# HAMMOND

## THE CHANGE CATALYST®

ENQIN GAO | HAMMOND RESEARCH & DEVELOPMENT DIRECTOR

SEPTEMBER 6, 2023



20TH ASIAN BATTERY
Conference and Exhibition

ESTABLISHED IN 1930

# WHO IS HAMMOND GROUP?

We are a specialty chemical company advancing lead-acid battery technology for advanced energy storage applications.

*We make:*

- **Advanced Expanders**
- **Battery Oxides**
- **Treated SureCure® (TTBLS)**
- **GravityGuard™ (Lead Silicate)**

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ORIGINAL & TREATED SURECURE®

# Tetrabasic Lead Sulfate Seed Crystals

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# HAMMOND R&D DEPARTMENT

**GORDON BECKLEY,** VP | Chief Operating Officer
B.S. Chemical Engineering – 42 years PbA battery exp., Gould, Gates Energy Products, GNB, Exide, GS Battery (JSB), Trojan

**ENQIN GAO,** Research & Development Director
B.S. Chemistry, M.S. Physical Chemistry, PhD studies in Materials Science and Engineering – 20 years PbA battery exp. Trojan Battery, Camel Group

**MARCO ROBOTI,** Materials Engineer
PhD Materials Engineering – 5 years PbA battery exp., Fiamm Energy Technology

**TOM WOJCINSKI,** Senior R&D Chemist
B.S. Chemistry – 20 years PbA battery additive experience HGI

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Metallurgist, Advanced Materials, Taguchi DOE
Lead-Acid Battery Expert - GNB Technologies

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**JOHN MILLER,** Industry Expert
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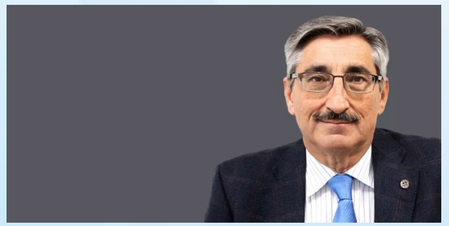
39 Years PbA Battery Industry; R&D & Engineering



**FRANCISCO TRINIDAD,** Industry Expert
PhD Electrochemistry, University of Madrid
Exide Technologies Europe – Director of Research
43 Years PbA Battery Industry; 24 articles,
65 presentations battery conferences, 14 patents

## THE FIRST STEP TO DEVELOPING THE NEXT GENERATION LEAD-ACID BATTERY:

# Positive Paste Structure

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# Background:

Adding small TTBLS (4BS ) crystals to positive paste has gained more acceptance in the lead acid industry. It eliminates the activation energy needed for 4BS formation and allows for a consistent optimized final particle/pore distribution in battery pastes. By increasing the PAM strength, it provides longer cycle life and cost savings due to the ability to reduce the density of lead in manufacturer's paste formulations.

From the successful 1st generation 4BS crystal SureCure® 100 (SC100), Hammond developed the next generation Treated SureCure®140 (TSC140). After years of testing, it maintains all the benefits of SC100 plus higher charge acceptance in formation and cycling.

# Background:

To better understand the effect of the positive paste structure's role in bipolar batteries, Hammond Group worked closely with Advanced Battery Concepts to evaluate the following positive pastes:

- 3BS no seed (regular 3BS paste )
- 4BS Steam Curing (steam cured 4BS paste)
- 4BS SureCure 100 (cured seeded 4BS paste with SureCure100 )
- 4BS Treated SureCure 140 (cured seeded 4BS by chemically treated 4BS seeds: Treated SureCure 140)

All batteries were manufactured based on current Advanced Battery Concepts process except 3BS no seed paste were cured and dried in lower temperatures to avoid 4BS crystal growth.

Full characterization of cured and formed PAM and battery tests were performed.

POSITIVE PASTE ADDITIVE STUDY

# Advanced Battery Concepts:

Special thanks to Advanced Battery Concepts for their support in this research project.

Advanced Battery Concepts


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## POSITIVE PASTE ADDITIVE STUDY

# Cured PAM XRD and BET:

| CURED PAM | 3BS | 4BS | α-PbO | β-PbO | BET ($m^2/g$) |
|---|---|---|---|---|---|
| 3BS No Seed | 40.4% | 11.0% | 43.0% | 5.6% | 1.05 |
| 4BS Steam Curing | 1.7% | 48.1% | 42.4% | 7.8% | 0.24 |
| 4BS SureCure100 | 3.8% | 65.9% | 26.4% | 3.9% | 0.35 |
| 4BS TreatedSureCure140 | 3.0% | 65.6% | 27.4% | 4.0% | 0.43 |

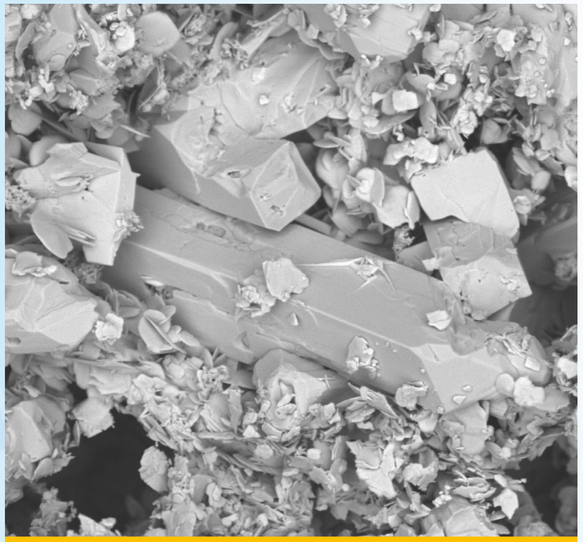
IN CURED PASTE:

- 3BS no seed cured paste has highest 3BS, α-PbO and BET surface area.
- 4BS Steam Curing has lowest BET surface area. Its low 4BS may be caused by test method variation.
- 4BS SureCure 100 and 4BS Treated SureCure 140 show highest 4BS content and medium BET surface area.

## POSITIVE PASTE ADDITIVE STUDY

# Cured PAM SEM:

3BS No Seed



4BS Steam Curing

4BS SureCure100

4BS TreatedSureCure140

IN CURED PASTE:

- 3BS no seed has small crystals with ~1 µm wide and ~4 µm long.
- 4BS Steam Curing has very big 4BS crystals more than 50µm long and 15 µm wide.
- 4BS SureCure 100 and 4BS Treated SureCure 140 show consistent well controlled 4BS crystals with 8~20µm long and 2~4 µm wide.

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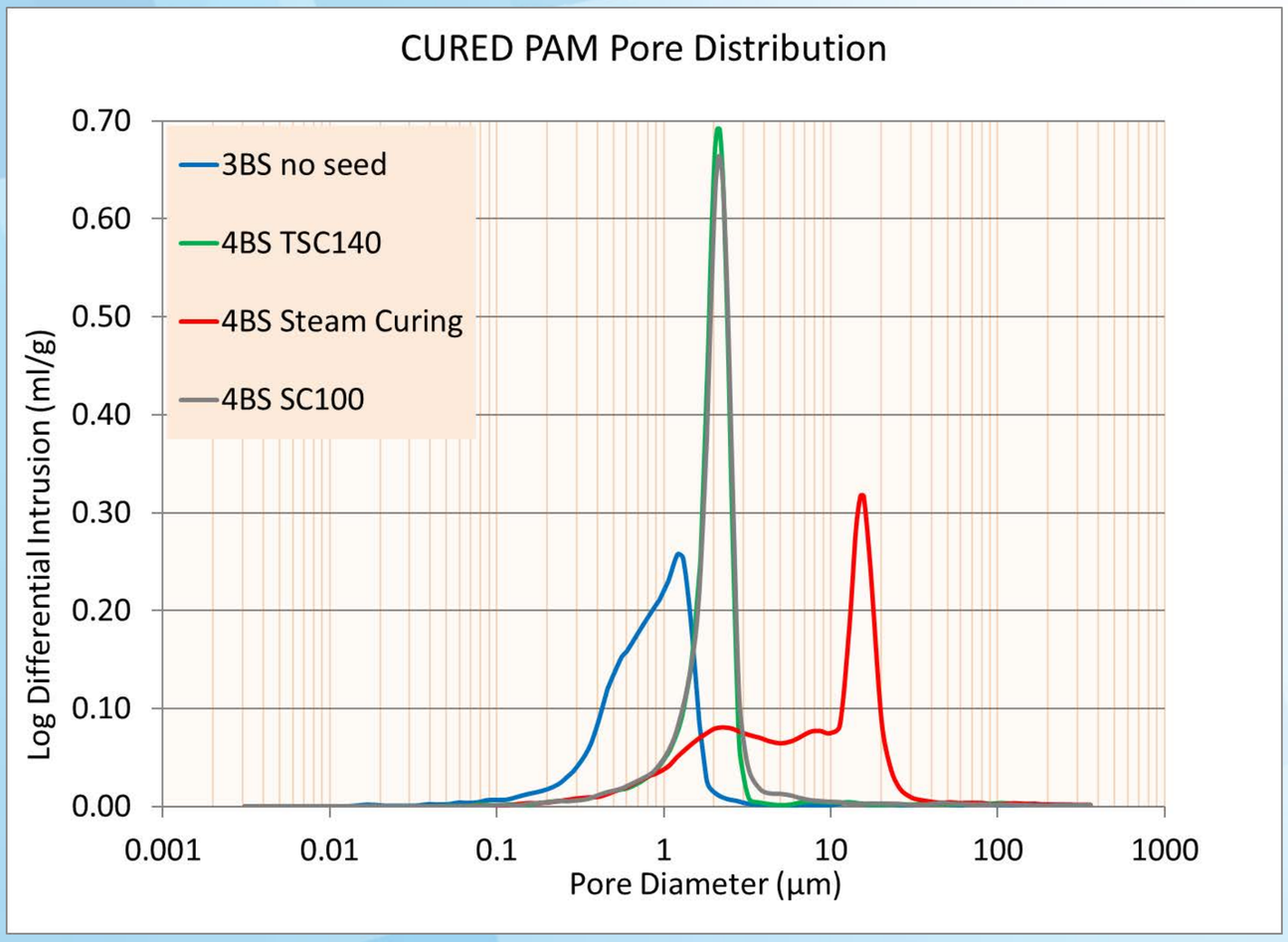
## POSITIVE PASTE ADDITIVE STUDY

# Cured PAM Pore Distribution:




IN CURED PASTE:

- 3BS no seed has smallest pores
- 4BS Steam Curing has very large pores
- 4BS SureCure 100 and 4BS Treated SureCure 140 achieve tight pore distribution and consistency.

## POSITIVE PASTE ADDITIVE STUDY

# Hg Porosimetry of Cured PAM:

| POROSITY CURED PAM | SA ($m^2/g$) | PORE SIZE (µm) | PORE VOLUME (ml/g) | POROSITY % |
|---|---|---|---|---|
| 3BS No Seed | 0.97 | 0.86 | 0.14 | 50.4 |
| 4BS Steam Curing | 0.22 | 7.97 | 0.15 | 53.1 |
| 4BS SureCure100 | 0.38 | 2.10 | 0.15 | 54.9 |
| 4BS TreatedSureCure140 | 0.40 | 2.06 | 0.15 | 53.0 |

IN CURED PASTE: Total pore volume for all the paste formula are very close: 0.14 to 0.15 ml/g.

- 3BS no seed has highest pore surface area and smallest average pore size.
- 4BS Steam Curing has smallest pore surface area and largest average pore size.
- **4BS SureCure 100 and 4BS Treated SureCure 140 provides pore surface area and average pore size.**

## POSITIVE PASTE ADDITIVE STUDY

# Formed PAM XRD and BET:

| FORMED PAM | α-$PbO_2$ | β-$PbO_2$ | $PbSO_4$ | α-PbO | BET ($m^2/g$) |
|---|---|---|---|---|---|
| 3BS No Seed | 7.1% | 76.1% | 10.6% | 6.2% | 5.05 |
| 4BS Steam Curing | 7.0% | 80.5% | 5.8% | 6.7% | 8.45 |
| 4BS SureCure100 | 8.1% | 81.6% | 4.0% | 6.3% | 5.51 |
| 4BS TreatedSureCure140 | 8.3% | 82.1% | 2.6% | 6.9% | 5.94 |

IN FORMED PASTE:

- 3BS no seed Active Material has highest $PbSO_4$ and lowest BET surface area.
- 4BS Steam Curing has highest BET surface area and 2nd high $PbSO_4$.
- **4BS Treated SureCure 140 shows highest $PbO_2$ content, lowest $PbSO_4$, and medium BET surface area providing improved formation efficiency.**
- Wet chemical test confirmed the $PbSO_4$ sequence of above formulae.

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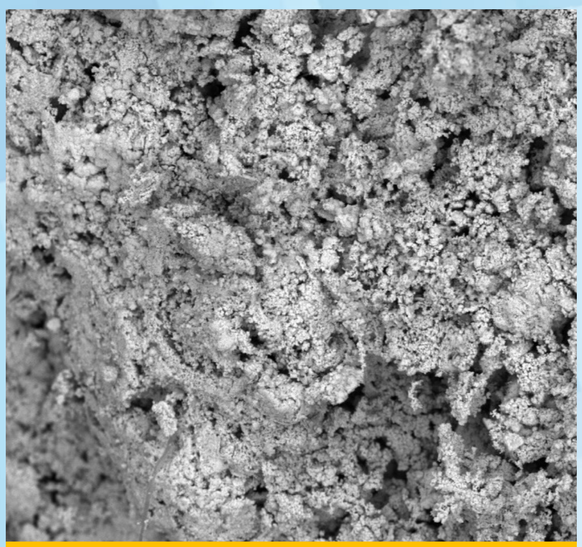
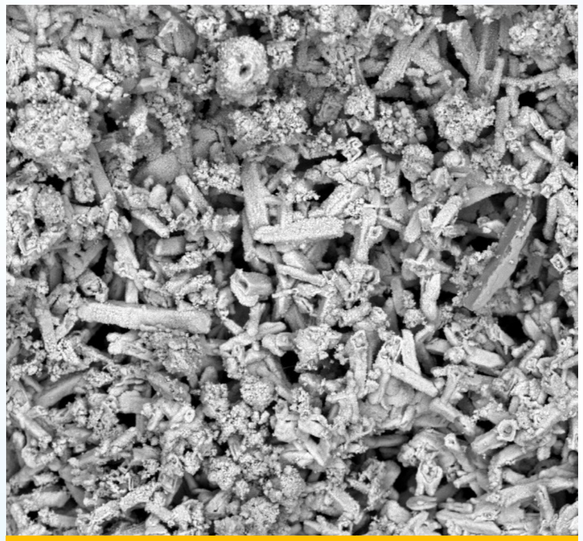
## POSITIVE PASTE ADDITIVE STUDY

# Formed PAM SEM:



3BS No Seed

4BS Steam Curing



4BS SureCure100

4BS TreatedSureCure140

IN FORMED PASTE: Formed Active Material to some extent inherited its cured paste Active Material structure/morphology.

- 3BS no seed has smallest crystals
- 4BS Steam Curing shows the morphology similar to its big 4BS crystals precursor with rough surface.
- **4BS SureCure 100 and 4BS Treated SureCure 140 maintains the strong Active Material structure after formation.**

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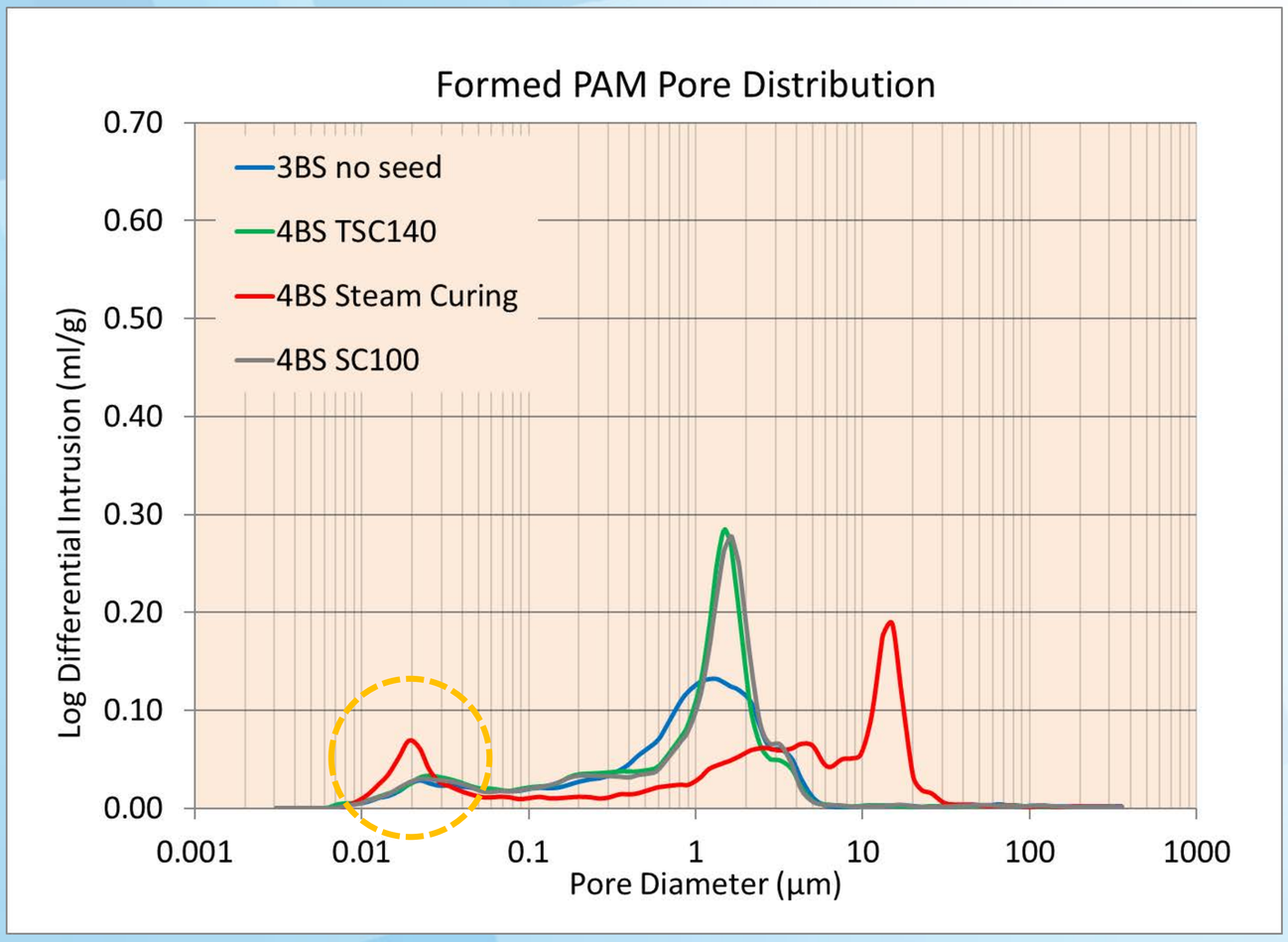
## POSITIVE PASTE ADDITIVE STUDY

# Formed PAM Pore Distribution:




IN FORMED PASTE:

- 3BS no seed has small and medium pores after formation
- 4BS Steam Curing has very small and very large pores after formation
- **4BS SureCure 100 and 4BS Treated SureCure 140 provides a consistent medium pore distribution.**

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## POSITIVE PASTE ADDITIVE STUDY

# Hg Porosimetry of Formed PAM:

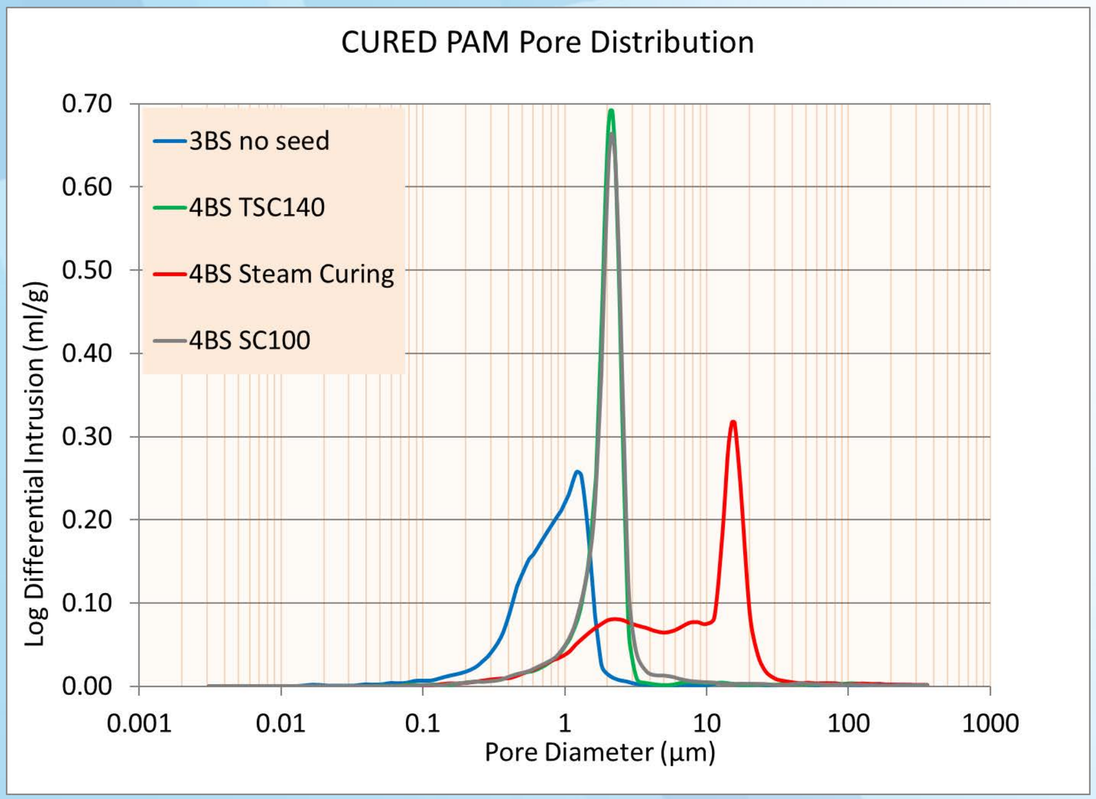
| POROSITY FORMED PAM | SA ($m^2/g$) | PORE SIZE (um) | PORE VOLUME (ml/g) | POROSITY % |
|---|---|---|---|---|
| 3BS No Seed | 3.56 | 0.98 | 0.14 | 52.4 |
| 4BS Steam Curing | 5.44 | 3.30 | 0.14 | 51.8 |
| 4BS SureCure100 | 3.79 | 1.33 | 0.15 | 54.9 |
| 4BS TreatedSureCure140 | 4.15 | 1.23 | 0.15 | 54.3 |

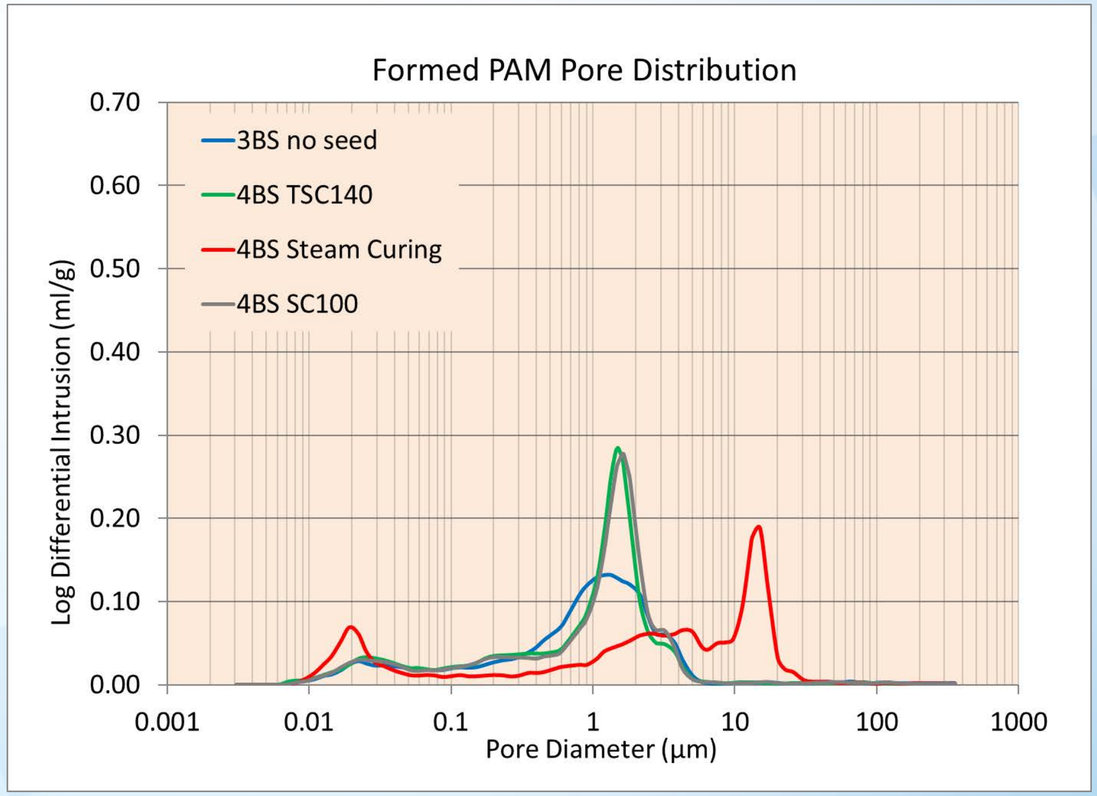
IN FORMED PASTE: Total pore volume for all the Formed Active Material are close to their Cured Active Material.

- 3BS no seed has lowest pore surface area and smallest average pore size.
- 4BS Steam Curing has highest pore surface area and largest average pores size.
- **Treated SureCure 140 provides higher pore surface area and smaller average pore size than SureCure 100.**

## POSITIVE PASTE ADDITIVE STUDY

# Cured vs. Formed PAM Porosimetry:




## COMPARING CURED AND FORMED PASTE:

- Formed PAM pore distribution is similar to that of cured PAM, except formed PAM has more small pores.

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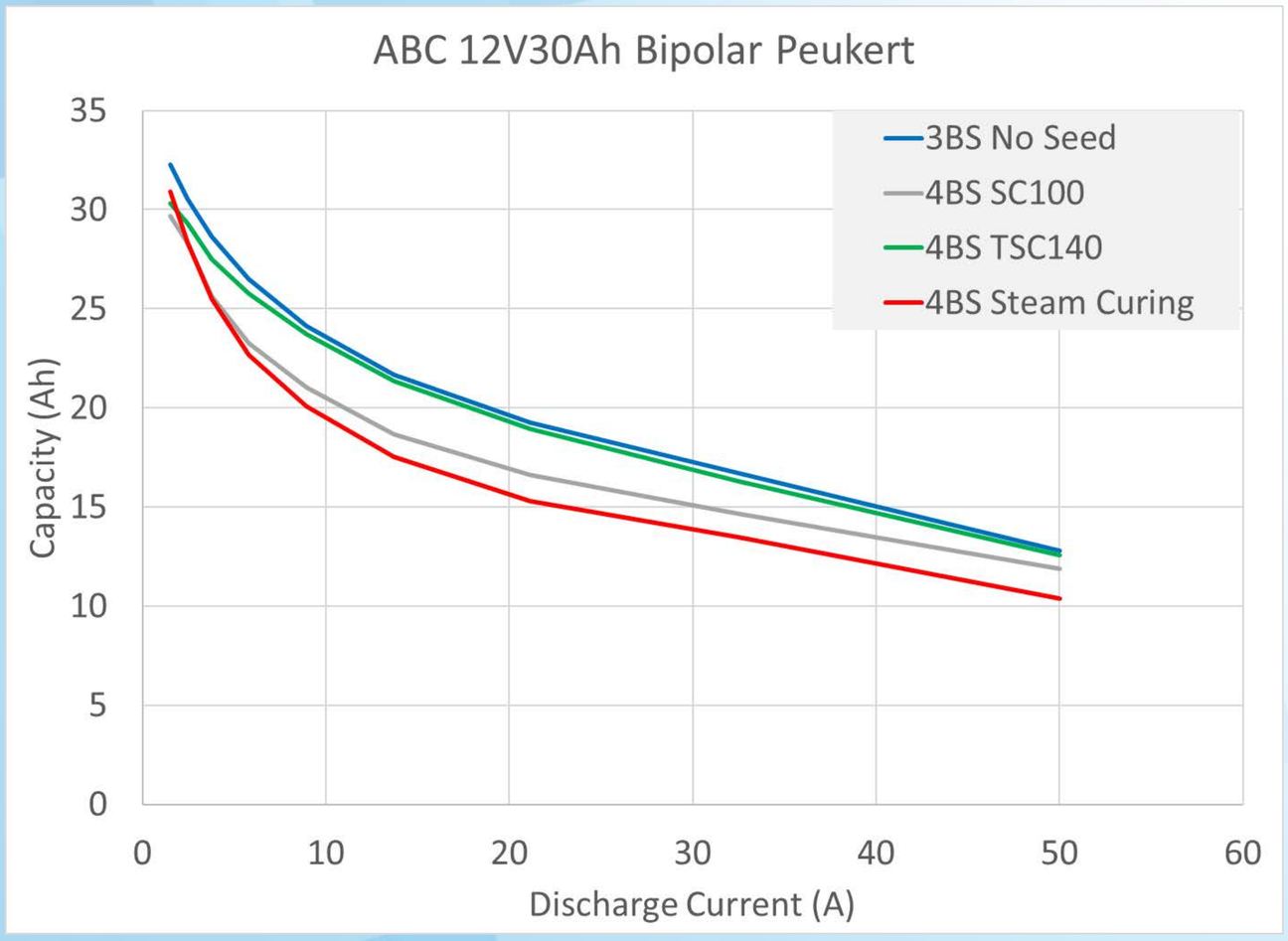
## POSITIVE PASTE ADDITIVE STUDY

# Peukert Curve:




PEUKERT TEST PROFILE: discharge at specified rate to 10.50v, charge at 6A to 14.40v, then 14.40v charge for different time specified by manufacturer. Lower rate discharge corresponds to longer time charge.

- At low rate discharge, capacity of all formulas tends to be same, showed the capacity was not limited by paste formula in low rate discharge.
- At medium rate discharge (0.1C20 to 6 C20), difference between different paste is big. 4BS Steam Curings show the lowest capacity and 3BS no seed showed highest capacity. **4BS Treated SureCure 140 capacity is very close to that of 3BS no seed.**
- When discharge rate further increases, the gap between different formulas gets smaller.

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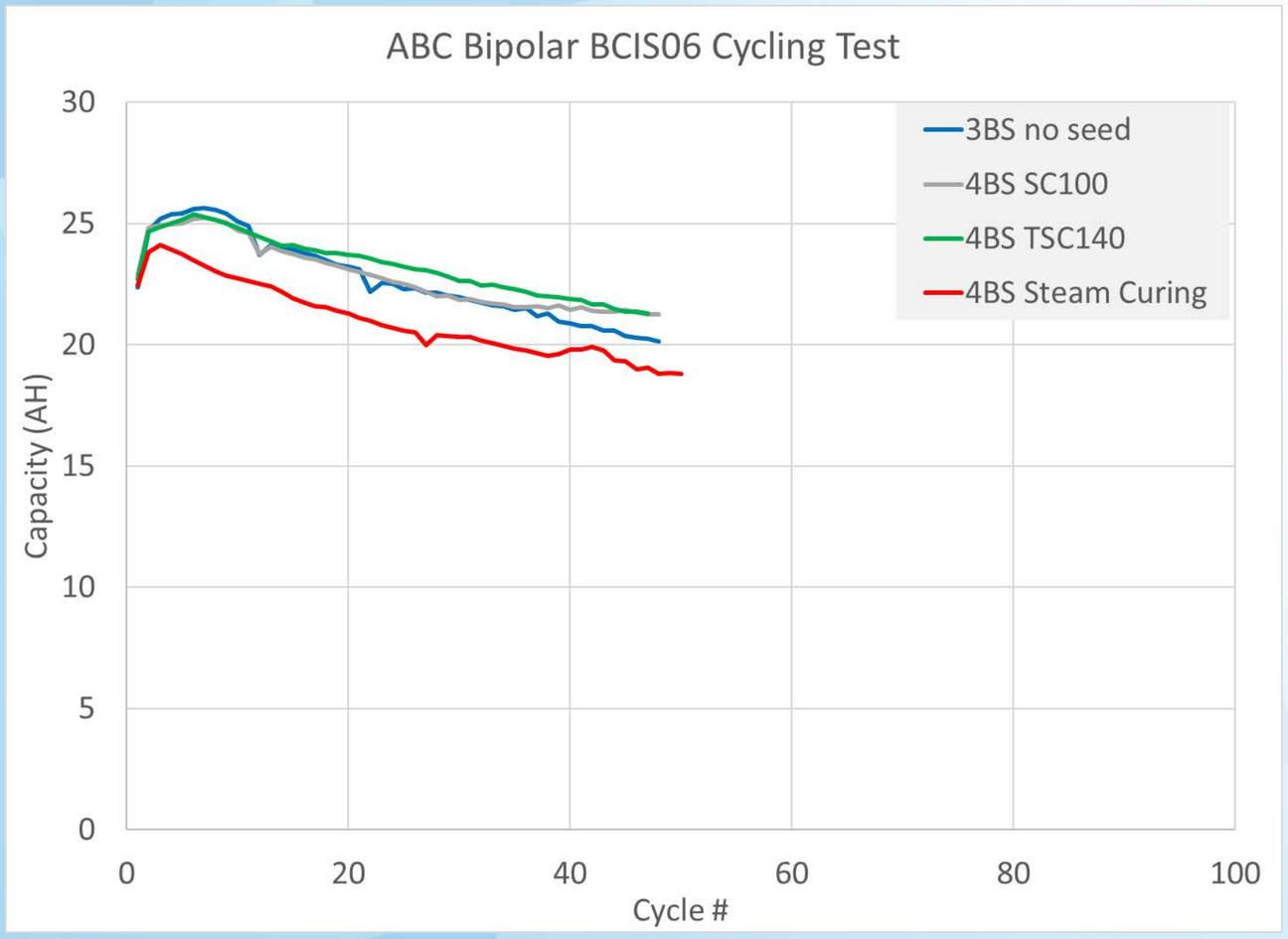
## POSITIVE PASTE ADDITIVE STUDY

# Cycling Chart:




BCIS06 CYCLING:
8.5A discharge to 10.5v, then charge at 6A to 14.40v, then 14.40v for 6h.

**In the first 50 cycles Treated SureCure 140 provides the best performance.**

Cycling test is still going on.

# Summary:

- **SureCure 100 and Treated SureCure 140 seeded PAM provide consistent cured and formed PAM structure, more than no seed 4BS formula.**
- After formation, formed PAM inherited some structure from its precursor cured PAM.
- Total porosity of cured and formed PAM are very close. During formation, porosity contribution from medium sized pores reduced, while that from smaller pores increased.
- **Treated SureCure 140 seeded PAM shows best formation efficiency compared to all 3 other paste formulas.**
- **Peukert tests showed Treated SureCure 140 seeded PAM has higher capacity than 4BS Steam Curing and 4BS SureCure 100 PAM, very similar to 3BS paste.**

## INNOVATION


# Hammond's research and development laboratories are dedicated to unlocking the next generation of lead-acid battery performance.

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