

CH5716

Processing of Materials

Ceramic Processing

Lecture MC2 – Review of Bulk Ceramic Processing

# Clay materials

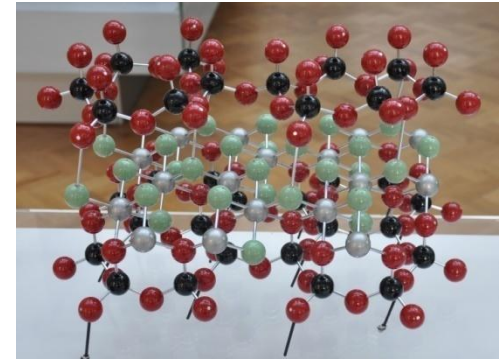
Clays are families of naturally occurring minerals

Formed from weathering of other rock materials eg feldspars

Found in deposits either where formed or build up by transportation

By nature very variable - with large number of variations

- Aluminosilicate nature with a layered structure
  - Alternating sheets of silica tetrahedra and octahedral alumina
  - Tetrahedral and octahedral be linked via bridging oxygen
  - Outer surfaces of octahedral sheet will be hydroxyl groups
  - This can form H bonds with adjacent tetrahedral layers
- Form platelet shaped particles
- Clays generally classified layer arrangement

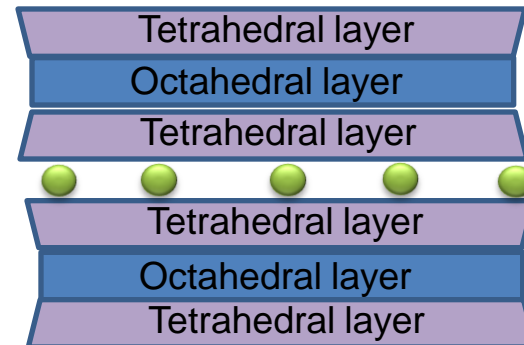
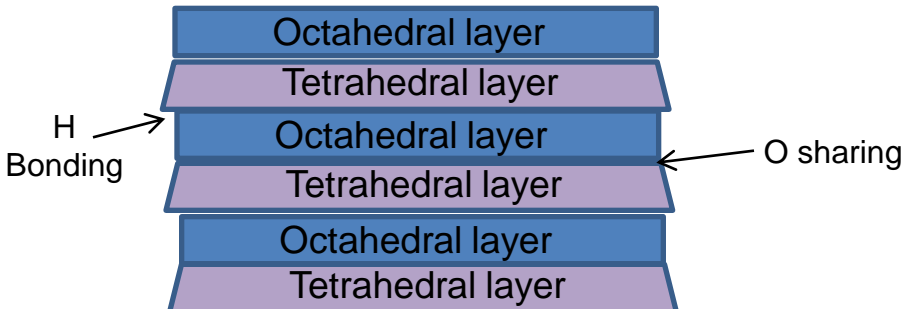


## 1:1 Clays equal number of Tet & Oct layers

- H bonding between layers
- Low propensity for water absorption
- Tend to be purest – Kaolinite

## 2:1 clays have 2 tet layers to every oct layer

- Tet – Tet faces can be stabilised by cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ )
- Can lead to greater water absorption and swelling
  - Can be good sorbent materials
  - Illite, smectite, bentonite



# Forming of Clay

- All clays will be lubricated by addition of water
  - Improves plasticity – too much and will become unworkable
  - Clay platelets separated by water molecules and held by H-bonding
- Bond will shear if force applied but has enough strength to retain form at rest
- Too much water then platelets become too separated – move to dispersion
- If this is stable can form a slip – thick creamy dispersion

## Forming by several means

- Hand building- coils, sheet forming
- Wheel throwing
- Extrusion
- Slip casting

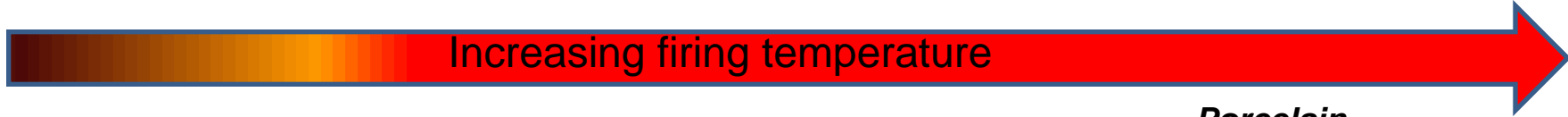


# Dry & Firing Clay

- Drying evaporates excess water
    - Platelets move closer together
    - Allows direct H-bonding between hydroxyl groups
  - Known as “leather hard” stage
    - Clay can still be recovered to plastic state by reintroduction of water
  - Shrinkage will occur (5% -15%)
    - lower in kaolinite and illite based clays
    - Therefore preferable as reduced structural failure
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- Initial heating on firing drives off further water
  - Decomposition of hydroxyl groups
  - Clay-OH-HO-Clay  $\rightarrow$  Clay-O-Clay + H<sub>2</sub>O<sub>(g)</sub> (chemically bound water)
  - This occurs  $\sim$  500°C and is irreversible
  - Formation of metakaolin
  - Loss of platelet structure, increase in amorphous phase
- Continues up to 1000°C known as biscuitware
  - Highly porous, good for application of glaze slips
- 950-1050°C vitrification begins
  - Further production of liquid/amorphous phases
  - Spinels (Si<sub>3</sub>Al<sub>4</sub>O<sub>12</sub>) may also be formed depending on initial composition of clay
- 1050-1200°C+ formation of mullite (3Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>) and cristoballite (SiO<sub>2</sub>)
  - Needle like structures appear
  - transformation temperatures can vary depending fluxing phases - enhanced by feldspar additions
- Pottery type often defined by the firing temperature

# Traditional Ceramics



## **Earthenware**

Relatively coarse red clays  
 Fairly low firing 950-1050°C  
 Minimal vitrification  
 Porous if not glazed

## **Stoneware**

Similar to Earthenware  
 Higher Firing 1200-1300°C  
 At least partially vitrified  
 Stronger & nonporous

## **Porcelain**

Appeared in T'ang Dynasty China 618-907AD  
 From fine kaolin clay, quartz & feldspar  
 Fully vitrified 1250-1300°C  
 White, translucent, resonant  
 Fine quartz grains in glassy matrix

## **Soft Paste Porcelain**

Lower kaolin, therefore alumina content

Allows lower Firing

less plastic unfired body

Not as tough, rare

## **Hard Paste Porcelain**

Higher kaolin & feldspar

Good plasticity and formability

But needs higher firing 1300-1400°C

1<sup>st</sup> European pieces ~1707AD in Saxony

## **Bone China**

Similar to HPP but with 50% animal bone

Calcium phosphate helps flux the vitrification

Improves strength, translucency & whiteness

Perfected by Josiah Spode, England end 18th century

Known as "Spode China" or "English China"



# Technical Ceramics

- Most likely raw material form will be a powder
- Powders are the general source of the ceramic material in thick film processing
- They form the heart of the system, other components will often be tailored round the powder
- Other ingredients basically facilitate the processing of the powder
- Hold it in form and shape until formed into a consolidated ceramic body during firing

Powders can be manufactured by several Methods

Solid State reactions

Sol-Gel

Combustion

Precipitation

Vapour Phase reaction

All will result in differing characteristics

***Surface Area , Size and Shape***

# Some Powder Definitions

- Primary Particle** - Smallest powder unit , cannot easily breakdown further in very fine ceramics may be a single crystallite, but most often polycrystalline grain
- Agglomerates** – Clusters of primary particles – what is generally in the bottle. Detrimental effect on processing, Need to be broken down by milling. Soft agglomerates are weakly bonded easy to break down, hard agglomerates have strong interparticle bonds – can be bad news.
- Particles** – General term, including both of the above.
- Granules** - larger agglomerates 0.1-1mm in diameter, often formed on purpose for dry flow characteristics for mass handling and mould filling in automated processes
- Flocs** - clusters of particles held together by electrostatic forces often in suspensions – very soft agglomerates
- Colloids** - Very fine particles (down to 10's nm scale), held in suspension by brownian motion, if good will be highly stable.
- Aggregates** - very large particles >1mm.

# Powder-Ceramic Relationships

## ***Dense Film***

- Particle Size – Fine (<1 $\mu$ m) preferred  
can be larger but higher firing required
- Size distribution – Narrow
- Shape – Spherical or equiaxed
- Agglomeration – Minimal

## ***Porous Film***

- Particle Size – larger OK (0.7 up to 5 $\mu$ m)
- Size distribution – wider or multimodal
- Shape – wider scope, not so  
critical for densification  
but can affect rheology
- Agglomeration – still low levels preferred  
for rheological reasons

# Other Powder Considerations

## Shape

### *Spherical*

- The “perfect” powder, most theoretical models assume spheres

### *Irregular*

- Most common
- SSA greater than equivalent sphere
- Will not pack as well as spheres

### *Porous*

- High SSA , pores may interact with solvent, dispersant & binder.
- Agglomerated or flocced systems may exhibit pseudo-porosity and time dependant rheology

### *Platelet*

- High aspect ratio, important feature in formability of clay based ceramics
- In slurries will have time dependant rheological properties
- May be difficult to attain good packing and green densities

## Density

- Most formulations based around wt% as mass is easy to deal with
- Although most interactions within a slurry occur with respect to vol%
- Therefore density is important when creating or modifying slurries
  - Ceramic densities can vary widely eg  $\text{SiO}_2$  at  $2.16\text{g/cm}^3$  to WC at  $15.6\text{g/cm}^3$
- Many slurries in the region of 25-35vol% of solid
  - Addition of pore former is another important aspect (graphite  $\sim 2.09\text{-}2.23\text{g/cm}^3$ ) and should always be initially considered in terms of volume
  - Density of ceramic is key, not to be confused with “bulk density” which is a measure of how well a powder packs

# Powder Dispersion

- Powders from bottles/storage will often be formed from agglomerates or floccs
  - This is especially true of finer powders
  - For dry processing a free-flowing granular powder will be preferred
    - Reduced blocking, better packing
    - For wet processing some form of milling mixing will be employed
    - Impart energy to breakdown agglomerates
    - Effects may be enhanced by use of dispersants
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- Ball milling – low energy,
    - Low viscosity systems – dispersion milling for slip based technologies
    - Impact action between balls and balls-container breaks down agglomerates
  - Attrition milling, Planetary Ball milling, vibratory milling
    - Higher energy approach – still impact based
    - Harder agglomerates, higher viscosity systems, size reduction
  - High shear mixing
    - Two/triple roll milling, Z-blade mixer, high intensity mixer
    - Dispersion of powders into very high viscosity mixes
    - Inks, pastes, dough
    - Application of shear disperses agglomerates

# Bulk Shaping Methods

Fall into 3 main Categories

- Powder Compaction
- Plastic Forming
- Casting

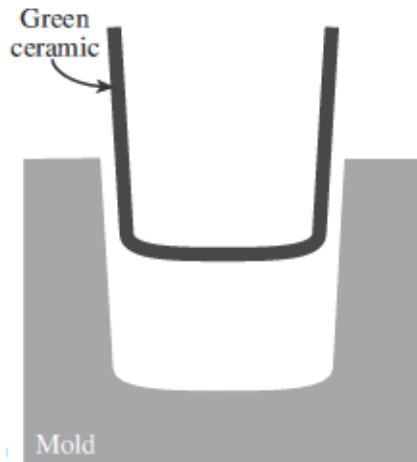
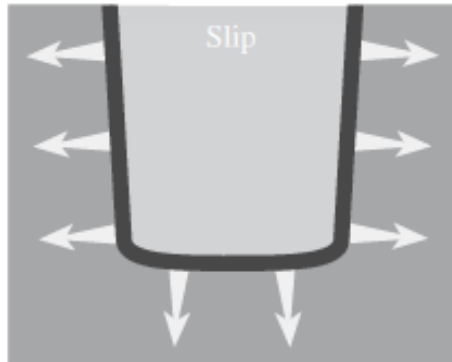
<i>Shaping method</i>	<i>Type of feed material</i>	<i>Type of shape</i>
Dry pressing	Free-flowing granules	Small and simple
Isostatic pressing	Fragile granules	Larger and more intricate
Extrusion	Plastic mass using a viscous polymer solution	Elongated with constant cross section
Injection molding	Organic binder giving fluidity when hot	Complex
Slip casting	Free-flowing cream	Mainly hollow

Plastic forming and Casting share many of the organic constituents as Thick film processing (to be discussed in a later lecture) however at much higher solids loading.

Aim is to end up with a green (unfired) form as close as possible to final fired shape (Net shape)

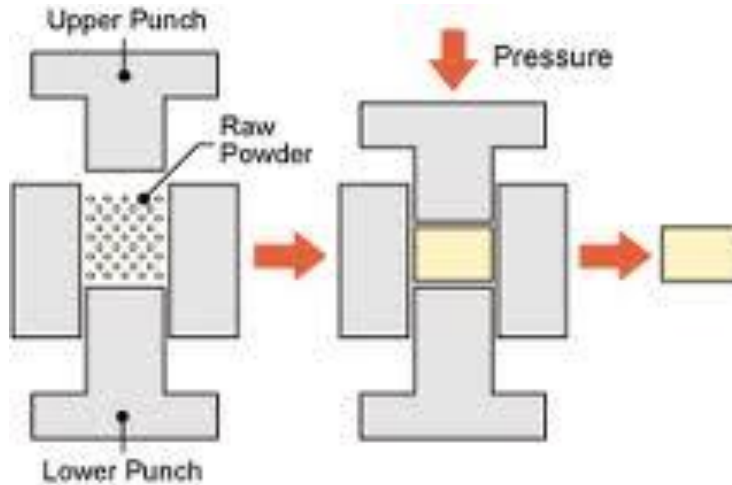
Minimise green machining or other post forming operations

# Slip Casting

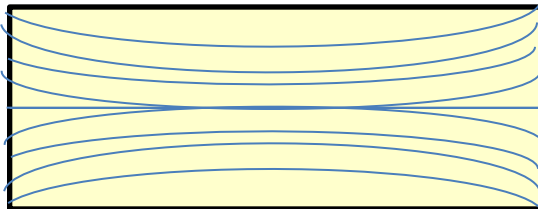


- Well established technique in pottery industry
  - Low cost and efficient for producing complex shapes
  - Most hollow ceramic objects (such as whitewares) produced this way
- A porous mould is created by casting plaster of paris ( $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ ) around master model of green part
  - Scaled to allow for shrinkage
- Aqueous based slip is poured into this mould
  - Good dispersion essential to prevent settling
- Water is drawn by capillary action from slip into mould walls
  - Creates a layer of dry ceramic on walls of mould
  - Once a sufficient thickness is built up excess slip drained away
- Green ceramic form removed from mould ready for final drying and firing

# Dry Pressing (Uniaxial)



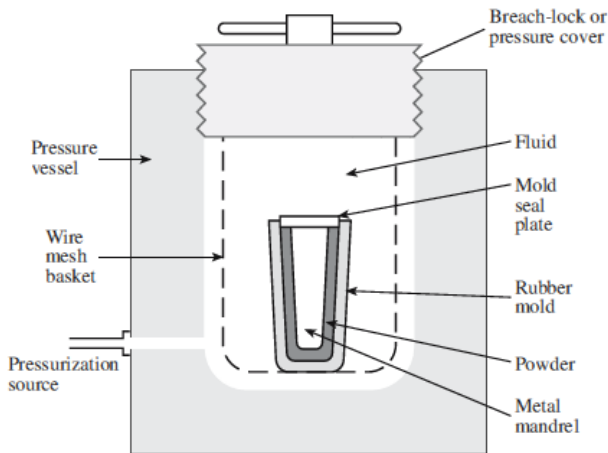
Schematic of uniaxial pressing



Representation of stress lines in uniaxially pressed pellet

- Suited to production of simple shapes
- Free flowing powder is best
  - Allows powder to move and pack during pressing operation
  - Larger particle sizes preferable for this
  - Often an application for granules
  - Fine particles may “block”
  - Leads to flaws in final piece
- Sometimes a small amount of binder can be added
  - Up to 5wt%
  - Helps green strength and handleability
- Uniaxial nature has uneven pressure distribution
  - can lead to stress fields in pellets
  - Cone & cup failures or subsurface cracking can result

# Cold Isostatic & Hot Isostatic Pressing



Wet Bag Isostatic Pressing

## **Cold Isostatic Pressing (CIP)**

Pressure applied by fluid (oil or water)

Even distribution of pressure onto powder

**Wet bag** is simplest form

Powder placed into rubber bag with any other formers

Bag placed into chamber and sealed

Chamber filled and pressurised

Pressure slowly released and bag removed

Wide range of sizes & shapes, simple tooling, uniform density

Only simple shapes, slow process

**Dry bag** incorporates rubber bag into mould

Powder introduced along with any formers

Fluid introduced and pressurised

Removal of pressure releases bag and part removed

Full automation possible, faster cycles, more complex parts

Spark plug Insulation classic example

**Hot Isostatic Pressing (HIP)** combines heat and pressure

Process referred to as HIPing, product is HIPed

Furnace inside pressure vessel

Preformed products used placed inside pressure vessel

2 flavours – Encapsulated with preform in deformable container

Non Encapsulated here presintered preform is used

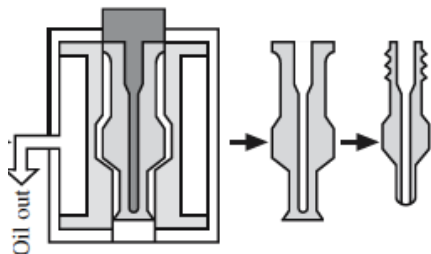
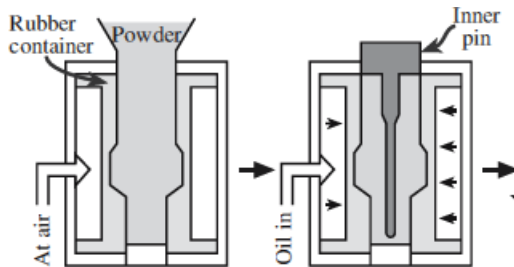
Gas such as argon used as pressurising fluid

Temps up to 2000°C have been used

Used for hard or refractory materials eg SiN

Also been used for piezoelectrics PZT, BaTiO<sub>3</sub>, SrTiO<sub>3</sub>

Good density with low grain growth – but costly



Dry Bag Isostatic Pressing

# ViscoPlastic Processing (VPP)

<i>Refractory alumina</i>	<i>Vol%</i>
Alumina (<20 $\mu$ m)	50
Hydroxyethyl cellulose	6
Water	44
AlCl <sub>3</sub> (pH > 8.5)	<1

Model VPP Formulation

- Number of processes revolve around VPP
  - This involves turning the ceramic into a plastic mass
  - Consistency varies between putty and bread dough
- Generally based around aqueous formulations
- Premixed under high shear conditions to break up agglomerates and evenly disperse ceramic
- Plastic mass has high solids loading and good formability and high green density
- Near net shape processes possible (injection moulding)



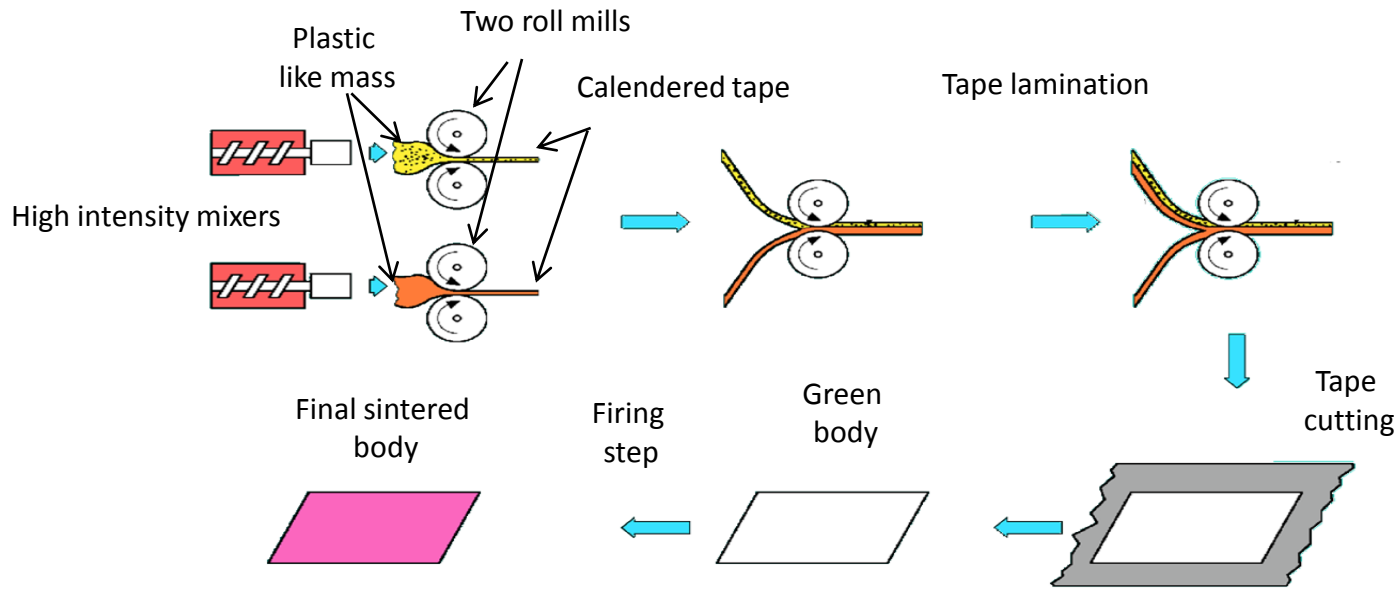
High Intensity Mixer



Two Roll Mill

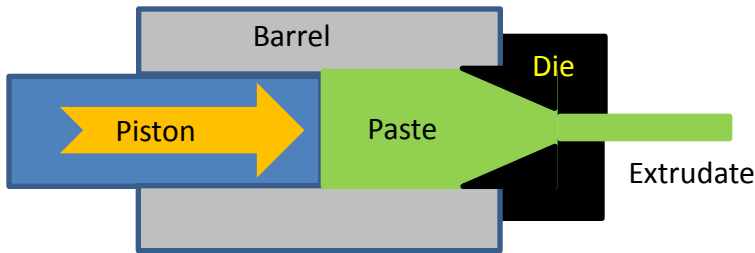


# Rolling/ Calendering

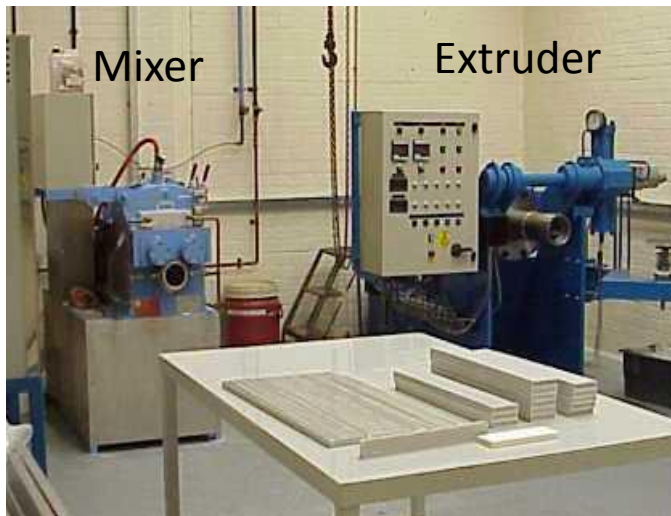


- Produces large sheets of material
- High shear process allows high solids loading
- Dough constancy allows thicker sheets (mm range) to be produced
- Sequential rolling can also result in layers of 1-5micron in thickness
- High solids loading can minimise firing shrinkage
- Careful control of green body characteristics to balance formability and sintering

# Ram Extrusion



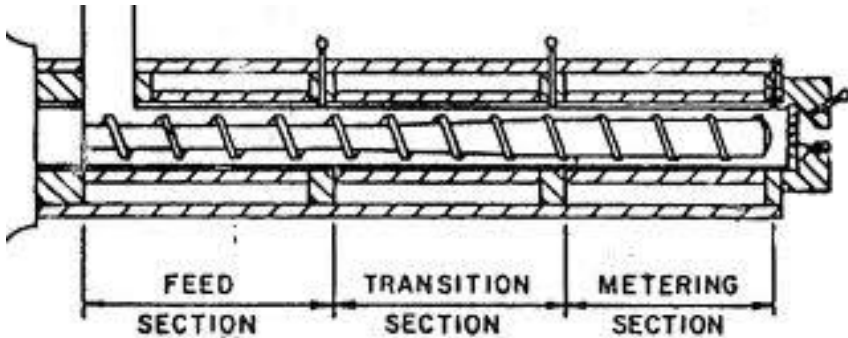
Schematic of ram extruder



High intensity mixer and ram extruder in industrial development lab

- Extrusion Produces controlled cross sections with high aspect ratio
- Forms may be solid or hollow
- Ram extrusion is the most basic extrusion process
  - Think toothpaste out of a tube
- Barrel is preloaded with VPP paste
- Piston is primed and pressure applied
- Forces paste out through die
  
- Extrudate can be cut to desired length dried then fired
- Batch Process with premixing required

# Screw Extrusion



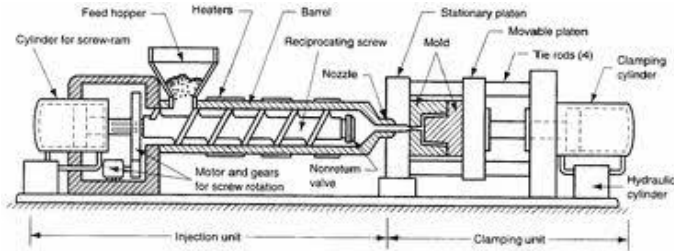
Cross section of screw extruder



Lab scale twin screw extruder for both mixing and extrusion

- General principles same as ram extrusion
  - Material is forced along barrel and out through controlled section die
  - This time transport mechanism is via Archimedean screw
- Increase in root diameter along length increases shear
  - Allows mixing and de-airs paste
  - Continuous process
- Ceramic can also be mixed with thermoplastic and extruded hot (150-200°C)
  - Heavily filled polymer processing
- Twin screw designs widespread
  - Improve transport
  - Promote mixing
- Can allow for elimination of initial high intensity premixing process

# Injection Moulding



Schematic of injection moulder



Selection of injection moulded parts

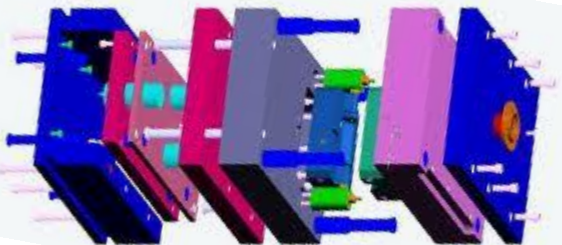


Diagram of injection moulding tool

Another polymer related process

Both ram and screw version exist

Can be used with VPP or thermoplastic processing

Again is it polymer or ceramic processing?

Other additives often used to modify rheology eg lubricants

## **Process**

As material moves along the screw it gathers at the tip

Screw moves back under this pressure

At a defined point the screw plunges forward

Material injected into mould

If Thermoplastic it cools and is then ejected

Cycle repeats

Transport phase overlaps cooling to minimise cycle times

Complex shapes can be produced

Although some shrinkage on firing

Moulds (tooling) complex and expensive

Limited use for prototyping

Better for long production runs of many 1000's units