

# Chemical Hazard Assessment

## Know your Chemical Hazards

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# Bob van Woezik

- Nationality: Dutch
- Marital status: Married, 3 boys
- Education: Chemical Process Engineer (MSc, MTD, PhD)

**1999 AkzoNobel**, a global manufacturer of e.g. Chelates, Micronutrients, Organic peroxides, Metal alkyls  
Functions: Process Engineer; Maintenance & Project manager; SHEQS manager; BG Process Safety program manager

**2015 OCI Fertilizers**, a global manufacturer of e.g. Methanol, Ammonia, Nitric Acid, Ammonium Nitrate  
Function: Corporate Process Safety & Occupational safety

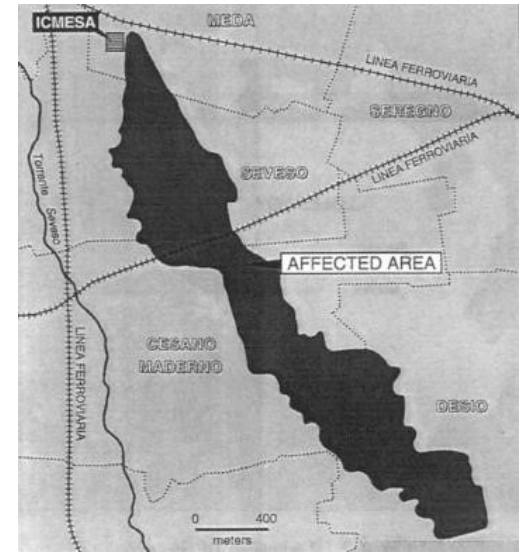
**2018 DSM Operations & Responsible Care**  
Function: Corporate senior expert Process Safety  
PS lead DSM Premix sites, Expert Chemical Hazard Assessments, Explosion Safety and protection

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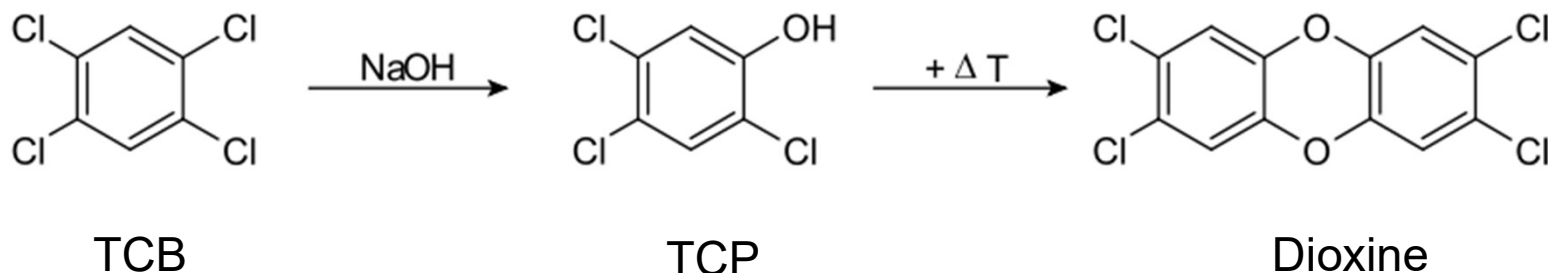
# Seveso - the consequences

- 10<sup>th</sup> July 1976, Icmesa chemical company
- Discharge of highly toxic dioxin from a bursting disk
- No one killed
- 250 people developed skin disease and land contaminated, many animals killed
- Seveso directive



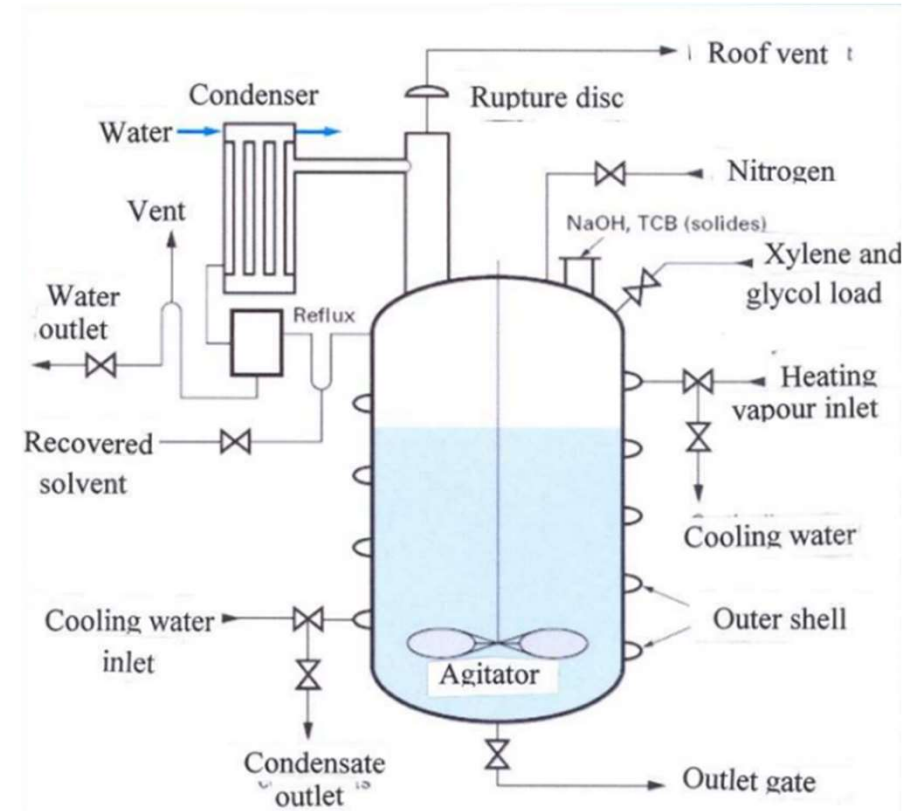
# Seveso - the chemistry

- Batch for the manufacture of 2,4,5-trichlorophenol. Temperature 140 - 170°C
- The company was aware of the hazardous characteristics of the main reaction. But did not foresee that a runaway could be triggered
- Post incident: Identified an exothermic decomposition ca. 250°C
- At high temperature 2,3,7,8-tetrachlorodibenzodioxin is formed (LD50 rat 0.02 mg/kg, TLV  $1.0 \times 10^{-8}$  mg/m<sup>3</sup>, carcinogenic and persistent)



# Seveso - the process

- Shut-down for the weekend (Italian law). Batch not finished, never stopped at this stage. 158°C last T measured
- 7 hours after shut-down, the runaway happened which released the reactor content
- The exothermic decomposition was initiated at 200 - 250°C and the reactor temperature increased uncontrolled to 450 - 500 °C
- To understand the chemical reaction behavior a Chemical Hazard Assessment is needed

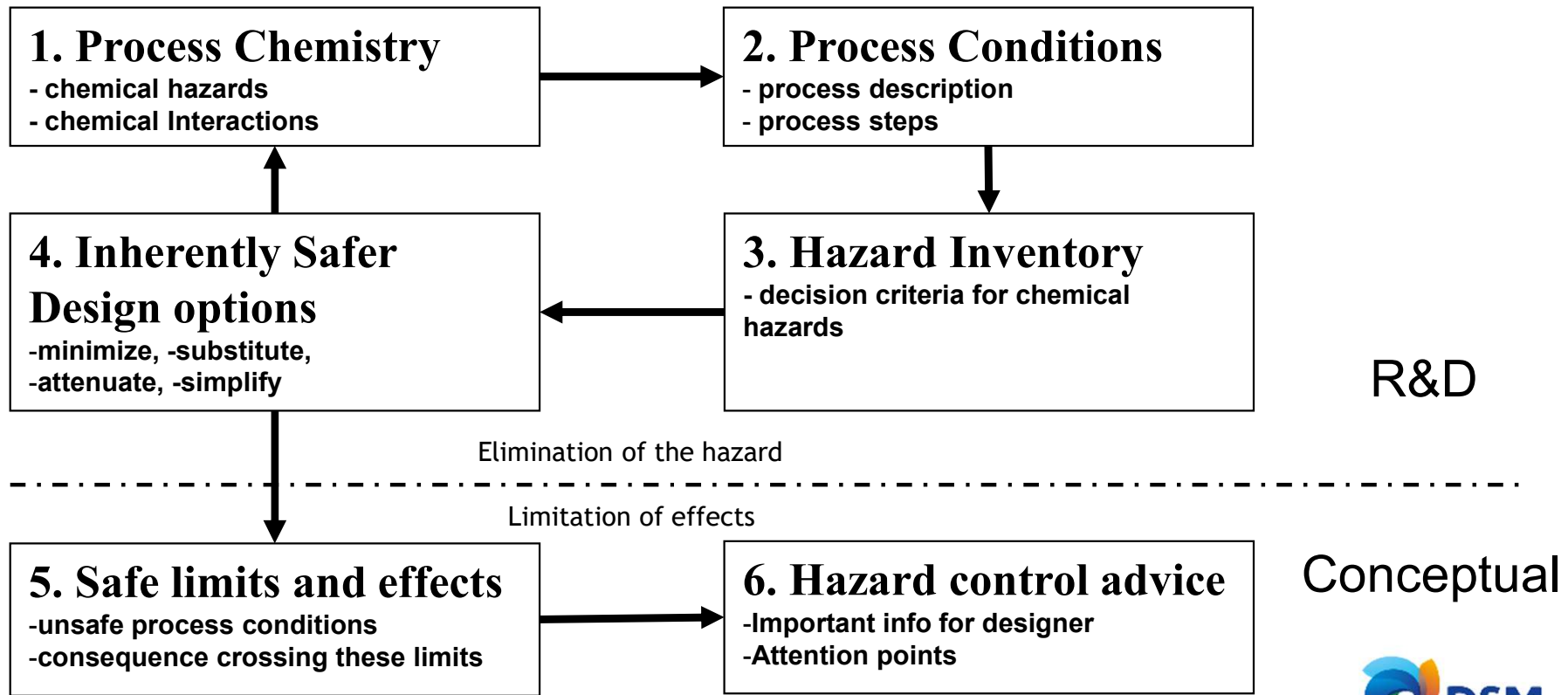


# Purpose of a Chemical Hazard Assessment

- CHA is a systematic approach to define the chemically related hazards of a process and its substances
- To challenge the process route and substances at an early stage
  - eliminating inherent chemical hazards
  - limiting of effects of remaining chemical hazards
- Documenting chemical hazard knowledge, used for design, operations, Management of Change

CHA is a fundamental document for process safety

# Chemical Hazard Assessment steps






# CHA report

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Chemical Hazard Assessment (CHA)


**Document- Nr.**  
**Site:**  
**Product:**  
**Step:**

**Vendor / Revision Index:**  
**Valid as per:**  
**Next review:**  
**File Name:**

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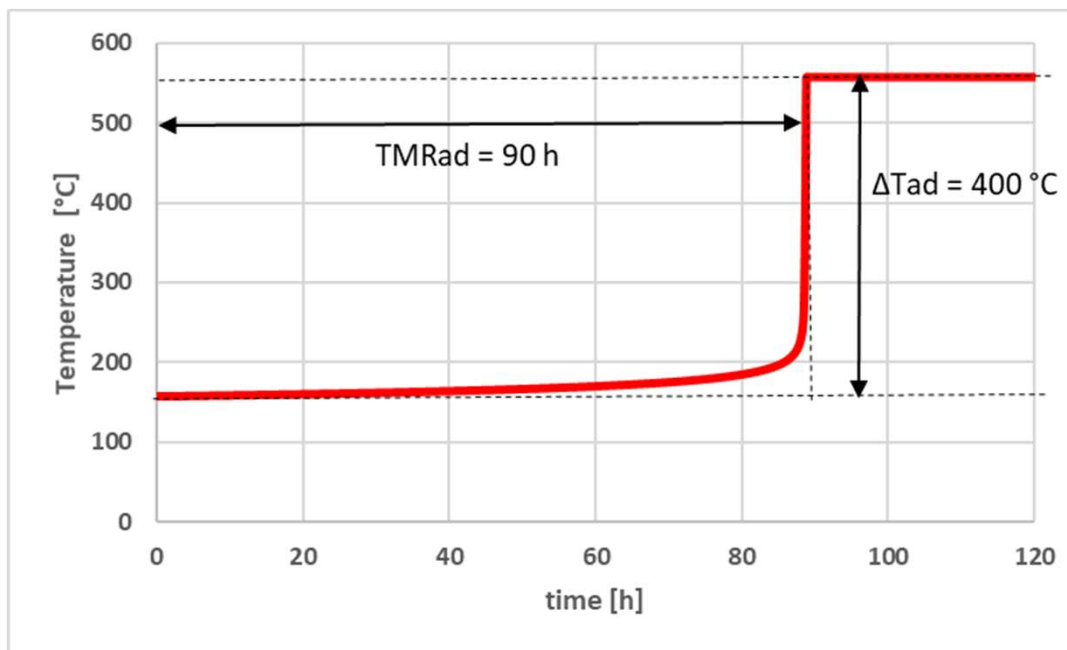
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# Unintended Decomposition reaction

Characterization of the decomposition reaction:

- Adiabatic temperature rise: consequence
- Time to maximum rate: probability



$$\Delta T_{ad} = \frac{c \cdot \Delta H_r}{\rho \cdot c'_p}$$

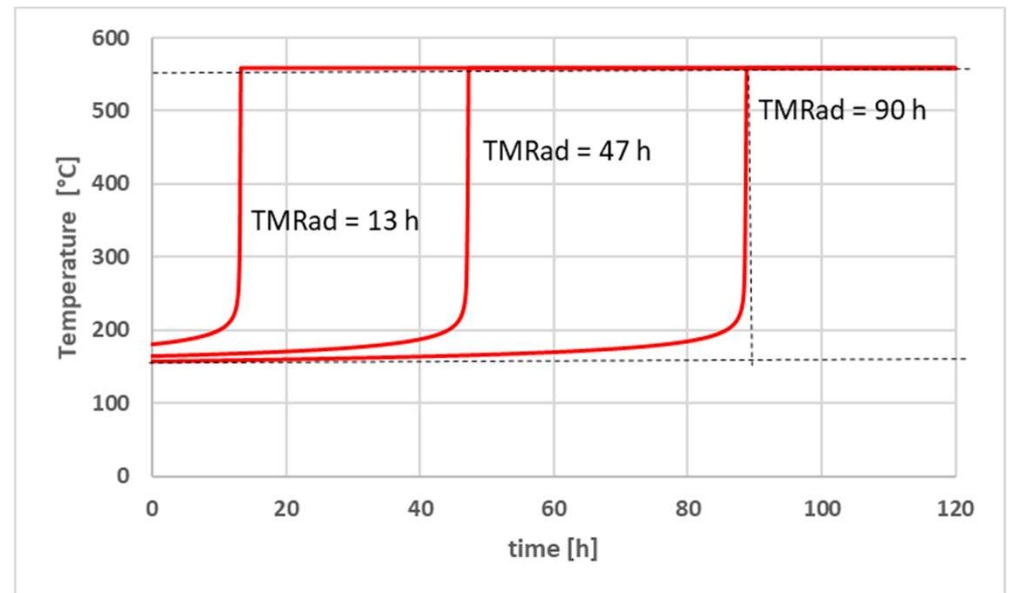
$$TMR_{ad} = \frac{c'_p \cdot R \cdot T_0^2}{q'_{(T_0)} \cdot E}$$

# Unintended Decomposition reaction

Decomposition reactions are sensitive to temperature.

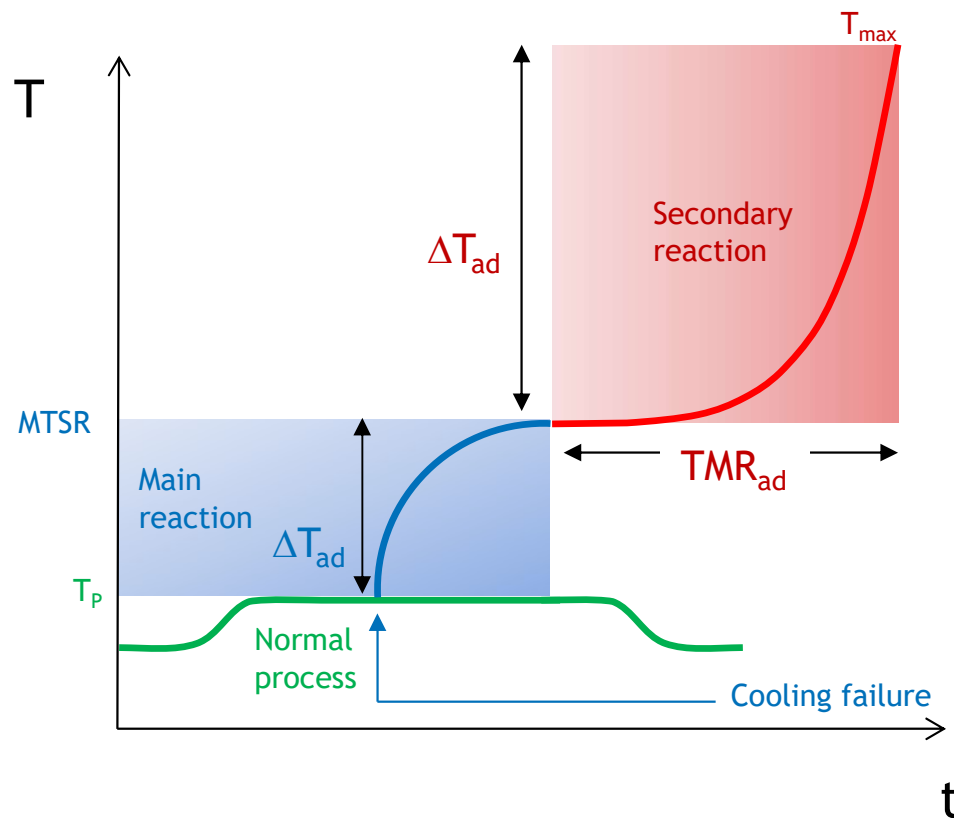
Evaluate TMRad at:

- Normal Process Temperature
- Maximum process temperature (MTSR)
- Maximum utilities temperature (steam temperature)



TMRad for 180 °C, 165 °C, 158 °C

# Cooling Failure Scenario



- Normal Process Temperature
- $\Delta T_{ad}$  synthesis reaction
- MTSR
- $\Delta T_{ad}$  decomposition reaction
- $T_{max}$
- $TMR_{ad}$

# Risk Diagram Criteria

Criteria	Consequence
Low	$\Delta T_{ad} < 50^{\circ}\text{C}$ and no pressure
Medium	$50^{\circ}\text{C} < \Delta T_{ad} < 200^{\circ}\text{C}$
High	$\Delta T_{ad} > 200^{\circ}\text{C}$

Criteria	Probability
Low	$\text{TMR}_{ad} > 24\text{h}$
Medium	$8\text{h} < \text{TMR}_{ad} < 24\text{h}$
High	$8\text{h} > \text{TMR}_{ad}$

NB. Probability Criteria are for reactions/reactors, not for storage, transport etc.

# Measurements

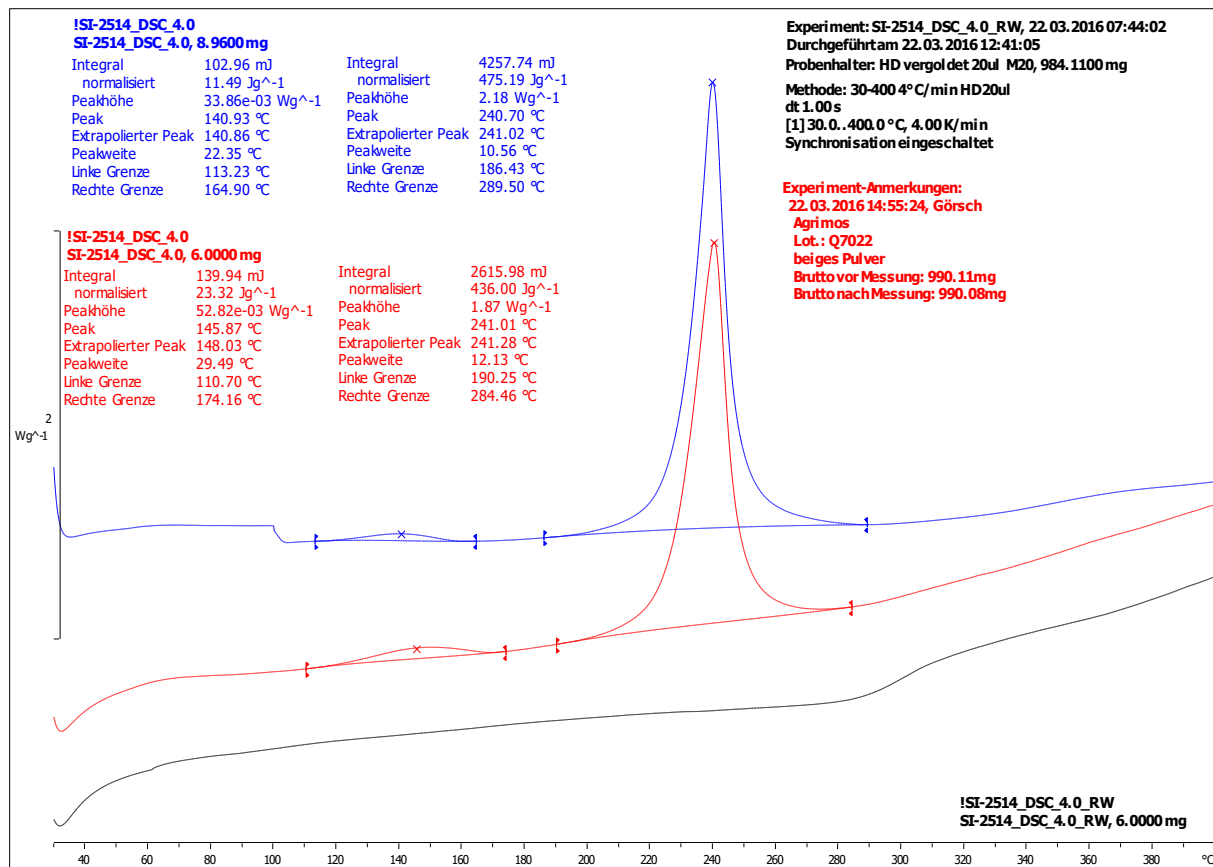
Screening tests for unintended decomposition reactions following KISS-Principle: Keep It Simple and Safe

- Differential scanning calorimetry DSC
- Calvet Calorimeter C80
- Thermo-kinetics software AKTS



- Small samples 50 mg – 1 g
- Fast screening
- Low costs

# Screening Tests



$$q_{\text{ref}} = 10 \text{ mW/g at } T_{\text{onset}}$$

$$T_{\text{onset}} = 186^{\circ}\text{C}$$

$$\text{Total heat} = 480 \text{ J/g}$$

$$\Delta T_{\text{ad}} = 269^{\circ}\text{C}$$

Criteria	Consequence
Low	$\Delta T_{\text{ad}} < 50^{\circ}\text{C}$ and no pressure
Medium	$50^{\circ}\text{C} < \Delta T_{\text{ad}} < 200^{\circ}\text{C}$
High	$\Delta T_{\text{ad}} > 200^{\circ}\text{C}$

# Estimation of the TMR

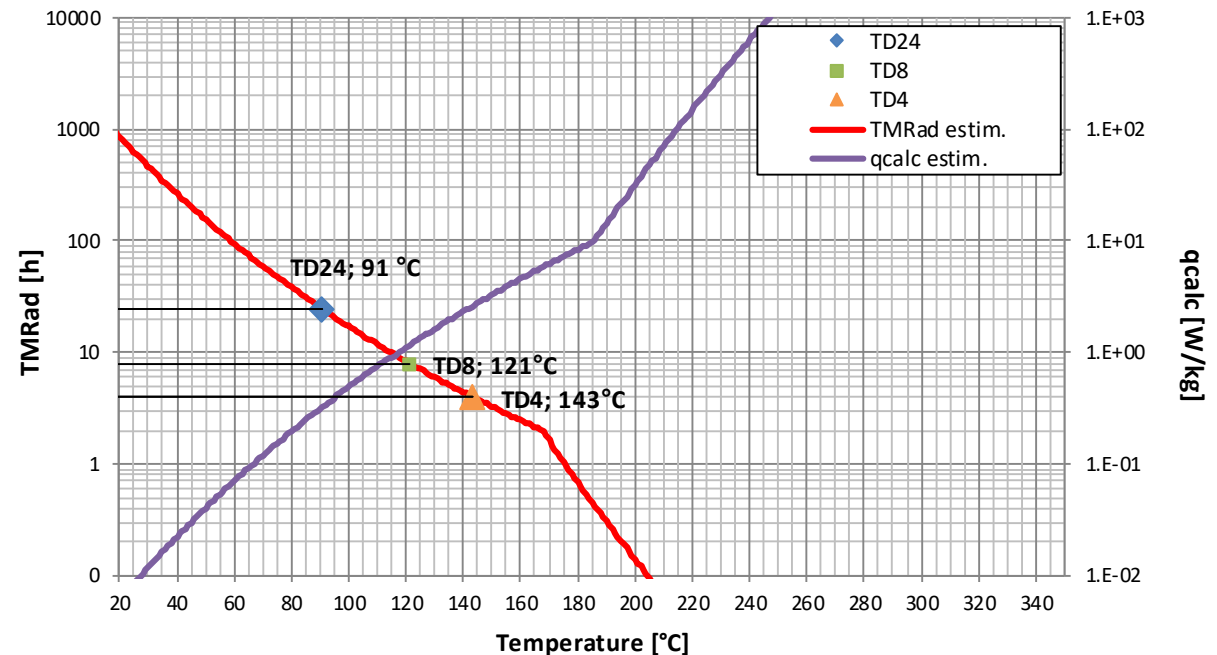
$q_{\text{ref}} = 10 \text{ mW/g at } T_{\text{onset}}$

$T_{\text{onset}} = 186^\circ\text{C}$

$$TMR_{ad}(T) = \frac{c'_p R T^2}{q_{(T)} E_a}$$

$$q_{(T)} = q_{(T_{\text{ref}})} \times \exp \left[ \frac{-E_a}{R} \times \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right]$$

Criteria	Probability
Low	$TMR_{ad} > 24\text{h}$
Medium	$8\text{h} < TMR_{ad} < 24\text{h}$
High	$8\text{h} > TMR_{ad}$





# Concluding: Safe Limits & Effects

**Effects:**  $\Delta T_{ad}$  decomposition = 400°C. Consequence is high: pressure build up by evaporation and/or reaction gas, and very fast decomposition.

Effects:  $T_{max} = 558^{\circ}\text{C}$ ,  $P_{max} \gg 30 \text{ bar}$

**Safe Limits:** TMR<sub>ad</sub> is 24 h for 212°C and 8 h for 238 °C

-Normal process Temperature 158 °C : TMR<sub>ad</sub> = 90 h

Low probability to trigger decomposition at 158 °C

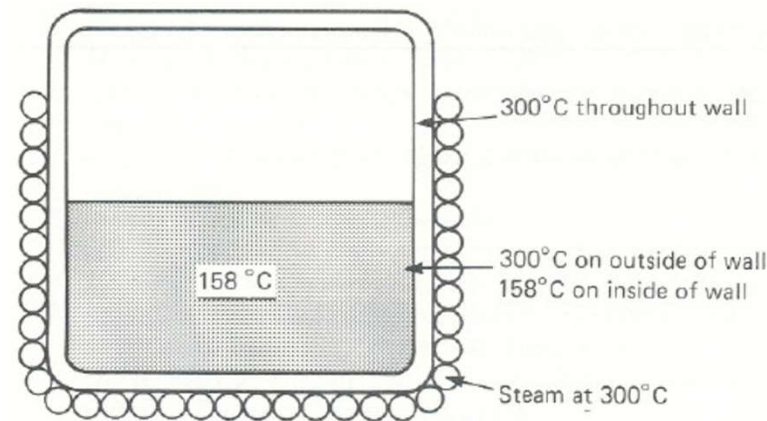
-Maximum utilities Temperature: steam of 300°C!

High probability in case of failure heating system.

To be reviewed during HAZOP.

A leaking steam valve initiated the release of Seveso

Criteria	Consequence	Probability
Low	$\Delta T_{ad} < 50^{\circ}\text{C}$ and no pressure	$\text{TMR}_{ad} > 24\text{h}$
Medium	$50^{\circ}\text{C} < \Delta T_{ad} < 200^{\circ}\text{C}$	$8\text{h} < \text{TMR}_{ad} < 24\text{h}$
High	$\Delta T_{ad} > 200^{\circ}\text{C}$	$8\text{h} > \text{TMR}_{ad}$



# Questions



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