Lessons Learned:
Developing Thermochemical Cycles for Solar Heat Storage Applications

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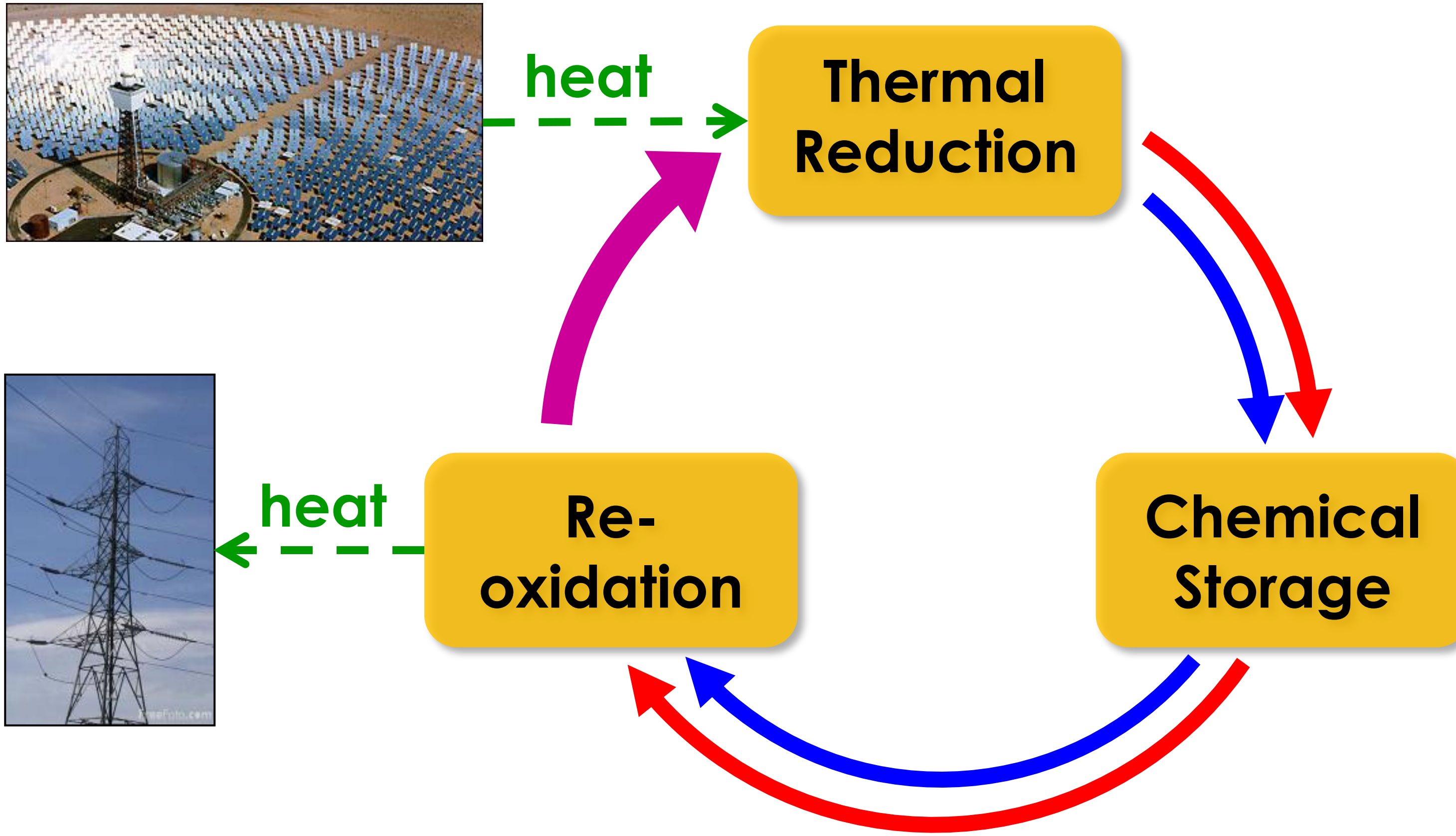
Outline

- Introduction
- Case Study I: Solid Oxide Decomposition
- Case Study II: Sulfur Based Cycle
- Conclusions

Solar heat is used to drive the reduction step of a thermochemical cycle



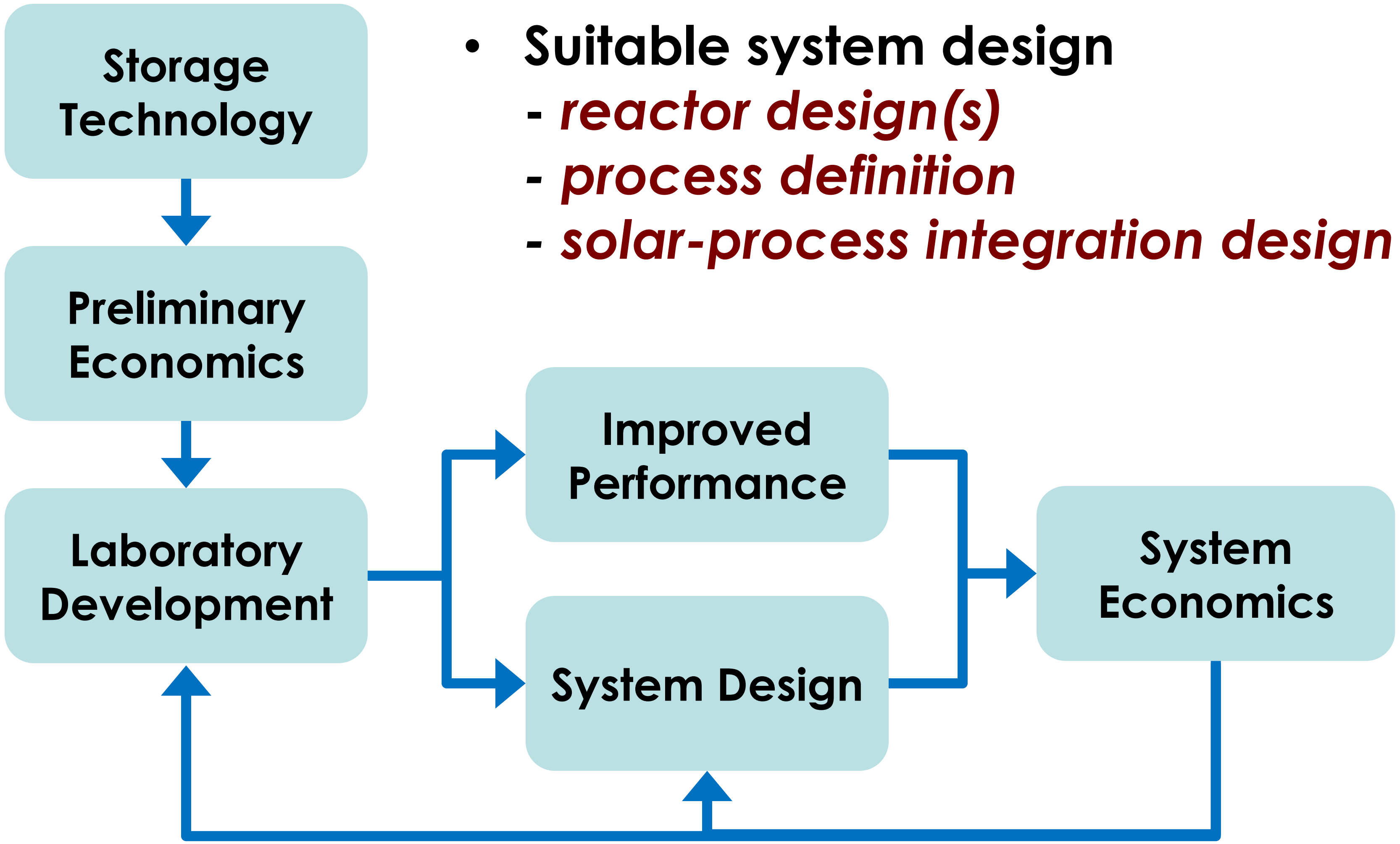
- Energy is stored in chemical bonds
- Energy is recovered upon chemical re-oxidation

Thermochemical heat storage can provide very high energy storage densities

Technology	Energy Density (kJ/kg)
Gasoline	45000
Sulfur	12500
Cobalt Oxide	850
Molten Salt (Phase Change)	230
Molten Salt (Sensible)	155
Lithium Ion Battery	580
Elevated water Dam (100m)	1

- **High energy density with low storage cost**
- **Ambient and long term storage**
- **Transportability**

An approach to develop and determine whether a TC suitable for TES has been established



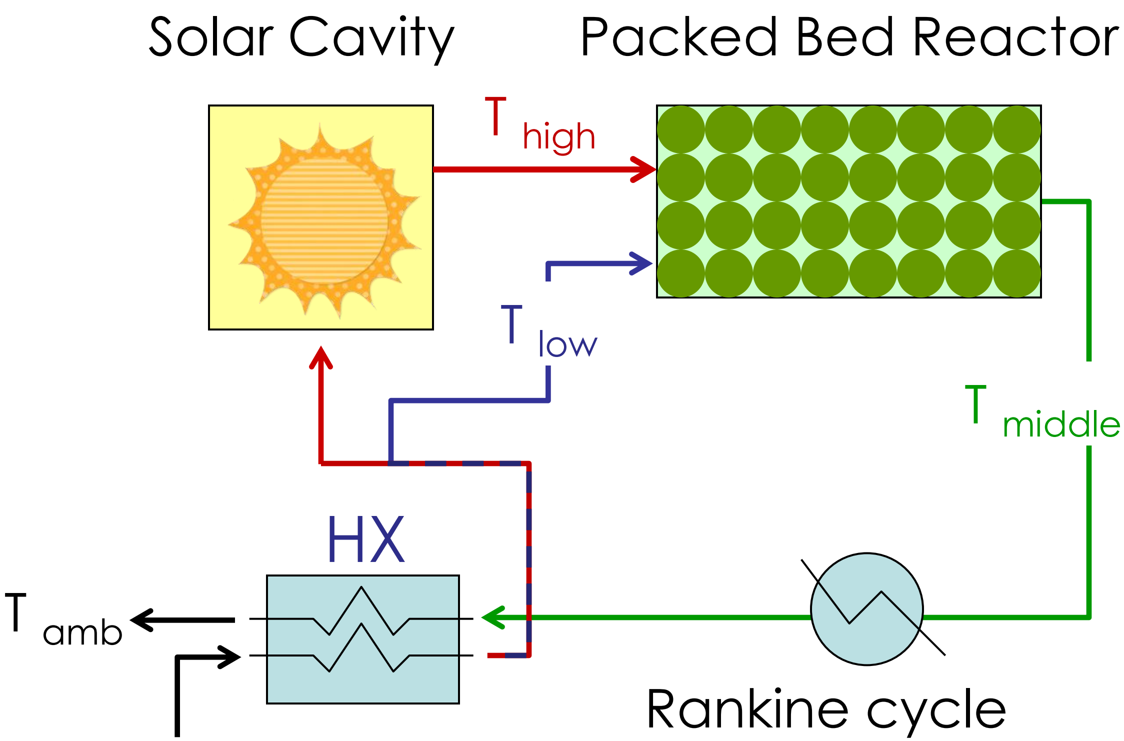
- **Suitable system design**
  - *reactor design(s)*
  - *process definition*
  - *solar-process integration design*

GA led two thermochemical energy storage projects that are supported by DOE

1. Solid Oxide Based Thermochemical Heat Storage*
   (DOE Advance TES program DE-FG-36-08GO18145)
2. Sulfur Based Thermochemical Heat Storage for Baseload*
   (DOE Baseload program DE-EE0003588)

* Project partner: German Aerospace Center (DLR)

A pair of solid oxide REDOX reactions were used to store and release heat



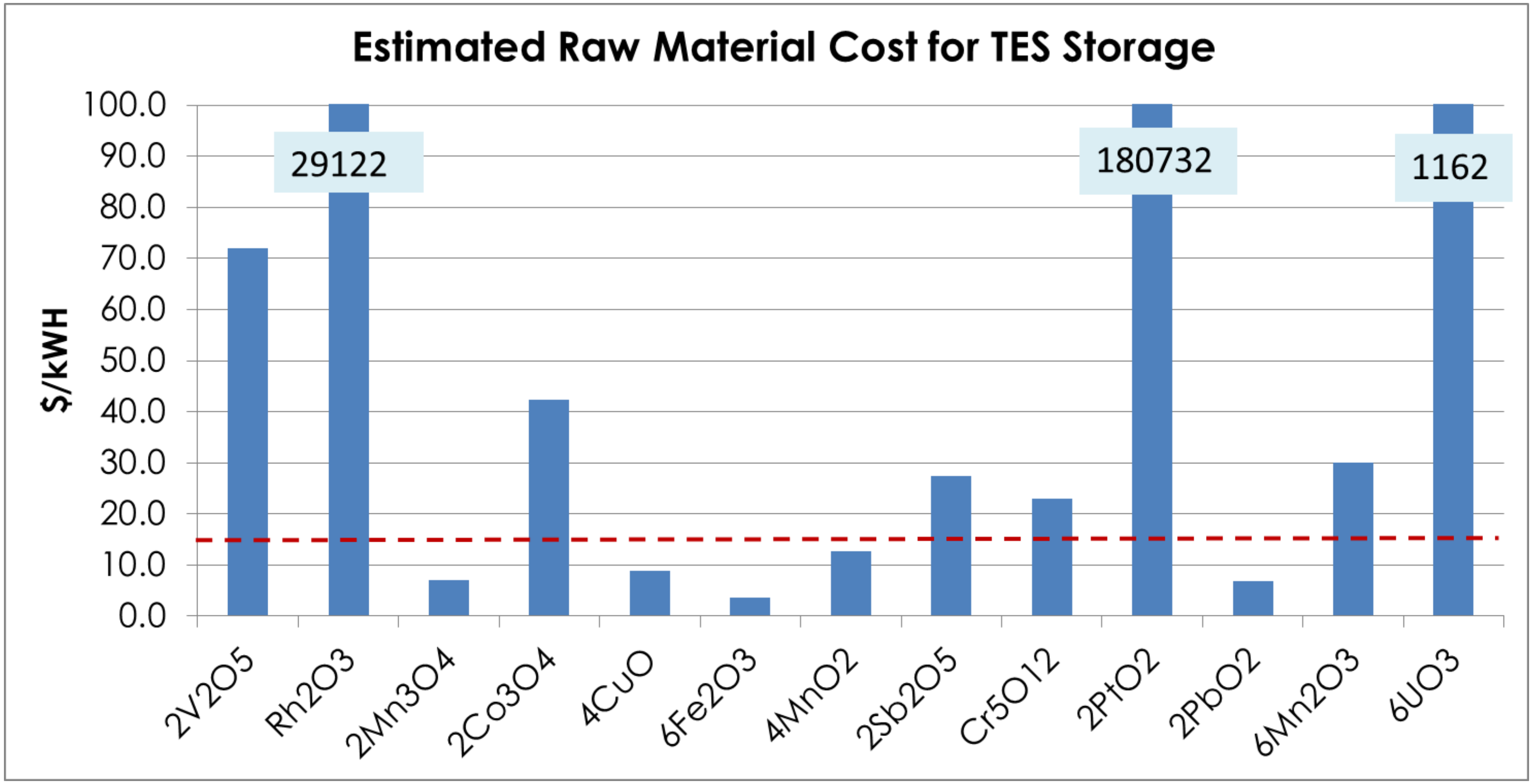
$T_{high} > T_{REDOX} > T_{middle} > T_{low} >> T_{amb}$

- **The heat transfer fluid (HTF) is also the reactant e.g. Air (O_2), CO_2 & H_2O**
- **Open System – no storage of HTF: oxides**
- **Closed System – HTF storage required: carbonates, hydroxides**

$MO_{2x+1} \rightarrow MO + xO_2$	$\longrightarrow$ **On sun**	**endo. (charge)**
$MO + xO_2 \rightarrow MO_{2x+1}$	$\longrightarrow$ **Off sun**	**exo. (discharge)**

Preliminary economics can be estimated through energy related costs

- **Energy related costs include raw materials, storage and process cost etc.**



- **Low raw material cost is required for large scale use**

Thermal reduction takes place readily in all candidate oxides

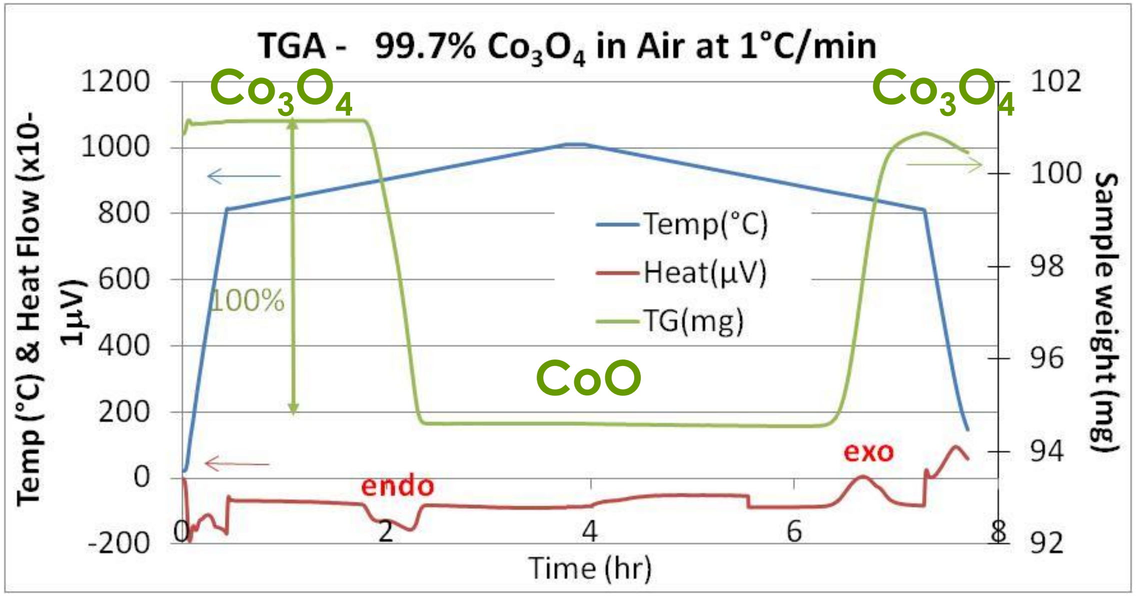
Reaction	HSC Temp (°C)	Exp Temp (°C)	Re-oxidation
$2PbO_2 \rightarrow 2PbO + O_2$	*405*	*NA*	*NO*
$2Sb_2O_5 \rightarrow 2Sb_2O_4 + O_2$	*515*	*NA*	*NO*
$4MnO_2 \rightarrow 2Mn_2O_3 + O_2$	*530*	*NA*	*NO*
$2BaO_2 \rightarrow 2BaO + O_2$	780	690	YES*
$2Co_3O_4 \rightarrow 6CoO + O_2$	900	870	YES
$6Mn_2O_3 \rightarrow 4Mn_3O_4 + O_2$	900	900	YES*
$4CuO \rightarrow 2Cu_2O + O_2$	1025	1030	YES
$6Fe_2O_3 \rightarrow 4Fe_3O_4 + O_2$	1300	1200	YES
$2V_2O_5 \rightarrow 2V_2O_4 + O_2$	1325	750*	YES*
$2Mn_3O_4 \rightarrow 6MnO + O_2$	1500	1400	YES

* incomplete

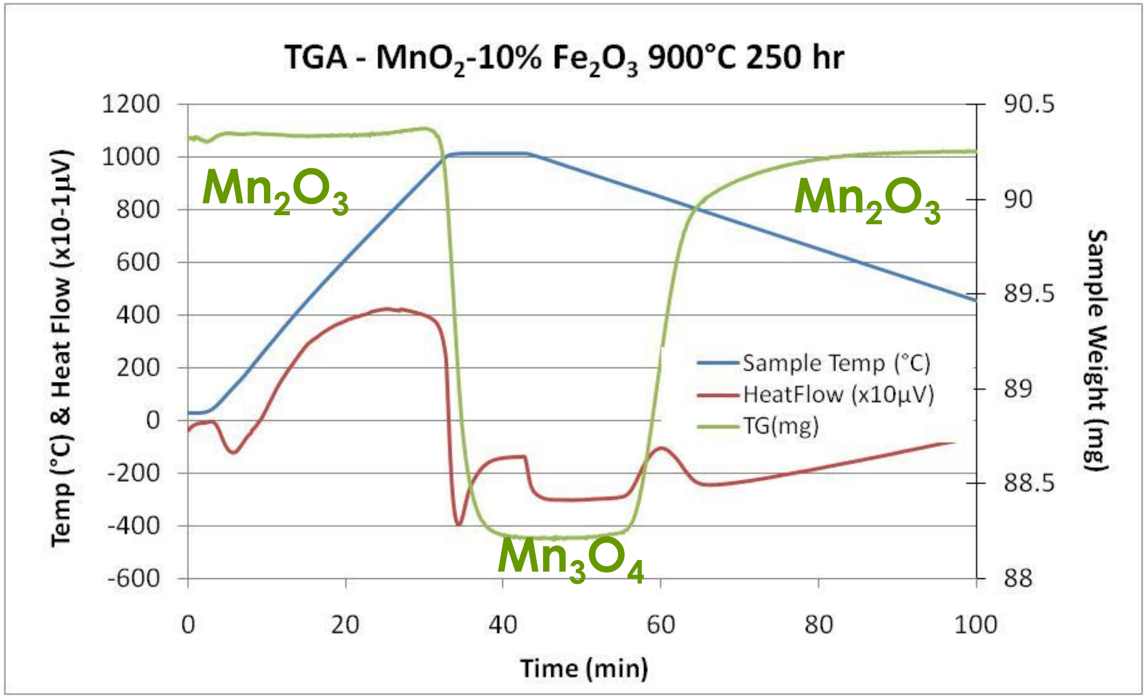
- Re-oxidation can be slow, especially at low temp
- Reaction kinetics needed to be improved

Four oxides underwent REDOX between 700-1100°C but only CoO demonstrated full re-oxidation

Reaction	Full Re-oxidation	Cyclic Repeatability
$2BaO_2 \rightarrow 2BaO + O_2$	No	Yes
$2Co_3O_4 \rightarrow 6CoO + O_2$	Yes	Yes
$6Mn_2O_3 \rightarrow 4Mn_3O_4 + O_2$	No	No
$4CuO \rightarrow 2Cu_2O + O_2$	No	No



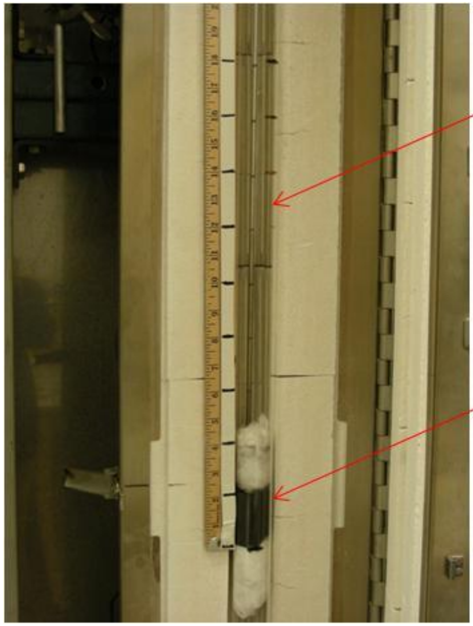
Secondary oxide addition was used to improve re-oxidation kinetics of manganese oxides



Doping	Max Re-oxidation (%)
Fe_2O_3	100
ZrO_2	42
CuO	25
None	6

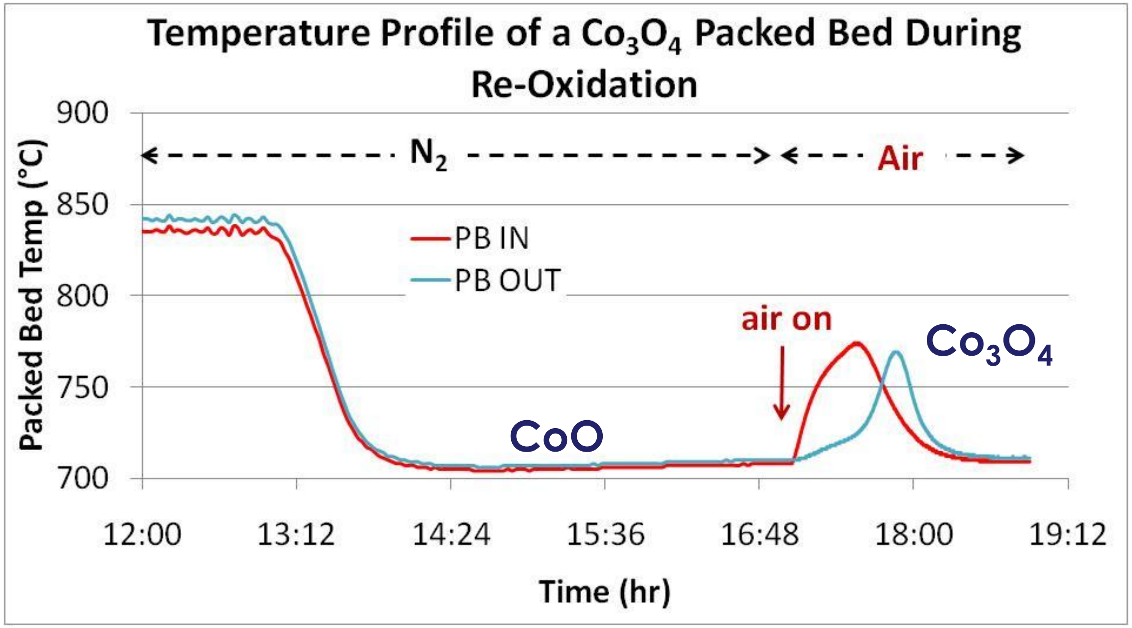
- **Full re-oxidation and cyclic repeatability were achieved with a 10wt%Fe_2O_3 addition**
- **REDOX reaction kinetics were obtained from laboratory measurements**

Thermal charging/discharging in a packed bed was demonstrated in the laboratory



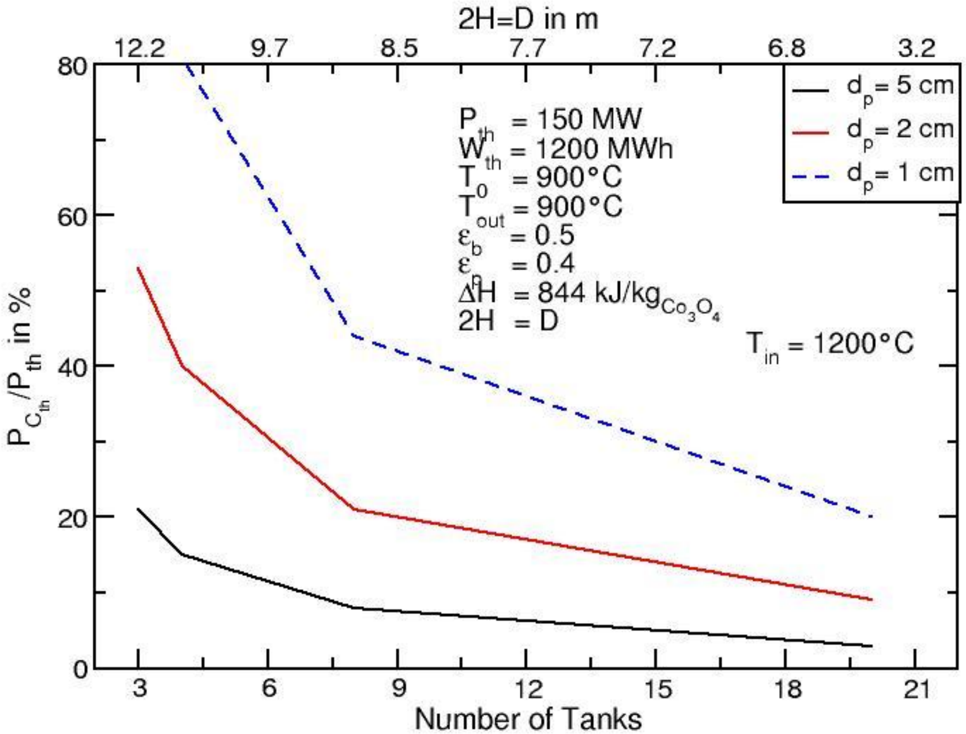
Quartz Tube

Packed Bed



- A materials compatibility study was carried out
- Process modeling was conducted using preliminary design and kinetics data
- Modeling data was used for final reactor design

Modeling results show pressure drop has significant impact on efficiency, process and reactor designs

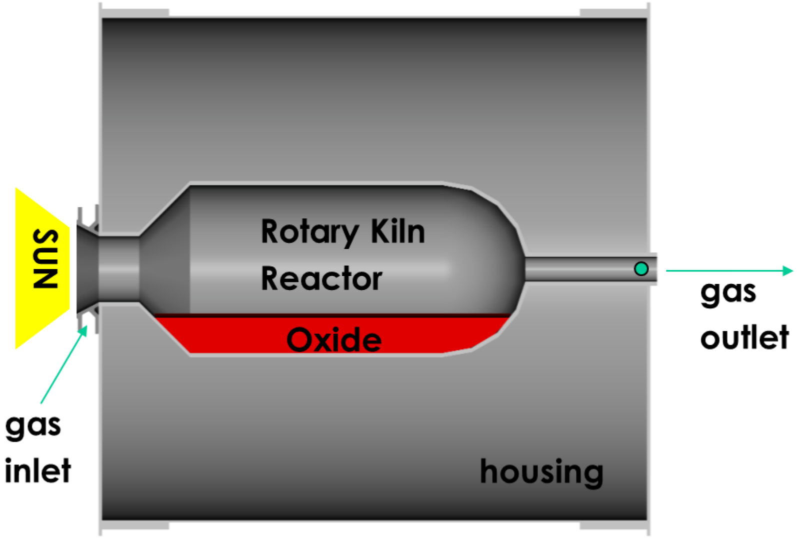


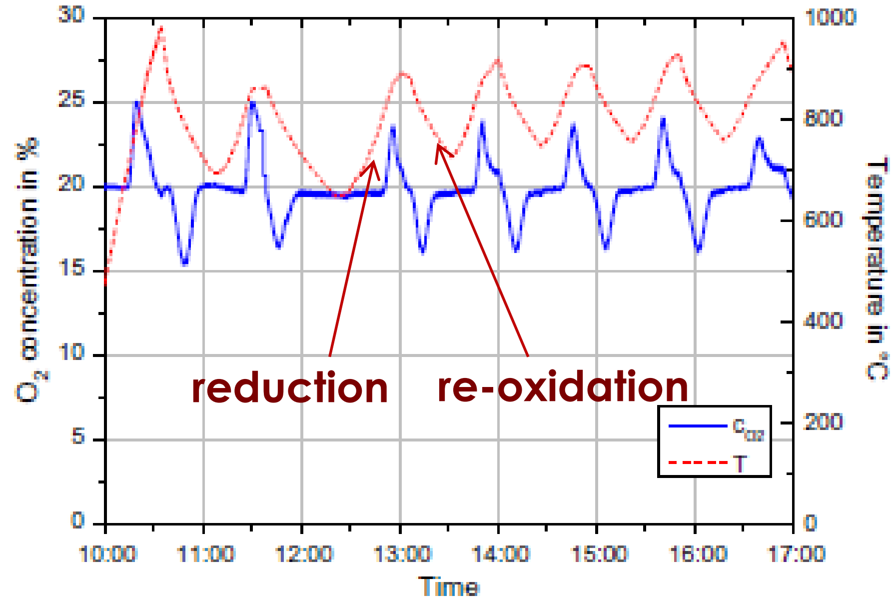
- **Higher inlet air temp is required (+300°C> eq)**
- **Larger pellets are necessary**
- **Multiple reactors are needed**

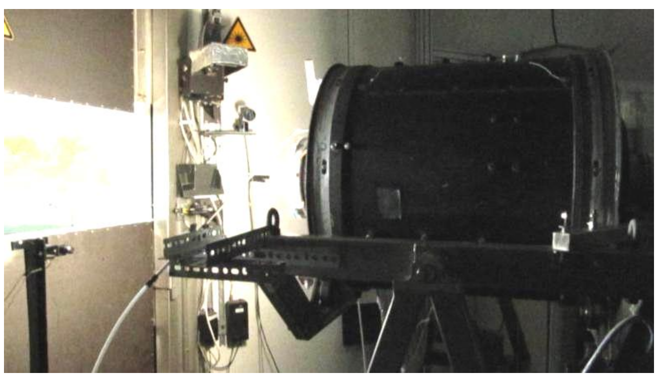
- **Indirect heat transfer is not suitable when high mass flow rates are required**
- **A directly irradiated design is preferred**

F. Schaube in GA Report A27230

A directly irradiated moving bed reactor design was adapted







A rotary kiln (moving bed) reactor

- **REDOX kinetics was much faster in a moving bed**
- **Maximize heat transfer rate to fully utilize solar heat**

M. Neises et al, Solar Energy (2012)

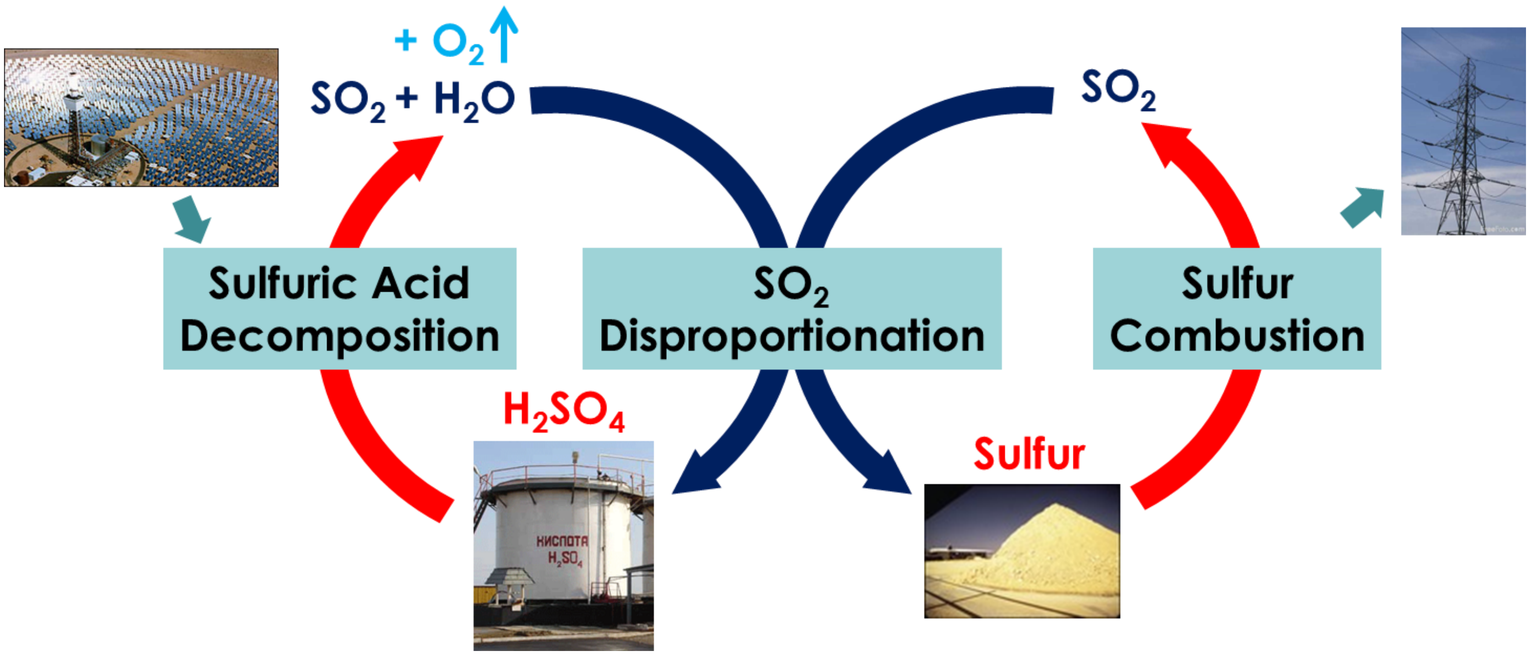
REDOX of solid oxide is applicable to thermochemical energy storage for CSP

- Material cost is the main driver of TES economics
- Mixed oxides greatly improve REDOX kinetics and cyclic repeatability
- A moving bed reactor is required to minimize parasitic cost

DOE Metric	Unit	2015	Mn-Fe	Co-Al
Storage Cost	$/kWh	15	15-35	50-100
LCOE	$/kWh	0.06	0.09-0.11*	0.13-0.17*
Efficiency	%	93	>93	>93

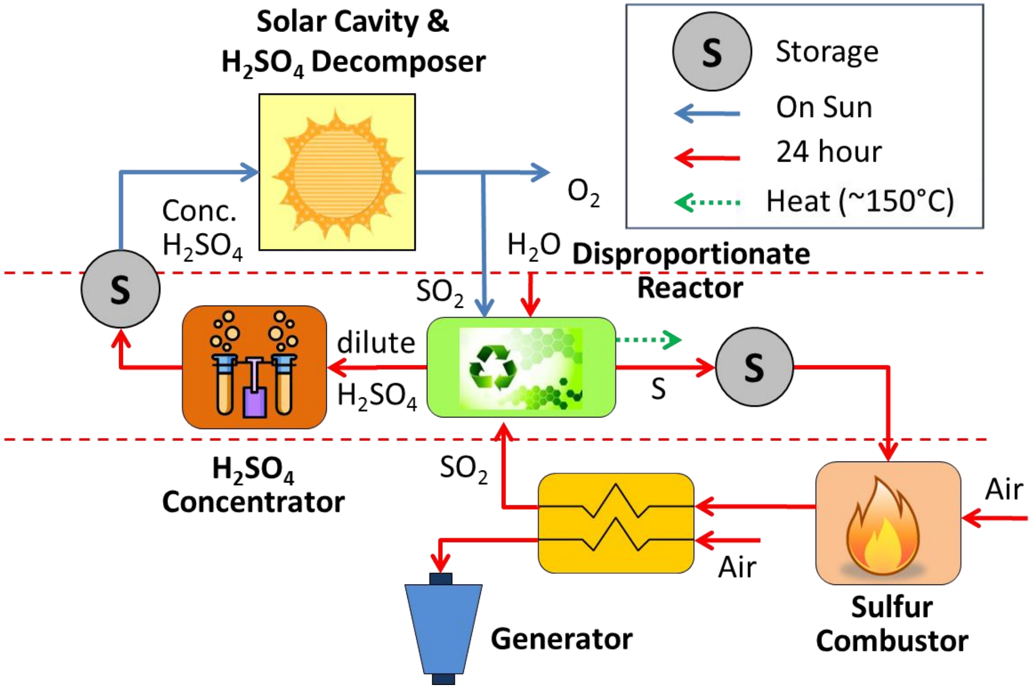
*SAM (NREL) using 2010 costs

Solar energy can be stored in elemental sulfur via a three step thermochemical cycle



	Reaction	Temp (C)
H_2SO_4 Decomposition	$2H_2SO_4 \rightarrow 2H_2O(g) + O_2(g) + 2SO_2(g)$	800
SO_2 Disproportionation	$2H_2O(l) + 3SO_2(g) \rightarrow 2H_2SO_4(aq) + S(l)$	150
Sulfur Combustion	$S(s,l) + O_2(g) \rightarrow SO_2(g)$	1200

Preliminary economics was assessed using a simplified process flowsheet



- *maximize solar capacity*
- *diurnal and seasonal energy storage*
- *constant daily/ year round power supply*
- *Brayton or combined cycle*
- *environmentally friendly*

DOE Metric	Capacity Factor	LCOE (¢/kWh_e)
SunShot Target	75%	6.0
CSP w/Sulfur Storage	>75%	8.7*

*SAM (NREL) using 2010 costs

Phase I – Determine the TC limits and address key process and design issues

Disproportionaton

Reaction Modeling

Verify Process Feasibility
- Improve kinetics
- Catalyst
- Sulfur Extraction

Decomposition

Decomposer Selection

On Sun and Materials Testing

Flowsheet

Process Pathways Comparison

System Design

CSP Plant Performance

Capacity Factor

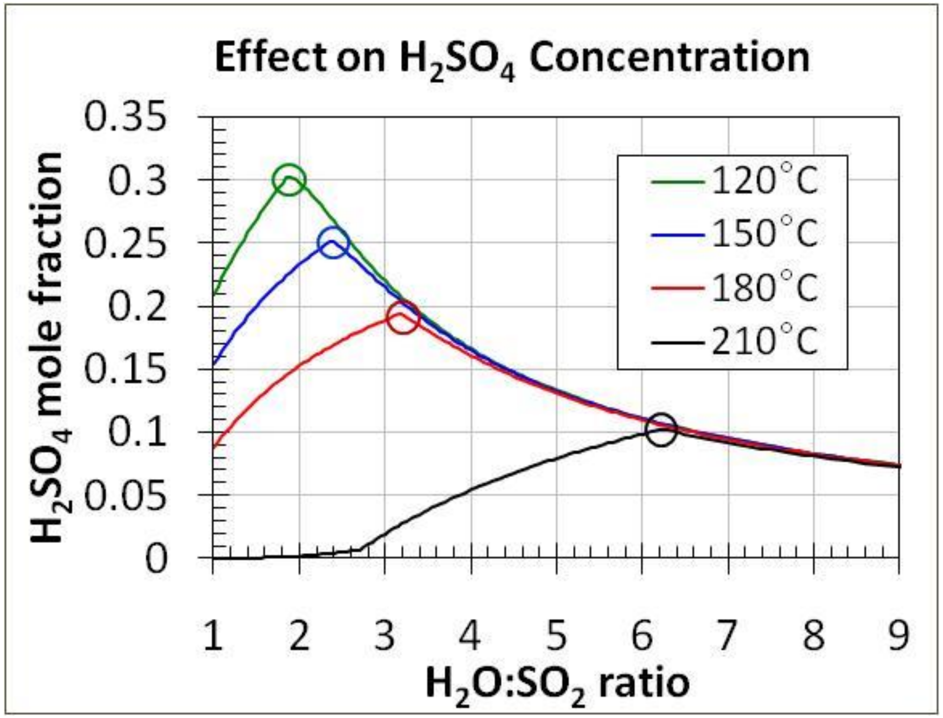
LCOE

GO NOGO

- Determine the thermodynamic limits for SO_2 disproportionation
- Maximize sulfur generation kinetics
- Establish a baseline system design – decomposer and materials compatibility

Effect of temperature and pressure on sulfur generation and H_2SO_4 conc. was modeled

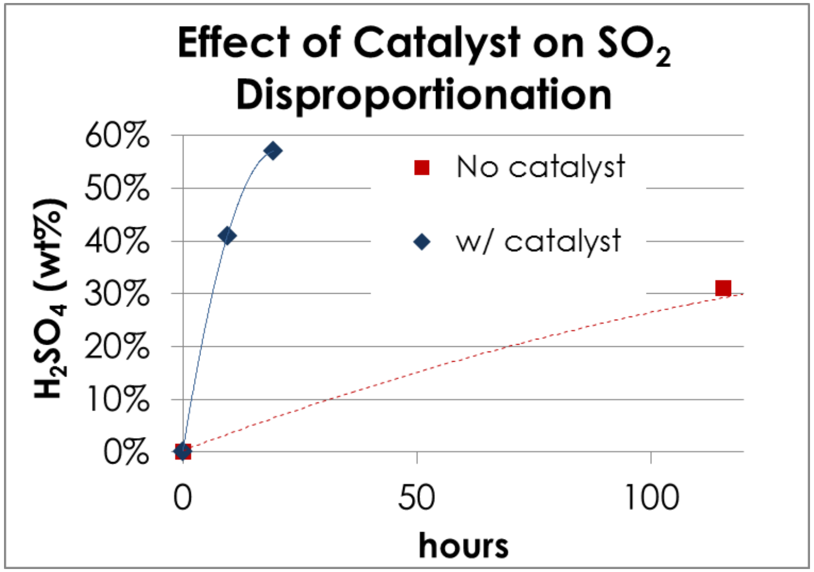
- **Results guided experimental work**
- **Data used for process and flowsheet designs**

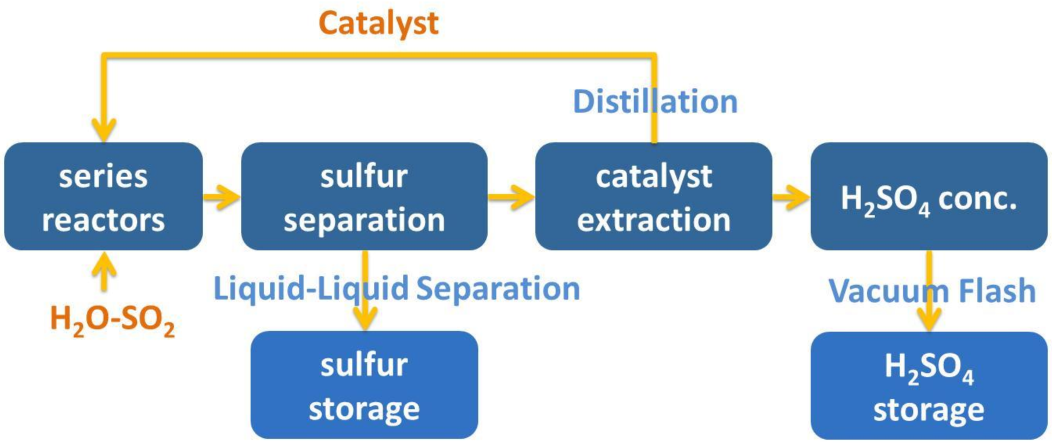


- ***Low temperature*** **and** ***high pressure*** **favor sulfur formation and high H_2SO_4 conc.**

Parameters	Range
Temp	120-150°C
Pressure	>10 bar
H_2O/SO_2	2 to 4
H_2SO_4 conc.	62wt%

Disproportionation kinetics was greatly enhanced with the use of catalyst

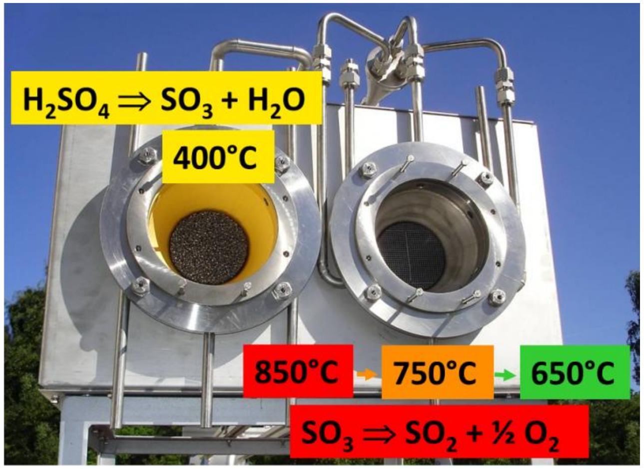




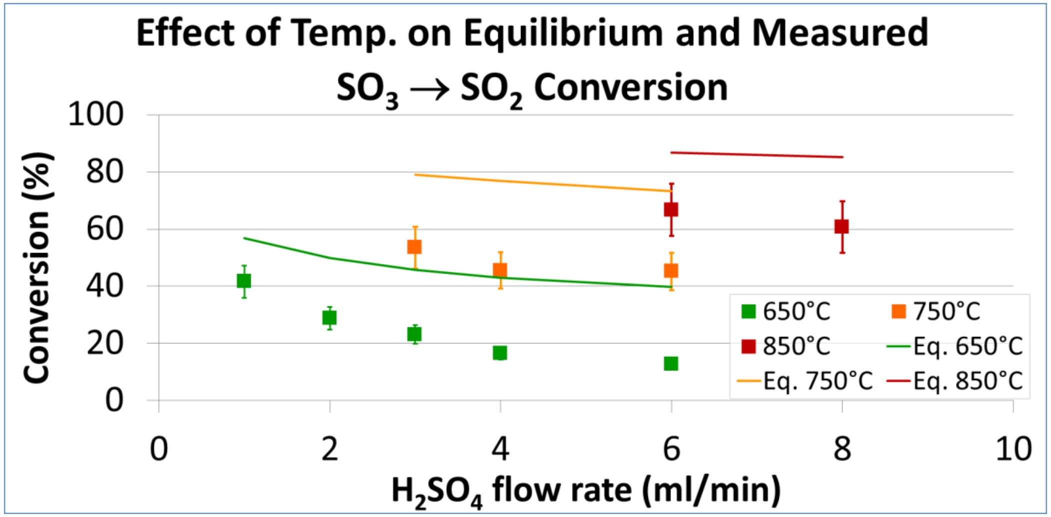
Process flow scheme for SO_2 disproportionation

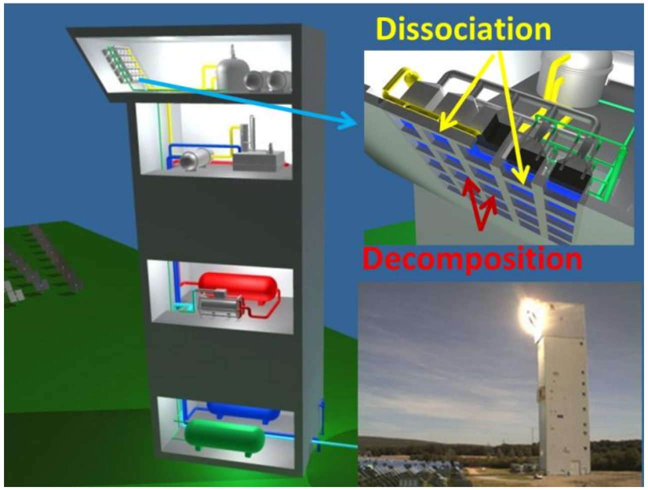
- Kinetics data defined reactor size and process cond.
- Means for sulfur extraction and catalyst recovery were established via laboratory work
- All processing steps for SO_2 disproportionation have been determined

Sulfuric acid decomposition was demonstrated on sun using a solar furnace



A dual chamber H_2SO_4 decomposer





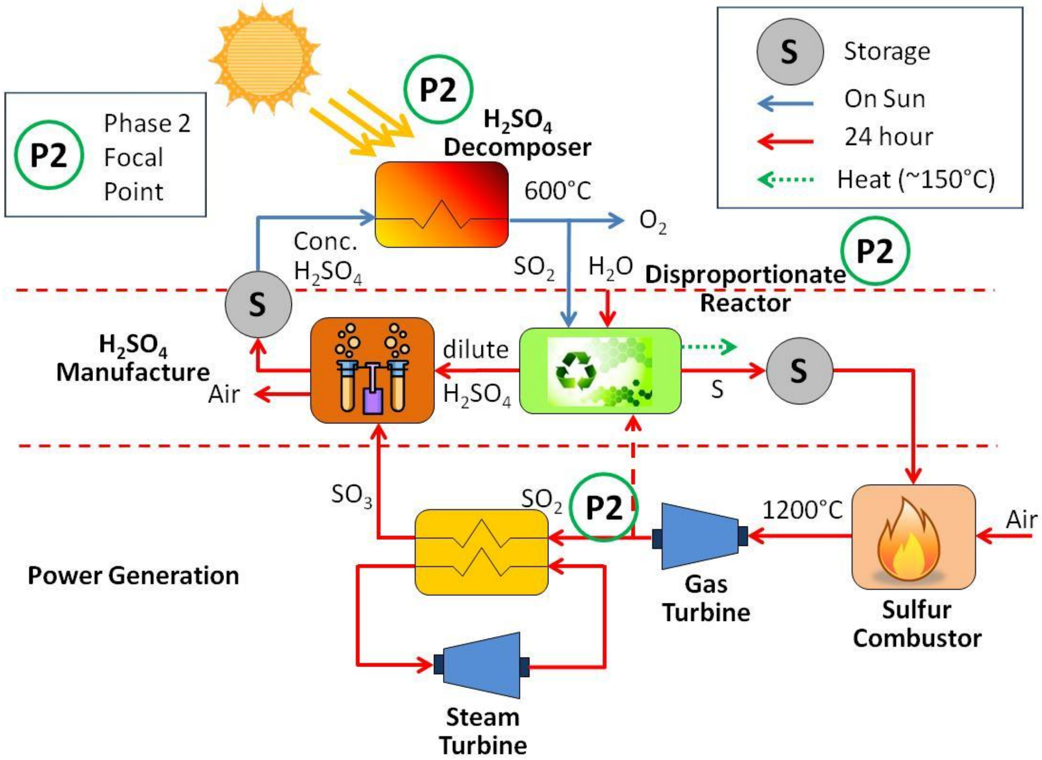
Conceptual scale up of a modular decomposer on a solar tower

- Process and decomposer refinement based on test data
- Lower decomp. temperature to reduce solar installation cost

D. Thomey et al., Int. Journal of Hydrogen Energy (2012)

A detailed flowsheet was established based on modeling and experimental data from Phase I

- **Plant design incorporated established processes from sulfuric acid manufacturing plant**



DOE Metric	LCOE (¢/kWh_e)
SunShot	6.0
CSP w/Sulfur Storage	8.1*

*SAM (NREL) using 2012 costs

- Storage cost is < $2/kWh
- LCOE is ~6¢/kWh_e based on proposed SunShot targets

Conclusions

- Chemical energy storage is well suited to CSP
- Energy related costs (materials and storage) need to be low
- Reaction kinetics of low temperature step can be a show stopper – improve kinetics
- Maximize process compatibility with solar reactor design – direct irradiation is preferred and always be beware of parasitic costs
- Maximize solar heat utilization and minimize solar installation cost in process and system designs
- When possible, incorporate established processes into your system design