Sulphuric Acid Plant Hydrogen Safety Workgroup - an Update -

Sheraton Centre, Toronto
11. November 2015

Preamble

A number of Hydrogen explosions have occurred in sulphuric acid plants over the past decade, some were reported, but many remain unconfirmed

Over the recent years the reported number of incidents/year has increased significantly.

A North American initiative with broad interests across the acid industry has made inroads into focusing global interest in this key safety issue for the industry.

Plant operator feedback now looks to the Workgroup for further guidance in specific related topics.

Workgroup Intent

A number of acid plant operators together with the core of the plant building industry undertook to discuss and consider if there are specific trends regarding these incidents and possibly draft up practical/ general guidelines for use by designers and operators to mitigate these situations in the future

Core Workgroup Members

- Jim Dougherty/Josh Every/ Nicole Christiansen
- George Wang
- Leonard Friedmann
- Rick Davis
- Hannes Storch/Collin Bartlett
- Michael Fenton/Rene Dijkstra
- Steve Puricelli – DuPont MECS

Mosaic

ECOSERVICES

Acid Engineering & Consulting, Inc.

Davis & Associates Consulting, Inc.

Outotec

CHEMETICS

MECS

Incidents recorded to date

Incident location

- Australia (2)
- Brazil (3)
- Holland (1)
- India (2)
- Italy (1)
- UK (1)
- US (6)
- Chile (2)

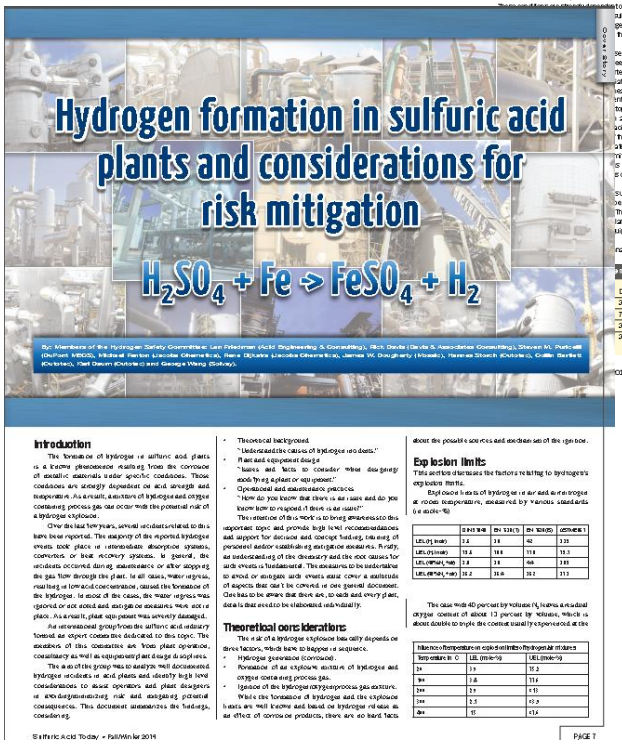
Cause of incident

- Acid Cooler leak (7)
- Boiler leak (2)
- Economizer leak (6)
- Tower/pump tank acid strength out of control (2)
- Chemical cleaning of the coolers (1)

Work carried out to date/1

Two technical papers published on the issue in the industry press in 2014

- Sulphur magazine
- Sulfuric Acid Today



Hydrogen formation in sulfuric acid plants and considerations for risk mitigation

$H_2SO_4 + Fe \rightarrow FeSO_4 + H_2$

By: Members of the Hydrogen Safety Committee: Len Friedman (Acid Engineering & Consulting), Rick Davis (Davis & Associates Consulting), Steven M. Puricelli (DuPont MECS), Michael Ferron (Jacobs Chemetics), Rene Dijkstra (Jacobs Chemetics), James W. Dougherty (Mosaic), Hannes Storch (Outotec), Collin Bartlett (Outotec), Yiet Deem (Outotec) and George Wang (Sinkey).

Introduction

The formation of hydrogen in sulfuric acid plants is a known phenomenon resulting from the corrosion of metallic materials under specific conditions. Those conditions are strongly dependent on acid strength and temperature. As a result, a mixture of hydrogen and oxygen containing process gas can occur with the potential risk of a hydrogen explosion.

Over the last few years, several incidents related to this have been reported. The majority of the reported hydrogen events took place in intermediate absorption systems, converters or heat recovery systems. In general, the incidents occurred during maintenance or after stopping the gas flow through the plant. In all cases, water ingress, resulting in low acid concentration, caused the formation of the hydrogen. In most of the cases, the water ingress was ignored or not acted and nitrogen purging was not in place. As a result, plant equipment was severely damaged.

An international group from the sulfuric acid industry formed an expert committee dedicated to this topic. The members of this committee are from plant operation, consultancy as well as equipment and design companies.

The aim of the group was to analyze well documented hydrogen incidents in acid plants and identify high level considerations to assist operators and plant designers in understanding risk and mitigating potential consequences. This document summarizes the findings, considering:

- Theoretical background
  - "Understanding the causes of hydrogen incidents."
- Plant and equipment design
  - "Issues and facts to consider when designing/modifying a plant or equipment."
- Operational and maintenance practices
  - "How do you know that there is an issue and do you know how to respond if there is an issue?"

The intention of this work is to bring awareness to this important topic and provide high level recommendations and support for decision making and concept finding, training of personnel and/or establishing mitigation measures. Firstly, the understanding of the chemistry and the root causes for such events is fundamental. The measures to be taken for avoidance/mitigation of such events must cover a multitude of aspects that can't be covered in one general document. One has to be aware that each case is plant specific and details need to be elaborated individually.

Theoretical considerations

The risk of a hydrogen explosion basically depends on three factors, which have to happen in sequence:

- Hydrogen generation (corrosion);
- Formation of an explosive mixture of hydrogen and oxygen containing process gas;
- Ignition of the hydrogen/oxygen/process gas mixture.

While the formation of hydrogen and the explosion limits are well known and based on hydrogen release as an effect of corrosion products, there are no hard facts about the possible sources and mechanisms of the ignition.

Explosion limits

This section addresses the factors relating to hydrogen's explosion limits.

Explosive limits of hydrogen in air and also in oxygen at room temperature, measured by various standards (vol-%)

	DIN 51649	EN 1839 (T)	EN 1839 (B)	ASTM E681
LEL (H_2 in air)	3.8	3.6	4.2	3.75
UEL (H_2 in air)	75.6	76.6	77.0	75.1
LEL (H_2 in O_2)	3.6	3.6	4.4	3.65
UEL (H_2 in O_2)	96.2	96.4	96.2	97.3

The case with 40 percent by volume N_2 leaves a residual oxygen content of about 13 percent by volume, which is about double to triple the content usually experienced at the

Influence of temperature on explosion limits of hydrogen/air mixtures

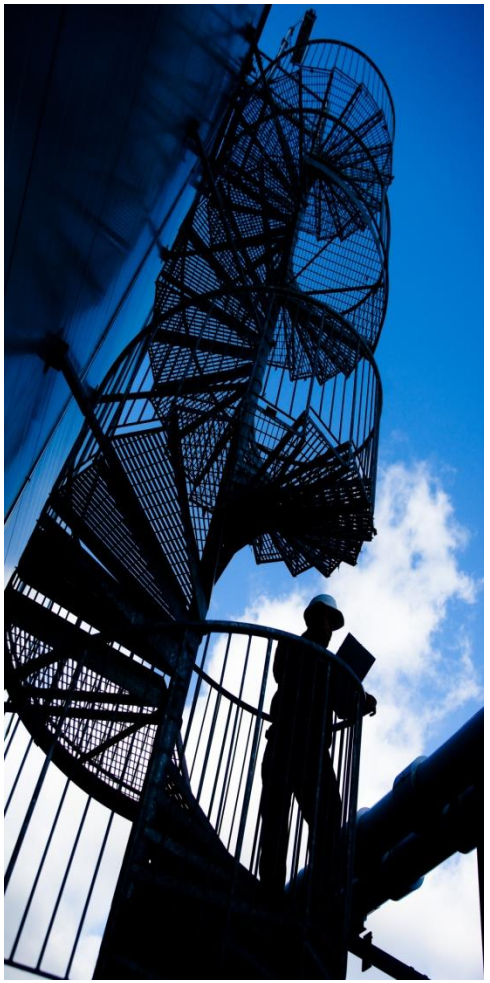
Temperature in °C	LEL (vol-%)	UEL (vol-%)
25	3.9	75.9
100	3.6	77.9
200	3.3	81.9
300	3.2	85.9
400	3.1	91.9

Hydrogen explosions on the rise

Generation of hydrogen in a sulphuric acid plant is a well-known phenomenon, but for some unknown reason, the incidence of hydrogen explosions has recently been on the rise. Fortunately, there have been no serious injuries to date. But, unless hydrogen safety is brought to the forefront of our thinking, the consequences could become more dire.

Work carried out to date/2

- A number of workshops and various presentations have been successfully organized at
  - AIChE, Clearwater/FL
  - Sulphur Conference/Paris
  - Maintenance Roundtable events
  - Various other industry conferences e.g. producer meetings
- These venues also allowed the workgroup to meet and confidentially discuss with operators incidents that have taken place at their facilities
- This has broadened the base of the Workgroup's incident database and allowed mitigation feedback to the operators

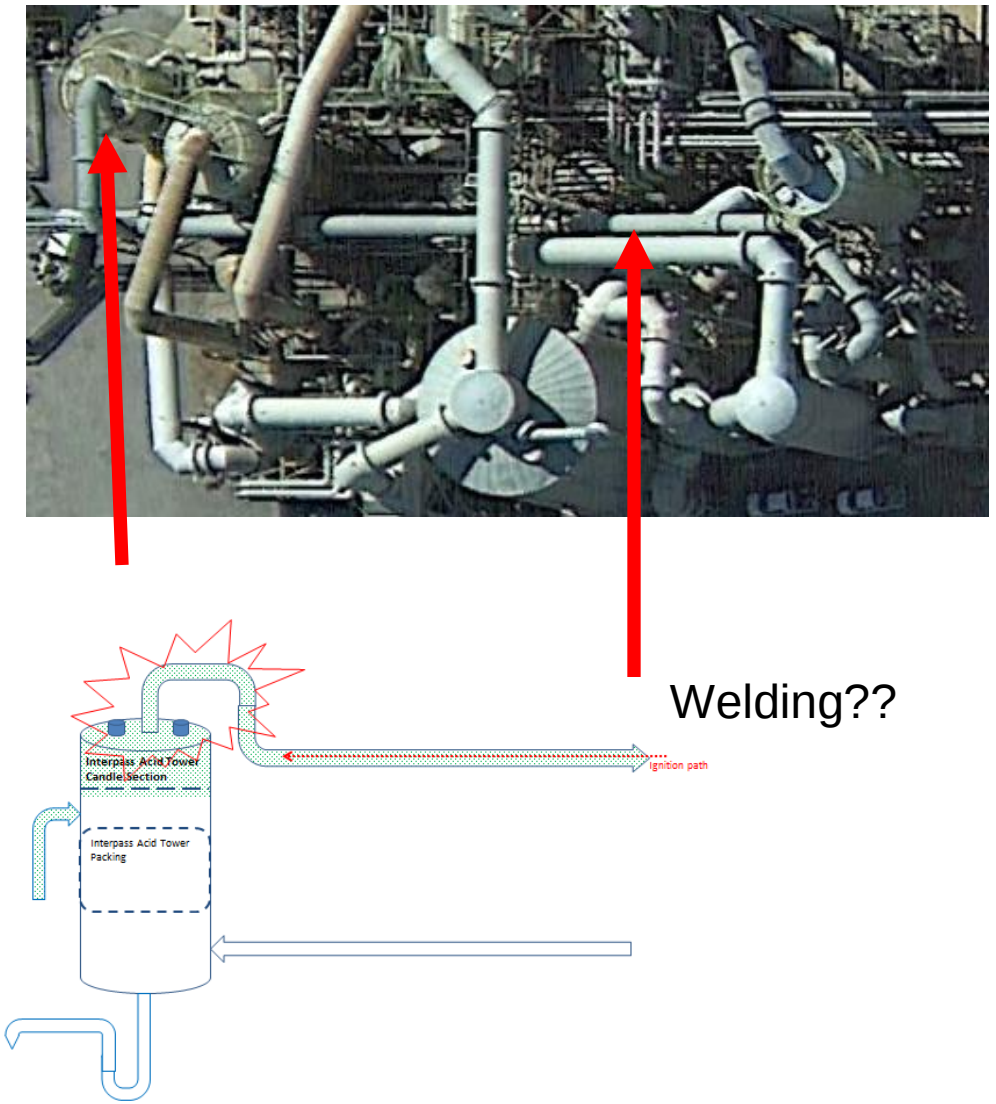


Key Workshop observations

- Based on the publications mentioned earlier, the key workshop observations are as follows:
  - The majority of incidents relate to weak acid events caused by equipment failures
  - Hydrogen incidents predominately occur when the blower is stopped
    - When weak acid is present, Hydrogen will be generated and has a very wide explosive limit
    - Ignition energy for Hydrogen is very low
  - Serious incidents share common causes
  - A new aspect for the Workgroup relates to Hydrogen safety issues during maintenance and shutdowns

Maintenance Case Study

- Event happened during a planned shutdown
- Hydrogen formation in cooler (weak acid)
- Formation of a ‘local explosive inventory’
- Ignition caused welding of duct nearby
- Severe damage of the tower and acid plant



Case Study Observations

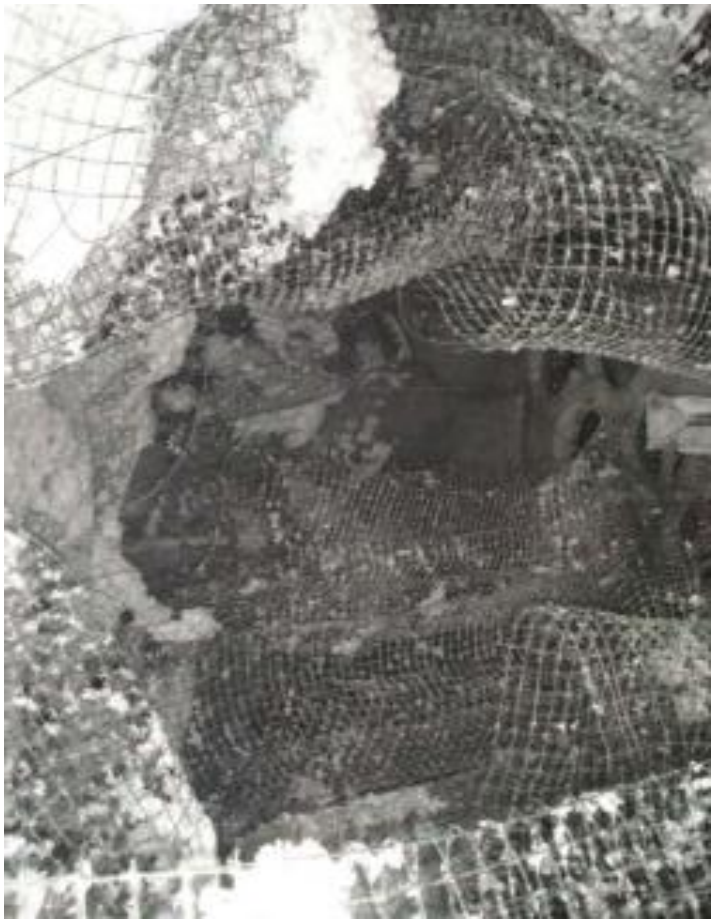
- Hydrogen can be formed during a shutdown:
  - e.g. water in equipment from backwashing
  - Acid film in equipment and air moisture
  - It does not have to be a weak acid event!!
  - Adhering to procedures will mitigate such events (backwashing, for example)
- If this situation occurs it normally results in a minor ‘pop’
- There are however situations where there is no ignition source (cold plant) and a potential for the formation of a larger ‘local explosive inventory’
- Maintenance work (e.g. welding) could have been the ignition source

Our work is far from complete……

- Ensure that plants operators are aware of the issue and the associated mitigation factors
- Further support of any operating site requiring our review/analysis of their incident
- Broaden operational guidelines to the industry at large to make it a safer place
- Develop guidelines for new topics, e.g. maintenance aspects

We are interested….!

- Do you have an incident you wish to discuss confidentially with the Workgroup?
- We want to hear from you and your incident
- We are here to help one another!



And finally…. Anti Trust Statement

It is not an objective, purpose or function of the team members to effect or participate in any understanding or conspiracy in restraint of trade or commerce. Pursuant to this statement, the team members undertake to desist carrying out any of the following: any activity related to sulphur based products and building of sulphuric acid plants with respect to prices and pricing practices, allocation of markets or customers, allocation or limiting of production, blacklisting, boycotting, refusals to deal, and any other activities that restrain competition in violation of the United States anti-trust laws.