# GravityGuard™

## An Additive for EFB Technology and Deep-Cycle Applications for Electrolyte Stratification Reduction


Working Together to Delight Our Customers & Drive the Advancement of Lead Acid Batteries

90 YEARS INDUSTRY LEADERSHIP

19 ABC 19th Asian Battery Conference & Exhibition

HAMMOND PERFORMANCE ADDITIVES

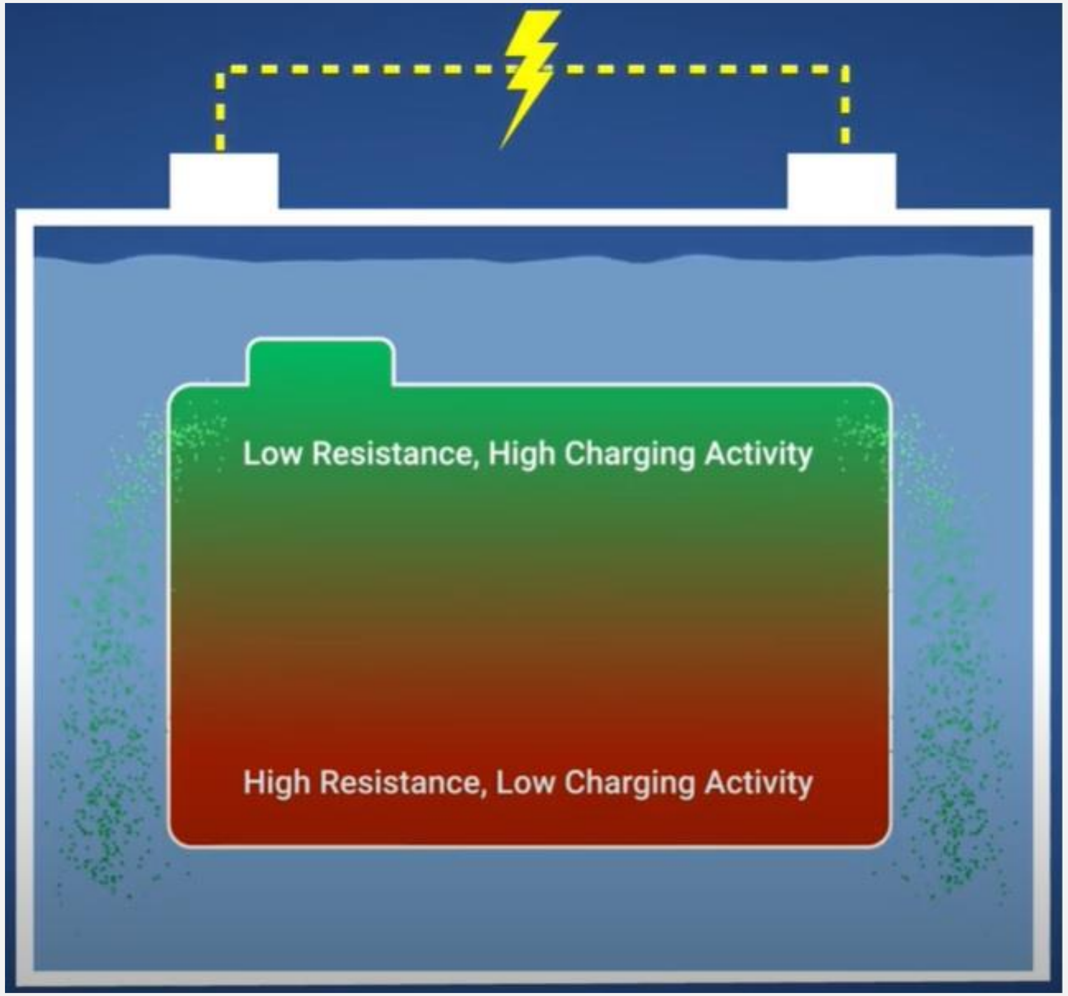
# An Age-Old Problem

Stratification of Electrolyte is as old as Lead Acid Battery Technology

Effects Batteries under heavy cycling duty at low states of charge or if recharge is inadequate

Higher density acid is expelled from the Active Material during charging.

Heavier acid sinks to bottom of cell case and as charging continues or battery sits idle after insufficient charging a density gradient is formed



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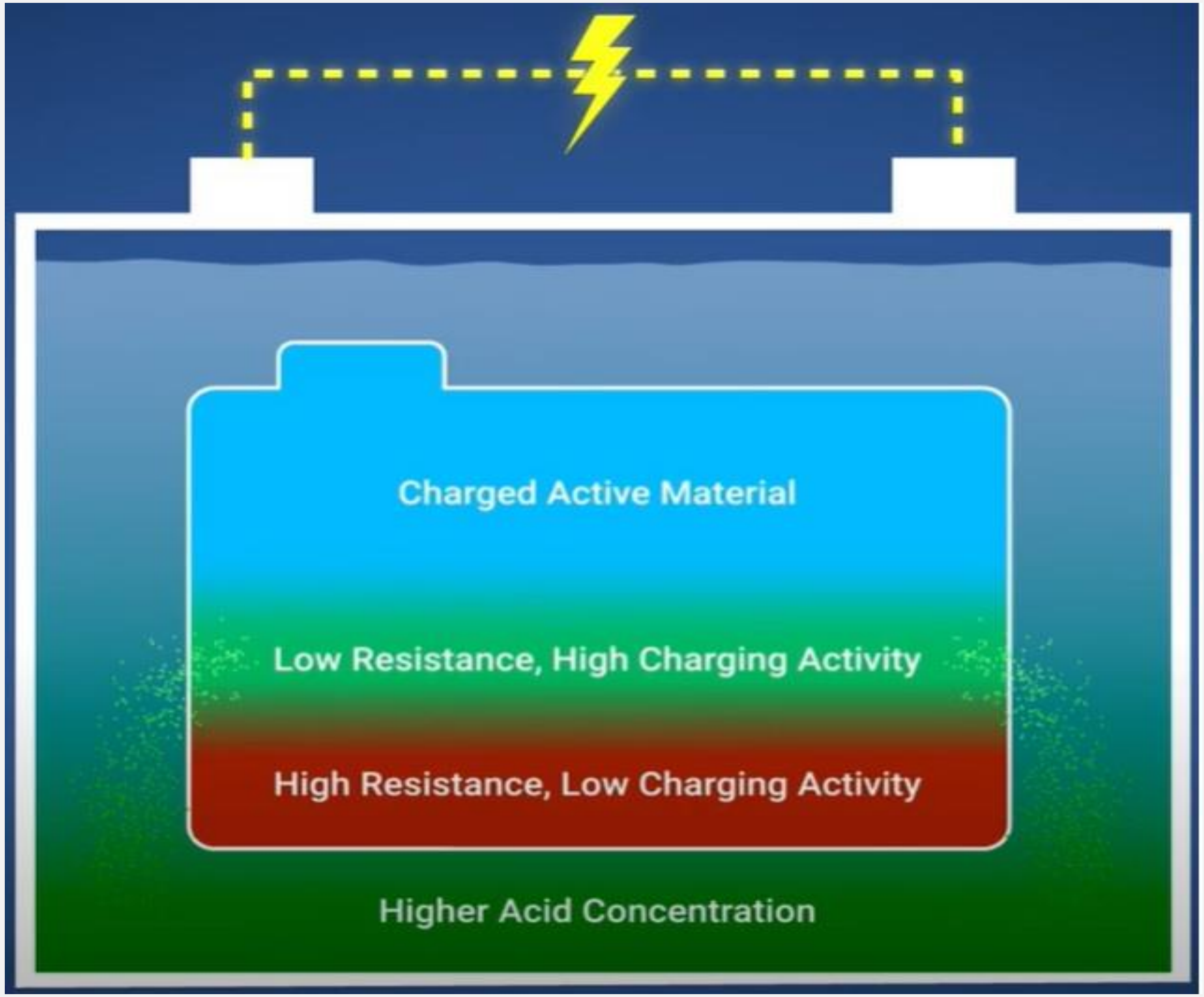
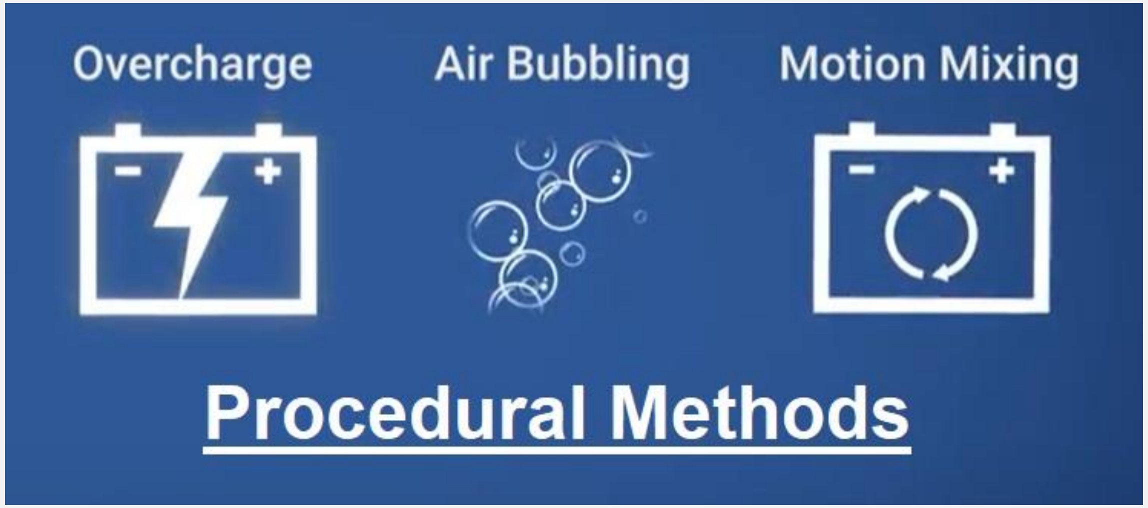
# Harmful Effects of Stratification

## Stratification Contributes To:

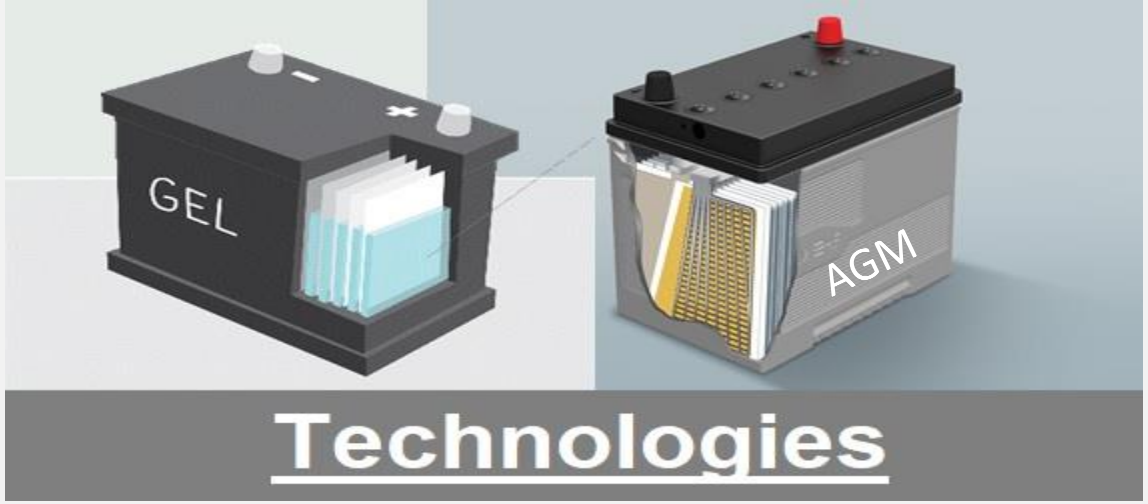
- Decreased Cycle Life
- Unequal Charge Across Plates
- Increased Corrosion
- Reduced Cold Crank
- Active Material Shedding
- Poor Overall Battery Performance



# Current Solutions to Stratification

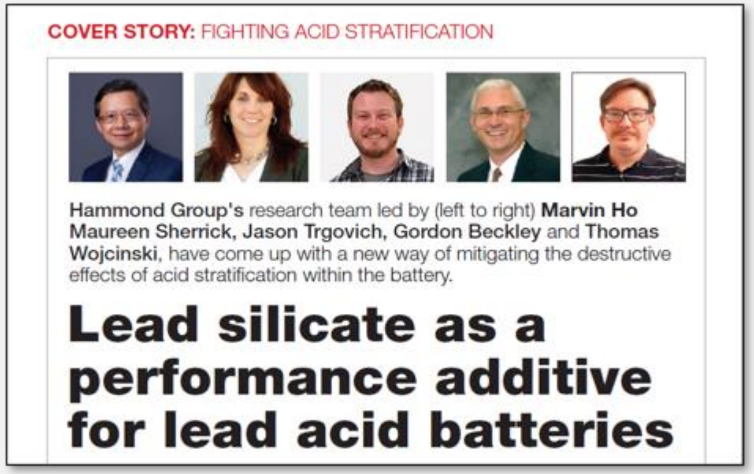



- Equalization Charging
  - Induces gassing to mix electrolyte
- Air Bubbling
  - Blowing compressed air through cell to cause mixing
- Shaking
  - Mixing by mechanical force
- Drawbacks
  - Increased abuse to battery and shorter life




- Gel Electrolyte
  - Form silica-sol gel from liquid electrolyte
- Glass Mat Separator
  - Use absorbent glass sponge separator
- Both seek to immobilize acid
- Drawbacks
  - More sensitive to abusive charging
  - 2 to 5 X the cost of typical flooded cells

# Innovation Through New Materials
# GravityGuard™

**COVER STORY:** FIGHTING ACID STRATIFICATION

**Hammond Group's** research team led by (left to right) **Marvin Ho Maureen Sherrick, Jason Trgovich, Gordon Beckley** and **Thomas Wojcinski**, have come up with a new way of mitigating the destructive effects of acid stratification within the battery.

**Lead silicate as a performance additive for lead acid batteries**

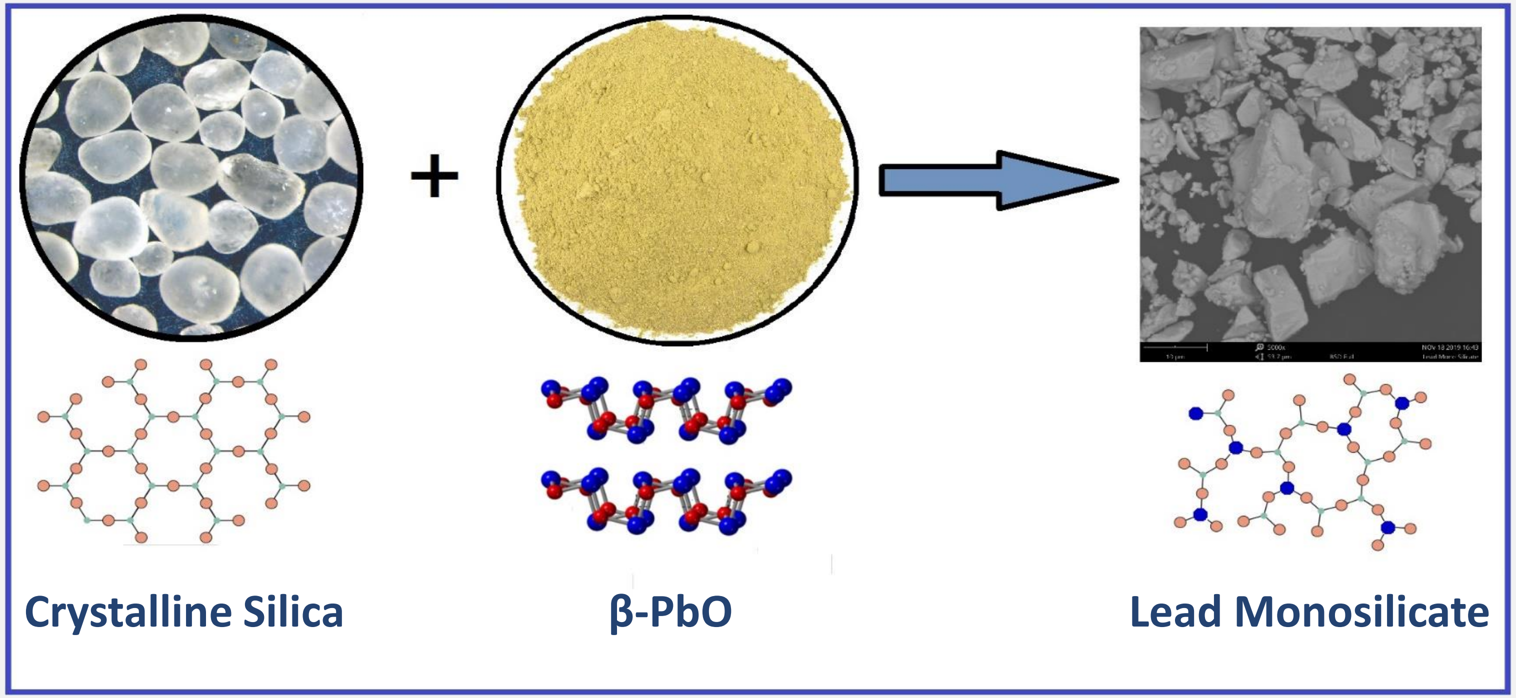

HGI Research Center began evaluation of Metal Silicate materials in 2018.

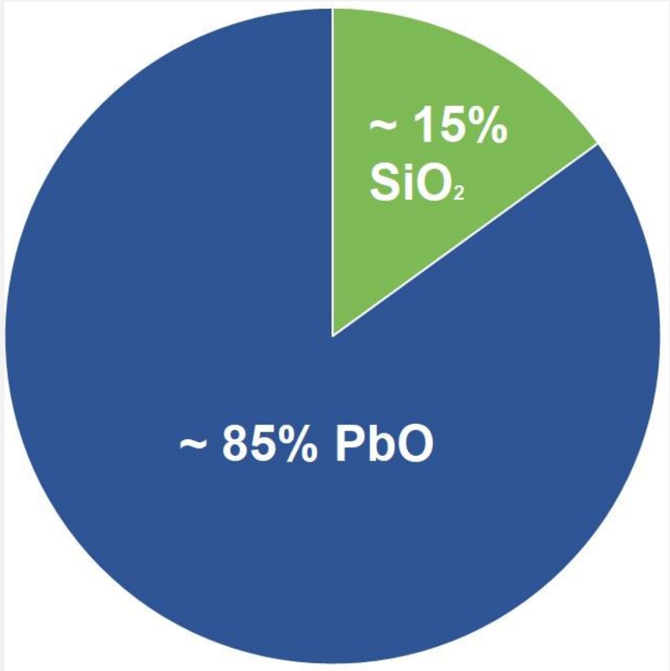
Discovery that Lead Silicates react with $H_2SO_4$ slowly and create gel structures plus $PbSO_4$.

These lead silicate materials could be a beneficial solution to the stratification problem.

Patent pending finding was awarded the 2021 BCI Sally Breidegam Miksiewicz prize for Innovation

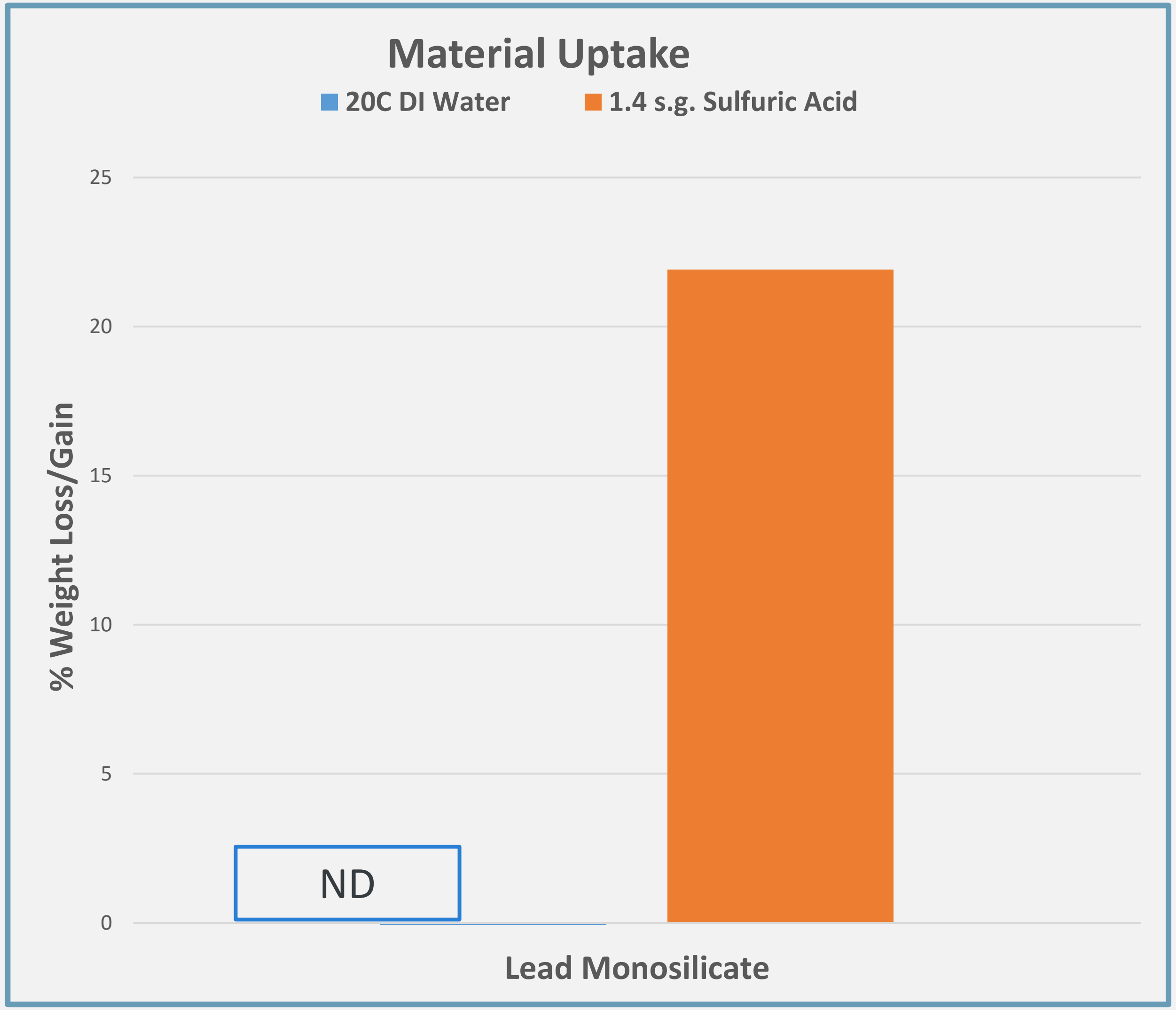
# Material Composition



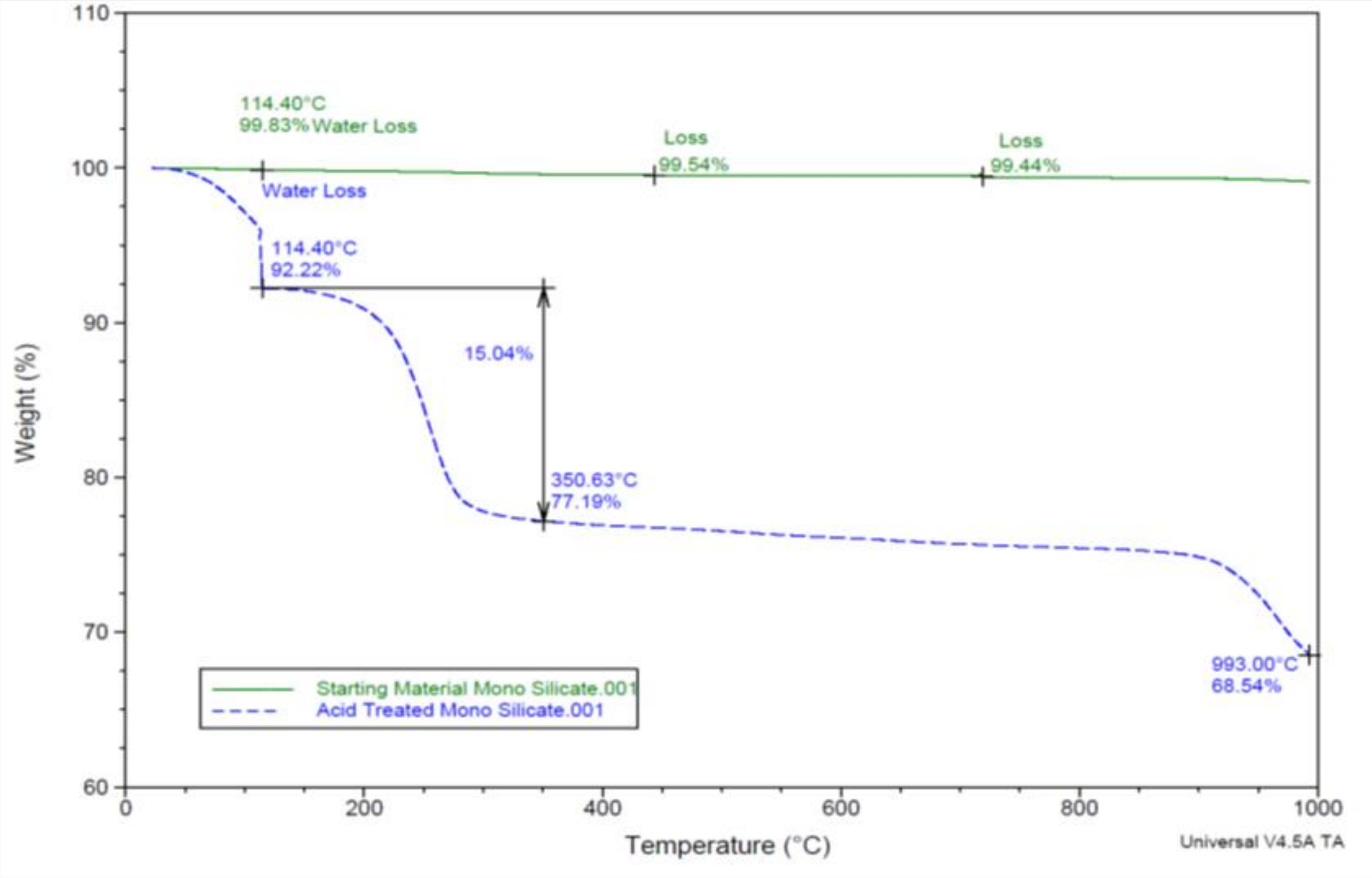

- Two main forms of lead silicate have been produced and evaluated by HGI: Lead Monosilicate & Lead Bisilicate
- Through experimental testing lead monosilicate was determined to be the most beneficial to the LAB
- The material is an amorphous glassy composition consisting of about ~ 15% Silica ($SiO_2$) with the remainder being β-PbO (PbO ~ 85%)
- Key material characteristics include a high composition of PbO relative to $SiO_2$, similar material density to lead oxide, low levels of harmful impurities, and insertion of Si into the PbO structure allowing for acid absorbing properties.

# Lead Silicate Reactions with Water and with Acid




- Initial Beaker Test –
  - Lead Monosilicate soaked in water or $H_2SO_4$
  - Samples filtered and dried
- Lead Monosilicate took up a considerable amount of weight upon reaction with sulfuric acid.
- Similar weight gain did not occur with DI Water
- Unlike fume silica, lead silicate does not react with water and its reaction rate with sulfuric acid is slow

# TGA analysis of Acid Washed Lead Monosilicate

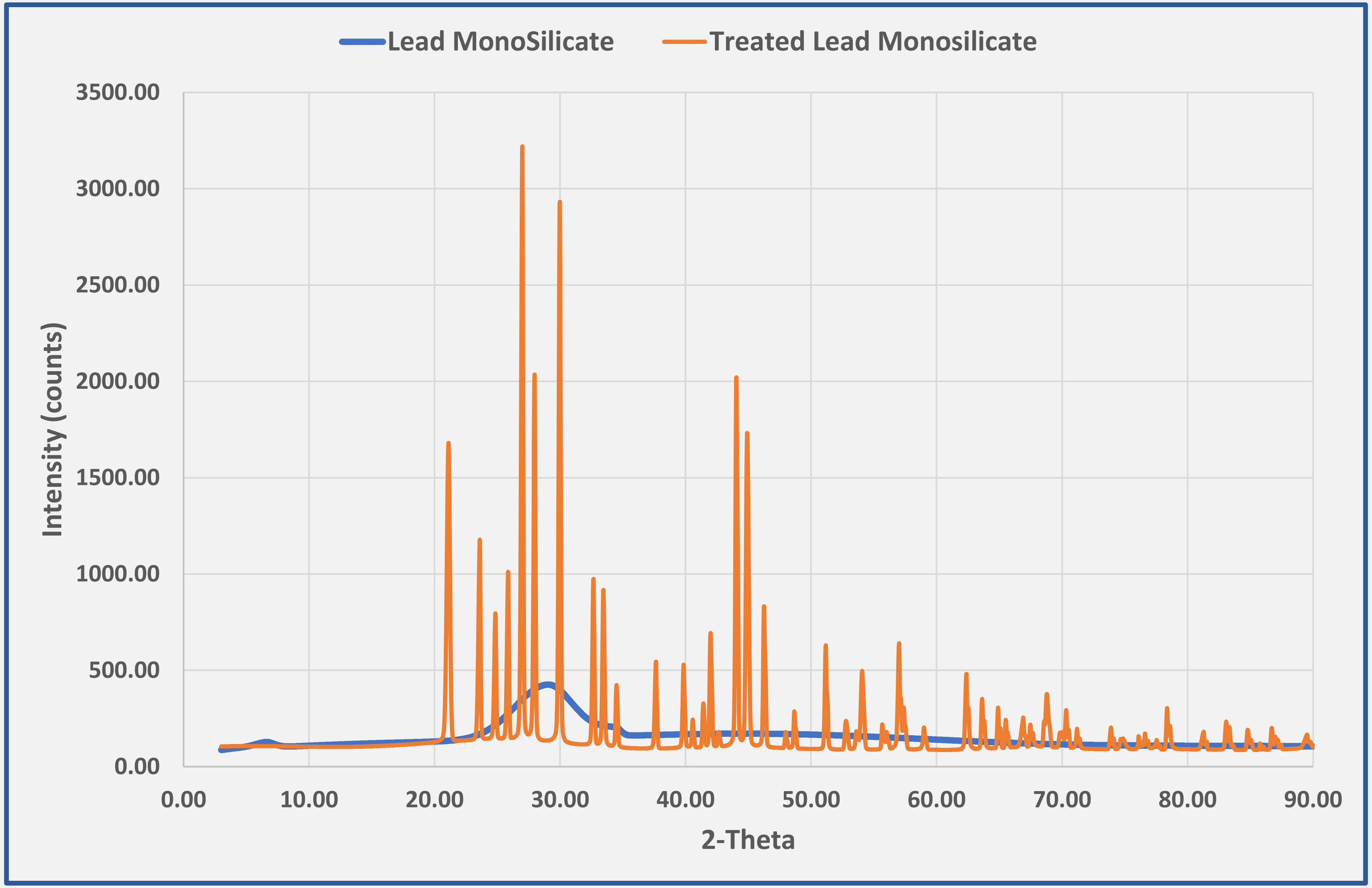



**TGA Analysis of the Raw Un-Washed Material and Acid Washed Products of Lead Monosilicate show a clear difference in weight loss characteristics**

**Un-washed base material shows very little weight loss up to 1000°C.**

**Treated Monosilicate shows loss of excess weight at temperatures corresponding to water vaporization (100°C) and sulfuric acid decomposition (>127°C for 50 wt.% $H_2SO_4$)**

# X-ray Diffraction Patterns of Washed & Un-Washed Lead Monosilicate

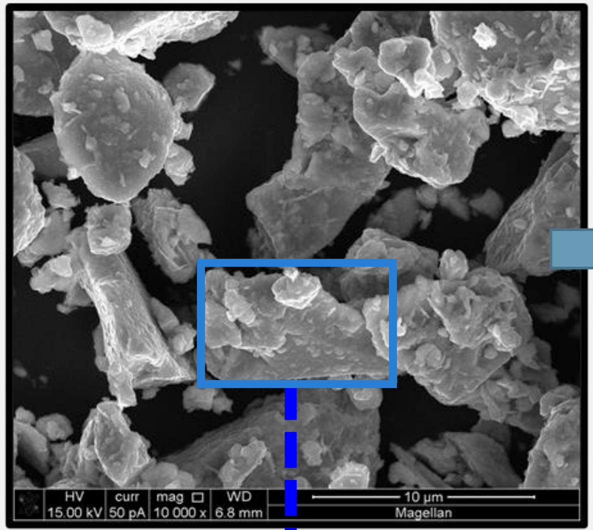



**Both the Raw Base Material and the Acid Washed Products were examined via XRD after drying**

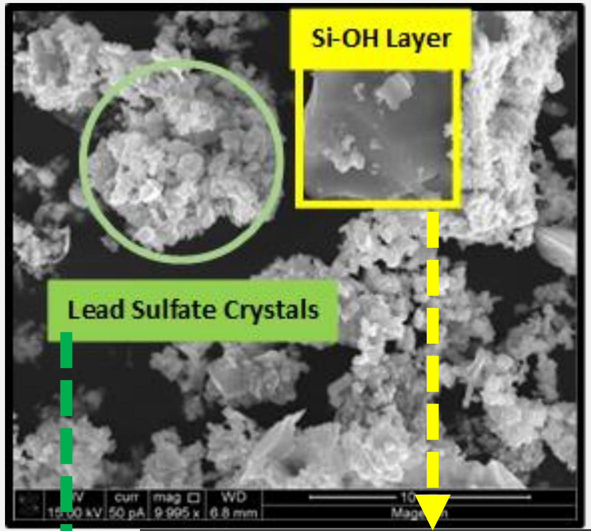
**A clear change in the crystalline structure of the Monosilicate sample was seen, shifting from Amorphous to more Crystalline**

**Comparison / Pattern Fitting of the Washed Products Scan shows good agreement with literature values for diffraction peaks of lead sulfate**

# SEM / EDS Analysis of Lead Silicate after Reaction with Sulfuric Acid

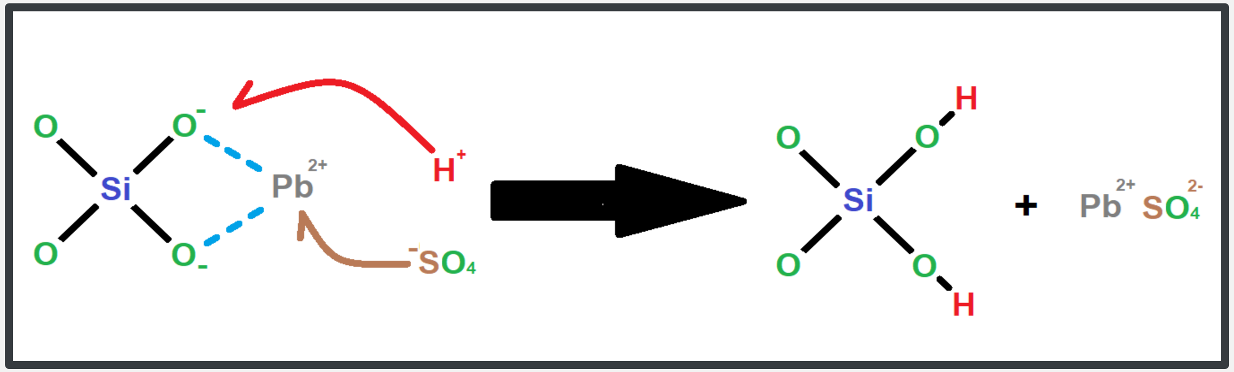



| Lead Monosilicate – Starting Material UnWashed | |
|---|---|
| Element Symbol | Atomic Conc. (%) |
| O | 55.9 |
| Pb | 30.1 |
| Si | 14.0 |




| Acid Treated Lead Monosilicate – Suspected Si-OH Particle | |
|---|---|
| Element Symbol | Atomic Conc. (%) |
| O | 62.6 |
| Si | 23.1 |
| Pb | 6.2 |

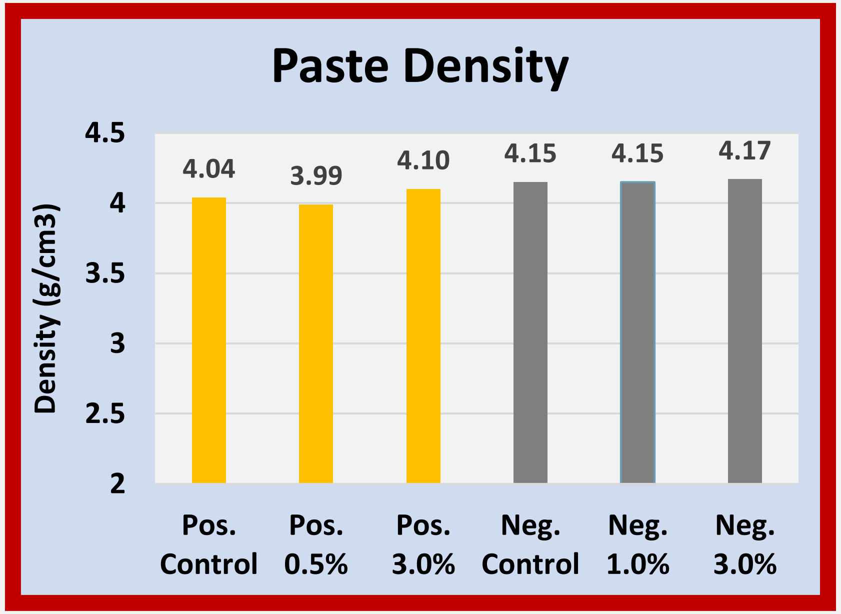
| Acid Washed Lead Monosilicate – Suspected Lead Sulfate Particles | |
|---|---|
| Element Symbol | Atomic Conc. (%) |
| O | 76.4 |
| Pb | 23.6 |
| Si | ND |



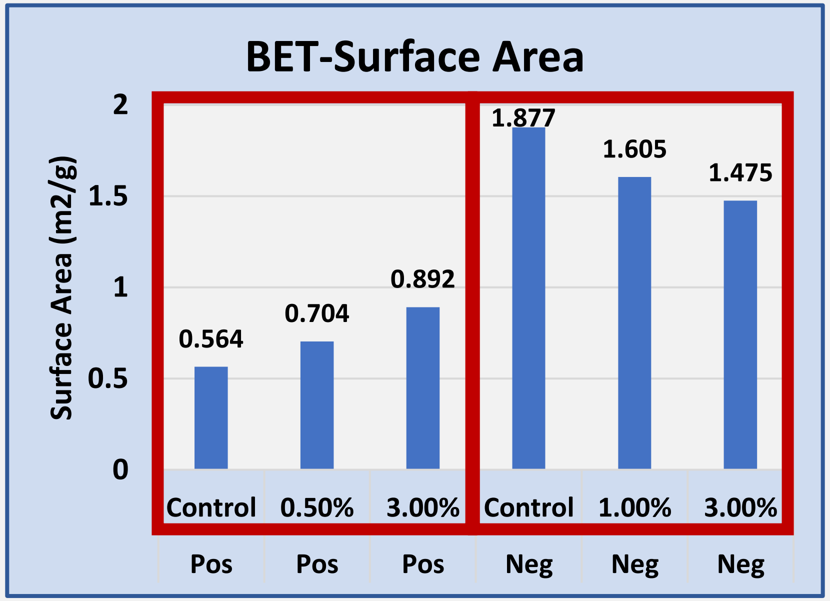

- Examination of the Unwashed and Washed product materials shows a change in crystal morphology.
- Elemental atomic concentrations of the raw Unwashed and Washed products, measured by Energy-dispersive X-ray spectroscopy (EDS), show differences in the amount of Pb or Si present in each of the new crystal structures observed.
- It is theorized that lead monosilicate reacts with sulfuric acid to form lead sulfate and silica gel structures

# Use of Lead Monosilicate as an Additive to the Battery Paste

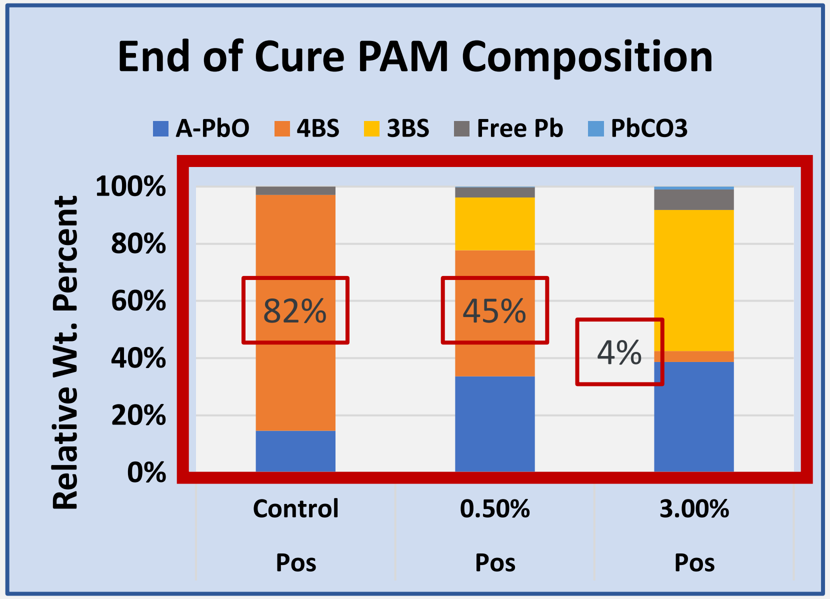
- Several typical positive (4BS cured) & negative paste mixes incorporating between 0.5 – 3.0% wt. Lead Monosilicate vs. lead oxide were prepared in the HGI Tech Center Laboratory using a CMC planetary mixer
- The resulting paste was cured at 55 °C for 72 Hours
- Analysis of the paste and dry cured materials yield the following data:




- No change (at loadings <3.0 wt.%) vs. Control




- Positive – Increased LMS = Increased SA
- Negative – Increased LMS = Decreased SA

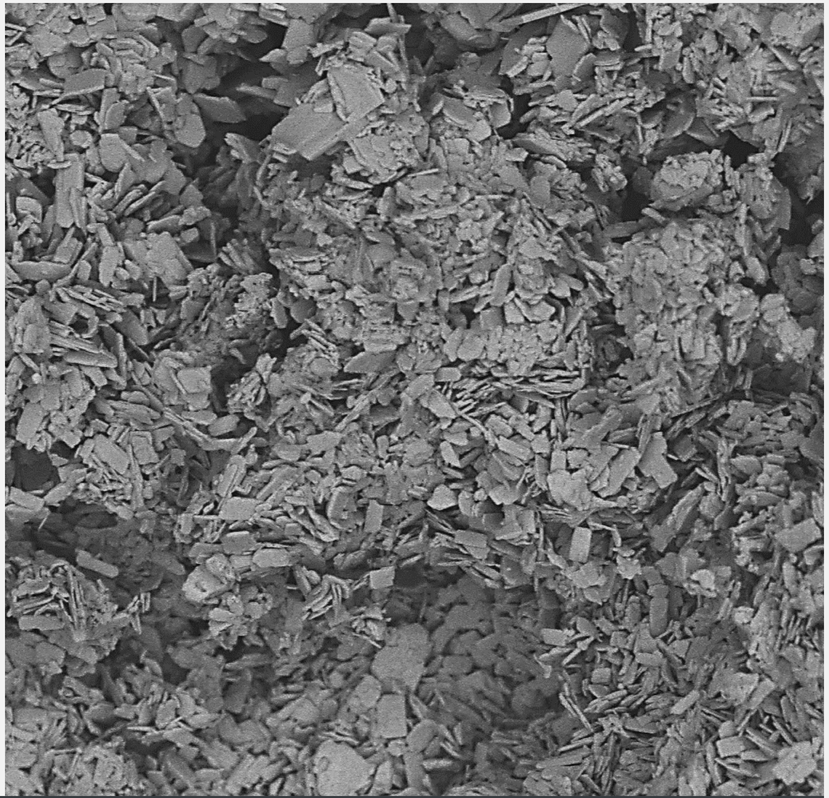



- Positive - Increased LMS = Decreased 4BS
- Negative – 3BS Similar in composition

# Cured Material
# SEM Images (Positives)

Control

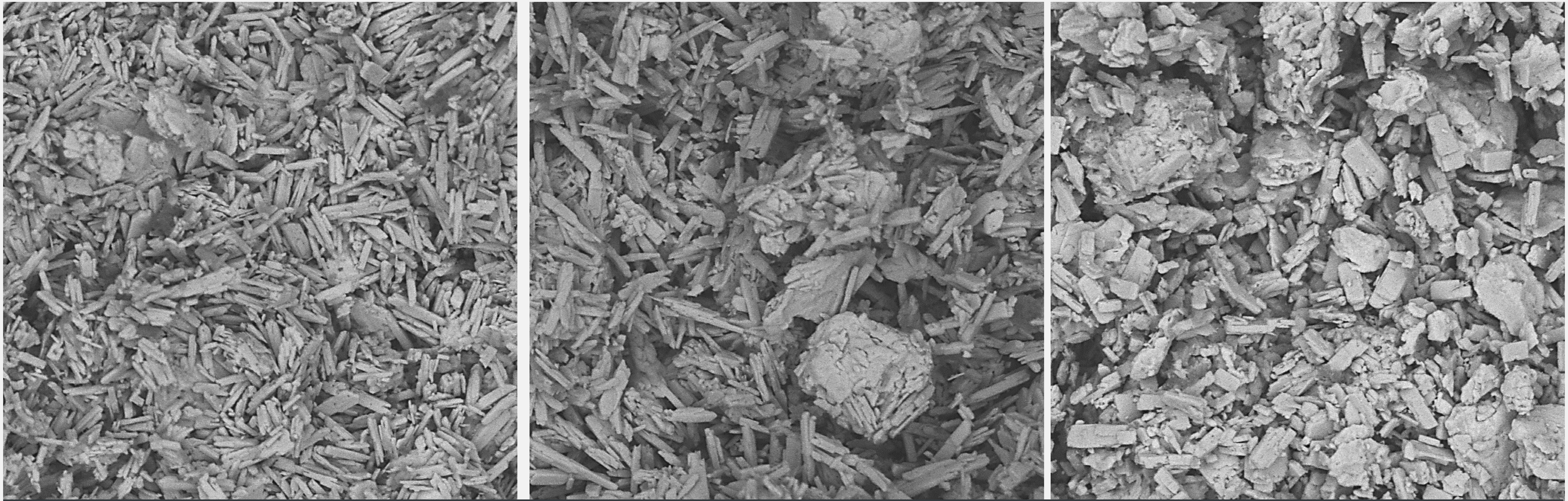
0.5% Lead Mono



3.0% Lead Mono

Crystal Structure of Cured Positive material shows good agreement with surface area measurements. Lead monosilicate influences the growth of 4BS crystals and modifies the overall crystal size of the cured material vs. control

# Cured Material
# SEM Images (Negatives)



Control | 0.5% Lead Mono | 3.0% Lead Mono

Crystal Structure of Cured Negative material also shows good agreement with surface area measurements. Lead monosilicate changes the morphology of 3BS crystals and modifies the overall crystal size of the cured material vs. control

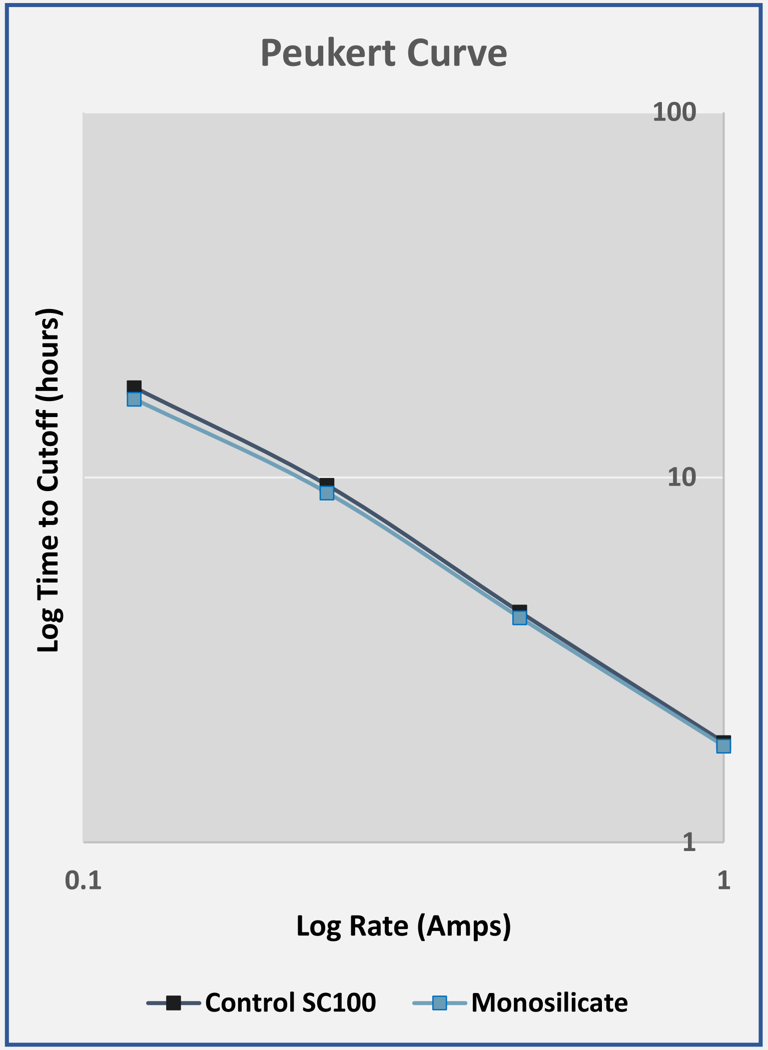
# Use of Lead Monosilicate as an Additive in Battery Cell Testing

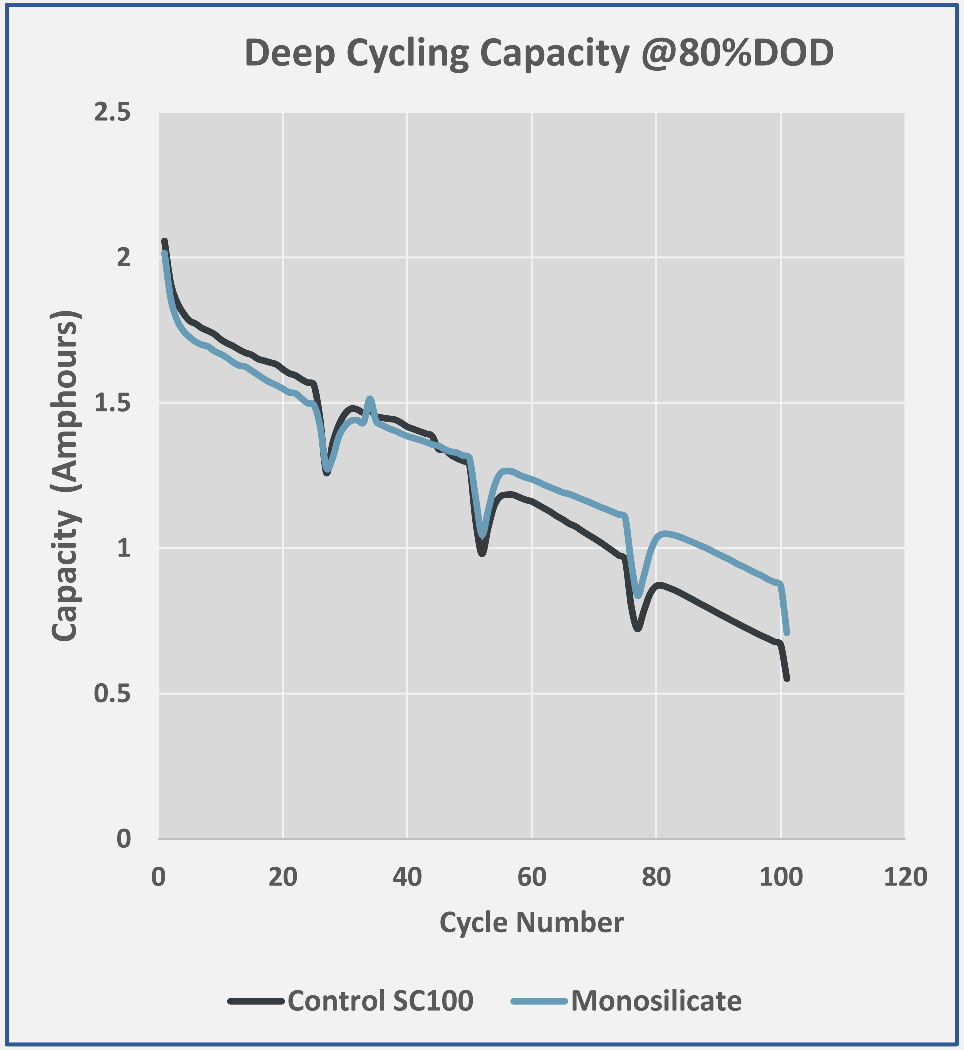
- Cell Testing Trials were performed to examine Lead Monosilicate's behavior in the Lead Acid Battery
- Lead Monosilicate was added into the negative and positive plates (both with & without 4BS seed crystals)
- Cells were built with a 3 Positive / 2 Negative element ratio with automotive-style separators following standard Hammond R&D procedures. Results are the average of 4 replicates.

| Curing Profile | Control | Experimental Positive | Experimental Negative |
|---|---|---|---|
| 55 °C Curing Temp<br>72 Hours | Positive<br>(1% 4BS Seeds – SureCure 100)<br>Negative<br>(HGI EFB Expander) | Mono vs. Oxide<br>(PAM: 1%) | Mono vs. Oxide<br>(NAM: 2%) |

# Peukert Curves/Cycling Test

## (Monosilicate: 1% in PAM and 2% in NAM)




- Control cells have 4BS structure in PAM
- Test Cells have 4BS seeds but little 4BS structure due to LMS
- All cells behave very similar in rating test and perform better in cycling test
- *There is no issue to use lead mono-silicate in both positive and negative plates*



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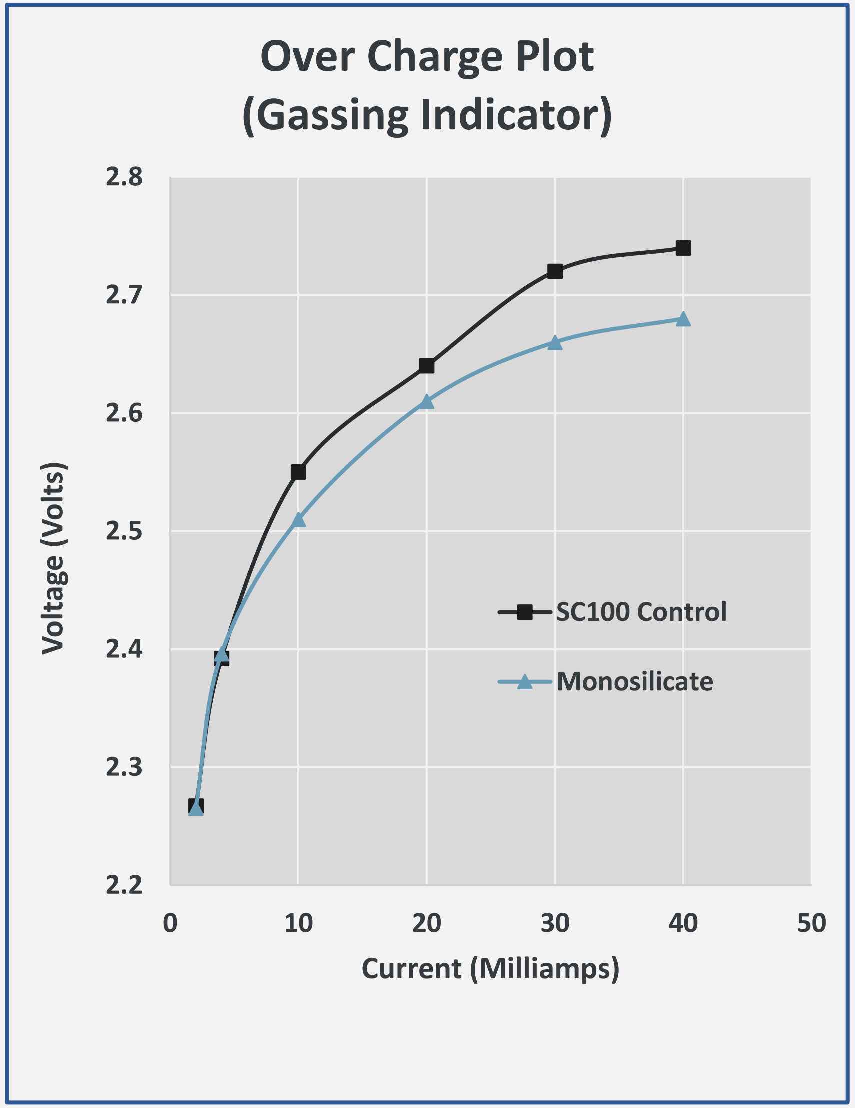
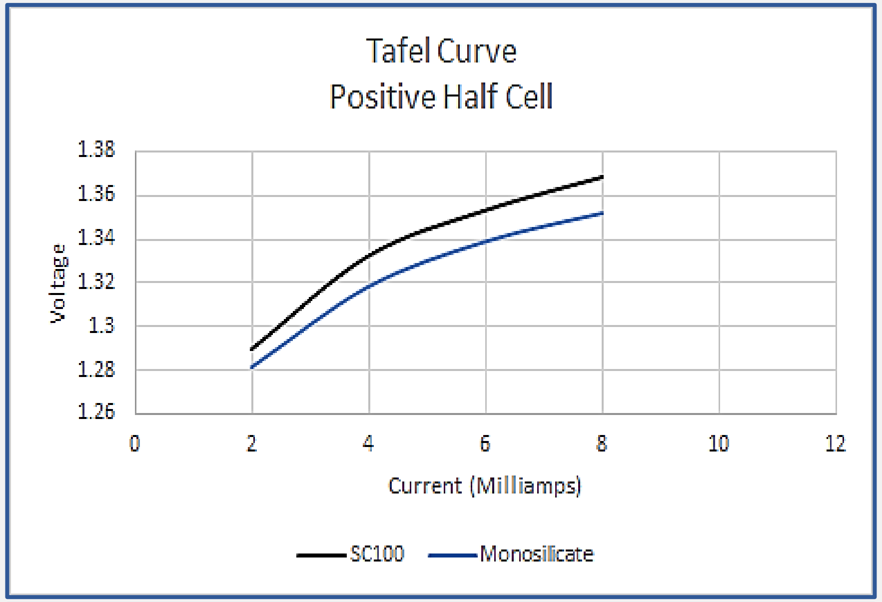
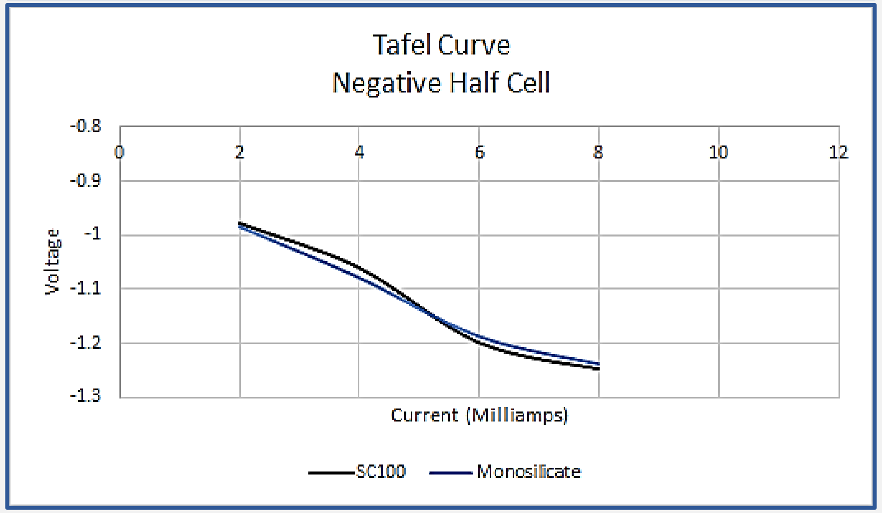
# Charging Characteristics – Over charge




- Positive plate with 1% lead mono-silicate shows higher gassing rate
- It is due to the lower half potential on positive plate (more oxygen evolution)
- This will improve the overall charge acceptance

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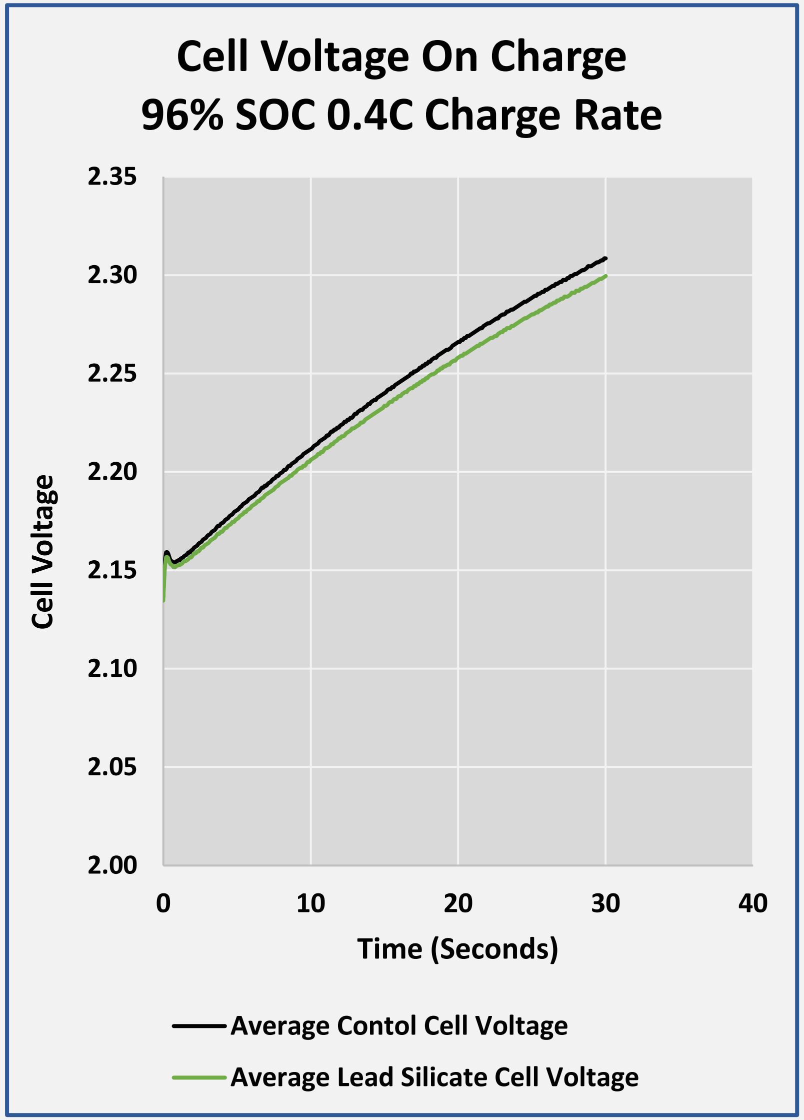
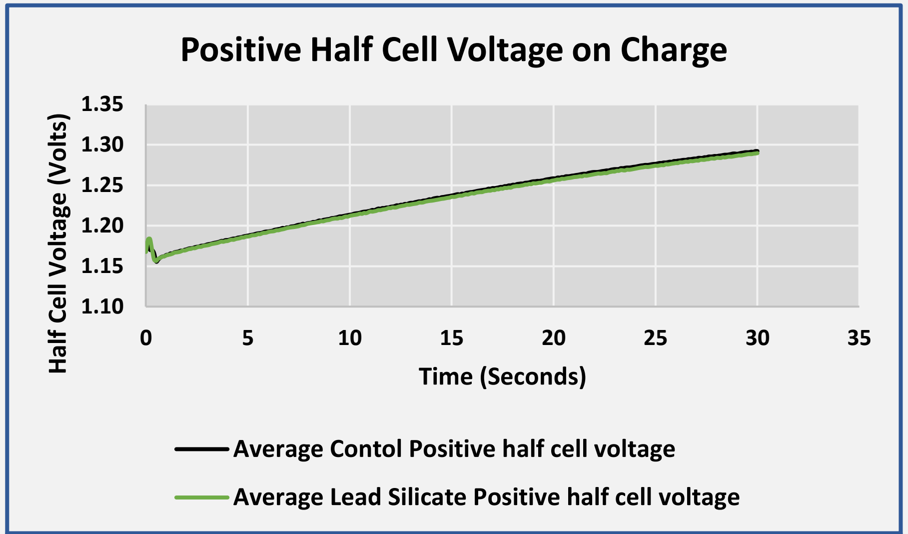
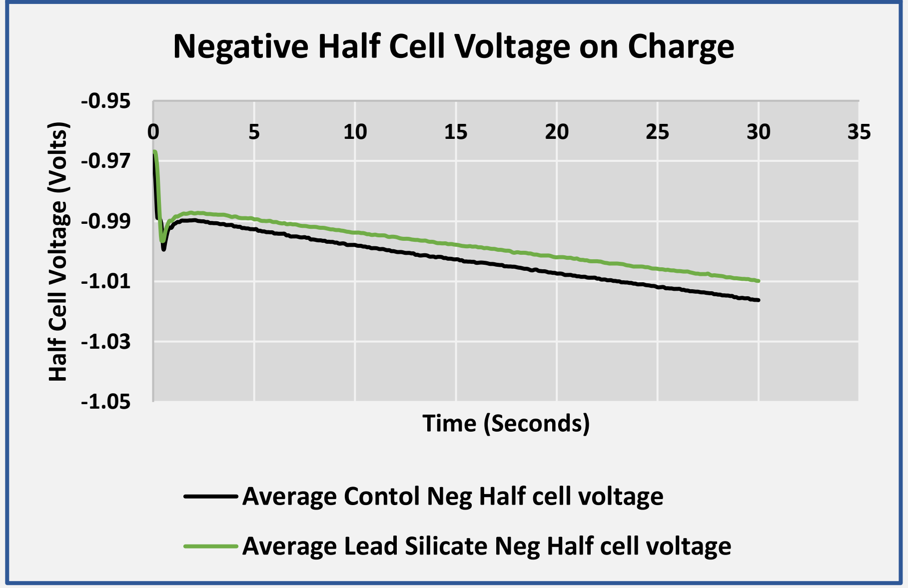
# Charging Characteristics – 0.4C @96%SOC

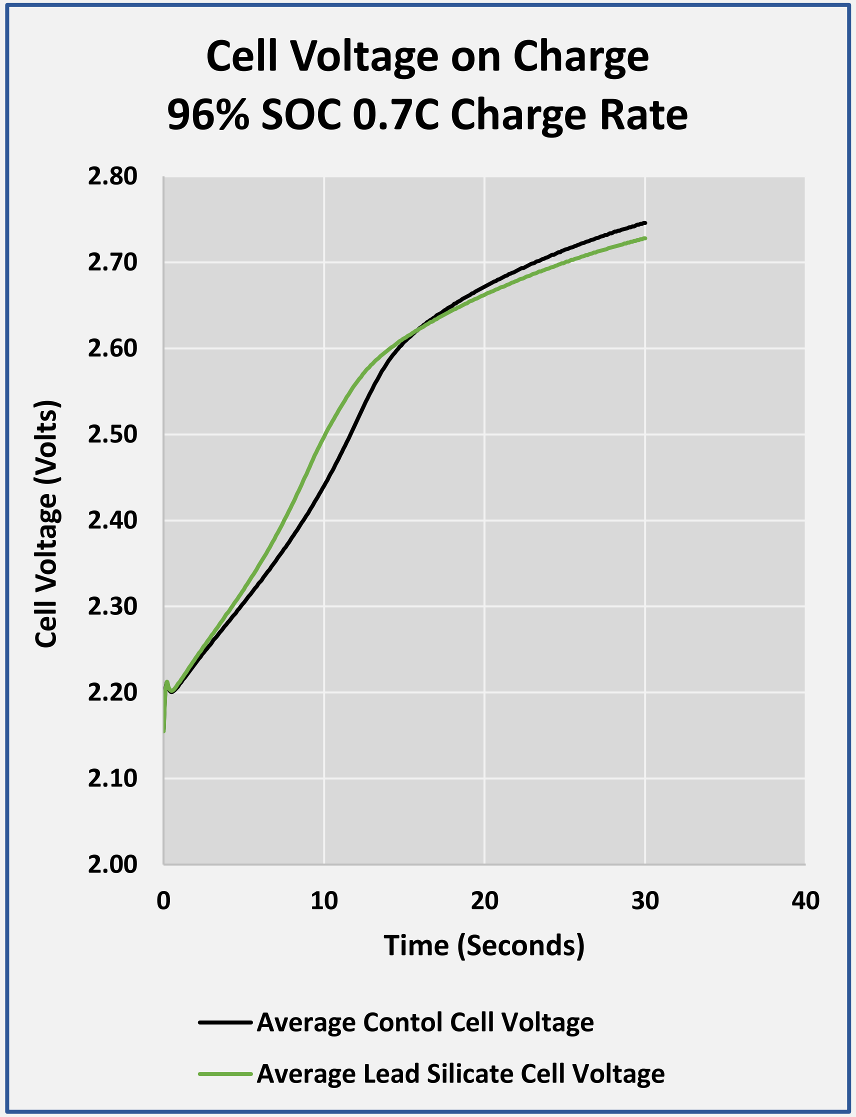


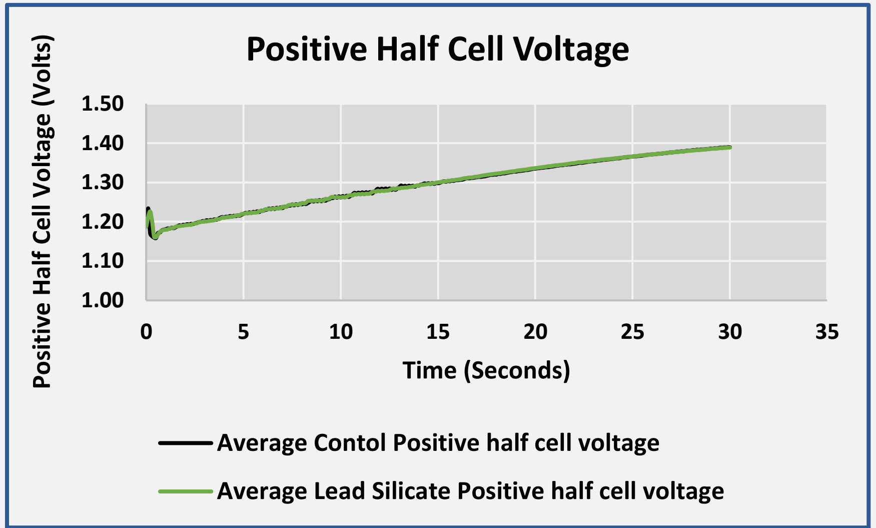



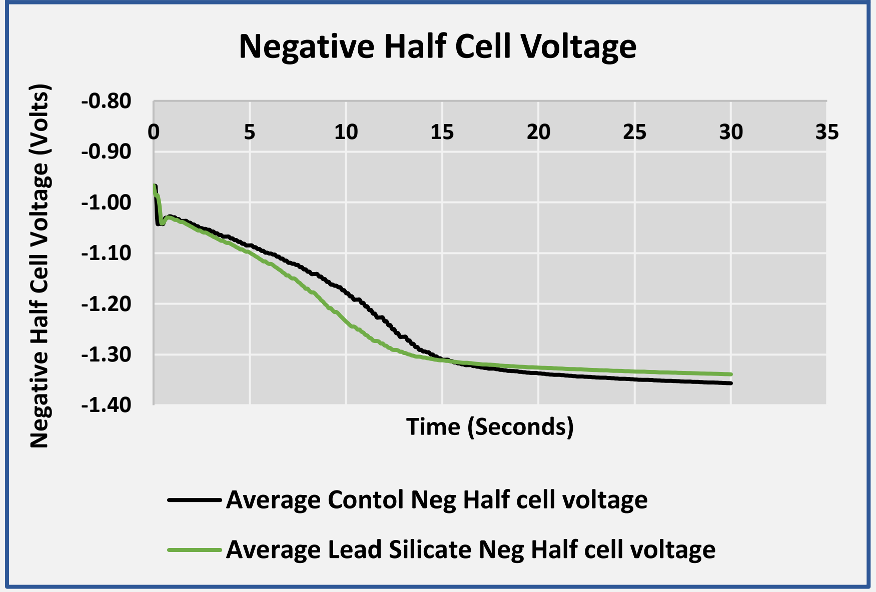




- Cell with lead mono-silicate shows better charge acceptance at 96%SOC
- The limiting factor is on negative plate (depolarization more)

# Charging Characteristics – 0.7C @96%SOC

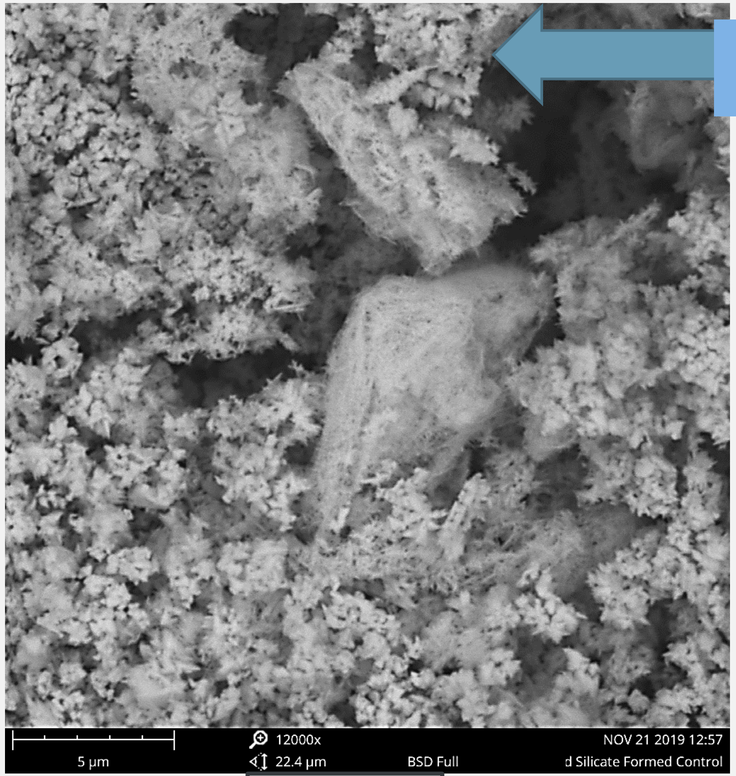


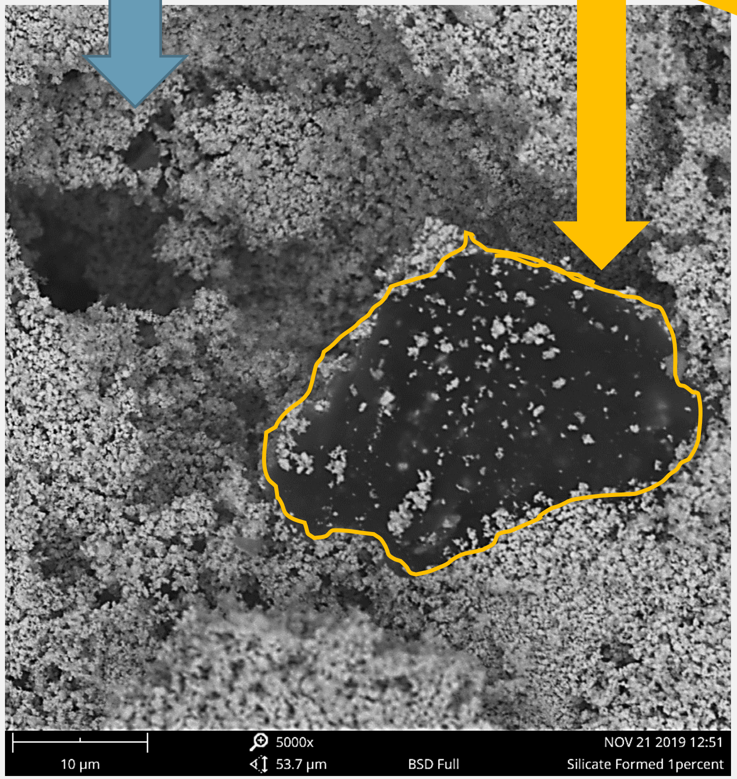




- Cell with lead mono-silicate show better charge acceptance at 96%SOC under high charge rate (0.7C)
- The limiting factor is on negative plate once again (depolarization more)
- This characteristic could potentially lead to lower carbon loading in expander

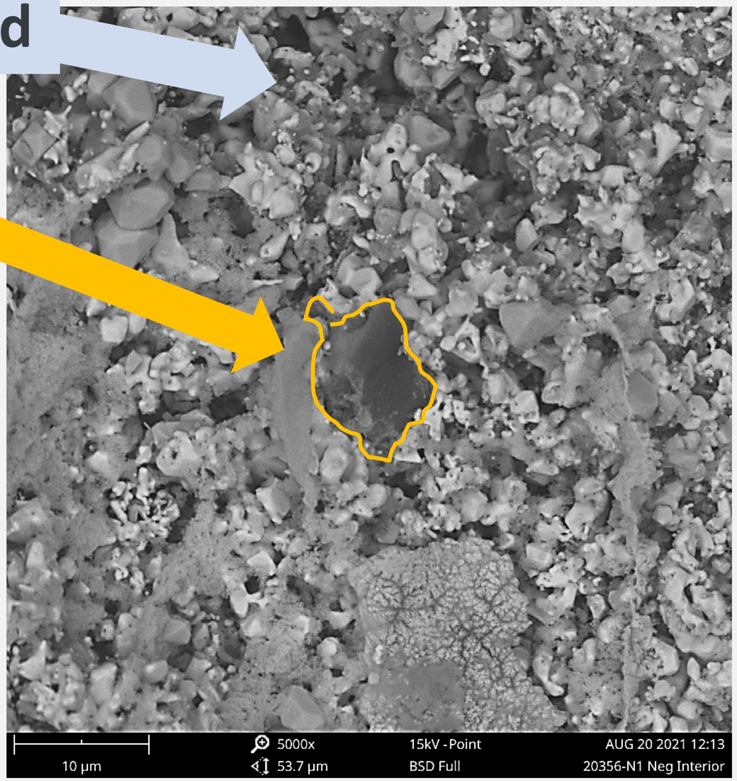
# SEM Images of Formed Plates




Control




PAM with 1% Lead Mono-silicate




NAM with 2% Lead Mono-silicate

# Full Scale Battery Test Results

**The following results are of lead monosilicate used as positive and negative active material additive by two Industry Partners**

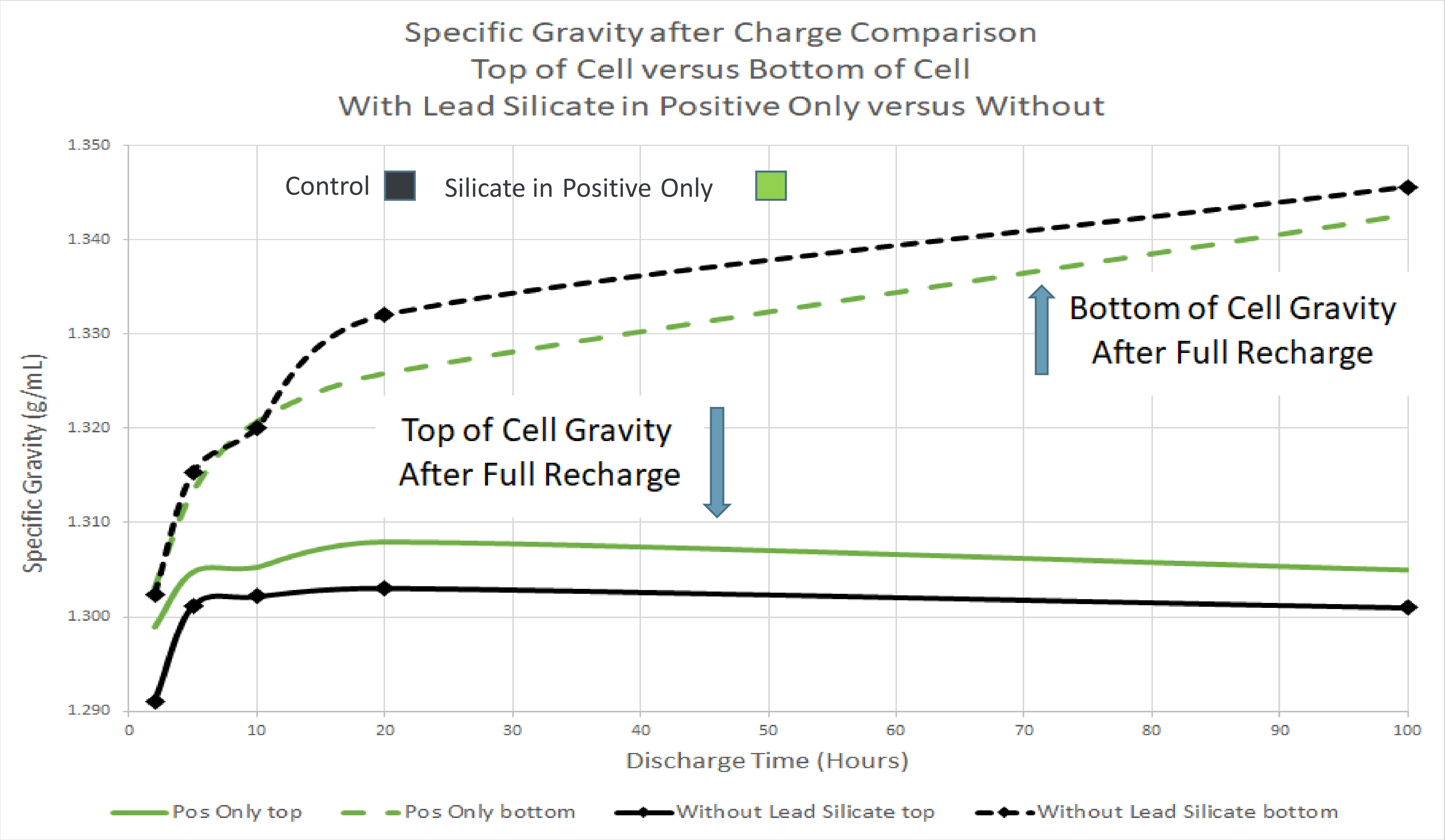
## Trial 1 –

- Effect on Acid Stratification
- Group 27 Flooded Marine Type Deep Cycle Batteries
- Series of discharges to 10.5v @26 °C
    - Before discharge, additional charging steps were applied to ensure no acid stratification.
    - ** Recharge profile: 115% of discharge energy + 15 Ah (boost charge step)
    - *** Specific gravity (SG) was measured by digital hydrometer in two cells. The results reported are the averaged value.

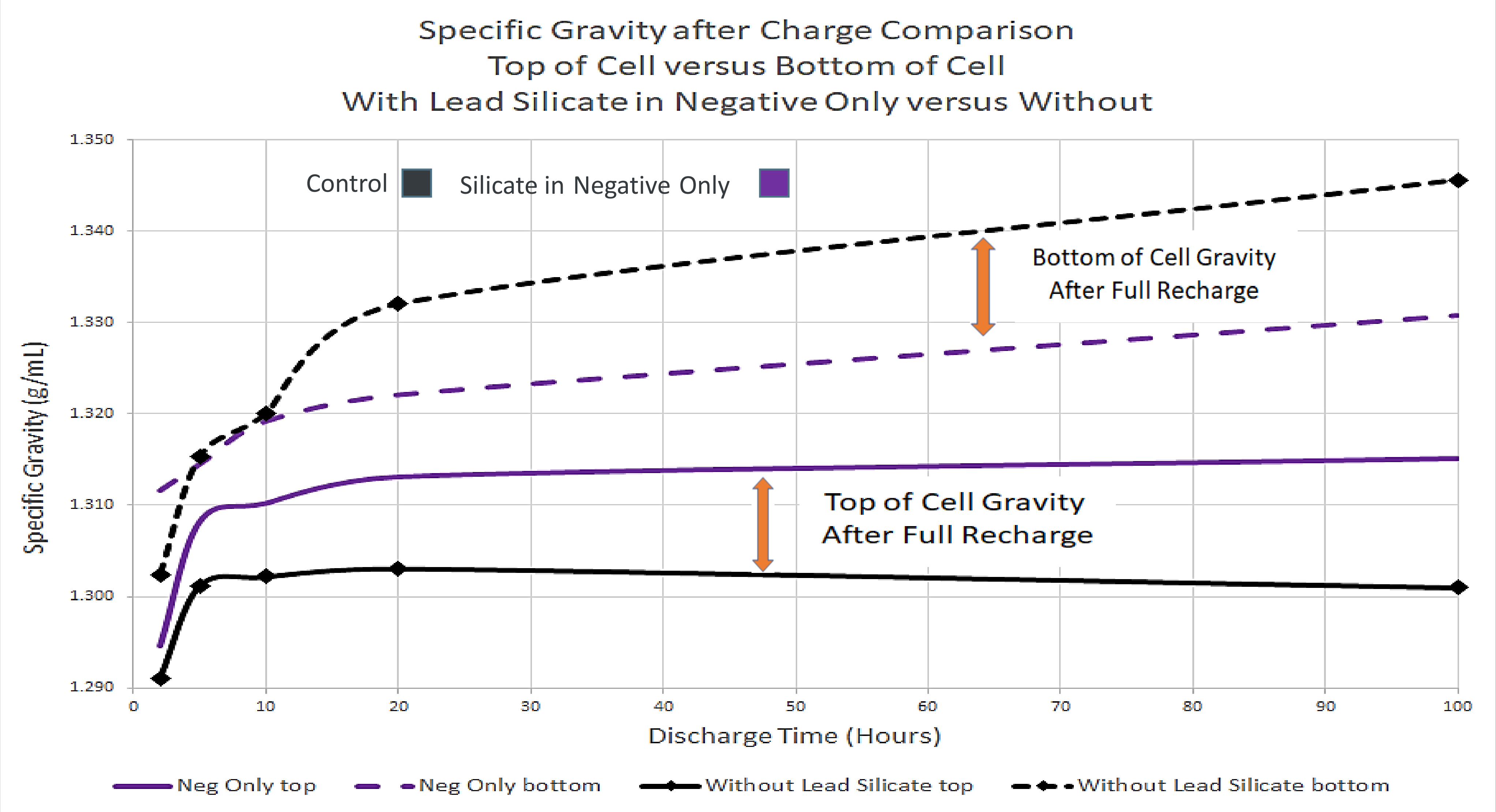
## Trial 2 –

- Test on Automotive OEM approved EFB-SLI type batteries.
- Testing Follows VW spec 75073
    - 20-hour Capacity Test (Section 7.1)
    - Cold Cranking Performance (Section 7.2)
    - Continuous 17.5% DoD Cycle Life Test (Section 7.6)

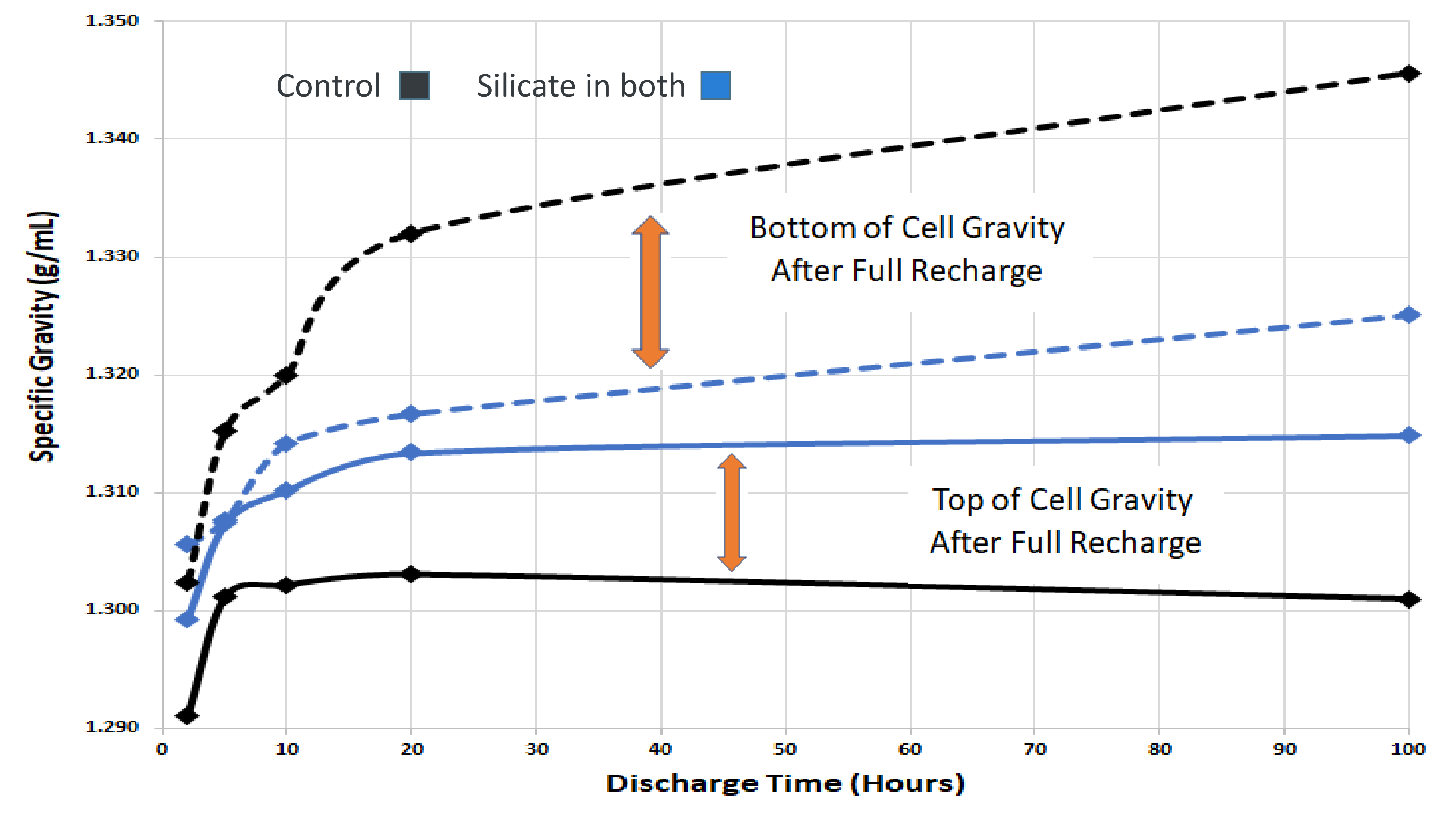
# Plant Scale Stratification Study: Group 27 Flooded Variable = 1% Lead Monosilicate in PAM Only



# Plant Scale Stratification Study: Group 27 Flooded Variable = 2% Lead MonoSilicate in NAM Only



# Plant Scale Stratification Study: Group 27 Flooded Variable = Lead Monosilicate in both the PAM & NAM



# Trial #2
# EFB Battery Test Results

| Test | Controls | 1% Lead Silicate, Positive Active Material | 1% Lead Silicate Positive & 2% Lead Silicate Negative, EFB02 Expander |
|---|---|---|---|
| C20 | 100% | 104% | 103% |
| CCA | 100% | 103% | 112% |
| 17.5% DOD, 26°C | 100% | 108% | 115% |

- VW spec 75073

# Conclusions/Benefits

- ❖Novel additive material is of similar composition to battery material matrix
- ❖GravityGuard™ creates gel-like domains in AMs as expected as well as non-harmful lead sulfate
- ❖GravityGuard™ reduces potential of 4BS crystal growth in PAM
- ❖The tests on charge characteristics indicate that cells with GravityGuard™ will have better charge acceptance
- ❖GravityGuard™ provides better overall capacity retention during cycle life
- ❖GravityGuard™ extends battery life by reducing stratification

# Thank You for your Attention!


GRAVITYGUARD
the cure for acid stratification

**customerservice@hmndgroup.com**

**Visit our Booth at the Virtual Asian Battery Conference**