

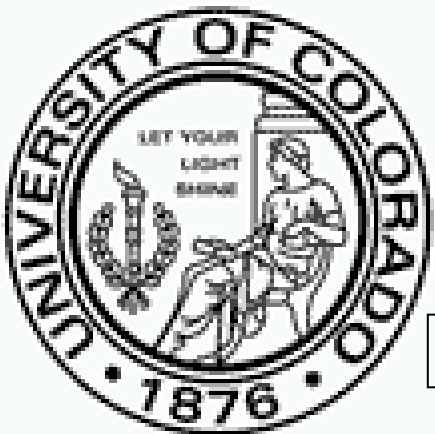
Fundamentals of a Solar-thermal $\text{Mn}_2\text{O}_3/\text{MnO}$ Thermochemical Cycle to Split Water

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University of Colorado

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Project ID No. PDP44



This presentation does not contain any proprietary or confidential information

Overview

Timeline

- 6-1-2005
- 5-31-2009
- 0%

Budget

- Total Project Funding

\$1,095,000 DOE

\$270,000 Cost share

- Funds received in FY04

\$0

Barriers

J. Rate of Hydrogen Production

M. Materials Durability

N. Materials and systems Engineering

P. Diurnal Operation Limitation

Q. Cost

R. System Efficiency

T. Renewable Integration

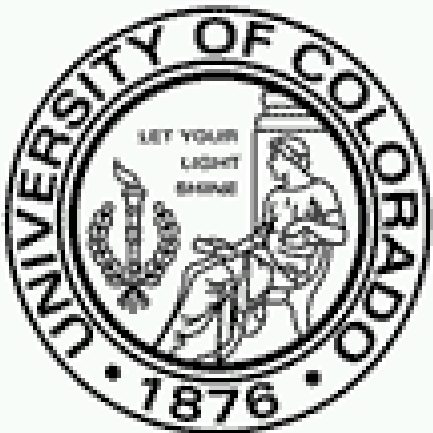
V. High and Ultrahigh Temperature Thermochemical Technology

W. High Temperature Materials

Y. Solar Capital Cost

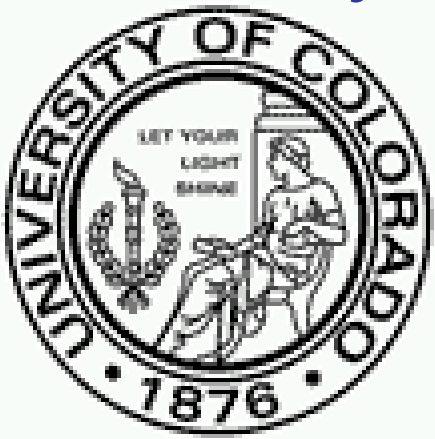
Partners

Swiss Federal Research Institute (ETH-Zurich)



Objectives

- Develop an understanding of the $\text{Mn}_2\text{O}_3/\text{MnO}$ 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



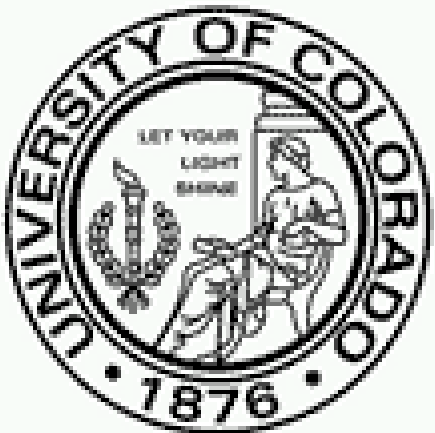
Approach

- 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



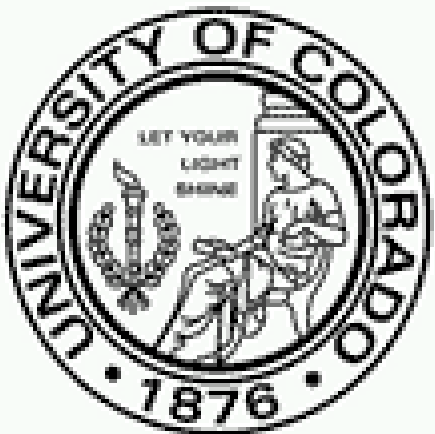
Technical Accomplishments/ Progress/Results

- 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 being developed

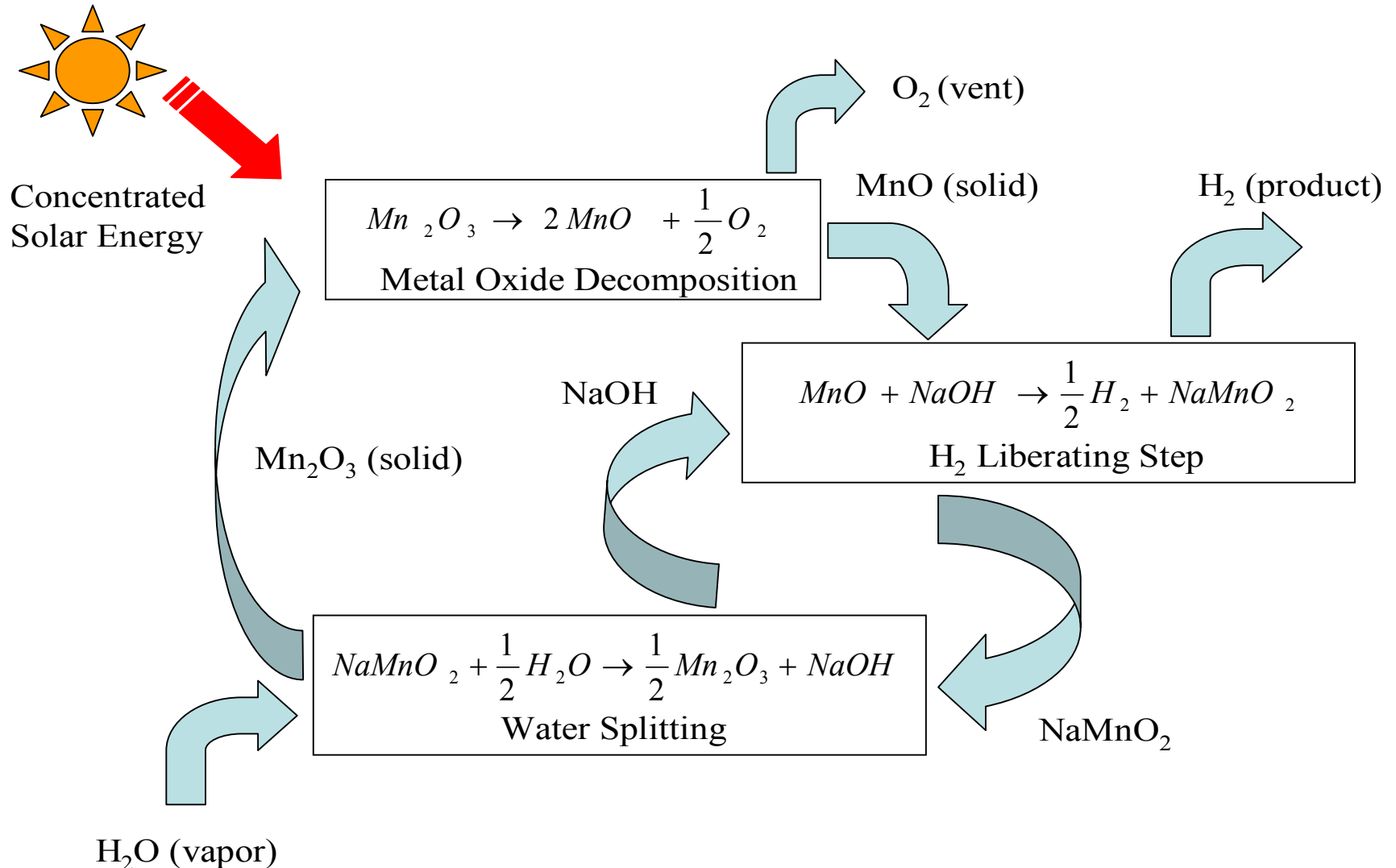


Literature Surveyed

- Sturzenegger, M., J. Ganz, P. Nuesch, and Th. Schelling, “Solar hydrogen from a manganese oxide based thermochemical cycle,” J. Phys. IV France, 9, 331-335 (1999).
- Sturzenegger, M. and P. Nuesch, “Efficiency analysis for a manganese-oxide based thermochemical cycle,” Energy, 24, 959-970 (1999).

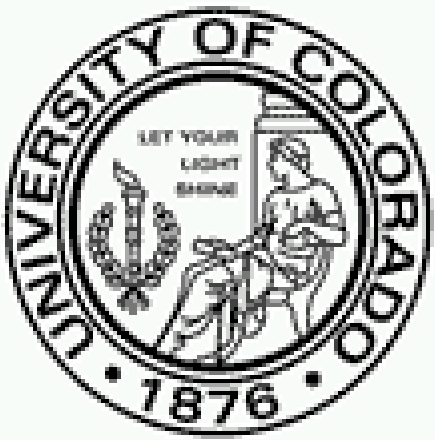


Literature Cycle



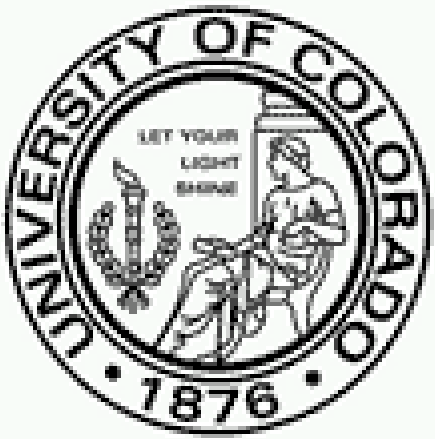
Preliminary Flowsheet Development

- 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



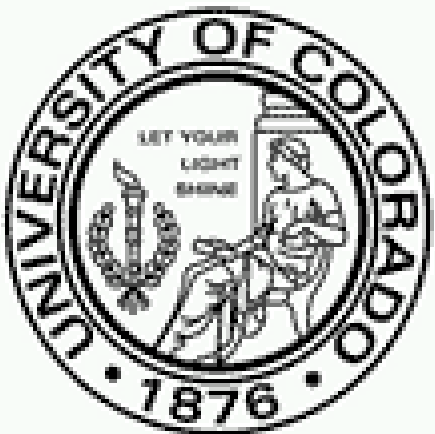
Process Design Premises

- 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



Process Economics Premises

- Economics by study estimate (factor) method using major purchased equipment costs (Lang's Factor)
- Base Case = 24 MW_{th} plant size; Integrated to 150,000 kg H₂/day
- 15 yr plant lifetime; 2453 hours per year (28 % on-sun)
- 12.5 % target IRR
- 25 % contingency
- Working capital = 18 % of FCI
- Equity funded
- 1.9% inflation; 7 yr MACR depreciation
- 228 operators in 150,000 kg H₂/day plant



Simplified Process Flowsheet:

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

Water Splitting

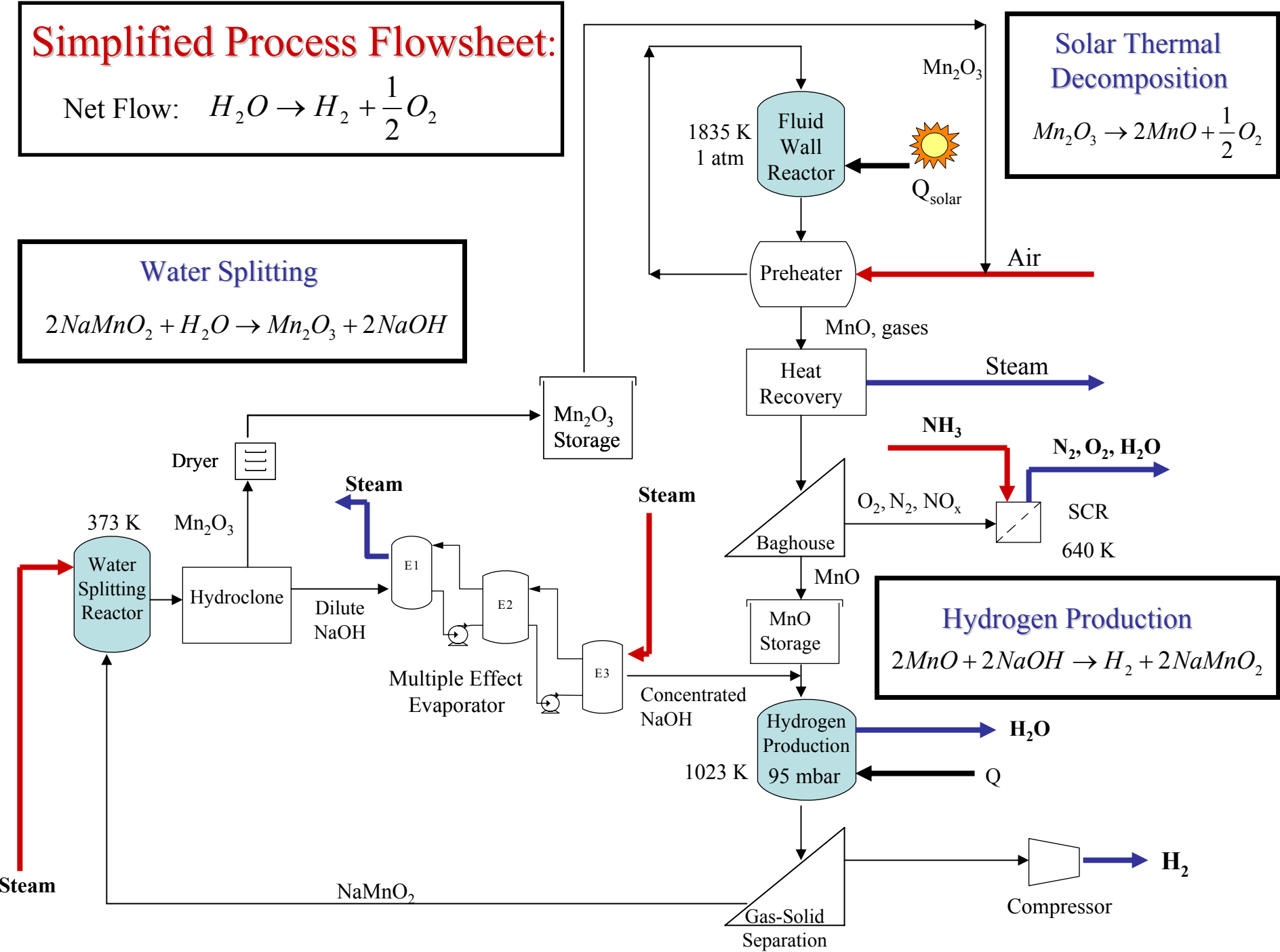
$2NaMnO_2 + H_2O \rightarrow Mn_2O_3 + 2NaOH$

Solar Thermal Decomposition

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

Hydrogen Production

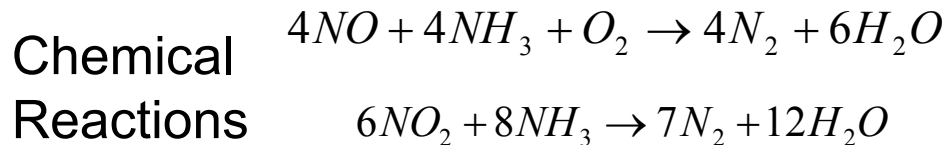
$2MnO + 2NaOH \rightarrow H_2 + 2NaMnO_2$



Safety, Environmental, and Health Considerations

Environmental Considerations

- Nitrogen oxides (NO_x) potentially formed at high temperature in solar thermal reactor
- NO_x can be reduced via selective catalytic reduction (SCR).

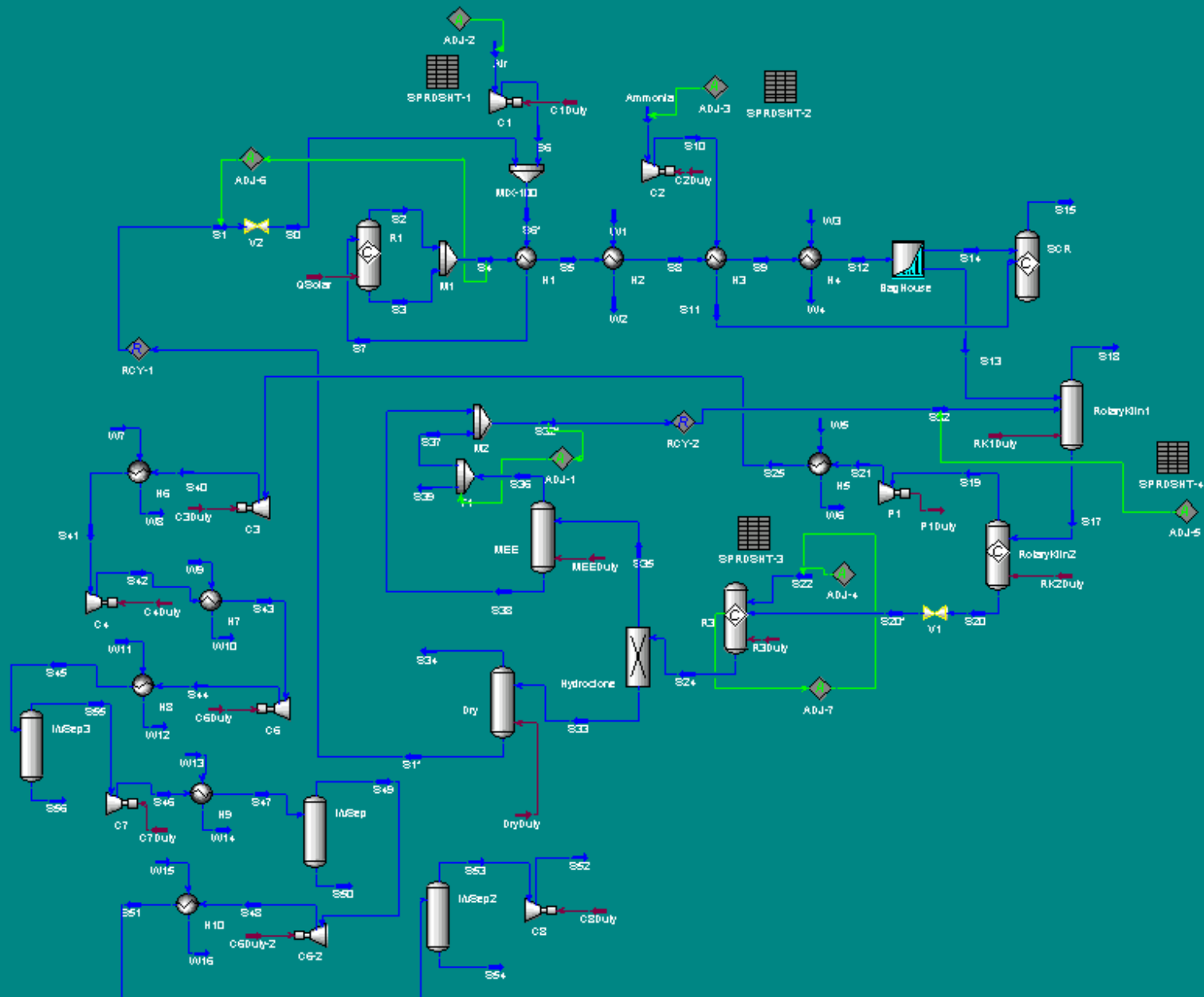


Catalyst: $\text{TiO}_2 / \text{V}_2\text{O}_5 / \text{WO}_3$

Safety and Health Considerations

- Corrosive chemicals (NaOH , NH_3)
- Flammability hazards (H_2 , O_2)
- Central nervous system effects from prolonged exposure (MnO , Mn_2O_3)

Process Simulation



Material Balance Summary*

	<u>Base Case: Single 24 MW_{th} solar thermal reactor</u>	<u>95 solar thermal reactors (each 24 MW_{th}) Single Back-end</u>
Products		
H ₂	235 kg/hr (1,579 kg/day), \$20.27/kg	22,325 kg/hr (150,024 kg/day), \$9.04/kg
Low Pressure Steam	2,491 kg/hr	236,645 kg/hr
Raw Materials and Utilities		
Ammonia	25 kg/hr	2,329 kg/hr
Low pressure steam	46,295 kg/hr	4,398,025 kg/hr
Cooling water	64,390 kg/hr	6,117,050 kg/hr
Natural Gas	21,275 scf/hr	2,021,082 scf/hr
Electricity	846 kWh/hr	80,370 kWh/hr

* Preliminary Process Design (12.5% IRR; 15 year lifetime)

Possible Cost Reducing Areas

- Equipment

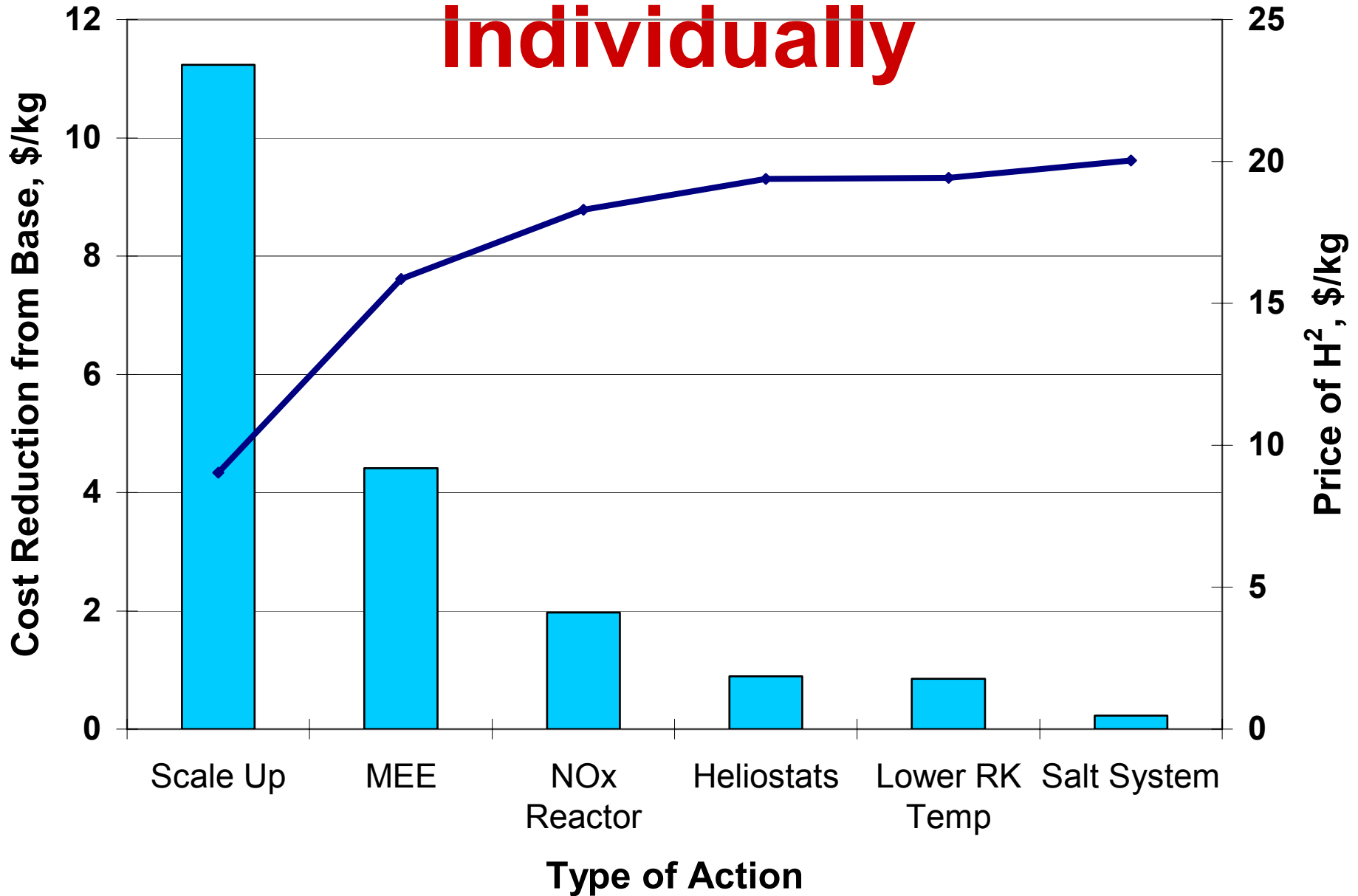
- Mult. Effect Evaporator – 16% total BMC
- Heliostats – 12% total BMC
- NOx Reactor – 11% total BMC
- Salt System – 2.3% total BMC

- Variable costs

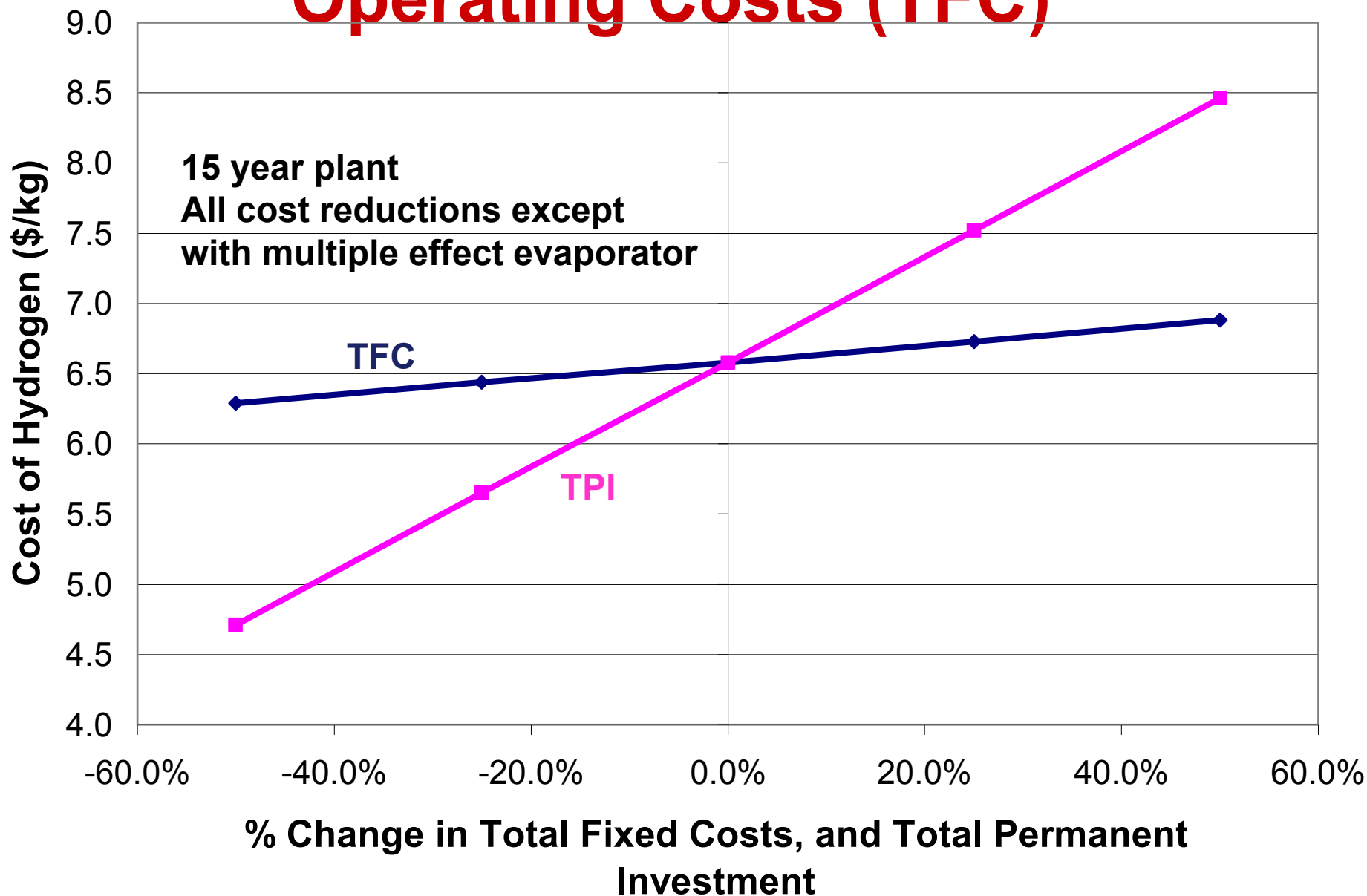
- Ammonia – 19% TVC
- Steam – 48% TVC
- Natural Gas – 17% TVC

Cost Reductions Applied

Individually

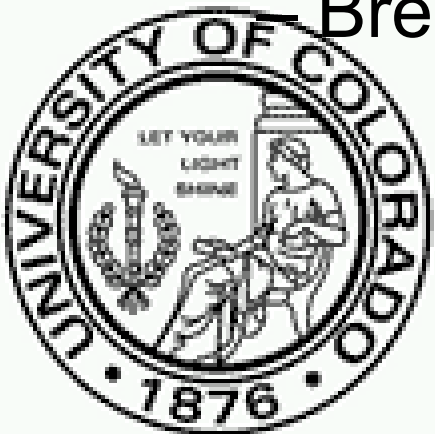


Sensitivity Analysis: TPI and Fixed Operating Costs (TFC)



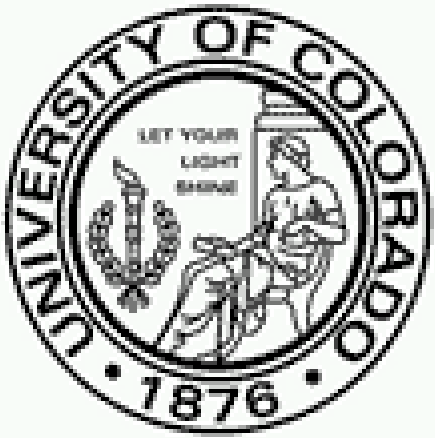
Impact of Cost Reductions

- All cost reductions except multiple effect evaporator:
 - \$829 million TPI
 - \$6.58/kg for 12.5% IRR (15 yr lifetime)
 - 8.8% ROI, 11.4 years PBP
- All cost reductions (40 yr plant life)
 - \$764 million TPI, \$3.01/kg for 10 % IRR
 - Break Even: \$1.50/kg H₂ selling price



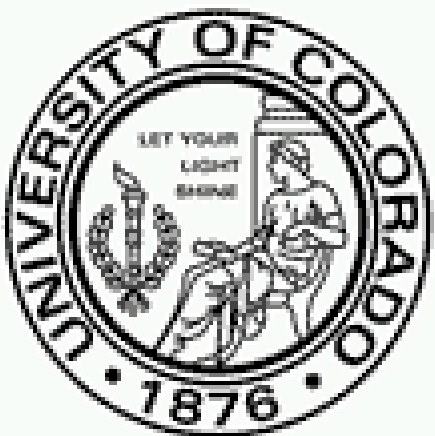
Key Areas for Research

- Integration of single secondary reaction step with multiple solar fields/reactors (\$11+/kg)
- NaOH recovery step using alternative technologies such as membrane separation, ...(\$4+/kg)
- Rapid $\text{Mn}_2\text{O}_3 \rightarrow 2 \text{MnO} + \frac{1}{2} \text{O}_2$ in air and in-situ mitigation of NOx (\$2/kg)
- Reduced heliostat costs (\$1/kg)
- Kinetics of $\text{Mn}_2\text{O}_3 \rightarrow 2 \text{MnO} + \frac{1}{2} \text{O}_2$ (lowest temperature) (\$1/kg)
- Consider alternative secondary reaction steps



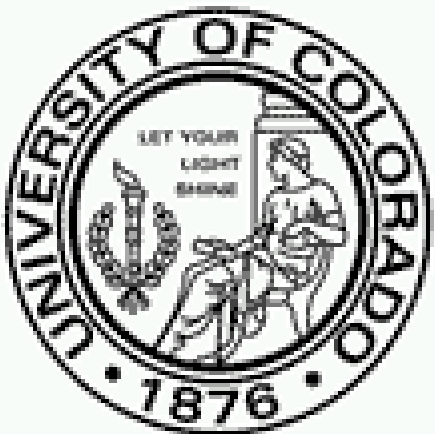
Experimental Work Plan Development

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



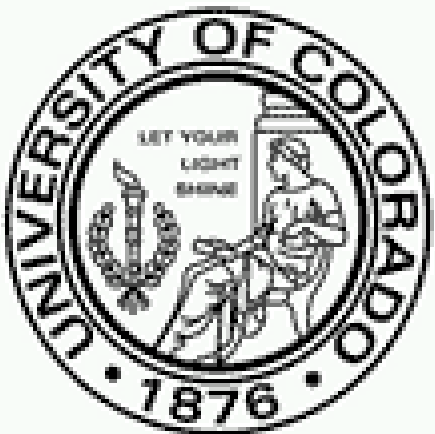
Hydrogen Safety

- At this stage of the project, H₂ quantities involved in the experiments are so minimal as to pose no H₂ safety risks
- The most significant current hazard is associated with ultra-high temperature (> 1500°C) operations
- Hazards mitigated with personnel training, well documented SOPs, and internal safety reviews



Conclusions/Summary

- The $\text{Mn}_2\text{O}_3/\text{MnO}$ cycle provides an opportunity for low cost renewable H_2
- Significant development needs made relative to process integration at large scale, NaOH recovery and NO_x mitigation



Acknowledgement

- DOE Hydrogen Program

