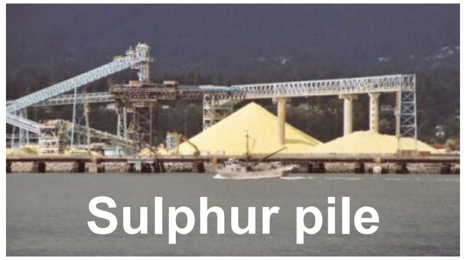
Sulphur Thermochemical Cycles

TWINSOLARSURF 1st Summer School, Athens, 2-6 June 2025

Dennis Thomey

Contents

Sulphur in industrial processes



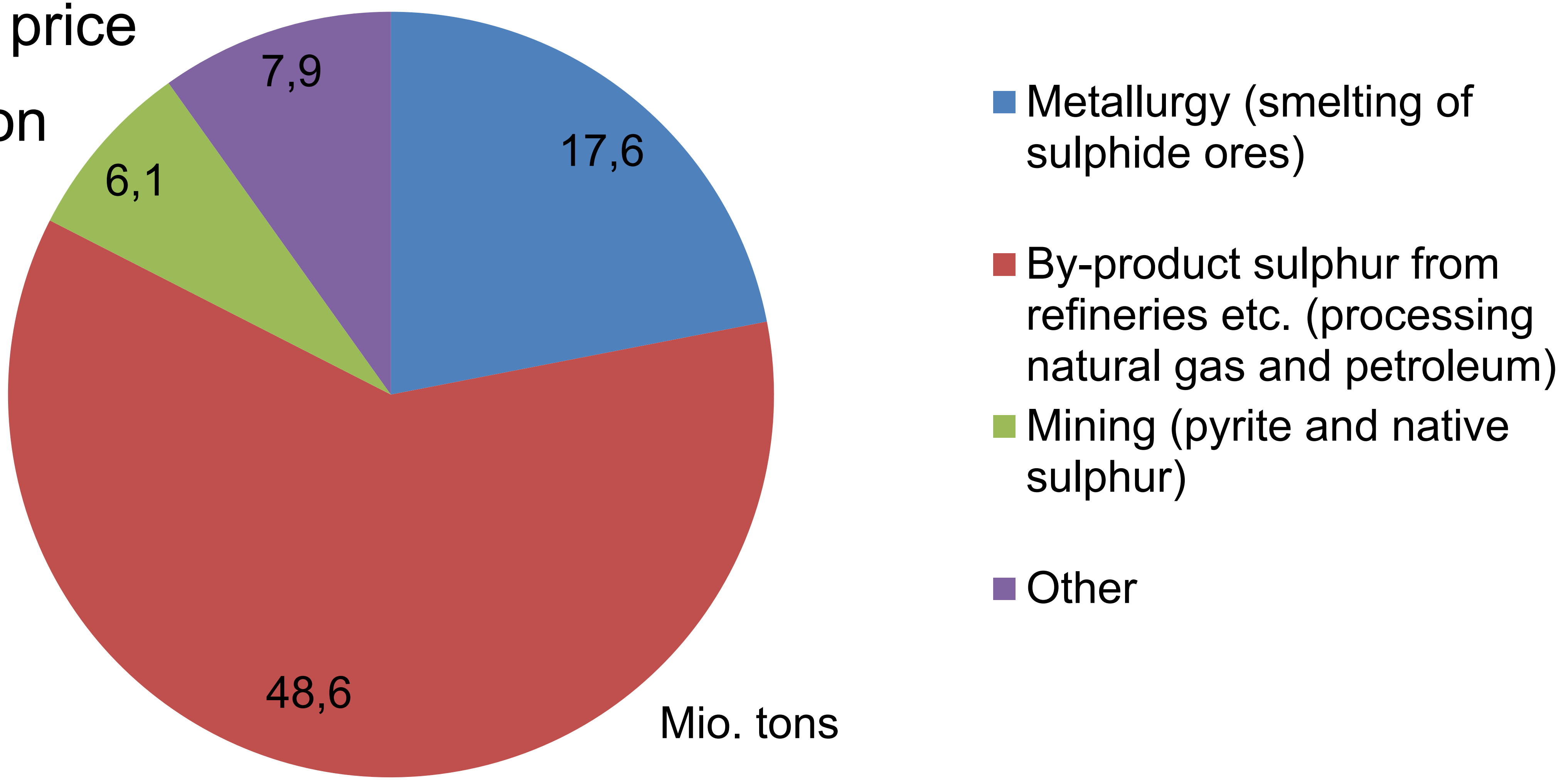
- Sulphur is required for **sulphuric acid** (SA) production
  - SA is world's most produced chemical
    $\Rightarrow$ Global annual rate **>200 Mio. tons**
  - SA is measure of industrial development
  - SA is mainly needed for **fertiliser production**

- Sulphur from **desulphurisation of hydrocarbons** via Claus process

- Sulphur is by-product of **metallurgic processes**

Sulphur
World Production

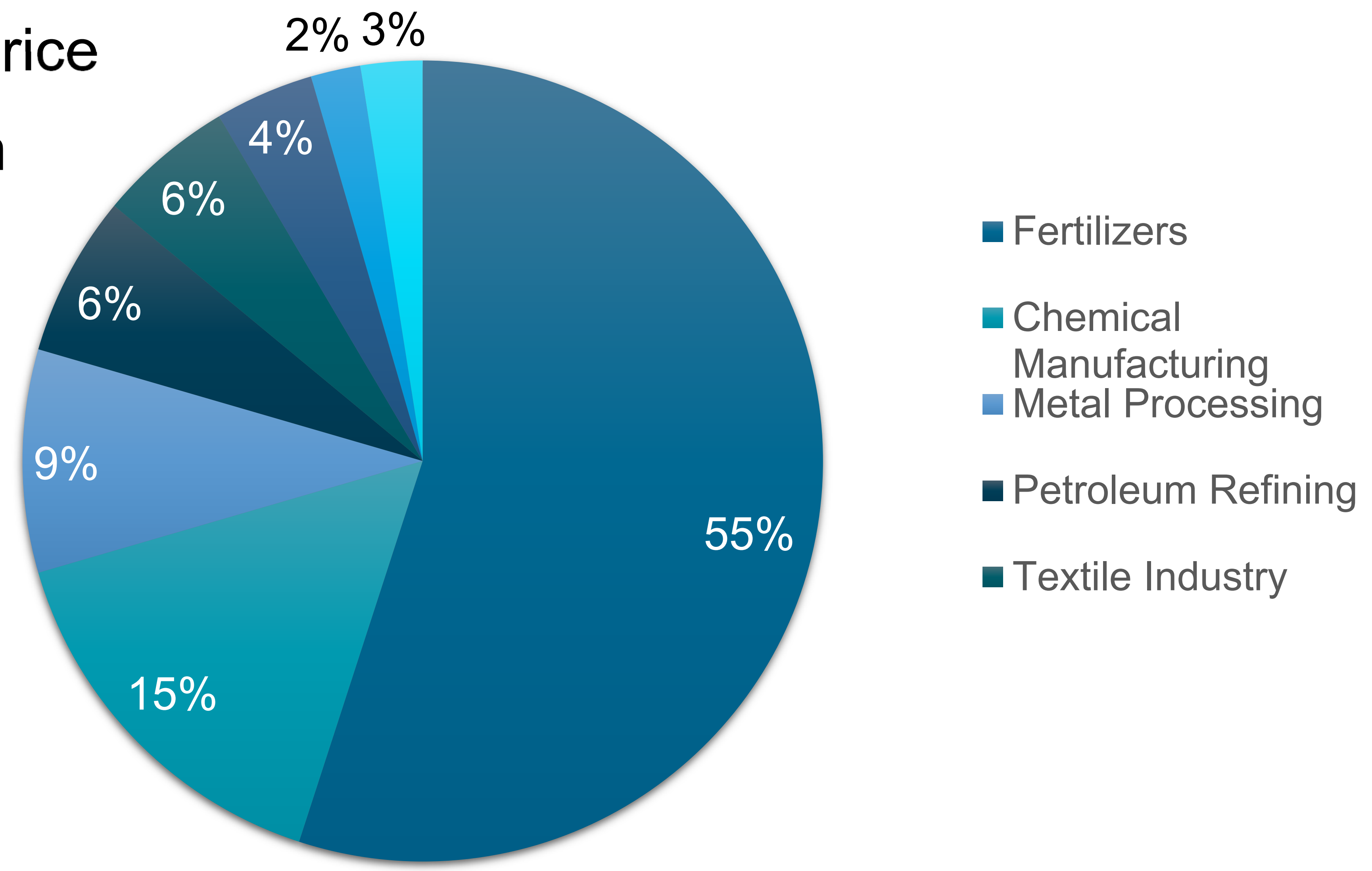
- Total of 82 Mio. Tons in 2022
- Very fluctuating world price
- Market US$ 13.2 Billion
- Avg. US$110 / ton



Source: 2022 Minerals Yearbook, U.S. Geological Survey

Sulphuric Acid
World Production

- Total of 231 Mio. Tons in 2024
- Very fluctuating world price
- Market US$ 23.1 Billion
- US$ 163 / ton in Sep.



Source: gm insight, 2024

Transportation and storage of sulphur
In solid or liquid form

Train

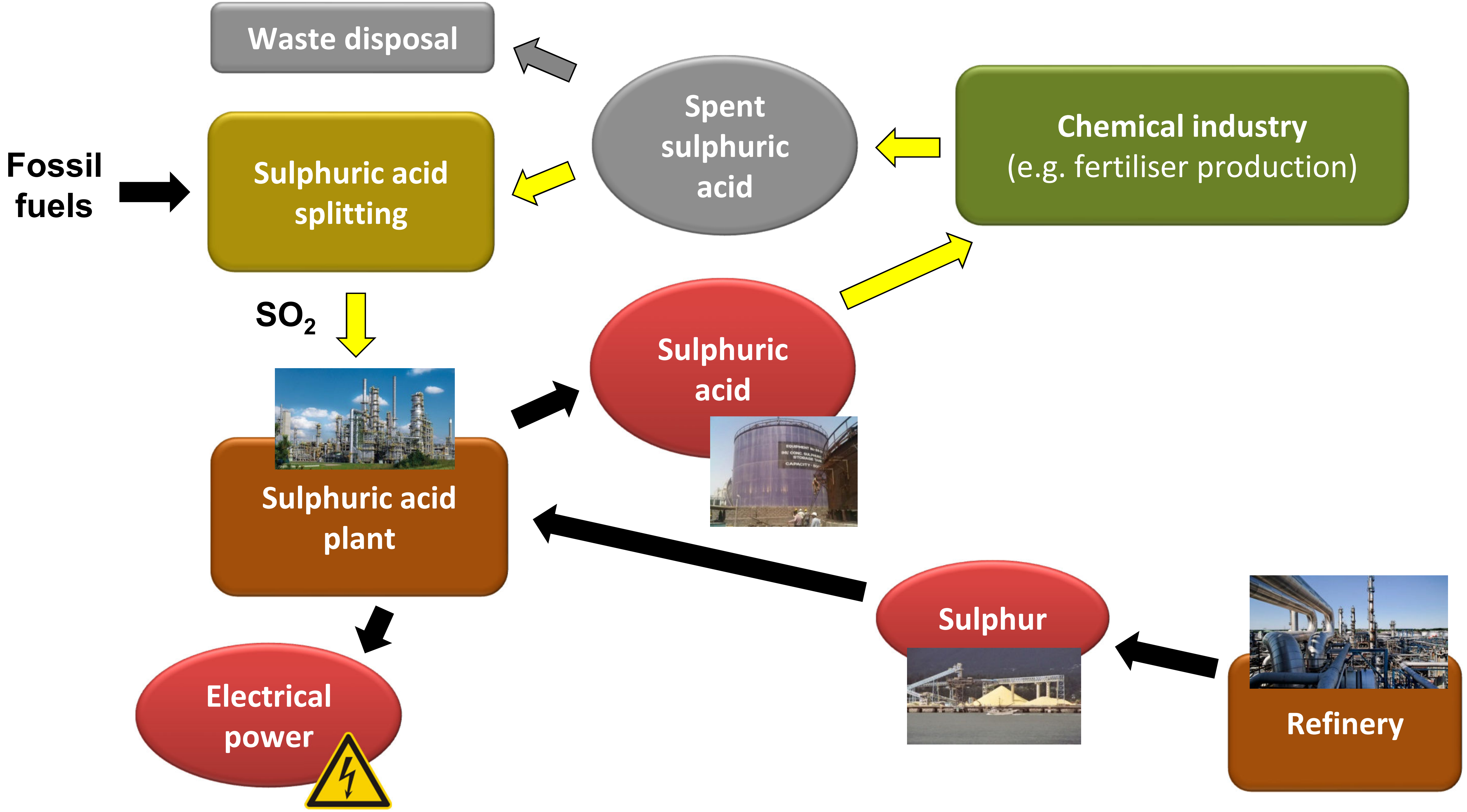
Pipeline

Molten sulphur in heated pipelines (~140 °C)

Ship

Truck

Sulphuric acid in the industry today



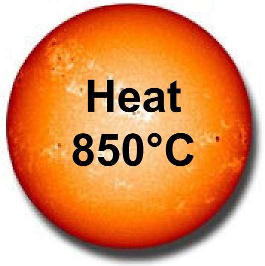
Contents

Solar hydrogen production from water
Efficiency comparison

Process	T [°C]	Solar plant	Solar-receiver + power [MW_{th}]	η T/C (HHV)	η Optical	η Receiver	η Annual Efficiency Solar – H_2
Elctrolysis (+solar-thermal power)	NA	Actual Solar tower	Molten Salt 700	30%	57%	83%	13%
High temperature steam electrolysis	850	Future Solar tower	Particle 700	45%	57%	76,2%	20%
Hybrid Sulfur-process	850	Future Solar tower	Particle 700	50%	57%	76%	22%
Hybrid Copper Chlorine-process	600	Future Solar tower	Molten Salt 700	44%	57%	83%	21%
Metal oxide two step Cycle	1800	Future Solar dish	Particle Reactor < 1	52%	77%	62%	25%

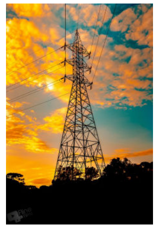
Siegel, et al. (2013) *Ind Eng Chem Res*

Hybrid Sulphur Cycle (HyS)



Thermal step $H_2SO_4 \leftrightarrows \tfrac{1}{2}\,O_2 + H_2O + SO_2$

Electrochemical step $2H_2O + SO_2 \leftrightarrows H_2SO_4 + H_2$



Water **Electricity*** **Hydrogen**

*) ~14 % of electricity demand of conventional water electrolysis

Brecher, et al. (1977) Int J Hydrogen Energ

DLR Research on Hybrid Sulphur Cycle

Timeline of projects

HySelect

Sul4Fuel

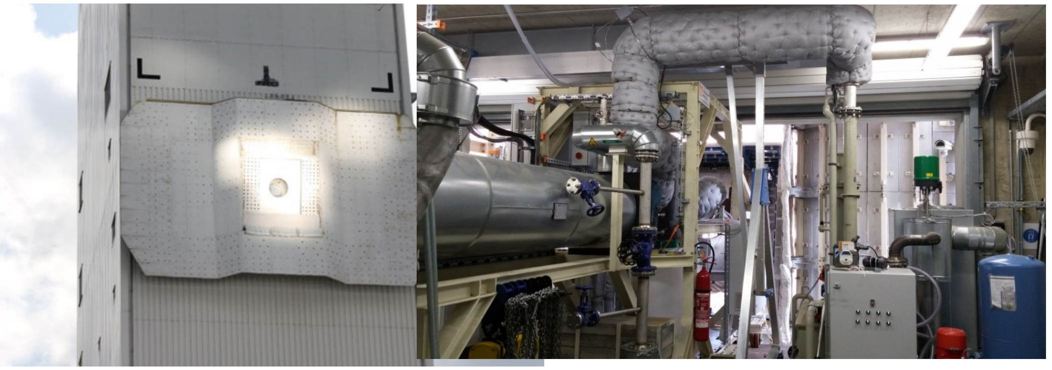
HybrEEn

HYTHEC

HycycleS

SOL2HY2

2005 | 2010 | 2015 | 2020 | 2025



Reactor separate chamber

Reactors from 1-2 kW

Directly irradiated

Upscale to Tower

TRL4

800-1000 °C

Indirect heating

Combined Tower and SDE

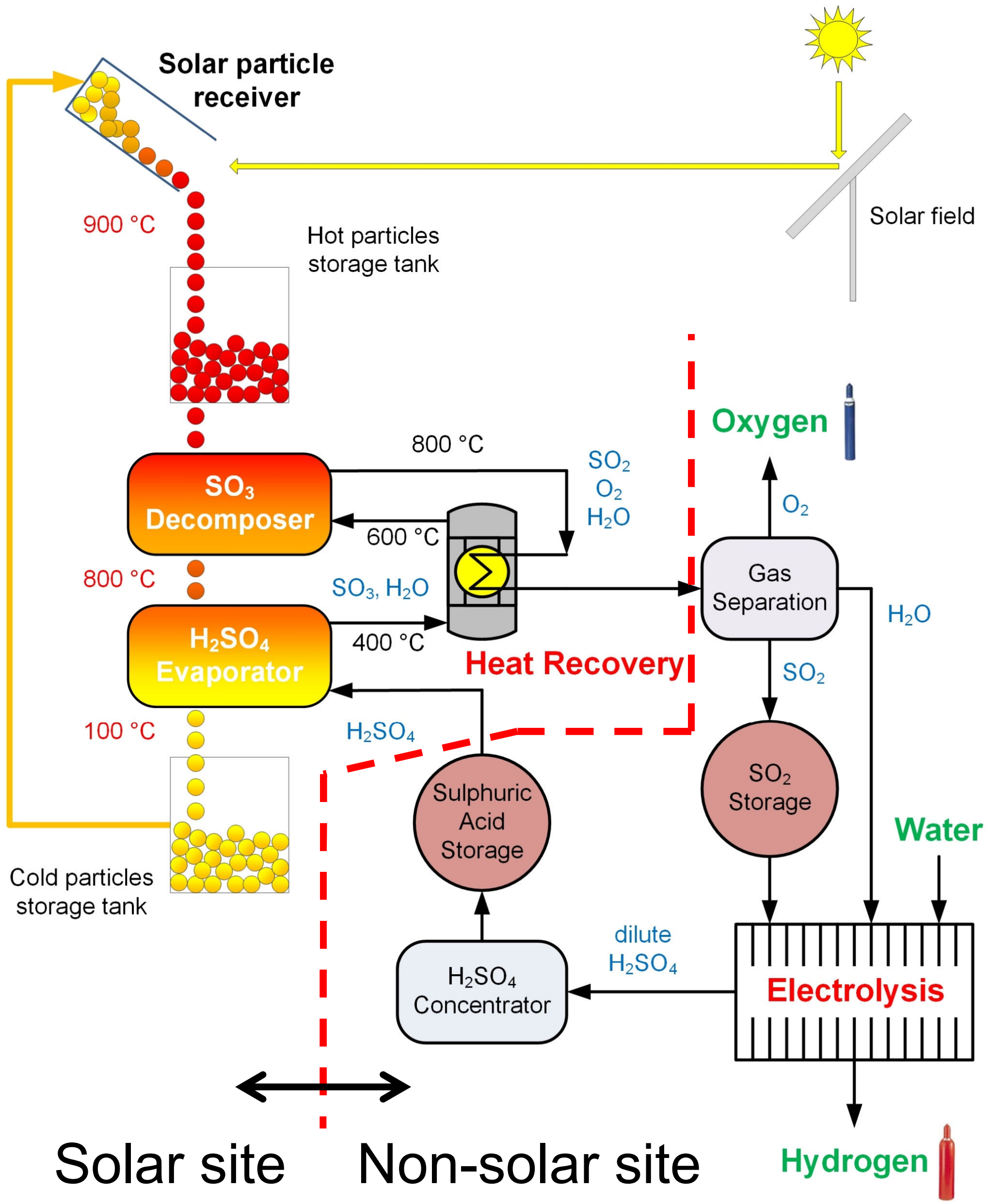
TRL6

efficiency target
>10 % solar to H_2

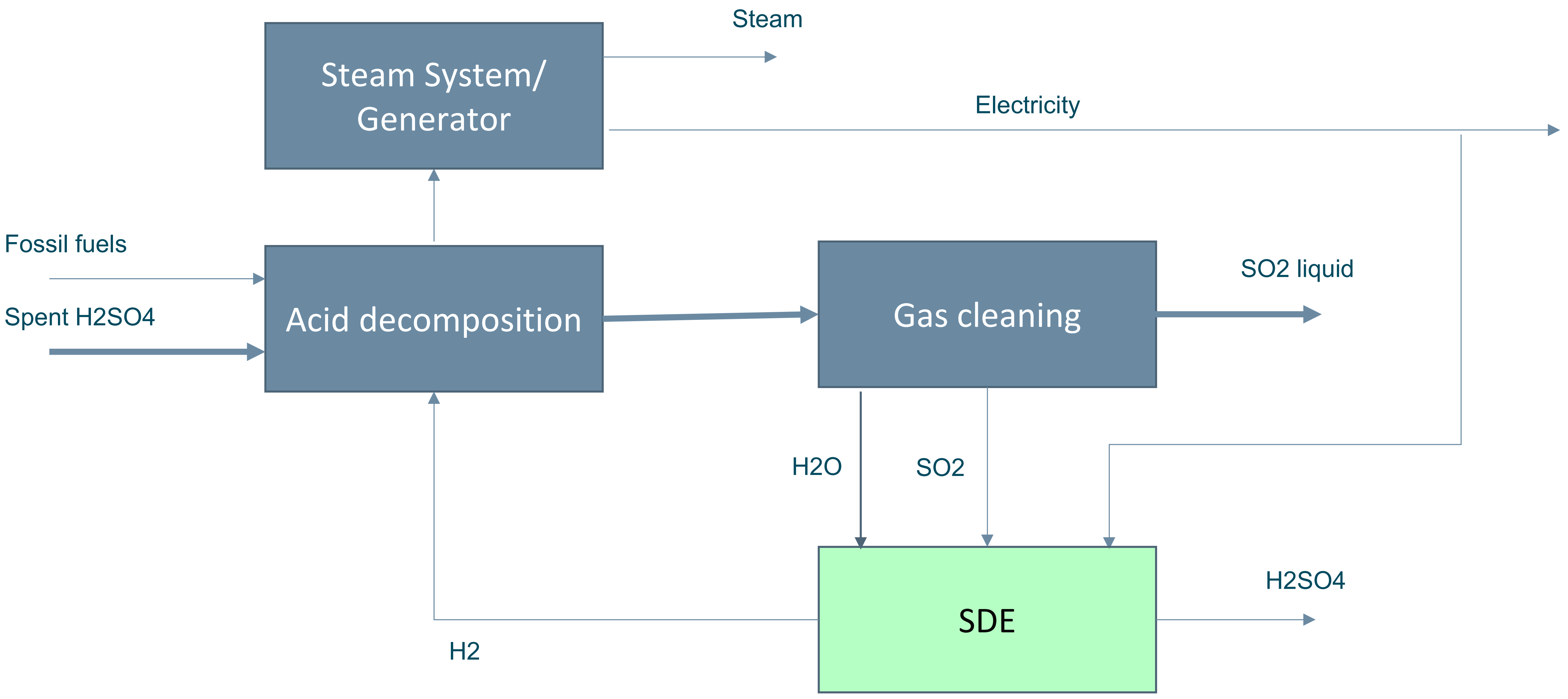
splitting reactor to 50-80 kW
solar receiver 750 kWth
thermal storage 4 MWh

*TRL = Technical Readyness Level

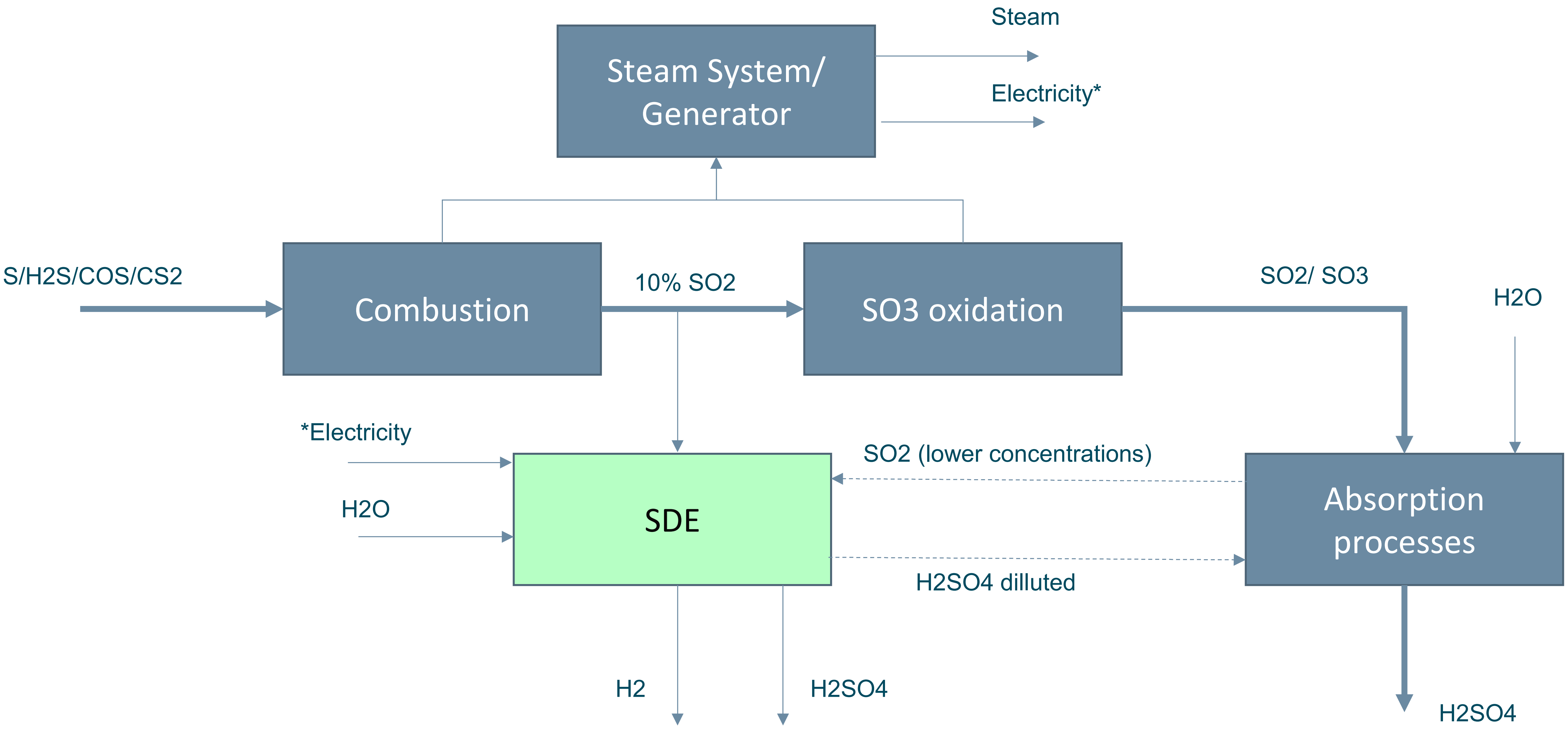
Solar hybrid sulphur cycle (HyS) process diagram
EU project HySelect



Industrial application of the SDE
Spent Sulphuric Acid Recycling Plant

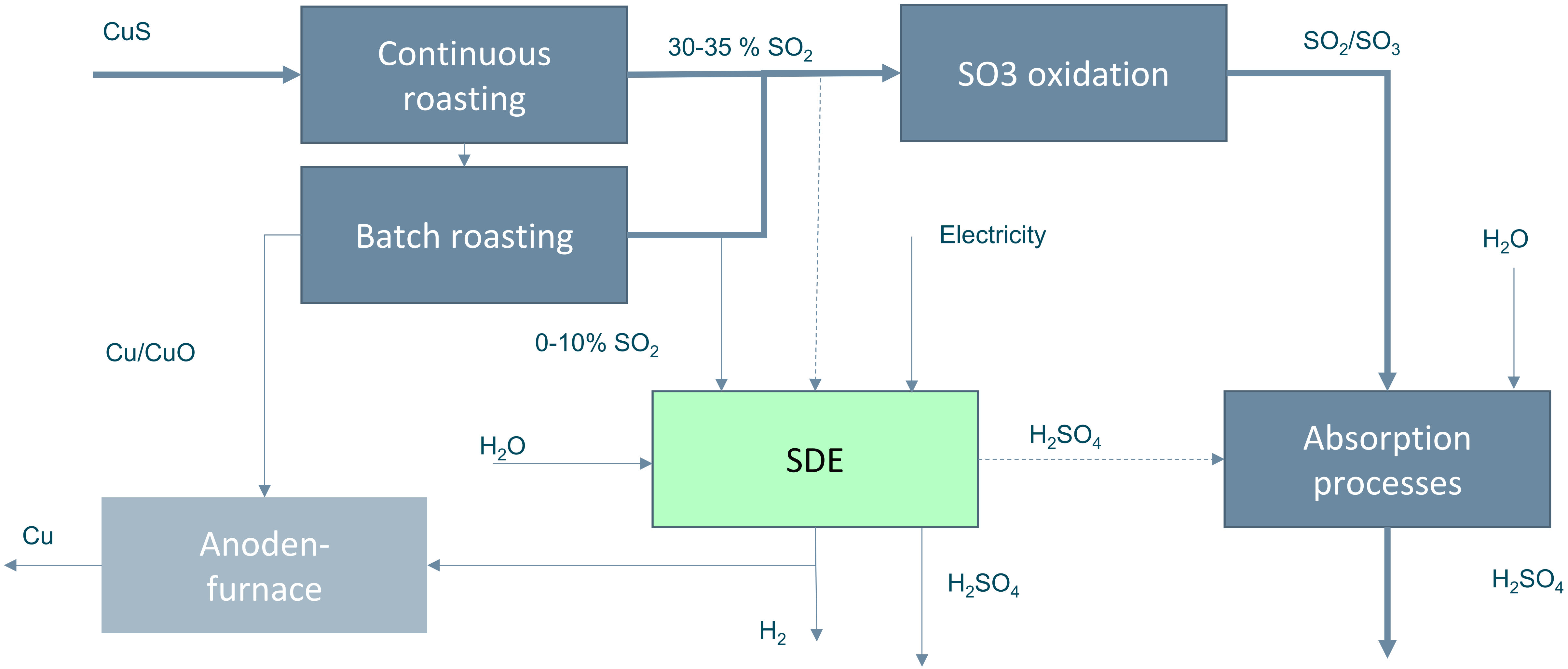


Industrial application of the SDE
Sulphuric Acid Production with Sulphur burner

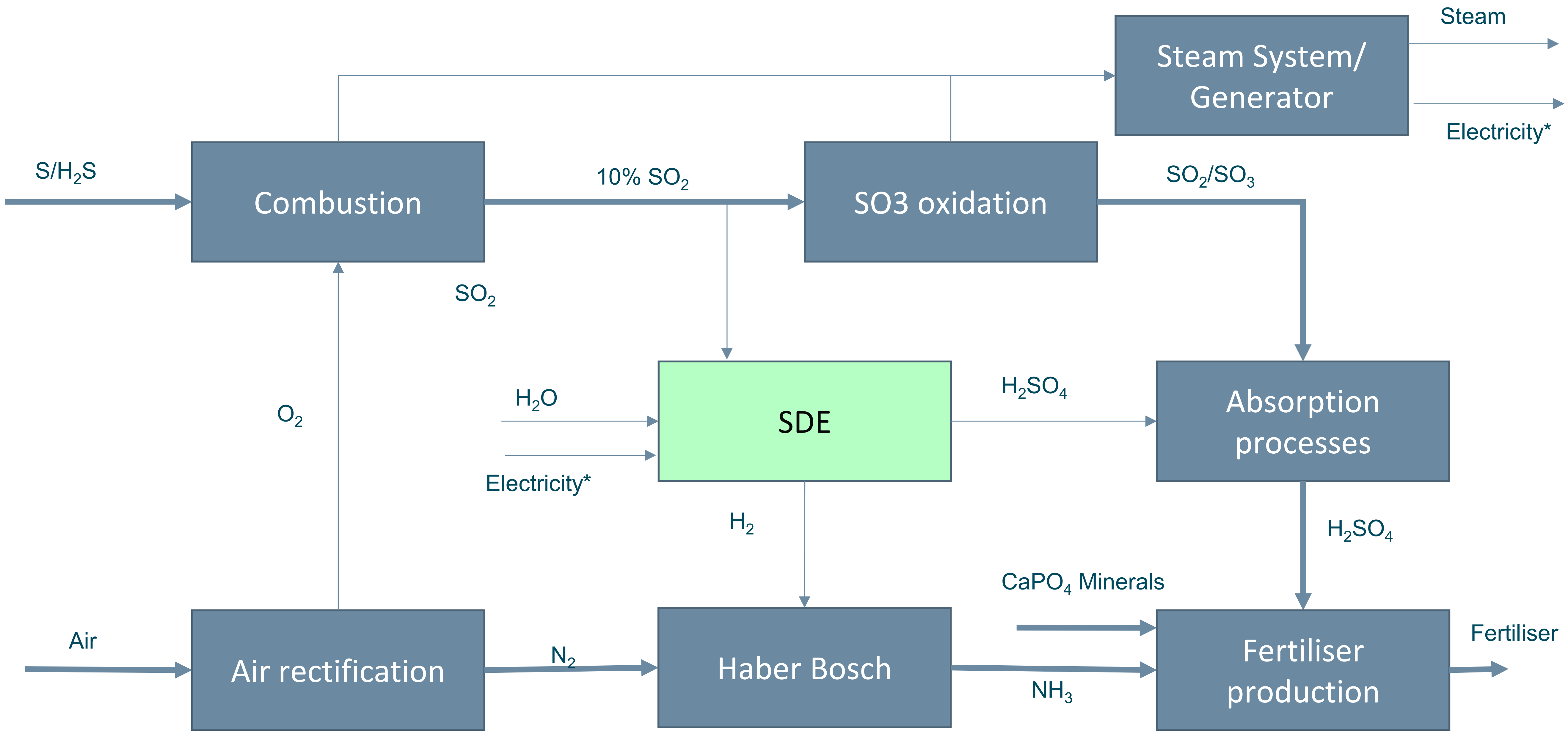


Industrial application of the SDE
Non-Ferrous Metal Industry

Example of CuS, other mineralic sulfides possible (Zn, Pb, Mo, Au, Pt etc.)

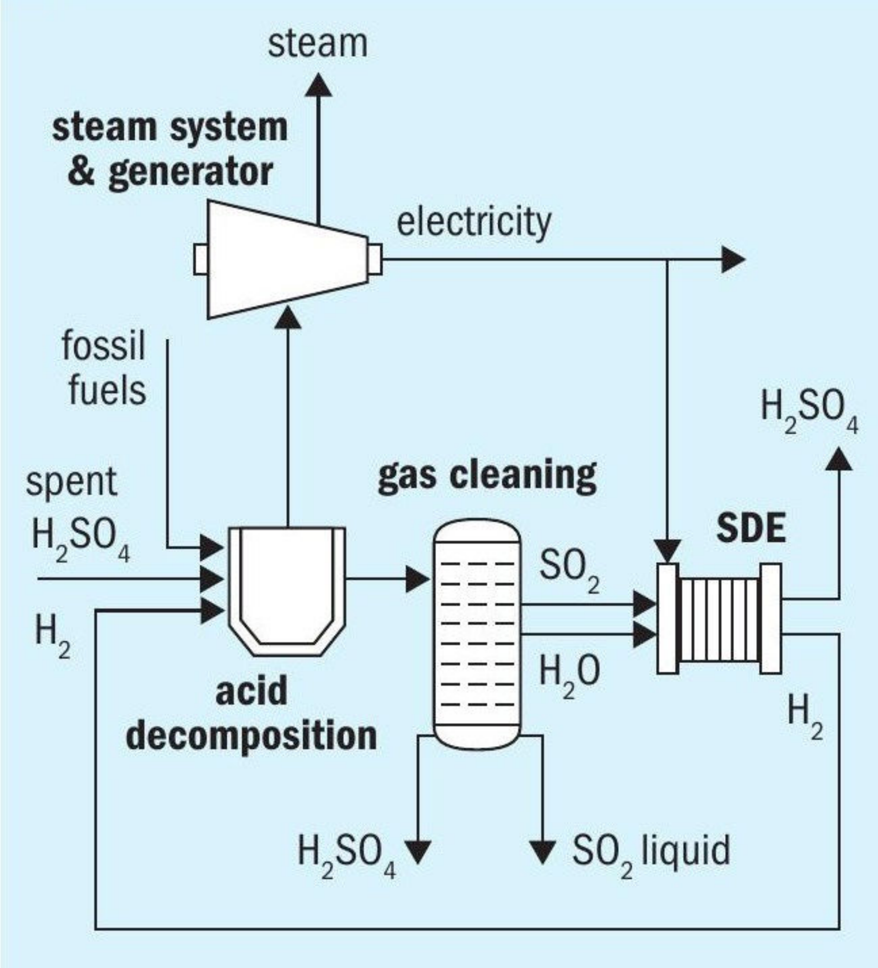


Industrial application of the SDE
Fertiliser Production



Sulphuric Acid Splitting – SAS

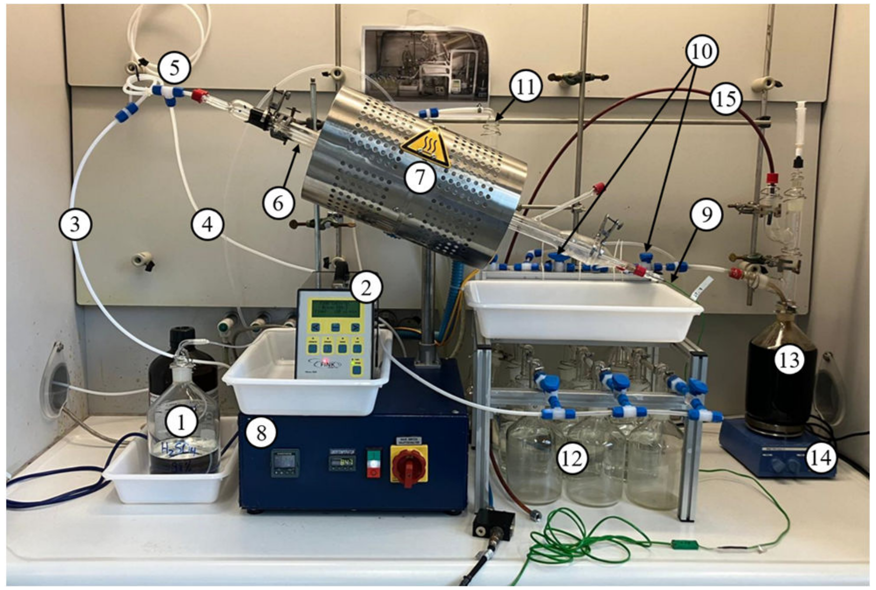
Catalytic acid decomposition

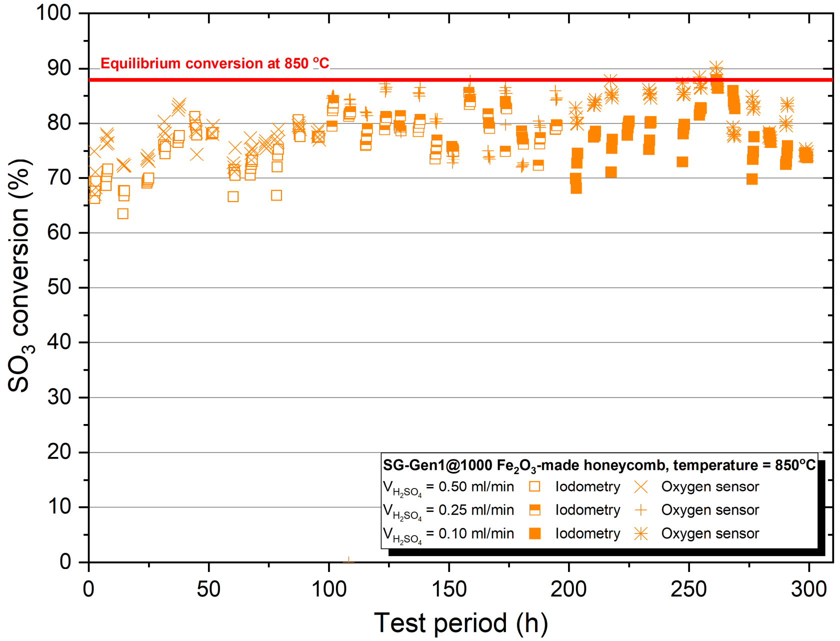


- thermal process ⟶ combustion of (fossil) fuels
- ⟶ catalytic process
- lower the required temperature
- no expensive PGM-based catalysts

Metal oxide structures[3, 4, 5] employed for catalytic Sulphuric Acid Splitting in DLR

- Iron & Copper oxide based compositions[1, 2, 3]





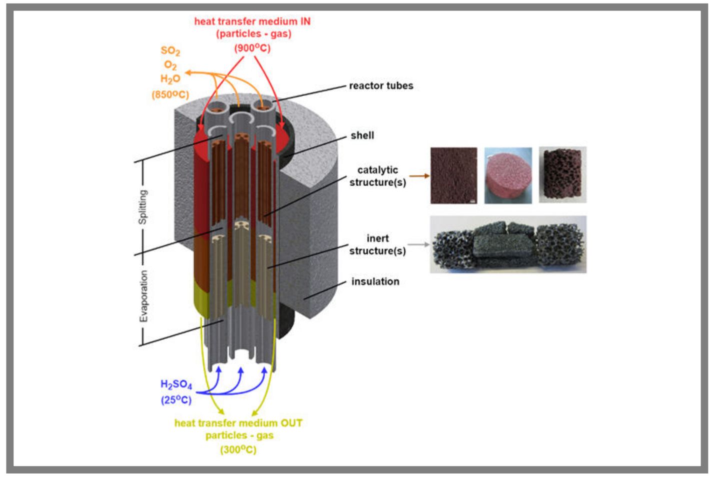
- temperatures of 800-900°C at 1 atm with conversions close to equilibrium
- long-term stability (≥500 h) and limited deactivation (2-7%)

1. Giaconia et al.; Int. J. Hydrog. Energ., 36 (2011) 6946-6509.
2. Karagiannakis et al.; Int. J. Hyd. En., 37 (2012) 8190-8203.
3. Karagiannakis et al.; Int. J. Hyd. En., 36 (2011) 2831-2844.
4. Agrafiotis et al., Applied Catalysis B: Environmental, 324 (2023) 122197
5. Tsongidis et al., AIP Conf. Proc. 2126 (2019), 210009

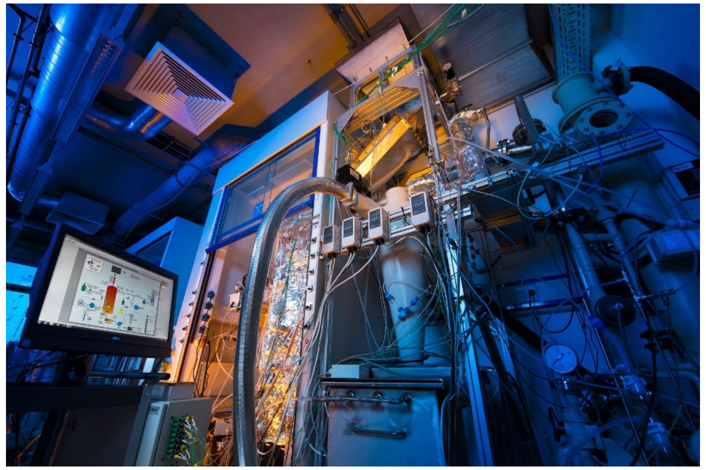
Sulphuric Acid Splitting – SAS

Catalytic acid decomposition with renewable heat

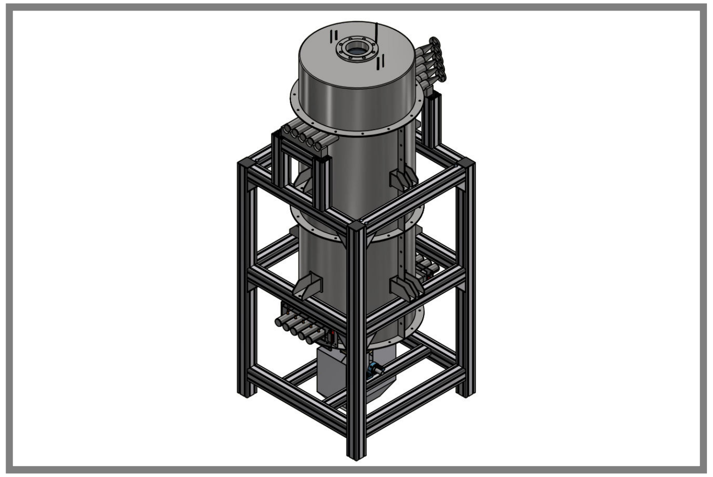
- heat transfer medium
- shell & tube HX design



allothermal reactor concept[1]



DLR-Pegasus 3kW$_{th}$ reactor[2]

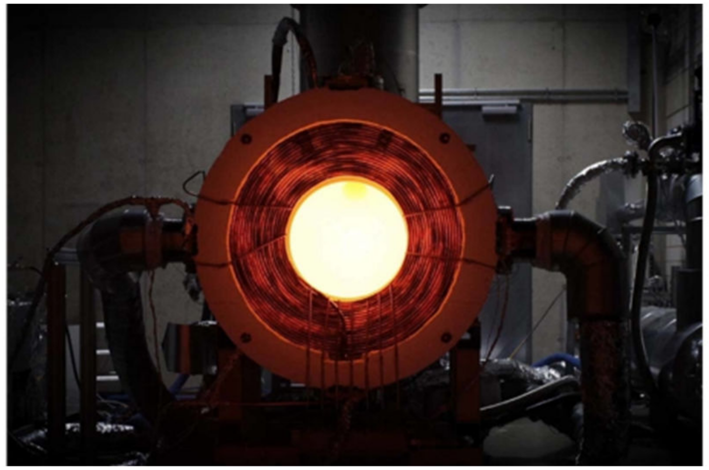


DLR-HySelect 50kW$_{th}$ reactor[3]

Sources of renewable heat

- Concentrating Solar Technologies
- options for renewable heat storage

CentRec® at the DLR tower[4]



Synhelion® solar receiver[5]

SiBox® for heat storage[6]

[1]Thanda et al., Allothermally heated reactors for solar-powered implementation of sulphur-based thermochemical cycles, (2023)
[2]https://cordis.europa.eu/project/id/727540/reporting/de
[3]https://hyselect.eu/
[4]https://www.dlr.de/en/images/2018/2/the-centrec-receiver-at-the-solar-tower-in-juelich-during-the-practical-test_30923
[5]https://synhelion.com/technology/solar-process-heat
[6]https://1414degrees.com.au/sibox-demonstration-module/

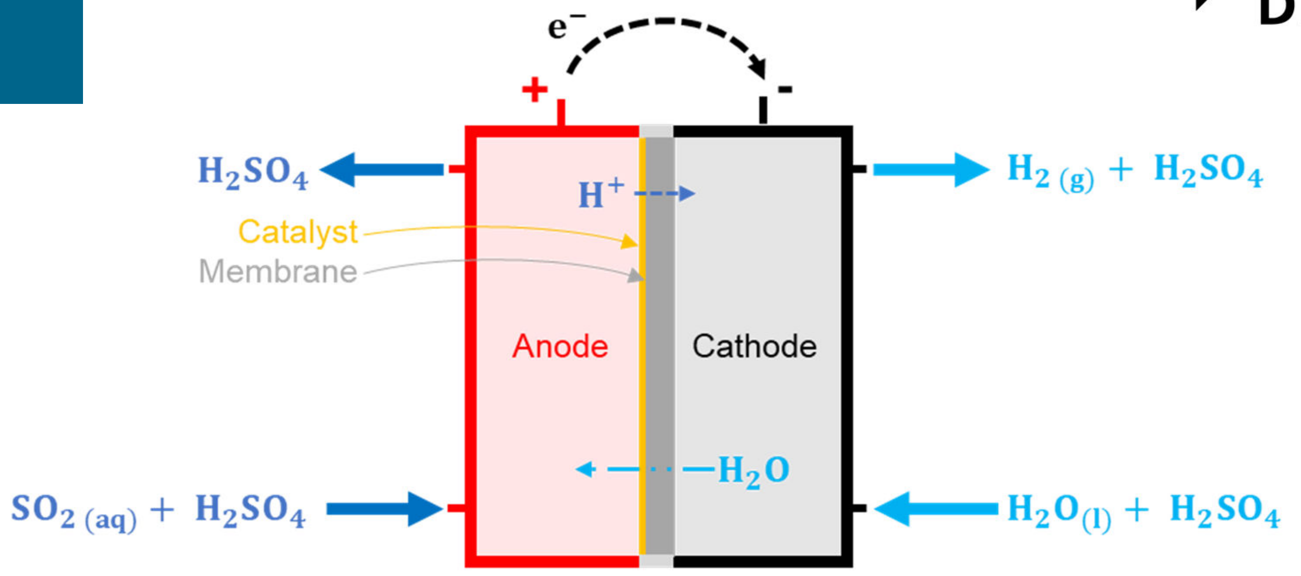
Sulphur dioxide Depolarized Electrolysis - SDE

Modified PEM (proton exchange membrane) **water electrolysis**

- producing Hydrogen and Sulphuric Acid from SO_2 and water

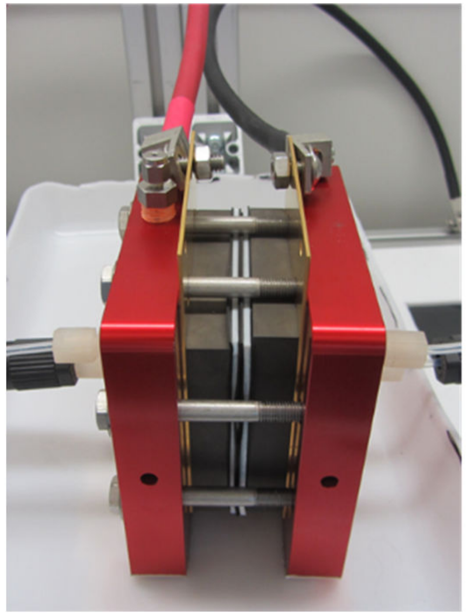
- theoretical cell potential of 0.17V
- ~14% of conventional water electrolysis 1.23V[1]

- cloned from water PEM stacks



- reliability of the process
- engineering challenges: SO_2 carry-over, corrosion resistance, scale-up
- catalysts, membranes, CCMs & MEAs w/o crit. materials (Pt-, Pd-), Au-

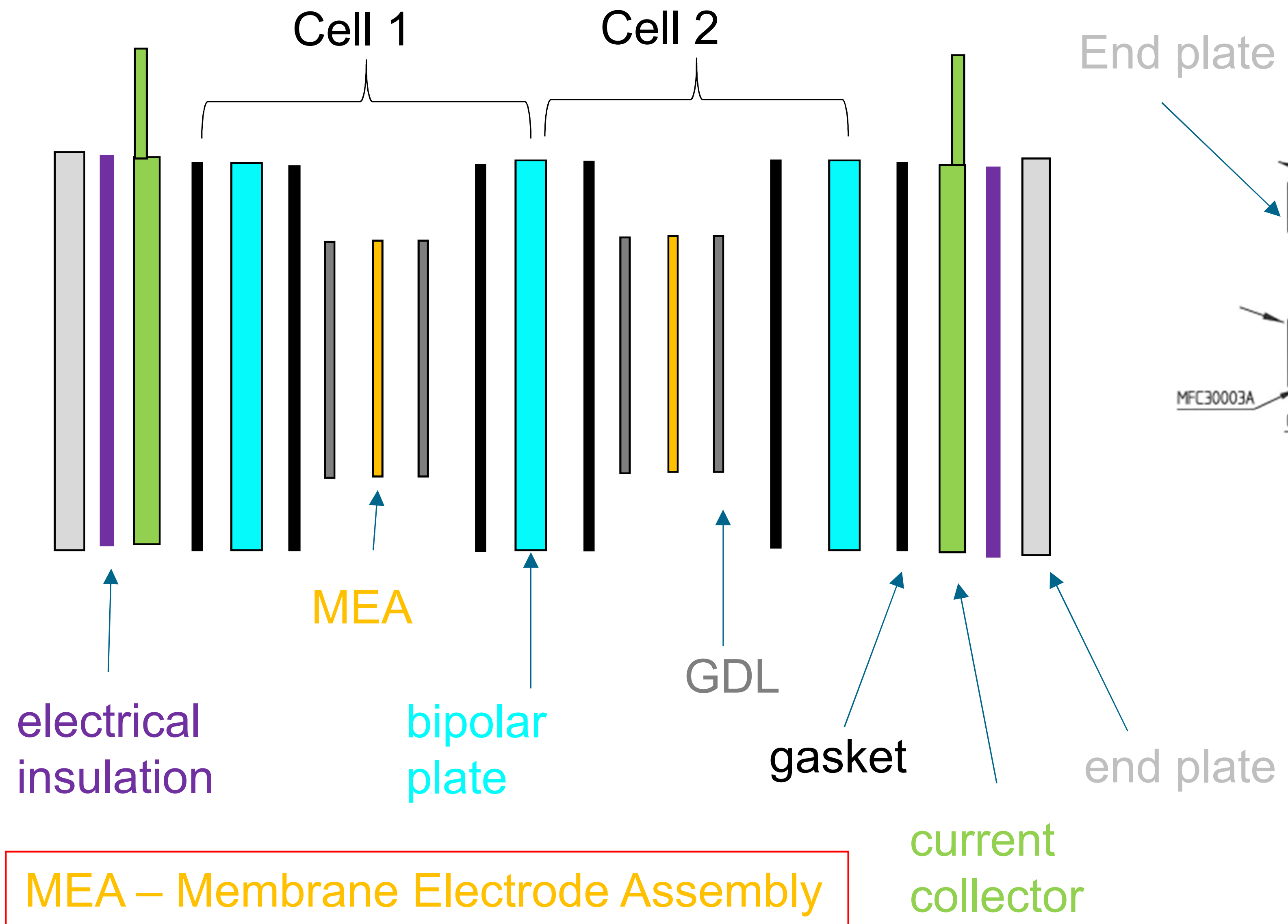
	Reaction	Temperature (°C)	Theoretical potential (V)
Electrolysis	$SO_2 + 2H_2O \rightarrow H_2SO_4 + H_2$	50	0.17
Anode	$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H^+ + 2e^-$		
Cathode	$2H^+ + 2e^- \rightarrow H_2$		

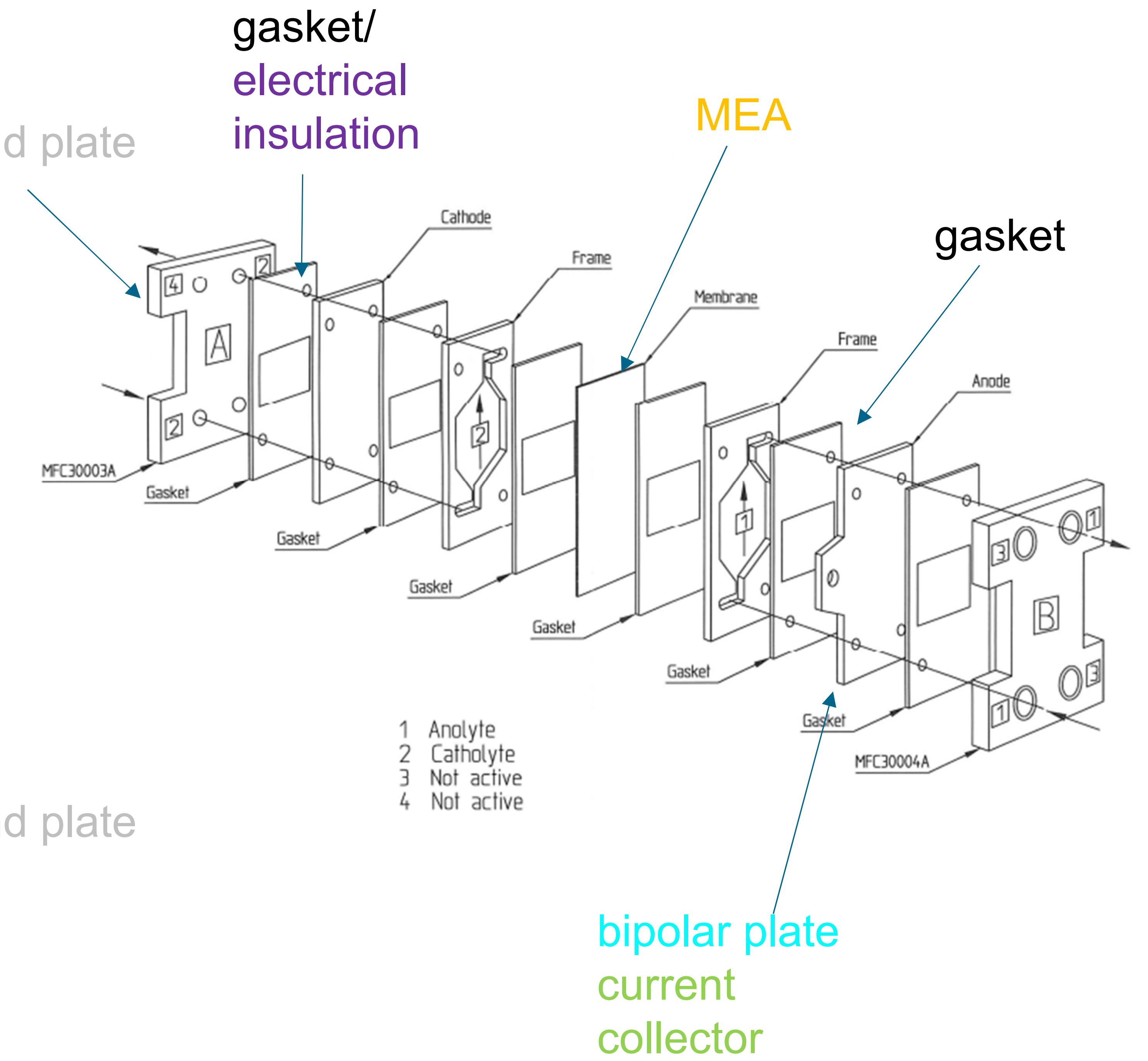


Cell and Stack for SDE in the experimental setup at DLR

[1]Sattler et al., Solar Energy, 156 (2017) 30-47

Cells, stacks & test rig for SDE – stacking

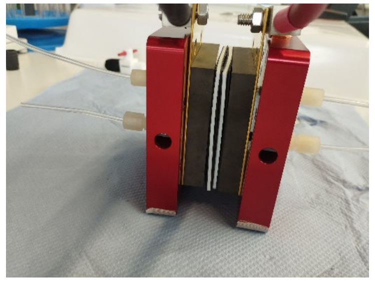




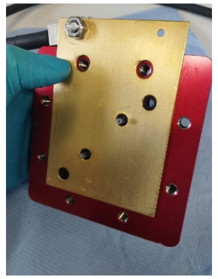
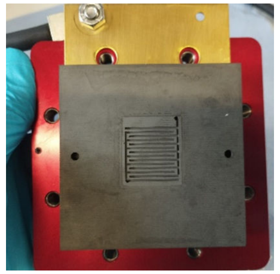
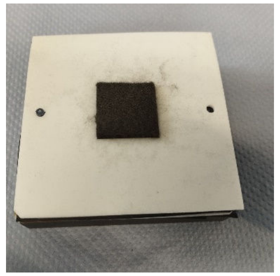
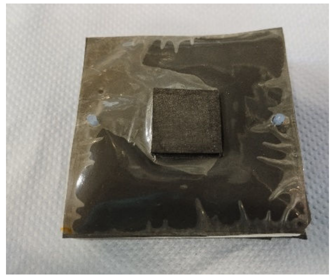
MEA – Membrane Electrode Assembly
GDL – Gas Diffusion Layer

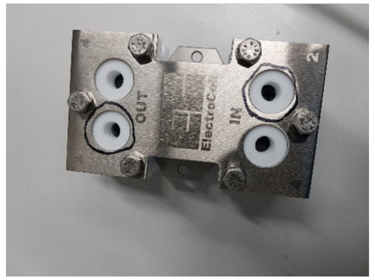
Cells, stacks & test rig for SDE – available cells

Cells and stacks in DLR

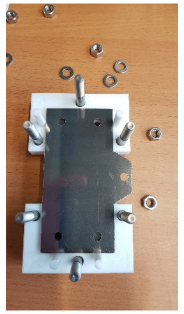
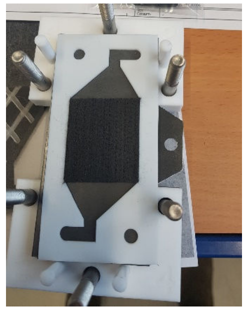


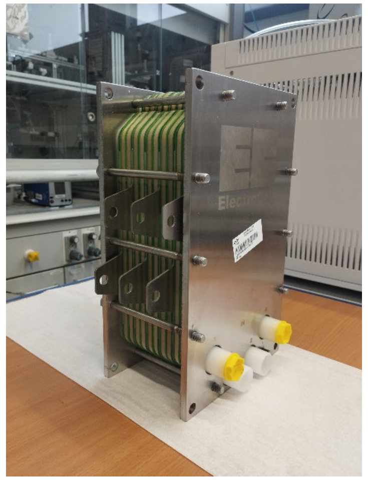
5 & 25cm^2

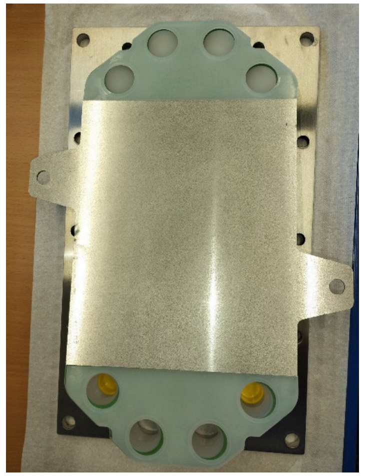


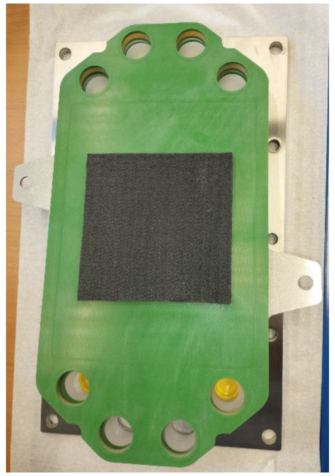
10 cm^2

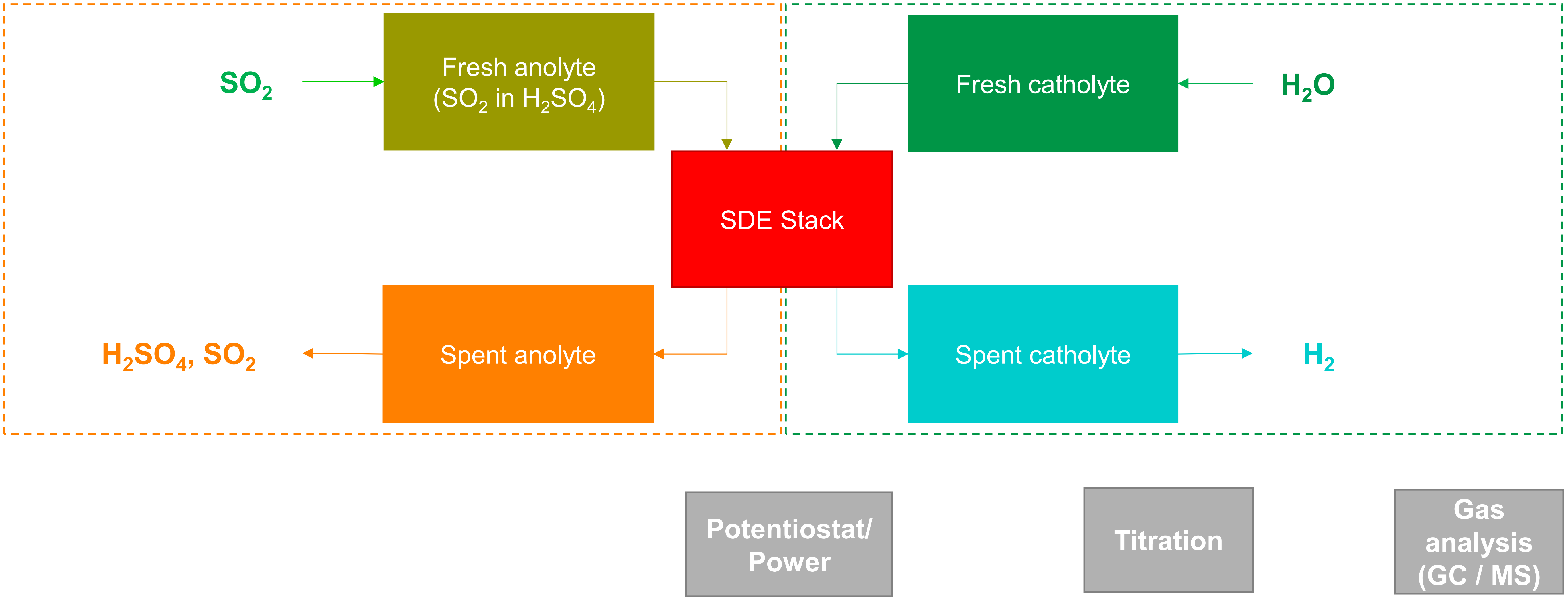



5x100 cm^2

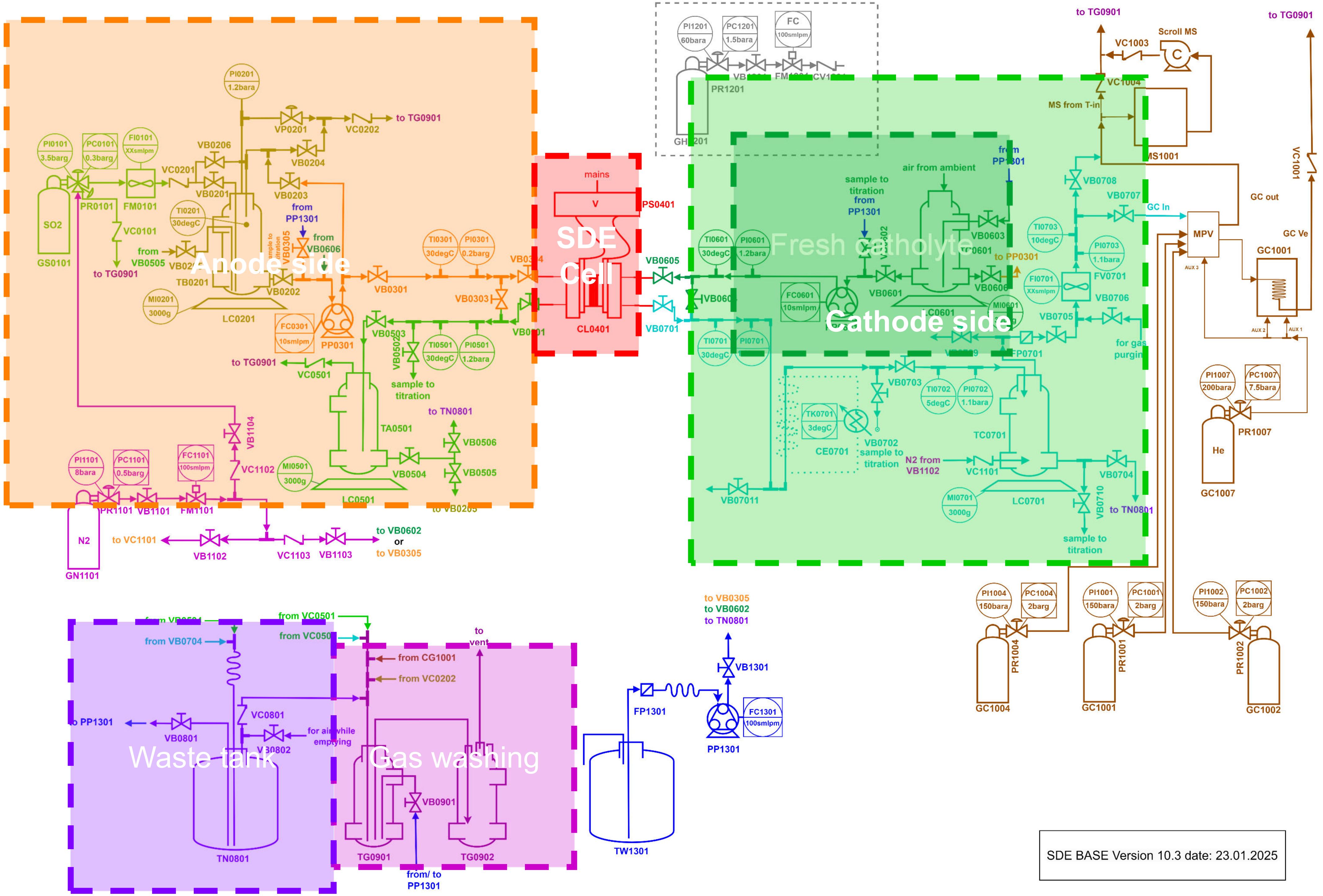





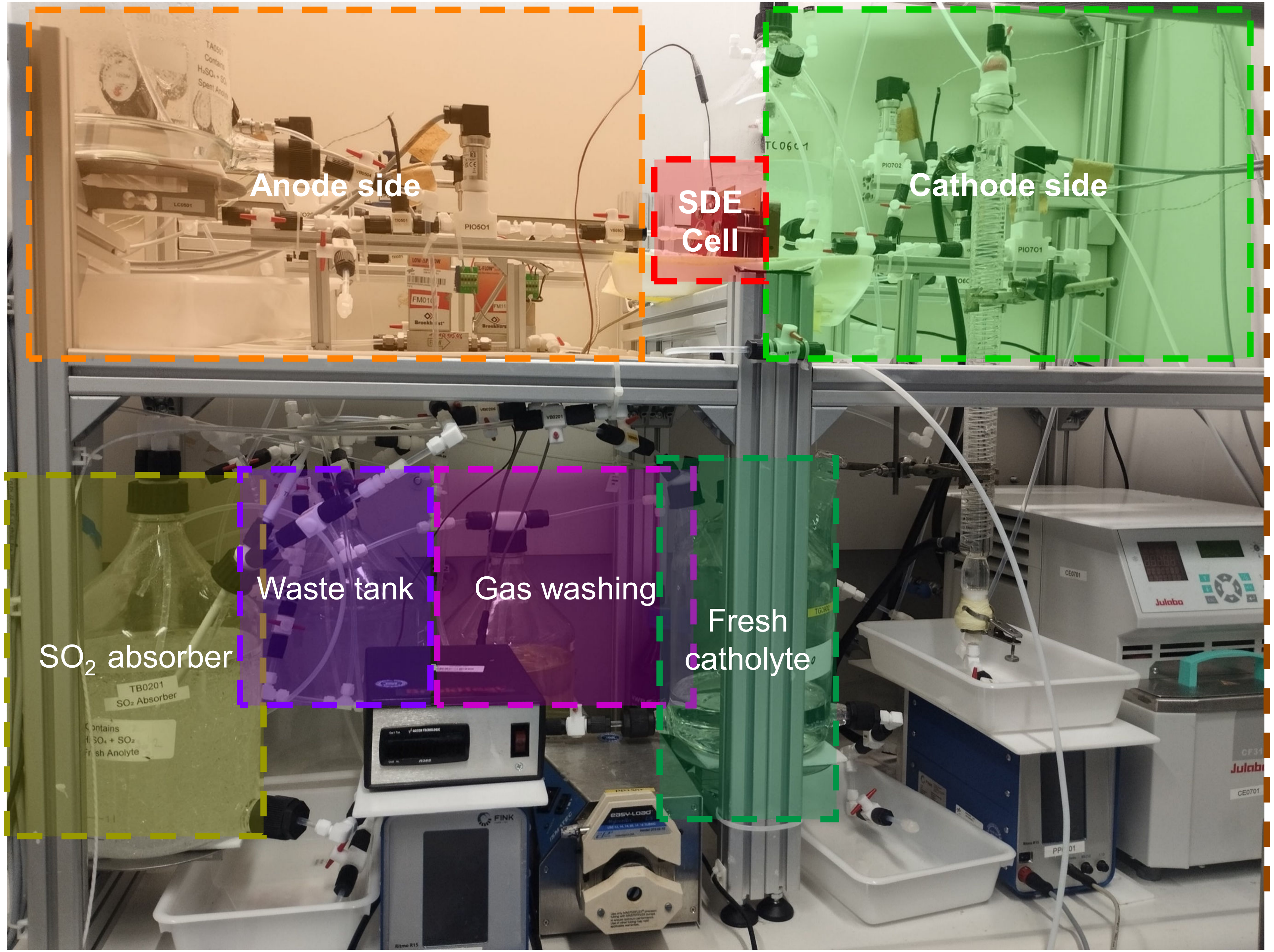
Simplified block flow diagram of the Sulphur dioxide Depolarized Electrolysis Unit



Cells, stacks & test rig for SDE – P&ID



Cells, stacks & test rig for SDE – experimental setup



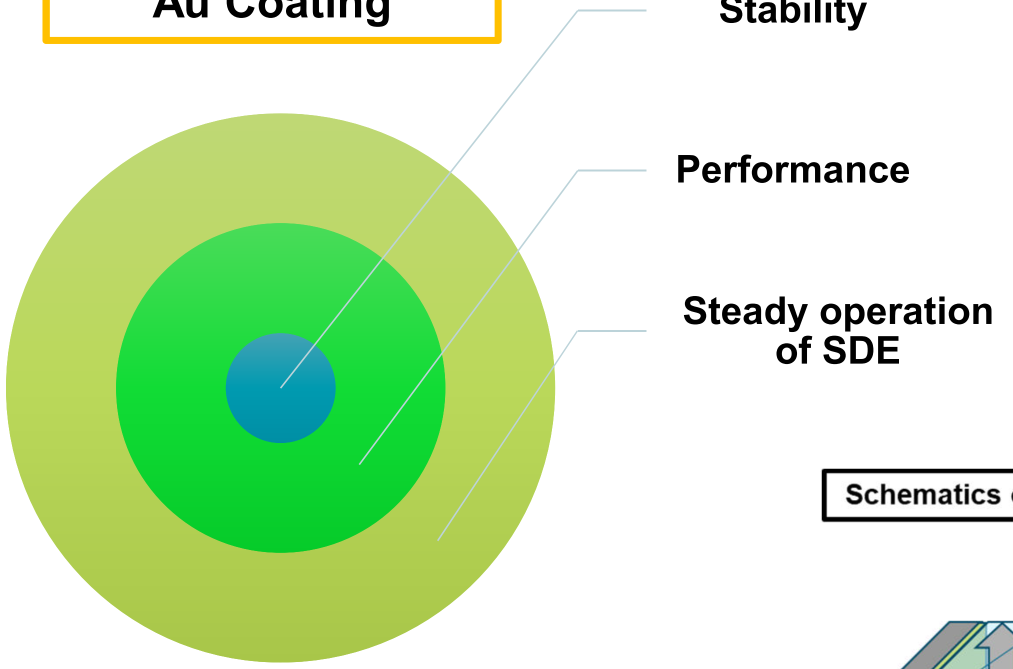
GC and MS

SDE component development – bipolar plates

- **Goal of our work is to ensure a steady operation of SO_2 Depolarized Electrolyzer**

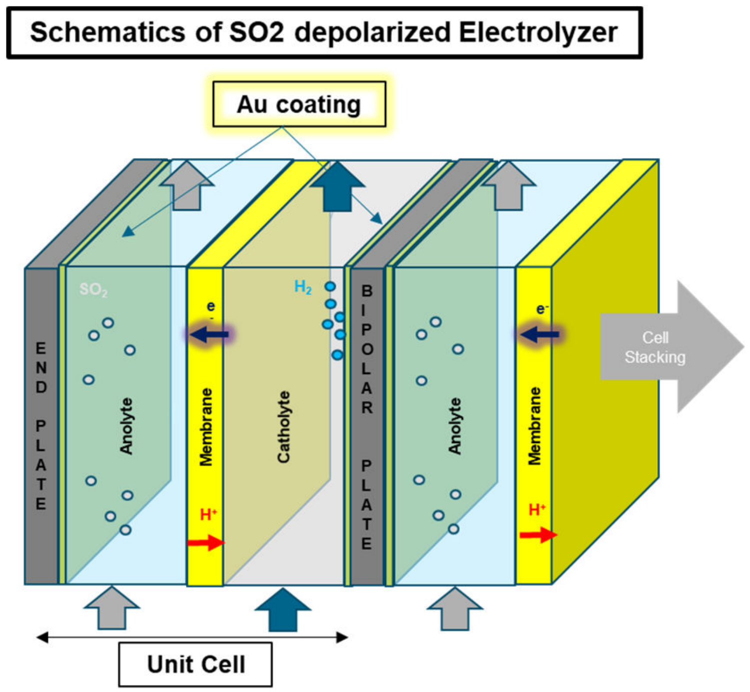
Bipolar Plates

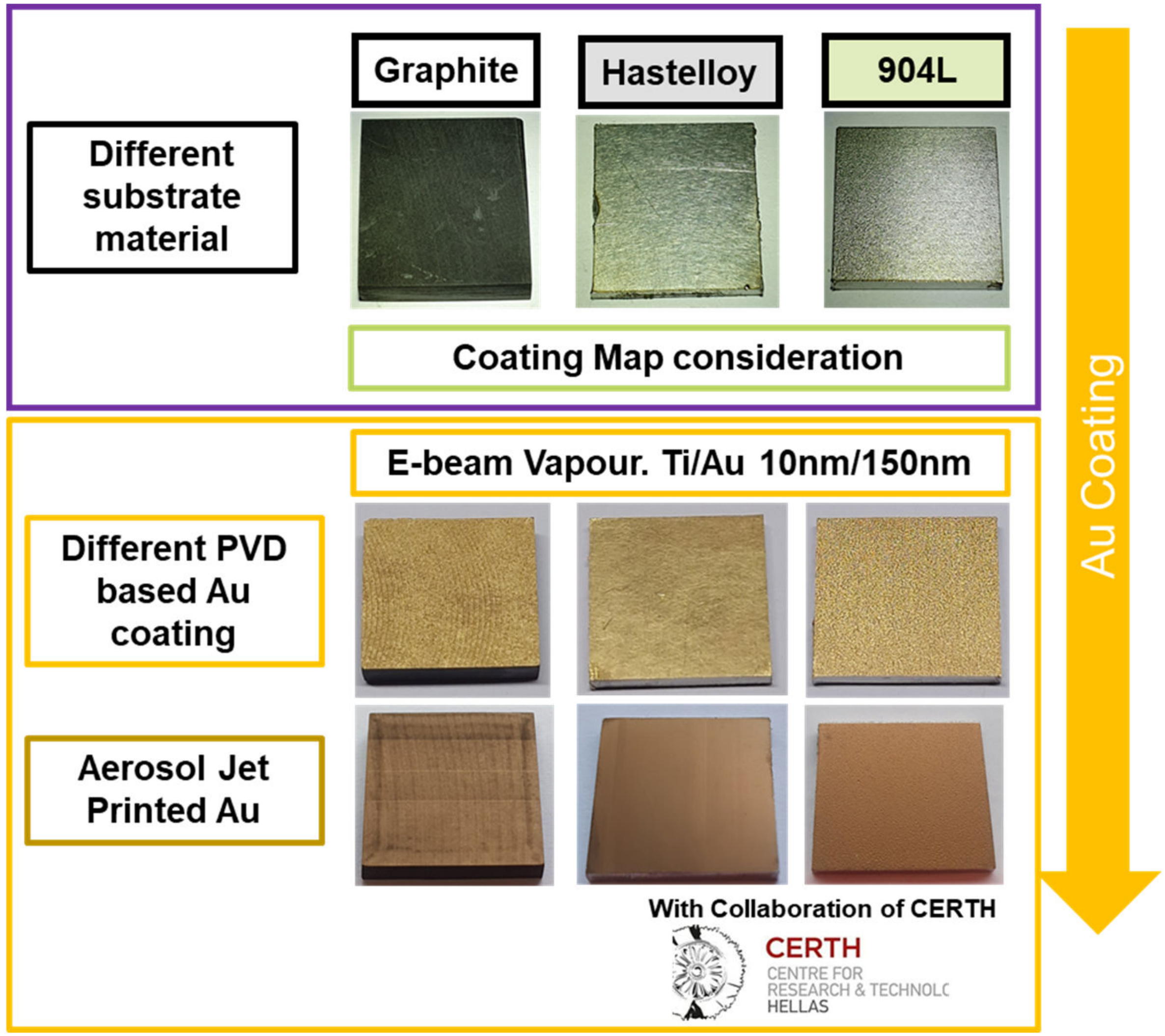
Au Coating



Requirements of Au coating

Chemical Stability
Mechanical Properties
Uniformity
Adhesion
Cost-Performance Ratio
Environmental & Safety

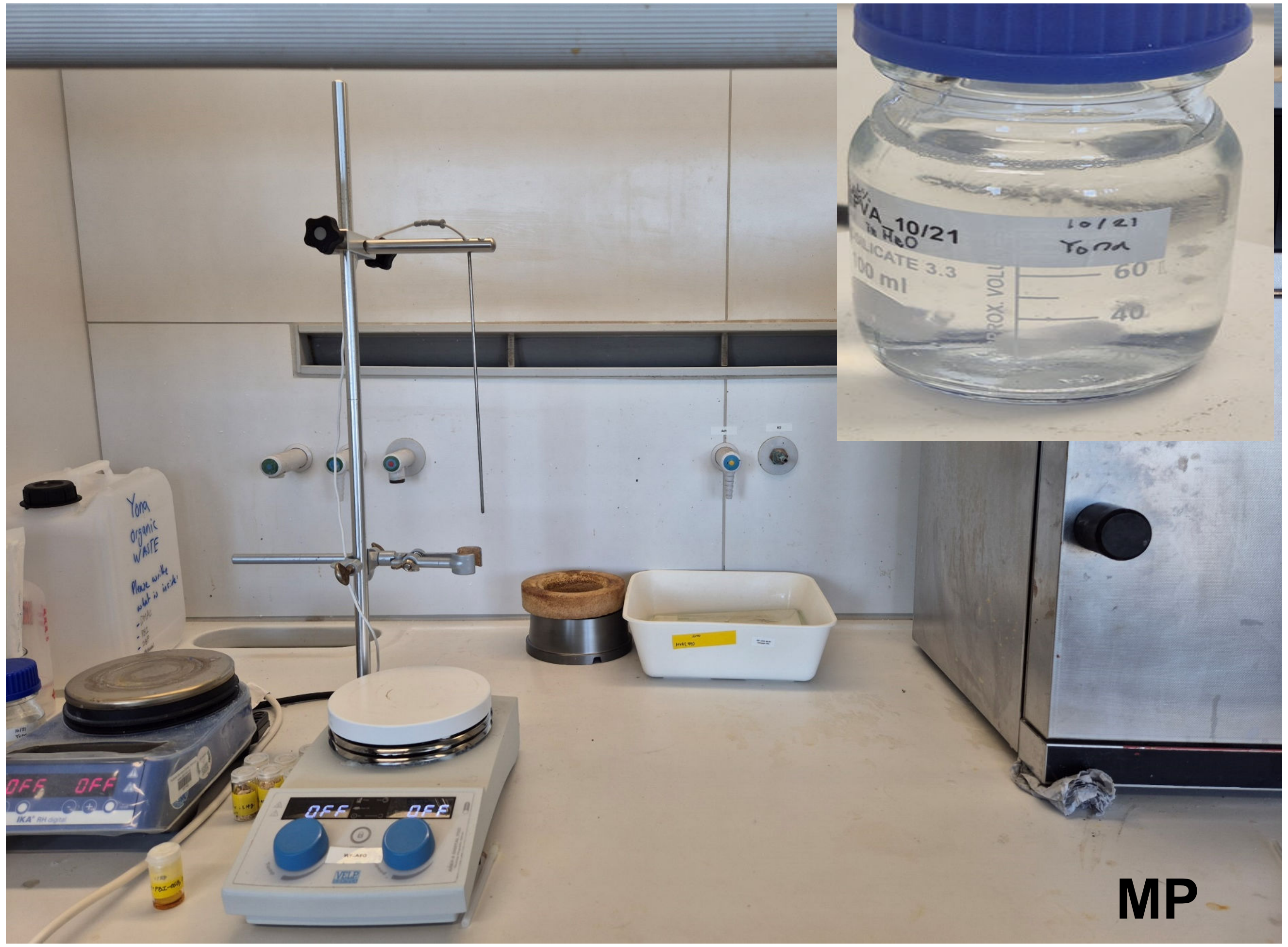


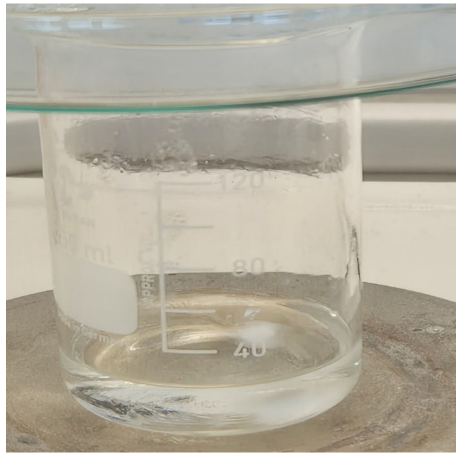


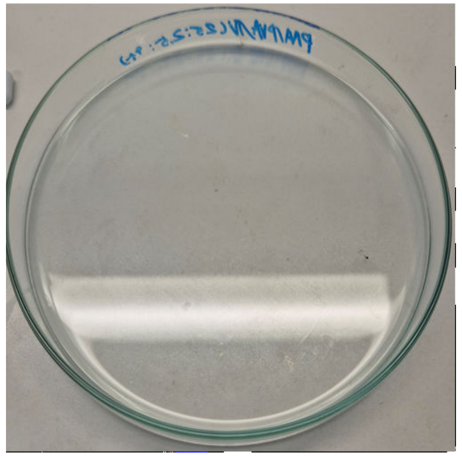
SDE component development – membranes

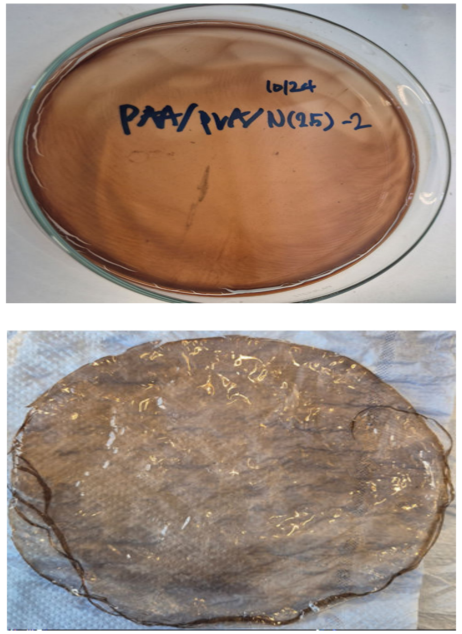
Preparation

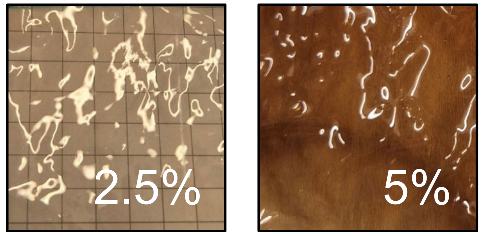
Preparing polymer solution → *Inducing reaction* → *Casting* → *Drying & Washing*



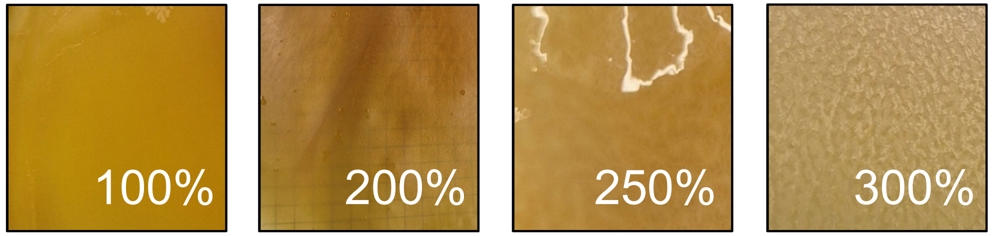








Cross-linked **Nafion** based membranes



Porous **PBI** (Polybenzimidazole) based membranes

SDE results – parameters

Input parameters
Potential
Gas/liquid feed
SO_2 anolyte concentration
H_2SO_4 anolyte concentration
H_2SO_4 catholyte concentration
Temperature
Pressure
Anolyte flowrate
Catholyte flowrate
Membrane type
Catalyst loading
Catalyst type
Single cell/stack

SDE

Output parameters
Current
H_2 production
SO_2 consumption
H_2SO_4 production

Metrics
Specific energy consumption
Conversion rates
Degradation
Other?

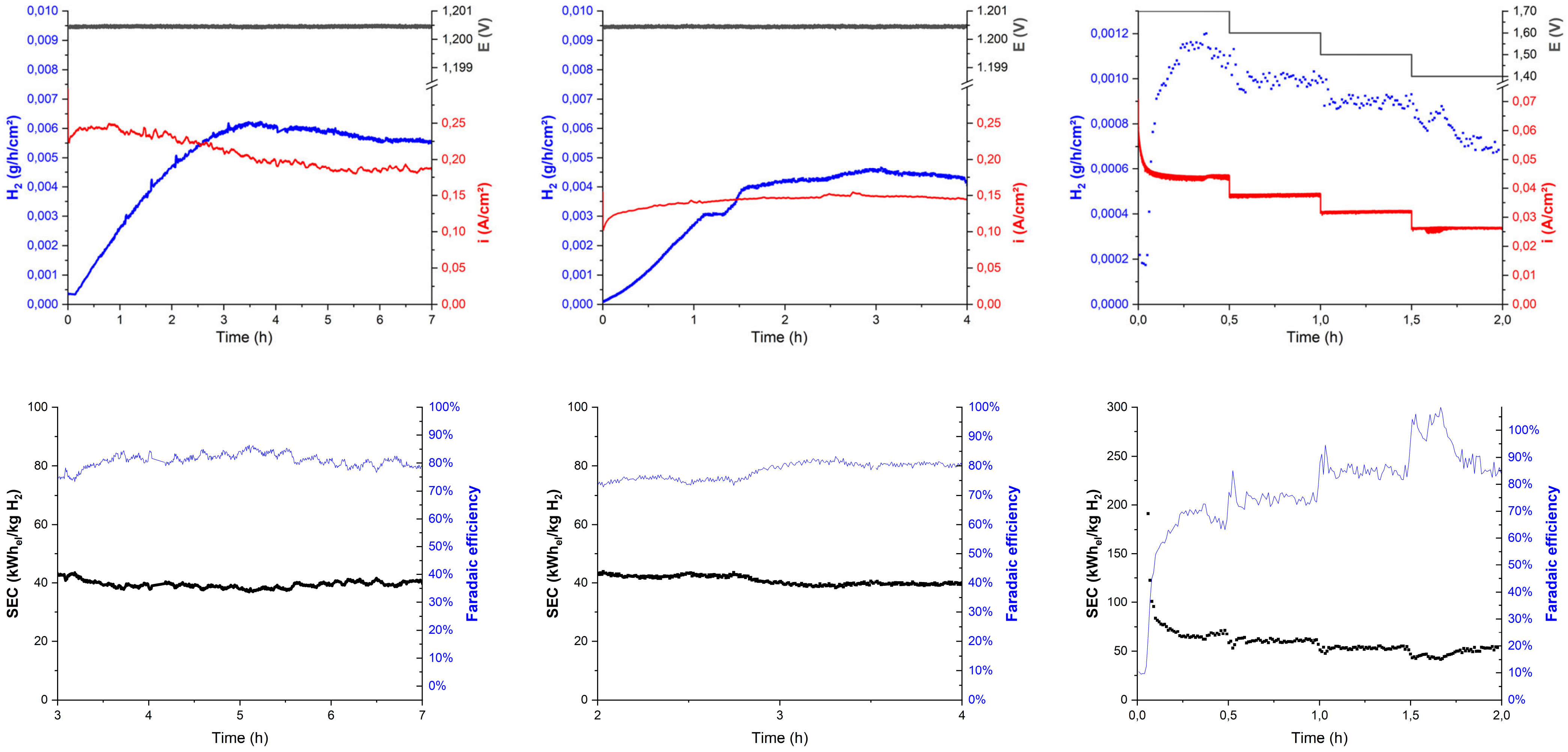
All experiments so far have been conducted with commercial of the shelf PEM components!!

Not optimal
Useful to establish baseline

Sulphur dioxide Depolarized Electrolysis - SDE

Results - lab scale

5 cm² **25 cm²** **100 cm²**



unpublished data

- off-the-shelf components
  - *not optimal for SDE*

- saturated SO_2 solutions
- 30% w/w Sulphuric Acid
- 1.2V & 1.5V

- quasi steady-state
- 0.15 - 0.2 A/cm^2

- **Specific Energy Consumption**
  - *energy input per kg H_2*

- **~40 kWh_{el}/kg H_2**
- promising results

- PEM water electrolysis target: 50 kWh_{el}/kg H_2

Sulphur dioxide Depolarized Electrolysis - SDE

Pilot SD electrolyzer

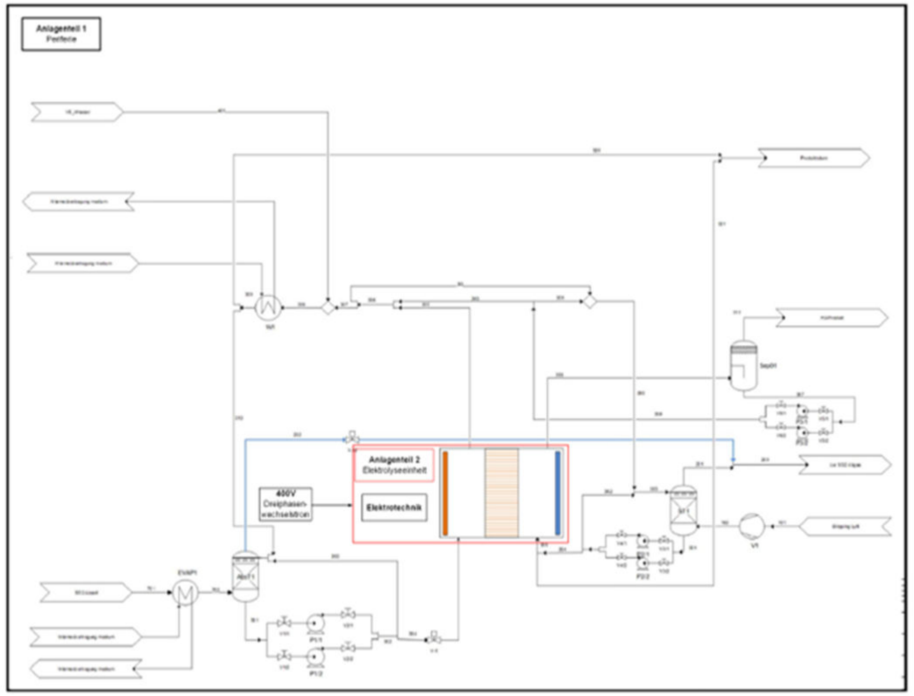
- **30-40 kW_{el}**

- Pilot design and P&ID in place
- Cost breakdown
- HAZOP analysis

- **Installation & operation in industrial environment**

GRILLO

HUGO PETERSEN
Verfahrenstechnischer Anlagenbau



Build up at the Grillo Site Duisburg

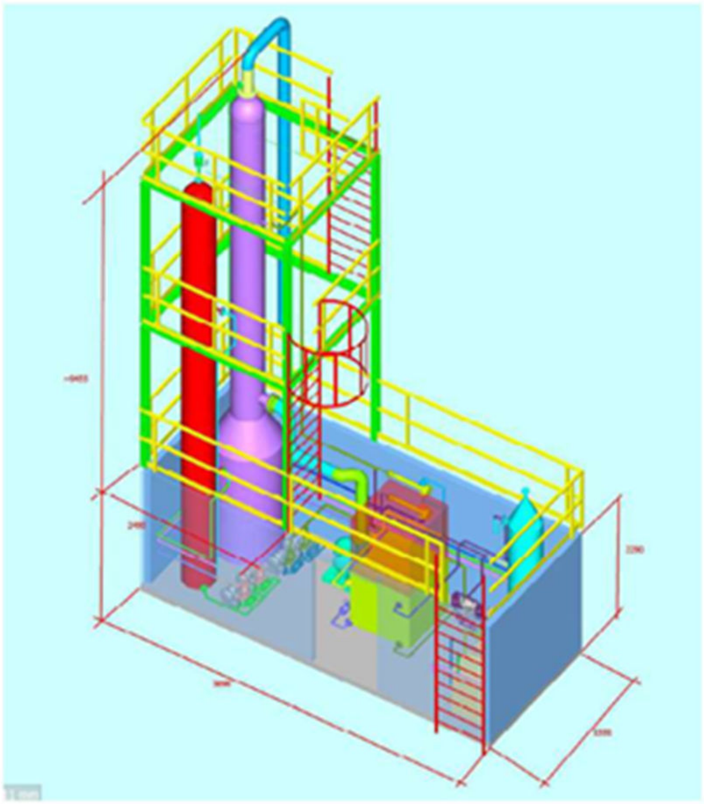


Abbildung 4: Bemaßung der Anlage für Platzbeschaffung der Pilotanlage in dem Fabrikgelände

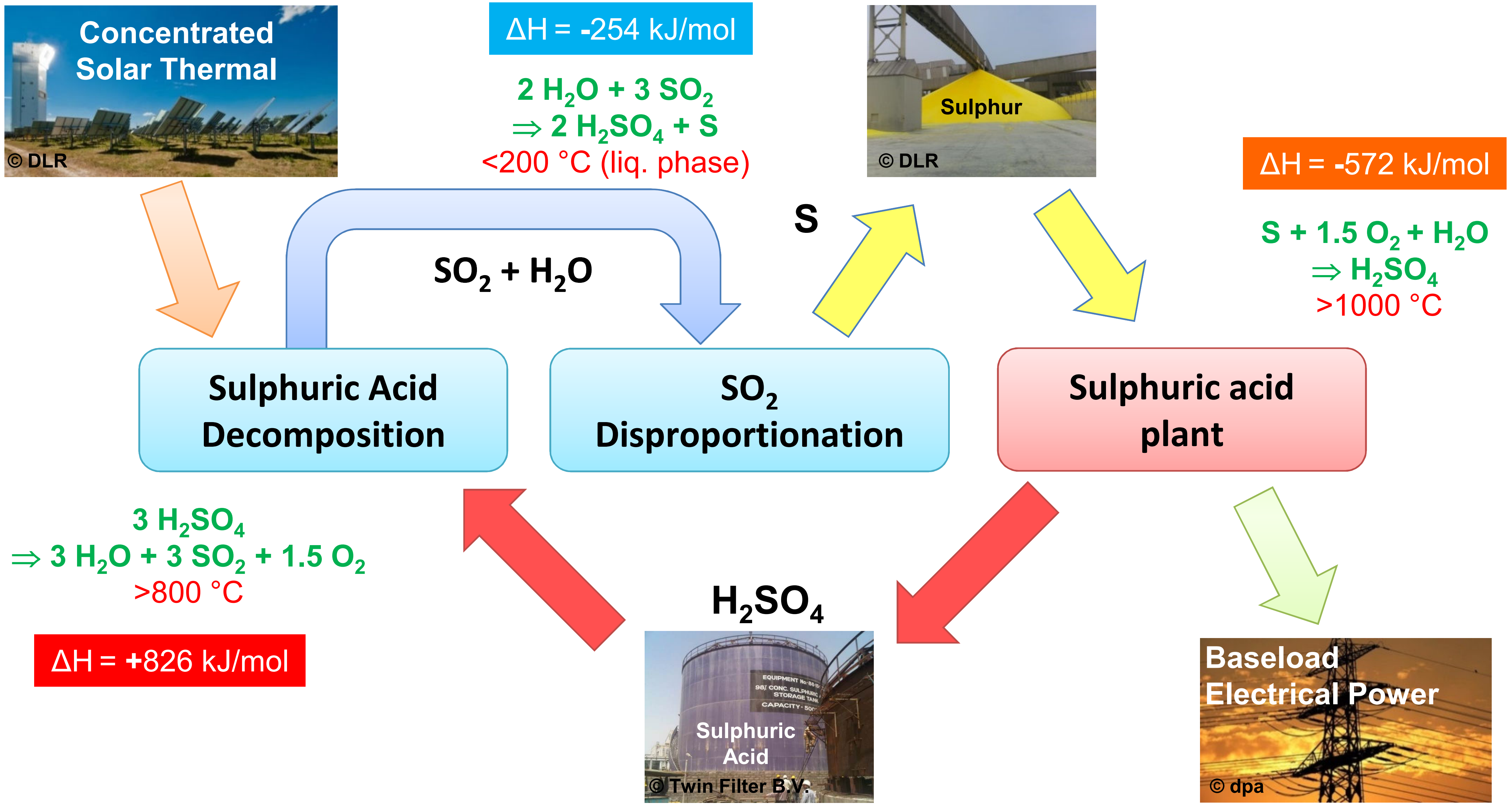
Contents

Comparison of energy storage densities

Technology	Energy density (kJ/kg)		Volumetric energy density (kJ/l)	
Hydrogen	141,886	1	~6,700	*
Gasoline	47,357	1	~35,000	
Sulphur	**9,281**	2	**~18,000**	
Lithium Ion Battery	580	2	~730	
Molten Salt	282	2	~540	
Elevated water Dam (100m)	1	2	~1	

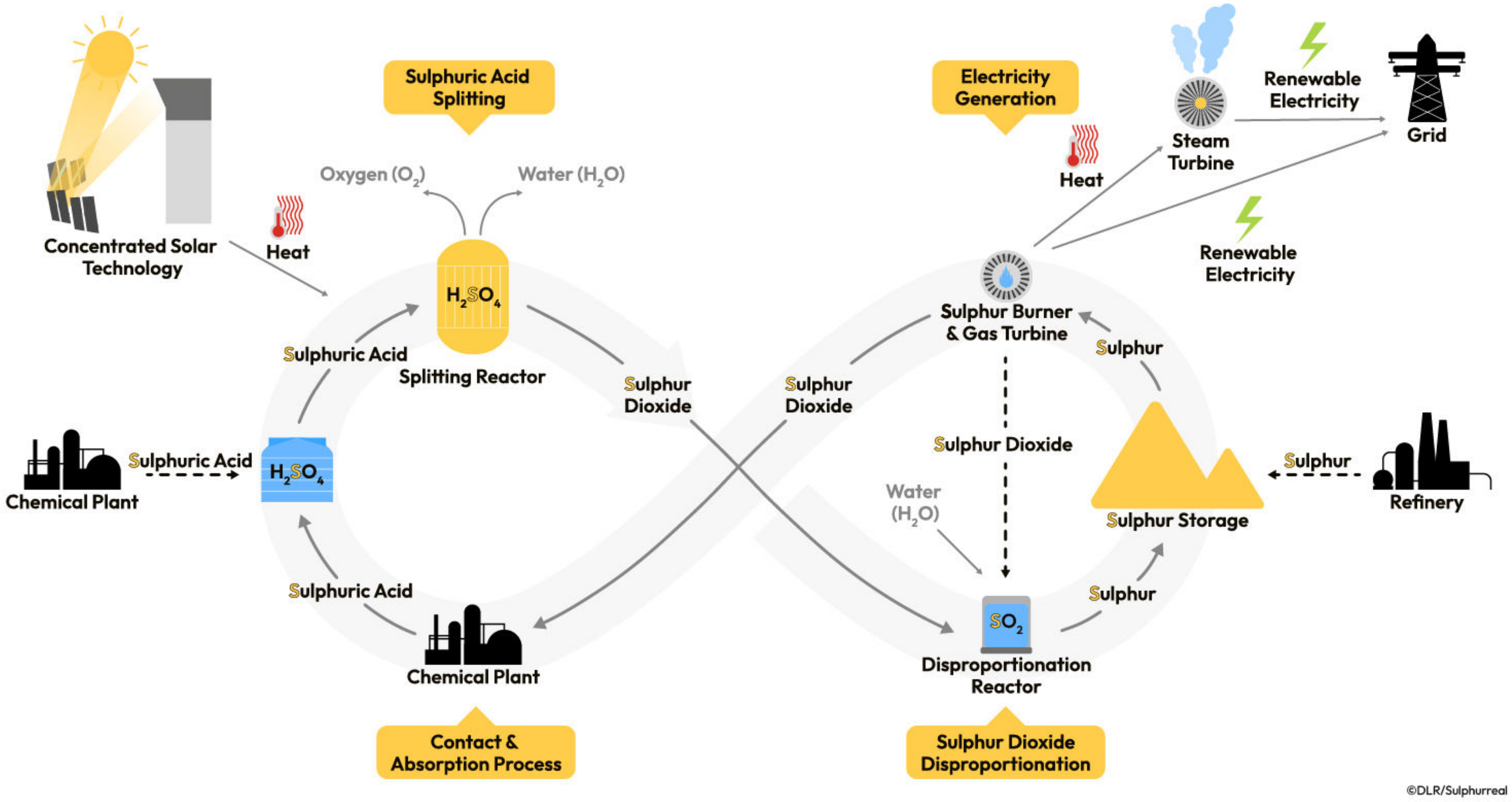
[1]College of the Desert
[2]General Atomics
*at 700 bar

Solid sulphur cycle for thermochemical storage
Baseload solar power production



Sulphur as an energy vector

Solid Sulphur cycle



https://sulphurreal.eu/project-overview/

- storage of (solar) energy in solid elemental Sulphur
- renewable heat stored in the form of elemental Sulphur is simple to store and transport
- outcome is high-quality Sulphur-combustion heat at T>1200°C
- S ready to be used as industrial energy carrier, dispatchable and on-demand when the energy is need
- “open cycle” operation: H_2SO_4, S, SO_2 from SA production or with desulphurization of flue-gas or natural gas

DLR Research on Solid Sulphur Cycle

Timeline of projects

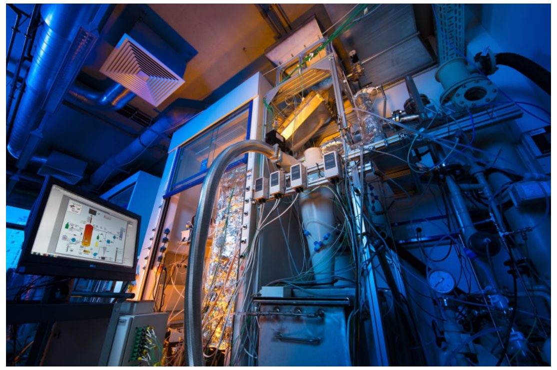
Baseload

PEGASUS

BaSiS

SULPHURREAL

2005 2010 2015 2020 2025



Centrifugal receiver prototype

500 kW prototype in Tower

H_2SO_4 splitting reactor

2 kW reactor
particle heated

2 kW reactor
continuous automated operation
hundreds of hours of catalytic splitting
low cost catalysts

Experimental testing of SO_2 disproportionation

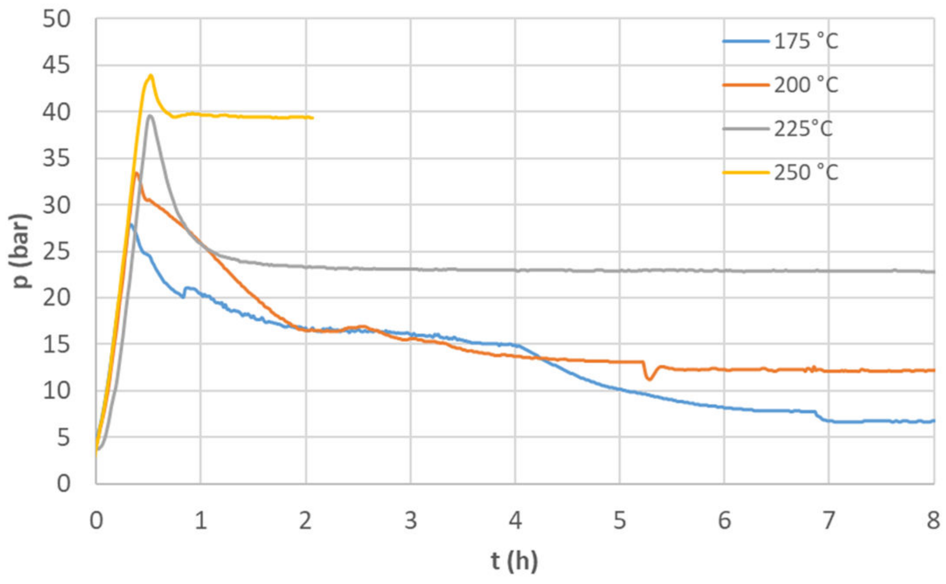
German national project BaSiS

EFRE.NRW Investitionen in Wachstum und Beschäftigung

EUROPÄISCHE UNION Investition in unsere Zukunft Europäischer Fonds für regionale Entwicklung

DLR

- Lab-scale autoclave reactor
- Internal tantalum coating
- Catalyst: hydrogen iodide (HI)
- T up to 250 °C, p up to 70 bar
- Work ongoing in PhD studies

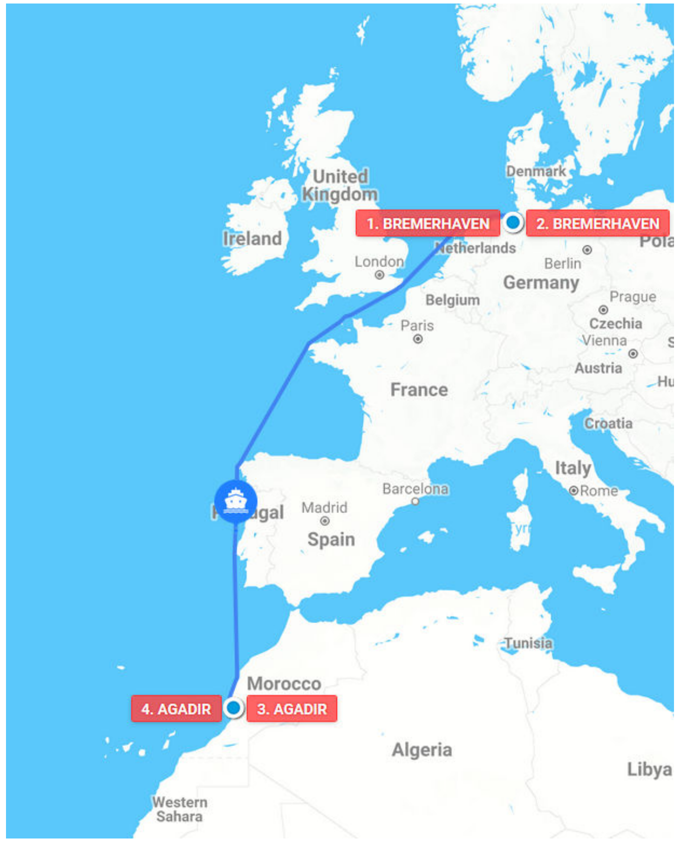


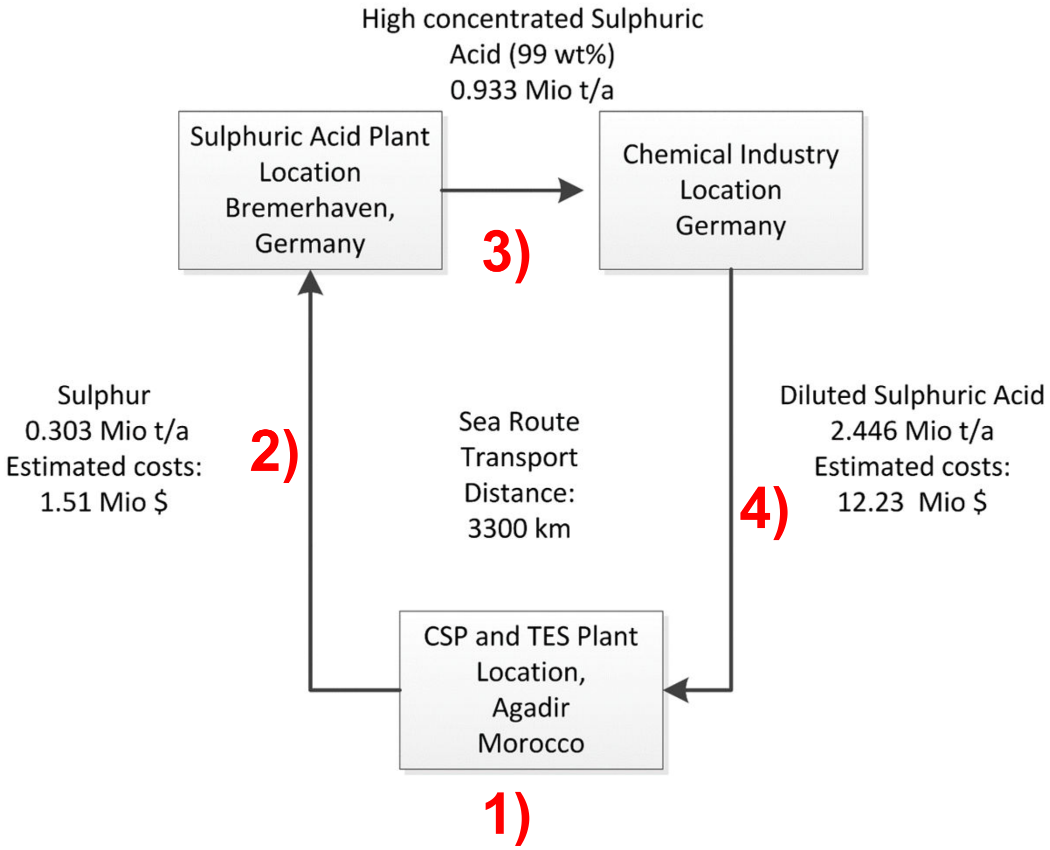
Source: DLR

Process simulation and techno-economic evaluation
Concept: Solar sulphur & combined sulphuric acid recycling

Exemplary application for Morocco/Germany

1. Solar recycling of spent sulphuric acid and sulphur production in Morocco
2. Transportation of solar sulphur to Germany
3. Sulphuric acid and baseload electricity production by chemical industry
4. Transportation of spent sulphuric acid back to Morocco





Solar to sulphur
$\eta_{sulphur}$ = 25 %

Solar to electricity
η_{electr} = 8.8 %

Economic competitiveness at CO_2 price of ~130 €/t

Source: A. Rosenstiel 2018

Summary

- Sulphuric acid is most produced base chemical and of high importance
- Sulphur based thermochemical processes applicable for
  - Efficient hydrogen production – hybrid sulphur cycle (HyS)
  - Long-duration energy storage – solid sulphur cycle (SoSu)
- Potential for integration of sulphur cycles into existing sulphuric acid plants
- Development of SO_2-depolarised electrolysis (SDE) at DLR
  - Development and testing of lab-scale prototype
  - Design of pilot for erecting on site of industrial partner Grillo in Duisburg, Germany
- Development of SO_2-disproporationation for sulphur generation at DLR
  - First testing completed, work ongoing

Thank you!

ptj projektträger jülich

Bundesministerium für Wirtschaft und Klimaschutz

Sul4Fuel

Wasserstoff in der Zink-/Schwefel-Industrie – Entwicklung und Testbetrieb einer Pilotanlage zur SO_2-depolarisierten Elektrolyse in den Grillo-Werken Duisburg

Clean Hydrogen Partnership

HySelect

hyselect.eu

European Innovation Council

Sulphurreal

sulphurreal.eu