Understanding the redox kinetics of oxygen carriers for chemical looping combustion

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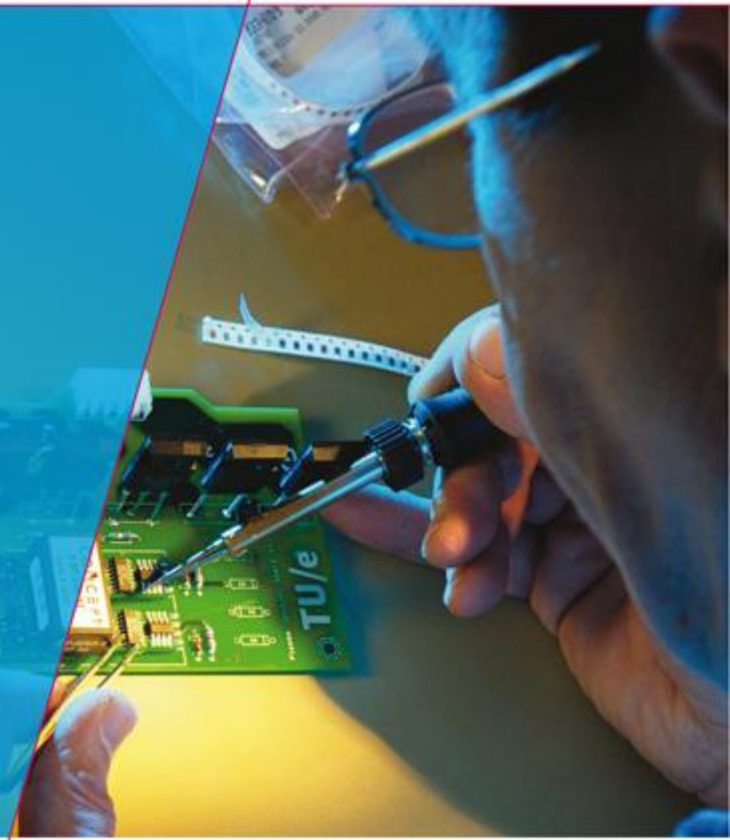
Understanding the redox kinetics of oxygen carriers for chemical looping combustion



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Chemical Process Intensification, Eindhoven University of Technology, The Netherlands

Multiphase Reactors Group
Department of Chemical Engineering & Chemistry

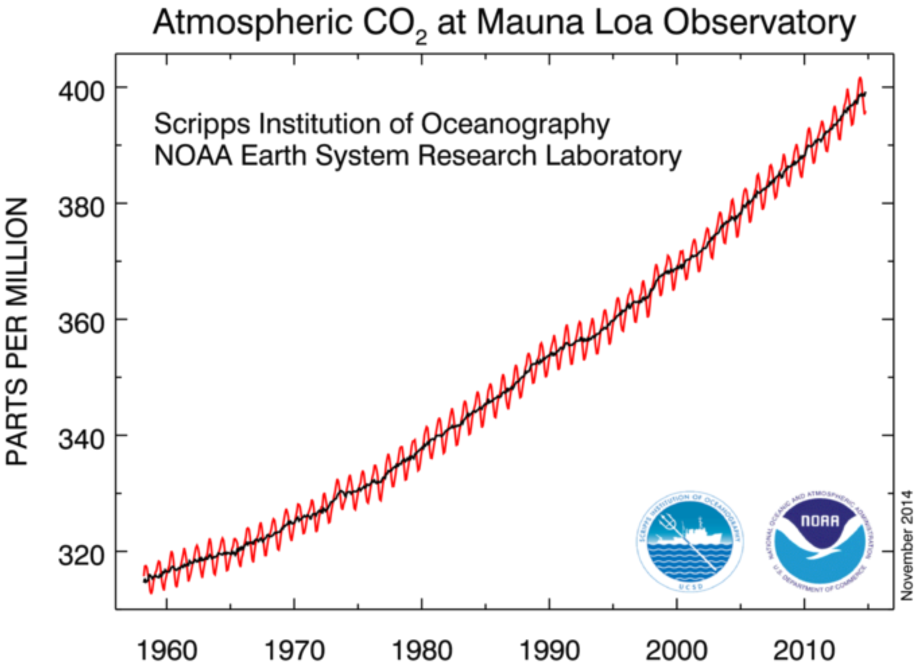
TU/e Technische Universiteit Eindhoven University of Technology

Where innovation starts

THE CO_2 PROBLEM

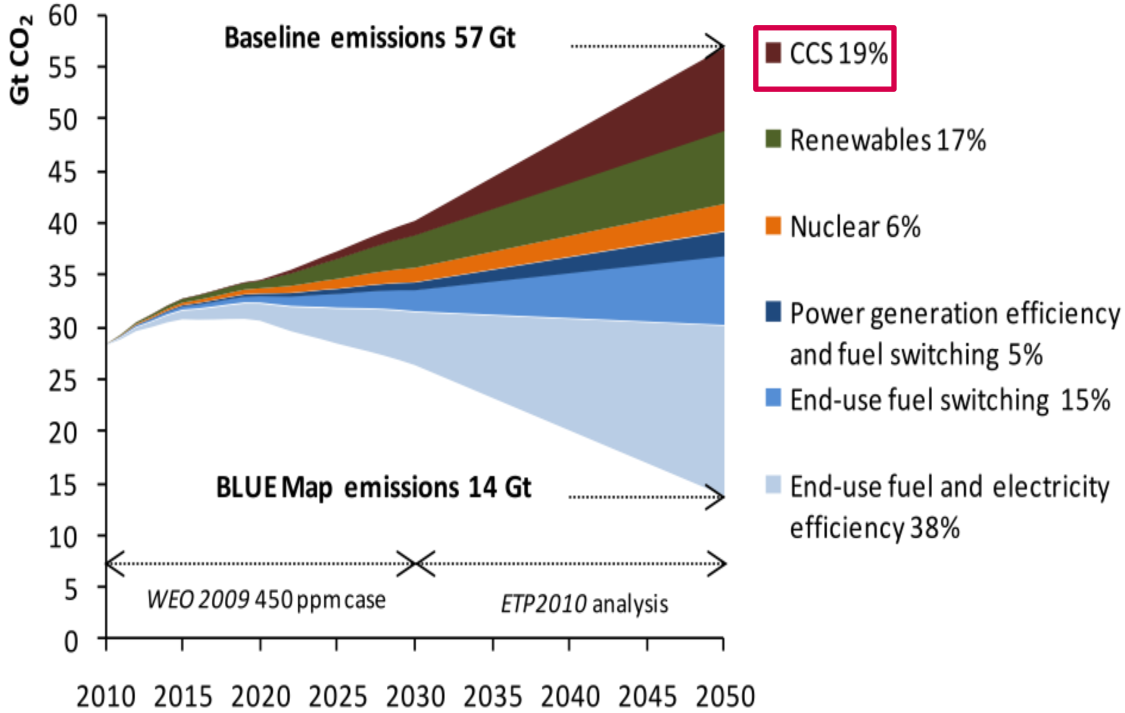
Emissions of greenhouse gases (**GHG**) to the atmosphere are expected to cause significant global climate change.

Carbon Dioxide (**CO_2**) is the primary greenhouse gas emitted through human activities.



THE CO_2 PROBLEM

CARBON CAPTURE AND STORAGE



Source: IEA Energy Technology Perspectives (2010) Scenarios and strategies to 2050

CCS: Important strategy for reducing CO_2 emissions from fossil based power plants

Chemical Looping is one of the most promising technologies of CCS as it presents the **lowest energy penalty**.

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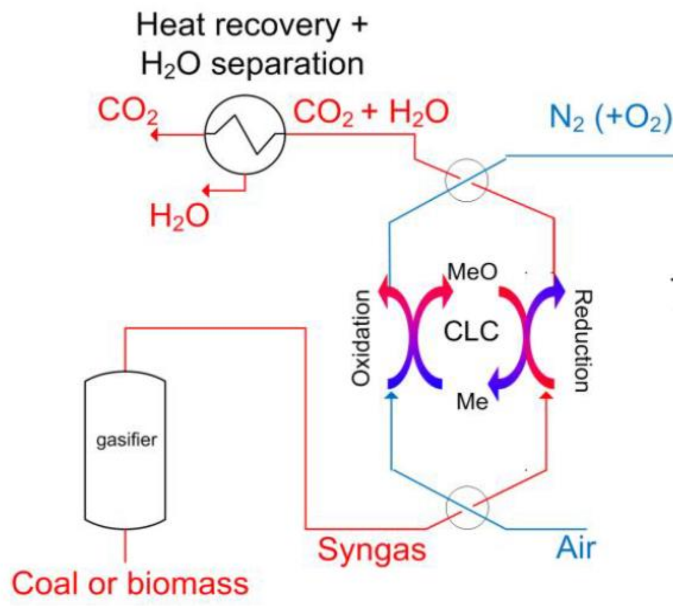
ENERGY PRODUCTION WITH CO_2 CAPTURE

Chemical Looping Combustion (CLC)



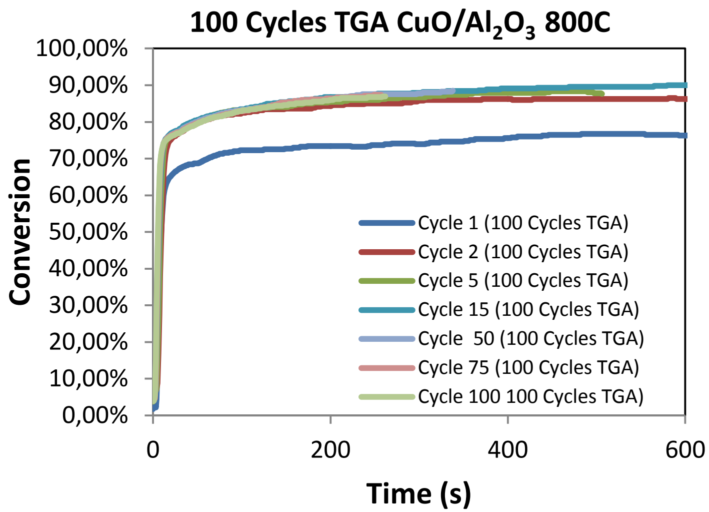
CLC involves

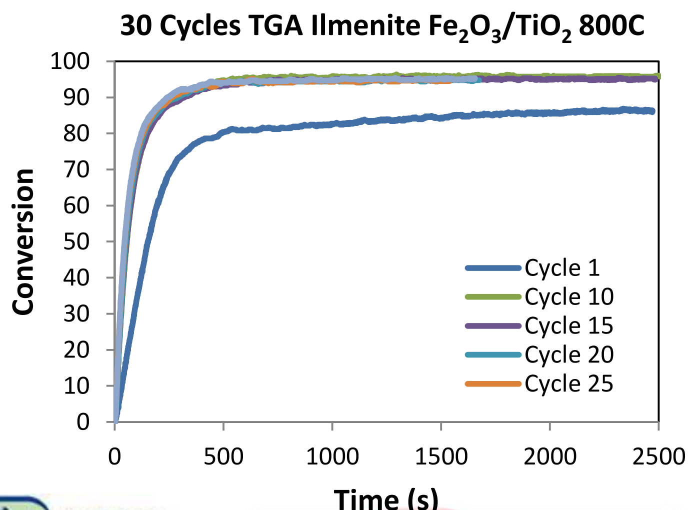
- Two Packed Bed Reactors (PBR)
  - Fuel reactor
  - Air reactor
- Redox chemistry (metal)
- Periodic operation

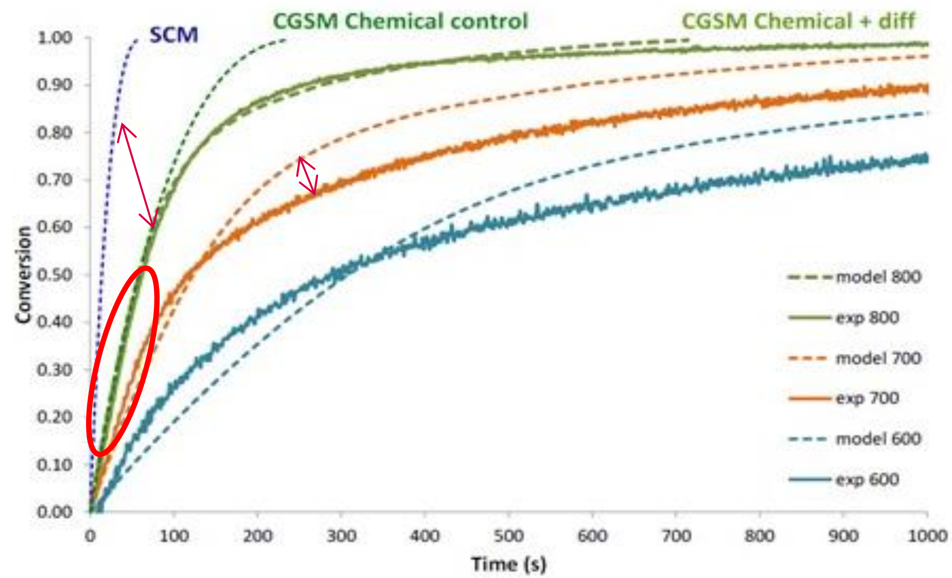
CLC can achieve

- High level of CO_2 capture
- Low energy carbon capture penalty

OXYGEN CARRIER KINETICS







Ilmenite conversion profiles as a function of time on stream (with 15% CO in N_2)

PBR: Conversion 0-100% every cycle

Important to predict the real final conversion

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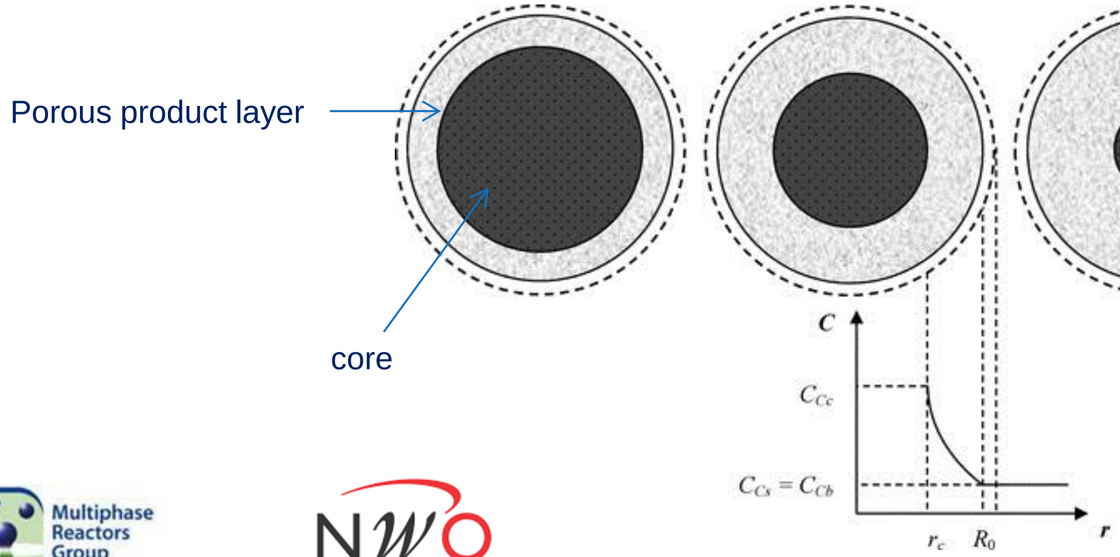
OXYGEN CARRIER KINETICS

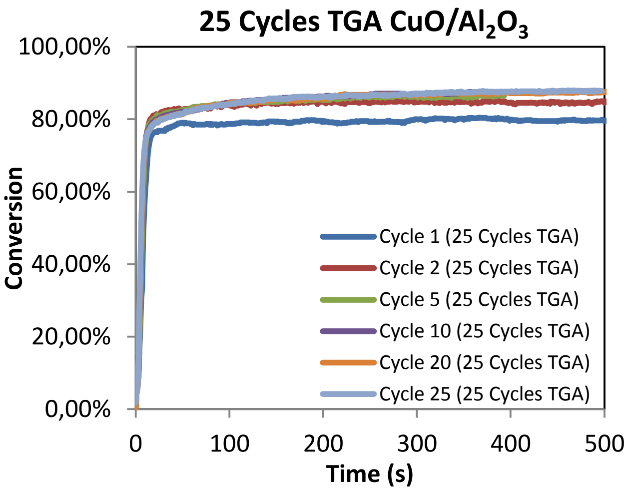
Shrinking Core Model Assumptions

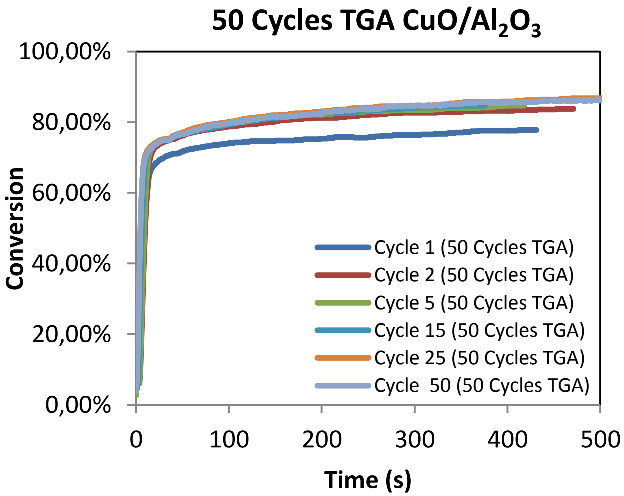
- Reaction located in the surface
- Porosity of the particle very small and uniform in each layer
- Resistance to gas diffusion very high
- Harmonic average effective diffusion coefficient
- Convection of the gas negligible if compared to the diffusive fluxes
- Kinetic is first order

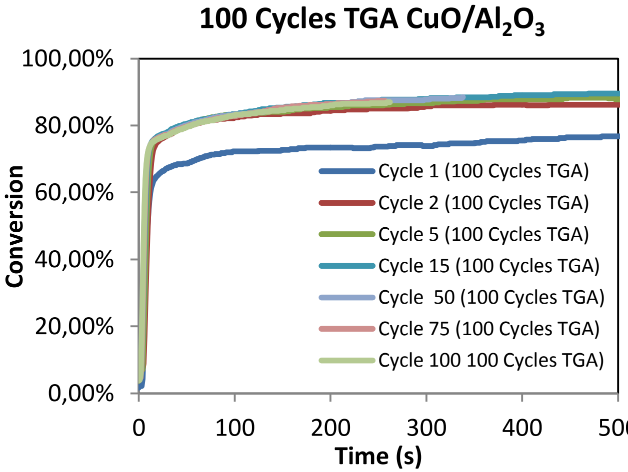


EXPERIMENTAL STUDIES

Thermo-**G**ravimetric-**A**nalysis (TGA)







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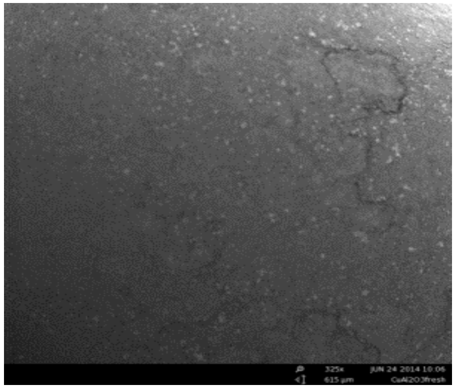
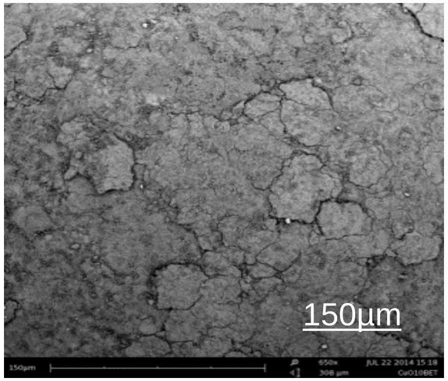
EXPERIMENTAL STUDIES

Scanning **E**lectron **M**icroscopy (SEM)

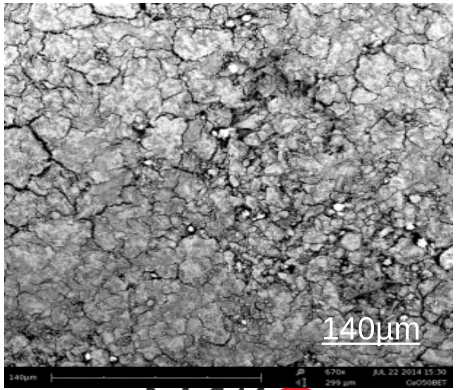
Fresh CuO/Al_2O_3



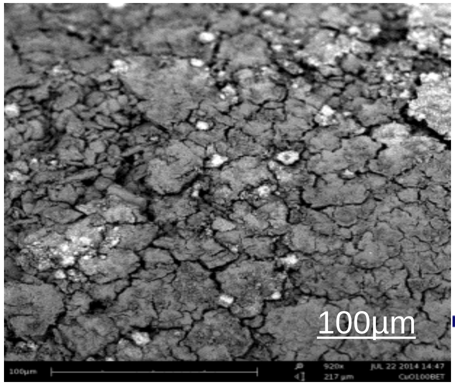
10 Cycles TGA CuO/Al_2O_3



50 Cycles TGA CuO/Al_2O_3



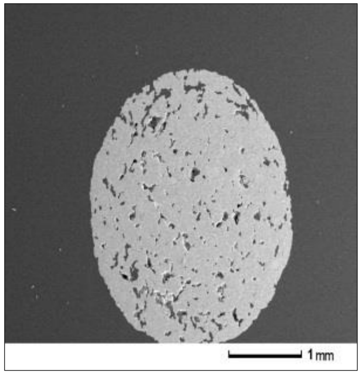
100 Cycles TGA CuO/Al_2O_3

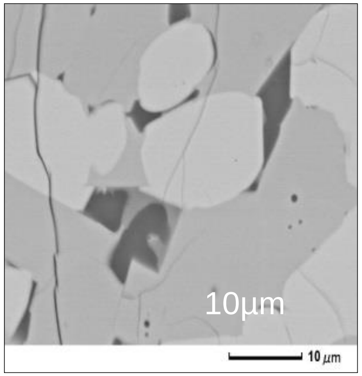


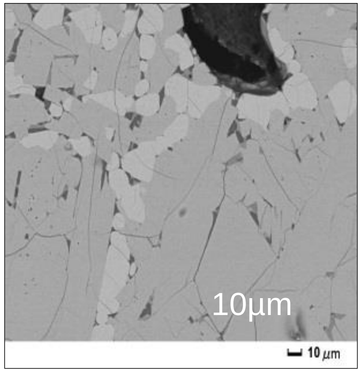
EXPERIMENTAL STUDIES

Scanning **E**lectron **M**icroscopy (SEM)

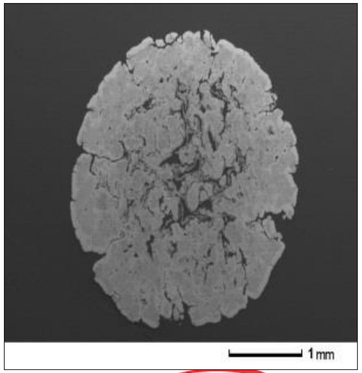
Fresh Ilmenite (Fe_2O_3/TiO_2)

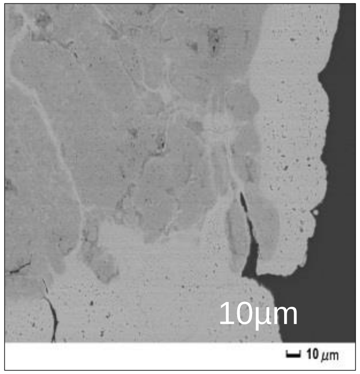


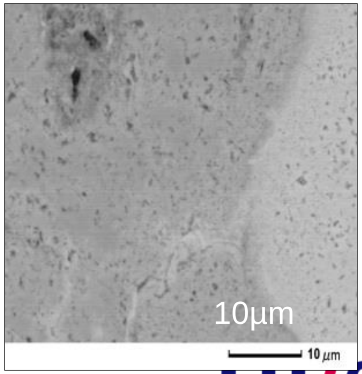




Activated Ilmenite (Fe_2O_3/TiO_2)



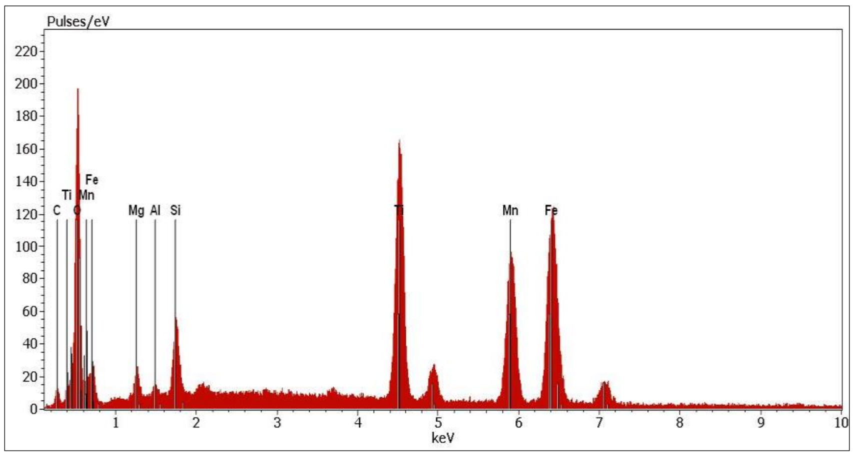


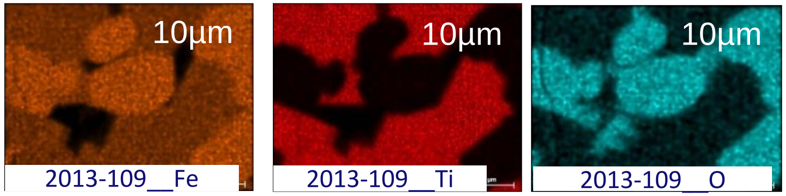


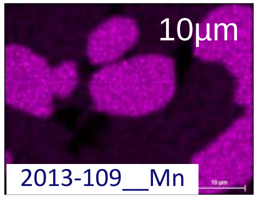
EXPERIMENTAL STUDIES

Scanning **E**lectron **M**icroscopy (SEM) + **E**nergy-**D**ispersive **X**-ray spectroscopy (EDX)

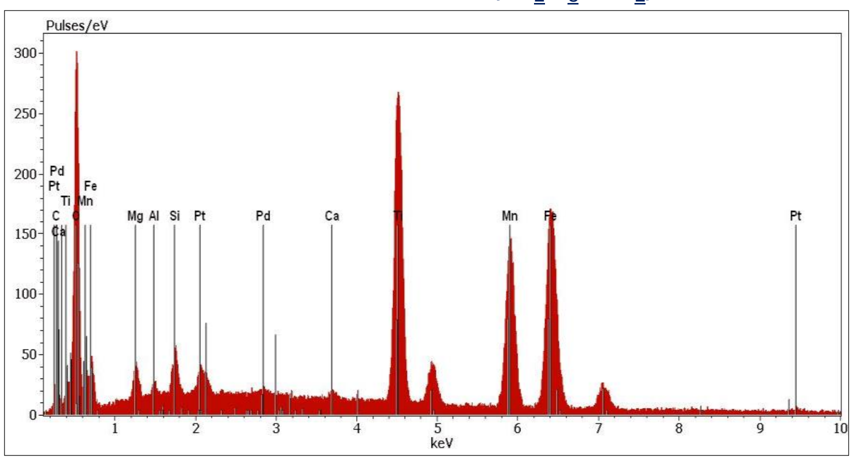
Fresh Ilmenite (Fe_2O_3/TiO_2)

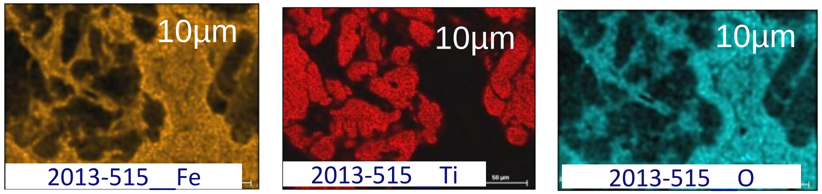


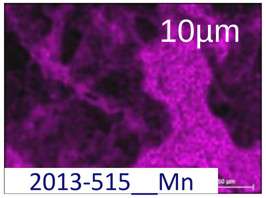




Activated Ilmenite (Fe_2O_3/TiO_2)







Thanks to VITO for the images

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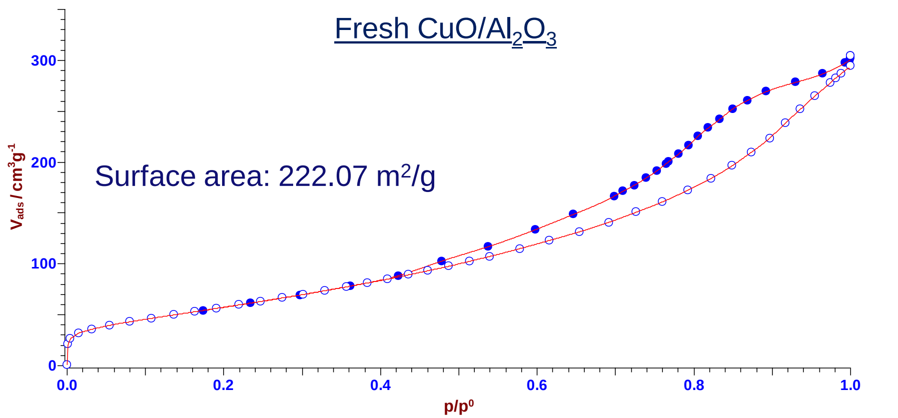
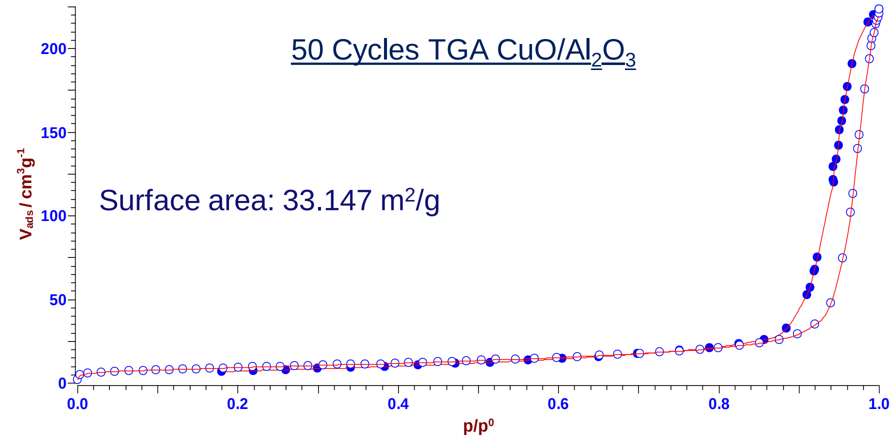
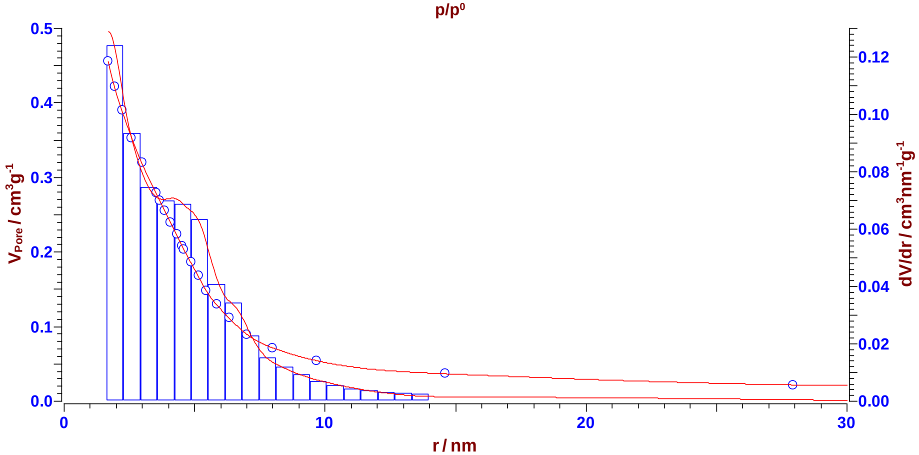
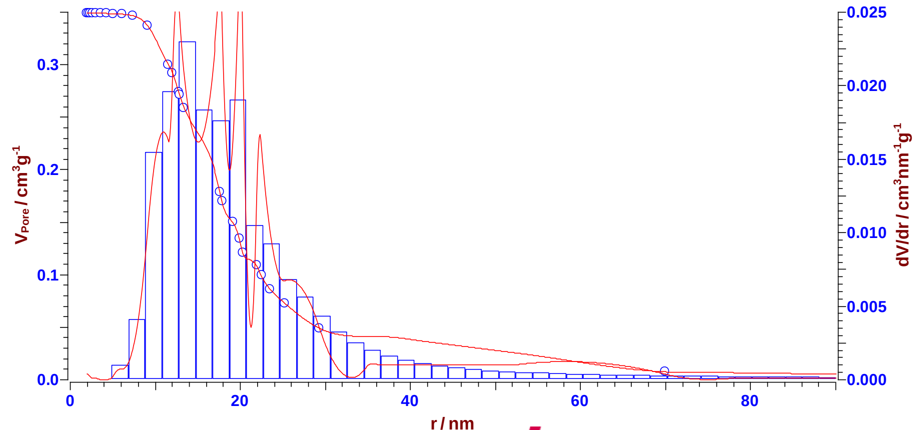
EXPERIMENTAL STUDIES

Physisorption with liquid nitrogen (BET)









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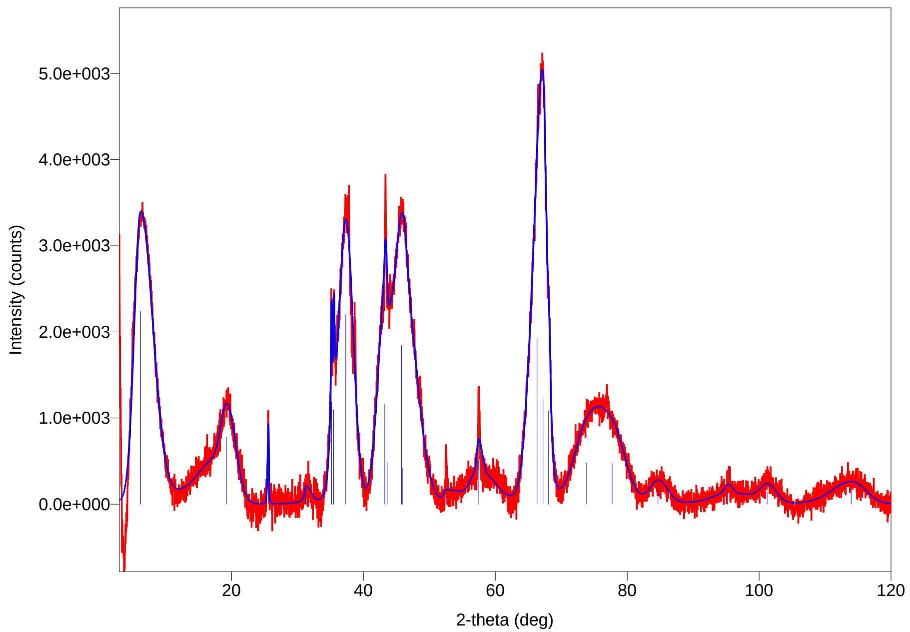
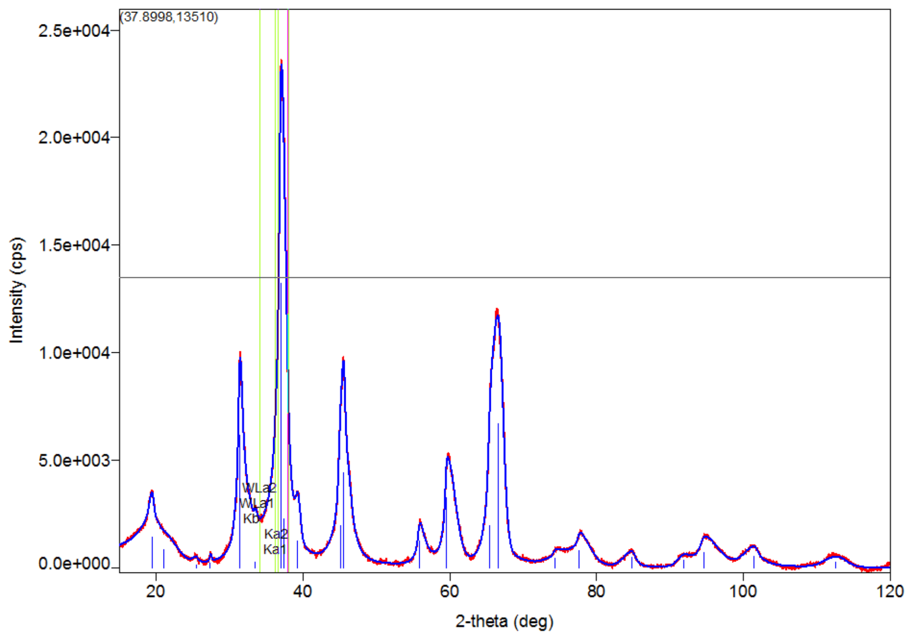
EXPERIMENTAL STUDIES

X-Ray Diffraction (XRD)

Fresh CuO/Al_2O_3



25 CYCLES TGA CuO/Al_2O_3



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EXPERIMENTAL STUDIES

X-Ray Diffraction (XRD)

Components	Fresh	25 Cycles	75 Cycles	100 Cycles
Tenorite (**CuO**)	X	X	X	X
Aluminium Oxide (**Al_2O_3**)	X	X	X	X
Spinel (**$CuAl_2O_4$**)	X	X	X	X
Gamma-alumina (**$Al_{2.67}O_4$**)	X	X	X	X
Copper aluminium oxide (**$CuAlO_2$**)			X	
Cuprite (**Cu_2O**)				X

$$CuO + H_2 \rightarrow Cu + H_2O$$
$$2CuO + H_2 \rightarrow Cu_2O + H_2O$$
$$Cu_2O + H_2 \rightarrow 2Cu + H_2O$$

$$Cu + \tfrac{1}{2} O_2 \rightarrow CuO$$
$$CuO + Al_2O_3 \rightarrow CuAl_2O_4$$
$$4CuAl_2O_4 \rightarrow 4CuAlO_2 + 2Al_2O_3 + O_2$$
$$4CuAlO_2 + O_2 \rightarrow 4CuAl_2O_2 + 2\,Cu_2O$$

New phases are formed while the number of redox reactions increases

These components can influence the kinetics of the OC

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PARTICLE MODEL

SCM Assumptions

- ~~Reaction located in the surface~~ SEM + XRD
- ~~Porosity of the particle very small and uniform in each layer~~ SEM
- ~~Resistance to gas diffusion very high~~ TGA
- ~~Harmonic average effective diffusion coefficient~~ SEM + BET
- ~~Convection of the gas negligible if compared to the diffusive fluxes~~ TGA
- ~~Kinetic is first order~~ XRD

⇓

New Particle Model

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PARTICLE MODEL

Kinetics of the components detected in the XRD analysis: Kinetics

Reduction:

$$\mathbf{CuO} + H_2 \rightarrow \mathbf{Cu} + H_2O$$
$$2CuO + H_2 \rightarrow \mathbf{Cu_2O} + H_2O$$
$$Cu_2O + H_2 \rightarrow 2Cu + H_2O$$

Oxidation:

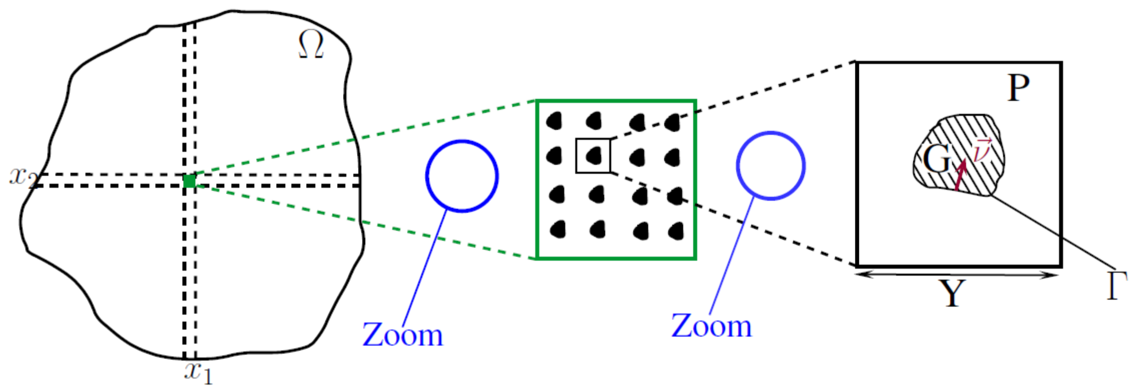
$$\mathbf{Cu} + \tfrac{1}{2} O_2 \rightarrow CuO$$
$$\mathbf{CuO} + Al_2O_3 \rightarrow \mathbf{CuAl_2O_4}$$
$$4CuAl_2O_4 \rightarrow 4\mathbf{CuAlO_2} + 2Al_2O_3 + O_2$$
$$4CuAlO_2 + O_2 \rightarrow 4CuAl_2O_2 + 2\ \mathbf{Cu_2O}$$

→

- **CuO**
- **$CuAl_2O_4$**
- **Cu_2O**
- **Cu**
- **$CuAlO_2$**

PARTICLE MODEL

Homogenization in porous media: Diffusion



Two sub-domains: the "inner" grain G surrounded by the pore P. With Γ being the boundary of G.

$$(P(x))\begin{cases} -\nabla \cdot \left(\boldsymbol{D_{eff}}(\boldsymbol{x})\nabla U\right) = f, & for\ all\ x \in \Omega \\ U = 0, & on\ \partial\Omega \end{cases}$$

Effective diffusion coefficient taking into account all the pore sizes and porosity.

CONCLUSIONS

- **The morphology in terms of porosity doesn't really describe the kinetics.**
- **The change can be due to thermodynamics or to solid diffusion.**
- **No constant or homogeneous pore size is observed in the experiments.**
- **New phases are formed in the redox cycles affecting the kinetics of the OC.**
- **The different phases and a better description of the effective diffusion coefficient (gas or solid) have to be included in the new particle model.**

ACKNOWLEDGMENTS

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Group of Chemical Process Intensification

- Prof. M. van Sint Annaland
- Dr. F. Gallucci
- Dr. I. Roghair

Thank you for your attention

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