

6/21-24 IFPRI suspension workshop @ U. Edinburgh  
*Suspensions and Slurries: Insights from New Physics*  
<https://ifpri.net/events/9th-ifpri-workshop-suspension-slurries-insights-new-physics>

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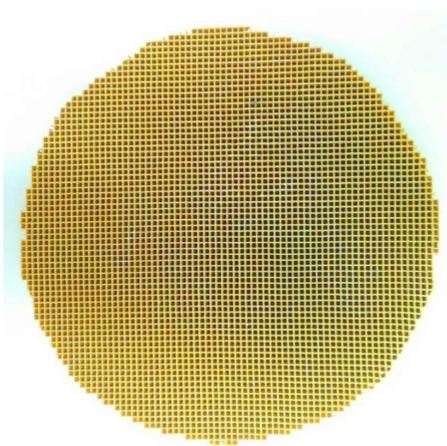
# *Getting and Keeping in Good Shape*

*plastic forming of particulate into a shape  
and keeping that shape*

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Corning Inc.

<http://www.corning.com/worldwide/en/innovation/materials-science/ceramics/how-it-works--extrusion.html>

5/31/18



### Abstract

The Celcor™ substrate is a ceramic honeycomb that is mostly air, structured air. Its shape begins with paste extrusion. The die exit and the extrudate are complementary: the lower the pressure-drop for airflow through the honeycomb, the higher its die extrusion pressure. Higher open frontal area means less pressure-drop and less thermal mass, resulting in faster acceleration and faster catalyst light-off for your car, something good for everyone, but challenging for honeycomb manufacturing.

The extrusion paste is a highly-filled polymer solution: inorganic and organic particles in a visco-elastic matrix. The paste is almost mathematically transformed by extrusion from a solid billet into a honeycomb twenty times longer. The honeycomb inhales air as it exits the die. Going from die entrance to exit is a mechanical inversion of the metal being the continuous phase (to hold shape against extrusion pressure) to the paste being the continuous phase (to hold shape against gravity and handling). Structured air is not load bearing, if not contained.

Upon leaving the supporting die, the paste must have sufficient yield stress to maintain its honeycomb shape through all the down-stream processes. The wet-green yield stress is significant, requiring high shaping pressure and resulting in plug-flow slip through the slots of the die.

Next, the shape is further fixed: the binder (aqueous polymer solution) is removed by drying and pyrolyzing, taking full advantage of the honeycomb's thin webs and open channels, leaving a honeycomb shape of assembled particles, which are reacted and sintered to become the porous ceramic honeycomb.

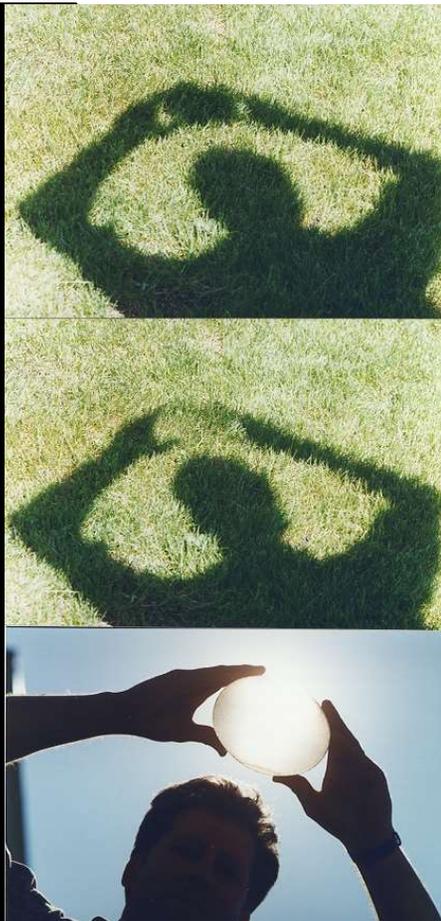
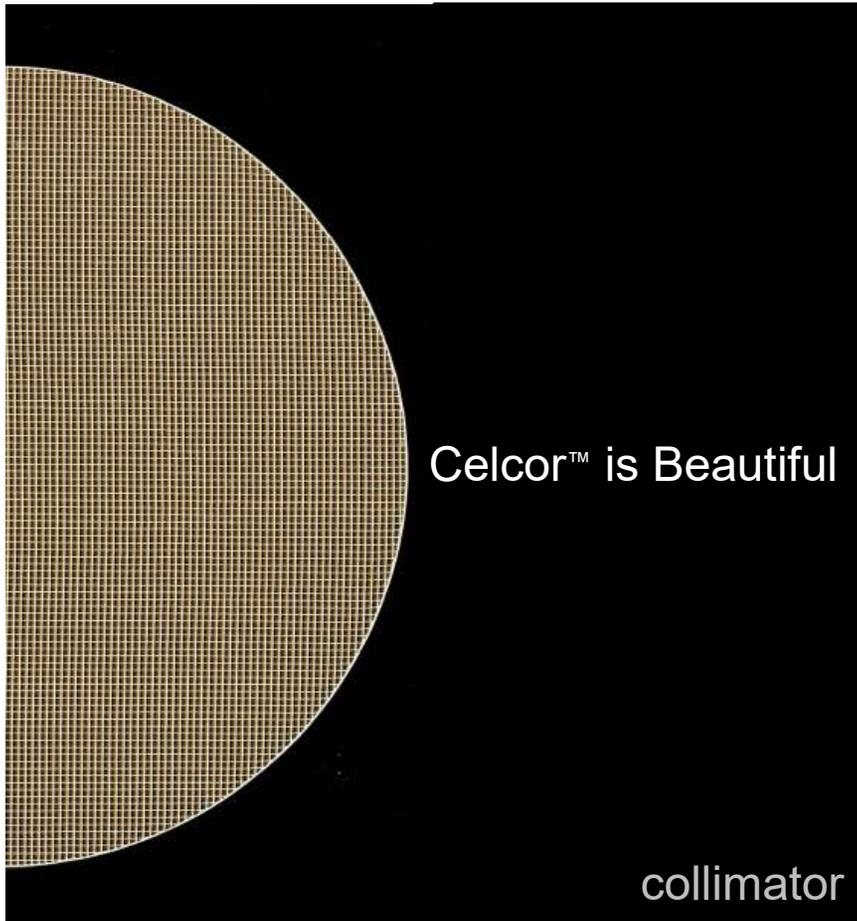
This assembly of particles exists before and after the shaping/extrusion die. The paste has an elastic modulus and yield stress, as does its wet-green honeycomb extrudate. Particles are touching within the paste and after pyrolysis. Touching is required for shape preserving yield stress and strength.

High solids-loading is required for pyrolysis strength and low sinter shrinkage. These stiff pastes are abrasive: particle-particle and particle-die contact result in wear, friction resistance, elastic strain and spring-back.

Extruding a particulate paste through progressively narrower and narrower slot goes from continuum to granular mechanics as the confining dimension approaches the particle size and level of mixedness. The market drives us to thinner webs for faster light-off. How thin can we go?

The final product requires a specific microstructure of particles, so the paste is not designed for optimum rheology. The paste is composed of platy particles that flow-texture to align co-parallel with the honeycomb web to achieve the desired fired microstructure. It is not a simple tribo-rheology problem, but it is a successful, enduring product. Every nonelectric car has a honeycomb.

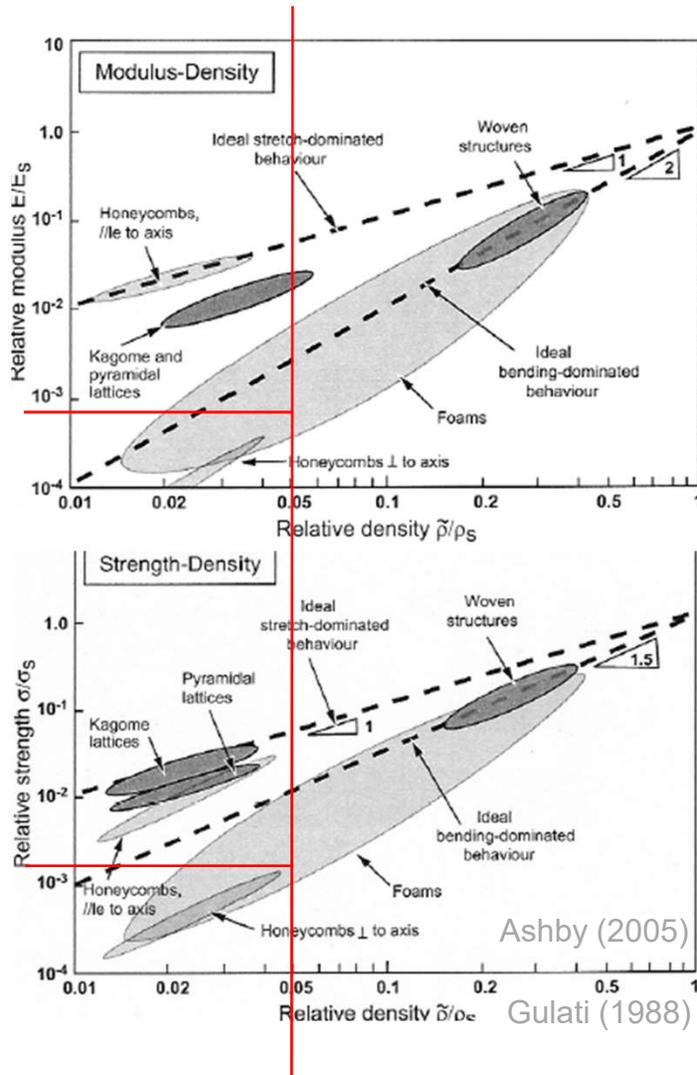
# the Celcor™ Substrate



# Random and Structural Porosity

honeycomb is linear porosity

hierarchical  
air distribution



## Ashby Plots

Two shapes for strength:

Shape of the object

Shape of the microstructure

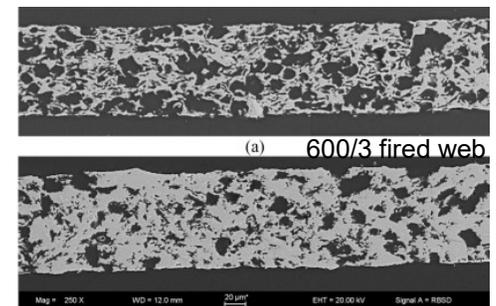
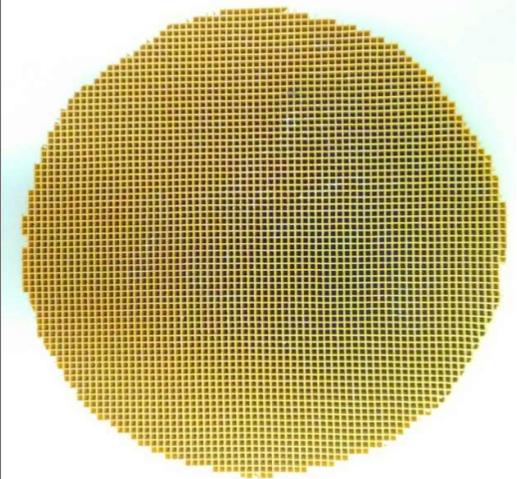
$P=0.55$

$P=0.35$

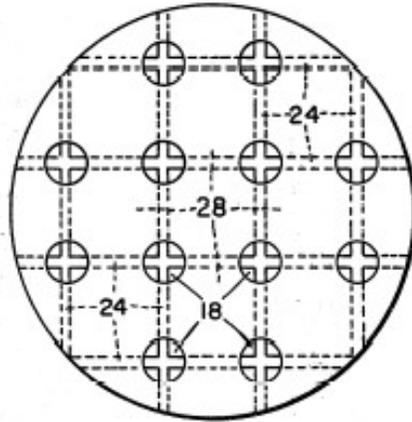
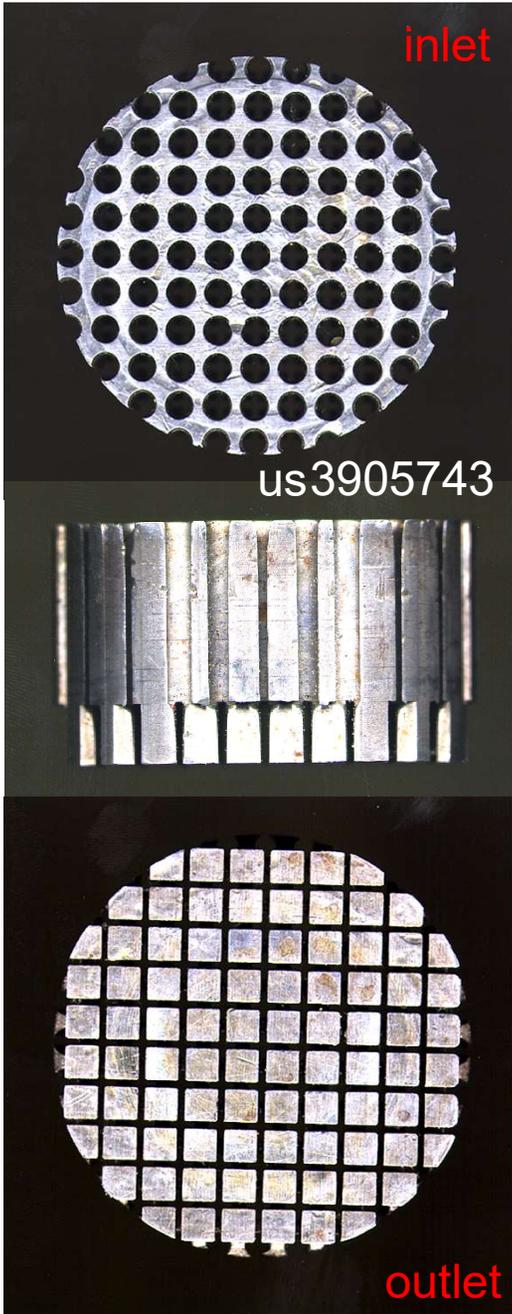
Tanner (2015)

# OFA

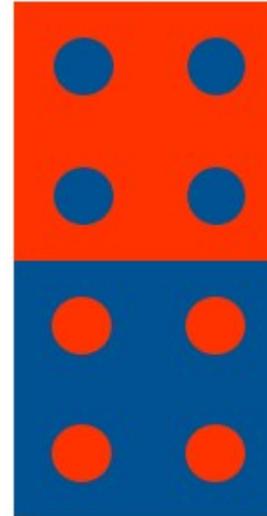
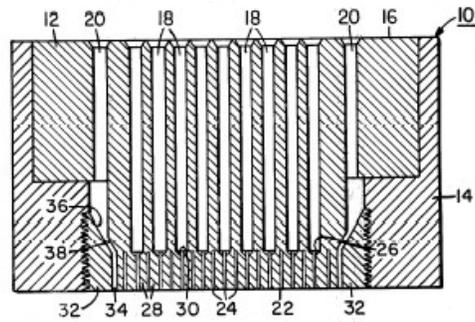
open frontal area



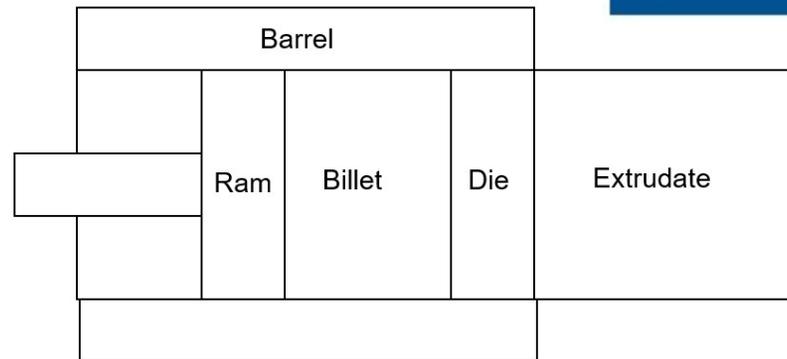
**P** porosity



but, the Celcor™ die is more perfect



*a mechanical inversion*

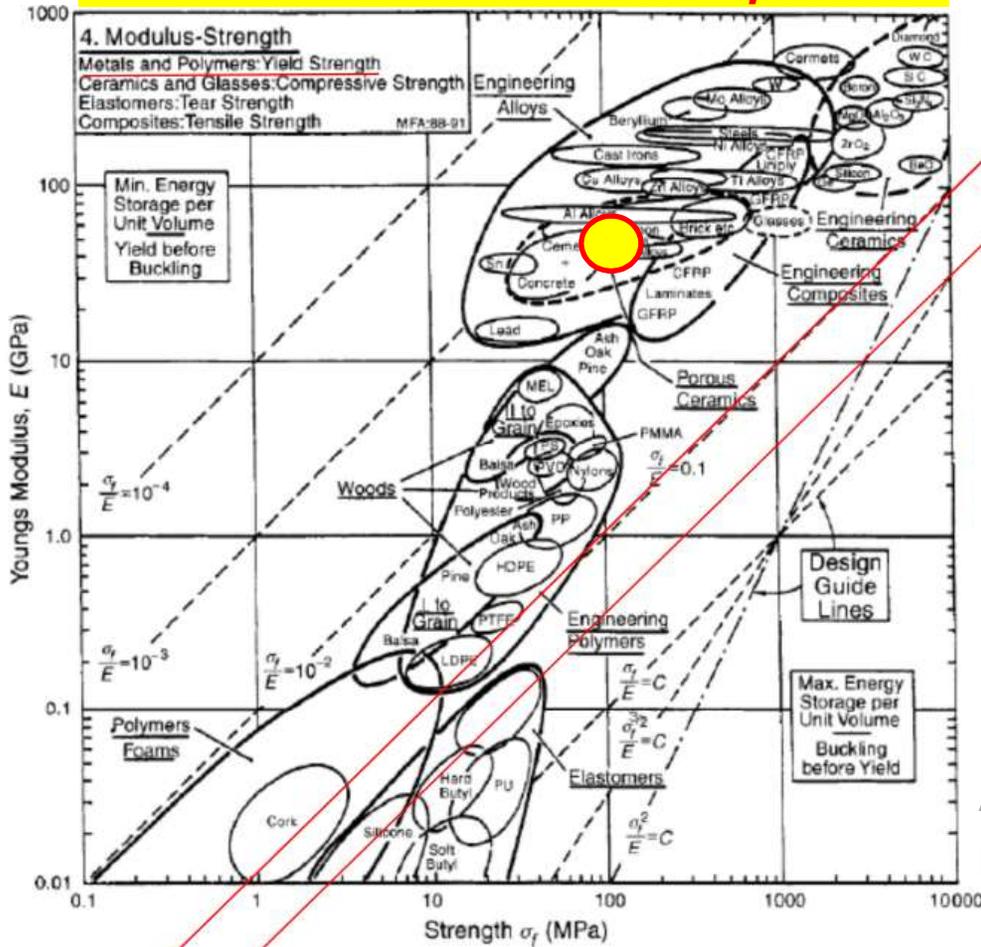


one length in and ten lengths out →

paste → ← air

# Soft Paste

## The Transient Composite



10% 20%

to tune  
the paste:  
change V  
change  $c_p$

Ashby (2009)  
materials map

mouth feel  
finger feel

Way down here we are in the land of easy deformable solids with good mouth and finger feel: food and cosmetics: cold peanut butter, pasta paste, cheese, lipstick etc

Recently, I've begun comparing my pastes to food, and looking at the mechanical properties of cheese. "Mouth Feel" instead of "Finger Feel".

Kamyab (1998)

# Die-entry *accelerating through the plastic zone*

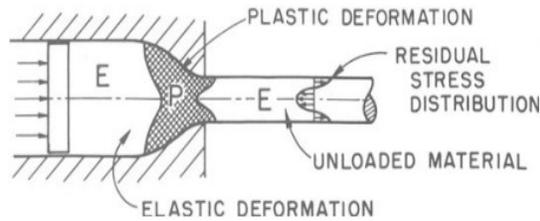


Fig. 1a. Extrusion configuration

plastic enough to change shape in die,  
but stiff enough to keep shape after die

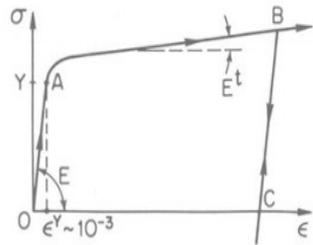


Fig. 1b. Elastic-plastic stress-strain relation

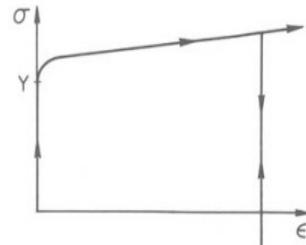
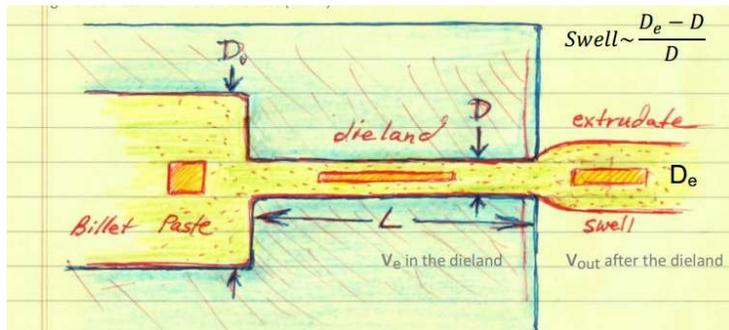


Fig. 1c. Plastic-rigid stress-strain relation



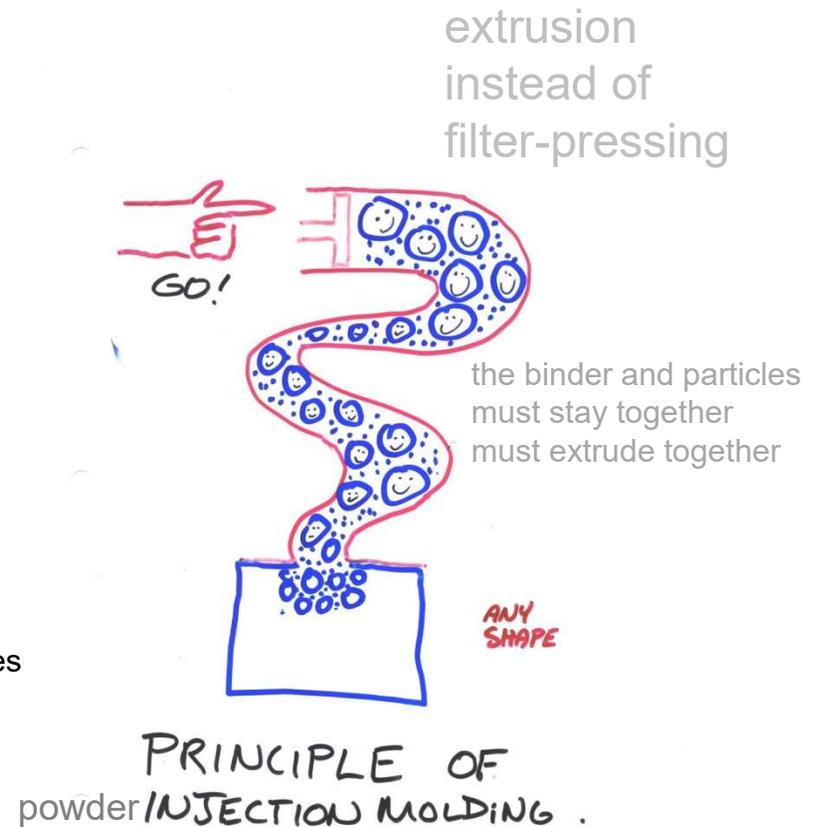
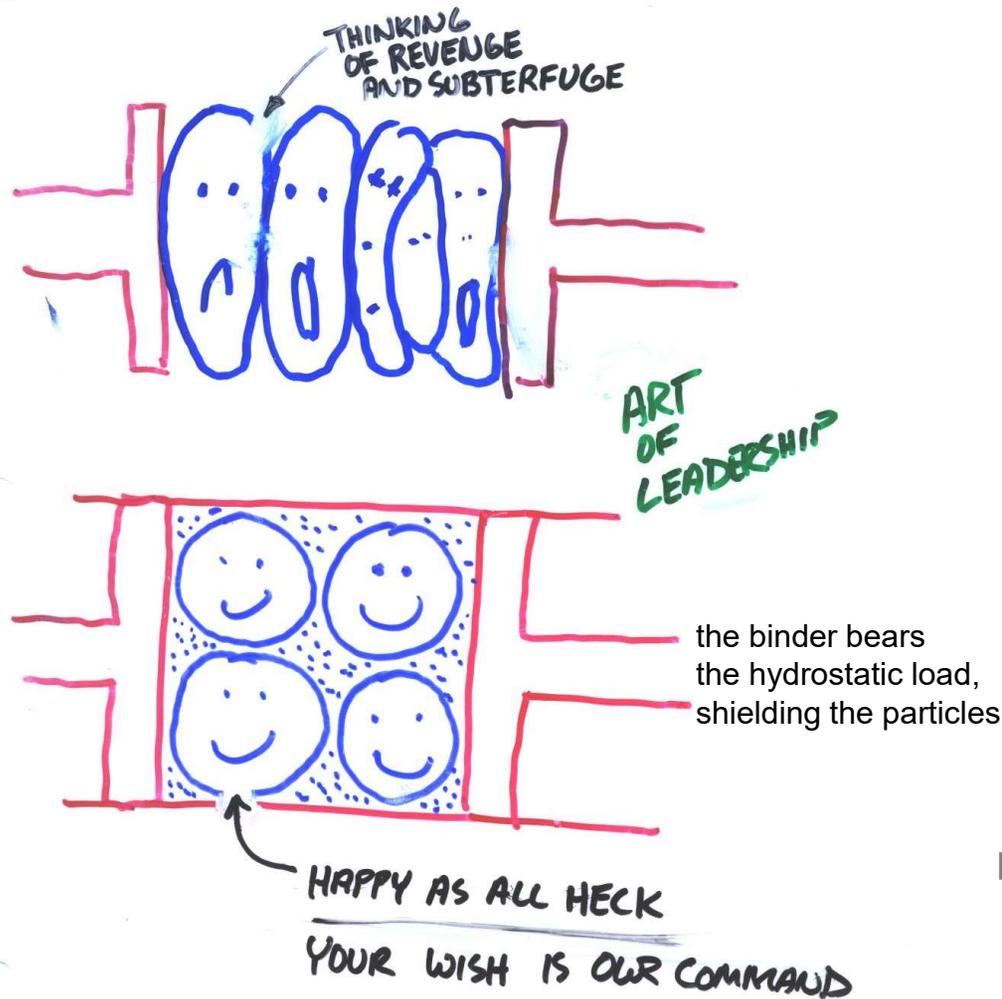
what is going on in here?

incipient flow  
critical state  
soil mechanics  
Wroth&Houlsby



The Need for Elastic Plastic Theory  
McMeeking (2013)

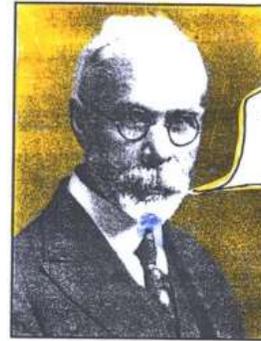
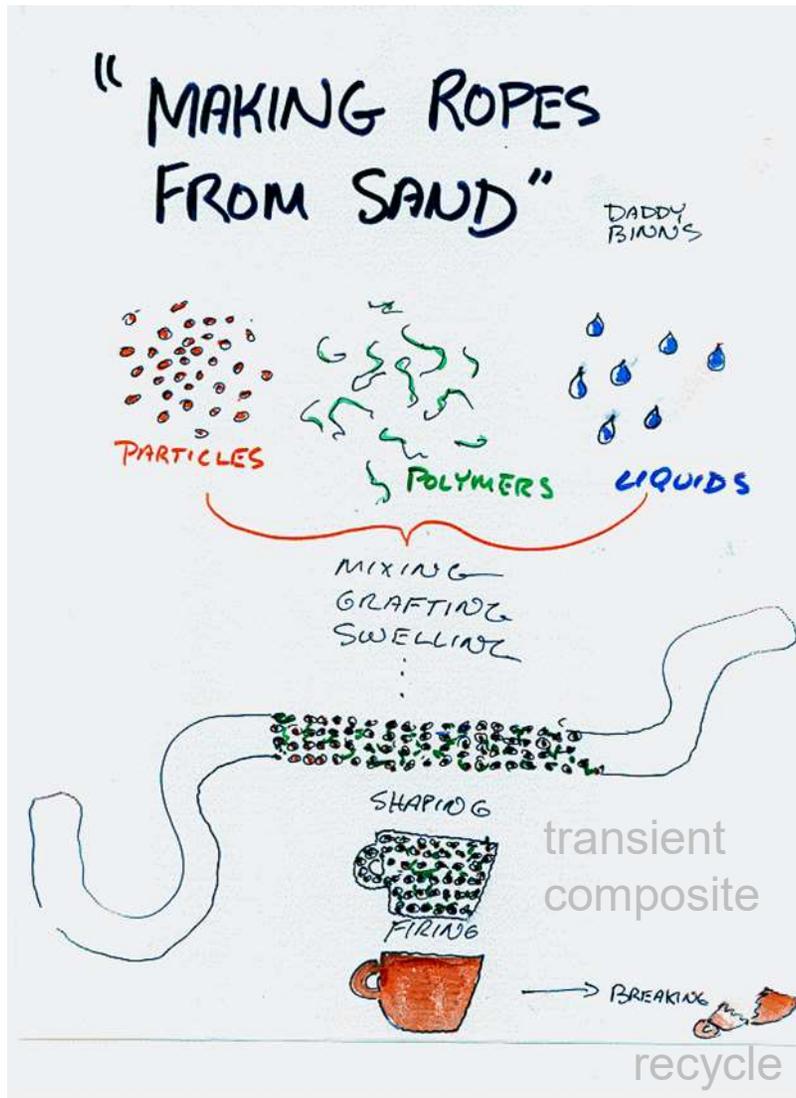
# Dry vs Wet *the Joy of hydrostatic pressure*



German (1990)

[soil mechanics]

# Making **stiff** paste

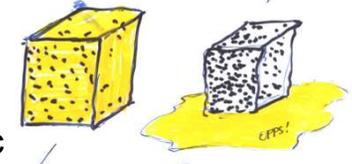


C.F. Binns  
1857-1934

... making ropes out of sand...



The extrusion paste is a highly-filled polymer solution: inorganic and organic particles in a visco-elastic matrix. Role of the liquid is hydrostatic support, so it must not seep.



The paste is plastic and must knit (cohesive, adhesive to itself)

self-healing:  
long, tough  
not short

**Knitting** is required by the massive parallel processing of assembling the array of flows within the die (unlike additive manufacturing).

$$\sigma_y < \sigma_f \quad \text{long, not short}$$

$$\sigma_y > \sigma_{ad} \quad \text{cohesive, not sticky}$$

# Think Pasta!

## Common Language

### Basic Egg Pasta

- 4 large eggs  
( $\frac{1}{8}$  cup [208 mL] eggs)
- 1 tbs (15 mL) water
- 3  $\frac{1}{2}$  cups (830 mL) sifted all-purpose flour
- $\frac{1}{2}$  tsp (2 mL) salt

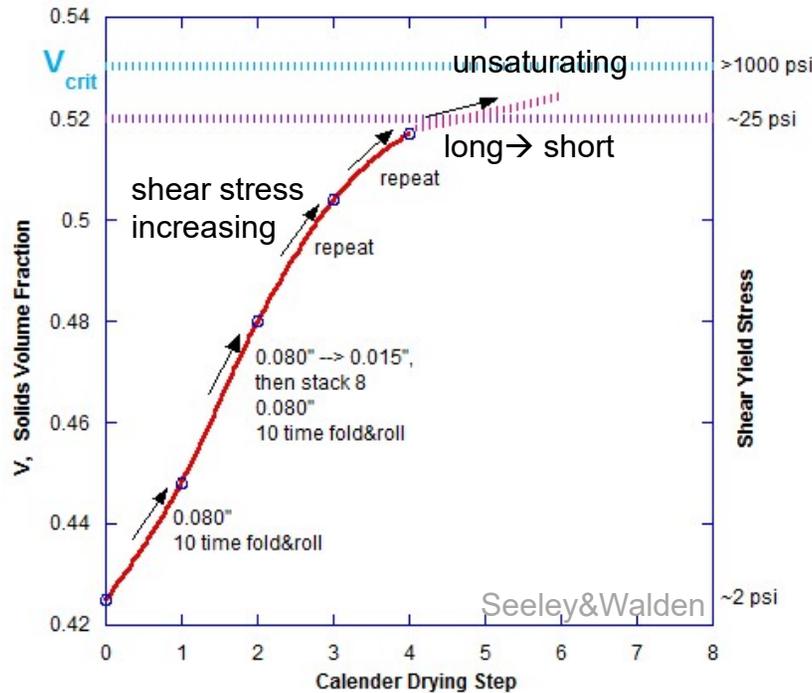
Place eggs, water, flour, and salt in mixer bowl. Attach bowl and flat beater. Turn to Speed 2 and mix 30 seconds. Exchange flat beater for dough hook. Turn to Speed 2 and knead 2 minutes. Remove dough from bowl and hand knead for 1 to 2 minutes. Let it rest for 20 minutes. Divide dough into 4 pieces before processing with Pasta Sheet Roller attachment.

Follow instructions in "Cooking Pasta."

Yield: 1  $\frac{1}{4}$  lbs (565 g) dough.



shear yield stress  
~ 2 psi

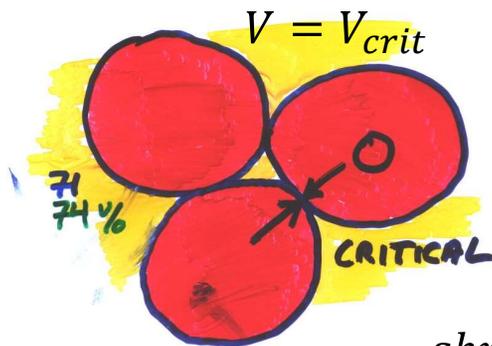


unsaturated  $\rightarrow$  saturated  
short  $\rightarrow$  long  
shear stress decreasing

# Useful in the lab for guidance

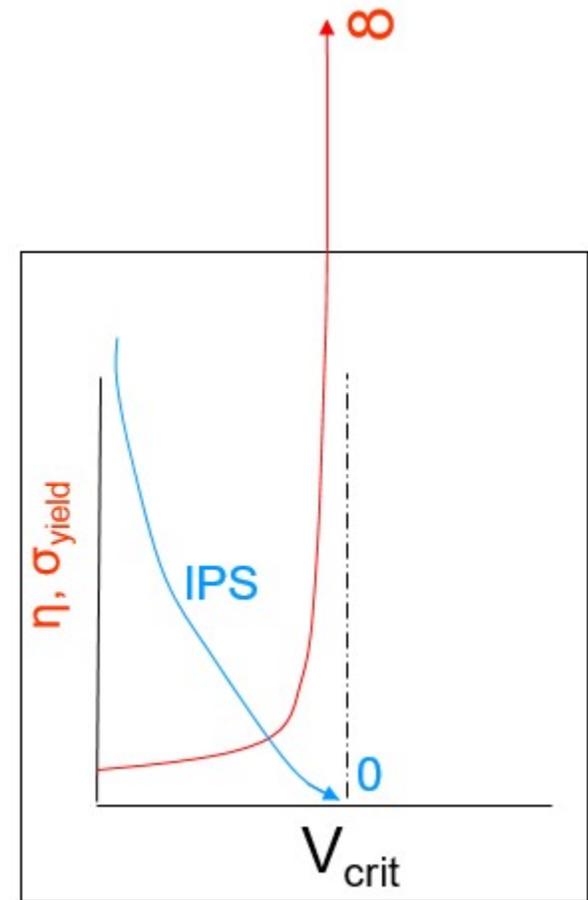
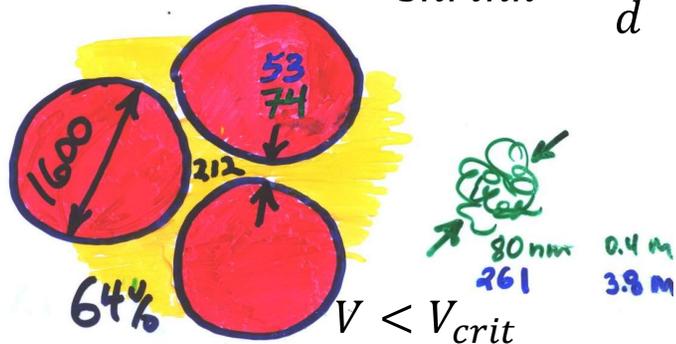
No-Hertzian-Contact  
Cartoon World

## HIGH SOLIDS LOADING



$$IPS = \frac{d}{3} \left( \frac{V_{crit}}{V} - 1 \right) \text{ Funk\&Dinger}$$

$$\text{shrink} \sim \frac{IPS}{d} \sim \frac{1}{3} \frac{1}{V} (V_{crit} - V) \propto \frac{1}{\tau_y}$$



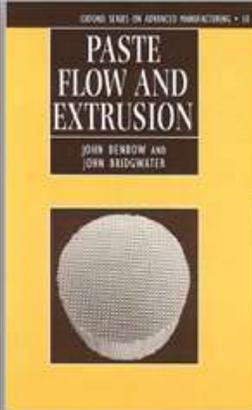
Blackburn reciprocal plots

what if  $V_{crit}$  is process dependent?

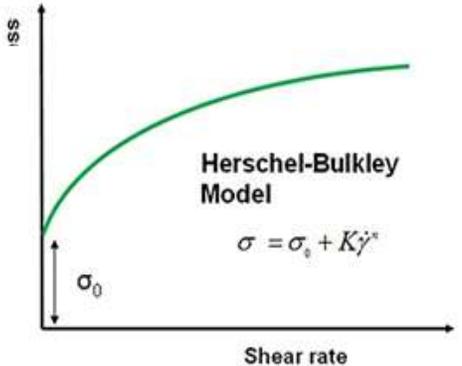
critical solids loading

jamming&breaking Yodel model

# Capillary Rheo (die-entry) Tribology (die-land) with plug-flow (...perk of significant yield stress at slow speeds)



## Benbow Paste



Benbow's equation for plug-flow extrusion:

$$P_{total} = P_{die-entry} + P_{die-land}$$

$$P_{total} = 2 \ln \left( \frac{D_o}{D} \right) (\sigma_{bo} + k_b v_e^n)_{die-entry} + 4 \left( \frac{L}{D} \right) (\tau_{fo} + k_f v_e^m)_{die-land}$$

speed dependent  
yield stress

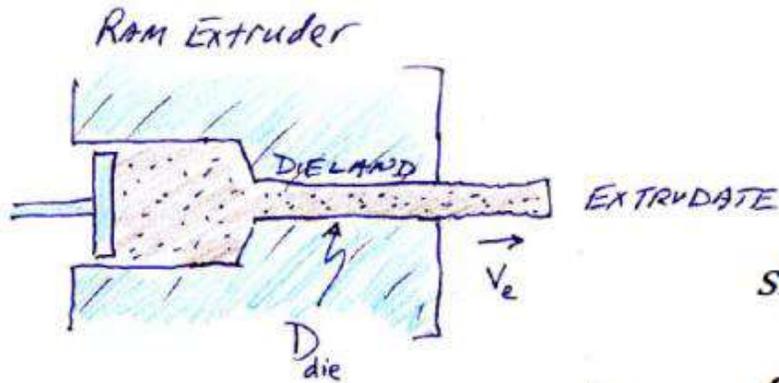
Here, die-entry is all plastic work: *no viscous and no elastic terms*

something empirical  
to guide one in the lab...

complementary flow is indentation Briscoe (1999)

# Linking together the die-entry and the die-land

No-Hertzian-Contact  
Cartoon World



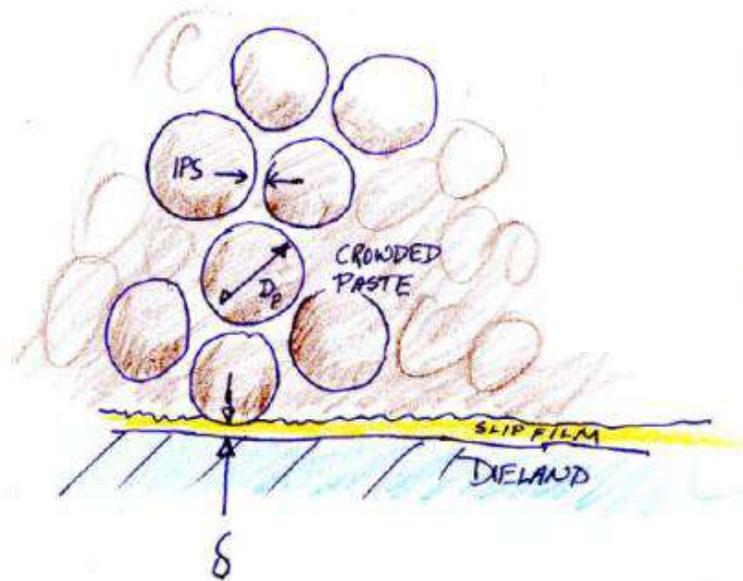
slip film thickness:

$$\delta = 3 \text{ IPS for } \delta \ll d \text{ and } D > 5d$$

when

$$\text{IPS} = \frac{d}{3} \left( \frac{v_{crit}}{v} - 1 \right) \text{ for } \text{IPS} \ll d$$

Funk&Dinger

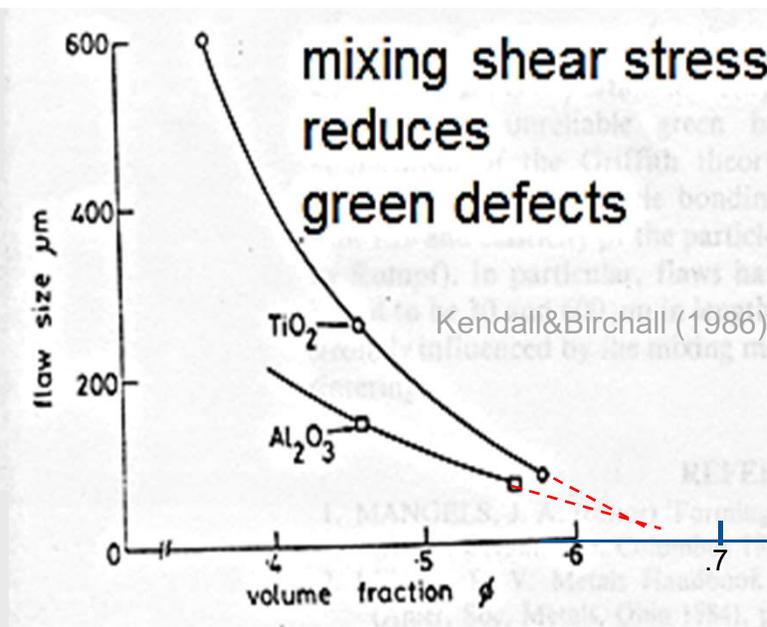
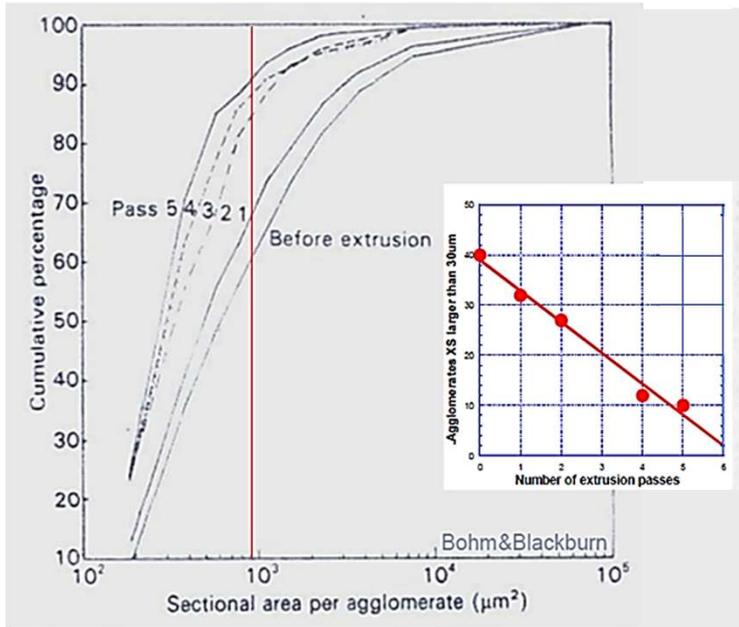


$$\frac{\delta}{d} = 1 - \frac{v}{v_{crit}}$$

Kalyon (2005)

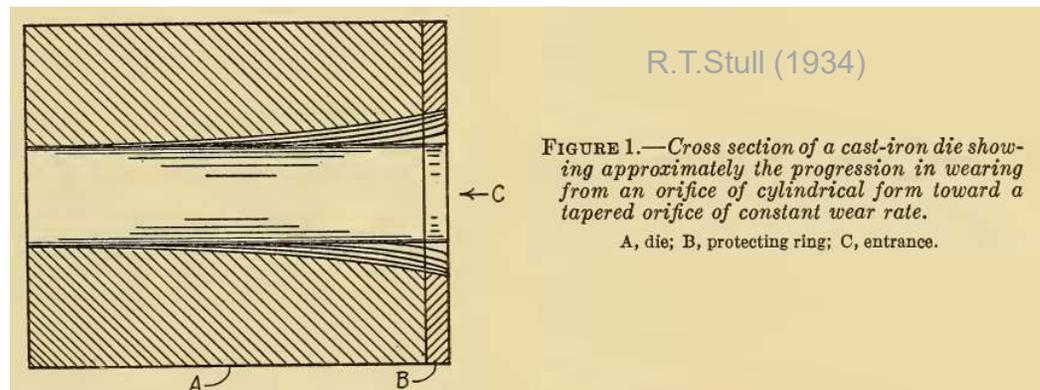
$$\frac{\dot{\gamma}_{slip}}{\dot{\gamma}_{IPS}} \sim \frac{1}{2} \frac{D}{d} \frac{\text{IPS}}{\delta} \rightarrow 1 \text{ as } 5d \rightarrow D$$

# A touching story of wear and comminution/attrition



particles contacting particles

Weibull and Birchall were all about paying attention to the tail of the distribution



particles contacting the die

# A Sticky Universe

K. Kendall (2001)  
*Molecular Adhesion and its Applications: The Sticky Universe*

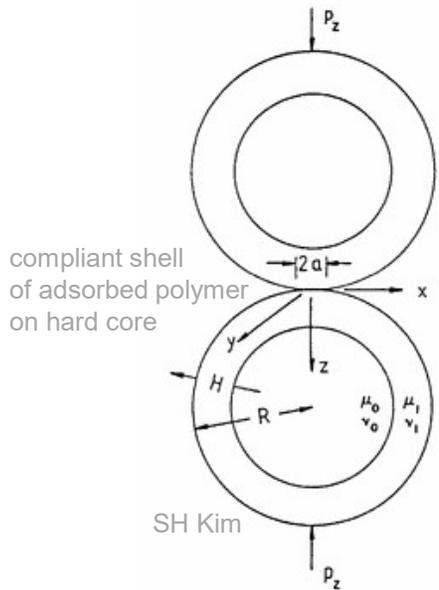


Fig. 1 Geometry of the problem

Reed&Sawyer

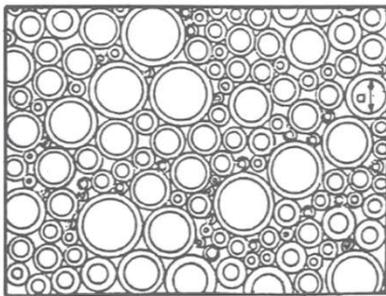
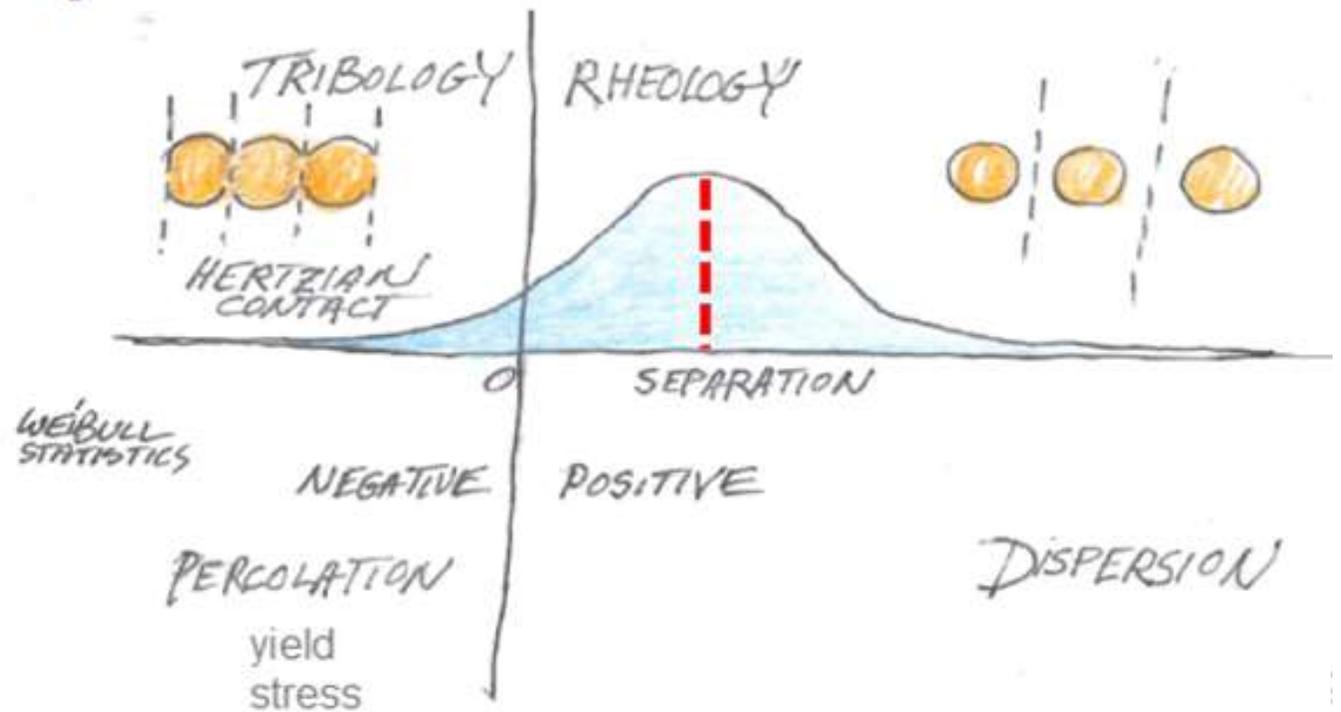


Fig. 14.6 (top) An added binder in liquid between particles influences consistency and flow of a slurry or paste and (bottom) compliant binder films on particles provides deformability needed for compaction and plastic extrusion.

Let them touch! ....contact patch, how hard are they touching?  
 allowing negative numbers  
 ....Hertzian contact



# Touching is good

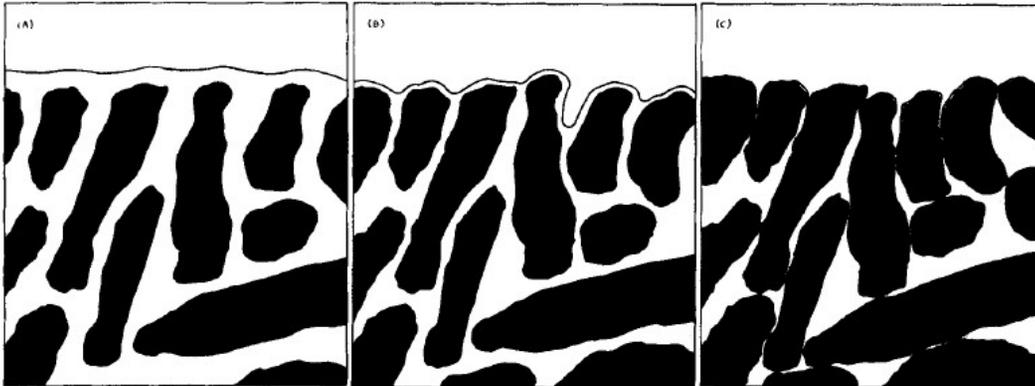


Fig. 2.—Magnified section of a plastic clay mass: (A) soft, (B) medium, (C) stiff.

Stress relaxation  
squeeze toy: evacuated  
bag of sand, whose  
granules are held in  
frictionous contact  
by the balloon's  
elastic membrane  
(modeling  
surface tension  
of a just  
saturated  
paste).



Norton (1948)

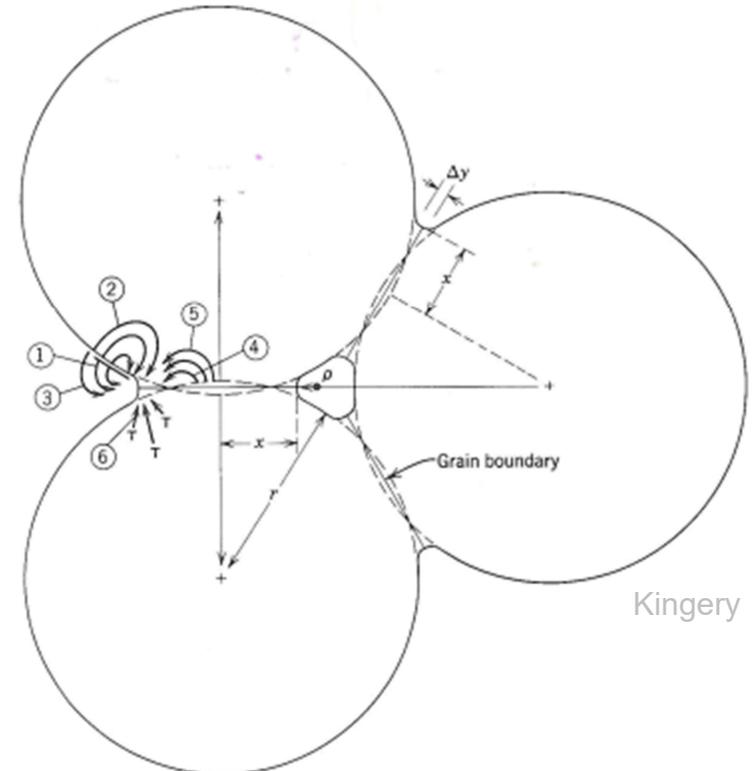


Fig. 10.21. Alternate paths for matter transport during the initial stages of sintering. Courtesy M. A. Ashby. (See Table 10.1.)

# non-ideal plastic body

It's Friction Lossy



very lossy

Astbury, Moore & Lockett (1966)  
cyclic torsion results from clay:

Norton Balloon

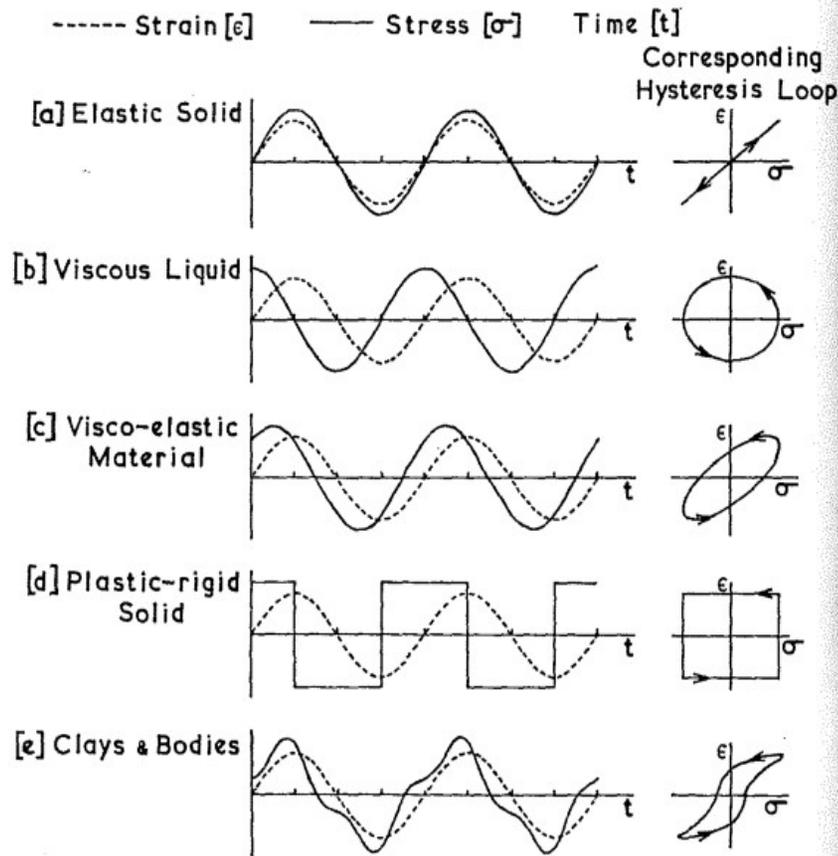


FIGURE 3.—The behaviour of various materials under sinusoidal strain.

*memory of clay*

NF Astbury, F. Moore & JA Lockett 1966

CYCLIC TORSION TEST FOR STUDY OF PLASTICITY 441

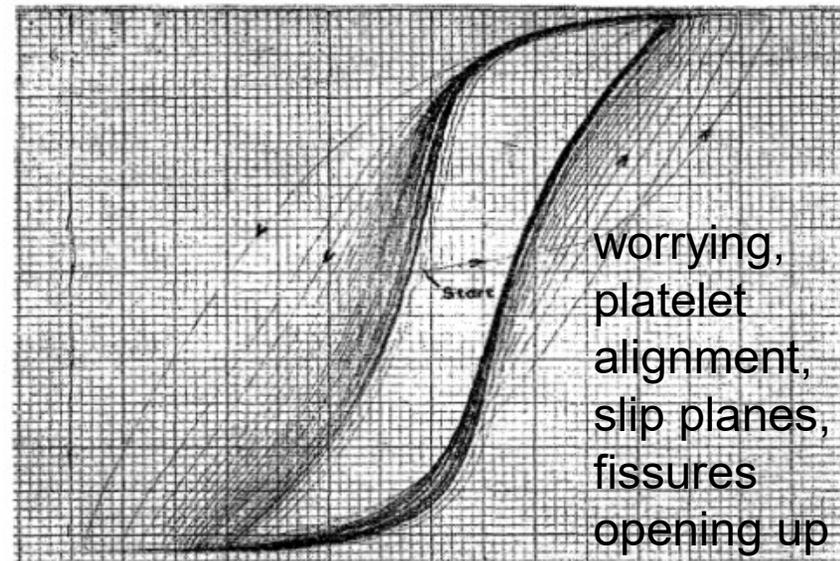
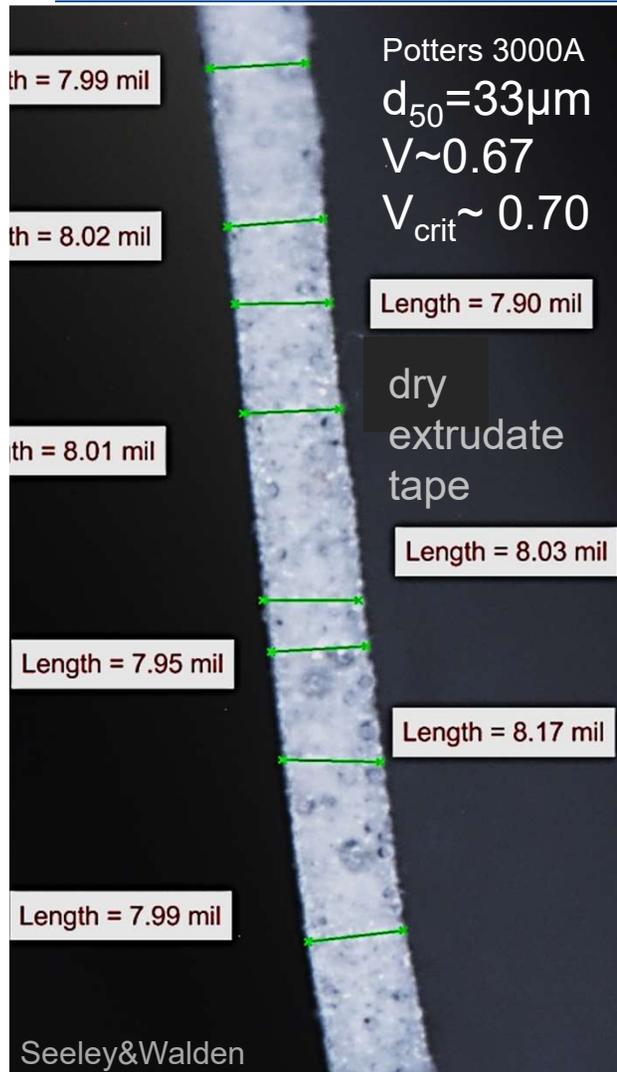
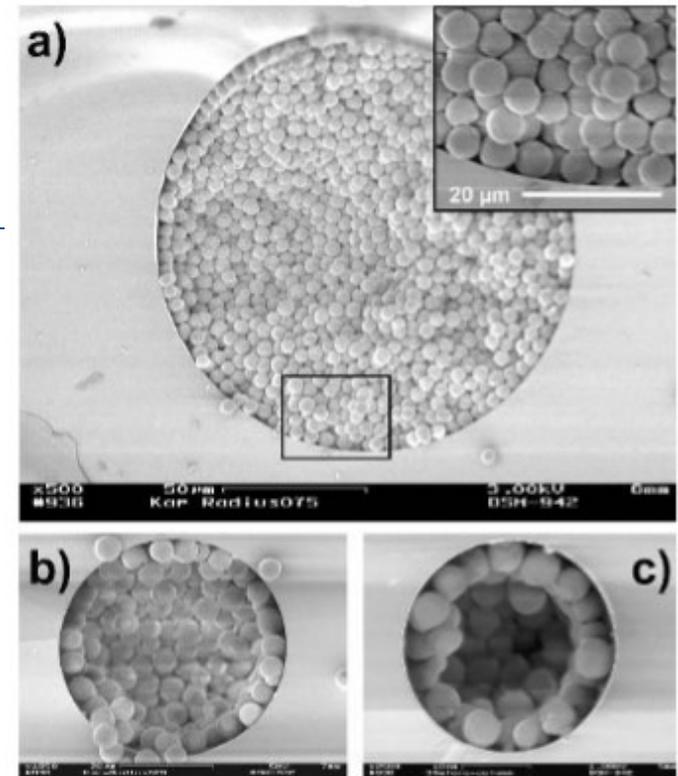


FIGURE 2.—Stress-strain record of torsion test on earthenware specimen at 29% moisture content. Vertical axis represents strain or angular displacement; horizontal axis represents stress or torque.

particle-particle  
particle-die geometric confinement  
**Crowding** of spheres



8.01±0.09 mil dry green  
7.06±0.12 mil slot  
(178µm slot ~5 particles)  
Die swell 8-14%



slurry  
**Figure 4.** Cross-sectional view on cut capillaries packed with the 5 µm-sized Zorbax SB-C18 particles: (a) 180 µm id, (b) 50 µm id and (c) 30 µm id capillary.

Nano-HPLC  
Ehlert (2008)

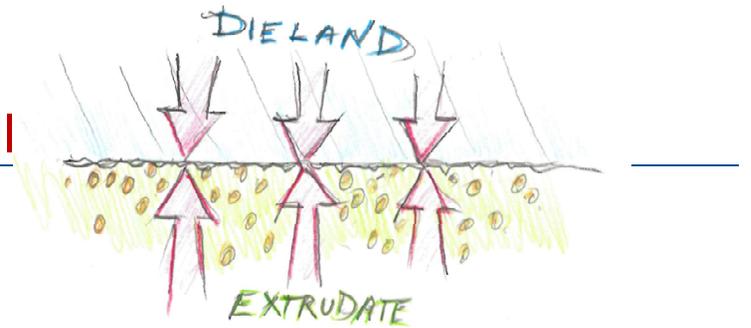
**wall-drag friction**  $\mu \rightarrow \frac{\tau_w}{\sigma_0} \sim 0.13$  plateaus as speed increases

...normal stress is related to yield stress

Blackburn (2006)

# Particles pushing particles against the die-wall

Bulk does not have a ready-made shear zone, but die-wall is a discontinuity, a ready-made shear zone



normal force of the particle assemble pushing against the die-wall is related to the yield stress of the paste

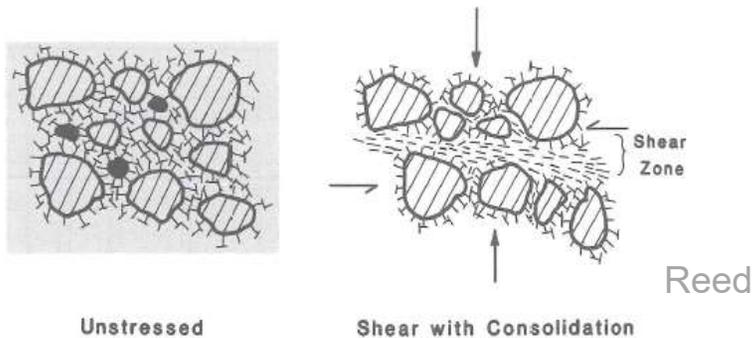


Fig. 15.24 Model of distribution of filler, finer clay particles of high aspect ratio/binder molecules, pores (dark regions) in plastic body, and formation of shear zone during plastic deformation.

Gumbel number for plug flow:

$$Gu = \eta_l \frac{v_e}{N}$$



Richard Stribeck  
1861-1950

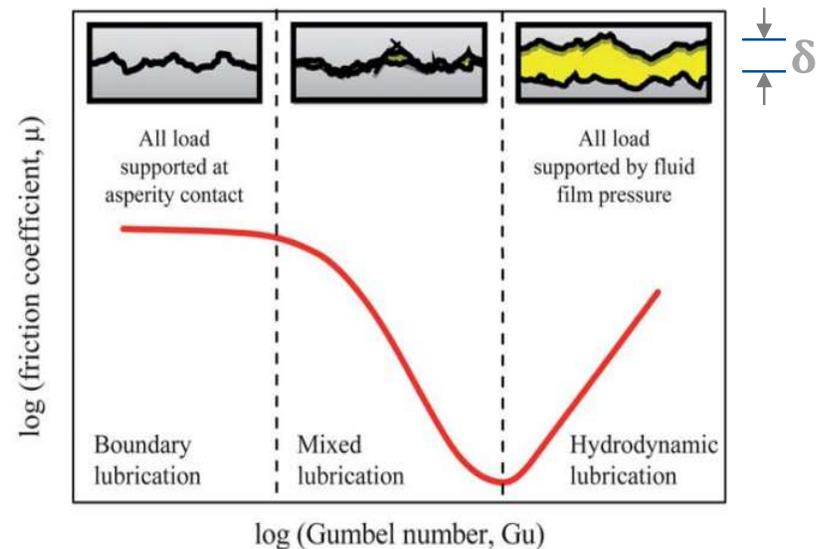


Fig. 1 Typical Stribeck curve showing the variation in frictional drag (expressed as the friction coefficient) with the Gumbel number for a lubricated contact. Andablo-Reyes

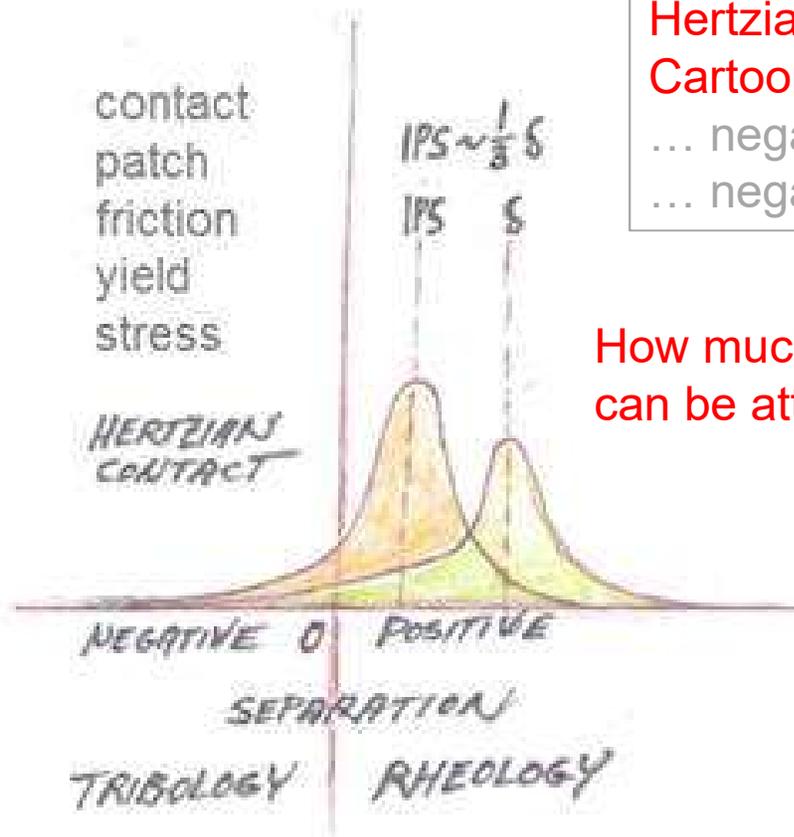
Can the die-entry and the die-land be related?

Perrot (2012)



Hertzian-Contact  
Cartoon World

... negative IPS  
... negative  $\delta$



How much of die-entry and die-land wall drag can be attributed to rheology and how much to tribology?

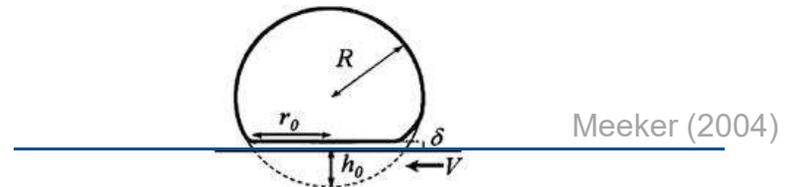


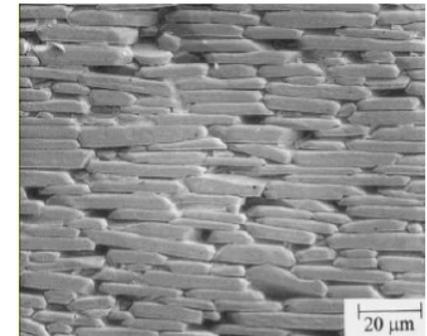
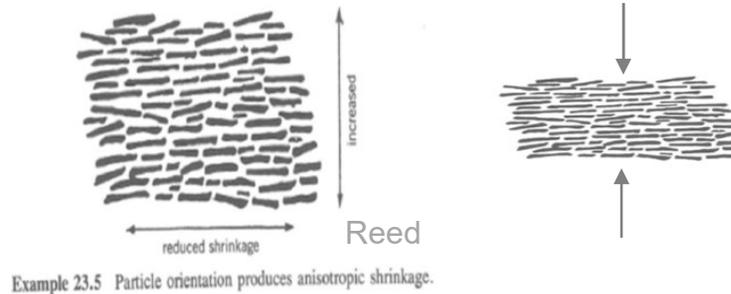
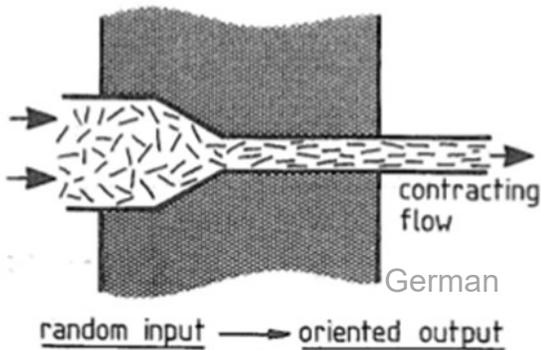
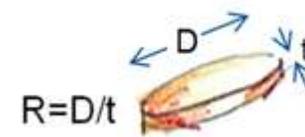
FIG. 11. Schematic representation of the facet and of the lubricated film formed when a soft particle is squeezed against a wall. For clarity, the shape of the upper part of the particle is approximated as the undisturbed spherical cap.

Meeker (2004)

negative examples:  
Kendall's elastic sintering and Meeker's hydroplaning,  
both based on consequences  
of Hertzian contact

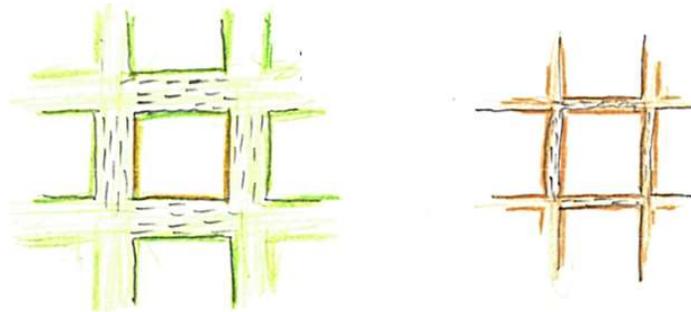
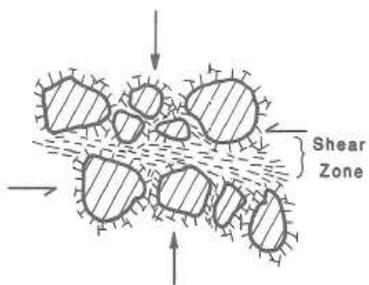
now .... no sphere particles:

# Texturing with platelets: alumina, clay and talc



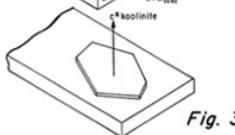
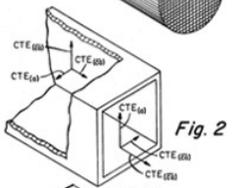
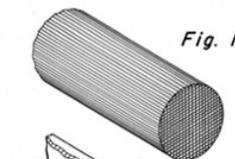
Messing

memory of clay



increasing  
OFA

Beall, us6506336

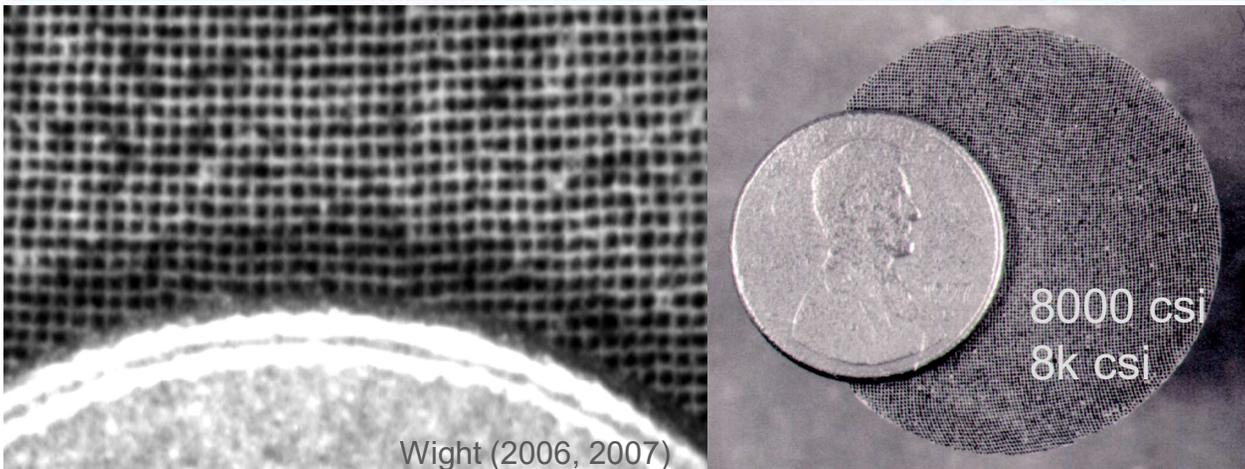
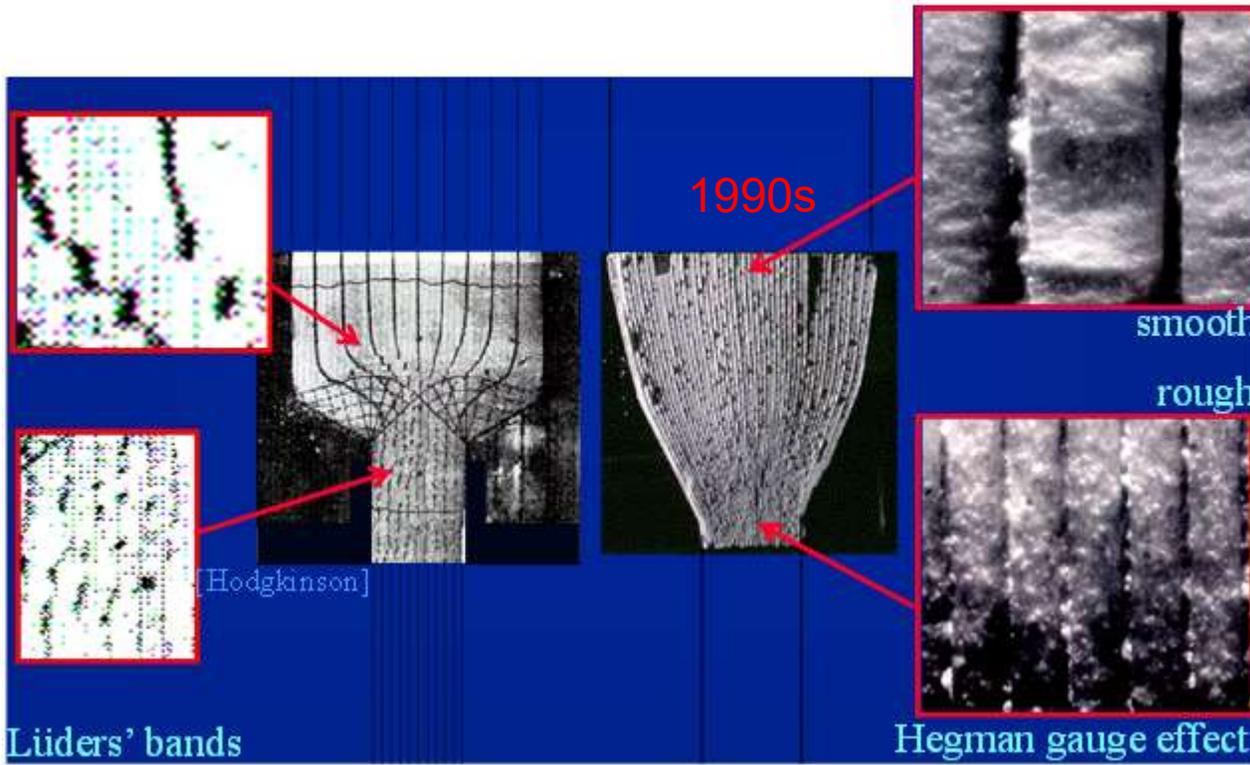


anisotropic ceramic:  
polycrystalline cordierite  
where negative expansion axis  
grows in the plane of the web

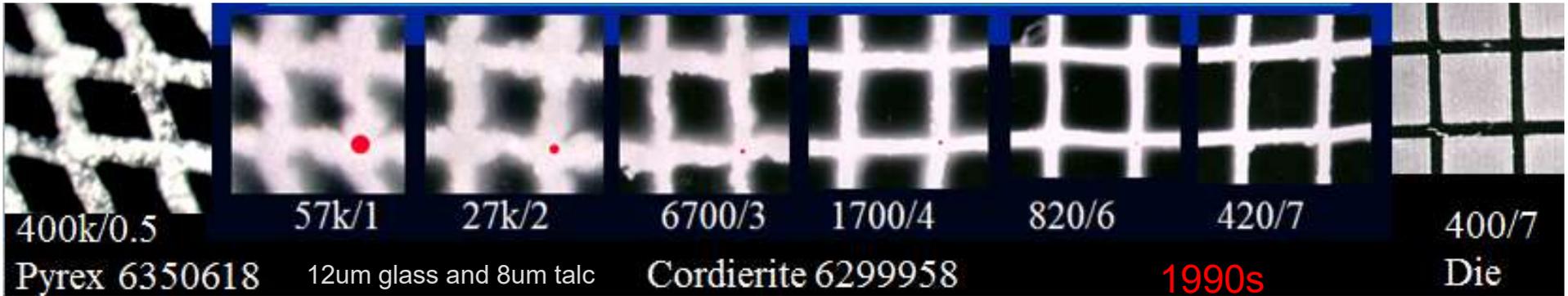
decreasing  
CTE

Lachman,us3885997

# Reduction extrusion reveals the granularity of the paste



Lange (1985)



## Granularity – loss of continuum

Interrogation of local rheology/microstructure

It might be easier to indent (Biscoe) than to extrude (Benbow) on the sub-mil scale.

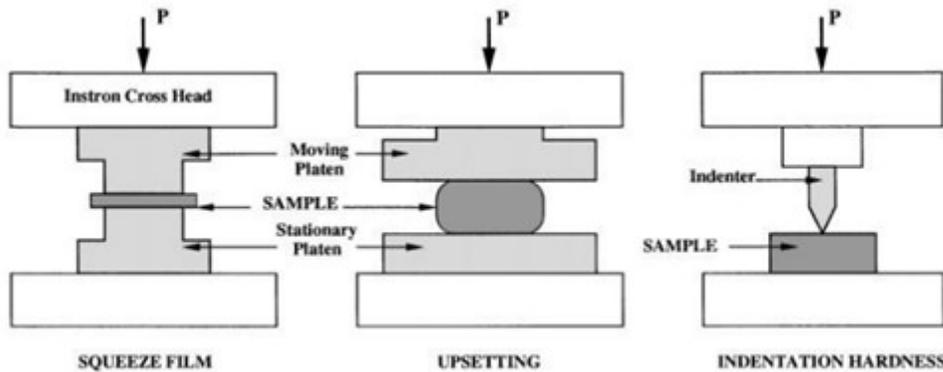
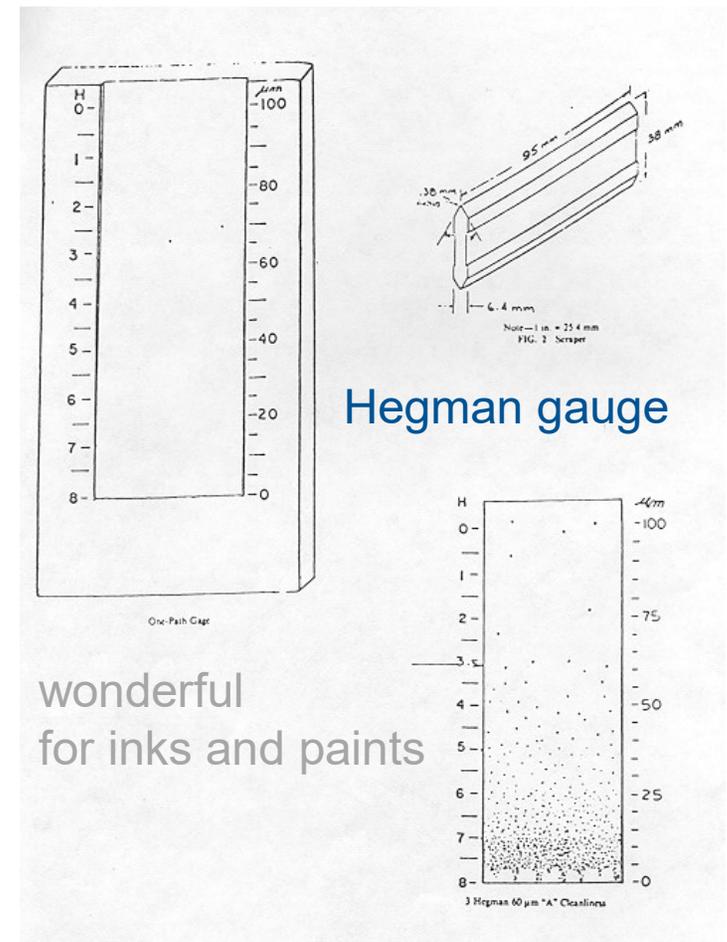


Fig. 1. Experimental test configurations.

Ozkan (1999)

Wight (2006, 2007)



Hegman gauge

wonderful for inks and paints

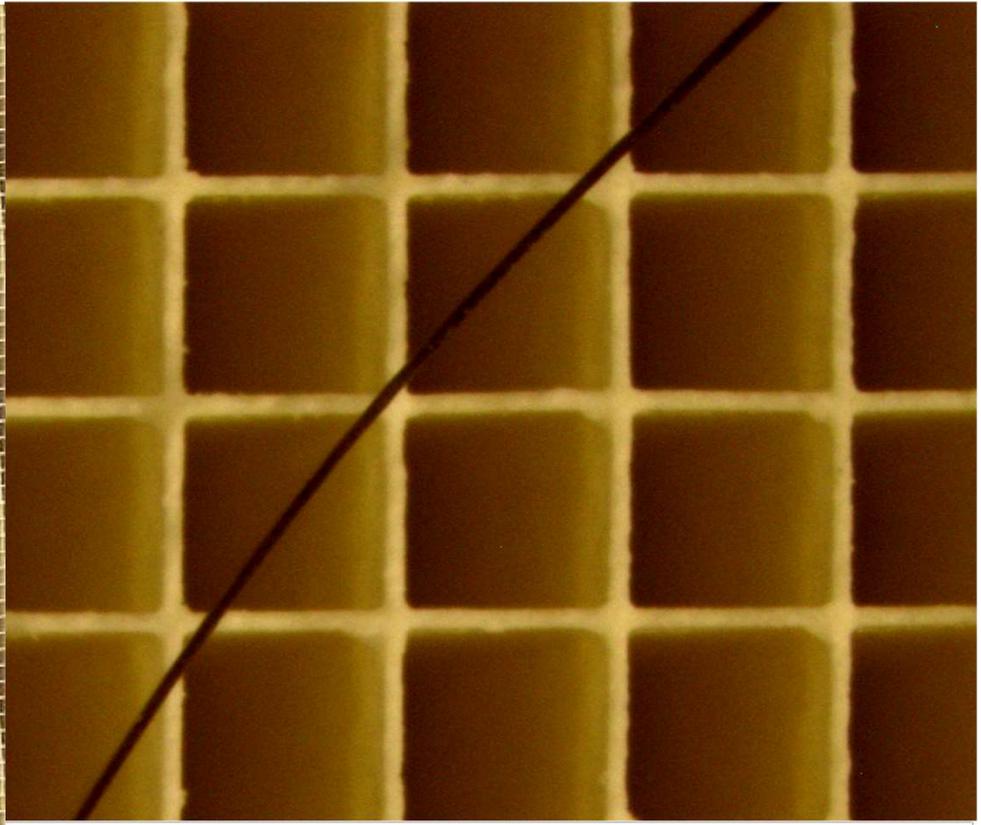
something to think about:

## Rheology and tribology on the same scale as the web

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900/3

600/3 ~ 83um



Corning's dime

my hair

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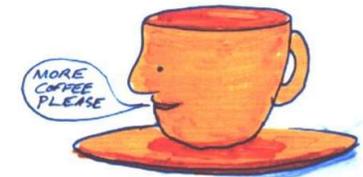
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