Introduction

- What is a Refractory ?

- What Raw Materials do we use to make them

What is a Refractory

- ‘Refractories are Non Metallic Materials that can withstand High Temperatures and Chemically Challenging Environments’
- “A material which is non-metallic, inorganic and does not soften at temperatures below 1500°C.”

What is a Refractory

- ‘Refractories are High Melting Point, Chemically Inert Metal Oxides’

- Materials that can withstand high temperatures and chemically challenging environments such as the Oxides of Aluminium, Silicon and Magnesium

What does a Refractory do?

Put simply:

‘Contain or work within high temperature environments’

To do this a refractory must be able to withstand :

- **high temperatures**
- **variable temperatures**
- **chemical attack by gases**
- **chemical attack by liquids**
- **physical stresses**
- **mechanical wear**

(both separately and in combination)

Refractory Applications

- Refractory materials are extremely important and affect the operation and costs of any plant in which they are employed.
- The steel industry is the largest consumer of refractories both in this country and worldwide.
- Approximately 2/3 of all refractories are used in the steel industry.
- Other major usage areas for Refractories:

Where do Refractory Raw Materials Come From?

- From out of the Ground
- Refractory Technology is as ‘Old as the Hills’
  - In fact that is where most of the Refractory Materials Come from
- As Science developed Materials that worked in Refractory applications were ‘Reverse Engineered’
- The best materials were found to be Metallic Oxides
  - These are extremely stable compounds
  - The Metal and Oxygen are in their most stable state when they are joined together
    - What does a Blast Furnace do? It strips oxygen from Iron
  - Since these Metallic Oxides are so stable they resist being broken down by High Temperatures or Chemically Aggressive environments

Which metal oxides?

- Obviously those oxides which have high melting temperatures
- For Blast Furnace Applications we are talking primarily about Alumino Silicates, (Combinations of Alumina and Silica), plus Pure Alumina

- 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

What are Refractories made from?

Refractories are usually metal oxides

(or combinations of them)

manufactured from Naturally Occurring

Raw Materials,

However, Refractory Technology has moved on a little and we have now developed

Semi Synthetic Raw Materials

and even

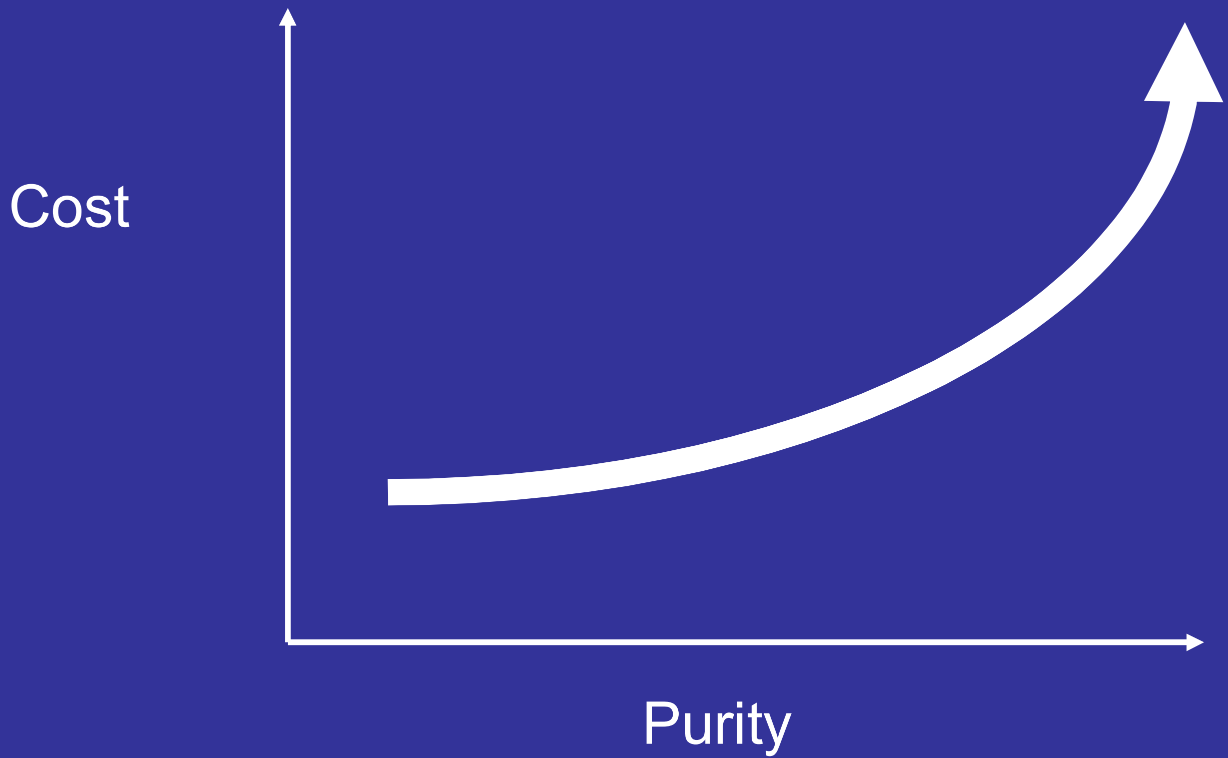
Fully Synthetic Raw Materials.

Cost and Purity

Relationship between cost and purity

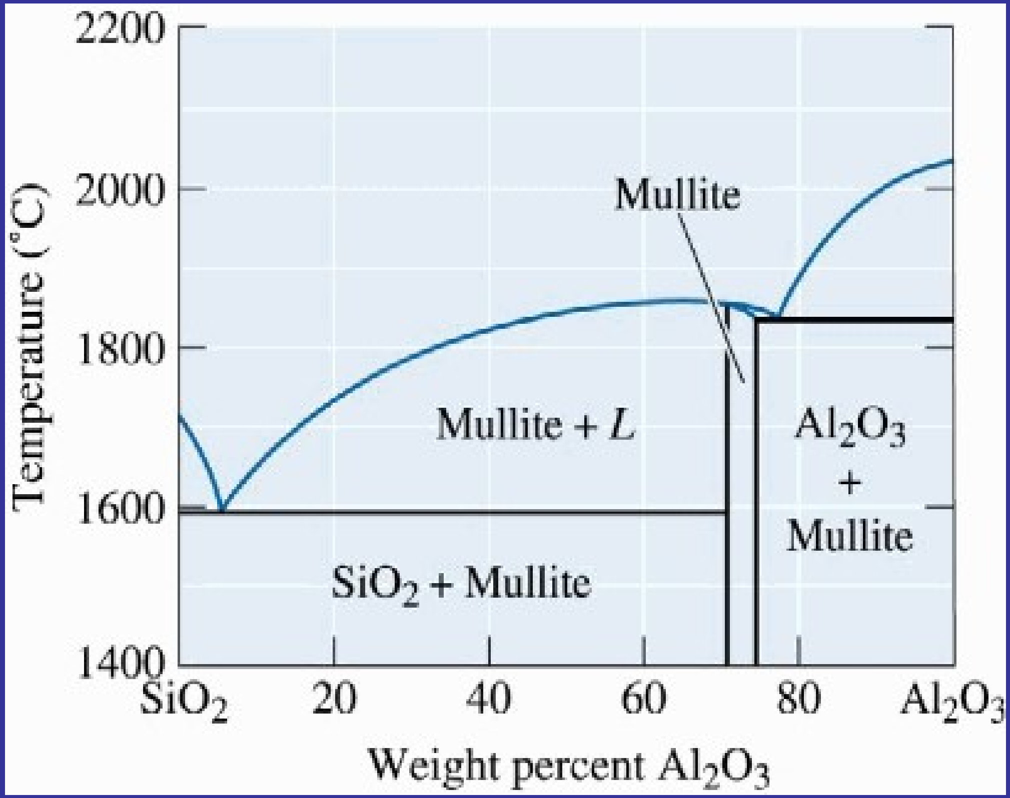
Naturally Occurring Raw Materials usually contain impurities and that can restrict the potential performance of a Raw Material when it is a component of a Refractory Product

For Blast Furnace Casthouse Applications we tend to use Semi Synthetic and Synthetic Raw Materials



Alumina Raw Materials
Silica – Alumina Binary Phase Diagram

- For Blast Furnace Runner and Taphole Clay Applications The Key Raw Materials will be Alumino Silicates, (Mixtures of Alumina and Silica), or Purer Alumina Based Raw Materials.



- Unfortunately, naturally occurring deposits of these Metal Oxides tend to be found combined with each other along with further components in what is a bit of a soup of potentially useful items
- Some naturally occurring deposits are refined to produce very pure forms of Alumina, Silica and Magnesia but this can be expensive
- Whilst with others we tend to work with what we have got and just compromise
  - Of course sometimes the mix of properties from the Hybrid materials are actually beneficial
- One of the most common combinations that you find is that between Alumina and Silica, The **ALUMINO SILICATES**

Semi Synthetic Raw Materials

These are natural raw materials that have undergone one or more industrial processes prior to use , such as:

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

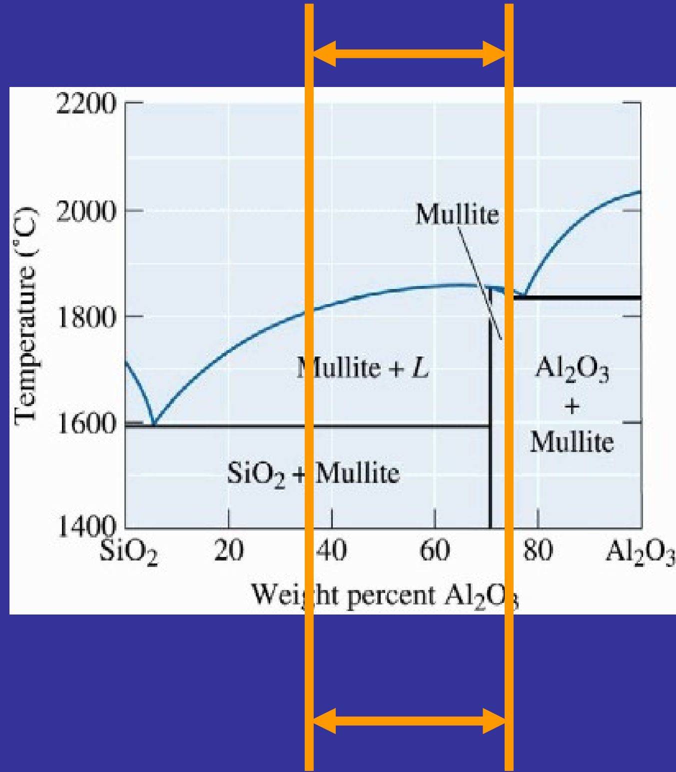
  H_2O from Kaolinite, bauxite etc

  CO_2 from carbonates and carbonaceous materials

Semi Synthetic Raw Materials

Calcined clay based aggregates eg, Molochite, Mulcoa 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(Al2O3.2SiO2.2H2O) 3Al2O3.2SiO2 + 4SiO2 +2H2O
- 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

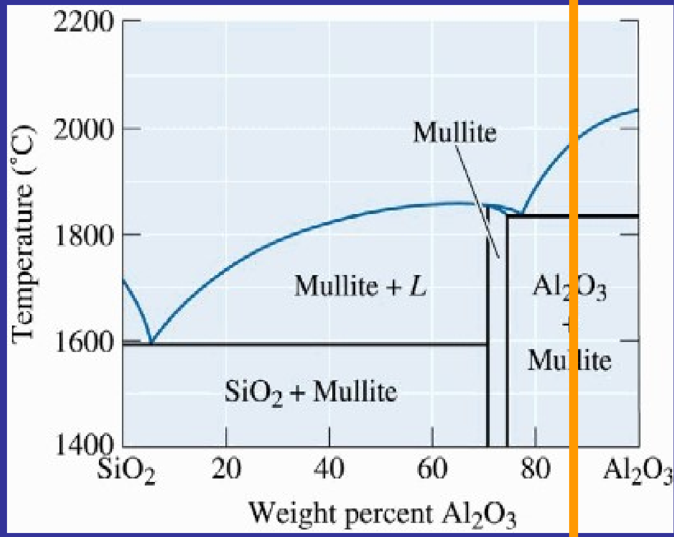


Semi Synthetic Raw Materials

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



Synthetic Raw Materials

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

- These are materials that do not occur naturally but they are 'Manufactured' from Naturally Occurring Raw Materials
- For Blast Furnace Casthouse Applications we are primarily interested in the first two on this list.
- These products are produced from Calcined Alumina / Bauxite

- 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

Synthetic Raw Materials

Tabular or Sintered Alumina

- Made from Calcined Alumina by forming into balls or 'Tablets', 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

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 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^{o}C, and bulk densities of x 3900kg/m3 (brown) and 3500/3700kg/m^3 (white)

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

Matrix Components and Bonds

- The Raw Materials that we have mentioned so far are the **'BULK ADDITIONS'**, the bigger, coarser components
- However a number of fine and ultrafine components can also be used and these are referred to as the **MATRIX,**
- The Matrix Components may consist of a variety of different materials that are used to engineer specific properties in the finished product. These can include:
  - Microsilica or Fumed Silica
    - That has an extremely fine particle size and spherical grain shape which enables it to modify flow properties in castable products. It is a by product of Ferro Alloy Production
  - High Alumina Cements
  - Binders
  - Other Additives
    - 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
    - Additives which may influence formation of in-situ compound formation, eg Si metal, Al metal in carbon containing products

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
- 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

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

- 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

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

What is Refractory Technology?

- The situation with Magnesia is slightly different
- Magnesia is actually produced from naturally occurring Magnesite, which is Magnesium Carbonate
- When this Magnesite is fired to 900c it converts to Magnesium Oxide, (Magnesia).
- If it is then fired further to 1600c it produces a more stable Dead Burned Magnesite
  - This is just to confuse people.
    - Magnesite is Magnesium Carbonate which when fired becomes Magnesia but when it is fired to 1600c we refer to it back by the Carbonate name but with a prefix to note that we have fired it to form the Oxide
- Of course naturally occurring Magnesite is not pure Magnesium Carbonate but generally contains Calcium Carbonate, (Lime) and Iron Carbonate, ($FeCO_3$).