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

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Overview

Timeline

- 6-1-2005
- 5-31-2009
- 25% completed

Budget

- Total Project Funding

  $330,000 DOE ($180,00 via UNLV)

  $ 82,500 Cost share

- Funds received in FY05

  $ 110,000 ($60,000 via UNLV)

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

Partners

Swiss Federal Research Institute (Aldo Steinfeld)

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

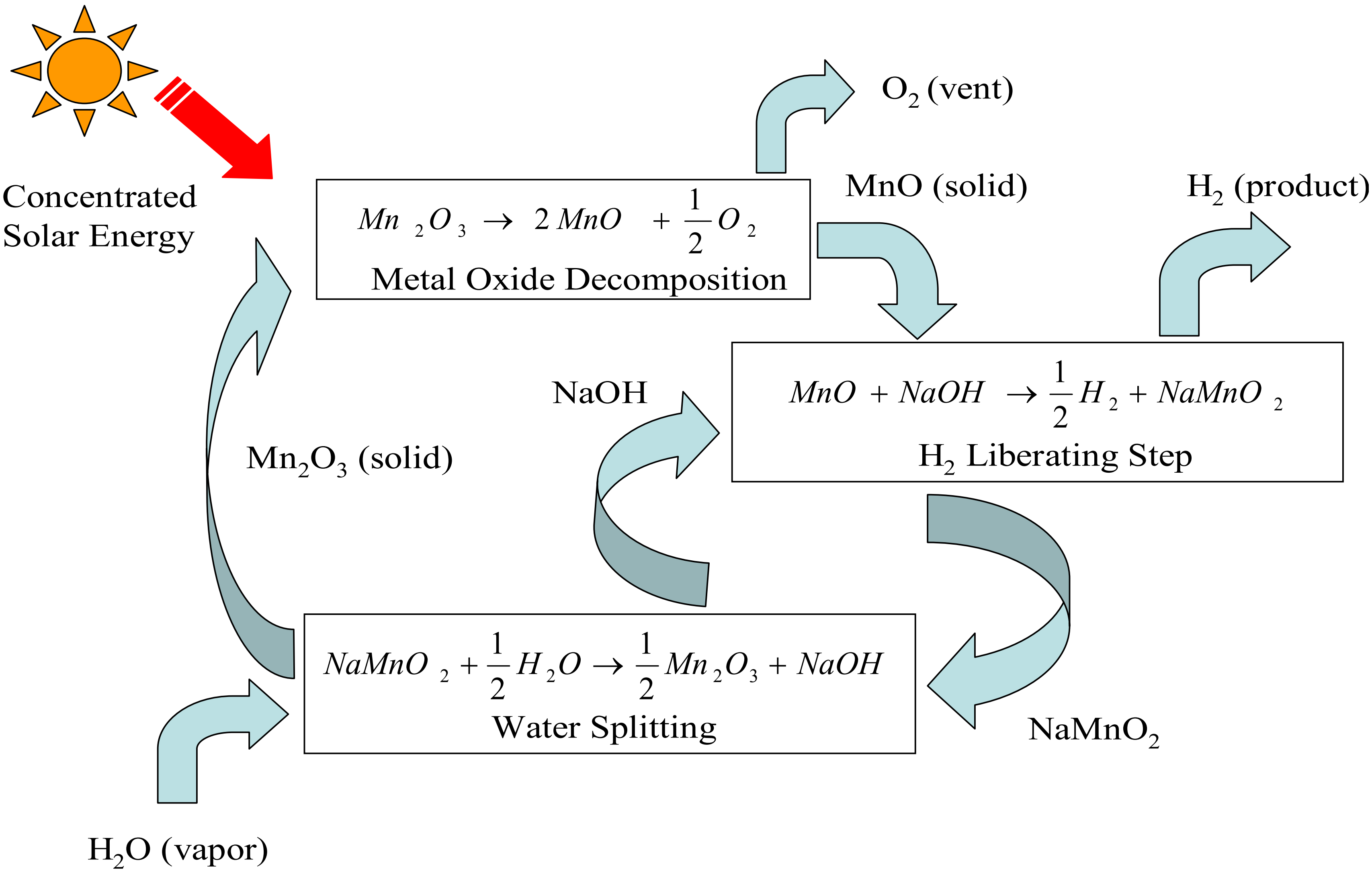
Approach

- Develop an initial process flow diagram based on available published information regarding the cycle; simulate integrated process; identify key areas for research and development
- Develop and carry out an experimental plan to evaluate the feasibility of all steps in the cycle
- Carry out CFD modeling and simulation to develop an understanding of solar-thermal reactor transport mechanisms
- Analyze cost and efficiency metrics for integrated cycle performance; provide final process flow diagram based on best scenario

Technical Accomplishments/ Progress/Results

- Literature surveyed
- Preliminary flow sheet developed based on literature information (conventional processing)
- Very preliminary economics carried out
- Preliminary key areas identified for research (based on preliminary simulations and economics)
- Experimental work plan underway for major reactions

Literature Cycle



Mn_2O_3/MnO Solar Cycle

- Advantages
  - Relatively low temperature (~1650 ^oC, or lower)
  - All solid/liquid species → no recombination
  - Can be performed in air
- Disadvantages
  - Corrosive nature of NaOH
  - Energy-efficient separation of NaOH/Mn_2O_3 difficult
  - Three step cycle has decreased efficiency
  - Multiple oxide species involved

Goals

- Perform high temperature reaction with small particles in an aerosol flow reactor
- Verify hydrogen formation when NaOH is added to MnO at elevated temperatures
- Optimize hydrolysis and separation of reaction products for recycle into 1st and 2nd steps
- Identify kinetics/mechanism

Key Challenges

- Solve separation problem in 3rd step for favorable economics: Currently 1 molar solution for 90% leaching necessary!
- Investigate effect of sodium carry-over to high-temperature reaction (10% residual)

Preliminary Flowsheet Development

- Based on literature only, a preliminary PFD was developed for the Mn_2O_3/MnO solar-thermal thermochemical cycle
- Only the most obvious and conservative unit operations were considered for this initial pass

Process Design Premises

- Mn_2O_3 dissociated (80%) in air at 1835 K
- NOx considered formed and dealt with via 640 K SCR
- Molten salt heat recovery system considered
- H_2 production step carried out at reduced P; H_2 removed to shift equilibrium to right (100%)
- 90% conversion assumed on water splitting step
- Multi-effect evaporator considered to recover NaOH
- H_2 supplied to pipeline at 300 psig

Simplified Process Flowsheet:

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

Water Splitting

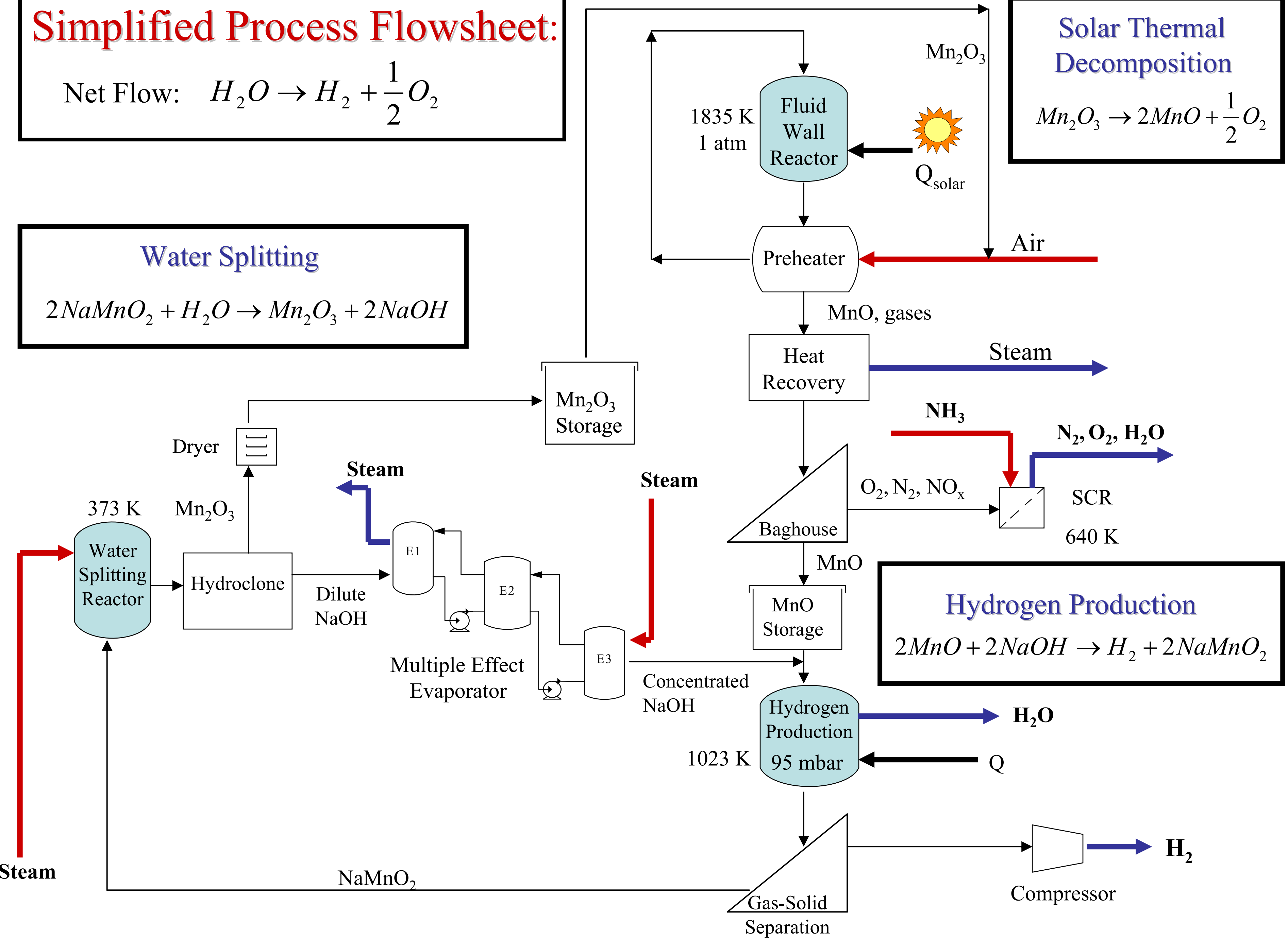
$$2NaMnO_2 + H_2O \rightarrow Mn_2O_3 + 2NaOH$$

Solar Thermal Decomposition

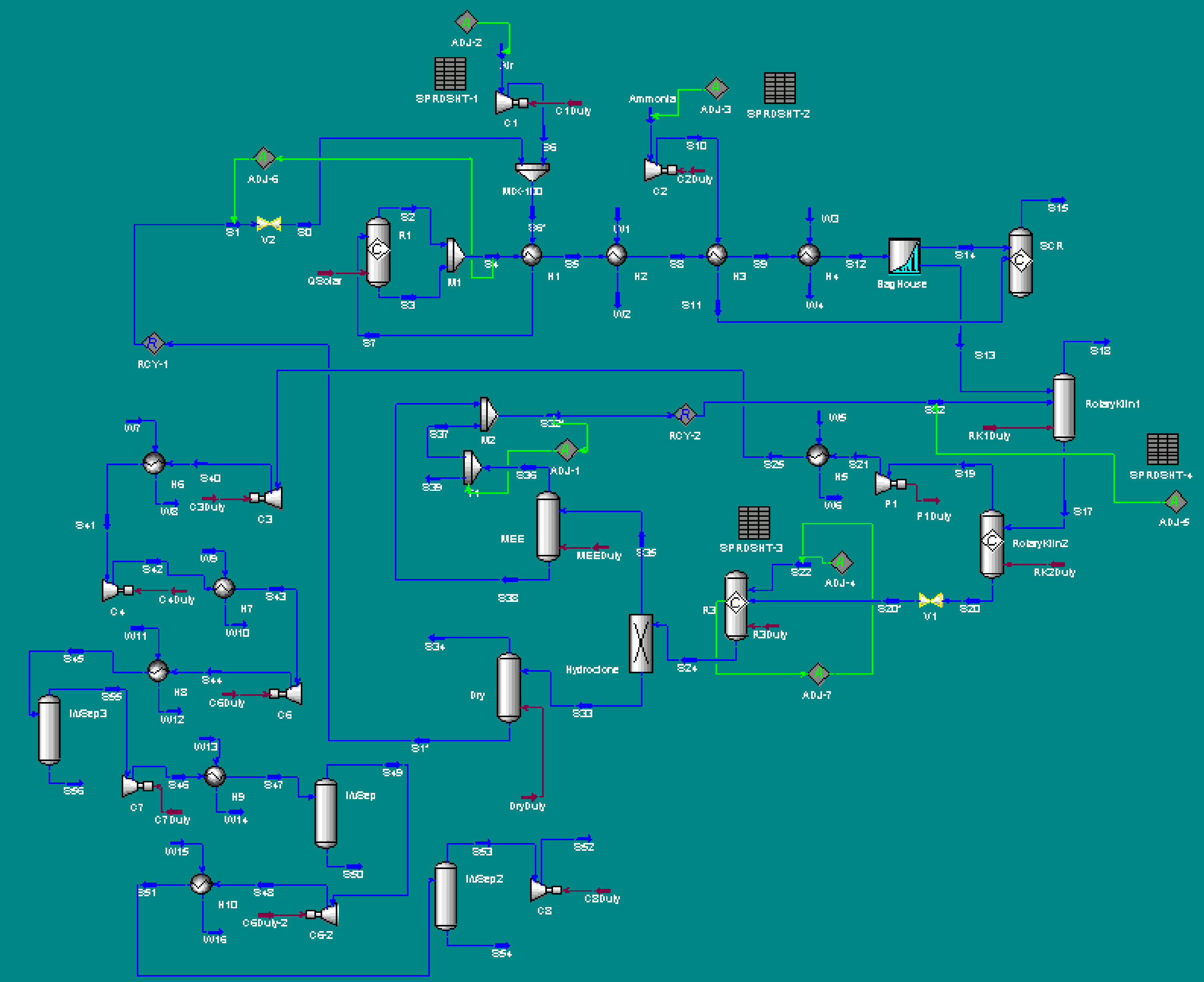
$$Mn_2O_3 \rightarrow 2MnO + \frac{1}{2}O_2$$

Hydrogen Production

$$2MnO + 2NaOH \rightarrow H_2 + 2NaMnO_2$$



Process Simulation



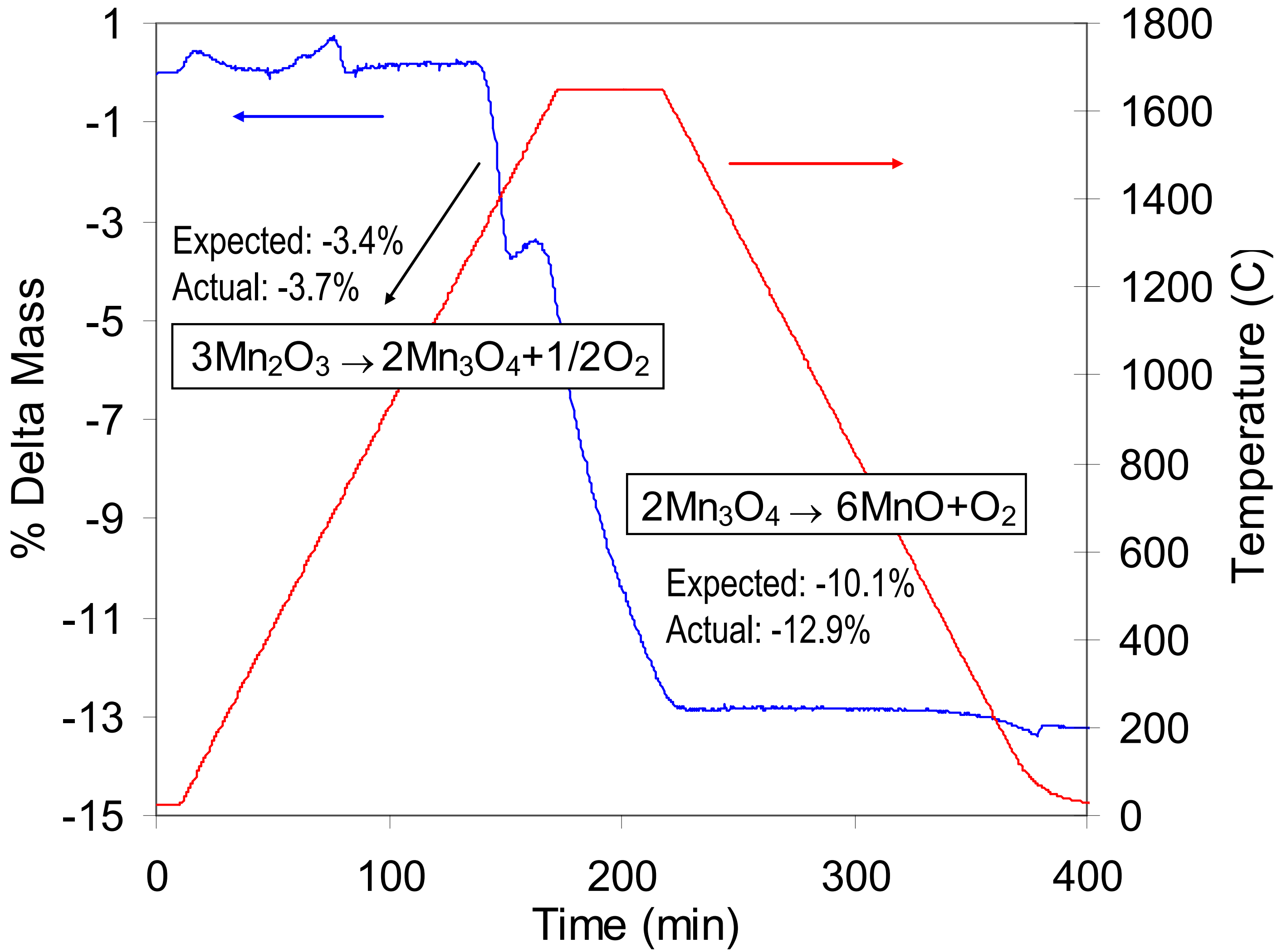
Key Areas for Research

- Kinetics of $Mn_2O_3 \rightarrow 2\ MnO + \frac{1}{2}\ O_2$ at reduced pressure to determine how low of a temperature the high step reaction can be carried out at (increases process efficiency)
- Demonstrate 2nd and 3rd steps in the cycle and verify pinch points
- Develop an alloy ($Mn_xMetal_yO_z$) providing for a Na salt with improved solubility in water (i.e. to reduce the amount of water that needs to be distilled off to recover NaOH)

Experimental Work

- Rapid dissociation kinetics ($Mn_2O_3 \rightarrow 2MnO + 1/2O_2$) investigation underway (SHGR funding in Yr 1)
- $MnO + NaOH \rightarrow 1/2H_2 + NaMnO_2$; preliminary H_2 liberating step experiments carried out
- $NaMnO_2 + ½\ H_2O \rightarrow 1/2\ Mn_2O_3 + NaOH$; preliminary water splitting step experiments carried out

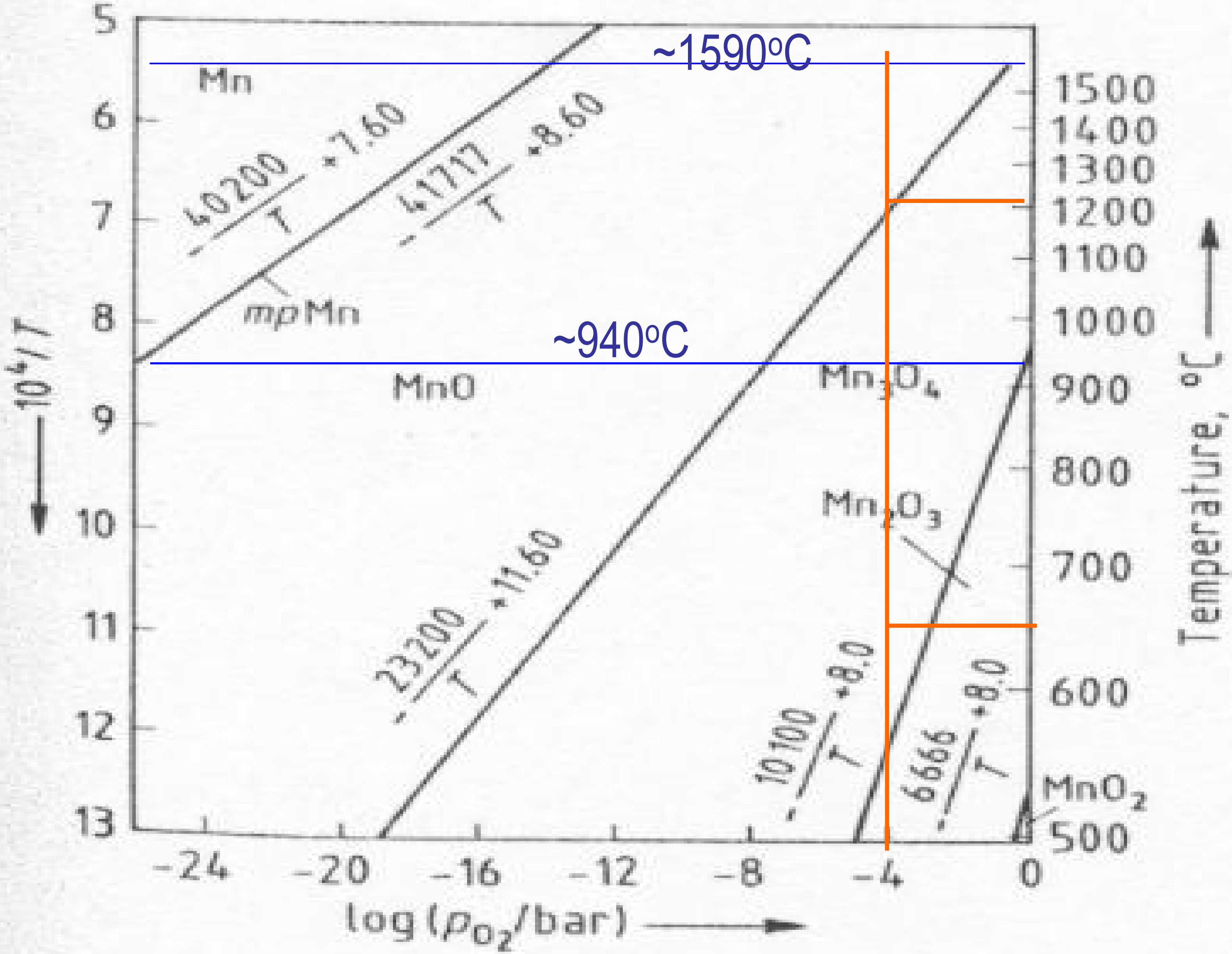
Mn_2O_3 TGA Decomposition
ZrO_2 crucible in argon @ 10 deg C/min

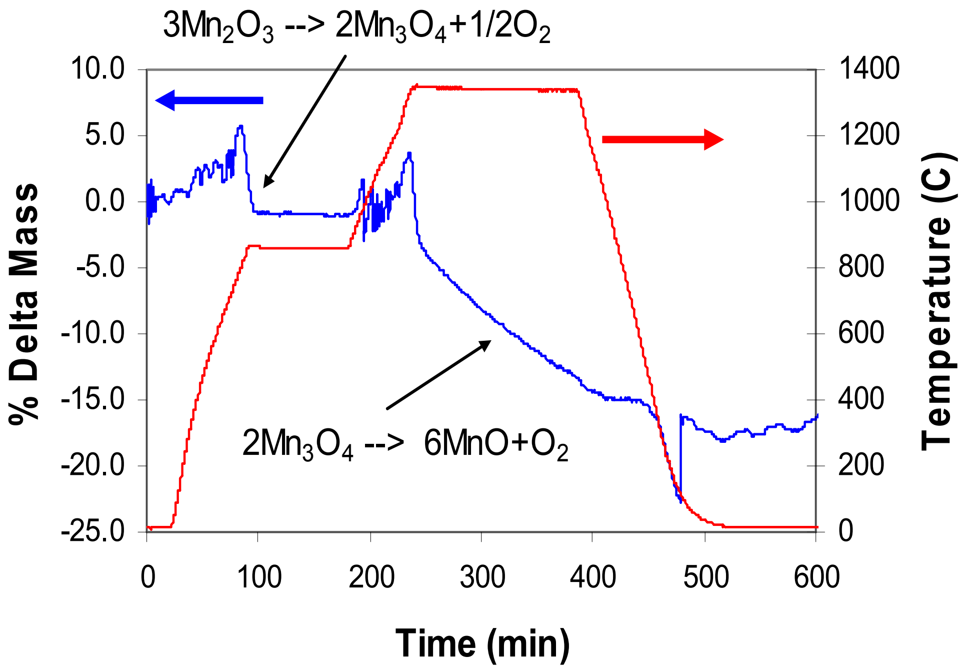


TGA Decomposition Challenges

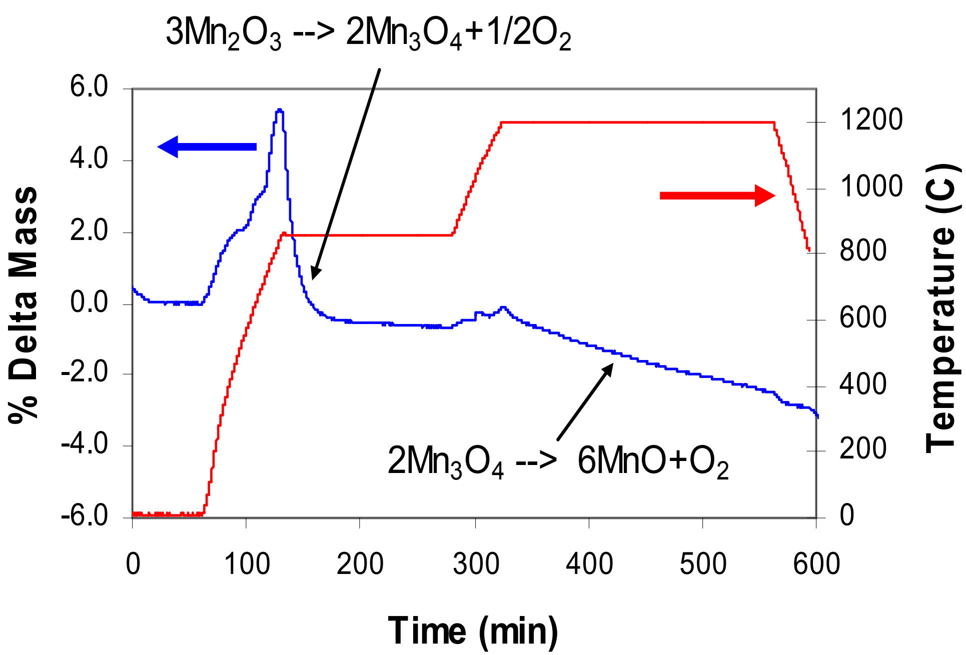
- Product sinters to crucible
  - No product analysis possible
- Solution → run under vacuum
  - Performed some preliminary runs
    - Have had initial problems keeping balance stable
  - Can obtain 500 mtorr atmosphere during run

Effect of Reduced Pressure





- 10 °C/min to 1310°C
- Sample mass = 600 mg
- Some sintering of product to crucible
- Dark greenish color (as MnO)
- Oxygen = 21.6% (MnO = 22.6%)



- 10 °C/min to 1200°C
- Sample mass = 870 mg
- No sintering of product to crucible
- Partial reaction – product contains both Mn_2O_3 (brownish-red color) and MnO (dark greenish color

Experimental Results Support Thermodynamics

Reaction 1

$Mn_2O_3 \rightarrow Mn_3O_4$

T = 650°C   P = 550 mtorr

Reaction 2

$Mn_2O_3 \rightarrow MnO$

T = 1220°C   P = 0.1 atm

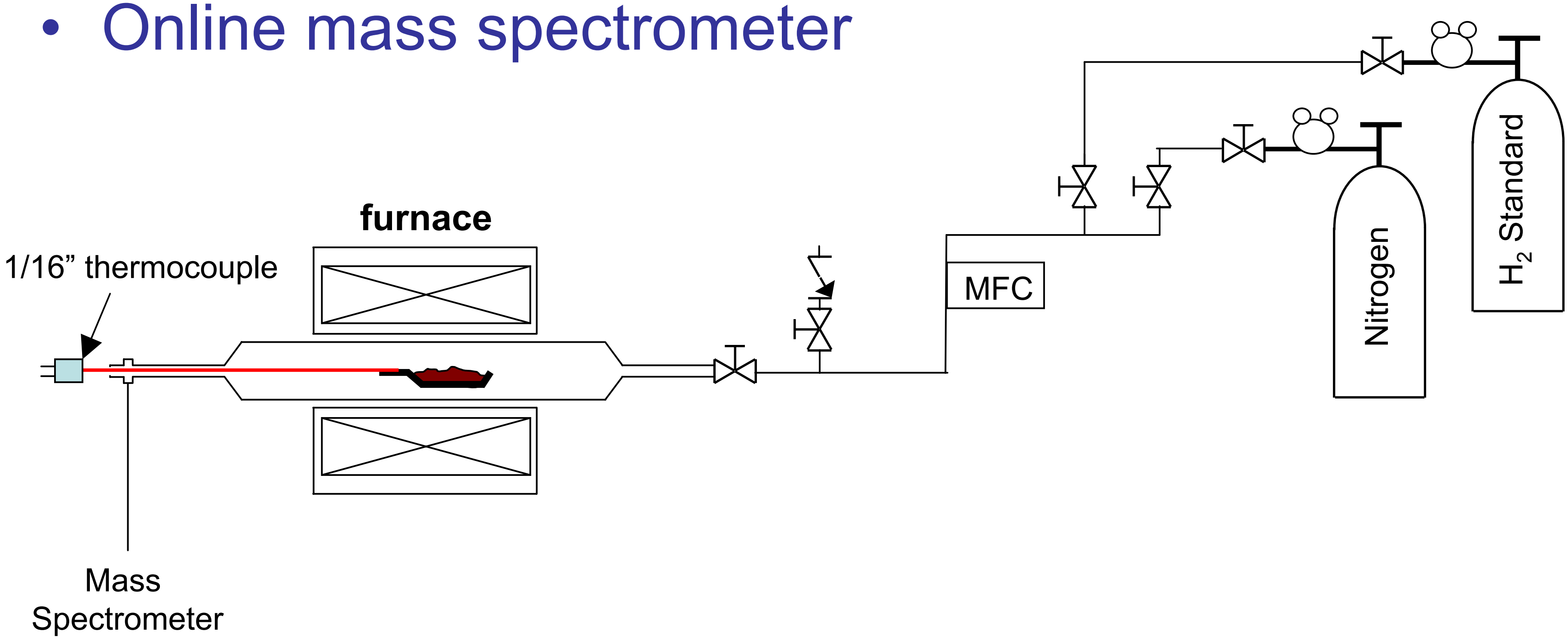
Reduced Pressure Studies Summary

	Argon Flow	Vacuum (500 mtorr)
$3Mn_2O_3 \rightarrow 2Mn_3O_4 + ½O_2$	1330 °C	750 - 850 °C
$2Mn_3O_4 \rightarrow 6MnO + O_2$	1580 - 1620 °C	1200 - 1310 °C

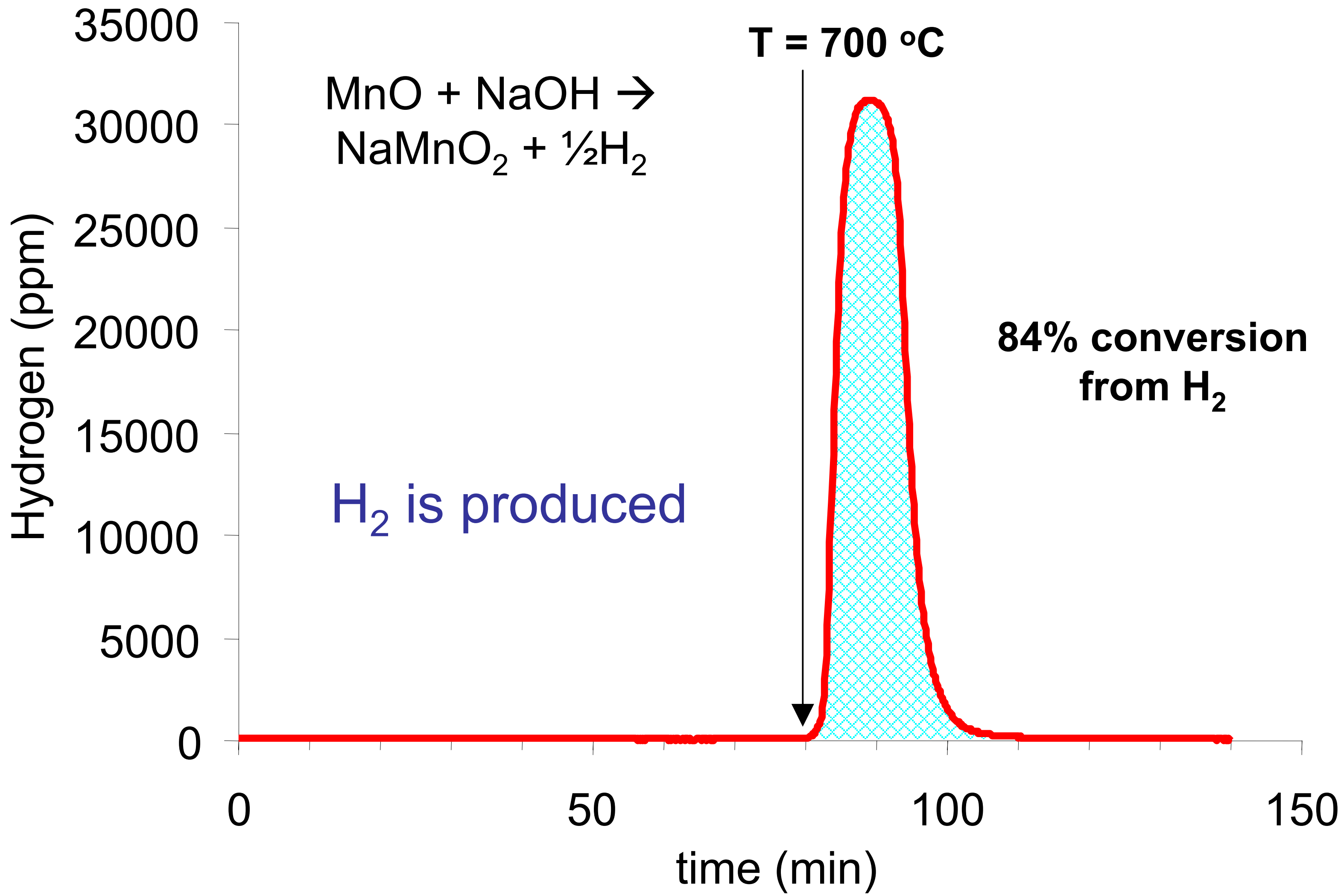
- Performing decomposition under reduced pressure conditions **does** reduce reaction temperatures
- Product oxygen mass content analyses indicate **full conversion** to MnO

Horizontal Tube Furnace

- For study of 2nd and 3rd steps
- Pull sample into hot zone at desired temperature
- Online mass spectrometer

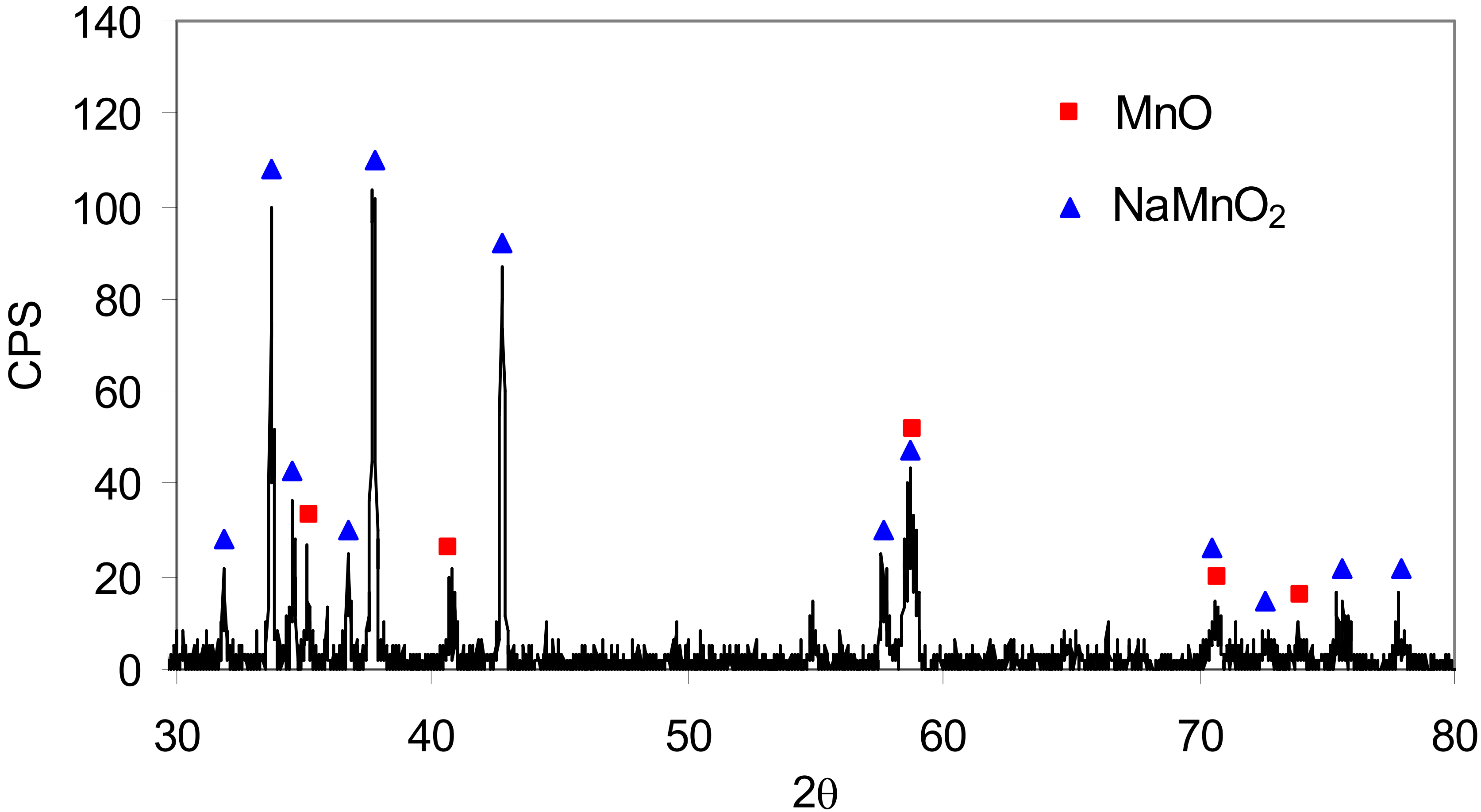


Mass Spectrometer Hydrogen Signal



XRD Product Analysis

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



$MnO + NaOH \rightarrow NaMnO_2 + \frac{1}{2}H_2$
$NaMnO_2 + H_2O \rightarrow \frac{1}{2}Mn_2O_3 + NaOH$

- Challenges
  - Optimize hydrogen production step
    - Grinding MnO/NaOH mixture appears to increase conversion
  - Separation of Mn_2O_3/NaOH solid species
- Further options
  - Temperature based phase separation
  - Mixed manganese oxides
    - Prepare $Mn_xFe_{1-x}O$ and $Mn_xZn_{1-x}O$ with sol-gel process
    - Verify hydrogen production with these mixed oxides
    - Investigate the separation efficiency with NaOH
      - Compare to Mn_2O_3/NaOH separation efficiency

Conclusions/Summary

- The Mn_2O_3/MnO cycle provides an opportunity for low cost renewable H_2
  - air in high temperature (HT) step
  - HT < 1250 ^{o}C (possible metal alloy receiver)
  - little MnO/O_2 recombination concern
- Significant development needs made relative to process integration at large scale, NaOH recovery and NOx mitigation

Major Collaboration

- ETH-Zurich is working with CU on the design of a solar-thermal transport tube reactor to interface to their High Flux Solar Simulator
  - reactor design
  - heat transfer modeling
  - experimentation

Acknowledgement

- DOE Hydrogen Program