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Sustainable ammonia production from sun, air and water

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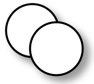
German Aerospace Center (DLR)
Institute of Solar Research

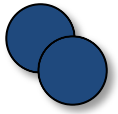
DLR

Ammonia and fertilizer production

Hydrogen
from natural
gas

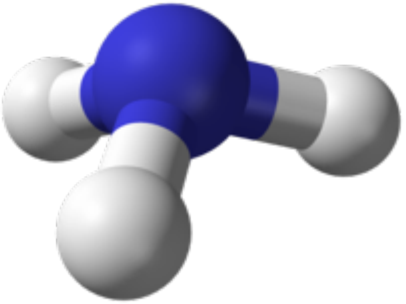


Nitrogen
From air
separation unit



Haber-
Bosch
process

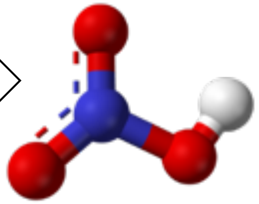
> 200 bar
> 400 °C
Fe/Al_2O_3



Ammonia (NH_3)

CSP?

Intermediates

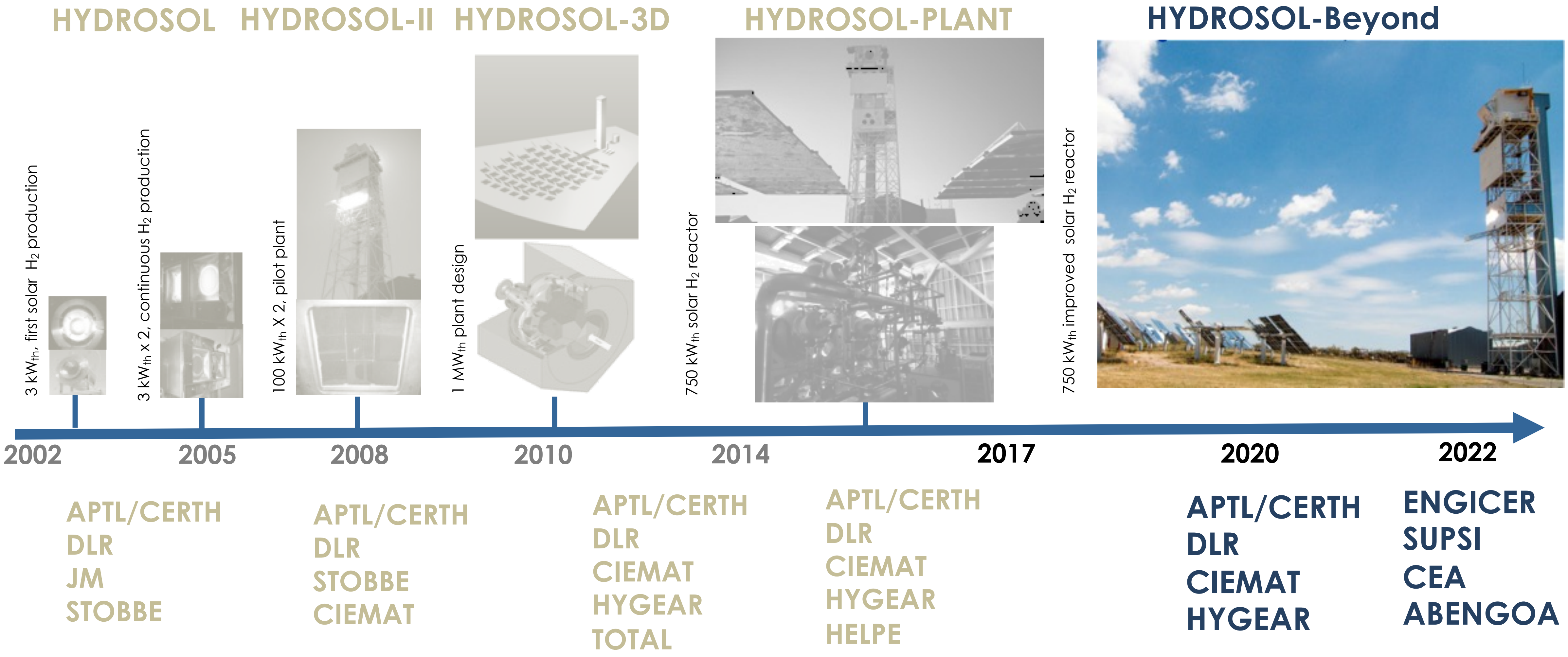


for instance:
nitric acid
HNO_3
+ additives

Nitrogen Fertilizer

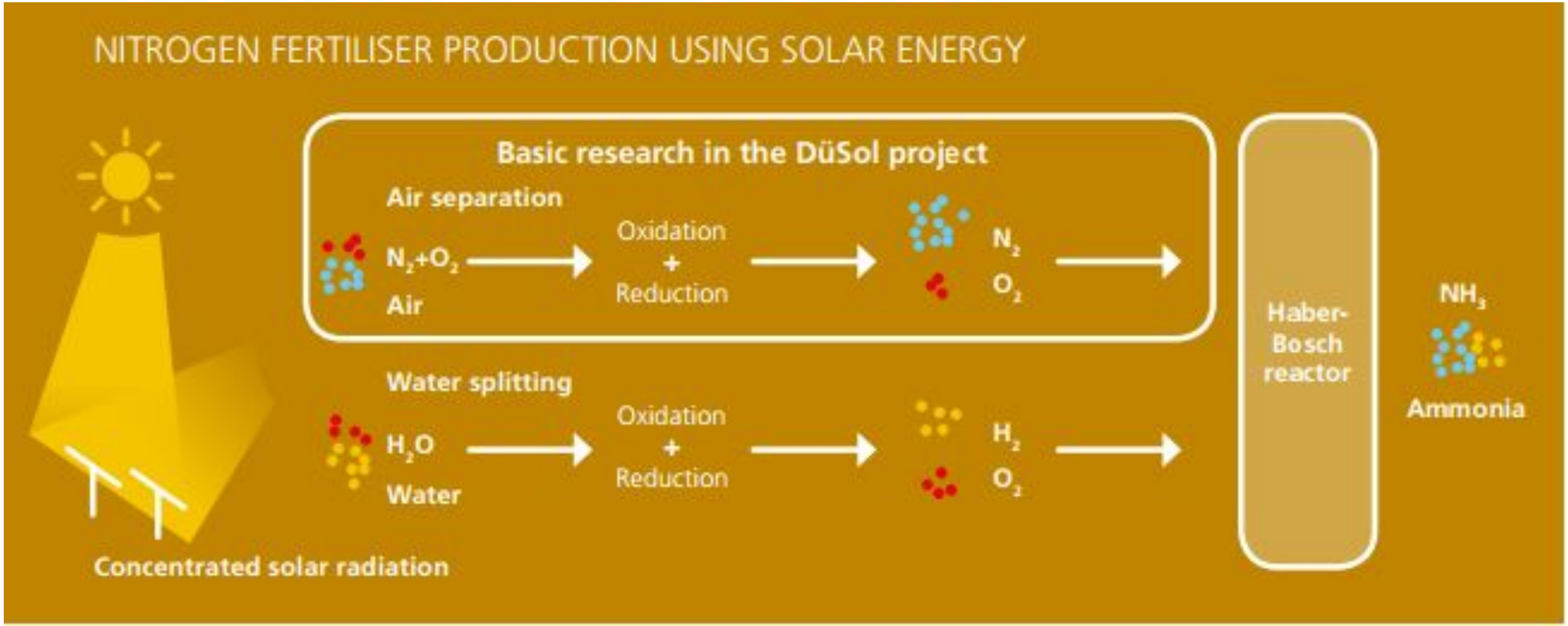
Thermochemical hydrogen production

Techno-economic Study:
LCOH: 6,7 – 13,0 €/kg [1]



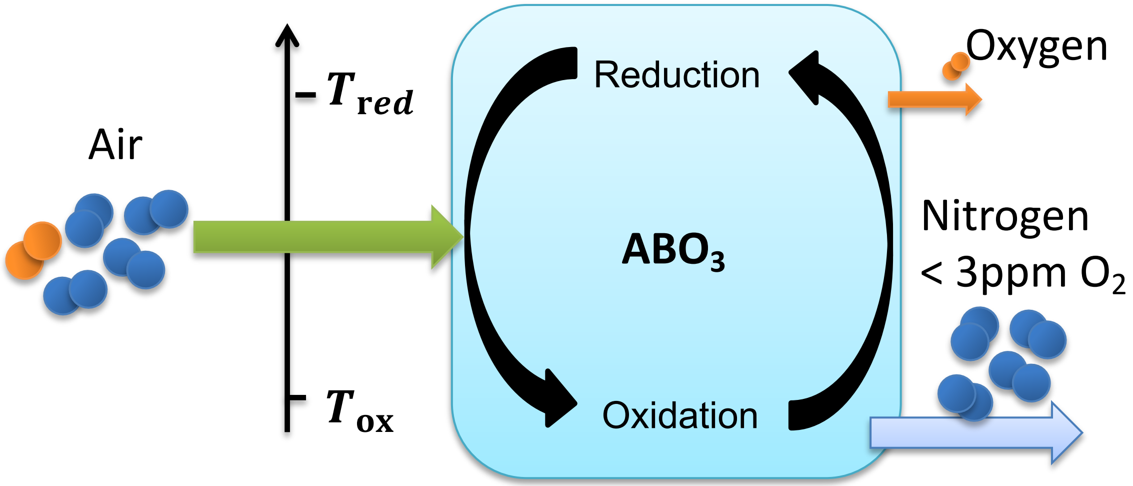
[1] Moser et al.
Energies **2019**, *12*, 352

Thermochemical air separation – Project Düsol



Thermochemical cycles for air separation

N_2 purification cycle



Choice of redox material

Perovskites - $SrFeO_x$

- Low temperature → low p_{O_2} ☑
- Rapid kinetics ☑
- Cycleability ☑
- Abundant materials ☑
- Low gravimetric O_2 capacity ☒

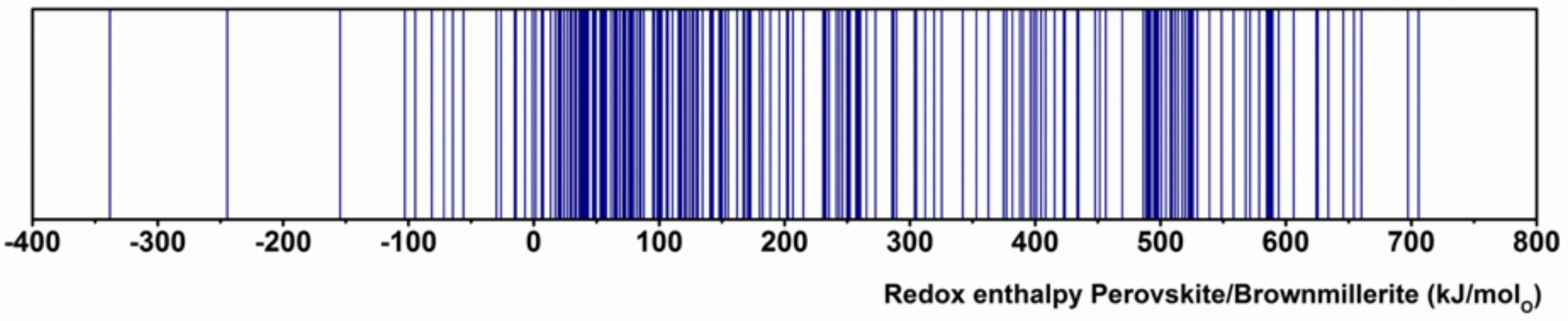
Perovskite Materials Design

Theoretical study of > 240 perovskites

Spectrum of redox enthalpies

harder to reduce → Higher reduction temperatures; More energy required

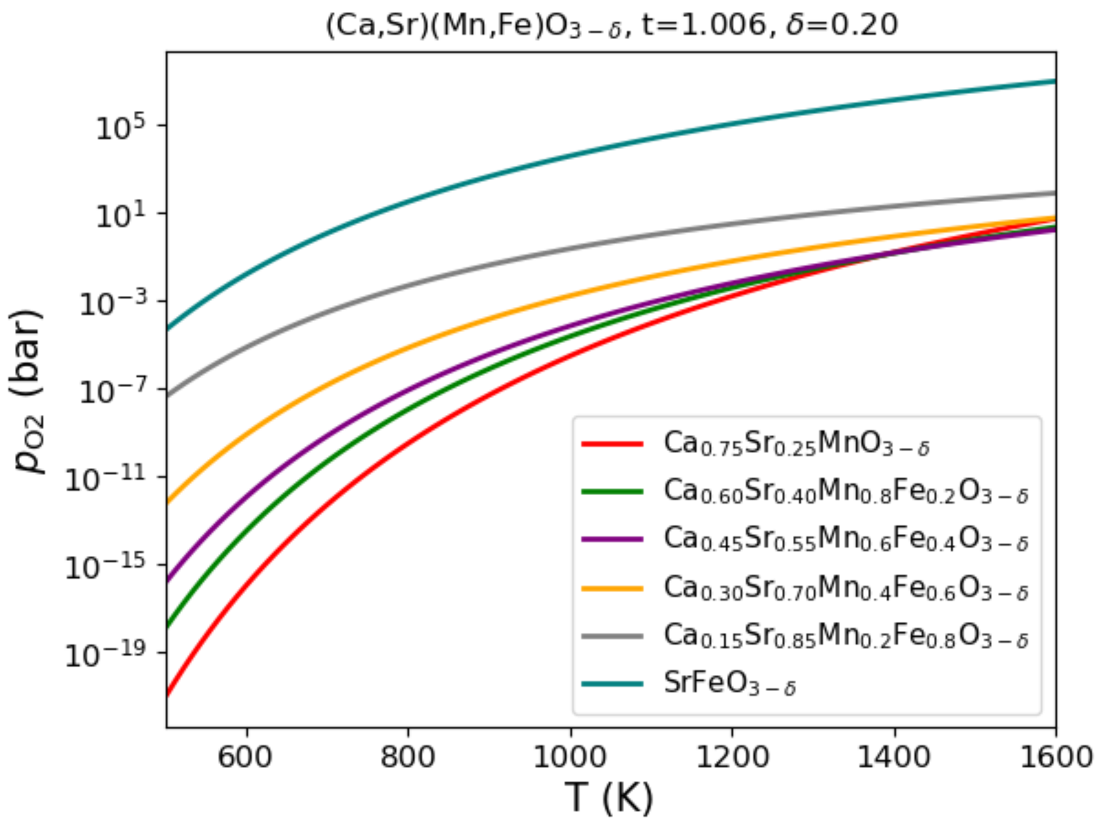
higher oxygen affinity → More effective air separation; lower oxygen partial pressures achievable



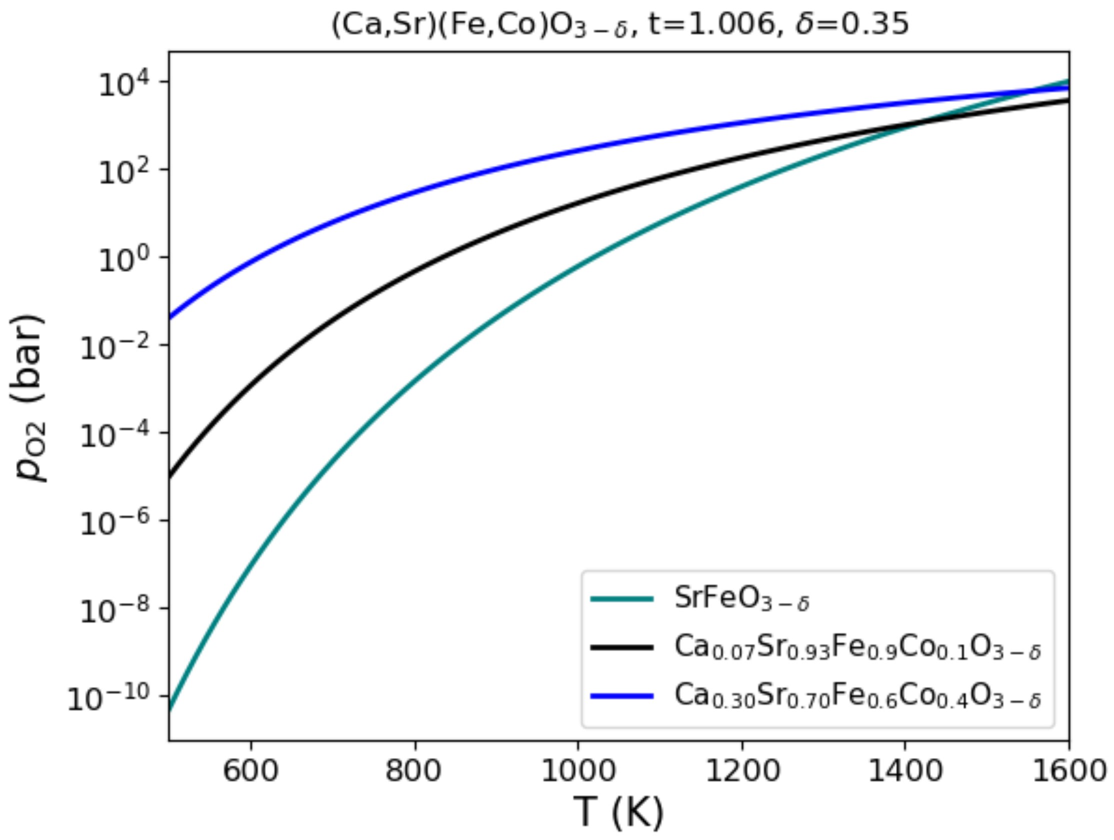
Vieten, J., et al., *Materials design of perovskite solid solutions for thermochemical applications.* Energy & Environmental Science, 2019. **12**(4): p. 1369-1384.

Example: $SrFeO_{3-\delta}$-based perovskites

Exchange some Fe by Mn ➔ Higher redox enthalpy



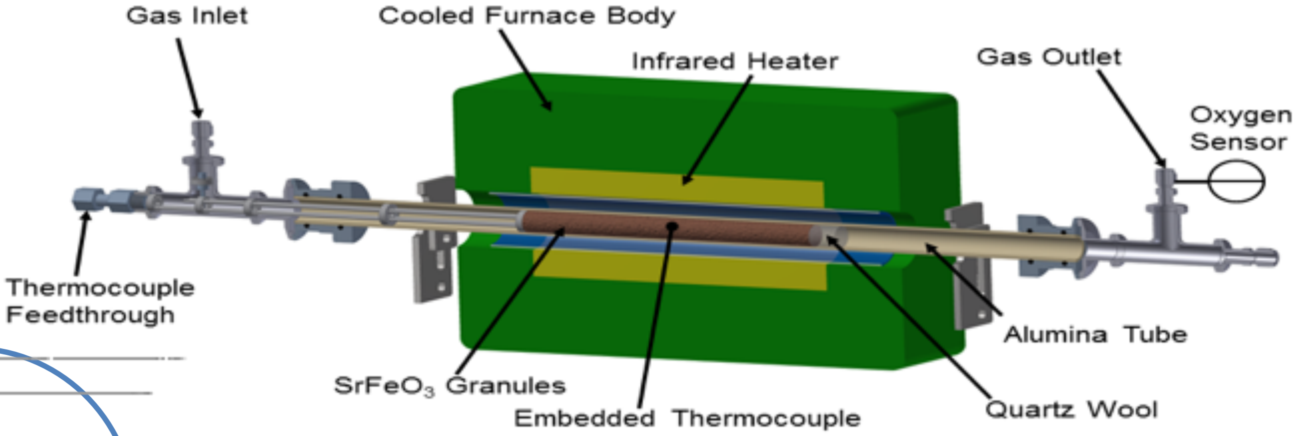
Exchange some Fe by Co ➔ Lower redox enthalpy



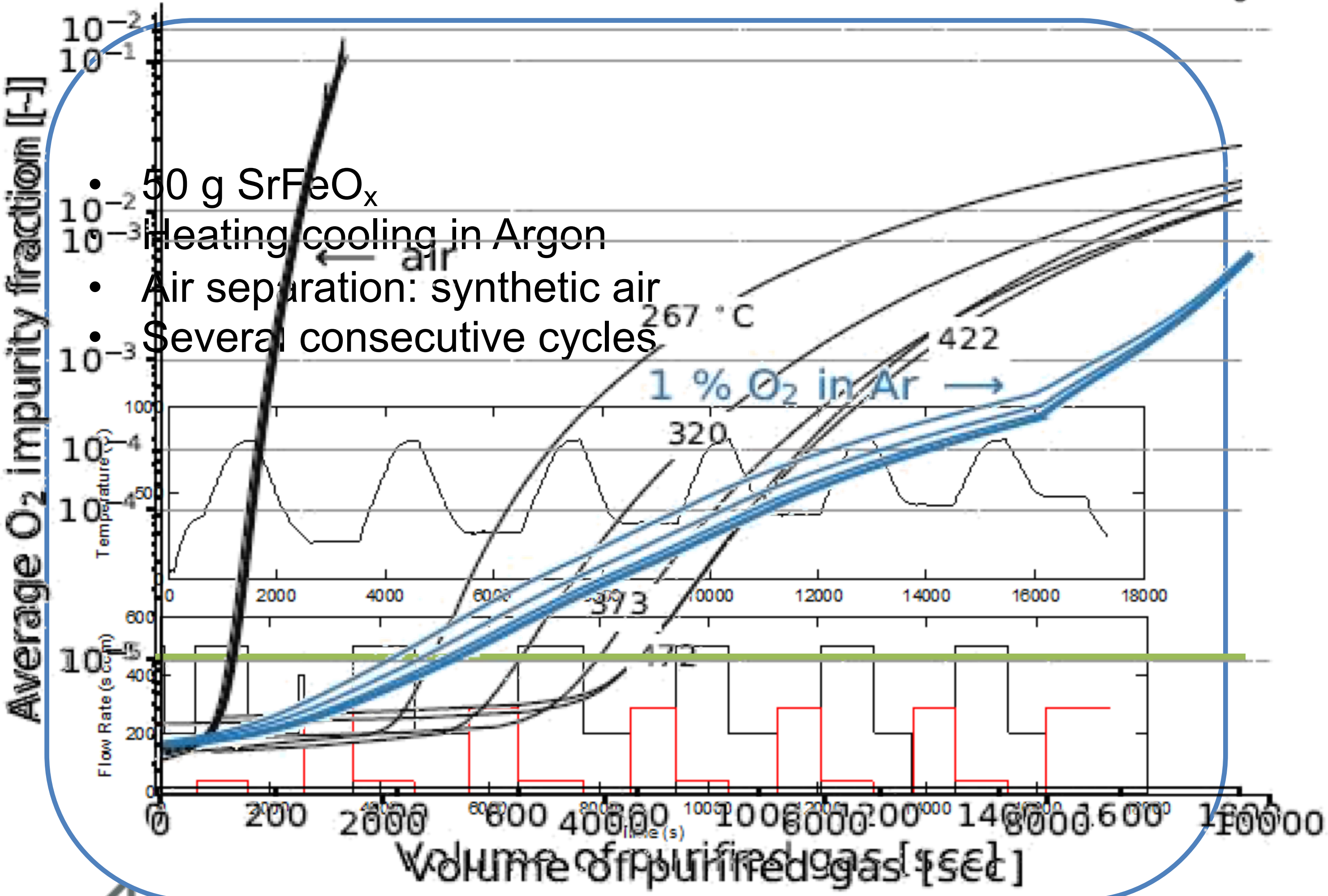
Vieten, J., *Perovskite Materials Design for Two-Step Solar-Thermochemical Redox Cycles*, 2019, PhD thesis, TU Dresden; DOI: 10.13140/RG.2.2.17964.92800

DLR

Laboratory scale air separation test



Experimental details



- 50 g $SrFeO_x$
- Heating/cooling in Argon
- Air separation: synthetic air
- Several consecutive cycles

50g material produced:

- 0.6 l purified N_2 from air
- 2 l purified N_2 from semi-purified stream

(purity suitable for the Haber-Bosch process)

Scaling up to 20 kW solar – reactor design

Reduction : $ABO_{3-\delta_{ox}} \xrightarrow{\text{heat in} \quad \Delta\delta\Delta H_O} ABO_{3-\delta_{rd}} + \frac{\Delta\delta}{2} O_2, \qquad T_{rd}$

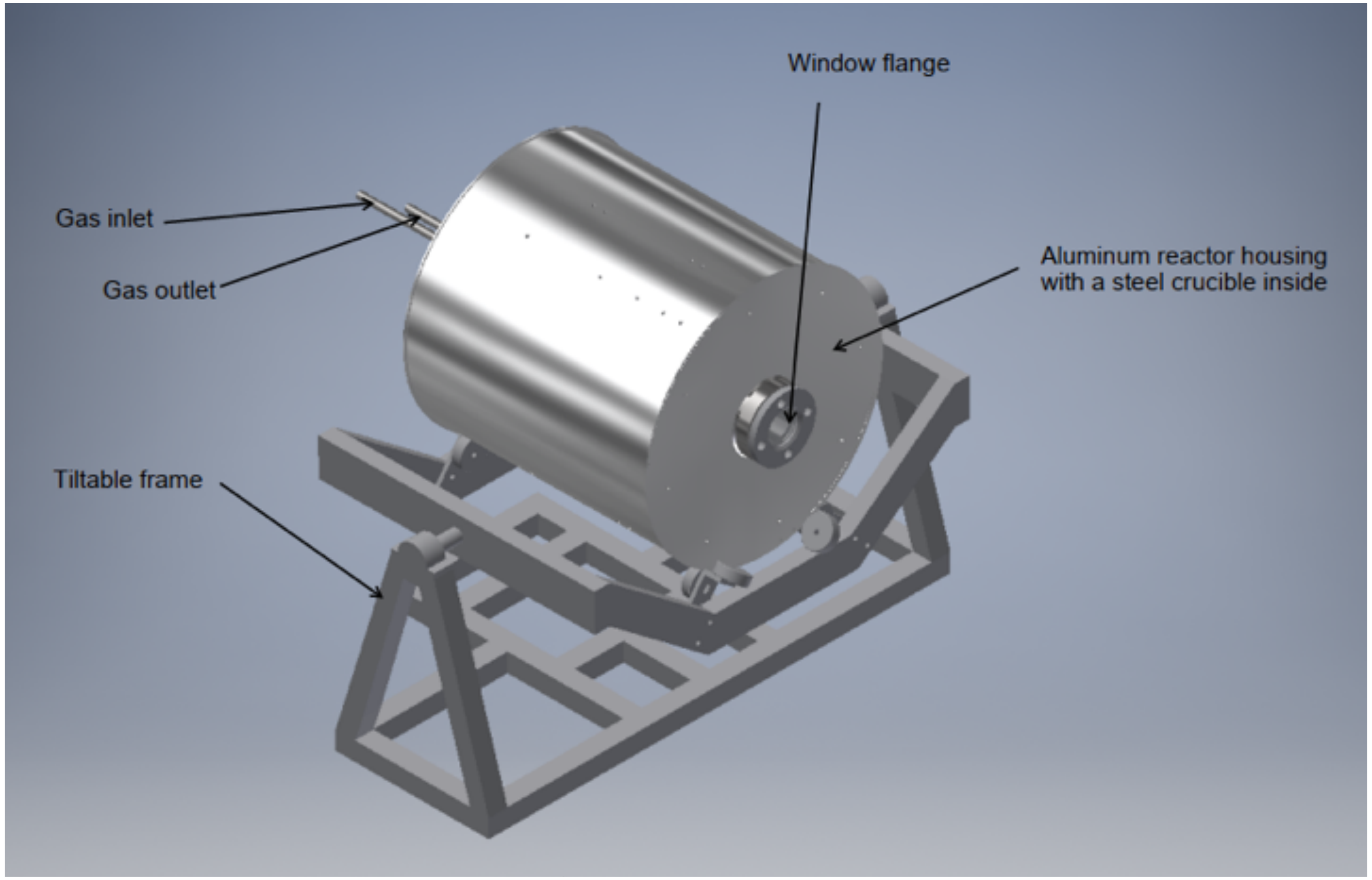
Material	T_{rd}	Atmosphere	T_{max}	p_{O_2}
$SrFeO_3$	800 – 1000 °C	Air	1150 °C	0.2 bar

Oxidation: $ABO_{3-\delta_{rd}} + \text{Air}(20\%\ O_2) \xrightarrow{\text{heat out} \quad -\Delta\delta\Delta H_O} ABO_{3-\delta_{ox}} + N_2\left(p_{O_2} \ll 0.2 bar\right), \qquad T_{ox}$

Material	T_{ox}	Atmosphere	T_{min}	p_{O_2}
$SrFeO_3$	300 – 500 °C	Air	250 °C	0.2 - ppm

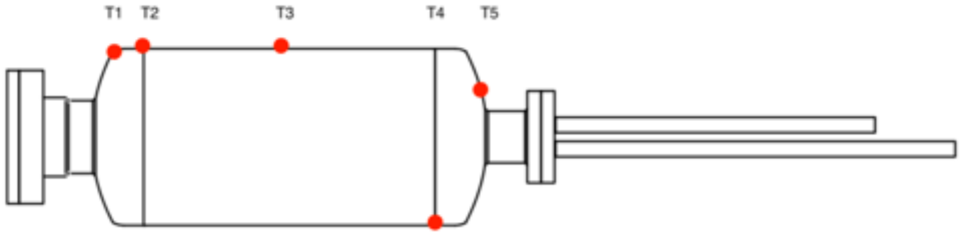
Solar rotary kiln

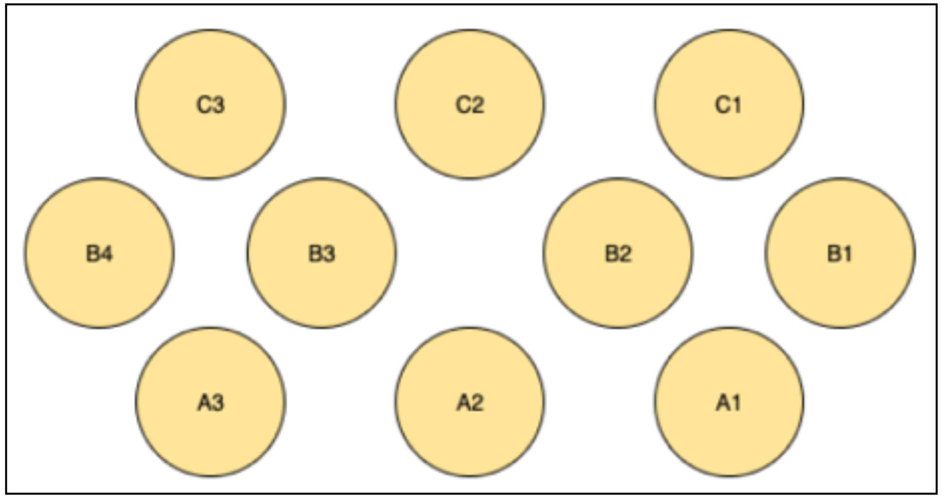
- Suitable for up to 2 kg redox material
- Stainless steel crucible (1.4828)
    - welded window flange and inlet-outlet pipes
    - 1.4828 because of its low amount of chrome
    - Temperature resistant up to 1000 ºC
- Zirconia coating
    - Increase heat and reaction resistance
- Gastight design with a quartz window
- Feedthrough flange for inlet and outlet pipe in the back of the crucible
- Bayonet thermocouples – 5 measurement points
- Mass flow controllers at the inlet and outlet pipe
- Oxygen sensor and filter

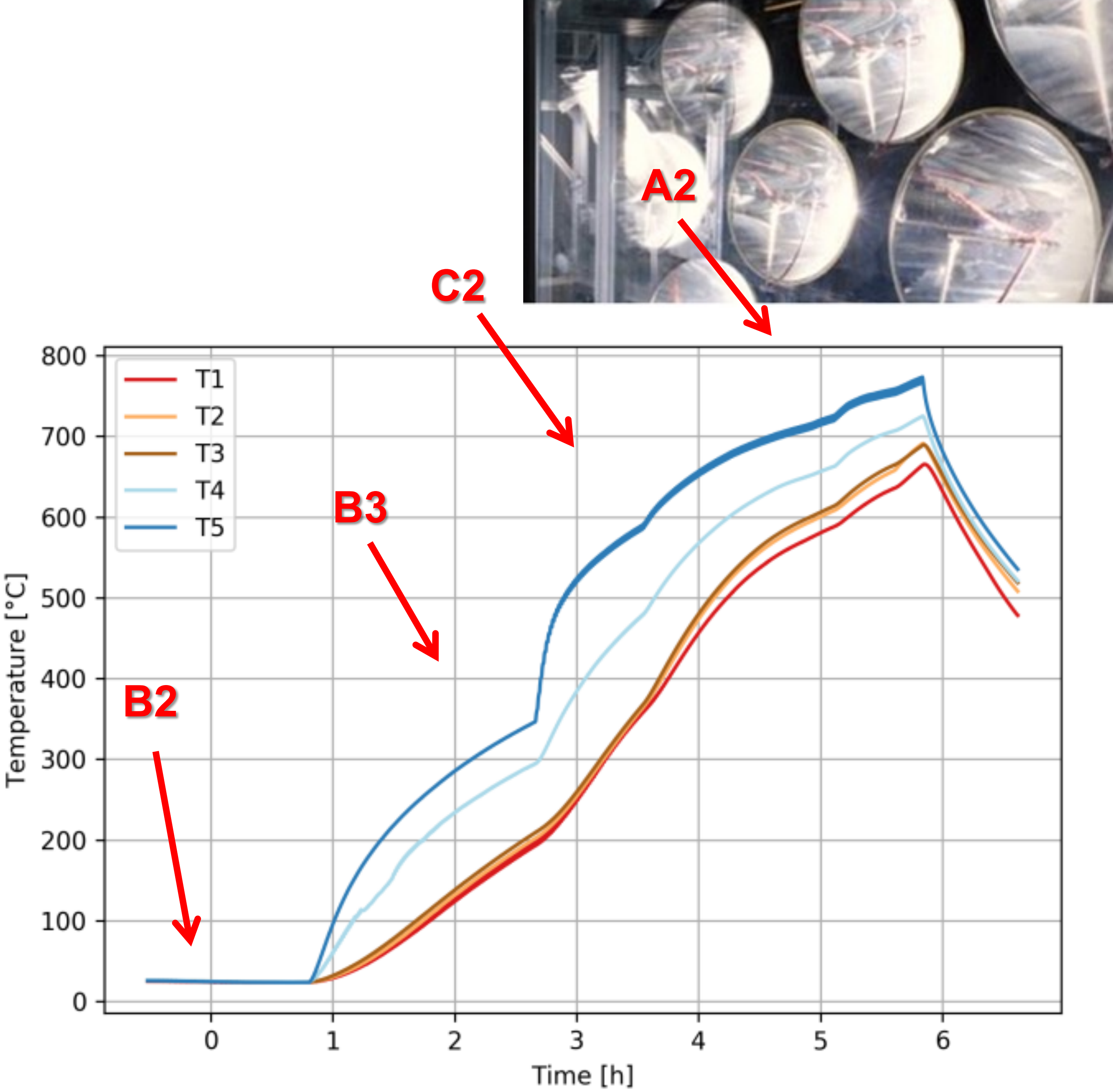


Experiments in the solar simulator

- Demonstration of thermal resistance
- Validation of design



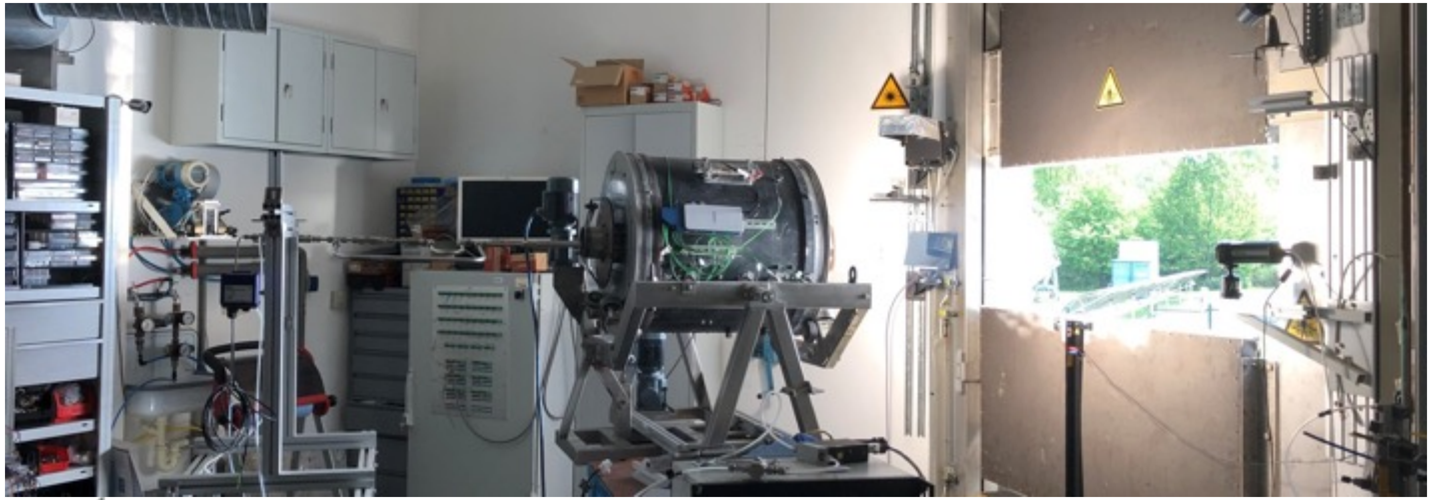




Solar air separation

Experimental details

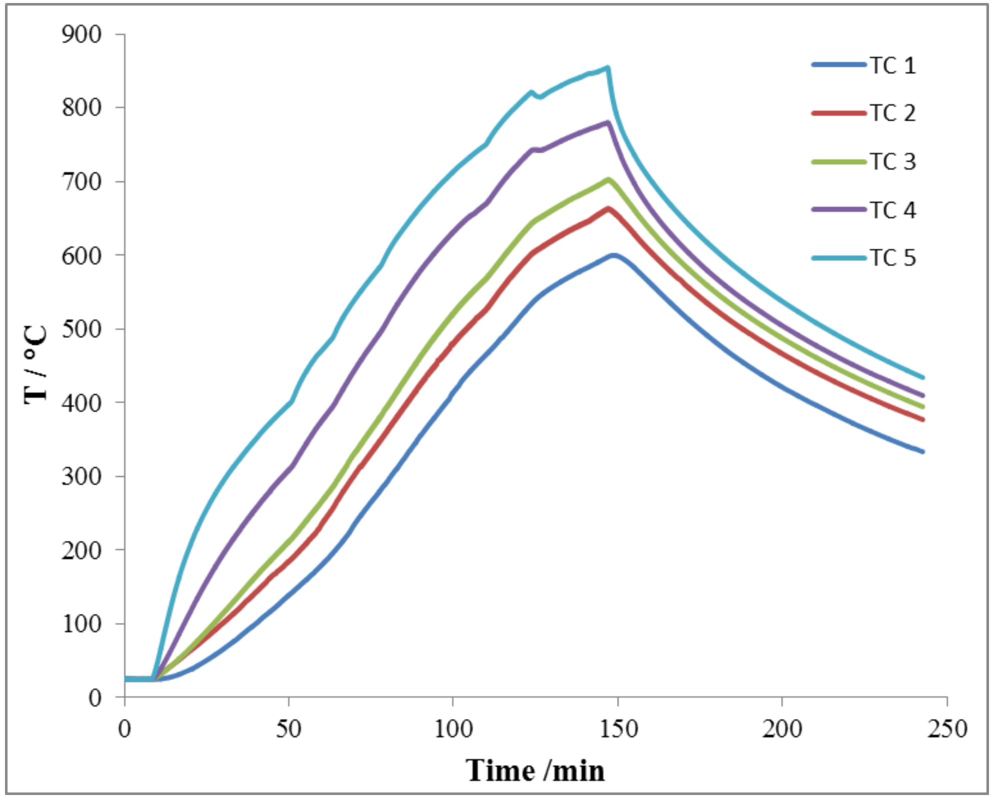
- Test in the solar furnace DLR Köln-Porz
- 250 g redox particle ($SrFeO_x$)
- Particle size 3-4.5 mm
- Rotation speed 1-6 rpm
- 1-4 l/min synthetic air flow



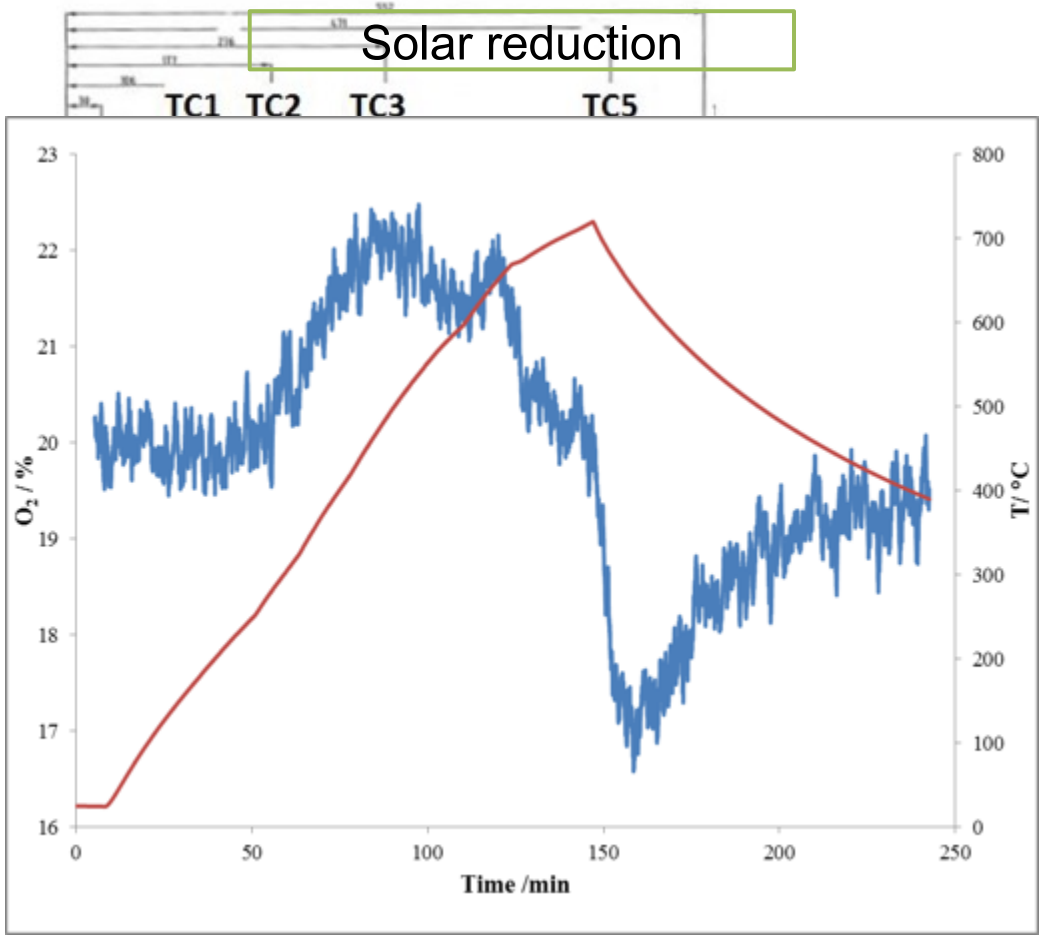
Solar air separation - results

With 250 g redox material:
Reduction: 4 l released oxygen
Oxidation: 3.6 l captured oxygen

Temperature distribution

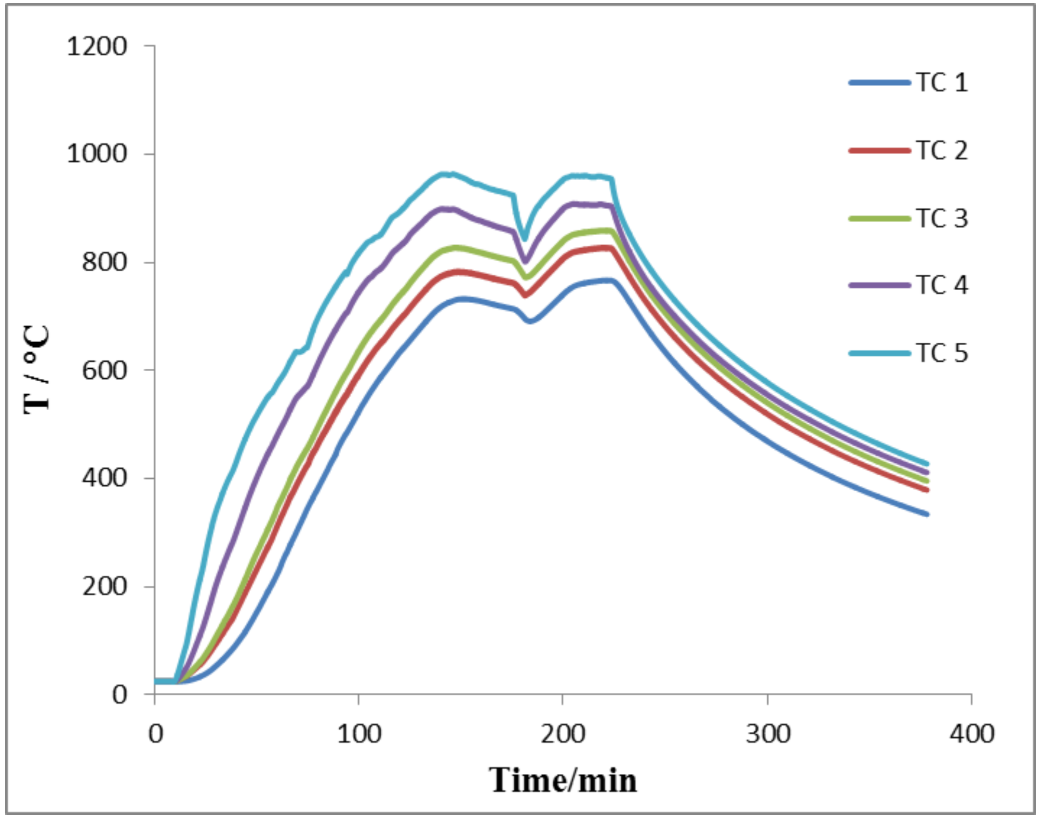


Solar reduction

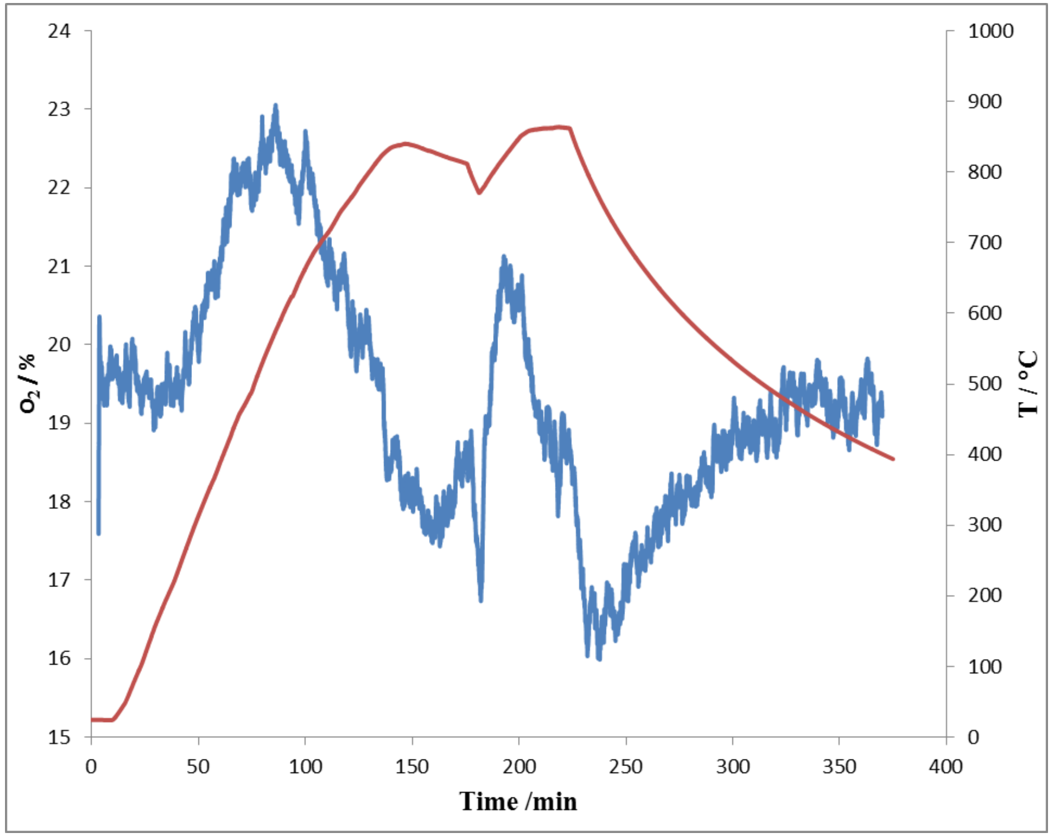


Solar air separation – multiple cycles

Temperature distribution



Solar reduction



Energy demand of thermochemical air separation

Model (based on equilibrium thermodynamics):

$$Q_{AS} = (Q_{chem} + Q_{sensible}) \cdot (1 - \eta_{solid-solid}) + Q_{pump}$$

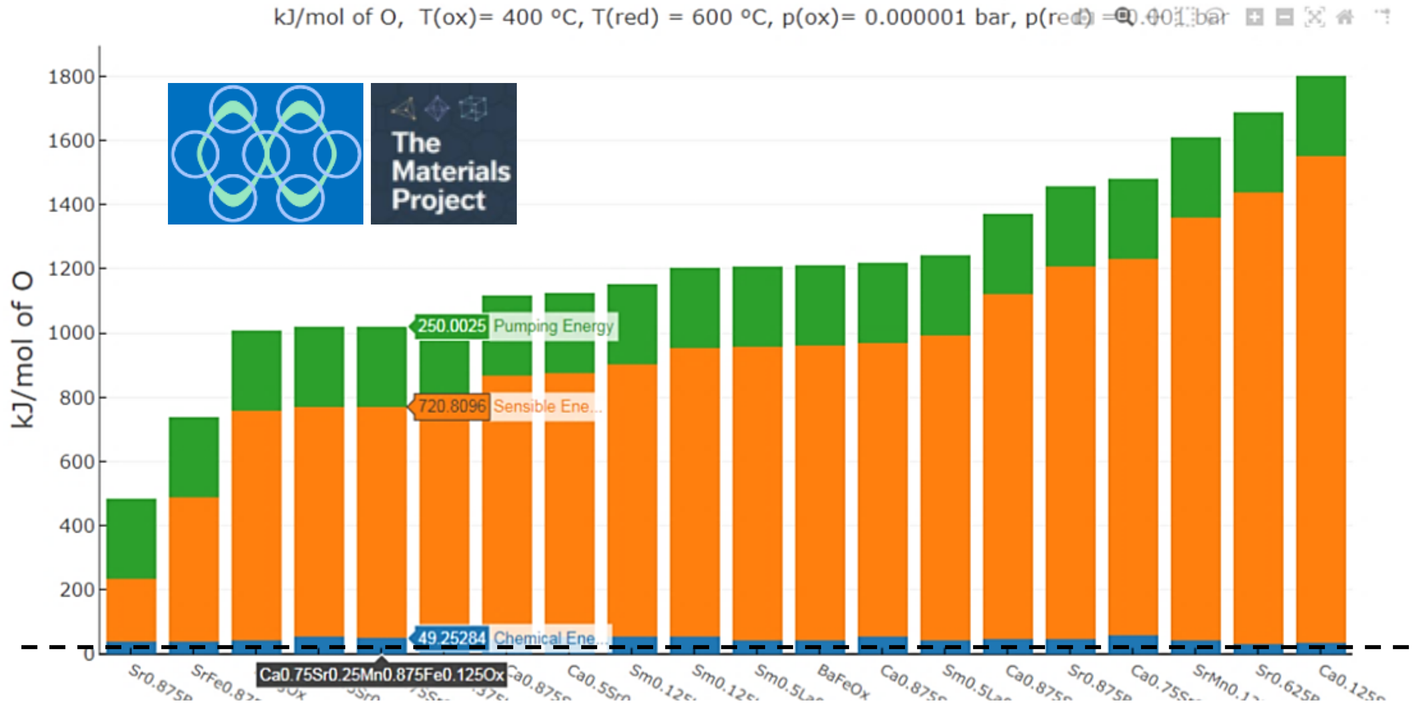
$$Q_{chem} = \int_{\delta_{ox}}^{\delta_{red}} \Delta H(\delta, T)\, d\delta$$

$$Q_{sensible} = \int_{T_{ox}}^{T_{red}} C_p(T, \delta_{ox}, \delta_{red})\, dT$$

Q_{pump}: mechanical pump envelope function, Brendelberger et. al

Brendelberger, S.; von Storch, H.; Bulfin, B.; Sattler, C. *Solar Energy* **2017**, 141, 91-102

$\eta_{solid-solid} = 0.6$



Data:
https://portal.mpcontribs.org/redox_thermo_csp/

State of the art: cryogenic air separation!

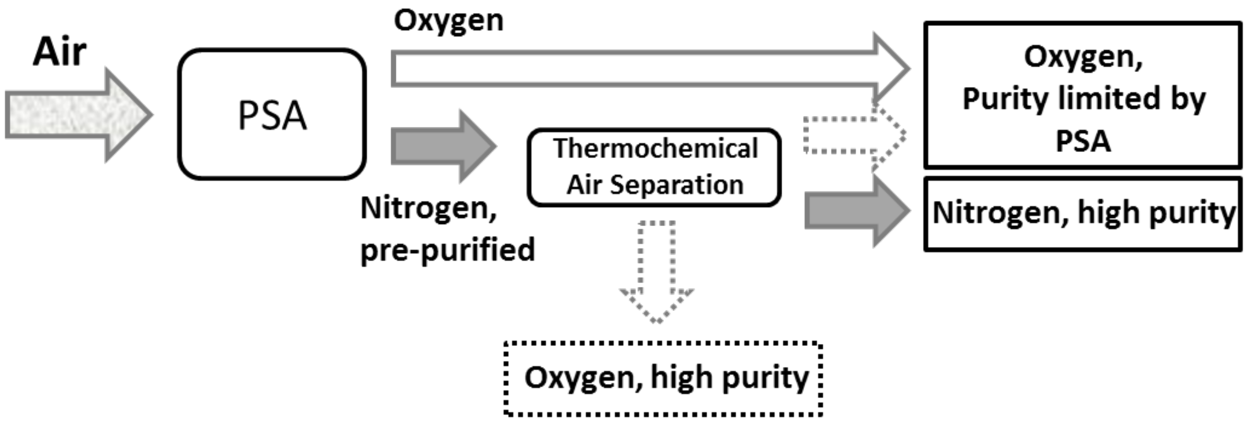
How can thermochemical air separation be more efficient?

- Improve heat recuperation?
  - Solid-solid heat recovery rates of > 97 % would be required for competitiveness! (virtually impossible, realistic maximum values are < 80 %, see Felinks et al.)

Felinks, J.; Brendelberger, S.; Roeb, M.; Sattler, C.; Pitz-Paal, R. *Applied Thermal Engineering* **2014,** 73 (1), 1006-1013

- Combine with other technology?
  - Pressure swing adsorption (PSA) is a very efficient technology for air separation, as long as the required gas purity is not very high

  - Combine PSA and thermochemical air separation!



Only a small fraction of the O_2 needs to be transported thermochemically

Vieten, J; Gubán, D.; Lachmann, B., Bulfin, B.; Kaunzner, D., patent application pending (file no DE 10 2019 126 114.7)

Energy balance of combined PSA and thermochemistry vs. state of the art

Per mol of nitrogen

PSA: $$w_{sep} = \ln\left[\left(\frac{p_{O_2,in}}{p_{O_2,out}}\right)^2\right] \cdot 1000\ \mathrm{Jmol^{-1}}$$

Cryogenic AS: $$w_{cryo} = 12\ \mathrm{kJmol^{-1}}$$

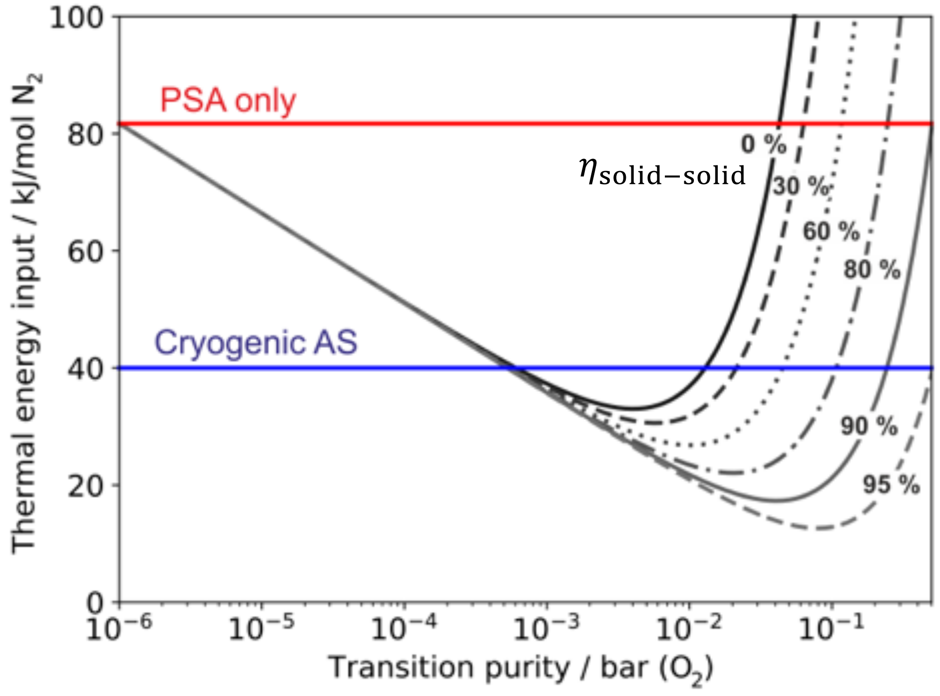
P.T. Krenzke, J.H. Davidson, *Energy & Fuels* **29** (2015) (2) 1045.
S. Li, V.M. Wheeler, P.B. Kreider, R. Bader, W. Lipiński, *Energy & Fuels* **32** (2018) (10) 10848.

Combined PSA + thermochemistry:

$$q_{sep} = \ln\left[\left(\frac{p_{O_2,in}}{p_{O_2,trans}}\right)^2\right] \cdot \eta_{elec}^{-1} \cdot 1000\ \mathrm{Jmol^{-1}}$$
$$+\, q_{thermochem} \cdot p_{O_2,trans} \cdot \eta_{solid-solid} \cdot \mathrm{mol\ bar^{-1}}$$

(1 bar total pressure)

with heat → electricity conversion efficiency $\eta_{elec} = 0.3$
$p_{O_2,in} = 0.21$ bar
$q_{thermochem}$ for $Sr_{0.875}Ba_{0.125}Fe_{0.875}Co_{0.125}O_{3-\delta}$,
reduction at 600 °C, $p_{O2} = 10^{-3}$ bar
oxidation at 400 °C, $p_{O2} = 10^{-6}$ bar

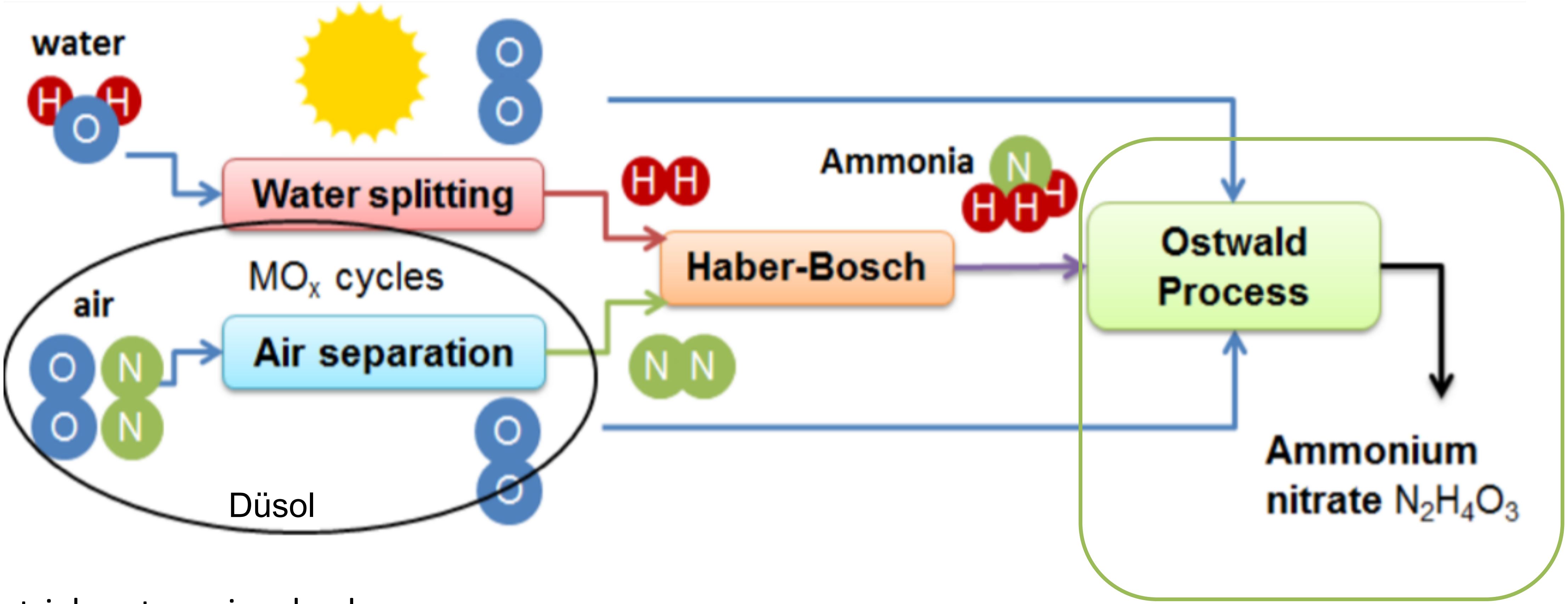


Combined system is more efficient that cryogenic AS

Vieten, J; Gubán, D.; Lachmann, B., Bulfin, B.; Kaunzner, D., patent application pending (file no DE 10 2019 126 114.7)

Follow-up project - outlook

Investigation of the entire value chain from hydrogen, nitrogen and oxygen to the fertilizer product



Industrial partners involved

Thank you for your attention!