NEWSLETTER

June 2016
Year IV - Edition LIVI

INSPECTION & ENGINEERING - SOLUTIONS & TRENDS

SPECIAL EDITION

Sulfuric Acid Safety and Mechanical Integrity

EDITORIAL

Dear readers, here we are moving fast into the second part of the year; and at this point we are proud of our safety performance; which includes not only our staff, but also our clients, contractors and suppliers. At the same time we have conscience that complacency is always around and mostly when we are good and successful in what we do.

With the threat of complacency around is always good to discuss about the safety and mechanical integrity focus that high consequences process and systems have developed, I'm talking about the aerospace and nuclear industry. It is well known that the safety factors applied to the design of components in aerospace and nuclear industry are high, but it is not fully understood the additional layers of protection they have developed. Where we could highlight very detailed operational hazards analysis, step by step procedures supported by checklists, extensive, intensive and continuous training, proactive risk management, formal processes for failure root cause and ultimately as the last layer of protection when all the above could fail, they are very strong in personal protection equipment discipline.

The safety and mechanical integrity culture developed in those industries is a reference and a model to follow when we have the determination to eliminate incidents and mechanical integrity failures. We don't need to work in the aerospace and nuclear to adopt this culture; in fact we have opportunities in critical high risk processes we deal with in the oil & gas industry.

We have dedicated this edition to one of these critical high risk processes and its challenges in safety and mechanical integrity. In this edition we are going to discuss details of Sulfuric Acid Safety and Mechanical Integrity

Francesco Solari
Inspfalca President.

ACHIEVED

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MAN HOURS WITH NO **ACCIDENTS**

INDUSTRY COLUMN

My experience working in refinery units that utilizes acid as catalysts

By Por Beth Thomas
Industrial Solutions

My first exposure to the refining mechanical integrity world was in alkylation units as Ultrasound Level I Inspector. I had the opportunity to work in both Sulfuric and Hydrofluoric Acid units and what I learned working in those units made me a more safety and mechanical integrity conscience person.

My first shocking experience was when I learned that in order to get into the unit special suits must we wear it and a step by step decontamination process must be followed in order to get out and remove the potentially exposed personal protective equipment (PPE) used; I thought "this is a serious business" and the things that came to my mind where What if a breach of the PPE occurs? Also how likely was an acid exposure?

I went through high quality training that allow me to reduce my legitimate fears and convert them into a safety and mechanical integrity focus that I carry even today in all I do.

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My today's understanding of the degradation mechanism in Sulfuric and Hydrofluoric Acid units and my understanding of all the risk mitigation protocols, makes me think that the likelihood to have incidents in these units is lower that other units where the respect, conscience and focus I developed is not commonly present.

My advice for those that have not had the opportunity to deal directly with these units is to get familiar with the safety and mechanical integrity details of Sulfuric and Hydrofluoric Acid units; which will make you a strong safety and mechanical integrity leader.

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LESSONS LEARNED

A story on complacency in sulfuric acid risk management

The U.S. Chemical Safety Board (CSB) motivated by a series of incidents that have been occurring in a refinery in the West Coast of USA; has recently released a report that includes key process safety findings related to safety culture, safety indicators, and the continued need for a proactive regulator to conduct preventive inspections.

On February 12, 2014, an incident occurred at this Refinery located in Martinez, California; which burned two workers and released an estimated 84,000 pounds of sulfuric acid. Less than a month later, on March 10, 2014, sulfuric acid sprayed and burned two contract workers during the removal of piping. Both incidents occurred in the refinery's alkylation unit – where high-octane blending components are produced for gasoline. This refinery also has a history of previous years acid sulfuric related incidents.

In the opportunity of the release of this report CSB Chairperson Vanessa Allen Sutherland said, "The CSB urges all refineries to review the key findings and conclusions of the board's case study and to apply those learnings to their own facilities. It is imperative that companies continually work towards improving their operations in an effort to prevent future incidents and ensure the safety of their workforce."

The CSB's case study examines this Refinery through the evaluation of previous incidents, worker statements, gaps in safety standards, deviations from established procedures and practices, and past efforts to assess and strengthen site safety culture.

The investigation found a number of safety culture concerns at the refinery, such as:

- Characterization of the February 2014 incident as a minor injury while the incident have been classified as the most serious type of process safety incident under industry guidelines;
- Exposure of alkylation unit workers to hazardous materials including vapors, acids, and corrosives;
- Failure to provide alkylation unit workers with necessary protective equipment;
- Existence of site-specific safety policies that were less protective than corporate policies and established industry good practice;
- Withdrawal from key national safety programs that workers believed were effective; and
- Perceived pressure on alkylation unit workers to expedite training and reduce cost.

Following recent CSB investigations into other accidents at petroleum refineries, the CSB recommended changes to strengthen refinery regulations in California and Washington.

The state of California has issued a draft refinery process safety management standard containing more rigorous safety regulations for the oversight of petroleum refineries, and the CSB is encouraged by these proactive changes to improve safety for workers and communities. The CSB's case study underscores the need for the proposed refinery safety reforms as well as individual refineries to continually assess and improve their process safety programs.

The CSB's case study emphasizes that regulators can use what are known as lagging process safety indicators, such as spills, fires, or gas releases, as well as leading indicators such as timely maintenance on safety critical equipment to focus inspections, audits, and timely closure of action items resulting from incident investigations to help drive process safety improvement.

"The continued recurrence of sulfuric acid incidents demonstrates the need for improvements at this refinery. We recommend that the refinery report process safety indicators to the regulator, said Lead Investigator Dan Tillema. "Regulators should monitor these indicators and conduct preventive inspections that lead to corrective actions --this is a critical component of an effective safety program - the ultimate goal is to ensure that risk is continually reduced."

We found this report as an excellent summary of lessons learned from a critical process like sulfuric acid alkylation, the human, systemic and latent causes identified here are behind same bad behaviors that cause incidents in other refinery units and other segments of the industry.
An active link to the CSB report follow: Link to report.

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Sulfuric Acid Degradation Mechanisms

The knowledge of corrosion by sulfuric acid has not changed much in the last quarter century, and there are many good references for it included in API RP 571 – Refining Degradation Mechanism. In the refining industry the most common place to experience sulfuric acid corrosion is in the sulfuric acid alkylation units where process control or water contents of acids deviates from design operation.

The alkylation process takes place in the alkylation unit of a refinery and occurs when isobutane combines with light olefins in the presence of a strong acid catalyst such as sulfuric acid. Alkylation is one of the most important processes in a modern refinery because it increases gasoline production by combining low value hydrocarbons such as propane and butane to produce a premium gasoline blend stock. The result is high-octane premium gasoline blending component, also known as high-octane alkylate.

The alkylation unit's spent sulfuric acid is highly corrosive, reactive, and can be flammable. In the event of contact, sulfuric acid can cause severe skin burns, serious eye damage, and respiratory irritation. To ensure the alkylation unit is operating within its safe operating limit the sulfuric acid concentration (strength) must be controlled, which requires frequent sampling and testing.

Some operators of sulfuric acid alky units have long believed that because of the sulfuric acid catalyst, that leaks are just part and parcel with the operation of such units. We now know that that just isn't true. With rigid control of acid concentration, fluid velocity, temperature and the avoidance of acid carryover, these units can be operated reliably with high integrity.

While much of a sulfuric acid alky plant can be constructed cost effectively out of carbon steel, there are a few places where upgrades to 316L, Alloy 20, and even Alloy B-2 and C276 may be needed. As with HFA alkylation units, sulfuric acid carryover into equipment and piping systems that were not constructed to resist sulfuric acid at certain concentrations and temperatures can lead to higher than design corrosion rates. Reactor effluent lines, reboilers, deisobutanizer overheads, caustic treating systems, and flare lines seem to be most vulnerable. Affected materials in order of increasing resistance are: carbon steel, 316L SS, Alloy 20, high silicon cast iron, high nickel cast iron, Alloy B-2 and Alloy C276.

Though corrosion from sulfuric acid is often general thinning, it can also be highly localized to weldments (especially HAZ), crevices and liquid vapor interfaces, as is often the case in flare lines because of the ingress of oxygen. It is not uncommon to see a knife-like line of corrosion at the tops of lines carrying concentrated sulfuric acid and at elbows, especially where maximum allowable velocities are exceeded. These types of localized corrosion are difficult to detect with point ultrasonic thickness measurements and require volumetric examinations such as raster pattern UT "B" or "C" scans.

Critical Factors for Sulfuric Acid Corrosion

- Acid concentration, temperature, alloy content, velocity, contamination and presence of oxidizers. Figure 1. shows a plot of carbon steel corrosion rates as a function of sulfuric acid concentration and temperature.
- Carbon steel corrosion rates increase significantly if the flow velocity exceeds about 2 to 3 fps (0.6 to 0.9 m/s) or at acid concentrations below 65%.
- Mix points with water cause heat to be released and high corrosion rates can occur where the acid becomes diluted.
- The presence of oxidizers can greatly increase the corrosion rate.

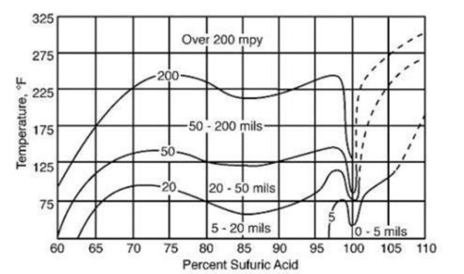

Figure 1 - Steel corrosion rates as a function of sulfuric acid concentration and temperature.

Prevention / Mitigation

- Corrosion is minimized through materials selection and proper operation within design velocities.
- Alloys such as Alloy 20, Alloy 904L and Alloy C-276 resist dilute acid corrosion and form a protective iron sulfate film on the surface.
- Acidified product streams can be washed with caustic to neutralize the acid.
- Inspection assisted with NDE with high effectiveness to detect and characterize very localized metal loss.

Industry publication and references

- NACE RP 0294 Design, Fabrication, and Inspection of Tanks for the Storage of Concentrated Sulfuric Acid and Oleum at Ambient Temperatures
- NACE Publ. 5A151 Materials of Construction for Handling Sulfuric Acid
- Sheldon W. Dean and George D. Grab, "Corrosion of Carbon Steel by Concentrated Sulfuric Acid," NACE Paper No.147

In the previous sections of this newsletter we discussed the severe consequences of a leak and exposure to sulfuric acid, now in this section we are discussing the degradation mechanism that could increase the likelihood of an acid sulfuric leak and the variables that could accelerate the degradation mechanism. It is clear now that sulfuric acid alkylation units are high risk, critical process units and all the knowledge and lesson learned around them is highly valuable. In Inspfalca we are ready to support your needs of risk reduction in these units or other critical process units.

upcoming events:

- **2016 API Fourth Annual Center for Offshore Safety Forum September 20, 2016 to September 21, 2016 Westin Houston Memorial City, Houston, Texas.**
- **2016 API Tanks, Valves, and Piping Conference & Expo October 10, 2016 to October 13, 2016 Aria Hotel, Las Vegas, Nevada.**
- **2016 API Pipeline Information eXchange and Pipeline Integrity Workshop October 11, 2016 to October 12, 2016 Hyatt Regency Houston Galleria, Houston, Texas.**
- **NACE Corrosion And Technology Week 2016 September 25 - 29, Royal Sonesta Houston, Texas.**
- **AFPM Cat Cracker Seminar 2016 August 23 - 24, Royal Sonesta Houston ,Texas.**