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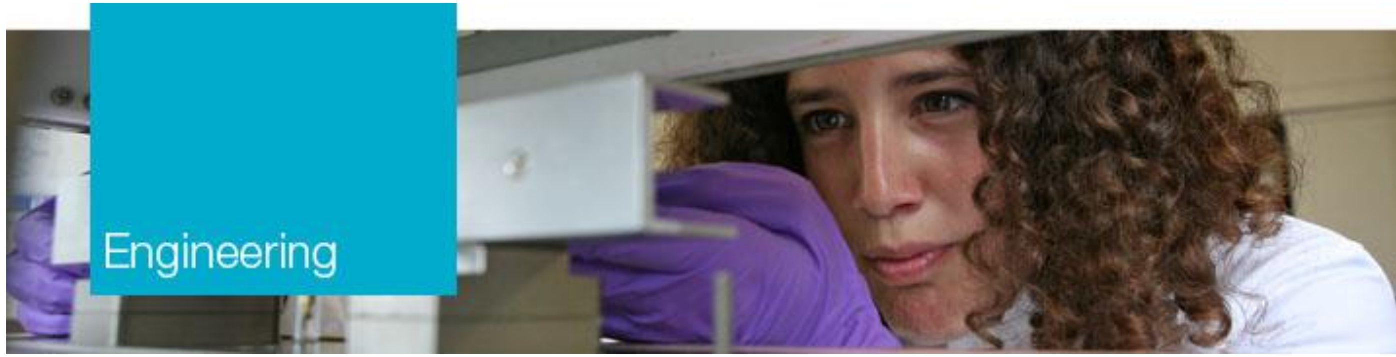


Synthesis of porous ceramics by spray-dried granules sintering

POLYTECH MONS

Outline

Introduction

Experimental results obtained with Spray-dried granules

- Alumina powder constituting the granules
- Granule characterization
- Expected structure
- Sintering of granule packing
- Effect of Thermal + pressure cycle on materials structure

Conclusions & perspectives

Introduction

Interest of using macroporous (>50 nm) ceramics

- Advantages of using ceramics
  1. High melting point
  2. High corrosion and wear resistance
  3. Surface functionalisation is possible

- Applications
  1. Molten metal and hot gas filtration
  2. fluid transfer or mixing
  3. Catalysis
  4. Refractory insulation

Objective

- To develop a new route for manufacturing macroporous ceramics with:
  - Highly interconnected porosity
  - Porosity fraction within a large range (30 to 80 %)
  - Good control of the pore size distribution (single or multimode)

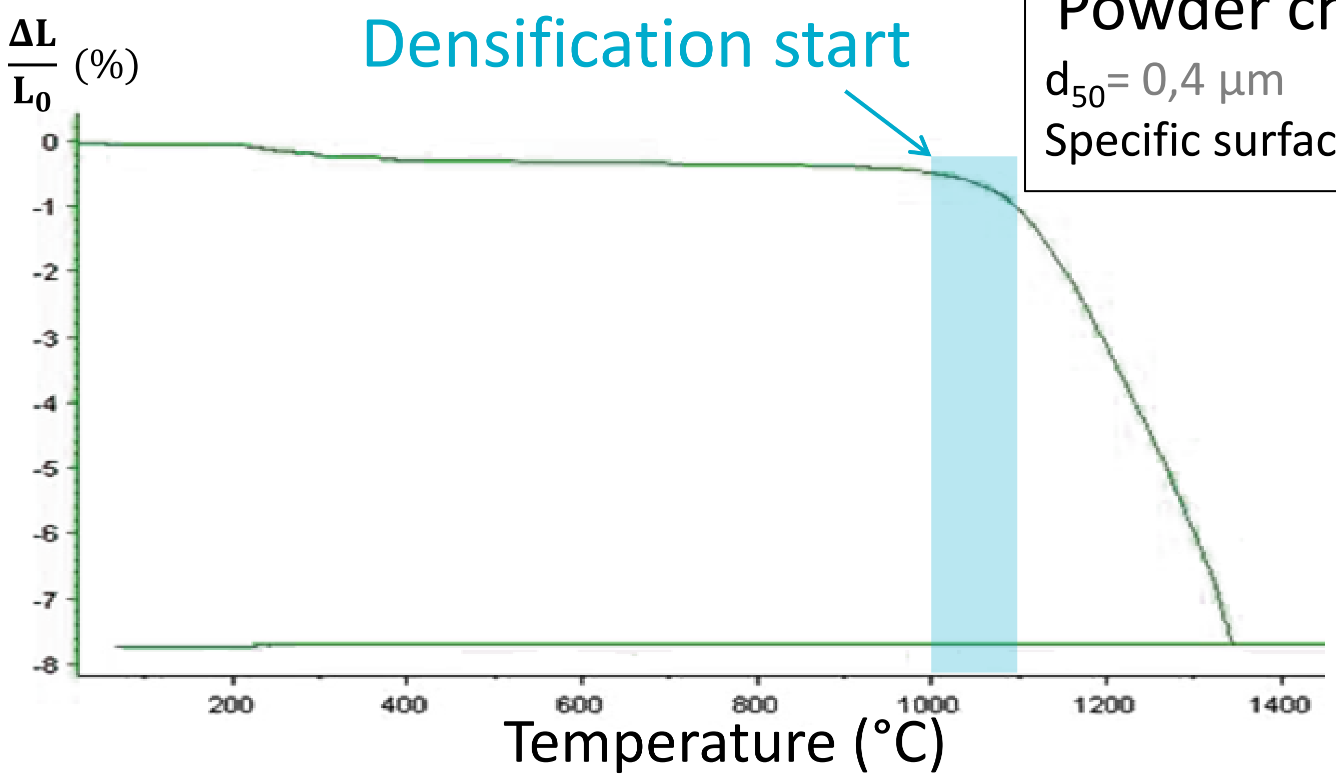
Methodology

- To "bridge", by sintering, packing of basic ceramic "units" (spheres, cylinders,…)
- Sintering must promote solid diffusion at interfaces between units with a limited densification to keep high porosity

Basic ceramic units

- Industrial granules obtained by spray-drying of alumina powder
  - d_{50}: 0,4 µm
  - Specific surface area : 8 m²/g

1. Alumina powder constituting the granules



Powder characteristics

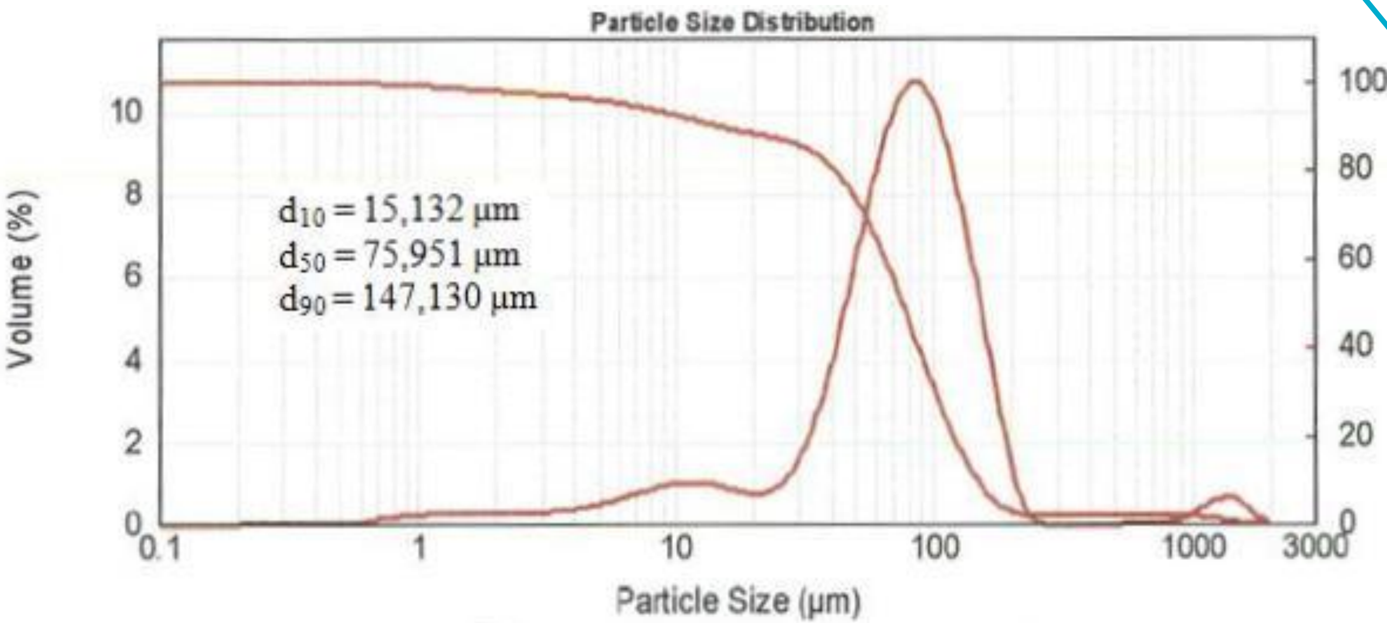
d_{50}= 0,4 µm

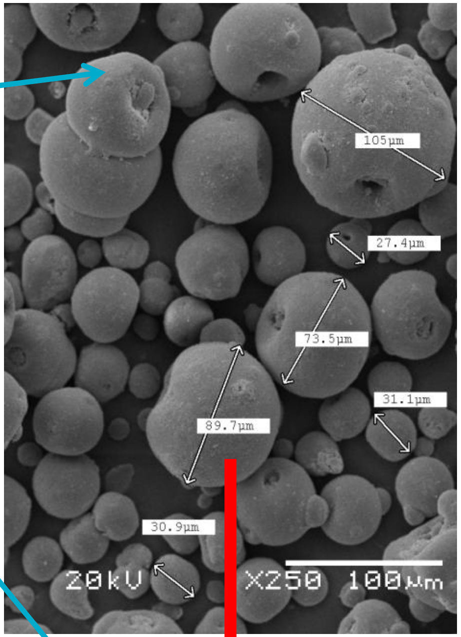
Specific surface area : 8,2 m²/g

- Densification begins between 1000°C and 1100°C
- After 1000°C specific surface area and porosity of the compact decrease

2. Granule characterisation

- **SEM:** The granules:
  - are spherical
  - have a porous structure
- **BET:** High specific surface area 6,7 m^2/g
- **Dry laser granulometry:**
  - d_{50} = 76 µm
  - Nearly unimodal distribution





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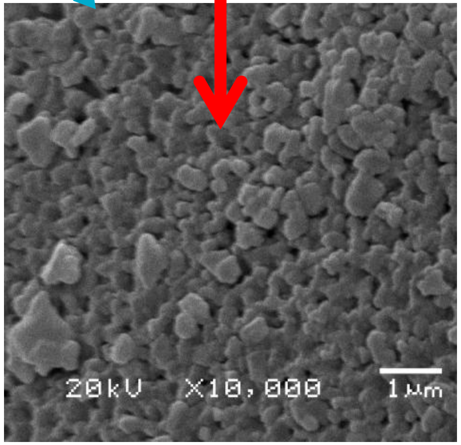
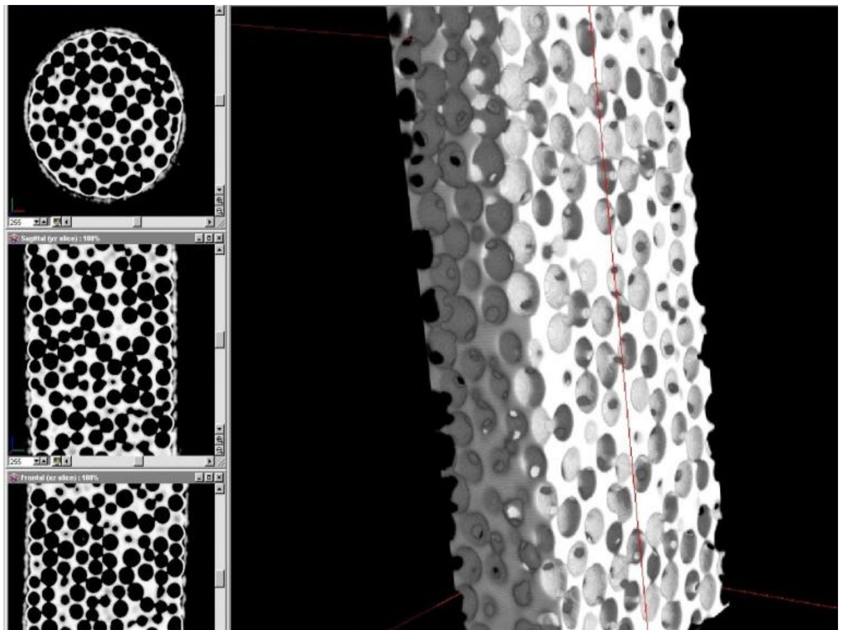
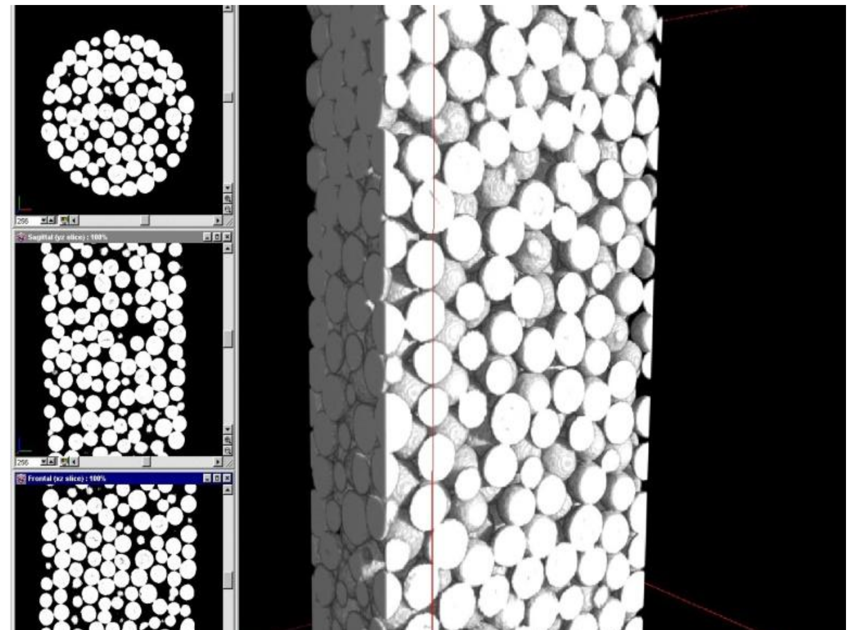


3. Expected structure

- Packing of basic ceramic units (granules) bridged together
- Negative image of the structure resulting of sacrificial methods using organic beads.

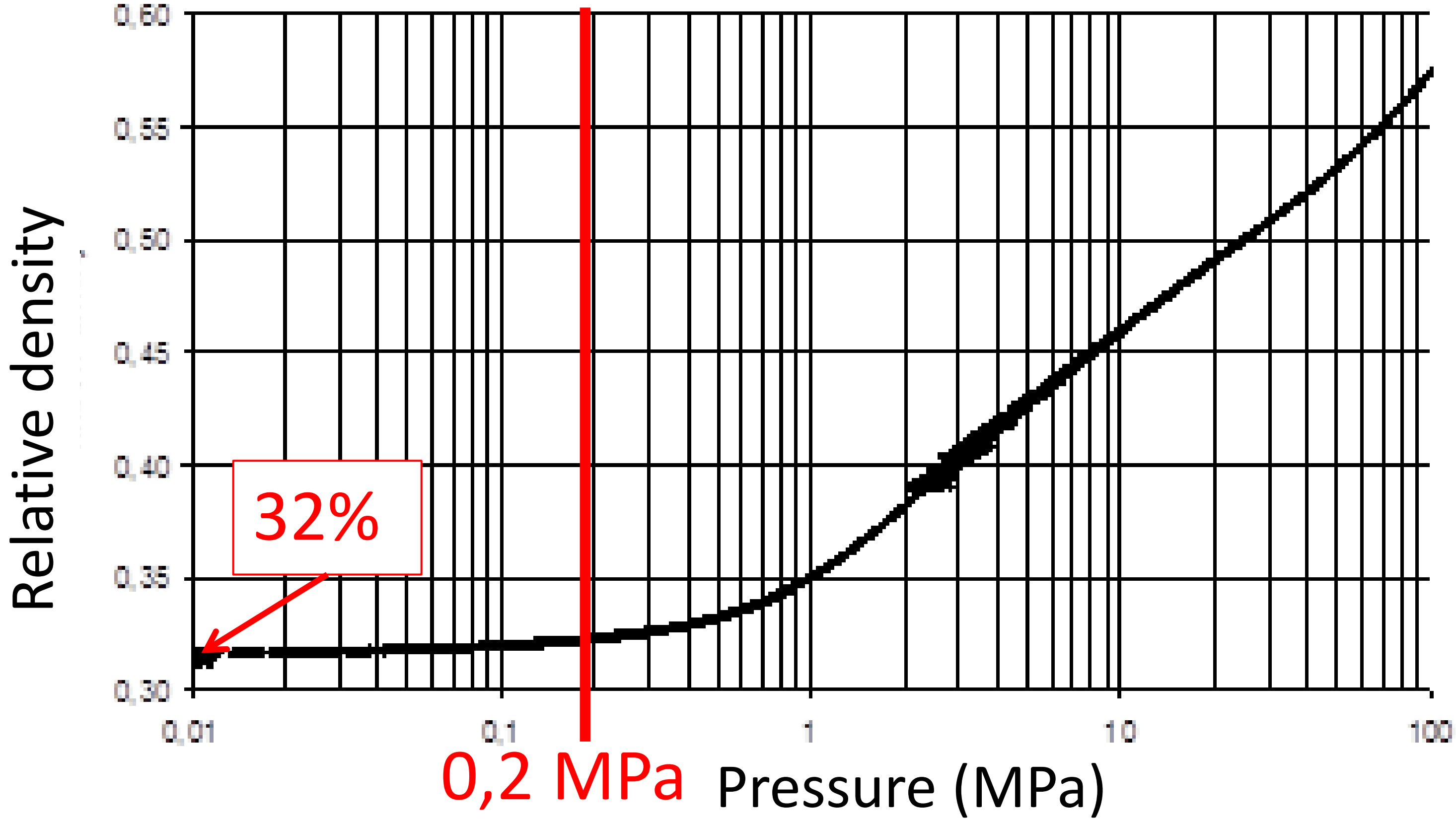


Sacrificial method



Expected structure

Compaction curve of spray-dried granules



- Pressureless, the total porosity fraction is 68% (maximum porosity can be achieved by bridging of granules' packing)
- Above 0,2-0,3 MPa the relative density increases due to the elimination of the intergranular porosity by plastic deformation

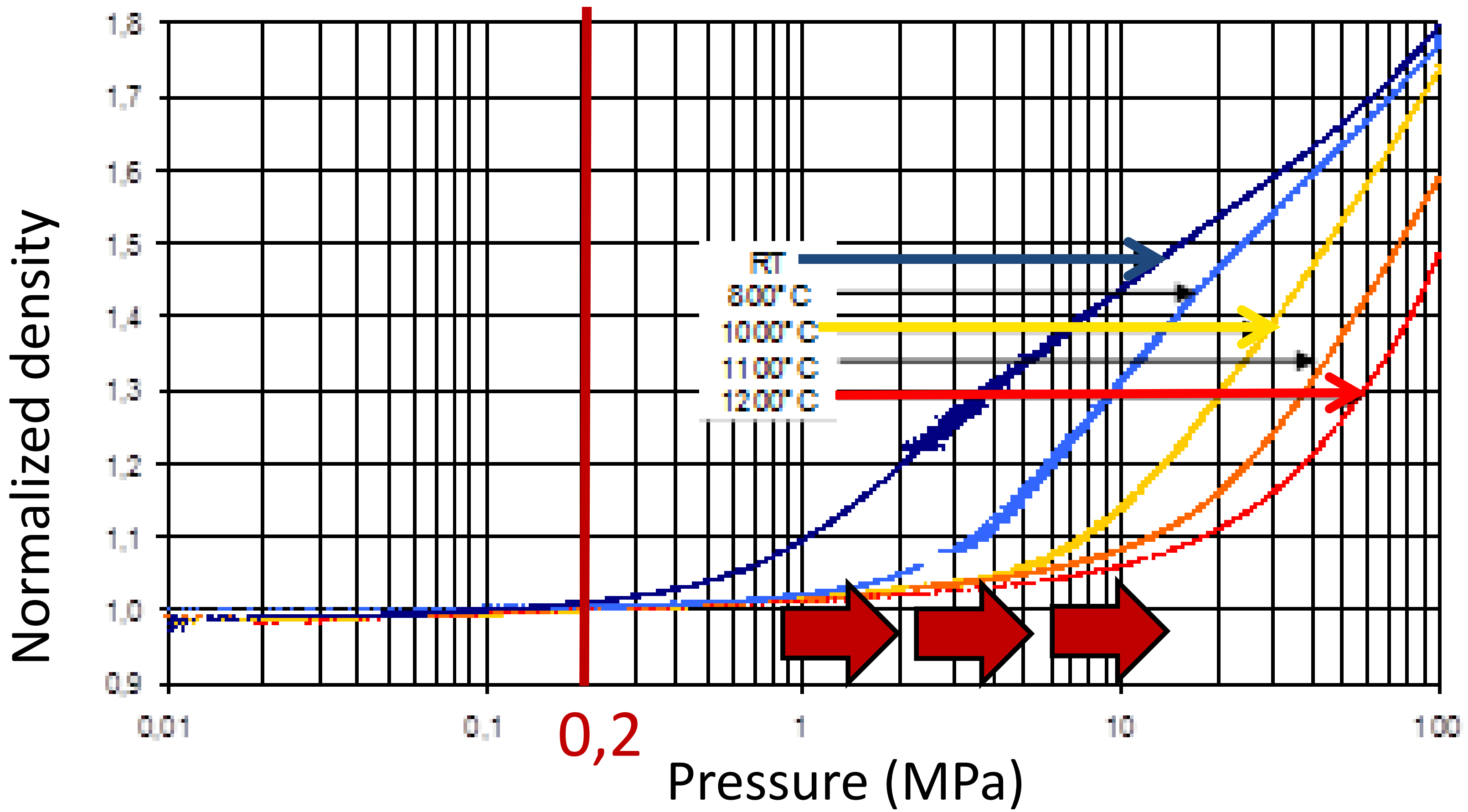
4. Sintering of granule packing

- Free sintering feasibility has been tried :
  - Compaction of the granules under 0,2 MPa in a die
  - Heating at 5°C/min up to 1600°C followed by 1h dwell
  - Natural cooling

➡ bad mechanical behavior was obtained

- Pressure during heat treatment can activate diffusion through the contact points of the granules.
- Mechanical resistance of the granules must previously be improved to avoid plastic deformation

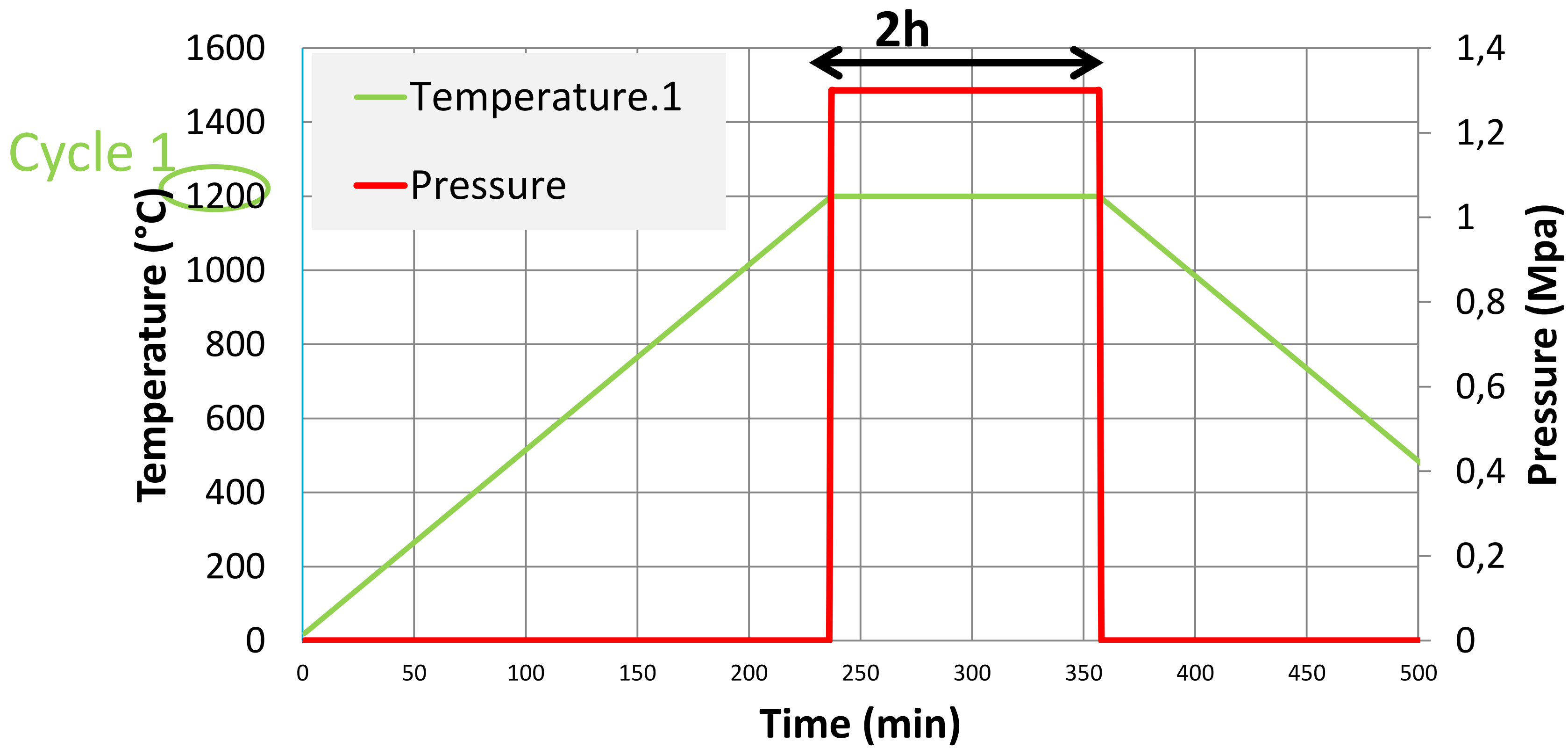
Compaction curves of the heat treated granules



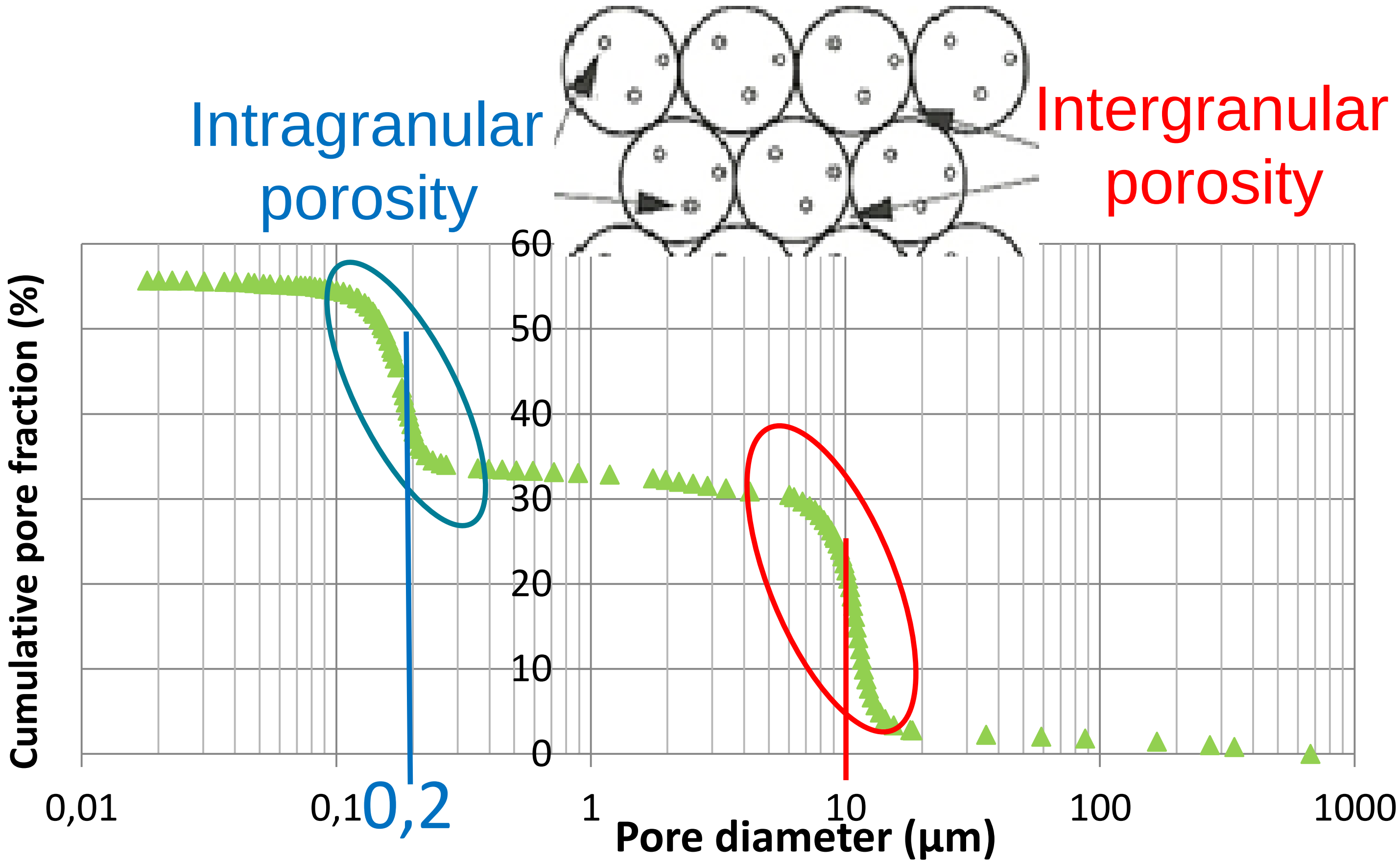
- Plastic deformation begins at much higher pressures when the temperature of the heat treatment increases
- There is a reinforcement of the granules' mechanical properties

5. Thermal and pressure cycle

- Heating at 5°C/min up to 1200°C without pressure (to avoid granules' plastic deformation);
- 2h dwell time at 1200°C under a pressure of 1,3 MPa;
- Natural cooling without pressure.



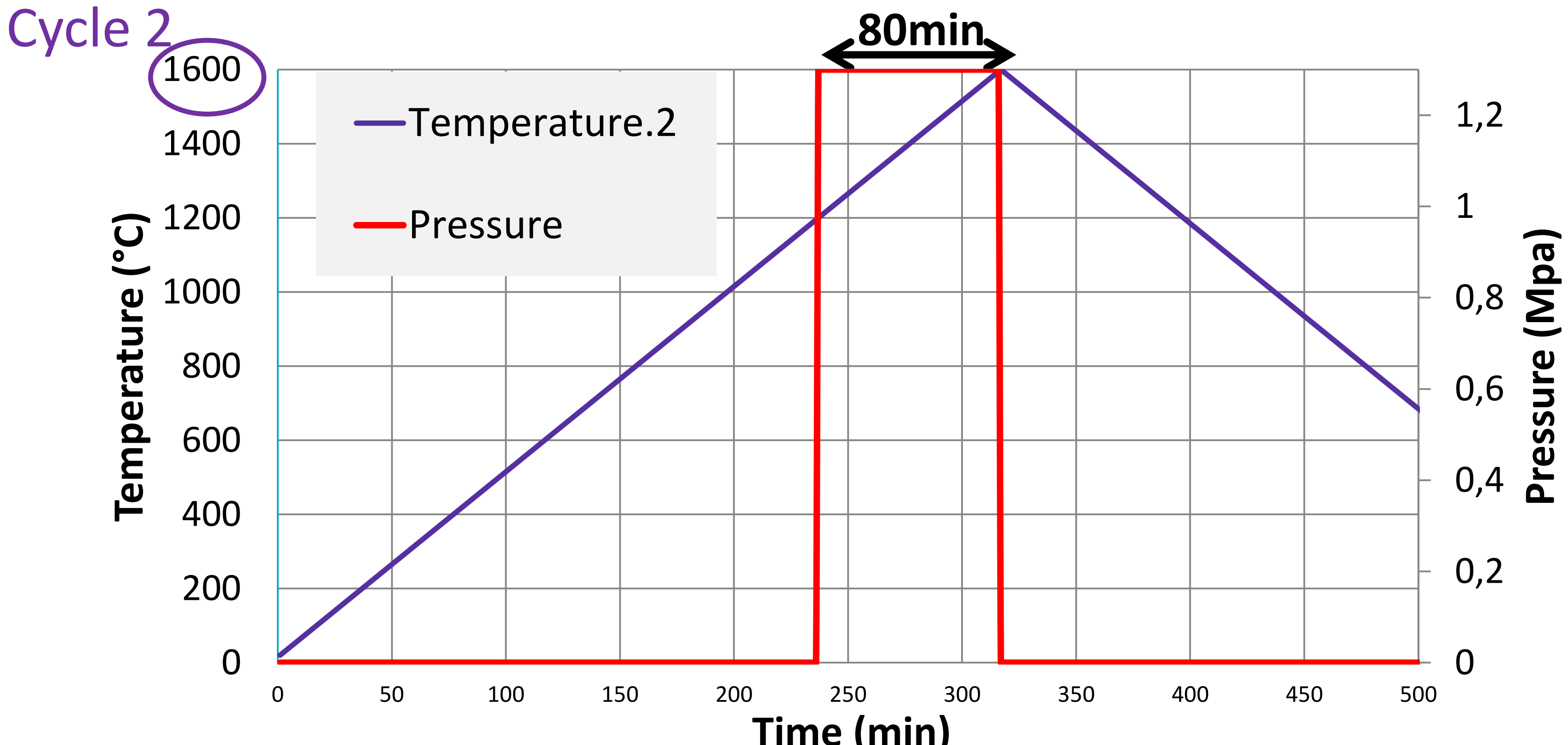
Pore size distribution (by Hg porosimetry)



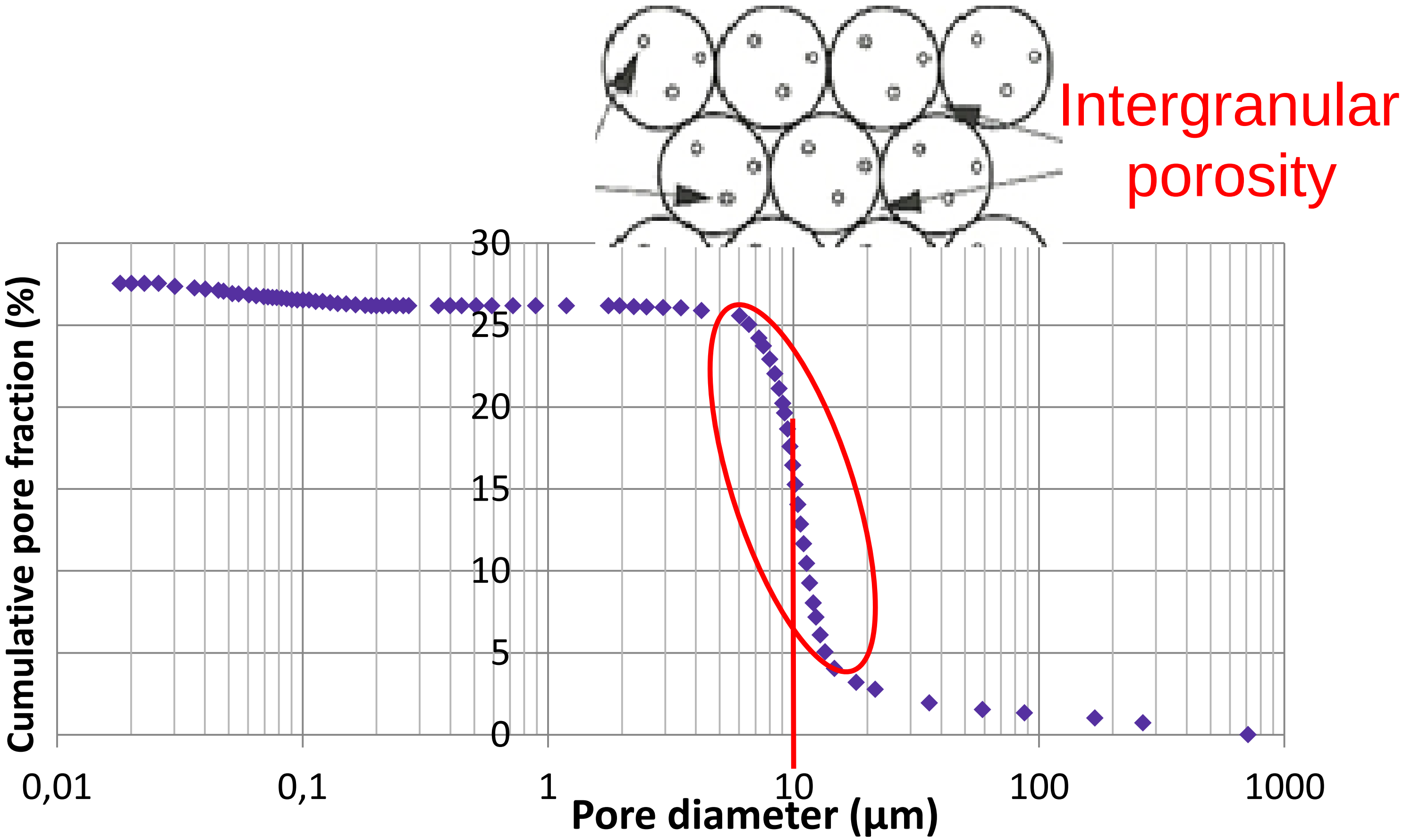
- A consolidated compact was obtained (compressive strength ≈7MPa)
  - Porosity fraction: 54%
  - Specific surface area : 3,7 m²/g (< Initial granules = 6,7 m²/g)

Thermal and pressure cycle

- Heating at 5°C/min up to 1200°C without pressure
- Heating at 5°C/min from 1200°C up to 1600°C under a pressure of 1,3 MPa
- Natural cooling without pressure



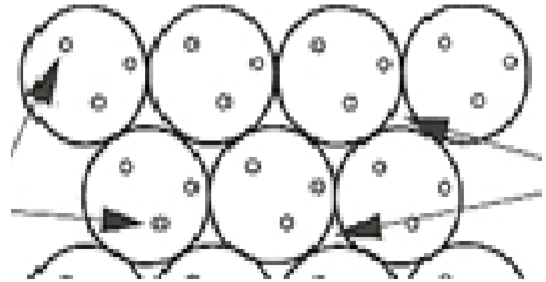
Pore size distribution (by Hg porosimetry)



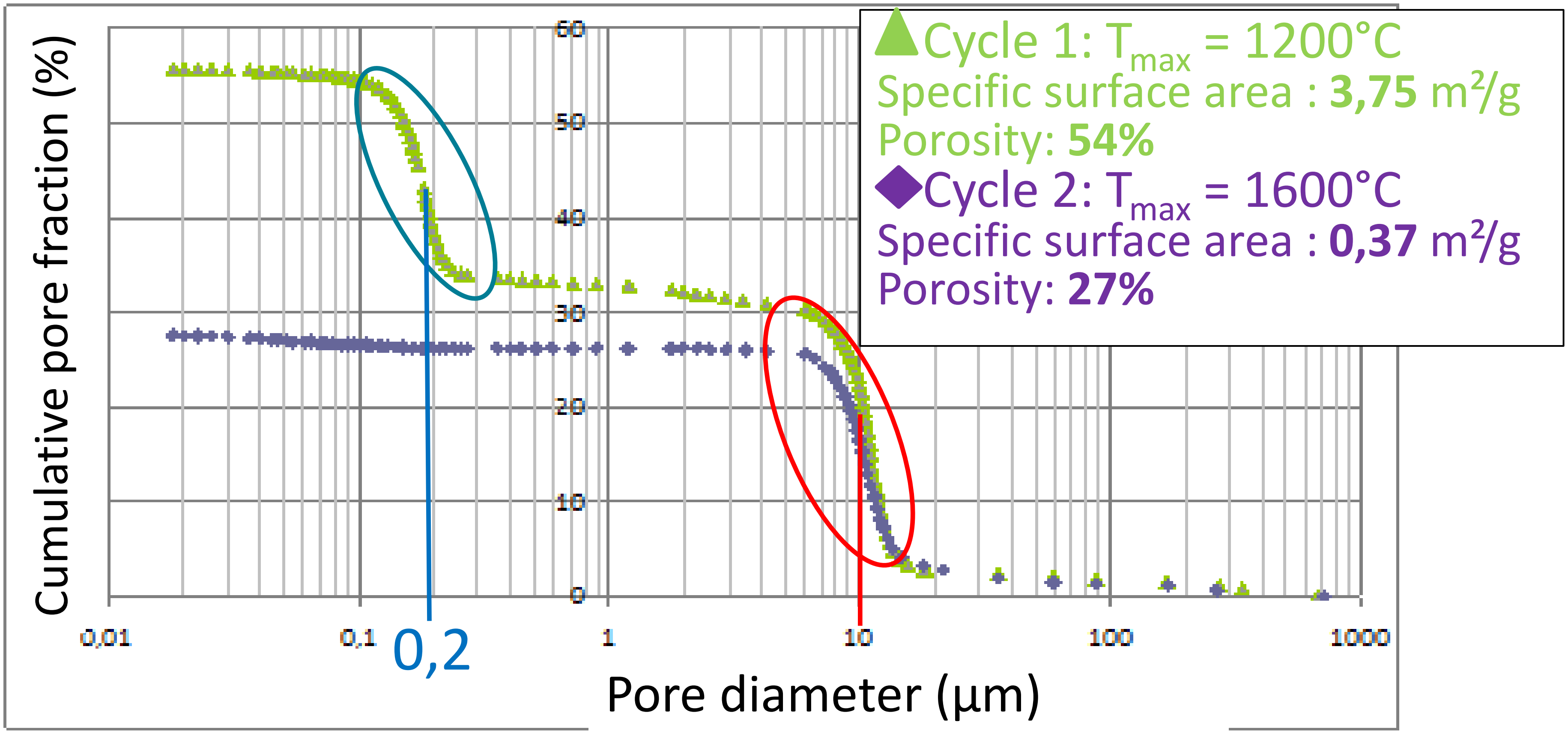
- A consolidated compact was obtained (compressive strength > 110 MPa)
  - Porosity fraction: 27%
  - Specific surface area :0,37m²/g

Pore size distribution (by Hg porosimetry)

Intragranular porosity



Intergranular porosity



Conclusions

1. Pressure applied on the compact induces the formation of necks between the granules
2. Porous alumina ceramics with porosity up to 55 % can be obtained by sintering of spray-dried granules compacts
3. The final material may exhibit only intergranular porosity or intergranular and intragranular porosities

Perspectives

1. Adding sacrificial template within or mix with the granules (to increase intra-interporosity)
2. Using Spark Plasma Sintering (SPS) technique
3. Replacing spray-dried granules by various basic ceramic units (ex : cylindrical units)
4. Transposing this process to another kind of ceramics (ex: cordierite)