Hydrogen Safety
For
Sulfuric Acid Plants

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SYMPTOMS OF ACID COOLER TUBE LEAK

DROP IN pH OF COOLING WATER FROM THE COOLER

- 0.05 wt% H_2SO_4 (~0.01N) has a pH of 2 (Δ~5,800 micro-mhos/cm^2)
- 0.5 wt% (~0.1N) H_2SO_4 has a pH of 1 (Δ ~24,000 micro-mhos/cm^2).

IF LEAK IS SUBSTANTIAL OUTLET WATER TEMPERATURE WILL INCREASE

- Making 5% ΔH_2SO_4 raises the CTW temperature by 15 ^oF

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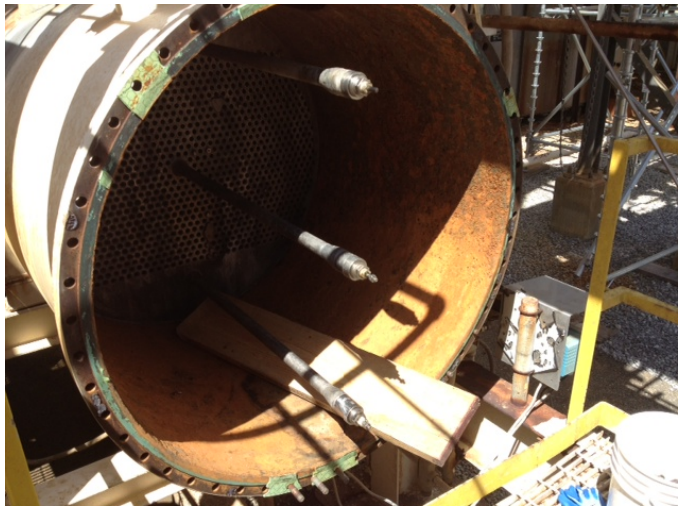
Hydrogen is also Present During Repairs

Brief Description :

Two employees were in the process of completing a weld repair on a shell-and-tube heat exchanger.

Tack welds were completed on the plug. When the employee initiated final welding on the plug, a flash fire occurred.

Due to close proximity to the work, both employees received minor burns from the flash.



Initial Findings:

- General work, confined space and line break permits were created and followed for the task
- Flammable vapor tests were conducted immediately prior to welding start with no issues detected
- Employee was wearing Nomex

Opportunities to Leverage:

- Ensure continuous monitoring during hot work
- PPE prevented more serious injury to employee
- Fuel source is likely hydrogen gas

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Hydrogen Safety Committee Observations and Conclusions

Members:

Solvay
Mosaic
Outotec
Chemetics
MECS
Rick Davis – Consultant
Lenny Friedman - Consultant

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$$Fe + H2SO4 \rightarrow FeSO4 + H2$$

$$H2 + 1/2\ O2\ \Delta Q/ > H2O$$

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General Observations

- A majority of water leak events occur without incident
- H_2 incidents predominately occur when
  - Substantial amounts of acid are diluted
  - Large surface area equipment is involved
  - The blower is stopped

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Weak Acid Excursion Causes

- Equipment failure
  - Nearing end of life expectancy
  - Malfunction
  - Defect
- Upstream sources
  - Significant waste heat boiler or superheater leak
- Operating/maintenance procedures
  - Incomplete or incorrect decontamination or commissioning
  - Lack of procedures or drains to remove condensed acid
- Inadvertent water dilution
  - Leaking dilution water control valve
  - Concentration control analyzer failure

Contributing Factors

- Recognition of the potential severity
  - Leaks rapidly escalate
  - Risk of collateral damage increases
  - Potential for damage outside of unit increases
    - acidification of cooling water circuit

- Response to a deteriorating situation
  - Sufficiency or ability to isolate/drain water
  - Ability to rapidly remove weak acid from the system

- Awareness of dangerous conditions
  - Corrosion of large surface area equipment results in high H_2 generation rates
  - Minimal oxygen is required (> 4 vol%)
  - Stagnant high spots allow mixture to reach the explosive limit

Conclusions

- When weak acid is present, H_2 will be generated
- H_2 was a wide explosive limit
- Ignition energy for H_2 is very low
  - (It will happen!)

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High Level Guidelines

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Hydrogen Safety Committee High Level Guidelines

•Minimize H2 formation by
- Separating weak acid from metal
  - Guidelines will be plant specific

- Minimize water ingress
  - Isolate the cooling water
  - Beware of H_2 formation in cooling systems
  - Provide economizer BFW bypasses

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Hydrogen Safety Committee High Level Guidelines

- Address H_2 accumulation
  - Blower purge
  - High point vents
  - N_2 purge
- Operational awareness / formal procedures
  - Emergency plans
  - Training
- Infrastructure
  - Expand Hazop scope to shared utilities
    - Cooling water systems

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Moving Forward

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Efforts Should Be Focused On:

- Early detection of leaks
  - pH or conductivity in acid coolers
  - Acid accumulation in economizers
- Mitigation
  - Shutdown procedures
  - Equipment evacuation
- Prevention
  - Avoiding the H2 explosive limit

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What Can Be Done To Prevent H_2 Incidents?

Technology suppliers

- Incorporate findings in HAZOP
- Adjust designs accordingly

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What Can Be Done To Prevent H_2 Incidents?

Operating companies

- Be on the lookout for indicators
- Keep training current
- Have written emergency procedures
- Regularly test pH/conductivity meters
- Transfer experience (Legacy planning and site to site)
- Test your operator's skills (Drills)

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A Final Thought

- Communicate information like what is being presented here to your operators!!
- Plan ahead. Prepare emergency procedures so that hasty decisions don't have to be made in a time of crisis.
- Adjust procedures based on experience

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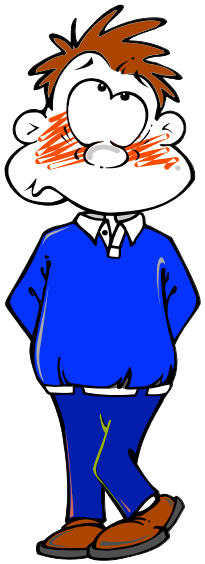

Sharing experiences might make you feel like you are standing naked in the sunshine…

But, feeling naked motivates one to become

"Stronger"!!

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Thank you!

The miracles of science™

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