Kinetic Model from Qr Measurement – assessment of heat accumulation and time-to-maximum rate

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Outline

- ❑ Background
- ❑ Energy balance
- ❑ Thermal hazard assessment
- ❑ Kinetic model to fit the heat of reaction (Qr) data
- ❑ *In-Silico* Evaluation of Heat accumulation
- ❑ Worst case scenario

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Project Background

- What does JM do…..
- Oxidation reactions with hydrogen peroxide in c

$$\text{Compound A} + H_2O_2 \xrightarrow[\text{Acid}]{} \text{Compound B}$$

- Peroxyacid formed *in-situ* is not thermally stable
- Control of the exotherm at production is important for safety and quality

- Understanding the total heat of reaction, the rate of heat generation and the rate of heat removal to achieve the energy balance on large reactors
- Control of heat accumulation and deviation of temperature during processing

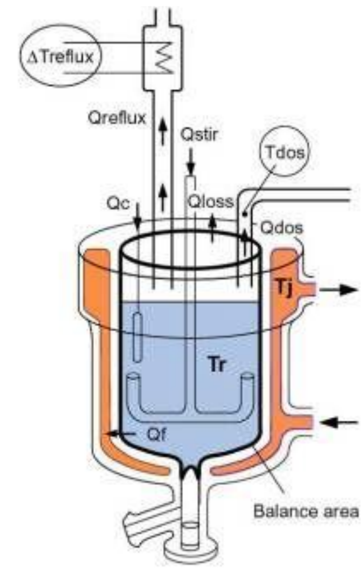
Energy Balance

- The total heat of reaction ΔH_r
  - Heat from individual reaction step, heat from mixing, dissolution, and phase change (evaporation, crystallization)
- In a jacket reactor,

$$Q_r = Q_{flow} + Q_{stir} + Q_{acc} + Q_{dos} + Q_{loss} + Q_{reflux}$$

  - Integration of the heat flow of reaction Qr over time

$$\Delta H_r = \int Q_r \cdot dt$$



- The heat flowing thru the jacket wall Q_{flow} can be determined by:

$$Q_{flow} = U \times A \times (T_r - T_j)$$

U = Heat transfer coefficient, W/(m^2·K)

A = the wetted inner surface area of the reactor, m^2

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Energy Balance

- In a batch process, the total heat of reaction can be simplified without the term of Q_{stir}, Q_{loss} and Q_{reflux} :

$$Q_r = Q_{flow} + Q_{acc}$$

- In a semi-batch process, the total heat of reaction can be simplified as:

$$Q_r = Q_{flow} + Q_{acc} + Q_{dos}$$

$$UA\left(T_r - T_j\right) + M_r \times C_{p,r} \times \left({}^{dT}/_{dt}\right) + M_d \times C_{p,d} \times (T_r - T_d)$$

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Heat Exchange Rate

- The heat exchange rate of a large scale jacket reactor is expressed by the heat transfer coefficient, U, in W/m²·K,
- The overall heat transfer coefficient is the sum of 6 separate heat transfer coefficients:

$$\frac{1}{U} = \frac{1}{h_i} + \frac{1}{h_{if}} + \frac{1}{h_l} + \frac{1}{h_w} + \frac{1}{h_{of}} + \frac{1}{h_o}$$

in which:

h_i	Inside (process) film coefficient
h_{if}	Inside (process) fouling factor
h_l	Lining coefficient
h_w	Wall coefficient
h_{of}	Outside (service) fouling factor
h_o	Outside (service) film coefficient

- U can be obtained from the regression of heating/cooling data with known A, or from DynoChem Estimate UA Utility based on the dimensions of the reactor, agitator and volume.
- Dynochem_UA Utility estimates a U value of 239 W/m^2K for reactor R1, comparing to the value 270 W/m^2K by regression of data from a heat-cool cycle

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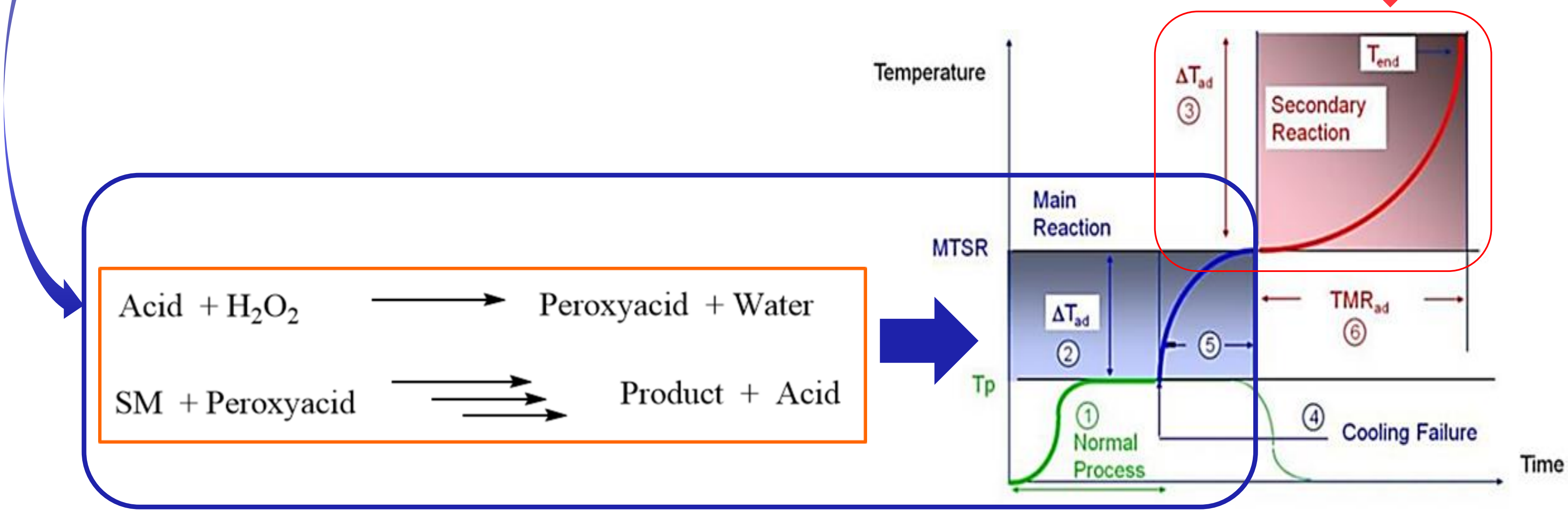
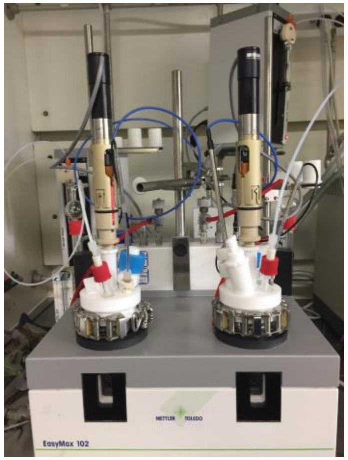
Risk Assessment of Thermal Hazard

- ❑ Consequences of loss control of process temperature (thermal runaway) and associated potential for gas evolution (over-pressurized reactors)
- ❑ Evaluations of both the desired reactions and possible secondary decomposition reactions
  - EasyMax, RC1 – desired reactions
  - DSC, TSu, ARC, etc. – secondary decomposition reactions



Risk Assessment of Thermal Hazard

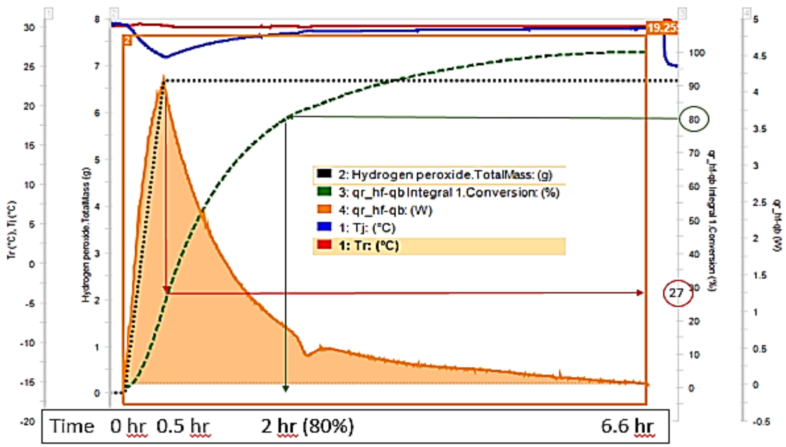
- EasyMax with the heat flow calibration option from Mettler Toledo
- Controlled addition of peroxide into the solution of SM in Acid
- Multi-step reaction



$$\text{Acid} + H_2O_2 \longrightarrow \text{Peroxyacid} + \text{Water}$$

$$\text{SM} + \text{Peroxyacid} \longrightarrow \text{Product} + \text{Acid}$$

- In the lab, the conversion of heat at the end of peroxide addition is near 30 % at 30°C



70% accumulation

- Risks associated with a semi-batch process of an exothermic reaction

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Modeling Qr

- ❑ Reaction kinetics is scale-independent
- ❑ Qr is a way to measure kinetics
- ❑ Feed rate, heat transfer, etc. are *scale-dependent*

$$rate = k\,[Acid] \times [H_2O_2]$$

$$\text{Acid} + \text{H}_2\text{O}_2 \longrightarrow \text{Peroxyacid} + \text{H}_2\text{O}$$

$$\text{SM} + \text{Peroxyacid} \longrightarrow \text{Product} + \text{Acid}$$

$$\boldsymbol{Qr = \left(\sum_i r_i(-\Delta Hr_i)\right)V} = Q_{flow} + Q_{acc} + Q_{dos}$$

Kinetic model from Qr

Predict temperature profile, accumulation of heat and heat effects on compositions as a function of operation conditions and reactor configurations

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DC Model to Fit Q_r

$$\text{Acid} + H_2O_2 \longrightarrow \text{Peroxyacid} + H_2O$$

$$\text{SM} + \text{Peroxyacid} \longrightarrow\longrightarrow\longrightarrow \text{Product} + \text{Acid}$$

$$Qr = \left(\sum_i r_i(-\Delta Hr_i)\right)V$$

Assuming the two most exothermic steps to fit the Q_r

$$\text{Acid} + H_2O_2 \longrightarrow \text{Peroxyacid} + H_2O$$

$$\text{SM} + \text{Peroxyacid} \longrightarrow \text{Epoxide} + \text{Acid}$$

Simplified fit-for-purpose model

$$Qr = (k_1[\text{Acid}][\text{H2O2}](-\Delta Hr_1) + k_2[SM][\text{Peroxyacid}](-\Delta Hr_2))V$$

DC Qr Model with Fixed Feed

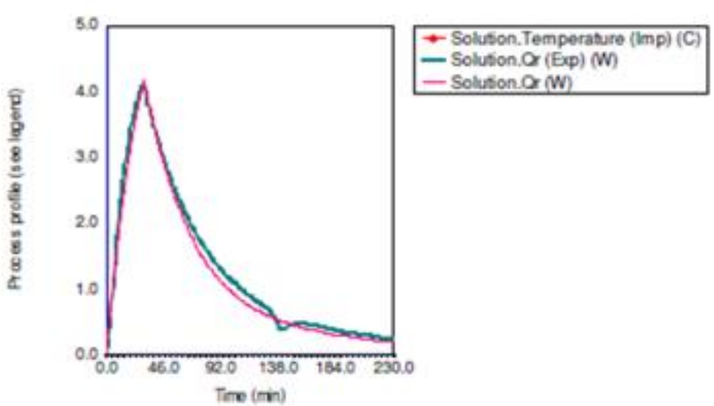
- A 2-line Dynochem model can fit >95% of the data points from EasyMax experiments
- The dip of the Q_r curve (endothermic event or side reactions) after the addition of peroxide is real, but ***not*** included in the simplified model

$$\text{Acid} + H_2O_2 \longrightarrow \text{Peroxyacid} + H_2O \quad (1)$$

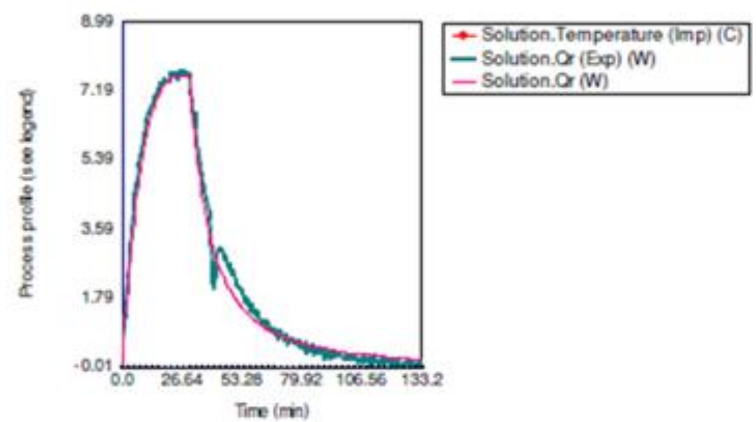
$$\text{SM} + \text{Peroxyacid} \longrightarrow \text{Epoxide} + \text{Acid} \quad (2)$$

	k (L/mole·s)	E_a (kJ/mole)	ΔH (kJ/mole)
Rxn 1	4.23E-05	58.58	-115.13
Rxn 2	2.20E-04	53.85	-250.40

Qr run 1 (30C, 30 min feed, 1.18 mol Peroxide /mol SM)



Qr run 2 (50C, 30 min feed, 1.21 mol Peroxide /mol SM)



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Model for Heat Accumulation

- DC multiline heat accumulation model to calculate the heat accumulation for multi-line reactions

$$\text{Acid} + H_2O_2 \longrightarrow \text{Peroxyacid} + H_2O \quad (1)$$

$$\text{SM} + \text{Peroxyacid} \longrightarrow \text{Epoxide} + \text{Acid} \quad (2)$$

- Dosing excess amount of peroxide, the max accumulation is at the stoichiometry point, where the number of moles of peroxide equals to the number of moles of SM at start
- Accumulation model runs twice – 1st run to get the total ΔH, 2nd run to calculate the accumulation
- The accumulation can be varied with the feed rate and the temperature
- The worst case scenario for the semi-batch process is the loss of process control at the max level of accumulation

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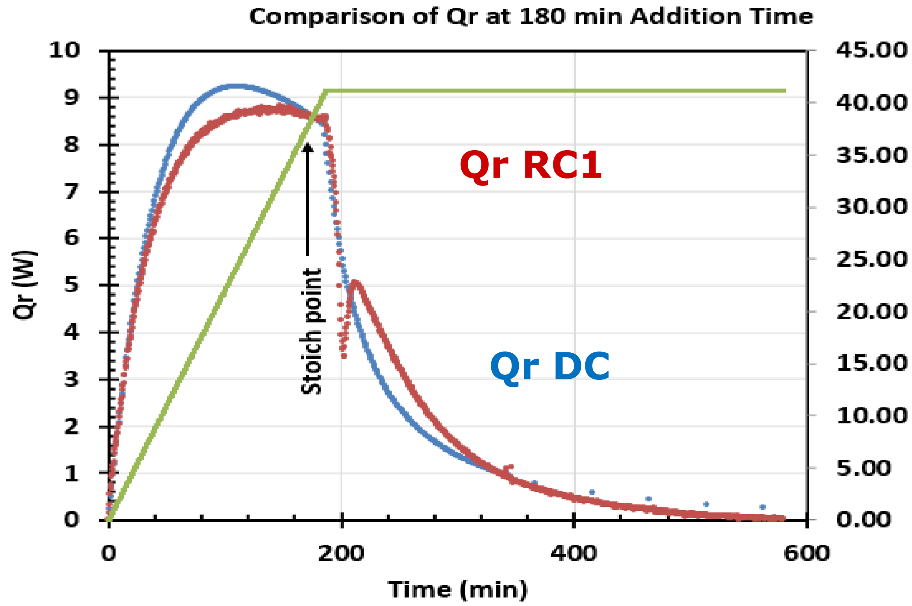
Verification of Heat Accumulation Model on RC1

- Executing reactions on RC1
- Imposing Tr data from RC1 into the accumulation model to calculate the max accumulation – 30 °C and 180 min



Mettler RC1

	Max accumulation from model	Max accumulation from RC1
30 °C and 180 min	38%	37%

DynoChem

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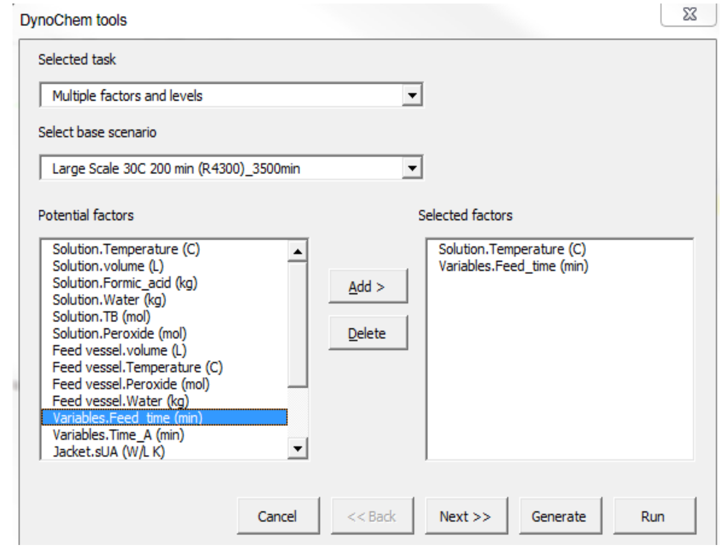
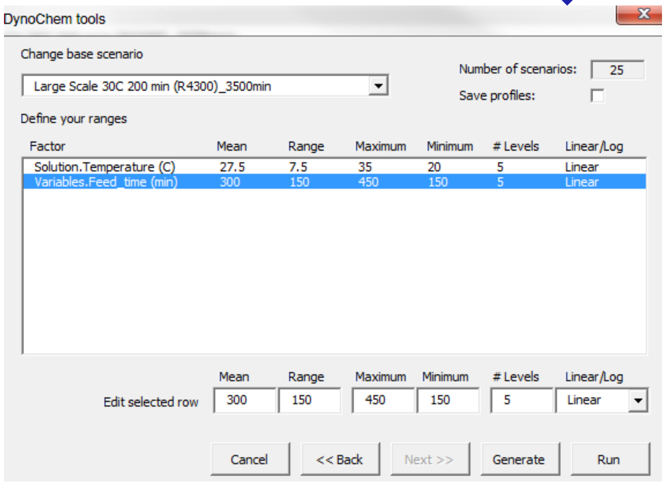
Optimization in Dynochem

- ❑ Heat accumulation model can provide the max accumulation in good agreement with reality.
- ❑ Simulate the process on the model for a range of temperature and feed time
- ❑ Large reactor R1, assuming Tj min = 0 C, and slow response of jacket temperature controller (low Kp value) in the model





Results of DynoChem simulations - Results 20170809-114746

		Solution Temperature C	Solution volume L	Solution Formic_acid kg
Variation 4 of Large Scale 30C 400 min feed (R4300)_T	time_3	37.5	1070	1109
Variation 5 of Large Scale 30C 400 min feed (R4300)_T	time_3	45	1070	1109
Variation 6 of Large Scale 30C 400 min feed (R4300)_T	time_3	15	1070	1109
Variation 7 of Large Scale 30C 400 min feed (R4300)_T	time_3	22.5	1070	1109
Variation 8 of Large Scale 30C 400 min feed (R4300)_T	time_3	30	1070	1109
Variation 9 of Large Scale 30C 400 min feed (R4300)_T	time_3	37.5	1070	1109
Variation 10 of Large Scale 30C 400 min feed (R4300)_'	time_3	45	1070	1109
Variation 11 of Large Scale 30C 400 min feed (R4300)_'	time_3	15	1070	1109
Variation 12 of Large Scale 30C 400 min feed (R4300)_'	time_3	22.5	1070	1109
Variation 13 of Large Scale 30C 400 min feed (R4300)_'	time_3	30	1070	1109
Variation 14 of Large Scale 30C 400 min feed (R4300)_'	time_3	37.5	1070	1109
Variation 15 of Large Scale 30C 400 min feed (R4300)_'	time_3	45	1070	1109
Variation 16 of Large Scale 30C 400 min feed (R4300)_'	time_3	15	1070	1109
Variation 17 of Large Scale 30C 400 min feed (R4300)_'	time_3	22.5	1070	1109
Variation 18 of Large Scale 30C 400 min feed (R4300)_'	time_3	30	1070	1109
Variation 19 of Large Scale 30C 400 min feed (R4300)_'	time_3	37.5	1070	1109
Variation 20 of Large Scale 30C 400 min feed (R4300)_'	time_3	45	1070	1109

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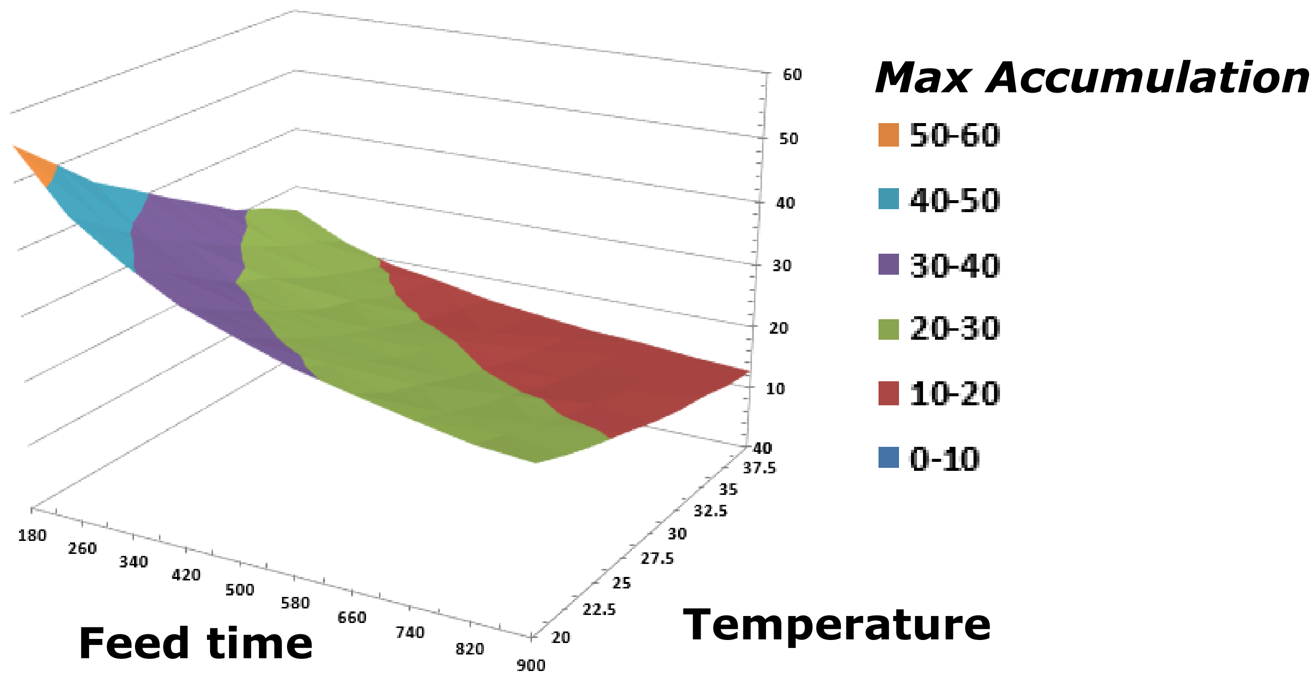
Optimization in Dynochem

- 3-D surface plot of max accumulation vs feed time and solution temperature (starting temperature)
- Assuming continuous feed of peroxide
- Faster feed of peroxide below 25 °C will cause higher accumulation >25%
- Optimize feed time and temperature based on accumulation
- Examine each scenario to avoid max solution temperature > 35 °C (current max allowable process temperature)



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Assessment of Thermal Hazard

- 100% accumulation of peroxide, adiabatic conditions
- Peroxide or peroxyacid undergoes thermal decomposition

$$HCOOOH \longrightarrow CO_2 + H_2O$$

$$HCOOOH \longrightarrow HCOOH + 1/2\ O_2$$

$$H_2O_2 \longrightarrow H_2O + 1/2\ O_2$$

- Create a combustible environment and pressurize the reactor
- The maximum temperature and pressure under the worst case scenario, adiabatic 100% accumulation

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Heat Balance in Adiabatic Condition

- Heat balance of exothermic reaction

$$UA(T_j - T_r) + M_s(-\Delta H_r)\frac{d\alpha}{dt} = M_s \times C_{p,s} \times \frac{dT}{dt} + M_c \times C_{p,c} \times \frac{dT}{dt}$$

$$\frac{d\alpha}{dt} = A \times \exp(\frac{-E_a}{RT}) \qquad \textit{Reaction rate}$$

- In full adiabatic conditions, $U = 0$

$$\frac{dT}{dt} = \frac{1}{\emptyset}\left(\frac{-\Delta H_r}{C_{p,s}}\right)\frac{d\alpha}{dt}$$

$$\emptyset = \frac{M_s \times C_{p,s} + M_c \times C_{p,c}}{M_s \times C_{p,s}}$$

- For batch reactors > 1 m^3, ϕ is approaching 1
- $T = f(t, kinetics, \Delta H_r, C_{p,s})$

Thermal Kinetic Model of Reaction Mixture

- Using DSC data from small scale 100% accumulation experiments at different ramp rates
- AKTS thermal kinetic model Isoconversional approach to perform numerical data analysis of kinetic experiments
- ***Apparent*** kinetic parameters without knowing detailed steps of thermal decomposition (model free)

AKTS
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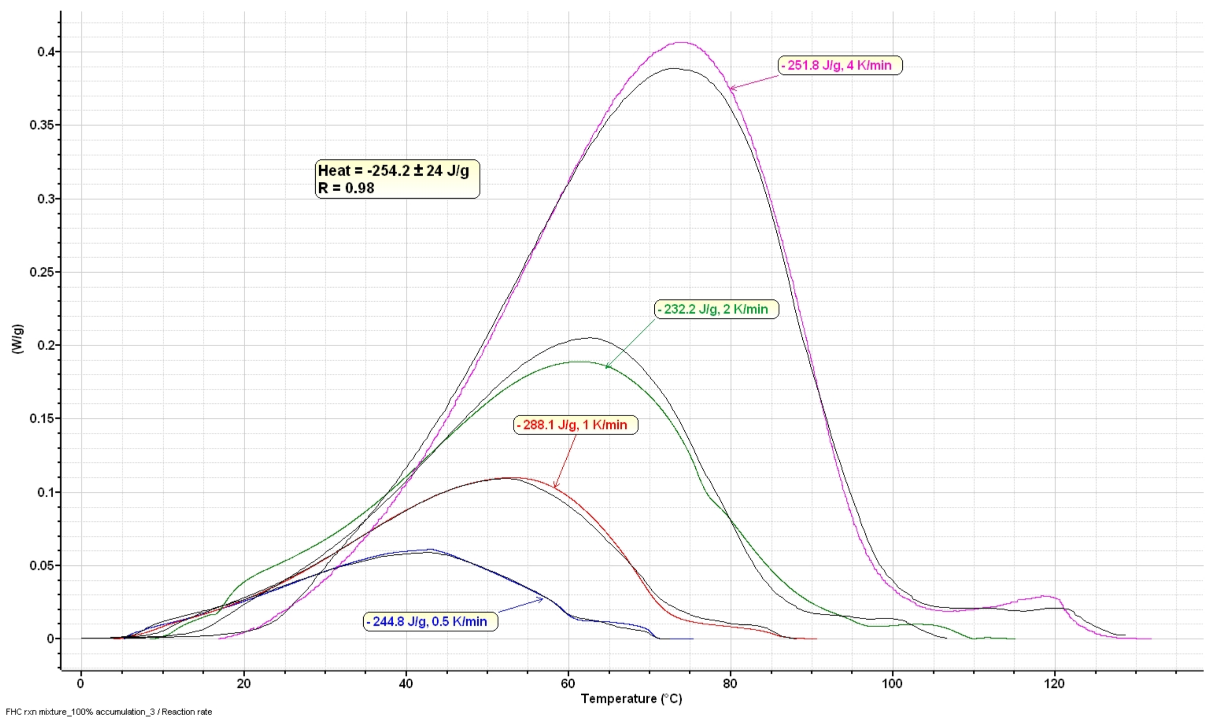

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TMR_{ad} of Reaction Mixture

- TMR_{ad}: Time-to-Maximum rate (TMR) under adiabatic conditions
- TMR_{ad} at ***100% accumulation*** from 30 °C is 25 min to reach the max temperature of 118°C

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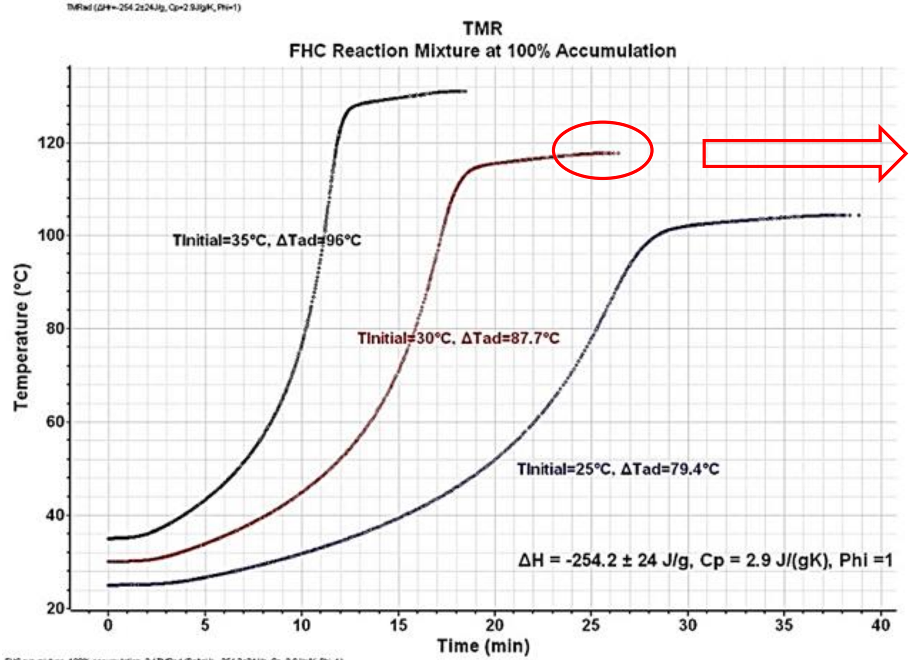

Calculated MTSR from calorimetry data:

MTSR (°C)	ΔT adiabatic (K)	Accumulation (%)
120	90	100
102	72	80
84	54	60
75	45	50
70	40	40
57	27	30
48	18	20

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TMR_{ad} of Reaction Mixture

- TMR_{ad}: Time-to-Maximum rate (TMR) under adiabatic conditions
- TMR_{ad} at ***40% accumulation*** from 30 °C is 80 min to reach the max temperature of 65°C

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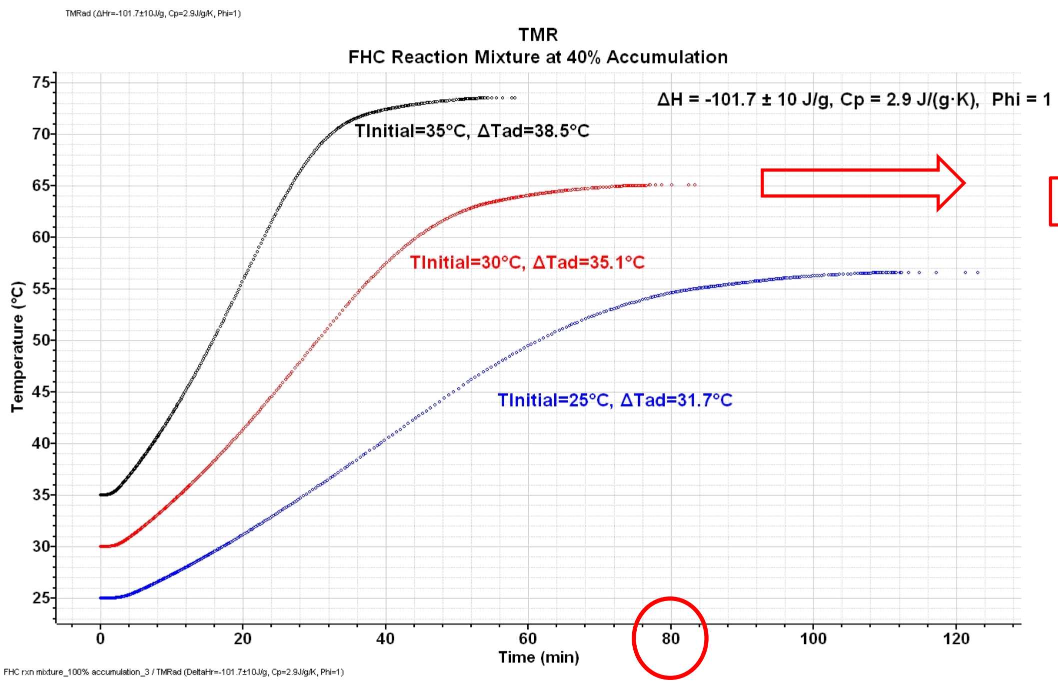

Calculated MTSR from calorimetry data:

MTSR (°C)	ΔT adiabatic (K)	Accumulation (%)
120	90	100
102	72	80
84	54	60
75	45	50
70	40	40
57	27	30
48	18	20

Process Vessel Characterization

Vessel R1	
Vessel MAWP (design Pressure)	100 psig
Vessel Volume When Empty	1013 gallons
Reactant Volume	600 gallons
Reactant Mass	2065 kg
Normal Operating Pressure	< 5 psig
Normal Operating Temperature	30 °C
Relief Device Set Pressure	65 psig

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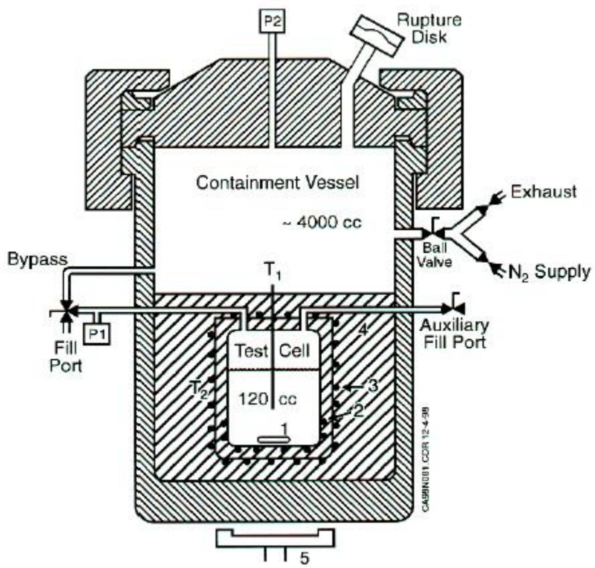
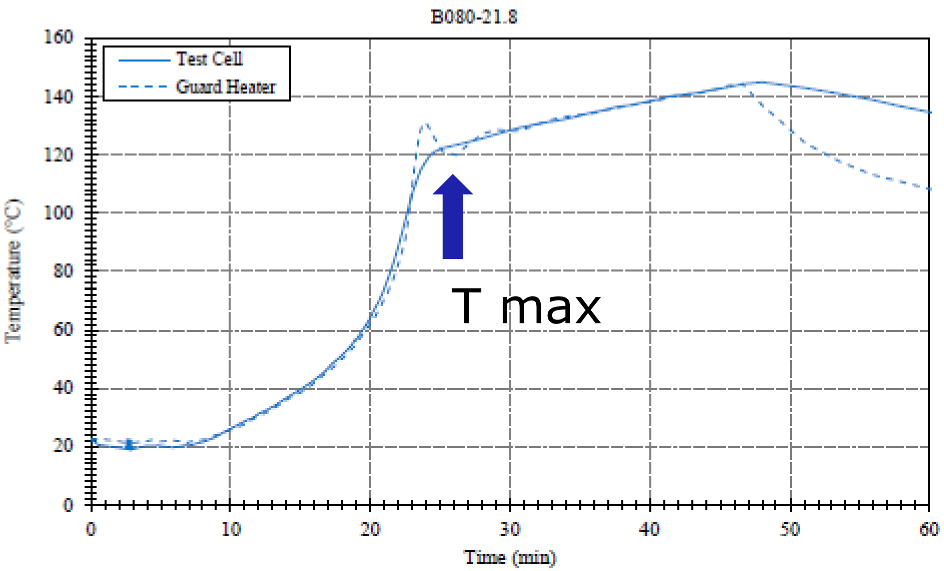
VSP2 Testing of Reaction Mixture

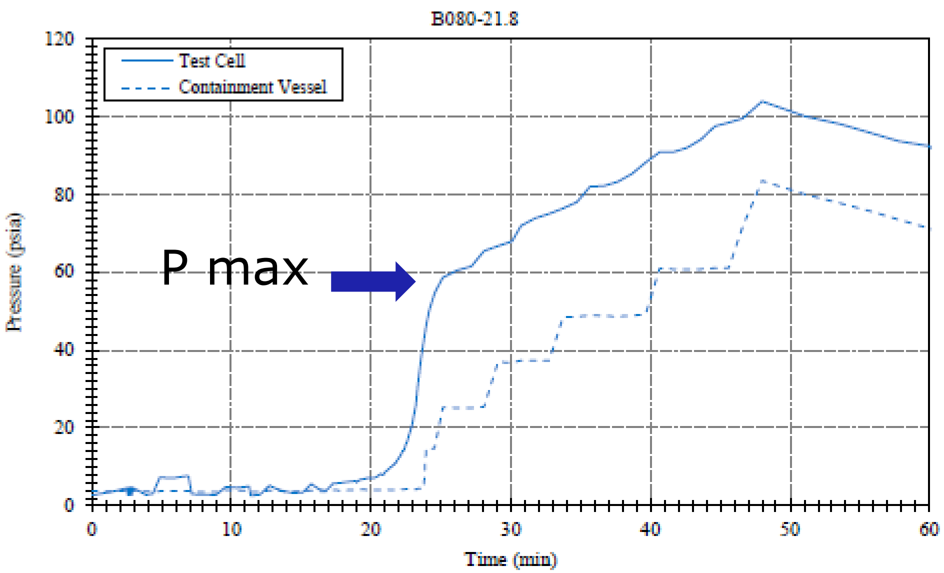
- The max pressure potential of the reaction mixture under adiabatic conditions in worst case scenario (100 % accumulation) is important for the pressure rating of vessel.
- The VSP2™ apparatus, based on DIERS (Design Institute for Emergency Relief Systems) research results, is designed to acquire data related to vent sizing.
- Hastelloy C test cell with an auxiliary heat to bring the testing mixture to the temperature.
- Hydrogen peroxide is added at once.
- A guard heater outside the test cell to maintain the same temperature as the inside sample temperature.
- Adiabatic conditions.



VSP2 Testing of Reaction Mixture

- 100% accumulation of peroxide
- Background heating rate ~ 1.0 °C/min
- The max temperature is approx. 125 °C, where the max pressure is approx. 58 psig
- The time to reach the max temperature and pressure is 25 min





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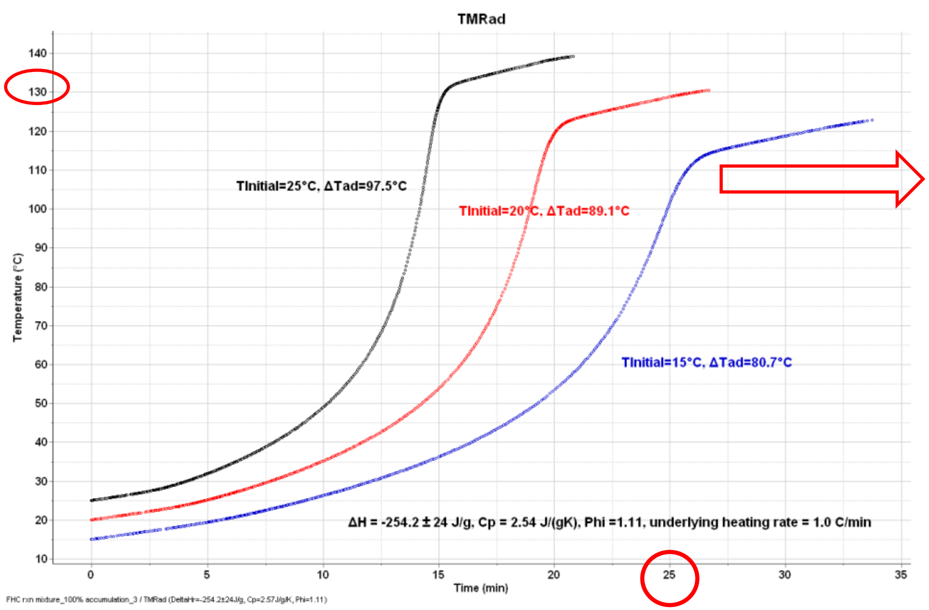
TMR$_{ad}$ of Reaction Mixture

- TMR$_{ad}$ from VSP2 at ***100% accumulation*** from 20 °C is 25 min to reach the max temperature of 125°C
- TMR$_{ad}$ from AKTS at ***100% accumulation*** from 20 °C is 27 min to reach the max temperature of 130°C

Time to max temperature from AKTS model:



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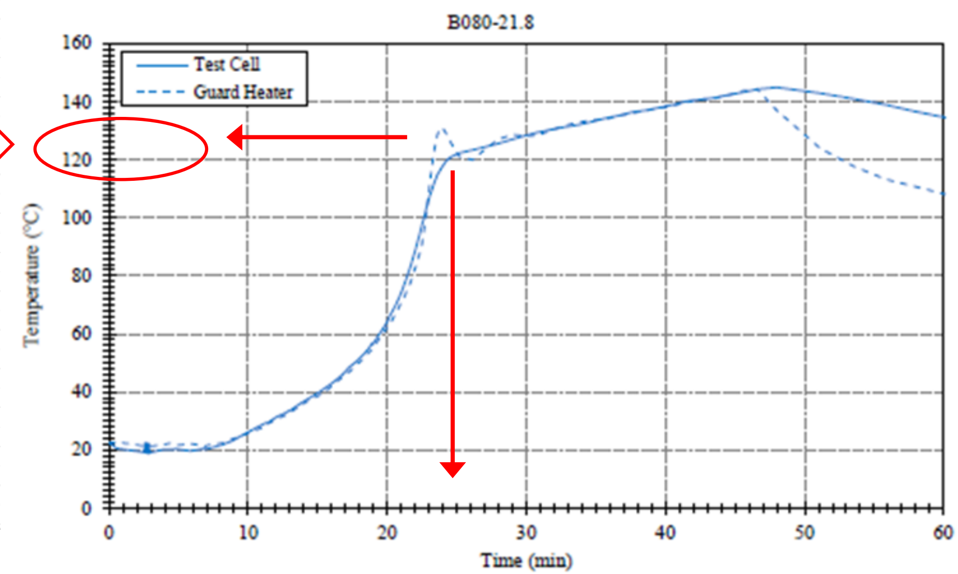
Time to max temperature from VSP2 testing:



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VSP2 Testing of Reaction Mixture

- The max pressure caused by the exothermic event at 100% accumulation is 58 psig
- At the worst case scenario, pressure generated from the exothermic reaction is **not** expected to challenge the pressure rating of vessel

Process vessel characterization:

Vessel R4300	
Vessel MAWP (design Pressure)	100 psig
Vessel Volume When Empty	1013 gallons
Reactant Volume	600 gallons
Reactant Mass	2065 kg
Normal Operating Pressure	< 5 psig
Normal Operating Temperature	30 C
Relief Device Set Pressure	65 psig

Summary

- A Dynochem kinetic model is able to fit > 90% of the calorimetry data (Qr) from Easymax.
- The heat accumulation model is verified with the experimental data from RC1.
- Dynochem_UA Utility estimates a U value of 239 W/m^{2}K for reactor R1. It is conservative comparing to the value 270 W/m^{2}K in report by Hargrove by regression of data from a heat-cool cycle.
- *In-silico* evaluation of the process conditions, equipment and control on the heat accumulation model with a range of feed time and temperature.
- Small scale dynamic DSC data and thermal kinetic model to predict the max temperature and time-to-maximum rate (TMR), and it matches the measured value from VSP2 testing.
- Empirical and computational approach – Safety-by-Design

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