14/06/2013

Manufacturing and characterization of oxygen carrier materials for fixed bed CLC

F. Snijkers[1], D. Tournigant[2], E. Louradour[2], M. Ortiz[3], F. Gallucci[3], Yngve Larring[4], J. Van Noyen[1]

[1] VITO nv, Belgium

[2] CTI sa, France

[3] TU/e, the Netherlands

[4] SINTEF, Norway

Outline

» Introduction

» Manufacture of oxygen carriers by extrusion

» Results and physico-chemical characterization of oxygen carriers

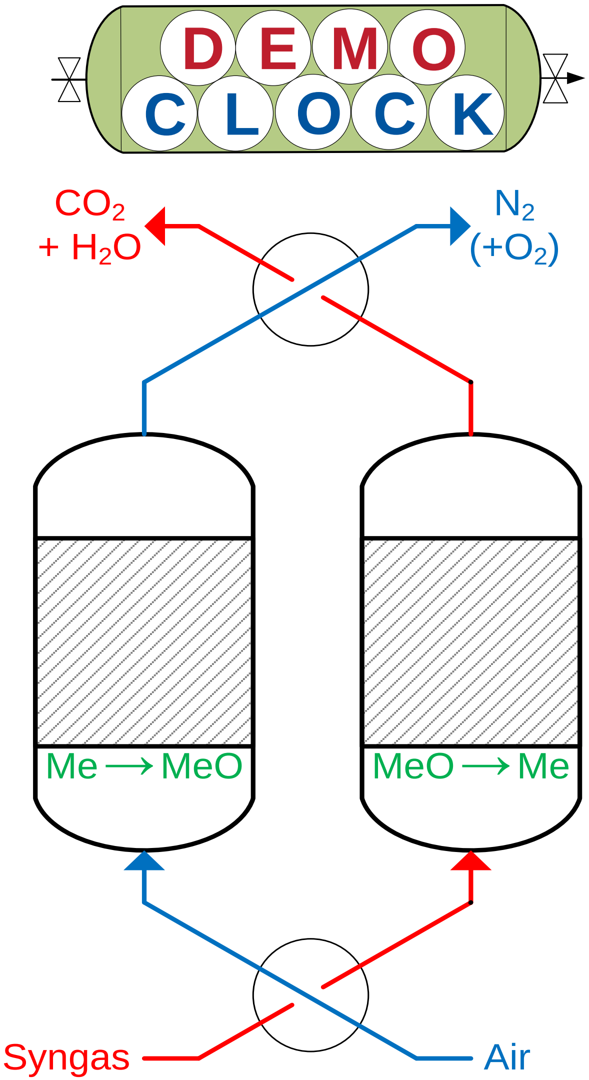
» Conclusions

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.



vision on technology

Introduction

Extrusion of oxygen carriers in DemoCLoCk

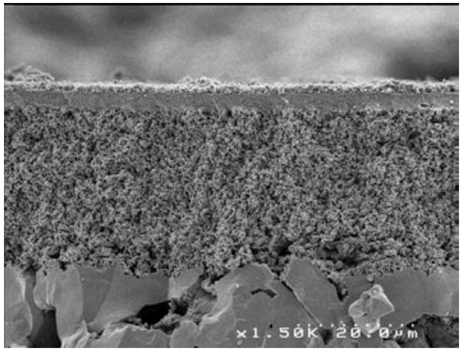
The ideal packed bed oxygen carrier material:

- 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.

CTI (www.ctisa.fr)
Filtration and catalysis

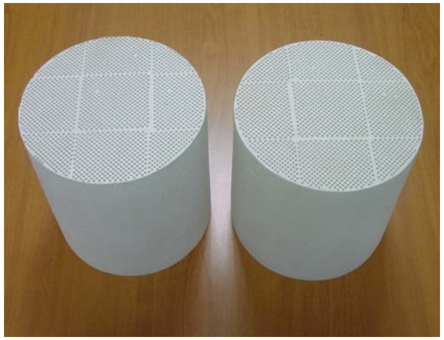
Membrane technologies


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

vito
vision on technology

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.

Outline

» Introduction

» Manufacture of oxygen carriers by extrusion

» Results and physico-chemical characterization of oxygen carriers

» Conclusions

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

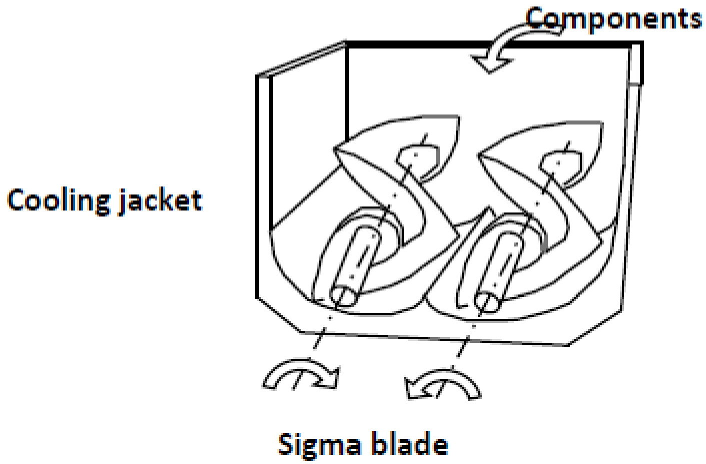
extruder

kiln

Manufacture by extrusion

Mixing

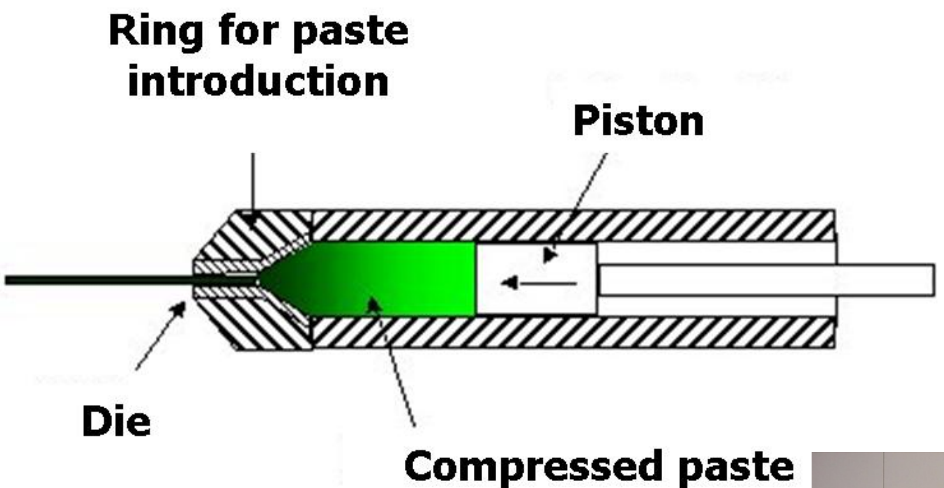
- Preparation of extrusion paste from constituents:
  - Ceramic powders
  - Dispersing agents: wettability, de-agglomeration, stability, viscosity
  - Binders for cohesion of the green body and in order to obtain a pseudo-plastic rheology
  - Plasticizers in order to decrease the vitreous transition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

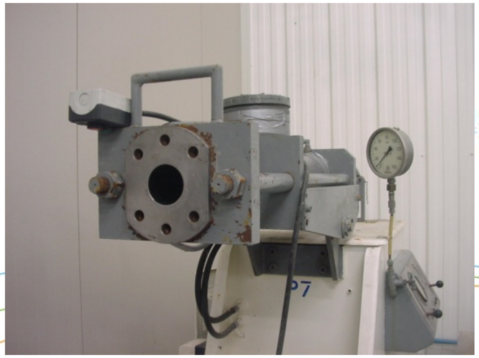


Manufacture by extrusion

Extrusion

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



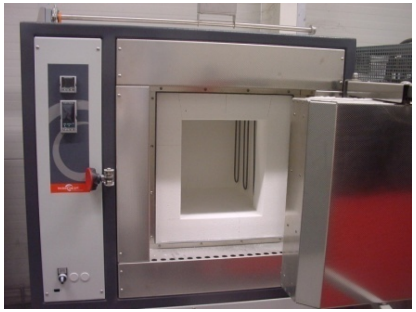


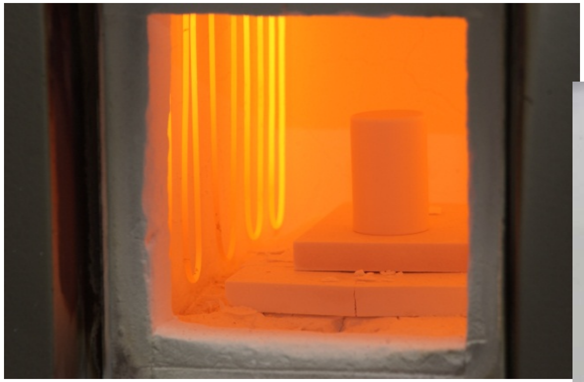
Granules shaping system

Manufacture by extrusion
Drying and firing

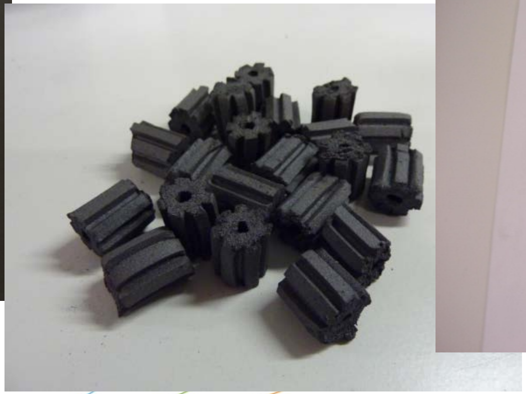
Lab tests: electrical furnaces

Production: gas fired industrial kiln





Fluted rings



Granules

Outline

- Introduction
- Manufacture of oxygen carriers by extrusion
- Results and physico-chemical characterization of oxygen carriers
- Conclusions

vision on technology

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:

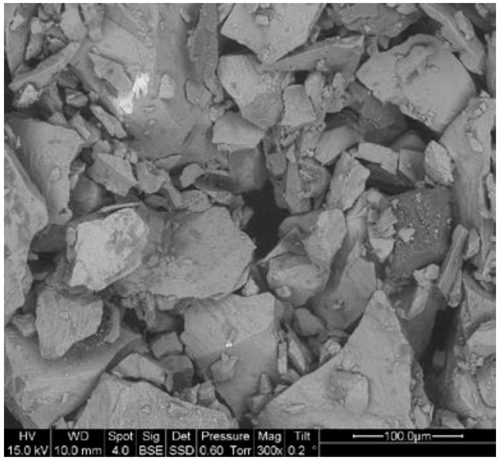
Synthetic material: $Ca_xMn_yTiO_3$

Higher cost

No inorganic binder needed

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

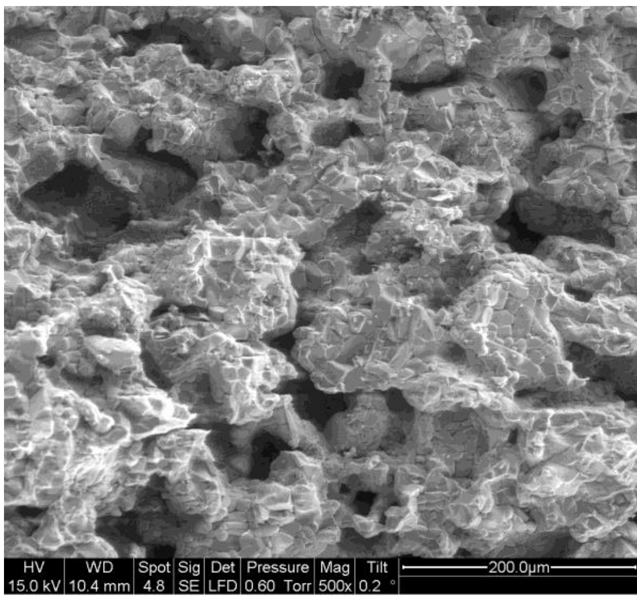
SEM of ilmenite powder



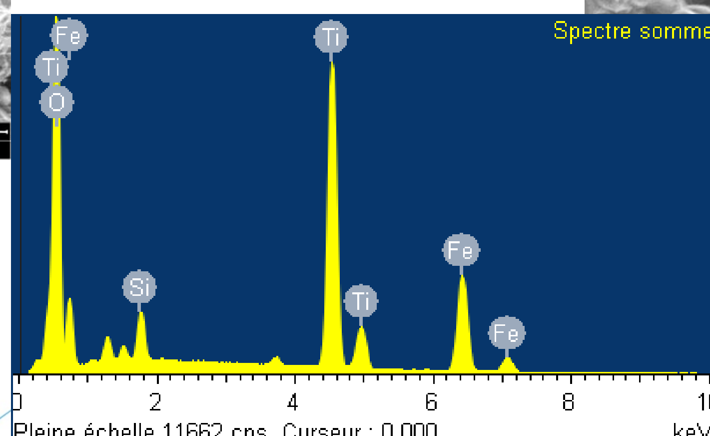
vito vision on technology

DemoCLoCk materials

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



SEM PICTURES



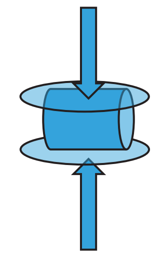
DemoCLoCk materials

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

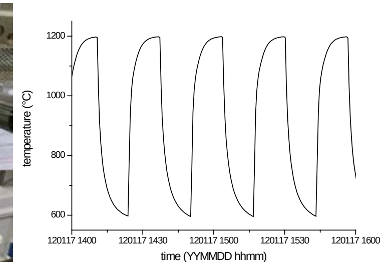
Mechanical tests: at a glance

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

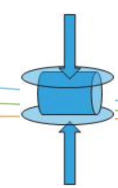


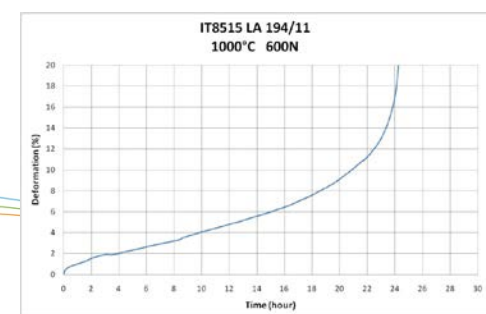
- Attrition: Spence method

- Thermal cycling tests (purely thermal effect)



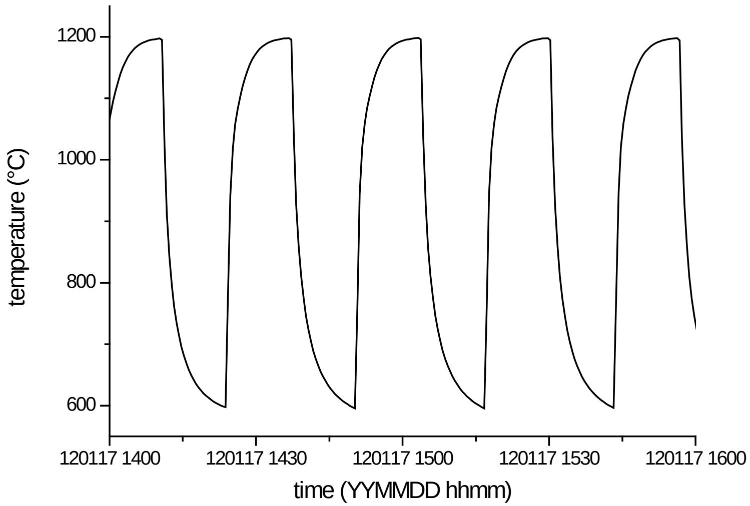
- Creep test (displacement ifo time) under load at high temperature

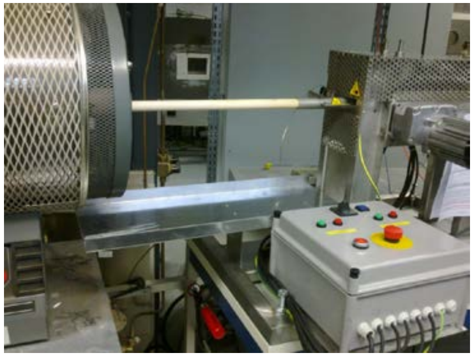




In house developed dedicated tests: thermal cycling and creep

» Thermal cycling test (purely thermal effect)

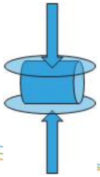




ΔT=600°C
Δt=30'
Max rate = 10°/s

» 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



vito vision on technology

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

Reactor cycling

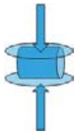
- G1
  - Degradation of mechanical properties
  - After 50 cycles: G1 well below target value, large variation
  - Strong increase in porosity, "breathing" of material

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

vito
vision on technology

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



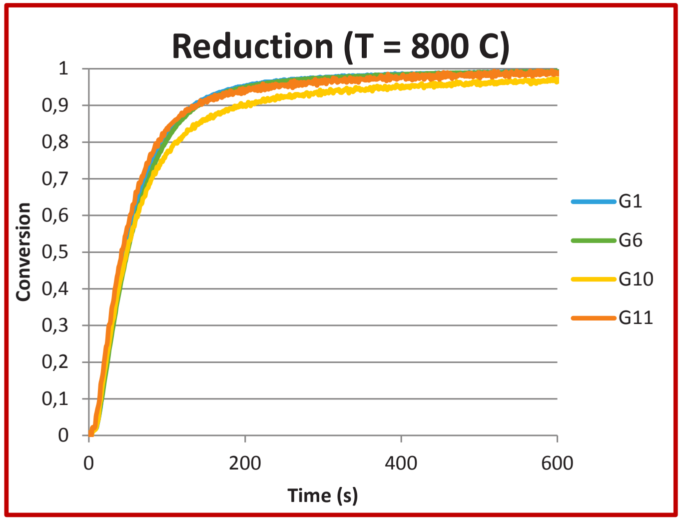
Sample	Temperature (°C)	Creep (% deformation/h)	Comment
G10	1200	0.073	95h test
G11	1200	0.193	76h test

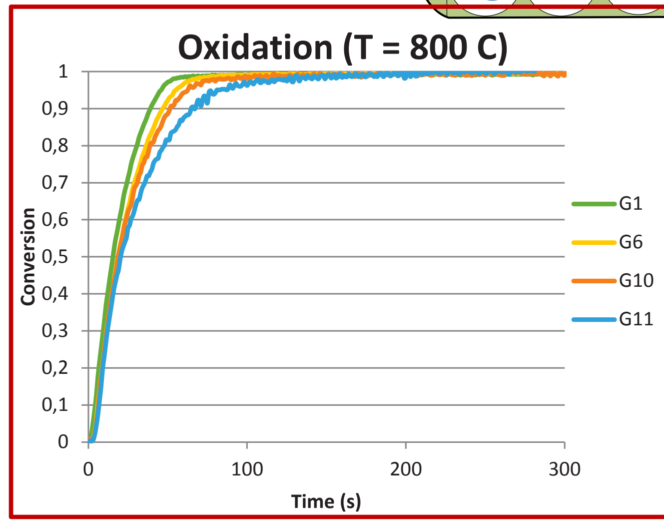
- Fluted rings fail at 1200°C after a short testing time
- Granules of the good composition show reasonable creep

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

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.

vision on technology

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 In TGA (in DaN/mm)	1.18	0.57	2.47	3.26

*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

Outline

» Introduction

» Manufacture of oxygen carriers by extrusion

» Results and physico-chemical characterization of oxygen carriers

» Conclusions

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