



Institute of Refractories Engineers

An Introduction to Refractories

Thursday 1<sup>st</sup> October 2009

Refractory Raw Materials

Alan Hey



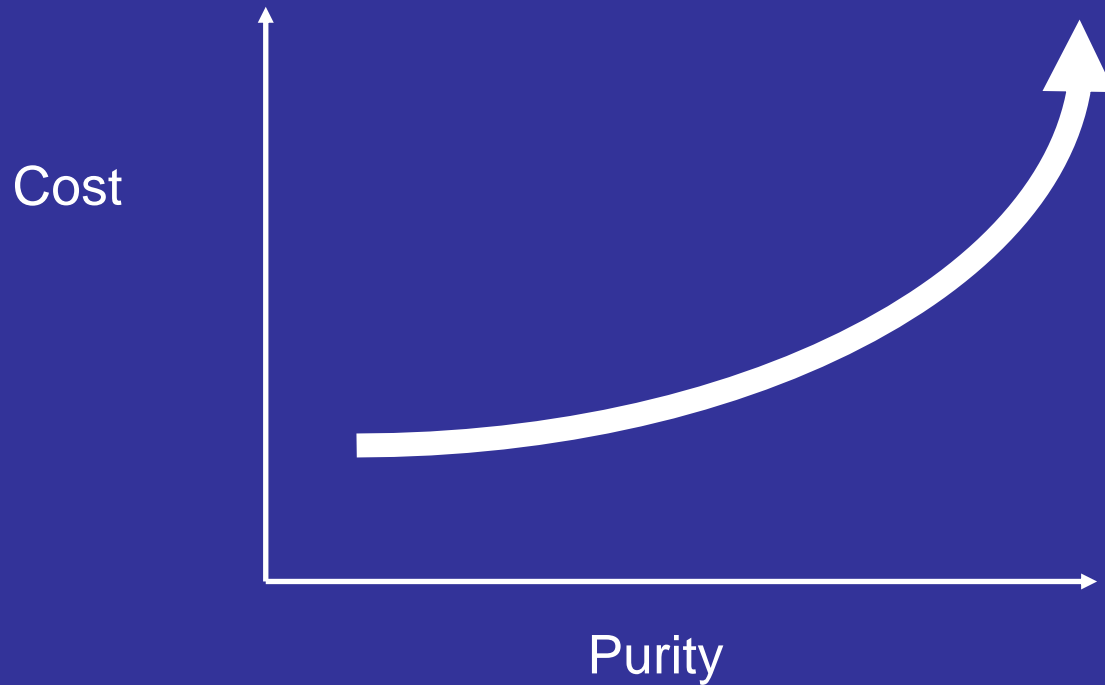
## Refractory Raw Materials

- Natural aggregates
- Semi-synthetic aggregates
- Synthetic aggregates
- Recycled and reclaimed aggregates
- Bonding and matrix materials
- Additives



# Refractory Raw Materials

Relationship between cost and purity





## Natural raw materials

- Quartz,  $\text{SiO}_2$
- Sillimanite Group,  $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$   
(~60%  $\text{Al}_2\text{O}_3$ )  
Sillimanite, Kyanite, Andalusite
- Zircon,  $\text{ZrO}_2 \cdot \text{SiO}_2$
- Clays
- Graphite



## Natural raw materials

- Quartz,  $\text{SiO}_2$  sources Sweden, Finland, Brazil, India, China
- Specific Gravity 2650kg/m<sup>3</sup>
- Melting point 1713°C
- Undergoes transformation to different crystal forms during heating and cooling, involving significant expansion and contraction – needs great care in producing fired products
- Principal use in silica bricks, now mainly manufactured overseas.
- Also used in monolithics, mainly induction furnace linings but also in form of quartzite used in clay based ramming, patching and gunning materials



## Natural raw materials

**Sillimanite Group,  $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  ~60%  $\text{Al}_2\text{O}_3$**

**Sillimanite, Kyanite, Andalusite**

- On firing, all convert to Mullite,  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  accompanied by a change in bulk density caused by changes in crystalline structure



- Kyanite undergoes significant expansion in the temperature range 1325 to 1410°C and this is of benefit in counteracting shrinkage in fired shapes but is a major advantage for monolithics especially.



## Natural raw materials

Kyanite lump



Kyanite sized





## Natural raw materials

**Clays** are found virtually everywhere in the world, and many types are suitable for refractories manufacture

- After mining, the clays are ground or pulverised for use in refractories.
- In the UK, Dorset, Devon and Cornwall are the main areas for production of high purity Ball Clays and China Clays
- All clays have essentially the mineral Kaolinite,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  as the principal component which imparts plasticity and binding power to the body in which it is contained whether it be a refractory or ceramic tableware.
- Special types of clays containing the mineral Montmorillonite are known as bentonite clays which have particularly high plasticity. Those originating from Wyoming in the USA are particularly well known for refractory applications in which small additions may be used





## Natural raw materials

### **Zircon,(zirconium silicate) $\text{ZrO}_2\text{-SiO}_2$**

- $\text{ZrO}_2$  content =66%, Bulk density=4560kg/m<sup>3</sup>
- Decomposes at around 1700°C
- Found in nature mainly as beach sand in Australia, S Africa and USA. Other sources are also being developed.
- Grain size is <0.3mm, also ground into flour sizes, eg -200 mesh
- Good corrosion resistance, used in refractories for iron & steel applications



## Natural raw materials

**Graphite** has a layer structure which leads to its anisotropic properties, ie, exhibiting widely differing thermal expansion and thermal conductivity depending on the crystal orientation

- It sublimates at  $3300^{\circ}\text{C}$  when no oxygen is present, **but is easily oxidised in the presence of air**. If reducing conditions can be maintained it is an excellent refractory
- it has excellent non-wetting properties and resistance to slag attack
- For refractories applications, natural crystalline graphites are mainly used
- There are synthetic and amorphous forms as well as natural material



## Semi- synthetic raw materials

These are defined as natural raw materials having undergone one or more industrial process prior to use , such as

- Beneficiation by removing impurities, or addition of pure material to modify chemistry and mineralogy during subsequent processing
- Briquetting or pelletising to densify the material
- Calcination or firing to stabilise minerals present and remove unwanted components, eg

$\text{H}_2\text{O}$  from Kaolinite, bauxite etc

$\text{CO}_2$  from carbonates and carbonaceous materials



## Semi- synthetic raw materials

- **Calcined clay based aggregates** eg, Molochite, Mulcoa range, Flint clays and Chamottes
- Calcined Bauxite based aggregates ranging from >80% to 90%  $\text{Al}_2\text{O}_3$
- Magnesite
- Dolomite



## Semi- synthetic raw materials

**Calcined clay based aggregates** eg, Molochite, Mulcoa 45, 60 &70, Flint clays and Chamottes

- These are usually mined, ground, briquetted or pelletised, and then fired. For higher alumina contents, eg 60 and 70%, bauxite is mixed with the clay prior to pelletising
- The firing process converts Kaolinite to Mullite. If additional alumina is present a higher amount of mullite is produced
- $3(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}) \rightarrow 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 4\text{SiO}_2 + 2\text{H}_2\text{O}$
- Kaolinite Mullite
- Water is driven off and the material is “shrunk” or densified to ensure it is stable on subsequent re-firing (or during use in the refractory product)
- The fired material is crushed and ground and graded by size fractions for use in the refractory product



## Semi- synthetic raw materials

### **Calcined Bauxite based aggregates ranging from >80% to 90% $\text{Al}_2\text{O}_3$**

The mineralogical basis of bauxite depends on where it originates

- Brazil and Guyana, the basis of the material is Gibbsite,  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
- Chinese material is based on the mineral Diaspore  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
- In order to use either material, it is necessary to remove the water by calcination, and depending on the calcination process, particularly for Chinese material, pelletisation of the mined raw material may or may not occur. Shaft kiln and Round kiln calcination usually takes place with lumpy material as mined.
- If a rotary kiln calcination process is used the raw bauxitic minerals are usually pelletised
- Calcined bauxite mainly consists of the mineral corundum,  $\alpha$ -alumina,  $\text{Al}_2\text{O}_3$ , with iron, silicon and titanium oxide impurities.
- It is used for many applications in fired and unfired shapes and monolithics



## Semi- synthetic raw materials



Calcined Chinese bauxite



## Semi- synthetic raw materials

**Magnesite,  $\text{MgCO}_3$**  is the natural mineral used to produce magnesia,  $\text{MgO}$

- Purity of the magnesite depends on where it is sourced, eg Austria has some high purity deposits, Korean and Chinese sources are less so
- Calcination of magnesite to form magnesia is often known as dead-burning which stabilises the material and reduces its tendency to hydrate. The calcined product may be referred to as magnesia clinker
- Hydration of magnesia, referred to as slaking, is a natural tendency of the material to revert to its stable form, so storage and use of the material has to be carefully managed because of this reactivity
- The high corrosion resistance to basic slags makes magnesia based products excellent for steelmaking processes





## Semi- synthetic raw materials



Calcined Chinese magnesite



## Semi- synthetic raw materials

**Dolomite** is a naturally occurring mineral, the double carbonate of calcium and magnesium,  $\text{Ca.Mg}(\text{CO}_3)_2$

- $\text{CaO-MgO}$  mixture has a melting point of  $>2300^\circ\text{C}$ , so aggregate made by calcination of raw dolomite has high refractoriness and resistance to basic slags.



- Although it can be stabilised by incorporation of iron oxide or silica, it has to be handled very carefully in order to avoid its rehydration or slaking tendency.
- It is used mainly for shaped products in steelmaking applications.



# Synthetic Raw Materials

- Tabular alumina
- Fused alumina
- Sintered magnesia
- Fused magnesia
- Sintered Mullite
- Fused Mullite
- Fused silica
- Silicon Carbide
- Spinels



# Synthetic Raw Materials

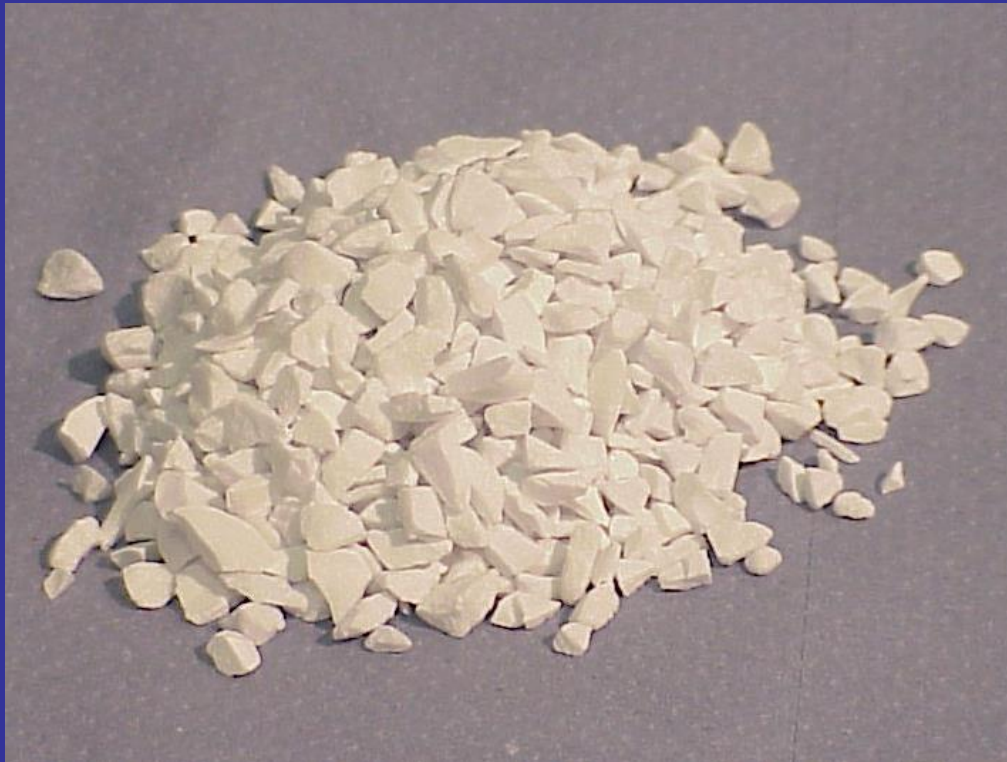
## Tabular or sintered alumina

- Made from calcined alumina by forming into balls, then calcining in a gas fired vertical shaft kiln at temperature  $>1800^{\circ}\text{C}$
- “Convertor Discharge” is then crushed and graded into various sized fraction
- Material is  $>99\%$   $\text{Al}_2\text{O}_3$  in the form of corundum or  $\alpha$ -alumina
- Sizes down to  $<20\mu\text{m}$  (MICRONS) are produced



# Synthetic Raw Materials

## Tabular or sintered alumina





## Synthetic Raw Materials

**Fused alumina** is produced essentially in two main types

- **Brown fused alumina** is produced by smelting bauxite in an electric arc furnace. The ingot formed is crushed into various grain sizes for refractories and abrasives use. Residual  $\text{TiO}_2$  gives the material its distinctive brown colour
- **White fused alumina** is processed in a very similar way except that the starting material is furnace grade alumina produced by the Bayer Process (see section on Calcined alumina)
- Both materials are highly refractory, having melting points of just under  $2000^\circ\text{C}$ , and bulk densities of  $\times 3900\text{kg/m}^3$  (brown) and  $3500/3700\text{kg/m}^3$  (white)





# Synthetic Raw Materials



Brown fused alumina



White fused alumina



## Synthetic Raw Materials

- Sintered magnesia** in high purity form is produced from sea water which contains magnesium chloride,  $\text{MgCl}_2$  at around 0.5% by weight
- The process involves precipitating magnesium hydroxide by adding hydrated lime to sea water.



- The magnesium hydroxide is then calcined to remove water and densify the product



Purity can be adjusted from 95% to >99.5%, the higher purities being used for more demanding steelmaking applications

**Fused magnesia** is produced by smelting sintered magnesia in an electric arc furnace followed by crushing of the ingot and sizing of the grains. Principal use is in high duty basic refractories for steelmaking applications





## Synthetic Raw Materials

- **Sintered Mullite** is made from a mixture of silica, bauxite and calcined alumina which are ground together and then pelletized or briquetted
- Following the drying process the material is calcined
- **Fused Mullite** uses similar starting materials but they are fused together in an electric arc furnace
- In common with all other fused material, because of slow cooling, large crystals of the mineral are formed



## Synthetic Raw Materials

### Silicon Carbide, SiC

- Silicon Carbide does not occur in nature but is produced from a mixture of silica sand and petroleum coke in an electric furnace at  $>2200^{\circ}\text{C}$
- It has good resistance to slag, and because of its high thermal conductivity has excellent thermal shock resistance.
- It is subject to oxidation, but surface oxidation of the SiC to silica can inhibit further oxidation in some circumstances



# Synthetic Raw Materials

## **Fused silica, $\text{SiO}_2$**

- High purity quartz sand is smelted above  $1720^\circ\text{C}$  in an electric furnace to produce a material which has a glassy, non-crystalline structure
- The material has extremely low thermal expansion and hence has excellent thermal shock resistance
- It has a limitation on usage temperature, since when heated above  $1200^\circ\text{C}$  it reverts to crystalline forms of silica in a process known as devitrification



# Synthetic Raw Materials

## Spinels, eg Magnesium Aluminate $\text{MgO} \cdot \text{Al}_2\text{O}_3$

- Spinels can be manufactured by either sintering or fusion routes
- It is possible to vary the chemistry and hence the physical properties by using  $\text{MgO}$  rich or  $\text{Al}_2\text{O}_3$  rich formulations, leading to a wide variety of compositions
- It is also possible to formulate products which will form spinel in the bonding system during firing of shaped products



# Recycled Raw Materials

## Recycled raw materials

- In a situation where imported raw materials costs are increasing , maximising recycling opportunities is vital
- In the manufacturing process, all producers of refractories recycle defective products to avoid waste, eg use of grog
- Used firebrick grog has been recycled into castables for some time
- Opportunities of recycling materials from related or other industrial processes, especially high value products
- Increasingly important area from an environmental point of view



# Recycled Raw Materials







# Recycled Raw Materials





## Matrix components and bonds

The fine and ultrafine components of a refractory product, referred to as the matrix, may consist of a variety of materials used to engineer specific properties in the finished product. Some examples are

- Calcined and reactive aluminas
- Microsilica, fumed silica, volatilised silica
- High alumina cements





## Matrix components and bonds

### Calcined alumina

- Calcined alumina is produced by treating impure natural bauxite with sodium hydroxide solution,  $\text{NaOH}$ , to remove impurities. This is known as the Bayer process
- A pure form of alumina hydrate  $\text{Al}(\text{OH})_3$  is produced, which is then calcined to produce alumina,  $\text{Al}_2\text{O}_3$
- Further purification produces aluminas with low soda content
- The products are fine ground (finer than  $63\mu$ ) by milling
- A variety of purities, crystallite sizes and grain surface area products are available



## Matrix components and bonds

### Microsilica or fumed silica

- Originally a by-product of ferroalloys production, the material has found widespread use in refractories, particularly in low cement castables where it replaces high alumina cement
- It has an extremely fine particle size and spherical grain shape which enables it to modify flow properties in castable products
- It is also an effective component in promoting mullite formation during service by reaction with fine alumina based components



# Matrix components and bonding materials

## High alumina cements

- High alumina cements ranging from 40 to 80%  $\text{Al}_2\text{O}_3$  can be manufactured by either a sintering or fusion route.
- Sintered products are most commonly used, predominantly 50, 70 and 80%  $\text{Al}_2\text{O}_3$
- A very wide range of castable products suitable for a variety of applications are possible using these cements
- Low cement castables are predominantly made with the 70%  $\text{Al}_2\text{O}_3$  product in combination with microsilica and special deflocculant additives



## Additives

**Additives may be used in order to engineer specific properties in the final product**

- Deflocculating additives such as sodium phosphates and polyphosphates etc are used in low cement castables to promote high fluidity at low added water contents
- Carbon, coal tar or petroleum pitch may be added to improve resistance to wetting by slag in monolithic materials
- Special additives may be used to improve resistance to attack by carbon monoxide, CO
- Additives which may influence formation of in-situ compound formation, eg Si metal, Al metal in carbon containing products



## Binders

In addition to other additives, special binders may be included in the formulation

- Temporary binders in fired products which retain the integrity of the material until the final ceramic bond is developed, eg dextrin, sodium lignosulphonate
- Glass formers based on boric oxide,  $B_2O_3$  to develop mid temperature strength
- Sodium silicate based materials to develop low temperature strength
- Aluminium phosphate based materials in either powder or liquid form to improve overall strength



## Binders

There are a number of binders used specifically in oxide-carbon based products which develop “carbon bonding”  
These may be used in combination depending on the product

- Coal tar and petroleum pitch
- Phenolic resins
- Coal tar in liquid form



# Institute of Refractories Engineers

- Wide variety of raw materials
- Globally sourced
- Cost versus purity major influence
- Effect of additives on engineered properties significant
- Available raw materials major influence on product development
- Importance of recycling



Institute of Refractories Engineers

An Introduction to Refractories

Thursday 1<sup>st</sup> October 2009

Refractory Raw Materials

Alan Hey