Sustainable nitrogen-based fertilizer production from sun, air, and water – the DüSol project

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Sustainable nitrogen-based fertilizer production from sun, air, and water

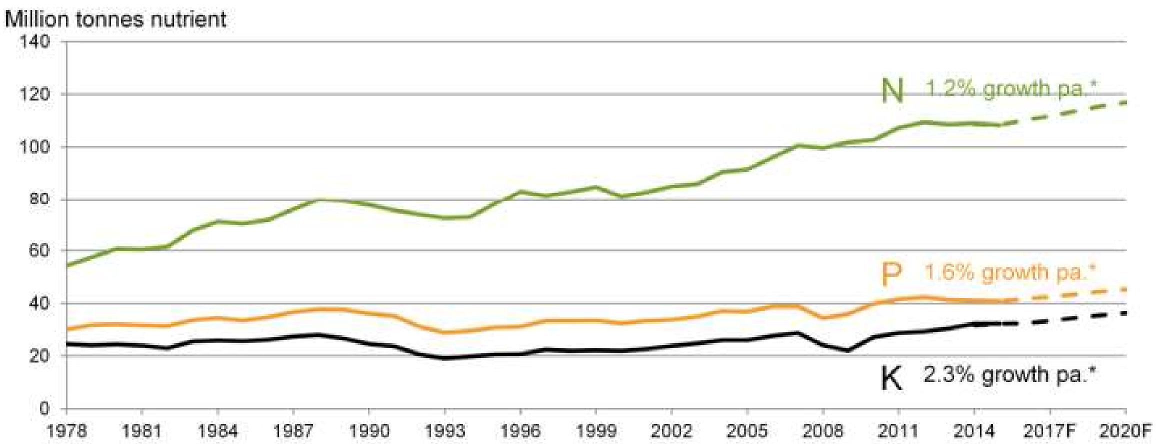
- *Projekt DüSol - Nachhaltige Düngerproduktion aus Sonne, Luft und Wasser*
- *Co-funded in the “Klimaschutzwettbewerb ErneuerbareEnergien.NRW” by the state of Northrhine-Westfalia, Germany, and the European EFRE fund.*
- *Partners:*
  - German Aerospace Center (DLR)
    Cologne, Germany
  - aixprocess
    Aachen, Germany
  - GTT-Technologies
    Herzogenrath, Germany

DLR Deutsches Zentrum für Luft- und Raumfahrt

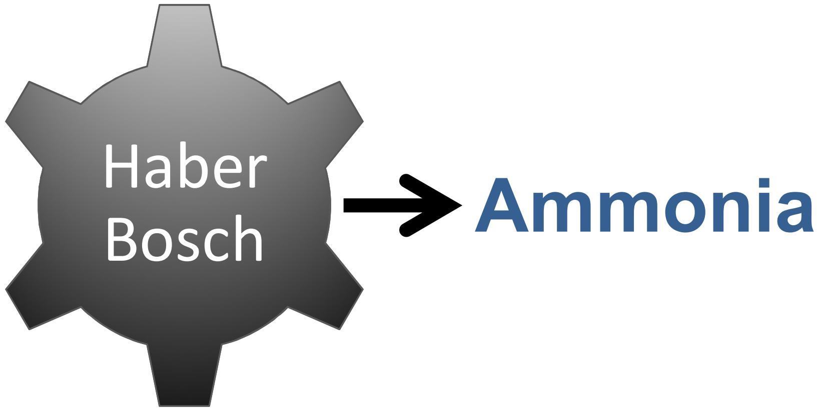
aixprocess

GTT-Technologies

Motivation



Nitrogen is the nutrient with highest consumption for fertilizers with an annual growth rate of 1.2%.



100-4000 Tons/Day
Plant Capacities

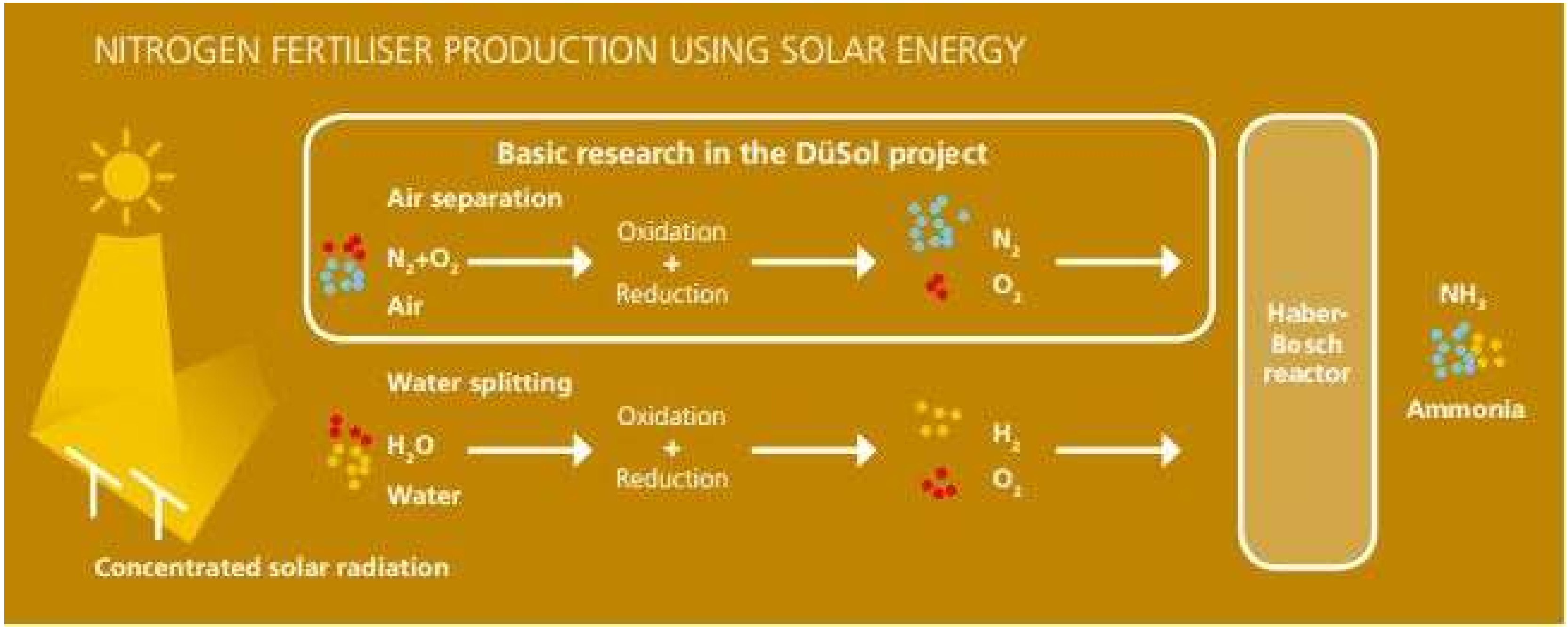
1-2 **% World's Annual Energy**

3-5 **% World's Natural Gas**

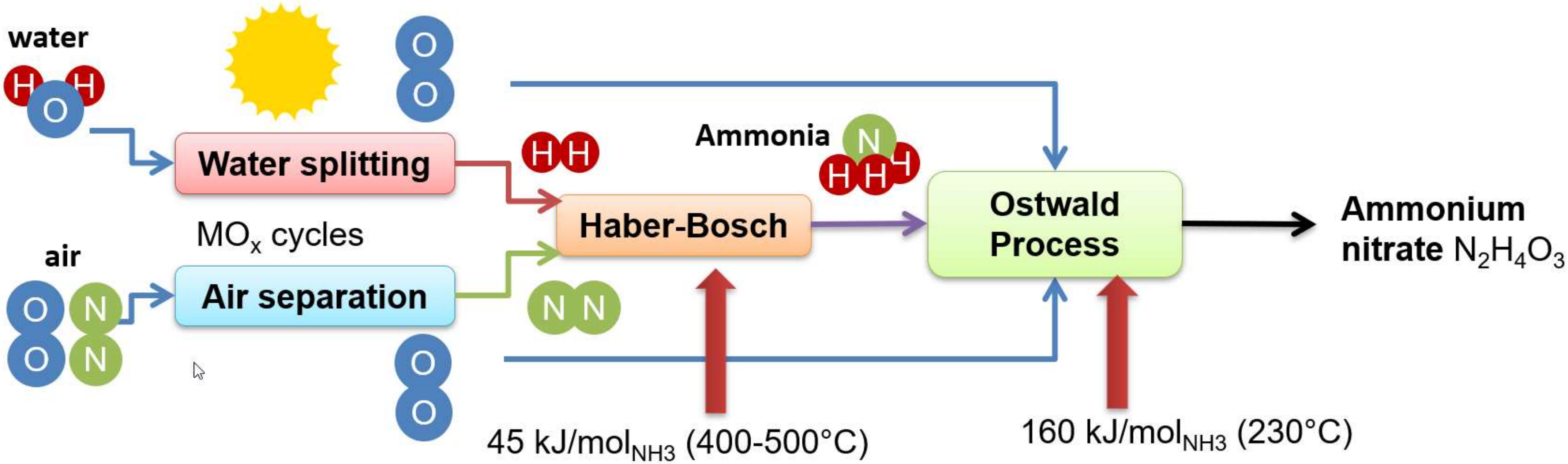
2.3 **Tons** **CO_2 eqv/Ton Ammonia**

International Fertilizer Association, Handbook 2016

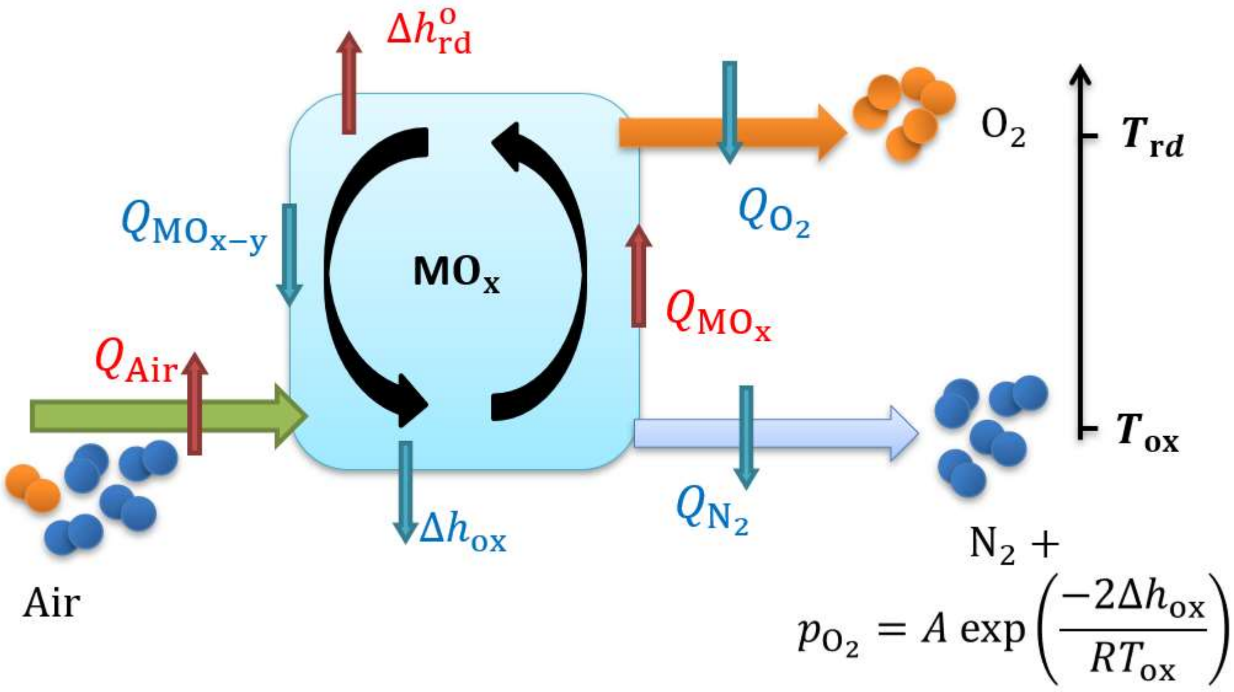
Process – introduction of solar energy



Process


water
H
O
H
O
O
Water splitting
H H
Ammonia
N
H H H
MOx cycles
Haber-Bosch
Ostwald
Process
Ammonium
nitrate N2H4O3
air
O
N
O
N
Air separation
N N
O
O
45 kJ/molNH3 (400-500°C)
160 kJ/molNH3 (230°C)

Thermodynamics of thermochemical air separation

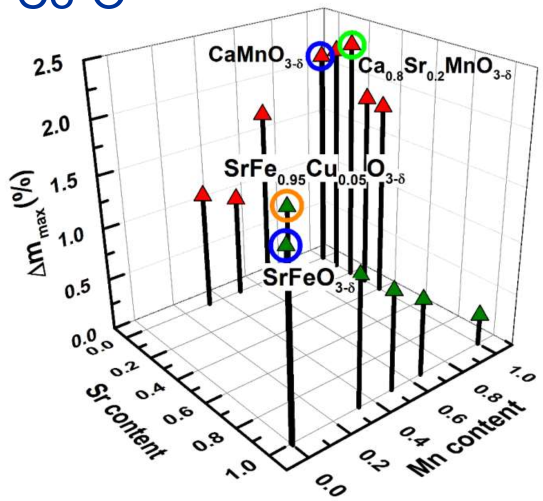


$$Q_{in} = 2\Delta h^{o}_{rd} + Q_{Air} + Q_{MO_x} = Q_{out} = 2\Delta h_{ox} + Q_{O_2} + Q_{N_2} + Q_{MO_{x-y}}$$

- For Haber-Bosch process < 3 ppm O_2 is needed

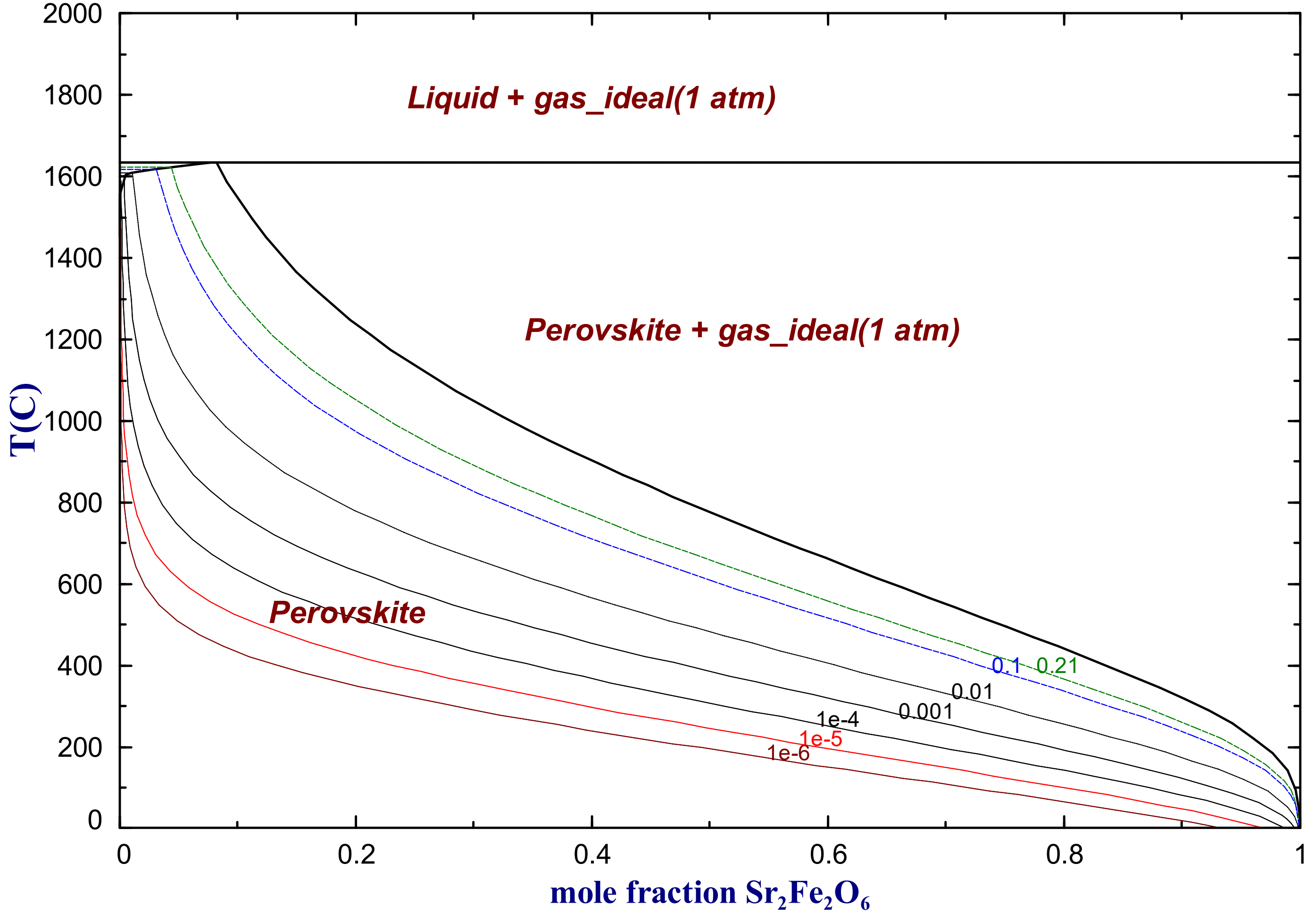
Selection of suitable redox materials

- Desired:
  - Low temperature → low $p_{(O2)}$
  - Rapid kinetics
  - Cycleability / mechanical stability
  - Abundant materials
  - Low energy demand/mol O_2
- Me-O systems:
  - Cu-O
  - Mn-O
  - Fe-O
  - Co-O
- Me1-Me2-O bimetallic systems:
  - Al-Mn-O
  - Fe-Mn-O
  - Co-Fe-O
  - Co-Cu-O
  - Co-Mn-O
  - Cu-Cr-O
  - Cu-Mn-O
  - Pb-Cu-O
  - Pb-Co-O
  - **Sr-Fe-O (Perovskite $SrFeO_{3-\delta}$)**

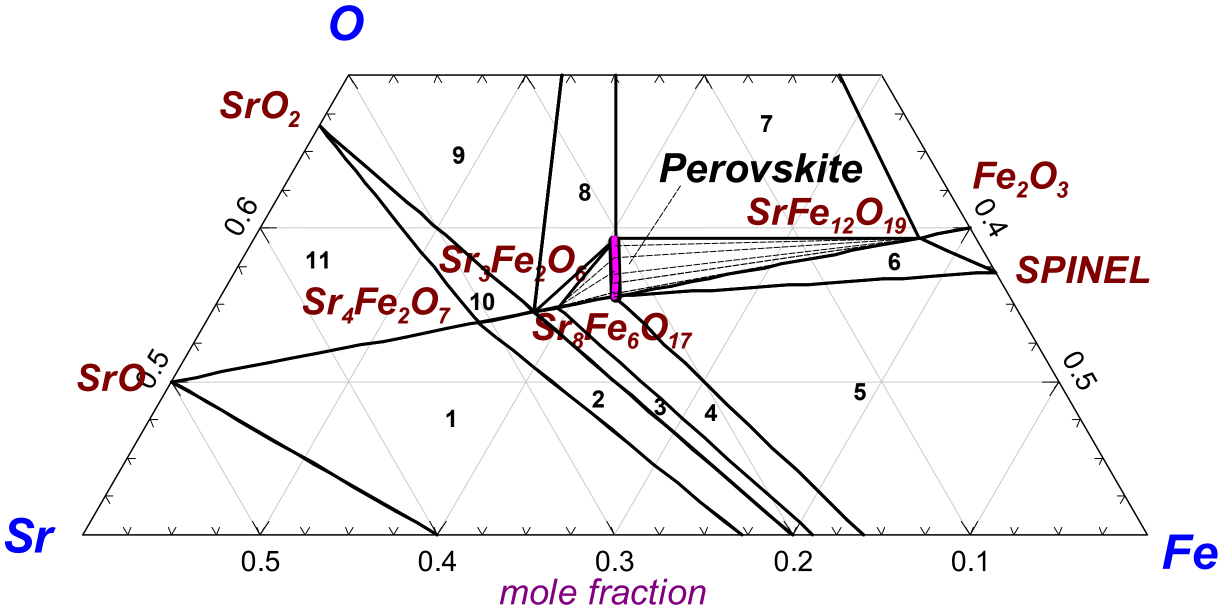


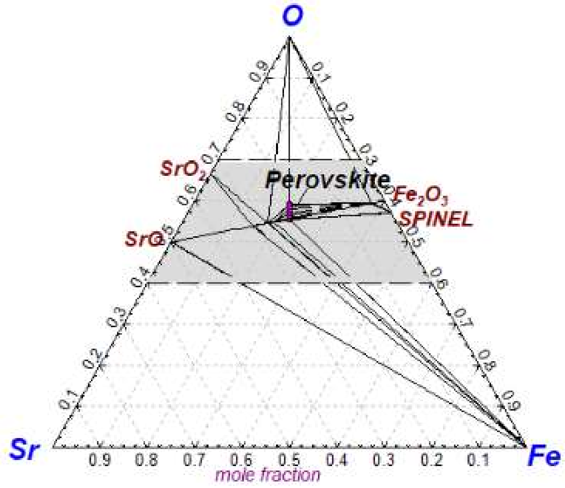
Vieten, J.; Bulfin, B.; Call, F.; Lange, M.; Schmucker, M.; Francke, A.; Roeb, M.; Sattler, C., Perovskite oxides for application in thermochemical air separation and oxygen storage. J.Materi. Chem. A 2016, 4 (35), 13652-13659.

Isoplethal section $Sr_2Fe_2O_5$-$Sr_2Fe_2O_6$ with isobars (in atm)

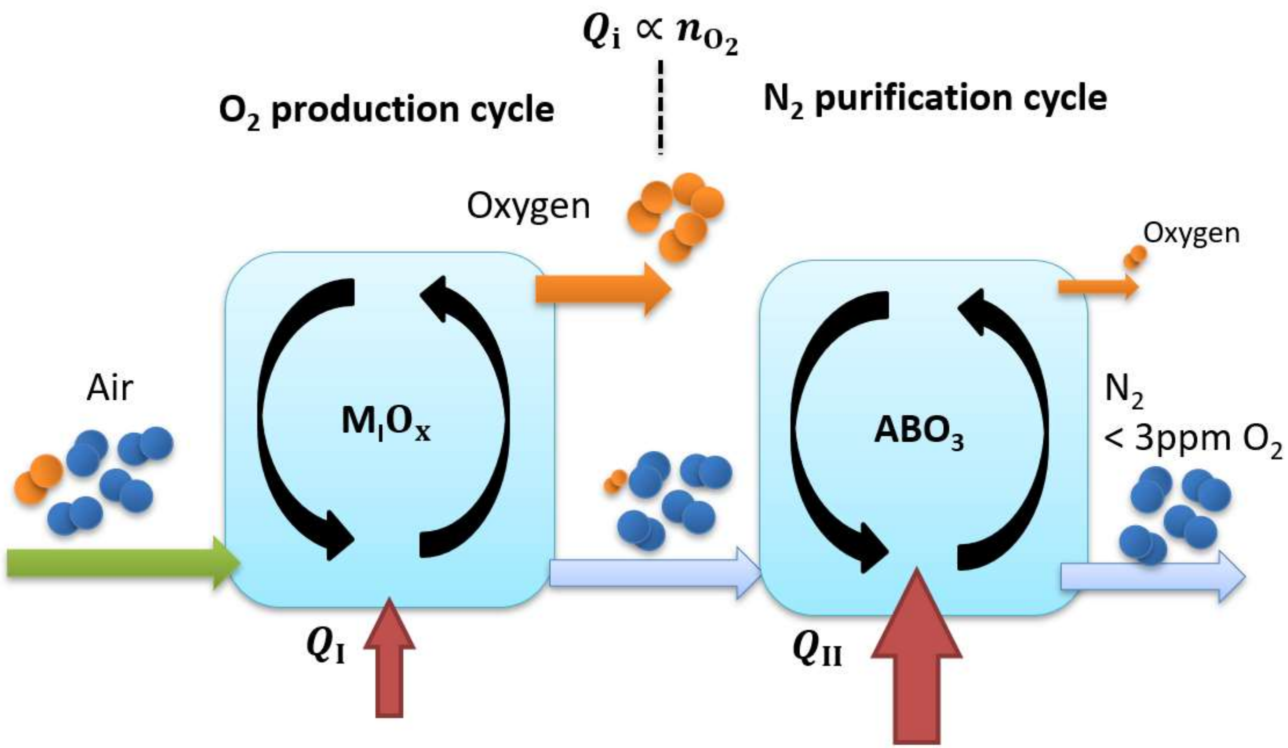


Calculated isothermal section at 400° C in the Fe-Sr-O system





Oxygen production then nitrogen purification. What have we learned so far?

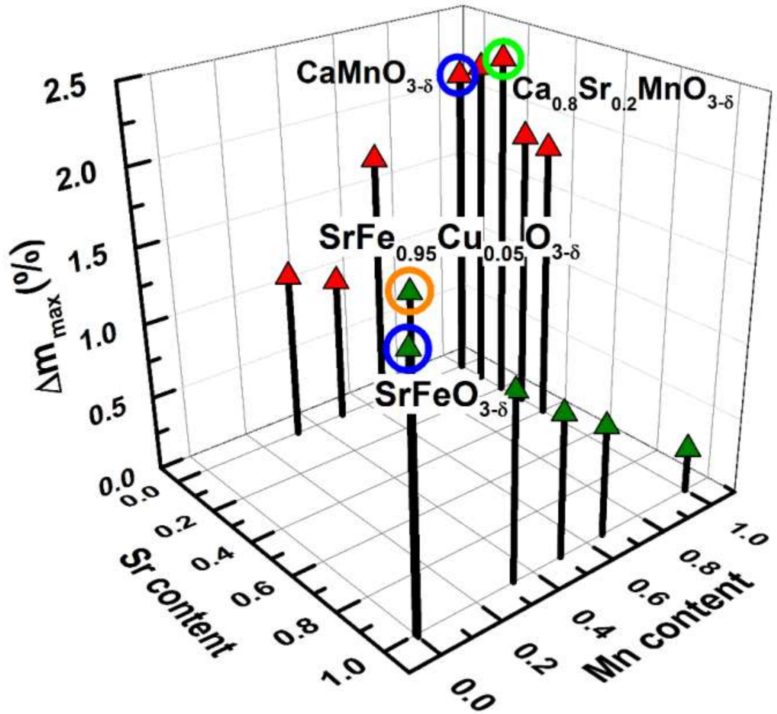


Perovskites

- Low temperature → low p_{O_2} ☑
- Rapid kinetics ☑
- Cycleability ☑
- Abundant materials ☑
- Low energy demand/mol O_2 ☒

Perovskites

- The screening process highlighted $CaMnO_3$ ($Ca_{0.8}Sr_{0.2}MnO_3$) and $SrFeO_3$ ($SrFe_{0.95}Cu_{0.05}O_3$).
- Extracted enthalpy and entropy of reduction for these materials via TGA scans and a van‘t Hoff method.
- Automated this analysis for TGA -> enthalpy and entropy data
- Characterized $SrMnO_3$-$SrFeO_3$ solid solutions

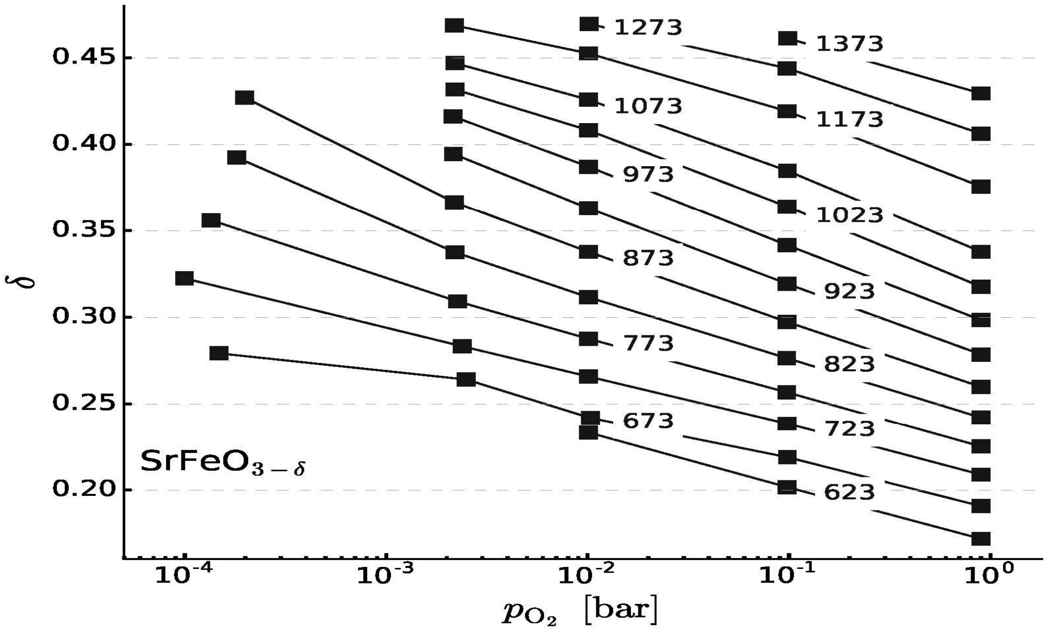


[1] Vieten, J.; Bulfin, B.; Call, F.; Lange, M.; Schmucker, M.; Francke, A.; Roeb, M.; Sattler, C., Perovskite oxides for application in thermochemical air separation and oxygen storage. Journal of Materials Chemistry A 2016, 4 (35), 13652-13659.

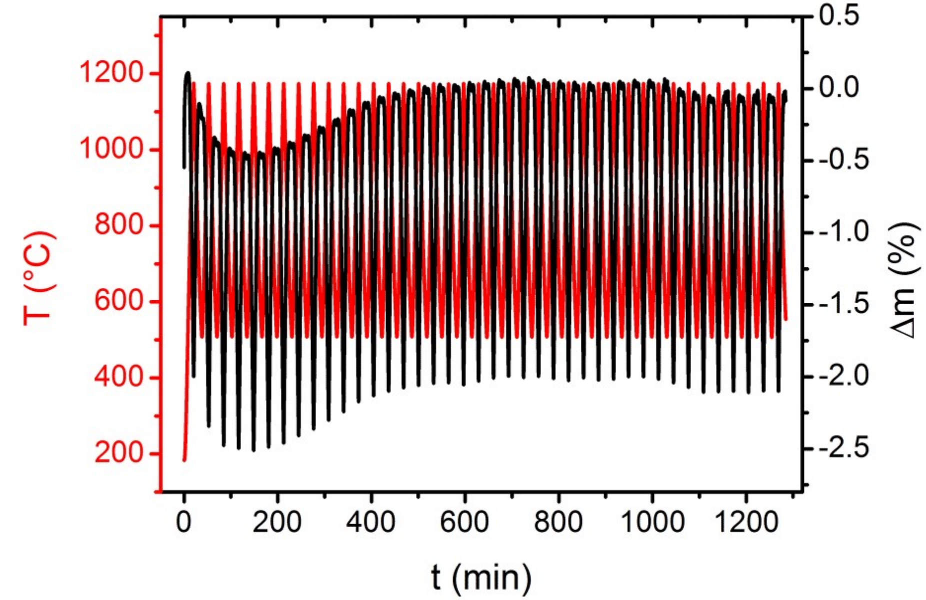
[2] Bulfin, B.; Vieten, J.; Starr, D. E.; Azarpira, A.; Zachaeus, C.; Haevecker, M.; Skorupska, K.; Schmuecker, M.; Roeb, M.; Sattler, C., Redox chemistry of CaMnO3 and Ca0.8Sr0.2MnO3 oxygen storage perovskites. Journal of Materials Chemistry A **2017**

[3] Vieten, J.; Bulfin, B.; Senholdt, M.; Roeb, M.; Sattler, C.; Schmücker, M. Redox thermodynamics and phase composition in the system SrFeO3 − δ — SrMnO3 − δ. Solid State Ionics **2017**, 308, 149-155

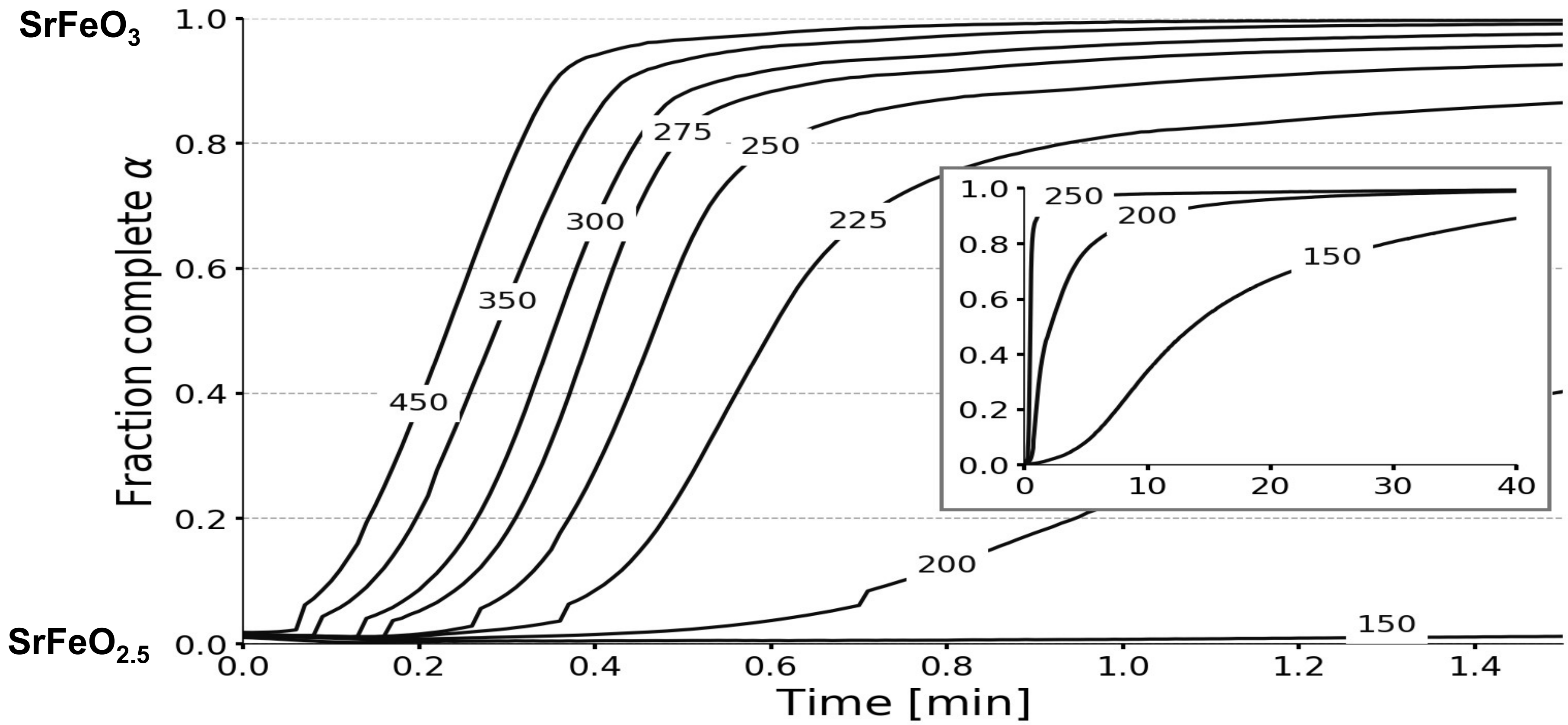
SrFeO$_3$ – TGA analysis



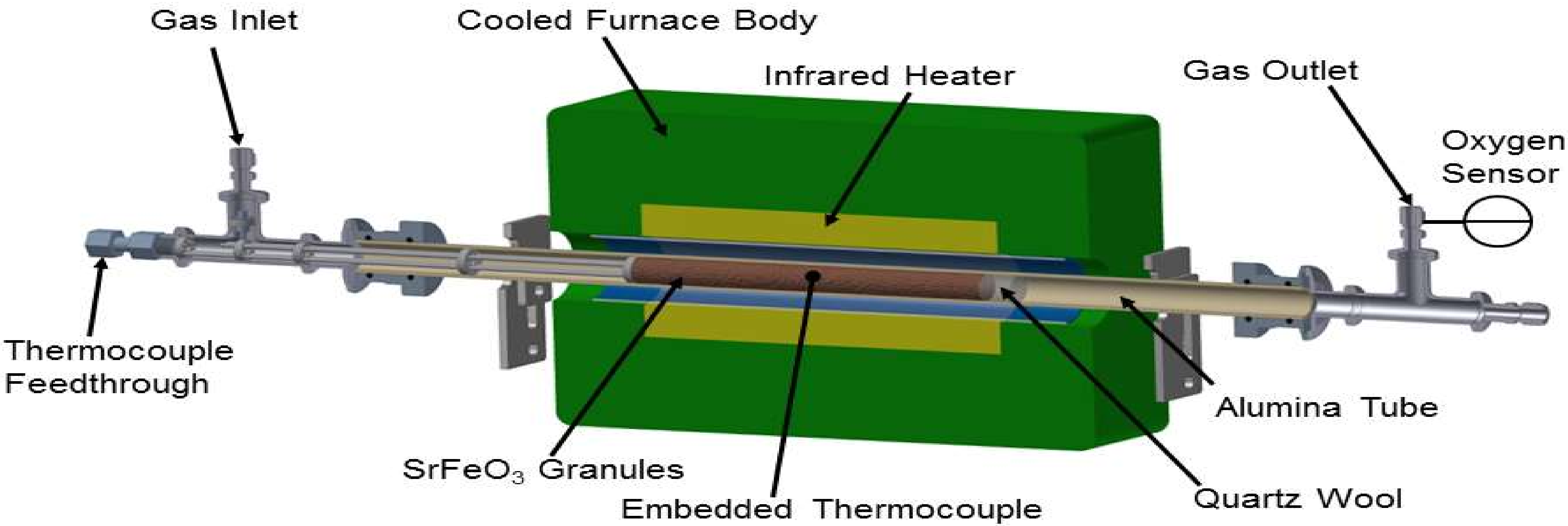
$$SrFeO_3 \xleftrightarrow{\delta(T, p_{O_2})} SrFeO_{3-\delta} + \frac{\delta}{2} O_2$$



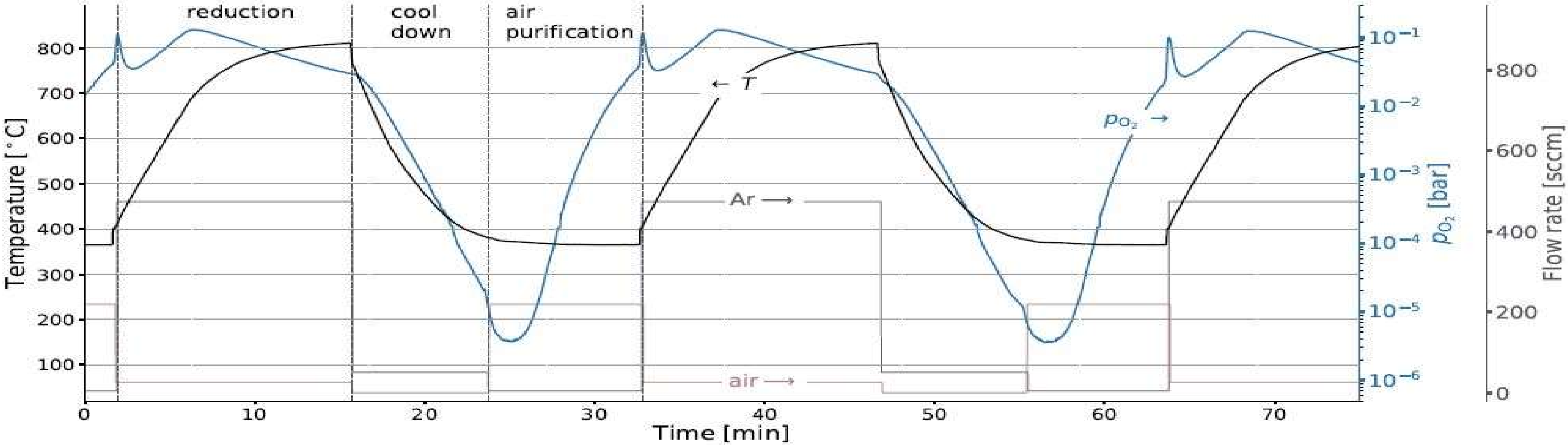
$SrFeO_3$ – TGA analysis



Technology Demonstration

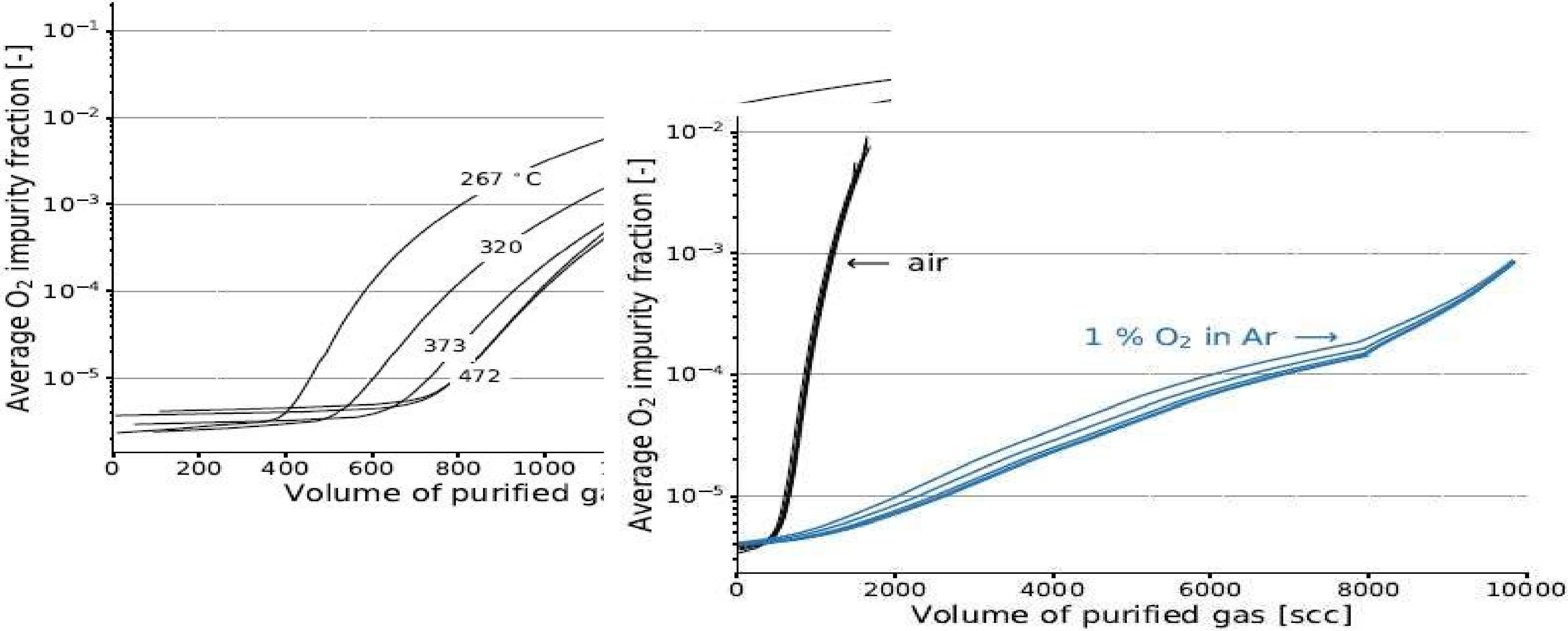


Proof of concept air separation test



cycle	T oxidation [°C]	O_2 produced [l]	O_2 absorbed [l]	p_{O_2} min. [bar]
1	267	0.516	0.480	2.45e-6
2	320	0.612	0.517	2.38e-6
3	373	0.640	0.526	2.93e-6
4	422	0.637	0.512	3.73e-6
5	472	0.608	0.526	4.091e-6

Air separation tests



Scaling up the reaction to 20 kW_{solar}

Reactions:

- **Reduction :** $\mathrm{ABO}_{3-\delta_{\mathrm{ox}}} \xrightarrow{\text{heat in} \;\; \Delta\delta\Delta H_{\mathrm{O}}} \mathrm{ABO}_{3-\delta_{\mathrm{rd}}} + \frac{\Delta\delta}{2}\mathrm{O}_2, \qquad T_{\mathrm{rd}}$

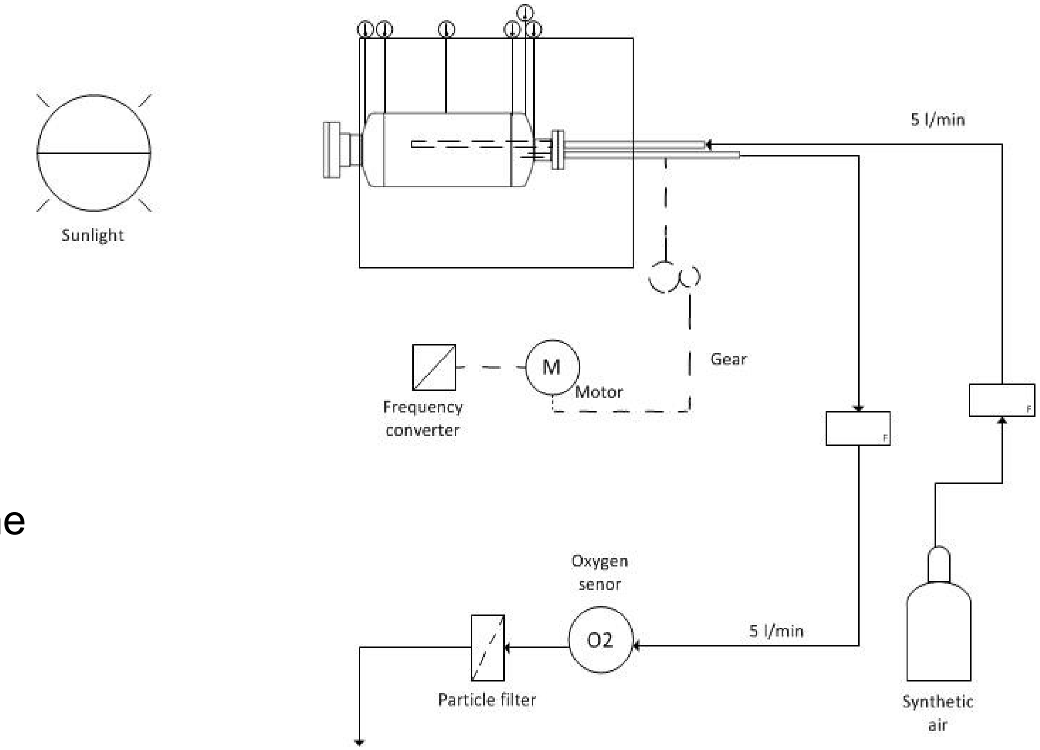
Material	T_{rd}	Atmosphere	T_{max}	p_{O_2}
$SrFeO_3$	800 – 1000 °C	Air	1150 °C	0.2 bar

- **Oxidation:** $\mathrm{ABO}_{3-\delta_{\mathrm{rd}}} + \mathrm{Air}(20\%\ \mathrm{O}_2) \xrightarrow{\text{heat out} \;\; -\Delta\delta\Delta H_{\mathrm{O}}} \mathrm{ABO}_{3-\delta_{\mathrm{ox}}} + \mathrm{N}_2(p_{\mathrm{O}_2} \ll 0.2bar), \qquad T_{\mathrm{ox}}$

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

Solar rotary kiln design

- 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



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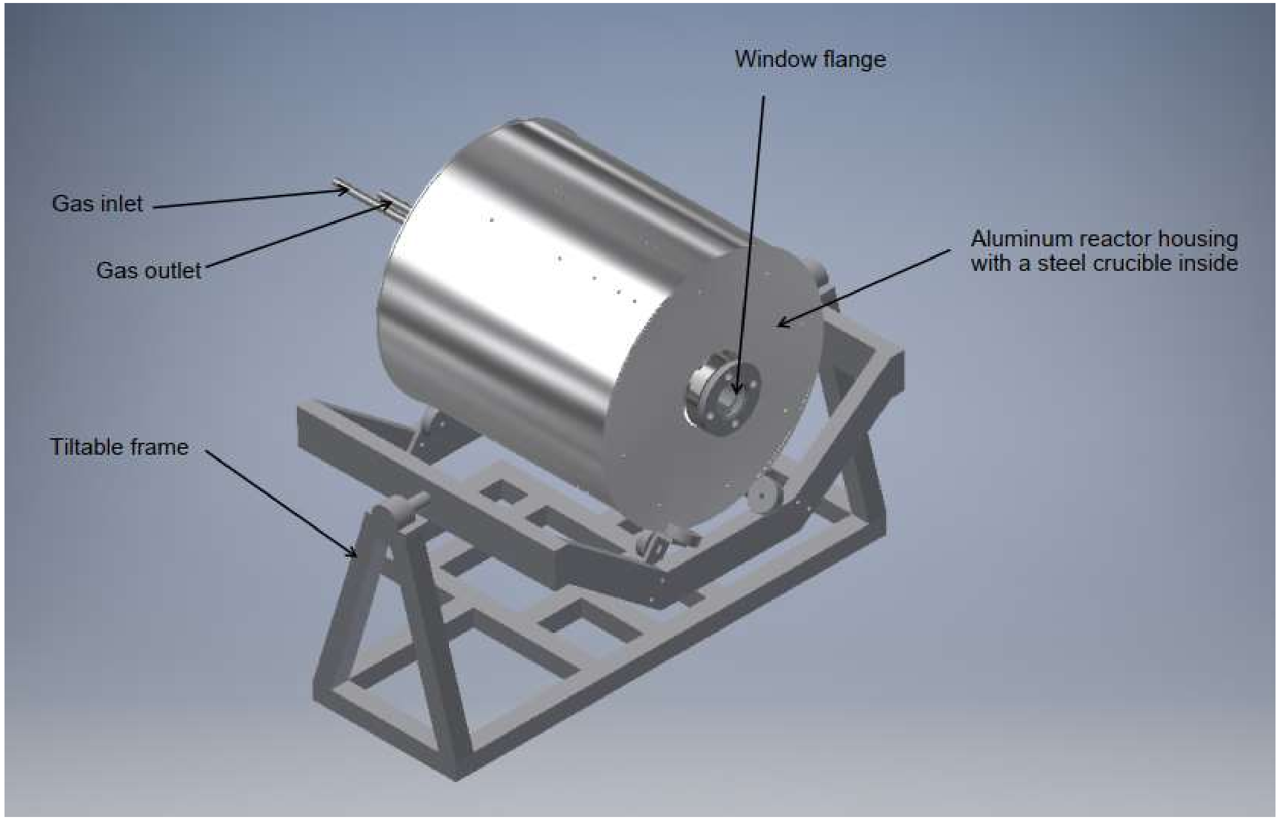
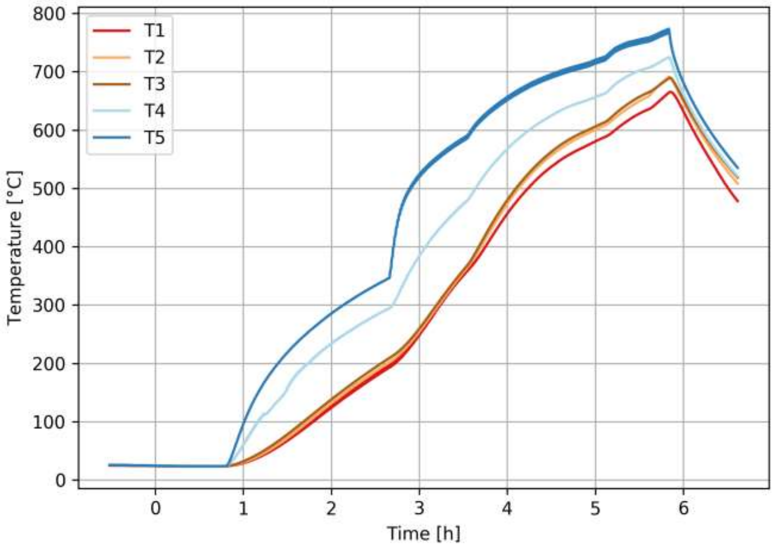


Experiments in the solar simulator

- 10 xenon spot-arch lamps 6 kW each

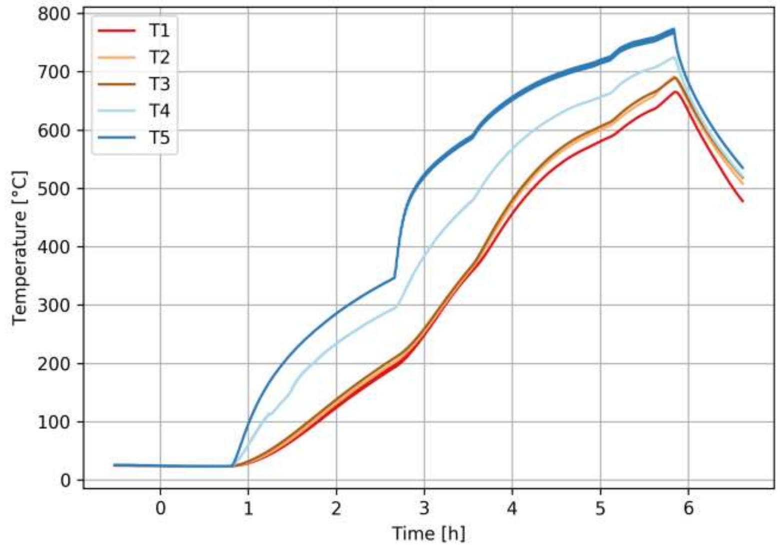
Thermal resistance and gas tightness of the reactor is validated



Experiments in the solar simulator

- 10 xenon spot-arch lamps 6 kW each
- Validate thermal resistance of gas tightness of the reactor

Next step: proof of concept air separation test



Aims and goals of CFD computations

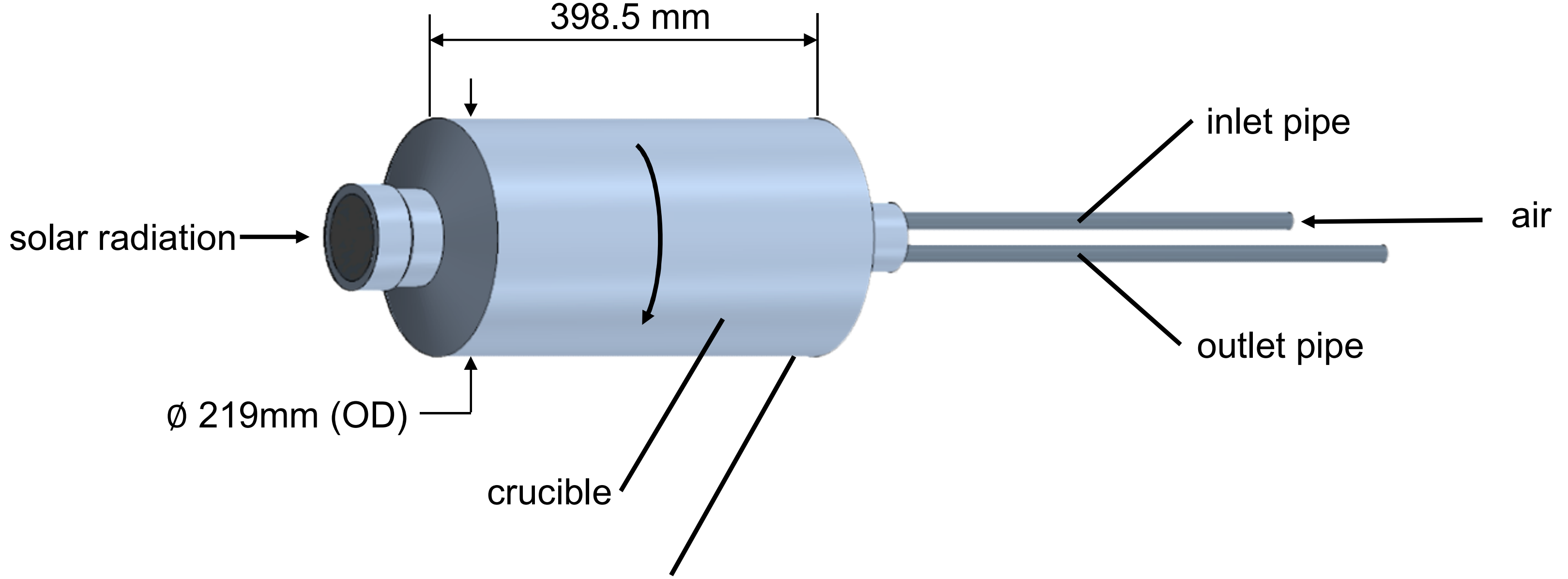
- CFD model of the experimental rotary kiln setup with the following aims:
  - Direct comparison of process parameters measured at the test setup and respective model calculations
  - Providing a validated „Digital Twin“ as numerical test setup for easy evaluation and assessment of parameter changes
  - Providing temperature ranges, zones and trajectories within the rotary kiln reactor as input for the process model
- Setup of the CFD model parallel to the setup of the test rig at DLR

current status

- Software: Star-CCM+ 13.0.6
- the CFD model currently features the following aspects:
  - Transient calculations
  - fully rotating geometry
  - gas flow through the rotary kiln reactor
  - calculation of radiative heat transfer by Discrete Ordinates Method (DOM)
  - particle movement in the solar rotary kiln (Discrete Elements Method (DEM))
  - particle heating by thermal radiation (thermal convection and conduction also considered)
- next step: inclusion of the oxidation-reduction chemical reaction system

current status

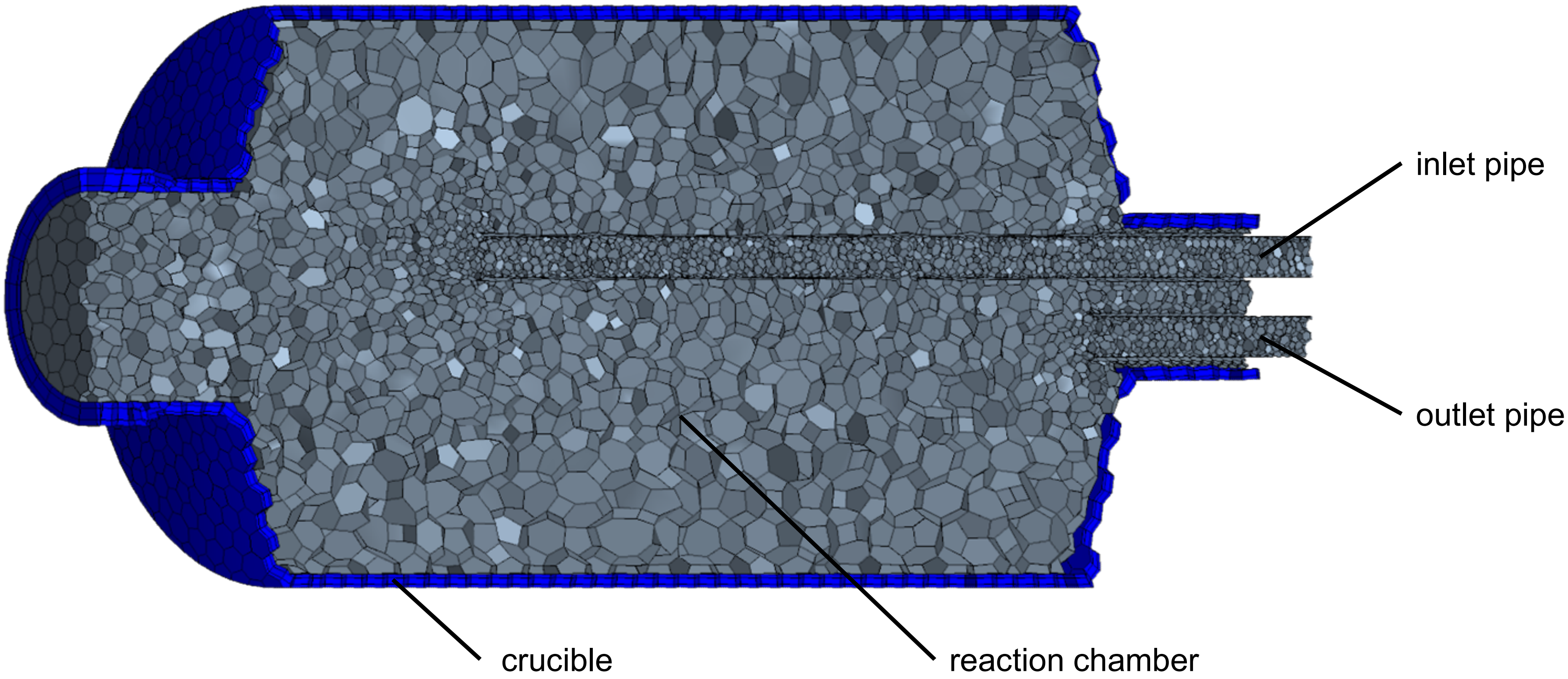
geometry and boundary conditions: Rotary kiln setup at DLR



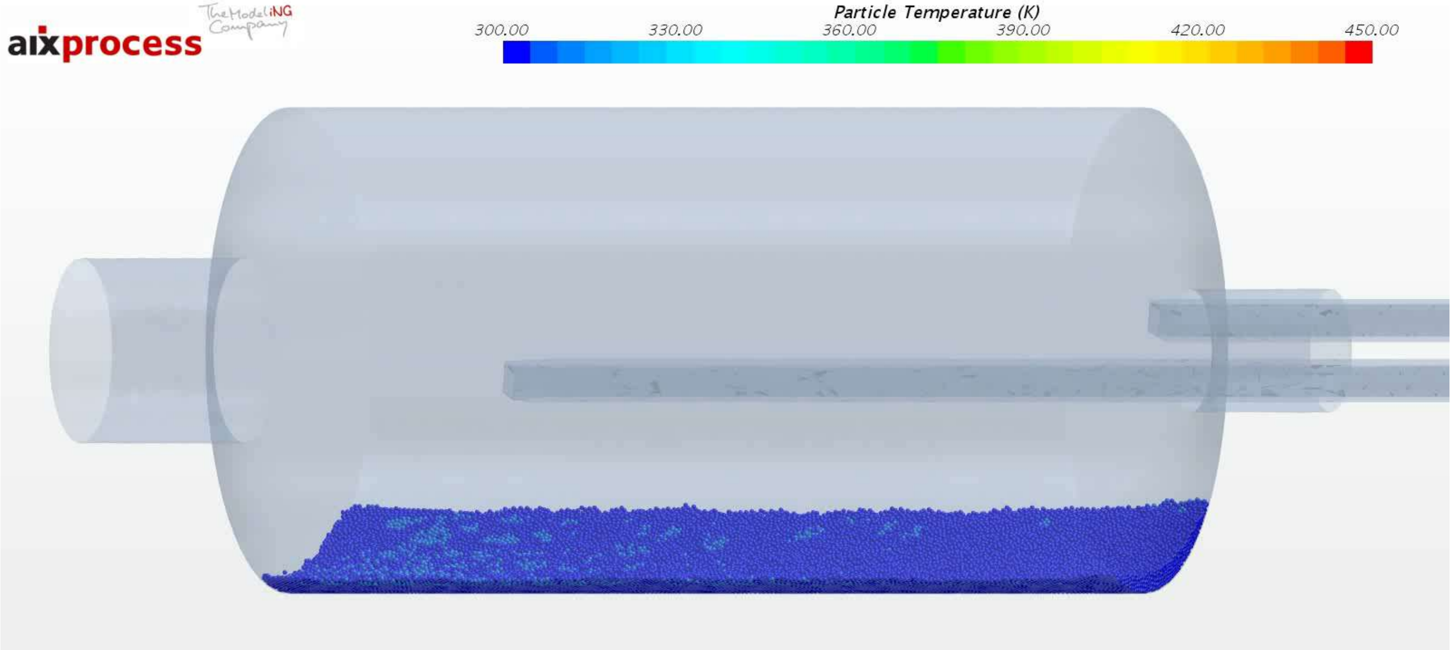
thermal insulation is considered as adiabatic wall (adiabatic wall does not allow the transfer of heat)

current status

mesh for CFD simulation



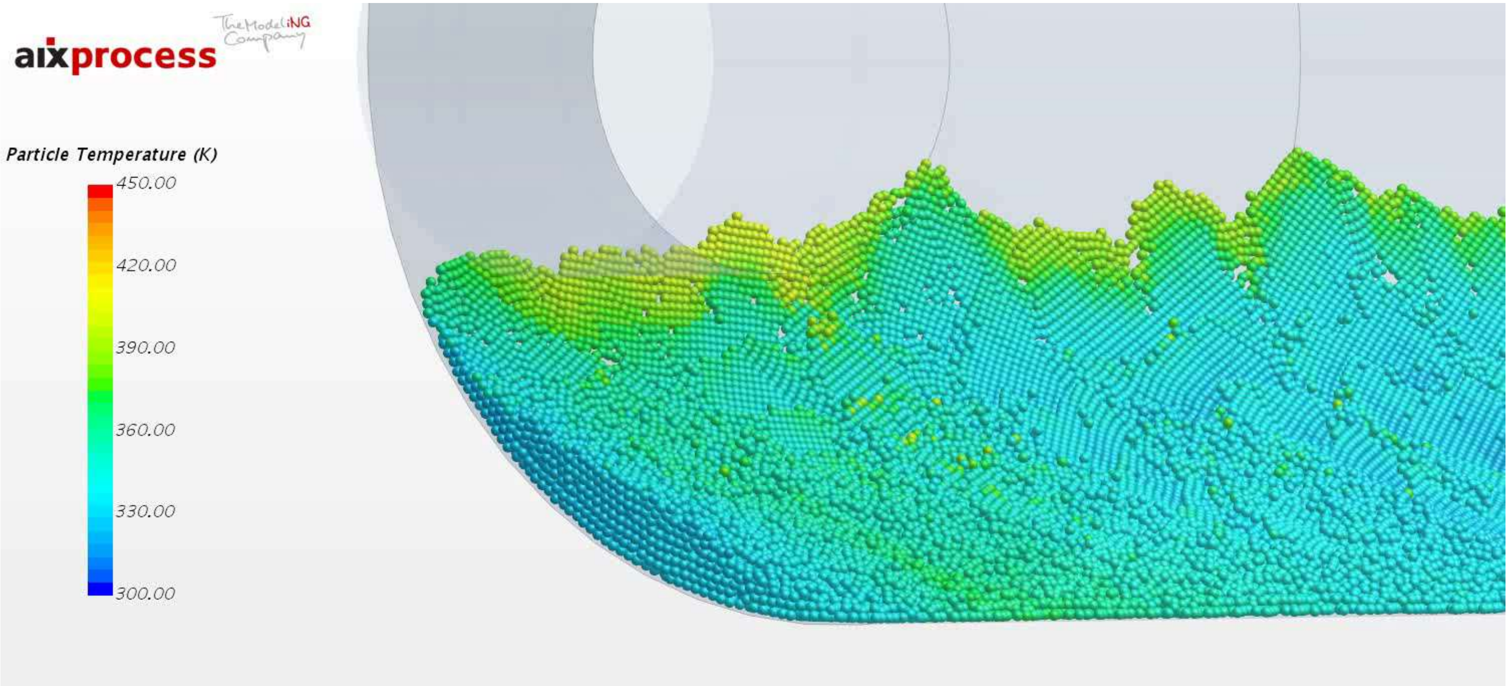
current status



- particle diameter: 2mm
- initial particle temperature: 300K
- total radiation power: 5 kW
- inlet air velocity: 1 m/s
- kiln rotation velocity: 2rpm
- simulated physical time: 30s

heating of 1 kg $SrFeO_3$ granulate (short heating duration)

current status



- discrete particle simulation:
  - consideration of particle-particle interaction (contact forces) by Hertz-Mindlin-model
  - individual heating of discrete particle by thermal radiation

detailed visualization of particle motion and temperature distribution

next step

chemical reaction

Inclusion of chemistry into CFD model

these assumptions will be used in the CFD simulation

- chemical equilibrium
- stoichiometric coefficient: δ = 0.5

$$SrFeO_3 \rightleftharpoons SrFeO_{3-\delta} + \frac{\delta}{2} O_2$$

input data into CFD simulation software

- equilibrium constant (from DLR measurement or from GTT calculations)

$$K = \frac{[SrFeO_{3-\delta}][O_2]^{\frac{\delta}{2}}}{[SrFeO_3]} = \frac{k_f}{k_b}$$

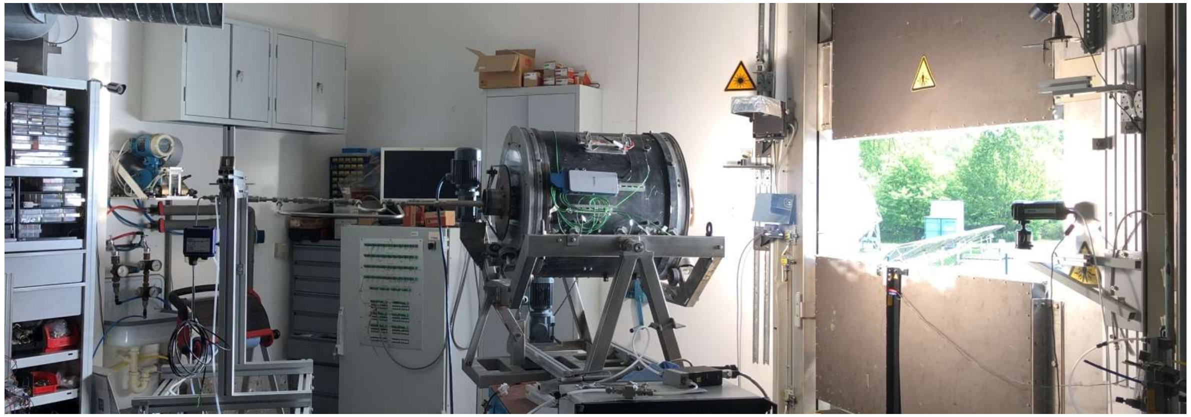
* the term $[X]$ is the concentration of the reactant X

* k_f and k_b designate the forward and the backward reaction rates, resp.

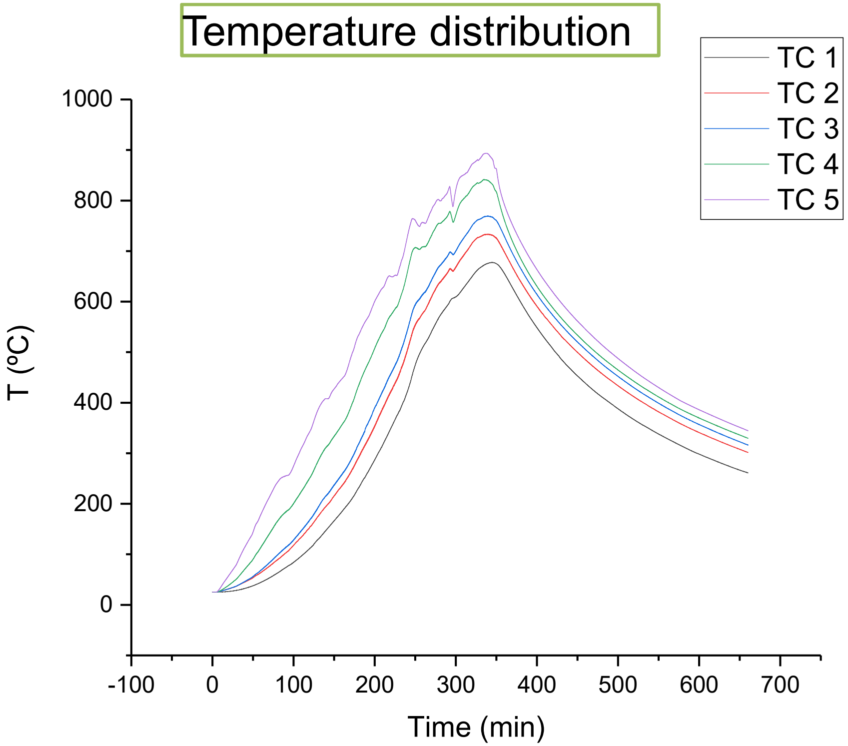
Solar air separation

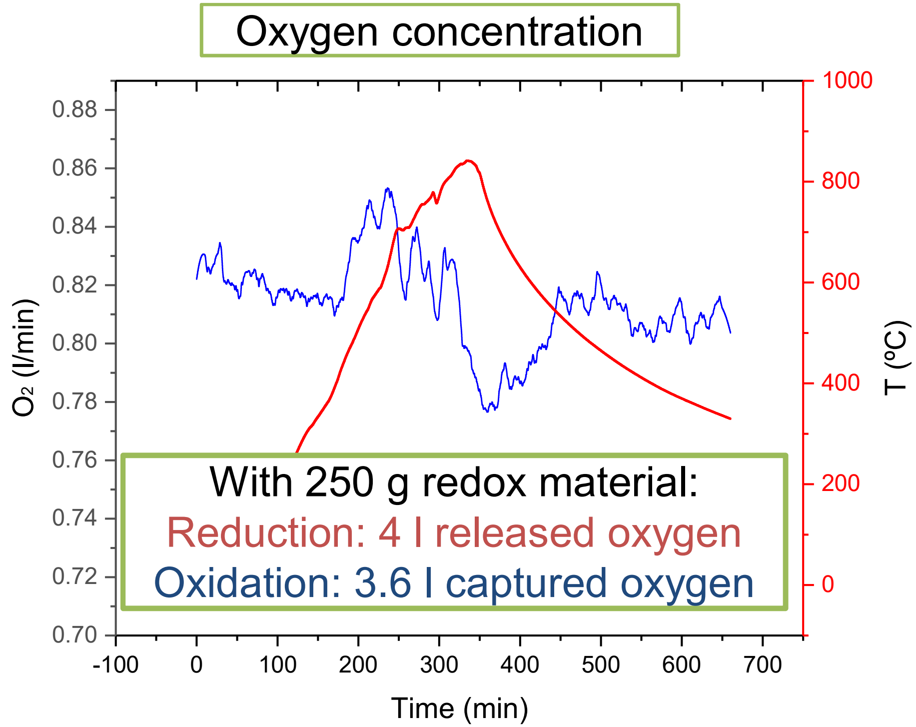
Experimental details

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



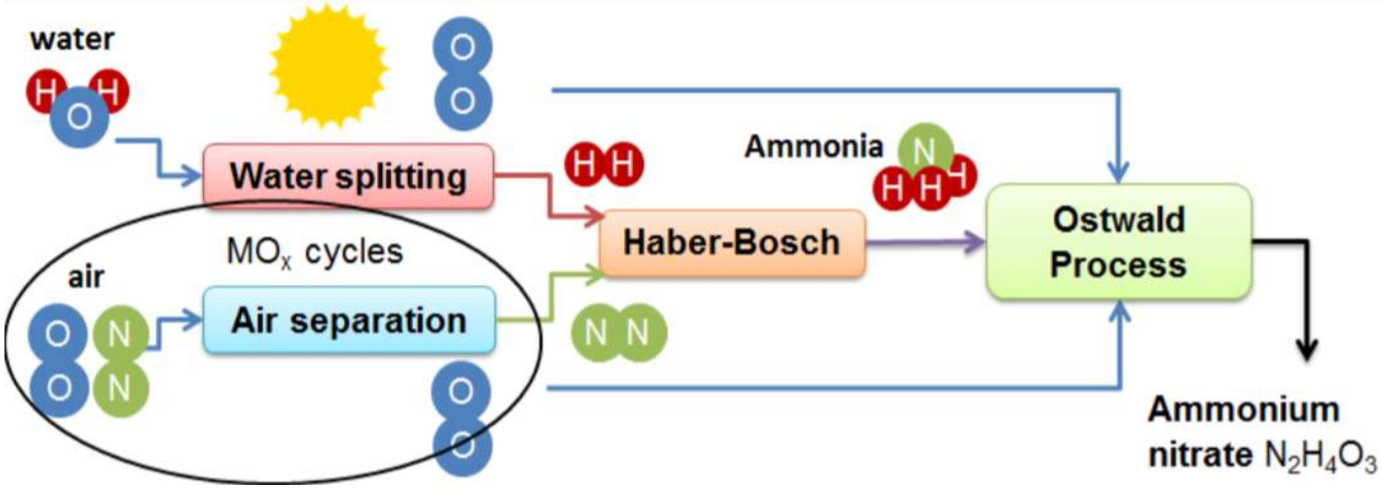
Solar air separation - results





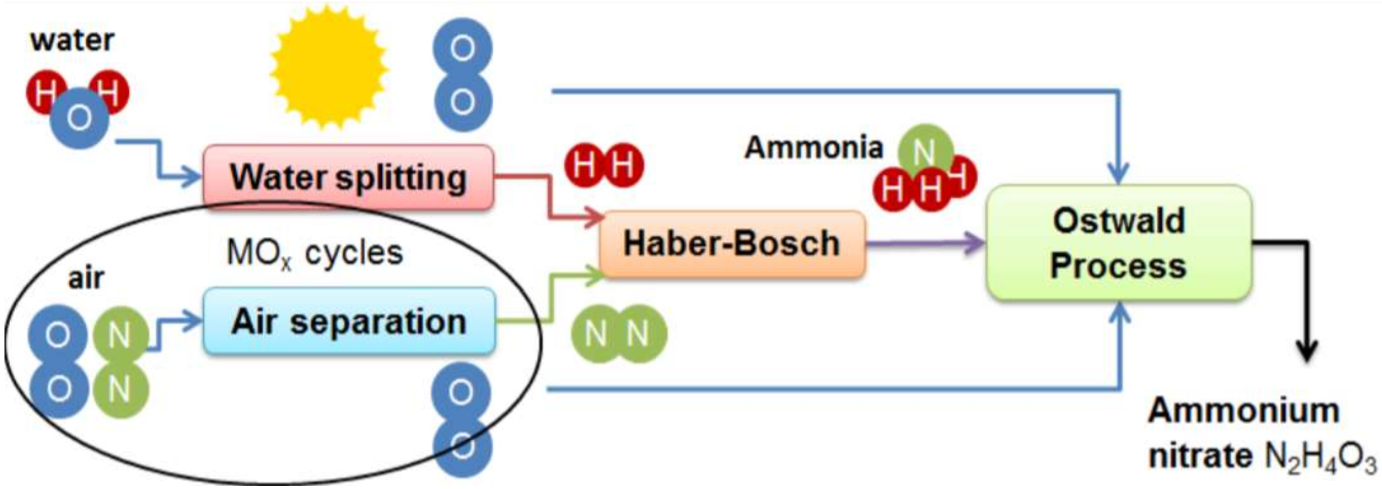
Next steps

- Inclusion of chemistry in CFD module ChemApp™
- Thermochemical process simulation SimuSage™
- Successive project will look at the value chain from hydrogen, nitrogen and oxygen to the fertilizer product



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!