Fuji Electric

Innovating Energy Technology

Hydrogen Permeation

Keywords :

- Hydrogen
- Corrosion
- Pressure sensors
- Membranes
- Measuring cell
- Static pressure
- Hydrogen permeation
- Materials

Hydrogen

Although hydrogen is not aggressive or corrosive, it can cause severe problems with pressure transmitters if the application is not properly examined. It may be very difficult to predict if transmitters will have such problems, because in two plants using the same process (or considered by user as same or very similar), transmitters may have the problem in one plant and not in the other. Reason is that only small difference in process conditions, or in combination of metals used in piping, or in piping geometry, may result, or not, in hydrogen permeation through the process diaphragms of the measuring cell.

When this phenomena occurs, the transmitters show crazy static pressure behavior, and very high and unpredictable zero drifts.

Consequence of hydrogen permeation is that accumulation of hydrogen gas occurs inside the transmitter's cell. Presence of gas makes that the filling fluid (Silicon or Fluorolube oil) becomes a compressible medium. The filling fluid is no longer a good medium to transmit the pressure from the process diaphragms to the sensing element.

Questions

- **Why hydrogen can penetrate through transmitters diaphragms?**
- **Which counter measures can be taken on the transmitter it self?**
- **Which materials should be preferred for piping?**

Hydrogen permeation

Hydrogen is the smallest atom element.
So, it can penetrate the thin metal process diaphragms of pressure transmiters.
Water, acids, bases, and the numerous organic compounds contain hydrogen.

Action on the diaphragm

Hydrogen is normally found in his molecular state H_2 (also called diatomic), composed of two hydrogen atoms.

H_2 molecules are big enough so that they will not penetrate diaphragms of pressure transmiters.

However, if H_2 molecule splits into hydrogen ions H+, it can penetrate

Examples of generation of H+ ions in the process fluid:

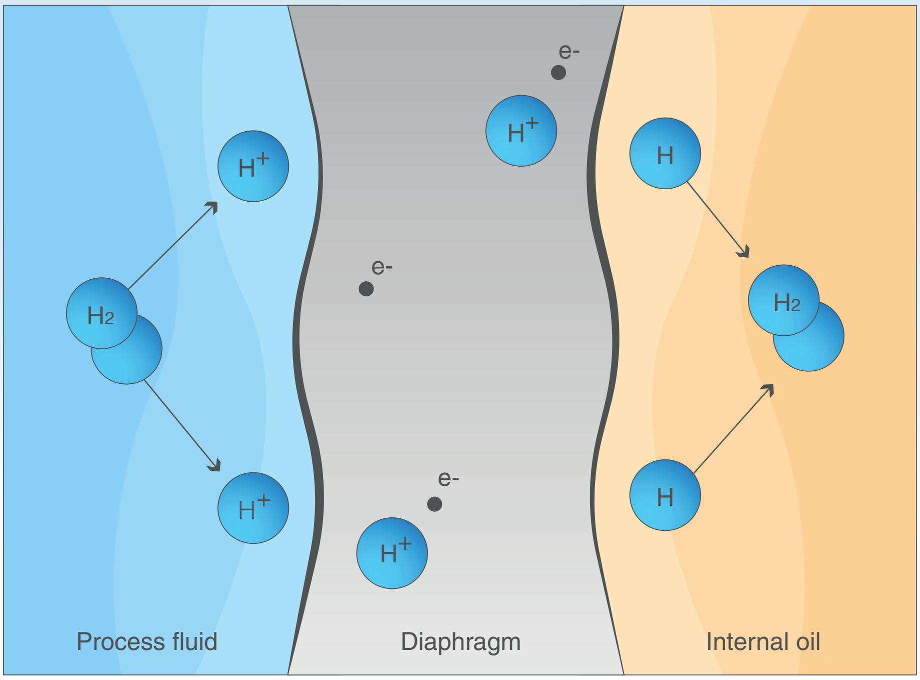
- $H_2 \rightarrow H^+ + H^+$
- $H_2O \rightarrow H^+ + OH^-$
- $H_2S \rightarrow H^+ + HS^-$

Combination of H+ ions and electrons in the diaphragm :

- $H^+ + e^- \rightarrow H$

Combination of H atoms in the internal oil of the cell:

- $H^+ + H \rightarrow H_2$

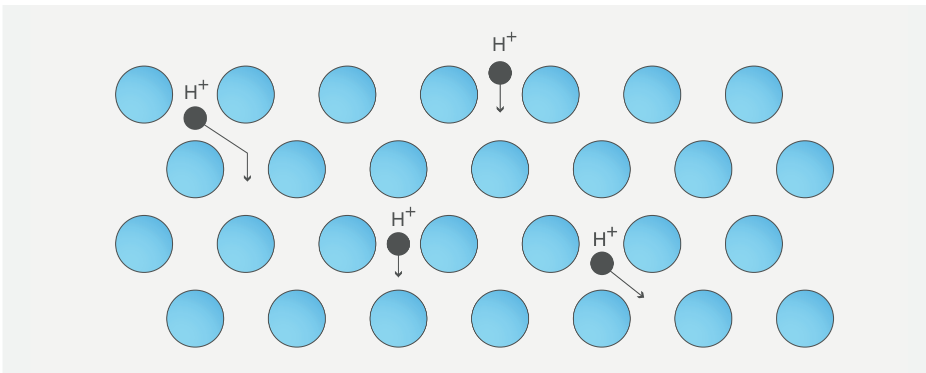


Interstitial mechanism

After passing through diaphragms, H+ ions will again combine into H_2 gas molecules. As internal medium of the transmitter's cell is electrically neutral and very stable, the H_2 molecules will not split again into H+ ions, H_2 will be definitely trapped inside the transmitter's cell, and hydrogen bubbles will appear.

It is a well known phenomena that atoms or molecules move from a high concentration medium (Process fluid) to a lowconcentration medium (Cell's fill fluid). Generally, H+ ions penetrate metal diaphragms by an interstitial mechanism.

Interstitial mechanism means that H+ ions pass from one intertitial site (free space between atoms) of the diaphragm material to the nearest intertitial site without permanently displacing any atoms of the diaphragm material.



Interstitial mechanism

Conditions generating H+ ions

H_2 molecules can randomly become dissociated into H+ ions in many ways, as explained hereafter.

Pure hydrogen

Applications where pure hydrogen is used, or where process contains H_2 gas are often suspected by users to result in hydrogen permeation. However, if H_2 is not split into H+ ions, there is no permeation. Tests made on pressure transmiters with pure H_2 gas at stable conditions of 100bar pressure and ambient temperature over one year showed no effect on performance of transmitter.

However, at high temperature or if important changes in operating pressure occur, hydrogen molecules collide with each other and surrounding material, H_2 atomic bonds are broken, resulting in generation of H+ ions.

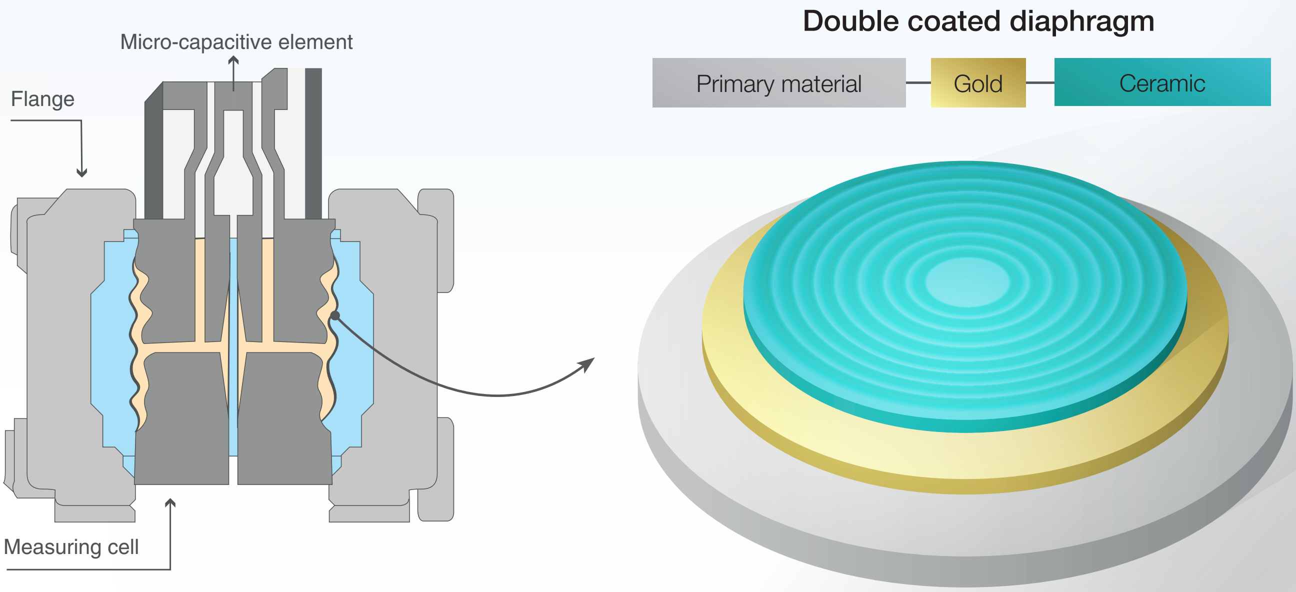
Steam at high temperature

It can cause corrosion of metals and generate H+ ions.

Galvanic reactions

This is the most common cause of H_2 dissociation. Process like seawater, weak electrolyte, Carbon Steel or Zinc plated impulse piping may cause corrosion and generate H+ ions. Care must be taken to prevent placing certain dissimilar metals in close proximity, and especially close to the pressure transmitters.

For example, cadmium or cadmium-plated parts placed near high-nickel alloys, such as Hastelloy or SST, in the presence of an electrolyte such as water, can result in a Ni-Cad electrochemical voltage generator. An electrolysis occurs, generating H+ ions. The use of Carbon Steel process covers (flanges) on pressure transmitters, is not recommended as it helps to create galvanic reactions in the measuring chamber of the transmitter (between process cover and diaphragm).



Sélection of diaphragm material

In applications where H+ ions are present, care must be taken to select diaphragm materials that are not susceptible to permeation. All metals show permeability to hydrogen.

By decreasin importance they are Steel, Hastelloy, Stainless Steel, Platinium, Silver, Gold. As brief summary, metals that contain a lot of nickel, like Hastelloy C and Monel should be avoided and Tantalum prohibited.

The gold-plated stainless steel diaphragms provide the best protection. The type of piping used should also affect diaphragm selection. High temperatures also increase the rate of permeation...

316 or 316L Stainless Steel	316 SST has a nickel content of approx 10 to14%. This Ni content, associated with chromium, allows good resistance to corrosion. 316 SST performs well against hydrogen permeation, and is approx. 10 times better than Hast C.
Hastelloy C	Hastelloy C has a nickel content of approx 55%. This Ni content, associated with chromium and molybdenum allows very good resistance to corrosion, especially to oxidizing conditions. Hastelloy C allows hydrogen permeation at a rate approx. 10 times higher than 316SST, and should be used with caution as a diaphragm material.
Passivated Hastelloy C	In the past, Fuji supplied passivated Hast C diaphragms as standard. Serious hydrogen permeation problems were experienced, and Fuji changed the standard material to 316L. Despite passivation improves slightly the protection against permeation, passivated Hast C should not be used when there is some fear of hydrogen permeation.
Monel	Monel has a nickel content of approx 67%. It has good resistance at ambient temperatures to most of the nonoxidizing and phosphoric acids, nonoxidizing salts and alkalis. Monel allows hydrogen permeation and should not been used in high hydrogen concentration applications or when the process is hydrogen gas.
Tantalum	Tantalum may suffer severe hydrogen embrittlement if process contains free hydrogen at any temperature. The diaphragm material becomes fragile, brittle, resulting in quick failure of the transmitter.
Gold-Plated Monel	This will provide protection against hydrogen permeation while providing the corrosion resistance of Monel. It is recommended for hydrofluoric acid applications.
Gold-Plated 316L SST	This will provide good protection against hydrogen permeation while providing also a good corrosion resistance. It is sufficient for most applications where there is a risk of hydrogen permeation. It is available from Fuji Electric France with a 5 µm gold layer.

Hydro Seal design

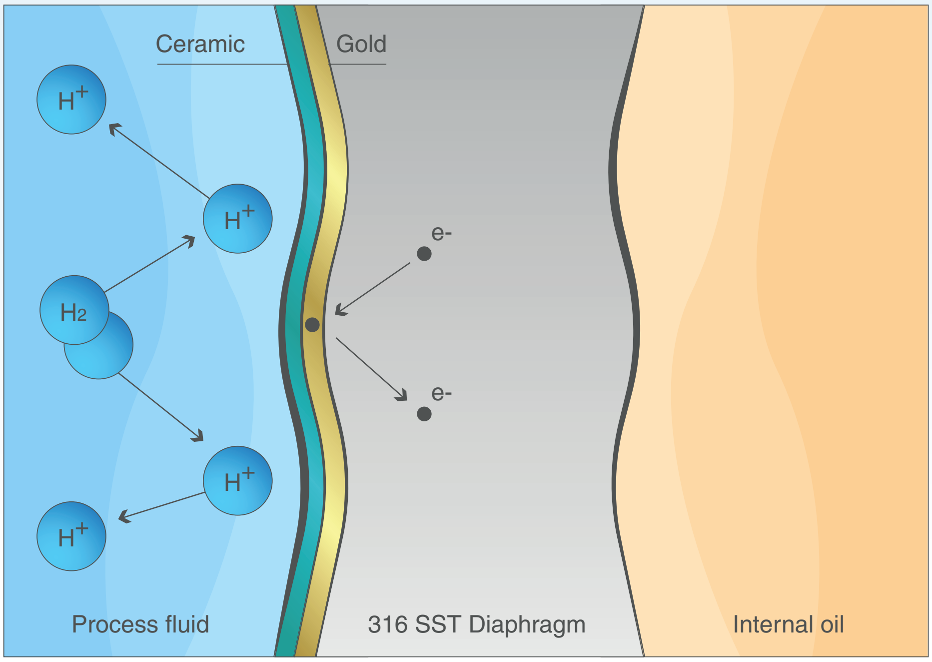
- This is a design developed by Fuji Electric.
- It will provide excellent protection against hydrogen permeation.
- It is recommended for the applications where hydrogen permeation has been experienced as most severe.

Action on the diaphragm

A 3 µm gold layer is applied on the 316L SST diaphragm, and a second layer of ceramic is applied on top of gold.

The ceramic layer provides an electrical insulation between the process fluid and the diaphragm, which prevents H+ ions from combining with electrons of the diaphragm.

This insulation minimizes the diffusion of hydrogen atoms through the diaphragm. Following figures show comparison of the performances of this design compared to HastC, 316SST, and Gold plated 3165SST.



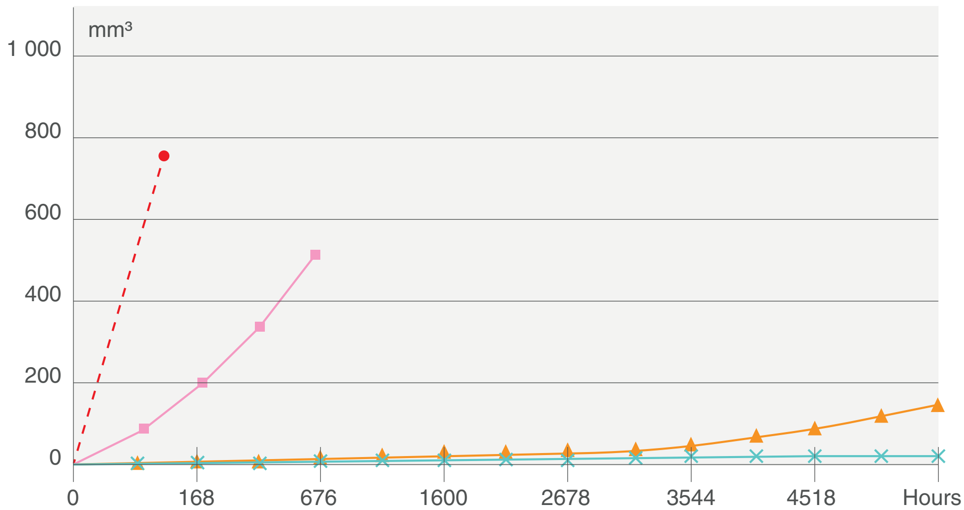
Benefits

- Minimizes generation of H+ ions and electrons due to galvanic reaction.
- Prevents H+ ions from combining with electrons.
- Minimizes the diffusion of hydrogen atoms through the diaphragm.

Comparison of Hydrogen permeability through different diaphragm materials:

Matériaux testé :

- Hastelloy C
- 316L Stainless Steel
- 316L Stainless Steel, gold plated
- Fuji Electric Hydro Seal gold + ceramic platings



Test conditions:

Medium: Water solution with hydrogen

Temperature : 80°C

Pressure : 100 bar

Vertical axis shows volume of hydrogen passing through the diaphragms (mm³)

Piping arrangement

Piping geometry, may result, or not, in presence of H+ close to transmitters process diaphragms. H+ and H_2 are very light weight, so they accumulate in upper parts of piping.

In case that hydrogen permeation occurs, it is advised to install the transmitters at a lower part of the piping, or at a lower position than impulse taps. This will avoid that Hydrogen accumulates inside measuring chambers of the transmitters.

Piping material

The type of piping may affect the hydrogen permeation rate and the selection of diaphragm material. Similar materials will prevent in most cases galvanic reactions, avoiding hydrogen permeation.

For example the selection of Stainless Steel for piping, process covers and diaphragms of transmitter is favourable configuration to avoid hydrogen permeation. At the opposite, dissimilar materials, such as the, use of zinc plated steel, of cadmium plated steel or of carbon steel, for piping or flanges close to the transmitter may generate H+ ions. In such cases it may be necessary to select gold plated or Hydro Seal diaphragms.

Generally, the tendency for corrosion and for generation of H+ ions to occur is governed by the magnitude of potential difference developed between dissimilar materials acting as the anode and the cathode in an acqueous solution. The metals with the highest potentials are at the anodic end of the galvanic series and metals with the lowest potentials are at the cathodic end. However, the potential generated may change depending on different process conditions.

In general, the farther apart the metals are positioned on the galvanic series, the more likely they are to corrode and generate H+ ions when placed closely together in an acqueous solution.

Refer to following list of "Galvanic Series of Metals" as rough information.

Fuji Electric policy

For the reasons explained previously, Fuji Electric has decided some years ago the following policy:

1. Stop to offer carbon steel flanges on transmitters.
2. Select 316SST diaphragms in place of Hast C.
3. Develop optional Hydro Seal protection for diaphragms.

Note : This technical data sheet has been made for reference only. Because each process conditions and installation configuration are unique, the material selection is the responsibility of the user.

Galvanique Series of Metals

Cathodic end
(protected)

- Platinium
- Gold
- Graphite
- Titanium
- Silver
- Hastelloy C
- Stainless steel passive
- Inconel passive
- Nickel passive
- Monel
- Copper-nickel alloys
- Bronzes
- Copper
- Brass
- Hastelloy B
- Inconel active
- Nickel active
- Tin
- Lead
- Stainless steel active
- Cast iron
- Iron or ateel
- Aluminium usual alloys
- Cadmium
- Pure aluminium
- Zinc
- Magnesium alloys
- Magnesium

Anodic end
(corroded)

How to check if there is H_2 gas inside transmitter's cell?

By changing position of transmitter :

1. Place the transmitter on a flat and stable surface, then by adjusting the Zero, set the output signal at a value between 4 and 20mA, such as 12mA.

2. Move the transmitter in every position, then place it in same position as step 1. The output signal should be same as recorded at step 1.

Repeat this test a few times. If the output signal changes significantly, this means that there is H_2 inside the cell.

By applying static pressure on DP transmitter:

Apply static pressure within the limits of specifications of the transmitter. If the zero drift is much outside specifications, this most probably means that there is H_2 inside the cell. The zero drift is even more important if negative static pressure is applied (below atmospheric pressure).

By examination of the cell's diaphragms :

1. If there is a lot of H_2 inside the cell, the diaphragms are much inflated, and it can be noticed at the first look.

2. If there is only a few gas, place the cell so that the diaphragm is upwards. Then hit the diaphragm with your finger. If the noise is atenuated / thump the cell should be OK, as it means there is oil behind the diaphragm. If the noise is clang as when you hit a paper or thin metal sheet it means that there is H_2 behind the diaphragm. If you have a doubt, compare with a new cell.

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