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Chemical Reaction Safety

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Chemical Reaction Safety

Safety and Chemical Reactions

Case Studies

Key Learning

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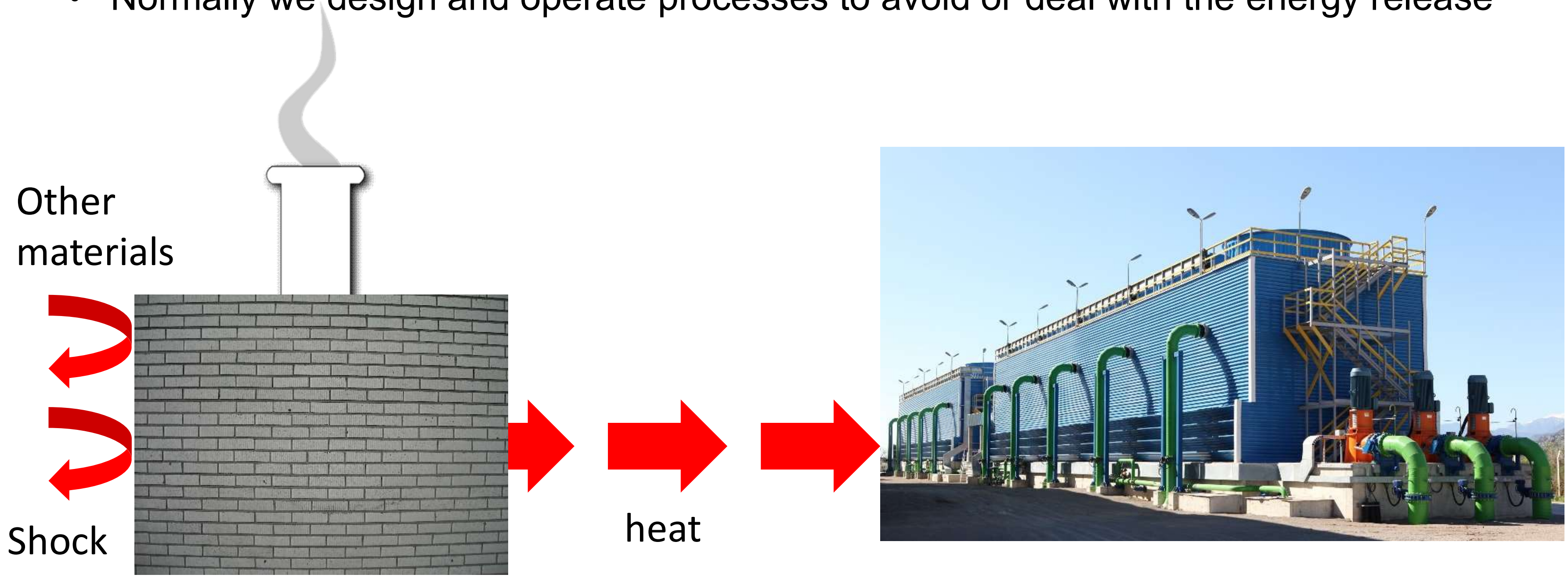
Safety and chemical reactions

- Chemicals may store a large amount of energy that can be released in a variety of ways
  - Chemical reactions often release a lot of energy as they progress
  - Accidental mixing of chemicals may give unwanted reactions
  - Some materials are shock-sensitive and may decompose violently
- Normally we design and operate processes to avoid or deal with the energy release



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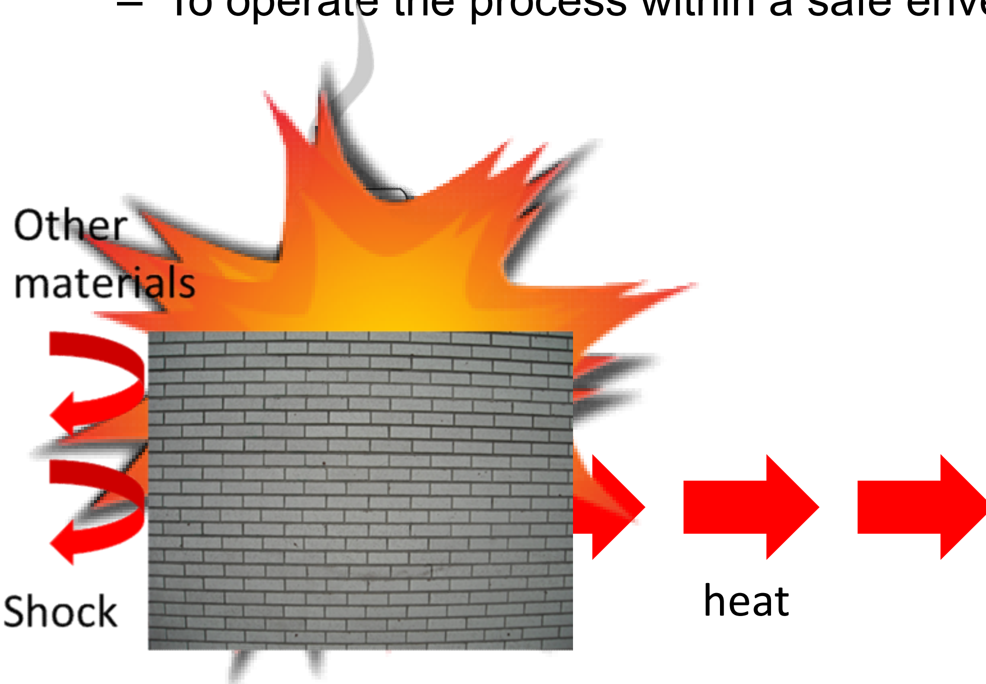
Safety problems from chemical reactions

- If we fail
  - To understand the process well enough
  - To design appropriate controls
  - To operate the process within a safe envelope



The consequences can be disastrous

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Types of reaction hazard

- Self-reactive chemicals sensitive to heat or shock
  - Heat or impact initiates rapid decomposition
- Runaway reactions
  - The rate of heat removal doesn't match generation, so the reaction accelerates and releases even more heat. Additional reactions may kick in as the temperature rises.
- Reaction between incompatible materials
  - Incompatible materials come in contact through error or equipment failure

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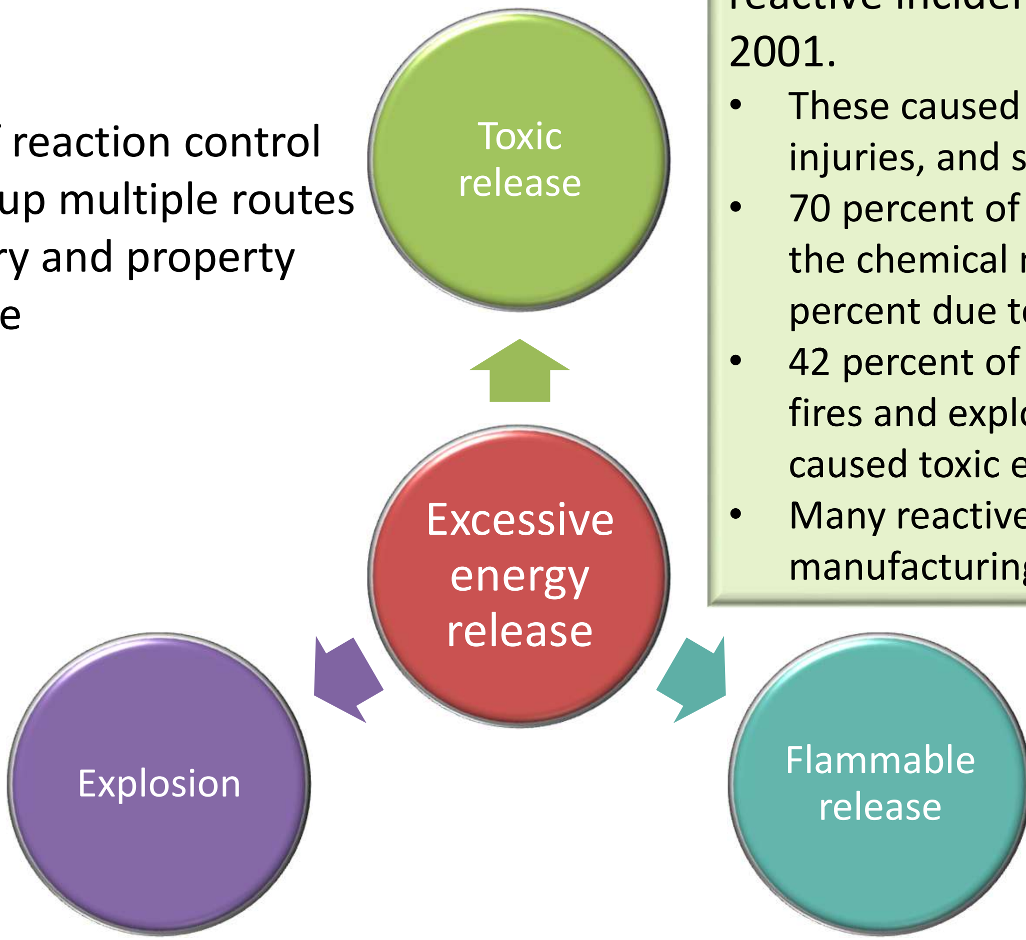
Safety problems from chemical reactions

Loss of reaction control opens up multiple routes to injury and property damage



CSB in The US looked at 167 serious reactive incidents over January 1980 - June 2001.

- These caused 108 deaths, hundreds of injuries, and significant public impacts.
- 70 percent of reactive incidents occurred in the chemical manufacturing industry, with 35 percent due to runaway reactions.
- 42 percent of reactive incidents resulted in fires and explosions, another 37 percent caused toxic emissions.
- Many reactive incidents occurred at small manufacturing sites.

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Root causes of reaction accidents

- We didn't know enough about the reactions before we operated at a dangerous scale
- We didn't implement sufficient or appropriate measures to control foreseeable problems
- We let the controls lapse and/or operated outside the safe envelope

Case studies

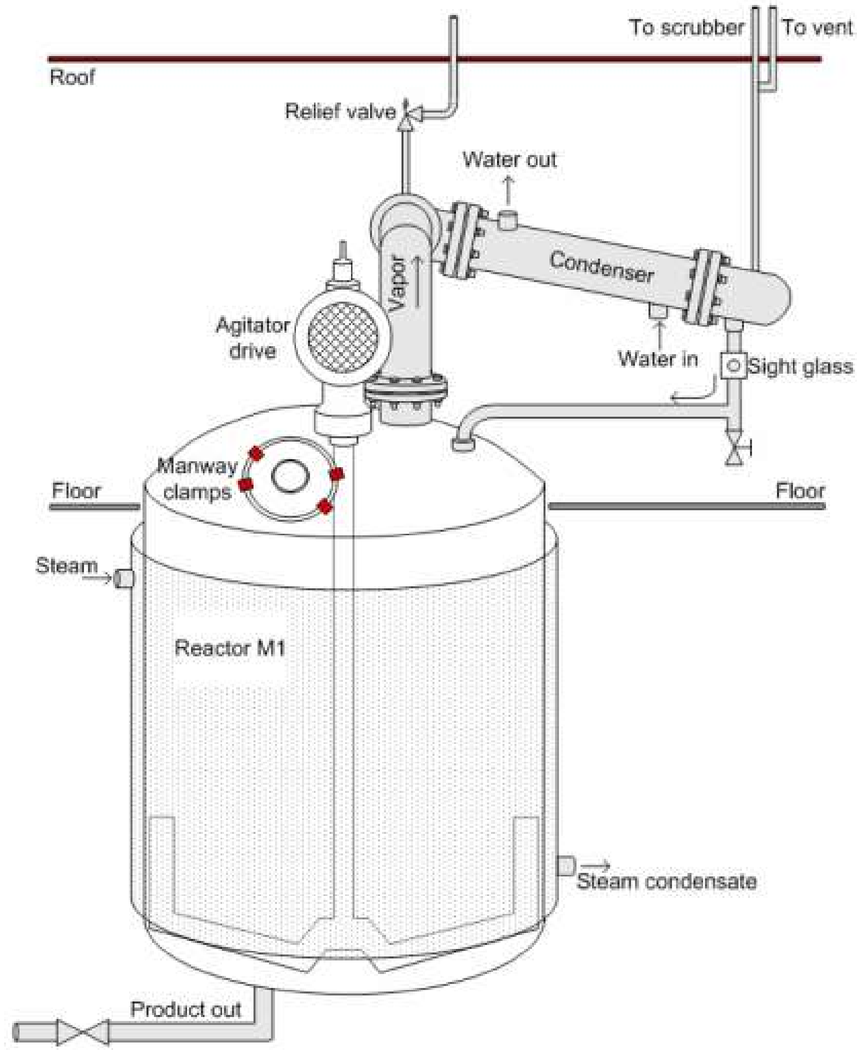
Case studies

- Many widely known examples
  - Bhopal, Seveso
- Other examples will be given here, picked because of the potential learning for Singapore
- Sources: US Chemical Safety and Hazard Investigation Board, Singapore WHSC

Ignorance is not bliss, experience is not safety…

Polymer coatings manufacture

- Synthron (Morganton, North Carolina) was a manufacturer of acrylic coatings and paint additives
- They carried our polymerization reactions in a 1,500 gallon reactor
- Solvents, acrylic monomers and initiators were mixed to various recipes
  - The reaction was heated with an initiator to start it
  - Once established, heat was removed continuously by condensing solvent/monomer vapour and returning liquid to the reactor
  - Excess heat could be removed by putting cooling water through the jacket



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Operating approach

- Small team ran the plant
  - None had any prior background in polymers
  - None in the company for more than 9 months
- No process hazard analysis or reaction risk assessment was used
- Typical process approach was to add solvent, half the monomer and initiator at the start then add rest of reactant slowly
  - Previous manager had scaled up new products based on past experience
  - Processes “evolved” by incremental changes, backing off if the condenser seemed to be struggling (flooding or pressure build-up)
- Various lax operating practices
  - Only bolting 4/18 bolts used to secure the vessel manway
  - Plant maintenance was limited
  - Poor safety culture, training, documentation and planning
  - Ineffective management of change processes

The incident

- A customer placed an order for 12% more than a standard batch
- The manager avoided making two part batches by modifying the process
  - Using extra monomer in the first charge (increase amount and conc.)
  - Reduced solvent quantity (reduced thermal mass)
  - Used more higher boiling solvent (increased reaction temperature)
- Result was to increase the peak reaction rate by a factor of 2.3
- The condenser could not cope and the pressure rapidly rose
- Solvent escaped through the inadequately sealed manhole into the factory
- Solvent ignited

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Outcome

- 1 fatality, 14 injured (2 seriously)
- Company filed for bankruptcy

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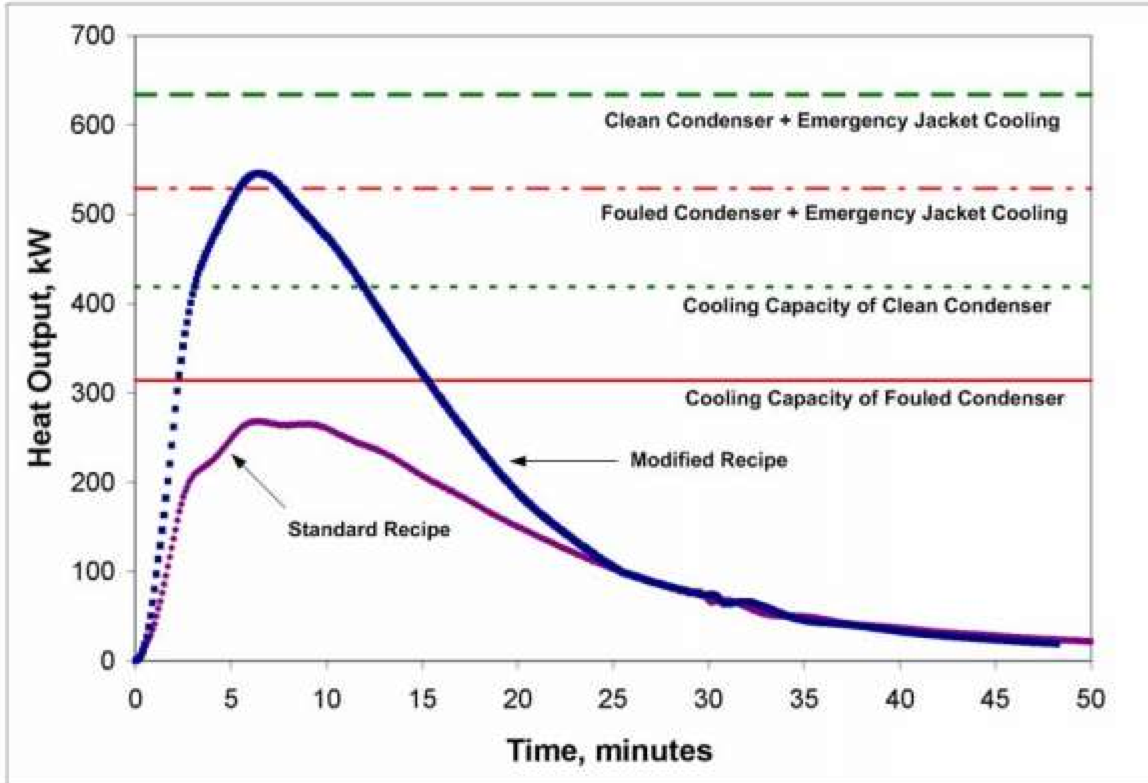
Learning from the accident

- Know your reaction and your plant
- Make sure your people, plant and methods are in good working order
- Manage change effectively



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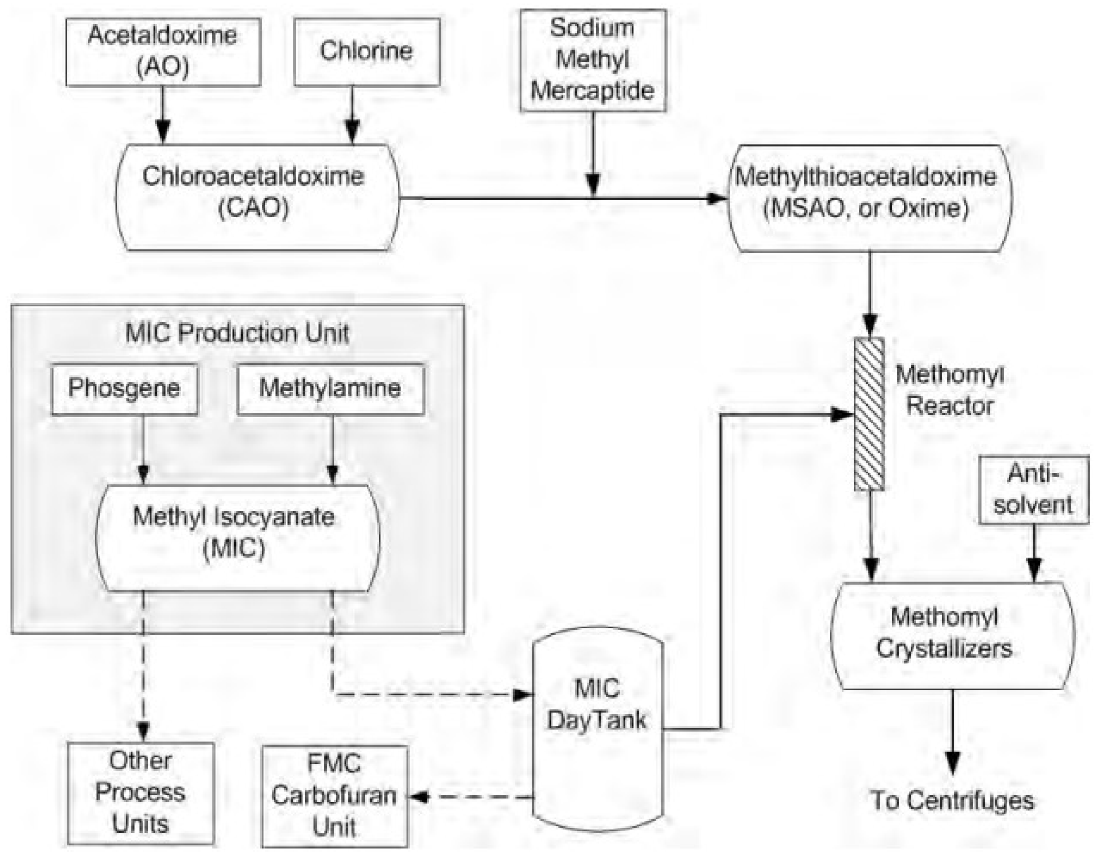
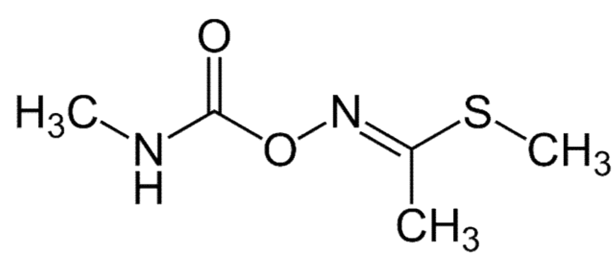
Change needs thought, and good memory…

Methomyl production

- Bayer CropScience operated a plant to manufacture Methomyl at Institute West Virginia
- Hazardous process involving several dangerous materials
  - Chlorine
  - Phosgene,
  - MIC
  - Methyl Mercaptan
- Risk of exothermic Methomyl decomposition well known and understood





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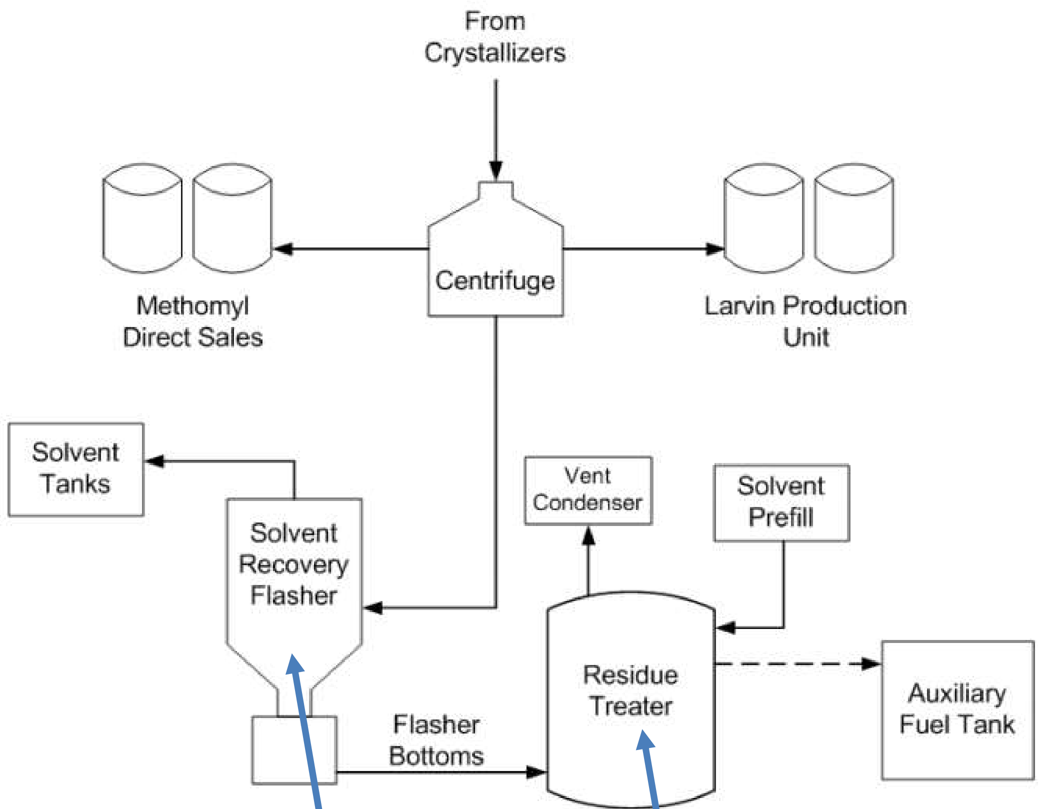
Methomyl production

- The post-filtration liquor was flashed to recover solvent
- The flasher bottoms were heated in the Residue Treater to decompose residual methomyl
  - Methomyl decomposes exothermically
  - Methomyl kept below 0.5% concentration by diluting in solvent and treated residue
  - Higher concentrations were known to generate too much heat (1% limit)
- The treated residues were used as a fuel



Should operate <80°C

Should operate >130°C

Changes in plant operations

- Various operational changes were being made or had occurred before the accident
  - Technical support for operations had been “thinned” with only one “technical adviser” covering Methomyl and another plant on day shifts
  - An ageing control system was being replaced with a modern DCS system
  - Various plant items were being replaced
- Assessment of the impact of the changes had been limited and of poor quality
  - Hazard assessment sessions had been brief and inappropriately staffed
  - Training of staff in use of the new control system had not been fully effective
  - A pre-existing culture of poor work practice had not been addressed
- The plant was being restarted

A catalogue of errors

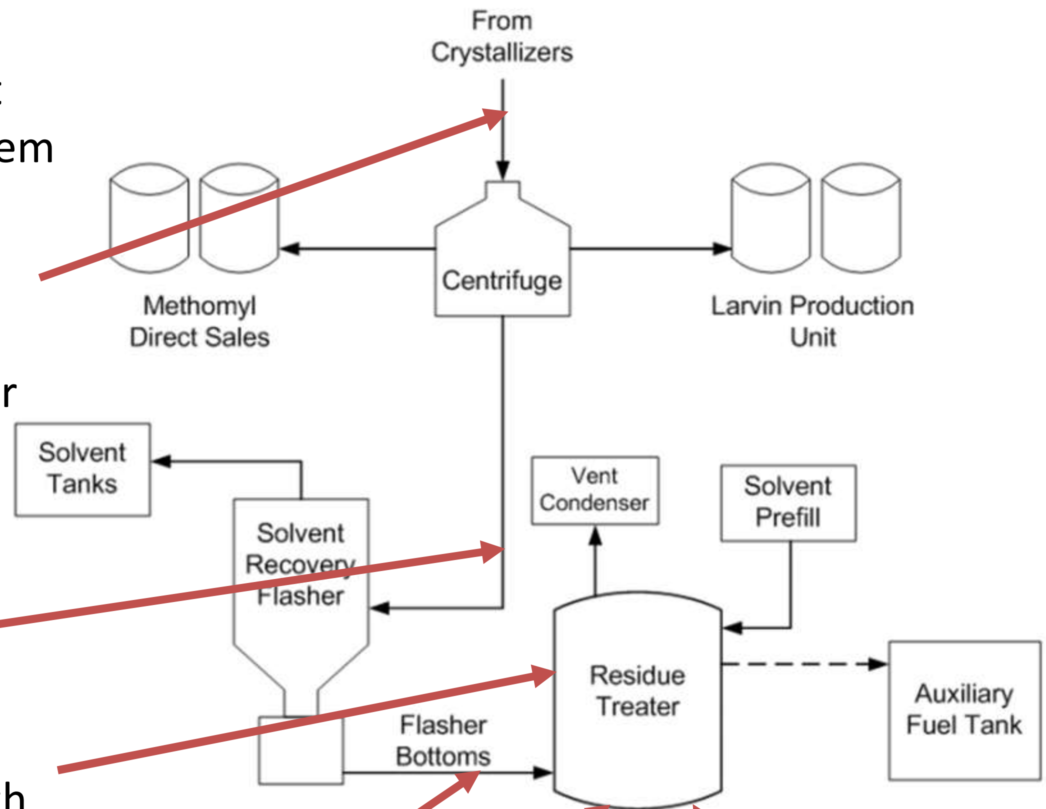
Operators were working from draft SOP not including new control system

The crystallization step failed but operators carried on.

Lab analysis of 4% Methomyl in liquor ignored in face of other problems

Liquor sent to centrifuges – and passed straight to Flasher

Residue Treater not pre-charged with solvent or pre-heated enough



Methomyl content of Flasher residue 40%, not 22%

Samples not taken to test for Methomyl content

Trips defeated to allow transfer into Cold Treater (65°C, not 130°C), and with low recirculation flow through heat exchanger

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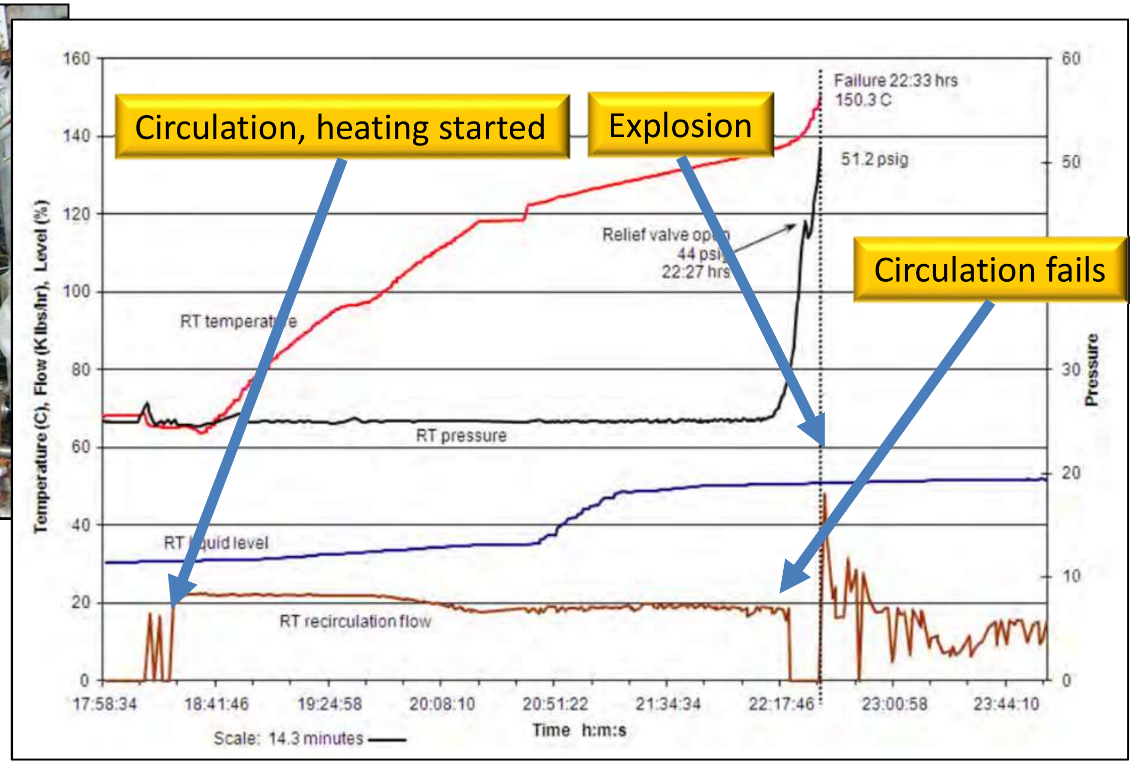
The event

- On the evening of 28th August a rapid pressure rise was noted in the Residue Treater
  - Two employees dispatched to investigate
- As they approached the unit it exploded violently
  - About 1 tonne of toxic residues and solvents sprayed out and ignited
  - Debris was thrown over a wide area



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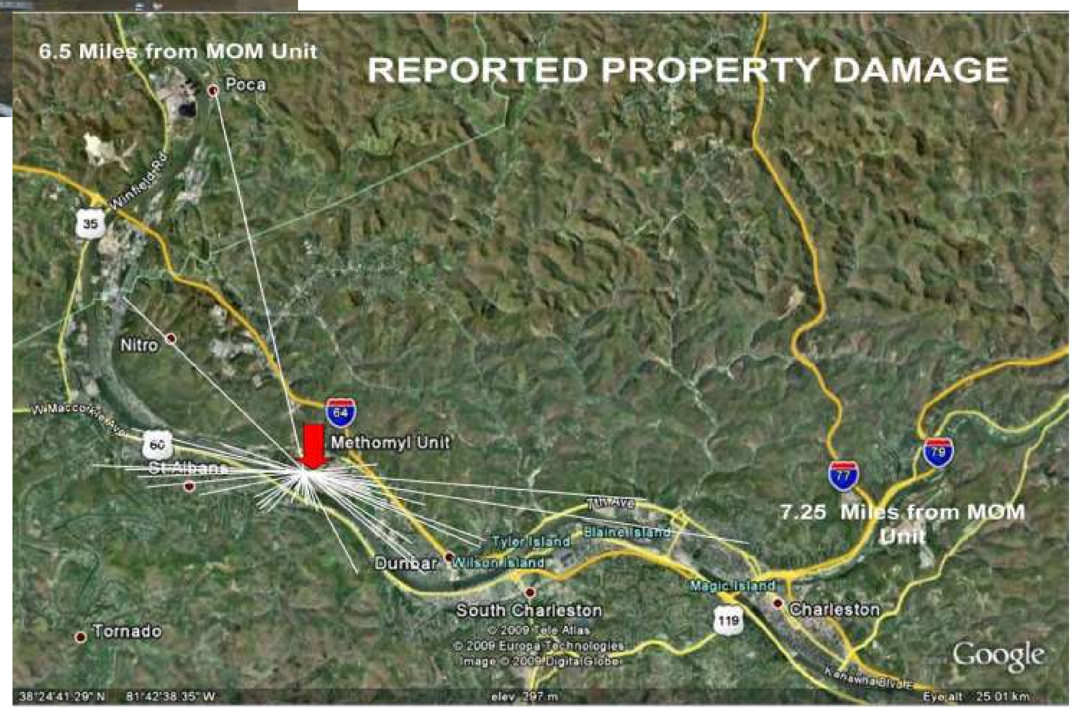
The accident

- The remains of the thermal treater ended up in a neighbouring unit
- 2 people dead
- 8 people inhaled toxic gas
- 40,000 advised to remain indoors



- Property damaged by flying debris at distances up to 11km distance

Some luck prevented worse problems

- Methyl isocyanate (MIC) stored in above-ground storage
  - Surrounded by protective cladding
- Some debris struck the storage
- Fortunately, none struck the protruding relief valve or transfer piping that could have released the contents

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Learning

- After any process or plant change there needs to be an appropriate and competent Safety review
- Commissioning can't be rushed
  - It's very dangerous to be fixing installation problems while trying to operate
  - Having people available in commissioning who understand the key safety issues is essential

Some things are better kept apart…

Specialty chemicals manufacture

- Hydrogen peroxide was being pumped down a line during a troubleshooting activity.
- A branch from the line, leading to a reactor and settler tank, had not been isolated properly
- Peroxide entered the reactor where it found residual sulphuric acid and isopropanol.
- The mixture reacted violently, raising the pressure until the reactor burst
- Fortunately, nobody was close at the time

The result of mixing incompatible chemicals

Remains of
the Reactor lid

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The reaction

- Concentrated Sulphuric Acid and Hydrogen Peroxide react to form “Pirahna Solution” – which is notorious as a rather unsafe cleaning agent

> “Piranha solution is very dangerous, being both strongly acidic and a strong oxidizer. Solution that is no longer being used should **never be left unattended if hot**. It should **not be stored in a closed container**. Piranha solution should **not be disposed of with organic solvents** (e.g. in waste solvent carboys), as **this will cause a violent reaction and a substantial explosion.**”
> (Wikipedia)

Root causes

- A suitable risk assessment had not been performed
- The operators had limited knowledge of the routes taken by pipes (ie where the peroxide could go)
- Equipment (reactor and settler) were not equipped to deal with the situation
  - Little instrumentation
  - Relief systems too small
  - Cooling system off
- Poor operational practices (leaving chemicals in vessels not in operation)

Key Learning ….

Learning

- **Assess thoroughly**
  - Including both planned reactions and credible deviations (e.g. side reactions and byproducts)
  - Process change / maintenance can introduce additional hazards
- **Design** to eliminate or mitigate risks
- **Operate** within the defined envelope / basis of safety
- **Manage change** effectively

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Thank you

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