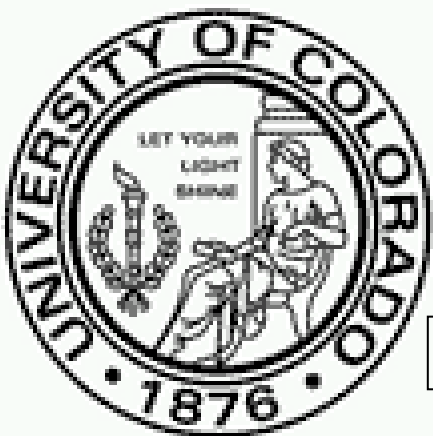


Fundamentals of a Solar-thermal $\text{Mn}_2\text{O}_3/\text{MnO}$ Thermochemical Cycle to Split Water

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Weimer; University of Colorado (Boulder, CO)

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Project ID No. PDP15

This presentation does not contain any proprietary or confidential information

Overview

Timeline

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

Budget

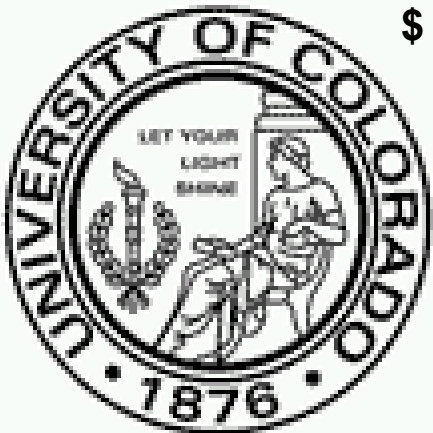
- Total Project Funding
 - \$330,000 DOE (\$180,000 via UNLV)
 - \$ 82,500 Cost share
- Funds received in FY05
 - \$ 110,000 (\$60,000 via UNLV)

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

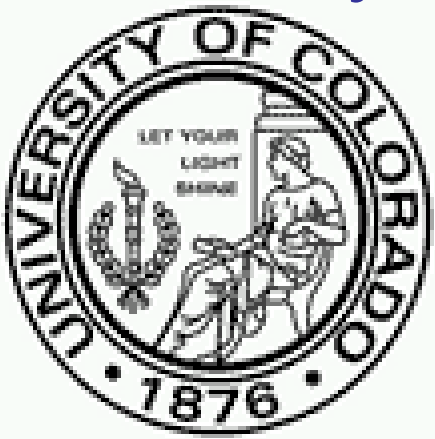
Partners

Swiss Federal Research Institute (Aldo Steinfeld)



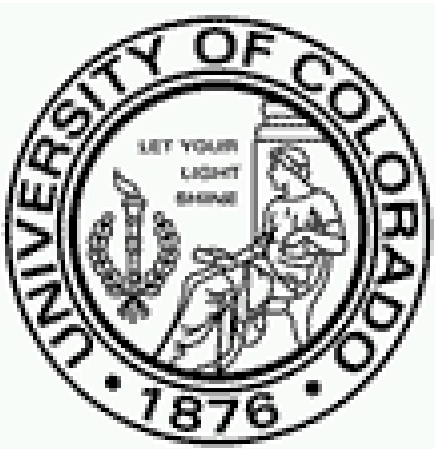
Objectives

- Research and develop a cost effective $\text{Mn}_2\text{O}_3/\text{MnO}$ 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



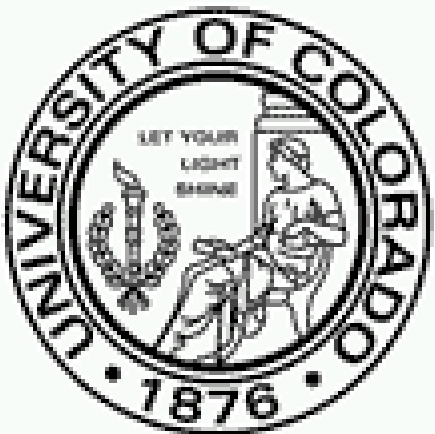
Approach

- 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

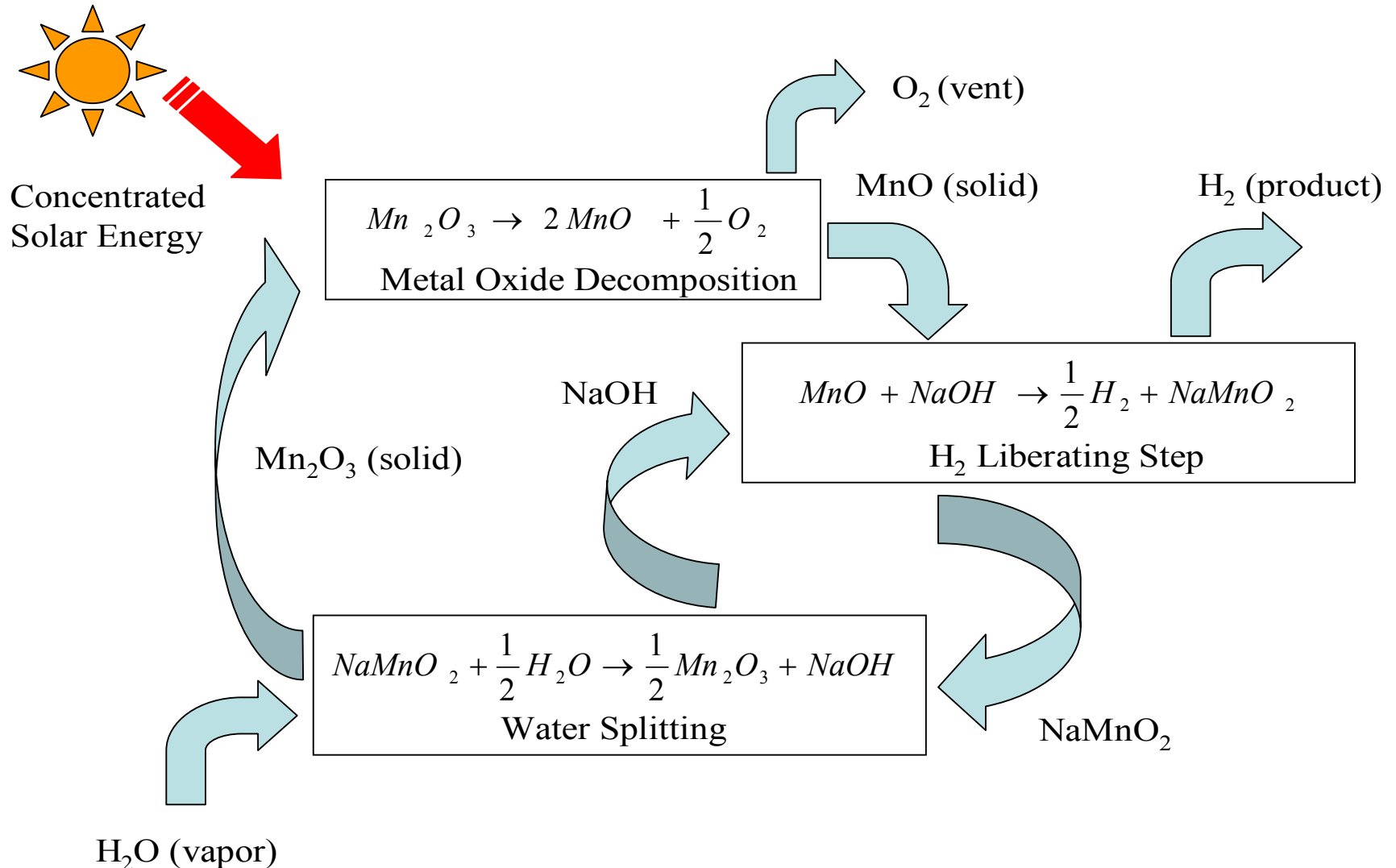


Technical Accomplishments/ Progress/Results

- 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



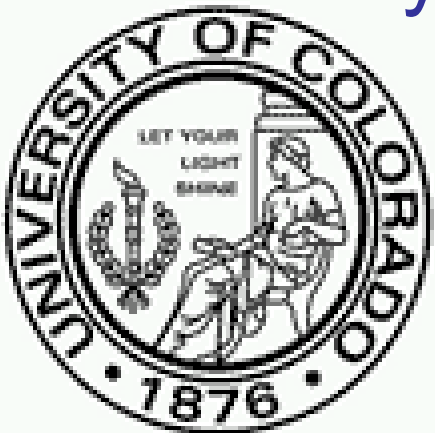
Mn₂O₃/MnO Solar Cycle

- Advantages
 - Relatively low temperature (~1650 °C, or lower)
 - All solid/liquid species → no recombination
 - Can be performed in air
- Disadvantages
 - Corrosive nature of NaOH
 - Energy-efficient separation of NaOH/Mn₂O₃ difficult
 - Three step cycle has decreased efficiency
 - Multiple oxide species involved



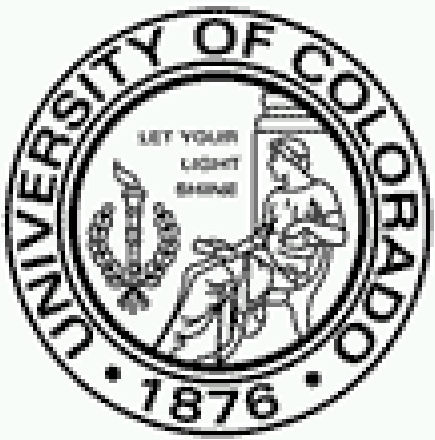
Goals

- 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)



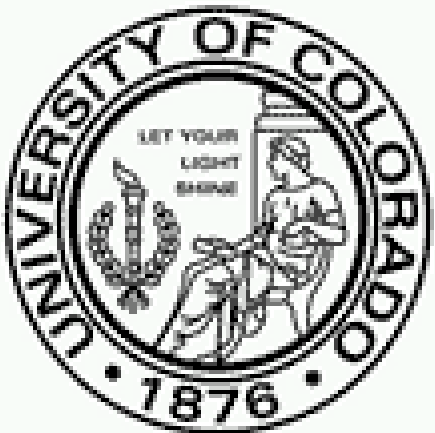
Preliminary Flowsheet Development

- Based on literature only, a preliminary PFD was developed for the $\text{Mn}_2\text{O}_3/\text{MnO}$ 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
- NO_x 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

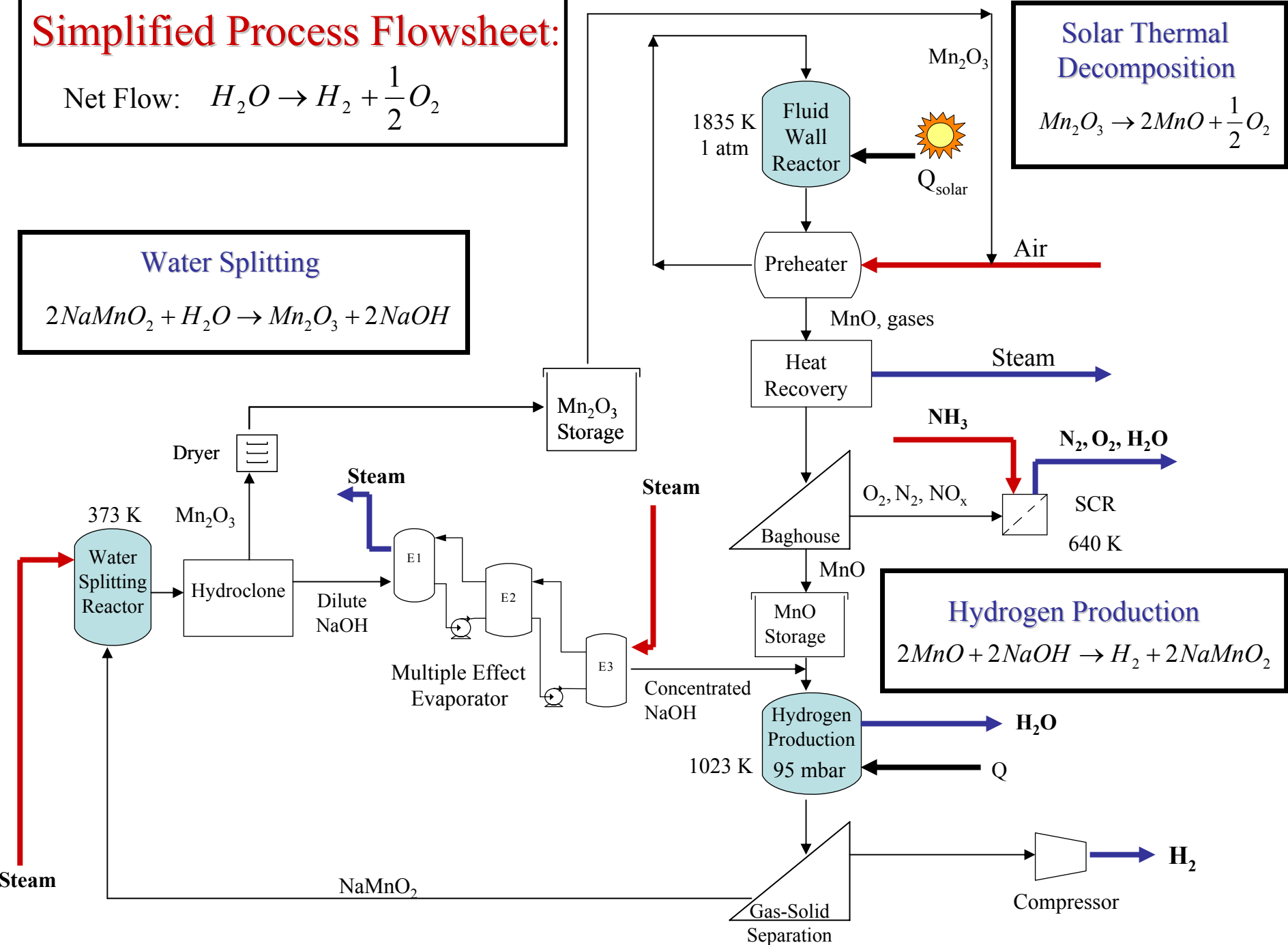
$2NaMnO_2 + H_2O \rightarrow Mn_2O_3 + 2NaOH$

Solar Thermal Decomposition

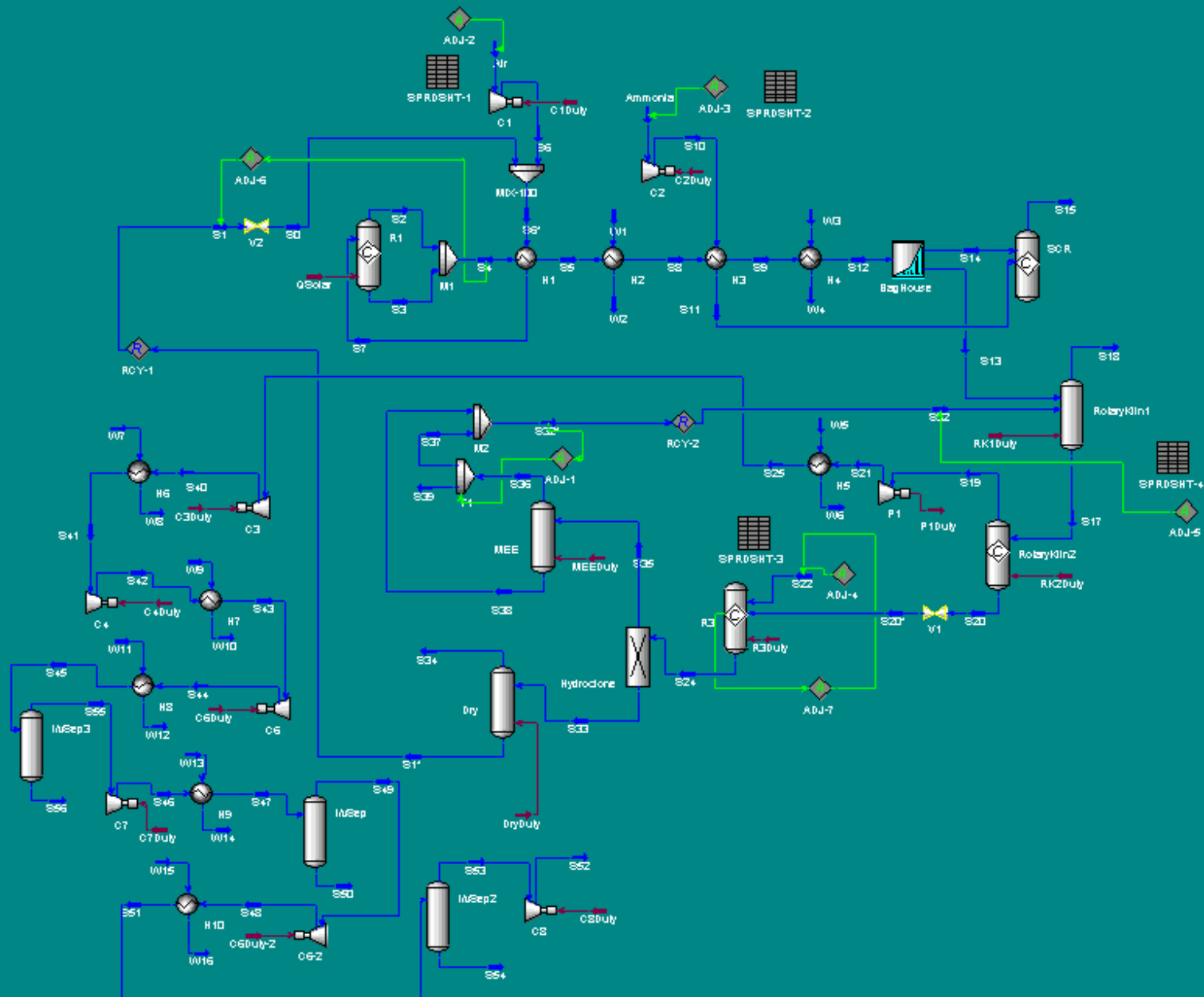
$Mn_2O_3 \rightarrow 2MnO + \frac{1}{2}O_2$

Hydrogen Production

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

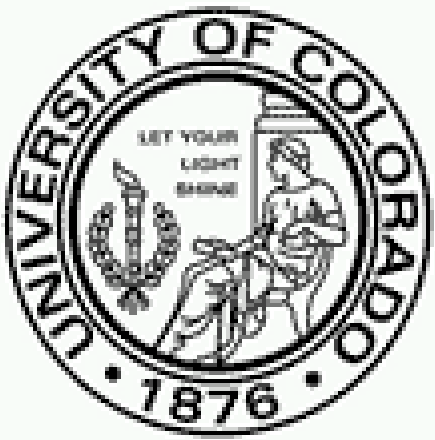


Process Simulation



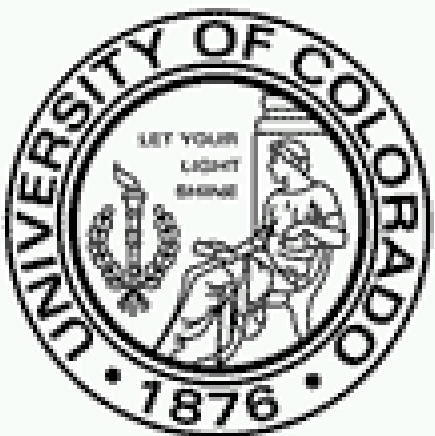
Key Areas for Research

- Kinetics of $\text{Mn}_2\text{O}_3 \rightarrow 2 \text{MnO} + \frac{1}{2} \text{O}_2$ 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 ($\text{Mn}_x\text{Metal}_y\text{O}_z$) 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)



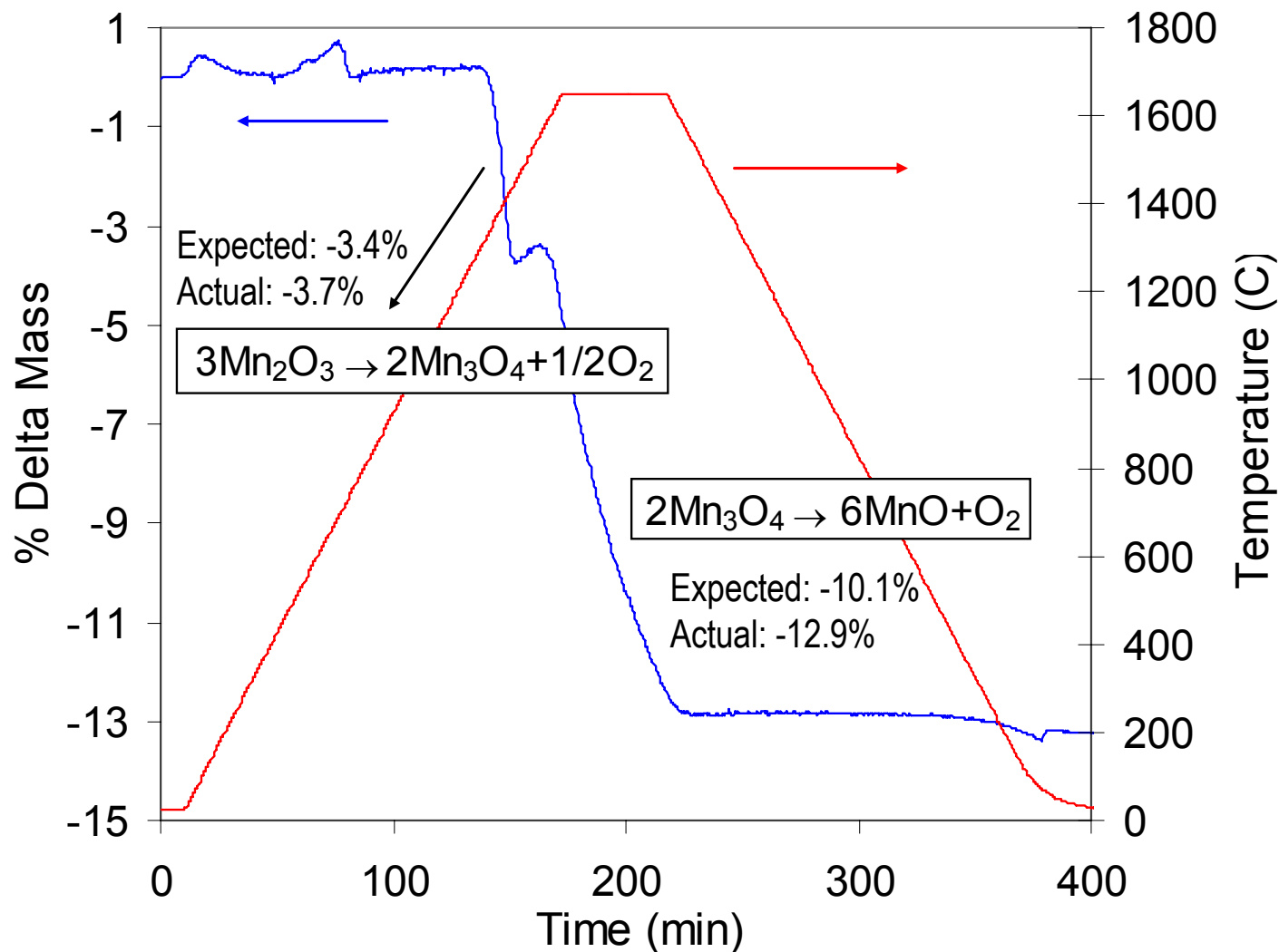
Experimental Work

- Rapid dissociation kinetics ($\text{Mn}_2\text{O}_3 \rightarrow 2\text{MnO} + 1/2\text{O}_2$) investigation underway (SHGR funding in Yr 1)
- $\text{MnO} + \text{NaOH} \rightarrow 1/2\text{H}_2 + \text{NaMnO}_2$; preliminary H_2 liberating step experiments carried out
- $\text{NaMnO}_2 + 1/2 \text{H}_2\text{O} \rightarrow 1/2 \text{Mn}_2\text{O}_3 + \text{NaOH}$; preliminary water splitting step experiments carried out



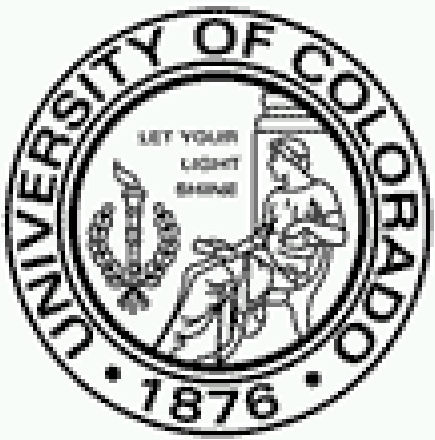
Mn₂O₃ TGA Decomposition

ZrO₂ crucible in argon @ 10 deg C/min

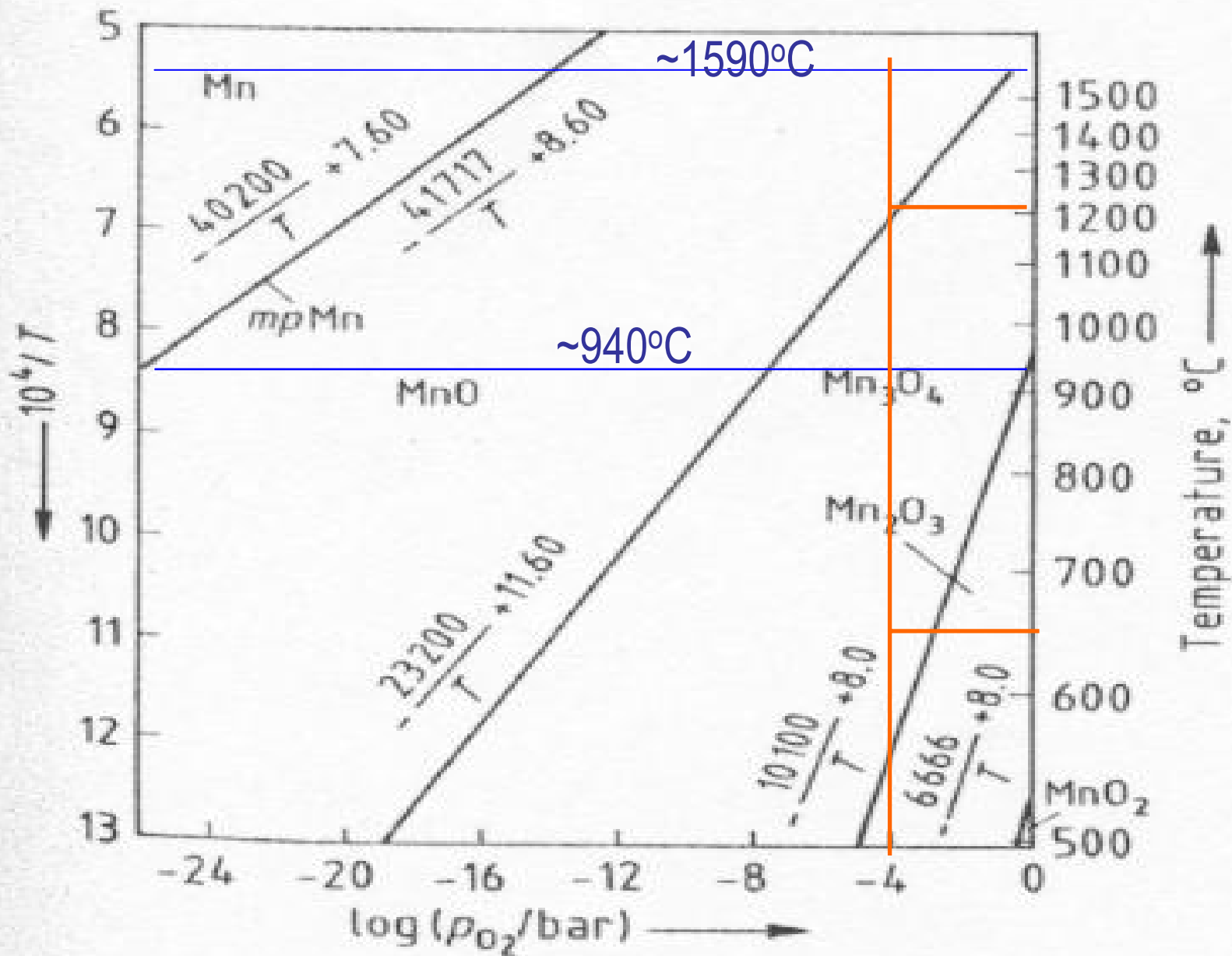


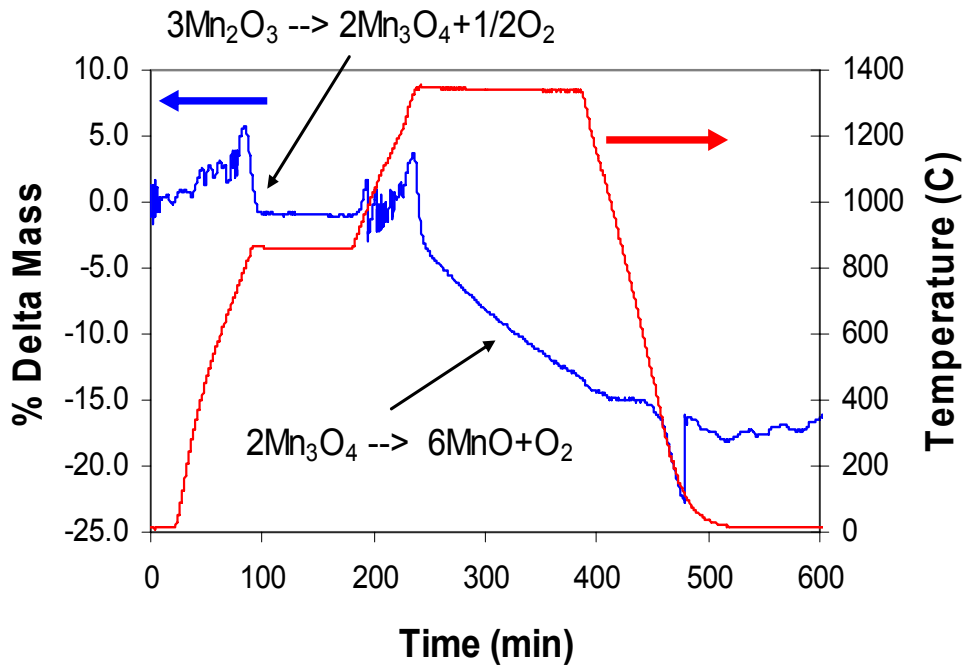
TGA Decomposition Challenges

- 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

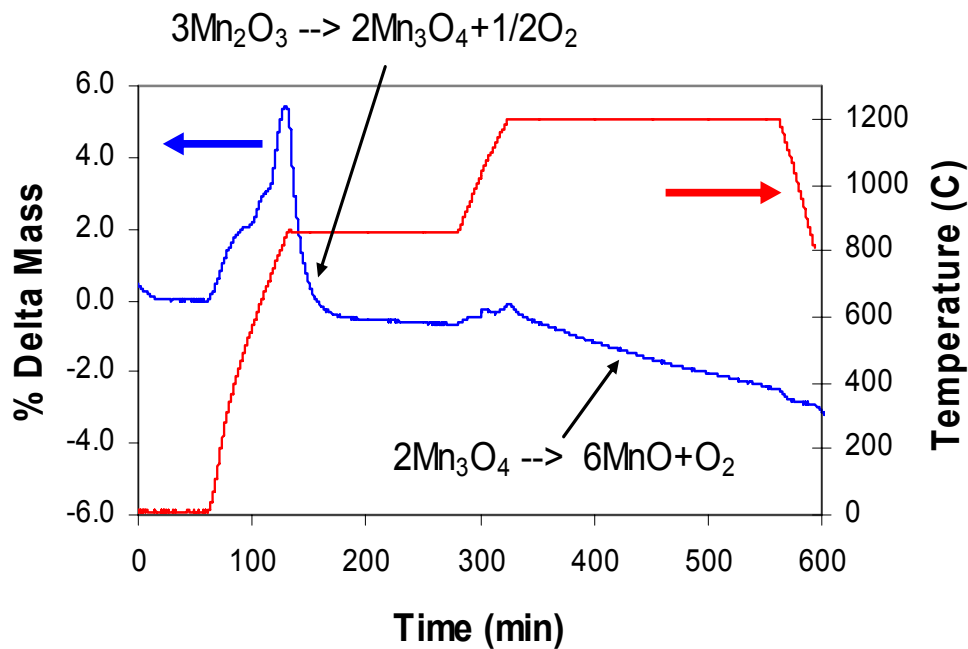


Effect of Reduced Pressure





- 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

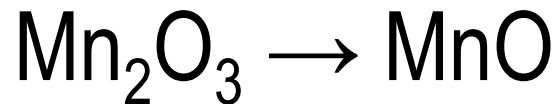
Support Thermodynamics

Reaction 1

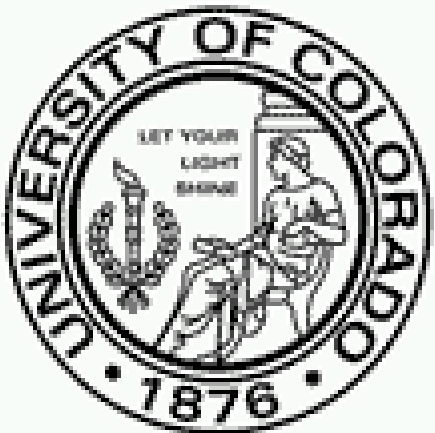


$$T = 650^\circ\text{C} \quad P = 550 \text{ mtorr}$$

Reaction 2



$$T = 1220^\circ\text{C} \quad P = 0.1 \text{ atm}$$



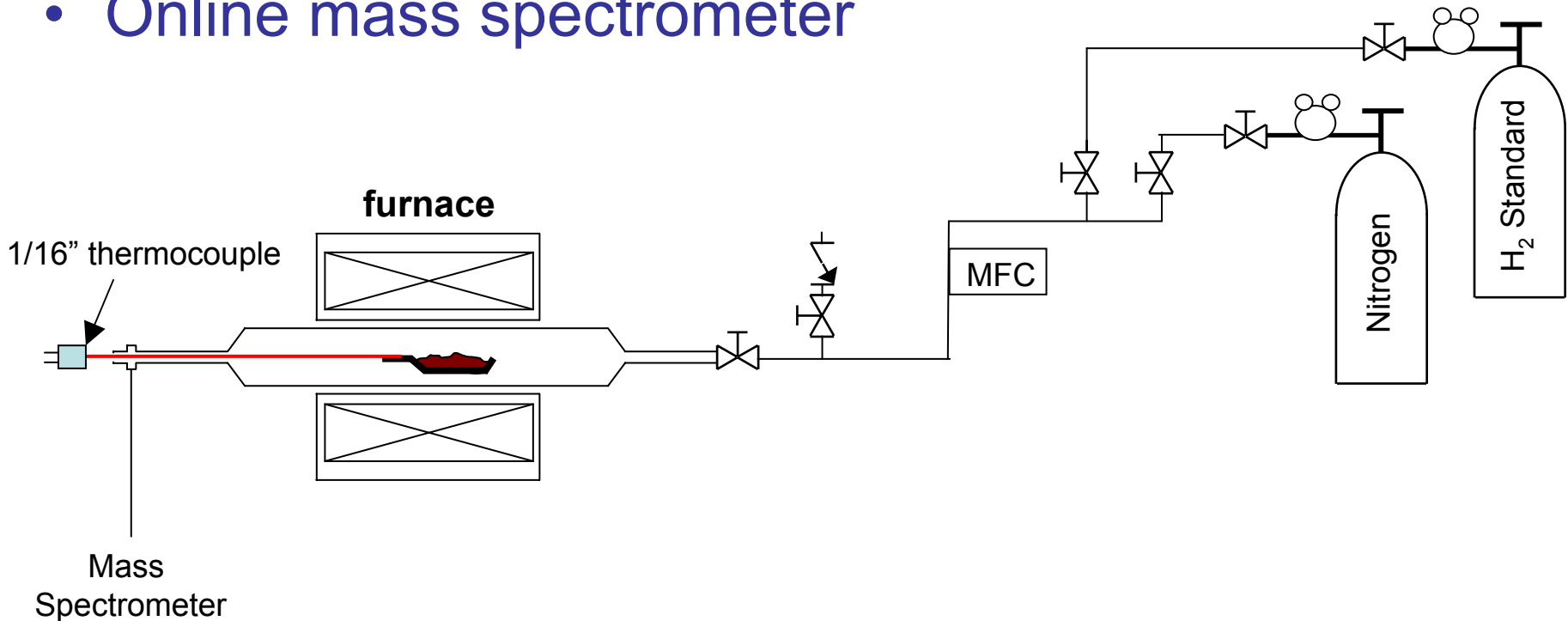
Reduced Pressure Studies Summary

	Argon Flow	Vacuum (500 mtorr)
$3\text{Mn}_2\text{O}_3 \rightarrow 2\text{Mn}_3\text{O}_4 + \frac{1}{2}\text{O}_2$	1330 °C	750 - 850 °C
$2\text{Mn}_3\text{O}_4 \rightarrow 6\text{MnO} + \text{O}_2$	1580 - 1620 °C	1200 - 1310 °C

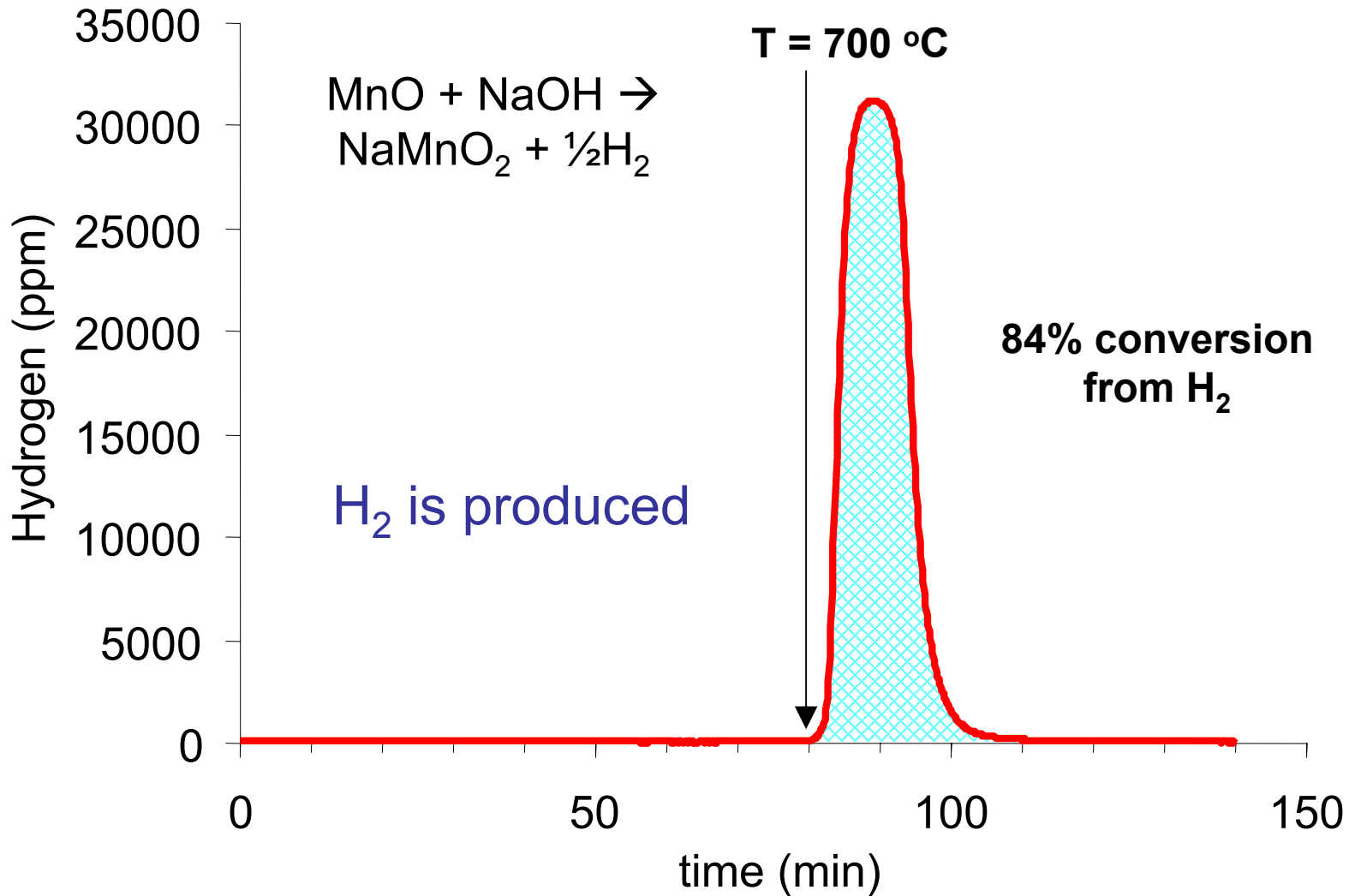
- Performing decomposition under reduced pressure conditions does reduce reaction temperatures
- Product oxygen mass content analyses indicate full conversion to MnO

Horizontal Tube Furnace

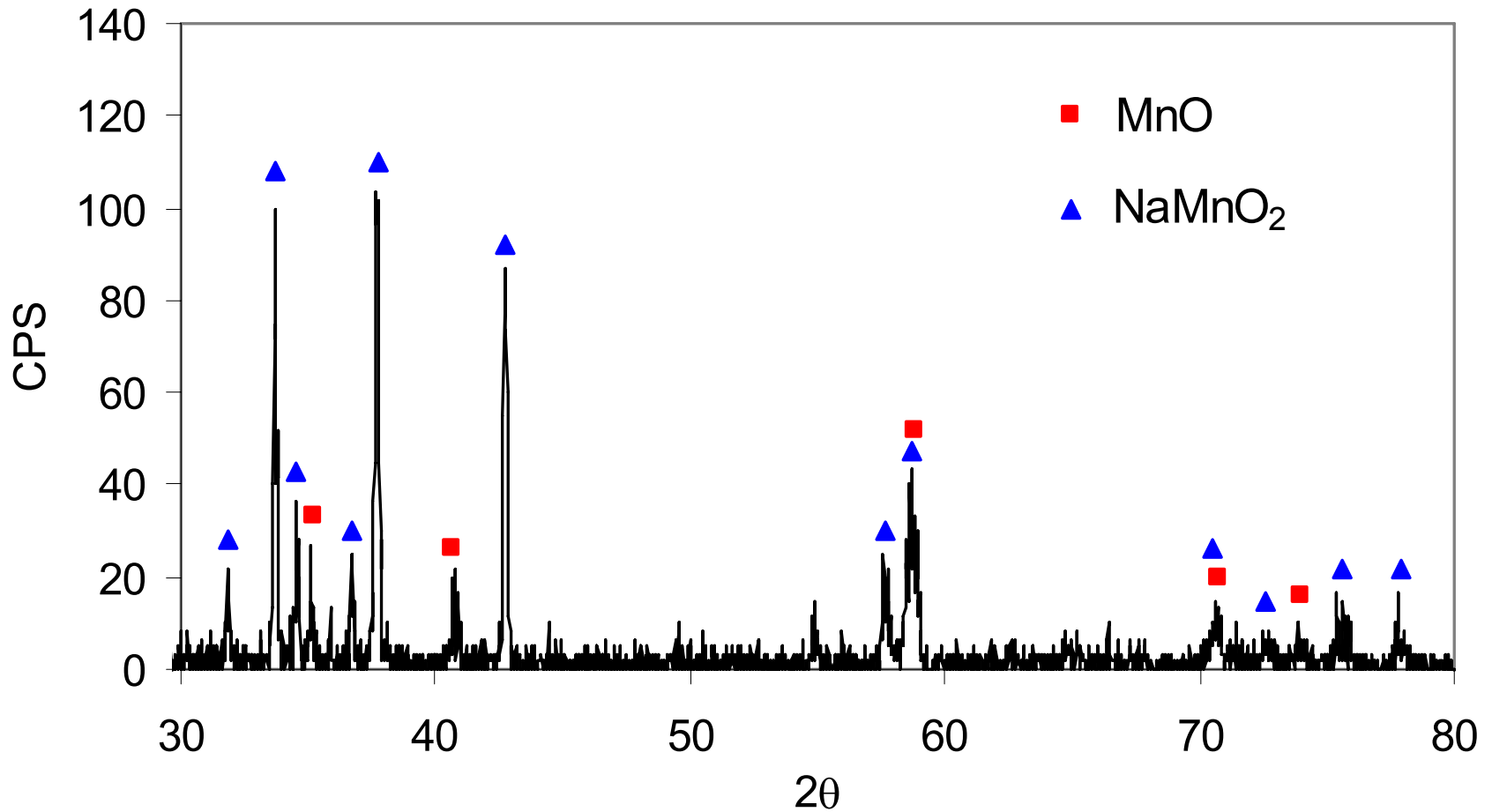
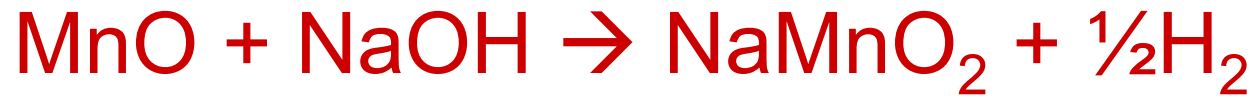
- For study of 2nd and 3rd steps
- Pull sample into hot zone at desired temperature
- Online mass spectrometer

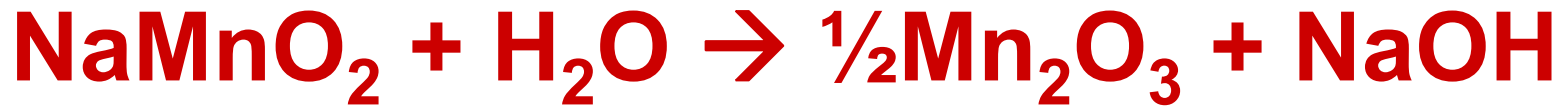


Mass Spectrometer Hydrogen Signal



XRD Product Analysis





- Challenges

- Optimize hydrogen production step

- Grinding MnO/NaOH mixture appears to increase conversion

- Separation of Mn₂O₃/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

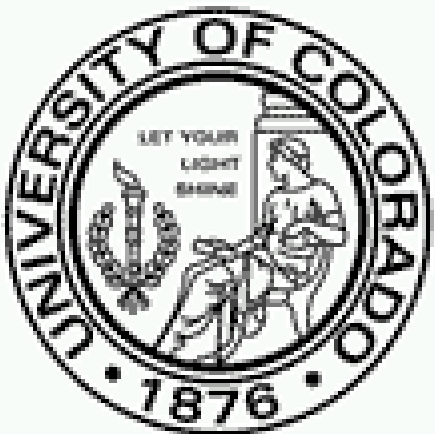
- Verify hydrogen production with these mixed oxides

- Investigate the separation efficiency with NaOH

- Compare to Mn₂O₃/NaOH separation efficiency

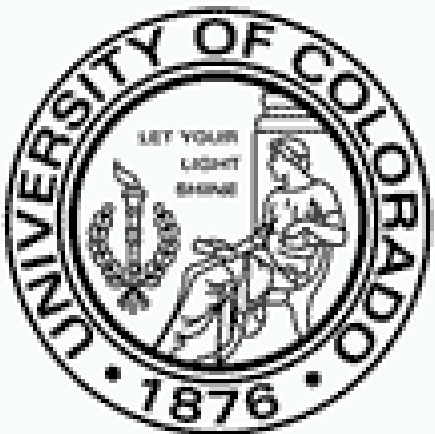
Conclusions/Summary

- The $\text{Mn}_2\text{O}_3/\text{MnO}$ cycle provides an opportunity for low cost renewable H_2
 - air in high temperature (HT) step
 - $\text{HT} < 1250\text{ }^\circ\text{C}$ (possible metal alloy receiver)
 - little MnO/O_2 recombination concern
- Significant development needs made relative to process integration at large scale, NaOH recovery and NO_x 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

