EN05.02.05: Materials for concentrated solar energy-driven sulphur-based thermochemical cycles

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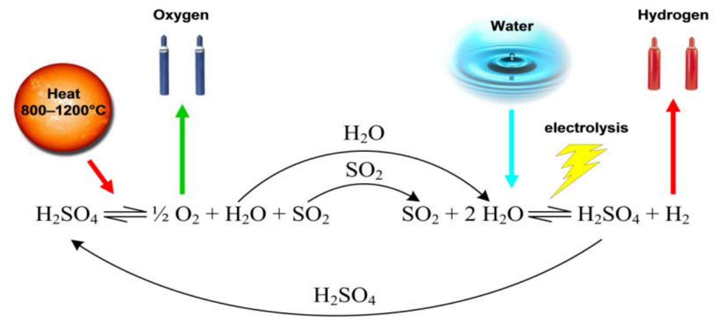
Sulphur-based thermochemical cycles

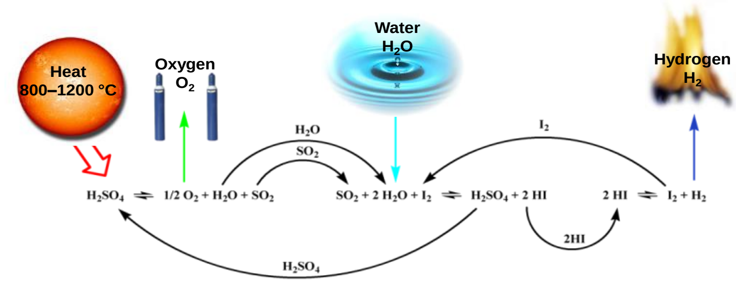
(a) the Hybrid Sulphur cycle

	Reaction	Temperature
Sulphuric acid decomposition	$H_2SO_4(aq) \rightarrow H_2O(g) + SO_3(g)$	450-500°C
	$SO_3(g) \rightarrow SO_2(g) + ½\ O_2\ (g)$	700-950°C
Electrolysis	$2\ H_2O + SO_2 \rightarrow H_2SO_4 + H_2\ (g)$	80°C
Anode:	$SO_2 + 2\ H_2O \rightarrow H_2SO_4 + 2\ H^+ + 2\ e^-$	
Cathode:	$2\ H^+ + 2\ e^- \rightarrow H_2$	



(b) the Sulphur-Iodine cycle

	Reaction	Temperature
Sulphuric acid decomposition	$H_2SO_4(aq) \rightarrow H_2O(g) + SO_3(g)$	450-500°C
	$SO_3(g) \rightarrow SO_2(g) + ½\ O_2\ (g)$	700-950°C
Bunsen reaction	$2H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2HI$	25-125°C
HI decomposition	$2HI \rightarrow I_2\ (g) + H_2\ (g)$	127-727°C



(c) 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

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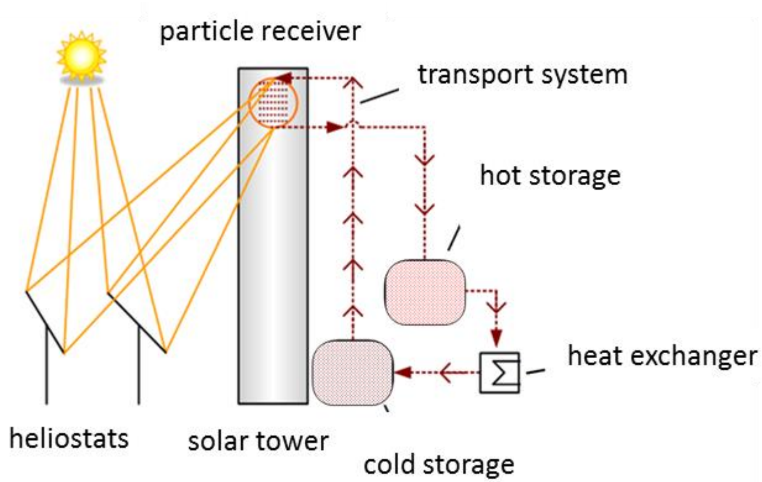
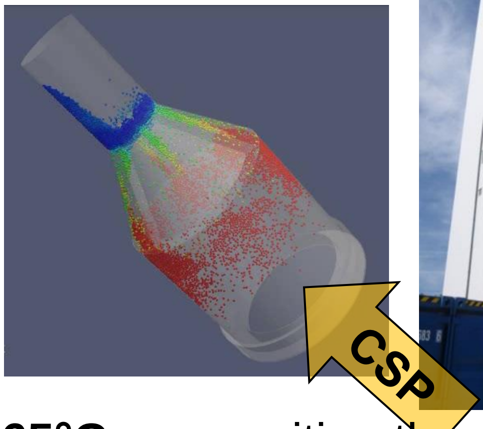
DLR: Solar particle receivers technology; Centrifugal receiver; solid particles streams as HTF

- Direct absorption ⇒ high efficiency and energy density
- Direct storage; receiver and storage at ambient pressure
- No freezing, no decomposition, low security requirements
- Can be “dirt cheap”: sand, ceramic proppants (sintered bauxite)
- SO_3 splitting catalysts: oxides (Fe/Cu/Mn-based)





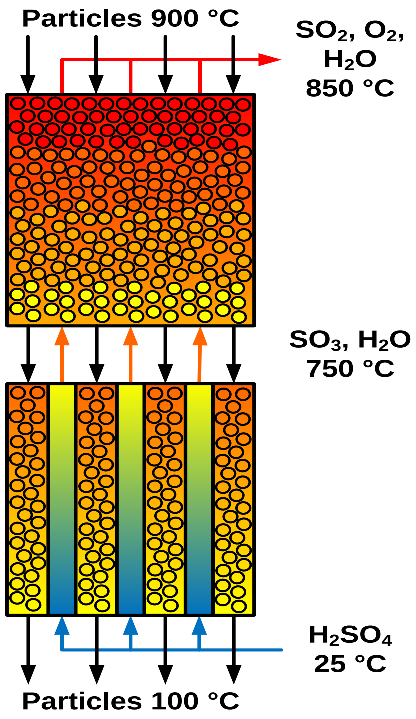
Demonstrated particle temperature of **T = 965°C** upon exiting the receiver

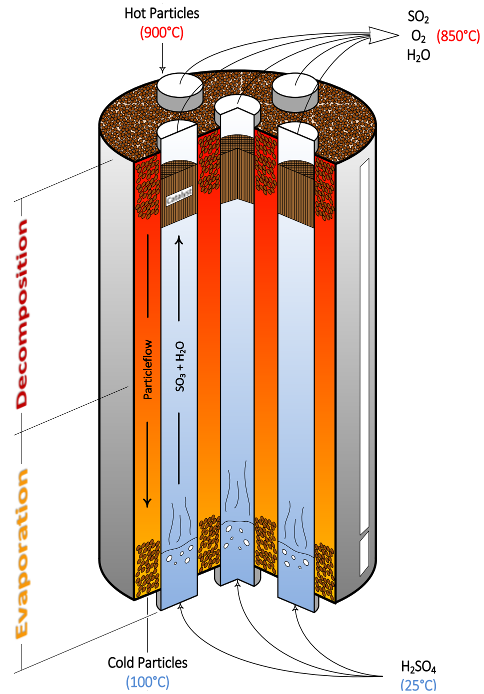
M. Ebert et al., AIP Conference Proceedings 2126, (2019) 030018.

Solar-driven SO_3 splitting reactor (H_2SO_4 decomposer) concepts downstream of solar receiver

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

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.**





In either case, particles can be fed from the hot storage tank off-sun and upon completion of evaporation, recirculated through the cold storage tank to the receiver on the top of the tower for a new cycle.

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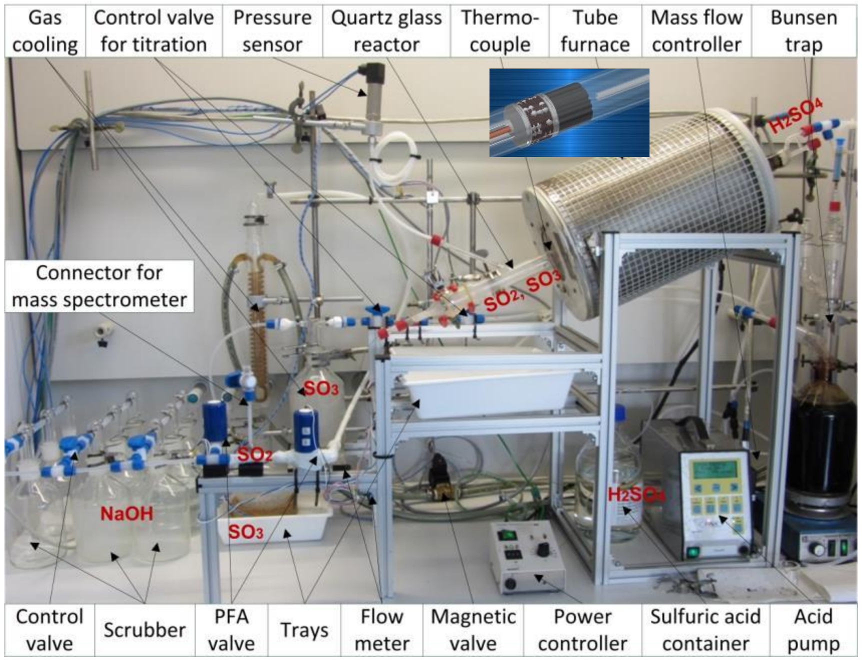
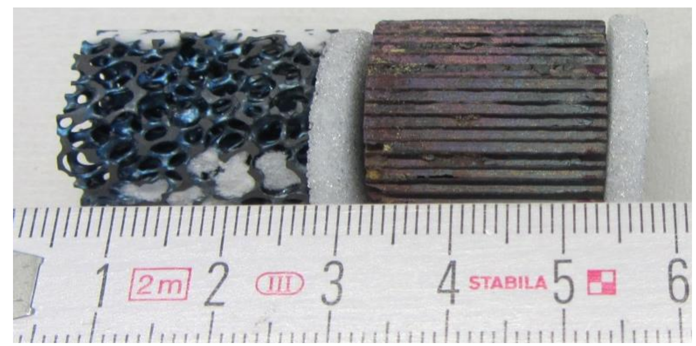
SO_3 splitting (H_2SO_4 decomposition) catalytic tests

Lab set-up for long-term catalyst testing





- Security system for 24 hours operation.
- Product gas analysis: iodometry, O_2 sensor.
- H_2SO_4 flow rates tested: 0.1/0.25/0.5 ml/min.
- Temperature: 800, 850, 900, 950°C.
- Testing times: from 100 up to > 1000 h.

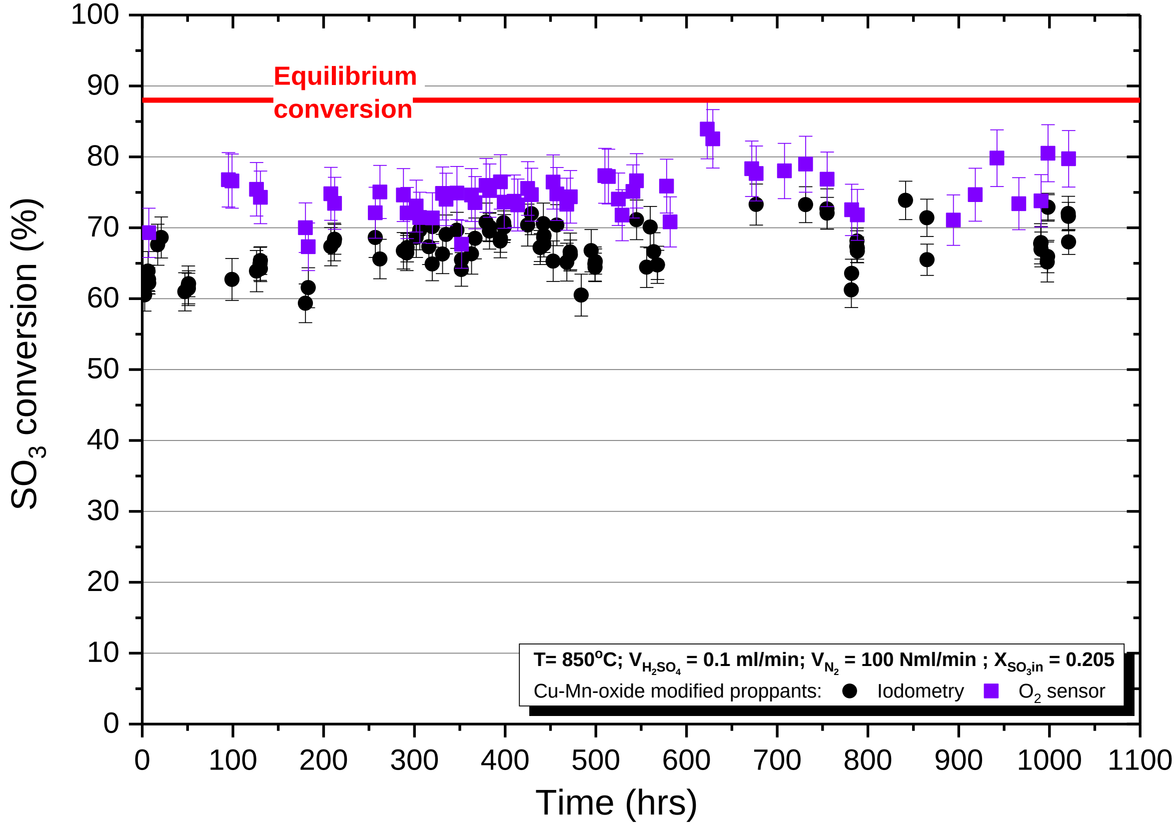
SO_3 splitting: long-term catalytic activity (> 1000 h), 850°C

Cu,Mn-oxide modified bauxite-based proppants were synthesized.

They exhibit:

- **High, constant conversion, 60-80%** (Eq. conv.=89 %).

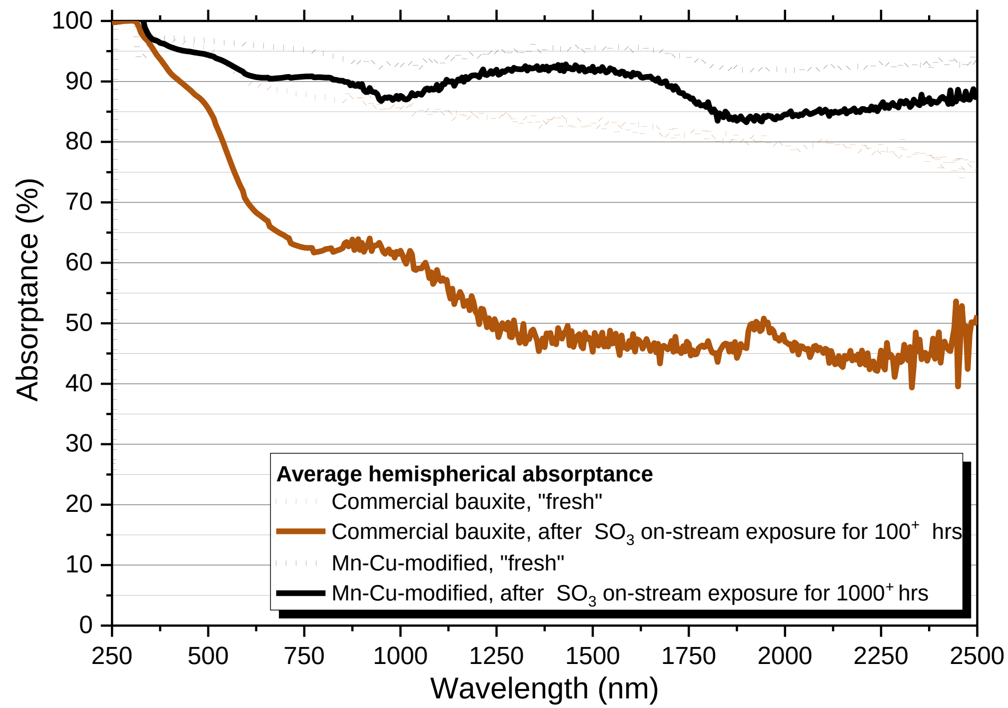
- **< 15% performance loss** after > **1000 h on** stream.



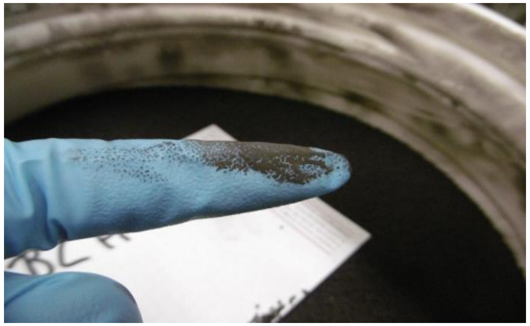
CSE-relevant properties

Cu,Mn-modified bauxite proppants exhibited **better absorbtance** than commercial ones and minor absorptance reduction after 1000 h on-stream exposure.

Yet, lower flowability (“sphericity”), mechanical strength and attrition resistance (creating “dust”).



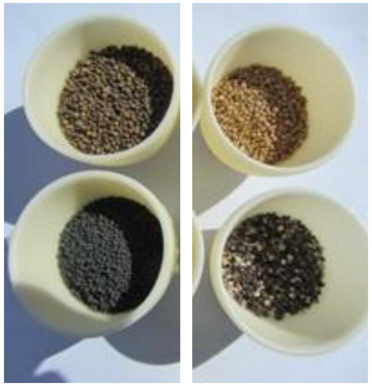
Expensive to be produced in pilot quantities.



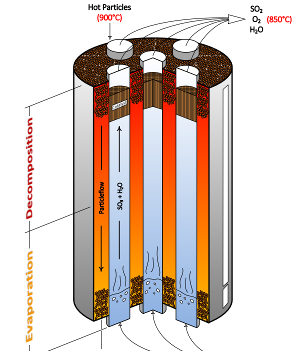
As-received After reaction

Commercial

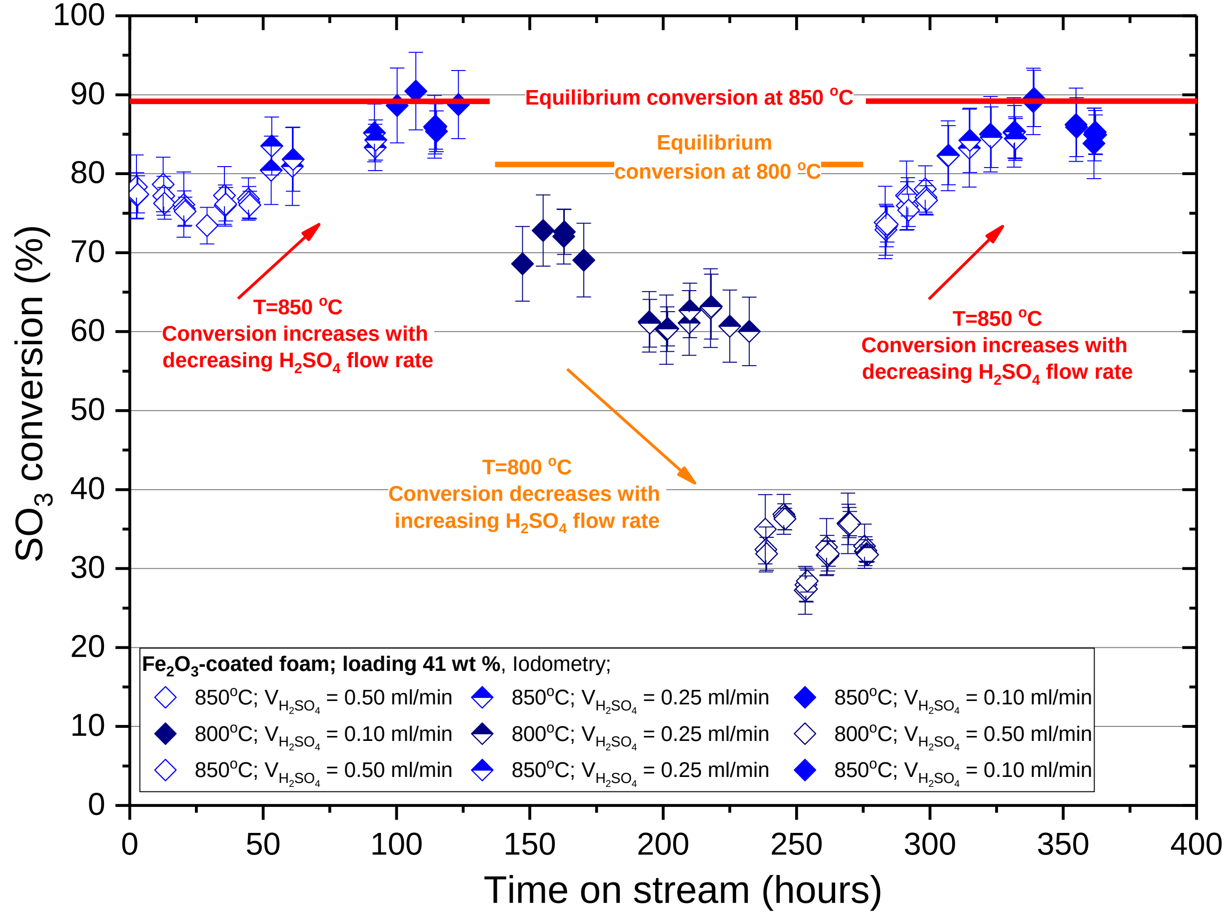
Modified



Indirectly heated reactor concept adopted



- Moving bed of inexpensive, non-catalytic commercial bauxite proppants (HTF) on the shell-side.
- Stationary Fe_2O_3 catalyst-coated foams inside the tubes (high catalyst loading, low pressure drop).
- Parametric experiments with same specimen, accumulating total 362 h on-stream.
- **Near-equilibrium conversion at 850°C** within a range of H_2SO_4 flow rates and fully reproducible.



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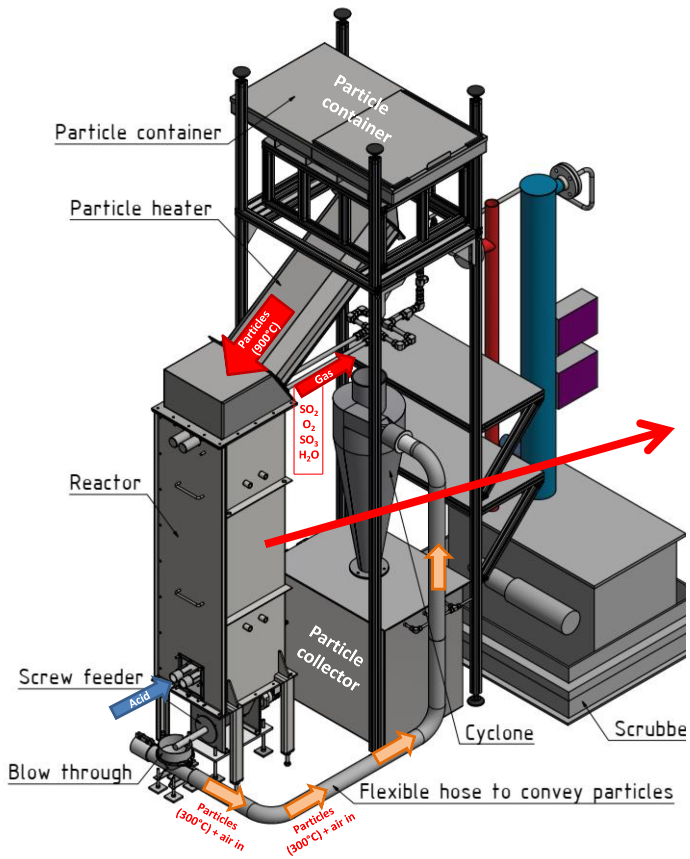
Sulphuric acid splitting reactor: Overview of setup at DLR, Juelich

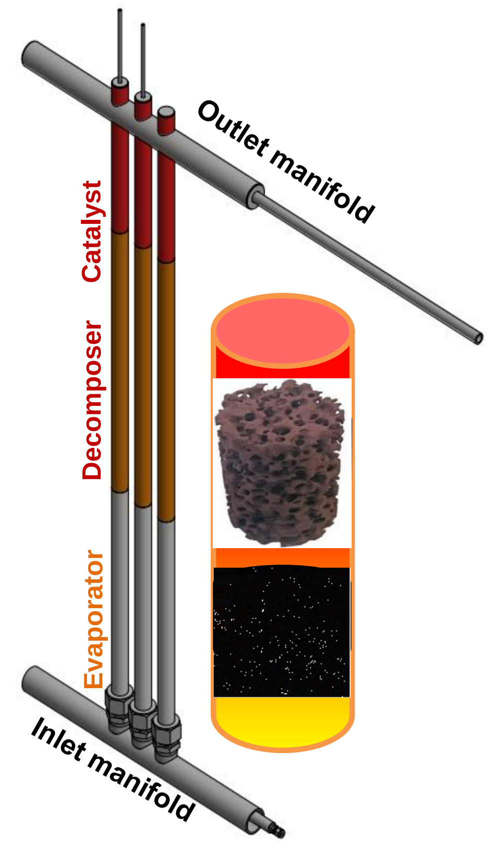
- Commercial bauxite particles (HTF) driven by gravity, flow rate controlled via a screw feeder.
- Electrical particle heater provides for hot particles.
- Evaporation, thermal and catalytic H_2SO_4 decomposition in one reactor.

- SiC foams coated with Fe_2O_3 catalyst for SO_3 splitting.
- SiC non-coated foams for thermal-only H_2SO_4 decomposition.

Sulphuric acid splitting reactor test setup

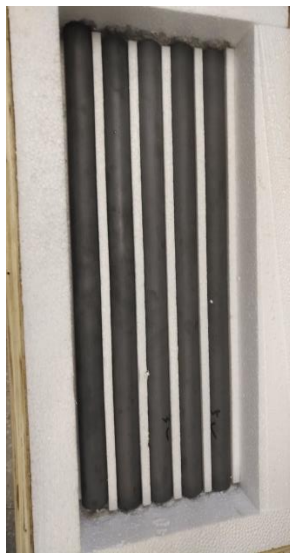


1 of 2 tube bundles



Lab-scale prototype reactor for sulphuric acid splitting

Stainless steel tubes



SiSiC tubes

Conclusions - Next steps

- The demonstrated potential of centrifugal particle receivers for providing hot particle streams of T ~ 950ºC opens new possibilities for performing endothermic chemical reactions like **the common SO_3 splitting step of all sulphur-based thermochemical cycles** downstream of the solar receiver.

- Direct and indirect heat transfer concepts between the moving hot particles stream and the reactant materials have been assessed; Cu-Mn-oxide modified bauxite proppants and Fe_2O_3-based structures have been extensively and long-term studied as SO_3 splitting catalysts, respectively.

- Fe_2O_3-coated SiC foams achieved near-equilibrium **SO_3 conversion** (**~ 89 %), at a temperature of 850º,** in principle reachable with hot particle streams.

- Construction of a lab-scale indirect contact catalytic reactor is almost completed and eventual proof-of-concept test is foreseen soon.

Thank you for your attention!

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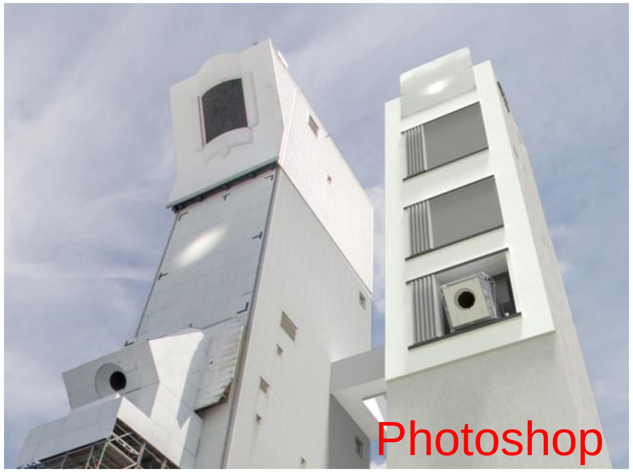

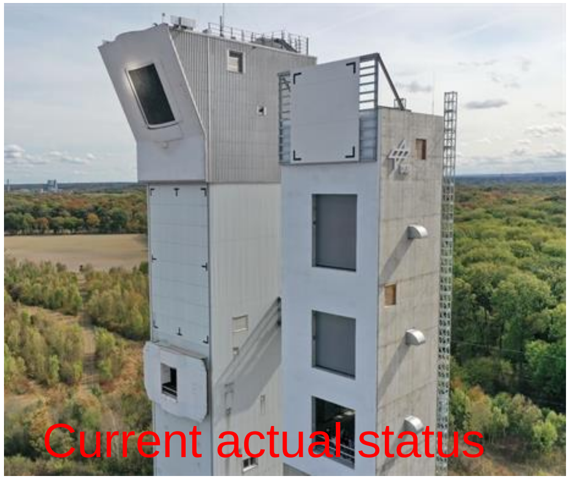

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