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Management of Leaks in Hydrogen Production, Delivery, and Storage Systems (U)

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EXECUTIVE SUMMARY

A systematic approach to manage hydrogen leakage from components is presented. Methods to evaluate the quantity of hydrogen leakage and permeation from a system are provided by calculation and testing sensitivities. The following technology components of a leak management program are described.

- Methods to evaluate hydrogen gas loss through leaks
- Methods to calculate opening areas of crack like defects
- Permeation of hydrogen through metallic piping
- Code requirements for acceptable flammability limits
- Methods to detect flammable gas
- Requirements for adequate ventilation in the vicinity of the hydrogen system
- Methods to calculate dilution air requirements for flammable gas mixtures
- Concepts for reduced leakage component selection and permeation barriers

INTRODUCTION

The safe production, storage, and delivery of hydrogen will be imperative to successfully implement the hydrogen economy. Hydrogen production, storage, and delivery have one common aspect in that all these processes will require pressure vessels and piping systems to safely contain hydrogen and avoid the hazard introduced if hydrogen were to escape the containment boundary. Hydrogen, like all other fuels and flammable gases, has inherent hazards, and process systems containing hydrogen must be carefully designed to control the special sealing requirements associated with light gases.

This report is prepared for Concurrent Technologies Corporation for the hydrogen pipeline life management program. The report describes the propensity for hydrogen gas to leak from process systems and provides methodologies to evaluate leakage. Code requirements for pre-service and proposed guidance for in-service leakage acceptance criteria based on flammable hydrogen-air mixtures are outlined. Recommendations are provided for component leak testing, for reduced system leakage with preferred joint designs, and for improved permeation barrier materials.

GASEOUS HYDROGEN LEAKAGE

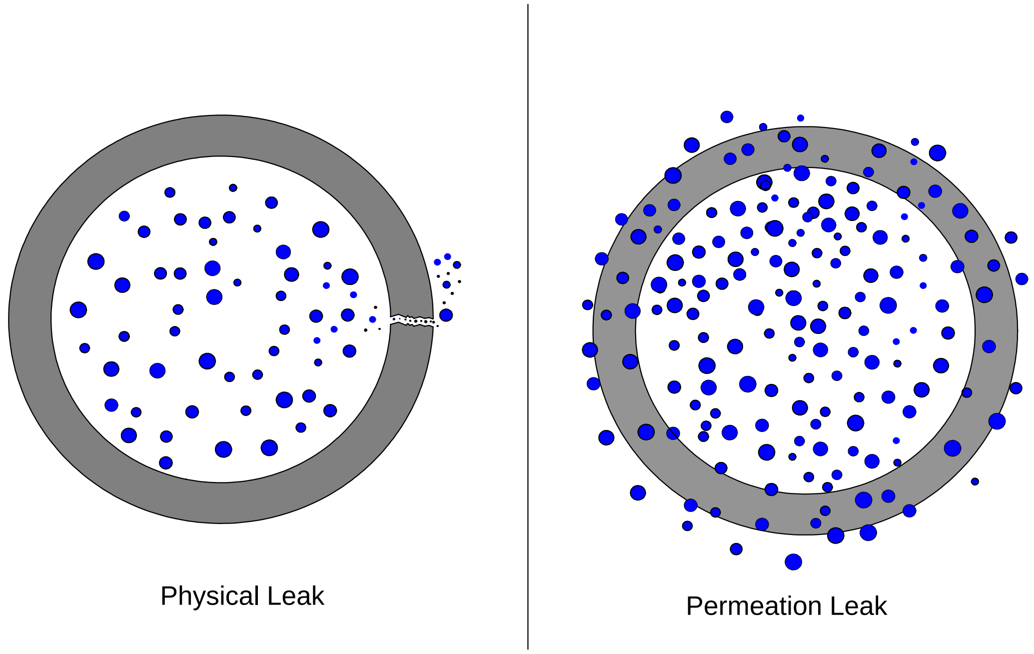
LEAK DESCRIPTION

Leakage is defined as the mass transfer of a fluid across a pressure or containment boundary. Two modes of hydrogen leakage are evaluated in this report, as illustrated in Figure 1. These include physical leaks and permeation leaks. Physical or path leaks occur from imperfections in joints, seals or defects in the pressure boundary. The imperfections manifest as a hole providing a leak path in the pressure boundary resulting in pneumatic gas flow. Path leaks usually occur because of defects in welds or brazed connections, flaws in sealing surfaces, or improper installation of mechanical joints.

Pre-service leak testing is required by construction codes. The main purpose of leak testing newly constructed piping systems and pressure vessels is to identify and repair physical leaks. Proper design, examination, and testing are required to control real leaks in hydrogen systems. The ASME Code for Pressure Piping [1,2] and the ASME Boiler and Pressure Vessel Code [3] provide the requirements for design and construction of hydrogen process equipment.

Hydrogen is permeable through metallic containment even if a component serving as a pressure boundary contains no flaws. Permeation takes place by atomic or molecular diffusion through the material. Permeation of diatomic molecules, such as hydrogen, oxygen, and nitrogen, through metals involves molecular adsorption onto the surface, dissociation of the molecule into surface atoms, solution of the atoms in the material, atomic diffusion through the material, and subsequent re-association of molecules and desorption from the material on the other side of the boundary. Hydrogen is unique in having a much higher permeation rate through metals compared to other common gases such as nitrogen and oxygen- between 15 and 20 orders of magnitude [4].

Permeation through polymers occurs with diatomic molecules transport directly without dissociating (into atoms). For both metals and polymers, the permeation rate increases with increasing pressure and temperature. Permeation rates are controlled through the proper selection of materials for the specific design application and also by increasing the thickness of the pressure boundary component.



Physical Leak

Permeation Leak

Figure 1 Concept of Path Leak or Pneumatic Flow and Permeation Leak

GASEOUS HYDROGEN LEAKAGE PARAMETERS

Hydrogen gas has several distinguishing attributes that are pertinent to safely contain it under pressure and for use in establishing leakage criteria for the acceptance of pressure retaining components. Both the physical properties of the fluid and the design parameters of the piping system will influence the leakage rate of the system. The major factors influencing leakage include:

Gas Properties

- Molecular mass or density
- Viscosity
- Molecular Diameter
- Mean Free Path

System Properties

- Deferential Pressure Across the Leak Path
- Absolute Pressure in the System (Design Pressure)
- Length and Cross Section of the Leak Path
- Material of pressure boundary
- Number and type of Joints in the system

Physical Properties of Hydrogen

A combination of physical properties affects the leakage characteristics of gaseous hydrogen. Hydrogen is the lightest element in the universe, fifteen times lighter than air. The viscosity of hydrogen is approximately half that of helium. Hydrogen is more prone to leak than other gases, because of its low viscosity and light molecular weight. Figure 2 provides a comparison of hydrogen to air and helium showing the difference in viscosity with temperature [5]. Specific properties of hydrogen that effect leakage as compared to other common gases are provided in Table 1 [6].

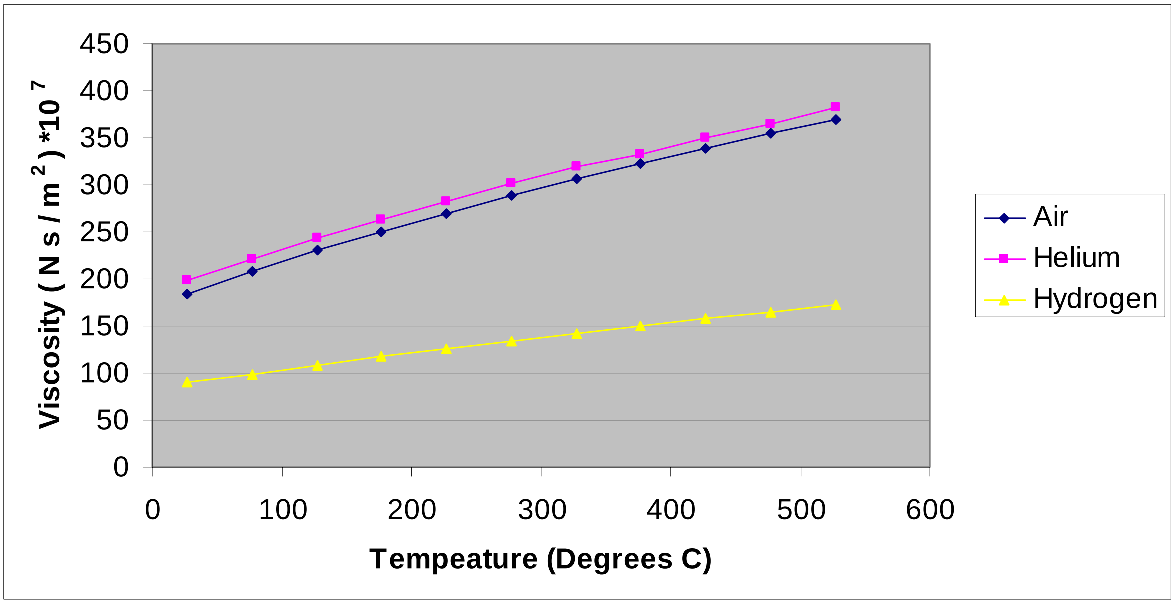


Figure 2 Comparison of Viscosity of Air, Helium and Hydrogen.

Table 1 Properties of Gases Compared to Hydrogen at 15ºC

Gas	Molecular Weight (g/mol)	Ratio To Hydrogen	Molecular Diameter (pm)	Ratio To Hydrogen	Viscosity (Pa-sec) X10^6	Ratio To Hydrogen
Air	29	14.5	-	-	18	2.1
Argon	39.9	20.0	288	1.2	22	2.6
Helium	4.0	2.0	190	0.8	19.2	2.2
Hydrogen	2.0	1.0	240	1.0	8.6	1.0
Methane	16.0	8.0	-	-	10.7	1.2
Nitrogen	28.0	14.0	315	1.3	17.3	2.0
Oxygen	32.0	16.0	298	1.2	19.9	2.3
Steam	18.0	9.0	-	-	9.3	10.8

LEAKAGE RATE MODELING

Leak rate modeling for two modes of hydrogen leakage, pneumatic flow and permeation, are described. Pneumatic flow occurs when the leak is by transfer of the gas through a small restriction in the pressure boundary. There are three basic modes of pneumatic flow to be considered in leak rate modeling: viscous, transitional, and molecular. Laminar flow and turbulent flow are subcategories of viscous flow, and a special case of viscous flow is choked flow.

The approximate ranges of flow rates for various pneumatic modes of gas flow are as follows [6].

- Turbulent flow occurs with leakage rate above 10^{-2} std. cc/sec.
- Laminar flow occurs with leakage rates in the range from 10^{-1} to 10^{-6} std. cc/sec.
- Molecular flow is most probable with leakage rates below 10^{-5} std. cc/sec.
- Transitional flow occurs in the gradual transition from laminar to molecular flow.
- Choked flow occurs when the flow velocity approximates the speed of sound in the gas.

Laminar and molecular flows are the predominant modes of leakage flow in the range of leakage rates of interest for hydrogen component leakage. Molecular flow is only an issue at low vacuum pressures where the mean free path of the gas molecule is equal to or exceeds the cross sectional diameter of the leak. Figure 3 shows the effect of pressure on the mean free path of hydrogen and air. The requirement for the molecular flow model at vacuum pressure is clearly indicated by the large increase in mean free path from near full vacuum pressure shown at the left axis of Figure 3 to atmospheric pressure at the right of the figure. At the proposed pressure conditions for hydrogen piping and pressure vessels (> 1000 psi), the flow rates will be viscous and in many cases will meet the requirements for choked flow.

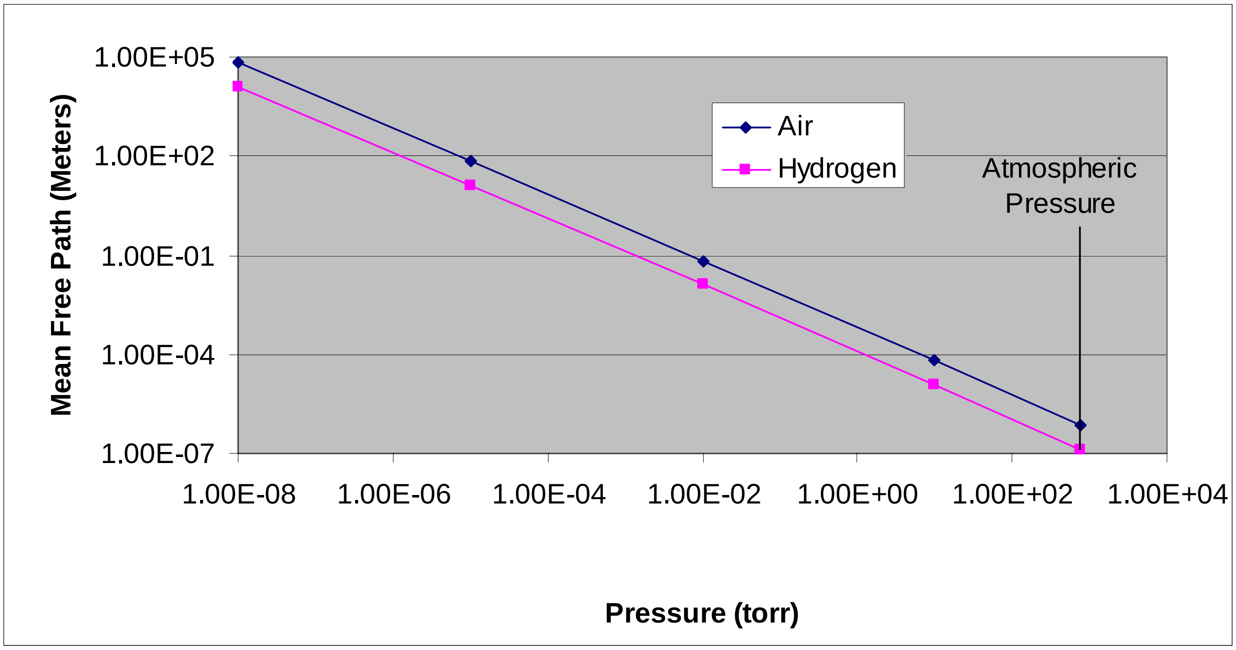


Figure 3 Mean Free Path of Air and Hydrogen vs. Absolute Pressure

When the diameter of a leak path is much larger (approximately 2 orders or magnitude) than the mean free path of the gas, the flow will be viscous. The viscous flow mode will always be the type of flow in high pressure leaks because the mean free path of a gas is inversely proportional to the pressure. The pressure drop across the leak path from the inside of a pressurized pipe or pressure vessel to atmosphere will be sufficient for viscous flow to control. This is the normal flow mode in leak testing pressurized systems. The flow rate from the leak will be proportional to pressure drop across the leak path. Quantitative models to evaluate both pneumatic flow and permeation are provides in Appendix A.

Leak rate comparisons between hydrogen and air at specified hole sizes are provided in Figure 4. The calculated leakage rates in the figure show that hydrogen leakage rates will be approximately twice those of air. When compared to natural gas, tests have shown the hydrogen will leak from the same system at a rate approximately 3 times faster on a volumetric basis [7]. The DOE has set a target goal to reduce the leakage rate of hydrogen for delivery systems to equivalent rates to the current natural gas systems by 2015.

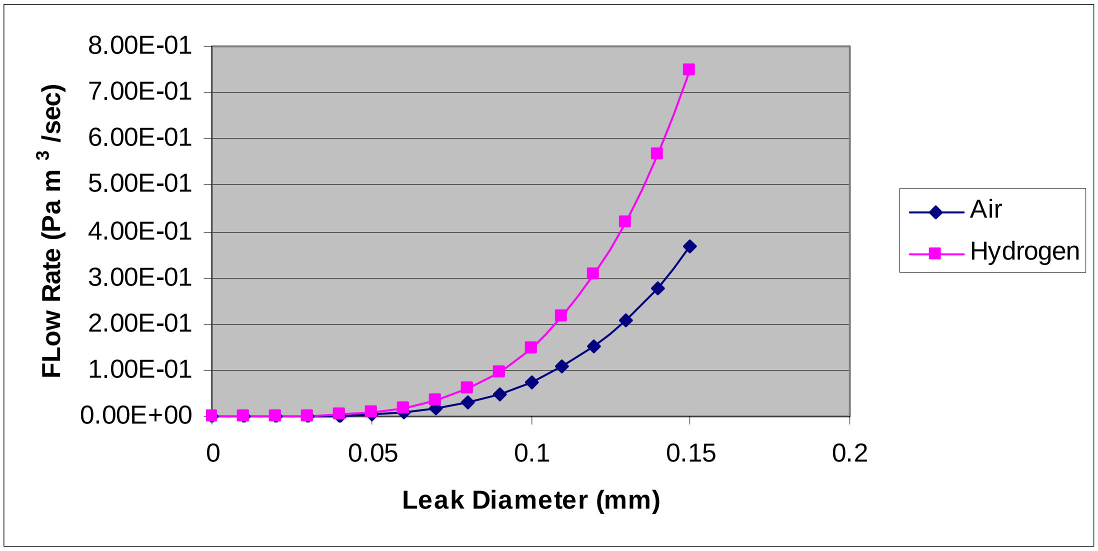


Figure 4 Standard Leak Rate vs. Leak Diameter for a 103421.4 Pa (15 psi) Pressure Differential with a Laminar Flow Model

HAZARDS ASSOCIATED WITH GASEOUS HYDROGEN LEAKAGE

HYDROGEN FLAMMABILITY

Hydrogen has a wider range of flammability in air than other common industrial fuel gases such as methane, propane, or gasoline as shown in Table 2 [8]. The minimum ignition energy at stoichiometric conditions is also an order of magnitude lower than the other industrial fuel gases. In evaluating hydrogen leaks the lower flammability limit (LFL) is the controlling parameter. For hydrogen the LFL is 4% by volume, compared for example to methane at 5.3%. The LFL limits for propane and gasoline are 1.7% and 1.0 % respectively. Required controls on the leakage of hydrogen would be similar to that for methane, where controls on propane and gasoline would be more restrictive. The much lower minimum ignition energy for hydrogen than the other gases in Table 2 is of little consequence since all these gases have low ignition energies. A weak static spark would ignite any of the gases. As a point of reference an electrostatic spark from the human body will produce about 10 mJ which is high enough to ignite any of the gases.

Ignited hydrogen-air mixtures will result in either a fire at a fixed point, a deflagration, or a detonation. The leakage rate of hydrogen from a point source can burn as a small flame to a jet depending in the velocity of the leak. Hydrogen-air mixtures in the open with no confinement will result in a deflagration. The resulting pressure increases for a deflagration event are on the order of 5 times the initial pressure. Turbulence can cause the deflagration flame front to accelerate and transition to a detonation. A detonation is a much more energetic event and can result in pressure levels as much as 30 times the initial pressure level.

The Nation Fire Protection Association publication NFPA 69 “Standard on Explosion Prevention Systems” [9] provides requirements for “Deflagration Prevention by Combustible Concentration

Reduction" in Chapter 6. For the condition for hydrogen leakage into a room, NFPA 69 would place a limit on the hydrogen concentration of 25% of the lower flammable limit. The allowable concentration of hydrogen in a room would then be 1 % by volume. The standard also requires the installation of sensors to detect hydrogen concentration level in the process spaces. The concentration limit of 25% of the LFL for NFPA 69 can be used to set ventilation requirement for process spaces.

Table 2 Ignition and combustion properties of air fuel mixtures of common fuels

Fuel	Lower Flammability Limit % Volume	Lower Detonation Limit % Volume	Stoichiometric Mixture % Volume	Upper Detonation Limit % Volume	Upper Flammability Limit % Volume	Minimum Ignition Energy mJ	Auto Ignition Temperature ºC
Hydrogen	4.0	18.3	29.5	59.0	75	.017	585
Methane	5.3	6.3	9.5	13.5	17	.274	537
Propane	1.7	3.1	4.0	9.2	10.9	.240	450
Gasoline	1.0	1.1	1.9	3.3	6.0	.240	215

CONTROL OF GASEOUS HYDROGEN LEAKAGE

JOINT DESIGN AND SELECTION

The propensity of hydrogen to leak requires special attention to the details in the design of the pressure boundary of a system, as well as the selection for components that will be used to control the system. The design codes such as ASME B 31.3 and B31.8 place requirements on all parts of the piping system, but there is the tendency to overlook these requirements for components such as valves and instruments. It will be important to rigorously apply the design codes to all components as the general public comes in contact with hydrogen systems. Hydrogen systems at present are controlled by very experienced users who understand the hazards posed by hydrogen and the tendency for hydrogen systems to leak. The need to control joint types and seal materials to those equivalent or superior to original manufacture's equipment in hydrogen systems will be paramount for safe operation.

A process or distribution system that contains hydrogen will always contain leaks. The selection of joint types and seal materials can be used to reduce leakage to minimum levels that can be safely controlled through ventilation.

Welded joints are the preferred method for joining materials in metallic piping systems. A weld made to the design code requirements will have the same strength as the joined material, but will have allowable flaws and porosity levels that are higher than the base material. The selection of the proper material to avoid hydrogen embrittlement is important for adequate system design, and the effect of welding on the base material needs to be evaluated to ensure crack-like flaws are not introduced or initiate or propagate through the weld metal and heat-affected-zone at accelerated rates as compared to the base material.

All types of mechanical joints have been used in hydrogen systems. There are several types of specialty fittings manufactured that provide very low leakage rates and that seal by means of highly localized plastic deformation. The most widely known manufactures of these fittings are Swagelok and Parker Hannifin. Compression fittings of this type would be the first choice of mechanical joints for application in hydrogen systems. However, compression fittings are limited in size and can only be applied to tubing systems.

Flange joints meeting the requirements of ASME B16.5 [10] that seal with face seals are acceptable for hydrogen service. When flanges are applied the application should be extensively reviewed. Raised face or ring joint flanges are preferred for their sealing ability. The proper selection of the gasket for compatibility with hydrogen is essential. The Compress Gas Association and NASA [11, 12] recommend the use of filled spiral-wound steel gaskets with raised face flanges and soft metallic, such as copper for ring joint flanges. Polytetrafluoroethylene (PTFE, one trade name is Teflon®) and graphite are the recommended fill materials for the spiral-wound gaskets. The DOE has had successful service with Helicoflex metallic gaskets, with copper and silver seals in hydrogen systems. The proper installation of the flanged joint will be the most important factor in obtaining an effective seal for flanged joints. ASME standard PCC1 “Guidelines for Pressure Boundary Bolted Flanged Joint Assembly” [13] provides the best guidance for flange installation.

Threaded joints have been used in hydrogen service, but their use is not recommended. When threaded joints are the only option, seal welding the threads to the requirements of ASME B31.3 [1] is recommended.

Hydrogen permeation through metals can be reduced by using a so-called permeation barrier coating. Common coating materials include gold, copper, and aluminum. The permeation rate of hydrogen through gold and copper is much less than through carbon steel, and the thicker these coatings are, the lower is the permeation rate. Aluminum is commonly applied to steels either using plasma spray or pack aluminizing. In the plasma spray process it is used much like the copper and gold coating. For the pack aluminizing coating, it is metallurgically diffused (bonded) at elevated temperature. This results in a stable intermetallic coating. The reduction of hydrogen permeation, up to a factor of 100, is thought to be caused by the formation of aluminum oxide at the surface of the aluminum rich compound; the oxide prevents dissociation of the diatomic hydrogen molecule and so permeation is dramatically reduced. The pack aluminized coating has been used in US Department of Energy applications. Other materials studied as coatings for hydrogen permeation reduction include TiN and tungsten.

ASME CODE LEAK AND PRESURE TESTING

Piping design codes all require a leak test prior to a system being placed into service. Leak testing is usually conducted at pressure levels at or below the system operating pressure. A pressure test as prescribed by design codes is performed at a factor times the design pressure of the piping system. The most applicable design codes for a hydrogen piping at this time are ASME B31.3 "Process Piping" and ASME B 31.8 "Gas Transmission and Distribution Piping". ASME is currently developing the B31.12 Code "Hydrogen Piping" that will address issues specific to hydrogen piping systems. The B31.12 Code will closely follow the existing requirements in the existing B31.3 and B31.8 for testing requirements based on their respective scopes. The main purpose of both of these tests is to verify the quality of construction of the piping. The pressure test as described in the Design Codes can be performed either as a hydrostatic or a pneumatic test. The pressure test is usually performed at 1.1 to 1.5 times the design pressure of the system. The code leak test is applies to test the pressure boundary of the piping system and not the isolation points in the system, such as the seats or seal in valves.

The most common locations for leaks in piping systems are at mechanical joints such as bolted flanges and threaded connections. Leaks can also occur at welds but are less common than leaks at mechanical joints. Even though weld defects do exist in piping systems, they do not usually extend through the wall of the piping system and result in leakage. Weld defects have resulted in the catastrophic failure of vessels during pressure testing. In cases where failure has occurred during pressure testing, brittle material behavior has been a contributing factor. The brittle material behavior was caused by the testing in cold ambient environments or with low temperature test fluids, in which the temperature fell below the materials ductile to brittle transition temperature (DBTT).

ASME Section V Article 10 [14] provides the requirements and guidance for leak testing methods. When testing for hydrogen leakage the sensitivity of the test method should be reviewed. Because of flammability issues with hydrogen the proper acceptance method for piping systems must be determined. When piping systems are in enclosed spaces, leakage can cause the hydrogen concentration in the room to rise to flammable levels. It is also important that the allowable leakage rate is chosen based on contribution for all possible leak sites. In closed spaces with multiple joints the leak rate will need to be lower than for a single leak site, as discussed above. Leak rates from pipelines are less of a concern because more of these systems are located outside where a flammable mixture cannot occur. Conditions that will trap gas from leaks and result in flammable mixtures must always be evaluated. The more common leak testing methods are reviewed below to provide guidance for performing hydrogen leak testing. The sensitivities associated with the these test methods can be used to determine bounding leakage rates for ventilation system design.

Hydrostatic testing is performed by filling the piping system with water to the specified test pressure. The test pressure is usually 1.25 to 1.5 times the design pressure. The piping being tested is isolated and filled with water to the test pressure. All joints, both welded and mechanical, are then visually inspected for leakage. The sensitivity of the hydrostatic testing method is in the range of 1 to 10^{-2} std. cc/sec [15]. One cubic centimeter per second is approximately one gallon per hour. In hydrostatic testing a sufficient period of time is required to allow the liquid to migrate through any restrictive path to the surface where a leak can be observed.

The pneumatic pressure is similar to the hydrostatic pressure test except the piping is filled with air or an inert gas and pressurized. The test pressure is lower than with a hydrostatic test to control the stored energy associated with the compressed gas. The B31.3 Code requires that the pressure be slowly increased to 1.1 times the design pressure. The pressure in the piping system is then reduced to the design pressure and all joints are inspected for leaks. A bubble solution is applied to the joints to aide in the visual identification of leak sites. The B31.8 piping code requires that all pipelines be tested for leaks with a gas test fluid, but only requires a maximum pressure of 100 psi. All the ASME codes provide specific caution and make recommendations for conducting pneumatic pressure tests because of the associated safety concerns with the stored energy in the compressed gas. The sensitivity of the pneumatic testing method is in the range of 10^{-2} to 10^{-4} std. cc/sec [15], significantly more sensitive than hydrostatic testing.

Bubble leak testing is specified in ASME Section V, Article 10, Appendix I. The test is performed by filling the component with air or an inert gas. This test is normally performed at low differential pressure across the pressure boundary in the range of 15 psi. Increasing the differential pressure across the pressure boundary will increase the sensitivity of the test. Lower viscosity test fluids will also improve the test sensitivity along with increased hold times needed for bubble formation at low leak rates. Helium is a good choice for a test gas when high sensitivity is required. A bubble solution is applied to the joints to aid in the visual identification of leak sites. If small components are being tested, the entire component can be immersed in a liquid bath. Leak sites can be detected on the pressure boundary by visual inspection. The sensitivity of the bubble testing method is normally in the range of 10^{-2} to 10^{-4} std. cc/sec [6]; sensitivities of 10^{-5} std. cc/sec can be achieved with refined test conditions.

The Pressure Change Test is described in ASME Section V, Article 10, Appendix VI. Pressure chance testing can be performed by several different methods. The two most common methods include pressure decay testing and rate of rise testing. In pressure decay testing a known pressure is applied to a component, and pressure is monitored over time to determine pressure decay. The pressure as a function of time can be used to determine the leak rate. The rate of rise test is similar to the pressure decay test except that the system pressure is initially lowered to a vacuum. The pressure rise is monitored with time, and the leak rate is calculated from the test data. Both of these pressure change methods are highly dependent on test duration. Test durations for small systems will be on the order of minutes where large system test durations will be on the order of hours, depending on the required test sensitivity. The precision of the pressure measurement instruments will affect the test results and the certainty of the calculated leakage rate. The sensitivity of the pressure change testing methods is dependent on system volume and test duration general value of sensitivity can not be provided.

Additional highly sensitive leak test methods are defined in ASME Section V, Article 10. These test methods require the use of a tracer gas such as helium. A differential pressure across the pressure boundary in the range of 1 atmosphere is usually specified. The tracer gas can be applied to either side of the component, and a vacuum pressure can be applied to achieve the required differential pressure. Leakage from the system is detected by use of sniffing probes or a mass spectrometer. Sensitivities as high as 10^{-10} std. cc/sec can be achieved by these highly sensitive methods [6]. One disadvantage to these methods is that they do not always provide a means to determine the location of the leak site.

MITIGATION AND MANAGEMENT OF GASEOUS HYDROGEN LEAKAGE

VENTILATION FOR HYDROGEN SYSTEMS

When using hydrogen or other flammable gases in closed spaces, the effect of leaks on the concentration level of the flammable gas in the air space must be evaluated. The leak rate must be determined based on the sensitivity of the leak testing method used. The use of adequate ventilation or placing limits on the gas quantities in rooms where hydrogen in used is required to control the concentration levels. Hydrogen accumulation must be controlled to acceptable levels in the atmosphere. Since hydrogen is much lighter than air, hydrogen can become trapped at high points resulting in pockets of hydrogen with high concentrations. Adequate amounts of ventilation flow must be provided to assure that no stagnant pockets exist.

The amount of ventilation required depends on the volume of the space and the maximum possible leakage rate into the space. In some cases hydrogen will also be stored in the space such as when bottled hydrogen is used as a supply source. The release of the stored volume may also need to be considered when evaluating the required ventilation levels and the maximum space concentration compared to the lower flammability limit of hydrogen. The control of hydrogen leakage is accomplished through proper system design, leak testing and ventilation.

The following methodology is suggested for estimating the required airflow rate [16]:

Nomenclature

V = Space Volume (ft^3)

V_H = Amount of hydrogen stored, (STD. ft^3)

H = Maximum Hydrogen Leakage Rate, (SCFM),

A = Ventilation Flow Rate (SCFM).

C = Limit of hydrogen concentration in air typically 25% of LFL (% volume)

t = Time, (min.)

S = $\frac{H}{H+A}$, assumed steady state concentration, (% volume)

T= $\frac{V}{H+A}$ Time constant, (min.)

Assume the atmosphere is well mixed and there is no hydrogen in the air before the leakage starts. Once the leakage begins, the hydrogen concentration will go up according to the correlation:

$$C = S(1 - e^{\frac{t}{T}}) \qquad (1)$$

Solving for t provides an equation for time to reach the flammability limit

$$t = T \ln(1 - \frac{C}{S}) \qquad (2)$$

The equations provided above provide for the review of three conditions to be evaluated to determine acceptable hydrogen concentrations.

Condition 1 Hydrogen stored in an unventilated space without leakage

The total volume of hydrogen can be released into the space as long as the final concentration level is within acceptable levels

$$\frac{V_H}{V} < 25\%\ \text{LFL}$$

Condition 2 Hydrogen leakage into a space with an unlimited supply and ventilation

For an unlimited amount of hydrogen to supply the leak, the ventilation flow rate must be at a level to insure that the flammability limit is not reached

$$\frac{H}{H+A} < 25\%\ \text{LFL}$$

Condition 3 Hydrogen leakage into a space with a limited supply and ventilation

The length of time that the leakage lasts can be calculated as follows

$$t_H = \frac{V_H}{H}$$

The time to reach the flammability limit can be calculated using equation 2

If $\mathbf{t} > \mathbf{t_H}$, the ventilation flow rate is sufficient

If $\mathbf{t} < \mathbf{t_H}$, the ventilation flow rate is not sufficient, and the flow rate will need to be increased or the leak rate will need to be reduced.

FLAMMABLE GAS DETECTORS[1]

Flammable gas detectors can make a valuable contribution to the safety of these processes. They can be used to trigger alarms if a specified concentration of the gas is exceeded. This can provide an early warning of a problem and help to ensure people's safety. However, a detector does not prevent leaks from occurring or indicate what action should be taken. It is not a substitute for safe working practices and maintenance.

Detectors can be fixed or portable. A 'fixed' detector is permanently installed in a chosen location to provide continuous monitoring of plant and equipment. It is used to give early warning of leaks from plants containing flammable gases, or for monitoring concentrations of such gases and within the plant. Fixed detectors are particularly useful where there is the possibility of a leak into an enclosed or partially enclosed space where flammable gases could accumulate.

A portable detector usually refers to a small, handheld device that can be used for testing an atmosphere in a confined space before entry, for tracing leaks or to give an early warning of the presence of flammable gas or when hot work is being carried out in a hazardous area.

Point detectors measure the concentration of the gas at the sampling point of the instrument. The unit of measurement can be:

- % volume ratio or ppm concentration;
- % lower explosion limit (LFL) for a flammable gas;

There are a number of different types of sensors used for gas detection. The choice of sensor depends on:

- the gas to be detected;
- the expected range of concentration;
- the presence of other gases that may affect readings or damage the sensor.

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1. The information provided on flammable gas detectors was adapted from reference 17

In many fixed gas detection systems, the sensor units are designed to use natural diffusion as the sampling method. The sensors are located at or near points where there is the possibility of a gas release.

If a specified gas concentration or set point is exceeded, the detector system should trigger an alarm. The alarm should not stop or reset unless deliberate action is taken. The alarm should be audible or visible or preferably both. The requirements for alarms are specified in performance standards such as NFPA 69.

The gas detector should be set to alarm at a level low enough to ensure the health and safety of people but high enough to prevent false alarms.

In determining the required alarm levels for fixed gas detection systems, the following should be taken into account:

- any industry standards and recommendations;
- the lower flammability limit of the gas
- the size of the potential leak and the time to reach a hazardous situation;
- whether the area is occupied;
- the time required to respond to the alarm;
- the actions to be taken following the alarm;

A suitable safety margin should also be incorporated to account for ventilation dead spots and the variability of natural ventilation. One option is to set two alarm levels. The lower alarm could act as a warning of a potential problem requiring investigation. The higher alarm could trigger an emergency response such as evacuation or shutdown or both. For leak detection purposes the first alarm level should be set as low as practical.

The purpose of a gas detector is to give a warning of a potential problem. The actions to be taken if the alarm sounds should be considered before the detector system is put into use. They should be documented in written procedures. These procedures may be operating procedures or emergency procedures and should be backed up by training and refresher courses.

Sensors should be positioned to detect any gas accumulation before it creates a serious hazard. Factors to consider are:

- the process plant and equipment;
- the type of sensor (see Appendix);
- the properties and dispersion characteristics of the gas;
- the ventilation patterns;
- other safety issues, eg location of personnel or equipment protection.

The number of sensors should also be considered. Failure or removal for maintenance, of an individual sensor should not compromise the safety of the area being monitored. Redundant sensors and control apparatus may be required for continuous monitoring and to prevent false alarms

The path of the gas or its dispersion characteristics will depend on the density of the gas and the ventilation patterns. The density can be used to determine at what height sensors should be positioned relative to the potential source.

The ventilation patterns for outdoor locations will depend on wind speed and direction, plant layout and topography. If necessary, smoke tests or computer models can be used to predict how a gas leak will behave and to determine the best place for sensors.

The sensors or sample points should not be positioned where they may be susceptible to excess vibration or heat, contamination, mechanical damage, or water damage.

Types of Flammable Gas Detection Sensors

Catalytic

The operating principle of this point detector is that heat is generated during the catalyzed reaction between the gas and oxygen in air. The resulting rise in temperature of the catalyst bead causes a change in electrical resistance of a platinum wire embedded in the bead, also acting as the heater, which is a measure of gas concentration. The heated wire is contained enclosure with a porous sintered metal insert that allows the gas to enter. This detector is small and is used for detecting flammable gases from 0-100% LFL.

Infrared

The operating principle is based on the absorption of infrared light by certain molecules which are detected by a decrease in transmitted radiation over a beam path. The detectors do not require oxygen, cannot be poisoned and are not ambiguous above the LEL. Unfortunately they cannot detect hydrogen and are inherently pressure-sensitive.

Thermal conductivity

The operating principle of this detector is that gases conduct heat at different rates. If a gas is in a mixture with a reference gas then the concentration can be determined by comparing the thermal conductivity of the mixture and the reference gas. This is typically done by measuring the heat dissipated by heated elements. The out-of-balance voltage from a resistance bridge is a measure of the gas concentration. The bridge compensates for ambient temperature changes. This detector is used in the range 0.1-100% v/v. It only works well when differences in thermal conductivity between the target gas and reference gas (air) are large and therefore works well with hydrogen or methane.

Flame ionization

This detector operates on the principle that an ionized gas will conduct an electrical current in proportion to the number of ions present. Hydrocarbon gases are easily ionized and the current flow produced is easily measured. The source of ionization is a hydrogen flame. This detector can be used for most hydrocarbon gases from ppm to % v/v levels. It needs hydrogen to generate the flame and a clean air supply

Flame temperature

This point detector operates by monitoring the temperature of a controlled hydrogen flame using a pyrometer. Flammable gas in the air supply to the flame causes the temperature of the flame to change. This change is a measure of gas concentration. This detector is large and is used for flammable gases from 0-100% LFL. It has a fast response but needs hydrogen to generate the flame and a clean air supply.

Semiconductor

The operating principle of this detector is that a surface interaction between a gas and a gas-sensitive semiconductor alters the conductivity of the semiconductor. Generally, reducing gases (eg hydrocarbons) drive the conductivity in one direction and oxidizing gases (eg oxygen) drive it in the opposite direction. The change in electrical conductivity of the semiconductor is a measure of the concentration of hydrocarbons in air. This detector can be used for most hydrocarbon gases from ppm to % v/v levels. It has a non-linear response and needs oxygen.

Ultrasonic

The operating principle is that the escape of gas from a high-pressure pipeline or other pressurized systems generates ultrasound, which when detected by an acoustic sensor, can provide a measure of the leak rate. This is a non-concentration based detector used to detect leaks from high pressure systems. Theoretically, it provides 360º coverage and does not require transport of the gas to the sensor. Care is needed in placement and false alarms may occur due to other ultrasonic emissions.

Photo ionization

The operating principle of this detector is the same as for the flame ionization detector, but the source of ionization is an ultraviolet lamp. The usage and range of this detector are dependent on the energy of the UV lamp. Its range is from ppm to % v/v levels. The detector is fast and sensitive but humidity may affect the readings. These detectors are small and can be handheld. They are used for leak detection at very low levels.

HYDROGEN SENSORS TECHNOLOGY AND STATUS

Sensors have been fabricated from materials that exhibit optical or physical changes when exposed to hydrogen. For example, there are both thick and thin film sensors that exhibit resistivity changes when hydrogen is incorporated in the lattice. There are thin film sensors, which undergo lattice changes with hydrogen incorporation; in addition, there are thin film sensors that demonstrate optical changes when reacted with dissociated hydrogen gas. All of the aforementioned sensor platforms have the potential for degradation mainly due to hydrogen cycling or contamination from impurities such as SO_2, CO or NO_x. In this section, a brief overview of the various types of commercialized or emerging hydrogen sensors will be given along with a discussion of the limitations of each.

Electrochemical Sensors

Electrochemical sensors generally consists of a H_2 sensing, a counter and a reference electrode. H_2 gas oxidizes at the sensing electrode which results in a change in the potential at the sensing electrode with respect to the reference. These sensors are usually selective for H_2 while having a working range from 100 to 1000 ppm H_2. Some inherent disadvantages are that electrochemical type sensors have a narrow temperature range, normally require oxygen for reversibility and have a short expected lifetime due to material oxidation. (Commercially Available)

Catalytic Bead Sensors

Catalytic bead sensors consist of 2 beads surrounding a wire heated to high temperatures (450°C). One bead is coated with a catalyst material to promote H_2 dissociation while the other is passivated. The 2 beads form two legs of a Wheatstone bridge, where changes in resistivity at the coated bead alters the bridge balance of the system and is detected. The sensor can generally be used over a wide temperature range and performs well in the 1 to 5 percent H_2 range. The catalytic bead sensors, however, are not H_2 selective and require 5 to 10% O_2 to operate. In addition, the sensors are known to be susceptible to poisoning by Pb, Si, P and S. (Commercially Available)

Semiconductor Sensors

Semiconductor sensors are comprised of mainly metal oxides which detect gases through variations in their resistance after gas adsorption into the crystal lattice. The resistivity of the semiconducting material is dependent on several factors such as temperature, humidity and chemical composition of the surrounding atmosphere. These sensors generally operate in the 0 to 1000 ppm H_2 range, but are only useful as general leak detectors since they are not H_2 selective. (Commercially Available)

Hydrogen Field Effect Transistors (HFETS)

HFETS are standard FETS while using palladium as the gate material. Thus, small changes in the resistivity of the palladium gate cause large changes in the current-voltage characteristics of the FET. These sensors work well in the 50 to 1000 ppm H_2 range while suffering from some of the same disadvantages as do palladium based sensors. (Commercially Available)

Resistive Palladium Alloy Sensors

Palladium alloy sensors use a wheatstone bridge architecture with two Pd/Ni sensor legs whose resistivity changes reversibly in the presence of H_2. Palladium acts as a catalyst material to dissociate H_2 that allows the monoatomic H dissolve into the metal layer. The palladium alloy sensors take advantage of the fact that Ni permits the palladium lattice to contract reversibly during hydrogen cycling. (Commercially Available)

Thermal Conductivity Sensors

Thermal conductivity H_2 sensors contain regions that act as “hot” and “cold” elements with controlled temperatures. Heat is transferred from the hot to the cold region via thermal conductivity through the gas phase (i.e. H_2). The power required to maintain the “hot” region serves as a direct measure of the gas conductivity. These sensors are not as sensitive as electrochemical or metal oxide sensors with detection values in the higher percent ranges, but could be useful as general leak detectors due to their sensitivity to light gases. (Emerging Technology)

Fiber Optic H_2 Sensors

Fiber Optic H_2 Sensors generally consist of portions of fiber optic coated with H_2 sensitive films. The films optical properties (i.e. refractive index, dielectric constant) are changed as hydrogen sorbs into the lattice of the films. Light is used to interrogate the films as it propagates down the optical fiber via total internal reflection. These types of sensors are traditionally immune to electromagnetic interferences, safe in potentially explosive environments (i.e. hydrogen) and show operating detection ranges from 0.1 to 100% H_2. Although, the coatings tend to suffer from cyclic instability in the films (delamination), optical effects from temperature and relative humidity. Emerging research in this area is addressing many of the limitations of past H_2 specific optical coatings. (Emerging Technology)

RECOMMENDATIONS

The management of leakage through a structural integrity /life management program is necessary for the implementation of a large scale hydrogen infrastructure. The technical components of a leakage management program for hydrogen systems have been described in this report. A program built from these components is an essential element for safety in hydrogen systems.

Additional development of the technology components and activities to enable practical implementation are recommended below

- Develop leak test standards for components in hydrogen service
- Develop pre- and in-service testing protocols for hydrogen systems
- Evaluate leakage from mechanical joints as a function of joint tightness
- Evaluate permeation rates for seals and gasket materials that address specific seal geometries
- Develop new membrane coating and method the apply the to existing installed systems
- Develop prototype devices to perform hydrogen permeation and leakage testing on in-service components
-

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APPENDIX A

QUANTITATIVE LEAK RATE MODELS

To calculate the leakage rate for a leak of a known size for laminar flow conditions, Poiseuille's Equation is applied. Equation 1 [18] models a leak as a circular tube of diameter d of length L, having internal pressure P_1 and external pressure P_2 as shown in Figure 1. The fluid property of interest is the dynamic viscosity, μ. Equation 2 [18] provides for laminar flow between parallel plates, having length L width B and separated by H as shown in Figure 2. Equation 2 can be applied to the condition of flow in a narrow annular space by replacing B with πd. A consistent set of units must be applied in all equations.

$$Q = \frac{\pi d^4}{128 \mu L}(P_1 - P_2) \quad \text{(Laminar Tube Model)} \qquad (1)$$

$$Q = \frac{BH^3}{12 \mu L}(P_1 - P_2) \quad \text{(Laminar Plate Model)} \qquad (2)$$

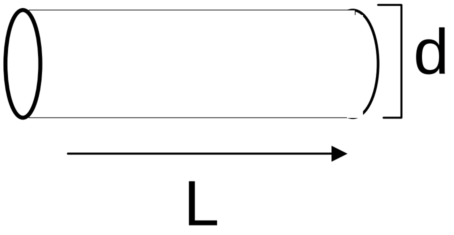

Figure 1 Schematic Viscous Leak Tube Geometry

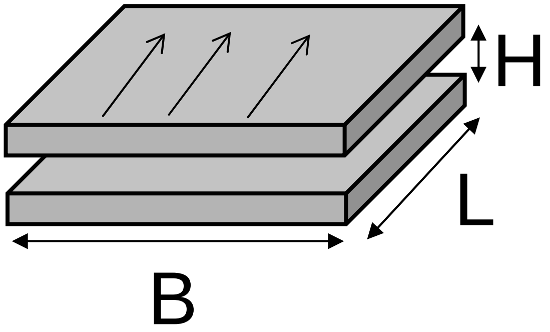

Figure 2 Schematic Viscous Leak Parallel Plate Geometry

Equations 1 and 2 provide the leakage rate in volume per time at the pressure and temperature conditions specific to the leak. The standard units for expressing dimensions for leakage are (pressure) X (volume) / (time), for example (Pa m^3 / sec. or Std cm^3 /sec.). When expressing flow rates in standard dimensions the flows are normalized to an average pressure across the leak $P_{avg} = (P_1 + P_2)/2$, Equations 1 and 2 then become Equations 3 and 4 respectively [6].

$$Q = \frac{\pi d^4}{256 \mu L}(P_1^2 - P_2^2) \quad \text{(Standard Leak Laminar Tube Model)} \qquad (3)$$

$$Q = \frac{BH^3}{24 \mu L}(P_1^2 - P_2^2) \quad \text{(Standard Leak Laminar Plate Model)} \qquad (4)$$

Equations 1 through 4 provide for the calculation of leakage in the laminar flow regime where the Reynolds number based on the velocity of the leakage through the leak is below approximately 2500. Most leakage rates, where calculation of the leakage rate is of interest, will be in the laminar regime.

As the flow rate from the leak site increases above the velocity restrictions for laminar flow, the leak size is of dimensions where a repair is most likely required. When the flow from the leak becomes turbulent, Equation 5 [6] can be applied to calculate the leakage in standard units.

$$Q = \pi d^{\frac{5}{2}}[\frac{RT(P_1^2 - P_2^2)}{16\, fML}]^{\frac{1}{2}} \qquad \text{(Turbulent Tube Model)} \qquad (5)$$

In the turbulent flow regime the frictional resistance to the flow can is no longer a function of Reynolds Number only. The friction factor f is applied in the turbulent flow equation to address the additional resistance to flow in this regime. The friction factor is a function for the roughness of the wall in the leak channel and the flow velocity. The value of f can range from .08 for leaks with high roughness to values as low as .037 [19]. When the data used from the leakage rate calculation is to be applied in calculations to evaluate the flammable atmospheres in rooms conservative estimates of leakage should be used.

In cases where the leak can be modeled as an orifice, the leakage rate can be calculated using equation 6 [19] for actual flow conditions, where equation 7 [6] provide the leakage rate in standard dimensions.

$$Q = \frac{\pi}{4} C_d Y d^2 \sqrt{2g(P_1 - P_2)} \qquad \text{(Orifice Model)} \qquad (6)$$

$$Q = [\pi d^2 P_1 C_d / 4M]/[RT_1 k(2/(k+1)]^{[k+1/k-1]} \quad \text{(Chocked Orifice Model)} \qquad (7)$$

Equation 6 is applicable to any gas flow where equation 7 is specific to choked flow. Choke flow across a leak path occurs when flow through the leak reaches sonic velocity. In choke flow a critical pressure ratio is reached where any additional increase in upstream pressure will not increase the flow rate through the leak. The critical pressure ratio (r_c) for hydrogen and air is .528 and for helium the ratio is .487. When applying equation 6 to the conditions of choked flow the term (P_1-P_2) should be replaced with the $P_1(1-r_c)$ [20]. In high pressure piping systems the conditions for chocked flow will usually exist. In equation 7, k is the ratio of specific heats, which is 1.4 for hydrogen and air and 1.67 for helium. Standard data for discharge coefficients C_d provides a value of .6 for the conditions of a small leak (hole) in a pipe or pressure vessel. A corresponding value of gas expansion factor (Y) is .86 [20].

Experimental data from Jackson [21] Lee et al. [22] has shown that defining the conditions of choked flow exclusively by the critical pressure ratio for small orifice sizes may not be sufficient. The work presented by Lee specifically addressed very small openings that are characteristic of leak sizes found in systems containing hydrogen leaks. The discharge coefficient in Lee's work increased with increased pressure above the choked condition defined by the critical pressure ratio. Discharge coefficients in the range of 0.86 to 1.0 were observed for orifice sizes in the range of 0.5 to 3 mils.

The leak rate models provided above require knowing the dimensions of the leak to calculate the leakage rate. The actual leak dimension, such as the characteristic diameter, is not easily obtained from the leak testing. The above flow models, especially the laminar flow models, are applied extensively in the design of components for light gas sealing. The models can also be applied for calculation of postulated opening sizes in the evaluation of gas release events and flammability hazards.

When the leakage rate is known or is determined from leak test data, the model can be applied to determine the leak cross sectional area. The leakage models can then be applied to calculate the effect of pressure changes. Leak tests on systems designed for flammable gas can be tested with air or helium and a leak rate determined. The cross sectional area of the leak can then be calculated. The hydrogen leak rate can then be determined from the models using hydrogen properties and the calculated cross sectional area. For flow rate in the laminar regime the values in Table 1 [10] can be applied to calculate leakage rates for different gases when the initial calculation or test was performed using helium.

Table 1 Viscous Flow Rates of Gases Relative to Helium Flow Rates.

Gas Flow Rate of :	Equivalent Helium Flow Rate
Air	1.08
Argon	.883
Helium	1.00
Hydrogen	2.23
Nitrogen	1.12
Water Vapor	2.09

LEAK RATE TEST

A standard method to calculate the leakage rate from a system is to perform a pressure decay test. Metallic pressure vessel and piping systems can be considered constant volume systems at test pressure levels. When highly accurate measurements are required, correction can be made for the system expansion due to both temperature and pressure at test conditions. The pressure decay test (or "rate of fall") is a standard test specified in ASME Section V to test for leakage. The leakage rate from the system can be calculated as follows [6, 14]:

Step 1 Calculate the initial mass in the system.

$$m_1 = \frac{P_1 V}{RT_1} \qquad (8)$$

Step 2 Calculate the final mass in the system.

$$m_1 = \frac{P_2 V}{RT_2} \qquad (9)$$

Step 3 Calculate the mass loss due to leakage from the system

$$\Delta m = m_1 - m_2 = \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right)\left(\frac{V}{R}\right) \qquad (10)$$

Step 4 Calculate the leakage rate

$$Q = \frac{RT_s}{t}(\Delta m) \qquad (11)$$

Where:

t is the time of the leak test and

T is test temperature.

The 4 step method described by the equations above provides the means to calculate a leak rate for system test data. The leakage rate provided for the pressure decay test method provides a general value of leakage for the system being tested and is not leak site specific. Tests used to determine leak rate will need to be considered for hydrogen systems to ensure the sufficient ventilation is available to maintain hydrogen concentration levels below the lower flammability limit.

LEAKAGAGE THROUGH PRESSURE BOUNDARY DEFECTS

Leak opening areas from crack like flaws in the pressure boundary of pressure vessels and piping systems can be calculated by applying fracture mechanics techniques. The leakage rate from these opening areas can then be determined by using one of the flow models discussed above. The orifice model will provide reasonable results for thin wall shells. The orifice diameter can be calculated by determining the equivalent diameter for a circular opening equal to the crack opening area. The evaluation of crack like flaws is often performed in hazard assessments of pressure retaining systems for postulated flaws in the pressure boundary. Two cases that address crack like flaws common to pressure vessels and piping systems are provided below [23].

Figure 3 illustrates a longitudinal crack in a pressure vessel. The load to open the crack is the circumferential or hoop stress driven by the applied pressure. Since the pressure load has the maximum effect on the hoop stress, this case will provide the worst case leak size for a postulated flaw in a system where the net section bending stress is low. This is the most common case for pressure vessels. Equation 12 provides the correlation between the applied hoop stress and the crack opening area. Figure 4 provides a plot of crack opening or leak areas verses applied hoop stress for several postulated crack lengths.

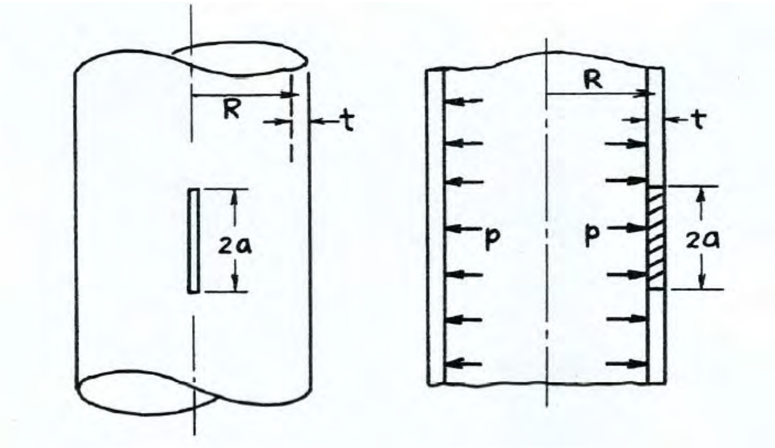

Figure 3 Longitudinal Flaw in a Shell

$$A_{Crack} = \frac{\sigma}{E}\left(2\pi Rt\right)\cdot G(\lambda) \qquad (12)$$

Where:

$$G(\lambda) = \lambda^2 + .625\lambda^4 \rightarrow \; for \rightarrow 0 < \lambda \leq 1$$

$$G(\lambda) = .14 + .36\lambda^2 + .72\lambda^3 + .405\lambda^4 \rightarrow \; for \rightarrow 1 \leq \lambda \leq 5$$

$$\lambda = \frac{a}{\sqrt{Rt}}$$

E = Modulus of Elasticity (Young’s Modulus)

σ = Applied Hoop Stress

In piping systems the controlling loads in the system are the net-section bending moments. Figure 5 illustrates a circumferential crack like flaw. The load to open this type of flaw is controlled by the net section bending moment on the cross section. Equation 13 provides the correlation between the applied stress and the crack opening area. Figure 6 shows the affect of an applied external bending load on the crack opening or leak area for several postulated crack lengths.

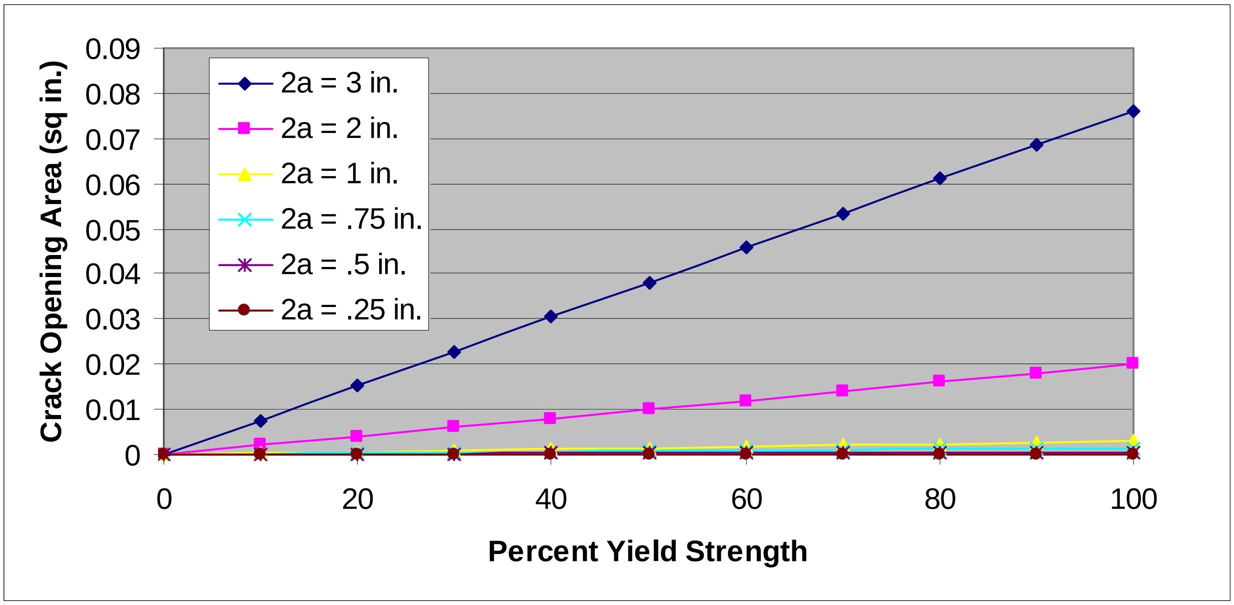

Figure 4 Crack Opening Area as a Function of Yield Strength and Crack Length for a 4 inch Schedule 40 Pipe with a 42 ksi Yield Strength

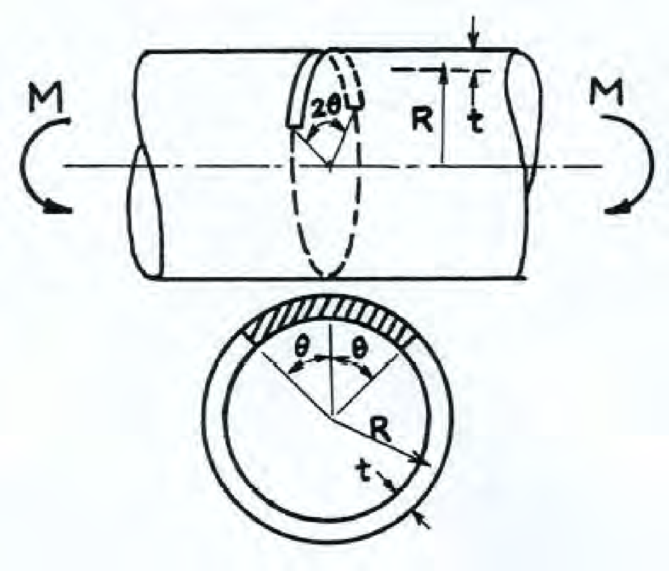

Figure 5 Circumferential Flaw in a Shell

$$A_{Crack}=\frac{2\sigma\pi(R\theta)}{E}\cdot I(\theta) \qquad (13)$$

Where

$$I(\theta)=1+\left(\frac{\theta}{\pi}\right)^{\frac{3}{2}}\left[8.2-12.7\left(\frac{\theta}{\pi}\right)+19.3\left(\frac{\theta}{\pi}\right)^{2}\right]+\left(\frac{\theta}{\pi}\right)^{3}\left[20.4-68.0\left(\frac{\theta}{\pi}\right)+165.2\left(\frac{\theta}{\pi}\right)^{2}-187.2\left(\frac{\theta}{\pi}\right)^{3}+146.7\left(\frac{\theta}{\pi}\right)^{4}\right]$$

E = Modulus of Elasticity (Young's Modulus)

σ = Applies Hoop Stress

θ = Half Crack opening angle, radians

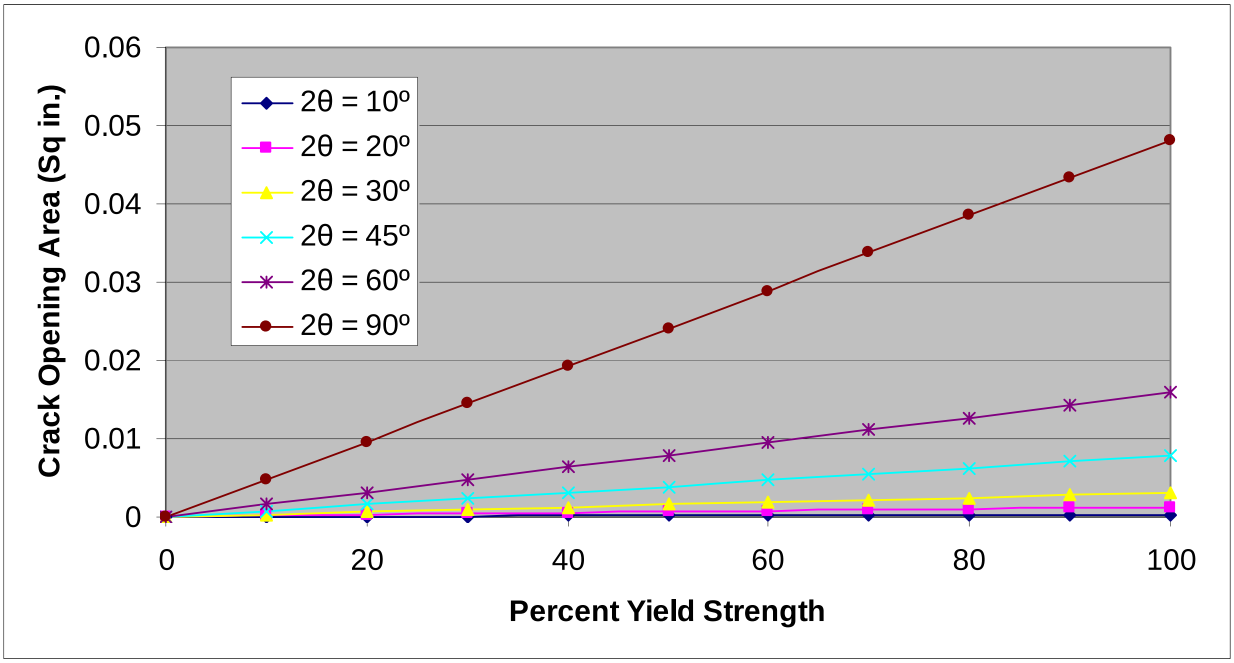

Figure 6 Crack Opening Area as a Function of Yield Strength and Crack Angle for a 4 inch Schedule 40 Pipe with a 42 ksi Yield Strength

HYDROGEN PERMEATION

As discussed earlier, hydrogen inside steel pipe will permeate the pipe wall to some degree. Current understanding of this phenomenon is fairly mature. The permeation rate of hydrogen out of pipe under given conditions can be estimated fairly well with literature data.

Diatomic gases such as hydrogen dissolve in metals as atoms according to Sievert's Law:

$$S=S_0\cdot\sqrt{p}\cdot e^{-\Delta H/RT} \qquad (14)$$

in which p is the partial pressure, ΔH the heat of solution, R the gas constant, T the absolute temperature, and S_0 the solubility constant. The solubility depends on the square root of the partial pressure because the hydrogen molecules dissociate at the surface and dissolve as atoms. The steel typically used for natural gas pipe is composed mainly of iron and has the same body-centered-cubic crystal structure as the form of iron existing at ambient conditions, called alpha iron. It is assumed that the permeability of hydrogen through natural gas pipe is the same as the permeation of hydrogen through alpha iron. This assumption is conservative because, in the limited number of systematic studies regarding diffusivity of hydrogen in iron-based alloys, the major alloying elements decrease or have no effect on hydrogen diffusivity [24]. For hydrogen dissolving in alpha iron, S_0 = 2.98 cc H_2 STP/cc metal/ $\sqrt{}$atm, ΔH = 6840 cal/mol, R = 1.987 cal/mol/Kelvin, p is the hydrogen isotope partial pressure in atmospheres, and T is temperature in degrees Kelvin [25]. The units of the quantity of hydrogen are cubic centimeters at standard temperature and pressure (cc H_2 @ STP), that is the volume of the quantity of gas when at 1 atm pressure and 273 K or 0 C. This can be converted to moles of gas n by:

$$n = \frac{(1atm)*[ccH_2\, @\, STP]}{R'*273} \qquad (15)$$

in which the gas constant R’ = 82.05 atm-cc/gram mol/Kelvin.

Once dissolved, hydrogen atoms diffuse in solid materials according to Fick’s Laws:

$$\mathrm{J} = -\mathrm{D}\cdot\frac{\partial c}{\partial x} \qquad (16)$$

and

$$\frac{\partial c}{\partial t} = \mathrm{D}\cdot\frac{\partial^2 c}{\partial x^2} \qquad (17)$$

in which J is the flux (amount of matter diffusing per unit area per unit time), D the diffusion coefficient (cm^2/s), and c(x,t) is the concentration which is a function of position x and time t. The diffusion coefficient normally varies exponentially with temperature:

$$\mathrm{D} = \mathrm{D}_0\cdot e^{-\mathrm{Q/RT}}. \qquad (18)$$

For hydrogen diffusing in alpha iron, the pre-exponential factor D_0 = 0.0016 cm^2/s and the activation energy Q = 1690 cal/mol (R and T have the same values and units as above) [25].

Equation 17 can be solved, with initial and boundary conditions, to find the concentration as a function of time and position in the wall, and then the flux permeating out of the pipe is calculated using Equation 16 evaluated at the outer surface of the pipe. Analytical solutions to Equation 17 exist for specific cases, and numerical solutions can be found for any case using finite difference methods. However, a simpler approach is to use the steady state approximation. Under the steady state approximation, the concentration no longer changes with time- $\frac{\partial c}{\partial t}$ = 0 in Equation 17. In this case the concentration varies linearly with position in the pipe wall:

$$c(x) = \mathrm{S} \cdot \left(1 - \frac{\mathrm{x}}{\mathrm{L}}\right) \quad (19)$$

in which the concentration varies from the solubility limit at the inner surface of the pipe, S (Equation 14), to zero at the outer surface; the pipe wall thickness is L. From Equation 16, the steady state flux of hydrogen out of the pipe is

$$\mathrm{J} = -\mathrm{D} \cdot \frac{\mathrm{S}}{\mathrm{L}} \quad (20)$$

Equation 19 represents the flux of hydrogen from inside the pipe out into the environment.

The permeability is defined as:

$$\Phi = \mathrm{D} \cdot \mathrm{S} \quad (21)$$

and so the steady state flux is:

$$\mathrm{J} = \frac{-\Phi}{\mathrm{L}} \quad (22)$$

The time to achieve steady state permeation is approximately [26]

$$\tau \cong 0.45 \cdot \frac{\mathrm{L}^2}{\mathrm{D}} \quad (23)$$

For a typical 4” schedule 40 pipe the wall thickness is 0.237” and at 50° F the time to achieve steady state is about 5 minutes (Equation 23). Thus the steady state approximation works very well for studying hydrogen permeation through steel pipe.

Permeation varies strongly with temperature. Figure 7 is a graph of the permeation rate per foot (length of pipe) of hydrogen out of a 4” schedule 40 iron pipe having a hydrogen pressure of 1000 psig as a function of temperature. The variation of permeation with temperature is normally represented in a so-called Arrhenius plot, in which the logarithm of the permeation rate is plotted as a function of the reciprocal temperature (Figure 8)

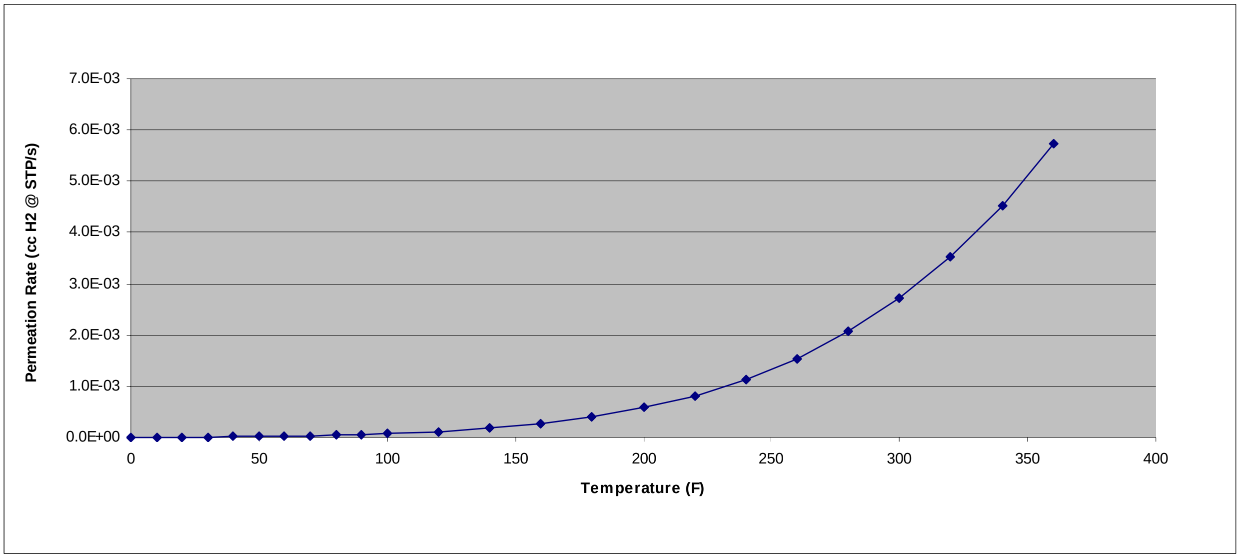

Figure 7 Permeation Rate (cc H_2 @ STP per second) of hydrogen per foot of length out of a 4" schedule 40 iron pipe at 1000 psig pressure as a function of temperature.

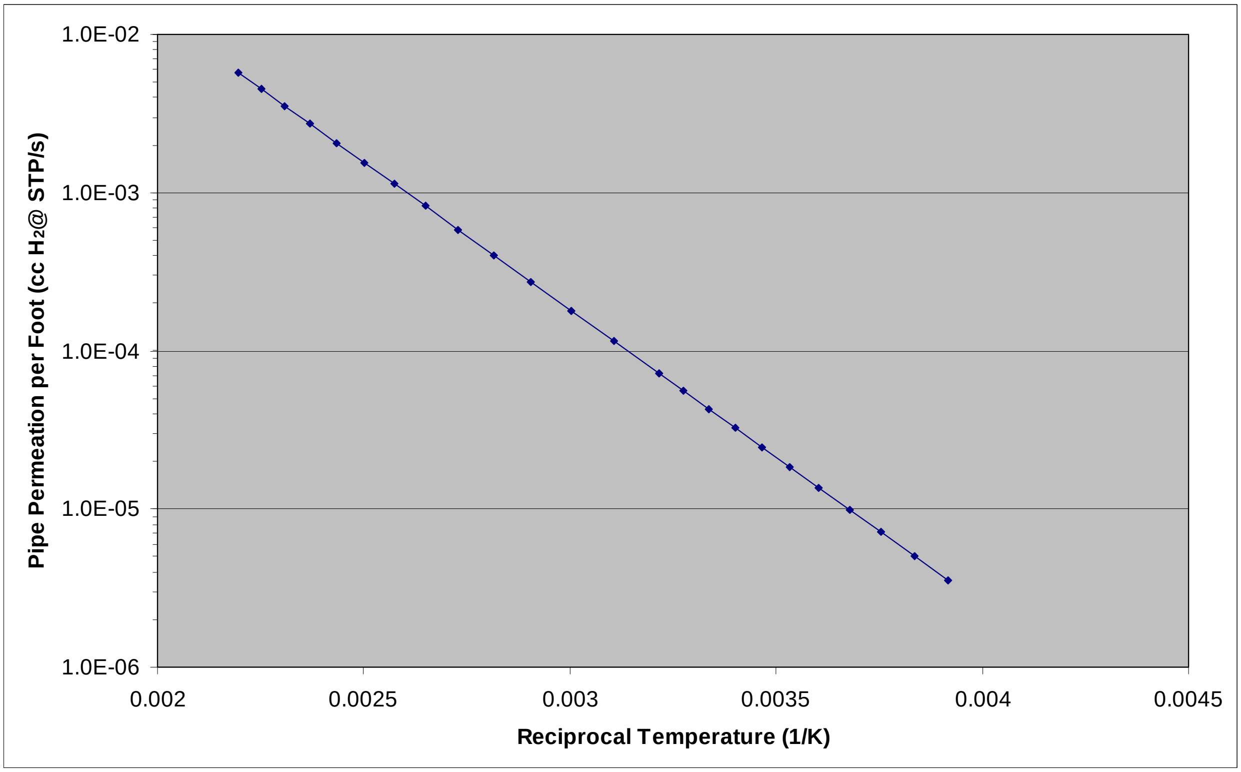

Figure 8 Logarithm of Permeation Rate (cc H_2 @ STP per second) of hydrogen per foot of length out of a 4" schedule 40 iron pipe at 1000 psig pressure as a function of reciprocal absolute temperature (1/Kelvin).

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