Institute of Refractories Engineers

An Introduction to Refractories

Thursday 25th September 2008

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

Cost

Purity

Natural raw materials

- Quartz, SiO_2
- Sillimanite Group, $Al_2O_3.SiO_2$ (~60%Al_2O_3)

  Sillimanite, Kyanite, Andalusite
- Zircon, $ZrO_2.SiO_2$
- Clays
- Graphite

Natural raw materials

- Quartz, SiO_2 sources Sweden, Finland, Brazil, India, China
- Specific Gravity 2650kg/m3
- Melting point 1713^oC
- 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, $Al_2O_3.SiO_2$ ~60%Al_2O_3

Sillimanite, Kyanite, Andalusite

- **On firing, all convert to Mullite, $3Al_2O_3.2SiO_2$ accompanied by a change in bulk density caused by changes in crystalline structure**

  $3(Al_2O_3.SiO_2)$ $3Al_2O_3.2SiO_2 + SiO_2$

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

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, $Al_2O_3.2SiO_2.2H_2O$ 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) $ZrO_2.SiO_2$**
- ZrO_2 content =66%, Bulk density=4560kg/m3
- Decomposes at around 1700oC
- 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 sublimes at 3300^{o}C when no oxygen is present, **but is easily oxidised ih 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

H_2O from Kaolinite, bauxite etc

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% Al_2O_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
- $3(Al_2O_3.2SiO_2.2H_2O)$ $3Al_2O_3.2SiO_2 + 4SiO_2 + 2H_2O$
- 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% Al_2O_3

The mineralogical basis of bauxite depends on where it originates

- Brazil and Guyana, the basis of the material is Gibbsite, $Al_2O_3.3H_2O$
- Chinese material is based on the mineral Diaspore $Al_2O_{3.}H_2O$
- 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, • -alumina,Al_2O_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

Magnesite, $MgCO_3$ is the natural mineral used to produce magnesia, 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

Dolomite is a naturally occurring mineral, the double carbonate of calcium and magnesium, $Ca.Mg(CO_3)_2$

- CaO-MgO mixture has a melting point of >2300°C, so aggregate made by calcination of raw dolomite has high refractoriness and resistance to basic slags.

$$Ca.Mg(CO_3)_2 \qquad CaO.MgO + 2CO_2$$

- 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^{o}C
- “Convertor Discharge” is then crushed and graded into various sized fraction
- Material is >99% Al_2O_3 in the form of corundum or • -alumina
- Sizes down to <20µm (MICRONS) are produced

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 TiO_2 gives the material its distinct 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^oC, and bulk densities of x 3900kg/m3 (brown) and 3500/3700kg/m^3 (white)

Synthetic Raw Materials

Sintered magnesia in high purity form is produced from sea water which contains magnesium chloride, $MgCl_2$ at around 0.5% by weight

- The process involves precipitating magnesium hydroxide by adding hydrated lime to sea water.

  $MgCl_2 + Ca(OH)_2 \qquad Mg(OH)_2 + CaCl_2$

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

  $2Mg(OH)_2 \qquad \text{heat} \qquad 2MgO + 2H_2O$

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^{o}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, SiO_2

- High purity quartz sand is smelted above 1720^{o}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^{o}C it reverts to crystalline forms of silica in a process known as devitrification

Synthetic Raw Materials

Spinels, eg Magnesium Aluminate $MgO.Al_2O_3$

- Spinels can be manufactured by either sintering or fusion routes
- It is possible to vary the chemistry and hence the physical properties by using MgO rich or Al_2O_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

Synthetic 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

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, NaOH, to remove impurities. This is known as the Bayer process
- A pure form of alumina hydrate $Al(OH)_3$ is produced, which is then calcined to produce alumina, Al_2O_3
- Further purification produces aluminas with low soda content
- The products are fine ground (finer than 63μ) 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% Al_2O_3 can be manufactured by either a sintering or fusion route.
- Sintered products are most commonly used, predominantly 50,70 and 80% Al_2O_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% Al_2O_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

- 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 25th September 2008

Refractory Raw Materials

Alan Hey