Sulfuric Acid Plant Hydrogen Explosions Why Now- What Can We Do

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Why Are We Talking About Hydrogen "Again"

- 16 Hydrogen Incidents in Last 15 Years
  - Fortunately No Personnel or Environmental Damage to Date
- Pictures Show Damage From Hydrogen
  - Economizers
  - Converters
  - Interstage Towers
  - Acid Coolers
  - Candle Mist Eliminators

Economizer Ruptured Tube

Economizer Baffle

Horizontal Economizer

Acid Cooler Damage

Acid Tower Dome

Acid Tower Dome

Candle Fibers

Candle Damage

Converter Damage

"Don't guess at the solution, tell me what happened and why and the solution will be obvious"

- Plant Damage Caused by Hydrogen Generation & Explosion
- Hydrogen Formed by Weak Acid Corrosion
- Hydrogen Builds-Up in Stagnant Areas
- Why Now and Not Before 2000
  - Design Changes??
  - Operation & Maintenance Changes??

Where Does Hydrogen Come From

- **Hydrogen is formed in the reaction of metal and Sulfuric Acid: M + H_2SO_4 = MSO_4 + H_2**
- **Hydrogen in acid plants for hundreds of years**
- **Corrosion of metals in acid plant by H_2SO_4 produces Hydrogen**
  - **Carbon Steel Equipment (converters, boilers, economizers, superheaters, ducts, etc.)**
  - **Stainless Steel Equipment (converters, towers, pump tanks, pumps, ducts, piping, etc.)**
  - **Cast Iron Piping**

Gas Side Hydrogen

- **Due to Water Vapor in Gas: Poor Drying or Water Leak in Equipment**
  - **Sulfur Gun, Boiler, Superheater, Economizer**
- **Water Plus Sulfur Trioxide = Sulfuric Acid**
- **Sulfuric Acid Plus Metal = Hydrogen**
- **Corrosion in Coolest Places – Economizer, Cold Heat Exchanger**

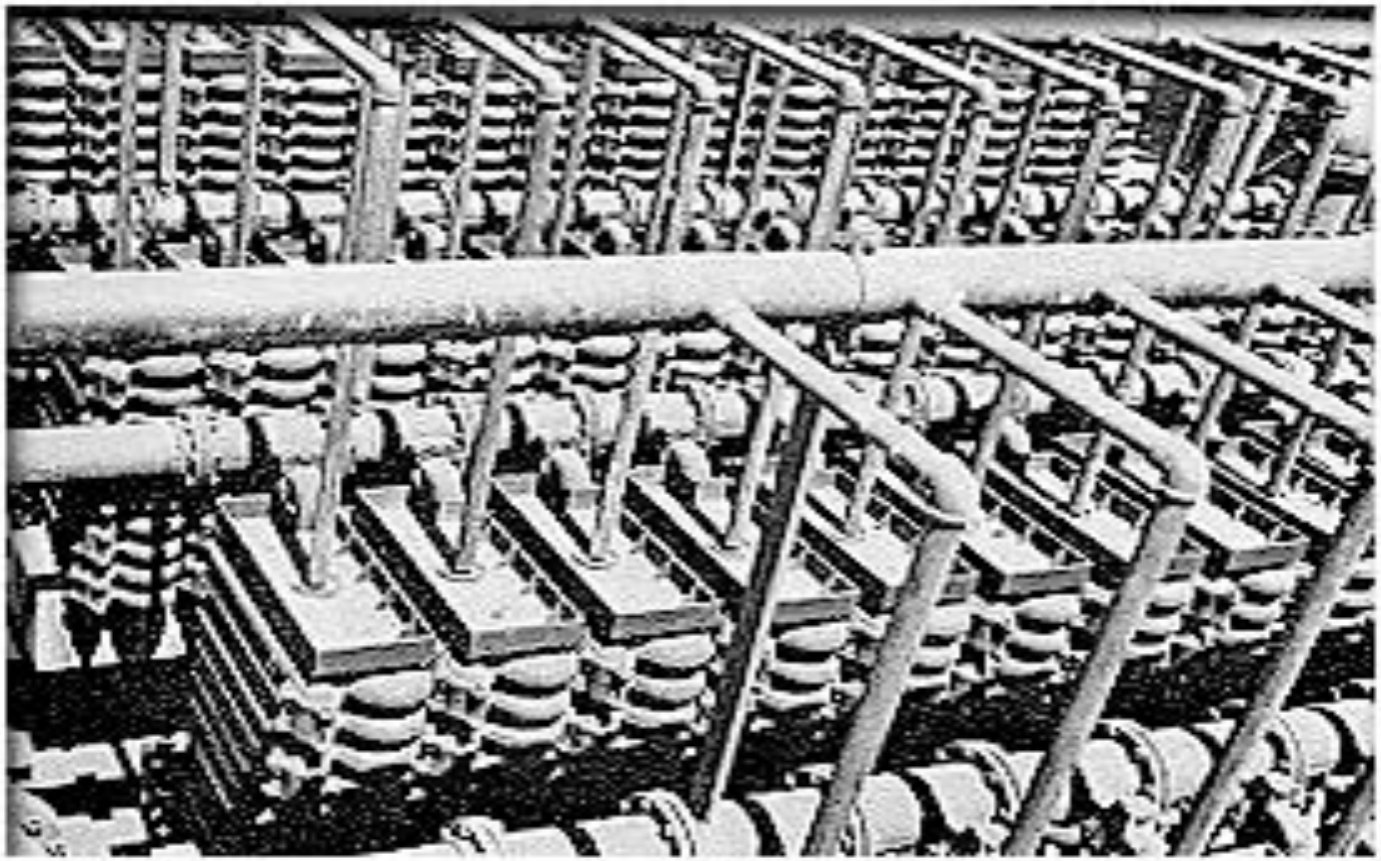
Hydrogen From Shell & Tube or Plate Acid Cooler Leak

- Leak of Water Into Acid When Acid Cooler Down Results in Rapid Corrosion & Hydrogen
- Shell & Tube Design For Over 45 Years
  - Keep Acid Pressure Above Water Pressure
  - So Leak of Acid to Water Will Not Cause Extensive Corrosion
- Explosions When Plant Shut-Down For Leak
  - Acid Off – Water On – Leak Water to Acid
  - Rapid Corrosion – Large Quantity of Hydrogen

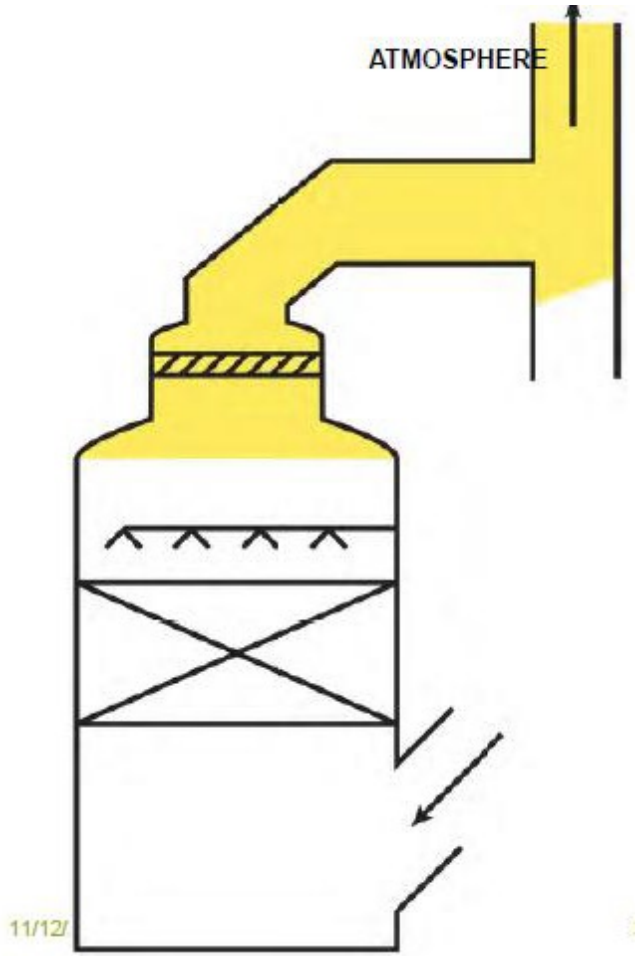
No Hydrogen Explosions Before 1970's- Minimum Exposed Metal, No Stagnant Areas & Draft Through Plant

- **Before 1970 Single Absorption Plants**
  - **Single Absorption Plants Draft to Stack**
  - **Draft Through Plant Purged Hydrogen**
  - **Acid Towers Acid Brick Lined, Internals Cast Iron**
  - **Absorber Top Out Exit Gas to Stack**
  - **Acid Piping Cast Iron**
  - **Acid Cooler Cast Iron AX Sections**
  - **Economizer Vertical In & Out – Cast Iron Gill Rings Over Tubes**

Cast Iron Sections



Absorber – to Stack



Change 1970's to 2000

- 1971 New Source Performance Standard 4#/Ton
- Double Absorption Essentially All New Plants & Most Existing Converted to Double Absorption
- Remainder Single Absorption Sodium/Ammonia Scrubbing
  - No Hydrogen Explosions in Single Absorption Plants

Design Changes 1970's On

- **Acid Cooler Changed From Cast Iron to Anodic Protected Stainless Steel Shell & Tube or Plate Type – early 1970's**
- **Economizer Changed From Cast Iron Gill Rings to Carbon Steel Finned Tubes**
- **Absorber Mist Eliminator Changed From Mesh Pads to High Efficiency Candle Type**
- **Double Absorption – No Draft Through Plant**

Acid Cooler Tube Leaks Caused Half of Hydrogen Incidents

- **Before 1970 Acid Cooling By Cast Iron "AX" Sections**
  - **Water Cascading Over Banks of Cast Iron "S" Shaped Sections**
  - **Could Not Leak Water Into Acid**
  - **Corrosion Hydrogen Into Air**
- **After 1970 - Shell & Tube Exchangers**
  - **Leak Water Into Acid Causes Corrosion & Hydrogen Into Plant Gas System**

Water to Acid When Plant Down

- **Early Cooler Designs – Cooler Vertical or Horizontal Above Pump Tank**
  - **Acid Pump Down –Acid Drains to Pump Tank, Water Drains Back to Cooling Tower**
  - **Problem Plugging Tubes & Changing Cathodes**
- **Design Changed to Horizontal at Grade**
  - **Acid Pump Down – Acid Stays in Cooler**
  - **Drain to Ground Or**
  - **Drain Pump to Remove Acid From Cooler**

Shell & Tube Acid Cooler

Cause of Hydrogen In Cooler

- **Acid Leak into Water Detected in Water**
- **No Valves in Water Side to Insure Full Water Flow at all Times**
  - **Full Water Flow Minimizes Tube Wall Temperature and Normal Corrosion**
- **Wrong – Cooler Tube Leak, Operator Shuts Down Acid Pump With Water Pump Still On**
  - **Acid Pump Down – Acid Stays in Cooler**
  - **Water Flows Into Acid – Rapid Corrosion**
  - **Hydrogen Into Gas Side of Plant**

One Hydrogen Incident 1970-2000

- **Incident at Farmland No 3 Plant - 1990**
  - **1960's Single Absorption Converted to Ammonia Scrubbing in 1975**
  - **Converted to Double Absorption 1980's**
    - **Horizontal Economizer**
      - **All Carbon Steel & Carbon Steel Finned Tubes**
      - **Same Elevation as Bottom of Converter**
    - **Interstage Absorber With High Efficiency Candles in Tower Upper Section With Side Gas Outlet**
    - **Double Absorption – No Draft Through Plant**

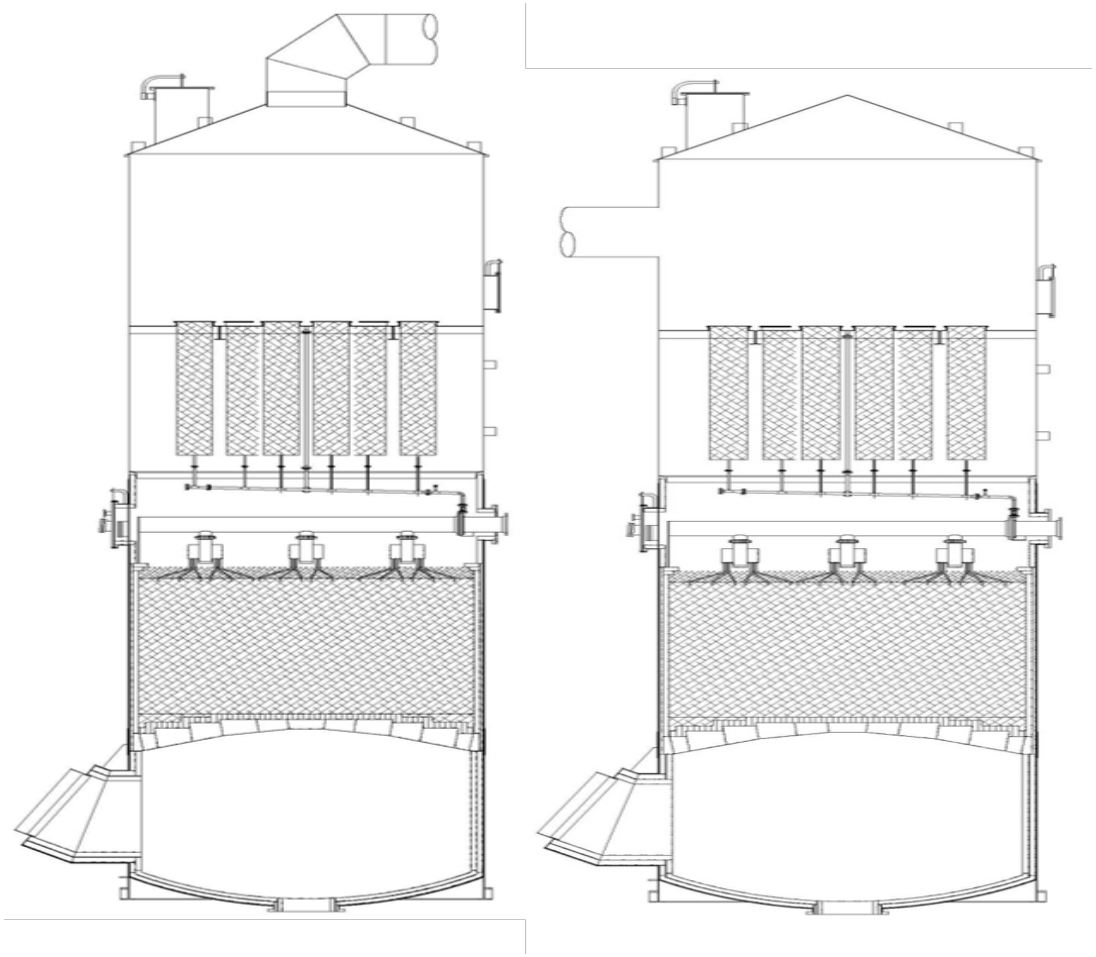
Farmland Incident

- Plant Shutdown – Could Not Get Sufficient Water to Boiler
- Economizer Leak – Horizontal Economizer
  - Weak Acid Filled Bottom of Economizer & Converter Floor
    - Corrosion of Bottom of Economizer & Converter & Coils Generates Hydrogen
- Hydrogen Builds-up in Top Section of Absorber – Stagnant Area Above Side Gas Outlet
- Hydrogen Explodes 1 Hour After Plant Shutdown & Economizer Drains Opened
  - Damage to:
    - Economizer & Gas Heat Exchanger, Gas Ducts
    - Absorber Mist Eliminator & Tubesheet
    - Absorber Acid Distributor & Packing

Farmland Incident - Why

- **Horizontal Economizer Provided Extended Surface For Corrosion & Hydrogen Generation**
- **Hydrogen Build-up in Top Section of Absorber – Stagnant Area Above Side Gas Outlet**
- **No Draft Through Plant - Double Absorption Design**

Top Vs Side Outlet – Stagnant Area



Design Changes 2000 On
16 Explosions in 15 Years

- **Anodic Protected Stainless Steel Shell & Tube or Plate Type Acid Cooler Located at Grade**
  - **Small Vent & Drain Connections**
  - **Operating & Maintenance Procedures – Tube Leak**
- **Absorber Mist Eliminator Candles**
  - **Top Outlet Changed to Side Outlet**
  - **Large Stagnant Area**
- **Economizer Drains – Small**
  - **Drains Not Checked for Water Leaks – Or Plugged**
- **Double Absorption – No Draft Through Plant**

Design Changes 2000 On

- **Alloy Equipment**
  - **Alloy Towers, Converters, Pump Tanks, Acid Coolers, Piping – No Correlation to Hydrogen**
- **HRS System All Alloy (1990) – 1-2 Incidents**
  - **Absorber Candles – Side Gas Outlet**
  - **Cooler/Boiler Steam Pressure Above Acid Pressure**
  - **Circulating Pump Designed to Fail on Dilute Acid**
  - **Cooler/Boiler Located Above Pump Tank**
  - **Acid Drains From Cooler & Piping, Steam Side Blocked & Vented**

What Can We Do to Minimize or Prevent a Hydrogen Incident

- **Eliminate Stagnant Areas for Hydrogen to Build-up**
  - **Use Absorber Top Gas Outlet**
  - **Use Single Absorption With Sodium or Ammonia Scrubbing**
- **Reduce Surface Area for Corrosion**
  - **Use Economizer Inlet Gas Flow Top Down and Outlet Gas Flow Vertical Up**
  - **Do Not Use Horizontal Economizer**

What Can We Do

- **Detect Steam & Water Leaks Early**
  - **Use large 3”-4” Cold Exchanger & Economizer Drains, Designed to be Rodded Out**
  - **Check Drains Regularly – Once Per Day Minimum**
  - **Design Drains for Operator Safety on Opening**

What Can We Do

- **Acid Cooler Installation**
  - **Install Acid Coolers Above the Pump Tank, Either Vertical or Horizontal**
  - **Install Interlock System to Stop Water Pump & Drain Water on Acid Cooler & Acid Pump Shutdown**
  - **Horizontal Coolers at Grade, Stop Water Flow & Drain Before Acid Flow**
  - **Drain Acid - Pump to Safe Place (Pump tank, Storage, Etc.)**
  - **Monitor & Manual Check Water Instruments (pH/ Conductivity) Minimum Once Per Day**
  - **Use Large Vent (1”) & Drain Connections (3”)**

What Can We Do

- **Purge Hydrogen From Plant**
  - **Single Absorption Plant Drafts Through the Plant & Purges Hydrogen**
  - **Double Absorption Plant Does Not Draft So Must:**
  - **Operate the Main Blower at Low Speed – Low Gas Flow to Purge Hydrogen From the Plant**
  - **Operate Main Blower Until All Weak Acid & Water are Drained From the Plant**

Acknowledgements & References

- **Hydrogen Study Group – Meetings, Discussions, Pictures and Presentations**
  - **Leonard J. Friedman - Acid Engineering & Consulting**
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  - **George Wang – Eco Services**
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  - **Rene Dijkstra & Michael Fenton – Chemetics-Jacobs**
  - **Bruce Garrett – MECSGlobal (New) & Steven Puricelli – Independent (Formally representing MECS)**
- **CIL-Chemetics Sulfuric Acid Cooler Operating Manual**
- **Manufacture of Sulfuric Acid by F.D. Miles, 1925**
- **Sulfuric Acid Manufacture – by A.M. Fairlie, 1936**
- **Manufacture of Sulfuric Acid – by W.W. Duecker & J.R. West, 1959**
- **Papers & Presentations by J.B. Rinckhoff & L.J. Friedman, 1973 to date**
- **Hydrogen Safety Presentations Can Be Obtained From Sulfuric Acid Today at www.h2so4today.com**

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