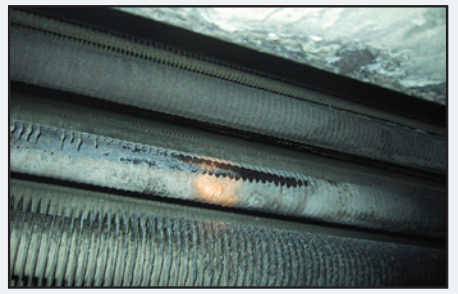
Hydrogen safety in the sulfuric acid industry

By: James W. Dougherty, Process Engineer, Mosaic Fertilizer LLC

ACID PLANT EQUIPMENT FAILURES

Acid cooler tube failures

Waste heat boiler tube failure



Economizer tube failure

Severe baffle plate weak acid corrosion damage

"It's not what you know you know, it's not even what you know you don't know, it's what you don't know you don't know that is dangerous" – Former United States Secretary of Defense Donald Rumsfeld

Hydrogen gas in sulfuric acid plants

"What we thought we knew we knew"

$$H_2SO_4 + Fe \longrightarrow FeSO_4 + H_2$$

It is well known and understood by all in the sulfuric acid industry that when sulfuric acid is exposed to steel the resulting chemical reaction produces hydrogen gas, but how many are familiar with all of the potential risks to sulfuric acid plants resulting from this reaction? Most plant operators are aware of hydrogen grooving in storage tanks and have experienced the minor hydrogen "bangers" that can happen when welding on high points in gas system ductwork or equipment. Fewer are familiar with incidents involving larger hydrogen explosions that can occur in sulfuric acid plants or the magnitude of the equipment damage that can result. Even fewer are familiar with the frequency that these incidents have occurred within the sulfuric acid industry in recent times.

Following the investigation of three such hydrogen related incidents, informal networking contacts throughout the industry have accumulated primary or secondary knowledge of a total of 13 hydrogen related incidents in sulfuric acid plants. Eleven of these 13 incidents have occurred within the past 10-years, equating to an alarming average rate of one per year! Three incidents have occurred to date in 2011 raising additional concern regarding what could potentially be further indication of an increase in the frequency of these serious incidents.

The incidents are typically initiated by steaming equipment or acid cooler leaks that result in severe weak acid excursions. The weak acid corrosion then generates enough hydrogen to accumulate explosive concentrations in various locations of the gas side process equipment, ultimately causing an incident. The equipment location where hydrogen gas accumulation most commonly occurs appears to be at the top of the interpass acid tower, but accumulations in drying towers, converter beds, heat exchangers, and ductwork have also been reported.

Boiler leaks, economizer leaks, acid cooler leaks and weak acid corrosion damage can all happen even at the best operated and maintained sulfuric acid plants. Most experienced sulfuric acid plant operations and maintenance personnel have probably seen equipment failures similar in nature to the types shown in the photos above. Most, fortunately, have not had the misfortune to experience any of the types of equipment damages shown in the photos below that can potentially result from the subsequent hydrogen explosion. This article highlights the critical knowledge learned so far from the investigation of the three incidents depicted in these photographs.

Incident investigations

"What we learned"

A Root Cause Failure Analysis (RCFA) was performed on each of these three incidents. Every known aspect of each plant's design, operating conditions, failure sequence of events and the resulting equipment damages was analyzed in an attempt to determine the mechanism of failure and develop the appropriate preventative measures and safeguards to minimize or eliminate the risks to acid plant equipment and operating personnel.

The first incident was initiated by a severe economizer tube failure that produced weak acid concentrations in the range of 85 percent. The resulting hydrogen explosion occurred in a high point of the ductwork for an internal hot pass heat exchanger of a radial flow converter design approximately 1-hour and 20-minutes after emergency plant shutdown. No ignition source was ever identified, but the operating temperature in the area of the converter (Catalyst Bed #2 Outlet) where the internal duct that the hydrogen is suspected to have accumulated is reasonably close to the auto-ignition temperature of hydrogen gas.

The second and third incidents were also initiated by economizer leaks, but in these scenarios the explosion occurred in the tops of IPA towers, one a traditional acid tower design and the other an alloy heat recovery acid tower design. Process gas temperatures present in the tops of acid towers are well below the known auto-ignition temperature of hydrogen so the ignition source in these cases is hypothesized to be a static charge buildup occurring in the non-conductive fiberglass bed of the acid mist eliminators. It is also notable that although the acid concentration (97.5 percent) in one of the tower incidents was nowhere near as weak as during the first incident, the accumulation of hydrogen gas reached explosive concentrations in approximately half the time. This may in part be interpreted as an indication that the higher acid temperatures and larger exposed metal surface areas are present in the heat recovery system tower resulted in a higher rate of hydrogen gas generation than during the incident involving the traditional IPA tower design.

Investigation results and hypothesis

"What we now think we know we know"

As part of the follow up to two of the investigations, estimates were made of the gas system process conditions and acid concentrations during the time leading up to the explosions. These conditions were then used along with a calculation of the area of the exposed metal surface in the acid system equipment as a basis to develop an "optimal approximation" of the volumes of hydrogen gas that was generated. In each case, these approximations indicated that it would not be unreasonable to expect that enough hydrogen gas was generated to result in the accumulation of explosive concentrations. Finite Element Analysis (FEA) was then used to estimate the forces that would have been required to cause the equipment damage observed in each incident. In both cases the forces estimated to be necessary to create the actual equipment damages reasonably approximated the forces that would be expected to have resulted from an explosion of hydrogen gas near its lower explosive limit concentration.

Furthermore, when compared to the third case and also to the other known sulfuric acid plant incidents, the degree of equipment damage in most of the incidents is strikingly similar. As a result of this commonality in the resulting equipment damages, it is being hypothesized that since the

RESULTING HYDROGEN EXPLOSION EQUIPMENT DAMAGE

Converter division plate damage viewed from below

Converter shell damage – 4" circumferential buckling

IPA tower mist eliminator candle damage

Heat Recovery System acid tower dome damage

hydrogen explosions all appear to be similar in magnitude that they are all being triggered as soon as lower explosive limit concentrations of hydrogen gas are reached and therefore a continual presence of some type of ignition source within the sulfuric acid plant equipment must exist.

Sulfuric acid plant design improvements

The apparent increasing trend in the frequency of hydrogen incidents may in part be inherent to the combination of improvements in plant designs that have taken place over the years. Single absorption plant designs have been upgraded to double absorption designs whose configuration of equipment and duct work typically results in a location near the top of the IPA tower or exit ducting where hydrogen that would have exited the tower to the stack in a single absorption plant now accumulates in the double absorption design. Installation of shell and tube acid coolers results in hydrogen gas being trapped inside the acid system as opposed to being released to the atmosphere as it was in the old cast iron acid cooler design. The change from brick lined acid towers and pump tanks to alloy equipment has dramatically increased the square footage of metal exposed to weak acid during excursions. Similarly, additional metal exposure has resulted from the increase in the number of acid distribution points per square foot from 1.5 in the old cast iron distributors to 4.0 in today's alloy distributors. Designing heat exchangers internal to radial flow converters can potentially result in configurations of internal ductwork that create high point trap areas which allow the accumulation of hydrogen gas in locations exposed to the elevated temperatures of the converter beds that previously did not exist (fig. 1). Each of these design changes has led to improved sulfuric plant operations, but now each should be evaluated from the point of view of their impact on hydrogen safety as well.

Ignition sources

"What we know we still don't know"

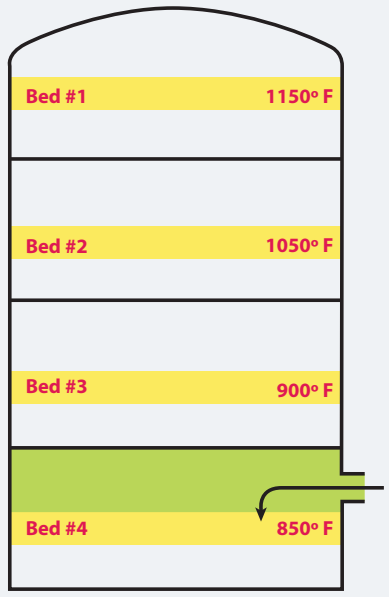
Results from efforts to identify the ignition source in each incident have been inconclusive. In most of the industry's incidents, the ignition occurs in the top of one of the acid towers and the source is hypothesized to be static charge build-up from the motion of the large volumes of acid mist particles that are commonly known to be generated when moisture leaks occur into the gas systems of sulfuric acid plants. In other cases, explosions have occurred in equipment locations with no apparent ignition sources present, but that have process conditions at or near the generally accepted auto-ignition temperature of hydrogen gas. Literature research uncovered a U.S. Patent application referencing static charge buildup in a chlorine plant drying tower constructed with non-conductive PVC materials. Extensive testing was completed to document the build-up of static charges on falling drops of sulfuric acid. Some discussion has already taken place regarding development of laboratory and/or field testing methods to determine if similar static charge build-up could occur in the non-conductive fiberglass beds of the mist eliminators, although given the extremely low ignition energy requirement for hydrogen, it is expected to be difficult to validate such low level charges are occurring in operating sulfuric acid plant equipment.

Hydrogen in sulfuric process conditions

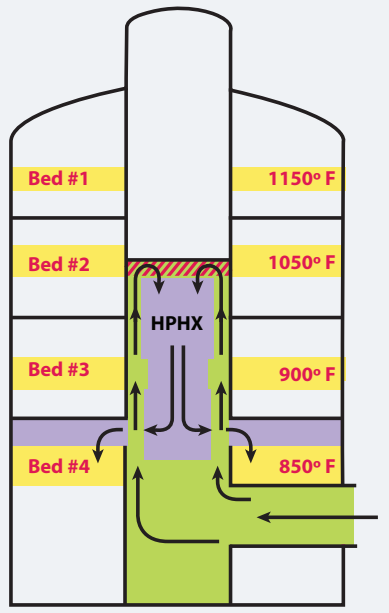
"What we don't know we don't know"

Published hydrogen gas auto-ignition temperature (AIT), lower explosive limit (LEL), and minimum ignition energy (MIE) requirements are all based on testing under atmospheric conditions. Literature research conducted to date has uncovered very little information regarding what these explosion characteristics of hydrogen gas would be in the process gas conditions of a sulfuric acid plant (SO_2/SO_3 /high nitrogen/reduced oxygen with trace quantities of NO_x compounds). Some of the published research encountered so far indicates that there are also factors present in the sulfuric acid process, particularly elevated operating temperatures and the presence of NO_x, having the potential to lower the AIT and LEL concentration of hydrogen gas, but it appears that no specific research has been conducted to define exactly what these impacts are. Further research and laboratory testing will be necessary to define all of the relevant characteristic explosion properties of hydrogen gas under sulfuric acid plant process conditions in order to ensure that all of the underlying science related to these incidents is fully understood. Only by completing this work can the sulfuric acid industry have confidence that the causes of these hydrogen incidents have been identified and the appropriate safeguards are developed in order to prevent them from occurring again in the future.

Fig.1:



TRADITIONAL CONVERTER: Hydrogen (green) enters converter contacting Bed #4 catalyst and chemically oxidizes.



RADIAL FLOW CONVERTER w/INTERNAL HPHX: Hydrogen (green) enters and collects in top of internal duct (red) before it can flow back down through HPHX (purple) and contact Bed #4 catalyst.

Plant safeguards

"What we are doing about it"

Given the current understanding of these two incidents, preventing hydrogen gas from reaching explosive concentrations appears to be the key to eliminating the risks to the sulfuric acid plants. The most effective plant safeguard available to accomplish this is the implementation of operating procedures to use the main air compressor to blow air through the gas system and purge out any hydrogen gas present in the equipment. This procedure should be executed during any plant shutdown that follows an equipment failure of the type that results in moisture leaking into the gas system or any major weak acid excursion. For most of these types of failure scenarios the plant must ultimately be cooled down to execute repairs anyway so the additional air purge time is not detrimental to the course of the repair outage. Computational Fluid Dynamics (CFD) modeling will be conducted in order to determine the minimum air flow requirement necessary to purge the hydrogen gas out of the system and validate the procedure's effectiveness. Other potential safeguards under consideration include: 1) increasing the minimum acceptable mechanical integrity levels for the plant's steaming equipment in order to reduce the risk of failures; 2) instrumentation that could potentially provide early detection of steaming equipment leaks; and 3) instrumentation capable of monitoring hydrogen gas concentrations in critical equipment locations.

It is clear that additional fundamental research substantiated by laboratory and field testing will likely be required in order to develop a comprehensive understanding of the underlying scientific principles associated with these types of hydrogen explosions in sulfuric acid plants. The sulfuric acid industry must now choose to make whatever efforts are necessary to continue on with the analysis started here and prosecute it until all that is needed to be known is finally known if risks associated with these hydrogen explosions are ever to be eliminated from our plants.

First sulfuric acid hydrogen safety presentation given in March 2011 at the Sulfuric Acid Maintenance Roundtable Conference.

Getting the word out

This article is a continuation of the efforts to get word out to the sulfuric acid industry and promote a better understanding of the potential risk for hydrogen explosions in sulfuric acid plants. Presentations have been made at the annual Sulfuric Acid Maintenance Roundtable and AIChE Central Florida Clearwater Conferences and another is planned for the upcoming Sulphur 2011 Conference in Houston. It is desired to continue collection of as much first hand information as possible to further the investigation of these incidents. Plans are in progress to develop a means to better facilitate collection of information from companies in the sulfuric acid industry with firsthand knowledge of these type of incidents. The proposed system includes options to allow collecting of information anonymously from any companies having concerns regarding the sensitive nature of these incidents. Continue to follow the progress in *Sulfuric Acid Today* magazine or contact me directly at james.dougherty@mosaicco.com for further information. ❑

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