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

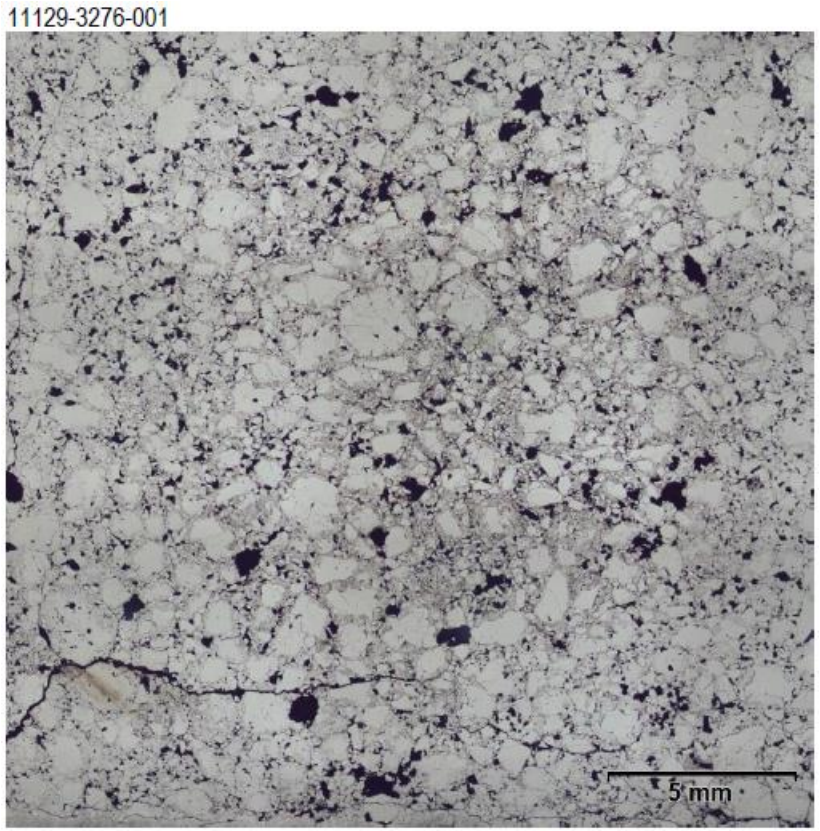
SUPRAL CA Tin Bath Bottom Blocks concept

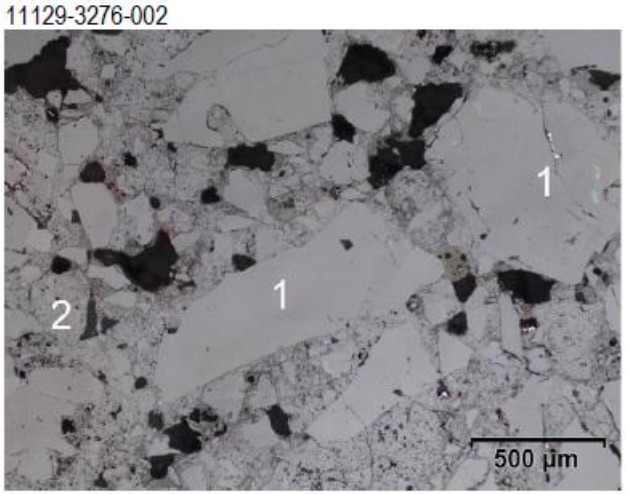
- Developed around ~20 years ago
- Tailored composition:
  - Based on **fused $CaO \cdot Al_2O_3$ grains; ~5%SiO2**
  - chemically **inert to alkali**: no *Nepheline* phase formation therefore no *peeling* phenomena typical of fireclay bottom blocks
  - chemically **inert to Sn**
- Low thermal expansion → 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





SUPRAL CA Microscopic view:

1. Large **fused CA grains**
2. Matrix

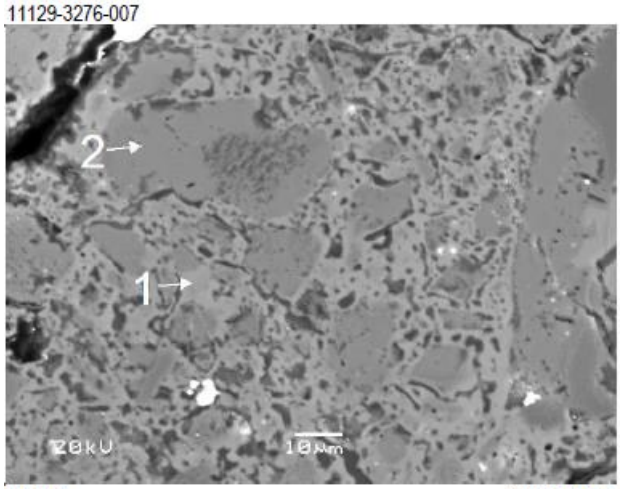


Fig. 7 SEM-BSE

SUPRAL CA Matrix view:

1. Gehlenite $Ca_2Al_2SiO_7$
2. Grossite $CaAl_4O_7$

SUPRAL CA Tin Bath Bottom Blocks

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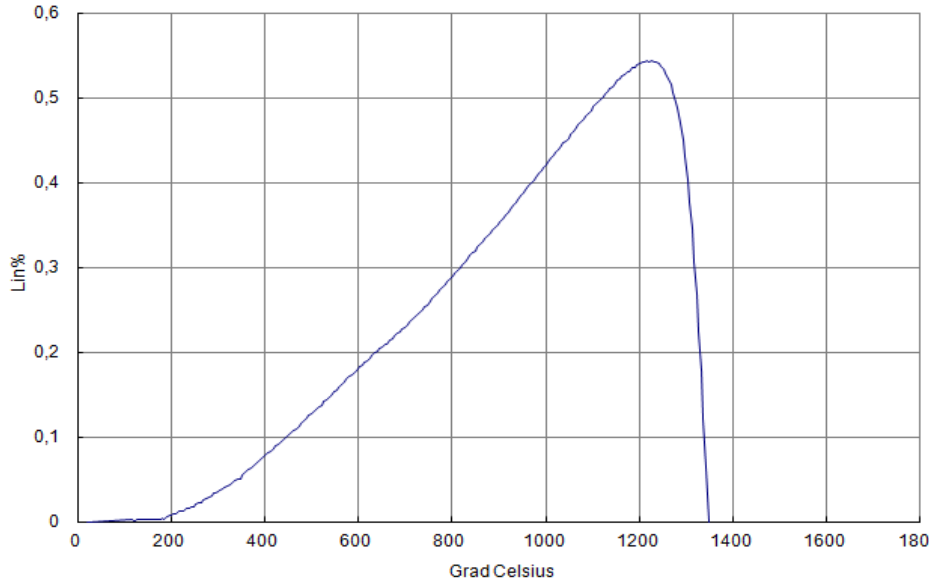
Supral CA temperature stability

- RUL of Supral CA

- T_0 = 1.216°C

- $T_{0.5}$ > 1340°C

Typical SUPRAL CA RUL curve



SUPRAL CA Post Mortem Analysis

Sample after 13 years in application

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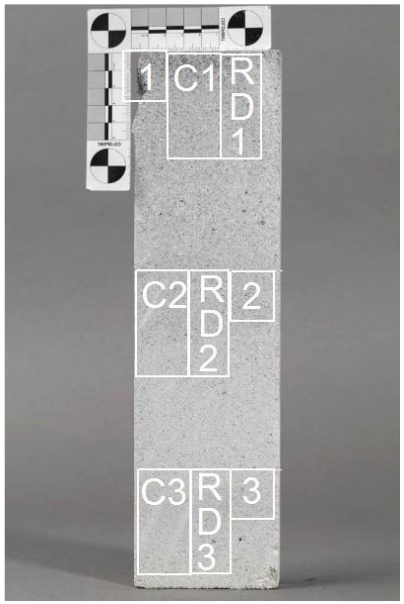
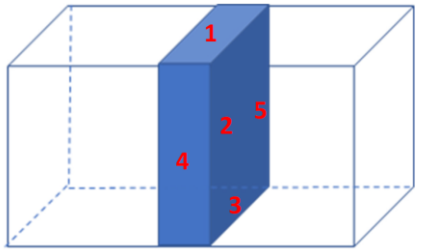
- Very good results after 13 years campaign – no *nepheline peeling* observed
- Very low Na infiltration
- No or very low Sn infiltration mainly in cracks or pores and only on a low mm depth
  → no chemical interaction with CA grains nor with the matrix
- Expected slight densification in the hot side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

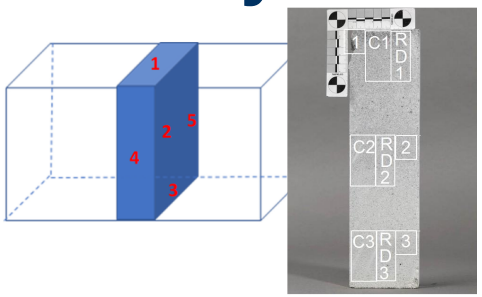




A slice was cut from the centre of the block.
Samples from hot side (tin contact), core and cold side were examined.

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_2O		0.23	0.25	0.24
MgO		1.80	1.74	1.77
Al_2O_3		68.7	69.0	68.6
SiO_2		4.89	4.84	4.93
SO_3		0.00	0.04	0.15
K_2O		0.05	0.11	0.14
CaO		24.1	23.9	24.0
TiO_2		0.03	0.03	0.03
Cr_2O_3		0.03	0.01	0.01
MnO		0.01	0.01	0.01
Fe_2O_3		0.10	0.07	0.09
Phasenanalyse (Röntgen-Diffraktometrie)[2]				
Mineralphase	**Formel**	**Gew.%**	**Gew.%**	**Gew.%**
Grossite, syn	$CaAl_4O_7/CaO{\cdot}2Al_2O_3$	>50%	>50%	>50%
Gehlenite, syn	$Ca_2Al_2SiO_7$	10-50%	10-50%	10-50%
Calcium Aluminum Oxide	$CaAl_2O_4/CaO{\cdot}Al_2O_3$	2-5%	2-5%	5-10%
Diaoyudaoite	$NaAl_{11}O_{17}$	0,5-2%	0,5-2%	0.5-2%
Spinel, syn	$MgAl_2O_4$	0,5-2%	0,5-2%	0.5-2%
Katoite	$Ca_3Al_2(OH)_{12}$	0,5-2%		
Gibbsite	$Al(OH)_3$	0,5-2%	0,5-2%	
Corundum, syn	Al_2O_3	0,5-2%	0,5-2%	
Physikalische Prüfdaten[2]				
Testmethode	**Einheit**			
Rohdichte (DIN EN993-1)	**g/cm³**	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)

Small phases alteration from the original sample

Top block side densification

New SUPRAL CA Phases distribution

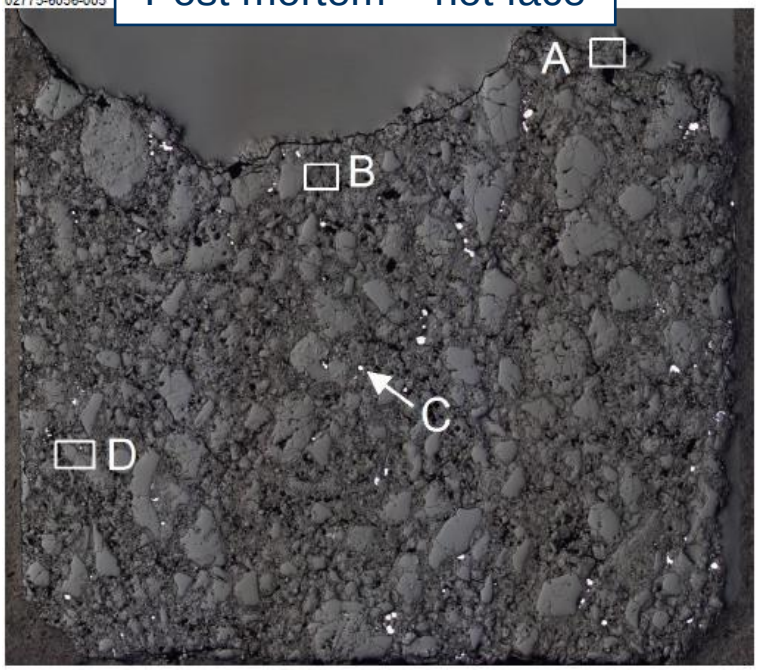
Phase analysis by x-ray diffraction[2]		
Mineral phase	**Formula**	**Wt.%**
Grossite	$CaAl_4O_7$	>50%
RV	%	61.10
Calcium Aluminum Oxide	$CaAl_2O_4$	10-50%
RV	%	15.30
Mayenite	$Ca_{12}Al_{14}O_{33}$	
RV	%	
Corundum	Al_2O_3	
RV	%	
Diaoyudaoite	$NaAl_{11}O_{17}$	0.5-2%
RV	%	0.80
Gehlenite	$Ca_2Al_2SiO_7$	10-50%
RV	%	17.20
Gibbsite	$Al(OH)_3$	2-5%
RV	%	5.60

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

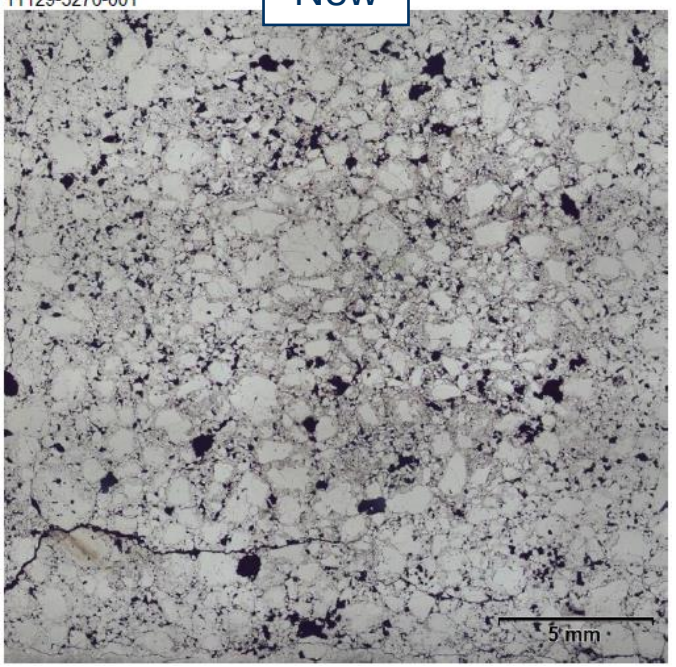
SUPRAL CA Post Mortem Analysis

Microstructure analysis – Post mortem vs. New

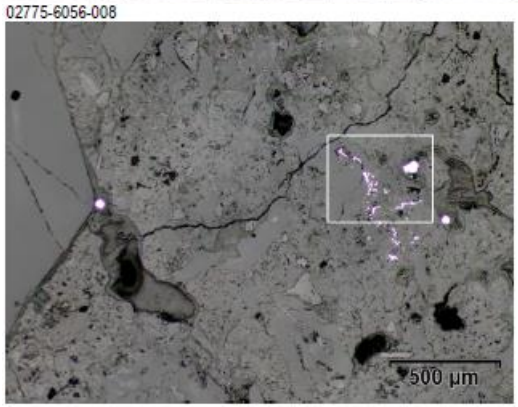
Post mortem – hot face



New



Detail B



- 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

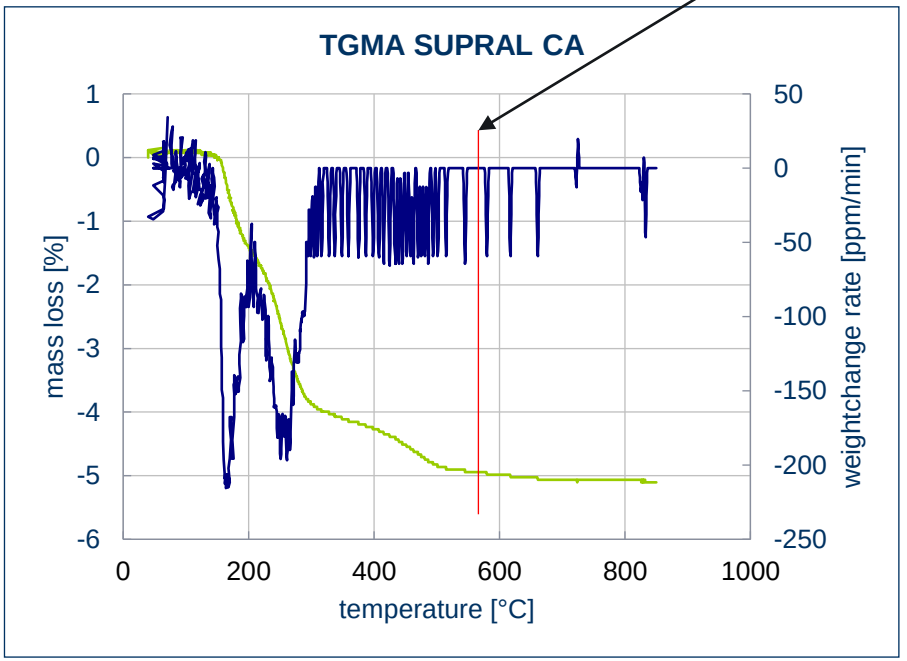
- Due to the raw material base, Supral CA tends to pick up water from the atmosphere
- In order to reduce the water content blocks are dried after finishing and packed into gas-tight Aluvac foil

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

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



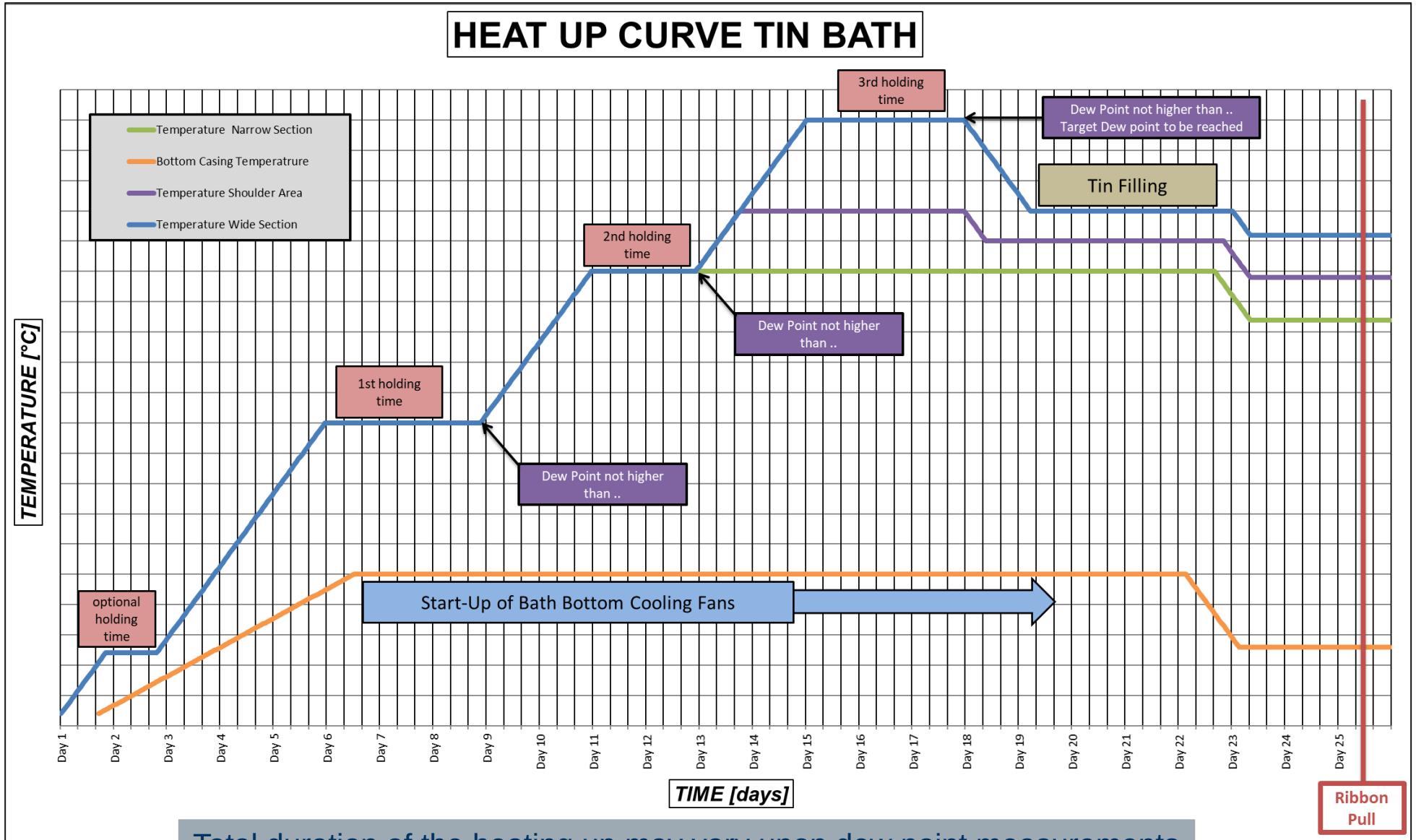
Tin bath Installation / Heating up procedures

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



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

Thank you for your attention

Get in Touch

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