Repurposing Existing Pipelines and New Pipelines Considerations for Gaseous/Blended Hydrogen and CO₂ Applications

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INTRODUCTION

Moving forward both existing and new pipelines will be evaluated for their overall capability to transport not only oil or natural gas, but also their capability to transport gaseous/blended hydrogen and CO₂. Flexibility in existing pipeline systems or any new pipeline systems built have in moving the various energy sources or being involved in CO₂ sequestering will be advantageous for efficient, economical, reliable, and safe operation. Efficient and economical operation typically requires the highest operating pressure possible. The question is what considerations need to be evaluated to determine the optimum operating pressure and more importantly for how long an existing pipeline or new pipeline system can operate at that pressure, in the most reliable manner, and the most important consideration that must be at the forefront of all decision-making processes is to keep the public as safe and out of harm’s way. There are many questions that need to be addressed in these fast-emerging steel pipeline applications to make the proper decisions.

DISCUSSION

What Do We Know

So, what can we truly say we do know of various attributes of oil, natural gas, gaseous hydrogen, and CO₂ pipeline transmission operation and steel design from our various number of years of operating these various pipelines both successfully and sometimes not so successfully:

- **Oil and natural gas pipelines** have been in existence for over 100 years, with a ramp up of pipelines built and in service since the 1950’s, 70+ years of steel/operating design and experience.
  - Various safety with some deaths and environmental damage leaks, Figure 1. [1,2]
    - PGE San Bruno – 2010 pipeline explosion 8 fatalities
    - Keystone XL – 2022 Kansas oil leak - environmental
    - BP Alaska – 2006 corrosion oil leak – environmental
  - Specifications (Examples)
    - API 5L/ISO 3183
    - Minimum requirements for chemistry, strength, ductility (CVN, DWTT), pipe dimensions, quality, etc.
    - Supplemental Specifications
      - SR5A, SR5B, etc.
    - PHMSA Title 49 CFR
      - Pipeline Company Internal Specifications
        - More specific min/max requirements for chemistry, strength, ductility (CVN, DWTT), pipe dimensions, internal/surface quality details, etc.
        - Agreed to Manufacturing Procedure Specifications (MPS)
          - Final technical agreement between the pipeline company/pipe producer/steel producer. Complete
details of steel and pipe production that will govern a specific transmission pipeline project.

- ASME B31.8, B31.3
  - Construction design codes minimum requirements.
    - Local State, County, Municipal Construction Design Codes

- Have developed the metallurgical technology for API X grades for H2S sour service applications successfully with approximately 45 years of successful operational experience.
Figure 1. PHMSA 2000-2019 pipeline incident summary report and API 2020 pipeline safety incidence summary report.

- Gaseous hydrogen transmission pipelines in service since about 1995 with the industrial gas companies. A few H2 lines were built prior, but most today are since about 1995 representing about 30 years of experience.
  - Operational/Safety Issues – none that were major reported, nothing reporting of fatalities noted since 1995. One Air Liquide purchased repurposed line 140 mile 8“ oil gathering line built 1940-1950, put into H2 service in 1998 at 700 psig for 6 months, rupture after 6 months due to corrosion, 75 mile section removed from service, remaining 65 miles derated to 350 psig H2 pressure and remaining in service. [3]
  - Low volumes needed.
  - Conservative approach to operation.
  - Operate at 50% or less design pressure.
  - Low strength steels, API X52 or lower.
  - H2 should be very pure, dry (IGC Doc 121-14: Water: less than 20 PPM (dew point @ 1 atmosphere = -55°C/-67°F, It is important to note that moisture is a critical contaminant in this context and this document should not be used for mixtures in which condensation of moisture may be expected to occur.)
  - Specifications
    - None typically used API 5L.
  - Low strength encourages higher ductility, finer grain, homogenous microstructures, etc.
  - Construction design code based on ASME B31.8 and B31.3 codes modified for H2 operation based on existing H2 data, very little in 2008 with more in 2019, IGC Doc 121-04 and input from several sitting B31.12 code members from the industrial gas companies running H2 pipeline systems. Option A (Prescriptive Design Method) for lower conservative operating pressure, 50% SMYS maximum, similar to the existing industrial gas company experience. Option B (Performance Based Design Method) for higher operating pressure to 21 MPa (210 Bar, 3000 psi) using Article KD-10 fracture toughness testing with a minimum KIH of 55 MPa-√m (50 KSI-√in).
  - Non-Mandatory Appendix G (2019) – Added as guidance information based on research into steel attributes that contribute to higher fracture toughness performance in gaseous hydrogen.
• CO2 transmission pipelines currently represent about 9500 km worldwide with 92% or approximately 8700 km operating in the US. This compares to a total of 2,252,035 km of oil/natural gas pipelines operating in the US today. The first US large scale CO2 pipeline was established in 1972 at the Terrell, TX, gas processing plant. Most CO2 pipelines in operation today have rather recently been put into service over the past 10 years. [7,8,9]
  - Various safety with some deaths and environmental damage leaks, Figure 1
  - 2001-2020, 5750 significant incidents were reported onshore and offshore resulting in over $10.7 billion worth of damages. [10]
  - While CO2 pipelines in the US only about 0.39% of the total km of pipelines in operation, they have represented a significant number of incidents and costs and already have had one serious rupture incident.
    - Denbury operated 24” OD CO2 pipeline in Yazoo County, Satartia, Mississippi, ruptured February 2020, Figure 2, that injured 45 people requiring hospitalization, some with ongoing health issues. The official cause was a girth weld failure due to excessive heavy rainfall and earth movement strain on the pipe.

![Figure 2. Satartia, Mississippi, CO2 pipeline rupture.](image)

In addition, what we know about these various applications for transmission pipes and their welds are as follows:

• Typical normal environmental conditions have external corrosion issues that affect current operating and new pipeline built today, such as Sulfide Stress Corrosion Cracking (SSCC), Stress Corrosion Cracking (SCC), etc.
• Each of the energy sources transmitted along with CO2 carbon capture via pipelines own unique needs of the ductility of the pipe body and HAZ welds:
  - All Gases (NG, H2, CO2) - Decompression crack speed upon rupture. This can be as high as the speed of sound (343 m/s or 1,125 ft/s) in a natural gas pipeline.
  - High Pressure Gaseous Hydrogen – must have sufficient ductility to withstand a 40-70% decrease in fracture toughness and a 10x plus increase in fatigue crack growth rate at operating temperatures down to -40 °C.
  - CO2 - Decompression resulting in liquid CO2 converting to gaseous CO2 very rapidly, requiring a much lower ductile to brittle transition temperature of the steel.
  - All Gases (NG, H2, CO2) – Potential corrosion mechanisms of H2S, NOx, SOx, moisture, etc. CO2 pipelines can tend to have a potential higher exposure to the additional corrosion mechanisms.
• Common denominators that need to be the focus for the steel and the welds for the pipelines are corrosion and ductility properties (fracture toughness and fatigue), are the two key components that need to be the focus in evaluation of repurposing pipes for these applications or in designing the alloy/processing for the through thickness microstructure that can create the optimum corrosion performance along with the ductility for the application and pressure needed for economical and most importantly safe operation.

• Various steel alloy/processing designs base metal and HAZ/weld metal perform better than others in the for natural gas applications, high-pressure gaseous hydrogen and SCC, Figure 3. [11,12,13,14,15] While these same attributes have not been tested in the presence of CO2 and other corrosion mechanisms, logically optimum ductility performance should be a desired attribute to assist in improved safe operation of a CO2 pipeline.

• Through thickness microstructures of polygonal ferrite/acicular ferrite offer improved ductility for API pipeline steels for oil, gas, and high-pressure hydrogen gas applications. Volume fractions of acicular ferrite between 10-70%, and recent work in the 10-40% range, work show optimum E1820 fracture toughness performance in high-pressure gaseous hydrogen.

• Development of ductility-based methodology and ranking system for prescreening of existing pipeline steels in service for repurposing along with new pipeline steels for high-pressure gaseous hydrogen service, Figure 4. [16,17] Work is currently ongoing at NIST to develop a similar methodology for pipe seam and grith HAZ/weld metal for high-pressure gaseous hydrogen service.
Figure 3. Examples of various fracture and fatigue performance for optimized alloy/processing design of the base metal and welds of API X grade pipeline steel developments in the past 4 years.
What Don’t We Know

There are still several key components that we need to address and understand as follows:

• B31.12 has a maximum hardness of 238 Hv10, typical API HIC Sour Service and EIGA CGC Doc 121-14 allows for 248 Hv10 maximum hardness, standard API X grades pipeline customer specifications typically allow for 260 Hv10 maximum hardness with the occasional negotiated opportunity to go higher to 270 Hv10 or 280-285 Hv10 for X80 grades. Is 300 Hv10 satisfactory for CO2 and hydrogen or blended hydrogen service?
  ○ Optimizing the through thickness base metal austenite grain size along with the proper distribution of the right size of Ti and Nb precipitates has shown in recent work to control the HAZ austenite grain size controlled which will reduce the potential for the harder microstructure phases to form. This has also shown to work in other structural steel welding applications.
  ○ Pcm vs. heat input may be another potential opportunity to optimize and find the proper balance for the hardness in these applications, Figure 5. [18]

• From the API data, corrosion is the biggest steel related issue in the standard API grade oil and natural gas applications today, what will happen to this issue when hydrogen or CO2 is introduced? There are already concerns that CO2 operation will have various corrosion components involved that the current API grades for oil and natural gas do not have to deal with. This can potentially make the “corrosion” related issues become larger than currently experiencing if nothing is done differently. What are the solutions? Optimum ductility shows improvement in SCC performance which may be a piece of the puzzle. What about atmospheric corrosion resistant alloy designs for scale formations that might be beneficial to add to the optimum ductility contribution. This has shown possibility in other structural
applications and is under study currently in China. What other metallurgical steel designs can be utilized or be developed?

- Hydrogen enters the steel matrix under 2 conditions, corrosion, and pressure. Corrosion allows for a higher volume of hydrogen to enter the steel matrix at a faster rate and under pressure the rate is slower, and volume is less, but less it will enter the steel matrix. What will happen in these applications when some corrosive element, i.e. moisture/condensation, etc., accidentally gets into the hydrogen or blended hydrogen application? What does that do to the amount of hydrogen that enters the matrix? We worry about hydrogen embrittlement mechanisms in high-pressure gaseous hydrogen applications, but how much hydrogen must enter the matrix to contribute to the embrittlement mechanisms and then how much must collect at areas of high stress intensity, such as microstructural banding, before the embrittlement mechanisms turn into a hydrogen induced cracking (HIC) mechanism that becomes a concern? We see separations forming in the fractures of the CT specimens in the E1820 samples in H2 testing where we have microstructural banding issues which we cannot ignore regarding long term exposure, Figure 6. [19] From years of hydrogen HIC production experience in structural steels, when the hydrogen content in the matrix is > 2 ppm the potential for HIC cracking can start to occur. [20] How many months, years, or decades will it take before either hydrogen embrittlement or even HIC may occur in these applications?

![Hydrogen Fracture Separations – Indication of Microstructural Phase Differences/Banding](image1)

![Hydrogen Fracture Separations – Indication of Microstructural Phase Differences/Banding](image2)

Figure 6. Example of separations in fracture surface of CT E1820 specimens tested at 5.5 and 21 MPa hydrogen pressure and microstructural banding. Note with increasing pressure there is increasing presence of separations depending on microstructural banding severity.

- We know that hydrogen is attracted to areas of high-stress intensity. We also know what steel components contribute to the overall residual stress of the pipe/welds. How can we design and measure the residual stress state to start the welded pipeline with the lowest possible residual stress state going into service to improve the potential for a longer service life?

There may be other key components that will need to be addressed for hydrogen, blended hydrogen and CO2 applications as more is understood that can be added to the list.
SUMMARY
What we have today for hydrogen is a better understanding of materials for the base metal of which we know some are better than others, it is all pressure dependent along as corrosion is not involved. Understanding the metallurgy of HAZ and welds is currently ongoing, and we are gaining knowledge quickly. We have very little knowledge regarding corrosion and CO2 applications, somewhat like where we were in 2005 regarding gaseous hydrogen and pipeline steels. However, we have experience with corrosion from other structural steel applications that we may be able to apply. We also have experience with sour service API applications and those microstructures and welds have performed well in high pressure gaseous hydrogen applications and pseudo versions made to ASME B31.12-2019 Non-Mandatory Guidance Appendix G microstructures are currently being marketed and implemented for hydrogen pipeline applications by three major pipe manufacturers.

CONCLUSIONS
The bottom-line issue in these emerging applications of high-pressure hydrogen, blended hydrogen and CO2 is that we have 40+ years of technology development and operational experience in oil, gas, (sweet and sour) and low-pressure pure hydrogen transmission pipelines that has resulted in the reported incidents shown in Figure 1. What we do not have is 40+ years of experience, of operating safely high-pressure gaseous hydrogen, blended hydrogen, or CO2 in the existing pipeline system. We are basically in the infancy stages of this experience in these applications. The million-dollar question is “If we start running high-pressure gaseous hydrogen or blended hydrogen up to 10-15 MPa (100-150 Bars, 1450-2175 psi) how many months, years, or decades can a pipeline/welds survive before an incident happens that creates a rupture that causes injury or fatalities? Every time, even if it is just a “one off” event, negative publicity can shut down an industry, cost millions of dollars, invite overzealous government regulatory controls, or all of them. The last time massive amounts of hydrogen were used in the public infrastructure was 1937, “Remember the Hindenburg”. We have the knowledge and expertise, we just need to use it wisely and work with many different disciplines who have experience in producing API grade steels, understanding key metallurgical attributes and how to achieve them to assure that the steel and the welds can deliver the best combinations possible for the next generation of challenging transmission needs for the world’s market. Most likely the answer to the type of steels and welds needed for the next generation of pipelines with applications for high-pressure gaseous hydrogen, blended hydrogen, or CO2 applications is one that is somewhere between the current pure API sour service metallurgy and current polygonal ferrite/acicular ferrite microstructures alloyed and processed for optimized ductility of the base metal and the HAZ of the seam/girth weld that will perform in the most economical, reliable and more importantly safest manner possible in high-pressure gaseous hydrogen, blended hydrogen, and CO2 applications.

REFERENCES
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