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

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Project ID No. PDP44

# 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

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## Partners

Swiss Federal Research Institute (ETH-Zurich)

# Objectives

- Develop an understanding of the $Mn_2O_3$/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

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# 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

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# 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

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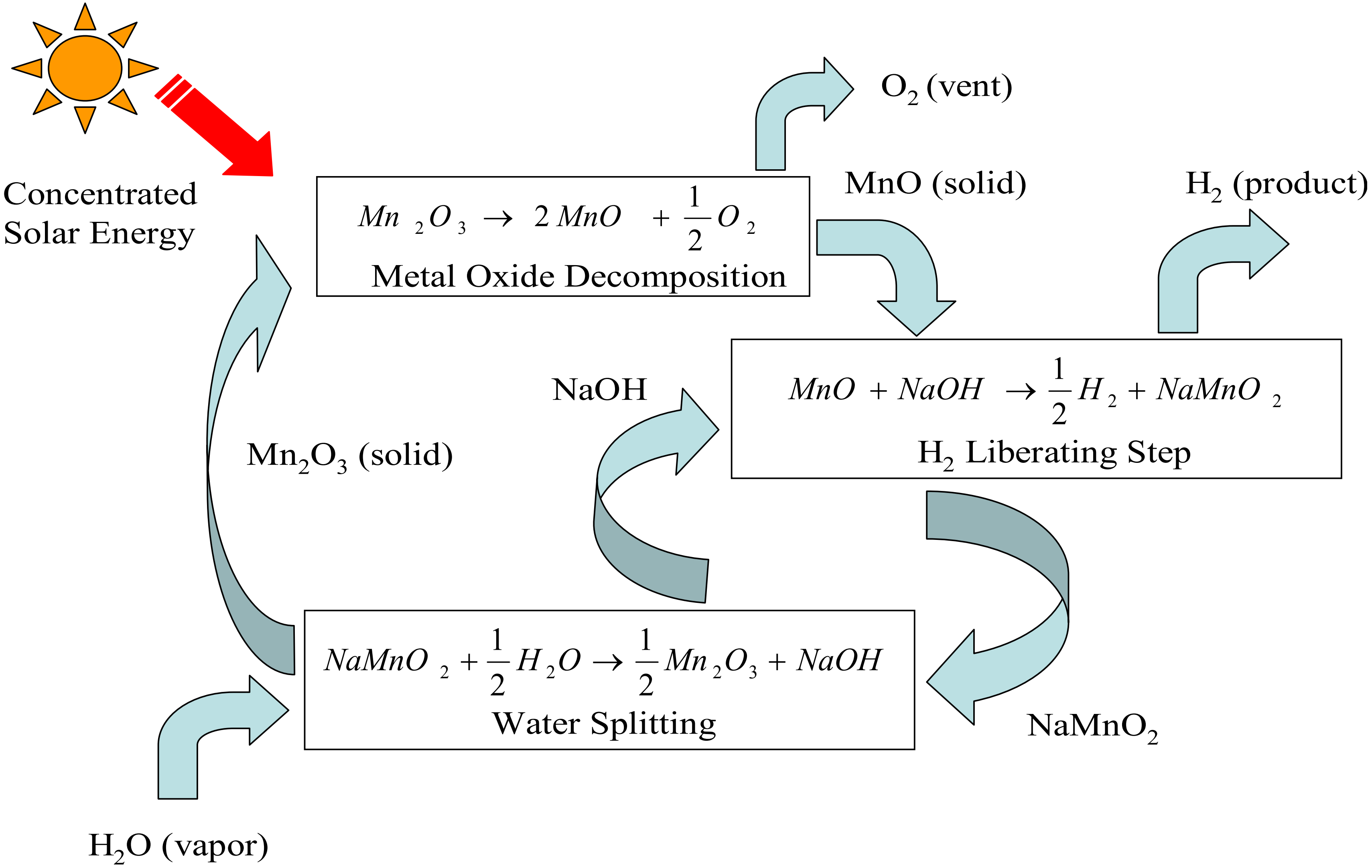
# Literature Surveyed

- 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



Concentrated Solar Energy

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

Metal Oxide Decomposition

$O_2$ (vent)

MnO (solid)

$H_2$ (product)

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

$H_2$ Liberating Step

NaOH

$Mn_2O_3$ (solid)

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

Water Splitting

$NaMnO_2$

$H_2O$ (vapor)

# 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

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# 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 $H_2$/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 $H_2$/day plant

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# Simplified Process Flowsheet:

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

## Solar Thermal Decomposition

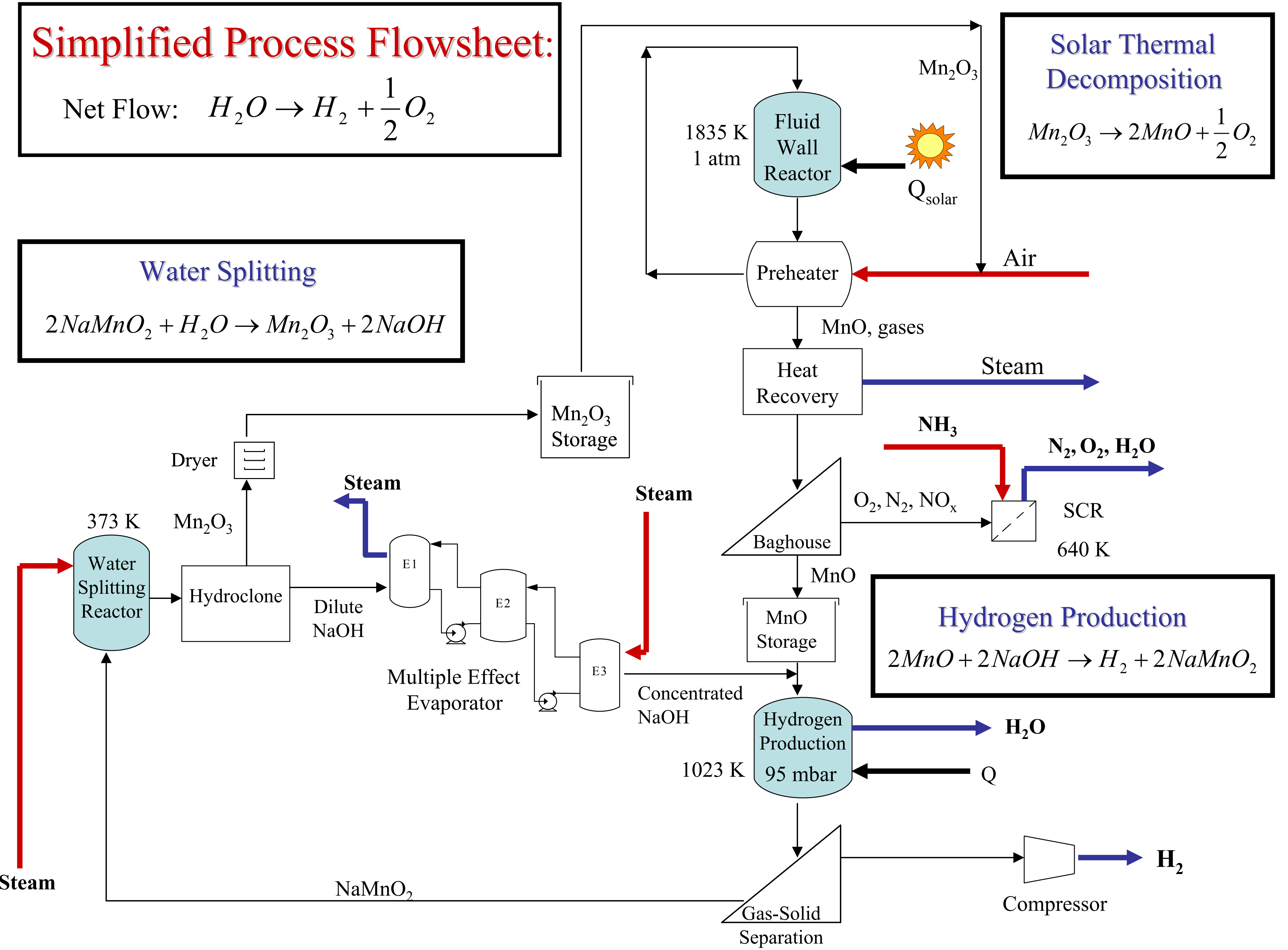
$$Mn_2O_3 \rightarrow 2MnO + \frac{1}{2}O_2$$

## Water Splitting

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

## 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).

Chemical Reactions

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

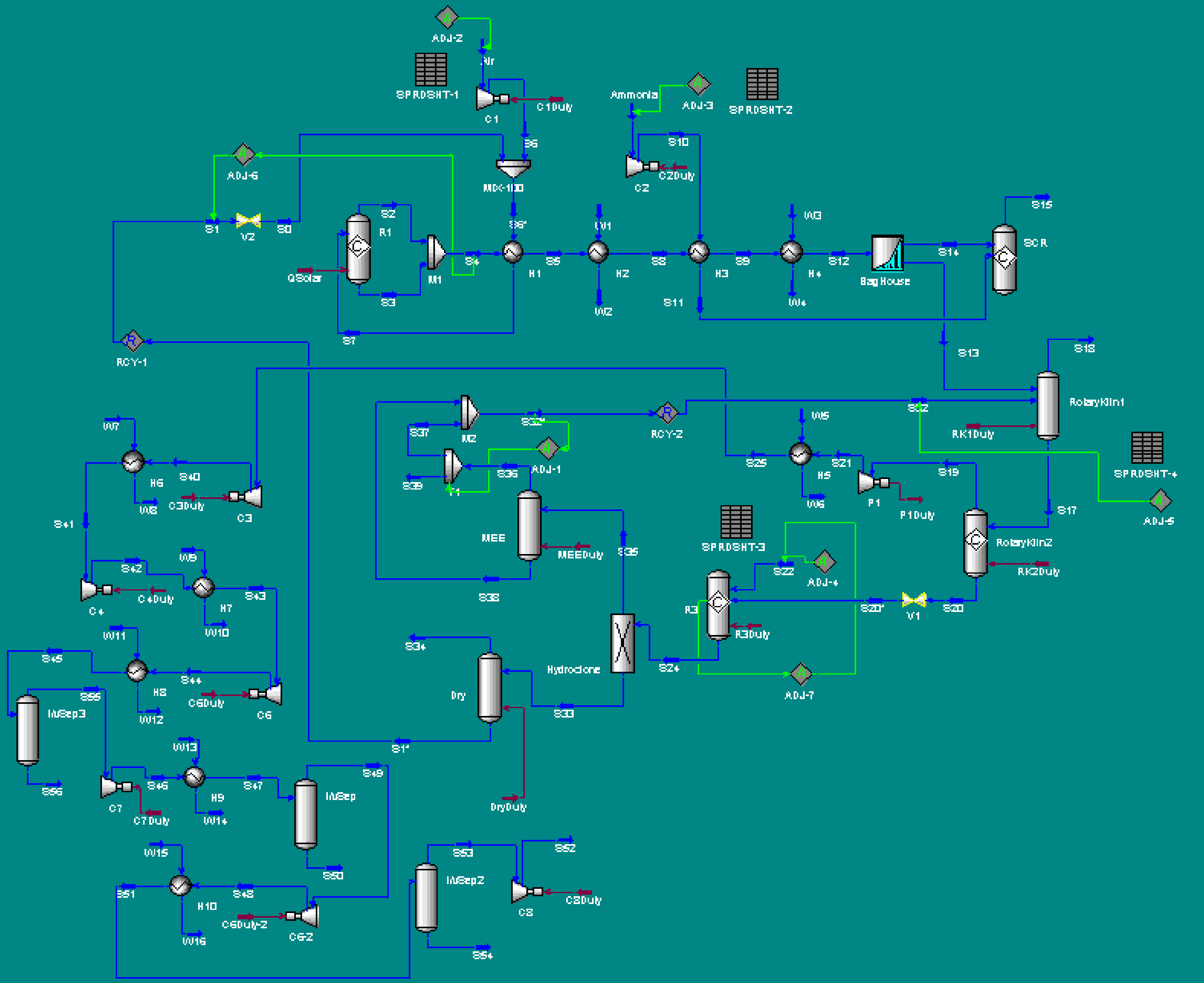
$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$$

Catalyst: $TiO_2$ / $V_2O_5$ / $WO_3$

## 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*

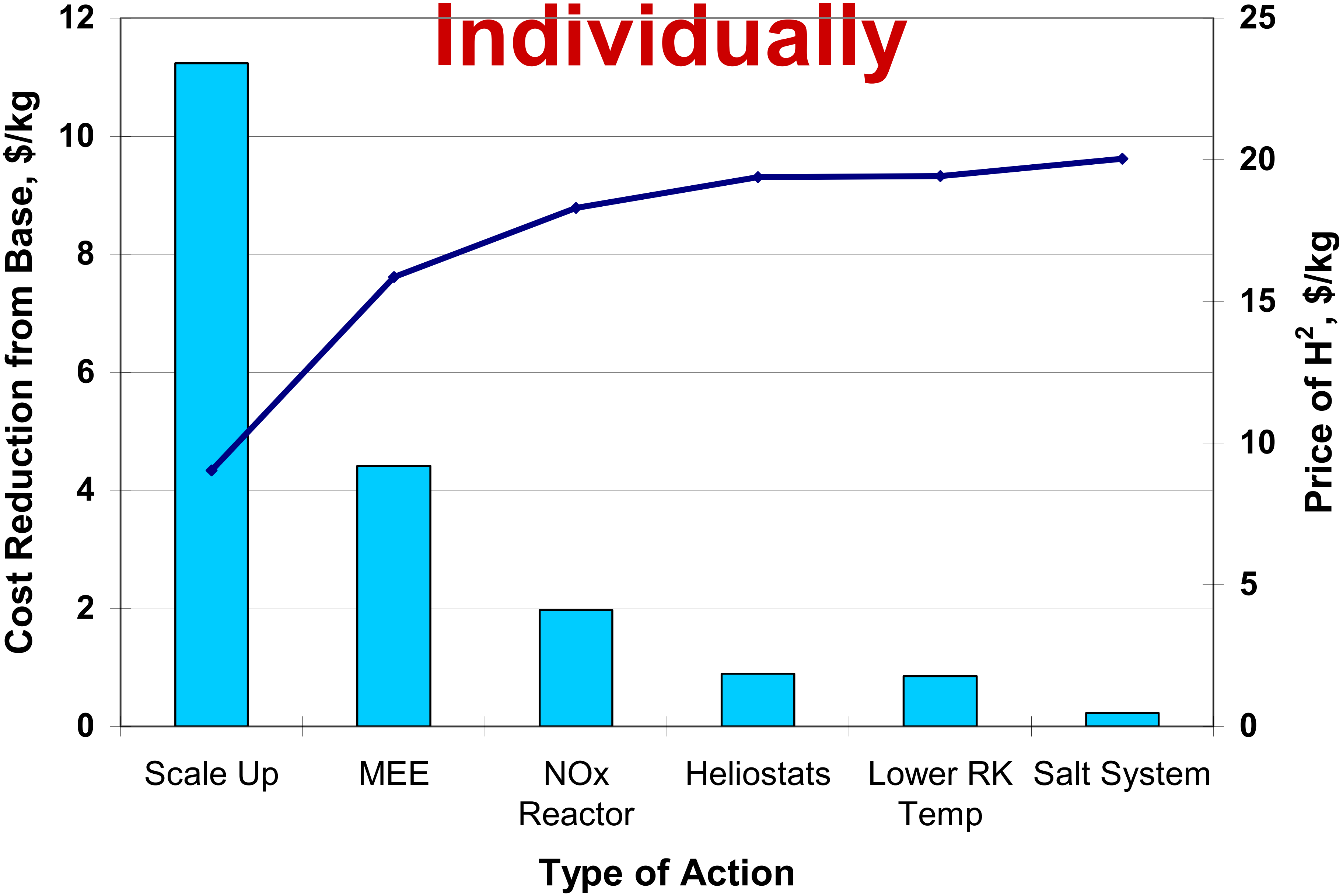
| | Base Case: Single 24 $MW_{th}$ solar thermal reactor | 95 solar thermal reactors (each 24 $MW_{th}$) Single Back-end |
|---|---|---|
| **Products** | | |
| $H_2$ | 235 kg/hr<br>(1,579 kg/day), $20.27/kg | 22,325 kg/hr<br>(150,024 kg/day), $9.04/kg |
| Low Pressure Steam | 2,491 kg/hr | 236,645 kg/hr |
| **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)

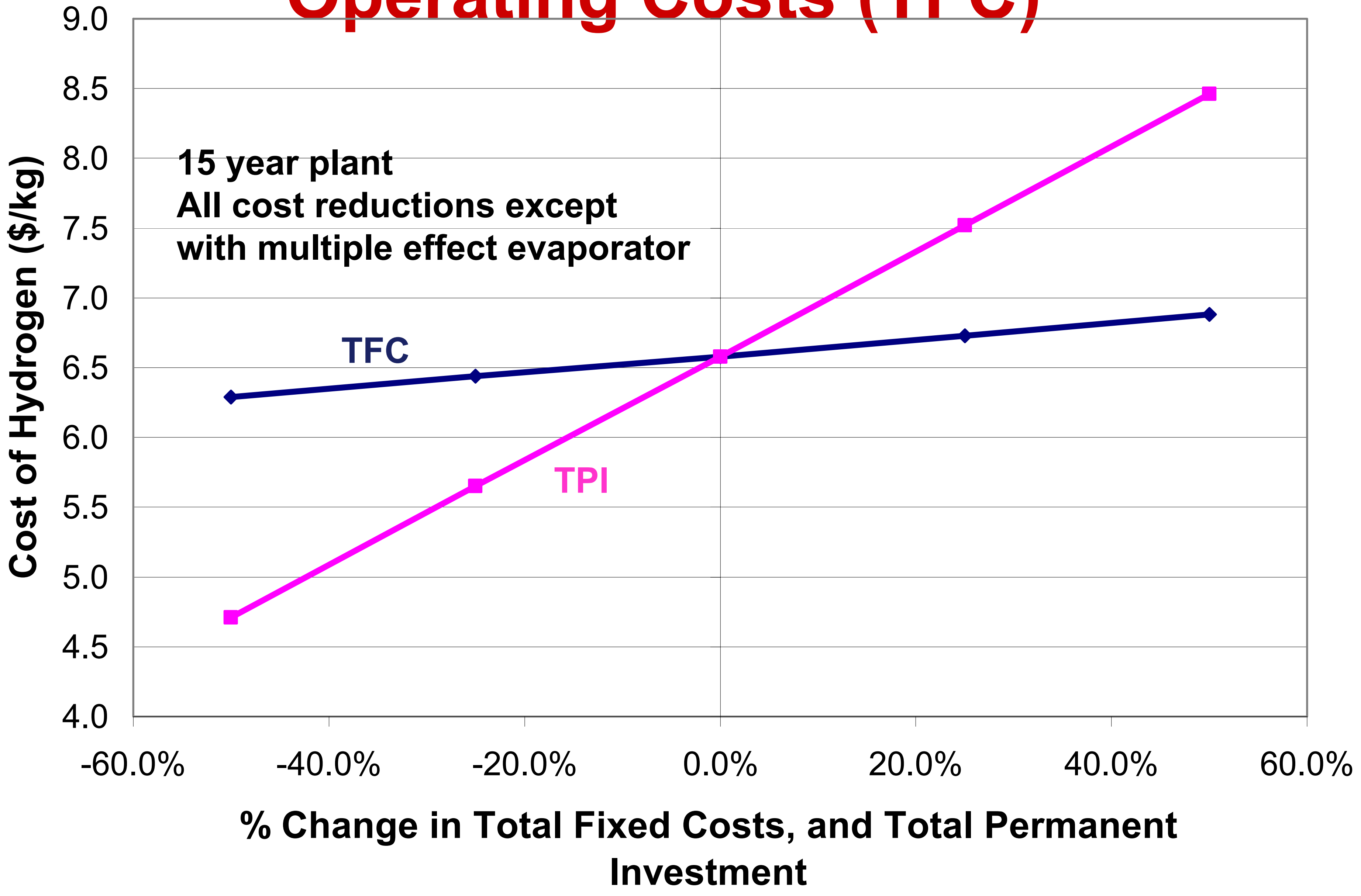
# Possible Cost Reducing Areas

- 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 $H_2$ 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 $Mn_2O_3 \rightarrow 2\ MnO + \frac{1}{2}\ O_2$ in air and in-situ mitigation of NOx ($2/kg)
- Reduced heliostat costs ($1/kg)
- Kinetics of $Mn_2O_3 \rightarrow 2\ MnO + \frac{1}{2}\ O_2$ (lowest temperature) ($1/kg)
- Consider alternative secondary reaction steps

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# Experimental Work Plan Development

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

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# Hydrogen Safety

- At this stage of the project, $H_2$ quantities involved in the experiments are so minimal as to pose no $H_2$ 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

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# Conclusions/Summary

- The $Mn_2O_3$/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 NOx mitigation

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# Acknowledgement

- DOE Hydrogen Program

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