

# Understanding the redox kinetics of oxygen carriers for chemical looping combustion

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Netherlands Organisation for Scientific Research

# Understanding the redox kinetics of oxygen carriers for chemical looping combustion

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**TU/e**

Technische Universiteit  
**Eindhoven**  
University of Technology

Where innovation starts

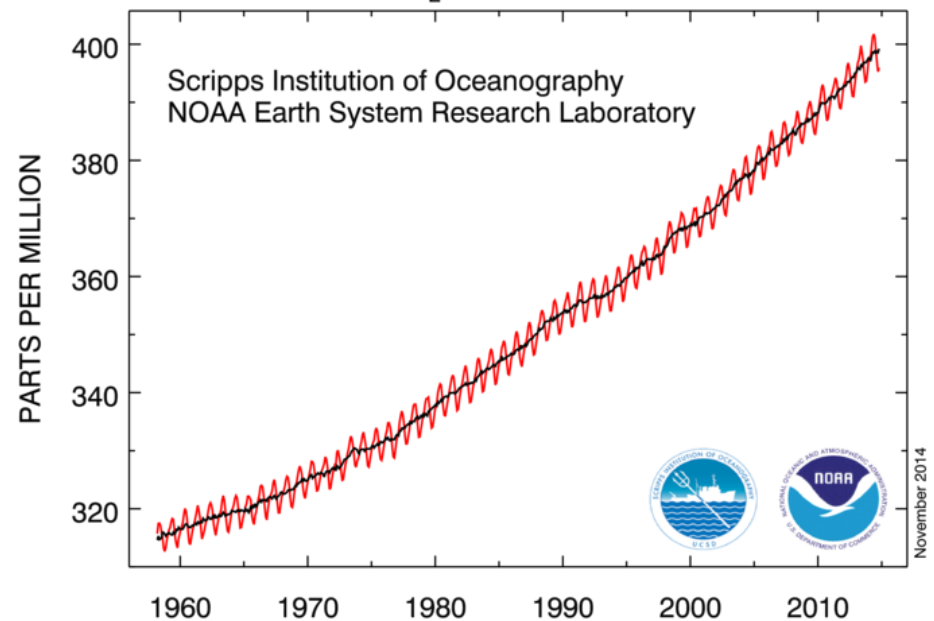
# THE CO<sub>2</sub> PROBLEM

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

Carbon Dioxide (**CO<sub>2</sub>**) is the primary greenhouse gas emitted through human activities.



Atmospheric CO<sub>2</sub> at Mauna Loa Observatory



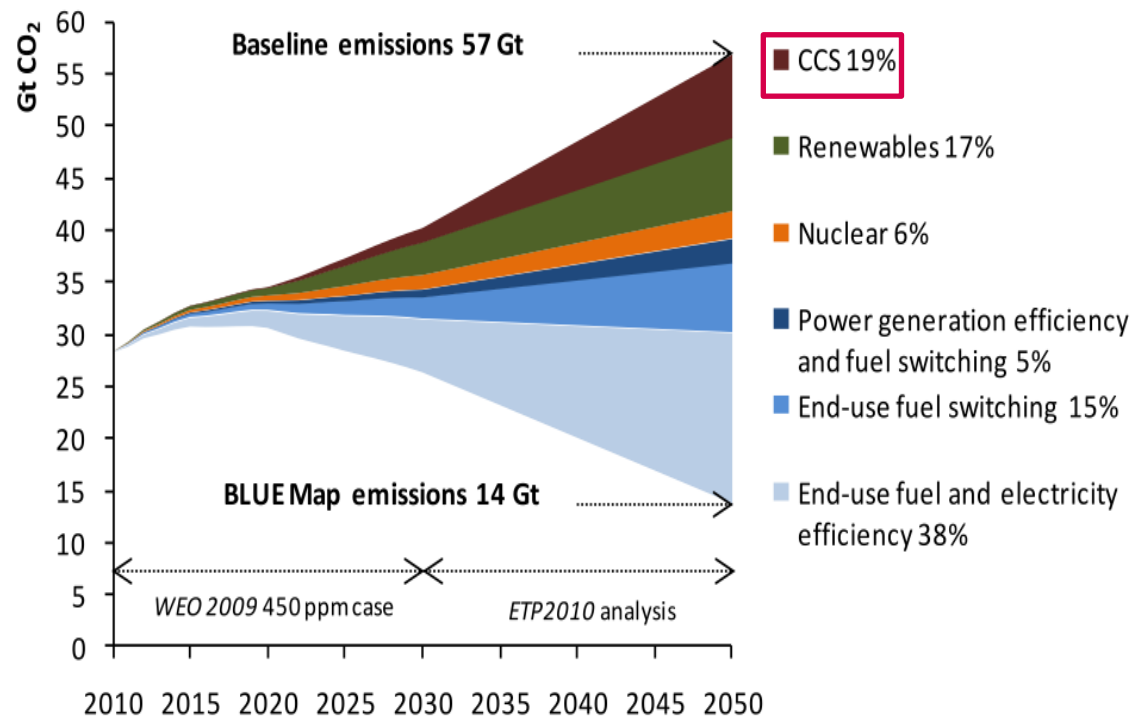
# THE CO<sub>2</sub> PROBLEM

## Introduction

Exp. Studies  
Particle Model  
Conclusions



# CARBON CAPTURE AND STORAGE



**CCS:** Important strategy for reducing CO<sub>2</sub> emissions from fossil based power plants



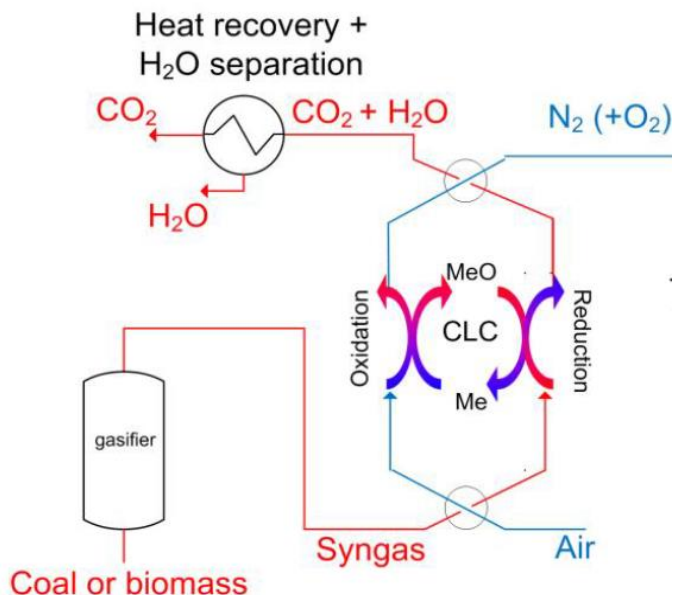
**Chemical Looping** is one of the most promising technologies of CCS as it presents the **lowest energy penalty**.

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



# ENERGY PRODUCTION WITH CO<sub>2</sub> CAPTURE

## Chemical Looping Combustion (CLC)



## CLC involves

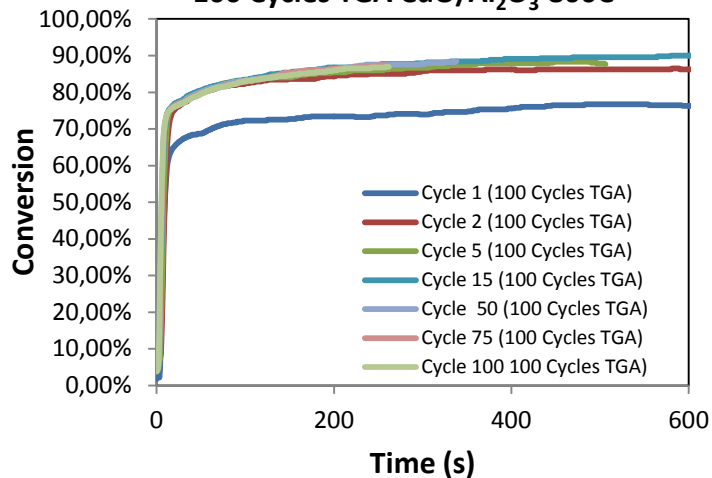
- Two Packed Bed Reactors (PBR)
  - Fuel reactor
  - Air reactor
- Redox chemistry (metal)
- Periodic operation

## CLC can achieve

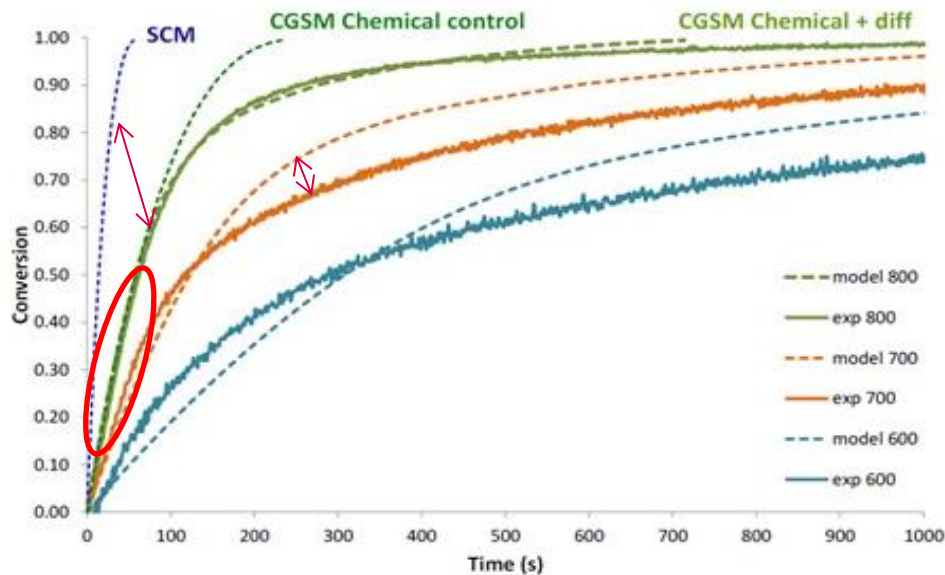
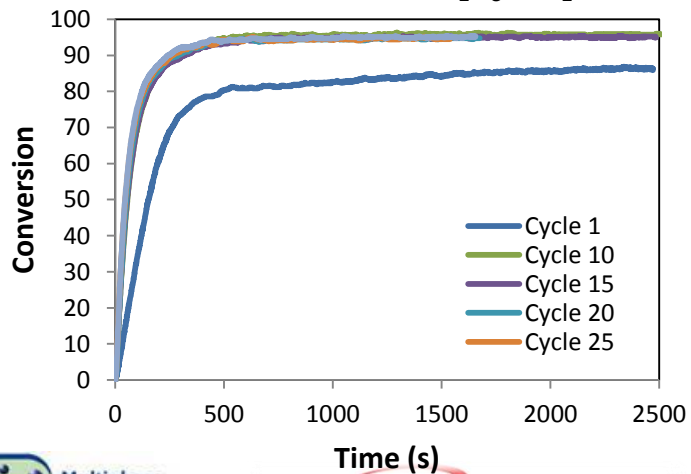
- High level of CO<sub>2</sub> capture
- Low energy carbon capture penalty

# OXYGEN CARRIER KINETICS

100 Cycles TGA CuO/Al<sub>2</sub>O<sub>3</sub> 800C



30 Cycles TGA Ilmenite Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> 800C



Ilmenite conversion profiles as a function of time on stream (with 15% CO in N<sub>2</sub>)

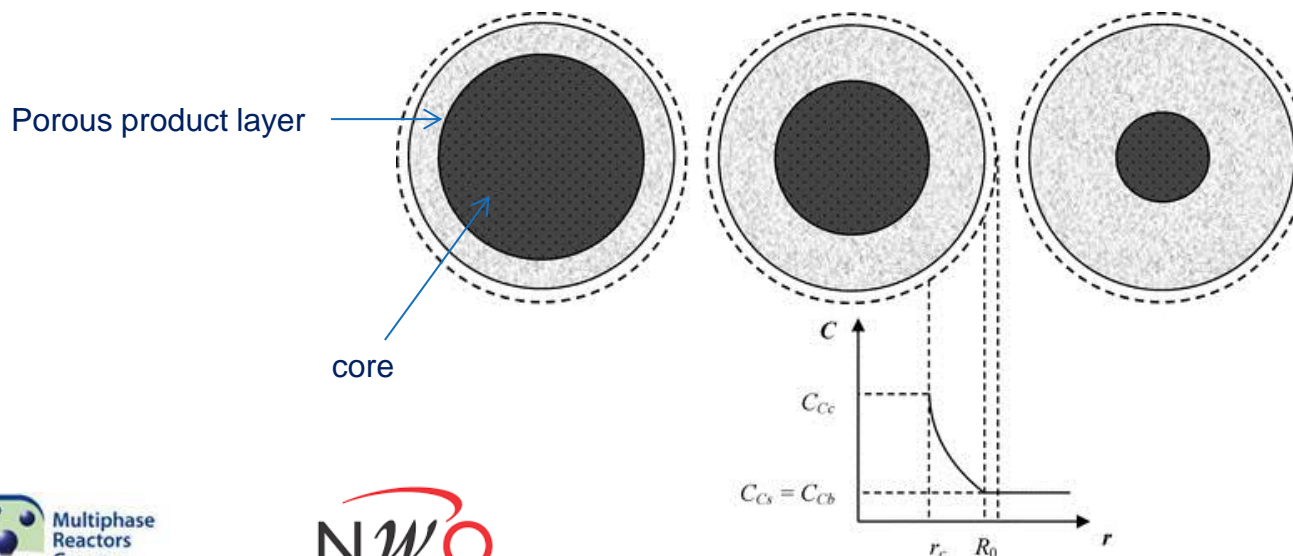
PBR: Conversion 0-100% every cycle

Important to predict the real final conversion

# OXYGEN CARRIER KINETICS

## Shrinking Core Model Assumptions

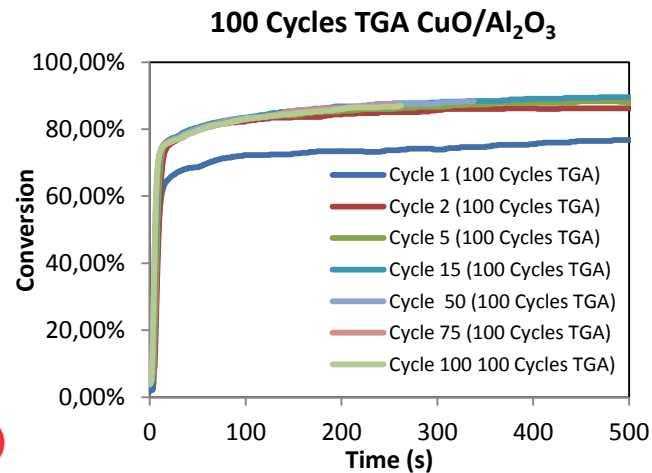
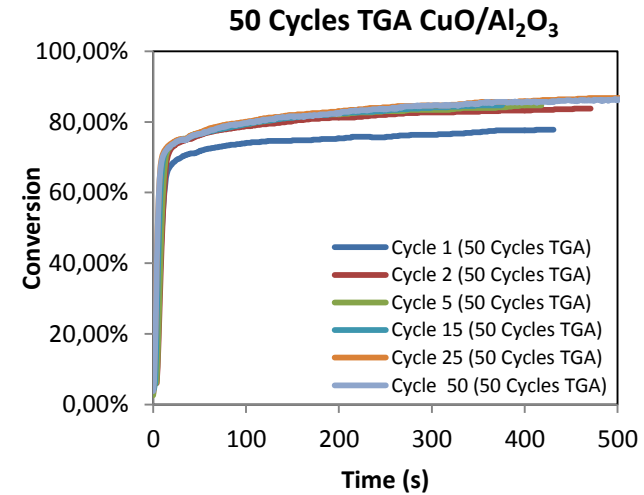
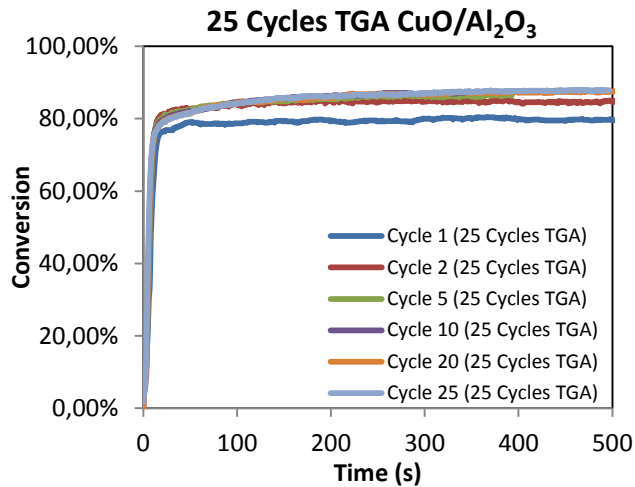
- Reaction located in the surface
- Porosity of the particle very small and uniform in each layer
- Resistance to gas diffusion very high
- Harmonic average effective diffusion coefficient
- Convection of the gas negligible if compared to the diffusive fluxes
- Kinetic is first order





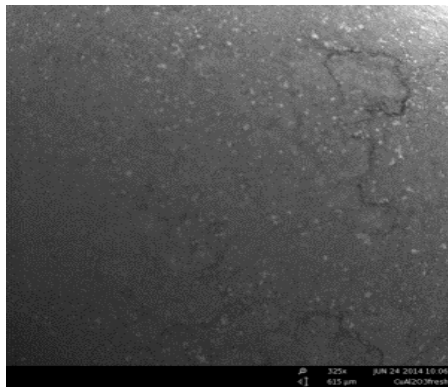
# EXPERIMENTAL STUDIES

## Thermo-Gravimetric-Analysis (TGA)

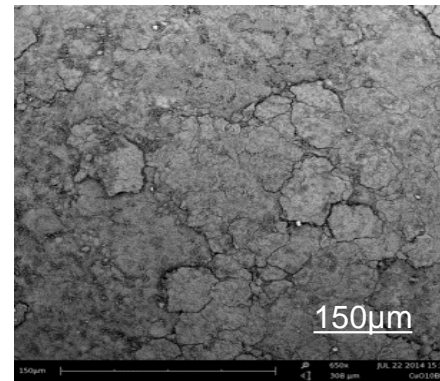


## Scanning Electron Microscopy (SEM)

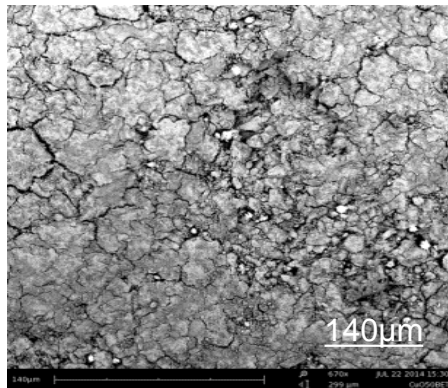
Fresh CuO/Al<sub>2</sub>O<sub>3</sub>



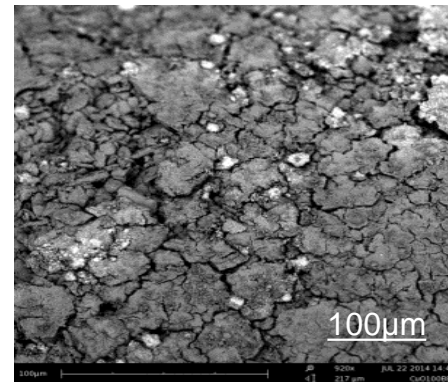
10 Cycles TGA CuO/Al<sub>2</sub>O<sub>3</sub>



50 Cycles TGA CuO/Al<sub>2</sub>O<sub>3</sub>

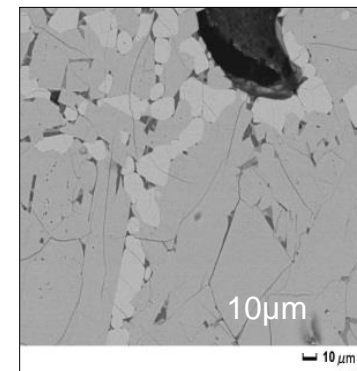
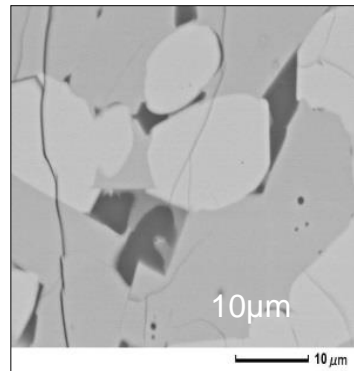
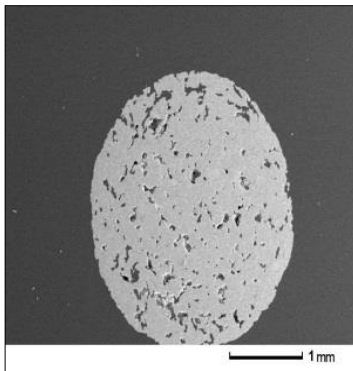


100 Cycles TGA CuO/Al<sub>2</sub>O<sub>3</sub>

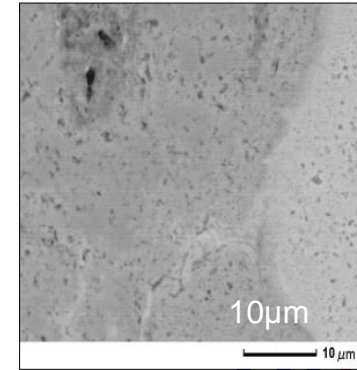
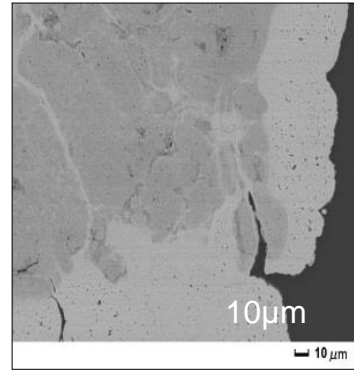
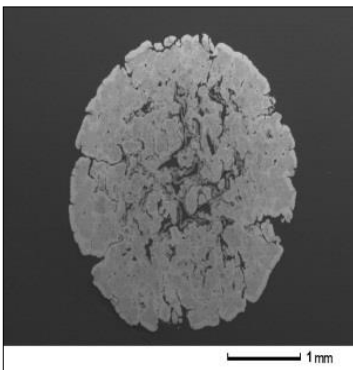


## Scanning Electron Microscopy (SEM)

Fresh Ilmenite ( $\text{Fe}_2\text{O}_3/\text{TiO}_2$ )



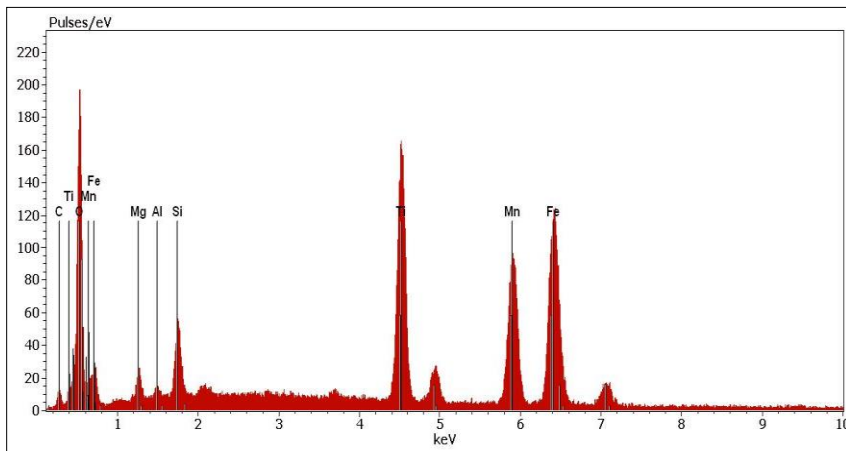
Activated Ilmenite ( $\text{Fe}_2\text{O}_3/\text{TiO}_2$ )



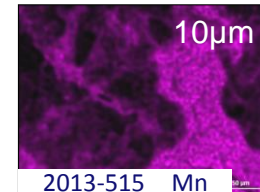
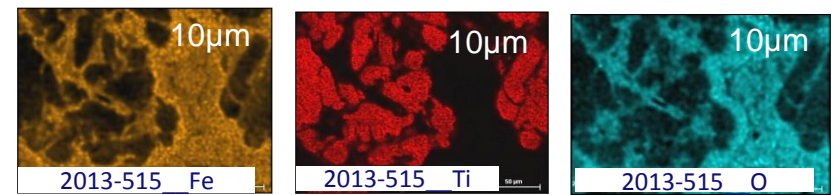
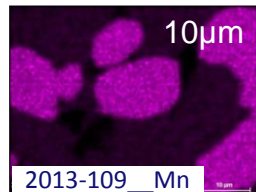
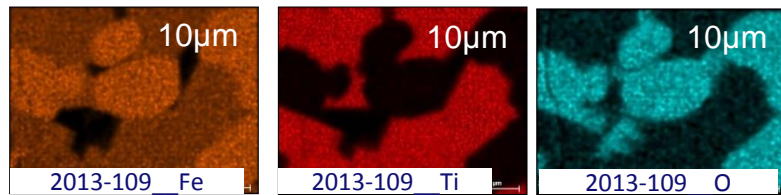
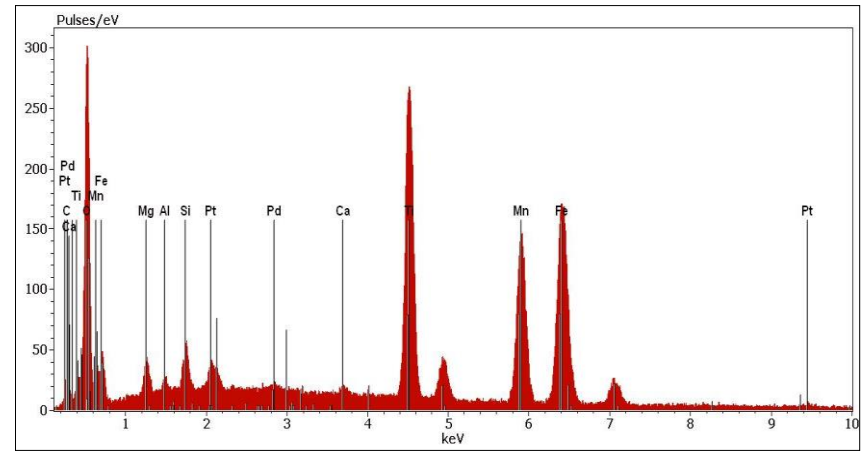
# EXPERIMENTAL STUDIES

## Scanning Electron Microscopy (SEM) + Energy-Dispersive X-ray spectroscopy (EDX)

Fresh Ilmenite ( $\text{Fe}_2\text{O}_3/\text{TiO}_2$ )



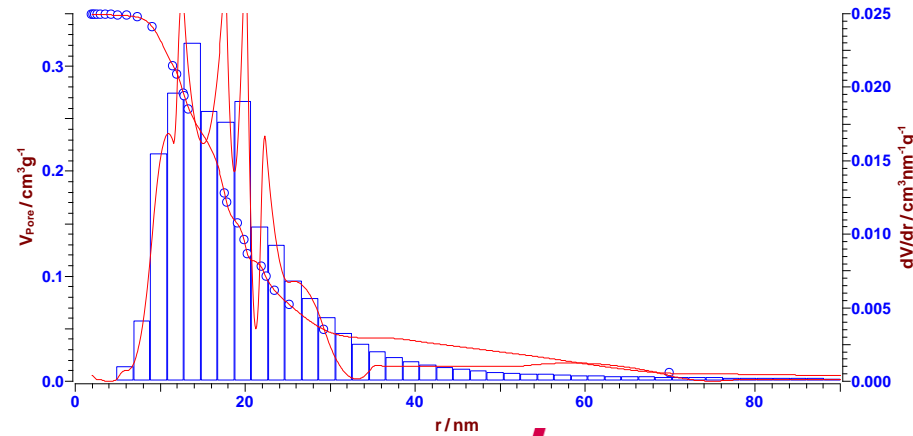
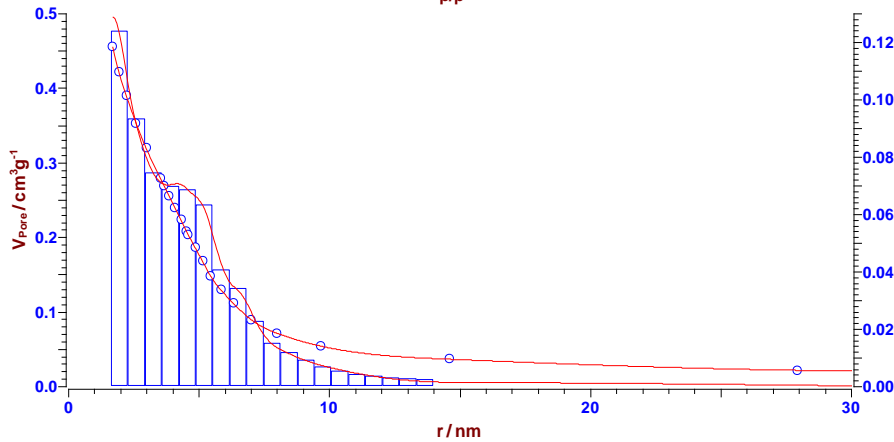
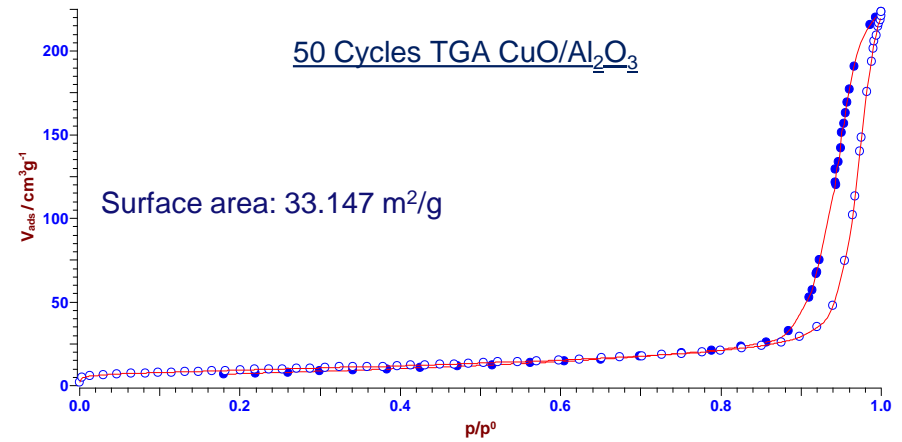
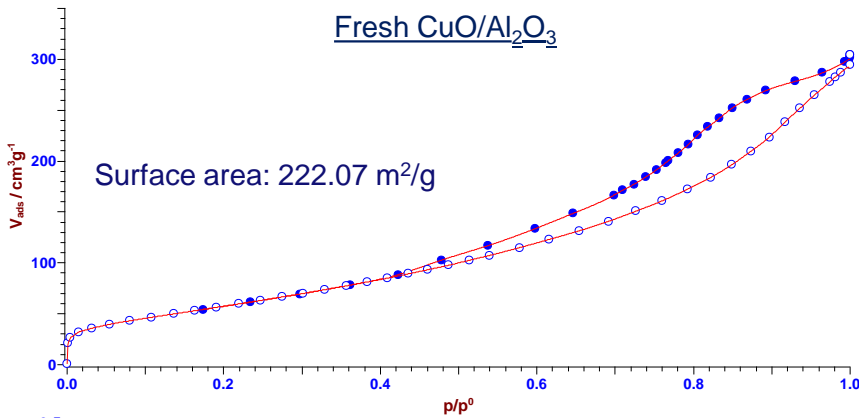
Activated Ilmenite ( $\text{Fe}_2\text{O}_3/\text{TiO}_2$ )



Thanks to VITO for the images

# EXPERIMENTAL STUDIES

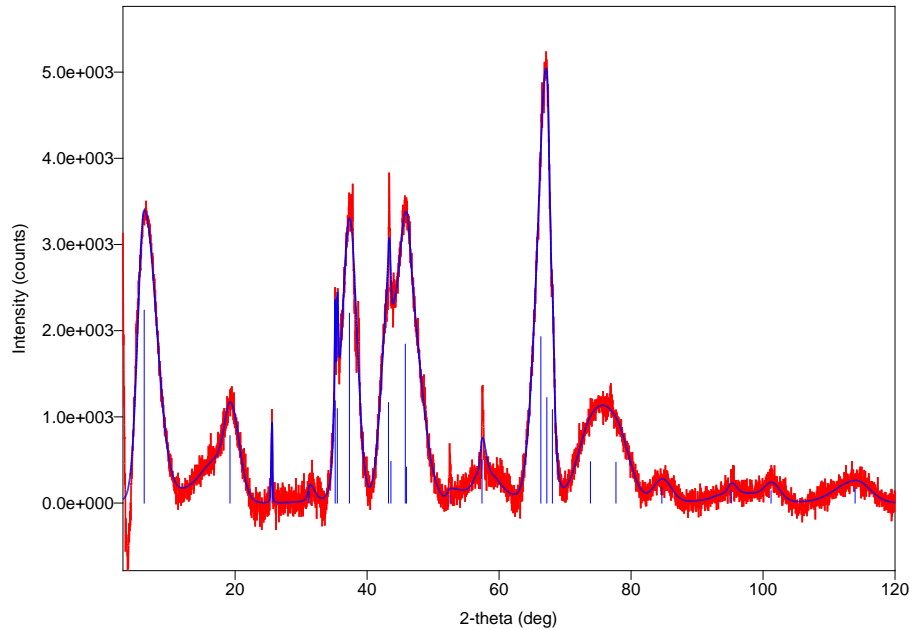
## Physisorption with liquid nitrogen (BET)



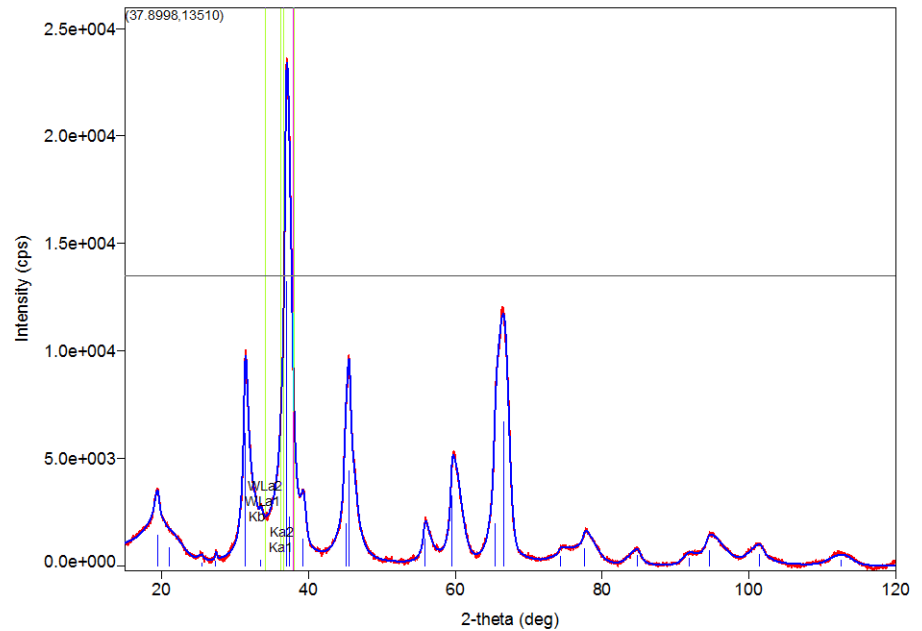


## X-Ray Diffraction (XRD)

Fresh CuO/Al<sub>2</sub>O<sub>3</sub>



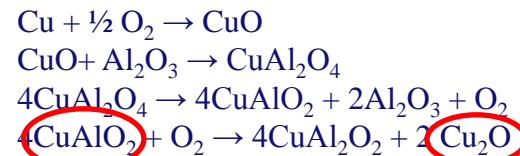
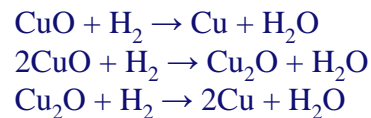
25 CYCLES TGA CuO/Al<sub>2</sub>O<sub>3</sub>



# EXPERIMENTAL STUDIES

## X-Ray Diffraction (XRD)

Components	Fresh	25 Cycles	75 Cycles	100 Cycles
Tenorite (CuO)	X	X	X	X
Aluminium Oxide (Al <sub>2</sub> O <sub>3</sub> )	X	X	X	X
Spinel (CuAl <sub>2</sub> O <sub>4</sub> )	X	X	X	X
Gamma-alumina (Al <sub>2.67</sub> O <sub>4</sub> )	X	X	X	X
Copper aluminium oxide (CuAlO <sub>2</sub> )			X	
Cuprite (Cu <sub>2</sub> O)				X



New phases are formed while the number of redox reactions increases

These components can influence the kinetics of the OC

## SCM Assumptions

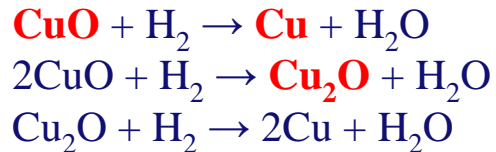
- ~~Reaction located in the surface~~ — SEM + XRD
- ~~Porosity of the particle very small and uniform in each layer~~ — SEM
- ~~Resistance to gas diffusion very high~~ — TGA
- ~~Harmonic average effective diffusion coefficient~~ — SEM + BET
- ~~Convection of the gas negligible if compared to the diffusive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



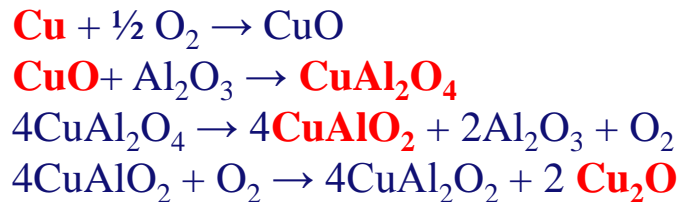
## New Particle Model

## Kinetics of the components detected in the XRD analysis: Kinetics

### Reduction:

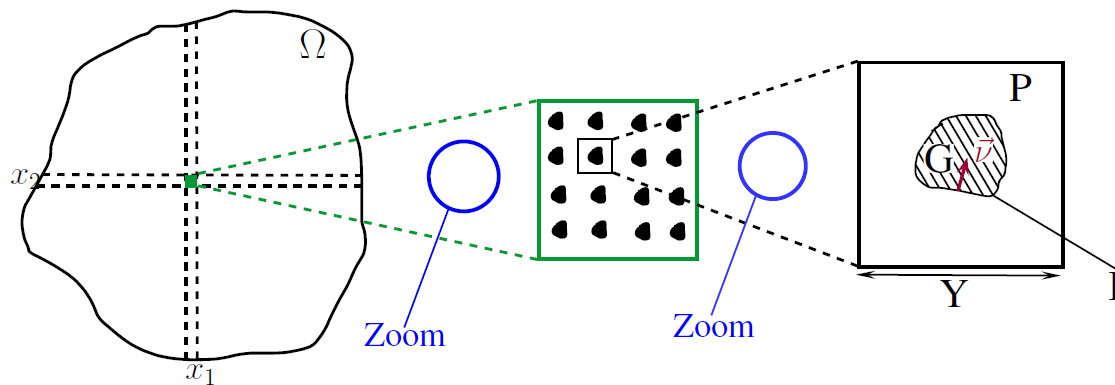


### Oxidation:



- CuO
- CuAl<sub>2</sub>O<sub>4</sub>
- Cu<sub>2</sub>O
- Cu
- CuAlO<sub>2</sub>

## Homogenization in porous media: Diffusion



Two sub-domains: the “inner” grain  $G$  surrounded by the pore  $P$ . With  $\Gamma$  being the boundary of  $G$ .

$$(P(x)) \left\{ \begin{array}{l} -\nabla \cdot (\mathbf{D}_{eff}(x) \nabla U) = f, \quad \text{for all } x \in \Omega \\ U = 0, \text{ on } \partial\Omega \end{array} \right.$$



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



- 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***