The manufacture of metakaolins

Virginie Soleil-Raynaut <virginie.soleil@imerys.com>
Product Manager Ground Clays & Calcined Clays
Imerys Refractory Minerals <www.imerys-refractoryminerals.com>
Imerys: 2016 Key figures

- **€4.2 bn** Revenue
- **€582 m** Current operating income
- **14.0%** Operating margin
- **16 000** Employees
- **260** Operating sites
- **50** Countries
- **8** R&D centers
- **#1 or #2** On most of our markets
- **€6.0 bn** Market capitalization
  - 54% of capital held by GBL
Imerys offers high value-added functional solutions

**Whiteness and toughness** of sanitaryware, floor and wall tiles

- World leader in ceramic bodies for sanitaryware

**Lifespan and fast charging** of electric vehicle lithium-ion batteries

- World leader in conducting additives (graphite, carbon black)

**Thermal and mechanical resistance** of industrial abrasives

- World leader in fused minerals for abrasives

**Resistance and lightness** of automotive plastic parts

- World leader in talc-based performance additives for plastics

**Softness** of natural mineral powders

- World leader in talc for health and beauty

**Watertightness and insulation** of roofs

- French leader in clay roof tiles

**Gloss and opacity** for paint

- World leader in wollastonite and talc for paint

**Filtration of liquids** (food or blood plasma)

- World leader in perlite and diatomite for filtration

**Whiteness and toughness** of sanitaryware, floor and wall tiles

- World leader in ceramic bodies for sanitaryware

**Resistance and lightness** of automotive plastic parts

- World leader in talc-based performance additives for plastics

**Softness** of natural mineral powders

- World leader in talc for health and beauty

**Watertightness and insulation** of roofs

- French leader in clay roof tiles

**Gloss and opacity** for paint

- World leader in wollastonite and talc for paint

**Thermal and mechanical resistance** of industrial abrasives

- World leader in fused minerals for abrasives

**Filtration of liquids** (food or blood plasma)

- World leader in perlite and diatomite for filtration
Imerys’ presence is diversified in many markets and regions.

The world leader in mineral-based specialties for consumer goods, industrial equipment and construction, with presence in more than 50 countries.
**What is a Metakaolin?**

- Metakaolin is an **amorphous state** of kaolinite obtained by firing the mineral at a temperature between 700 and 950°C.

- It is a **pozzolanic** material, i.e. it reacts with lime in the presence of water.
  - In cementious materials, metakaolin reacts with the lime released by the cement during its hydration; it also reacts with the lime added in some mortars.
  - Pozzolanic reaction:

  ![Chemical Reaction Diagram](attachment:image.png)
What is Metakaolin?

Thermal transformation of Kaolin / Kaolinite

Kaolinite : $2\text{SiO}_2 \text{Al}_2\text{O}_3, 2\text{H}_2\text{O}$

Deshydroxylation

Water

$500-550^\circ\text{C}$

Métakaolinite

$2\text{SiO}_2 \text{Al}_2\text{O}_3$

$750-950^\circ\text{C}$

Si-Al Spinelle

$\text{Si}_3\text{Al}_4\text{O}_{12}$

Over-heating = densification and loss of pozollanicity

$960-980^\circ\text{C}$

Mullite

$3\text{Al}_2\text{O}_3 2\text{SiO}_2$

$1100-1150^\circ\text{C}$

Chamotte

$11/07/17$ The manufacture of metakaolins

![Diagram of thermal transformation of Kaolin/Kaolinite](image-url)
What is Metakaolin?

XRD shows the transformation of kaolinite to amorphous. Amorphous state is the one of interest for Geopolymer.

KAOLINITE BRUTE
K : Kaolinite
Q : Quartz

METAKAOLIN
V : verre
Q : Quartz
The manufacture of metakaolin: processes of calcination

- There are several industrial processes to calcine a kaolin clay, some known since Antiquity.
- Two main processes used within Imerys:
  - **Continuous furnaces:** wherein loads are moved through temperature zones continuously or intermittently
    - Herreshoff multilevel kiln: UK, USA
    - Rotary kiln: France (Clérac), Ukraine (Vatutine), USA (Andersonville)
  - **Flash kilns:**
    - Torbed calciner: UK
    - Flash kiln FCB type: France (Clérac)
Processes of calcination: rotary kiln

Rotary kiln at Imerys Refractory Minerals Clérac (France)

L = 34 m; Ø 2.5 m

Throughput: 10 tonnes per hour

Fuel oil + Biogas + Sawdust

www.cementkilns.co.uk
Processes of calcination: rotary kiln

**Advantages**
- The technology is reliable and robust (similar to a cement plant).
- Efficient energy consumption: 800-1200 kWh/t
- Good throughput rate: 10-12 tonnes/h

**Drawbacks**
- Dehydroxylation control after heating: need to have a good knowledge of the process.
- The feed material is shaped as pellets → temperature gradient in the pellet.
- Product has to be milled after calcination.
- The kiln has to be run continuously so need of a certain volume or combination with other materials.

**Products available:**
- ARGICAL M-1000 (France)
- MK-40 (Ukraine)
Processes of calcination: Herreshoff kiln
## Processes of calcination: Herreshoff kiln

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technology is reliable and robust (similar as rotary kiln).</td>
<td>Dehydroxylation control after heating: means to have a good knowledge of the process</td>
</tr>
<tr>
<td>Efficient energy consumption: 600-1200 kWh/t</td>
<td>Thermal inertia of the kiln</td>
</tr>
<tr>
<td>Good control of temperature of calcination</td>
<td>Huge investment: 1.5-2 times more than a rotary kiln.</td>
</tr>
</tbody>
</table>

### Product available:
- METASTAR 501 (USA)
Processes of calcination: Flash kiln

Very short calcination time (second)

Powder inlet
## Processes of calcination: Flash kiln

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Really flexible: Target temperature quickly reached.</td>
<td>Complex operational system.</td>
</tr>
<tr>
<td>Precise control of temperature, thus of dehydroxylation.</td>
<td>Important cost of investment.</td>
</tr>
<tr>
<td>Limited energy consumption: 400 to 800 kWh/t</td>
<td>Milled material needed for feed.</td>
</tr>
<tr>
<td>Capacity of kiln adapted by initial design (1 tonne/h at Clérac).</td>
<td></td>
</tr>
<tr>
<td>Can produce very fine metakaolin (pre milling).</td>
<td></td>
</tr>
</tbody>
</table>

**Product available:**
- ARGICAL M-1200S (France)
The quality of the metakaolin is directly linked to the quality of the starting material, i.e. the deposit the kaolin clay is coming from.

- Primary deposit: low levels of TiO2 and Fe2O3, high level of K2O, low surface area
- Secondary deposit: more impurities but higher surface area.

The amount of kaolinite in the hydrous kaolin (starting material), reflected by the total chemical analysis, is a main parameter for the reactivity of the final product (metakaolin).

The process and parameters (time and temperature) of calcination are key parameters for reactivity, and the processing of the starting material has also an influence:

- Pelletisation by pressing before the rotary kiln
- Drying / milling / air classification before the flash kiln

Particle size distribution (fineness) plays a role, but to a lesser extent: a poorl-reactive metakaolin cannot be improved only by milling.

A regular quality control of the final product is carried out to ensure: reactivity, quality of the calcination, reliability, reproductibility.
Metakaolins for Geopolymers

Which metakaolin is the best for geopolymers?

- Parameters that are important for the reactivity:
  - Alumina content (Al/Si ratio)
  - Amount of amorphous phase
  - Calcination process
  - Fineness

- Any metakaolin can be used in a geopolymer system. There is no ideal metakaolin for geopolymers; the choice depends on the parameters sought after:
  - Setting time
  - Rheology
  - Mechanical resistance
  - …

- Tell us what you are looking for!
<table>
<thead>
<tr>
<th>Product</th>
<th>Country</th>
<th>Calcination process</th>
<th>Pozzolanic index</th>
<th>Colour</th>
<th>Surface area BET (m²/g)</th>
<th>d50</th>
<th>Cost basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>METASTAR 501</td>
<td>USA</td>
<td>Herreshoff</td>
<td>1400</td>
<td>+++</td>
<td>14</td>
<td>1 µm</td>
<td>5</td>
</tr>
<tr>
<td>ARGICAL M-1200S</td>
<td>France</td>
<td>Flash</td>
<td>1370</td>
<td>++</td>
<td>23</td>
<td>1.5 µm</td>
<td>2</td>
</tr>
<tr>
<td>ARGICAL M-1000</td>
<td>France</td>
<td>Rotary</td>
<td>1150</td>
<td>++</td>
<td>19</td>
<td>10 µm</td>
<td>1</td>
</tr>
<tr>
<td>MK-40</td>
<td>Ukraine</td>
<td>Rotary</td>
<td>1100</td>
<td>+</td>
<td>15</td>
<td>20 µm</td>
<td>1</td>
</tr>
</tbody>
</table>
Thank you for your attention