Supporting decarbonization with new approaches in the Sulphuric Acid industry

M. Kuerten - Grillo, D. Dimitrakis - DLR

GRILLO

Oil | Gas | Fertilizers | Metallurgy | Industrial
CRU Sulphur + Sulphuric Acid 2024 Conference & Exhibition
4-6 November 2024 • Hyatt Regency, Barcelona, Spain

DLR

Agenda

1) Introduction Grillo
2) Applications Sulphur Dioxide Depolarised Electrolysis (SDE)
3) Introduction Research Center Deutsches Zentrum für Luft- und Raumfahrt
4) SDE Current status
5) Sulphuric Acid Splitting
6) Sulphur as an energy carrier

Grillo Group Added value in 4 egal entities

1

METAL
Zinc Wire, Zinc Coils. Zinc Powder, Zinc Anodes, ZAMAK®Z, ZEP®, Grillo-Concrete Protection (KKS)

2

CHEMIE
Sulfur Chemicals (Acids, Oxides, Sulfates, Sulfites), Dimethylether und Dimethylsulfat, Zincsalts, Recycling of sulfur containing waste

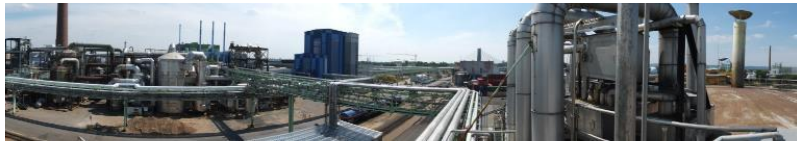
3

ZINC OXIDE
For Electronics, Chemistry, Pharmacy/Cosmetics, Food and Feed

4

RHEINZINK
For Construction Applications
Roof, Facades, Roof Drainage, Interior

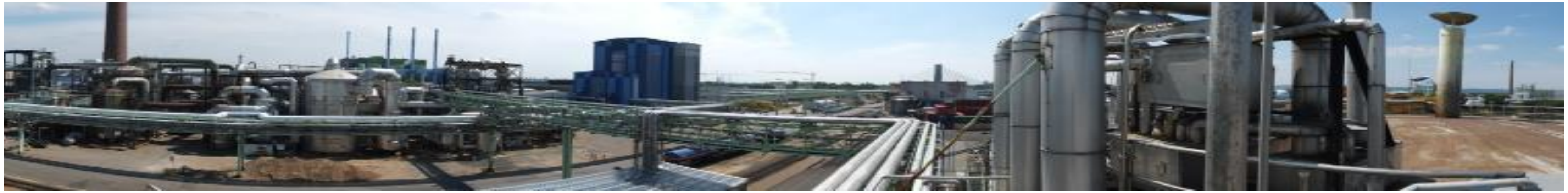
INDUSTRIEPARK FRANKFURT-HÖCHST



DUISBURG

CHEMICALS DIVISION

Industriepark Frankfurt-Höchst



Integrated site for sulphur chemicals

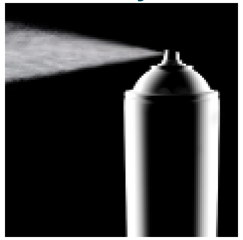
- Starting point: Burning sulphur
- Electricity and steam production w/o greenhouse gases

Sulphuric Acid

Sodium Pyrosulfite

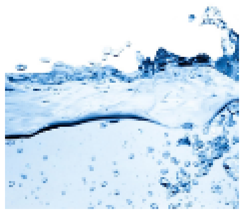
Sodium Bisulfat

Dimethylether



Oleum

Sodium Bisulfite



Dimethylsulfate

CHEMICALS DIVISION

Duisburg

Site focus on the recycling of waste streams

- Contaminated Acids
- Zinc Ashes

Recycling – Acids

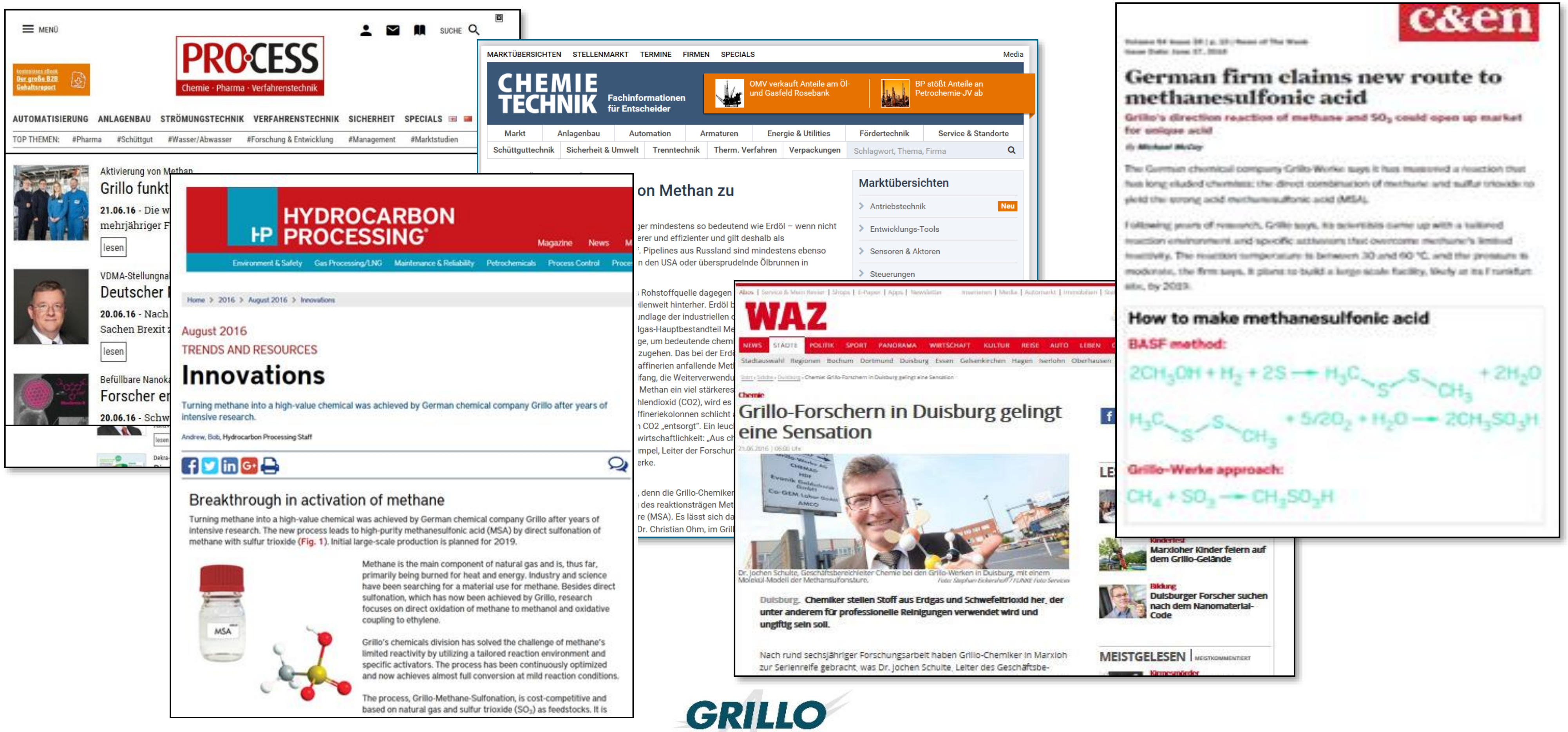
Sulphur Dioxide

Zinc Sulfate

Values for Grillo – Innovation

Methane Activation

Published in Science, March 2019



MENÜ SUCHE

PROCESS
Chemie · Pharma · Verfahrenstechnik

AUTOMATISIERUNG ANLAGENBAU STRÖMUNGSTECHNIK VERFAHRENSTECHNIK SICHERHEIT SPECIALS

TOP THEMEN: #Pharma #Schüttgut #Wasser/Abwasser #Forschung & Entwicklung #Management #Marktstudien

Aktivierung von Methan
Grillo funkt
21.06.16 - Die w
mehrjähriger F
lesen

VDMA-Stellungna
Deutscher
20.06.16 - Nach
Sachen Brexit
lesen

Befüllbare Nanok
Forscher er
20.06.16 - Schw

MARKTÜBERSICHTEN STELLENMARKT TERMINE FIRMEN SPECIALS Media

CHEMIE TECHNIK Fachinformationen für Entscheider

OMV verkauft Anteile am Öl- und Gasfeld Rosebank

BP stößt Anteile an Petrochemie-JV ab

Markt | Anlagenbau | Automation | Armaturen | Energie & Utilities | Fördertechnik | Service & Standorte

Schüttguttechnik | Sicherheit & Umwelt | Trenntechnik | Therm. Verfahren | Verpackungen

on Methan zu

Marktübersichten
Antriebstechnik Neu
Entwicklungs-Tools
Sensoren & Aktoren
Steuerungen

HYDROCARBON PROCESSING

Magazine News

Environment & Safety | Gas Processing/LNG | Maintenance & Reliability | Petrochemicals | Process Control

Home > 2016 > August 2016 > Innovations

August 2016

TRENDS AND RESOURCES

Innovations

Turning methane into a high-value chemical was achieved by German chemical company Grillo after years of intensive research.

Andrew, Bob, Hydrocarbon Processing Staff

Breakthrough in activation of methane

Turning methane into a high-value chemical was achieved by German chemical company Grillo after years of intensive research. The new process leads to high-purity methanesulfonic acid (MSA) by direct sulfonation of methane with sulfur trioxide (Fig. 1). Initial large-scale production is planned for 2019.

Methane is the main component of natural gas and is, thus far, primarily being burned for heat and energy. Industry and science have been searching for a material use for methane. Besides direct sulfonation, which has now been achieved by Grillo, research focuses on direct oxidation of methane to methanol and oxidative coupling to ethylene.

Grillo's chemicals division has solved the challenge of methane's limited reactivity by utilizing a tailored reaction environment and specific activators. The process has been continuously optimized and now achieves almost full conversion at mild reaction conditions.

The process, Grillo-Methane-Sulfonation, is cost-competitive and based on natural gas and sulfur trioxide (SO_3) as feedstocks. It is

MSA

WAZ

NEWS STÄDTE POLITIK SPORT PANORAMA WIRTSCHAFT KULTUR REISE AUTO LEBEN

Chemie

Grillo-Forschern in Duisburg gelingt eine Sensation

Dr. Jochen Schulte, Geschäftsbereichleiter Chemie bei den Grillo-Werken in Duisburg, mit einem Molekül-Modell der Methansulfonsäure.

Duisburg. Chemiker stellen Stoff aus Erdgas und Schwefeltrioxid her, der unter anderem für professionelle Reinigungen verwendet wird und ungiftig sein soll.

Nach rund sechsjähriger Forschungsarbeit haben Grillo-Chemiker in Marxloh zur Serienreife gebracht, was Dr. Jochen Schulte, Leiter des Geschäftsbe-

Marxloher Kinder feiern auf dem Grillo-Gelände

Bildung
Duisburger Forscher suchen nach dem Nanomaterial-Code

MEISTGELESEN

c&en

German firm claims new route to methanesulfonic acid

How to make methanesulfonic acid

BASF method:

$$2CH_3OH + H_2 + 2S \rightarrow H_3C{-}S{-}S{-}CH_3 + 2H_2O$$

$$H_3C{-}S{-}S{-}CH_3 + 5/2O_2 + H_2O \rightarrow 2CH_3SO_3H$$

Grillo-Werke approach:

$$CH_4 + SO_3 \rightarrow CH_3SO_3H$$

GRILLO

Values for Grillo – Quality & Environmental Protection

INTEGRATED MANAGEMENT-SYSTEM / CERTIFICATIONS:

- DIN EN ISO 9001 (Quality)
- DIN EN ISO 14001 (Environment)
- DIN EN ISO 22000 (Food)
- DIN EN ISO 50001 (Energy)
- FAMI-QS (Feed)

Authorised waste management company

HACCP-System

Certified for:
Koscher
Halal
NSF

GRILLO

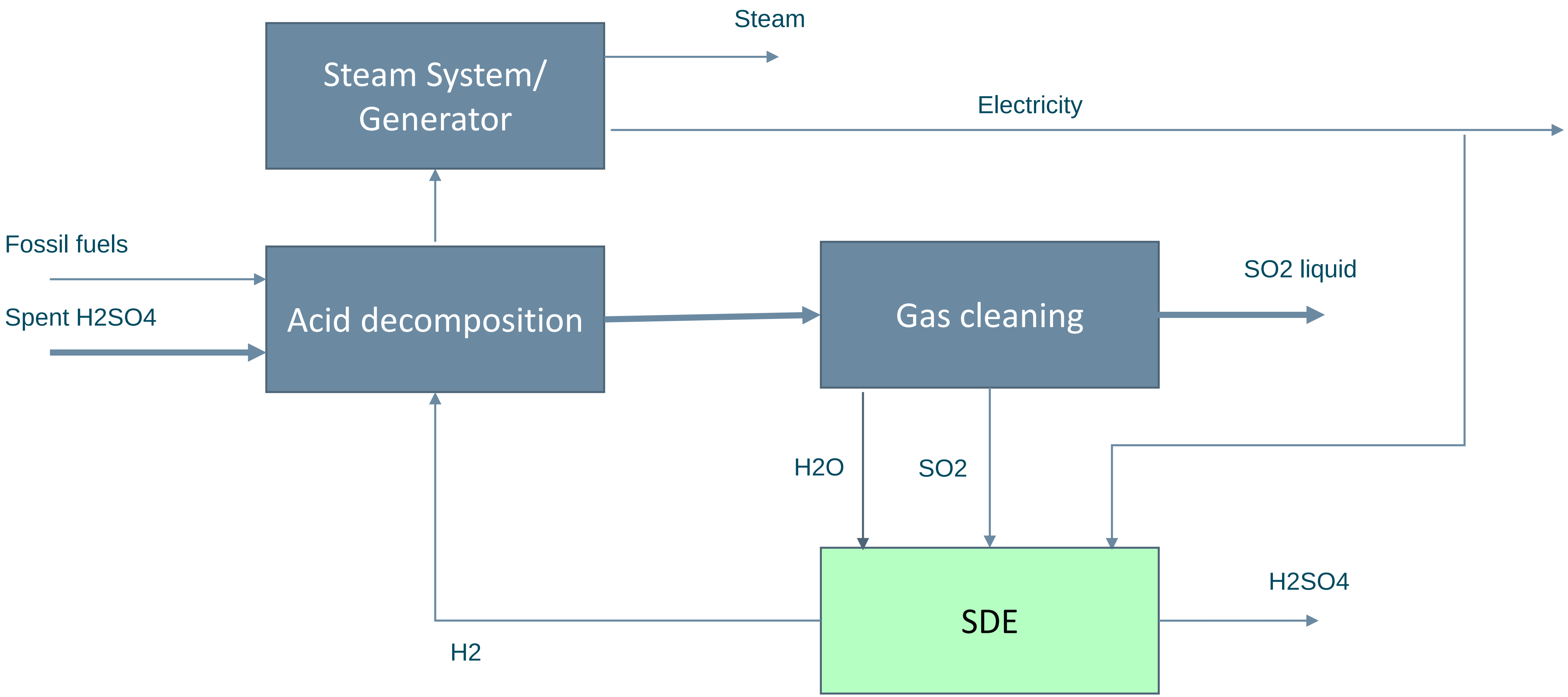
Industry decarbonisation

What is our industry doing?

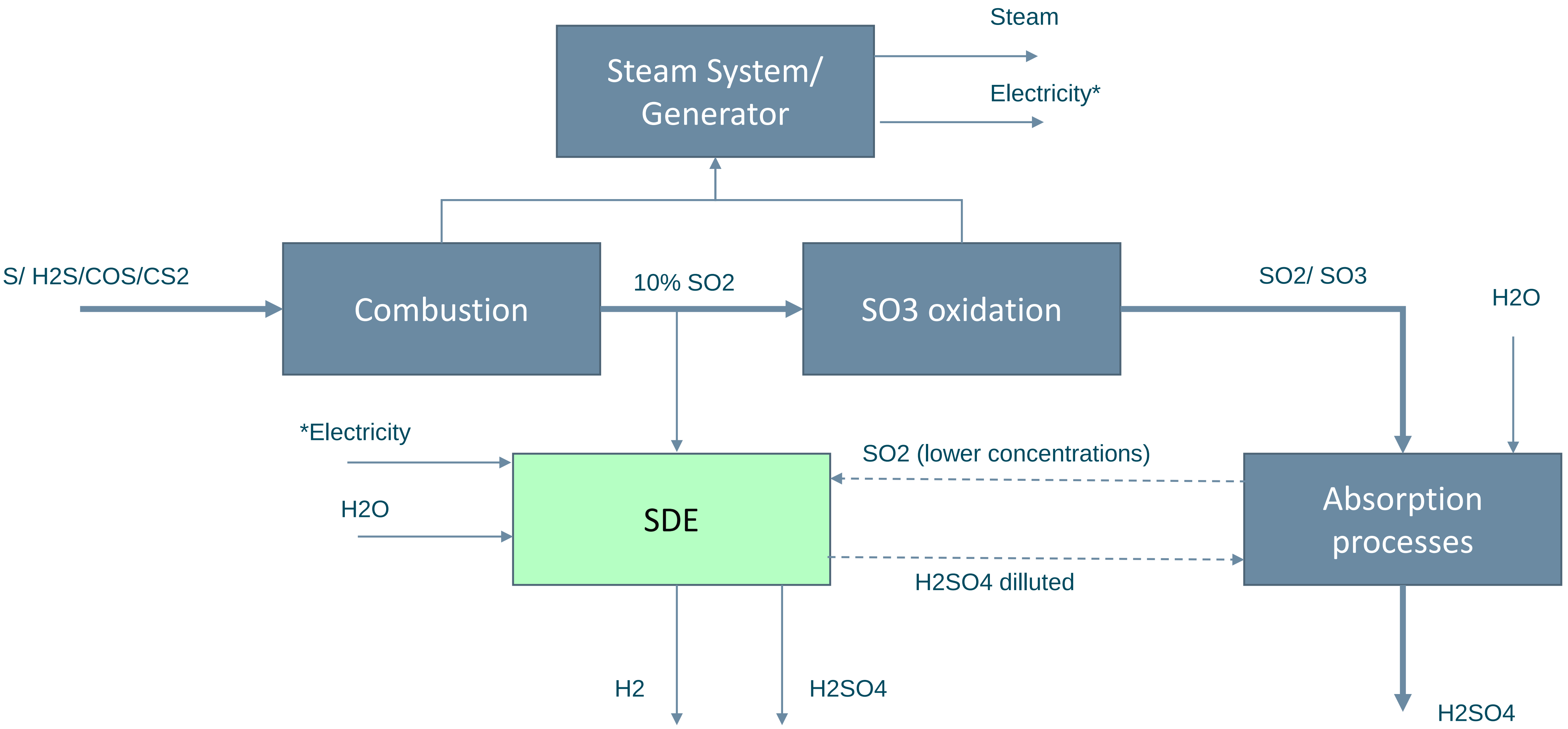
Sulphur Dioxide Depolarised Electrolysis (SDE)

$$SO_2 + 2H_2O \xrightarrow{\text{Electricity.}} H_2SO_4 + H_2$$

Application of the SDE in Duisburg **Spent Sulphuric Acid Recycling Plant**

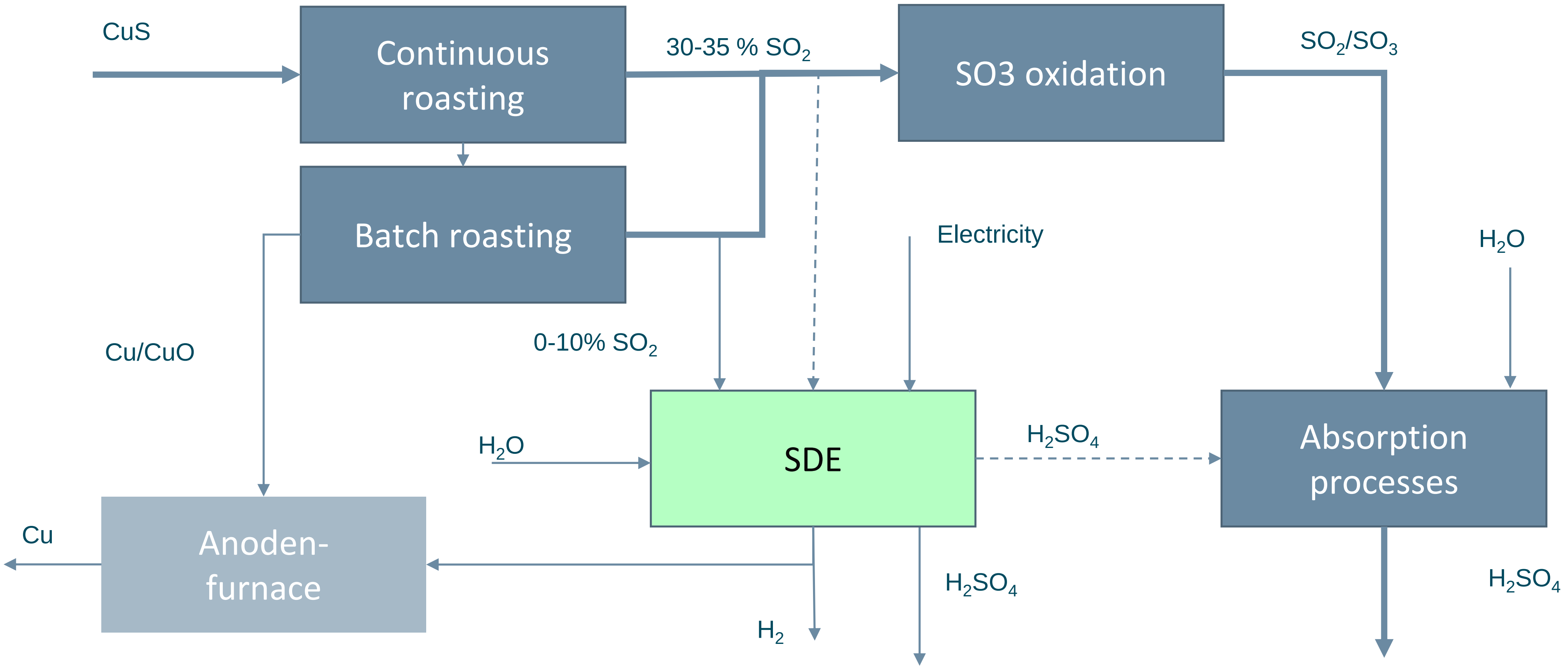


Application of the SDE in the **Sulphuric Acid Production with Sulphur burner**

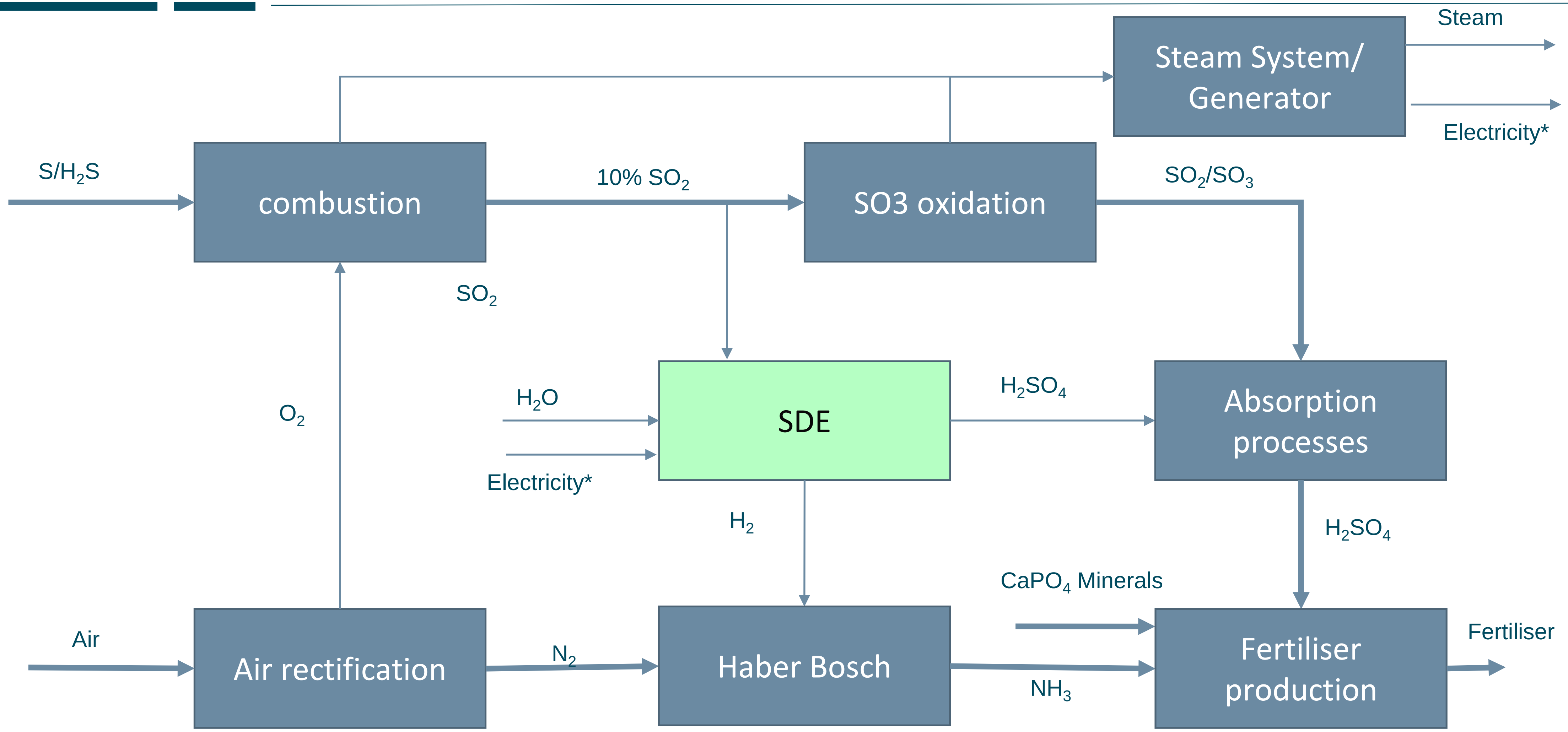


Implementation of the SDE in the **Non-Ferrous Metal Industry**

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



Implementation of the SDE in the **Fertiliser Production**



The Institute of Future Fuels

Development of alternative chemical energy carriers

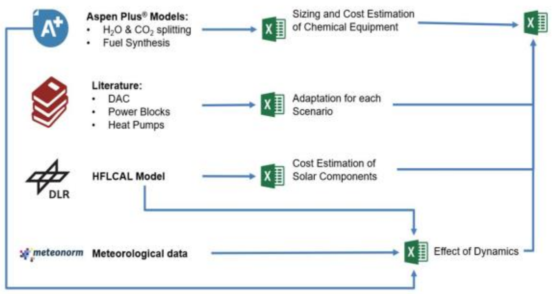
Technology development for an efficient and economic production of energy carriers for a global renewable energy industry

Solar-chemical Processes

Material- and Component Design

Demonstration

Evaluation



- Sites: Jülich and Cologne, growing to 120 employees
- Supporting structural change in the Rhenish mining area
- Contributions to the defossilization of energy, aviation and transport
- Infrastructure and large-scale facilities for process development

Renewable Production Pathways

DLR

Base Materials

Production of inorganic Pigments
Metal Melting and Recycling
Reduction of Metal oxides
Treatment of Metal Ores
Glass production

Sulphur

Sulphur as Storage Medium
Sulfuric Acid Recycling
Hybrid-Sulphur Cycle
Sulphur as Fertiliser
Sulphur Dioxide disproportionation

$Ca(OH)_2$-Looping
$CaCO_3$-Looping
Cement
Clinker
Lime
Alumina
Phosphate

Calcination

Nitrate
Ammonia
Fertilisers
Molten Salts
Air separation
Ammonia-Nitrate

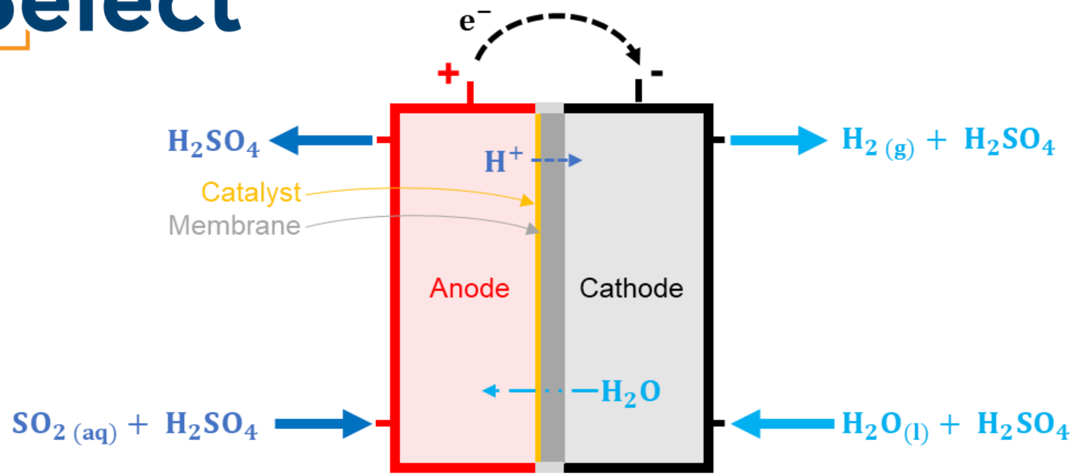
Nitrogen

PEC
HTSE
Cracking
Reforming
Gasification
Coal Drying
Coal Gasification
Syngas Production
CO_2 and H_2O splitting

Fuels

Sulphur dioxide Depolarized Electrolysis - SDE

	Reaction	Temperature (ºC)	theoretical potential (V)
Electrolysis	$SO_2 + 2\ H_2O \rightarrow H_2SO_4 + H_2$	50	0.16
Anode	$SO_2 + 2\ H_2O \rightarrow H_2SO_4 + 2\ H^+ + 2\ e^-$		
Cathode	$2\ H^+ + 2\ e^- \rightarrow H_2$		

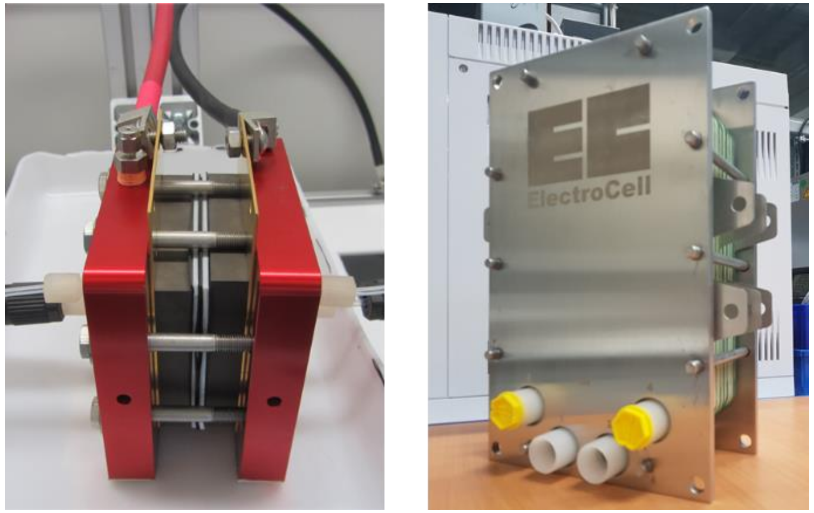


Modified water electrolysis

- producing Hydrogen and Sulphuric Acid out of SO_2 and water
- theoretical cell potential of only 0.16V
- corresponds to ~14% of conventional water electrolysis 1.23V[1]

- cloned from water PEM stacks
- 0.7-0.9V at current densities 0.2-0.4A/cm^2 at 60-80°C
- SO_2 carry-over through the PEM membrane

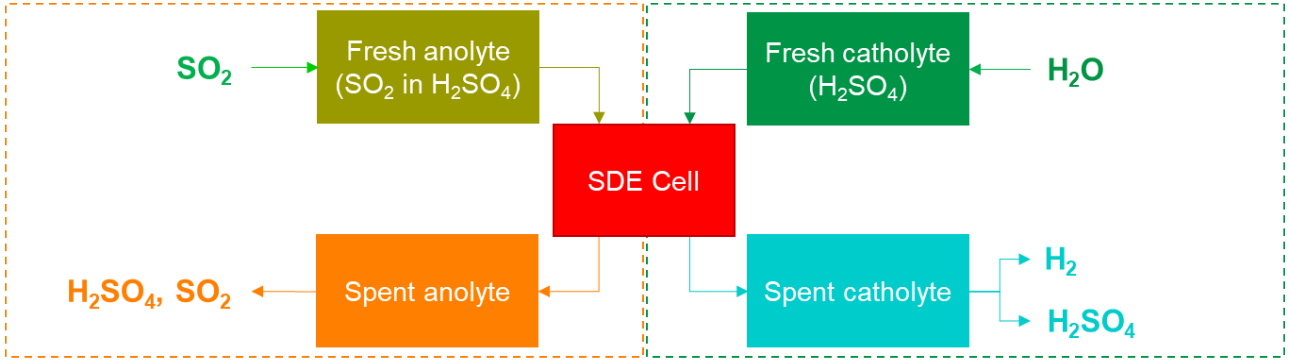
- reliability of the process
- engineering challenges: SO_2 carry-over, corrosion resistance, scale-up
- catalysts, membranes, CCMs &MEAs w/o crit. materials (Pt-, Pd-), Au-

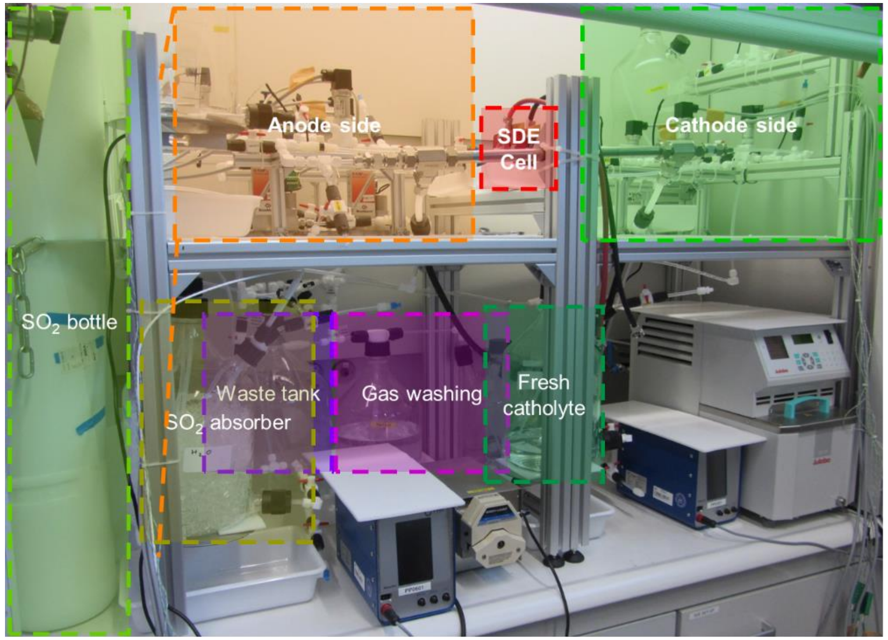


Cell[2] and Stack[3] for SDE in the experimental setup at DLR

[1]Sattler et al., Solar Energy, 156 (2017) 30-47
[2]https://www.scribner.com/products/redox-flow-cell-testing/redox-flow-cell-test-fixture/
[3]https://www.electrocell.com/products/electrochemical-flow-cells/electro-mp-cell

Sulphur dioxide Depolarized Electrolysis - SDE

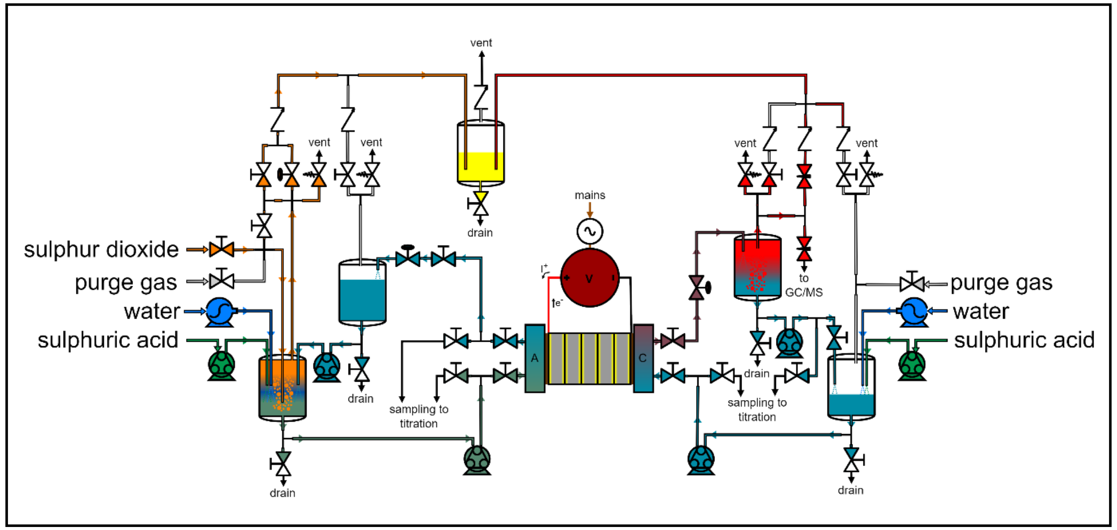




GC and MS

Experimental setups in DLR

- to guide the jump from the lab-scale to a pilot unit electrolyzer
- Lab-scale
  - single cells & stacks
  - 5, 25 & 100cm^2
  - commercial PEM components
  - custom & modified components
- Pilot electrolyzer
  - 30-40kW$_{el}$
- Installation & operation in industrial environment



Sulphur dioxide Depolarized Electrolysis - SDE

Results

- commercial components
- not optimal

- applied potentials
  - 0.60 – 0.95 V
- flowrates of single cells
  - ~10 mL/min
- several test runs in the order of 10-15h each

- **H_2 production**
  - ~6,3% H_2 in N_2, GC spectra

Sulphur dioxide Depolarized Electrolysis - SDE

Results

- commercial components
  - total of >40h of operation
- Calculated specific energy consumption
  - **25-30 kWh/kg H_2**
  - cf. PEM: 50 kWh/kg H_2
- Long-term runs
  - ~100h
  - Continuous multi-cycle operation
  - Baseline
- Modified components
- **Promising results!**

Sulphuric Acid Splitting - SAS

	Reaction	Temperature (ºC)	ΔHº (kJ/mol S)
Sulphuric Acid Splitting - SAS	$H_2SO_4(g) \rightarrow SO_2(g) + H_2O(g) + 1/2\ O_2(g)$		
Sulphuric Acid Dissociation - SAD	$H_2SO_4(g) \rightarrow H_2O(g) + SO_3(g)$	450-500	+98
	or equivalent:		
	$H_2SO_4(l) \rightarrow H_2O(l) + SO_3(l)$		+134
Sulphur trioxide splitting - STS	$SO_3(g) \rightarrow SO_2(g) + 1/2\ O_2$	650-950	+99

HySelect

Sulphurreal

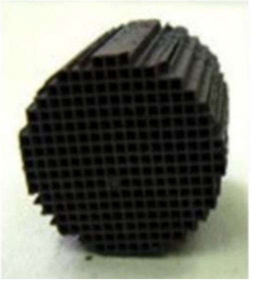
DLR

Catalytic splitting

- use catalysts to lower the required temperature of the splitting reaction
- no expensive PGM-based catalysts → single/mixed oxides of abundant transition metals[1, 2, 3]
- certain MOx compositions show catalytic activity close to Pt/Al_2O_3 benchmark catalysts[4, 5]

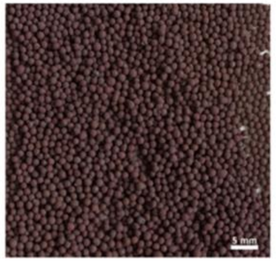
- iron oxide (Fe_2O_3) or CuO-based compositions[6, 7, 8]
- long-term stability (≥500h) and limited deactivation (2-7%)
- temperatures of 800-900ºC at 1atm to achieve conversions close to equilibrium

CuO– coated SiSiC honeycomb



Fe_2O_3– coated SiSiC foams

Fe_2O_3 granules

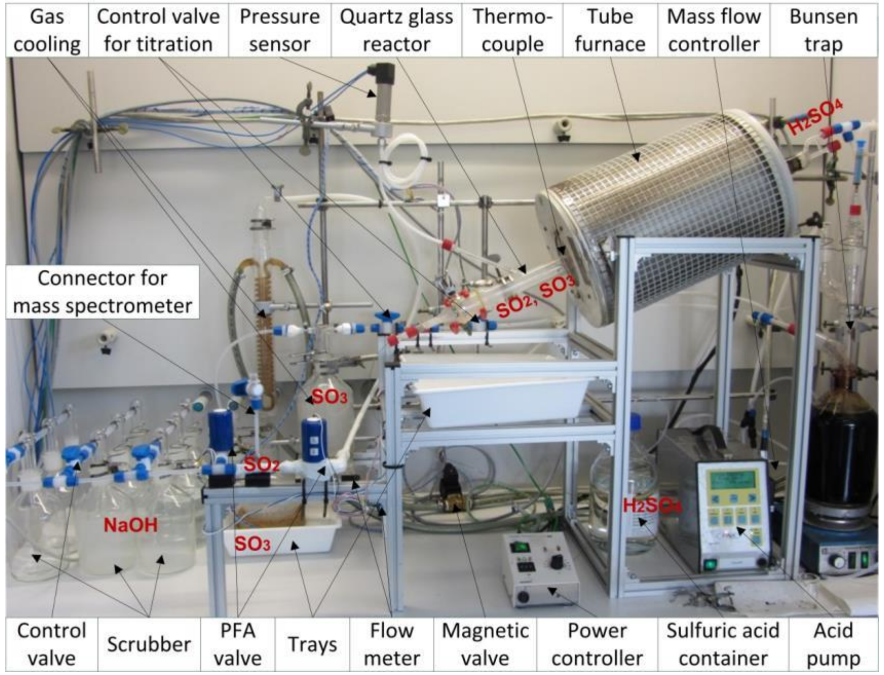


Metal oxide structures[8, 9, 10] employed for catalytic Sulphuric Acid Splitting in DLR

1. Norman et al.; Int. J. Hydrogen Energy, 7 (1982) 545-556.
2. Brittain and Hildenbrand, J Phys Chem, 87 (1983) 3713-3717.
3. Dokiya et al., Bull. Chem. Soc. Jpn., 50 (1977) 2657-2660.
4. Barbarossa et al.; Int. J. Hyd. Energ., 31 (2006) 883-890.
5. Brutti et al.; Ind. & Eng. Chem. Res., 46 (2007) 6393-6400.
6. Giaconia et al.; Int. J. Hydrog. Energ., 36 (2011) 6946-6509.
7. Karagiannakis et al.; Int. J. Hyd. En., 37 (2012) 8190-8203.
8. Karagiannakis et al.; Int. J. Hyd. En., 36 (2011) 2831-2844.
9. Agrafiotis et al., Applied Catalysis B: Environmental, 324 (2023) 122197
10. Tsongidis et al., AIP Conf. Proc. 2126 (2019), 210009

Sulphuric Acid Splitting - SAS

Sulphurreal HySelect DLR



DLR lab reactor for catalytic Sulphuric Acid Splitting[1]

- Evaluation by lab-and pilot scale reactors
- Long-term performance (100s of hours)
- 850°C, ambient pressure
- conversions close to equilibrium

- Formation of stable sulphates common problem for both oxides and noble metals supported on oxides
- Deactivation more significant at lower T
- Metal V-based formulations ≤ 650°C
    - Cu-V[2] & partially molten phase vanadates[3]

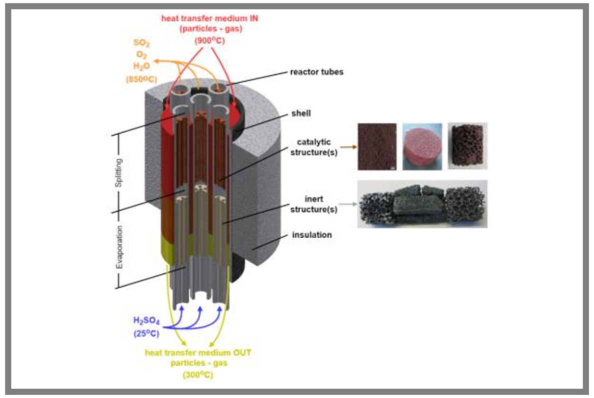
[1]Agrafiotis et al., Applied Catalysis B: Environmental, 324 (2023) 122197
[2]Machida et al.; Chem. Comm., 47 (2011) 9591-9593, Chem. Mater., 24 (2012) 557-561
[3]Kawada et al.; Catal. Sci. Technol., 4 (2014) 780-785, Ind. Eng. Chem. Res., 55 (2016) 11681-11688

Sulphuric Acid Splitting - SAS

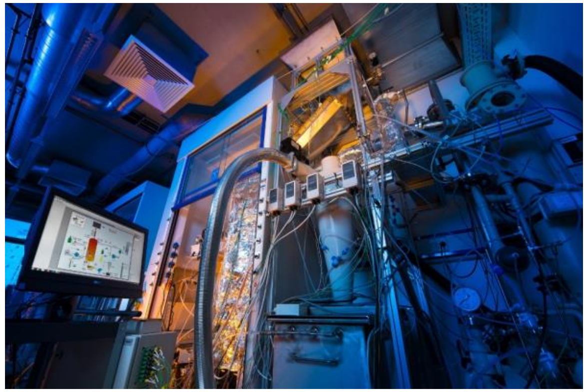
Catalytic splitting with renewable heat

- heat transfer medium
- shell & tube HX design

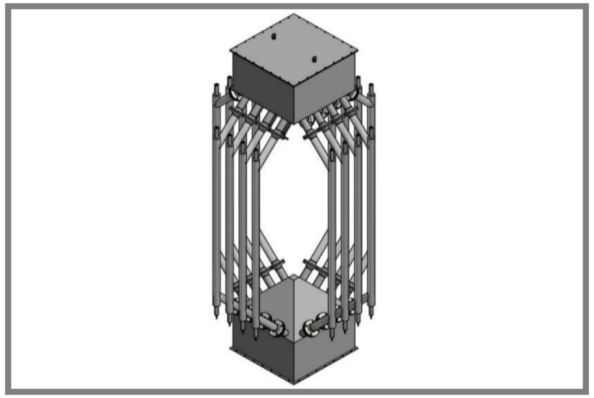
- non-moving catalytic bed
  - granules
  - pellets
  - honeycombs
  - foams



allothermal reactor concept[1]



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



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

Sources of renewable heat

- Concentrating Solar Technologies
  - solar tower

- Options for renewable heat storage
  - latent heat or
  - chem. energy

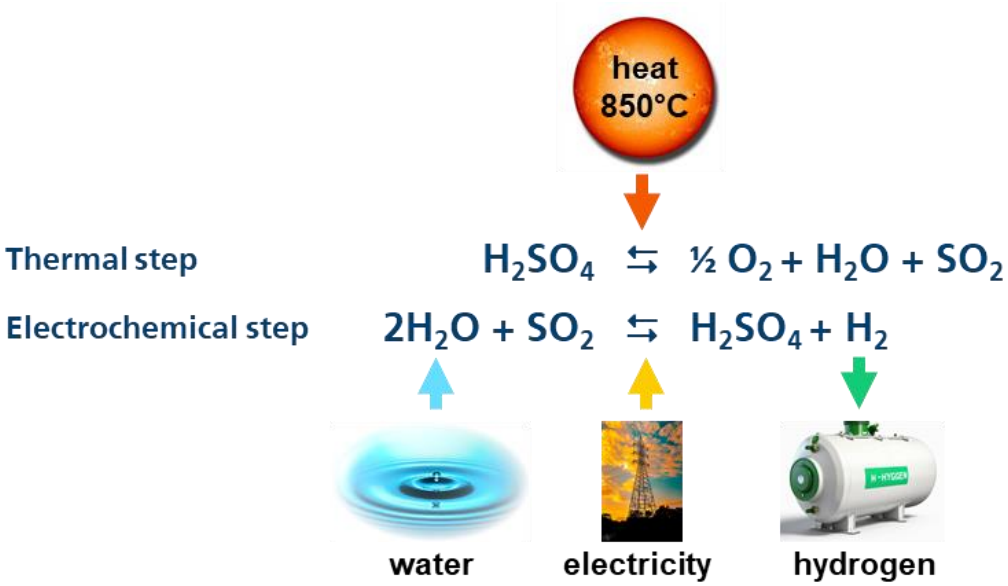
CentRec® at the DLR tower[4]

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/

The Hybrid Sulphur Cycle



Hydrogen Europe, Clean Hydrogen Production Pathways, Report 2024

HyS cycle*

- thermochemical water splitting
- Sulphuric acid splitting + SDE
- outcome is H_2 and sulphuric acid which is completely recycled in the process
- demo HyS plant (kg/day H_2) planned operation 2026
- “open cycle” operation: H_2SO_4, SO_2 from SA production

www.hyselect.eu

*Brecher LE, Wu CK, United States Patent 3888750: Westinghouse Electric Corporation (Pittsburgh, PA); 1975

Sulphur as an energy vector

Wong et al.; Sol. En., 118 (2015) 134-44

	Reaction	Temperature (°C)	ΔH° (kJ/mol S)
Sulphuric Acid Decomposition	$3\ H_2SO_4(aq) \rightarrow 3\ SO_2(g) + 3\ H_2O(g) + 3/2\ O_2(g)$	650-950	+826
Sulphuric Acid Disproportionation	$3\ SO_2(g) + 2H_2O(l) \rightarrow 2\ H_2SO_4(aq) + S(s)$	50-200	-254
Sulphur combustion	$S(l) +\ O_2(g) \rightarrow SO_2(g)$	500-1500	-297
Contact process	$SO_2(g) + 1/2\ O_2(g) \rightarrow SO_3(g)$	*380-635*	*-99*
Absorption	$SO_3(g) +\ H_2O(g) \rightarrow H_2SO_4(aq)$	*55-280*	*-176*

Solid Sulphur cycle*

Sulphurreal

www.sulphurreal.eu

- thermochemical direct storage of (solar) energy to solid elemental Sulphur
- renewable heat stored in the form of elemental Sulphur is simple to store and transport

- decomposition of H_2SO_4 + SO_2 disproportionation + elemental Sulphur combustion

- 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

*Norman, J.H, General Atomics, Sulfuric acid-sulfur heat storage cycle, US Patent 4,421,734, (1978)

Outlook

Focus

- Sulphur dioxide Depolarized Electrolysis
- Catalytic Sulphuric Acid splitting
- Sulphur as an energy vector

Approach

- actively pursued as viable add-on or supplementary technologies
- a meaningful next step in decarbonization of the industry
- significant commercialization potential
- involvement of industry enables a positive outlook for a sustainable future

Contact

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Clean Hydrogen Partnership

Co-funded by the European Union

HySelect

Efficient water splitting via a flexible solar-powered Hybrid thermochemical-Sulphur dioxide depolarized Electrolysis Cycle

www.hyselect.eu

HySelect EU-Project

@HySelect

This project is supported by the ***Clean Hydrogen Partnership*** *and its members* ***Hydrogen Europe*** *and* ***Hydrogen Europe Research*** *under the Grant Agreement Nr. 101101498.*