Packed Bed Reactor Design For High Temperature Thermochemical Energy Storage Using Metal Oxide Redox Reaction

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PACKED BED REACTOR DESIGN FOR HIGH TEMPERATURE THERMOCHEMICAL ENERGY STORAGE USING METAL OXIDE REDOX REACTION

by

Nasser Vahedi

A Dissertation

Presented to the Graduate and Research Committee
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PACKED BED REACTOR DESIGN FOR HIGH TEMPERATURE THERMOCHEMICAL ENERGY STORAGE USING METAL OXIDE REDOX REACTION

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NUMENCLATURE

ACRONYMS

TES     Thermal Energy Storage
TCES    Thermochemical Energy Storage
CSP     Concentrating Solar Power
REDOX   Reduction / Re-Oxidation
HTF     Heat Transfer Fluid
TGA     Thermo-Gravimetric Analysis
DSC     Differential Scanning Calorimetry
SEM     Scanning Electron Microscope
XRD     X-Ray Powder Diffraction
O&M     Operation and Maintenance
SFR     Split Flow Ratio
CLOD    Chemical Looping and Oxygen Decoupling
PV      Photovoltaics
FULL SCRIPT

$\Delta H$ Enthalpy of reaction, $J/mol$

$C_p$ Specific heat, $J/kg.K$

$E$ Activation energy, $J/mol$

$k$ Reaction rate constant, $1/Sec$

$K$ Bed permeability, m2

$M$ Molar mass, $kg/mol$

$P$ Pressure, Pa

$T$ Temperature, K

$t$ Time, sec

$h$ Overall heat transfer coefficient, $W/m^2.K$

$u$ Velocity of gaseous phase, m/s

$X$ Conversion, (-)

$R$ Rate of reaction, $kg/m^3.sec$

$Re$ Reynolds number, (-)

$ini$ Initial

$in$ Inlet

$out$ Outlet

$Q$ Heat

$L$ Latent heat

$h$ Concentration

$d$ Diameter, m

$S$ Source term

$A$ Pre-exponential constant
GREEK SYMBOLS

\( \varepsilon \) Porosity
\( \mu \) dynamic viscosity, Pa-s
\( \lambda \) Thermal conductivity, W/m.K
\( \rho \) density, kg/m³
\( \eta \) Efficiency
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ABSTRACT

Thermochemical energy storage (TCES) compared to other energy storage solution is more suitable due to possibility of storage at higher density and even higher temperatures. Thermal energy is stored/released using a reversible endothermic/exothermic reaction. For large-scale high temperature heat storage, TCES is nearly the only solution compared to the sensible or latent heat storage. However, high temperature TCES is at research stage and has not been commercialized yet. Among several potential reversible chemical reaction, metal oxide reduction/re-oxidation (redox) reaction have several advantages. They usually have high reaction temperature with high enthalpy of reaction, which make the thermochemical energy storage a better fit for large-scale applications. In metal redox reaction, air can be used as both heat transfer fluid and reactant. Using air will simplify the system considerably as the HTF storage system can be eliminated and air flow can be directly used in reactor eliminating any required intermediate heat exchangers. For new generation of large scale Concentrated Solar Power (CSP) plants, the thermochemical energy storage operating at high temperature is a tailor made for design requirements. Cobalt and manganese oxide are among the promising candidates for high temperature storage redox systems. In this study, the packed bed reactor has been selected as a storage reactor for redox system at high temperature. Cobalt oxide and Iron-doped manganese oxide are selected as redox reactant for the packed bed reactor. A mathematical model is developed including available reaction kinetics and mass, momentum and energy transport within the reaction bed and heat transfer fluid. Equations governing mass, momentum, and heat transport in the bed with the reaction kinetics are solved using finite element method. A simple packed bed reactor is selected as a base system for storage simulation study. Complete storage cycle simulation together with parametric study was implemented for two-dimensional model.
Developed model is used for application into other different design configurations. To address main drawbacks of simple packed bed reactors, a modified split flow design configuration is proposed in which the HTF flow is split into direct and indirect contact mode. Parallel flow configuration of proposed modified split flow reactor is simulated. It was shown that flow splitting will reduce pressure drop along the reaction bed considerably while increasing the storage duration. It was shown that gained energy saving for pressure reduction is totally justified compared to the reduction in overall storage performance. Split design provides more control over the bed properties variations during cyclic storage operation and also the reactor is more stable in variation of bed properties after several successive storage cycles.

Experimental analysis was conducted on pure cobalt and manganese oxides to characterize the reaction kinetics. Pure manganese oxide passing two successive reduction during storage half cycle in which only the second one is partly reversible. Thus only modified systems such as doped type of manganese oxide can be applied for TCES application. For cobalt oxide system, it was shown that even pure sample can complete storage cycle and the reaction was complete for considered heating and cooling rate. There was a shifting and transition detected at initial cycles for the discharge half-cycle. The system behaved more stable condition after passing initial cycles. Morphological analysis was conducted on the pure sample after a few initial cycles to better understanding the detected transition. It was shown using SEM results that there was considerable grain growth observed after few cycles. In order to differentiate the effect of reaction and temperature for transient condition and considerable grain growth, temperature analysis conducted via putting sample at certain temperatures below and above reaction temperature. It was shown that the grain size growth occurred mostly at 1000 C and the effect of reaction on the grain size was not strong. It was inferred that the detected transient behavior in reaction at later cycles could be due to grain size variation at high temperature.
1 INTRODUCTION

1.1 MOTIVATION

Continuous operation of new generation of high temperature air operated Concentrated Solar Power (CPS) plants required integration a sophisticated high-density thermal energy storage system operating at high temperature. Thermochemical energy storage is the only current energy storage method that can meet both requirements, and thus, has been selected for this research. Among available reversible chemical reactions, cobalt oxide and doped manganese oxide have proven unique features best fitted for storage requirement, especially possessing high-energy density and high reaction temperature. In order to apply selected reactant for large-scale operation, packed bed reactor has been selected due to its remarkable design simplicity that makes it cost-effective, and thus appealing for storage application. The motivation of this research is to focus on the design of packed bed reactor for high temperature thermochemical energy storage using Cobalt or doped Manganese oxides as storage reactant. Different packed bed reactor configurations have been proposed and their related performance is compared. Beside design configuration, more in detail study is conducted to understand the physics of the selected redox reactant to address the sintering and oxygen diffusion limitation for packed bed application.

This study plan to make the packed bed reactor configuration more efficient for small and large-scale storage applications. Proposed design configuration will serve wide range of applications of high temperature compact storage system, which can be used in CSP plants, large boilers, furnaces, and several other high temperature applications where efficient storage system is critical.
1.2 TECHNICAL BACKGROUND

Fossil fuel supply the major part of world current energy demand. Having high energy
density, ease of transportation and storage has made them widely used around the world. Beside
advantages, fossil fuel resources are exhaustible and depleting trend is even increased due to
ever-increasing world energy demand. Large volume application of fossil fuels and their products
has made several environmental crises such as greenhouse effect, global warming and climate
change. CO\textsubscript{2} emission is one of the major concern of fossil fuels as they generate CO\textsubscript{2} as
combustion by-products. NO\textsubscript{x}, SO\textsubscript{x} and Ozone are among the other pollutant by-products, which
has made fossil fuel applications to be limited and even expensive. Increasing energy demand of
the world and limited available fossil fuel resources have made application of alternative energy
resources as a must rather than an option [1,2].

Renewable energy, among one of the alternative, are gaining more attentions considering
environmental compatibilities. The main feature of them is their inexhaustible nature, which
justify any investment with no concern in resource depletion and limitation. Wind, solar, tidal,
geothermal are among the most developed commercialized renewables. Other renewable
resources are available such as bio-fuel or bio-ethanol in which an environmental friendly process
such photosynthesis is used with the aid of other renewables such as solar to generate product
for energy applications. Among all the renewable energies, solar energy has some unique traits,
which has made it more attractive, compared to other resources. Solar energy is the most
abundant renewable resources. The rate of receiving solar energy per hour to the earth is about
430 EJ which is about the total annual current energy consumption of the world [3]. Solar energy
is nearly available all over the world with varying intensity. Another unique characteristic of solar
energy is the possibility of its concentration, which is very critical for its large scale and efficient
application. Renewable energy has some major shortcomings such as intermittence and
fluctuating nature. This is very dominant for solar energy in which its intensity changes day and night, seasonal, even hourly due to cloudy condition and change of angle of radiation. In addition to non-constant availability, the finished cost of the renewable energy, especially solar energy, is high considering current technology and current price of the fossil fuels.

Solar energy application includes thermal process and electricity generation. The former focuses on solar radiation collection and transforming it into thermal energy. Collected heat can be provided at different temperature levels depending on applications. Electricity generation can be done directly using PV panels in which received solar energy is directly converted into electricity. In Concentrated Solar Power (CSP) plant, the collected solar heat is first converted into mechanical energy and then the mechanical energy is converted into electricity power generation [4].

One of the major problem with solar energy applications is the fluctuation of incident solar radiation that causes mismatch between energy supply and demand. In order to provide the chance of continuous and demand compatible solar energy using CSPs, suitable thermal energy storage is required to be integrated in the CSP plant. The energy storage system will store excess energy when it is available and release stored energy when it is needed. Thus, storage system is an integral part of CSP plant for continuous demand based operation.

CSP plants includes solar collector, receiver, and thermal energy storage and power generation system. Solar collector collects and concentrates received solar radiation that is converted into thermal energy and is transferred to the Heat Transfer Fluid (HTF) in the receiver. Collected heat is transferred with HTF to the storage system in which additional available heat is stored. Required amount of the heat for running the power cycle is supplied to the power generation system for electrical energy generation based on the required demand.
According to the type of solar energy concentration method, CSPs are classified into two major groups, point or line concentrator. At point concentrators, collected solar radiations are concentrated at a single point which then the heat is absorbed by the receiver which is mounted at concentration point. In line concentrators, the incident solar radiation is concentrated along a line in which the linear receiver is mounted.

**Figure 1: Solar collectors classification based on types of concentration**

Line concentrators usually have simpler design and are cost-effective. As the concentration is focused along a line, then the focal point movement along a focal line may not affect the collector performance and the system can operate with only single tracking. Possibility of application of single tracking control, simplify the system configuration even more. Beside above mentioned advantages, having a line concentration increases the heat losses from focal line to the ambient through radiation and convection. In addition, the length of collector focal line is limited as in the extended collectors, the concentration line works as a heat dissipation surface for losing collected heat. Another major drawback of the line concentrators is higher-pressure losses for heat transfer fluid flow through the collector header. This may become more critical for larger plants that needs more collector surface area. Considering the line concentrator limitation, they are mostly used for medium scale CSPs. Two major typed of line concentrators
are Fresnel and parabolic trough. Fresnel collectors have a simpler design and are easy to install with simple operation and control. Parabolic troughs are among the most commercialized type of solar collectors for medium scale CSP plants. The major concern for parabolic trough collector is their limited collector dimension due to structural stability especially against wind loads, which results in lower surface area per each module and thus, higher finished cost.

![Diagram of solar collector components](image1.png)  
![Photo of solar collectors](image2.png)

**Figure 2: Line concentration solar collectors a) Parabolic trough b) Fresnel**

At point concentrators, the received solar radiation is concentrated at a single point, which is the focal point of the collector or tip of the tower. Point collectors are perfect for direct use of collected heat such as heat source in a heat engine for power generation since the point concentration can provide heat at higher temperature, which is preferred for heat engines. Sterling engine is among one of the commercialized types of heat engines that can be mounted at the concentration point. Point concentration will reduce the heat loss and provide more
concentration ratio compared to the line concentration. Due to point concentration, collectors need dual tracking system that make the design and control more complex. In addition, the collector performance is highly dependent to the tracking performance as the concentration efficiency will degrade considerably even with very little focal point offset.

For dual tracking dish collector systems, the dish should be movable in two directions. Hence it requires sophisticated movable structure that limits the size of the collector, especially because of the wind loads. In this regard, the size of the dual tracking dish collector is not justified to increase more than a certain limit. For larger plants, it requires number of collectors to be installed in series that will increase the cost. Thus, dish collectors are used for medium to small
size of the CSPs. In addition, the receiver should be installed at the focal point that needs a support. Receiver and its support may prevent part of solar radiation to be received by the dish and consequently will lose part of available incident energy.

Figure 4: Aerial view of Gemasolar plant, Torresol Energy, Spain

In solar tower systems, a set of mirrors called heliostat with dual tracking control system reflects the received radiation to the tip of a solar tower. Solar receiver installed at the tower tip absorbs the concentrated radiation and transfers it to the heat transfer fluid. In this system, the collector surface, solar field, is not limited and can be larger than the other types of collectors. The solar towers are currently best option for large scale CSP plants since the collector area is not limited and also due to point concentration, higher temperature can be achieved.

Regarding the concentration point of view, dual tracking dish collector has the highest concentration. They can reach higher temperature with less energy losses since the concentration is very close to the point concentration condition. Solar towers have a lower concentration ratio and a lower efficiency of concentration at higher temperature compared to dish collectors, but their thermal performance exceeds the other types of solar collectors, especially the parabolic trough. For large-scale solar power generation, dish collectors are limited to the plant size and cannot compete with solar tower collectors. Among currently available technologies, the solar
tower is the best option for large scale CSP plants collector because of the size and high temperature of the receiver [5].

![Figure 5: Performance efficiency of solar collectors at different temperatures](image)

**Figure 5: Performance efficiency of solar collectors at different temperatures**

![Figure 6: Trend for lowering cost of unit power generated in CSPs](image)

**Figure 6: Trend for lowering cost of unit power generated in CSPs**

The collected solar radiation converts into heat at solar receiver and then it is transferred to the Heat Transfer Fluid (HTF). Various types of HTF could be used for different types of solar systems. The HTF can be classified into three main groups: liquid; gas; and moving solid particles. Molten salts, oils, liquid metals (such as sodium), water are among the common types of liquid HTFs. Air and CO$_2$ are typical gases used as HTF such as plant with supercritical CO$_2$ power cycle. As new proposed technology, falling solid particles are used as heat transfer fluid in the air receiver to absorb the heat at the receiver and moves to the storage tank for storage. Proper
selection of HTF mostly depends on the temperature range in which the HTF is chemically stable and its thermal and physical properties remains stable. Gases are more stable at higher temperatures but they have poor thermal properties. The receiver system can be designed in both direct and indirect form. In direct form, the HTF and working fluid of power cycle are the same and absorbed heat at the receiver is used directly in the power system. In indirect design, the HTF and power system working fluid have two separate cycles. HTF should exchange absorbed heat to the working fluid in a separate heat exchanger to keep the both cycles isolated.

```
Heat Transfer Fluid (HTF)

Gas
Liquid
Moving Particle (Solid)
```

*Figure 7: Types of Heat Transfer Fluids used in solar receivers*

![Diagram of Heat Transfer Fluids](image)

*Figure 8: Moving particle solar receiver CSP plant [6]*

The typical thermal power cycles, which are used in power block, are Rankine, Brayton and combined cycle. According to thermodynamics, for all the possible power cycles, the
efficiency of heat to electricity conversion will increase if the temperature of the heat source increases. Thus for solar power generation, one of the main ways of reduction of finished cost of generated solar power is to increase the temperature of the heat source. The higher temperature of collected solar heat, the higher the efficiency of the solar power cycle. Beside temperature of the solar collector, increase in the size of the plant can help for reduction of finished cost of generated solar power. Among different solar collectors, the solar tower system can be used for large-scale plants together with high temperature of collected solar heat. Thus, new generation of efficient large scale CSP plants are based on solar tower collectors operating at high temperature (near 1,000°C)[5]. Air is used as HTF in these types of CSPs plants since it has high stability at such high operating temperatures. Air is cheap and abundant, and the most important feature of air is no need for HTF storage, which simplifies the plant configuration.

Air operated high temperature solar towers are the leading new generation of cost effective large-scale CSP plants. For these plants, continuous operation requires the integration of proper thermal energy storage system. Such thermal energy storage system should have high-energy storage density at high storage temperature.

1.2.1 PART I - ENERGY STORAGE SYSTEM

The solar radiation is intermittent in nature. Beside the availability of solar radiation, the power demand has its own fluctuations that may not match with the solar energy availability. In order to generate and supply the power based on the demand, a storage system needs to be integrated into the CSP plant to work as an accumulator or storage.
In the power generation process, the storage can be installed before power block to store collected heat before converting into power or can be fit after the power block to store generated power. Generate power storage requires conversion of generated AC power to DC and store it in electro-chemical batteries, and when it is needed, convert DC to AC again and supply for demand. The AC to DC and reverse process will have some losses, which reduce overall storage efficiency, and the electro-chemical batteries are very expensive for large-scale applications. In addition, a loss of stored power, considering conversion efficiency, nearly equals to three times of equivalent heat energy, thus the storage efficiency in generated power storage system is very critical. Electrical batteries has a time dependent degradation resulting in energy loss, and thus, they
cannot be used for long-term energy storage. The other option is to store collected heat in the proper storage system and convert it into power when it is needed. The main concern for thermal energy storage is energy density, which is more critical for large-scale storage system. Studies show that considering current available technologies for heat and electricity storage, thermal energy storage is cheaper for large-scale with longer storage period (9hr and longer) [7]. A suitable thermal energy storage system integration is a solution for continuous demand base operation of CSP plants.

![Diagram of electrical storage batteries for storage of generated power](image)

**Figure 11: Schematic for electrical storage batteries for storage of generated power**

THERMAL ENERGY STORAGE

Thermal storage system is an integral part of CSP plants. The integration of thermal energy storage system becomes more critical when it constitutes about 20% of total plant cost. Thus, the storage density and efficiency are critical parameters for section and design of storage system, which directly affect the finished cost of the system and generated power. In addition to energy density and storage performance (charge and discharge duration and rates), the temperature range of storage system is very critical. Thermal stability, storage efficiency, system design and the finished cost of storage system are totally dependent on the storage temperature. The storage temperature is also critical for integrated power block affecting the power generation
efficiency as well. The higher the storage temperature, the higher efficiency of power generation in the power block.

Discharge temperature in thermal energy storage system is very critical since the power block operation during discharge is based on the availability of the released heat. In this regard, the storage system exergy efficiency is defined as $\eta_{ex}$ that characterizes the storage performance based on the availability of discharge energy compared to the given stored energy.

$$\eta_{ex} = \frac{\text{Released exergy at discharge}}{\text{Stored (Given) exergy at charge}} = \frac{Q_{out} (1 - \frac{T_C}{T_{\text{disch.}}})}{Q_{in} (1 - \frac{T_C}{T_{\text{ch.}}})}$$

Where $Q_{in}$ and $Q_{out}$ are heat stored during charge and recovered heat during discharge, respectively. $T_{\text{disch.}}$ is the discharge temperature, $T_{\text{ch.}}$ is the charge temperature, and $T_C$ is the heat sink temperature. Exergy efficiency depends on ratio between recovered and stored energy and the difference between discharge and charge temperature. Thus, degradation in the quantity and quality (temperature) of stored energy should be minimized for increasing storage exergy efficiency. The higher temperature discharge provides more availability for power block and electricity generation and is one the most critical design parameter for thermal energy storage systems [8].

Thermal energy storage can be classified according the storage mechanism as sensible, latent and thermochemical energy storage [9]. In sensible heat storage (SHS), the thermal energy is stored in sensible form in which the temperature of storage material is increased. In Latent Heat Storage (LHS) system, the thermal energy is stored in latent heat form during phase change process. In thermochemical energy storage, the thermal energy is stored in the form of enthalpy of reaction that is recovered using a reversible chemical reaction.
Based on the type of application and operating condition for storage systems, some of the key characteristics should be considered for storage method and storage material selection, which are listed in table below.

<table>
<thead>
<tr>
<th>STORAGE SYSTEM AND MATERIAL KEY DESIGN PARAMETERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy storage density</td>
</tr>
<tr>
<td>Cyclic and thermal/chemical stability</td>
</tr>
<tr>
<td>Operating temperatures (Charge/Discharge)</td>
</tr>
<tr>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>High storage rate (kinetics) for charge and discharge</td>
</tr>
<tr>
<td>High mechanical stability (low thermal stress, limited volume change)</td>
</tr>
<tr>
<td>Toxicity, flammability and corrosion</td>
</tr>
<tr>
<td>Cost (Capital / Operation and maintenance)</td>
</tr>
</tbody>
</table>

*Table 1: Storage system and material key design parameters*

SENSIBLE ENERGY STORAGE

In sensible energy storage, the heat is as sensible form via increasing the temperature of storage medium.

\[
Q_{Sensible} = \rho V C_p \Delta T
\]  

(2)

Where \( \rho \), \( V \) and \( C_p \) are density, volume and specific heat of the storage material and \( \Delta T \) is the temperature changes during the storage process. The sensible storage capacity depends on density and specific heat of the storage material and the range of changes of temperature during storage process. Storage materials can be solid or liquid. Liquids such as water, oils (mineral, synthetic), molten salts (nitrides and nitrates, \( NaNO_3 \) – \( KN_3 \)).
Liquid storage material have temperature limitation, which prevents them from high temperature applications. Molten salts have reasonable stability at high temperatures but they are less stable at lower temperatures. The corrosion is another main concern, especially for higher temperature applications. Using liquid metals are among the alternatives for high temperature sensible storage.

Solid storage materials usually have a higher density and higher specific heat with a better high temperature stability. Rocks, sands, concrete, refractory and ceramic are among the commons solid storage materials. The thermal stability of solid materials is much higher compared to liquid one. Application of solid storage can be in passive or active form. In passive form, they are packed to form a storage bed. In active form, heated particles are stored in hot silo while the particles are stored in the separate tank. Based on the requirement for energy release, hot particles are fed to a fluidized bed system for proper heat exchange.

![Figure 12: Two tank sensible storage configuration](image)

Another very common and cost effective active storage system is the thermocline with single tank configuration. In this system, the tank is packed with high specific heat materials and hot fluid is entered from the top and cold flow leave the tank from the bottom for both charge and discharge mode. This configuration is much cheaper as one of the storage tanks is eliminated
and it can be used for short term storage with high energy desecration that could only be justified regarding the finished cost of the system.

**Figure 13: Thermocline storage system schematic**

Sensible storage systems have simple system design with wide range of storage temperatures, which can be even applied for very high temperatures using suitable solid storage materials. However, they have a low energy density and high-energy degradation, especially at high temperatures, which their applications are not justified for large-scale high temperature CSP plants.

**LATENT HEAT ENERGY STORAGE**

In Latent Heat Storage (LHS) system, the latent heat of phase change is used for thermal storage. The main phase change process used in LHS is solid to liquid phase change or solidification / melting process. The stored energy depends on the latent heat of phase change process and the mass of storage material.

\[
Q_{\text{Latent}} = mL_f
\]  

(3)

Where, \(Q_{\text{Latent}}\) is the stored heat, \(m\) and \(L_f\) are mass of storage material and latent heat of melting/solidification respectively. Latent heat storage has higher energy density as most of the energy transferred is used for phase change at constant temperature. Thus, for specific
temperature changes, LHS can store much more energy compared to SHS due to the phase change process and its required heat absorption.

![Diagram showing latent heat storage versus sensible]

**Figure 14: Latent heat storage versus sensible**

The storage material in latent heat storage is known as Phase Change Material (PCM). There are several different PCM available for LHS application at various storage temperatures. They are classified based on types into organic and inorganic. Organic compounds usually have a lower melting temperature and are used for low and mid-temperature storage applications (< 250°C). Inorganic materials have a better storage performance operating at higher temperature. PCM usually have a low thermal conductivity. The thermal conductivity is even lower when the phase change happens and the system contains two phase or transient condition. There are several techniques such as extended surfaces have been proposed to improve heat transfer performance of LHS systems.

LHS systems have a higher energy storage density compared to sensible storage with an acceptable thermal and cyclic stability. In LHS systems, the storage/release of thermal energy could be achieved at a constant temperature. Beside unique features of LHS, low thermal conductivity, volumetric changes during storage, low rate of charge and discharge, corrosion
concern, limitation for high temperature applications are among the main drawbacks and application concerns for these type of storage systems.

THERMOCHEMICAL ENERGY STORAGE

For Thermochemical Energy Storage (TCES) systems, energy is stored as enthalpy of reaction for a reversible chemical reaction. During the forward endothermic reaction, energy is stored as an enthalpy of forward reaction and new materials are formed. The energy can be stored for a long time with less degradation of stored energy. For release of stored energy, the reverse exothermic reaction is used. During the reverse reaction, the stored energy is released and original material is reformed. In simple storage cycle, during charging step (storage), the reactant A is transformed into products B and C through forward endothermic reaction and enthalpy of reaction $\Delta H_r$ is absorbed. During the discharge process, the reactant B and C are recombined through exothermic reverse reaction and stored energy is released.

$$A + \Delta H_r \leftrightarrow B + C$$ (4)

![Figure 15: Mechanism for Thermochemical Energy Storage](image)
In TCES, the stored energy depends on mass of the reactants:

\[ Q_{TC} = m_{\text{Reactant}} \Delta H_r \]

(5)

where \( Q_{TC} \) is the stored energy of TCES, \( m_{\text{Reactant}} \) and \( \Delta H_r \) are the mass of reactant contributing in the storage and enthalpy of reaction, respectively. The formed material after forward reaction (B and C) can be stored separately for longer duration with less degradation, which provides the possibility of long-term storage. High enthalpy of reaction of typical chemical reactions provides higher energy storage density, which is one the main advantages of TCES for large volume storage applications. In addition to long term storage and higher energy storage density, the TCES systems has more thermal and cyclic stability, wide range of storage temperature at higher temperatures and nearly constant charge and discharge temperatures. Despite unique advantages of TCES compared to other storage systems, they have complicated system due to having reaction and heat transfer together.

<table>
<thead>
<tr>
<th>STORAGE DENSITY</th>
<th>SENSIBLE</th>
<th>LATENT</th>
<th>THERMOCHEMICAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>kWh/m³</td>
<td>~25</td>
<td>~100</td>
<td>~500</td>
</tr>
<tr>
<td>kWh/ton</td>
<td>10~50</td>
<td>50~150</td>
<td>120~250</td>
</tr>
</tbody>
</table>

*Table 2: Storage system performance comparison*

Based on the phase of the reactants, TCES systems can be classified into gas/gas, gas/liquid and gas/solid reactions. Gas/Gas and Gas/Solid systems are the most common reactions, which are used for storage applications. Steam/methane reforming and ammonia dissociations are among the gas/gas storage systems, which have been extensively studied. Gas/solid system is more common for storage systems such as metal hydrides, hydroxides, carbonates, oxides. Gas/solid system can be classified into open and closed systems. In closed systems, reactant in gas phase is stored for reuse for reverse reaction while in open system there is no storage required for reactant gas that simplifies the storage system considerably. The
hydrides, hydroxides and carbonate systems are among the closed system in which $H_2$, $H_2O$ and $CO_2$ should be stored in a suitable storage system for reuse in the next part of storage cycle. Metal oxide systems are the most common types of open systems in which air is used as reactant and it is not stored in a storage system for reuse. In closed system, despite complexity, the pressure and concentration of the gas reactant can be adjusted for controlling the reaction kinetics and overall storage cycle performance while in open system, the concentration is dependent to the quality of the ambient air and is not adjustable.

![TCES Reactions Diagram](image)

*Figure 16: Thermochemical Energy Storage reaction classification*

Among the available thermal energy storage systems, TCES systems have higher energy density and can operate at high temperatures (high storage temperature) with low degradation and reasonable cyclic stability. These features make thermochemical energy storage systems among the best candidates for large-scale storage applications. For proper selection of TCES system, below parameters should be considered:

- High enthalpy of reaction or storage density (Reduce the required storage volume)
- Reaction reversibility and not having the possibility for side reactions
- Less degradation both thermal and cyclic
- Fast reaction kinetics
1.2.2 PART II - THERMOCHEMICAL ENERGY STORAGE SYSTEMS

AMMONIA BASED SYSTEM

The ammonia-based storage system was proposed in the mid-1970s as one of the earliest thermochemical energy storage system [10]. This system is one of the most studied system among other thermochemical storage systems. The system uses ammonia dissociation into hydrogen and nitrogen for storage using the reaction:

$$2NH_3(g) + \Delta H_r \leftrightarrow N_2(g) + 3H_2(g)$$

(6)

$$\Delta H_r = 66.88 \frac{kJ}{mol} = 3.9 \frac{MJ}{kg} @20 \text{ MPa and 300K}$$

The endothermic dissociation reaction happen through absorption of heat at around 700°C within the endo-reactor. The formed $N_2$ and $H_2$ are stored in the storage tanks. The reverse reaction which is the ammonia synthesis happens in a separate reactor, which is called the exo-reactor in which exothermic discharge reaction happens usually at temperature ranges 350°C to 550°C. Both reactions require catalyst in the packed bed type of reactor.

*Figure 17: Schematic for Ammonia storage system [11]*
Ammonia storage system has several advantages: well-known reaction, commercialized system for ammonia synthesis applications, no side reactions, and high energy density at high temperature. Despite several advantages the system has several major drawbacks: a requirement for high pressure reactor (100~300 bar) [10], a requirement of catalysts, a toxic reactant, a considerable temperature offset between charge and discharge temperatures, hydrogen handling at high pressure, a complexity in operation, and high cost of the system. Considering above-mentioned disadvantages of ammonia dissociation system, it cannot be a good storage system for high temperature applications [12].

HYDROCARBON-BASED HEAT STORAGE

Methane reforming is another reversible reaction for thermochemical energy storage applications. Forward reaction can be done using either \( H_2O \) (steam) or \( CO_2 \) resulting in formation of \( CO \) or \( H_2 \). This reaction is well known as it is currently used for hydrogen generation.

\[
CH_4(g) + H_2O(g) + \Delta H_r \leftrightarrow 3H_2(g) + CO(g) \\
\Delta H_r = 250 \frac{kJ}{mol} \ @ \sim 1,000^\circ C
\]

\[
CH_4(g) + CO_2(g) \leftrightarrow 3H_2(g) + 2CO(g) \\
\Delta H_r = 247 \frac{kJ}{mol} \ @ \sim 1,000^\circ C
\]

Side reaction can be run in this system especially for steam used reforming in which the proportion of \( H_2 \) may be increased, which is one of the main concern for application of these systems. Handling and storage of \( H_2 \) and \( CO \), especially \( CO \) due to its toxicity, using steam or even \( CO_2 \), and the cost are among the other main drawbacks for application of this system.
SULFUR-BASED HEAT STORAGE

The sulfur-based storage system includes three steps following three processes. The overall process of the system includes Sulfuric Acid Decomposition, SO₂ disproportionation and sulfur combustion as shown below:

\[ H_2SO_4(aq) \rightarrow H_2O(g) + \frac{1}{2}O_2(g) + SO_2(g) \] (9)

\[ 2H_2O(l) + 3SO_2(g) \rightarrow H_2SO_4(aq) + S(l) \] (10)

\[ S(l) + O_2(g) \rightarrow SO_2(g) \] (11)

The first step, sulfuric acid decomposition, happens via absorbing the collected solar heat. This reaction happens in two steps in which the sulfuric acid is decomposed into SO₃ first and is transformed into SO₂ and O₂. The first step happens at about 500°C while the second step takes place between 650 and 900°C. At the sulfur formation step, the SO₂ is used to recover the sulfuric acid and sulfur is formed. The formed sulfur can be used in an incinerator or combustor for burning and releasing the stored heat. The sulfur burning can release heat at 1,200°C, which is perfect for running the power block for efficient power generation. The sulfur-base system has some unique advantages such as higher discharge temperature rather than the storage temperature, high energy density of about 9 MJ/kg. The sulfur recovery and formation process is well-known process and its technology is well-developed, which is ready to be used for industrial applications.
Having three-step process requires more equipment, which increase in capital and operational cost. Sulfur and its products are highly corrosive at high temperatures, which requires application of corrosion resistant materials at higher cost. Considering the unique advantages of sulfur system has made it as one of the best potential TCES systems but complicated process together with high capital cost requires more system improvement for its commercialization.

HYDRIDES-BASED HEAT STORAGE

Metal hydrates are another candidates for TCES application. The energy stored during forward dehydrogenation process of metal hydride (MH), which forms hydrogen and pure metal. For energy release, the backward reaction is used in which the generated hydrogen is used for formation of metal hydrides.

\[ MH(s) + \Delta H_r \leftrightarrow M(s) + \frac{1}{2} H_2(g) \]  

(12)

Metal hydrides have high energy density that is suitable for large-scale storage applications. Some of the MH systems have a high reaction temperature that is suitable for high temperature applications.
The metal hydrogenation / dehydrogenation process is well-known for hydrogen storage application. Hydrogen storage and handling still is a main concern for application of these systems. One of the limiting parameters for proper storage application is the low thermal conductivity of the formed MH that reduces the storage rate, especially during discharge. In addition, a high-pressure requirement for operation makes the storage system more expensive.

HYDROXIDE BASED HEAT STORAGE

The reversible reaction used in hydroxide based storage system is the hydration/dehydration reaction of metal hydroxide. In forward reaction during charge mode, the heat is absorbed and metal hydroxide dehydrates and forms metal oxide and water (steam). For reverse reaction during discharge mode, the steam is used for hydration of metal oxide and releasing the stored energy.

<table>
<thead>
<tr>
<th>Metal Hydrides</th>
<th>Theoretical Heat Storage Capacity (kJ/kg)</th>
<th>Operating Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNO$_2$/KNO$_3$</td>
<td>150 per 100°C</td>
<td>&gt;290</td>
</tr>
<tr>
<td>Mg$_2$NiH$_4$ $\rightarrow$ Mg$_2$Ni + 2H$_2$</td>
<td>1158</td>
<td>250–400</td>
</tr>
<tr>
<td>MgH$_2$ $\rightarrow$ Mg + H$_2$</td>
<td>2811</td>
<td>300–400</td>
</tr>
<tr>
<td>Mg$_2$FeH$_6$ $\rightarrow$ 2Mg + Fe + 3H$_2$</td>
<td>2096</td>
<td>350–550</td>
</tr>
<tr>
<td>NaMgH$_2$ $\rightarrow$ NaH + Mg + H$_2$</td>
<td>1721</td>
<td>430–585</td>
</tr>
<tr>
<td>NaMgH$_4$ $\rightarrow$ Na + Mg + 1.5H$_2$</td>
<td>2881</td>
<td>&gt;585</td>
</tr>
<tr>
<td>TiH$_4$ $\rightarrow$ Ti + 0.86H$_2$</td>
<td>2842</td>
<td>700–1000</td>
</tr>
<tr>
<td>CaH$_2$ $\rightarrow$ Ca + H$_2$</td>
<td>4934</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>LiH $\rightarrow$ Li + 0.5H$_2$</td>
<td>8397</td>
<td>&gt;850</td>
</tr>
</tbody>
</table>

Table 3: Metal hydrides storage performance [13]
\[ M(OH)_2(s) + \Delta H_r \leftrightarrow MO(s) + H_2O(g) \]  

<table>
<thead>
<tr>
<th>REACTION</th>
<th>STORAGE TEMPERATURE(°C)</th>
<th>STORAGE DENSITY (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(OH)_2(s) + \Delta H_r \leftrightarrow MgO(s) + H_2O(g)</td>
<td>350</td>
<td>1,340</td>
</tr>
<tr>
<td>Ca(OH)_2(s) + \Delta H_r \leftrightarrow CaO(s) + H_2O(g)</td>
<td>400~600</td>
<td>1,406</td>
</tr>
</tbody>
</table>

Table 4: Promising Metal Hydroxide storage characteristics

Mg hydroxide has high energy density and low cost, but the low charging temperature and difference in rate of forward and reverse reaction limit its application to low temperature storage only. Ca hydroxide has a higher reaction temperature based in the steam pressure used for hydration. The discharge temperature ranges from 400~600°C at steam pressure ranging from 0.1~5 bar. Beside high discharge temperature, it has high energy density at even lower cost compared to Mg hydroxide, which has made it among good candidates for high temperature storage applications. Beside favorable characteristics for TCES application, Ca hydroxide has low thermal conductivity and high volumetric expansion during hydration/dehydration cycle. Agglomeration and sintering is another concern for application of Ca hydroxide. Steam handling and storage is another major limiting factors for large scale applications. As the discharge pressure is dependant to the steam pressure, higher pressure system required more complicated reactor and storage system. The highest storage temperature for Ca hydroxide system is still well below the required temperature of new generation of high temperature storage systsems. Beside several significant operating concerns, due to low cost and well-known reaction, the Ca hydroxide still has a chance for commercialization for TCES application [14].
CARBONATE BASED HEAT STORAGE

Carbonation / Decarbonation is another reversible reaction which can be applied in TCES systems. During the forward endothermic reaction, the metal carbonate is decomposed and it absorbs the enthalpy of reaction. After decomposition, $CO_2$ and metal oxide are formed. The products should be stored for discharge phase in which the metal oxide is carbonated through reverse reaction consuming the generated $CO_2$ to form the metal carbonates. The Carbonation / Decarbonation is a gas-solid system that should be run in a closed cycle, as the released $CO_2$ should be stored for reuse in the reverse reaction [15].

$$MCO_3(s) + \Delta H_r \leftrightarrow MO(s) + CO_2(g)$$  \hspace{1cm} (14)

<table>
<thead>
<tr>
<th>reaction</th>
<th>storage temperature($^\circ C$)</th>
<th>storage density (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CaCO_3(s) + \Delta H_r \leftrightarrow CaO(s) + CO_2(g)$</td>
<td>850</td>
<td>1,790</td>
</tr>
<tr>
<td>$SrCO_3(s) + \Delta H_r \leftrightarrow SrO(s) + CO_2(g)$</td>
<td>1,200</td>
<td>1,585</td>
</tr>
</tbody>
</table>

**Table 5: Promising Metal Carbonates storage characteristics**

Handling $CO_2$ is one of the main drawback of these systems since the formed $CO_2$ needs compression that reduces total availability of storage system. $CO_2$ can be handled using absorbent bed rather than compression storage in which amines, metal organic frameworks and zeolite are used as absorption bed. The $CaCO_3$ system has gain more attention as it can be used together with postcombustion $CO_2$ capture system that is known as Ca-looping (CaL) cycle. The reverse carbonation reaction happens at about 850$^\circ$C, which can be also adjusted using different pressure for $CO_2$. The reaction temperature is fairly high and suitable for several CSP receivers working at high temperature. The energy density is high enough for large-scale storage applications. The $CaCO_3$ is abundant, inexpensive, non toxic, and the storage cycle can be completed without any side reactions. Beside unique features, sintering and agglomeration and less cyclic stability are
among the main concern for application of such appealing system in high temperature storage conditions.

**REDOX BASED HEAT STORAGE**

Redox based thermochemical energy storage system is based on reversible reduction / re-oxidation reaction of metal oxides. During the charging mode, the heat is absorbed via a forward reaction during which the metal oxide is reduced and oxygen is released. Released oxygen can be stored for reuse and also can be released into air since air contains enough oxygen for reverse reaction. For discharge mode, the metal is re-oxidized and it releases the stored energy reforming the metal oxide

\[
MO_x(s) + \Delta H_r \leftrightarrow MO_{x-y}(s) + \frac{y}{2}O_2(g)
\]  

(15)

![Diagram](image-url)

*Figure 19: Schematic for metal oxide packed bed storage system integration in CSP Plant*

Air is used as both heat transfer fluid (HTF) and reactant during the reverse re-oxidation process. Using air provides the possibility if running the system with open cycle mode in which there is no need for storage of air during the storage cycle. These storage systems can be easily
integrated into air operated solar receivers in which hot air can be recirculated through the solar receiver. This possibility eliminates any need for application of intermediate heat exchangers for transferring the collected heat in the receiver to the HTF for storage system that simplifies the overall system and reduce related capital and operating costs. Metal oxide redox system is gas-solid system in which air is a gas phase and metal oxide forms the porous solid reactant. Among the other important advantages of metal redox systems is the possibility of running the system even at ambient pressure. This eliminates sophisticated high temperature compression system that justifies the large-scale system application. Using open cycle of air system with gas-solid type of reactor has made the overall system design more simplified but operating at high temperatures and complexity of reaction, heat transfer, oxygen penetration and simultaneous sintering effect, have made these system more complex. There are several metal redox reactions available for high temperature TCES applications.

1.2.3 PART III - TCES USING METAL OXIDE REDOX REACTION

There are several metal oxide available. There was a screening project in which several metal oxides were reviewed as a potential for TCES applications. Some of them were removed for the first round of screening due to very low (Cr\textsubscript{5}O\textsubscript{12}, Li\textsubscript{2}O\textsubscript{2}, MgO\textsubscript{2}) or very high (V\textsubscript{2}O\textsubscript{5}) reaction temperature, toxic nature (U\textsubscript{2}O\textsubscript{3}, PbO\textsubscript{2}), and very high price (PtO\textsubscript{2}, Rh\textsubscript{2}O\textsubscript{3}). Few of them were not able to complete re-oxidation reaction, and thus, not capable of completing the storage cycle (Sb\textsubscript{2}O\textsubscript{5}, MnO\textsubscript{2}). Among the screened metal oxides, BaO\textsubscript{2}/BaO, Mn\textsubscript{2}O\textsubscript{3}/Mn\textsubscript{3}O\textsubscript{4}, Co\textsubscript{3}O\textsubscript{4}/CoO, CuO/Cu\textsubscript{2}O and Fe\textsubscript{2}O\textsubscript{3}/Fe\textsubscript{3}O\textsubscript{4} were potential candidates for TCES applications at high temperature[16]. Potential metal oxide candidates are reviewed considering the possibility of their applications for high temperature TCES systems.

BARIUM OXIDES (BaO\textsubscript{2}/BaO)
Barium-based redox TCES has the capability of application for prolong redox cycling, availability, high-energy storage density (474 kJ/kg) and reasonable working temperatures (800°C charge and 600~700°C discharge). The layering effect and cyclic stability are major impediment for TCES application. The temperature offset between charge and discharge is another concern, which reduces the performance of storage system and needs to be improved. Another concern for Barium base system is its reactivity with $H_2O$ and $CO_2$ which would influence the overall reactant stability during cyclic operation. To prevent this side reaction, air purification process should be applied to control the $H_2O$ and $CO_2$ level of the air flow that increases the operational cost.

COPPER OXIDES ($CuO/Cu_2O$)

The copper based redox reaction has high energy density (811 kJ/kg) that is perfect for TCES applications. One of the main concern is that the reaction temperature, 1,120°C, and the melting temperature of $Cu_2O$, 1,232°C, make it difficult to control and operate while preventing the reactant from melting and disintegration its porous structure. The slow rate of re-oxidation process is another limiting parameter resulting in not complete conversion.

IRON OXIDE ($Fe_2O_3/Fe_3O_4$)

The iron oxide system operates at very high temperature. For reduction of $Fe_2O_3$ to form $Fe_3O_4$, temperature close to 1,400°C must be reached that is very difficult to handle. The energy storage capacity, 600 kJ/kg, is acceptable for TCES application. Beside very high reaction temperature, the transformational stress during reduction will induce porosity and crack on the bulk of the system resulting in degradation and loss of integrity of porous bed or reactant.
COBALT OXIDE \((\text{Co}_3\text{O}_4/\text{CoO})\)

The cobalt oxide based system has high energy storage density 884 kJ/kg together with high reaction temperature. The reaction temperature is about 900°C that have made it as one the most suitable systems for high temperature applications [17–22]. The Cobalt is much more expensive compared to the other redox reaction despite its availability as 32th available element on the earth [23]. The Cobalt oxide is toxic that limits its application and handling. In cobalt base storage system, the re-oxidation process for pure cobalt oxide is slower but its kinetics is much faster compared to the other potential redox reaction during re-oxidation. Although operating at high temperature, the system maintain its integrity even after several cycles [24].

MANGANESE OXIDE \((\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4)\)

There are several oxide systems available for Manganese: \(\text{MnO}_2\), \(\text{Mn}_2\text{O}_3\), \(\text{Mn}_3\text{O}_4\) and \(\text{MnO}\). There are some other transitional oxides are available which are not stable. Considering several different oxides, various transitions can happen. At lower temperature, the \(\text{MnO}_2/\text{Mn}_2\text{O}_3\) system does not exhibit redox cycle reversibility and re-oxidation may not happen. The most suitable redox transition is \(\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4\) since it shows reversibility at high temperatures. The energy storage density is about 202 kJ/kg that is not as high as the other oxides, but is acceptable. The low price may justify its application for large-scale systems [23]. The re-oxidation reaction has considerably slow kinetics and sintering causes low cyclic stability. Another major drawback is the high thermal hysteresis offsets temperature between reduction and re-oxidation reaction and reduce storage system overall efficiency. Considering the abundant and low cost, non toxic and reasonable energy density at high temperature has made the \(\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4\) system suitable for high temperature TCES applications. There are several research conducted focusing on improvement of re-oxidation reaction kinetics and improving the cyclic stability especially using doping agents [24].
PEROVSKITES

Perovskites are mixed metal oxides in the form of \(ABO_3\) in which \(A\) is a large cation and \(B\) is a transitional metal cation of smaller size. Redox cycles of perovskites are currently the subject of investigation for several energy-related applications, such as thermochemical solar fuel production [25], membranes for \(H_2\) production or \(CO_2\) reforming [26,27], oxygen separation or as oxygen carriers for chemical looping combustion [28]. The main difference between redox cycles of perovskites and stoichiometric metal oxides is that for perovskites reduction is accompanied by the creation of a limited amount of oxygen vacancies and generally do not involve the formation of a different phase with well-defined stoichiometry. In contrast with stoichiometric oxides, perovskites do not show well-defined redox transition but, beyond a certain threshold temperature, which strongly depends on oxygen partial pressure, exhibit a continuous, quasilinear oxygen release/uptake within a very wide temperature range. This leads to a more gradual weight loss/gain during Thermo-Gravimetric experiments when compared to the sharp transitions of stoichiometric materials. During oxidation, such vacancies are re-occupied by oxygen anions through an exothermic reaction and release of heat. Thus, the main advantage of perovskites compared to stoichiometric oxides is that there is not any crystallographic transition in redox cycle resulting in higher structural stability. In addition, reduction and re-oxidation kinetics of perovskites are much faster than other stoichiometric oxides, which is due the improvement in oxygen penetration. Even though perovskites have the desirable properties for TCES applications, they require extensive processing and their application in large quantities is uncertain [29].

As a conclusion, Cobalt oxide and Manganese oxide are among the best current redox systems, which can be used for high temperature and high-density storage application. The pure
Cobalt oxide prove reasonable cyclic behavior while the Manganese oxide needs some doping for kinetic improvement and lowering the thermal hysteresis.

1.2.4 PART IV - REDOX SYSTEM REACTOR CONCEPT

The reactor configurations proposed for gas-solid reactions can be classified into three main group as fixed bed, fluidized bed and moving bed based on the reaction bed [30].

Figure 20: Gas-Solid reactors classification based on the reactor configuration

In the fixed or packed bed configuration, the solid reactant forms a porous bed in which the HTF will react while passing through the reaction bed. Due to direct contact between gas and solid phase, they usually have good thermal and reaction performance but the main concern is the considerable pressure loss for gas flow passing through the bed. Although the gas and solid phase are in direct contact during the reaction, the thermal conductivity of solid phase is one of the critical design parameters affecting the reactor performance. Solid beds with low thermal conductivity will lose part of their storage performance due to the lower kinetics due to slow heat diffusion. The possibility of sintering and grain grown directly affect the porosity and oxygen diffusion, and thus, reactor overall performance. In this regard, these type of reactors required more particle size control and also some precautions should be considered for controlling the performance degradation due to sintering and oxygen penetration. The packed bed reactors have a very simple configurations and the solid phase particles are not moving thus there is no need for solid particle handling system to be integrated into the reactor. This fixed solid phase, simplifies the design of the reactor especially at high operating temperatures. Despite operational
drawbacks, simplicity in design and operation and consequently lower cost of these types of reactors justify more improvement for application in TCES systems [31].

\[ Image \]

**Figure 21: Honeycomb coated with cobalt oxide packed bed reactor [32]**

For the fluidized bed reactor, the solid phase is not fixed and it is pushed with direct contact of HTF flow. These gas-solid reactors are used mostly for the materials with low thermal conductivity and mass diffusivity. For solid reactants having a large volume change due to reaction and temperature changes, fluidized bed reactor is a better option since the volumetric changes do not have strong influence on the reactor performance. Motion of solid reactant also reduces the chance of sintering and particle size growth as the contact time of fluidized particle is not sufficient for sintering. The sintering may happen during the material handling and storage for reuse. Fluidized bed reactors require more control on the particle size to keep them below requirement for fluidizing [33]. Since particle size is a critical item that should be controlled during operation, crushing particle could be needed to control the size of particles for storage operation. Another drawback for fluidized bed reactor is the required power for circulating HTF (air) through the reactor to fluidize the bed. The recirculation requires a considerable amount of power and also the blower system should be capable of handling HTF at very high temperatures. Solid
material handling and moving reactant between reactors or storage system is another complicated part of these types of reactors that increases the capital and maintenance cost. For high temperature systems, the heat loss for material handling could be considerable. Having moving components and fluidized bed operation has made these types of reactors more complex [34].

The third type of reactors is the moving bed reactors in which the bed is moving either with gravity or other external forces applied [35]. In gravity driven system, the solid particle fall down and the reaction happen while they are moving down within the reactor. Several type of gravity driven reactors are available such as vertical column, inclined bed, slit type and roof type [36].

![Falling particle receiver and reactor configuration](image.png)

*Figure 22: Falling particle receiver and reactor configuration* [37]
Forced moving bed reactors have forced move for the bed such as rotary kiln and screw beds. In these types of reactor, the bed moving speed can be adjusted and also can handle larger volume of reactant. One of the main concerns, specially for rotary kiln type reactor, is the mechanism for feeding and removal of reactants after reaction completion. Despite higher heat transfer between solid reactant and HTF, handling solid particles and having movable components at high temperature make the system more complex [36].
Reactors for solar applications can be classified as direct irradiated or indirect heated reactors. In direct irradiated the solar radiation is concentrated into the reactor in which the reactant directly heated with concentrated irradiation. In indirect system, the HTF such as air, absorbs the collected heat within the receiver and then transfer it to the reaction bed within the reactor.

**Figure 25: Schematic for direct irradiated reactor configuration**

**Figure 26: Schematic for indirect heated reactor configuration**
In packed bed reactor, both charge and discharge reactions happen in one reactor and there is no need for application of two separate reactors (one for charge and the other for discharge). For fluidized and moving bed, usually they use one reactor for charge and another reactor for discharge. In which the reactants are moved from one reactor to the other. Having two separate reactor make the system more complex. An additional reactor and material handling system will increase the finished cost of the system considerably.

Among proposed reactors, the packed bed type has remarkable advantages for high temperature applications: design simplicity, ease of operation, lack of moving component at such high operating temperature, single reactor for both charge and discharge, no need for reactant storage between charge and discharge mode, possibility of design at even very small scales, and modular scale up possibility. But any application of packed bed system requires resolving the issues of high pressure drop and chance of sintering of solid reactants.
1.3 LITERATURE REVIEW

Research on metal oxide redox reaction application for high temperature storage applications dated back to 1976. At that time, the oil crises forced research and development activities in renewable energy, especially for solar energy applications. Wentworth et al. proposed that the reversible chemical reactions can be applied for thermal energy storage applications [40]. Bowrey et al. conducted the experimental analysis for energy storage performance of $BaO_2/BaO$ [41]. Fahim et al. developed the kinetics for the reaction of $BaO_2/BaO$ system [42]. Chadda et al. performed experiments on $CuO/Cu_2O$ system for energy storage application [43]. For about two decades, there were a few studies focusing on this area due to the drop in oil price and lack of interest for renewable energy application and thermal energy storage systems. Recently, there is a push for application of renewable energy, the thermochemical energy storage has regained attention [44].

STATE OF THE ART ON HIGH TEMPERATURE REDOX ENERGY STORAGE

Wong et al. studied the potential metal redox reactant systems suitable for high temperature thermal energy storage application in a joint project between General Atomic and German Aerospace Center (DLR) [16]. The potential metal oxides were screened focusing on possibility in cyclic operation for thermal energy storage at high temperature. At the early stage of the research, several metal oxides were eliminated due to low or very high storage temperature, toxicity and high price for storage applications. At the next stage, the reversibility analysis were conducted on the remaining oxides and many metal oxides such as $Sb_2O_5$ and $MnO_2$ were eliminated irreversible nature of reaction. After complete screening $BaO_2/BaO$, $Mn_2O_3/Mn_3O_4$, $Co_3O_4/CoO$, $CuO/Cu_2O$ and $Fe_2O_3/Fe_3O_4$ were among the candidates of pure metal oxide that met the minimum requirements for high temperature thermal energy storage.
applications [16]. Based on this fundamental study and screening, suitable metal oxide system were studied further by different research group.

**COBALT OXIDE REDOX SYSTEM (Co$_3$O$_4$/CoO)**

Among available metal oxide redox reactions, Co$_3$O$_4$/CoO system is the most suitable system for high temperature thermal storage applications. The high energy density at high temperature and good reversibility have attracted the attention of several research groups. Despite a high price and a potential toxicity, the system is interest for the thermochemical storage since the performance is somehow unique compared to other pure metal oxides. Several initial researches were focused on characterization of the reaction by performing Thermal Gravimetric Analyses (TGA).

Theoretical enthalpy of reaction was reported to be within the range of 816~844 kJ/kg that is considerably higher compared to other pure metal redox. The high enthalpy of reaction provides high energy storage density, which is one of the critical selection parameters for large-scale thermochemical energy storage applications [16]. These reported values were theoretical and were calculated using reaction simulations, but the lower values were observed in experiments. Nieses et al. measured the energy storage density of 400 kJ/kg using a rotary kiln reactor [39]. Karagiannakis et al. obtained even different values for powder and pellet form of reactant using a tube heater. The reported energy storage density was measured 495 kJ/kg and 525 kJ/kg [45] for powder and pellet cobalt oxide, respectively. These measurements were conducted using a reactor rather than TGA analyzer and it was justified that the lower measured values are due to reactor performance and incomplete reaction. Pagkoura et al. used honeycomb type of packed bed reactor and reported the energy density estimation of 549 kJ/kg, which was greater than other measured values implying better performance of the reactor compared to the others [46].
The redox reaction of cobalt oxide system happens in the temperature ranges between 700°C to 900°C depending on the experimental set up and purge gas used. Andre et al. reported that theoretical reaction temperature for cobalt oxide system is 935°C while the experimental results in air with 20% O₂ concentration reported 790°C for the reaction temperature [47]. Niese et al. reported 800°C for a rotary kiln reactor [39]. Agrafiotis et al. reported 885 - 905°C for the forward reduction temperature [17]. Muller et al. verifies the effect of oxygen concentration on the reduction temperature using TGA [25]. They showed that in lower oxygen concentration atmosphere, the reduction occurred at a temperature range of 480 - 630°C [48].

The reversibility of cobalt oxide system redox reaction were studied in several experiments. Muroyama et al. studied cobalt oxide powder using TGA and shown that the weight variation remains stable even after 10 successive cycles [49]. Karagiannakis et al. estimated the reversibility using pellet type reaction bed and verified that no degradation after 10 cycles [45]. Pagkoura et al. verified reversibility after initial cycles for designed honeycomb structure [46]. They verified the reversibility for 30 cycles with a minor degradation. Hutchings et al. investigated pure cobalt oxide powder using TGA and found no decrease of reactivity over 100 cycles between 870 °C and 955 °C. Wong et al. conducted a 500-cycle test for a pure sample with temperature ranging from 700 °C and 900 °C to study the morphological evolution of the sample [16]. It was shown that a considerable grain growth and sintering happened when the number of cycles is increased.

Heating/cooling rate effect on storage performance were studied Agrafiotis et al. [17]. Wong et al. considered different heating rates ranging from 1°C/min to 30°C/min and showed that the lower heating/cooling rate provides more chance for re-oxidation reaction completion as the kinetics of re-oxidation is slower compared to reduction. At 30°C/min part of the re-oxidation
reaction not complete, and thus, the conversion rate was reduced due to an incomplete reverse reaction [16].

There are several reaction kinetics models proposed for the cobalt oxide redox reaction based on TGA measurement for both forward and reverse reaction. Hutchings et al. used TGA experiments to quantify thermodynamics of reaction for feasibility study using redox reaction in oxygen generations and storage applications. He proposed preliminary kinetics based on the available experimental measurements [50]. Wong et al. measured the activation energy for forward reduction reaction as 960 kJ/mol [16]. Muroyama et al. studied the redox reaction kinetics of cobalt oxide and determined apparent kinetic parameters with Arrhenius type temperature dependencies [49]. Karagiannakis et al. compared the redox reaction of dense cobalt powder and pellet form and verified faster kinetics in pellets due to higher conduction rates [45].

Utility scale application of cobalt oxide redox system were studied by Schrader et al. [49]. It was shown that the application of cobalt oxide redox system and Brayton power cycle has the potential of reaching efficiency of 44%[49].

MANGENESE OXIDE REDOX SYSTEM

Manganese has several transitional oxides formed at different temperature. Four of these transitional manganese oxides are stable, and among these $Mn_2O_3/Mn_3O_4$ has a reversible reaction at the ambient pressure.

$$MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$$

(16)

The $Mn_3O_4/MnO$ has a high reaction temperature, and thus it is not applicable for practical applications [48]. Zaki et al. were conducted TGA analysis on pure manganese oxide and proved that the $Mn_2O_3/Mn_3O_4$ is the only oxide system which can go for reversible reaction for temperature ranges between 500 °C to 1050 °C. Wong et al. conducted similar TGA analysis and
verified cyclic performance of $Mn_2O_3/Mn_3O_4$ system but for a very small mass fraction. They concluded that due to the formation of oxide layer at the outer surface of the manganese, the oxygen penetration is hindered, and thus, a fraction of reactant contributes in a cyclic operation. They concluded that the pure system cannot be applied as storage reactant and further improvement for oxygen penetration during re-oxidation reaction should be considered [16]. Karagiannakis et al. conducted similar experiment for cobalt oxide and verified that the pellet type of solid reactants has better performance and reaction kinetics compared to the powdered form [45].

The energy storage density of manganese oxide system $Mn_2O_3/Mn_3O_4$ is theoretically measured to be 202 kJ/kg. The energy density is not as high compared to that of cobalt and barium redox system. The high reaction temperature, low price, no toxicity still make the system a promising candidate for high temperature thermochemical energy storage applications.

**MIXED METAL OXIDE**

Pure metal oxides have some drawbacks for storage performance such as slow redox reaction, low cyclic stability, sintering and grain growth, and too high reaction temperature. Even for promising candidates such as Cobalt and Manganese, these drawbacks should be improved for commercialization. Slow redox reaction and sintering are the most important shortcomings of these two promising candidates, especially for Manganese system. Mixed oxides as a doping effect could alleviate these problems [16,47]. Theoretically, charge imbalance and lattice strain are formed due to the differences in the oxidation states and atomic sizes of two metal oxides. Therefore, the oxygen vacancies and interstitials can be enhanced leading to the increase of oxygen mass transfer and the enhancement of oxidation. The mixed approach may also improve reaction reversibility and enable an adjustable operating temperature. Proper selection of
secondary doping agent could enhance oxygen penetration and controlling the grain growth and sintering kinetics to improve cyclic stability of the reactants. The mixing process has strong influence on the effectiveness of doping process. The mixing processes are classified as physical and chemical based on the mixing type. The mechanical mixing is a sort of solid solution in which no solvent is used during the mixing. Typical mechanical mixings are rolling, co-firing and calcination [16]. For the chemical mixing method, material candidates are synthesized from a solution followed by heating, stirring, filtering, grounding and calcining [51].

Cobalt oxide based mixed metal oxide systems:

Carrillo et al. compared the redox behaviors of mixed manganese and cobalt oxides [52]. They studied $Co_3O_4$ system doped with $Mn_2O_3$ at about 10 mol% of manganese. The doped system showed good reversibility and fast kinetics but at narrower temperature range and considerably lower energy storage density. They proved that this doped system is not suitable since several critical storage performance parameters are adversely affected and system performance is downgraded considerably [52]. Wong et al. accidentally found that the addition of 0.5% Cr improved the oxidation rate of $Co_3O_4$ system. It was shown that after 500 redox cycles the Cr-doped samples present a greater oxidation rate compared to pure sample [16].

As another potential doping metal oxide for pure cobalt oxide system is $Fe_2O_3$. The problem with pure $Fe_2O_3$ was very high reaction temperature and material stability at high temperature preventing it from direct application for TCES systems. Block et al. studied the mixed $Co_3O_4/Fe_2O_3$ with mass ration of about 14% for $Fe_2O_3$. They found that the reversibility has been improved compared to pure cobalt oxide for a larger number of cycle. They reported that the enhanced cyclic stability is due improved microstructural stability. However, the energy storage density was reduced compared to pure oxide because of the doped $Fe_2O_3$. The optimum doping level was shown to be about 10% of $Fe_2O_3$ which yields improved reversibility with the
enthalpy of reaction about 460 kJ/kg [53]. Similar study conducted by Wong et al. documented that 23.3% ration for $Fe_2O_3$ insertion has the oxidation rate of up to 81% with reasonable energy storage density [16].

$Al_2O_3$ was proposed as another metal oxide to form a better binary system with cobalt oxide. Wong et al. studied different ratio for $Al_2O_3$ insertion. They increased the ratio and measured oxidation rate and shown that there is a peak at 5% ratio. The reversibility improvement was shown to be considerable although some drop in activation energy and energy storage density was found. They also studied the cyclic stability of the optimum sample and it was shown that the $Al_2O_3$ insertion has mitigated grain growth rate considerably [16]. The 5% ratio binary system of $Co_3O_4/Al_2O_3$ performance was verified by testing within a rotary kiln reactor [39]. It was shown that the sample retain its reversibility even after 30 cycles. They also reached much faster reaction compared to packed bed system due the improved heat transfer and oxygen diffusion within the rotary kiln reactor. Pagkoura et al. studied honey comb structure using the same binary system. They indicated that the $Al_2O_3$ insertion improves the structural stability. They verified that the doped system has a lower energy density compared to the pure system.

$CuO$ similar to cobalt oxide has high energy storage density, thus, it is a good mixing agent. Block et al. studied the mixed system with ration of 10% for $CuO$. It was shown that the structural stability and reversibility was improved. They also verified remarkable stability in the microstructure even after 40 redox cycles. It was shown that sintering was reduced and greater surface area was still available for the system [44]. The insertion ratio for $CuO$ is limited due to the possibility of melting of the oxide at high temperature resulting in a formation of new component that degrades the system performance. Pagkoura et al. tested other nonmetallic doping agents and improved storage performance but the doped system lost structural integrity after several cycles [54].
Several mixed oxide were studied for manganese based systems. Wong et al. used $Fe_2O_3$ and proved that the doping is very effective for improving the oxidation kinetics. The mixing was not only improved cyclic performance of the pure manganese oxide, but also maintained the reaction temperature at high level. Despite considerable improvement in the re-oxidation process, the kinetic is still too slow for large-scale applications [16]. Block et al. verified the effect of $Fe_2O_3$ mixing to manganese oxide system by considering a wide range of mixing [44]. Andre et al. proposed 15% mol ratio mixture while Wokon et al. suggested 25 mol% to have good reversibility after several cycles [23,55]. Carrilo et al. confirmed the improvement in re-oxidation of mixed $Mn_2O_3/Fe_2O_3$ system. They explained that the $Fe_2O_3$ insertion might reduce the bond energy between $Mn$ and oxygen that increases the mobility of oxygen through the lattice during re-oxidation [56]. The energy density of mixed $Mn_2O_3/Fe_2O_3$ system was shown to be higher compared to pure $Mn_2O_3$ system. The cyclic stability was verified for more than 75 cycles with remarkable performance and nearly no degradation [56]. The mixed system of $Mn_2O_3/Fe_2O_3$ has proven good performance and remarkable reversibility together with even higher energy storage densities compared to the pure manganese oxide. Due to availability of the components and very low price of the ingredients, this binary system has a very good potential for high energy density storage at high moderate to high temperature ranges for large-scale applications.

Pure manganese oxide redox system has two main drawbacks, the low reversibility and thermal hysteresis (temperature gap between charge and discharge). Based on previous studies, it was shown that $Fe_2O_3$ mixing can address the low reversibility. Carrilo et al. proposed $CuO$ as another co-doped agent together with $Fe_2O_3$ in order to be able to resolve the temperature gap between charge and discharge. They tested $Mn_2O_3$ mixed system consisting of 20% and 5% mole fraction $Fe_2O_3$ and $CuO$. The temperature was shown to be reduced from 225°C in pure
$Mn_2O_3$ to 81°C for co-doped mixed system considered. The addition of $CuO$ although improved the temperature gap for $Mn_2O_3$ but it affected the kinetics of both forward and reverse reaction and resulted in lowering reaction temperature for both reduction and re-oxidation processes [57].

Another potential candidates for using in mixed system of manganese oxide is $Al_2O_3$. Block et al. studied the mixed system of $Al_2O_3/Mn_2O_3$ and shown that the system energy storage density was not changed compared to the pure manganese oxide system. The re-oxidation rate was very slow making the system not applicable for cyclic storage applications. Despite effectiveness of $Al_2O_3$ in performance of cobalt oxide system, it is not effective for manganese oxide system [44].

$Li_2O$ is another oxide which has been studied as a doping agent and it was shown that the mixed system may not be effective for pure manganese oxide system performance. Varsano et al. identified the feasibility of using the synthesized $Li_2O_2$ and $MnO$ as the energy storage material. It was shown that the reaction kinetic was fast and reversibility was acceptable. It was verified that the synthetized $LiMnO_2$ has high potential for high temperature energy storage applications, but the drawback is the low energy density.

**REACTOR DESIGN**

Based on developed characterizations of metal oxide redox reactions for commercial storage applications, a proper reactor design should be applied. Several studies have been conducted on proposing suitable design configuration for high temperature storage applications [58]. One of the simplest design configuration is packed bed design mostly used for lab-scale tests due to simplicity in design. Wong et al. used a simple cycle packed bed for lab-scale study using cobalt oxide redox reaction [16]. Wokon et al. studied manganese oxide doped with iron as a reactant using a packed bed reactor. The tube heater used for heating the packed bed. The system
performance together with parametric study was reported. It was shown that no degradation occurred after 17 cycles but the sintering was observed [59]. Pagkoura et al. used pellets of pure cobalt oxide and several other mixed system based on cobalt in the packed bed to study the reactor performance. Among several proposed composite used for pellet formation, cobalt oxide – alumina and cobalt oxide – iron oxide shown better thermal and mechanical stability during a reactor operation. But the overall mechanical stability of pellet was not sufficient for long term cyclic operation [54]. They also considered honey comb structures using cobalt oxide composited and cordierites coated structures with cobalt oxide. The coated structure shown better mechanical stability for a cyclic operation [46]. Tescari et al. used cordierites coated structures with cobalt oxide to substitute a storage bed of existing sensible storage system. Proposed coated structure works as a hybrid sensible and thermochemical energy storage. It was shown that the thermal energy storage density was doubled due to the application of cobalt oxide slurry as coating [32]. Several other Moving or fluidized bed reactors were proposed. Neises et al. used a directly irradiated solar rotary kiln using mixed cobalt oxide with 5% \( Al_2 O_3 \) as reactant. The cyclic performance were studied for 30 complete redox cycles [39]. A numerical model that described the behavior of such reactor was further developed by Tescari et al. and validated with experimental results [60]. The experimental set up were used for fixed sample of reactant and the main concern was the feed and discharge of the system requiring intermittent operations for loading and unloading. Tescari et al. proposed a concept of the rotary kiln reactor in which the system can operate continuously without any interruption for loading and unloading the reactant [61]. Babiniec et al. proposed a new update based on packed bed reactor. They proposed a moving bed packed reactor in which the reactant are pushed into the packed bed and reaction bed gradually shifted to the reactor discharge [36]. They also proposed a gravity driven dilute particle flow reactor in which particles were flowing downward by gravity while air flows from the bottom
in the opposite direction. This concept was the indirect heated gravity driven moving bed reactor which was proposed for application of solid fuel preparation for Brayton cycle operation [36]. Schrader et al. proposed a moving bed concept reactor but with direct irradiation in which the redox reaction occurs on a gravity driven directly irradiated reactor. Reduction transpires within the storage reactor and the reduced solid cobalt oxide is stored in a storage tank. For discharge, a separate counter flow reactor were proposed in which the solid cobalt oxide is fed to the top of the reactor and counter air flow coming from the bottom is heated while re-oxidation process proceeds. Hot air leaves at the top of the reactor and oxidized solid reactant are collected and feed for reuse in the next cycle. This configuration of directly irradiated gravity driven reactor for storage and counter flow reactor for discharge configuration were proposed to be integrated within a Brayton cycle power block in which hot air leaving discharge reactor feeding the gas turbine directly [38]. In order to eliminate the sintering effect and improve oxygen release and especially penetration during re-oxidation reaction, fluidized bed reactor design were proposed for applications with metal redox reactants.
1.4 OUTLINE OF DISSERTATION

In this study, as a basic approach for efficient packed bed reactor using redox reactant, the mathematical model has been developed and simulations has been conducted. In chapter 2 the mathematical model and numerical method is presented. In chapter 3, developed mathematical method is used for simulation of storage cycle for simple packed bed reactor with direct contact flow. In chapter 4, the split flow reactor concept is introduced and its performance is compared with conventional direct contact flow reactor and its improvement in overall reactor performance is verified. In chapter 5, the experimental analysis of pure cobalt oxide and manganese oxide is provided. Single and multiple cycle response of the reactant is presented. Temperature effect and morphology variation study is also provided for cobalt oxide system. In chapter 6, the summary and conclusion together with proposed future studies are provided.
2 MATHEAMTICAL MODELS AND NUMERICAL METHODS

Thermochemical energy storage systems have gained attention recently for development in CSP plant and demand for high temperature and high density energy storage. The development is at an early stage and testing and research is conducted mostly at lab-scale level. Experimental research was mostly focused on material characterization for a small amount of sample. A few studies was considered a reactor scale testing. Any development on large-scale application requires a detailed mathematical model to be used for design and optimization of reactor. In this study, the mathematical model was developed for packed bed reactor using metal redox as a reactant. Developed model was used for performance analysis and optimization for proposed design configurations.

2.1 INTRODUCTION

Metal oxide redox reaction is used as reversible chemical reaction for thermochemical energy storage. Thermal energy is stored in the form of enthalpy of reaction during forward reduction reaction during which heat is absorbed and oxygen is released. The stored energy is released through the reverse re-oxidation reaction during which the stored energy is released and reduced reactant is re-oxidized. The reactor concept is a packed bed reactor using air as both reactant and heat transfer fluid. Single reactor is used for both charge and discharge modes of operation with packed bed configuration in which the solid reactants are fixed for all storage period. The redox reactant are packed inside the reactor to form a porous bed that allows air passing through with direct contact to the porous structure of the bed. During charging mode, hot air is fed to the bed to trigger the forward endothermic reduction reaction. Released oxygen is swept away by flowing air. After completion of reactor charging, the cold air is fed to the reactor heated through the release of enthalpy of reaction during discharge mode.
The thermochemical storage reactor is a complicated system in which porous flow, heat transfer and chemical reaction occur all together within reaction bed. In addition, forward and reverse reactions have different kinetics requiring a separate analysis for charge and discharge modes of operation. Complete reactor simulation is very complicated and due to lack of available details and related computational cost, several assumptions are considered.

- Solid reactant is assumed to be as a continuous medium despite its porous structure. Thus, developed model for solid phase is continuous porous model and the particle approach is not considered for solid bed analysis.

- The reactor is considered to be well insulated - heat losses from the walls are neglected.

- The effect of cyclic operation of reactor for storage performance and material properties are not considered - the operation is considered for single storage cycle.

- Bed porosity is assumed to be constant throughout the storage process - the sintering effect and its related effect on bed porosity is neglected.

- The porous bed thermal conductivity is assumed to be constant – the effect of porosity variation as a result of sintering on the thermal conductivity is not included.

- Air is used as both HTF and reactant. It is assumed that air behaves as an ideal gas at such high temperature and normal pressure.

- Radiation heat transfer between solid and gas phase is neglected due to small temperature difference.

2.2 GOVERNING EQUATION

FLUID PHASE

The mass conservation equation for gas phase flow is
\[
\frac{\partial (\varepsilon \rho_g)}{\partial t} = -\nabla (\rho_g u) - R
\]  

(17)

where \( \varepsilon \) is bed porosity, \( \rho_g \) is gas (air) density, \( u \) is air velocity, and \( R \) is rate of reaction. The rate of reaction term included as source term in gas-phase continuity equation. The oxygen is released from the solid bed during reduction and part of oxygen contents of air is consumed during re-oxidation reaction. The effect of oxygen consumption, oxygen release, and the temperature variations on air density is considered using ideal gas equation of state for gas flow. The oxygen concentration variation can be found based on gas density variation and rate of reaction as below

\[
\varepsilon \rho_g \frac{\partial (w_{O_2})}{\partial t} + \rho_g u \cdot \nabla (w_{O_2}) = -(1 - w_{O_2})R
\]

(18)

where \( w_{O_2} \) is oxygen concentration.

The momentum equation for gas phase flow through the porous bed is

\[
\frac{\rho_g}{\varepsilon} \left( \frac{\partial u}{\partial t} + (u, \nabla) \frac{u}{\varepsilon} \right) = \nabla \cdot \left( -P + \frac{\mu}{\varepsilon} (\nabla u + (\nabla u)^T) - \frac{2}{3\varepsilon} \mu (\nabla \cdot u) \right) - (\mu K^{-1})u
\]

(19)

where \( P \) is pressure, \( \mu \) is dynamic viscosity of the air, and \( K \) is bed permeability. The bed permeability is a function of bed porosity and particle size defined by

\[
K = \frac{d_p^2 \varepsilon_b^3}{180(1 - \varepsilon_b)^2}
\]

(20)

The energy equation for gas phase flow is

\[
\frac{d(\rho_g C_p T_g)}{dt} + \nabla \cdot (u \rho_g C_{pg} T_g) - \nabla \cdot (\lambda_g \nabla T_g) = S_g
\]

(21)

where \( T_g \) is gas (air) temperature, \( C_{pg} \) is specific heat, and \( \lambda_g \) is thermal conductivity of the air at \( T_g \) temperature. \( S_g \) is the source term for gas flow energy equation. The volumetric convection with solid porous structure and diffusion are included in the gas-phase energy
equation while the radiation heat transfer is neglected. The source term for gas phase heat
transfer include solid-gas volumetric heat convection.

\[ S_g = \frac{h_{sg}}{\varepsilon} (T_s - T_g) \]  \hspace{1cm} (22)

SOLID PHASE

The mass conservation for solid phase is

\[ \frac{d\rho_s}{dt} = R \]  \hspace{1cm} (23)

where \( \rho_s \) is bed density. The solid bed density variation can also be calculated indirectly from
the rate of conversion and average density of reactant before and after the conversion
(reduction/oxidation).

The energy equation for solid phase is

\[ \frac{\partial (\rho_s C_{p,s} T_s)}{\partial t} + \nabla \cdot (-\lambda_s \nabla T_s) = S_s \]  \hspace{1cm} (24)

where \( C_{p,s} \) is bed specific heat, \( T_s \) is solid bed temperature, \( \lambda_s \) is bed thermal conductivity,
\( \Delta H \) is enthalpy of reaction, and \( S_s \) is the source term for energy equation. The source term
for solid phase include the volumetric heat transfer with air together with exchanges energy
as enthalpy of reaction for conversion at both forward and reverse reaction.

\[ S_s = R \Delta H + \frac{h_{sg}}{(1 - \varepsilon)} (T_g - T_s) \]  \hspace{1cm} (25)

The energy equation for gas and solid phases is coupled by the convective heat transfer. The
radiation heat transfer is neglected for the solid-phase, and thus, the volumetric convection and
diffusion are the mode of heat transfer for the solid phase. The volumetric convection heat
transfer coefficient is calculated based on the conductive resistance of the solid particle and
convective resistance between the solid particle and air flow. The volumetric heat transfer
coefficient is proposed based on Ginielinski as below
\[ h_{sg} = \frac{6(1 - \varepsilon)}{d_p} \left( \frac{1}{h_g} + \frac{d_p}{10 \lambda_s} \right)^{-1} \]  

where \( d_p \) is solid particle diameter, and \( h_g \) is air heat transfer coefficient at that specific temperature. The volumetric heat transfer coefficient can be modified to include the radiative heat transfer at higher temperature differences.

### 2.3 REACTION KINETICS

#### 2.3.1 DEFINITIONS

According to the provided list of governing equations, the reaction rate, \( R \), is a critical parameter included in the continuity and energy equation for both gas and solid phases. Due to the existing reaction in which both mass and heat transfer occur together between two phases, the modeling is more complicated compared to conventional flow and heat transfer case [62].

For development of reaction kinetics, the weight variation measured by Thermo Gravimetric Analysis (TGA) is needed. Sudden change of weight is an indication of reaction initiation and proceeding. During the reduction (endothermic) reaction due to oxygen release, the weight drops while during re-oxidation reaction, the weight increases. There will be no weight changes after reaction is completed. Thus, the reaction temperature and rate of reaction can be estimated based on TGA experimental measurement [63]. Due to direct measurement of conversion, most of gas solid kinetics are proposed based on conversion value defined for both forward and reverse reactions.

\[ X_{\text{red}} = \frac{w_{\text{initial}} - w_t}{w_{\text{initial}} - w_{\text{final}}} \]  

where \( X_{\text{red}} \) is conversion for reduction reaction, \( w_t \) is the current weight of sample, and \( w_{\text{initial}} \) (before reduction) and \( w_{\text{final}} \) (after reduction) are initial and final weight of the sample, respectively. The reduction reaction conversion is estimated based on the ration of weight loss.
compared to the total expected weight variation. Similarly, for re-oxidation reaction, the reaction conversion can be defined as below

\[ X_{\text{oxi}} = \frac{w_t - w_{\text{initial}}}{w_{\text{final}} - w_{\text{initial}}} \]  

(28)

where \( X_{\text{oxi}} \) is conversion for reduction reaction, \( w_t \) is the current weight of sample, and \( w_{\text{initial}} \) (before oxidation) and \( w_{\text{final}} \) (after oxidation) are initial and final weight of the sample, respectively. During oxidation reaction, the reaction proceeding (weight gain ratio) is estimated based on the difference between instantaneous weight of the sample and initial weight compared to the total expected weight gain. The rate of conversion, which indicates the rate of weight loss and gain (for reduction and re-oxidation), is directly proportional to the rate of reaction. Rate of reaction is defined based as below

\[ R = \frac{dX}{dt} (1 - \varepsilon)(\rho_{s,\text{max}} - \rho_{s,\text{min}}) \]  

(29)

where \( X \) is the conversion reduction or re-oxidation reactions, and \( \rho_{s,\text{max}} \) and \( \rho_{s,\text{min}} \) are maximum and minimum solid density, respectively.

For gas-solid reaction system, it is experimentally validated that the rate of reaction is controlled by three main parameters: temperature, reaction mechanism, and pressure.

\[ \frac{\partial X}{\partial t} \propto \text{Temperature & Reaction mechanism & Pressure} \]  

(30)

Based on that, the general form of rate of conversion for heterogeneous gas-solid reaction system as a widely accepted empirical expression is proposed [64]

\[ \frac{\partial X}{\partial t} = K(T_g).f(X).h(pO_2,pO_{2,eq}(T_g)) \]  

(31)

where \( \frac{\partial X}{\partial t} \) is the rate of conversion for reduction or re-oxidation reactions, \( K(T_g) \) is temperature dependence of reaction rate constant, \( f(X) \) reaction mechanism function and \( h(pO_2,pO_{2,eq}(T_g)) \) is the function including the effect of the partial pressure of oxygen.
The temperature dependence of the reaction rate is included in the rate of conversion and $K(T_s)$. This dependence term is defined based on Arrhenius equation

$$K(T) = A \cdot \exp\left(-\frac{E_a}{R \cdot T}\right)$$

where, $A$ is pre-exponential factor, which is a measure of collision rate of the reactants. $E_a$ is the activation energy and $R$ is the universal gas constant. $K(T)$, as it is named, is the inclusion of temperature effect in the reaction rate. The effect of the reaction mechanism on the conversion is included by $f(X)$. The pre-exponential factor $A$, the activation energy and the reaction mechanism $f(X)$ represent are called kinetics triplet of the reaction [64]. In most cases, the pressure variation (partial pressure of reactant) is small, so the pressure term is neglected in the overall rate of conversion. Based on the proposed rate of conversion and related rate of reaction, different kinetics are proposed according to different TGA analysis. It is difficult to assess the kinetic data directly from a large-scale experiments due to multiple affecting factors and the complexity of the simultaneously occurring phenomena. On the other hand, the conditions in a lab-scale set up, like the TGA analyzer, allows the interpretation of the redox couple kinetics under relatively simplified conditions, but it may not be the exact rate in prototype systems. Even for the lab scale analysis, there are several parameters affecting the measured values such as sample purity, set up calibration status, the purge gas composition, type of sample holder and crucible, type of the set up and its accuracy, etc. Due to these potential deviations, it is not possible to propose a unified reaction rate for specific type of reactant. The recommended approach is to determine model parameters of rate of conversion based on the conducted TGA results of a sample.
2.3.2 COBALT OXIDE SYSTEM

The cobalt oxide redox system is based on reduction of $Co_3O_4$ in which the oxygen is released and the enthalpy of reaction is stored. For reverse reaction, oxygen is brought into contact with $CoO$ for oxidization and the stored energy is released. The reversible pure cobalt oxide gas-solid system chemical reaction is as below

$$Co_3O_4(s) + \Delta H_r \leftrightarrow 3CoO(s) + \frac{1}{2}O_2$$

(33)

For atmospheric condition ($O_2$ concentration equal to 21%), the enthalpy of reaction is about 844 kJ/kg, and reaction temperature of forward reaction about 890°C. Despite several experimental TGA analysis conducted on pure and mixed cobalt oxide system, there still a few kinetics model is available [65]. Hutchings et al. were among the first group which studied the cobalt oxide redox reaction kinetics [50]. They studied Cobalt oxide system for feasibility study of oxygen absorption/desorption applications. They intended to use Cobalt oxide redox system as a stable reversible redox reaction for oxygen generation purpose. They investigated the role of kinetics and thermodynamic factors on oxygen absorption and desorption of pure cobalt oxide. They conducted TGA analysis on pure cobalt oxide sample to develop kinetic model. They verified that the weight loss of about 6.64% occurs during reduction. The reaction temperature measured to be 891°C for using air as purge gas while it was 938.5°C when pure oxygen was used. They also verified that the volumetric change for conversion of 3 moles of $CoO$ to $Co_3O_4$ was 13.6%. As they were interested in application for oxygen storage and handling, they proposed the reaction kinetics just for desorption (reduction) reaction based on the measured TGA/DTA analysis. The proposed reduction reaction rate is

$$R = A \left( \frac{1}{T_0} - \frac{1}{T} \right) \exp(- \frac{E_a}{RT})$$

(34)
where $T_0$ is the temperature where $\Delta G = 0$, $T$ is the temperature and $E_a$ is the activation energy. They measured activation energy for reduction reaction to be 439 kJ/mol and verified that it is high compared to range between 80 to 135 kJ/mol for a diffusion process [50]. Wong et al. conducted several non-isothermal and isothermal TGA analysis with air at atmospheric pressure and calculated the kinetic constant and activated energy of forward and reverse reaction for pure and mixed cobalt oxides. The mixed oxide considered was cobalt oxide with 5% aluminum oxide as doping agent [16]. They reported kinetic constant parameters based on experimental measurement, as listed in Table 5.

<table>
<thead>
<tr>
<th></th>
<th>Pure $Co_3O_4$ Reduction</th>
<th>Mixed with 5% $Al_2O_3$ Reduction</th>
<th>Mixed with 5% $Al_2O_3$ Re-Oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a (\frac{kJ}{mole})$</td>
<td>960</td>
<td>731</td>
<td>165</td>
</tr>
<tr>
<td>$A (\frac{1}{s})$</td>
<td>1.98e+39</td>
<td>1.01e28</td>
<td>1.26e9</td>
</tr>
</tbody>
</table>

*Table 6: Pre-exponential factors and activation energies calculated for Pure $Co_3O_4$ and mixed with 5% $Al_2O_3$ using TGA analysis* [16]

They also provided rate of conversion for mixed system with 5% $Al_2O_3$ as below

For reduction reaction:

$$\frac{\partial X}{\partial t} = K(T)(1 - X)(- \ln(1 - X))^2\frac{1}{\gamma}$$

$$K(T) = 1.01 \times 10^{28} \exp(-\frac{731}{RT})$$

(35)

For re-oxidation reaction:

$$\frac{\partial X}{\partial t} = K(T)(1 - X)(- \ln(1 - X))^2\frac{1}{\gamma} \left(\frac{P}{P_{eq}} - 1\right)$$

$$K(T) = 1.26 \times 10^{9} \exp(-\frac{165}{RT})$$

(36)
\( P_{eq} \) is related to the equilibrium temperature as

\[
\ln(P_{eq}) = -\frac{25422}{T_{eq}} + 20.01 \tag{37}
\]

There were no further details provided. The proposed rates of reaction are listed in the appendix of the report and has not been published officially [16].

Pagkoura et al. prepared a pellet out of mixed cobalt oxide and used them as a reaction bed for a tube heater reactor equipped with oxygen analyzer [54]. The reaction rate was controlled based on variation of oxygen concentration. As the oxygen variation was very small compared to the total oxygen content of air flow, the effect of oxygen concentration variations were neglected in the proposed simplified kinetics model for forward and reverse reaction.

\[
\frac{\partial X}{\partial t} = K_{\text{red}} \cdot (1 - X) - K_{\text{Oxi}} \cdot X \tag{38}
\]

where \( K_{\text{red}} \) and \( K_{\text{Oxi}} \) are reaction constants for reduction and re-oxidation reaction, respectively.

The equilibrium condition is given by setting the rate of conversion equal to zero in which

\[
\frac{\partial X_{eq}}{\partial t} = K_{\text{red}} \cdot (1 - X_{eq}) - K_{\text{Oxi}} \cdot X_{eq} = 0 \tag{39}
\]

\[ X_{eq} = \frac{1}{1 + \frac{K_{\text{Oxi}}}{K_{\text{red}}}} \tag{40} \]

The rate of conversion can be rewritten based on calculated \( X_{eq} \)

\[
\frac{\partial X}{\partial t} = K \left( 1 - \frac{X}{X_{eq}} \right) \tag{41}
\]

With simulation for open system with constant air flow, the \( X_{eq} \) is evaluated as a function of temperature as below
\[ X_{eq} = \frac{1}{(1 + \frac{P_1}{T} \exp(\frac{P_2}{T}))} \]  

(42)

where \( P_1 \) and \( P_2 \) are constant coefficients determined by curve fitting based on available experimental data. Thus, the final proposed rate of conversion is

\[ \frac{\partial X}{\partial t} = K \left( 1 - \frac{X}{X_{eq}} \right), \quad X_{eq} = \frac{1}{(1 + \frac{P_1}{T} \exp(\frac{P_2}{T}))} \]  

(43)

where \( P_1 \) and \( P_2 \) are determined based on experimental results and \( K \) is a function of temperature. The kinetics constant is different for reduction and re-oxidation reactions as they have different rates, but \( P_1 \) and \( P_2 \), which determine \( X_{eq} \), are the same for both forward and reverse reactions. The kinetics constant \( K \) is determined using Arrhenius type function of temperature.

\[ K(T) = A \exp\left(\frac{-E_a}{R \cdot T}\right) \]  

(44)

where, \( A \) is pre-exponential factor, \( E_a \) is the activation energy and \( R \) is the universal gas constant.

The \( K \) is determined for reduction and re-oxidation separately [54]. Thus, based on simplified linear approximation and considering that the variations of oxygen concentrations are minor, the proposed kinetics can be applied for storage cycle. The \( K \) value is determined as a function of temperature for each of reaction modes separately. \( X_{eq} \) is considered to be constant for both forward and reverse reactions.

Muroyama et al. studied the oxygen concentration effect on system performance [49]. The reason that they have considered the effect of oxygen concentration of the proposed kinetics was the plan for application of the cobalt oxide redox reaction in the Brayton cycle power generation. In the proposed configuration, the reduction is planned to happen in a gravity driven directly irradiated reactor in which the oxygen concentration can be controlled. Reduced cobalt oxide is used in a separate counter flow direct contact reactor in which the re-oxidation happen.
and the heat is released and used as heat source to run the Brayton cycle [38]. As both considered reactors were supposed to operate in a non-atmospheric condition, the oxygen partial pressure effect should be considered in the proposed reaction kinetics. They conducted several isothermal and non-isothermal TGA analysis at various values of temperature and atmosphere (oxygen concentration). For oxygen partial pressure integration in the proposed reaction kinetics, the Avrami-Erofeyev model with power rate term was integrated to resolve the effect of oxygen partial pressure variations [64]. For gas-solid system proposed rate of reaction is

\[
K \left(1 - \frac{P_{O_2}}{P_{O_{2,eq}} \cdot T}\right)^\gamma \cdot (t - t_0) = \left[-ln(1 - X)\right]^{\frac{1}{n}}
\]

(45)

where \(P_{O_2}\) is oxygen partial pressure, \(P_{O_{2,eq}}\) is oxygen partial pressure which is determined using thermophysical property data, \(\gamma\) is the reaction order determined based on reaction mechanism, \(t_0\) is the offset time required for switching the atmosphere in isothermal TGA analysis. The kinetic constant \(K\) is determined based on Arrhenius type temperature dependency similar to the previous models. Based on the above considered model, the proposed kinetics for reduction and re-oxidation were derived.

For reduction reaction, it was shown that the rate of reaction is very sensitive to the oxygen concentration, thus the reaction mechanism is a function of oxygen partial pressure. The reduction kinetics is

\[
K \left(1 - \frac{P_{O_2}}{P_{O_{2,eq}} \cdot T}\right)^\gamma \cdot (t - t_0) = \left[-ln(1 - X)\right]^{\frac{1}{n}},
\]

\[
\gamma = 1.506 \pm 0.022 \quad n = 1.968 \pm 0.058,
\]

(46)

The kinetic constant is

\[
K(T) = A. \exp \left(-\frac{E_a}{R \cdot T}\right)
\]

(47)
\[ A = 1.104 \pm 0.043 \times 10^9 \frac{1}{s} \quad E_a = 247.21 \pm 0.38 \frac{kJ}{mol} \]

Surprisingly, they verified that the oxygen partial pressure is not affecting the re-oxidation kinetics since the reaction kinetics is mostly governed by cobalt cation and oxygen anions movement rather than oxygen diffusion. They proposed a reaction kinetics for re-oxidation with no term for oxygen partial pressure term. The re-oxidation kinetics is

\[ Kt = \left[ 1 - (1 - X)^{\frac{1}{3}} \right]^2 \]  \hspace{1cm} (48)

With the kinetic constant

\[ K(T) = A \exp \left( -\frac{E_a}{R \cdot T} \right) \]  \hspace{1cm} (49)

\[ A = 22.16 \pm 1.2 \frac{1}{s} \quad E_a = 58.07 \pm 0.26 \frac{kJ}{mol} \]

Considering the above listed proposed reaction kinetics, it should be noticed that each result set is provided based on the internal TGA experiment, which depends on several parameters such as type of the sample (purity, particle size etc.), TGA machine accuracy, type of measurement (isothermal and non-isothermal), and many other uncertainties that affect the final proposed kinetics. In this study, since we are dealing with a packed bed reactor operating as atmospheric condition and the reactor is not pressurized, we apply the proposed kinetics by Pagkoura et al. [54]. Since they have conducted the analysis for packed bed tube heater with pellet type bed, the test condition is closer to the considered packed bed reactor that we plan to study. We assumed that the reactor is operating at atmospheric pressure and it has not been pressurized for operation. Below is the summary of considered rate of reactions for simulation analysis of cobalt oxide system. The reaction kinetics system is

\[ \frac{\partial X}{\partial t} = K \left( 1 - \frac{X}{X_{eq}} \right), \quad X_{eq} = \frac{1}{(1 + \frac{p_1}{T} \exp(\frac{p_2}{T}))} \]  \hspace{1cm} (50)
\[ K(T) = A \exp(-\frac{E_a}{T}) \]  \hspace{1cm} (51)

For REDUCTION reaction
\[ A = 2.12 \times 10^{27} \frac{1}{s}, \quad E_a = 87,000K, \quad P_1 = 10^{-7} K, \quad P_2 = 25,000K \]  \hspace{1cm} (52)

For RE-OXIDATION reaction
\[ A = 1.4 \times 10^{-15} \frac{1}{s}, \quad E_a = -30,000K, \quad P_1 = 10^{-7} K, \quad P_2 = 25,000K \]  \hspace{1cm} (53)

### 2.3.3 MANGANESE OXIDE SYSTEM

Alonso et al. investigated pure manganese oxide using solar driven Thermogravimeter with reactant directly exposed to high flux thermal irradiation. They derived kinetics related to \( \text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4 \) and \( \text{Mn}_3\text{O}_4/\text{MnO} \) \cite{66}. There were several studies on pure manganese oxide showing that the pure system is not suitable for thermochemical energy storage due to very low re-oxidation reaction and thermal hysteresis \cite{16,45,67}. Due to other suitable characteristics manganese oxide is considered for thermochemical energy storage applications. The storage performance of manganese oxide system could be improved by mixing manganese oxide with other metal oxide. Among several mixed combinations, mixed manganese and iron oxide system has proven good storage performance \cite{23,44,55}. Carrillo et al. considered the 1:4 Fe/Mn mass ratio mixture as a modified mixed storage reactant. They conducted several TGA analysis and developed kinetics for both forward and reverse reactions \cite{55} to demonstrate that the mix is good after 75 cycles. Considered mixed system was
\[ 6(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{O}_3(s) + \Delta H_r \leftrightarrow 4(\text{Mn}_{0.8}\text{Fe}_{0.2})_3\text{O}_4(s) + \text{O}_2(g) \]  \hspace{1cm} (54)
Based on conducted experimental TGA analysis together with in-situ XRD, they proposed the reaction kinetics as below

\[
\frac{\partial X}{\partial t} = K(T)X^l(1-X)^m(-\ln(1-X))^n
\]  

\[
K(T) = A.\exp\left(-\frac{E_a}{T}\right)
\]

where \( K(T) \) is defined as Arrhenius type function of temperature. The kinetics parameters for both reduction and re-oxidation are as below

For REDUCTION reaction

\[ l = 1.75, \quad m = 0.7, \quad n = -0.75 \]  

\[ A = 4.2 \times 10^{19} \frac{1}{\text{min}}, \quad E_a = 371.2 \frac{kJ}{\text{mol}} \]

For RE-OXIDATION reaction

\[ l = 1.26, \quad m = 0.522, \quad n = -0.59 \]

\[ A = 2.3 \times 10^3 \frac{1}{\text{min}}, \quad E_a = 74 \frac{kJ}{\text{mol}} \]

In the proposed kinetics for 1:4 Fe/Mn mixed system, they have not considered the effect of oxygen partial pressure effect since the test was conducted in atmospheric condition.

Beside 1:4 Fe/Mn mixed system, different ratio has been proposed and system operation performance analysis were conducted. Wokon et al. considered 1:3 Fe/Mn system in which the mixture was prepared in a specific granulation process in order to have the granular shape reactant for application in hybrid sensible-thermochemical packed bed reactor. The mixed metal system is

\[ 6(Mn_{0.75}Fe_{0.25})_2O_3(s) + \Delta H_r \leftrightarrow 4(Mn_{0.75}Fe_{0.25})_3O_4(s) + O_2(g) \]
Using results of thermogravimetric analysis (TGA) they proposed a reaction kinetics constant (function of temperature), reaction mechanism and oxygen partial pressure [55].

Proposed reaction kinetics system is

\[
\frac{\partial X}{\partial t} = K(T) \cdot l \cdot X \cdot (1 - X) \cdot (-\ln(1 - X))^{(1 - \frac{1}{m})} \cdot \left(1 - \frac{pO_2}{pO_{2,eq} \cdot T}\right)^n
\]  \hspace{1cm} (62)

\[K(T) = A \cdot \exp\left(-\frac{E_a}{T}\right)
\] \hspace{1cm} (63)

Thus the related reaction mechanism is proposed for both forward and reverse reaction as below

For REDUCTION reaction

\[l = 1.95, \quad m = 1.95, \quad n = 4.55\] \hspace{1cm} (64)

\[A = 2.74 \times 10^{13} \quad \frac{1}{s}, \quad E_a = 355.72 \quad \frac{kJ}{mol}\] \hspace{1cm} (65)

For RE-OXIDATION reaction

\[l = 1.38, \quad m = 1.38, \quad n = 7.06\] \hspace{1cm} (66)

\[A = 1.78 \times 10^{16} \quad \frac{1}{s}, \quad E_a = 463.53 \quad \frac{kJ}{mol}\] \hspace{1cm} (67)

For manganese oxide packed bed reactor analysis, since the system is operating at atmospheric condition, the pressure effect term will be neglected. In the analysis for manganese oxide in this study, the proposed model by Wokon et al. is employed with neglected pressure term. Thus as a conclusion, our reaction kinetics model for the reactor design analysis is based on 1:3 Fe/Mn mixed system. The reaction kinetics is as below

\[
\frac{\partial X}{\partial t} = K(T) \cdot l \cdot X \cdot (1 - X) \cdot (-\ln(1 - X))^{(1 - \frac{1}{m})}
\] \hspace{1cm} (68)

\[K(T) = A \cdot \exp\left(-\frac{E_a}{T}\right)
\] \hspace{1cm} (69)

For REDUCTION reaction
\[ l = m = 1.95 \]  
\[ A = 2.74 \times 10^{13} \frac{1}{s}, \quad E_a = 355.72 \frac{kJ}{mol} \]

For RE-OXIDATION reaction

\[ l = m = 1.38 \]
\[ A = 1.78 \times 10^{16} \frac{1}{s}, \quad E_a = 463.53 \frac{kJ}{mol} \]

### 2.4 MATERIAL PROPERTIES

Material properties can be classified as for gas or solid bed. For gas phase properties, air is treated as an ideal gas. For solid phase, the instantaneous extensive properties are estimated based on average ratio considering the converted portion of the reactant. Thus, the average density and specific heat are calculated as below

\[ \rho_s = (1 - X_{\text{reduction}}) \cdot \rho_{Co_3O_4} + X_{\text{reduction}} \cdot \rho_{CoO} \]  
\[ \rho_s = X_{\text{oxidation}} \cdot \rho_{Co_3O_4} + (1 - X_{\text{oxidation}}) \cdot \rho_{CoO} \]

where \( \rho_s \) is average instantaneous solid bed density, \( \rho_{Co_3O_4} \) density of \( Co_3O_4 \), \( \rho_{CoO} \) density of \( CoO \) and \( X_{\text{reduction}} \) and \( X_{\text{oxidation}} \) are conversion ratio of reduction and re-oxidation reaction respectively. Similarly, for specific heat, the average value is defined as

\[ C_{ps} = (1 - X_{\text{reduction}}) \cdot C_{p,Co_3O_4} + X_{\text{reduction}} \cdot C_{p,CoO} \]  
\[ C_{ps} = X_{\text{oxidation}} \cdot C_{p,Co_3O_4} + (1 - X_{\text{oxidation}}) \cdot C_{p,CoO} \]

where \( C_{ps} \) is average instantaneous solid bed specific heat, \( C_{p,Co_3O_4} \) is specific heat of \( Co_3O_4 \), \( C_{p,CoO} \) is specific heat of \( CoO \), and \( X_{\text{reduction}} \) and \( X_{\text{oxidation}} \) are conversion ratio of reduction and re-oxidation reaction, respectively. The temperature effect on specific heat is considered as linear function of temperature for both materials.
Physical parameters for Cobalt oxide system is listed in Table below [16].

<table>
<thead>
<tr>
<th>DESCRIPTION</th>
<th>SYMBOL</th>
<th>VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density of $Co_3O_4$</td>
<td>$\rho_{Co_3O_4}$</td>
<td>6,110 [kg/m$^3$]</td>
</tr>
<tr>
<td>Density of $CoO$</td>
<td>$\rho_{CoO}$</td>
<td>6,450 [kg/m$^3$]</td>
</tr>
<tr>
<td>Specific Heat of $Co_3O_4$</td>
<td>$C_{p,Co_3O_4}$</td>
<td>0.55$T_s$ + 328.6 [J/kg.K]</td>
</tr>
<tr>
<td>Specific Heat of $CoO$</td>
<td>$C_{p,CoO}$</td>
<td>0.12$T_s$ + 628 [J/kg.K]</td>
</tr>
<tr>
<td>Bed porosity</td>
<td>$\varepsilon$</td>
<td>0.6</td>
</tr>
<tr>
<td>Bed thermal conductivity</td>
<td>$\lambda$</td>
<td>1 [W/mK]</td>
</tr>
<tr>
<td>Enthalpy of reaction</td>
<td>$\Delta H_r$</td>
<td>196.2 [kJ/mol]</td>
</tr>
</tbody>
</table>

*Table 7: Physical properties of Cobalt Oxide system*

Similarly, for mixed manganese oxide, the physical properties can be estimated as average ratio based on converted portion of the reactant.

The average density and specific heat are calculated as below

$$
\rho_s = (1 - X_{\text{reduction}}) \cdot \rho_{Mn_2O_3} + X_{\text{reduction}} \cdot \rho_{Mn_3O_4}
$$

(78)

$$
\rho_s = X_{\text{oxidation}} \cdot \rho_{Mn_2O_3} + (1 - X_{\text{oxidation}}) \cdot \rho_{Mn_3O_4}
$$

(79)

where $\rho_s$ is average instantaneous solid bed density, $\rho_{Mn_2O_3}$ is density of $Mn_2O_3$, $\rho_{Mn_3O_4}$ is density of $Mn_3O_4$, and $X_{\text{reduction}}$ and $X_{\text{oxidation}}$ are conversion ratio of reduction and re-oxidation reaction, respectively. The average specific heat is defined as

$$
C_{p,s} = (1 - X_{\text{reduction}}) \cdot C_{p,Mn_2O_3} + X_{\text{reduction}} \cdot C_{p,Mn_3O_4}
$$

(80)

$$
C_{p,s} = X_{\text{oxidation}} \cdot C_{p,Mn_2O_3} + (1 - X_{\text{oxidation}}) \cdot C_{p,Mn_3O_4}
$$

(81)

where $C_{p,s}$ is average instantaneous solid bed specific heat, $C_{p,Mn_2O_3}$ is specific heat of $Mn_2O_3$, $C_{p,Mn_3O_4}$ is specific heat of $Mn_3O_4$, and $X_{\text{reduction}}$ and $X_{\text{oxidation}}$ are conversion ratio of reduction and re-oxidation reaction, respectively. The temperature effect on specific heat is considered as linear function of temperature for both martials.
Considered physical properties for 1:3 Fe/Mn mixed system are listed in Table below.

<table>
<thead>
<tr>
<th>DESCRIPTION</th>
<th>SYMBOL</th>
<th>VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density of $Mn_2O_3$</td>
<td>$\rho_{Mn_2O_3}$</td>
<td>4,500 [kg/m$^3$]</td>
</tr>
<tr>
<td>Density of $Mn_3O_4$</td>
<td>$\rho_{Mn_3O_4}$</td>
<td>4,860 [kg/m$^3$]</td>
</tr>
<tr>
<td>Specific Heat of $Mn_2O_3$</td>
<td>$C_{p,Mn_2O_3}$</td>
<td>$0.39T_s + 30.85$ [J/kg.K]</td>
</tr>
<tr>
<td>Specific Heat of $Mn_3O_4$</td>
<td>$C_{p,Mn_3O_4}$</td>
<td>$0.55T_s + 43.83$ [J/kg.K]</td>
</tr>
<tr>
<td>Bed porosity</td>
<td>$\varepsilon$</td>
<td>0.6</td>
</tr>
<tr>
<td>Bed thermal conductivity</td>
<td>$\lambda$</td>
<td>1 [W/mK]</td>
</tr>
<tr>
<td>Enthalpy of reaction</td>
<td>$\Delta H_r$</td>
<td>271 [kJ/kg]</td>
</tr>
</tbody>
</table>

*Table 8: Physical properties of mixed manganese oxide system*

### 2.5 INITIAL AND BOUNDARY CONDITIONS

Due to difference in kinetics and thermal conditions (initial condition and boundary conditions) of reactor for charge and discharge, the simulations are done for two separate modes and the conditions are adjusted for each mode separately.

**BOUNDARY CONDITION**

\[
\text{@Inlet}\begin{cases}
    u = U_{in} & \text{Inlet velocity} \\
    \dot{m} = m_{in} & \text{Inlet mass flow rate} \\
    T = T_{in} & \text{Inlet temperature}
\end{cases}
\]  

(82)

For inlet condition based on the type of simulation either inlet velocity or mass flow rate will be used. Inlet temperature is adjusted based on the mode of operation at can be either constant or variable based on operating condition.

\[
\text{@Outlet}\{ P = P_{out} & \text{Outlet pressure} \}
\]

(83)

\[
\text{@Walls}\{ n \cdot \nabla T = 0 & \text{Well insulated} \}
\]

(84)
INITIAL CONDITION

\[
\begin{aligned}
P_{in} &= P_{out} = P_{ini} \\
T_s &= T_g = T_{ini} \\
u_g &= 0 \\
\rho_s &= \rho_{s1} \text{@Charge} = \rho_{s2} \text{@Discharge}
\end{aligned}
\]  

(85)

2.6 NUMERICAL METHOD

Finite element method is used for solving the system of differential equations. The rate of conversion differential equation is solved to determine the conversion instantaneously. The conversion rate depends on the solid bed temperature that is updated as the reaction proceeds. Based on the conversion and its rate, material properties and rate of reaction are calculated. The momentum and energy equations are solved based on calculated rate of reaction. Flow physics in a porous medium is considered for heat transfer and fluid flow through the reaction bed. The velocity, pressure and temperature field is determined at each point at a given instant. Air properties are calculated based on instantaneous temperature and pressure using the state equation considering the ideal gas behavior of HTF. Due to the existence of reaction and related local temperature difference between solid bed and heat transfer fluid, non-isothermal model is applied for solid and gas interphase condition. Energy equation for both gas and solid phase is calculated and the temperature of each phase is updated based for the next loop. The conversion proceed along the bed until the reaction completes which results in removal of the source terms from continuity and energy equations. The system switches to the conventional heat transfer problem until the bed reaches to the inlet temperature and the system become stable.
Figure 27: Numerical method overall flow chart
3 PACKED BED REACTORS

Simulations were conducted for a complete storage cycle of two redox systems in a simple packed bed reactor. Cobalt oxide and Iron doped Manganese oxide system were considered as storage reactants using gas-solid redox reaction for thermochemical energy storage. Complete storage cycle including charge and discharge were simulated using mathematical model and available developed reaction kinetics. Transient two dimensional axisymmetric model is used for both system analysis. Due to different reaction kinetics, the simulation was conducted in two separate half cycle for charge and discharge mode.

Parametric study considering effect of porosity, inlet air flow rate on reactor performance and pressure drop was conducted. It is shown that porosity has a strong influence on reactor performance as a higher porosity will increase storage rate but the overall storage density will be reduced. It was shown that discharge bed outlet temperature is a critical design parameter that should be considered for setting other parameters such as porosity and inlet flow rate. The transient simulations were also conducted for system analysis in three dimensional reactors. It was shown that based on uniform inlet air distribution and well insulation at side walls, the two dimensional approximation is a reasonable approach for treating conventional cases.

Simple packed bed reactor configuration is considered for this study. The reactor is used for complete storage cycle which includes both charge and discharge phases. Considered reactor has cylindrical cross section and reactant are packed within the middle of the reactor tube. The heat transfer fluid (HTF) enter from inlet and passing through the reaction porous bed. Then it flow out from the reactor tube outlet. Same reactor is used for both charge and discharge half cycles and charge and discharge case will happen based on the type of operating condition. It is assumed that the reactor walls are well insulated and there is no heat losses from side walls. Inlet
properties considered to be uniform across the inlet and no changes happen radially at the reactor inlet. The reactor discharge is connected to the ambient and outlet condition is at atmospheric pressure. At the beginning of each mode of storage cycle, the bed initial condition is assumed to be uniform and bed temperature is equal to initial temperature. It is also assumed no flow condition initially and heat transfer fluid (air) and solid porous bed are in equilibrium condition.

Due to axial symmetry of the reactor, two-dimensional axisymmetric transient model is used for solving the governing equations.
3.1 STORAGE CYCLE

The complete storage cycle includes two separate half cycle in which the charging occurs at the first half cycle and the stored energy is released during the next half cycle. Each half cycle is completed when the bed temperature reaches the inlet temperature of HTF and the system equilibrates.

![Figure 28: Reaction bed configuration and related probe points](image)

CHARGE HALF CYCLE

Before the charging process is initiated, the bed is in fully discharged at the initial temperature $T_{ini}$. The inlet condition for HTF is set for charging at a fixed velocity, $u$, and temperature, temperature $T_{in}$ to commence the charging process. The hot air entering the bed heats up the reactant, and when the bed temperature reaches the reaction temperature the reaction is triggered. A reaction front will be formed and it will proceed along the reactor. The storage cycle continues until the HTF discharge temperature from the reactor equals to the inlet temperature and the system reaches an equilibrium condition.

DISCHARGE HALF CYCLE

It is assumed that the reactor is at fully charged condition before discharge half cycle starts. The air is in equilibrium with the porous bed at initial temperature $T_{ini}$. To initiate the discharge process, the air inlet condition is set at a constant speed and temperature, $u$ and $T_{in}$ (discharging temperature). The air entering the bed cools down the bed and the reaction will starts as the reaction temperature is reached. The reaction front will be formed and it will proceed
along the bed until the conversion is completed. The heated air passing through the porous bed leaves the bed at \(T_{g,\text{out}}\). The discharge mode continues until the bed reaches to the inlet temperature and the equilibrium condition is maintained.

Formed reaction front splits the reaction bed into three zones: region ahead of front, reaction front, and region behind the front. The endothermic/exothermic reaction occurs at the reaction front as the temperature has reached to the reaction temperature. The thermochemical energy (the enthalpy of formation) of the storage system is exchanged at the reaction front. In the other two zones located ahead and behind the reaction front, the heat exchange is in the sensible mode. During the charge process, the downstream region is preheated to reach reaction temperature and the upstream region is heated up to the inlet temperature. During the discharge process, it is in reverse mode as downstream air flow receive stored sensible heat from the reaction bed to cool down up to reaction temperature while the upstream section absorb remained sensible heat after reaction to cool down the bed up to the inlet temperature. The thermochemical energy storage and release occurs in a small region around the reaction front and the rest of the reactor region exchanges the sensible heat with heat transfer fluid. As the kinetics for forward and reverse reaction and related initial and boundary conditions are different for each half cycle (charge and discharge), then the simulation is done for each mode separately. The criteria for each half cycle completion is based on bed temperature which should reach to the air inlet temperature to be considered as completed. The real charge and discharge completion condition is based on bed conversion status. In this study, each half cycle duration is based on reaching the inlet temperature which implies completion of both thermochemical and sensible part of storage. The reactor is a hybrid a thermochemical and sensible energy storage unit; the sensible form of energy is not negligible. In this regards, in order to consider real operating condition of the reactor, the thermal equilibrium condition is set as the storage completion
criteria. In some studies, in order to concentrate on the thermochemical portion of the storage, special operating condition can be set in which the system is reached to an equilibrium condition the temperature at the level below the reaction temperature, but the reaction prevented due to lack of oxygen or excess partial pressure for oxygen. For reaction to be triggered, the atmosphere (oxygen partial pressure) is changed in addition to inlet condition of heat transfer fluid. Thus, only thermochemical of storage is utilized. This condition is mostly used for discharge or re-oxidation in which the system cooled down to below reaction temperature using nitrogen as purge gas. Due to lack of oxygen, the re-oxidation may not happen although the temperature is below reaction temperature. In order to start the discharge reaction, the purge gas is switched to air. Under such condition, there is no need for sensible heat exchange to make bed reaching the reaction temperature to initiate the conversion. For reactor performance analysis, both sensible and thermochemical parts should be considered since the sensible storage is an integral part of the system and affects overall system performance. In this study, by the complete system is considered unless otherwise stated.

3.2 COBALT OXIDE SYSTEM
A simple packed bed reactor using cobalt oxide as storage reactant is considered for study. The reaction temperature is about 890°C, thus the system is designed to operate between 700°C and 1,000°C. For charging mode, the hot air at 1,000°C enters the reactor and continues until the bed temperature everywhere reaches 1,000°C. For discharge operation, cold air enters the reactor for reheating at 700°C and continues until the bed temperature reaches 700°C. Five equal spacing probe points are considered along the reaction bed to monitor the temperature in the bed. The first one near the inlet and measuring the inlet HTF temperature and the last one close to the outlet recording HTF outlet temperature. One of the critical performance parameters for
reactor operation is the HTF outlet temperature which is monitored at point 5 through the storage cycle.

![HTF temperature monitoring points along the reaction bed](image)

*Figure 29: HTF temperature monitoring points along the reaction bed*

### 3.2.1 TWO DIMENSIONAL MODEL

A simple cylindrical packed bed is considered for this study. As the reaction bed is well insulated, a two-dimensional axisymmetric model is used for simulation of the system. Similar approach can be applied for rectangular cross section reactors with high aspect ratio as the side-wall effect can be neglected.

**CHARGING MODE:**

It is assumed that the bed is fully discharged and maintained at 700°C with no air flow. At the beginning the charge half cycle, the hot air at 1,000°C and uniform inlet velocity is fed into the reactor at the inlet. $Re$ number of HTF at inlet is maintained at 1,700 to keep the flow condition in laminar mode along the reactor. The reactor discharge condition is atmospheric and there is no back pressure considered at the outlet. Inlet hot air warms up the reaction bed until the reduction reaction is triggered and reaction front is formed. The initiated endothermic reduction reaction proceed along the reaction bed through the formed reaction front. Hot air flow temperature drops as it enters the reaction bed and it loose more energy at the reaction front because of the enthalpy of reaction exchange. After passing the reaction front, the HTF further cools down due to exchange of heat with the cold porous bed. Reaction happens at reaction front and
endothermic reaction stores the energy as reaction completes. Downstream part is preheated to reach to reaction temperature as the reaction front reaches. The upstream section, heats up the bed in sensible mode to reach to the inlet temperature. Charging duration is controlled by rate of gas-solid heat exchange and the kinetics of forward reaction.

**Figure 30: Reaction front proceeding along the bed during charge mode at different time steps**

The HTF temperature at probe points along the reaction bed together with the conversion variations throughout the charging process are shown in below Figure 30. It was assumed that the bed and heat transfer fluid being in equilibrium condition at 700°C, thus the temperature of the point close to the inlet increase rapidly as hot air stream enters the reactor. The temperature of the bed near the inlet increases rapidly at the early stage and the change becomes gradual as the bed temperature is increased, and reaction is triggered. The average conversion ratio of the bed, indicator of the overall reaction process, is shown in Figure 30.
Despite very sharp temperature rise at the beginning at point 1, the slope of temperature rise is reduced as the reaction triggered. The endothermic reaction absorbs part of inlet energy for storage resulting in slower temperature increase of HTF although the inflow is maintained at 1,000°C. The temperature rise at point 2 is delayed until the hot inlet air flow reach to that point. Similar trend is observed at all downstream locations but more gradual increase of temperature as the temperature of air flow decreases due to upstream energy absorption of the bed. The lowest rate of temperature rise is at the outlet as it is located at the farthest point compared to the inlet. The average conversion value indicates the reaction progress. The conversion complete much earlier before the charging completes implying that the thermochemical heat storage is completed in a short time. The bed continues to store energy in sensible form until the bed temperature reaches to inlet temperature of HTF.

![Figure 31: HTF temperature at controlling points along the bed during charge mode](image)

It can be seen from the temperature signal at the outlet (point 5) that the time required for sensible heating is much longer after the conversion is completed. This is indicated by the lower existing temperature gradient at the outlet. The volumetric heat transfer coefficient is very critical in the overall storage rate of the reactor since pre and post heating of the bed can be
accelerated with the higher heat transfer coefficient. Another important consideration is that the outlet temperature of the reactor during charging mode indicates the rate of storage and is one of the measuring parameters for reactor performance analysis. In addition, discharge temperature of the reactor at the outlet is an indicator of how much energy is stored by the bed. Running the reactor with higher outlet temperature is justified up to the level in which the stored amount of energy being higher than required energy for maintaining the air flow through the reactor.

DISCHARGING MODE:

For the discharge process, HTF enters the bed at 700°C. At the porous bed front, oxidation reaction starts as soon as the oxygen absorption from the air in the porous bed occurs. The exothermic oxidation reaction releases the enthalpy of reaction that is transferred to HTF. This results in an increase of temperature of HTF in the stream-wise direction. The temperature of the air at HTF channel inlet is maintained at 700°C, which is well below the reaction equilibrium temperature of 890°C. As the reaction front proceeds, the upstream bed sections cool via HTF flow passing through the bed. The cooling process continues until the entire bed is cooled down to HTF inlet temperature.
The temperature at various probe points and the conversion for discharge mode is shown in Figure 31. Oxidation reaction occurs rapidly resulting in a temperature peak compatible with the variation of rate of conversion. After the completion of the conversion, the cooling process continues for a much longer time. The fraction of the released reaction energy is used to heat up the bed and stored as sensible energy within the bed by increasing the bed temperature. This stored sensible energy within the bed is released during the cooling process, which takes more time compared to the fast oxidation reaction. The outlet pressure is set to the ambient pressure, and it remains constant throughout the simulation. Inlet mass flow rate is maintained constant and the flow is laminar at Re = 1,700.
EFFECT OF BED POROSITY

For packed bed reactor design, among several influential parameters, bed porosity is the most critical one. The increase of the bed porosity improves HTF flow, and as a result, the rate of convective heat transfer increases along the bed. The increase of heat transfer rate leads a rapid increase of the bed temperature and in turn an increase of the rate of reaction. The rate of oxygen penetration will improve by increasing voids throughout the solid structure and further surface area available for oxygen diffusion. The influence of porosity on the HTF outlet temperature and the rate of reaction is studied for the design and optimization of reactors at different operating conditions.

For the charge mode, the bed outlet temperature and the average conversion are shown for three different porosity values. As the bed porosity increases the rate of reaction increases. Higher porosity enhances the fluid flow in the bed and thus increases the rate of heat transfer, which expedites the overall charging process. Increasing porosity improves the rate of reaction and charging performance, but it reduces the amount of storage material that can be packed.
Higher porosity reduces the energy density of the system, which is very important for large-scale storage modules. The total stored energy is one the performance parameters of the reactors, which needs to be optimized along with the rate of reaction and the outlet temperature.

Figure 34: Average outlet temperature and conversion for different bed porosities – Charge mode

For the discharge mode, porosity variations result in significant performance changes. Increasing porosity while keeping other parameters unchanged, enhance the reaction rate. The bed outlet temperature decreases as the porosity of the bed is increased. Higher porosity increases the flow rate and enhances the convective heat transfer and results in faster cooling of the reactor bed.
Similar to the charging mode, despite improving reaction rate, the porosity increase reduces the total stored energy and reduces the total reactor capacity. Another undesirable effect of the porosity increase in discharge mode is the reduction in the maximum bed outlet temperature. The maximum temperature of the bed during the discharge process is the reaction temperature which is reached at the reaction front. Increasing porosity results in higher HTF flow rate and improved convection heat transfer, but reduces the bed outlet temperature. In CSP plant, the downstream power block performance is highly dependent on the bed outlet temperature. The reduction of the outlet temperature should be avoided for maintaining power generation efficiency at a reasonable level. The optimum selection of the porosity level, which is more critical for the discharge mode than charging, should be included in bed design optimization.

Bed particles microstructure can be changed after a cyclic operation of the bed (several charge and discharge operations). Such changes are more dominant for the re-oxidation process, and those variations should be included in the cyclic performance analysis of storage for future studies. One of the main drawback for this type of simple packed bed reactors is the lack of controlling parameter for porosity variations. Porosity has a dominant effect on the reactor...
performance for both parts of storage cycle, especially at discharge. If any changes happen to bed porosity, the only controlling parameter to maintain the reactor performance and prevent from degradation is to increase HTF flow rate that would result in higher-pressure losses.

It can be inferred from both charging and discharge processes that heating and cooling phases after completion of the reaction, takes most of the time of storage. The rate of heat transfer through the bed should be enhanced to improve the charge and discharge rates and the overall reactor performance. Any improvements in the rate of convective heat transfer between porous bed and HTF enhance the post-reaction phase and improve the overall storage performance.

3.2.2 THREE DIMENSIONAL MODEL

Two dimensional approximation may not be acceptable due to non-uniformities of surface temperature, side cooling etc. We conducted transient simulations in a three dimensional rectangular cross section reactor.

The reactor has a rectangular cross section with low aspect ratio thus the side-wall should be included and two dimensional approximation is not acceptable. Hot air is fed from the bottom during the charge mode and cooled air for the discharge cycle. Both charge and discharge half-cycles are simulated along the bed using reaction kinetics and developed three-dimensional numerical model. The HTF flows in the vertical direction from the bottom for both charge and discharge modes. The uniform velocity profile, a plug flow, is applied at the reactor bed inlet. The inlet and outlet sections ahead and behind the porous reaction bed have not been included in the simulation. The probe locations where HTF temperature signals are acquired during the charging and discharging mode are also shown in Figure 35.
Figure 36: a) Schematic of rectangular prism-shaped porous bed reactor as computational domain,   b) The probe locations for controlling HTF temperature during storage cycle

CHARGE MODE

For the charging process, the bed is maintained at 700°C as the initial temperature before the charging process commences. It is triggered as hot air enters the bed from the bottom at the charging temperature of 1,000°C. The constant inlet temperature of HTF is maintained throughout the charging process, and the charging mode is completed as the whole bed temperature reaches the inlet temperature. The reduction (dissociation) reaction starts at the porous bed inlet and forms a reaction front that proceeds along the bed until the entire solid bed is converted (reduced). The flowing hot air at the inlet increases the temperature of the bed reaching the reaction temperature. High inlet temperature maintains the bed temperature above the reaction equilibrium temperature at the formed reaction front. The heat transfer between HTF and the porous bed is assumed to be only via volumetric convection. As the reaction front proceeds, the converted part of the bed is further heated until reaching the inlet temperature.
The high porosity facilitates the rapid mass and heat transfer along the bed, which affects the rate of reaction and overall charging period.

Figure 37: Instantaneous temperature contour at t=10,000 sec – Charge mode

In Figure 37, the instantaneous solid bed temperatures are depicted at t = 10,000. The storage process is classified into two modes based on the storage mechanism. At the reaction front, the storage is in thermochemical form due to the reaction and the conversion of reactants, and the rest of the bed, which is heated and its temperature is increased, the energy is stored in the sensible form. Although the porous bed is good sensible storage capacity, the major part of stored energy is still in the thermochemical form, which is the main reason that the system has a higher energy density compared to other available systems.
Figure 38: Instantaneous iso-surfaces of solid bed temperature at t=10,000 sec – Charge mode

The instantaneous contours of the HTF temperature in the stream-wise direction are rendered. It is shown that due to the uniform flow along the porous bed, the temperature variations are mostly along the bed axis rather than in the lateral directions. The temperature distribution for the HTF during charging demonstrates that the two-dimensional mass, heat and momentum transport modeling of the reaction bed is a reasonably accurate representation as long as the uniform inlet flow and the well-insulated wall conditions are considered.
The temperature evolutions of HTF at various locations along the bed are depicted in Figure 39. The temperature signals are acquired at equally spaced probes located at the center of the reactor from the bottom to top. After the completion of the conversion, the storage is in a sensible mode in which the temperature of the bed increases to the air inlet temperature. It is shown that the time required for the sensible storage is significantly longer than the time required for the thermochemical storage, especially after conversion is completed. This can be verified from the trend of conversion variation along the bed.
DISCHARGE MODE

After the completion of the charging half-cycle, the reactor is ready for the discharge mode. During the discharge phase, HTF enters the bed at 700°C and is heated while passing through the reactor to reach the desired outlet temperature. The cold inlet air is preheated via using stored sensible heat within the porous structure. This phase is continued until the bed temperature is reduced to the reaction temperature at which the reverse reaction is triggered.

At the reaction front, conversion proceeds and the stored thermochemical energy is released. The exothermic oxidation reaction releases the absorbed enthalpy of reaction and transfers it to the passing HTF. As a result, the temperature of HTF in the stream-wise direction increases. The temperature of the air at the reactor inlet is maintained at 700°C, which is well below the reaction equilibrium temperature of 890°C. At the inlet of the bed, since the temperature difference between inlet air and the solid bed is higher, the rate of sensible heat transfer is higher compared to that in the region downstream of the bed. The formed reaction front can be distinguished within the bed. Inlet air pre- and post-sensible heating regions can be seen along the bed, which are separated by the formed reaction front. At the narrowly formed
reaction front, the conversion proceeds and the reverse re-oxidation enthalpy of reaction is released. Similar temperature patterns are observed for the porous solid bed.

![Instantaneous temperature contour at t=15,000 sec – Discharge mode](image)

*Figure 41: Instantaneous temperature contour at t=15,000 sec – Discharge mode*

Instantaneous iso-surfaces of bed temperature are depicted in Figure 41. The trend is similar as in charging mode, but the conversion time is significantly different due to the difference in the reaction rates. The approximate uniform temperature distribution at the lateral planes within the bed is observed due to the insulated side-walls and uniform inlet conditions. The uniform temperature distribution of HTF at lateral planes in the stream-wise direction is also observed during the discharge process.
Figure 42: Instantaneous iso-surfaces of solid bed temperature at $t=15,000 \text{ sec}$ – Discharge mode

Figure 43: HTF temperature contours along the reaction bed at $t=10,000 \text{ sec.}$ – Discharge mode
In Figure 43, the time evolution of HTF temperature at various equally spaced locations along the central plane of the bed is shown. The points are located from the bed inlet (T1) to the outlet (T4), and the last curve (T4) shows the reactor outlet temperature evolution which is a critical performance parameter of the system. As the HTF outlet temperature is the maximum available heat for the storage module, the efficiency of the power generation unit depends on it. After the re-oxidation conversion is completed, the stored sensible heat is released. Due to the reduced level of temperature difference, this last stage of the discharge mode takes place much longer compared to the rest of the half-cycle.

Figure 44: Conversion variation and HTF temperature at control points along the reactor – Discharge mode

CONCLUSION
In order to investigate the three-dimensional behavior of the packed bed reactor, a rectangular prism type packed bed reactor has been selected for this study. Simulations were conducted for square cross-section reactor with cobalt oxide as reactant agent for high-temperature storage applications. The study conducted for a single storage cycle including the charge and discharge phase separately. It was shown that uniform inlet velocity profile and
laminar flow along the porous bed retain its profile along the bed considering the no-flux condition at the side walls. An isentropic form of the porous bed and uniform temperature distribution helps the uniform trend to be maintained throughout the bed. It can be inferred that two-dimensional system approximation is reasonable during complete storage cycle. The thermochemical storage occurs within the reaction front, and sensible storage takes place inside the rest of the porous bed. The rate of thermochemical storage is much faster compared to the sensible storage. In the region downstream of the reaction front where the temperature difference between HTF and the bed is low, the sensible storage is very slow. For an overall increase in storage rates, it is needed to enhance the sensible heat transfer, especially at last part of the reactor. It can also be implemented by decreasing the bed length while increasing the cross-section. Increasing the bed length reduces overall pressure loss of the bed, but reaching the required outlet temperature becomes challenging. Increasing the bed cross section makes maintaining the uniform inlet velocity more difficult. Any non-uniformity in inlet velocity results in more complicated bed performance. In order to improve the bed performance, especially the rate of charge and discharge, one of the critical parameters is the bed aspect ratio.

3.3 MANGANESE OXIDE SYSTEM
Pure manganese oxide was not applicable for TCES application due to oxygen penetration limitation which results in slower re-oxidation reaction rate, and thus, a lower amount of reactant participates in a storage cycle [16]. Another drawback of the manganese oxide compared to the others is the existence of intrinsic hysteresis which results in an offset between charge and discharge temperatures for complete storage cycles. Abundance, non-toxicity, and high enthalpy of reaction have made manganese oxide system as a competitive option to cobalt oxide system. In order to make the use of manganese oxide as a feasible redox agent, several investigations
have been conducted [68]. The mixed manganese and iron oxide have been selected and studied by several research groups. The different molar ratio of Fe/Mn such as 1:4[52,56,57,69], 1:2 [44] and 1:3 [16] have been proposed for improvement of pure manganese oxide performance. Wokon et al. conducted thermal analysis and thermodynamic study for Fe/Mn with 1:3 molar ratio. They also developed kinetics for the forward and reverse reactions [55]. In this study, a similar reactant is considered, and simulations are conducted based on the proposed reaction kinetics.

\[ 6(Mn_{0.8}Fe_{0.2})_2O_3(s) + ΔH_r ↔ 4(Mn_{0.8}Fe_{0.2})_3O_4(s) + O_2(g) \]  \hspace{1cm} (86)

\[ ΔH_r = 271 \text{kJ/kg} \hspace{1cm} \text{Reaction Temperature} = 980°C \]  \hspace{1cm} (87)

A cylindrical porous reaction bed is considered. The reactor configuration is similar to two-dimensional model considered for cobalt oxide system. The HTF enters the porous bed at the left side and leaves from other end. The steady uniform plug flow is assumed at the inlet for complete storage cycle. For the charging half cycle, hot air flows into the bed from the bottom. For the discharging half-cycle, cold air enters the reactor from the bottom. In order to evaluate the performance of the reactor, the HTF temperatures are measured at four equally spaced points throughout the bed. It is assumed that the outer wall of the bed is well insulated and there is no heat flux from the sidewalls. The charge and discharge mechanism is similar to cobalt oxide system with different set of the inlet temperature. The system operates at 800°C up to 1,040°C range with the reaction initiating at 980°C.

**CHARGE MODE**

It is assumed that the whole bed is maintained at 800°C as the initial cold temperature of storage. In order to start the charging process, the high-temperature hot air at 1050°C is supplied uniformly from the left side of the reactor. The inflow uniform flow pattern and temperature remain unchanged until the completion of the charging mode. The forward endothermic reaction
(reduction) is triggered resulting in the formation of the reaction front. The heat transfer between HTF and the porous bed is assumed to be only via the volumetric convection. As the reaction front proceeds, the converted part of the bed is further heated until reaching the inlet air flow temperature. The forward reaction takes place in a narrow region around the reaction front, and the thermochemical form of energy is stored.

The HTF temperature at four equally spaced locations along the bed axis is shown as a function of time in Figure 44. The conversion curve is also provided representing the reaction completion trend. The first point (T1) which is closer to the inlet is heated rapidly via passing heat flow and passing the reaction front. The heating rate in regions closer to the inlet is higher due to the greater temperature difference between HTF and the reaction bed. Since the HTF stream and the solid bed are in non-equilibrium, the solid bed temperature could be different from HTF temperature at each point. This means that although the reaction front is passed and the conversion is completed at some points, the HTF temperature could still be below the reaction temperature. For analysis of the reaction performance, it is important to characterize the HTF temperature variations since the rate of storage and storage system performance are strongly dependent on the HTF temperature. The conversion rate and the rate of convective heat transfer between the solid and gas phase are key parameters affecting the HTF temperature and related reactor performance.
Figure 45: Conversion variations and HTF temperature changes at controlling points along the bed - Charge mode

DISCHARGE MODE

The charging process continues until the uniform temperature reached inside the bed. The charged bed is then ready for the discharge half-cycle to release the stored energy and complete the full cycle. During the discharge mode, the initial bed temperature is assumed to be 1,050°C, which is well above the reverse reaction temperature. The HTF at 800°C is fed to the bed at the inlet uniformly and maintained until the completion of the discharge mode. At the bed inlet, the cold air is rapidly preheated passing through the high-temperature solid bed. At the early stage, due to the existing high-temperature difference between HTF and the bed, the rate of heat transfer is greater, and thus HTF temperature rapidly approaches the bed temperature. When the porous bed cooled down to the reverse reaction temperature, the reverse exothermic reaction is initiated, and the stored enthalpy of reaction is released at the reaction front. The reaction front formed at the inlet proceeds along the bed. The conversion trend indicates the approximate location of the reaction front. The conversion parameter is defined as the ratio of
the converted section to the whole bed; thus with a good approximation, the conversion can indicate the location of the reaction front at each time.

In Figure 45, the time evolution of HTF temperature at four successive equally spaced locations along the bed center is shown. The similar temperature trend is observed as in the charge mode; the HTF temperature near the inlet rapidly changes due to the higher temperature difference between the HTF and the bed in this region. HTF near the entrance (T1) is heated rapidly and quenches the solid bed to the reaction temperature. The reaction front is formed at the lower temperature compared to the charging mode due to existing hysteresis for storage reactants. The formed reaction front propagates along the bed until the complete conversion of the porous solid bed is attained. The HTF temperature near the outlet is heated more gradually. One of the critical performance parameters for the reactor bed design is the HTF outlet temperature during the discharge mode. The main reason for consideration of a storage system is to provide higher HTF temperature for a longer period of the discharge phase. The intrinsic hysteresis of the reactant results in temperature offset of leaving HTF temperature at the discharge process, but the release of stored thermochemical energy helps to maintain a high-temperature outlet for a longer portion of the discharge half-cycle. After the completion of the conversion, the heat release from the solid bed is in the form of sensible energy. This stage of the discharge process lasts much longer compared to the previous phases.
EFFECT OF AIR INFLOW RATE:

The effect of inlet air flow rate on the storage performance is examined in the parametric study. The bed outlet temperature is considered as the key performance parameter of the reactor for the charge and discharge mode of operations. Three values of the air flow rate are considered in the parametric study. The conversion and the HTF temperature at the bed outlet are depicted as a function of time, during the charge mode. The conversion rate improves as the flow rate is increased but the effect of air flow rate on bed outlet temperature is more pronounced, as shown in Figure 46 and Figure 47.

Figure 46: Conversion variations and HTF temperature changes at controlling points along the bed - Discharge mode
It is expected that the increased airflow rate results in increased input energy, and thus the remarkable changes in the outlet temperature is justified, but for the overall performance of the bed, the required pressure work for maintaining the higher flow rates through the porous bed should be considered.
For discharge half cycle, the effect of the inlet air flow rate is shown. As expected, the higher inflow rate of cold air to the reactor results in a more rapid temperature drop during the discharge mode. As a critical bed performance parameter, the bed outlet temperature drop is not favorable despite faster discharge process. Increasing the inlet air flow rate improves the charging rate, and thus, improves one of the main performance parameters of the reactor, but it increases the parasitic load or required pressure work for maintaining the flow rate through the porous bed. One of the other critical drawbacks of the increased airflow rate is lowering the bed outlet temperature at the discharge mode, which is the most critical performance parameter and should be considered carefully during the reactor design.

![Graph showing HTF temperature at the bed outlet for inlet air flow rate of 5, 10 and 15 lit/min during discharge half-cycle.](image)

**Figure 49: HTF temperature at the bed outlet for inlet air flow rate of 5, 10 and 15 lit/min - Discharge half-cycle**

EFFECT OF BED POROSITY:

As one of the main design parameters of the packed bed reactors, the effect of the porosity has been studied by considering three values of the bed porosity. The evolution of the bed outlet temperature at the charging mode is shown for the bed porosity of 0.5, 0.6 and 0.7.
The bed outlet temperature increases more rapidly as the bed porosity is increased; implying the conversion rate is increased with increasing bed porosity.

*Figure 50: HTF temperature at the bed outlet for the bed porosity $\varepsilon = 0.5, 0.6$ and $0.7$ - Charge half-cycle*

The influence of the bed porosity on the discharge process is shown in Figure 50. As expected, increasing bed porosity improves gas flow through the bed, and thus the rate of convective heat transfer between HTF and the bed is increased. The increased rate of heat transfer results in a higher temperature drop at the bed outlet. Improvements in the heat transfer increase the outlet temperature while the higher flow rates result in the higher temperature drop at the outlet. Thus, the porosity effect on the outlet temperature is not as critical as the inflow rate effect during the discharge mode. Porosity variation has a considerable effect on the total energy density and the pressure drop across the bed, which should be considered in the overall bed design process.
CONCLUSION

A cylindrical packed bed reactor is selected as the reaction bed for a thermochemical energy storage module using the gas-solid redox reaction. The iron doped manganese oxide (Fe:Mn 1:3 molar ratio) is selected as a redox agent for the reactor analysis. The bed performance during the charge and discharge mode is studied. Since the sensible heat transfer after complete conversion of the bed lasts much longer, the overall storage cycle timing is increased significantly. The prolonged cycle timing is not favorable for the system performance. Heat transfer improvement and proper aspect ratio selection could mitigate the storage time issue. Aspect ratio adjustment should be optimized as the shorter bed length increases the chance of temperature drop at the discharge mode and the higher aspect ratio makes the uniform flow distribution at such temperatures more complicated. As a preliminary parametric study, the effect of inflow HTF rate and bed porosity on the system performance is studied. It was shown that the increased flow rate increases the heat input and improves the charge and discharge rates, but it results in lower outlet temperature at the discharge mode and higher pressure drop across the bed. It was shown
that the increased bed porosity improves the storage rate, but the storage density as a critical performance parameter shall be reduced.
4 MODIFIED SPLIT FLOW REACTORS

For high temperature thermal energy storage applications using redox reaction, suitable design configuration should be applied. Packed bed reactor, compared to moving bed and fluidized bed reactors has simpler design with no moving component, uses a single reactor for charge and discharge mode. It is cost-effective and more appealing for high temperature storage applications. Despite unique advantages, they have higher pressure drop and are prone to sintering, which affect overall reactor performance. The inlet flow condition is only control parameter and this makes it difficult for keeping the system performance at efficient level after several cyclic operation. Based on the physics of solid redox reaction, a novel simple modification is proposed to address most of intrinsic drawbacks. Hybrid direct and indirect heat transfer mechanism achieved by the split flow system is proposed as a main modification for conventional design. In split flow system, a fraction of air is passed through reaction bed providing direct contact heat transfer and the rest is passed through side channels providing indirect heat transfer to the bed. Considerable reduction in inlet pressure drop could be achieved with an acceptable level of reduction in storage performance. Parametric study was conducted on a circular cross-sectioned reactor and it was shown that optimization is required at design stage for proper selection of design parameters. Different types of split type design configuration could be applied depending on applications.
Tescari et al. proposed a hybrid sensible-ThermoChemical energy storage system in which a cobalt oxide coated cordierite honeycomb structure were used as reaction bed. Good cyclic performance was observed together with nearly doubling storage density compared to pure sensible one. The bounding of the coating to the structure and low energy density are among the main drawbacks of this design [32].

*Figure 52: a) Coated cordierite with cobalt oxide honeycomb structure b) honeycomb cordierite structure used for sensible storage c) packed bed reactor using coated blocks as storage [32]*

Pagkoura et al. used honeycomb structures made of cobalt oxide as a packed bed reactor [46]. For improving structural rigidity of formed honeycombs, they used alumina composites. Difficulty in formation (extrusion) and structural stability after several cyclic operation are among the main concerns of this type of design configuration for large-scale applications [70].
Pagkoura et al. proposed wafers made of cobalt oxide to be used as a reaction bed. A special preparation method is used to form the wafers [46,54]. Similar to the previous design (structure honeycomb design), although fabrication process improved stability, but the system didn’t display a good stability after cyclic operation.
Strohle et al. proposed a hybrid sensible and TCES system with discharge temperature control [71,72]. Modified packed bed design is mostly for sensible storage while the discharge temperature is controlled using a closed loop TCES. This design configuration, is mainly sensible storage and may not be considered as modified TCES system. Applied thermochemical storage at discharge location, has the same concerns for packed bed reactors.
Deficiencies of packed bed configurations were not resolved despite several attempts by various groups. In order to address this drawback of a simple packed bed design, better understanding of the reaction physics is required. In gas-solid redox system, air works both as HTF and reactant. Heat transfer by air is required for both forward and reverse reaction to supply and release energy to the reactor. The forward reduction reaction can proceed without air as oxygen release do not need to availability of air. Thus, air serves as HTF for forward reaction, but serves as HTF and reactant for reverse reaction [73].

![Diagram of reaction physics](image)

**Figure 56: Air flow role in gas-solid redox system storage cycle**

Required amount of oxygen compared to the total air mass flow rate is very little, and thus, there is a flexibility in setting the airflow rate without affecting the required oxygen level for re-oxidation reaction. The gas-solid redox system cannot be run in indirect mode as air is required for reverse reaction but there is nearly no limitation regarding the oxygen supply through adjustment of air flow rate. Considering the reaction requirements, as an innovative design configuration, split flow design system, is proposed in which the system operates in hybrid of direct and indirect mode. In split flow system, part of air flows through the bed and the rest flows in channels surrounding the reaction bed. Splitting will reduce the required mass flow rate through the bed as part of heat transferred is handled through indirect heating of the bed. Reducing mass flow rate passing through reaction bed will result in considerable reduction in pressure loss along the bed. Reduction of air flowing through the bed may not affect the re-
oxidation reaction performance as the oxygen content of air flowing through the bed is still far above required level for reverse reaction.

In this modified design, the mass flow rate passing through the reaction bed can be adjusted based on different operating conditions and can be tuned according to the variations of the bed properties during cyclic operation of the reactor. Compared to simple packed bed design, the system has more controlling parameters and can be operated more efficiently. In split flow design there will be less concerns about uniform flow distribution across the reaction as any non-uniformity can be controlled through heating from sidewalls. The split flow ratio is defined as the ratio of air mass flow rate passing through the bed over the total mass flow rate of air flow:

\[
SFR = \frac{\text{Mass flow rate passing through the bed}}{\text{Overall mass flow rate}}
\] (88)

Proposed split flow design configuration can be classified into parallel and cross flow design, as illustrated in Figure 56. In parallel flow, the outer flow is parallel to the reactor bed axis while in cross flow, the outer flow is normal to the reaction bed axis. Based on the type of cross section of the reactor, parallel flow can be designed in rectangular cross section (wafer type, see Figure 57) or circular cross section (annulus type, see Figure 58), as depicted in Figure. For cross flow design, based on the type of the looping for flow passing through the reaction bed, the configuration can be classified into closed and open loop system. In open loop system, the two split flows (outer flow and bed flow) merge after passing the reactor while in closed loop system, the bed flow passing a separate loop compared to the outer flow.
Figure 57: Split flow design classifications

Figure 58: Wafer type parallel flow configuration
4.1 PERFORMANCE COMPARISON

For study of performance improvement using split flow system compared to conventional direct contact packed bed reactor, a wafer type split flow reactor is selected. Simulations were conducted in the same reactor bed dimension using cobalt oxide redox system as reactant. A conventional direct contact packed bed reactor with a rectangular cross-section has been selected as a reference reactor. In this reactor, HTF flows through the bed in a vertical direction. The uniform velocity profile, a plug flow, is applied at the reactor bed inlet. The inlet and outlet sections ahead and behind the porous reaction bed have not been included in the simulation. The considered porous bed reactor is the only region of the computational domain. The uniform inlet airflow enters the bed at the bottom of the reactors and exits from the top during the charge and discharge mode of operation. The bed schematic with probe locations where HTF temperature signals are acquired during the charging and discharging mode are also shown in Figure 59.
The proposed split flow reactor design has two separate HTF flow channels adjacent to the porous reactor bed. The split flow ratio is set to $SFR = \frac{1}{3}$, thus one third of the total mass flow rate is passed through the bed and the rest of inflow is split equally between two side channels. It is assumed that the laminar flow condition is maintained throughout the storage cycle in side flow channels. The flow scheme is the same for both charge and discharge cycle. A complete storage cycle consisting of the charge and discharge mode is considered for the performance analysis. During the charge mode, hot air is passed through the bed and energy is stored within the bed. During the discharge mode, the cold air is heated within the reactor by using the stored energy. It is assumed that each mode will start after completion of the previous mode. Due to different kinetics and inlet conditions, the storage cycle is studied in separate charge and discharge mode.
Figure 61: Wafer type split flow packed bed reactor with control points along the bed axis

CHARGE MODE

During the charging process, the bed is maintained at 700°C as the initial temperature before the charging process commences. The charging is triggered as hot air enters the bed from the bottom at the charging temperature of 1,000°C. The constant inlet temperature of HTF is maintained throughout the charging process, and the charging mode is completed as the whole bed temperature reaches the inlet temperature. The reduction (dissociation) reaction starts at the porous bed inlet and forms a reaction front proceeding along the bed until all the solid bed being converted (reduced). The flowing hot air at the inlet increases the temperature of the bed reaching the reaction temperature. High inlet temperature maintains the bed temperature above the equilibrium reaction temperature at the formed reaction front. As the reaction front proceeds, the converted part of the bed is further heated until reaching the inlet temperature. The high porosity facilitates the rapid mass and heat transports along the bed, which affect the
rate of reaction and overall charging period. In Figure 61, the temperature variations for HTF along the bed are shown during the charging mode for the reference and proposed split flow bed. The temperature variation and the conversion of the charging mode are similar for each reactor. In the split flow reactor, $2/3$ of the total hot air mass flow rate is passed through side channels resulting in side heating of the bed rather than direct contact compared to the reference bed. This side heating expedites heat transfer to the bed and compensates the lack of efficient heat transfer in direct contact. With the split flow reactor, the convergence is delayed for about 2,000 sec during which outlet temperature is less than 50 °C below the direct contact average outlet temperature.
The bed outlet remains at atmospheric pressure; thus the bed inlet pressure indicates the overall pressure drop along the bed. In Figure 62, the average inlet pressure of porous bed is shown for both reactors during the charge mode. It is shown that the inlet pressure is reduced less than half of the inlet pressure of the reference bed. This remarkable drop in required pressure work for the novel split reactor design is achieved while the charging performance is deteriorated.
modestly compared to the conventional direct packed bed reactor. The improvement in power requirement could be a major factor for the large-scale applications of TCES systems consisting of gas-solid packed bed reactors.

![Graph showing average inlet gauge pressure for split flow reactor versus direct contact reference bed – Charge mode](image)

*Figure 63: Average inlet gauge pressure for split flow reactor versus direct contact reference bed – Charge mode*

The completion of the charging mode could be determined from the average outlet temperature of the bed. When the outlet temperature approaches the inlet temperature, it can be inferred that the charging process has been completed. In Figure 63, the average outlet temperature for both reactors is compared. It is shown that the trends for outlet temperatures of both designs are similar, but the bed charging duration of the split reactor is delayed for about 2,000 sec while the temperature is within an acceptable range. In the split reactor, a similar level of the outlet temperature is achieved with about 5% drop.
Figure 64: Bed HTF outlet temperature for split flow reactor versus direct contact reference bed – Charge mode

In Figure 64, the reaction front in both reactors is shown at the same instance for a better comparison. In the split reactor, the reaction front is bent due to heating from side channels. The lack of heat transfer due to the reduction in mass flow rate is compensated through heat transfer from side channels.
DISCHARGE MODE

During the discharge phase, HTF enters the bed at 700°C and is heated while passing the reactor to reach the set outlet temperature. It is assumed that the bed is at a cold temperature (700°C) to emphasize on the thermochemical portion of stored energy. The discharge trend is similar for the reference direct-contact and split flow reactor. The discharge duration, which is critical for reactor performance, is elongated. During the elongated period, the outlet temperature in the split flow reactor is in the acceptable range, as shown in temperature signals probed at various location in Figure 65.
Discharge mode duration is longer compared to the charging mode. This is mainly due to consideration of a thermochemical portion of discharge energy resulting in lower temperature gradient and consequently lower heat transfer rates. The airflow temperature at bed discharge centerline is the last point that will be cooled during the discharge mode, and thus, the temperature at this probe is an indicator of discharge process completion. The inlet pressure
dropped is shown in Figure 66 in both reactors. In the split flow reactor, the average inlet pressure is reduced by less than half of the pressure drop obtained in the direct contact reference reactor. Reduced pressure drop through the reactor results in a considerable reduction of required power for maintaining the passing airflow through the reactor.

Figure 67: Bed HTF outlet temperature for split flow reactor versus direct contact reference bed – Discharge mode

The average reactor outlet temperature of each reactor is compared. The outlet temperature is elevated by about 5% in the split reactor, as shown in Figure 67. It is shown here that that the reactor performance is deteriorated modestly during the discharge mode while the required pressure work has been dropped considerably.
Figure 68: Bed HTF outlet temperature for split flow reactor versus direct contact reference bed – Discharge mode

The reaction front in each reactor rendered at the various instant is compared in Figure 68. The reaction front in the split flow reactor is curved as a result of heat transfer from side channels. Curved reaction front increases the front length which compensates the effect of the reduced mass flow rate and related heat transfer reduction in the bed. The compensation avoids the reactor performance deterioration any further. Further enhancement in heat transfer from the side channel can improve the bed performance considerably in the split reactor.
It can be inferred from both charging and discharge mode of the storage cycle that the pressure loss and related pressure work has been reduced considerably compared to conventional direct contact flow reactor with manageable performance reduction. This improvement is very critical for widespread application of packed bed reactors that have simpler design and are cost-effective compared to moving bed reactors.

4.2 PARAMETRIC STUDY

For better understanding of the effect of design parameters on performance of split flow reactor, parametric study is considered for a typical reactor. A split flow packed bed reactor with cylindrical cross section is considered as a reaction bed. The porous bed is surrounded with parallel HTF flow in an annulus. It is assumed that the laminar flow condition is maintained throughout the storage cycle. The flow scheme is the same for both charge and discharge mode. The uniform inlet airflow enters the bed at the bottom of the reactors and exit from the top for both the charge and discharge mode of operation. The reactor schematic with a porous bed and HTF annulus are shown in Figure 69.
In split flow reactors, split flow ratio and HTF channel flow dimension are among the extra design parameters available for reactor design. These added controlling options provide more flexibility in operation compared to conventional direct contact packed beds while improving the performance considerably.
SPLIT FLOW RATIO EFFECT

Split flow ratio is an important controlling parameter that influences heat transport rather than oxygen diffusion for the reaction. There is a trade-off between the rate of heat transfer within the porous bed and pressure drop through the bed. Increasing flow rate through the porous bed improves heat transfer between HTF and reaction bed while resulting in considerably higher pressure drop. The split flow ratio of 1/2, 1/3 and 1/4 are selected to determine the storage duration and pressure drop along the bed. The study is conducted for both charge and discharge modes.

In Figure 70, the area-averaged HTF temperature recorded at the reactor outlet is shown for the split ratio of 1/2, 1/3 and 1/4 during the charge mode. The shorter storage duration is observed for higher values of split ratio (SFR). With the increase of the split flow ratio, the direct contact packed bed regime is approached, and the heat transfer rate between the HTF and the porous bed is increased.

![Figure 71: Average HTF temperature at bed outlet for different Split Flow Ratios (SFR) values – Charge mode](image)

The related average inlet pressure is shown in Figure 71 for three selected split flow ratios during the charging mode. As the outlet pressure of the reactor remains constant for all cases,
the average inlet pressure represents the overall pressure drop through the bed. The pressure drop increases as the split ratio is increased. For lower values of SFR, although the storage duration is elongated the average outlet temperature is within 50°C margin with respect to the set temperature when the charging mode is closer to the completion. It can be inferred that compensation of storage duration and outlet temperature may be justified while having a considerable reduction in pressure drop. This trade-off condition should be considered during the design stage.

![Average inlet gauge pressure for different Split Flow Ratios (SFR) values – Charge mode](image)

*Figure 72: Average inlet gauge pressure for different Split Flow Ratios (SFR) values – Charge mode*

For the discharge mode, the average bed temperature is shown in Figure 72 for different split flow ratios. Similar to the charge mode, reducing SFR value results in increasing storage duration, and this increase is higher compared to the charge mode. This stronger influence of the split ratio is due to the lower temperature gradient during the discharge mode.
Average inlet pressure as a function of time is shown in Figure 73 for a split flow ratio. As the split flow rate is reduced from 1/2 to 1/3, the reduction in average pressure drop is considerable. The increase in the storage duration is due to the lower surface heat transfer between the bed and HTF at the outer wall compared to the direct contact heat transfer within the bed. The wall heat transfer rate can be improved via application of some modification within the bed for increasing the bed conductivity. Application of such thermal conductivity improvement measures can improve storage duration and justify using lower SFRs.
HTF ANNULUS CLEARANCE EFFECT

The laminar flow of HTF in the annulus is maintained for all storage cycle. With such constraint, the annulus clearance is adjusted to change the flow velocity within a limited range of laminar flow regime. The effect of annulus clearance is studied for charge and discharge mode of operation. The annulus clearance is reduced into half for $SFR = 1/2$ operation, and the results are provided for both modes of operations. With the increase of HTF flow speed, the charging duration is reduced significantly during the charging mode, as shown in Figure 74. It is demonstrated here that the performance of the reactor could be controlled by the HTF channel dimensions.
Figure 75: Average HTF temperature at bed outlet for different annulus clearance – Charge mode

The average outlet temperature of HTF is provided for the discharge mode in Figure 75. The discharge duration is hardly changed with the increase of the HTF speed, which is mainly due to the lower existing temperature difference.

Figure 76: Average HTF temperature at bed outlet for different annulus clearance – Discharge mode

Annulus flow condition directly affects the rate of heat transfer between HTF fluid and the bed, and thus, any changes in the HTF speed influences the bed performance. Annulus clearance reduction maintains the flow regime within laminar mode as it is assumed the mass
flow rate remains unchanged. The mass flow rate in the annulus is determined via the SFR of the reactor. Thus flow condition within annulus is controlled by both SFR and clearance size.

There is no constraint to maintain flow regime within laminar mode in the annulus, and a higher Reynolds number can be considered. It should be noted that any changes in flow condition in annulus will affect the pressure drop along the channel directly. Having different pressure drop in the annulus and porous bed in a split flow reactor requires a supply of inlet flow at two different pressures for bed and HTF annulus. Handling of air at different pressures is not practical as it makes the air supply and handling system for the reactor more complicated. If the reactor air supply is provided at the same constant pressure, thus there should be another constraint added for channel flow adjustment to keep pressure drop equal to the related drop along the bed. Hence, channel dimension and split flow ratio controlling parameters may not be independent.

With the equal pressure drop constraint, the split flow ratio should be optimized based on reactor performance requirements, and then the HTF channel dimension should be adjusted based on the pressure drop requirement. Elimination of equal pressure drop constraint provides more flexibility in design and control of the reactor while making the air supply system more complicated. In that case, the variable SFR system can be applied to adjust the SFR at an optimum level for different modes of operation and performance requirements.
5 EXPERIMENTAL ANALYSIS

For design of an efficient reactor, the physics of reaction and applicable and compatible construction material for reactor fabrication are very important. In this section for better understanding the physics of redox reaction, experimental analysis were performed using various samples. Compatibility of some candidates for reactor bed fabrication is also investigated experimentally.

5.1 COBALT OXIDE SYSETM

In order to bench marking the characterization of cobalt oxide system, pure cobalt oxide sample was selected for study. The sample is in powder form and no further pretreatment were conducted. The powdered form was selected as for initial analysis, as the particle size effect is supposed to be considered in future studies.

<table>
<thead>
<tr>
<th>DESCRIPTION</th>
<th>SOURCE</th>
<th>PURITY</th>
<th>PARTICLE SIZE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt Oxide</td>
<td>Reade International Corp.</td>
<td>99.9%</td>
<td>400 mesh (38 µ)</td>
</tr>
</tbody>
</table>

Table 9: Pure cobalt oxide sample specification

Thermo-Gravimetric Analysis (TGA) is used to measure the weight variations throughout the test during a storage cycle. TGA analysis measures weight loss during reduction reaction and weight gain during re-oxidation. Differential Scanning Calorimetry (DSC) is used to measure the enthalpy of reaction and the net heat flow measurement for the sample. DSC is used for heat flow measurement to the sample via measuring the amount of heat required to increase the temperature of a sample and an empty reference pan as a function of temperature. TGA and DSC analysis can be conducted in two separate set ups or can be done simultaneously in a combined machine [17–22]. In this study high precision, true differential TGA/DSC instrument is utilized for simultaneous measurement of weight change (TGA) and true differential heat flow (DSC) using
the same sample for the range of temperature from an ambient condition temperature to the maximum operating temperature of 1,000°C [48].

TA Instrument Simultaneous DSC and TGA (SDT) Q600 is used for the experimental analysis. The analyzer uses a horizontal dual beam design with automatic beam growth compensation. Alumina pans are used for both sample and reference. The system is tarred initially with empty samples located at dual cantilever beams. Then the sample is loaded into the sample pan for precise weight measurement. The size of the alumina sample cup was 90µlit that was loaded with 53mg of \( \text{Co}_3\text{O}_4 \) sample. Air is used as purge gas with a constant flow rate of 100 ml/min. Due to the constant airflow rate, the heating and cooling rate is controlled by the heating rate of the furnace. After loading of the system and initial weight measurement, the preheating phase triggered. The furnace is set to preheat from ambient temperature up to 700°C. During the pre-heating stage, some weight loss was detected which is mostly due to moisture loss and degasification of the sample. The lower and upper limit of the temperature is set for 700°C and 1,000°C respectively to ensure reaction completion in each half cycle.

Figure 77: Simultaneous TGA/DSC set up configuration [74]
Complete single storage cycle consist of successive charge and discharge half cycles. The charge half cycle starts at 700°C as initial temperature, ramps up with 10°C/min rate up to 1,000°C, and dwells at maximum temperature for 10 minutes. The discharge half cycle starts right after completion of charge stage in which it ramps down with 10°C/min cooling rate up to 700°C and dwells at that temperature for 10 minutes. The storage cycle ends at the end cold dwelling stage. The next cycle will begin after that with the same temperature variation trends. The single cycle temperature curve is shown in Figure 81.

![Figure 78: Single storage cycle temperature variation details for TGA/DSC analysis – For Cobalt Oxide system](image)

### 5.1.1 SINGLE CYCLE ANALYSIS

The results for single cycle analysis of pure cobalt oxide is provided using the defined temperature trend specifically with 10°C/min heating rate for both heat up and cool down section. At the beginning of the cycle, the weight starts to drop down as the temperature ramps up. The initial minor drop in weight is due to release of moisture and gases as the temperature increase. At the temperature of about 900°C, the forward reduction reaction starts. Due to fast kinetics of
forward reaction, there is a weight loss of about 6.6% within a short time period. There is very little weight variations following the sudden weight change; implying that the reaction has been completed. Similarly, at dwelling period, the system is stable with nearly no weight change.

For reverse reaction, there is no weight change until about 875°C at which the reverse re-oxidation reaction is started. Sudden weight gain because of re-oxidation occurs during that short time period. The rate of weight gain decreases at the end of reaction compared to initial stage and there will be nearly no weight gain at below 800°C. The weight loss during the forward reaction is nearly regained during the reverse reaction that indicates that cobalt oxide has a good reversibility for the heating trend applied for a single cycle.

![Image: Weight changes versus time for single cycle, pure cobalt oxide, TGA results](image)

**Figure 79: Weight changes versus time for single cycle, pure cobalt oxide, TGA results**

The weight variation versus temperature is also provided. The sharp slope of forward reaction compared to the reverse reaction indicates faster kinetics for reduction compared to re-oxidation reaction. The weight change after reduction, during dwelling time and before reverse reaction, is negligible; proving that reaction is completed before reaching the maximum
temperature. The kinetics of reverse reaction are slower at the end of re-oxidation reaction, as depicted in Figure 83. The temperature difference between charge and discharge temperature is clearly indicated in Figure 83.

Figure 80: Weight variation versus Temperature for single cycle, pure cobalt oxide, TGA results

For heat flow analysis, the DSC results are illustrated in Figure 84 for a single cycle. The first drop is for reduction reaction and heat absorption while the next peak is for discharge. The narrow shape of the extrema indicates that the reaction and related heat flow transpired at a short time period. The charge well is narrower compared to the discharge peak, which is due to faster kinetics for forward reaction compared to reverse one. The peak area for both reactions are very close; proving that the stored energy during charging is released in the reverse reaction and overall storage system is nearly reversible. The nearly linear heat flow variations at the rest of the curve is because of sensible heat exchange via temperature variations. The discharge peak ending is not sharp, which is consistent with the slower rates at the end of re-oxidation reaction.
Figure 81: Heat flow variations versus time for single cycle, pure cobalt oxide, DSC results

The heat storage mechanism is clearly shown in heat flow variation versus temperature plot, as depicted in Figure 85. The storage starts with sensible heating - the linear part of charging plot – and sensible heating (storage) continues until the reaction temperature at which the thermochemical storage section is triggered. The formed well represents the enthalpy of reaction for forward reduction reaction. After reaction completion, sensible heating continues until reaching to the maximum temperature. For reverse reaction, the sensible cooling starts as the temperature decreases. It continues until the reverse re-oxidation temperature is reached. As the oxidation reaction starts, the discharge mode is changed to thermochemical as indicated by the peak in heat flow curve. After reaction is completed, the sensible cooling continues.
5.1.2 MULTIPLE CYCLE ANALYSIS

For a single cycle, it was shown that both reactions were completed considering the assigned heating and cooling rate for the pure cobalt oxide sample. Multiple cycle test was conducted to see the cyclic stability and overall system cyclic performance.

5 CYCLES TEST
The weight changes variations for 5 successive cycles is provided in Figure 86. The weight variation shows good reversibility at each cycle. Considered heating trend is acceptable for the system as the both reactions (forward and reverse) are completed before reaching the dwelling temperature. The degradation between cycles is minor and not easily distinguishable in Figure 86.
In weight variation versus temperature plot, it is shown that the weight and temperature follow nearly the same pattern for the reduction period at each cycle with minor changes. The weight changes are minimal when the temperature is further away from the reaction temperature, which proves that the reaction completion is nearly attained before reaching the maximum temperature or the temperature of the dwelling. The slope of the weight changes curve is a measure of the rate of reaction considering the temperature difference from the reaction temperature. The reduction curve is steeper which is due to the high rate of forward reaction. The nearly flat trend of the curve remains the same even for following cycles. The thermochemical energy is stored within a narrow margin of temperature which is desirable for the storage system. The weight change at the dwelling period is very little, and thus indicates that the duration of the dwelling period has a negligible influence on the storage process.
For the re-oxidation period, the trend is slightly different from the reduction one. The weight change versus temperature curve at each cycle follows the same path except during the re-oxidation section. As the sample cools down from the peak temperature, there is nearly no weight variation until the reaction temperature reached and the reverse reaction commences. At each cycle, the re-oxidation launches at the same temperature which indicates that there is a negligible or no shifting occurs for the reaction temperature. There is a slight deviation in the re-oxidation weight change until the large portion of weight gain is completed. It can be inferred that the reverse reaction (re-oxidation) will be more sensitive to the rate of cooling as its rate is slower and the rate of heat transfer within the sample might be comparable with the rate of reaction. The weight-temperature curves of all cycles merge again toward the end of the reaction and follow the same path up to the low-temperature dwelling period. The slope for the last part of the curve is even smaller which implies that the reaction is very slow during this period of the cycle. This could justify that the re-oxidation reaction starts from the outer layer of the sample in which oxygen penetration is faster. After the conversion of the outer layer of the sample, the rate of oxygen penetration is reduced, and thus for the reaction within the inner layers of the sample is much slower. This process can be verified with further study of the surface area, particle size and arrangement variation concerning temperature. The initial weight is completely regained, which proves good cyclic performance of pure cobalt oxide and also sufficient low-temperature dwelling period. The offset between the temperature of charge (reduction) and discharge (re-oxidation) indicates the difference in charge and discharge temperature of the storage cycle or the presence of the intrinsic hysteresis of the reactant.
Figure 84: Weight variation versus temperature for 5 cycle test of pure cobalt oxide sample

The heat flow variation versus time is provided for 5 cycle operation, as depicted in Figure 88. During the reduction (charging) process of the cycle, the heat flow variation is similar for all cycles that proves the similar condition is achieved during all charging cycles. The fast reduction results in a rapid conversion, and thus the release of enthalpy of reaction occurs in a small range of temperature. The rapid discharge results in a valley in the heat flow curve (minimum heat flow) which occurs nearly at the reaction temperature. The valley (minimum) location and its value is the nearly same at each cycle that agrees with the stable performance during the reduction process of the cycle. The approximate linear trend of heat flow during this period shows that the specific heat varies linearly with temperature. The peak (maximum) value of the heat flow at the reduction reaches rapidly up to 2 W/g; validating that the released heat is transferred to HTF rapidly, and thus, the heat transfer within the sample and from sample to air stream is not a
limiting parameter for the system operation. The peak at discharge is reduced and widen, but the changes of total heat flow for each half cycle is almost the same for each cycle.

![Figure 85: Heat flow versus time for 5 cycle test of pure cobalt oxide sample](image)

The existing transition in heat flow variation can be seen in heat flow versus temperature plot. It is shown that the peak value is decreased and shifted for the existing transition during the discharge reaction. The variation in the peak value is dependent on the rate of reaction at a given temperature. The reduction in the peak value matches with the assumption of reduction in reaction kinetics. It is also shown that the reaction proceeds in a longer duration during the later cycles. This behavior can be justified with the limitation formed for oxygen penetration within the inner layers. Thus, the oxygen transfer within the reactor is more critical than heat transfer at the discharge mode. Further study is required for the oxygen transfer process in the reactor for the proper design and optimization of the energy storage module. At the constant temperature condition, there is some heat flow initially, which is due to the continuation of the reaction, but the heat flow curve becomes nearly flat later. The shifting is only
for re-oxidation reaction duration and successive operation do not change the start and end point of the reaction which is a function of temperature.

![Figure 86: Heat flow versus temperature for 5 cycle test of pure cobalt oxide sample](image)

Simultaneous TGA and DSC provide the chance of having both weight variations and heat flow in one plot. The respective point from each curve is marked in Figure 90. Initiation of both forward and reverse reactions are coincident for both heat flow and weight variation curves. For forward reaction, the weight drop duration is shorter than the related heat flow duration indicating that the reaction kinetics of forward reaction is faster compared to the rate of heat transfer. Thus, the heat flow will continue even after the reaction is completed (weight changes stopped). For reverse re-oxidation, the case is different, the weight variation and heat flow begins and terminates nearly at the same point. It means that the re-oxidation kinetics is not faster compare to heat transfer rate and the released heat can be transferred as the reaction transpires. As there is no changes in heat transfer mechanism of the system, it means that the re-oxidation
kinetics is slower compared to reduction and the released heat can be handled without any build up or delay.

Figure 87: Simultaneous weight variation and heat flow for 5 cycle test of pure cobalt oxide sample

Simultaneous weight change, heat flow and temperature versus time is provided in Figure 91. It provides overall picture of the pure cobalt oxide system after 5 successive cycles. The weight variation is stable and there is no considerable changes between two successive cycles. For heat flow, the charge section is the same but there is a shift during the discharge mode of successive cycles. The peak for the discharge curve is reduced while it has been widen. The overall discharge heat seems to be identical but the timing for its release is shifted.
Figure 88: Simultaneous weight variation and heat flow 
Heat flow versus time for 5 cycle test of pure cobalt oxide sample

30 CYCLES TEST

For better analysis of the storage system, the 30 cycle testing has been performed. The weight variation versus time is provided in below Figure 92 and Figure 94. The peak of weight regain is reduced after several cycle but the weight loss is increased. It is mostly like a shifting for weight variation. The overall changes and degradation in weight variation is less compared to the shifting. The overall system performance using a pure sample is acceptable for 30 successive cycles. There is some degradation after multiple cycle but it is less than the overall shifting values.
Figure 89: Weight and temperature variations versus time for 30 cycle test using pure cobalt oxide sample
Figure 90: Weight variations versus time for 30 cycle test using pure cobalt oxide sample

The weight variations versus temperature is provided in Figure 94 and Figure 95. The shifting discussed earlier can be seen in successive cycles. The shifting in weight variation is more dominant for the overall weight changes and degradation is little and even for a pure system showing reasonable reversibility. The trend is similar in all cycles in which there is a transition and the system is approaching to an asymptotic condition after several cycles. The transition rate is higher especially at the initial cycles and it reduces for the next cycles. The asymptotic trend is clearer in the complete cycle plots in which after initial cycles, the system behavior approaches a more stable condition and shifting rate is reduced.
Figure 91: Weight variations versus temperature at selected cycles for 30 cycle test using pure cobalt oxide sample

Figure 92: Weight variations versus temperature for 30 cycle test using pure cobalt oxide sample
5.1.3 MORPHOLOGICAL ANALYSIS

In order to check the coarsening and grain growth after cyclic operation of the system SEM imaging analysis was conducted for the sample before and after completion of five cycles. The results are provided at different magnifications for better understanding the coarsening progress. Although, the comparison is done for samples after only five cycles, there still some grain growth and rounding effects that can be seen between images, especially at higher magnifications. This indicates that there is a grain growth after five cycles. This grain size results in variation in available surface area for oxygen penetration. Thus, the oxygen diffusion rate is expected to be affected, which is more critical during re-oxidation or discharge mode. Rendered images justify the transition detected in the heat flow curves during discharge. However, it should be considered that the weight variations, which is strongly dependent on reaction progress, do not have such variations in the discharge part of TGA results.
Initial sample @ 5k

After 5 cycles sample @ 5k

Initial sample @ 10k

After 5 cycles sample @ 10k

Initial sample @ 20k

After 5 cycles sample @ 20k
5.1.4 TEMPERATURE EFFECT ANALYSIS

In last section, it was shown that the bed morphology changes after a few cycles. Temperature variation during each cycle and the oxygen diffusion may affect the bed condition. In order to isolate the effect of temperature, the sample is heated up to certain temperature and maintained for 3 hours letting the system reach to a stable condition and then cooled down to the room temperature. For storage cycle, the temperature varies from 700°C to 1,000°C and the reaction happen in the interval between 850°C and 900°C. The test temperature is varied with the test. Selected temperatures are 700, 800, 850, 900 and 1,000°C. The 700°C and 800°C are selected as well below the reaction temperature. The 850°C and 900°C are selected right before and after the reaction to see the immediate effect of reaction and 1,000°C is selected as the maximum temperature of the cycle. The SEM results are provided in Figure 100 for the sample maintained at the selected temperature for three hours. The grain coarsening occur at 900°C. The slight variation in the grain size is observed before and after reaction. It can be inferred that the reaction has not made a considerable change in the system morphology. However, from 900°C to 1,000°C,
there is a remarkable grain growth, as displayed in Figure 100d and 100e. It can be inferred that during cyclic operation, the maximum temperature has a profound influence on the rate of grain growth. Induced changes in grain size will reduce available surface area for oxygen diffusion which in turn reduces reaction kinetics. The transient behavior of the reactant after the initial cycle can be justified with the grain growth at maximum temperature.
Figure 94: The SEM pictures of the sample after heat treatment at constant temperature of a) 700°C, b) 800°C, c) 850°C, d) 900°C and e) 1,000°C for pure cobalt oxide sample
5.2 MANGANESE OXIDE SYSTEM

Similar to cobalt oxide system, pure manganese oxide has been selected for pure sample analysis. The sample is in powder form with 40 micron particle size and it is used for analysis without any further treatment. Pure Manganese has several oxides at different temperatures.

Two oxides systems are in the temperature range of above 500°C as below:

\[
MnO_2(s) + \Delta H_r \leftrightarrow Mn_2O_3(s) + O_2(g) \quad @ \quad T_{reaction} \approx 550°C
\]

\[
Mn_2O_3(s) + \Delta H_r \leftrightarrow Mn_3O_4(s) + O_2(g) \quad @ \quad T_{reaction} \approx 900°C
\]

As reaction temperatures for both reactions are considered as high temperature storage case, thus the temperature for analysis is set at 200°C to 1,100°C.

<table>
<thead>
<tr>
<th>DESCRIPTION</th>
<th>SOURCE</th>
<th>PURITY</th>
<th>PARTICLE SIZE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manganese((MnO_2))</td>
<td>Fisher Scientific</td>
<td>99.9%</td>
<td>400 mesh ((38 \mu))</td>
</tr>
</tbody>
</table>

*Table 10: Pure manganese oxide sample specification*

TGA / DSC was conducted for study the kinetics of the pure sample. The charge half cycle starts at 200°C as initial temperature and then it ramps up with 10°C/min rate up to 1,100°C. Then dwells at maximum temperature for 10 minutes. The discharge half cycle starts right after completion of charge stage in which it ramps down with 10°C/min cooling rate down to 200°C and dwells at that temperature for 10 minutes. The storage cycle ends at the end cold dwelling stage. The single cycle temperature curve is shown in Figure below.
5.2.1 SINGLE CYCLE ANALYSIS

The results for single cycle analysis of pure manganese oxide are provided using the defined temperature trend. Initial minor weight losses right after the test initiations are for moisture and volatile removal from the sample. As the temperature reaches 550°C, the first forward reaction is triggered as the weight starts to drop suddenly. The forward reaction of $\text{MnO}_2(s) \rightarrow \text{Mn}_2\text{O}_3(s)$ occurs at this temperature. After completion of this reaction, temperature increases and the second reduction occurs at temperature of about 900°C. The forward reaction of $\text{Mn}_2\text{O}_3(s) \rightarrow \text{Mn}_3\text{O}_4(s)$ occurs during the second weight loss. There is no further weight change up to the maximum temperature. The weight changes for both reactions are very sudden implying fast forward reaction kinetics. After dwelling at high temperature, the system is cooled down with the same rate to the initial temperature. During cooling process, there is a minor weight gain at temperature of 900°C. It shows that the weight gain is for reverse reaction of $\text{Mn}_3\text{O}_4(s) \rightarrow \text{Mn}_2\text{O}_3(s)$, but the portion of the weight gain in reverse reaction is very
small. As there is no further weight changes at lower temperature, it proves that the $Mn_2O_3(s) \rightarrow MnO_2(s)$ is irreversible at least in atmospheric condition.

![Graph showing weight changes versus temperature](image)

**Figure 96: Weight changes versus time for single cycle, pure Manganese oxide, TGA results**

The weight change versus temperature is shown in Figure 107. Overall weight loss after complete one cycle is highlighted which indicates considerable irreversibility in pure system even for a single cycle.
**Figure 97: Weight variation versus Temperature for single cycle, pure Manganese oxide, TGA results**

The heat flow versus temperature is shown in Figure 108. The two wells are for the first and second forward reaction while the minor peak is for portion of reverse reaction at discharge. For a single cycle, it is shown that the system store considerable amount of heat but release small portion of it.
Figure 98: Heat flow variations versus temperature for single cycle, pure manganese oxide, DSC results

Simultaneous weight changes, heat flow, and temperature versus time is shown in Figure 109. The wells and single peaks are coincident with weight losses and regain, respectively.
Figure 99: Combined weight changed, heat flow and temperature versus time for single cycle, pure Manganese oxide system

It was verified that the single cycle of pure manganese oxide powder is mostly irreversible and only small portion of heat stored is recovered. Such storage characteristic is not acceptable for TCES applications. The reaction temperature for reversible portion of the reaction is about $900^\circ C$ together with a good enthalpy of reaction make the system attractive given the irreversibility issue being resolved.

5.2.2 MULTIPLE CYCLES

The cyclic test results of the pure system after seven successive cycles are provided in Figure 110. In weight losses, a small portion of mass participates in a complete storage cycle in which the minor weight fluctuations can be seen. The weight fluctuation after successive cycle is small compared to overall weight loss after the forward reaction of the first cycle.
Figure 100: Weight changes versus time for multiple cycles, pure Manganese oxide system

Heat flow variations show nearly stable response after successive cycles as the portion contributing in storage will complete the reaction and the trend is stable with nearly no changes between cycles.
Figure 101: Heat flow versus temperature for multiple cycles, pure Manganese oxide system

Figure 102: Simultaneous weight changes, heat flow and temperature versus time for multiple cycles, pure Manganese oxide system
In combined variation plots, the heat flow variation at each cycle is evident and the trend with heat flow is nearly the same, as shown in Figure 113. The weight variations are minor compared to overall initial weight loss. The weight changes after each cycle is more evident when the initial weight loss portion is subtracted.

Figure 103: Simultaneous weight changed, heat flow and temperature versus time for multiple cycles, pure Manganese oxide system – Focused on cyclic part
6 CONCLUSIONS

The main objective of this study is the design of efficient and cost-effective packed bed reactor for high temperature thermochemical energy storage. Two promising metal redox systems were considered as storage reactant within the reactor, Cobalt oxide and Iron-doped Manganese oxide systems. Simulations were conducted in three-dimensional packed bed reactors using a complete storage cycle. Flow through a porous medium, heat and mass transport, reaction kinetics were included in the mathematical model to determine the performance characteristics of thermochemical energy storage module using metal redox system. The coupled set of governing equations for transient heat and mass transport within and from/to the reaction bed along with redox reaction kinetics are solved numerically using finite element method handles by commercial software COMSOL. Various packed bed reactor configurations considering heat transfer between solid reaction bed and heat transfer fluid for charge and discharge mode. It was shown that the propagating reaction front split the bed storage into two major parts regarding heat storage mechanism, sensible and thermochemical. The thermochemical portion of heat storage/release is handled only at reaction front in which reaction happen and solid reactant is converted. In regions behind and ahead of reaction front, the bed stores a sensible heat only. Any improvement in heat exchange between solid reactant and porous bed will improve overall reactor performance considerably. The rate of heat transfer is a limiting parameter for the bed performance.

Effect of bed porosity on the unit storage performance was studied for both charge and discharge mode. Increasing bed porosity is expected to improve HTF flow and the heat transfer between solid and gas phase, but reduce storage density of reaction. It was shown that the effect of the bed porosity is more pronounced for re-oxidation (discharge) phase. It was also shown that
the bed porosity plays a dominant role in the reactor performance, and optimized condition should be assigned for the design of the reactor.

In order to investigate the three-dimensional behavior of the packed bed reactor, a rectangular prism type packed bed reactor has been considered. Simulations were conducted for square cross-section reactor with cobalt oxide as reactant agent for high-temperature storage applications. The study conducted for a single storage cycle including the charge and discharge phase separately. It was shown that uniform inlet velocity profile and laminar flow along the porous bed retain its profile along the bed considering the no-flux condition at the sidewalls. It was shown that two-dimensional system approximation is reasonable during complete storage cycle. For an overall increase in storage rates, it is needed to enhance the sensible heat transfer especially at last part of the reactor as the temperature gradient decreases. Decreasing the bed length while increasing the flow cross-sectional area aid in improving the heat transfer. Increasing the bed length reduces overall pressure loss of the bed, but reaching the required outlet temperature becomes challenging. Increasing the bed cross section makes maintaining the uniform inlet velocity be difficult. In order to improve the bed performance, especially the rate of charge and discharge, one of the critical parameters is the bed aspect ratio, which should be considered as a design and optimization parameter.

In order to improve packed bed reactor performance, a split flow design configuration is proposed in which portion of mass flow is passed through the bed and the rest through outer HTF channels. A simple rectangular cross-section packed bed reactor with a large aspect ratio is considered as a benchmark and its performance compared with the same size split flow reactor. Two channels at each side of the reaction bed considered for HTF outer flow as an indirect heat transfer in split flow design configuration.
It is shown that for the charge and discharge mode, the temperature signals at the bed outlet are similar for the simple and split flow reactors. The performance of the reactor is aggravated with a longer conversion time, while the pressure drop along the bed is reduced significantly. The reduction in the pressure drop results in a considerable reduction in the pumping power required for maintaining the flow along the bed. It improves the high-pressure drop concern of the packed bed considerably with a minor loss of performance, especially storage duration.

Parametric study was conducted for a cylindrical split flow packed bed reactor is considered. It was shown that higher Split Flow Ratio values result in faster storage and greater pressure drop along the bed. Lower split flow reactor performance is mainly due to the slower rate of indirect heat transfer between HTF and porous bed. The indirect heat transfer rate can be improved to compensate for performance changes. The proper SFR should be selected considering the trade-off between performance deterioration and improved pressure drop. The HTF channel dimension, another controlling parameter for the split flow reactor, has a strong influence on bed performance. Reduction in channel dimension improves bed performance while increasing pressure drop along the channel and related pressure work. SFR as the main design parameter for a split flow reactor should be selected during the bed design optimization. Heat transfer improvement within the bed provides more flexibility in design and control of the split flow reactors and can be applied for bed design optimization process.

In order to better understand the physics of the reaction and reactant behavior during storage cycle, simultaneous TGA and DSC tests were conducted to evaluate weight variations together with heat flow curves as a function of temperature. A constant heating and cooling rate equal to 10°C was selected for further investigation. The temperature variation trend including the heating/cooling rate and dwelling period was proven to be suitable for pure cobalt oxide TES cycling, as the weight changes indicate that the reaction is nearly completed in each ramp and
there is nearly no weight changes was detected at dwelling condition. For the particular heat flow, it was shown that the cobalt oxide trend of charge is nearly the same for successive cycles, but there was a shifting after a few initial cycles of discharge. A study of coarsening and surface area variation, using SEM imaging, was performed before and after cyclic tests. It was shown that coarsening and grain variations were remarkable even for few initial cycles. It was inferred that heating of pure cobalt oxide at a selected rate and dwelling period is suitable for the storage cycle. Heat flow transition was detected in the discharge part of a few initial cycles, which needs further investigation. There was degradation detected between successive cycles that implies that a more cyclic stability study is required, especially for larger numbers of storage cycles.

Pure manganese oxide in powder form is studied for several storage cycles. It is shown that pure manganese oxide have a considerable irreversible initial mass loss for initial reduction. As temperature increased, secondary partially irreversible reduction occurs. Cyclic operation is based on that a small percentage of the sample. Pure manganese oxide cannot be used in storage application directly and a kinetic improvement using doping is needed.

It was shown that temperature effect on sintering and grain growth is dominant compared to reaction and oxygen diffusion. Formed sintering and grain growth at higher temperature will reduce available surface area and prevent oxygen penetration. Any controlling of sintering process or reducing its rate will results in less reduction in oxygen diffusion rate and consequently reaction kinetics. It was also shown that there is a transient condition after initial couple of cycles. It can be inferred that proper pretreatment, especially the heat treatment should be implemented before the system operation and keep the reactant at more stable form for the rest of cyclic operation.

Proposed modified split flow packed bed reactors can resolve the main drawbacks of conventional direct flow type of reactors and will help commercialization of packed bed reactors.
for large-scale applications. Despite having more controlling parameter for efficient operation of reactor, design optimization should be considered.

6.1 FUTURE WORKS

More comprehensive numerical model can be considered for future simulation. Simplified assumptions such as neglecting the radiation heat transfer between gas and solid phases and system losses from sidewalls can be relaxed for accurate representation of the actual system.

Considered material properties especially thermal conductivity and bed porosity and particle size are based on few available experimental analysis. Further study of material characterization is needed for future analysis.

In this study, a single cycle storage was considered and due to cyclic operation of the system, simulations spanning several cycles is required, in which the effect of property variation especially bed porosity and thermal conductivity between successive cycles should be considered.

There are limited reaction kinetics available developed based on simplified experimental analysis or formulation approximation. For future studies, more accurate kinetic model is required based on different selected samples. The kinetic model should include the effect of cycle operation and cyclic variation of reaction. Oxygen partial pressure variations effect can be studied for future kinetics model developments.

In split flow design, as part of overall heat transfer is handled via conduction between the outer wall and reaction bed, thus the bed thermal conductivity become more critical compared to conventional design. Increasing split flow ration (SFR) factor is preferred for reducing the pressure drop and related required pressure work but it is limited to rate of heat conduction from side channels which is dependent to thermal conductivity of the porous bed. In order to further improve performance of split flow reactors, the rate of heat conduction should be increased.
Increase in rate of heat conduction can be among the future works which can be achieved by increasing the porous bed thermal conductivity or application of extended surfaces for heat transfer enhancement.

Another design configuration for split flow reactor is cross flow system. In cross flow design, the split flow passing normal to the reaction bed, see Figure below. The reactor is located in air flow channel in which the split flow is passed normal to the reactor axis. As the split flow rate is adjustable, the desired range of outlet temperature can be reached.

![Cross flow split type reactor design schematic](image)

*Figure 104: Cross flow split type reactor design schematic*

Similar to parallel flow, heat transfer enhancement can be applied in cross flow design reactors. The heat transfer enhancement can be implemented via increasing the thermal conductivity of solid reactant or using extended surfaces for improving heat transfer. Proper fin
arrangement shall be designed based on temperature profile along the bed and heat transfer requirements.

Based on the type of looping for direct flow and split flow streams, cross flow reactors can be designed as open loop and closed loop. In open loop design, the direct flow after passing through the bed is merged again with the split flow and there is only one stream which return back for the cycle. But in closed loop design, the direct flow and side streams pass through two separate loops, thus the stream condition for each system can be independently adjusted. The schematic for open loop system is shown in Figure below. Flow splitter located at flow channel inlet, split the inflow into cross flow which is passed through the flow channel and direct flow portion which is forced to go through the reaction bed. In open loop system the porous bed outlet is connected to flow channel thus maintaining equal pressure at porous bed and flow channel discharge.

![Flow Diagram](image)

*Figure 105: Open loop cross flow split reactor design schematic*
In closed loop design, the direct flow stream is passing a totally separate loop from flow passing through the channel, see Figure below. Thus the direct flow stream condition such as pressure, temperature, flow rate and oxygen partial pressure can be adjusted independently from channel flow stream. Having more possibility for direct flow condition adjustment provide more controlling parameter for reactor performance tuning for different operating conditions. Beside more flexibility in control, having two separate stream will make the system more complicated and expensive which should be considered for justification of application.

**Figure 106: Closed loop cross flow split reactor design schematic**

For cross flow design, different arrangement for reactors within the flow channel can be considered which provide more efficient design for large scale operation. In Figure below the linear arrangement of multiple reactors in cross flow design is shown. The main concern for multiple reactor configuration is the lack of sufficient temperature gradient for downstream reactors which will affect the rate of convection from the side stream. Proper arrangement for reactor elements within the flow channel is very critical parameter at design stage. In addition,
flow rate of direct flow stream for down-stream reactors can be adjusted to compensate lack of convective heat transfer and maintain uniform heat transfer for each reactors.

Figure 107: Multiple linear arrangement of cross flow split design schematic

Development of more stable reactant is one of the critical path for commercialization of packed bed reactors. Further study of sintering kinetics and bed variations is required. Application of doping, palletization and other stabilization processes can improve system performance considerably.

Most of the study and characterization are conducted at TGA scale in which a very tiny amount of sample is used for experimental analysis. The reactant material response at higher
scales especially for packed bed condition should be studied. It is proposed to analyze the system
response for packed bed scale using tube heater and monitoring the oxygen level for cycle control.
REFERENCES


[29] L. André, S. Abanades, Investigation of metal oxides, mixed oxides, perovskites and


[52] A.J. Carrillo, J. Moya, A. Bayón, P. Jana, V.A. De La Peña O’Shea, M. Romero, J. Gonzalez-
Aguilar, D.P. Serrano, P. Pizarro, J.M. Coronado, Thermochemical energy storage at high
temperature via redox cycles of Mn and Co oxides: Pure oxides versus mixed ones, Sol.

[53] T. Block, N. Knoblauch, M. Schmücker, The cobalt-oxide/iron-oxide binary system for use
as high temperature thermochemical energy storage material, Thermochim. Acta. 577

[54] C. Pagkoura, G. Karagiannakis, A. Zygogianni, S. Lorentzou, M. Kostoglou, A.G.
Konstandopoulos, M. Rattenburry, J.W. Woodhead, Cobalt oxide based structured bodies
as redox thermochemical heat storage medium for future CSP plants, Sol. Energy. 108

investigation of a technical grade manganese-iron binary oxide for thermochemical

[56] A.J. Carrillo, D.P. Serrano, P. Pizarro, J.M. Coronado, Understanding Redox Kinetics of
Iron-Doped Manganese Oxides for High Temperature Thermochemical Energy Storage, J.

thermochemical energy storage: Modulating temperatures of redox cycles by Fe-Cu co-

[58] L. Farcot, N. Le Pierrès, B. Michel, J.F. Fourmigué, P. Papillon, Numerical investigations of

on technical grade manganese-iron oxide in a lab-scale packed bed reactor, Sol. Energy.


reactive gas atmospheres: Probing redox compositions in the decomposition course


[73] G. Azimi, H. Leion, M. Rydén, T. Mattisson, A. Lyngfelt, Investigation of different Mn-Fe oxides as oxygen carrier for chemical-looping with oxygen uncoupling (CLOU), Energy and
VITA

I finished my high school at 1999 and then started my Bachelor’s degree at Tehran Poly Technics University of Technology, right after. I finished my BSc. in mechanical engineering at 2004 and then applied for Master Program. I started my master program at Tehran University in mechanical engineering, Thermal science. I received my Master degree at 2007 and then started my industrial career. I worked in several energy projects especially utility, oil & gas and power generation for about 8 years. Then I decided to refresh my academic background through PhD program. I joined Lehigh University in 2015 to start my PhD in Mechanical Engineering. I was awarded research assistantship from IAC program for all my study at Lehigh running Lehigh University Industrial Assessment Center (IAC). I finished my degree in August 2019 and plan to go back to business with recent degree following my professional career more productive.