Renewable Power Generation by Solar Particle Receiver Driven Sulphur Storage Cycle

SO_3 splitting catalytic systems development

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AEROSOL & PARTICLE TECHNOLOGY LABORATORY

The reaction – background information & challenges

The Solid Sulphur Cycle

	Reaction	Temperature
Sulphuric acid decomposition	$2H_2SO_4(aq) \rightarrow 2H_2O(g) + 2SO_3(g)$	450-500°C
	$2SO_3(g) \rightarrow O_2(g) + 2SO_2(g)$	700-950°C
Disproportionation	$2H_2O(l) + 3SO_2(g) \rightarrow 2H_2SO_4(aq) + S(s)$	50-200°C
Sulphur Combustion	$S(l) + O_2(g) \rightarrow SO_2(g)$	500-1500°C

Common for all sulfur-based thermochemical cycles

Catalyst	Temperature	Performance	Conclusion
Pt/Al_2O_3 (TiO_2)	700-800°C	Activity close to thermodynamic, Pt sublimation, sulfidation	Not currently considered
Fe_2O_3	**800-900°C**	**Fair bur lower activity cf. best performers, stable long-term**	**Benchmark catalyst, low cost**
Cr_2O_3	800-900°C	High activity, Cr leaching	Not currently considered
$Fe_xCr_{1-x}O_3$	800-900°C	High activity, eventual Cr leaching, structural changes	Not currently considered
CuO	800-900°C	High activity, structural changes	Cost issue
CuO/Al_2O_3	**800-900°C**	**High activity, stable long-term**	**Promising,** minimize Cu content
Cu-Fe-Al mixed ox.	800-900°C	High activity, structural changes / not sufficiently tested	Likely not preferred option
$Cu_{1-x}V_xO_z$	**600-650°C**	**High activity but with dilute SO_3, stable, partial liquefaction**	**Promising but challenging**

Main challenge: *Chemically & thermally harsh conditions for catalysts & reactor construction materials*

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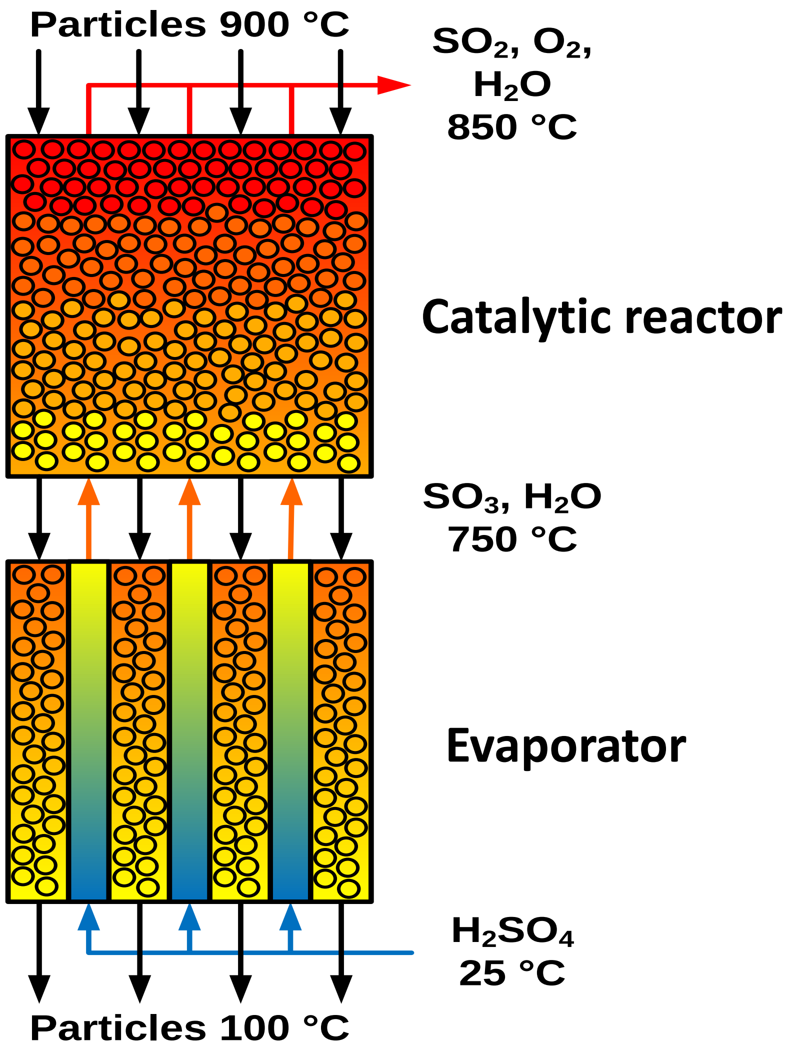
The PEGASUS approach – straightforward concept (I)

Catalytically-modified particles (proppants) as **both HTF & catalyst** for SO_3 splitting

Reactor downstream the particle receiver

"Catalytic" Fe/Cu/Mn-modified bauxite proppants → moving catalyst bed → direct contact with SO_3 vapours ($SO_3 \rightarrow SO_2 + O_2$); downstream indirect evaporation of H_2SO_4 in SO_3 and $H_2O_{(g)}$ in a counter-flow cascade-like configuration.



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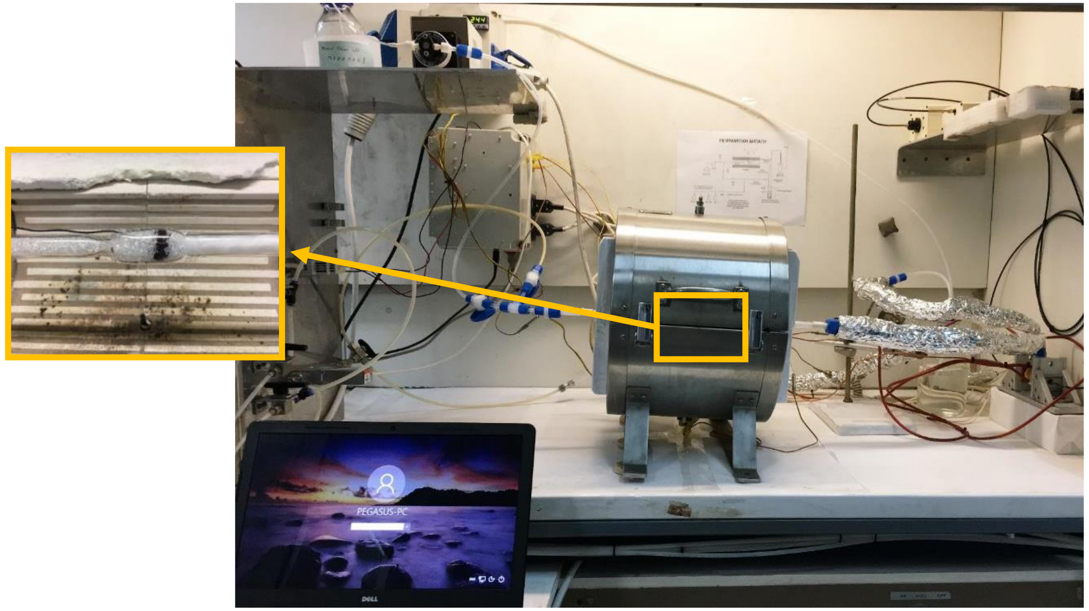
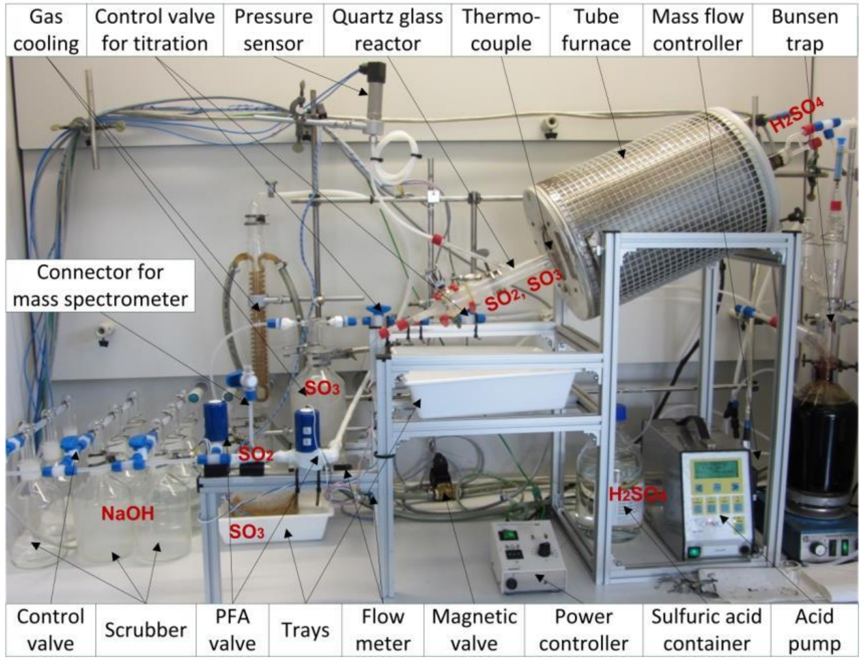
Catalytic evaluation of particles & proppants (II)

Catalytic & thermomechanical evaluation of > 60 samples:

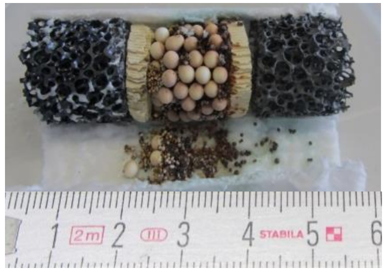
- ✓ *Modified & unmodified bauxite-based proppants*
- ✓ *Iron oxide-based dense particles*
- ✓ *Copper oxide-based dense particles*



Screening setup (1 – 10 h)



Long-term stability setup (100 - > 1000 h)



- Evaluation in fixed bed reactors with concentrated sulfuric acid feed @ 800-900^oC
- Analysis by: SO_2 via UV-Vis spectrometry, O_2 measurements, titration

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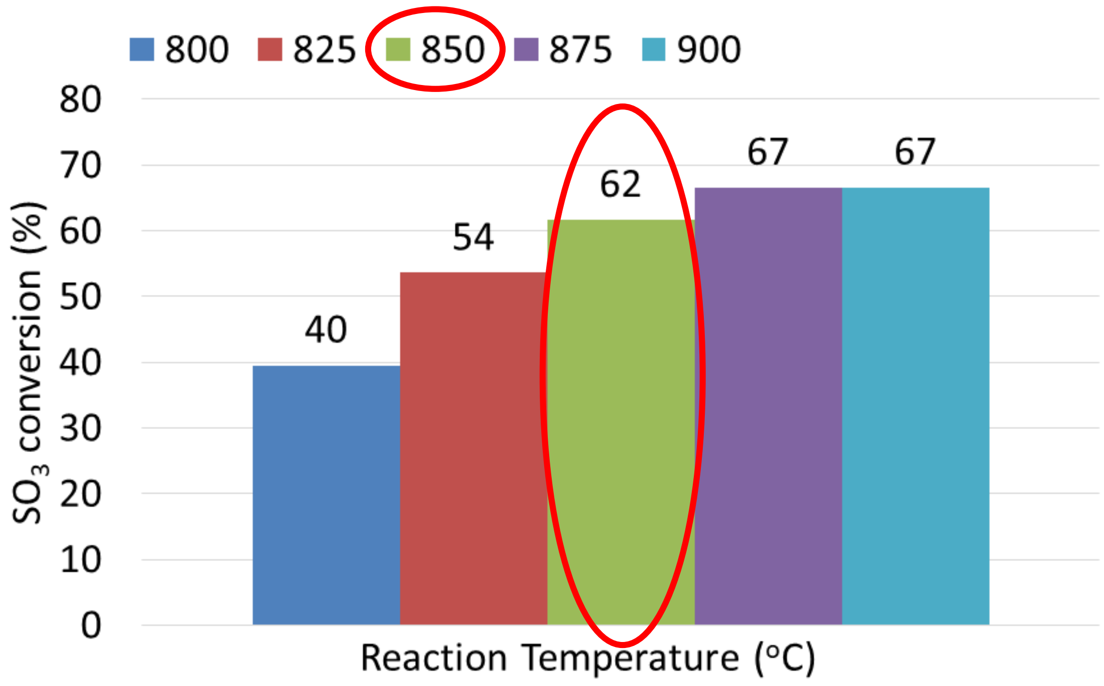
Catalytic evaluation of particles & proppants (III)

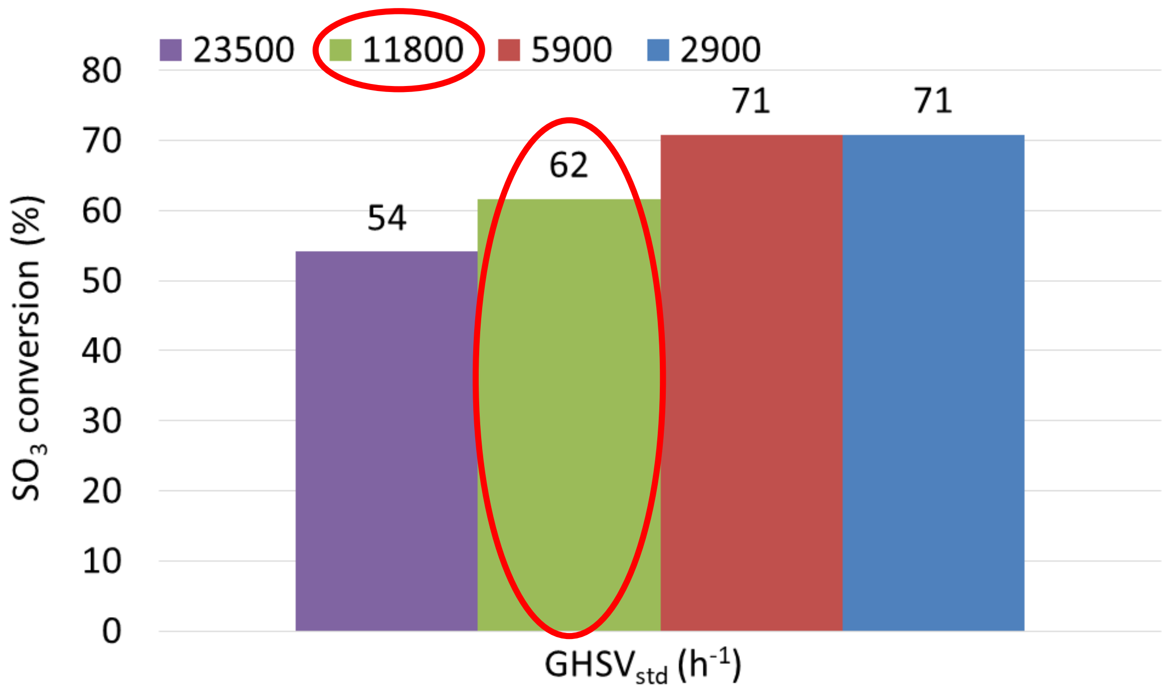
Parametric tests: effect of reaction temperature & residence time/GHSV on SO_3 conversion

Sample: Cu-Mn-O modified proppant

@850°C



GHSV = 11800 h^{-1}



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Catalytic evaluation of particles & proppants (IV)

Most promising samples from screening studies - overview

No	Sample name	SO_3 conversion (%) @850°C	Crushing Strength (in N)		CS % change
			Fresh particles	Used particles	
1	CuO_clay=15/85_1 dense particles	**63.9**	16	18	**+12.5**
2	CuO_clay=15/85_2 dense particles	**63.4**	15	22	**+46.7**
3	BCH-18 (Cu-modified proppants)	**62.4**	102	77	**-24.5**
4	BCH-25 (Cu-Mn-modified proppants)	**61.6**	55	57	**+3.6**
5	BCH-26 (Cu-Mn-modified proppants)	**59.4**	53	53	**0**
6	CuO_clay=75/25 dense particles	**59.3**	32	33	**+3.1**
7	BCH-19 (Cu-modified proppants)	**59.3**	74	69	**-6.8**
8	Fe_2O_3 particles dense particles	**54.8**	23	29	**+26.1**

- Choice on the basis of combined high SO_3 conversion, thermomechanical stability (i.e. CS parameter) & in-principle production scalability
- Additional purpose-designed attrition tests indicated that thermomechanical stability still needs to be improved

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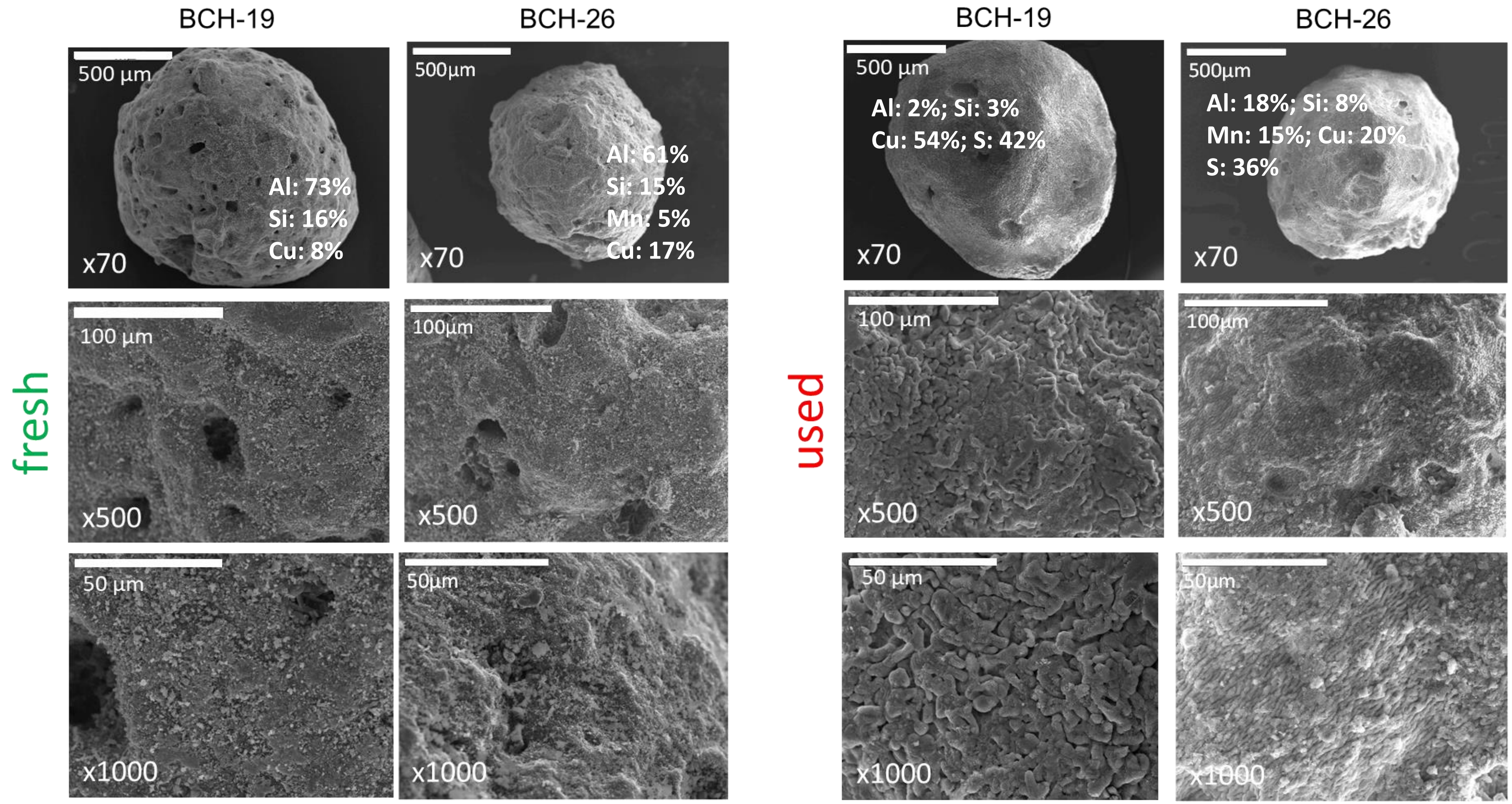
Post characterization of exposed samples – indicative results (I)

Comparative physicochemical characterization of pristine (fresh) & exposed (used) samples



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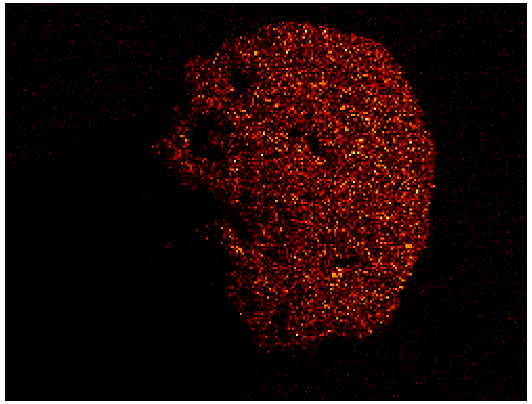
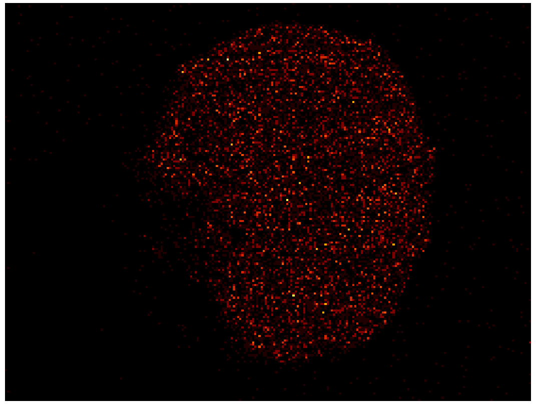
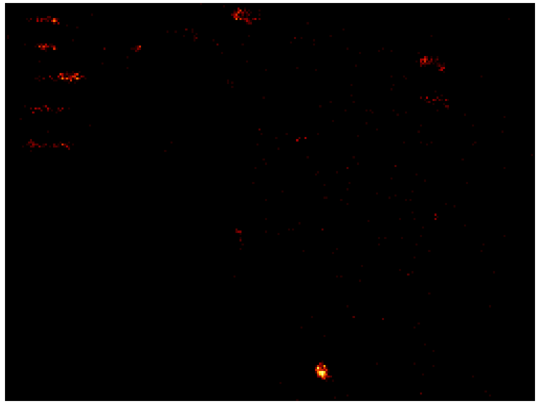
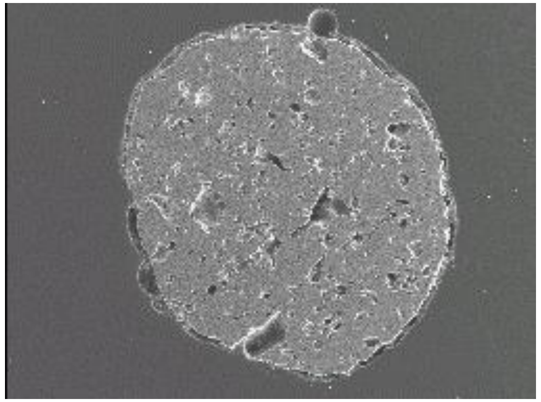
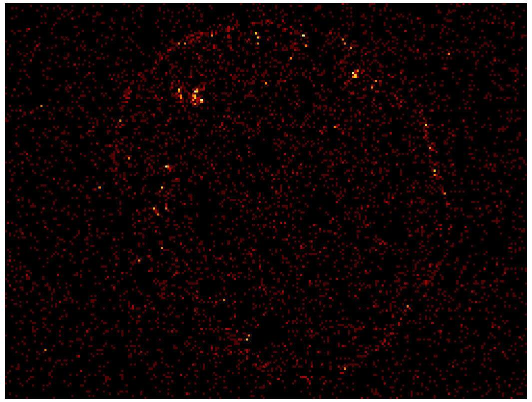
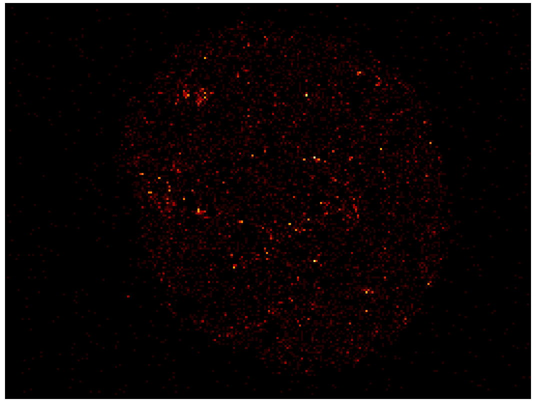
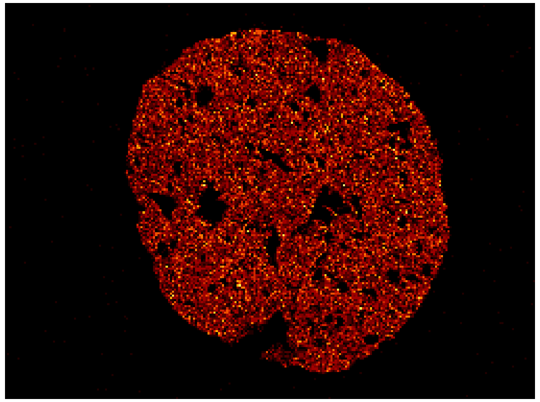
- Macroporosity visible in the fresh/used samples. Signs of sintering in used samples
- Atomic analysis (wt%): Al, Si, Cu & Mn as main phases; S clearly detected in the used samples

Post characterization of exposed samples – indicative results (II)

Sample view		Element		
		S	Cu	Al
Surface				
Cross-section				

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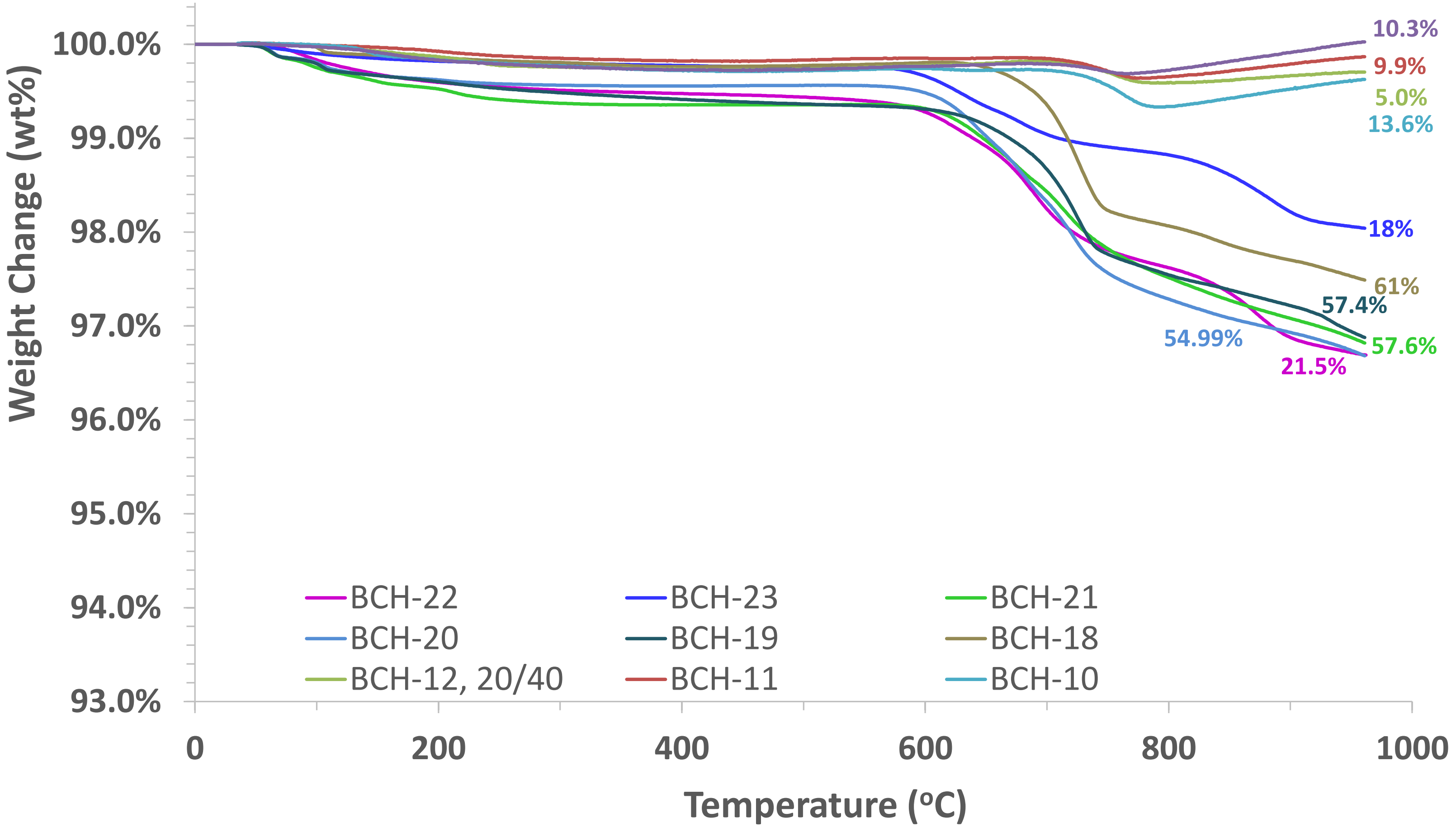
- Strong indication for the formation of a surface CuO-rich layer
- Sulfur detected mostly on the surface (spatial correlation with CuO)

Post characterization of exposed samples – indicative results (III)



- Weight loss due to sulphates decomposition is directly proportional to catalytic activity
- Reaction mechanism via cyclic sulphates formation & decomposition:

$$MO + SO_3 \leftrightarrow MSO_4 \leftrightarrow MO + SO_2 + 0.5O_2$$

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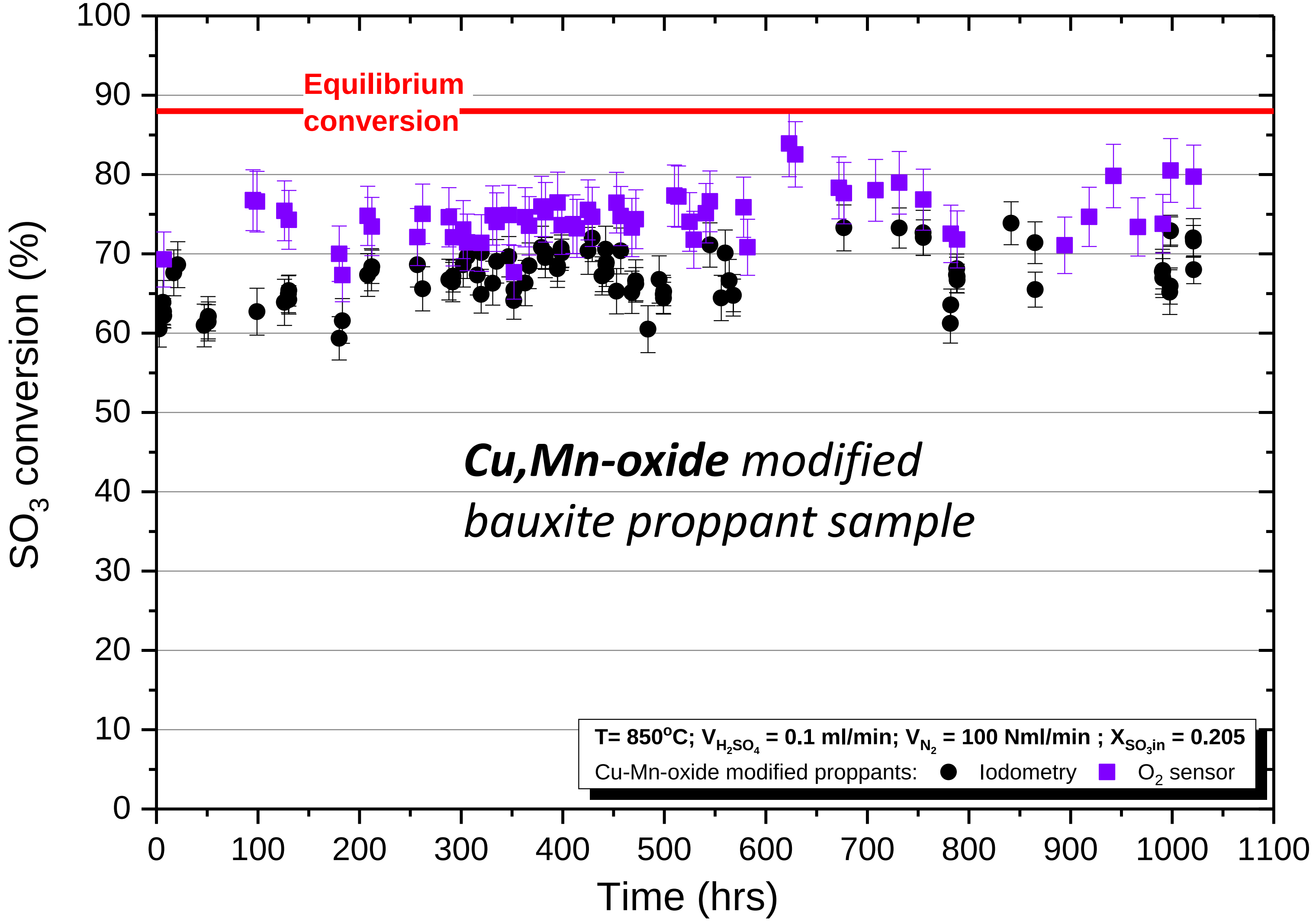
Long-term exposure test of best performing modified proppants



- High & stable conversion @ 60-80% (equilibrium conversion @ conditions employed ~ 89 %)
- No performance loss after > 1000 h on stream

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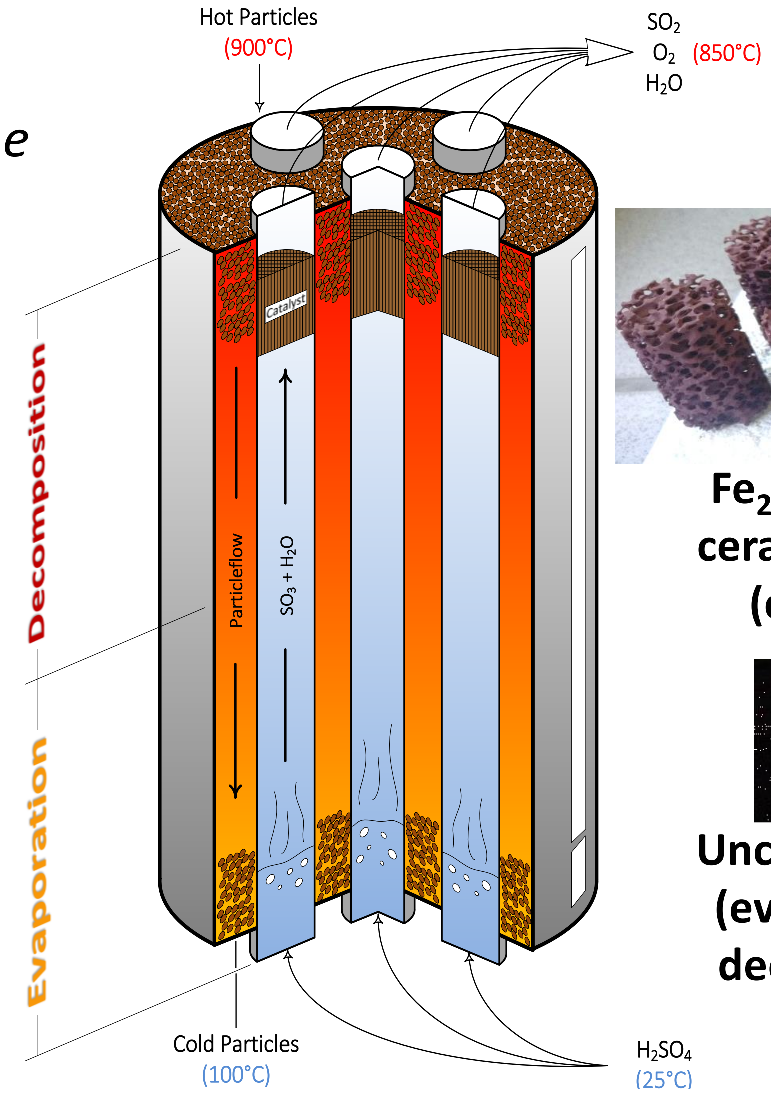
The PEGASUS approach – revised concept

Challenges of straightforward concept:

- ✓ *Catalytic modified proppants: costly, complicated production & of low thermomechanical stability*
- ✓ *Directly exposed particles likely to cause corrosion to the receiver (due to residual sulphates)*

Non-catalytic, cheap, “plain” bauxite proppants → shell-and-tube sulphuric acid evaporator/SO_3 splitting reactor cascade → **indirect heat transfer** between the particles on the shell-side and fluid (H_2SO_4 vapours) on the tube-side, which therein will come into contact with **a non-moving catalyst bed.**

<u>Concept adopted in the project for experimental validation → tbd in the next presentation</u>



Fe_2O_3-coated ceramic foams (catalyst)

Uncoated foam (evaporator + decomposer)

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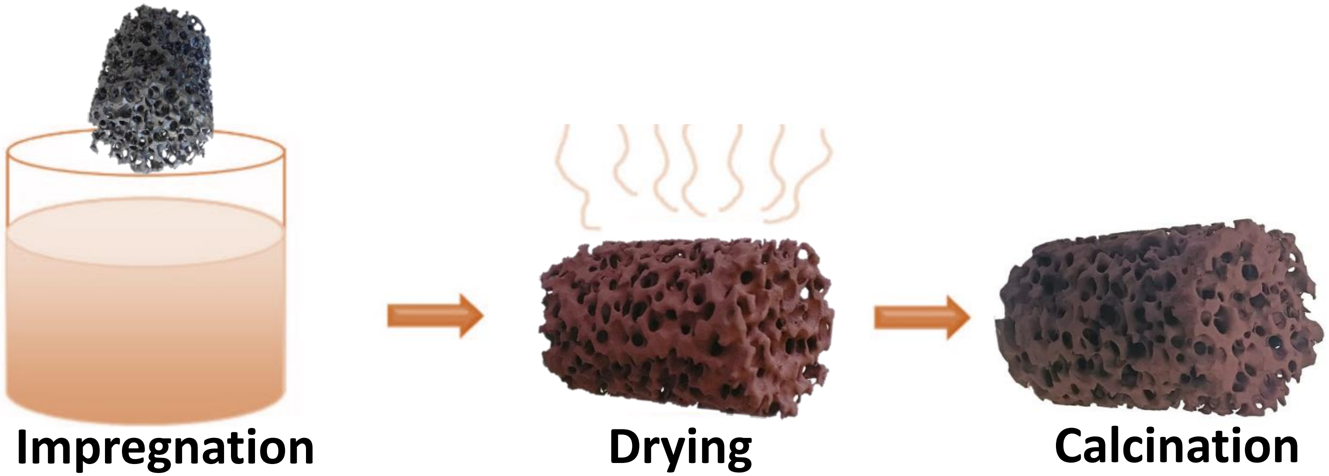
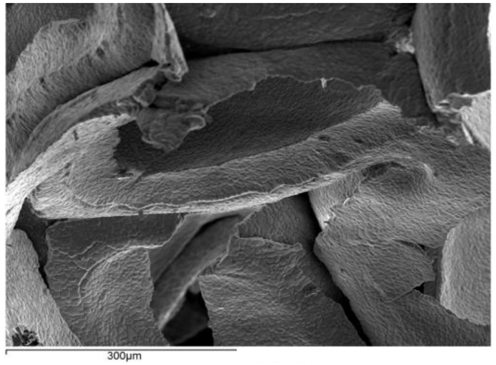
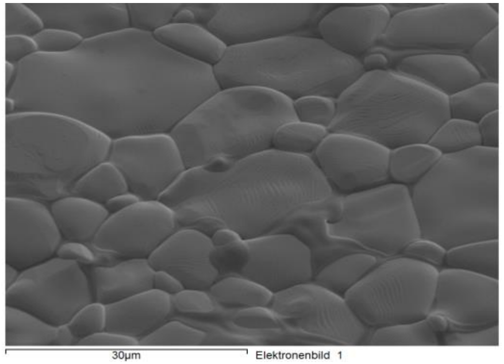
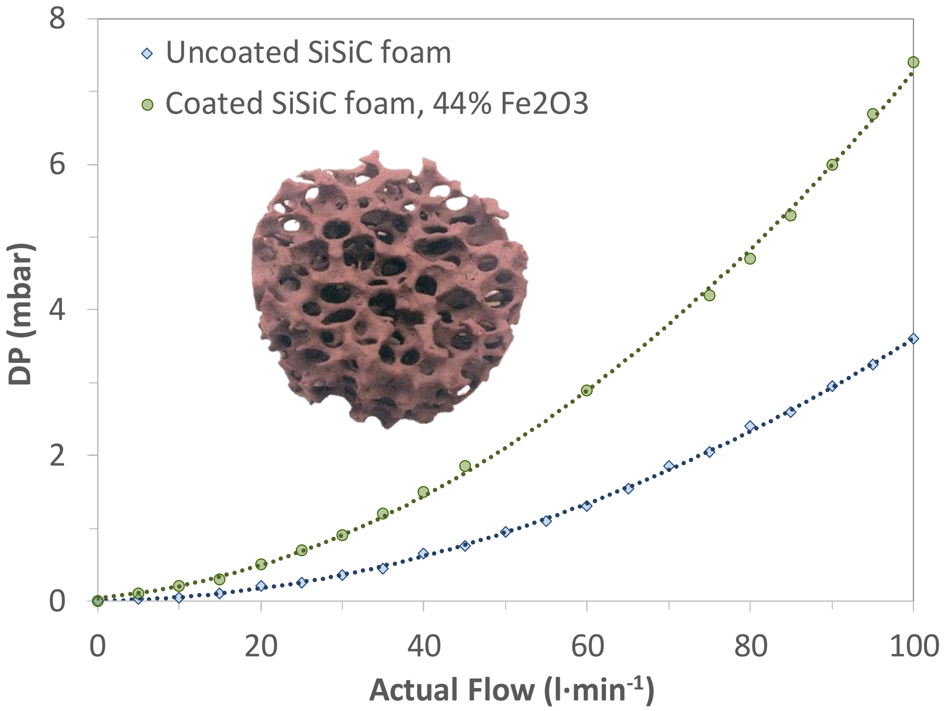
The PEGASUS revised concept – preparation of catalytic structures

Slurry/dip coating of SiSiC foams → Fe_2O_3









- Coating of 24 segments of Ø24 mm x 40 mm in total → decomposer setup @DLR
- Average loading (Fe_2O_3 mass/clean foam mass): 37.5 wt%
- Homogeneous coating & low pressure drop of coated segments

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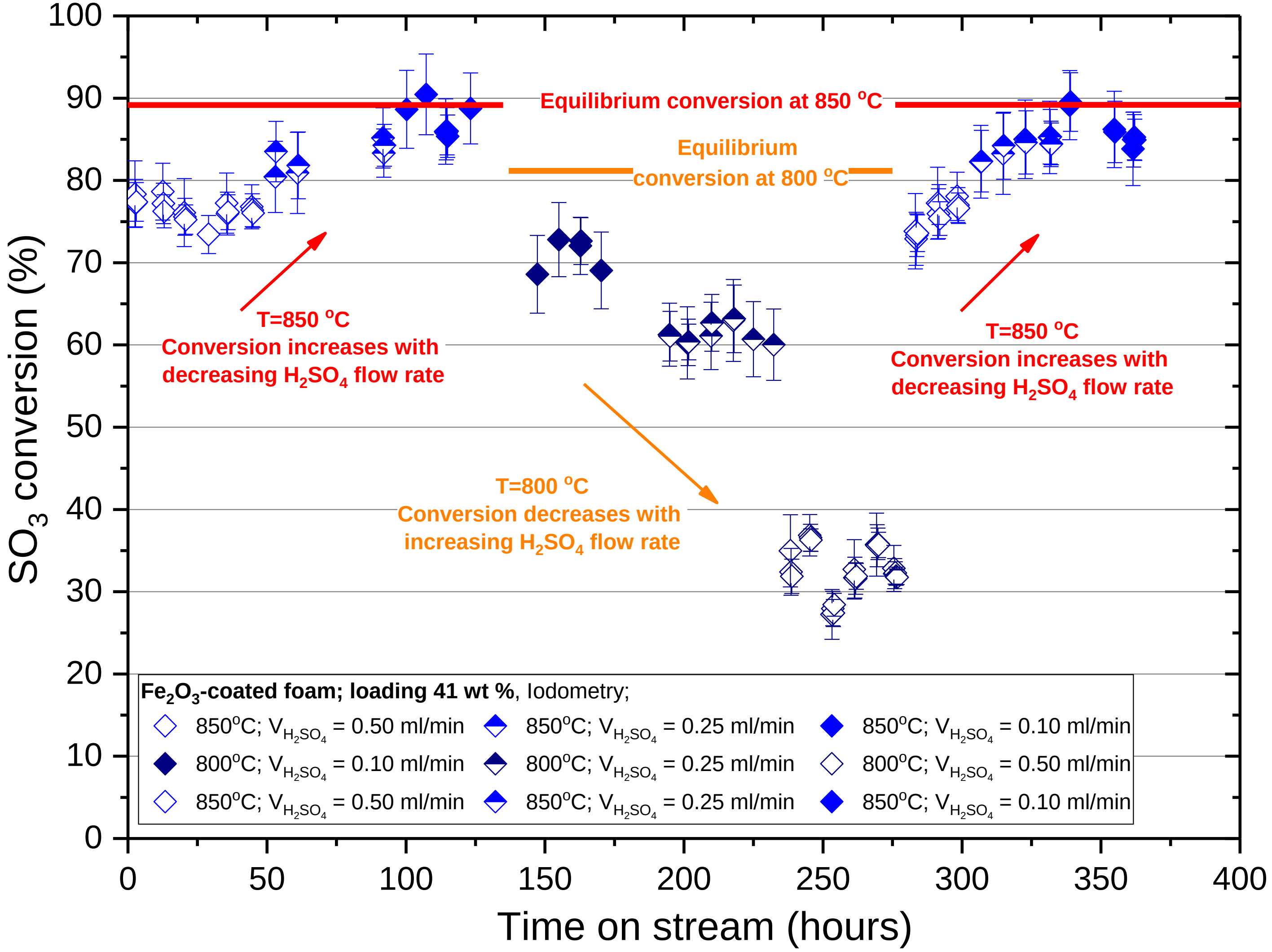
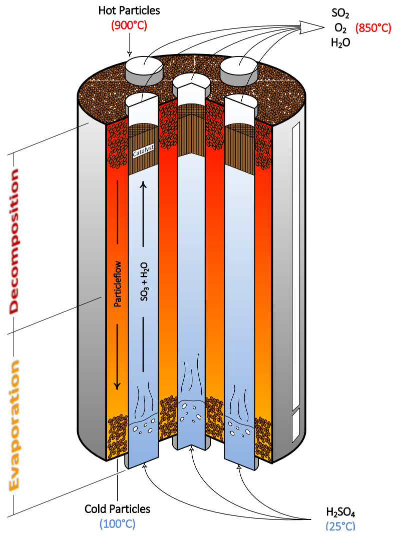
Long-term exposure of a Fe_2O_3-coated foam





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- Parametric experiments with same specimen, accumulating 362 h on-stream in total
- Near-equilibrium conversion @ 850°C within a range of H_2SO_4 flow rates & reproducible

Conclusions & future recommendations

- Modified proppants manufacturing to **combine high SO_3 splitting catalytic activity and HTF possible but far from optimized**:
  - ✓ *w.r.t. expected real operational environment → receiver's corrosion risk is high*
  - ✓ *Scaling-up feasibility → modified proppants manufacturing complicated & costly*
- Long term exposure (up to > 1000 h) under ideal lab-scale conditions → promising results
- Focus on the **indirect heat transfer concept** by using cheap proppants & catalytically active structures of high gas-solid contact area
  - ✓ *Careful design and room for optimization to achieve **efficient solid-solid heat transfer***
- Work to achieve validation under more realistic conditions & for long-term operation
- Development of a next version of decomposer reaction **@ high pressure** (P > 10 bar)

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Thank you for your attention!

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