## INTRODUCTION TO BENTONITE & PERLITE MINERALS: KEY ATTRIBUTES & FUNCTIONALITIES



# **Group Presentation**





merys oners nigh value-added functional solutions...

#### Imerys draws on its know-how

Portfolio of high-quality mineral resources

Knowledge of its customers' applications

- Wide range of exclusive technologies and processes
- Materials science expertise

#### ... to develop an offering based on:

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









Filtration of edible liquids



Gloss and opacity for paint



**Lifespan** of lithium-ion batteries to improve electric vehicle autonomy



Conductivity of ceramic hobs



Strength and lightness of vehicle bumpers



Protection of crops



Watertightness and insulation of roofs



Whiteness and toughness of sanitaryware



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The world leader in mineral-based specialties for consumer goods, industrial equipment and construction, with presence in 50 countries

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The Energy Solutions & Specialties business group manufactures and sells high-performance mineral solutions for various demanding industries: the consumer goods and paper sectors with Carbonates, high-temperature industries served by Monolithic Refractories, Graphite & Carbon applications linked to mobile energy, and oil and gas exploration served by the Oilfield Solutions division.

#### Carbonates

Natural (GCC) and Precipitated (PCC) Calcium Carbonates used as filling or coating pigment for paper production and functional additives for paints, rubber, plastics.

#### **Monolithic Refractories (Calderys)**

Unshaped refractory materials used to protect industrial equipment from high temperatures in heavy industries (steel, cement, power generation, petro-chemicals). Protection for furnaces, kilns, crucibles and incinerators.

#### **Graphite & Carbon**

High performance graphite powder for mobile energy, electronics and engineering, refractories for the transport and automotive markets.

#### **Oilfield Solutions**

Production of proppants and mineral solutions for non-conventional oil and gas exploration.



The **Filtration & Performance Additives** business group enjoys many high quality minerals and products (bentonite, diatomite, perlite, vermiculite, talc, wollastonite and steel casting fluxes) supplied to many industries including agriculture, food, beverages, steel, construction, horticulture, plastics, paints, rubber, catalysts, paper, pharmaceuticals, beauty and personal care.

#### Performance Additives

The division addresses fast growing markets in which additional performance is key. The solutions offered consist
of functional additives derived mostly from mica, talc, wollastonite, diatomite, perlite or vermiculite used for paints,
plastics, polymers, rubbers, adhesives, sealants, pharma & personal care.

#### Minerals for Filtration

• Mainly diatomite and perlite used as filter aid for edible liquids (beer, wine, oil, fruit juice). The division is the world's leading supplier of diatomite and expanded perlite-based products for filtration.

#### Performance Additives for Metallurgy

- Serves the metallurgy market along the whole metal production chain, from raw materials through to the casting of the final products.
- Includes Steel Casting Fluxes, Bentonite & Perlite Intermediates, and Metalcasting Performance Additives.

## Bentonite: a Smectitic Clay with hundreds of applications



# **Bentonite mineralogy and attributes**



### **Bentonite's Structure**

# Bentonite is a volcanic **rock** composed dominantly of clay minerals belonging to Smectite group.

- Consists of 3-layer platelets: an octahedral layer comprising of Mg, Fe, Al and OH-groups, sandwiched between two tetrahedral layers with Si-O tetrahedrons.
- One smectite mineral is the di-octahedral Montmorillonite (part of Al<sup>+3</sup> is replaced by Mg<sup>+2</sup> and Fe<sup>+2</sup> while Si<sup>+4</sup> is replaced by Al<sup>+3</sup>)
- Due to isomorphic substitution, all layers are electrically charged and this is counterbalanced by hydrated "exchangeable" cations occupying the space between platelets
- All key-properties are attributed to this "chargedlayer/cations" couple. i.e. H<sub>2</sub>O Absorption, Swelling,
- Thixotropy, Thickening







## Bentonite's (Montmorillonite's) behavior in aquatic environment

- Montmorillonite's performance is due to its ability to:
  - 1. disperse in colloidal particles («easy cleavage» vs. other clays like e.g. kaolinite)
  - 2. absorb and immobilize big amounts of H<sub>2</sub>O and ions
  - 3. form thixotropic slurries and thick pastes
- Montmorillonite's performance in H<sub>2</sub>O systems is maximized
- by Exchanging Ca<sup>+2</sup> by 2Na<sup>+1</sup> (e.g. Na<sub>2</sub>CO<sub>3</sub> treatment, called Activation),
- Electrolytes and Polymers addition
- Montmorillonite's performance in non-H<sub>2</sub>O systems (e.g. crude oil, resins, organic solvents, edible oils and fats) requires treatment with other molecules and compounds (e.g. quaternary amines, partial acid leaching with mineral acids, etc.)



Fig. 2: Smectite and kaolinite under the electronic microscope





# General Functionalities of Montmorillonite in H<sub>2</sub>O environment

Application wise ("mineral" with 1,000 uses") Montmorillonite can be seen as:

1. Binder

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Thixotropic agent (gelling, sealing, thickening) 2.

1nm

water

- 3. Absorbent
- Functional additive 4.



# How key-attributes relate to Applications



### Bentonite in Foundry application

• Bentonite is used as a binder for the making of moulds.

• Mechanism: Wetted bentonite powder is mixed with Quartz sand grains. Hydrated Smectite platelets are delaminated and cover the sand particles. Bonding takes place through adhesion and cohesion based on the surface properties of the wet clay platelets attached to the quartz surface.

• It is economic and environmentally friendly since the majority of the sand and binder is reused in a cyclic system

- Key specs for bentonite are:
- rich in Montmorillonite content
- High thermal durability at 550 C















## Bentonite in Paper manufacturing

Bentonite yields a huge number of **electrically charged platelets** in water environment, thus, improving the **sieve retention** on the paper machine and the **binding of impurities** as resin conglomerates. Also it performs well in **process** Water treatment and purification:

1. Retention: Bentonite and Polymers connect paper fibers and fillers forming a

better fiber web and resulting in less loss through the sieve. Yield (Retention) and Devatering are increased upgehine's the sieve or wastepaper (stickers,

binders, glue...) and form agglomerates which disturb the process and the quality of the paper. Bentonite **binds** such substances to the fibers before **4**99<sup>lor</sup>**Wate binds control and water recycling:** In water treatment

**microflotation** is applied to separate particles and fibres from water by using air. Bentonite and Polymer flocculate these particles and make flotation more effective. Bentonite also adsorbs very fine particles improving the water clarity













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## Bentonite in Paints, Plasters and similar pastes

- Viscosity and plasticity of bentonite improve thixotropic and pseudo plastic flow behavior. Bentonite works in :
- 1. Water-borne paints & coatings
- 2. Plasters, sealants
- 3. Ceramic masses
  - Bentonite's performance is enhanced through soda overactivation and additional treatment with PEO, MgO, polymers and inorganic salts:
    - High gel strength / High yield point
    - Thixotropic & pseudoplastic flow behavior
    - Anti-settling properties
    - Inhibits running or sag
    - Synergy effect with organic thickeners
    - can produce a surfactant free emulsion (interfacial barrier that allows for the formation of isolated water droplets)
    - Improved mechanical stability of coatings
  - Key properties: 1)strong rheological behavior, 2)high whiteness, 3)ultra-fine particle size 4)stability against electrolytes
  - Organoclays and (synthetic) hectorite dominate the clay additives subsegment in P&C market







Rheology of Bentonite Dispersions



Model for Dispersions of Bentonite: a: sol - exfoliated particles

- b: 3-dimensional band-type gel
- c: 3-dimensional cardhouse-type gel
- d: aggregates (flocs)



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## **Bentonite as Animal Feed additive**

Smectitic Clay is used:

1. As binder for Animal Feed pellets (group: binders, anticaking agents, substances for control of radionuclide contamination, EC Reg.No: 1m558i)

1. Additionally, as an **additive for the absorption of harmful aflatoxin** (group: substances for reduction of the contamination of feed by aflatoxin B1, Reg.No

1m5

Bentonite's performance **as binder** and active

- inglediantellar structure and surface chemistry contribute to binding, anti-eaking and flowing agent properties during pellet processing and conservation
  - 2. By its swelling action slows down the intestinal tract and increases the absorption of nutrients (proteins, lipids)
  - 3. Better environment by livestock manure management
    - Animal waste management by water absorption
    - Management of odor emissions by absorption of ammonia

4. Buffering capacity of clay leads to reduction of acidosis hazard for ruminants.

- Bentonite 's performance as **Mycotoxins** absorber: Bentonite containing >70% **dioctahedral smeetite** is added to the feed to:
- 1. decrease mycotoxins bioavailability, reduce mycotoxins uptake,
- 2. reduce distribution to the blood and target organs,
- 3. prevent future contamination

flatoxins are Produced by fungi. Various **absorption mechanisms** have been proposed. The most probable ones:

A. Ion-dipole interactions and coordination between exchange cations and carbonyl groups

**B. Water bridging effect** - H bonding between carbonyl groups and H<sub>2</sub>O in hydration shells of exchange cations



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### **Bentonite as Pet Litter absorbent**

Granular bentonite is used for the formation of cohesive Clumps (when in contact with pet's urine)

• Cat's urine creates tight clumps which are then scooped and removed

Recently bentonite along with expanded perlite were used for the development of a new lightweight PL

• Expanded perlite granules are used as core material, which is coated - through balling process- with a layer of a bentonite powder

PARTICULATE

FINES

REJECT

ADDITIVES

FINISHED

• Lightweight PL (patented by Nestle) offers the strength of traditional clumping litters at almost



¥ 34

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PACKAGING

SPURINA.

CATS

LightWeight

TIDY

#### New Applications under consideration (NPD projects)

• Bleaching clays: used for edible oils purification. Bentonites are acid treated at Acid Activates T=80-120C. Smectite is attacked (selective leaching) in order t surface area. Classification: HPBE (Acid Activated Bentonite), SMBE (Acid treated Attapulgite), NBE (Attapulgite or other)

• OrganoClays: Na<sup>+</sup> or Ca<sup>2+</sup> ions are replaced by long chained organic cations, particularly quaternary ammonium salts ("Quats"). Organoclays are used in Oil drilling Muds, Solvent based paints, waxes, etc.

 Geosynthetic Clay Liners (GCLs): develop resistant bentonites to high alkalinity bigh conductivity effluents.

• Nuclear Waste sealing: Highly compacted bentonite products (rings, pellets or bricks) ensuring their sealing properties for 100s of years for radioactive wastes permanent disposal Aflatoxine absorbent (in animal feed): Na-Mont adsorbs aflatoxing and thus reduces or eliminates toxicity of the mycotoxins to animals and humans Seed Growth: seeds are coated with a bentonite slurry which provides the water to promote rapid sprouting of the seed when planted (gardens and greenhouses).

 NanoClavs: bentonite is purified and platelets are dispersed in the size of nanometers. By organophilization Nanoclays are produced suitable as resin fillers, e.g. for reinforcing PP and Nylon 6 composites.

 Cosmetics: Na-activated, organoclays, and white bentonite are used in formulations. Small quantities provide thixotropic and suspension aids

Future(?): 1)Catalysts: Ca-Monts' and Acid Activated provide catalytic activity and are used in Petrochemical industry. Acid-treated Monts are used for dimerization reactions of unsaturated fatty acids. etc. 2)Pillared Clays: Monts pillared with inorganic cations (e.g. Al hydrated Complexes) are used as catalysts, selective sorbents, membranes. 3) Pesticides Carrier: pesticides are absorbed on the granular particle which is incorporated in fertilizers or spread directly on the ground. Calcination is sometimes required.









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# **Perlite: an expandable Volcanic glass**



## Key Perlite and Volcanic glasses attributes

Perlite is :

- A Volcanic glass containing 70-76% amorphous silica. It is a solid solution of Alkalis (K, Na) in SiO2 matrix
- **Expands 5-30 times** its original volume, when rapidly heated to its softening temperature range (>870 °C), due to the presence of 2-5% "combined" H2O and Alkalis (6-10%)
- "Combined" H2O is exists mainly the form of Silanol groups [SiOH] Also present: OH-,  $H_2O$  absorbed by few exchangeable ions,  $H_2O$  bound through Hydrogen bonding

**Unexpanded perlite (milled, graded)** is used in industry due to its: 1)amorphous SiO2 (70-76%), which is **chemically very reactive** against certain chemical solutions, 2)abrasiveness

**Expanded perlite** has exceptional physical properties, making it appropriate for numerous applications in **Construction and Building**: 1)**Light weight** (apparent density: 30-150 kg/m<sup>3</sup>), 2)**Low thermal conductivity** (0.035-0.06 W/m×K at 24°C), 3)**Multi-Cellular** structure

#### Functionality of Perlite in BCMs Applications:

- 1. Reduction of the end-product weight ("Lightweight")
- 2. Enhancement of acoustical and thermal insulation properties (high porosity)
- 3. Improved flow characteristics and workability of bulk products (mortars, plasters)
- 4. Chemically inertness
- 5. Economically attractive





Fig. 1 Schematic structures of silicate tetrahedral units  $Q_n$ , with *n* denoting the number of oxygen atoms bridging two silicon centers ( $\emptyset$  = bridging oxygen atom)

## **Established applications of perlite**



## **Expanded Perlite in Ceiling Tiles and Acoustical Boards**

Acoustical ceiling tiles are manufactured from mineral wool, cellulose fibers, starch, clay, fiberglass and expanded perlite. The raw graded perlite is expanded and the added proportion in the formulation can vary tremendously (from 10 to 75 w/w%) depending on the required properties of the finished product.

Expanded Perlite is added to increase the porosity of the tile, to enhance their acoustical properties as well as to provide bulk volume in order to reduce tile weight





#### Expanded Perlite in Lightweight concrete (LWC), plasters (LWP) and mortars (LWM)

Perlite improves physical properties when added to construction mixes. Primarily reduces the density of the product and enhances thermal insulation characteristics

Perlite is a vital ingredient in lightweight gypsum plasters or mortars LWP, LWM), which are specially formulated to be mechanically sprayed on the wall. Functionality:

- enhanced fluidity of the paste during pumping
- higher workability when pressing and compacting
- substantial increase of insulation properties
- smooth release of water during hardening (no cracking)

Lightweight) concretes (LWC) are used in roofing decks to reduce the weight that has to be supported by load-bearing structures. At the same time, thermal insulation ability is improved and transmission of noise reduced. Perlite also improves flow characteristics of cement or concrete and so is used in self-leveling floor screeds. LWCs are also used to insulate spaces around heating, steam, coolant pipes or bases for ovens, furnaces and cold storage tanks.



Type of end-product	Function				
	Masonry Mortar : Bind materials together.				
	Plaster : For leveling or smooth finish to the wall.				
	Render: Protect against weathering (Monocouche for France)				
	Insulating Render: Improve thermal insulation of walls.				
	Screed: For leveling or smooth finish to the floor				
	Tile Adhesive: Binding materials together				
Other -8/3/2016 Bentonite and Perlite A	Dry Concrete: Pre-packed & Ready-mix concrete for DIY Colored Render: Decorative coatings mainly to historical buildings (renovation)				

## **Expanded Perlite for Loose fill insulation in masonry construction**

Expanded perlite is used as loose fill insulation material:

- in cavity walls
- for filling the hollow cores of masonry blocks
- in fire doors
- to improve thermal insulation and fire resistance









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# **Horticulture applications (1)**

Expanded perlite increases the production yield and improves the quality of agricultural products as it:

- 1. provides good aeration and optimum moisture retention for plant growth (due to high porosity)
- 1. regulates drainage rate
- 1. has a reasonably stable pH (almost neutral)
- 2. is sterile (due to the high temperatures prevailing during expansion)
- 3. is weed-free
- 4. can be recycled





This garden had approximately 2 inches of fine grade perlite tilled into the soil early in the growing season. The results after an extremely dry summer with almost no watering!



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# Horticulture applications (2): Hydroponics and Growing media

#### Hydroponic cultivation: growing of plants in a non-soil, supporting media

- Allows delivery of controlled amounts of water and specific nutrients to the plants.
- Either in greenhouses, or in the open air with plants in grow bags filled with perlite.



Green house container growing

Perlite advantages:

- Strong capillary action while retaining good drainage: plants draw up water and nutrients at the needed rate
- it can be recycled
- it retains more air than the other materials, optimising root development



Typical "soil-less mix" with perlite (20-40% by volume):

- pH 5.9-6.7
- moisture content 11-45%
- apparent density 95-130 kg/m<sup>3</sup> (0,09-0,13 g/ml)
- sieve size < 9,5 mm

• "soil-less mix" provides a growing medium for plant propagation, eliminating the risk of contamination by disease, insects and herbicide residues

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### Expanded Perlite in Cryogenics, Low Temperature Insulation and Special Industrial Insulation

A. Expanded Perlite insulates Low temperature and Cryogenic vessels used for the transportation or storage of very cold liquids. Storage tanks are double walled : the space between the inner and outer wall is evacuated (only for special cryogenic service) and simultaneously filled with fine expanded perlite. Perlite is ideal because of its free flowing nature.

- "low temperature applications" : liquids at temperatures 4°C down to -100°C
- "cryogenic applications" : liquids at temperatures lower than -100°C

# B. Preformed expanded perlite-silicate Products for Special Industrial Insulation

Expanded perlite granules are bonded with the use of a suitable binder (Liquid sodium silicate or potassium silicate) to form rigid shapes for a wide range of insulating applications. The produced shapes ("Sproules") are usually provided in the form of half shells for pipe insulation or in blocks:

1. are water resistant (<10%

WA), do not corrode ("corrosion inhibitors") the item to be enclosed

2. are thermally efficient (0,058 W/m.K at 120 DC)

3. fire resistant and stable (up to 650°C) throughout their temperature range of performance.







# **Chemical industry:** H3PO4 production for Fertilizers

Medium-fine raw graded perlite (<0,8 mm) is used as modifier in the production of phosphoric acid with the "Wet" process (Wet process Phosphoric Acid-WPA):

$$Ca_{10}(PO^{4})_{6}F_{2} + 10H_{2}SO_{4}$$
 10CaSO<sub>4</sub> + 0H<sub>3</sub>PO<sub>4</sub> + 2HF

Main advantages of perlite addition:

1. Reduction in overall plant corrosion caused by HF (6HF + SiO<sub>2</sub> (perlite)  $H_2SiF_6 + 2H_2O$ )  $H_2SiF_6$  then precipitates as  $Na_2SiF_6$ ,  $KSiF_6$  or  $NaKSiF_6$ .

- Target: to correct the active SiO<sub>2</sub>/F ratio to at least 0.53

- adjust the  $_{\mbox{Al2O3/P2O5}}$  rate, to approx 0.020

## 1. Reduction of the HF emission to the atmosphere

- 1. Increased efficiency in the filtration and washing stages of the <sub>H3PO4</sub> production (avoid Gypsum needles)
  - The gypsum crystal needle then changes from to a cluster-like shape whose specific surface area is significantly smaller
- 1. Less <sub>P2O5</sub> residues left in the filtering cake



### **Volcanic glasses in Cement and Concrete**

#### 1. Puzzolane Cement

Natural pozzolans are used in the production of CEM II and CEM IV pozzolanic cements. Addition has a positive effect on: 1)heat of hydration, 2)alkali silica reaction, 3)permeability

- Perlite-based Pozzolans and super-Pozzolans are volcanic glasses
- high amorphous state, used in the production of pozzolanic cements

#### 1. HPC Concrete

High-performance concrete (HPC) complies with properties that lead to long service life in severe environments: 1)strength, 2)water and chloride permeability, 3)resistance to alkali silica reaction

HPC is specified in the most of infrastructure projects such as bridges, airports, highways and in demanding projects like skyscrapers and high rising buildings.

• Micrasil is a new, effective, mineral based material of high consistency, being thus an attractive substitute of Supplementary Cementitious Material (SCM) like silica fume, natural pozzolans, fly ash or slag



## **Phyllomat: Reinforcing filler or Functional additive**





- Phyllomat is jet-milled expanded perlite, lamellar-shaped and free of quartz (silane coated or uncoated)
- suitable to work as a functional filler in polymers and plastics and other formulations
- Morphology: platelets with aspect ratio of 10:1 20



## **Projects in Pipeline: Micrasil**



Micrasil is a highly performing SCM. It reacts with the free lime, by-produced during the hydration of cement, providing:

- 1. Higher strength (due to additional hydraulic bonds)
- 2. Lower Porosity (due to the formation of calcium silicates in the interstitial spaces)
- 3. Enhanced Durability (lower chloride penetration, lower alkali-silica reactivity)
- 4. Improved Workability

In very demanding climate conditions (extreme heat & cold) and in aggressive soil (Cl<sup>-1</sup>, SO<sub>4</sub><sup>-2</sup>), SCMs are inevitable component for construction in order to achieve concrete durability for more than 50 years.

- Typical SCMs used are silica fume, fly ash and GGBS and all of them are by products/ wastes of the silicon, coal energy or pig iron industry
- On the contrary, Micrasil is an industrial product with guaranteed physical and chemical profile and functionality





Compression strength data (MPa) ■ 7% SF ■ 10% Micrasil



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## Projects in Pipeline: Geopolymers (based on perlite and/or clays)

The Challenges for the construction industry are set under the "20-20-20 objective"

- Embodied energy may account for 20% of the building's energy use
- Building components with improved thermal properties

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IMERYS' Solution: Development of a new generation of inorganic, incombustible, insulation materials and building masonry components ("3I") based on minerals with lower embodied energy (>50%), lower cost (15%) and upgraded properties compared to the commercial CBMs



#### merys represents o% or global and 20% or EU peritonite production



sources: Annual Reports, 10-K reports, Roskill 2015, Imerys market intelligence

Leading position in almost all major bentonite applications, particularly foundry and iron ore selletizing (IOP)



sources: Annual Reports, 10-K reports, Roskill 2015, databases with import/export data, Imerys market intelligence





sources: Annual Reports, 10-K reports, Roskill 2015, Imerys market intelligence

	Gerr	nany	Fra	nce	Italy		
	kT	MS%	kT	MS%	kT	MS%	
Imerys	301	33%	59	27%	67	31%	
Mineral Technologies	0	0%	0	0%	0	0%	
Clariant	361	39%	113	52%	24	11%	
Huettenes Albertus	26	3%	8	4%			
Ashapura	25	3%			12	1%	
Laviosa			5	2%	69	32%	
Others	211	23%	32	15%	55,5	26%	
Total market	924	100%	217	100%	215	100%	

#### USA Demonite consumed at a giance



	Foundry		Construction		IOP		Drilling		Others		Total
	kT	MS%	kT	MS%	kT	MS%	kT	MS%	kT	MS%	kT
lmerys*	162	22%									162
Mineral Technologies	574	78%	220	80%			150	17%	497,5	44%	1.442
Clariant											0
BPM					200	48%	250	28%	397,5	35%	848
MI-SWACO					150	36%	350	39%			500
Others			56	20%	70	17%	150	17%	233	21%	509
Total market	736	100%	276	100%	420	100%	900	100%	1.128	100%	3.460

sources: Annual Reports, 10-K reports, Roskill 2015, Imerys market intelligence

BPI 5 Year Plan

#### merys represents ∠5% or global and 45% or ⊏EA penile production



\*:British Geological Survey (BGS) estimate: Iran is producing around 1.1 mio MT pa (not included) \*\*: PERGEM is JV (50/50) of Imerys with IPM (Turkey)

sources: Annual Reports, 10-K reports, Roskill 2011, Imerys market intelligence

#### LEA Fenile consumed at a giance





*EEA: EU- including TR + CIS* sources: Annual Reports, 10-K reports, Roskill 2011, Imerys market intelligence



sources: Annual Reports, 10-K reports, Roskill 2011, Imerys market intelligence

# Thank you for your attention



