Distinguishing Features of a Carbonization Line Designed for Heavy Tows

GOCarbonFiber
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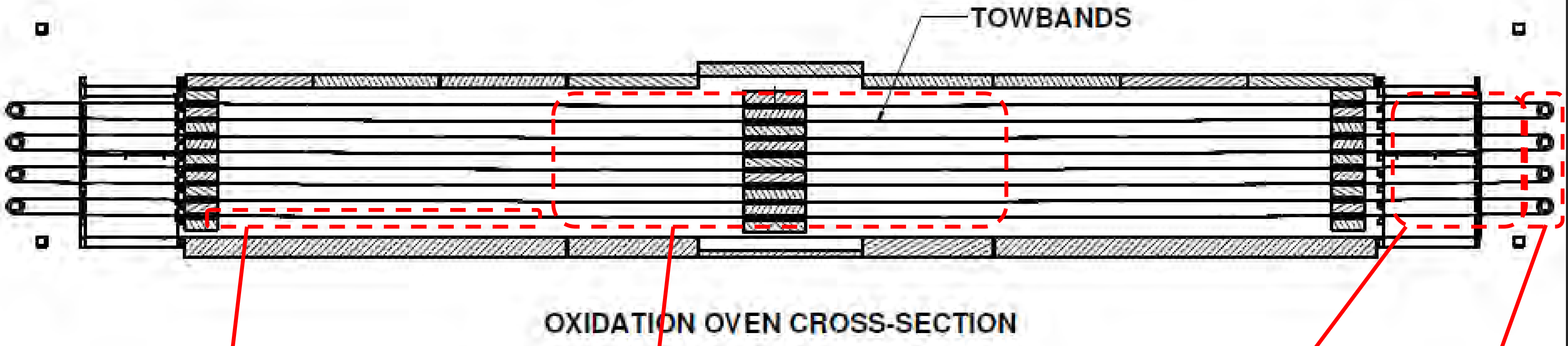
About Harper

- Headquartered in Buffalo, NY, USA
- An employee-owned business
- State-of-the-art Technology Center
- Access to carbon fiber piloting facilities
- Multi-disciplined engineering talent
  - Chemical
  - Ceramic
  - Mechanical
  - Electrical
  - Industrial
  - Process & Integration

Agenda

1. Thermal model of light and heavy tows in an oxidation oven
2. Highlight differences of heavy tows and how this guides the equipment design and operation

Oxidation Oven Thermal Model



Heat up time of tows entering the oven

Exothermic tow temperature rise above the oven setpoint

Tow cooling between oven and passback rolls

Heat transfer to passback rolls and roll temperatures

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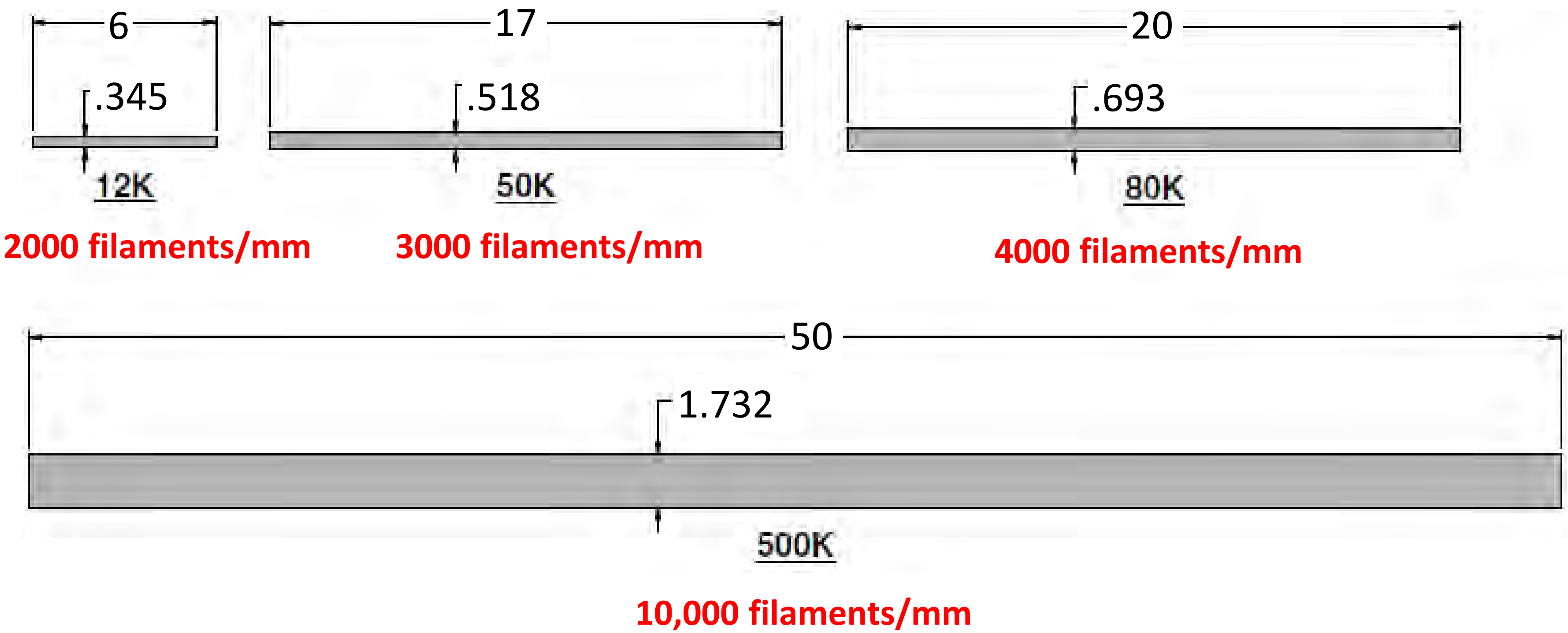
Model Assumptions

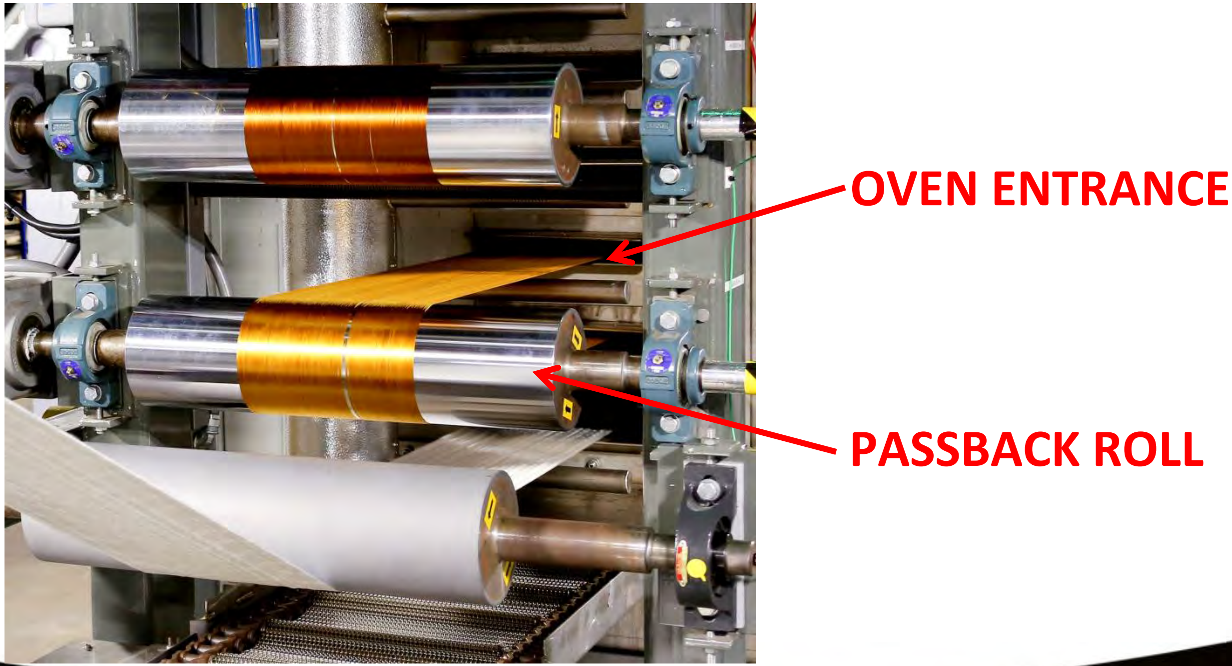
- PAN filaments are round with 11.5 micron diameter
- Filament volume fraction 0.6 [1]
- PAN emissivity = 0.85 [2]
- Other properties and constants at end of slide set

Comparison of Tow Cross-Sections (mm)

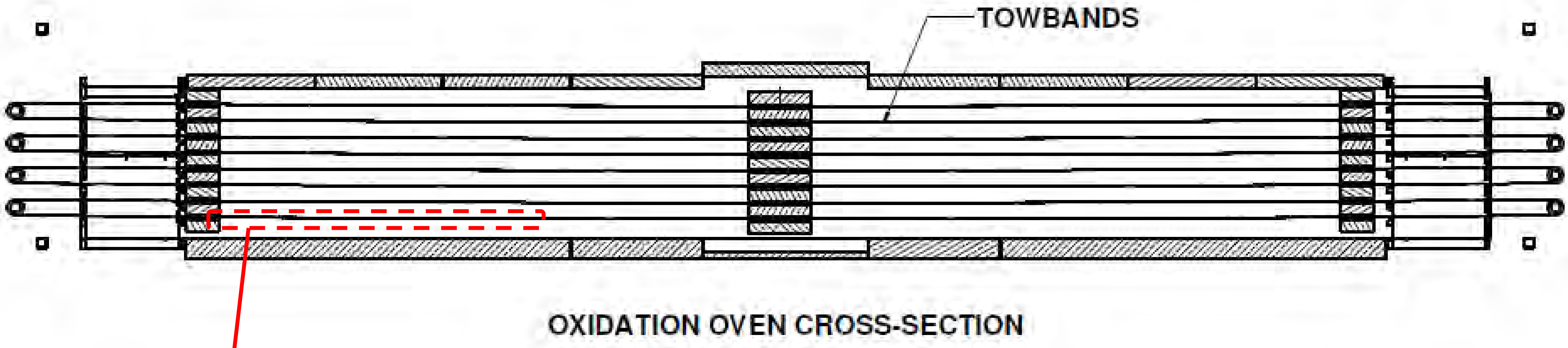


Additional Model Assumptions

- All significant heat and mass transfer is in the vertical direction
- Exothermic energy is only significant when the tow temperature is near the oven temperature

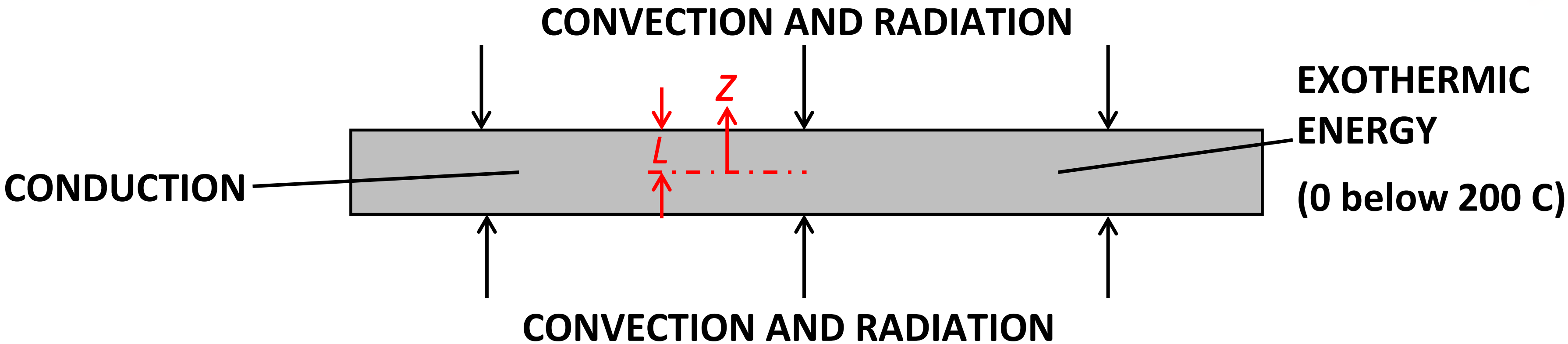


Oxidation Oven Thermal Model

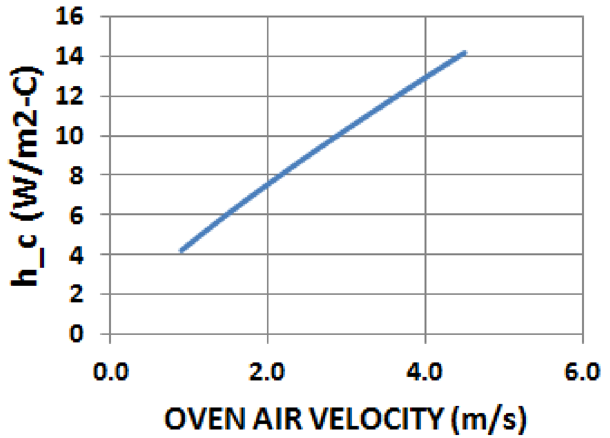


Heat up time of tows entering the oven

Thermal Model of Tows Heatup



Convection [3]: $$h_c = \left(\frac{k}{d}\right)\left[8.1 + 0.019\left(\frac{Vd}{\nu}\right)^{.83}\right]$$



Radiation [4]:

$$h_{r,T_0\to T_1} = \sigma\epsilon F\,\frac{\int_{T_0}^{T_1}(T_1^4 - T^4)dT}{\int_{T_o}^{T_1}(T_1 - T)dT} = \frac{2\sigma\epsilon F}{(T_1 - T_0)^2}\left[\frac{4T_1^5 + T_0^5}{5} - T_1^4 T_0\right]$$

Solution Equation for Tow Heatup [5]

$$\frac{T(z,t)-T_1}{T_0-T_1} = 2\sum_{n=1}^{\infty}\left(\frac{\sin\mu_n L}{\mu_n L+\sin\mu_n L\cos\mu_n L}\right)e^{-\alpha_{tow}\mu_n^2 t}\cos\mu_n z$$

Where:

$$\tan\mu_n L = \frac{h_c+h_r}{\mu_n k_{tow}}$$

And:

$$\frac{1}{k_{tow}} = \frac{\theta_{fiber}}{k_{fiber}} + \frac{1-\theta_{fiber}}{k_{air}}$$

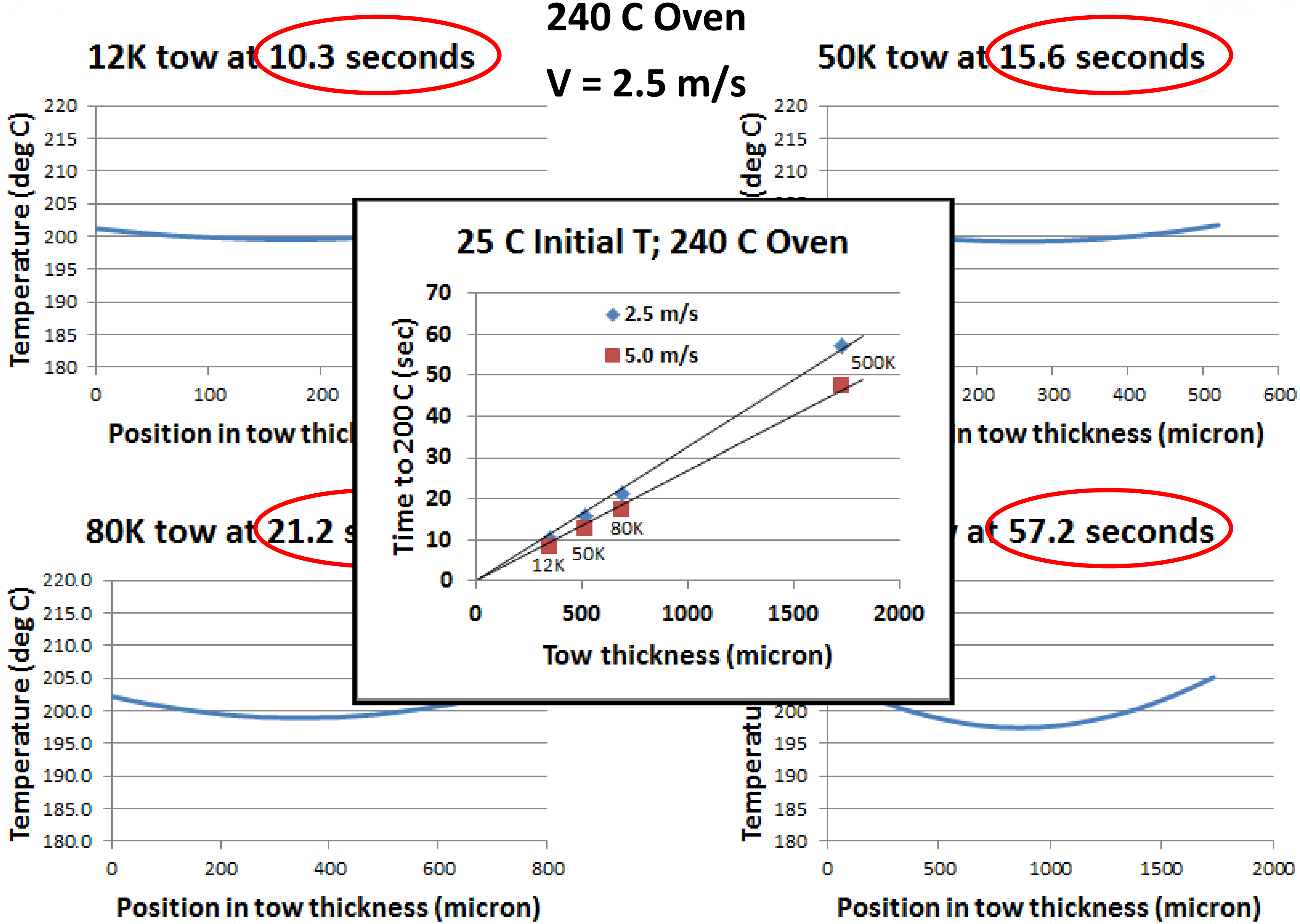
And:

$$\alpha_{tow} = \frac{k_{tow}}{\rho_{tow}c_{p,tow}}$$

Thermal Calculations – Heatup

240 C Oven

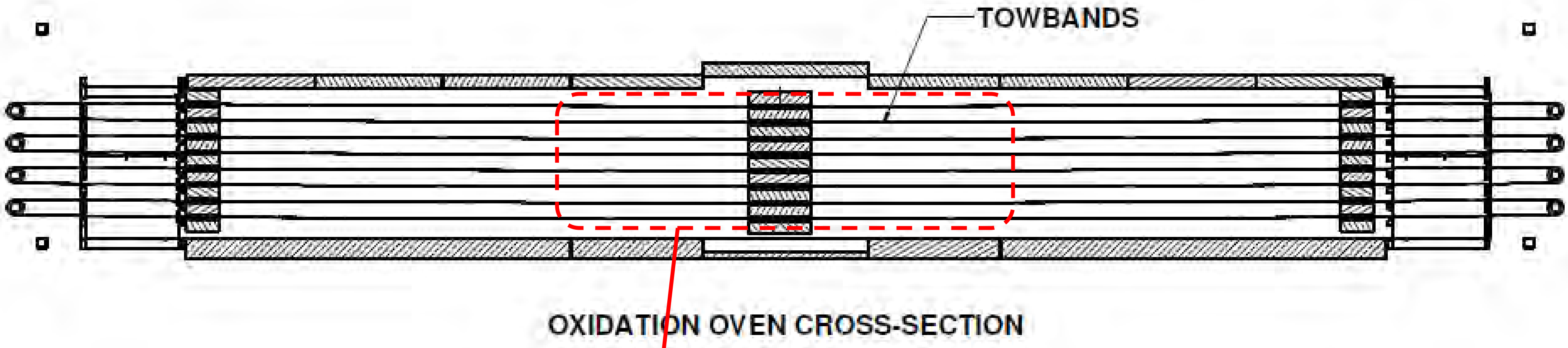
V = 2.5 m/s



Discussion

- Increasing tow thickness leads to a significant portion of the pass length being used just for heat up
  - This favors slower line speeds (wider)
  - This favors ovens with fewer passes (longer)
- Increased oven air velocity only helps a little (does not change radiation)

Oxidation Oven Thermal Model



Exothermic tow temperature rise above the oven setpoint

Temperature Rise Due to Exothermic Energy Release

Solution equation:

$$T(z) - T_1 = \frac{\ddot{u}L^2}{2k_{tow}}\left[1 - \left(\frac{z}{L}\right)^2 + \frac{2k_{tow}}{h_c L}\right]$$

Where:

$$\ddot{u} = \frac{\eta \rho_{tow} \Delta H}{\tau_{Residence}}$$

And:

$$\eta = \frac{Peak\ Local\ Exotherm}{Mean\ Exotherm} = \frac{4}{3}$$

A rule of thumb is 1/3 of the exotherm is in the first half of the residence time and 2/3 is in 2nd half of the residence time.

Exothermic Temperature Rise - Calculations

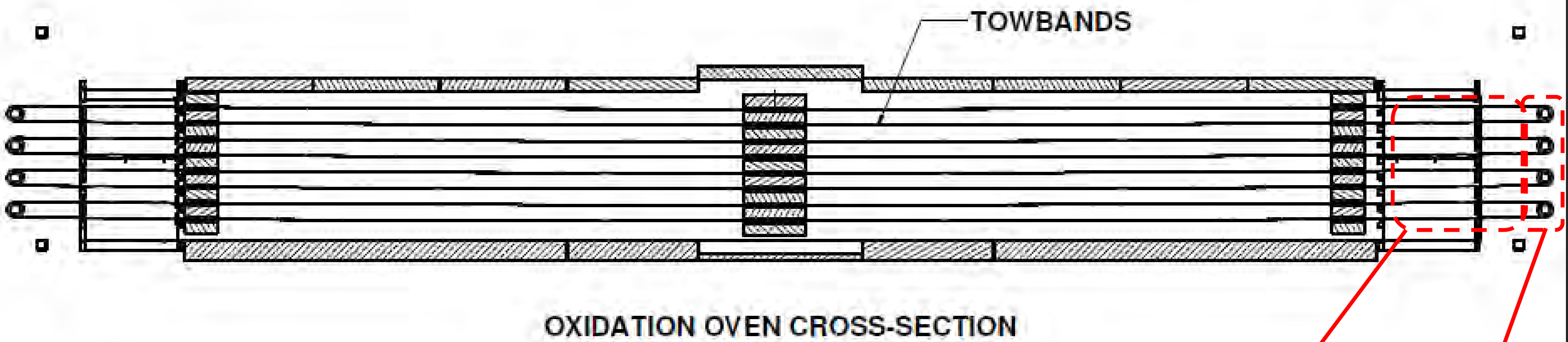
			12K	50K	80K	500K
60 Minutes Residence Time	Oven velocity		12K	50K	80K	500K
	2.5 m/s	Max Rise ^{0}C	10	15	20	53
	5.0 m/s	Max Rise ^{0}C	6	9	12	32
	Tow Delta (z = 0 to z = L)		0.1	0.3	0.6	3.6

120 Minutes Residence Time	Oven velocity		12K	50K	80K	500K
	2.5 m/s	Max Rise ^{0}C	5	8	10	26
	5.0 m/s	Max Rise ^{0}C	3	4	6	16
	Tow Delta (z = 0 to z = L)		0.1	0.2	0.3	1.8

Discussion

- Increasing tow thickness means significant differences between the tow temperature and the oven setpoint temperature
- Oven air velocity is the important variable – radiation does not help – which suggests that heavy tow ovens be designed for higher air velocities

Oxidation Oven Thermal Model



Tow cooling between oven and passback rolls

Heat transfer to passback rolls and roll temperatures

Tow Cool Down

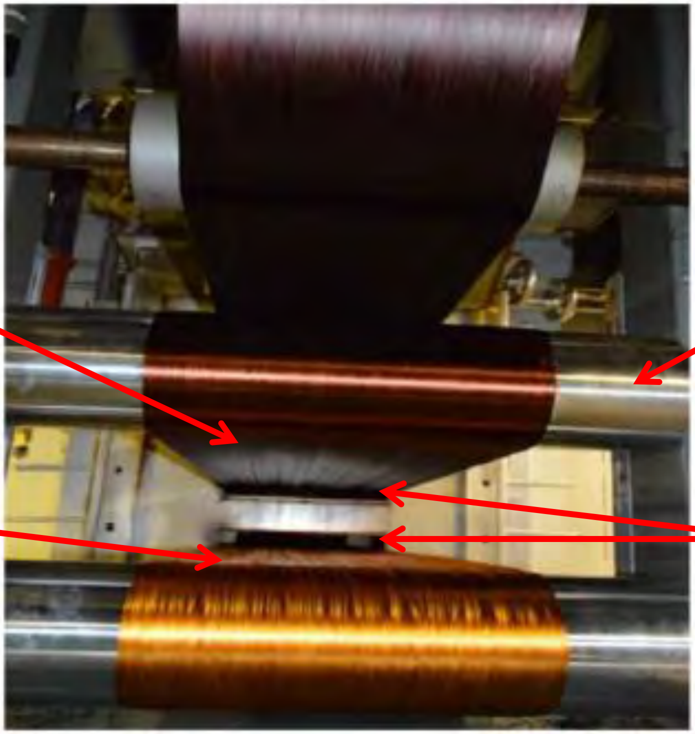
Same solution equation as tow heatup, except that there is no forced convection

Instead there is natural convection

$$h_c = \left(\frac{k}{d}\right)\left[0.27\ Ra^{1/4}\right];\ Bottom\ side$$

$$h_c = \left(\frac{k}{d}\right)\left[0.14\ Ra^{1/3}\right];\ Top\ side$$

$$Ra = \frac{(T_{tow} - T_{ambient})}{(T_{ambient} + 273)}\frac{gd^3}{\alpha\nu}$$



Passback Roll Temperature

The roll temperature balances heat flowing in from the tows with heat flowing out to ambient

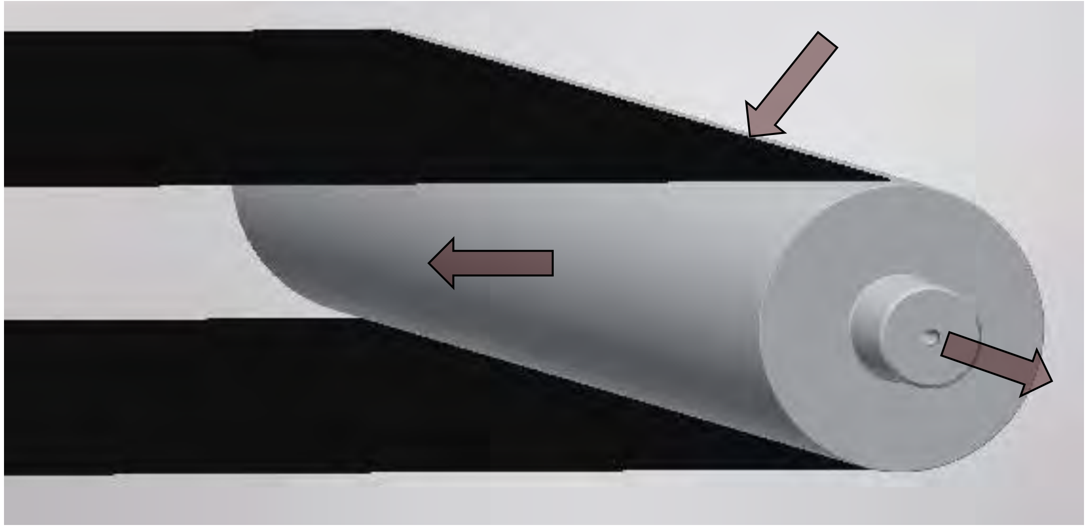
Heat out of the rolls by convection and radiation

$$(h_c + h_r)A'_{roll}(T_{roll} - T_{ambient})$$

Heat into the rolls from the tows

$$h_{tow \rightarrow roll} A_{roll} (T_{tow} - T_{roll})$$

$$h_c = \left(\frac{k}{d_{roll}}\right)\left[0.39Ra^{1/4} + 0.04\left(\frac{V_{roll} d_{roll}}{\nu}\right)^{0.8}\right]$$

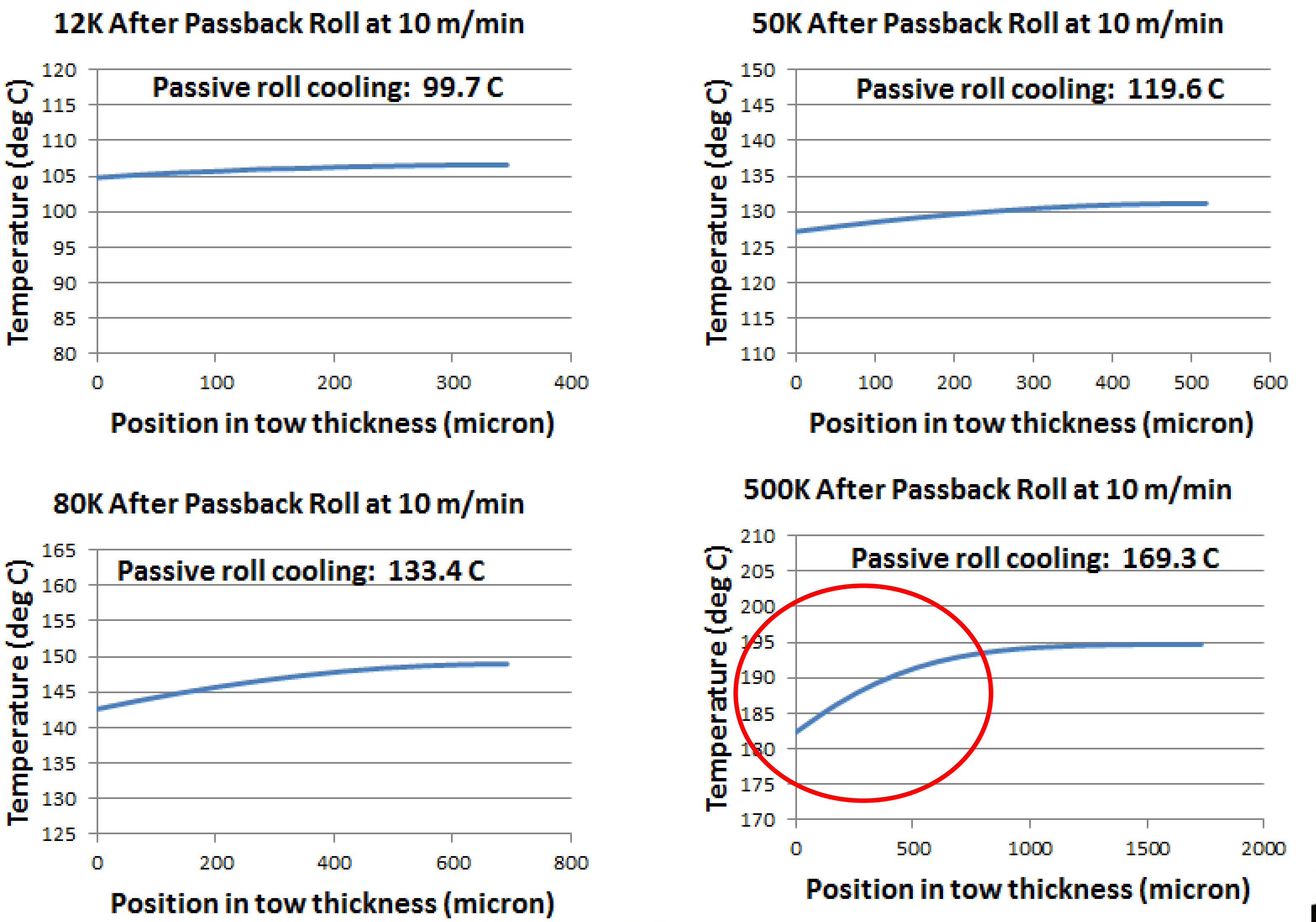


Heat out of the rolls by conduction at the journals

$$2\left(\frac{KA}{L}\right)_{Journal}(T_{roll} - T_{ambient})$$

Thermal Calculations – Tows Just After a Roll

240 C Oven



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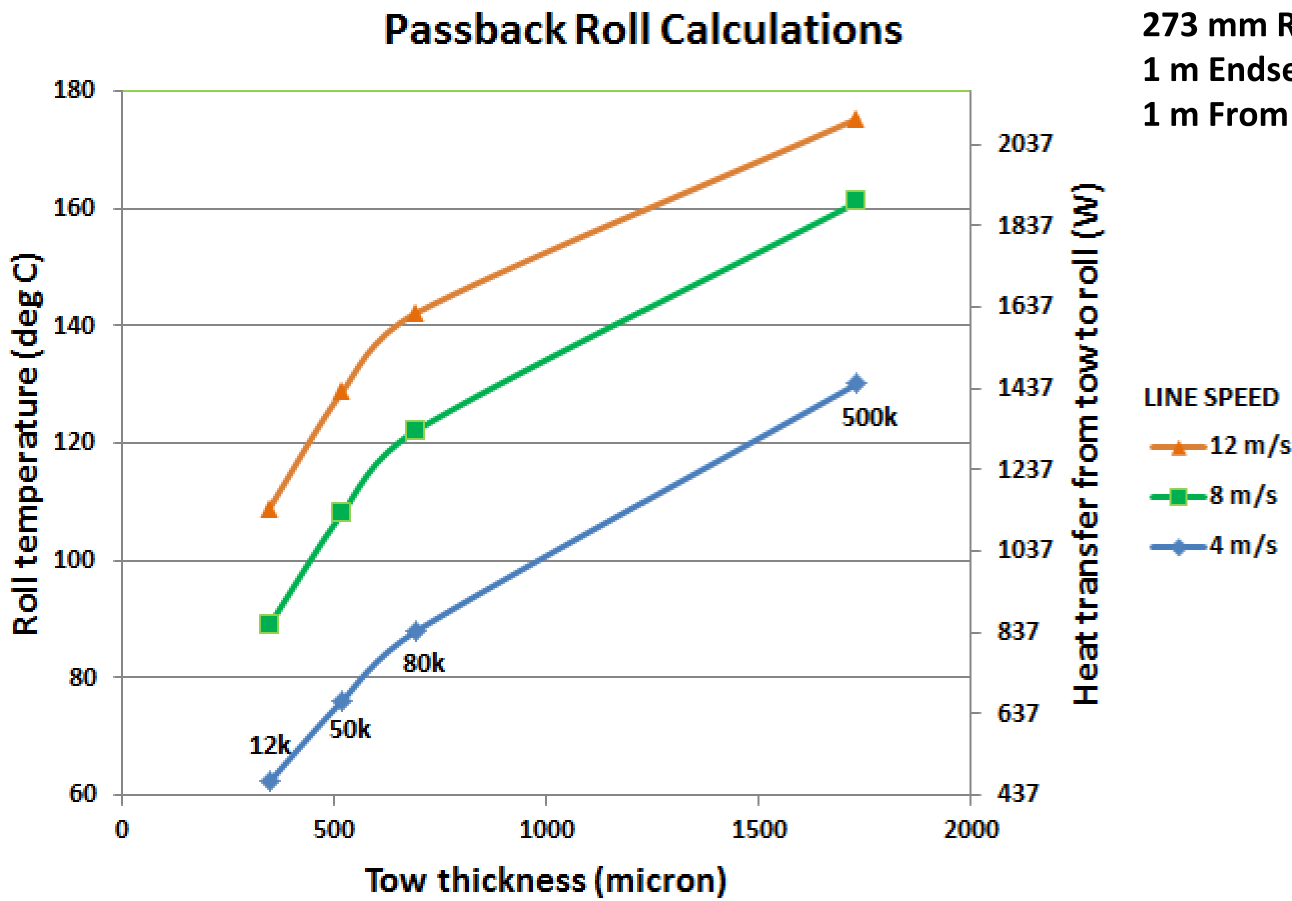
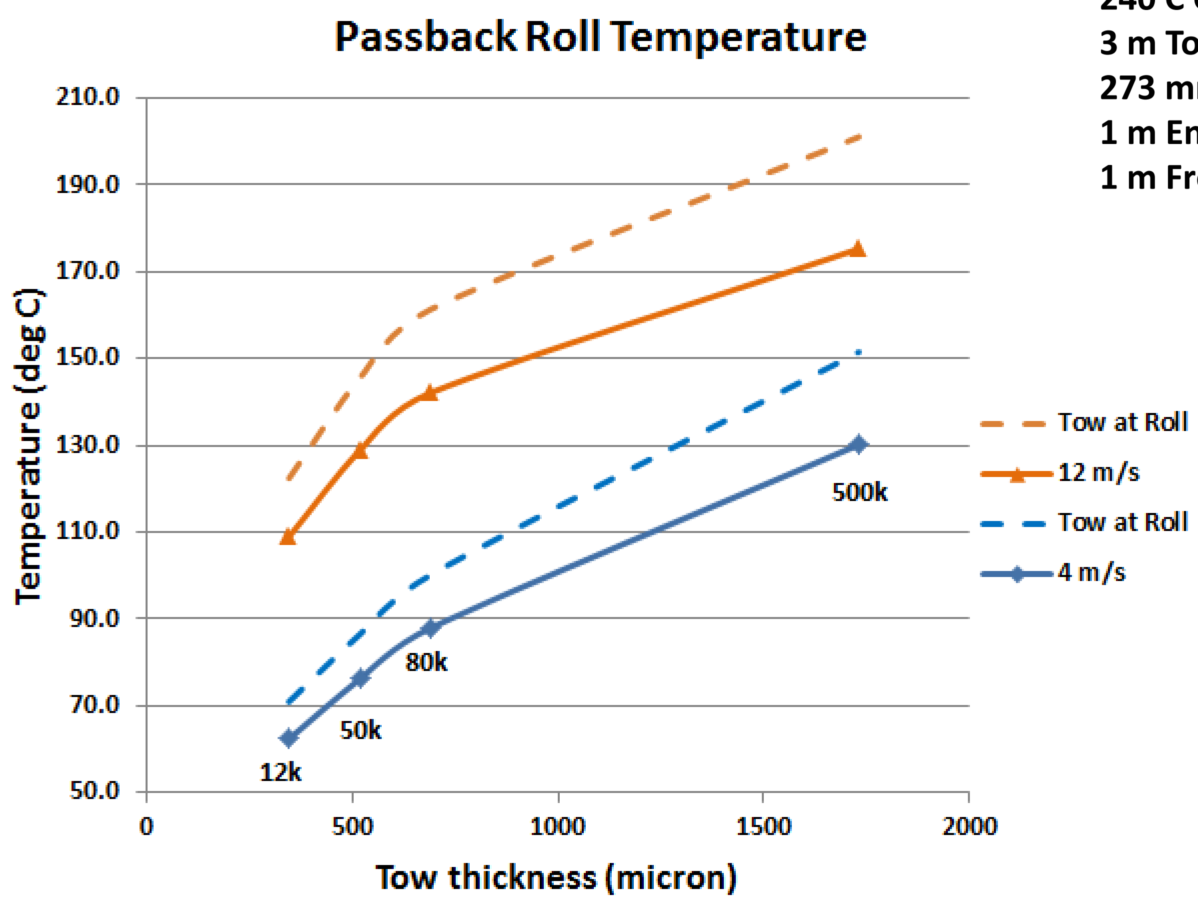
Tow Cool-Down Calculations



240 C Oven
3 m Towband
273 mm Roll
1 m Endseal Length
1 m From Endseal to Roll

Tow Cool-Down Calculations

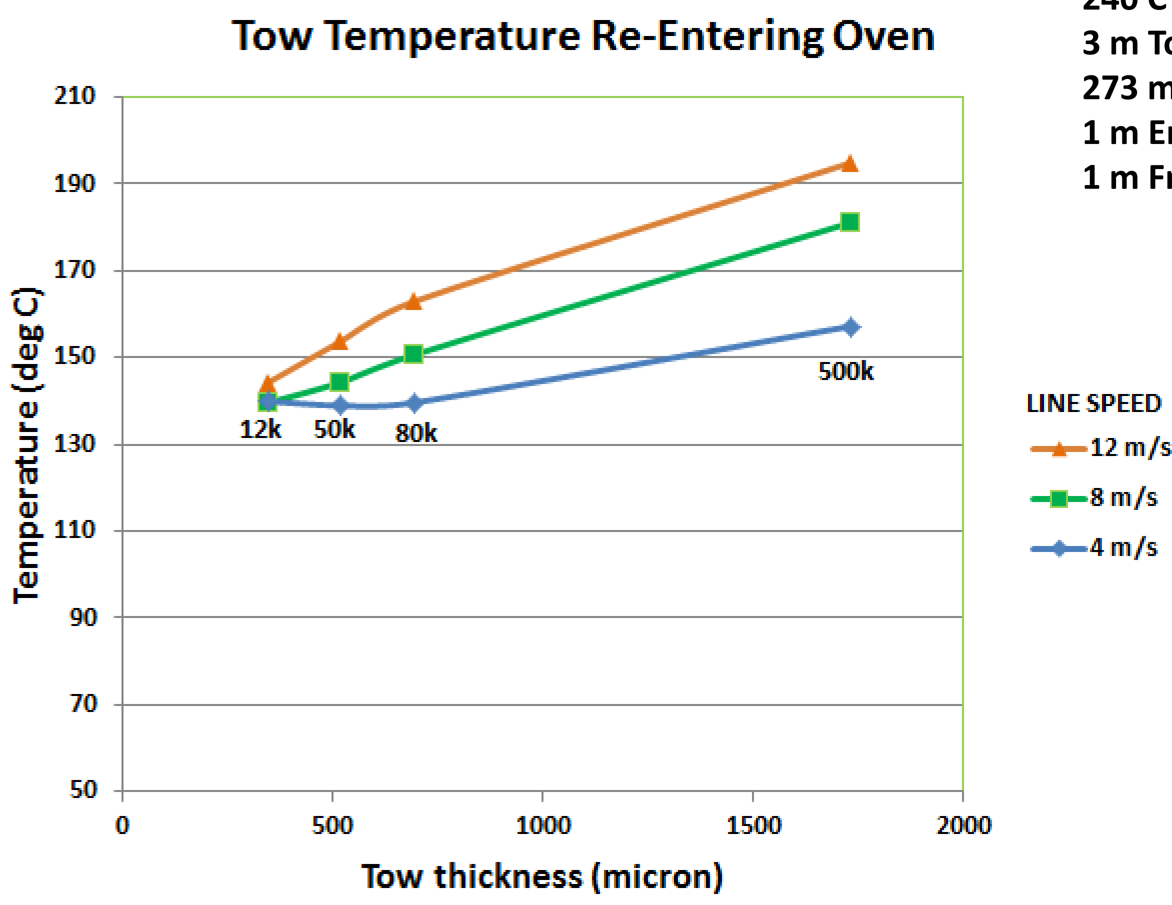


240 C Oven
3 m Towband
273 mm Roll
1 m Endseal Length
1 m From Endseal to Roll

Discussion

- The heavier the tow, the higher the roll temperatures
  - Passive cooling is inefficient to shed heat from tows
  - Active cooling may be required on heavy tow lines
- Heavy tow lines at lower line speeds will have less problem

Thermal Calculations – Tow Re-Entry Temperature



240 C Oven
3 m Towband
273 mm Roll
1 m Endseal Length
1 m From Endseal to Roll

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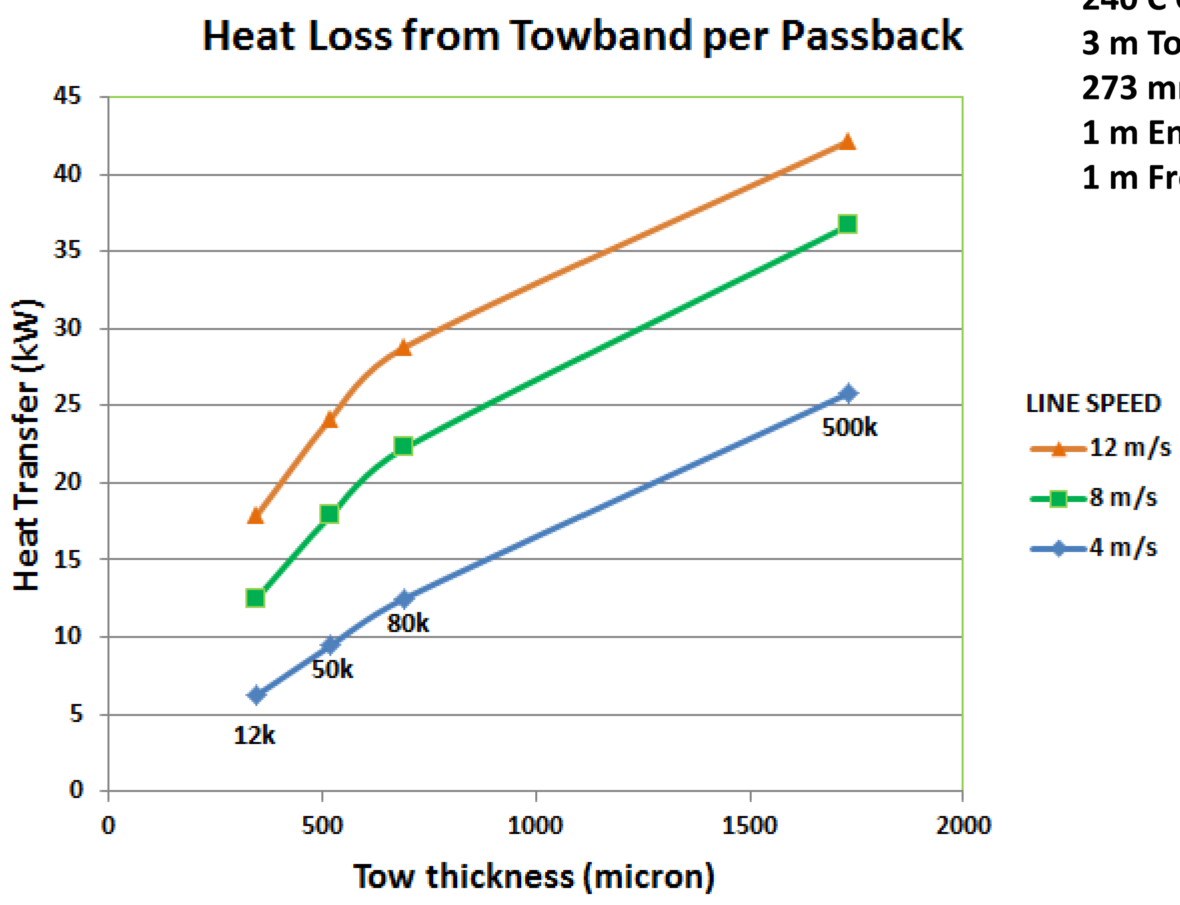
Thermal Calculations – Heat Loss Per Pass



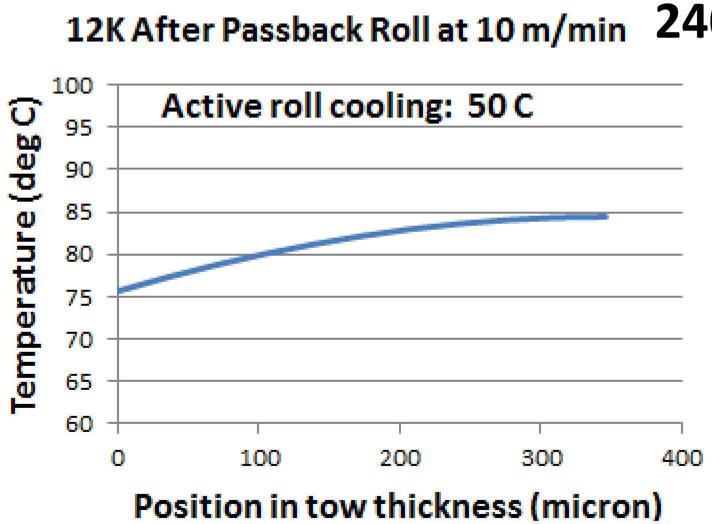
240 C Oven
3 m Towband
273 mm Roll
1 m Endseal Length
1 m From Endseal to Roll

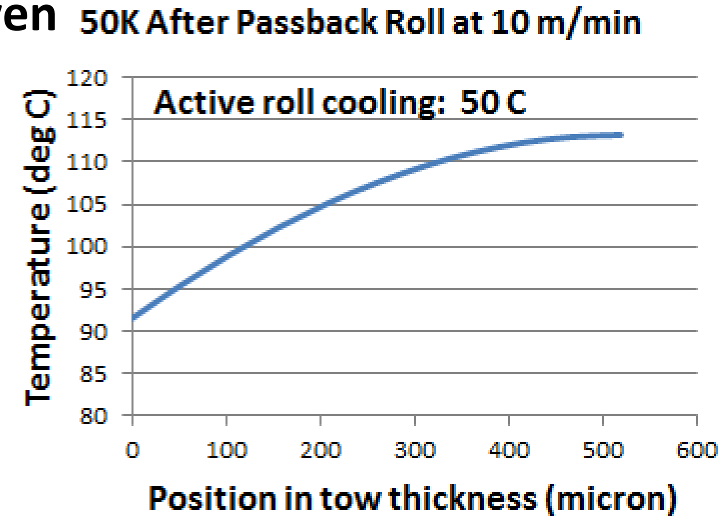
Discussion

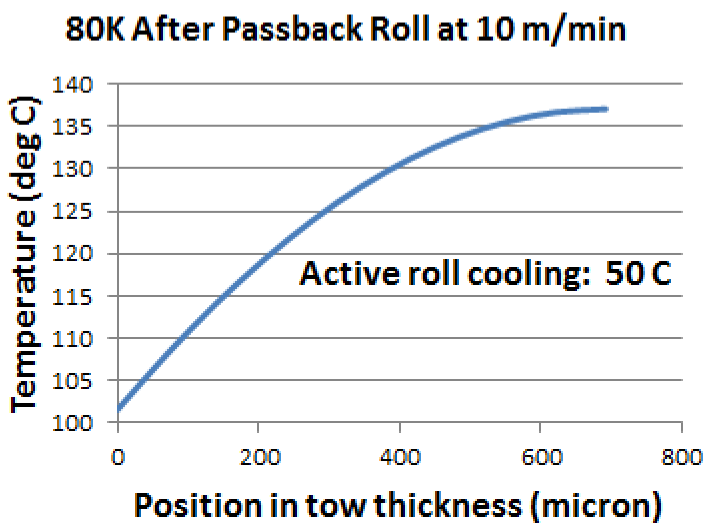
- End-seals have beneficial energy exchange
- Heavy tows will increase the energy penalty for many passes
  - This suggests longer ovens with fewer total passes
  - If active cooling used on rolls, will increase the energy penalty

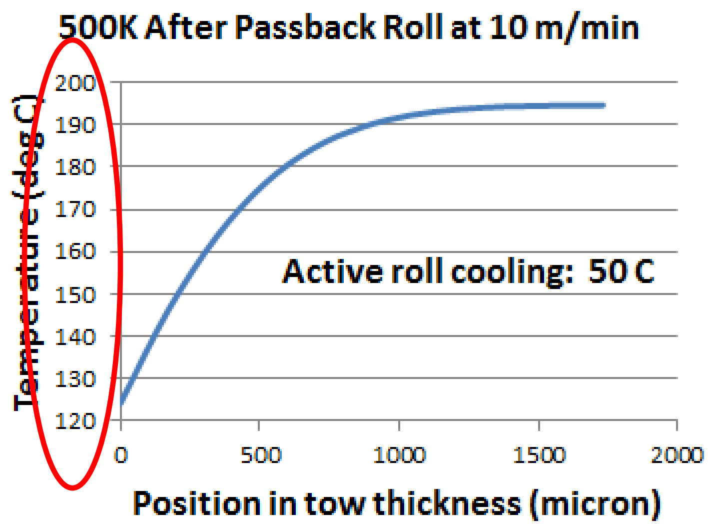
Thermal Calculations –
Tows Just After an Actively Cooled Passback Roll

240 C Oven









Comparisons of Passive and Active Roll Cooling

240 C Oven; 3 m Towband; 273 mm Roll
1 m Endseal Length; 1 m From Endseal to Roll

Heat transfer from tows to roll (kW) at Linespeed of 10 m/s		Passive roll cooling	Active roll cooling (50 C)
Tow K	Z (micron)		
12K	346	1.0	4.8
50K	519	1.3	6.9
80K	693	1.5	8.3
500K	1731	2.1	12

Tow temperature re-entering oven (deg C) at Linespeed of 10 m/s		Passive roll cooling	Active roll cooling (50 C)
Tow K	Z (micron)		
12K	346	142	128
50K	519	149	134
80K	693	157	143
500K	1731	189	179

Heat loss from towband per passback (kW) at Linespeed of 10 m/s		Passive roll cooling	Active roll cooling (50 C)
Tow K	Z (micron)		
12K	346	15	17
50K	519	21	25
80K	693	26	30
500K	1731	40	48

Discussion

- Unclear impact of temperature gradient inside tow
- The heavier the tow, the more significant the energy penalty from active cooling the rolls




Final Thoughts

- The different heating and cooling behavior of light and heavy tows leads to differences in the ovens and passback rolls
  - Wider – Slower – Longer
  - Passive cooling ⟶ Active cooling
- Mass transfer, such as diffusion of oxygen into the tow, likely also an important difference with heavy tows

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Material Properties and Constants

Filament volume fraction in the tow [1]: $\theta_{fiber} = 0.6$

PAN filament thermal conductivity [1]: $k_{fiber} = 0.090 \ \frac{W}{m\ C}$

PAN specific heat [7]: $c_p = 1280 \ \frac{J}{kg\ C}$

PAN density [7]: $\rho_{fiber} = 1170 \ \frac{kg}{m^3}$

PAN emissivity [2]: $\epsilon = 0.85$

PAN oxidation, overall heat of reaction [1,9]: $\Delta H = 1.96 \ \frac{MJ}{kg}$

Heat transfer coefficient, tow to roll [8]: $h_{tow \to roll} = 100 \ \frac{W}{m^2\ C}$

Various air properties from [4] or Wikipedia

References

[1] Dunham and Edie, *Carbon,* Vol. 30, No. 3, pp. 435-450, 1992.

[2] Mason and Coleman, *Technical Report 67-86 –CM,* U.S.Army Natick Laboratories, 1967.

[3] Kops and Arenson, *15th Brazilian Congress of Mech. Engr.*, 1999.

[4] Lienhard, J.H., *A Heat Transfer Textbook*, 1981.

[5] Arpaci, V.S., *Conduction Heat Transfer*, 1966.

[6] Burmeister, L. S., *Convection Heat Transfer*, 1883.

[7] Polymer Properties Database, *www.polymerdatbase.com*, 2015.

[8] Stry, W.J., *Back Calculated Heat Transfer Coefficient (Harper internal memo),* 2008.

[9] Sprague, P.S., *US Patent #6,776,611*, 2004.

Thank you for your time!
We welcome any questions…

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