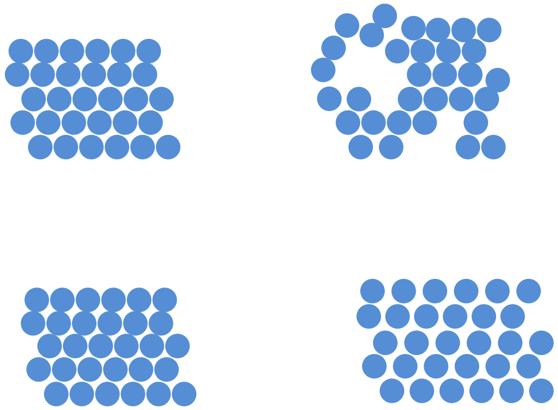
EMA5646
Ceramic Processing
6 Green Body Formation

Introduction

❑General requirements for green body formation

Rahaman (2003), p. 328

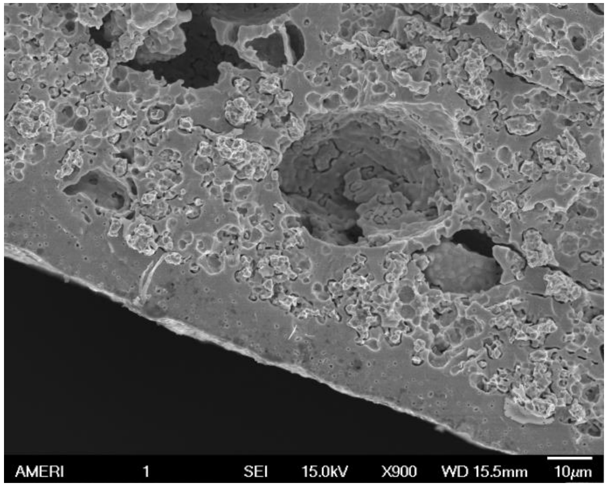
- **<u>Homogeneous packing of particles</u>**
  Severe variation in powder packing will lead to heterogeneity in final product microstructure and, in most cases, inferior properties (mechanical or thermal)
- **<u>High packing density of particles</u>**
  Higher powder packing density leads to higher density after sintering



❑Special scenarios

- Introducing heterogeneity
  - Example: functional graded coating or electrodes
- Reducing packing density
  - Example: high porosity wanted for electrodes for fuel cells

NiO-YSZ/YSZ bilayer co-sintered Cross-section (SEM by Shichen Sun)



Methods for Green Body Formation (1)

❑Mechanical compaction

Rahaman (2003), p. 328-329

Pressing dry or semi-dry powders in metal dies with mechanical pressure (uniaxial or isostatic)

- Advantages: simplest, fast process
- Disadvantages: limited shape and microstructure uniformity

❑Casting

Casting ceramic powder slurry/suspension with low enough viscosity that flows under its own weight

- Advantages: form complex shape
- Disadvantage: involves drying of solvent, volume shrinkage might be large

❑Plastic forming

Plastically shaping thick ceramic powder paste/doll by applying mechanical stress

- Advantages: fast, continuous production
- Disadvantages: limited shape

Dry-pressing die

http://www.ebay.co.uk/itm/20mm-Diameter-ID-Pellet-Press-Steel-Dry-Pressing-Die-Set-Mold-/200438956668

Press

Tape-casting green ceramic tape

Tape-casting green ceramic ware

http://www.cgcri.res.in/page.php?id=43
http://www.veniceclayartists.com/african-pottery-arts-traditional-contemporary/

Extruded ceramic parts after sintering

Extrusion of ceramic honeycomb

http://www.ikts.fraunhofer.de/en/research_fields/processes_and_components/Shaping/Extrusion.html

Methods for Green Body Formation (2)

Forming method	Feed material	Shape of green body
Mechanical pressing		
Die compaction	Powder or free flowing granules	Small simple shape, mostly pellets or short cylinders
Isostatic pressing	Powder or free flowing granules	Large, more intricate shapes
Casting		
Slip casting	Free-flowing slurry with **low** binder content	Thin walled shape, can be intricate
Tape casting	Free-flowing slurry with **high** binder content	Thin sheets/tapes
Plastic forming		
Extrusion	Thick paste of powder and binder solution	Elongated shape with uniform cross-section
Injection molding	Granulated mixture of powder and solid binder	Small intricate shapes

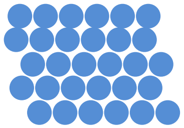
Table after Rahaman (2003), p. 329

Packing of Powders

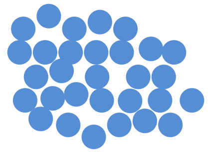
Rahaman (2003), p. 330

❑Models for powder packing

- **Regular (or ordered) packing**
  Mathematically simple



- **Random packing**
  More realistic



❑Parameters used to describe powder packing

- **Packing density**

$$\text{Packing density} = \frac{V_{solid}}{V_{total}} = \frac{V_{solid}}{V_{solid} + V_{space}}$$

- **Apparent volume (or relative bulk volume)**

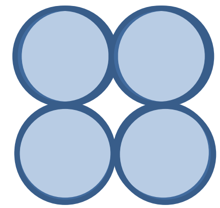
$$\text{Apparent volume } \mathrm{V_a} = \frac{V_{solid} + V_{space}}{V_{solid}} = \frac{1}{\text{Packing density}}$$

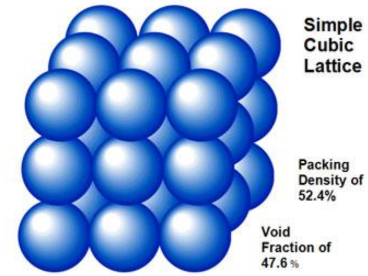
- **Coordination number (CN)**
  The number of particles that are in direct contact with a particular particle

Regular Packing of Monosized Spheres

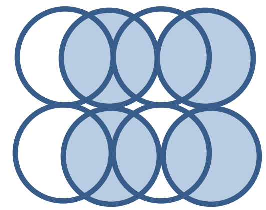
❑Examples of regular packing

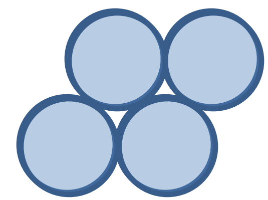
- (Simple) Cubic
  - Packing density 52.4%
  - CN = 6



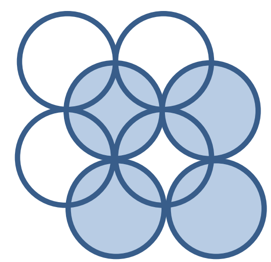


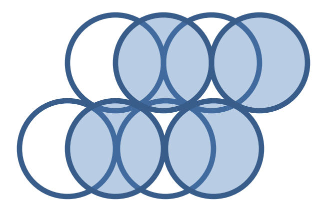
- Orthorhombic
  - Packing density 60.5%
  - CN = 8



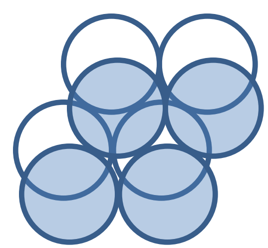


- Tetragonal-sphenoidal
  - Packing density 69.8%
  - CN = 10





- Rhombohedral (like in FCC or HCP)
  - Packing density 74.0%
  - CN = 12



Rahaman (2003), p. 330-332

Random Packing of Particles

❑Loose random packing

Powders are loaded into a container and are not allowed to re-arrange to as favorable state as possible

- This gives the so-called **<u>poured density</u>** or **<u>freely settled density</u>**

❑Dense random packing

Powders are loaded into a container and vibrated or tapped to reach a state of highest packing density

- This gives the so-called **<u>tap density</u>**

http://www.quantachrome.com/density/autotap.html

Rahaman (2003), p. 331-332

Random Packing of Monosized Particles

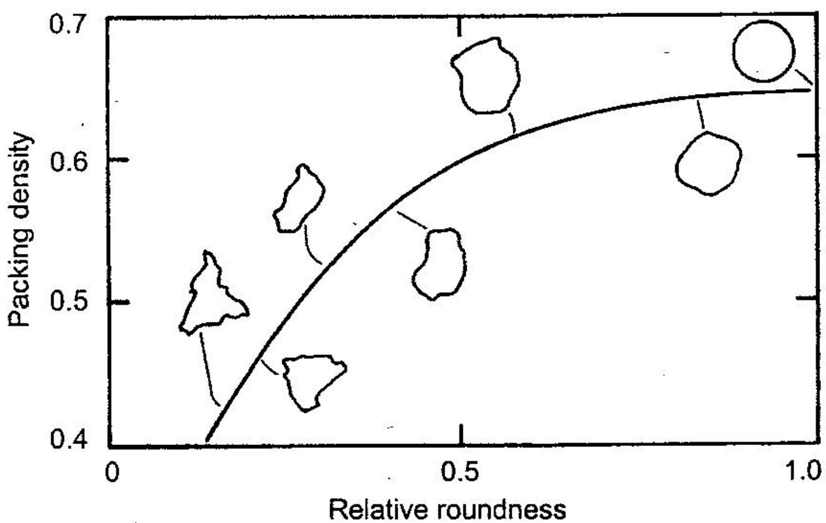
❑For <u>mono-sized spheres</u>

Rahaman (2003), p. 332-334

- Upper limit packing density for random packing of monosize sphere is ~63.5-64%
- Loose random packing gives packing density of ~57-61%
- The non-uniformity is local and, often small beyond 3 sphere diameter

❑Practical systems

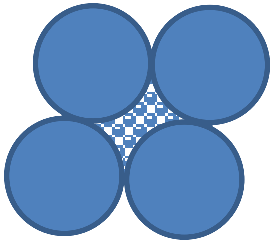
- Particle particles deviate from spheres and, often, the further it is away from sphere or equiaxial shape, the lower the packing density
- Anisotropic particles (e.g., needles or plates) usually give lower packing density; but they can give packing high density if there is preferred orientation/ordering



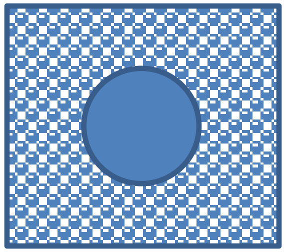
Particle shape	Aspect ratio	Packing density
Sphere	1	0.64
Cube	1	0.75
Rectangle	2:5:10	0.51
Plate	1:4:4	0.67
Plate	1:8:8	0.59
Cylinder	5	0.52
Cylinder	15	0.28
Cylinder	60	0.09
Disk	0.5	0.63
Tetrahedron	1	0.5

Random Packing of Bimodal Sized Spheres

- **Packing density could improve for bimodal spheres compared with monosized spheres**
  - For large particles → filling of interstitials between large spheres with smaller particles gives higher packing density



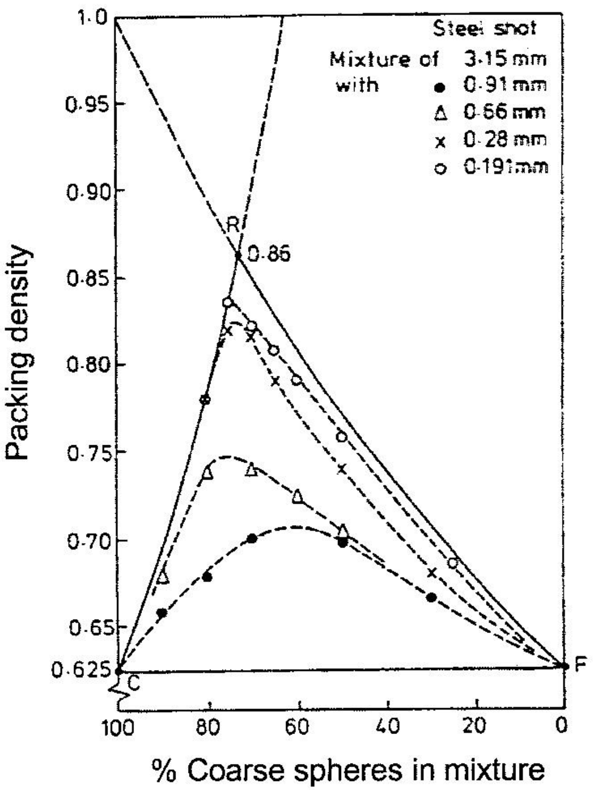
  - For small particles → replacing of regions of small spheres packing with large, dense particles also gives higher packing density

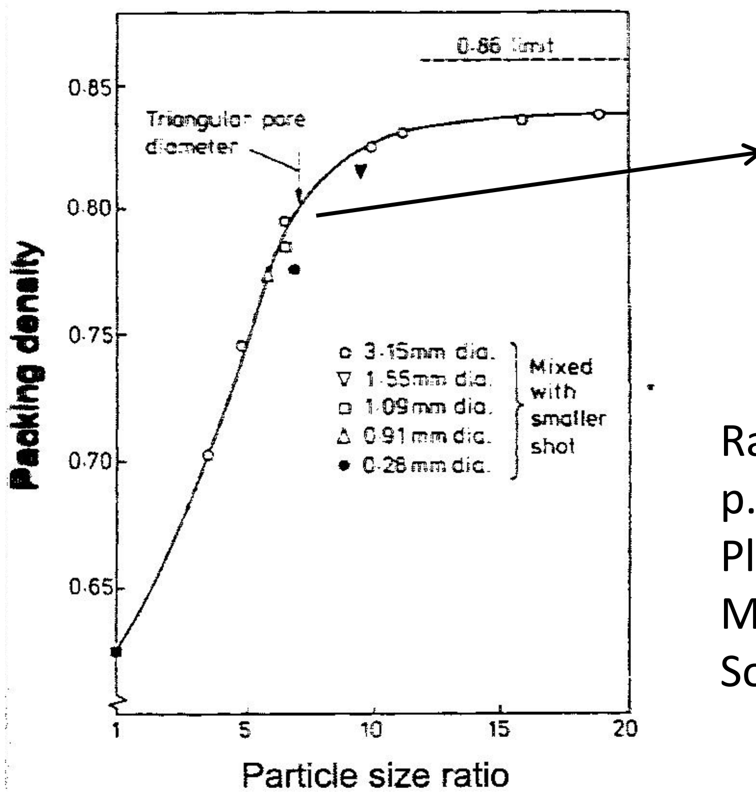


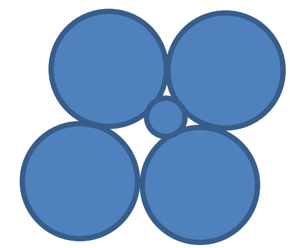
- **The packing density for bimodal sized spheres is a function of**
  - Ratio of sphere diameters
  - Fraction of large (or small) spheres

Size and Fraction Effect on Random Packing of Biomodal Sized Spheres

- For the same size ratio, at intermediate weight fraction for large particles equals ~0.733, the dense random packing density reaches highest, which, theoretically could reach ~0.86
- Dense random packing density increases as particle size ratio increases, reaching plateau at size ratio of ~15



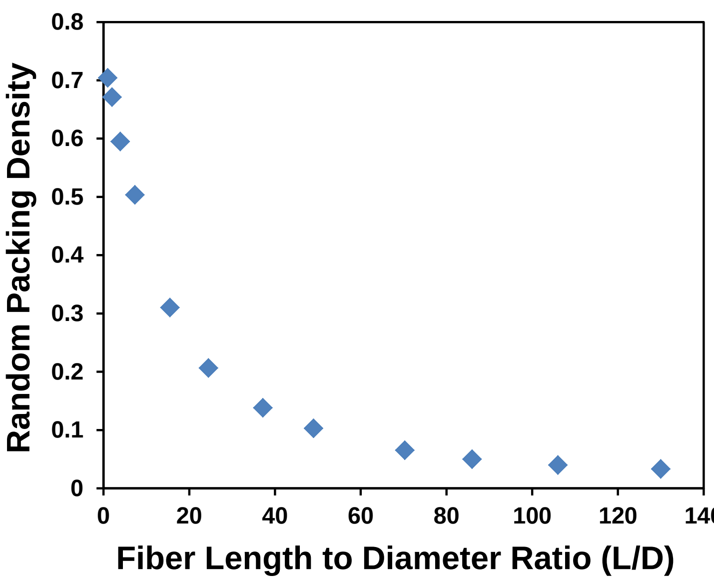




Rahaman (2003), p. 334-337
Plots original data from McGeary, J Am Ceram Soc, 1961 vol. 44, p513

Random Packing of Bimodal Sized Nonspherical Particles

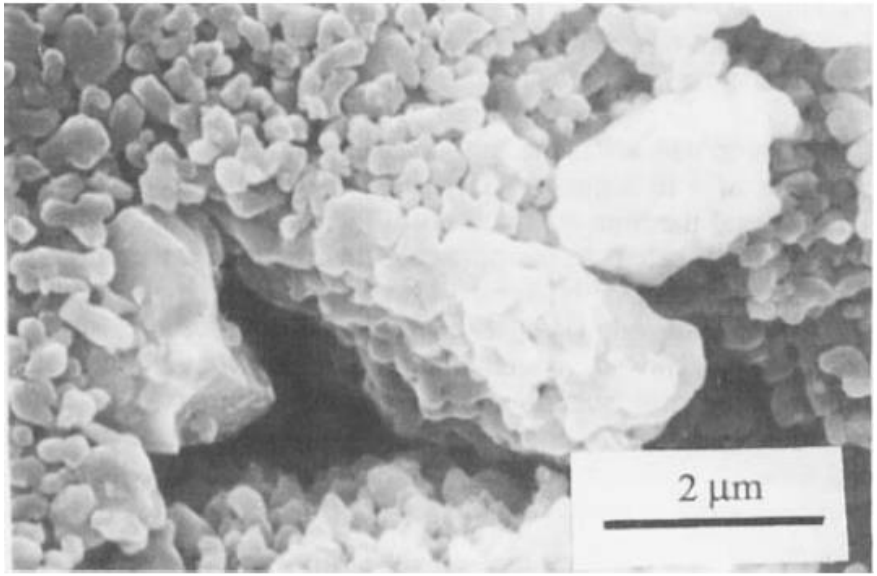
- ❑ **Similar to spheres, random packing of bimodal sized non-spherical particles also leads to increased packing density**
- ❑ **Packing density generally depends on**
  - Size ratio between two modes of particles
  - Weight fraction of larger (or smaller) particles
  - Particle shape
    - E.g.: fibers/whiskers give low packing density and it gets worse as whisker length to diameter aspect ratio increase → generally whiskers L/D ratio kept in range of 15-20

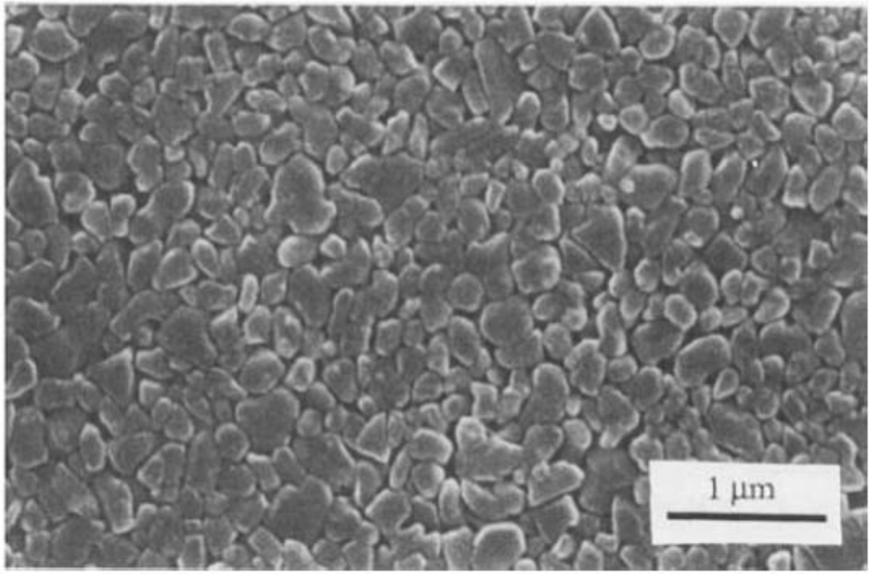


Whisker		Particle Dia. /Whisker D ratio				
L/D	Vol. %	0	0.11	0.94	14.30	∞
3.91	25	68.5	68.5	61.7	74.6	82.0
3.91	50	76.4	74.6	61.7	72.5	75.9
15.52	25	68.5	66.7	59.9	54.1	65.0
15.52	50	61.7	55.6	50.7	44.3	48.1
37.10	25	50.0	48.0	42.0	33.1	41.3
37.10	50	25.7			22.6	25.6

Random Packing of Particles with Continuous Size Distribution

- ❑Practical powders have continuous size distribution
- ❑Particles with continuous size distribution could, in principle, pack to very high density, and normally, the wider the distribution, the higher the density
- ❑Draw backs of using powders with very wide size distribution: possibility of non-uniformity in green body and defects in sintering





Rahaman (2003), 341-344; Figures from Roosen, J Am Ceram Soc, 1988 vol. 71, p970

Mechanical Compaction

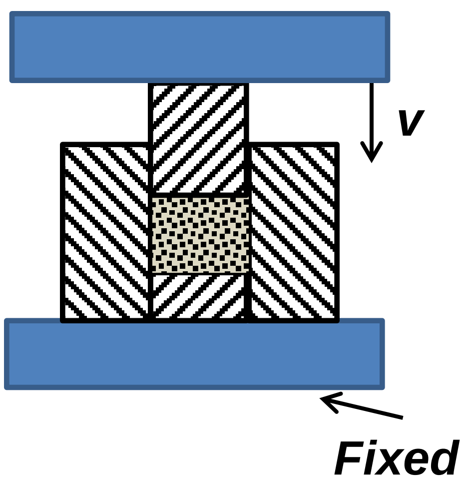
❑General features

- Moisture content in powders for dry and semi-dry pressing
  - < 2 wt% of water for dry pressing
  - < 5-20 wt.% for semidry pressing

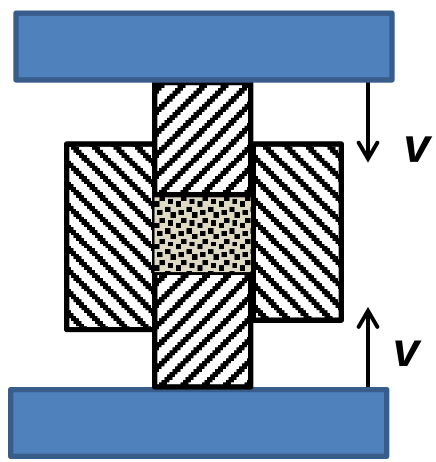
❑Die compaction

- Used for simple shapes – mostly disks and short cylinders
- Modes of operation:

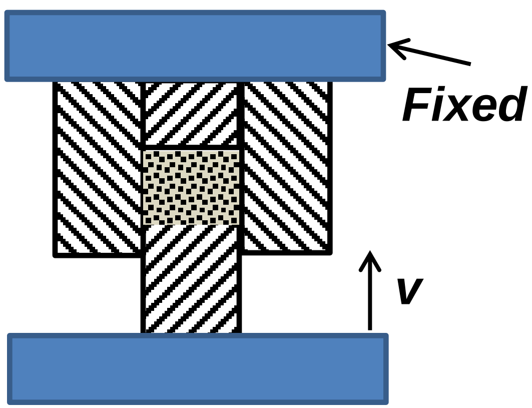
Single action mode



Dual action mode



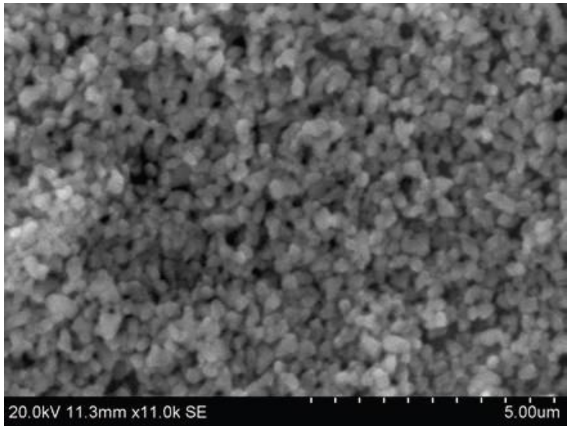
Floating mode

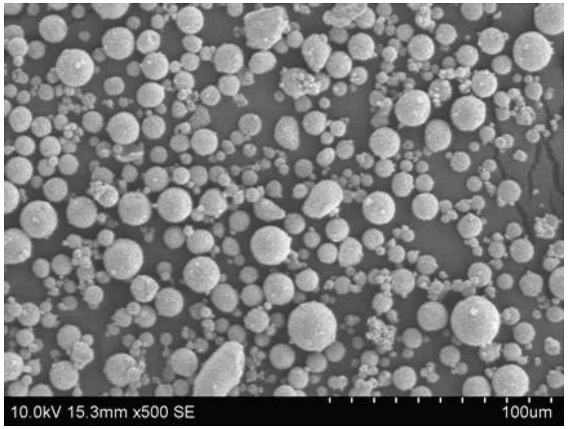


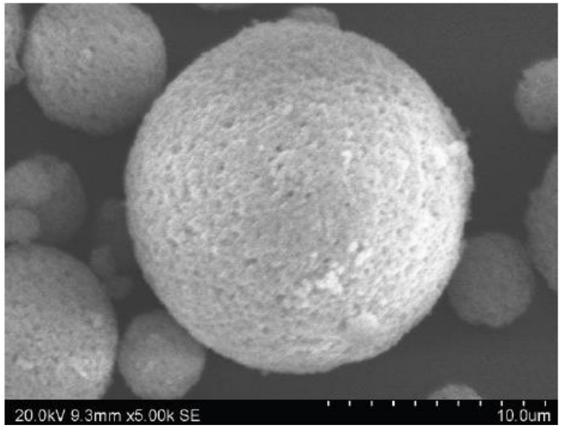
Powders & Granules for Die Filling

❑Powders used

- Fine powders
  - OK for lab, but poor flowablity for industrial production
- Granules (e.g., made by spray drying)
  - Size often ~10-400 μm
  - Improves flow capability
  - Often contain additives (e.g., PVA binder)







Abhisek Choudhary, ISRN Ceramics, 2013, 264194

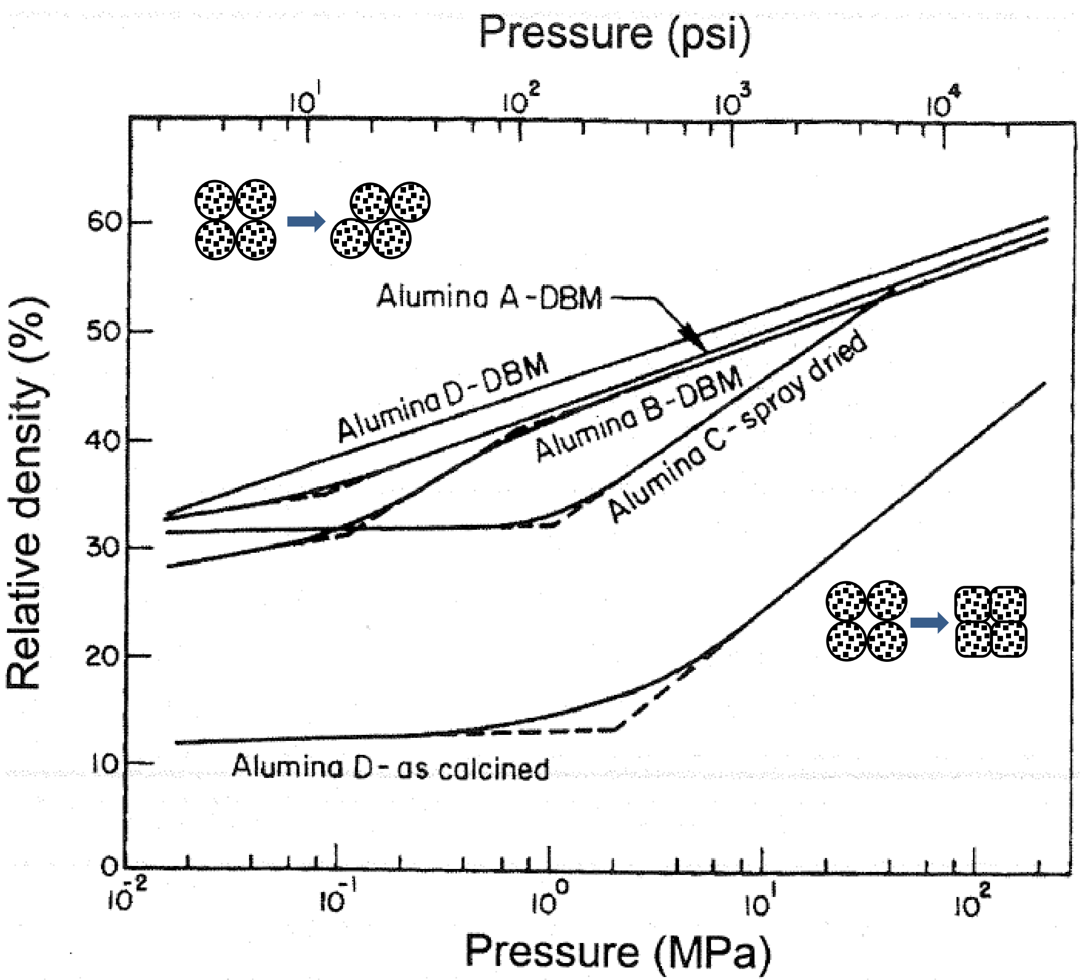
❑Die filling density: ~20-35%

Packing density of ~45-55% within each granule and ~60% for packing of granules

Die Compaction – Primary Powders vs. Granules

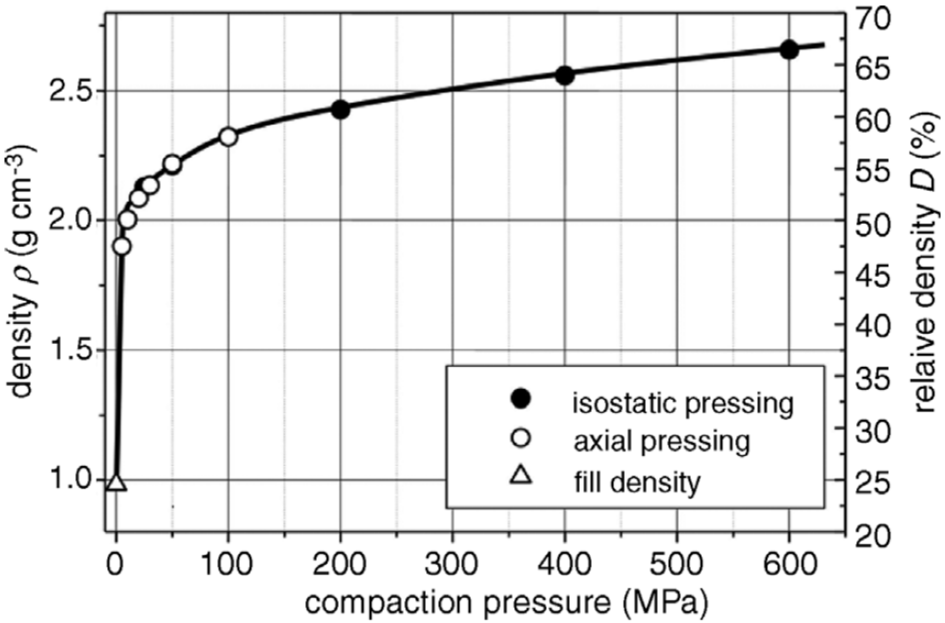
- **<u>One-stage</u> compaction for primary particles**
  - Packing density increases directly with pressure due to re-arrangements and fractures at higher pressure
- **<u>Two-stage</u> compaction for large granules/agglomerates**
  - Low pressure: packing density increases very slowly
    - Reduction of large voids by rearrangement of granules
  - Higher pressure: packing density increases more rapidly
    - Deformation and fragmentation of granules

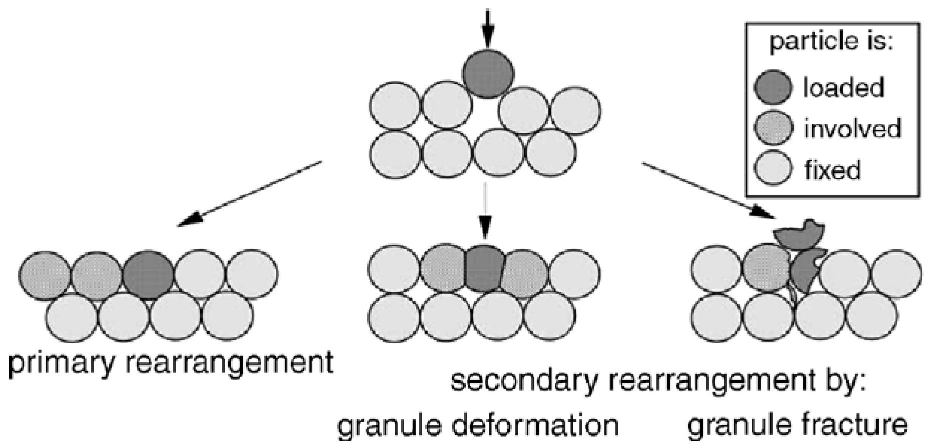
Rahaman (2003), 362-371; Figure from Niesz, D E et al. Mater Sci Research: Processing of Crystalline Ceramics; , v 11, 1978 p. 41



Die Compaction – Pressure Effects: Rearrangement, Deformation, & Fracture

- Generally, higher pressure leads to higher packing density, but saturates at ~random close packing density
- Different processes occur as pressure is applied including re-arrangement, deformation, and fracture

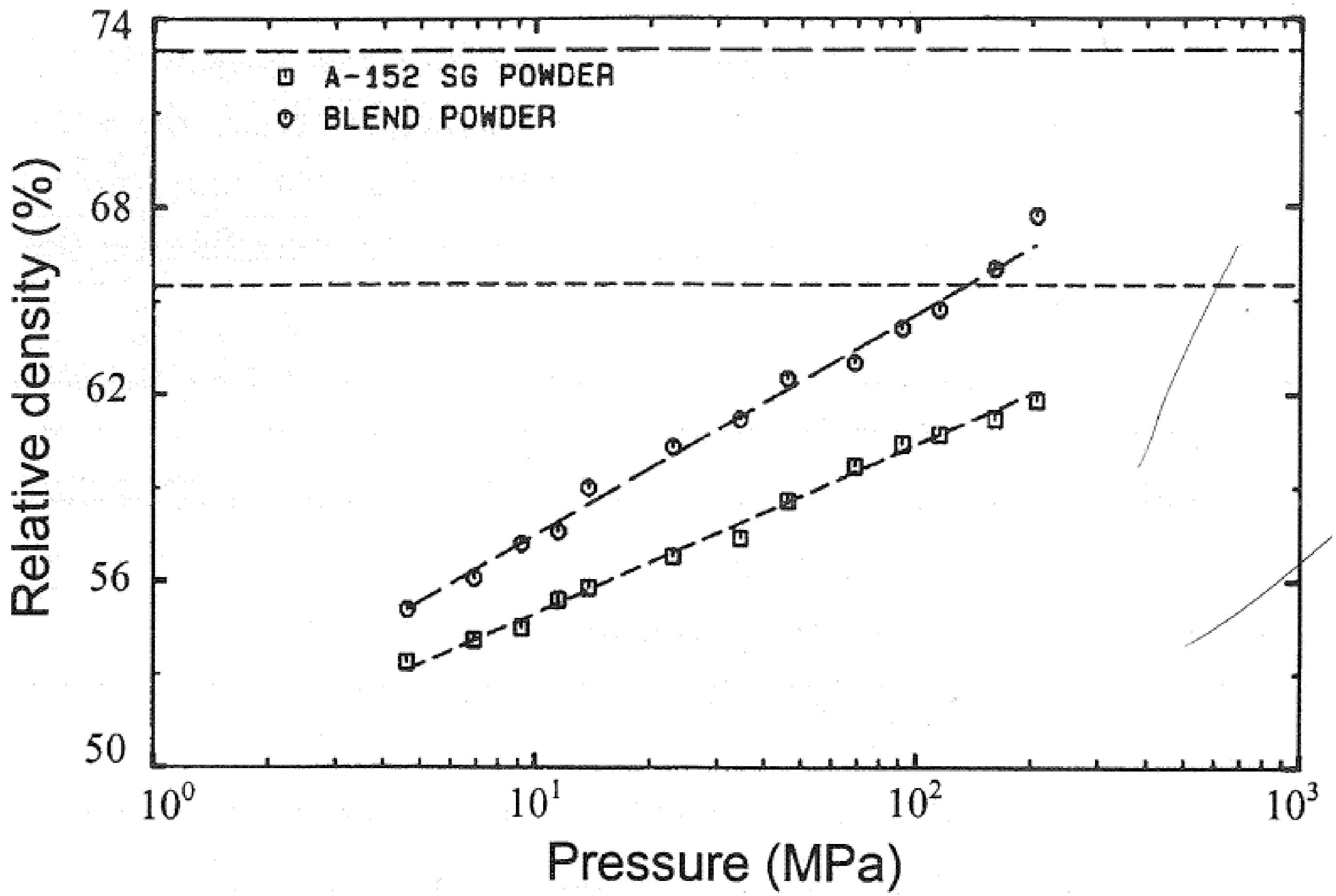




Rahaman (2003), 362-371; Figures credit of R Roberacker, Powder Compaction by Pressing, in Ceramics Science and Technology, Volume 3, Synthesis and Processing, 2012, p. 1-37

Die Compaction – Powder/Granule Size Distribution Effect

- Wider granule (or powder) size distribution (e.g., via blending) gives higher density

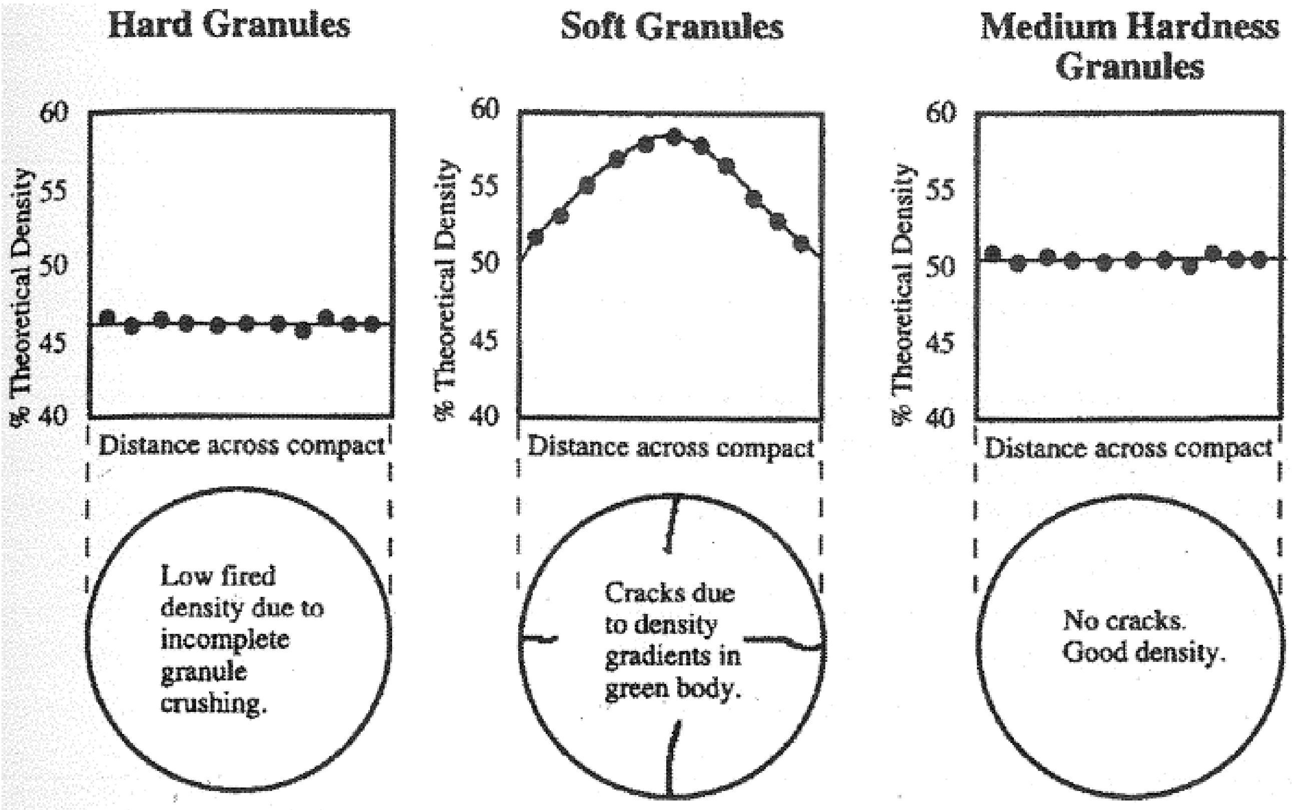


Rahaman (2003), 362-371; Figures credit of R. Zheng, J. Am. Ceram. Soc. 1988, Vol. 71, p. C456

Die Compaction – Granule Hardness Effect (1)

❑Granule hardness effect

- Too **hard** granules give low packing density due to intergranules pores
- Too **soft** granules give high packing density but possibly severe non-uniformity
- Medium hardness granules give high packing density and good uniformity

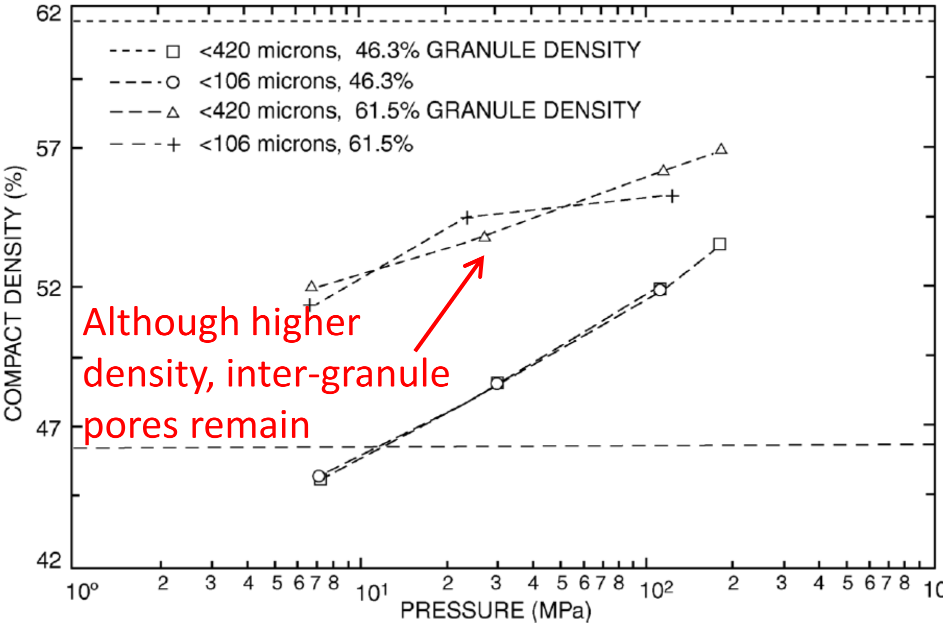


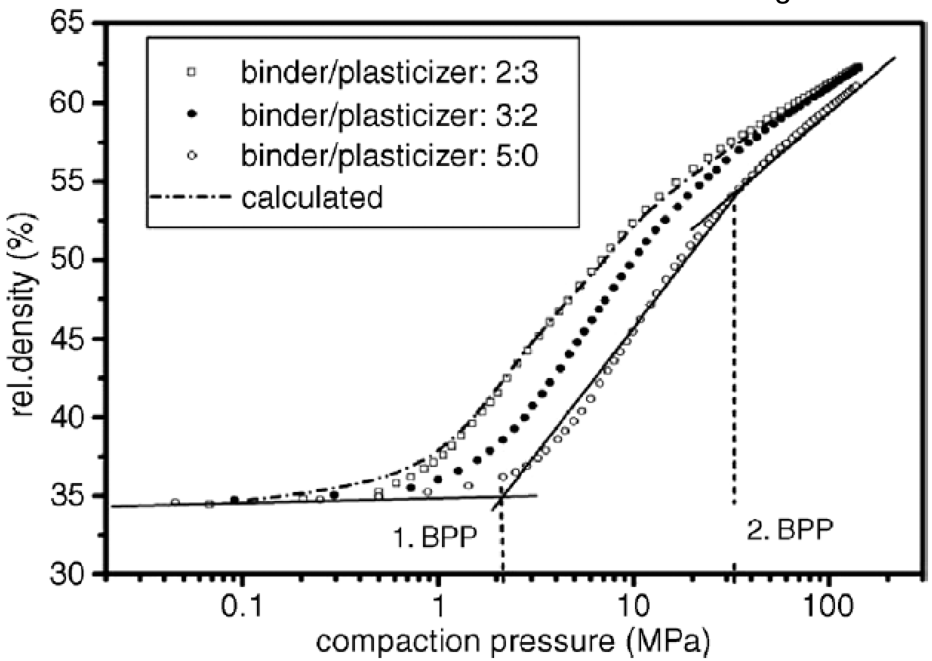
Rahaman (2003), 362-371; Figure credit of Glass SJ, MRS Bulletin, 1997 Vol. 22 (12), p. 24

Die Compaction – Granule Hardness Effect (2)

❑Granule hardness can be changed by

- Controlling dispersion of powders, e.g., use of partially floccutated slurry instead of fully stable colloidal slurry
- Using polymer binder with lower T_g or adding (more) plasticizer to reduce T_g





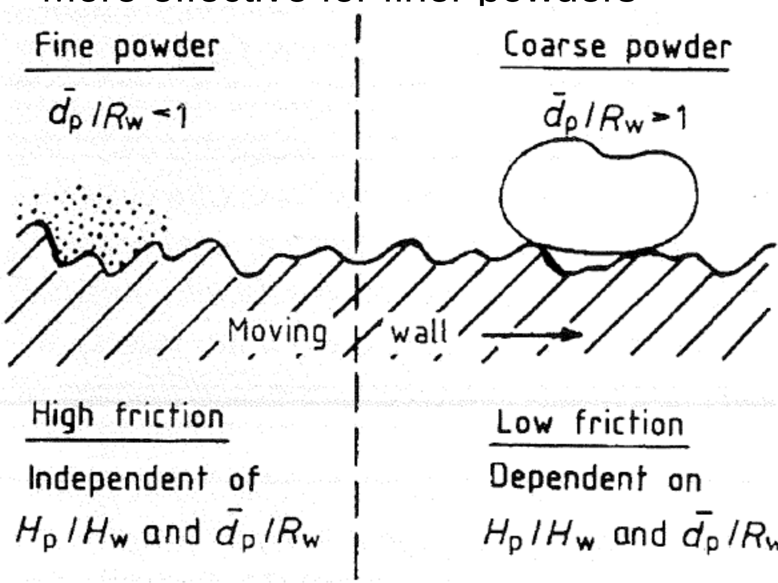
Rahaman (2003), 362-371; Figures credit of R. Zheng, J. Am. Ceram. Soc. 1988, Vol. 71, p. C456 and Agniel, Y. (1993) Bedeutung der Einzelgranalieneigenschaften zur Defektvermeidung in trockengepressten keramischen Modellpulvern. Ph.D. dissertation, Universit€at Karlsruhe, 1992, Institute for Ceramics in Mechanical Engineering IKM 009

Die Compaction –
Die and Powder Interaction Effects

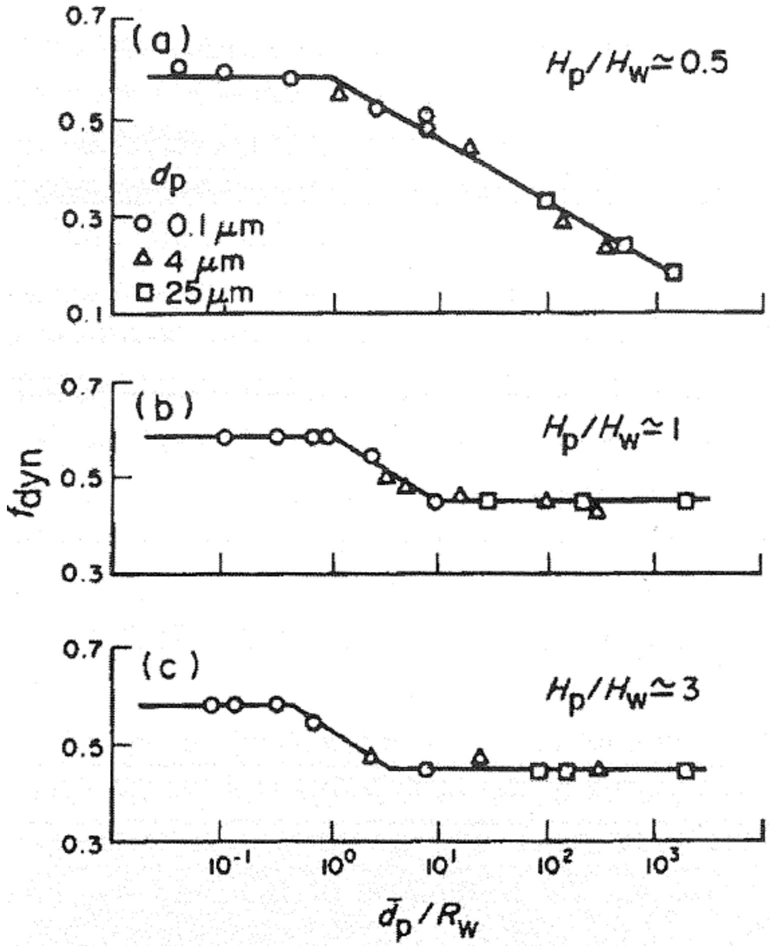
❑Factors influencing powder compaction

- Particle size d_p vs. die wall roughness R_w
  - Rougher the die wall or smaller the particles, higher the friction coefficient until plateauing
- Hardness of particles H_p vs. die wall H_w
  - Harder the die wall, lower the friction coefficient
- Direction of grooves on die wall
- Lubricant
  - More effective for finer powders

Slip within powder compact



Slip between powder and wall



Rahaman (2003), 362-371; Figures credit of van Groenou, Powder Metallurgy Int, 1978, vol. 10, p.206 and Strijbos S. Powder Technol, 1977, vol. 18, p.209

Release of Powder Compact after Pressing

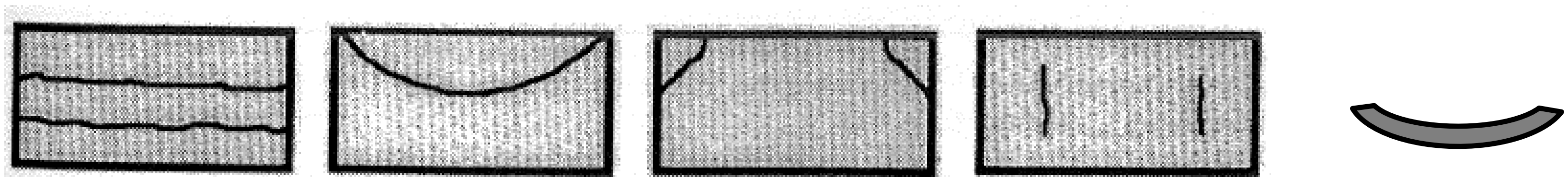
❑Phenomena of "Spring back"/Strain recovery

- After applied pressure is released, powder compact expands slightly and releases stored elastic energy
- Features
  - Generally more significant for higher pressure and/or higher organic contents
  - May increase friction between powder compact and sample and also cause damage to the sample
  - Lubricants (e.g., stearic acid) could help reduce friction and reduce pressure for ejection

Defects in Pressing

❑Defects

Delamination **Capping** **Ring capping** **Vertical cracks** **Warping/bending**



- Origins: pressure and/or density variation due to internal/wall frictions and inhomogeneous die filling

❑Approaches to mitigate defects

- Ensure uniform die filling: use power with good flow capability and uniformity
- Use organic binder
  - Increase compact strength
- Use lubricants
  - Reduces friction with wall and between particles
  - Decrease pressure needed and spring back
- Use small thickness to diameter ratio ***t*/*D***
  - generally <0.5 for single action <1 for double action

Rahaman (2003), 362-371

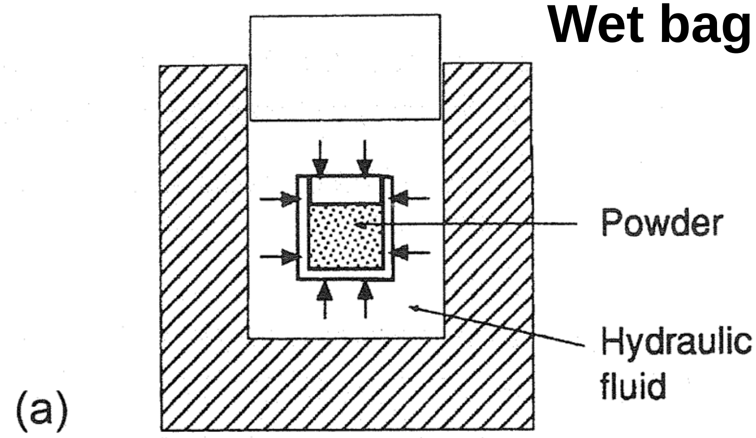
Isostatic Pressing

- **Use of fluid to transfer pressure in pressing process**
- **Advantages**
  - Uniform pressure
  - Higher pressure allowable
- **<u>Wet bag</u> isostatic pressing**

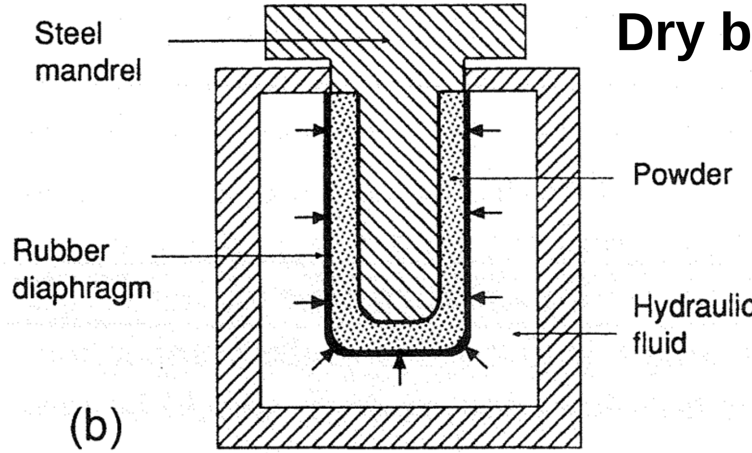
  Pre-shape the sample, load in soft bag, (vacuum) and immerse in hydraulic fluid, apply high pressure
  - Used for complex shape and large size sample
- **<u>Dry bag</u> isostatic pressing**

  Load powder in rubber thick rubber bag, with rigid core or support, then apply pressure
  - Easier for automation and used for small sample or simple shape

Wet bag



Dry bag



Rahaman (2003), 371-372

Casting

❑Casting

Casting ceramic powder slurry/suspension with low enough viscosity that flows under its own weight, followed by removal of liquid that leads to consolidation of powders

❑General requirements

- Homogeneous particle packing
- Green density as high as possible → High particle content in slurry
- Reasonable rheology → Not too high particle content in slurry

❑Advantages

- Low cost process capable of making complex (thin walled) shapes or thin sheets

❑Major categories

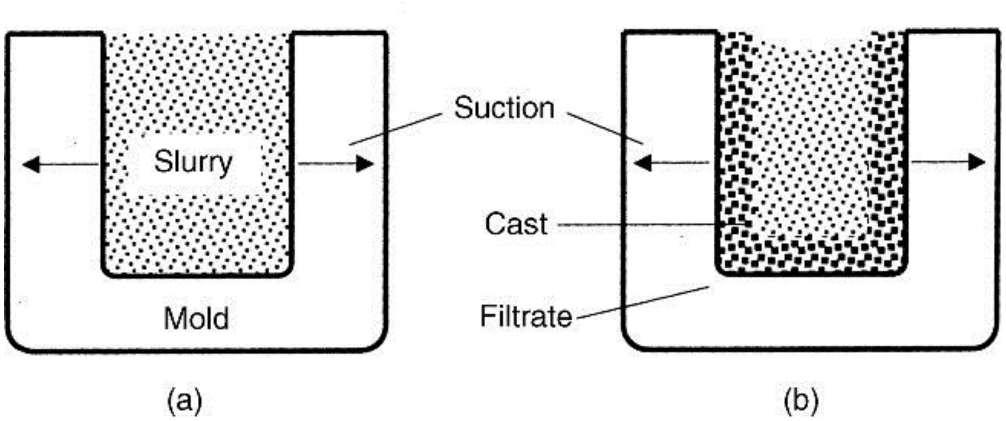
- Slip casting
- Tape casting
- Pressure casting
- Gel casting
- Electrophoretic deposition

Rahaman (2003), 362-371

Slip Casting (1)

❑Process description

Slurry (slip) is poured into porous mold, which suck solvent (e.g., water) away by capillary force



❑General slip casting mechanism

- Darcy's law

Solvent flux ***J***

$$J = \frac{K}{\eta_L} \cdot \frac{dp}{dx}$$

Implications: solvent flux ***J*** (i.e., casting rate) will increase if

- K Permeability of the porous medium (consolidated layer and porous mold) increases
- η_L Solvent viscosity decreases
- dp/dx Pressure gradient (in this case due to capillary suction) increases

Rahaman (2003), 372-391

Slip Casting (2)

- Thickness of cast L_c grows/increases with time following parabolic law

$$L_c^2 = \frac{2K_c p}{\eta_L (V_c / V_s - 1)} t$$

K_c	Permeability for the consolidated cast body
p	Pressure difference across the cast body
η_L	Solvent viscosity
V_c	Volume fraction of solid in the cast body
V_s	Volume fraction of solid in the slurry

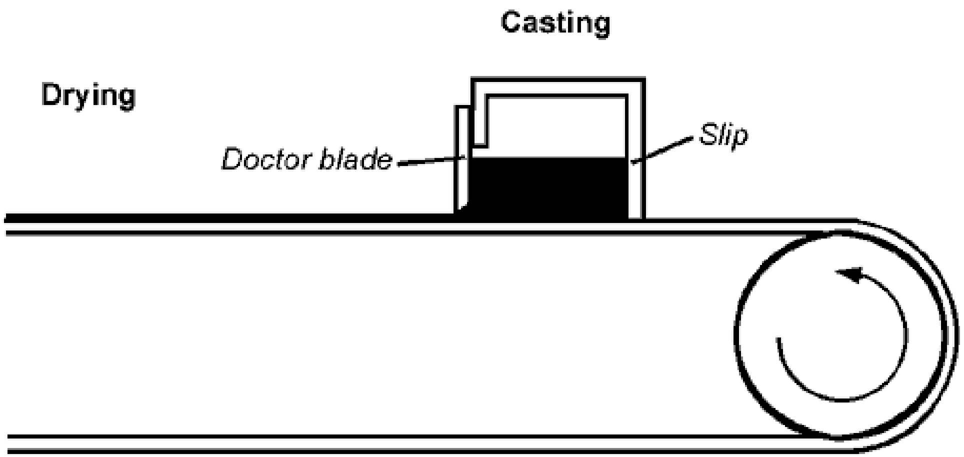
Implications:

- Cast thickness growth rate decreases with time (or cast thickness)
- Optimal pore size in mold for compromise between p and K_c
- Slurry should be partially stabilized to prevent too dense cast (which gives too low permeability) and too loose cast (which gives non-uniform microstructure)
- Increasing solid content or decreasing viscosity (e.g., via increasing temperature) lead to increased cast thickness growth rate

Rahaman (2003), 372-391

Tape Casting

- **Slurry cast onto carrying tape with thickness controlled by the gap between blade and tape**



http://www.keramverband.de/pic/ebild57.gif

- **Use**

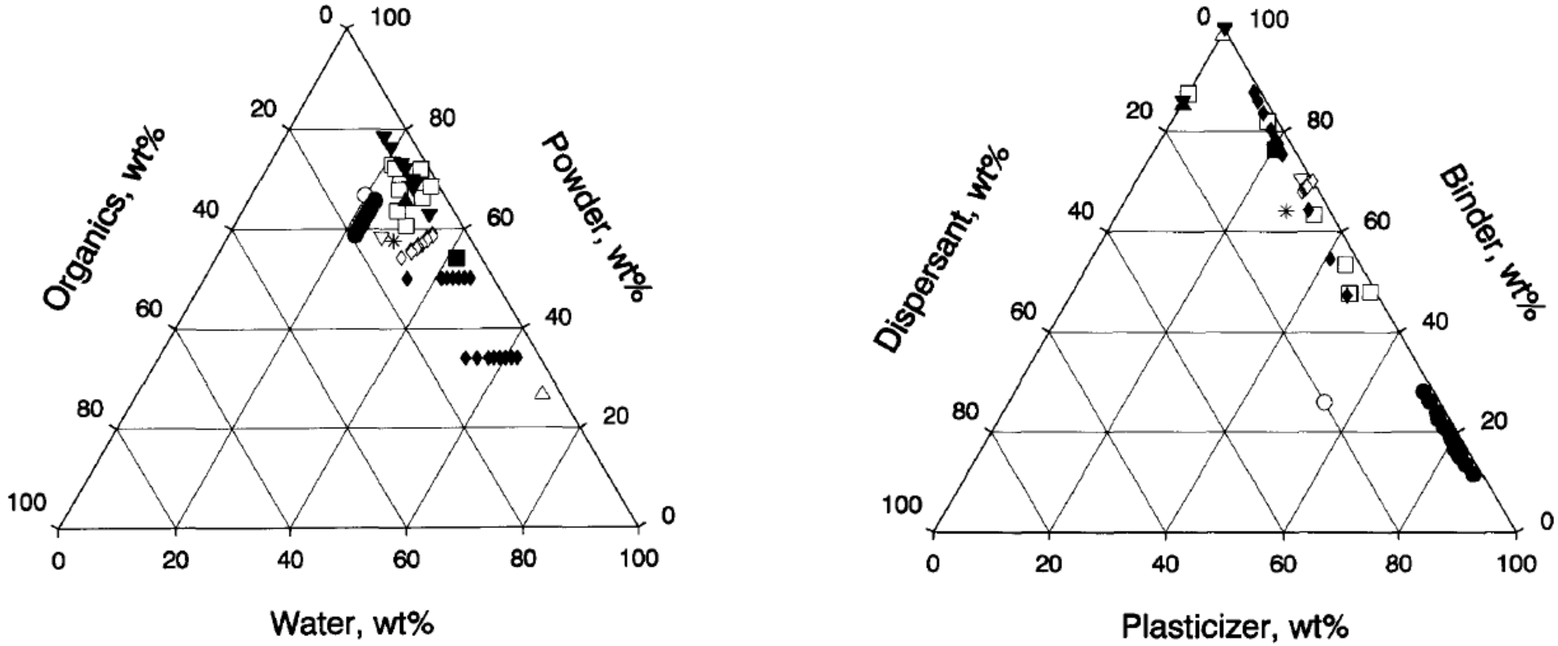
  For production of film/tapes with thickness ~10-1000 μm

- **Slurry formulation considerations**
  - Solvents:
    - Usually organic: Acetone or MEK for thin tapes and Toluene for thicker tapes (>0.25 mm)
    - Aqueous solvent getting more common: see Hotza and Greil, Mater Sci & Eng: A Vol202 (1-2), 1995, p 206
  - Ceramics: 30-80 wt%
  - Binder: ~1-5 wt% (~2-30 vol.%)
  - Plasticizer: 1-3 wt%
  - Dispersant: <~1 wt%

Rahaman (2003), 372-391

Tape Casting - Aqueous System Formulation

❑Ratios



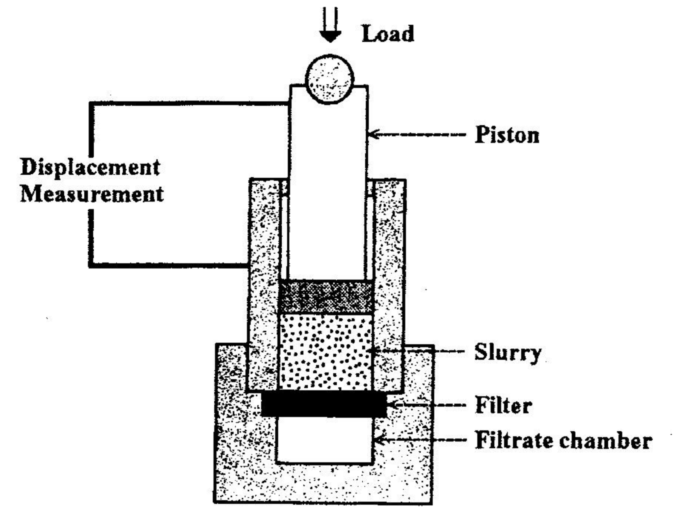
❑Examples:

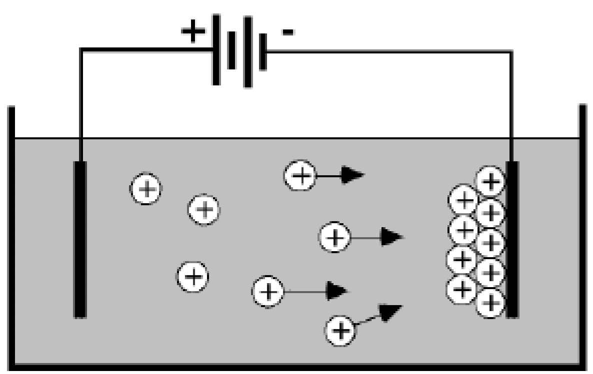
- Binder: PVA, PAA, PVAc, NH_4PA, cellulose ether, acrylic polymer and co-polymer
- Plasticizer: PEG, glycerol, PPG
- Dispersant: polyelectrolytes such as acryl sulfonic acid, NH_4PMA, NH_4PA

See Hotza and Greil, Mater Sci & Eng: A Vol202 (1-2), 1995, p 206

Other Casting-Based Techniques

- **Pressure casting**
  - Applying pressure in casting process
  - Advantage: faster consolidation/solvent removal
- **Gel casting**
  - Add organic monomer to cast slurry, which undergoes gelation (polymerization) process and prevents particle settling or segregation and also strengthen the body to withstand capillary stress during drying.
  - Advantage: thicker green body with low polymer content for easier burn out
- **Electrophoretic deposition**
  - Depositing green body from stable colloidal suspension via electrophoresis
  - Advantage: better controllability

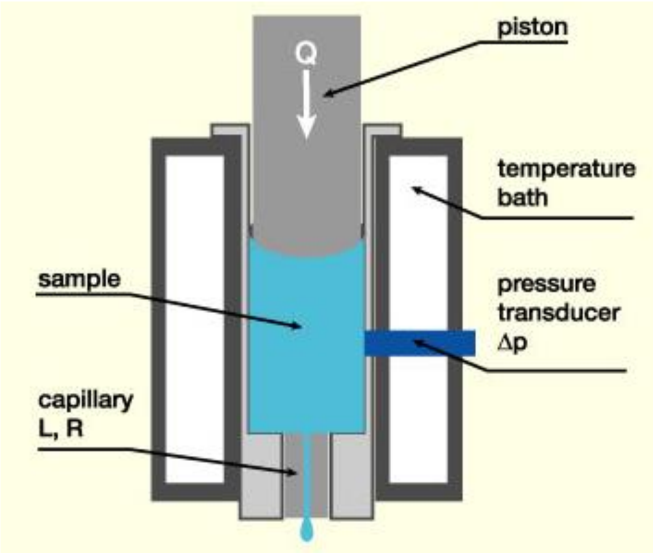




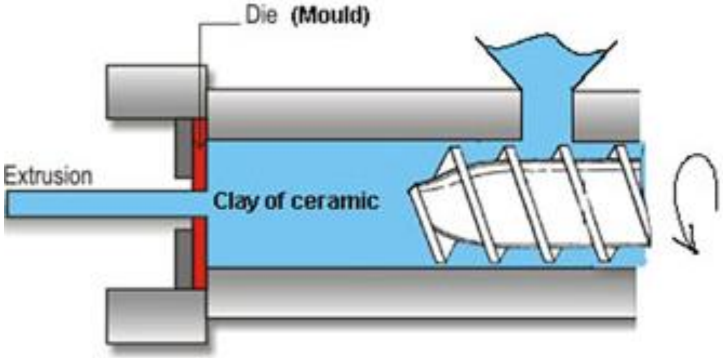
Rahaman (2003), 372-391; http://www.vtscience.com/EPD_Pages/What_is_EPD.html

Plastic Forming

- ❑ **Forming ceramic green body from moldable or plastic powder-additive mixtures**
- ❑ **Major categories**
  - Extrusion
  - Injection molding
- ❑ **Basic requirements of ceramic paste**
  - Moldable - plastic deformation above certain stress level
  - Ability to withstand deformation under own weight
- ❑ **Extrusion instrument**
  - Piston type
  - Screw type



http://www.adhesivesmag.com/articles/85163-tailoring-psa-dispersion-rheology-for-high-speed-coating



http://www.dsource.in/course/ceramics-II/plastic_state_forming(extrusion-pressing)/index.html

Rahaman (2003), 391-399

Extrusion Formulation

❑Manipulating plastic behavior of feed material

- For clay: powder water interaction
- For technical ceramics: addition of organic binder, usually high molecular weight binder polymer such as methyl cellulose, polyacrylimides, PVA

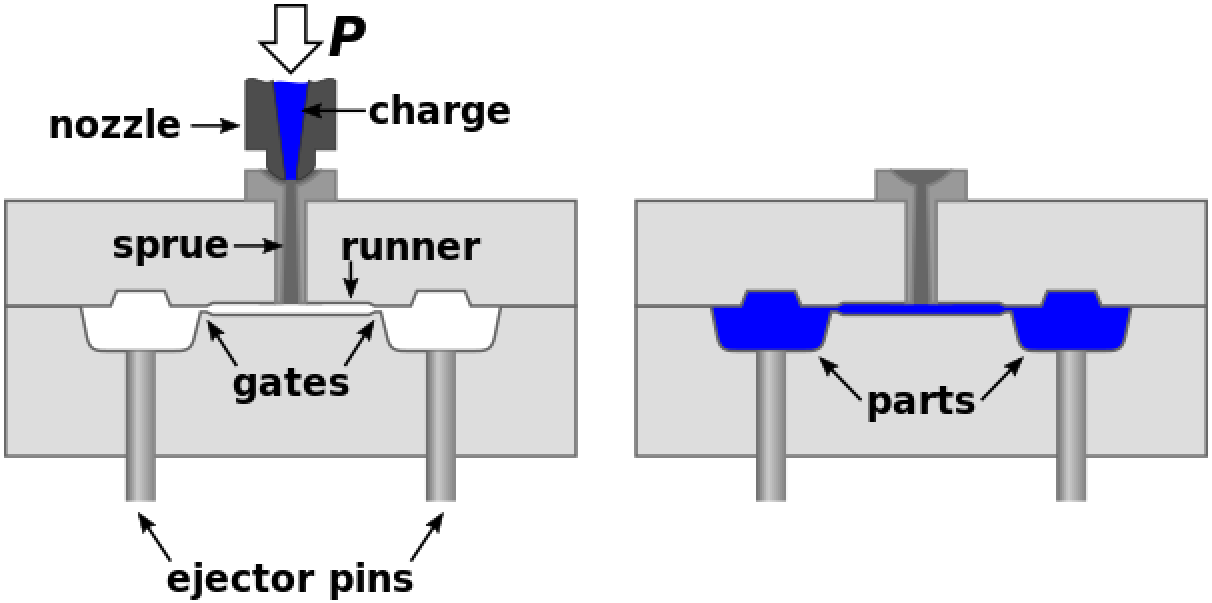
❑Formulation example

Whiteware		Technical Ceramics	
Material	Concentration (vol.%)	Material	Concentration (vol.%)
Kaolin	16	Alumina	45-50
Ball clay	16	Water	40-45
Quartz	16	Ammoniul polyacrylate (dispersant)	1-2
Feldspar	16	Methyl cellulose (binder)	5
Water	36	Glycerin (plasticizer)	1
CaCl2	<1	Ammonium stearate (lubricant)	1

Rahaman (2003), 391-399

Injection Molding (1)

- ❑ **Injection of thick ceramic powder paste with plastic behavior into mold to shape it**



"Injection molding diagram" by ariel cornejo - Own work. Licensed under CC BY-SA 4.0 via Commons - https://commons.wikimedia.org/wiki/File:Injection_molding_diagram.svg#/media/File:Injection_molding_diagram.svg

- ❑ **Application**

  Production of high volume, small ceramic articles with complex shapes

Rahaman (2003), 391-399

Injection Molding (2)

❑Example formulation

- Binder content generally higher than (e.g., double or even triple) other ceramic processing method to ensure plasticity

Component	Formulation 1	Formulation 2
Powder	1 μm alumina, 85 wt.%	20 μm silicon?, 82 wt.%
Major binder	Paraffin wax, 14 wt.%	Polypropylene, 12 wt.%
Minor binder		Microcrystalline wax, 4 wt.%
Other additives	Oleic acid, 1 wt.%	Stearic acid, 1 wt.%

❑Limited industrial application of injection molding in ceramics

- High tooling cost
- High polymer content (often >~10 wt% or ~30 vol%) necessary for injection molding make the organics removal process more difficult
- Much more complicated than injection molding of polymers due to higher density, viscosity, modulus, and thermal conductivity and lower fracture toughness

Rahaman (2003), 391-399

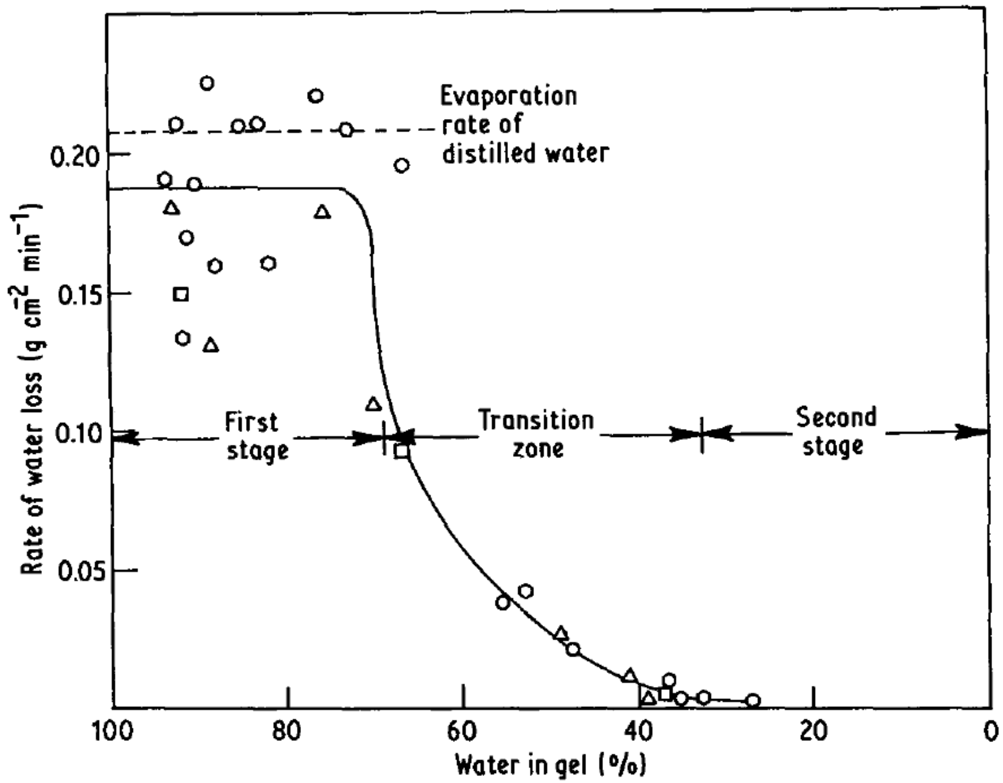
Drying (1)

- **Casted or plastically formed parts need to be dried before subsequent binder removal and sintering**

  Casted or extruded body typically contain moisture of 20-35% by weight, and the more solvent, the greater shrinkage in drying

- **Multi-stage drying**
  - Constant rate period (CRP)
    - Liquid (almost) covers entire surface
    - Powder compact shrink in overall size due to capillary compression exerted by liquid
  - Falling rate period (FRP)
    - No further reduction in compact size due to particles close touching
    - Gradual decreasing evaporation rate

Drying of alumina gel



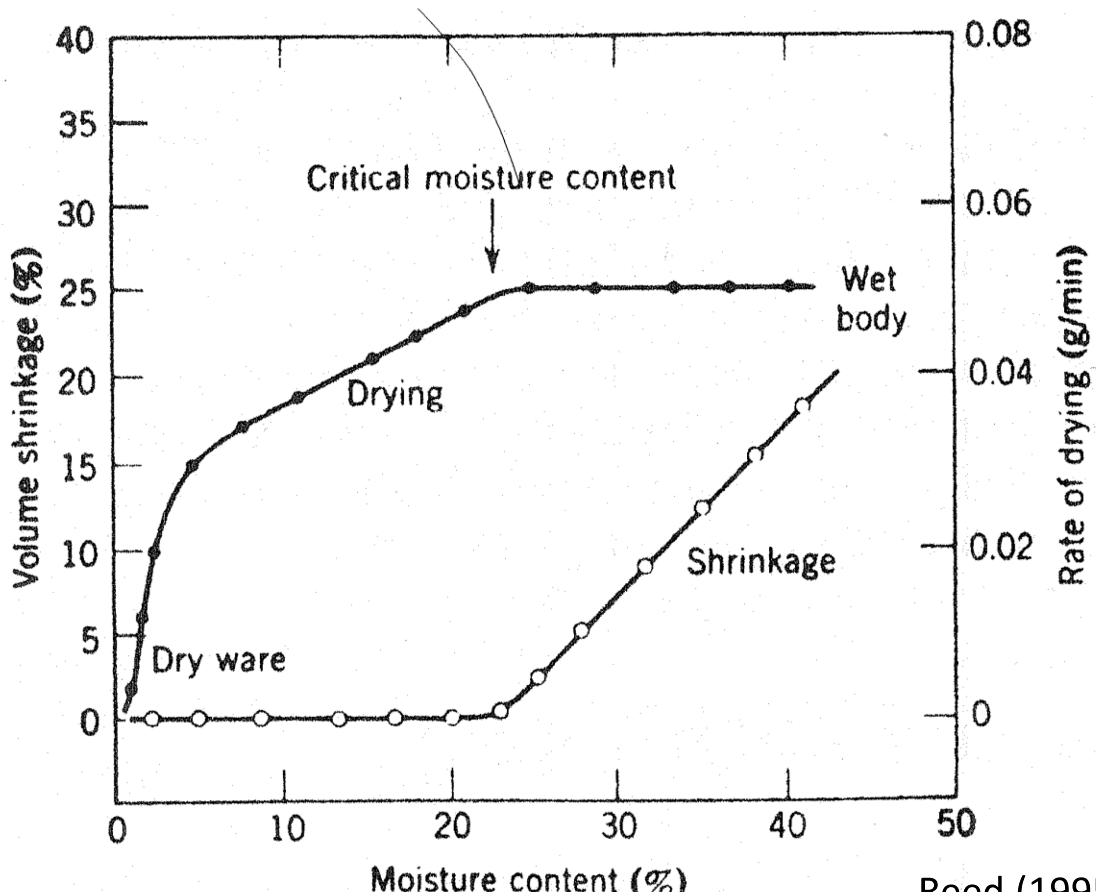
Rahaman (2003), 405-410

Dwivedi, J. Mater Sci Lett, 1986 vol. 5, 373

Drying (2)

❑Drying shrinkage

- Small when the solvent content is less than ~20 wt.%
- Large when the solvent content is larger than ~20 wt.%



Reed (1995), 549-558

Drying (3)

❑Complications

Capillary action in drying, which,
if not controlled properly, may lead to non-uniformity and even cracking

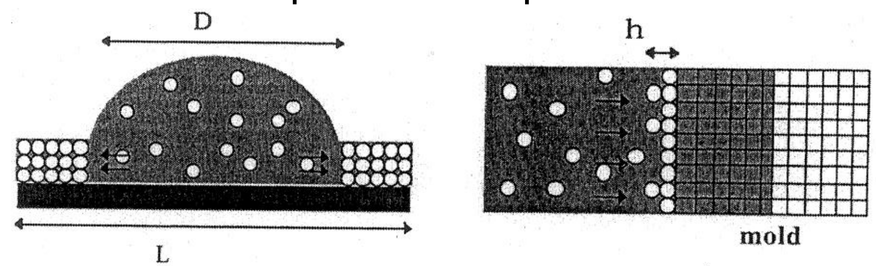
❑Drying defects

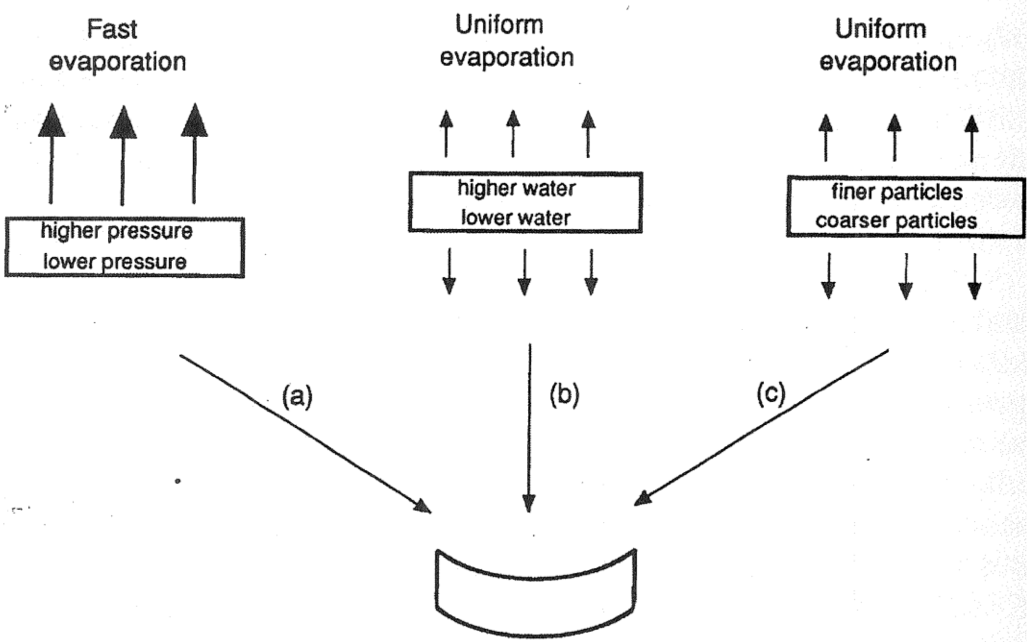
- Deformation such as bending
- Crack formation

❑Ways to mitigate drying defects

- Increase drying time: even days for large body in production
- Increase particle size - not too practical
- Increase drying temperature (which decreases viscosity) while maintaining high humidity (for water as solvent)

Schematics illustrate drying or solvent removal over semi-dried powder compact





Rahaman (2003), 405-410

Binder Removal

❑Ways of binder removal

- Capillary flow
  - Green body placed in powder bed or a porous substrate that absorbs the melted binder
- Solvent extraction
  - Used to remove the soluble component of the binder system
- Thermal debinding
  - Stage 1: Softening of binder at temperature of ~150-200 ^{o}C
  - Stage 2: Thermal degradation of the polymer binder by breaking into smaller molecules or, when oxygen is present, oxidation into smaller molecules at ~200-400 ^{o}C
  - Stage 3: Remaining binder removal at > ~400 ^{o}C
- Combined method

❑Practical thermal debinding

- Less critical if binder volume content < 5 vol.%
- Critical for tape casted or extruded body with much higher binder content
- Need balance between binder removal rate and avoidance of structural defects – sometimes debinding take days to finish
- Generally debinding at slightly lower temperature in oxidizing atmosphere than in inert atmosphere

Rahaman (2003), 409-418

Green Body Characterization

- **Green body quality determines, to a large extent, the quality of sintered ceramics**
- **Characterization of green body**
  - Relative density or porosity
    - Dimension-weight measurement for regular sample (e.g., pellet)
  - Pore size distribution
    - Mercury porosimetry
    - SEM and associated image analysis
  - Other techniques
    - Impregnation with polymers (low viscosity epoxy or MMA monomer followed by hardening to secure the structure) followed by cross-sectioning and image analysis

Homework

- For the plots below for random packing of bi-model sphere mixtures (one large sphere and one small sphere), explain <u>with simple calculation</u> why the highest packing density reachable is ~0.86 and also estimate the weight fraction of coarse sphere within the total bi-model sphere mixtures when the system reaches the highest packing density
- Due Wed Nov 25 class

Rahaman (2003), p. 334-337
Plots original data from McGeary, J Am Ceram Soc, 1961 vol. 44, p513