Materials Compatibility Webinar Q&A

Key Words: materials, embrittlement, gas, liquid, polymer, elastomer, metal

The information in this document provides answers to the questions that were raised during the Center for Hydrogen Safety March 30, 2022 webinar.

1. Is H.E. a problem with the transport of cryogenic (liquid) hydrogen?

The question with liquid hydrogen exposure is whether atomic hydrogen can enter the metal. In the event that atomic hydrogen does enter the metal, then hydrogen embrittlement can certainly be a problem for liquid hydrogen transport.

Here is a link to a publication in 2021 looking into the effects of H.E. at cryogenic temperatures by Merkel et al. https://doi.org/10.1115/PVP2021-62436

2. Are there specific heat treatment processes that can improve the resistance to H2 embrittlement of steels?

There are two effects from heat treatment of steels that may impact hydrogen embrittlement: 1) heat treatment can modify the steel strength level, and 2) heat treatment can alter the steel microstructure. Heat treatment that lowers the steel strength level will improve resistance to hydrogen embrittlement, while heat treatment that may create a more hydrogen embrittlement-resistant microstructure is an active area of research.

3. Are the "Nelson Curves" a reliable guide for application limits for metals?

The Nelson Curves only apply to steels exposed to hydrogen gas at elevated temperature, in which the degradation mechanism is high-temperature hydrogen attack (HTHA)

4. Are there any studies on the effect of hydrogen on fittings, valves, etc. Any standards or guidance documents available?

The CSA/ANSI documents (e.g., CSA/ANSI HGV 4.4 for valves) is recommended.

5. Does a weak acid create more of an HE issue?

Weak acids can promote hydrogen embrittlement in structural metals.

6. Can heat treatment under reducing atmosphere be a source of exposure to hydrogen?

Yes.

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7. How can we best analyze austenitic materials to ensure that they will be suitable for hydrogen use?

One starting point is to perform materials testing in hydrogen gas following the CSA/ANSI CHMC1 standard.

8. When thinking of the strength of the metal is there a difference in Tensile and Yield strength, or what would be most important?

Hydrogen embrittlement susceptibility correlates with either the yield or tensile strength of the metal. The preferred correlation often depends on the common practice in certain technology sectors.

9. Have you any experience with tritium? Do the same rules hold true? Additional considerations?

The fundamental principles of hydrogen embrittlement also apply to tritium embrittlement, but there is one essential additional consideration for tritium embrittlement. When metals are continuously exposed to tritium for extended periods of time (e.g., years), some fraction of the tritium that enters the metal transmutes to ^{3}He and forms nanometer-sized bubbles. These ^{3}He bubbles exacerbate embrittlement activated by the hydrogen isotope in the metal.

10. What are the key characteristics of failure by Hydrogen embrittlement?

Unlike conventional material failure modes at ambient temperature, hydrogen embrittlement is time-dependent. In addition, in many cases, hydrogen embrittlement involves crack propagation along grain boundaries in the metal (intergranular cracking).

11. Is there a site or database available for general public access that gives non-material scientists an idea of which materials are acceptable for use in certain pressure/temperature/stress regimes for both metals and polymers?

This is definitely a need. One emerging trend that may enable such guidance for lower-strength steels is that the fatigue limit (endurance limit) does not appear to be degraded by hydrogen.

A datahub is under development on H-Mat.org for providing data for the general public. There are also a list of publications and presentations from the H-Mat program available to the general public. Polymers have been much less studied and has a smaller body of knowledge. The H-Mat program is working to expand that body of knowledge. The question of pressure/temperature/stress regimes is an excellent question. I would add that polymers can also be susceptible to depressurization rates and hydrogen saturation levels in the polymer.

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12. What are the cost to quality ratios of the materials you mentioned, stainless steel, lithium, alloy?

There is certainly a trade-off between cost and performance in hydrogen gas for the austenitic stainless steels (higher cost, higher performance) and ferritic steels (lower cost, lower performance). Aluminum alloys have an attractive balance between cost and performance in hydrogen gas.

13. It is common in the literature to use SSRT to assess the material susceptibility to hydrogen embrittlement? What is your opinion about it? The acting mechanisms in this low strain rate condition may not be analogous to those seen in materials in service?

Slow strain rate testing (SSRT) may be effective for material screening, but the data cannot be employed in quantitative analyses (e.g., design or fitness-for-service).

14. Any thoughts as to where killed carbon steel falls in this discussion for hydrogen pipeline applications?

Current evidence from materials testing in hydrogen gas is that variations in steel composition and microstructure do not have first-order effects on hydrogen embrittlement susceptibility.

15. Can you speak a little to the impact of surface condition (e.g. roughness, presence of scale, etc.) on H2 absorption in metals, in the absence of any defects? Is there evidence that the surface condition can be impactful on the material response in any way?

There is evidence that air-formed oxides can impede hydrogen uptake into ferritic steels exposed to hydrogen gas. The open question is whether the oxide offers this protection long term during continuous hydrogen gas exposure.

16. Would you say there is a difference in material selection for service, storage and transportation versus hydrogen generation?

Material selection depends on the nature of applied stresses in components as well as hydrogen gas pressure and temperature. Assuming these vary for different applications, it may be expected that material selection varies as well.

17. Are the reactions and cracks you mentioned ever seen in liquid hydrogen tanks?

Hydrogen-assisted cracking has been reported for steel cylinders containing hydrogen gas. Similar hydrogen-assisted cracking has not been documented for liquid hydrogen tanks.

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18. Now that the price of SS is high, how does other cheap polymer options like PTFE, PFA and PVDF lined CS piping behave under the same condition?

I'm not exactly sure what are the same conditions the question is referring to; however, polymers as a barrier to limiting H.E. to metals is not a good solution. All polymers are semi-permeable and hydrogen gas is no exception when it comes to the permeation of polymers. H.E. will happen in polymer lined CS pipes similar to unlined.

19. To minimize hydrogen embrittlement, is there an advantage of using low-carbon austenitic stainless steels; e.g., 316L vs. 316 at a particular pressure and temperature?

The hydrogen embrittlement susceptibility of the 300-series stainless steels is governed by nickel content. Any difference in hydrogen embrittlement susceptibility for 316L vs. 316 can be attributed to nickel content and not carbon content.

20. What level of cold strain be avoided in 304 and 316 for high pressure hydrogen applications? Is there a general rule of thumb?

Any detrimental effect of cold work on hydrogen embrittlement susceptibility can likely be attributed to the formation of strain-induced martensite. The relationship between level of cold work and amount of strain-induced martensite depends on alloy composition, such as nickel and carbon contents. Ideally, austenitic stainless steels in hydrogen applications do not contain any strain-induced martensite.

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21. Are there any material considerations specific for hydrogen application in subzero temperatures, high altitudes, or coastal zones?

For certain structural metals such as austenitic stainless steels, hydrogen embrittlement is more severe at subzero temperatures.

22. Can you comment on how the hydrogen to material incompatibility considerations you spoke of in sealing/gasketing components compare or contrast to those of barrier layer components?

Yes, there are three different areas that could be categorized as polymer components; static seals, dynamic seals, and barriers. The materials selection can be different in each case, for example, elastomers, and thermoplastics, and in some cases, both are used together. Each of these seals and barrier systems has different use case requirements. Static seals are concerned with volume change with hydrogen exposure with decompression, especially rapid gas decompression, O-ring groove design, operating temperature, and compression set. Compression set increases caused by hydrogen can result in premature leakage. Dynamic seals have some similar demands as the static seal but also have the addition of friction coefficient and wear rate changes. There has been research that indicates hydrogen can influence both and if volume change is increased further complications with operations will be impacted. Lastly, barrier performance with polymers would be more related to void formation from gas pressure changes where the voids coalesce. There is also some evidence of environmental stress cracking in some materials.

23. Is hydrogen in polymers still considered chemically inert with the main interaction resulting from physisorption rather than chemisorption?

The answer to this is complicated. The polymer itself can be chemically inert, but caution should be used to say all polymers. However, polymers are not pure material systems. Polymer material systems often contain additive packages for processing, environmental, and property performance enhancement. We find that additives can influence the hydrogen performance in these polymer systems. For example, elastomers can often have plasticizers added to lower Tg, but hydrogen has been found to cause plasticizer migration and increases in hydrogen diffusion coefficients. We have also found sulfur cured systems behave differently than peroxide cured systems. Some of these differences were due to the ZnO/S interface where hydrogen collects at the interface which forms voids on decompression. We have also noticed that polyamides with some types of toughners can also be influenced by hydrogen exposure with rapid gas decompression.

24. Will the final decision of metal and or polymer be asked to include carbon intensity for each in pursuit of decarbonization of energy industry?

Not that I'm aware of. Oftentimes, the use of polymers offsets the long-term impacts of decarbonizations with their use.

25. I still remember the 1986 Challenger O-rings catastrophic incident (in SpaceX terminology, uncontrolled combustion or failure) and the discussions that happened for several years after. Are we better informed now than 1986 or before to deal with hydrogen and material compatibility for terrestrial h2 infrastructure applications?

I believe that the O-ring wasn't a hydrogen material compatibility issue as it was used outside of its operational design space (below freezing temperatures in Fl). I believe metals are further along in their understanding than polymers. There are still some understandings that need to be researched further. There are some polymer systems that appear to work well and have had long-term exposure and performance data.

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26. With the radiological waste treatment/handling/storage processes, radiolysis creates hydrogen from the breakdown of organics; are there studies which have evaluated or documented hydrogen embrittlement in these systems?

The work of Dr. Fraser King may address this issue.

27. Material compatibility is the basic and essential (and critical) part of design considerations but often gets lost in the hype of something new. Is this due to lack of information or knowledge or both or due to the hype created by vested interests?

I agree. I have found it to be both. The more information that is available and shared the more knowledge that can be gained. We often have individuals from companies reaching out to us to help them understand the issues to look for with material selection. The design can also influence the performance of the material in operation too.

28. How do we assess the natural gas pipelines to ensure they are ok for H2 use?

There are multiple initiatives worldwide that are addressing this question.

29. You mentioned that moisture enhances the embrittlement, but what effect does salt water have on embrittlement?

Hydrogen embrittlement may occur in structural metals exposed to aqueous environments, including salt water environments.

30. In terms of low pressure applications how would time affect embrittlement and do we know how long before embrittlement would begin to be an issue?

Even in low-pressure hydrogen gas applications, the manifestations of hydrogen embrittlement such as accelerated crack growth do not require extended periods of time to activate. The more important question is whether sufficient hydrogen can enter the metal in low-pressure applications to activate embrittlement.

31. What is your opinion on FCG mitigation on steel by oxygen at long terms?

For lower-strength steels exposed to hydrogen gas, the long-term mitigation of accelerated fatigue crack growth (FCG) by oxygen impurities is an open question. There is clear evidence that oxygen mitigates hydrogen-accelerated fatigue crack growth for cyclic loading periods as long as 10^2 to 10^3 seconds, but such mitigation is an open question when loading periods are substantially longer.

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32. Will the polymer service experience extrapolation issue be similar to the metals issue?

Yes, I have seen this in the oil and gas industry where polymer materials used in components for natural gas are being used in hydrogen that have long-term durability issues. The amount of hydrogen that saturates in the polymer varies and causes completely different behavior in the polymer than another gas which has very low levels of gas in the polymer. It is recommended to use a known polymer material that has been tested for hydrogen performance and not to extrapolate service experience with other gases.

33. Are there elastomer seals in H2 ball valves that are approved for high-pressure service >3500 PSI?

There are elastomer materials that have been tested up to 12,000 psi with less than 3-4% swell that may be appropriate. You would need to test and evaluate.

34. TI-alloys are used in PEM water electrolyzers. How is H2 embrittlement handled in those applications?

If these are Ti alloys with alpha phase that are subjected to stress and hydrogen gas exposure, then caution is certainly warranted.

35. When blending H2 in methane rich pipelines, is there a limitation for Carbon Steel pipelines? If yes, till what % of H2?

There are multiple initiatives worldwide that are addressing this question.

36. Is there a difference between Ortho and Para hydrogen in terms of embrittlement?

Molecular hydrogen at ambient temperature is an equilibrium mixture of ortho and para hydrogen, and the question then is how the dissociative chemisorption reaction on metal surfaces may be different for the two isomers.

37. In addition to sealing, do you think plastics can be used at H2 fittings, housing or storage of a component that has H2 medium inside?

Yes, depending on the application and stress levels. The design aspect would be critical. It is not uncommon to see plastic tubing used with hydrogen.

38. How does one incorporate the element of accelerated aging in H2 environments in testing so we do not have to wait long times under service environments?

This is a challenge for all of us. In polymers, we often use temperature to accelerate aging, however, when adding hydrogen, the interaction with the polymer changes and makes it difficult to assume that the influence is similar to long exposure times. We have done long-term exposures to 60 days on polyethylene pipeline materials, and we do not see a decrease in performance. We do see an initial drop in the crystallinity and material density with the PE material and are evaluating whether this impacts long-term creep, fatigue, or fracture performance. For elastomers, we don't know if there is migration of materials or if migration comes to equilibrium or continues, which could impact long-term performance.