Chemical Incident Investigation

Millennium Inorganic Chemicals (MIC)

Stallingborough UK, 2010

May 2019

HSE Science and Research Centre

Contributors

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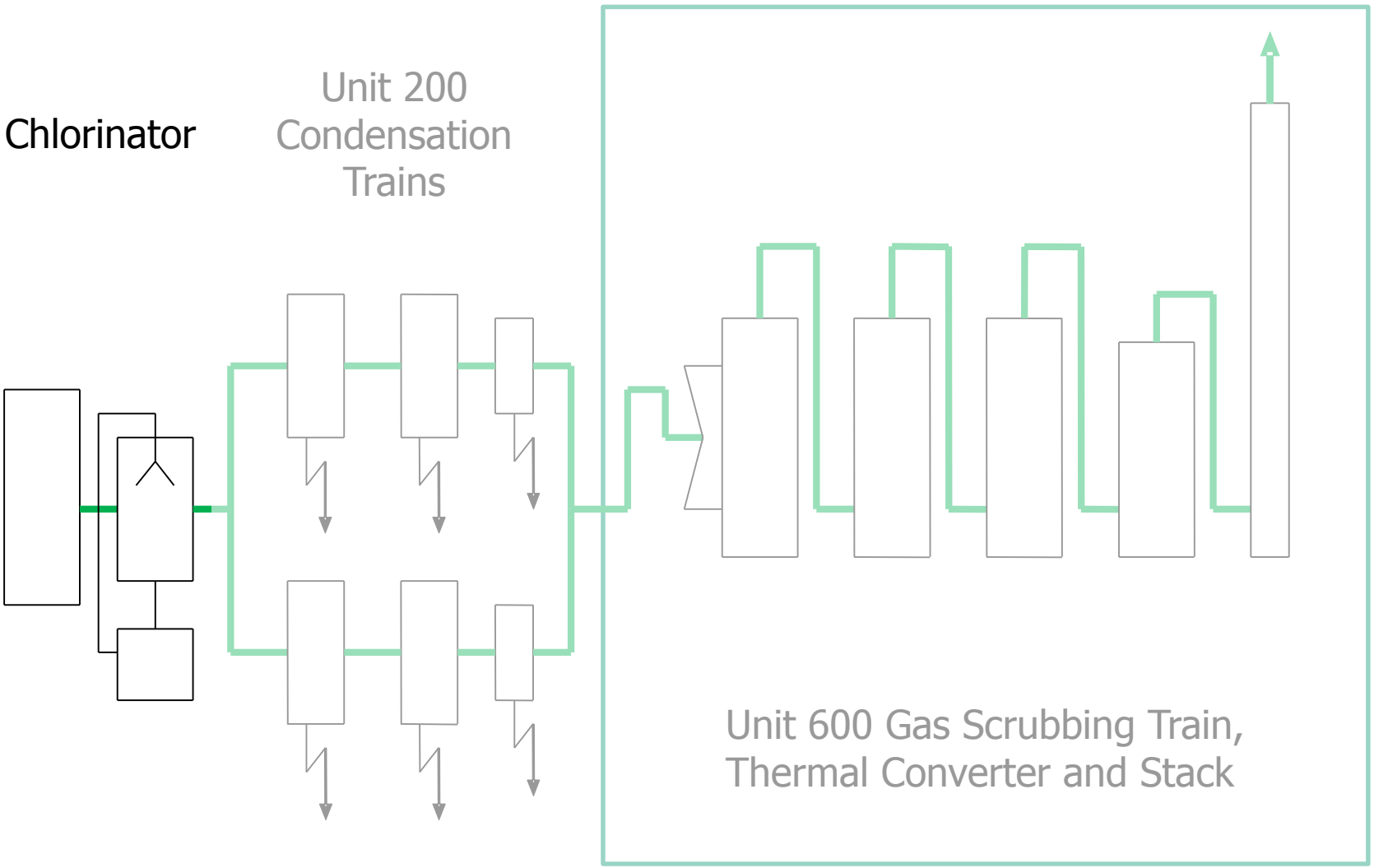
Titanium Dioxide- The Chloride Process

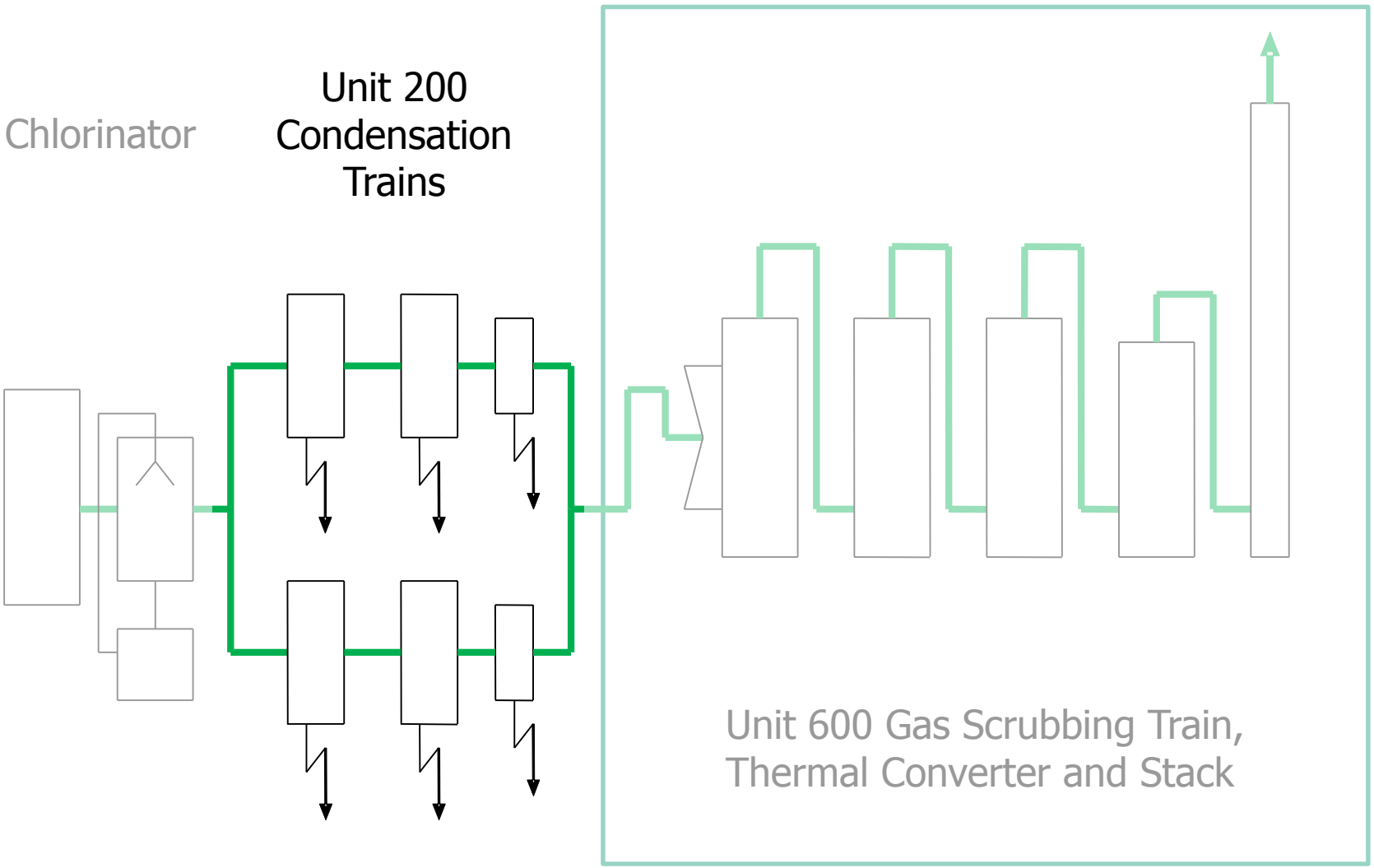
$TiO_{2\ (ore)} + 2Cl_2 + \text{impurities} \rightarrow \mathbf{TiCl_4} + CO_x + \text{impurities}$

$\mathbf{TiCl_4} + 2O_2 \rightarrow TiO_2 + 2Cl_2$

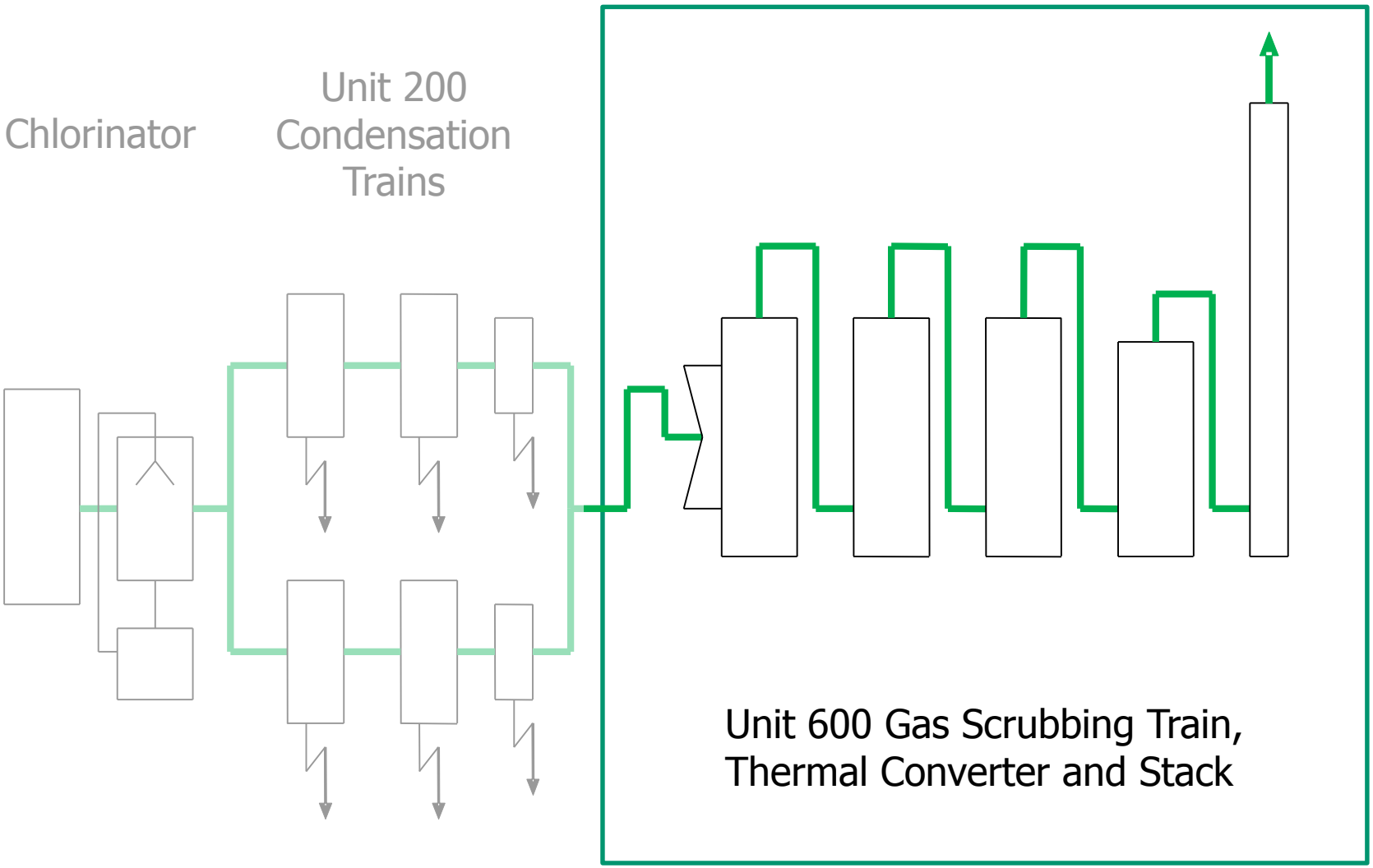
Plant Schematic



Plant Schematic



Plant Schematic



Unit 600: Scene of a Violent Reaction

D650

D650

Two of the Investigation Challenges

Only residual amounts of $TiCl_4$ are expected to be in the gas stream when it enters D650 and it was evident early on in the investigation that an unknown amount of liquid $TiCl_4$ had entered the vessel resulting in a violent reaction and causing catastrophic failure

- 1st Challenge was to find out how the liquid $TiCl_4$ had passed over from the condensation train and why it had failed at that particular time

- 2nd Challenge was to understand if the white cloud which left site posed a risk to members of the public

So why did Vessel D650 fail…?

"Unexpectedly large volume of $TiCl_4$ reacted at once"

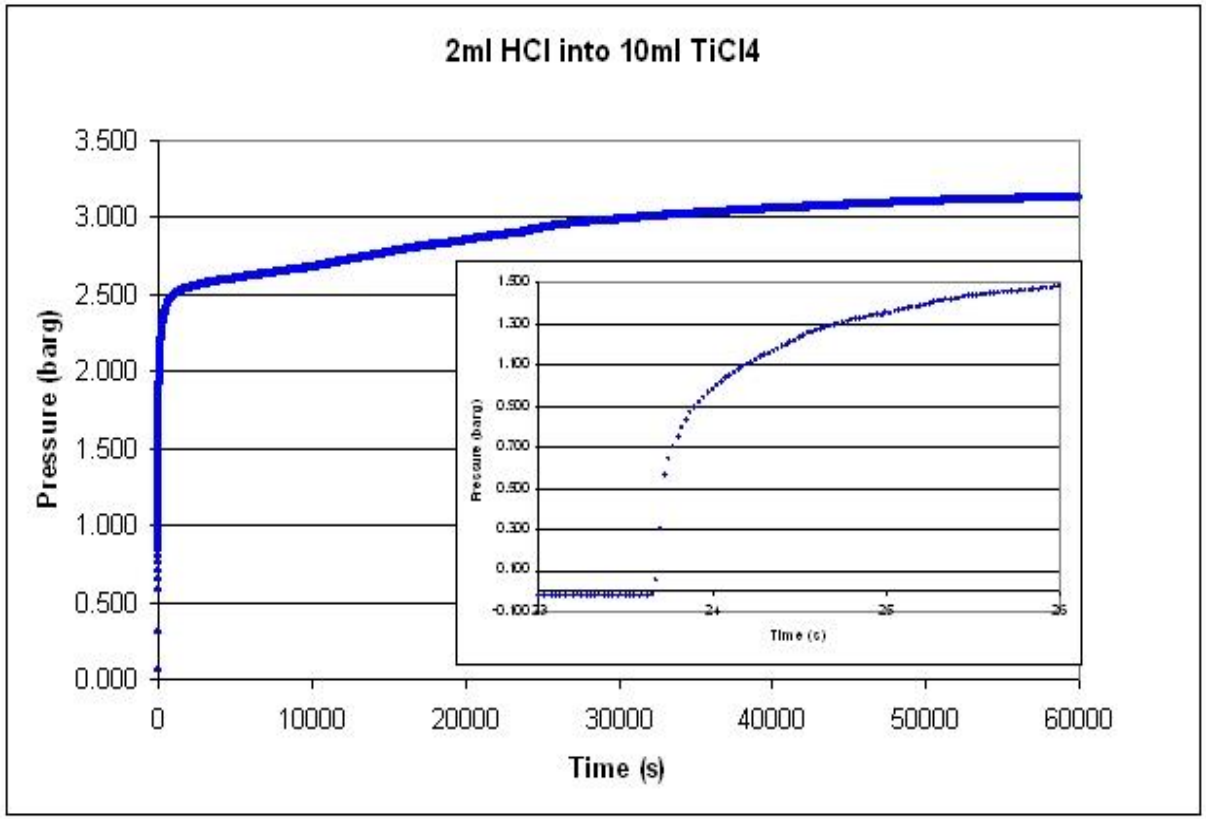
The Reaction:

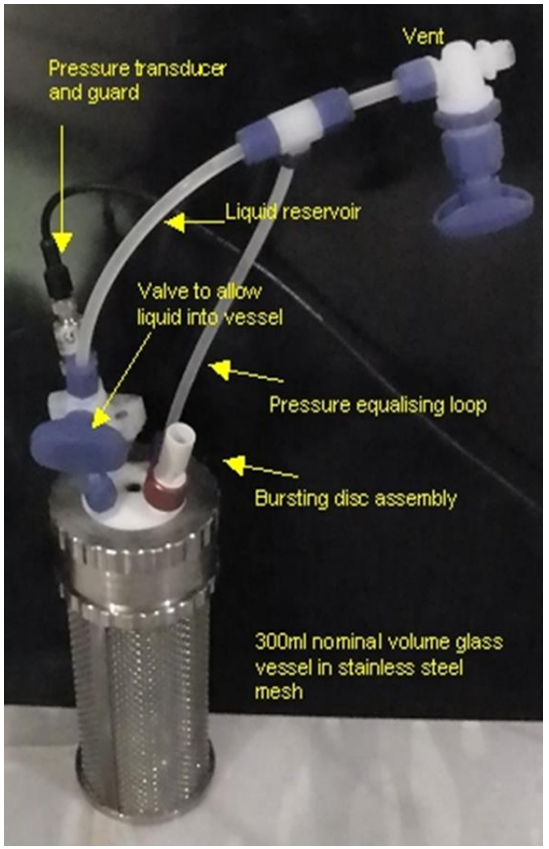
$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4\ HCl$$

Second example of violent reaction between $TiCl_4$ and water

21st March 2011

Pressure Increases





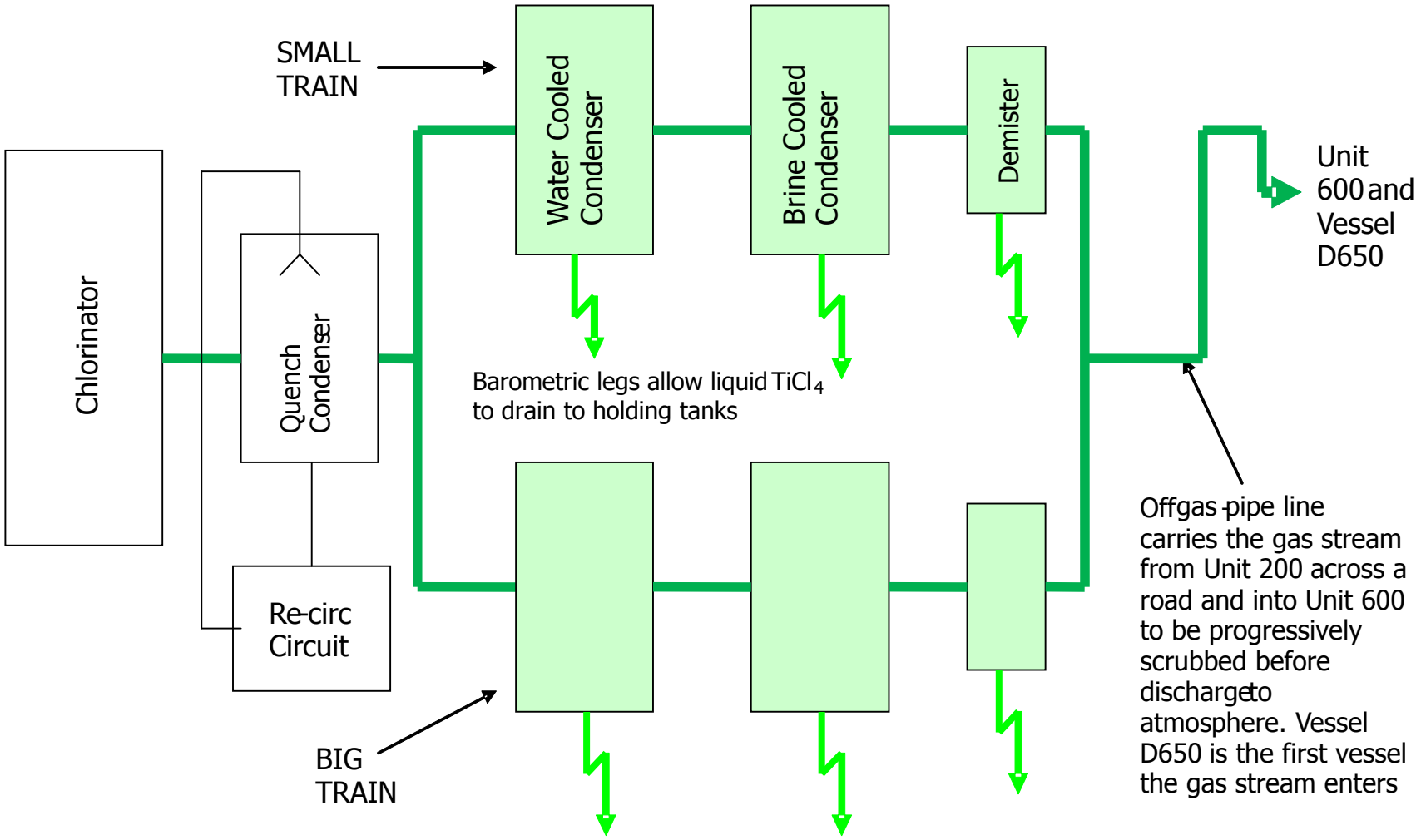
- Pressure rise 0-1 bar about 400ms
- Final Pressure 3.13 bar
- 1.3 bar could be from hydrochloric acid

So why did Vessel D650 fail…?

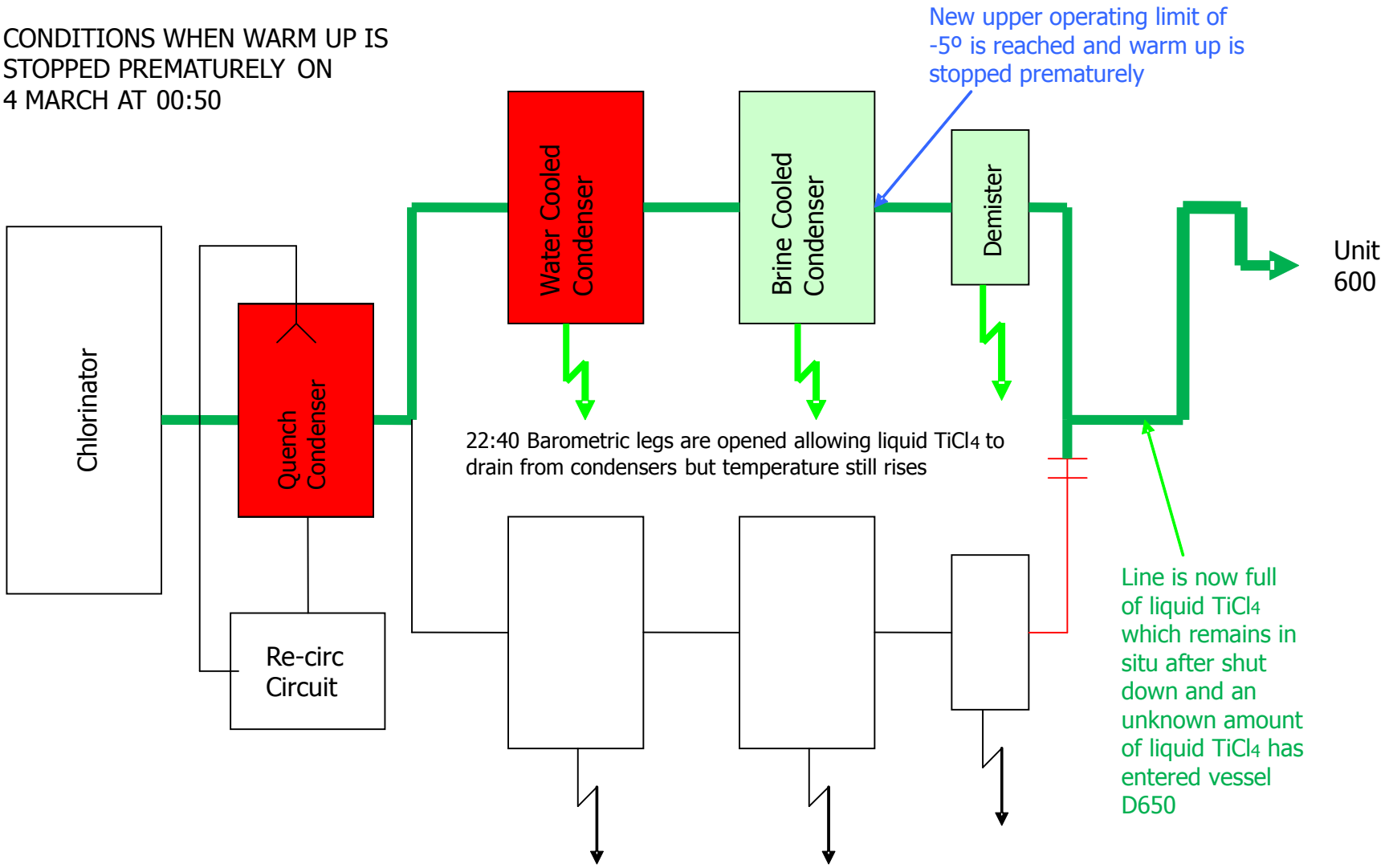
"Unexpectedly large volume of $TiCl_4$ reacted at once"

Where did the $TiCl_4$ come from?

Unit 200 Condensation Train



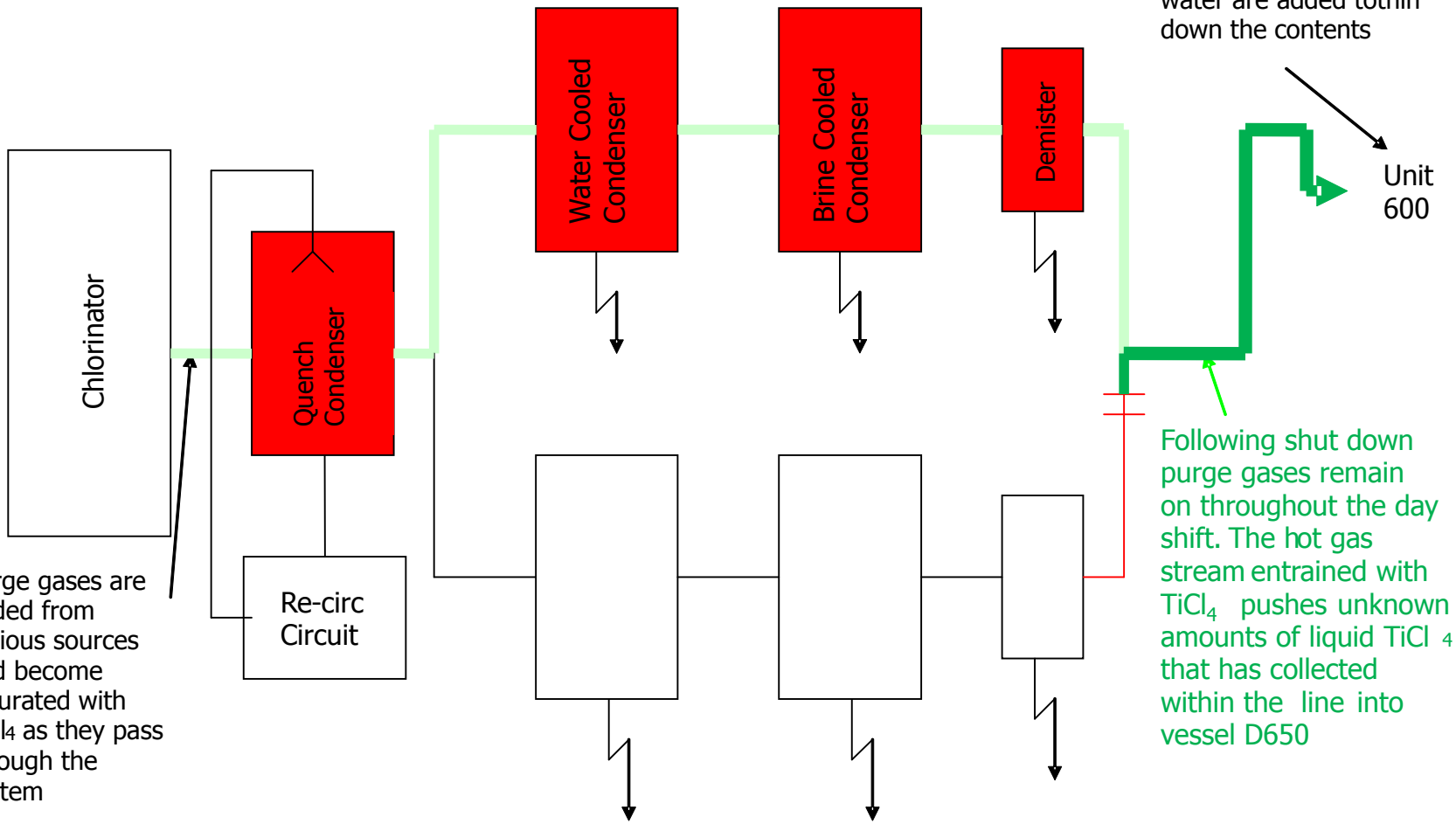
CONDITIONS WHEN WARM UP IS STOPPED PREMATURELY ON 4 MARCH AT 00:50



CONDITIONS DURING THE DAY SHIFT 4 MARCH

Water and brine off to enable repair

Significant quantities of $TiCl_4$ enter D650. Unknown quantities of water are added tothin down the contents



Purge gases are added from various sources and become saturated with $TiCl_4$ as they pass through the system

Following shut down purge gases remain on throughout the day shift. The hot gas stream entrained with $TiCl_4$ pushes unknown amounts of liquid $TiCl_4$ that has collected within the line into vessel D650

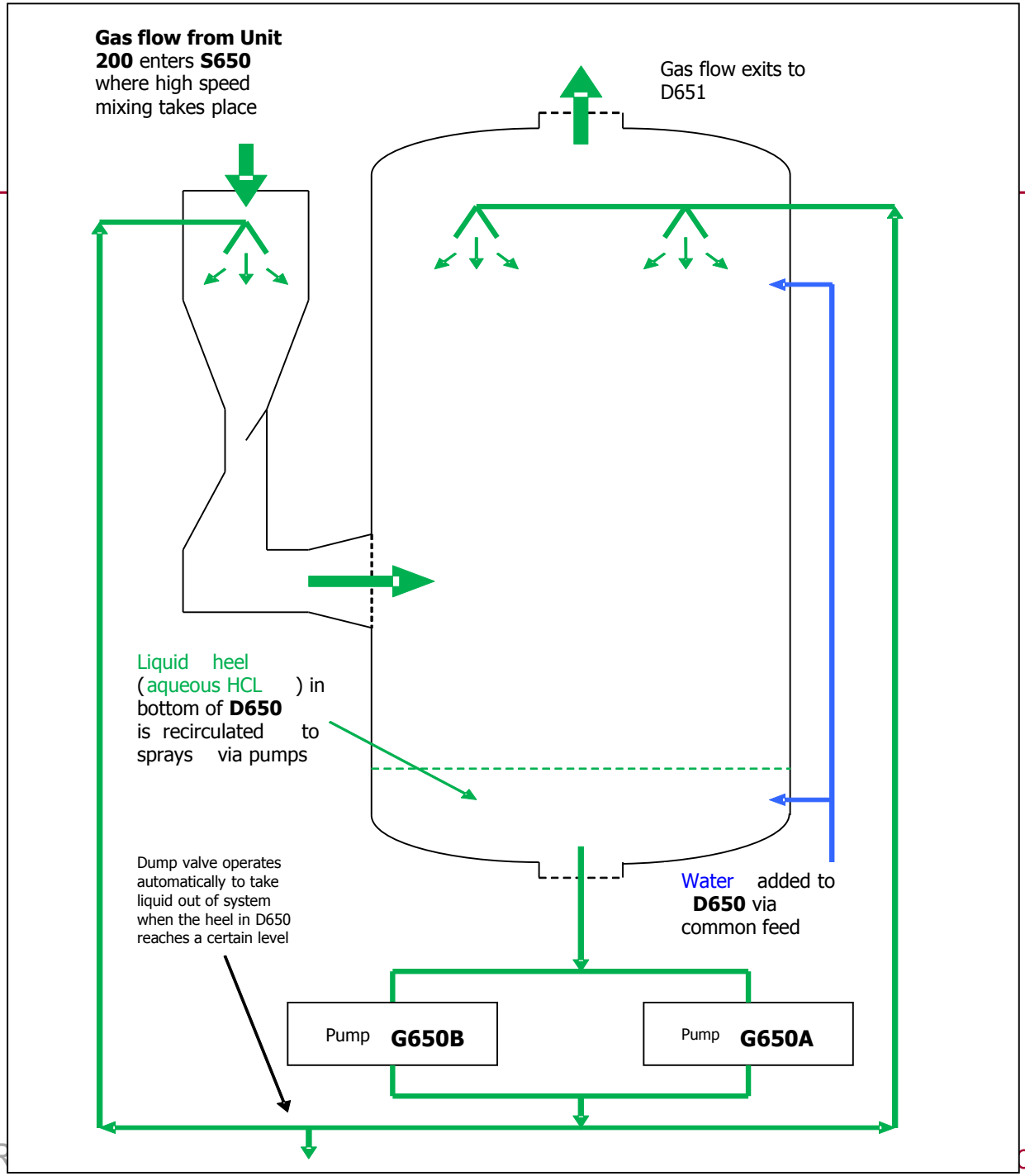
So why did Vessel D650 fail…?

"Unexpectedly large volume of $TiCl_4$ reacted at once"

How did the $TiCl_4$ arrive and cause the vessel to fail?

Two options

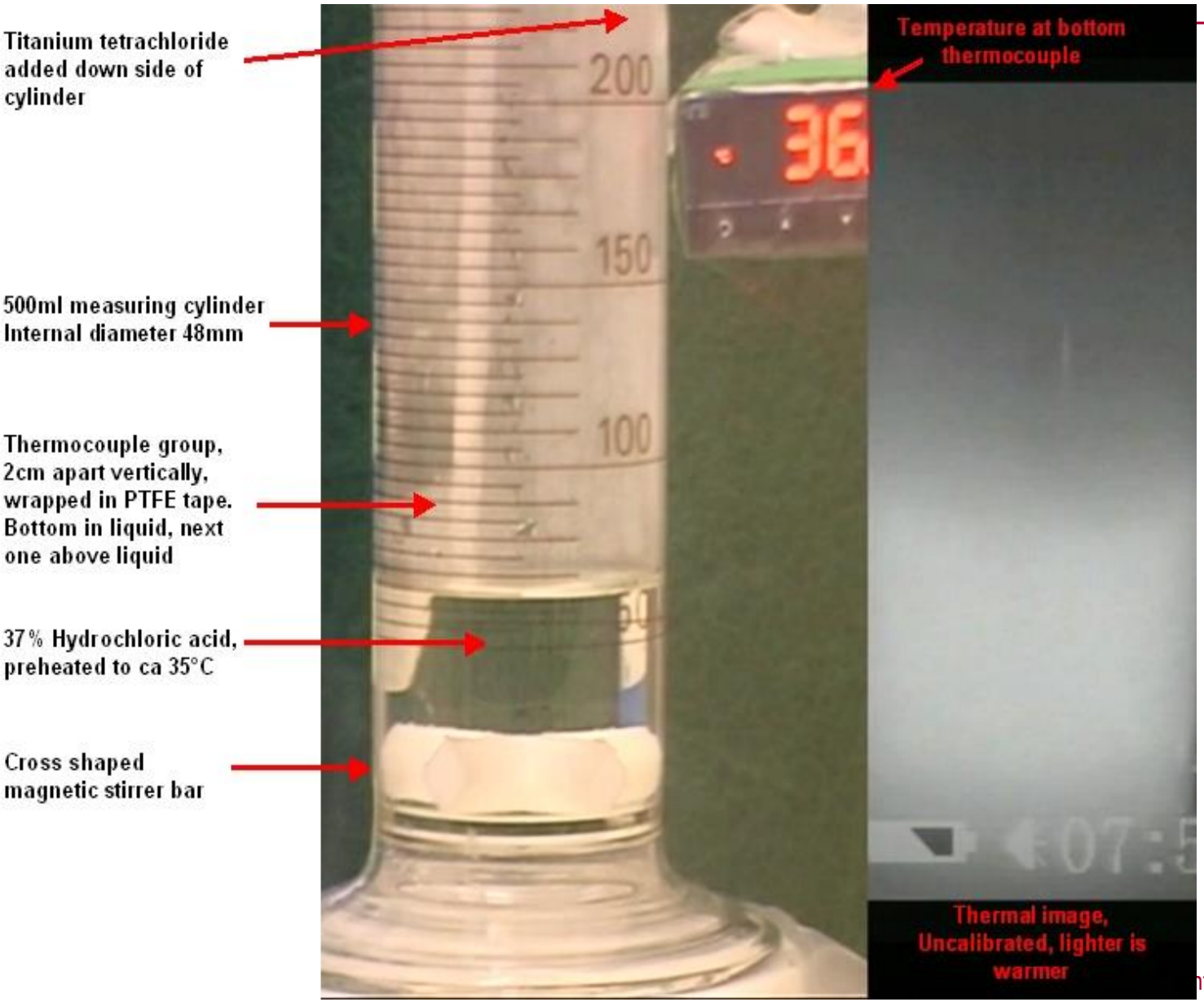
D650



Base of Unit 650; Pumps

Pump Bolts

Foam formation: 500ml cylinder

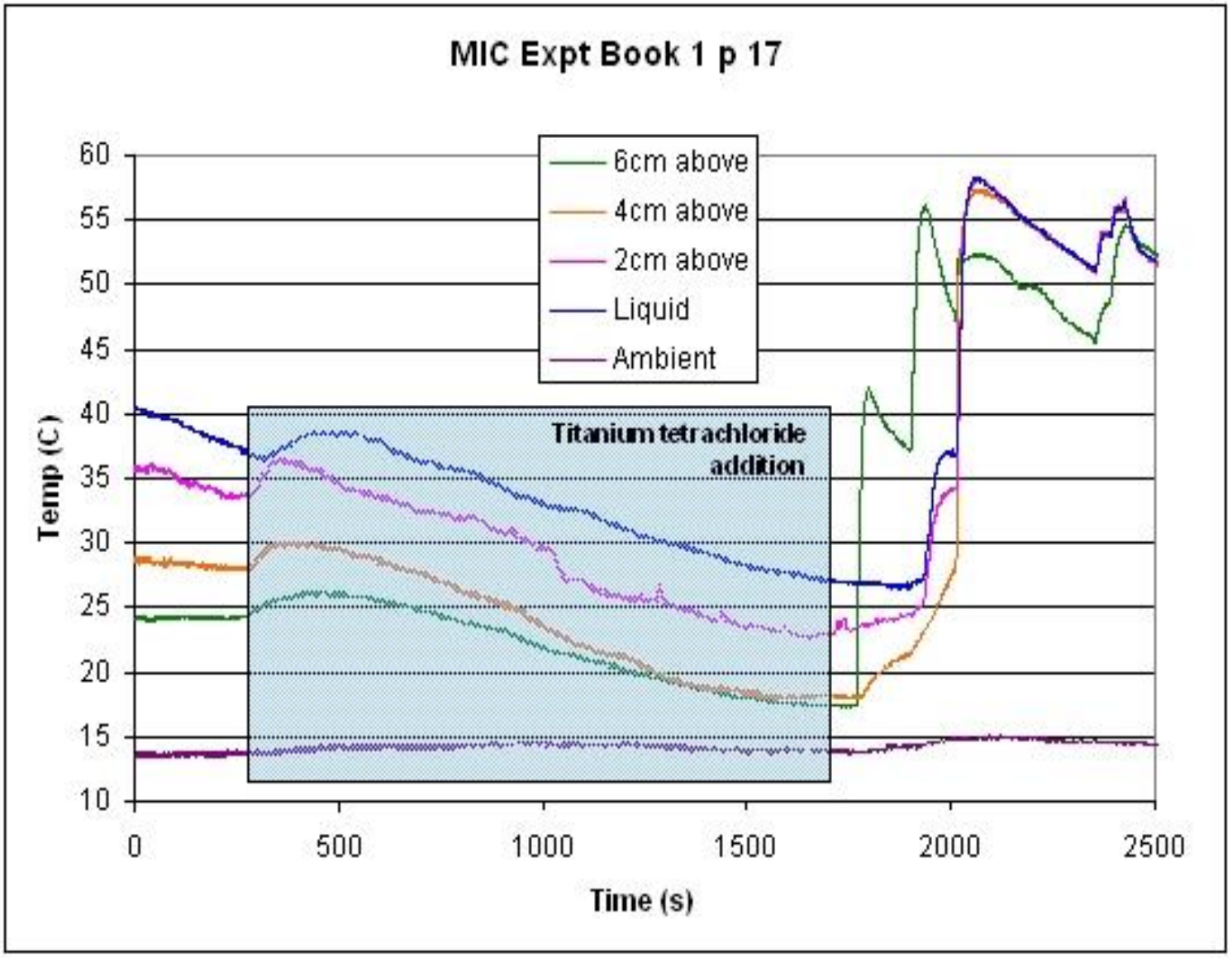


Example of crust formation

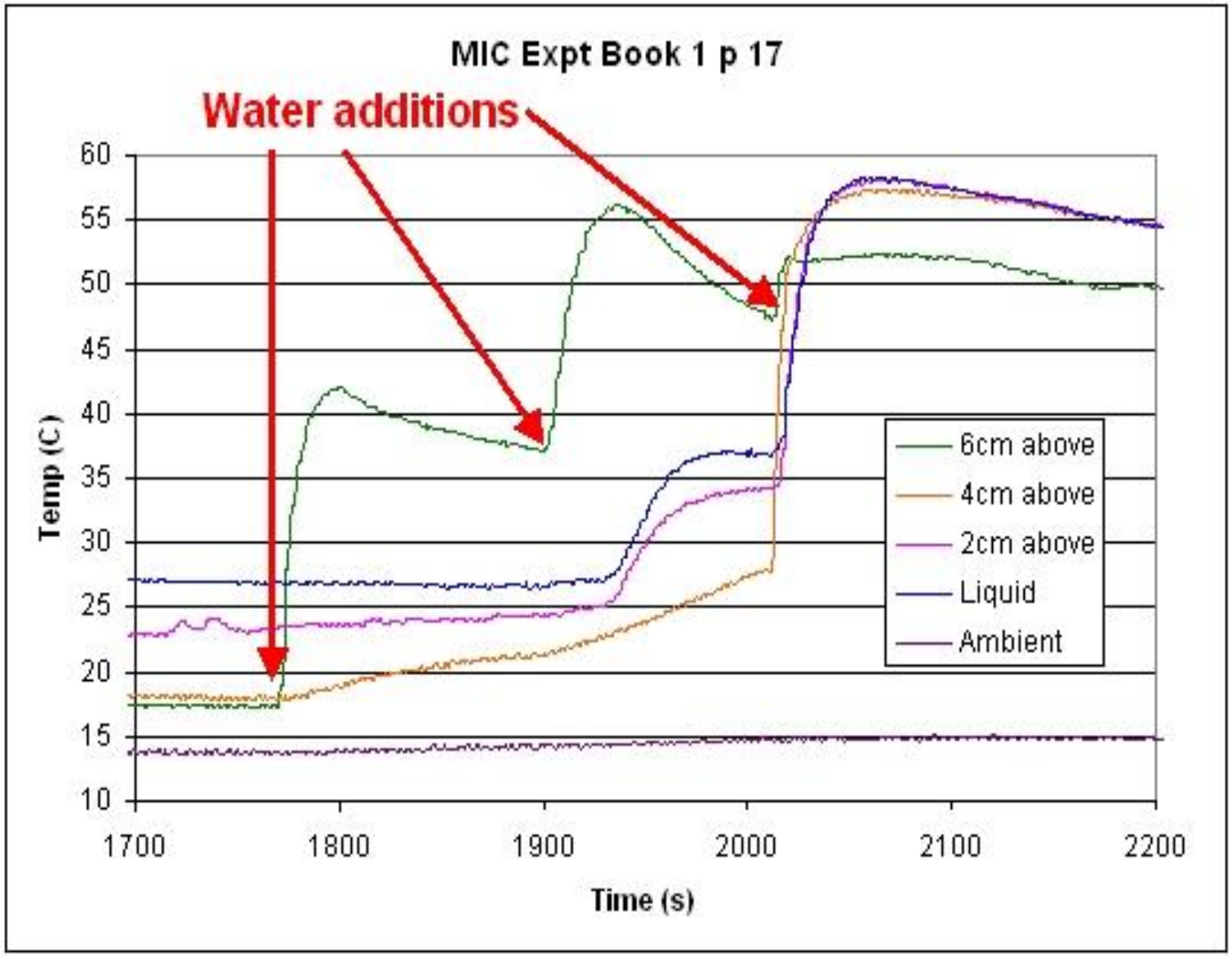
Addition of $TiCl_4$ to HCl

13th December 2010

Foam formation: 500ml cylinder



Foam formation: 500ml cylinder



Subsequent sequence of events

- Warm-up / Start-up continued on 5th March
- Less than optimal conditions in **D650**
  - Blockages / Twaddle Readings
- Additional water added to dilute the scrubbing mixture
- Pump stopped to clear sampling ports
- Pump turned back on

Subsequent sequence of events

- Fume seen from pump
- Decision to switch over to auxiliary pump

VESSEL RUPTURED

- Rescue of injured
- COMAH Emergency plan initiatied

Subsequent consequences

- Harm to people
- Dense white cloud left site, closing Humber to traffic
- Company submitted guilty pleas (to all three charges) in May 2016

Generic Lessons

Questions?