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Hydrogen – Autoignition and Leak Testing

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(From a paper dated May 2, 2001 in response to a project's need to install hydrogen piping.)

This paper addresses two issues. One concerns autoignition and the other concerns leak test parameters.

AUTOIGNITION

Much of the following information on autoignition is from the NASA Glenn Safety Manual revised June 2000. The various definitions including the text in quotes, has been taken directly from that manual. In conjunction with autoignition this paper will also address some of the other volatility issues and parameters with regard to hydrogen

Autoignition is dependent upon temperature, not pressure. Some of the properties of hydrogen regarding its volatility are:

1. The Autoignition Temperature of gaseous hydrogen in air is 1084°F.
   a. Autoignition is the phenomenon in which a mixture of gases or vapors ignites spontaneously with no external ignition source. It is also referred to as "Autogenous Ignition" or "Spontaneous Ignition".
   b. Autoignition Temperature is the lowest temperature at which a fuel, in contact with air or an oxidizer, will self-heat to ignition without an external ignition source. The Autoignition Temperature for a monopropellant is the temperature at which it will self-heat to ignition in the absence of an oxidizer.

2. Minimum Spark Ignition Energy for gaseous hydrogen in air at 1 atm Btu (mJ) = 1.9×10^{-8} (0.02).
   a. Ignition Energy is the amount of energy needed to initiate flame propagation through a combustible mixture. The Minimum Ignition Energy is the minimum energy required for the ignition of a particular flammable mixture at a specified temperature and pressure.

3. Explosive Limits, upper and lower, vol. % hydrogen in air mixture is 18.3% and 59%
   a. Explosive Limits are the maximum and minimum concentrations of vapor, mist, or dust in air or oxygen at which explosions occur. The size and geometry of the environment as well as the concentration of the fuel control the limits. "Detonation Limit" is sometimes used as a synonym for "Explosive Limits".

"The major hazards associated with gaseous hydrogen are fires and explosions. Hydrogen gas can burn in two modes, as a deflagration or as a detonation:

"In a deflagration, the ordinary mode of burning, the flame travels through the mixture at subsonic speeds. This happens, for instance, when an unconfined cloud of hydrogen-air mixture is ignited by a small ignition source. Under these circumstances, the flame will travel at a rate anywhere from ten to several hundred feet per second. The rapid expansion of hot gases produces a pressure wave. Witnesses hear a noise, often a very loud noise, and may say that an explosion occurred. **The pressure wave from rapid unconfined burning may be strong enough to damage nearby structures and cause injuries to personnel.**

"In a detonation, the flame and the shock wave travel through the mixture at supersonic speeds. The pressure ratio across a detonation wave is considerably greater than that in a deflagration. The hazards to personnel, structures, and nearby facilities are greater in a detonation. A detonation will often build up from an ordinary deflagration that has been ignited in a confined or partly confined mixture. This can occur even when ignition is caused by a minimal energy source. It takes a powerful ignition source to produce detonation in an unconfined hydrogen-air mixture. However, a confined mixture of hydrogen with air or oxygen can be detonated by a relatively small ignition source. The pressure ratio across a detonation wave in a hydrogen-air mixture is about 20, as indicated when the wave passes a detector mounted flush in a confining wall. (A pressure ratio of 20 means 300 psi if the mixture is at atmospheric pressure.) When the wave strikes an obstacle, the pressure ratio seen by the obstacle is between 40 and 60. Even larger pressure ratios occur in the region where a deflagration builds into a detonation.

"Mixtures of hydrogen with air, oxygen, or other oxidizers are highly flammable over a wide range of compositions. The flammability limits, in volume percent of hydrogen, define the range over which fuel vapors ignite when exposed to an ignition source of sufficient energy.

"The flammable mixture may be diluted with either of its constituents until it is no longer flammable. Two limits of flammability are defined: the lower limit, the minimum amount of combustible gas that makes a mixture flammable; and the upper limit, the maximum amount of combustible gas in a flammable mixture.

"The flammability limits based on the volume percent of hydrogen in air (at 14.7 psia) are 4.0 and 75.0. The flammability limits based on the volume percent of hydrogen in oxygen (at 14.7 psia) are 4.0 and 94.0. Reducing the pressure below 1 atmosphere tends to narrow the flammability range by raising the lower limit and lowering the upper limit. No mixture of hydrogen and air has been found to be flammable below 1.1 psia.

"Temperatures of about 1050 F are usually required for mixtures of hydrogen with air or oxygen to autoignite at 14.7 psia. However, at pressures from 3 to 8 psia, autoignitions have occurred near 650 F.

"The primary hazard of using hot hydrogen (1050 to 6000 F) is that a large leak at temperatures above the autoignition temperature will almost always result in a flash fire. Other safety criteria are the same as for ambient temperature gaseous hydrogen. System construction materials must be suitable for use at the elevated temperatures.

"Hydrogen-air mixtures can ignite with very low energy input, 1/10th that required to ignite a gasoline-air mixture. For reference, an invisible spark or a static spark from a person can cause ignition.

"Hydrogen-oxygen and hydrogen-pure air flames are colorless. (Any visible flame is caused by impurities.) Colorless hydrogen flames can cause severe burns.

LEAK TESTING

When installing a piping system as potentially volatile as hydrogen a procedure should be established that not only sets forth thorough and definitive guidelines, but also identifies the best suitable means of assuring system integrity.

Part of that assurance lies with the pressure and leak testing process. It is suggested that helium be used as the pneumatic test gas with a maximum acceptable leak rate that will be discussed later.

Aside from hydrogen's potential volatility, its molecular size, with an atomic mass of 1.00794, creates a containment problem. Helium, with an atomic mass of 4.002602, provides a very close approximation of that containment problem. Nitrogen, with an atomic mass of 14.00674 would not provide the same assurances found when using helium as the test gas. I would recommend against using a heavier gas, such as nitrogen, by extrapolating the results of a nitrogen leak rate to determine what the leak rate might be if it were hydrogen.

When testing potentially volatile or lethal piping systems for leaks, a maximum allowable leak rate should be predetermined and specified in any testing procedure. The quantitative aspect of a hydrogen leak can be determined under two separate criteria:

1. Is the piping inside a building?
    a. Is the building well ventilated?
    b. Are there potential ignition sources within close proximity to the piping?
    c. Is the piping in an area that could pocket and accumulate hydrogen emission?

2. Is the piping in open air?
   a. Are there potential ignition sources within close proximity to the piping?

Two different acceptable leak rates could be established for inside piping systems and for outside piping systems. The high diffusion rate of helium makes it difficult to test for minute quantities of helium on an inside installation, and even more difficult on an outside installation. For that reason, and because hydrogen would probably not have a place to accumulate outside, a higher leak rate could be acceptable for an outside installation.

Detecting leaks can be accomplished with a soapy water solution like Snoop. However, this is not the best method for locating the relatively small leaks that could occur with helium. Nor does it provide a means to determine the leak rate.

Using a helium probe (spectrometer), leak rates can be determined to a level of 10^{-6} cm^3/sec. This allows leaks to not only be located but to be quantified as well. Determining and specifying the maximum allowable leak rate for gaseous hydrogen is a plant, or Owner specific, issue that is based on a plant by plant circumstance.

If it is determined that a single maximum allowable leak rate would apply to both inside and outside installations then the basis for a worse case inside installation would determine the leak rate. In making that determination a scenario would have to be created whereas a leak would occur at a joint, at an assumed leak rate, inside a building, in still air, with a vaulted or penthouse type ceiling; a space above the leak where hydrogen could accumulate

Assuming good design practices have been followed, the main concern regarding this discussion is with gaseous hydrogen discharge from a leak accumulating in an enclosed building. The following Table 1 lends some perspective when assessing the magnitude of a leak rate:

Leak Rate	Unit of Measure	Hours to Accumulate 1ft^3	ft^3/Year
10^{-4}	cm^3/sec	78669	.11
10^{-3}	cm^3/sec	7866.9	1.11
10^{-2}	cm^3/sec	786.7	11.13
10^{-1}	cm^3/sec	78.7	111.31

Table 1 – Leak Rate Accumulation

When setting a value for an allowable leak rate it should be assumed that the above mentioned "good design practices" were not adhered to. Even though a good design, particularly where hydrogen is concerned, would not allow a building to be designed without good ventilation, and would not allow a penthouse type ceiling without ventilation, it should be assumed otherwise.

As a reference, ASME B31.3 – Process Piping provides for a Sensitive Leak Test in Para. 345.8. This paragraph states, in part, "Sensitivity of the test shall be not less than 10^{-3} atm·ml/sec(100 Pa·ml/s) under test conditions." This is an additional testing requirement for Category M fluids.

SUMMARY

Autoignition, in most cases, should not be a real concern. Ensuring that designers adhere to good design practices there should be no circumstance that would allow hydrogen to autoignite. The heat required for hydrogen to autoignite would have to come from an outside source.

Leak rates for hydrogen, or any other volatile or lethal service, should be researched, evaluated, discussed and specified in a company's engineering guideline. In pressure/leak testing, determining system integrity through pressure loss or by applying Snoop for a bubble test is acceptable for the majority of services. However, for services such as hydrogen a more definitive and quantifiable method should be adopted.

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