

Development of catalytic particles for SO₃ decomposition of the thermochemical energy storage scheme based on elemental sulfur

<u>Kyriaki G. Sakellariou</u>, Nikolaos I. Tsongidis, Chrysoula Pagkoura, George Karagiannakis and Athanasios G. Konstandopoulos

Aerosol & Particle Technology Laboratory, CPERI/CERTH, Thessaloniki, Greece



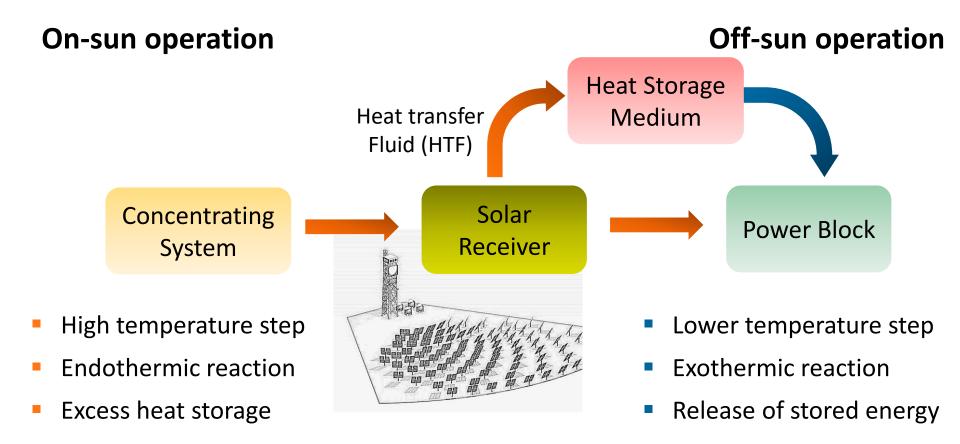
CYI, Nicosia, Cyprus November 14th, 2017





THERMOCHEMICAL ENERGY STORAGE APPLICATION

- \diamond CSP technologies issue: intermittence of solar energy \rightarrow process inefficiencies
- \diamond Need for high energy density storage systems \rightarrow reversible chemical reactions



ACKNOWLEDGEMENTS

Renewable Power Generation by Solar Particle Receiver Driven <u>Sulphur Storage Cycle</u>

The European Commission for funding of this work through the Horizon 2020 project *PEGASUS (G.A. No: 727540)*





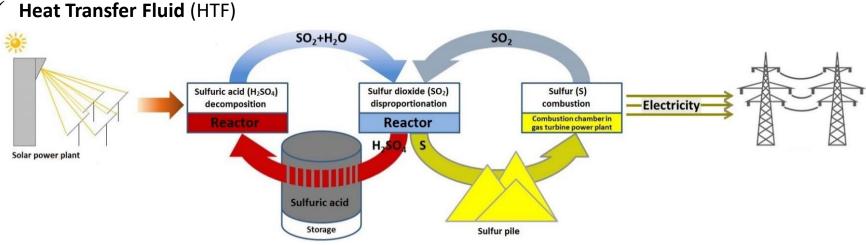
OUTLINE

- Description of PEGASUS Concept
- **TCS** reaction scheme
- **Our role in the project**
- **Preliminary results:**
 - ✓ Materials characterization
 - ✓ Materials evaluation

CONCEPT

 \checkmark

- **Novel power cycle** for renewable electricity production
- Coupling of a centrifugal particle receiver for solar towers & a compact sulfur-based Thermo-Chemical energy Storage (TCS) scheme
- □ High operating temperatures with high energy density storage potential
- Development of **oxide-based particles with a double role.** Used both as:
 - \checkmark Catalysts for the SO3 dissociation reaction (primarily) and

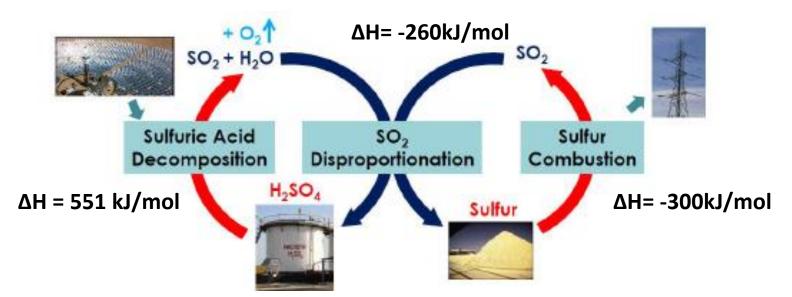


- Advantages of the suggested scheme:
 - ✓ Very high energy density: approx. 12,500 kJ/kg cf. 300 kJ/kg for molten salts
 - ✓ Cost-effective material (<60 €/tn cf. ~400 €/tn for molten salts) and cheaply stored in piles under ambient conditions
 - \checkmark Constant temperature heat recovery and possibility for higher temperature stored energy retrieval cf. original heat input 5/11

THERMOCHEMICAL SULFUR STORAGE CYCLE

Endothermic reaction steps (charge)

 $\begin{array}{l} 2H_{2}SO_{4(aq)} \rightarrow 2SO_{3(g)} + 2H_{2}O_{(g)} \ T=450\text{-}500^{\circ}\text{C} \\ 2SO_{3(g)} \rightarrow 2SO_{2(g)} + O_{2(g)} \ T=700\text{-}900^{\circ}\text{C} \end{array}$



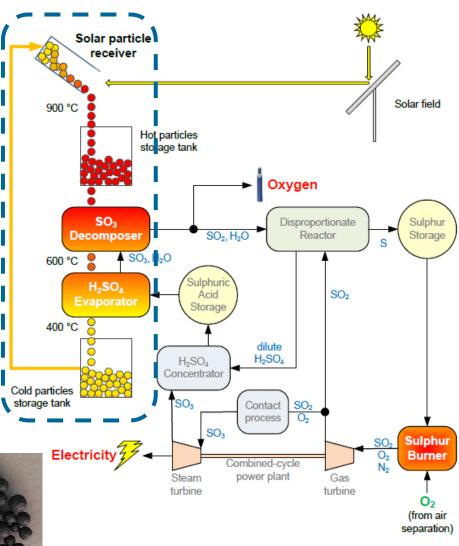
Exothermic reaction steps (discharge)

 $\begin{array}{l} 2H_2O_{(I)} + 3SO_{2(g)} \rightarrow 2H_2SO_{4(aq)} + S_{(s)} T = 50\text{-}200^{\circ}\text{C} \\ S_{(I)} + O_{2(g)} \rightarrow SO_{2(g)} T = 500\text{-}1500^{\circ}\text{C} \end{array}$

OUR ROLE IN THE PROJECT

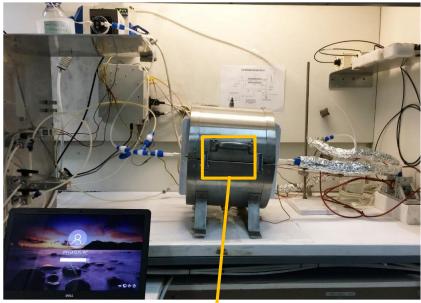
- Development of oxide-based materials with double role: SO₃ dissociation catalysts & HTF
- Fe₂O₃ & CuO enriched particles
- Nearly spherical formulations manufacturing
- Main requirements:
 - \checkmark High catalytic activity
 - ✓ High thermo-mechanical strength & resistance
 - ✓ Black or blackish color for high solar absorbance
- Physicochemical characterization (XRD, BET, Hg-porosimetry, SEM/EDS, TGA)
- Mechanical properties evaluation (crushing strength measurements)
- Preliminary evaluation upon catalytic activity

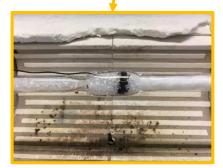




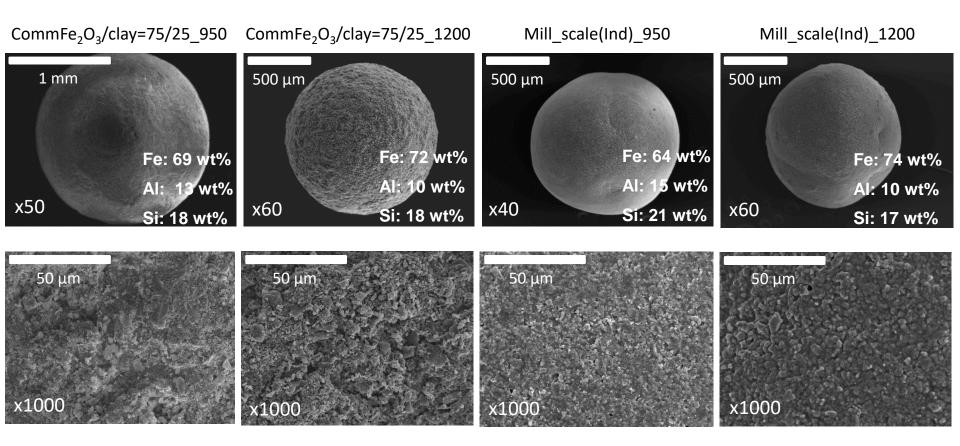
EVALUATION SETUP & EXPERIMENTAL CONDITIONS

- Quartz tube reactor filled with quartz beads (left side) and quartz wool (right side). Particles in fixed bed formulation
- □ SO₂ analysis by UV-Vis spectrometry in a heated (212°C) quartz cuvette
- Experimental conditions set for the preliminary tests
 - ✓ Reaction temperature: 850°C
 - ✓ Pressure: 1 bar
 - ✓ Feed: conc. sulfuric acid (95-98%), 0.12 ml/min
 - ✓ GHSV = \sim 50,000 h⁻¹ / LHSV = \sim 14 h⁻¹
 - ✓ Catalyst quantity per test: 1 g
 - ✓ Daily SO_2 calibration (prior to each test)
 - ✓ Dilution of reactor outlet with N_2 flow to achieve measurable SO_2 concentration values (0.5 – 3 std lt/min)
 - ✓ On-stream exposure per test: 60 min



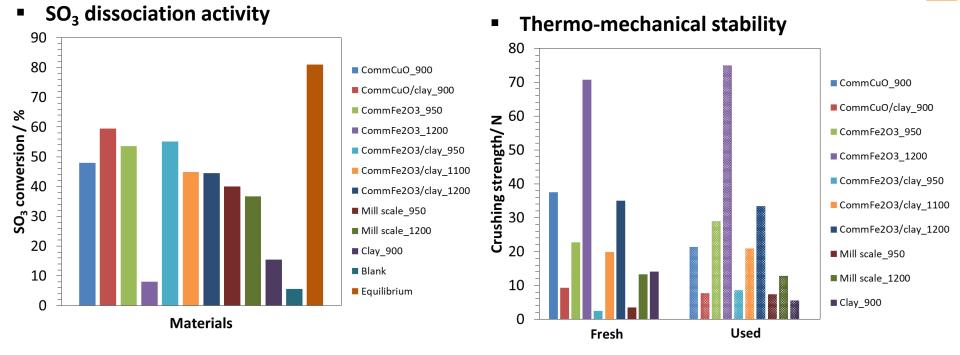


CHARACTERIZATION OF $F_{e_2O_3}$ -BASED PARTICLES



- ✓ Clay used as additive
- ✓ No mixed Fe_2O_3 clay phases identified by XRD
- ✓ Major elements present: Fe, Al, Si
- $\checkmark\,$ Higher calcination temperature \rightarrow more sintered structures

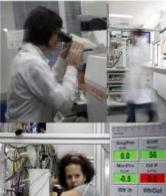
PRELIMINARY **R**ESULTS



✓ Fe_2O_3 materials:

- Samples calcined at 950°C more active cf. the ones calcined at 1200°C, but lower structural stability
- Higher calcination temperature \rightarrow improved CS \rightarrow Improved structural stability
- Sintering at 1200°C detrimental to catalytic activity
- ✓ CuO materials:
 - CommCuO/clay with high conversion (i.e.~50%)
 - Clay presence favored catalytic activity, however, caused deterioration in stability
 - Characterization results pending











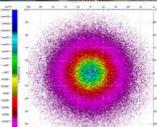












Thank you for your attention!





http://apt.cperi.certh.gr ksakella@cperi.certh.gr