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)

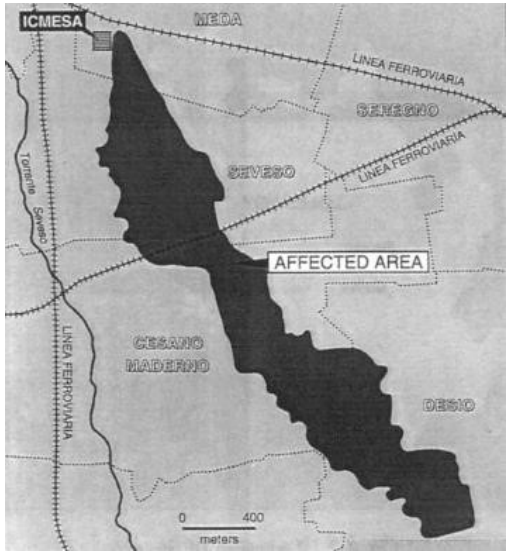
1999 AkzoNobel, a global manufacturer of e.g. Chelates, Micronutrients, Organic peroxides, Metal alkyls
Functions: Process Engineer; Maintenance & Project manager; SHEQS manager; BG Process Safety program manager

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

Seveso - the consequences

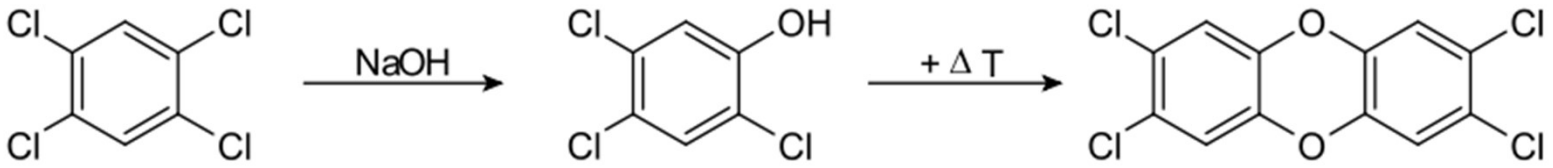
- 10th July 1976, Icmesa chemical company
- Discharge of highly toxic dioxin from a bursting disk
- No one killed
- 250 people developed skin disease and land contaminated, many animals killed
- Seveso directive



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

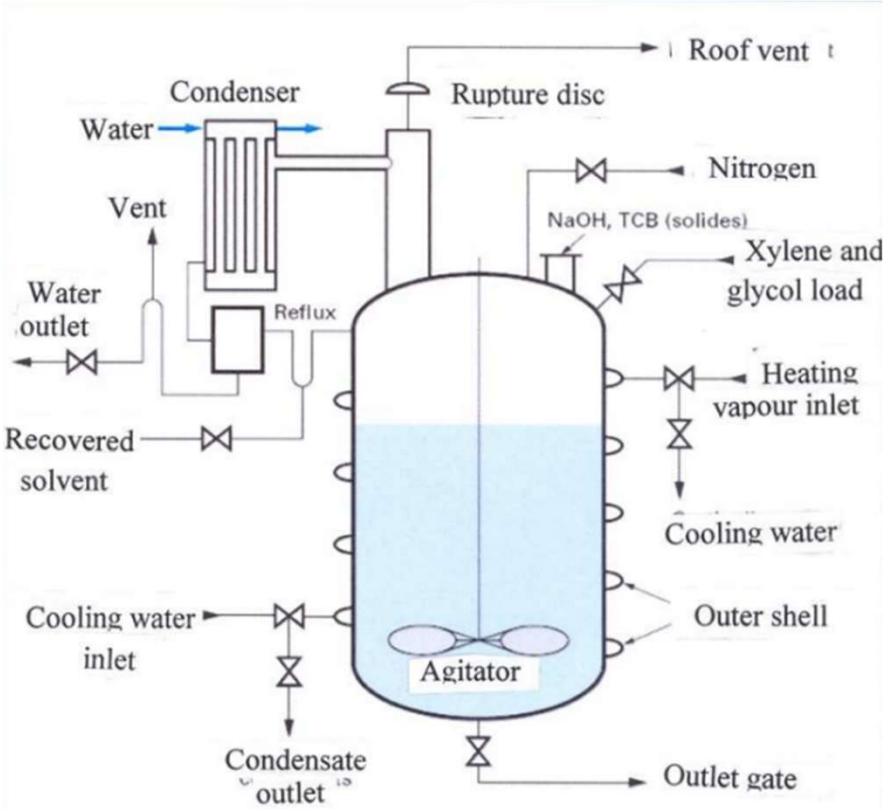
- Post incident: Identified an exothermic decomposition ca. 250°C
- At high temperature 2,3,7,8-tetrachlorodibenzodioxin is formed (LD50 rat 0.02 mg/kg, TLV 1.0 * 10^{-8} mg/m³, carcinogenic and persistent)



TCB TCP Dioxine

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

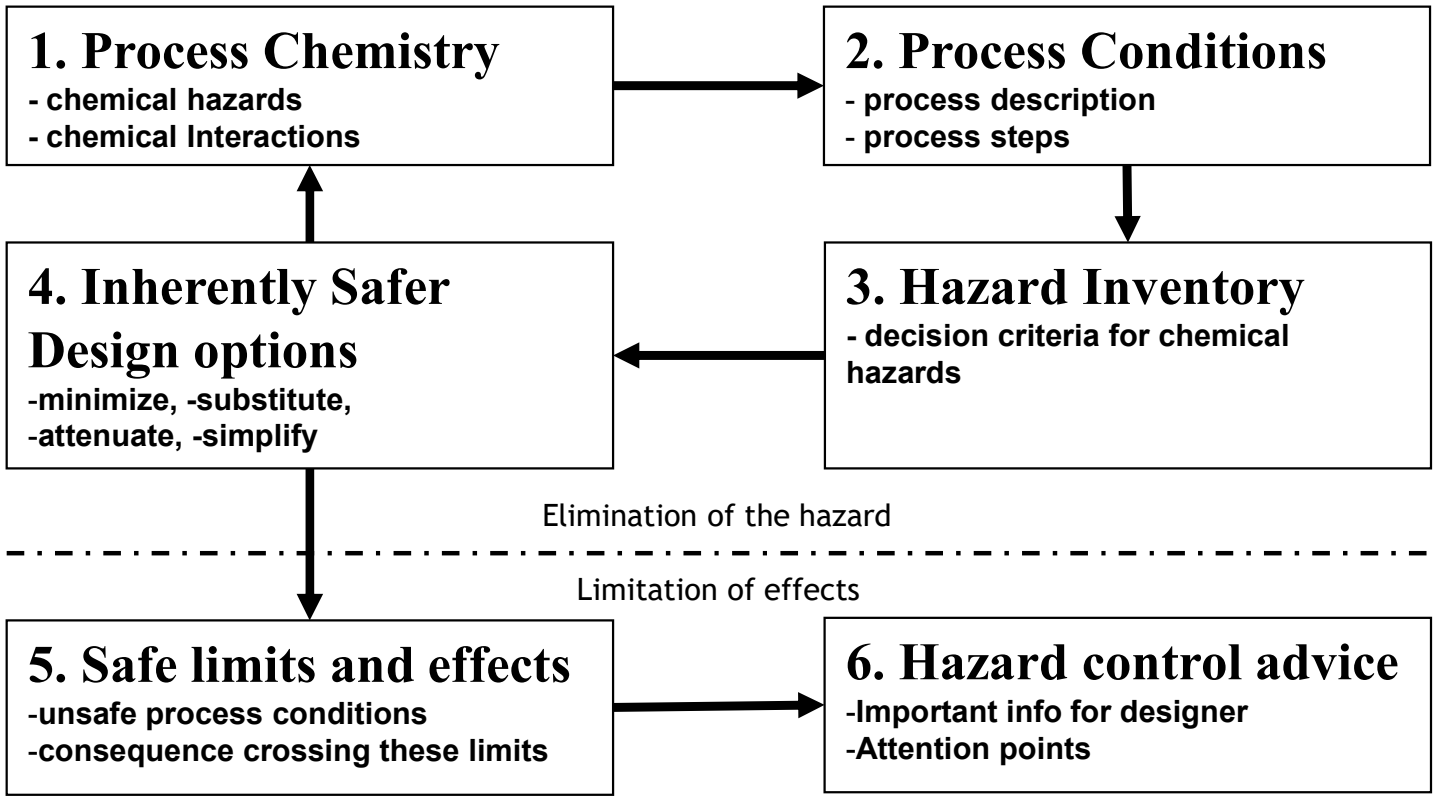
- CHA is a systematic approach to define the chemically related hazards of a process and its substances

- To challenge the process route and substances at an early stage
  - eliminating inherent chemical hazards
  - limiting of effects of remaining chemical hazards

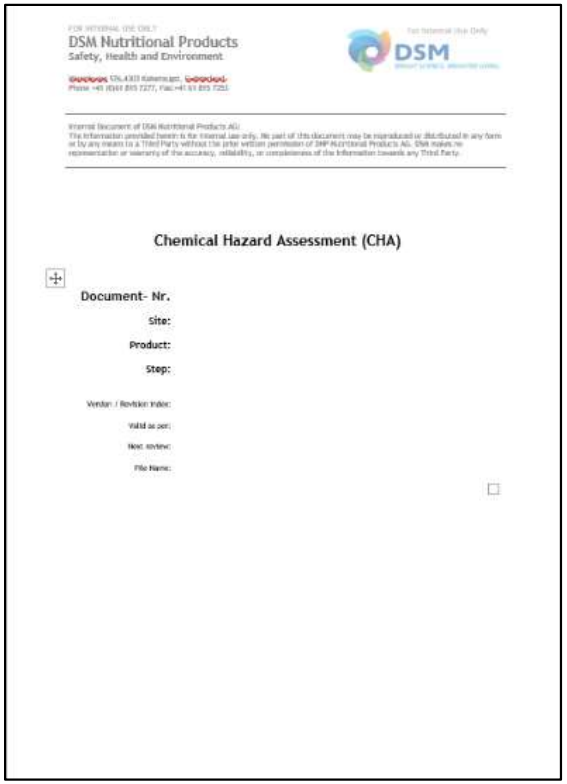
- Documenting chemical hazard knowledge, used for design, operations, Management of Change

CHA is a fundamental document for process safety

Chemical Hazard Assessment steps



CHA report



DSM Nutritional Products
Safety, Health and Environment

Chemical Hazard Assessment (CHA)

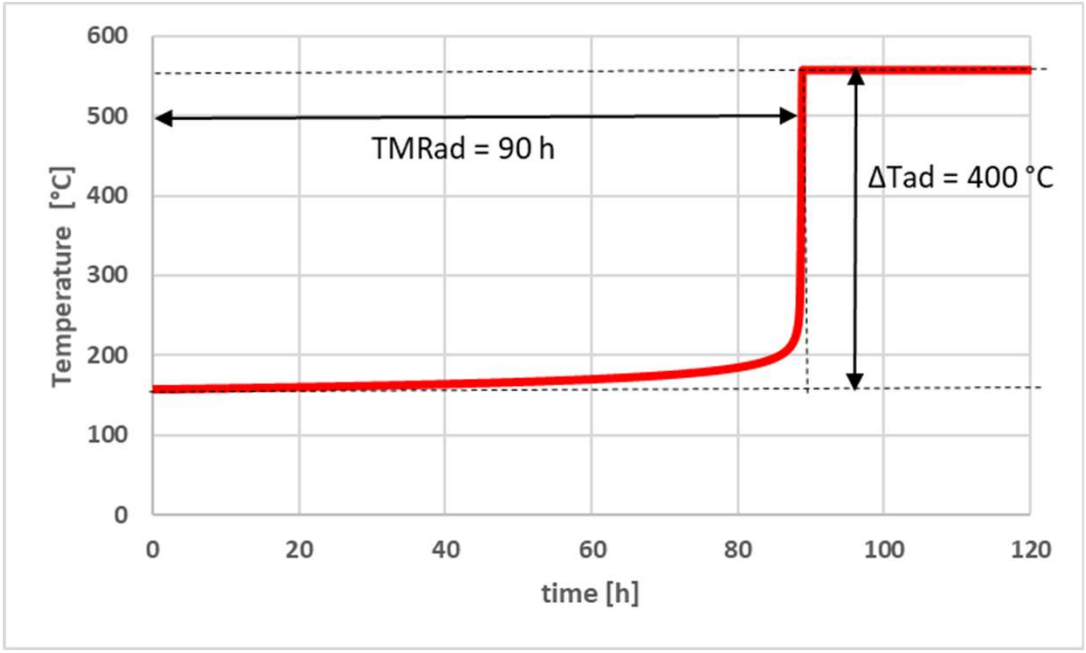
Document- Nr.
Site:
Product:
Step:

Table of Content

Unintended Decomposition reaction

Characterization of the decomposition reaction:

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



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

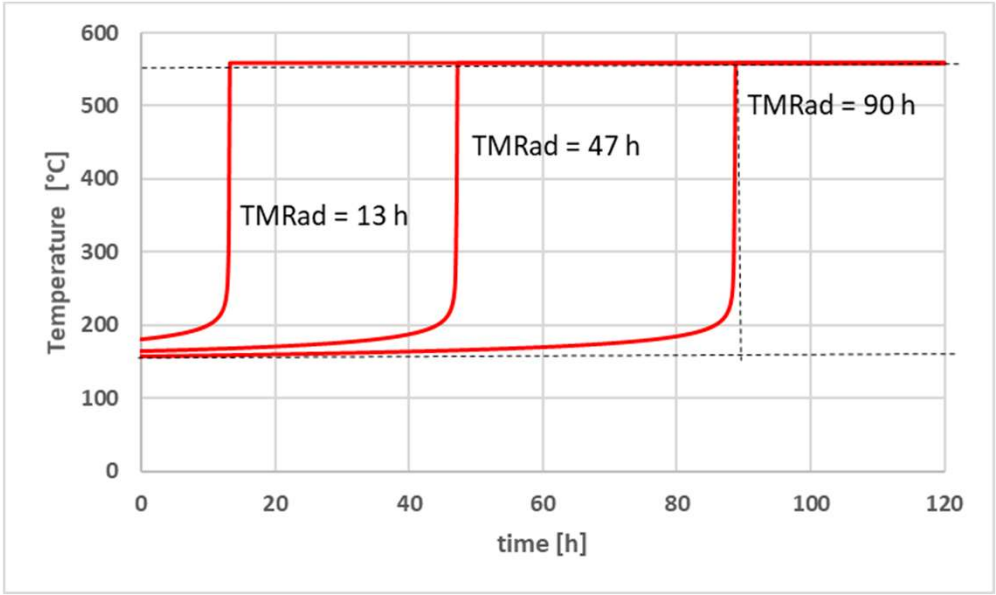
$$TMR_{ad} = \frac{c'_p \cdot R \cdot T_0^{\,2}}{q'_{(T_0)} \cdot E}$$

Unintended Decomposition reaction

Decomposition reactions are sensitive to temperature.

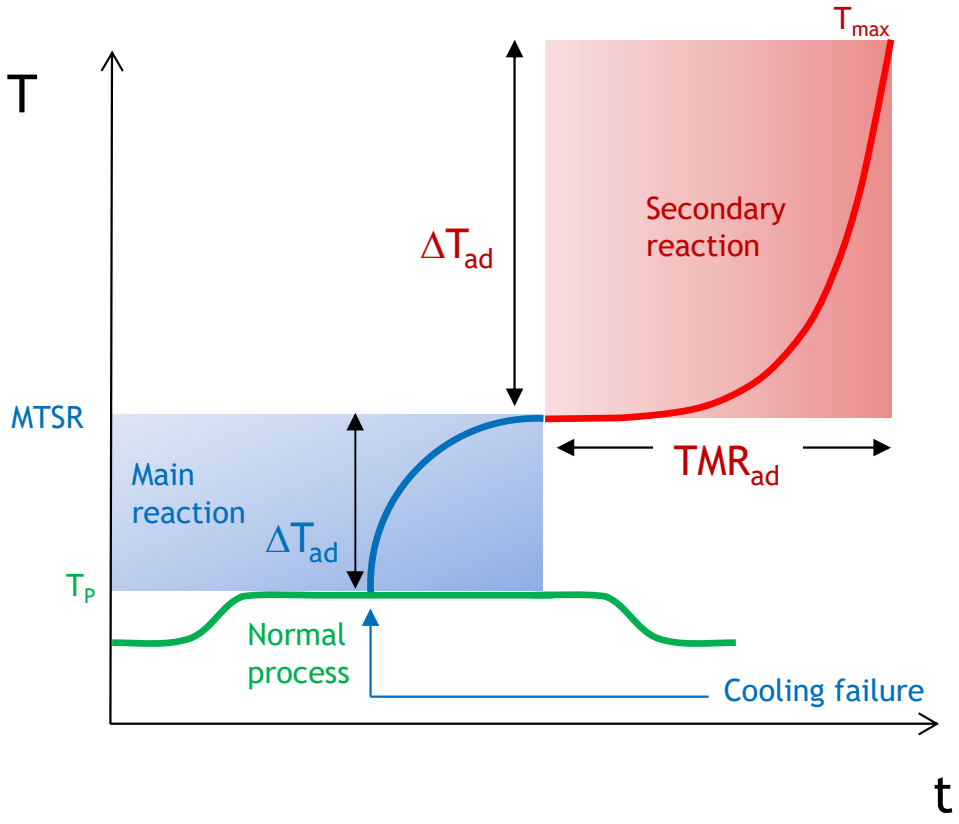
Evaluate TMRad at:

- 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
- ΔTad synthesis reaction
- MTSR

- ΔTad decomposition reaction
- Tmax
- TMRad

Risk Diagram Criteria

Criteria	Consequence
Low	ΔT_{ad}<50°C and no pressure
Medium	50°C<ΔT_{ad}<200°C
High	ΔT_{ad}>200°C

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

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

More details see: Thermal Safety of Chemical Processes by Francis Stoessel

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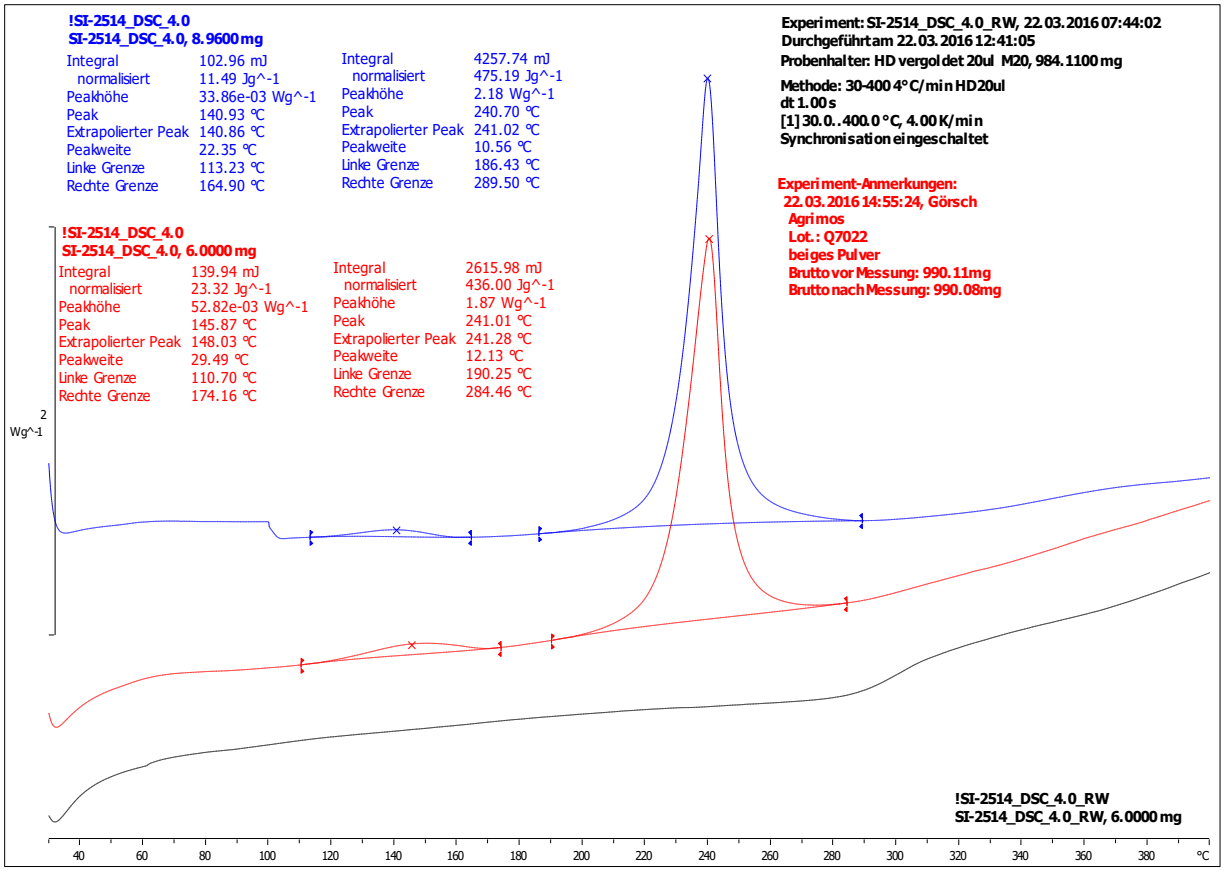
Measurements

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_{ref} =10 mW/g at T_{onset}
T_{onset} =186°C

Total heat = 480 J/g
ΔTad = 269 °C

Criteria	Consequence
Low	ΔT_{ad}<50°C and no pressure
Medium	50°C<ΔT_{ad}<200°C
High	ΔT_{ad}>200°C

Estimation of the TMR

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

T_{onset} =186°C

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

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

Criteria	Probability
Low	TMR_{ad}> 24h
Medium	8h<TMR_{ad}<24h
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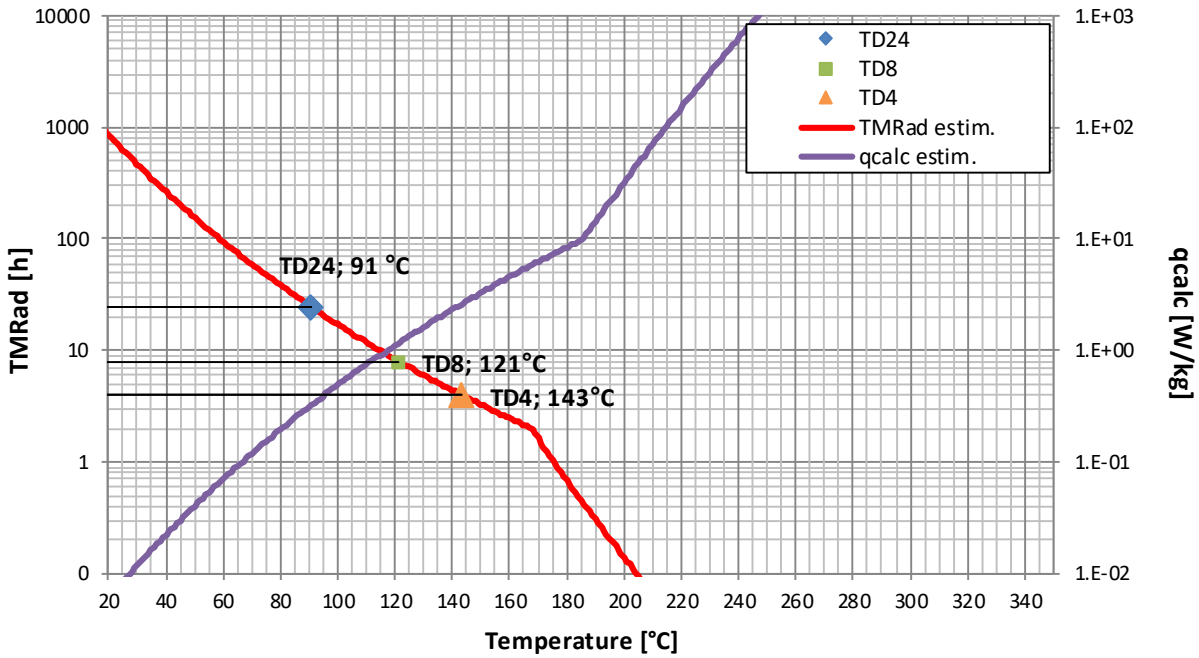


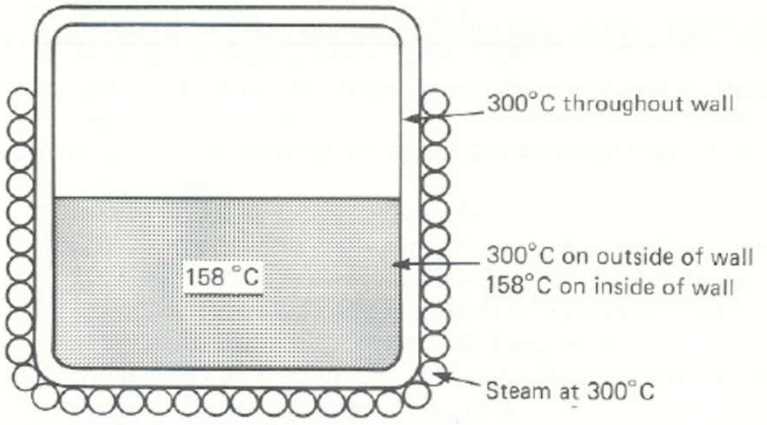
Concluding: Safe Limits & Effects

Criteria	Consequence	Probability
Low	ΔT_{ad}<50°C and no pressure	TMR_{ad}> 24h
Medium	50°C<ΔT_{ad}<200°C	8h<TMR_{ad}<24h
High	ΔT_{ad}>200°C	8h > TMR_{ad}

Effects: ΔTad decomposition = 400°C. Consequence is high: pressure build up by evaporation and/or reaction gas, and very fast decomposition.
Effects: Tmax = 558°C, Pmax >> 30 bar

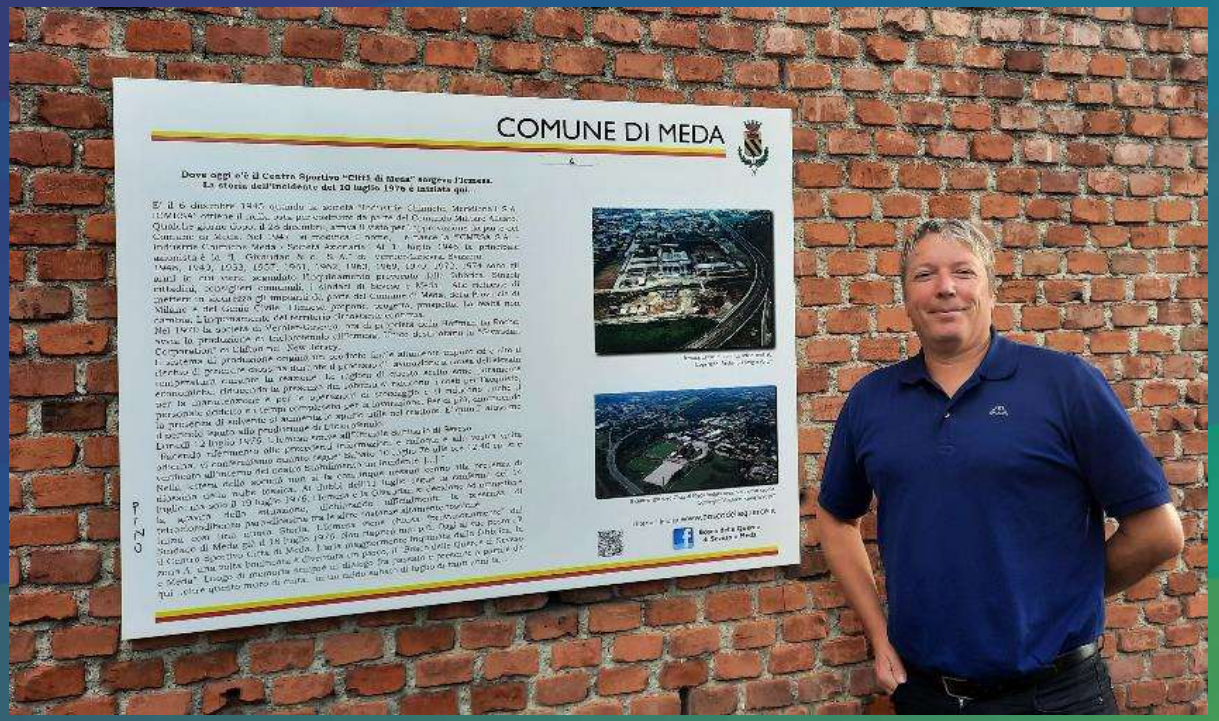
Safe Limits: TMRad is 24 h for 212°C and 8 h for 238 °C
-Normal process Temperature 158 °C : TMRad = 90 h
Low probability to trigger decomposition at 158 °C

-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

Questions



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