

Understanding the redox kinetics of oxygen carriers for chemical looping combustion

Citation for published version (APA):

San Pio Bordejé, M. A., Roghair, I., Gallucci, F., & Sint Annaland, van, M. (2014). Understanding the redox kinetics of oxygen carriers for chemical looping combustion. In *Proceedings of the Modification of Porous Media Workshop, 11-12 November 2014, Bad Soden, Germany*

Document status and date:

Published: 01/01/2014

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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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

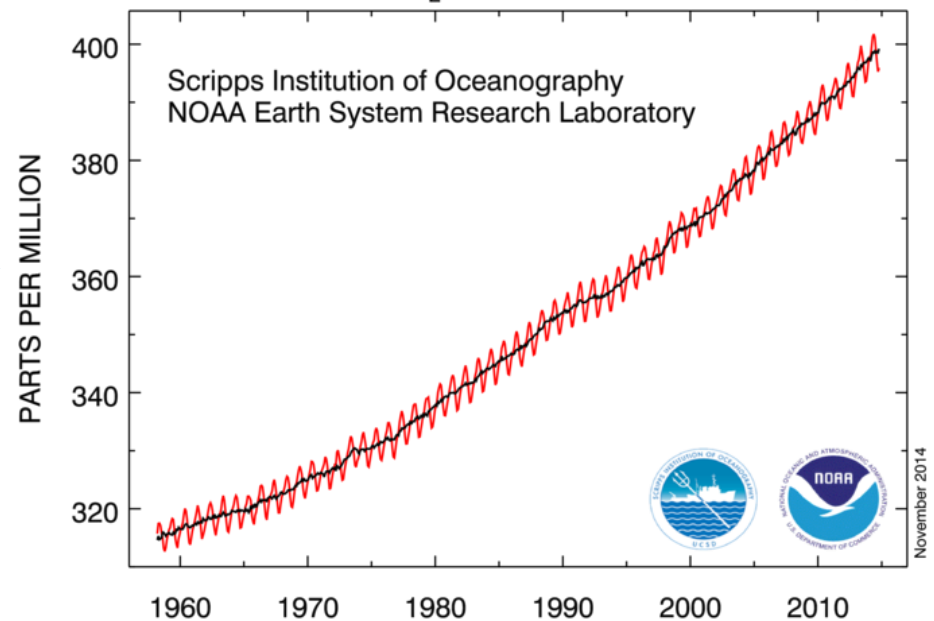
THE CO₂ PROBLEM

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

Carbon Dioxide (**CO₂**) is the primary greenhouse gas emitted through human activities.



Atmospheric CO₂ at Mauna Loa Observatory



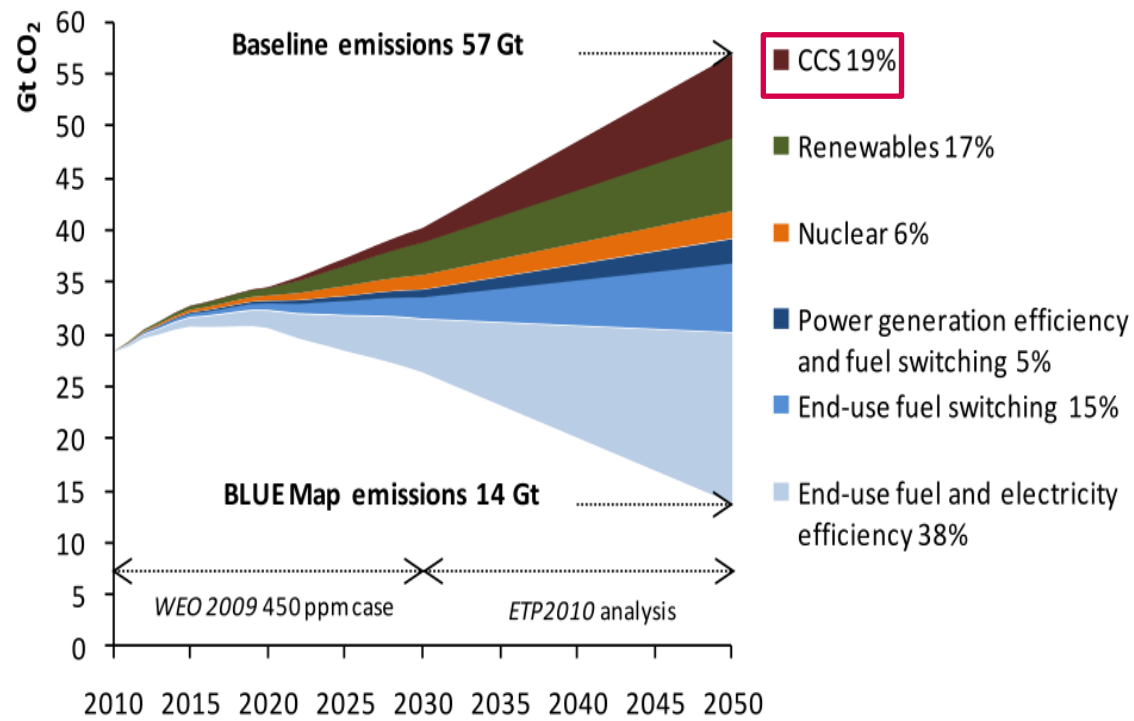
THE CO₂ PROBLEM

Introduction

Exp. Studies
Particle Model
Conclusions



CARBON CAPTURE AND STORAGE



CCS: Important strategy for reducing CO₂ emissions from fossil based power plants

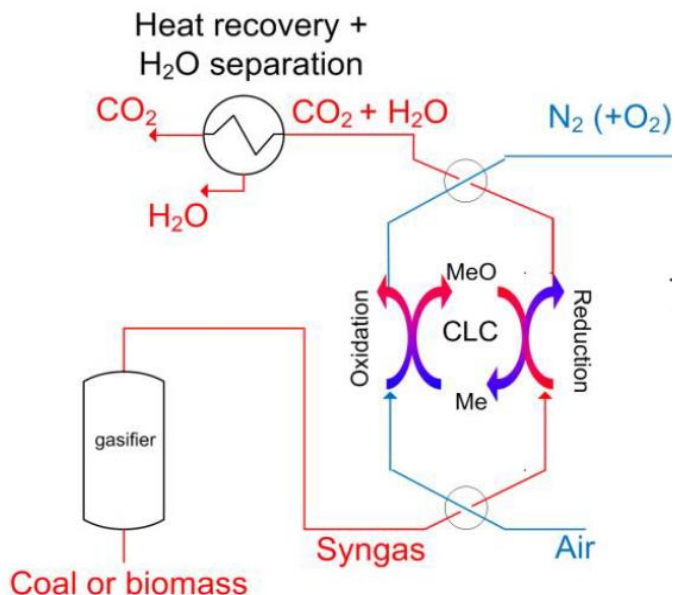


Chemical Looping is one of the most promising technologies of CCS as it presents the **lowest energy penalty**.

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

ENERGY PRODUCTION WITH CO₂ CAPTURE

Chemical Looping Combustion (CLC)



CLC involves

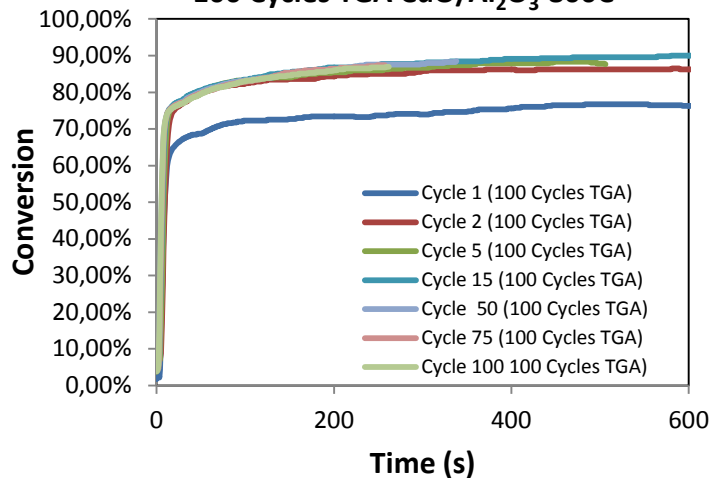
- Two Packed Bed Reactors (PBR)
 - Fuel reactor
 - Air reactor
- Redox chemistry (metal)
- Periodic operation

CLC can achieve

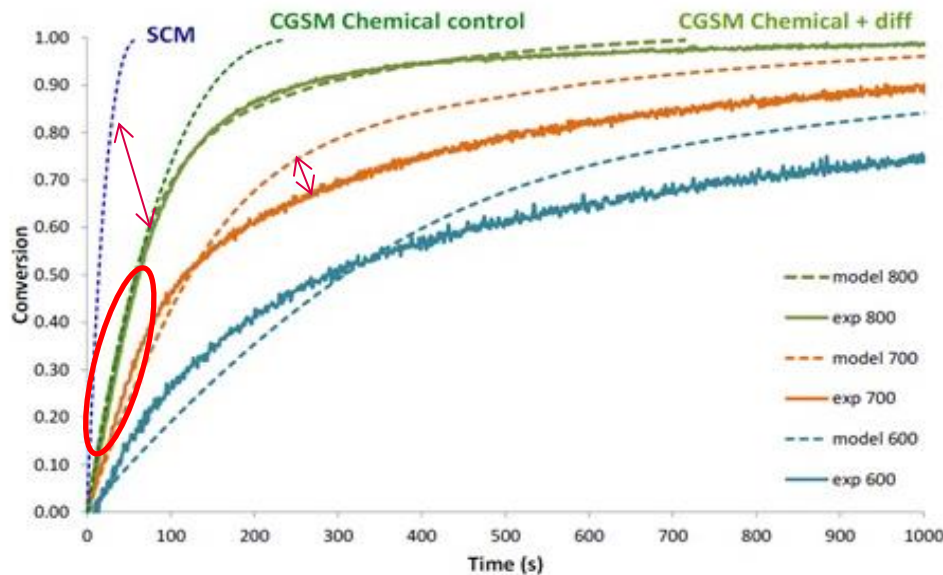
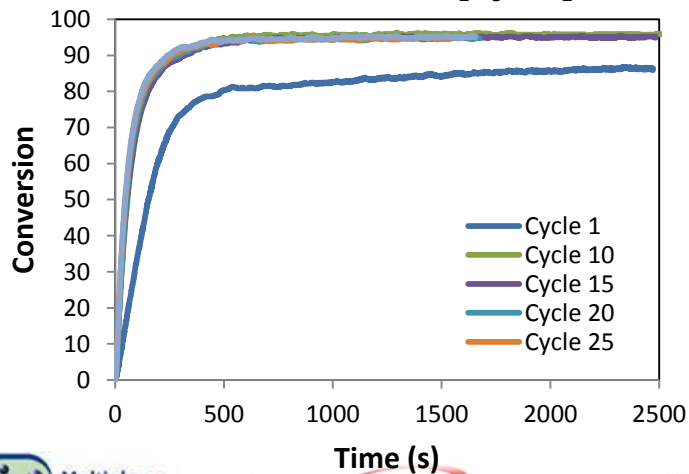
- High level of CO₂ capture
- Low energy carbon capture penalty

OXYGEN CARRIER KINETICS

100 Cycles TGA CuO/Al₂O₃ 800C



30 Cycles TGA Ilmenite Fe₂O₃/TiO₂ 800C



Ilmenite conversion profiles as a function of time on stream (with 15% CO in N₂)

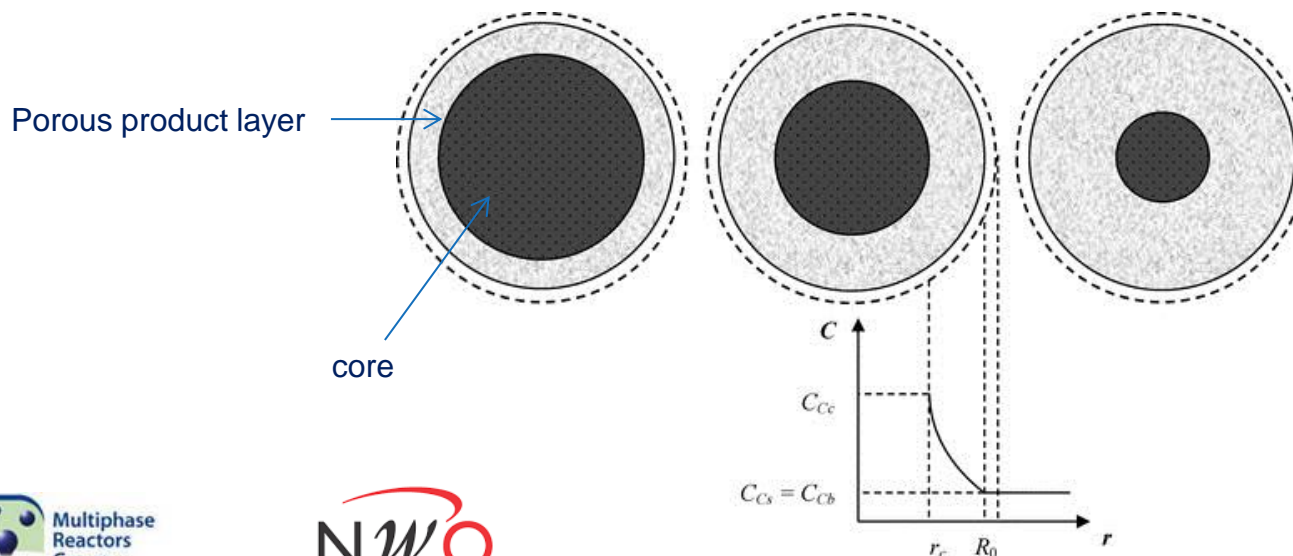
PBR: Conversion 0-100% every cycle

Important to predict the real final conversion

OXYGEN CARRIER KINETICS

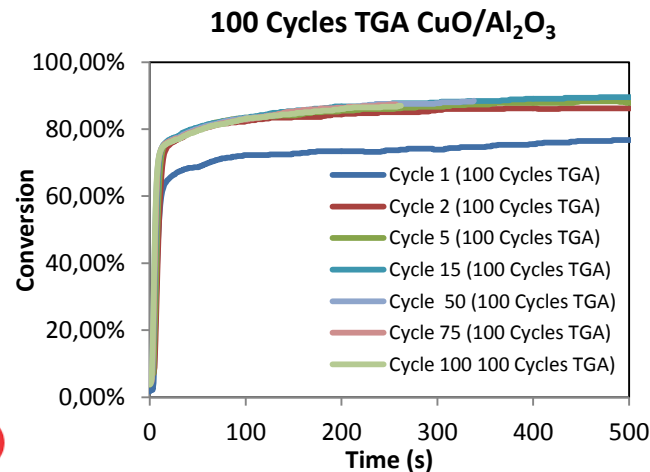
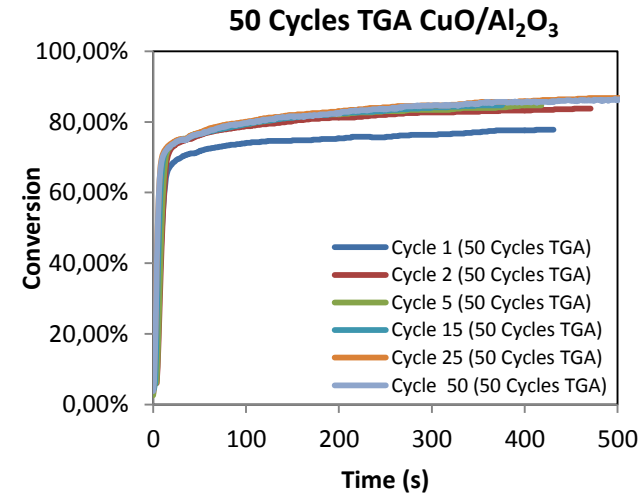
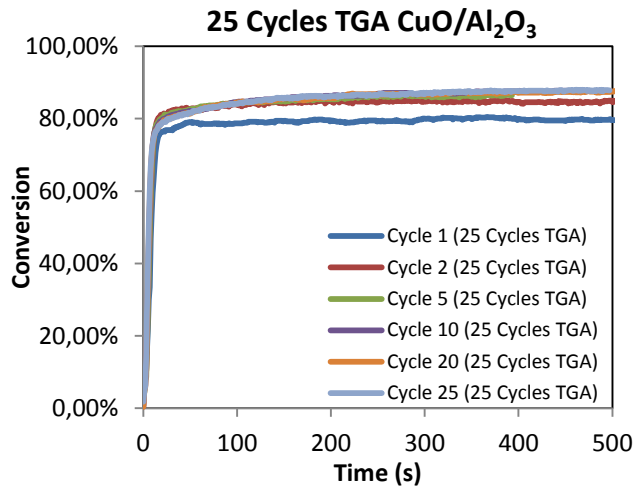
Shrinking Core Model Assumptions

- 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



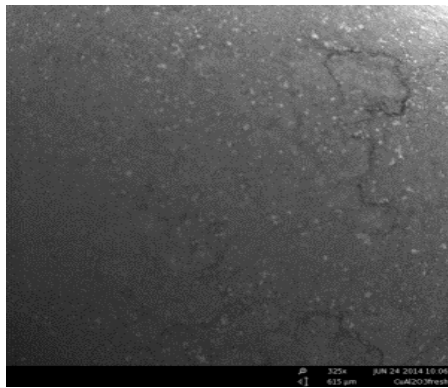
EXPERIMENTAL STUDIES

Thermo-Gravimetric-Analysis (TGA)

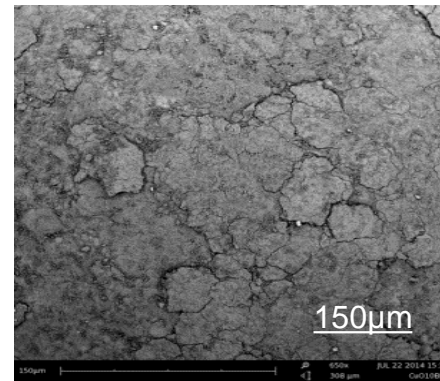


Scanning Electron Microscopy (SEM)

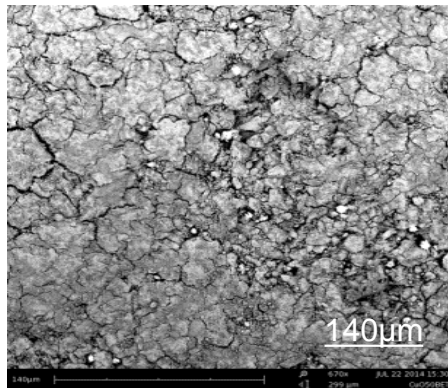
Fresh CuO/Al₂O₃



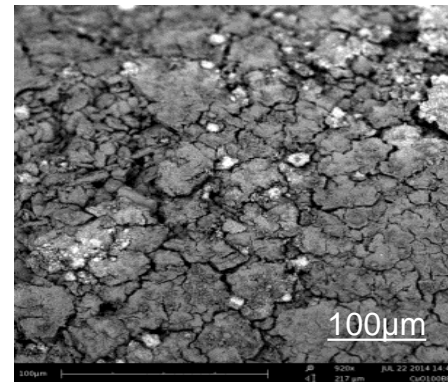
10 Cycles TGA CuO/Al₂O₃



50 Cycles TGA CuO/Al₂O₃

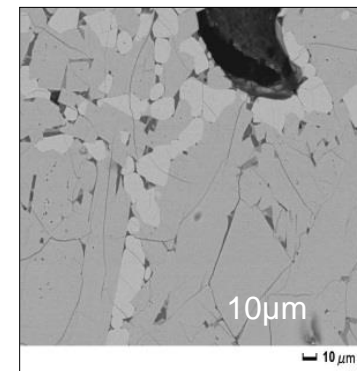
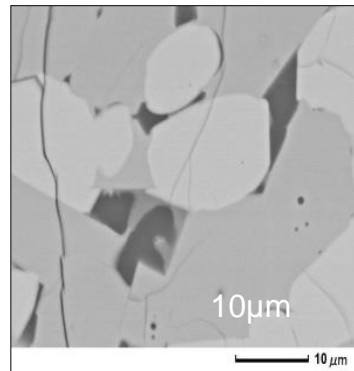
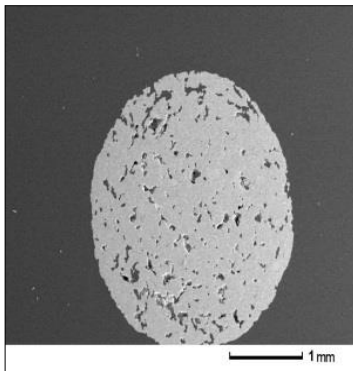


100 Cycles TGA CuO/Al₂O₃

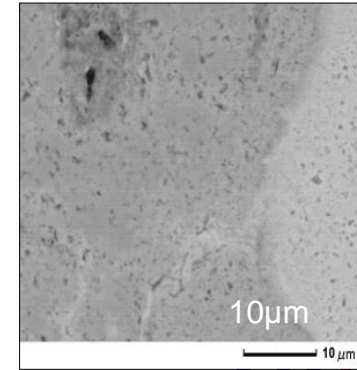
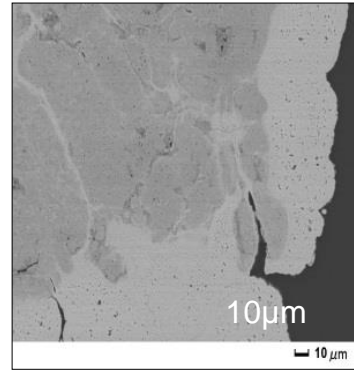
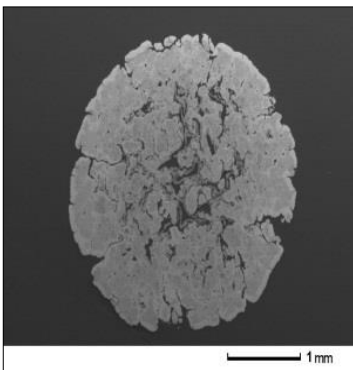


Scanning Electron Microscopy (SEM)

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



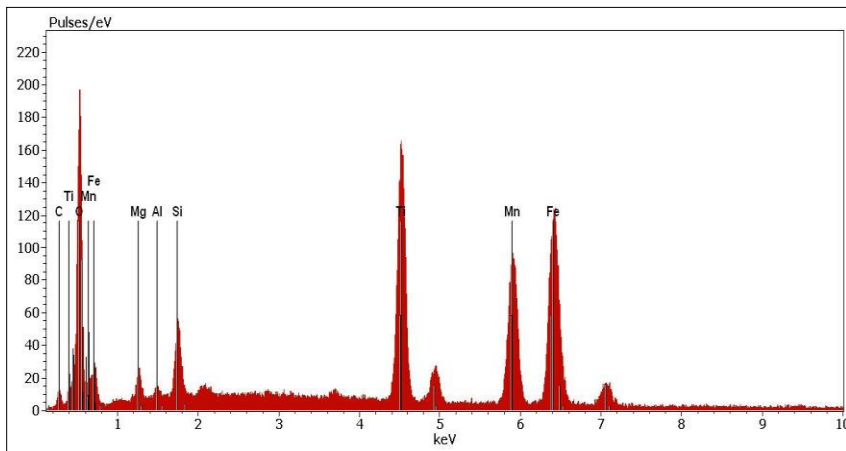
Activated Ilmenite ($\text{Fe}_2\text{O}_3/\text{TiO}_2$)



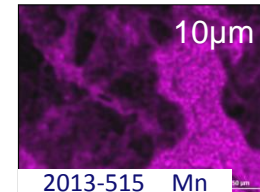
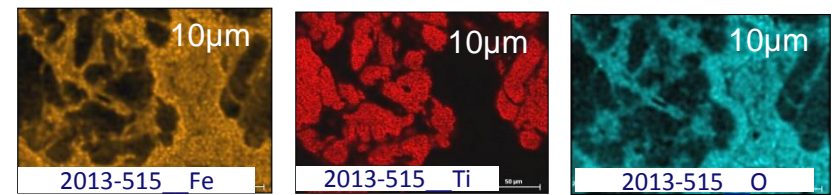
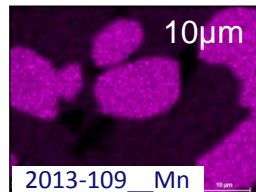
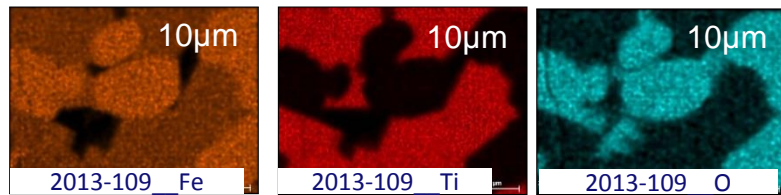
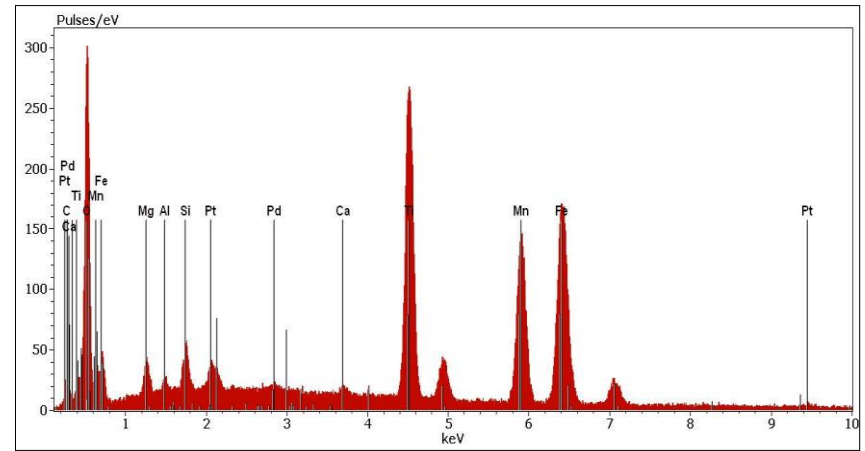
EXPERIMENTAL STUDIES

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

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



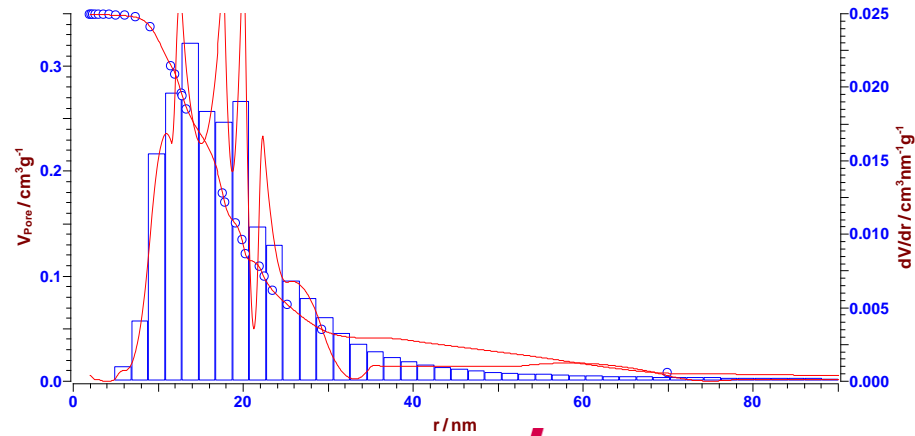
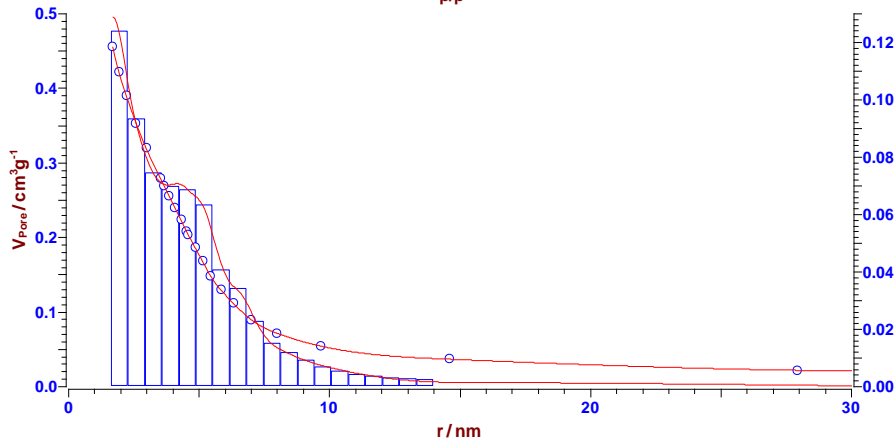
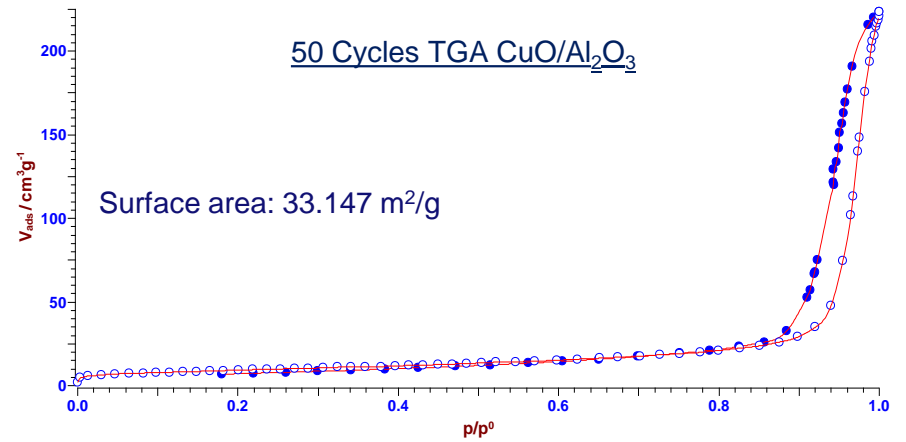
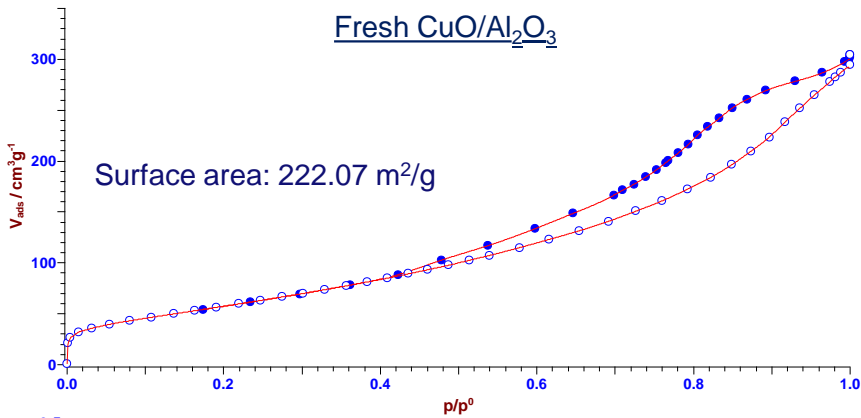
Activated Ilmenite ($\text{Fe}_2\text{O}_3/\text{TiO}_2$)



Thanks to VITO for the images

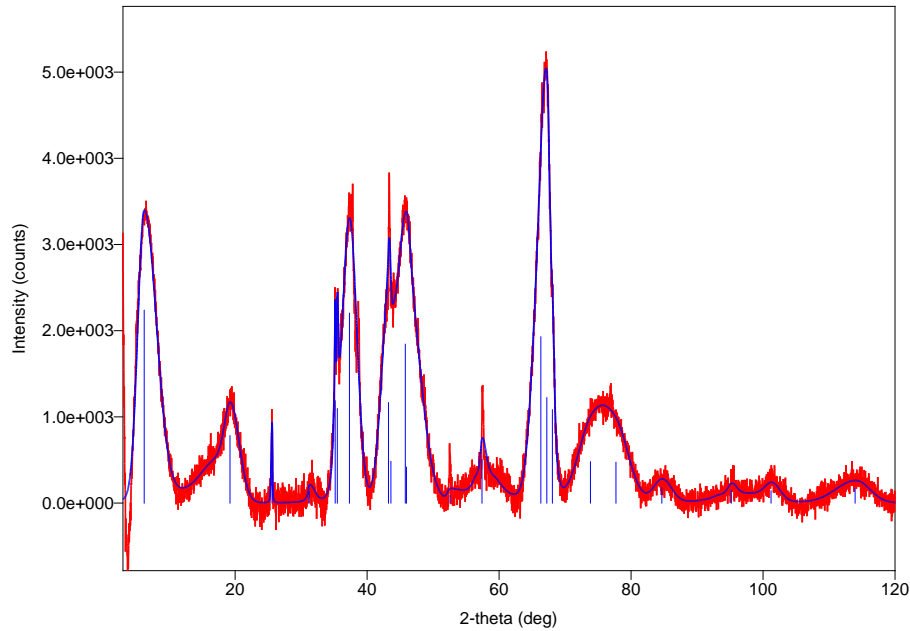
EXPERIMENTAL STUDIES

Physisorption with liquid nitrogen (BET)

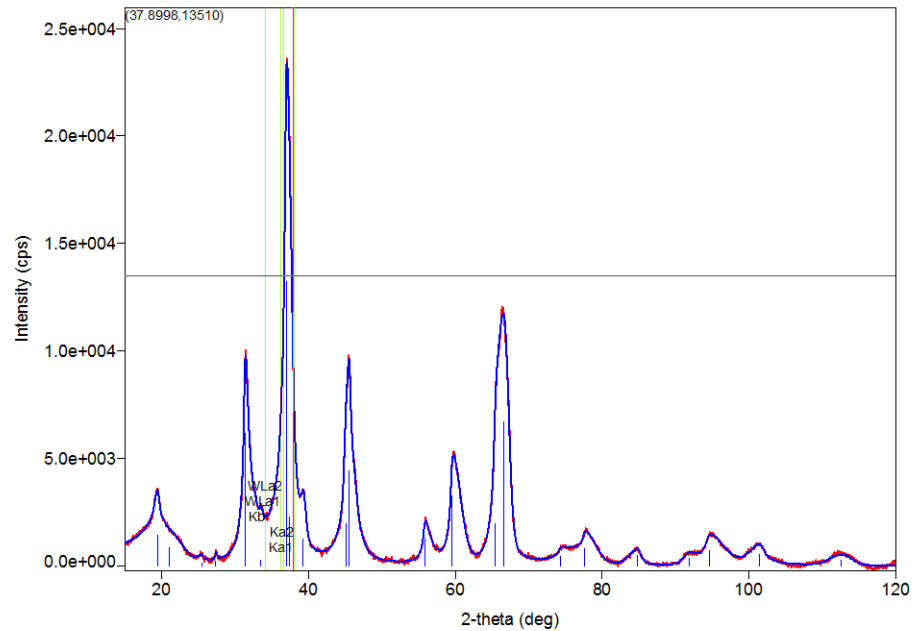


X-Ray Diffraction (XRD)

Fresh CuO/Al₂O₃



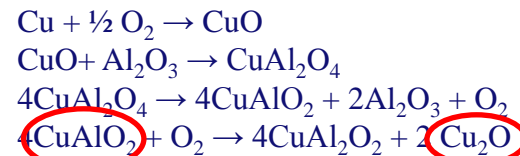
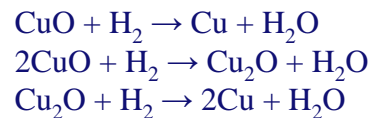
25 CYCLES TGA CuO/Al₂O₃



EXPERIMENTAL STUDIES

X-Ray Diffraction (XRD)

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

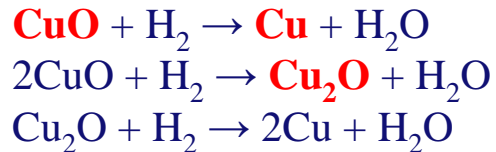


New Particle Model

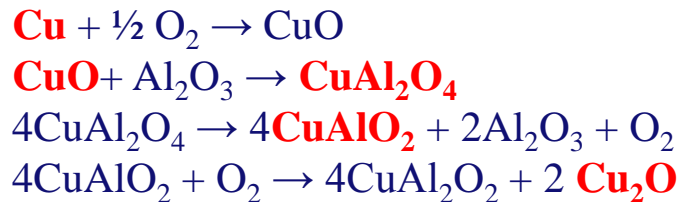
PARTICLE MODEL

Kinetics of the components detected in the XRD analysis: Kinetics

Reduction:

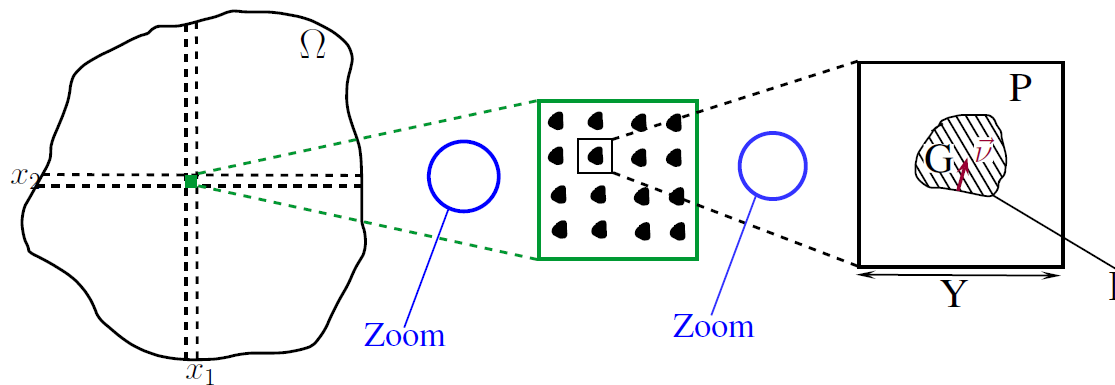


Oxidation:



- CuO
- CuAl₂O₄
- Cu₂O
- Cu
- CuAlO₂

Homogenization in porous media: Diffusion



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

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



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

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***