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Fall/Winter 2014



## SPREADING HYDROGEN SAFETY WORLDWIDE

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# Hydrogen formation in sulfuric acid plants and considerations for risk mitigation



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## 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 noted and mitigation measures were 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/plant design disciplines.

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 avoiding/minimizing risk and mitigating potential consequences. This document summarizes the findings, considering:

- Theoretical background  
“Understand 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 and concept finding, training of personnel and/or establishing mitigation measures. Firstly, an understanding of the chemistry and the root causes for such events is fundamental. The measures to be undertaken to avoid or mitigate such events must cover a multitude of aspects that can't be covered in one general document. One has to be aware that there are, to each and every plant, details that 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 mechanism of the ignition.

## Explosion limits

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

Explosion limits of hydrogen in air and air/nitrogen at room temperature, measured by various standards (in mole-%)

	DIN 51649	EN 1839(T)	EN 1839(B)	ASTM E681
LEL (H <sub>2</sub> in air)	3.8	3.6	4.2	3.75
UEL (H <sub>2</sub> in air)	75.8	76.6	77.0	75.1
LEL (40% N <sub>2</sub> + air)	3.6	3.6	4.4	3.65
UEL (40% N <sub>2</sub> + air)	38.2	38.4	38.2	37.3

The case with 40 percent by volume N<sub>2</sub> leaves a residual oxygen content of about 13 percent by volume, which is about double to triple the content usually experienced at the

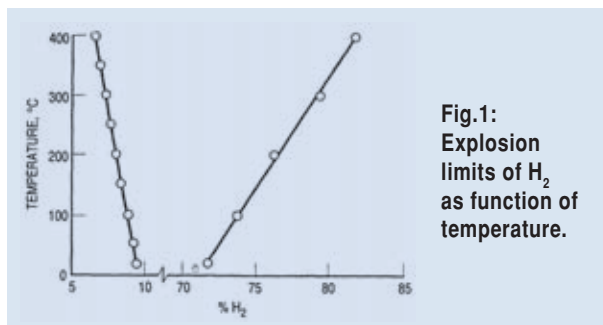
Influence of temperature on explosion limits of hydrogen/air mixtures		
Temperature in °C	LEL (mole-%)	UEL (mole-%)
20	3.9	75.2
100	3.4	77.6
200	2.9	81.3
300	2.1	83.9
400	1.5	87.6



intermediate absorber. Thus, it is to be expected that the UEL in this case will be below the tabled figures.

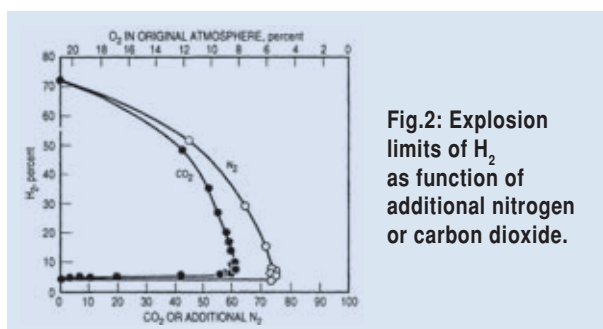
It appears that the explosion range widens with increased temperature, which is important to consider at the prevailing conditions of acid plant operation. The minimum self-ignition temperature amounts to 585 degrees C.

Fig. 1 shows the variation of the explosion limits as a function of the temperature ( $H_2$  in air).



**Fig.1:**  
Explosion  
limits of  $H_2$   
as function of  
temperature.

The presence of additional  $N_2$  or  $CO_2$  in the gas (air) will reduce the oxygen content. Subject to the residual  $O_2$ , the explosion limits vary significantly, as presented in Fig. 2.



**Fig.2:** Explosion  
limits of  $H_2$   
as function of  
additional nitrogen  
or carbon dioxide.

The diagram in Fig. 2 is based on a NASA report (1993) and suggests that the LEL remains virtually stable and constant with increased  $N_2$  content, while the UEL significantly decreases. Once the oxygen content of the gas reaches a level below 4-5 percent, the  $H_2$  is outside of any critical composition. This is very close to a typical gas at the exit of an intermediate absorber and hence one must not expect the formation of an explosive gas composition at “normal” operation. Obviously, no considerable amount of  $H_2$  would be released at such “normal” operation.

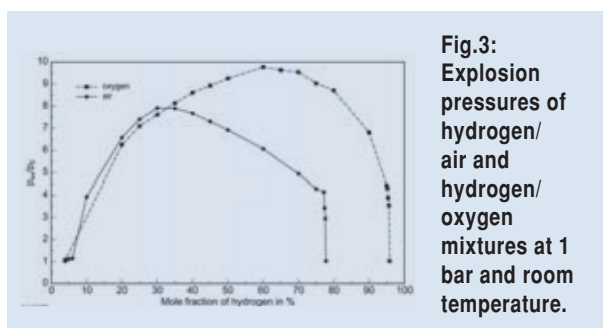
However, release of  $H_2$  is much more important during plant shutdown and periods of maintenance.

## Explosion pressure and ignition energy

The energy involved in a hydrogen explosion/reaction is determined by the equations:



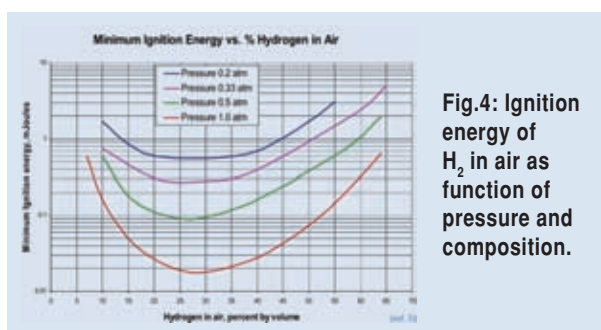
The reaction is highly exothermic and the high value of reaction enthalpy  $\Delta H$  indicates that the result of an explosion can be devastating. Fig. 3 shows the



**Fig.3:**  
Explosion  
pressures of  
hydrogen/  
air and  
hydrogen/  
oxygen  
mixtures at 1  
bar and room  
temperature.

explosion pressure generated.

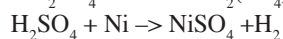
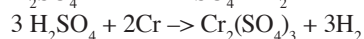
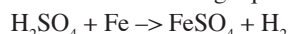
Ignition of hydrogen/air mixtures, particularly when these mixtures are within the flammability limits, takes place with only a very slight input of energy. A spark with such low energy that it is invisible in a dark room can ignite such a mixture. Common sources of ignition are sparks from electrical equipment, and sparks caused by the discharge of a small accumulation of static electrical charges. Even though a mixture is below the limit of flammability, some combustion can occur with a source of sufficient size and intensity. The minimum energy of ignition at a volumetric hydrogen concentration of 30 percent (stoichiometric) is only 0.02 mJ (while in pure oxygen, it is only 0.007 mJ). The ignition energy sharply increases at leaner or richer hydrogen concentrations and reaches 10 mJ, which represents a typical static discharge from a human body. This example shows that when there is the accumulation of an explosive hydrogen/oxygen mixture the likelihood of an ignition is extremely high.



**Fig.4:** Ignition  
energy of  
 $H_2$  in air as  
function of  
pressure and  
composition.

## Hydrogen formation rate

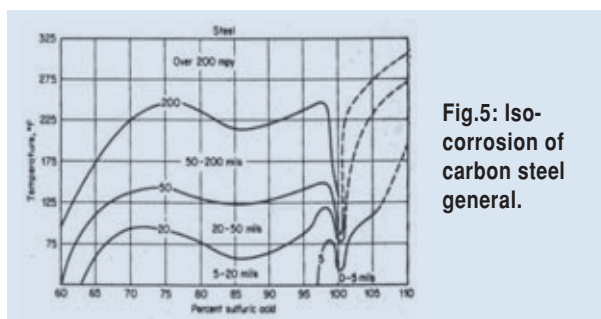
Stoichiometric corrosion chemistry is trivial and conforms to the following equations:



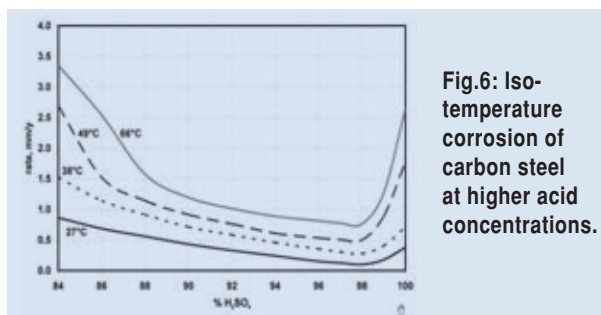
In practical terms, those equations describe that:

- For each 1 kg of Fe, an amount of 0.0361 kg of  $H_2$  is generated (equivalent to 0.40  $Nm^3$ ).
- For each 1 kg of Cr an amount of 0.0582 kg of  $H_2$  is generated (equivalent to 0.65  $Nm^3$ ).
- For each 1 kg of Ni an amount of 0.0344 kg of  $H_2$  is generated (equivalent to 0.38  $Nm^3$ ).

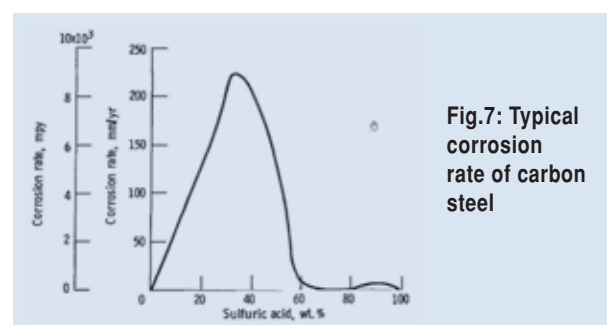
Typical corrosion rates of usual metals in acid plants are known, for example, as shown in Fig. 5 through Fig. 8. These diagrams can be used to quantify the amount of hydrogen generated.



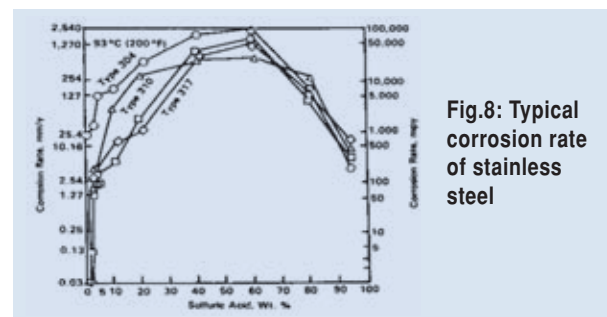
**Fig.5:** Iso-  
corrosion of  
carbon steel  
general.



**Fig.6:** Iso-  
temperature  
corrosion of  
carbon steel  
at higher acid  
concentrations.



**Fig.7:** Typical  
corrosion  
rate of carbon  
steel



**Fig.8:** Typical  
corrosion rate  
of stainless  
steel

Based on those data, the amount of hydrogen generated can basically be determined, at least as an order of magnitude. For example, the corrosion rate of a 1000  $m^2$  heat exchanger when exposed to 100 degrees C acid at 80 percent  $H_2SO_4$  is in the range of 10 mm/year. Low alloy stainless steel, e.g. 304 or 316 type, offers slightly less corrosion, but still in the range of 6 mm/year.

If such a heat exchanger is exposed to 80 percent acid at 100 degrees C for about 4 hours, then the amount of hydrogen produced would amount to 37 kg or 406  $Nm^3$ .

When a plant is idle for such time and the hydrogen accumulates at the top of the intermediate absorption tower, which may have a volume of 700  $m^3$  (or even less when considering only the “dead” volume on top of the gas exit duct, say 150  $m^3$ ), then the  $H_2$ -concentration can be anywhere from 50-100 percent. The rest of the gas obviously must contain some oxygen, which is the case when <100 percent  $H_2$  is present. These figures are well within the range to generate an explosion, provided that sufficient oxygen is present.

Obviously it has to be considered that such an explosive mixture could accumulate—depending on the plant configuration—in other areas. For example, in one reported case the explosion occurred not in the top of the tower, but below the candle filter tube sheet.

## Normal variation or excursion of acid concentration during operation

The earlier example and case studies clearly show that such events occur only under atypical conditions. It has to be understood that variations of acid concentration at normal operation, e.g. failure to control process water addition, can be regarded as non-critical with regard to the potential formation of hydrogen as a result of corrosion. Despite the higher corrosion rate as a function of operating outside the pre-determined design figures/operating windows, and as long as the possible material window of concentration and temperature are adhered to, the potential amount of hydrogen formed is negligible.

It can be concluded that:

1. The small amount of  $H_2$  will not reach the explosion range during operation.
2. Normal operation offers a gas composition where the  $O_2$  content is very low.
3. By having a continuous gas flow through the plant, the hydrogen concentration will be negligible and well below the lower explosive limit.

Operating windows are to be determined in accordance with process boundaries, e.g. an absorber cannot be operated outside of 98.0-99.0 percent  $\text{H}_2\text{SO}_4$  and a drying tower not outside of 92-98.5 percent  $\text{H}_2\text{SO}_4$ , without generating other detrimental effects, such as extreme  $\text{SO}_3$  plume or heavy condensate formation. Obviously such circumstances would force a plant shutdown prior to entering into the tolerable material window.

The material window is defined to be the range where the corrosion rate is still tolerable for a short period of time (up to, say, 1 mm/year), despite being the typically acceptable range of 0.1 mm/year.

As long as operation parameters are contained within said limits, one must not expect an exceeding formation of hydrogen during operation. Shut down conditions are very different, however, as the hydrogen may accumulate and thus form an explosive composition.

## Plant and equipment design considerations

It is a given that, in every plant, equipment can fail due to nearing the end of operational life, malfunction or defect. For the formation of hydrogen, the equipment that causes excessive water ingress is most relevant. That equipment is mainly steam related (waste heat boilers, economizers or superheaters) or water related (acid coolers or water dilution control valves).

As explained earlier, hydrogen is formed by the reaction of weak and/or hot acid with stainless steel, e.g. acid coolers, economizers, stainless steel towers, piping and other metallic components. The formed hydrogen will find, in every plant, stagnant areas where gas can accumulate and form an explosive hydrogen/oxygen/process gas mixture.

As all of that equipment is required and the plant layout will not allow an elimination of those stagnant areas (e.g. in one reported incident, the hydrogen reacted below the tube sheet), different measures that can be taken during design or operation to minimize risk need to be discussed. Of course, based on the studied cases, there are contributing factors to consider. For example:

- Delayed leak detection, e.g. due to leak size or not maintaining/installing instruments.
- Inability to isolate/separate the water from the acid system.
- Inability to remove weak acid from the system, which causes further corrosion.
- Insufficient operation manuals addressing such events.

Keeping those generic aspects in mind will certainly help to increase the awareness of the issue of hydrogen incidents. The expert committee elaborated on more specific high level considerations. Those considerations should serve as a help for designers, operators and consultants in the sense of *...am I aware of the potential consequences... or ...have I considered that....* Please note that obviously such a list cannot cover all the specific elements of a plant, equipment, etc., and is meant as a list of typical considerations that complement rather than replace design guidelines, operation manuals or procedures. Such plant-specific documents can and should be expanded with regard to the hydrogen issue during the respective project-specific discussions.

## High level considerations

### Avoiding hydrogen formation

The mechanism of hydrogen formation is well understood, as described earlier. It is crucial to transfer this knowledge into the design and operation in order to minimize the risk of hydrogen formation, which actually

means avoiding rapid corrosion. It is of utmost importance to consider the entire plant/operation and understand potential effects of local modifications to other plant areas.

- Consider the characteristics of construction materials:
  - Bricklined vs. stainless steel towers/vessels (material resistance, drain concept, etc.).
  - Cast iron vs. stainless steel equipment (irrigation system, piping, etc.).
- Ensure separation of weak acid from metallurgical surfaces, for example:
  - Drain acid from acid coolers; consider drain valve location and size of valve and ensure drain piping is sufficiently dimensioned.
  - Acid can be drained from other stainless steel equipment, e.g., towers, pump tank, piping, etc.
  - Acid distributors, tube sheet can be drained to avoid risk of local hydrogen formation.
- Minimize water ingress using these design considerations:
  - Cooling water isolation.
  - Boiler feed water bypasses around economizer.
- Consider measures to identify water ingress early on, for example:
  - Additional instrumentation to measure, e.g., dew point and opacity.
  - Intelligent data management system for analyzing flow rate, temperature, production deviation, etc.
- Consider related infrastructure in plant safety concept/HAZOP studies, especially the cooling water system:
  - Ensure that water pressure is always lower than acid pressure.
  - Ensure that acid contaminated cooling water can be drained.
  - Ensure cooling water quality is monitored.

### Avoid hydrogen accumulation

The key to safe operation is avoiding hydrogen formation. However, one has to consider that despite all efforts, the risk of hydrogen formation exists—even only nominally. Hence the design of plant/equipment as well as operational procedures must take this into consideration.

- Use these design considerations to minimize areas of potential hydrogen accumulation:
  - Fit acid tower with top, not lateral, gas outlet.
  - Minimize volumes of gas accumulation through the design of the equipment, see example later in this article.
- Ensure that proper shutdown and purge procedures are in place:
  - Those procedures have to be established considering the individual plant characteristics and local standards.
  - Potential procedure: ongoing purging of the plant by main blower following an event, until all weak acid is removed from system and equipment is isolated.
- Minimize potential  $\text{H}_2$  accumulation by, for example:
  - Purging blower.
  - Installing high point vents.
  - Purging nitrogen (depending on local infrastructure).

### Equipment specific aspects

Equipment design and operation should consider specific aspects for risk mitigation. Listed below are three examples of equipment that represent prominent sources of hydrogen formation, accumulation and ultimately explosion. Please note that equipment other than those listed could also be analyzed in a similar fashion.

### Acid coolers

Acid coolers offer a huge surface area, and hence have the highest potential for hydrogen formation. However weak acid in cooling water circuits can also result in hydrogen formation in the respective equipment (e.g., air coolers with closed loops). Consider the following aspects of acid cooler operation:

- The main reason for an acid cooler leak is related to water quality.
  - Is the cooler chosen for the cooling water quality?
  - Does the actual and the specified quality of the cooling water match?
  - Is the cooling water quality regularly monitored and are treatment procedures in place and maintained?
- The acid pressure should be higher than the water pressure.
  - While this is correct at start-up, is this still valid after years of operation?
  - How is this considered/mitigated at heat recovery coolers/evaporators, where this demand can generally not be adhered to?
  - How is this ensured in abnormal situations, e.g., acid pump shutdown, filling of tanks etc?
- As plant capacities increase, acid coolers are getting larger. Is the increased capacity considered in the design?
  - Is the drain number and size correctly dimensioned?
  - Is a vent valve installed to support faster drainage?
  - Where are water and acid drained to?
- Is the maintenance of acid coolers done in a proper way?
  - Are there procedures available and are personnel aware of them?
  - The washing of coolers can result in:
    - Residual water in plugged tubes. Note: Tubes can be blocked by fouling on the water side, which creates a corrosive environment (hot spots).
    - Residual water in the shell.
- Is an adequate leak response ensured?
  - Can the water side of the cooler be isolated and drained?
  - Are the drains/vents easily accessible even during upset conditions?

### Economizer

In economizers the water pressure is always significantly higher than the gas pressure, so a leak will force water into the gas stream. Once water has entered the gas stream weak sulfuric acid will potentially be formed. The result can be rapid corrosion (hydrogen formation) of the finned tubes and other downstream equipment.

- Water entering the gas stream can end in acid towers and dilute the acid strength.
- Consider draining the economizer.
  - Bottom drains can easily be blocked by small debris or sulfate.
  - Is it part of maintenance practice to inspect such drains at every shut down?
  - Is there a safe location to drain to?
- Are upset operations and cool down phases adequately considered?
  - Can the water side be fully isolated?
  - Is a gas or water bypass around the economizer needed for the cool down procedure?

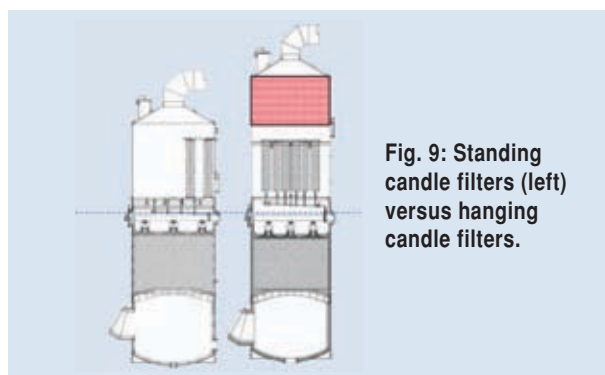
### Absorption towers

Irrespective of a leak occurring in an economizer, waste heat boiler or acid cooler, ultimately the water will enter the absorption tower, eventually resulting in circumstances where the acid strength can't be controlled anymore, hence the sub-system of the intermediate absorption tower is the

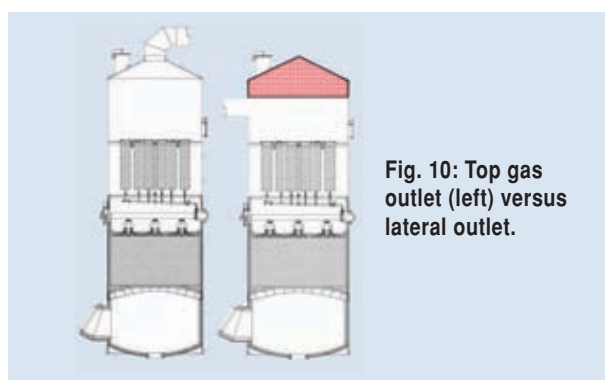


area of the highest potential for hydrogen formation.

- What are implications of construction materials?
  - Stainless steel towers are easy to install, however they offer a reduced operation window. Can it be ensured that the towers can be drained in case of upset operation (weak acid)?
  - Bricklined towers are significantly more robust and less exposed to corrosion and so weak acid could remain stored in the tower sump or pump tank for some time. Has the material decision been triggered by the draining concept?
  - Consider a design to minimize vapor and stagnant gas spaces.
  - Consider standing vs. hanging candle filters, as in Fig. 9.
  - Consider top vs. lateral gas outlet, as in Fig. 10.
  - Consider the maintenance concept: in-tower candle replacement vs. cutting of roof.
  - Consider options to remove hydrogen from the potential areas in the tower:
    - Purging using main blower after acid pumps are out of operation.
    - Purging using nitrogen (if available).
    - Purging using high point purging vents.



**Fig. 9: Standing candle filters (left) versus hanging candle filters.**



**Fig. 10: Top gas outlet (left) versus lateral outlet.**

## Operation and maintenance

Irrespective of implementing previous suggestions, the key to avoiding such events is operator and maintenance personnel **awareness** of the theory behind hydrogen formation and the potential consequences. Operators have to plan and be prepared for such events, ensuring early detection, mitigation and prevention.

- Do the following operational/maintenance procedures cover such events?
  - Regular and emergency shutdown procedures.
  - Equipment evacuation procedures.
- Do operators have the chance to practice for such events?
  - How is it ensured that the procedures will work?
    - Transfer experience (legacy planning).
    - Test operator skills.

- Do operators understand to look out for early warning signals?
- How are new operators trained?
- Is the equipment regularly inspected/tested?
  - Ensure that bypass and drain valves work.
  - Ensure the drain line and disposal area is not blocked.
  - Ensure that drains are cleaned at every shut down.
- Early warning of a problem is vital.
  - Are sufficient instruments installed?
    - Analyzers on cooling water return, one per cooler.
    - Consider water and acid temperature measurement.
    - Redundancy of acid measurement in cooling water (pH-meter, conductivity, etc.).
  - Are instruments maintained regularly, including cooling water loops?
- Is the available information used in a “smart” way?
  - Is a data management system used, e.g., acid plant water balance system?
  - Are historical trends used?
  - Is the anodic protection understood? Changes in current/voltage indicate a problem at a very early stage.
- Do maintenance procedures consider adequate purging and flammable gas testing?

## Conclusion

Generation of hydrogen in a sulfuric 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. There are many potential causes for the increased incidence of hydrogen explosions, including the age of operating sulfuric acid plants, the increased use of stainless steel equipment in lieu of traditional brick and cast iron materials, new maintenance practices, new safety and environmental regulations that limit the ability of operators to perform traditional operational checks (such as draining drip acid from equipment) and a loss of operating experience, due to demographics.

Moving forward, all parties involved must recognize that equipment failures are inevitable and when water is involved, a weak acid excursion can occur. This article has shown that the conditions leading to the formation of an explosive mixture can occur rapidly and immediate action is required that can only be achieved via thorough planning and procedures. By disseminating this information, the hope is that operators and designers alike become more aware of the hazards, making new plants better equipped for hydrogen safety and helping existing plants stay out of potentially dangerous situations.

Any questions pertaining to hydrogen-related incidents, redesigns or operations can be brought to the attention of the Hydrogen Safety Committee by contacting any member of the group via email. Len Friedman, email: acideng@icloud.com; Rick Davis, email: rick@consultdac.com; Steven Puricelli, email: steven.m.puricelli@mecsglobal.com; Michael Fenton, email: Michael.Fenton@jacobs.com; Rene Dijkstra, email: Rene.Dijkstra@jacobs.com; James W. Dougherty, email: James.Dougherty@mosaicco.com; Hannes Storch, email: hannes.storch@outotec.com; Collin

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## 2015 Sulfuric Acid Roundtable set for Florida

COVINGTON, La.—*Sulfuric Acid Today* is pleased to announce that the 2015 Sulfuric Acid Roundtable is scheduled for March 23-26, 2015. This year's roundtable will take place at the newly constructed Streamsong Resort in central Florida.

Attracting an international audience of professionals in the phosphate, metallurgical/smeltering and acid regeneration industries, this biennial conference provides a venue for participants to learn the latest sulfuric acid technologies and exchange best practices. The schedule will closely follow the model of previous meetings. It will consist of two and a half days of informative presentations from the conference's co-sponsoring firms along with insightful producing plant presentations, maintenance panel discussions, a keynote address on the global sulfuric acid market for 2015 and an update on hydrogen safety. There will be ample networking opportunities to meet co-sponsor representatives and peruse their exhibits of acid plant supplies and services.

This year's location will also allow roundtable attendees to take advantage of many recreational activities, including golf, fishing, hiking and clay shooting. An exciting new feature of this year's roundtable will be a tour of Mosaic's New Wales Phosphate Fertilizer Complex in Mulberry, Fla. The New Wales site, which has been in operation since 1975, sports five sulfuric acid plants producing 14,000 TPD and three turbine generators capable of producing over 100 MW of electricity. The site manufactures over 4 million TPY of phosphate fertilizers and is also one of the largest producers of animal feed supplements in the world.

For more information on the roundtable or to register, please visit [www.acidroundtable.com](http://www.acidroundtable.com). For sponsorship opportunities, please contact Kathy Hayward, (985) 807-3868 or email [kathy@h2so4today.com](mailto:kathy@h2so4today.com). □