Caking of Bulk Solids and Its Prevention

Greg Mehos, Ph.D., P.E.
Greg Mehos & Associates LLC
greg@mehos.net
978-799-7311

Goals

- Understand caking mechanisms
- Recommend caking test methods
- Solve caking problems

Goals

Goals

Caking

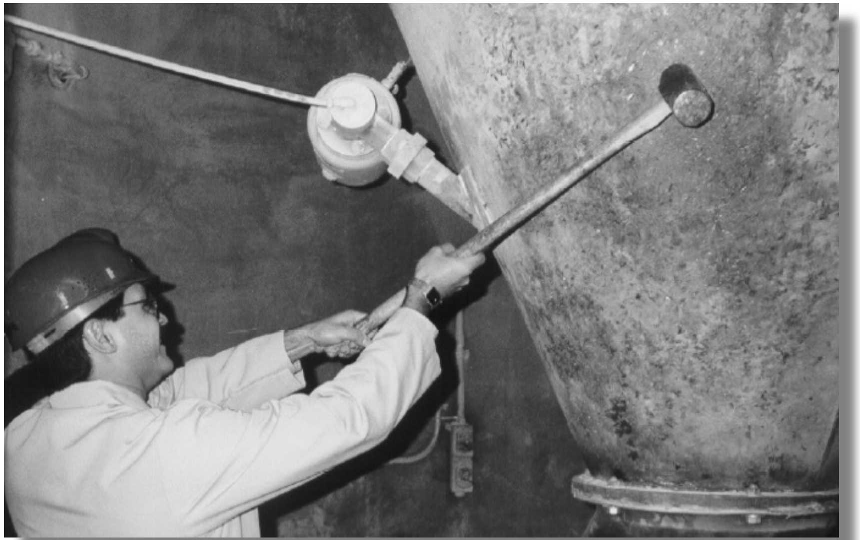
- Challenges
  - Caking not immediately observed
    - Manufacturing site
    - Customers
  - Difficult to measure or predict
- Definition
  - No. of lumps?
  - Strength of caked material?

Consequences of caking

- Misperception of quality
- Customer dissatisfaction
- Loss of sales

Consequences of caking

- Misperception of quality
- Customer dissatisfaction
- Loss of sales
- Downtime
- Higher operating costs
- Loss of revenue



Causes of caking

- Moisture content/relative humidity
- Temperature
- Storage/packaging (stress)
- Composition/purity
- Particle size

Caking mechanisms

- Dry solid cohesive forces
- Liquid and solid bridges
- Plastic creep and sintering

Caking mechanisms

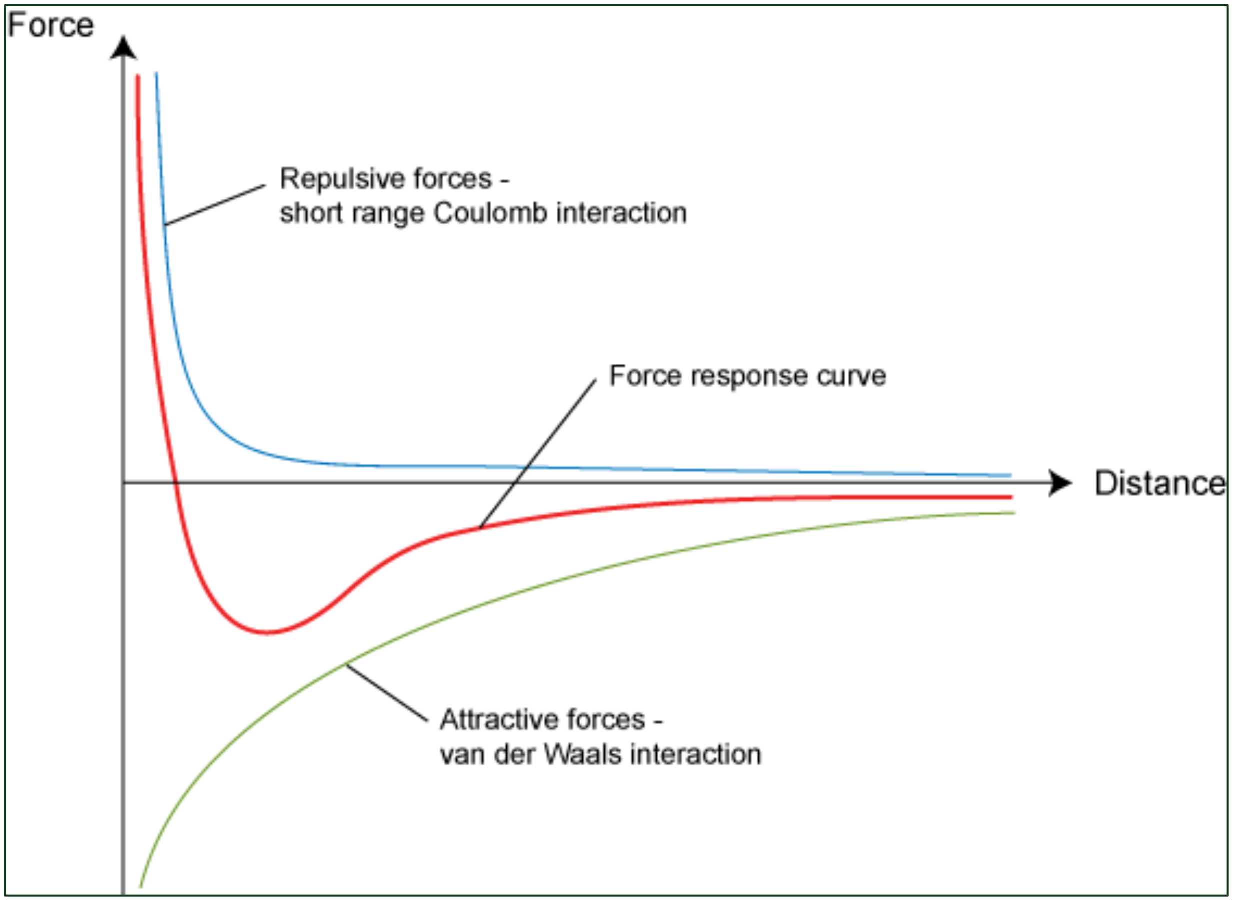
- Dry solid cohesive forces
- Liquid and solid bridges
- Plastic creep and sintering

Dry solid cohesive forces

- Non-polar
- Polar

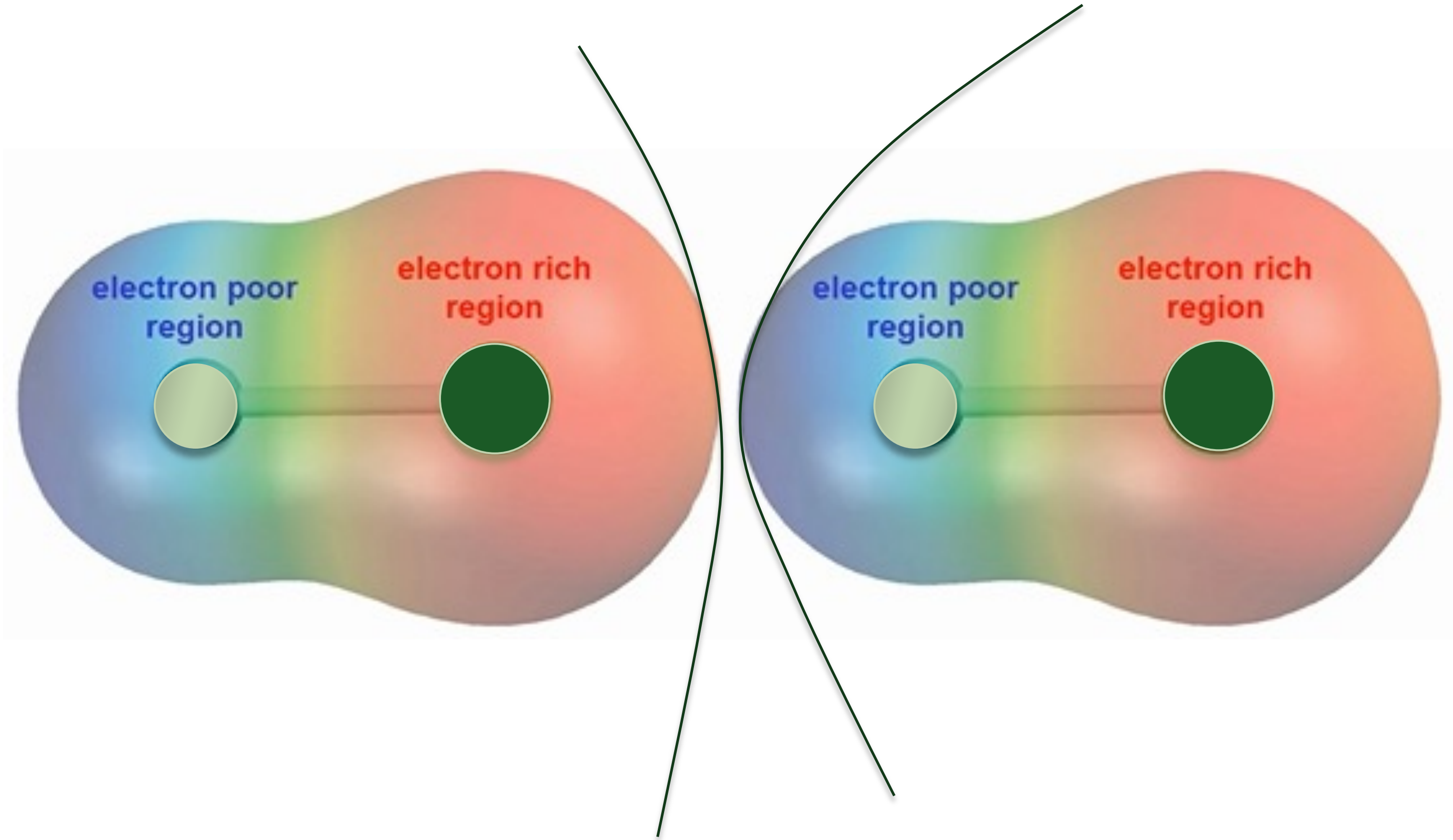
Dry solid cohesive forces

van der Waals and Coulomb forces

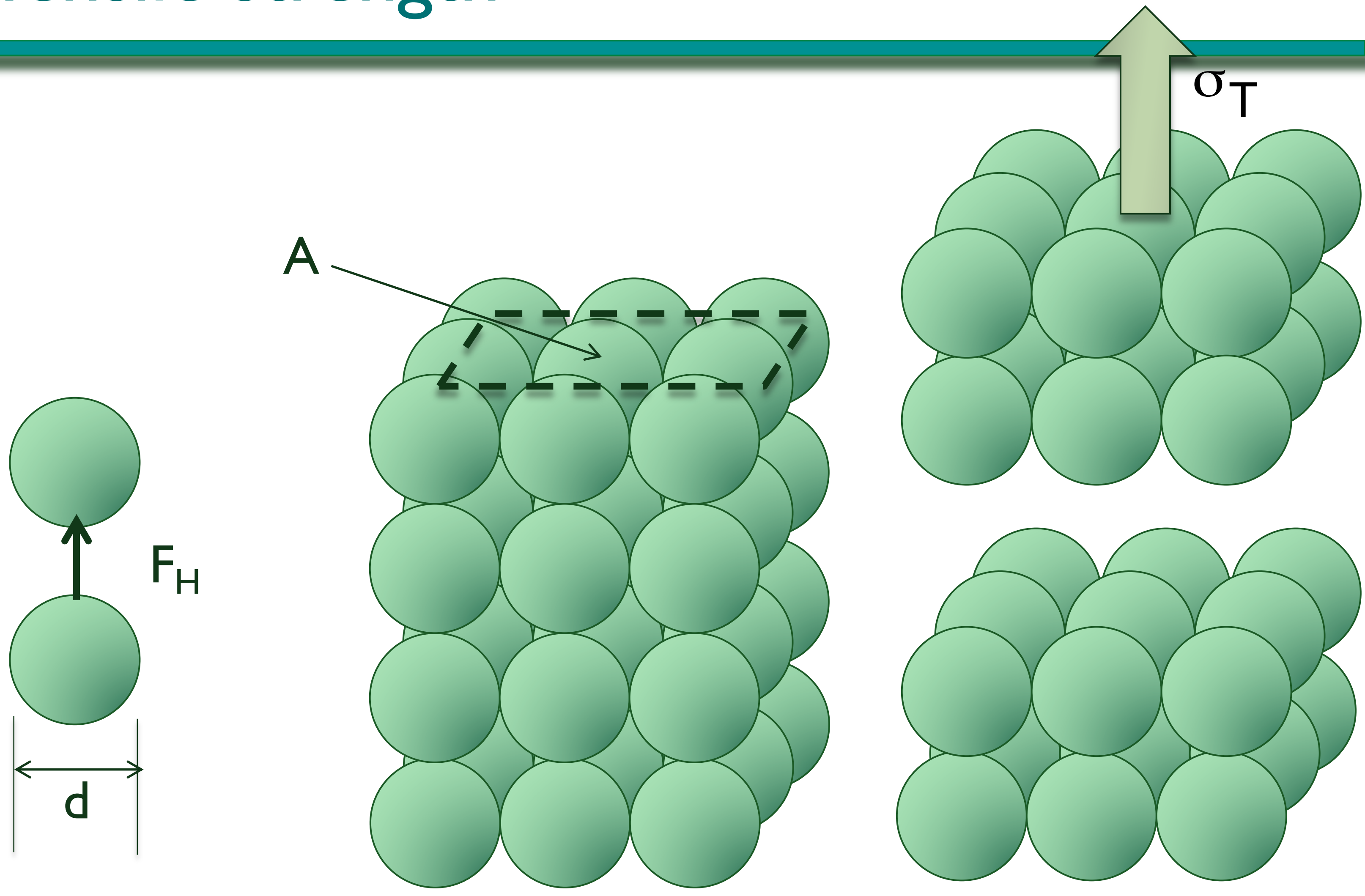


Dry solid cohesive forces

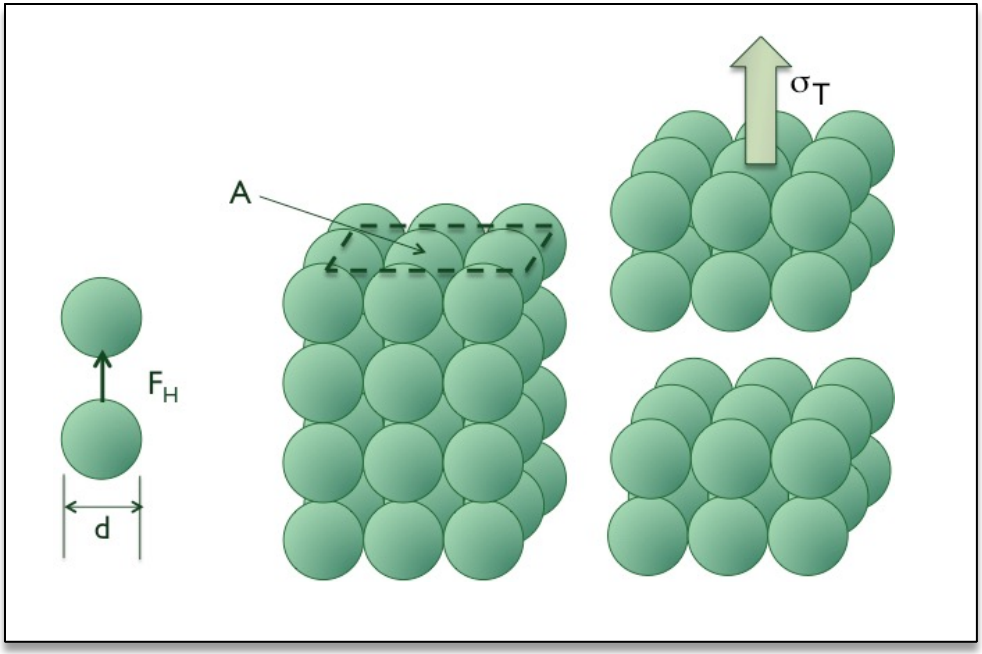
Polar interactions



Tensile strength



Tensile strength



$$\sigma_T = \frac{nF_H}{A} \propto \frac{nd}{nd^2} \propto \frac{1}{d}$$

Cohesive strength inversely proportional to particle diameter

Caking mechanisms

- Dry solid cohesive forces
- Liquid and solid bridges
- Plastic creep and sintering

Liquid and solid bridges

- Moisture content
  - Bound
  - Unbound

Liquid and solid bridges

- Moisture content
  - Bound
  - Unbound
- Capillary condensation/liquid bridges
- Viscous layering

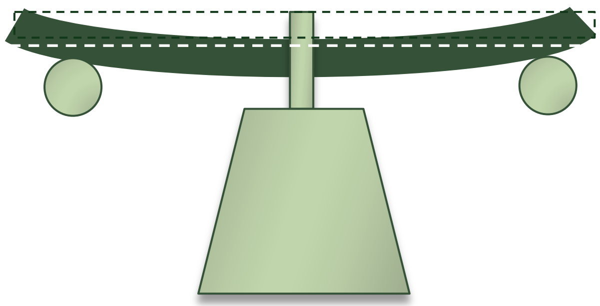
Liquid and solid bridges

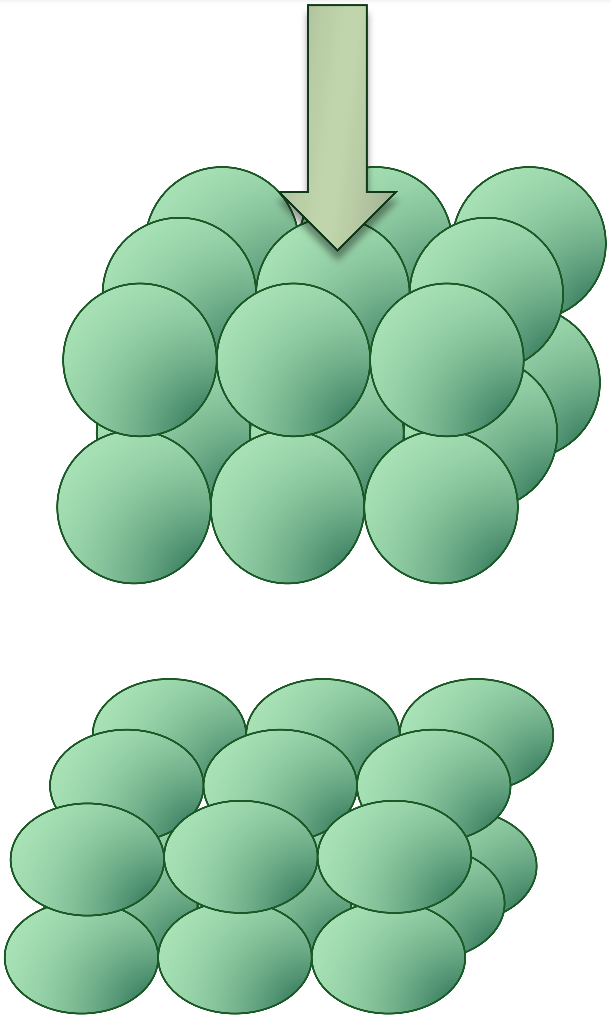
- Moisture content
  - Bound
  - Unbound
- Capillary condensation/liquid bridges
- Viscous layering
- Crystalline/solid bridges

Caking mechanisms

- Dry solid cohesive forces
- Liquid and solid bridges
- Plastic creep and sintering

Plastic creep/sintering





Test program

- Develop hypothesis based on likely caking mechanisms
- List possible independent variables that can be controlled

Test program

- Develop hypothesis based on likely caking mechanisms
- List possible independent variables that can be controlled
- Conduct tests in which caking is *quantified*
- Select control variables
  - Process control
  - Product specification
- Modify process or product

Common control variables

- Moisture content/relative humidity
- Temperature
- Storage/packaging
- Particle size
- Composition/purity
- Surface energy or modification

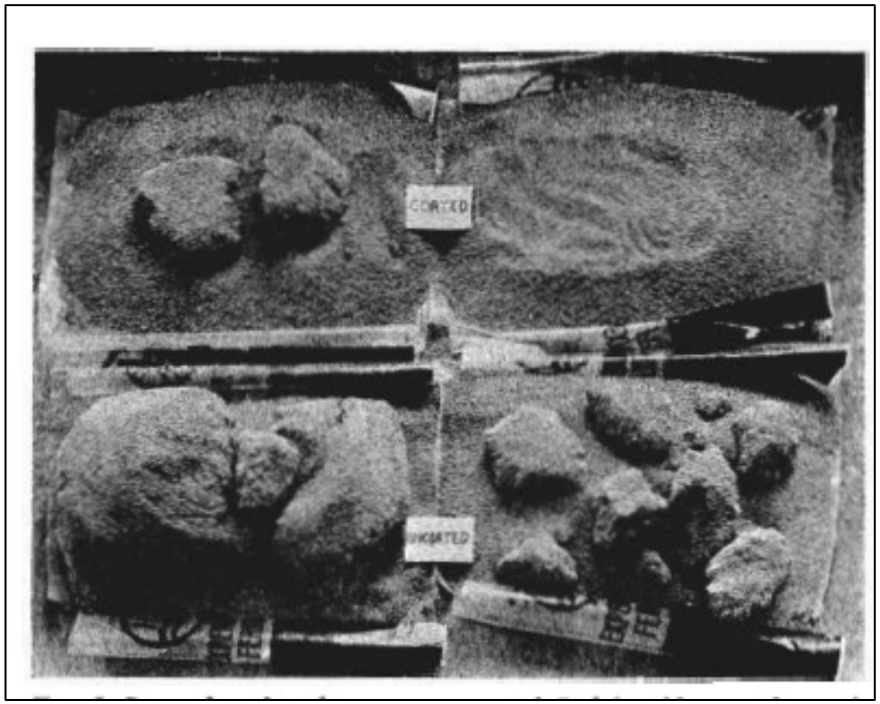
Testing

- Strength tests
- Engineering strain
- Moisture sorption

Strength tests

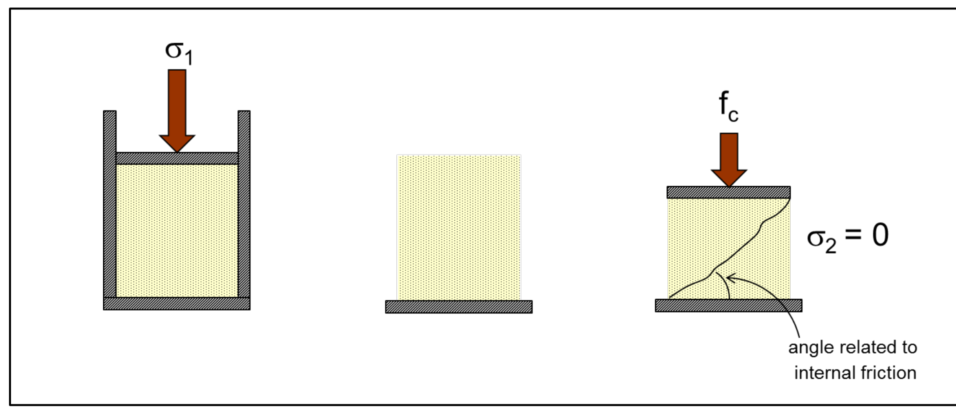
- Qualitative
- Quantitative

Qualitative



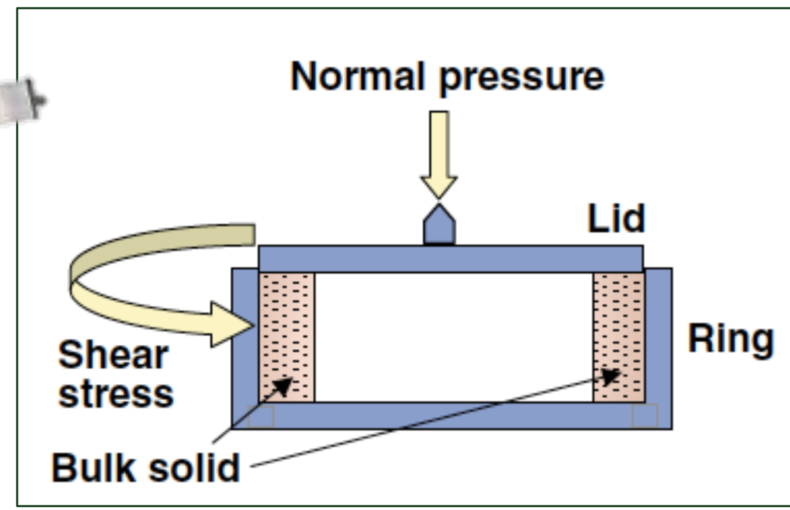
Penetrometers

Uniaxial compression



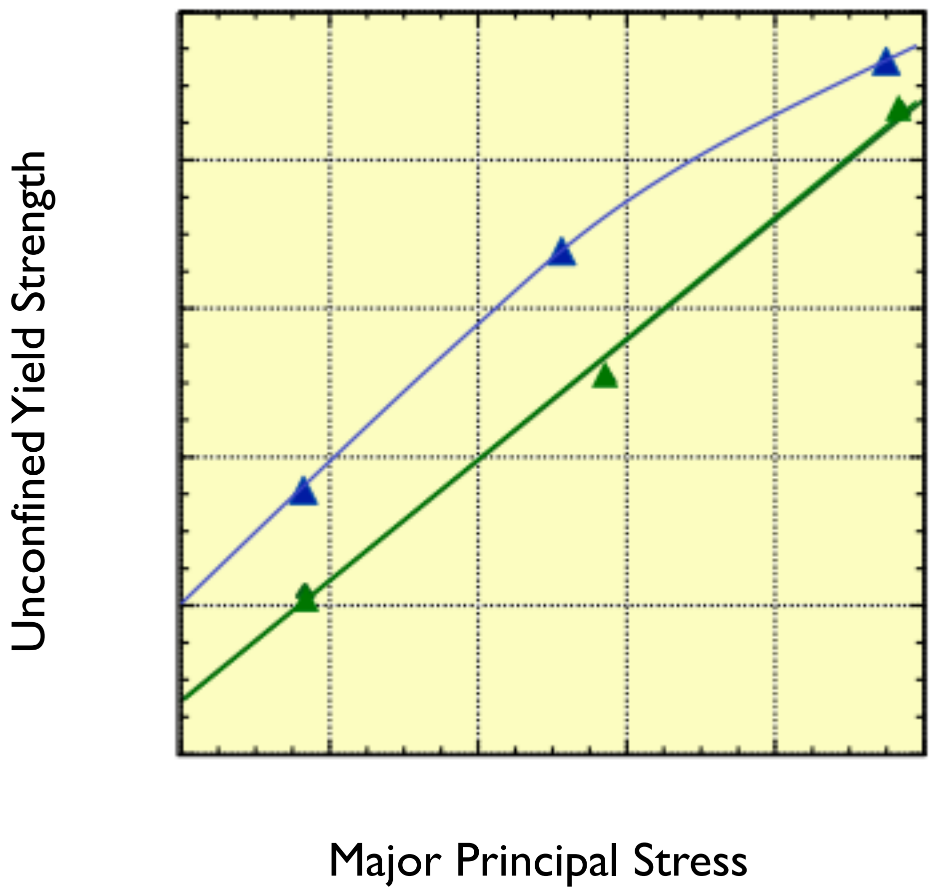
Freeman Technology Uniaxial Powder Tester (not its FT4)
No longer commercially available

Shear cell testers



Schulze RST-XS.s

Shear cell testers



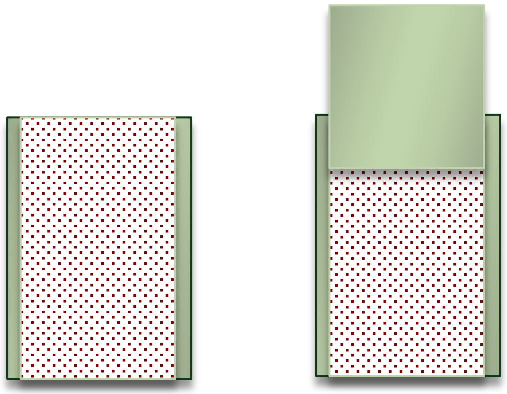
Shear cell testers

- Measure cohesive strength as function of
  - Solids stress
  - Time
- Also used in hopper design
  - Outlet size
  - Hopper angle
  - Flow behavior in existing bins

Testing

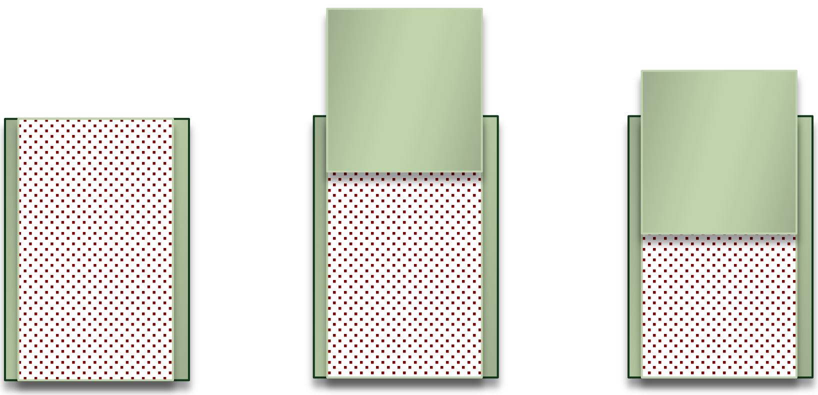
- Strength tests
- Engineering strain
- Moisture sorption

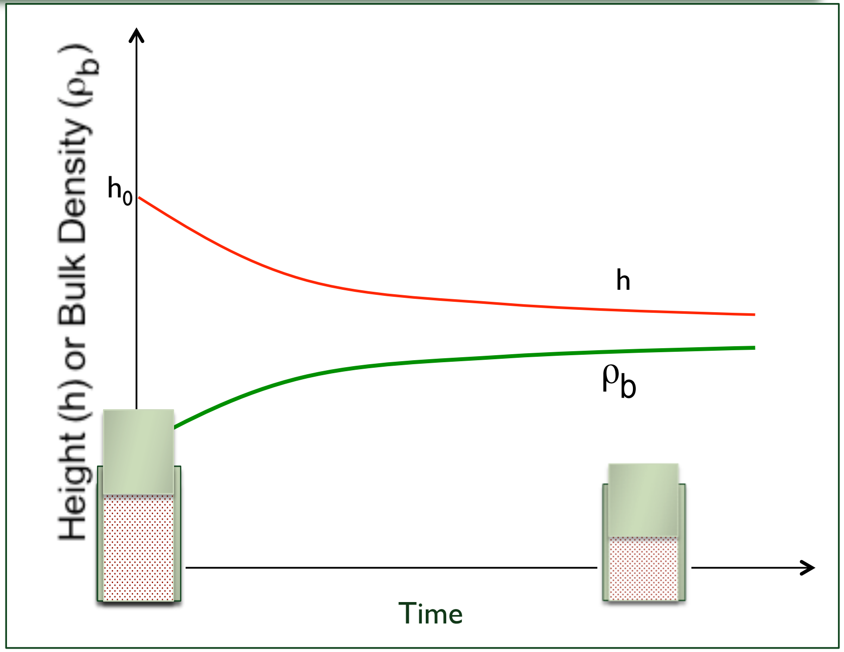
Engineering strain



Schulze RST-XS Consolidation Bench

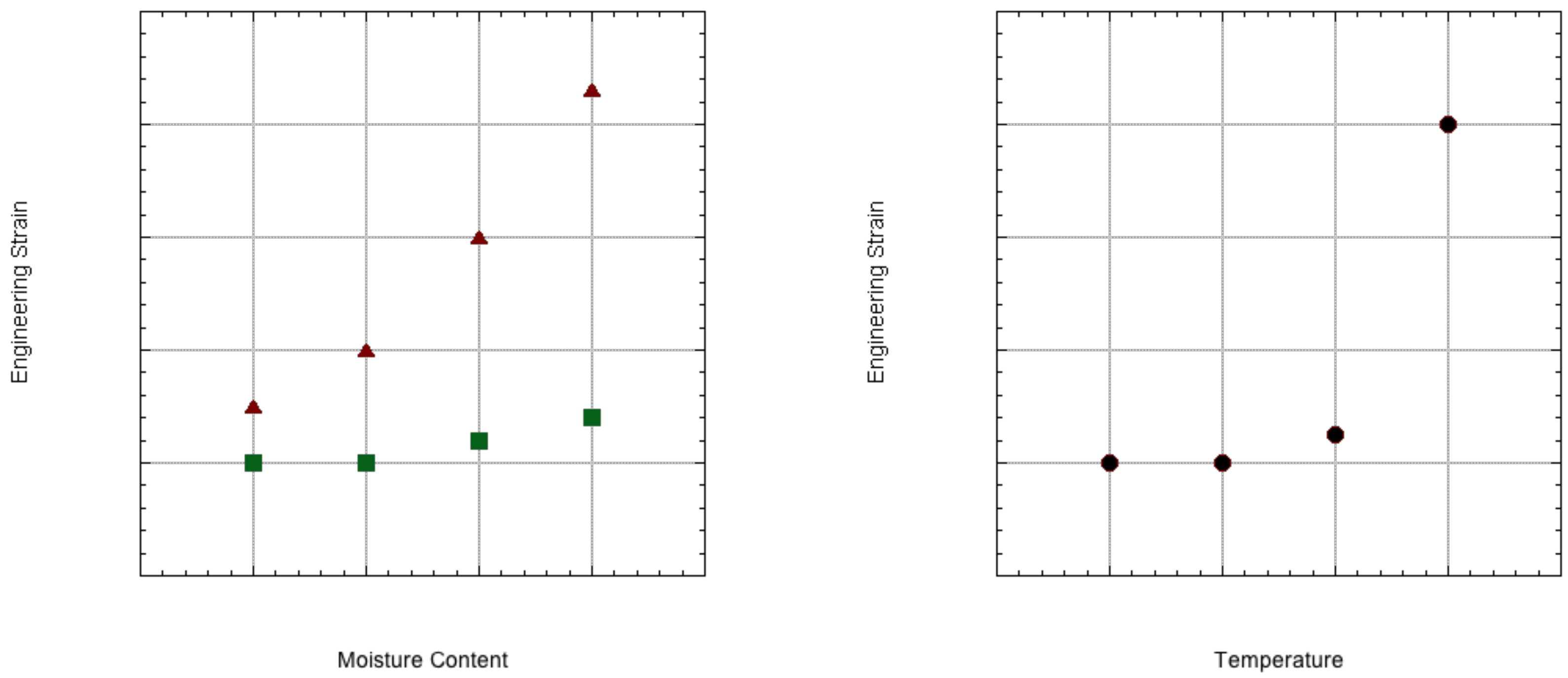
Engineering strain





Engineering strain: $\varepsilon = \dfrac{\Delta h}{h_0}$

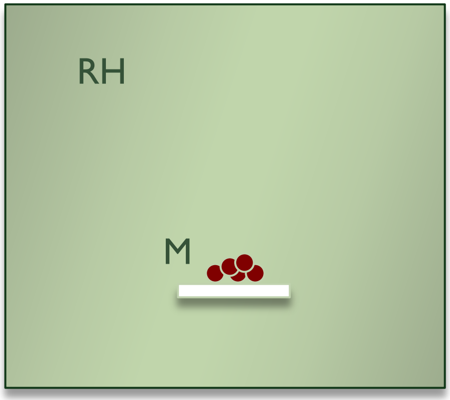
Engineering strain



Testing

- Shear cell testing
- Engineering strain
- Moisture sorption

Moisture sorption

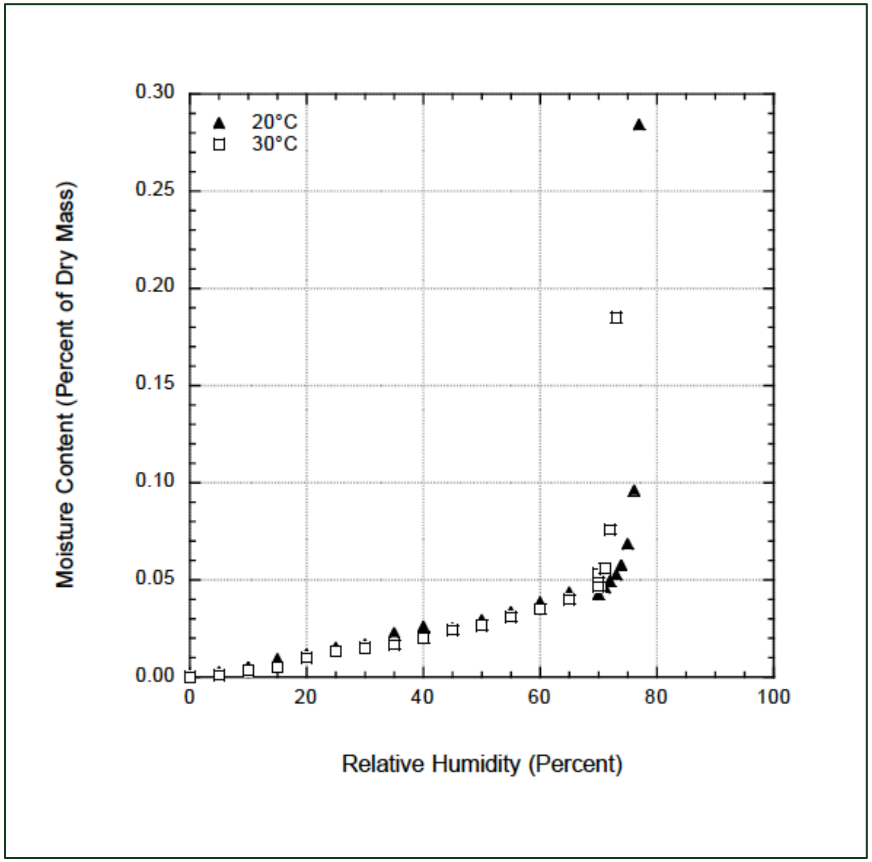


Relative humidity chamber

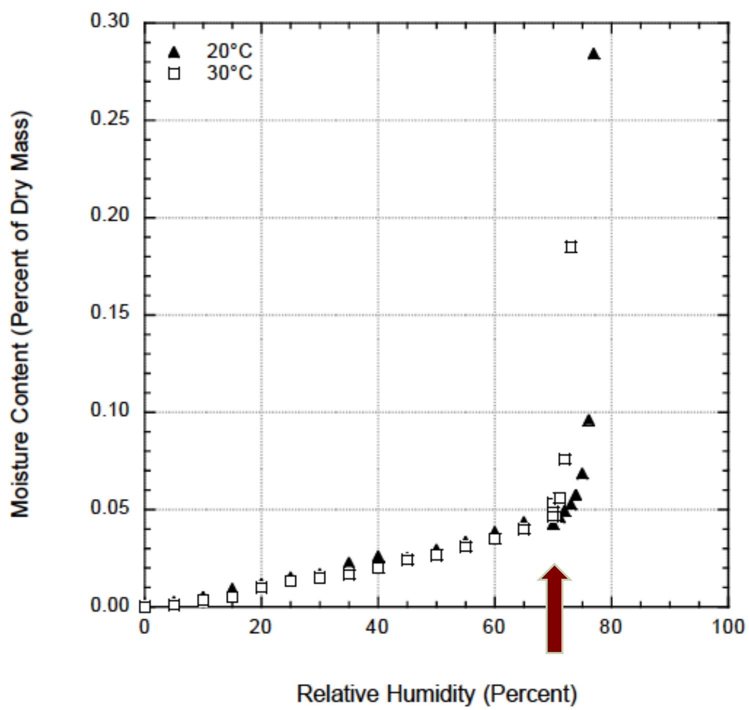
Saturated Salt Solutions

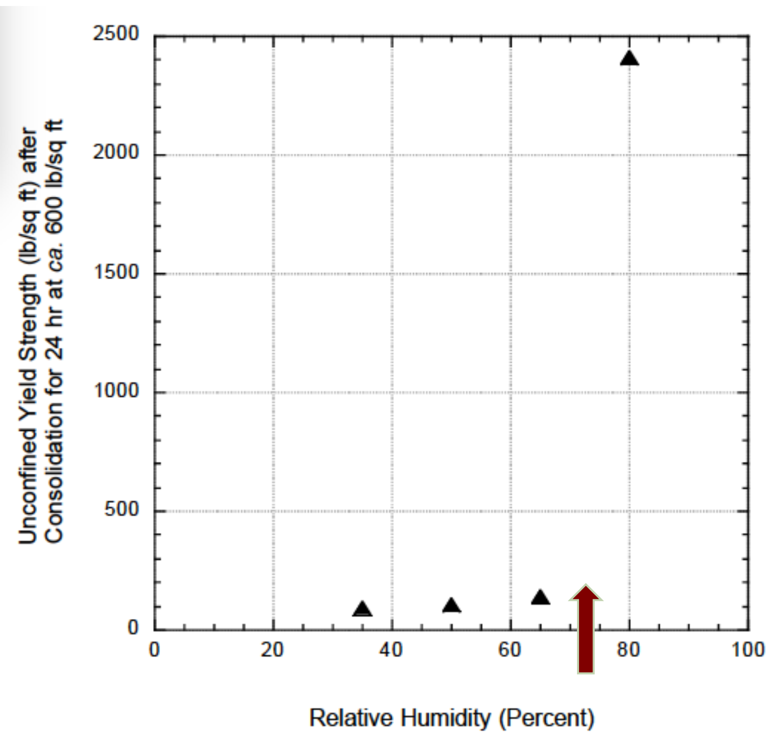
Saturated Salt Solution	Temperature (°C)										
	0	5	10	15	20	25	30	35	40	50	60
	Relative Humidity over the Salt Solution (%)										
Ammonium nitrate - NH_4NO^3			75	70	67	64	60	53			
Ammonium sulphate - $(NH_4)_2SO_4$	82	82	82	82	81	81	81	80	80	79	
Lithium chloride - LiCl [1)]					11.31	11.35	11.28	11.25	11.21	11.10	10.95
Magnesium chloride - $MgCl_2$	34	34	33	33	33	33	32	32	32	31	29
Magnesium nitrate - $Mg(NO_3)_2$	60	59	57	56	54	53	51	50	48	45	
Natrium Cloride - NaCl [1)]	75.51	75.65	75.67	75.61	75.47	75.29	75.09	74.87			
Potassium sulphate - K_2SO_4	99	98	98	98	98	97	97	97	96	96	
Potassium nitrate - KNO_3	96	96	96	95	95	94	92	91	89	85	
Potassium chloride - KCl	89	88	87	86	85	84	84	83	82	81	80
Potassium acetate - CH_3CO_2K			23	23	23	23	22				
Potassium hydroxide - KOH		14	12	11	9	8	7	7	6	6	5
Sodium chloride - NaCl	76	76	76	76	75	75	75	75	75	74	75
Sodium nitrite - $NaNO_2$					65	64	63	62	61		
Sodium dichromate - $Na_2Cr_2O_7$	61	59	57	57	55	54	53	51	50	49	47

Moisture content and cohesive strength



Moisture content and cohesive strength

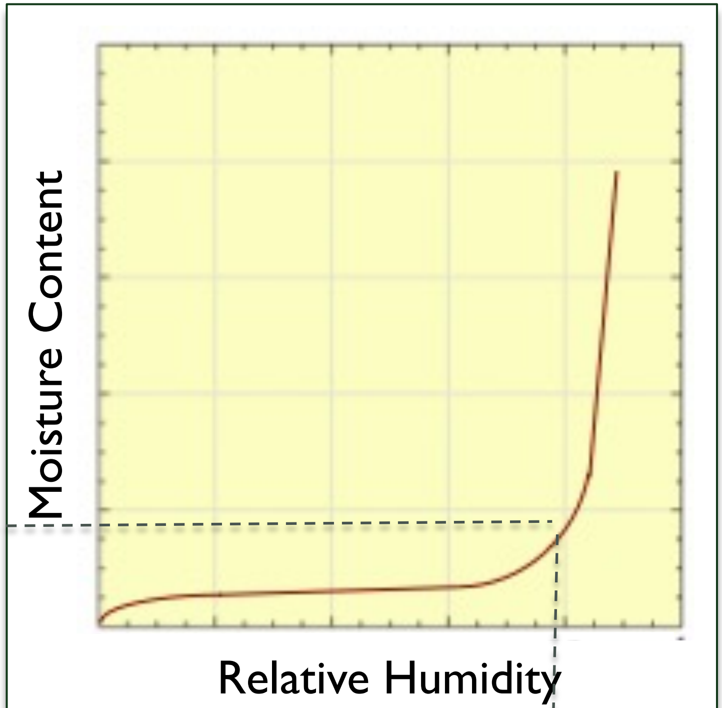




RH *vs.* water activity

$$a_w = \frac{RH}{100}$$

Moisture isotherms



Critical MC

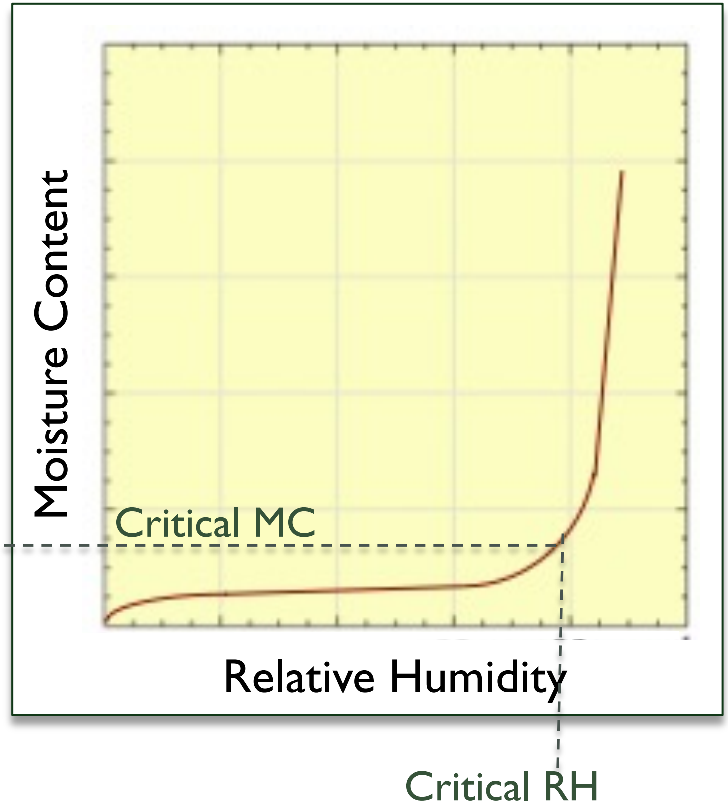
Moisture content to avoid liquid bridging

Critical RH

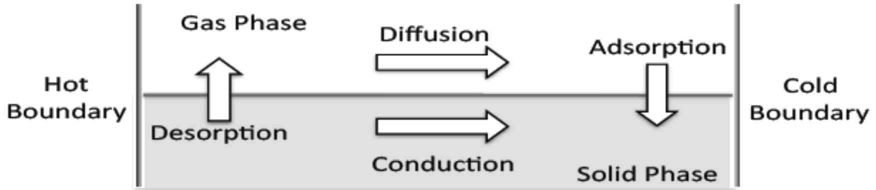
Relative humidity to prevent capillary condensation

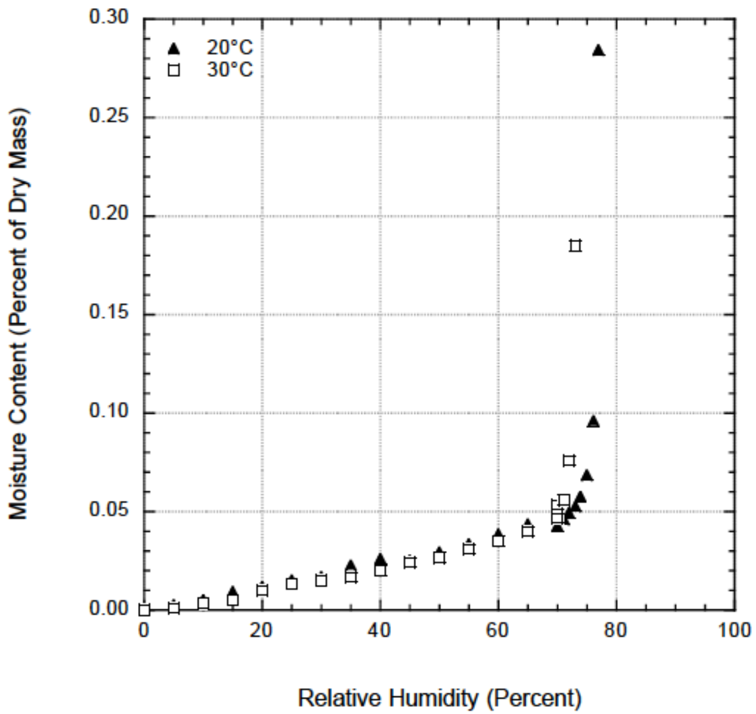
Liquid and solid bridges

- Moisture migration can lead to local regions w/ high moisture content
- If powder dries after reaching capillary state, <u>solid bridges</u> may form



Moisture migration

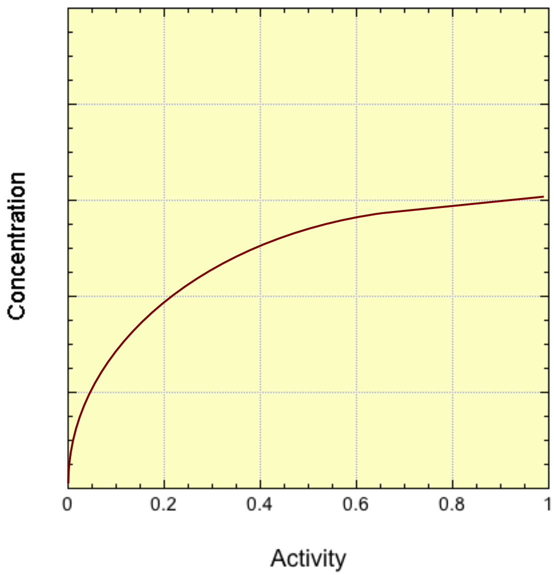




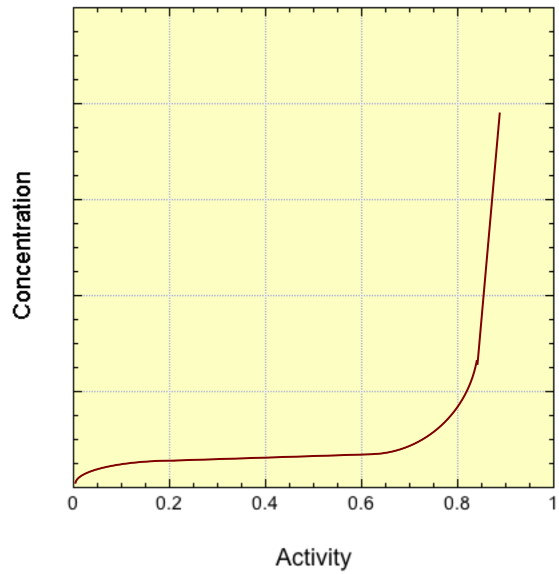
Moisture isotherms

Brunauer *et al.* (1940)

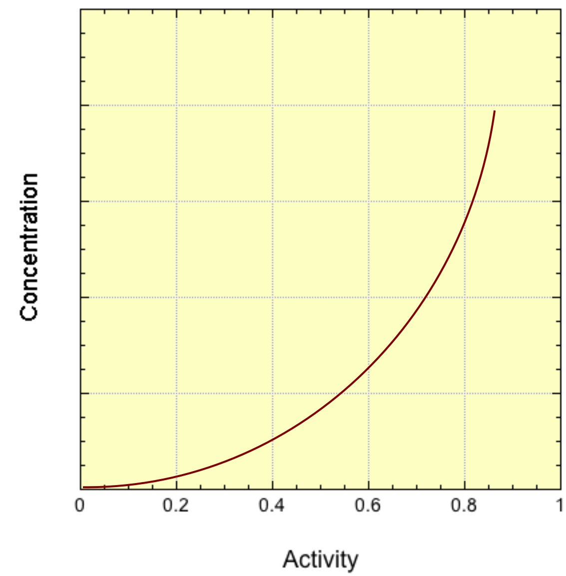
Type I



Type II



Type III



Langmuir

GAB
(Guggenheim, Anderson, and de Boer)

Flory-Huggins

Testing

- Shear cell testing
- Engineering strain
- Moisture sorption
- Inverse gas chromatography

Test program

- Develop hypothesis based on likely caking mechanisms
  - Dry solid cohesive forces
  - Liquid and solid bridges
  - Plastic creep and sintering

Test program

- Develop hypothesis based on likely caking mechanisms
  - Dry solid cohesive forces
  - Liquid and solid bridges
  - Plastic creep and sintering
- List possible independent variables that can be controlled
  - Moisture content
  - Relative humidity
  - Temperature
  - Particle size
  - Composition
  - Surface energy

Test program

- Conduct test program
  - Process control, e.g., temperature, moisture content, process variable
  - Product specification, e.g., moisture content, particle size
- Perform characterization and strength tests
  - Shear cell testing
  - Engineering strain
  - Sorption testing

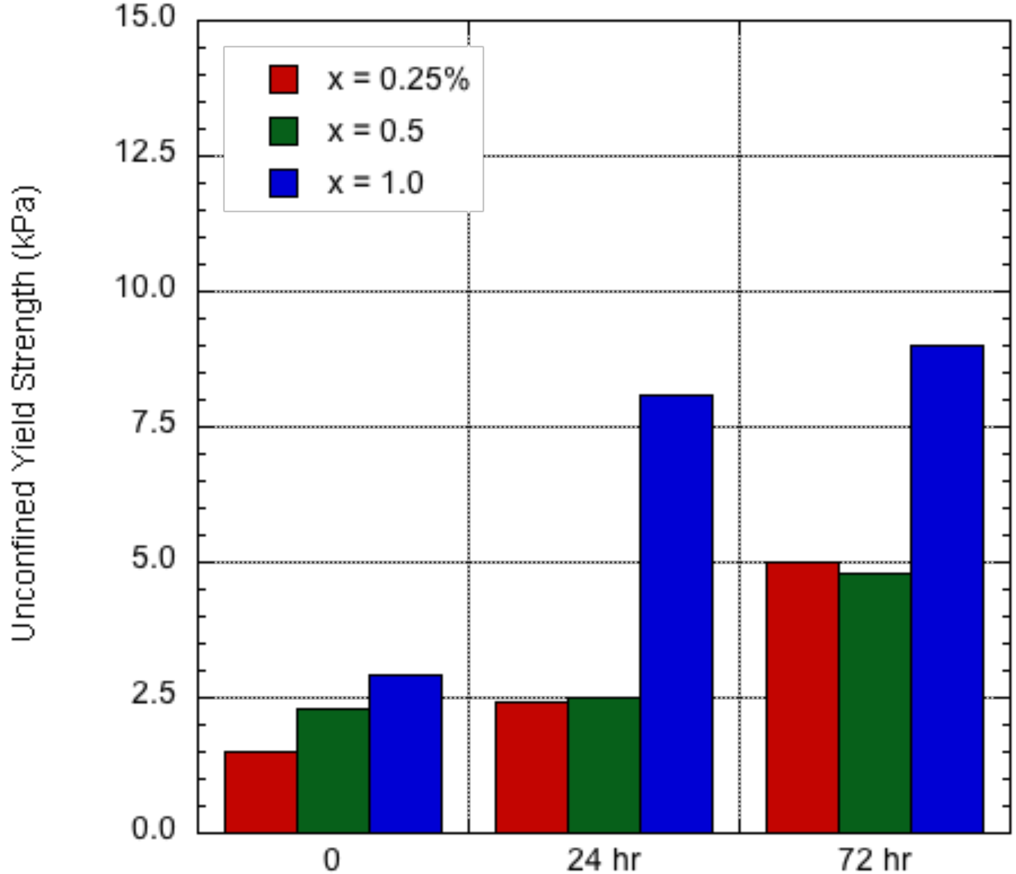
Solutions to flow problems

- Modify process
  - Operating conditions
  - Equipment
- Modify product
  - Aggressive product specs
  - Flow aid
  - Granulation
- Change storage conditions
  - Container type/size
  - Environment

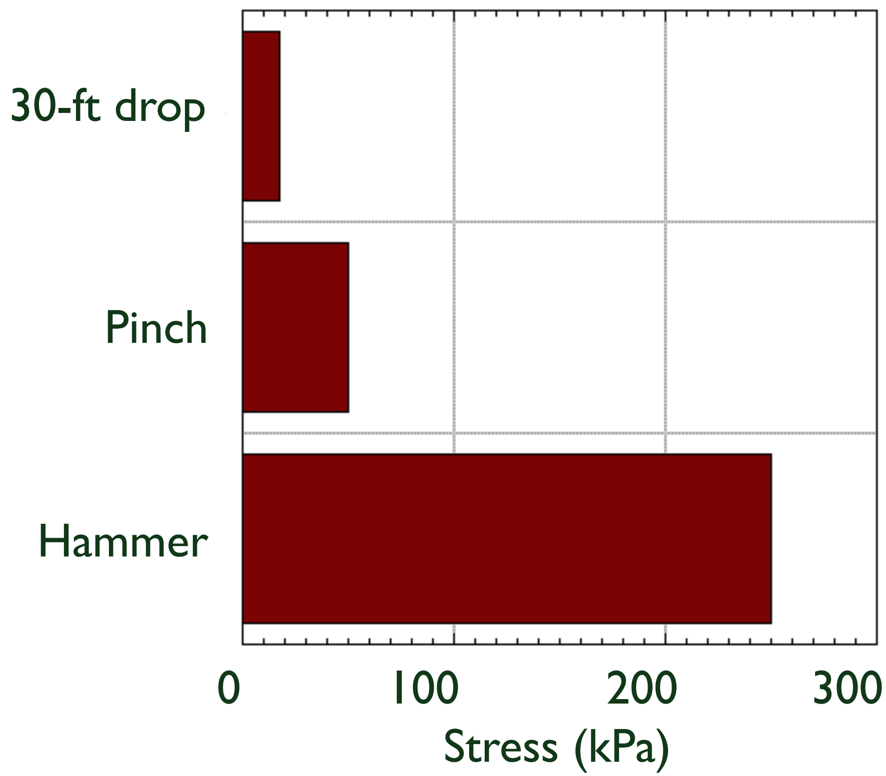
Case study

- Root cause: high moisture content
- Solution: Improve drying

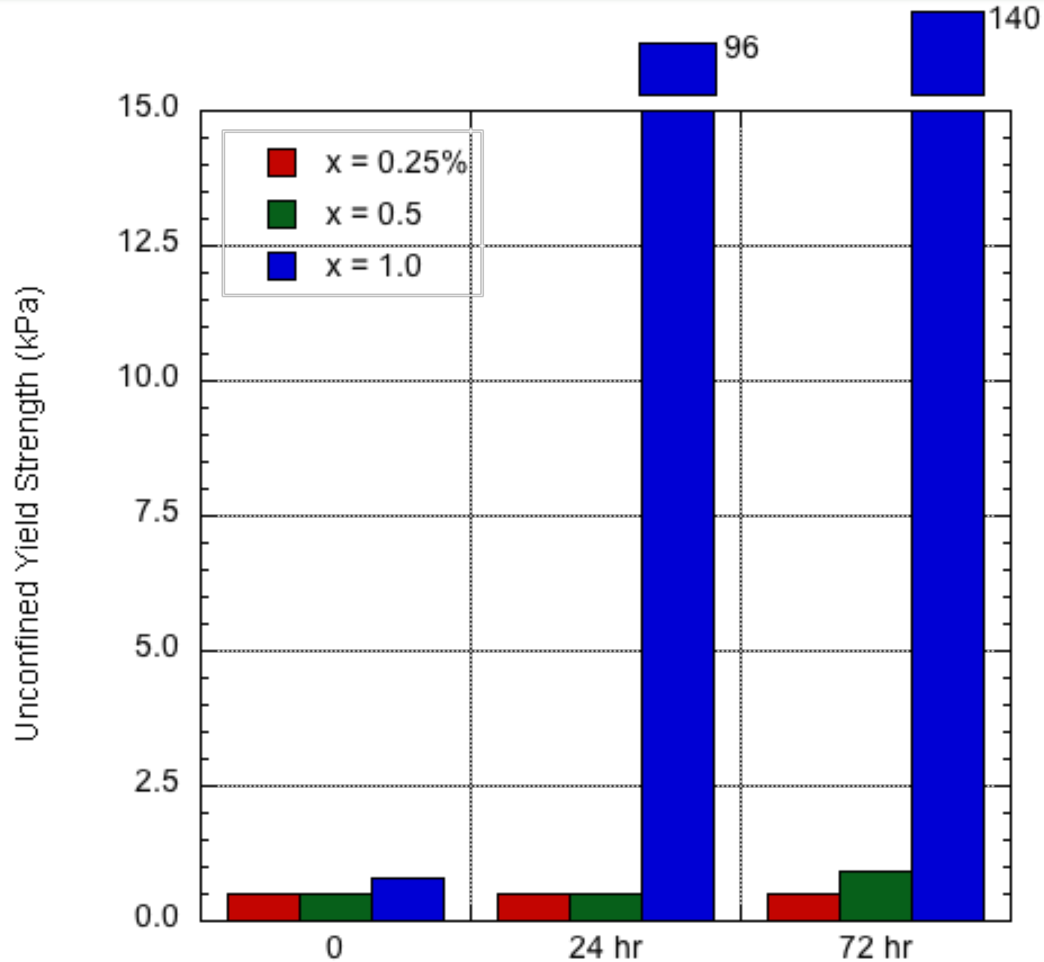
Storage conditions



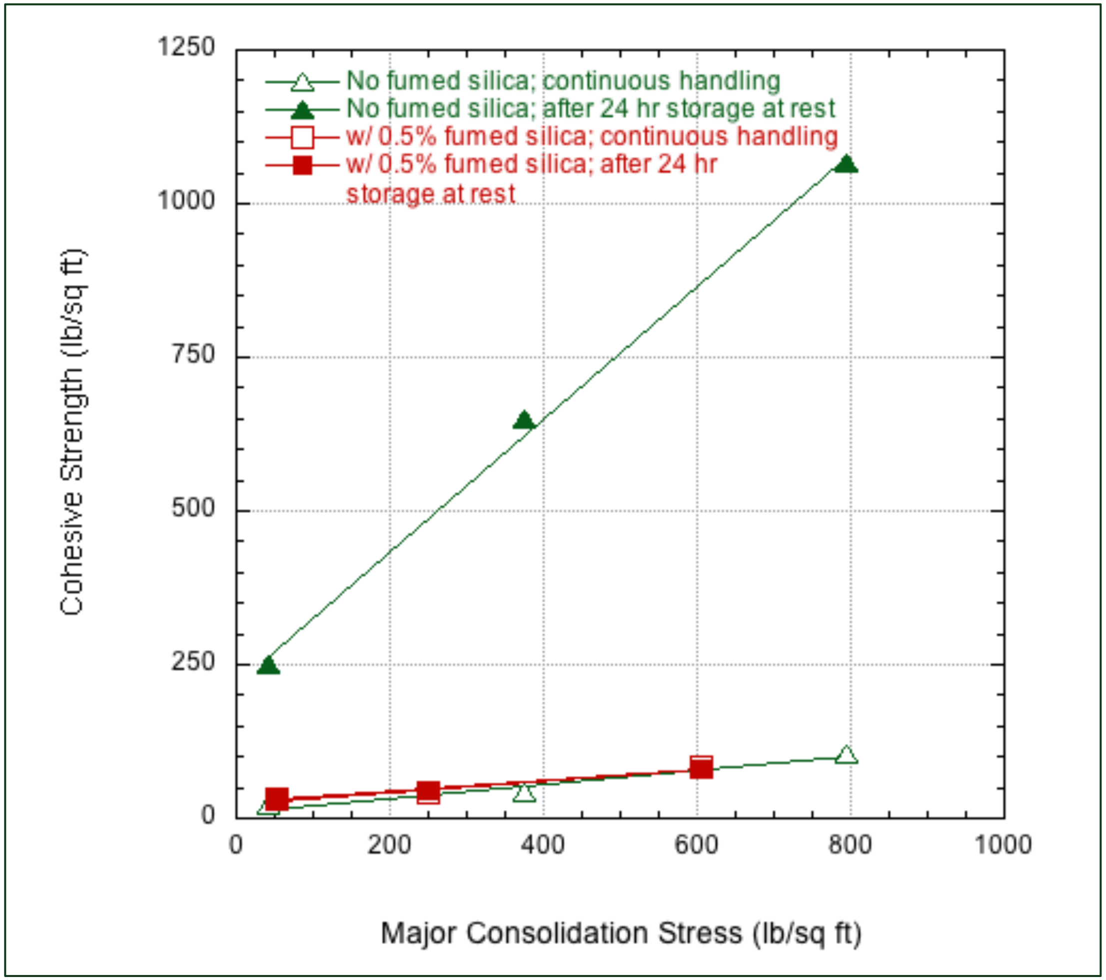
Storage conditions



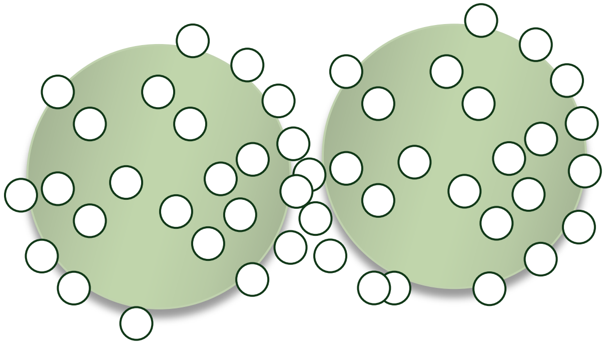
Storage conditions



Case study



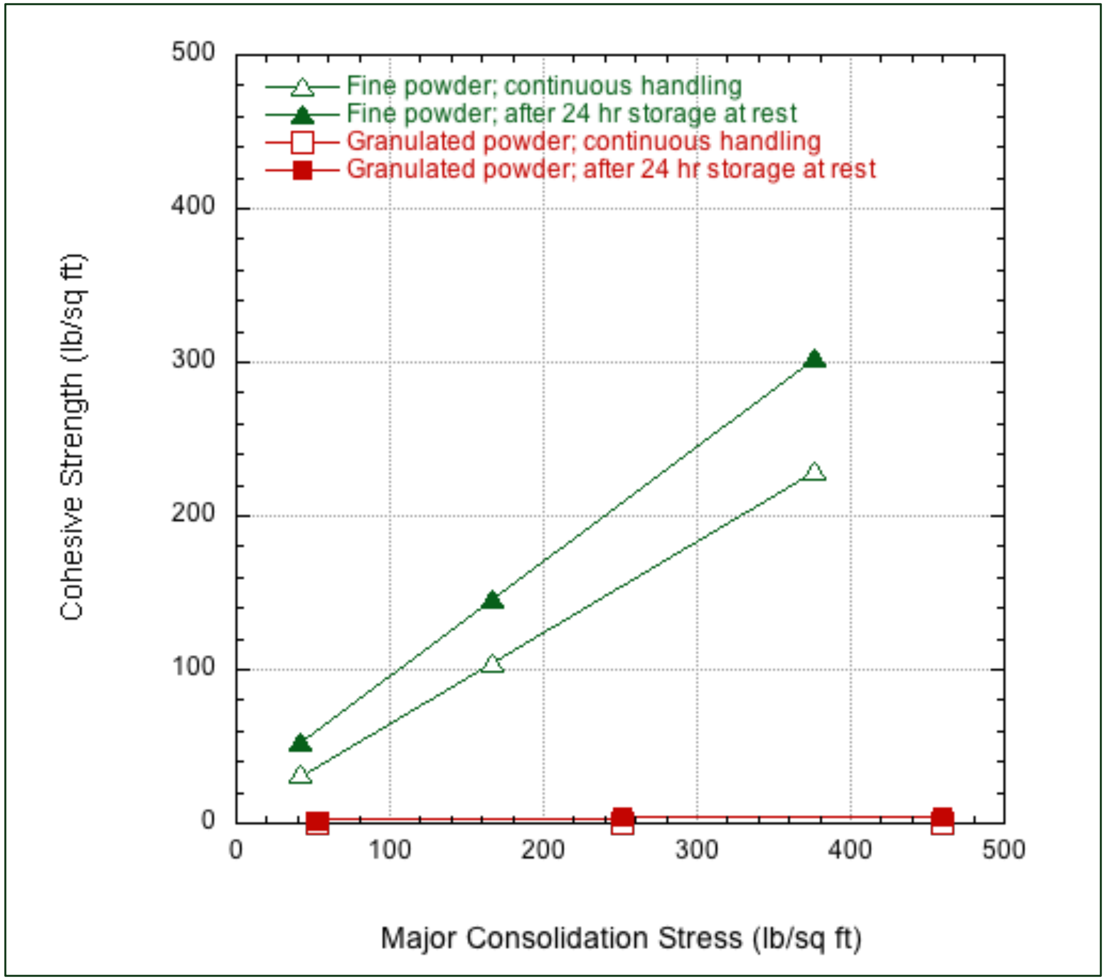
- Root cause: strong interactions between particles
- Solution: addition of flow aid



Parting agents

- Silicon dioxide
  - Fumed
  - Precipitated
- Magnesium stearate
- Calcium carbonate/stearate

Case study

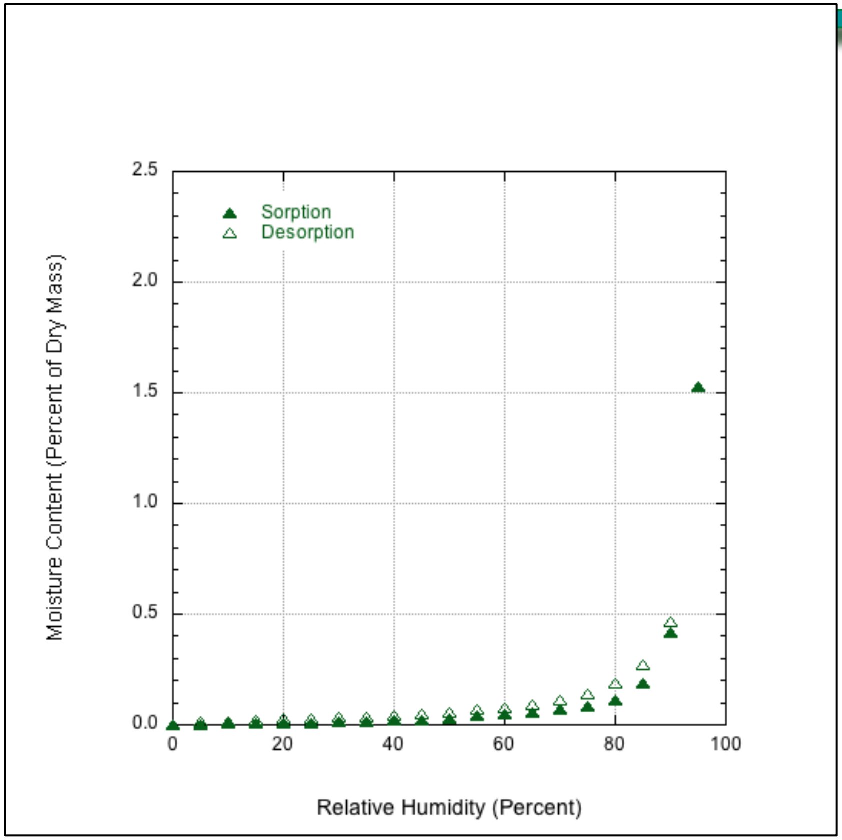


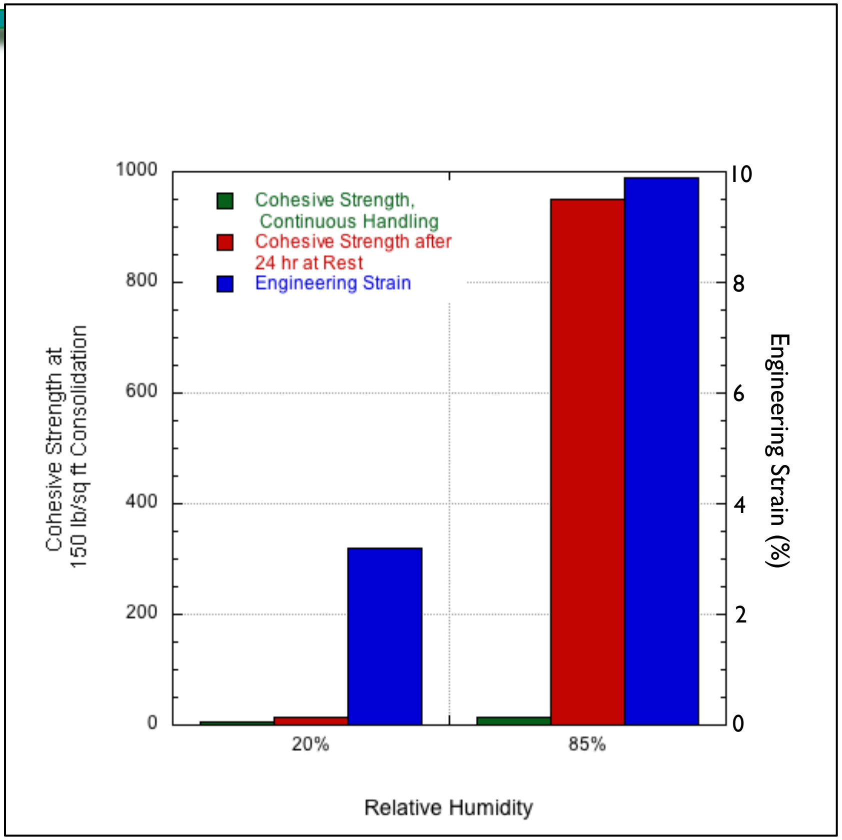
- Root cause: strong interactions between particles
- Solution: granulation

Agglomeration methods

- Pressure
  - Tableting
  - Extrusion
  - Briquetting
- Granulation
  - Pin and paddle mixers
  - Disk agglomerators
  - Rotary drums

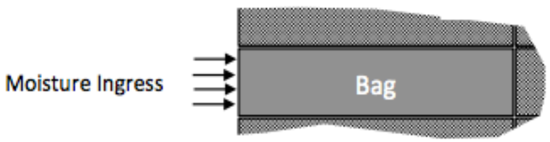
Case study

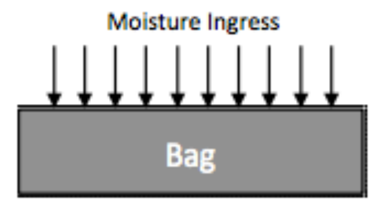




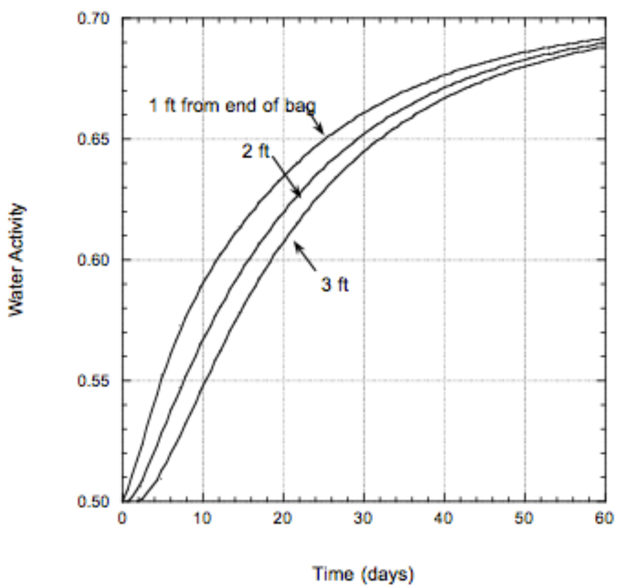
- Root cause: exposure to high relative humidity caused capillary condensation, plasticization
- Solution: reduce product moisture content; store in packages impervious to moisture

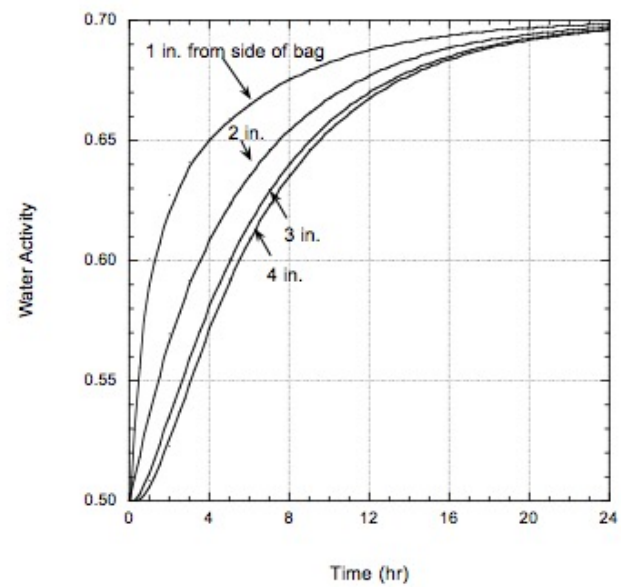
Moisture ingress



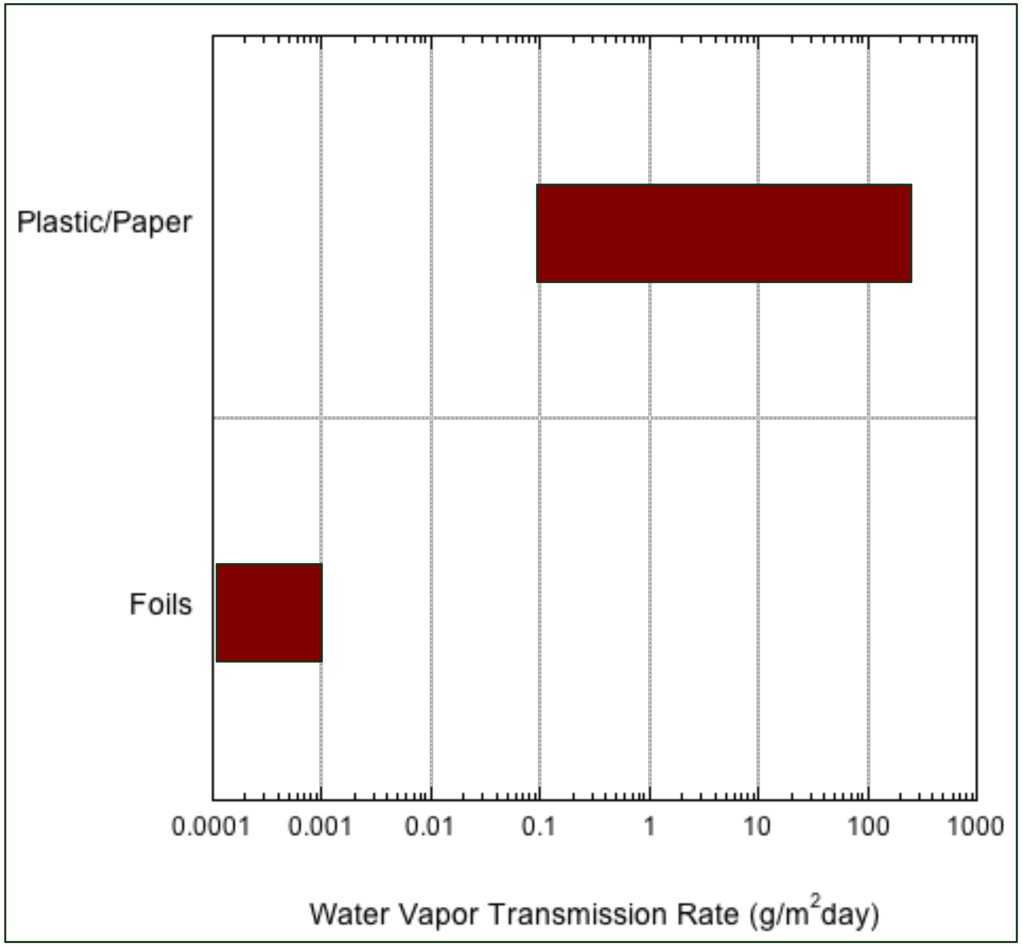


WVTR of paper/PE bag: 3.6 g/m^2day

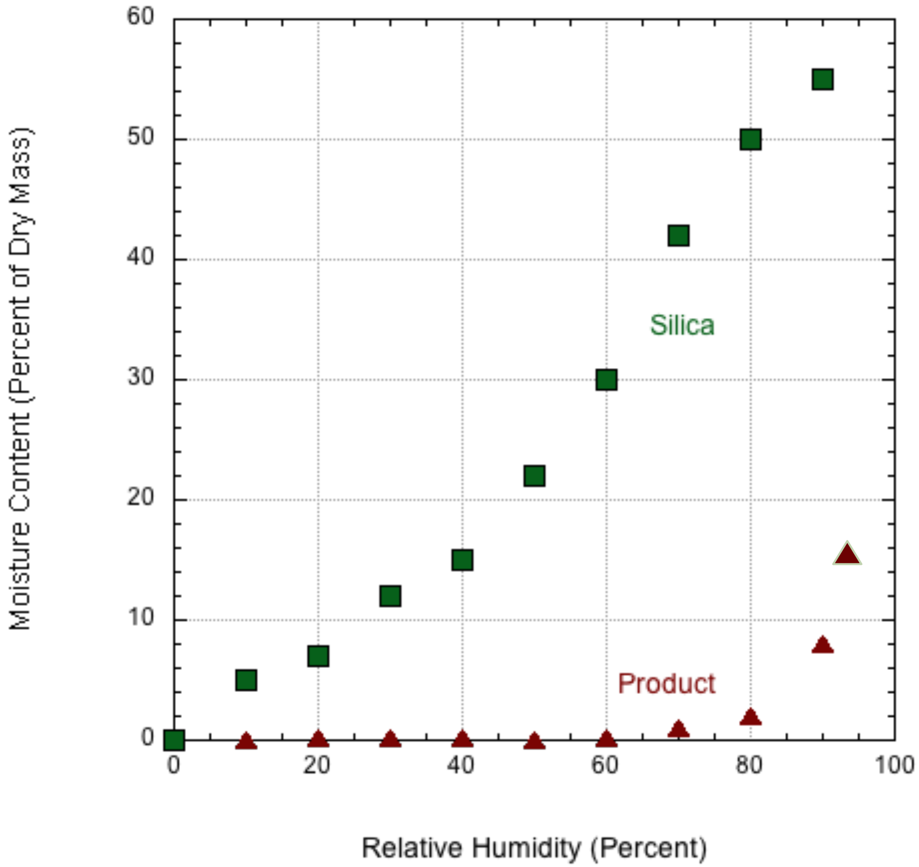




Moisture ingress



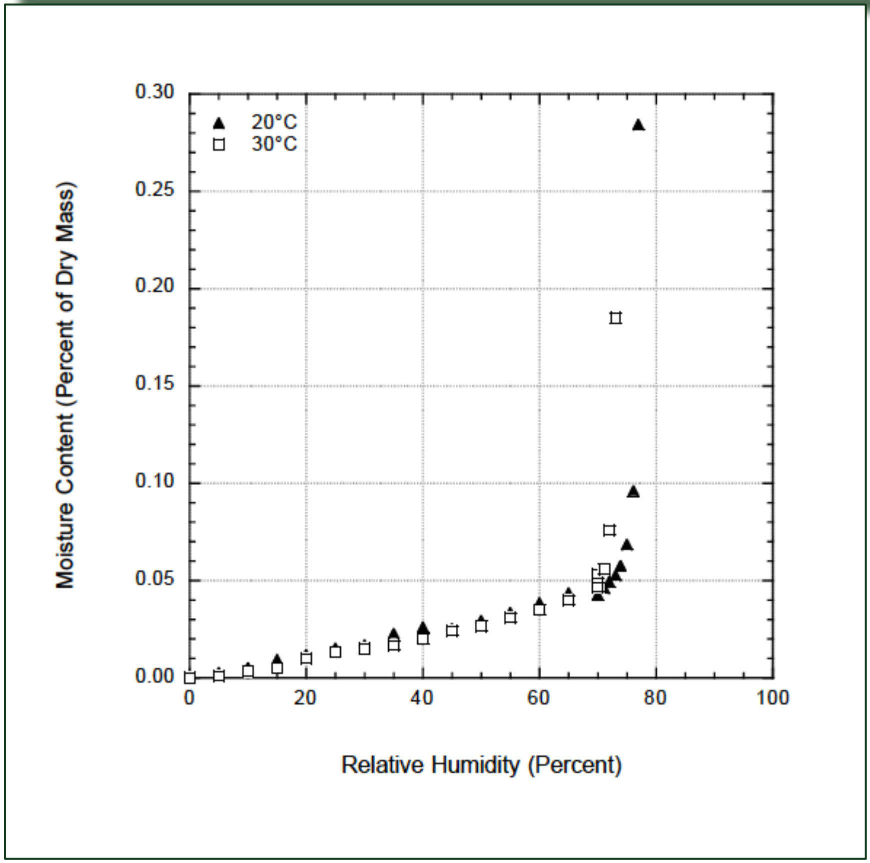
Desiccants

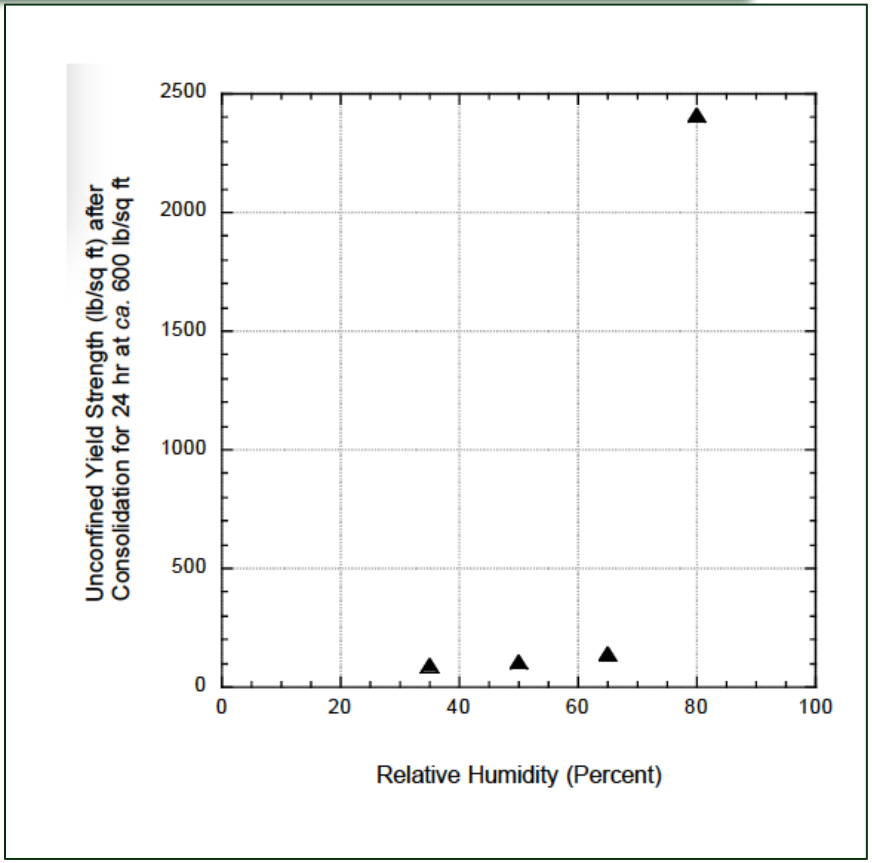


Moisture Content (Percent of Dry Mass)
60
50
40
30
20
10
0
0
20
40
60
80
100
Relative Humidity (Percent)
Silica
Product

Dessiccants

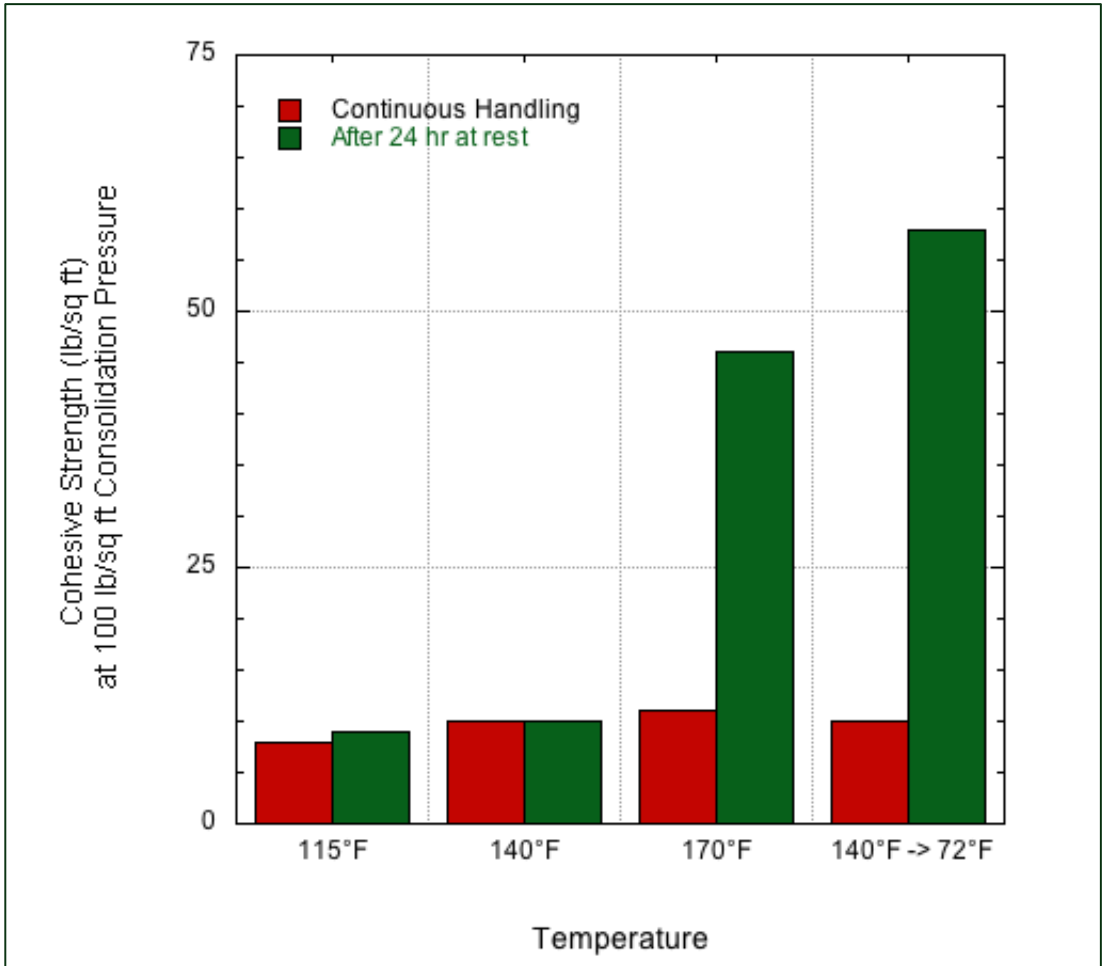
Case study





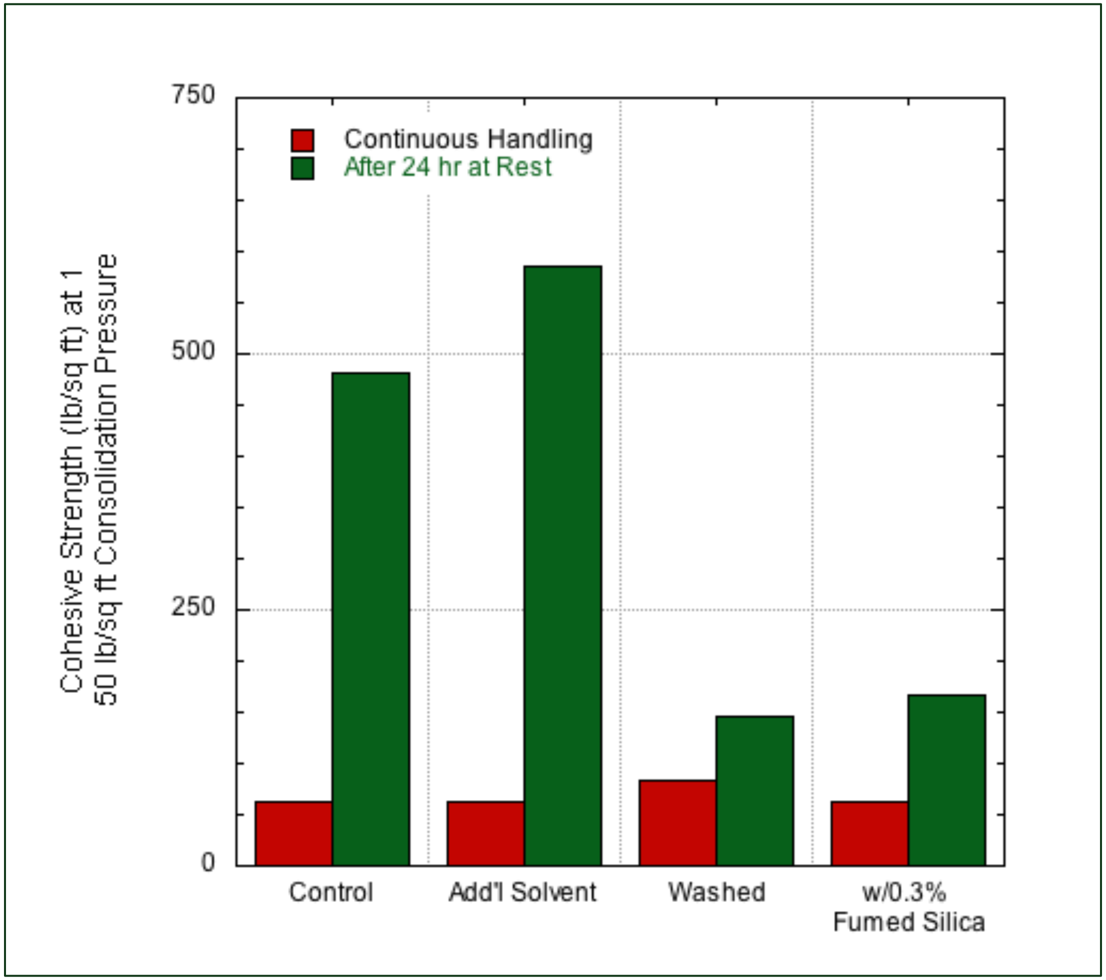
- Root cause: caking still occurs when moisture content is very low
- Solution: target *water activity* instead of moisture content

Case study



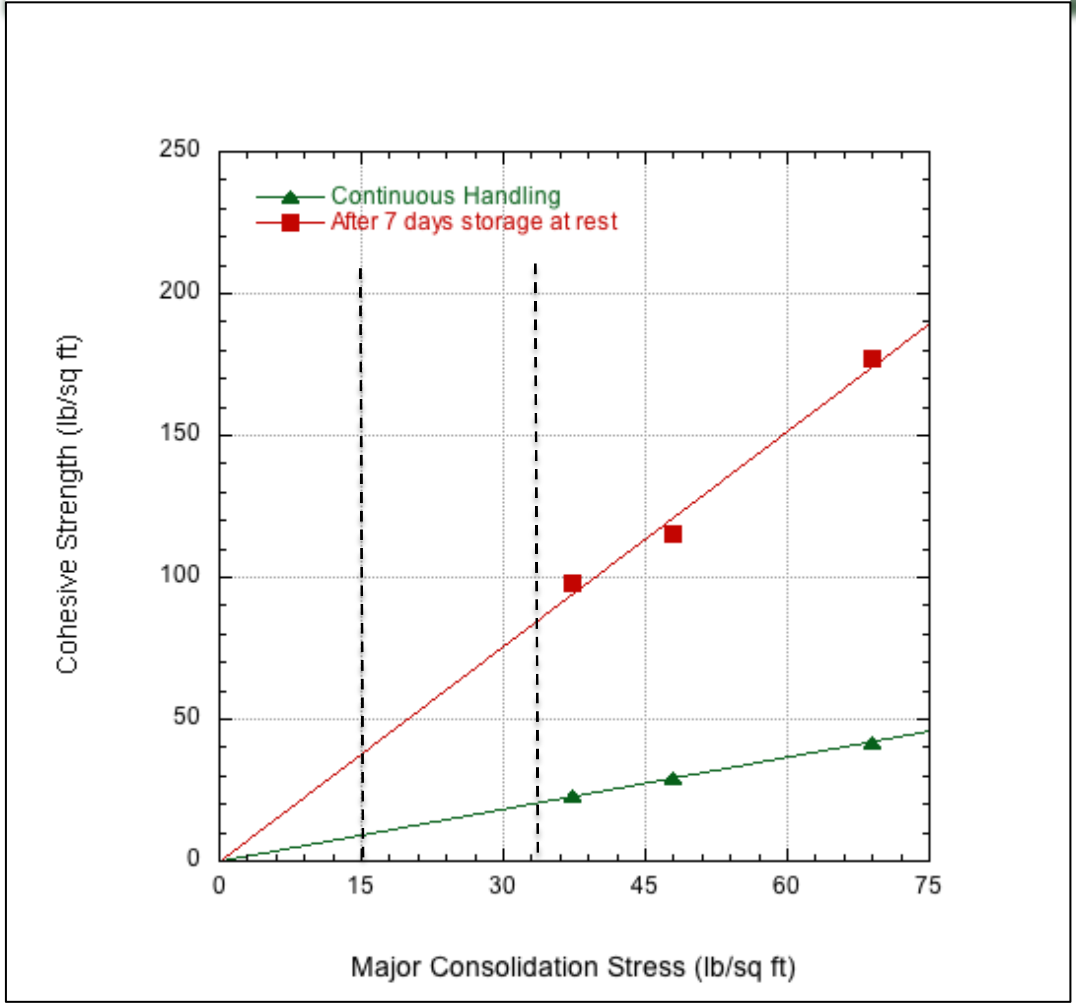
- Root cause: temperature above Tg caused plastic creep, annealing
- Recommended solution: install cooler downstream of extruder

Case study



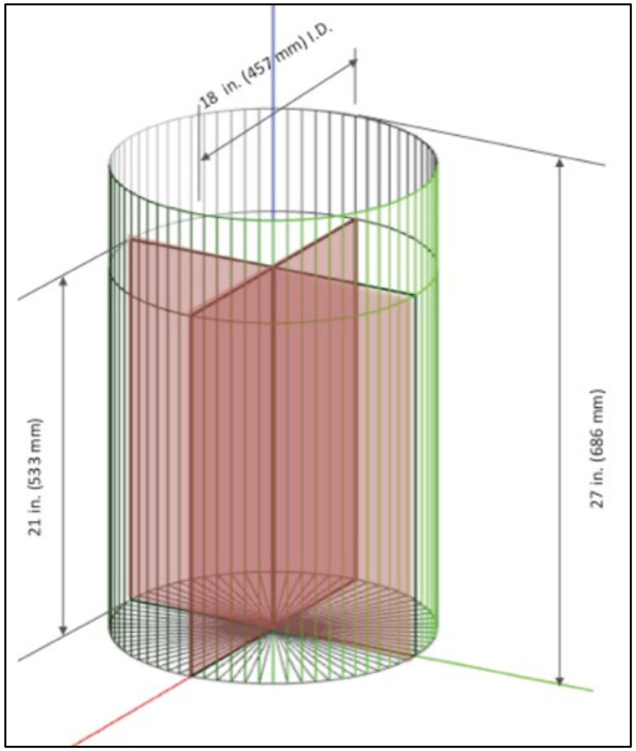
- Root cause: impurities had strong interactions
- Solution: install washing step or add flow aid

Case study

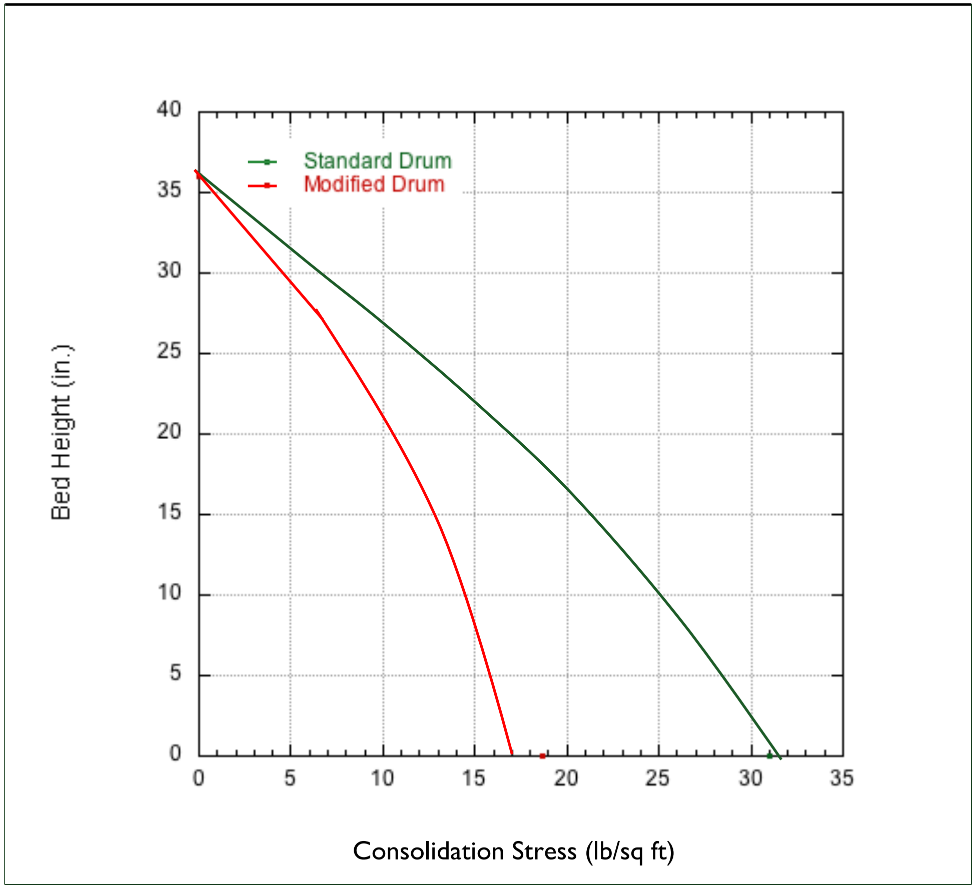


- Root cause: consolidation in drums results in caking
- Recommended remedy: modify packaging to reduce solids stress

Packaging

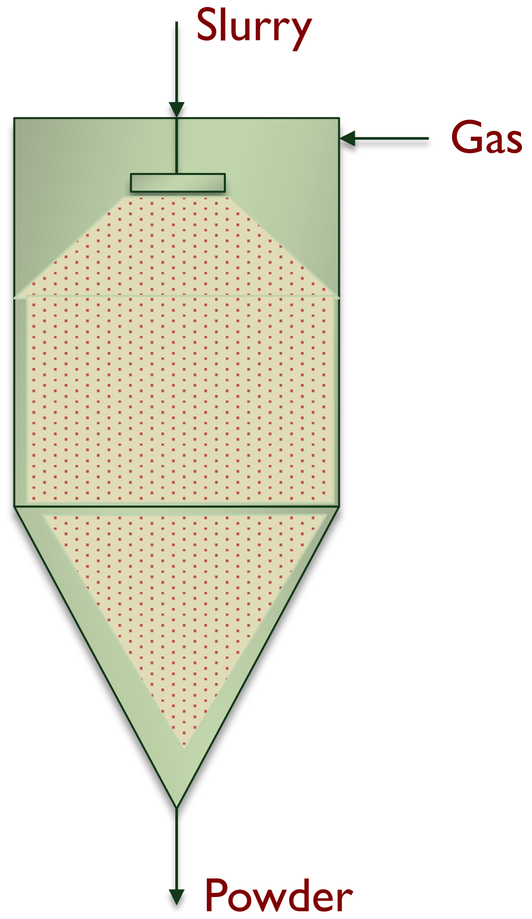


18 in. (457 mm) I.D.
21 in. (533 mm)
27 in. (686 mm)



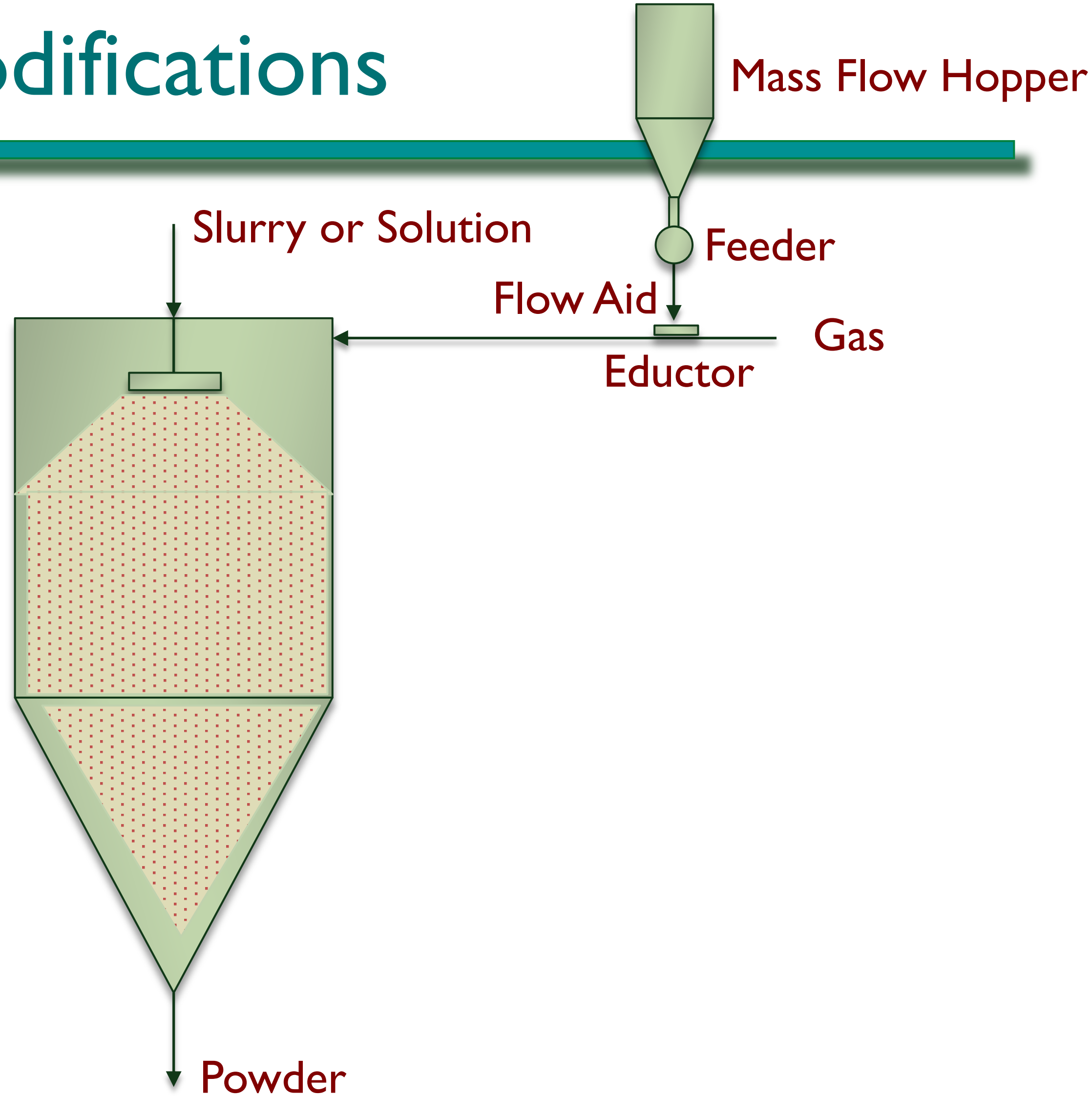
Standard Drum
Modified Drum
Bed Height (in.)
Consolidation Stress (lb/sq ft)
0
5
10
15
20
25
30
35
40

Case study

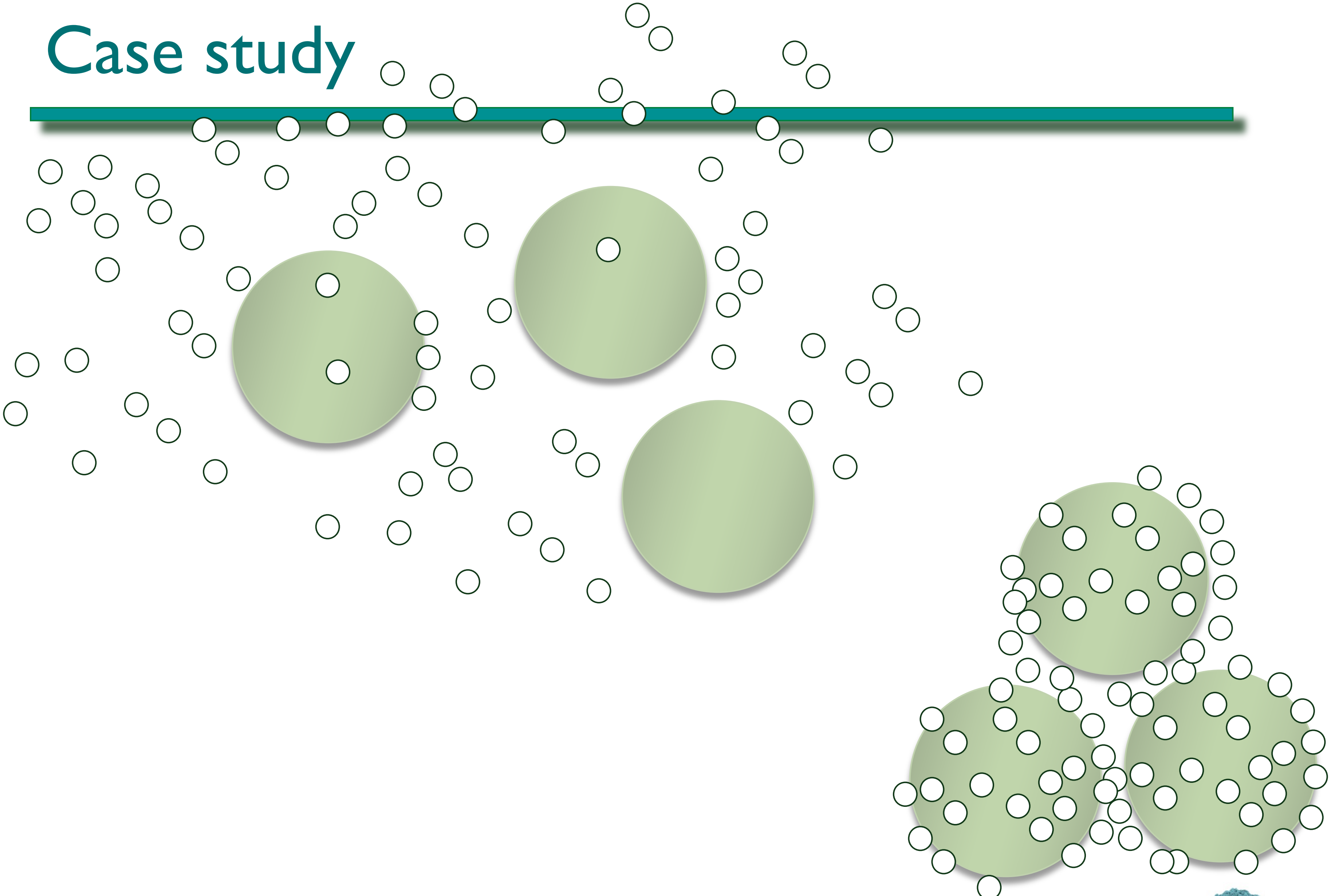


- Root cause: flow aid unavailable to act as parting agent
- Modified flow aid introduction

Spray dryer modifications

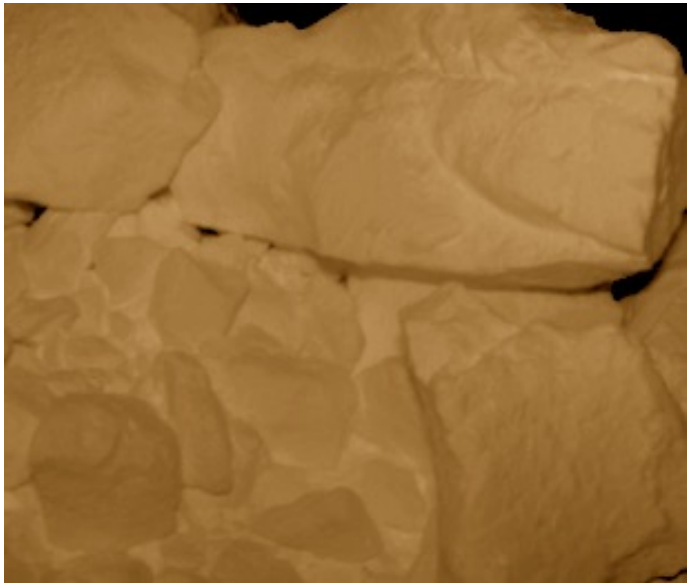


Case study



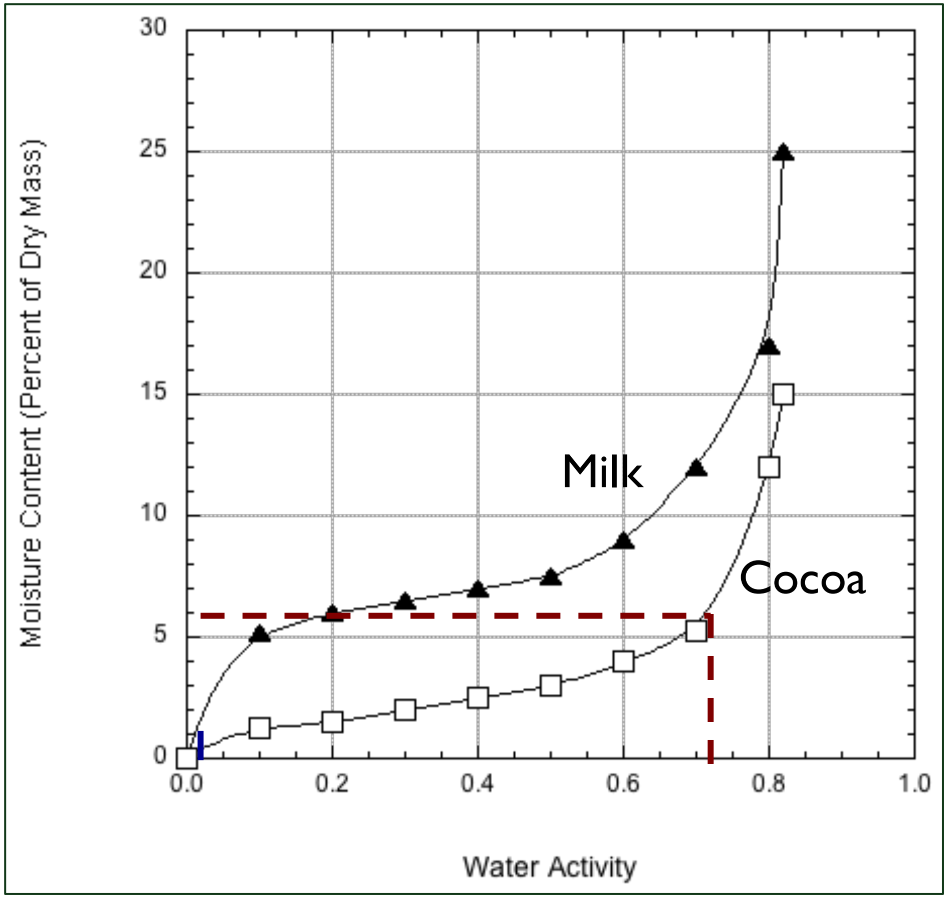
Case study

Re-worked blend does not cake

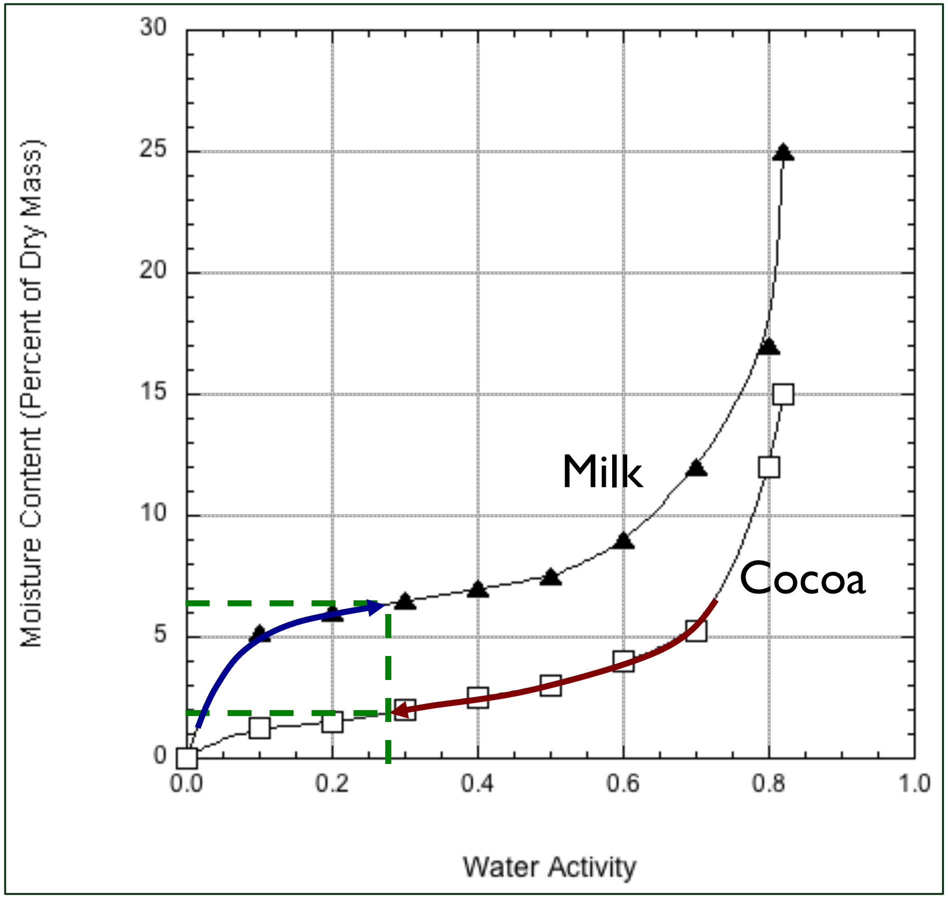


- Root cause: moisture migration after blending
- Pre-dry one component

Moisture migration



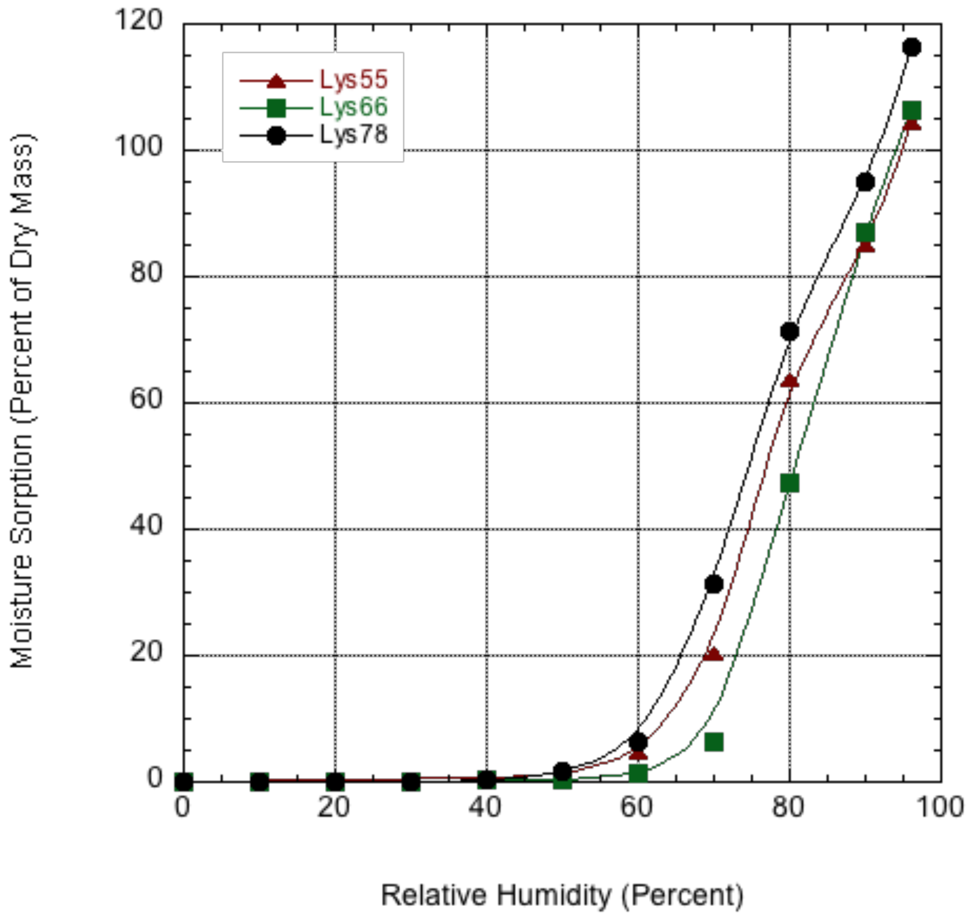
Moisture migration



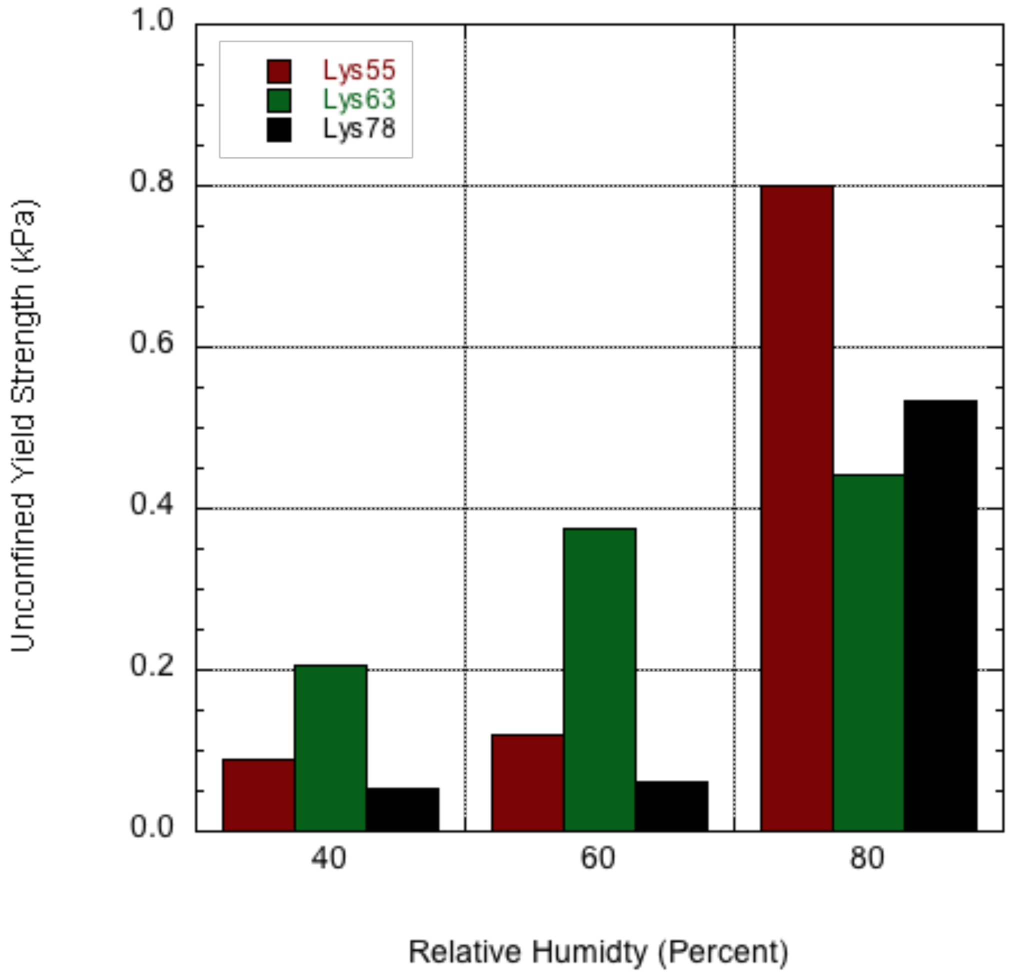
L-Lysene

- Lys65
- Lys55 - Lys65 + additives
- Lys78 – alternative process

Sorption test results

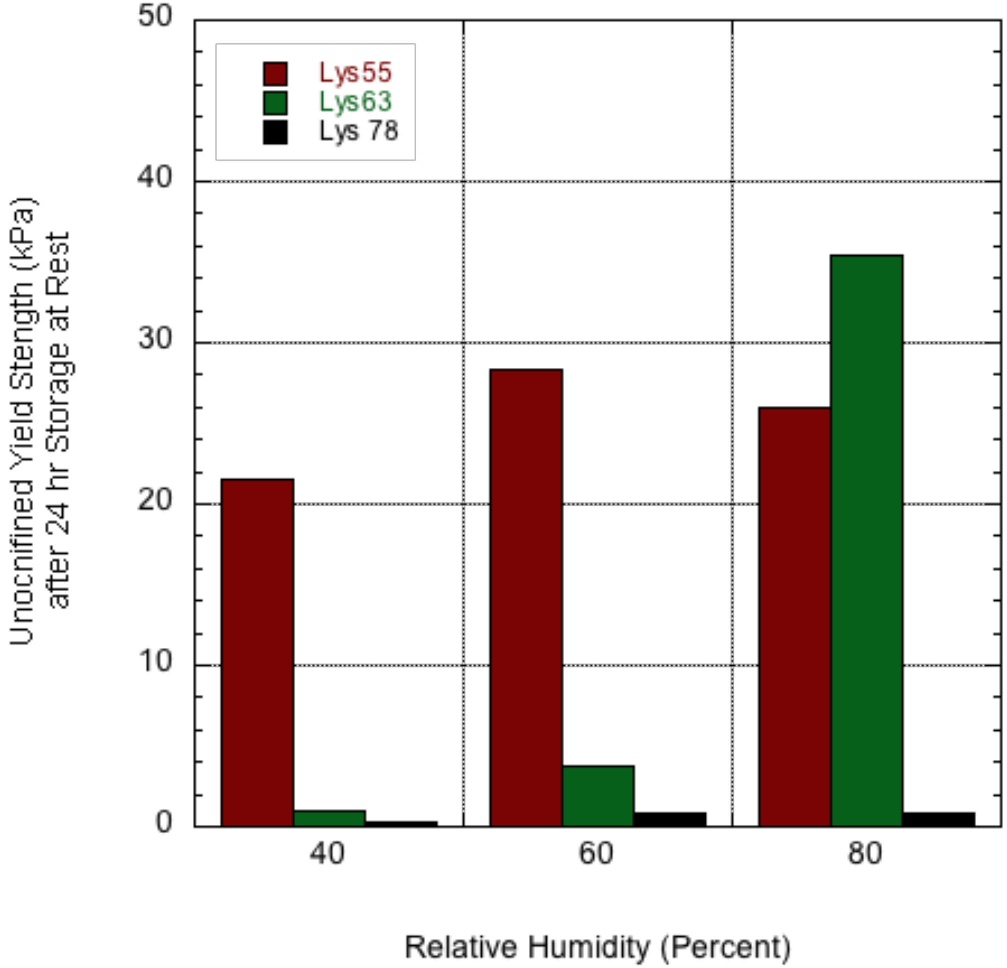


Shear cell test results



Continuous Handling

Shear cell test results



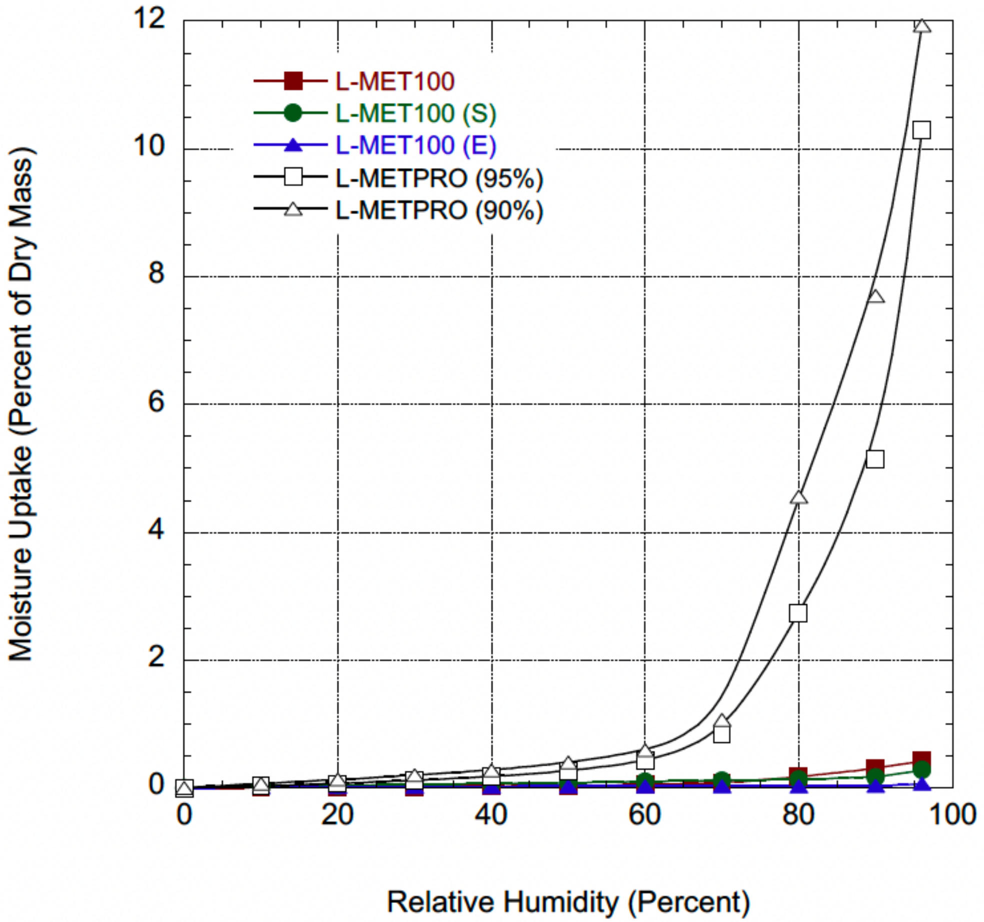
After 24 hr Storage at Rest

GM&A

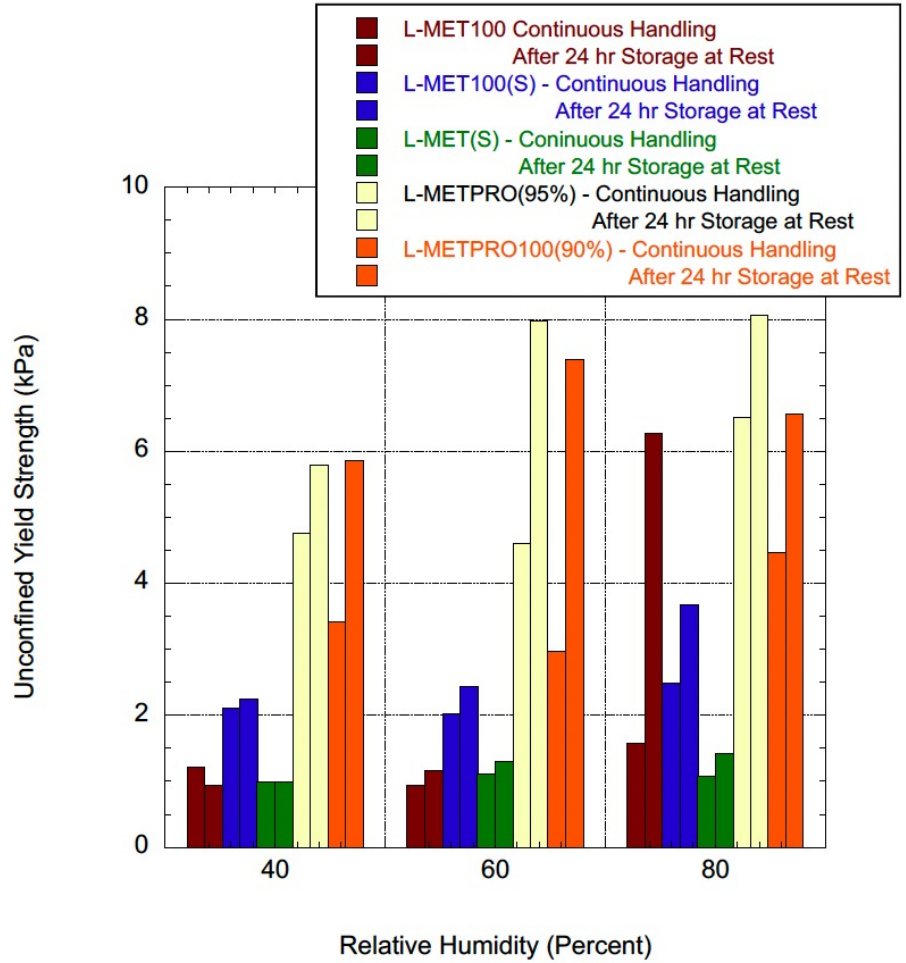
Competitive materials

- MET100
- MET100(S)
- MET100(E)
- METPRO(95%)
- METPRO(90%)

Sorption test results

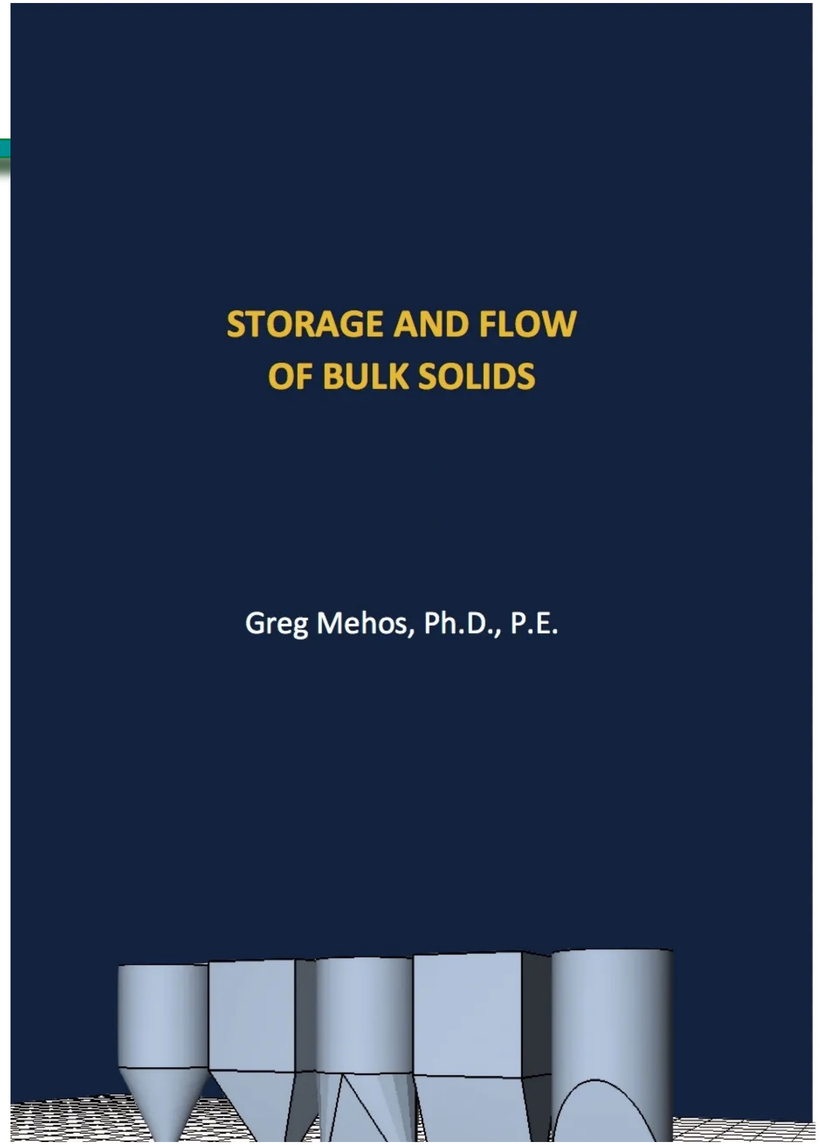


Shear cell test results



Summary

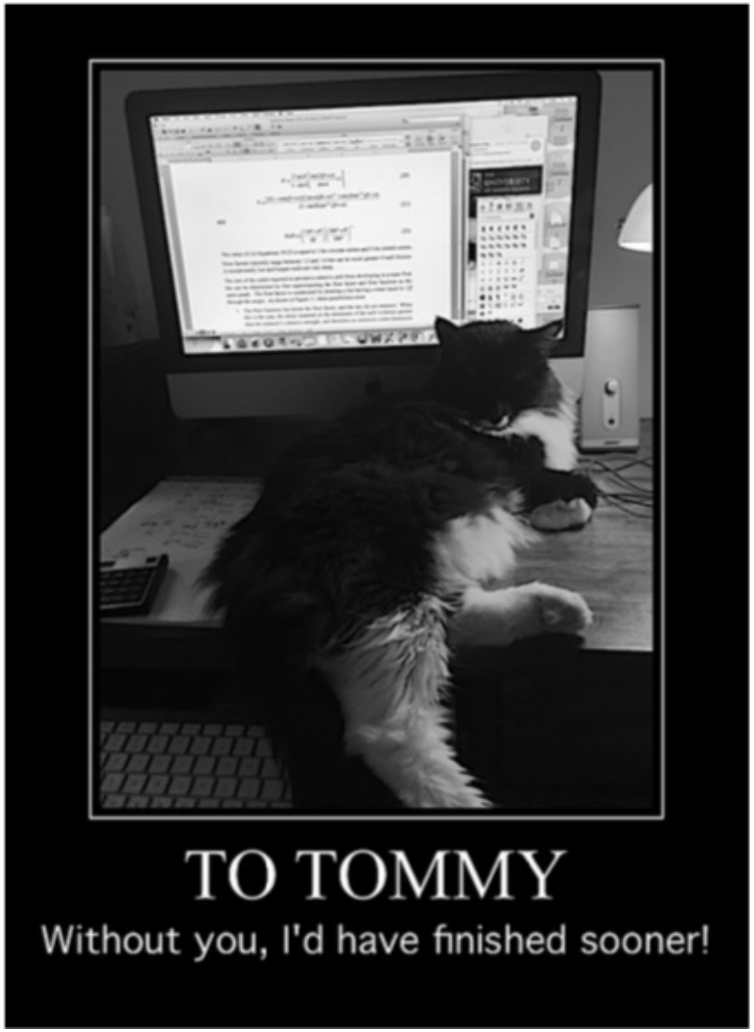
- Mechanisms
  - Dry solid cohesive forces
  - Liquid forces and solid bridges
  - Plastic creep and sintering
- Solutions
  - Measure cohesive strength (under conditions that simulate storage at rest under consolidation) to determine root cause of caking
  - Identify key process control variables
  - Control process (e.g., set process set points or product specifications) or environment (e.g., RH, packaging) or modify product (e.g., granulate, add flow-aid)


STORAGE AND FLOW
OF BULK SOLIDS
Greg Mehos, Ph.D., P.E.

www.mehos.net/downloads

URI Notes

Password: Tommy



9. BETTER REFERENCES THAN THIS ONE

1. Arnold, P., A. Roberts, and A. McLean, Bulk Solids: Storage, Flow, and Handling, TUNRA, Newcastle, Australia, 1978.
2. Bates, L., User Guide to Segregation, British Materials Handling Board, Marlow, England, 1997.
3. Bates, L., Guide to the Design, Selection, and Application of Screw Feeders, Cromwell Press, Trowbridge, England, 2000.
4. Fayed, M. and L. Otten, Handbook of Powder Science and Technology, Van Nostrand Reinhold Company, New York, 1997.
5. Jenike, A., Storage and Flow of Solids – Bulletin 123, University of Utah, Salt Lake City, Utah, 1964.
6. Kulwiec, R., Materials Handling Handbook, John Wiley and Sons, Hoboken, NJ, 1985.
7. McGlinchey, Bulk Solids Characterization, Blackwell Publishing Co., Carlton, Victoria Australia, 2005.
8. McGlinchey, Bulk Solids Handling – Equipment Selection and Operation, Blackwell Publishing Company, Ames, IA, 2008.
9. Rhodes, M. Introduction to Particle Technology, John Wiley and Sons, Hoboken, NJ, 2008.
10. Schulze, D., Powders and Bulk Solids: Behavior, Characterization, Storage and Flow, Springer, Berlin, 2008.
11. Shamiou, P., Handling of Bulk Solids – Theory and Practice, Butterworths, London, 1990.
12. Woodcock, C. and J. Mason, Bulk Solids Handling: An Introduction to the Practice and Technology, Springer Science, New York, 1987.