of the model.

Step one of the modeling approach is to isolate the linear portion of the oxygen absorption kinetic curve as shown in Figure 4, and then fit the data to the rate coefficient (slope) $k_1$ in Equation 2.

$$q_{abs} = k_1t$$  \hspace{4cm} (2)

The approach above is justified by observing the oxygen composition in the TGA effluent gas during the TGA run. As Figure 5 shows, the linear areas of Figure 4 (Left) correspond to times when the oxygen composition in the effluent gas is at or near 0. This implies that all oxygen entering the experimental system is being absorbed by the perovskite. Graphs of oxygen composition in the effluent as a function of time specific to the NETL perovskite were not
available from NETL experiments but are assumed as the general absorption and desorption behavior of the NETL perovskite is similar to the \( Ba_{1-x}Sr_{x}Co_{0.8}Fe_{0.2}O_{3-\delta} \) perovskite from He et al. (2009).

Figure 5: Mole fractions of oxygen in the effluent gas measured during TGA experiment for \( Ba_{1-x}Sr_{x}Co_{0.8}Fe_{0.2}O_{3-\delta} \) at various \( x \) values, 500°C from He et al. (2009).

Step two of the modeling approach is to isolate the curved portion of the data in Figure 4 and to fit it to a pseudo-second order form like Equation 3.

\[
\frac{q_{abs}}{dt} = k_2 (q_{eq} - q_t)^2
\]  

(3)

Here, \( \frac{q_{abs}}{dt} \) represents the change in oxygen capacity over time, \( q_{eq} \) is the equilibrium capacity of oxygen in the perovskite matrix, and \( q_t \) is oxygen capacity at some point in time. \( k_2 \) is the 2\(^{nd}\) order rate coefficient. To make the fitting, Equation 3 is integrated with respect to \( t \) yielding Equation 4.

\[
\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq} t}
\]  

(4)

This kind of linear form is called a Lagergren equation and is sometimes referred to as a linear force model. To find the associate constants in the form, the data of Figure 4 is replotted as time versus \( \frac{t}{q_{abs}} \), as shown in Figure 6.
Figure 6: Data from Figure 4 recast to a form similar to Equation 4 in order to capture 2nd order kinetic rate constants: (Left): Ba_{1-x}Sr_{x}Co_{0.8}Fe_{0.2}O_{3-δ} at various x values, 500°C from He et al. (2009) in min-\text{g perov}/mmol_{O2}; (Right): Typical oxygen absorption linear force model kinetic curve for Sr_{1-x}Ca_{x}FeO_{3-δ} at x = 0.30, 450°C in s-kg\text{perov}/kg_{O2} (NETL data).

Note that NETL data is collected in s-kg\text{perov}/kg_{O2} instead of min-\text{g perov}/mmol_{O2} to better support unit conversion in simulation efforts. This choice does not influence the veracity of the model.

Referencing Equation 4, \( q_{eq} \) can be isolated through slope, and \( k_2 \) by extending a curve to its natural y-axis intercept. Once the modeling parameters, \( k_1 \), \( k_2 \), and \( q_{eq} \) are isolated, they can be applied back through Equations 2 and 4 to model a kinetic rate for perovskite in isothermal conditions.

### 2.2.1 NETL Perovskite Parameters Derived Using The Methods Of He

Using isothermal TGA data, kinetic parameters \( k_1 \), \( k_2 \) and \( q_{eq} \) were derived conditionally as shown in Table 1. Data was resolved in an Excel workbook, then visually manipulated to discern linear and curved portions. A best fit linear approximation approach was used to isolate \( k_1 \), \( k_2 \), and \( q_{eq} \), as described in Section 1.2.

**Table 1: Kinetic Constants and Model Input Derived using the Methods of He for NETL Perovskite at Isothermal Temperatures**

<table>
<thead>
<tr>
<th>Material and Temperature Setting</th>
<th>( k_1^{(abs)} )</th>
<th>Mass Flow Rate</th>
<th>( k_2^{(abs)} )</th>
<th>( q_{eq}^{(abs)} )</th>
<th>( k_2^{(des)} )</th>
<th>( q_{2eq}^{(des)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Sr_{0.75}Ca_{0.25}FeO_{3-δ} )</td>
<td>( \frac{kg_{O_2}}{kg_{\text{perov}} \cdot s} )</td>
<td>( \frac{kg}{s} )</td>
<td>( \frac{kg_{\text{perov}}}{kg_{O_2} \cdot s} )</td>
<td>( \frac{kg_{O_2}}{kg_{\text{perov}}} )</td>
<td>( \frac{kg_{\text{perov}}}{kg_{O_2} \cdot s} )</td>
<td>( \frac{kg_{O_2}}{kg_{\text{perov}}} )</td>
</tr>
<tr>
<td>450°C</td>
<td>0.00046690</td>
<td>0.000637</td>
<td>41.82</td>
<td>0.0240</td>
<td>0.606</td>
<td>0.00</td>
</tr>
<tr>
<td>( Sr_{0.70}Ca_{0.30}FeO_{3-δ} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>450°C</td>
<td>0.00020130</td>
<td>0.000275</td>
<td>5.97</td>
<td>0.0224</td>
<td>1.660</td>
<td>0.00</td>
</tr>
<tr>
<td>500°C</td>
<td>0.00015325</td>
<td>0.000209</td>
<td>2.97</td>
<td>0.0185</td>
<td>9.405</td>
<td>0.00</td>
</tr>
</tbody>
</table>
2.3 METHODS OF BULFIN

A multi-step method for deriving kinetic rates for perovskite from TGA data is described below. The methodology is adopted from a pressure swing adsorption process applied to a fixed bed of $SrFeO_{3-\delta}$ perovskite (Bulfin et al., 2020a). In Bulfin’s example, the extent of conversion, $X(t)$, is used to quantify the non-stoichiometry ($\delta$) of perovskite at any given time. The conversion rate, $\left(\frac{dX}{dt}\right)$, is then expressed with a temperature-dependent Arrhenius rate constant which allows the model to be used over a range of temperatures and oxygen partial pressures, with a single set of kinetic parameters.

To build the model, first assume that the extent of conversion is defined through Equation 5.

$$X(t) = \frac{\Delta\delta_0 - \Delta\delta(t)}{\Delta\delta_0 - \Delta\delta_\infty}$$

(5)

$\Delta\delta_0$ is the non-stoichiometry of the perovskite at time = 0. $\Delta\delta_\infty$ is the equilibrium value of the non-stoichiometry, based on ambient temperature and partial pressure of oxygen. $\Delta\delta(t)$ is the non-stoichiometry of the perovskite at some time = $t$.

The extent of conversion with time, $\frac{dX}{dt}$, is then cast through a dependence on temperature, $k(T)$, a function of conversion extent, $f(X)$, and local gas concentrations of oxygen, $c_{O_2}$ as given in Equation 6.

$$\frac{dX}{dt} = k(T)f(X)c_{O_2}^n$$

(6)

The value of $n$ is a constant representing the order of oxygen concentration dependence and is determined experimentally.

$k(T)$ is an Arrhenius rate constant of the form given in Equation 7.

$$k(T) = k_0 \exp\left(\frac{-E_a}{RT}\right)$$

(7)

$k_0$ is an experimentally fitted pre-exponential factor. $E_a$ is an experimentally derived apparent activation energy. $R$ is the gas constant and $T$ is temperature.
\( f(X) \) is given as a power law function as shown in Equation 8.

\[
f(X) = (1 - X)^m
\]  

(8)

\( m \) is a constant depending on the reaction mechanism.

Applying Equations 7 and 8 to Equation 6 yields a specific kinetic equation that defines the rate of conversion over time. This is shown as Equation 9.

\[
\frac{dX}{dt} = \left( \frac{dX}{dt} \right)_{t=0} (1 - X)^m = k_0 \exp \left( \frac{-E_a}{RT} \right) c_{O_2}^n (1 - X)^m
\]  

(9)

The key to using the Bulfin model successfully is defining the constant values, \( k_0, E_a, m \) and \( n \).

Using Bulfin’s data (Bulfin et al., 2020b) for \( SrFeO_{3-\delta} \), the process for finding these constants is now described.

Step one is to find \( n \). TGA data for \( SrFeO_{3-\delta} \) was taken at oxygen partial pressures of \{0.01, 0.05, 0.2, 1.0\} bar and temperatures of \{523, 573\} K. In this range, it was noticed that the change in mass, \( \left( \frac{dm}{dt} \right)_{t=0} \), was directly proportional to extent of conversion \( \left( \frac{dX}{dt} \right)_{t=0} \). Because of that, a log-log plot of \( \left( \frac{dm}{dt} \right)_{t=0} \) vs. \( c_{O_2} \) would yield \( n \) through its slope. So, a graph like Figure 7 would yield \( n \).

![Figure 7: Initial slope (dm/dt; t=0) plotted against oxygen concentration at 523 K (n = 0.71) and 573 K (n = 0.68). This is Figure 3 from Bulfin et al. (2020a).](image-url)
The effect of oxygen concentration is unique to absorption (oxidation), as desorption does not require the presence of oxygen to proceed. In the context of the Bulfin model, this is managed by assuming $n = 0$ during desorption (reduction).

Step two is to find $m$. Assuming that Equation 8 governs reaction rate, data is purposefully fitted to determine $m$. Plotting $\frac{dx}{dt}$ against $(1 - X)$ using log-log format, one chooses various $m$ to create best fit lines through the data points. Best fit can be determined through standard statistical error measures, like $R^2$. Figure 8 shows a typical $m$ fitting at different temperatures. Each temperature series results in a different $m$, but a single $m$ with error bars is used for all temperatures in the model.

![Figure 8: Plots of (dX/dt) vs. (1–X) with log-log scale showing fitting of m at different temperatures. This is Figure 5 from Bulfin et al. (2020a).](image)

Step three is to cooperatively determine $E_a$ and $k_0$. Values for activation energy are isolated by considering constant values of conversion. Imagining Equation 9 with constant $X$, $m$ and $n$, the equation is reordered like Equation 10.

$$c_{O_2}^{-n} \left( \frac{dX}{dt} \right)_{X=const} = k_0 \exp \left( \frac{-E_a}{RT} \right) (1 - X)_X^{m=const}$$  \hspace{1cm} (10)

Then, a logarithm is applied to both sides of the equation and the form is reimagined as shown in Equation 11.

$$\log \left( c_{O_2}^{-n} \left( \frac{dX}{dt} \right)_{X=const} \right) = \left( \frac{-E_a}{RT} \right) + \log (k_0 (1 - X)_X^{m=const})$$  \hspace{1cm} (11)
From this form, plotting \( c_o^{-n} \left( \frac{dx}{dt} \right)_{X=const} \) with logarithmic scale against \( \frac{10^3}{RT} \) will isolate \( -E_a \) in slope (with units kJ/mol) and \( k_0 (1 - X)^m_{X=const} \) at the intercept. Figure 9(b) illustrates this methodology. Figure 9(a) shows a companion graph of \( X = const \) at constant temperatures over time which is used to derive \( \left( \frac{dx}{dt} \right)_{X=const} \).

![Graph](image)

Figure 9: (a) Conversion extent versus time at temperatures between 453–553 K in 10 K increments; (b) Capturing the value for activation energy and rate constant using lines of constant conversion extent. This is Figure 7 from Bulfin et al. (2020a).

### 2.3.1 Bulfin-Based Rate Equations Used in MFiX Simulations

Multiphase Flow with interphase eXchanges (MFiX) requires kinetic rate equations expressed in terms of change of mass per unit time \( \left( \frac{dm}{dt} \right) \). However, the Bulfin rate equations, given in the above derivation, are expressed in terms of extent of conversion \( \left( \frac{dx}{dt} \right) \). So, for successful implementation in MFiX, a translation of form must be made.
The non-stoichiometry ($\delta$) of perovskite is calculated from mass change. Equation 12 shows this correlation.

$$\Delta \delta(t) = - \left( \frac{\Delta m(t)}{m_{\text{ref}}} \right) \left( \frac{MW_{\text{ref}}}{MW_{O_2}} \right)$$

Here, $\Delta m(t)$ is mass change over a particular time-frame, $m_{\text{ref}}$ is the mass at a reference condition which is used as the basis for recording all mass change measurements, $MW_{\text{ref}}$ is the molecular weight of perovskite at the same reference time point, and $MW_{O_2}$ is molecular weight of oxygen.

Figure 10: Relative non-stoichiometry, $\Delta \delta(t)$, is plotted against oxygen partial pressure for a range of temperatures (623 K–803 K). This is Figure 1 from Bulfin et al. (2020a).

Figure 10 reveals the complexity of the non-stoichiometry condition, as it varies with oxygen concentration in effluent gas as well as temperature. One must be careful to select the appropriate stoichiometric condition to represent an appropriate reference mass.

Substituting Equation 12 into Equation 5, conversion extent can be recast through mass as shown in Equation 13.

$$X(t) = \frac{\Delta \delta_0 - \Delta \delta(t)}{\Delta \delta_0 - \Delta \delta_\infty} = \frac{m_0 - m(t)}{m_0 - m_\infty}$$

Then, a derivative with respect to time is applied to Equation 13 to make Equation 14.
\[
\frac{dX}{dt} = \frac{-1}{m_0 - m_\infty} \frac{dm}{dt} = \frac{1}{m_\infty - m_0} \frac{dm}{dt}
\]  

(14)

Isolating \(\frac{dm}{dt}\), Equation 14 is recast to Equation 15.

\[
\frac{dm}{dt} = (m_\infty - m_0) \frac{dX}{dt}
\]

(15)

Then, \(\frac{dX}{dt}\) is replaced by its equality through Equation 9.

\[
\frac{dm}{dt} = (m_\infty - m_0)k_0\exp\left(-\frac{E_a}{RT}\right)c_{O_2}^n(1 - X)^m
\]

(16)

As already described, the values for \(k_0, E_a, m\) and \(n\) are derived from TGA data and are specific to absorption and desorption. Values for \(m_\infty\) and \(m_0\) are specific to simulation and represent mass of perovskite at its equilibrium condition and mass of perovskite in its initial condition. The infinity conditions are calculated through Equations 12 and 13 as given in Equation 17.

\[
m_\infty = m_{ref} \left[1 + \left(\delta_{ref} - \delta_\infty\right) \frac{MW_{O_2}}{MW_{ref}}\right]
\]

(17)

The reference mass is likewise found through Equations 12 and 13 as given in Equation 18.

\[
m_{ref} = \frac{m_0}{1 + \left(\delta_{ref} - \delta_0\right) \frac{MW_{O_2}}{MW_{ref}}}
\]

(18)

Recall that the non-stoichiometry (\(\delta\)) of perovskite, including values of \(\delta_\infty, \delta_{ref},\) and \(\delta_0\) are determined from TGA data collected at various temperatures and partial pressures of oxygen.
2.3.2 Reported Perovskite Parameters

Table 2 contains kinetic parameters for SrFeO$_{3-\delta}$. These were collected from Bulfin et al. (2020) and used in subsequent MFiX simulations.

Table 2: Kinetic Constants Derived from the Methods of Bulfin for SrFeO$_{3-\delta}$

<table>
<thead>
<tr>
<th>Swing Direction</th>
<th>$E_a$ ($kJ/mol$)</th>
<th>$E_a$ ($kJ/mol$)</th>
<th>$k_0$ ($\frac{1}{s\cdot m^3}$)</th>
<th>$m$ (--)</th>
<th>$m$ (--)</th>
<th>$n$ (--)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(all tests)</td>
<td>(used for modeling)</td>
<td>(all tests)</td>
<td>(used for modeling)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Absorption</td>
<td>92 ± 17</td>
<td>95.3</td>
<td>$1.652 \times 10^7$</td>
<td>3.94 ± 0.5</td>
<td>3.94</td>
<td>0.695</td>
</tr>
<tr>
<td>(Oxidation)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Desorption</td>
<td>144 ± 16</td>
<td>145.5</td>
<td>$1.270 \times 10^9$</td>
<td>2.10 ± 0.9</td>
<td>2.10</td>
<td>0.000</td>
</tr>
<tr>
<td>(Reduction)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Experiments to support the derivation of kinetic constants specific to NETL’s perovskite material, Sr$_{0.75}$Ca$_{0.25}$FeO$_{3-\delta}$, are ongoing. Initial CFD simulations shared in this report where the Bulfin model was implemented use the constants given in Table 2.
3. **CFD RESULTS**

Two general simulation campaigns are presented in this report. The first is a demonstration of the successful implementation of the He model for isothermal absorption/desorption of oxygen over perovskite. The second is a demonstration of the successful implementation of the Bulfin model for non-isothermal absorption/desorption of oxygen over perovskite.

3.1 **MATERIAL PROPERTIES**

3.1.1 **Sr\(_{1-x}\)Ca\(_x\)FeO\(_3-\delta\) and SrFeO\(_3-\delta\)**

NETL experimentalists suggested that an appropriate particle density for Sr\(_{1-x}\)Ca\(_x\)FeO\(_3-\delta\) and SrFeO\(_3-\delta\) was equal to ~5,200 kg/m\(^3\).

After further discussion with NETL experimentalists, thermal parameter values for Sr\(_{1-x}\)Ca\(_x\)FeO\(_3-\delta\) and SrFeO\(_3-\delta\) were also assumed equivalent for these CFD studies. A literature search related to SrFeO\(_3-\delta\) yielded a value for specific heat equal to 630 J/kg-K (Haavik et al., 2003). Thermal conductivity was approximated at 1.2 W/m-K (Labus and Labus, 2018).

3.2 **CFD SET-UP USING THE METHODS OF HE**

A bench scale pressure swing adsorption (PSA) device was modeled using MFiX discrete element method (MFiX-DEM) and two fluid method (MFiX-TFM). A user defined function was created and linked to MFiX solver version 20.2 to incorporate the effects of He-style oxygen absorption and desorption. This can be found at: https://mfix.netl.doe.gov/gitlab/applications/perovskite/-/tree/dc/DEM_Validate_DC

To demonstrate the He model implementation, the perovskite sorbent was simulated as a solid made of two species: (1) an inert perovskite and (2) a reactive “solid” phase O\(_2\). In reality, oxygen is part of the crystal structure of the oxygenated perovskite, but the solid labeling is necessary to track oxygen between solid and gaseous phases. For DEM simulations, 3.1 mm particles of Sr\(_{1-x}\)Ca\(_x\)FeO\(_3-\delta\) were dropped into an imagined 0.021-m diameter tube of length 0.305 m and allowed to settle into a fixed bed. For TFM simulations, the same geometry is assumed but with a prescribed solids fraction of 0.60. Initial conditions for the absorption model defined the particles as fully inert perovskite (no O\(_2\) solid-phase). Synthetic air (20% O\(_2\), 80% N\(_2\)) at constant temperature is introduced from one end of the prescribed tube, with a mass flow rate per Table 1.

Initial conditions for the desorption model defined the particles as fully oxygenated, where the solid phase oxygen species fraction was calculated from TGA data. Pure N\(_2\) at constant temperature was introduced from one end of the prescribed tube, with a mass flow rate per Table 1. In both DEM and TFM models, grid was set to 4 x 55 x 4 with size 0.00525 m x 0.00527 m x 0.00525 m. In both cases, Gidaspo drag and stiff chemistry were assumed, and MFiX’s default numeric solver settings were employed. Figure 11 shows a basic lay-out for these CFD simulations.
3.2.1  **MFiX-DEM and TFM Results**

The He model was validated against NETL’s experimental TGA data for absorption and desorption.

**3.2.1.1 Isothermal Validation Absorption/Desorption (no heat of reaction)**

These simulations assume fully isothermal conditions, with no heat of reaction. This assumption is valid as the TGA experiments are conducted in a temperature-controlled setting. It should also be noted that the He model is missing the temperature dependence of absorption and desorption rates and capacities.

Figure 12 illustrates that at constant temperature, the He model, as applied in both MFiX-DEM and MFiX-TFM simulations, does capture oxygen absorption characteristics of NETL’s perovskite well. However, the desorption of oxygen appears too quick, as compared to experiment, and this effect is consistent across both MFiX-DEM and MFiX-TFM simulations.

Two additional cases were considered for validating the MFiX implementation of the He model with the TGA data. Similar trends as in Figure 12 were observed. The results are presented in the appendix.
Figure 12: (Left) Matching experimental isothermal (723 K) absorption curve with no heat of reaction for Sr$_{0.70}$Ca$_{0.30}$FeO$_{3.6}$ using MFiX-DEM and MFiX-TFM; (Right) Matching experimental isothermal (723 K) desorption curve for Sr$_{0.70}$Ca$_{0.30}$FeO$_{3.6}$ using MFiX-DEM and MFiX-TFM.

3.2.1.2 Non-Isothermal Absorption/Desorption Validation (with heat of reaction)

NETL experimentalists reported that the absorption of oxygen is exothermic, and desorption of oxygen is endothermic for Sr$_{1-x}$Ca$_x$FeO$_{3.6}$. The experimentalists were able to measure the heats of reaction from experiments. These values were input into the model along with assumed thermophysical properties obtained from literature as discussed in Section 2.1.1.

The small-scale validation simulations shown here do not exhibit significant thermal swings (<100 K), but as the mass of the modeled perovskite system increases, expectations are that these temperature differences may become more consequential.

To begin to imagine the O$_2$-front and thermal characteristics of the small-scale computational experiment described in Section 2.2, a MFiX-DEM simulation of an absorption/desorption swing based on TGA time scales is presented in Figure 13 and Figure 14.
Figure 13: Gas enters from top and moves downward. (Left) Solid phase oxygen composition, (Right) Gas phase oxygen composition; Stages of visualization: (a) time = 0 s, Absorption swing begins (no O\textsubscript{2} in solid phase or gas phase); (b) time = 30 s, O\textsubscript{2} appears in both solid and gas phases; (c) time = 390 s, perovskite has absorbed as much O\textsubscript{2} as it can; (d) time = 400 s, desorption swing begins; (e) time = 430 s, O\textsubscript{2} has been released from solid phase; (f) t = 600 s, desorption complete.

Figure 14: Gas enters from top and moves downward. (Left) Solid phase temperature (K), (Right) Gas phase temperature (K); Stages of visualization: (a) time = 0 s, Absorption swing begins (no O\textsubscript{2} in solid phase or gas phase); (b) time = 30 s, O\textsubscript{2} appears in both solid and gas phases; (c) time = 390 s, perovskite has absorbed as much O\textsubscript{2} as it can; (d) time = 400 s, desorption swing begins; (e) time = 430 s, O\textsubscript{2} has been released from solid phase; (f) t = 600 s, desorption complete.
Figure 13 and Figure 14 demonstrate that the He model can capture absorption and desorption physics for perovskite qualitatively. However, the He model should be limited to simulations that maintain an essentially isothermal profile as it is derived for discrete temperatures and oxygen concentrations. Effectively, the He model represents a system that will absorb O\textsubscript{2} at the same rate until a maximum O\textsubscript{2} concentration is met or desorb O\textsubscript{2} until a minimum O\textsubscript{2} concentration is met without regard to local temperature or oxygen concentration profile. Figure 14, in particular, demonstrates that when thermal characteristics of perovskite are incorporated into simulations that isothermal conditions are definitely NOT maintained.

Exploratory cases were run with adjustments to the oxygen saturation capacities based on local gas phase temperatures. However, these models are still missing the changes to the rates of reactions which are also sensitive to temperature. There are no terms in the kinetic rates that incorporate a thermally dynamic system. Additionally, changes in the oxygen concentrations in the gas stream cannot be handled by the He model. Shown in Figure 15, it is known from literature (Miura et al., 2016) that varying oxygen concentrations in the gas stream impacts the absorption rate as well as saturation capacity.

![Figure 15: Oxygen content for SrFeO\textsubscript{3-δ} and Sr\textsubscript{0.75}Ca\textsubscript{0.25}FeO\textsubscript{3-δ} samples at 550°C as a function of ambient oxygen concentration; this is Figure 5 from Miura et al. (2016).](image)

For these reasons, it was necessary to implement a model that has temperature as well as oxygen concentration dependence, such as the Bulfin model.

### 3.3 CFD SET-UP USING THE METHODS OF BULFIN

A user-defined function was created and linked to MFiX solver version 20.2 to incorporate the effects of Bulfin-style oxygen absorption and desorption kinetic rates. A sister user-defined function was subsequently translated from fortran (MFiX’s native language) to C++ (Fluent’s
To demonstrate the Bulfin model implementation, the perovskite sorbent was simulated as a solid made of two species: (1) an inert perovskite and (2) a reactive “solid” phase \( \text{O}_2 \). As previously described, oxygen is part of the crystal structure of the oxygenated perovskite, but the solid labeling is necessary to track oxygen between solid and gaseous phases.

### 3.3.1 Unit-Scale Simulations

To test Bulfin kinetic rates quickly, a 3 x 3 x 3 cell block was created representing a 1 x 1 x 1 (units) cube. For TFM simulations, 3.1 mm particles of \( \text{Sr}_{1-x}\text{Ca}_x\text{FeO}_3-\delta \) are imagined in a fixed bed. The prescribed solids fraction is 0.6.

Initial conditions for the absorption model defined the particles as fully inert perovskite (no \( \text{O}_2 \) solid-phase). Pure \( \text{O}_2 \) at constant temperature (513 K) is introduced from one edge of the prescribed block, with a velocity inlet magnitude of 0.09 m/s.

Initial conditions for the desorption model defined the particles as fully oxygenated, where \( \delta \) was derived from TGA data and translated to an associate mass of oxygen that was incorporated into the user function. Pure \( \text{N}_2 \) at constant temperature (723 K) was introduced from one edge of the prescribed block, with a velocity inlet magnitude of 0.09 m/s.

### 3.3.1.1 MFiX-TFM Unit-Scale Absorption/Desorption Rates Validation

The Bulfin kinetic rates model was validated against experimental measurements (Figure 17). Recall that Table 2 in Section 1.3.2 outlines the associate kinetic rate constants.

![Figure 16: (Left) Matching experimental isothermal (723 K) absorption curve with no heat of reaction for \( \text{Sr}_{0.70}\text{Ca}_{0.30}\text{FeO}_3-\delta \) using unit-test MFiX-TFM; (Right) Matching experimental isothermal (723 K) desorption curve for \( \text{Sr}_{0.70}\text{Ca}_{0.30}\text{FeO}_3-\delta \) using unit-test MFiX-TFM.](image)
3.3.2 First Mid-Scale Simulation

Bulfin kinetic rates were applied to ~2.3 tonₘ (perovskite) PSA unit, made of a 0.55-m diameter cylinder, 1.1-m tall with 4 inscribed square cross-section tubes, each 0.22 m x 0.22 m. Grid is 60 x 50 x 60. The unusual geometry is a consequence of heat-transfer limitations within the MFiX code which requires internal surfaces to lay along grid lines. Figure 19 is a simple illustration of this unit.

![Figure 17: Visualization of mid-scale MFiX-TFM perovskite PSA unit geometry with square tubes.](image)

To incorporate heat transfer through the internal steel walls, minor modifications were made to the heat transfer routines within MFiX. Copies of the modified subroutines are included in the NETL Gitlab repository at: [https://mfix.netl.doe.gov/gitlab/applications/perovskite/](https://mfix.netl.doe.gov/gitlab/applications/perovskite/)

All walls within the simulation are no-slip. The interior walls are 0.055-m thick. Set-up is MFiX-TFM with a prescribed solids fraction of 0.63. Roughly 634 kg of sorbent fill the 4 square tubes, with 1,685 kg in the remaining annulus.

Absorption and desorption swings are set to occur in 1,200-s increments in counter-flow. Initially, unit temperature and inlet gas temperatures are set to 723 K. Air (mass flow rate = 0.10 kg/s, specified as a velocity inlet of 1 m/s) is introduced at the top (moving downward) within the square tubes representing absorption, while N₂ (mass flow rate = 0.27 kg/s, specified as a velocity inlet of 1.1 m/s) is introduced at the bottom (moving upward) in the annulus representing desorption. After 1,200 s, N₂ (mass flow rate = 0.09 kg/s, specified as a velocity inlet of 1 m/s) is introduced at the top (moving downward) within the square tubes representing desorption, while air (mass flow rate = 0.30 kg/s, specified as a velocity inlet of 1.1 m/s) is introduced at the bottom (moving upward) in the annulus representing absorption. The mass flow rates are scaled based on sorbent mass in the respective regions. This 2,400 s cycle is repeated once.
3.3.2.1 MFiX-TFM Mid-Scale Demonstration PSA Unit With Square Tubes

Figure 18: Visualization of mid-scale MFiX-TFM perovskite PSA unit with square tubes in counterflow: (Top Row) $O_2$ in solids fraction; (Bottom Row) solids temperature in unit.

Figure 19: Visualization of mid-scale MFiX-TFM perovskite PSA unit with square tubes in counterflow: (Top Row) $O_2$ in solids fraction; (Bottom Row) solids temperature in unit.
Figure 20: Visualization of mid-scale MFiX-TFM perovskite PSA unit in counterflow (Top Row) solids temperature in unit; (Bottom Row) O2 in solids fraction square tubes only.

Figure 20 through Figure 22 show a time sequence through 1,200 s absorb/desorb sweeps. The top row in each of the figures shows oxygen in solid concentration (the oxygen that is absorbed by the perovskite). Red indicates fully oxygenated (the largest amount of O2 in perovskite) and blue indicates fully deoxygenated (the least amount of O2 in perovskite). The bottom row shows how temperature swings imitate the exothermic reaction of absorption (by turning red) and the endothermic reaction of desorption (by turning blue).

This demonstration case gives a glimpse of the thermal swing in mid-scale unit (~50 K) when temperature change is incorporated into the kinetic model. This case also demonstrates that the Bulfin kinetic methodology does capture absorption/desorption phenomenon at mid-scale.

Some differences in temperatures can be observed in the second cycle (2,400 s–4,800 s). For example, the t= 600 s temperature contour is different from the t = 3,000 s (this is t = 600 s in the second cycle). The average temperatures in the core region are much less at 3,000 s than at 600 s which indicates the benefit of switching between absorption and desorption towards thermal management. The same trend can be observed in the annulus region too.

Note: Experimentalists feel this temperature swing is qualitatively too low for NETL perovskite. Most likely the low value is a consequence of the activation energy, $E_a$ of the perovskite in the model. Recall that the current set-up is for published kinetic parameters of SrFeO$_{3-\delta}$, not Sr$_{0.75}$Ca$_{0.25}$FeO$_{3-\delta}$. Experiments are underway that will allow calculation of the kinetic parameters specific to NETL perovskite.
3.3.3 Second Mid-Scale Simulation
Bulfin kinetic rates were applied to ~2.3 ton\textsubscript{m} (perovskite) PSA unit, made of a 0.55-m diameter cylinder, 1.1-m tall with 4 inscribed stair-stepped cross-section tubes, made to imitate 4 coarsely round tubes of 0.22-m diameter. Grid is 60 x 50 x 60. The unusual geometry is a consequence of heat-transfer limitations within the MF\textsc{i}X code which requires internal surfaces to lay along grid lines. Figure 23 is a simple illustration of this unit. To incorporate heat transfer through the internal steel walls, minor modifications were made to the heat transfer routines within MF\textsc{i}X. Copies of the modified subroutines are included in the NETL Gitlab repository at: https://mfix.netl.doe.gov/gitlab/applications/perovskite/-/tree/dc/MFiX\_stairstep

![Figure 21: Visualization of mid-scale MF\textsc{i}X-TFM perovskite PSA unit geometry with stair-stepped tubes.](image)

All walls within the simulation are no-slip. The interior walls are 0.055-m thick. Set-up is MF\textsc{i}X-TFM with a prescribed solids fraction of 0.63. 421 kg of sorbent fill the 4 stair-stepped tubes, with 1,960 kg in the annulus.

Absorption and desorption swings are set to occur in counter-flow. Absorption lasts for 300 s, then desorption for 100 s. Initially, unit temperature and inlet gas temperatures are set to 723 K. Air (mass flow rate = 0.09 kg/s, specified as a velocity inlet of 1 m/s) is introduced at the top (moving downward) within the stair-stepped tubes representing absorption, while N\textsubscript{2} (mass flow rate = 0.30 kg/s, specified as velocity inlet of 1.1 m/s) is introduced at the bottom (moving upward) in the annulus representing desorption. After 1,200 s, N\textsubscript{2} (mass flow rate = 0.09 kg/s, specified as a velocity inlet of 1 m/s) is introduced at the top (moving downward) within the square tubes representing desorption, while air (mass flow rate = 0.30 kg/s, specified as a velocity inlet of 1.1 m/s) is introduced at the bottom (moving upward) in the annulus representing absorption. The mass flow rates are scaled based on sorbent mass in the respective regions. This 2,400 s cycle is repeated once.
3.3.3.1 MFiX-TFM Mid-Scale Demonstration PSA Unit With Stair-Stepped Tubes

The addition of the stair-stepped geometry does not change or improve results dramatically. Thermal swing is still limited to ~50 K. Detailed results are presented in the appendix.

While there is some improvement with this new methodology, until kinetic rate constants specific to NETL’s Sr$_{0.75}$Ca$_{0.25}$FeO$_{3-\delta}$ are available, predictive capability remains limited.
4. CONCLUSIONS AND FUTURE WORK

This work demonstrates that both the He-model and Bulfin-model for kinetic rate constants can be applied successfully to simulations of O\(_2\) absorption and desorption as it relates to perovskite. By assumption, the He-model is limited to isothermal simulations for predictive work. It is also rate-limited by calculations of oxygen capacity that are embedded locally in every simulation. Even so, this report successfully demonstrated how the He-model does capture absorption and desorption of O\(_2\) at constant temperature for NETL’s Sr\(_{0.75}\)Ca\(_{0.25}\)FeO\(_3\)\(_{\delta}\) as simulations matched associate experimental TGA data well.

On the other hand, the Bulfin-model is more robust overall, allowing the examination of non-isothermal conditions at varying oxygen concentrations. Like the He-model, this report successfully demonstrated how the Bulfin-model does capture absorption and desorption of O\(_2\) at constant temperature for SrFeO\(_3\) as simulations matched associate experimental TGA data well (Bulfin et al., 2020).

Early Bulfin-model simulations were limited by a calculation of the non-stoichiometry of perovskite (how much O\(_2\) it can hold) based on initial and boundary conditions only. With these assumptions, using published physical and kinetic data for SrFeO\(_3\), (Bulfin et al., 2020a), it was shown that temperature rise associated with absorption and desorption processes was limited to around 50 K, regardless of geometry. It is expected that this value may be higher for NETL’s Sr\(_{0.75}\)Ca\(_{0.25}\)FeO\(_3\)\(_{\delta}\).

Current simulations that utilize the Bulfin-model have incorporated the non-stoichiometry of perovskite as a cellular calculation. This allows simulations to better predict absorption/desorption based on local conditions of temperature and O\(_2\)-concentration and has revealed temperature rise limits for SrFeO\(_3\) to be around 30 K.

However, square and stair-stepped tubes are unreasonable limitations to the current implementation of the Bulfin model in MFiX-TFM. Consequently, user defined functions that govern the Bulfin model have been migrated to the Ansys Fluent platform; Fluent already has a fully developed conjugate heat transfer methodology for internal surfaces. This will allow the development of more physically accurate geometry for mid-scale PSA units, and an improved simulation process for examining different absorption/desorption cycle times to evaluate O\(_2\) production flow rates. This work is already ongoing. Additionally, from a process design standpoint, optimization of geometry, cycle times and timing will be necessary. It is planned that these will be analyzed with the Fluent implementation of the model.

Likewise, the experiments necessary for the development of Bulfin-specific kinetic rate constants under varying oxygen concentrations are nearing completion. Once these data are fully in hand, the methodology of Section 1.3 will be applied, and new kinetic constants validated in a simple model will be extended to larger scale simulations. NETL lab scientists will then tackle a new series of experiments to better understand the effects of steam (and possibly CO\(_2\)) on Sr\(_{0.75}\)Ca\(_{0.25}\)FeO\(_3\)\(_{\delta}\) absorption and desorption characteristics. As these data become accessible to simulation scientists, associate kinetic constants will be calculated and incorporated into new simulations, moving the predictive capability closer to a realistic implementation of an oxygen regeneration unit based on perovskite chemistry with industrially inexpensive effluent gas (rather than pure N\(_2\)/O\(_2\)).
5. REFERENCES


APPENDIX

A.1 CFD RESULTS USING THE METHODS OF HE

These results are presented as an extension to Section 3.2.1.1. Results from a different base temperature simulation and from a different perovskite simulation are presented in Figure A1 and Figure A2. These figures illustrate that at constant temperature, the He model, as applied in both MFiX-DEM and MFiX-TFM simulations, does capture oxygen absorption characteristics of NETL's perovskite well. However, the desorption of oxygen appears too quick, as compared to experiment, and this effect is consistent across all cases.

Figure A.1: (Left) Matching experimental isothermal (773 K) absorption curve including heat of reaction for Sr_{0.70}Ca_{0.30}FeO_{3-δ} using MFiX-TFM; (Right) Matching experimental isothermal (773 K) desorption curve for Sr_{0.70}Ca_{0.30}FeO_{3-δ} using MFiX-TFM.

Figure A.2: (Left) Matching experimental isothermal (723 K) absorption curve including heat of reaction for Sr_{0.75}Ca_{0.25}FeO_{3-δ} using MFiX-TFM; (Right) Matching experimental isothermal (723 K) desorption curve for Sr_{0.75}Ca_{0.25}FeO_{3-δ} using MFiX-TFM.
A.2 CFD SET-UP USING THE METHODS OF BULFIN

Detailed results for Section 3.3.3 are presented in Figure A3 through Figure A5. The flow and composition behavior are very similar to the description from Section 3.3.2.1.

Figure A.3: Visualization of mid-scale MFiX-TFM perovskite PSA unit with stair-stepped tubes in counterflow (Top Row) O₂ in solids fraction; (Bottom Row) solids temperature in unit

Figure A.4: Visualization of mid-scale MFiX-TFM perovskite PSA unit with stair-stepped tubes in counterflow: (Top Row) O₂ in solids fraction; (Bottom Row) solids temperature in unit.
Figure A.5: Visualization of mid-scale MFiX-TFM perovskite PSA unit with stair-stepped tubes in counterflow: (Top Row) \( \text{O}_2 \) in solids fraction; (Bottom Row) solids temperature in unit.
This page intentionally left blank.