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Manufacturing and characterization of oxygen carrier materials for fixed bed CLC

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Outline

» Introduction

» Manufacture of oxygen carriers by extrusion

» Results and physico-chemical characterization of oxygen carriers

» Conclusions

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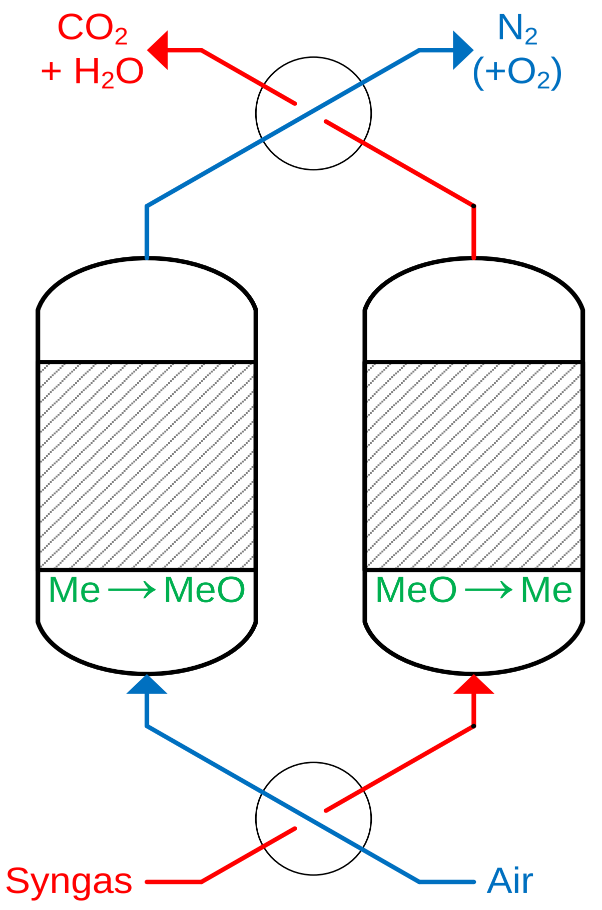
Introduction

- DemoCloCk: packed bed CLC

- Aim of project activity:
  - oxygen carrier development and manufacturing of oxygen carriers that combines a high capacity for oxygen transfer, suitable reactivity and kinetics to limit reactor size, a shape to support a flow pattern that allows for ‘intimate’ interaction with the fuel (gasified coal) or air, with a minimum pressure drop and according packing density, an acceptable strength to make a lifetime of above 20.000 hours of operation possible, and sulphur poisoning resistance in the sense that the other targets can be met.



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Introduction

Extrusion of oxygen carriers in DemoCLoCk

The ideal packed bed oxygen carrier material:

- High capacity for oxygen uptake and release
  - High activity through high and accessible surface area
- Maximal conversion of syngas
- Shaped for low packing density enabling high flow and low pressure drop
- Resistance to poisoning
- Structural integrity, for good multicycle - performance and long service life
- Cost, including environmental and safety costs.

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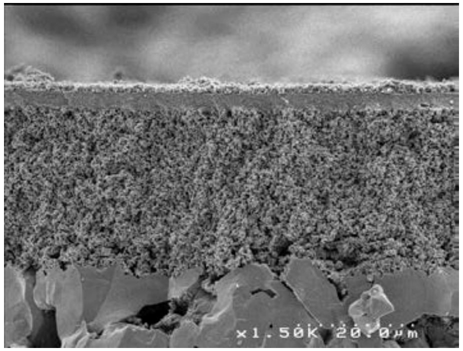
CTI (www.ctisa.fr)
Filtration and catalysis

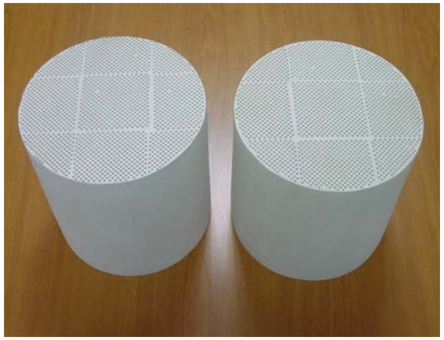
Membrane technologies

supports



Inorganic membrane
(ultra, micro)

Gases purification and treatment



DPF

Ceramic candles : SiC support with membrane for high temperature gas filtration

Catalysis and alternative Energies

Ceria catalyst

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Introduction: fabrication of OC

Diameter: 2-3mm
Lenght: 3-10mm (2-25)

Granules

Diameter: 10-12mm
Lenght: 12-18mm
(10-22)

Fluted rings

Catalysts and catalyst support can be fabricated with different shapes and from a variety of materials, mainly from mixtured of oxides (alumina,….) by extrusion
The characteristics like size, porosity, pore size, mechanical properties are defined in function of the application.

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Manufacture by extrusion

» Main steps and components for the extrusion process

raw materials and conditioning

↓

mixing, paste preparation

↓

shaping: extrusion

↓

Drying, calcining and sintering

mixer

extruder

kiln

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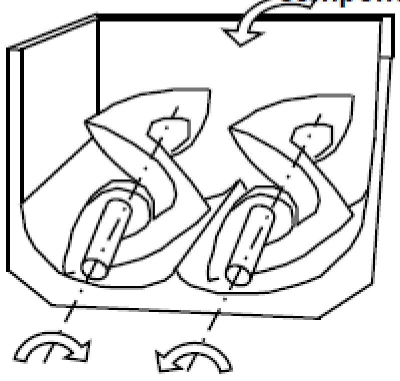
Manufacture by extrusion
Mixing

- Preparation of extrusion paste from constituents:
  - Ceramic powders
  - Dispersing agents: wettability, de-agglomeration, stability, viscosity
  - Binders for cohesion of the green body and in order to obtain a pseudo-plastic rheology
  - Plasticizers in order to decrease the vitreous transition temperature of the binders
  - Lubricants: minimize friction
  - Solvents: ideally water



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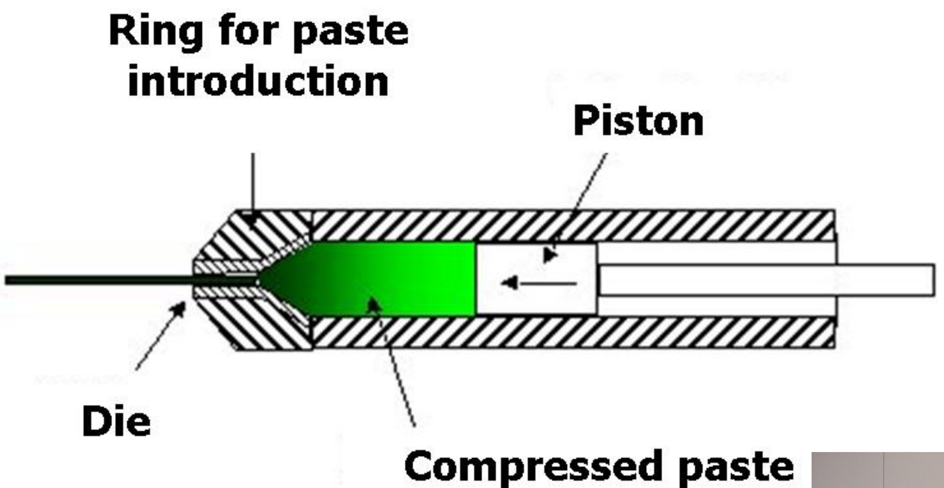
Manufacture by extrusion

Extrusion

After mixing into a paste, the paste is shaped through a die by extrusion



Granules shaping system

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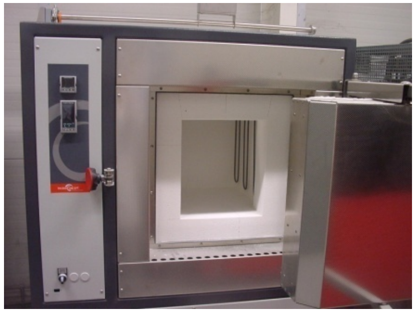
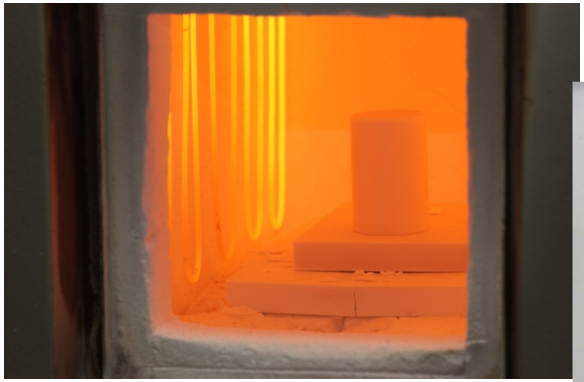
Manufacture by extrusion
Drying and firing

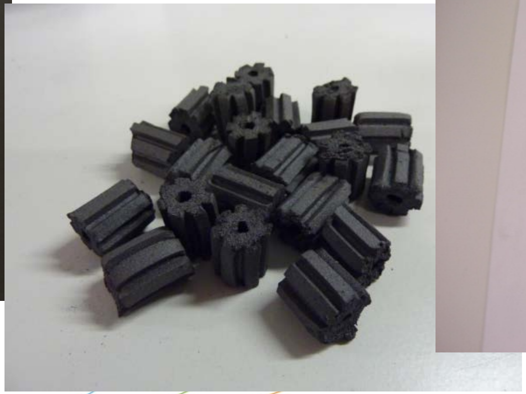
Lab tests: electrical furnaces

Production: gas fired industrial kiln





Fluted rings



Granules

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DemoCLoCk materials

First choice:

Naturally occuring material: Ilmenite ($FeTiO_3$) :

Interest: low cost

Difficulty: natural mineral with particle size D_{50} = 150µm

Mineral binder needed: Al_2O_3, TiO_2 , Fe_2O_3, Mn_2O_3, clays,..

Second choice:

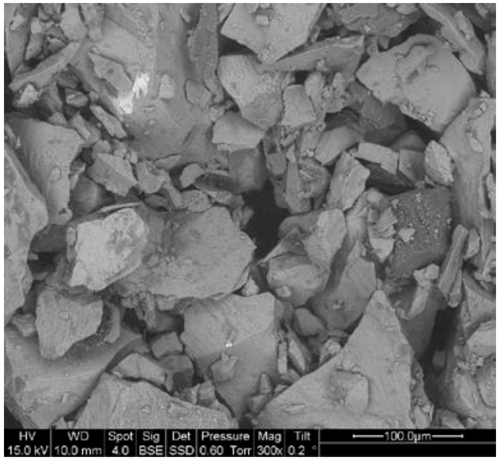
Synthetic material: $Ca_xMn_yTiO_3$

Higher cost

No inorganic binder needed

For both composition: thermal treatment 1300°C - 10 h

SEM of ilmenite powder



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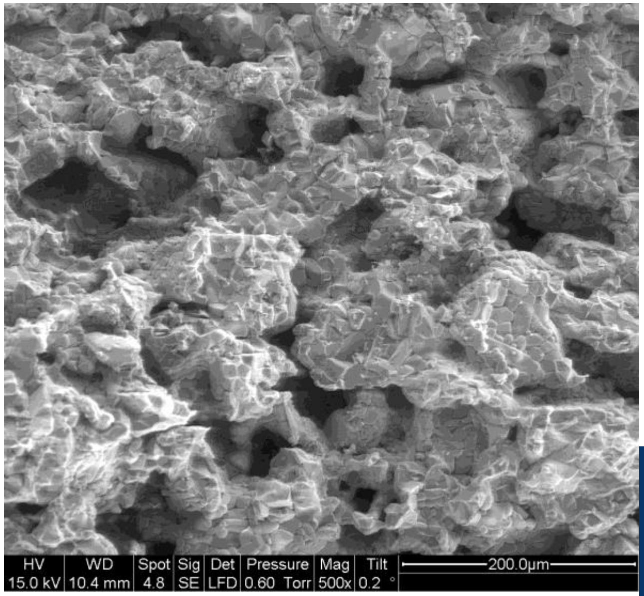
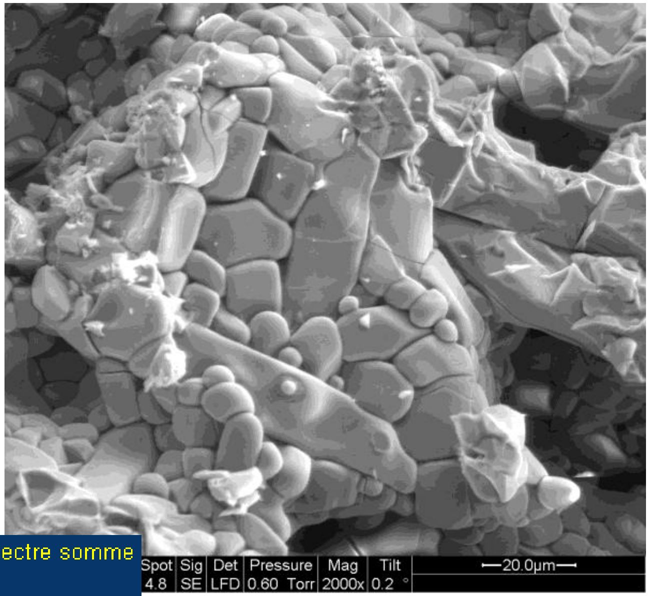
DemoCLoCk materials

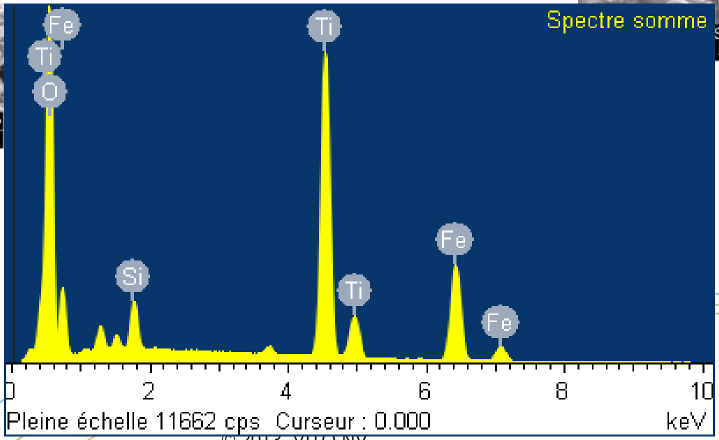
DEMO CLOCK

80% Ilmenite – 20% TiO_2 (% in weight)
after sintering 1300°C - 10h



SEM PICTURES





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DemoCLoCk materials

Physical Characteristics	F1 – Granules	F4– Porous Granules
Average external diameter (mm)	2.6 ± 0.2	2.6± 0,2
Average length (mm)	7.5 ± 5.0	6.6 ± 5,0
Grain bulk density	4.03	3,08
Grain Porosity (%)	1.22	30
Mechanical characteristics		
Individual particle crushing strength (DaN/mm) >2	2.29	2,91
Attrition (Spence method) (%)	5.8	2,15
Attrition by sieving (850µm) (%)	0.5	-

Mechanical characteristics of porous CMT82>> dense CMT82:
Porosity limits the grain growth

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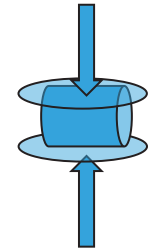
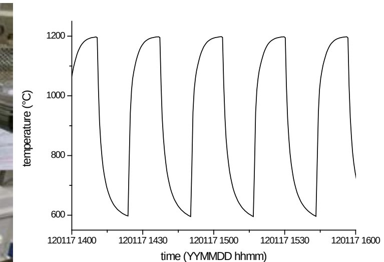
Mechanical tests: at a glance

- Crush strength (target 2 DaN/mm)
  - Fresh
  - After cycling

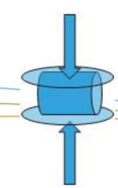


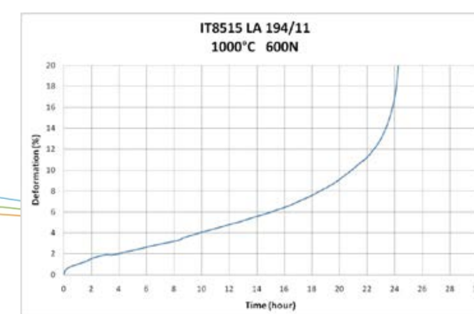
- Attrition: Spence method

- Thermal cycling tests (purely thermal effect)



- Creep test (displacement ifo time) under load at high temperature





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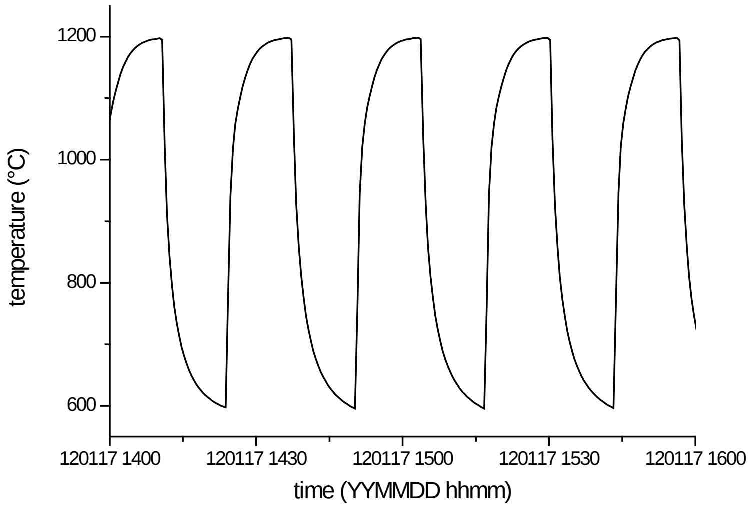
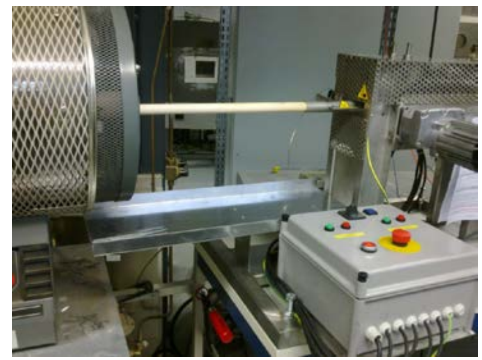
In house developed dedicated tests: thermal cycling and creep

» Thermal cycling test (purely thermal effect)

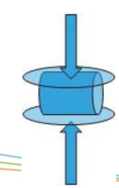




ΔT=600°C
Δt=30'
Max rate = 10°/s

» Creep test (displacement ifo time) under load at high temperature, mimicking packed bed conditions

Loads calculated with bed height of 2.5m
Isothermal at 1200°C under air, 1 atm



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Thermal cycling

- Granules subjected to thermal cycles (under air)
- Mechanical strength evaluated after up to 200 cycles

sample	# cycles	Crush strength (DaN/mm)	Stdev.	Stdev %	Min CS (DaN/mm)	Max CS (DaN/mm)
Granule G10	0	10,2	3,14	30,8	5,84	17,05
Granule G10	50	5,48	1,12	20,4	3,98	8,05
Granule G10	100					
Granule G10	200	3,34	1,1	32,93	1,42	5,12
Granule G11	0	17,3	3,5	20,2	11,46	21,2
Granule G11	50	9,67	3,82	39,5	4,5	17,9
Granule G11	100					
Granule G11	200	11,75	4,71	40,09	3,03	16,16

- G10: clear deterioration
- G11: only slight deterioration?: not very clear trend

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Reactor cycling

- G1
  - Degradation of mechanical properties
  - After 50 cycles: G1 well below target value, large variation
  - Strong increase in porosity, “breathing” of material

sample	# cycles	Crush strength (DaN/mm)	Std dev.	Stdev %	Min CS (DaN/mm)	Max CS (DaN/mm)	Poros. (Hg, %)
G1	0	9,26	1,94	20,9	6,34	12,9	
G1	10	13,43	4,74	35,3	7,52	23,26	14
G1	20	4,83	1,28	26,5	3,45	7,38	23
G1	50	**1,18**	0,44	37,3	0,63	1,79	32

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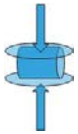
Creep tests

- Displacement in function of temperature under load
  - Loads calculated with bed height of 2.5m, 1.5kg
  - Isothermal at 1200°C under air, 1 atm



Sample	Temperature (°C)	Creep (% deformation/h)	Comment
G10	1200	0.073	95h test
G11	1200	0.193	76h test

- Fluted rings fail at 1200°C after a short testing time
- Granules of the good composition show reasonable creep

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Mechanical tests: first conclusions

- Creep tests
  - Fluted rings fail under load at high temperature
  - Granules withstand load, even at 1200°C

- Thermal cycling tests
  - Fluted rings degrade after several cycles, depending on composition, to below target value
  - Granules show no clear trend, but mechanical strength is still above critical value

- **Granules** are the **prefered shape** over fluted ring shape

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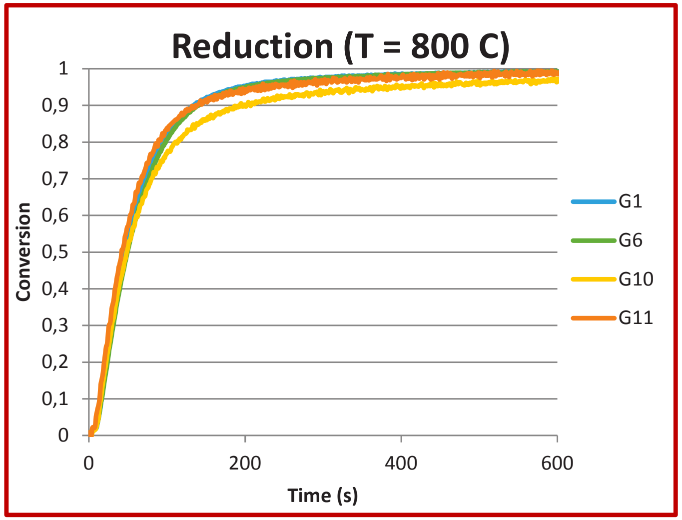
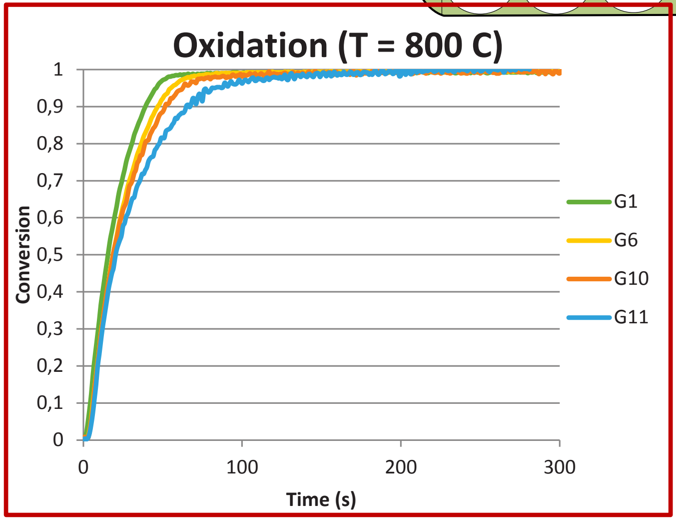
TGA tests





15/20/65 H_2/CO/inert-mixture

- At 800°C, the different oxygen carrier samples showed similar reactivity during the reduction and the oxidation. Oxidation is faster than reduction.
- The reaction rate increased with the fuel concentration and/or the temperature.
- The reduction with H_2 is faster than with CO
- The kinetics, assessed using the changing grain size model with a combination of chemical reaction and diffusion through the product layer, of the different oxygen carriers are similar.

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Mechanical tests

	G1	G6	G10	G11
Individual particle crushing strength as produced (DaN/mm*)	2.86	1.97	2.13	2.91
Attrition (Spence method) %	12.1	10.4	10.3	2.2
Crushing strength after 50 redox cycles	1.18	0.57	2.47	3.26

In TGA (in DaN/mm)

*Target value for cata: 2 DaN/mm.

- If the oxygen carrier shows a low crushing strength, the granules would break and the pressure drop in the reactor will increase dramatically
- The crushing strength of the particles after 50 redox cycles in the TGA at TU/e, was analyzed at VITO

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Outline

DEMO CLOCK

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Conclusions and highlights

» Extrusion is an industrial manufacturing technique for PB oxygen carrier application.

» 18 different compositions and two shapes (27 samples) have been prepared for lab scale evaluation in TGA and packed bed CLC with comparable results.

» Degradation of material is attributed mainly to chemical stress. Quite different behaviour has been observed for different compositions.

» One composition has been selected which will be scaled up (awaiting 'go/no go') to ton-scale production for the 500kW demonstration plant in Puertollano, Spain

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