Thermochromical Heat Storage for Concentrated Solar Power Based on Multivalent Metal Oxides

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Outline

• Project Description and Objectives
• Challenges
• Reaction Kinetics Improvements
• Solar HX Designs
• Fixed Bed Reactor Modeling and Design
• Rotary Kiln Reactor Testing
• Summary
• Recommendations
Thermochromical cycles utilize a pair of reduction and oxidation reactions (REDOX) to store and release heat.

Solar Cavity Fixed/Moving Bed Reactor

- The heat transfer fluid (HTF) is also the reactant e.g. Air (O₂), CO₂ & H₂O
- Open System - no storage of HTF: oxides
- Closed System - HTF storage required: carbonates, hydroxides

T<sub>high</sub> > T<sub>REDOX</sub> > T<sub>middle</sub> > T<sub>low</sub> > T<sub>amb</sub>

MnO<sub>2x+1</sub> → MO + xO₂ → On sun endo. (charge)
MO + xO₂ → MnO<sub>2x+1</sub> → Off sun exo. (discharge)
A conceptual on sun demonstration design was to be established at the end of Phase III.

**Phase I**
- Down Select
- Experiments
- Economics
- Modeling (DLR)
- Packed Bed

**Phase II**
- Development
  - 400-1000°C Systems
  - Kinetics Improvement
  - Materials Compatibility
  - Cost Reduction
  - Flowsheet Improvement
- TES Reactor (DLR)
  - Modeling & Design
  - Solar HX Design

**Phase III**
- Development
  - >1000°C Systems
  - Prototype Design
  - Simulator Testing
  - Conceptual On Sun Demo. Design

**Timeline**
- 4/1/09
- 5/1/12
Challenges were encountered in Phase I

- Re-oxidation kinetics are slow and incomplete
- Long term kinetics are unknown
- Oxide materials cost can be substantial

Solutions

- Improved oxygen mass transfer
- Developed oxides with stable REDOX properties
- Reduced total materials and system cost

<table>
<thead>
<tr>
<th>TES Reaction</th>
<th>Temp (°C)</th>
<th>Density (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2\text{Co}_3\text{O}_4 \rightarrow 6\text{CoO} + \text{O}_2$</td>
<td>870</td>
<td>844</td>
</tr>
<tr>
<td>$6\text{Mn}_2\text{O}_3 \rightarrow 4\text{Mn}_3\text{O}_4 + \text{O}_2$</td>
<td>900</td>
<td>202</td>
</tr>
</tbody>
</table>
The incorporation of a secondary oxide has been shown to increase electrical conductivity

- Replace the primary cation with another e.g. $\text{Mn}^{3+}$ w/ $\text{Fe}^{3+}$, or $\text{Co}^{2+}$ w/ $\text{Al}^{3+}$
- Oxidation state and atomic size differences resulted in charge imbalances and lattice strain
- Lattice vacancies density is increased which leads to higher oxygen mass transfer through the lattice

- Mixed oxides can potentially reduce raw materials cost (reduce high cost material fraction)
- Long term REDOX performance can be improved by inhibiting grain growth with secondary oxide additions
Manganese Based Mixed Oxides

- Iron oxide was most effective in enhancing re-oxidation of manganese oxide ($\text{Mn}_3\text{O}_4 \rightarrow \text{Mn}_2\text{O}_3$)

- A 16 fold improvement in re-oxidation was obtained
Optimal composition for fast re-oxidation was determined to be MnO$_2$-10\%Fe$_2$O$_3$

- Thermal storage capacity decreases with increasing Fe$_2$O$_3$ fraction
- Highest TES capacity for as processed mixed oxide was obtained at 10\% Fe$_2$O$_3$

*theoretical weight reduction at 3.4%
REDOX properties of manganese-iron mixed oxides improved with thermal cycling

- Reduction approaches the theoretical value (3.4%) in cycled samples with higher iron oxide content
- Optimal composition is estimated to be at 18% Fe₂O₃
Microstructural analysis showed re-crystallization in cycled specimens with high iron oxide content.

<table>
<thead>
<tr>
<th></th>
<th>5% Fe$_2$O$_3$</th>
<th>10% Fe$_2$O$_3$</th>
<th>15% Fe$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As annealed</td>
<td>500 cycles</td>
<td>As annealed</td>
<td>200 cycles</td>
</tr>
<tr>
<td>200 cycles</td>
<td>500 cycles</td>
<td>1000 cycles</td>
<td></td>
</tr>
</tbody>
</table>

- Low iron oxide content leads to sintering.
- Fine grain size helps to improve REDOX properties.
Additions of $\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3$ all resulted in re-oxidation kinetics enhancement.

Fastest re-oxidation kinetics were obtained at 5% $\text{Al}_2\text{O}_3$. 
**REDOX properties of cobalt-aluminum mixed oxide improved with thermal cycling**

- Cobalt-iron oxide showed very stable REDOX properties wrt thermal cycling
- Iron oxide replaces a larger fraction of cobalt oxide
- Cobalt-iron oxide is best suited for concept validation
Two solar HX options were selected based on demonstrated pathways.

### Indirect HX
- **Pros**
  - No solid movement
  - Demonstration ready
- **Cons**
  - Indirect HX (large $\Delta T$)
  - Pressure loss parasitic
  - Possible attrition issue

### Direct HX
- **Pros**
  - Direct irradiation (small $\Delta T$
  - Fast HX
  - Less attrition sensitive
- **Cons**
  - Solid movement
  - Scale up issues
  - Heat retrieval design
A fixed bed reactor model was established based on measured kinetics of cobalt-aluminum oxides

- Baseline design is for a $50\,MW_e$ output
- Parasitic losses due to pressure drop is kept at below 20%

![Graph showing baseline design points]

**Baseline design points**

- $d_p \geq 3$ cm
- $T_{in} - T_{eq} \geq 300$ C
- 8 tanks, $2H=D=8.6$ m
  - $18.75\,MW_{th}$ each
- $T_{out} = 900$ C
Fixed bed reactor performance is limited by pressure drop and mass flow rate

- Reactor has good thermal performance
- Good heat transfer for particle with diameter up to 10 cm
- Mass flow of 55 kg/sec is required
- Total storage capacity is between 120-190MWth
- Design is promising
REDOX of solid metal oxide in a rotary kiln has been validated ON SUN

- **Directly irradiated solar receiver reactor**
  - Housing
  - Reaction chamber
  - Gas outlet
  - Secondary concentrator

On Sun Cobalt oxide REDOX in a Rotary Kiln

- **Proof of concept was successful using pure cobalt and Co-Al mixed oxides**
- **Fast reaction kinetics compared to fixed bed**
The open-cycle flowsheet structure for TC heat storage is similar for all cycles.

On Sun:
- Ambient Air to Receiver
- Charging Thermal Storage
- Steam Generator and Power Turbine
- Return Air Condenser

Off Sun:
- Receiver
- Discharging Thermal Storage
- Steam Generator and Power Turbine
- Return Air Condenser
• Storage cost was reduced by between 20-30% with the use of mixed oxides

- Co-Fe-O
- Mn-Fe-O

<table>
<thead>
<tr>
<th>TES Chemical Storage Cost (Baseload)</th>
</tr>
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<tbody>
<tr>
<td>Co oxide</td>
</tr>
<tr>
<td>140</td>
</tr>
</tbody>
</table>

**LCOE (¢/kWh)**

<table>
<thead>
<tr>
<th></th>
<th>Co-Fe-O</th>
<th>Mn-Fe-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotary Kiln</td>
<td>~17</td>
<td>~10</td>
</tr>
<tr>
<td>Fixed Bed</td>
<td>26</td>
<td>18</td>
</tr>
</tbody>
</table>

- Pressure drop parasitic, high ΔT and mass flow resulted in high LCOE for fixed bed reactor
- Rotary kiln reactor can provide significant cost savings
- Direct irradiation is the only economical means
Summary

- **REDOX kinetics of cobalt and manganese oxides have been greatly enhanced via secondary oxide additions**
- **Long term thermal cyclic testing showed REDOX properties of mixed oxides to be stable**
- **Reactor modeling work showed fixed bed reactors with practical dimensions**
- **REDOX of solid metal oxide in a rotary kiln has been demonstrated ON SUN**
- **TES and LCOE are above current DOE targets**
Recommendations

- Employ the mixed oxide concept for other REDOX applications e.g. syngas production or water-splitting
- Further investigate the use of rotary kiln reactors for solid based thermochemical reactions
- Study the use of other direct irradiation means for materials charging