Innovations in Red Lead – Enhancing Formation Efficiency *by Structural Control with Functionalised Oxides*

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Agenda

- Targets & Introduction
- “Functional Oxides” – what are the advantages?
- PAM: Optimising Structure and Active Interface
- Formation Study – extended study (2023 – 2025)
- Understanding of Parameters – Approach “Structure impacting Performance”
- *Side-view: 12V mass battery testing – top-down approach*
- Findings & Summary

Introduction

Targets: Analyse the Limits of the Positive Active Mass (PAM) in terms of:

- Effective Formation by the addition of optimal grade RL
- Functional RL+ in cured and transformation to formed PAM
- Optimal performance of PAM (over an extended time)

Study Elements:

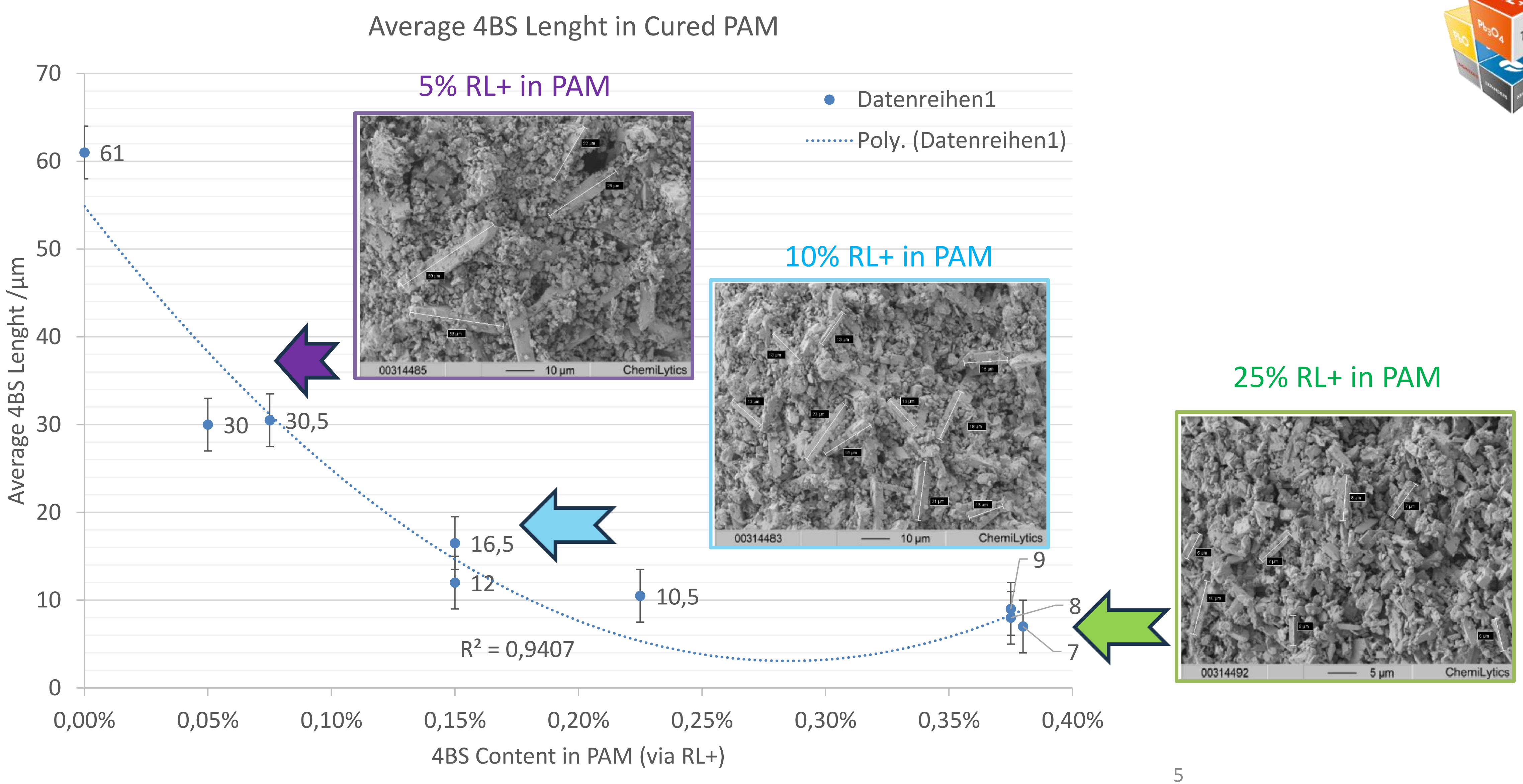
- Extended Formation study using different dosing of RL+ @45°C
- PbO2 and structural conversion in formation – using Laser microscopy
- Understanding “Peukert” - Capacity study based on PAM porosity parameters

Formation Study (extended)

- **PAM Mixes:**
  - Standard: Red lead (RL) with d50 = 4.5 µm and Lead dioxide (PbO_2) 25 to 27%
  - Red lead: *0% (Reference), 5 w% to 50 w%* - ***with focus on 5 w% to 25w%***
  - Comparison of cured positive active masses (PAM): **tri-basic (3BS)** vs **tetra-basic (4BS)**

- **Conditions of the Formation study:**
  - 45°C Standard formation profile (as presented in ABC 2023)
  - Laser microscopic study of cured plate (non-destructive), after formation, and again after several C20, C5 cycles (first phase of operation – entropy analysis, ongoing study)
  - Including “interrupted” formation to investigate the structural changes during formation

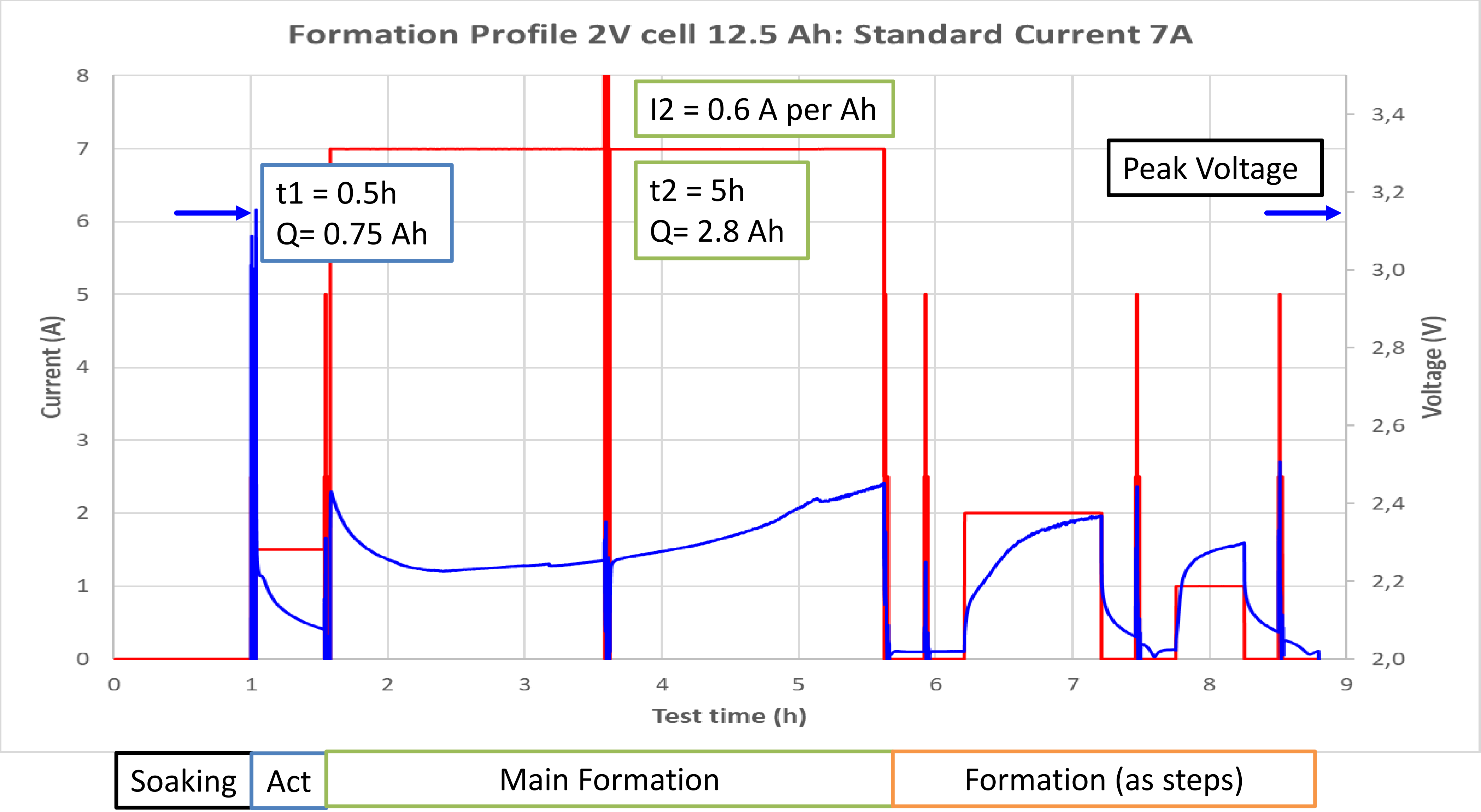
RL+ => Impact on 4BS cured PAM Structure



RL+ => Impact on 4BS cured Structure

- **Cured Plates (templated structure):**
  - Allows control of the porosity by RL+ Dosing
  - Crystal length can be systematically varied
  - Pore size and pore interconnection can be controlled and influenced
  - This structure has a direct influence on the mass transport and the conductive backbone of the PAM
- **Formed Plates (transformed structure):**
  - The target is to keep the beneficial structure generated in the curing process
  - The transformation process in formation (cured to formed PAM) was investigated
  - Optimal porosity structure was investigated

Formation Profiles (Standard, 25% RL+, FF =2.5)



Formation Factor (FF) & Formation Energy (FE)

$$\textbf{Formation Factor (nom. or } \textbf{\textit{act.}}\textbf{)} = \frac{\textbf{Formation Charge Q (Ah)}}{\textbf{Nominal or } \textit{Actual} \textbf{ Capacity (Ah)}}$$

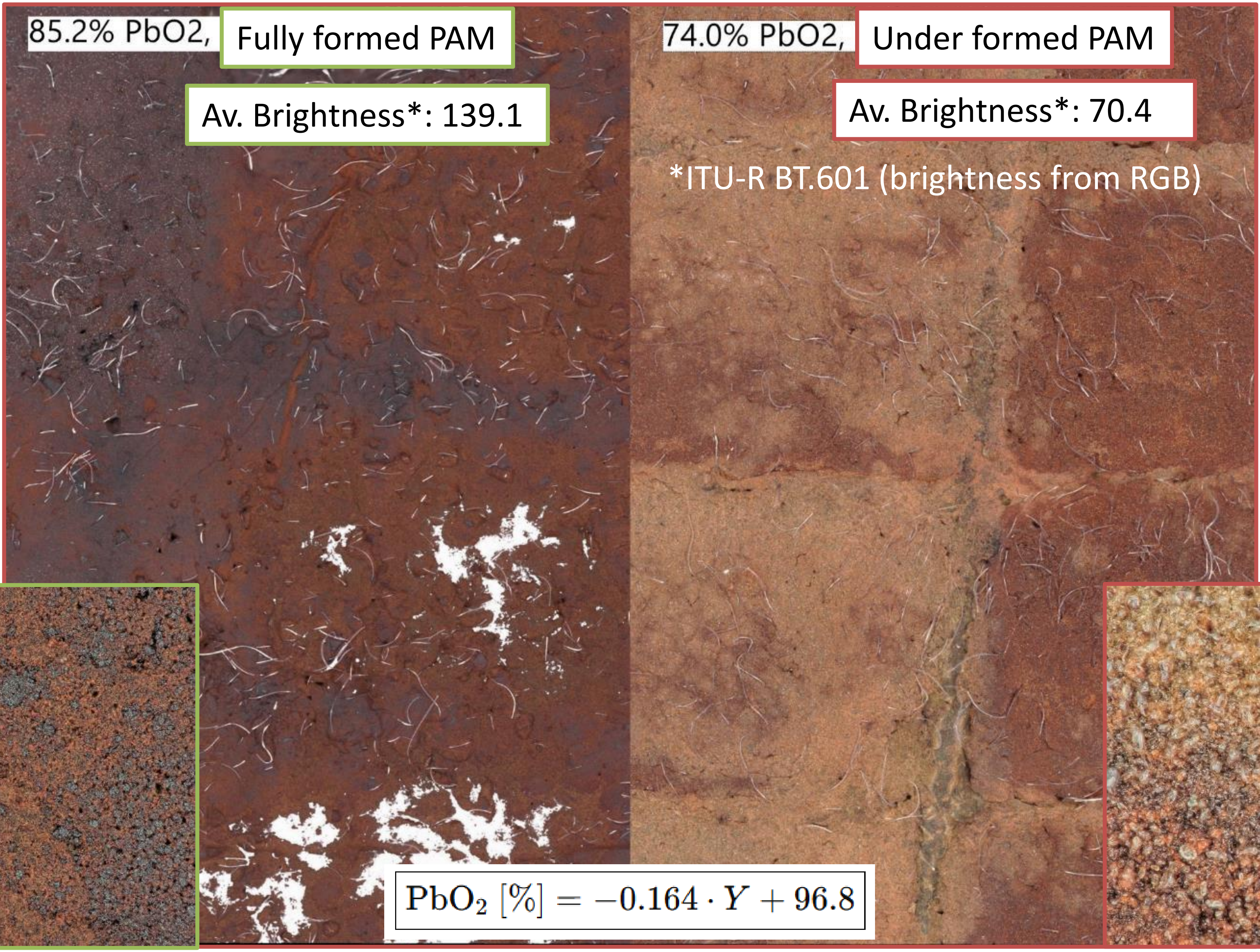
There are two different definitions of the formation factor: **nominal capacity-based** and **actual capacity-based**. Depending on the definition, mass utilisation affects the formation factor.

$$\textbf{Formation Energy (specific)} = \frac{\text{Formation Energy (Wh)}}{\textbf{Weight of PAM (DuF)}}$$

The **Formation Energy** allows for easy calculation of Energy savings.
For simplicity, the value refers to the weight of the dry unformed (DuF) Positive Active Mass (PAM)

Local Resolution of Formation Grade (LM)

Mag.: 100x



$$PbO_2\,[\%] = -0.164 \cdot Y + 96.8$$

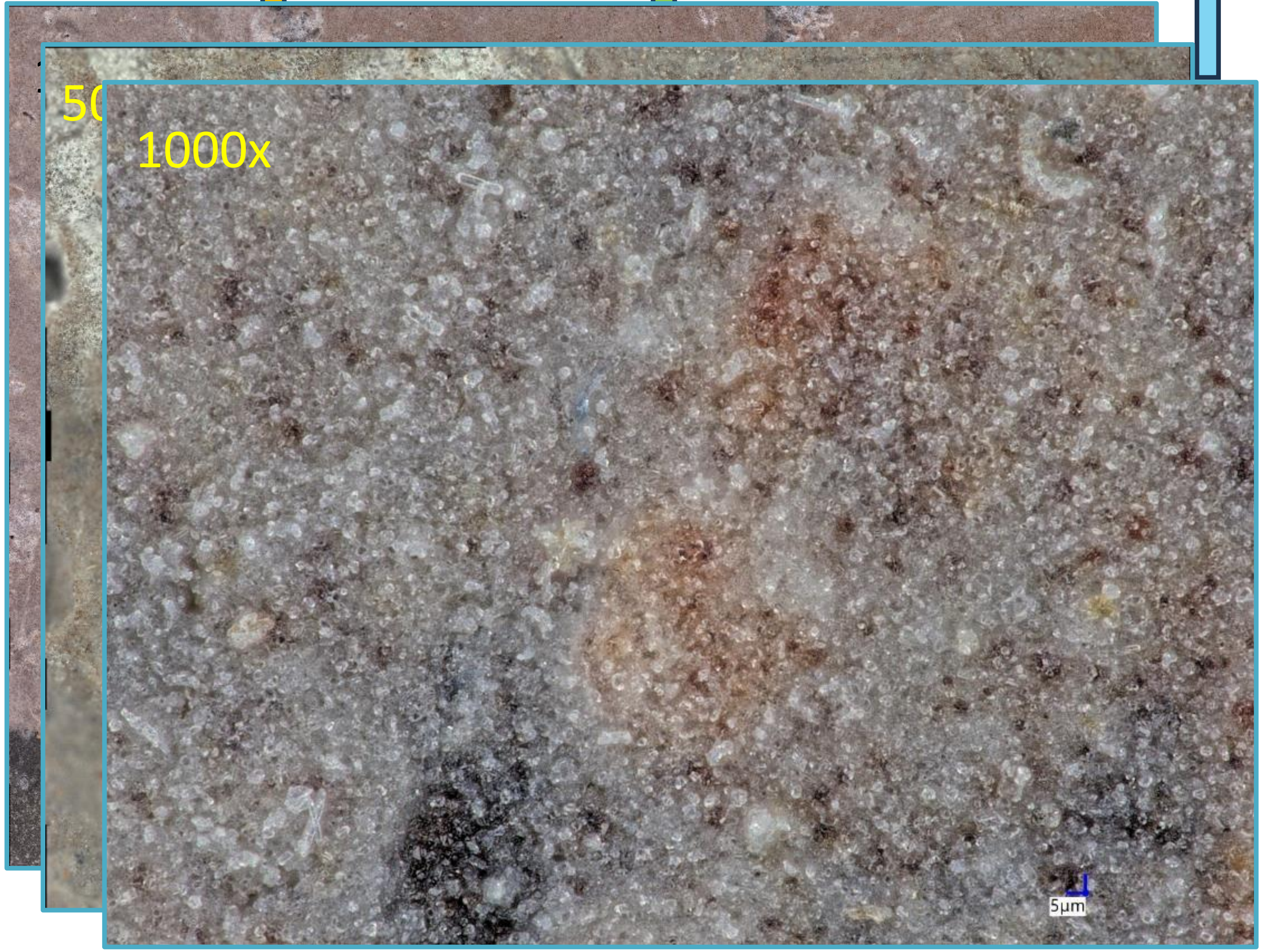
Mag.:500x

Mag.:500x

Formation monitored by ***Laser Microscopy***

Soaking | Act | Main Formation | Formation (as steps)

Stop 0



25 w% of RL+

Stop 0:
After „Activation Step“
t1 = 0.5h
Q= 0.75 Ah
⇒ 30% of C20 (2.5 Ah)

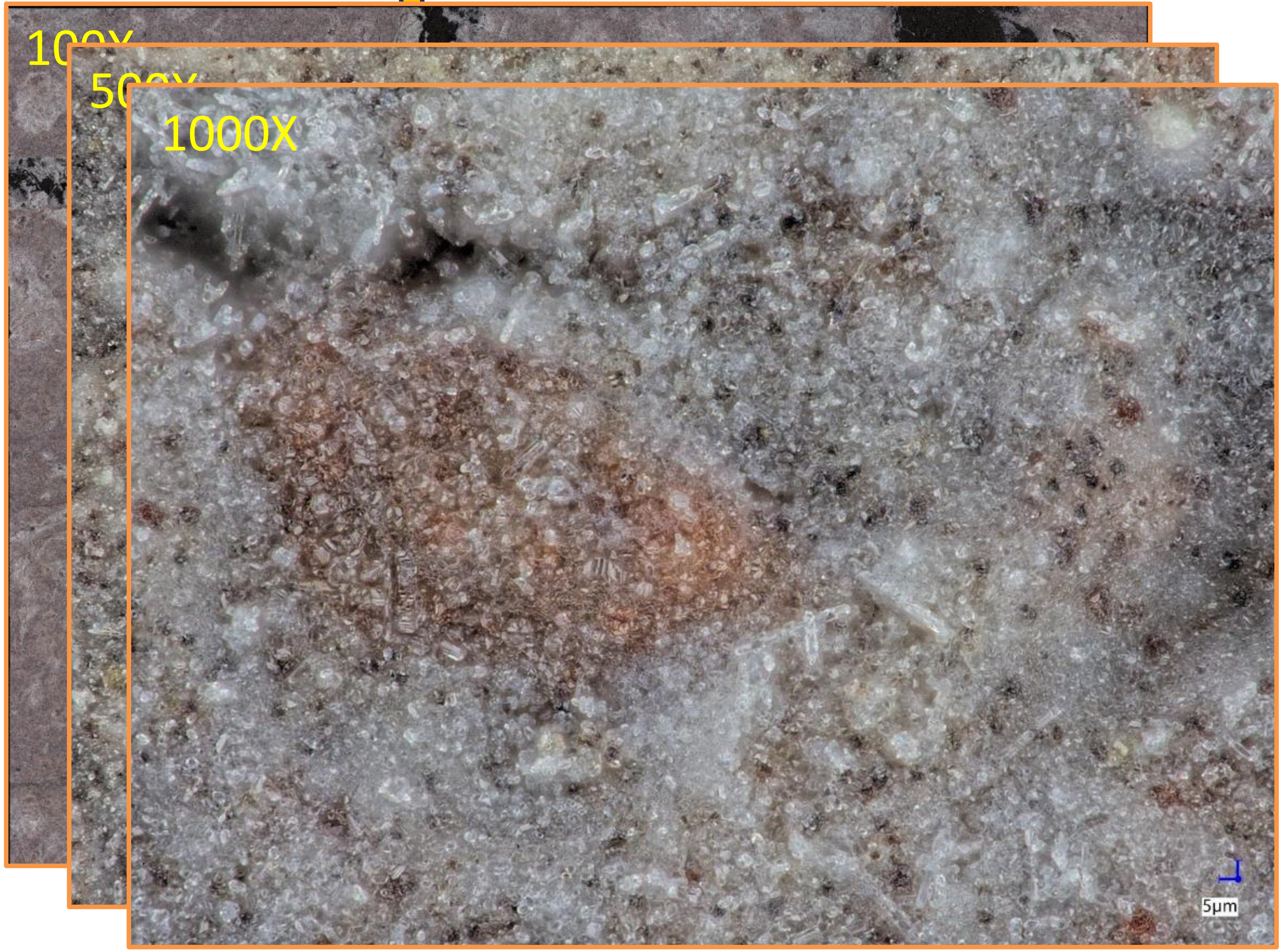
⇒ 11% of total Q formation

PbO2 measured was ~5%

Surface is sulphated!

Formation monitored by ***Laser Microscopy***

Soaking | Act | Main Formation



Stop 1:
Mid of „Main Formation Step"
T2 /2 = 2.5h (of 5h)
Q = (0.7 + 1.4) = 2.1 Ah

⇒ 80% of C20 (2.5 Ah)

⇒ 34% of total Q formation

PbO2 measured was **52%**

Surface is sulphated!

Formation monitored by *Laser Microscopy*

Soaking | Act | Main Formation

Stop 2:
End of „Main Formation Step"
T2 = 5h
Q = (0.7 + 2.8) = 3.5 Ah

⇒ 140% of C20 (2.5 Ah)

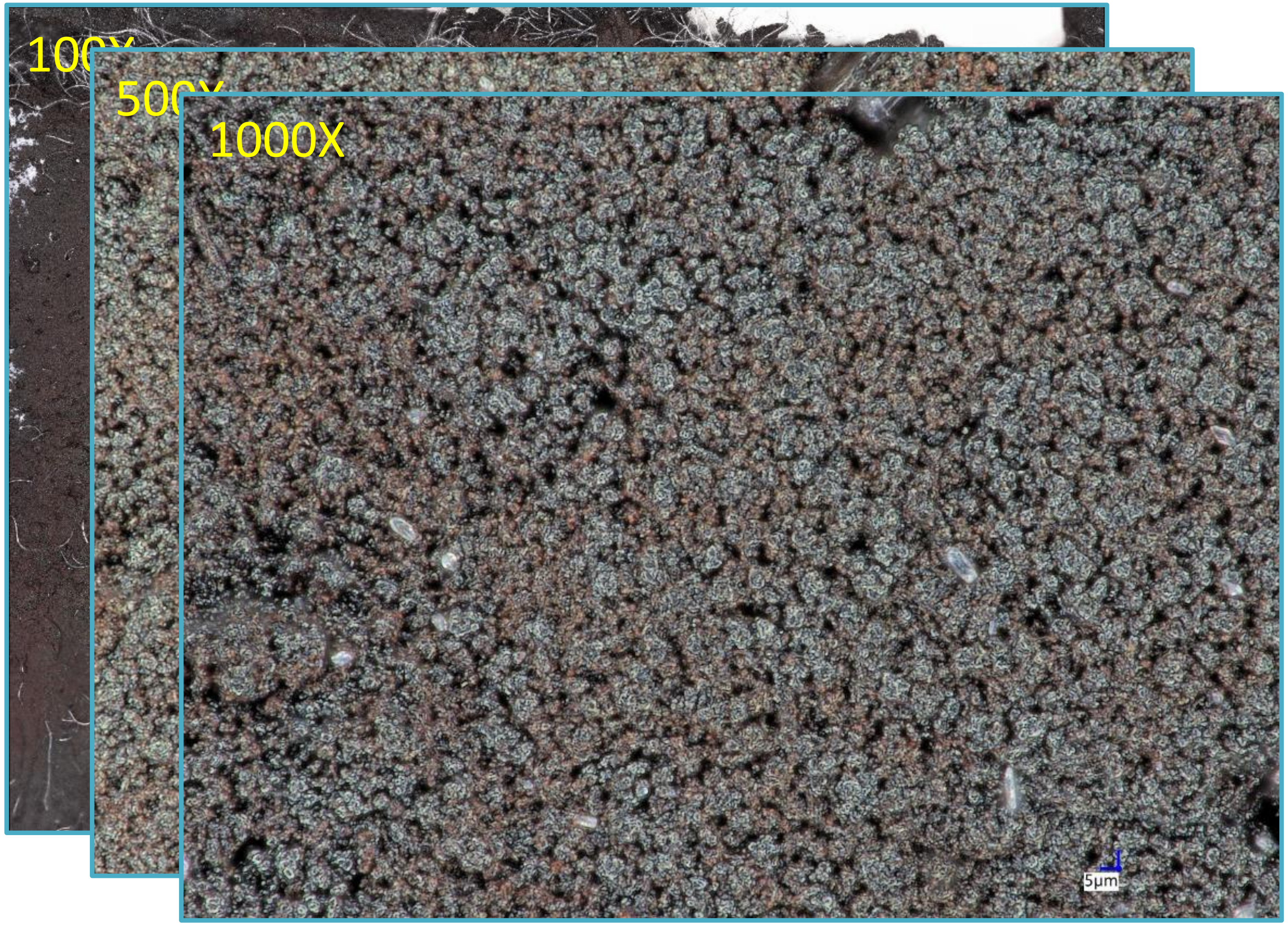
⇒ 56% of total Q formation

PbO2 measured was **75%**

Structure is visible!
Some remaing electrolyte visible

Formation monitored by ***Laser Microscopy***

Soaking | Act | Main Formation | Formation (as steps)



Stop 3:
End of Formation
T3 = 8h
Q = 6.3 Ah

⇒ 250% of C20 (2.5 Ah)

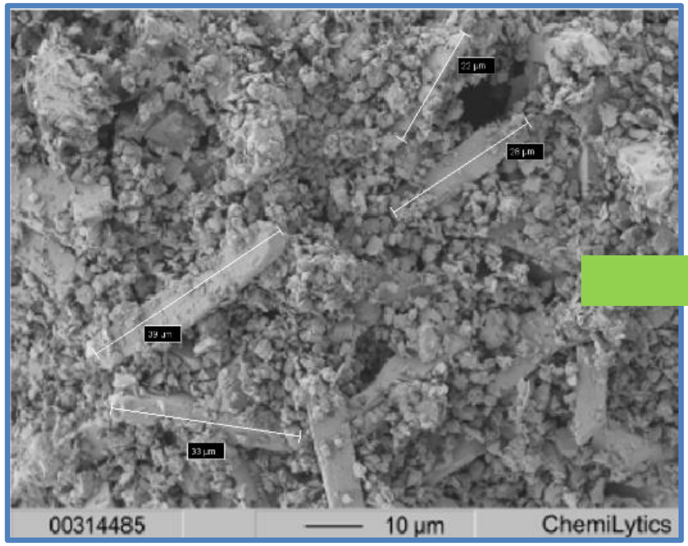
⇒ 100% of total Q formation

PbO2 measured was **84%**

Structure fully developed

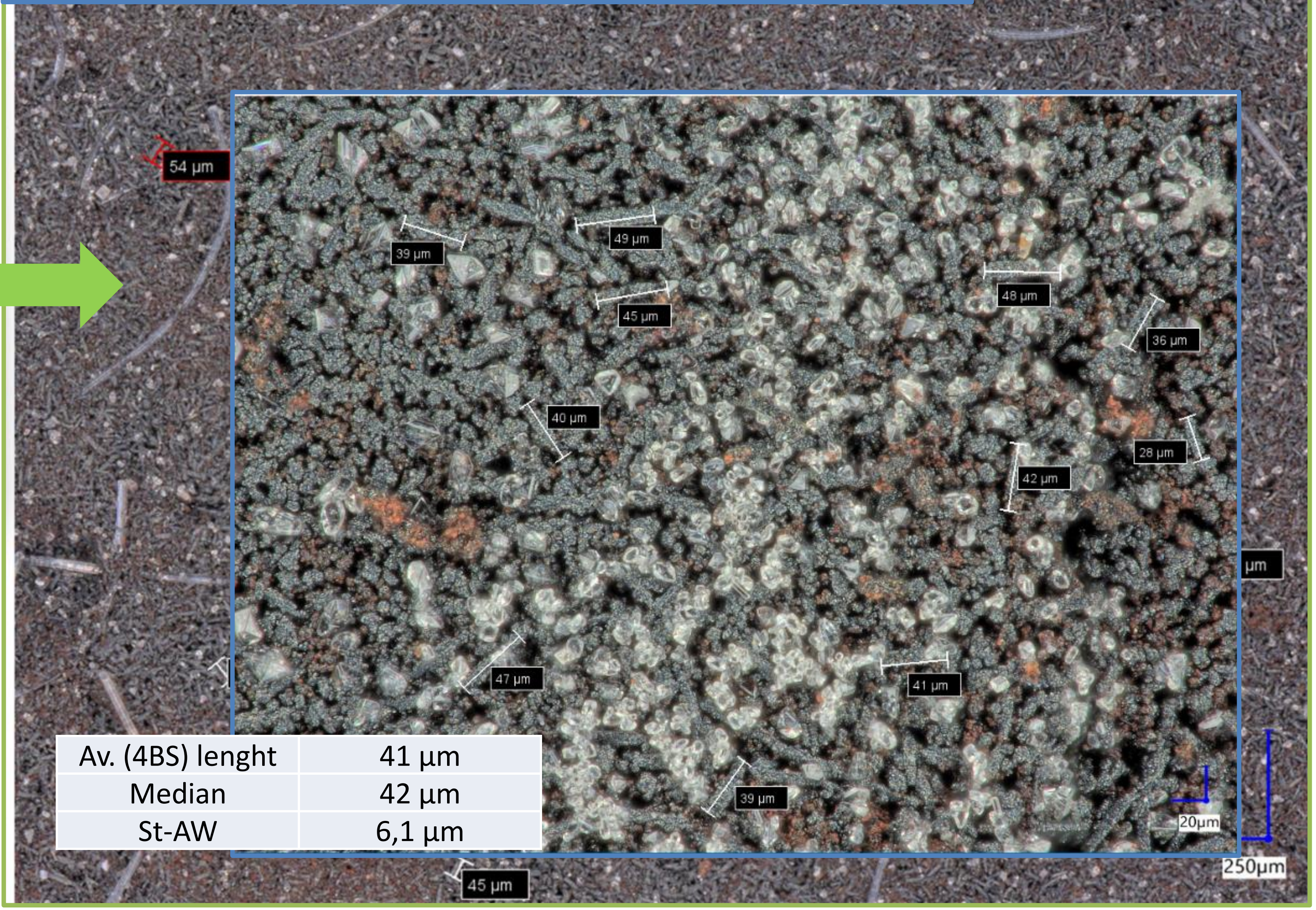
Cured (0.3% 4BS = 5 % RL+) => Formation

Cured PAM 5% RL+ & 20% RL



Av. (4BS) lenght	30,5 µm
Median	30,5 µm
St-AW	7,2 µm

Formed PAM 5% RL+ (= 0.3% 4BS) and 20% normal RL

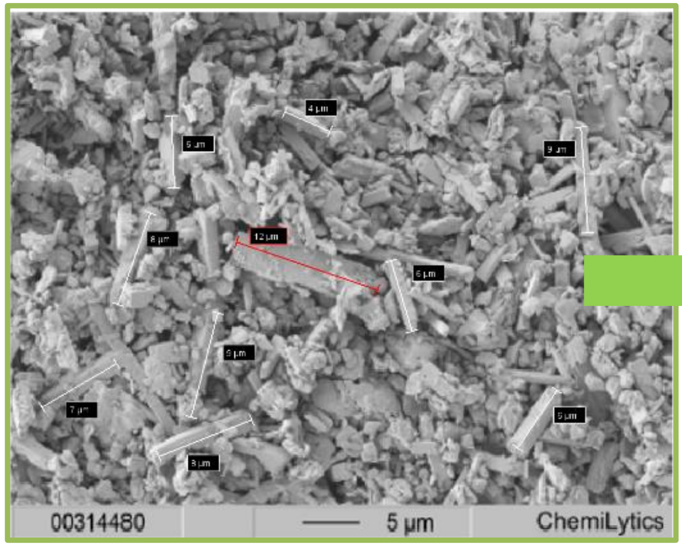


Av. (4BS) lenght	41 µm
Median	42 µm
St-AW	6,1 µm

Source: ABC 04_ Gereifte PAM_ PV 1.4_5%RL+ &20%RL

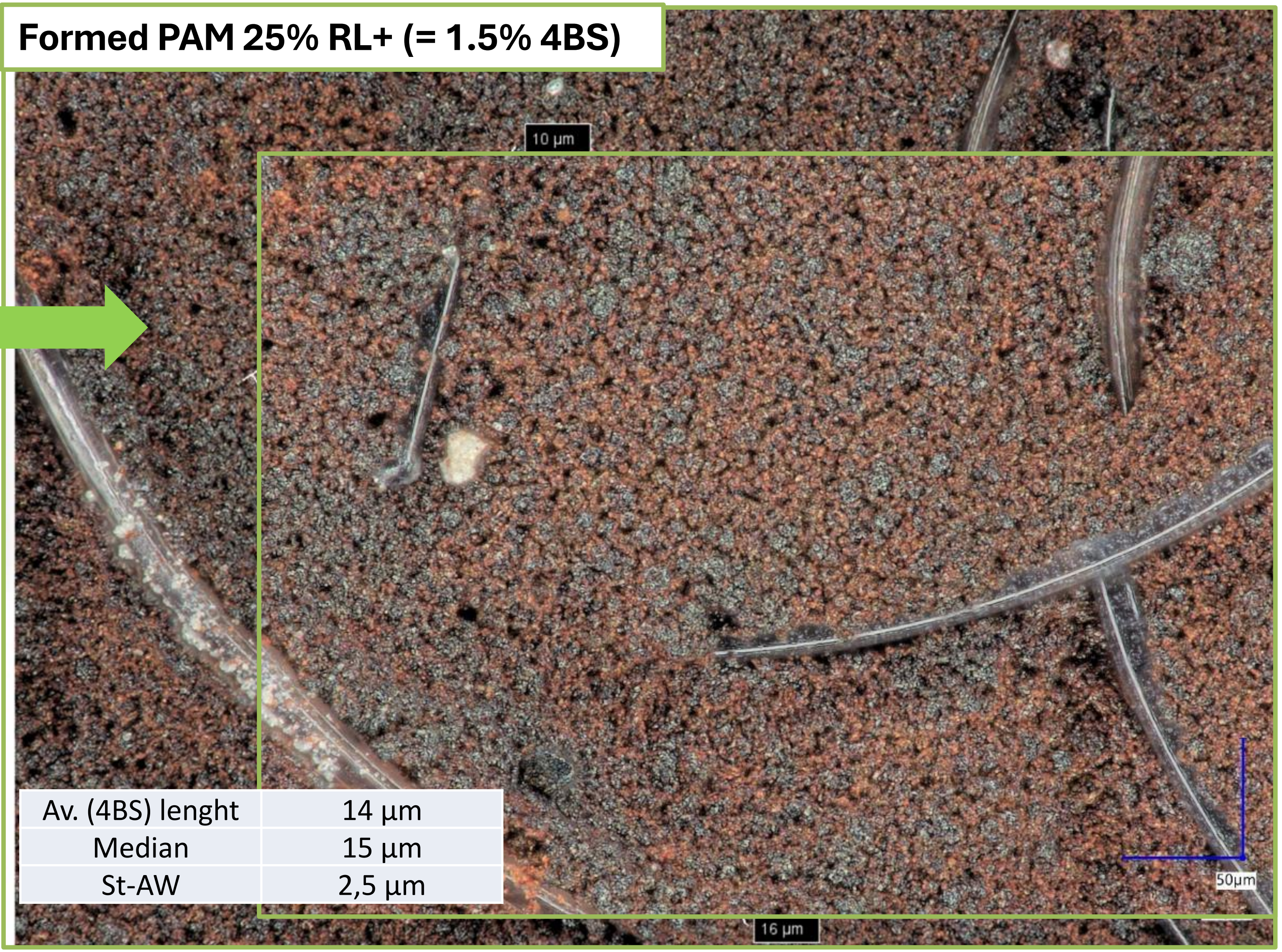
Cured (1.5 % 4BS = 25 %RL+) => Formation

Cured PAM 25% RL+



Av. (4BS) lenght	7,5 µm
Median	7,5 µm
St-AW	2,2 µm

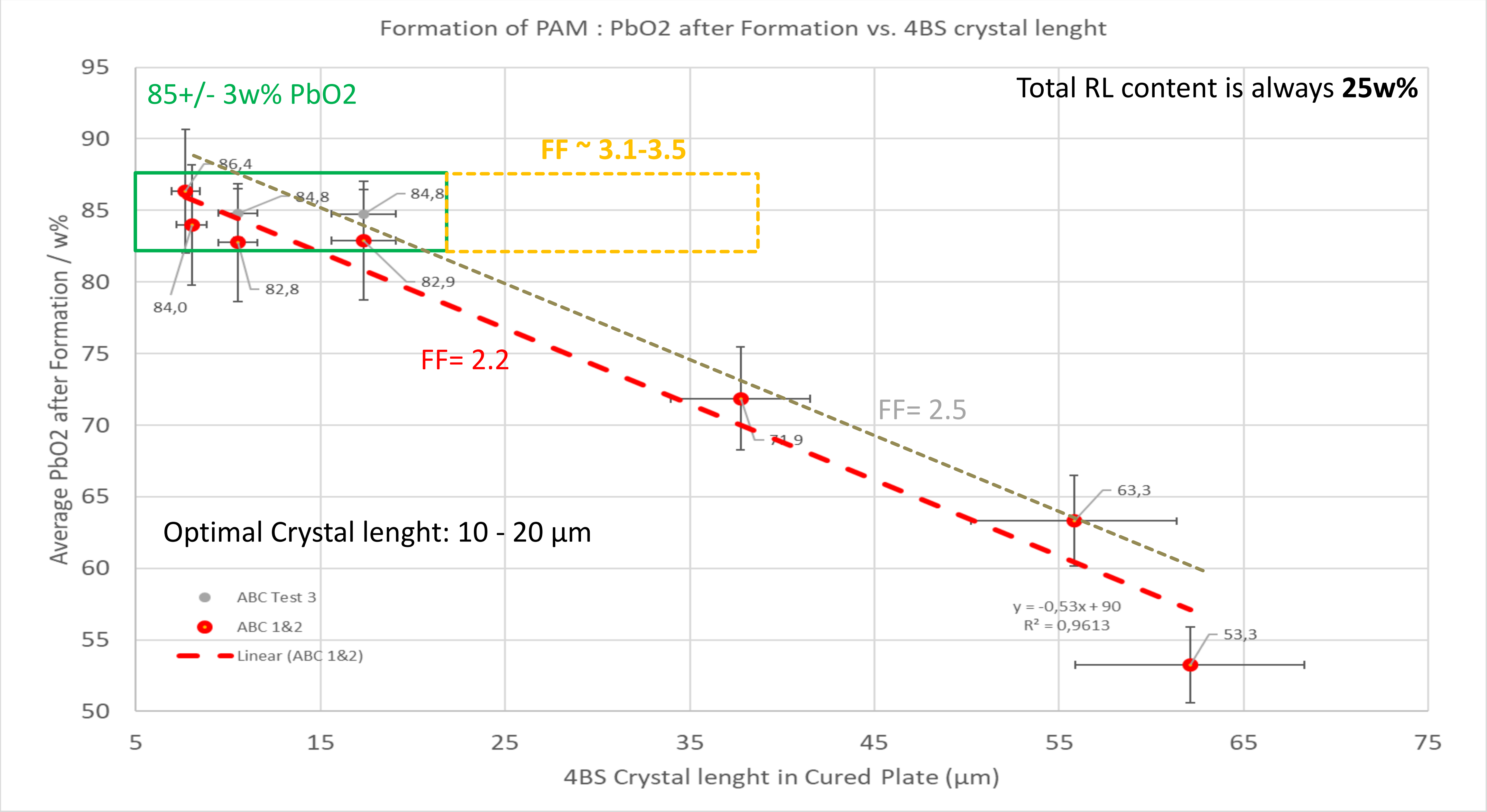
Formed PAM 25% RL+ (= 1.5% 4BS)



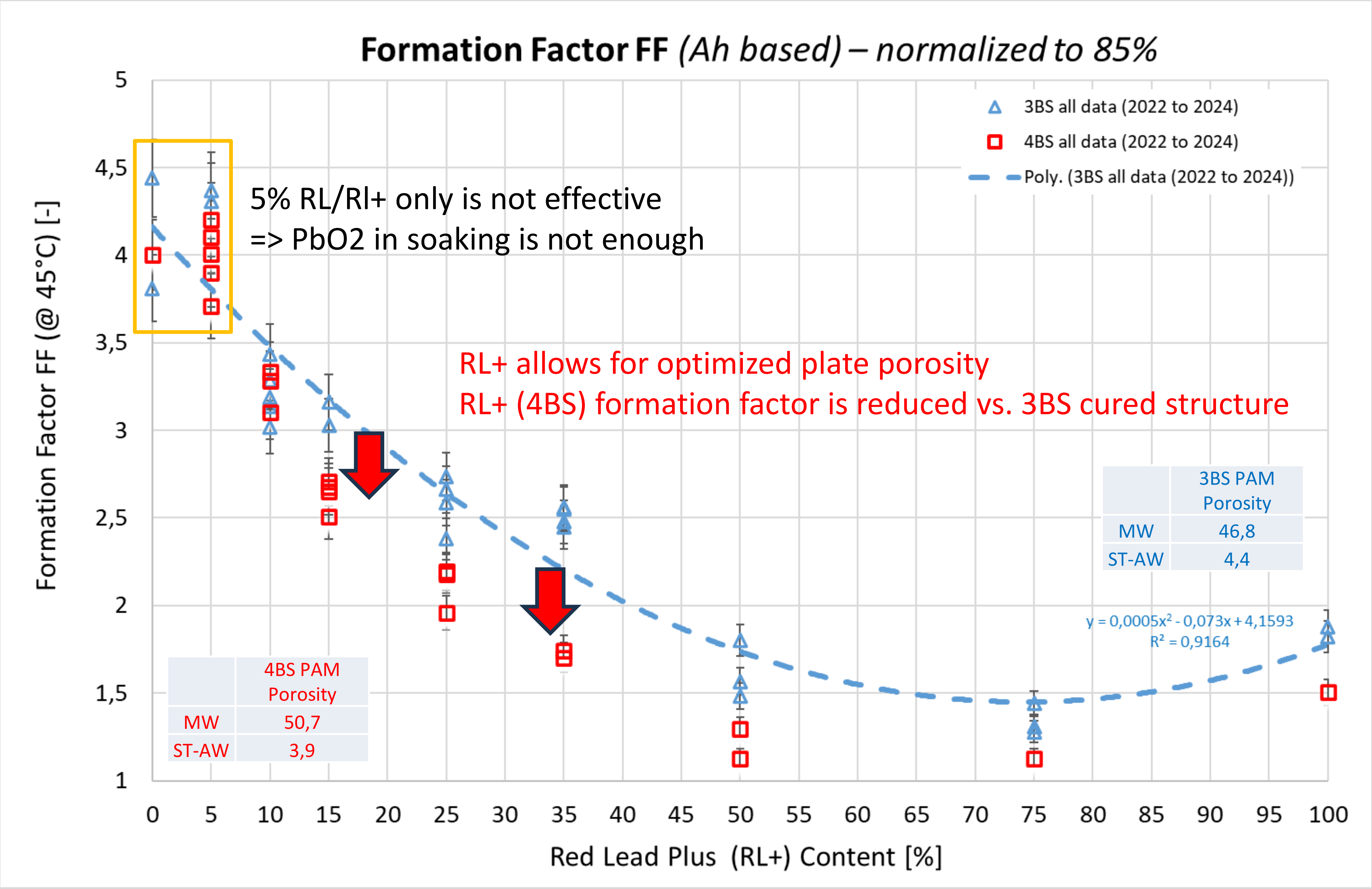
Av. (4BS) lenght	14 µm
Median	15 µm
St-AW	2,5 µm

Source: ABC _Gereifte PAM_ PV 1.1_25%RL+

Impact on 4BS Crystal Length on FF and PbO2



Formation Factor – RL+ for 4BS / RL for 3BS



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Optimal Formation with RL+

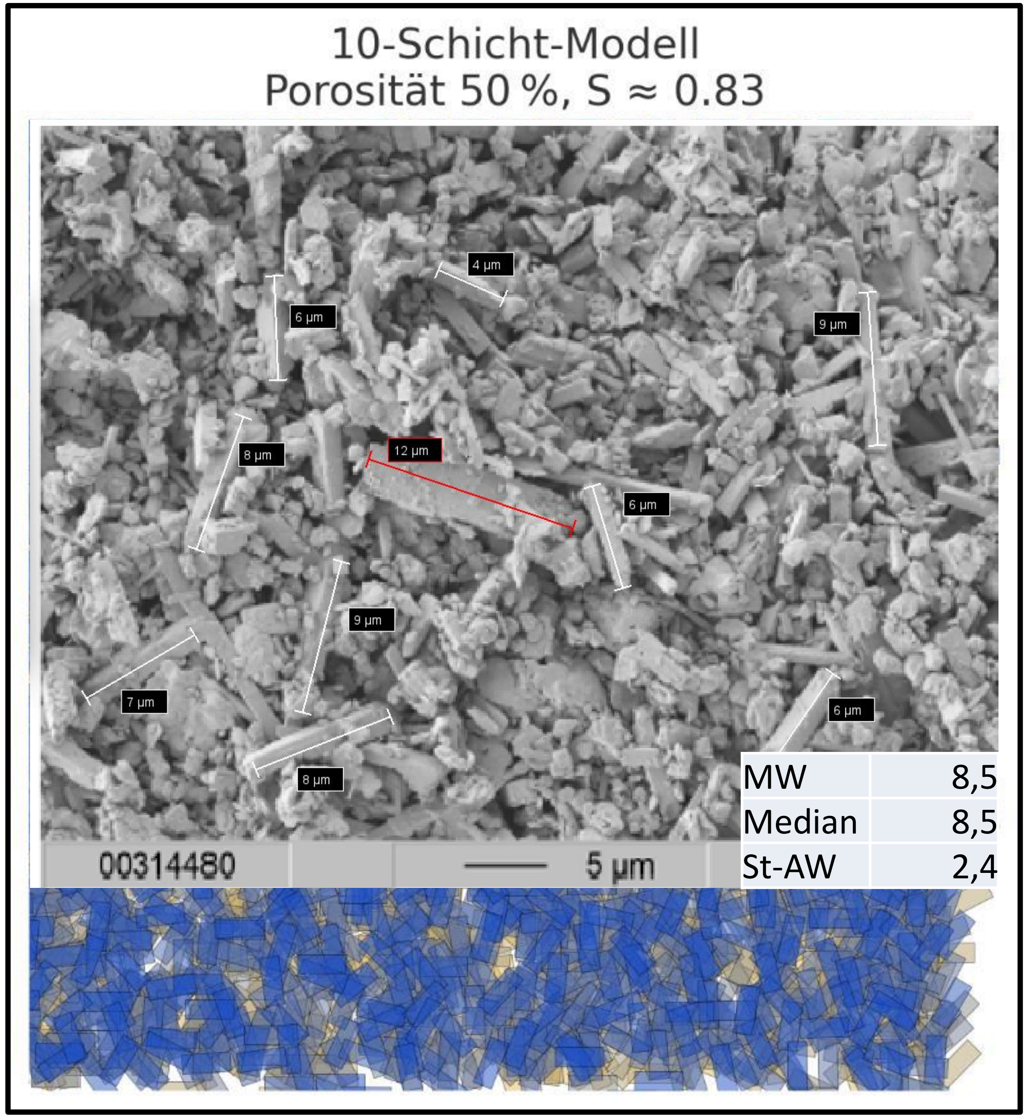
- **Using RL allows for the reduction of formation energy by, e.g. increasing conductivity**
- **Initial conductivity is enlarged by the decomposition of RL, forming active PbO_2**
  - Please remember that RL needs to be decomposed to PbO_2 during soaking step (T >30°C)!

- **RL+ between 10w% and 25w% is allowing for a beneficial structure of the PAM**
  - Optimal 4BS crystal size is about 10 to 20 µm in cured PAM
  - Larger 4BS crystals (>>30 µm) require significantly higher formation factor and energy
  - Cured PAM can be transformed into a formed PAM with a similar structure

  - In the laser microscopic study, we have seen the growth of prismatic crystals similar in length and width to the tetrabasic lead sulphate crystals
  - Thus, the 4BS seeding allows systematic control of the structure of the formed PAM
  - Battery ageing by cycling is presently investigated by laser microscopy

  - Remember: Typically, smaller 4BS crystals (< 10 µm) create a less stable structural template

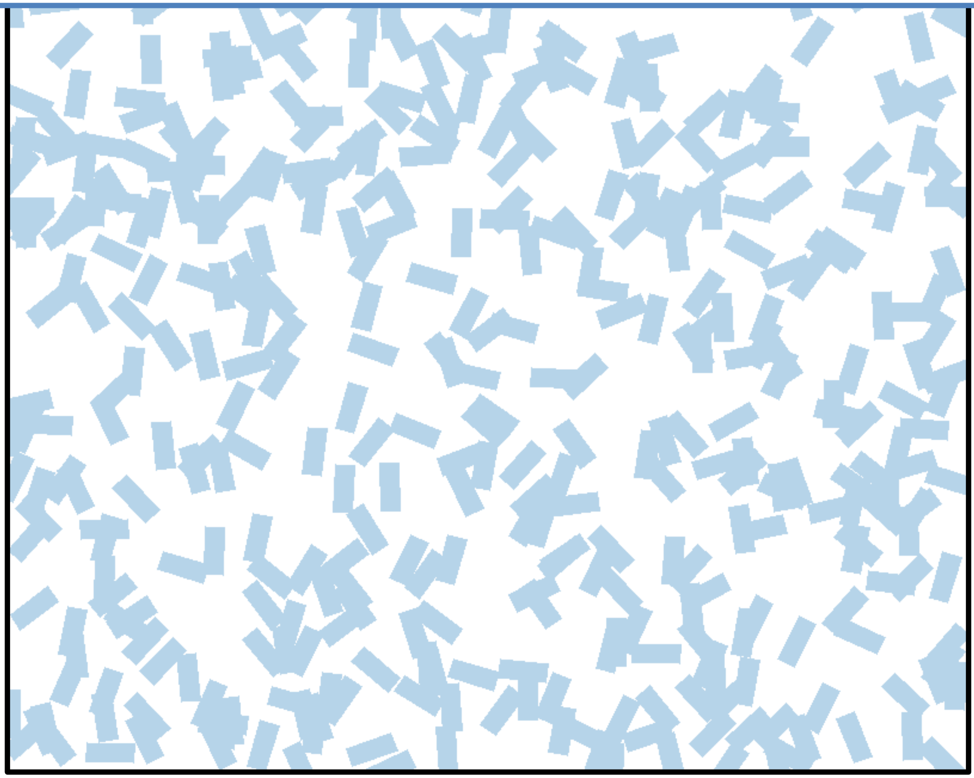
4BS in PAM – Simple Modelling



MW	8,5
Median	8,5
St-AW	2,4

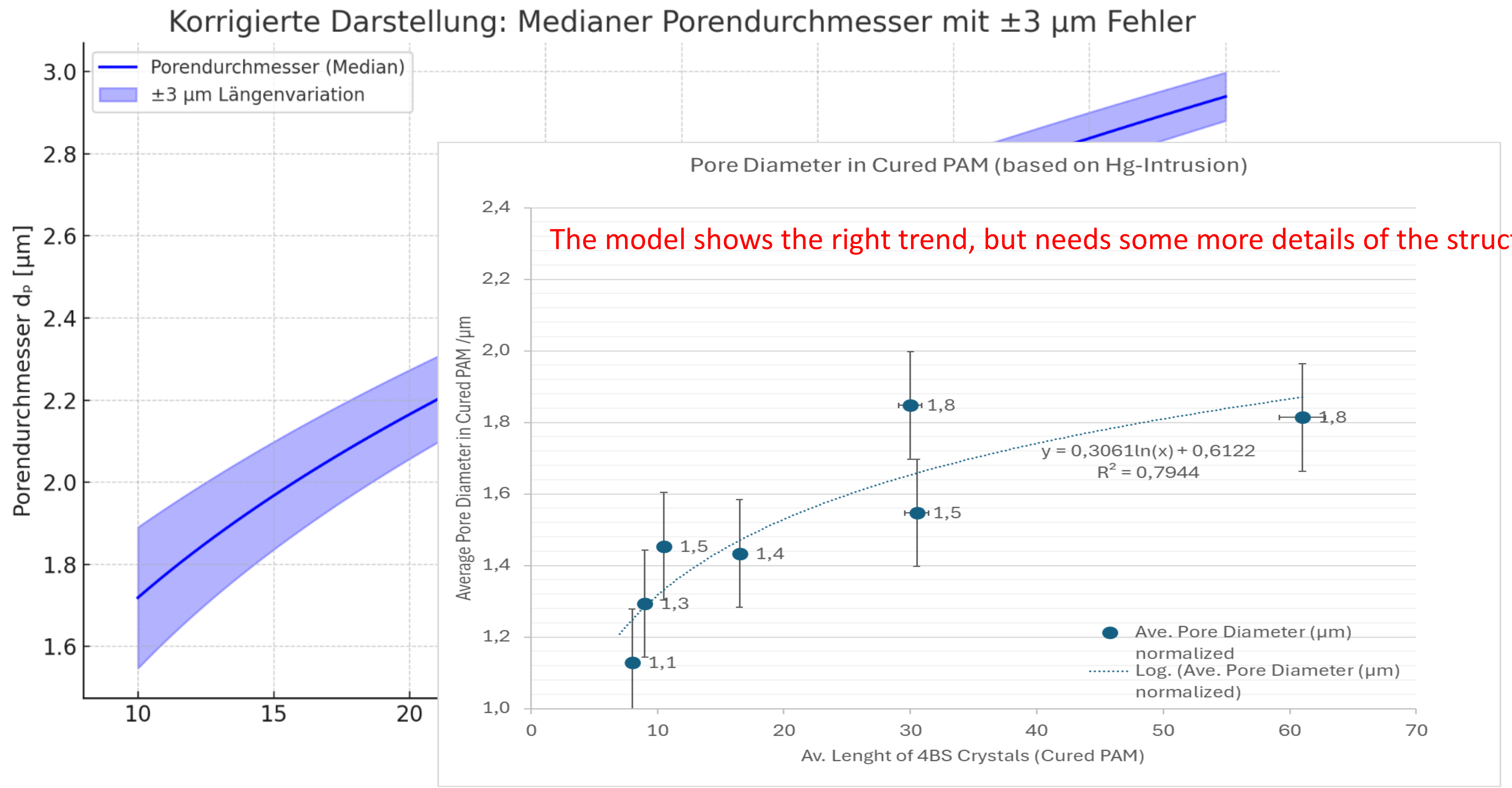
Overlay of „4BS Crystals" as projected rectangular structures

- 10 layers with defined orientation entropy are calculated
- Porosity per layer is 50%
- Pores are calculated from this overlay structure
- Length of 4BS crystals is without variation (could be included)



MW	10
Median	10
St-AW	**0**

Porosity Modell (simple Model)

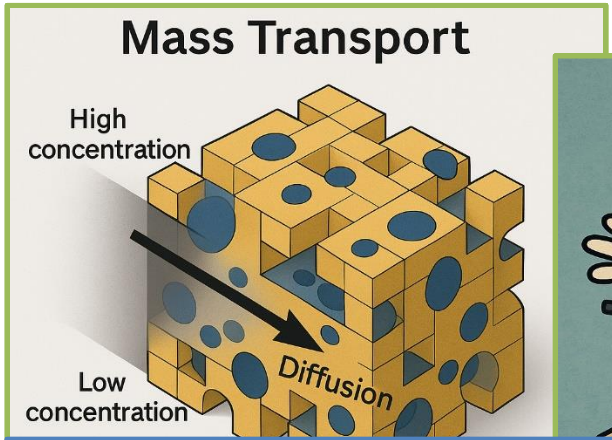


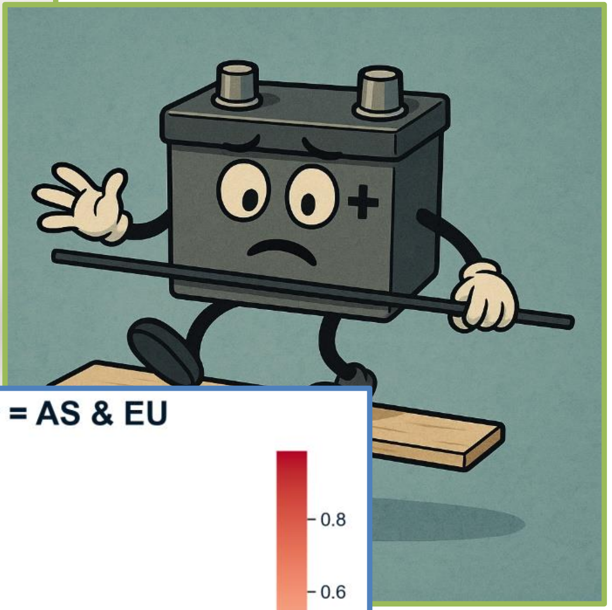
The model shows the right trend, but needs some more details of the structure.

PENOX *Side View – Structure Impact* vs. Top Down

Structure Impact:

- In this presentation, PENOX discussed the impact of electrode structure on performance
- Structure impacting *local conductivity, mass transport, and degradation while cycling*





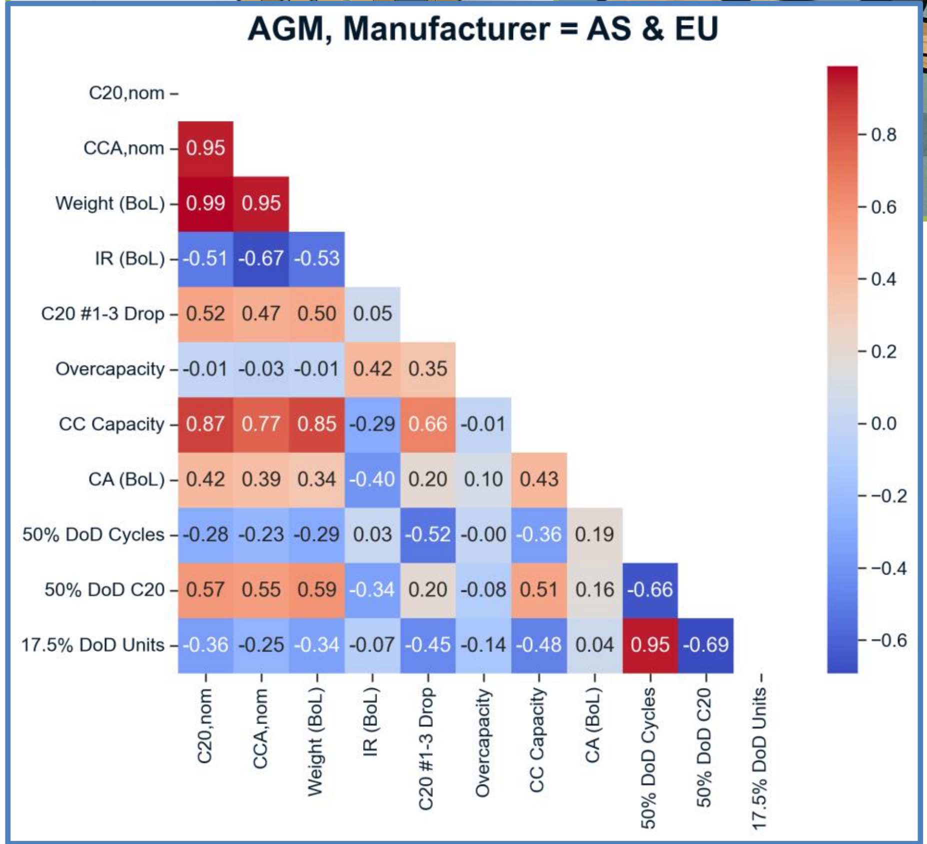
Top Down (Cooperation with ABR): Austrian Battery Research Laboratory GesmbH.

In parallel, PENOX is investigating massive data from 12V battery testing (norm-based) and field battery testing

The main target is to understand design trends and their relative performance.

Furthermore, the evolution of technology and *"key-survival criteria" for battery operation.*

Presentation by Martin Wieger et al. (ABR) and Micha Kirchgeßner, 05.09.2025 - 9:50 am – 10:15 am



Summary & Outlook

- The impact of different **RL** grades on formation energy and time was systematically investigated
- The 4BS - cured structure is more effective by about 2 Wh per kg of PAM in a 2V cell—about 1.7 kWh per 60 Ah 12 V (E20 = 0.72 kWh) automotive battery. *The likely reason is the more effective mass transport in the porous structure with a wider pore diameter, which enhances mass transport for sulfuric acid.*
- **RL+**, which combines the functions of RL and 4BS, is a cost-effective bi-functional material.
- Using a **4BS structure** allows **higher mass utilisation than a 3BS structure.** *However, the maximum is reached for a* ***porosity of about 50 to 55 %*** *of the formed positive active mass*.

- PENOX is using Laser Microscopy to investigate structural changes of the PAM while cycling
- The idea is to link capacity and capacity evolution by structural data from Laser Microscopy

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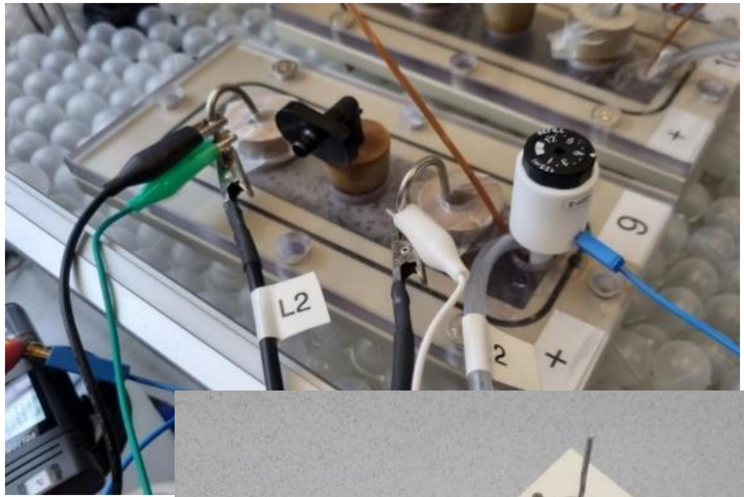
R&D Team & Center in Germany

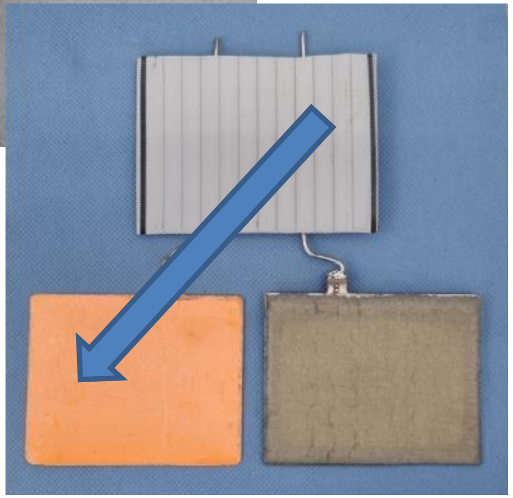
Thank you for your kind interest

Test Setup in PENOX Laboratory

- Cell Set-up:
  - Grid technology is gravity cast grids
  - One positive plate (1p) with C20: 12 Ah nominal
  - Two negative plates (2n)
  - PAM : NAM ratio in weight equals: 1 : 1.8*
  - Electrolyte: 300 g, density 1.28 +/- 0.05 g/cm³
  - C20, **C5** was tested at 20 to 22 °C

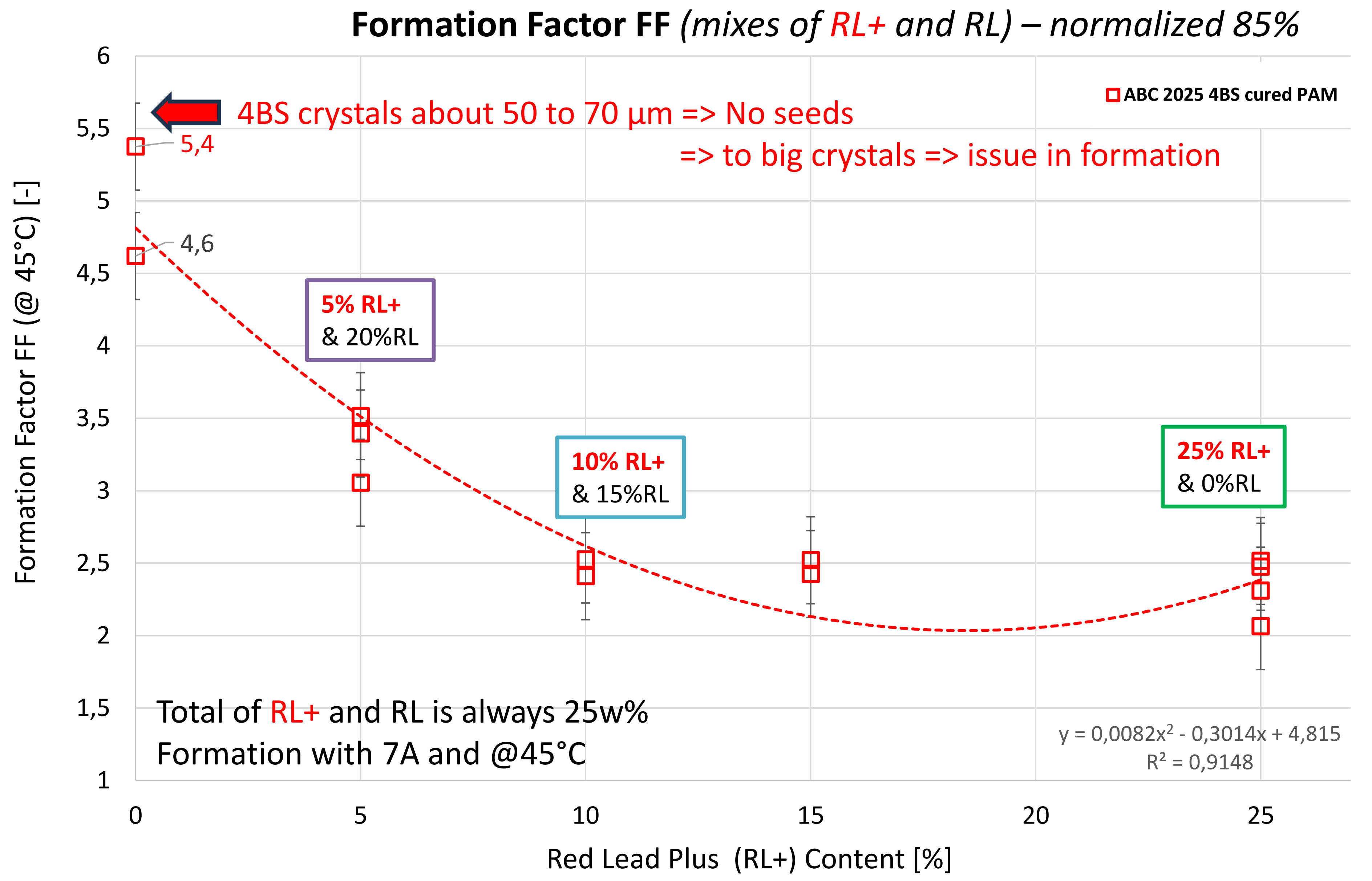
- Variation of the reference:
  - M-neg. plate is a ***standard negative***
  - J-neg. plate is a ***negative plate with advanced carbon***





*This high NAM content is reducing the impact of the NAM, as this study focuses on PAM. PENOX is comparing, e.g. (5p/4n), for a more exact data comparison.

Formation Factor – Mix of RL+ and RL



Formation Factor – RL+ for 4BS / RL for 3BS