

Raw materials for tomorrow's ceramics: emphasis on rare earths and magnesite

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Raw materials for tomorrow's ceramics: emphasis on RE & magnesite

1. Definition: What are ceramics?
2. Applications
3. Raw materials
4. The case of rare earths [RE]
5. The case of magnesite
6. Futurology

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1. What are ceramics?...

- Historical: Greek *keramikos*, from *keramos*: potter's clay, pottery
- objects produced by shaping & heating clay, especially when considered as art
- of or relating to the manufacture of any product (as earthenware, porcelain, or brick) made essentially from a nonmetallic mineral (as clay) by firing at a high temp
- Modern: those things made from materials which when heated are permanently changed - on the molecular level, which also changes the physical characteristics of the object. Limited melting or fusion takes place → a glass or vitrified phase → a permanent bond within the articles → gives them their permanence and utility.

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...1. Main classes of ceramics...

- Building/architecture: tiles, sanitaryware etc
- Tableware
- Refractories
- Foundry
- Engineering ceramics
- Other

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...1. The commercial setup -- International ceramic tile industry

- Italy, China, Brazil,...
- 2009 fall, 2011 pick-up
- 'US demand for decorative tile to increase by 4.4% pa by 2013'
- Shift to Asia → China's sanitaryware industry: 174 mi pieces, → 220 mi in 2015
- Italian machinery: 75% of turnover = exports
- Antidumping: Sept 15, '11: Definitive EU duties 26.3 - 69.7% on 97 Chinese companies
- EU 'Made In' label to clearly state country of origin on non-EU imported goods excl. Turkey, Norway, Iceland, Lichtenstein. Welcomed by Cerame-Unie
- Spain's ceramics sector is the number one consumer of natural gas

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2. Applications: Building and Tableware Ceramics...

Examples:

- **Frits:** Materials used as bases of manufacturing for the rest of ceramic tile products
- **Glazes:** Homogeneous mixtures of compounds in liquid or solid state chosen in the basis of such chemical and physical properties as rheology, refractivity and thermal expansion in order to adapt them to each client's particular application and firing specifications.
- **Printing Powders:** Their use may range from the application of protective layers to ceramic tile pieces to the preparation of different types of printing inks. \
- **Ceramic Stains:** Stains for glazes are obtained by burning and sintering processes. Controlled grain size and colour fastness are important factors. Stains for ceramic body colouring can be used to colour ceramic bodies externally.

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...2. Applications: Refractory Ceramics...

- All major European material industries [iron & steel, cement, glass, chemicals & petrochemicals] are energy intensive & use refractory ceramics as a protective lining in their high temp reactors to limit corrosion & reduce heat loss
- **European refractory industry** produces 5,5 mi tpy refractory ceramics @3,6 bi €. Main products, mi tpy
 - Magnesia refractories 2,4 mi
 - Fireclay refractories 1,2
 - High alumina refractories 0,8

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...2. Applications: Refractory and Foundry Ceramics...

- Cookson's Ceramics division: refractories & foundry businesses. Vesuvius & Foseco
- Steel: tundish tube changer and ladle shroud products, linings
- foundry castings
- fused silica → crucibles for photovoltaic panels & tempering rollers for the glass industry

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...2. Applications: Engineering ceramics

- ceramic capacitors
- crucibles
- nozzles
- semiconductors
- lasers
- dental
- oxygen sensors
- capacitors for electronic applications,...

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3. Raw materials...

- Identification
- Procurement issues
- Search for substitutes
- New functions

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...3. Raw materials for ceramics for tiles, sanitaryware, tableware...

Contain oxides of Al, Si, Mg, Ca, Fe, alkali metals (Na, K), + traces of other elements

–Clays

–Feldspar [Na, K] for glaze, polishing, tile. Shortage. USGS: In 2010, Italy no1 feldspar 4.7 mit, Turkey no2 4.5 mit, China no3 2 mit

–Kaolin, Quartzite, Silica

–Rare Earths

–Magnesite and magnesia: Ceramics tiles engobe, frits & glazes, Also floors, panels.

–Important: UK-based ceramics experts combined recycled glass & ceramics → a sustainable material for architecture & interior design.

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...3. Raw Materials for Refractory Ceramics

- Magnesia, from $MgCO_3$ or synthetically eg Grecian Magnesite SA or Premier Magnesia LLC, deadburned or electrofused
- Alumina, from bauxite
- Graphite, natural or synthetic
- Olivine
- Zirconia
- other

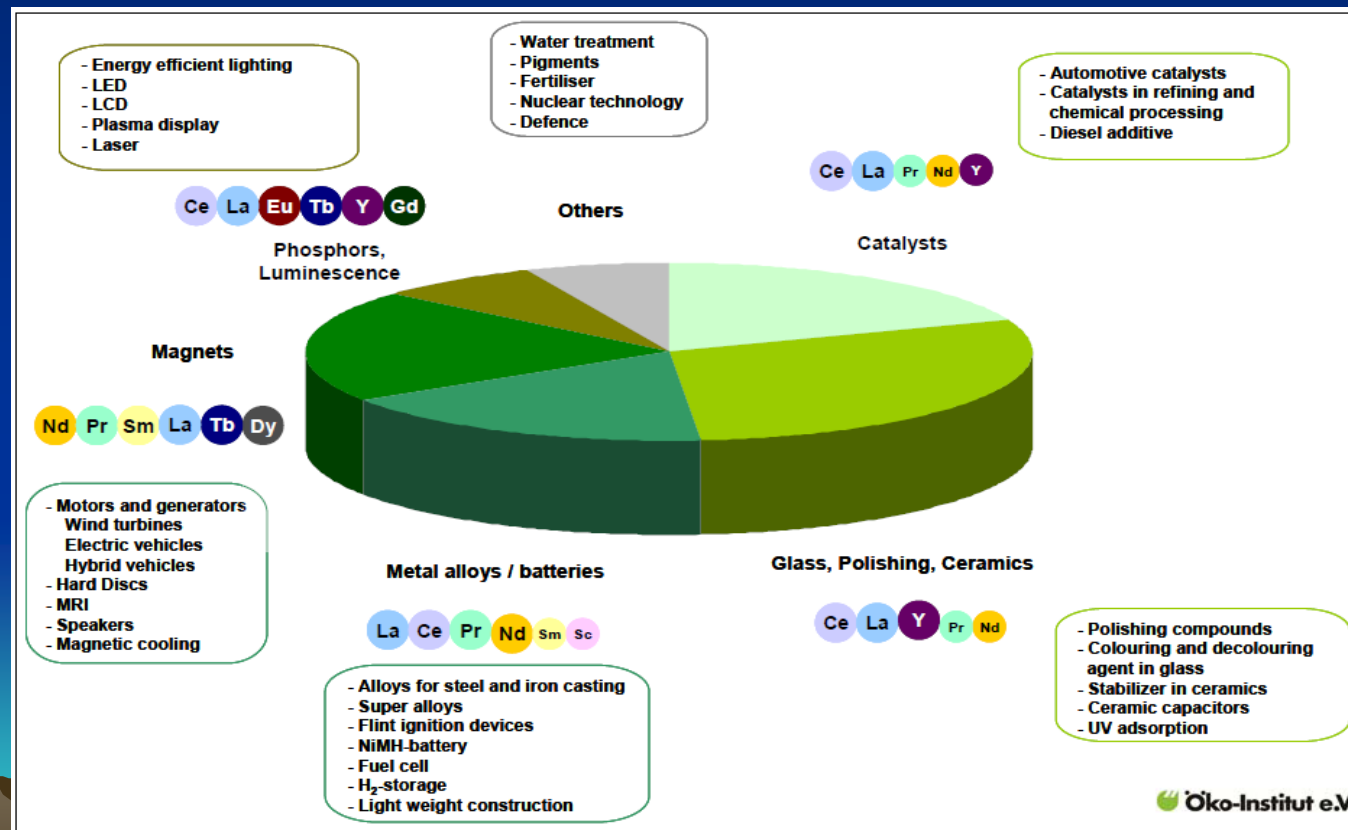
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4. The case of RE – Intro...

- 'Rare Earths Worldwide: An Industry & Policy Analysis', Natural Resources GP, 2011
- Milano presentation, 2011
- Industrial Minerals: news piece and VN article, both 2011

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...4. The case of RE -- Global applications of REE...



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Main applications in ceramics

Application	Major REE
Ceramics	
Ceramic capacitors, semiconductors and other components for LCD and electronics	La, Ce, Pr, Nd
Stabiliser for ceramic material	Y, Ce
High-temperature superconductors	Y
Pigments in ceramics	Pr, Y, Nd
Refractory material	Y, Ce
Laser	Y
Dental ceramics	Ce

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...4. The case of RE -- Global applications of REE...

- **Glass, polishing, ceramics & catalysts: relevant in volume, less relevant in value: the cheaper REE cerium & lanthanum are used very frequently for these applications**
- **Neodymium compounds help stabilize electrical properties in ceramic capacitors**
- **Yttrium ceramics as crucibles for melting reactive metals & as nozzles for jet casting molten alloys. Cars contain O2 sensors composed of yttrium based ceramic materials.**

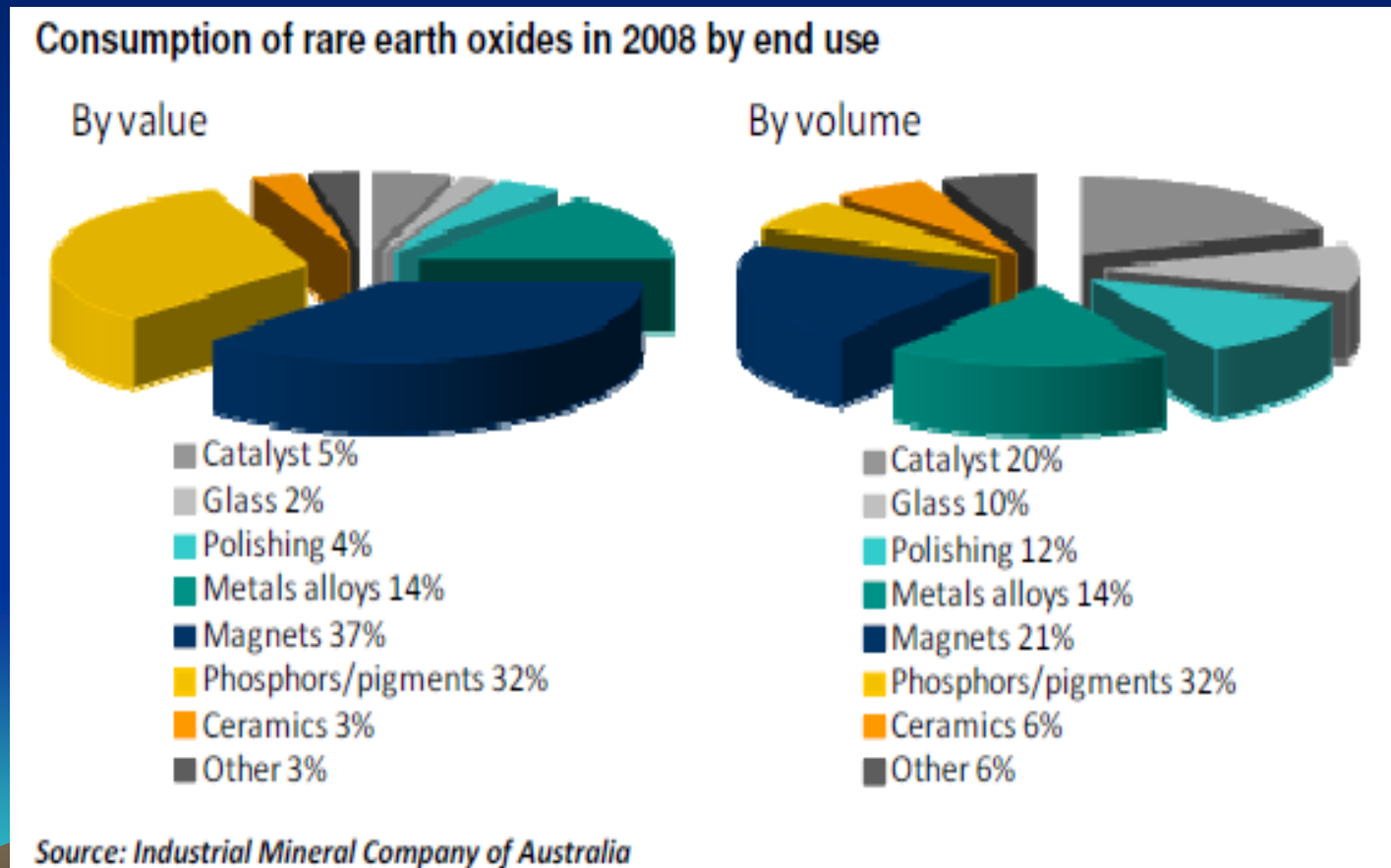
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...4. The case of RE -- Global applications of REE...

- **Cerium oxide** in zirconia → high temp engineering ceramic; exceptional toughness, good strength. US Space Shuttle: engineering ceramics w/ Cerium. High refractive index, opacifying agent in enamel compositions in protective coatings on metals.
- **Praseodymium**, common coloring pigment; w/ **Nd**, used to filter certain wavelengths of light. Its color allows producing pigments for coloring products eg. [vibrant yellow] ceramic tile & glass
- **Yttrium**: Cars contain O₂ sensors composed of Yttrium based ceramics, for most efficient use of fuel & less pollution
- **Dysprosium**: popular heavy; helps make electronic components smaller & faster. Oxide: additive in special ceramic compositions for high-capacitance, small-size capacitors for electronic applications

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...4. The case of RE -- Global applications of REE...

- Glass polishing 15000 t REO (44 %)
- Glass additives 12000 t REO (35 %)
- Ceramics 7000 t REO (21 %)

Kingsnorth (2010) for 2008

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...4. The case of RE -- applications in ceramics...

- Annual production of praseodymium oxide : 200 Ton
- Annual production of cerium oxide: 1000 Ton
- Eg. C.C. Bonet large assortment of products used in different ceramic-tile decoration processes
- Frits > Spray-dried glazes > Pellets
- Glazes > Engobes > Ceramic Stains
- Grits > Printing Powders -- Cerium oxide
- Stains -- Praseodimium oxide

CCBonet glazes, Milano presentation

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5. The case of Magnesite...

- Intro
- in building ceramics: Ceramics tiles [frits & glazes]. Eg. Grecian Magnesite *KERMA* magnesium carbonate, esp. in Italy, Spain, Greece, Portugal
- Engobio: applied on reverse side of tiles, just before introduction into kiln. Its high refractoriness prevents tiles from sticking on kiln rollers at high temperatures → trouble-free production. Compared w/ other minerals used, eg. Al_2O_3 , magnesium carbonate: low abrasion → protects kiln rollers fm wear. 'Superwhite' → attractive finish to reverse side of tiles.

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...5. The case of Magnesite...

'For Magnesium-rich frits & glazes

- magnesium carbonate ensures high quality frits & glazes at both low & high temperatures
- At high temperatures, functions as active fluxing agent & produces glazes with smooth, buttery surface
- At low temperatures, is refractory & provides opacity and matteness'

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...5. The case of Magnesite...

For high performance ceramics

- Quality improvement of gres porcelanato tiles
- Addition of 2-4% improves feldspar performance
- MgO + albite → fluxing phases → final product w/ very low porosity
- The most efficient fluxing agent for low quality feldspars
- Energy cost savings: addition into body of porcelain tiles decreases firing temp & thermal cycle
- Dimensional stability of end products and enhanced mechanical properties: decomposes at 600 °C, lower than decomposition temp of rival products (> 800 °C to >900°C). Ceramic body still porous → CO₂ does not cause deformation, cracks and bubbles.

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...5. The case of Magnesite

For refractories



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6. Futurology...

Imagine...

- microminiaturization of electronic devices. Ceramic engineers will turn nonfunctional packaging parts into functional components of the device; microminiaturization of components → incorporation of opto-electronic integrated circuits
- High temp superconductors → magnetic levitation vehicles, cheap electricity, improved MRI (magnetic resonance imaging): w/ micro-applications of superconductors through thin film tapes in sensors & memory storage devices → use of superconductors will take-off

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6...Futurology

Imagine...

- Automobiles: 30kgs ceramics/car, ceramics to improve motion sensors, gas compositions, electrical & thermal changes & light weight, high strength and high temp engine components
- Conservation of energy & environmental protection: in ceramic fuel cells, batteries, photovoltaic cells, & fiber optic transmission of energy – more coming
- Ceramic applications in medical diagnostic instruments, bioceramics for bone replacement & chemotherapy release capsules is here. More use to be seen w/ improvements in strength, nonreactivity, compatibility, longevity, porosity for tissue growth, & lower costs
- Ceramic proppants: beads, keeping fractures in hydrocarbon reservoirs open
- Etc...

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Thank you very much!

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