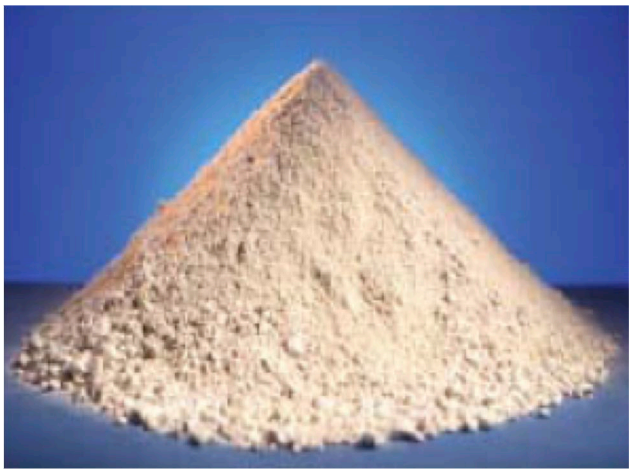
The manufacture of metakaolins



Geopolymer Camp
10 July 2018

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Product Manager Kaolins & Chamottes

IMERYS
TRANSFORM TO PERFORM

IMERYS: Key figures for 2017

IMERYS, WORLD LEADER
IN MINERAL-BASED SPECIALTIES FOR INDUSTRY

Through the added-value transformation of its mineral resources and the development of synthetic minerals, Imerys develops solutions that boost the performance of many products across all markets. In this way, the Group puts its technological, materials science and application-specific expertise to work for its customers in supporting their commitment to innovation.

€4,6Bn Revenue

€648M Current operating income

18,300 employees

14.1% Current operating margin

12.5% of revenue generated by new products

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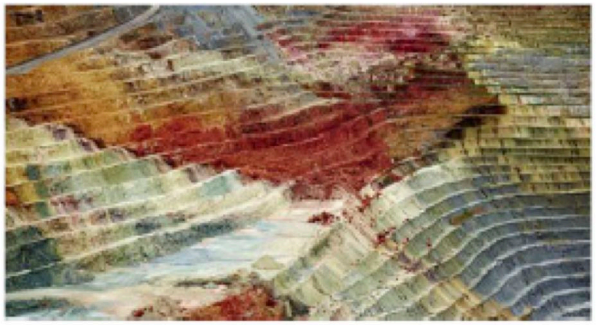
Imerys offers high value-added functional solutions...

- **Beneficiated mineral resources** (clay, bentonite, diatomite, feldspar, kaolin, mica, wollastonite, etc.)
- **Formulations** (ceramic bodies, continuous casting fluxes for steel, monolithic refractories, etc.)
- **Synthetic minerals** (synthetic graphite, zirconia, etc.)

- from high quality assets:
  - Unique portfolio of mineral resources
  - Wide range of exclusive technologies and processes
  - Materials science expertise
  - Know how and customers' applications knowledge



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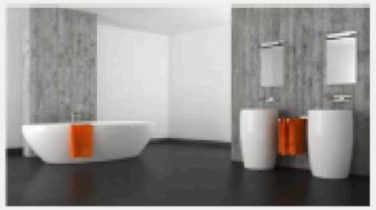
...that bring essential properties to its industrial customers' products

Whiteness and toughness of sanitaryware, floor and wall tiles



World leader in ceramic pastes for sanitaryware

Lifespan and fast charging of electric vehicle lithium-ion batteries

World leader in conducting additives (graphite, carbon black)

Gloss and opacity for paint

World leader in wollastonite and talc for paint

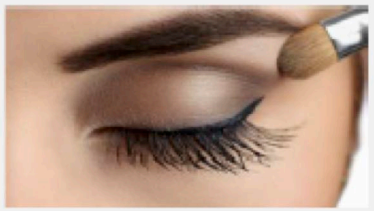
Thermal and mechanical resistance of industrial abrasives

World leader in fused minerals for abrasives

Resistance and lightness of automotive plastic parts

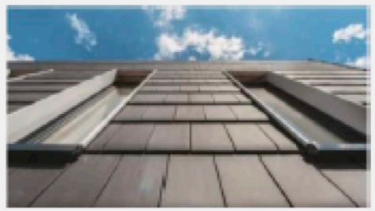
World leader in talc-based performance additives for plastics

Softness of natural mineral powders



World leader in talc for health and beauty

Watertightness and insulation of roofs



French leader in clay roof tiles

Filtration of liquids *(food or blood plasma)*

World leader in perlite and diatomite for filtration

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Imerys has a diversified presence in more than 50 countries

IMERYS Aluminates

The manufacture of metakaolins

Structure of metakaolin

Industrial processes & Product range

Key properties

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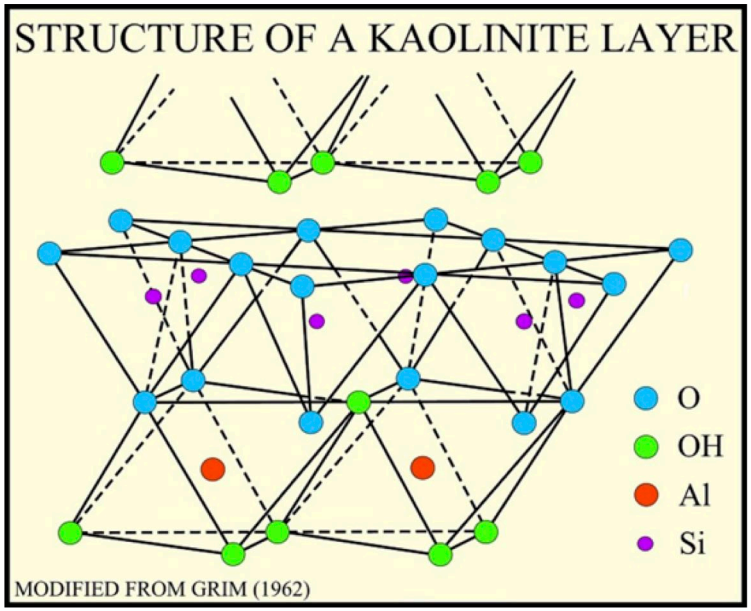
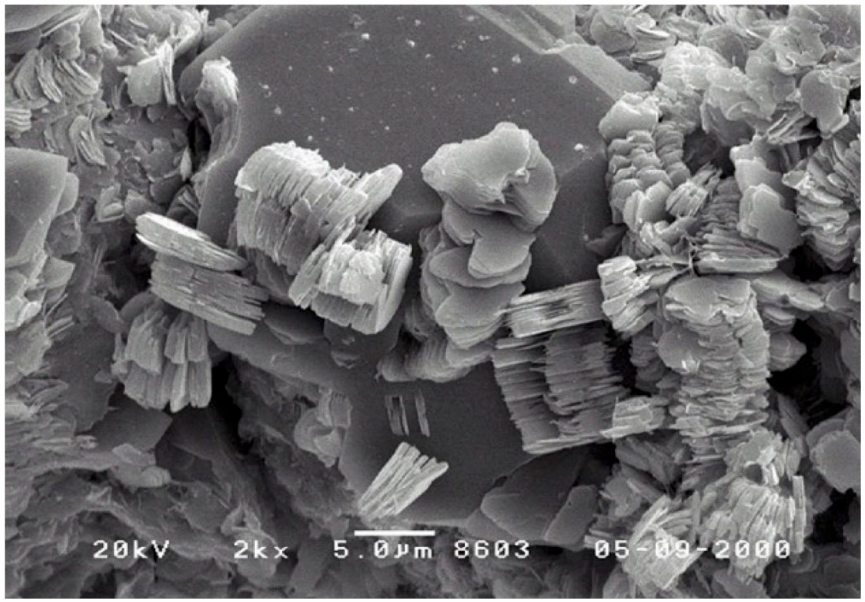
Structure of kaolinite

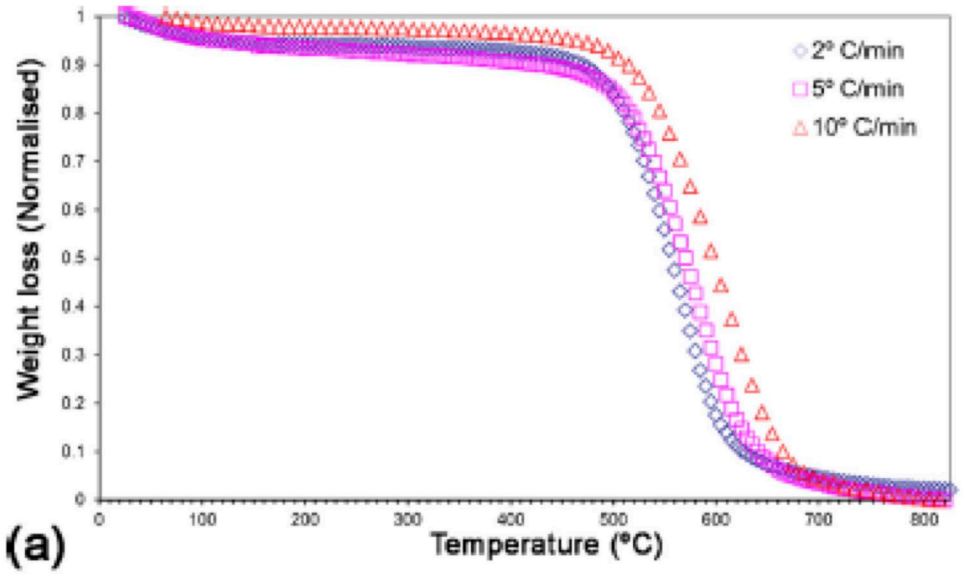
- **Kaolinite** is a hydrous aluminium silicate: $Al_2Si_2O_5(OH)_4$ or Al_2O_3 . 2 (SiO_2) . 2 (H_2O)

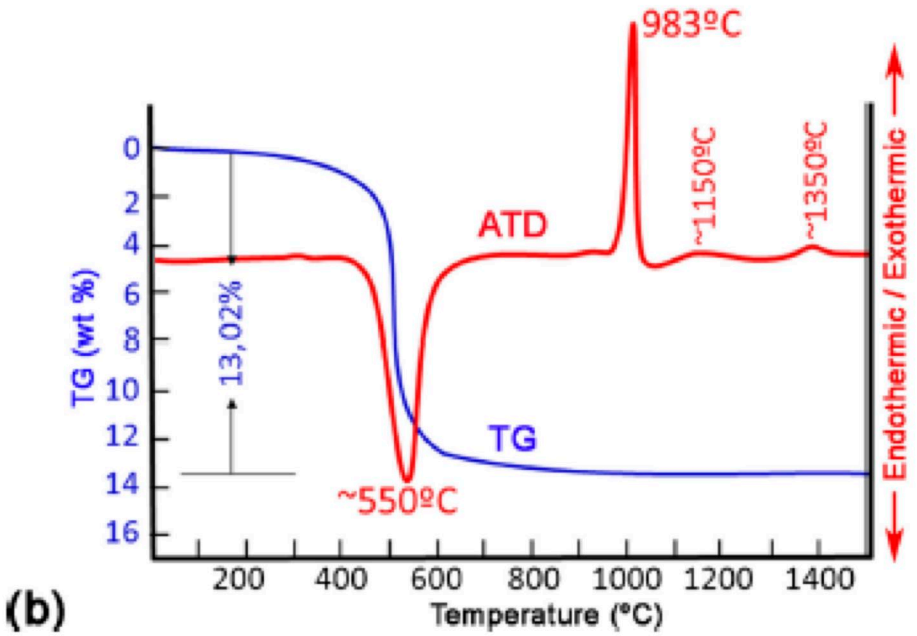




- With heat, water is released from the crystalline structure and the structure is modified.

Transformation of kaolinite





The DTA curve shows a broad endothermic peak at 550°C and a sharp exothermic peak at 983°C.

The main endothermic peak (~550◦C) is associated with the weigh-loss on the TG curve.

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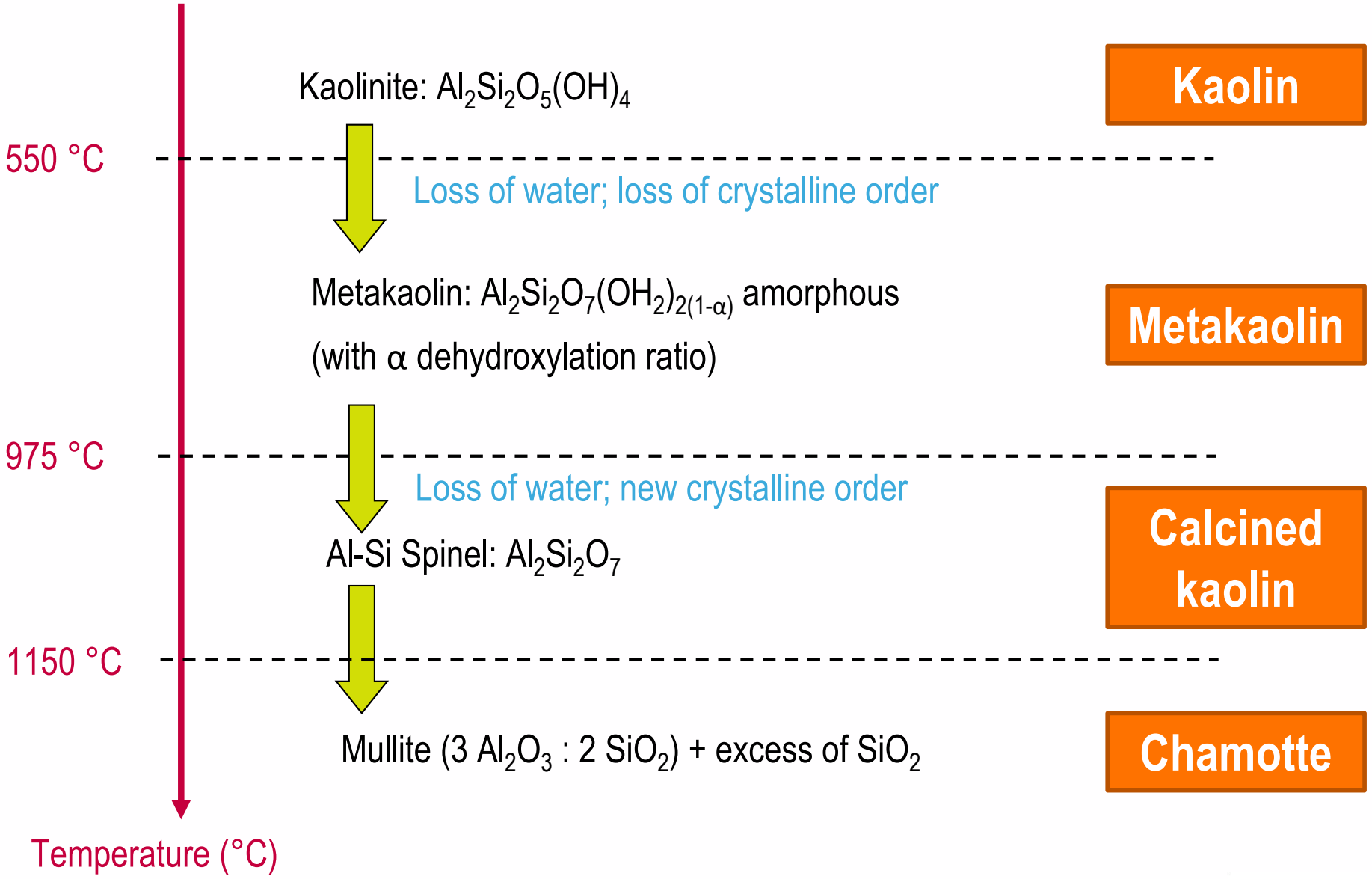
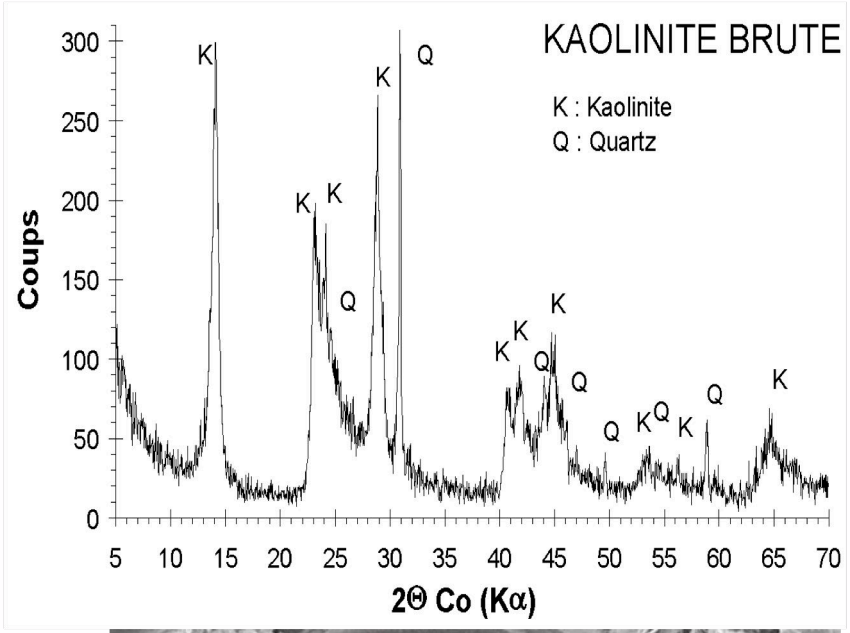
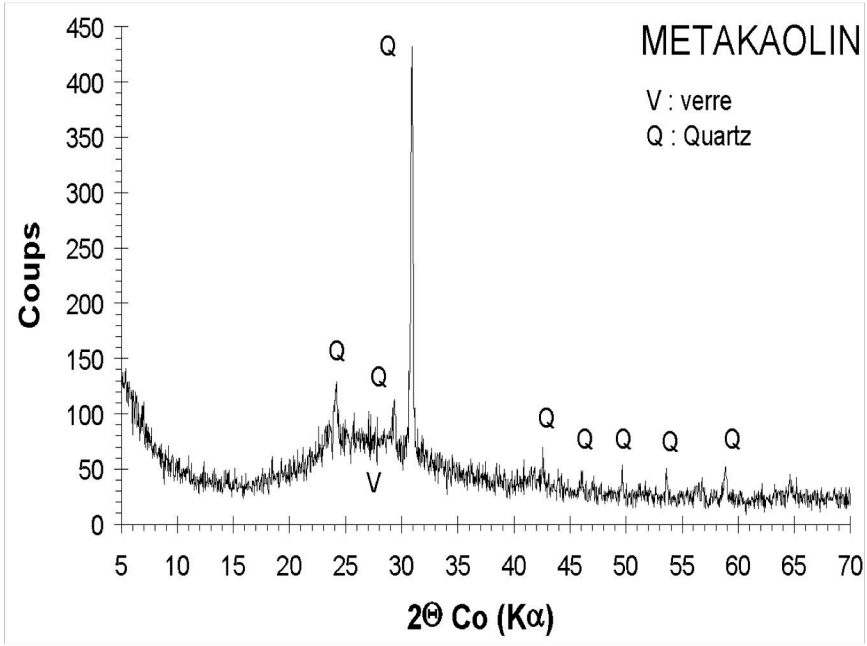
Transformation of kaolinite

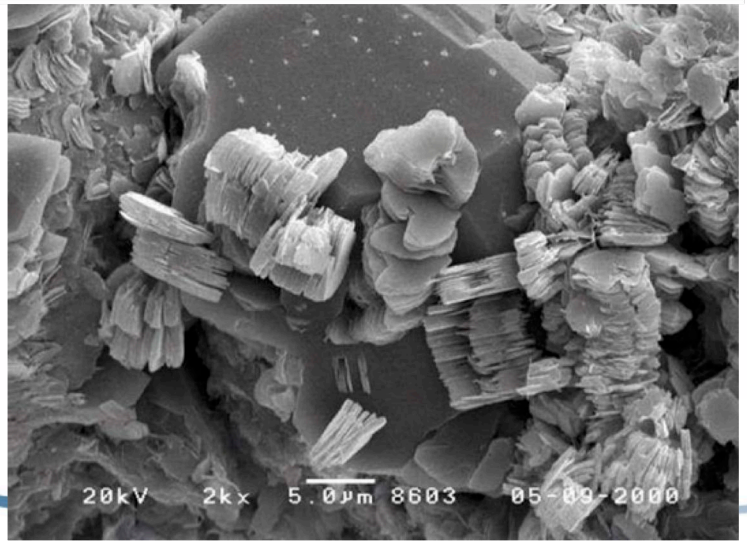


What is metakaolin?

XRD shows the transformation of kaolinite to amorphous.







Transformation of kaolinite

	Structure	^{27}Al NMR	^{29}Si NMR
Kaolinite	• Al^{3+} in octahedra. • Si^{4+} in tetrahedra.	• Al_{VI} signal (–3 ppm)	• Si_{IV} signal (–90 ppm)
Metakaolin	• Destruction of Al^{3+} octahedra. • Si^{4+} in a polymer of tetrahedra.	• Al_{VI} transforms into Al_{IV} (70ppm) & Al_V (35 ppm).	• "metakaolin signal" (–100 ppm)
Al-Si Spinel		• Al_{IV} (70ppm) • The Al_V signal disappears and an Al_{VI} signal (–2ppm) appears [mullitisation].	• The "metakaolin signal" shifts to –110 ppm. • The Si_{IV} signal (–90ppm) of mullite starts to appear.
Mullite	• Al3+ in octahedra and tetrahedra. • Si4+ in tetrahedra.	• one Al_{VI} signal (5 ppm) • two Al_{IV} signals (60 & 45 ppm)	• Si_{IV} signal (–90 ppm)

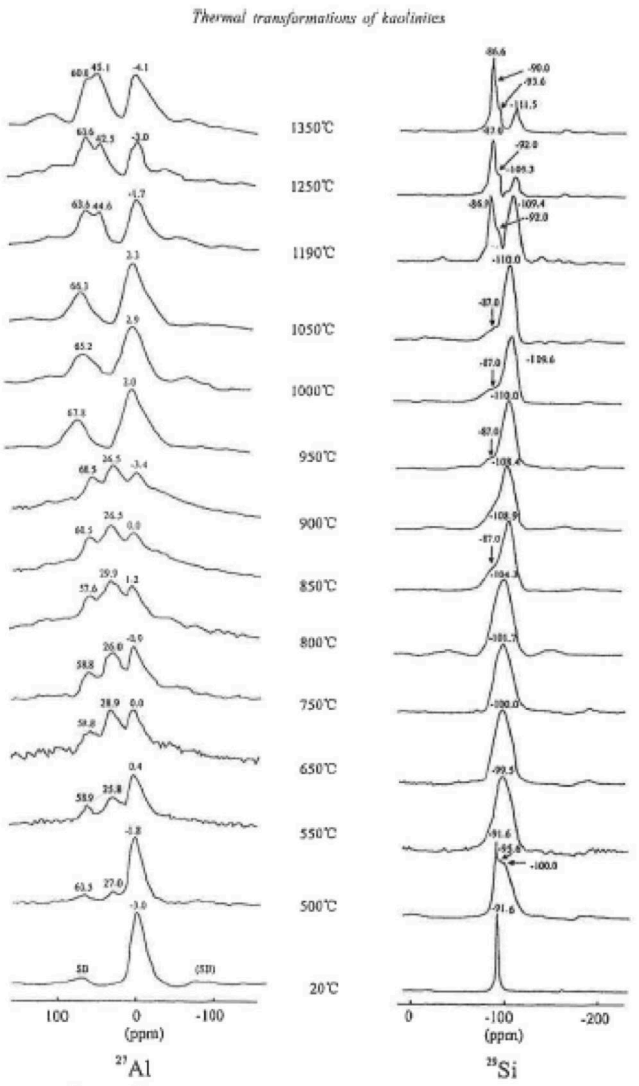


FIG. 3. ^{27}Al and ^{29}Si MAS NMR spectra of the kaolinite heated at different temperatures.

The manufacture of metakaolins

Structure of metakaolin

Industrial processes & Product range

Key properties

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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 of 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

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)

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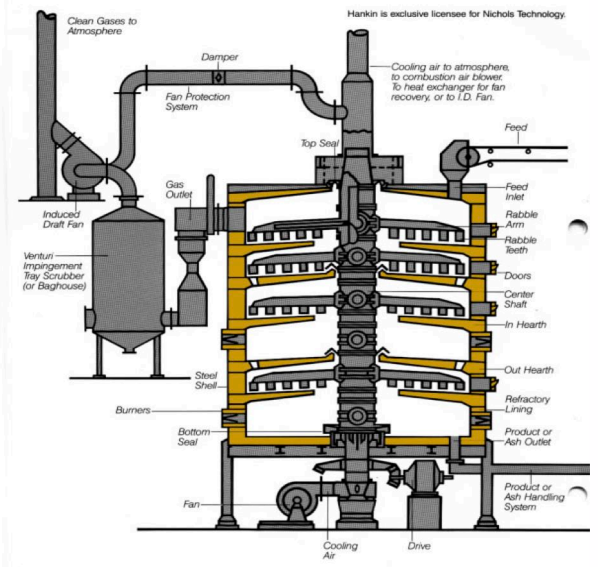
Processes of calcination: Herreshoff kiln

Advantages

- Technology is reliable and robust (similar as rotary kiln).
- Efficient energy consumption: 600-1200 kWh/t
- Good control of temperature of calcination

Drawbacks

- Dehydroxylation control after heating: means to have a good knowledge of the process
- Thermal inertia of the kiln
- Huge investment: 1.5-2 times more than a rotary kiln.



Product available:

❖ METASTAR 501 (USA)

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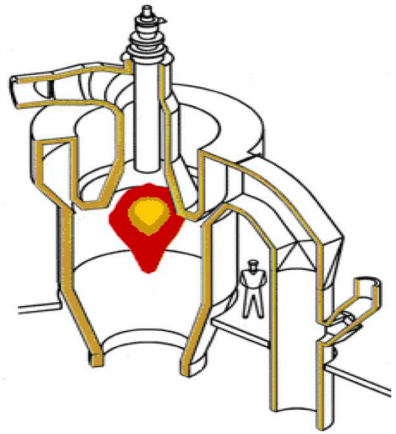
Processes of calcination: Flash kiln

Advantages

- Really flexible: Target temperature quickly reached.
- Precise control of temperture, thus of dehydroxylation.
- Limited energy consumption: 400 to 800 kWh/t
- Capacity of kiln adapted by initial design (1 tonne/h at Clérac).
- Can produce very fine metakaolin (pre milling).

Drawbacks

- Complex operational system.
- Important cost of investment.
- Milled material needed for feed.



Product available:

❖ ARGICAL M-1200S (France)

Product Range

Product	Country	Calcination process	Pozzolanic index	Colour	Surface area BET (m^2/g)	d50	Cost basis
METASTAR 501	USA	Herreshoff	1400	+++	14	1 µm	5
ARGICAL M-1200S	France	Flash	1370	++	23	1.5 µm	2
ARGICAL M-1000	France	Rotary	1150	++	19	10 µm	1
MK-40	Ukraine	Rotary	1100	+	15	20 µm	1

The manufacture of metakaolins

Structure of metakaolin

Industrial processes & Product range

Key properties

The manufacture of metakaolin: important parameters

- 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 TiO_2 and Fe_2O_3, high level of K_2O, 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 poorly-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.

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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!**

IMERYS Refractory Minerals

Thank you for your attention!

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