Sulfuric Acid Plant Hydrogen Explosions From Unusual Source

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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**

Why Gas Side Hydrogen Explosions Now and Not Past??

- **Past (Before 1970) Single Absorption Plants**
  - **Single Absorption Plants Drafted to Stack**
  - **Draft Through Plant Purged Hydrogen**
- **Double Absorption Plants Draft to Dry Tower**
  - **Draft Very Little – Valve At Dry Tower Inlet**
  - **Hydrogen Builds-Up at High Points: in Interstage Absorber Top & Dry Tower Top**
  - **Ignition by Hot Heat Exchanger or Furnace Gas**

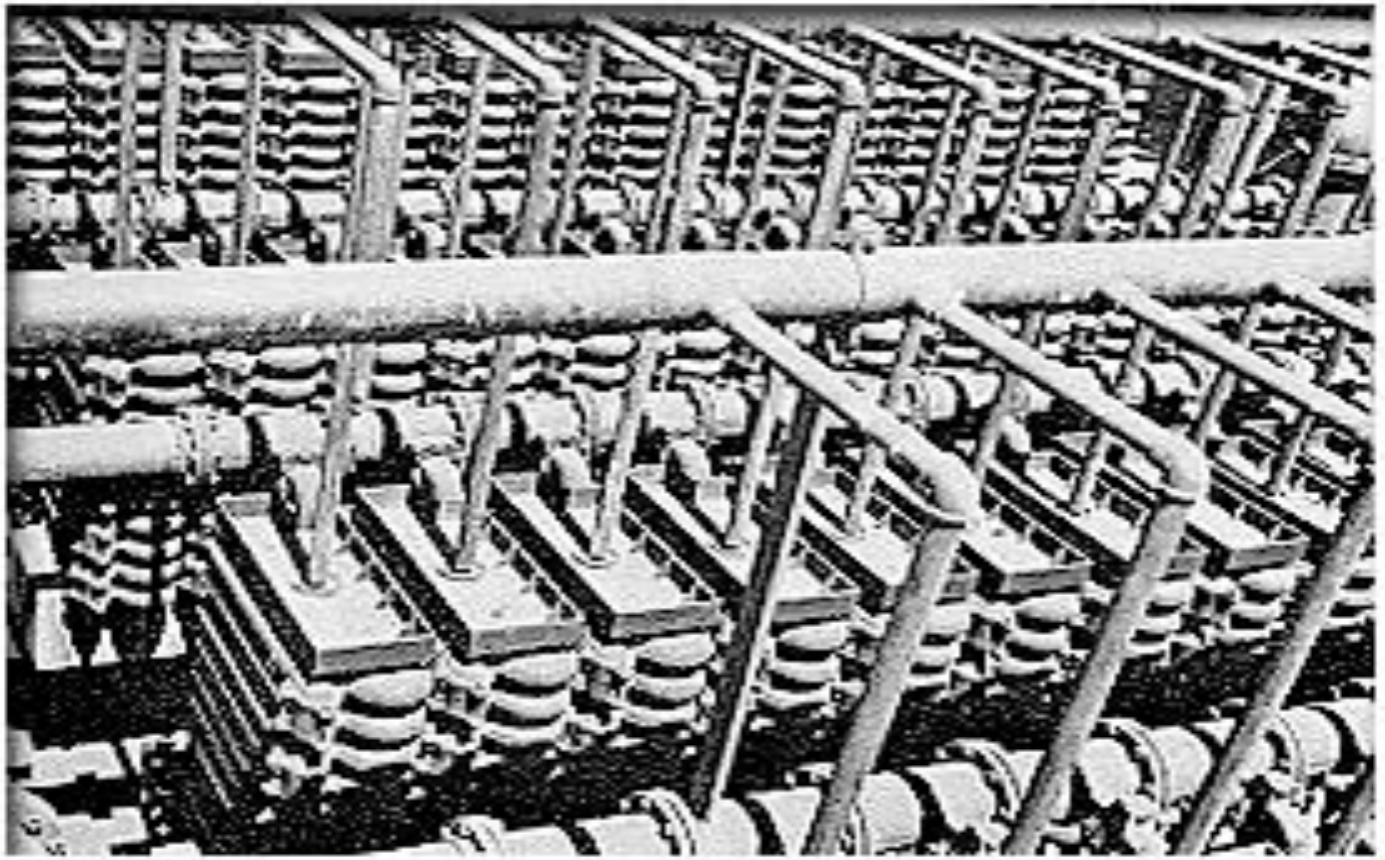
Hydrogen From Unusual Source "Acid Cooler Leak"

- **Leak of Water Into Acid When Acid Cooler Down Results in Rapid Corrosion & Hydrogen**
- **Shell & Tube Design For Over 40 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**

Why Acid Cooler Caused Explosions Now & Not Past?

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

Cast Iron Sections



Water to Acid When Plant Down

- **Early Cooler Designs – Exchanger Vertical**
  - **Acid Pump Down –Acid Drains to Pump Tank**
  - **Problem Plugging Tubes – Acid in Face**
- **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**
- **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**

Prevention of Acid Cooler Hydrogen Explosion

- Install Cooler Vertical So will Free Drain Acid
- Install Horizontal Cooler Above Pump Tank So Will Free Drain Acid
- If Cooler is at Grade:
- Stop Cooling Water Pump Before Acid Pump
  - Open & Drain Cooling Water Side of Cooler
- Stop Acid Pump & Start Drain Pump to Remove Acid From Cooler

Conclusion

- **HAZOP – Address Question of Acid Cooler Hydrogen Explosion**
- **Operations to Review Procedures When Acid Cooler Leak to Minimize Corrosion & Hydrogen**
- **Review:**
  - **Cooling Water Drain Valve Sizes**
  - **Need for Cooling Water Isolation Valves**
  - **Acid Side Drain Pump Connection & Sizing**

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