Fundamentals of a Solar-thermal Mn_2O_3/MnO Thermochemical Cycle to Split Water

Todd Francis, Freya Kugler, Oliver Kilbury, Paul Lichty, Melinda Channel, Casey Carney, Hans Funke, Roger Rennels & Alan Weimer

University of Colorado – Boulder

11 June 2008

Project ID No. PDP1

Overview

Timeline

- 6-1-2005
- 5-31-2009
- 70%

Budget

•**Total Project Funding**

$797,702

$199,426 Contractor share

•**Funds received in FY07**

$ 420,000

•**Funds received in FY08**

$ 102, 298

Barriers

- U. High-Temperature Thermochemical Technology
- V. High-Temperature Robust Materials
- W. Concentrated Solar Energy Capital Cost

Partners

Swiss Federal Institute of Technology

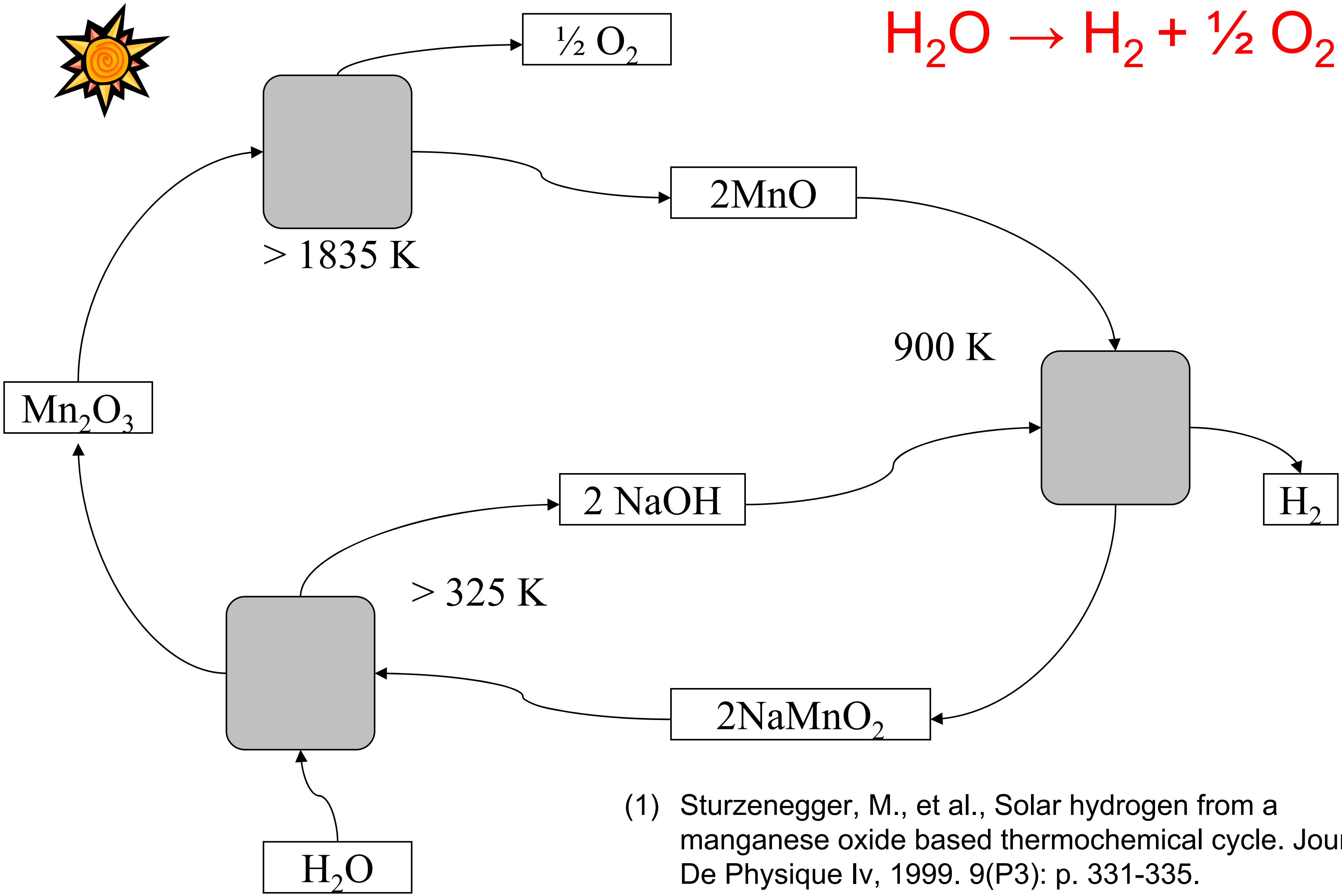
University of Nevada – Las Vegas

Objectives

- Research and develop a cost effective Mn_2O_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

Mn_2O_3/MnO Cycle

$$H_2O \rightarrow H_2 + \frac{1}{2} O_2$$



(1) Sturzenegger, M., et al., Solar hydrogen from a manganese oxide based thermochemical cycle. Journal De Physique Iv, 1999. 9(P3): p. 331-335.

Approach

- Thermodynamic assessment of the cycle
- Experimental investigation
  - Investigate Mn_2O_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

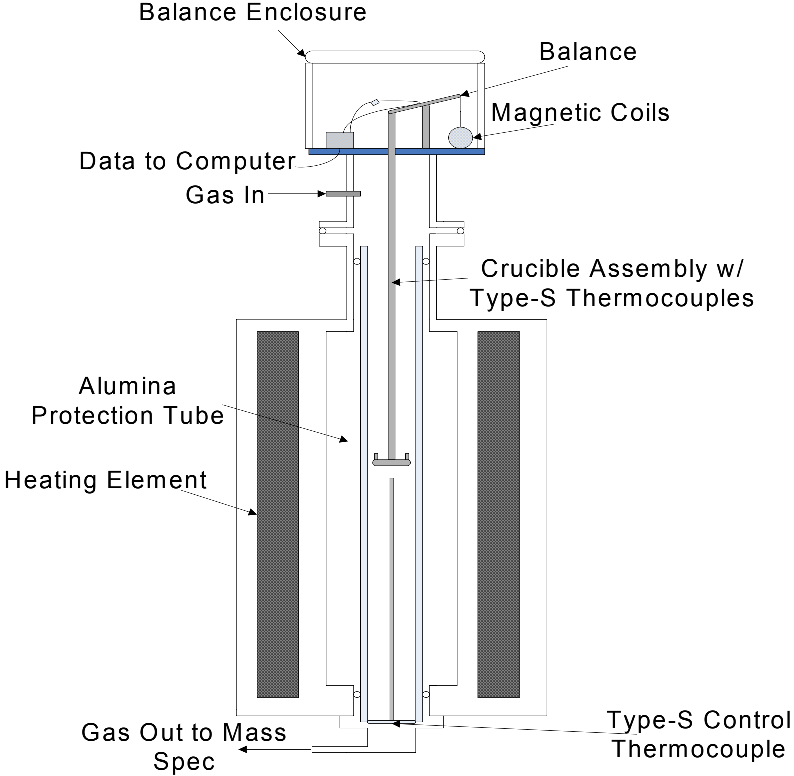
Technical Accomplishments / Progress / Results

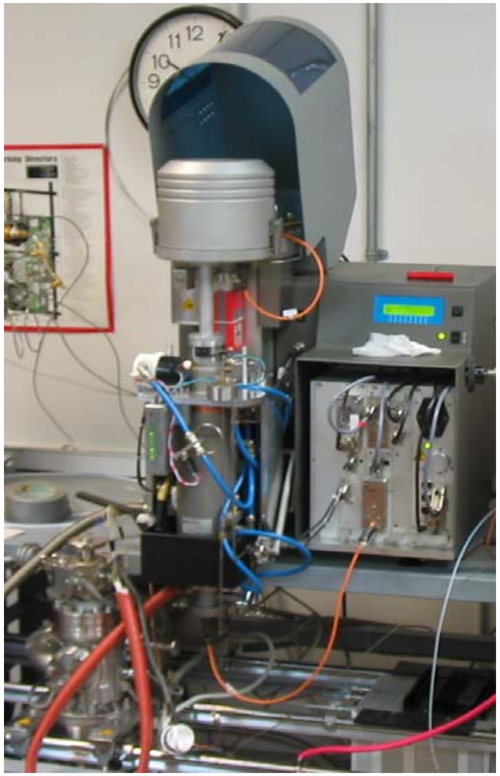
- Found a probable mechanism for manganese oxide dissociation
- Used mixed manganese oxides to study H_2 generation and NaOH recovery
- Investigated solid state synthesis of mixed oxide production
- Completed initial PFD

Reaction Kinetics From a TGA

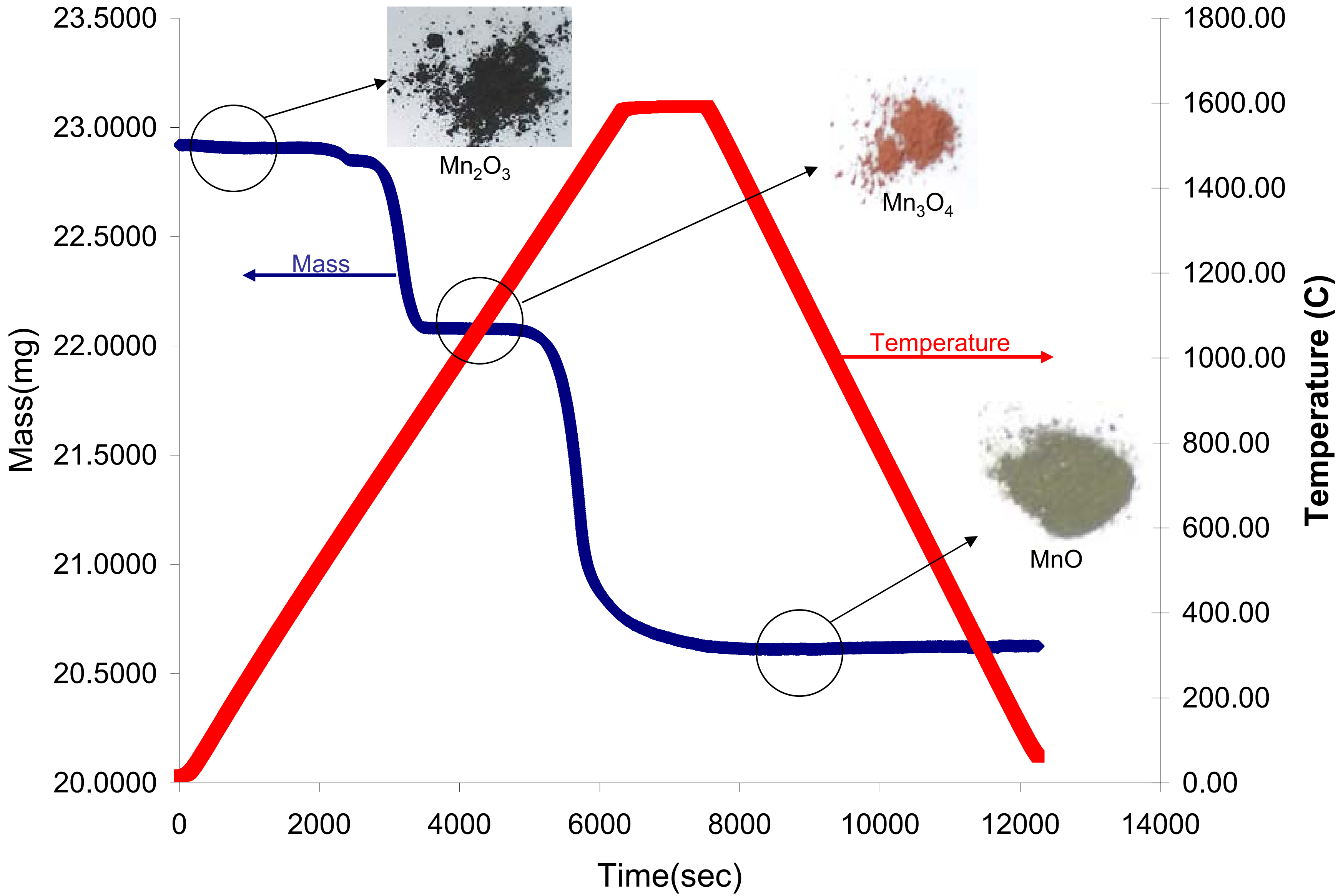
- Used TGA to understand mechanism and derive initial reaction kinetics
  - Reaction proceeds in two steps

$$3Mn_2O_3 \rightarrow 2Mn_3O_4 + \frac{1}{2} O_2 \rightarrow 6MnO + O_2$$

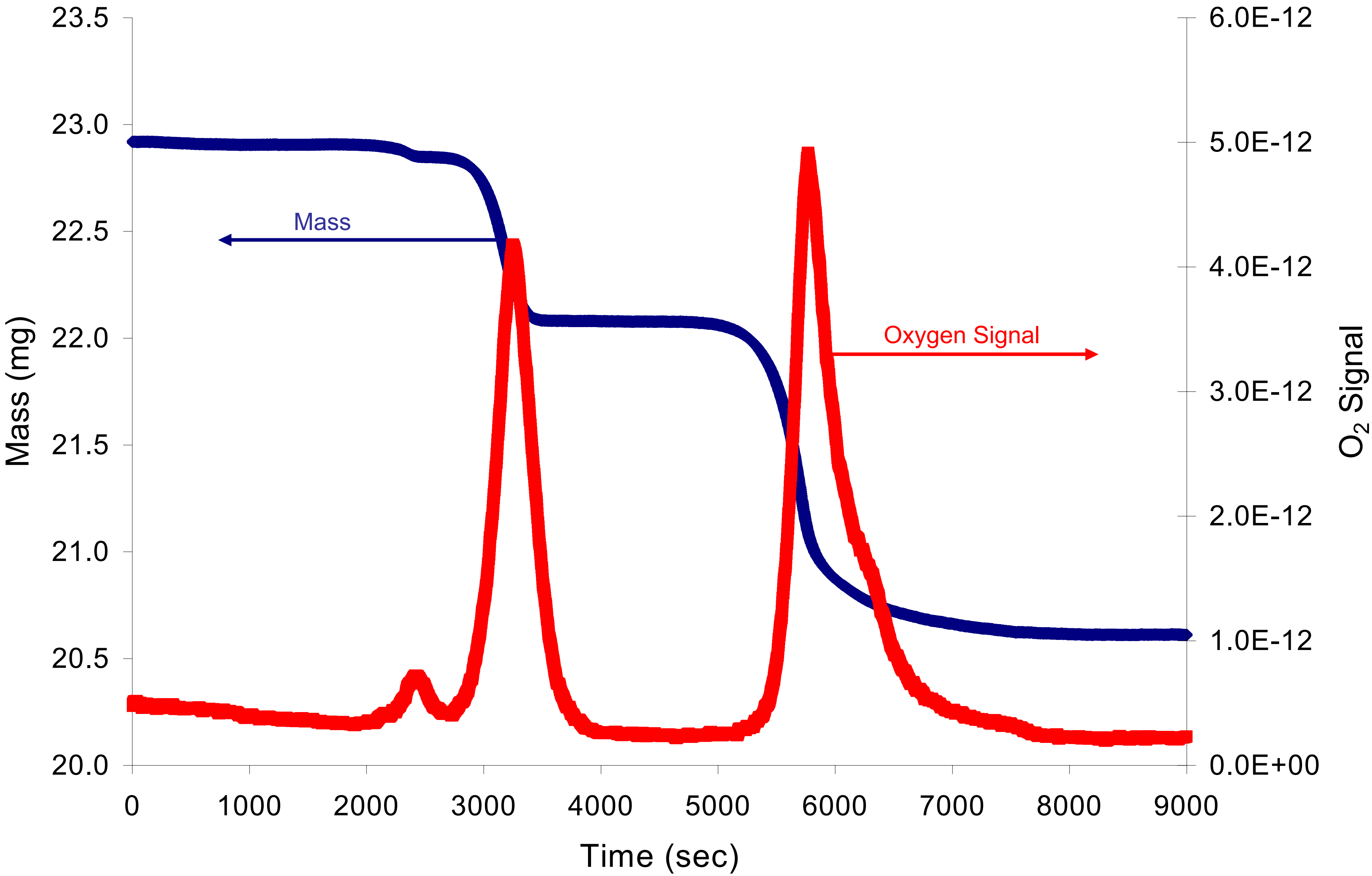




TGA Mass Trace



Mass Trace with Mass Spec Data

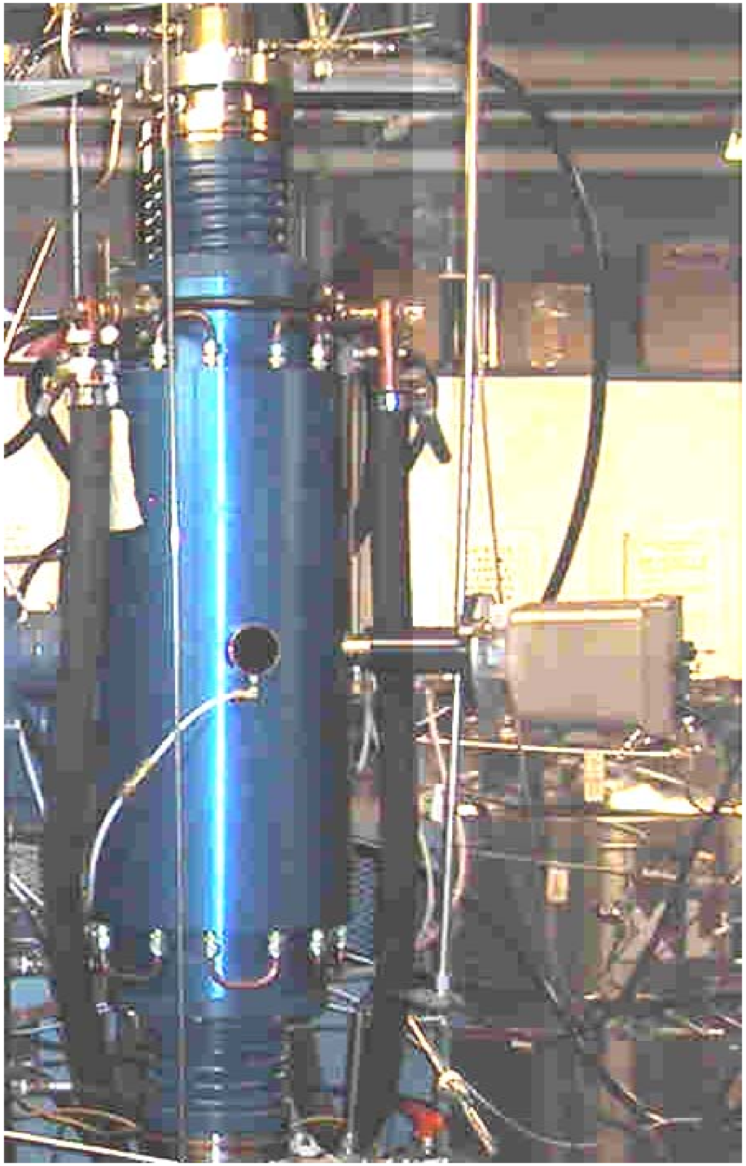


TGA Mechanism Progress

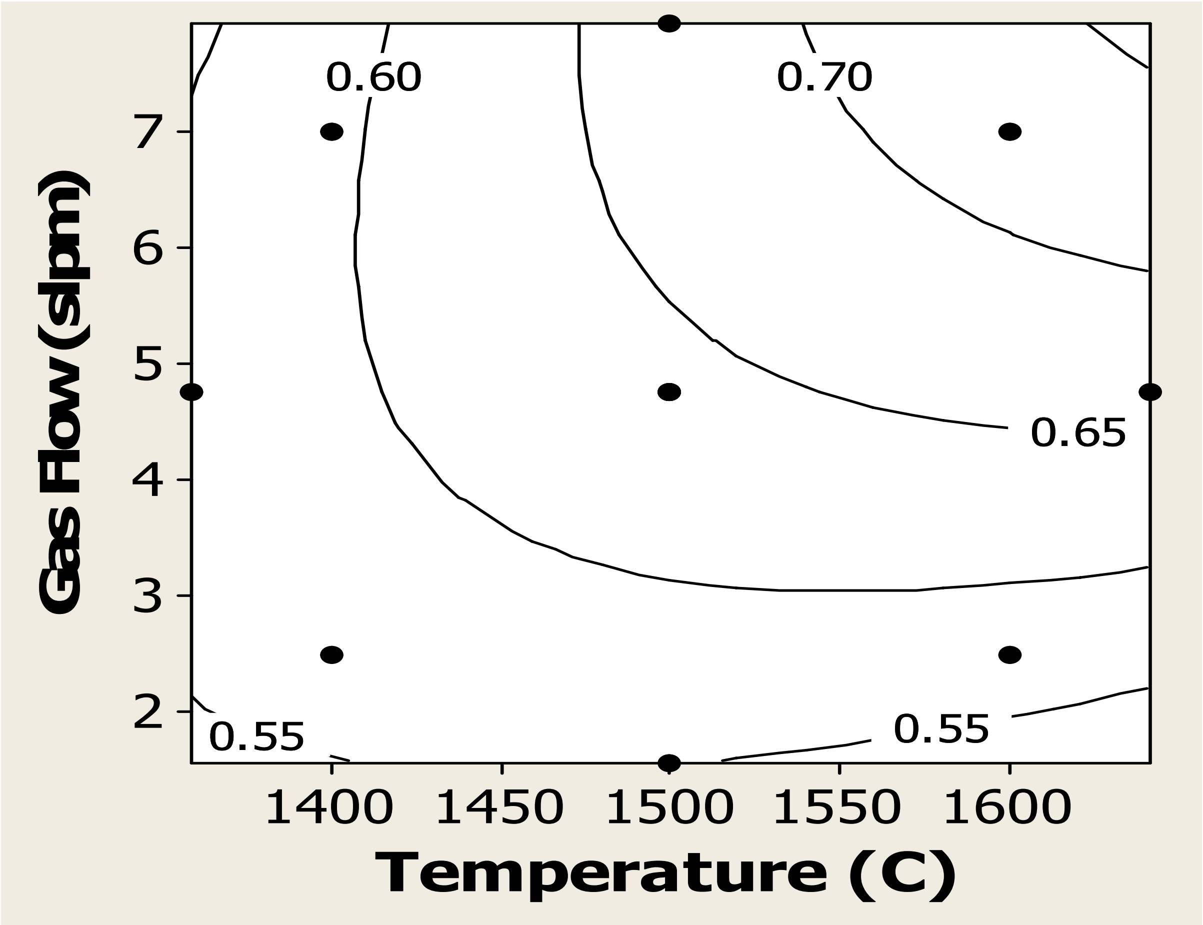
- An Avrami-Erofeev type mechanism is hypothesized to control both reactions
  - Parameters were calculated
- Hypothesized diffusion resistances control part of the $Mn_3O_4 \rightarrow 3MnO + ½O_2$ transition

Mn_2O_3 Dissociation in an AFR

- Study manganese oxide dissociation in an Aerosol Flow Reactor
  - Diffusion resistances are limited
  - Reactor ideal for high volume processes
- Understand how oxygen can affect the reaction

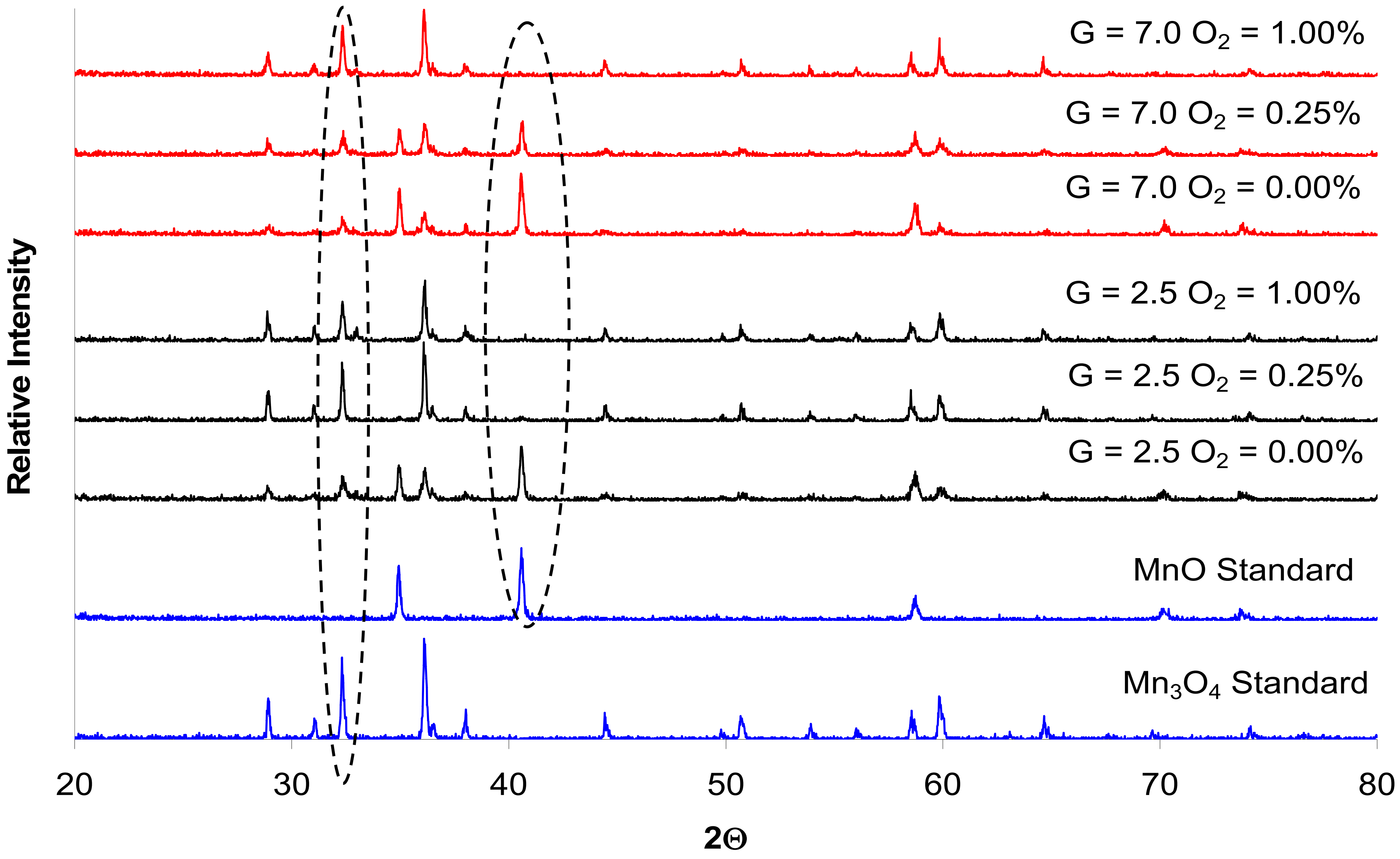


Reactor Conversions



Conversions ranged between 50 and 75%. Highest conversions achieved with high temperature and gas flow rate.

XRD Spectra 1400 °C



Reactant Regeneration Step

$$2\ \alpha\text{-NaMnO}_2 + H_2O \rightarrow 2\ NaOH + Mn_2O_3$$

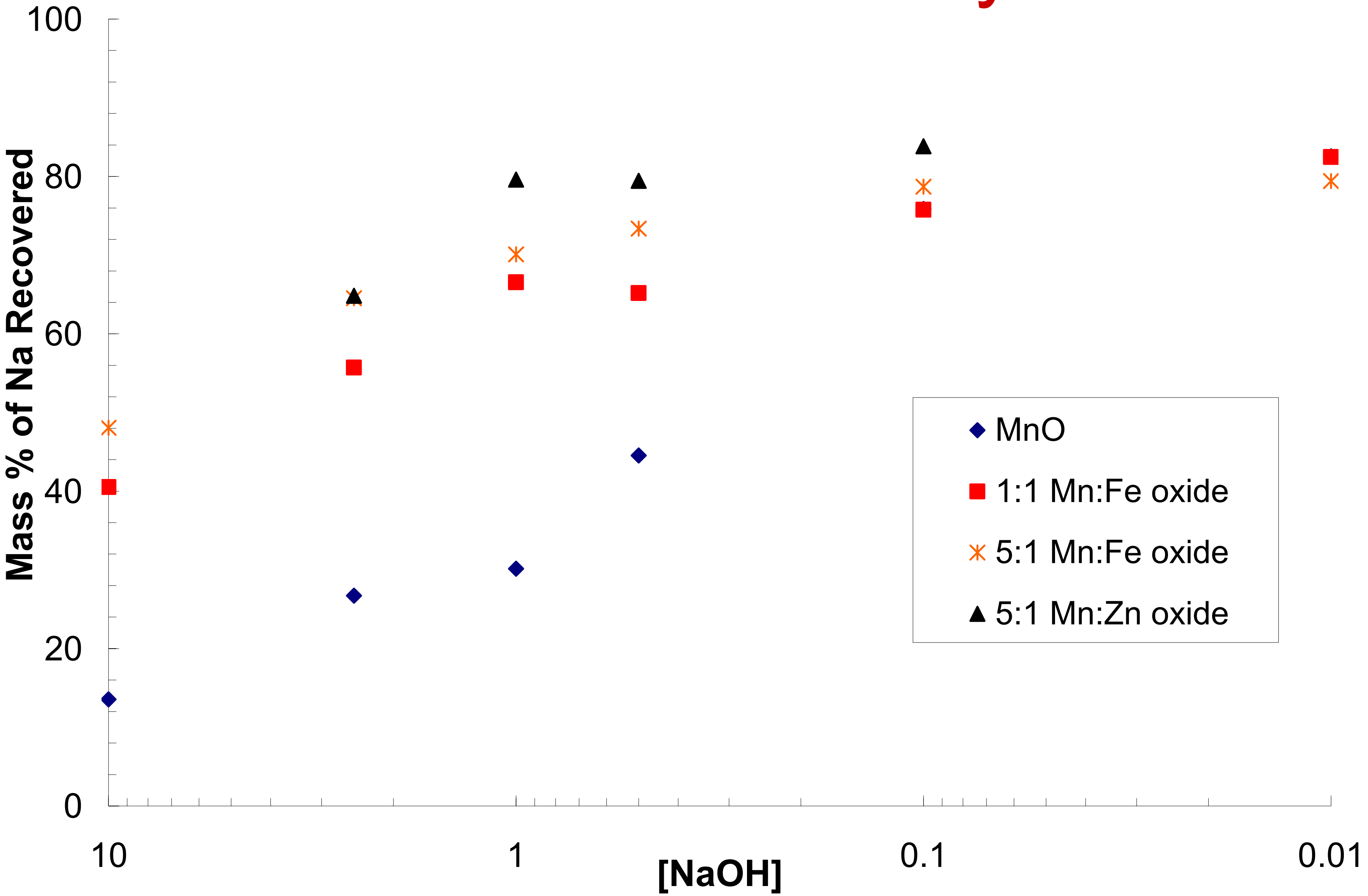
Issue: NaOH recovery

- 80 – 90% of NaOH can be removed with H_2O
- High energy requirement

Solution: Mixed Manganese Oxides

- Rationale: Iron-analog $NaFeO_2$ can be hydrolyzed completely
- Test ratios Mn/Fe and Mn/Zn oxides

NaOH Recovery

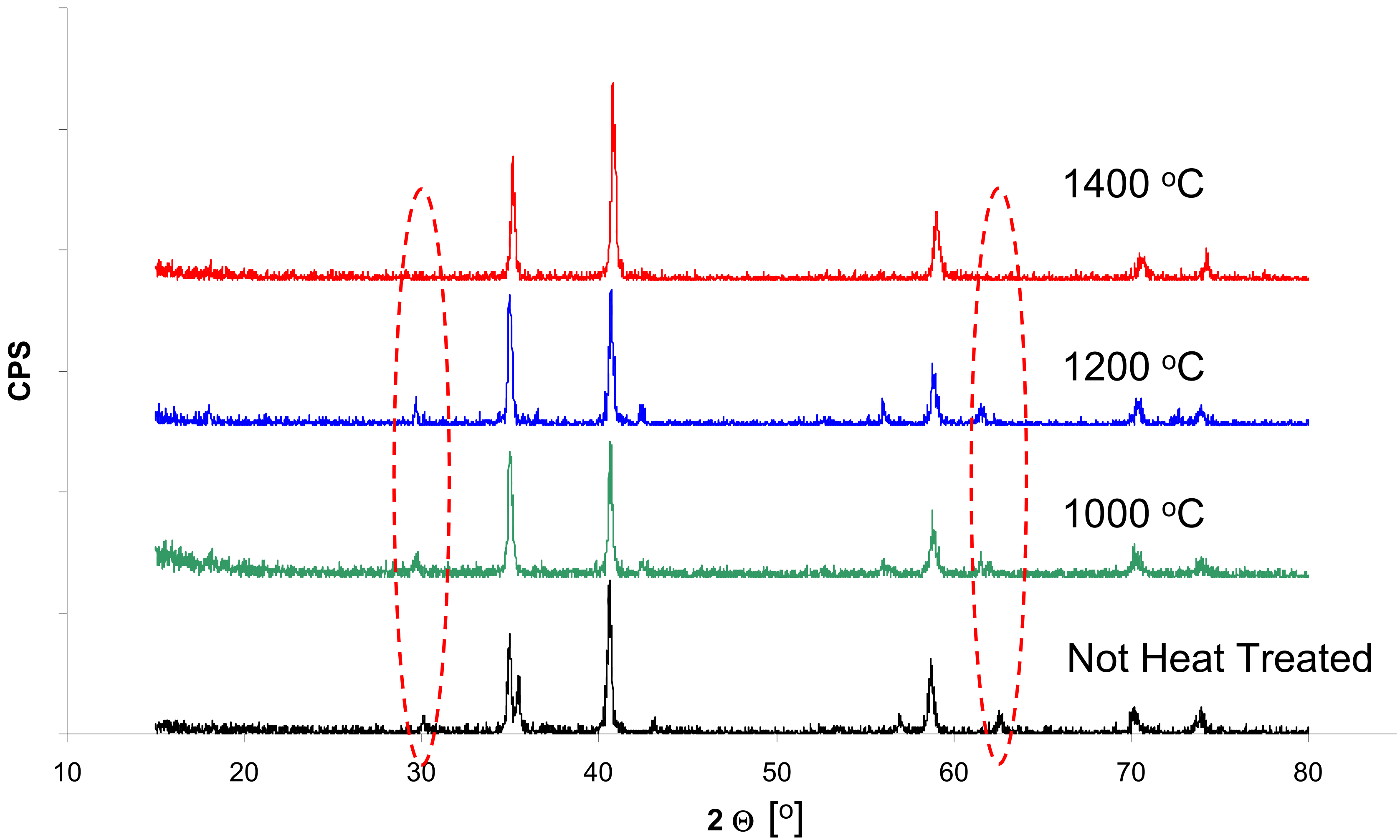


Synthesis of Mixed Metal Oxides

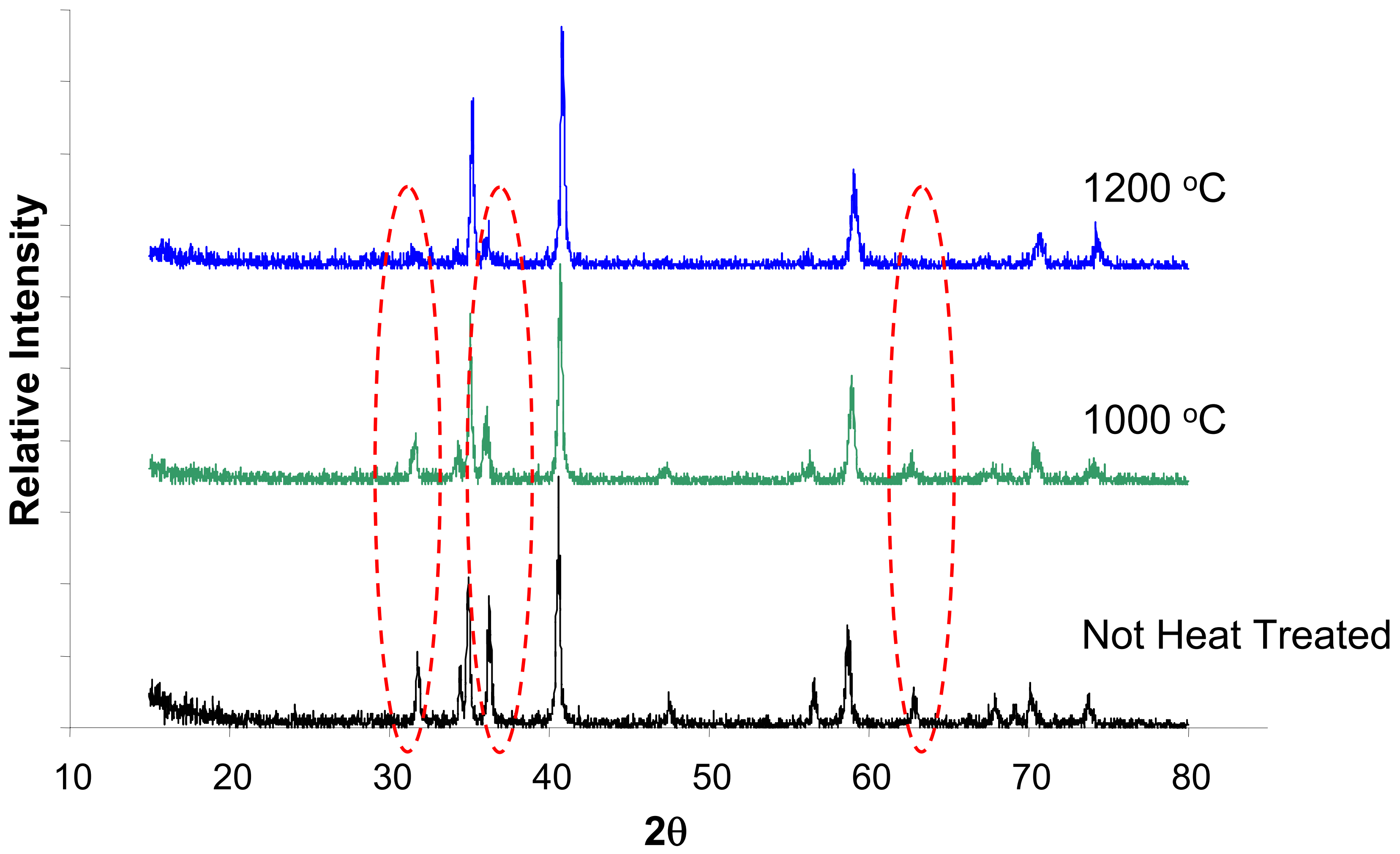
- **Solid state synthesis**
  - Provides control over composition
  - High temperature required
  - Large quantities easy to synthesize
  - Simple procedure

- **Method**
  1. Mill stoichiometric amounts of metal oxides
  2. Heat treat

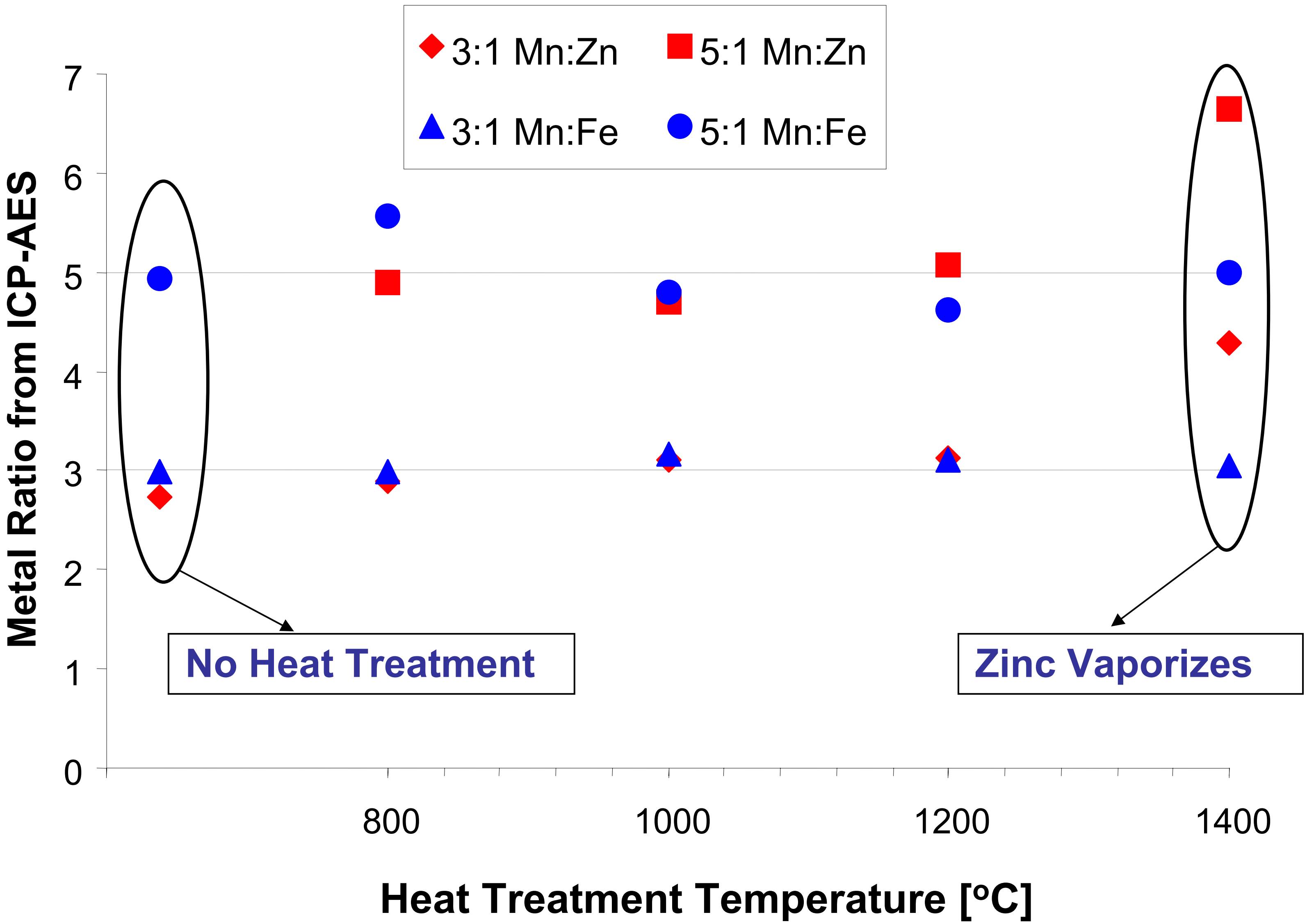
XRD Spectra of $Mn_{0.75}Fe_{0.25}O$



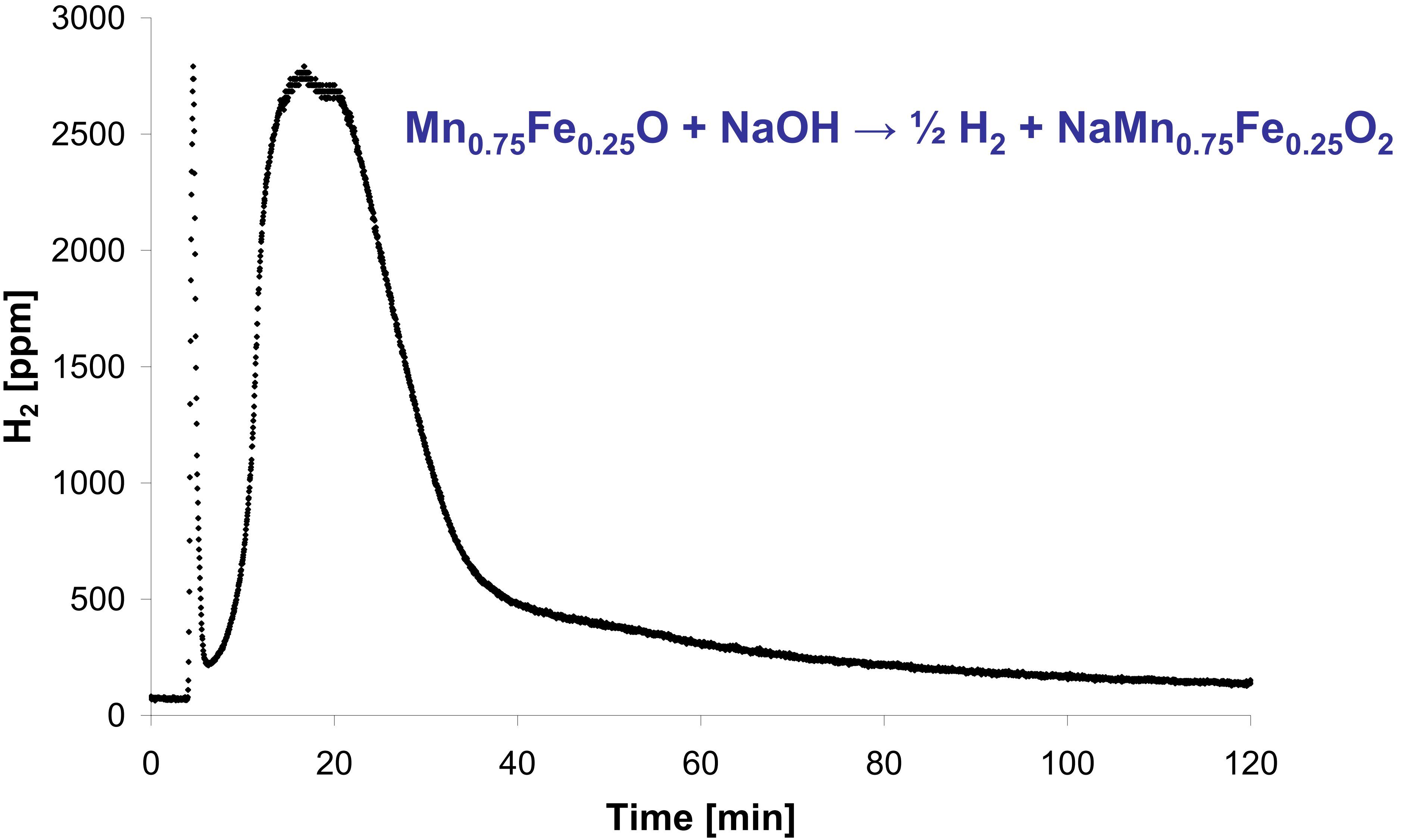
XRD Spectra of $Mn_{0.75}Zn_{0.25}O$



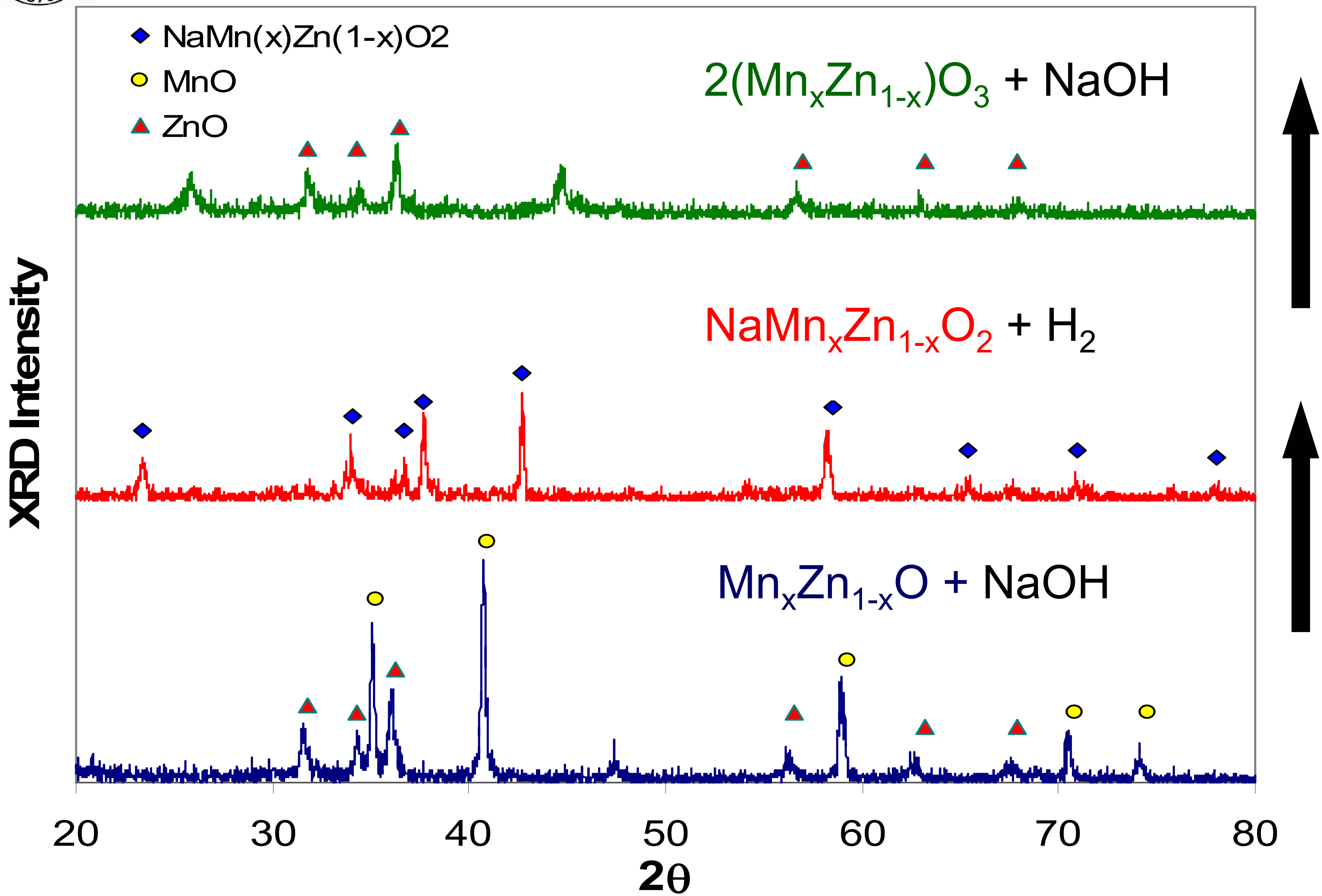
ICP of Mixed Mn Oxides



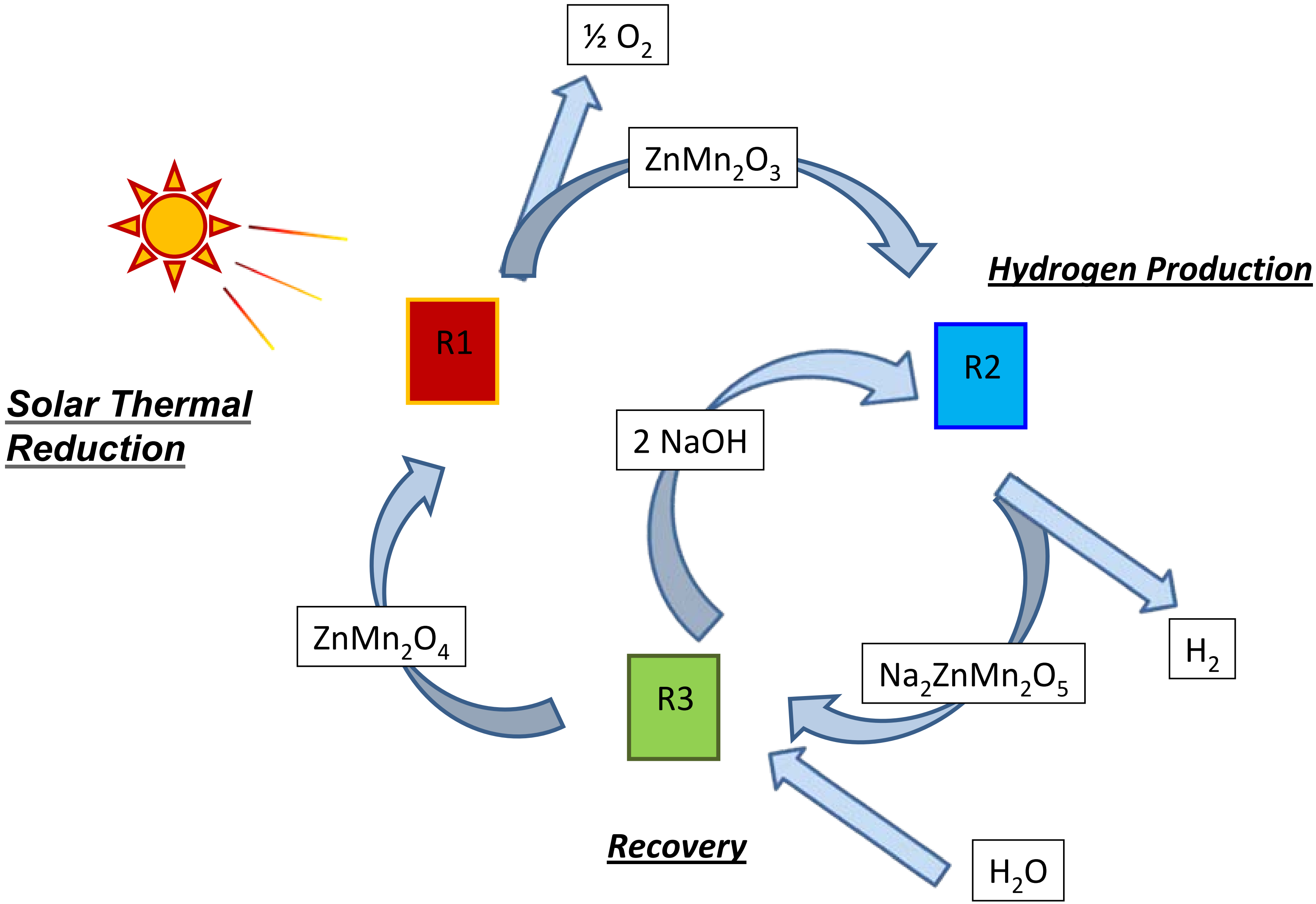
H_2 Generation From Mixed Oxide



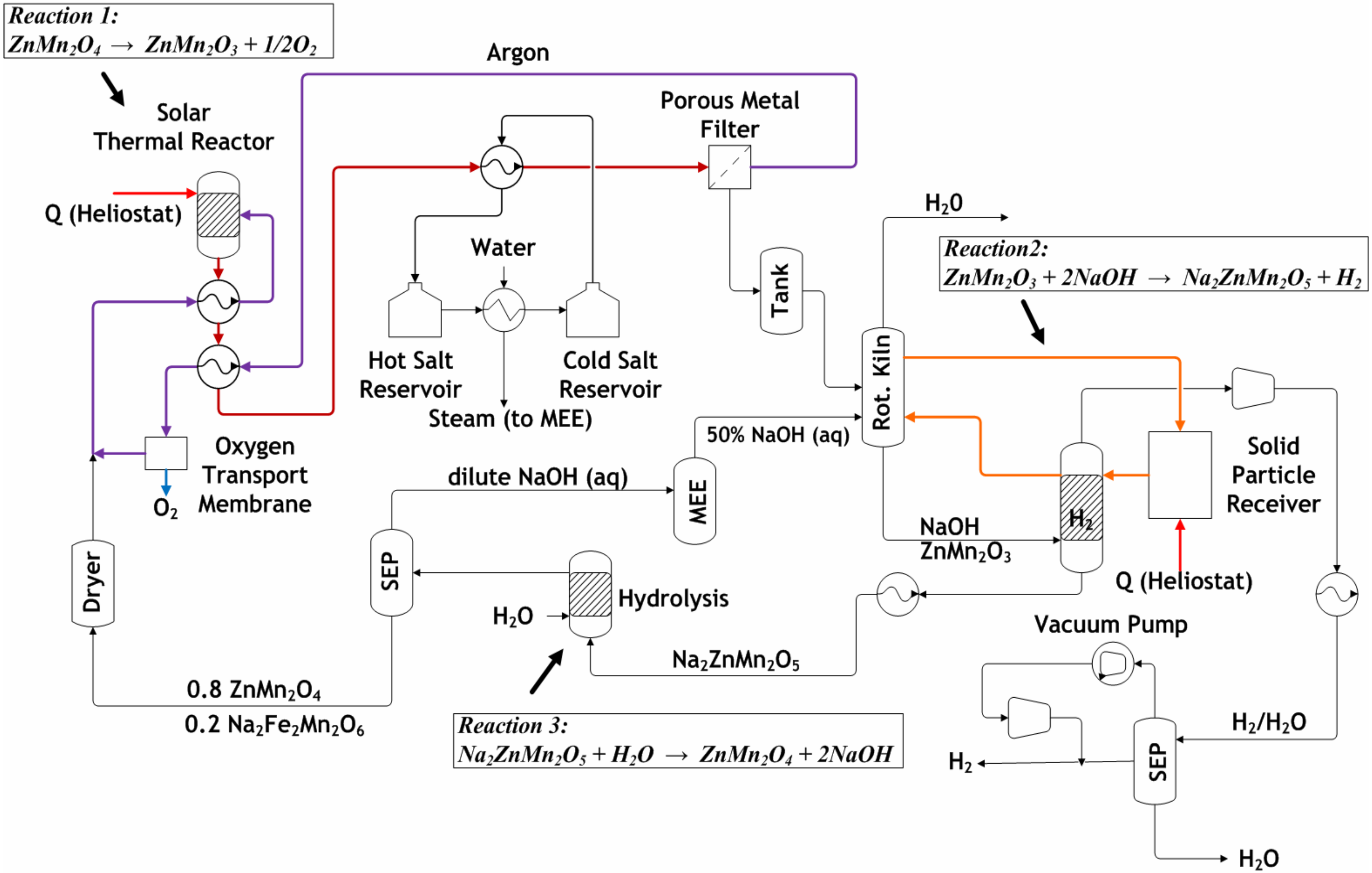
2nd and 3rd Steps Demonstrated



Mixed Metal Oxide Solar Thermal Cycle



$ZnMn_2O_4/ZnMn_2O_3$ – Process Flow Diagram



H2A Specifications

- Produce 100,000 kg H_2 per day at 300 psi
- 2012 startup at current inflation rate 2.4%
- 40 year economic analysis period
- Hydrogen cost goal of $2-3 per kg

Economic Sensitivities

Carrier gas (Argon vs. Air)

- Best Case: Oxygen Transport Membrane

Heat recovery (Molten Salt)

- Heat feed stream
- Send steam to multiple effect evaporator
- Drive turbine to make electricity

NaOH recovery

- Improve chemistry to reduce water requirement

Compression

- Vacuum pump to draw off H_2

Future Work

- Testing of $Mn_{2-x}Zn_xO_3$ dissociation
  - Evaluate whether reaction mechanism is the same as Mn_2O_3
- Continue work on mixed manganese oxide synthesis
- Gain better understanding of H_2 generation with mixed manganese oxides
- Update process flow diagram with new results to reassess the $Mn_{2-x}Zn_xO_3$ /$Mn_{1-x}Zn_xO$ cycle

Conclusions/Summary

Significant progress has been made with the Mn_2O_3/MnO cycle

- A reaction mechanism has been hypothesized for Mn_2O_3 dissociation
- Mixed manganese oxides have been shown to improve the product recovery steps
- Experimental investigation using a mixed manganese oxide is ongoing
  - Mn/Zn Oxide