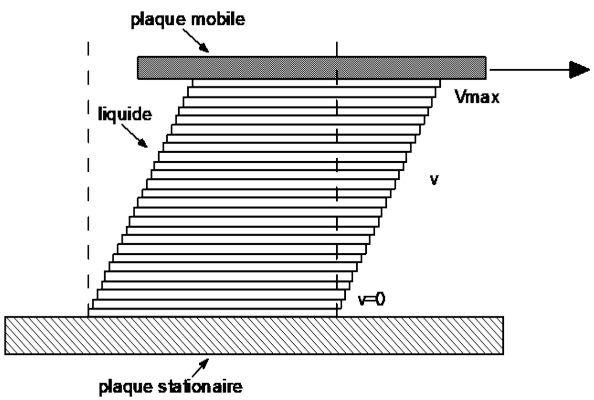
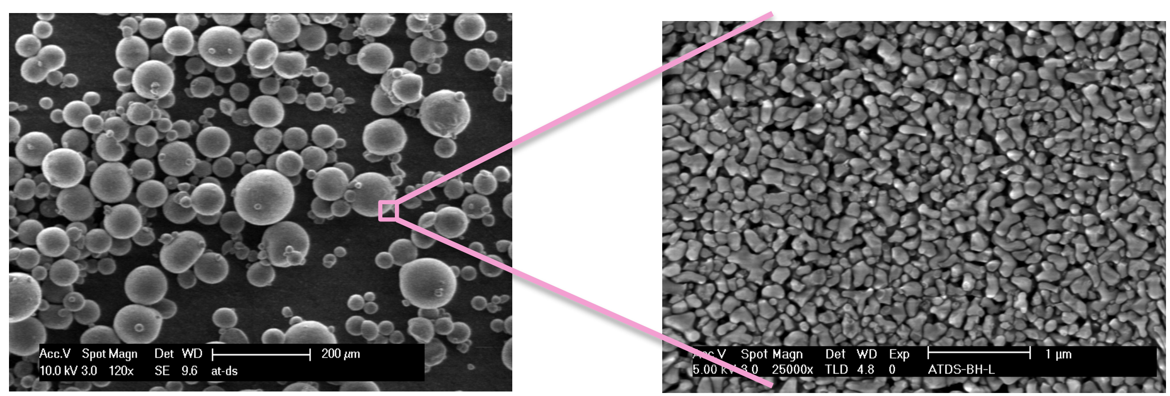
Week 10

10. Powder Treatment (3)
Rheology, mixing and granulation

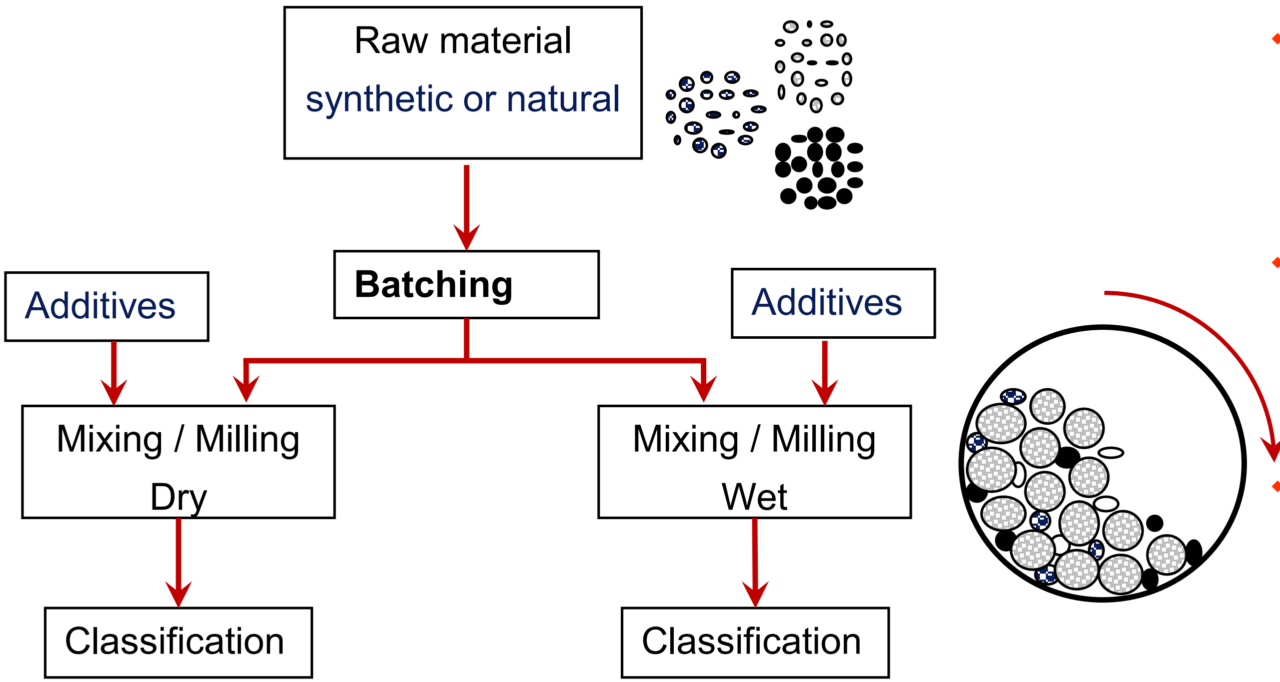
A. Testino





Pages; 169-178, 185-204, Les Céramiques, Les Traité des Matériaux, Volume 16, PPUR, 2005

Ceramic Processing – 1 - Powders

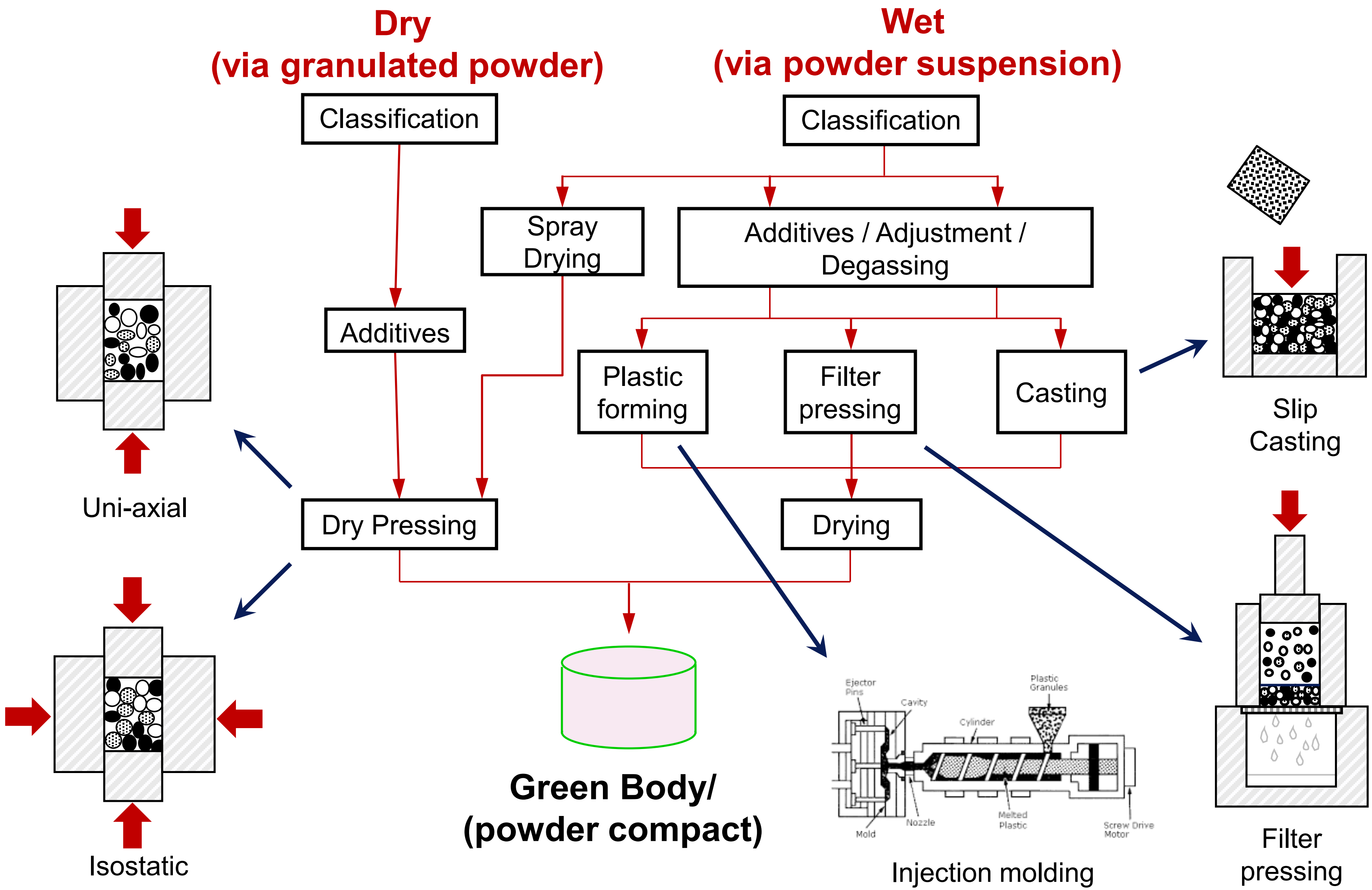


- Commercial powders, often modified for application
- Milling step in order to break up the agglomerates,
- Synthesized by solid route or by precipitation
- Different types of equipment - practical aspects and some scientific principles

- known chemical purity,
- good reactivity

(size ~1 µm and specific surface ~ 5-15 m^2/ g) and
- good homogeneity - physical and chemical.

Manufacture of Ceramics - Ceramic Processing



moulding (UK); molding (US)

Les Céramiques, J. Barton, P. Bowen, C. Carry & J.M. Haussonne, Les Traité des Matériaux, Volume 16, PPUR, 2005

Summary

Rheology

- The resistance of a liquid to an applied shear is known as viscosity.
- For perfectly elastic solids, the energy applied is fully restored as soon as the force ceases to be applied.
- For liquids, the deformation is irreversible and there is flow.
- For ceramic suspensions or slips e.g. shaping by tape casting, slip casting, injection moulding or even on the potter's wheel it is very important to know what the flow will be under the applied stresses.
- The viscosity η of a fluid can be described by:

$$\eta = \frac{\tau}{\dot{\gamma}} \qquad \tau = \frac{F}{A} \qquad \dot{\gamma} = -\frac{dv}{dy} \qquad \gamma = \frac{dx}{dy} \qquad \upsilon = \frac{dx}{dt}$$

viscosity, shear stress, shear rate, shear strain, speed

η or μ [pressure · time = Pa · s = M L t^{-1}] is *dynamic* viscosity.

The *kinematic* viscosity is $\upsilon = \frac{\mu}{\rho}$, where ρ is the density [M L^{-3}]. Therefore, υ unit is [L^2 t^{-1}]

η:eta, μ:mu

Rheology

- Liquid between two parallel plates of surface A
- The upper plate is moved by applying a force F to it to give it a speed Vmax.
- Shear stress (τ) – stress that causes successive parallel layers of a material body to move in their own planes
- Shear strain (γ) – relative in plane displacement, x, of two parallel layers in a material body divided by their separation distance y,
- Shear rate - rate of change of shear strain - $d\gamma/dt$ or $\dot{\gamma}$

shear stress

When $$\eta = \frac{\tau}{\dot{\gamma}}$$ is linear

shear rate

we have a Newtonian Liquid

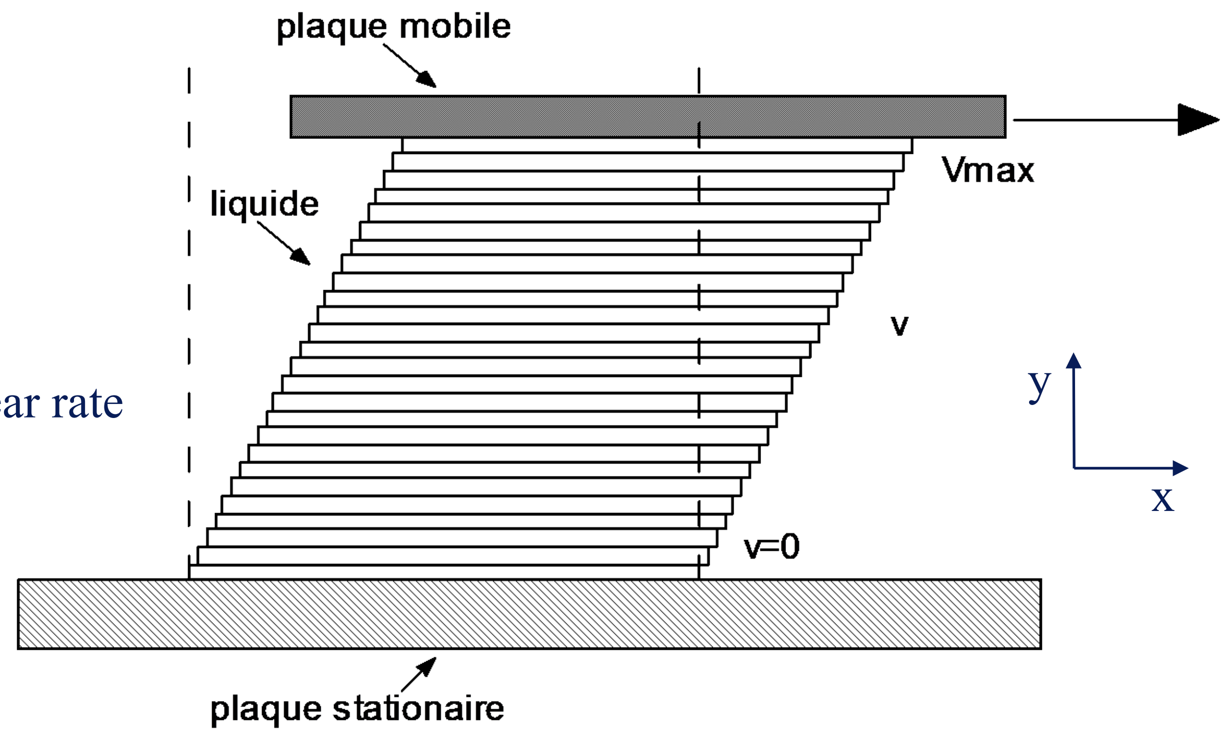
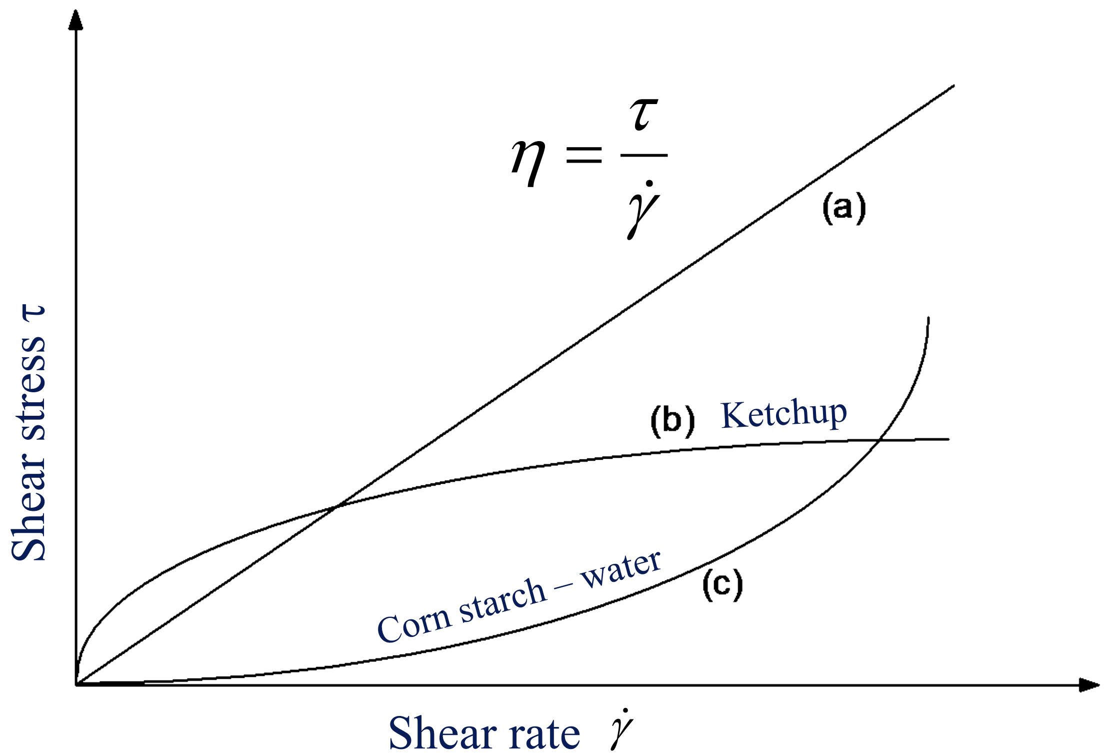


Fig 3.4.20 *Diagram of the flow of a liquid between two parallel plates*

Types of liquids



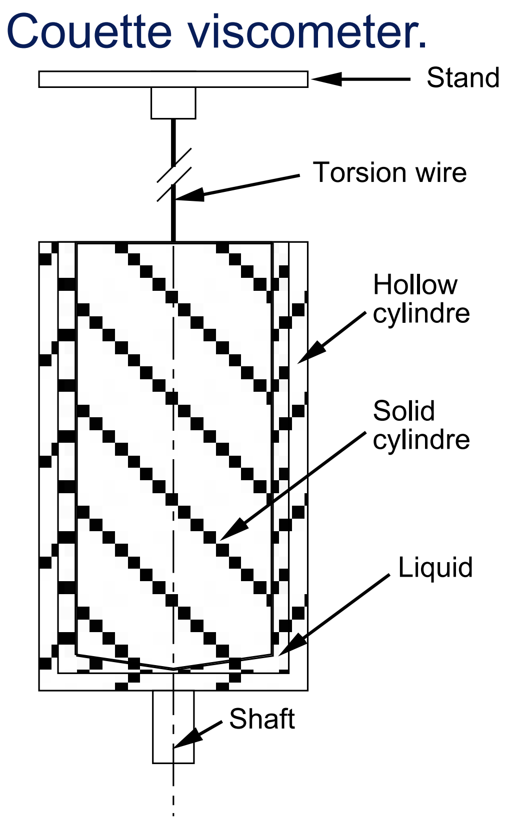


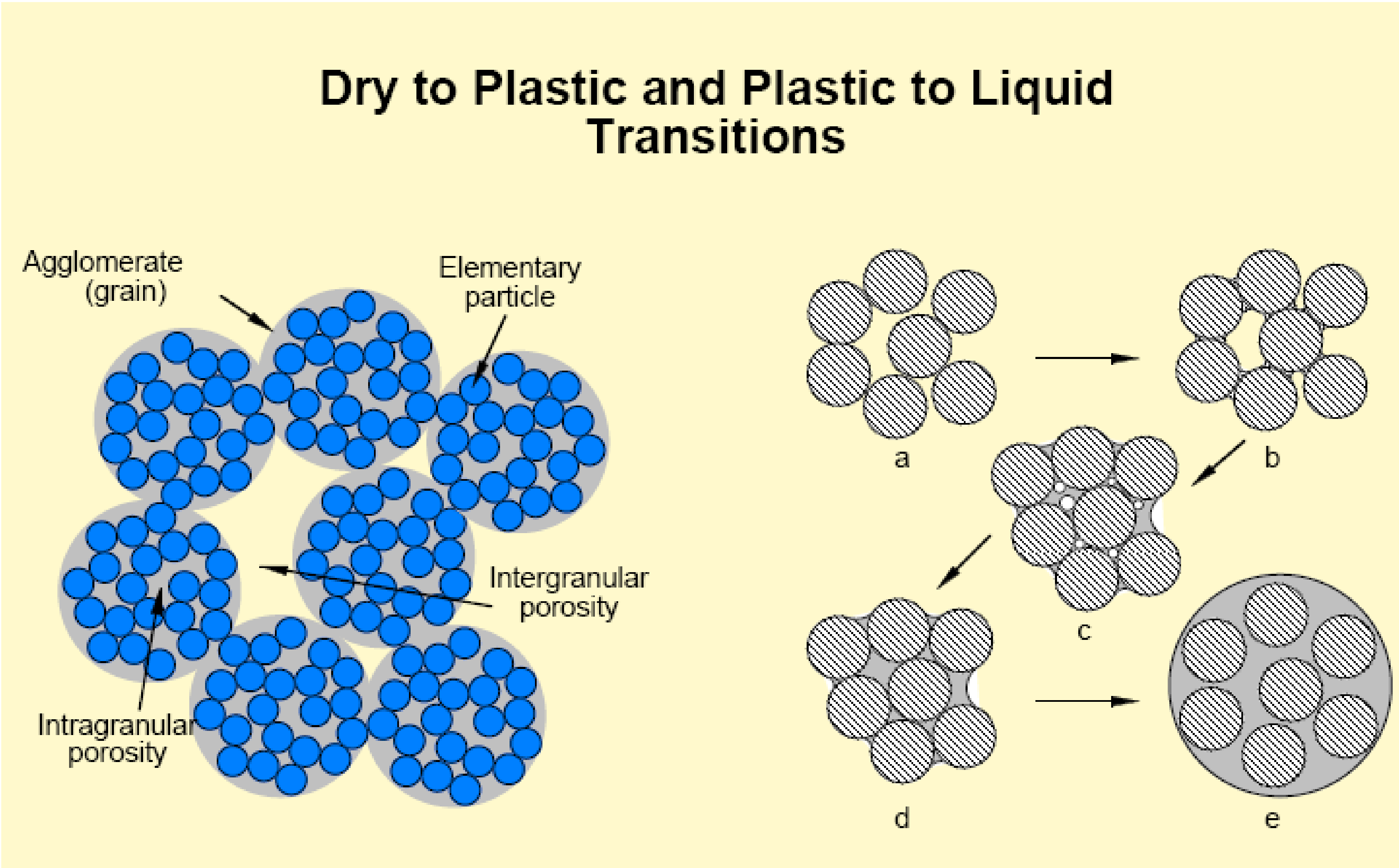
Figure 3.4.21. *Flow curves for different types of fluids*

(a) Newtonian fluid (b) shear thinning fluid (c) shear-thickening fluid

Oil	Water	Mercury	Orange juice	Blood	Olive oil	Honey	Bitumen
0.65	1.0	1.5	2-5	4-15	100	12'000	1'000'000

Table 3.4.6. Typical viscosity values for well-known liquids at 20˚C mPa · s.

Wetting of powders - to produce flowing suspension



Flow Threshold – Yield Stress

- Some suspensions only flow when minimal stress is applied.
- Flow threshold. τ_y
- Typical of systems in which there are networks of attractive forces - cement
- Alumina – session exercise 9.7 - secondary minimum
- From Van der Waals or electrostatic forces.
- Linear after – yield stress ideal Bingham fluid (if not, non-ideal)

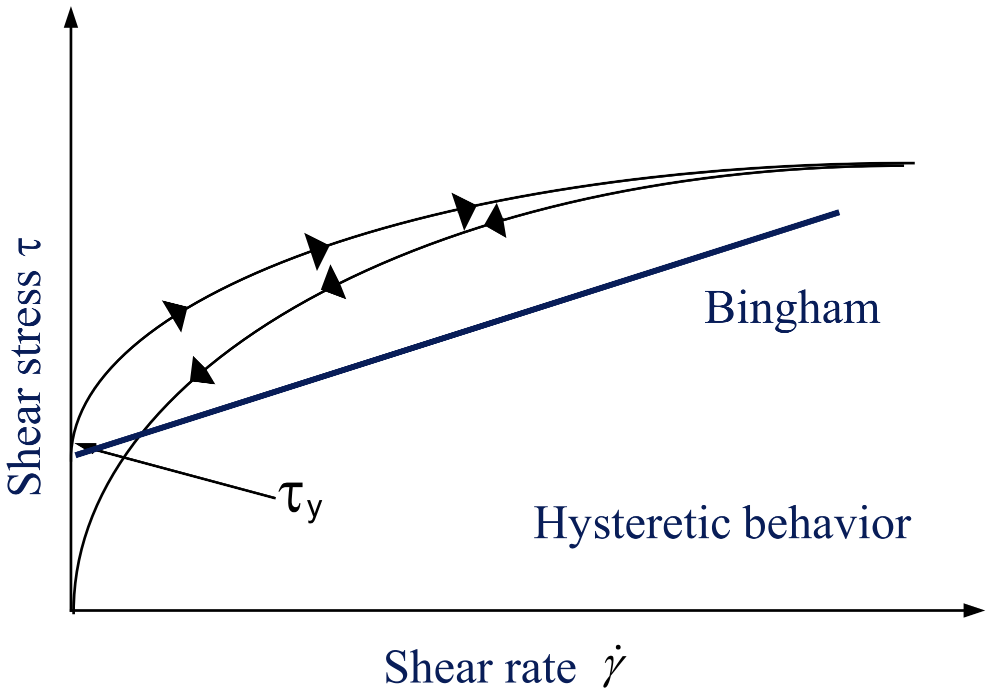


Figure 3.4.21. Flow curve for a shear thinning liquid with a yield stress, τ_y.

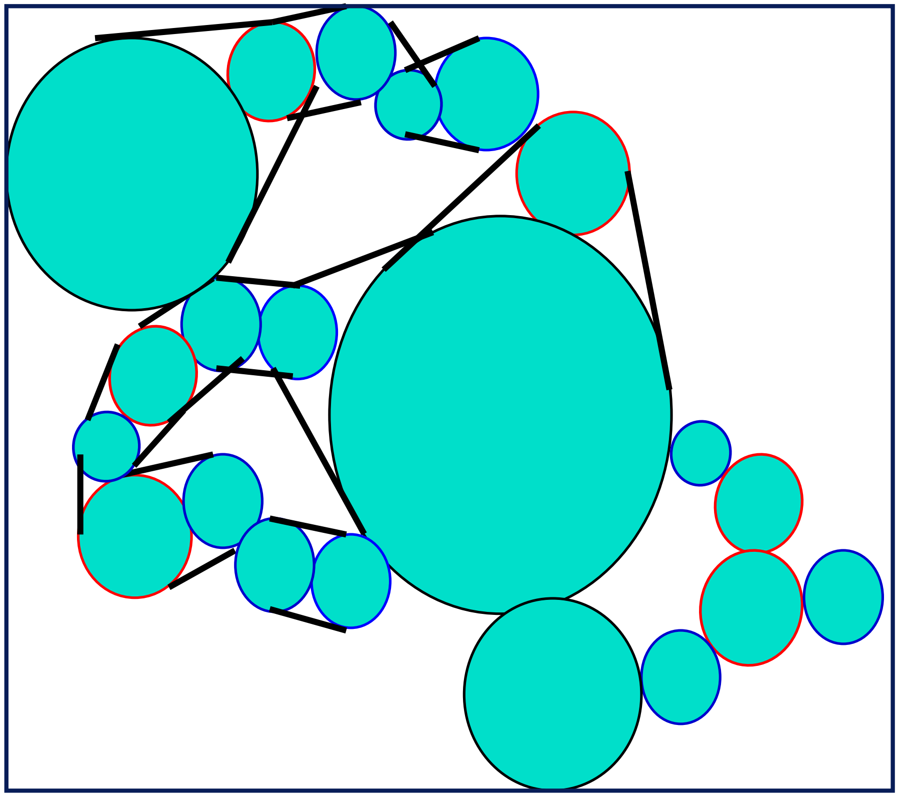
- If the viscosity varies with time for a constant shear rate
- The behavior is said to be **thixotropic**

  (bifidus or petite Suisse ...)

Yield Stress

- What is the stress required to break the attractive network and give a fluid behavior?

- EXAMPLE
- Cement rheology



Example Cement - Ordinary Portland Cement (OPC)

LIMESTONE
SAND
CLAYS

→ 1450ºC → CLINKER

GYPSUM → ↓

PORTLAND CEMENT (OPC)

ALTERATION OF LANDSCAPES

HIGH ENERGY REQUIREMENTS

EMISSION OF GREENHOUSES GASES

1 ton of cement < > 0.815 ton of CO_2

- Raw materials: 0.425 ton of CO_2
- Fuel: 0.390 ton of CO_2

- Slag[1] often mixed with OPC – no need of activation – waste product no energy or CO_2
- Pure AAS[2] cements still need alkali but energy consumption still much lower OPC

- Cement industry contributes about 7-9% of the worldwide CO_2 emission
- [1]Slag: e.g. blast furnace slag, see metallurgy and cast iron production (4% of global CO_2 emission)
- [2]AAS: alkali-activated slag, pH needs to be high (alkaline) to dissolve slag

Cement rheology - Why AAS ?

➢World-wide need to reduce the **energy** consumption

➢Reduce **greenhouse gases emitted** during cement manufacture

➢Pursuit of more eco-efficient materials – blast furnace slag is a waste product from the iron industry with chemical composition close to cement – can replace cement and reduce carbon footprint

ALKALI-ACTIVATED SLAG (AAS)

⇨ Obtained by mixing granulated slag & highly alkaline solutions (low reactivity)

⇨ AAS cements - mechanical and durable properties comparable or even higher than Ordinary Portland Cement (OPC)*.

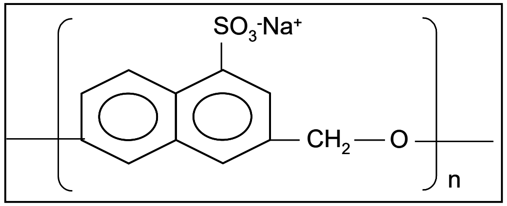
- ⇨ high early strength, low heat of hydration,
- ⇨ high resistance to acid, seawater, sulphate media
- ⇨ low reinforcement corrosion

•*C. Shi. Cem. Concr. Res., 26 (1996) 1789-1799,
•*Puertas et al Mater. Construcc. 52 (267) 55-71

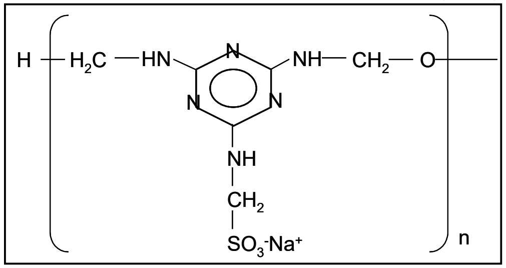
Superplasticizers – polymers – steric or electrostatic?

Admixture	M_w (Da)	M_n (Da)	PDI (M_w/M_n)
Naphthalene-based (NF)	5,384	3,338	1.6
Melamine-based (M)	15,804	8,498	1.9
Vinyl copolymer (V)	28,800	13,814	2.1
Polycarboxylate-ether PCE1	24,275	11,962	2.0
Polycarboxylate-ether – PCE2	32,000	6,200	5.2
Polyacrylic acid PAA	10,000	-	-

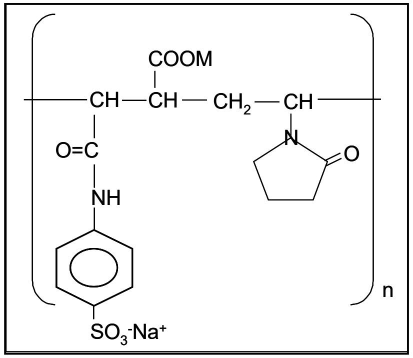
Naphtalene derived (NF)



Melamine derived (M)



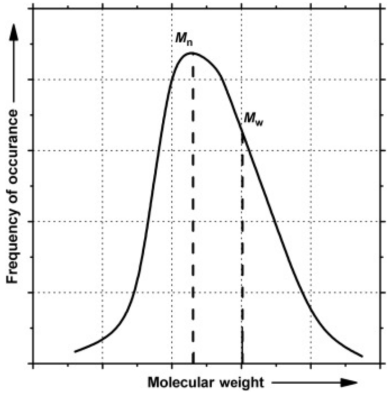
Vinyl copolymer (V)



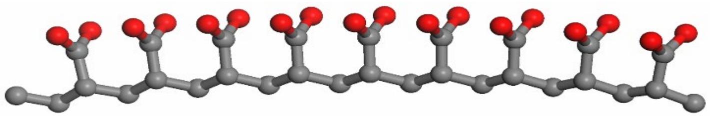
Mw: Weight average molecular weight

Mn: Number average molecular weight

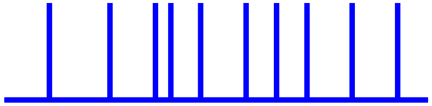
PDI – polydispersity index – broadening of the distribution of molecular weight



Polyacyrlic acid –(PAA)

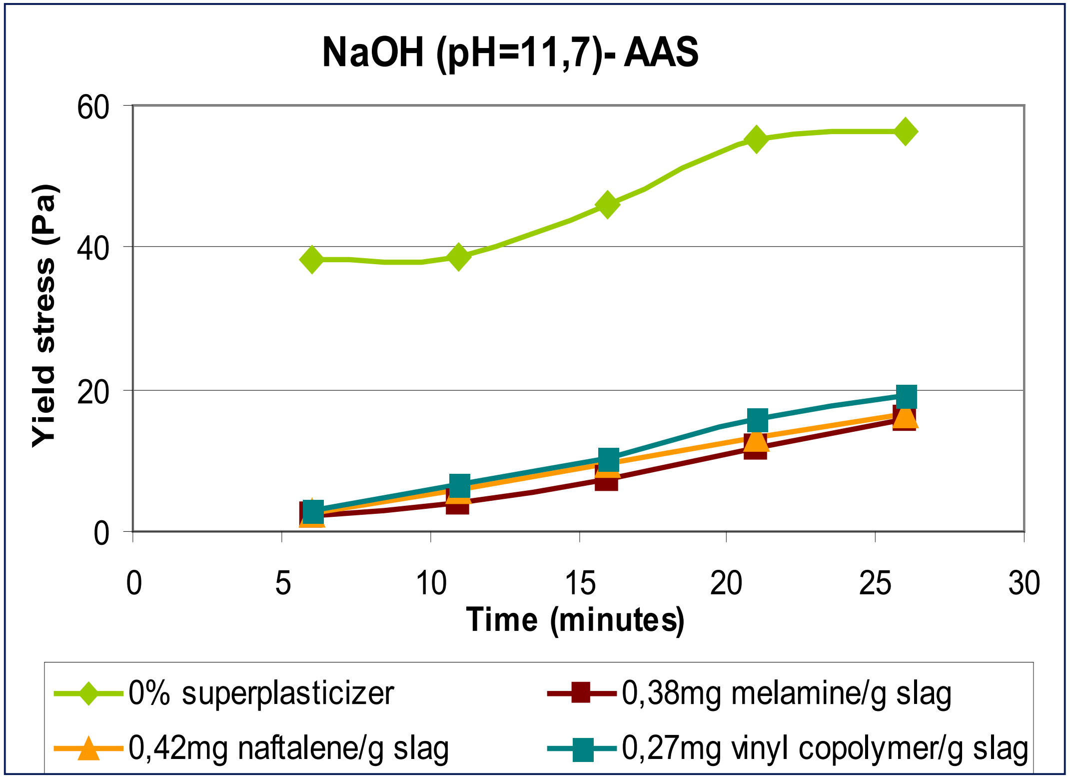


Polycarboxylate-ether



Yield Stress - Slag cements - steric repulsion

- Initial cement has significant yield stress – 40 Pa
- All polymers (Superplasticizers, SPs) reduced Yield stress significantly
- All SPs only induce a small change in the zeta potential (Slag -2.9 mV)
- Steric or electrostatic main dispersion mechanism? Hamaker* and Yodel#

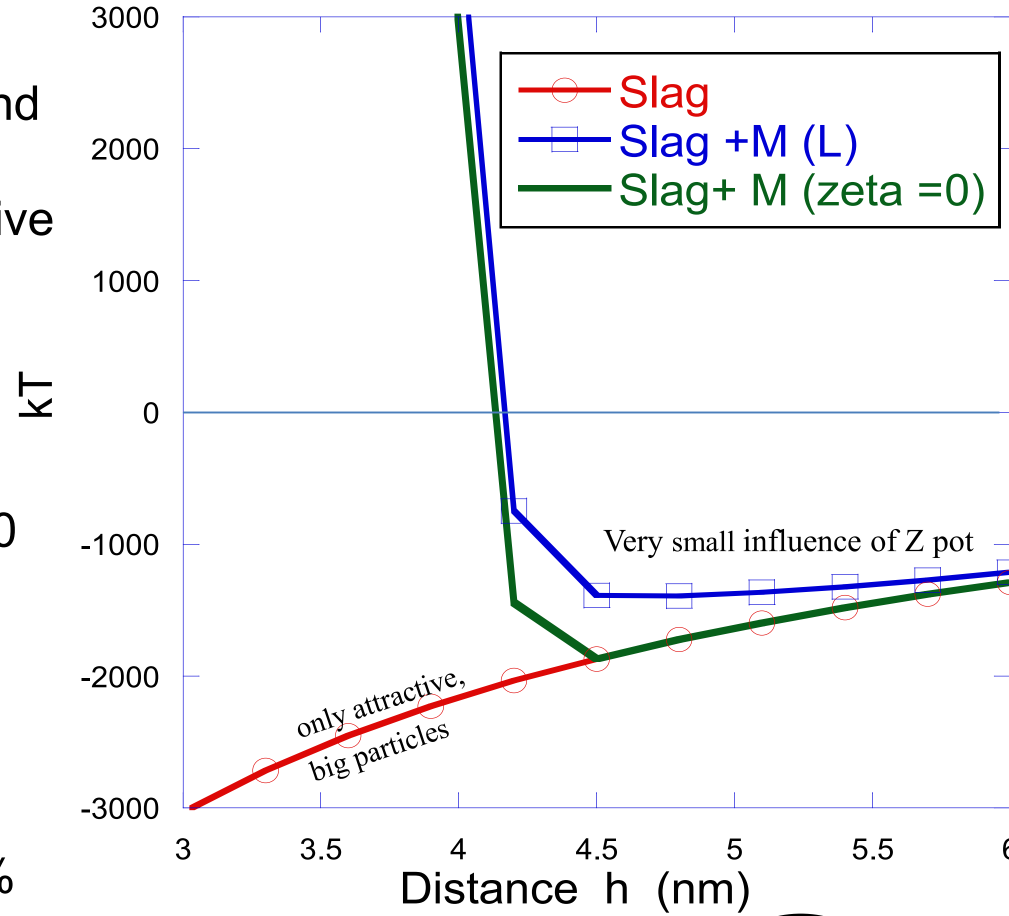


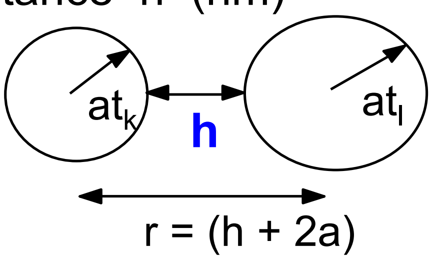
Admixture	Zeta (slag) pH-11.7
Naphthalene-based (NF)	- 8.9
Melamine-based (M)	-10.4
Vinyl copolymer (V)	-9.4
Polycarboxylate-ether PCE1	-3.3
Polycarboxylate-ether – PCE2	-1.7
Pure slag	- 2.9

* Mr. Palacios, P. Bowen , M. Kappl, HJ. Butt, M. Stuer, C. Pecharromán, U. Aschauer, F. Puertas "Repulsion Forces of Superplasticizers on Alkali Activated Slag Pastes" Materials of Construction, 489-513, 62 (308), 2012
#Robert J. Flatt, Paul Bowen, J. Am. Ceram. Soc., 89 [4] 1244–1256 (2006)

Interparticle Potentials Hamaker* - Slag cements & SPs

- Dispersants used in all cements
- Concrete – mixture of cement and sands ,gravel….etc
- All SPs still show a small attractive minimums between particle surfaces-
- At 3-7 nm
- Little Change in depth & distance of minimum with zeta = 0
- i.e. Steric dominating
- If zeta plane is placed at Labs (adsorbed layer thickness)
- Electrostatic contributions <25%
- Low zeta and moderate ionic strength - slag pH 11.7
- **Steric component dominates**

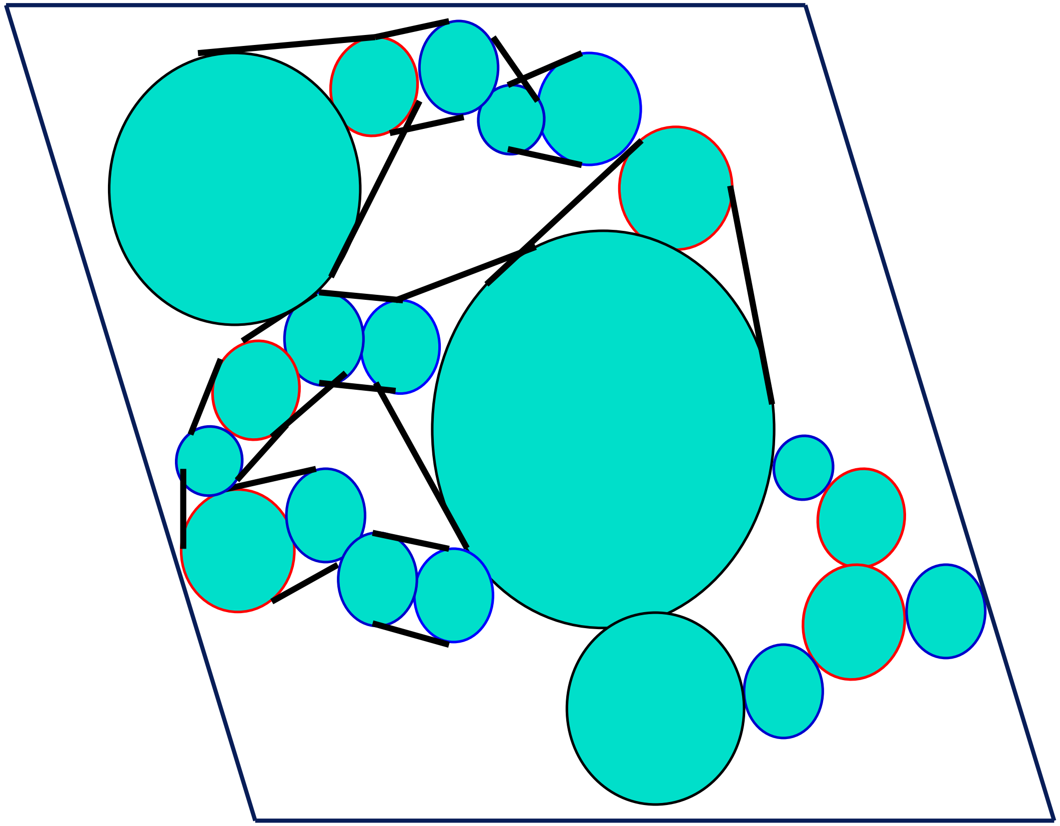




* M. Palacios, P. Bowen , M. Kappl, HJ. Butt, M. Stuer, C. Pecharromán, U. Aschauer, F. Puertas "Repulsion Forces of Superplasticizers on Alkali Activated Slag Pastes" Mat.Contrucion489-513, 62 (308), 2012

Yield Stress

- What is the stress required to break the attractive network and give a fluid behaviour?



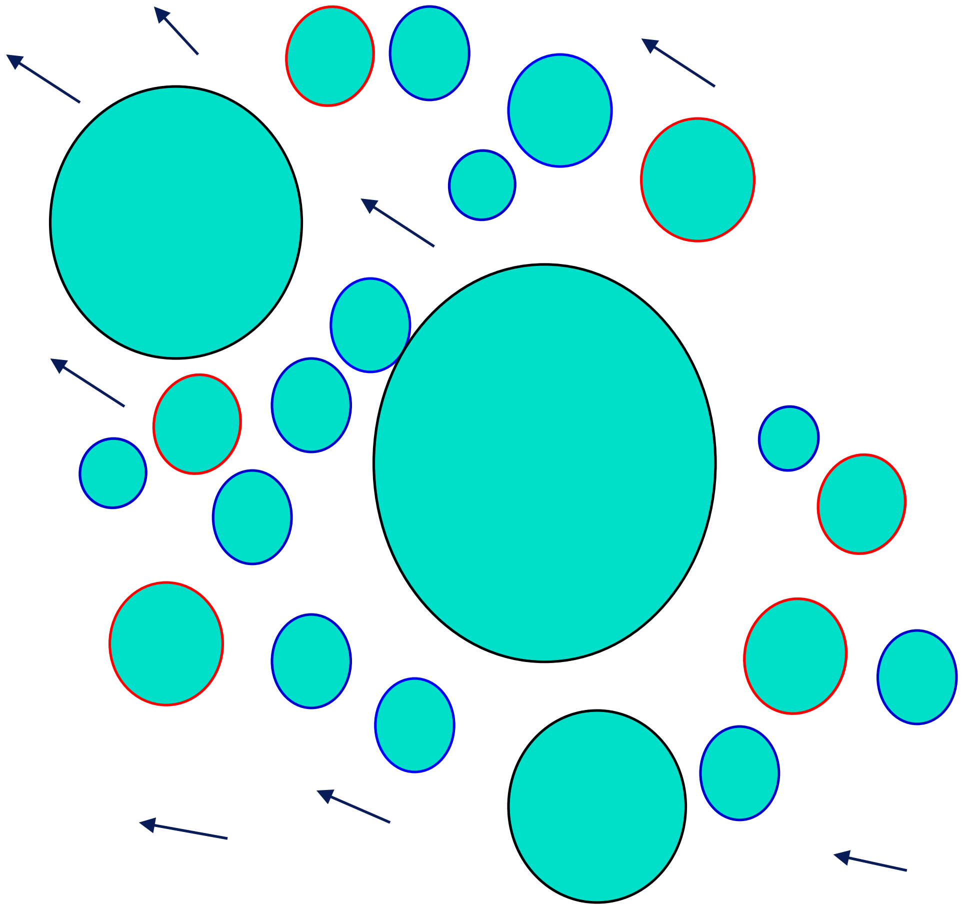
Yield Stress

- What is the stress required to break the attractive network and give a fluid behavior?

- How to calculate from basic suspension characteristics
- PSD and physicochemical parameters – fundamental (Z potential, adsorbed layer thickness, Hamaker constant, …)

- Research topic at LMC

- RJ Flatt, P. Bowen, "YODEL: a Yield stress MODEL for suspensions " J.Amer.Ceram.Soc., 89 (4) 1244-56, (2006)



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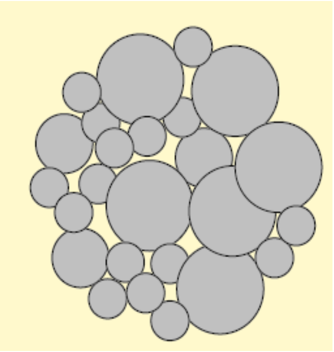
Rheology of suspensions

- The main factors controlling the type of behavior are
  - the volume fraction of the particles,
  - particle size distribution as well as
  - their morphology
  - Interparticle forces (colloidal stability),
  - the type of polymeric additives in the dispersing liquid



- For diluted suspensions, ignoring the interparticle forces, Einstein derived the expression for the viscosity of a suspension

$$\eta_s = \eta_l \left(1 + \alpha\phi\right)$$ Eq. 3.4.22

- η_s of the suspension, the volume fraction ϕ particles, η_l the viscosity of the liquid
- α is a constant depending on the morphology of the particle - 2.5 for spheres
- $\alpha > 2.5$, for anisotropic particles
- agglomerated particles, liquid will be trapped - will not facilitate movement of particles - the effective volume of solids is increased relative to the actual volume of solid put into suspension.

Volume fractions> 2%

2

- Einstein's relationship good for ϕ by 2%
- $\phi > 2\%$ - must be completed by the higher order terms of a Taylor series
- To take into account interparticle interactions (multibody interactions)

$$\eta_s = \eta_l \left(1 + \alpha\phi + \beta\phi^2 + \chi\phi^3 + \ldots\ldots\right) \qquad \text{Eq. 3.4.23}$$

- For ultrafine particles (<100nm) - the effective volume increase resulting from the double layer and / or the adsorbed layer.
- Can be very significant ….
- Especially for suspensions with low ionic strengths e.g. 10^{-5} M
- Particles of 10nm can have an effective radius of 100nm (Tadros, 1995).

Effect of Volume fraction

Rigid spheres model (hard sphere) - Silica in cyclohexane

- behaviour shear thinnng - between the viscosity limit values
  - low shear rate η_0 and to
  - high shear rate η_∞.
- For η_0, the limit of ϕ is <0.64,
- which corresponds to maximum random packing of monosized spherical particles.
- For η_∞ $\phi > 0.64$ suggests that there is some degree of organization in the structures
- ex: compact hexagonal where $\phi = 0.74$
- allowing the flow of these microstructures with a high degree of arrangement *(Russel 1991)* ***e.g. hexagonal close packed layers***
- **Elegantly demonstrated experimentally by Henri van Damme in Paris** *(Lootens et al PRL 95, 268302 (2005))*

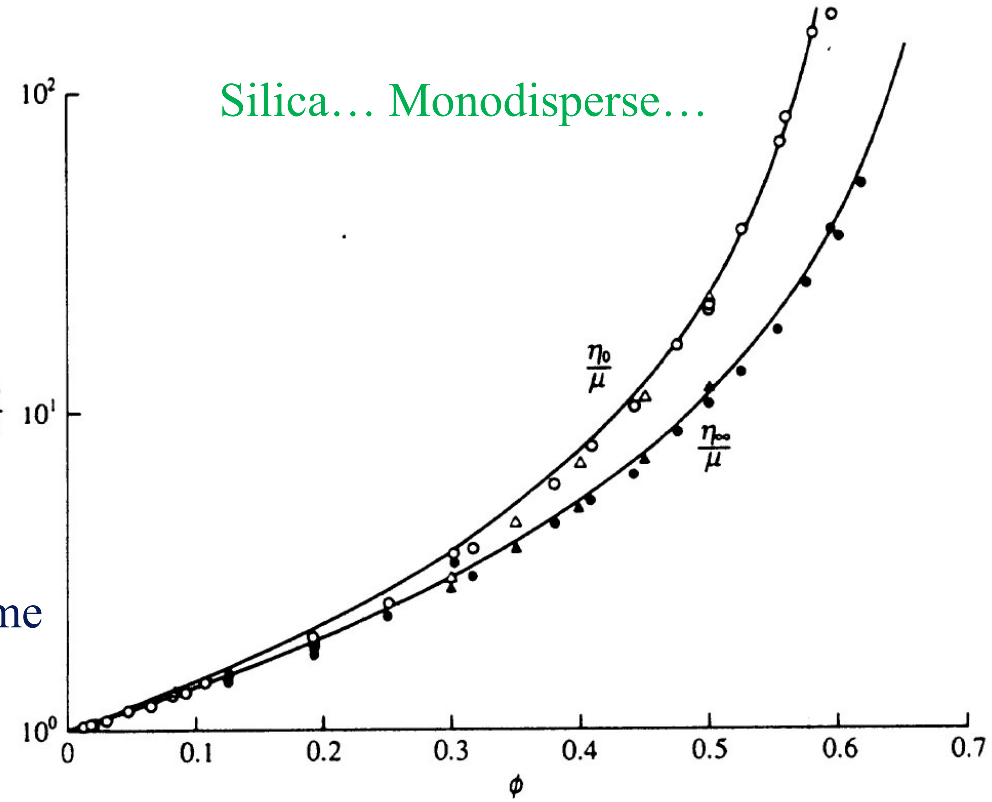
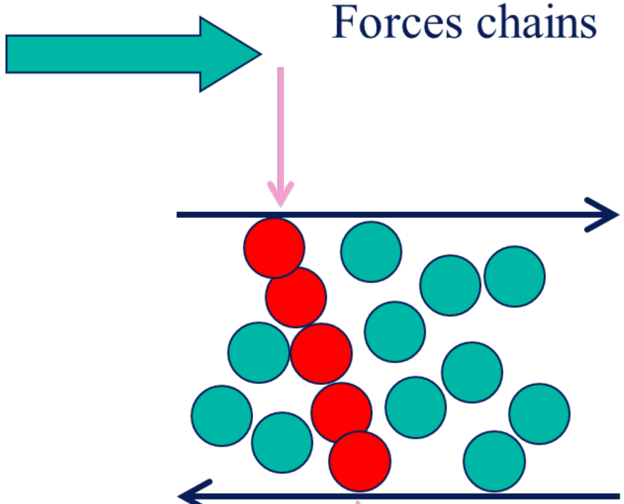


Figure 3.4.23. *Effect of volume fraction on the relative viscosity of a suspension - for rigid spheres (a) low shear rate η_0 (b) high shear rate η_∞(Russel, 1991).*

Dilatant Flow of Concentrated Suspensions of Silica Particles

- Dilatant = shear thickening = *Increase in viscosity with increased shear rate*
- Dilatant above critical shear rate.
- Very low yield stresses <1 Pa - "good" colloidal stability



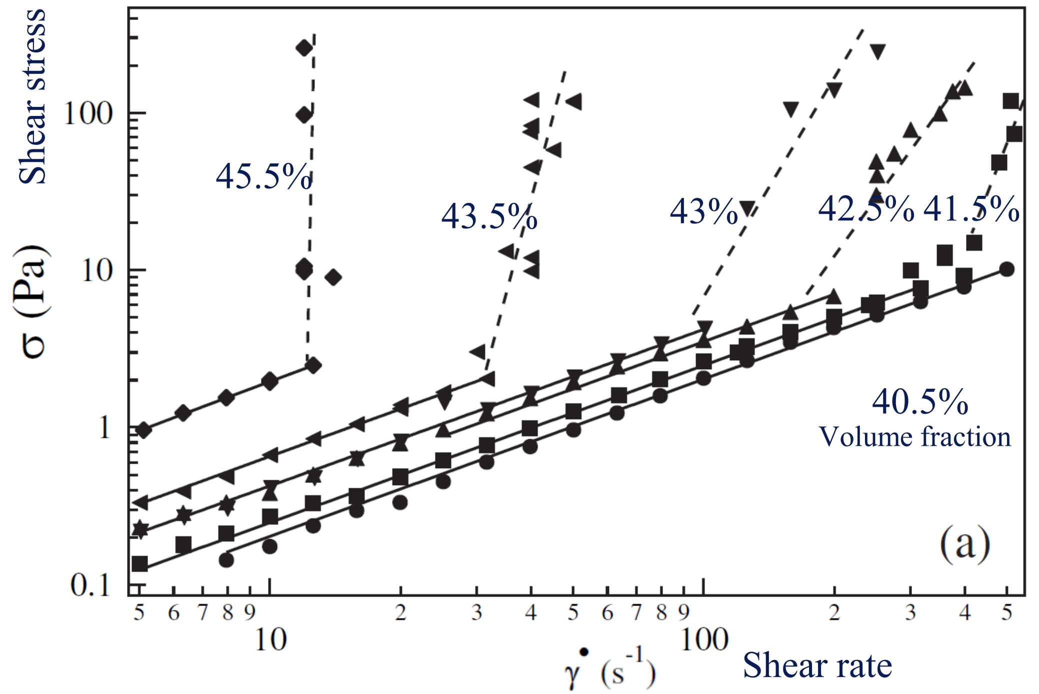


FIG. 2. (a) Shear stress increase as a function of the shear rate for different particle volume fractions (40.5% ;, 41.5%; 42.5%; , 43%; , 43.5%; , 45.5%).

→ Increasing particle volume fraction, jamming transition starts at lower shear rate

Lootens et al PRL **95, 268302 (2005)**

Shear-induced order : Lootens et al PRL **95, 268302 (2005)**

3

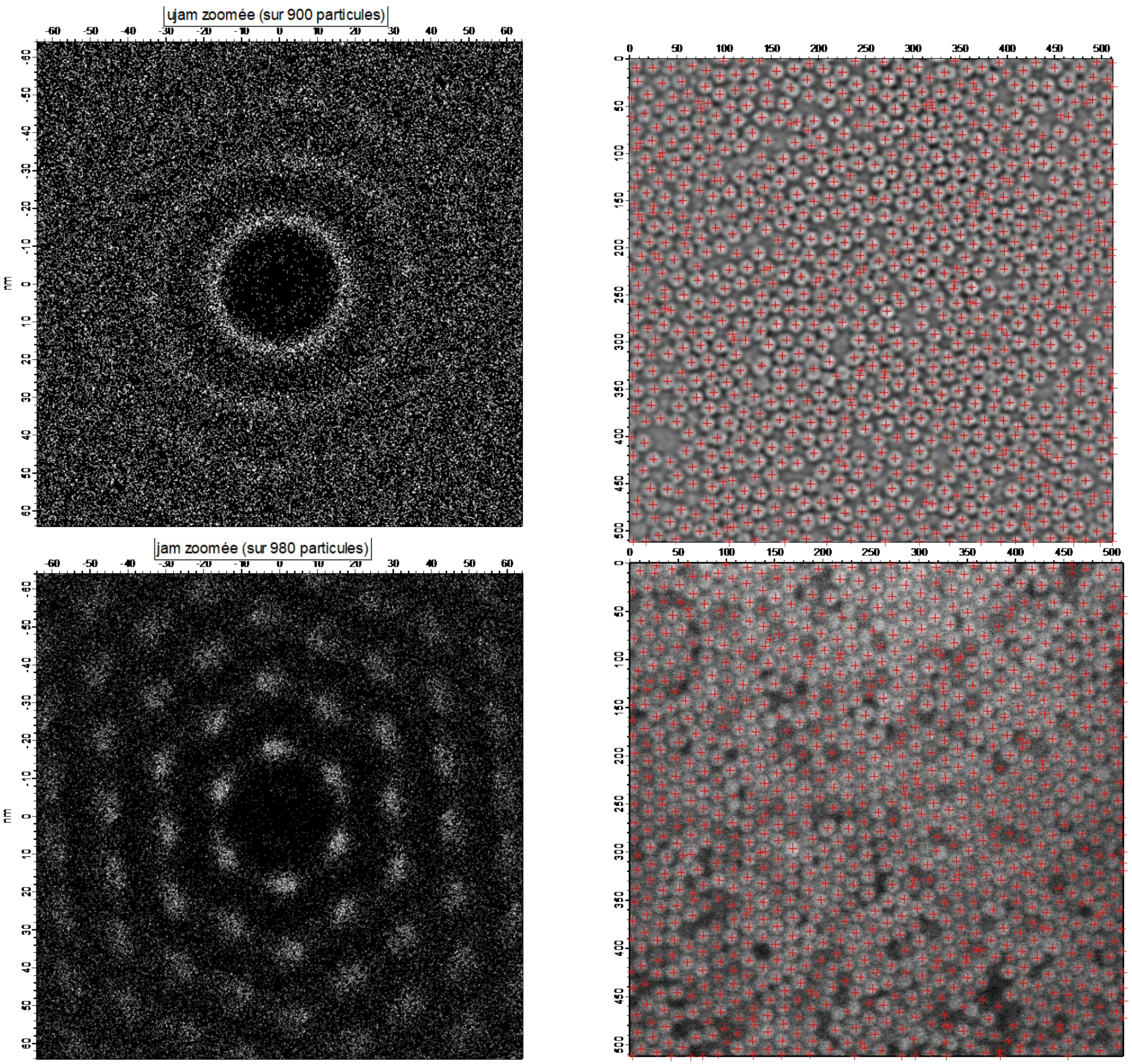


FIG. 5

Confocal microscope images of suspensions

(a) at rest, low shear

Fourier transforms of the centers of the particles are shown.

ϕ is 50%, silica particles (2 μm) in a mixture water /glycerol 23 / 77, *wt %.*

(b) just after shear above the jamming transition

Viscosity and potential zeta

The key factors

- **effective volume**

fraction of particles

- Interparticle interactions
- Evolution of the viscosity of a suspension as a function of the pH and the zeta potential….

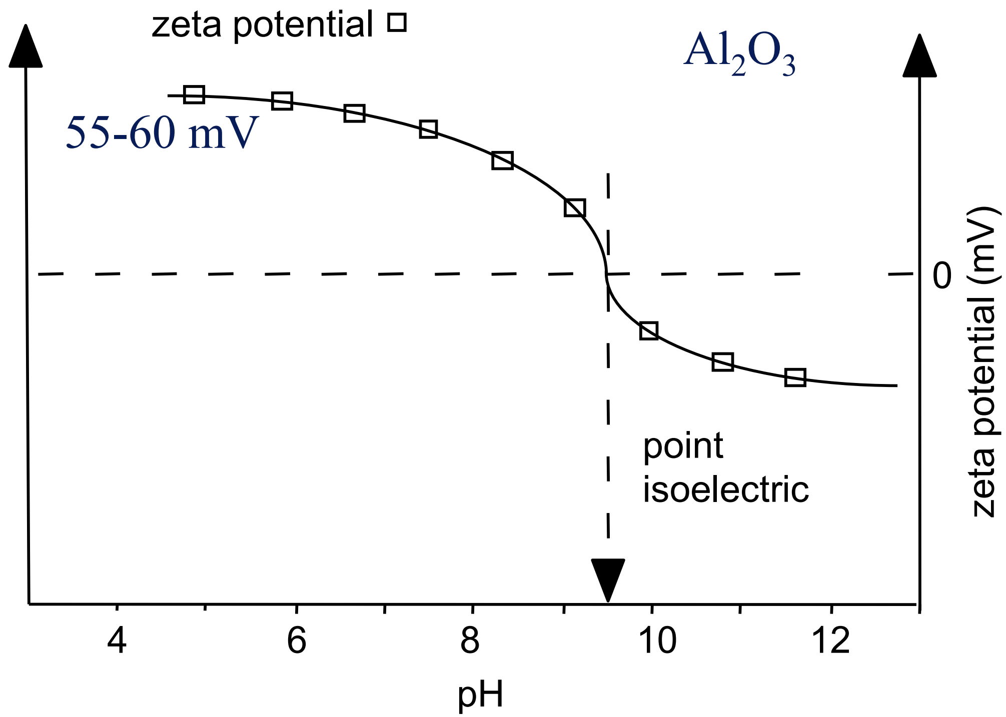


Figure 3.4.24. *Effect of the pH and consequently of the zeta potential on the evolution of the viscosity of a ceramic suspension.*

Viscosity and potential zeta

The key factors

- **Effective volume** fraction of particles
- Interparticle interactions (attractive VdW, repulsive electrostatic/steric)
- Evolution of the viscosity of a suspension as a function of the pH and the zeta potential….
- Far from the isoelectric point (iep) viscosity is low
- maximum viscosity at the iep.
- If pHs excessively high or low,
- the double layer (≈1/κ) begins to be compressed - increase in ionic concentration (ionic strength)
- Dissolution – increase of ions in solution…double layer compressed
- Attractive forces… van der Waals - secondary minimum .. viscosity increases…..

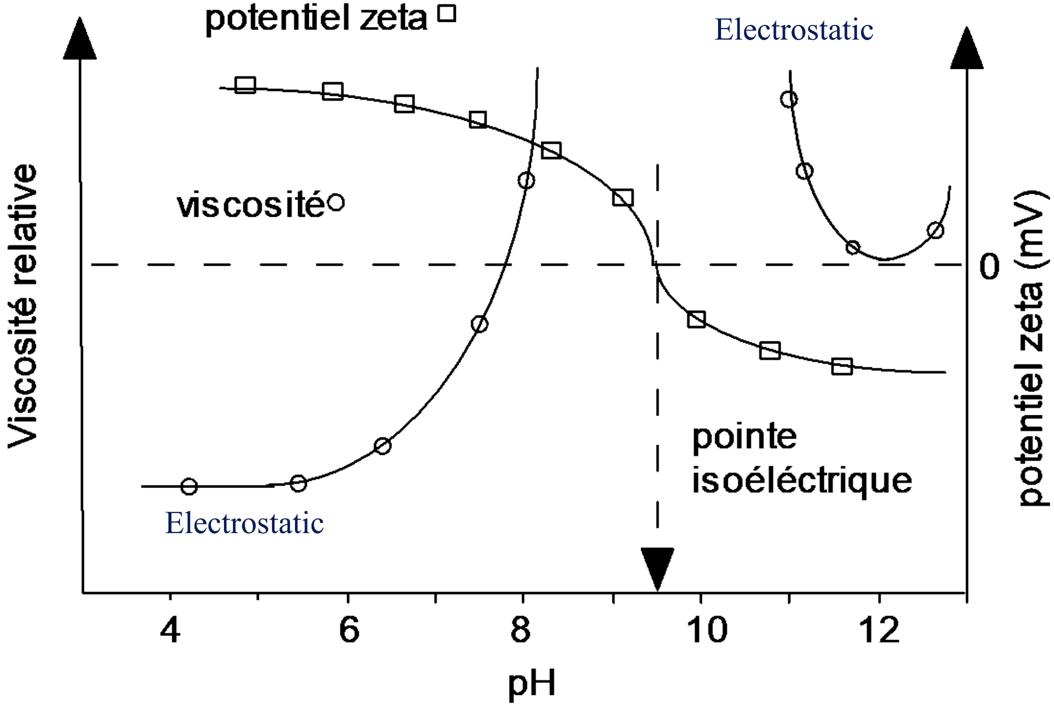


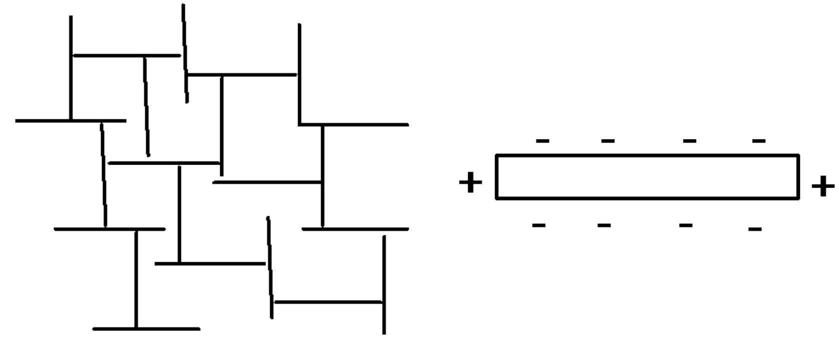
Figure 3.4.24. *Effect of the pH and consequently of the zeta potential on the evolution of the viscosity of a ceramic suspension (Al_2O_3)*

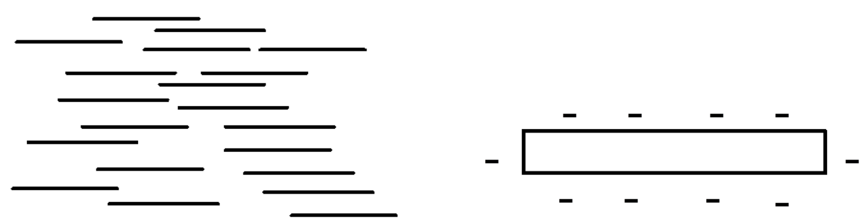
$$\frac{1}{\kappa} = \left(\frac{\varepsilon_o \varepsilon_r kT}{\sum_i (z_i e)^2 c_{io}} \right)^{1/2} \qquad (3.8.13a)$$

Rheology of ceramic pastes: shape effect

- For traditional ceramics, the rheology is even more complicated by the **anisotropic shape** of the particles and the **inhomogeneous distribution** of the charges.
- At pHs < 6,
- kaolinite platelets carry negative charges on their basal planes and positive charges on their edges.
- This leads to a house of cards type microstructure which at high volume fractions leads to a continuous attractive network and a yield point.
- At pHs > 8,
- all surfaces become negative and a minimum in viscosity is observed (Figure 3.4.25, next slide).

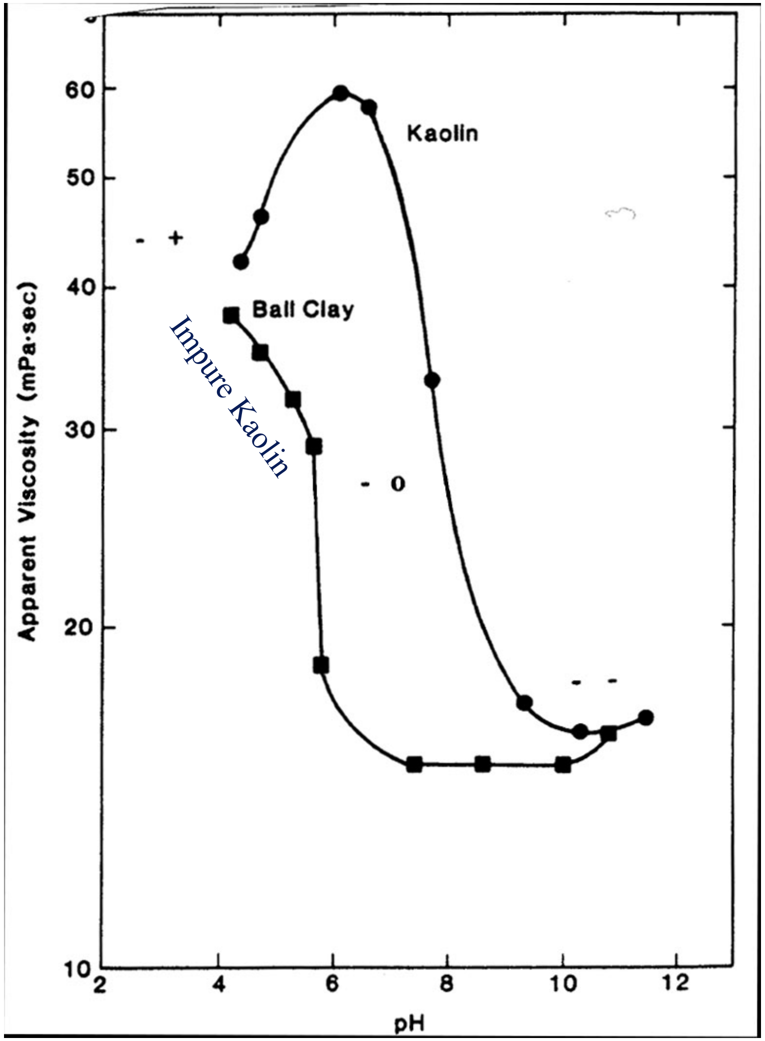
pH <6





pH> 8

Rheology - traditional ceramic pastes



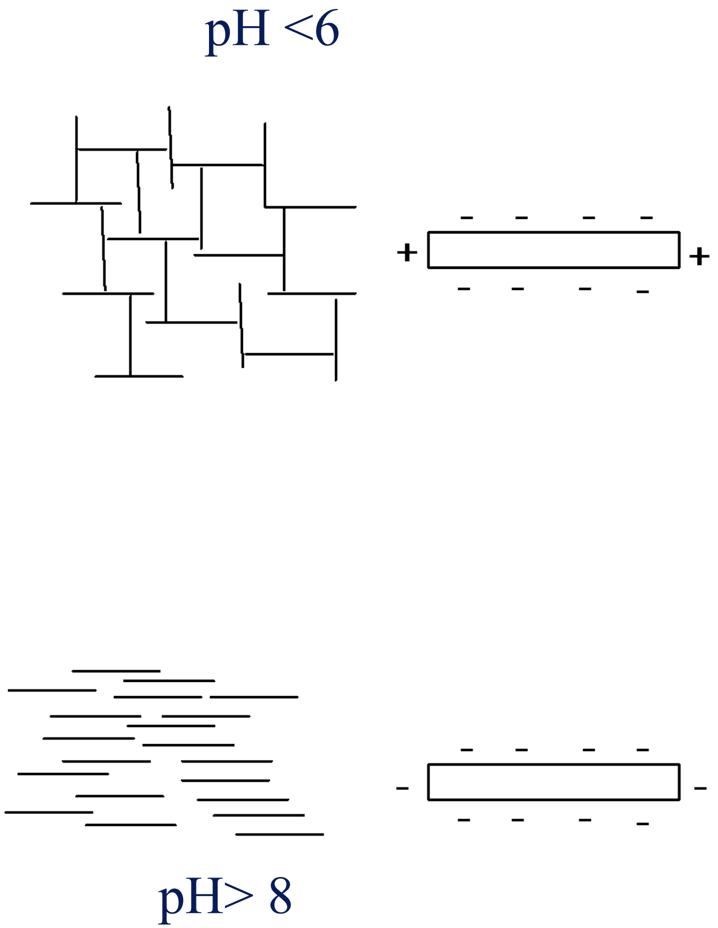


Figure 3.4.25. *Change in viscosity of Kaolin suspensions and a "ball clay "as a function of the pH (Reed, 1995) and schematic representation of the microstructure of the suspension.*

1

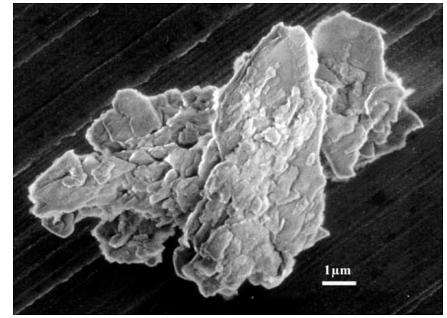
3.4.4 Mixing

- The mixing of different compounds is important in several industries: pharmacy, detergents and ceramics.
- Traditional ceramics - porcelain – is a mixture of quartz, feldspar and kaolin.
- Most ceramics contain sintering additives in powder form (e.g. MgO for Al_2O_3).
- Mixtures of powders - synthesis of mixed oxides* - $K_{1/2}Na_{1/2}NbO_3$ - peizoelectrics without Pb
- The absence of homogeneity can lead to the formation of secondary phases which adversely affect the final electrical properties

Kaolin

(50-55%)

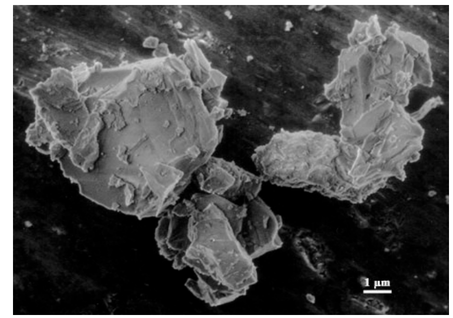
Plasticity



Feldspar

(25%)

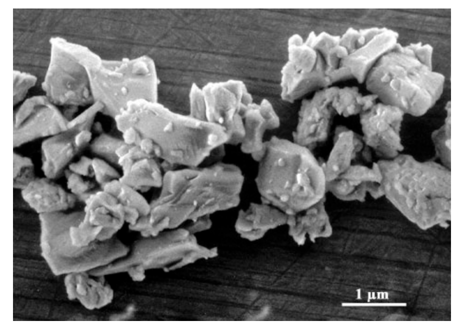
Lower T



Quartz

(20-25%)

Mech. Prop.



Porcelain

(*E. Hollenstein, M. Davis, D. Damjanovic and N. Setter, Appl. Phys.Lett., **87**, 182905-1-3 (2005)

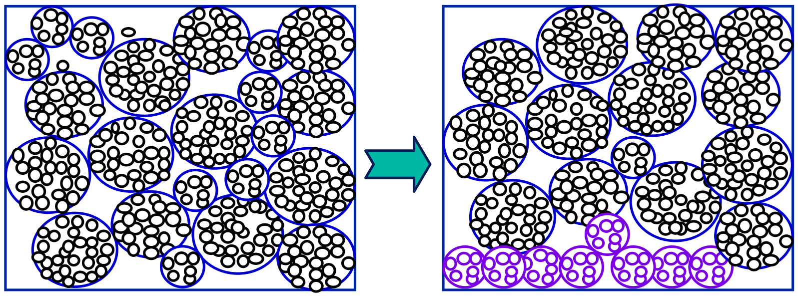
Piezoelectric properties of Li- and Ta-modified „$K_{0.5}Na_{0.5}NbO_3$ ceramics (2016 - 725 citations…)

(K, Na carbonate + oxide of Nb)

Mixing - Segregation

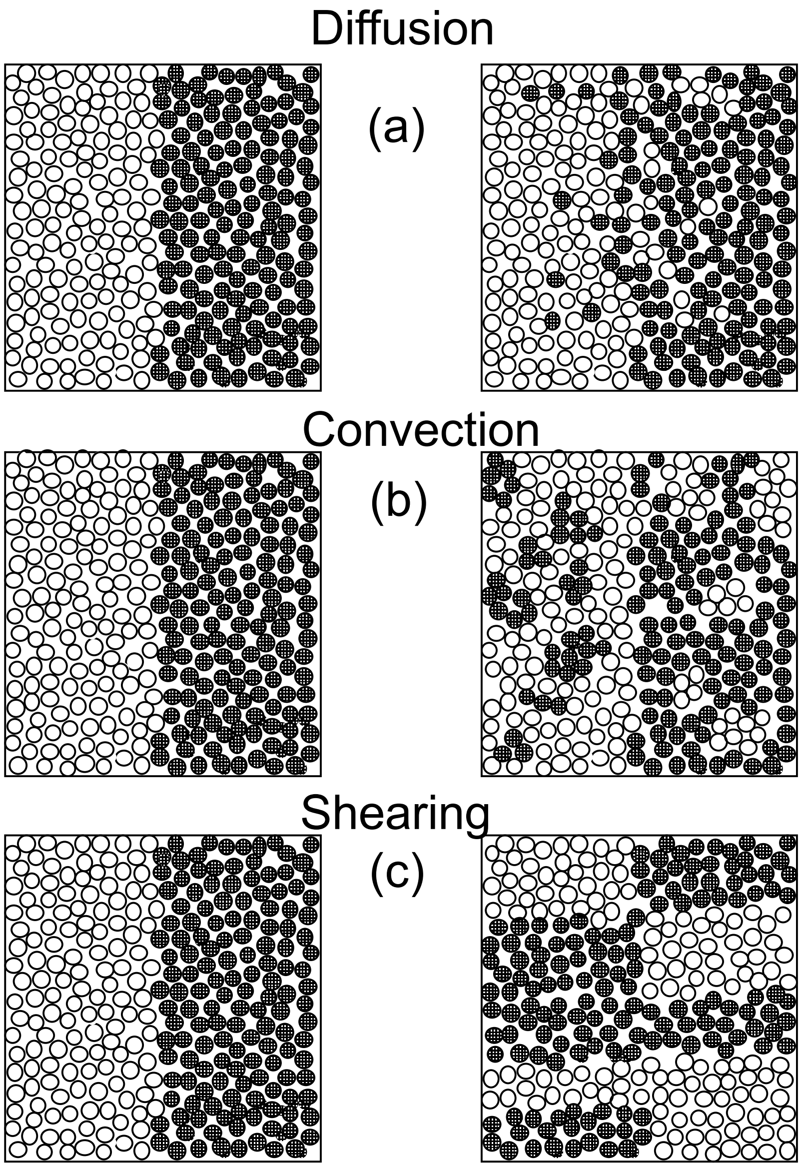
- Mixing - goal - obtain a "homogeneous" distribution of the constituents.
- It depends on their size, shape, density, surface properties, chemistry and volume fraction.
- Depends on whether the mixing is done wet or to dry,
- Humidity or static charges can play important roles.
- Mixing and segregation are concurrent processes - choose the method to not promote segregation
- In general, the segregation of dry powders strongly depends on the cohesion
- Powders that flow freely have a higher tendency to segregation, the opposite is true for powders with more cohesion.

> ♦ Possibility of segregation
>
> ♦ Who eats cornflakes or muesli?



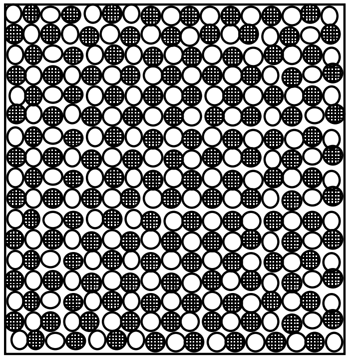
Mechanisms

- There are three types of mixing mechanisms:
  - diffusion,
  - convection or
  - shearing.
- It is rare that only one of these mechanisms operates at a time in a mixer,
- but often one dominates

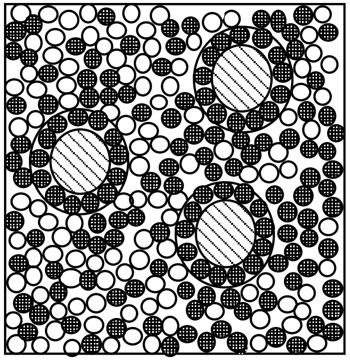


Microstructure of a mixture

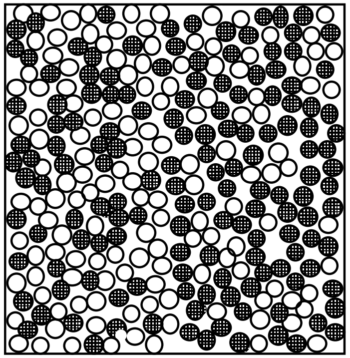
- The microstructure of a mixture can be described:
  - ordered
  - partially ordered
  - random
- ordered mixture - covering large particles with finer particles
  - carbon black (40nm) with powders of SiC (µm's) (Nass 1995).
- partially ordered mixture - two major components - one is covered with a third component.
- For random mixtures at a 50/50 ratio, the probability of finding any one of the constituents at such a point is the same.
- The majority in practice are random mixtures
- The degree to which mixtures approach a perfectly ordered or random mixture is both difficult to define and to measure.



(a) ordered mixture.



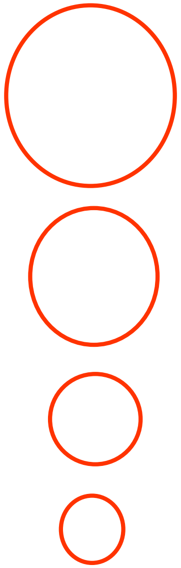
(b) partially ordered mixture

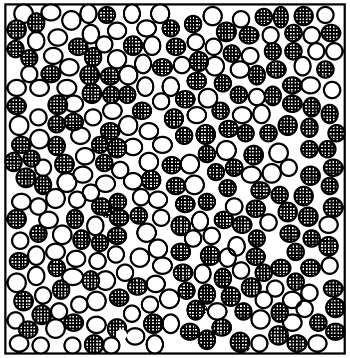


(c) Random mixture

Degree or quality of mixing

- The definition of the degree or quality of mixing is complex
- More than 40 different mixing indices have been proposed (Poux et al, 1991).
- Length scales, such as proposed by Mort and Riman (1995), are a good solution for mixtures of ceramic powders.
- The definition of the length scale is the radius of the sphere whose volume is equal to that of the sampled volume.
- The sampling method and the volume considered are also very important and will depend on the size distributions and volume fractions of the different components of the mixture.
- e.g. the Mort & Riman approach was to decrease the size of the sampled volume (radius of sphere) and analyze the composition of the volume and compare it to the nominal total overall composition





2

Mixing quality - 5 powders

- A complex mixture of 5 powders for the production of a metal ceramic composite (Cermet) $TiC_{0.5}N_{0.5}$ - TiN - Al_2O_3 - Mo_2C - Ni

	$TiC_{0.5}N_{0.5}$	TiN	Al_2O_3	Mo_2C	Ni
% Volume	45%	15%	20%	5%	15%

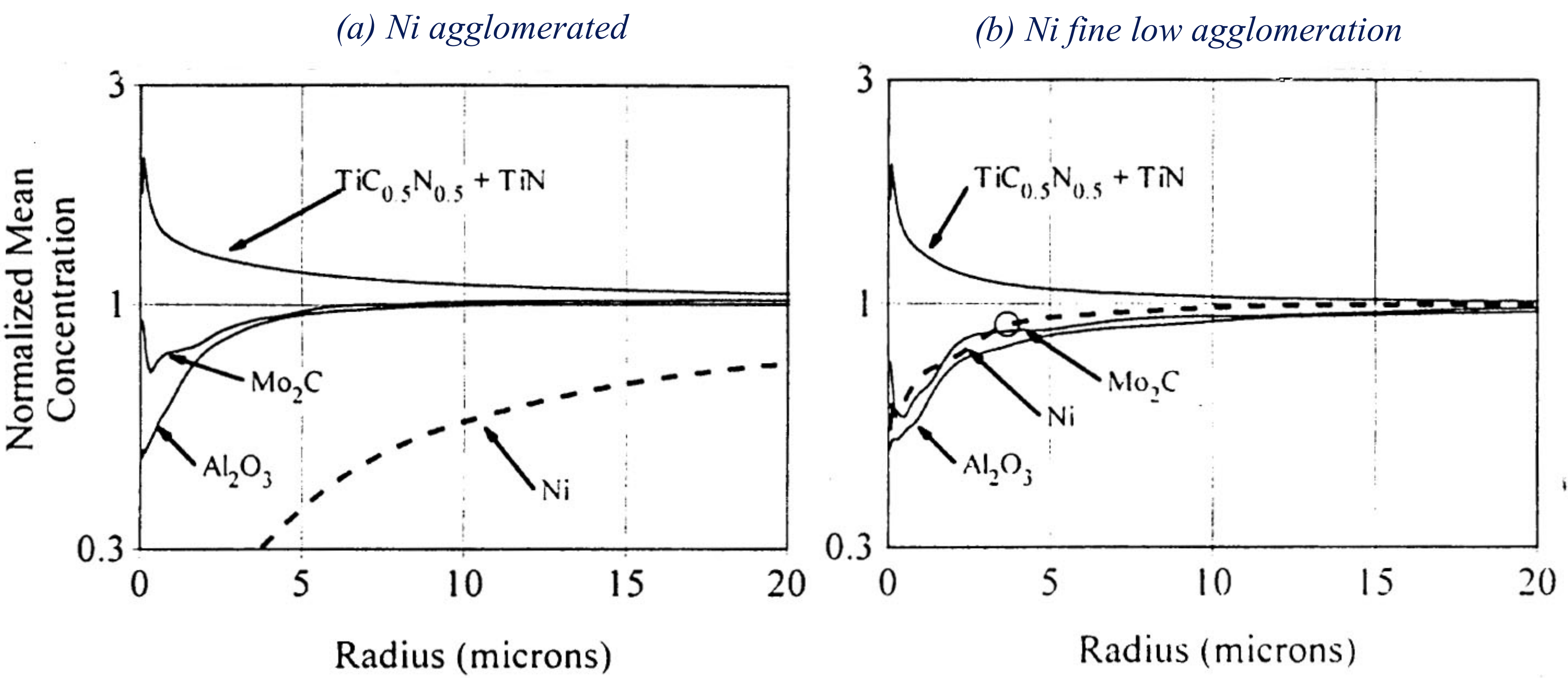
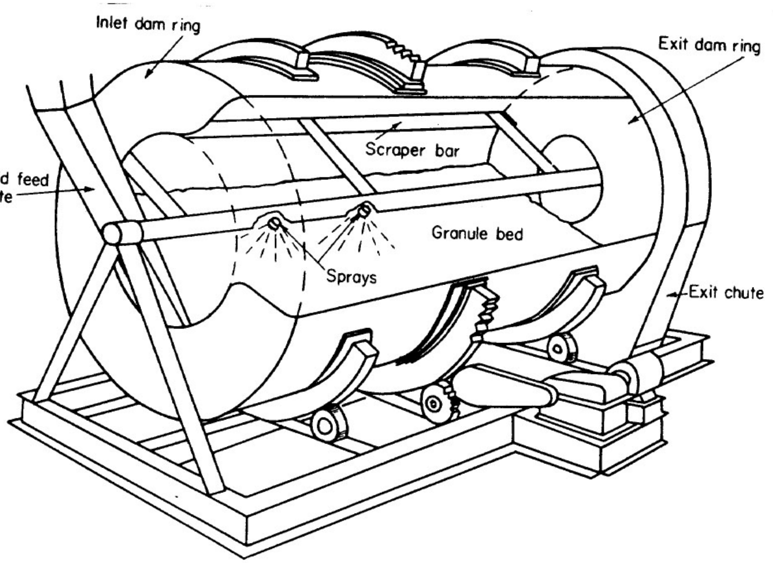


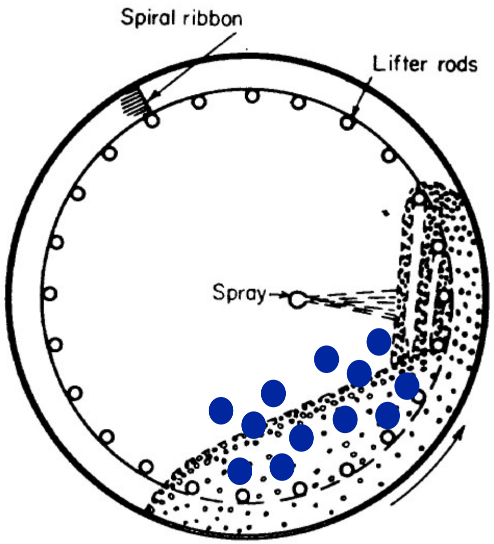
Figure 3.4.28. *Analysis of the degree of homogeneity of a mixture of 5 powders with two different Ni powders (a) Ni agglomerated (b) Ni fine low agglomeration(Gulliver et al (2000)).*

Mixers - Diffusion

- Different types of mixers for powders, pastes or slurries.
- They are classified according to the mechanism dominating the mixture.
- Mixers where diffusion dominates are drum mixers
- most often used for dry powders
- A small amount of beads can also be added to help break up cohesive powders
- With the addition of an internal nozzle can also be used for simultaneous granulation.

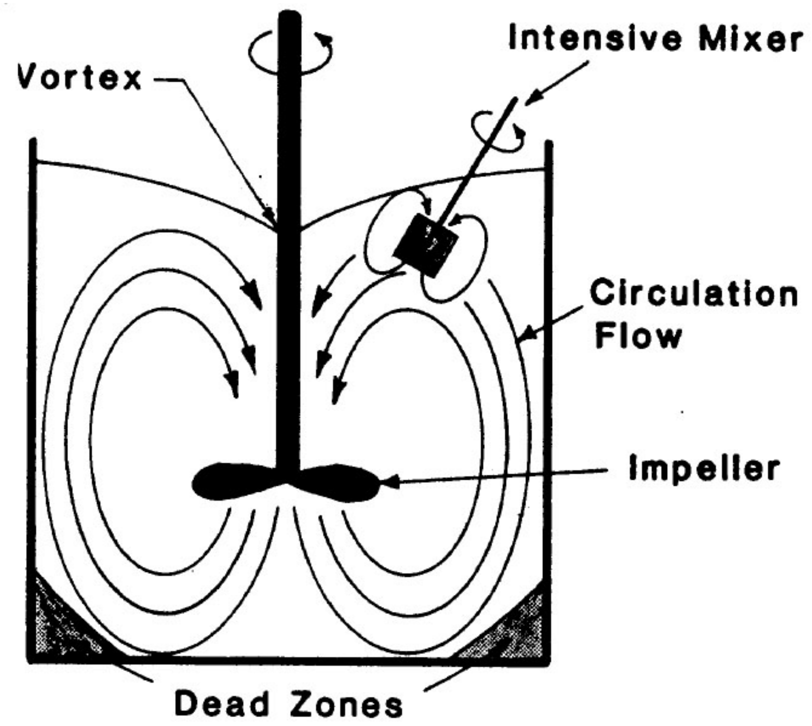
Diffusion





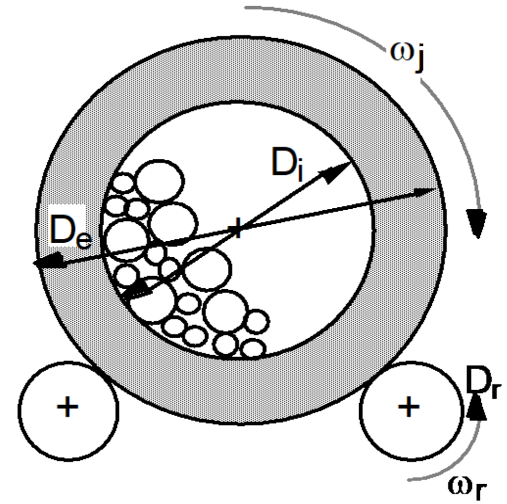
Convection mixers

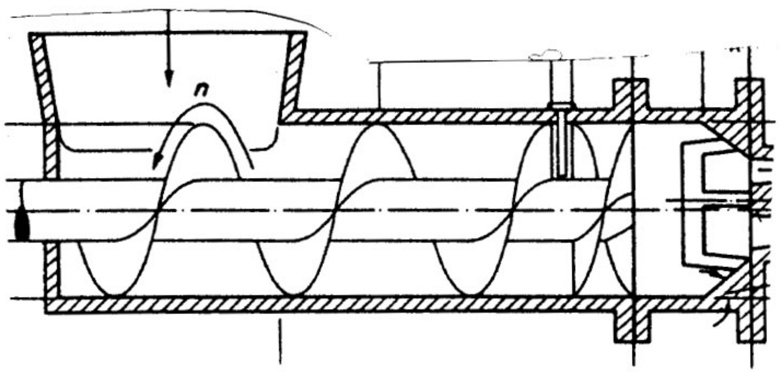
- Convection mixers include paddle, mortar, propeller and screw mixers.
- These are often used for pastes
- Paddle-impeller mixers invariably have dead zones
- The highest shear rates at the edges of the blades and between them and the walls.
- These large shear forces can sometimes break agglomerates.



Shear mixers

- Mixers with shearing forces dominating are kneaders, roller mills, screw extruder and simple ball mills.
- Ball mills - simultaneously mixing and mill
  - simple and inexpensive to use.
  - good for suspensions
- More viscous pastes
  - E.g. for injection molding,
  - screw extruders are needed

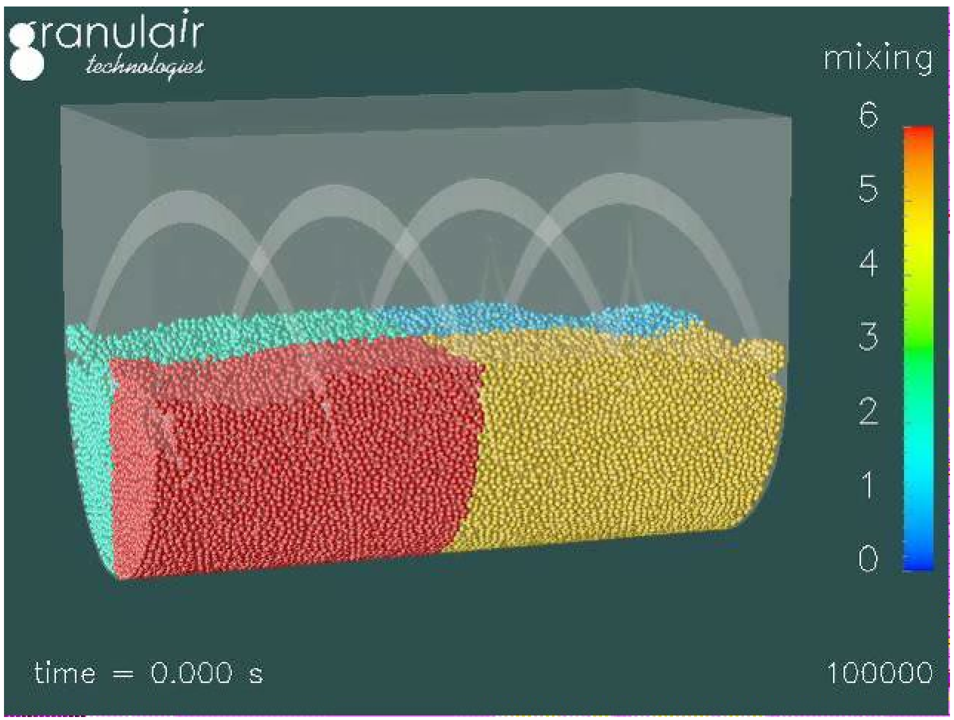




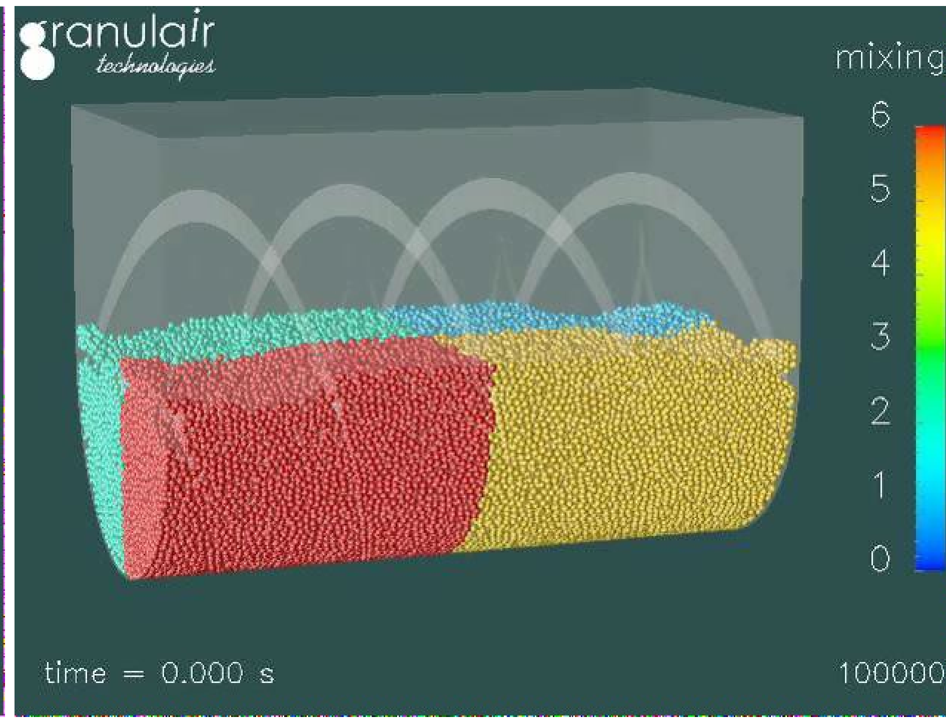
Discreet Element modeling

- Dr. Mark Sawley - EPFL (lin.efpl.ch)
- Ribbon blender - 500mm X 300mm container - dual ribbons move particles in opposite directions
- 100,000 spherical particles - 6mm dia. Particles colored according to original position

Low cohesion

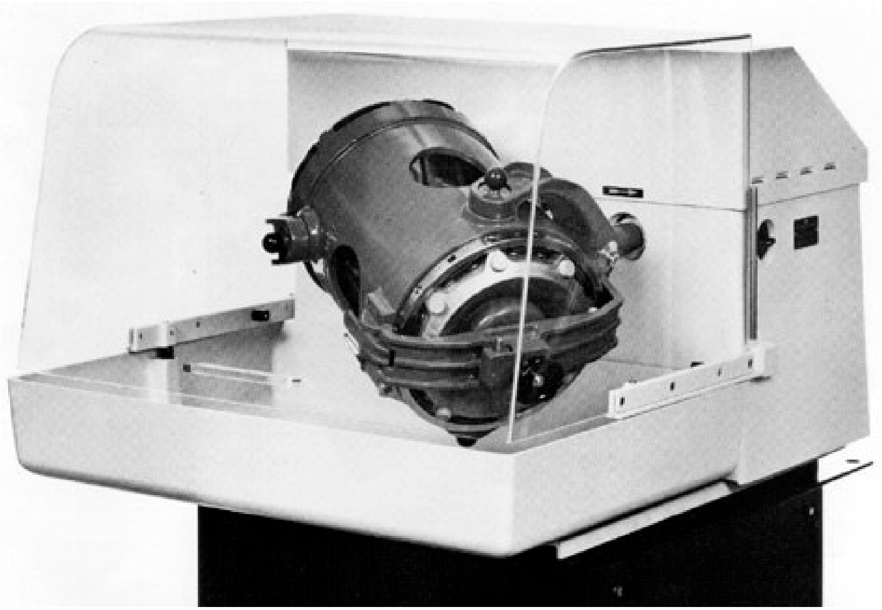


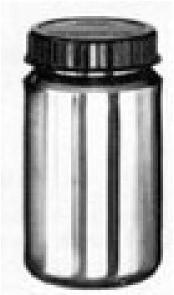
High cohesion (x10)

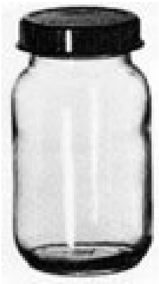


Turbula

- Typical mixer of random movements
- The pot oscillates in a moving cradle along 2 axes - rotating in the opposite direction.
- Mixing occurs when the mixture is divided and then recombined, with movements that combine rotation, translation and inversion.
- This involves both convection and shear mechanisms
- Often useful in the laboratory for mixing e.g. cements for research

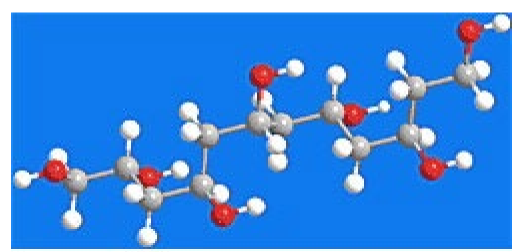






3.4.5 Granulation

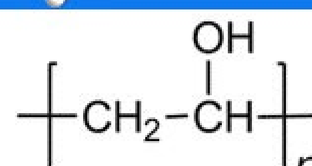
- Powders used in ceramic processes often ~μm,
- Cohesive powders that do not flow freely.
- Problems both for transport and filling dies in automated dry pressing machines.
- Fine powders are usually granulated to form larger particles or granules (25-500 μm)
- Interparticle interaction are due to van der Waals forces, electrostatic or capillary (liquid bridging) or chemical (solid bridging – chemical bonds…aggregates).
- In most cases in ceramics, the cohesion within the granules is ensured by organic polymers, binders
- Polyvinyl Alcohol - PVA



Gray - carbon

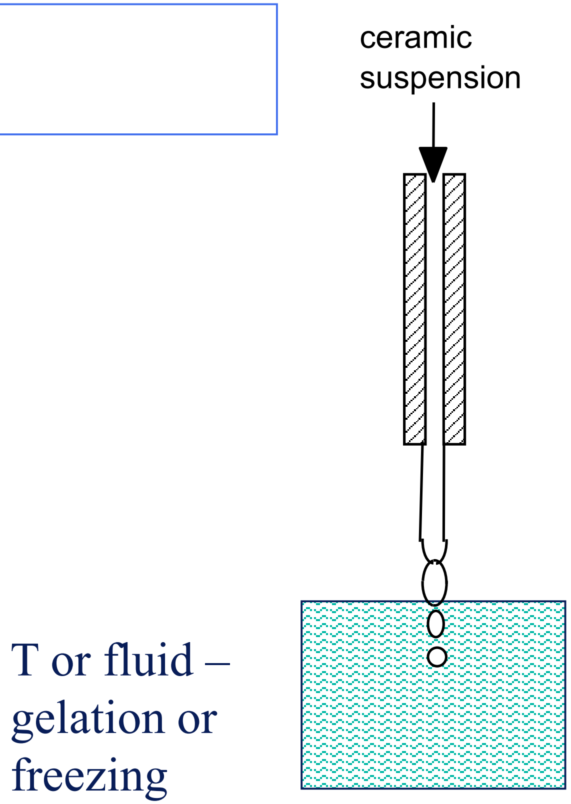
Red - oxygen

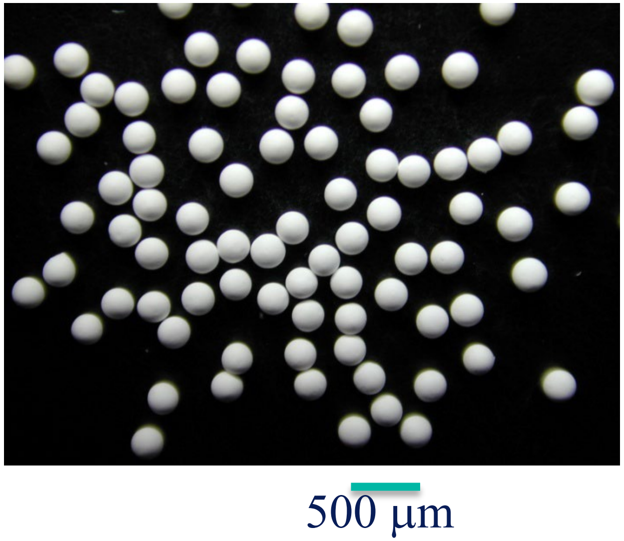
White - hydrogen



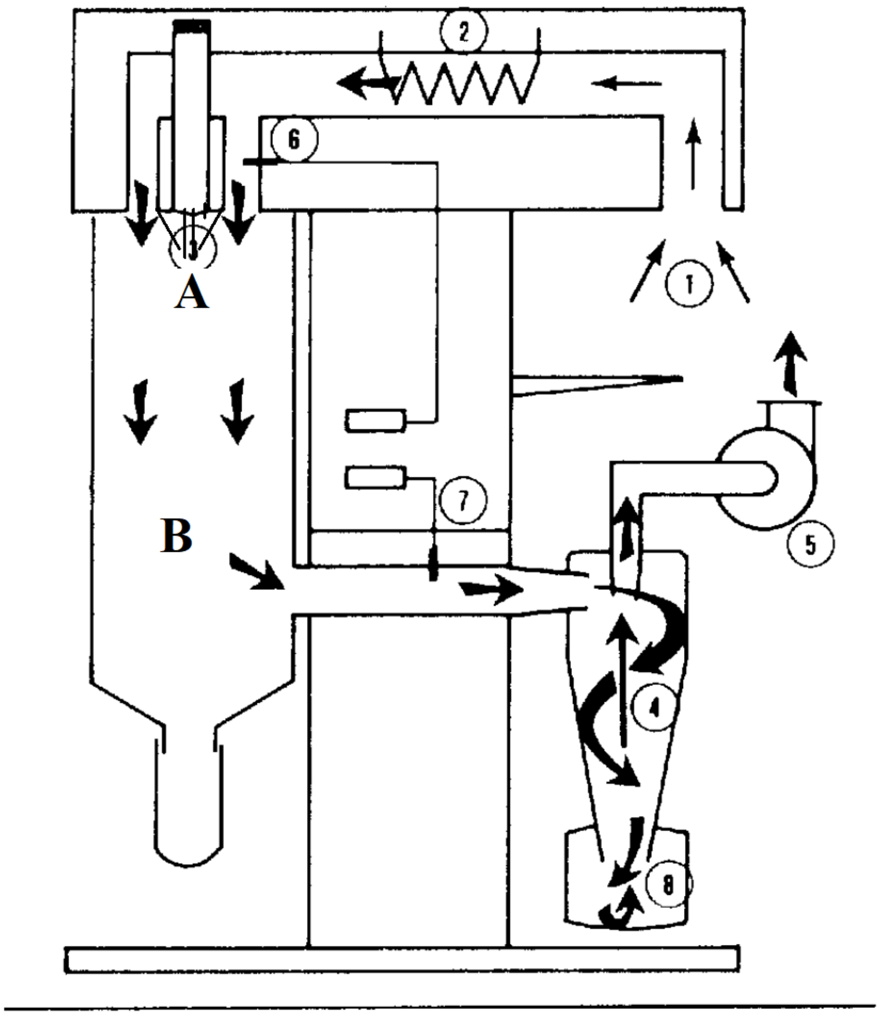
Granulation methods

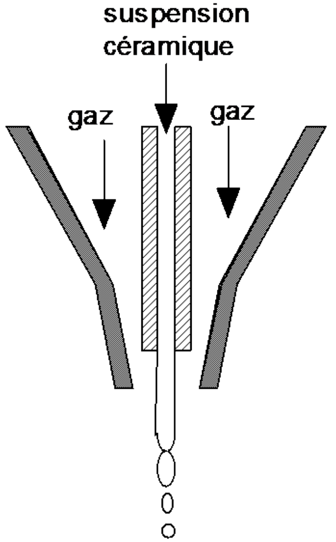
- Pelletization,
- Drum granulators,
- Fluidized beds,
- Extrusion (and chopping),
- Atomization (Spray drying)
- Gelation techniques
- Freeze granulation (e.g. using liquid nitrogen as freezing fluid)
- Each techniques has a range of granule size,
- For ceramic powders, the most popular method is atomization
- Special applications - biocements,
  - granules with narrow size distribution
  - produced by gelation or freezing of droplets produced with a vibrating nozzle



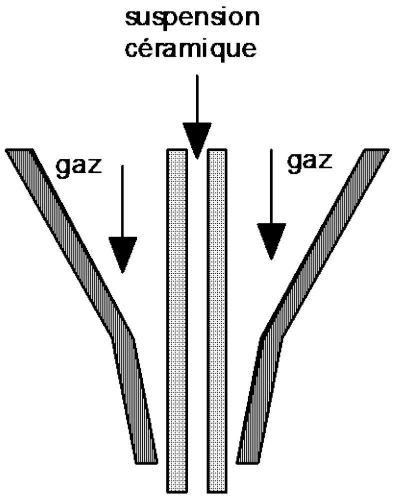


Atomization – Spray Drying





(c) internal mixing nozzle



(d) external mixing nozzle

Atomization with rotating discs

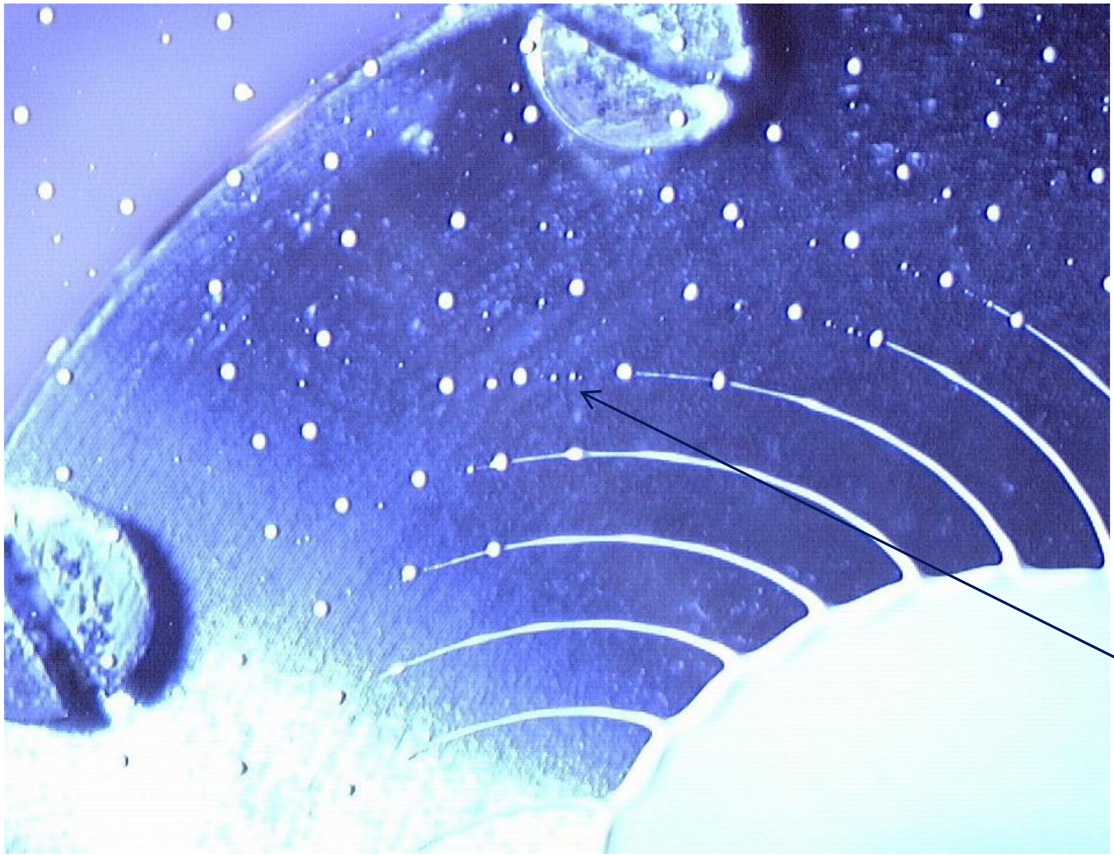
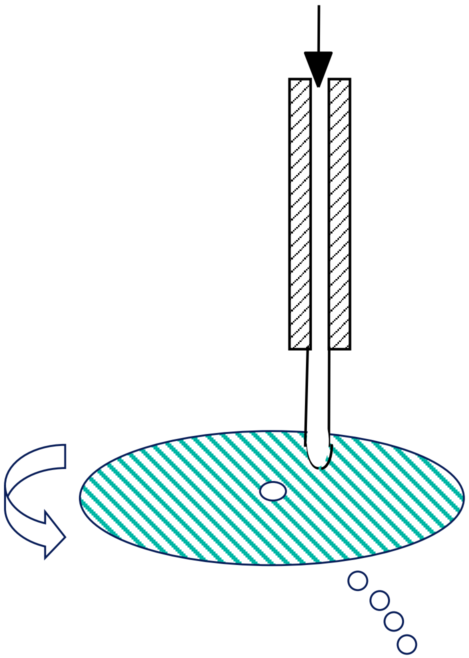


Figure 3.4.32. ((b) *rotating disc atomizer*

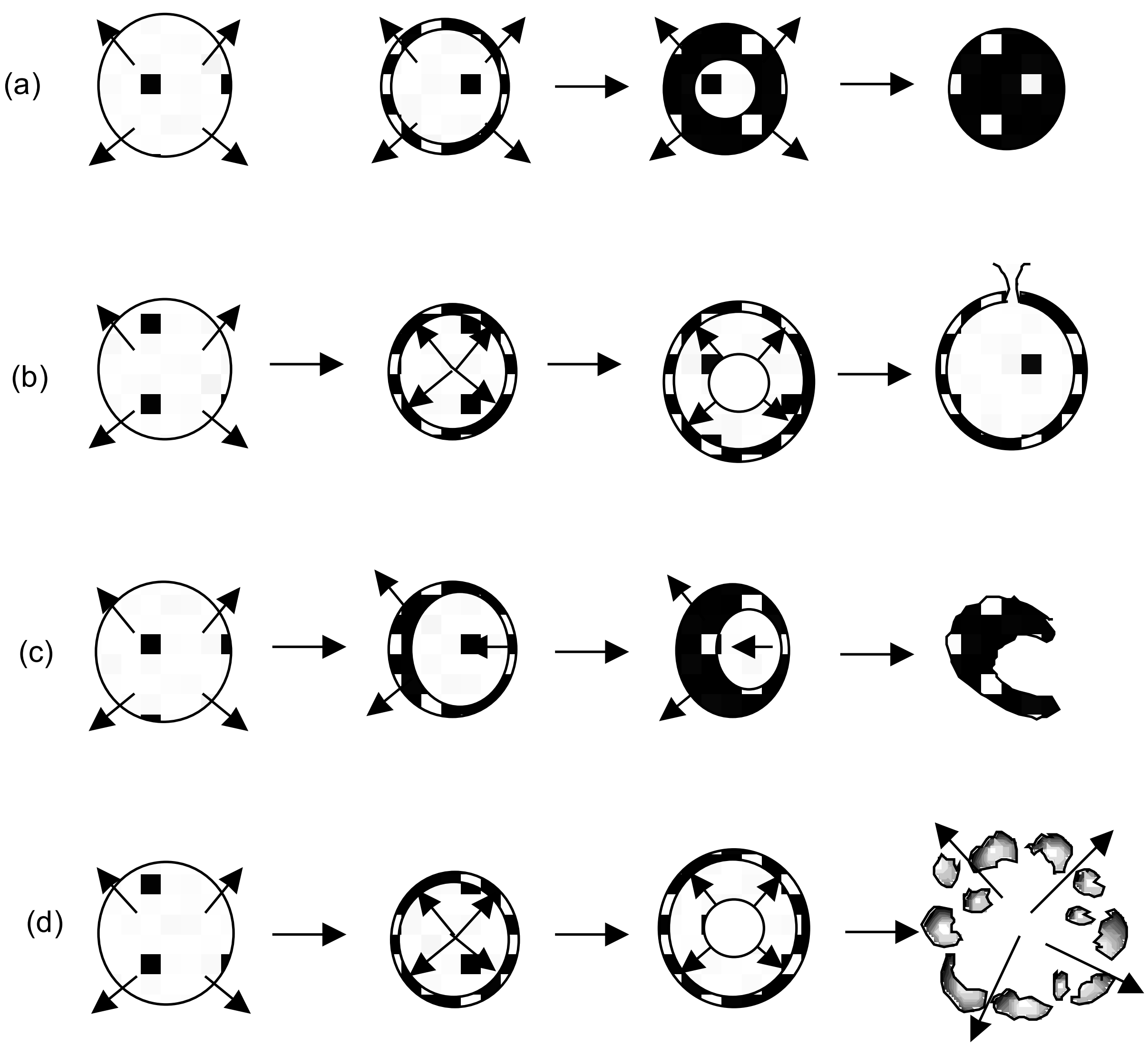


Satellites - hard to avoid

- sieving is needed

- Industrial 5-10% of fines and
- 5-10% coarse removed by sieving
- Improves green body homogeneity and final ceramic mechanical properties

Drying of a suspension droplet



(a) dense granule
(desired)

(b) hollow granule
(not desired)

(c) collapsed granule
(not desired)

(d) granule explodes into fragments
(not desired)

Granules - defects

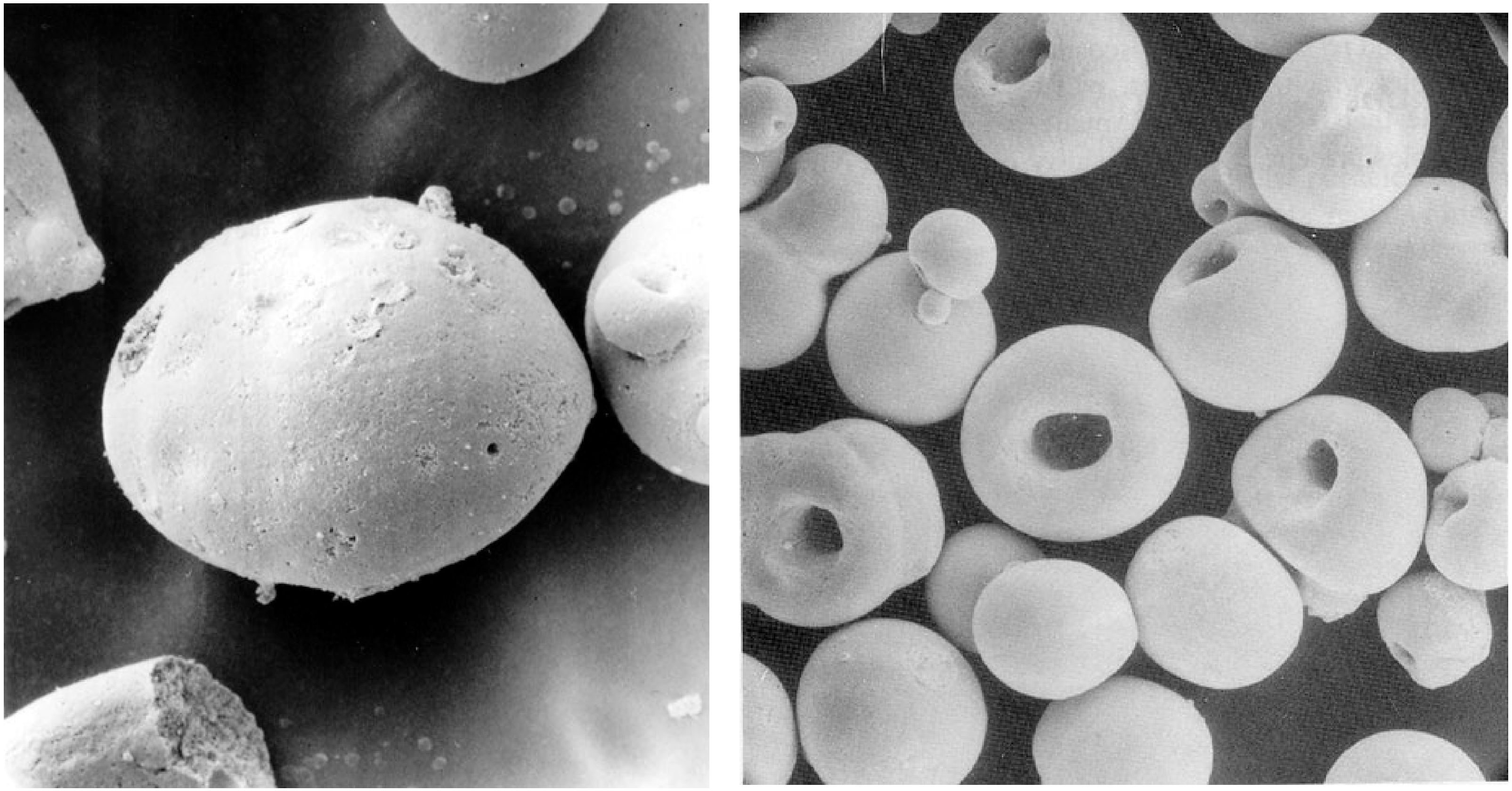
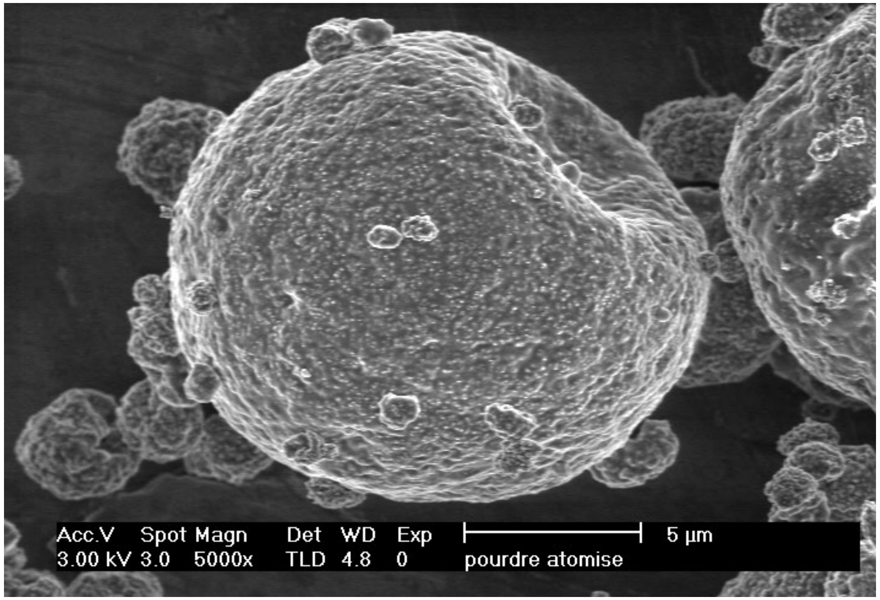


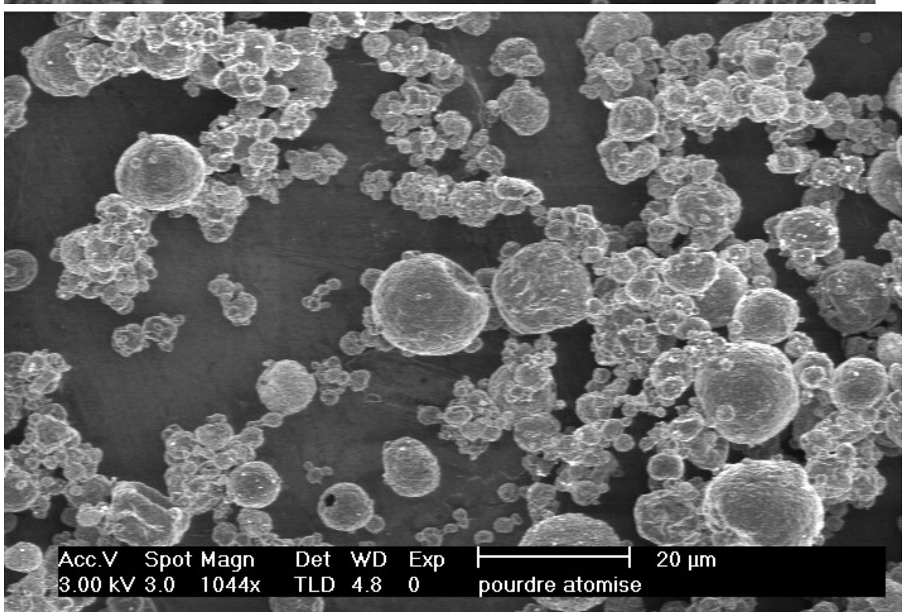
Figure 3.4.34. *Typical commercial granules (100µm) showing (a) granules with homogeneous density (b) hollow spheres with depression.*

Primary particles - 1 µm !!

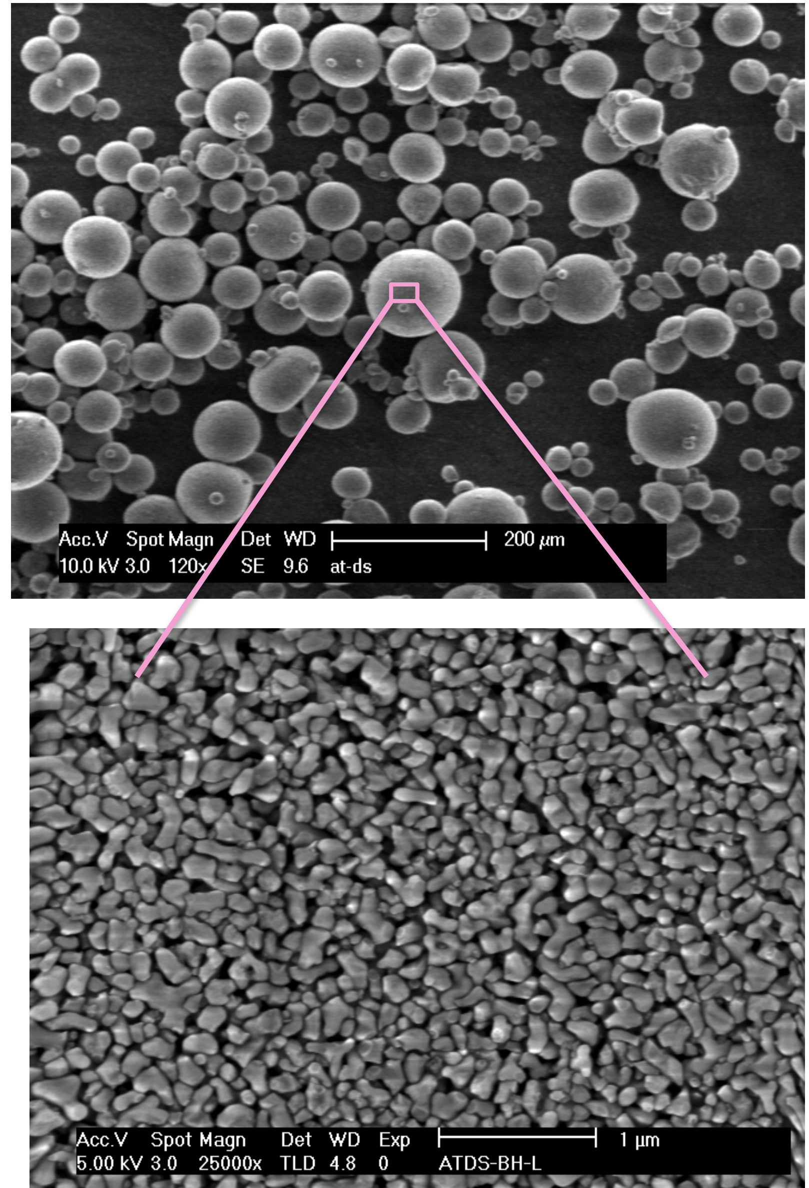
Granules from atomization

- Laboratory scale - Al_2O_3





- Industrial Scale Al_2O_3



1

Manufacture of Ceramics - Ceramic Processing