Technical University of Varna
Annual Journal
https://doi.org/10.29114/ajtuv.vol8.iss2.323
Vol. 8 Issue 2 (2024)
Published: 2024-10-18
ISSN 2603-316X (Online)

Steel X65 acc. API 5L behaviour under the influence of CO_2 and H_2

Diyan Nikolov[1], *Georgi* Antonov[1]

1- Technical University of Varna, Department of Materials Science and Technology, 9010, 1 Studentska street, Varna, Bulgaria

Corresponding author: antonov@tu-varna.bg

Abstract. *The paper focuses exclusively on the study of the gas pipeline steel X65 (acc. API 5L) behavior when subjected to the influence of CO_2 (carbon dioxide) and H_2 (hydrogen). Research and development of this type of document is necessary due to the needs of minimizing the CO_2 in the atmosphere produced by cement manufacturing during the process of decarbonization of limestone and clay in the cement kiln. With the expensive carbon emissions costing about 63 EUR/ton for the first quarter of 2024, it is reasonable CO_2 to be utilized. Additionally, coal-fired power plants must be transformed due to the high price of their electricity. Along with the cost for mining coal, the EU adds additional costs for emissions. The market cannot afford to provide unprofitable energy to customers. The power sector somehow must take necessary action to comply with the latest government and environmental requirements.*
One possible approach to address the transformation needs is to switch to green H_2 fuel or a mixture with H_2, or implement Carbon Capture and Storage (CCS) processes. Both gases have their specific problems that need to be overcome. The behavior of the already laid pipelines made by low carbon steel material exposed to these gases has not been fully assessed. Future experiments and tests will determine how these gases will affect the life cycle or design life of pipeline transportation systems.

Keywords: CO_2 transportation, corrosion, running ductile fracture, hydrogen induced corrosion

I. Introduction

Most of the companies are trying to decrease the impact of the latest imposed requirements by minimizing CO_2 emissions or changing fuels by investing money in developing new economical processes for the utilization of greenhouse gasses. In 2021, the European Union provided grants for the development of a cost-effective process for CCS. For the transportation of CO_2, the logical approach is to use old pipelines. Choosing the cost-effective method does not guarantee safety or risk-free operation. Corrosion engineers are challenged to prove that pipelines not designed for CO_2 service will be safe enough to handle these new conditions. Since this is a new field of engineering, it has not been sufficiently studied. Each case will be specific, with different parameters, materials, residual service life, existing pipeline fittings and equipment condition, and service requirements.

The oil and gas industry is also affected by these new regulations to achieve Net Zero by 2050 (Neele F., Koenen, M. et all., 2011). However, the only difference is that O&G companies own most of the pipelines, depleted wells for storages, budget, technologies, and competent engineers. The processing of fossil fuels a major producer of greenhouse gasses, but regrettably, the EU environmental regulations cover only the European countries. The Brevik project has been developed for large-scale CCS in Norway, where CO_2 from a cement factory is transported by ship to the already depleted oil wells in North Sea. The Northern lights project, also in Norway, designed to store 1.5 million tons per year, is expected to be commissioned in 2024. As stated by the Global CCS Institute, there are 19 projects in operation with large-scale capacity, totalling 40 million tons of CO_2 (https://www.brevikccs.com/en/). Based on

https://doi.org/10.29114/ajtuv.vol8.iss2.323
Vol. 8 Issue 2 (2024)
Published: 2024-10-18
ISSN 2603-316X (Online)

the above, the need for studying specific pipelines used for the transportation of CO_2, H_2, or mixtures with those gases must be assessed.

II. What is the purpose of this study?

The aim of this paper is to clarify the steel behaviour under the influence of CO_2 and H_2. The most common steel used for pipeline manufacturing is X65 acc. API 5L. Due to the fact that most of the pipeline systems are old, and many of the drilled O&G wells are depleted, it is reasonable and cost-effective for operators to explore possibilities to use those old pipelines and already depleted wells for carbon transportation and storage, or transportation of natural gas mixed with green H_2.

The study hereto discussed and the related experiments will reveal the resulting negative consequences in the event of failure in the transportation and storage of CO_2. This means that the state of the gas is no longer in the desired supercritical region. The experiments clearly show that the issue with the highly corrosive media is the water-gas contact, or the place where free water is mixed with the CO_2. An important finding from the experiments will be recognizing which zone of the pipe is most susceptible to damage. Last but not least, for the steel affected by CO_2, experiments will show how the mechanical characteristic are changed. The tasks mentioned above should provide operators with proper guidance on the utilization of this specific gas, along with potential hazards to avoid.

Regarding the Hydrogen gas, the present study will highlight the issue with HIC corrosion. Transportation using the old pipelines and old infrastructure for this gas with practically the smallest molecule is impossible. The latest intentions are for H_2 to be mixed with the natural gas in order for the calorific value to be increased, but such an approach must be considered dangerous because of the ability of H_2 to cause steel embrittlement and cracks.

III. Detailed account of the issue with CO_2 in steel pipes.

Understanding CO_2 behavior is very important because the phases of the product will affect direct on the design of the pipelines. Additionally, due to the varying impurities in the CO_2, the phase diagram holds particular significance. Figure 1 shows the relationship between pressure and temperature, which presents the phases of CO_2. Some pipeline operators work in dense phase, while others transport CO_2 in gas phase. All this depends on factors such as pipe diameter, pipeline length, pipe materials, and required throughput. It is important for the process to avoid two phases (Cole, I. S., Corrigan, P., Sim, S., & Birbilis, N. 2011).

For the purposes of the experiment that will be presented, conditions of 60 Bar pressure and 25 DegC are used. Under these conditions, specimens or coupons of steel X65 acc. API5L are placed in a small pressure vessel made of SS316 stainless steel rated up to 150 Bar. At 60 Bar, it is evident from the phase diagram that the coupons are tested in the gas phase of CO_2. The aim of the examination is to provide data in case the transportation process fails, and the CO_2 decreases in the pressure or temperature, moving the situation from the supercritical region to the gas region. In the supercritical fluid phase, CO_2 has a density similar to a liquid, but the viscosity is closer to the gas phase. In this state, the CAPEX cost is lower, and the distance of the pipeline can be significantly longer.

Technical University of Varna
Annual Journal
https://doi.org/10.29114/ajtuv.vol8.iss2.323
Vol. 8 Issue 2 (2024)
Published: 2024-10-18
ISSN 2603-316X (Online)

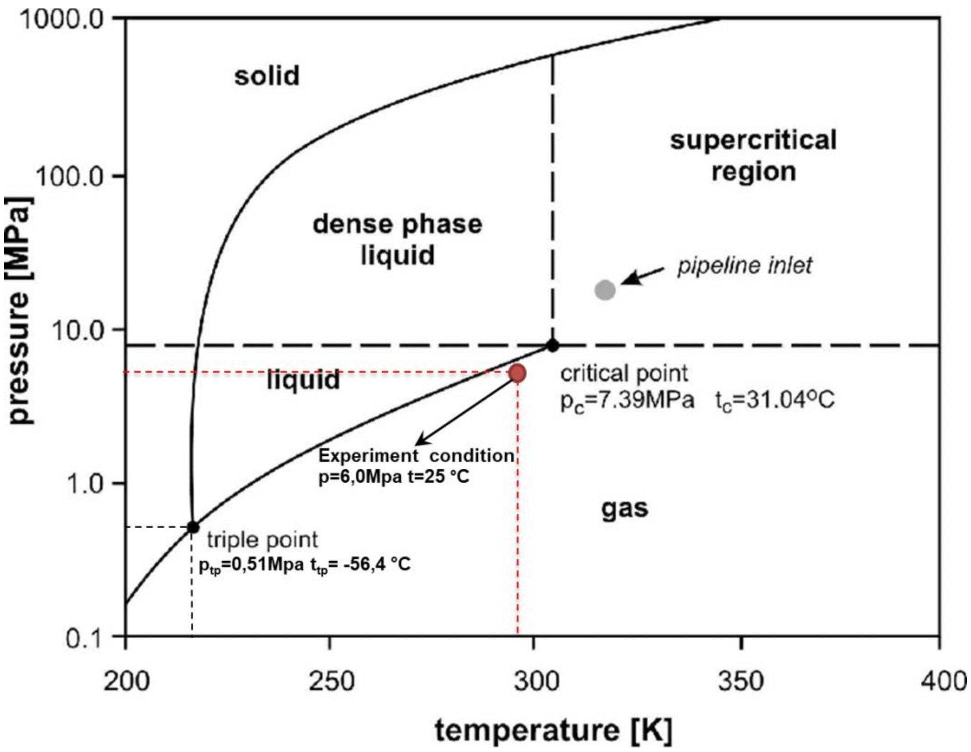

Figure 1 Phase diagram for CO_2 (Witkowski, A., Rusin, A., Majkut, M., & Stolecka, K. 2014)

Table 1. Elemental analysis for the carbon steel (API 5L X65) used in the corrosion tests in (%):

C	*Mn*	*P*	*S*	*Cr*	*Ti*	*Ni*	*Mo*	*Al*	*Fe*
0,059	1,36	0,016	0,003	0,0292	0,0197	0,0227	0,0066	0,032	Bal-ance

Most O&G pipelines are designed and manufactured with X65 carbon steel. This steel is popular due to its good mechanical properties, with a yield point of about 500 MPa and tensile strength of about 600MPa. Besides, it has good corrosion resistance and weldability, making it one of the most commonly used steel grades for pipelines onshore and offshore. Undoubtedly, the welds are critical and extremely sensitive points of concern when the pipes are under load.

Test equipment was specially designed in order for the specimen to be inserted in a solution of CO_2 and H_2O as an additive. Presented below is a simple schematic diagram.

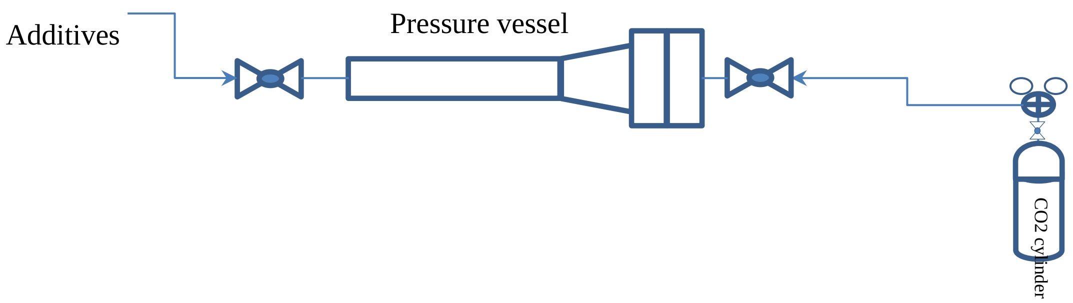

Figure 2: Process diagram of testing equipment with internal volume of 400ml

https://doi.org/10.29114/ajtuv.vol8.iss2.323
Vol. 8 Issue 2 (2024)
Published: 2024-10-18
ISSN 2603-316X (Online)

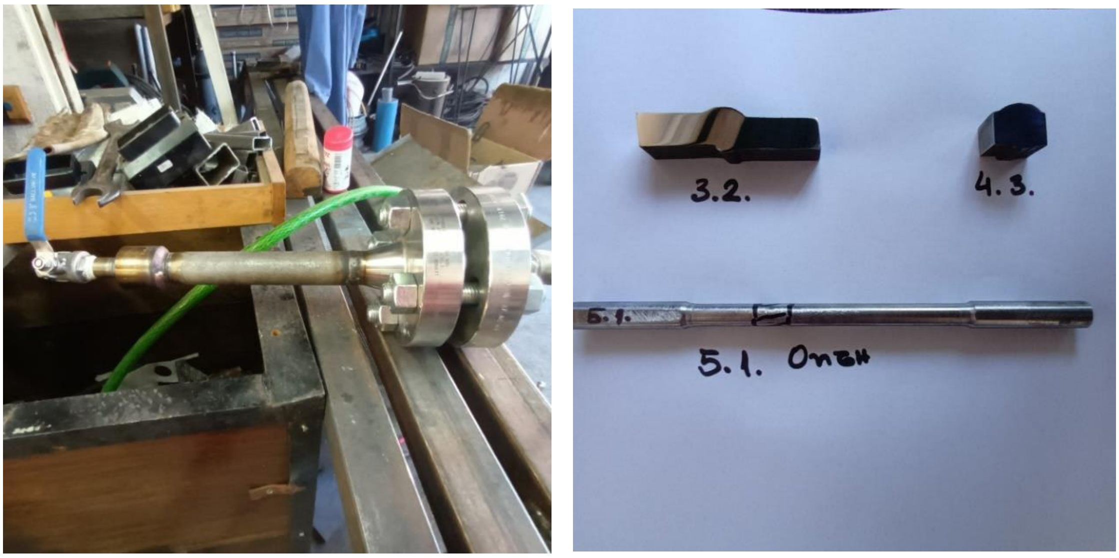

Figure 3: Pressure vessel and Test specimens

Three pieces of test specimens have been prepared as shown in Figure 3:

3.2. Specimen - Transverse weld including main steel material put for 100 hours in a media of 100% CO_2, and 10 ml H_2O – will be XRD tested (X-ray diffraction analysis) in order to determine the phase identification of the alloy;

4.3. Specimen – Transverse weld put for 100 hours in media of 100% CO_2, and 10 ml H_2O – will be macro examined;

5.1. Specimen – Produced for tensile testing. Includes the transverse weld (marked on the surface) and main steel material. Partially immersed in solution of 100% CO_2 and 50 ml of H_2O for 2 weeks.

Test Results

After 100 hours of testing, **Specimen 3.2.** shows severe signs of corrosion due to the aggressive solution of carbonic acid. The oxide layer, then, which is in contact with the oxygen in the air, starts peeling off almost immediately. Correspondingly, the acid in the gas water contact inside the testing equipment was able to etch the weld. The weld passes are visible in Figure 4. (Root pass made with TIG method with OK Tripod 12.64, and Hot passes made with SMAW method with OK 48.00). The oxidizing process is concentrated in the weld zone and the zones where the load of the rolling machine has been applied, due to the pipe forming from steel plate in the factory.

https://doi.org/10.29114/ajtuv.vol8.iss2.323
Vol. 8 Issue 2 (2024)
Published: 2024-10-18
ISSN 2603-316X (Online)

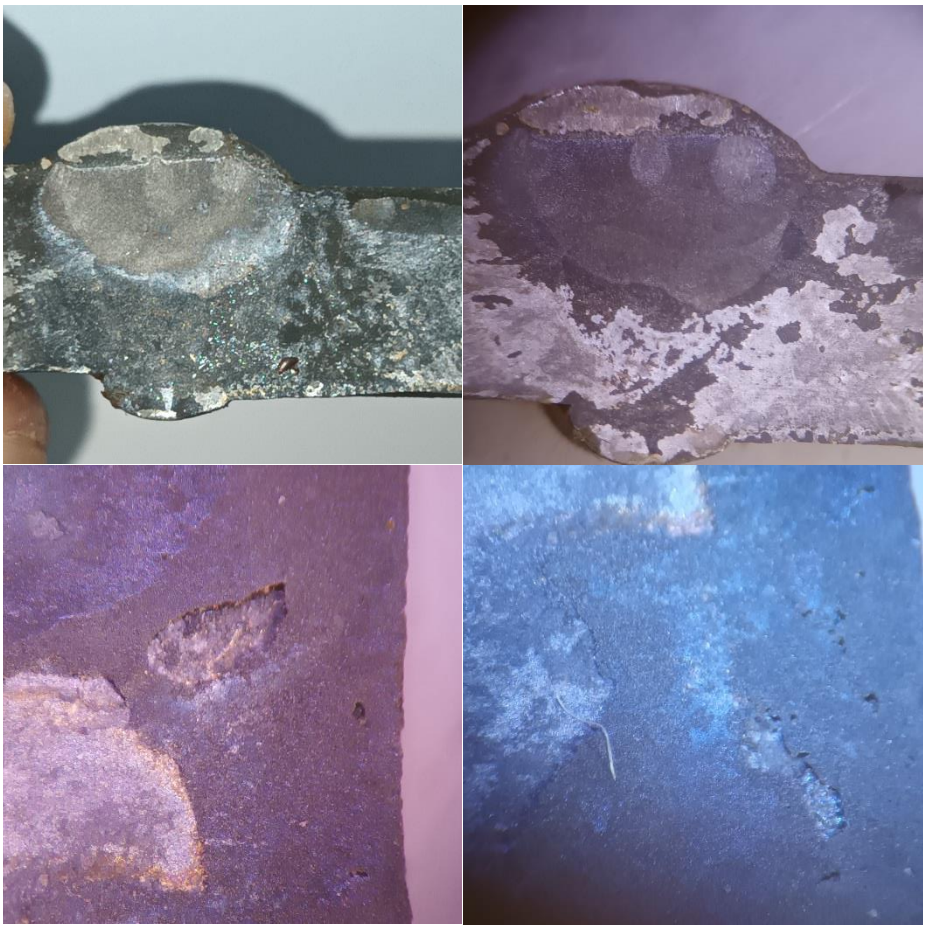

Figure 4. Macro examination of the specimen 3.2

Specimen 3.2. has been prepared, and the backside polished in order for the XRD devise to examine the base material, oxidized zone, and the area between. The specimen dimensions have been further machined to fit the XRD holder. Figure 5.

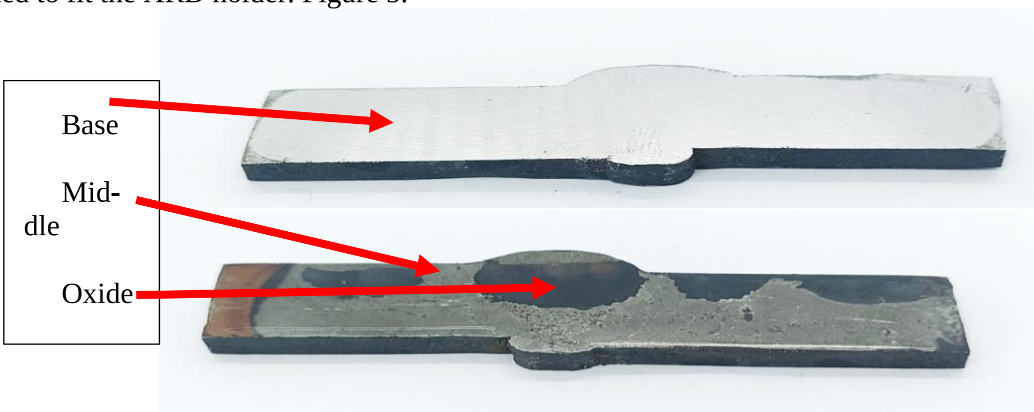

Figure 5. Specimen 3.2 ready for XRD examination

https://doi.org/10.29114/ajtuv.vol8.iss2.323
Vol. 8 Issue 2 (2024)
Published: 2024-10-18
ISSN 2603-316X (Online)

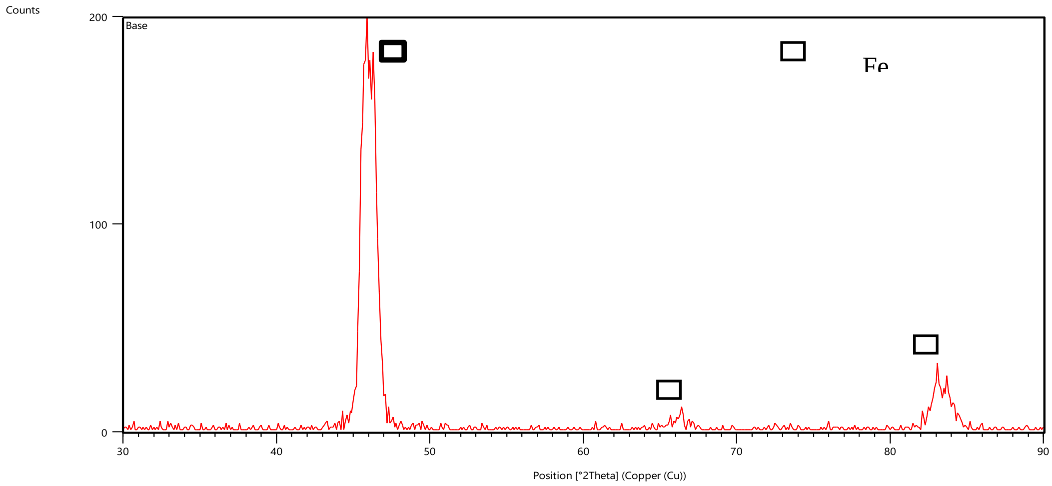

Figure 6. Base/main material results

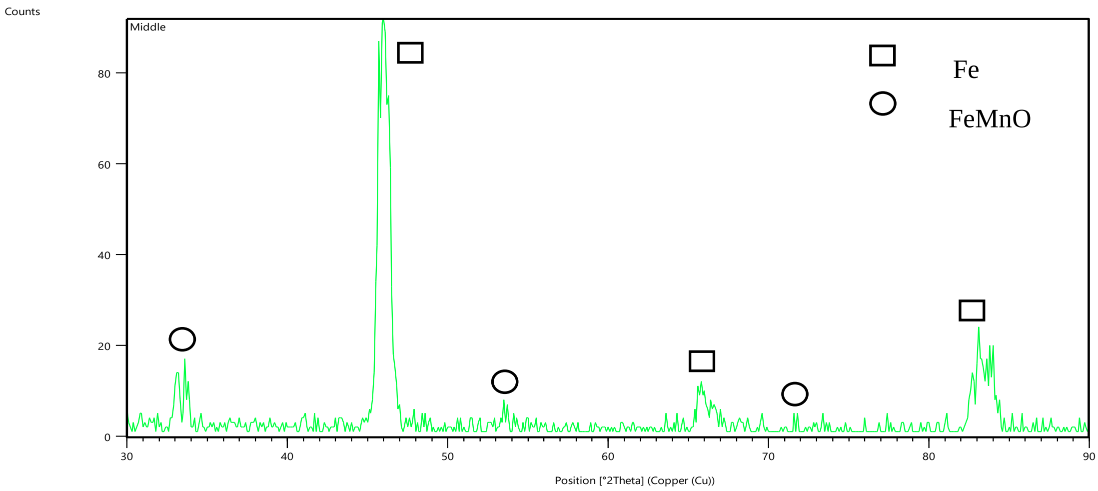

Figure 7. Middle zone results

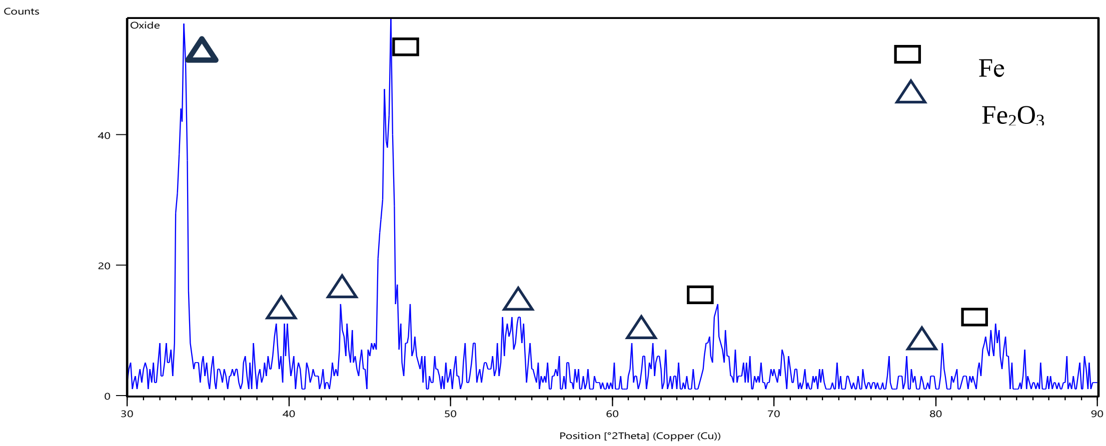

Figure 8. Oxidized zone results

https://doi.org/10.29114/ajtuv.vol8.iss2.323
Vol. 8 Issue 2 (2024)
Published: 2024-10-18
ISSN 2603-316X (Online)

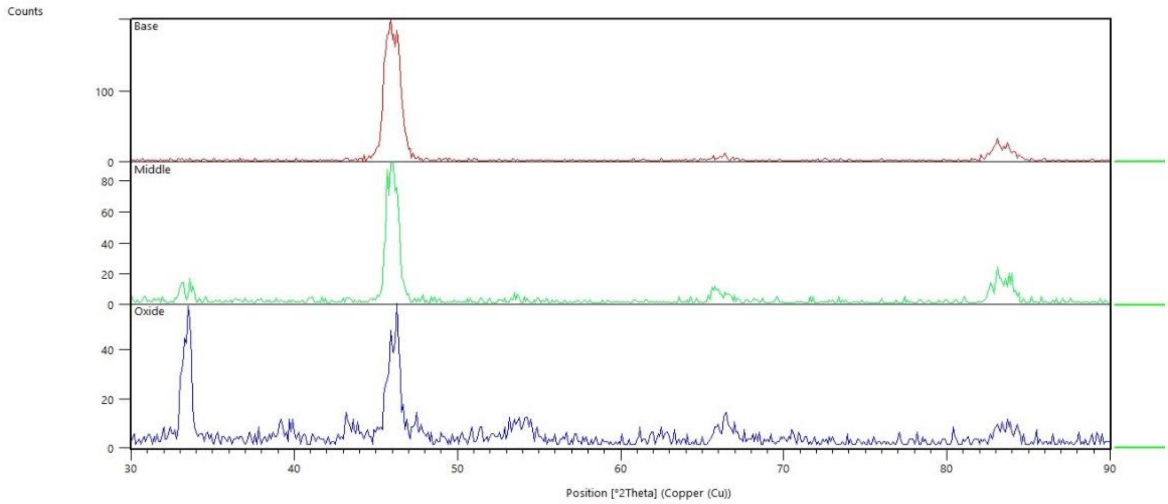

Figure 9 a. Combined results

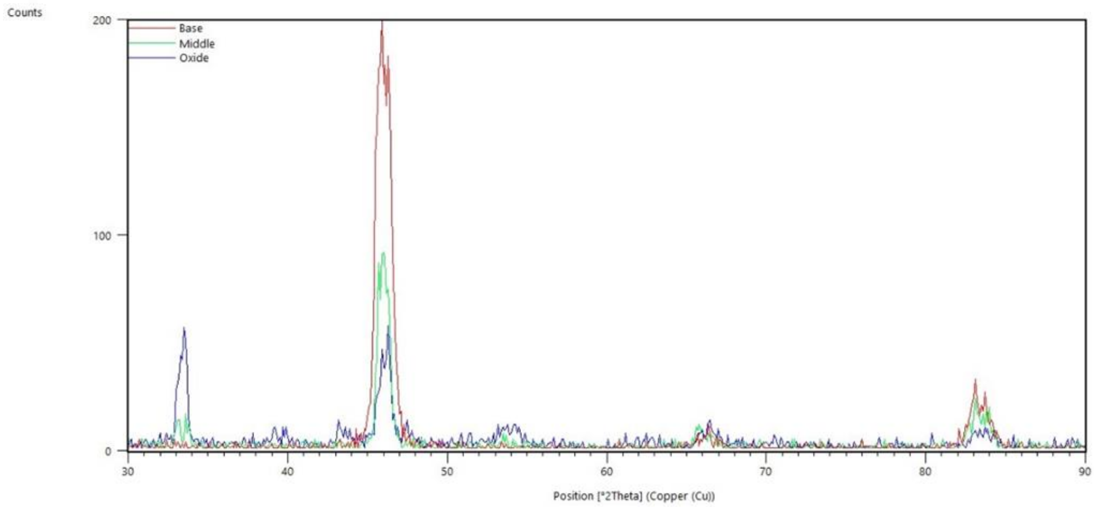

Figure 9 b. Combined results

4.3. Specimen has been partially immersed in water. The part near the water gas contact has a severe corrosion layer.

Technical University of Varna
Annual Journal
https://doi.org/10.29114/ajtuv.vol8.iss2.323
Vol. 8 Issue 2 (2024)
Published: 2024-10-18
ISSN 2603-316X (Online)

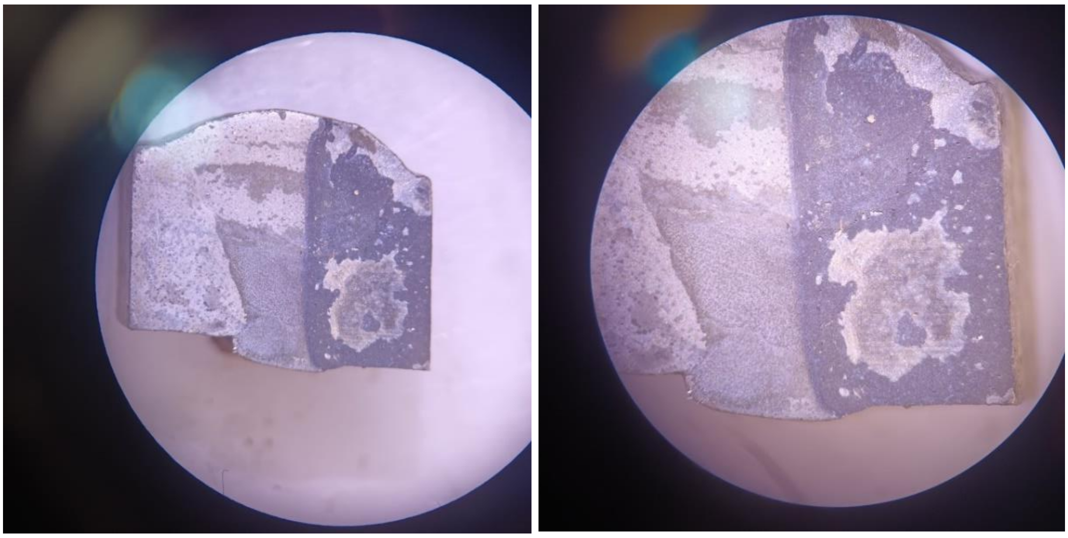

Figure 10. Polished side with etched weld and corrosion layer on the not submerged part of the specimen

5.1. Specimen – Partially immersed in a solution of 100% CO_2 and 50 ml of H_2O for 2 weeks, has been tensile tested and compared to the same specimen with the same weld but not affected by the solution of CO_2 and water.

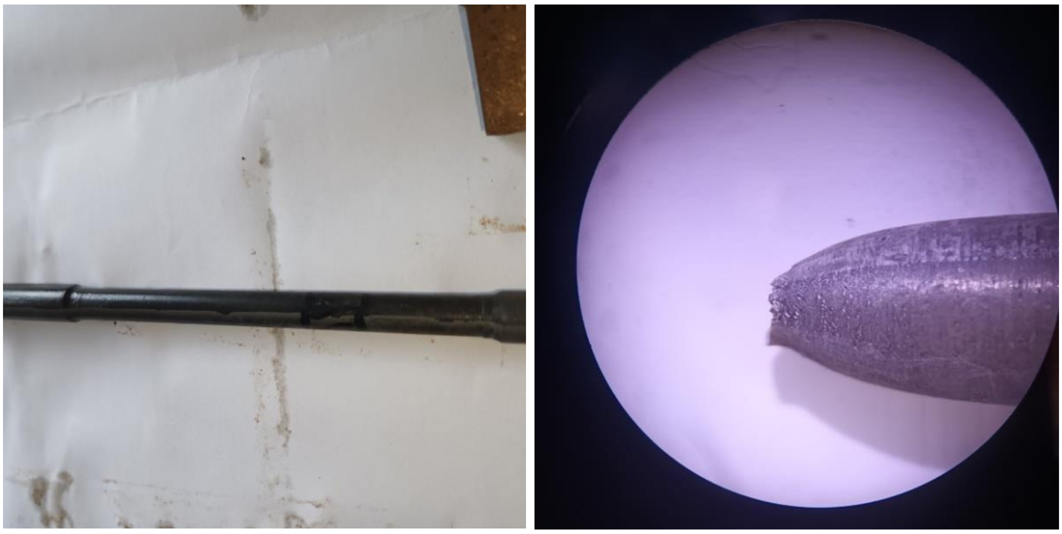

Figure 11. Specimen 5.1.

Reported in Table 2 are the results compared between 2 identical tensile strength specimens. As mention earlier, 5.1. was affected by the corrosion solution while 2.13 was not. A slight difference is observed between Re and Rm due to the corrosion caused by the carbonic acid. Moreover, the fracture analysis of the zone around the fracture surface shows small cracks within the corroded zone.

Table 2 Results from tensile test experiments

Speci-men	do	L0	S0	du	Lu	Su	Fe	Fm	Re	Rm	A	Z
	mm	mm	mm2	mm	mm	mm2	N	N	MPa	MPa	%	%
2.13	8	80	50,24	3,6	90,4	10,17	24250	28600	**482,68**	**569,27**	13	79,75
5.1	8	80	50,24	4,4	92,5	15,2	22700	26050	**451,83**	**518,51**	15,63	69,75

https://doi.org/10.29114/ajtuv.vol8.iss2.323
Vol. 8 Issue 2 (2024)
Published: 2024-10-18
ISSN 2603-316X (Online)

The water added inside the testing equipment together with the CO_2 serves as the primary catalyst for the corrosion process. The gas phase, in addition, poses potential issues for the low carbon steel pipelines. Therefore, it is imperative that pipelines remain free from any water or impurities. The case under consideration is of utmost importance, as the results demonstrate the possible consequences for welds in the event of a process failure.

IV. Hydrogen "green" problem and solution

The novel approach to the utilization of old pipelines is to use them for other fluids for which they are not designed. Hydrogen is one of the potential gases which has been nominated by many organizations that could save our polluted environment. Numerous ideas exist on how to use this gas, but many of them present serious technical challenges. In view of the small molecule size, it is very hard to keep the hydrogen "inside" the system for many existing oil and gas facilities. Much of the equipment is not suitable to accommodate this gas, as leaks will appear immediately, for example, the packing and seals on the valves.

There are two ways to utilize this gas, which are applicable in the industry. The first and the more expensive option is to design and build entirely new facilities specifically for hydrogen. In this case, materials, equipment, and processes will be suitable for the use of this tiny molecule.

The other way, and less expensive, is to mix this gas with other gases, for example, natural gas. This approach will collect the "green" hydrogen from the producers, for example, from electrolysis where the gas is produced using renewable energies, and mixed in the national pipeline grid (Topolski, Kevin, Reznicek, Evan P., et all, 2022). This could increase the natural gas caloric value, and the burn process will be more effective.

However, pipeline operators face the following issues. Transportation and distribution are dangerous processes in terms of safety. Hydrogen has the ability to embrittle materials.

Defined, below, will be two of the major issues.

Hydrogen-induced corrosion or HIC is the process where small hydrogen atoms diffuse into the spaces of inclusions in materials such as carbon steel, for instance. Figure 12 features HIC corrosion in a vulnerable metal (Gabani Amit, Founder of Bhavy industrial testing services, March 29/2023).

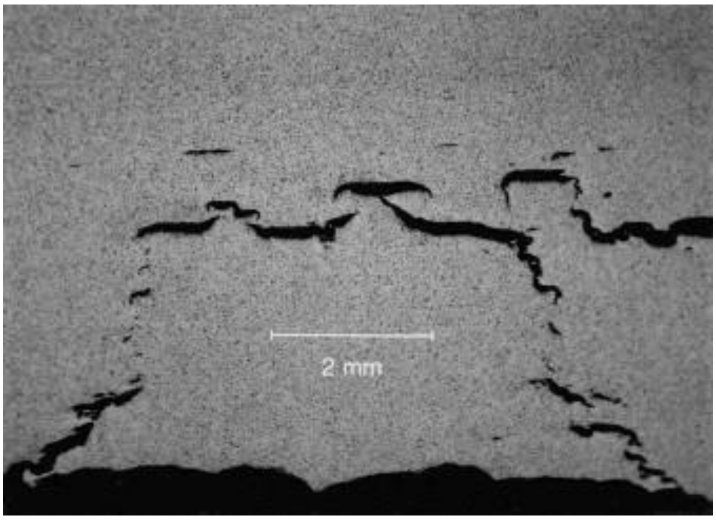

Figure 12. Image of HIC corrosion in vulnerable metal

Hydrogen embrittlement occurs when hydrogen atoms penetrate into the pre-formed cracks as a result of corrosion, or steel impurities from inclusions. They form brittle compounds and may increase cracking. Because of this mechanism, the H_2 concentration in the mix must be controlled and inspected.

https://doi.org/10.29114/ajtuv.vol8.iss2.323
Vol. 8 Issue 2 (2024)
Published: 2024-10-18
ISSN 2603-316X (Online)

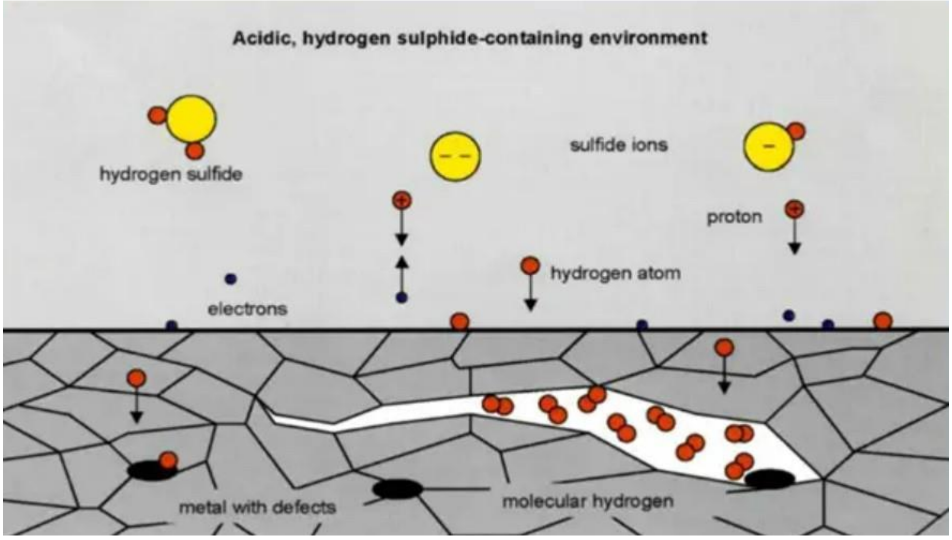

Figure 13. Mechanism of appearance of Hydrogen embrittlement in metals exposed to hydrogen gas or certain hydrogen-containing compounds (Gabani Amit, Founder of Bhavy industrial testing services, March 29/2023).

The aim of the proper assessment of the process of transporting, distributing, and blending H_2 is to avoid the risk of the issues stated above. This can be done by checking the steel materials compatibility, or using materials for use in hydrogen service (NACE materials).

As usual, welds are the sensitive points of any equipment, so a thorough analysis of the welding procedures (WPS) should be done.

Stress-affected and contraction zones should be avoided.

Constant inspections of the chemical and mechanical characteristics of the materials must be carried out as preventive measures.

Chemical solutions such as inhibitors can be used in order to minimize the negative effects of the hydrogen.

V. Conclusion

Using existing pipelines for products, or mixtures with gases, designed for other services, especially those operating at the limits of their mechanical properties, is a very dangerous approach, regardless of the environmentally friendly intentions behind such actions. The capture and transportation of CO_2 require careful analysis, taking into account all relevant factors to prevent catastrophic depressurization and other inherent issues that could result in immeasurable costs.

The same issue arises with hydrogen transportation. Special pipelines should be designed and manufactured, implementing the latest industry requirements. The problems outlined above are unavoidable factors in our quest for environmental transformation and greener future.

Acknowledgment:

The present study was developed in accordance with the doctorate project PD11/2023, Methodology for evaluating the operational reliability of underwater marine gas pipelines, funded by the Technical University of Varna.

https://doi.org/10.29114/ajtuv.vol8.iss2.323
Vol. 8 Issue 2 (2024)
Published: 2024-10-18
ISSN 2603-316X (Online)

References:

Capelle, J., Furtado, J., Azari, Z., Jallais, S., & Pluvinage, G. (2013). Design based on ductile–brittle transition temperature for API5L X65 steel used for dense CO2 transport. Elsevier Ltd. Retrieved from https://www.researchgate.net/publication/273413639

Cole, I. S., Corrigan, P., Sim, S., & Birbilis, N. (2011). Corrosion of pipelines used for CO2 transport in CCS: Is it a real problem? International Journal of Greenhouse Gas Control, 5(4), 749–756. https://doi.org/10.1016/j.ijggc.2011.05.010

Gabani, A. (2023, March 29). Founder of Bhavy industrial testing services.

Veselinov, D., Skulev, H., Yankova, R., & Koeva, V. (2023). Performance of selective plated copper coatings on stainless steel 316L and nickel alloy Ni201: Microstructure, microhardness, wear resistance, and corrosion resistance. Institute of Metal Science, Equipment and Technologies with Hydro- and Aerodynamics Centre "Acad. A. Balevski" Bulgarian Academy of Sciences. https://doi.org/10.7546/CRABS.2023.10.12

Neele, F., Koenen, M., van Deurzen, J., Seebregts, A., Groenenberg, H., & Thielemann, T. (2011). Large-scale CCS transport and storage networks in North-West and Central Europe. Energy Procedia, 4, 2740-2747. https://doi.org/10.1016/j.egypro.2011.02.176

Silva, S. C. D., de Souza, E. A., Pessu, F., & others. (2019). Cracking mechanism in API 5L X65 steel in a CO2-saturated environment. Engineering Failure Analysis, 99, 273-291. https://doi.org/10.1016/j.engfailanal.2019.02.031

Topolski, K., Reznicek, E. P., Erdener, B. C., San Marchi, C. W., Ronevich, J. A., Fring, L., Simmons, K., Fernandez, O. J. G., Hodge, B.-M., & Chung, M. (2022). Hydrogen blending into natural gas pipeline infrastructure: Review of the state of technology. United States. https://doi.org/10.2172/1893355

Witkowski, A., Rusin, A., Majkut, M., & Stolecka, K. (2014). The analysis of pipeline transportation process for CO2 captured from a reference coal-fired 900 MW power plant to sequestration region. Chemical and Process Engineering, 35(4), 497–514. https://doi.org/10.2478/cpe-2014-0037

Witkowski, A., Majkut, M., & Rulik, S. (2014). Analysis of pipeline transportation systems for carbon dioxide sequestration. Archives of Thermodynamics, 35, 3–8. https://doi.org/10.2478/aoter-2014-0008

Advisory Council of the European Zero Emission Technology and Innovation Platform (ETIP ZEP). (2019). CO2 storage safety in the North Sea. Zero Emissions Platform. Retrieved from https://zeroemissionsplatform.eu/wp-content/uploads/ZEP-report-CO2-Storage-Safety-in-the-North-Sea-Nov-2019-3.pdf

Corrtest Instruments. (n.d.). Corrtest Electrochemical workstation CS350 User manual. Wuhan Corrtest Instruments Corp., Ltd.

NACE International. (2003). Corrosion control of steel fixed offshore structures associated with petroleum production (NACE Standard RP0176-2003). Houston, TX: NACE International.

https://brevikccs.com/en/

https://zeroemissionsplatform.eu/wp-content/uploads/ZEP-report-CO2-Storage-Safety-in-the-North-Sea-Nov-2019-3.pdf

https://zeroemissionsplatform.eu/wp-content/uploads/ZEP-Future-CCS-Technologies-report-12-January-20171.pdf