THE ROLE OF SILICA IN SEPARATOR TECHNOLOGY

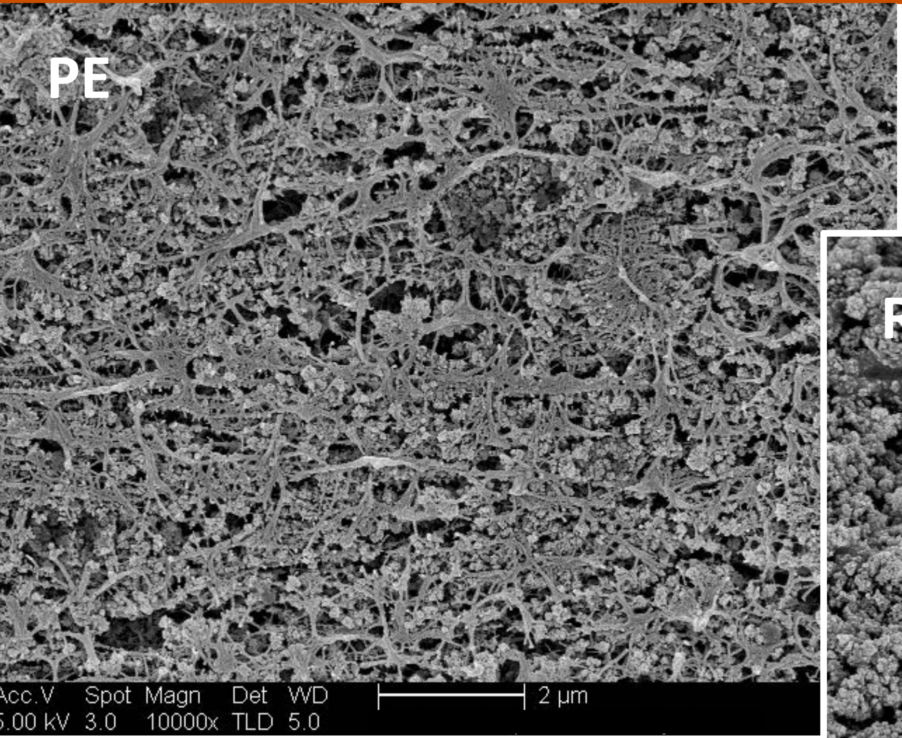
M. Kawachi, M. Onishi, M. Takuo, M. Platz, J. Moore, A. Brown, D. Merritt,
S. Downes, E. Hostetler, C. Rogers, C. La, R. Waterhouse, and R.W. Pekala

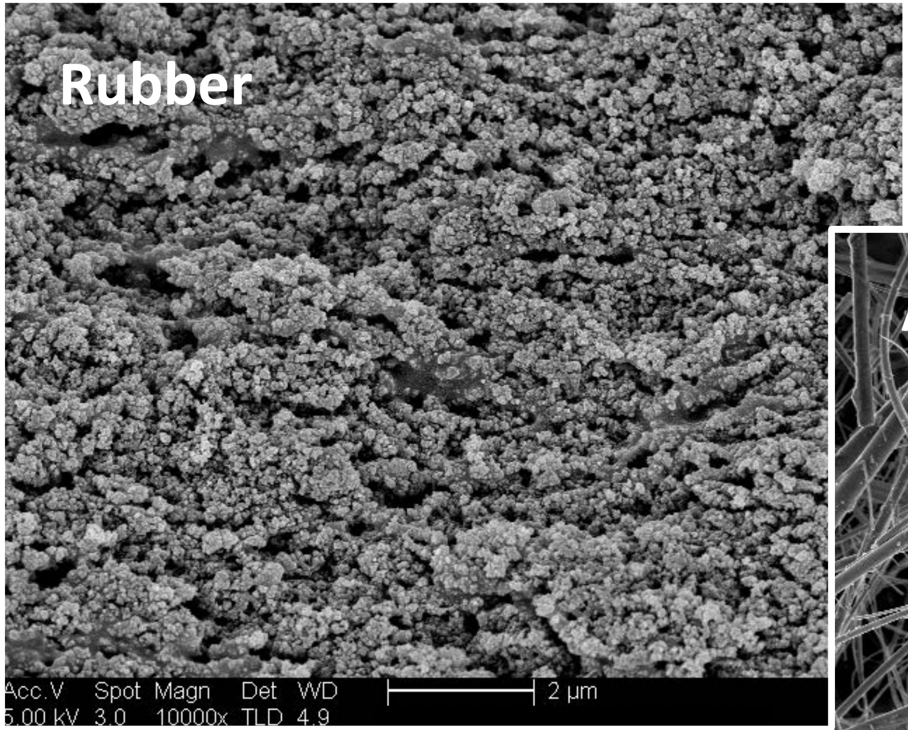
ENTEK International LLC • ENTEK International LTD. • ENTEK Asia International

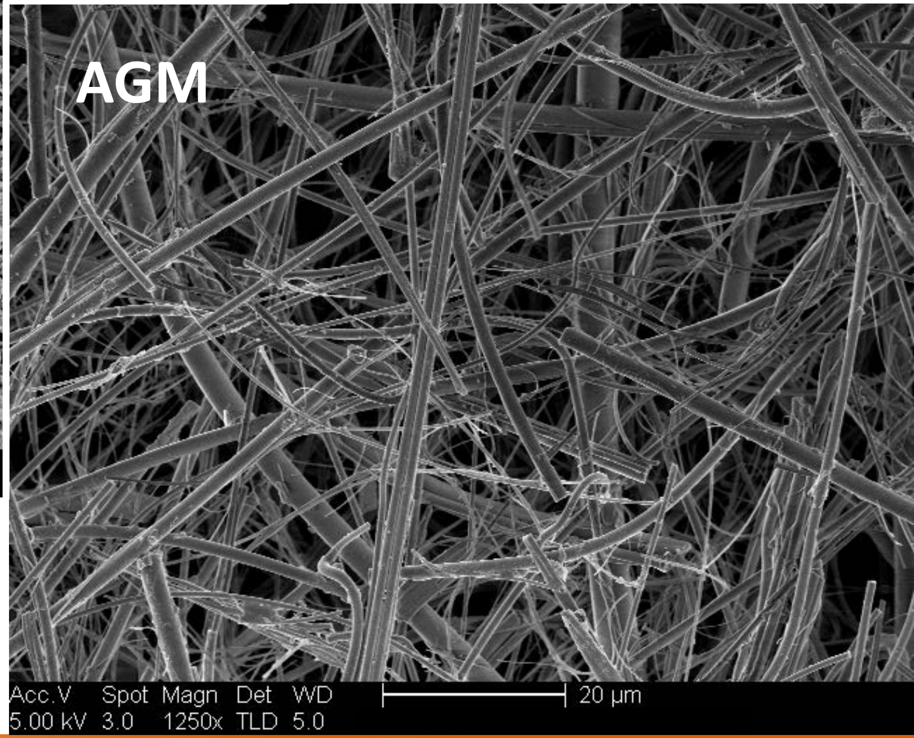
ELBC
6–9 September
Lyon, France 2022

September 8, 2022

COMMON PB-ACID SEPARATORS



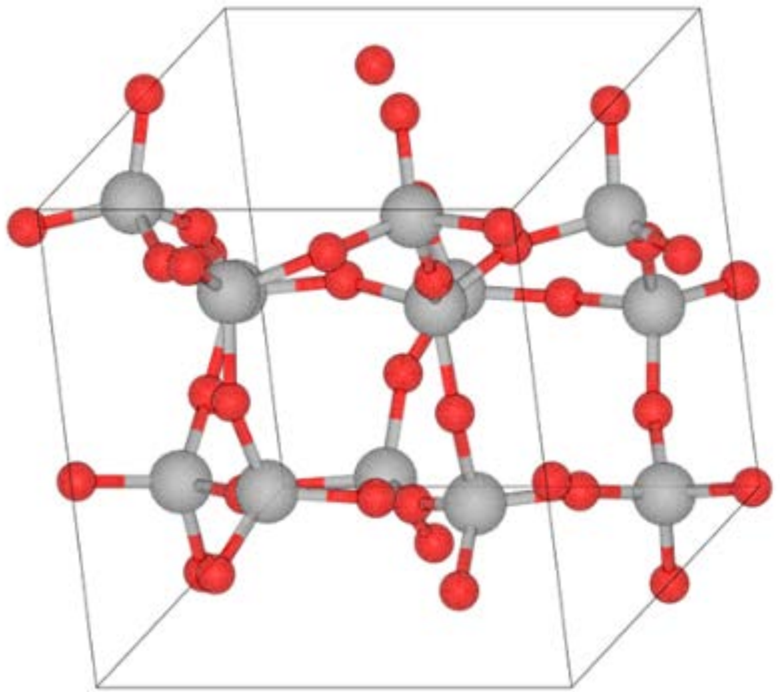




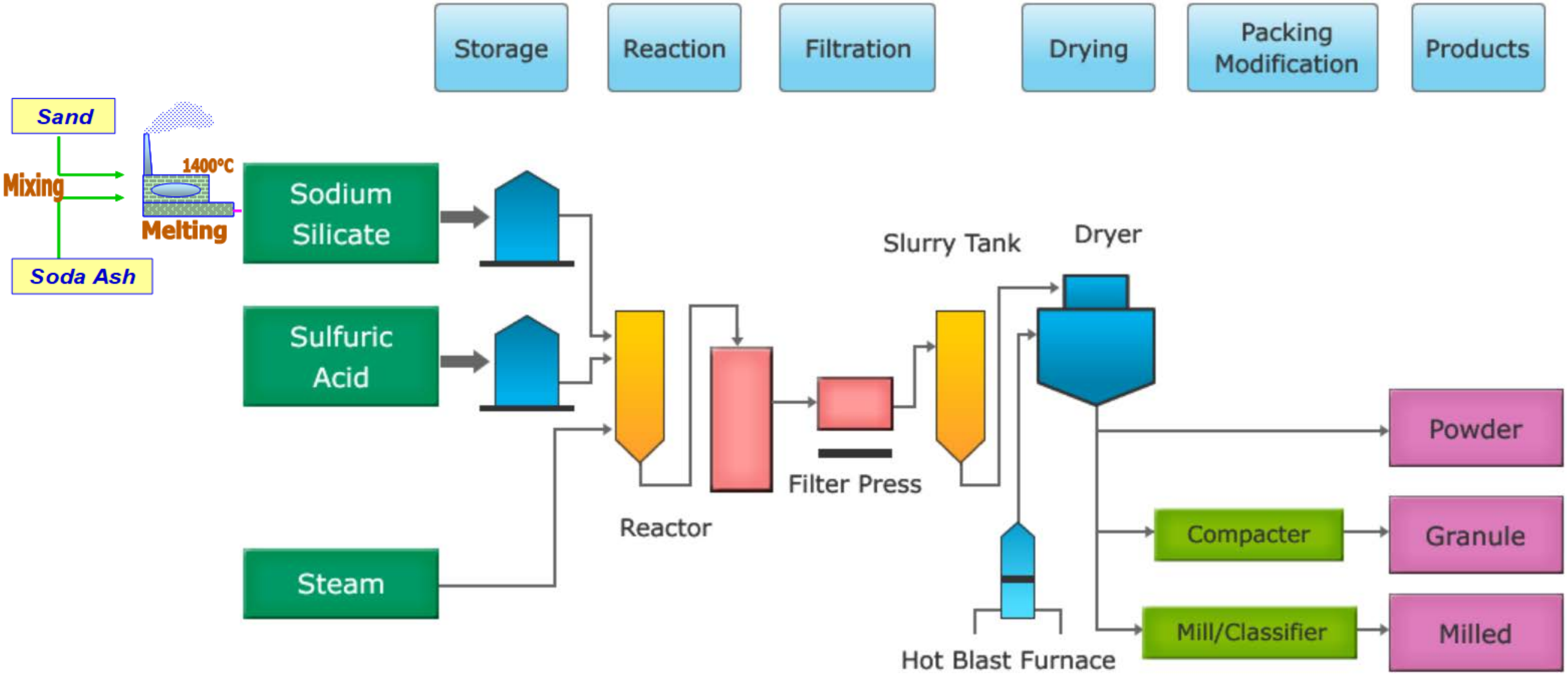
The terms -- "PE" and "Rubber" separators -- are misnomers since each contain large percentages of precipitated silica

SILICA FACTS

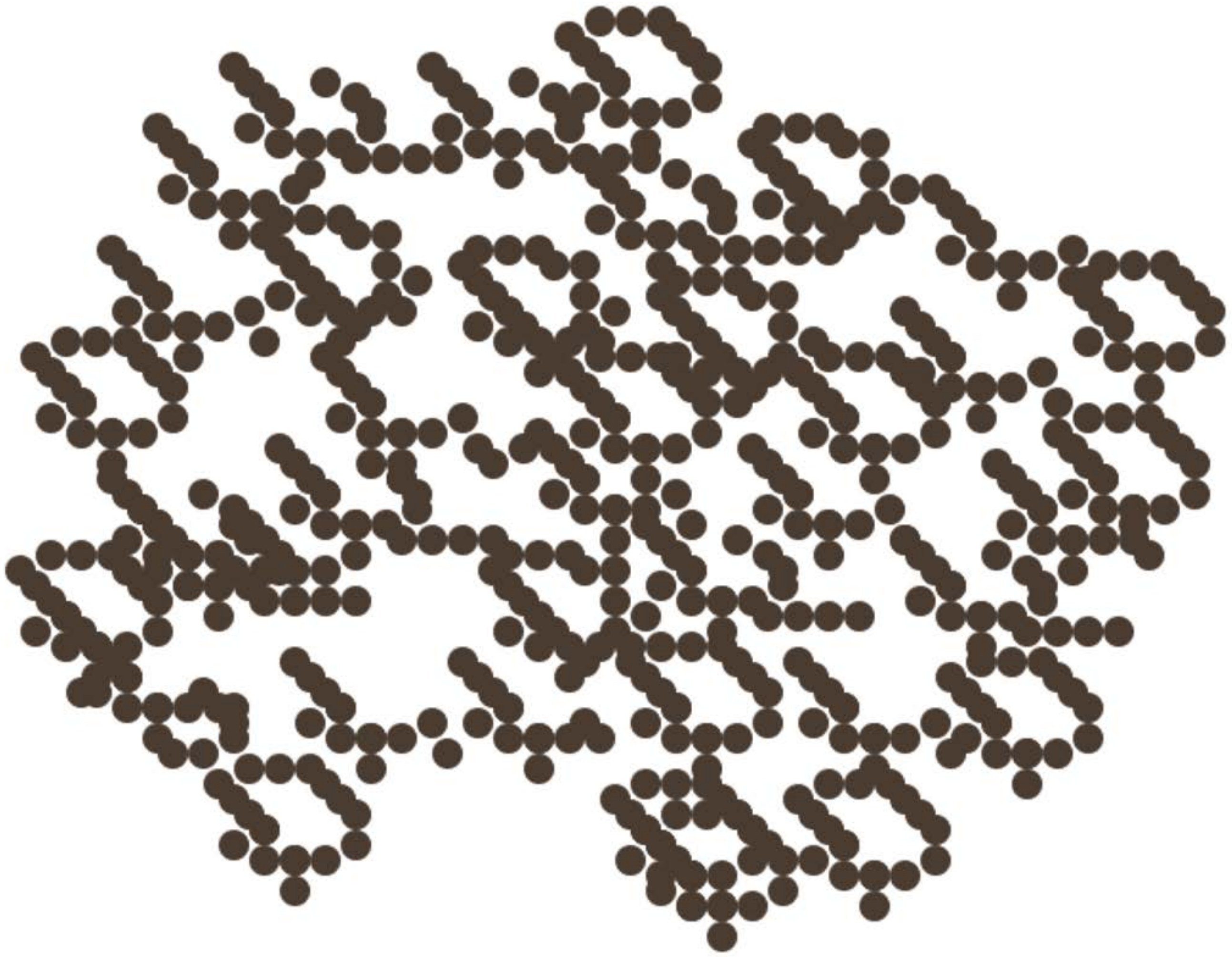
- Silica or silicon dioxide is one of the most common materials in the earth's crust
- Silica exhibits tetrahedral coordination between 1 silicon atom and 4 oxygen atoms
- Silica occurs in both ***crystalline*** and ***amorphous*** forms
- Crystalline forms of silica include ***quartz***, tridymite, and cristobalite
- Quartz is a raw material input for the production of glass fiber used in absorptive glass mat
- Amorphous silicas are generally produced in either a "wet" or thermal synthetic process
- The "wet" process is used for the production of ***precipitated silica*** and the thermal process is used to manufacture ***fumed silica***
- Precipitated silica is most commonly used in Pb-acid battery separators



PRECIPITATED SILICA

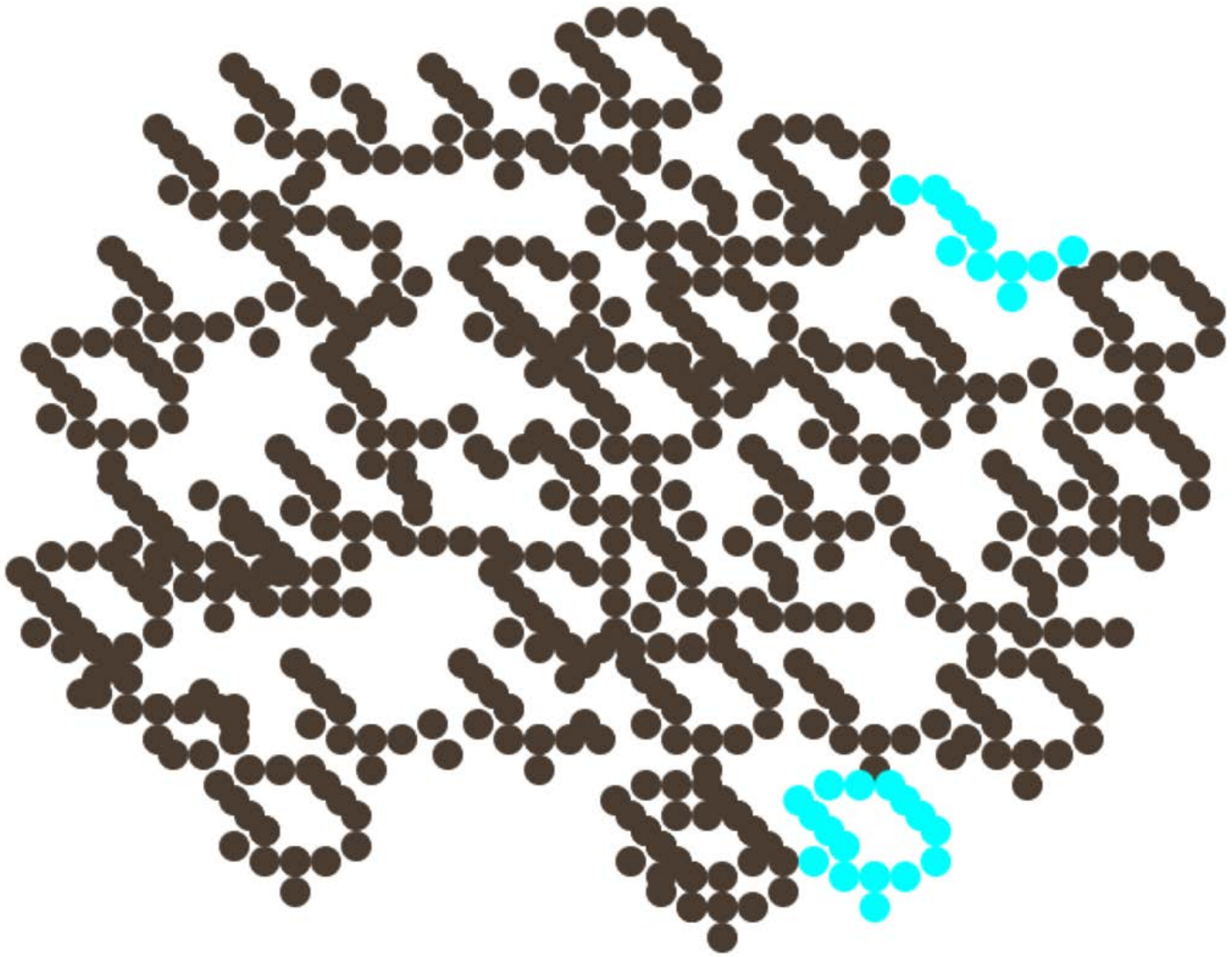


PRECIPITATED SILICA STRUCTURE



Particle size = 10- 100 um

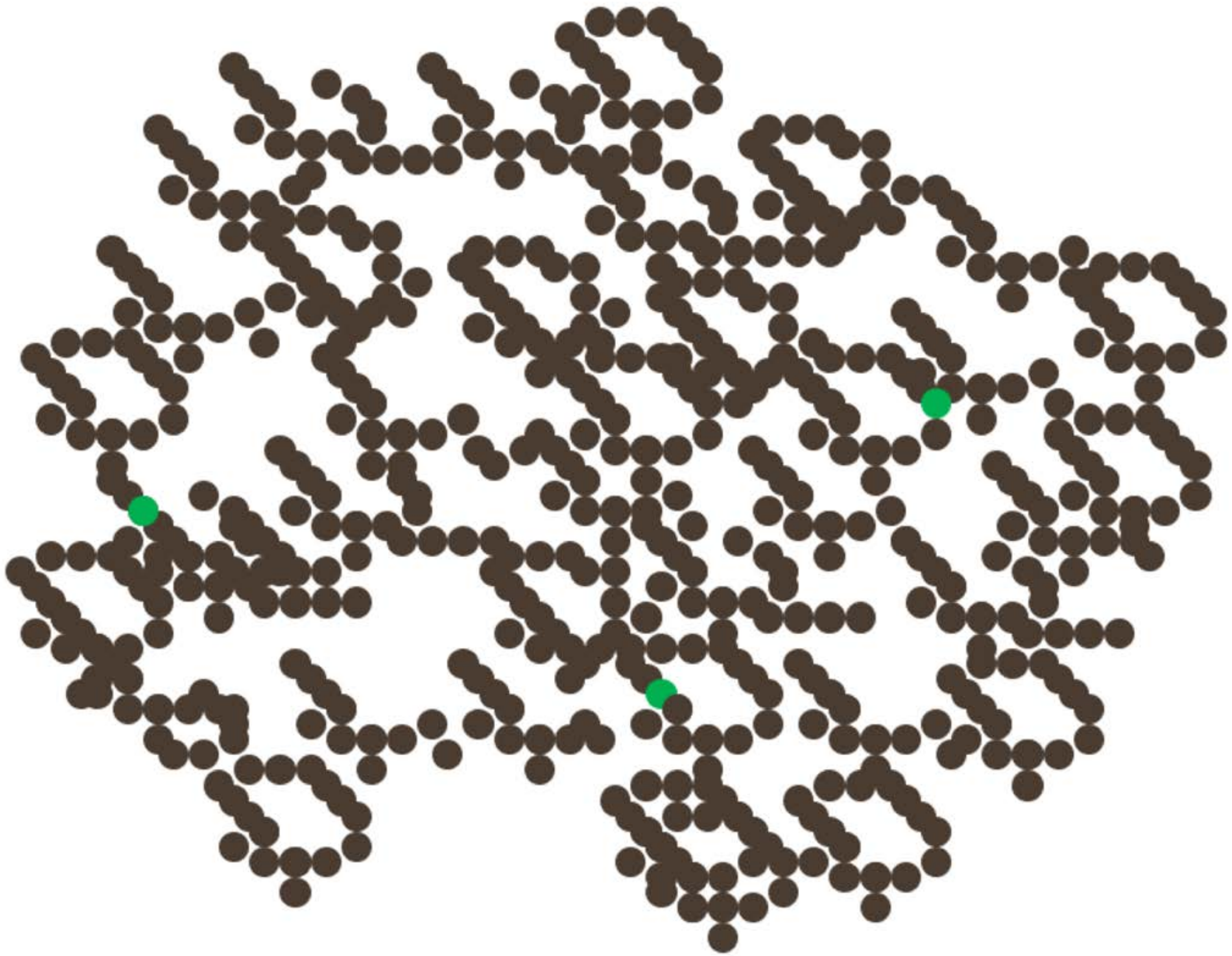
PRECIPITATED SILICA STRUCTURE



Particle size = 10- 100 um

Aggregate size = 0.1-0.3 um

PRECIPITATED SILICA STRUCTURE

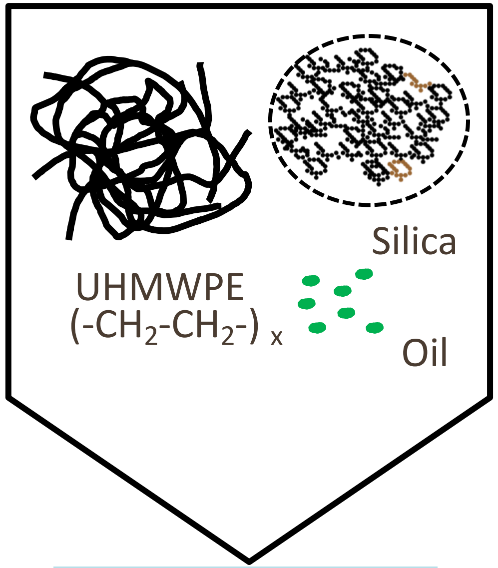


Particle size = 10- 100 um

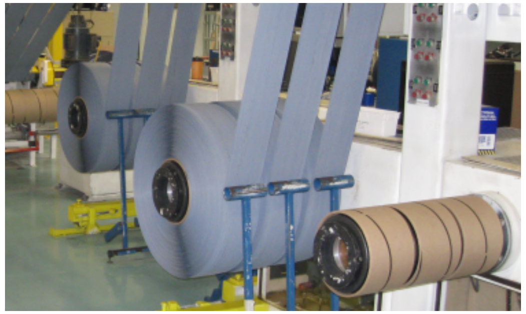
Aggregate size = 0.1-0.3 um

Primary particle size = 0.02 um

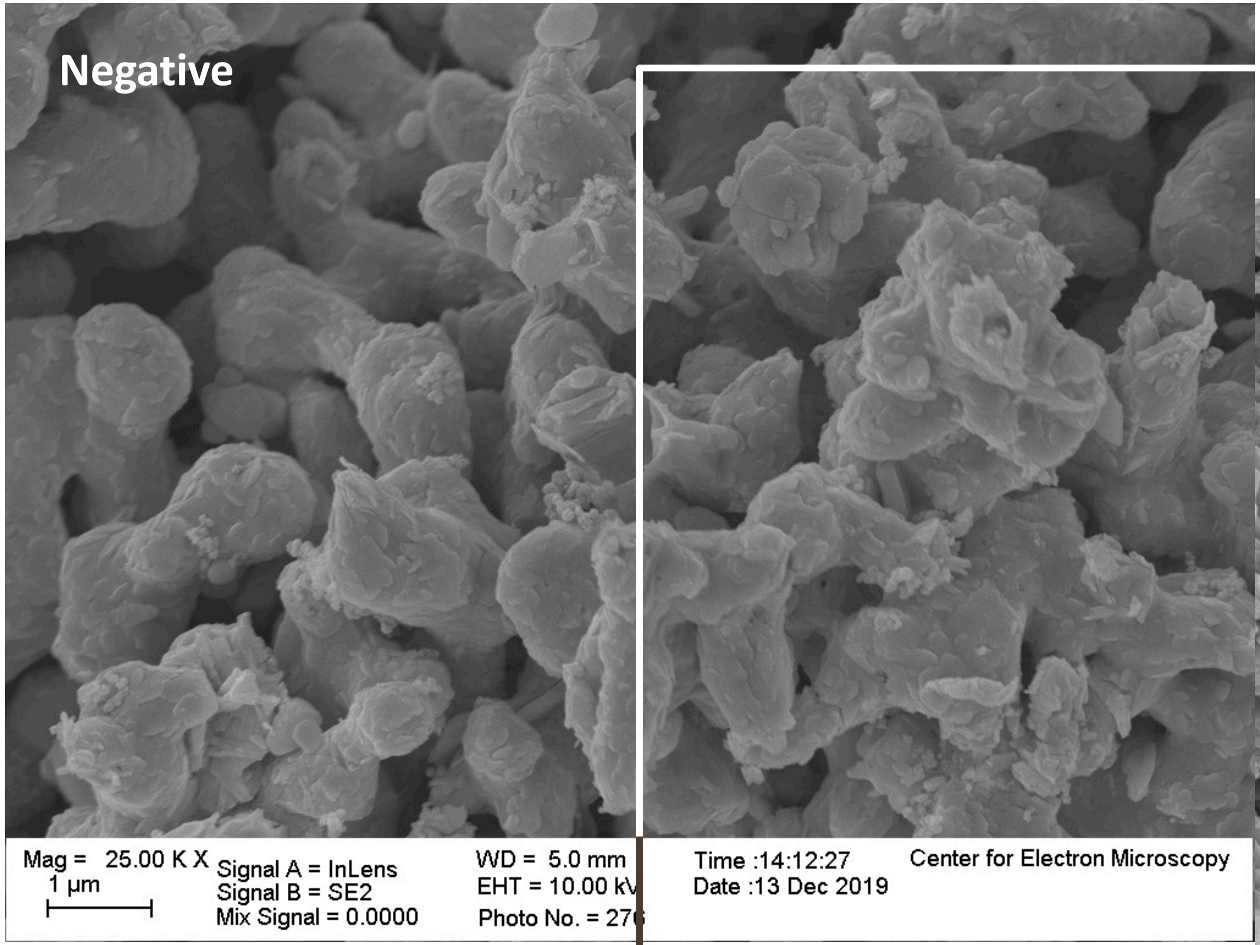
KEY RAW MATERIALS AND SEPARTOR MANUFACTURING PROCESS

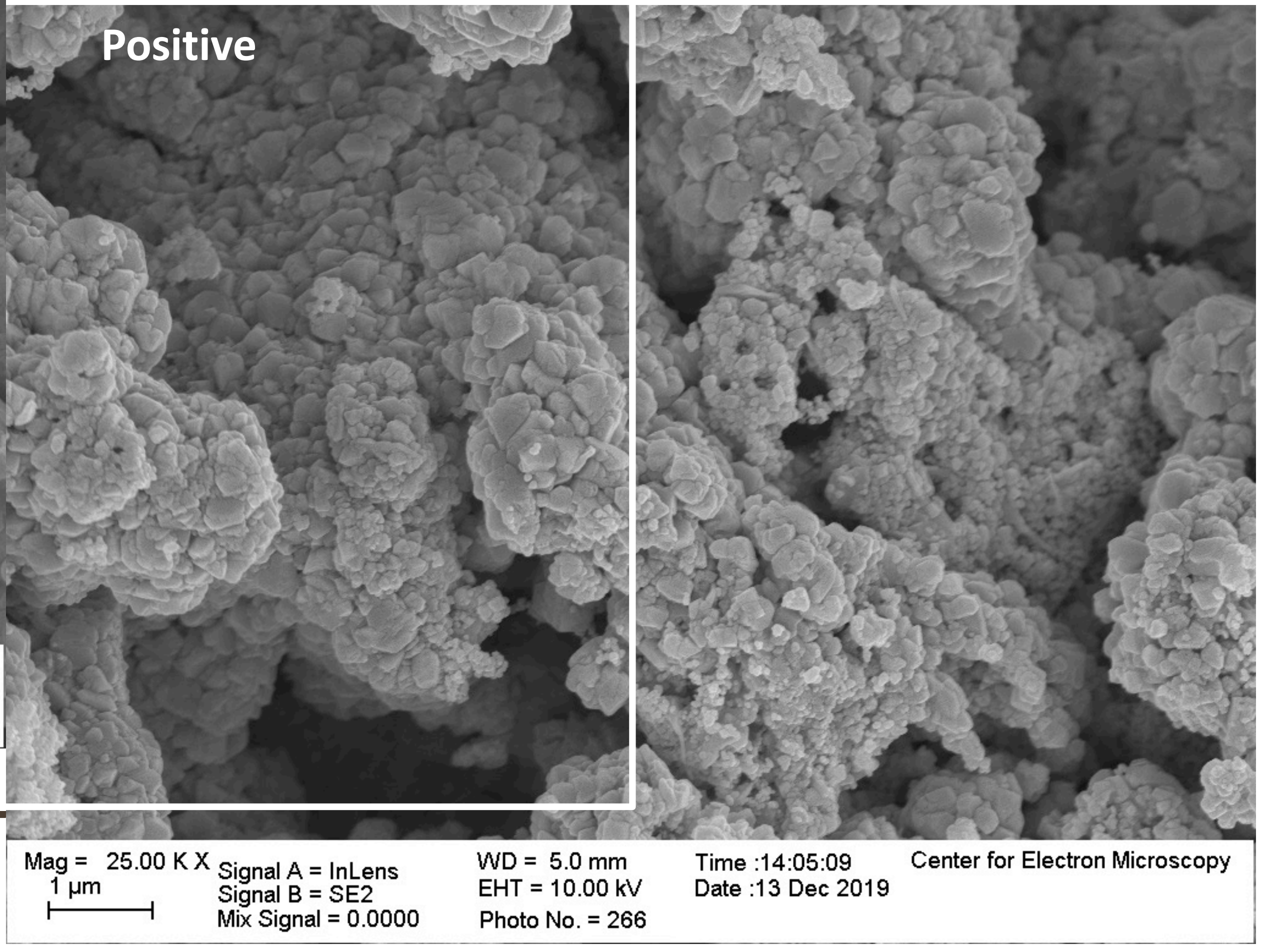


Extrusion → Calender → Extraction → Drying → Hot Air Oven → Slit & Wind →

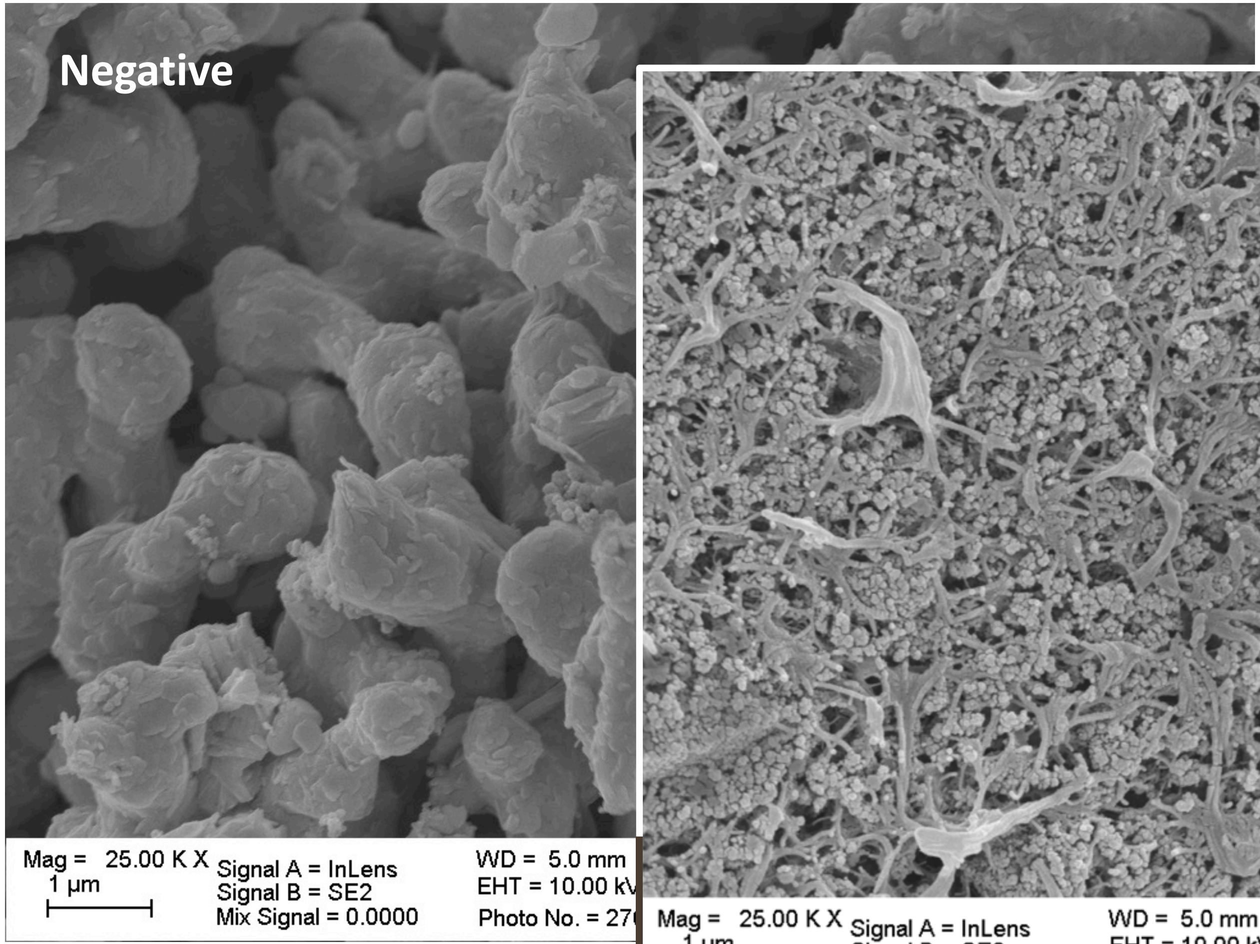


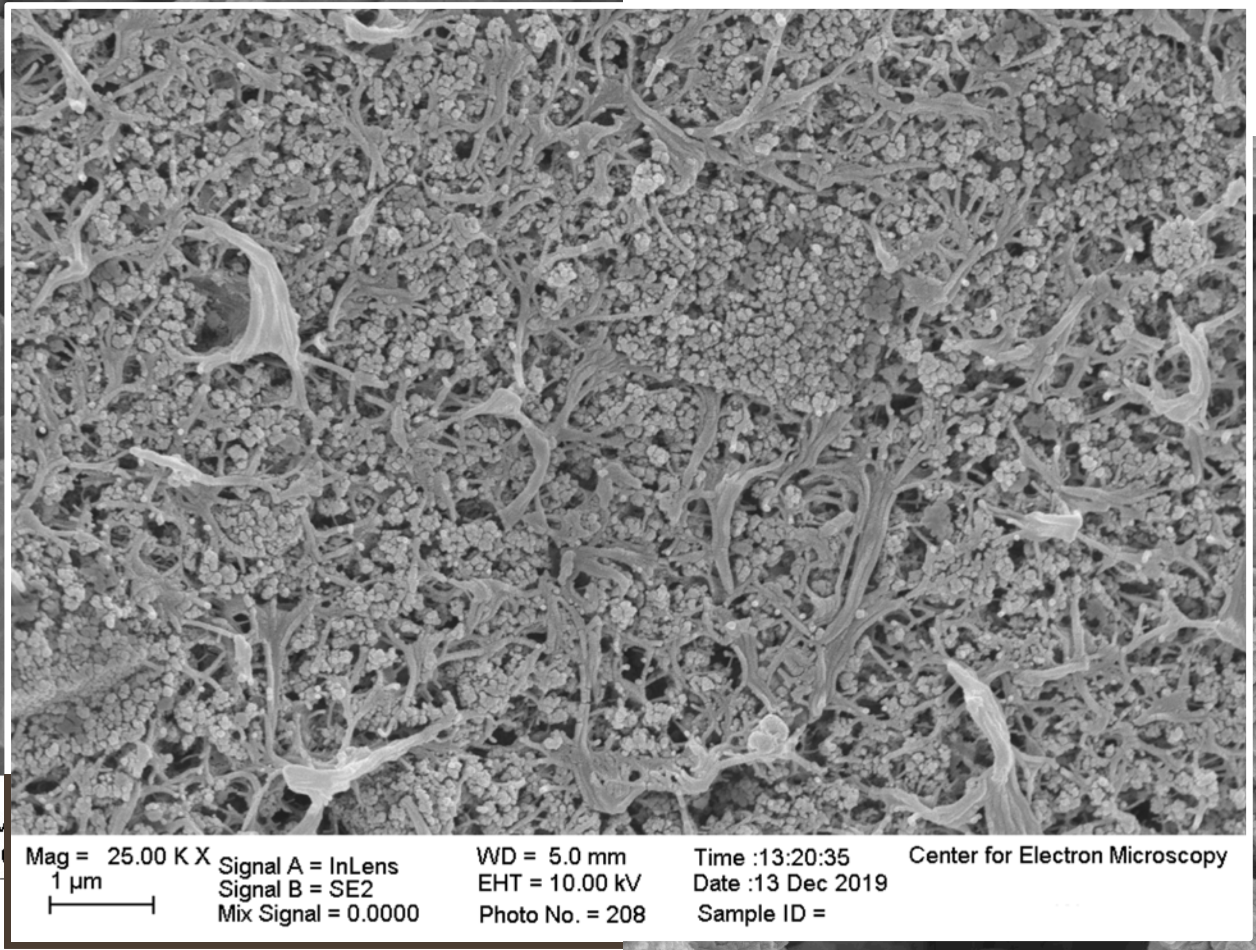
SEM – PARTICLE/PORE STRUCTURE OF ELECTRODES VS SEPARATOR

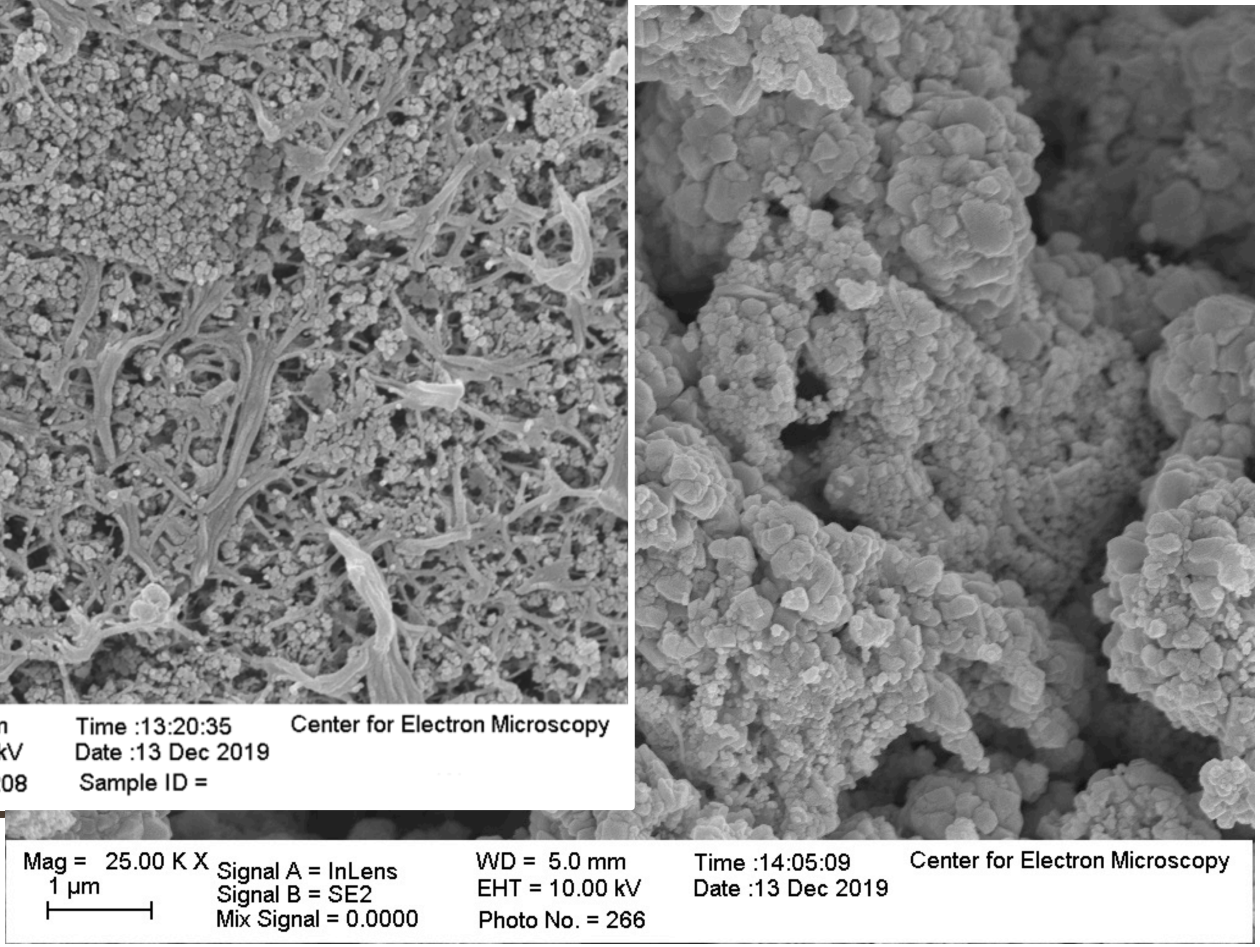


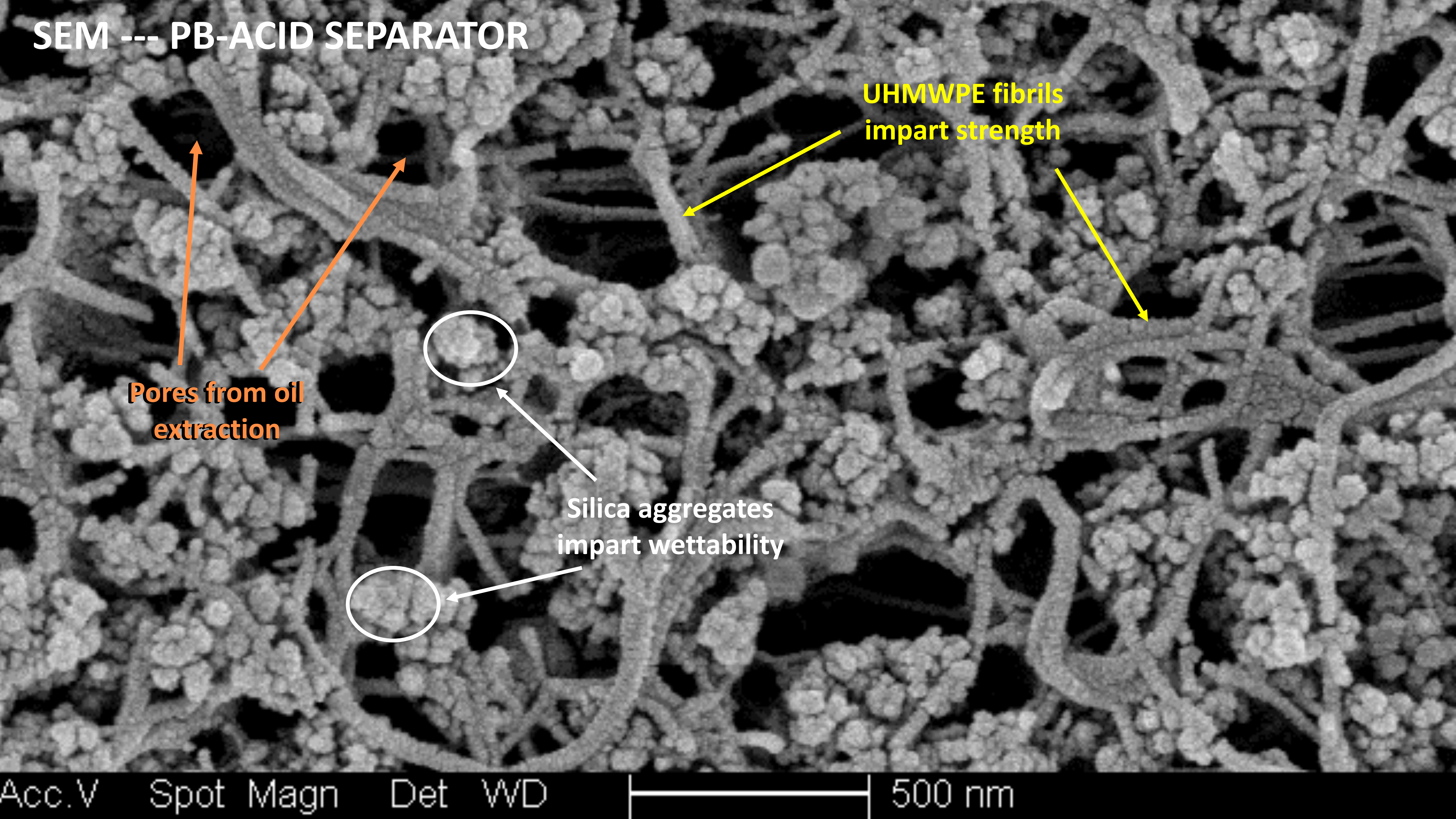


SEM – PARTICLE/PORE STRUCTURE OF ELECTRODES VS SEPARATOR

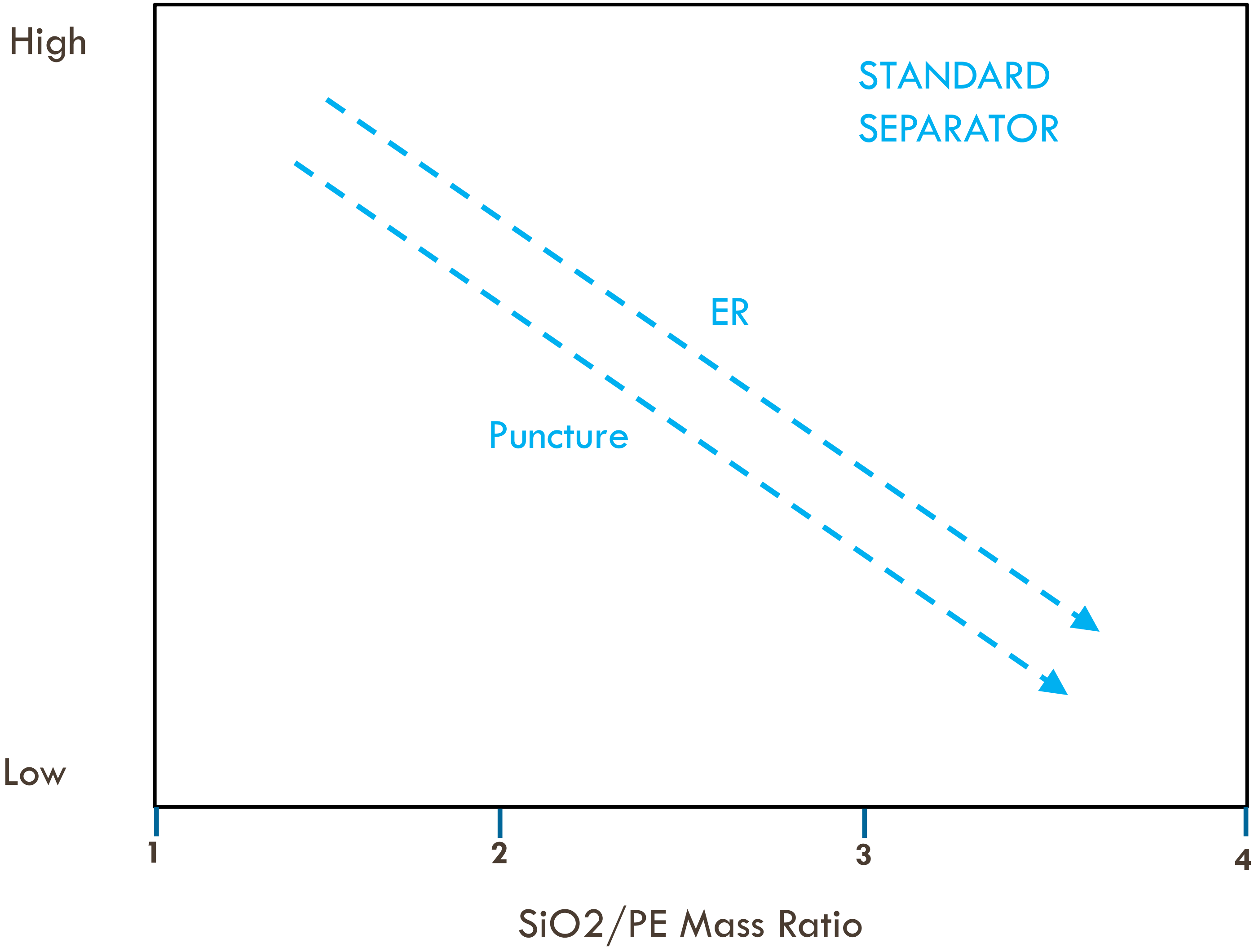







SEM --- PB-ACID SEPARATOR
UHMWPE fibrils impart strength
Pores from oil extraction
Silica aggregates impart wettability
Acc.V Spot Magn Det WD
500 nm

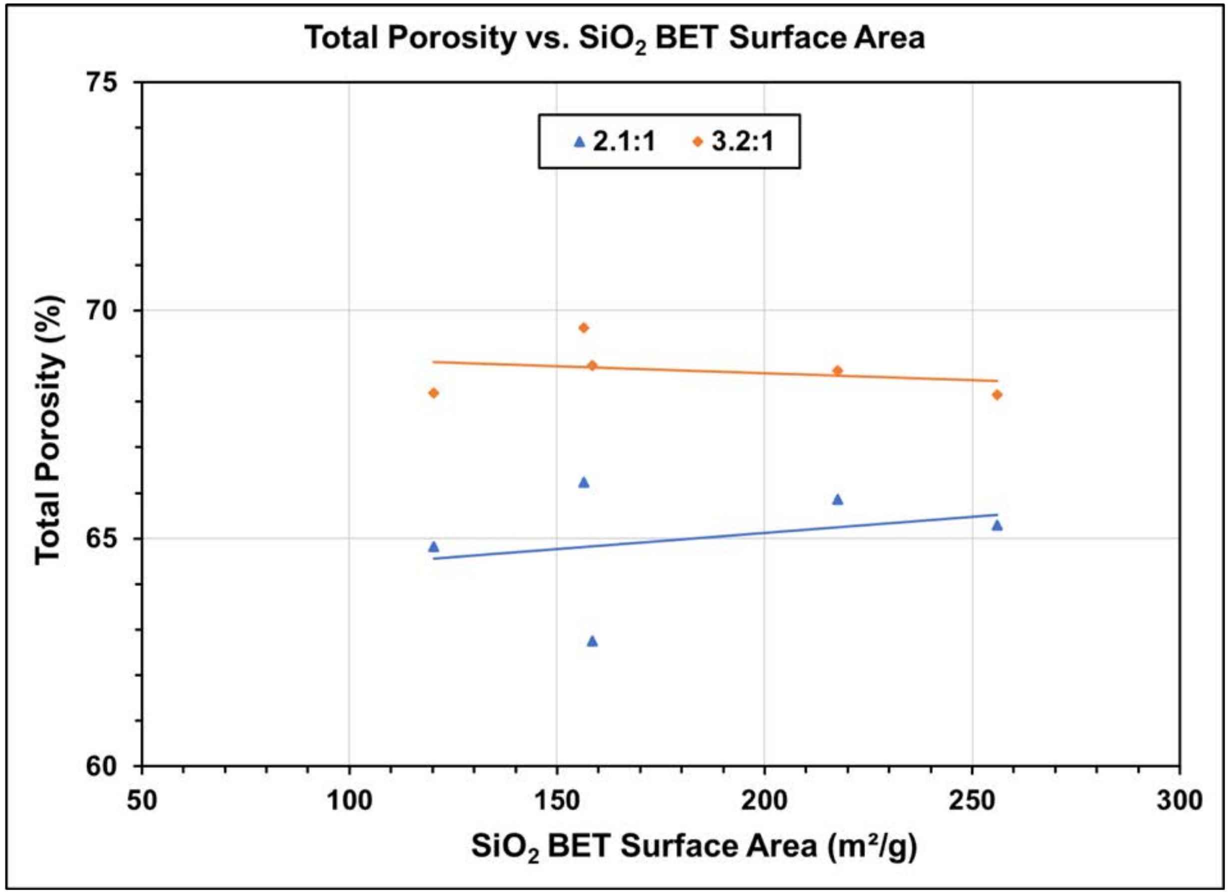
KEY SEPARATOR CHARACTERISTICS VS COMPOSTION

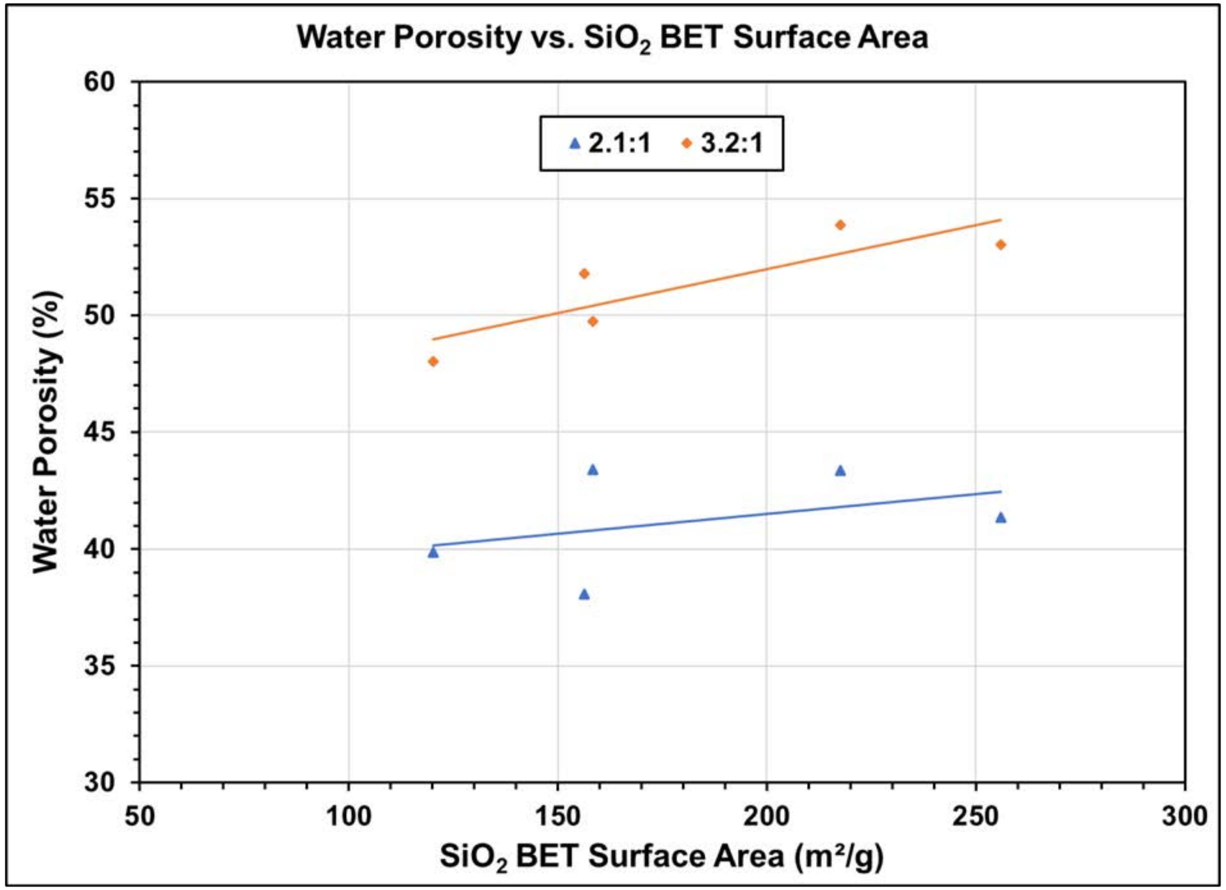


Material Parameters
- Silica Dispersibility
- Polymer Molecular Weight

Process Parameters
- Throughput
- Cooling rate
- Orientation

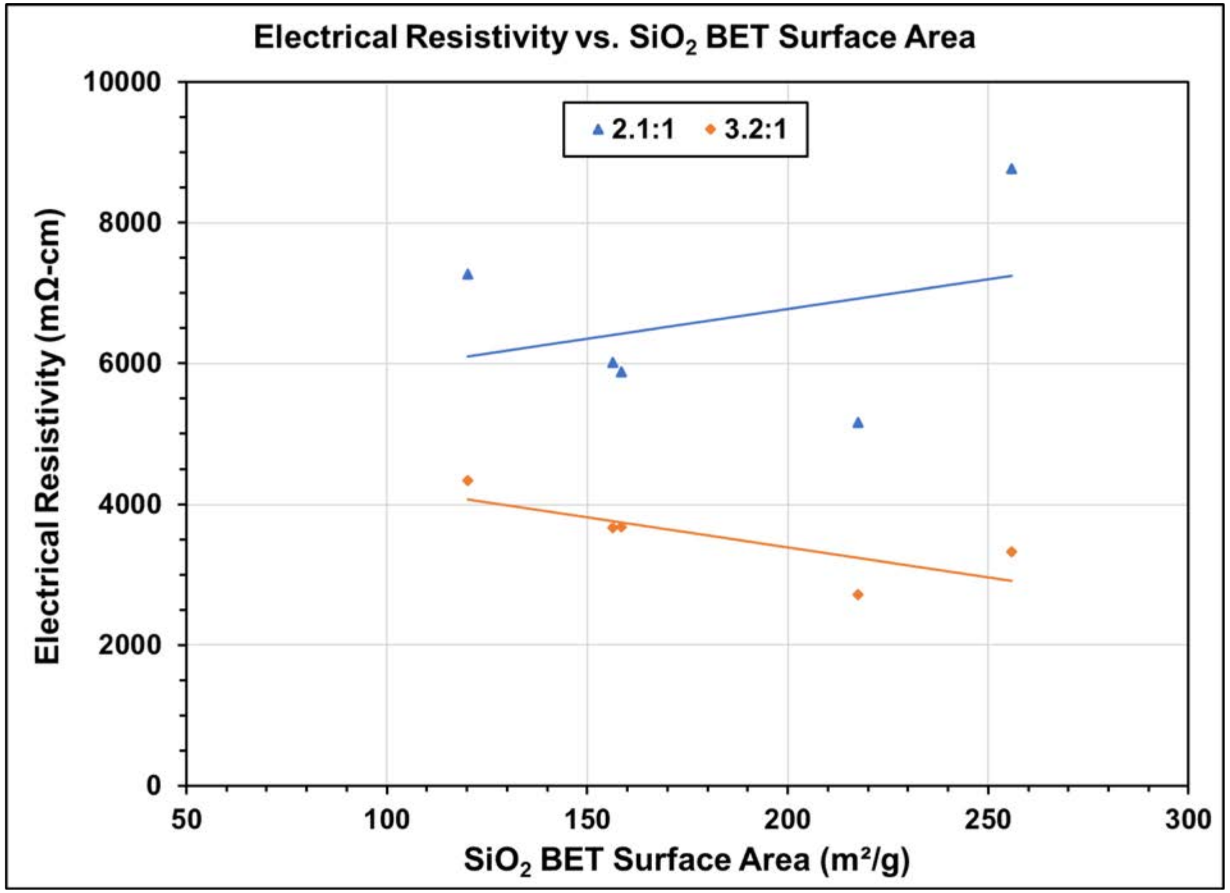
LAB EXTRUSION TRIAL WITH SILICAS HAVING DIFFERENT SURFACE AREAS

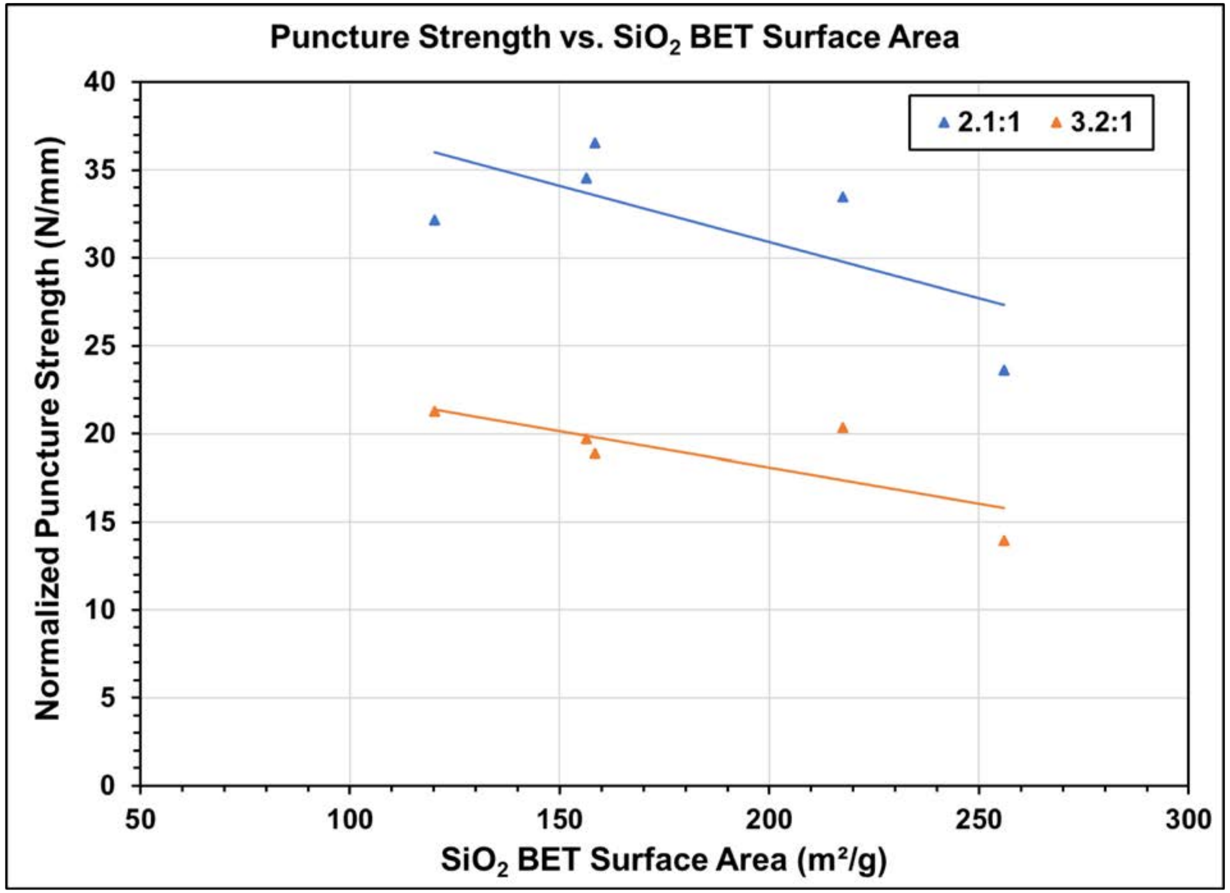




Water porosity results indicate that not all available pores are wetted out, but a higher percentage are at SiO2/PE = 3.2

ELECTRICAL RESISTIVITY + PUNCTURE STRENGTH TRENDS





Expected trends observed for ER and puncture vs. SiO2/PE ratio; however, large differences in absolute values dependent upon silica surface area

EXPECTED PARTICLE SIZE TRANSFORMATION DURING EXTRUSION

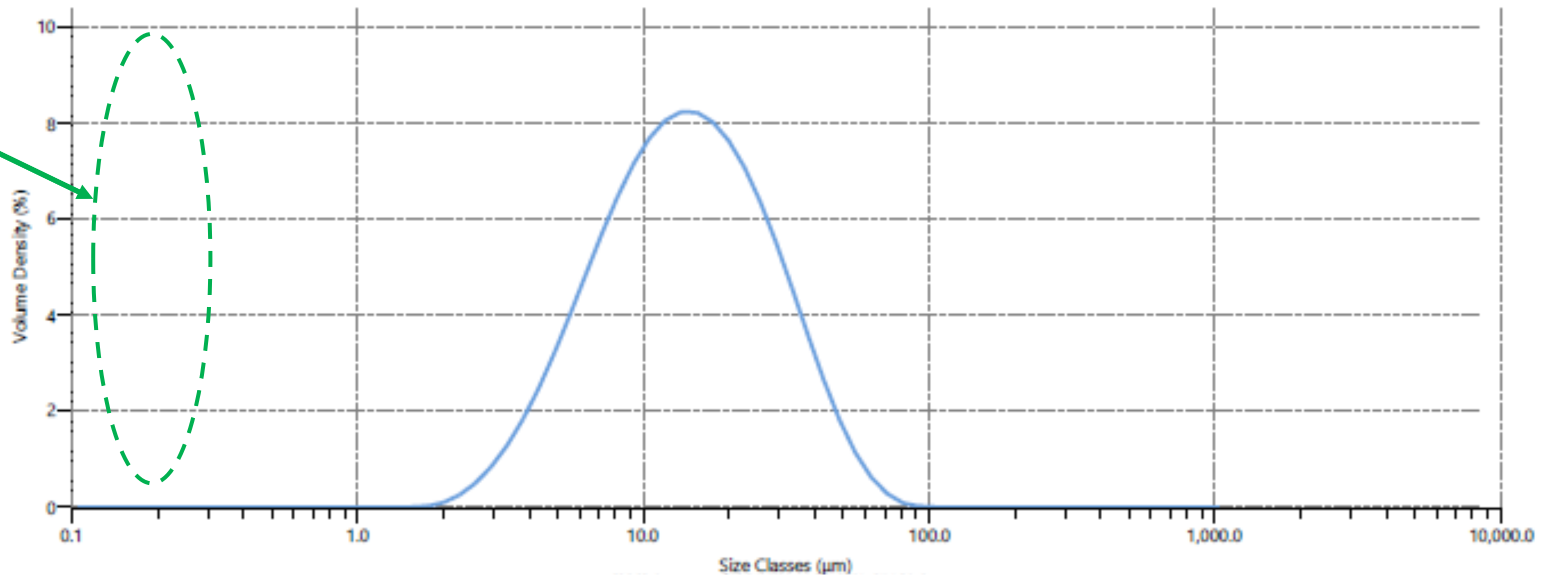
Malvern Instruments

Malvern

Measurement Details	
Operator Name	
Sample Name	Silica S
Analysis Date Time	
Measurement Date Time	

Optical Properties	
Particle Refractive Index	1.457
Particle Absorption Index	1.000
Particle Refractive Index Blue	
Particle Absorption Index Blue	
Dispersant Refractive Index	1.330
Residual	0.10 %
Weighted Residual	0.11 %

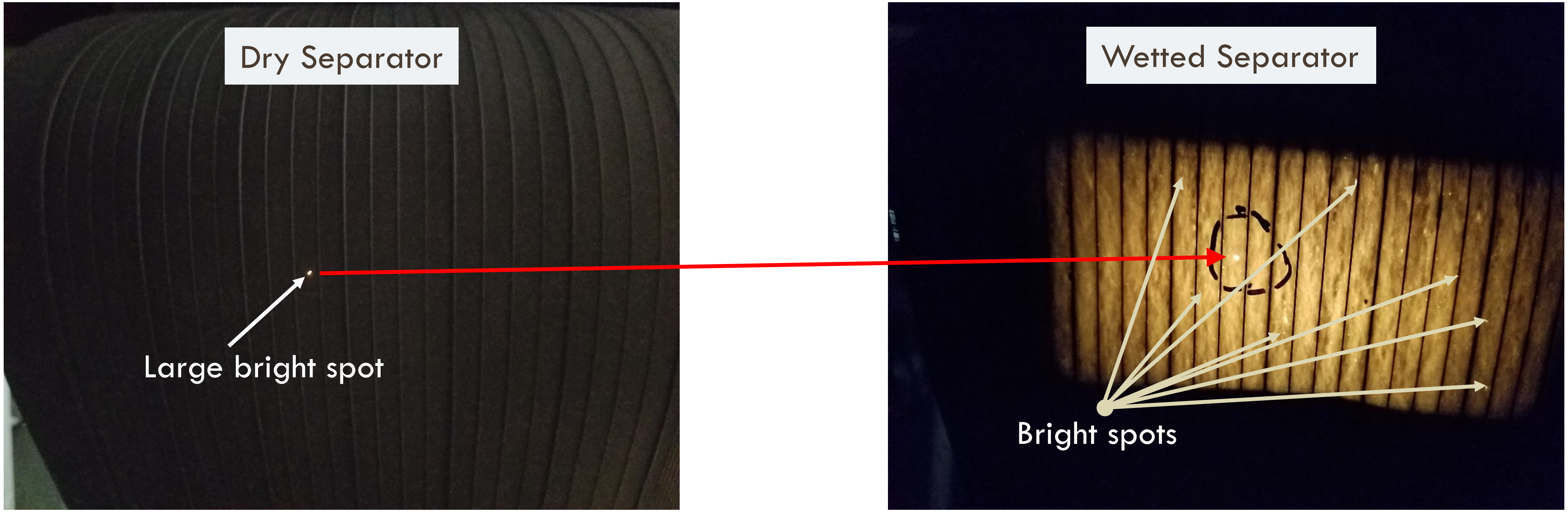
Frequency (compatible)



Typical Silica aggregate size within separators

Dv (10) 5.50 μm
Dv (50) 13.9 μm
Dv (90) 33.5 μm
Dv (99) 57.1 μm
Dv (99.9) 74.0 μm

OPTICAL CHARACTERISTICS: BRIGHT SPOTS



- When the separator is wet, the air is displaced from the pores and the difference in refractive index between the pores and the solid structure is greatly reduced. Scattering of light is also greatly reduced (but not eliminated), and much more light is transmitted through the separator. The transmitted light is very diffuse.
- Absorption of light by the carbon is still in effect, but the carbon is dilute.
- So, what are the bright spots?

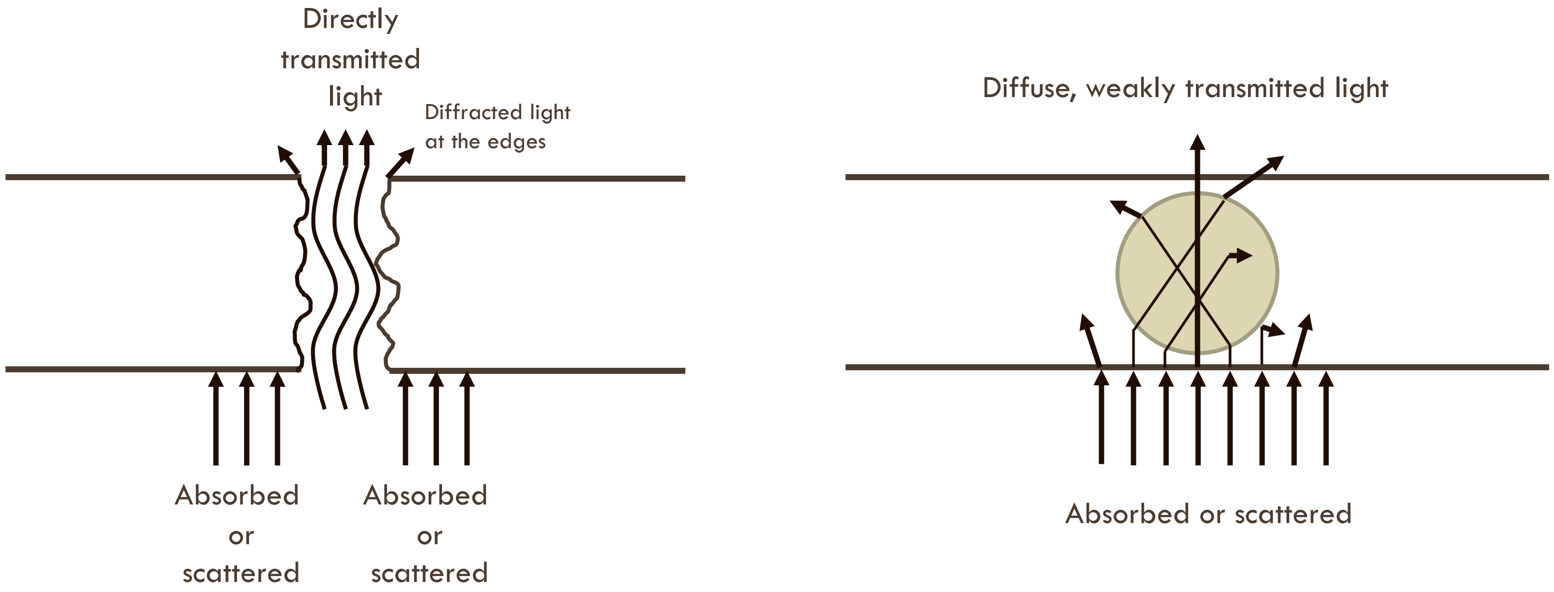
A LARGE SILICA AGGLOMERATE OR GLASSY PARTICLE

- The presence of a large silica agglomerate or glassy particle may impact porosity in a microscopic region
  - Reduced ion conduction through that spot gives higher local resistivity.
    - There may be a small reduction in current density in the electrode regions directly facing the silica particle.
    - The reduction is made small by the high conductivity of the acid electrolyte and the small fraction of separator surface involved (<<1%).
- The particle is held in place by the surrounding UHMWPE/silica matrix and will not be dislodged.
  - The particle cannot become a hole with normal handling.
    - Prior studies have shown that the particle remains in place, despite mechanical stresses such as bending, stretching and ultrasonic vibration.
  - The particle may lower the mechanical strength in that spot, but we have not been able to measure a reduction, since the pin used in puncture testing is much larger than the particle.

A silica agglomerate or glassy particle should have no observable impact on the performance of the separator or the lead acid battery.

WHY NOT A PINHOLE?

- The bright spots identified in our internal investigation were all the result of transmission of diffuse light, requiring wetting of the separator with water and a very bright light source to be observed.
- A pinhole, by definition, is a hole through the separator that allows light transmission unimpeded by any absorption or scattering (except from the edge of the hole). A vision system is used to monitor pinholes on all production lines (> 100 um diameter), and they are observable in the laboratory without wetting the separator.



SEPARATOR SHRINKAGE OBSERVED DURING BATTERY TEARDOWN

- One of the principal attributes of precipitated silica is its stability in sulfuric acid (low pH)
- It is, however, possible to create local regions of high pH and high temperature at the top of a lead acid battery cell
- The above dissolution may occur as a result of over-discharge or acid stratification
- Under these conditions, silica may dissolve into the electrolyte, resulting in a lower SiO_2/PE mass ratio and shrinkage of the separator in that region
- The dissolution can also be observed in DUF batteries that have become exposed to a humid or “wet” environment

SILICA SOLUBILITY

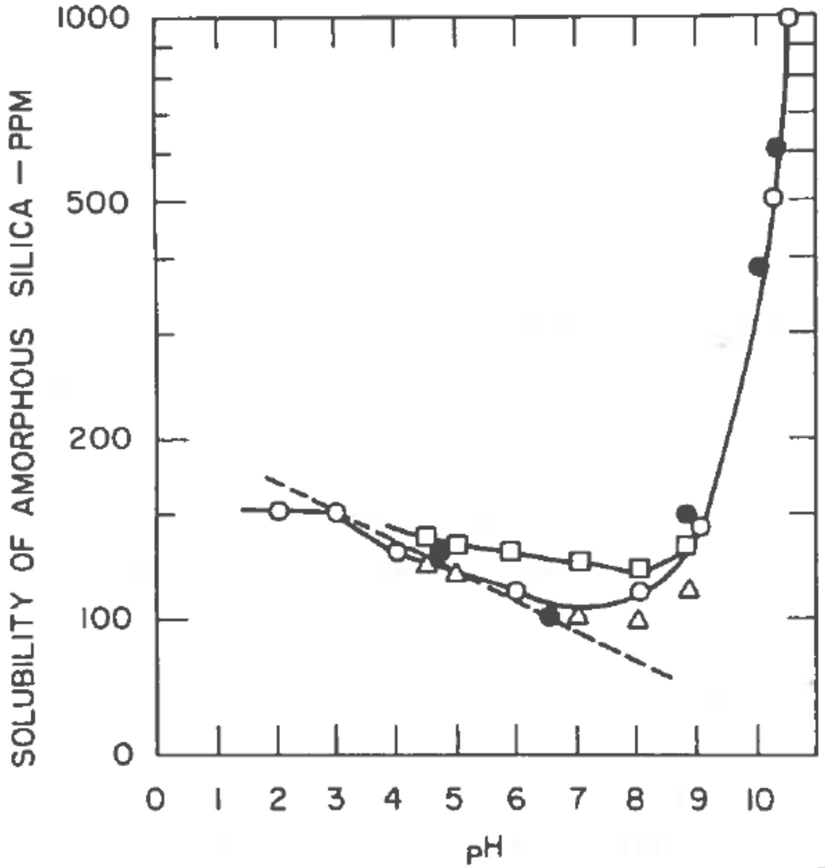


Figure 1.6. Solubility of amorphous silica versus pH: O, Alexander, 25°C; ●, Cherkinskii and Knyaz'kova (160) 19°C; Δ Baumann, 20°C; □ Baumann, 30°C; Dashed line from Cherkinskii equation: log $C_M = -2.44 - 0.053$ (pH).

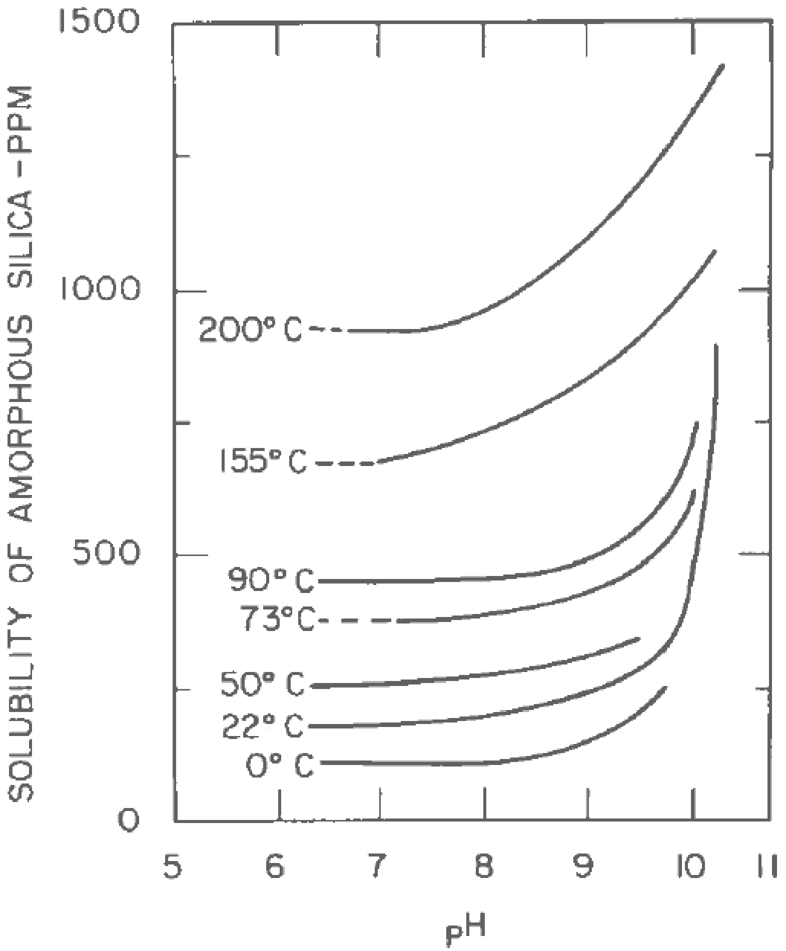


Figure 1.7. Solubility of amorphous silica versus pH at different temperatures [from Goto (167a)].

Reference: R.K. Iler, *The Chemistry of Silica*, 1979

THERMOGRAVIMETRIC ANALYSIS (TGA) OF DISTORTED ENVELOPES

- Envelopes were washed with water & solvent-extracted with IPA, TCE, & HFE to preserve pore structure

sample	moisture (%)	oil (%)	PE (%)	carbon black (%)	SiO2 (%)	SiO2/PE
Top of failed envelope	1.42	2.26	46.18	2.43	47.70	1.03
Top of envelope repeat	1.50	2.23	39.77	2.00	54.50	1.37
Middle of failed envelope - near shoulder	2.11	1.47	31.43	1.92	63.04	2.01
Good wet envelope	3.95	1.85	29.59	1.74	62.87	2.12
Dry envelope	3.41	1.09	27.35	1.04	67.10	2.45

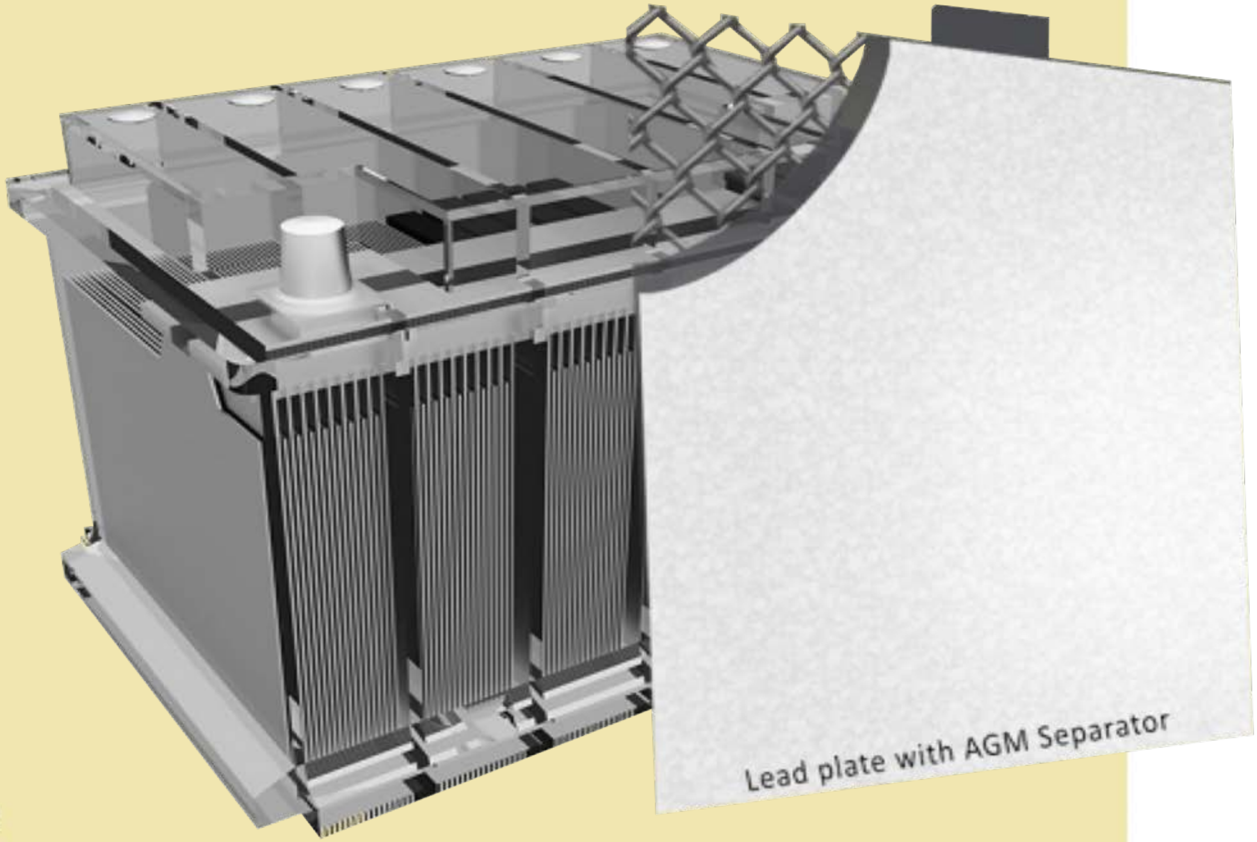
- Large variation of Silica/PE ratio in the failed envelope
- Silica/PE ratio is very low in failed envelope
- Measuring the silica concentration in the electrolyte or as a precipitate during a battery teardown may provide useful information about acid stratification

TGA results show a reduction in the silica content of the distorted envelopes.
Low silica content at the top of the envelope is consistent with electrolyte stratification.

ABSORPTIVE GLASS MAT

VRLA batteries are used in a variety of applications that require certain features of the AGM separator. Depending on the customer need, ENTEK AGM is available in three types and can be generally described as follows:

1. **All-glass fiber AGM**: is typically used in applications were maximum capacity and battery life are concerned.
2. **Hybrid-AGM**: used where mechanical strength is important for, e.g., high-speed battery assembly, where there is a narrow distance between the poles, and/or where the battery is subject to vibration during use.
3. **Hybrid-PLUS-AGM**: used in similar applications as Hybrid-AGM, especially where there is a requirement for long-life cycle batteries or where batteries are concerned with dendrite short-circuit.



GLASS COMPOSITION CONSIDERATIONS FOR FIBER FORMATION

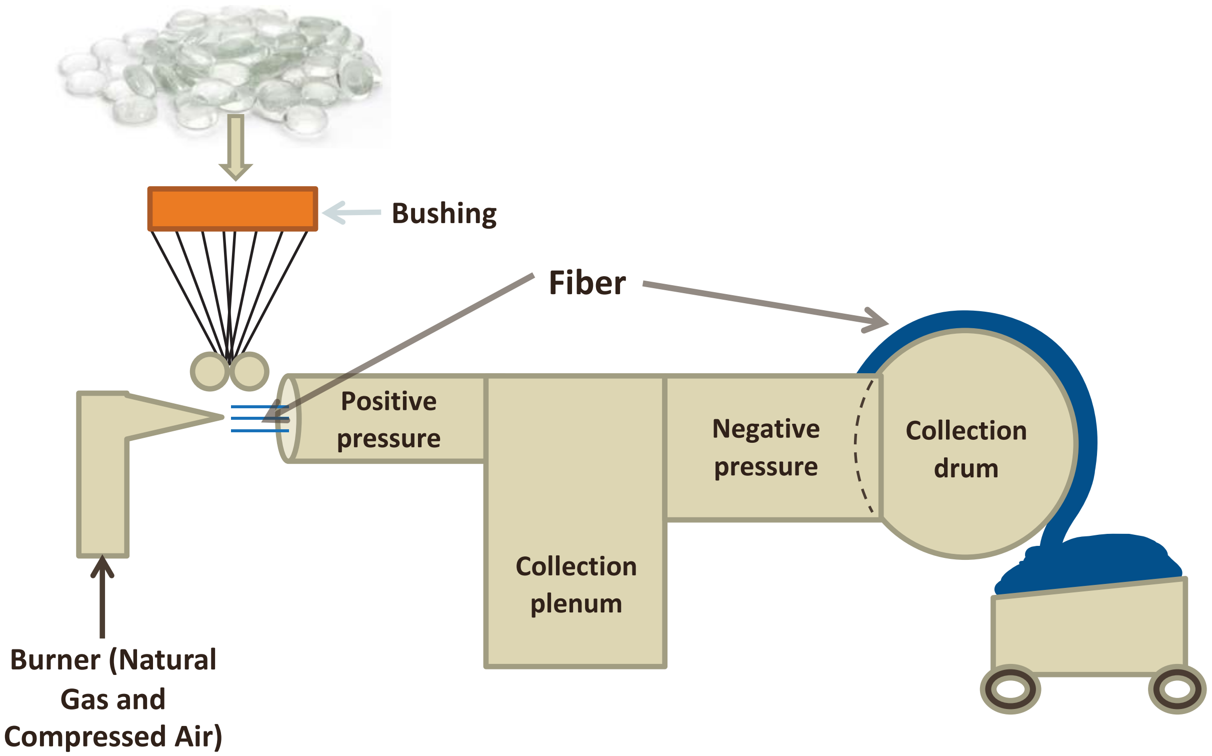
- Raw material costs
- Viscosity
- Liquidus temperature
- Melting enthalpy
- Surface tension
- Fiber tensile strength
- Elastic modulus
- Chemical durability
- Density
- Refractive index
- Surface reactivity and chemical sizing

% Oxide/Glass Type	A-glass	B-glass	C-glass	E-glass
SiO_2	70.50	60.00	65.00	51.50
Al_2O_3	3.25	5.50	4.00	14.50
B_2O_3	0.09	9.50	5.50	7.75
K_2O	5.25	2.50	1.00	0.40
Na_2O	11.25	11.50	15.50	0.60
MgO	3.00	1.00	3.00	5.50
CaO	6.00	3.00	5.50	19.50
BaO		4.50	0.10	
ZnO		3.50	<0.1	
Fe_2O_3		0.20	<0.2	
F_2			<1.0	0.10

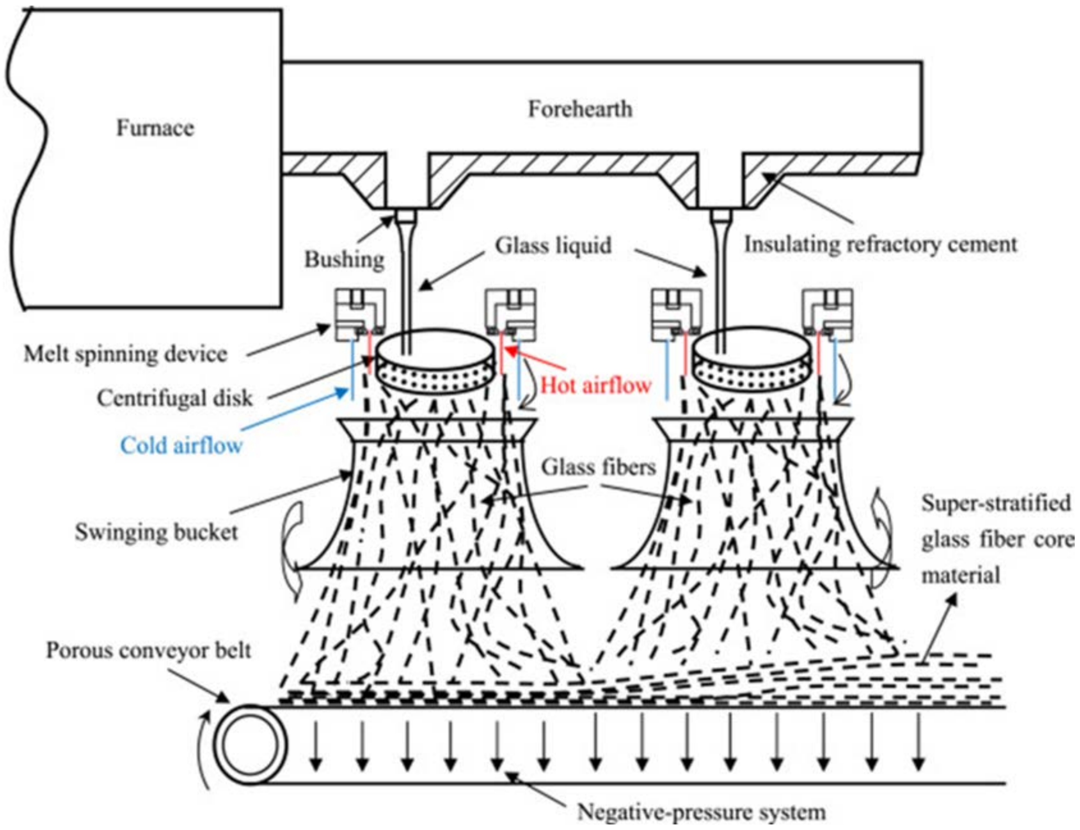
A-glass: low boron, alkali silicate
B-glass: general borosilicate
C-glass: acid resistant borosilicate
E-glass: calcium aluminoborosilicate

COMMERCIAL FIBERIZING PROCESS RESULT IN DIFFERENT SIZE DISTRIBUTIONS

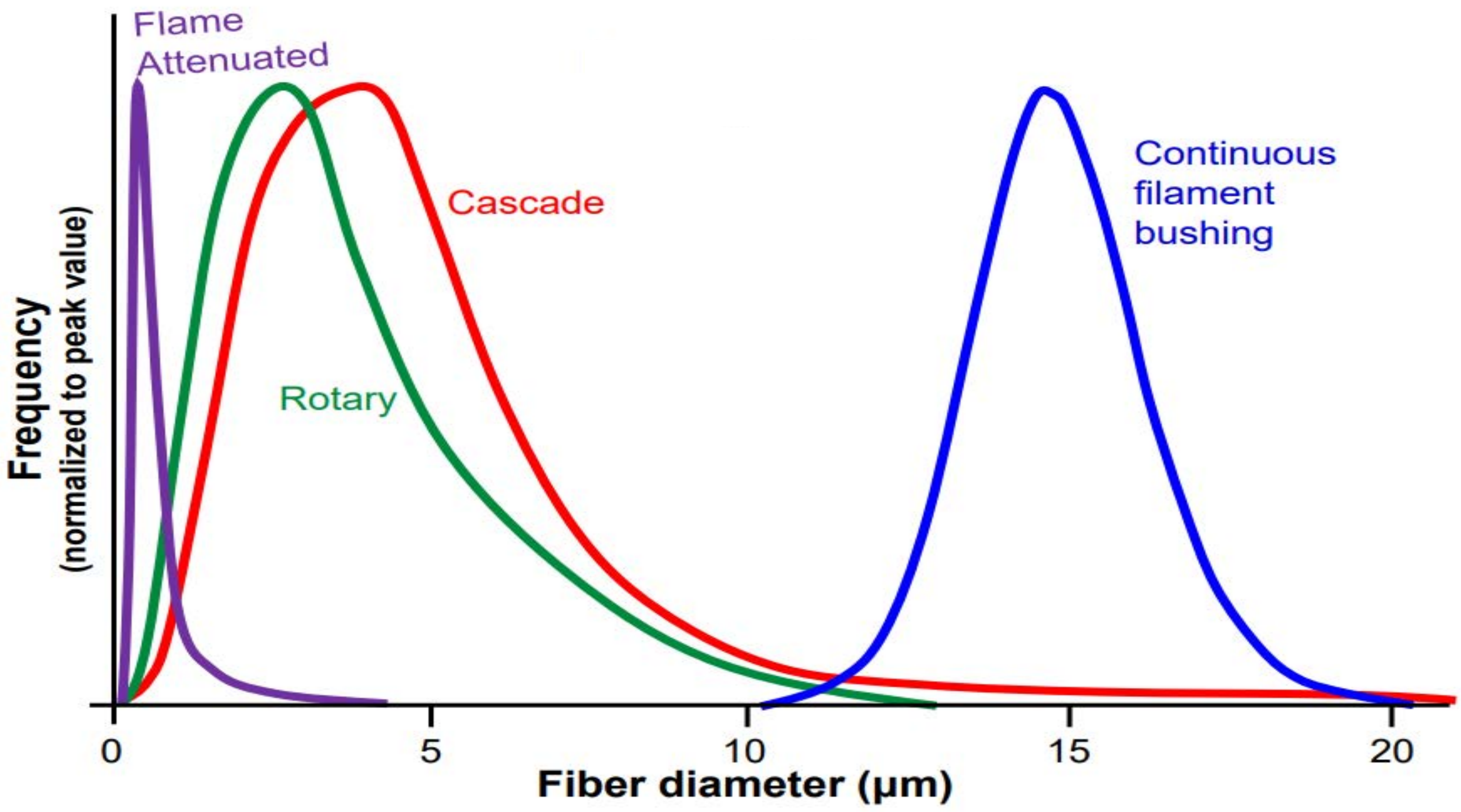
Flame Attenuation



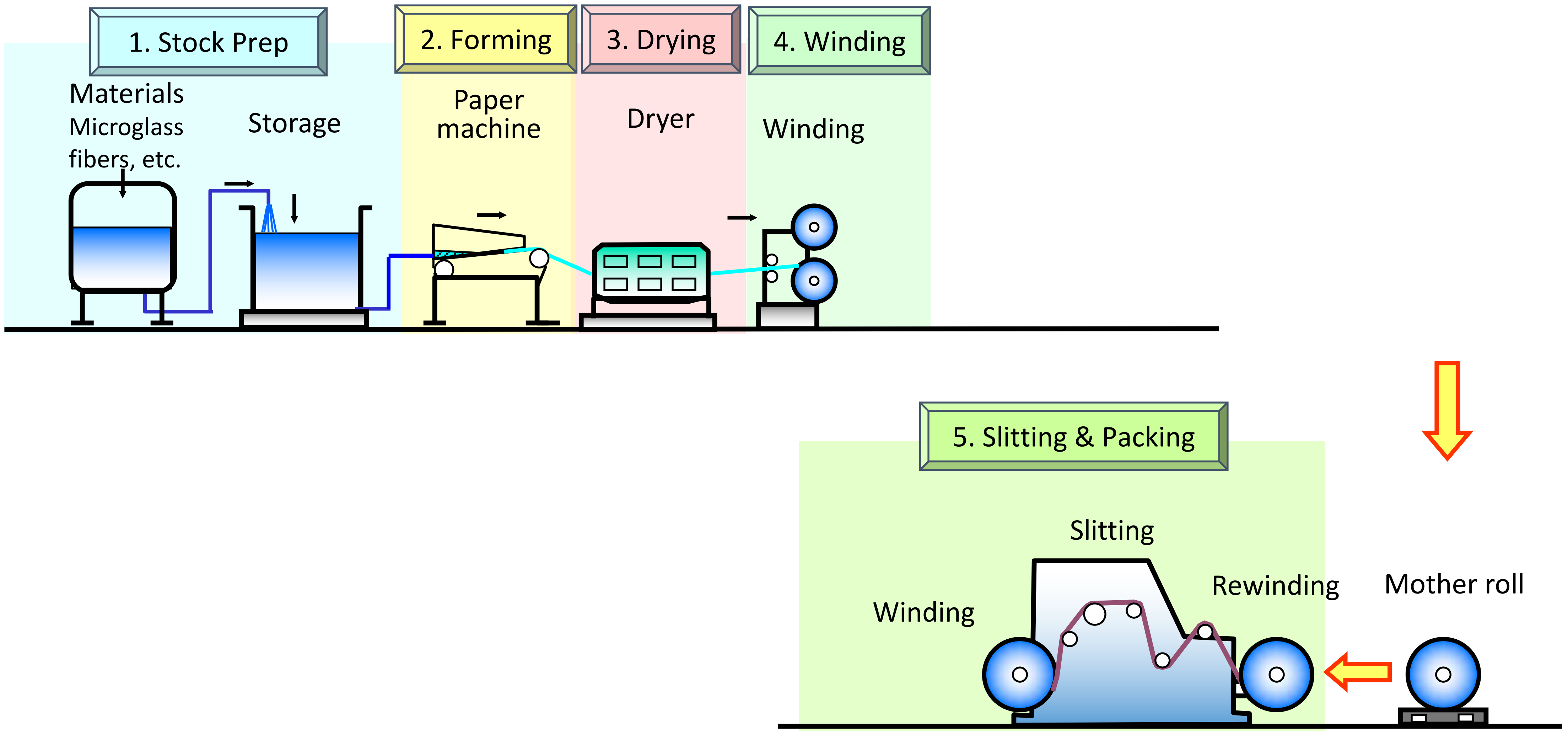
Rotary Attenuation



COMMERCIAL FIBERIZING PROCESS RESULT IN DIFFERENT SIZE DISTRIBUTIONS

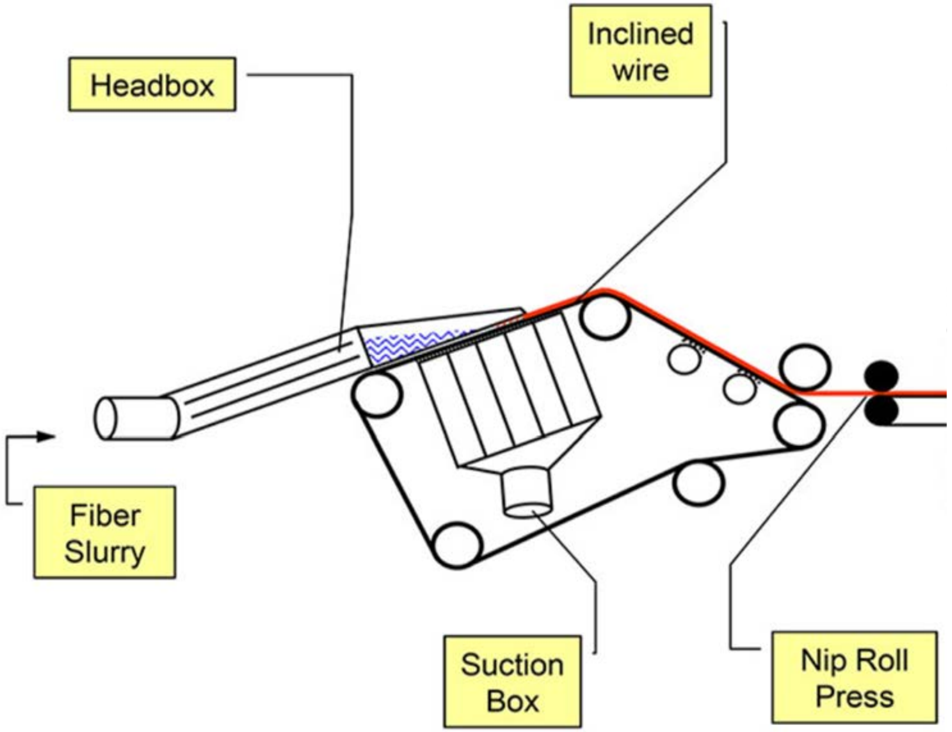


AGM PAPER MANUFACTURING

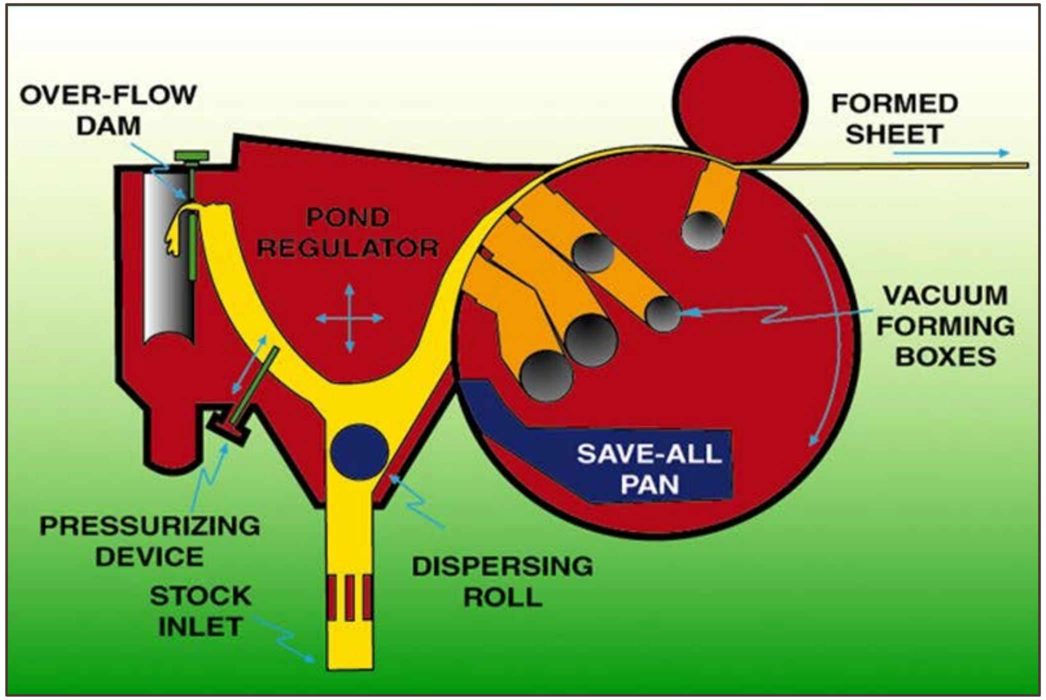


AGM FORMING STEP

Inclined Wire Former



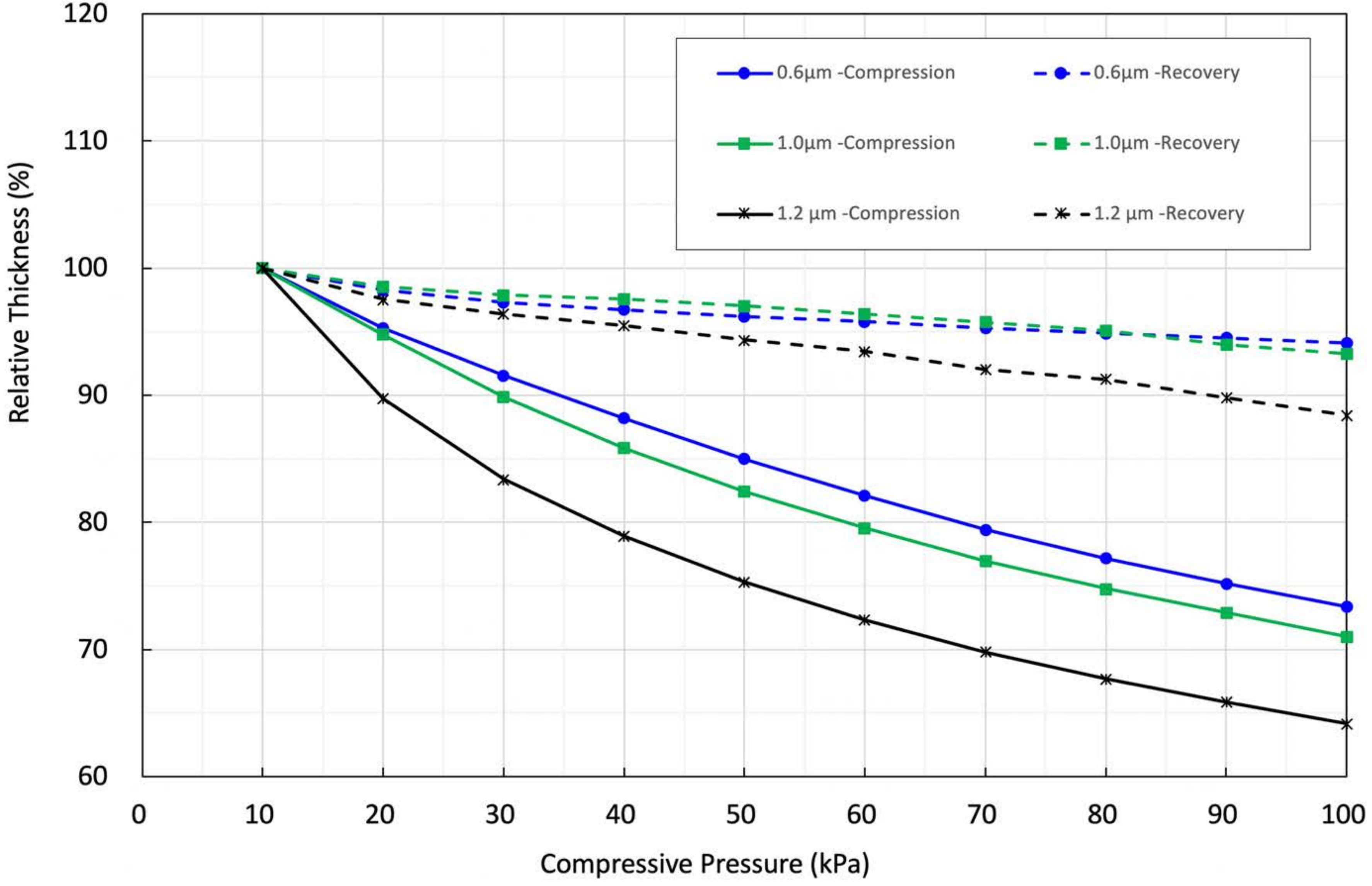
Cylinder Former



ALL-GLASS FIBER AGM SEPARATOR

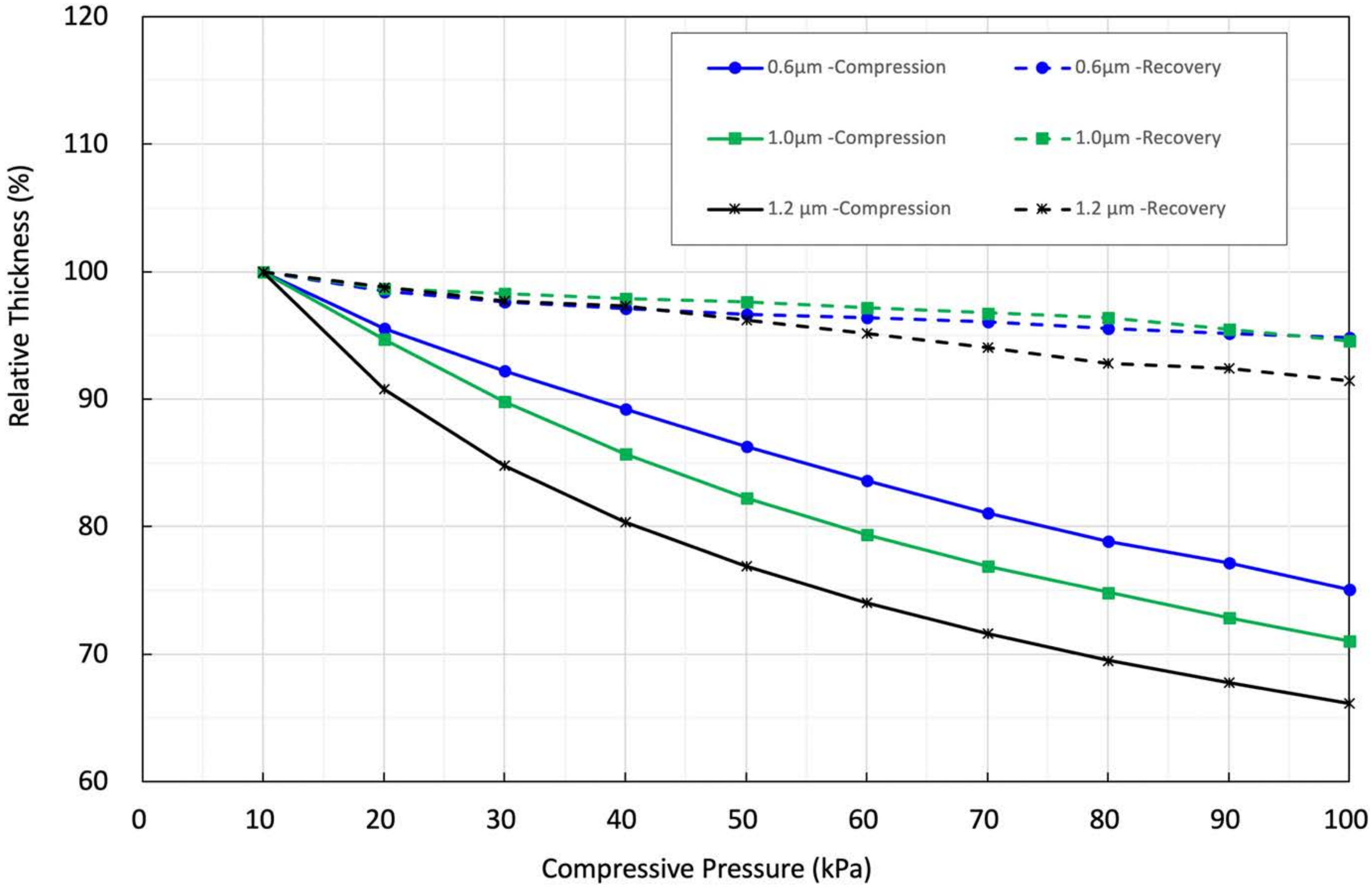
- Conventional product family
- We have developed various types of AGM to support customer needs:
  - High capacity
  - High CCA performance
  - Stratification resistance

Grade	BET Specific Surface Area (m^2/g)	Density [@10kPa] (g/cm^3)	Loss on Ignition (%)	Tensile Strength [MD] ($N/10mm^2$)
BMS-A6	1.4	0.150	0.4	5.3
BMS-5	1.5	0.130	0.4	4.5
BMS-Y18	1.6	0.153	0.4	8.0
BMS-AT	2.0	0.150	0.4	8.5
BMS-FJ	1.5	0.130	0.4	3.2



What is the impact of fiber diameter on compression-recovery ?

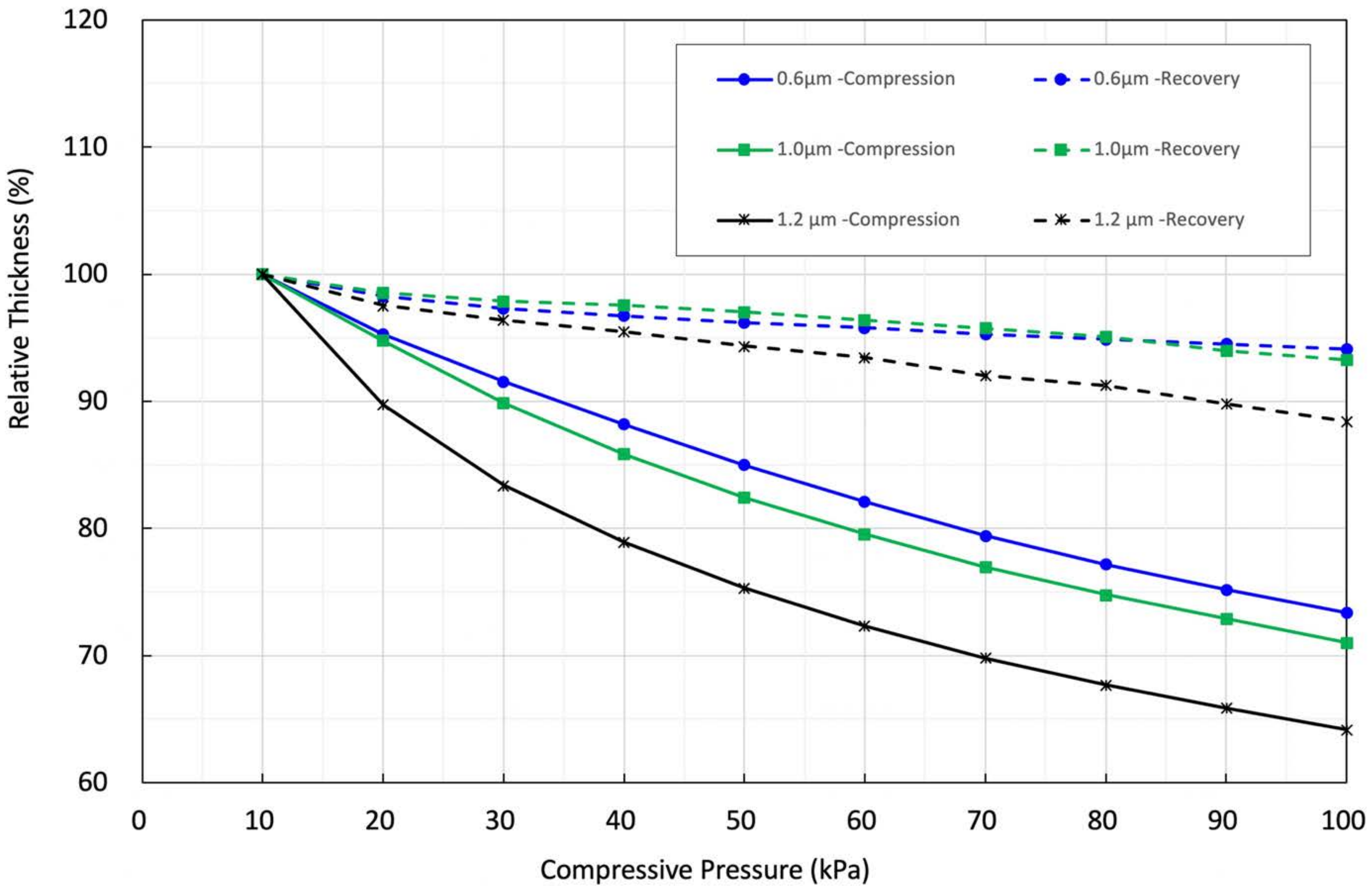
DRY (25 C)



What is the impact of fiber diameter on compression-recovery ?

DRY (25 C)

H_2SO_4 (25 C)



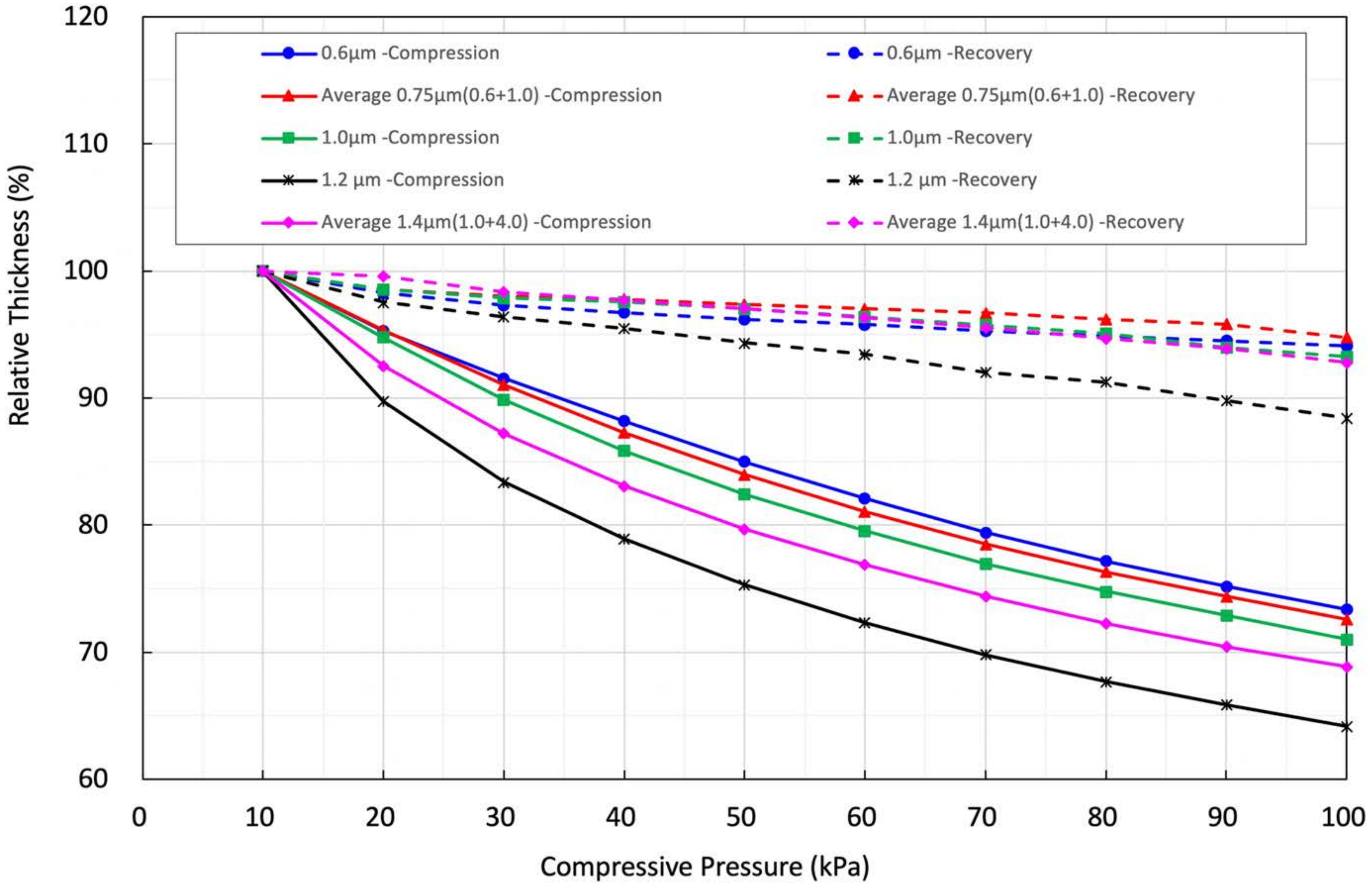
What is the impact of fiber diameter on compression-recovery ?

DRY (25 C)

H_2SO_4 (25 C)

H_2SO_4 (40 C)

www.entek.com



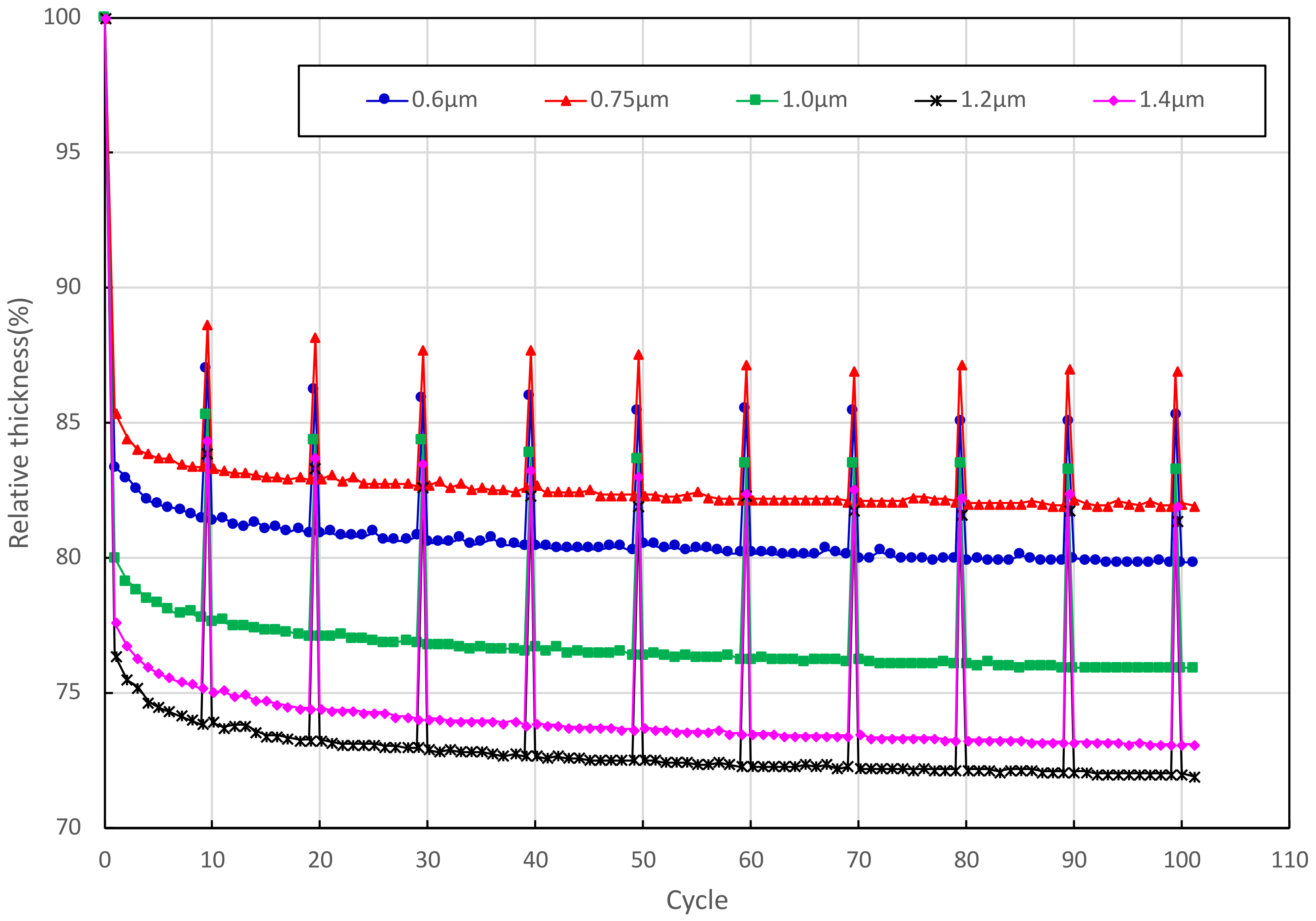
What is the impact of fiber diameter on compression-recovery ?

DRY (25 C)

H_2SO_4 (25 C)

H_2SO_4 (40 C)

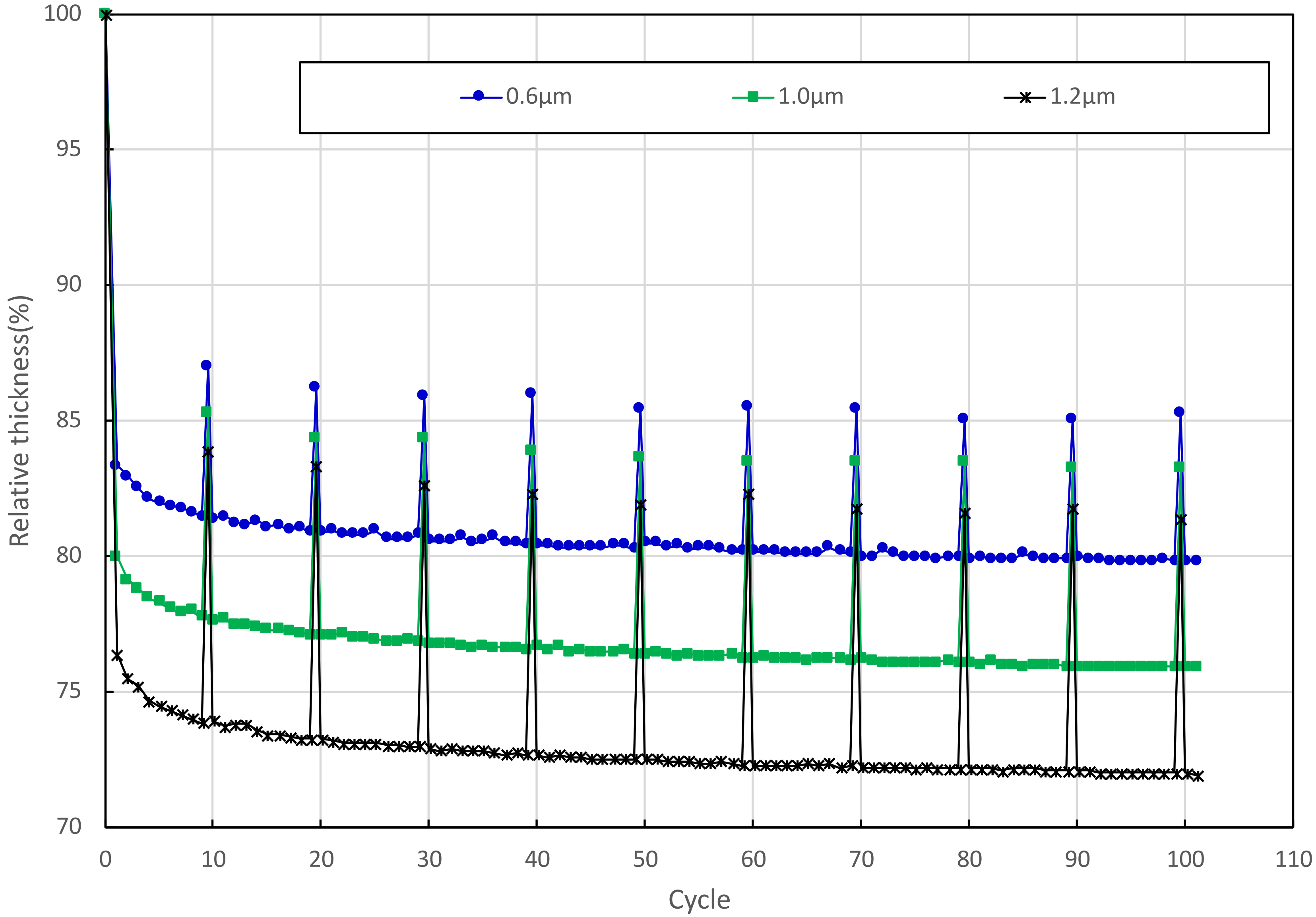
H_2SO4 (40 C)



How does fiber diameter impact continuous compression-recovery cycling ?

Methodology

Using a horizontal compression tester, 10 sheets are soaked in sulfuric acid and continuously compressed and released from 10 kPa to 50 kPa. Thickness at 10kPa is recorded every 10 cycles.



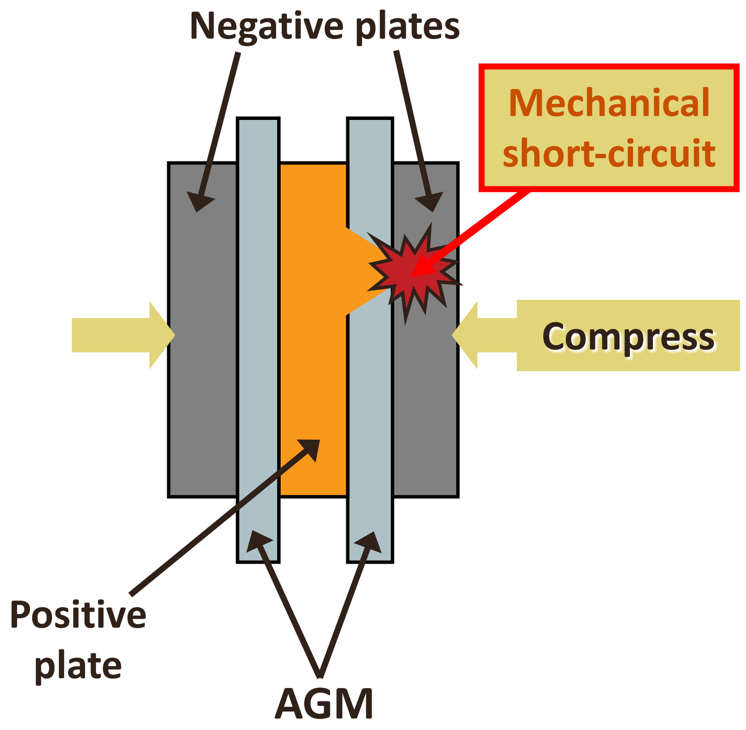
How does fiber diameter impact continuous compression-recovery cycling ?

Methodology

Using a horizontal compression tester, 10 sheets are soaked in sulfuric acid and continuously compressed and released from 10 kPa to 50 kPa. Thickness at 10kPa is recorded every 10 cycles.

HYBRID AGM (GLASS FIBER + POLYMER)

- It has the following advantages:
  - ✓ Higher tensile strength for increased productivity
  - ✓ High puncture strength to prevent mechanical shorts

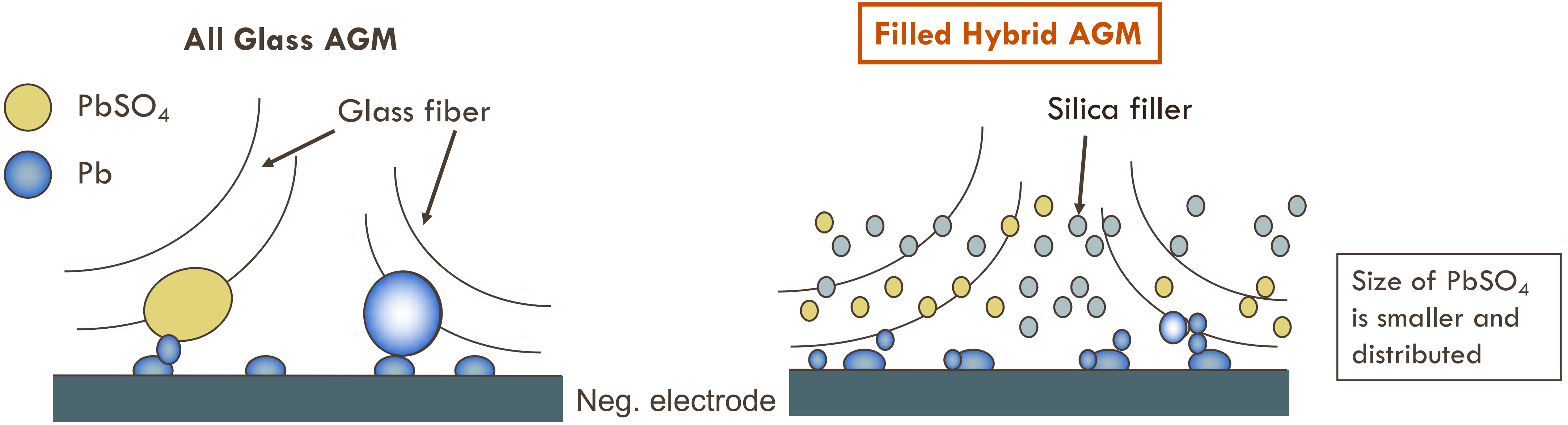


Grade	BET Specific Surface Area (m^2/g)	Density [@10kPa] (g/cm^3)	Loss on Ignition (%)	Tensile Strength [MD] ($N/10mm^2$)	Puncture Strength (N/mm)
BMS-Z46	1.3	0.150	8	8.0	4.5
BMS-Z47	1.2	0.147	16	9.0	6.5
BMS-Z44	1.9	0.150	8	8.5	5.5
BMS-Z45	1.8	0.147	16	11.0	7.5
BMS-A6[1)]	1.4	0.150	0.4	5.3	2.6

HYBRID *PLUS* AGM (GLASS FIBER + POLYMER + SILICA FILLER)

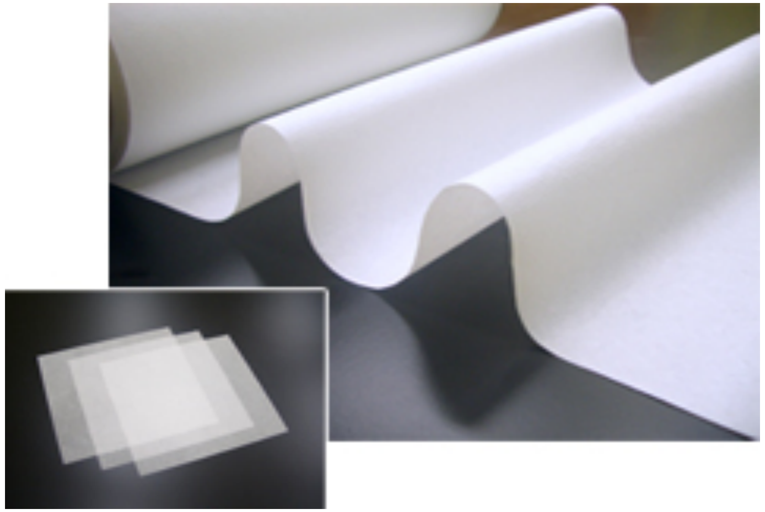
- Since the amount of the electrolyte is small in VRLA, sulfuric acid in the electrolyte is consumed and tends to be close to neutral, and dendrite short circuit is likely to occur
- Filling AGM with silica has the effect of complicating the structure of the AGM separator and preventing lead growth

Grade	BET Specific Surface Area (m^2/g)	Density [@10kPa] (g/cm^3)	Loss on Ignition (%)	Tensile Strength [MD] ($N/10mm^2$)	Puncture Strength (N/mm)
BMS-74	35	0.195	10	6.5	6.4
BMS-620	20	0.195	30	21.7	16.1
BMS-A6[1)]	1.4	0.150	0.4	5.3	2.6



AGM PASTING PAPER

- Engineered to enhance AGM separator performance and serve as a process aid to retain active materials using continuous grid pasting technology.
- Depending on customer requirements, this product is composed of 100% acid-resistant glass fiber or a blend of acid-resistant glass and polymer fibers.



Grade	BET Specific Surface Area (m^2/g)	Thickness [@10kPa] (mm)	Basis weight (g/m^2)	Loss on Ignition (%)	Tensile strength [MD] (N/25mm)
GPP-36A	2.2	0.2	36	0.4	5
HPP-38A	1.6	0.2	38	15	9
HPP-28B	1.6	0.2	28	11	7

SUMMARY

- Silica is an often forgotten material that has a large impact on the performance of Pb-acid batteries
- The control of silica particle size or silica fiber diameter is critical to the manufacture and key characteristics of PE/SiO2 and AGM separators, respectively.
- Assuming 1.5 m^2 of separator in a Pb-acid battery, there will be ~ 100-350 g of silica in a battery, dependent upon whether a PE/SiO2 or AGM separator is used.
- While silica is generally stable in sulfuric acid, a Pb-acid battery can undergo severe stratification, resulting in dissolution of silica into the electrolyte.
- ENTEK looks forward to working with manufacturers to further optimize the value proposition of Pb-acid batteries.

THANK YOU!

VISIT:
www.entek.com

ELBC
6–9 September
Lyon, France 2022