HYDROGEN PERMEATION CAUSES AND PREVENTION

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INTRODUCTION

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Hydrogen (H) is the simplest and smallest atom element in nature. It exists not only in its natural Hydrogen molecule (H_2) but also in numerous organic compounds, acids, bases, and even water. While hydrogen is not considered corrosive, it can cause problems with pressure transmitters through permeation if the application is not properly evaluated.

Hydrogen is normally found as in a diatomic state as a molecule composed of two hydrogen atoms (H_2). In this state, molecules will not penetrate the thin metal barrier diaphragms. However, if the hydrogen splits into two hydrogen ions (H^+ atoms), it can penetrate barrier diaphragms because H^+ ions are smaller than the space between the molecules of the barrier diaphragm metal.

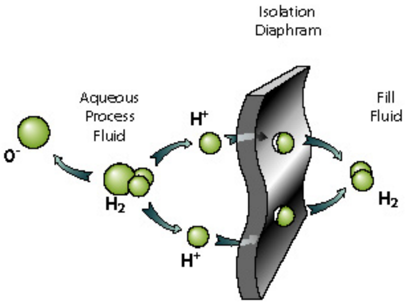
The source of the hydrogen gas (H_2) significantly influences the way migration affects a transmitter. The worst possible case is where (H_2) is cathodically generated on the face of the diaphragm. All it takes to create a galvanic cell is a weak electrolyte (water serves very well) coupled with zinc- or cadmium-plated transmitter flanges, a galvanized pipe, or fittings near the stainless-steel diaphragm.

Zinc or cadmium plating serves as limited but significant types of corrosion protection when the base metal cannot provide the needed protection. For applications that do not require maximum protection, zinc or cadmium offers an inexpensive solution. Due to environmental protection limitations, cadmium is no longer offered and zinc is now mainly used.

Zinc is applied as a thin coating sufficient to withstand normal atmospheric corrosion. However, its resistance to corrosion by most chemicals is low. Zinc acts as a sacrificial anode. This means the underlying metal is protected at the expense of the zinc plating — even when the zinc plating is scratched or nicked, exposing the metal substrate.

A potential difference results when the electrically connected zinc-plated heads or galvanized piping (anode) and the positive diaphragm (cathode) are separated in a conductive medium (water). This potential difference causes positively charged particles to flow from the anode to the cathode through the conductive medium. To complete the circuit, the negatively charged electrons flow from the anode to the cathode through the metal-to-metal contact between the heads and diaphragm.

The loss of electrons by the zinc plating is called oxidation, and it causes the metal to become positively charged. The positively charged ions on the surface (Zn^{++}) attract negative ions found in the aqueous process to form new compounds. This new compound no longer has its former metallic characteristic, but rather takes on a new form, such as zinc oxide (ZnO_2). The gain of electrons at the diaphragm is referred to as reduction and allows the metal to retain its metallic properties while liberating monatomic hydrogen (H^-) and oxygen (O) in the process. Some of the monatomic hydrogen (H^-) migrates through the diaphragm; the remainder combines to form hydrogen gas (H_2), which bubbles away harmlessly.



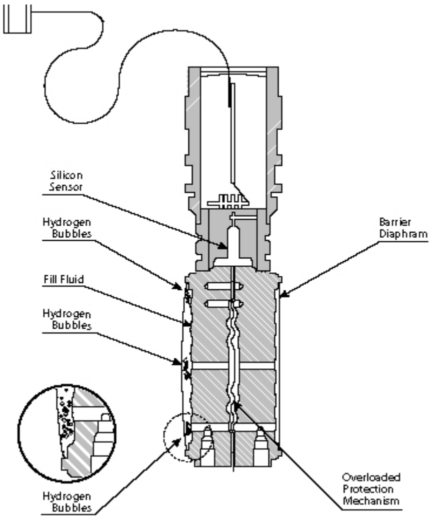
Changes can occur at high temperature or high pressure in hydrogen-rich processes. In a pure hydrogen environment, hydrogen molecules collide with each other and bonds are broken. In applications where hydrogen is part of large molecules, hydrogen ions can randomly become dissociated from molecules in many ways.

After passing through the barrier diaphragms, H^+ ions will re-combine into H_2 molecules, which become trapped. Gradually the H_2 molecules dissolve into the transmitter's fill fluid, and over time the fill fluid becomes saturated. The concentration of trapped H_2 depends on the operating pressure (static pressure) of the system and the temperature. The moment the static pressure is relieved, the trapped H_2 gas expand and a bubble appears.

Hydrogen gas trapped inside a transmitter causes zero and span shifts over time as the trapped gas increases degrading performance of the transmitter. As the hydrogen gas builds up, it causes outward expansion ('bulging') of the barrier diaphragms, leading to cracks and transmitter failure through the loss of fill fluid.

A typical pressure transmitter diaphragm measures 0.002 inches (0.025 to 0.050 mm) thick. If the permeation continues long enough, permanent distortion of the diaphragm takes place as the diaphragm continues to expand.

This distortion is most evident and damaging once the static or operating pressure is relieved from the transmitter with the trapped (H_2) still at the static pressure behind the diaphragm. The trapped hydrogen gas occupies a greater volume than the liquid fill fluid and 'bulges' or 'blows-out' the diaphragm.



APPLICATIONS

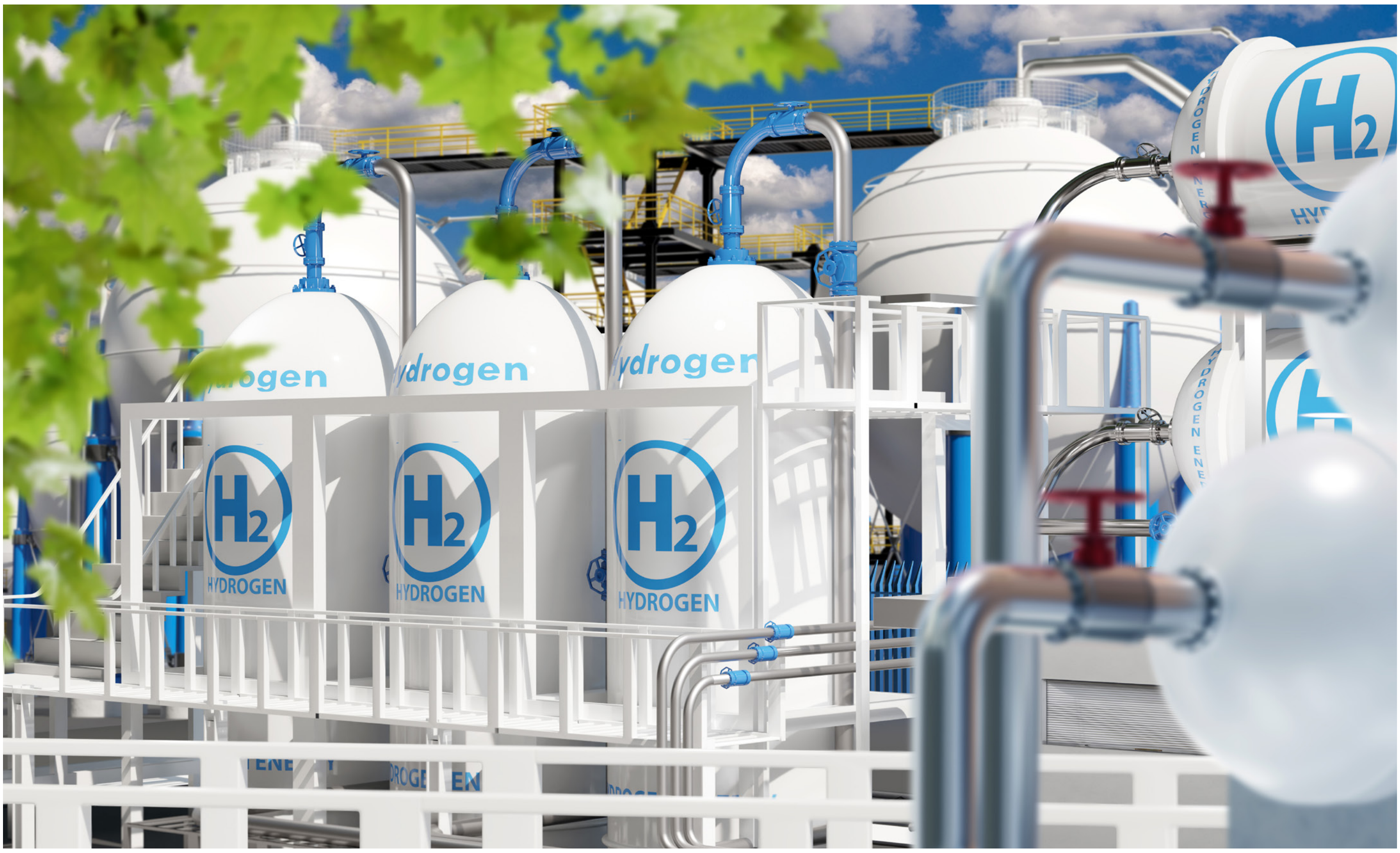
Where to watch for galvanic H_2 permeation?

2

Pure hydrogen applications are the obvious source of hydrogen permeation. However, H_2 permeation can occur in applications where hydrogen is not the main component. Examples of this are as follows:

- Hydro forming or alkylation processes using hydrofluoric acid (HF) can lead to the same problems when hydrogen ions are liberated
- Steam at high temperatures can cause corrosion of metal diaphragms, and hydrogen ions can be generated
- Water applications with galvanized process heads, impulse piping, 2/3-way manifolds, fittings, valves, etc. in the process are the obvious sources of hydrogen permeation. Water applications include steam or steam generating applications.

However, hydrogen permeation can occur in applications where water is not the main component present in its liquid form. Water in its vapor form as moisture can lead to the same problems when the vapor condenses. This can include combustion-air or compressed-air applications where moisture is present in the air. Water vapor condensing out due to compression or temperature changes collects inside a transmitter and leads to the same problems.



DIAPHRAGM MATERIALS

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Diaphragm metal material affects the rate of hydrogen permeation because molecular lattice spacing is different in each metal. The nickel (Ni) content of the metal also affects the rate of hydrogen permeation. While not totally understood, the rate of hydrogen permeation increases exponentially with the nickel content.

Stainless steel has the lowest nickel content and is the diaphragm material of choice for most applications. Nickel-based metals, like Hastelloy C-276 and Monel, should be avoided as well as Tantalum.

Hastelloy C-276
Hastelloy C-276 adds chromium and molybdenum to nickel to help improve resistance to oxidizing, but, also retains some resistance in non-oxidizing conditions; making the material suitable for general use. Unfortunately, Hastelloy C-276 is susceptible to hydrogen permeation due to its loose latticework. A material of tighter latticework on the surface of the Hastelloy yields a diaphragm with all the benefits of the Hastelloy and better resistance to hydrogen permeation. The key is for the introduced material to not interfere with the spring rate of the diaphragm. Chromium (II) oxide (CrO) and gold (Au) are two such materials; both offer a different degree of protection against hydrogen permeation.

The Chromium (II) oxide (CrO) is applied via the process of passivation. Passivation involves the creation of a light coating of CrO on the surface of the diaphragm to add a protective coating with a tighter latticework without interfering with the spring rate of the base material. The resulting latticework gives the Hastelloy the same resistance to hydrogen permeation found in Stainless Steel.

Monel
Monel, like the Hastelloy C-276, is a nickel-based metal but, it introduces copper and a small amount of iron, manganese, carbon, and silicon to the mix. Commonly, Hydrofluoric (HF) acid applications use a transmitter with Monel diaphragm material because of its unique corrosive properties. However, the process produces hydrogen ions when the weak bond between the hydrogen and fluoride breaks. Given the loose latticework of the nickel-based Monel, hydrogen permeation occurs. Gold-plating the Monel is the only solution for this type of application.

However, by keeping the temperature at the diaphragm as low as possible, the diffusion of those ions into the fill fluid slows. Material selection with a correct additional coating/plating can also slow the rate of permeation.

SOLUTIONS AND PREVENTION

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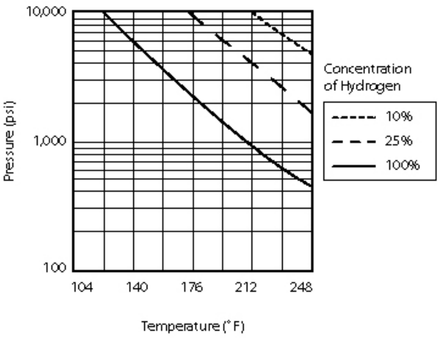
Permeation

Eliminating hydrogen permeation cannot be achieved; but, the rate of diffusion can be reduced, thus extending the life of the transmitter. The rate of hydrogen permeation depends on the temperature of the diaphragm, the concentration of hydrogen in the process, and the type of metal chosen for the diaphragm. Two of these factors are controllable.

Below chart provides relation between the operating conditions and resistance to permeation.



Operating Conditions

Acceleration of hydrogen permeation occurs when the temperature of the isolation diaphragm is high. Reducing the temperature slows the diffusion of the hydrogen ions thus extending the life of the diaphragm. It is difficult to define what temperature is value 'high.' As a general rule, the higher the concentration of hydrogen, the lower the temperature needs to be.

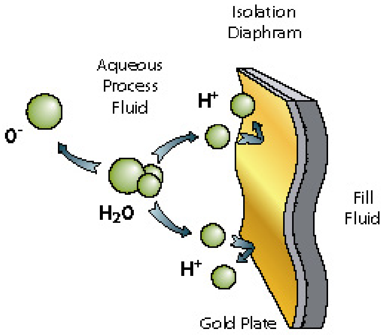
Thus, the process temperature at the diaphragm surface is a dominant factor in the mobility of the hydrogen ions, and any measure taken to reduce the temperature will significantly extend the operating life of a transmitter in hydrogen service.

Material Selection

Although expensive, gold-plating the barrier diaphragms offers the best protection. A thin layer (0.00012 inch (3 µm) thick) of 99.9% pure gold virtually eliminates hydrogen permeation without itself being affected by the process. Increasing the thickness of the gold plating can account for applications having more free hydrogen ions. However, the thicker the gold, the more it affects the spring rate of the diaphragm.

However, do not use gold plating to enhance resistance to corrosion. The gold plating is too thin and too porous to provide an effective barrier to corrosion.

The expected operating life of a transmitter is typically extended 5 to 10 times by gold plating.



The best prevention is afforded by the proper installation and the correct choice of metals in hydrogen applications. Contaminants, such as hydrogen sulfide, are commonly associated with hydrogen processes. In particular, if the hydrogen sulfide is wet, this can lead to Stress Corrosion Cracking (SCC).

SUMMARY

- **Do not** use Hastelloy diaphragms with zinc-plated carbon steel process heads. Zinc is extremely anodic compared to the highly cathodic Hastelloy and rapid zinc corrosion can release excessive hydrogen ions and initiate rapid ion migration.
- **Do not** use zinc-plated carbon steel process heads with stainless steel diaphragms. Stainless steel process heads should be used for this application.
- **Gold plate** the diaphragms whenever hydrogen ion migration is a threat.

Honeywell provides no assurances or guarantees as to their appropriateness in a specific application. These guidelines are just that - guidelines. Each process is unique, the end user's experience with their process is the best source of information for the engineering of the solution. It is customer experience that is paramount.

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