# Composite particles as active catalysts for the $SO_3$ dissociation reaction of the thermochemical storage scheme based on elemental sulfur

Nikolaos I. Tsongidis[1,2], George Karagiannakis[1], Kyriaki G. Sakellariou[1,2], Chrysoula Pagkoura[1], Athanasios G. Konstandopoulos[1,2], Dariusz Janus[3], Marek Zagaja[3], Daria Pomykalska[3]

[1]Aerosol & Particle Technology Laboratory, CPERI/CERTH, P.O. Box 60361, 57001, Thessaloniki, Greece

[2]Department of Chemical Engineering, Aristotle University, P.O. Box 1517, 54006, Thessaloniki, Greece

[3]Baltic Ceramics, 30/63 Swietokrzyska St, 00116, Warsaw, Poland

## Introduction

The work is in the framework of definition & validation of a novel power cycle via coupling of a centrifugal particle receiver[1] for solar towers & a compact sulfur-based Thermo-Chemical Storage (TCS) scheme. The concept combines high operating temperatures with high energy density storage (12.5 MJ/kg S) potential.

**Endothermic reaction steps (charge)**

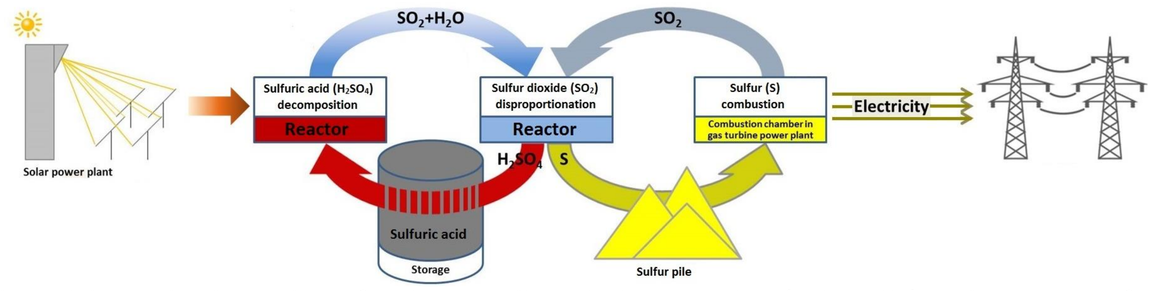
$H_2SO_{4(aq)} \rightarrow 2SO_{3(g)} + 2H_2O_{(g)}$ T= 450-500°C

$2SO_{3(g)} \rightarrow 2SO_{2(g)} + O_{2(g)}$ T= 700-900°C ΔH= +560kJ/mol

**Exothermic reaction steps (discharge)**

$2H_2O_{(l)} + 3SO_{2(g)} \rightarrow 2H_2SO_{4(aq)} + S_{(s)}$ T= 50-200°C ΔH= -260kJ/mol

$S_{(l)} + O_{2(g)} \rightarrow SO_{2(g)}$ T= 500-1500°C ΔH= -300kJ/mol




The present work focuses on the development and experimental evaluation of oxide-based particles as both catalysts for the $SO_3$ dissociation reaction (primarily) and Heat Transfer Fluid (HTF). Main requirements are high thermo-mechanical strength, resistance to chemically harsh environment & suitable particle color. The study includes structural, morphological, mechanical & catalytic activity results.

## Structural, Morphological & Mechanical Properties

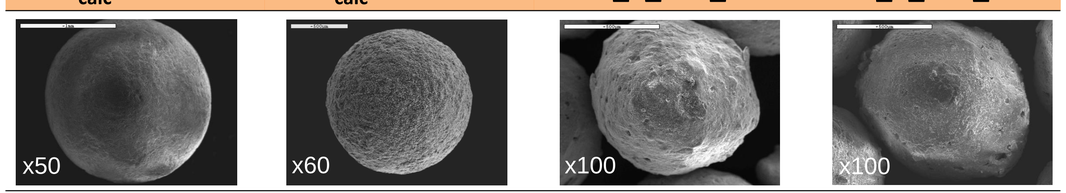
❖ Structural characterization by X-Ray Diffraction

❖ Mechanical strength by Crushing Strength (CS) measurements

| | Material | $T_{calcination}$ /°C | Phases identified | $Cs_{fresh}$/N |
|---|---|---|---|---|
| APTL | **Commercial $Fe_2O_3$** | **950** | **$Fe_2O_3$** | **22.8** |
| | Commercial $Fe_2O_3$ | 1200 | $Fe_2O_3$ | 70.7 |
| | $CommFe_2O_3$/clay=75/25 | 950 | $Fe_2O_3$, $SiO_2$ | 2.5 |
| | **$CommFe_2O_3$/clay=75/25** | **1200** | **$Fe_2O_3$, $SiO_2$** | **35.0** |
| | Mill-scale (Ind) | 950 | $Fe_2O_3$, $SiO_2$ | 3.5 |
| | Mill-scale (Ind) | 1200 | $Fe_2O_3$, $SiO_2$ | 13.2 |
| | $IndFe_2O_3$/clay=75/25 | 950 | $Fe_2O_3$ | 11.7 |
| | **$IndFe_2O_3$/clay=75/25** | **1200** | **$Fe_2O_3$** | **107.5** |
| | Clay | 900 | $SiO_2$, $Al_2O_3$, $Al_2SiO_5$ | 14.1 |
| Baltic Ceramics (BCR) | BCR_1_425_850 | **1280** | $Al_2O_3$, traces of $FeTi_2O_5$, $Fe_2O_3$, $Mn_2O_3$ | >100 |
| | **BCR_2_425_850** | | **$Al_2O_3$, $Al_2(Al_{2.5}Si_{1.5})O_{9.75}$, traces of $FeTi_2O_5$, $Fe_2O_3$, $Mn_2O_3$** | |
| | **BCR_2_850_1180** | | ***same composition as BCR_2_425_850*** | |
| | BCR_3_425_850 | | $Al_2O_3$, traces of $FeTi_2O_5$ | |
| | BCR_4_425_850 | | $Al_2O_3$, traces of $FeTi_2O_5$, $Fe_2O_3$ | |
| | BCR_4_850_1180 | | *same composition as BCR_4_425_850* | |
| | **BCR_5_841_1680** | | **$Al_2O_3$, $SiO_2$, traces of $Fe_2O_3$, $3Al_2O_3 \cdot 2SiO_2$** | |

❖ Morphological characterization via SEM

| $CommFe_2O_3$/clay composite | | BCR proppants | |
|---|---|---|---|
| $T_{calc}$=950°C | $T_{calc}$=1200°C | BCR_1_425_850 | BCR_2_425_850 |



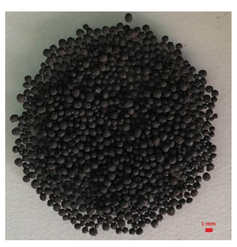

Near spherical; size range 425-1680 μm (BCR), 700-1400 μm (APTL)

***APTL samples:***

- ✓ Low crystallinity & absence of clear $Al_2O_3$ & Al-Si-O peaks
- ✓ Higher calcination temperature → more sintered structures & improved CS → Improved structural stability
- ✓ Major elements (EDS): Fe, Al, Si
- ✓ BET showed low surface area & no porosity (Hg-porosimetry)

***BCR samples:***

- ✓ Bauxite-based proppants with main phases: $Al_2O_3$ & aluminosilicates. Small amounts of $Fe_2O_3$, $Mn_2O_3$ & $FeTi_2O_5$
- ✓ SEM results for same particle size (425-850 μm) very similar
- ✓ Major elements (EDS): Al, Mn, Si. Also present Ca, Ti & Fe
- ✓ Negligible surface area (BET) & no porosity



## Catalytic Activity Evaluation

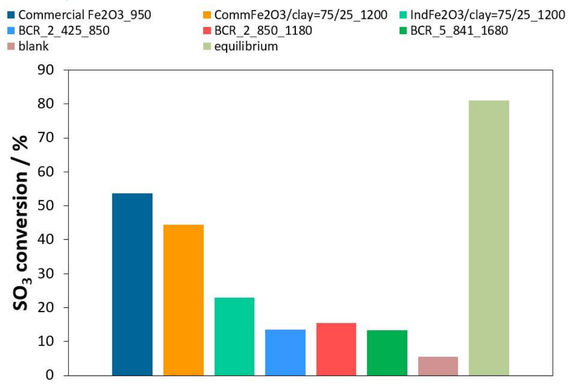
❖ $SO_2$ analysis by UV-Vis spectrometry in a setup for catalytic activity measurements

- On-stream exposure duration per test: 60 min
- Temperature: 850°C; Pressure: 1 bar
- Feed: concentrated sulfuric acid (98%), 0.12 ml/min
- Catalyst quantity per test: 1 g

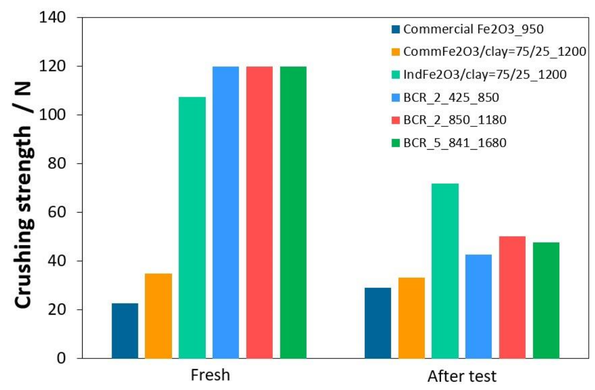
| | Material | $SO_3$ conversion/% | Particle Color | $CS_{after\ exp.}$/N |
|---|---|---|---|---|
| APTL | **Commercial $Fe_2O_3$_950** | **53.6** | **dark red-blackish** | **29.0** |
| | Commercial $Fe_2O_3$_1200 | 8.0 | blackish-black | 74.9 |
| | $CommFe_2O_3$/clay=75/25_950 | 55.1 | medium red | 8.6 |
| | **$CommFe_2O_3$/clay=75/25_1200** | **44.4** | **dark red-blackish** | **33.4** |
| | Mill-scale (Ind)_950 | 40.0 | dark brown-blackish | 7.3 |
| | Mill-scale (Ind)_1200 | 36.8 | blackish | 12.9 |
| | **$IndFe_2O_3$/clay=75/25_1200** | **23.0** | **blackish** | **71.9** |
| | Clay_900 | 15.4 | light yellow | 5.6 |
| BCR | BCR_1_425_850 | 10.3 | black | 61.3 |
| | **BCR_2_425_850** | **13.6** | **black** | **42.7** |
| | **BCR_2_850_1180** | **15.5** | **blackish** | **50.2** |
| | BCR_3_425_850 | 9.9 | blackish | 52.0 |
| | BCR_4_425_850 | 5.0 | black | 52.9 |
| | BCR_4_850_1180 | 4.1 | black | 57.9 |
| | **BCR_5_841_1680** | **13.4** | **blackish** | **47.7** |

- Equilibrium 81%
- Blank conversion 5%

❖ $SO_3$ conversion %




❖ Mechanical properties evaluation




***Indicative comparative results of $SO_3$ conversion and CS measurements***

- ***APTL particles rich in $Fe_2O_3$ high efficiency***
  - ✓ Samples calcined at 950°C more active cf. the ones calcined at 1200°C, but lower structural stability
  - ✓ Sintering at 1200°C detrimental to catalytic activity
  - ✓ Stable CS values before & after testing for selected samples
- ***BCR proppants relatively low performance***
  - ✓ Absence or low content of catalytically active phases
  - ✓ No significant effect of particle size
  - ✓ CS reduced by >50% after 60 min of exposure → but still high

## Conclusions

- ✓ Extremely high mechanical integrity leads to low catalytic activity in the BCR proppants → lack of sufficient catalytically active phases + no porosity
- ✓ **$CommFe_2O_3$/clay=75/25_1200 most promising material so far → combines $SO_3$ conversion >40%, CS > 20 N & dark color** → Further improvement to be closer to s.o.a. performance [2],[3]
- ✓ Combination of both approaches to create modified proppants relatively rich in catalytically active phases (e.g. $Fe_2O_3$, **CuO**) and high mechanical integrity
- ✓ Preliminary results on **CuO-containing BCR proppants** showed **$SO_3$ conversion >50%**

## References

1. Ho C., Christian J., Gill D., Moya A., Jeter S., Abdel-Khalik S., Sadowski D., Siegel N. Al-Ansary H., Amsbeck L., Gobereit B., Buck R., Energy Procedia, 49 (2014), 398-407
2. Karagiannakis G., Agrafiotis C.C., Zygogianni A., Pagkoura C., Konstandopoulos A.G., Int. J. Hydrogen Energy, 36 (4) (2011) 2831-2844
3. Giaconia A., Sau S., Felici C., Tarquini P., Karagiannakis G., Pagkoura C., Agrafiotis C., Konstandopoulos A.G., Thomey D., de Oliveira L., Roeb M., Sattler C., Int. J. Hydrogen Energy, 36 (11) (2011) 6496-6509

## Acknowledgements

We would like to thank the European Commission for funding of this work through the Horizon 2020 project **PEGASUS** - GA No: 727540.

Contact: Nikolaos I. Tsongidis | Tel: +30 2310 498 256 | Fax: +30 2310 498 190 | e-mail: ntsongid@cperi.certh.gr | Web: http://apt.cperi.certh.gr