
Hydrogen Incident December 2010

“To Learn and Share”

(To help others know what they don't know)

Background

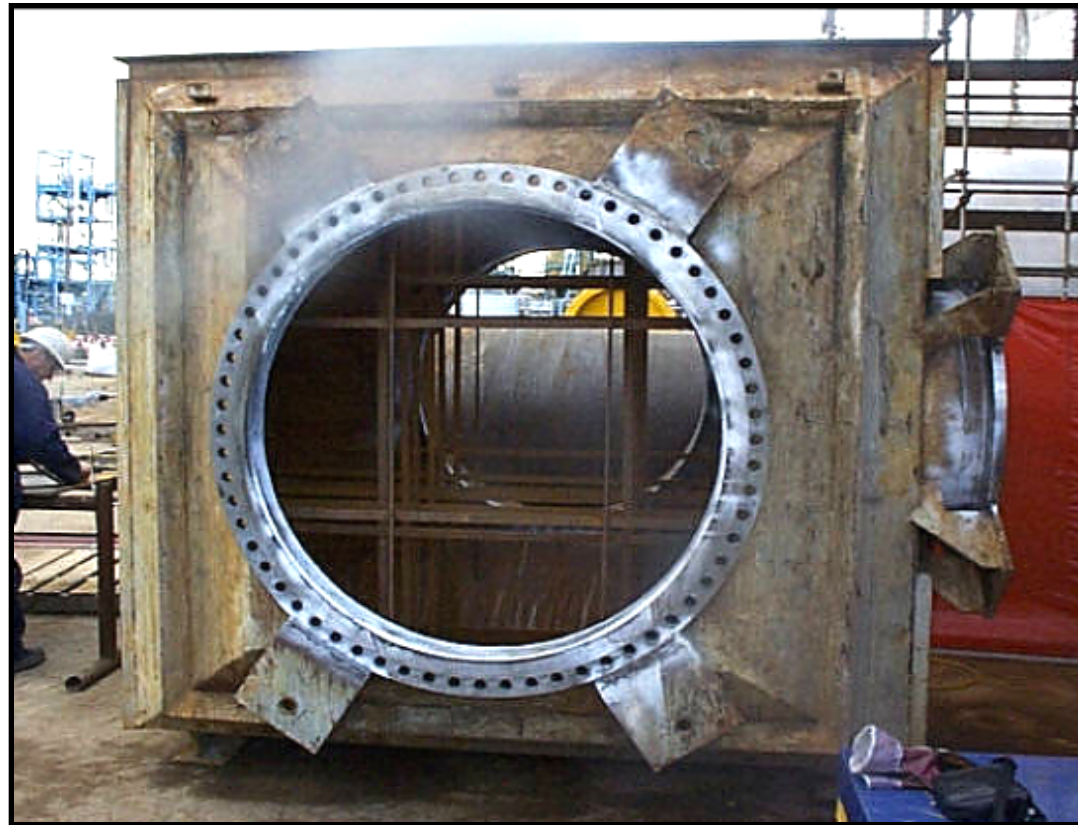
- ▶ ~900 Te/day, vintage 1972, double absorption
 - ▶ Supplier to the UK on Sulphur burnt compounds;
 - ▶ 98%, 96%
 - ▶ 20% Oleum
 - ▶ Ultra Pure (<0.5ppb purity, electronic grade)
 - ▶ Liquid SO₂
 - ▶ Liquid SO₃
 - ▶ Dilutes (77%)
 - ▶ PS3 (100% strength)
 - ▶ Located very close proximity to town's population (200 metres), schools, wildlife, main arterial highways.
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SAC Schematic

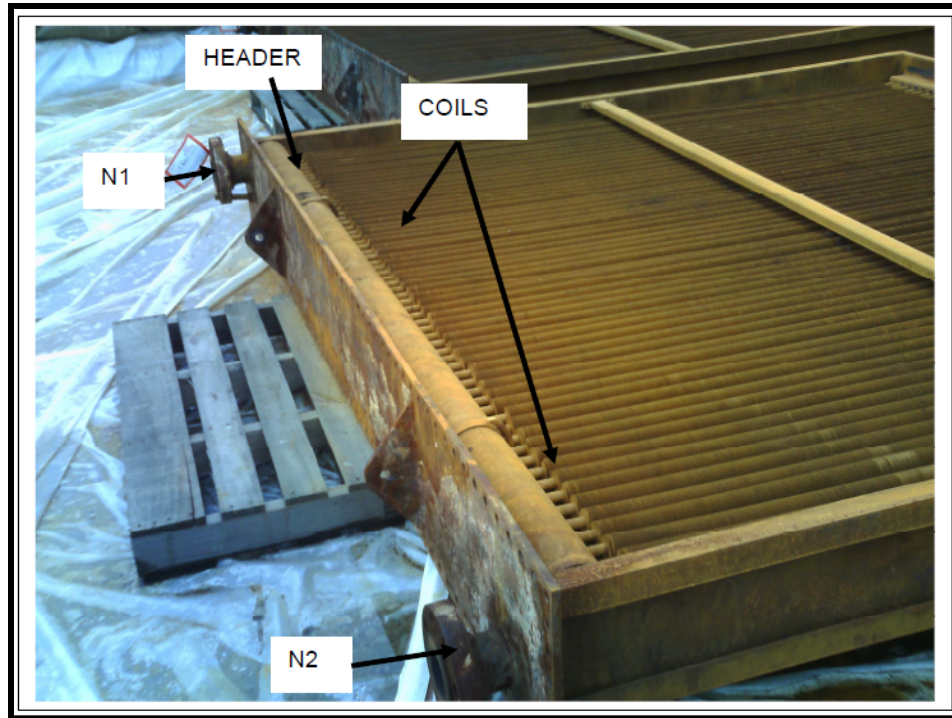
The diagram illustrates the Sulfuric Acid (SAC) production process. It begins with **sulphur** (orange arrow) entering a **Furnace**. The output of the furnace goes to **Boiler 1**, which then feeds into a **Converter**. The **Converter** is a large vertical vessel with multiple stages. The output of the converter goes to **Boiler 2**, which then feeds into a **Superheater**. The output of the superheater goes to a series of **Intermediate Heat Exchangers**. The output of the intermediate heat exchangers goes to a **Heated pipe (ex- 3rd pass gas)**, which then feeds into an **Oleum Absorber**. The output of the oleum absorber goes to an **Intermediate Absorber**. The output of the intermediate absorber goes to a **Final Absorber**. The output of the final absorber goes to a **Stack**. The process also includes a **Drying Tower** (receiving input from the furnace), a **Blower**, a **Steam turbine**, and **Oleum Evaporators**. A **Secondary Economiser** (highlighted in red) is also shown, which is part of the heat recovery system. The **SO3** (green arrow) is shown entering the **Oleum Evaporators**.

Secondary Economiser Shell - Before

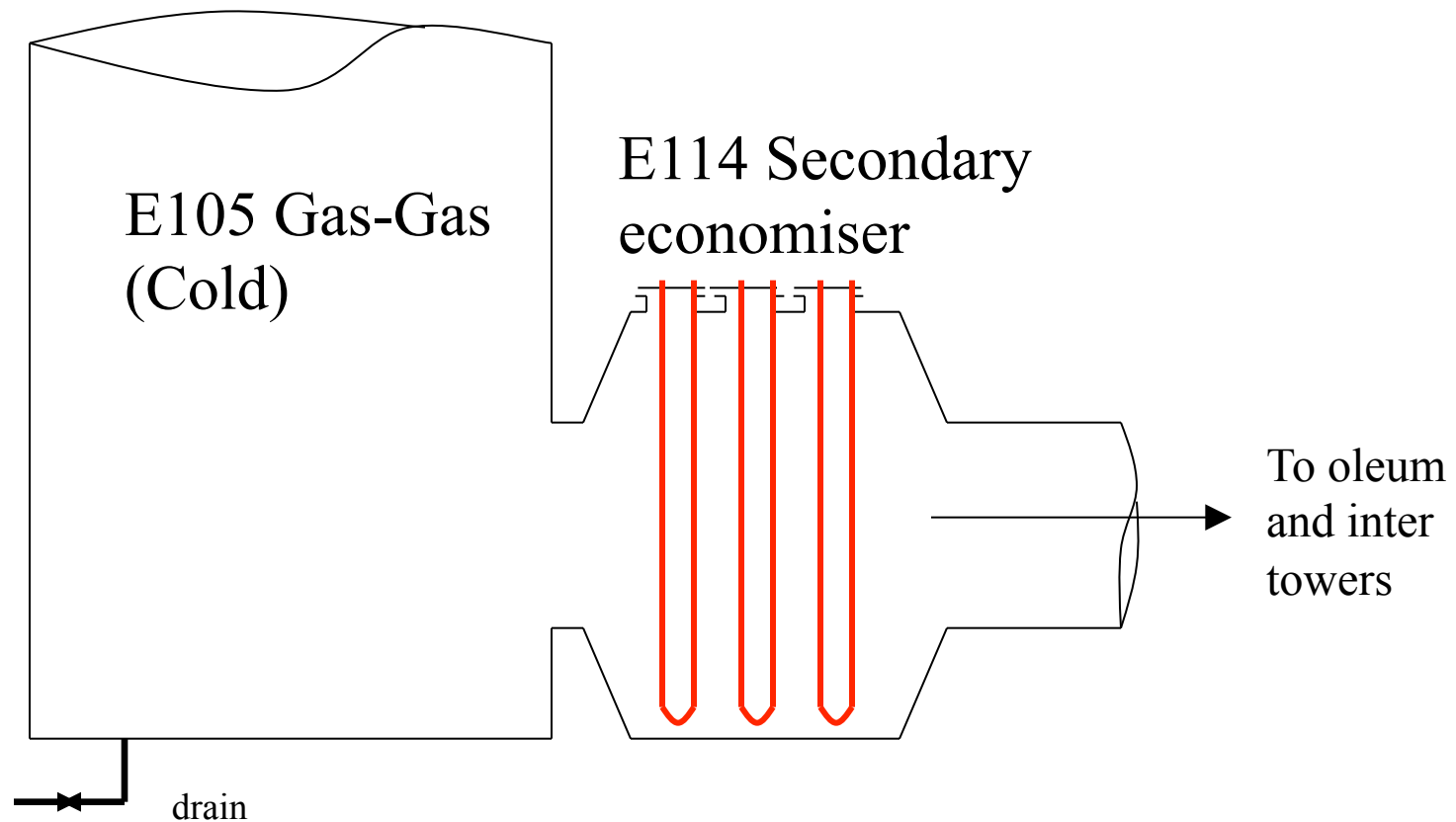
- ▶ What the old vessel shell used to look like minus the HE elements



Secondary Economiser HE Elements - Before



Gas-Gas/Secondary economiser schematic



The Aftermath – initial environmental spillage



The Aftermath - Inside of the Secondary Economiser

- ▶ Resultant state of secondary economiser, vast corrosion of steel



The Aftermath - Secondary Economiser Bundles

- ▶ Resultant condition of tube bundles – Lost approx 1 metre from all three bundles



What happened?

- ▶ We rolled the dice....we didn't know what we didn't know.
- ▶ The secondary economiser had been installed in 1984 for energy/absorption efficiency, complete with drain.
- ▶ Drain removed from it in 1996, reason unknown.
- ▶ December 2010 - tube bundle(s) failed - resulting in weak acid being produced in the gas side of the unit
- ▶ Lead to rapid corrosion of tube bundles in vessel and large scale strength control excursion in towers/circs/coolers.
- ▶ Corrosion generated significant quantities of hydrogen, which collected at the top of the inter-absorber, one of the high points of the plant.
- ▶ The hydrogen, which has low activation energy, caused pressure excursion when it found source of ignition.

Timeline

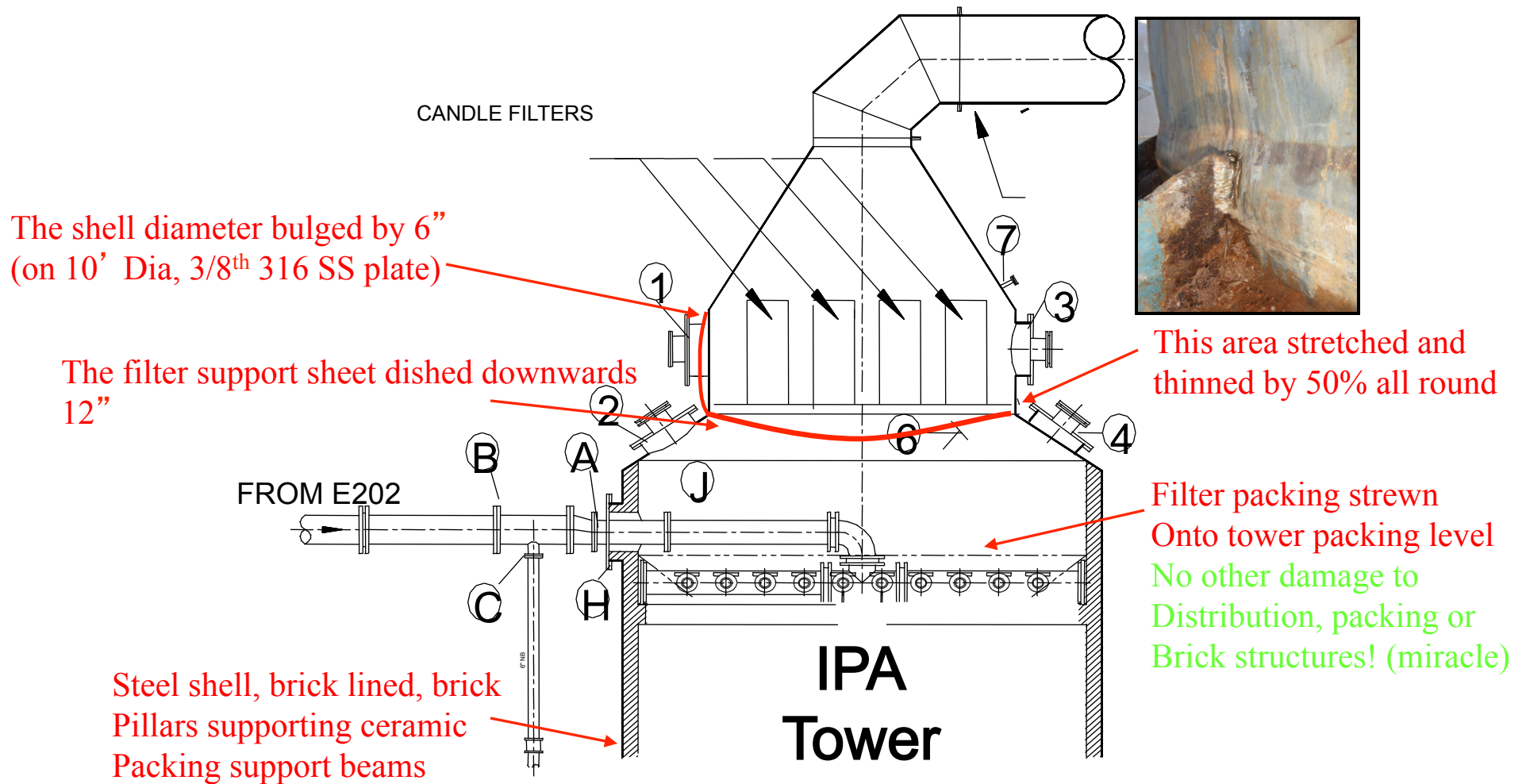
- ▶ 23rd Sept 2010 – Plant begins scheduled turnaround including final installation of new converter/ducts – 37 Day Outage – longest so far recorded.....
 - ▶ 30th October – Plant restarts
 - ▶ 30th October to 15th December –unprecedented sequence of protracted outages (8 long days offline for repairs in a 6 week period)
 - ▶ 15th December - Outage for further repairs followed by failure of the secondary economiser leading to acid spill to outfall major plant upset, acid spill to outfall and Hydrogen explosion in top of inter pass tower.
 - ▶ Immediate All stop – “Force Majeure” invoked 1 day later
 - ▶ Massive response required from a standing start!
 - ▶ Significant inspections and investigations beyond the obvious damage to the secondary economiser and inter pass tower.
 - ▶ 11th February – 58 days after failure – plant restarts
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What happened?

- ▶ The pressure generated resulted in damage (deformation, bulging and cracks) to the top of inter-absorber tower and destruction of the candle filters in the tower



Taking the strain.....



Dimensions

- ▶ ~ 900kg (2000lbs) of steel corroded in the secondary economiser
 - ▶ ~ 33kg (75lbs) of Hydrogen evolved
 - ▶ At ambient pressure volume = 600m^3 ($21,000\text{ ft}^3$)
 - ▶ Fills parts of the system with ease when the plant is SD
 - ▶ When running, the H_2 conc was $<0.4\%$ even with a corrosion event occurring
 - ▶ When stopped H_2 stagnated by buoyancy in high spots, mainly top of inter pass tower in this case.
 - ▶ Flammable range 3% to 75%
 - ▶ Very low activation energy – $\text{NO}_x/\text{SO}_2/\text{SO}_3/\text{Nitrosyl}$ acid effects
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Impacts

- ▶ We were very lucky.....we rolled the dicemany things could have happened....no-one was hurt, there were minor effects on environment, but....
 - ▶ Force Majeure
 - ▶ 58 days offline – working flat out – 2 rest days – Christmas Day and New year's day – 150 staff engaged in total
 - ▶ Worst weather conditions on record – plant became 1 large and very dangerous ice block.
 - ▶ 27 VIP International Inc (Louisiana, USA) staff landed on 1/1/11, to repair and inspect all towers, were finished and gone by 10/1/11 – great job!
 - ▶ Response in terms of inspection and repairs cost circa \$4.5million.
 - ▶ Business loss \$VERY large
 - ▶ Massive confidence loss – our customers (1 of which had to enter Force Majeure themselves) and ourselves
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**December 16th 2010 – start of the coldest UK
winter for many years**



It could have been much worse...

- ▶ The top of the IPA could have massively ruptured, causing fragments –large or small – to damage other sensitive equipment.
 - ▶ The pressure wave could have destroyed the internals in the Inter Pass Absorber Tower
 - ▶ Personnel could have been injured, both in the initial event and then in the huge rapid response that followed – they were not.
 - ▶ The environmental impact could have been significant.
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Initial modification to re-establish operation



Root Cause (Most probable)

- ▶ Sequence of outages led to repeated condensation in the secondary economiser.
 - ▶ The removal of the gas drain in 1996 meant that this vessel shell was not drained of that liquor.
 - ▶ The liquor pool corroded the base of the U-tubes
 - ▶ Massive water ingress caused rapid further acidic corrosion, liberating significant hydrogen which filled the system while the plant was SD.
 - ▶ Plant gas paths were stagnant because the plant was stopped.
 - ▶ Hydrogen migrated by buoyancy and gathered in the top section of the inter pass tower.
 - ▶ The hydrogen in the top of the inter-pass tower was ignited (static) and caused the confined explosion.
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What we have or will do differently....

- ▶ Re-established regular gas drain checks and corrected our pressure drop survey regime.
 - ▶ Revised blow through procedures when SD
 - ▶ Introduced absorber acid strength rate of change instrumentation linked to the DCS and alarms.
 - ▶ Re-designed and installed a new secondary economiser to match a new gas-gas HE' s.
 - ▶ We are engaging the industry on a number fronts ;
 - ▶ Discussing Hydrogen generation awareness – two way process!
 - ▶ Progressing how to detect water breakthrough from boilers, superheater, economisers (Acoustic monitoring)
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Permanent Modifications to plant (So far)



New secondary economiser. No fins.
Top of gas inlet is well below lowest of the tubes
(Self limiting safety feature)



Moisture detection pot with resonant
type detector with alarms

Permanent Modifications to plant (So far)



New secondary economiser.
No fins on internal tubes.
Much Larger!

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- ▶ The incident had widespread implications to us and our business.
 - ▶ BUT....It could have been much worse!
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