Institute of Refractories Engineers

Refractory Raw Materials

Training Day 2015

Introduction

Sam Franklin

Practicalities

- Breaks
- Handout
- Exercises
- Timing
- Phones
- Questions
- Certificates

Course Aim

To provide an understanding of

- refractory raw material types
- the selection of raw materials
- the combination of raw materials in refractories

Schedule

Introduction
Aggregate Materials
Binders
Exercise
Material Design
Exercise

Reminder - What Are Refractories

BS 3446

"A non-metallic material or product (but not excluding those containing a proportion of metal) having heat-resisting properties."

•Classification by Form

- Shaped
  - Bricks
  - Blocks
  - Pre-cast

- Un-Shaped – Monolithics
  - Castable
  - Rammable
  - Mouldable
  - Gunnite

•Classification by Chemistry

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

•Use in increasingly ACID environments

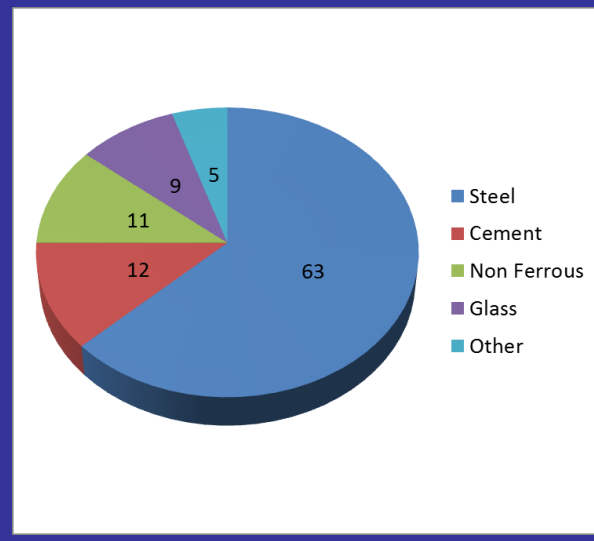
•Acidic or Siliceous	*•Basic or Limey*
•Slags.	*•Slags.*

•User Industries

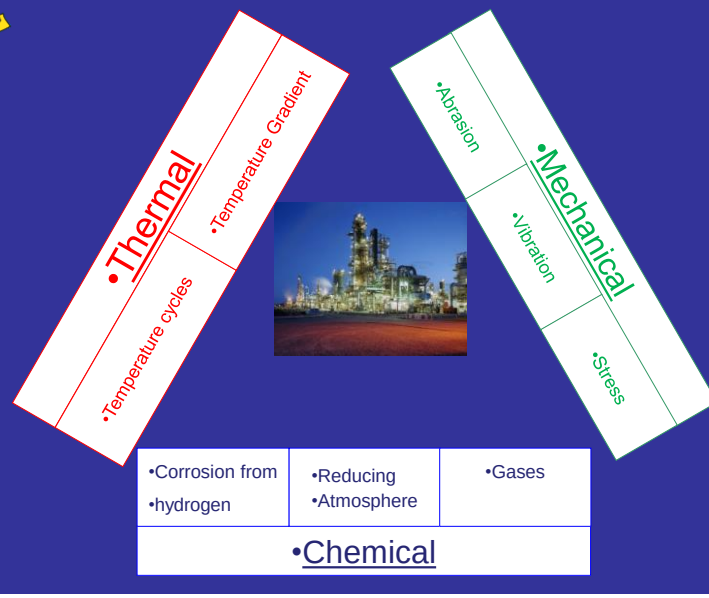
Refractories are used in ALL thermal processing industries

- **Metals**
- **Chemicals**
- **Glass**
- **Ceramics**
- **Waste Processing**
- **Cement**
- **etc**

•User Industries



•Wear of Refractories



What are Raw Materials ?

The ‘stuff’ we make refractories from

- Usually solid
- Wide range of particle size
  - 20mm to 1/10,000 mm (0.1μm)
- Wide range of chemistry

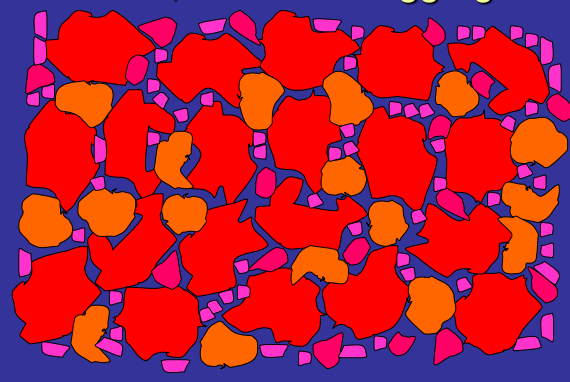
Why are raw materials important

Final properties

- Chemical
- Thermal
- Mechanical

Can’t put it right later

Binders, Fillers and Aggregate



Large Particles – Aggregate – 20-0.1mm

Binder – Glues the aggregate together – liquid or fine powder

Filler – Fine articles that do not contribute to initial bond

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Aggregates and Selection

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Pure Compound Melting

- 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

Natural Raw Materials

- Mining costs
- Transport
- Impurities

- Beneficiation
- Crushing and Grading

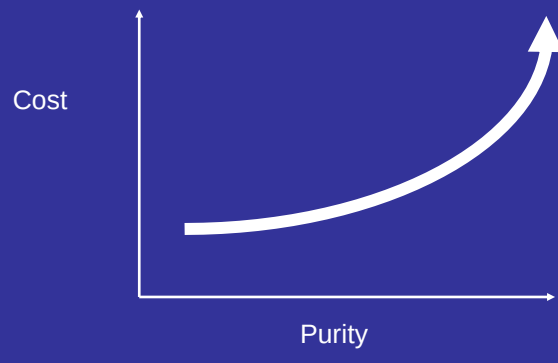
Raw material treatment

- Thermal Treatment
  - Chemical decomposition
  - Calcination
  - Densifying
  - Fusing
- Chemical Treatment

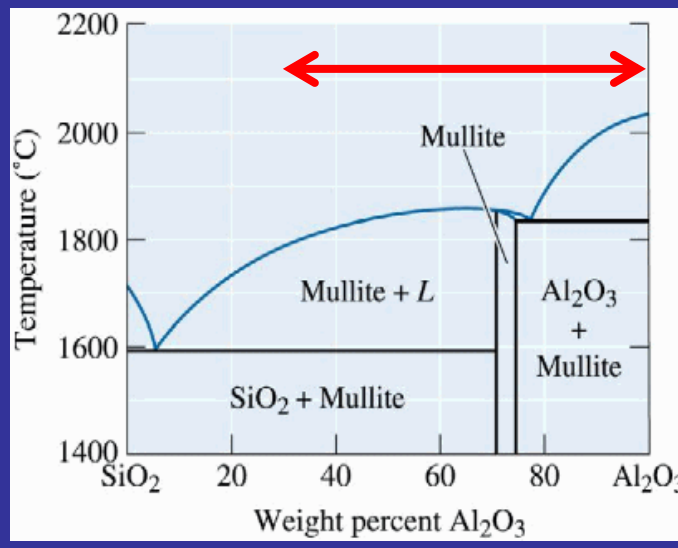
Higher Temp

Raw material cost

- Abundance
- Transport
- Amount of Treatment



Raw Material Chemistry



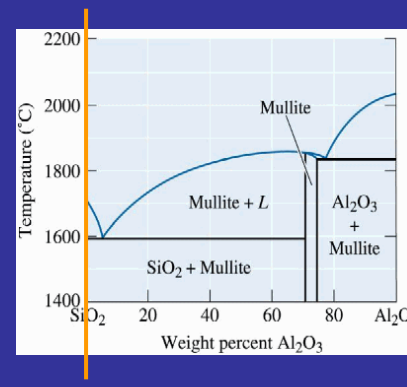
Natural raw materials

- 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

Quartzite,

- Widely found in nearly pure deposits in many places
- Only some deposits suitable for refractories
- Specific Gravity 2650kg/m3
- Melting point 1713°C
- Has complex crystal phase transformations and expansions
- Used in silica bricks, for glass and iron industry
- Also used in monolithics, mainly induction furnace linings



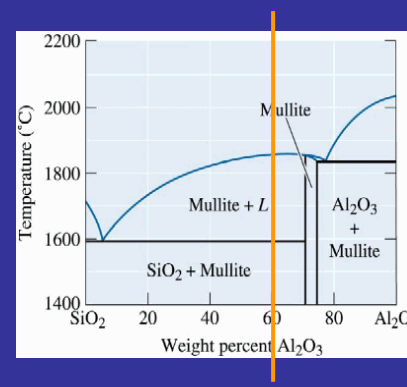
Natural raw materials

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**

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



Natural raw materials

KYANITE – Transforms at 1325 -1410°C

Often used to counter shrinkage in fired shapes and especially monolithics

ANDALUSITE – Transforms at 1450-1500°C

A range of sources in Europe, Africa and S America

Commonly used in making shaped refractories

SILLIMANITE – Transforms >1550°C

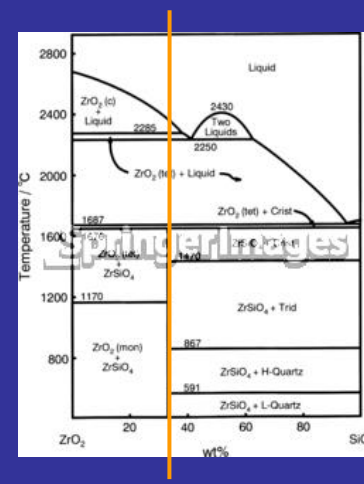
Few commercial sources outside India

Needs high firing temperature to convert

Natural raw materials

Zircon,(zirconium silicate)
$ZrO_2.SiO_2$

- ZrO_2 content =66%,
- Bulk density=4560kg/m3
- Decomposes at around 1700ºC
- From Australia, S Africa and USA. Grain size is <0.3mm, also ground into fines 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 3300ºC 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

Synthetic raw materials

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

- 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
- Fusing – melting and re-solidfying
- Chemical Processing

- COMBINATIONS of these

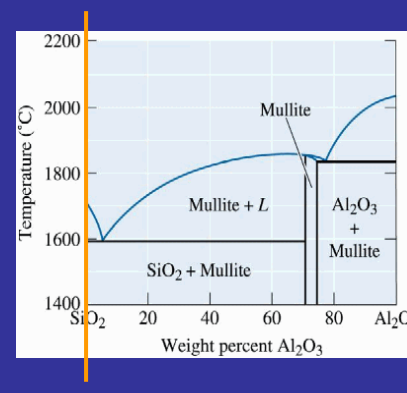
Synthetic raw materials

- **Calcined clay**
  - eg Molochite, Mulcoa range, Flint clays and Chamottes
- Calcined Bauxite
- Tabular alumina
- Fused alumina
- Sintered Mullite
- Fused Mullite
- Fused silica
- Silicon Carbide
- Spinels

Synthetic Raw Materials

Fused silica, SiO_2

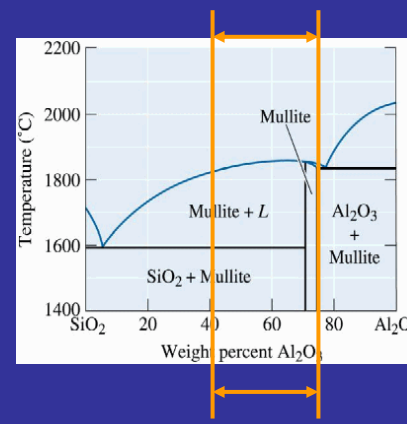
- High purity quartz sand is melted >1720°C in an electric furnace
- Glassy, non-crystalline structure
- Low thermal expansion
- Excellent thermal shock resistance
- MST ~1100°C



Synthetic raw materials

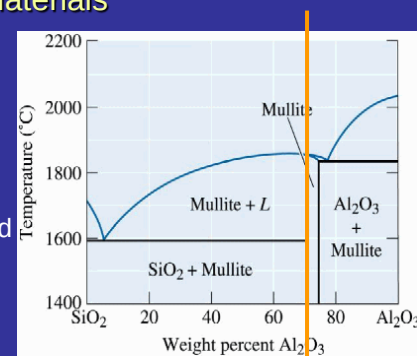
Calcined clay based aggregates
Examples
Molochite,
'Mulcoa' brand
Flint clays and Chamottes

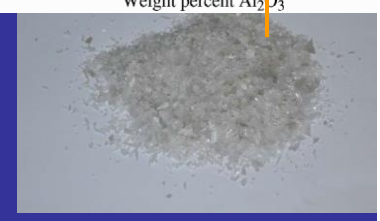
- Simple process
  - Mine, Briquette, Firing, Crush and grade
  - Material may be blended first or natural blends
- Firing converts Kaolinite to Mullite.
- Higher alumina content … more mullite
  $3AS_2H_2$ → A3S2 + 4S +2H
  Kaolinite Mullite Silica Steam
- Material shrinks during process



Synthetic Raw Materials

- **Sintered Mullite**
- 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 fired
- **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

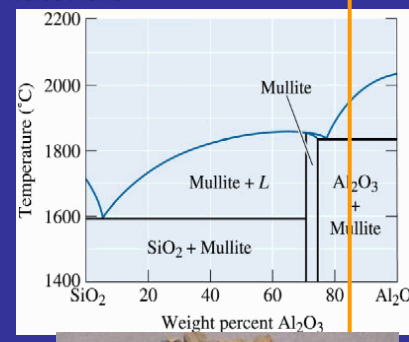




Synthetic raw materials

Calcined Bauxite
80% - 90% Al_2O_3

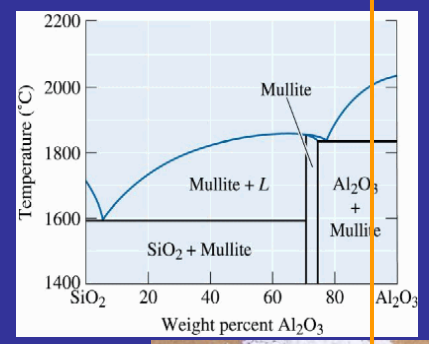
- Bauxite is a aluminium based mineral
- Refractory grades sourced in China and S America
  - Brazil and Guyana, mineral Gibbsite, Al2O3.3H2O
  - China, mineral Diaspore Al2O3.H2O
- Water must be removed – calcination
- Rotary kiln material – pelletised first
- Calcined bauxite made up of corundum with iron, silicon and titanium oxide impurities.
- It is used for many applications in fired and unfired shapes and monolithics



Synthetic Raw Materials

Calcined alumina

- Produced by chemical treatment of natural bauxite to remove impurities. This is known as the Bayer process
- A pure form of alumina hydrate $Al(OH)_3$ is produced
- This is calcined to remove water
- Further chemical purification reduces alkali content
- The products are ground by milling
- A variety of purities, crystallite sizes and grain surface area products are available

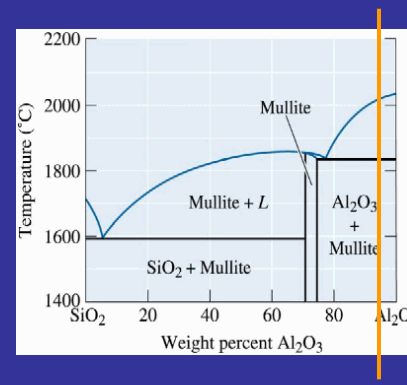


Synthetic Raw Materials

Fused alumina

- Starting material is melted in an electric furnace, >2000°C
- Cast into an ingot
- Crushed and graded

- Brown fused alumina
  - Raw material is bauxite
  - Higher TiO2 level from impurities
  - Used for abrasives and refractories
  - Density 3900kg/m3
- White fused alumina
  - Raw material is calcined alumina
  - Density 3900kg/m3



Synthetic Raw Materials

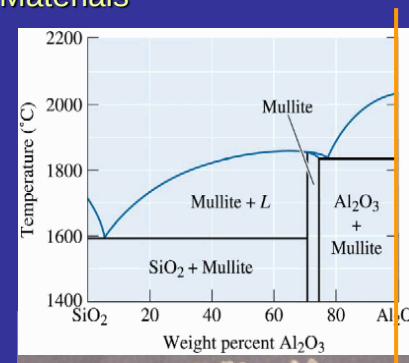
Brown fused alumina

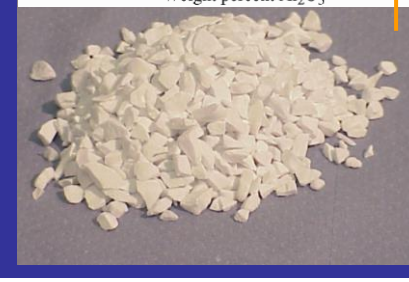
White fused alumina

Synthetic Raw Materials

Tabular or sintered alumina

- Calcined alumina formed into balls
- Heated in shaft kiln >1800°C
- Crushed and graded into sized fraction
- Material is >99% Al_2O_3 in the form of corundum
- Sizes down to <20µm (MICRONS) are produced





Synthetic Raw Materials

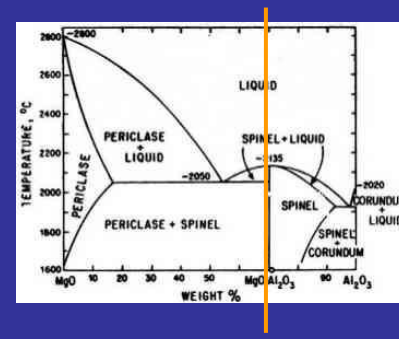
Silicon Carbide, SiC

- Silicon Carbide does not occur in nature
- Silica sand and petroleum coke in an electric furnace at >2200°C
- It has good resistance to slag,
- high thermal conductivity
- excellent thermal shock resistance.
- It is subject to oxidation

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

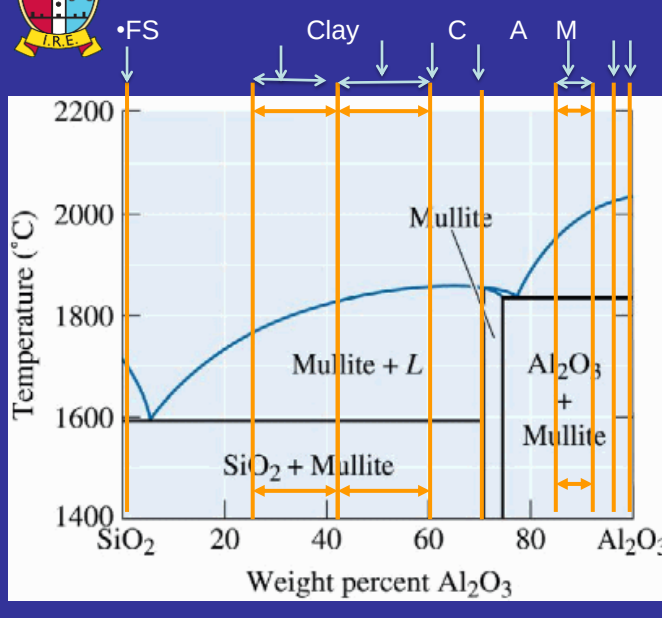


Recycled Raw Materials

Recycled raw materials

- Recycling reduces cost
- In house scrap – grog
- Used brick is sorted, chrushed and resold
- Increasingly important area from an environmental point of view

Phase Diagram

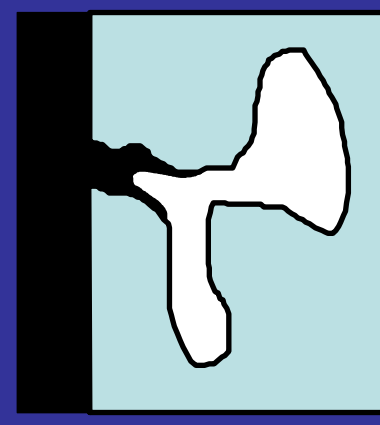


FS Fused Silica
C Chamotte
A Andalusite
M Mullite
B Bauxite
FA Fused Alumina
TA Tabular Alumina

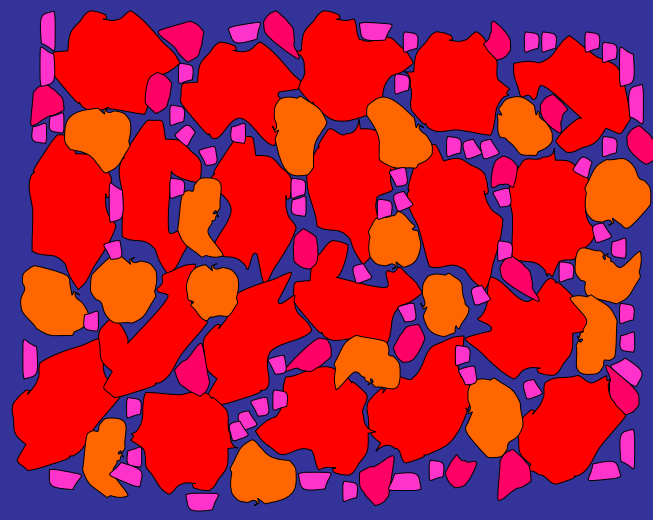
Why Porosity matters

- Porosity can promote chemical attack, especially slag penetration.
- As pores get filled with slag, the corrosion goes on from inside and not only the outside surface.
- High porosity also reduces abrasion resistance
- For hot face materials, porosity is minimised

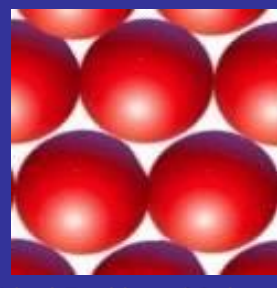
- For insulation materials, a high porosity entrains more air and



Size Distribution

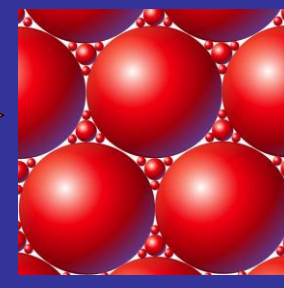


Ideal Particle Packing

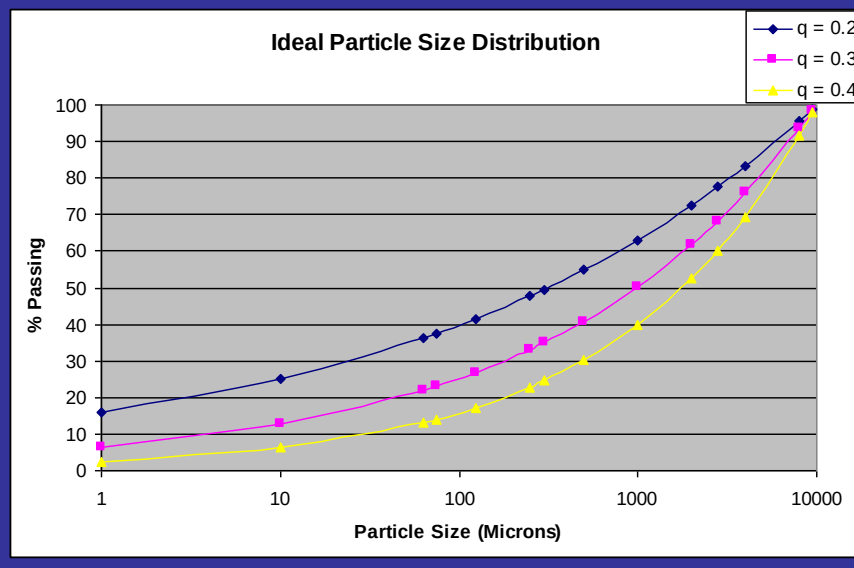


•Ideal Packing of Spheres

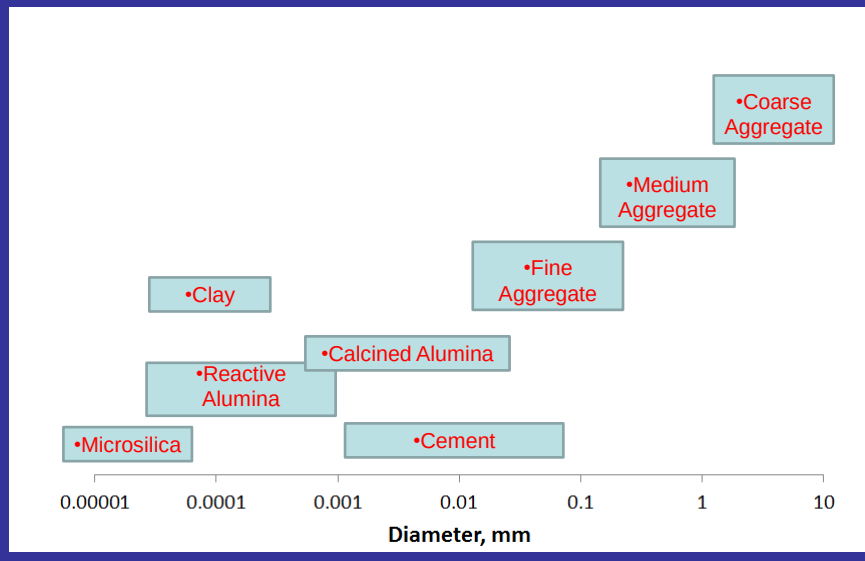
•Voids are filled using progressively smaller particles



Andreasen Distribution Curves



Particle Size



Example Mix

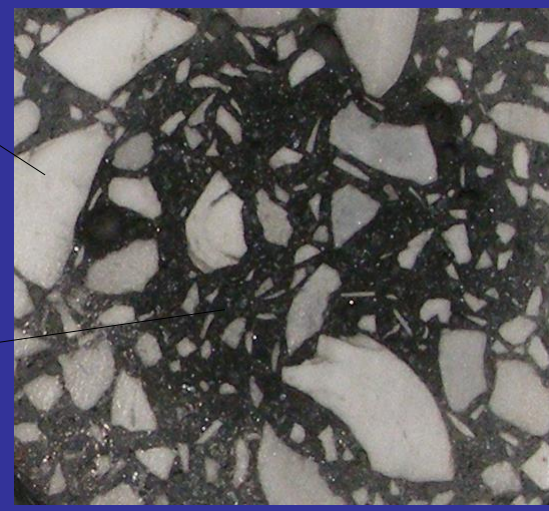
Materials	Size	% (by weight)
Fused Alumina	-10+5	25.0
Fused Alumina	-5+1	20.0
Fused Alumina	-1+0	25.0
Calcined Alumina	<10μm	15.0
Volatilised Silica	<1μm	5.0
Cement	<1μm	10.0
Additives		+0.1

Example Mix

Example Mix

•Aggregate

•Matrix



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- 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

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Thank You