Hydrogen Gas Incidents

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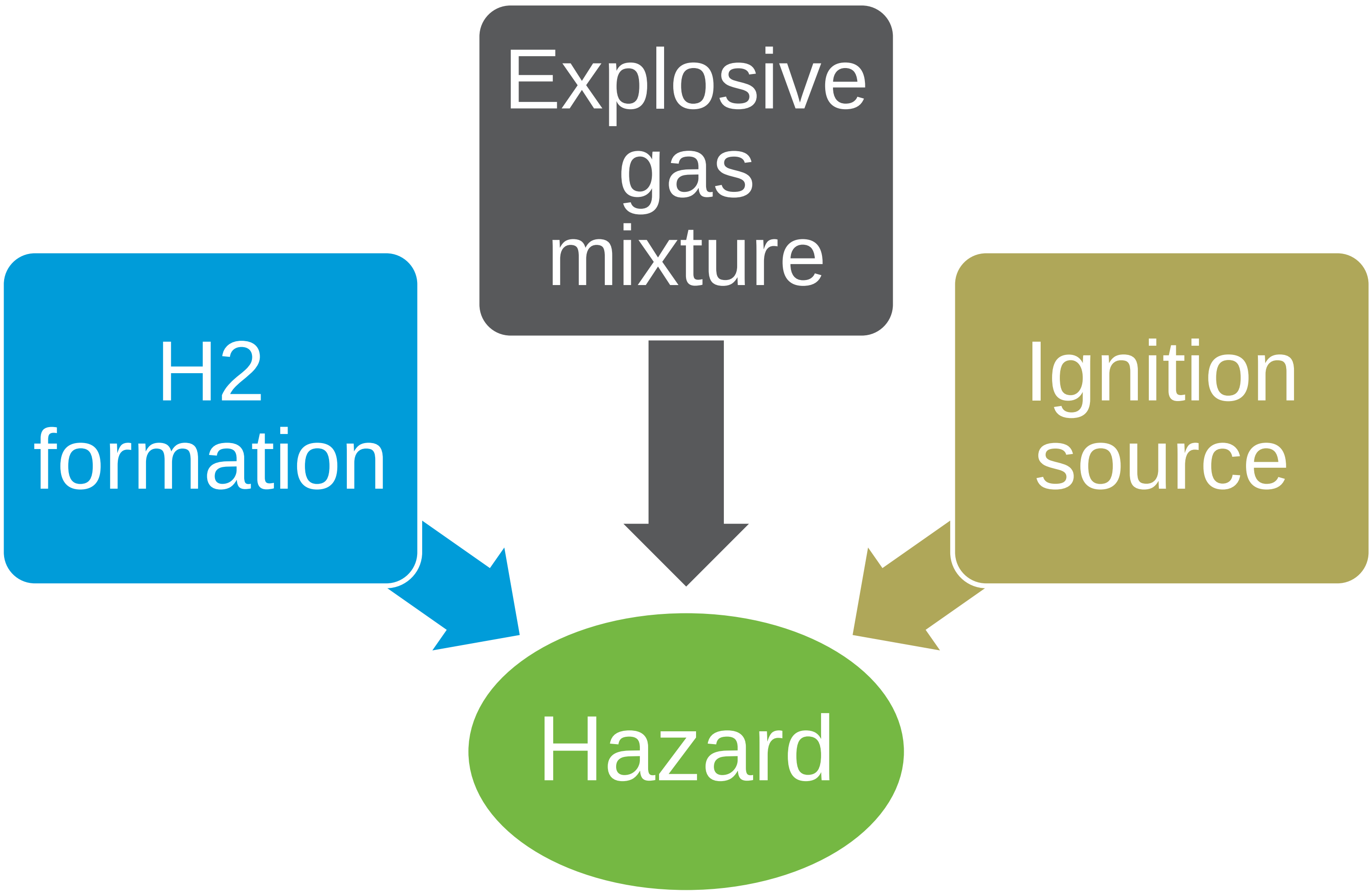
Agenda

- Theoretical considerations
  - Hazard formation
  - Physical properties of H_2/Air mixtures

- Case Study

- Considerations

Hazard formation



Explosion limits

- Explosion Limits of hydrogen in air and air/nitrogen at room temperature, measured by various standards (in mole-%)

	DIN 51649	EN 1839(T)	EN 1839(B)	ASTM E681
LEL (H_2 in air)	3.8	3.6	4.2	3.75
UEL (H_2 in air)	75.8	76.6	77.0	75.1
LEL (40% N_2 +air)	3.6	3.6	4.4	3.65
UEL (40% N_2 + air)	38.2	38.4	38.2	37.3

- 2nd case residual oxygen content is approx. 13%-vol. (~ double the content at the intermediate absorber)
- UEL in this case will be below the tabled figures as the addition of increasing chemically inert substances to mixtures of hydrogen and air causes the upper and lower limits of explosion to approach each other, and ultimately to met.

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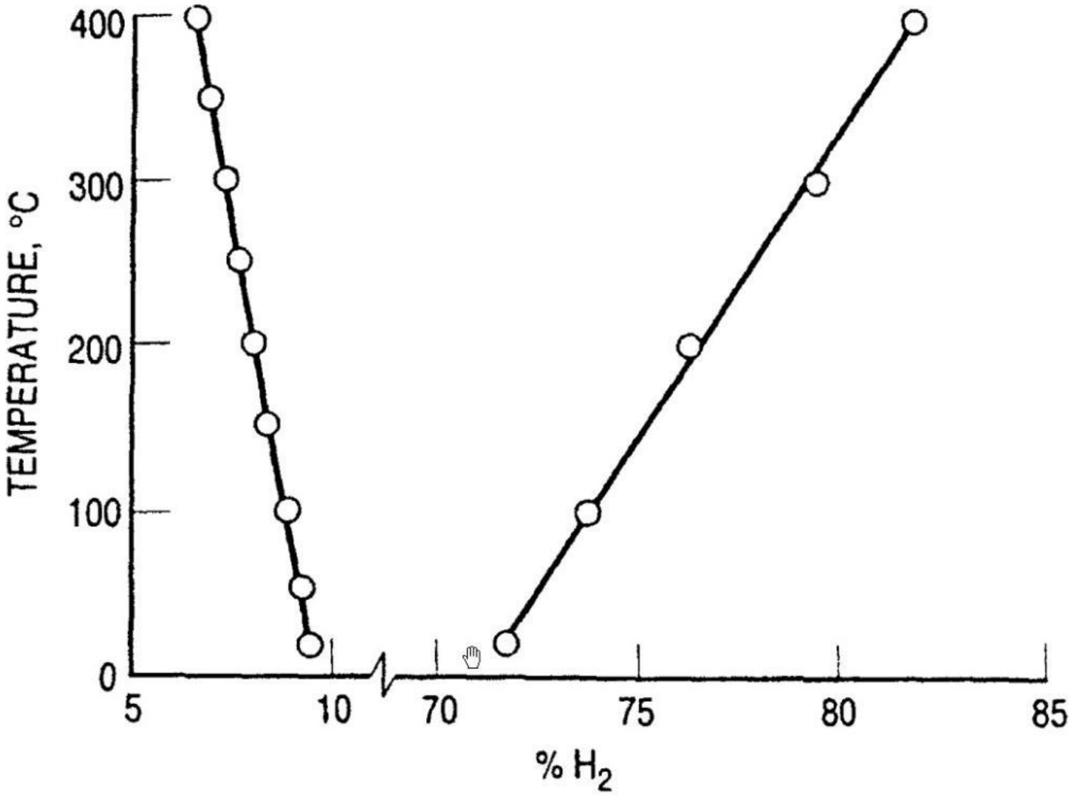
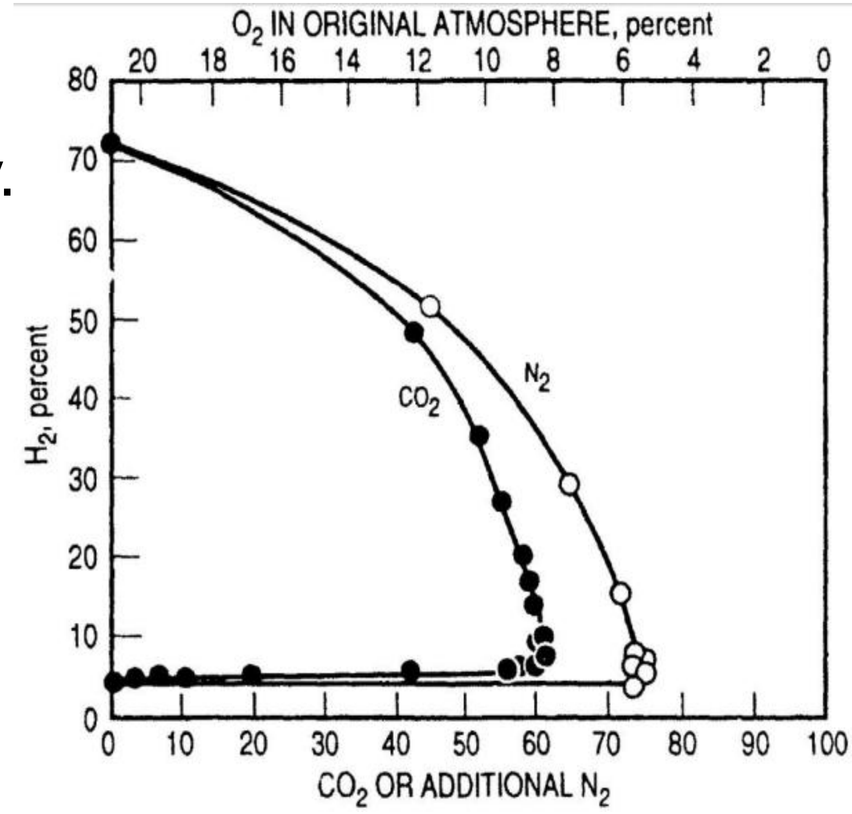
Influence of gas temperature

- Explosion range of hydrogen – air mixtures widens with increased temperature, which is important at our prevailing conditions



Influence of additional N2 or CO2

- The presence of additional N_2 or CO_2 in the gas (air) will reduce the oxygen content.
- Subject to the residual O_2 , the explosion limits vary significantly.
- No crititcal compositions at O_2 contents below 4…5%



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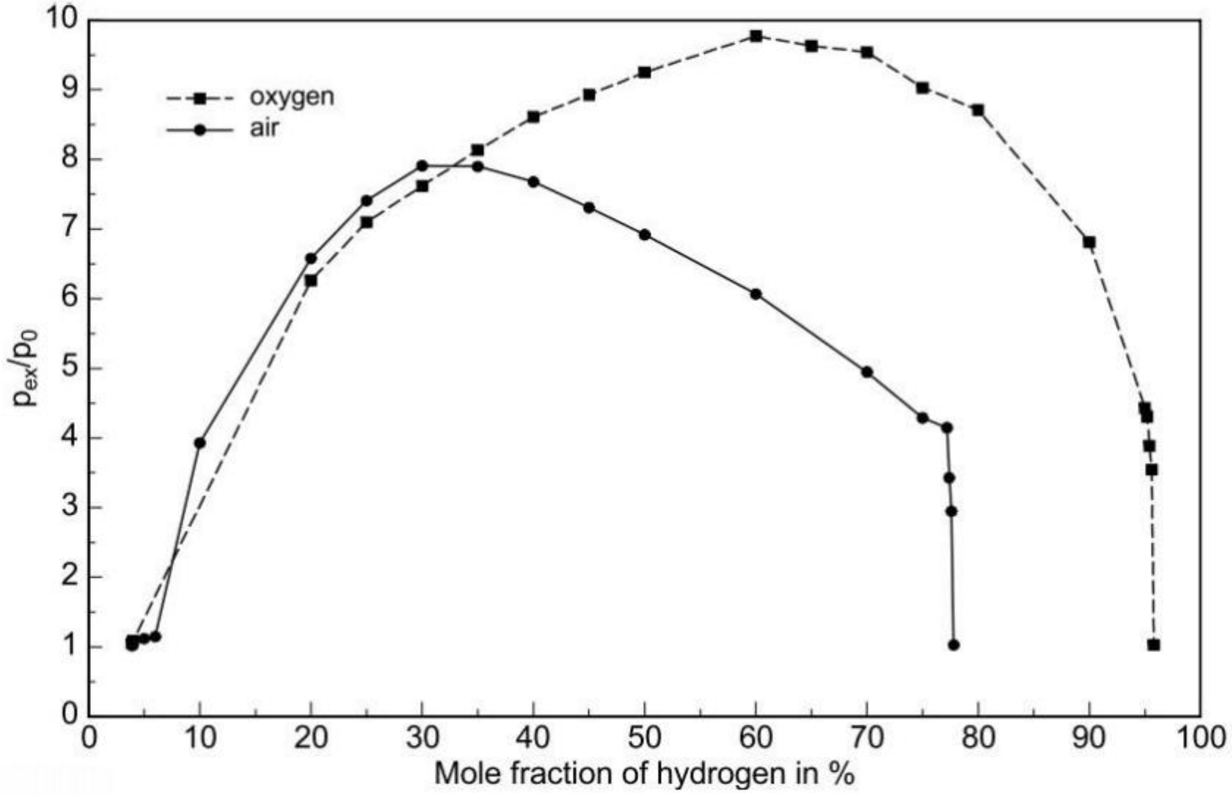
Reaction energy

$2\ H_2 + O_2 = 2\ H_2O$ -> ΔH= -483 kJ/mol
High pressure generation due to explosion



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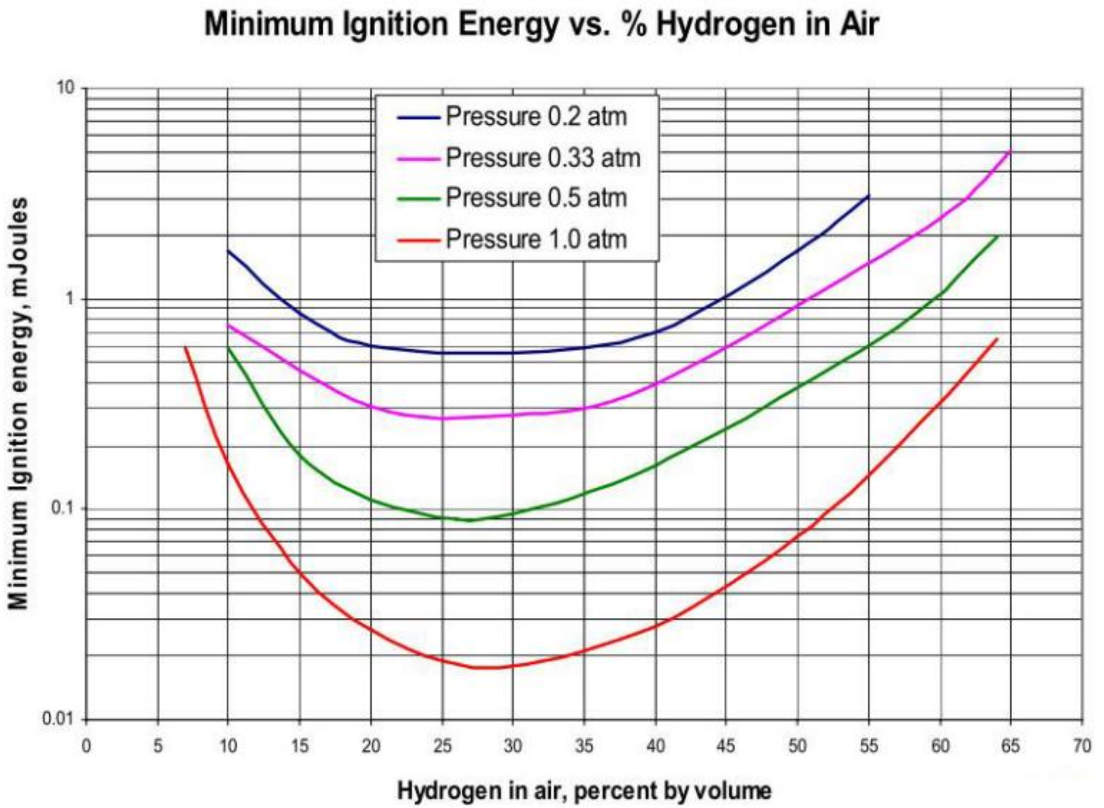
Required ignition energy

- Very small input of energy required for ignition: only 0.02 mJ at 30 % H_2 in air



H_2 generation – an example

- Scenario: Catastrophic corrosion of a 1000 m^2 heat exchanger:
- Assumption:
  - Acid (100C, 80%) leads to a corrosion rate of 10 mm/y
  - Amount of H_2 after 1 hour : approx. 9 kg (or 100 Nm^3)
- Volume of IP tower top ~ 700 m^3 (or less if only „dead“ volume is considered on top of exit, say 150m^3)
- H_2 concentration after one hour is between 15 and 65 vol-%, which is well within explosion limits (UEL reached after 5 – 20 minutes)

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Case Study: Hydrogen Explosion

After a short period after re-commissioning of Plant an Hydrogen-Explosion occured, this event was originated by ***acid cooler leak in closed loop system.***

Reason for leak could be: tube sheet failure, tube leak from acid/water side, maintenance, anodic protection, etc.

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Case Study: Hydrogen Explosion

What has happened?

Plant operated at partial load.

At a certain time high temperature in cooling water loop was realized, but communication failed.

+ 1:30 First local samples were taken

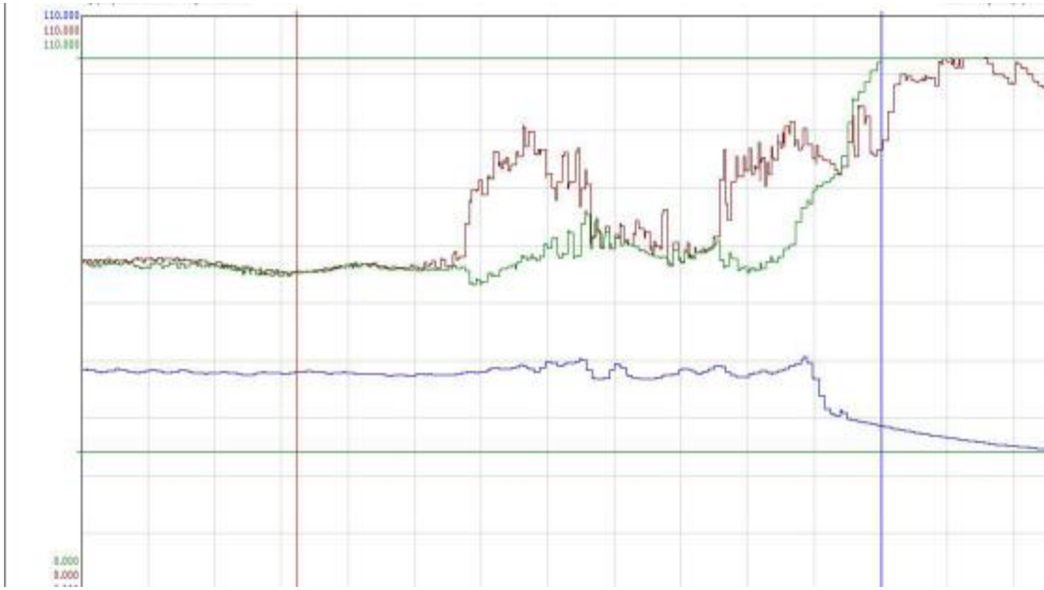
+ 2:05 Confirmation of result and shut-down initiated

+ 2:30 Acid concentration below 91%; CW pressure > Acid pressure

→ Cooling water stopped

→ Acid circulation and blower stopped

+ 3:00 First explosion



Intermediate Absorber
Cooling water temperature, out: red (cooler 1)
green (cooler 2)
blue (main blower)

Less than 30 minutes between stop of blower and explosion!!

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Case Study: Hydrogen Explosion

Have there been Warnings?

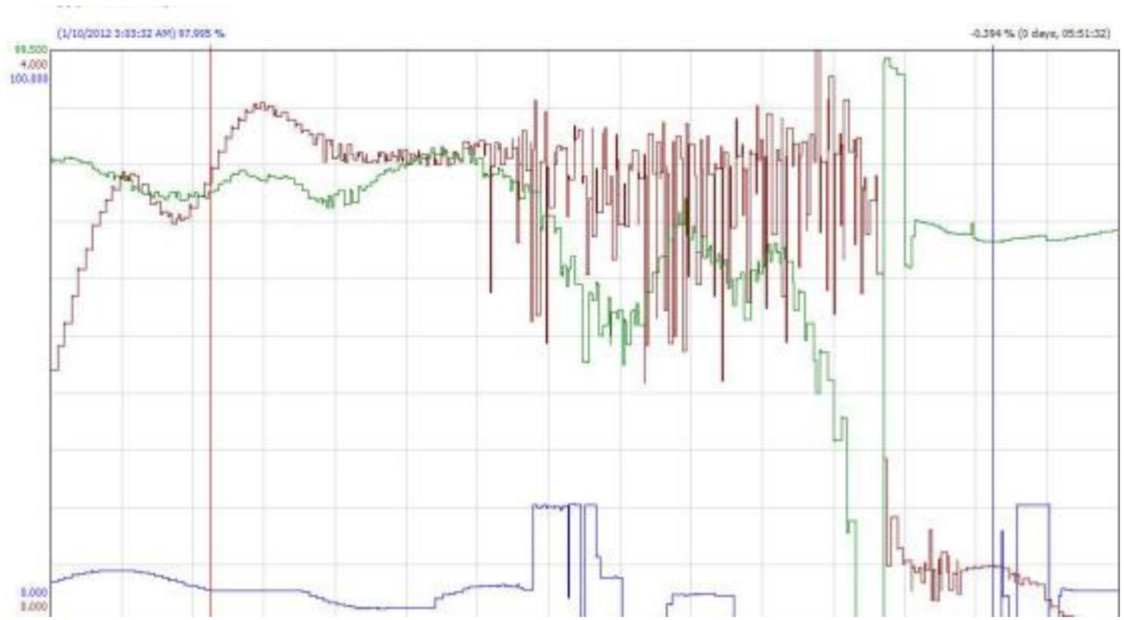
Cooling water temperatures

Pressure of cooling water in closed loop system (red)

Acid concentration (grün)

Dilution water (blue)

Anodic protection system (n.a.)



Instabilites in trend are good indication of up-set conditions!!

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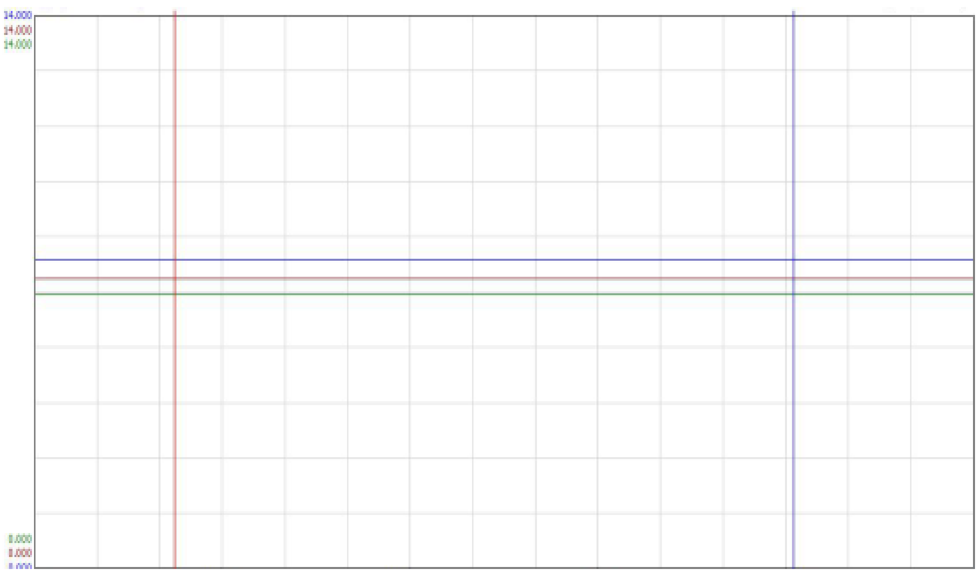
Case Study: Hydrogen Explosion

Why was the leak detected so late?

Each cooler is monitored by a pH-measurement.

No alarms during operation (!) .... as probes have not been re-installed (in other cases instruments bypassed, alarm ignored, etc.)



Static trends can tell something too!!

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Case Study: Hydrogen Explosion

What else supported the incident?

Closed loop cooling water systems have pressure levelling device to maintain cooling water pressure < acid pressure.

If this is not in operation; reaction in cooler a far more violent as water enters into acid.

Closed loop systems have typically smaller water inventory, which support formation of weak acid.

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Case Study: Hydrogen Explosion

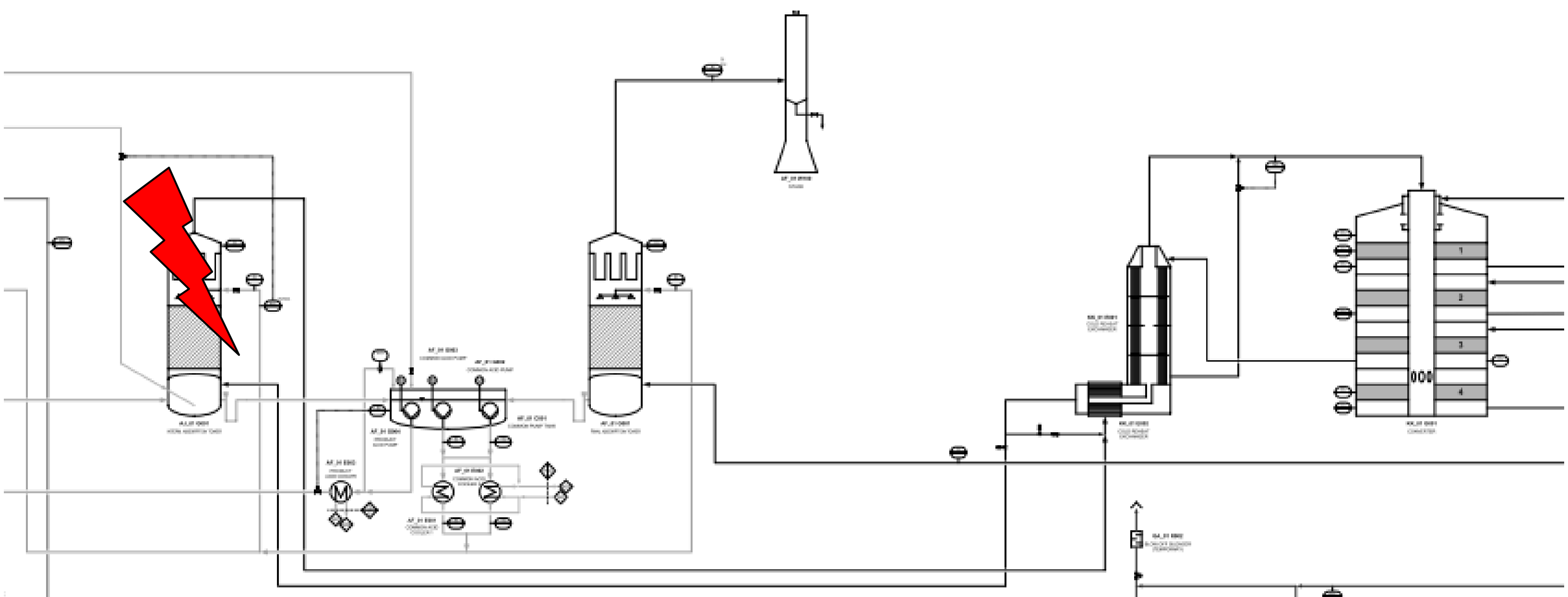
Which equipment was affected?

Damage must be expected by (I) weak acid, (II) explosion, (III) repair time

(I) Cooling water system, acid piping system, acid cooler, acid pumps, irrigation, system

(II) IAT (Candle filters, dome, packing), Cold Re-heat exchanger, Converter, Blower, (T/G-set)

(III) Acid piping, irrigation systems, catalyst etc.



Case Study: Hydrogen Explosion

Which equipment was effected?

Acid coolers: Completly
damaged

Acid Piping: Circulation was stopped early, no damage

Pump tank: No damage in bricklined tank (despite the fact, that acid of 85% was stored for extended time)

Acid Pumps: Removed imediately, no damage

Case Study: Hydrogen Explosion

Which equipment was affected?

Intermediate Absober

Candle Filters: Destroyed

Tube Sheet: Deformed

Packing: Contaminated by fibers

Dome and brickwork: No Damage

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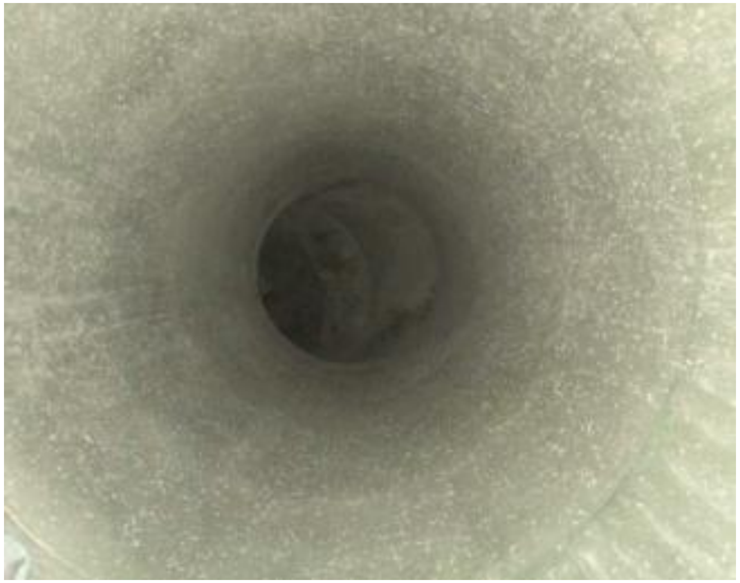
Case Study: Hydrogen Explosion

Which equipment was affected?



Heat Exchanger: Baffles damaged

Converter: No damage

Blower: No damage

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Conclusion

What can we learn ......

…. Hydrogen formation can be extremly fast under certain conditions. Due to the wide explosion range and low explosion energy the risk of hazardous situation is high.

..... A failure in an acid cooler (or boiler, economizer etc) can and will happen.

...... An early detection and fast isolation can help to avoid hydrogen explosions

...... Good operation and maintenance practice is fundamental (Interpret process data)

….. Consider infrastructure in adequate way

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Sustainable use of
Earth's natural resources