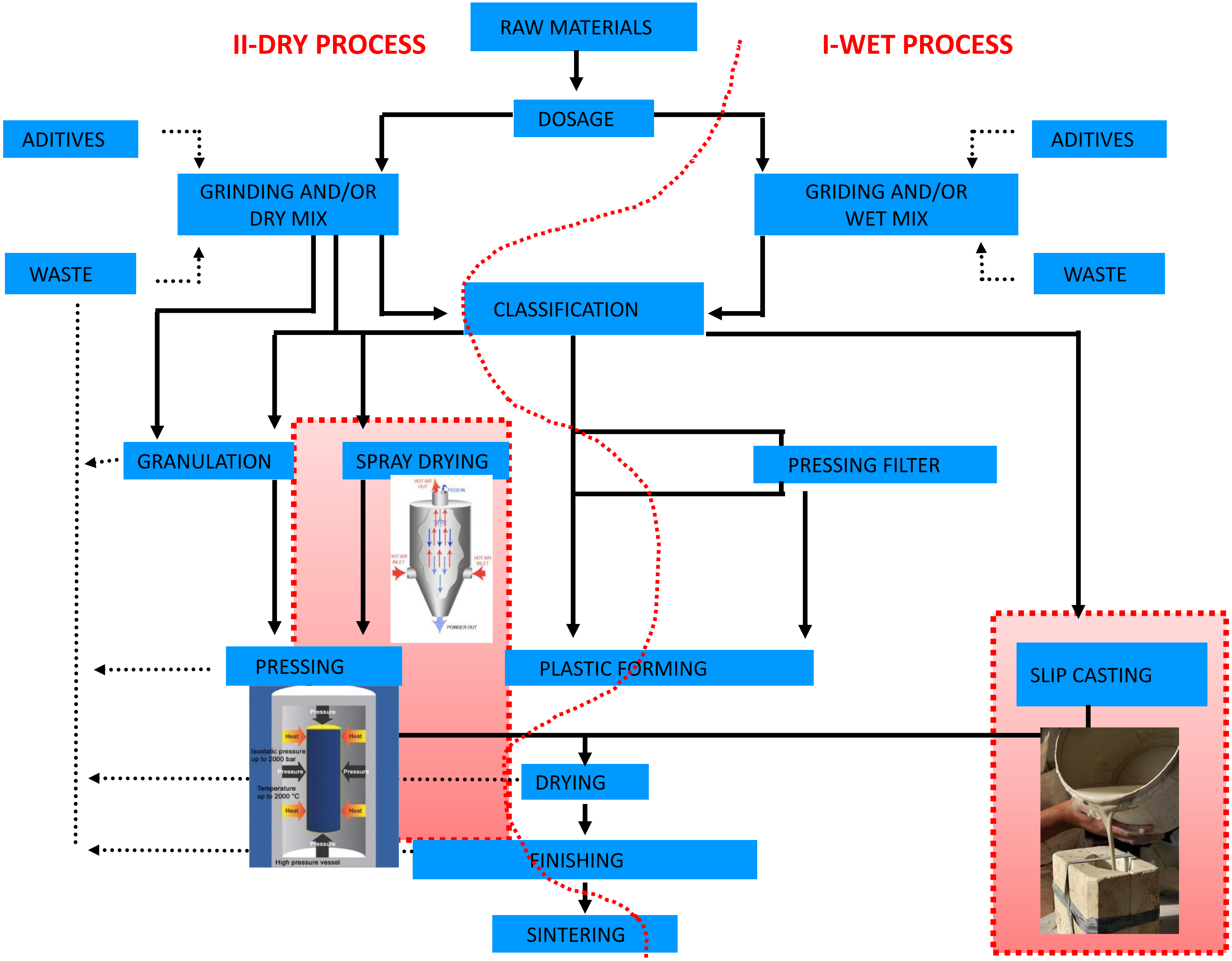
TECNOLOGIA DOS MATERIAIS CERÂMICOS

V – FORMING AND PREDENSIFICATION


II-DRY PROCESS
RAW MATERIALS
I-WET PROCESS
DOSAGE
ADITIVES
GRINDING AND/OR DRY MIX
ADITIVES
GRIDING AND/OR WET MIX
WASTE
WASTE
CLASSIFICATION
GRANULATION
SPRAY DRYING
HOT AIR OUT
FEED IN
HOT AIR INLET
HOT AIR INLET
POWDER OUT
PRESSING FILTER
PRESSING
Pressure
Heat
Heat
Isostatic pressure up to 2000 bar
Pressure
Pressure
Temperature up to 2000 °C
Heat
Heat
Pressure
High pressure vessel
PLASTIC FORMING
SLIP CASTING
DRYING
FINISHING
SINTERING

I – Wet process

I – Wet process: Slip casting

Filling the mold

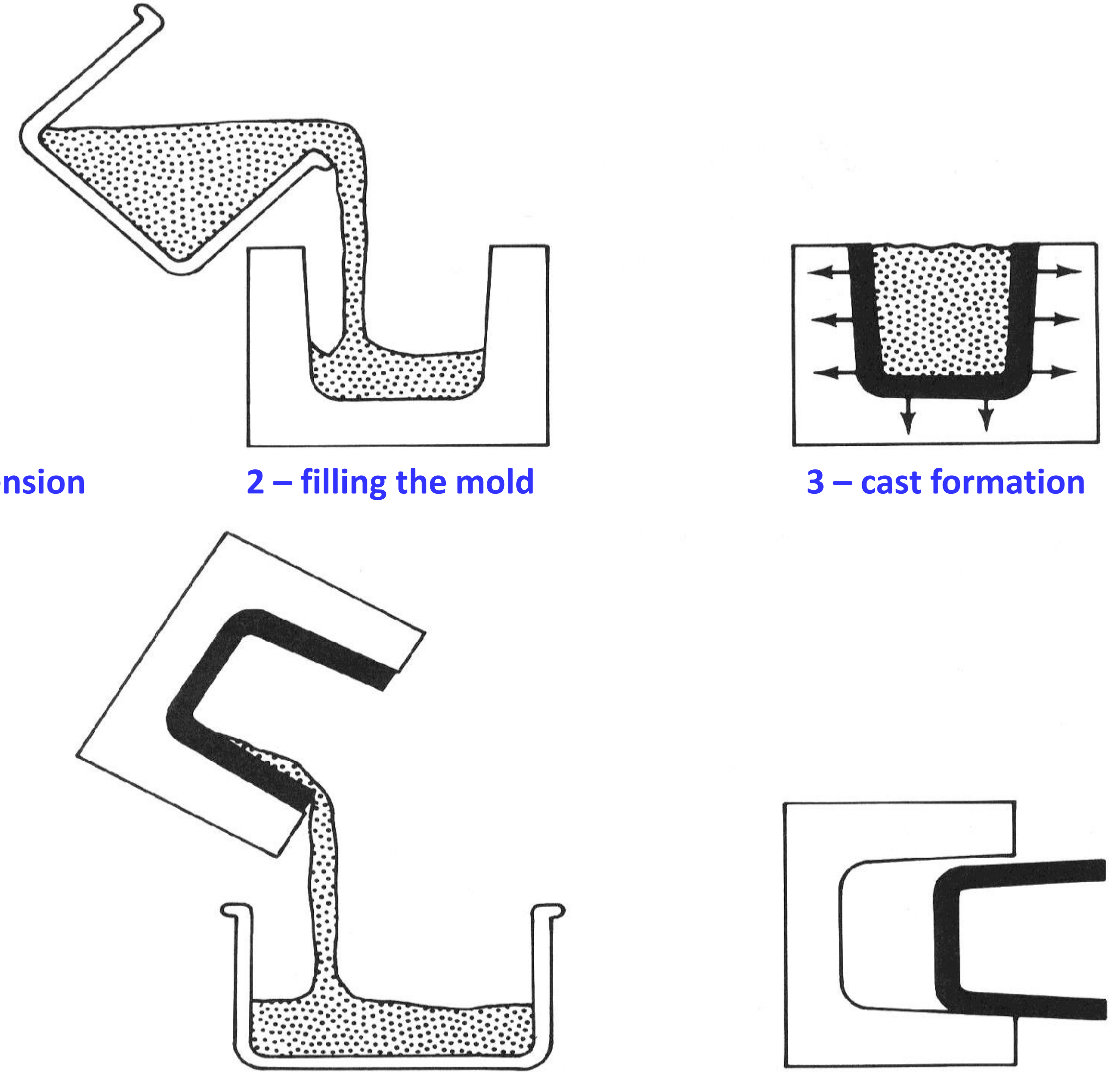
I – Wet process: Slip casting

Plugging and separation

I – Wet process: Slip casting

Plugging and separation

I – Wet process: Slip casting



1 – slurry/slip/suspension preparation

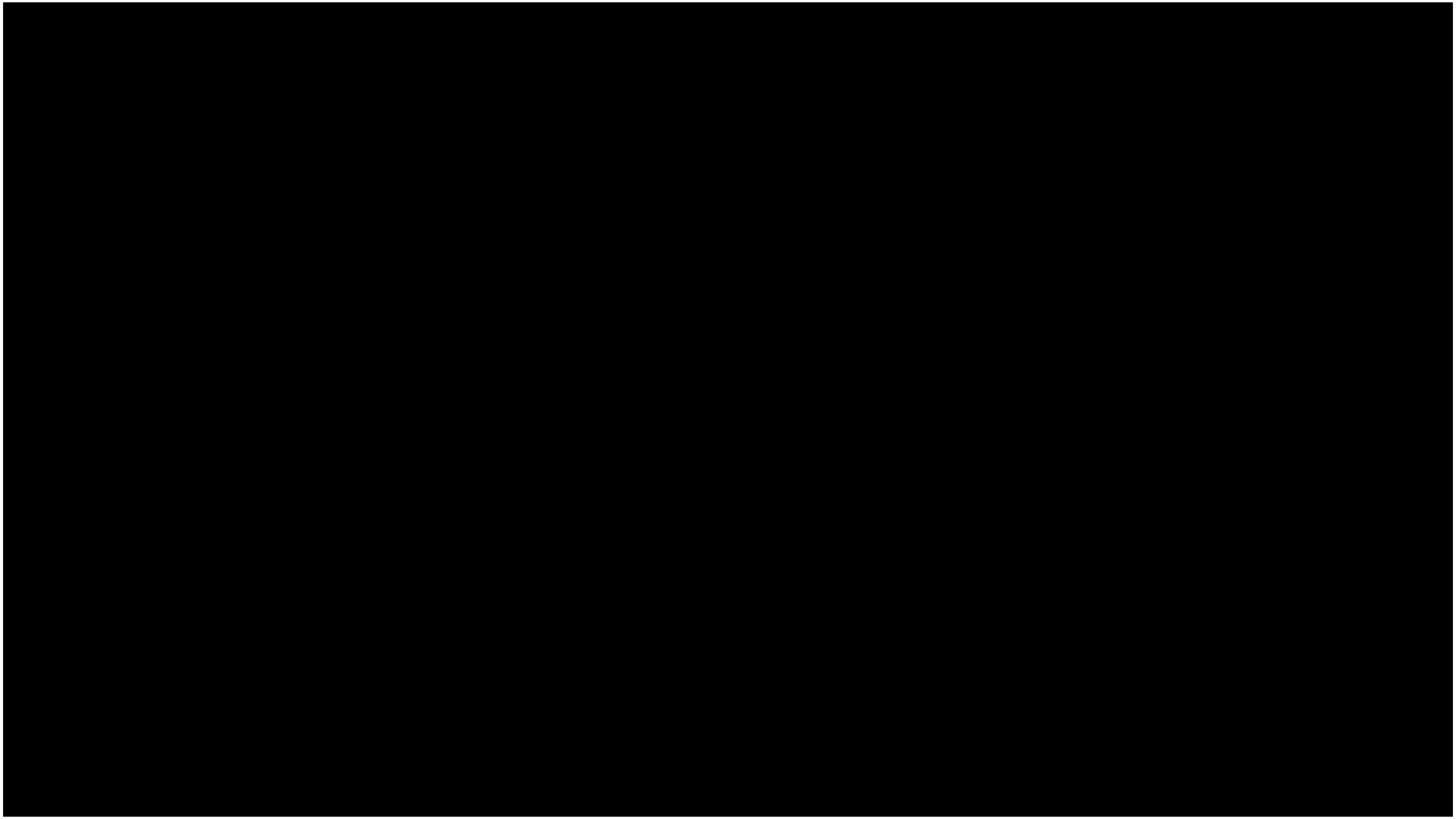
2 – filling the mold

3 – cast formation

4 – draining

5 – plugging and separating

Drain casting illustration. (a) Permeable mold is filled with slip. (b) Liquid is extracted from the mold, while forming compacts along mold walls. (c) Excess slip is drained. (d) Casting is removed after partial drying.



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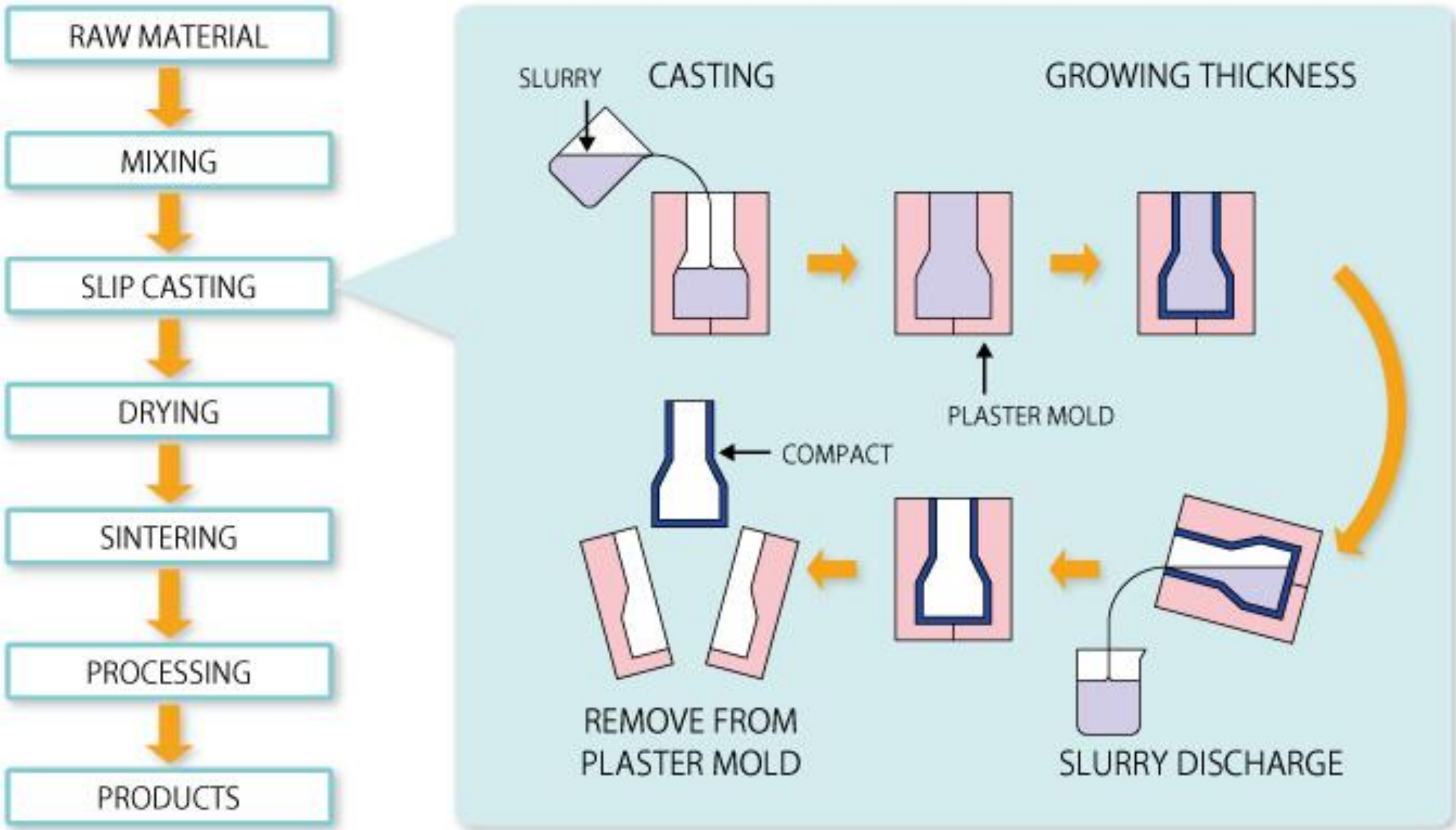
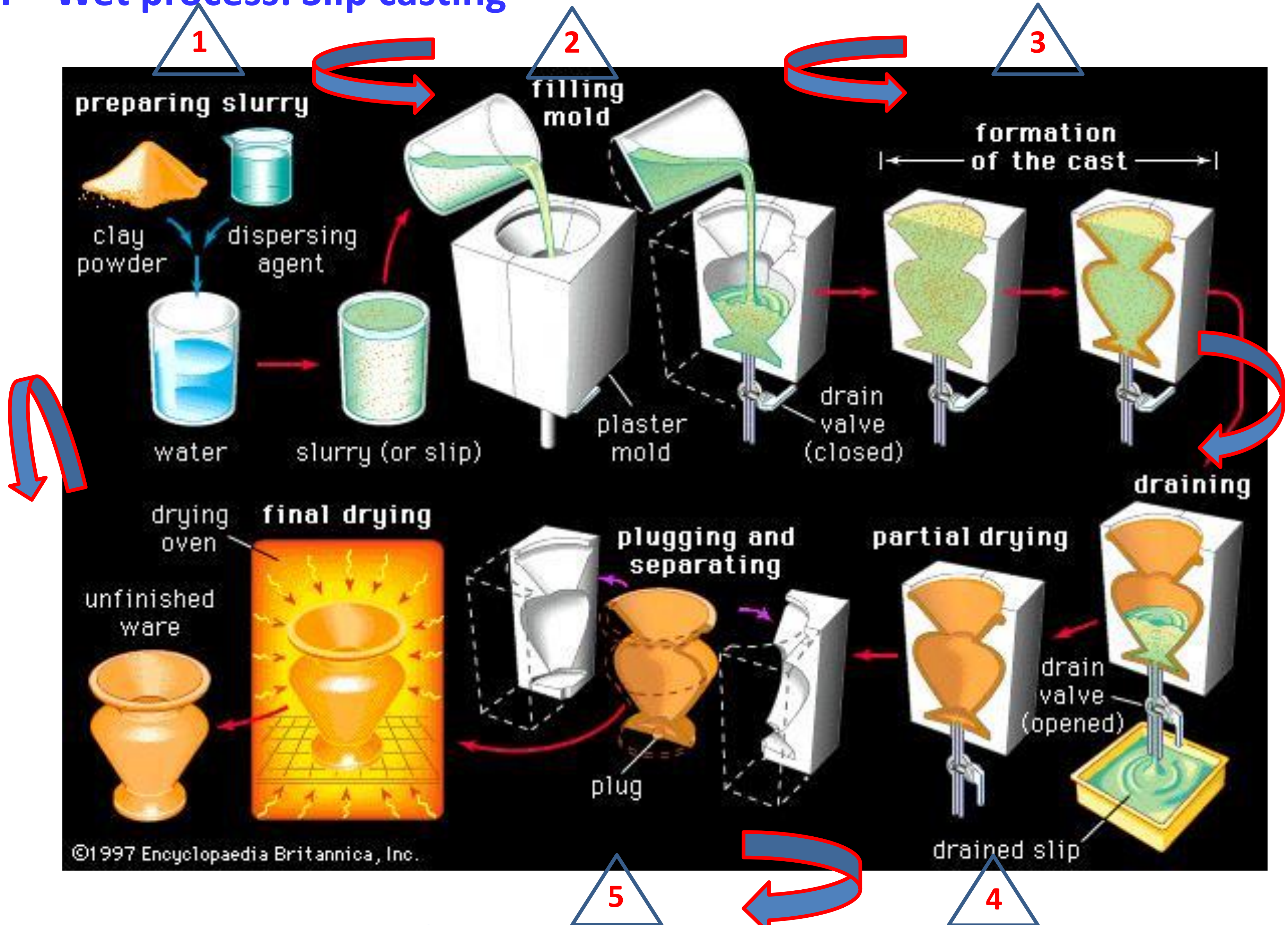

RAW MATERIAL
MIXING
SLIP CASTING
DRYING
SINTERING
PROCESSING
PRODUCTS
SLURRY
CASTING
GROWING THICKNESS
PLASTER MOLD
COMPACT
REMOVE FROM PLASTER MOLD
SLURRY DISCHARGE

I – Wet process: Slip casting



I – Wet process: Slip casting

Casting processes are used to porduce a self-suporting shape called a cast from a specially formulated slurry.

The yield strength of the cast may be increased by the partial removal of the liquid, which concentrate the solids, or by gelation, polymerization, or crystallization of the matrix phase.

In slip casting, the slurry is poured or pumped into a permeable mold having a particular shape; capillary suction and filtration oncentrate the solids into a cast adjacent to the wall of the mold.

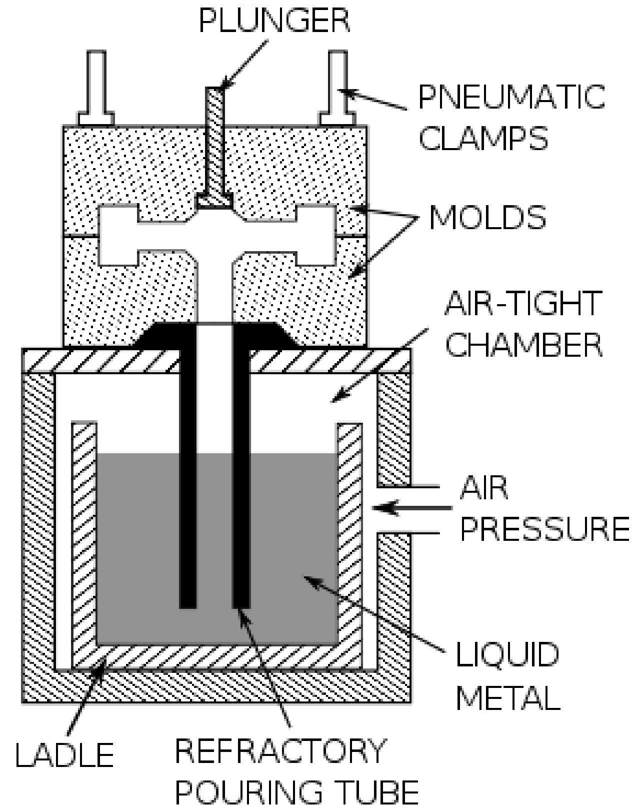
The motivation force for the separation of the liquid may also be pressure applied to the slurry (pressure casting), a vacuum aplied to the mold (vacuum-assited casting) or centrifugal pressure.

Slip is drained from the mold after the desired wall thickness has been achieved using a drain casting mode.

Drain casting is the traditional porcess used to porduce a variety of porcelain products with a complex shape, such as bathroom fixtures, chemical porcelain components, dense refractories that are of a complex shape or massive in cross section, highly porous thermal insulation, and traditional fine china and dinnerware.

I – Wet process: Slip casting

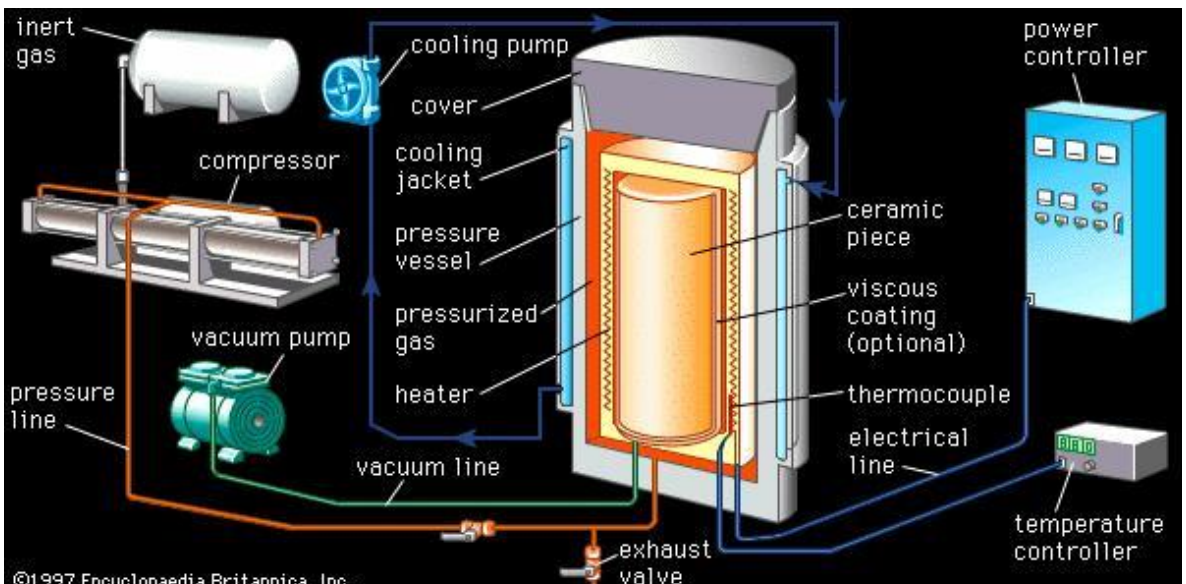
Vacuum draining



Vacuum casting is widely used for forming very porous refractory insulation having a **complex shape**.

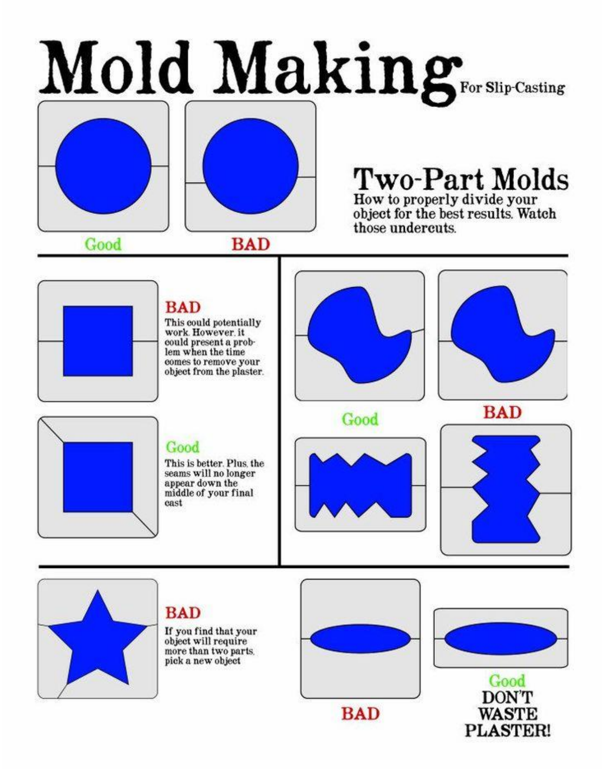
After the desired wall thickness has been cast, the preform is withdrawn and removed for drying and chemical set.

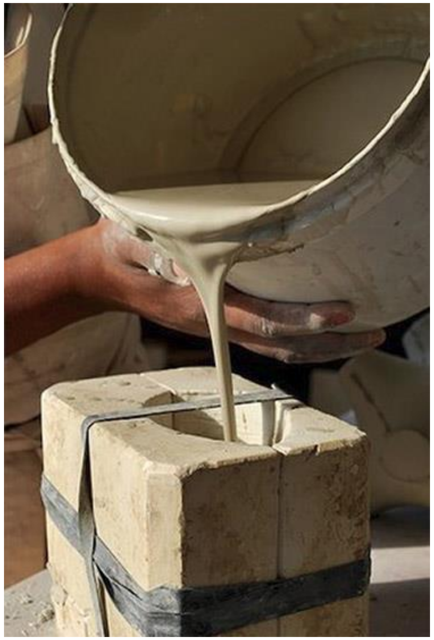
The external surface of a gypsum mold may also be subjected to a vacuum to effectively increase the parameter ΔP_T and the casting rate in slip casting.

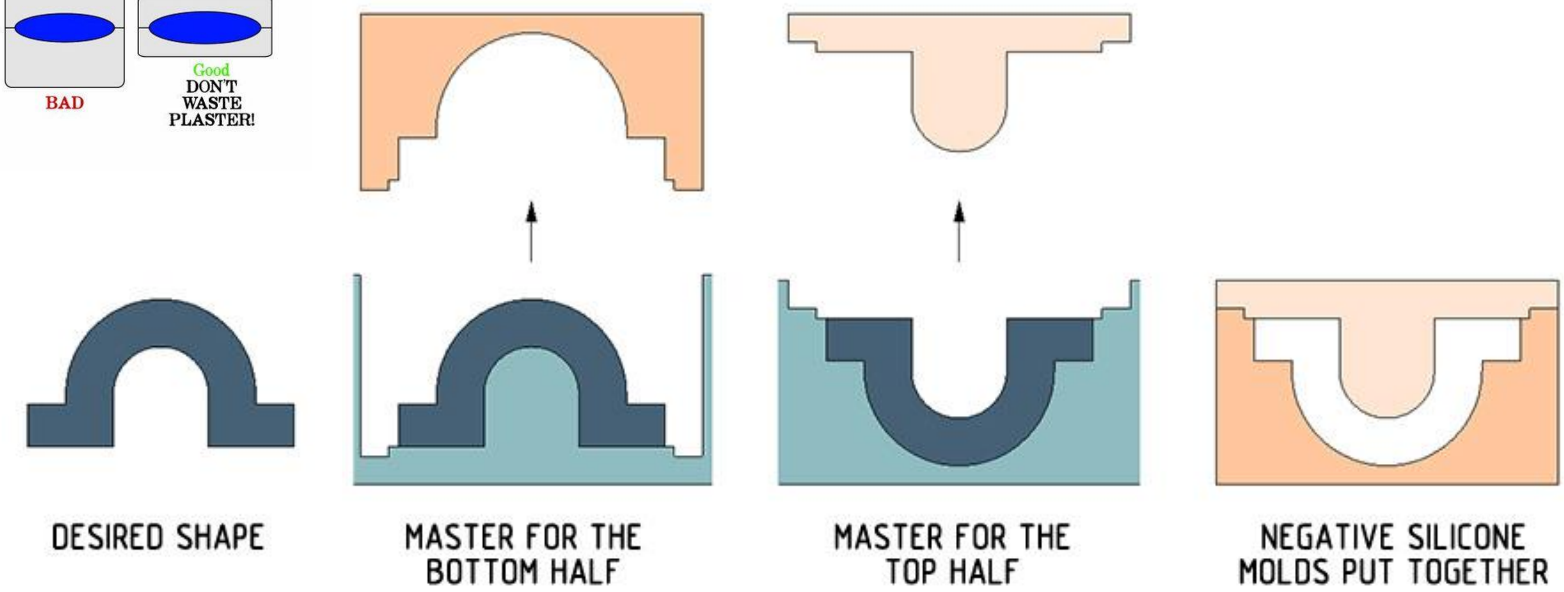


I – Wet process: Slip casting

Mold making







I – Wet process: Slip casting

Mold characteristics

GYPSUM MOLD

$CaSO_2.H_2O$ POLYCRYSTALINE MATERIAL

Gypsum crystals diameter ∅ 2 – 5 μm

Gypsum crystal length L = 20 μm

CONTINUOUS NETWORK OF OPEN POROSITY

gypsum porosity diameter ~ 0.1 μm- 4 μm

gypsum porosity irregularly shaped / continuous capillarity

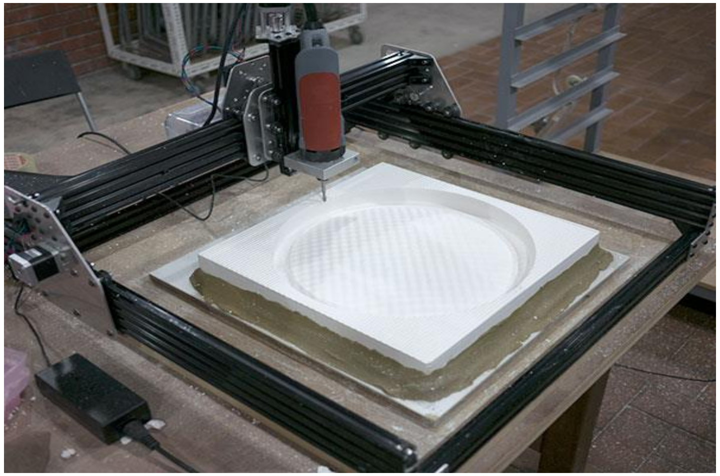
GYPSUM MOLD CLEANING TREATMENT

mold cleaning temperature < 50ºC

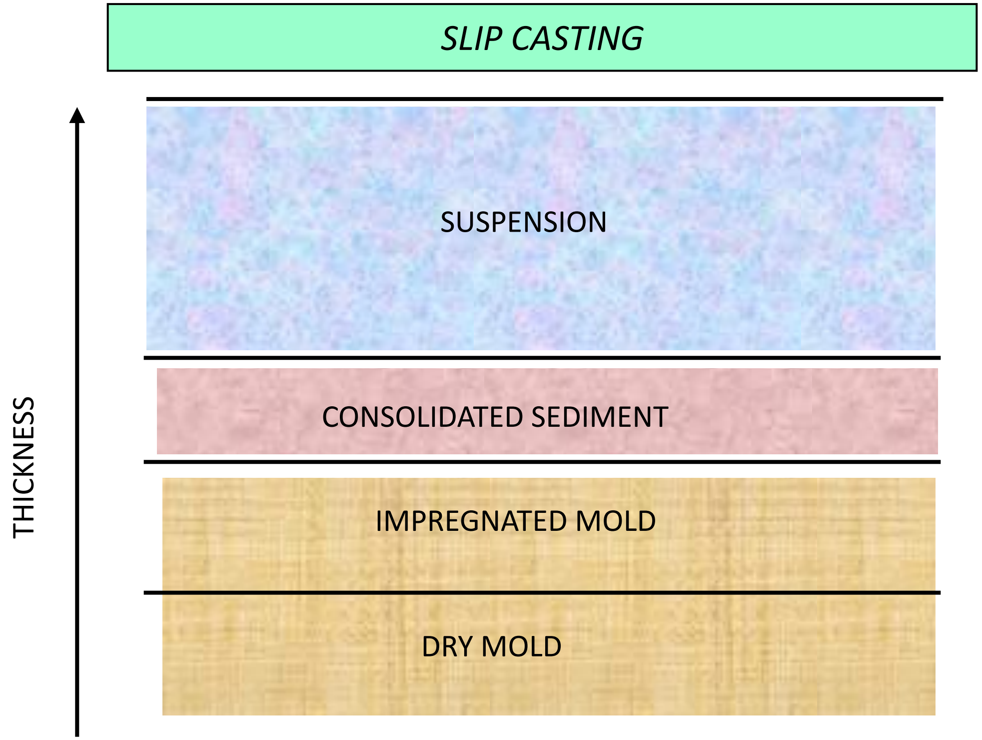
drainage velocity 0.1 kg / m^2

LOW COOLING RATE TO AVOID CRACK FORMATION

Pay attention to any organic present in the slurry! They may penetrate or simply stick on to the mold surface, decreasing it drainage power and consequently changing the ceramic piece thickness profile.



I – Wet process: Slip casting



LAPLACE EQUATION $$P = S\sigma \cos\gamma$$

P – capillarity (**0.03 – 0.1 MPa; 4.5 – 14.5 psi)**)

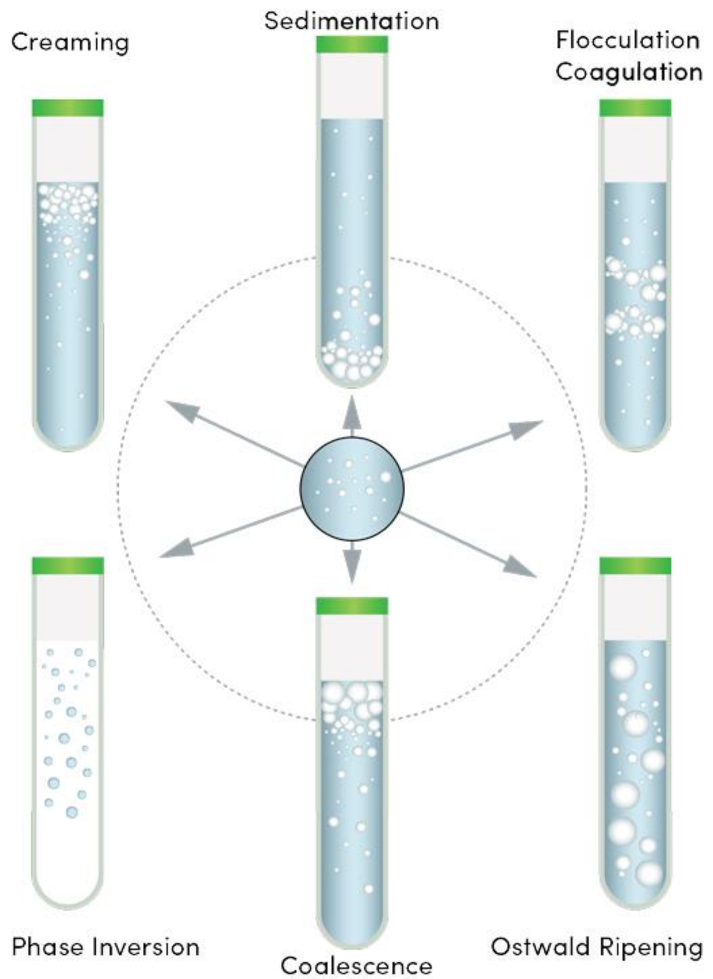
S – gypsum specific surface area

σ – H_2O surface tension

γ– contact angle (**$\cos\gamma = 1$**), high wettability

I - Slip casting: slip requirements

Which slip suit better the casting performance?



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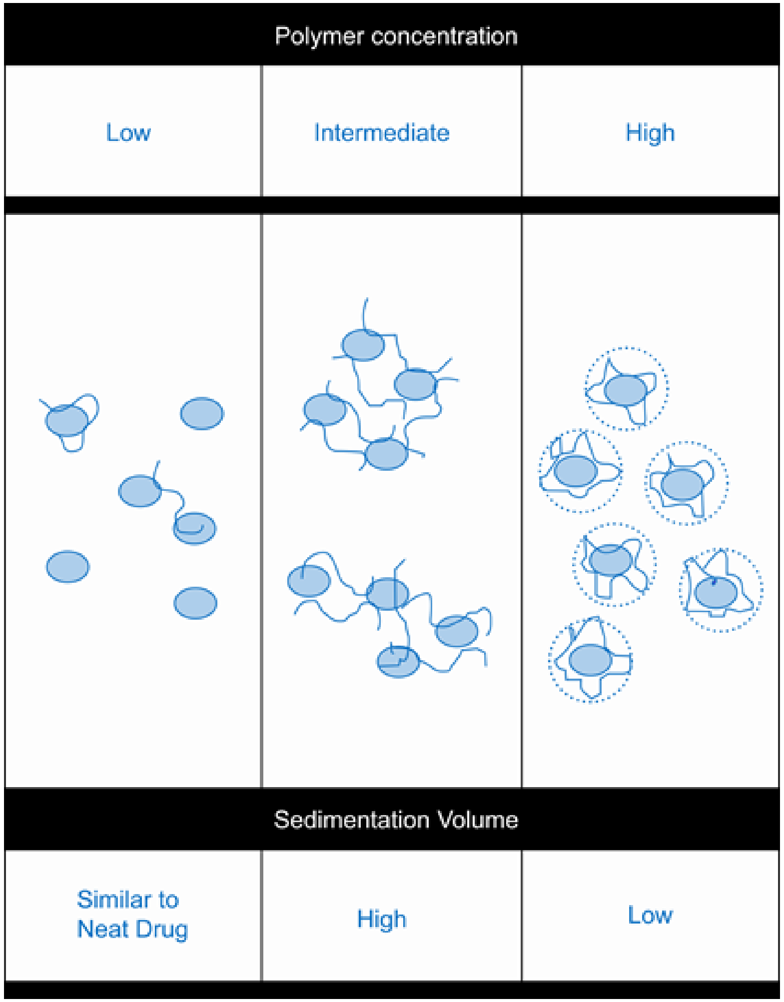
I - Slip casting: slip requirements

Which slip suit better the casting performance?



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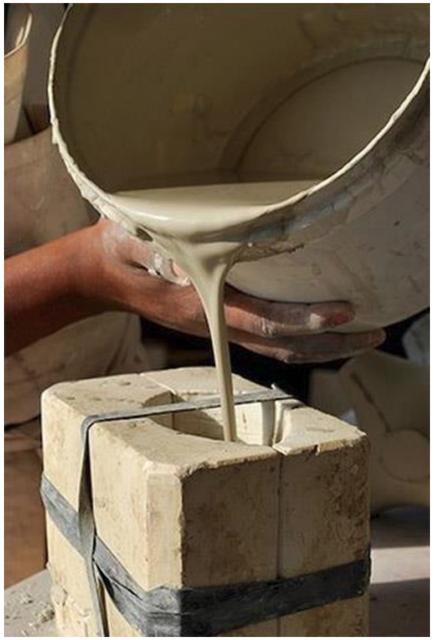
I - Slip casting: slip requirements

Mandatory!

- **low η (< 1 Pa.s)**
- **high solids concentration (up to 60 % v/v)** } !!

  (we want to maximize both drainage velocity and green density)

- **Gaussian distribution of particles diameters** (to maximize packing, thus decreasing shrinkage during drying and sintering !)
- **homogeneous microstructures**
- **high kinetic stability** (no floccule or coagula formation)
- **high drainage velocity**
- **no bubbles**



To avoid!

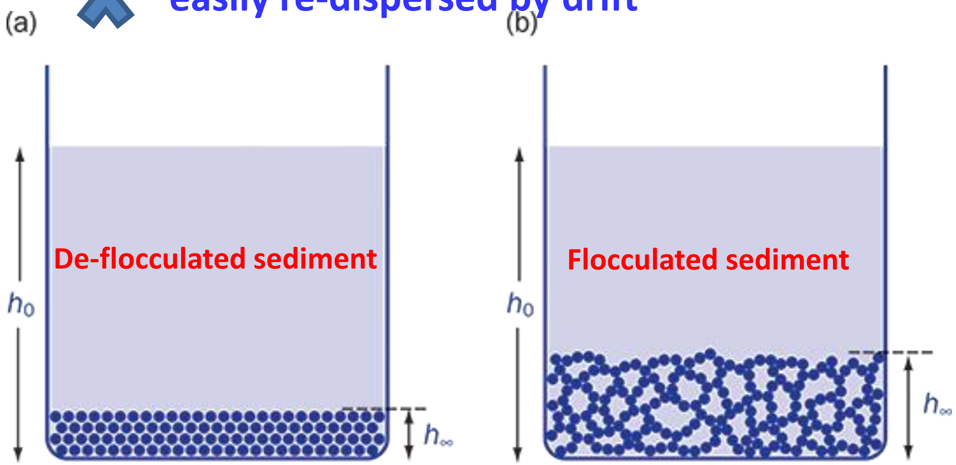
- **solid particles segregation (by size, shape, surface energy,…)**
- **density heterogeneities (volume density)**
- **fracture during drying**
- **fracture during sintering**

I - Slip casting: slip requirements

Which slip suit better the casting performance?

Flocculated suspension (pseudo-plastic and/or toxitropy and low drainage velocity)

- **low density sediment**
- **sediment with low cohesion**
- **permeable and porous**
- **high volume**
- **easily re-dispersed by drift**



De-flocculated suspension

- **high density sediment**
- **sediment with high cohesion**
- **non-permeable**
- **low volume**
- **difficult re-dispersed by drift**

I – Wet process: Slip casting

In the **porcelain slip**, the clay content of 15-20 % is needed to obtain the proper fired microstructure. The clays used should be sufficiently coarse and relatively free of bentonite.

Generally, clay slips are only partially deflocculated, and the working viscosity is higher than the minimum that is possible for the solids loading. The type and amount of additives used to control the state of partial defoloculation depend on the type and amount of colloids present, soluble impurities in the raw materials, and impurities in the water.

I – Wet process: Slip casting

Slurries for casting oxides, **carbides**, **nitrides**, etc. range more widely in composition. A fraction of a percent of an organic binder increases the pseudoplasticity of the slurry and the strength of the cast but reduces the permeability of the cast and the casting rates. A slurry that is partially deflocculated will cast more rapidly, but the cat will be more porous.

Binder migration, which reduces the liquid permeability of the cast, is reduced by using a binder or medium molecular weight.

A deflocculated slurry with adequate colloids and a minimal binder content will produce a cast with a narrow range of pore size and na adequate green strength for carefull handling; however the casts are brittle and relatively intolerant of surface finishing prior to sintering.

Compositions containing a small amount of a fine clay and na organic binder are more plastic and more tolerant to stresses in finishing and handling.

I – Wet process: Slip casting

Whiteware casting slips are generally only partially deflocculated and are yield-pseudoplastic and thixotropic. During casting the slight removal of water and gelation increase the apparent viscosity and apparent yield strength of the cast.

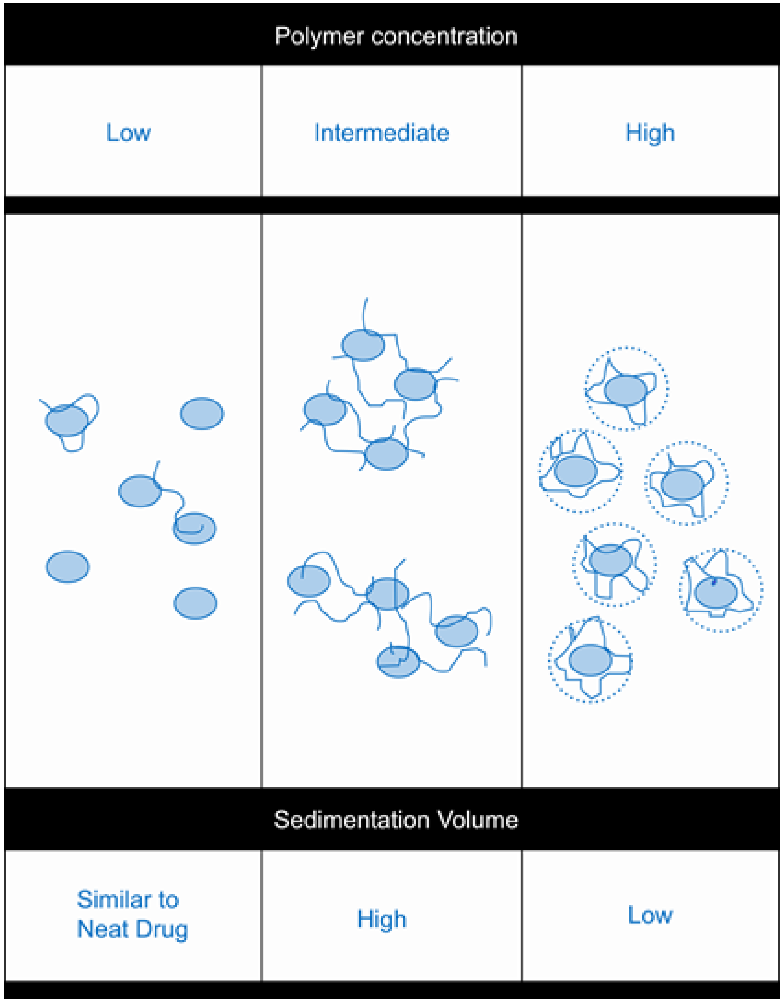
The oartially deflocculated slip contains agglomerates (flocs) which may be of a controlled size and solids content. Gel formation in the cast is critical, and the gel strength varies with the proportions of raw materials used, colloid content, flocculation (colloid coagulation) caused by chemical additives, and casting time.

A cast with a balance between firmness, density and plasticity is require to prevent fracture or shape distortion during trimming, handling, drying, and surface finishing. A more uniform distribution of both the liquid and particle sizes throughout the cast reduces stress and distortion on drying and firing.

Gelation minimizes mold staining and imporves mold release by reducing the mobility of colloids through the cast.

I - Slip casting: slip requirements

Which slip suit better the casting performance?



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II – Dry process

II – Dry process: ceramic tiles

Powders from chemical solution techniques

Pressing techniques with **powder mixtures** being compressed in almost **dry conditions** are preferred for forming ceramic products with appropriate geometries.

Ceramic starting powders are normally milled down to the micrometer range in order to increase their sintering capacity. On the other hand, attractive forces arise at the particle surfaces and lead to **uncrontrolled agglomerations** and a **bad processability**. In order to optimize the flowability and to increase both the bulk density and the storing capability of comminuted powders in silos and hoppers **they are granulated before further processing**.

Spray drying is the most common thermal granulation process in ceramic production.

Horizontal fluid bed granulation and spray freeze granulation are also thermal processes but have never approach the importance of spray drying.

II – Spray drying

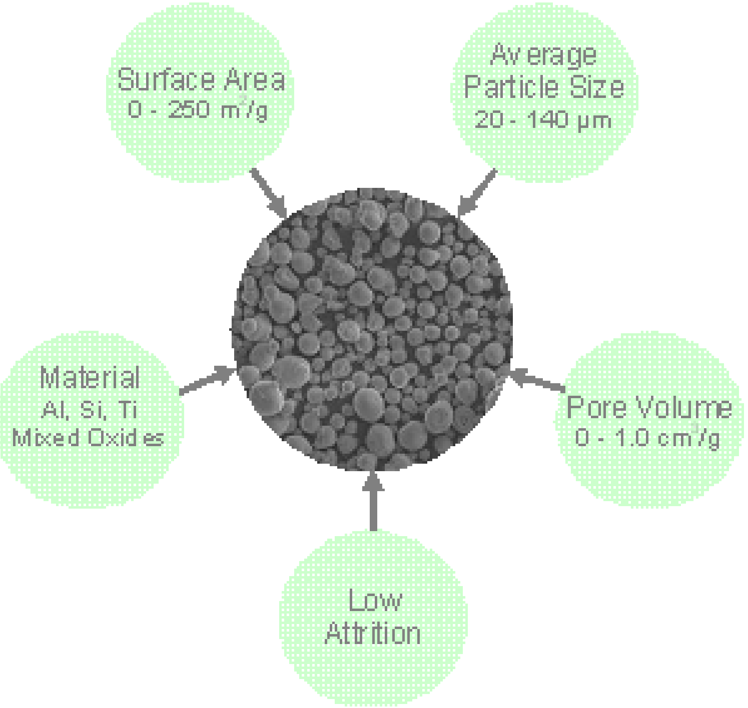
Powders from chemical solution techniques

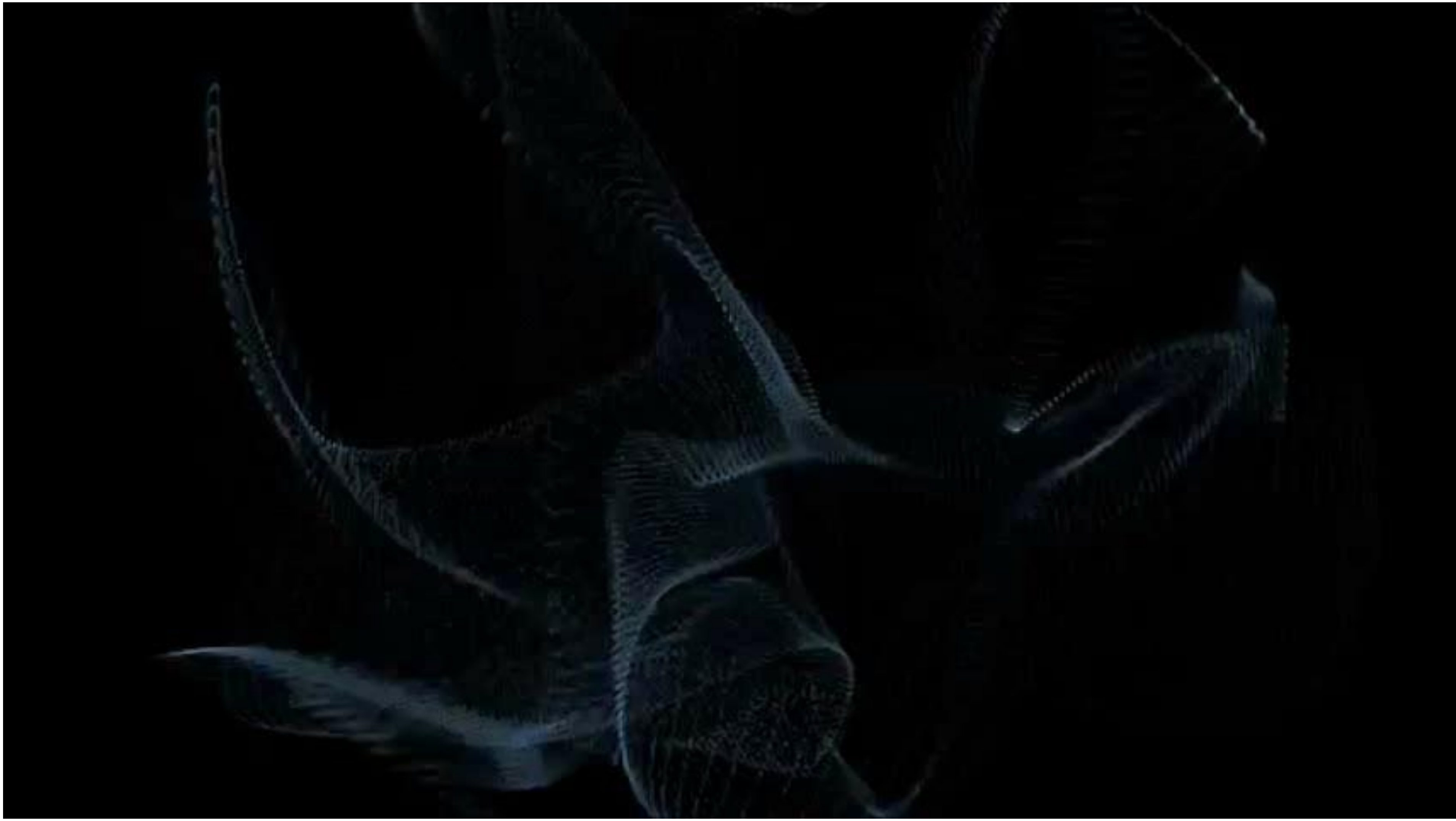
Spray-drying is used widely for preparing granulated pressing fed from powders of ferrites, titanates, other electrical ceramic compositions, alumina, carbides, nitrides, and porcelain bodies.

Batch mixing in a slurry form and atomizing facilitate **mixing** and the achievement of **mixedness**.

When properly controlled, spray-drying produces **nearly spherical**, **relatively dense granules larger than 20 μm in size** which flow and compact well in pressing operations.

Capacities of industrial spray-dryers range from **less than 10 to several 100 kg/h**.





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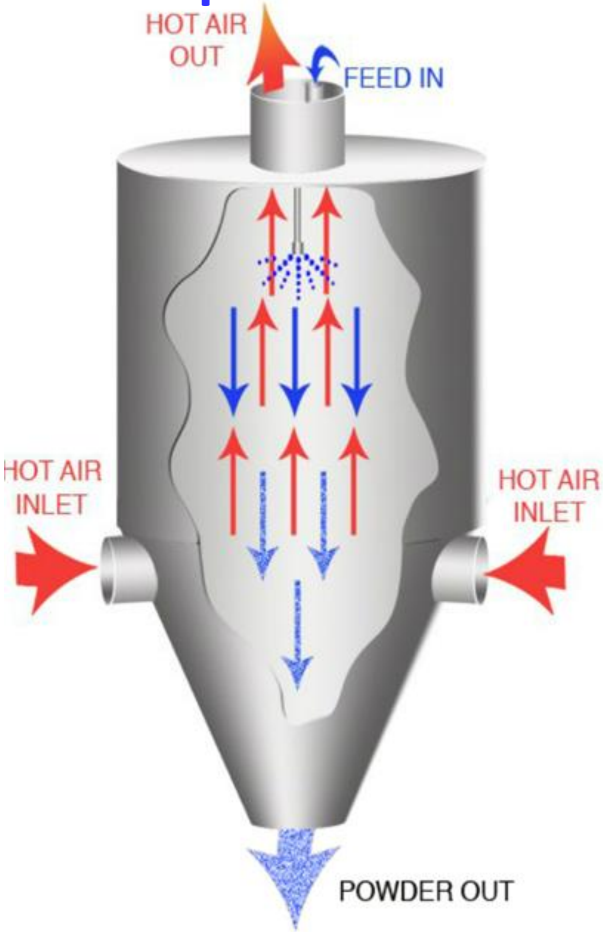
II – Spray drying

Powders from chemical solution techniques



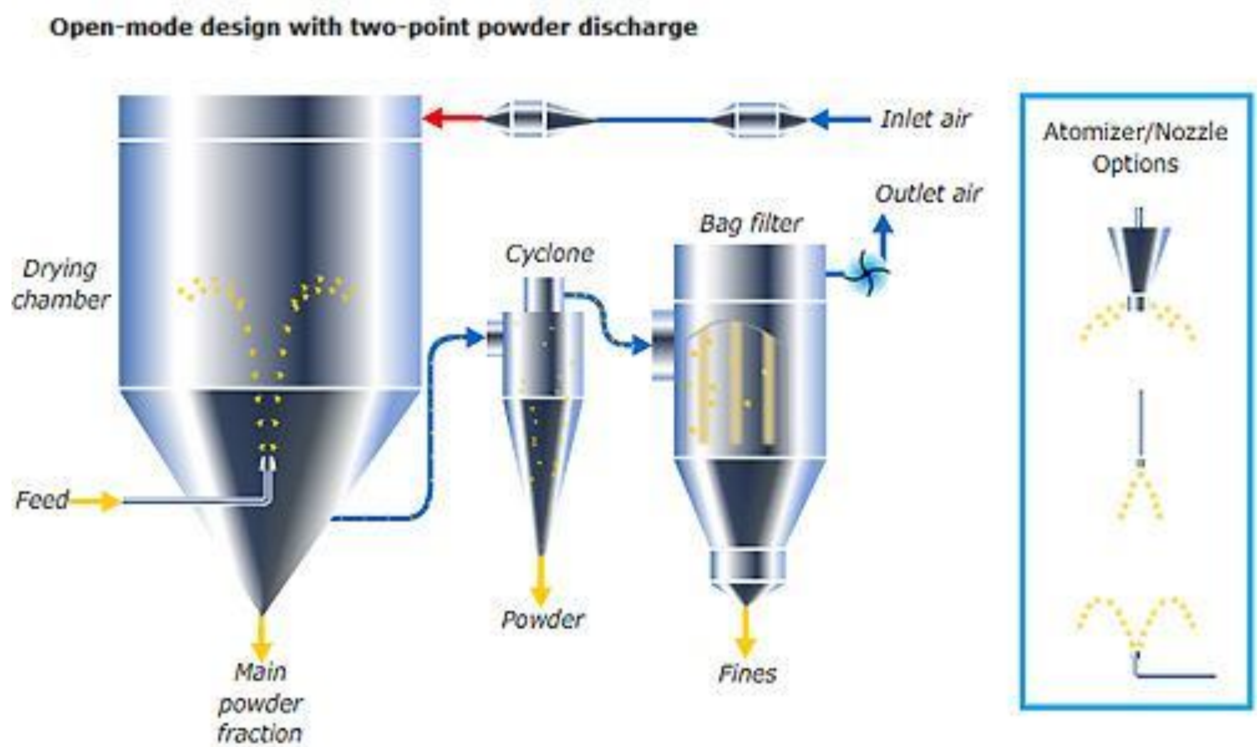
In spray-drying **the solution containing the ions** of interest **is dispersed** into **microscopic volumes** followed by the **remotion of the solvent** as a **vapor,** forming a **salt**.

Maintenance of atomic-scale homogeneity will be possible for multicomponent systems only when the components are of about equal solubility or when the salts forms extremely rapidly.

Spray-drying has been used to produce dry salt particles of **10-20 μm** in diameter.

II – Spray drying

Powders from chemical solution techniques



If a hot furnace is combined with the **spray-drying**, drying and calcination are operated in one single step; because the heating rate is several hundred degrees per second, complete decomposition occurs only if the salt decomposes at a relatively low temperature.

II – Spray drying

Powders from chemical solution techniques

Variables in spray-drying unit operation

i) suspension composition, concentration and rheology

ii) chamber design

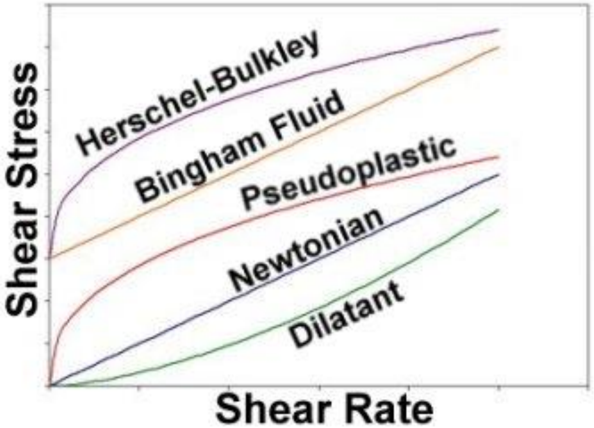
iii) droplet size

iv) temperature and flow pattern of the air in the drying chamber

(P= 1 atm, T = 300-600ºC, filtered dry air)

Powders from chemical solution techniques

i) Suspension composition, concentration and rheology

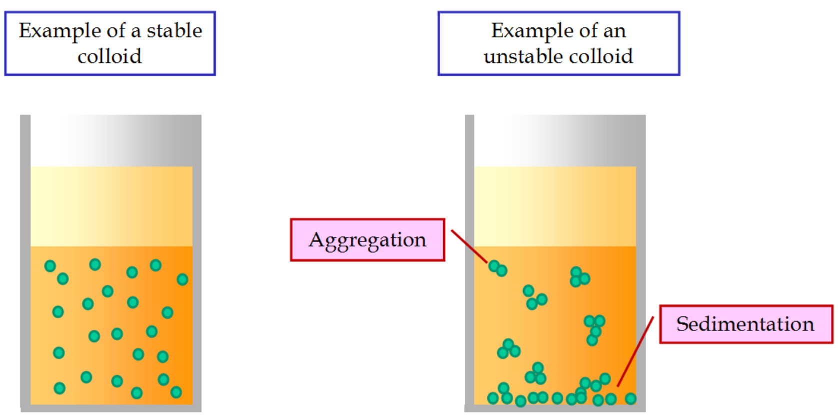


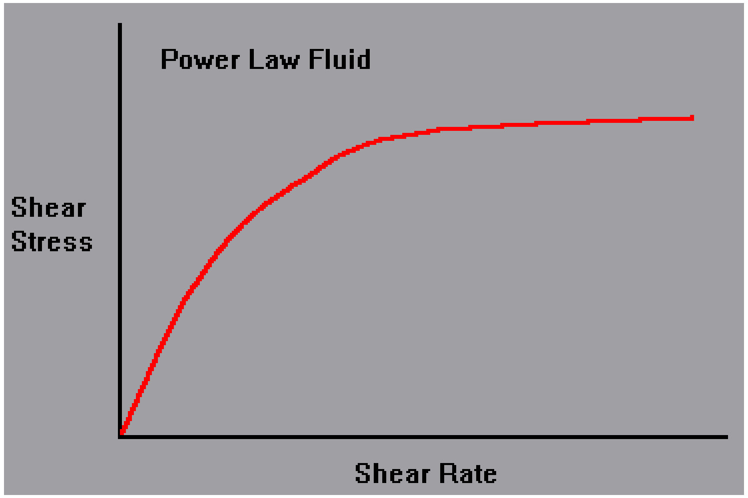
deflocculated suspension

pseudo-plastic behavior

η has to be measured over a large shear rate interval, to garanty **no dilatancy behavior** (shear velocity may be higher than 10^4 s^{-1} during spray-drying)

high solids concentration





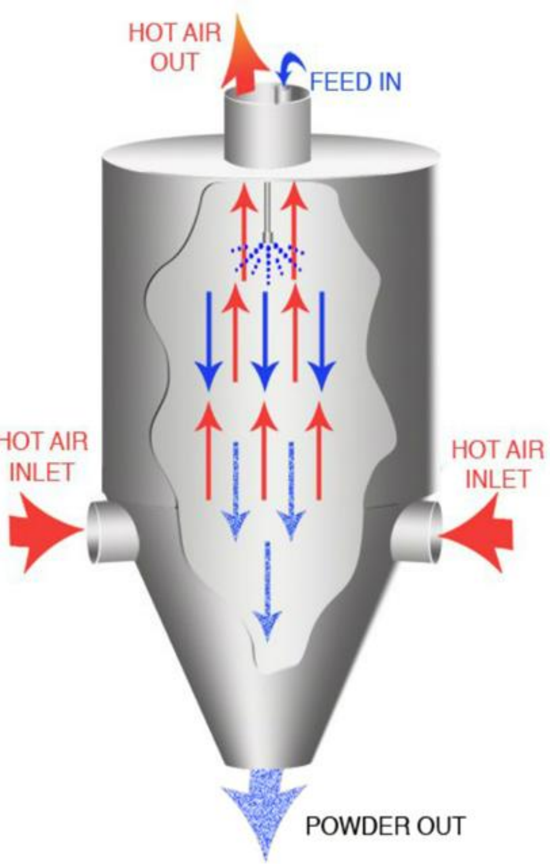
II – Spray drying

Powders from chemical solution techniques

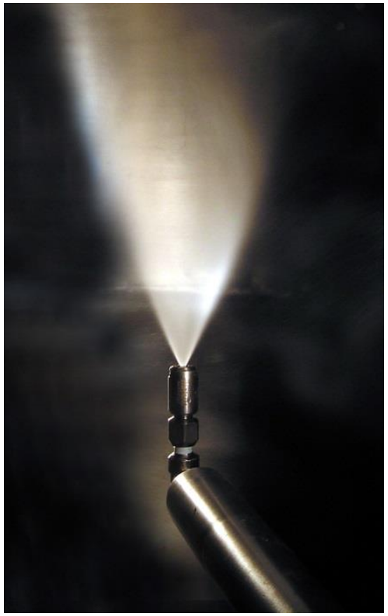
ii) Chamber design

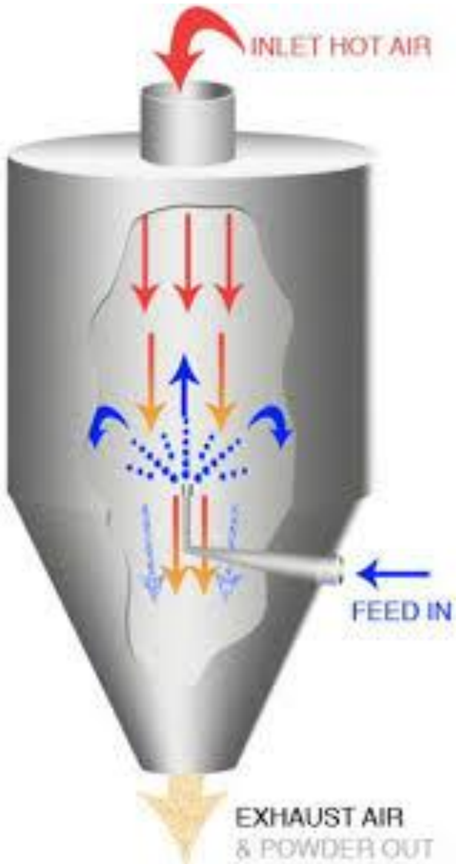
In this thermal granulation process a ceramic slip is atomized to create fine spherical shaped drops which are dried in a hot gas stream.

We have to distinguish in the main between **rotary** and **nozzle atomization** as they will lead to different distributions of the granule sizes.



rotary spray drying

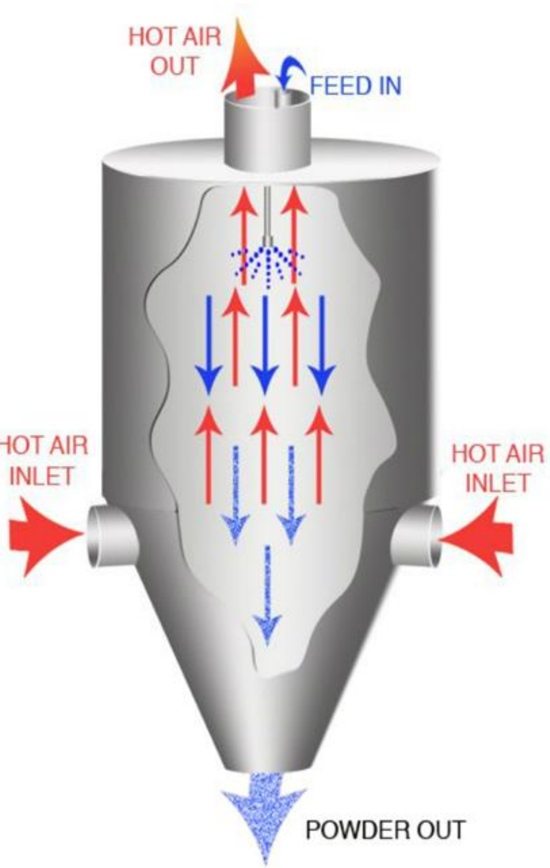




nozzle spray drying

Powders from chemical solution techniques

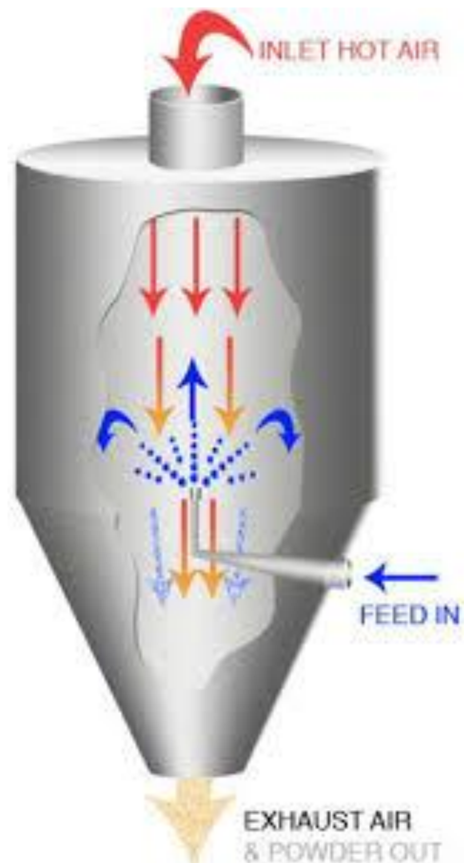
ii) Chamber design



rotary spray drying

In a **pressure nozzle**, slurry accelerating through small channels breaks up into droplets. Pressure nozzles are relatively inexpensive but are subject to blocked flow, and the high operational pressures ranging up to **10 MPa** increase abrasion rates.

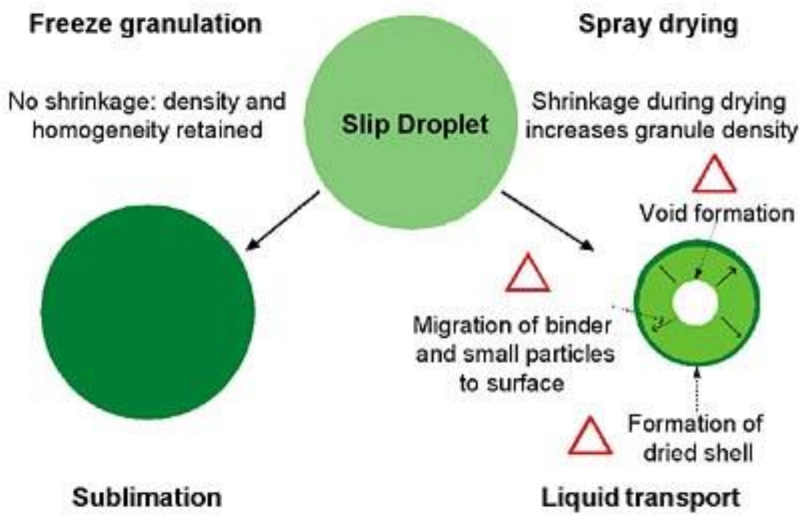
In a **two fluid nozzle**, a high velocity gas is mixed with the slurry o produce turbulence and droplets; operating pressures may be reduced to **less than 1 MPa**; external mixing produces a **smaller droplet size**.



nozzle spray drying

Powders from chemical solution techniques

iii) Droplet size



The **droplet size** in the spray increases with:

i) **turbulence** produced in the nozzle

ii) **slurry viscosity**

iii) **solids content of the slurry**

iv) and **inversely with the flow velocity**

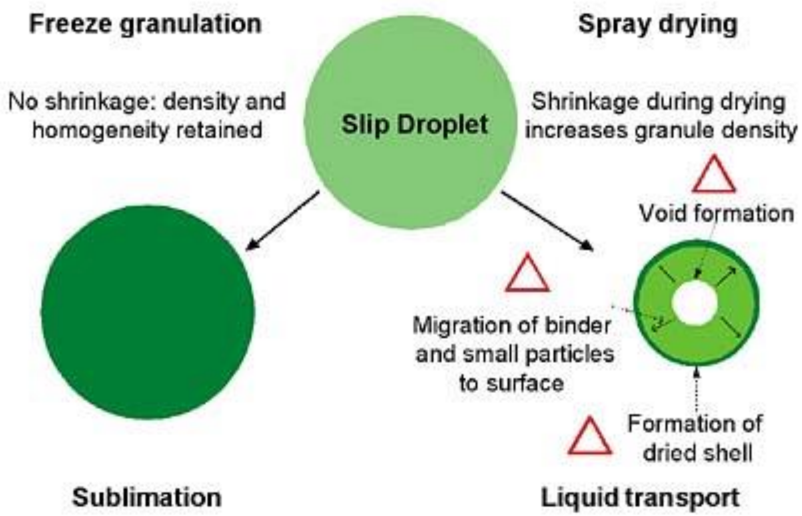
Granules ranging up to about 400 μm may be produced using pressure nozzles, and sizes up to about 150 μm using a rotary atomizer.

Relative to a pressure nozzle, a two fluid nozzle usually produces a greater fraction of sizes < 44 μm.

II – Spray drying

Powders from chemical solution techniques

iii) Droplet size



Considerable evaporation must occur during the first few miliseconds of drying to prevent the formation of agglomerated granules and a coating of sticky agglomerates on the wall of the dryer.

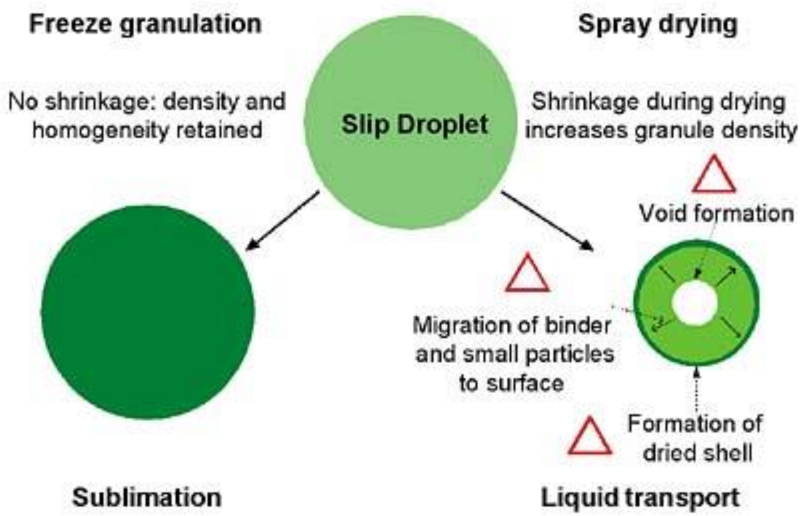
Filtered drying air is commonly heated to a temperature in the range of 300-600ºC.

The product temperature is normally lower than the outlet air temperature and is usually maintained below 100ºC when using organic binders and additives.

II – Spray drying

Powders from chemical solution techniques

iii) Droplet size



The evaporation rate increases initially as the droplet is heated, and a skin is formed. The drying rate remains high as long as the surface is saturated with liquid.

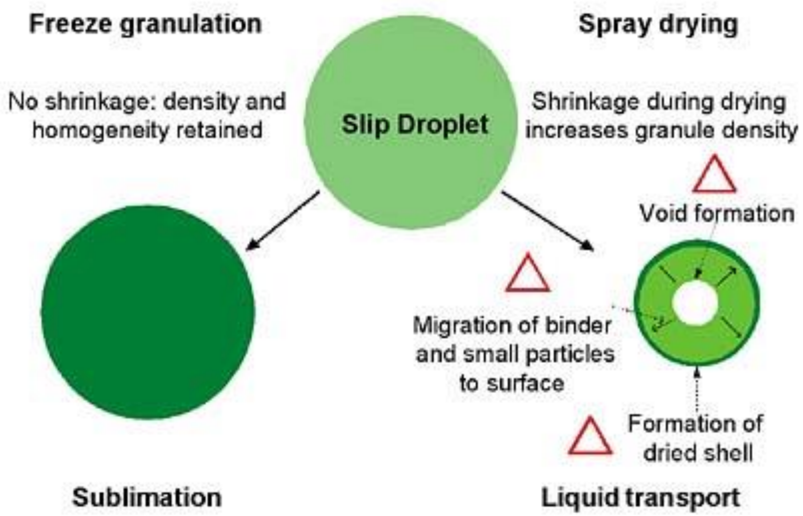
Evaporation retards the heating of the product. Rapid capillary flow and slower evaporation (i.e. a relatively low inlet air temperature and/or a relatively high relative humidity) extend the duration of evaporation from the surface.

Cappilary flow is reduced by parameters that reduce the permeability such as binder molecules and the migration of fine particles or precipitated salts into pores near the surface.

II – Spray drying

Powders from chemical solution techniques

iii) Droplet size



Rapid heating may cause liquid to evaporate within the droplet forming a vapor bubble, which may expand the agglomerate. When the bubble breaks through the skin and collapses and the agglomerate is plastic, a **donut shape is formed**.

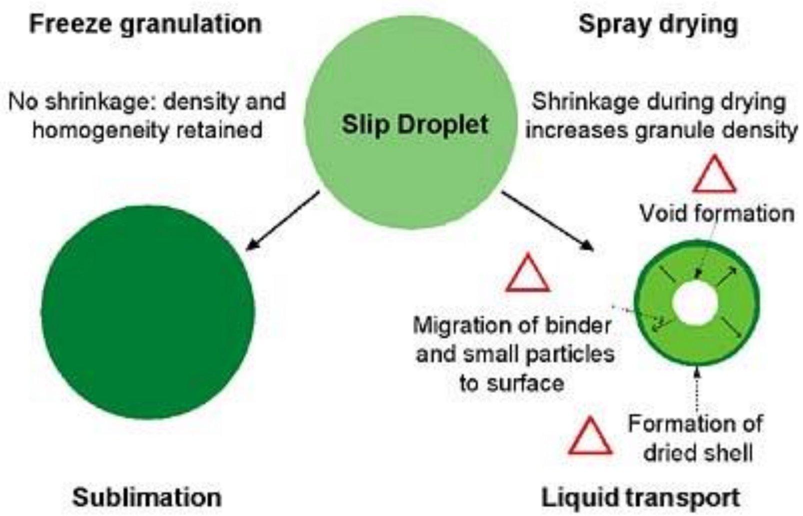
The evaporation rate decreases when the evaporation front recedes below the surface, and the agglomerate becomes less plastic.

The granule is nearly in equilibrium with the warm, moist air leaving the dryer, and the outlet gas temperatures is controlled to maintain a constant moisture content.

II – Spray drying

Powders from chemical solution techniques

iii) Droplet size

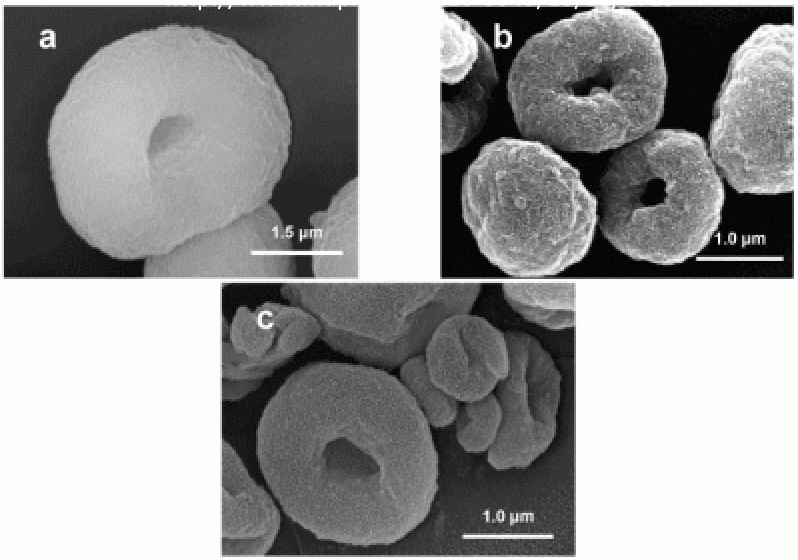


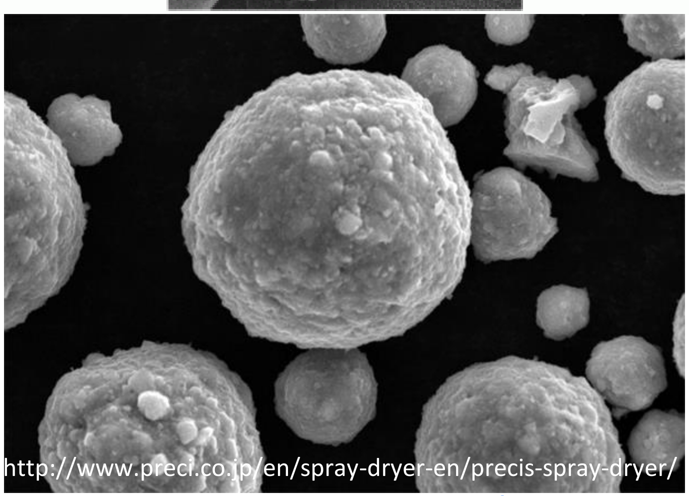
In order to acheve **sufficient green strength** after the shaping process, mostly organic binders are added to the suspensions. They enrich at the surfaces on the granules during the drying process, due to their higher evaporation temperatures compared to pure water, so that further transport of water vapor is hindered and a uniform water transport is no longer possible. This lead to **cavitation** or, in case of high vapor pressure inside the granules, the **thin granule wall may burst open**.

The humidity and binder content of the granules will affect their compressibility in the subsequent pressing process and has to be adapted to the respective requirements.

Powders from chemical solution techniques

iii) Droplet size





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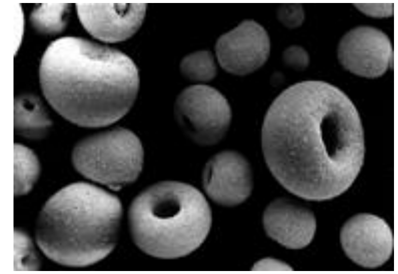
http://coen.boisestate.edu/rickubic/teaching-research/mse-421/



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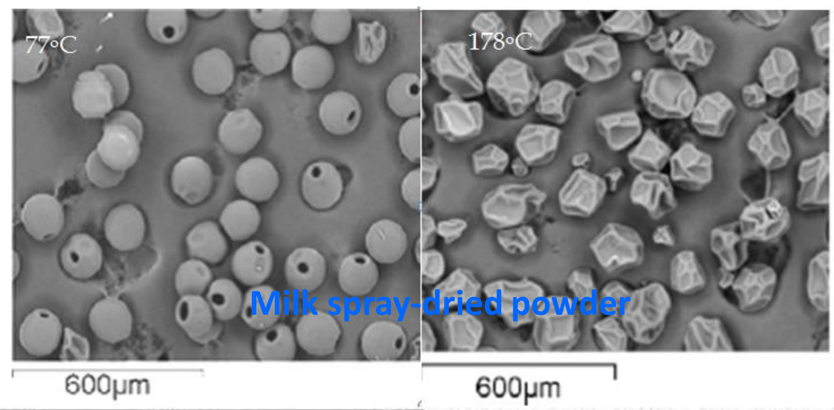

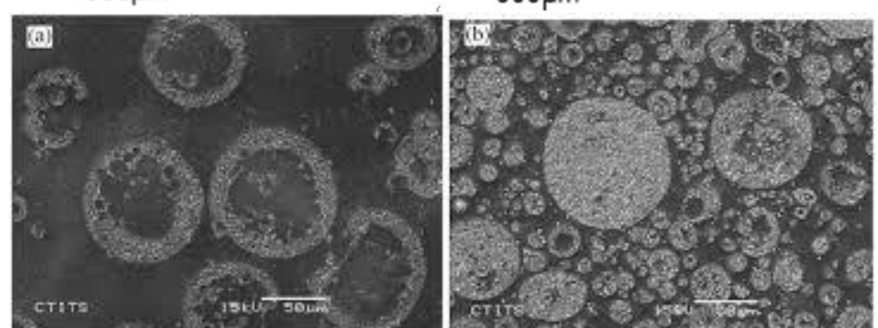

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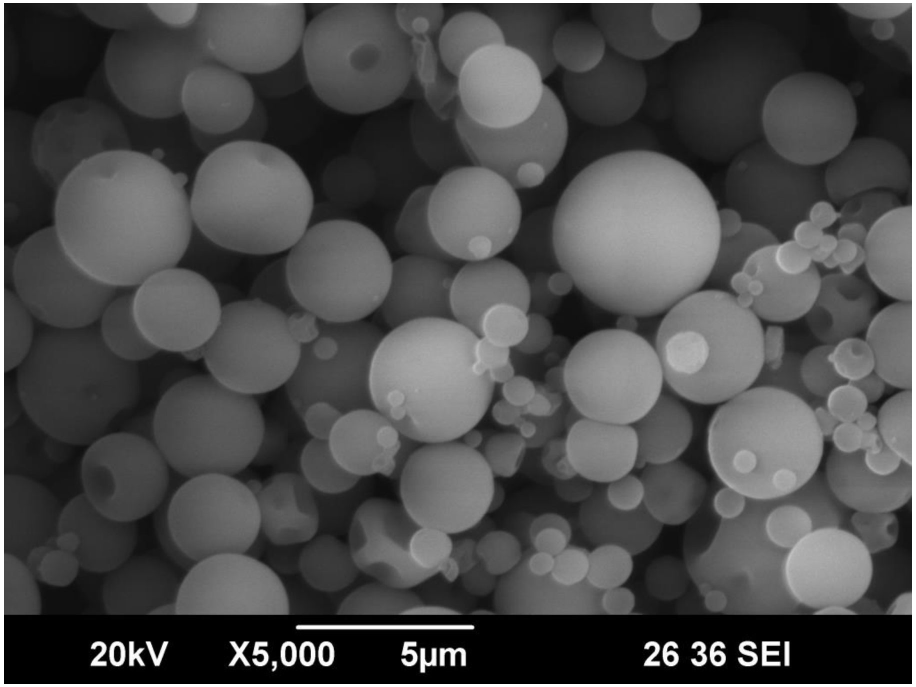
II – Spray drying

Powders from chemical solution techniques

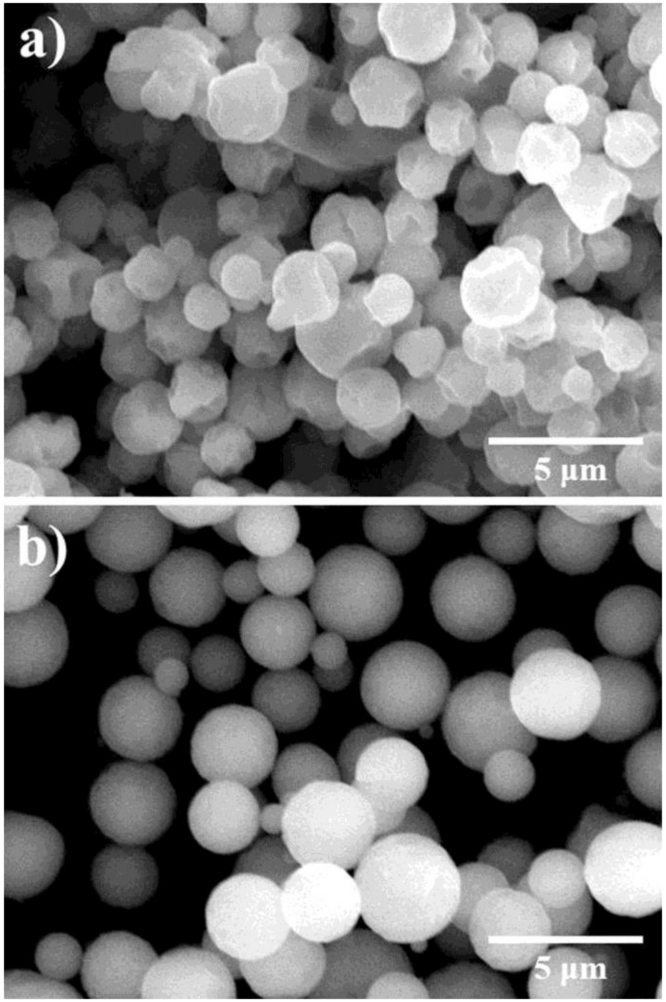
iii) Droplet size

http://chobotix.cz/research-2/encapsulation-technologies/spray-drying/



Chitosan spray-dried powders

http://www.nature.com/articles/srep05857?message-global=remove

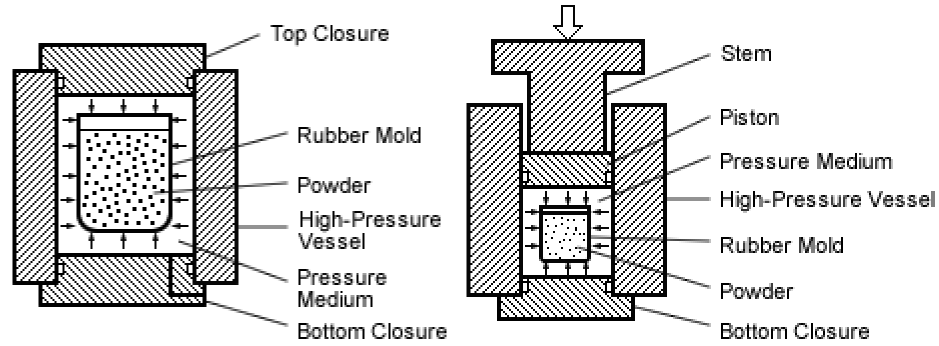


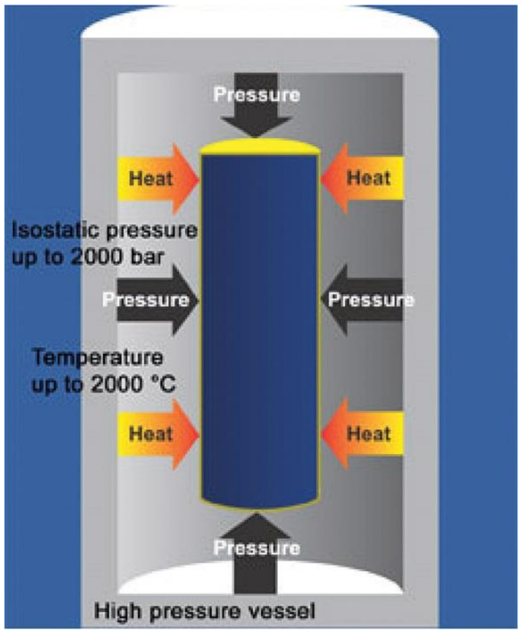
$ZnFe_2O_4$ spray-dried powders

III – Isostatic pressing

Powders from chemical solution techniques

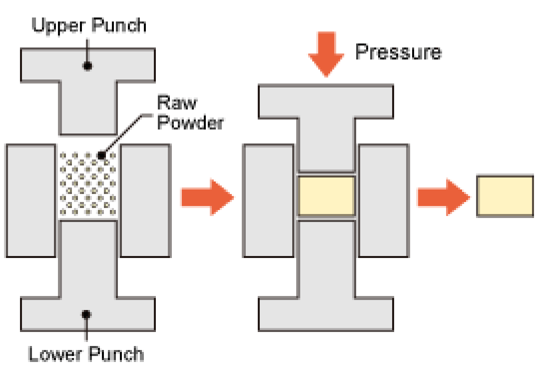
III – Isostatic pressing





Pressing is the simultaneous compaction and shaping of a powder or granular material confined in a rigid die or a flexible mold. Powder feed for industrila pressing is in the form of controlled granules containing processing additives produced by spray-drying or spray granulation.

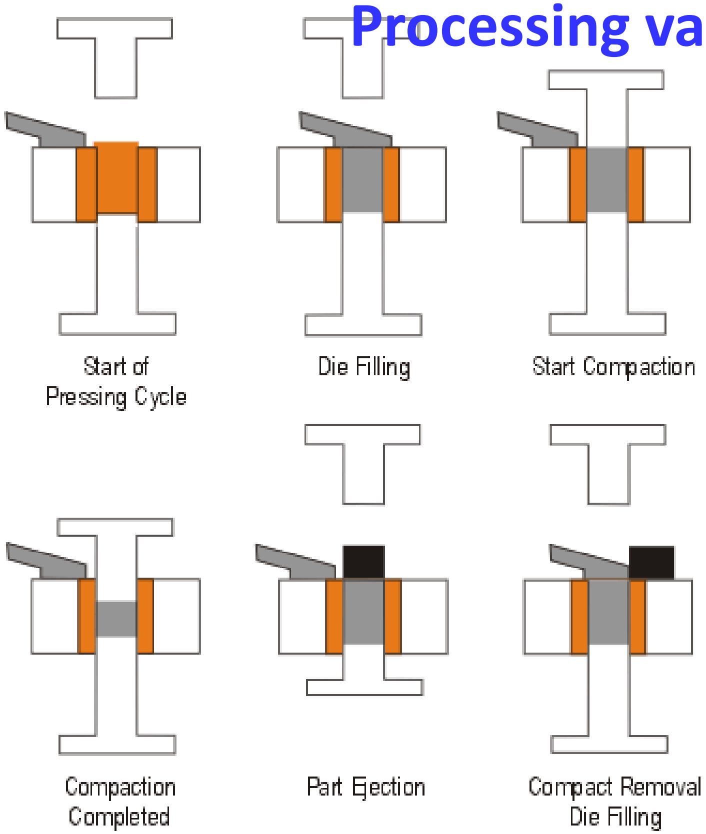
For reasons of produtivity and the ability to porduce parts ranging widely in size and shape to close tolerances with essential no drying shrinkage, pressing is the most widely praticed forming process.

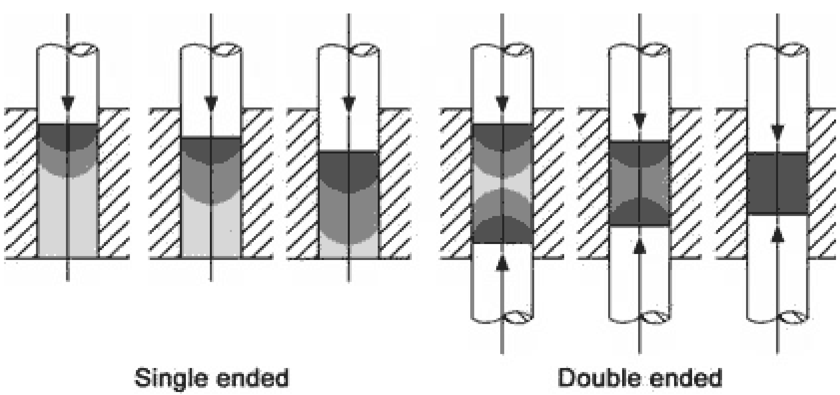


Products produced by pressing include a wide variety of magnetic and dielectric ceramics, various fine-grained technical aluminas including clip carriers and spark plugs, engineering ceramics such as cutting tools and refractory sensors, ceramic tile and porcelain products, and coarse-grained refractories, grinding wheels, and structural clay products.

III – Isostatic pressing

Processing variables in dry-pressing





i) **filling of the die**

ii) **compaction and shaping**

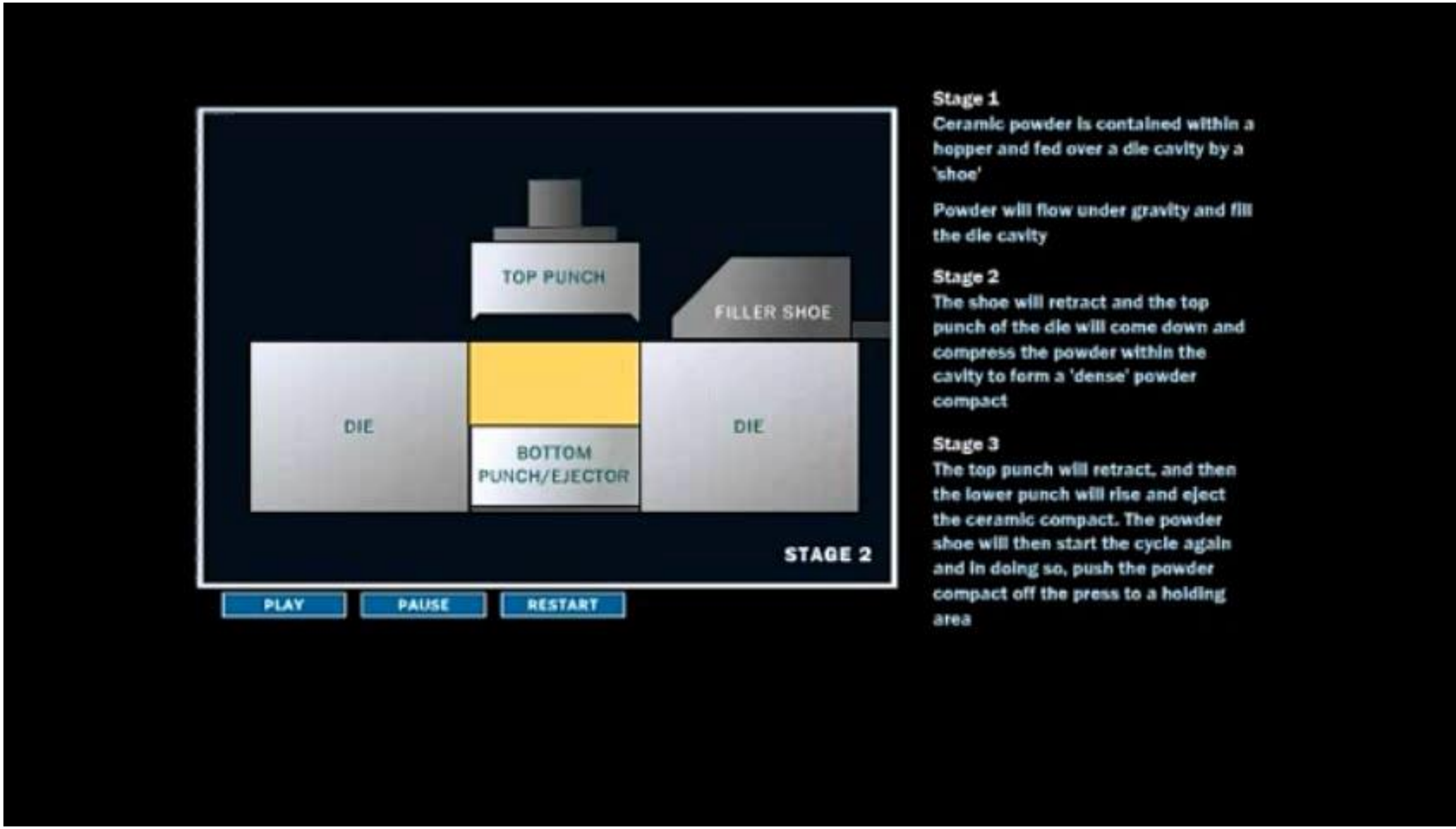
iii) **ejection**

Tooling for dies and punches is commony constructed of hardened steel, but special steels and carbide or ceramic inserts are used in high-wear areas.

The clearance between the die and punchis about 10-25 mm when pressing micron-size powders and up to 100 mm when pressing granular particles.

Die-set life may range up to several hundred thousand pieces for a simple die and a low pressing pressure.

Advertised tolerances are now better than ± 1 % in mass and ± 0.02 mm in thickness.


TOP PUNCH
FILLER SHOE
DIE
DIE
BOTTOM
PUNCH/EJECTOR
STAGE 2
PLAY
PAUSE
RESTART
Stage 1
Ceramic powder is contained within a hopper and fed over a die cavity by a 'shoe'
Powder will flow under gravity and fill the die cavity
Stage 2
The shoe will retract and the top punch of the die will come down and compress the powder within the cavity to form a 'dense' powder compact
Stage 3
The top punch will retract, and then the lower punch will rise and eject the ceramic compact. The powder shoe will then start the cycle again and in doing so, push the powder compact off the press to a holding area

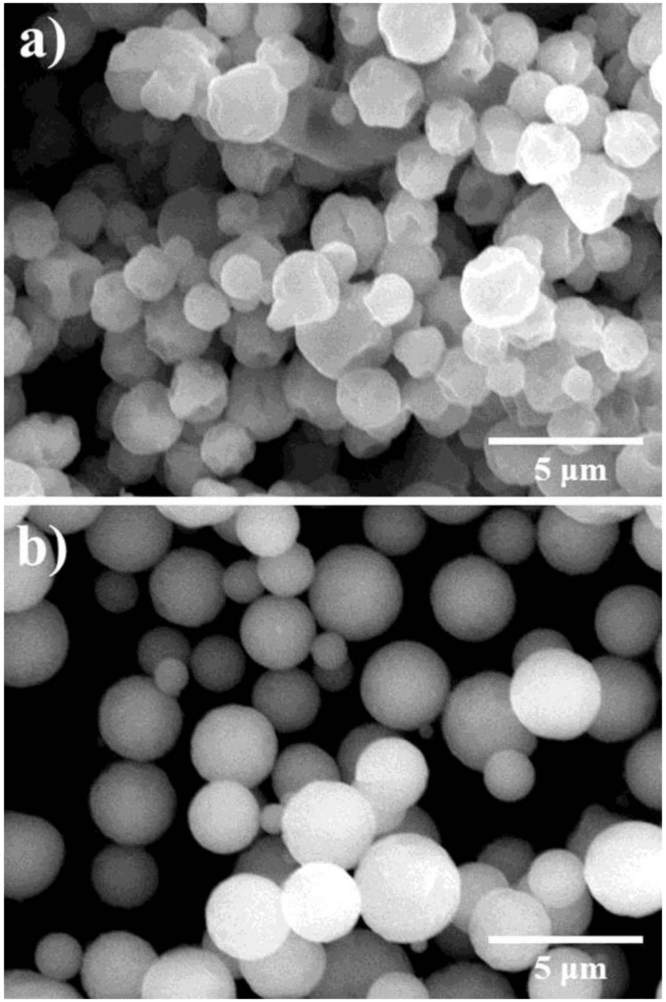
III – Isostatic pressing

Powders characteristics

Dense, **nearly sherical particles** or **granules** with **smooth**, **nonsticky surfaces** that are **coarser than about 40 μm** have **good flow behavior** and are preferred for pressing.

The presence of more than 5% of a finer size may sometimes stop flow altogether, and fines may enter the annulus between the punch and die wall, causing friction and reducing the escape of air.

Extremely large granules are usually irregular in shape, and the bridging action between coarse granules may impede flow and the achievement of a uniform bulk density when powder flows into the die. They should removed by sieving.



$ZnFe_2O_4$ spray-dried powders

Powder Pressing

Sintering - powder touches - forms neck & gradually neck thickens

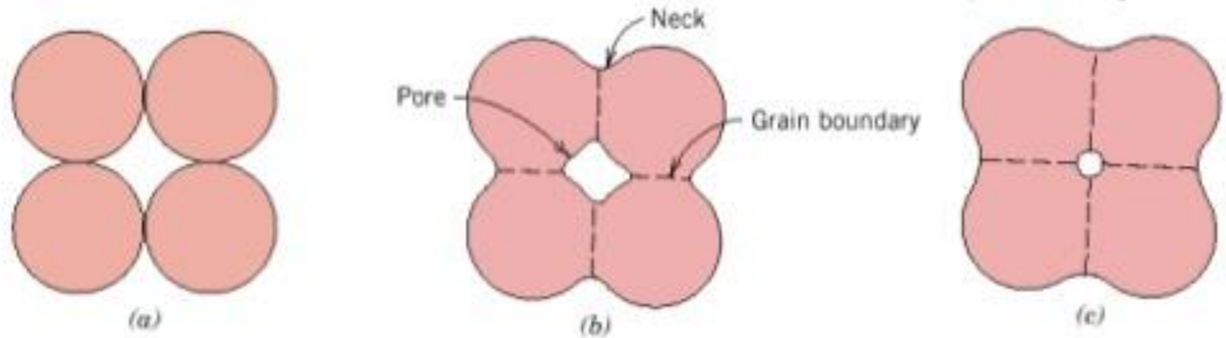
- **add processing aids to help form neck**
- **little or no plastic deformation**

Uniaxial compression - compacted in single direction

Isostatic (hydrostatic) compression - pressure applied by fluid - powder in rubber envelope

Hot pressing - pressure + heat

Adapted from Fig. 13.16, *Callister 7e*.



III – Isostatic pressing

Compaction behavior

Three compaction stages may be identified when the dependence of compact density on log (punch pressure) is examined.

In Stage I, slight densification above the fill density (Df) may occur owing to the sliding and rearrangement of granules. Interstices among granules are much larger than the average pores within the granules.

In Stage II granules deform on fracture, reducing the volume of the relatively large interstices. The apparent yield pressure (Py) of the granules is less than 1 Mpa when the binder system is soft and ductile.

$$D_C = D_f + m\ln\left(P_a / P_y\right)$$

The densification in Stage II may be approximately by the equation:

$$D_C = D_f + m\ln\left(P_a / P_y\right)$$

where DC is the compact density at na applied pressure Pa and m is a compaction constant that depend on the deformability and packing of the granules.

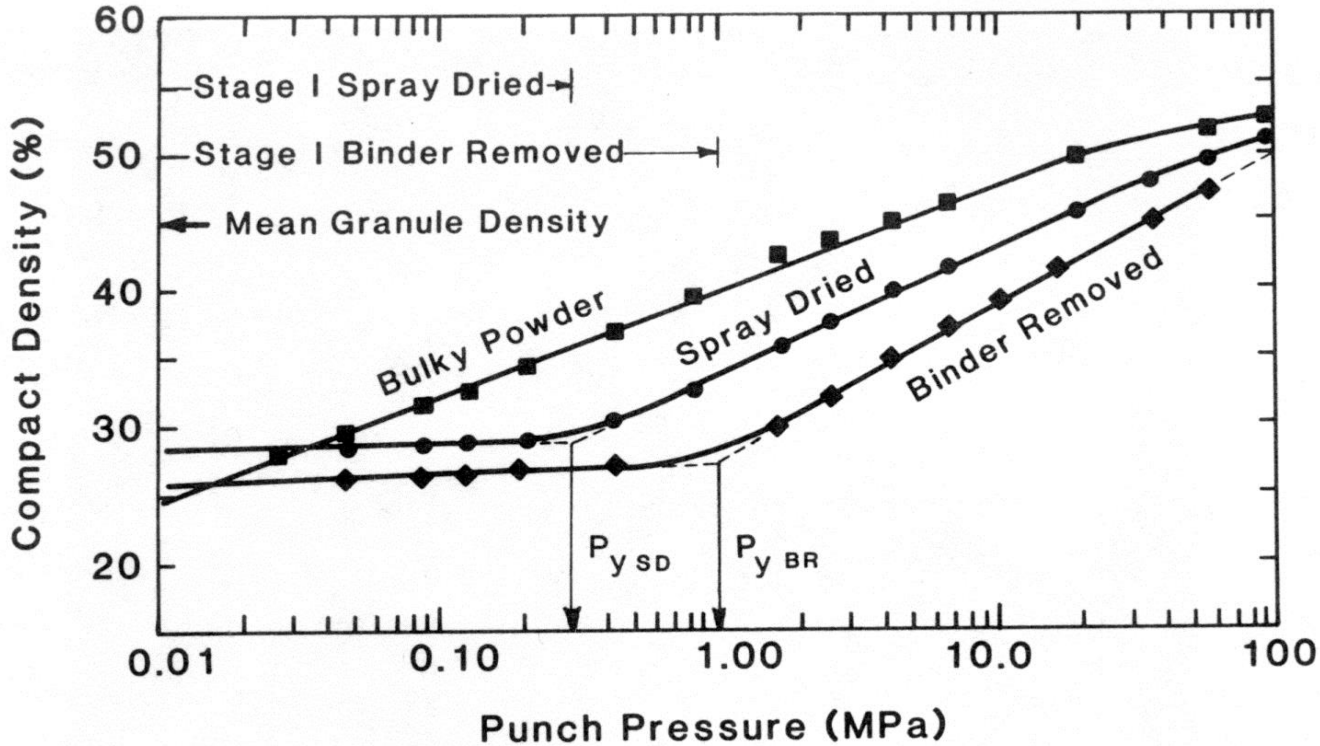


Fig. 20.12 Compaction behavior of MnZn ferrite feed in granular form with and without polyvinyl alcohol binder phase and comminuted granules (bulky powder) containing binder. (After S. J. Lukasiewicz and J. S. Reed, *Am. Ceram. Soc. Bull.* **57**(9), 798–801,805 (1978)).

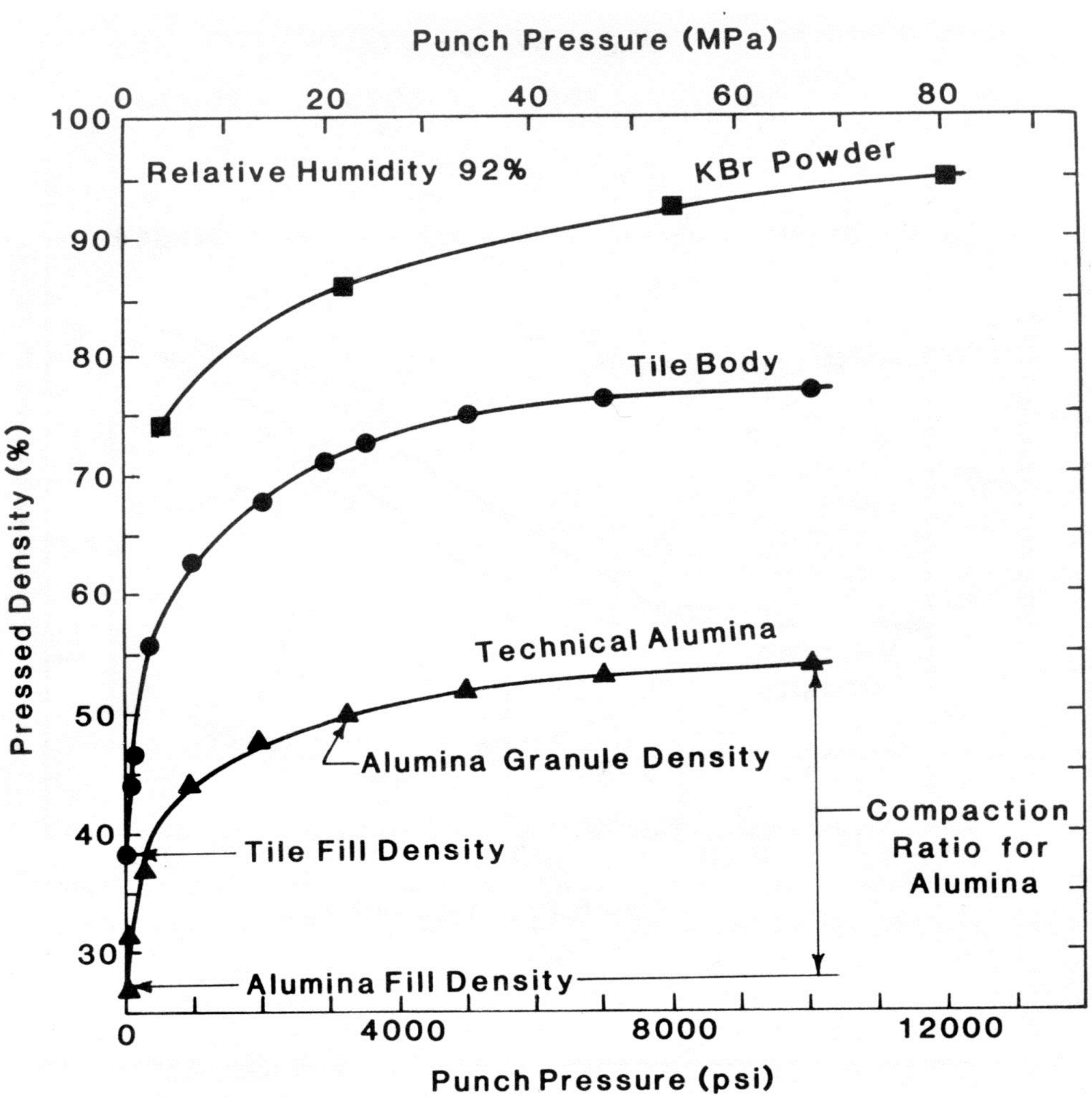


Fig. 20.6 Compaction behavior of spray-dried alumina and tile body granules and a KBr powder as a function of punch pressure (density calculated on inorganic basis).


Quintus
TECHNOLOGIES

Further reading

- **Spray Drying Handbook**. F. W. Bakker-Arkema**,** *4th ed. John Yiley, New York, NY (2007)*
- **Spray Drying Handbook**. K. Masters, *4th ed. John Yiley, New York, NY (1985)*
- **Slipcasting (Ceramics Handbooks).** S. Wardel, University of Pennsylvania Press; 2nd edition (July 5, 2007)