Chemical Process Safety – an Introduction

ENG 431 Safety of chemical Processes
Module 1

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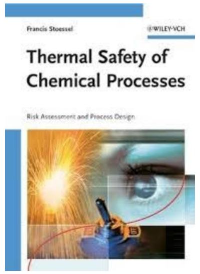
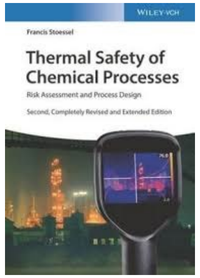
In this presentation

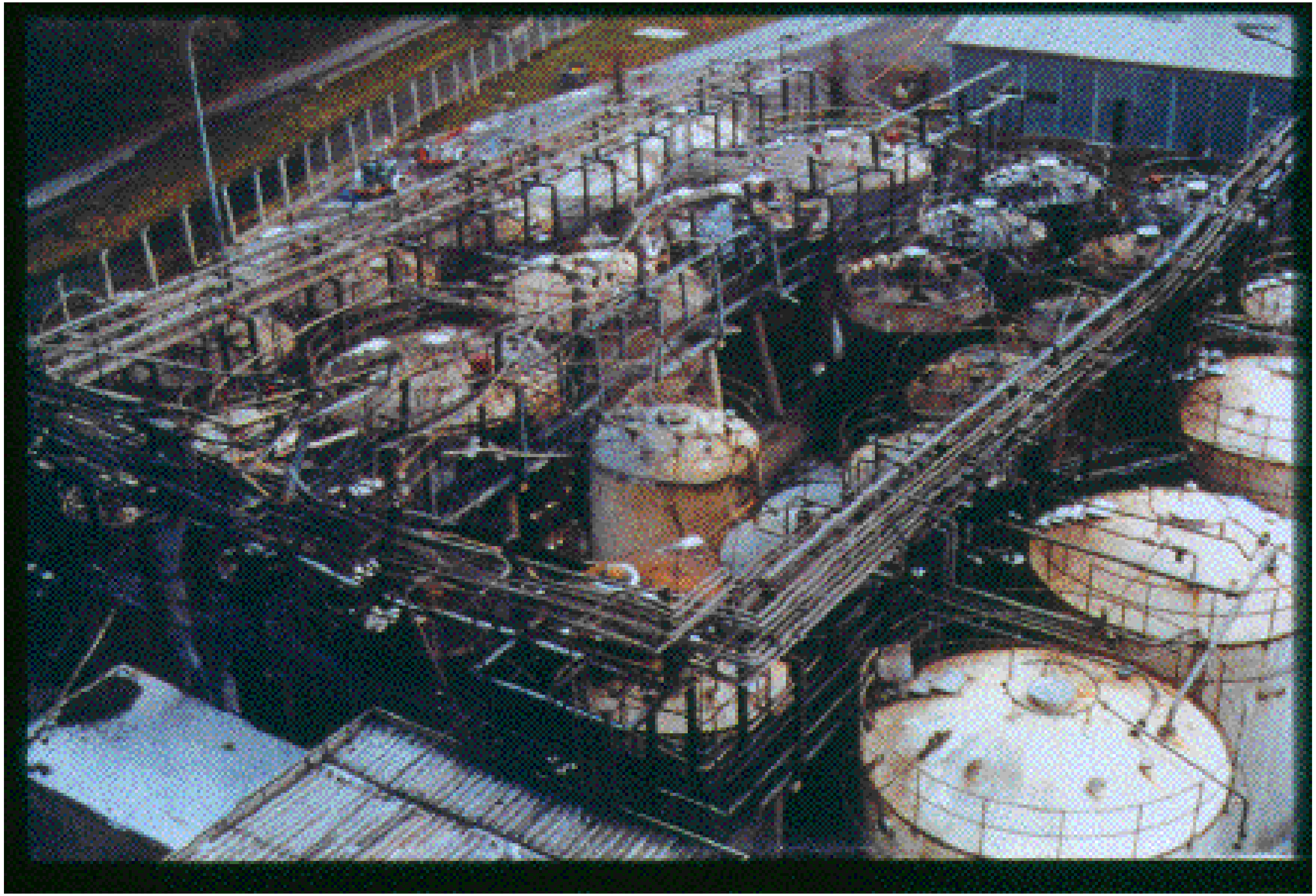
- Introduction to Process Safety
- Incidents – case histories
- A few definitions



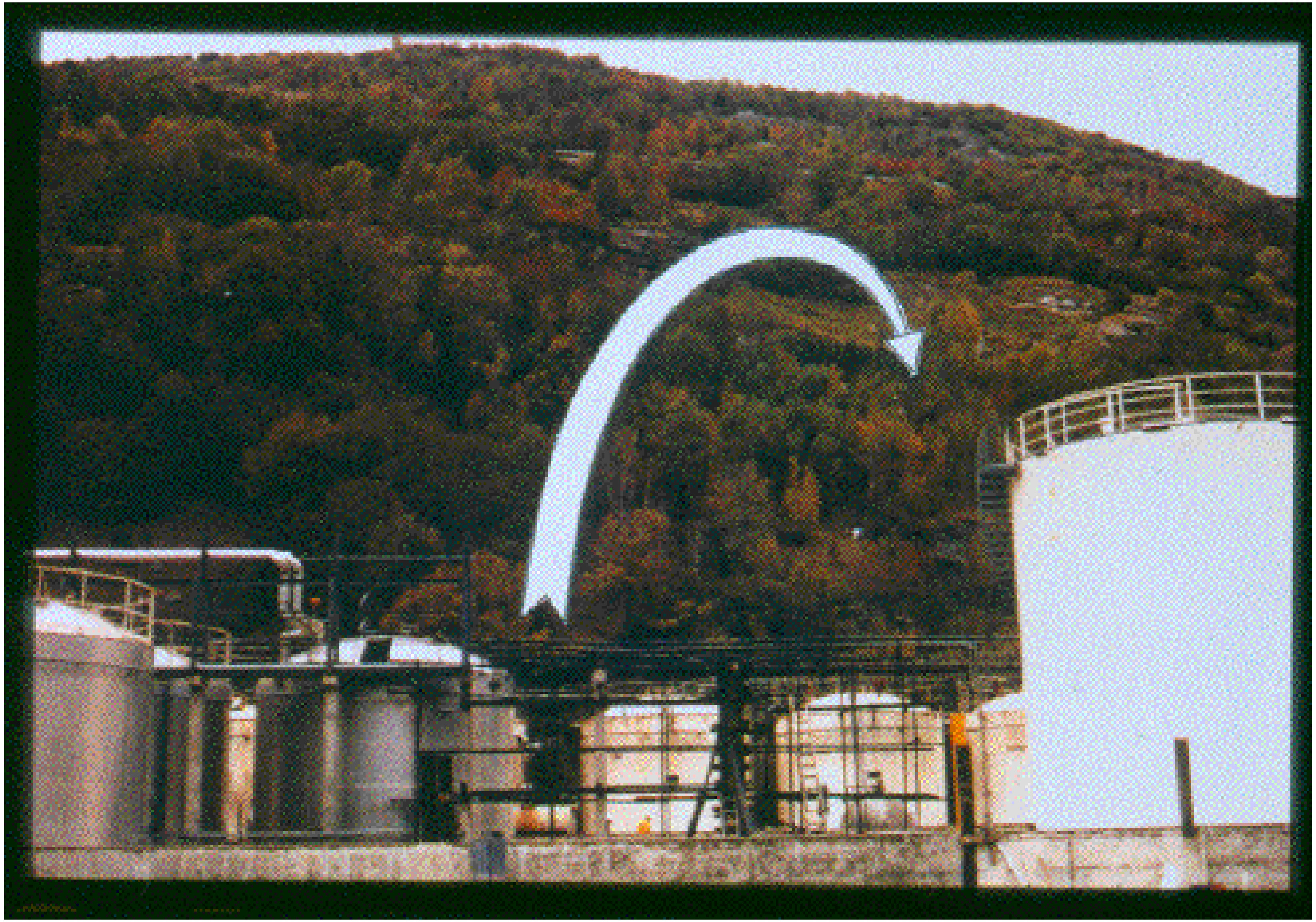


Chapter 1.1

Storage tank



Storage tank



Storage tank

Explosion in Leverkusen, Germany

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

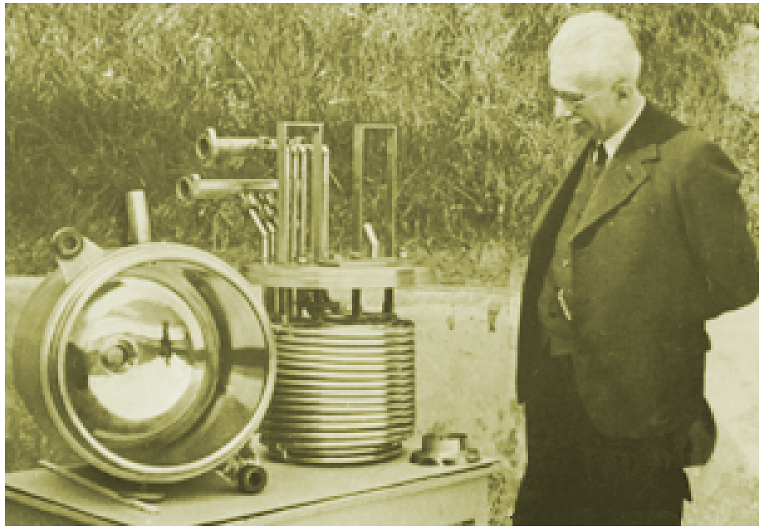
Explosion im Entsorgungszentrum Bürrig (currenta-info-buerrig.de)

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

Process Safety

- Process safety definitions (CCPS):
  - a discipline that focuses on the prevention of fires, explosions, and accidental chemical releases
  - Prevention of, preparedness for, mitigation of, response to, or restoration from catastrophic releases of chemicals or energy from a process
- ≠ occupational safety: focus on personal safety (prevent harms from falls, cuts, sprain, strains, being stuck by objects, repetitive motion injuries etc)

Nitroglycerine nitration reactor in 1875
https://www.nobelprize.org/alfred-nobel/alfred-nobel-in-scotland/



Continuous nitroglycerine reactor in 1935 (Biazzi)
http://www.biazzi.ch/page/history.php/

Process safety

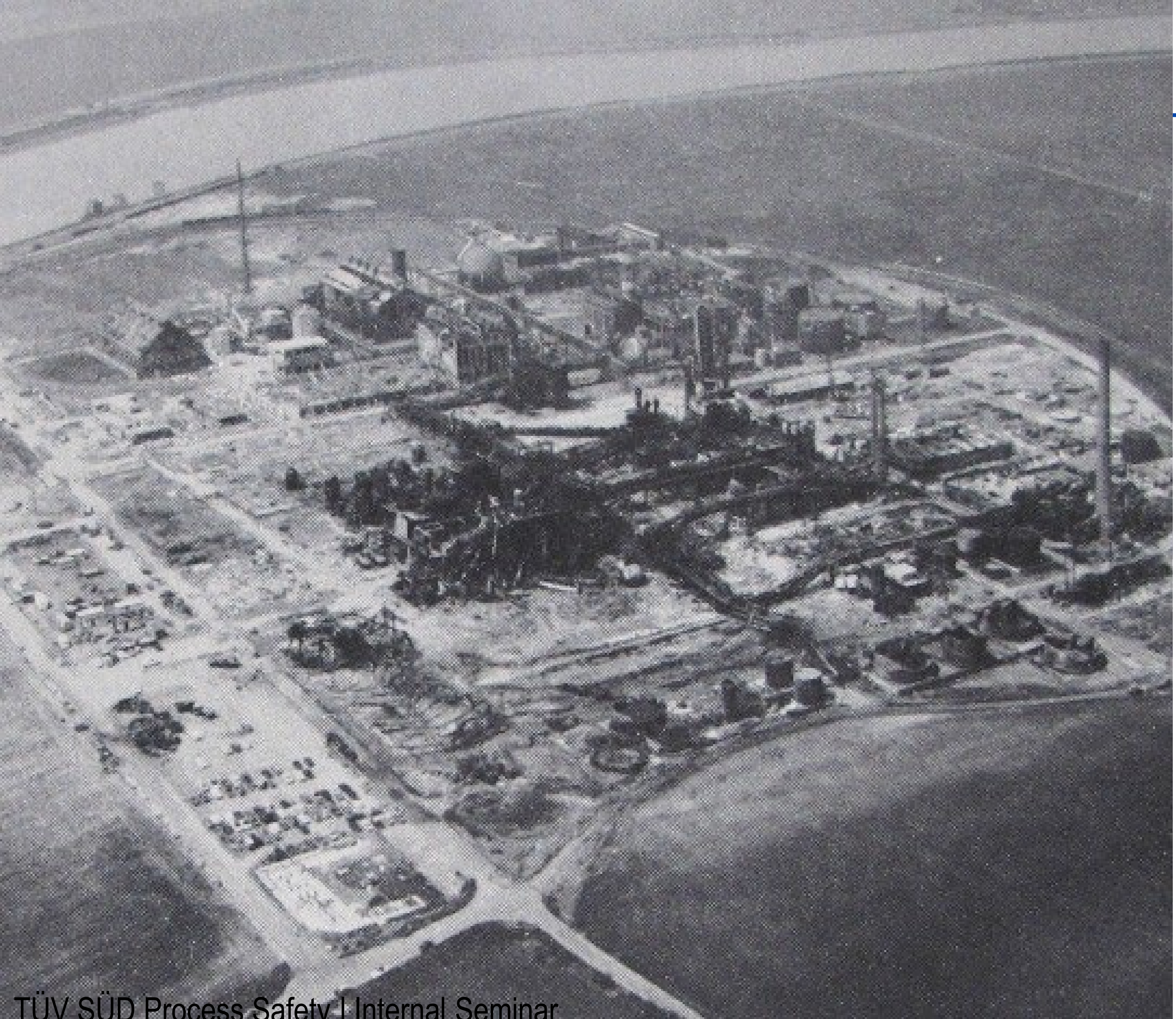
- What could be deviations that lead to fires, explosions, and accidental chemical releases?

- Example of accidents?

Accidents

- Flixborough 1974
- Seveso 1976
- Mexico City 1984
- Bhopal 1984
- Schweizerhalle 1986
- Piper Alpha 1988
- Toulouse 2001 (AZF explosion)
- BP Texas City Refinery 2005
- Buncefield 2005
- Deepwater Horizon 2010
- Port of Tianjin 2015
- Beirut 2020
- Leverkusen 2021
- ..

Flixborough



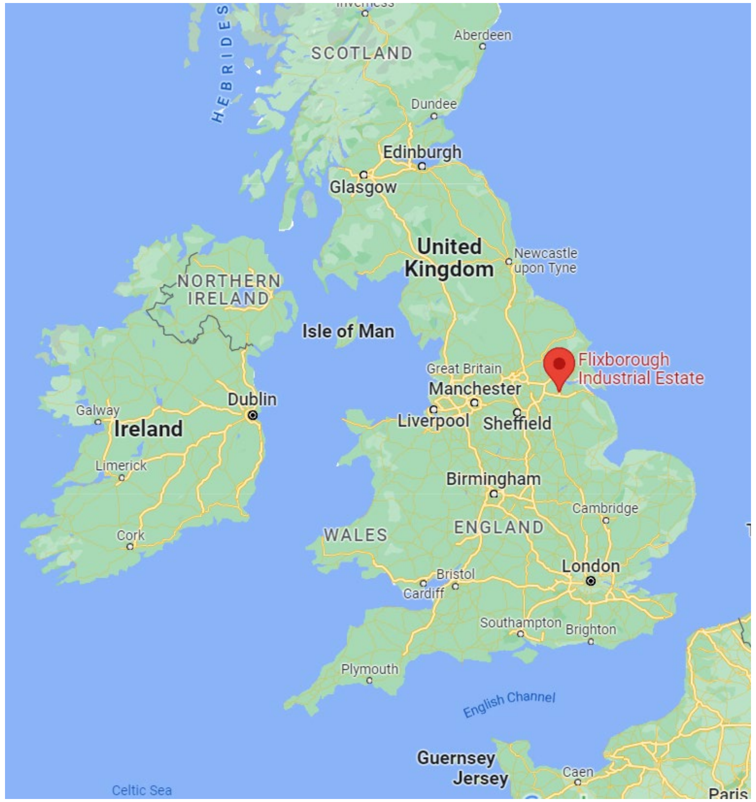
- June 1st 1974 16:58
- Killed 28 people, injured 36 onsite and > 57 off site
- Lead to development of safety and loss prevention
- Increased efforts in industry and demand from the public controls on such plants
- https://youtu.be/8A1xSCUtB-M

Flixborough (accident site)

- Farmland, 260 km north of London, 800m from villages of Flixborough and Amscott, 3-5 km from larger towns

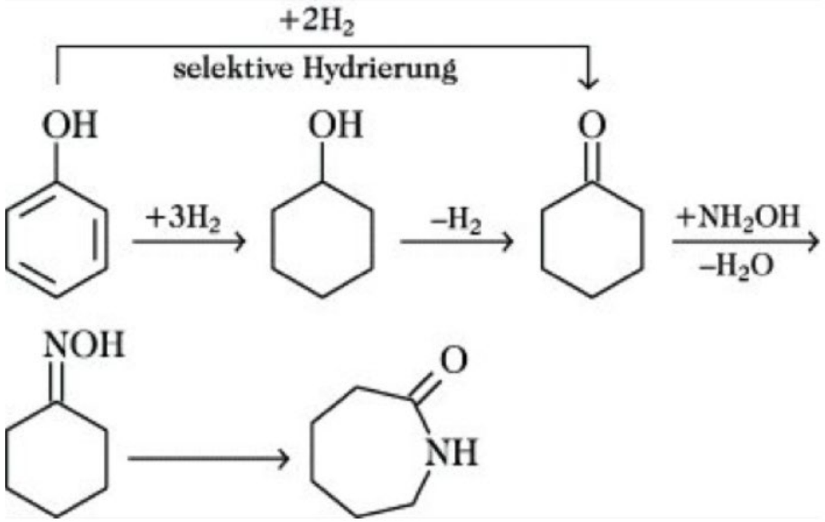
- 1974: occupied 550 people
- Plant built in 1938 to produce fertilizer
- 1964 changed ownership with the aim to produce caprolactam (owned by DSM and National Coal Board (NCB))

- Produced first 20’000 t/y caprolactam by means of phenol hydrogenation (1967)
- 1972 increased capacity (70’000 t/y) with construction of a new unit: this unit uses cyclohexane oxidation

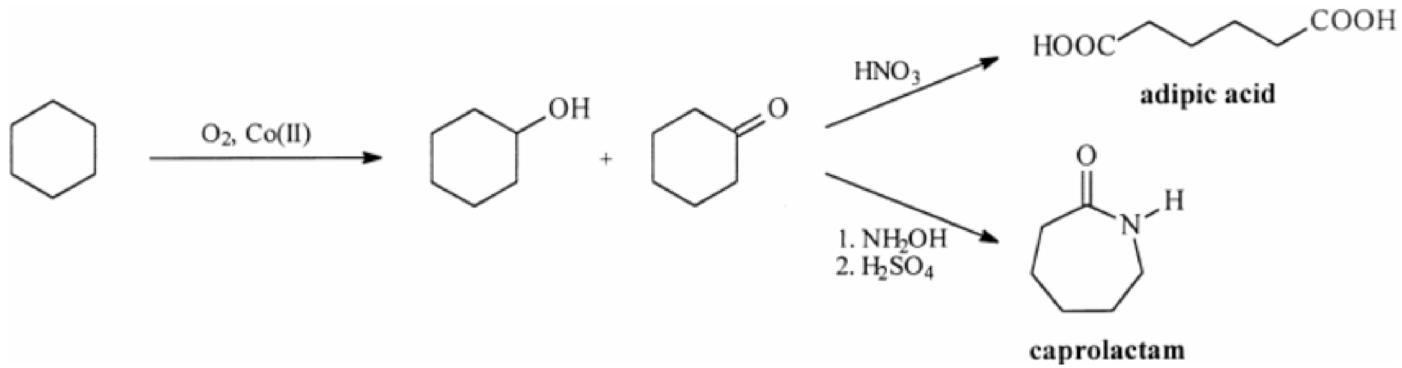


Chemistry

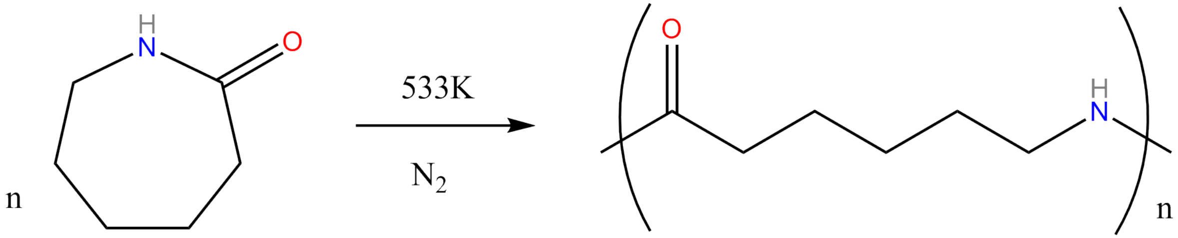
- Phenol hydrogenation:



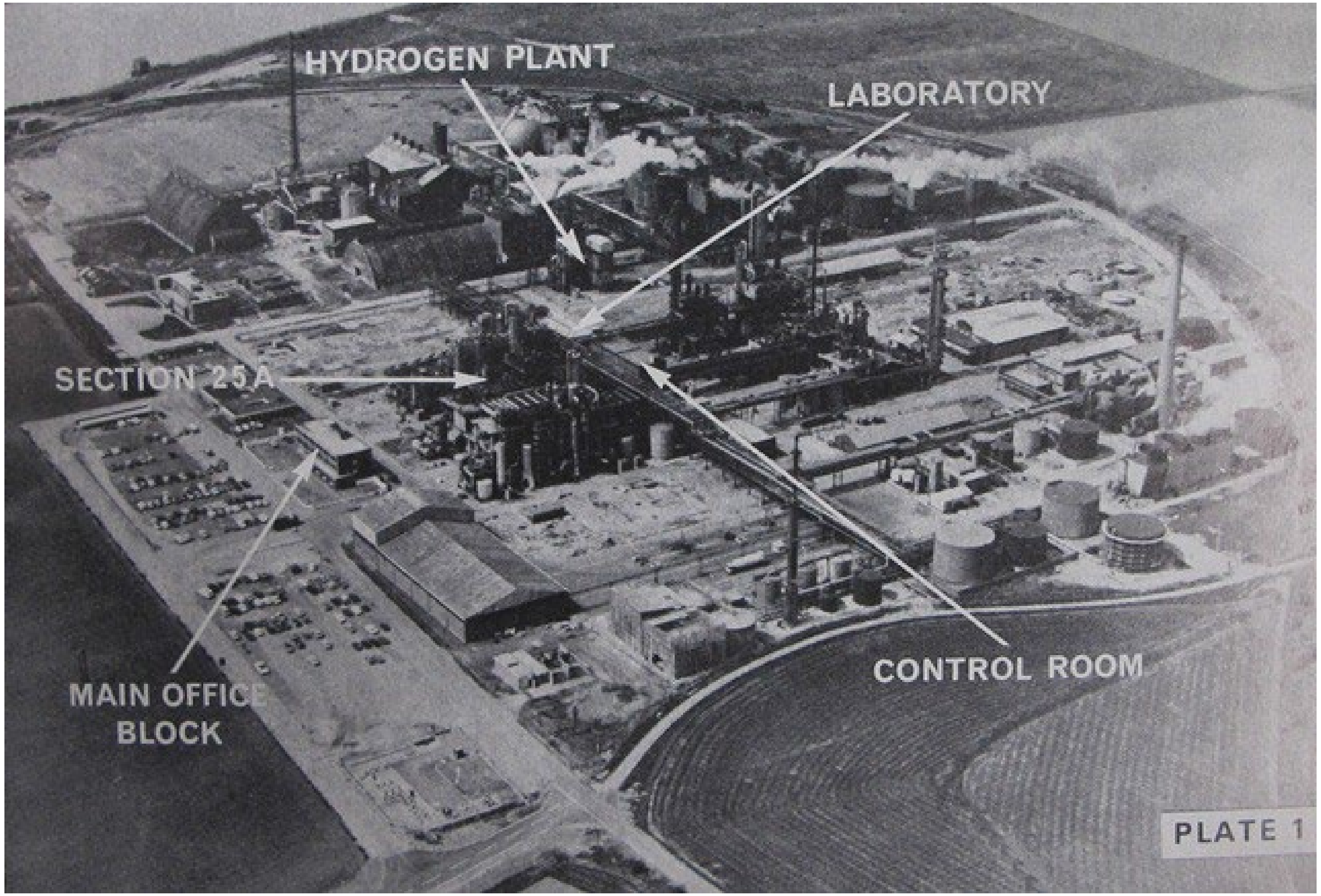
- Cyclohexane oxidation



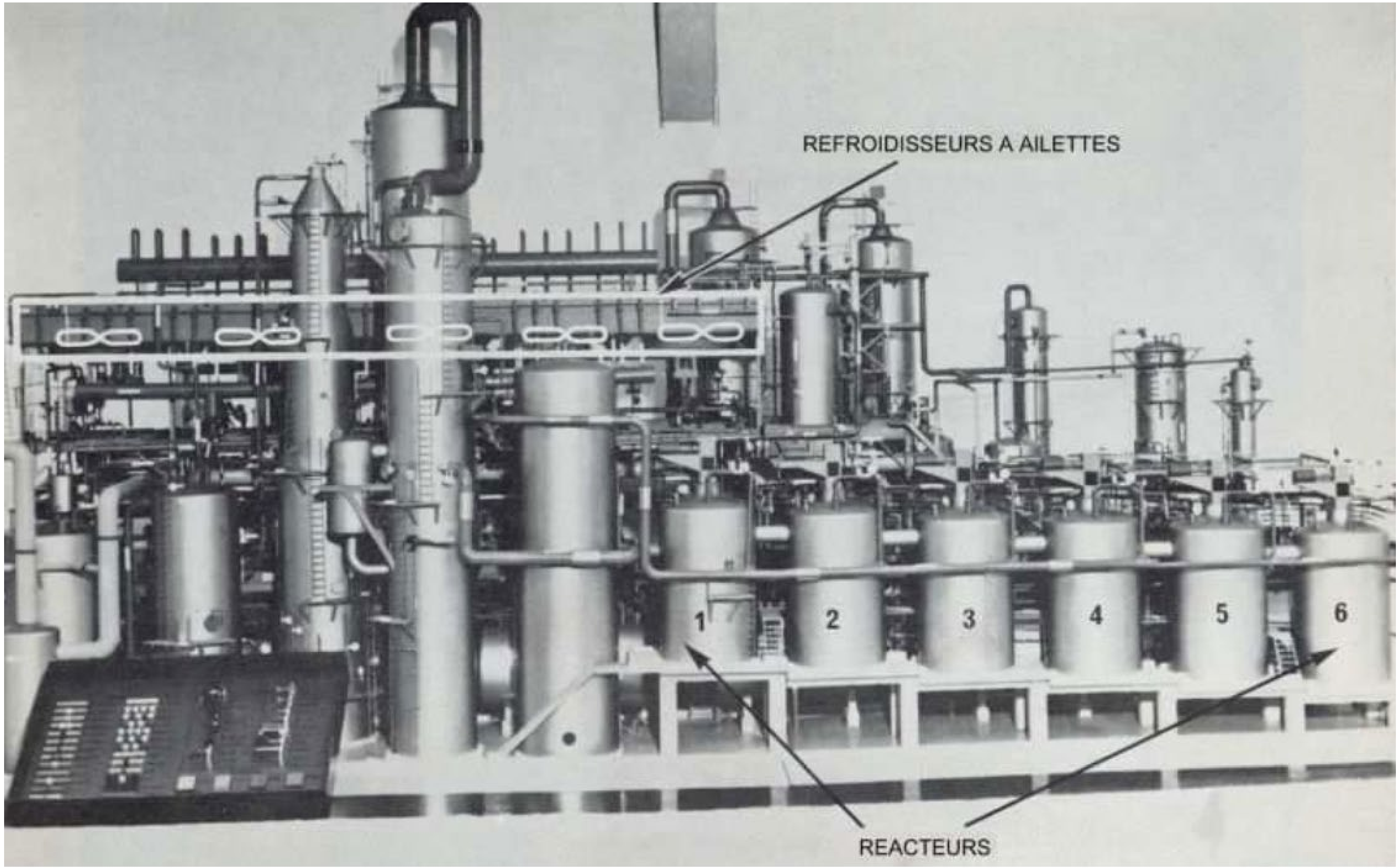
- Caprolactam use → nylon production



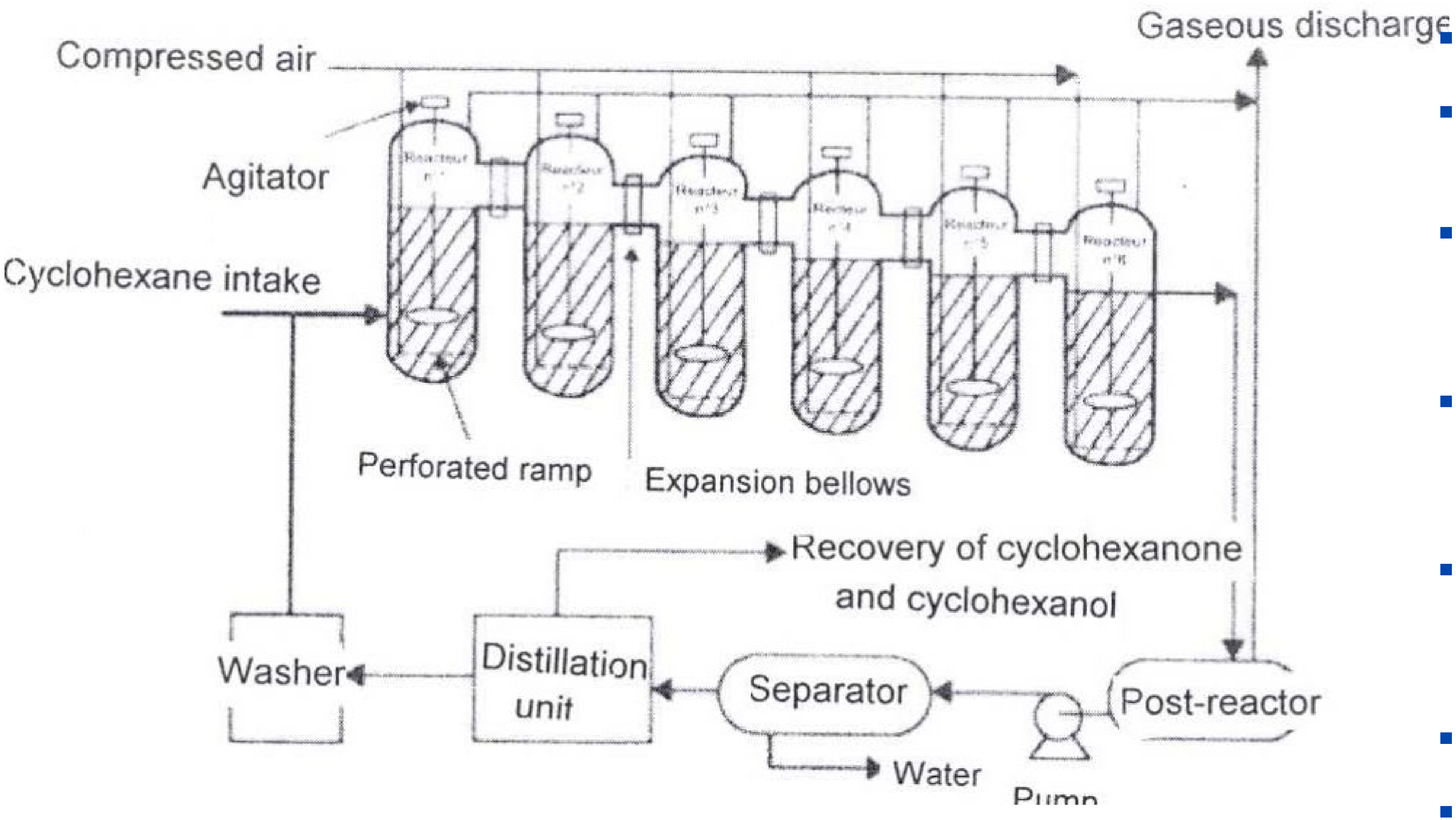
Plant layout



Process



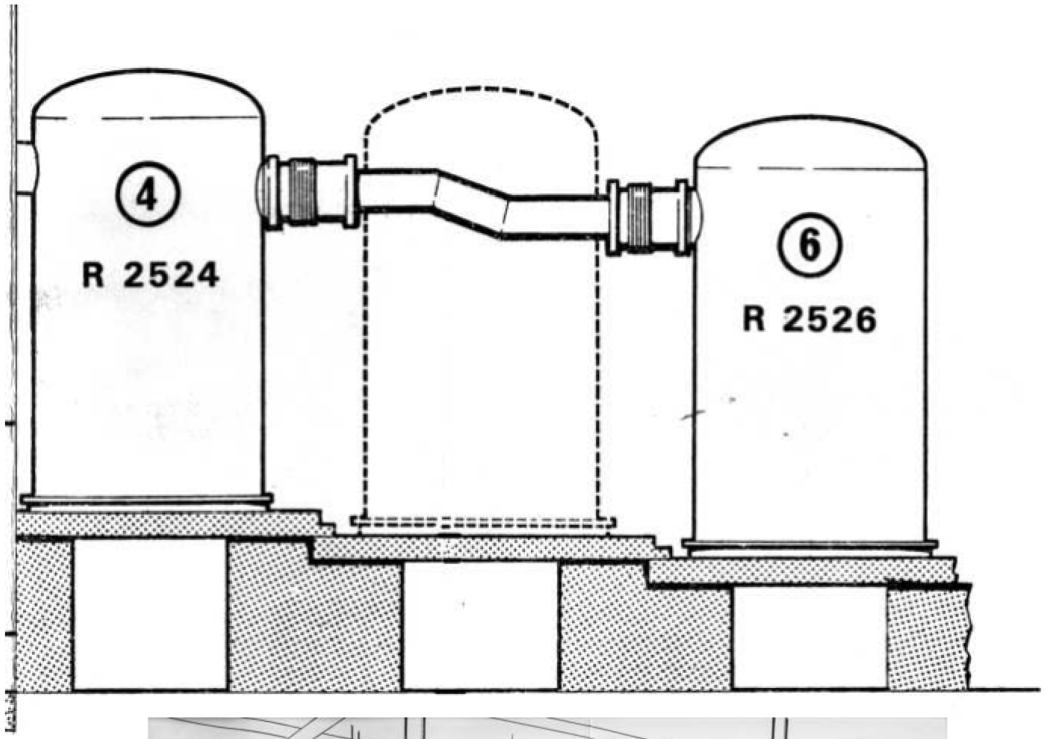
Process

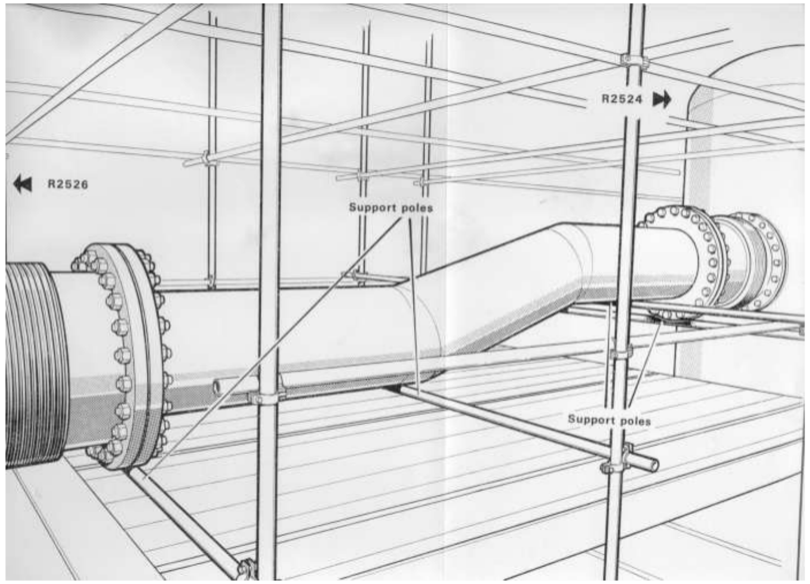


- 6 reactors of 45 m^3 each
- Compressed air injected through perforated ramp
- $25m^3$ cyclohexane in the reactors at 155°C and 8.8 bar of pressure (+ catalyst)
- Low output of cyclohexanone and cyclohexanol → recirculation of cyclohexane
- 250 -300 m^3/h liquid flow between reactors via 711 mm diameter pipes fitted with expansion bellows
- Installation inert (nitrogen)
- PRV 11 bar

The accident

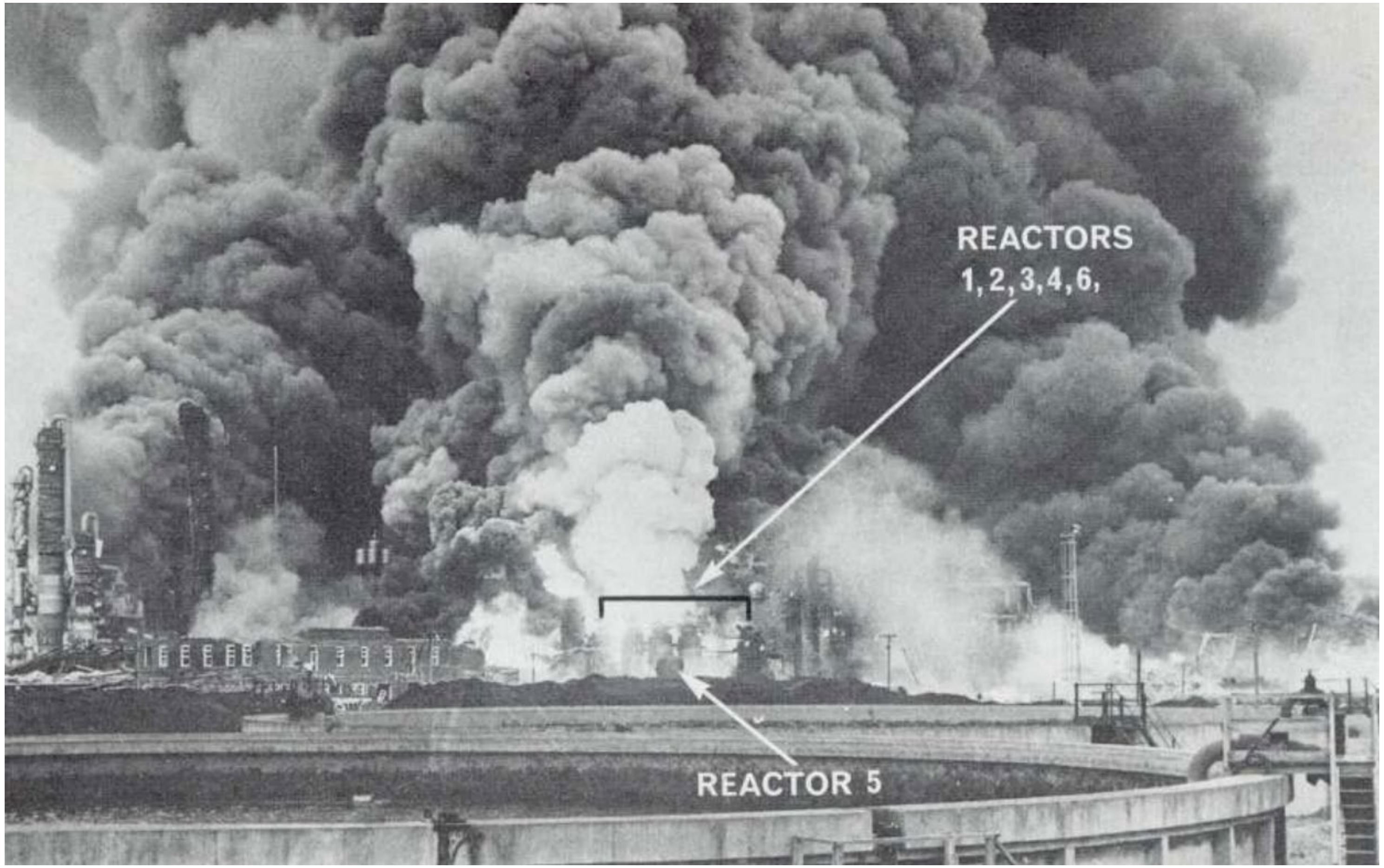
- March: difficulties
  - March 27th cyclohexane leak on reactor 5 (vertical crack)
  - March 28th crack is 2 meter long
  - Stop and inspection of reactor 5 scheduled
  - Resume production quickly → build a bypass between Reactors 4 and 6
  - Leak test on 1st of April, restart process with 508 mm elbow pipe (fabricated onsite) connecting the two expansion bellows on Reactors 4 and 6 via a plate flange. Entire assembly supported by scaffolding
  - Until May 29th installation operated without any special problem
  - May 29th: cyclohexane leak --> shut down, repair, test restart early morning 1st June
  - June 1st 4:00: new cyclohexane leak, followed by several others → installation stopped and restarted 1 hour later
  - Shortly after: new leak → stop production





The accident

- June 1st 7 am back into service but problems with T and P
- June 1st 4:53 pm deflagration
  - Noticeable 50 km away
  - Flames 70-100m high
  - Pressure of the explosion destroyed stationary fire fighting equipment
  - All building within 600m were destroyed
  - 72 individuals present on the site: 28 killed, 36 injured (lucky it was wk)
  - 1987 houses and retail businesses were damaged (72 of 79 houses in Flixborough, 73 from 77 in Amscott, 644 of 756 in Burton)
  - Large piece of equipment found 6 km away, debris up to 32 km away



The causes of the accident

- Difficult to determine exactly because
  - absence of witnesses (all staff present in the control room died in the accident)
  - Destruction of all unit instrumentation
- According to the investigation report:
  - Failure at the level of the two connecting bellows on the temporary pipe placed between reactor 4 and reactor 6
  - Massive leak of hot and pressurized cyclohexane
  - Release of of 40-60 ton cloud of cyclohexane ignited 25 to 35 seconds later (ignition: reforming tower of the hydrogen unit)
  - Cause: amateurism by removing reactor 5 and constructing bypass.
    - No verification (only leak test with nitrogen 9 bar)
    - No calculation, no drawings
    - No reference to standard or guidelines
    - Nothing to prevent movements of the bypass (scaffolding inadequate)
      - No account of turning moment that would be placed on the pipe due to flow of fluid and proces P
      - No account for sehar forces on the bellows (not designed for that)
    - Leak on reactor 5 not investigated
  - Other causes also described in literature

What would you change to avoid this?

The context

- New caprolactam unit at full capacity since beginning of 1974
  - technical and labour problems before:
    - miner strikes, only 3 day of power per week (November 1973 to January)
    - Plant can’t adapt → work on backup energy generation → reactor agitation turned off
    - Agitation of reactor 4 deteriorated and was not put back on
  - Beginning of 1974 plant produced 47’000 tones/year → prospect of financial loss →ask Government’s pricing commission to authorize 48% price increase but was refused
  - Considerable economic and commercial pressure
- Personnel
  - Plant maintenance engineer post vacant since beginning of 1974
    - Former maintenance engineer’s subordinate (technician with 10 years experience in electricity and 4 years in maintenance)
    - Mechanical engineering competence in the plant low (Director and Technical Director are chemists/chemicl engineers, no qualification in mechanical engineering)

The actions taken and lessons learnt

- Need to strengthen public authority control → Health and Safety at Work Act was introduced in the UK
- Together with Seveso accident in 1976 led to the «Seveso directive»
- 18 people died in the control room → carefully design the layout and location of control rooms (occupied building)
- Limit the hazard potential onsite
- Any modification, no matter how small, can engender risk –> MOC
- Preventive maintenance preferable to emergency intervention
- Management of feedback (cracks in other reactors reported but escaped investigation) → safety culture
- Competence from staff crucial (only a well-skilled and experienced workforce will be able to recognize precursor signals of an accident → competence and organisational changes
- Personnel should not be faced with having to chose between safety and productivity. Goal of a company must be to produce under safe conditions

The actions taken and lessons learnt

- Management of change
  - Piper Alpha (1988)

- Unconfined vapour cloud explosions have to be better understood
  - Developpment of TN
  - TNO model (rather than only TNT equivalents)
  - Buncefield 2005, BP Texas City refinery (2005) ….

- Occupational buildings
  - Guidance on location and design of occupied buildings
  - Hickson and Welch (1992), BP Texas City refinery (2005)

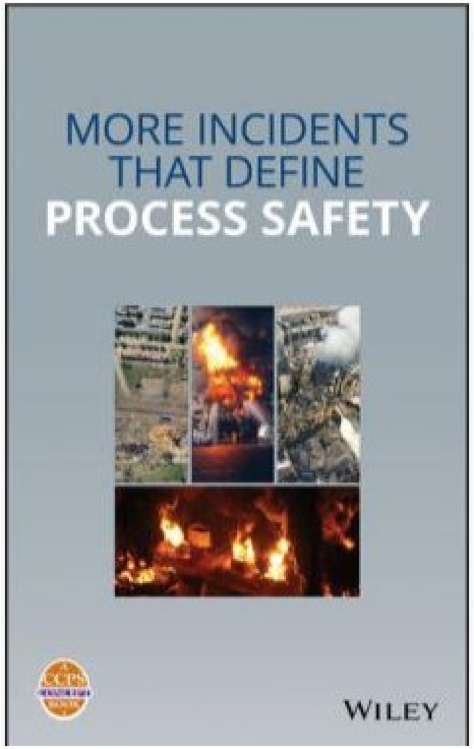
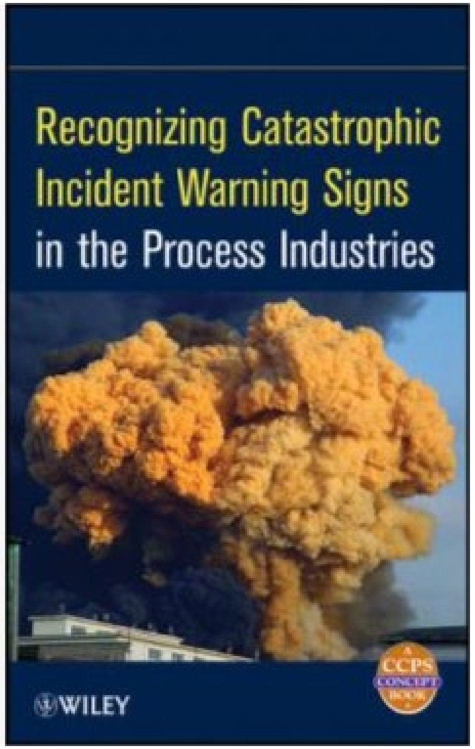
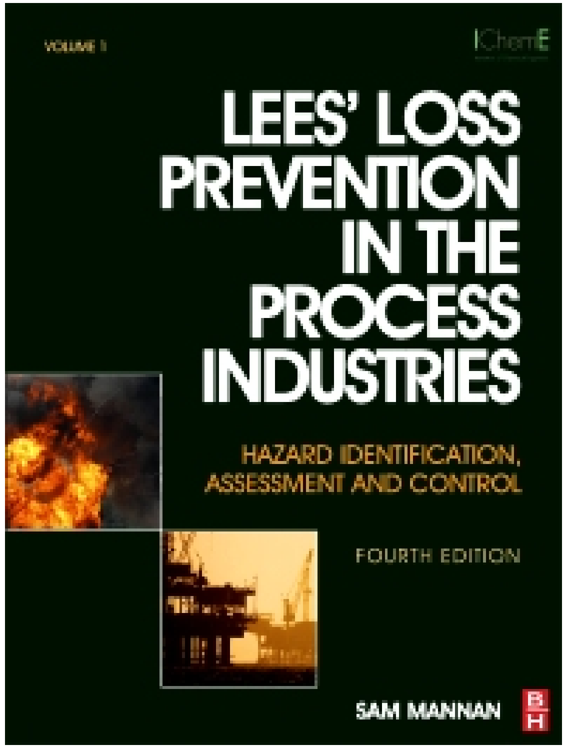
- Qualification, competence is key
  - Piper Alpha Explosion, Buncefield, BP Texas City…

- Safety culture
  - Need mature safety culture in the company when dealing with high hazard operations

Databases for accidents

- CSB: chemical safety board: https://www.csb.gov/
- ARIA: French database (but also site in english): https://www.aria.developpement-durable.gouv.fr/?lang=en
- AICHE: database, but nead AICHE access: https://www.aiche.org/ccps/resources/psid-process-safety-incident-database
- European database https://minerva.jrc.ec.europa.eu/en/minerva --> look into emars and also links to other databases
- Zema (German database): https://www.infosis.uba.de/index.php/en/site/13947/zema/index.html
- IOGP (association of oil&gas producers): https://safetyzone.iogp.org/Main.asp
- Japanse database (looks like not updated anymore (up to ~ 2003): http://www.sozogaku.com/fkd/en/
- BGRCI (need to have access code: ask Thomas): https://www.bgrci.de/ereignisinformationssystem/
- OSHA: https://www.osha.gov/pls/imis/accidentsearch.html
- Processnet: https://processnet.org/ereignisdb.html
- Factsonline (some info free other over licence): http://www.factsonline.nl/
- International disaster database: some infos: https://www.emdat.be/
- More historical: http://explosionconsultancy.co.uk/
- HSE: https://www.hse.gov.uk/index.htm

Literature

- 
Edition 6
What Went Wrong?
Case Histories of Process Plant Disasters and How They Could Have Been Avoided
IChemE

MORE INCIDENTS THAT DEFINE PROCESS SAFETY
WILEY

Recognizing Catastrophic Incident Warning Signs in the Process Industries
WILEY
CCPS CONCEPT BOOK

VOLUME 1
IChemE
LEES' LOSS PREVENTION IN THE PROCESS INDUSTRIES
HAZARD IDENTIFICATION, ASSESSMENT AND CONTROL
FOURTH EDITION
SAM MANNAN

Accidents

- Flixborough 1974
- Seveso 1976
- Mexico City 1984
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- Port of Tianjin 2015
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Process Safety

- Process safety programs focus on
  - Design and engineering of facilities
  - Hazard assessments
  - Management of change
  - Inspection
  - Testing
  - Maintenance of equipment
  - Effective alarms
  - Effective process control
  - Procedures
  - Training of personnel
  - Human factors

Themes of the lecture

1. Introduction
2. Thermal risks assessment
3. Calorimetric methods
4. Decomposition reactions
5. Heat accumulation conditions and Autocatalytic reactions
6. Mastering exothermal reactions
7. Risk reducing measures
8. Gas/Vapor and Dust Explosions

Objectives of the lecture on Chemical Process Safety

• Mastering	• Assessment techniques for thermal risks: desired and decomposition reactions
• Basic knowledge	• Allowing the selection and design of risk reduction measures • Explosion protection

Incident - Case Histories

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Case Histories

- Max 7 minutes per group

Questions:

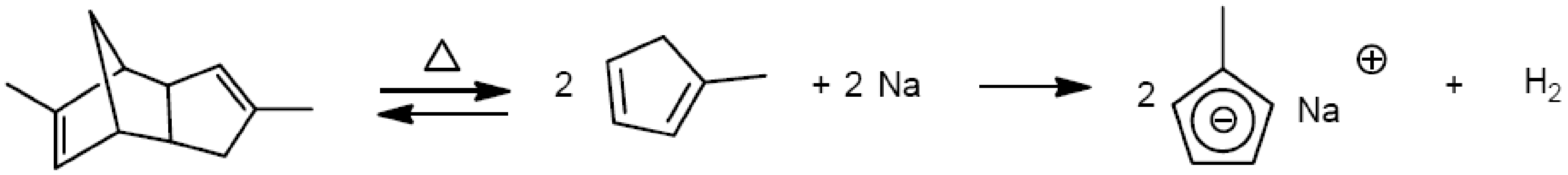
1. *What is the chain of event and what are the causes for the incident?*
2. *Which barriers failed (technical, organizational?) Why did the accident not happen before?*
3. *What is the origin for the released energy (the consequences)?*
4. *What appropriate risk reducing measures (barriers) would be required to restart the production? How would they hinder the chain of event of the incident? What type (technical, organizational) of barriers are those?*
5. *What are the potential problems linked with these measures?*

T2 Laboratories

- Video (https://www.youtube.com/watch?v=C561PCq5E1g&feature=youtu.be)

T2 Laboratories - Chemistry

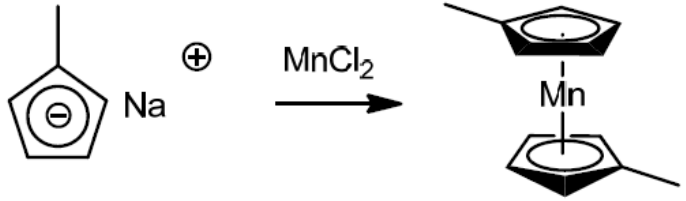
- Metalation Step of MCMT (Methylcyclopentadienyl Manganese Tricarbonyl) process



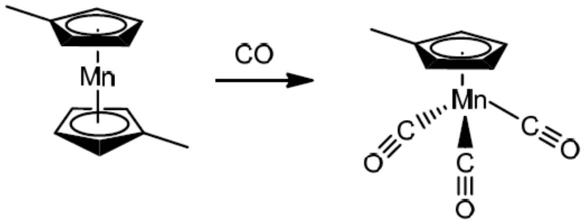
- Reactants: MCPD (Methyl cyclo pentadiene)
  Sodium Molten
- Products: NaMCPD (Natrium methyl cyclo pentadiene)
  H2 Hydrogene
- Solvent: Diglyme (Diethylene glycol diethyl ether)

T2 Laboratories - Chemistry

- Substitution



- Carbonylation



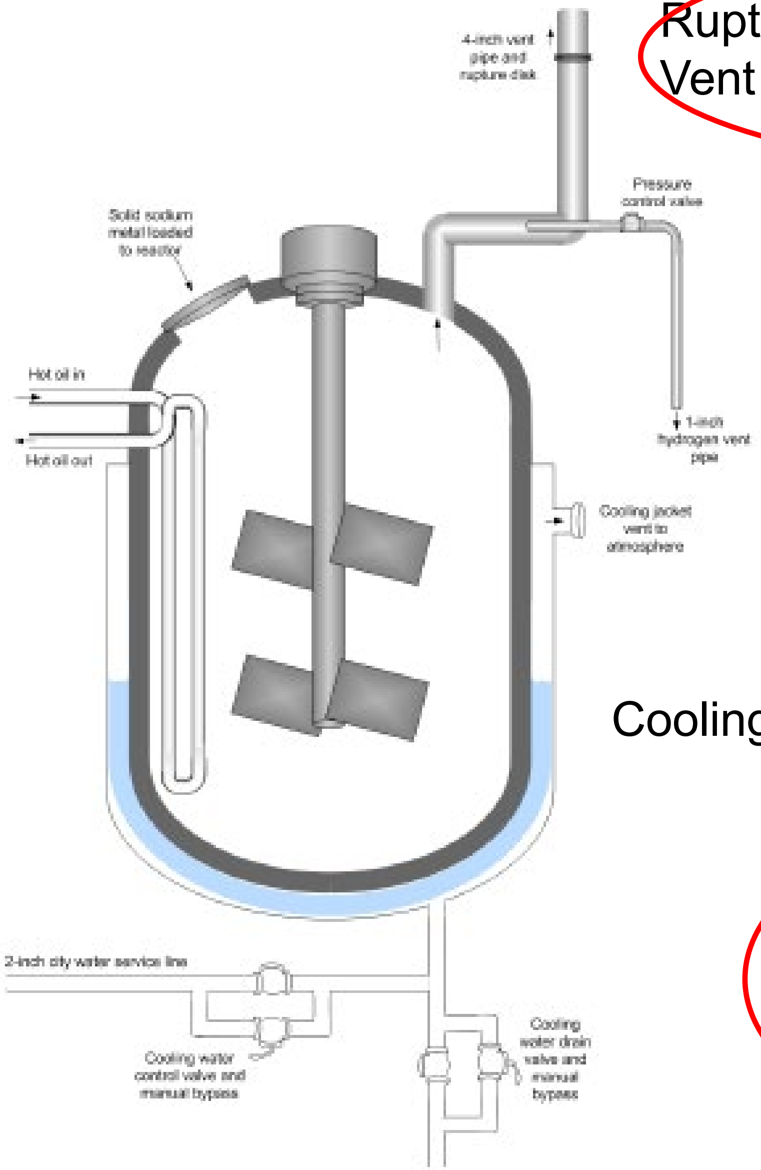
T2 Laboratories – Summary of manufacturing procedure

- Feed of MCPD dimer and Diglyme
- Addition of sodium metal (15 cm opening)
- Heating with oil at 182°C
- Reactor pressure control set to 3.45 barg
- Operator starts agitation at 99°C
- Operator stopps Heating at 149°C
- Operator starts Cooling at 182°C

T2 Laboratories - Reactor

Rupture disk (Pset = 28 barg (400 psig))
Vent pipe (∅ 10cm)

Heating
(∅ 8cm)



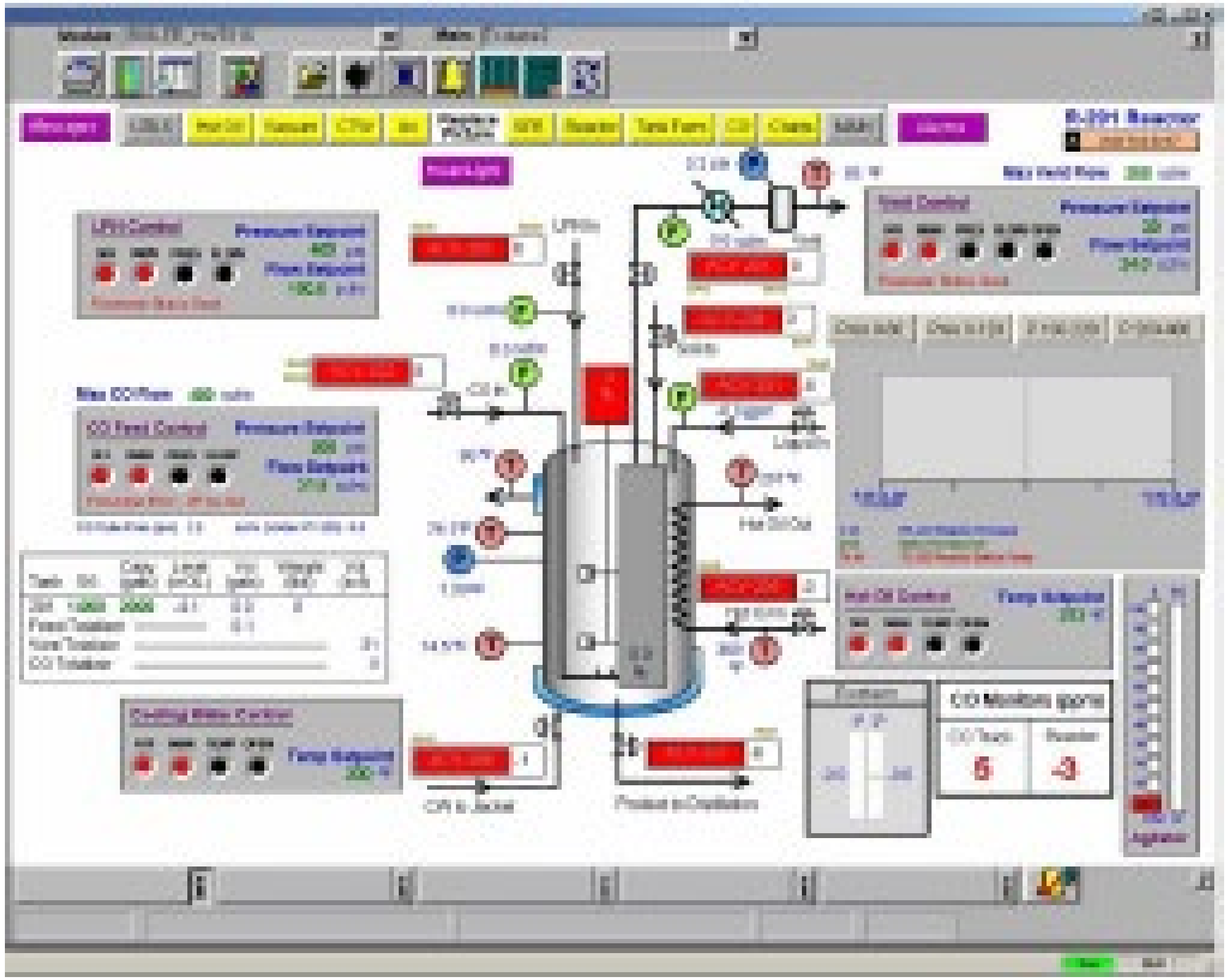
H2-Venting (Pressure controlled; ∅ 3cm)

Cooling jacket

$V = 10\ m^3$
P_{Design} = 83 barg (1200 psig)
MAWP = 41 barg (600 psig)

T2 Laboratories – Process Control

- Batch-Process



T2-Laboratories - Consequences

- Energy: 1400 lbs TNT eq. = 636 kg TNT eq.

Explosion on 19. December 2007, killed 4 people and injured 32. Destroyed several nearby businesses

Process safety

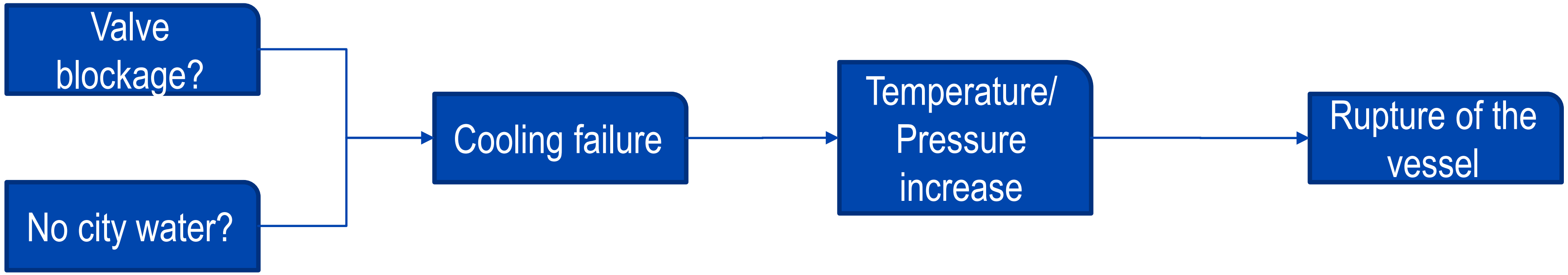
- Causes for fires, explosions, and accidental chemical releases?

T2-Laboratories

1. *What is the chain of event and what are the causes for the incident?*
2. *Which barriers failed (technical, organizational?) Why did the accident not happen before?*
3. *What is the origin for the released energy (the consequences)?*
4. *What appropriate risk reducing measures (barriers) would be required to restart the production? How would they hinder the chain of event of the incident? What type (technical, organizational) of barriers are those?*
5. *What are the potential problems linked with these measures?*

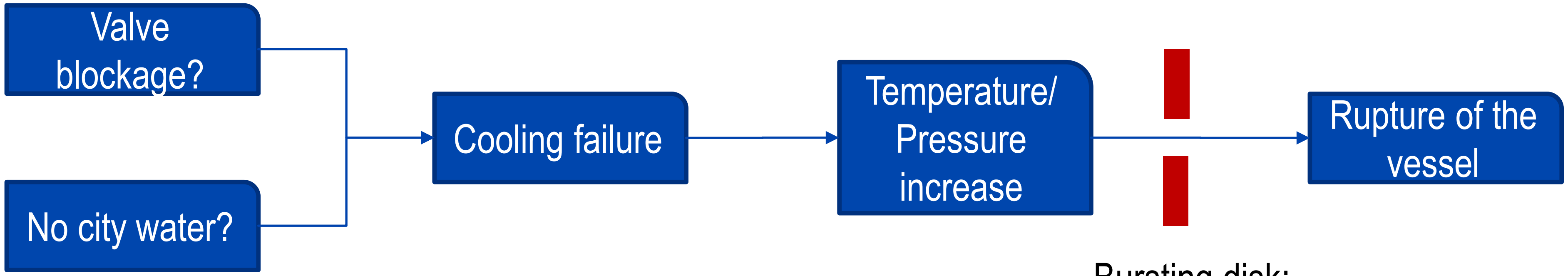
T2-Laboratories

1. *What is the chain of event and what are the causes for the incident?*



T2-Laboratories

2. *Which barriers failed (technical, organizational?) Why did the accident not happen before?*



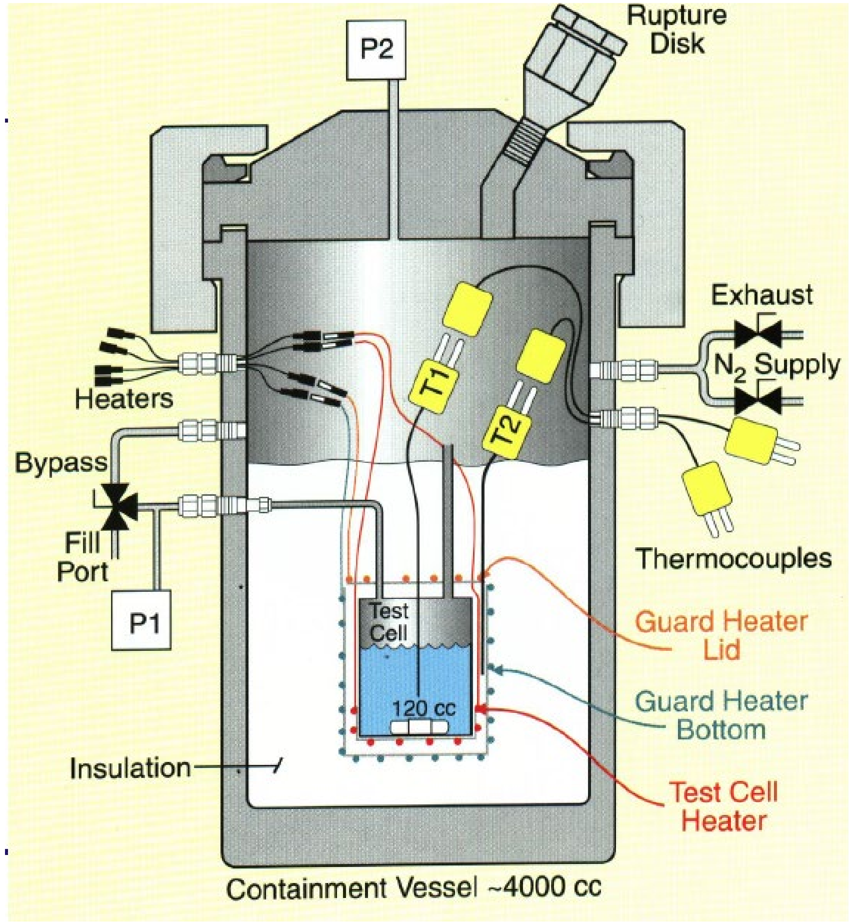
Bursting disk:
Design (size, opening pressure) not appropriate
Technical failure, human failure (engineering)

T2-Laboratories

3. What is the origin for the released energy (the consequences)?

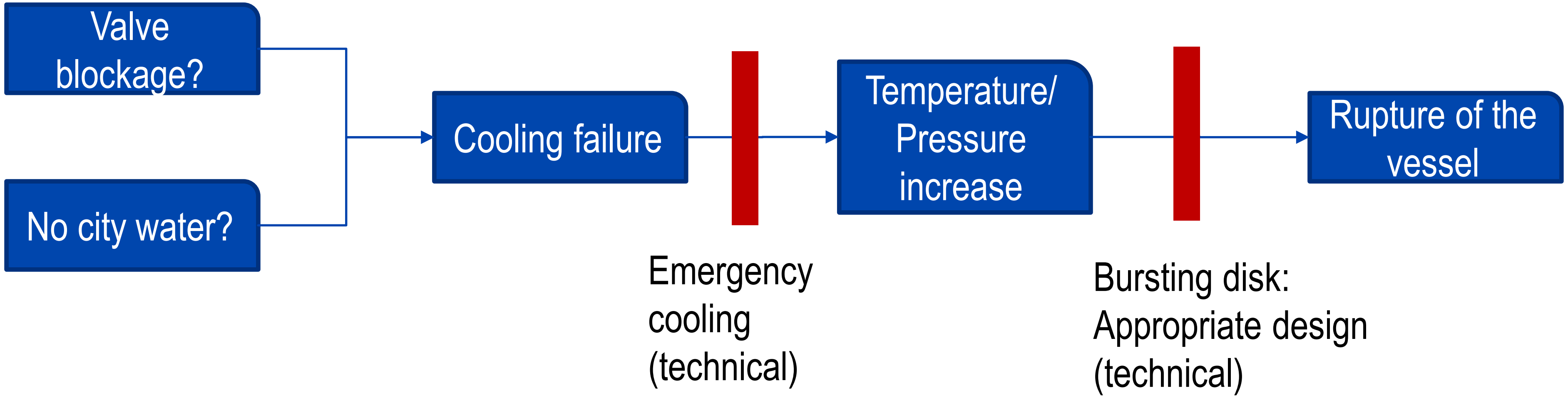
- 2 Exothermal effects observed:
  - 1st from ca. 177°C (desired reaction)
  - 2nd from ca. 199°C (secondary reaction: Na with solvent)

- Temperature and pressure increase rates of 2nd reaction:
  - dP/dt = 37 bar/s
  - dT/dt = 22°C/s



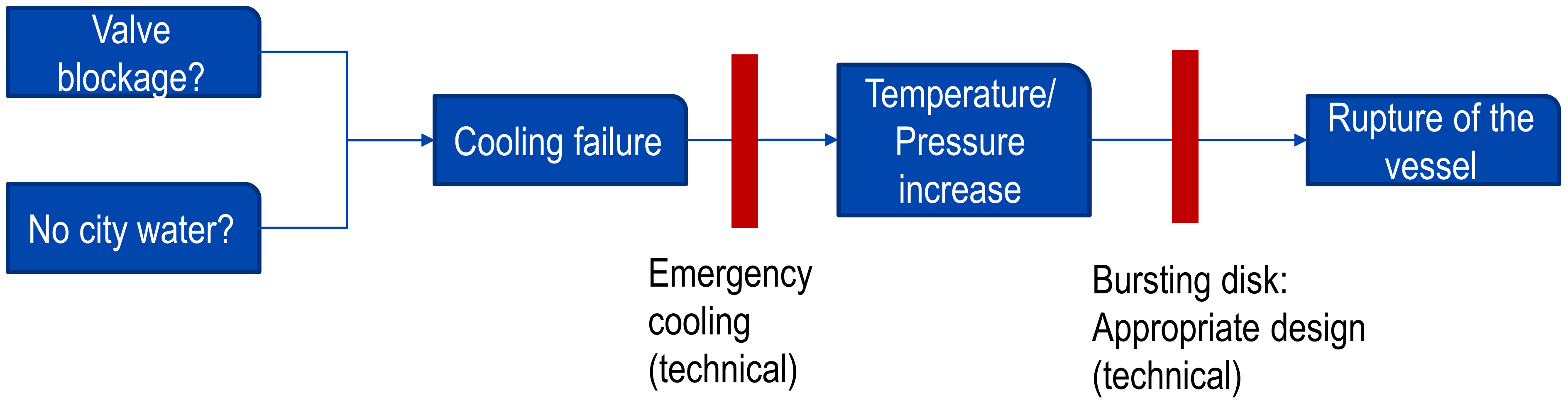
T2-Laboratories

4. *What appropriate risk reducing measures (barriers) would be required to restart the production? How would they hinder the chain of event of the incident? What type (technical, organizational) of barriers are those?*



T2-Laboratories

5. *What are the potential problems linked with these measures?*



CCPS Risk based Process Safety

- Commit to Process Safety
  - Process Safety Culture
  - Compliance with Standards
  - Process Safety Competency
  - Workforce Involvement
  - Stakeholder Outreach
- Understand Hazards and Risk
  - Process Knowledge Management
  - Hazard Identification and Risk Analysis
- Manage Risk
  - Operating Procedures
  - Safe Work Practices
  - Asset Integrity and Reliability
  - Contractor Management
  - Training and Performance Assurance
  - Management of Change
  - Operation Readiness
  - Conduct of operations
  - Emergency Management
- Learn from Experience
  - Incident Investigations
  - Measurement and Metrics
  - Auditing
  - Management Review and Continuous Improvement

A few definitions

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Hazard / Risk

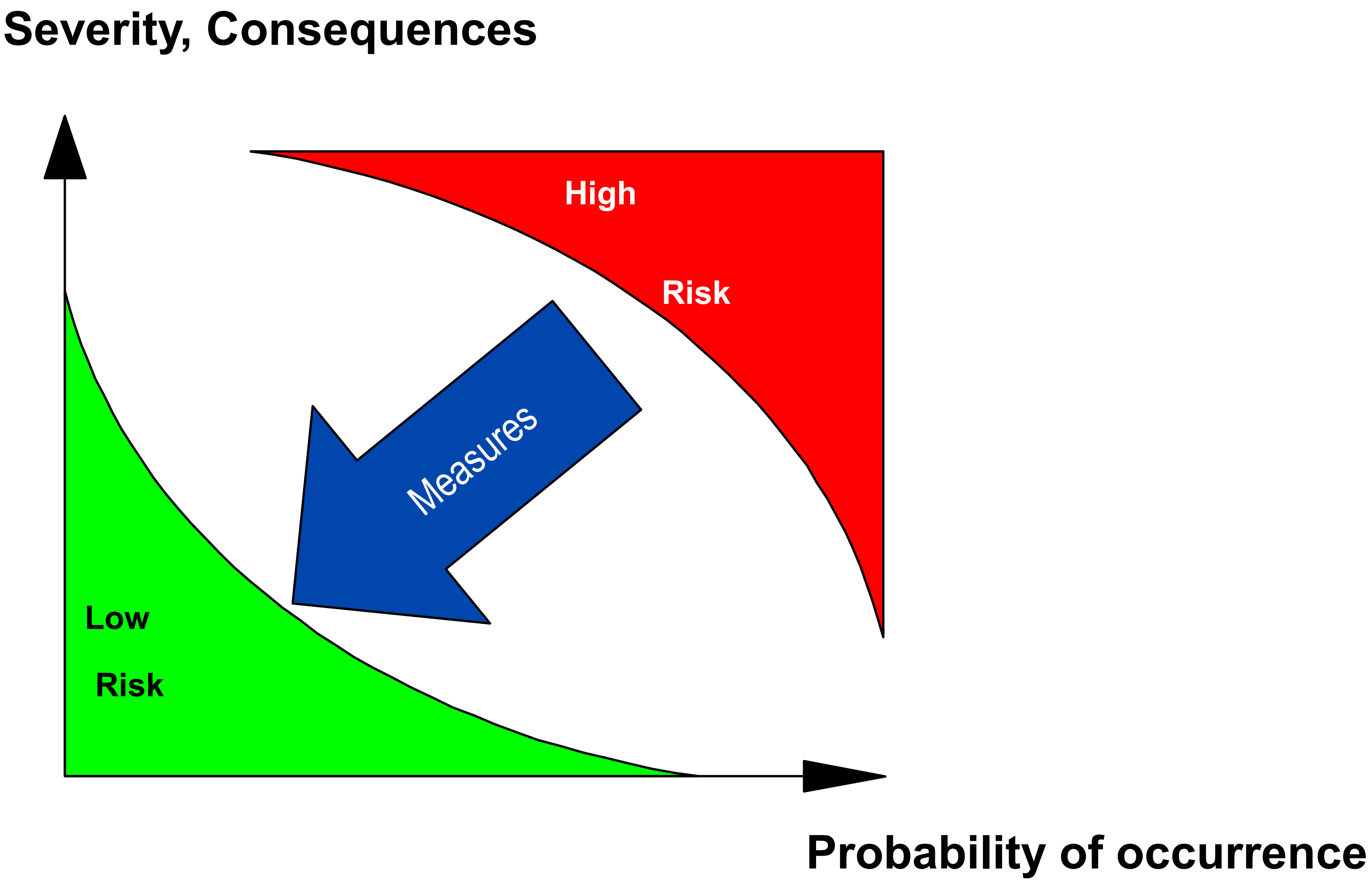
- Hazard (EFCE)
  Situation presenting a potential for causing harm to human beings, environment or goods.

- Risk (EFCE)
  A measure of the loss potential for human beings, environment or goods in terms of severity and probability.

  Risk= Severity x Probability

- https://www.youtube.com/watch?v=p4WJ3bo4r0LA

Risk Diagram



From Hazard to Incident