



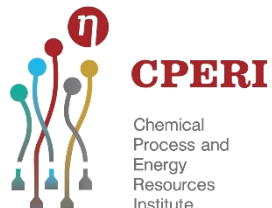
Solar-aided Thermochemical Cycle using Sulphur as an Energy Vector

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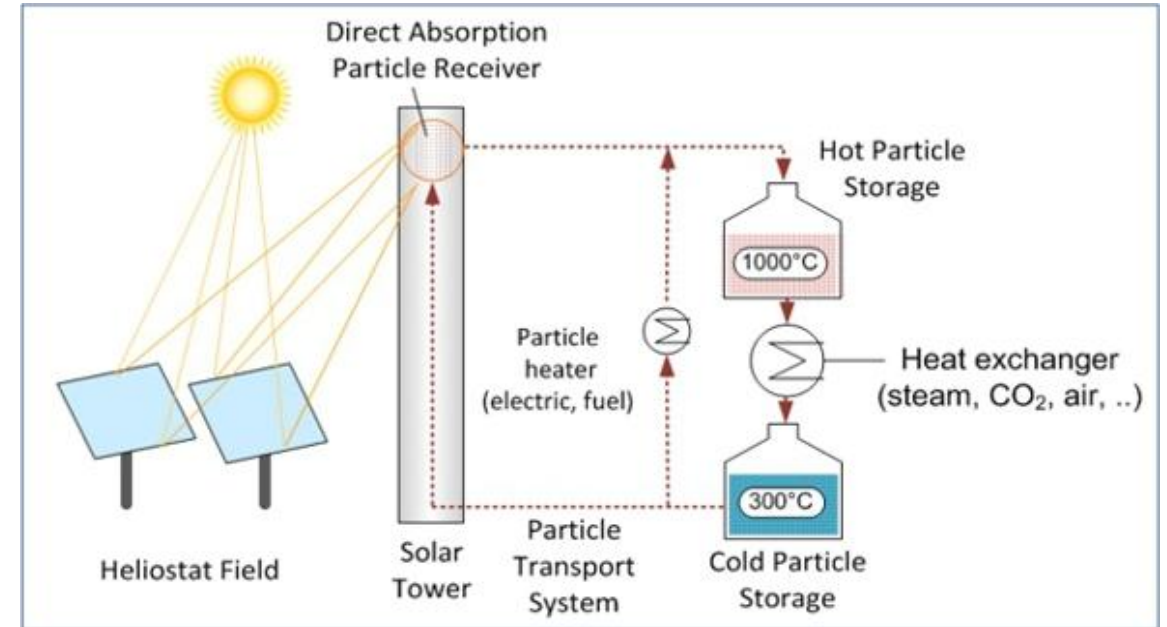
Presentation Outline

- ❑ Introduction to Solar Thermal Energy Storage & Materials
- ❑ Materials' Synthesis, Shaping & Characterization
- ❑ Catalytic Activity Tests Unit
- ❑ Evaluation
- ❑ Conclusions & Next Steps

The Role of Concentrated Solar Power (CSP) Plants



DLR solar field: [DLR \(CC BY-NC-ND 3.0\)](#)



- ❖ Mirrors are used to reflect and concentrate solar energy on a specific point (receiver)
- ❖ Solar energy from the sunlight is converted to thermal energy (heat)
- ❖ The heat is transferred into a working liquid
- ❖ Heat exchanger (steam)
- ❖ *Electricity generation*

The Role of Concentrated Solar Power (CSP) Plants



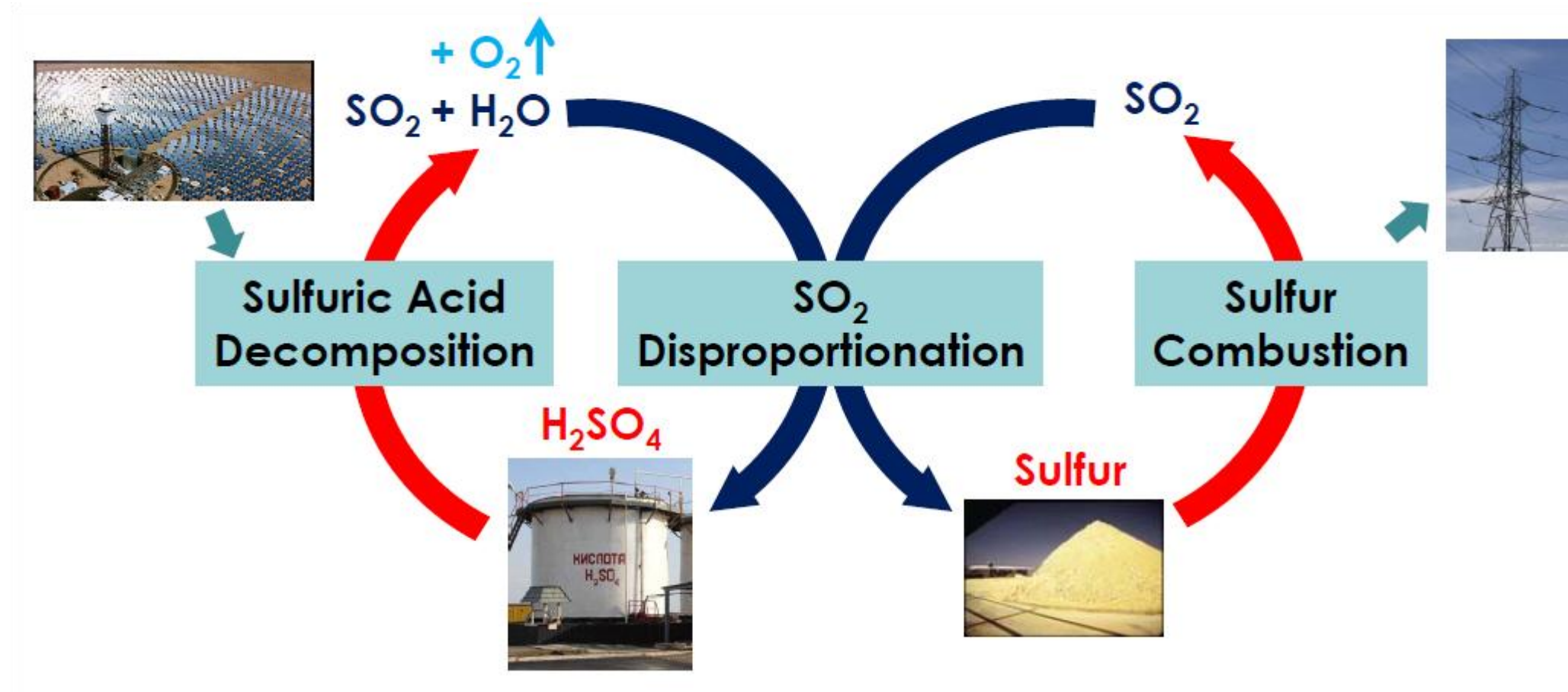
DLR solar field: [DLR \(CC BY-NC-ND 3.0\)](#)



DLR's 1000° C direct absorption particle receiver (DLR)

- ❖ Mirrors are used to reflect and concentrate solar energy on a specific point (receiver)
- ❖ Solar energy from the sunlight is converted to thermal energy (heat)
- ❖ The heat is transferred into a working liquid
- ❖ Heat exchanger (steam)
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Solar Thermal Energy Storage: A Sulphur cycle to make unlimited thermal energy storage



(B. Wong, 2015)

Why Sulphur?

❑ High-Energy Density Fuel

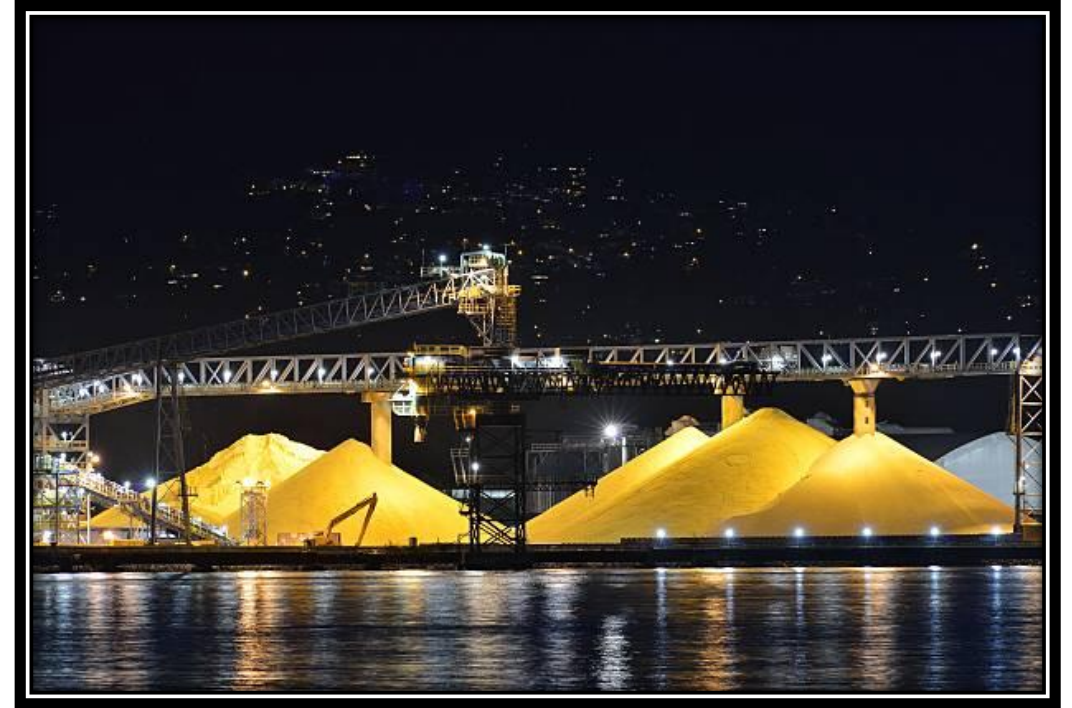
❑ Low Cost

Media	Energy Density (kJ/kg)	Materials Cost (\$/kWh _t)
Sulfur	12500	0.018
Gasoline	45000	0.108
Molten Salt (Phase Change)	230	7.56
Molten Salt (Sensible)	155	11.22
Elevated water Dam (100m)	1	-

Sulphur energy density / cost compared @ [Allothermally Heated Reactors for Solar-Powered Implementation of Sulphur-Based Thermochemical Cycles](#)

Why Sulphur?

- ❑ High-Energy Density Fuel
- ❑ Low Cost
- ❑ Easy Storage & Transportation



Waterfront sulfur piles, Port of Vancouver (konxinzhu)

Why Sulphur?

- ❑ High-Energy Density Fuel
- ❑ Low Cost
- ❑ Easy Storage & Transportation
- ❑ Endless SA Cycle -
“Open” or “Closed”
- ❑ CO₂-free Circular Economy

Main reactions of the elemental Sulphur thermochemical cycle and main operational parameters

	Reaction	Reaction enthalpy kJ/mol S	Indicative temperature °C
1a	$3\text{H}_2\text{SO}_4(\text{aq}) \rightarrow 3\text{SO}_3(\text{g}) + 3\text{H}_2\text{O}(\text{g})$	-826	450 - 500
1b	$3\text{SO}_3(\text{g}) \rightarrow 3\text{SO}_2(\text{g}) + 1.5\text{O}_2(\text{g})$		650 - 900
2	Disproportionation $3\text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2\text{SO}_4(\text{aq}) + \text{S}(\text{s})$	-254	50 - 200
3	Sulphur combustion $\text{S}(\text{l}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})$	-297	500 - 1500
4a	Contact process & $\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g})$	-99	400
4b	Absorption $\text{SO}_3(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{aq})$	-176	< 200

Why Sulphur?

- ❑ High-Energy Density Fuel
- ❑ Low Cost
- ❑ Easy Storage & Transportation
- ❑ Endless SA Cycle -
“Open” or “Closed”
- ❑ CO₂-free Circular Economy

- ❑ Sustainable Synergies with the SA Industry
- ❑ Can be Combusted on Demand
– Adjustable Combustion Temperature
- ❑ Baseload or Dispatchable Electricity

Materials' Synthesis

	Reaction	Reaction enthalpy kJ/mol S	Indicative temperature °C
1a	$3\text{H}_2\text{SO}_4(\text{aq}) \rightarrow 3\text{SO}_3(\text{g}) + 3\text{H}_2\text{O}(\text{g})$	-826	450 - 500
1b	$3\text{SO}_3(\text{g}) \rightarrow 3\text{SO}_2(\text{g}) + 1.5\text{O}_2(\text{g})$		650 - 900

Highly Endothermal/Catalyst Needed

Route 1: Dissolution-Evaporation-Precipitation



Powder Calcination



Route 2: Dry Mixing



Materials' Synthesis & Characterization

- Fe-,Cu-,Ce- based synthesized materials -Unsupported / Supported (Kaolin)
 -**Single** / Mixed Oxides

Material	XRD Phases	BET Surface (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (nm)
Fe ₂ O ₃	Fe ₂ O ₃	1.5	0.014	93.7
Fe ₂ O ₃ _com/Kaolin 15/85%_DM	Fe ₂ O ₃ , SiO ₂ , Fe(Al ₂ O ₄)	10.8	0.119	40.8
Fe ₂ O ₃ _wet/Kaolin 15/85%_DM	Fe ₂ O ₃ , SiO ₂ , Fe(Al ₂ O ₄)	10.4	0.295	69.9
Fe ₂ O ₃ _com/Kaolin 45/55%_DM	Fe ₂ O ₃ , SiO ₂ , Fe(Al ₂ O ₄)	7.8	0.073	40.07
CuO_com/Kaolin 15/85%_DM	CuO, CuAl ₂ O ₄ , Al ₆ Si ₂ O ₁₃ , SiO ₂	~ 0	~ 0	~ 0
CuO_wet/Kaolin 15/85%_DM	Cu ₄ O ₃ , CuAl ₂ O ₄ , Al ₆ Si ₂ O ₁₃ , SiO ₂	~ 0	~ 0	~ 0
CuO/Kaolin 15/85%_WM	CuAl ₂ O ₄ , SiO ₂ , Al ₆ Si ₂ O ₁₃	1.3	0.011	168.9
CeO ₂ _wet/Kaolin 15/85%_DM	CeO ₂ , SiO ₂	11.3	0.493	93.5
CeO ₂ /Kaolin 15/85%_WM	CeO ₂ , SiO ₂ , Al ₆ Si ₂ O ₁₃	5.5	0.065	51.7

Materials' Synthesis & Characterization

- Fe-,Cu-,Ce- based synthesized materials -Unsupported / Supported (Kaolin)
- Single / **Mixed** Oxides

Material	XRD Phases	BET Surface (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (nm)
Fe ₂ O ₃ _com/CuO_com (molar ratio Fe:Cu=1:1) _DM	CuFe ₂ O ₄ , CuO	0.2	0.010	21.9
Fe ₂ O ₃ _com/CuO_com (molar ratio Fe:Cu=2:1) _DM	CuFe ₂ O ₄ , CuO	0.1	0.003	212.6
Fe ₂ O ₃ _com/CuO_com (molar ratio Fe:Cu=2:1)/ Kaolin_DM	CuFe ₂ O ₄ , CuO, SiO ₂ , Al ₆ Si ₂ O ₁₃	1.9	0.017	74.9

Materials' Shaping

- ❑ Catalysts were shaped into spherical and nearly spherical particles



Spheronizer



CuO_{com}/Kaolin_DM



CuO_{wet}/Kaolin_DM



CuO/Kaolin_WM



Fe₂O₃_{com}/Kaolin_DM

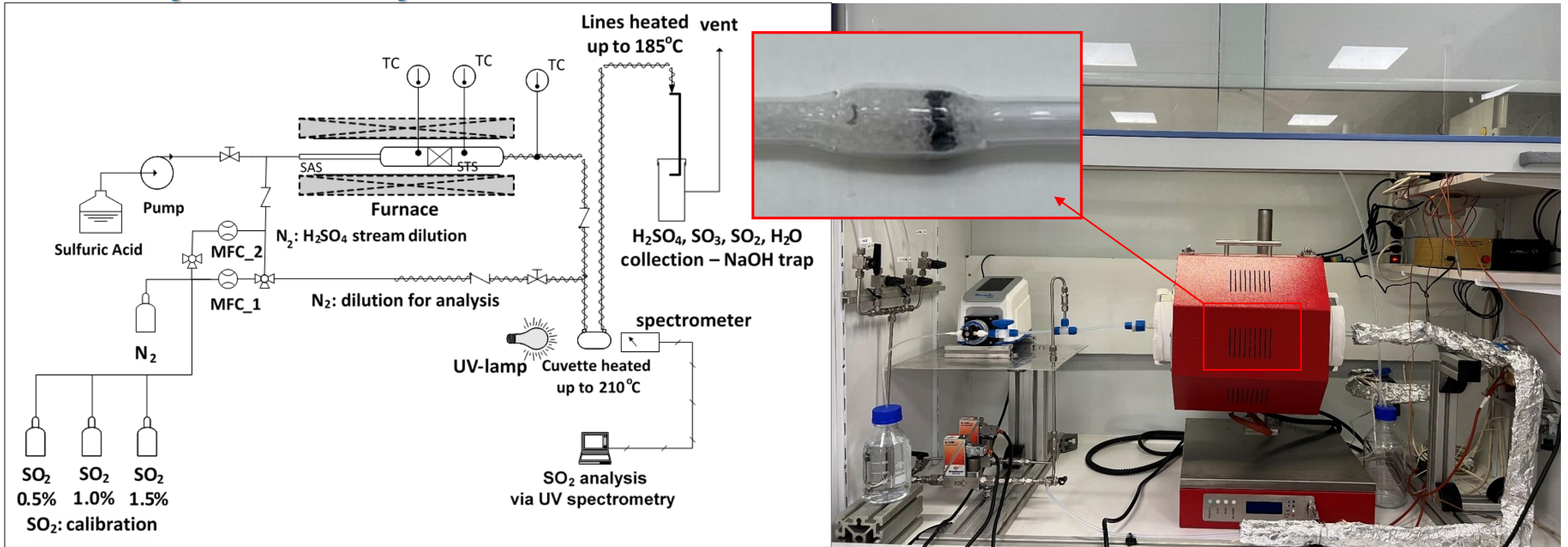


CeO₂/Kaolin_WM



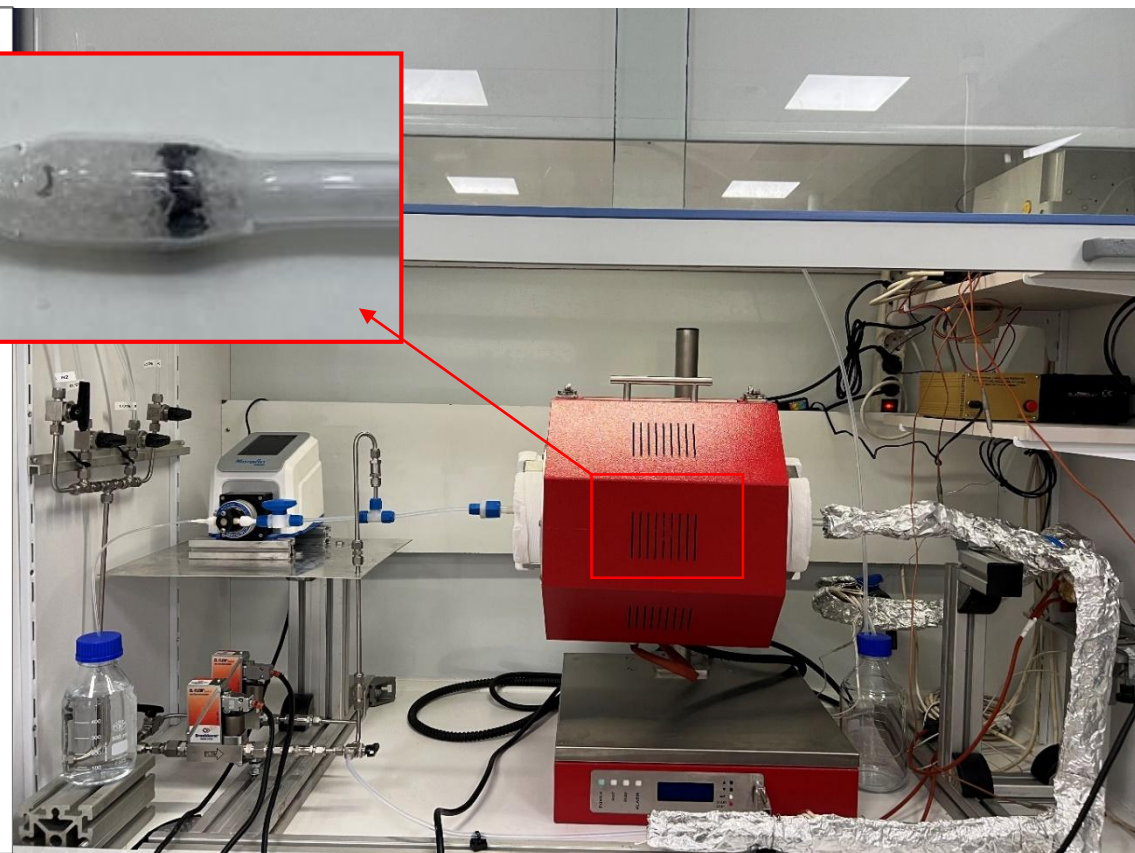
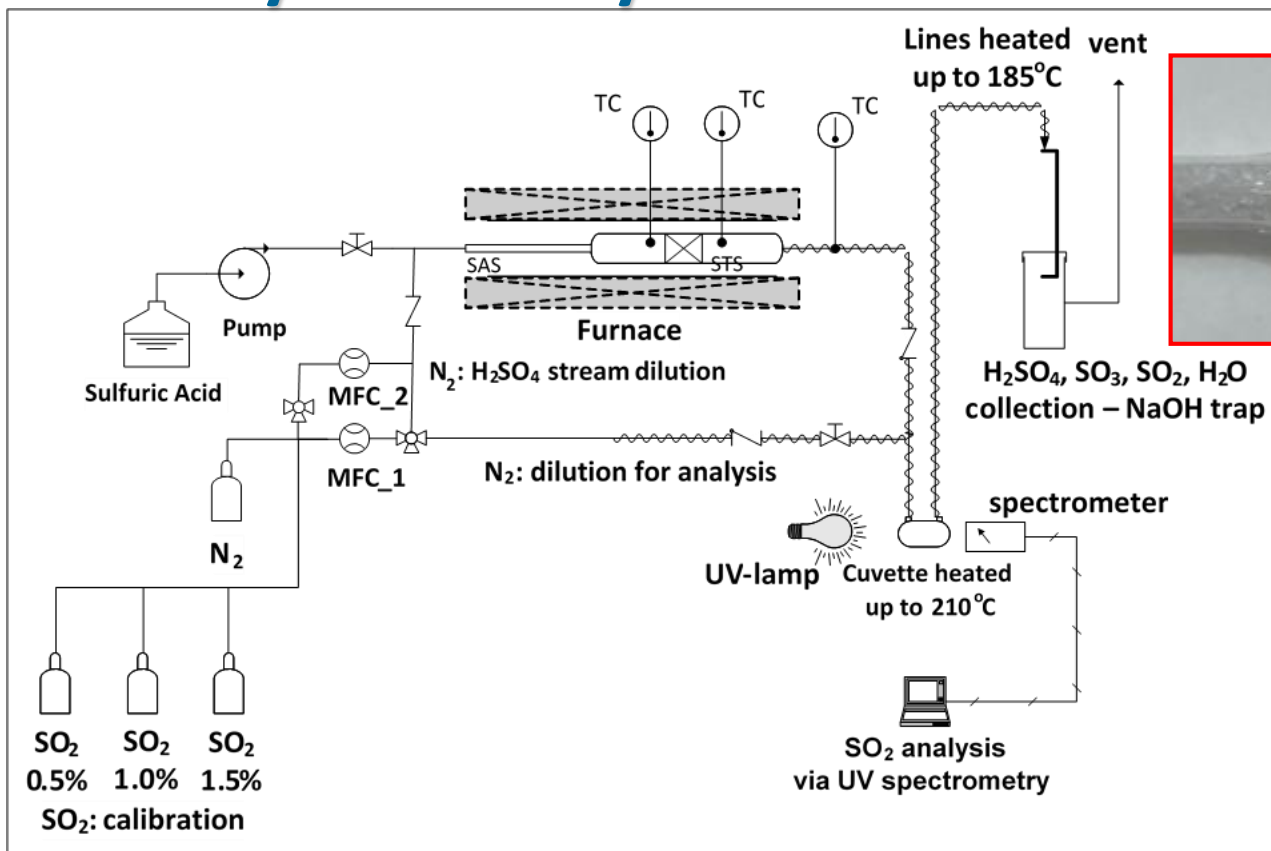
Fe₂O₃/CuO (Fe:Cu=1:1)

Catalytic Activity Tests Unit



- Quartz tube reactor filled with quartz beads (left side) and quartz wool (right side). Fixed bed formulation
- SO_2 analysis by UV-Vis spectrometry in a heated (212°C) quartz cuvette

Catalytic Activity Tests Unit



Reaction temperature (°C)	Pressure (bar)	H ₂ SO ₄ feed conc.	H ₂ SO ₄ feed rate (ml/min)	Mole fraction, x _{SO3} (-)	GHSV (h ⁻¹)	WHSV (h ⁻¹)	Catalyst quantity (g)	On-stream exposure (min)
850	1	96.5 %	0.12	0.500	11,500	13.2	1	60



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Introduction to Solar Thermal
Energy Storage & Materials

Materials' Synthesis, Shaping
& Characterization

Catalytic Activity Tests Unit

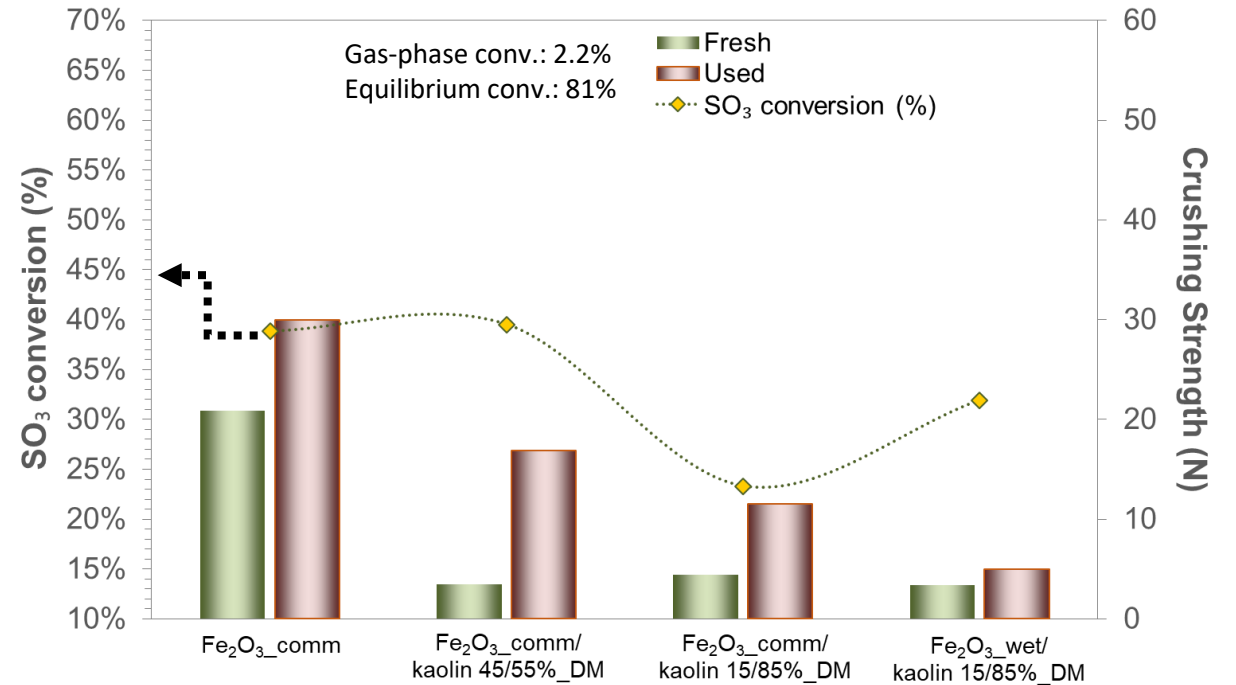
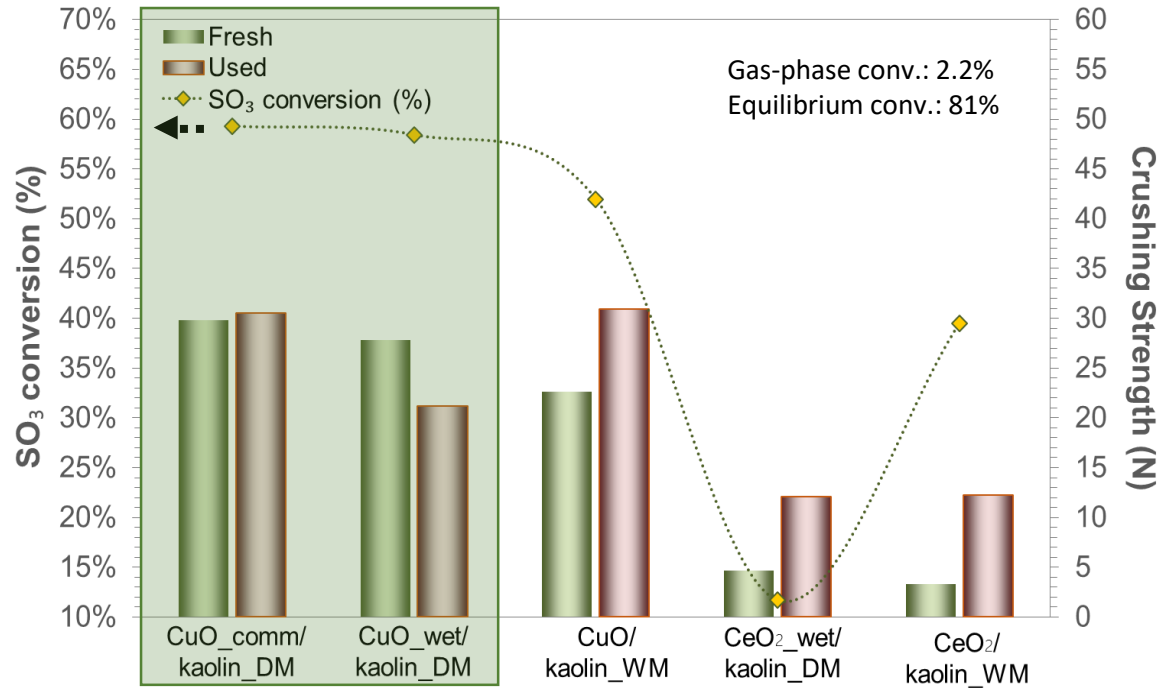
Evaluation

Conclusions & Next Steps



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Process &
Energy
Resources
Institute

Evaluation

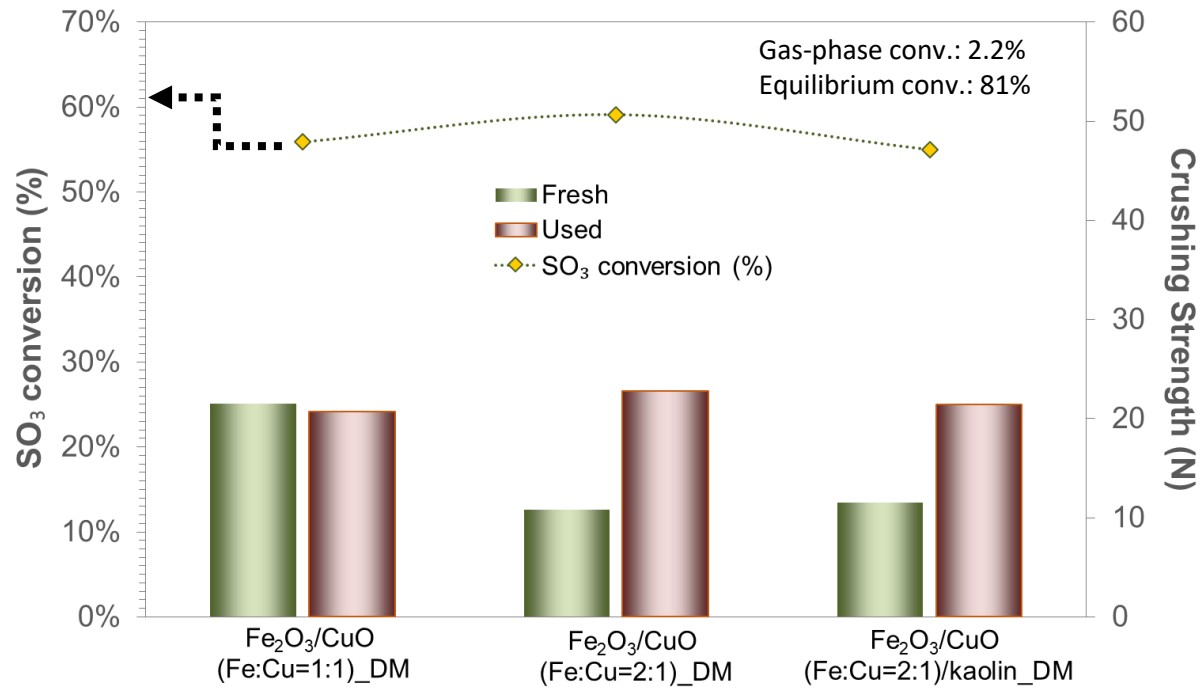


- ✓ Crushing Strength (CS) improved after experiment: Sintering
- ✓ Copper Oxides: High catalytic activity
- ✓ DEP synthesized CeO₂/Kaolin: better catalytic activity

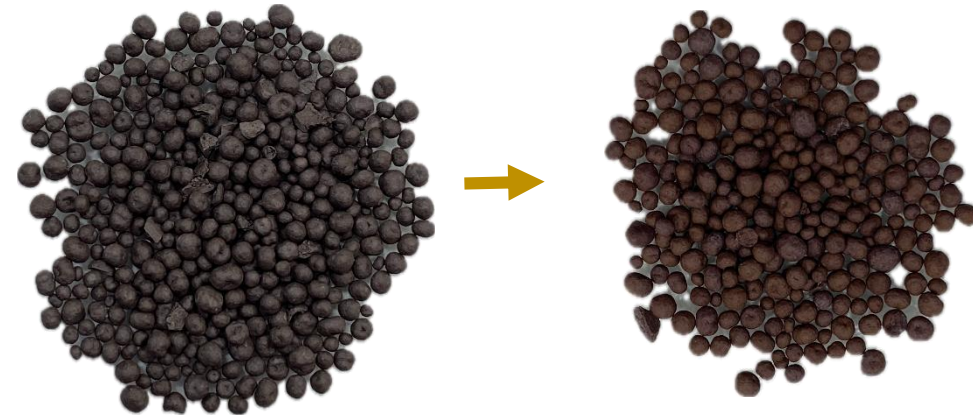


Fresh
Used
CuO /kaolin (15/85 wt%)

Evaluation



- ✓ Mixed phases such as CuFe₂O₄ detected- enhanced the catalytic activity
- ✓ Crushing Strength (CS) improved after experiment: Attributed to sintering



Fresh

Used

*Fe₂O₃_com/CuO_com
(molar ratio Fe:Cu=2:1)/ Kaolin_DM*

Indicative physicochemical characterization (*CuO_com/Kaolin_DM*)

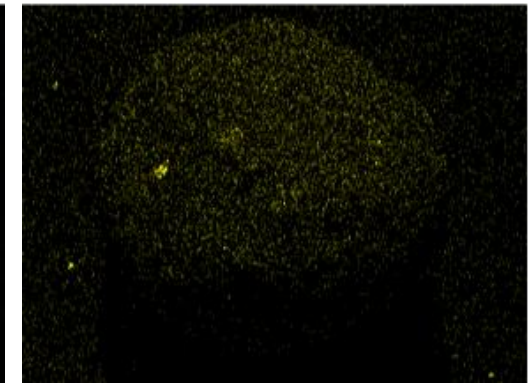
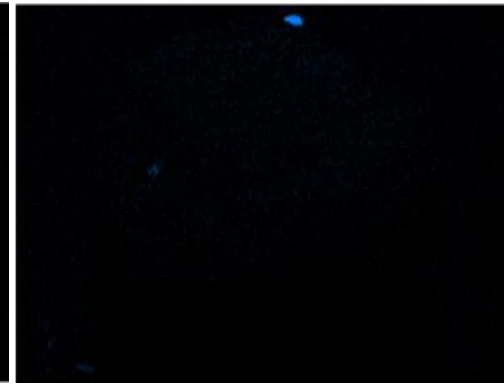
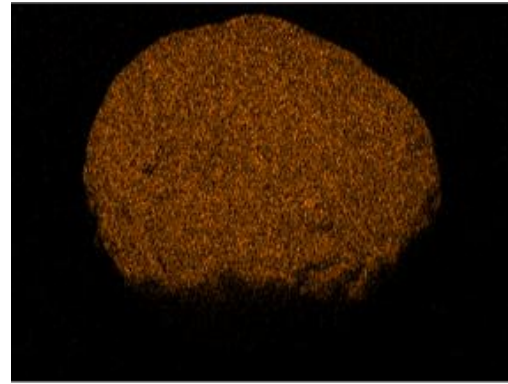
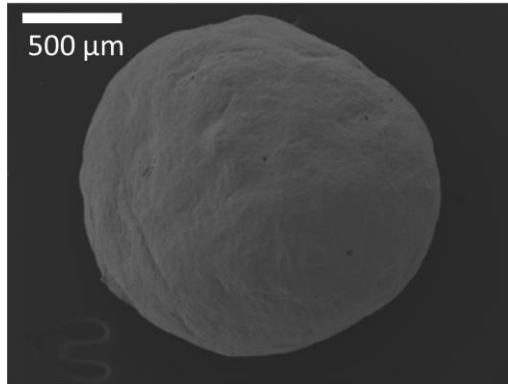
Fresh

Cu

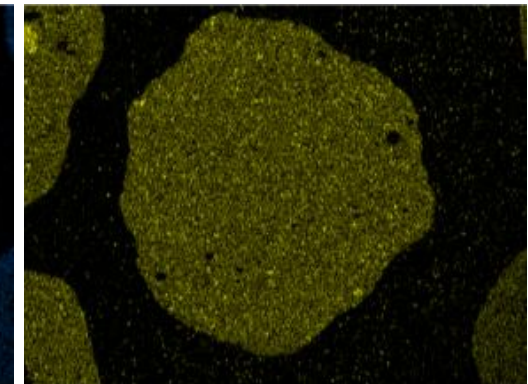
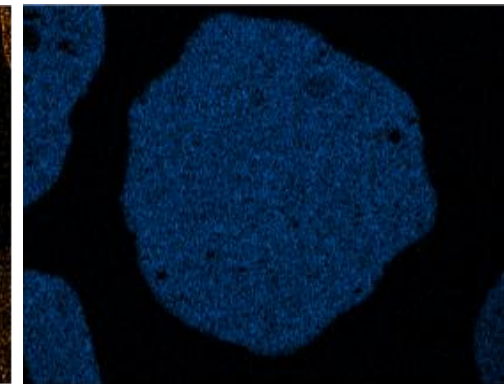
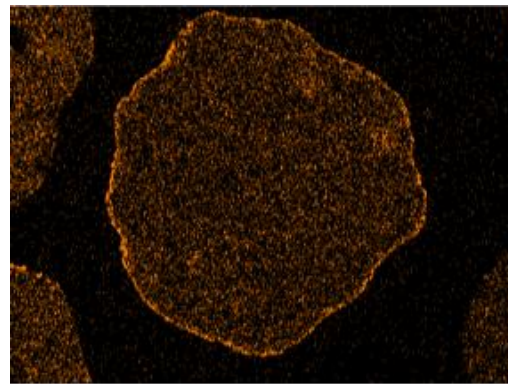
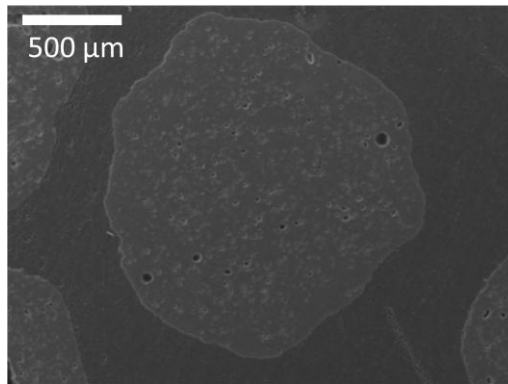
Al

Si

Surface



Cross Section



- ❖ *Identified peaks:* CuO, CuAl₂O₄, Al₆Si₂O₁₃, SiO₂, O₂
- ❖ *Negligible* surface area, pore volume and pore size in the fresh sample
- ❖ Copper mainly on *surface*; Al/Si internally

Indicative physicochemical characterization (*CuO_com/Kaolin_DM*)

Used

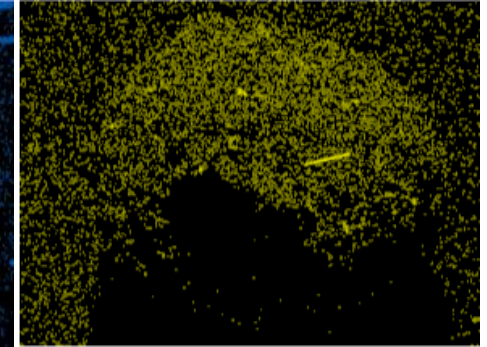
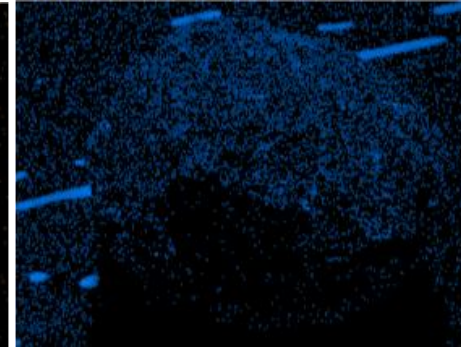
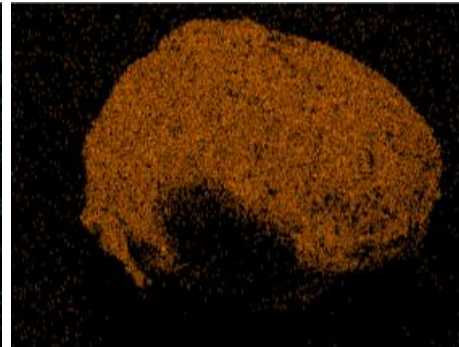
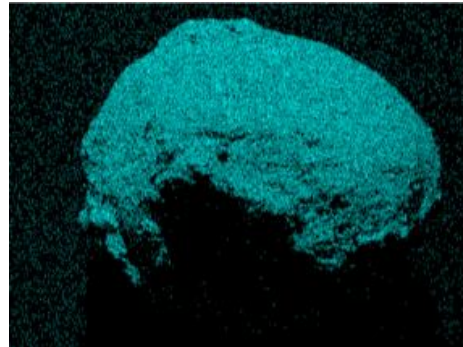
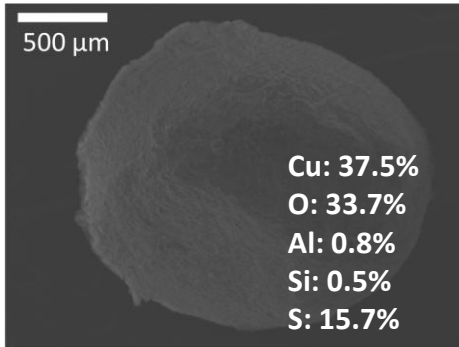
S

Cu

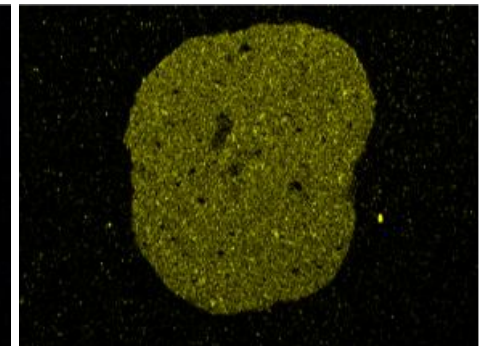
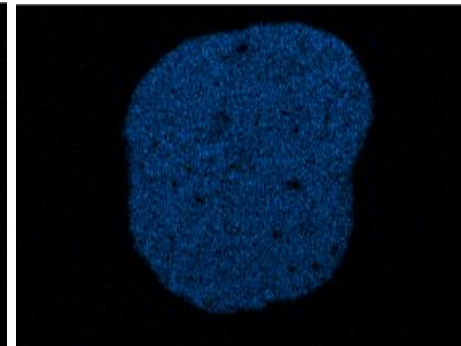
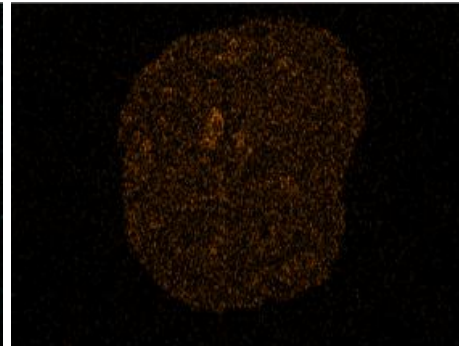
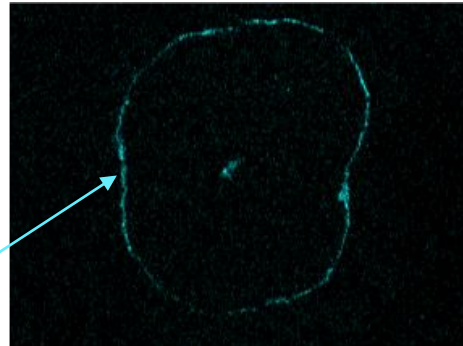
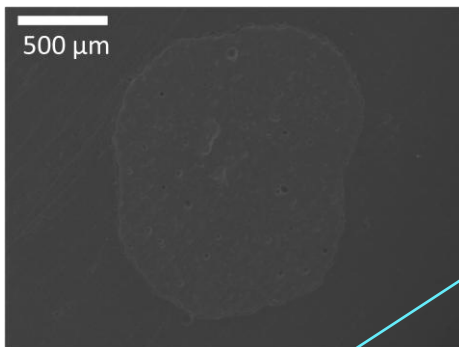
Al

Si

Surface

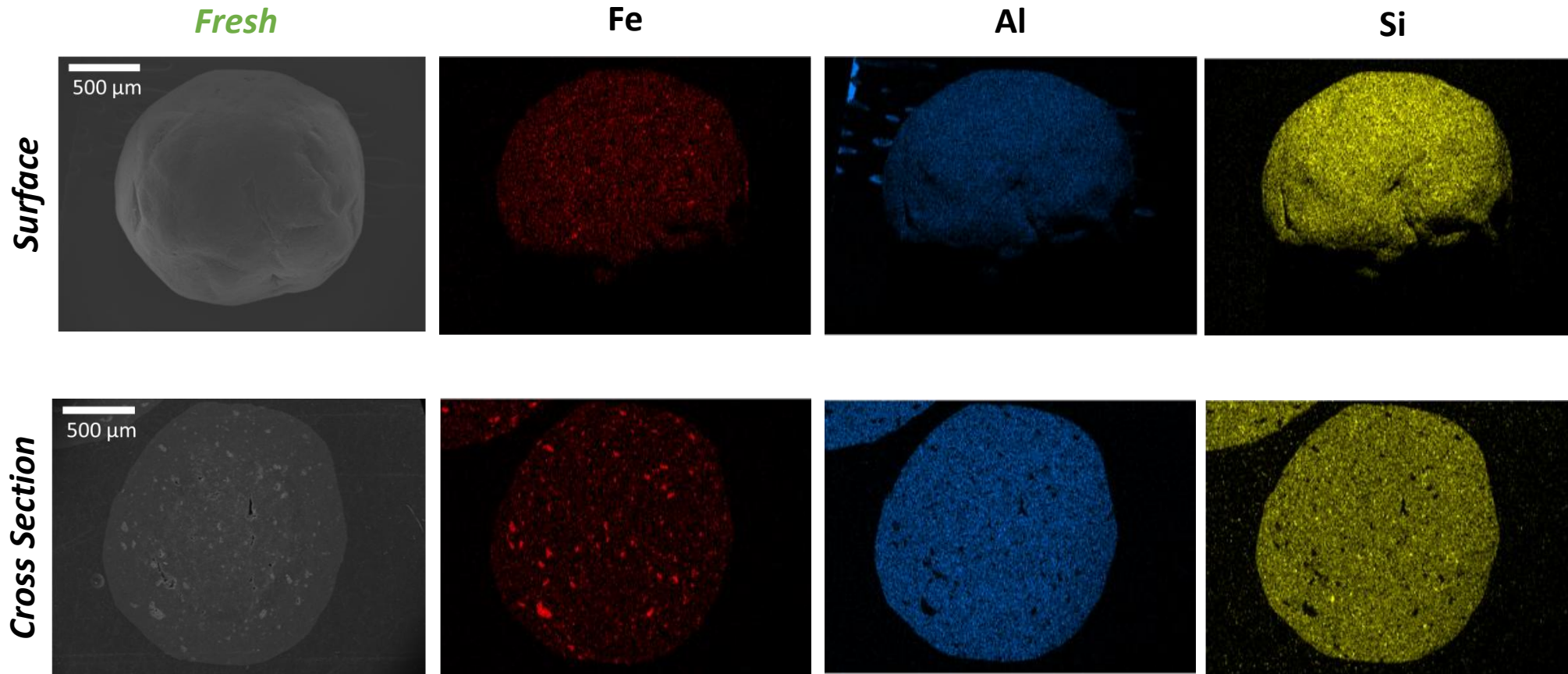


Cross Section



- ❖ *Identified peaks:* CuO , Cu_4O_3 , SiO_2 , CuAl_2O_4 , $\text{KAl}(\text{SO}_4)_2$, $\text{Al}_6\text{Si}_2\text{O}_{13}$, $\text{K}_2\text{S}_2\text{O}_3$
- ❖ $0.6 \text{ m}^2/\text{g}$ BET surface area, $0.024 \text{ cm}^3/\text{g}$ pore volume and 93.0 nm pore size
- ❖ *Reaction: taking place mainly on the surface of the particles*

Indicative physicochemical characterization (Fe_2O_3 _wet/Kaolin_DM)



- ❖ *Identified peaks:* Fe_2O_3 , SiO_2 , $Fe(Al_2O_4)$
- ❖ 10.4 m²/g BET surface area, 0.295 cm³/g pore volume and 69.9 nm pore size
- ❖ Al/Si internally

Indicative physicochemical characterization (Fe_2O_3 _wet/Kaolin_DM)

Used

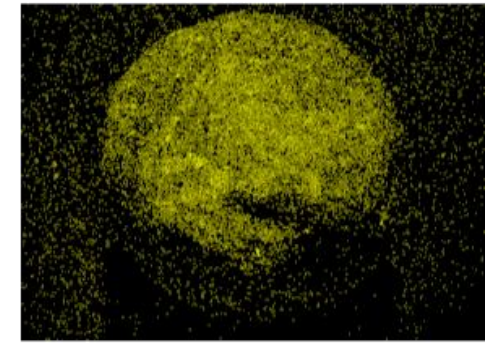
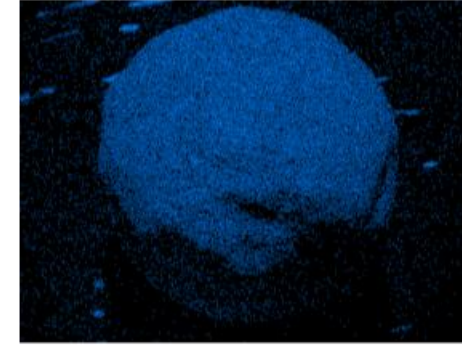
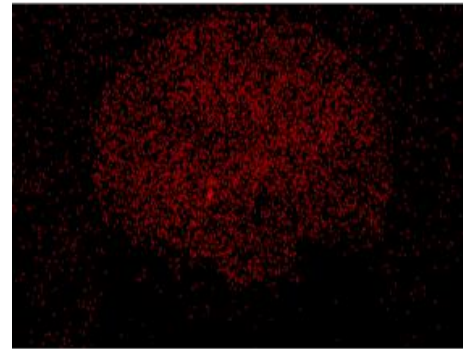
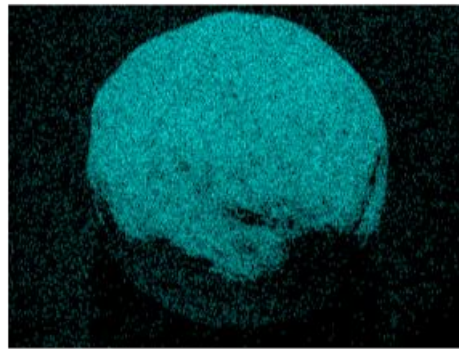
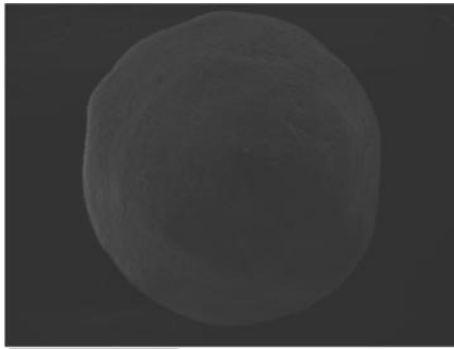
S

Fe

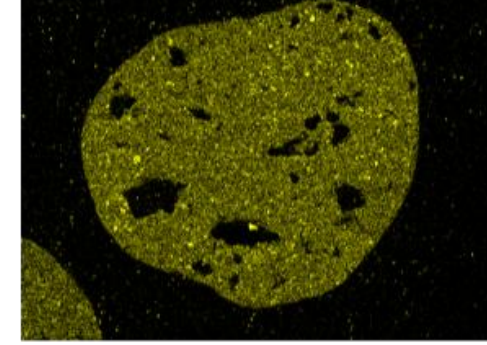
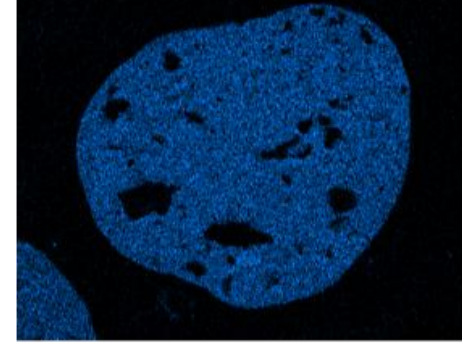
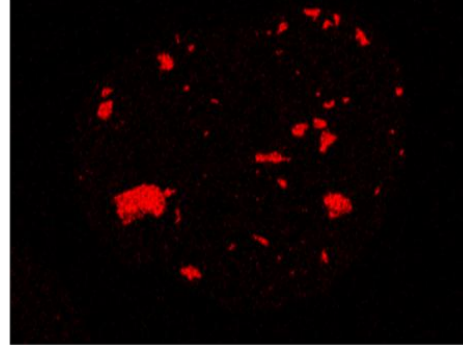
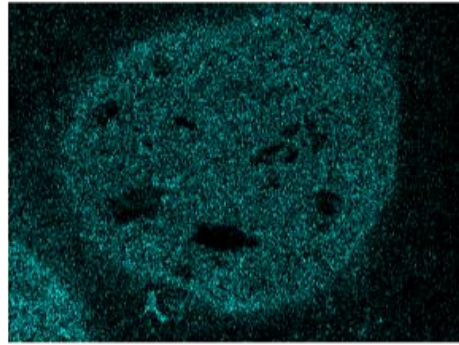
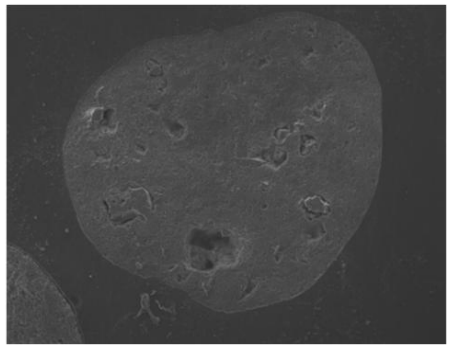
Al

Si

Surface

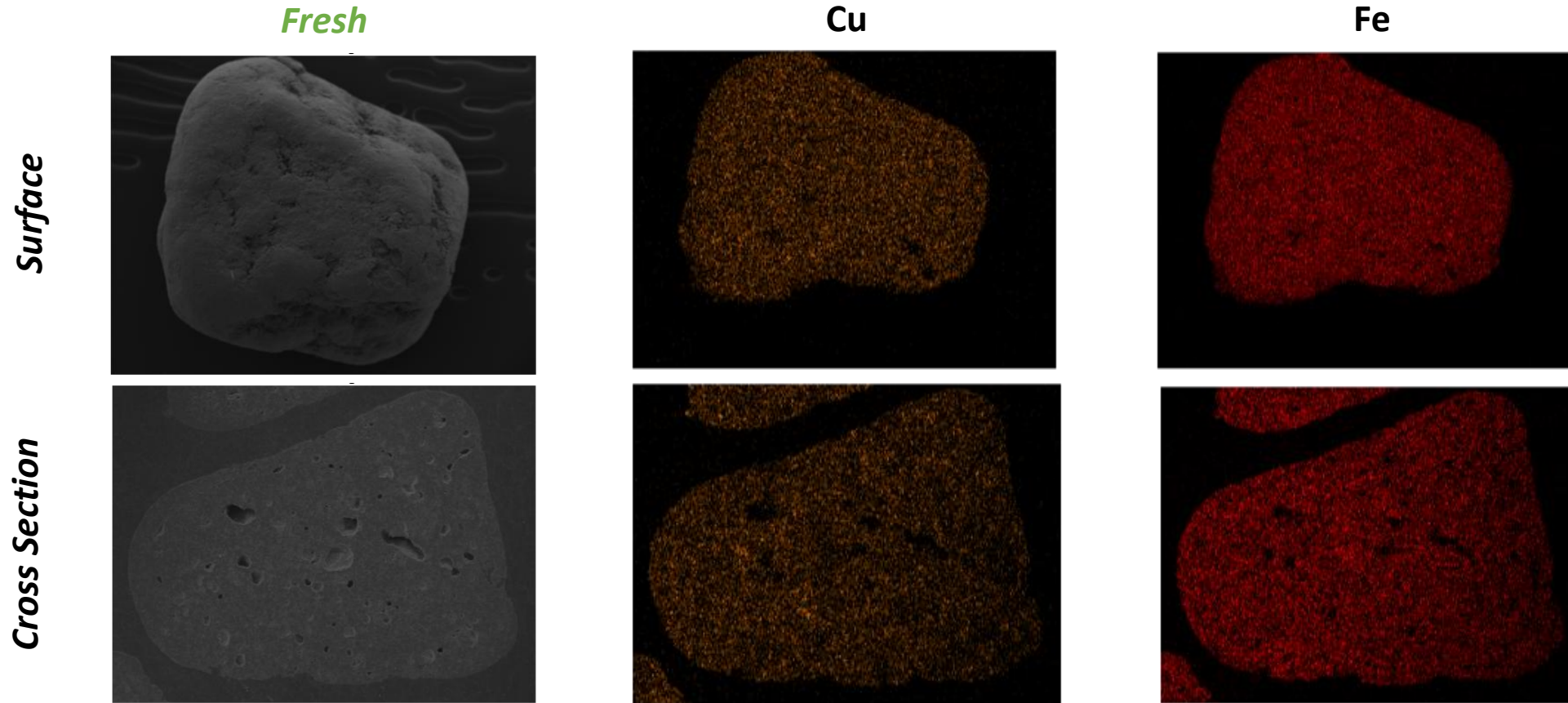


Cross Section



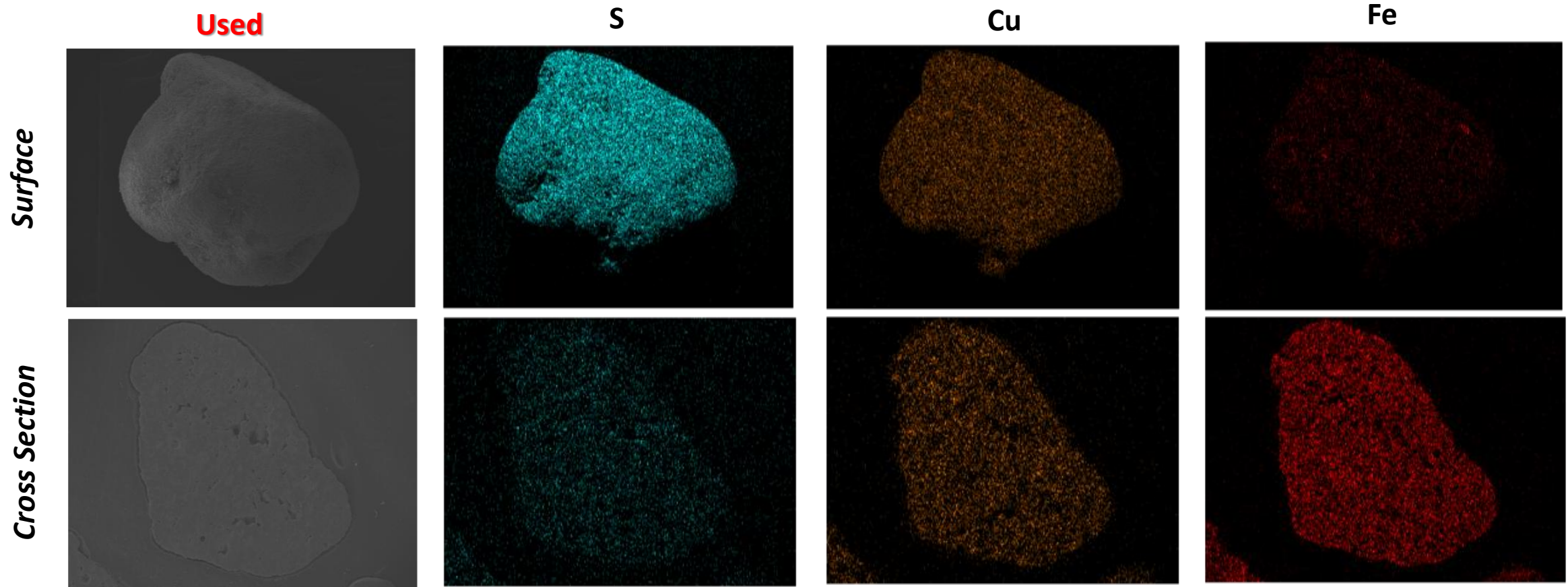
- ❖ Identified peaks: Fe_2O_3 , SiO_2 , $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, $KAl(SO_4)_2$, $(Al(H_2O)_6)_2(SO_4)_3(H_2O)_5$
- ❖ 2.2 m²/g BET surface area, 0.038 cm³/g pore volume and 81.2 nm pore size
- ❖ Reaction: taking place mainly on the surface of the particles

Indicative physicochemical characterization ($\text{Fe}_2\text{O}_3/\text{CuO}_{DM}$ - $\text{Fe}:\text{Cu}=1:1$)



- ❖ Identified peaks: Fe_2O_3 , CuO
- ❖ $0.2 \text{ m}^2/\text{g}$ BET surface area, $0.010 \text{ cm}^3/\text{g}$ pore volume and 21.9 nm pore size
- ❖ Copper and Iron all over the structure

Indicative physicochemical characterization ($\text{Fe}_2\text{O}_3/\text{CuO_DM}$ -Fe:Cu=1:1)



- ❖ Identified peaks: CuFe_2O_4 , Fe_2O_3 , $\text{Cu}(\text{SO}_4)$, $\text{Cu}_2\text{O}(\text{SO}_4)$
- ❖ 0.9 m^2/g BET surface area, 0.076 cm^3/g pore volume and 93.5 nm pore size
- ❖ Reaction: taking place mainly on the surface of the particles

Conclusions & Next Steps

- ❑ Dissolution-evaporation-precipitation: finer particles and more mixed phases cf. dry mixing
- ❑ Sufficient distribution of active phases- mainly on the surface and Al/Si internally- mechanical stability
- ❑ The reaction is mainly taking place on the surface of the catalysts
- ❑ Best catalytic performance: CuO_comm/kaolin_DM (59.3%) - CuO, CuAl₂O₄ active phases and Fe₂O₃_com/CuO_com (Fe:Cu=2:1)_DM (59.1%) - CuFe₂O₄, CuO active phases

Next Steps

- ❑ Synthesis & Evaluation of medium temperature catalysts (~650 °C) – Vanadium-based
- ❑ New synthesis methods and additional mixed materials

Acknowledgements

European
Innovation
Council



Funded by
the European Union



An innovative thermochemical cycle based on solid Sulphur
for integrated long-term storage of solar thermal energy

This study has received funding by the European Commission through the HORIZON EUROPE project “SULPHURREAL” under Grant Agreement number 101115538.

Thank you for your Attention!

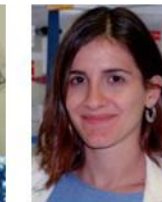
Questions?



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