Chemical Hazard Assessments: need and practices

Dr Christine Fannes & Dr Annik Nanchen

EPSC Conference Barcelona, 2nd December 2024

Christine Fannes

Main expertise: Process Safety Testing and Advice, Thermal Process Safety (reactive hazards), Risk analysis

1987	Master in Chemistry
1987 – 1992	PhD Synthetic Chemistry
1992 – 1996	Assistant Laboratory Leader and Quality Assurance manager for the department of Intermediates
1996 – 2001	Customer Support and sales representative for high tech lab equipment
2001 – 2024	Principal Scientist
2024 – now	Senior Principal Scientist

Annik Nanchen

Main expertise: Risk analysis, Thermal Process Safety (reactive hazards), Design of Pressure Relief Systems

EPFL	2002	Chemical engineer
ETH zürich	2002 – 2005	PhD Biotechnology
Codexis	2006 – 2007	Analytical Biochemist
swiss / TÜV SÜD Process Safety	2007 – 2014	Process Safety Consultant
DSM	2014 – 2015	Process Safety Specialist
TÜV SÜD Process Safety	2015 – now	Process Safety Consultant
EPFL	2016 – now	Lecturer

Iowa State University; DTU Technical University of Denmark

Accidents due to chemical runaways

Sources: CSB report T2 laboratories, Currenta, https://www.eti-swiss.com/internationales-2/chemikalien-konventionen/basler-konvention/, *getty Images/AFP/STR*, https://www.downtoearth.org.in/health/bhopal-38-years-ago-while-the-world-slept-its-worst-industrial-disaster-unfolded-in-the-heart-of-india-68232

Goals Chemical Hazard Assessment

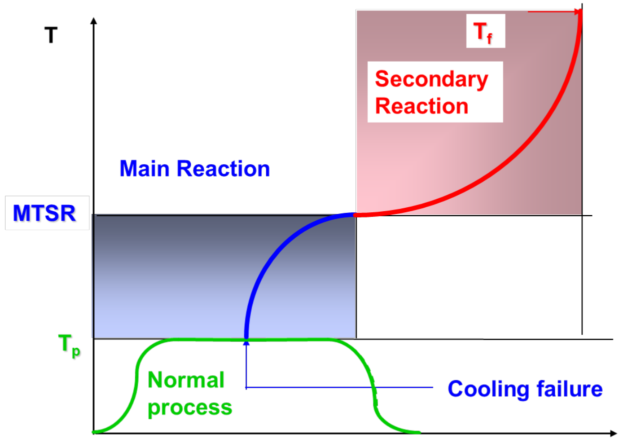
- **Collection of data → Goal 1**
  - Properties of chemicals

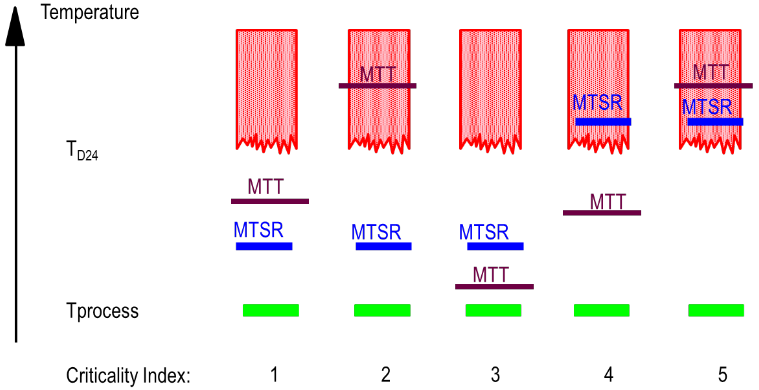
  - Interactions

	ACETIC ACID, GLACIAL	ACETONE	Alcohols and Polyols	Conjugated Dienes (P)	DICHLOROMETHANE	Esters, Sulfate Esters, Phosphate Esters, Thiophosphate Esters, and Borate Esters
ACETONE	Compatible					
Alcohols and Polyols	Caution Flammable Generates gas Generates heat Intense or explosive reaction Polymerization hazard	Caution Explosive Unstable when heated				
Conjugated Dienes (P)	Compatible	Compatible	Compatible			
DICHLOROMETHANE	Compatible	Compatible	Compatible	Compatible		
Esters, Sulfate Esters, Phosphate Esters, Thiophosphate Esters, and Borate Esters	Compatible	Compatible	Compatible	Compatible	Compatible	
ISOPROPANOL	Caution Flammable Generates gas Generates heat Intense or explosive reaction Polymerization hazard	Caution Explosive Unstable when heated	Compatible	Compatible	Compatible	Compatible

Reference: Cameo

- Reactivity (synthesis and side/decomposition reactions)





Reference: Stoessel, Thermal Safety of Chemical Processes

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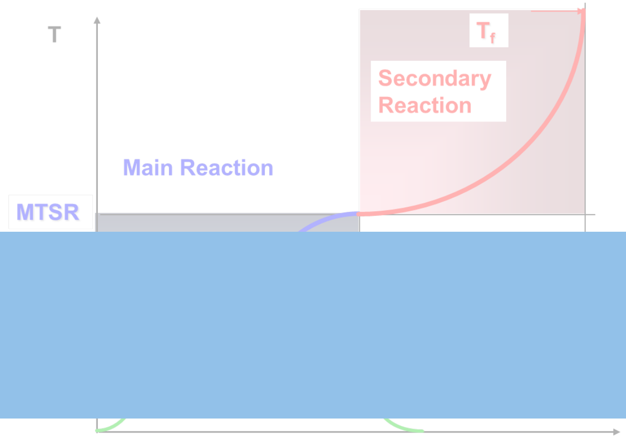
- Reactivity (synthesis and side/decomposition reactions)



Interpretation of Data → Goal 2
→ Definition of safe limits & safety concept

Alcohols and Polyols	Caution Flammable Generates gas Generates heat Intense or explosive reaction Polymerization hazard	Caution Explosive Unstable when heated	Alcohols and Polyols			
Conjugated Dienes P	Compatible	Compatible	Compatible	Conjugated Dienes P		
DICHLOROMETHANE	Compatible	Compatible	Compatible	Compatible	DICHLOROMETHANE	
Esters, Sulfate Esters, Phosphate Esters, Thiophosphate Esters, and Borate Esters	Compatible	Compatible	Compatible	Compatible	Compatible	Esters, Sulfate Esters, Phosphate Esters, Thiophosphate Esters, and Borate Esters
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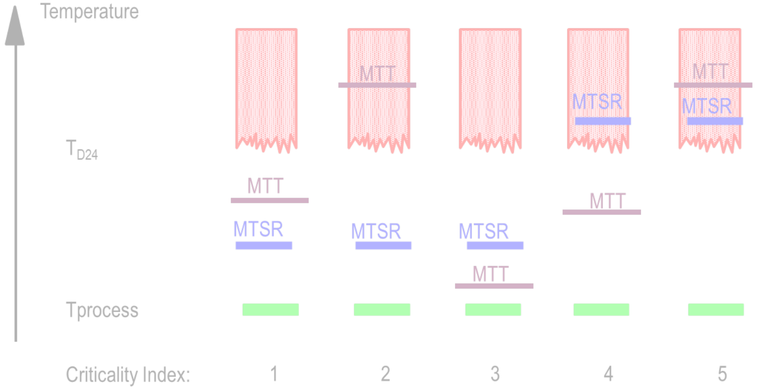


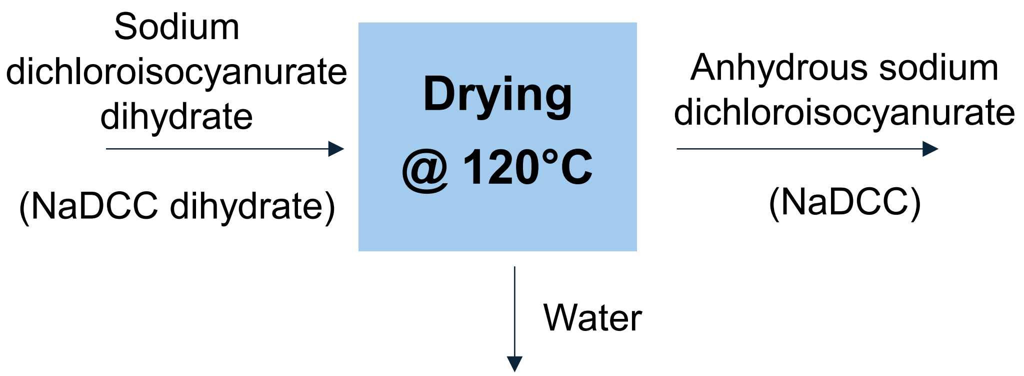
Chemical Hazard Assessment - Steps

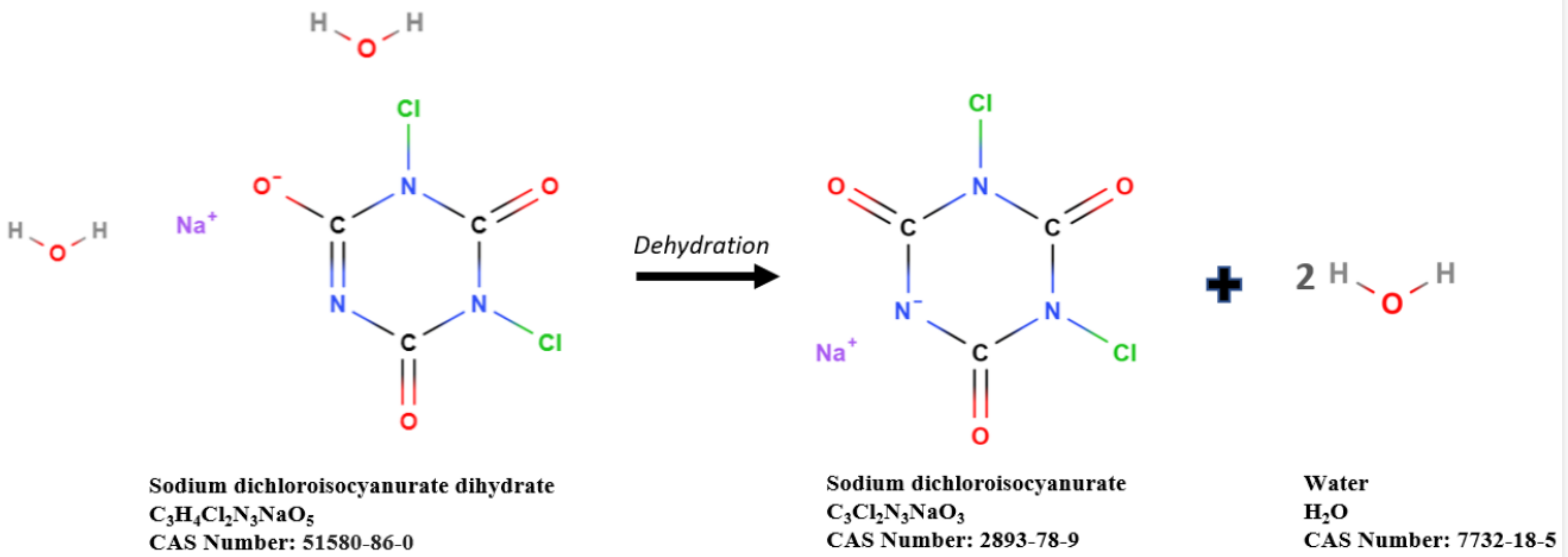
1. Data Collection
2. Data Interpretation
3. Safety concepts, safe limits
4. Transfer of information
5. Life cycle – Update information

Example: Drying of NaDCC dihydrate

Process Information:

Drying in a fluidized bed dryer





Source: https://www.csb.gov/optima-belle-explosion-and-fire/

Chemical Hazard Assessment - Steps

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2. Data Interpretation
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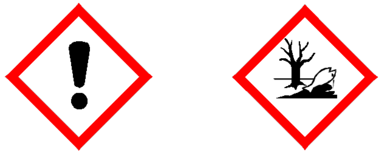
Example: Drying of NaDCC dihydrate

Collecting information on starting material and finished product

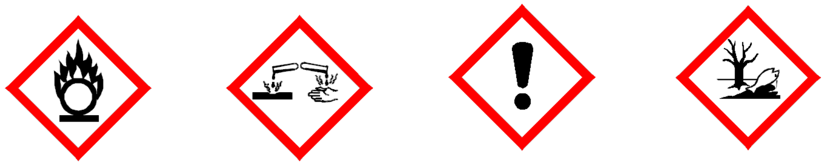
NaDCC dihydrate



EUH031: contact with acids liberates toxic gas

Decomposition T > 240°C

NaDCC



EUH031: contact with acids liberates toxic gas

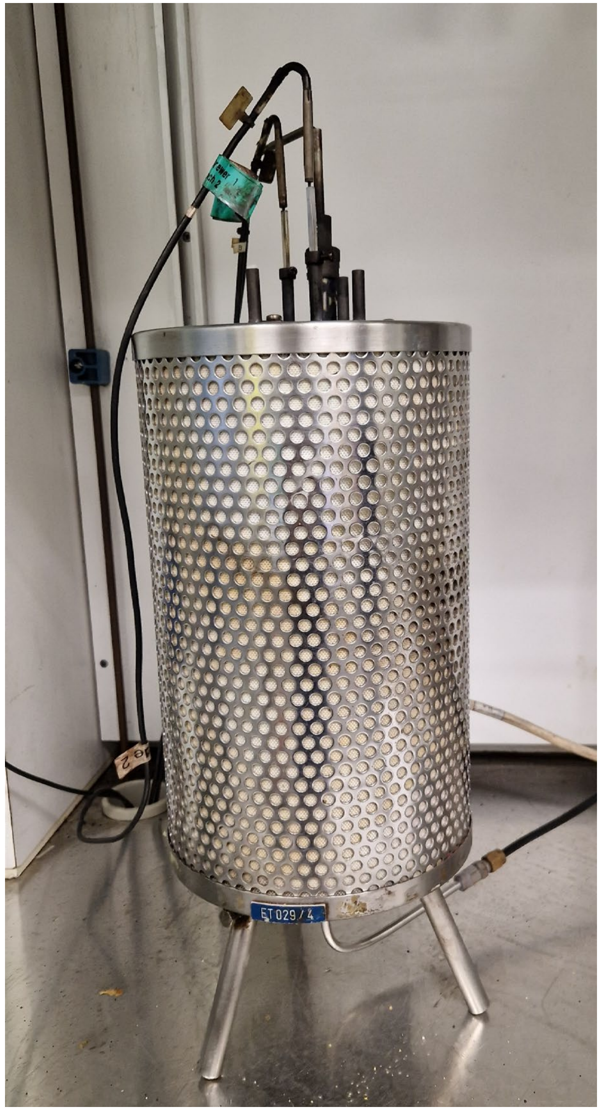
Decomposition T 240°C – 250°C

Data from Gestis (https://gestis-database.dguv.de/)

Example: Drying of NaDCC dihydrate

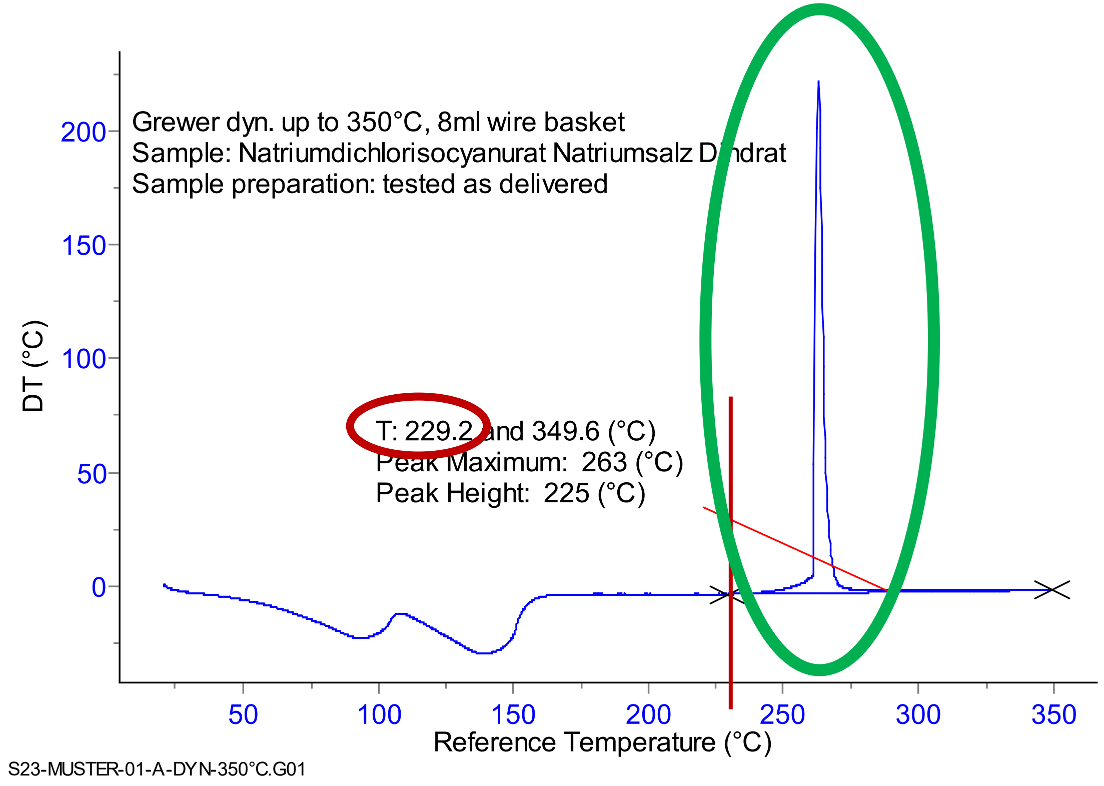
Evaluation of drying conditions

- Grewer measurement

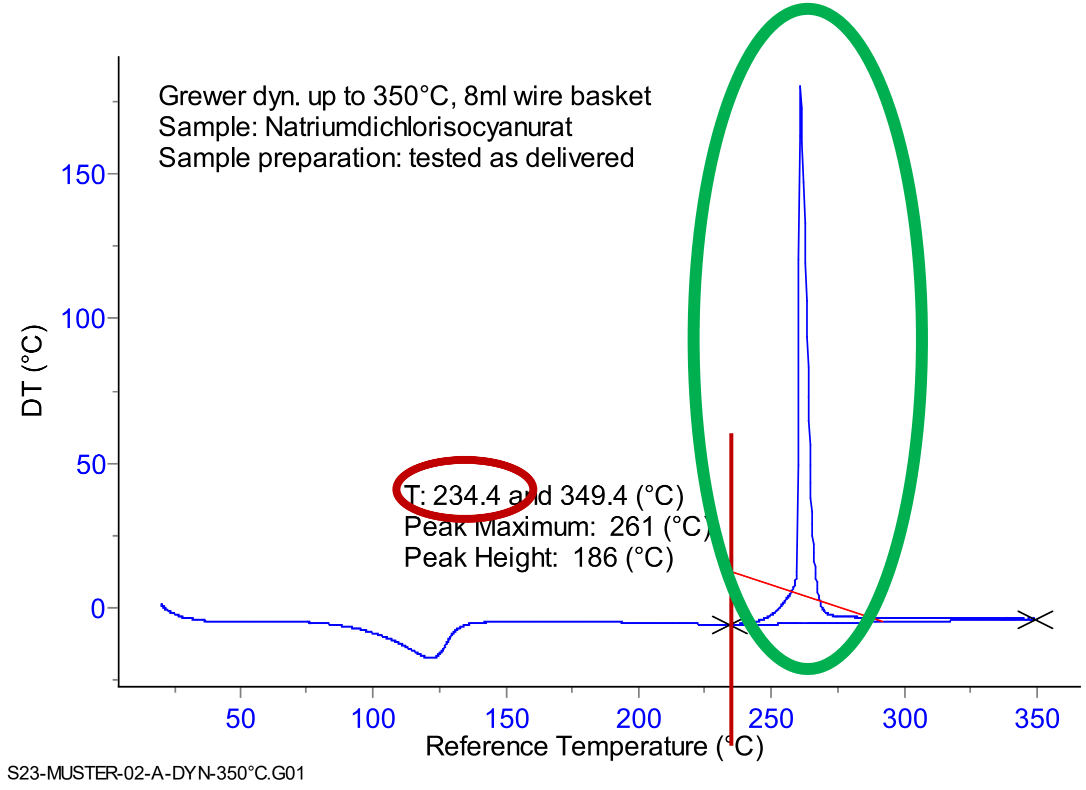


Example: Drying of NaDCC dihydrate

- NaDCC dihydrate Grewer



- NaDCC Grewer

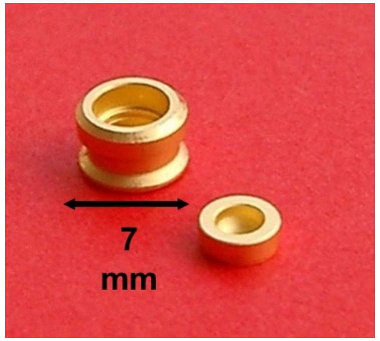


Confirm decomposition temperature ranges mentioned in Gestis (or other MSDS)

Example: Drying of NaDCC dihydrate

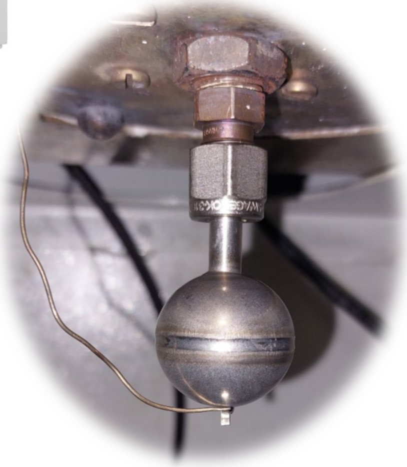
Assessing decomposition:

DSC



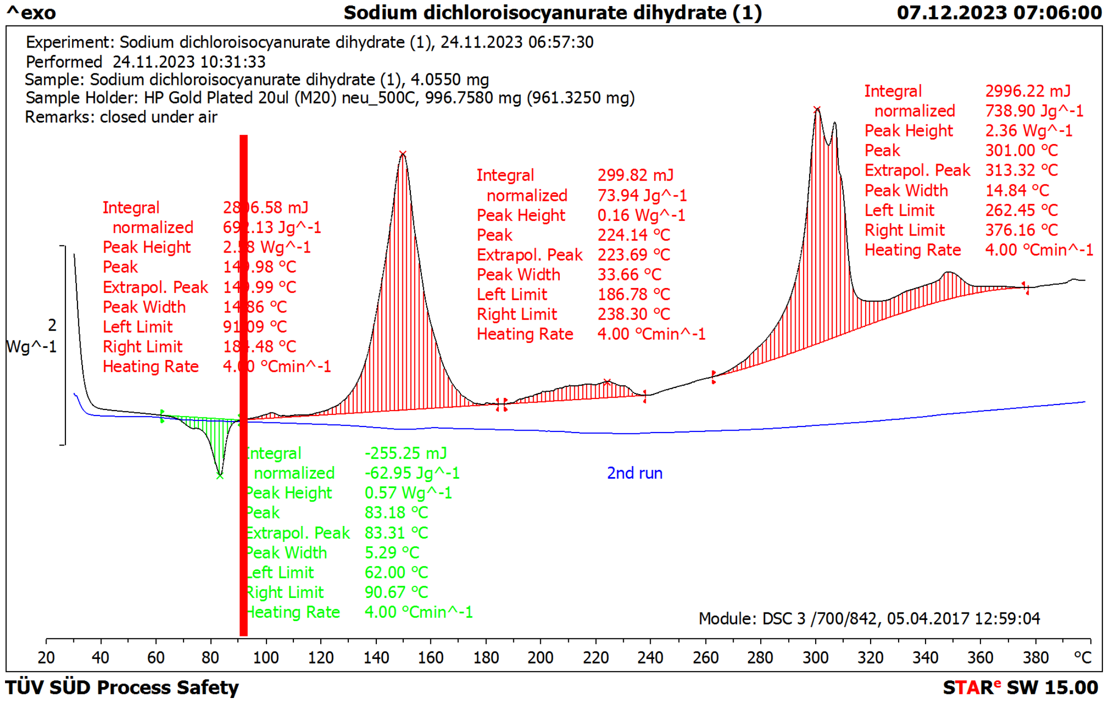
Calvel Calorimeter C80

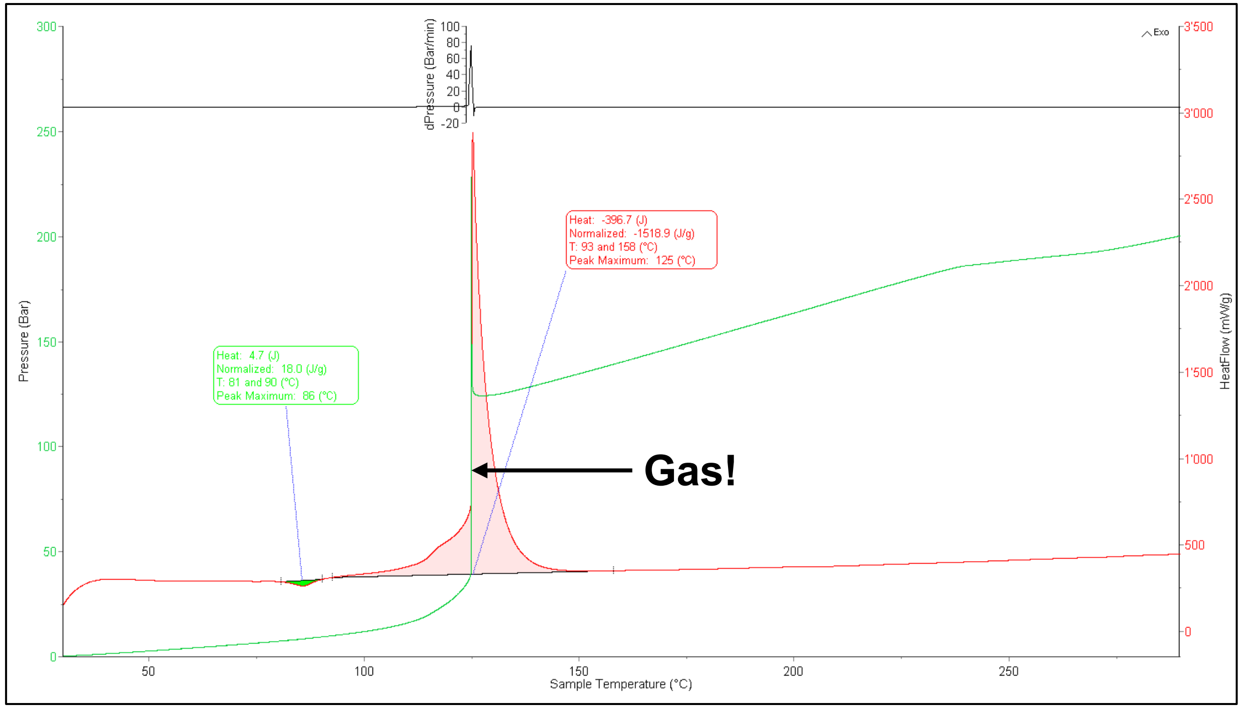
ARC



Example: Drying of NaDCC dihydrate

- NaDCC dihydrate DSC
- NaDCC dihydrate C80



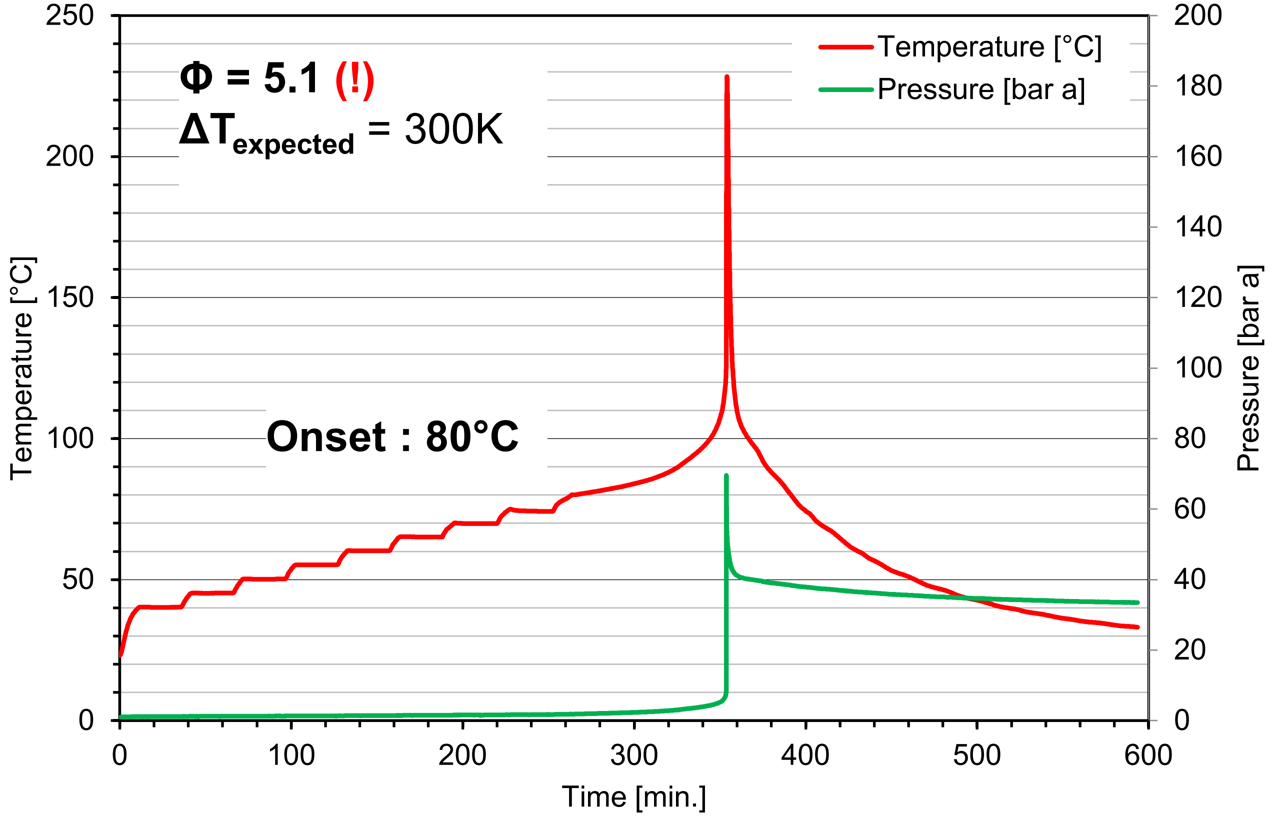


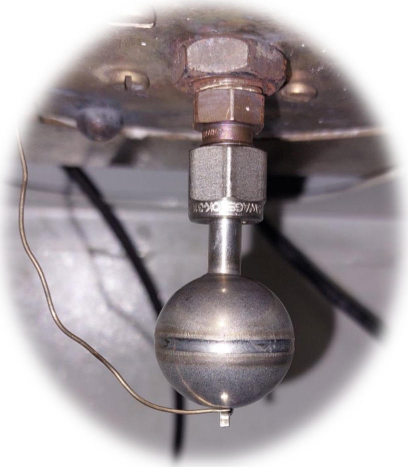
- Total of 1500 kJ/kg decomposition energy
- Decomposition measured from ~90°C

- Important pressure increase
- Total of 1500 kJ/kg decomposition energy
- Decomposition measured from ~90°C

Example: Drying of NaDCC dihydrate

- NaDCC dihydrate ARC (pseudo-adiabatic – Heat-Wait-Search)





~ 50% of the overall event could be measured

Chemical Hazard Assessment - Steps

1. Data Collection
2. **Data Interpretation**
3. **Safety concepts, safe limits**
4. Transfer of information
5. Life cycle – Update information

Safe limits and effects

Parameter	Deviation	Storage	Reactor	Distillation	Drying
-	Normal process				
Amount	More/less/none				
Concentration	More/less				
Substance	Other				
Temperature	More/less				
Pressure	More/less				
Time	Early/late/ too fast/too slow				
Mixing	No/less/more				
Sequence	Wrong (B before A)				
Transient	Start/stop				
Other					

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Safe limits and effects → reactivity

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Safe limits and effects → reactivity

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Time	Early/late/ too fast/too slow Too long/too short				
Mixing	No/less/more				
Sequence	Wrong (B before A)				
Transient	Start/stop				
Other					

Example: Drying of NaDCC dihydrate

Safe limits and effects

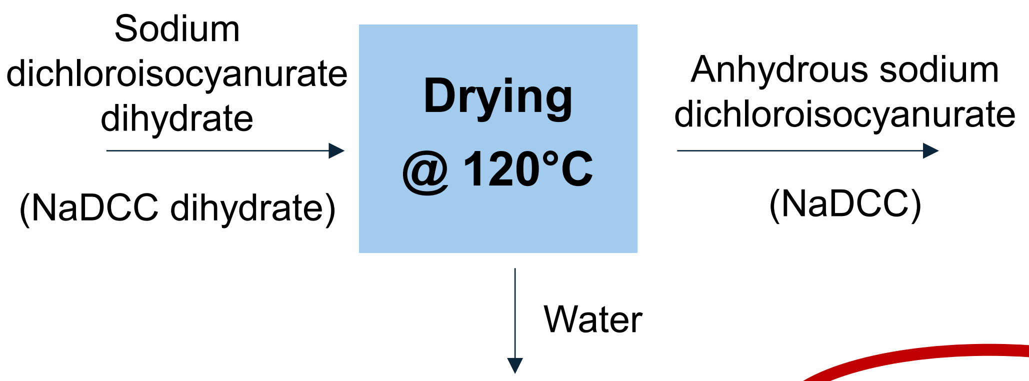
1. Assess normal process conditions
   - Severe decomposition (temperature increase > 1000°C)
   - In an open system (e.g. fluidized bed dryer) → maximum drying temperature ~ 120°C

2. Assess response of process to deviations
   - **Closed system, layers of products**:
     - decomposition with high severity (T and P) and T_{D24}~20°C (very high probability)
     - Violent gas production → pressure relief might be difficult
   - **Temperature too high**: Gas production around 100 l/kg (in open system @ 350°C)

Chemical Hazard Assessment - Steps

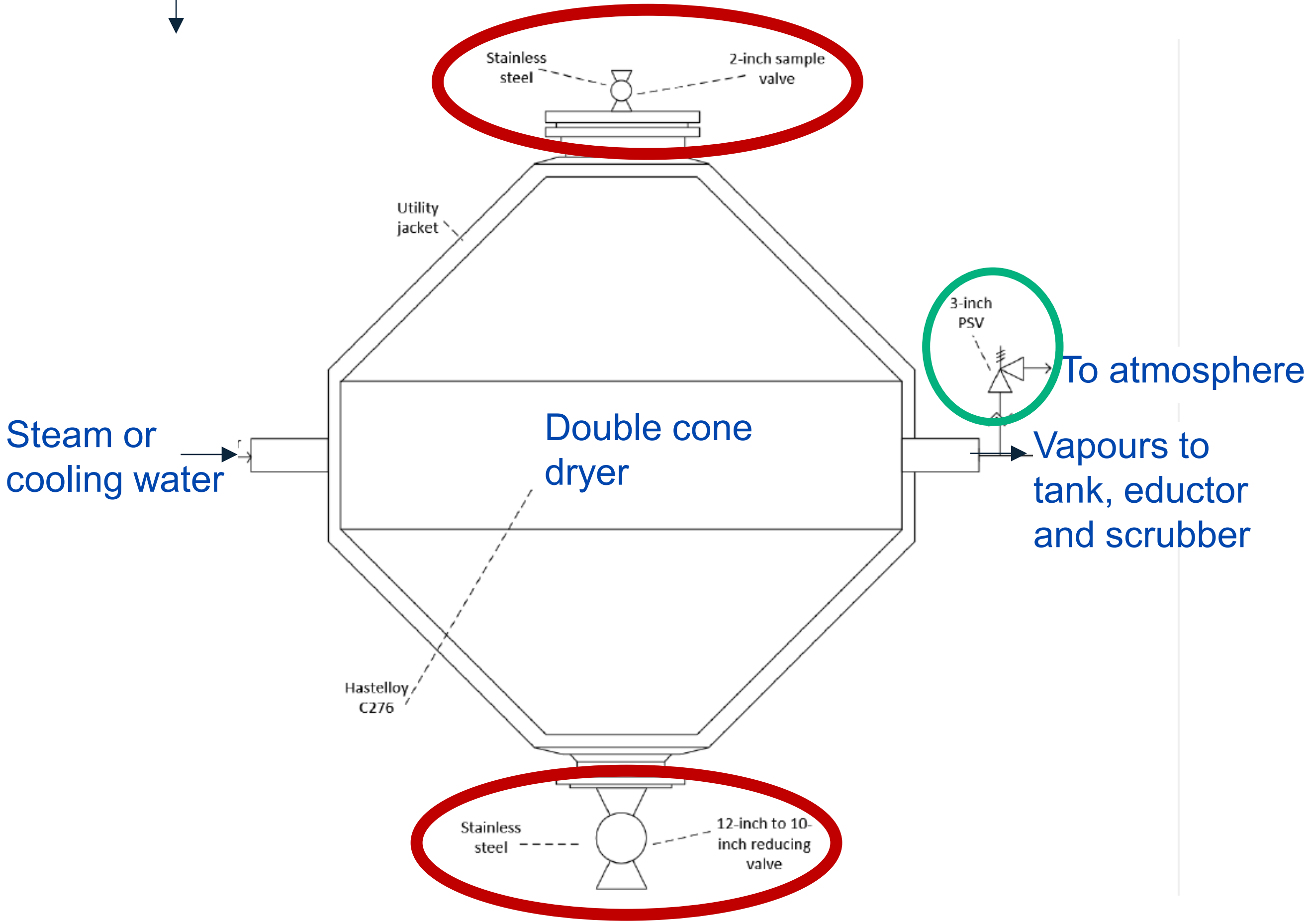
1. Data Collection
2. Data Interpretation
3. Safety concepts, safe limits
4. **Transfer of information**
5. **Life cycle – Update information**

Example



Process Information

- Process conditions for fluidized bed
- Company looking for third party to dry NaDCC dihydrate
- Option found: rotary double cone dryer (pressure equipment)
- Tests directly in $4 m^3$

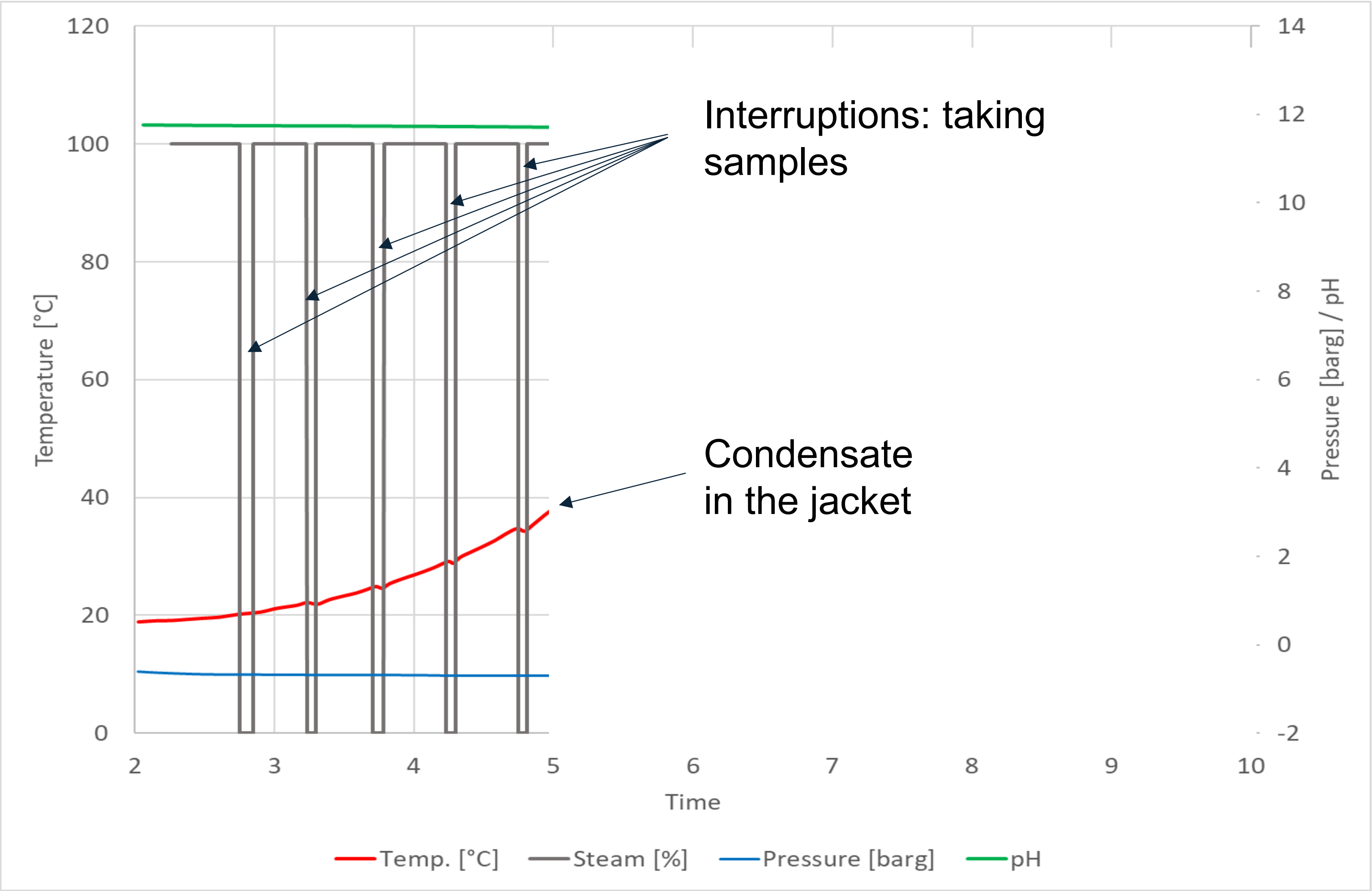


Source: https://www.csb.gov/optima-belle-explosion-and-fire/

Example: Drying of NaDCC dihydrate

- **Process Data Batch 1**

Figure 2. Optima Belle's rotary double cone jacketed dryer. (Credit: Optima Belle)



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Example: Drying of NaDCC dihydrate

- **Process Data Batch 1**

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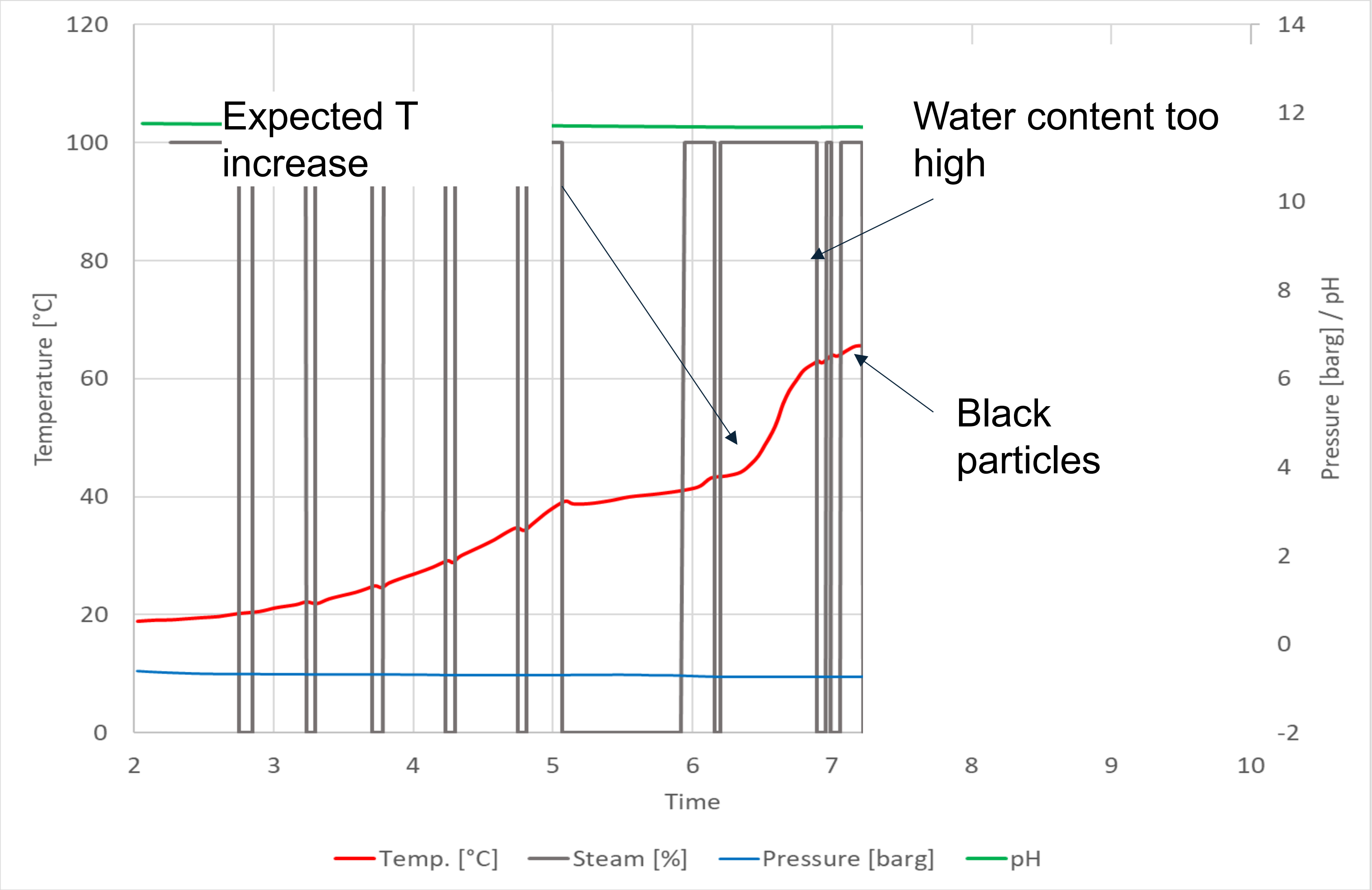

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Example: Drying of NaDCC dihydrate

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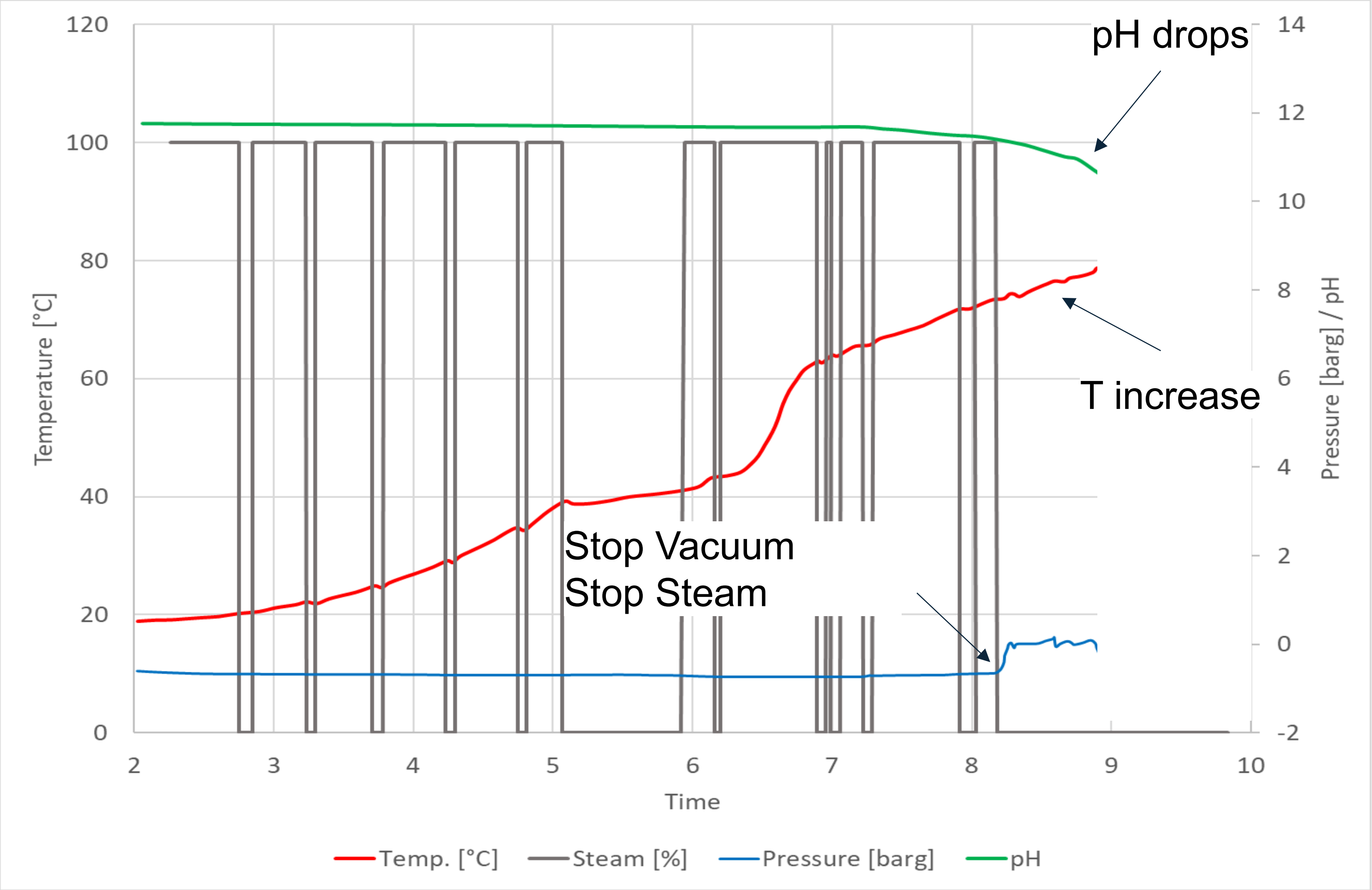

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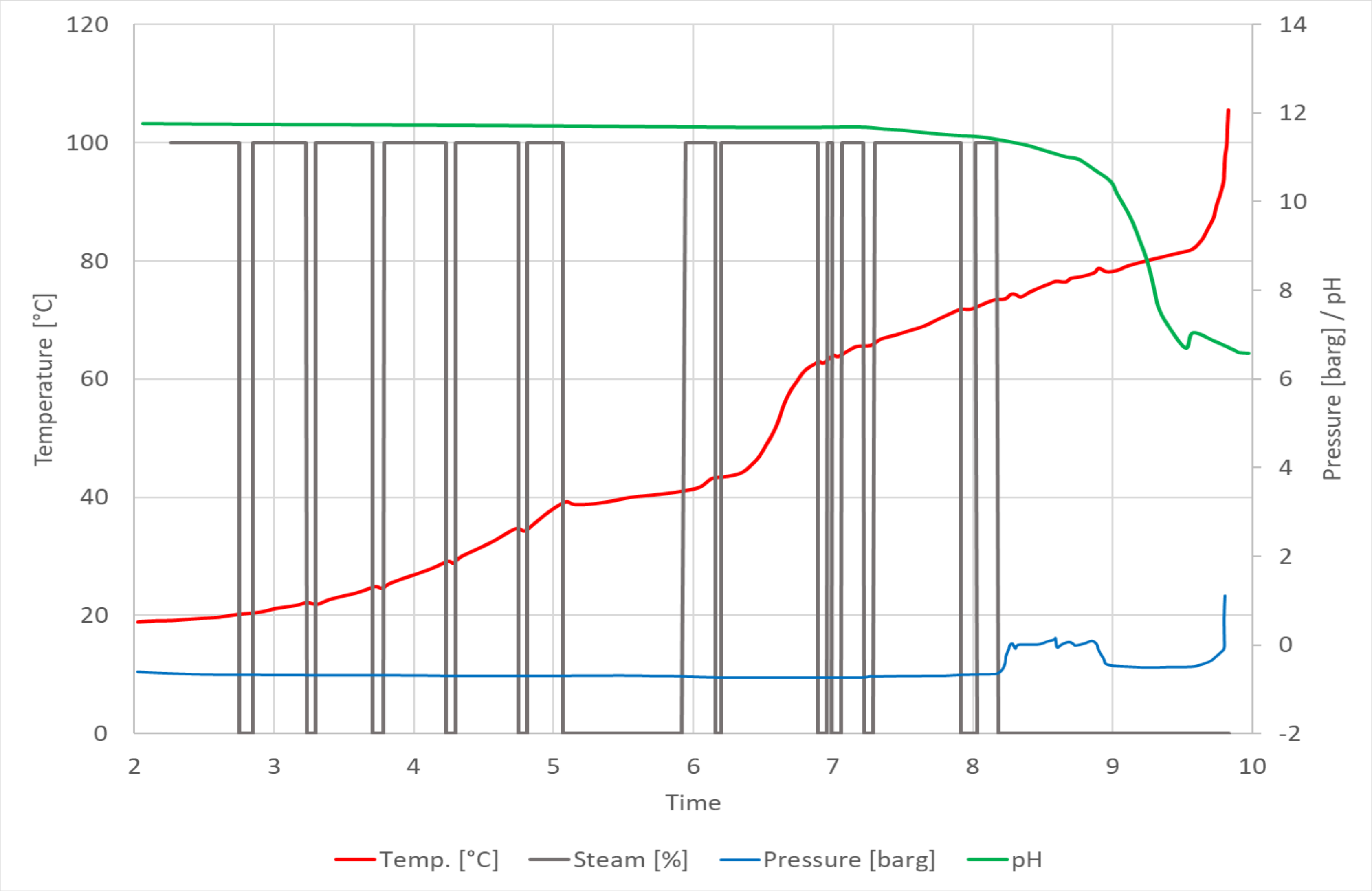
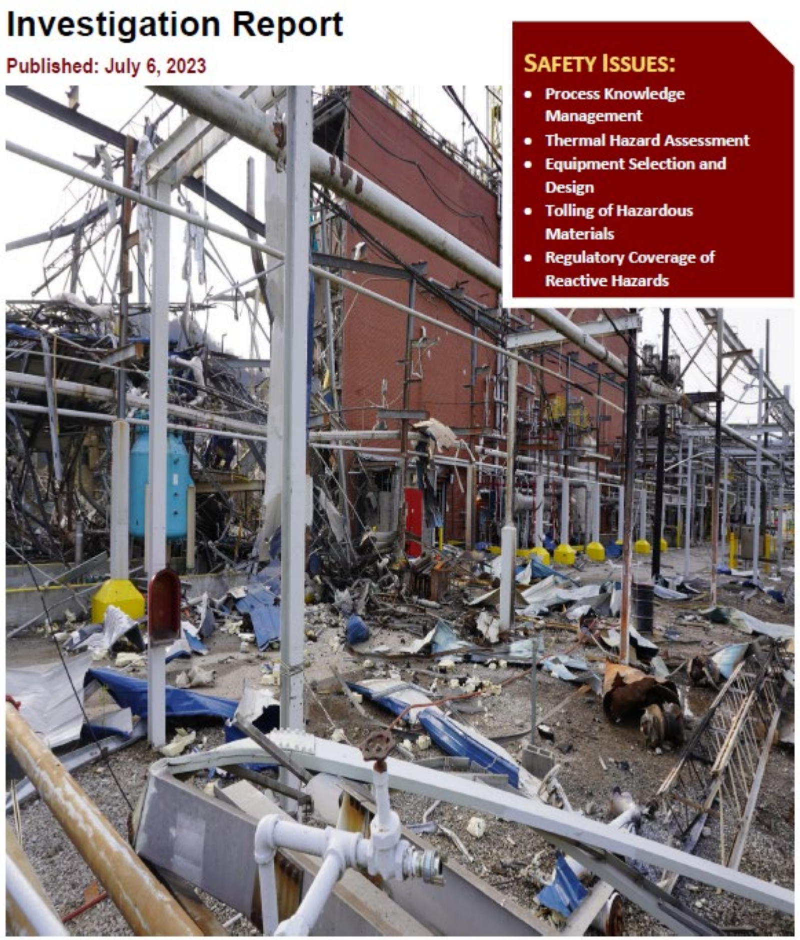


Source: https://www.csb.gov/optima-belle-explosion-and-fire/

Example: Drying of NaDCC dihydrate

- 8th December 2020
  - One employee fatally injured, two others respiratory irritation
  - Debris found ~ up to 800 m away from the site

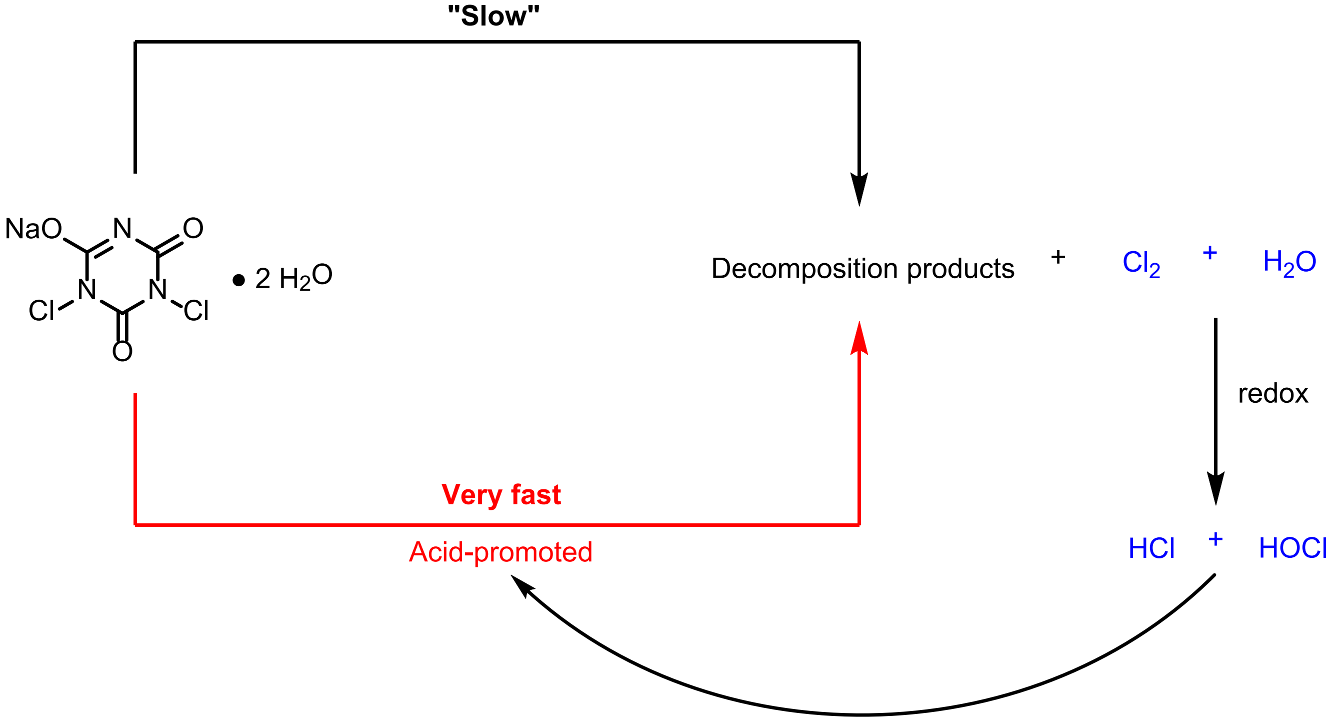
Source: CSB investigation report July, 6, 2023
 «Fatal Chemical Decomposition Reaction and Explosion at Optima Belle LLC»



Example: Drying of NaDCC dihydrate

Explanation

- Double cone dryer: closed system
- While vacuum was applied, decomposition gases were removed
- Atmospheric conditions: decomposition gases do not escape and accelerate the decomposition (autocatalytic behavior)



Example: Drying of NaDCC dihydrate

Conclusions made based on the example

- Chemical Hazard Assessment is key
  - Before introduction of a process into a plant → even for processes without a synthesis reaction
  - To gather relevant data for a process and define safety concept and safe limits of a process
    - Required data might be process dependent → difference «open» drying vs «closed» drying
    - Are mostly installation/scale independent

CHA good practice

1. Data Collection
2. Data Interpretation
3. Safety concepts, safe limits
4. Transfer of information
5. Life cycle – Update information

Multipurpose equipment @ J&J

- From lab scale to chemical plant: 10 L - 6000 L
- No dedicated equipment
- 1 plant for multiple chemical processes
- 1 HAZOP for the equipment and multiple chemical hazard analyses (CHAs)

Pilot plant scale

Lab scale

Chemical production

Waste treatment included

Risk Analysis @ JNJ

	Hazop	CHA	PHA
	Hazard and Operability Analysis	Chemical Hazard Analysis	Process Hazard Analysis
When?	@ installation of new equipment	@ introduction of new chemical process	@ introduction of new chemical process
Focus	Capabilities of equipment with worst case chemistry	Chemical reaction	Capabilities of the plant
Responsible	Chemical plant	Development	Chemical plant
Redo	Changes in equipment and worst-case chemistry	Changes in chemistry	Every 5 years, review (**PHR**) and changes in chemistry and plant

Process Safety Center - **PSC**

Therapeutics Development & Supply

→ Chemical Process R&D

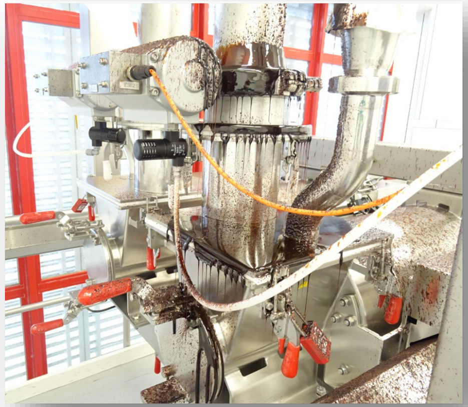
→ Technology & Engineering

→ Process Safety Center

Center of Excellence for safety testing and advice

To avoid …

Lab scale –
peroxide chemistry



Powder unit plant –
thermal decomposition
of sticky powder

Waste treatment – side product
from Suzuki reaction

Safety testing at PSC

A large battery of tests available:

Thermal Stability

- DSC
- Open Vessel (gas)
- Grewer + AIT powders
- Thermogravimetry – mass spectrometry (TG-MS)
- Thermal Screening Unit (TSU + Phitec I)
- AKTS thermal stability

Explosive Properties

- Shock Sensitivity (screening)

Calorimetry

- Reaction Calorimetry (RC1)
- Phi-Tec II (Adiabatic Calorimetry)

Flammability

- Burning behavior
- Flash point
- Auto Ignition Temperature liquids (AIT - screening)
- Minimum Ignition Temperature dust cloud (MIT) *
- Layer ignition Temperature 5mm layer (LIT) *

Conductivity

- Electrical Volume Resistivity (EVR) *
- Liquid conductivity

Dust Explosion Characteristics *

- Minimum Ignition Energy (MIE)
- Dust Explosion 20 L vessel (Pmax, dP/dt -> KSt)

* Outsourced from 2019

DSC: Differential Scanning Calorimetry
AIT: Auto-ignition Temperature
AKTS: Advanced Kinetics and Technology Solutions

Process safety: A Risk based approach

Lab Scale → → → Pilot Plant → → → Chem. Prod.

Lab Scale
< 10 L

- Screening Thermal stability
- Shock sensitivity
- Theor. Evaluation
- Identification critical reactions
- Risk evaluation (CHA)

Pilot Plant
< 1600 L

- Adv. Thermal stability
- Compatibility
- Flammability
- Calorimetric studies
- Safety advice
- CHA

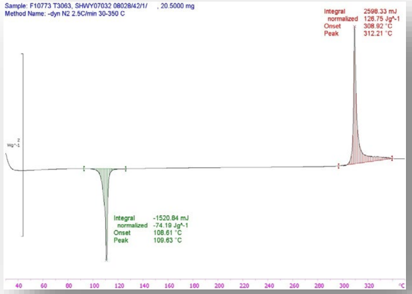
Chem. Prod.
± 6000 L

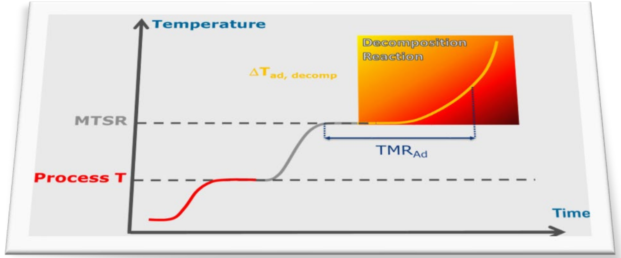
- Dust explosion-characteristics
- Ignition temperatures
- Conductivity
- Intro new reagents
- SWIFT
- CHA + PHA

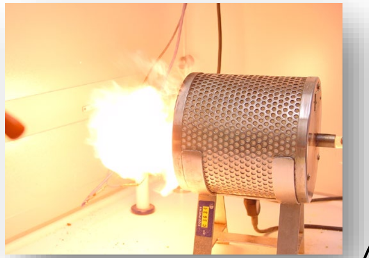
Higher Risk, more testing

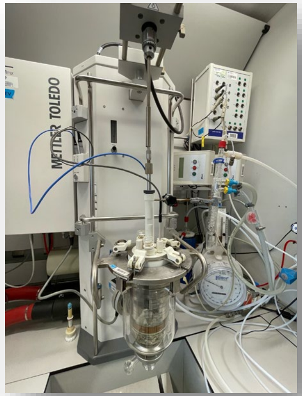
CHA: Chemical Hazard Analysis
PHA: Process Hazard Analysis
SWIFT: Structured What-If Technique

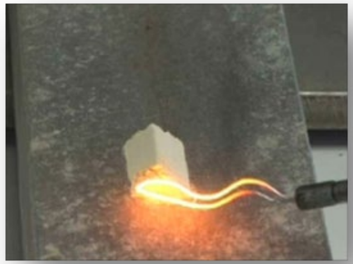
Risk Analysis @ PSC











Products

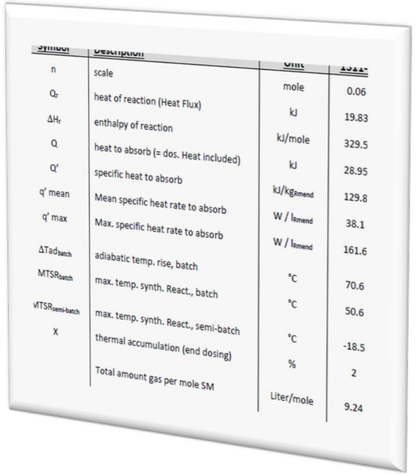
- Thermal stability
- Explosive properties
- Compatibility
- Flammability
- Ignition temperatures
- Dust explosion
- Conductivity

CHA

Approval (Go/No Go) for CDXP
&
Preparation PHA for Com. Prod.

Processes

- Calorimetry
- Gas production
- Runaway potential
- What if scenarios



Symbol	Description	Unit	[illegible]
n	scale	mole	0.06
Q_r	heat of reaction (Heat Flux)	kJ	19.83
ΔH_r	enthalpy of reaction	kJ/mole	329.5
Q	heat to absorb (= dos. Heat included)	kJ	28.95
Q'	specific heat to absorb	kJ/kg_{Rmend}	129.8
q' mean	Mean specific heat rate to absorb	W / l_{Rmend}	38.1
q' max	Max. specific heat rate to absorb	W / l_{Rmend}	161.6
ΔTad_{batch}	adiabatic temp. rise, batch	°C	70.6
$MTSR_{batch}$	max. temp. synth. React., batch	°C	50.6
$MTSR_{semi-batch}$	max. temp. synth. React., semi-batch	°C	-18.5
X	thermal accumulation (end dosing)	%	2
	Total amount gas per mole SM	Liter/mole	9.24

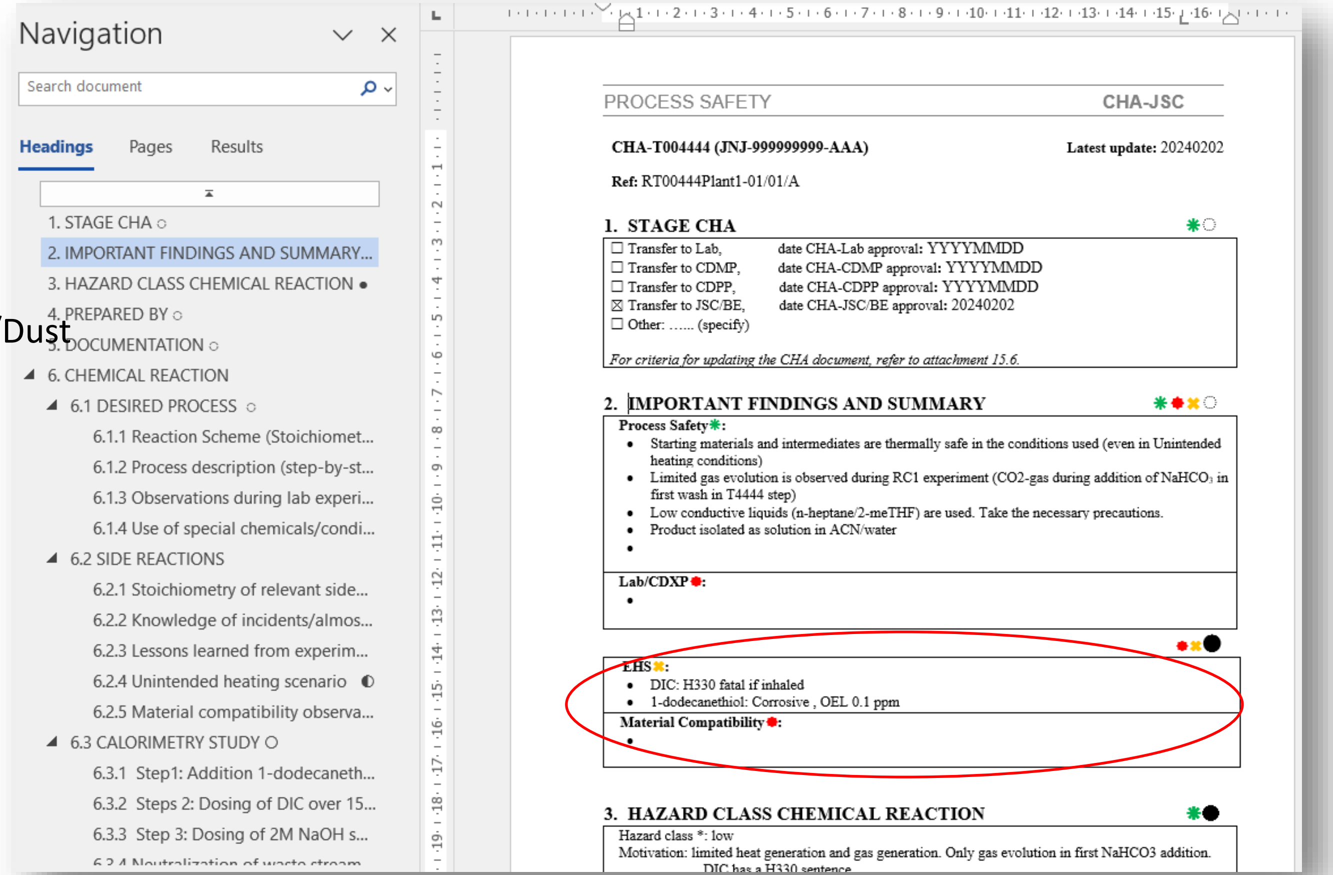
CHA: Chemical Hazard Analysis Process

1. Data collection
2. Data interpretation
3. Safety concepts, safe limits
4. Transfer of information
5. Life cycle – update information

CHA: Data collection

Word-doc

- Chemical reaction (desired / side reactions)
  - Reaction scheme (mass balance!)
  - Process description
  - Observations in the lab
  - Calorimetry study (PSC exp)
- Safety information of chemicals (used and produced)
  - Thermal stability/Shock sensitivity/Flammability Conductivity/Dust explosion characteristics
  - Compatibility chemicals and environment
- Process waste streams
  - Composition / destination
  - Reactivity (Hazardous properties) + chemistry
  - Compatibility waste streams and environment
- Capabilities of plant
  - Cooling and venting capacity
- What if – analysis
- Actions and recommendations



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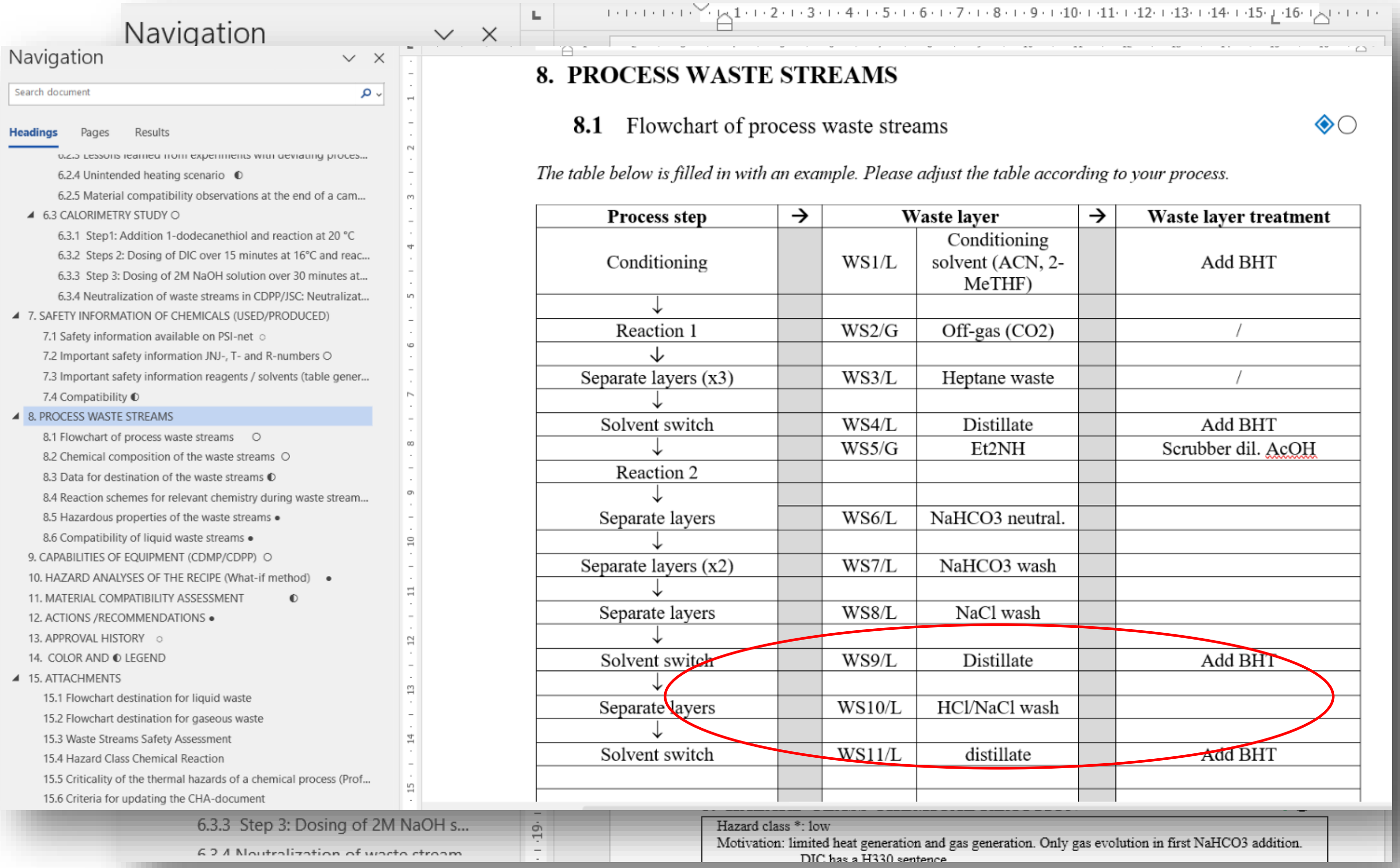

Navigation

Headings Pages Results

8. PROCESS WASTE STREAMS

8.1 Flowchart of process waste streams

The table below is filled in with an example. Please adjust the table according to your process.

Process step	→	Waste layer		→	Waste layer treatment
Conditioning		WS1/L	Conditioning solvent (ACN, 2-MeTHF)		Add BHT
↓					
Reaction 1		WS2/G	Off-gas (CO_2)		/
↓					
Separate layers (x3)		WS3/L	Heptane waste		/
↓					
Solvent switch		WS4/L	Distillate		Add BHT
↓		WS5/G	Et2NH		Scrubber dil. AcOH
Reaction 2					
↓					
Separate layers		WS6/L	$NaHCO_3$ neutral.		
↓					
Separate layers (x2)		WS7/L	$NaHCO_3$ wash		
↓					
Separate layers		WS8/L	NaCl wash		
↓					
Solvent switch		WS9/L	Distillate		Add BHT
↓					
Separate layers		WS10/L	HCl/NaCl wash		
↓					
Solvent switch		WS11/L	distillate		Add BHT

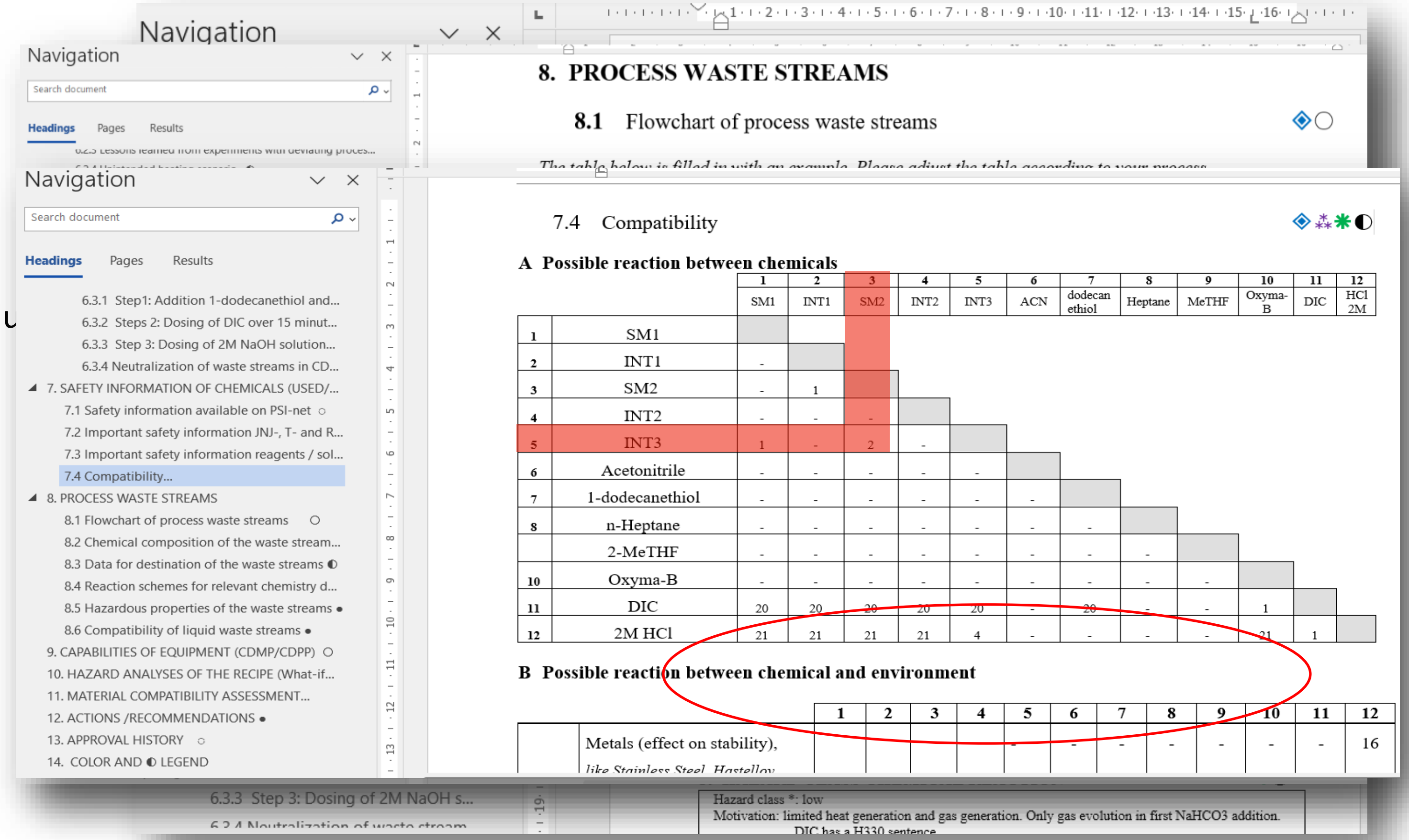
6.3.3 Step 3: Dosing of 2M NaOH s...

Hazard class *: low
Motivation: limited heat generation and gas generation. Only gas evolution in first $NaHCO_3$ addition. DIC has a H330 sentence

CHA: Data collection

- Chemical reaction (desired / side reactions)
  - Reaction scheme (mass balance!)
  - Process description
  - Observations in the lab
  - Calorimetry study (PSC exp)
- Safety information of chemicals (used and produced)
  - Thermal stability/Shock sensitivity/Flammability Condu
    explosion characteristics
  - Compatibility chemicals and environment
- Process waste streams
  - Composition / destination
  - Reactivity (Hazardous properties) + chemistry
  - Compatibility waste streams and environment
- Capabilities of plant
  - Cooling and venting capacity
- What if – analysis
- Actions and recommendations

Word-doc



		1 SM1	2 INT1	3 SM2	4 INT2	5 INT3	6 ACN	7 dodecan ethiol	8 Heptane	9 MeTHF	10 Oxyma-B	11 DIC	12 HCl 2M
1	SM1												
2	INT1	-											
3	SM2	-	1										
4	INT2	-	-	-									
5	INT3	1	-	2	-								
6	Acetonitrile	-	-	-	-	-							
7	1-dodecanethiol	-	-	-	-	-	-						
8	n-Heptane	-	-	-	-	-	-	-					
	2-MeTHF	-	-	-	-	-	-	-	-				
10	Oxyma-B	-	-	-	-	-	-	-	-	-			
11	DIC	20	20	20	20	20	-	20	-	-	1		
12	2M HCl	21	21	21	21	4	-	-	-	-	21	1	

CHA: Data collection

- Chemical reaction (desired / side reactions)
  - Reaction scheme (mass balance!)
  - Process description
  - Observations in the lab
  - Calorimetry study (PSC exp)
- Safety information of chemicals (used and produced)
  - Thermal stability/Shock sensitivity/Flammability Condu… explosion characteristics
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- Process waste streams
  - Composition / destination
  - Reactivity (Hazardous properties) + chemistry
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  - Cooling and venting capacity
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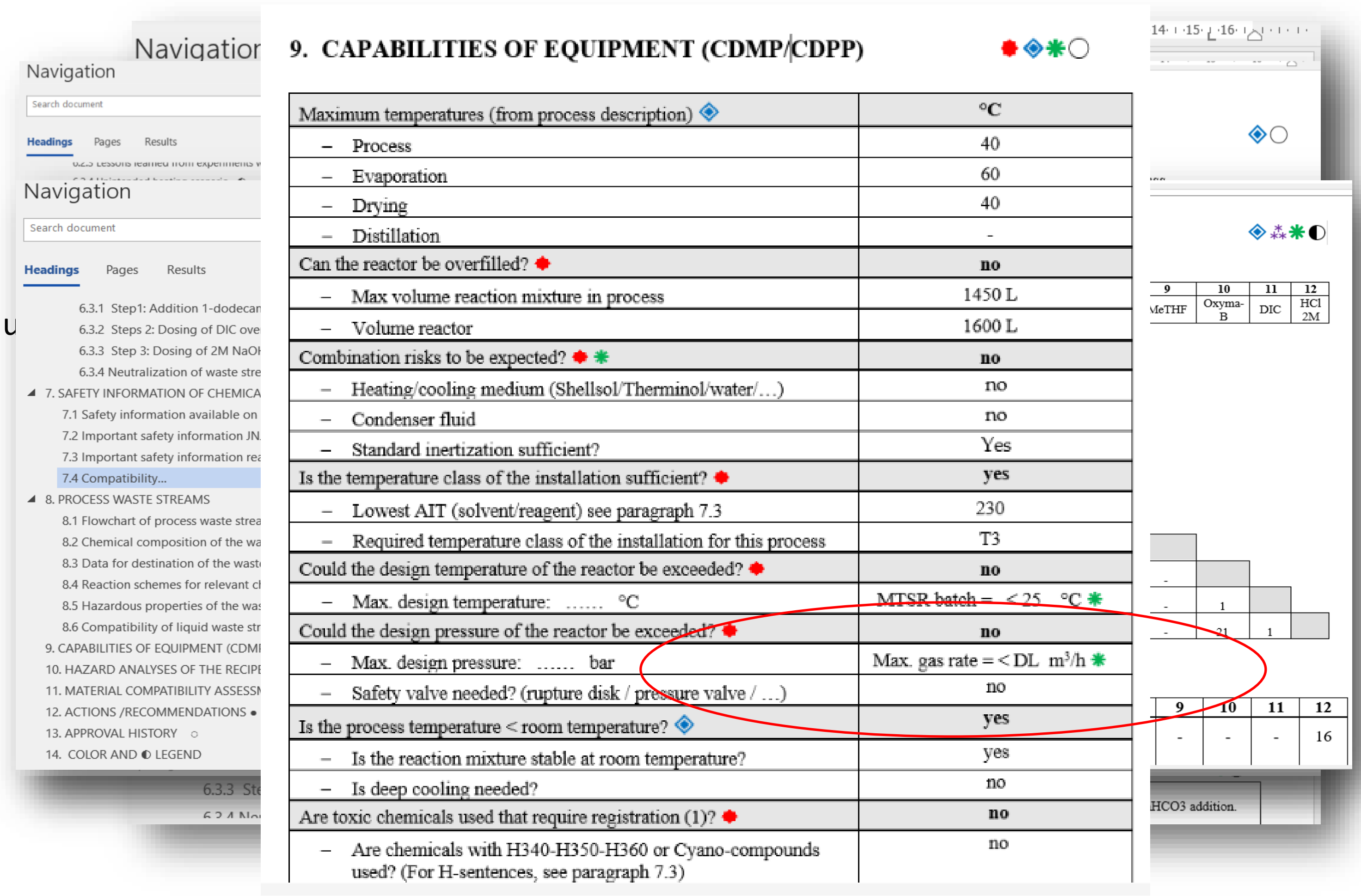
- Actions and recommendations

Word-doc



Navigation

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13. APPROVAL HISTORY
14. COLOR AND LEGEND

9. CAPABILITIES OF EQUIPMENT (CDMP/CDPP)

Maximum temperatures (from process description)	°C
– Process	40
– Evaporation	60
– Drying	40
– Distillation	-
Can the reactor be overfilled?	no
– Max volume reaction mixture in process	1450 L
– Volume reactor	1600 L
Combination risks to be expected?	no
– Heating/cooling medium (Shellsol/Therminol/water/…)	no
– Condenser fluid	no
– Standard inertization sufficient?	Yes
Is the temperature class of the installation sufficient?	yes
– Lowest AIT (solvent/reagent) see paragraph 7.3	230
– Required temperature class of the installation for this process	T3
Could the design temperature of the reactor be exceeded?	no
– Max. design temperature: …… °C	MTSR batch = < 25 °C
Could the design pressure of the reactor be exceeded?	no
– Max. design pressure: …… bar	Max. gas rate = < DL m^3/h
– Safety valve needed? (rupture disk / pressure valve / …)	no
Is the process temperature < room temperature?	yes
– Is the reaction mixture stable at room temperature?	yes
– Is deep cooling needed?	no
Are toxic chemicals used that require registration (1)?	no
– Are chemicals with H340-H350-H360 or Cyano-compounds used? (For H-sentences, see paragraph 7.3)	no

CHA: Data collection

- Chemical reaction (desired / side reactions)
  - Reaction scheme (mass balance!)
  - Process description
  - Observations in the lab
  - Calorimetry study (PSC exp)
- Safety information of chemicals (used and produced)
  - Thermal stability/Shock sensitivity/Flammability Condu
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  - Compatibility chemicals and environment
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  - Composition / destination
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  - Cooling and venting capacity
- What if – analysis
- Actions and recommendations

Word-doc

Navigation 9. CAPABILITIES OF EQUIPMENT (CDMP/CDPP)

10. **HAZARD ANALYSES OF THE RECIPE (What-if method)**

Step	Product / Item	Deviation (more/less/none) (higher/lower) (faster/slower) (shorter/longer)	Discussion	Action nr
1	Conditioning of equipment	No	**No** conditioning: no safety issue	
2	Inertization	No	**No**: potential explosive atmosphere	
3	Add to reactor at once SOLVENT (775 KG)	No More/less	**No**: high exothermicity without solvent! **More:** (= diluted): no safety issue **Less:** less solvent to capture heat generation → runaway? cooling capacity in the plant?	x
4	Start stirring, rpm: 70 t./min	No	**No:** hot spots during addition of reagent B	
5	Add to reactor at once REAGENT A (20 KG)	No More/less	**No:** no safety issue: no reaction, reagent B is stable at 60 °C **More:** no safety issue, reagent A is stable at 60 °C **Less:** no safety issue, reagent B is stable at 60 °C	
6	Heat to 60 °C (0.5 °C/min)	No Faster/slower Higher/lower	**No:** no safety issue **Faster/slower:** no safety issue **Higher:** no safety issue up to 100 °C (RM is thermally stable at 100 °C) **Lower:** no safety issue	
7	Dose to reactor at 60 °C, over 30 minutes REAGENT B (30 KG)	No More/less Faster/slower	**No:** no reaction, reagent A is stable at 60 °C **More:** no safety issue, reagent B is stable in RM at 60 °C **Less:** no safety issue, reagent A is stable in RM at 60 °C **Faster:** higher exothermicity & faster gas evolution → simulation of cooling & venting capacity needed in the plant **Slower:** no safety issue	x
8	Stirring at 60 °C for 2 hours	No Shorter/longer	**No/Shorter:** no safety issue, reaction not completed, no issues during workup **Longer:** no safety issue, RM stable at 60 °C (Q?) **Slower:** no safety issue	
9	…			

– Are chemicals with H340-H350-H360 or Cyano-compounds used? (For H-sentences, see paragraph 7.3)

CHA: Data collection

CHA- preparation by multidisciplinary team

Word-doc
> 40 pages

Risk based

14. ✱COLOR AND ◐ LEGEND

- ◈ Process Owner Chemical Process R&D
- ✱ Process Safety Center (PSC)
- ✖ EHS Expert
- ✹ Plant Engineer
- ⁂ Material Compatibility Expert

- ◌ Minimum requirement Lab
- ○ Minimum requirement CDMP
- ◐ Minimum requirement CDPP
- ● Minimum requirement JSC/BE

7.2 Important safety information JNJ-, T- and R-numbers ◈✱✖○

JNJ-, T- or R-number ◈	✱ Maximum reaction temperature (°C)	✱ Maximum drying temperature (°C)	✱ Maximum evaporation temperature (°C)	✱ Drying Class	✱ Safety Class dry Powder	✖ PBOEL-HHC Class	✖ Hz2xx: Process Safety	✖ Hz3xx: Toxicity/health	✖ Hz4xx: Environment
Starting Material 1 (SM1)	100	100	-	1	1B	3A*	-	H314	-
Intermediate1	130	-	130	-	-	3A*		Not tested	
Starting Material 2 (SM1)	120	120	-	1	1B	3A*	-	-	H401
Intermediate 2	130	130	-	1	1C	3A*		Not tested	
Intermediate 3	120	120	-	1	1B	3A*		Not tested	

CHA: Chemical Hazard Analysis Process

1. Data collection
2. Data interpretation
3. Safety concepts, safe limits
4. Transfer of information
5. Life cycle – update information

CHA: Data interpretation

Chemical reaction (desired and side reactions)

- Reaction scheme (mass balance!)
- Process description
- Observations in the lab
- Calorimetry study (PSC exp)

Are all reaction products known?

Are side reactions known?

Lessons learned from deviating conditions?

Chemistry below room temperature?

Foaming observed?

Heat and gas evolution?

T2 laboratories

Source: CSB report

CHA: Data interpretation

Safety information of chemicals (used and produced)

- Thermal stability
- Shock sensitivity
- Flammability
- Conductivity
- Dust explosion characteristics
- Compatibility chemicals and environment

What is the start of the decomposition?

Decomposition energy?

Is the product flammable?

Is the powder sensitive for dust explosion?

Are low conductive solvents used?

Compatibility issues?

Sugar refinery

AB specialty silicones

AZF Toulouse

Sources: CSB reports

CHA: Data interpretation

Process waste streams

- Composition
- Destination of the waste streams
- Reactivity (Hazardous properties) + chemistry
- Compatibility waste streams and environment

Reactive chemicals present?

Hazardous properties of waste streams?

Low conductive layers?

Neutralization of waste layer needed?

Can waste layers be combined?

Waste treatment company

Reference: Indaver 2016

Waste treatment – **side product from Suzuki reaction**

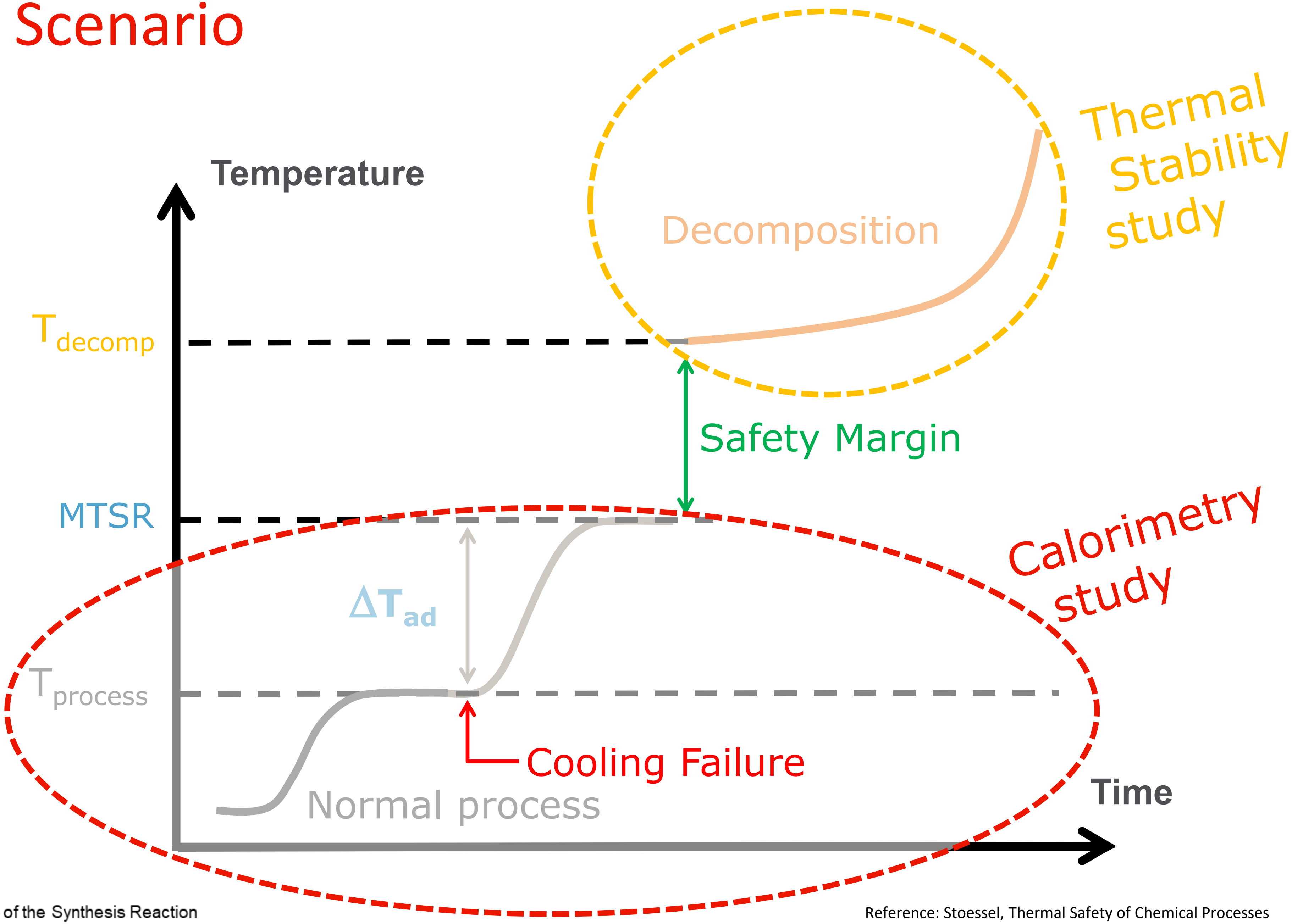
CHA: Chemical Hazard Analysis Process

1. Data collection
2. Data interpretation

   Capabilities of the plant: heat and gas evolution during the process

3. Safety concepts, safe limits
4. Transfer of information
5. Life cycle – update information

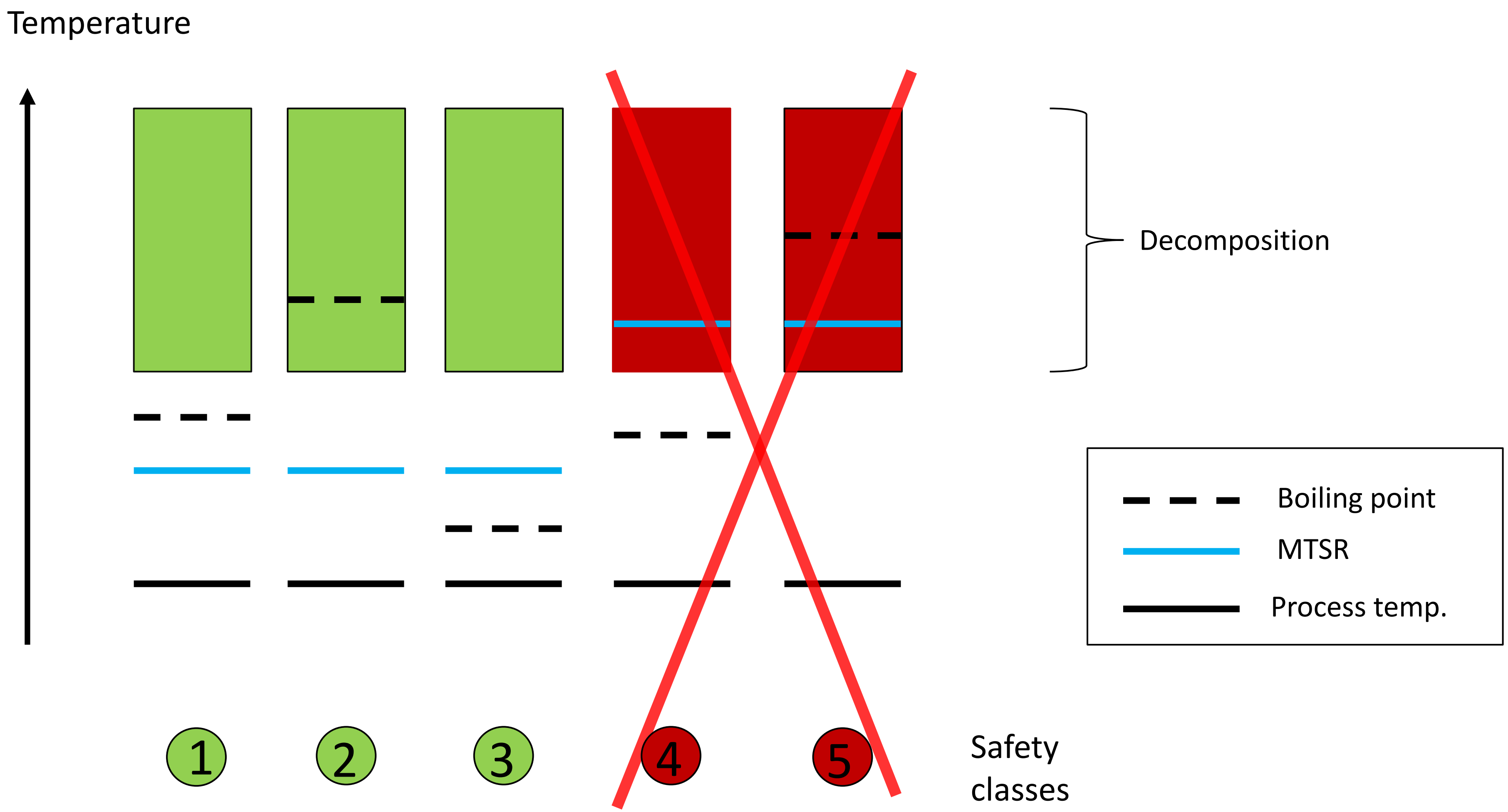
Runaway Scenario



MTSR: Maximum Temperature of the Synthesis Reaction
ΔT_{ad}: Adiabatic Temperature rise

Reference: Stoessel, Thermal Safety of Chemical Processes

Safety Classes - cooling failure scenario

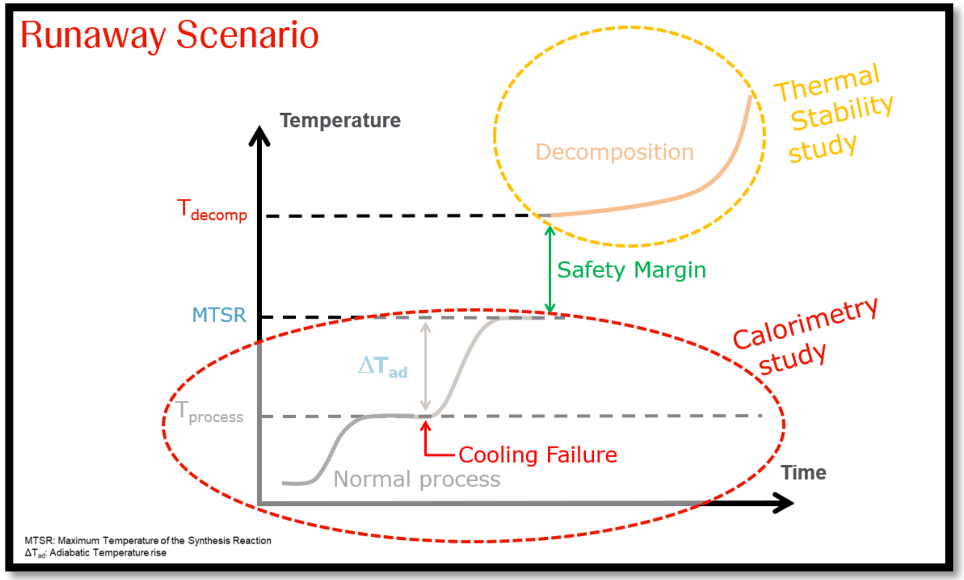


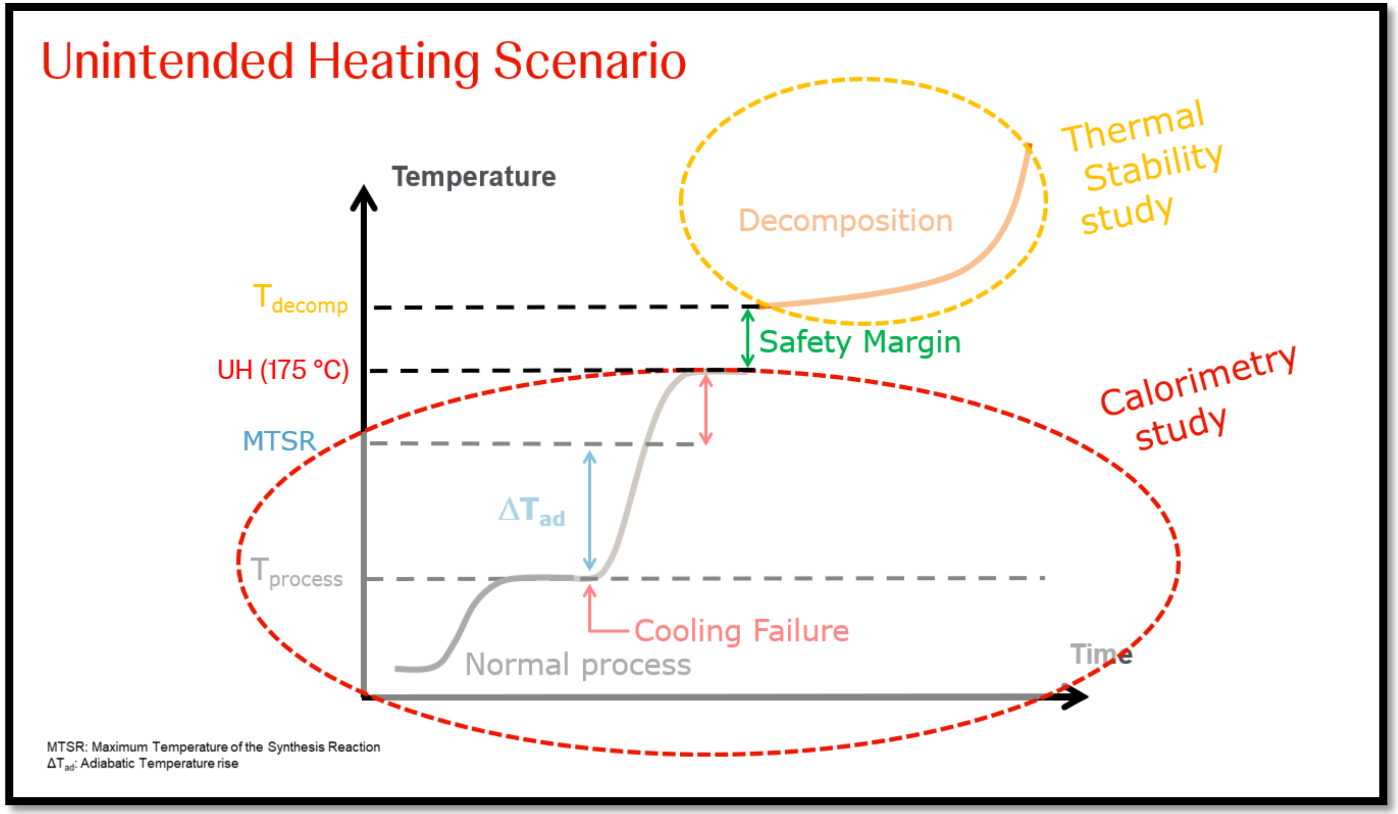
Reference: Stoessel, Thermal Safety of Chemical Processes

Scenario's

Cooling Failure

Temperature rise → MTSR
→ Criticality Classes





Unintended Heating

Failure of Basic Process Control System (BPCS)

CHA: Chemical Hazard Analysis Process

1. Data collection
2. Data interpretation
3. Safety concepts, safe limits
4. Transfer of information
5. Life cycle – update information

CHA: Safety concepts, safe limits

Reactive limits

Define max allowable temperatures for each chemical

(Thermal stability study)

Shock sensitive compound?

(Impact energy test, screening)

Required cooling and venting capacity?

(Calorimetry experiments)

Flammability limits

Is the powder flammable?

(Burning rate test)

Temperature classification of the equipment

(Auto ignition temperature for liquids & powders

Layer/Cloud ignition temperature for powders,

ATEX: Safe Temperature: 2/3 MIT, LIT-75 °C)

Extra safety measures needed for electrostatic issues?

Conductivity of liquids (> 10 000 pS/m)

Compatibility

→ **Material and environment**

→ **Other chemicals/solvents**

Dust explosion characteristics

→ **Sensitivity** (MIE)

→ **Severity** (Pmax, Kst)

CHA: Chemical Hazard Analysis Process

1. Data collection
2. Data interpretation
3. Safety concepts, safe limits
4. Transfer of information
5. Life cycle – update information

CHA: Transfer of information

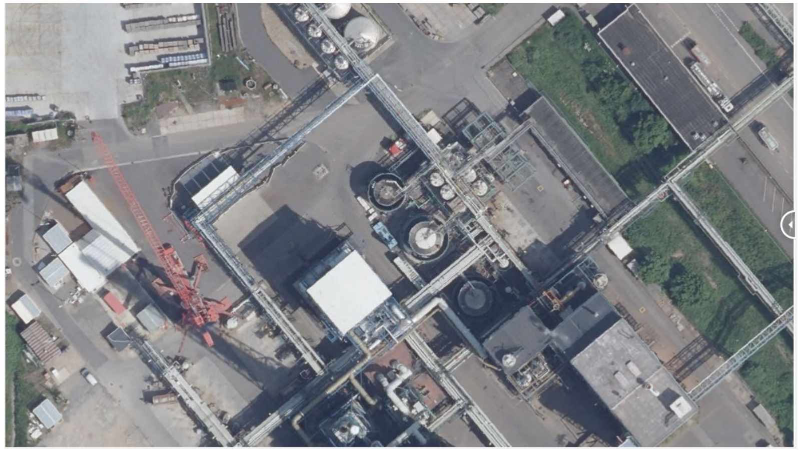
1. Collected data in the CHA doc is reviewed during the CHA meeting
2. CHA is archived at PSInet

   (= platform for safety reports/notes/risk assessments)

3. CHA doc is on SharePoint
4. Transfer to pilot plant: approval of Master batch record by PSC
5. Transfer to chemical production: CHA is preparation for PHA

Explosion in Leverkusen, Germany

- 27^{th} July 2021 9:40
- 7 people killed, 32 people injured
- Company: Currenta



Explosion im Entsorgungszentrum Bürrig (currenta-info-buerrig.de)

- Explosion im Entsorgungszentrum Bürrig (currenta-info-buerrig.de) https://www.currenta-info-buerrig.de/

CHA: Chemical Hazard Analysis Process

1. Data collection
2. Data interpretation
3. Safety concepts, safe limits
4. Transfer of information
5. Life cycle – update information

CHA: Chemical Hazard Analysis – living document

CHA = Chemical Hazard Analysis
PHA = Process Hazard Analysis

Lab < 10 L

CHA-lab (check list)

Lab > 10 L

CHA-CDMP

Mini Plant < 400 L

CHA-CDPP

Pilot Plant <1600 L

CHA-CP + PHA

Chem. Prod. ± 6000 L

Limited impact/risk --→ High risk

Screening Safety tests --→ Full Safety tests

Management of Change (MoC)

If chemical process changes → update risk analysis (CHA/PHA)

But what constitutes as a change?

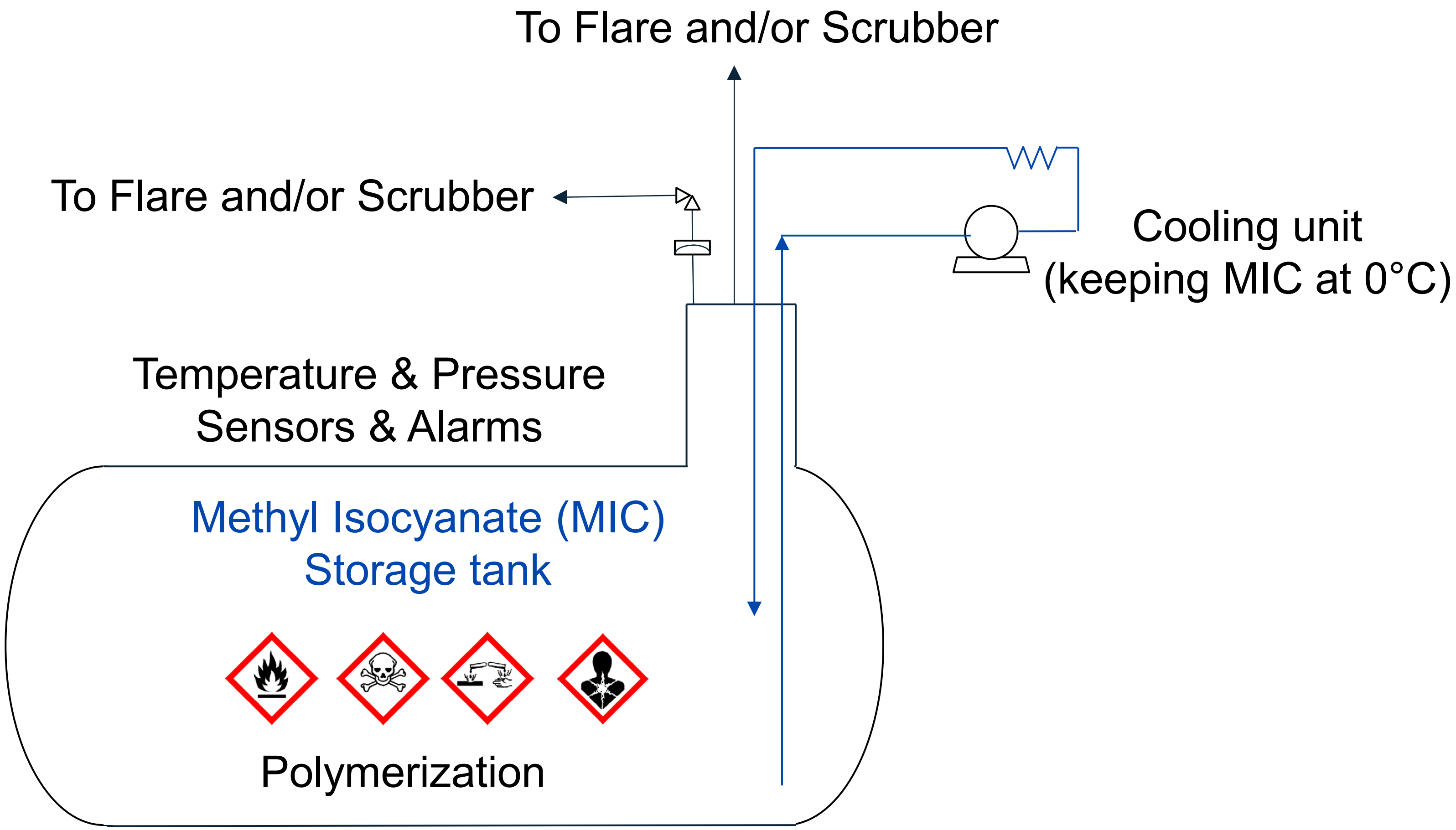
- Use of new chemicals in the process (reagents, solvent, …)
- Change in quality of a raw material
- Change in order of addition
- Larger batch size (more than 50% added)
- Change in process parameters (temperature, pressure, …)
- Change in concentration (more than 5%)
- Any change in ratios of reagents
- Faster dosing of chemicals
- Higher heating rate
- Change the way the reaction mixture is heated
- A new treatment of waste layers
- …

Changes during development

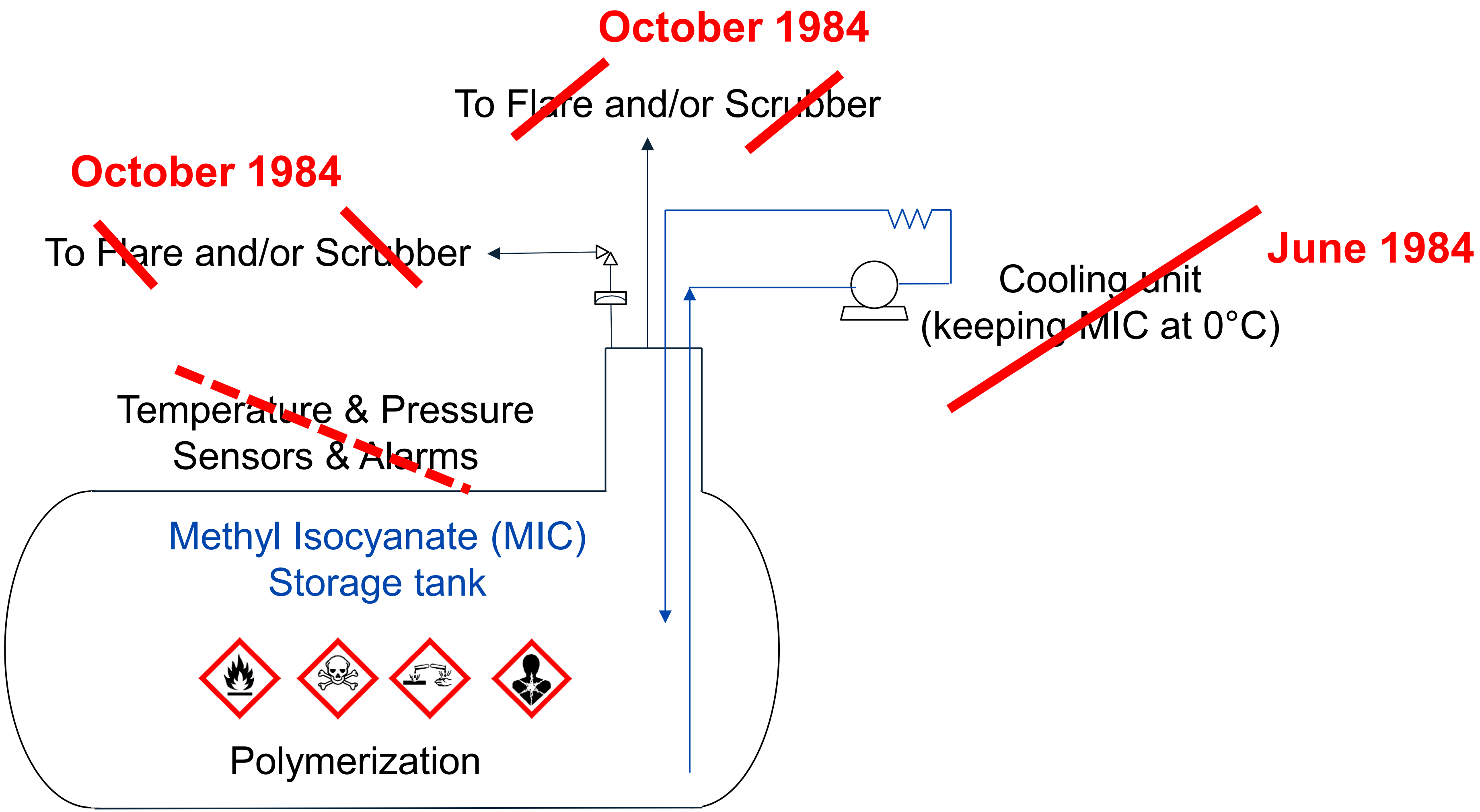
No changes possible after validation

Needs to be well defined!

Bhopal Accident



Bhopal Accident

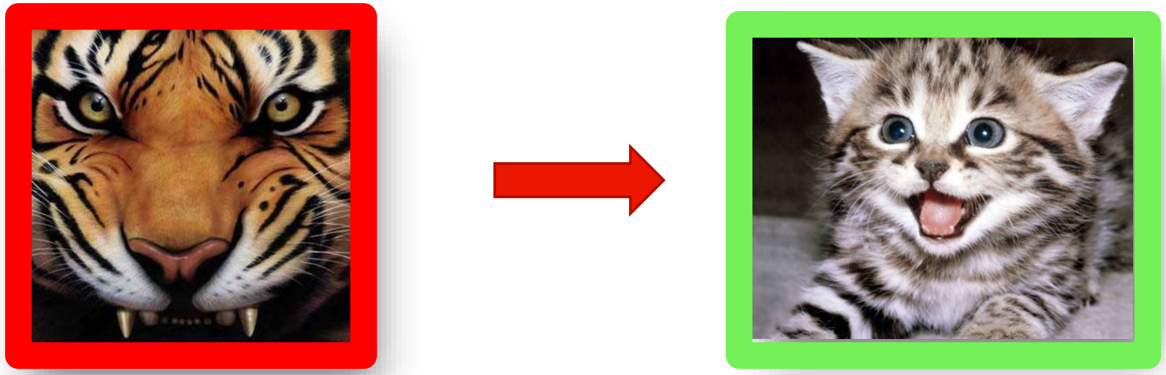


Why do we need an intrinsically safe process?

"What you don't have, can't leak"

Ground-breaking paper by Trevor Kletz: (Chemistry and Industry, 6 May 1978, pp 287-292)

Inherently safer design



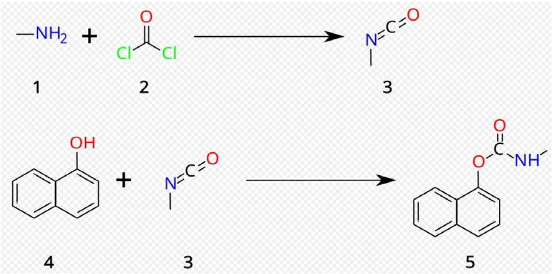
Minimize
Substitute
Attenuate
Simplify

1. **Minimize :** Eliminating or reducing a hazard,
2. **Substitute :** Substituting with a less hazardous material,
3. **Attenuate :** Using less hazardous process conditions,
4. **Simplify :** Designing a process to reduce the potential for, or consequences of, human error, equipment failure, or intentional harm.

Inherently safer design

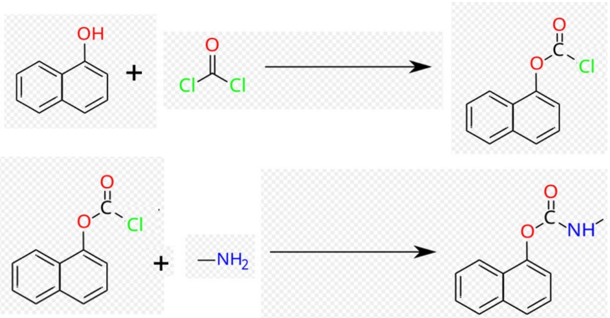
Synthesis of Cabaryl

Methylamine + phosgene → Methyl isocyanate (MIC)
Methyl isocyanate with 1-naphtol → Carbaryl



Minimization: store less MIC at the facility

Substitution: alternative process with formation of less hazardous chloroformate (change the order of addition)



Moderation: MIC stored at < 0 °C (standard procedure) instead of ambient temperature

December 3, 1984, Bhopal

“How to Make Inherent Safety Practice a Reality”, Khan & Amyotte, *Feb 2003, Canadian Journal of Chemical Engineering, Vol 81, pp. 2-16.*

Conclusion

Sources: CSB report T2 laboratories, Currenta, https://www.eti-swiss.com/internationales-2/chemikalien-konventionen/basler-konvention/, *getty Images/AFP/STR*, https://www.downtoearth.org.in/health/bhopal-38-years-ago-while-the-world-slept-its-worst-industrial-disaster-unfolded-in-the-heart-of-india-68232

Conclusion

- CHAs
  - Are necessary before introduction of a process into a plant
  - Are key to define safety concept and safe limits of a process
  - Are mostly installation/scale independent
  - Should be done on all steps of a process
  - Are key for preparation of further risk assessments (PHA, HAZOP, ATEX, LOPA, SIL….)

- CHA is a group effort: process safety and chemistry experts, EHS, plant engineers and operators

- Inherently safer design
  - Continually look for ways to reduce or eliminate hazards throughout the process life cycle
  - Start early with the CHA → change process when it is still possible

Johnson&Johnson Innovative Medicine

TÜV SÜD

Thank you for your attention

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