Understanding the redox kinetics of oxygen carriers for chemical looping combustion

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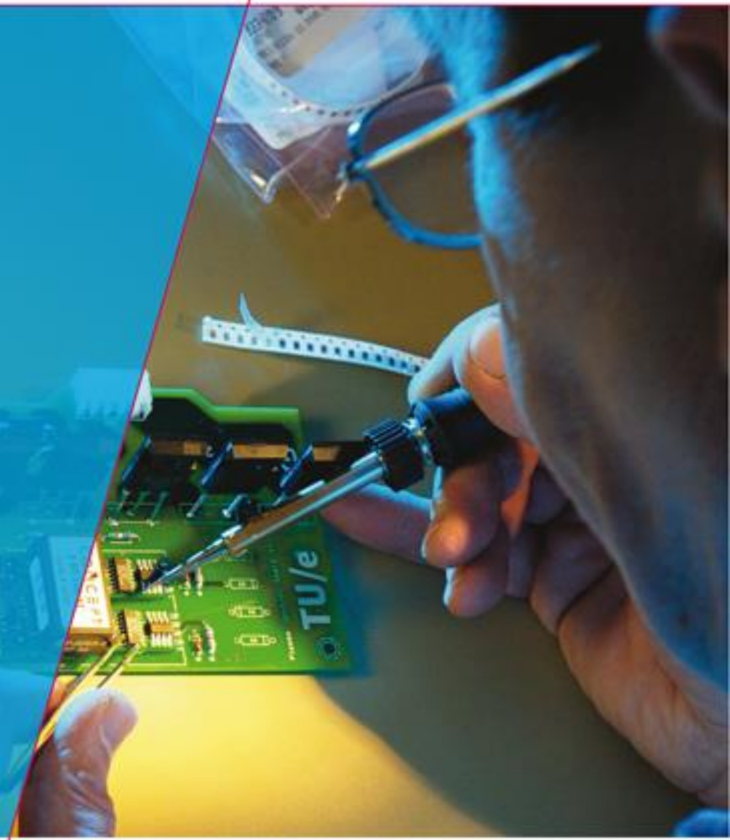
Understanding the redox kinetics of oxygen carriers for chemical looping combustion



M. A. San Pio Bordeje, I. Roghair, F. Gallucci,
M. van Sint Annaland

Chemical Process Intensification, Eindhoven University of Technology, The Netherlands

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Department of Chemical Engineering & Chemistry

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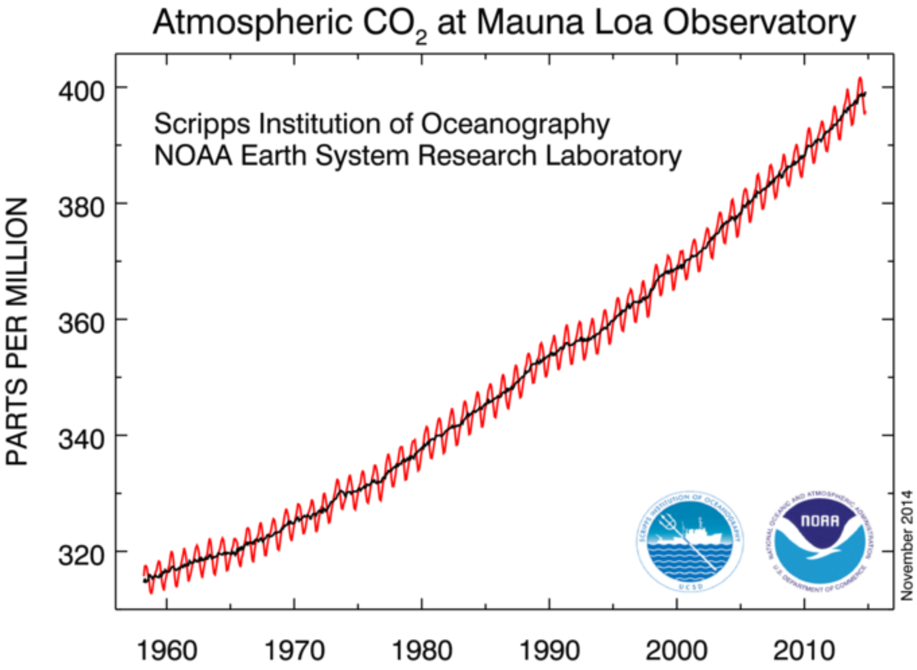
Where innovation starts

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.



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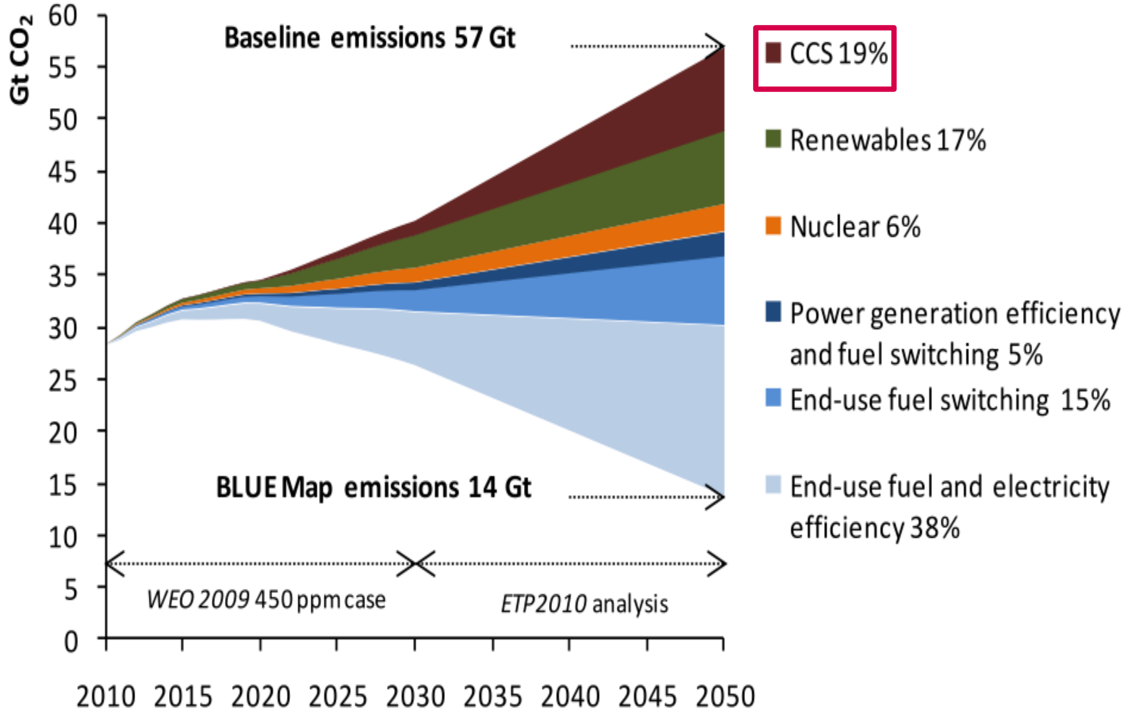
THE CO_2 PROBLEM

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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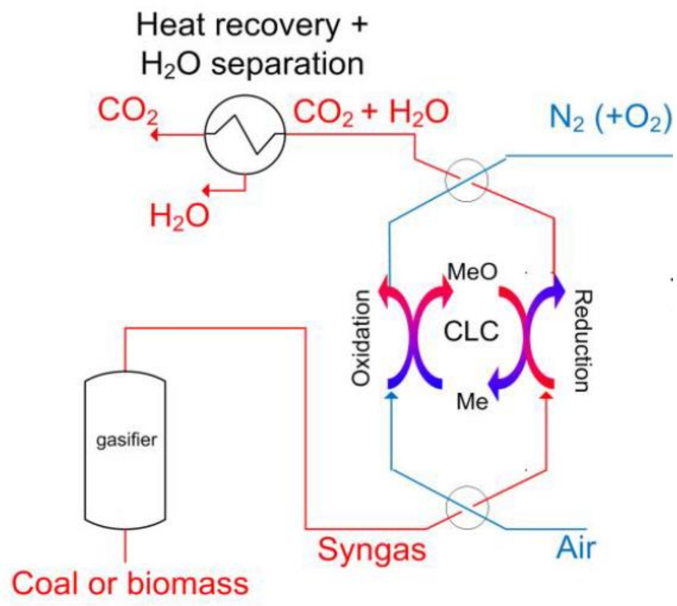
ENERGY PRODUCTION WITH CO_2 CAPTURE

Chemical Looping Combustion (CLC)



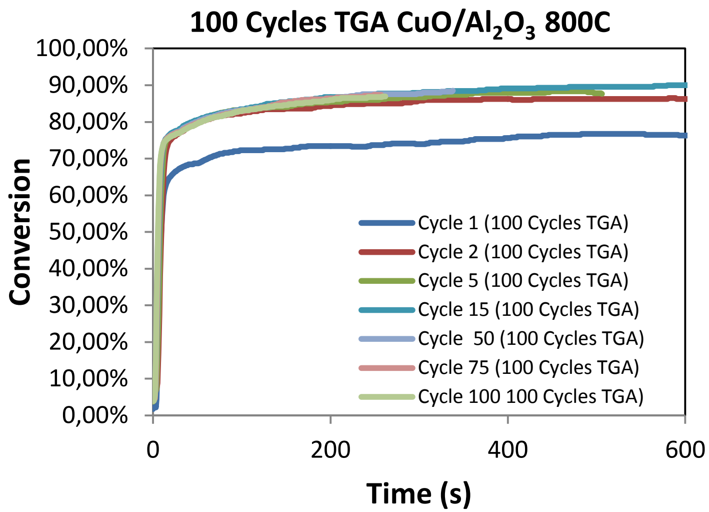
CLC involves

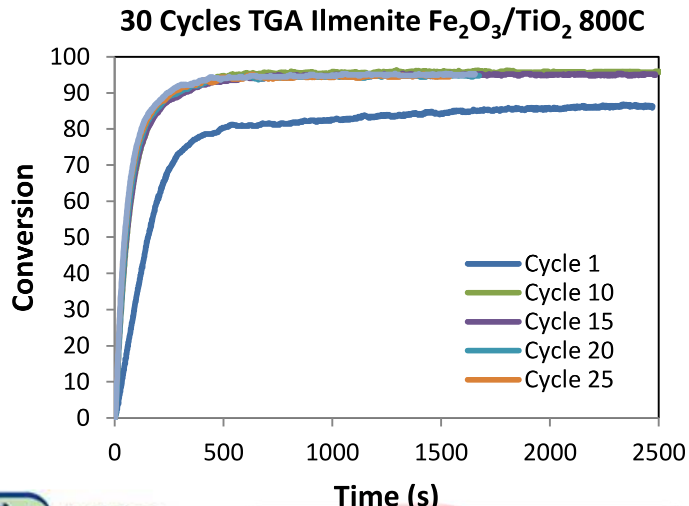
- Two Packed Bed Reactors (PBR)
  - Fuel reactor
  - Air reactor
- Redox chemistry (metal)
- Periodic operation

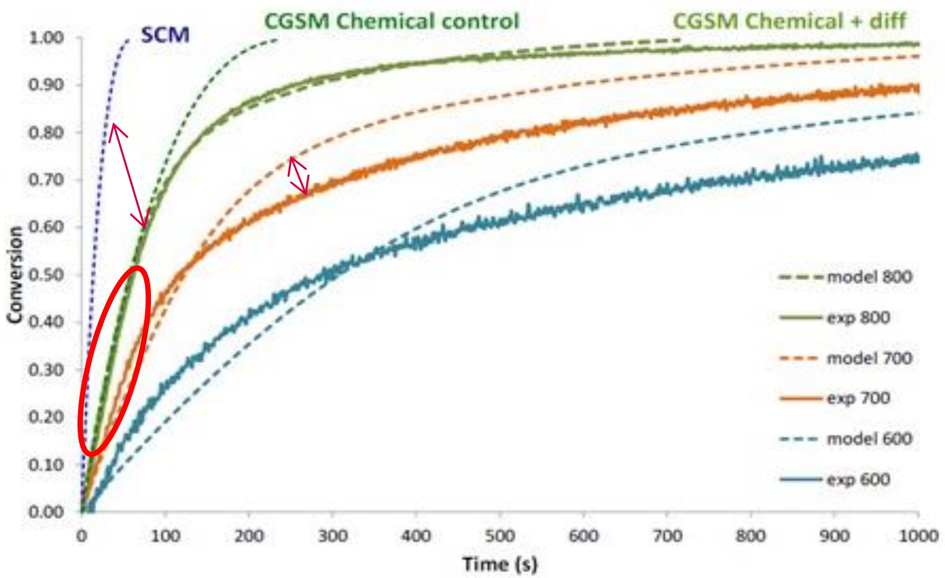
CLC can achieve

- 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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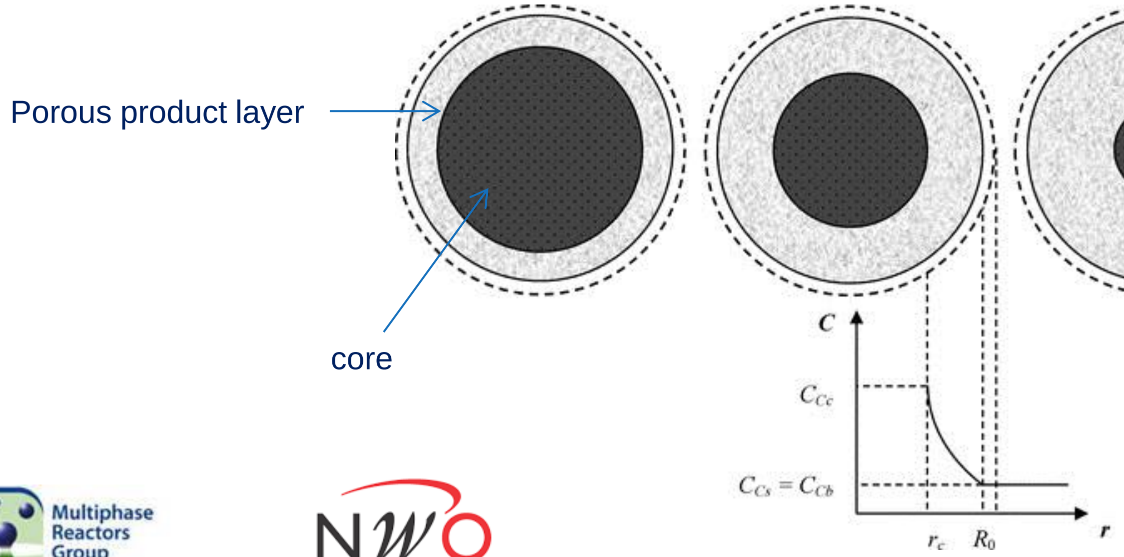
OXYGEN CARRIER KINETICS

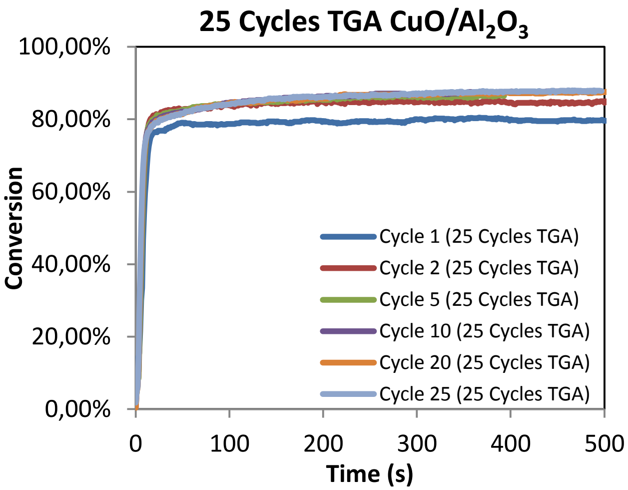
Shrinking Core Model Assumptions

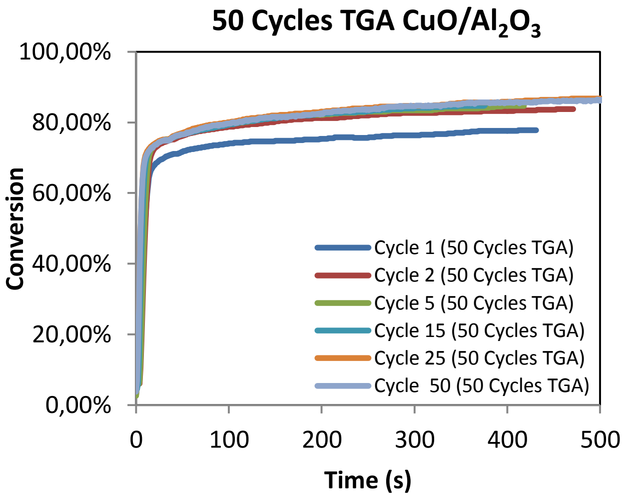
- Reaction located in the surface
- Porosity of the particle very small and uniform in each layer
- Resistance to gas diffusion very high
- Harmonic average effective diffusion coefficient
- Convection of the gas negligible if compared to the diffusive fluxes
- Kinetic is first order

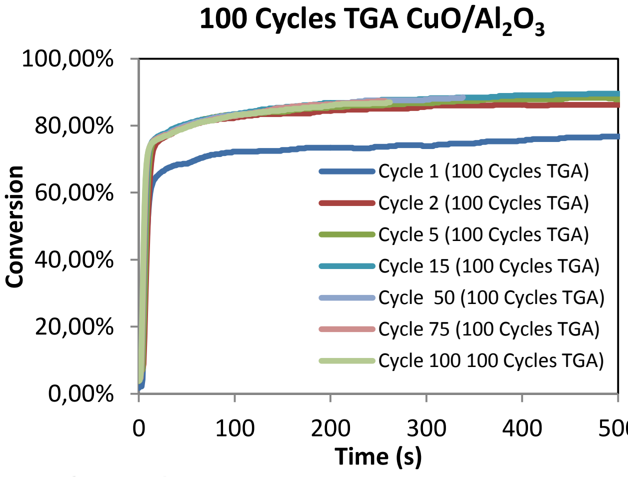


EXPERIMENTAL STUDIES

Thermo-Gravimetric-Analysis (TGA)



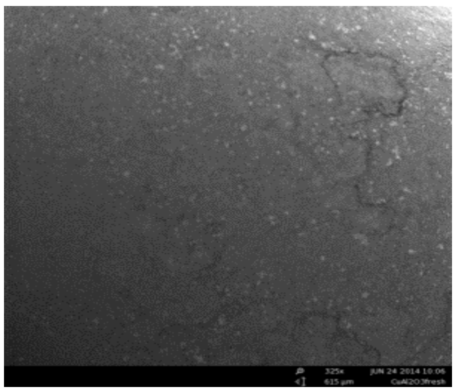




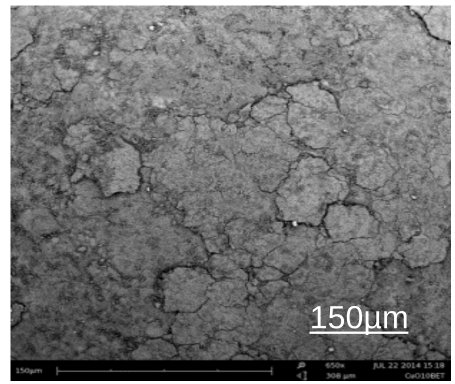
EXPERIMENTAL STUDIES

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

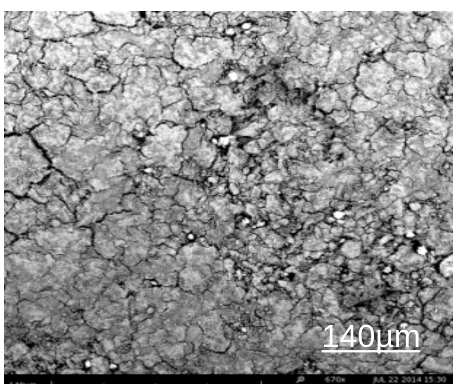
Fresh CuO/Al_2O_3



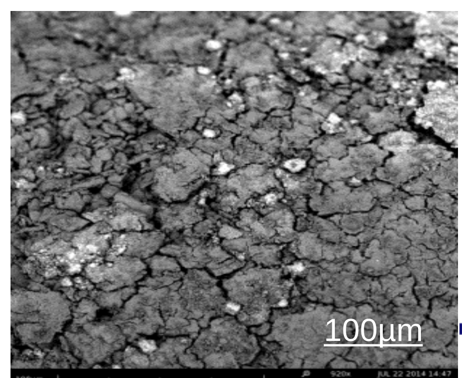
10 Cycles TGA CuO/Al_2O_3



50 Cycles TGA CuO/Al_2O_3



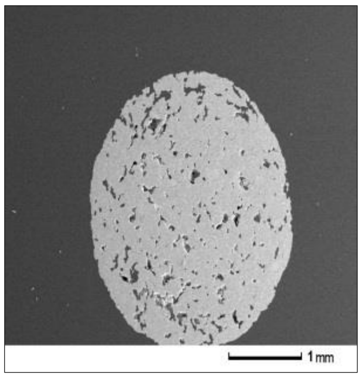
100 Cycles TGA CuO/Al_2O_3

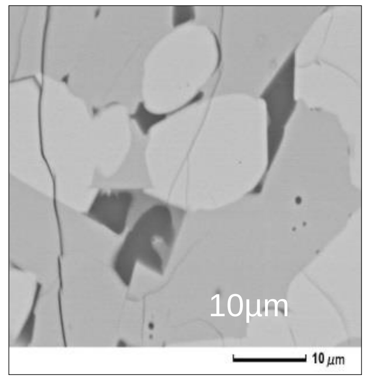


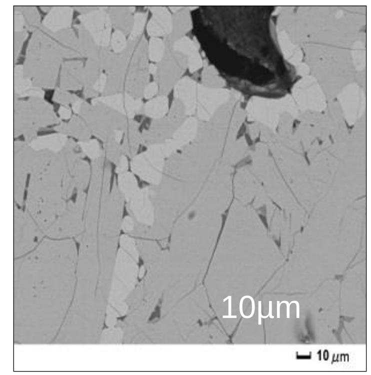
EXPERIMENTAL STUDIES

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

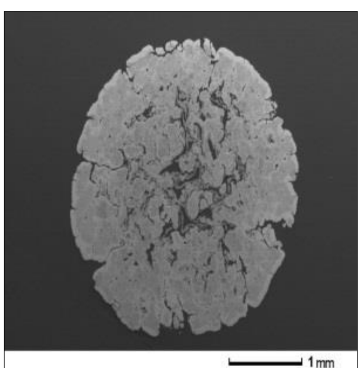
Fresh Ilmenite (Fe_2O_3/TiO_2)

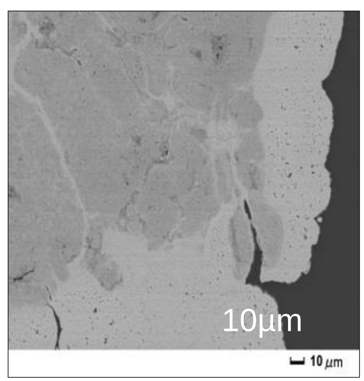


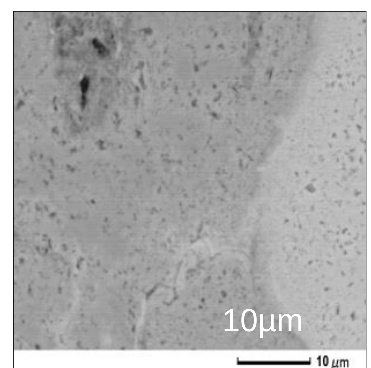




Activated Ilmenite (Fe_2O_3/TiO_2)



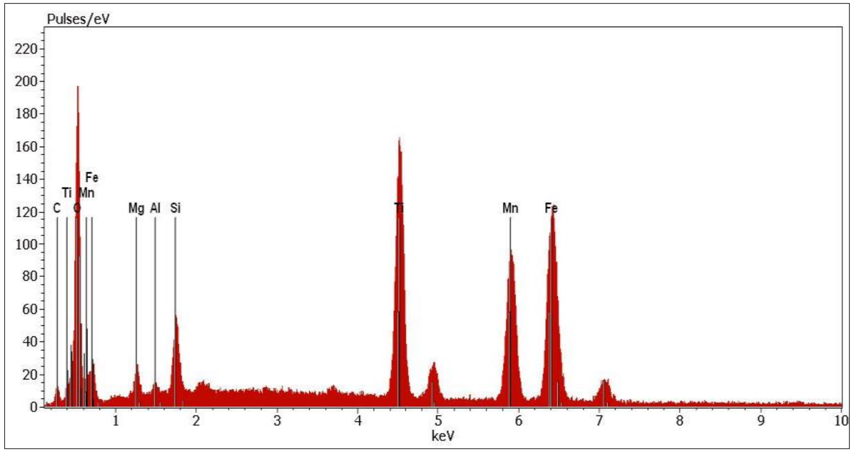


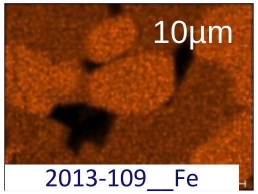


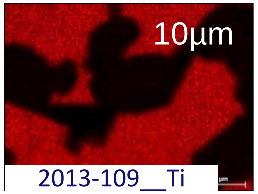
EXPERIMENTAL STUDIES

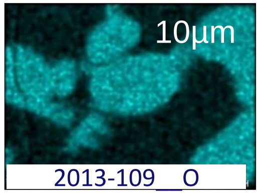
Scanning **E**lectron **M**icroscopy (SEM) + **E**nergy-**D**ispersive **X**-ray spectroscopy (EDX)

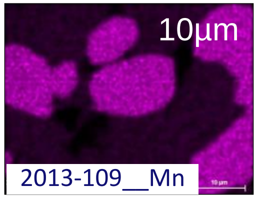
Fresh Ilmenite (Fe_2O_3/TiO_2)



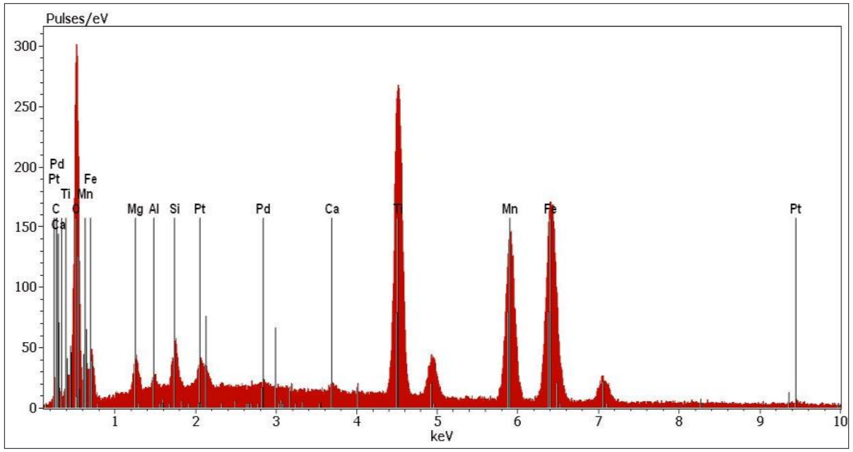


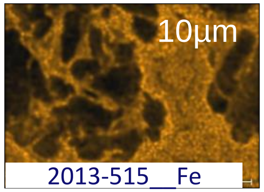


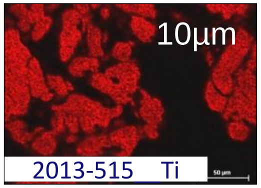


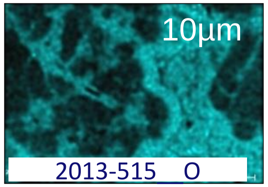


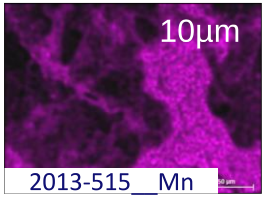
Activated Ilmenite (Fe_2O_3/TiO_2)











Thanks to VITO for the images

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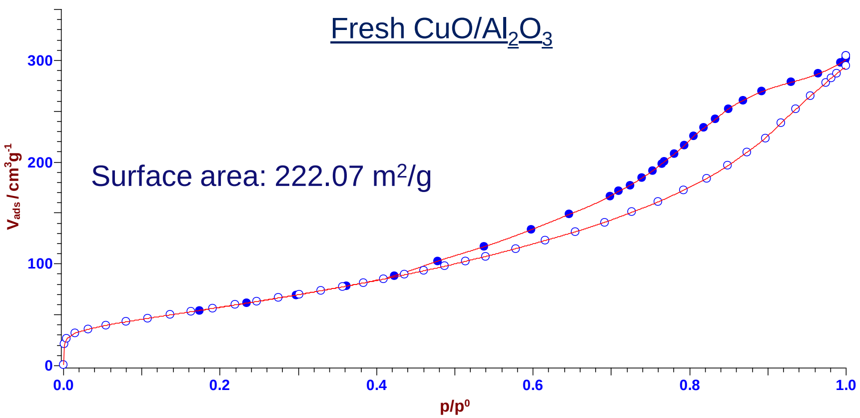
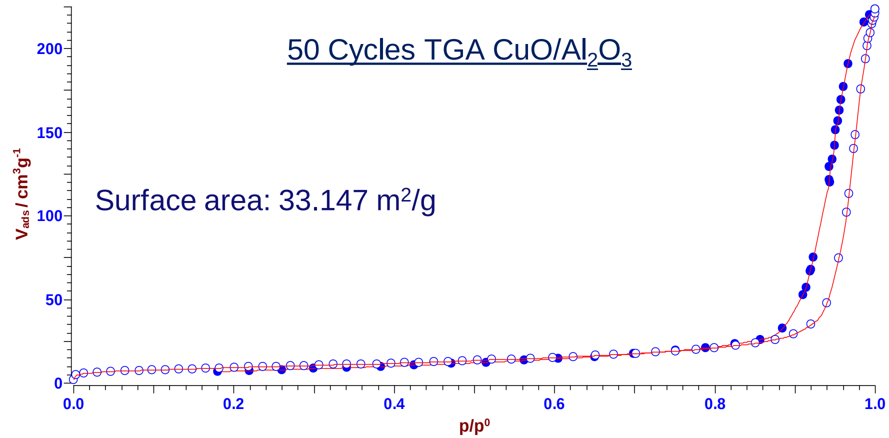
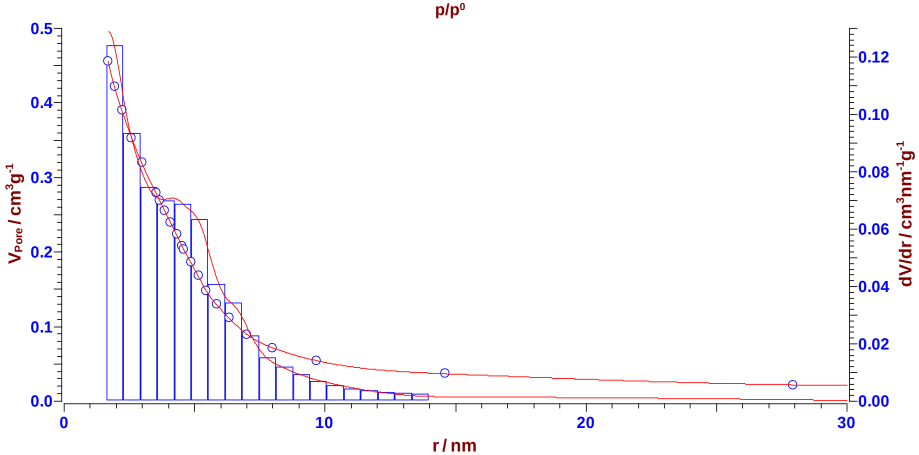
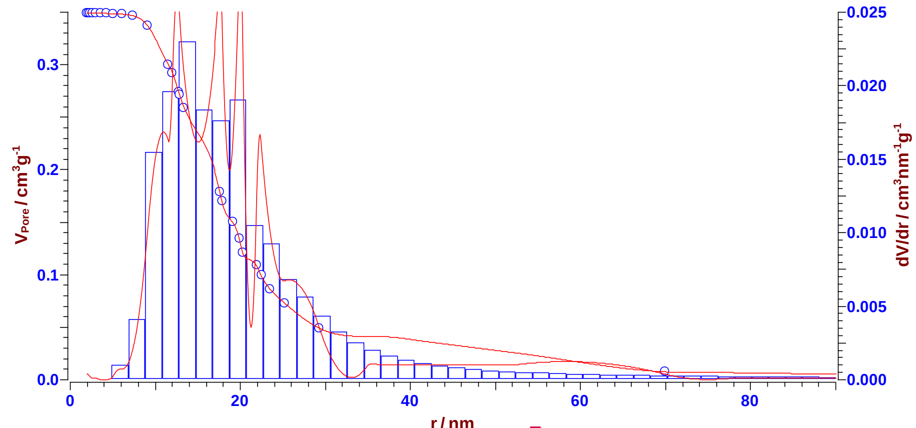
EXPERIMENTAL STUDIES

Physisorption with liquid nitrogen (BET)









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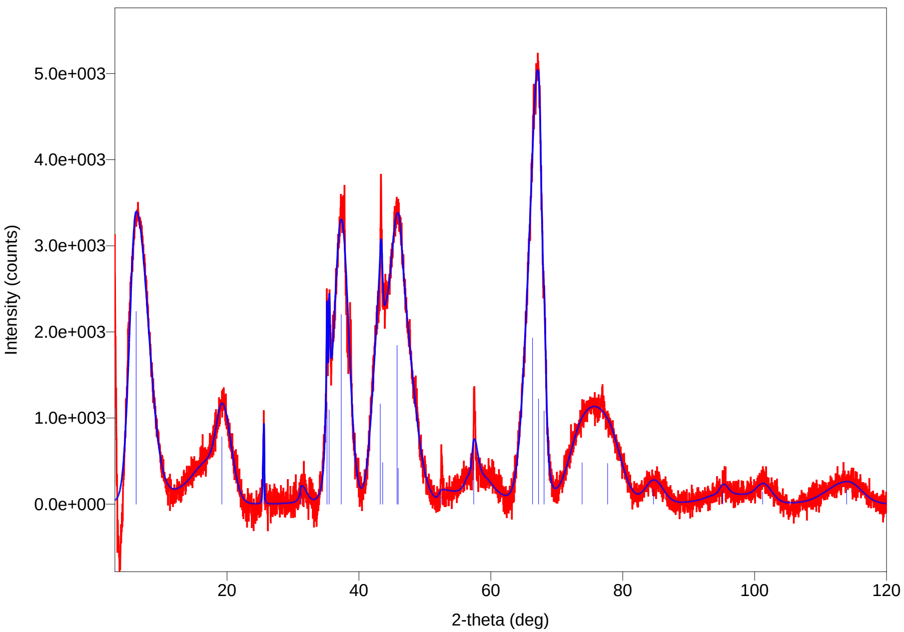
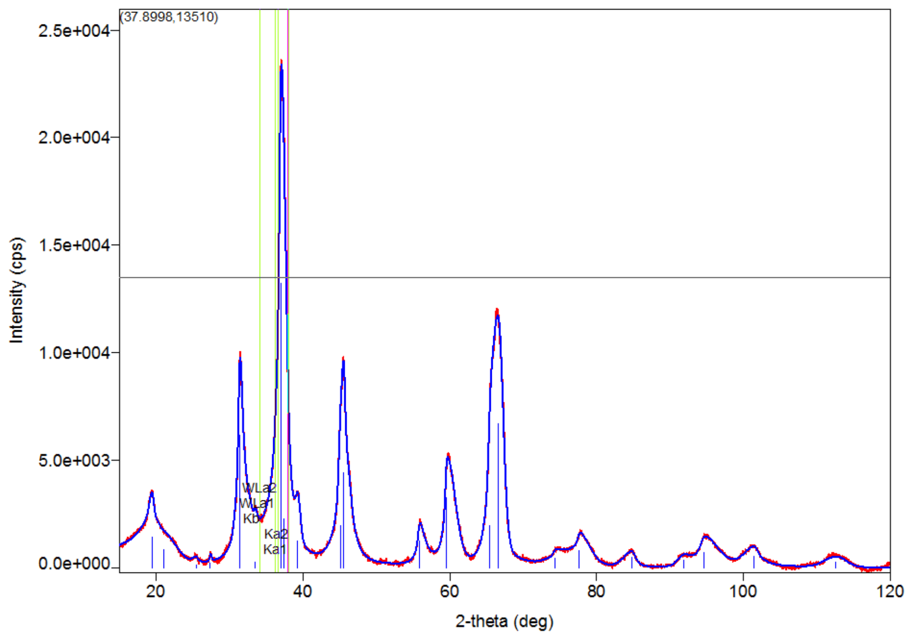
EXPERIMENTAL STUDIES

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

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

$Cu + ½ O_2 \rightarrow CuO$
$CuO + Al_2O_3 \rightarrow CuAl_2O_4$
$4CuAl_2O_4 \rightarrow 4CuAlO_2 + 2Al_2O_3 + O_2$
$4CuAlO_2 + O_2 \rightarrow 4CuAl_2O_2 + 2 Cu_2O$

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:

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

Oxidation:

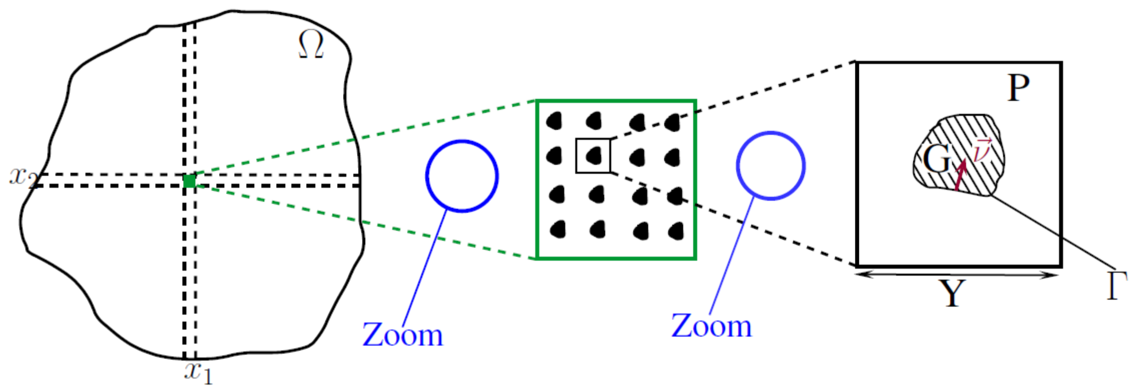
$Cu + ½ O_2 \rightarrow CuO$
$CuO + Al_2O_3 \rightarrow CuAl_2O_4$
$4CuAl_2O_4 \rightarrow 4CuAlO_2 + 2Al_2O_3 + O_2$
$4CuAlO_2 + O_2 \rightarrow 4CuAl_2O_2 + 2 Cu_2O$

→

- 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.

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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

NWO for the financial support of this project under the ECHO-STIP grant 717.013.007

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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