Refractory Raw Materials

What are refractories made from?

- **'Refractory Materials'!**

•Refractories are usually metal oxides

•(or combinations of them)

•manufactured from:

• naturally occurring raw materials

•synthetic materials generated from processing naturally occurring raw materials

Which metal oxides?

- Importantly - oxides which have high melting temperatures (or carbon/carbides).
- Pure materials are rarely if ever used because of their high cost and properties that are not appropriate for meeting the conditions in a steelmaking environment.
- The melting temperature of some pure oxides are far in excess of those encountered in the intended applications.

Silica	SiO_2	1726°C
Alumina	Al_2O_3	2054°C
Magnesia	MgO	2800°C
Zirconia	ZrO_2	2700°C
Mulite	$Al_6Si_2O_{13}$	1828°C
Spinel	$MgAl_2O_4$	2135°C
Lime	CaO	2600°C

•However, the melting temperature is generally decreased by impurities in the same way as salt decreases the melting point of ice.

Types of refractories: Chemistry

Classification of Refractories: Chemistry

Acid	Neutral	Basic
Silica	Alumina	Magnesia
Mulite	Bauxite	Doloma
Fireclay	Zirconia	Magnesia-Chrome
Andalusite	(Carbon)	Magnesia-Carbon

Use in increasingly ACID environments

Acidic or Siliceous Slags.

Basic or Limey Slags.

Refractory Raw Materials

- Natural aggregates
- Semi-synthetic aggregates
- Synthetic aggregates

Natural raw materials

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

  Sillimanite, Kyanite, Andalusite
- Graphite

Natural raw materials

- Quartz, SiO_2 sources Sweden, Finland, Brazil, India, China
- Specific Gravity 2650kg/m3
- Melting point 1713^{o}C
- Undergoes transformation to different crystal forms during heating and cooling, involving significant expansion and contraction – needs great care in producing fired products
- Silica bricks, now mainly manufactured overseas.

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

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**

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

- **Kyanite undergoes significant expansion in the temperature range 1325 to 1410^oC and this is of benefit in counteracting shrinkage.**

Natural raw materials

Kyanite lump

Kyanite sized

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 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

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

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
- $3(Al_2O_3.2SiO_2.2H_2O) \longrightarrow 3Al_2O_3.2SiO_2 + 4SiO_2 + 2H_2O$
- 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, α-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

Calcined Chinese bauxite

Synthetic Raw Materials

- Tabular alumina
- Fused alumina
- 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 α-alumina
- Sizes down to <20μm (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 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
- Both materials are highly refractory, having melting points of just under 2000^{o}C, and bulk densities of x 3900kg/m3 (brown) and 3500/3700kg/m^3 (white)

Synthetic Raw Materials

Brown fused alumina

White fused alumina

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