SAND2015-5336C

# Maximizing Efficiency in Two-Step Solar-Thermochermical Fuel Production

**Ivan Ermanoski**

**Sandia National Laboratories**

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

# Chasing Carnot, Stefan and Boltzmann

**Ivan Ermanoski**

**Sandia National Laboratories**

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.



Sandia National Laboratories

# Acknowledgements

**James Miller and Anthony McDaniel**

**Sandia National Laboratories**

**Nathan Siegel**

**Bucknell University**

**Funding**

**U.S. Department of Energy Fuel Cell Technologies Office**



Sandia National Laboratories

# Two-Step Thermochemical Fuel Production

**A theoretically simple process: "pouring water on a hot rock" ™**

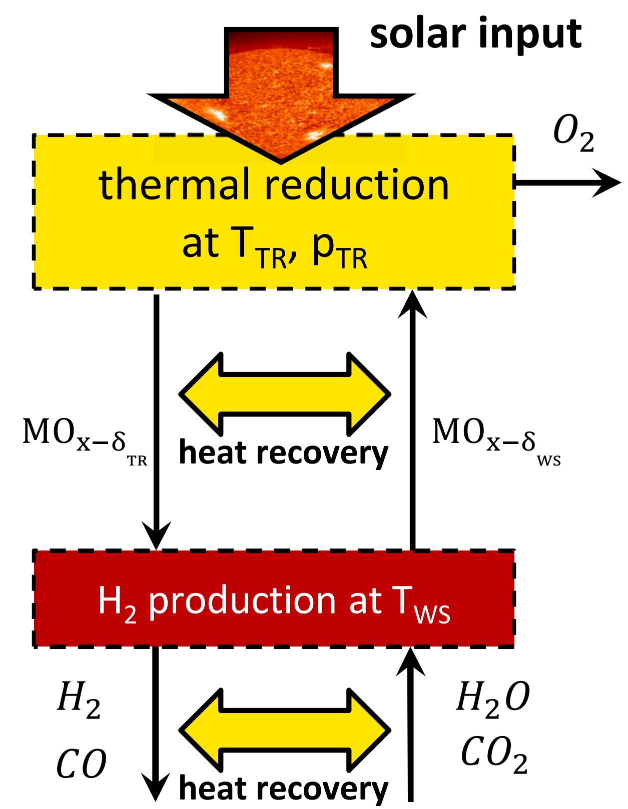
**Thermal reduction**

$$\frac{1}{\delta_{TR}-\delta_{WS}} MO_{x-\delta_{WS}} \rightarrow \frac{1}{\delta_{TR}-\delta_{WS}} MO_{x-\delta_{TR}} + \frac{1}{2} O_2$$

**Water/$CO_2$ splitting**

$$\frac{1}{\delta_{TR}-\delta_{WS}} MO_{x-\delta_{TR}} + H_2O \rightarrow \frac{1}{\delta_{TR}-\delta_{WS}} MO_{x-\delta_{WS}} + H_2$$

$$\frac{1}{\delta_{TR}-\delta_{WS}} MO_{x-\delta_{TR}} + CO_2 \rightarrow \frac{1}{\delta_{TR}-\delta_{WS}} MO_{x-\delta_{WS}} + CO$$

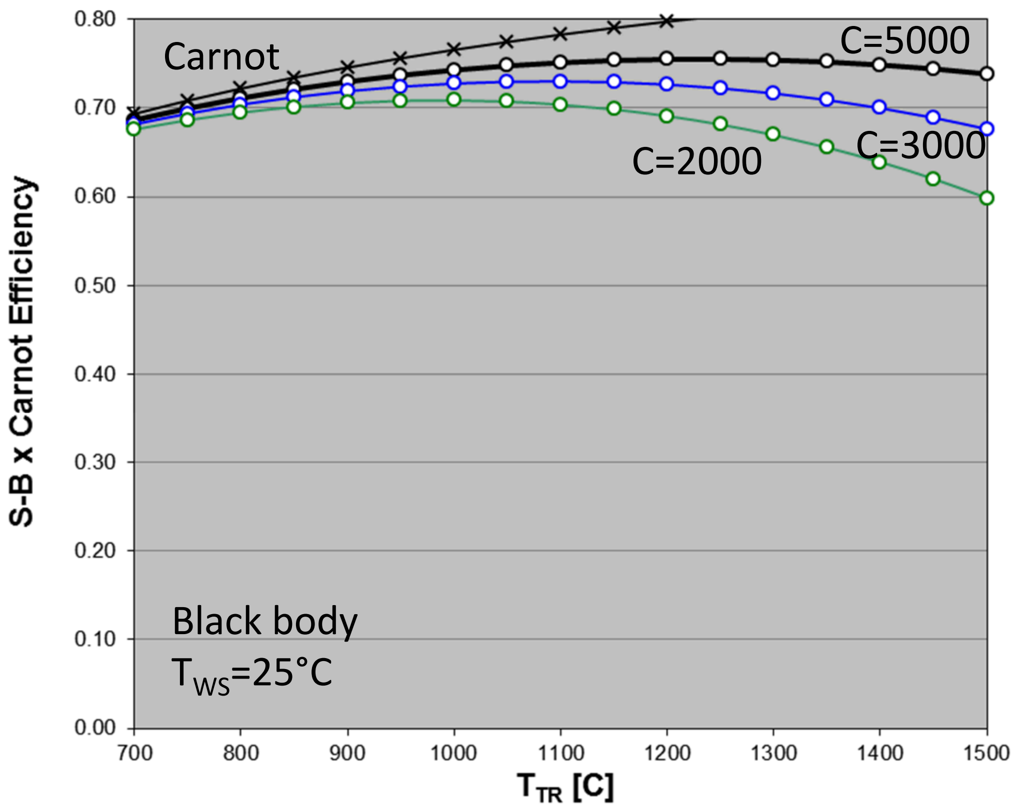


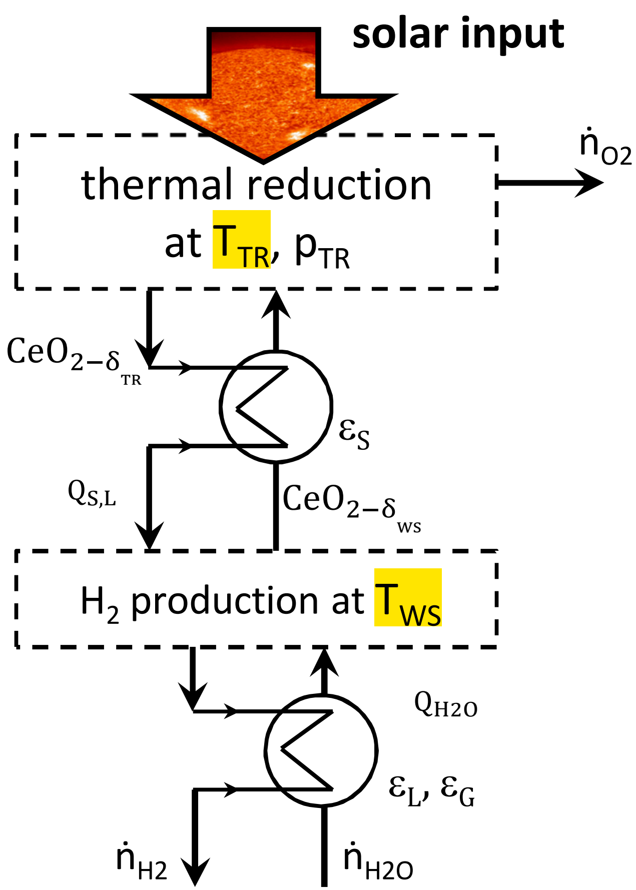

**STC converts heat to chemical work.**
**The trick is doing it efficiently.**

# Solar Heat Engine: Thermodynamic Limits

**Stefan-Boltzmann:** $P_{rad} = \sigma T_{TR}{}^4$

**Carnot:** $\eta = \dfrac{T_{TR} - T_{WS}}{T_{TR}}$




**Doing well!**

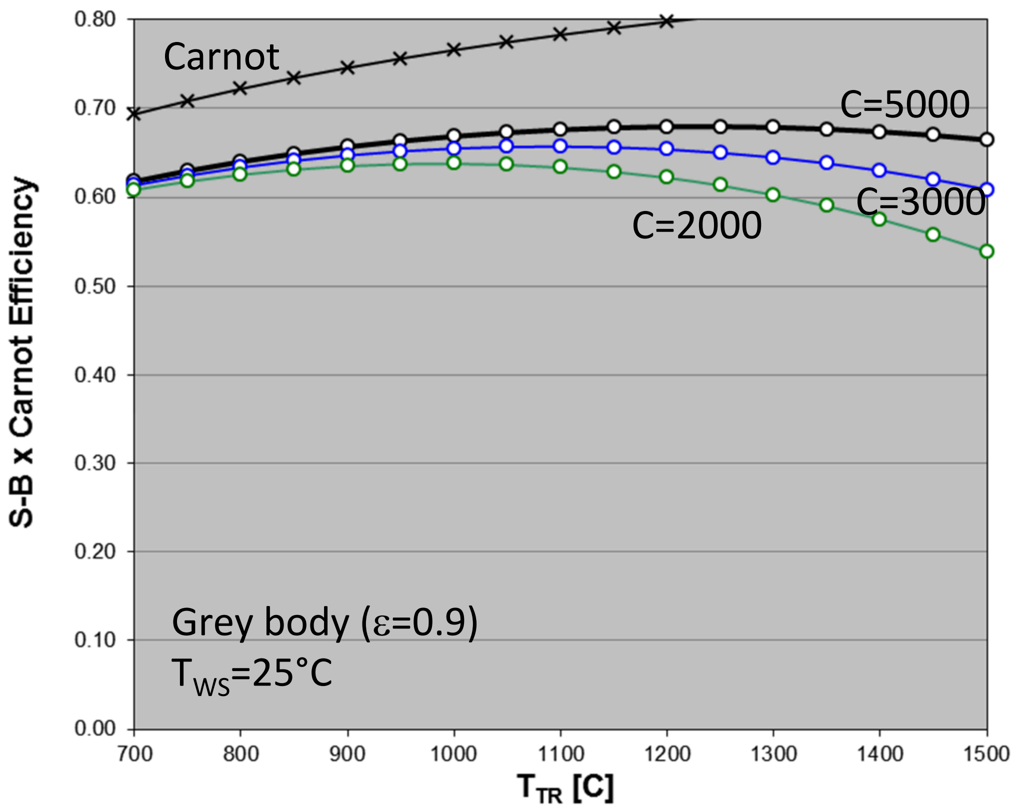


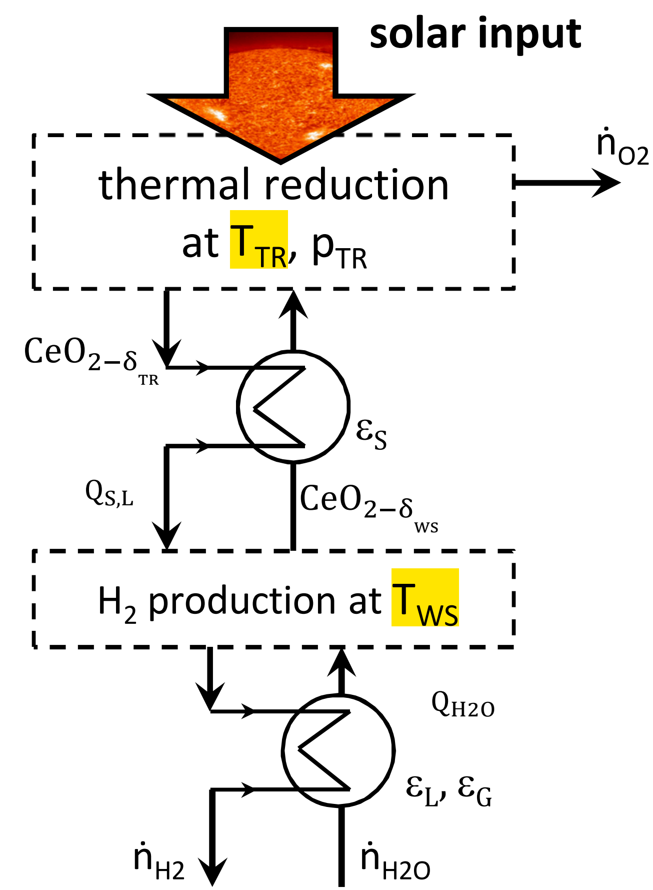
Sandia National Laboratories

# Solar Heat Engine: Thermodynamic Limits

**Stefan-Boltzmann:** $$P_{rad} = \sigma T_{TR}{}^4$$

**Carnot:** $$\eta = \frac{T_{TR} - T_{WS}}{T_{TR}}$$



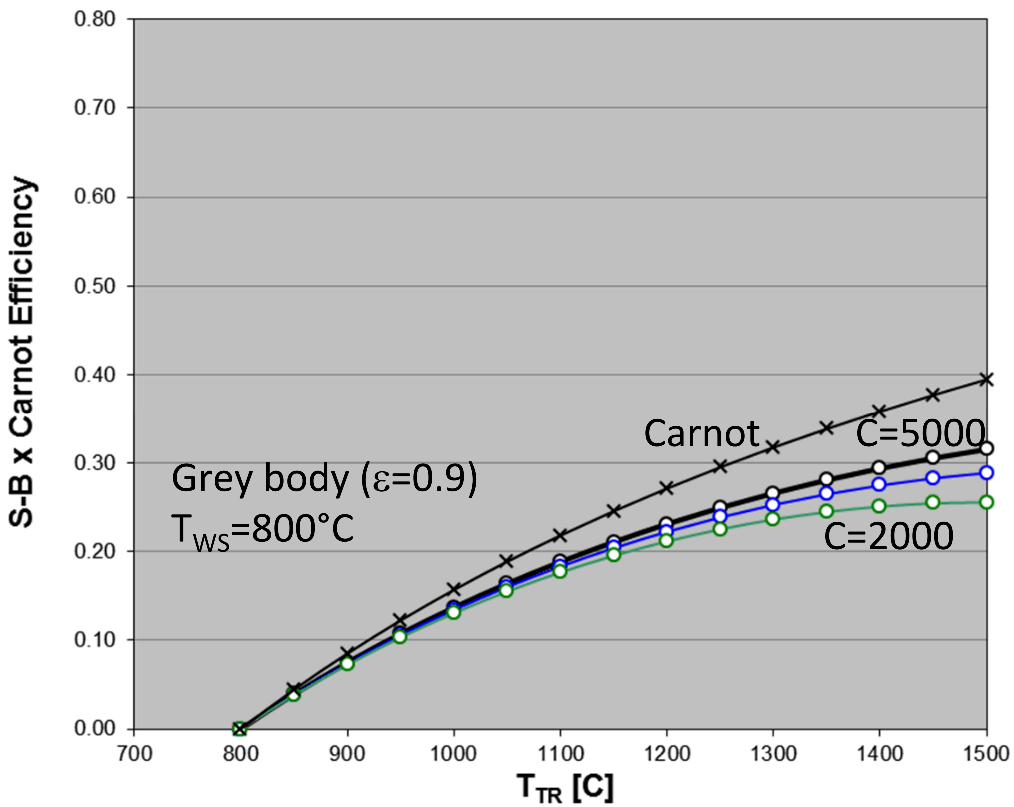



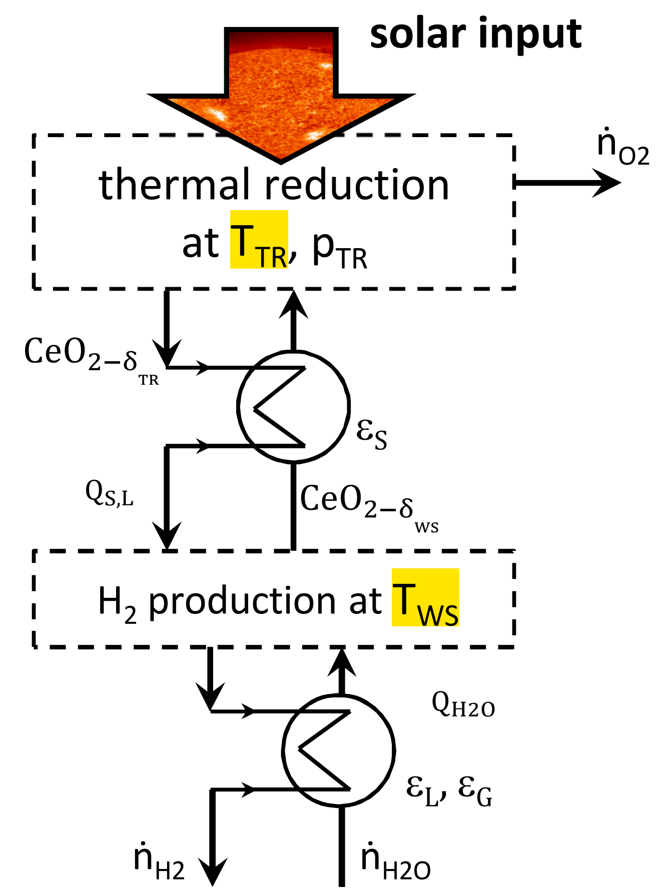

**Doing well!**

# Solar Heat Engine: Thermodynamic Limits

**Stefan-Boltzmann:** $$P_{rad} = \sigma T_{TR}{}^4$$

**Carnot:** $$\eta = \frac{T_{TR} - T_{WS}}{T_{TR}}$$



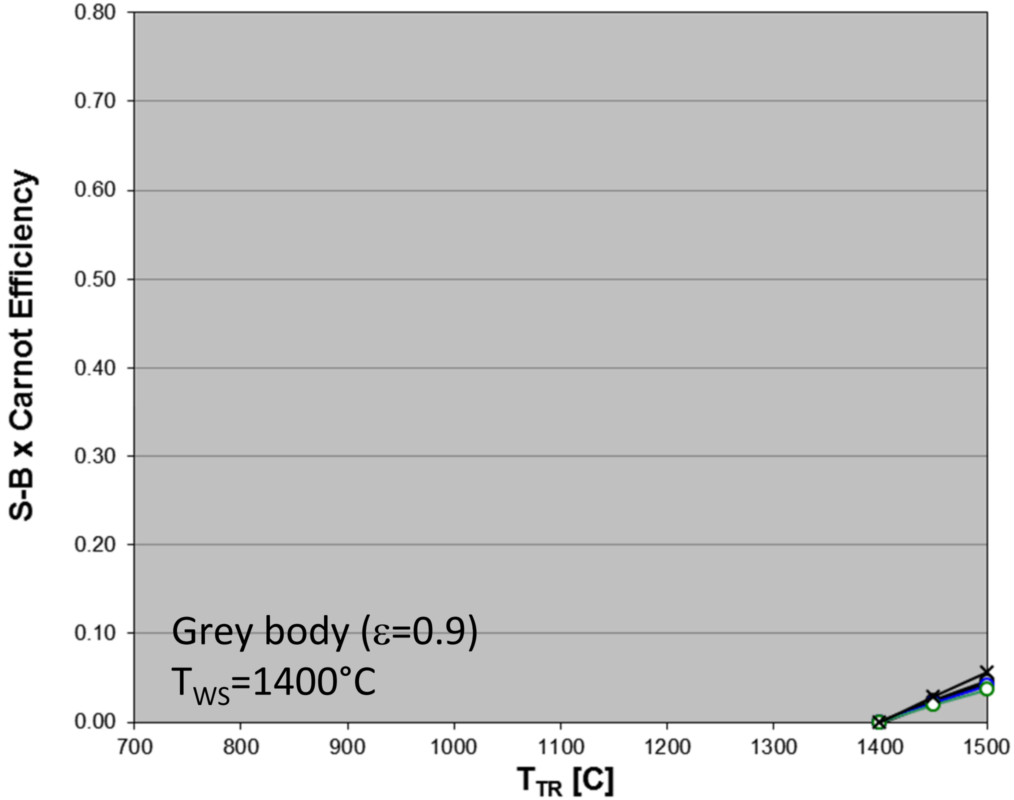



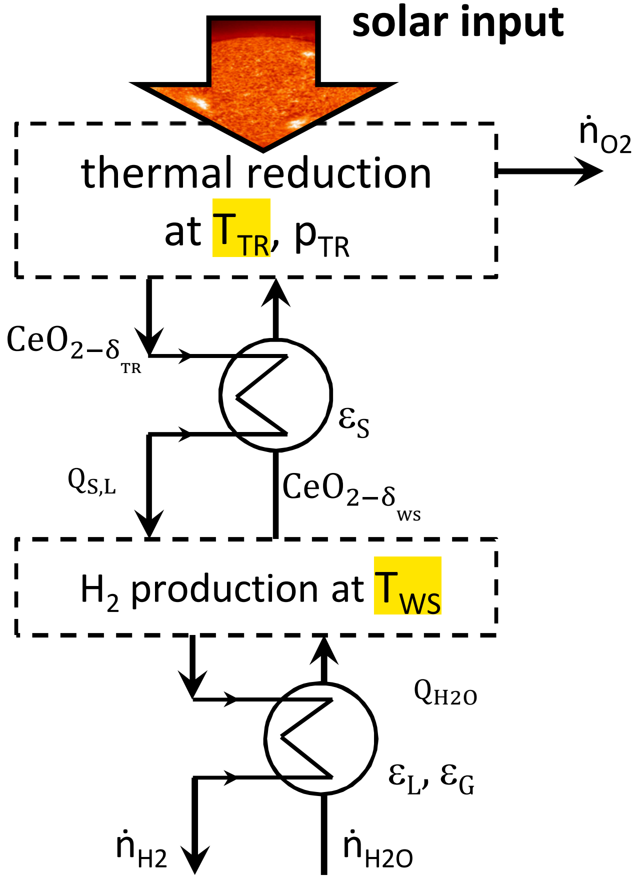

**In trouble…**

# Solar Heat Engine: Thermodynamic Limits

**Stefan-Boltzmann:** $P_{rad} = \sigma T_{TR}{}^4$

**Carnot:** $\eta = \frac{T_{TR} - T_{WS}}{T_{TR}}$




**Dead!**



Sandia National Laboratories

# Specifics of Reactor Efficiency

$$\eta_R = \frac{\dot{n}_{H_2} HHV_{H_2}}{\dot{Q}_A}$$

$$\dot{Q}_{TH} = A\dot{Q}_A - P_{rad}$$

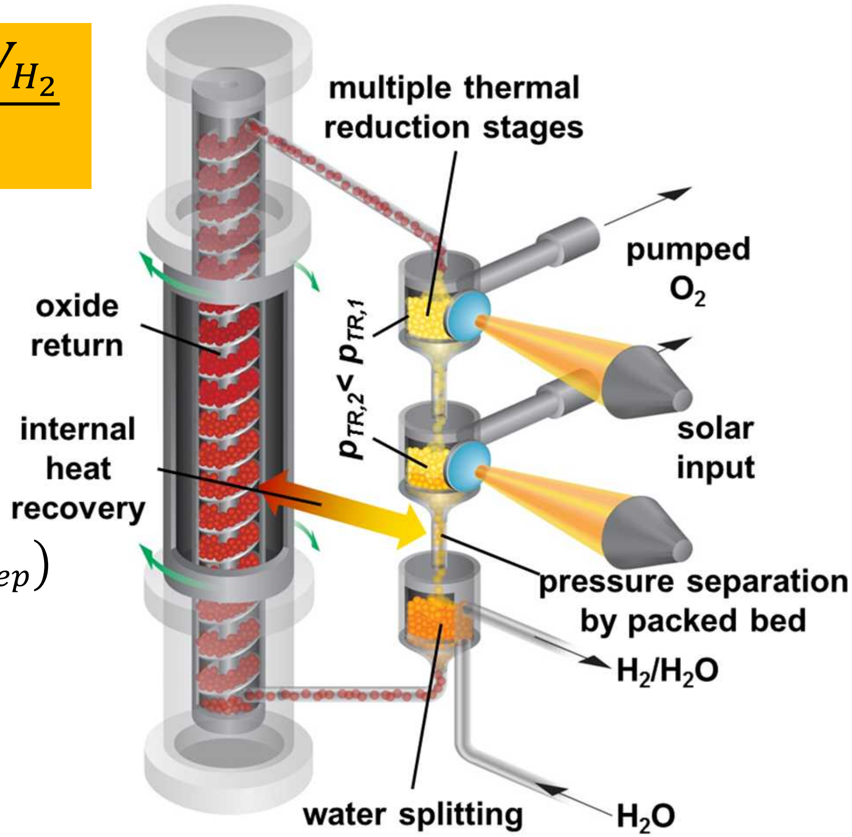
$$Q_{mol} = Q_{TR} + Q_S + Q_{AUX}$$

$$\dot{n}_{H_2} = \frac{\dot{Q}_{TH}}{Q_{mol}}$$

$$Q_{AUX} = \left(Q_{H_2O} + Q_{pump} + Q_{mech} + Q_{sep}\right) - \left(Q_{ROX} + Q_{S,L} + Q_{O_2}\right)$$

$$Q_S = \frac{C_{p,S}}{\Delta\delta}\Delta T(1 - \varepsilon_S)$$

$$Q_{H_2O} = n_{w/h}\left[C_{p,L}\left(T_{bp} - T_0\right)(1 - \varepsilon_L) + \Delta H_{vp}(1 - \varepsilon_G) + C_{p,G}\left(T_{WS} - T_{bp}\right)(1 - \varepsilon_G) + Q_{pump,vp}\right]$$



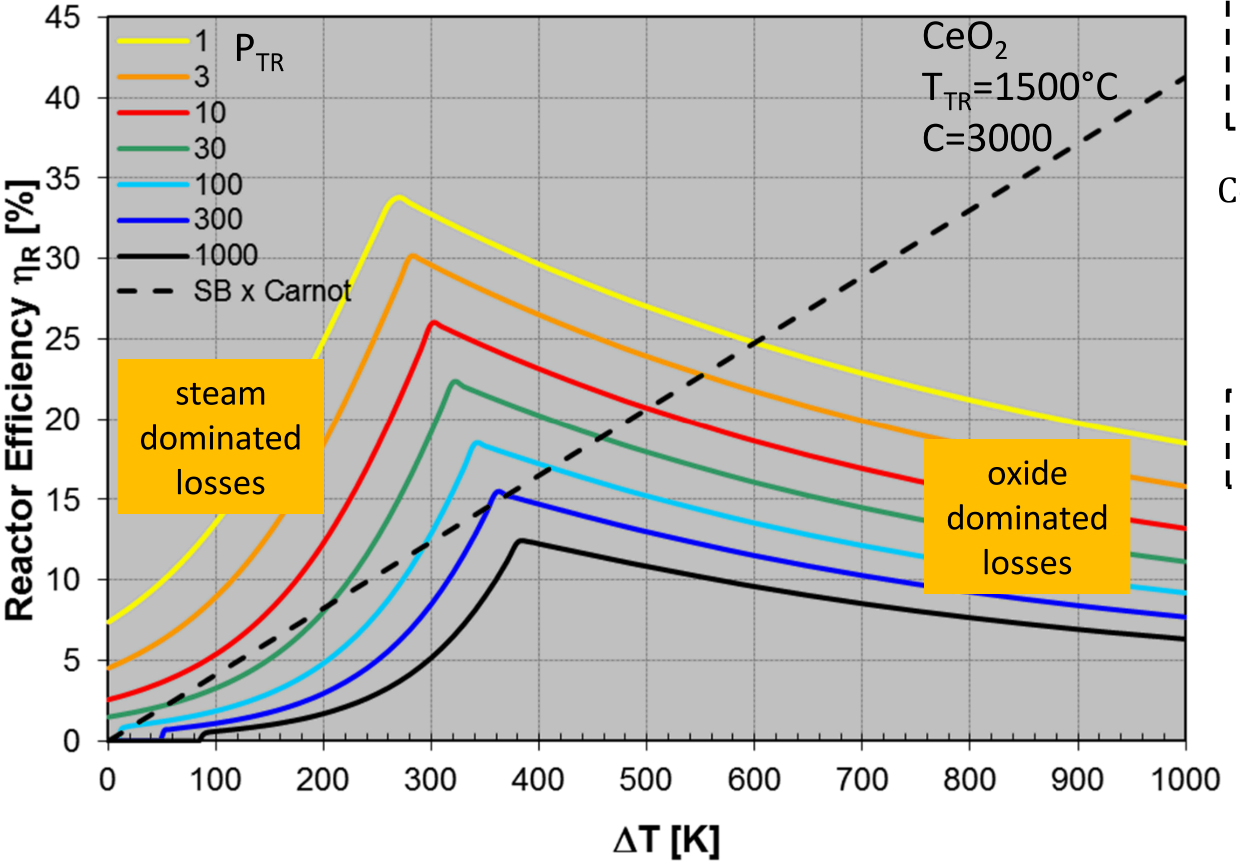

**Includes all major energy requirements and losses**

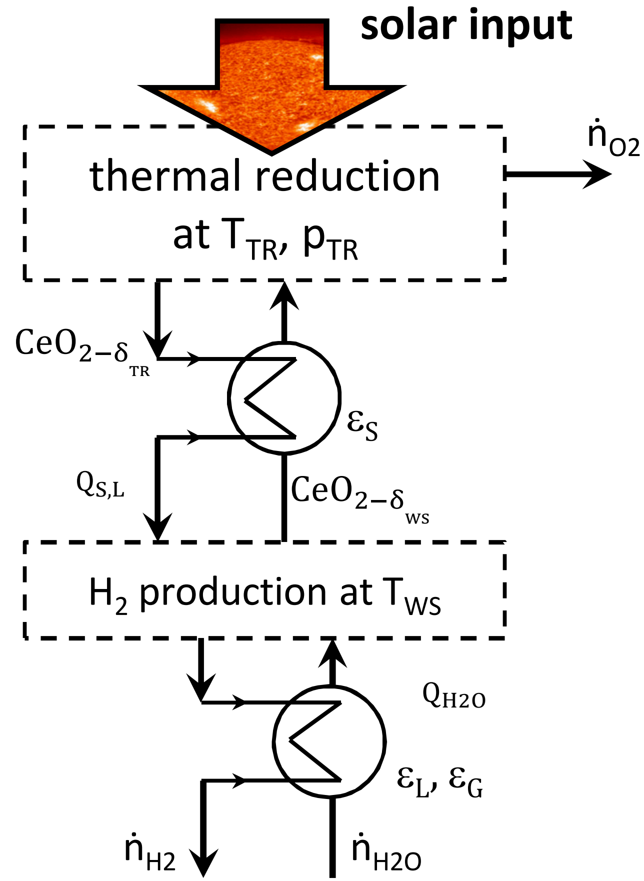


Sandia National Laboratories

# Efficiency Peak in (Un)expected Place

$$\eta_R = \frac{\dot{n}_{H_2} HHV_{H_2}}{\dot{Q}_A}$$

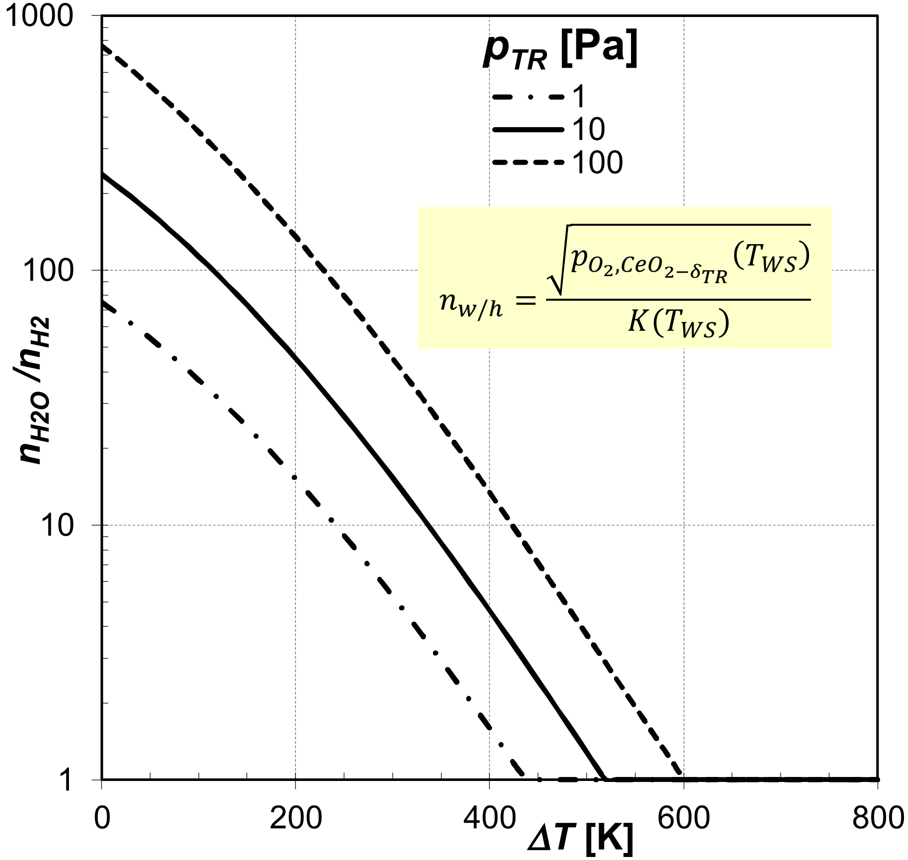


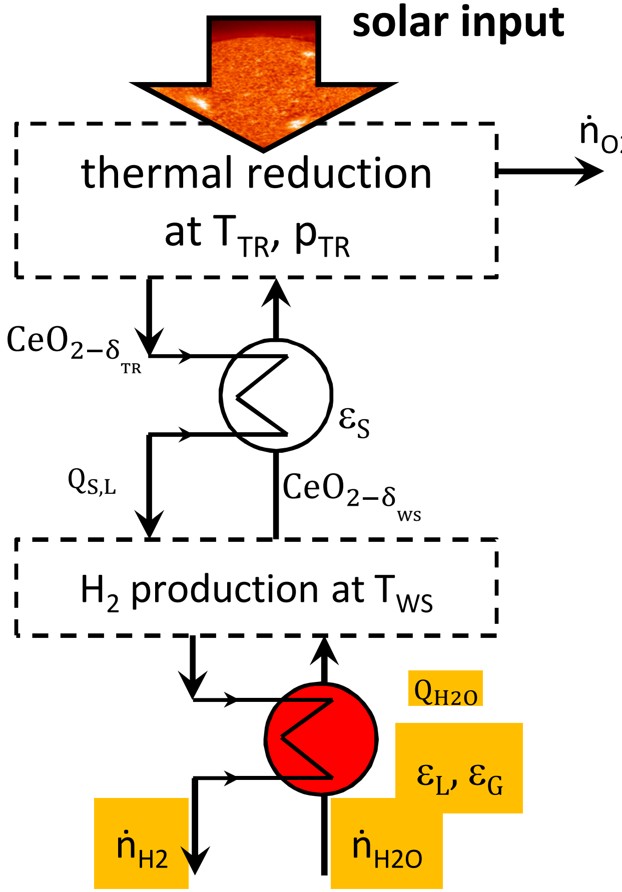

**Peak efficiency: Oxide and steam heating loads are roughly equal.**

# Key Material Requirements: Steam

**How much steam per mole $H_2$?**



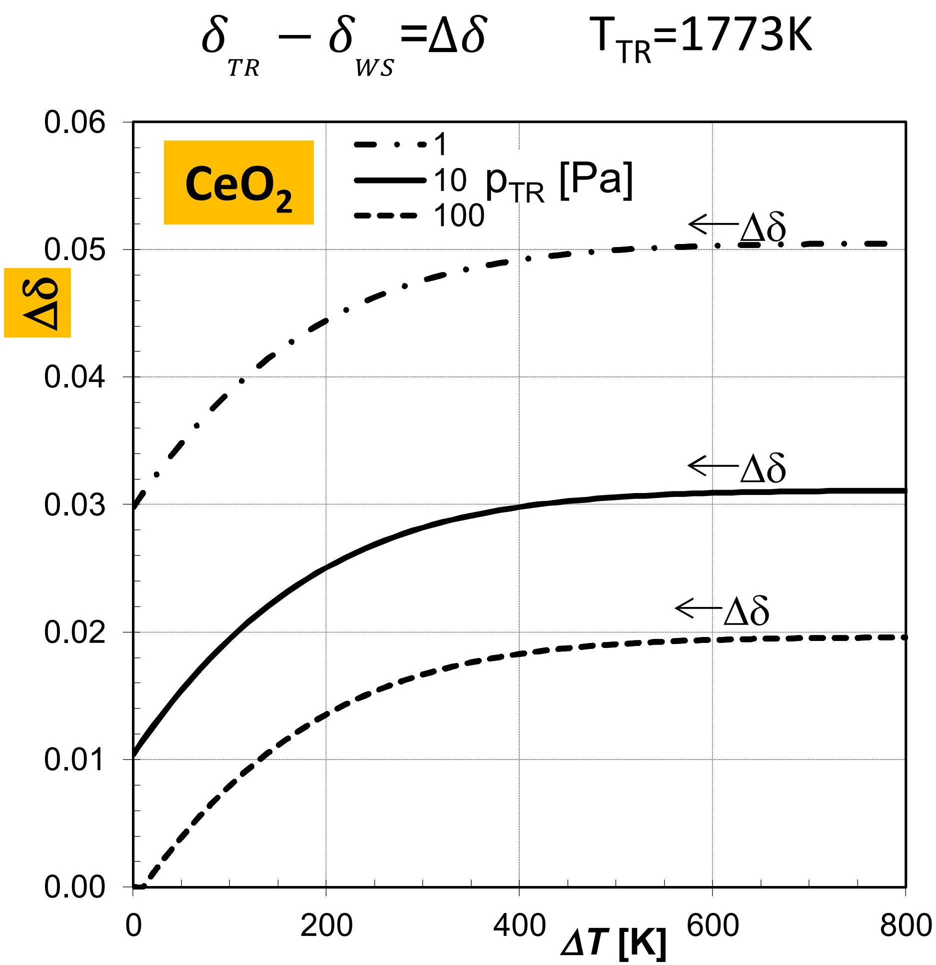

$$n_{w/h} = \frac{\sqrt{p_{O_2,CeO_{2-\delta_{TR}}}(T_{WS})}}{K(T_{WS})}$$

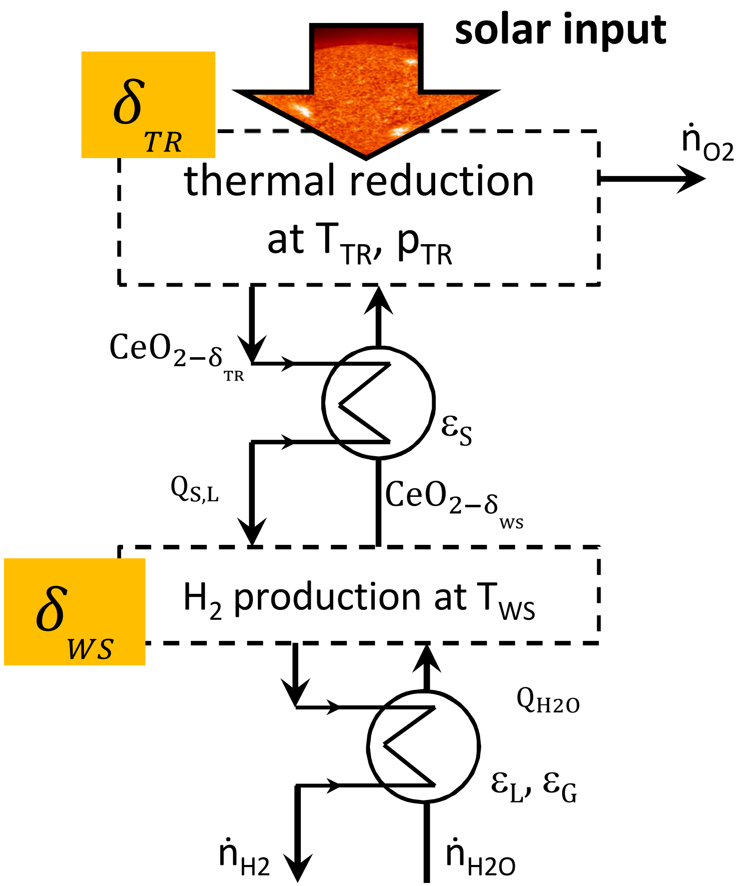



**Low ΔT or high reduction pressure leads to a high steam/$H_2$ ratio**

# Key Material Requirements: Reactive Oxide

**How much $CeO_2$ per mole $H_2$?**



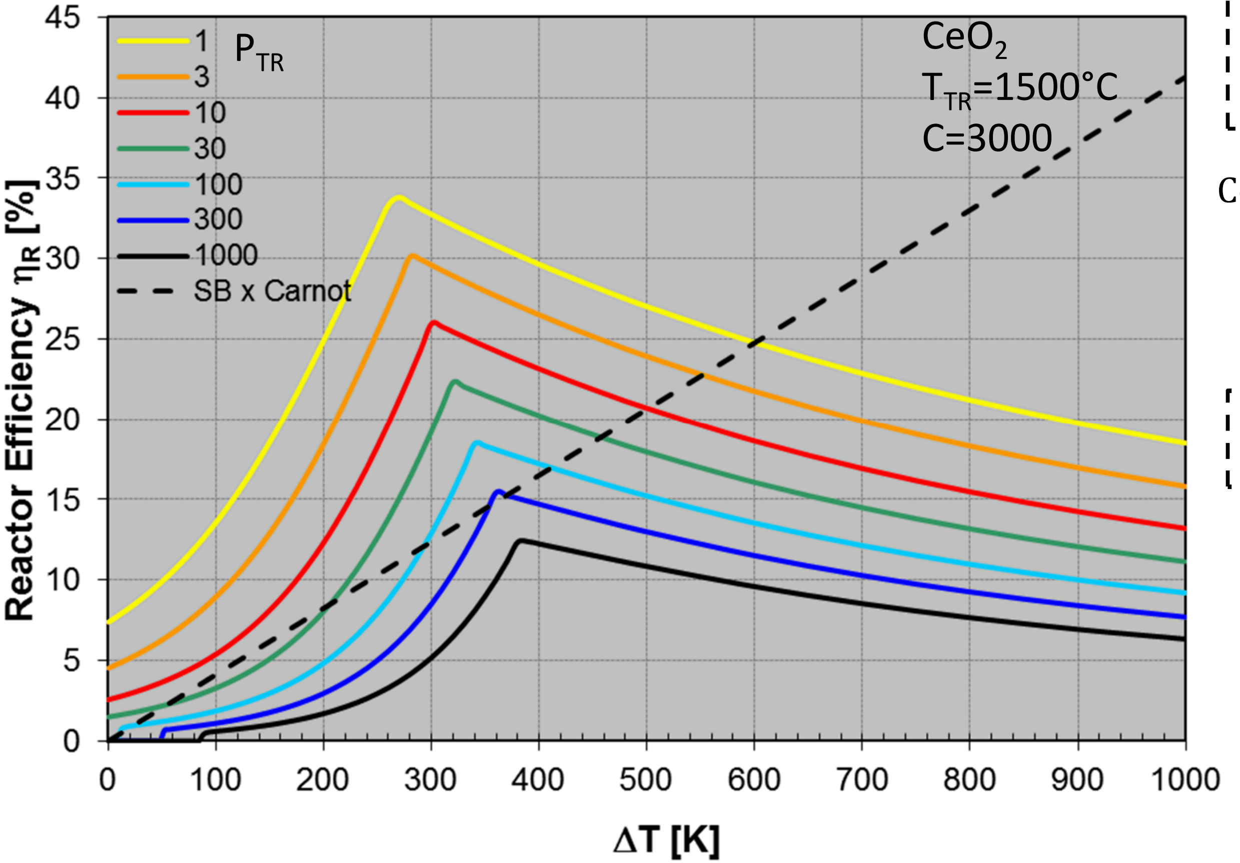

**The reversible oxygen capacity can be very low!**

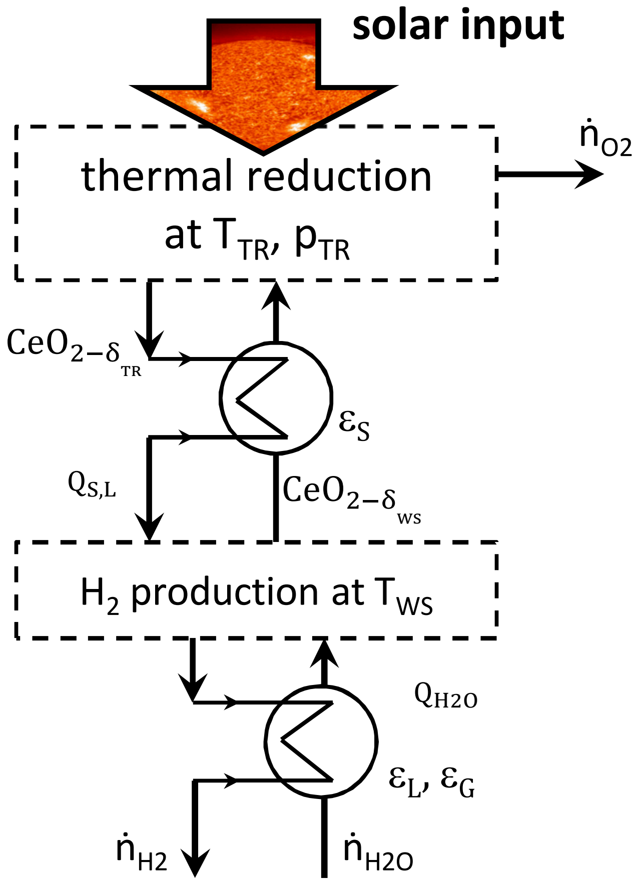


Sandia National Laboratories

# Efficiency Peak in (Un)expected Place

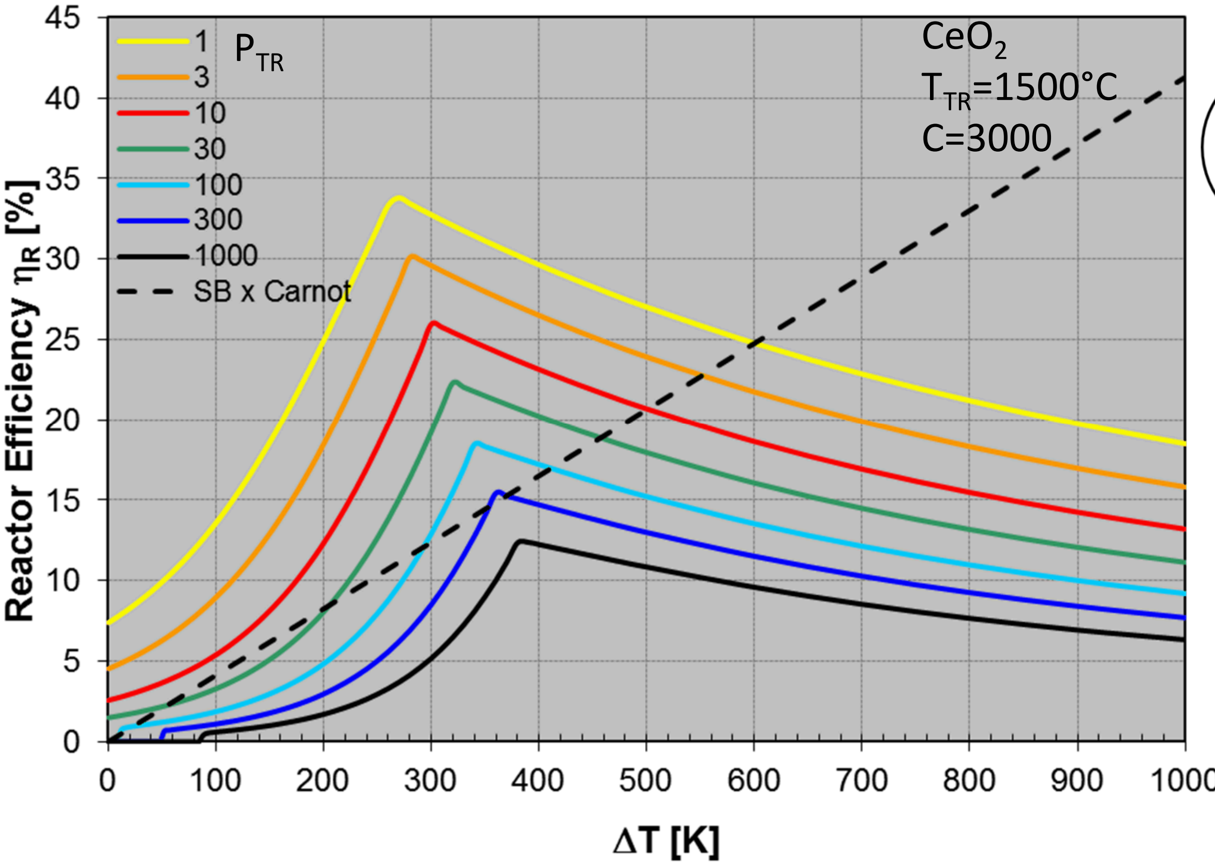
$$\eta_R = \frac{\dot{n}_{H_2} HHV_{H_2}}{\dot{Q}_A}$$

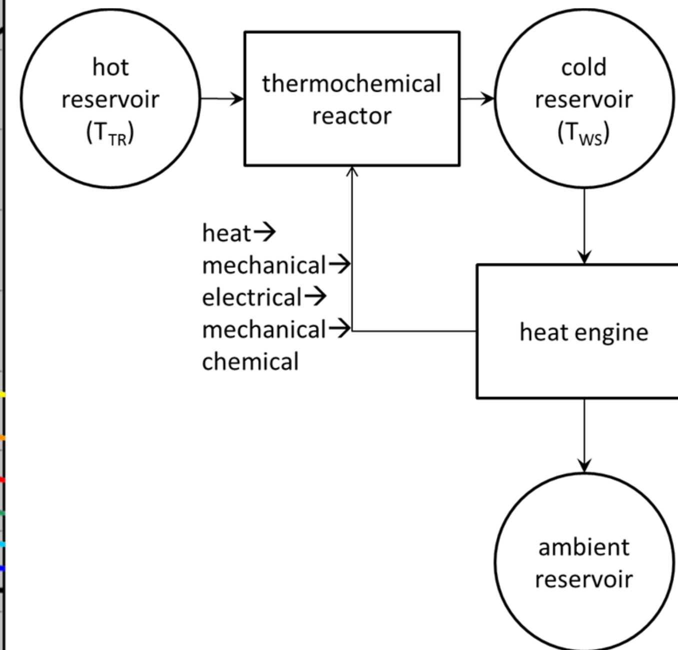



**Carnot predicts efficiency terribly!**
**(But it's not his fault.)**

# $T_{WS}$ is Not the “Real” Cold Reservoir…



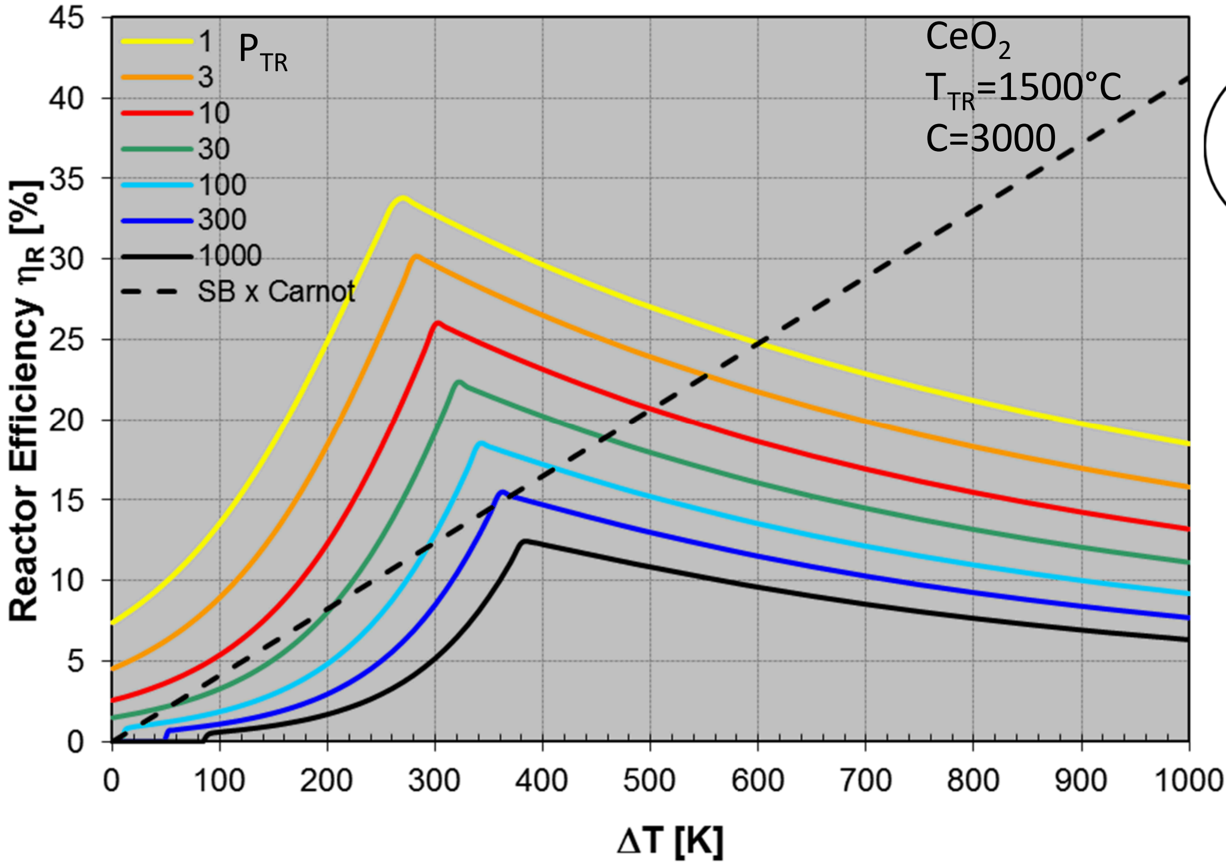



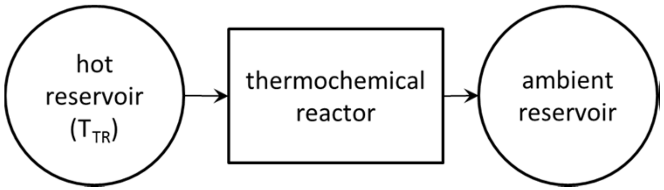

**Carnot predicts efficiency terribly…**
**because of the explicit use of output heat for work.**

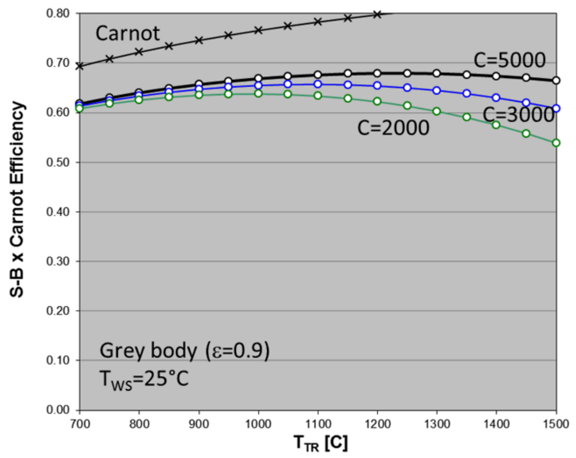


Sandia National Laboratories

# …But it Should Be



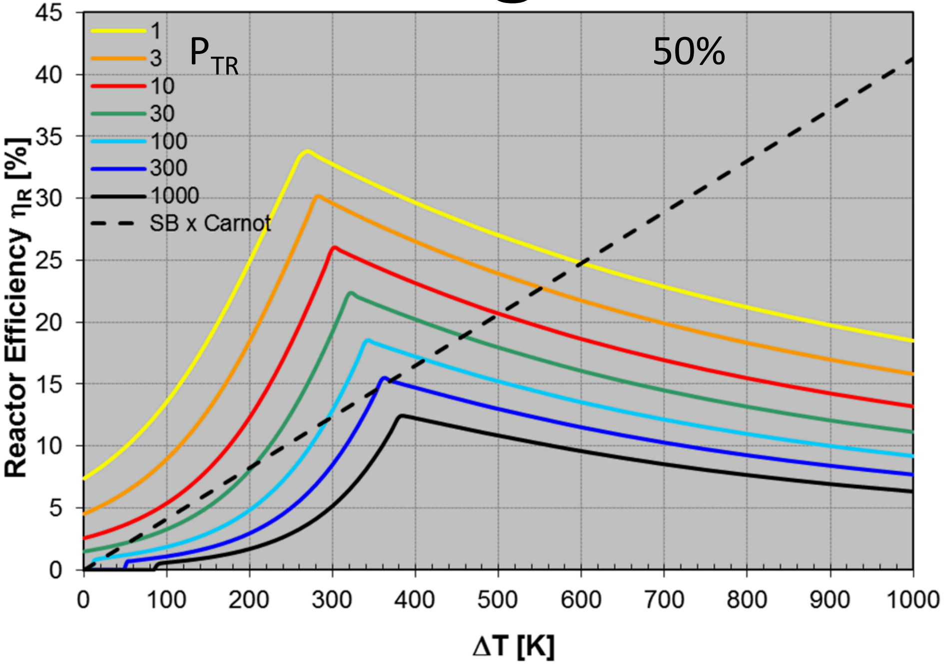




**Lowering $T_{WS}$ would approach the ideal Carnot process and increase efficiency.**

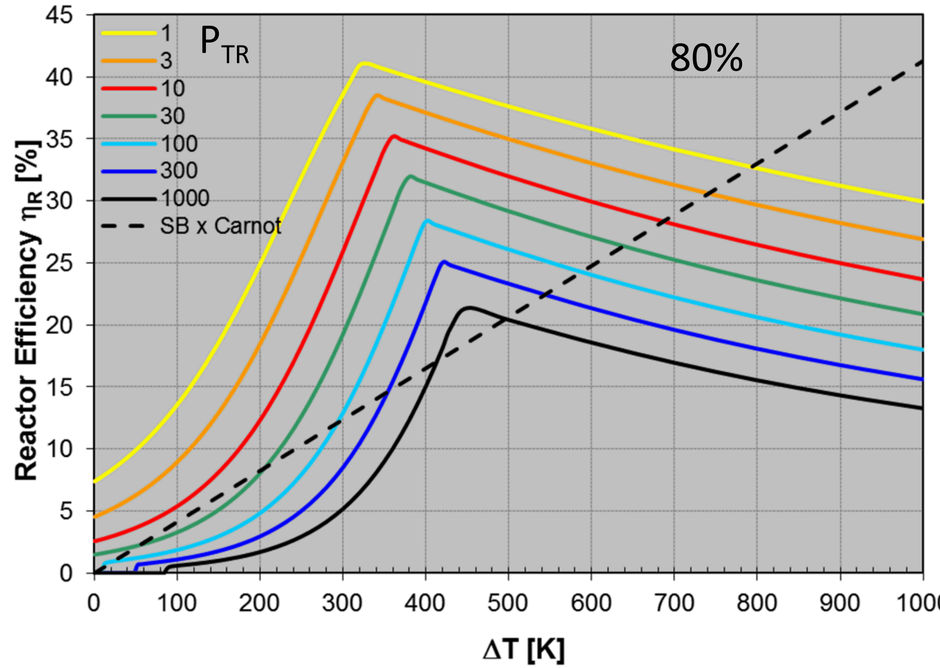


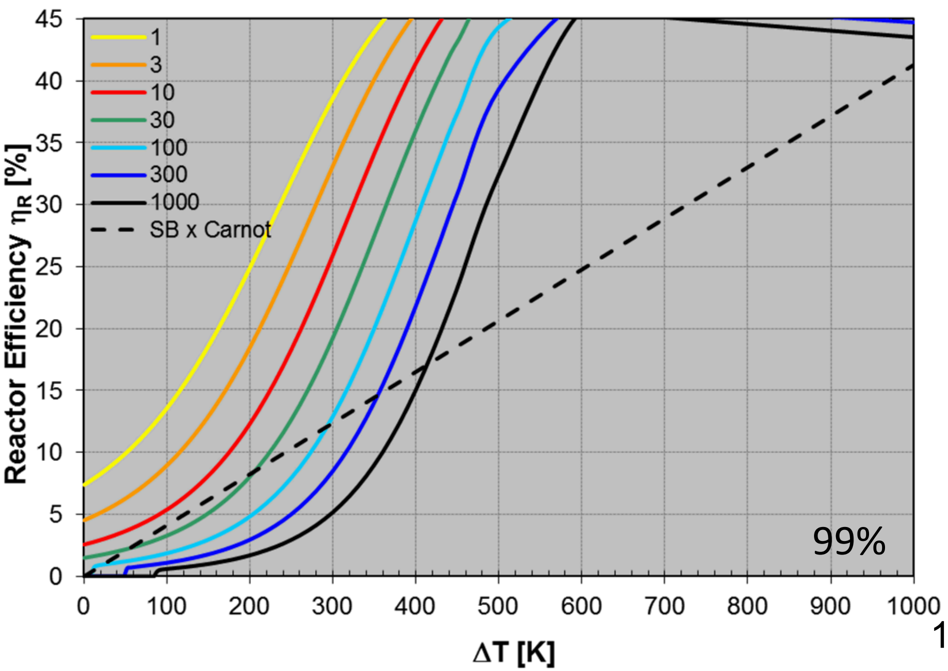
Sandia National Laboratories

# Chasing Carnot: Solid Heat Recovery



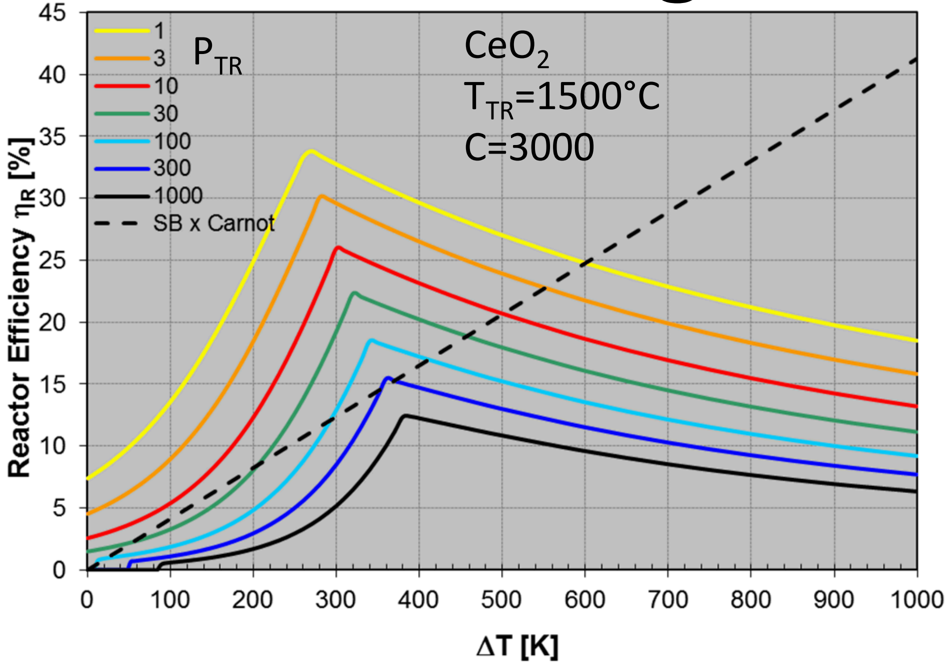

$CeO_2$
$T_{TR}$=1500°C
C=3000

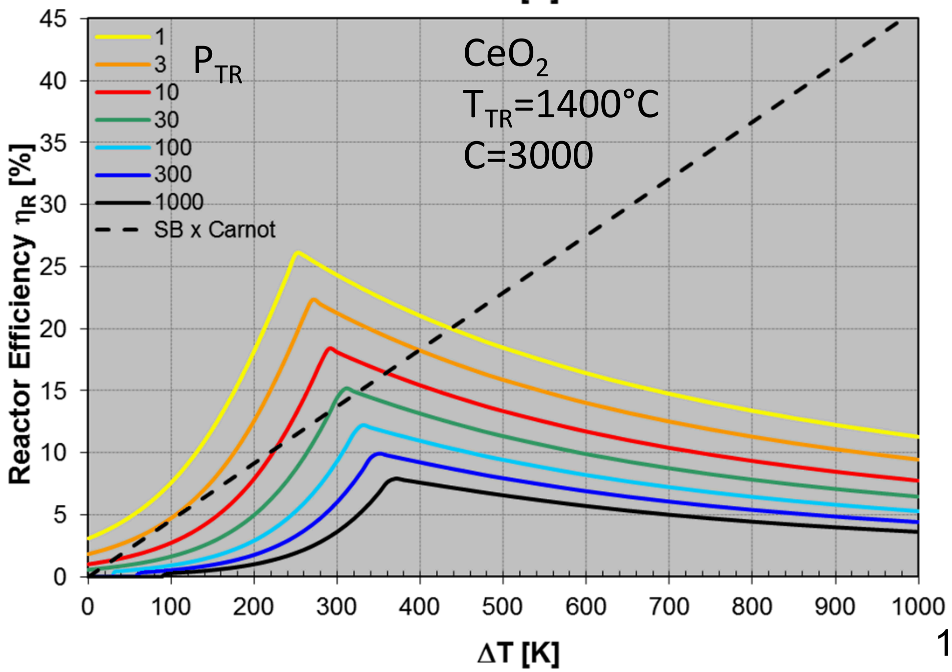


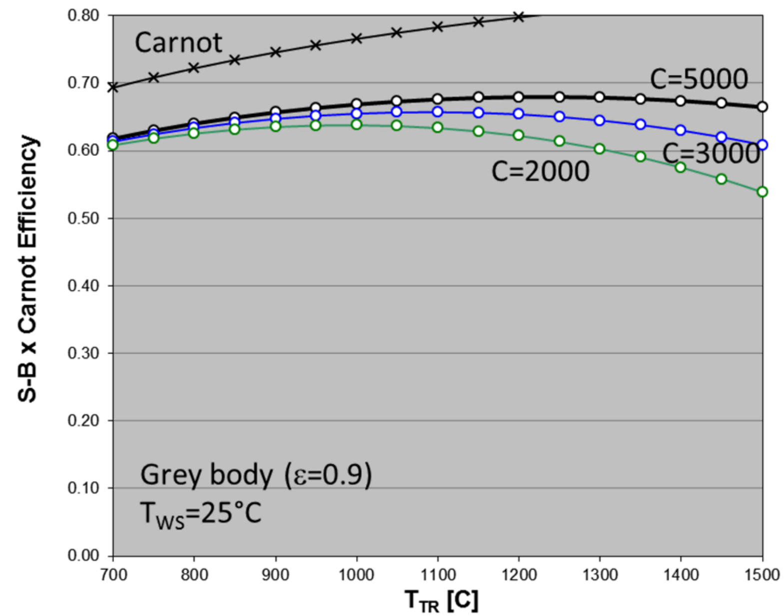




**More heat recovery brings the process somewhat closer to the ideal Carnot cycle – at the cost of engineering unfeasibility.**

# Reactor Chasing Stefan-Boltzmann – No Gain

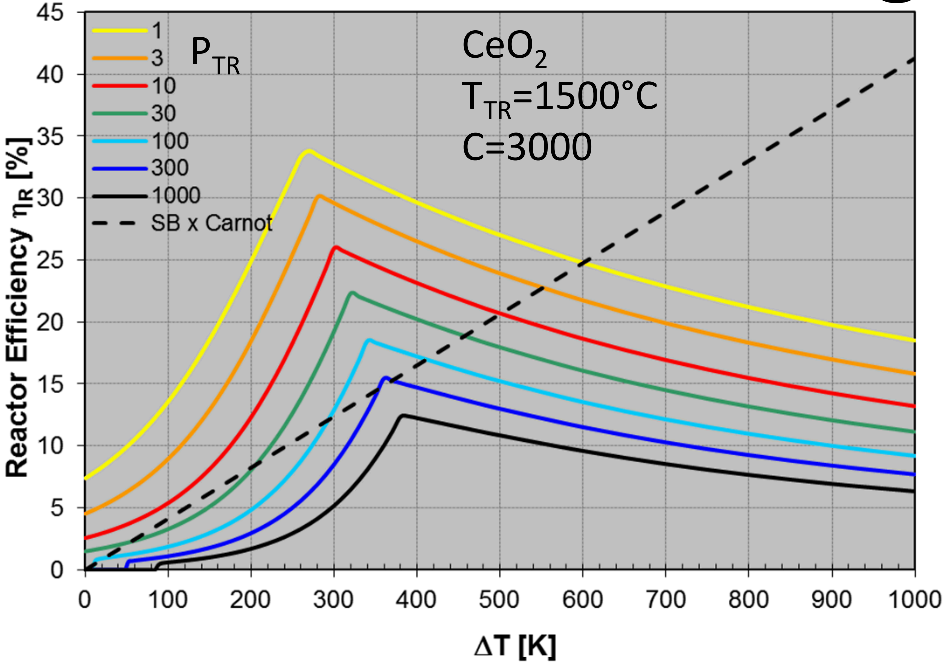


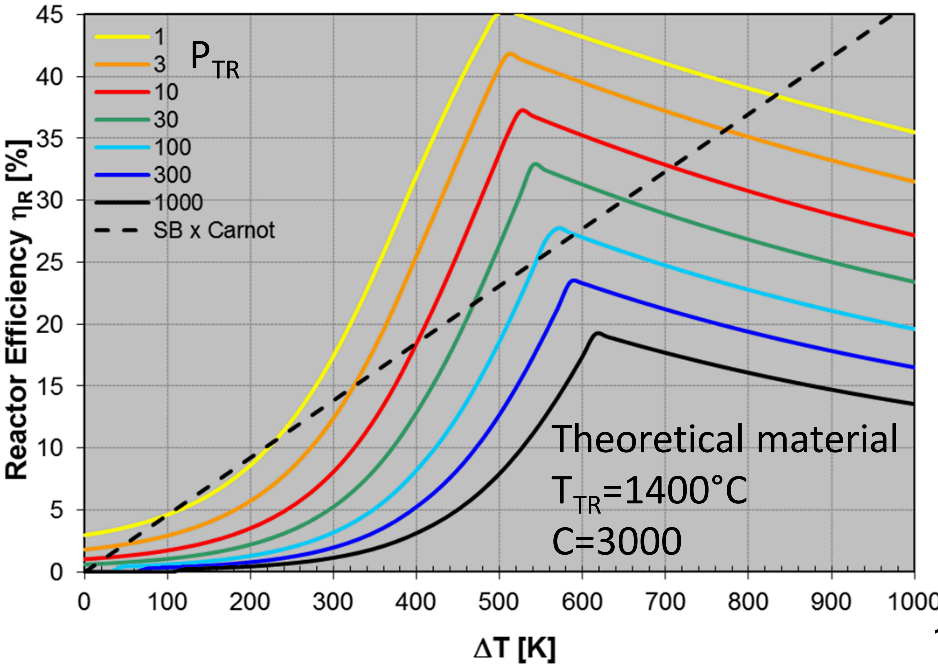




**Decreasing $T_{TR}$ decreases efficiency, despite the opposite theoretical prediction. The problem? $CeO_2$.**

# Material Chasing Stefan-Boltzmann



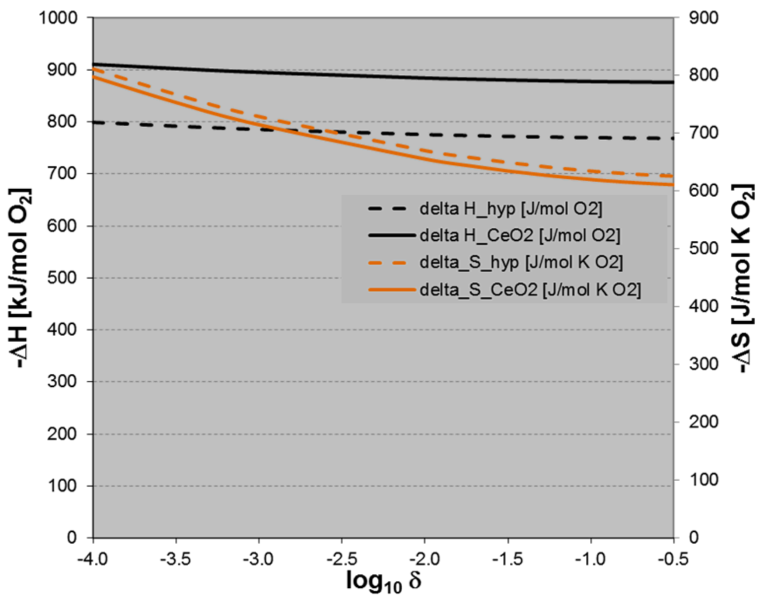




Theoretical material:

$p_{TR}$: ceria x 1000

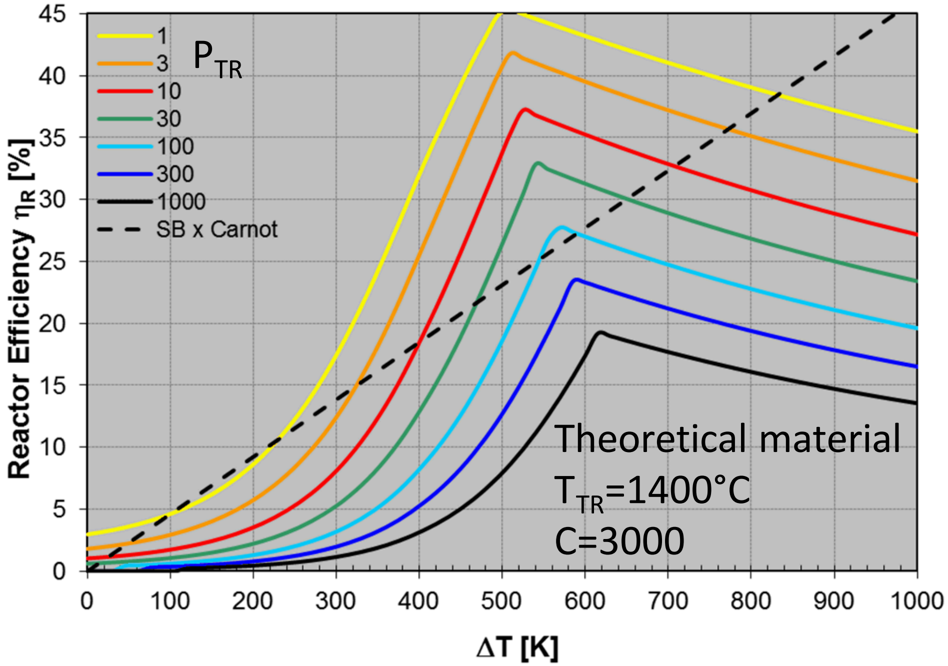
$T_{TR}$: ceria-100°C

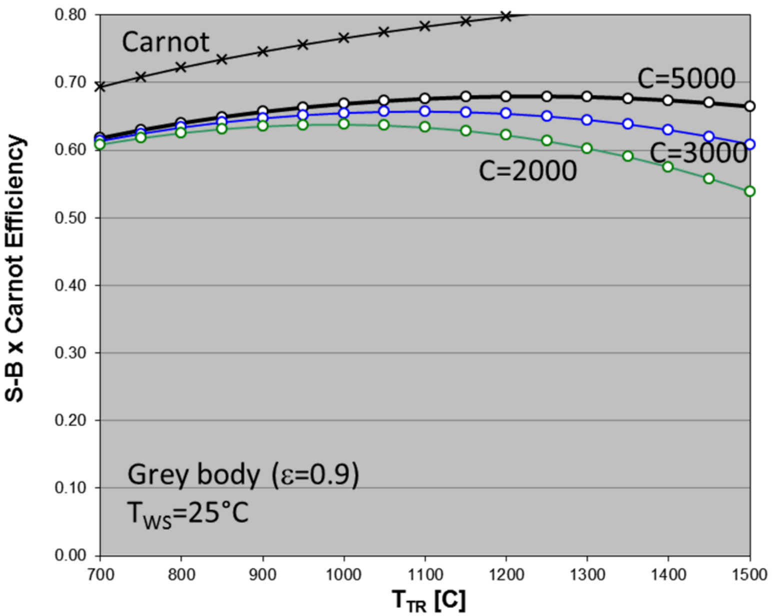
$c_p$: 140 J/mol K (vs. 80 J/mol K for ceria)




**A material with the right thermodynamic properties can help approach the ideal Carnot cycle and increase efficiency.**

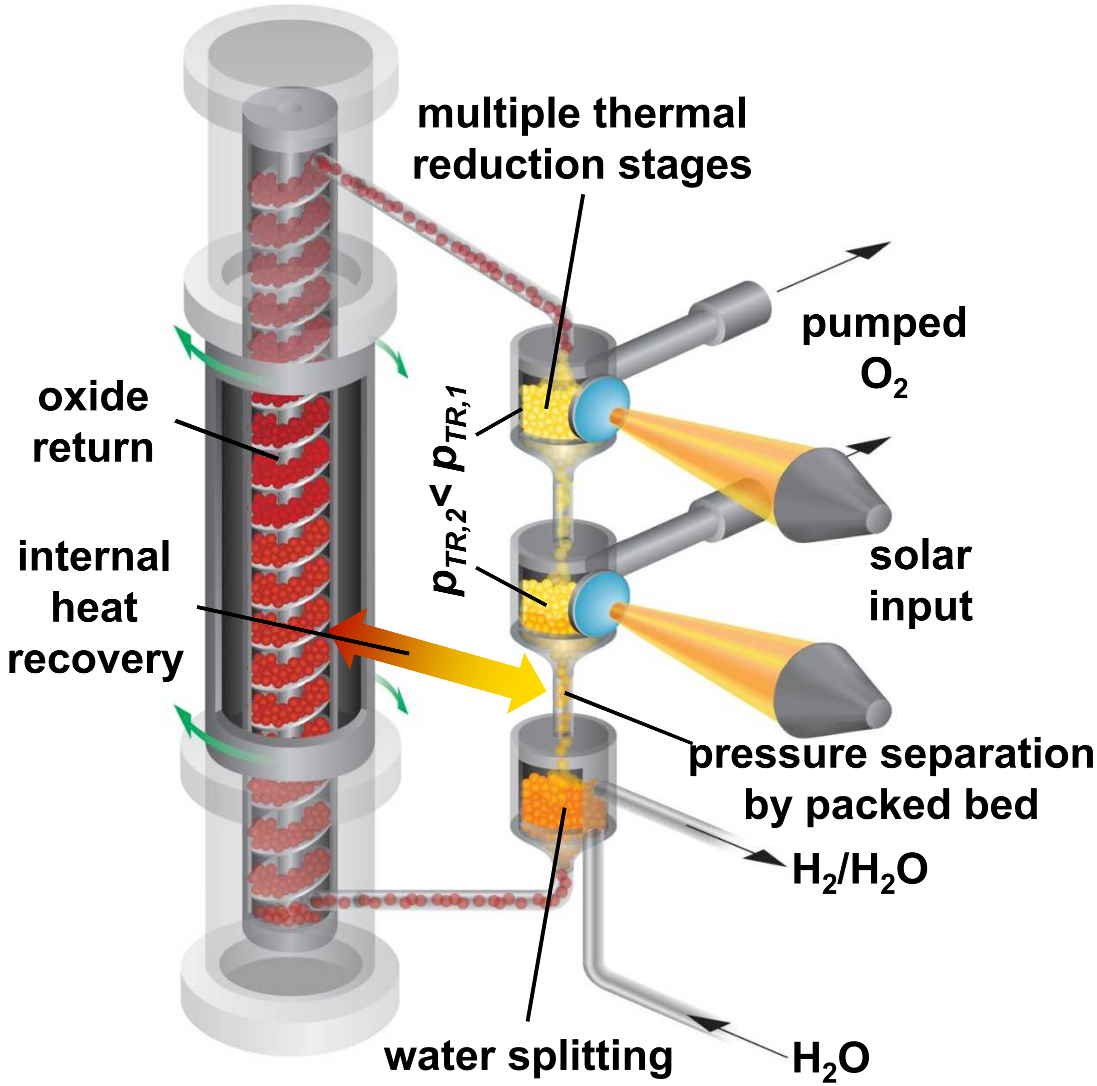
# Material Chasing Stefan-Boltzmann




**A material with the right thermodynamic properties can help approach the ideal Carnot cycle and increase efficiency.**

# Staged Reduction Reactor for Low Pressure




**Incrementally pumping $O_2$ reduces the overall flow volume and velocity**



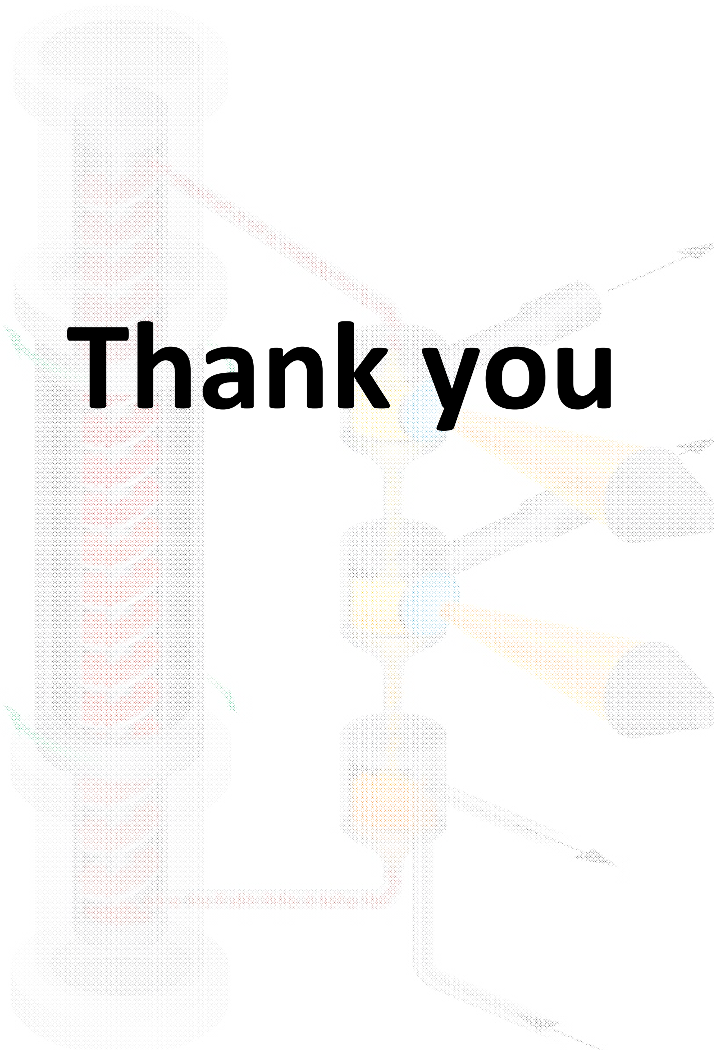
Sandia National Laboratories

# Summary/Interesting questions

- Materials with low $\Delta\delta$ pose a mass flow challenge
- Optimal $\Delta T$ can be found to maximize efficiency
- Thermal reduction pressure limited by $O_2$ flow
- A >10x pressure decrease feasible in staged reduction
- Best results by combining $\Delta T_{opt}$, staged pumping and advanced reactive oxides

- Field design for multiple chambers?
- Operation control to maintain optimal $\Delta T$ for variable DNI?

# Thank you

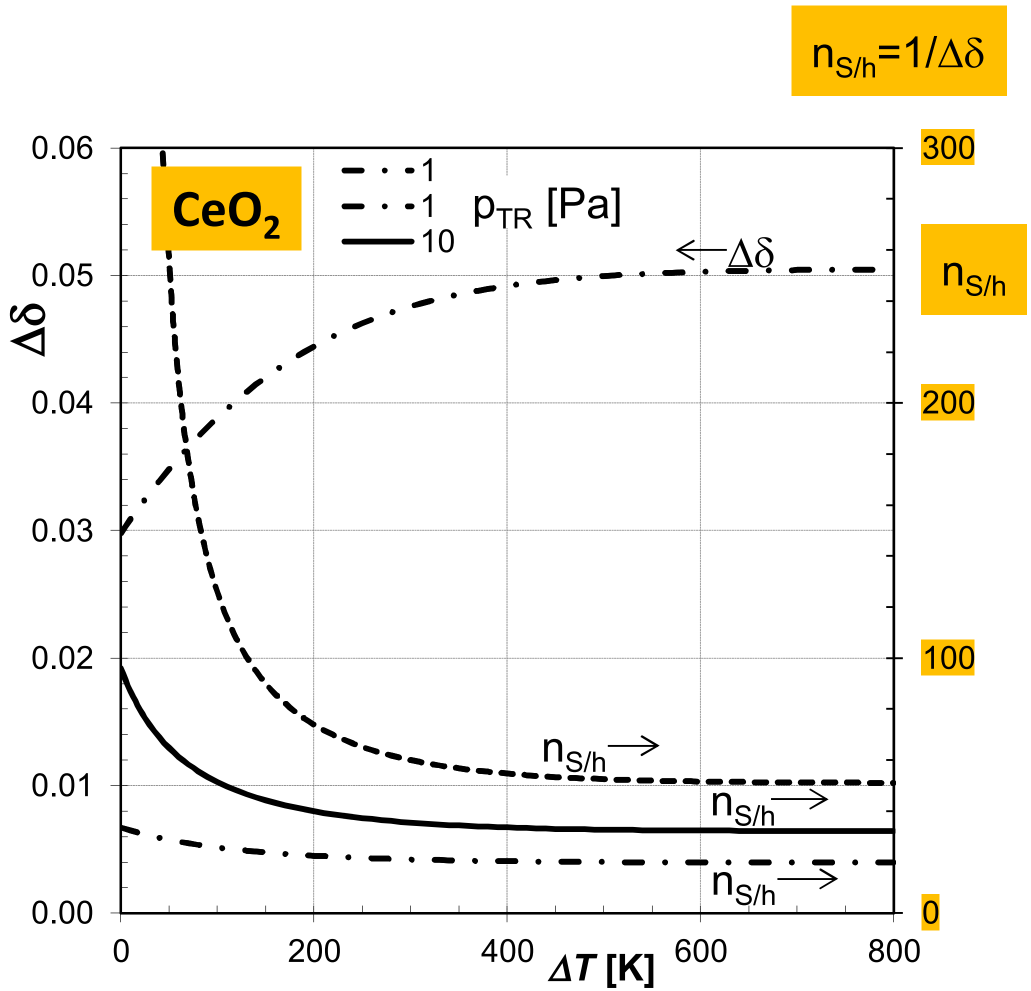


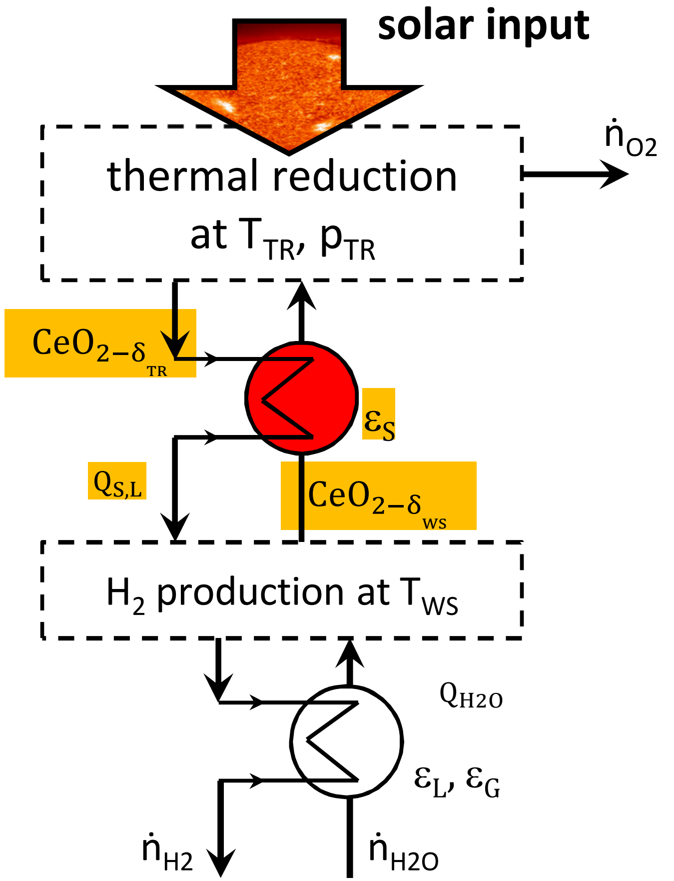
Ivan Ermanoski iermano@sandia.gov

Sandia National Laboratories

# Key Material Requirements: Reactive Oxide

**How much $CeO_2$ per mole $H_2$?**

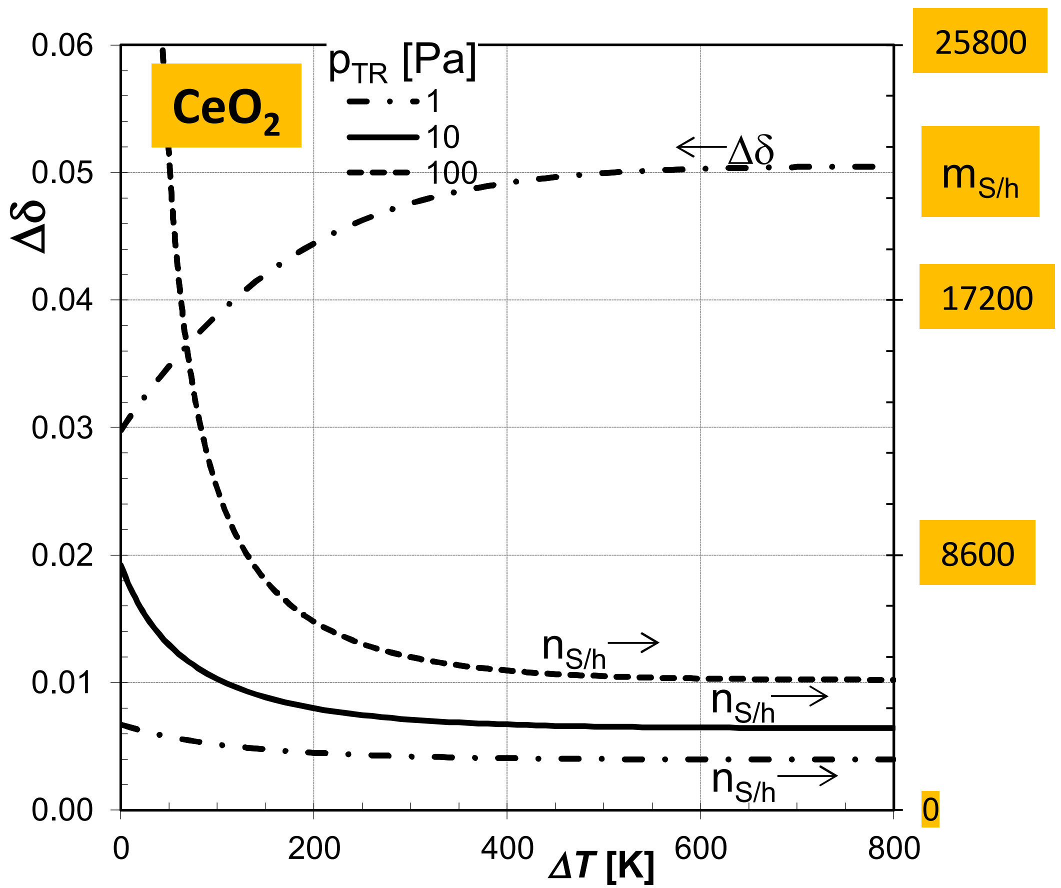


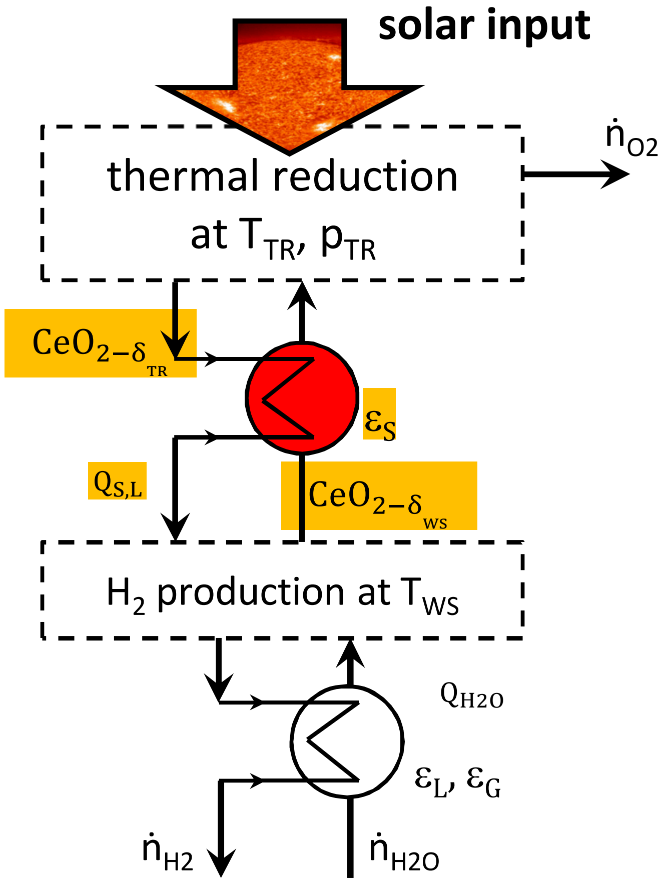




**A low reversible oxygen capacity leads to a very high oxide/$H_2$ ratio and excessive oxide mass flow and heat recovery requirements**

# Key Material Requirements: Reactive Oxide

**How much $CeO_2$ per mole $H_2$?**



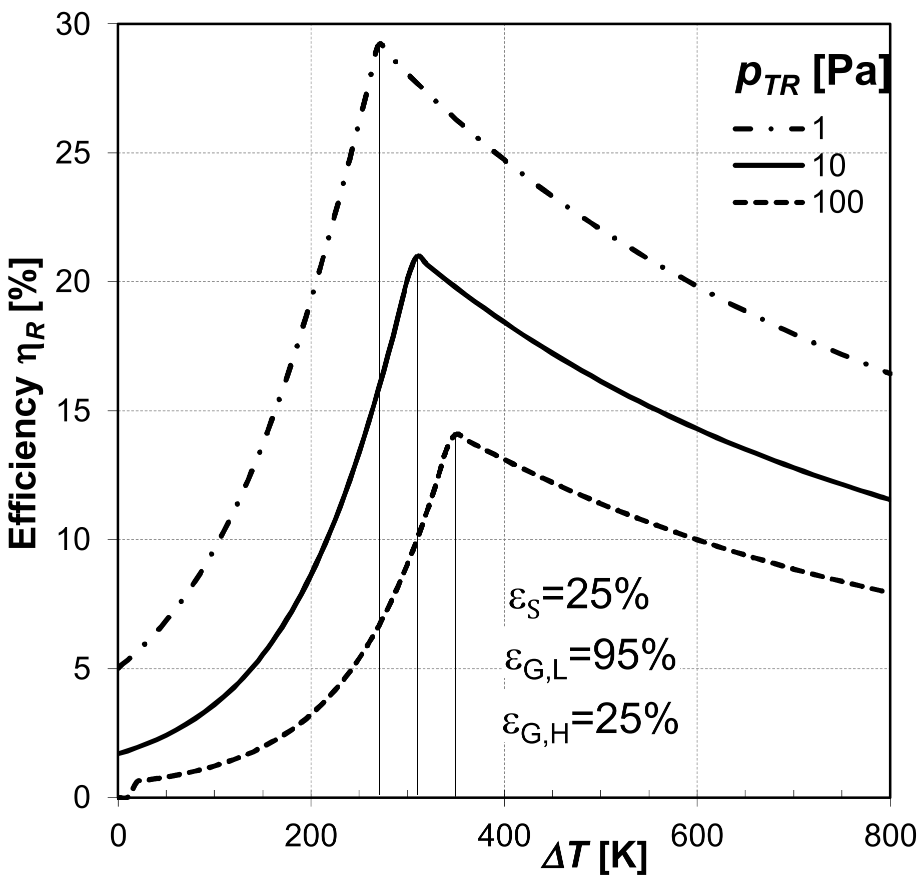



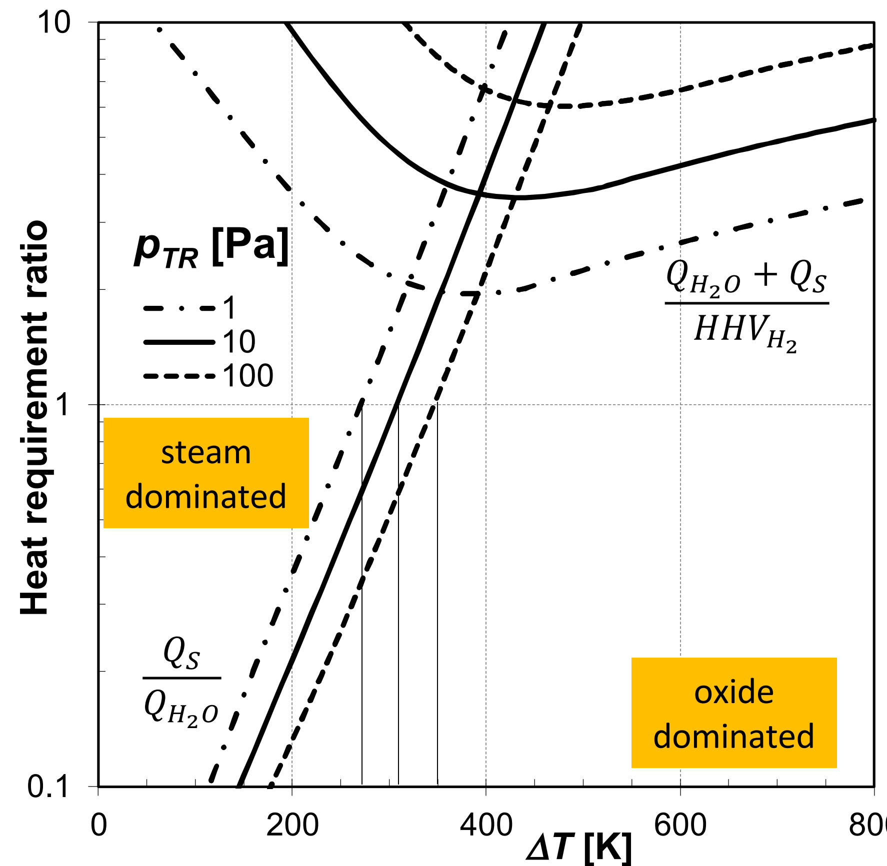

**A low reversible oxygen capacity leads to a very high oxide/$H_2$ ratio and excessive oxide mass flow and heat recovery requirements**

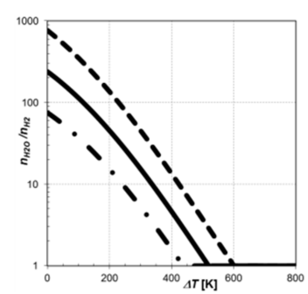


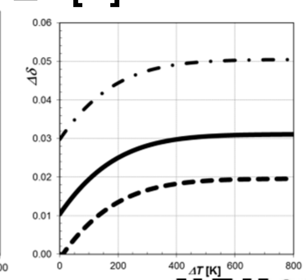
Sandia National Laboratories

# Maximizing Efficiency: Solid/Steam Heating Balance and a Low Reduction Pressure



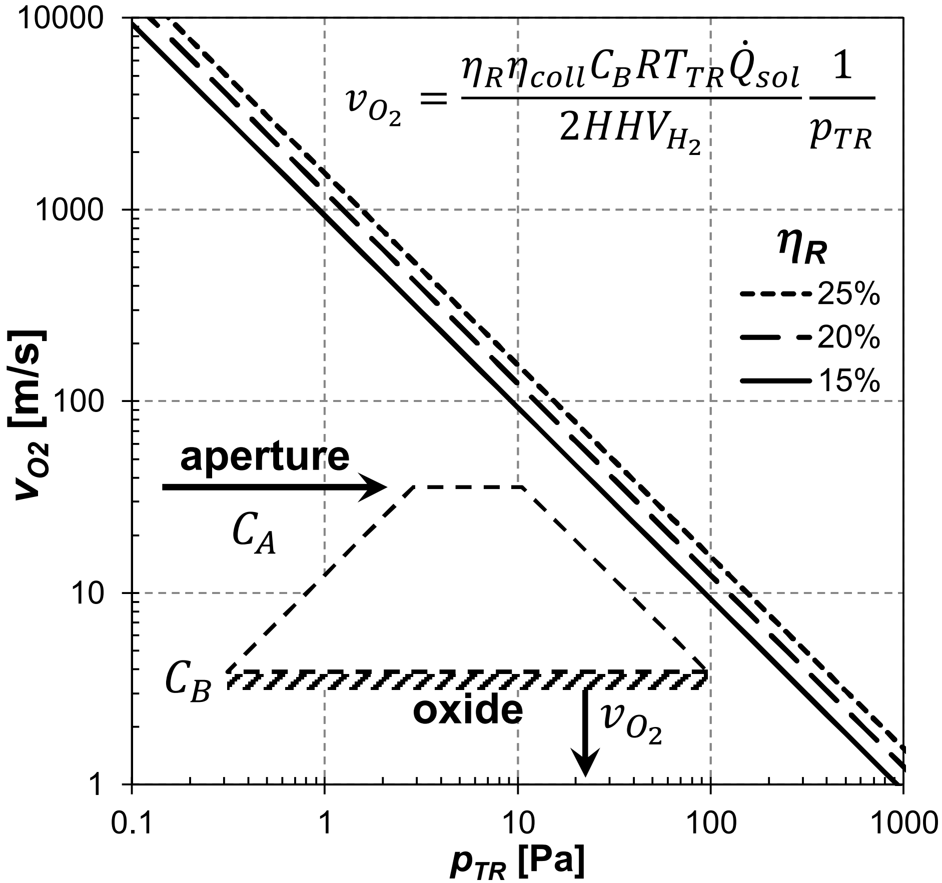



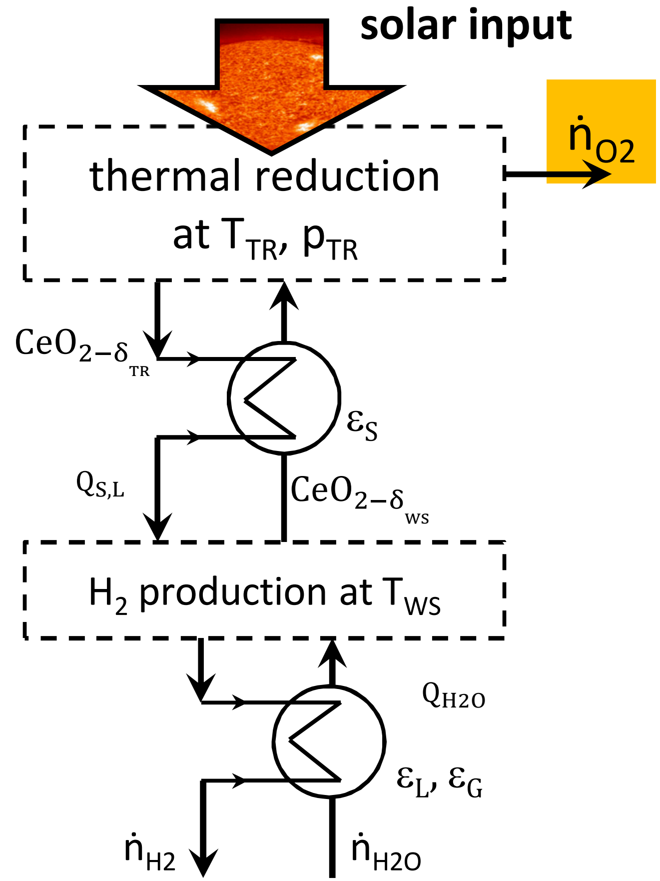

**Efficiency is the highest when:**

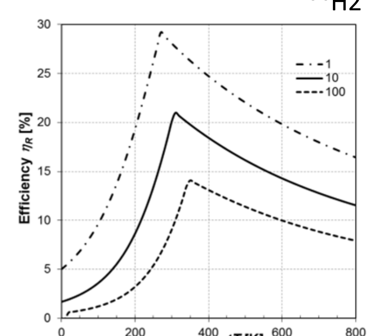
- **Oxide and steam heating loads are roughly equal**
- **Thermal reduction pressure is low**

# $O_2$ Pressure Limits: Flow Volume and Speed

**Is 1Pa accessible?**



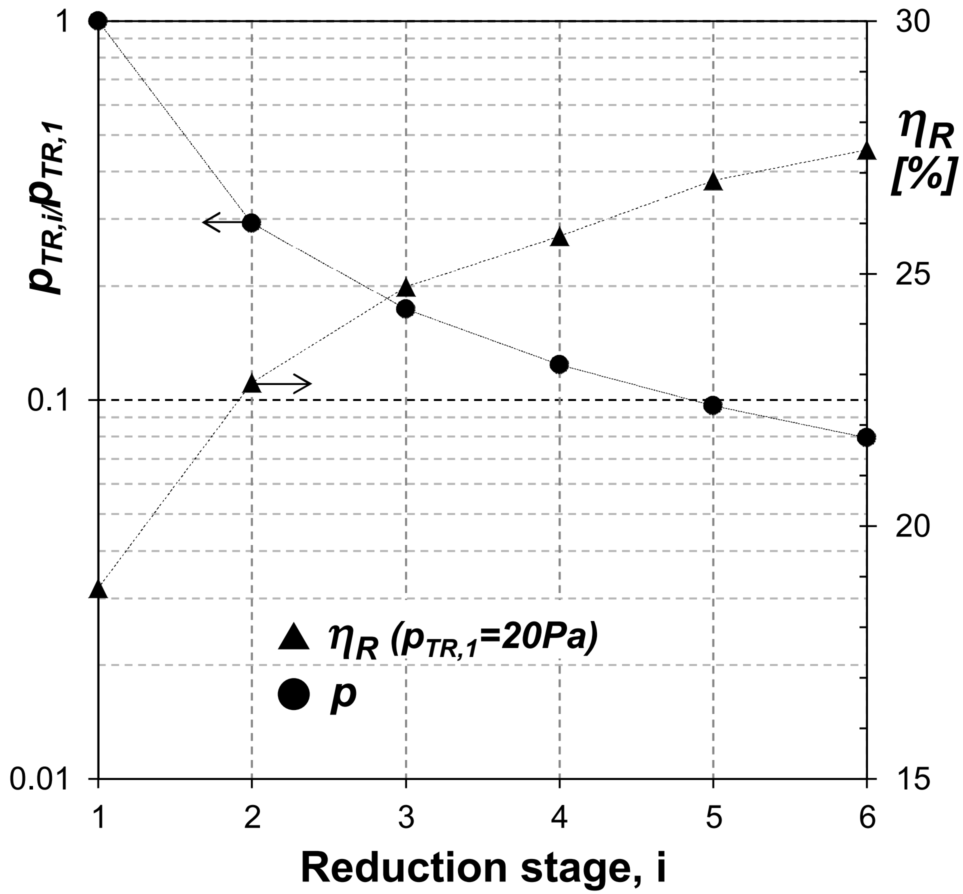



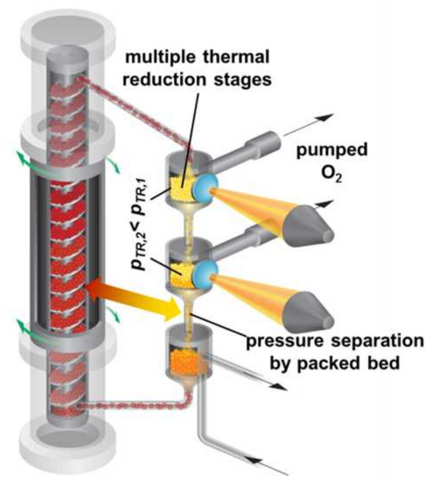

**At low pressure required flow volumes and velocities are astronomical!**



Sandia National Laboratories

# Staged Reduction for Low Pressure




$$p_{TR,i} = \dot{n}_{ox} R T_{TR} \frac{\delta_{TR,i} - \delta_{TR,i-1}}{2\dot{V}_{O_2}}$$

**Efficiency is the highest when:**

- **10x pressure decrease possible with as few as 5 chambers**
- **Decreased pump work and size**



Sandia National Laboratories

# Next Generation Redox Active Materials

Energy & Environmental Science

RSC Publishing

COMMUNICATION

View Article Online
View Journal

**Sr- and Mn-doped $LaAlO_{3-\delta}$ for solar thermochemical $H_2$ and CO production†**

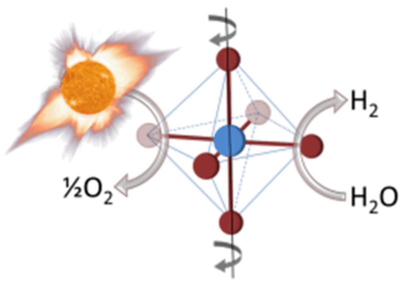
Cite this: DOI: 10.1039/c3ee41372a

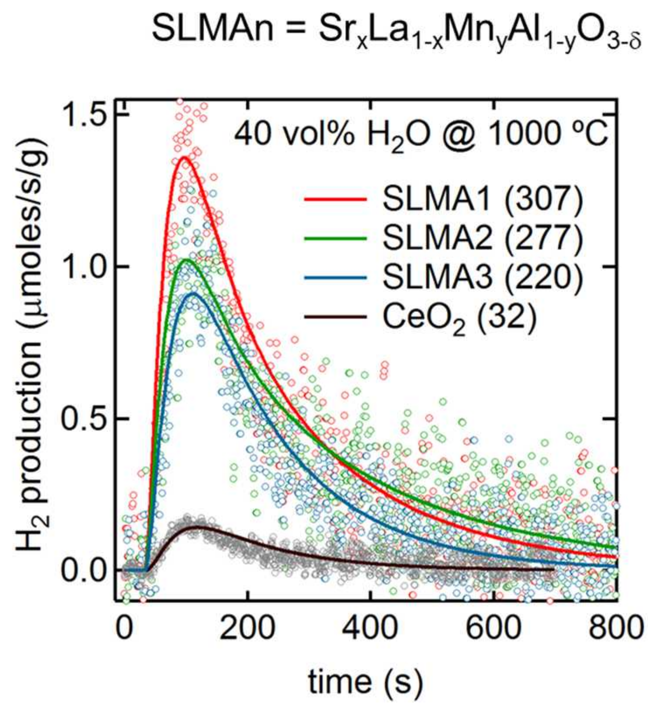
Received 22nd April 2013
Accepted 4th June 2013

DOI: 10.1039/c3ee41372a

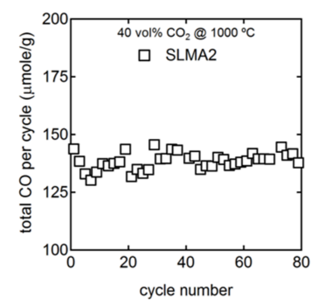
www.rsc.org/ees

Anthony H. McDaniel,[*a] Elizabeth C. Miller,[‡ab] Darwin Arifin,[§a] Andrea Ambrosini,[b] Eric N. Coker,[b] Ryan O'Hayre,[c] William C. Chueh[¶a] and Jianhua Tong[*c]




- Perovskite compounds split $H_2O$ in a thermochemical cycle.
  - First of a kind observation, also demonstrated durability
- Kinetics benchmarked against $CeO_2$.
  - Similarly fast oxidation rates
- Make ~9× more $H_2$ than $CeO_2$ at $T_{TR}$ = 1350 °C.



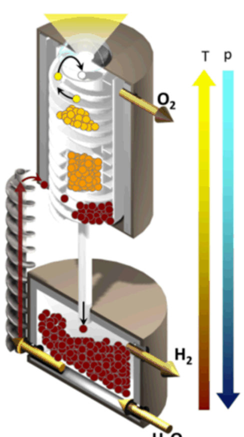

Sandia National Laboratories

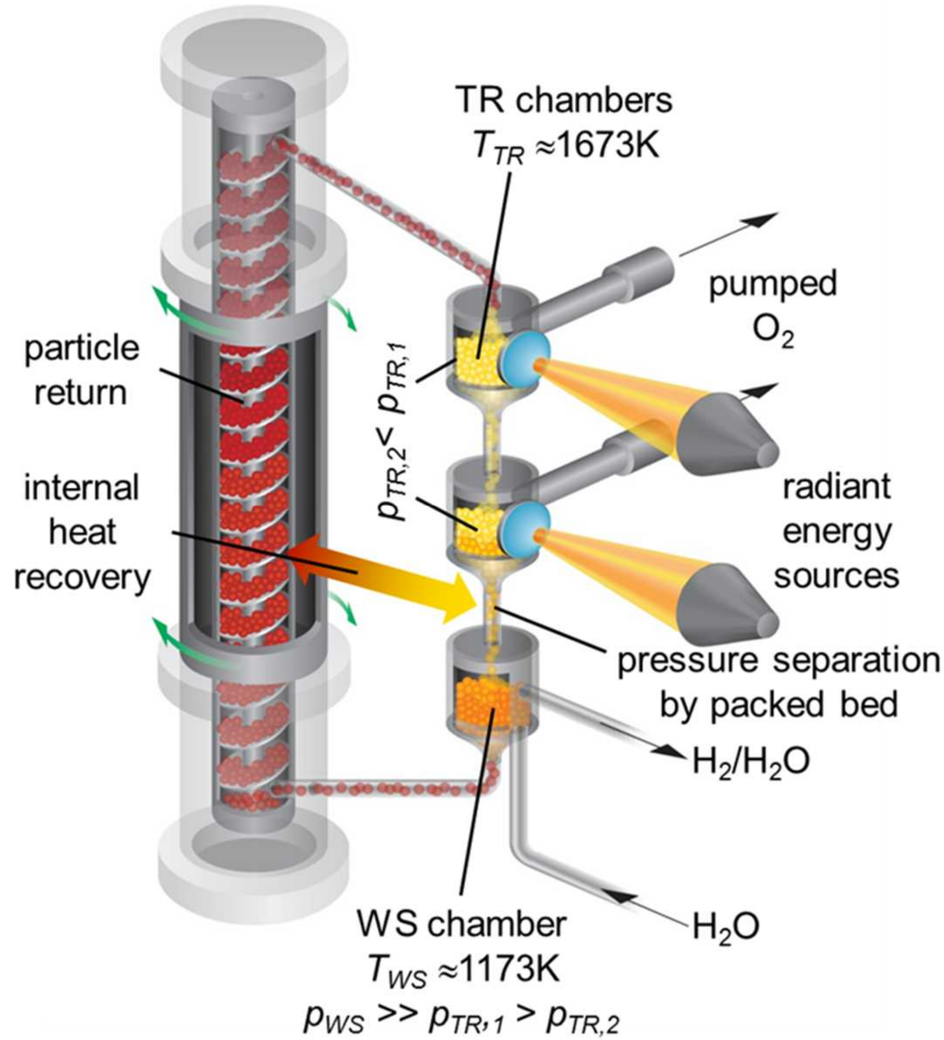
# Staged Reduction Reactor for Low Pressure

**An improvement of an earlier moving packed bed concept**

- Direct solar absorption
- Internal heat recovery between $T_{TR}$ and $T_{WS}$
- Continuous on-sun operation
- Temperature and product separation
- Pressure separation (thermal reduction step vacuum pumping )
- Non-monolithic oxide
- Reaction kinetics decoupled from reactor operation

- Thermal reduction pressure (0.1-10Pa)
- Decreased solid-solid heat recovery requirement
- Decreased pump work requirement
- Compatibility with MW-scale plant






Sandia National Laboratories