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Hydrogen Incidents in Sulfuric Acid Plants Why Now – What Can We Do

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INTRODUCTION

Contact sulfuric acid plants in their current form with vanadium catalyst have been operating since the 1920's with few if any reported hydrogen incidents. In the last fifteen (15) years there have been over thirty (30) major hydrogen incidents around the world, where hydrogen built-up in the sulfuric acid plant stagnant areas has detonated causing major damage to plant equipment, requiring extensive downtime for repairs. To date, fortunately, no major personnel injuries or environmental damage has resulted.

The question is: Why Now, and not in the 100 years before. What has changed? What are we doing different in the design and/or operation and maintenance of sulfuric acid plants today??

And of course, the most important question is: What Can We Do to reduce the potential for or prevent a hydrogen incident in sulfuric acid plants?

An industry group was formed a few years ago, including representatives from consultants, design engineering contractors, and operating companies, to study and analyze the hydrogen incidents around the world to determine the cause and suggest ways to mitigate the potential for hydrogen incidents. The main function of the hydrogen study group is to get the word out about hydrogen and suggest ways to reduce the potential for hydrogen incidents.

This presentation looks at the changes to the design and/or operation and maintenance of sulfuric acid plants that has led to the significant increase in hydrogen incidents. And provides recommendations to both designers and operators of ways to reduce the potential for hydrogen incidents. The presentation complements/extends the information and mitigation suggestions of the hydrogen study group.

WHERE DOES HYDROGEN COME FROM

The reaction of metals with sulfuric acid produces metal sulfate and hydrogen by the following reaction: M (metal) + H_2SO_4 (sulfuric acid) = MSO_4 (metal sulfate) + H_2 (hydrogen). The metals normally found in a sulfuric acid plant are carbon steel, various types of stainless steel, and/or cast and ductile iron. The amount of hydrogen produced and the rate of hydrogen production is a function of the metal and its corrosion rate in sulfuric acid (the concentration and temperature of the sulfuric acid, the acid velocity, etc.), and the surface area of metal exposed to the sulfuric acid. The metals; carbon steel, stainless steel and cast iron have relatively low corrosion rates when exposed to high concentration sulfuric acid in the range of 90% to 99.9% at normal temperatures and velocities. The corrosion rates increase significantly as the sulfuric acid concentration is reduced, and the temperature and/or velocity are increased. That is why the gas in the plant is dry, and gas cooling is by dry air quench or indirect exchangers; economizers, boilers, superheaters, gas-gas or air cooled exchangers, etc. A leak in any of the gas cooling devices results in moisture (water) entering the gas stream causing dilute sulfuric acid to condense in the cooler places in the plant – normally the economizer or cold gas heat exchanger. The resulting low concentration sulfuric acid condensate increases the corrosion rate of the metal in the exchanger causing hydrogen generation.

Another source of hydrogen is the shell and tube or plate type sulfuric acid coolers. The coolers normally operate with sulfuric acid at 93% to 99.9% concentration with cooling water providing the cooling medium. If there is a leak in the acid cooler tube or plate and the acid pressure is above the water pressure, acid will leak into the cooling water where it will be detected by the pH/conductivity instruments in the cooling water exit the cooler, and action taken to shut down the plant, drain the water then acid from the cooler and repair the leaking tube. On the other hand, if the water pressure is above the acid pressure during normal operation or when the plant is shut down, the water flowing into the acid will dilute the acid causing rapid corrosion of the metal and hydrogen generation.

Moisture or steam/water leaking into the gas stream and condensing as dilute sulfuric acid or water leaking into the sulfuric acid in the acid cooler diluting the acid, results in generation of significant quantities of hydrogen. That hydrogen builds-up in stagnant areas of the plant and detonates – normally when the plant is shut-down to correct the leak problem. The energy required to ignite the hydrogen is very low, so as soon as the hydrogen builds into the explosive range (about 3% to 96%) the hydrogen will explode. Prior to the 1990's there were no reported hydrogen incidents (explosions). However, in the last fifteen years or so there have been over 30 hydrogen explosions in double absorption sulfuric acid plants, most caused by

leaks in shell and tube or plate type sulfuric acid coolers, with steam system (economizer, boiler and superheater) leaks a distant second, and all when the plant was being or just shut-down to repair the leaking device, or when the device is being cleaned.

WHY NOW??

Sulfuric Acid Plant Design Prior to the 1920's

Before the mid 1920's essentially all sulfuric acid was produced by the "Nitration" or "Chamber" process (first introduced in 1746). In the Chamber process nitrogen oxide compounds are used to enhance the gas phase oxidation reaction of sulfur dioxide with oxygen and water vapor. The reactions are complex with the formation of the intermediate nitrosylsulfuric acid (HOSO_2NO or HSO_3NO_2 or SO_5NH), followed by the decomposition of nitrosylsulfuric acid by water in dilute acid (acid less than 80% H_2SO_4) to form sulfuric acid and nitrogen oxide (NO). The nitrogen oxide is regenerated by oxygen or air in the burner gas to nitrogen dioxide (NO_2), and the combination of nitrogen compounds (NO & NO_2 or N_2O_3) are recycled to the sulfur dioxide oxidation step. Large lead chambers, some as large as 500,000 ft³ for each 20 STPD acid production, were used for the oxidation step, providing reaction time and for the removal of the heat of reaction (hence the process name "Chamber" process). Gay-Lussac and Glover towers (named after the people who developed them) were used to react the nitrosylsulfuric acid produced in the Chambers with water in dilute (<80%) acid and to regenerate the nitrogen compounds. Product acid from the Glover tower is 60 Baume (77.67%) sulfuric acid. The acid could be concentrated by heating to 66 Baume (93.19%). Note: Today nitrosylsulfuric acid is formed in a contact acid plant by the reaction of sulfur dioxide with nitrogen oxides formed in the furnace and collected with the concentrated sulfuric acid mist in the absorption tower high efficiency mist eliminator. Brown nitrogen oxide gas is released when the high efficiency mist eliminator is opened and water or moisture in the air dilutes the nitrosylsulfuric acid, decomposing it to sulfuric acid and nitrogen oxides.

Chamber process materials of construction were lead and acid brick with little if any metals exposed to sulfuric acid, so little chance for hydrogen. In addition the continuous movement of gas in the plant from the draft up the Gay-Lussac tower to the stack provided little if any stagnant areas for hydrogen or other compounds to build-up. The stack gas leaving the Gay-Lussac tower normally contained about 1,000 PPM SO_2 and about 12%-18% of the nitrogen entering the plant as NO, NO_2 , and N_2O_4 . There were no metals to corrode, so hydrogen was not a problem (little if any generated), or even considered in the plant design or operation.

No hydrogen incidents were recorded in over 200 years of Chamber process operation.

The Contact Process 1900 to 1970

The early contact plants (before 1900 to middle 1920's), producing about twenty tons per day in a single train, bear little resemblance to today's plant. Early plants used platinum catalyst and required extensive gas cleaning systems ahead of the converter to minimize poisoning of the platinum catalyst (from halogens, arsenic, etc.). With the development of vanadium catalyst in the early 1900's (1899 through 1928) the contact process was on its way. A breakthrough in 1927 by Chemico with the development of the pressurized sulfur furnace with spray sulfur guns, combined with the use of vanadium catalyst produced a flow sheet very similar to today's design. Contact plants from the late 1920's to the early 1970's were single absorption and gradually increased in capacity from a few hundred tons per day to about 1,500-2,000 tons per day.

Why Not Before 1970's

Although there were some differences in plant design and equipment, the basic equipment arrangement, design, and materials were similar for all plants through the 1930's to early 1970's, until the clean air act of 1971 forced changes. The early plants were all single absorption with acid brick lined acid towers, and metals in the plant cast iron or cast ductile iron. Acid coolers were stacks of cast iron "AX" sections with the water flowing outside (open atmosphere side) of the cast iron. Acid piping was cast iron or cast ductile iron. One sulfuric acid plant designer/operator (Allied-General Chemical) owned a foundry, beat to a different drummer, and from the 1950's on used cast iron towers with acid reservoir in the tower base, stainless steel acid coolers (non-anodically protected) and stainless steel piping, with no hydrogen incidents.

Hydrogen explosions in a plant requires the production of hydrogen and an area for the hydrogen to build-up. The following is required for a hydrogen explosion:

Hydrogen generation - sulfuric acid corrosion of exposed metal.

Stagnant area(s) in the plant for the hydrogen to build-up.

Corrosive sulfuric acid – water or steam into the gas or acid system to dilute the sulfuric acid to increase the corrosion rate of the metal, increasing hydrogen production.

Increased surface of exposed metal that increases the amount of hydrogen produced.

The plant design prior to the early 1970's did not have the conditions (used corrosion resistant materials) for the generation of significant amounts of hydrogen, or stagnant areas of the plant for any hydrogen generated to build-up.

No hydrogen incidents (explosions) were reported during the period (1930's to early 1970's) in single absorption sulfuric acid plants. In fact, no hydrogen incidents in single absorption plants to date have been reported. Note: There may have been hydrogen incidents in the early period and in recent years that were kept secret (confidential) by plant operators at the request of their lawyers and insurance company. However, it is hard to believe that a hydrogen incident that damages the plant and equipment, shutting the plant down for 3 to 6 months, with costs to repair the plant, and the cost of lost production could be kept secret and would not be noticed anywhere in the world. The single absorption sulfur burning plant design included a main blower either before or after a drying tower, an acid brick lined drying tower with ceramic packing, cast iron acid distributor, and entrainment separator (metal or Teflon mesh pad, quartz pebbles, or ceramic saddle packing) above the main tower packing with a top gas outlet. The tower with a top gas outlet did not have a stagnant area and the system had little metal surface for the generation of hydrogen. The gas then flowed to the sulfur furnace and furnace boiler. Leaks in a boiler tube would add significant water into the gas stream, but at the temperatures, low sulfur trioxide (SO₃) levels, and high oxygen concentration, any hydrogen produced in the boiler was rapidly oxidized to water in the furnace and converter. Major water leaks (rupture of a boiler tube) would produce minor amounts of hydrogen when the plant was shut-down (limited SO₃ and sulfuric acid produced to corrode the metal), that would be drafted to the converter and oxidized to water. Hydrogen in the gas to the converter during plant operation would be oxidized by the oxygen in the gas, the high temperature and the vanadium oxidizing catalyst to water. Gas cooling around the converter included; converter boiler, superheater (internal or external), and air heaters (internal or external). Again, any water leak into the gas stream during plant operation would produce some hydrogen that would oxidize in the converter, and during plant shut-down, the draft through the plant would pass the hydrogen over the catalyst to be oxidized to water. The key to minimizing hydrogen effects on plant shutdown is the draft through the plant to the stack and the lack of a stagnant area in the acid towers.

The gas leaving the converter system would flow through an economizer to cool the gas before entering the absorption tower. The economizer, being the coolest surface in the gas stream, would condense any sulfuric acid from a water leak in the steam system into the gas. Initial condensation in the economizer would be Oleum and not be corrosive to carbon steel. Additional water would reduce the sulfuric acid concentration and become more and more corrosive to the steel. The economizer was constructed of a carbon steel casing with carbon steel tubes covered with cast iron gill rings, providing the surface for heat transfer and low corrosion cast iron to minimize corrosion if there were a water leak in the plant systems. Little hydrogen was generated in the cast iron gill ring economizer – low corrosion rate for cast iron over a wide range of sulfuric acid concentrations. Any hydrogen generated due to a water leak in the plant would flow with the gas from the economizer to the absorption tower. The absorption tower was an acid brick lined vessel with ceramic packing, cast iron acid distributor and entrainment separator similar to the dry tower. The gas outlet from the absorption tower flowed from the top of the tower to the stack. The stack was either mounted on top of the tower or to the side. The warm gas flowing up the tall stack to the cooler atmospheric air created a buoyant force, "draft" through the entire plant. Air-gas flowed from the inlet to the plant at the dry tower through the entire gas system and absorption tower up the stack to atmosphere. When the plant was down and the equipment was warm or hot the flow of gas (draft) would purge the plant of any hydrogen up the stack to the atmosphere.

The acid system included the acid brick lined drying and absorption towers, acid brick lined acid pump tanks, and cast iron (or cast ductile iron) acid piping, all with very low corrosion rates. Acid coolers were cast iron AX Sections consisting of extended surface stacks with the acid flowing inside the “S” shaped sections and water running down the outside. Any acid leak would flow to the water and to the water collection pit. The arrangement of the AX sections prevented water from entering the acid side and producing hydrogen.

Spent acid regeneration and metallurgical plant designs were similar to the sulfur burning plant design but had the sulfur furnace and steam system equipment replaced by gas-gas heat exchangers that used the heat generated in cooling the converter SO₂ to SO₃ oxidation reaction gas to heat the cool gas from the drying tower and blower to converter catalyst inlet temperatures. With that exception, equipment and materials were the same as the sulfur burning plant, with even less chance for acid corrosion and hydrogen generation since most if not all of the steaming equipment is eliminated.

Reason No Hydrogen Incidents Before Early 1970's

The reason there were no reported hydrogen incidents before the early 1970's was due to a number of factors: Minimum surface for acid corrosion; Corrosion resistant materials; No stagnant areas for hydrogen to build-up; and a Draft through the plant on plant shut-down:

The design of the drying and absorption towers had the exit gas flowing from a top center outlet, with no stagnant area for hydrogen build-up.

The single absorption plant design with warm-hot gas flowing from the top of the absorption tower to the stack created a draft through the plant on plant shut-down that purged the plant of any hydrogen produced.

The plant equipment provided little surface for hydrogen generation.

The acid cooler has acid inside the cast iron AX section stacks and water running on the outside, so any leak would be from acid to water and not into the gas stream or acid. No acid side corrosion or hydrogen generation to the plant system.

Towers, pump tanks and other equipment were acid brick lined. No corrosion or hydrogen generation.

Economizer steel tubes were covered with cast iron gill rings (extended surface) with no steel exposed (except casing and vessel bottom). Minimal corrosion surface and hydrogen generation.

Acid piping and tower acid distributors were cast iron or cast ductile iron. Minimal corrosion and hydrogen generation.

Changes 1970's to 1990's – Clean Air Act and Double Absorption

In December 1971 the U.S. EPA enacted the clean air act with regulations for sulfuric acid plants. The regulations limited emissions for new sulfuric acid plants to 4 Lbs. SO₂/Ton of acid produced and sulfuric acid mist to 0.15 Lbs. H₂SO₄/Ton. Existing sulfuric acid plants were regulated by the individual states (final approval by EPA) to meet a normal emission limit of 10 Lbs. SO₂/Ton before 1975. In all cases (except for a few grandfathered plants) the single absorption process alone was no longer adequate. Essentially all new sulfuric acid plants were double absorption, a process originally developed in the early 1900's to protect platinum catalyst from various poisons, and later rediscovered and patented by Bayer in the late 1960's. The Bayer double absorption process was licensed to and used by all of the designers around the world (Monsanto, Parsons, Chemico, Lurgi, Hugo Peterson, ChemiBau, etc. and their licensees). Original single absorption plants were either converted to double absorption or added a sodium or ammonia based scrubbing system to meet the new regulations.

Single Absorption–Scrubbing–No Reported Hydrogen Incidents

Many existing single absorption sulfuric acid plants met the new SO₂ emission regulations with the addition of ammonia or sodium based SO₂ scrubbing systems. The scrubbing systems were constructed of fiber reinforced plastic (FRP) towers and FRP or stainless steel (corrosion resistant to sodium and ammonia scrubbing solutions) tower internals (packing, trays, supports. etc.), and piping. Scrubber stacks were mounted on top of the scrubbing tower to elevations of 100 feet to 200 feet above grade. The potential for hydrogen generation did not increase with the addition of scrubbing systems, and draft through the plant continued.

No reported hydrogen incidents have occurred in single absorption-scrubbing plants to date.

Double Absorption-Over 30 Hydrogen Incidents

Essentially all new sulfuric acid plants used the double absorption process along with many of the existing sulfuric acid plants that were converted to double absorption. All had an absorption tower with gas-gas heat exchangers in the center of the process that created a cold trap, minimizing the plant draft to the stack. In addition, plants with a blower ahead of the drying tower were required to have a tight close valve to prevent back flow of furnace SO₂ gas to atmosphere via the dry tower and blower, preventing a draft through the plant. The intermediate absorption tower mist eliminator was of two types: Two stage mesh pads by Otto York Co. and Begg Cousland; or High efficiency "Brownian Motion" candles from ICI-Begg Cousland, Koch and Monsanto, with top center outlets from the tower.

The change from stacks of cast iron AX sections to anodically protected shell and tube acid coolers in the early 1970's was a major change in the potential for an acid cooler tube leak to generate large quantities of hydrogen. In addition, the energy crisis in 1973 increased the value of the energy recovered from the sulfur burning sulfuric acid plant. Recovering heat from the gas in the economizer ahead of the absorption towers became economical. The old wives tale of one designer that the gas to the absorbers could not be cooled in the economizer below 400 F was discarded and the gas to the absorbers was cooled to 300 F – 330 F with no effect on economizer acid condensation. The heat exchange surface area required for the additional cooling increased significantly (as the gas to boiler feed water delta T decreased), and the cast iron gill ring design could not be used. The economizer heat exchange surface became extended surface carbon steel finned tubes.

Design Changes 1970's to 1990's

The major changes to the sulfuric acid plant design in the period from the early 1970's to early 1990's were:

Interstage absorption system addition – Interstage absorption system increased SO₂ conversion efficiency to the required 99.7% or 4 Lbs. SO₂/Ton. But, added a cold place in the middle of the plant that essentially stopped the draft through the plant on shutdown.

Plants with the blower before the dry tower required a tight close valve at the blower discharge (ahead of the dry tower) to prevent back flow of hot SO₂ gas from the furnace through the dry tower and blower to atmosphere on blower shutdown, preventing a draft through the plant.

Acid coolers were changed from stacks of cast iron AX sections to stainless steel shell and tube exchangers, providing the potential for generating large quantities of hydrogen from an acid cooler tube leak.

Economizer design changed from cast iron gill ring covered tubes to carbon steel finned tubes to provide sufficient heat transfer surface area for the required additional energy recovery.

Economizer designs continued the use of vertical down inlet gas flow over the coils and vertically up exit gas flow, limiting exposed metal to the leaking tube coil and the bottom surface of the economizer, reducing exposed surface corrosion and hydrogen generation. Some designers used horizontal economizers in a few installations, providing increased metal surface for corrosion and hydrogen generation.

Plant size increased from about 1,500 STPD to about 3,000 STPD.

Hazop analysis during the period "did not" include consideration for hydrogen generation or explosion, as there were no reported hydrogen incidents until 1990.

Why Only One Hydrogen Incident in Period 1970's to 1990's

With the design changes outlined above; double absorption process eliminating draft through the plant, shell and tube or plate type acid cooler generating hydrogen on a tube or plate leak, and carbon steel extended surface economizer providing greater surface for hydrogen generation, it is surprising there was only one reported hydrogen explosion incident – Farmland No. 3 plant in 1990.

The Farmland No. 3 plant was a 1960's single absorption unit converted first to ammonia scrubbing (1975), then to double absorption (1980's) to meet Florida state SO₂ emission standards for existing sulfuric acid plants. The double absorption design included a horizontal economizer connected to the bottom (3rd) stage of the existing converter at the converter outlet elevation, and an absorption tower with candle mist eliminator and side mounted gas outlet. A leak in the economizer coils allowed weak sulfuric acid to cover the economizer bottom and bottom coils, along with the bottom (floor) of the converter. This provided a large extended surface for hydrogen generation. The hydrogen flowed to the absorption tower and collected in the stagnant area in the top section of the tower. About one hour after the plant was shut down and economizer drains were opened the hydrogen that collected in the top section of the absorption tower exploded. Investigation indicated the horizontal economizer allowed weak acid to corrode the floor and lower coils of the economizer, and the bottom of the converter, providing a large surface area for corrosion and hydrogen generation. The side gas outlet from the interstage tower provided a stagnant area for hydrogen to build up.

The Farmland hydrogen incident was presented by John Friedman of Farmland in 1991 to the local Florida section AIChE group at a monthly meeting in Lakeland with over 200 attendees representing most of the Florida fertilizer-sulfuric acid industry. The group's response to the Farmland incident was typical, "We have been operating sulfuric acid plants for many years and this has not happened to me or others I am aware of, so why worry". The subject of hydrogen generation or explosion was still not considered in a Hazop (hazard and operability analysis), MOC (management of change) or PSD (prevention of significant deterioration) review.

Shell & Tube Acid Coolers – Development - Shell and tube acid coolers have been used for many years (since the mid 1950's-early 1960's) in Allied-General Chemical (now Chemtrade) plants. The coolers are constructed of 304 stainless steel and operate in 99+% absorber acid and cold (<120 F) 93% drying acid. The Allied-General Chemical spent acid regeneration plants were originally single absorption with top gas outlets to the stack, and later converted to add-on double absorption with top outlet high efficiency candle mist eliminator vessels. Non-anodically protected stainless steel shell and tube acid coolers are still being used in many of these plants. The key to successful operation is operation of the absorber cooler at acid concentrations above 99%, and dry tower coolers at acid concentrations above 93% at acid temperatures below 120 F. The coolers are mounted in an elevated position, above the pump tank or tower acid reservoir, and free drain on acid/water shutdown. No hydrogen incidents have occurred in over 55 years. Other attempts with non-anodically protected shell and tube acid coolers at other operating conditions were not successful, with useful life less than one year.

In the late 1960's-early 1970's Canadian Industries Ltd. (CIL) technical group supporting the operation of the pyrite roasting sulfuric acid plant at the INCO Copper Cliff, Canada copper/nickel smelter, worked on the development of shell and tube acid coolers to replace the normal cast iron AX section acid coolers for a new plant to be added to the site. They first tried non-anodically protected shell and tube stainless steel exchangers (as used by Allied-General Chemical) and found a life of less than 6 months. The literature indicated anodic protection of metals as a means of corrosion protection, and they tried the Continental Oil developed Anatrol System, supplied by Magna Corporation. Bench scale and pilot tests were made. The group added anodic protection to the 316 stainless steel shell and tube acid coolers and found a range of voltage potential that would hold the corrosion protective oxide film in place. Other modifications resulting from early failures, included a no tube in baffle window design, and expanded acid nozzles to reduce velocity and turbulence. The early coolers were mounted vertically in the acid flow from the pump to the tower. Extended life with near zero corrosion resulted, and the Chemetics division of CIL was formed to fabricate and market the new anodic protected shell and tube sulfuric acid cooler to the industry.

To minimize corrosion of the exchangers a number of design and operating rules were required by CIL-Chemetics for the guarantees and proper operation:

The acid pressure must be maintained above the water pressure at all times - during normal operation and on shutdown, to prevent water from a leaking tube entering and diluting the acid causing low acid concentration corrosion of the stainless steel tubes.

During operation, must maintain the water velocity high to minimize water side fouling. Minimizing tube wall temperature, and acid tube wall temperature induced corrosion. Control acid temperature by acid side bypass, not water flow, to minimize acid temperature and velocity.

Must continuously monitor exit water pH/conductivity to rapidly detect a tube leak.

On a tube leak, must rapidly drain the water side first, then acid side of the exchanger to maintain the acid pressure above the water pressure.

Note: There was no mention in the cooler operating manual or any acknowledgement of acid leak corrosion producing hydrogen.

Initially the anodically protected shell and tube acid coolers were mounted vertically from the pump discharge to the tower inlet. Some were arranged horizontally above the acid pump tank. In both cases on shutdown the acid would drain from the cooler and acid piping back to the pump tank, and cooling water would drain back to the cooling tower basin, leaving the cooler and piping (water and acid) empty with no hydrogen generation. During the initial years of operation there were sporadic acid tube leaks, and a gun was developed to rapidly inject a plug in leaking tubes. Some plants indicated difficulty plugging tube leaks, or changing cathodes once every 2-3 years in vertical and elevated acid coolers. In response to operator's requests, most designers changed the cooler arrangement to locate the coolers at grade in a curbed area. Most installed a cooler drain pump to pump out acid from the cooler and piping on a tube leak or a shut down for maintenance. Water was drained to the ground in the curbed area to a pit.

The reasons for only one hydrogen explosion during the period 1970's to 1990's in double absorption plants are as follows:

Interstage Tower Stagnant Areas - There were essentially no stagnant areas in the interstage tower.

The interstage tower exit gas mist eliminator used by all but one designer was a pad type mounted in a reduced diameter stainless steel section at the top of the tower with center top gas outlet. No stagnant area.

One designer used high efficiency candles in the interstage tower with a top center outlet. Although the upper section of the tower was large with dished head and full tower diameter, the center top gas outlet provided minimum stagnant area for hydrogen build-up (except the Farmland tower that had a side gas outlet that provided a large stagnant area for hydrogen to build-up).

Operation and Maintenance Practice – With the relatively new double absorption process (from mid 1970's), good operation and maintenance practices were followed and included:

Economizer and cold heat exchanger drains were checked regularly, once per shift and later once per day, to check for acid condensation – water leaks. This was especially needed in plants with a high efficiency mist eliminator in the interstage tower that removed even the fine acid mist so a water leak did not produce a visible stack.

Proper shell and tube acid cooler operating procedures were closely followed.

Water side leak detection pH and conductivity meters were monitored and checked regularly for proper operation to rapidly detect an acid cooler tube leak. Manual operator pH/conductivity tests were made once per shift to once per day to confirm instrument readings.

Water side pressure drop was monitored regularly to insure maximum water flow at all times.

When there was a tube leak, the water was shut off and drained before the acid pump was shut down and acid was drained by the acid cooler drain pump. To maintain acid pressure above the water pressure.

Plant Purge-Removing one Protection – The draft to the stack on plant shut-down was eliminated by the interstage system and prevented by the blower discharge valve in blower before dry tower plants. Plants with a blower after the dry tower had a short time, about 3-5 minutes, gas purge from the turbine driven main blower rolling to a stop on shutdown.

WHY NOW

Changes 1990's to Date – Over 30 Incidents in 15 Years

There have been over 30 reported major hydrogen explosion incidents around the world since the late 1990's, all in double absorption sulfuric acid plants. All except one resulted in the explosion taking place in the top of the interstage tower alone or along with the dry tower, or in a few cases, the interstage tower exit duct. Essentially all tower explosions have been in towers with candle mist eliminators with side tower gas outlets (stagnant areas) or in the high point of the interstage tower exit duct. In one case the explosion occurred in the stagnant area in the top channel of a converter internal heat exchanger. Hydrogen generated in more than half of the incidents was from an acid cooler leak, two were from horizontal economizers, one from heat recovery system boiler and concentration control, and the remainder from standard steam system – boiler, superheater, and economizer leaks-corrosion.

Changes in the last 15 to 20 years that increased the potential for hydrogen generation and explosion.

Acid plant capacity increased from 3,000 STPD to about 6,000 STPD. Equipment increased in size.

Interstage Stagnant Area - The designers replaced pad type entrainment separators and mist eliminators in the interstage tower and many dry towers with either impaction candles or high efficiency candles. All towers now had a large diameter section on top of the tower. The change was made to increase acid particle removal efficiency, and for safety during maintenance of the entrainment separator/mist eliminator. It is safer to stand on a tubesheet to work on or replace a mist eliminator candle, than on an acid wetted slippery 4" or 6" stainless steel beam 8'-10' above the acid distributor to repair or replace a pad mist eliminator.

Many designers relocated the center top gas outlet to the side of the tower upper section. The side outlet saves a duct elbow, some duct length, and opens the tower dome for easier candle removal-replacement. This change provided a large stagnant area in the tower upper section for hydrogen to build-up.

Acid Cooler – Shell and tube acid coolers grew in size along with plant size. Most remained anodically protected, but some designers installed non-anodically protected shell and tube coolers using austenitic silicon stainless steel (18Cr-18Ni-5Si-2%Cu, an alloy used for many years in nitric acid service) marketed under the trade names, Saramet and Sandvik SX (and recently Zecor).

Essentially all acid coolers were located at grade. Most designers included an acid drain pump, others provided a drain connection for a pump out truck.

Acid and water side vents and drains remained small, the same size (3/4", 1" & 2") as the original small heat exchangers, significantly increasing acid cooler water and acid drain time.

Operator and Maintenance Practice - Long term leak free operation of acid coolers results in a loss of proper operation monitoring, and shutdown and draining procedures. Operator and maintenance attention to the acid cooling system was reduced by the long term leak free operation of the acid cooler. Monitoring of instrumentation (water pH and conductivity, water delta P, Anatrol meters and alarms, etc.), was replaced by computer system control by exception mode of operation, and operator attention moved to more pressing operation and monitoring duties.

Economizer – Safety concerns with opening economizer and cold heat exchanger drains blowing hot SO₃ gas and acid, along with extended periods of steam system and economizer leak free operation, resulted in operators extending the time between checking drains for acid condensate, from once per shift or day, to weekly or monthly, or not at all. When not operated regularly, the drains would plug with sulfate and debris and be useless for early detection of water leaks in the plant.

Some designers installed horizontal economizers (economic decision), without considering or understanding the additional exposed surface for acid condensate corrosion and hydrogen risk.

Heat Recovery System – In the late 1980's Monsanto Enviro-Chem recognized/noted the corrosion free operation of austenitic stainless steel at high temperature in acid at concentrations above 99% used since

the 1950's in Allied-General Chemical plants, and patented that use as the basis of its heat recovery system (HRS). From the early 1990's, Monsanto has installed many heat recovery systems operating with 99+% sulfuric acid at temperatures above 400 F, using 310 (austenitic) stainless steel, with a steam boiler used to cool the hot acid. The boiler operates with the water pressure well above the acid pressure. A boiler leak flows water to acid, diluting the acid, corroding the boiler, and circulating pump, stopping the acid flow. The acid cooler/boiler is located above the acid pump tank. When the acid flow is stopped, the elevated cooler/boiler drains the acid to the pump tank, while interlocks vent the steam and drain the boiler feed water. The circulating pump failure and acid cooler-boiler located above the pump tank minimizes corrosion and hydrogen generation. The design purposely constructs the circulating pump of materials to fail if the acid is diluted, and the elevated cooler/boiler drains the acid from the boiler and circulating piping on circulating pump failure (stopped acid flow). The change to elevated cooler/boiler, and failure prone circulating pump was done to stop circulating corrosive hot dilute sulfuric acid and reduce overall HRS system corrosion, not to reduce hydrogen generation, although it had that effect.

The HRS tower uses high efficiency candles and a side tower gas outlet, so one would expect more than the 1-2 hydrogen explosion incidents. The elevated acid cooler-boiler is the key to avoiding large amounts of hydrogen generation and additional incidents. The HRS system equipment is constructed of 310 stainless steel providing a large surface for weak acid corrosion and hydrogen generation. However, the failure of the acid circulating pump, stopping acid circulation on dilution of the acid and the elevated boiler/acid cooler minimizes hydrogen generation.

Alloy Equipment (converters, towers, pump tanks, acid piping, acid coolers, etc.) - During the 1990's, sulfuric acid plant equipment gradually changed from acid brick lined and cast iron to stainless steel. Stainless steel has been used for sulfuric acid plant equipment since the 1950's by Allied-General Chemical, but not widely used by others due to its cost being more than twice the standard materials of construction of acid brick, carbon steel, and cast iron.

The major change to stainless steel started in 1970 with the development of the anodic protected shell and tube acid cooler that gradually took over acid cooler service by the mid 1970's. A stainless steel converter design was proposed by Chemetics in 1979-1980 using an updated central tube design developed in the early 1950's by Chemico, Dorr Oliver, etc., substituting stainless steel for carbon steel and cast iron used in the earlier designs. For a replacement converter the stainless steel converter, although higher in cost, could be built remotely and lifted into place to replace a carbon steel cast iron converter in about one-third the time, saving plant down time. Alloy (stainless steel) towers and pump tanks of Saramet and Sandvik SX followed for the same reason – build remotely and lifted into place to replace old equipment, saving down time. By the mid 1990's, new plants were being built with alloy converters, towers and pump tanks. All of the alloy equipment went through a long learning curve (over 15 years) of various failures (scale of converter, and corrosion of towers and pump tanks). Eventually the cause of the problems became known and solutions were found.

The hydrogen incident history of plants with alloy equipment (over 25 years) indicates (except for acid coolers) they are not a significant contributor to hydrogen generation or explosions, even in the all alloy HRS system with one hydrogen explosion in 25 years of operating plants.

Purge Gas–No Draft through Plant – A draft through the plant on shutdown purges hydrogen from the plant equipment and is a significant contributor to minimizing hydrogen build-up and the potential for a hydrogen explosion. Single absorption plants alone or with a tail gas scrubbing system have not had a reported hydrogen incident from the 1920's to date, and the purge or draft through the plant on shutdown is a significant reason. All of the hydrogen explosion incidents have occurred in double absorption plants where the draft or purge on shutdown is minimum or eliminated.

What Can We Do??

“Don't guess at the solution, tell me what happened and why and the solution will be obvious”, were the words my first boss drummed into me 51 years ago (to a just out of school nuclear and chemical engineer) working in the technical group of a nuclear power reactor fuel reprocessing plant where much of the equipment was located behind 5 feet of high density concrete. With radiation and nuclear criticality issues, not a place for guessing solutions to problems. The above review of hydrogen incidents in this presentation

of “Why Now – What Has Changed” follows those well proven words. The review in the previous sections of this paper outlines what has changed in sulfuric acid plant design and operation in the last 15-20 years that resulted in over 30 hydrogen incidents (explosions) around the world in double absorption sulfuric acid plants, and not in the first 80 years of single absorption sulfuric acid plant operation, or the first 20-30 years of double absorption plant operation.

The knowledge, analysis and incite of the hydrogen study group combined with the above analysis of Why Now, leads to the following Acid Engineering & Consulting, Inc (AE&C) recommendations of design and/or operating changes to minimize or eliminate the potential for a hydrogen incident-explosion in sulfuric acid plants. Many of the suggestions are the result of public presentations by members of the hydrogen study group.

Eliminate Stagnant Areas for Hydrogen to Build-up

Use top outlet absorption and dry tower gas exit to eliminate stagnant areas

Consider adding automated high point vents to purge hydrogen on economizer and acid cooler leaks

Use single absorption with sodium or ammonia based scrubbing process – no stagnant areas and purge-draft through plant

Reduce Potential for Corrosion - Hydrogen Generation

Reduce Surface Area for Corrosion - Economizer

Use vertical down inlet gas and vertical up exit gas to minimize exposed metal (limited to leaking coil and vessel bottom)

Avoid use of horizontal economizer arrangement

Detect Steam System Water Leaks Early – Cold Exchanger & Economizer

Use large (3”-4”) cold exchanger and economizer drains to detect water leaks, design to be rodded out

Check cold exchanger and economizer drains regularly – once per day minimum for early detection of water leaks. Install drains designed for operator safety when opening and closing

Acid Cooler Installation to Minimize Potential for Corrosion and Hydrogen Generation

Install acid coolers above the acid pump tank either vertical or horizontal, so they free drain on acid circulation shutdown. Install system (interlock, etc.) to drain water (to ground or back to cooling tower basin) on acid cooler and acid pump shutdown.

If acid coolers are located at grade, shutdown and drain cooling water before stopping the acid flow.

Install interlock system to trip cooling water flow and drain water (to the ground in curbed area) on cooler leak shutdown and on acid pump shutdown.

Install an acid cooler acid drain pump to rapidly remove acid from the cooler to the acid pump tank, acid storage tank, or other safe location

Use large vent and drain connections to facilitate rapid draining of water and acid. Use 1” minimum vents and 3” minimum drains on the water and acid side of the exchanger

Monitor acid cooler instrumentation (pH/conductivity, etc.) both online and with once daily (minimum) manual operator checks to insure instruments are working correctly and to detect water leaks early

Purge Hydrogen from the Plant on Shutdown – Purging hydrogen from the plant on shutdown is a contributor to minimizing hydrogen build-up and hydrogen explosions.

Plants with tower side gas outlets should modify the tower outlet to a top outlet to eliminate stagnant areas in the tower, and/or:

Operate the main blower at low speed to purge the plant of hydrogen until the water and acid are drained from the acid cooler or economizer.

Single absorption plants with or without sodium or ammonia tail gas scrubbing draft to the stack and purge hydrogen from the plant. The plant draft-purge is a contributing reason there have been no reported hydrogen incidents/explosions in single absorption plants in the last 100 years of plant operation.

Double absorption plants do not draft on shutdown due to the cold trap (interstage absorption system), and the tight close valve in plants with the main blower ahead of the dry tower. A purge of the plant by the main blower should be done in plants with side tower gas outlets until the water and acid are drained from the cooler and economizer, also a good idea in plants with top gas outlets.

Consider adding automated high point vents to purge hydrogen on economizer and acid cooler leaks

Operation and Maintenance – Continued operator training for both normal operation, and handling of upsets and shutdowns (moving the plant to a safe down position, and preparation for maintenance) is necessary to insure operators are prepared for unusual plant upsets or acid or steam leaks that may occur infrequently.

Acid Coolers - Long term leak free operation of acid coolers results in a loss of proper operation monitoring, and shutdown and draining procedures. Operator and maintenance attention to the acid cooling system was reduced by the long term leak free operation of the acid cooler. Monitoring of instrumentation (water pH and conductivity, water delta P, Anatrol meters and alarms, etc.), was replaced by computer system control by exception mode of operation, and operator attention moved to more pressing operation and monitoring duties.

Monitor acid cooler instrumentation (pH/conductivity, Anatrol system and alarms, dilution water flow, etc.) both online and with once daily (minimum) manual operator checks to insure instruments are working correctly and to detect water leaks early.

When an acid cooler leak is detected,

Shut off the sulfur or SO₂ gas feed and reduce the main blower to a minimum flow setting to purge the plant.

Then shutoff the cooling water and drain the water side of the acid cooler to the curbed area or sump.

After the water side is drained, stop the acid circulating pump and drain the acid from the cooler using the drain pump if provided, or if not, by hose to a portable pump to a safe location or area.

Continue the gas purge by the main blower until the leaking acid cooler is drained (water and acid).

When the acid cooler is drained (water and acid), stop the main blower plant purge.

Economizers – Cold Heat Exchangers – Safety concerns with opening economizer and cold heat exchanger drains blowing hot SO₃ gas and acid, along with extended periods of steam system and economizer leak free operation, resulted in operators extending the time between checking drains for acid condensate, from once per shift or day, to weekly or monthly, or not at all. When not operated regularly, the drains would plug with sulfate and debris and be useless for early detection of water leaks in the plant.

Check economizer and cold heat exchanger drains once per shift or at a minimum of once per day to detect water leaks into the gas system early.

When a water leak is detected and the leaking equipment (boiler, superheater, economizer) is located,

Shut off the sulfur or SO₂ gas feed and reduce the main blower to a minimum flow setting to purge the plant. Continue the gas purge by the main blower until the acid condensate in the economizer or cold exchanger is drained.

When the acid condensate is drained from the economizer and cold exchanger, adjust the main blower flow to purge the plant in preparation for cool down to repair the steam/water leak.

SUMMARY

The intent of this presentation was to answer the questions, Why Now? and What Can We Do? to minimize and/or prevent hydrogen incidents-explosions in sulfuric acid plants. The recommendations are the result of the analysis of the incidents, the changes in the design and operation of sulfuric acid plants in the last 100 years, and the changes that resulted in the over 30 hydrogen explosions in double absorption plants in the last 15 years. The work of the hydrogen study group provided significant knowledge and analysis of the many hydrogen incidents around the world and formed a basis of this review.

The recommendations presented should be used together with the suggestions of the hydrogen study group, and others, in a Hazop of existing and new sulfuric acid plants.

Acknowledgements & References

Hydrogen Study Group – Meetings, Discussions, Pictures and Presentations

Leonard J. Friedman - Acid Engineering & Consulting

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Rene Dijkstra & Michael Fenton – Chemetics-Jacobs

Bruce Garrett – MECSGlobal (New) & Steven Puricelli – Independent (Formally representing MECS)

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PICTURES

Economizer Tube









Converter









