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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
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.
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.
Membrane technologies

Inorganic membrane (ultra, micro)

supports

Gases purification and treatment

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

Catalysis and alternative Energies

DPF

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

**Introduction: fabrication of OC**

- **Granules**
  - Diameter: 2-3mm
  - Length: 3-10mm (2-25)

- **Fluted rings**
  - Diameter: 10-12mm
  - Length: 12-18mm (10-22)

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Manufacture by extrusion

- Main steps and components for the extrusion process

1. Raw materials and conditioning
2. Mixing, paste preparation
3. Shaping: extrusion
4. Drying, calcining and sintering

- Images:
  - 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.
Manufacture by extrusion
Drying and firing

Lab tests: electrical furnaces

Production: gas fired industrial kiln

Fluted rings

Granules
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**First choice:**
Naturally occurring material: Ilmenite (FeTiO$_3$):
- Interest: low cost
- Difficulty: natural mineral with particle size $D_{50} = 150\mu$m
- Mineral binder needed: Al$_2$O$_3$, TiO$_2$, Fe$_2$O$_3$, Mn$_2$O$_3$, clays,..

**Second choice:**
Synthetic material: Ca$_x$Mn$_y$TiO$_3$
- Higher cost
- No inorganic binder needed

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

80% Ilmenite – 20% TiO₂ (% in weight) after sintering 1300°C - 10h

SEM PICTURES
DemoCLOCK materials

<table>
<thead>
<tr>
<th>Physical Characteristics</th>
<th>F1 – Granules</th>
<th>F4– Porous Granules</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average external diameter (mm)</td>
<td>2.6 ± 0.2</td>
<td>2.6 ± 0.2</td>
</tr>
<tr>
<td>Average length (mm)</td>
<td>7.5 ± 5.0</td>
<td>6.6 ± 5.0</td>
</tr>
<tr>
<td>Grain bulk density</td>
<td>4.03</td>
<td>3.08</td>
</tr>
<tr>
<td>Grain Porosity (%)</td>
<td>1.22</td>
<td>30</td>
</tr>
<tr>
<td><strong>Mechanical characteristics</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Individual particle crushing strength</td>
<td>2.29</td>
<td>2.91</td>
</tr>
<tr>
<td>(DaN/mm) &gt;2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Attrition (Spence method) (%)</td>
<td>5.8</td>
<td>2.15</td>
</tr>
<tr>
<td>Attrition by sieving (850µm) (%)</td>
<td>0.5</td>
<td>-</td>
</tr>
</tbody>
</table>

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)

\[ \Delta T = 600^\circ C \]
\[ \Delta t = 30' \]
Max rate = 10\(^\circ\)/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
Thermal cycling

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

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

- 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

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Creep (% deformation/h)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>G10</td>
<td>1200</td>
<td>0.073</td>
<td>95h test</td>
</tr>
<tr>
<td>G11</td>
<td>1200</td>
<td>0.193</td>
<td>76h test</td>
</tr>
</tbody>
</table>

» 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 preferred shape over fluted ring shape
TGA tests

- 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 H₂ 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.

15/20/65 H₂/CO/inert-mixture
Mechanical tests

<table>
<thead>
<tr>
<th></th>
<th>G1</th>
<th>G6</th>
<th>G10</th>
<th>G11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Individual particle crushing strength as</td>
<td>2.86</td>
<td>1.97</td>
<td>2.13</td>
<td>2.91</td>
</tr>
<tr>
<td>produced (DaN/mm*)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Attrition (Spence method) %</td>
<td>12.1</td>
<td>10.4</td>
<td>10.3</td>
<td>2.2</td>
</tr>
<tr>
<td>Crushing strength after 50 redox cycles</td>
<td>1.18</td>
<td>0.57</td>
<td>2.47</td>
<td>3.26</td>
</tr>
<tr>
<td>in TGA (in DaN/mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*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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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.