Existing Pipeline Materials and the Transition to Hydrogen

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Abstract
The climate emergency is one of the biggest challenges humanity must face in the 21st century. We all need to be involved in the process of moving towards a decarbonized economy. At the same time, the advancing global energy transition faces many challenges when it comes to ensuring a sustainable, reliable and affordable energy supply. For this reason, gas will continue to play an important role in the future energy system. An emphasis on decarbonizing the existing gas infrastructure will inevitably lead to greater penetration of greener fuels, such as hydrogen, ultimately produced from renewable energy. While the replacement of natural gas with hydrogen and the introduction of hydrogen into modern natural gas transmission and distribution networks creates challenges, there is nothing new or inherently impossible about the concept of hydrogen pipelines. Indeed, more than 4,000 kilometers of pipelines are currently in operation. These pipelines, however, were (almost) all built in accordance with specific hydrogen codes, which tend to be much more restrictive in terms of material properties than their natural gas equivalents. This in turn means that the conversion of natural gas pipelines made from “standard” grades can be challenging.

This paper will investigate the role of material properties in terms of susceptibility to hydrogen damage as part of a Hydrogen Framework that includes characterizing the material properties of existing natural gas pipelines through ILI based on ROSEN’s Pipeline DNA process. It will describe the application of this framework to develop a “hydrogen-ready” pipeline in order to help enable the safe, economic and successful introduction of hydrogen into the natural gas network.

1 Introduction

Hydrogen pipelines are not new. The first hydrogen pipeline is thought to have been constructed in the 1930’s in Germany, and today there are more than 4,500 km of hydrogen pipelines in operation (1). Equally, natural gas pipelines are not new. There are thought to be more than 2,000,000 km of natural gas pipelines worldwide. The vast majority of these pipelines, both hydrogen and natural gas, are constructed out of the same types of material carbon-manganese steel, generally manufactured in accordance with the same base specifications (typically API 5L (2)). It is therefore easy to assume that materials, proven reliable through decades of service, to be suitable for natural gas service, will also be suitable for hydrogen service. The counter-argument is that most hydrogen pipelines have been purpose built and manufactured in accordance with specific hydrogen codes (e.g. ASME B31.12 (3)). These hydrogen-specific codes tend to be more restrictive in their material requirements than their natural gas equivalents (for example restricting the chemical composition and allowable strength levels). The logical consequence of these restrictions is that materials that are suitable for natural gas service are unsuitable for hydrogen service. Therefore, the materials of existing natural gas pipelines may be unsuitable for hydrogen service.

This paper will explain the various code restrictions and investigate their scientific basis. The role of material properties in terms of susceptibility to hydrogen damage will be clarified. The paper will show how these material properties should be taken into account as part of a wider Hydrogen Framework, and demonstrate how ILI technology can assist in understanding the materials within an existing pipeline and ensuring that they are suitable to enable the safe, economic and successful introduction of hydrogen.

2 Code Requirements

The most common design codes for hydrogen pipelines are ASME B31.12 and the AIGA / EIGA guidelines (4).

ASME B31.12 explicitly allows the use of grades up to X80 / L555 for hydrogen service, but the allowable stresses and operating pressures are restricted to such an extent (over and above the additional restrictions for hydrogen service compared to natural gas service for lower grade materials) that there is very limited value in using higher grades. In addition, the hardness of welds is limited to a maximum of 237 BHN, which implicitly restricts the allowable grades. Impact testing requirements differ between ASME B31.12 and API 5L, and it is therefore possible that pipelines, which were manufactured strictly in accordance with API 5L, do not meet the requirements of ASME B31.12. Non-mandatory Appendix A of ASME B31.12 explicitly states that only grades up to X52 / L360 are proven for service in hydrogen gas, and references the AIGA / EIGA guidelines for material selection purposes.

The AIGA / EIGA guidelines appear to be somewhat confused in terms of material requirements. Lower strength steels (grades X52 / L360 or lower) are recommended, and the guidelines differentiate between "carbon steels" and "microalloyed steels", with there being significantly more restrictions to the latter. Somewhat surprisingly, microalloyed steels are referred to purely in the context of electric resistance welded (ERW) line pipe and there is no recognition that microalloying could be applied to other product forms (e.g. seamless or SAW). The AIGA / EIGA guidelines also restrict the use of microalloyed steels to grades X42 / L290 and X52 / L360 (i.e. higher grades, or materials intended for higher strength grades, are not allowed). The AIGA / EIGA material requirements are summarized in Table 1.

Property	**AIGA / EIGA Carbon Steels Requirement**	**AIGA / EIGA ERW Microalloyed Steels Requirement**
Manufacturing Process	-	Basic oxygen or electric furnace steel that is fully killed and continuously cast.
Heat Treatment Condition	Normalized steels are preferred, seam welded pipes should be locally normalized (this appears to also apply to SAW pipe, although this is not	Weld seam and HAZ shall be heat treated so as to simulate a normalizing heat treatment.

	standard practise for SAW pipe mills)	
Chemical Composition	The use of lower sulphur and phosphorous steels should be considered for severe applications. All intentional alloy additions to be reported.	Maximum sulphur shall not exceed 0.01%. Maximum phosphorous shall not exceed 0.015%. All intentional alloy additions to be reported.
Metallographic and Microscopic Examination	-	Final ferrite grain size shall be ASTM 8 or finer. Weld samples to be cut once every 100 lengths and examined to ensure proper weld fusion.
Carbon Equivalent (CE[1])	0.43 maximum	0.35 maximum
Hardness	22 HRC / 250 HB maximum	95 HRB maximum
Strength	800 MPa (116 ksi) UTS maximum is recommended	Actual yield and tensile strengths shall be less than the following maximum above the minimum specified for different API 5L grades X52 24,000 psi (165 MPa) X42 25,000 psi (172 MPa)
Toughness	Impact test requirements in the applicable API / ASTM specifications. Reference to some additional requirements which should be considered	Both transverse (acceptance of 71 J individual, 94 J average) and longitudinal samples (acceptance of 88 J individual, 118 J average) are required. Minimum shear requirement of 60% individual, 75% average.

Table 1 - AIGA / EIGA Material Requirements

Appendix D of the guidelines outlines the metallurgical factors affecting hydrogen toughness and brittle fracture mechanisms.

[1] $CE_{IIW} = C + Mn/6 + (Cr+Mo+V)/5 + (Ni+Cu)/15$

Although not exhaustive, the above demonstrates that there are significant additional restrictions in place for materials for hydrogen pipelines compared to their natural gas equivalents. Both ASME B31.12 and the AIGA / EIGA guidelines recognise this, and as part of their guidance on repurposing pipelines recommend destructive laboratory testing at a minimum frequency of 1 sample per 1.6 km (1 mile). Within Europe, the German DVGW guidelines (5) refer back to ASME B31.12.

This in turn begs the questions, what are the metallurgical reasons for these restrictions and how can existing natural gas pipelines, whose materials may not meet the restrictions, be safely repurposed?

3 Metallurgical Effects of Hydrogen

The fundamental mechanisms of hydrogen damage are still very much a topic of current research, and there is probably a lack of understanding of the effects of hydrogen among the wider pipeline community. In particular, there are two major shibboleths, which need to be addressed.

It can often be casually assumed that, since any form of hydrogen damage requires that the hydrogen be absorbed into the pipe wall in atomic (or ionic) form, and since hydrogen pipelines transport gaseous molecular hydrogen, that there is no risk of hydrogen damage. Unfortunately, as quantified in Sieverts' Law (named after the eponymous Adolf Sieverts and first formulated in 1929 (6)), molecular hydrogen will dissociate at the pipe wall and hydrogen will therefore be absorbed into the metallic pipe wall matrix and can cause damage. This effect of gaseous hydrogen on various mechanical properties and susceptibility to damage has been widely documented, for example in the Sandia Technical Reference (7).

The second assumption is that gaseous hydrogen will inevitably lead to issues, and potentially failure, especially in higher strength carbon steel pipelines. This belief is probably born out of the widely documented occurrences of hydrogen related failures (e.g. through sour cracking or hydrogen embrittlement). The long, and successful, track record of production, storage, and transportation of gaseous hydrogen in carbon steel offers a convincing empirical refutation of this.

To understand the effects of gaseous hydrogen on pipeline steels it is therefore necessary to understand the behavior of steels in gaseous hydrogen, and contextualize this behavior when compared to other service conditions.

The bulk concentration of hydrogen within a pipe wall resulting from dissociation and absorption of gaseous molecular hydrogen following Sieverts' law can be shown to be orders of magnitude lower than the hydrogen concentrations resulting from other "typical" pipeline service conditions, for example an active cathodic protection system, welding (even with a low hydrogen welding process) or sour service. However, it is generally accepted that the bulk hydrogen concentration is of secondary importance with the most important factor being the localized concentration at the tip of a pre-existing defect. The relative importance of the reduction in cohesive energy or Hydrogen Enhanced DEcohesion (HEDE), Hydrogen Enhanced Localized Plasticity (HELP) and Adsorption Induced Dislocation Emission (AIDE) induced by this localized concentration have been much discussed (8) and it is fair to say that the exact mechanism(s) involved are still up for debate. Despite this, it appears to be agreed that the most important source of hydrogen is direct dissociation of gaseous hydrogen at the defect (crack) tip, rather than redistribution and diffusion of bulk hydrogen to high stress defect tips. This importance of localized dissociation and concentration means that gaseous hydrogen is less benign, at least in the presence of pre-existing defects or cracks, than it may appear.

The nature of the hydrogen attack will depend on the metallurgical structure of the steel. As discussed by Thompson and Bernstein (9), it will depend on various factors including the chemical composition, distribution and morphology of phases, grain structure (size, shape, texture) and the segregation and distribution of intentional alloying elements and precipitates as well as impurities. Koyama et al. (10) give an overview of recent progress in microstructure specific hydrogen mapping, while various other researchers have looked more in depth at the specific mechanisms. While the use of lower strength steels has been historically proven in gaseous hydrogen service, there does not appear to be any fundamental metallurgical reason why lower strength steels are suitable, while higher strength grades are not. Some of the risk factors, which increase the chance of hydrogen attack (for example the presence of martensite or the amount and lamellar spacing of pearlite), will also act to increase the strength and hardness of a steel, while others (for example the amount and proportion of non-metallic inclusions) will not. This microstructural dependence means that areas within a pipeline of a different microstructure to the bulk parent material (for example welds or hard spots) may be more prone to hydrogen attack than the parent itself.

Sour service steels offer convincing evidence that, if the microstructure is correctly controlled, high strength steels can be resistant to hydrogen attack with X70 / L485 sour service steels being common. Equally, sour service failures have been recorded even in lower strength (X52 / L360) grades. This reflects the differences, which can exist between pipes supplied to nominally the same grade, a modern European X52 / L360 linepipe will have been manufactured using different process conditions, and have an entirely different microstructure, to a vintage X52 / L360 pipe originally manufactured in the 1950's. In addition, there is the known discrepancy between specified minimum properties and actual properties; it is not unusual to for X52 / L360 steel to have actual strengths that would satisfy the minimum requirements of X60 / L415, or even X65 / L450.

The effects of gaseous hydrogen on pipeline steels are primarily to reduce ductility, reduce fracture toughness, and increase fatigue crack growth rate compared to air or natural gas (7). It therefore follows that relatively low ductility, or low fracture toughness pipes, even if these properties are acceptable for natural gas service, may be unacceptable for hydrogen service. Importantly, neither ductility nor fracture toughness are specified in common line pipe supply standards. Total elongation and Charpy impact values are normally specified, but these are only proxies for uniform elongation and fracture toughness and the specified values do not differ hugely between lower strength and higher strength grades. Indeed API 5L (2) currently requires higher Charpy impact energies for higher strength grades for PSL 2 pipe.

Grade	Minimum Total Elongation (50 mm gauge length, 12.7 mm diameter round specimen) / %	Full-Size CVN Absorbed Energy Min. / J, Pipe OD < 508 mm / 20”
X52 / L360	21	27
X 56 / L390	19	27
X60 / L415	18	27
X65 / L450	18	27
X70 / L485	17	27
X80 / L555	16	40

Table 2 – Selected Pipe Body Property Requirements for PSL 2 Pipe - from API 5L

The simplistic assumption that lower strength grades will always be suitable, while higher strength grades will not, is therefore flawed. Material-specific testing is required to show suitability.

4 Conversion of Existing Pipelines

As demonstrated above, if pipelines are to be repurposed, existing codes recommend destructive testing of material samples at a minimum frequency of one sample per mile. It has been further demonstrated that the mechanical property and chemical composition requirements are significantly more onerous for hydrogen pipelines than for their natural gas equivalents, and therefore there is a high probability that the destructive test results will not meet the requirements for hydrogen service. There is a lack of guidance within the codes regarding what can be done in these situations.

To cut this Gordian knot, ROSEN believes that it is necessary to obtain a detailed understanding of the materials within a pipeline. In recent years, ROSEN has introduced the RoMat family of in-line inspection services. These include the Pipe Grade Sensor (PGS) technology (11) and the DMG hard spot technology, with the aim of supporting operators through the processes of material verification.

The RoMat PGS service is based on high-resolution eddy current measurements, with the signal response being a function of specific aspects of the pipe chemistry and microstructure. Proprietary algorithms are then used to translate the response into values for yield strength (YS) and ultimate tensile strength (UTS) for each joint. The RoMat DMG service uses dual field magnetic flux leakage (MFL) technology to detect internal and external volumetric martensitic hard spots (12).

Outputs from these services can then be incorporated with data from other sources (both ILI and historical records) to fully characterize the pipeline and separate out individual pipe “populations”. Each individual population is defined by a unique set of shared characteristics (including strength, wall thickness, nominal joint length, pipe type etc.), as a result of this a single population can therefore be confidently associated with a single construction campaign and original pipe mill. This population approach defines the “Pipeline DNA” and allows more robust assessments of the pipeline, and its suitability for hydrogen service.

The initial output from a PGS run is an estimation of the YS or UTS associated with each pipe or bend within the inspected pipeline, as shown in Figure 1.

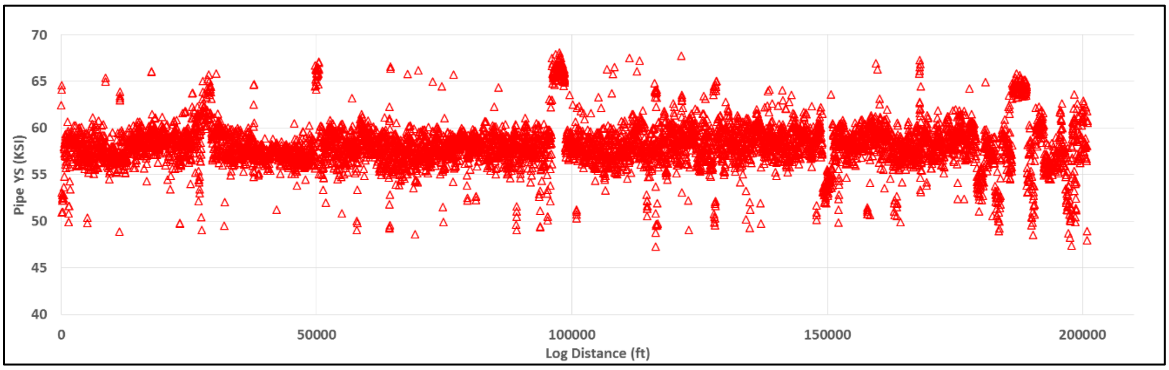

Figure 1 - YS along the pipeline

In the above graph, each point represents a single pipe joint (normally ~12 m length). This output can be used as a stand-alone resource to identify potential strength outliers, however full value is achieved when the data is integrated with other sources to define populations, fully characterize the pipeline, and identify the "Pipeline DNA". A completed example is shown in Figure 2, where each data point represents the median strength value attributed to a single pipe. Each population is defined by a unique colored symbol in the plot.

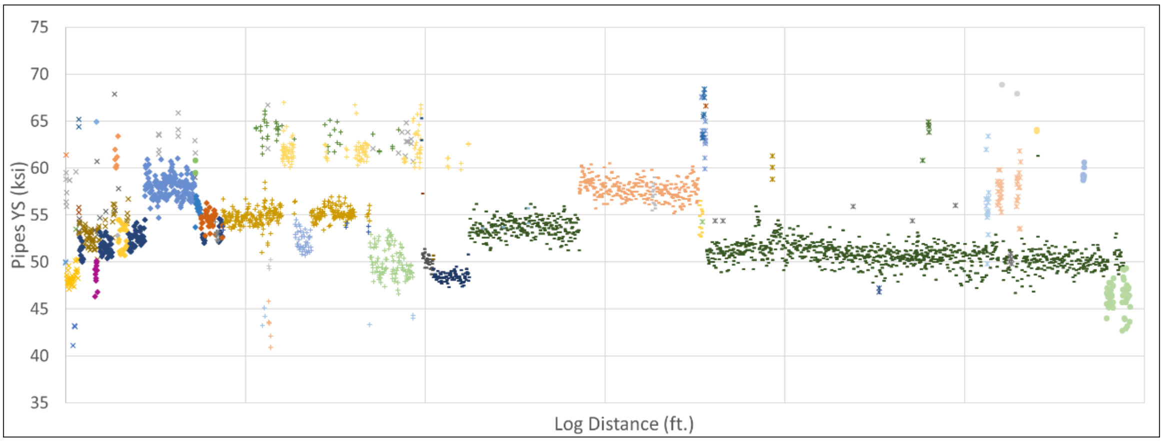

Figure 2 - Populations identified along the full pipeline length

The "Pipeline DNA" can then be overlaid with other datasets, for example suspect crack-like indications from an EMAT inspection or hard spot locations from the RoMat DMG service, to identify if these hard spots are associated with individual populations.

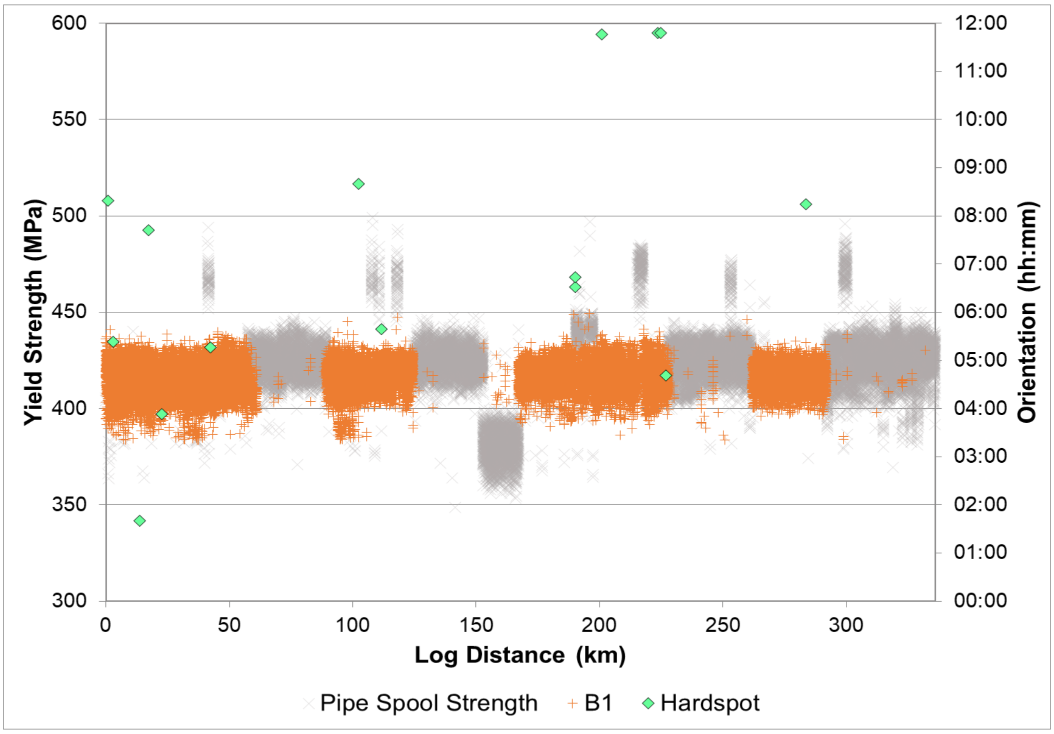

Figure 3 – Hard spots concentrated in a single population

Figure 3 shows an example of this approach, where it can be seen that all 15 hard spots identified in an over 300 km long pipeline were present in population B1, and thus associated with a single mill and construction campaign. No hard spots were identified in any other populations.

This "Pipeline DNA" approach enables a step-change in the approach to assessing materials for their suitability for hydrogen service. Rather than the recommended, but blunt, approach of destructive testing once a mile, testing can be targeted at individual populations. This approach has multiple benefits over the standard recommendations. Firstly, it ensures that no populations are missed. If sampling occurs once a mile then it is very probable that short diversions, repairs or other small populations will be not be sampled, while multiple samples will be taken from the main population and therefore they would effectively be repeats. Secondly, verification testing can be targeted at areas which may be of concern, for example, if a particular population has an anomalously high strength, a high concentration of hard spots or crack-like indications, then these can be targeted during verification digs. Additional confidence can be gained in the representative nature of any features that are excavated. For example, if all reported hard spots are concentrated in a single population, there is more likelihood that they will be of the same morphology and created by the same mechanism than if they were in different populations. Assessment techniques can therefore be used with more confidence. Destructive testing and evaluation can be targeted at the highest risk locations, both increasing confidence in the test results and minimizing the number and cost of verification digs required.

5 The Transition to Hydrogen

The approach outlined above is an example of how one specific aspect (material suitability) of the transition to hydrogen can be managed. It is best understood as part of a wider hydrogen integrity framework, as outlined in Figure 4.

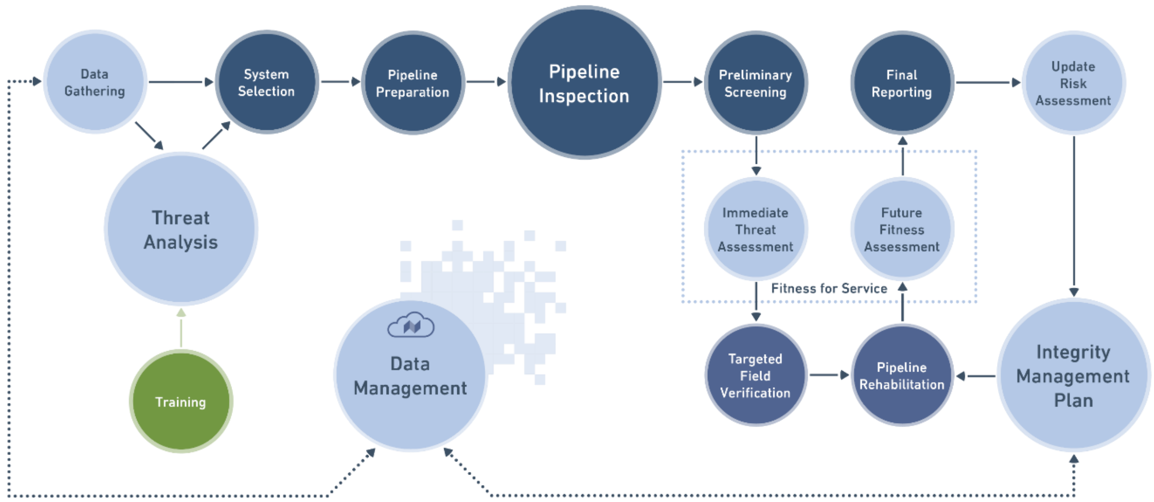

Figure 4 – ROSEN Hydrogen integrity framework

As outlined above, the first stage in any transition to hydrogen is to gather data and identify potential threats. In this case, it is axiomatic that material susceptibility to hydrogen attack is a potential threat, and that often times, existing data is insufficient to quantify this threat. Once this gap has been acknowledged, appropriate steps can be taken (a mixture of analysis of existing records, ILI and destructive testing) to fill the gap and ensure that the potential threat is fully understood, characterized and mitigated against.

ROSEN firmly believe that this approach, combining an in-depth understanding of the effects of hydrogen and world-leading ILI and testing technology, can enable the safe introduction of hydrogen into existing pipelines.

6 REFERENCES

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