Fundamentals of a Solar-thermal Mn$_2$O$_3$/MnO Thermochemical Cycle to Split Water

Todd Francis, Michael Schmid, Oliver Kilbury, Casey Carney, Hans Funke, & Alan Weimer

University of Colorado – Boulder
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Overview

Timeline
• Start: 6-1-2005
• End: 5-31-2009
• 40% Complete

Barriers
• AU. High-Temperature Thermochemical Technology
• AV. High-Temperature Robust Materials
• AW. Concentrated Solar Energy Capital Cost
• AX. Coupling Concentrated Solar Energy and Thermochemical cycles

Budget
• Total Project Funding
  $410,000 DOE ($180,00 via UNLV)
  $102,500 Cost share
• Funds received in FY06
  $ 80,000

Partners
Swiss Federal Institute of Technology
University of Nevada – Las Vegas
Objectives

• Research and develop a cost effective Mn$_2$O$_3$/MnO solar-thermal thermochemical cycle through theoretical and experimental investigation

• Based on the above, develop a process flow diagram and carry out an economic analysis of the best process option
Literature Cycle

Concentrated Solar Energy

\[ Mn_2O_3 \rightarrow 2MnO + \frac{1}{2}O_2 \]

Metal Oxide Decomposition

O₂ (vent)

MnO (solid)

H₂ (product)

NaOH

\[ MnO + NaOH \rightarrow \frac{1}{2}H_2 + NaMnO_2 \]

H₂ Liberating Step

Mn₂O₃ (solid)

H₂O (vapor)

\[ NaMnO_2 + \frac{1}{2}H_2O \rightarrow \frac{1}{2}Mn_2O_3 + NaOH \]

Water Splitting

NaMnO₂
Approach

• Thermodynamic assessment of the cycle
• Experimental investigation
  – Investigate Mn$_2$O$_3$ dissociation and mechanism
  – Investigate H$_2$ generating step
  – Investigate ways in which to recover NaOH after H$_2$ generating step
  – Develop alternative methods in which to close the cycle
• Use H2A framework to economically evaluate the cycle
Technical Accomplishments / Progress / Results

• Demonstrated high conversions of Mn$_2$O$_3$ dissociation in an Aerosol Flow Reactor (AFR)
• NaOH removal by vaporization was investigated
• Explored carrying residual NaMnO$_2$ through the cycle
• Testing in progress with mixed manganese oxides for more efficient NaOH recovery
Mn$_2$O$_3$ Dissociation

Experiments are being conducted with a two factor Central Composite Design (CCD)

Temperature (1500 – 1600°C)

Gas Flow Rate (2.5 – 7 slpm)
Mn$_2$O$_3$ Dissociation Results

Significant oxygen generation is seen in situ during a typical experimental run.

Results show increasing temperature and gas flow rate resulted in the highest conversion. This indicates that recombination of oxygen may have a significant effect.
XRD spectra show a strong MnO spectrum and a weak Mn$_3$O$_4$ spectrum. A dotted line helps illustrate that all of the peaks can be seen from the MnO standard and only the major peaks from the Mn$_3$O$_4$ standard.
Dissociation Objective Progress

• Demonstrated high conversions in an AFR
  – Oxygen generation detected in situ
  – XRD confirmed MnO presence
  – $O_2$ analysis showed conversions as high as 82%

• More experimental work to come
  – Investigation of recombination rates
  – Thermogravimetric mechanistic studies
Steps 2 - 3 in Manganese Cycle

- **NaOH separation is the biggest challenge**
  - 10% sodium residual
  - 100 torr H₂

- **Solutions – Currently investigating**
  - Thermal separation of NaOH
  - Processing residual NaMnO₂
  - Mixed manganese oxides

- **More Potential Solutions**
  - Different M-OH sources (Potassium, …)
  - Different separation approaches
Thermal Separation of NaOH

Vaporize NaOH to separate it from Mn$_2$O$_3$

- $2^5_{-2}$ screening design

<table>
<thead>
<tr>
<th>Factors</th>
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<tr>
<td>Sample Mass</td>
<td>Non-Isothermal/Isothermal</td>
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<tr>
<td>Gas Flow Rate</td>
<td>Temperature Hold Time</td>
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A horizontal tube furnace is utilized to conduct experiments

- Pull sample into hot zone at desired temperature and time
Results indicate that a significant amount of NaOH was not vaporized. In addition, a statistical analysis shows that there are no significant effects. This indicates that within the ideal operating ranges selected for the factors that it is not possible to achieve a high vaporization rate of NaOH.

For the vaporization to proceed at an ideal rate a high temperature is required

- Likely problems with a higher temperature
  - Reverse reaction to NaMnO$_2$
  - Partial reduction of Mn$_2$O$_3$ to Mn$_3$O$_4$

**Conclusion:** Vaporization of NaOH is not a viable method to separate Mn$_2$O$_3$ and NaOH.
Processing Residual NaMnO$_2$

High temperature step with NaMnO$_2$

\[ 2\text{NaMnO}_2(s) \rightarrow \text{Na}_2\text{O}(\text{vapor}) + 2\text{MnO}(s) + \frac{1}{2}\text{O}_2 \]

\[ \text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH} \]

- Attempt proof of concept at Mn$_2$O$_3$ dissociation operating conditions
  - Use a Thermal Gravimetric Analyzer (TGA)
Proof of Concept Results

It has been demonstrated using a TGA that MnO is formed at 1500°C

- What form does the sodium take?
- Will the reaction kinetics become faster when diffusion resistances are negligible?

• Future work
  – Study sodium product gas with a mass spectrometer
  – Look at reactions kinetics in an AFR
Mixed Manganese Oxides

Use of mixed metal oxides may potentially improve Mn$_2$O$_3$/NaOH separation

- Research divided into 3 phases
  1. Synthesize Mn$_x$Fe$_{1-x}$O and Mn$_x$Zn$_{1-x}$O
  2. Verify hydrogen production with these mixed oxides
     
     \[
     \text{Mn}_x\text{Fe}_{1-x}\text{O} + \text{NaOH} \rightarrow ? \text{NaMn}_x\text{Fe}_{1-x}\text{O}_2 + \frac{1}{2}\text{H}
     \]
  3. Investigate the mixed oxide – NaOH separation efficiency
     - Compare with Mn$_2$O$_3$ - NaOH separation
Mixed Oxide Identification

Currently mixed manganese oxides are showing mixed oxidation states. It is necessary to produce these with only the +2 oxidation state.

Next steps
- Calcine with reducing atmosphere
- Reduce existing mixed oxide into lower oxidation state
  - This will verify hydrogen production

Sol-gel precipitation reaction in basic solution from metal salts
- Calcination of precipitate (air, N2)
Future Work

• On sun testing of Mn$_2$O$_3$ dissociation
  – Reactor design and construction
  – Materials testing
    • Alumina
    • Silicon Carbide

• Continue future work plans detailed earlier in the presentation
  – Mn$_2$O$_3$ decomposition
  – Processing residual NaMnO$_2$
  – Mixed manganese oxide investigation

• Update H2A analysis with new experimental results
Conclusions/Summary

Significant experimental progress has been made with the Mn$_2$O$_3$/MnO cycle

- High conversions for Mn$_2$O$_3$ have been demonstrated
- Potential solutions for NaOH recovery have been identified and investigations have begun
- Studies in alternative ways to close the cycle are ongoing
  - Mixed manganese oxides