The importance of hydrogen safety

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The formation of hydrogen resulting from the corrosion of metallic materials is well known. In the sulfuric acid industry, though, the risks posed by the presence of hydrogen had not been sufficiently recognized. Over the last few years, several incidents in the sulfuric acid industry related to the presence of hydrogen have been reported (see Table 2). In many cases plant equipment was severely damaged. This lead an international group from the sulfuric acid industry to form an expert committee in 2013 that was dedicated to this topic with the aim to improve the understanding of underlying causes and to bring wider attention to the issue. The members of this committee are from plant operation, consultancy, and equipment/plant design disciplines. The work of the group resulted in presentations at several conferences in 2014 and 2015 and the publication of two major articles in *Sulfuric Acid Today* (Fall/Winter 2014) and *Sulphur* (#355 Nov/Dec 2014). This shorter article is intended to remind people in the sulfuric acid industry that the risks of hydrogen in acid plants are real and continued vigilance is required.

Theoretical considerations

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

1) Hydrogen generation: Hydrogen generation results from corrosion of metallic surfaces in contact with sulfuric acid. Generally this corrosion can be described by the following equation:

Metal + $H_2SO_4 \rightarrow H_2$ + Metal-Sulfate

Metals typically found in acid plants are carbon steel, stainless steel, and stainless steel alloys containing Fe, Cr, and Ni. If safe acid concentrations or temperature limits for the material in question are exceeded, the production of hydrogen cannot be prevented. Corrosion rates and safe areas of operation can be determined from corrosion diagrams. (See Fig. 1).

2) Formation of an explosive mixture of hydrogen and oxygen-containing gas: Hydrogen and oxygen readily form flammable mixtures at ambient conditions when the oxygen content of the mixture is above 4.3 percent volume. As long as sufficient oxygen is present, the lower explosion limit is highest at ambient temperature and becomes lower when gas temperatures increase (see Table 1). This lower threshold cannot be reached during normal operation of the acid plant as long as gas flow through the plant is maintained. Abnormal operations, such as emergency stops (i.e. gas flow interruptions), cooling/heating periods of the plant (at reduced flow and increased oxygen content) and maintenance periods therefore pose the highest risk.

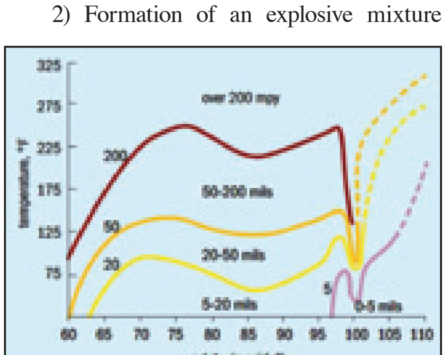

Fig. 1: Corrosion rates for carbon steel.

Temperature °C	LEL vol%	UEL vol%	LOC vol% O2
20	4.1	75.6	4.3
100	3.4	77.6	4.0
200	2.9	81.3	3.2
300	2.0	83.9	2.3
400	1.4	87.6	1.3

Table 1: DIN Effect of temperature on hydrogen flammability.

3) Ignition of the hydrogen/oxygen/process gas mixture: The ignition of hydrogen/air mixtures when these mixtures are within the explosive limits requires only a very small input of energy, such as the build-up of static energy. It was the conclusion of the workgroup that ignition sources could likely not be prevented in acid plants and hence emphasis should be placed on prevention of hydrogen formation and the formation of flammable mixtures.

Plant and equipment design considerations

It is a given that 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 (see Table 2). This equipment is mainly steam related (waste heat boiler, economizer, or superheater) or water related (acid coolers or water dilution control valves). Any leakage in this equipment can quickly result in weak and/or hot acid which allows the formation of hydrogen on metallic surfaces in the plant.

Often the generated hydrogen can find stagnant areas in the plant where the gas can accumulate and form an explosive hydrogen/oxygen/process gas mixture. Plant layout requirements will often not allow the elimination of those stagnant areas. Therefore, measures that can be taken during design or operation to minimize these risks need to be discussed. Based on the studied cases, several contributing factors have been identified that played a role in the chain of events.

Number of incidents	Primary equipment failure
7	Acid Cooler Leak
6	Economizer Leak
3	Boiler Leak
2	Loss of Acid concentration control
1	Acid Cooler Cleaning

Table 2: Reported hydrogen related incidents with plant damage.

—Delayed leak detection, e.g. due to small initial leak size or not maintaining/installing instruments that allow earlier detection.

—Inability to isolate/separate the water from the acid system.

—Inability to remove weak acid from the system, which causes further corrosion.

—Insufficient information in operation manuals/procedures addressing such events.

Keeping those generic aspects in mind will certainly help to increase awareness of hydrogen incidents. The expert committee in the previous articles elaborated further on more specific, high level considerations. Those considerations, as summarized below, should serve as an aid for designers, operators, and consultants in the sense of "Am I aware of the potential consequences" or "Have I considered that…."

Avoid hydrogen formation by:

—Understanding the characteristics and limitations of construction materials.

—Ensuring that it is possible to separate (weak) acid from the metallic surfaces.

—Minimizing further water ingress as soon as possible.

—Considering the use of additional instrumentation for monitoring and early detection.

—Considering all aspects of the plant during design and safety reviews to prevent issues caused by design choices or project interfaces.

Avoid hydrogen accumulation by:

—Minimizing areas where hydrogen can accumulate during plant design and equipment replacement.

—Ensuring proper shutdown and purge procedures are established that take into account the possible presence of hydrogen.

—Shutting down the acid plant blower after hydrogen formation has been stopped.

Share information related to hydrogen formation and its risks by:

—Including it in safety studies, change management, tool box talks, etc.

—Discussing the operating and maintenance procedures and identifying whether they cover hydrogen formation events.

—Practicing emergency procedures to ensure operating personnel are familiar with the tasks required to safely bring the plant off-line.

Obviously, any such list cannot cover all the specific elements of a plant, equipment, etc., and is merely meant to point out typical considerations that complement—rather than replace—design guidelines, HAZOP studies, operation manuals, and procedures. Any plant-specific documents can and should be expanded with regard to hydrogen formation issues, either during the initial project or in cooperation with consultants and/or the original licensors for plants that are already in operation.

Conclusion

Generation of hydrogen in a sulfuric acid plant is a well-known phenomenon, but for some unknown reason, the number of reported hydrogen explosions has recently been on the rise. Fortunately, there have been no serious injuries reported to date and damage has been restricted to plant equipment. It is further encouraging that since 2014 the number of reported cases has seen a reduction. But, unless hydrogen safety is maintained at the forefront of our thinking, incidents will continue and consequences could become more severe.

This article has attempted to remind the acid industry that the conditions leading to the formation of an explosive mixture can occur rapidly and immediate action is required. The correct actions 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, acideng@icloud.com; Rick Davis, rick@consultdac.com; Steven Puricelli, steven.m.puricelli@dupont.com; Michael Fenton, Michael.Fenton@jacobs.com; Rene Dijkstra, Rene.Dijkstra@jacobs.com; James W. Dougherty, James.Dougherty@mosaicco.com; Hannes Storch, hannes.storch@outotec.com; Collin Bartlett, collin.bartlett@outotec.com and George Wang, georgewang3815@gmail.com. ❑