Incidents in Sulfuric Acid Plants - What Can We Learn?

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Abstract

Over the last ten years there have been a number of incidents in sulfuric acid plants causing equipment damage, lost production, releases to the environment, and danger or injury to personnel. The lack of dissemination of information (secrecy) on incidents has resulted in the repeat of incidents in other plants.

The Hazard and Operability Analysis required of all existing and new plants or changes to existing units, is a formal procedure to identify potential hazards and institute design or operating procedure changes to prevent the hazard (incident) from occurring. However, Haz-Ops have not been successful in the bringing about the incorporation of design changes or preventing many repeat incidents in sulfuric acid plants. Our long operating history and familiarity with the sulfuric acid plant and process causes us to overlook many potential hazards - because they have not happened in our plants.

This paper reviews a number of sulfuric acid plant incidents, indicating the cause and outlining potential changes to prevent the incident from happening. The ultimate goal is to identify hazards to improve the value of the Haz-Op in preventing incidents and to encourage others to disseminate information on incidents, potential hazards and design and/or operating changes to prevent incidents.

Hazard and Operability Analysis

The Hazard and Operability Analysis (Haz Op) is a formal procedure to identify potential operating problems or hazards and develop changes in the design to prevent the problem or hazard from occurring. The Haz Op is conducted by a team composed of a facilitator or leader with representatives from operating, maintenance, instrument, safety and engineering groups. Haz Ops are required of all existing and new plants or changes to existing units. The formal Haz Op procedure was developed to insure a uniform and thorough analysis of new and existing plant designs "independent" of the knowledge and experience of the Haz

Op team with the particular plant or process. The Haz Op questions are uniform for all Haz Ops and are geared to identify all aspects of operating and equipment variation, malfunction or abnormality.

Sulfur burning sulfuric acid plant Haz Ops have taken from one day to two - three weeks depending on the composition of the team and the thoroughness of the questioning and answers. Longer Haz Ops however, do not necessarily mean a more complete analysis. From participating in numerous Haz Ops I conclude the thoroughness of a Haz Op to identify potential hazards is a function of the team members, their knowledge and experience the sulfuric acid process, equipment and operation, and most important, their knowledge of previous incidents, hazards, and problems with their or other sulfuric acid plants. In many cases, being overly familiar with the plant or process (many years of sulfuric acid plant operating or design experience) leads many to gloss over potential hazards - because they have not happened to them. We have all heard the statement "I've been running (or designing) sulfuric acid plants for over twenty years and have never seen that happen".

the key to a complete and thorough Haz Op to insure a good operating, safe plant complying with environmental regulations and avoiding incidents that could damage equipment, injure personnel or release contaminants to the environment is a Haz Op team with sulfuric acid design and operating experience and knowledge of incidents in other sulfuric acid plants.

Acid Plant Incidents

The following section describes a number of acid plant incidents that have occurred numerous times in plants around the world. In most cases, the incidents occurred in plants that have undergone rigorous Haz Ops and plants with many years of operating experience. A review of many plants operating today will show few with designs or systems to prevent the hazards outlined below.

Superheater Tube Rupture - Conversion heat in many sulfuric acid plants (sulfur burners and some high gas strength regeneration and metallurgical plants) has been used to produce superheated steam in boilers, combination superheater - economizers, and superheaters for over fifty years. These units are typically constructed of carbon steel. In the last fifteen years, many designs have incorporated a steam superheater to cool the gas between the first and second catalyst bed or to upgrade an existing plant by augmenting the furnace or converter boiler with a superheater. The hot gas (high tube wall temperature) requires a structurally strong material at the elevated temperature and one resistant to high temperature SO2 scale. Installations have used alonized chrome - moly steel and stainless steel tubes and fins. Use of stainless steel has become common in sulfuric acid plant gas streams; in converters, hot gas heat exchangers, hot ducts and hot steam superheaters.

There have been a number of failures of stainless steel steam superheaters in the last fifteen years, some failing in less than one year, and some after five to ten years. The failures have occurred in the tube return bends and were attributed to caustic stress corrosion cracking. The caustic was from boiler water carry-over attacking the more highly stressed stainless steel return bend in the superheater. A literature search reveals a paper presented at the NACE meeting in 1985 " Corrosion 85" by Dean, Grab, and Watkins Jr., of Air Products and Chemicals, Inc., titled "Superheater Design Criteria to Avoid Cracking of Austenetic Stainless Steel by Caustic". The paper analyzes a number of stainless steel superheater failures in Air Products petrochemical plants, identifying caustic stress corrosion cracking as the cause. the paper recommends means to prevent the problem - minimize boiler water carry-over, and use stainless steel above a minimum temperature.

The information on stainless steel superheater tube failures was in the literature, available to all in 1985. Failures have occurred in sulfuric acid plants since the late 1980's, and we are still designing and operating plants with stainless steel superheaters as if no problems have ever occurred. Repeated Haz Ops have not identified a potential problem or hazard, even though one clearly exists.

Metal Dry Tower Corrosion - There has been a move in the industry (pushed by some acid plant contractors) to install the more expensive and less flexible silicon stainless steel (Saramet or Sandvik SX) "metal tower". A few installations have been dry towers. Use of metal towers in dry tower service has led to severe corrosion (leaks in the tower shell) in the area of the tower below the gas inlet. The corrosion rate of silicon stainless steel is dependent on the acid concentration and temperature. Corrosion in dry towers occurs when the moisture in the gas is absorbed into the acid near the wall of the tower below the gas inlet, diluting the acid. One band-aid method of protecting the tower shell near the gas inlet is to spray acid from the pump tank on the tower wall. A more positive protection is to brick line the lower section of the tower. Haz Ops apparently did not uncover the acid dilution - tower corrosion problem, and metal dry towers continue to be marketed and sold.

Sulfur Explosion - There have been a number of sulfur explosions in sulfur burning sulfuric acid plants. These have occurred with sulfur feed to the plant and the main blower put into surge by rapidly closing off the gas flow (closing dampers - closing both the boiler exit and bypass dampers, etc.). This causes the blower to go into surge (cycle of air flow then no air flow) with sulfur vapor reaching an explosive mixture in the plant equipment. In one case the explosion occurred in the back of the furnace and inlet to the boiler, twisting the furnace and boiler, forcing them apart, and bending the boiler risers and downcomers. In another case, the explosion occurred on top of the first bed in the converter, blowing a portion of the converter top head and inlet duct about 50 - 100 feet. In both cases an operator inadvertently closed a bypass and exit damper with the blower surge protect plant trip bypassed, jumpered or not there at all. Fortunately, in both cases no one was injured. A simple low-low blower discharge pressure plant and blower trip is all that is required to safely shutdown the blower and sulfur feed, preventing an explosion.

AE&C was involved in a recent project where the sulfuric acid plant contractor refused to trip the blower on a surge condition, insisting on a high pressure blower trip (does nothing) and a black box surge system from a compressor sub-vendor. So even proven experience of hazardous conditions and a thorough Haz Op can not deter lack of knowledge and the fear of admitting one does not know everything. The Haz Op procedure was developed to overcome people problems - but is not effective in all cases.

Acid Pump Tank Explosion - A rupture of the pump tank roof and rapid release of pressure (explosion) occurs in a strong acid pump tank when steam generated by the rapid dilution of acid causes overpressure in the tank leading to catastrophic failure of the pump tank roof and connecting acid piping. The hazardous situation is the result of the dilution water valve leaking into a pump tank with the circulating pump down. The water (sp.gr. 1) forms a layer on top of the acid (sp.gr. 1.8). When the pump is started, rapid dilution of the acid raises the temperature producing steam, overpressureing the tank.

Many plants have recognized the problem, requiring the operator to manually close the dilution water block valves when the pump is down. Occasionally an operator forgets or is busy with something else (an acid leak many times is the reason the circulating pump is shut down). Modern plants trip the dilution water auto valve and require the operator to close the block valves, hoping the auto valve closes fully (nothing in the seat) and the operator remembers to close the block valves. A more positive means is required to protect the plant from this hazard. A simple double block and bleed on the 1" or 2" water line, activated whenever the pump is shut down prevents the hazard.

Heat Recovery System (Diluter) - The problems with the HRS system are a prime example of secrecy perpetuating and preventing solutions to serious problems, and how operators sharing problems and attempts at solutions have gone a long way to making a bad situation almost livable. The HRS diluter has been a major problem area since the first HRS unit started up. During initial operation dilution of the hot (>400 F) acid with water resulted in steam generation in the stream and severe vibration from the bubbles collapsing. The vibration severely damaged the Teflon lined piping and acid distributor, resulting in severe dilute acid corrosion of the tower internals, mist eliminator and gas heat exchanger. The designer envisioned dilution problems in the initial design, locating the diluter as close to the acid inlet to the tower as possible. The vibration required extensive bracing of the first units structure. Concern with the vibration caused the designers to locate succeeding units diluter on the ground with significant anchoring, However, no changes were made to solve the vibration and equipment damage problem. The designers maintained a high level of secrecy concerning the many HRS problems, denying publicly at technical meeting around the world any problems existed. Sales presentations indicated no operating or equipment problems. Eventually, HRS units were built in the U.S. HRS plants in Florida and North Carolina became, in the words of one HRS system operator "full scale pilot plants", trying to solve problems kept secret for many years.

Had the problems been public, the concerted effort of sulfuric acid plant designers and operators could have attacked the problems and gone a long way toward solving them. Instead, new HRS plants were installed with the anticipation of trouble free, reliable operation, only to find the new unit to be a 2000 STPD - 3000 STPD pilot plant.

Haz Ops were performed on each of the HRS systems installed in the U.S. without uncovering the potential problems -hazards. Again the Haz OP procedure could not overcome the lack of knowledge of problems in other plants (secrecy). Operators sharing information have contributed to mutually overcoming many of the problems with the HRS system - many remain.

Tower Packing Failure - There have been a number of incidents where the acid tower packing support has failed, dropping the packing into the bottom of the tower. Causes of packing support failure vary from mechanical failure, thermal shock, to an acid wave knocking over the packing support arch or dislodging the packing support itself. In each case prevention is simple and low cost.

Thermal shock failures occur when the converter is heated with the acid circulation off. As the heating cycle continues, hot gas enters the absorption tower, heating the packing support. When the acid circulating pump is started, the cold acid causes rapid cooling of the support beams (thermal shock) resulting in beam failure. A simple interlock to prevent blower operation when the acid pump is not running prevents the hazard.

Acid surge knocking over the packing support arches or displacing the packing support beams occurs when the acid level in the tower increases to partially block the gas inlet. The gas flow - pressure causes an acid wave in the tower, resulting in packing support failure. In elevated towers, acid builds up when a brick or other object partially restricts the acid flow from the tower to the pump tank. Level instrument failure in towers at grade can result in excessive level in the tower. A simple independent high-high level alarm and plant trip can prevent the problem. In fact, acid towers are not designed to be liquid full, so proper design practice requires an overflow or separate high alarm - trip.

Mechanical failure of packing supports can be due to a manufacturers defect, damage to the beams or support blocks during installation, or damage from operation (temperature excursions, bumping the packing, etc.). Inspection during turnarounds usually detects cracks or damaged beams or supports many months before failure. Tower inspection at each turnaround (every one - two years) is well worth the effort.

Haz Ops routinely fail to identify the thermal shock and high level hazards, even though high temperature and high level are specific questions in the Haz Op procedure. AE&C is not aware of an acid plant with an elevated tower with a high level alarm, and very few towers at grade have independent high level alarms - trips.

Mist Precipitator Explosion - Metallurgical and regeneration type sulfuric acid plants use tube type wet electrostatic precipitators to remove sulfuric acid mist and solids from the SO2 gas. Some of these plants have high hydrocarbon levels in the SO2 gas stream. Lead sinter gas and copper roaster gas are examples of gas streams where the ore flotation reagents (hydrocarbons) are vaporized into the gas stream to the acid plant. Problems with fuel burners in regeneration plants at start-up can also put high levels of hydrocarbons into the gas. If the power is turned on the electrostatic precipitator with high levels of hydrocarbons in the gas an explosion can occur. Many precipitator explosions have occurred in sulfuric acid plants over the years. The prevention is simple and low cost - provide a purge of the system to remove the hydrocarbon laden gas before permitting power to the precipitator (main blower running for five to ten minutes before power can be turned on to the precipitator). An equipment purge is similar to a burner control system where a purge of hydrocarbons from the furnace is required before the pilot can be lit.

Conclusion

There are many more incidents that have occurred in sulfuric acid plants over the years. Each operator has experienced their own. We all can learn form our own experience and from the experience of others. Sharing information on incidents and hazards is an effective means of preventing bad things from happening, damaging equipment, injuring personnel, or releases to the environment. The Haz Op and our own experience has given us a false sense of security.

The intent of this work was to demonstrate a major deficiency in the Haz Op analysis in preventing damaging and hazardous incidents, and by illustration the vulnerability of many plants to incidents that have happened in other plants. It would be hard to live with oneself if withholding information on a hazard resulted in the severe injury or death of someone. The paper is a plea to the industry to share information on incidents and hazards.