

Metal Oxides in Solar Thermochemical Cycles: Gaining Breathing Room Through Reactor Design

Ivan Ermanoski

Sandia National Laboratories

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Outline

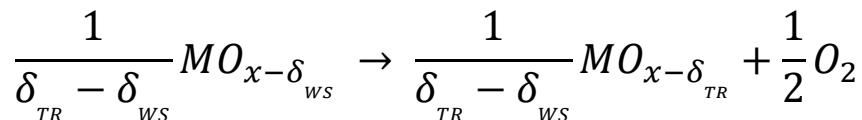
- **Materials role and requirements in two-step cycles**
- **Key efficiency drivers**
- **Achieving low thermal reduction pressure**
- **Electrically forcing reduction and water splitting**
- **Increasing temperature**
- **Fantasy materials**

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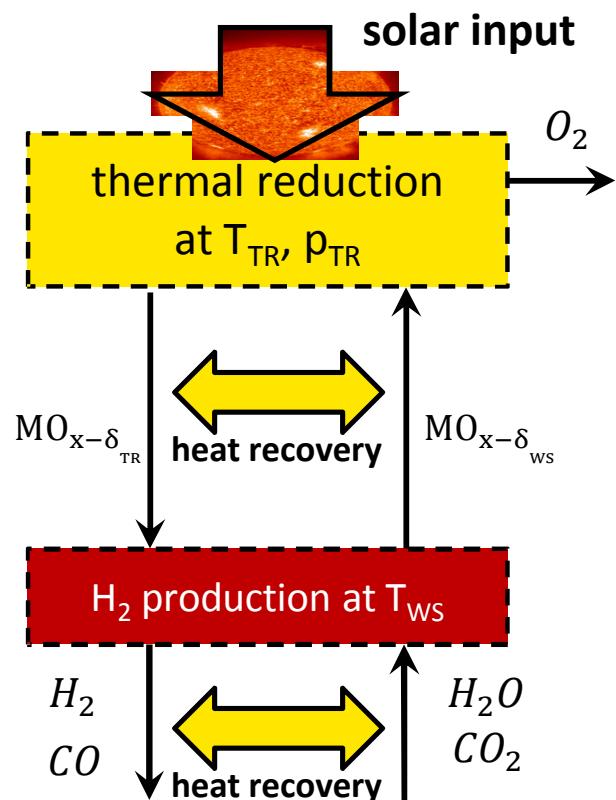
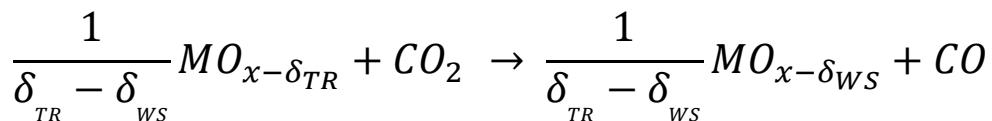
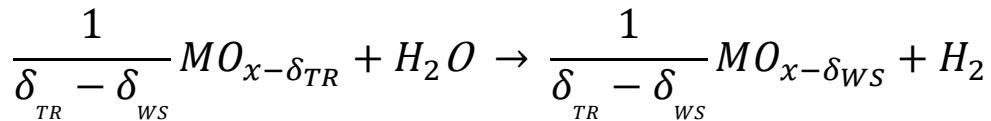
Two-Step Thermochemical Fuel Production

A theoretically simple process

Thermal reduction



Water/CO₂ splitting

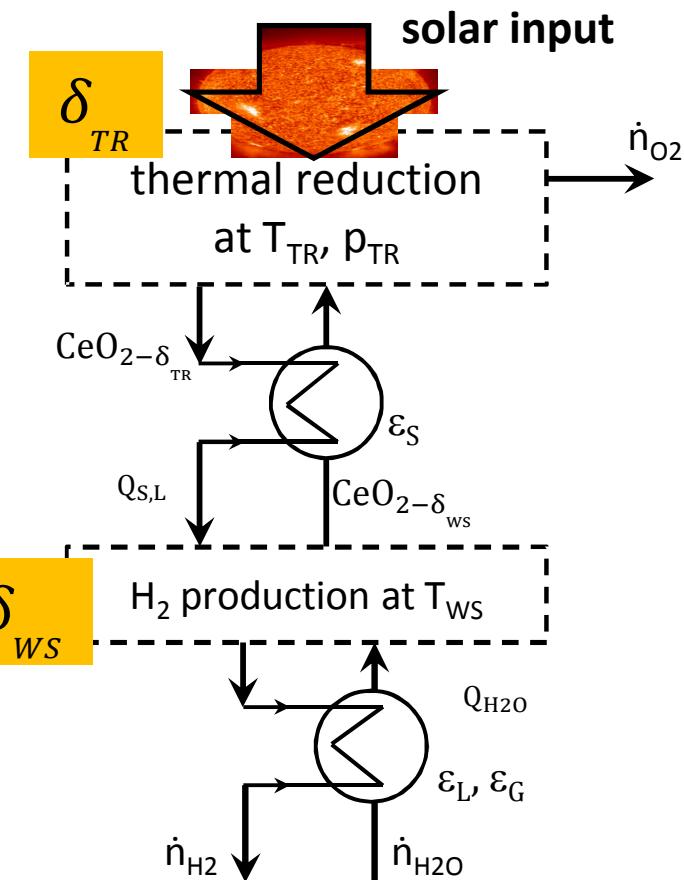
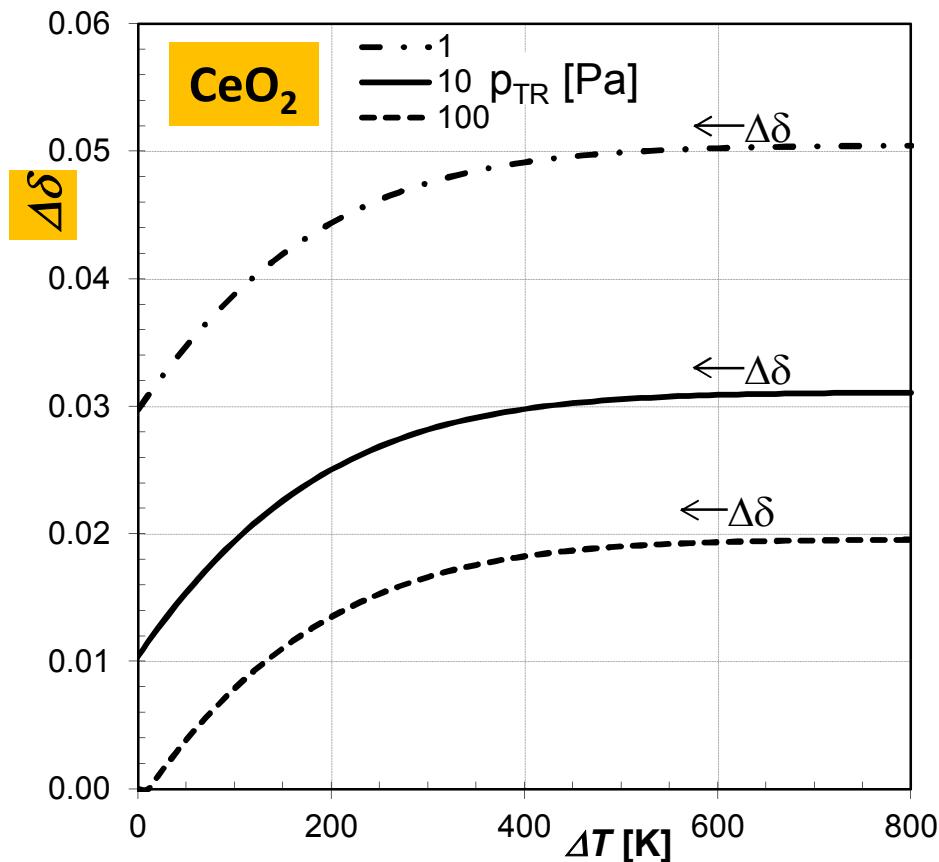


Key Material Requirements: Reactive Oxide

How much CeO_2 per mole H_2 ?

$$\delta_{TR} - \delta_{WS} = \Delta\delta$$

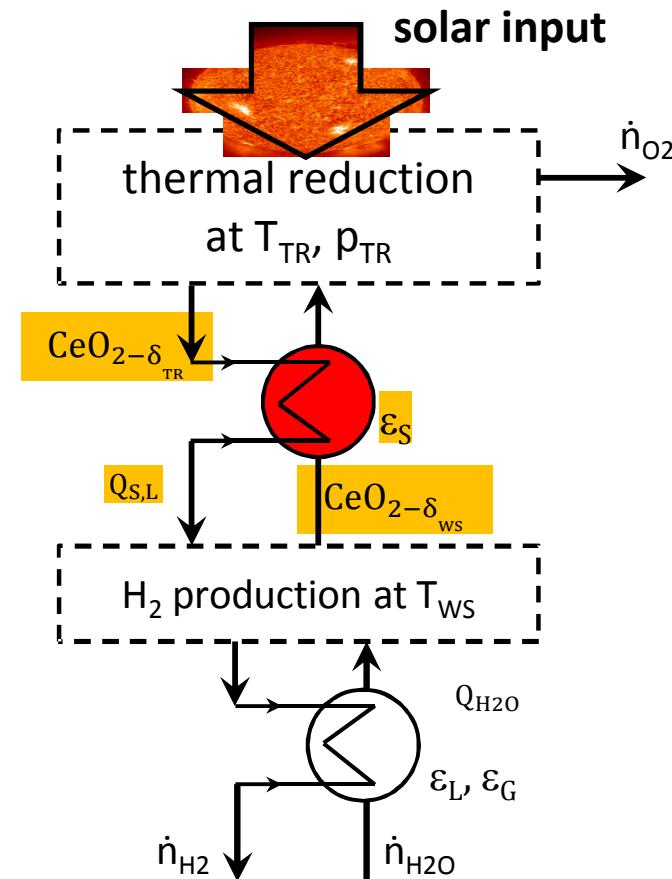
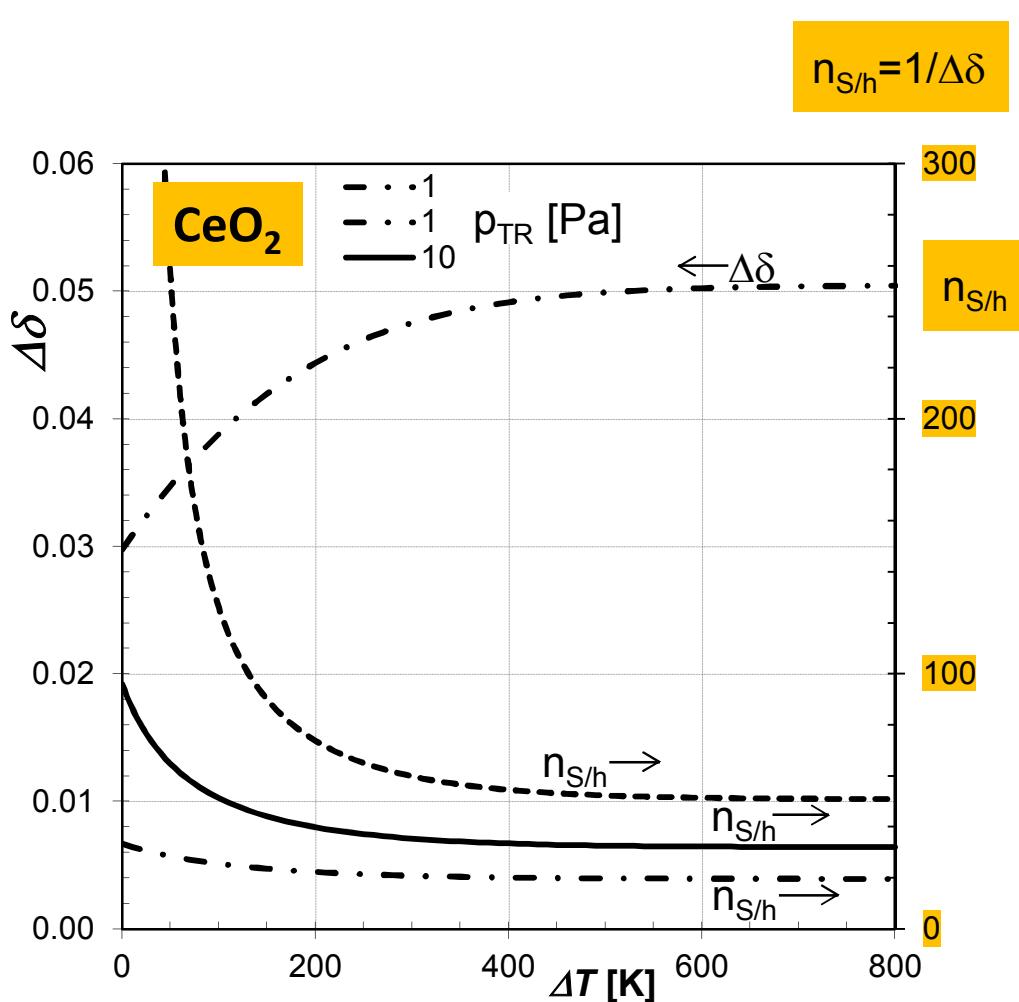
$$T_{TR} = 1773\text{K}$$



The reversible oxygen capacity can be very low!

Key Material Requirements: Reactive Oxide

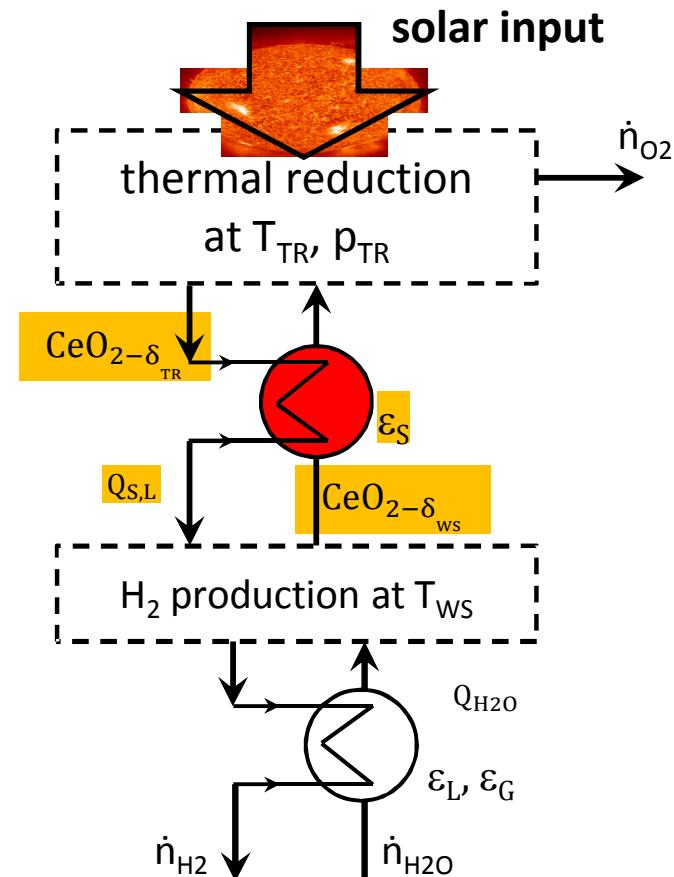
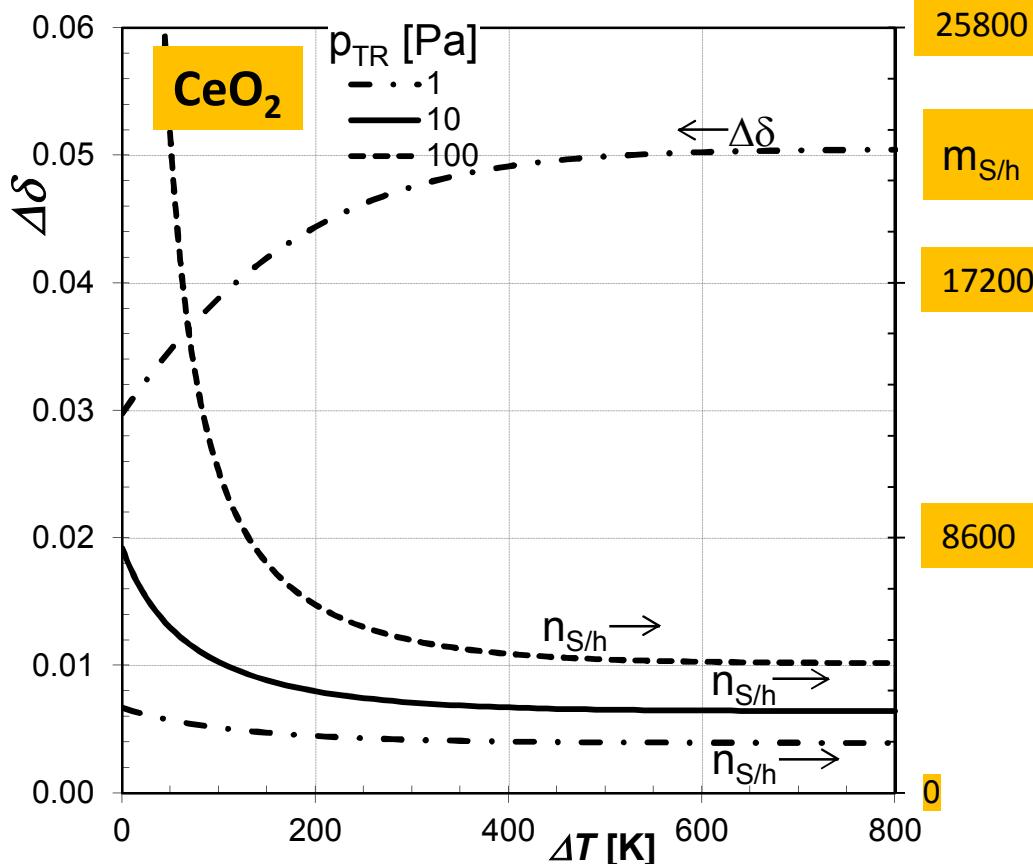
How much CeO_2 per mole H_2 ?



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

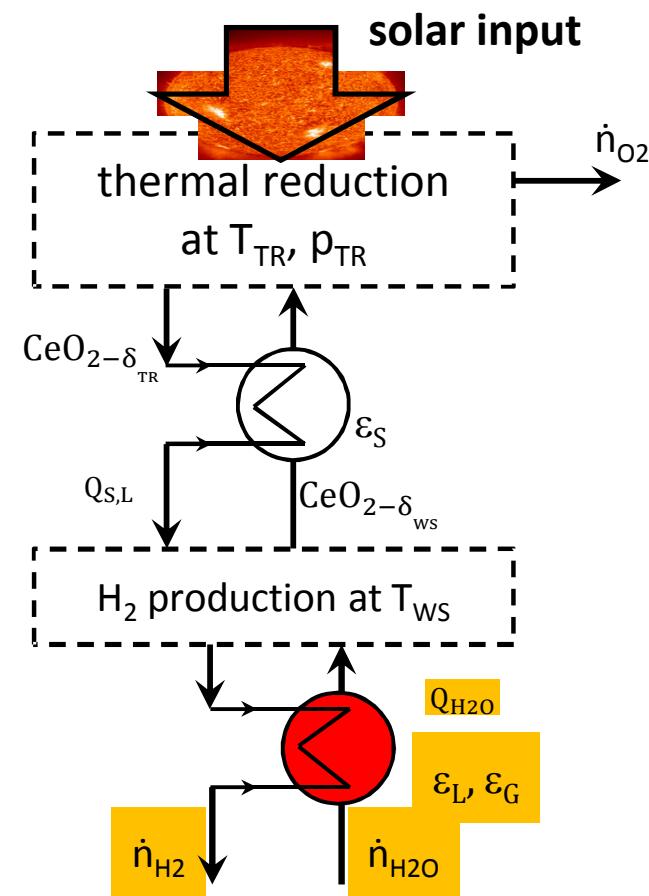
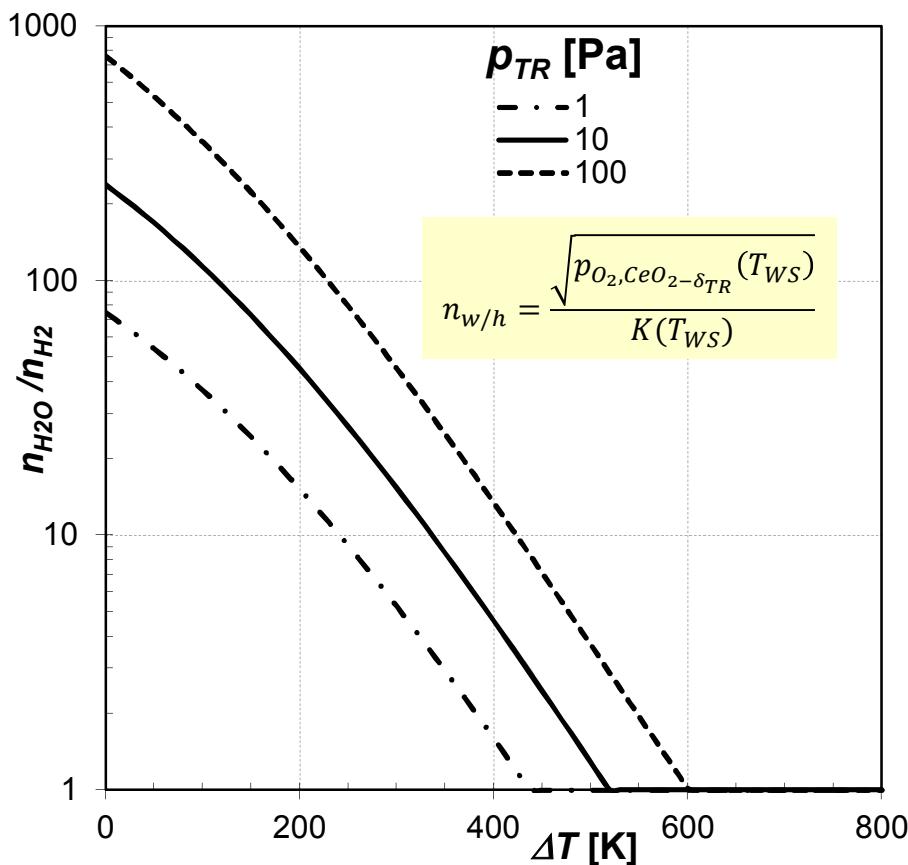
How much CeO_2 per mole H_2 ?



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Key Material Requirements: Steam

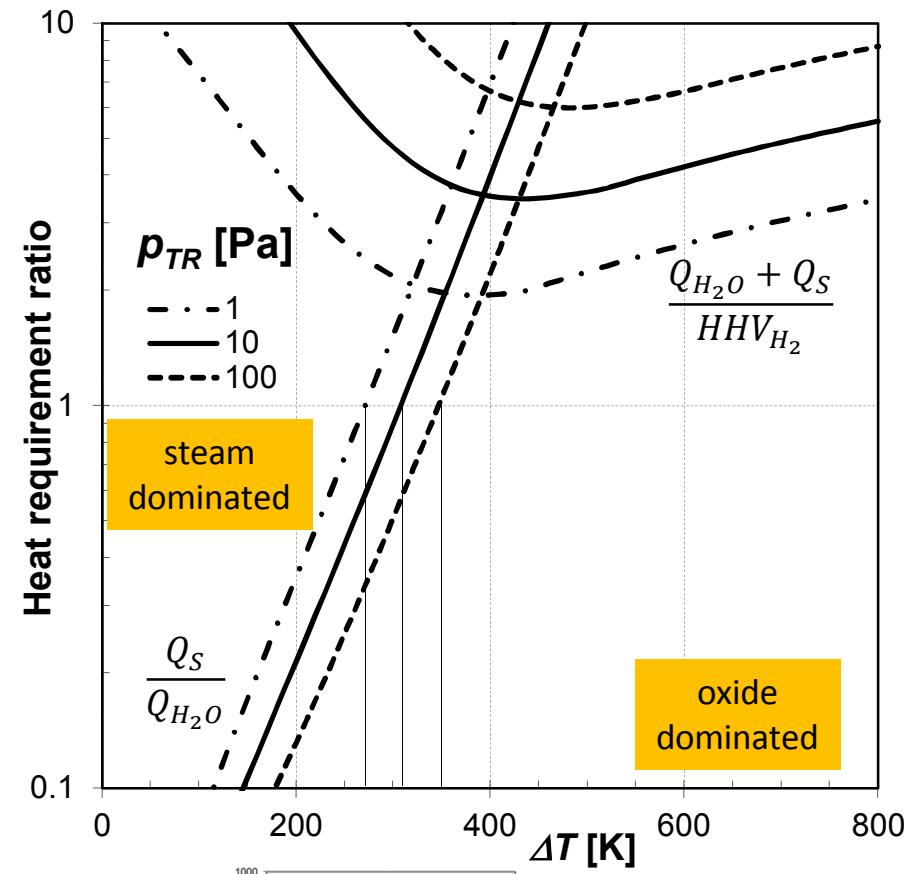
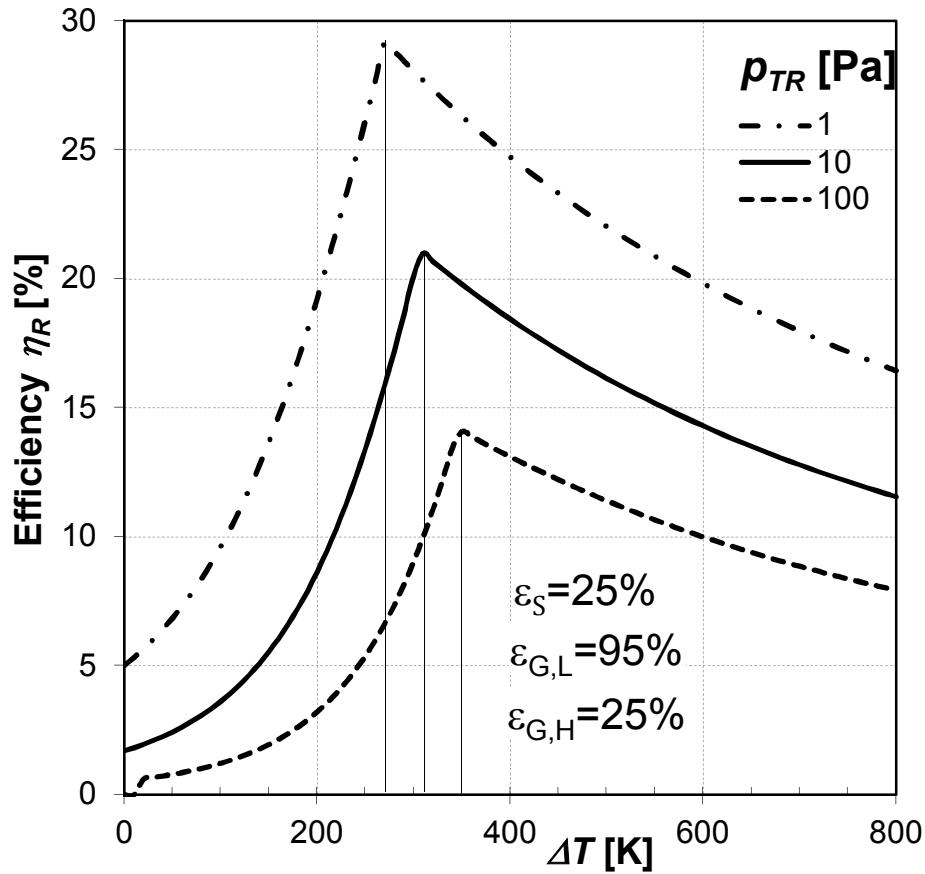
How much steam per mole H₂?



Low ΔT or high reduction pressure leads to a high steam/H₂ ratio

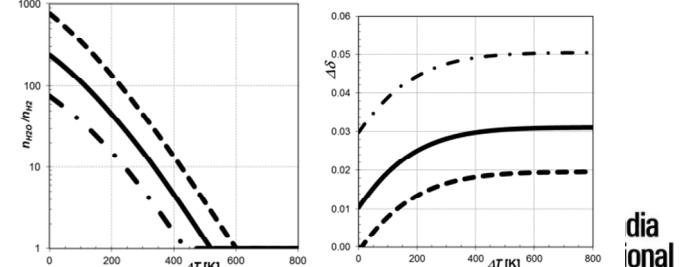
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Maximizing Efficiency: Solid/Steam Heating Balance and a Low Reduction Pressure



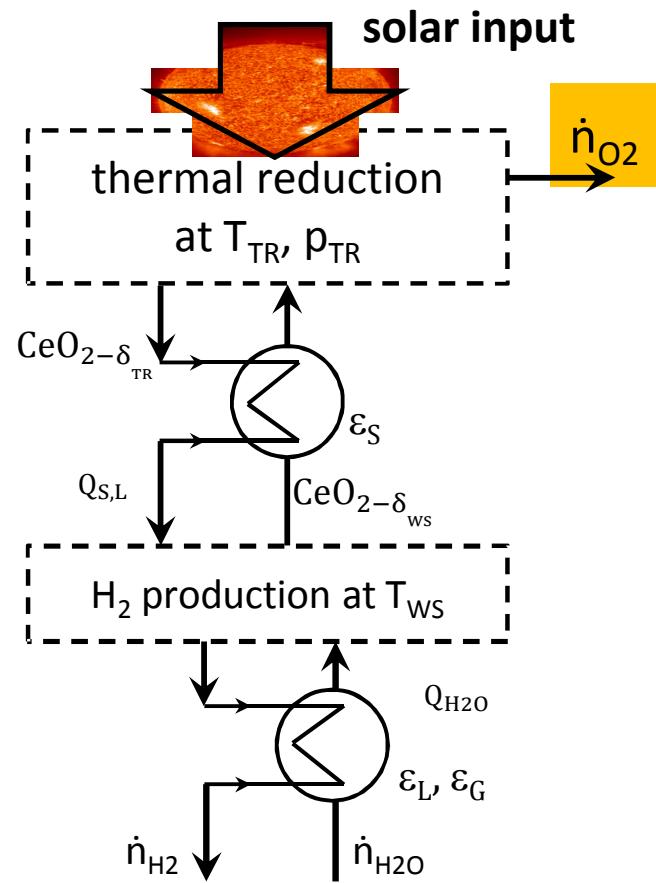
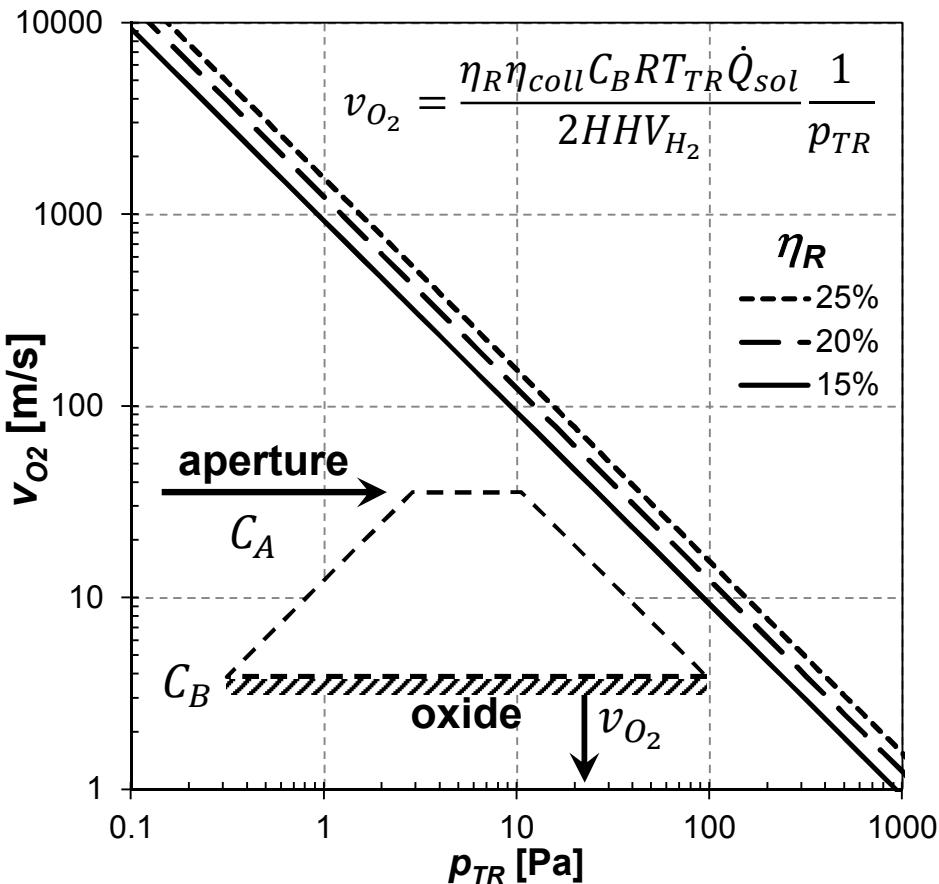
Efficiency is the highest when:

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

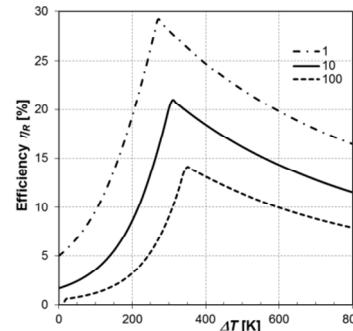


O₂ Pressure Limits: Flow Volume and Speed

Is 1Pa accessible?

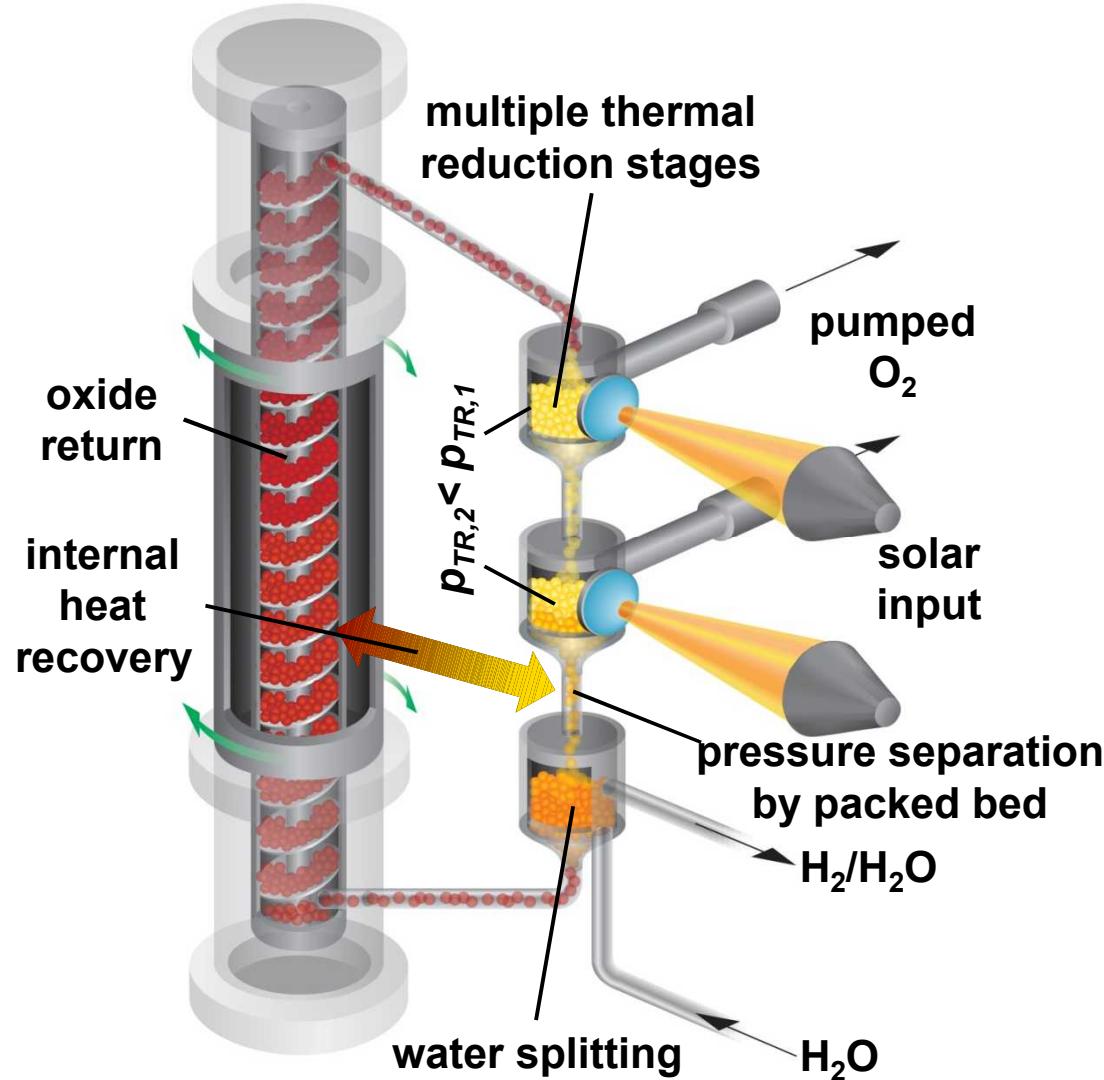


At low pressure required flow volumes and velocities are astronomical!



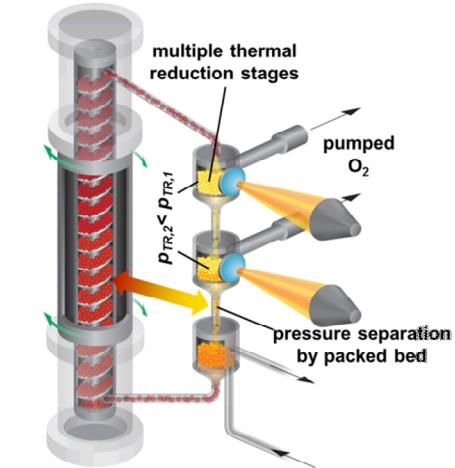
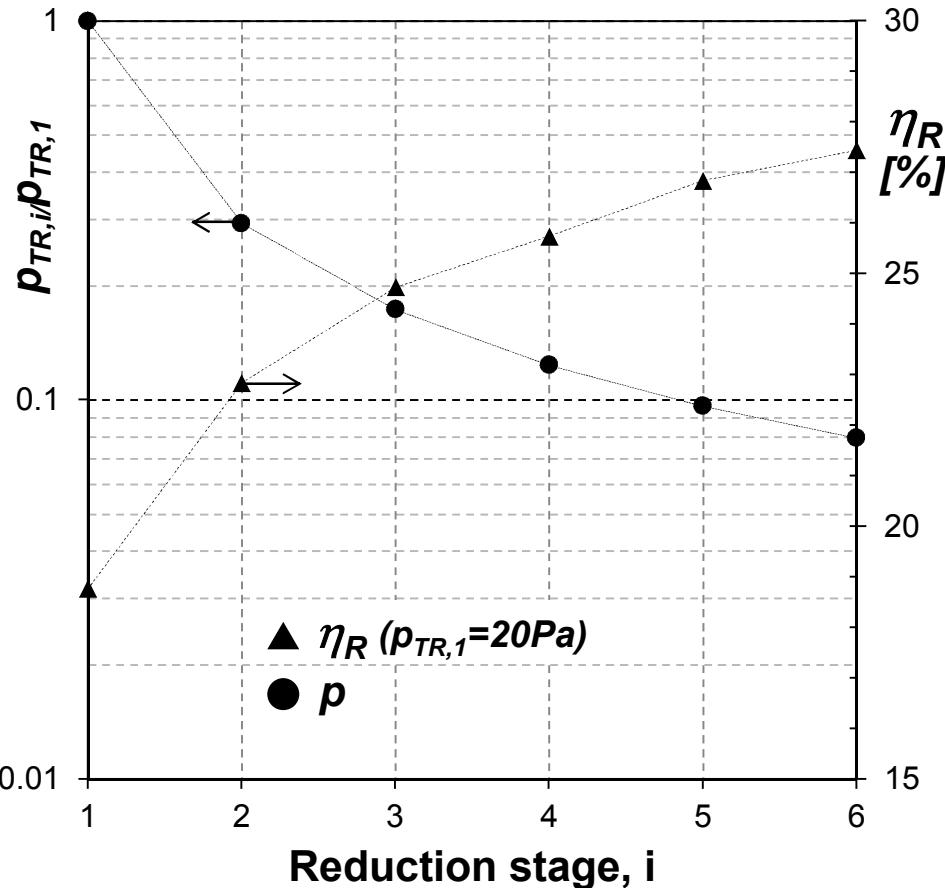
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Staged Reduction Reactor for Low Pressure



Incrementally pumping O_2 reduces the overall flow volume and velocity

Staged Reduction for Low Pressure

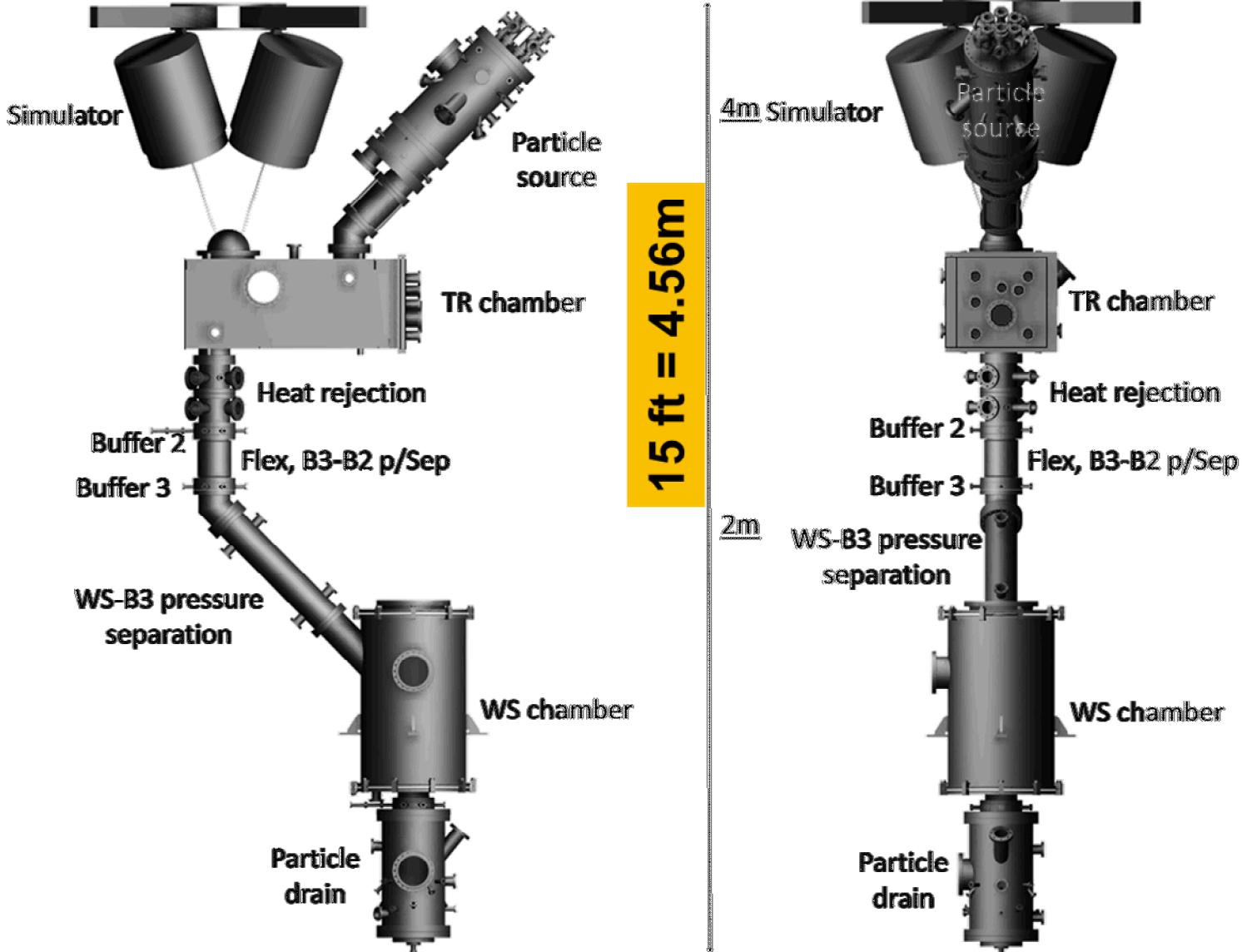


$$p_{TR,i} = \dot{n}_{ox} R T_{TR} \frac{\delta_{TR,i} - \delta_{TR,i-1}}{2 \dot{V}_{O_2}}$$

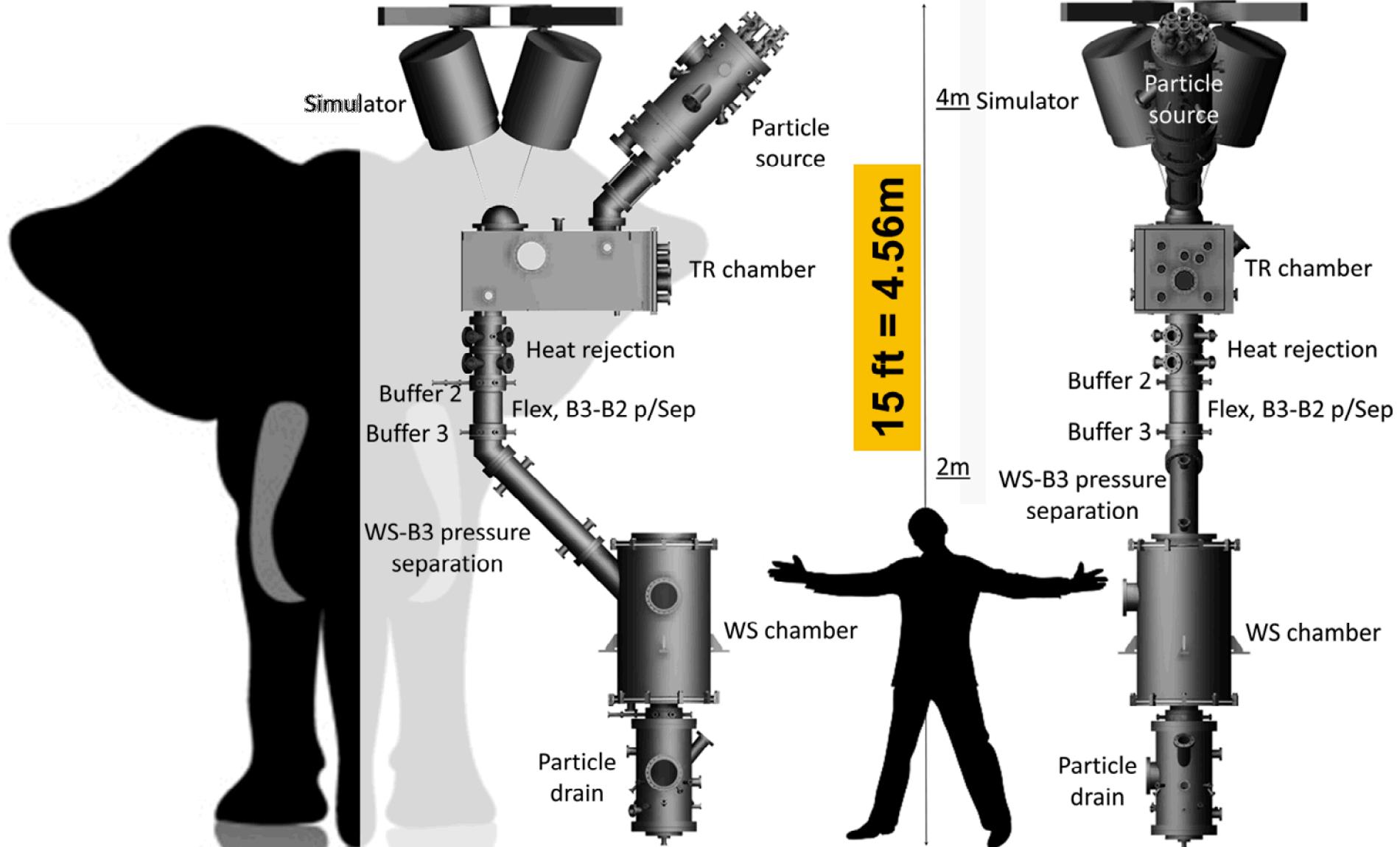
Efficiency is the highest when:

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

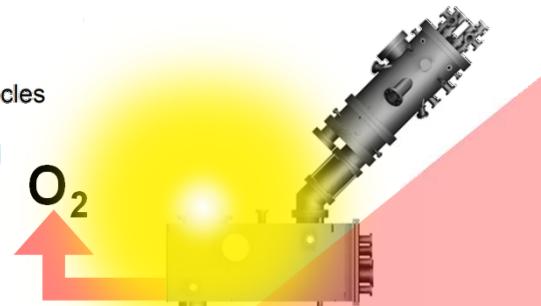
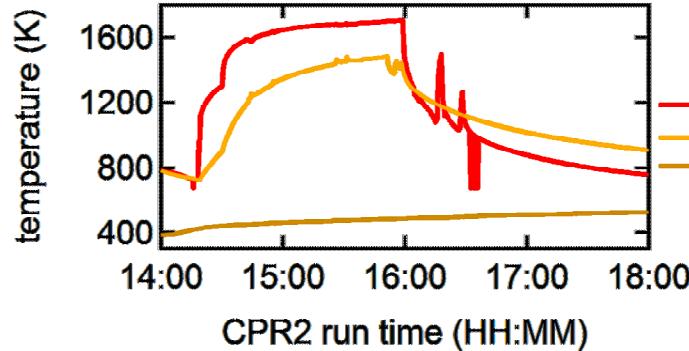
Vacuum and Staged Reduction in Practice



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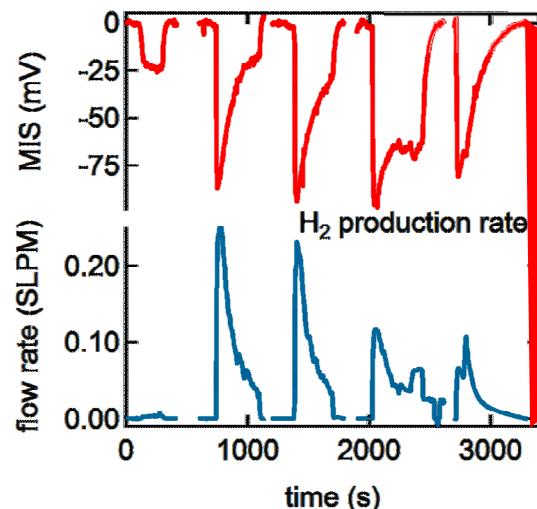


Vacuum and Staged Reduction in Practice

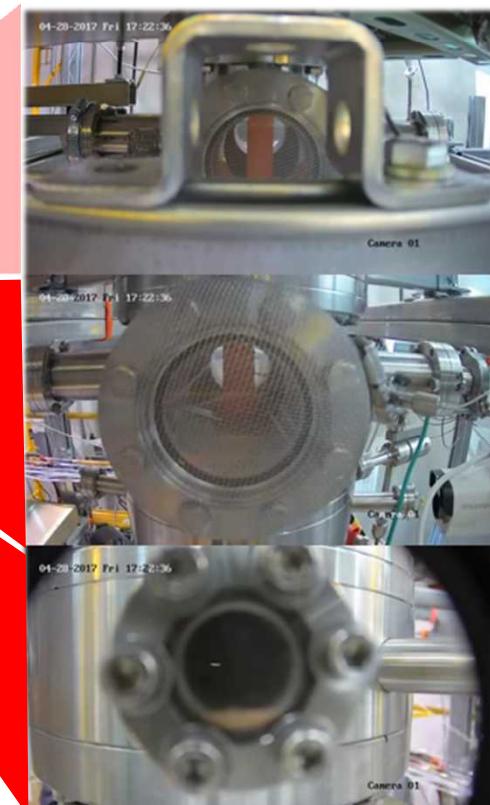


$T_R \sim 1700$ K

0.25 SLPM peak H₂ rate

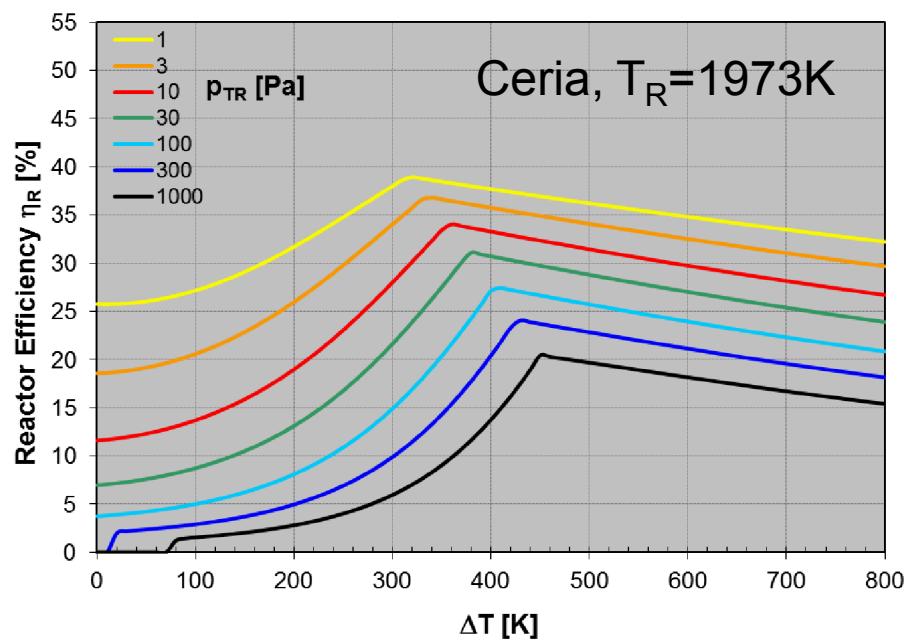
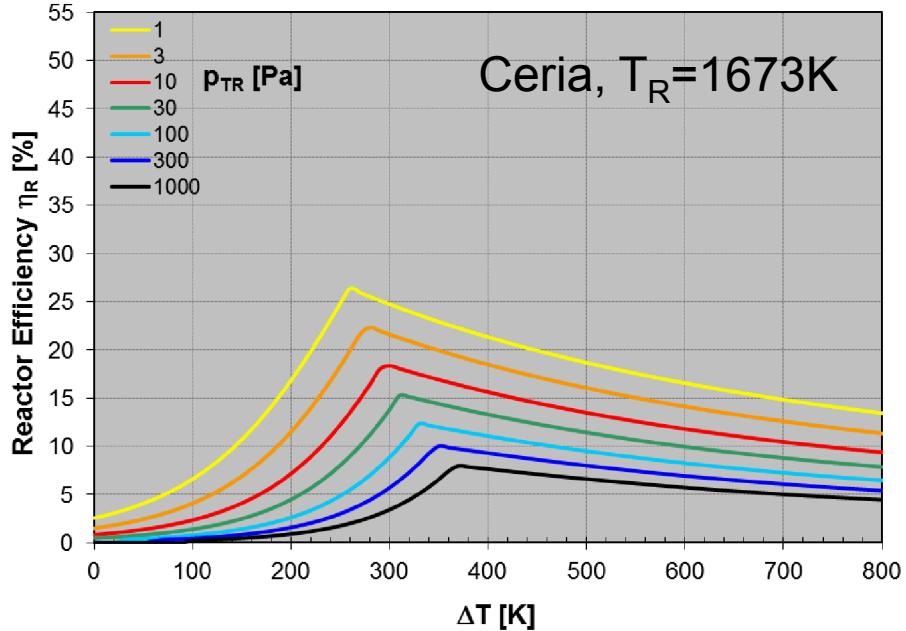
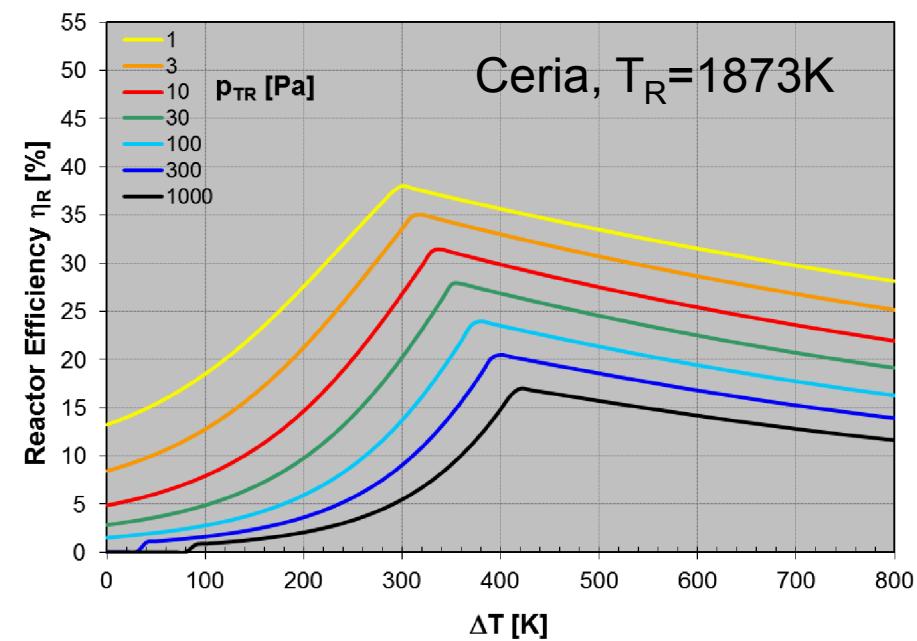
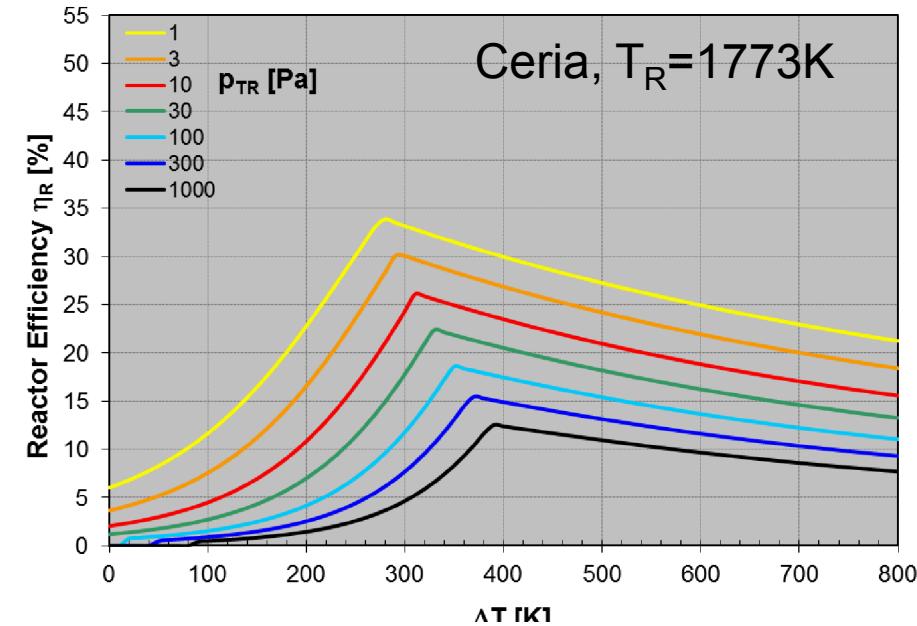


↑ H₂O



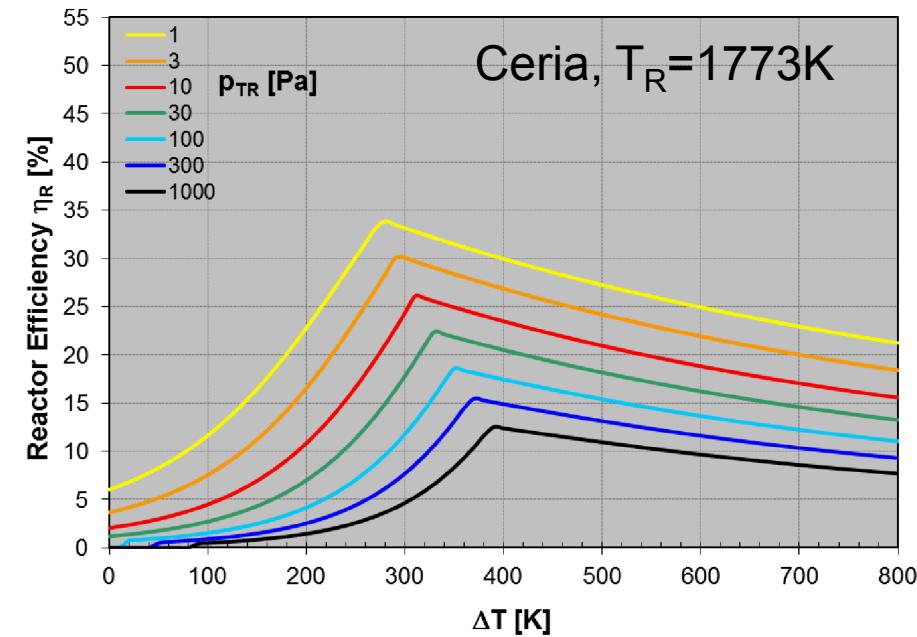
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Playing With Reduction Temperature



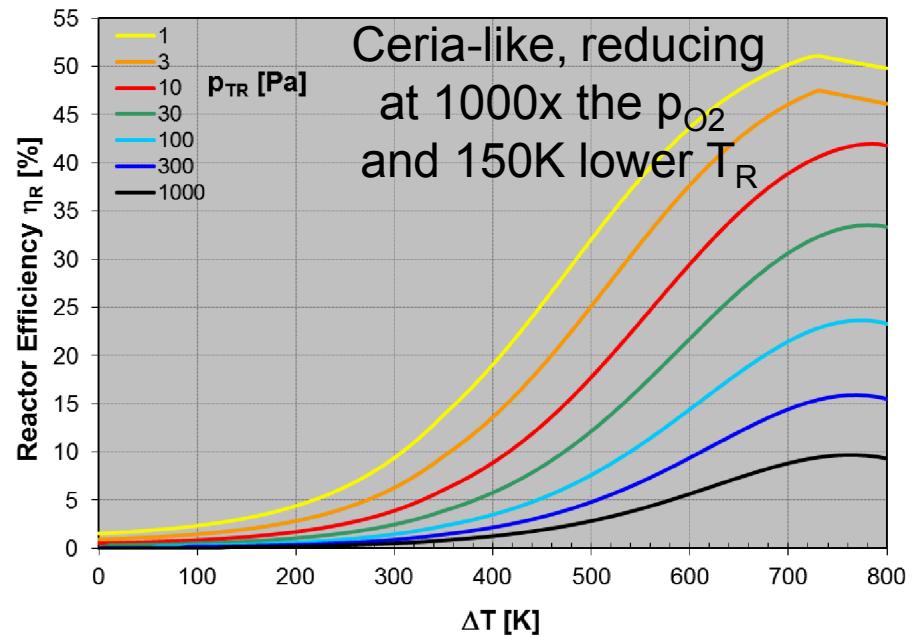
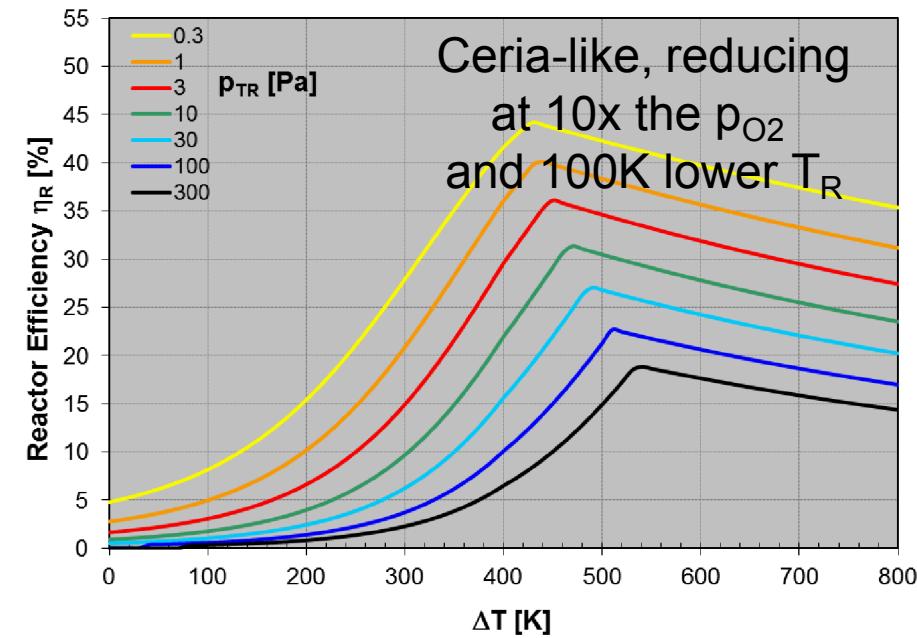
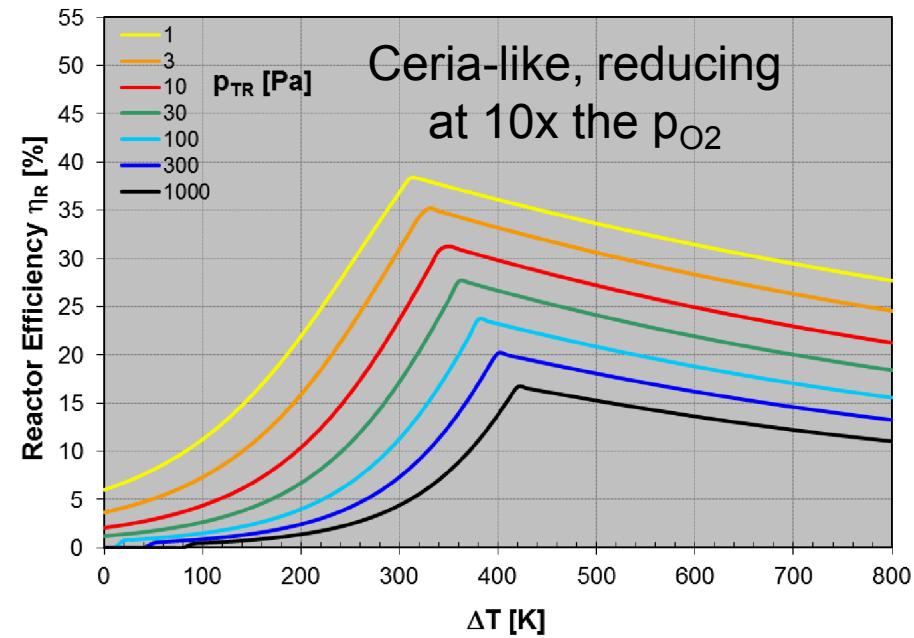
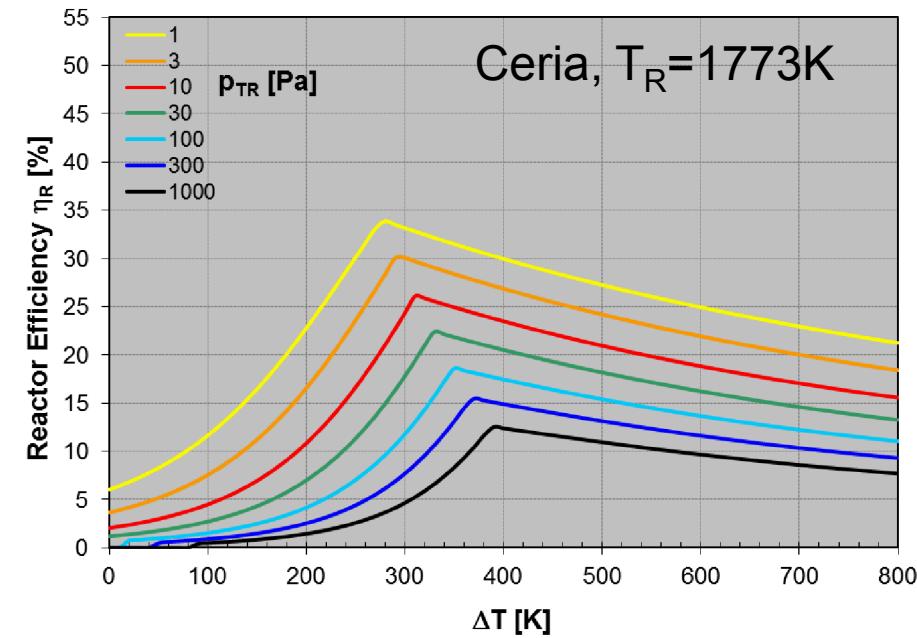
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Playing With Materials Properties

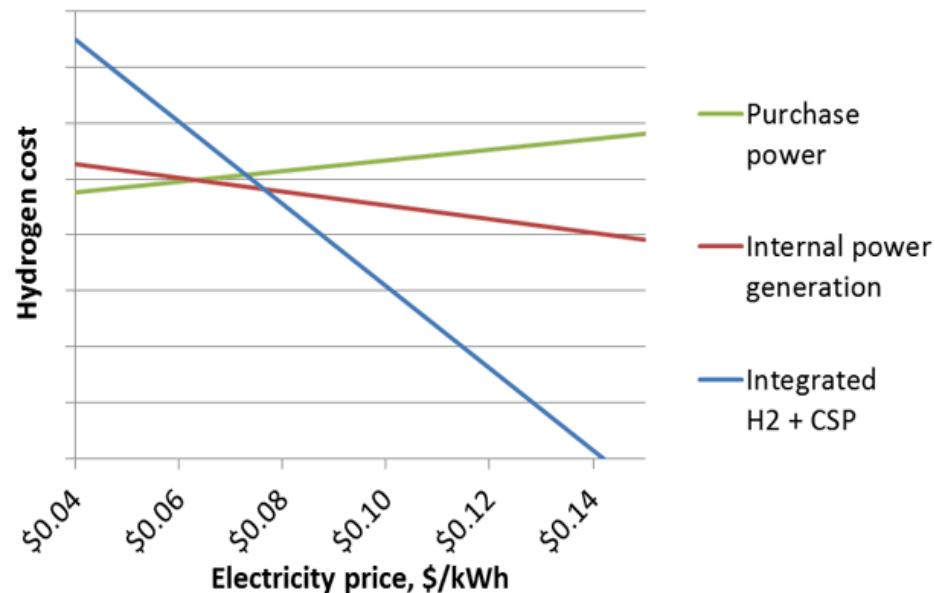
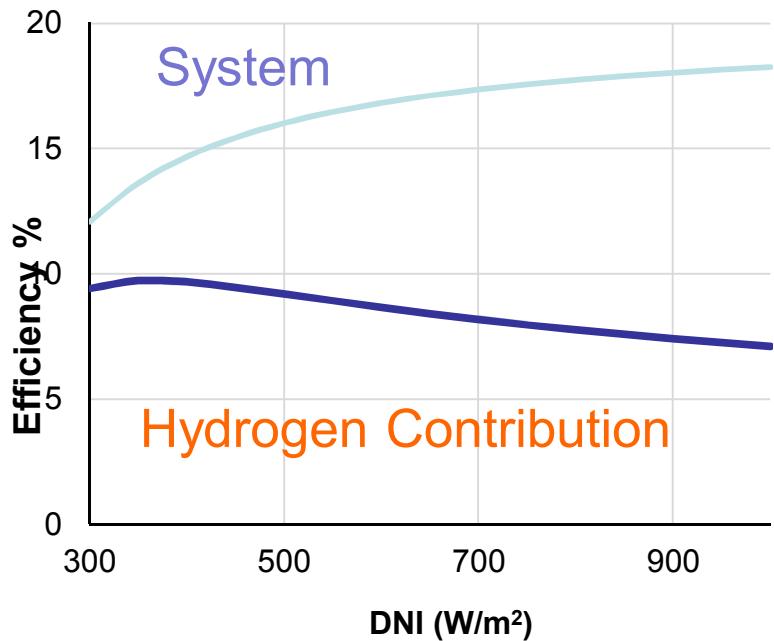


Family of efficiency curves for a
 CeO_2 reactor.

Playing With Materials Properties



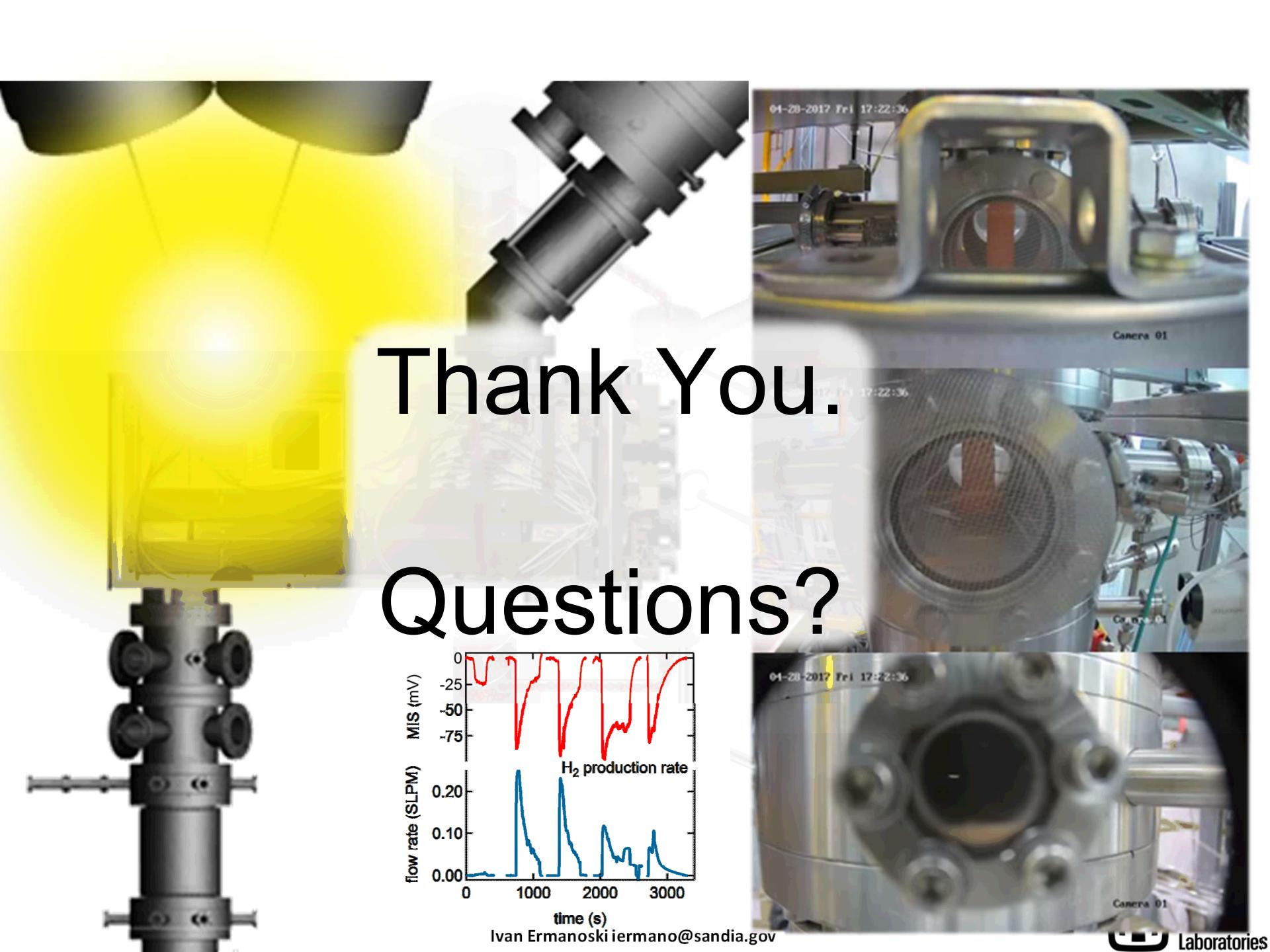
Cogeneration



- Electricity production from waste heat can offset H₂ cost.
 - Ratio of H₂:Electricity dependent on DNI
 - System efficiency is more complex
 - Impact of high-temperature waste heat amplified by integration with CSP

Summary/Interesting questions

- Materials with low $\Delta\delta$ pose a mass flow challenge
- Optimal ΔT 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 ΔT_{opt} , staged pumping and advanced reactive oxides
- Future advances in receiver technology for higher T_R ?
- Advanced materials?
- Cogeneration?



Thank You.

Questions?

