

Tin Bath Bottom Blocks RHI Magnesita solutions

19-9-22 – TC11 Meeting - Düsseldorf



Agenda

- 1 CA Tin Bath Bottom blocks concept – SUPRAL CA
- 2 SUPRAL CA post-mortem analysis
- 3 CA hydration potential and countermeasures
- 4 RHIM Tin Bath Heating Up Service

SUPRAL CA Tin Bath Bottom Blocks concept

- Developed around ~20 years ago
- Tailored composition:
 - Based on **fused $\text{CaO}\cdot\text{Al}_2\text{O}_3$ grains**; ~5% SiO_2
 - chemically **inert to alkali**: no *Nepheline* phase formation therefore no *peeling* phenomena typical of fireclay bottom blocks
 - chemically **inert to Sn**
- Low thermal expansion → reduce the expansion joints
- Low thermal conductivity → comparable to fireclay blocks
- First installation in 2007
- Supplied **~40 lines** worldwide → **No peeling problem reported**
- Pressed, fired and post processed in plant Niederdollendorf (Germany)

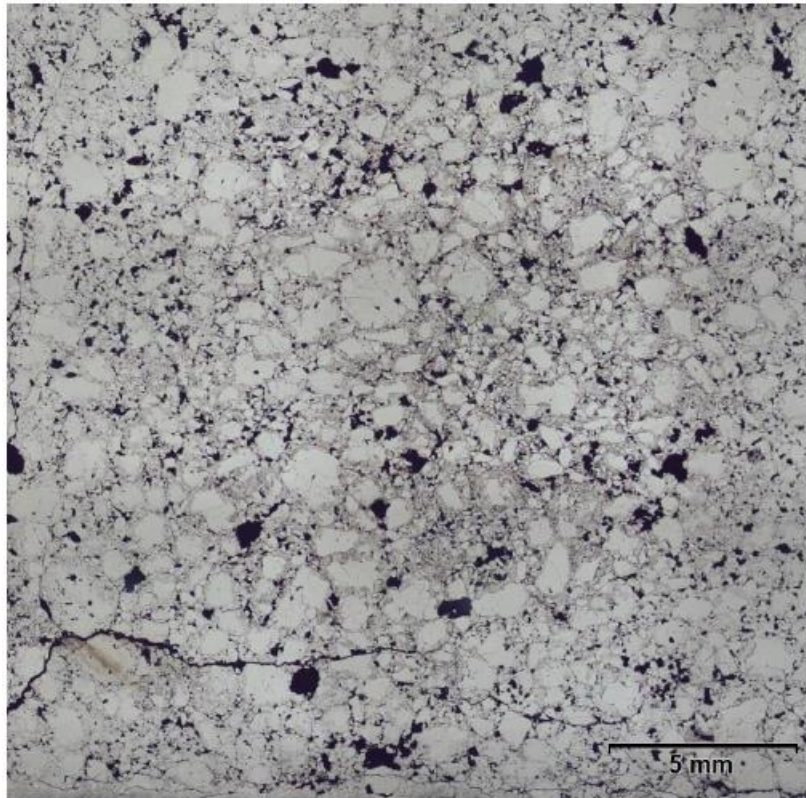


SUPRAL CA Tin Bath Bottom Blocks

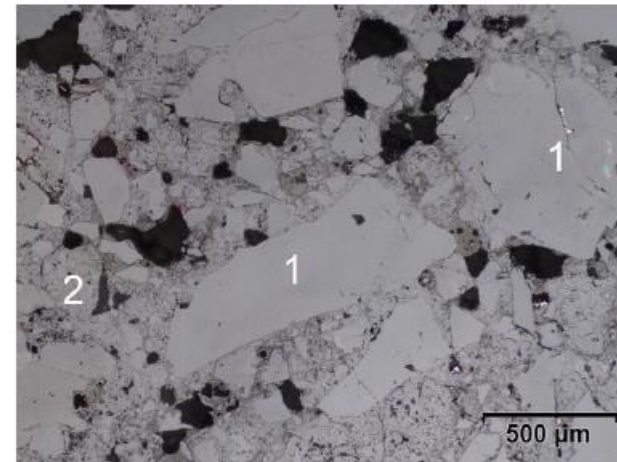
Microstructure

SUPRAL CA Microstructure

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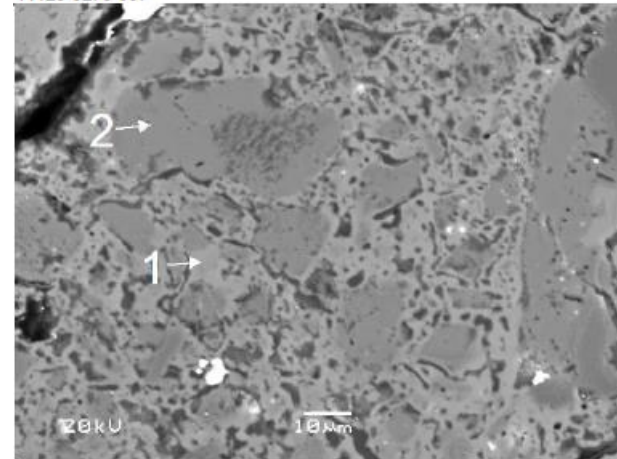


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- SUPRAL CA
Microscopic view:
1. Large **fused CA grains**
 2. Matrix

11129-3276-007



- SUPRAL CA
Matrix view:
1. Gehlenite
 $\text{Ca}_2\text{Al}_2\text{SiO}_7$
 2. Grossite
 CaAl_4O_7

Fig. 7

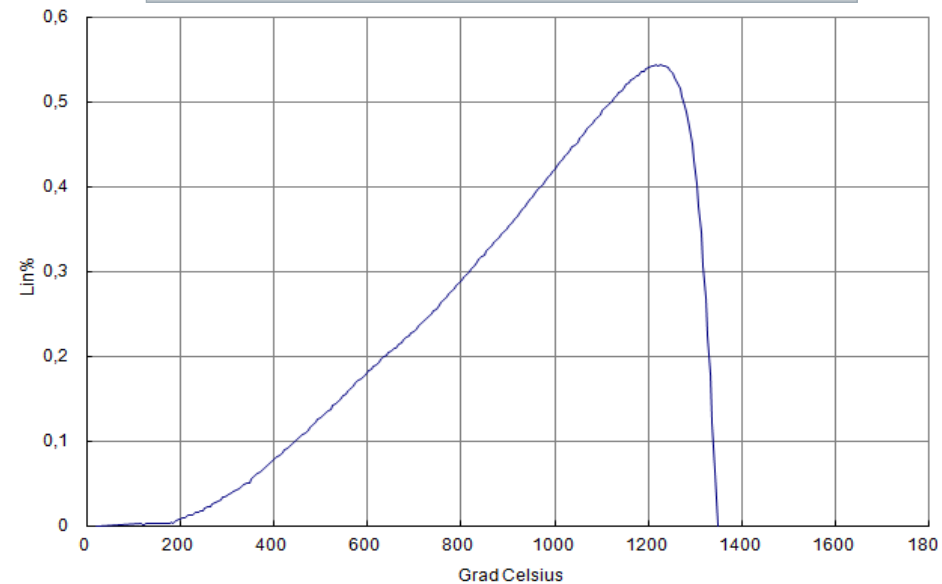
SEM-BSE

SUPRAL CA Tin Bath Bottom Blocks

Supral CA temperature stability

- RUL of Supral CA
 - $T_0 = 1.216^\circ\text{C}$
 - $T_{0.5} > 1340^\circ\text{C}$

Typical SUPRAL CA RUL curve

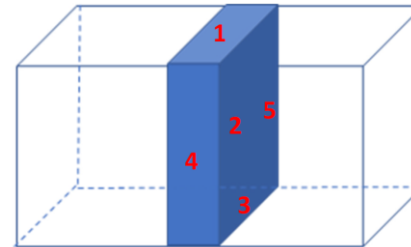
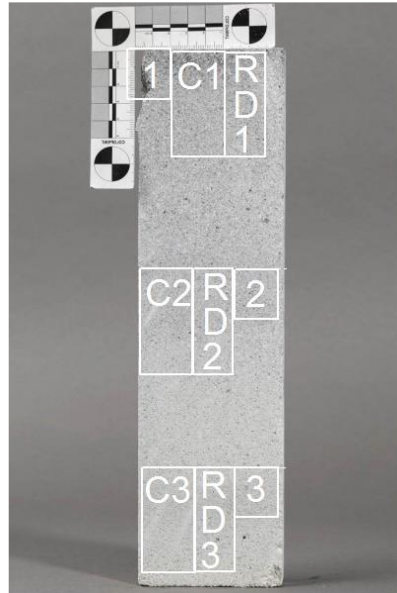


SUPRAL CA Post Mortem Analysis

Sample after 13 years in application



- Very good results after 13 years campaign – no *nepheline peeling* observed
- Very low Na infiltration
- No or very low Sn infiltration mainly in cracks or pores and only on a low mm depth
→ no chemical interaction with CA grains nor with the matrix
- Expected slight densification in the hot side due to long thermal exposure;
core and cold sides remain almost unchanged

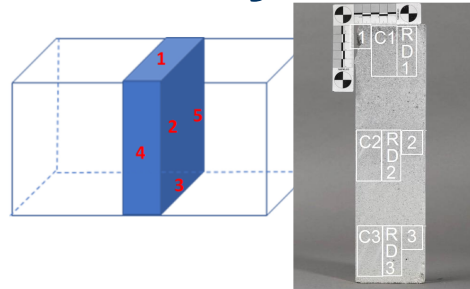


A slice was cut from the centre of the block. Samples from hot side (tin contact), core and cold side were examined.

SUPRAL CA Post Mortem Analysis



Probennahme [mm]	0-60	120-180	240-400	
Chemische Analysen				
Glühverlust (1050 °C) (ISO 26845)				
	Gew. %	Gew. %	Gew. %	
Glühverlust	5.43	2.51	4.23	
Bestimmung mit RFA ¹⁾ (ISO 12677)				
Na ₂ O	0.23	0.25	0.24	
MgO	1.80	1.74	1.77	
Al ₂ O ₃	68.7	69.0	68.6	
SiO ₂	4.89	4.84	4.93	
SO ₃	0.00	0.04	0.15	
K ₂ O	0.05	0.11	0.14	
CaO	24.1	23.9	24.0	
TiO ₂	0.03	0.03	0.03	
Cr ₂ O ₃	0.03	0.01	0.01	
MnO	0.01	0.01	0.01	
Fe ₂ O ₃	0.10	0.07	0.09	
Phasenanalyse (Röntgen-Diffraktometrie ²⁾)				
Mineralphase	Formel	Gew. %	Gew. %	Gew. %
Grossite, syn	CaAl ₄ O ₇ /CaO·2Al ₂ O ₃	>50%	>50%	>50%
Gehlenite, syn	Ca ₂ Al ₂ SiO ₇	10-50%	10-50%	10-50%
Calcium Aluminum Oxide	CaAl ₂ O ₄ /CaO·Al ₂ O ₃	2-5%	2-5%	5-10%
Diaoyudaoite	NaAl ₁₁ O ₁₇	0,5-2%	0,5-2%	0,5-2%
Spinel, syn	MgAl ₂ O ₄	0,5-2%	0,5-2%	0,5-2%
Katoite	Ca ₃ Al ₂ (OH) ₁₂	0,5-2%		
Gibbsite	Al(OH) ₃	0,5-2%	0,5-2%	
Corundum, syn	Al ₂ O ₃	0,5-2%	0,5-2%	
Physikalische Prüfdaten ²⁾				
Testmethode	Einheit			
Rohdichte (DIN EN993-1)	g/cm ³	2.48	2.41	2.39
Offene Porosität (DIN EN993-1)	Vol. %	13.2	18.5	17.7



Very low Na infiltration (determined by ICP)

New SUPRAL CA Phases distribution

Small phases alteration from the original sample

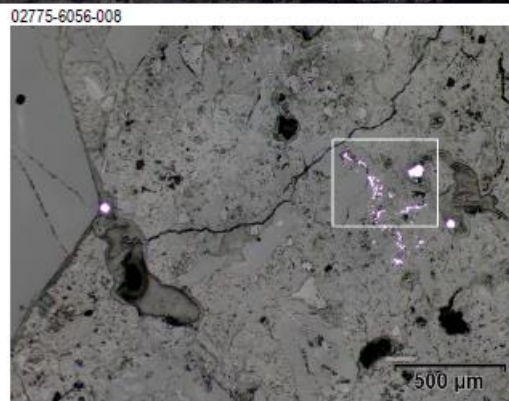
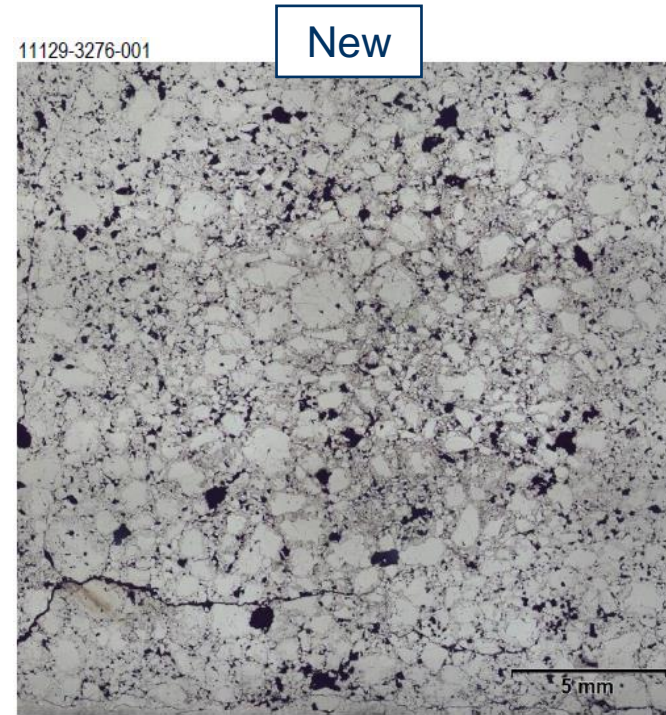
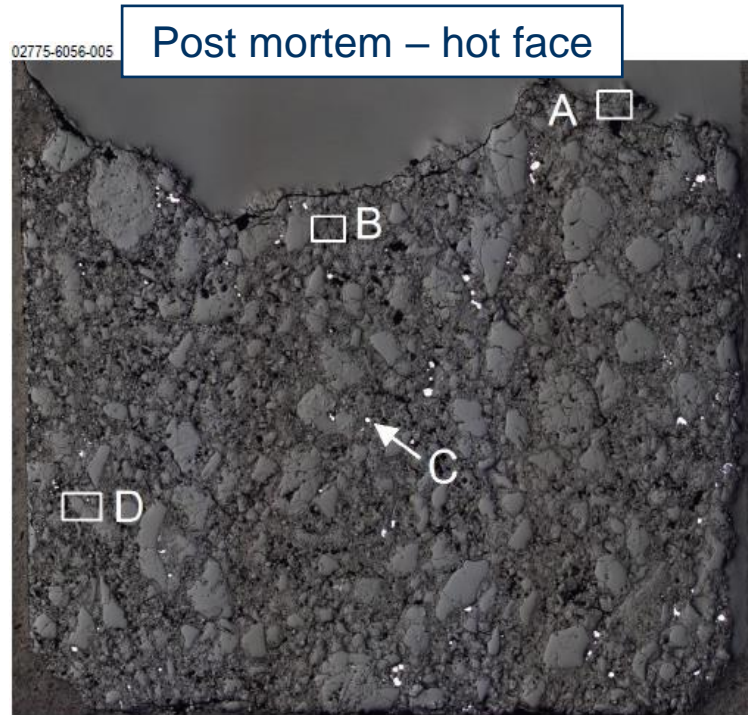
Top block side densification

Phase analysis by x-ray diffraction ²⁾		
Mineral phase	Formula	Wt. %
Grossite	CaAl ₄ O ₇	>50%
RV	%	61.10
Calcium Aluminum Oxide	CaAl ₂ O ₄	10-50%
RV	%	15.30
Mayenite	Ca ₁₂ Al ₁₄ O ₃₃	
RV	%	
Corundum	Al ₂ O ₃	
RV	%	
Diaoyudaoite	NaAl ₁₁ O ₁₇	0.5-2%
RV	%	0.80
Gehlenite	Ca ₂ Al ₂ SiO ₇	10-50%
RV	%	17.20
Gibbsite	Al(OH) ₃	2-5%
RV	%	5.60

¹⁾ On ignited sample (1050 °C) by X-Ray Fluores

SUPRAL CA Post Mortem Analysis

Microstructure analysis – Post mortem vs. New



- Metallic Sn is present only on the surface (first 20mm) as droplets especially in cracks and/or porosities
- No reaction with the refractory material can be detected

SUPRAL CA Tin Bath Bottom Blocks

Hydration – Packaging - Aluvac foil bag

- Due to the raw material base, Supral CA tends to pick up water from the atmosphere
- In order to reduce the water content blocks are dried after finishing and packed into gas-tight Aluvac foil



SUPRAL CA Tin Bath Bottom Blocks

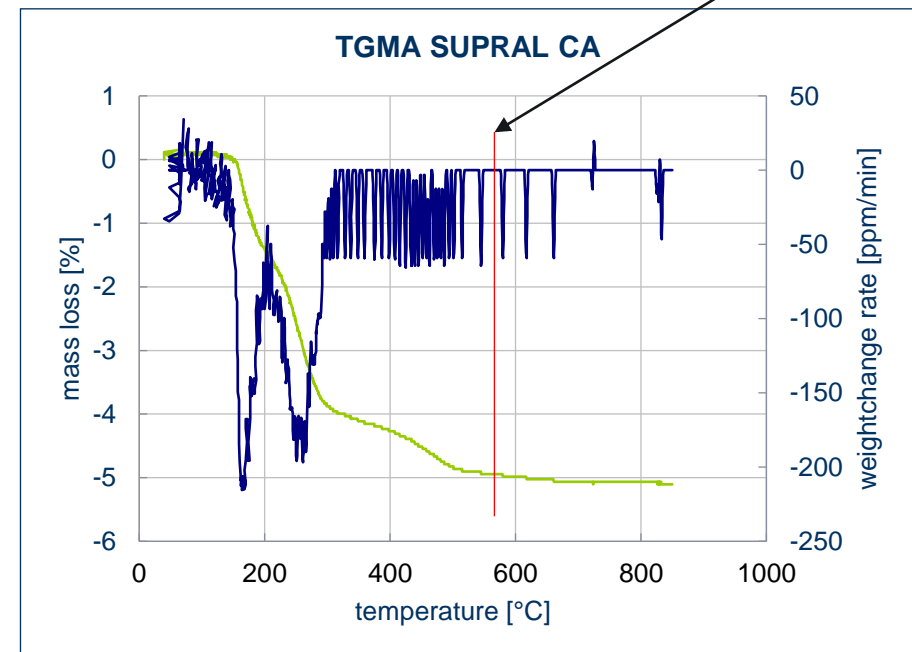
Hydration

- SUPRAL CA hydration:
 - E.g. humid locations, long installation procedure, water leakage accidents
→ water diffused in porosities can potentially react with CA grains forming *CA hydrated phases*
 - If installation and warming up procedure are not correctly handled, hydrated phases could lead to bubbling

550÷600°C
majority of
chemically
bonded water
removed



CA hydrated phases are drastically removed with a correct **warming up procedure** avoiding bubbling risk



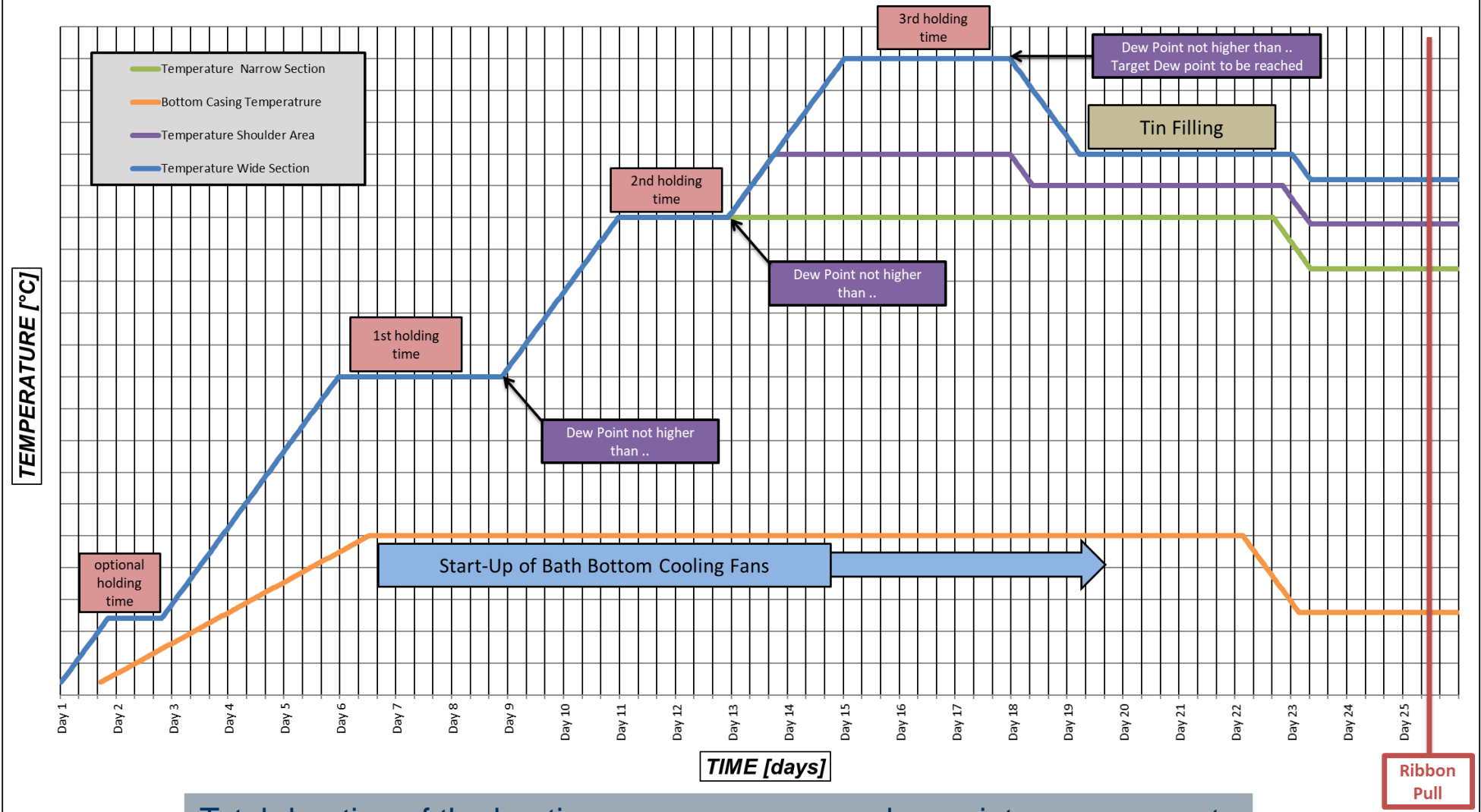
Tin bath Installation / Heating up procedures

RHI Magnesita Tin Bath Heating Up service

- Installation recommendations
- Adjustment of the heating up curve before start up as well as during the process
- Heating up recommendations :
 - Top blocks and bottom casing temperature; tin bath parameters
 - Onsite regular Dew Point measurements to monitor water presence in the tin bath atmosphere during whole heating up procedure with a portable device along tin bath length
- RHIM technical project team available to assist heating up processes onsite
- Service already offered successfully → no bubbling observed

Example of adapted heating up curve

HEAT UP CURVE TIN BATH



Total duration of the heating up may vary upon dew point measurements

Thank you for your attention



Get in Touch

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