STRESS ENGINEERING SERVICES INC.

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Guideline for Repurposing Existing Carbon Steel Pipelines for CCS and CCUS Projects

Final Report

Prepared for:
PCOR Partnership
Energy & Environmental Research Center
University of North Dakota
Grand Forks, ND

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Grand Forks, ND

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Forward

Stress Engineering Services, Inc. (SES) was contracted by PCOR Partnership to prepare this comprehensive guideline for repurposing existing carbon steel pipelines for use in carbon capture and sequestration (CCS) and carbon capture utilization and sequestration (CCUS) projects. The guideline was developed to provide PCOR membership with a basic guideline with considerations to be used for the following possible applications:

1. A pipeline that had not previously been exposed to H_2S transporting a stream of CO_2 now containing H_2S
2. A pipeline that had been previously exposed to H_2S but now will be repurposed for use with a clean CO_2 stream without H_2S

It is important to recognize that the selection of existing carbon steel pipelines previously used for transport of oil and/or gas cannot be based on standard industry practices. First and foremost, standard oil and gas pipelines are not designed for transport of supercritical CO_2 (SC-CO_2). This dedicated use requires significant modeling of CO_2 phase behavior during a possible leak and the subsequent requirement for modeling the minimum Charpy impact toughness to arrest a running ductile fracture. These requirements are not commonly applied to oil and gas pipelines and are not trivial tasks. This document is a general guide to the requirements necessary to assess the potential repurposing of existing pipelines for SC-CO_2 transport.

This guideline represents the opinions of the authors and incorporates feedback from individual members of the PCOR Partnership who have reviewed this document and its provisions. The intent of this document is to summarize current best practices, and it is not intended to replace education, experience, and the use of engineering judgment. Safety issues other than those expressly covered are not addressed in this document.

Table of Contents

List of Tables

List of Figures

1. Introduction

Stress Engineering Services, Inc. (SES) was contracted by PCOR Partnership to prepare a comprehensive guideline for repurposing existing carbon steel pipelines for use in carbon capture and sequestration (CCS) and carbon capture utilization and sequestration (CCUS). This guideline primarily covers two pipeline scenarios: a pipeline that ***had not*** previously been exposed to H_2S is being considered for a stream of CO_2 now containing H_2S, and a pipeline that ***had*** been previously exposed to H_2S is now being considered for use with a clean CO_2 stream without H_2S.

2. Factors that Impact Steel Pipeline Performance – General Considerations

This section discusses various factors and their impacts on pipe performance. It is interesting to note that while there is currently considerable discussion and work on standards and best practices for repurposing hydrocarbon pipelines for transport of SC-CO_2, many of these efforts are entirely focused on pressures, temperatures, and hydraulics with relatively little mention of potential corrosion and materials issues. More concerning is that most of the papers presented on this subject completely ignore the most significant consideration that existing hydrocarbon pipelines are not designed for the extremely high fracture toughness needed to prevent a running ductile fracture, possibly resulting in terminating such a project. As an example, see the work presented by Seevam, et al. discussing the feasibility of reusing existing pipelines [1].

2.1 CO_2 Stream Composition

There are numerous compositions of CO_2 streams slated for current and future CSS and CCUS projects. However, some of the more common CO_2 stream compositions are presented in Table 1, summarized from various sources. Implicit in this table is the concentration of $CO_2 \geq 95\%$.

Table 1. Examples of the Streams from Various Sources

Industries	Typical Impurities
Power Generation – Coal Fired Plants *(IPCC, Carbon Capture and Storage, Working Group III, 2005)*	0-0.5% SO_2, ~ 0.01% NO, 0-0.6 % H_2S, 0- 2.0 % H_2, 0-0.4 % CO, 0.01-3.7 % N_2/Ar/O_2
Power Generation – Gas Fired Plants (*IPCC, Carbon Capture and Storage, Working Group III, 2005*)	0-0.1 % SO_2, ~ 0.01% NO, < 0.01 % H_2S, 0-1.0 % H_2, 0-0.04 % CO, 0.01-4.1 % N_2/Ar/O_2
Chemical Plants	N_2, O_2 and H_2O
Other Industries such as natural gas plants (but primarily for EOR)	0 – 1 % H_2S, 2% CH4, 0-4% N_2, 0-10 ppm O_2, ≤ 0.1% H_2O

Industries	Typical Impurities
Ethanol plants	0% SO_2, ~ 1.5% N_2, < 2% O_2
Fertilizer plants	0.07% H_2, 0.44% N_2, 0.055% O_2, 0.01% Ar, 2.4 wt % H_2O

These various concentrations of impurities can have a profound effect on corrosion of steel pipelines if liquid water is present; however, the vague limits of less than certain concentrations are inadequate for proper evaluation of the role of each impurity in the corrosivity of the stream. Therefore, only generalizations can be made in this section of the report regarding how detrimental each species may be for a given pipeline.

Of particular note are Table 2 and Table 3 from Peletiri [2], which show the wide range of typical H_2S concentrations in CO_2 streams. It is the impact of H_2S specifically that is pertinent to this guideline.

Table 2. CO_2 Stream Composition in mol% of Some Existing Pipelines

	Cortez Pipeline	Canyon Reef Carriers	Sheep Mountain	Central Basin Pipeline	Bravo Dome	Weyburn	Jackson Dome
CO_2	95	85–98	96.8–97.4	98.5	99.7	96	98.7–99.4
CH_4	1–5	2–15	1.7	0.2		0.7	Trace
N_2	4	<0.5	0.6–0.9	1.3	0.3	<0.03	Trace
H_2S	0.002	<0.02		<0.002 wt		0.9	Trace
C_{2+}	Trace		0.3–0.6			2.3	
CO						0.1	
O_2				<0.001 wt		<0.005 wt	
H_2						Trace	
H_2O	0.0257 wt	0.005 wt	0.0129 wt	0.0257 wt		0.002 v	

Table 3. Minimum and Maximum Mole Percentages of Typical Impurities in CO_2 Streams

	CO_2	N_2	O_2	Ar	SO_2	H_2S	NO_x	CO	H_2	CH_4	H_2O	NH_3
Min.%	75	0.02	0.04	0.005	$<10^{-3}$	0.01	<0.002	$<10^{-3}$	0.06	0.7	0.005	$<10^{-3}$
Max.%	99.95	10	5	3.5	1.5	1.5	0.3	0.2	4	4	6.5	3

2.2 Temperature and Pressure

The design and operating temperatures and pressures of supercritical CO_2 (SC-CO_2) pipelines are typically set within a narrow range in order to ensure the CO_2 being transported remains in the supercritical state. Typical operating temperatures and pressures range from 55 °F – 111 °F (13 – 44 °C) and 1232 – 2174 psi (84.9 – 149.9 bar) [2]. Generally, increasing pressure and temperature increase corrosion rates.

2.3 Water Content

In recent years there has been a considerable effort to study the role of water content in SC-CO_2 streams from a corrosion standpoint. Unlike the typical water limits for natural gas pipelines of about 7 lbs/MMscf, the solubility of water in SC-CO_2 is a strong function of temperature, pressure, and impurities. Figure 1 shows significant increase in water solubility when CO_2 goes through a phase change from gas to liquid with increasing temperature and pressure [3].

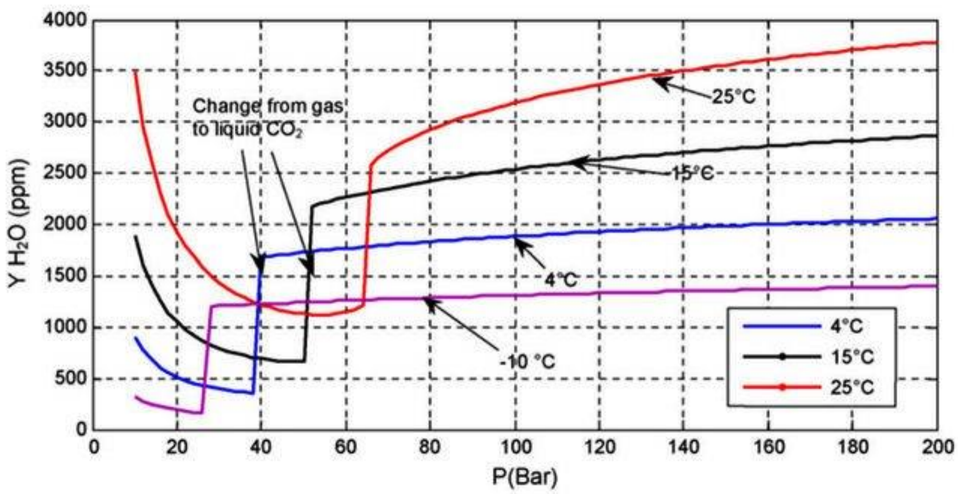

Figure 1. Increase in water solubility as CO_2 has a phase change from gas to liquid

Figure 2 shows the effect of nitrogen on the water solubility at constant temperature of 40 °C [4].

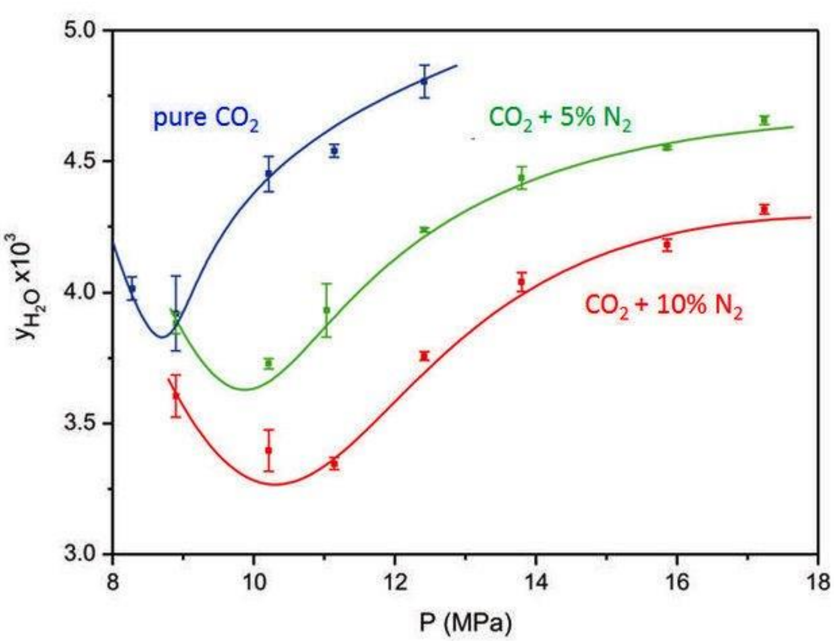

Figure 2. The effect of N2 on the solubility of water in CO_2 at 40 °C

Typical SC-CO_2 pipeline specifications for water range from 50 – 650 ppm. The 650 ppm limit for water is the standard Kinder Morgan specification which has served that company well for many years. As long as water remains soluble in the SC-CO_2 phase and there is no liquid water phase in the pipeline, corrosion will not occur. This fact is substantiated by the long successful history of the oil industry in West Texas using carbon steel pipelines for transport of SC-CO_2.

Zhang et al. studied the effect of water mist in contact with SC-CO_2 as well as a separate water phase [5]. They found that droplets of water mist saturated with CO_2 caused minor corrosion with some pitting. For the separate water phase, corrosion rates ranged from 197 – 590 mpy (5 – 15 mm/y) depending on the temperature. Other researchers have found the same high corrosion rates when a separate water phase is present.

Water dropping out of the SC-CO_2 phase will have no buffering of pH so the resulting pH of such water will be very low. Numerous studies have shown the same results for pH as presented in Figure 3. Here the SC-CO_2 conditions at 1070 psi (73.8 bar) and 31 °C demonstrate that, for these conditions and higher, the pH is 3.0 – 3.1 [6].

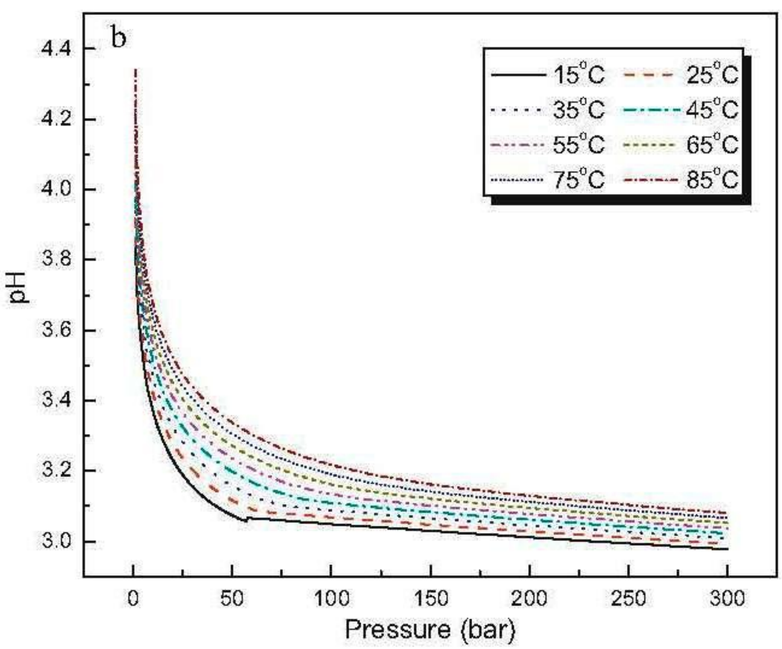

Figure 3. Variation of pH as a function of pressure and temperature

Even more deleterious is the further drop in pH caused by impurities in the CO_2 such as SO_2 and NO_2. Ayello et al. found that adding as little as 100 ppm SO_2 to SC-CO_2 at 1,099 psi and 104 °F reduced the pH another decade below that shown in Figure 3 to approximately 2.5 [7].

2.4 H_2S Content

A comparatively large number of studies have been performed considering the effect of H_2S on corrosion of steels in SC-CO_2. However, much like the situation for other impurities, there are contradictory results that show either no increase in corrosion rate with H_2S present or a significant increase in corrosion rate. Ding et al. [8] found almost no effect of H_2S contents ranging from 5 to 200 ppm on corrosion from SC-CO_2; however, these authors did not present a base case corrosion rate in the absence of H_2S. Sui et al. [9] found that for 1000 ppm H_2S at various temperatures, the corrosion rate depended on the temperature and pressure (see Figure 4).

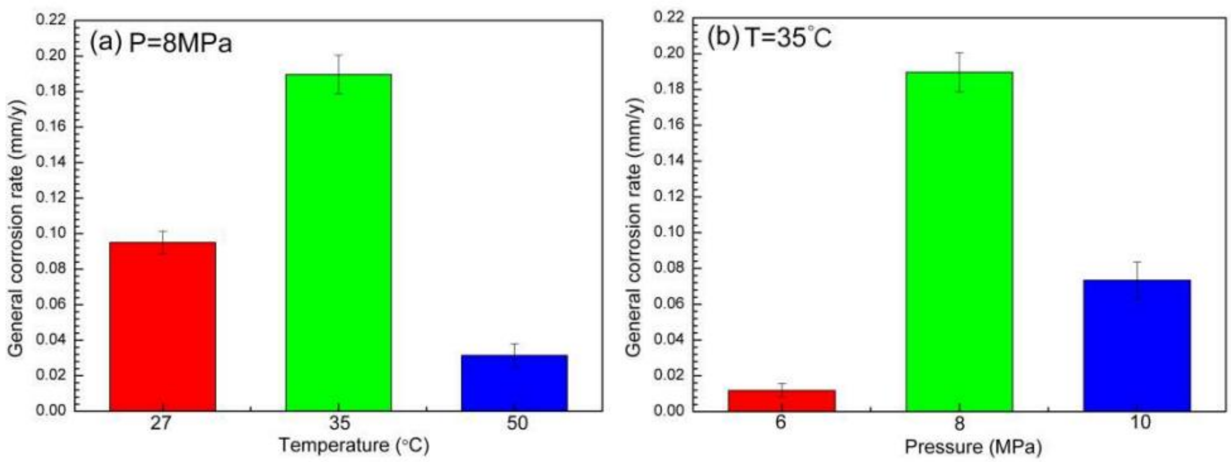

Figure 4. Corrosion rate of X65 steel exposed to water-saturated supercritical CO_2 containing 1000 ppmv H_2S impurity for 72 h at different conditions: (a) 8 MPa with different temperatures; (b) 35 °C with different pressures

Zhang et al. evaluated carbon steel in SC-CO_2 at 1,956 psi and 176 °F for 96 hours [10]. Table 4 shows the results as a function of H_2S content. The presence of increasing H_2S shows significant increases in corrosion rate over the base case with no H_2S.

Table 4. X65 Corrosion Rates vs. H_2S Content

H_2S Concentration, ppm	Corrosion Rate, mpy
0	614.6
3-5	858.9
300-400	1,375.1

Choi et al. [11] showed that the presence of 200 ppm H_2S dramatically increased the corrosion rate of carbon steel in CO_2 that was water saturated. Under dewing conditions, the corrosion rate increased from 6 mpy to 32 mpy when 200 ppm H_2S was present.

One other potential issue when H_2S is present but which has not received adequate attention is the potential for cracking associated with H_2S. The specific forms that could be operative are sulfide stress cracking (SSC) and Hydrogen Induced Cracking (HIC), both of which are addressed in NACE MR0175/ISO 15156 [12]. However, this standard is specifically related to the potential for SSC and HIC in upstream petroleum production; it does not address the risk in SC-CO_2 systems. Craig [13] published a short note raising the issue of whether this standard is applicable to SC-CO_2 and whether either SSC or HIC could be the same risk as in oil and gas production and transportation. Little work has been performed to date to examine this question. Paul [14] considered the potential for SSC by testing X65 stressed specimens in an environment of 1435 psi CO_2 and 14.5 psi H_2S at 104 °F (40 °C). They found that H_2S reduced the overall corrosion rate due to the formation of an iron sulfide film (mackinawite), and while no sharp cracks were observed, they noted "fine scale features". These so called fine scale features have been identified numerous times in the past as trenches and are a precursor to SSC. Therefore, the risk of SSC in X65 in the presence of H_2S is a real possibility and should be considered in SC-CO_2 pipelines when H_2S is present. It is likely that higher strength pipe steels such as X70 and X80 will be at even greater risk of SSC in H_2S-bearing streams.

The potential for HIC has not been evaluated for SC-CO_2 systems, but since most pipelines that transport SC-CO_2 are relatively large diameter, they are typically manufactured with welded longitudinal seams. Most modern transmission line pipe is seam welded by high-frequency electric resistance welding (HFW), but thick wall pipe may use submerged arc welding (SAW), and older pipe may have been made using low-frequency electric welding (LF-ERW) or other obsolete long seam techniques. Welded steel pipe is known to be more susceptible to HIC than seamless pipe; therefore, this risk should be addressed for SC-CO_2 pipelines.

The NACE MR0175/ISO 15156 standard sets a threshold partial pressure of H_2S (pH_2S) for SSC at 0.05 psia; however, this value was determined based on oil and gas systems and is specific to the gas phase. Since SC-CO_2 and any impurities are not correctly defined by partial pressures, the correct term for stating the contribution of components to the overall mix is fugacity. Therefore, fH_2S must be determined using software to arrive at the actual contribution of H_2S. Figure 5 presents an analysis of the variation of pH_2S and fH_2S with increasing pressure of CO_2 starting in the gas phase and continuing into the dense phase [15]. Note the significant drop in pH_2S and fH_2S once there is a phase change of the CO_2 from gas to dense phase. Since this work was based on a pH_2S of 1.5 psia, Figure 5 suggests that SC-CO_2 containing certain concentrations of H_2S would not strictly follow the 0.05 psia limit in NACE MR0175 and, thus, could possibly tolerate higher pH_2S before SSC were a risk. Much more work on this including parallel SSC tests needs to be performed in order to define an fH_2S limit.

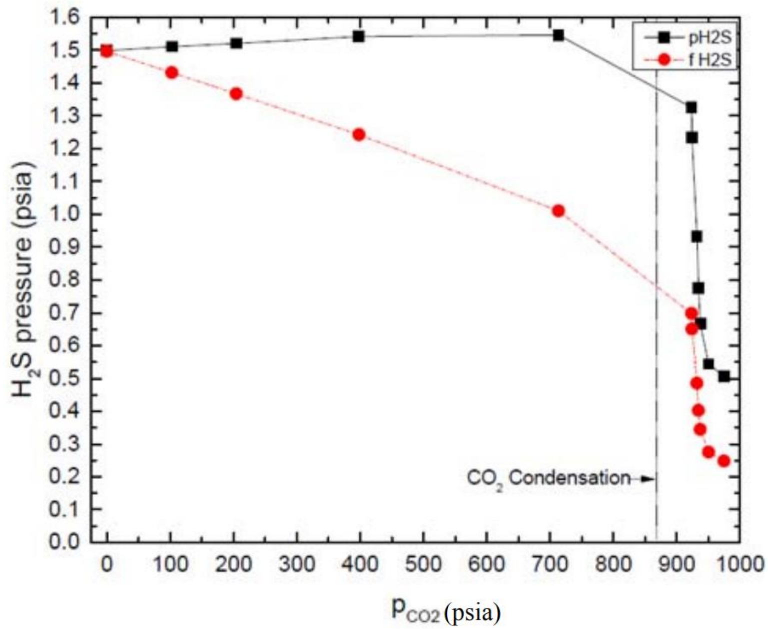

Figure 5. Effect of increasing CO_2 on partial pressure and fugacity of 0.41 g H_2S (starting pH_2S of 1.5 psia) at 75 °F with 60,000 ppm chloride brine in a 2 L autoclave

2.5 Oxygen

The limited work on the role of O_2 is somewhat contradictory. For example, Choi [16] reported an increase in corrosion rate when O_2 was present at 50 °C, however, Hua [17] evaluated 20, 50, and 1000 ppm O_2 at 35 °C and found the effect was to reduce the general corrosion rate but encourage local attack by pitting. Zhang also found an increasing corrosion rate with O_2 levels up to 400 ppm [10].

2.6 Nitrogen Oxides (NO_x)

Dugstad and Halseid studied the effect of combinations of SO_x, NO_x and O_2 impurities on corrosion of steel and found that NO_x was far more detrimental to corrosion, leading to higher rates than either of the other two [18].

2.7 Sulfur Dioxide (SO_2)

Choi and Nesic found that for 1% SO_2 in SC-CO_2 with 650 ppm water, the corrosion rate was 146 mpy, and with the addition of small amounts of O_2 the corrosion rate increased slightly [19]. These authors and others indicate the detrimental effect from SO_2 is the formation of sulfuric acid.

Li et al. found that as little as 100 ppm SO_2 significantly increased the corrosion rate in SC-CO_2 [20].

When a combination of SO_2 and O_2 are present, it has been suggested that either sulfurous or sulfuric acid can form. This is confirmed by the observation on steel coupons of the presence of $FeSO_3$ and $FeSO_4$. As Barker et al. stated, the nature of the corrosion products that form can either reduce or inhibit corrosion or accelerate attack [21].

2.8 Other Impurities (Hydrogen, CO, etc.)

Currently there does not appear to be any research or testing specific to any role of hydrogen in the corrosion of steels in SC-CO_2. However, Healy et al. [22] have studied the potential for breakout of H_2 from SC-CO_2, and results indicated that under some conditions a separate H_2 gas phase of up to 20 mol % could form. This could be a significant issue from a materials standpoint since H_2 gas in an environment where the solution pH is near 3 could lead to various forms of hydrogen cracking.

Many SC-CO_2 streams contain measurable quantities of CO; however, few studies have been performed to illuminate the role of this species. One set of tests showed no effect of CO on corrosion [9]. The potential role of CO still warrants more investigation since a well-recognized form of stress corrosion cracking occurs in the H_2O-CO-CO_2 system [23].

There are also many possible trace compounds that could be present in the SC-CO_2 stream that should be evaluated such as glycols, methanol, etc. and their degradation products.

2.9 Corrosion Product Films

As shown in Figure 3, the pH of water condensing from SC-CO_2 is likely to be around 3, which would not be expected to result in a corrosion product according to thermodynamic considerations. In systems with CO_2 as a gas in the presence of water at temperatures of around 140 °F to 176 °F (60 °C to 80 °C) and a higher pH of 6, a semi-protective $FeCO_3$ scale forms on the pipe walls that can significantly reduce the corrosion rate [24]. However, as shown in Figure 6, no such product would be expected at pH 3 and for temperatures typical of SC-CO_2 [25]. Only ferrous ions (Fe^{2+}) are expected unless the electrochemical potential is high enough to form Fe_2O_3.

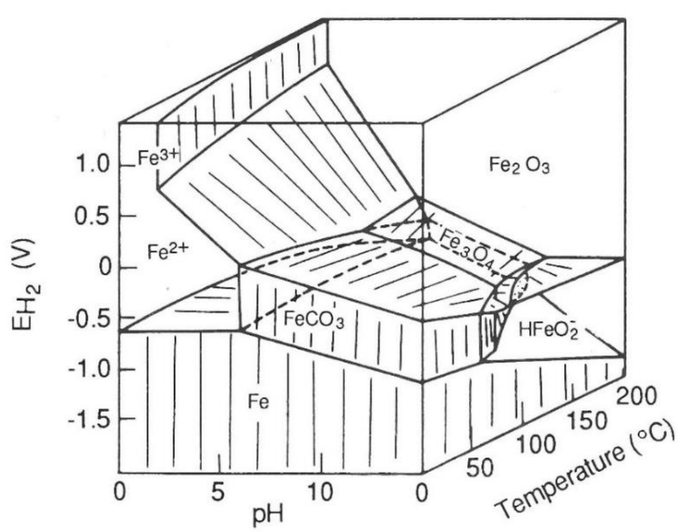

Figure 6. E_H-pH diagram showing the species present for the Fe-CO_2-H_2O system

More recently, these same regions have been confirmed by Tanupabrungsun et al. [26]. Yet, as will be discussed in this guideline, research has often shown that corrosion products do appear on steel surfaces, contrary to what is expected based on the E_H-pH diagrams. As explained by Tanupabrungsun, the pH of 3 is that of the bulk solution, and the actual pH at the steel surface can be much higher, as high as 6.2 when the bulk pH is 4 according to work of Han [27]. At higher surface pH, the expected corrosion product would be $FeCO_3$, which these researchers confirmed was indeed present. While these studies were not performed at supercritical pressures, the results are still expected to apply.

Morland et al. [28] observed a thin nonhomogeneous layer of $FeCO_3$ corrosion product formed for all their test conditions in dense phase CO_2. Thin nonhomogeneous scales are not considered protective whereas thicker homogeneous scales can be. Cabrini et al. [29] noted the presence of thick protective $FeCO_3$ scales in their tests at 140 °F and 1,160 psi CO_2. The reason for these contrary findings is due to experimental factors such as the temperature, pressure, and water content to name a few.

The same inconsistent results of corrosion product formation and composition occurs when impurities are considered in the tests. For example, Sun et al. [30] found the corrosion rate depended on the combination of impurities (see Figure 7).

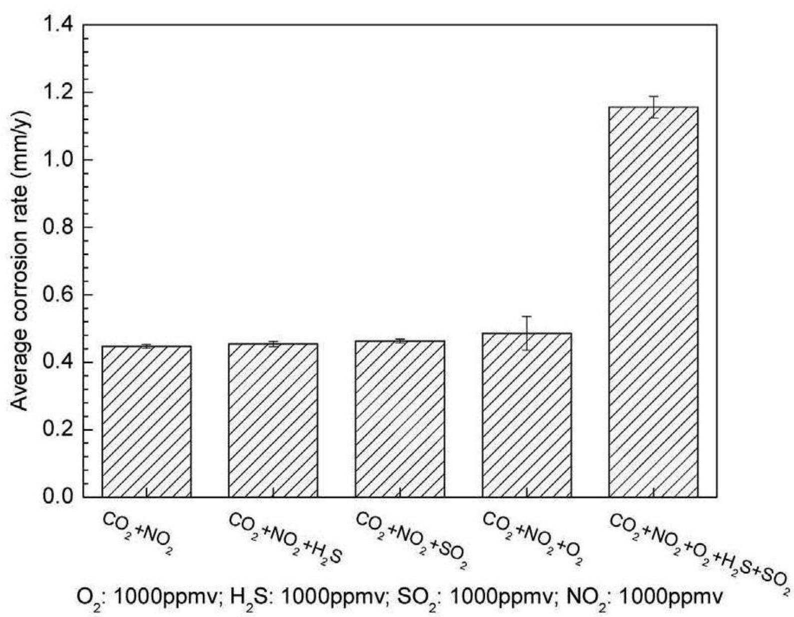

Figure 7. Corrosion rates of X65 in water saturated SC-CO_2 containing impurities at 1450 psi and 122 °F

They also observed a variety of corrosion products formed depending on these combinations of impurities. For example, for the combination of $CO_2 + NO_2 + O_2 + H_2S + SO_2$, the corrosion product was composed of $FeSO_4{\cdot}4H2O$, S, $FeCO_3$, and FeS. Therefore, it is apparent that no generalization can be made on what corrosion product will form in a specific environment because of the wide variety of possible impurities, and no reliable prediction of the protective qualities of these products can be proposed.

Of specific interest to this guideline is the case of SC-CO_2 with H_2S present. Li et al. [31] found that an FeS scale predominated with as little as 50 ppm H_2S present, but increasing the temperature to 200 °C and/or including O_2 greatly increased the corrosion rate. Moreover, contrary to the work presented by Paul [14], they did not find SSC at 100 ppm H_2S in their tests. However, they did not closely examine the stressed surfaces like Paul did, so trenching cannot be ruled out in their work. Choi [11] observed that for pure CO_2 conditions the corrosion product was $FeCO_3$, but the inclusion of 200 ppm H_2S caused the corrosion product to be predominantly FeS.

2.10 Other Factors to Consider

2.10.1 Metallurgy of the Pipe and Welding

The metallurgy of steel pipelines is an entire subject of its own; however, for SC-CO_2 pipelines it is common practice to specify a relatively high strength grade (i.e., X70 and X80) in order to reduce the total cost of steel and allow for high transport pressures. As stated before, in the absence of a liquid water phase there is no measurable corrosion, and this is true regardless of the steel metallurgy. However, if water is present, a large body of research has shown that steel microstructure can have a significant effect on the corrosion from CO_2. Carbon steels with banded ferritic/pearlitic microstructures have poor corrosion resistance compared to steels with fine-grained, unbanded, tempered martensite microstructures [32]. High strength pipeline steels are produced with low carbon content for good weldability and fracture toughness through various processes such as thermomechanical treatments (TMCP) which develop a fine ferritic microstructure with essentially no pearlite. While such processing does not make the steel resistant to CO_2 corrosion, TMCP pipe should exhibit relatively reduced corrosion rates compared to lower strength linepipe steels that are banded ferrite/pearlite.

By and large, no studies have been performed on the resistance of various welding processes to corrosion in SC-CO_2. Likewise, no studies on the best filler metals from a corrosion standpoint have been performed.

2.10.2 Hydrotesting of Pipelines and Water Removal

As stated in DNV-RP-J202 [33]:

> *Special attention should be given to dewatering of pipeline system prior to filling with CO_2. The high solubility of water in dense phase CO_2 may be beneficial as to ease the requirement to drying compared to gaseous state. It should, however, be noted that in the initial stage of the first-fill, the CO_2 will be in gaseous phase.*

It is generally felt in the industry that small amounts of water remaining in the pipeline will be reabsorbed into the CO_2 due to its high solubility; however, as stated above, care should be taken if large amounts of water remain since gaseous CO_2 and water can be very corrosive.

Some operators use a combination of dry air and pigs followed by filling with dry CO_2, while others use drying and initial filling with nitrogen at a dew point of -29 °F (-34 °C). Subsequently, the nitrogen is exchanged with dry CO_2 during the filling of the pipeline.

Pipelines should be fitted with pig launchers and receivers to allow for debris removal and any standing water. Such facilities will also aid in-line inspection efforts.

2.10.3 Frequency and Duration of Upsets

The frequency and duration of upsets leading to a separate liquid water phase dropping out can be a corrosion concern if SC-CO_2 and water remain in the pipeline for a considerable length of time. However, this concern is typically overridden by the larger risk of hydrates that can block and interrupt the immediate startup of a pipeline. This can be a much more significant issue than corrosion, but the risk of corrosion during such downtimes should not be ignored.

2.11 The Need for Subject Matter Experts (SMEs)

As can be appreciated from the above discussion, this area is very complicated and warrants the assistance of an SME in several disciplines to assist in navigating all of the many issues.

3. General Considerations for Repurposing Existing Pipelines for SC-CO_2 Service

The considerations discussed in this section apply for both repurposing a sweet pipeline to carry SC-CO_2 containing H_2S and repurposing a sour pipeline to carry SC-CO_2 without H_2S.

3.1 Original Design Conditions and Actual Operating History

Information should be gathered regarding not only the original design conditions but, more importantly, the actual operating conditions such as MAOP, temperature, water content, frequency of pigging, etc. Most importantly, it should be determined whether the preexisting pipeline was designed for SC-CO_2 conditions or not. If the pipeline was originally designed for SC-CO_2, then design details such as minimum fracture toughness to resist a running ductile fracture and the modeling to support this should be confirmed for the new operation since differences in the source CO_2 impurity content can significantly affect the phase behavior and thus the necessary minimum fracture toughness. If the pipeline was not designed for SC-CO_2 transport, it may not be suitable for this application since acceptable fracture toughness may not be achievable even if crack arrestors are added. This can only be determined by modeling the required fracture toughness to arrest a running ductile fracture using methods such as the Battelle Two Curve Method (BTCM) [34]. In general, most oil and gas pipelines, including transmission pipelines, are only designed to the API Specification 5L minimum Charpy impact toughness; therefore, they are completely inadequate for the significantly higher fracture toughness required for arresting a running ductile fracture. If crack arrestors are considered for installation on existing pipelines, it should be pointed out that currently there are no standards from which crack arrestor designs can be made. Furthermore, it will be necessary to perform a risk analysis to consider the proximity of populated areas as well as other risks such as road crossings. It is highly advisable that an SME be contracted for this work.

3.2 Materials of Construction

The first step to consider for an existing pipeline is to gather all available data regarding the following:

- Grade and method of manufacturing/processing of the linepipe (i.e., X65 ERW, etc.). PSL Level 1 or 2, heat treatment condition such as normalized, as-rolled, TMCP, quenched and tempered, etc.
- The same as above for fittings generally ordered to ASTM standards, valves, and other in-line components.
- Welding procedures for installing the pipeline including procedure qualification records and whether the procedures were in accordance with API 1104 or ASME Section IX.

One of the most common problems for converting pipelines from one service to another, i.e., gas to oil, is incomplete records. This is a frequent problem in hydrocarbon transport and is expected to be more so for conversion to SC-CO_2 service. Many times, existing pipelines have been passed through many operators and owners with no or incomplete transfer of the original design and construction information. This could be a major problem for conversion to SC-CO_2 service for many reasons: steel pipe for pipelines are often made from numerous heats of steel that have variable mechanical properties, multiple welding procedures may be welded together with various filler metals, wall thicknesses may vary across sections that have been replaced over time, etc.

In the United States, federal regulations for converting pipelines to CO_2 service have not been clearly established. Per the Council on Environmental Quality (CEQ) Report to Congress on Carbon Capture, Utilization, and Sequestration submitted June 2021:

> *While USDOT is responsible for the regulation and oversight of safety for liquid CO_2 pipelines, and PHMSA has conducted research and analysis regarding the applicability of existing regulations to gaseous CO_2 pipelines, the agency has not conducted an analysis on the identification or prioritization of existing pipelines for expanded CCUS…*

Regulatory frameworks for CCS/CCUS are often established by states within their boundaries, and the requirements may vary from state to state. Generally, SC-CO_2 transmission is regulated under CFR Part 195, "Transportation of Hazardous Liquids by Pipeline", in which carbon dioxide is defined as, "a fluid consisting of more than 90 percent carbon dioxide molecules compressed to a supercritical state." Under this part, conversion to service is covered in §195.5, but the guidance in this section is not specific to SC-CO_2 and associated material concerns.

Nonetheless, there is relevant regulatory guidance for pipeline service conversion, generally. As detailed in PHMSA Advisory Bulletin ADB-2014-04, "Guidance for Pipeline Flow Reversals, Product Changes and Conversion to Service," PHMSA advises caution converting existing pipelines under the following conditions:

- Grandfathered pipelines that operate without a Part 192, Subpart J pressure test or where sufficient historical test or material strength records are not available.
- LF-ERW pipe, lap welded, unknown seam types and with seam factors less than 1.0 as defined in §§ 192.113 and 195.106.
- Pipelines that have had a history of failures and leaks most especially those due to stress corrosion cracking, internal/external corrosion, selective seam corrosion or manufacturing defects.
- Pipelines that operate above Part 192 design factors (above 72% SMYS).
- Product change from unrefined products to highly volatile liquids

The practical application of this guidance to repurposing pipelines for SC-CO_2 is that modern pipelines with good service history, integrity programs, and well-documented properties are the best candidates for conversion.

Some operators elect to employ nondestructive pipe grading techniques in order to determine unknown pipe properties without destructive testing. These methods include hardness testing, instrumented indentation, and scratch testing. All three techniques can fairly determine tensile strength, and instrumented indentation and scratch testing are reasonably good at approximating yield strength. However, because only the surface of the pipe material is tested, resulting tensile properties may vary from API Specification 5L tensile tests.

The major shortcoming of nondestructive pipe grading is the inability to reliably determine fracture toughness. While vendors of these services often claim that fracture toughness can be estimated from the test data, this has not gained wide industry acceptance. Even if pipe body fracture toughness could be believed, these grading techniques have no way of estimating the fracture toughness of the long seam. Destructive testing is still the best method for establishing unknown pipe properties. Because the pipe properties, specifically the fracture toughness, are so critical to SC-CO_2 pipeline design, destructive testing is worth considering for property verification even in cases where the existing pipe properties are documented. In most cases, destructive testing is the only way to determine fracture toughness, as correlations from Charpy impact properties are only approximate.

3.3 Current Pipeline Condition

Pipelines may have accumulated wall loss and pitting corrosion damage over the course of their lives. Mechanical features such as dents and gouges may exist as well, which would put a SC-CO_2 pipeline at risk. Inspection is critical in order to identify and characterize such damage in order to assess whether the pipelines can be salvaged for conversion.

The long length of transmission pipelines, often traversing many miles, typically precludes the use of manual nondestructive examination (NDE) methods. The most efficient and most effective methods of pipeline inspection by far are in-line inspection (ILI) tools, commonly referred to as pigs. There are a large array of pigs available to operators, broadly categorized as "smart" pigs and "dumb" pigs. Any ILI typically requires that a cleaning tool (dumb pig) be initially run to clear away debris for the ILI tool (smart pig).

Pigs may utilize calipers, magnetic flux leakage (MFL), ultrasonics, other advanced inspection technology, or some combination of these. A review of in-line inspection technologies is an entire subject of its own and is outside the scope of this guideline. This guideline recommends that a suitable combination of techniques be used to adequately capture existing pipeline damage, both internal and external.

To ensure the integrity of external surfaces is maintained, the cathodic protection system for buried pipelines should be surveyed to verify that it is adequately protecting the pipeline. Repairs should be made immediately to prevent or limit damage, as external corrosion can occur whether or not the pipeline is in service. It is also important to perform a geological survey to assess earth movement, particularly in steep terrain. Earth movement poses a threat to the integrity of all pipelines, but at least one high profile failure of a SC-CO_2 pipeline has occurred due to the geological conditions.

4. Existing Pipelines Repurposed for Transport of SC-CO_2 Containing H_2S

The considerations discussed in this section apply when repurposing a sweet pipeline to carry SC-CO_2 containing H_2S. These considerations are in addition to those discussed above in Section 3.

4.1 Materials of Construction

First and foremost, the introduction of H_2S into an existing pipeline system requires considering the potential for SSC and HIC. If the pipeline is constructed from seamless pipe, the risk of HIC is likely low. If the pipeline is constructed from seam-welded pipe, then both possibilities must be considered. These issues are addressed in more detail in Section 4.3.

The compatibility of non-metallic components such as seals, gaskets, etc. with CO_2 containing H_2S as an impurity must also be considered. The non-metallic components used for typical hydrocarbon pipelines are not necessarily resistant to SC-CO_2 with H_2S and thus may require replacement before exposure to H_2S-bearing SC-CO_2 streams.

4.2 Composition of Transported Fluids

If the only components in the fluids being transported are CO_2, H_2S, and water, which may or may not condense to a separate water phase, the potential corrosion problems are reasonably well understood, as discussed below in Section 4.3. However, if there are other impurities such as SO_2, NO_2, and O_2, then additional corrosion concerns may also be present. These are discussed below as well. Because the presence of even small amount of impurities can substantially affect pipeline corrosion, it is of utmost importance that a complete analysis of the fluids being transported, including possible upsets, be undertaken in order to anticipate the potential corrosion issues that may arise.

4.3 Potential Corrosion Problems (Wall loss, pitting, SSC, HIC)

In the case of H_2S alone as the only impurity in the SC-CO_2 stream, there are potentially any number of corrosion/cracking mechanisms that can be operative depending on the pH_2S (fH_2S). As discussed in Section 2.9, even small amounts of H_2S in the CO_2 stream can produce an FeS corrosion product on the surface of the steel. There are numerous variables that determine whether this corrosion product will be protective or not such as temperature, fH_2S, water chemistry, etc. and therefore cannot be generalized herein. Suffice it to say that a non-protective FeS scale can lead to localized pitting which can be difficult to detect. Also, depending on the fH_2S, the water chemistry, the grade of pipe (i.e., yield strength), and whether it is long seam welded or not, the risk of SSC and HIC may be present.

As mentioned earlier in this guideline, the conversion of a non-sour pipeline to one which will transport fluids containing H_2S should at a minimum conform to the requirements of NACE MR0175/ISO 15156. This would require resistance to both SSC and HIC. While it was shown earlier for SC-CO_2 that the correct factor for describing the severity of H_2S is fH_2S, as a first preliminary evaluation of any existing pipeline, the conservative analysis would be to simply consider the pH_2S and determine whether the amount of H_2S reaches or exceeds the 0.05 psia threshold. If it does, then a more comprehensive analysis may be required, which is best handled by an SME.

If other impurities such as SO_2, NO_2, and O_2 may be present in combination with H_2S, then the risk of pitting, SSC, and HIC could be higher. For example, as stated in this guideline, the presence of SO_2 and NO_2 separately can reduce the pH of a free water phase and lead to very high corrosion rates, as shown in the work by Ayello et al. [7]. However, when they are present together, the corrosivity has been demonstrated by Dugstad et al. to be minimal [35]. The inclusion of O_2 to this mix can dramatically increase the corrosion rate, as was shown in Figure 7 [30]. Due to the complexity of these various interactions between impurities, there are currently no means to predict whether corrosion will take the form of uniform wall thinning, pitting, or some form of environmental cracking. It would be advisable to perform corrosion tests under simulated pipeline conditions in order to better understand what types of corrosion attack may be anticipated.

4.4 Effect of Internal Surface Products

It is impossible to address all of the possible surface deposits such as mill scale and corrosion products that might be present along the internal surfaces of existing pipelines. In the case of the former, the mill scale is generally a combination of iron oxides such as FeO, Fe_3O_4, and Fe_2O_3. Since these are not typically removed from the internal surfaces of pipelines during construction, and there are not typically any significant issues with their presence in pipeline service, these compounds will not be discussed further in this guideline. As regards corrosion products, this becomes more difficult since the corrosion products that may form are a direct result of steel corrosion in the presence of whatever fluid is being transported. In many cases, these products will be iron carbonate ($FeCO_3$) from CO_2-containing streams and/or iron sulfides (FeS) when H_2S is present. However, unlike the single corrosion product from CO_2, there are a whole host of possible iron sulfides that may form which can be protective or not. These are addressed in more detail in Section 5.3. Based on the differentiation addressed in this report between repurposing existing pipelines to carry SC-CO_2 with H_2S and those which have already been exposed to H_2S, it is assumed that the preexisting pipelines in this section have not been exposed to H_2S in the fluid being transported. As such, FeS is not expected to be present, and any preexisting corrosion products should not be an issue for conversion to SC-CO_2 service.

Prior to transitioning a pipeline to SC-CO_2 service, it is advisable to run inline inspection to define the status of the pipeline with respect to existing corrosion damage, pits, and cracks. The impact of these findings and the decision whether the pipeline is suitable for SC-CO_2 service is beyond the scope of this guideline.

A summary guideline for the repurposing of a pipeline to carry SC-CO_2 containing H_2S is provided in Appendix A.

5. Existing H_2S-Containing Pipelines Repurposed for Transport of SC-CO_2 without H_2S

The considerations discussed in this section apply when repurposing a sour pipeline to carry SC-CO_2 without H_2S. These considerations are in addition to those discussed above in Section 3.

5.1 Materials of Construction

It is assumed for this guideline that a candidate preexisting pipeline that has been exposed to H_2S was designed, constructed, and operated in compliance with NACE MR0175/ISO 15156 in order to minimize the risk of SSC and HIC. This would mean the highest strength pipe would be Grade X65 or possibly in some cases Grade X70. Construction and purchase records confirming the specified minimum yield strength, tensile strength, and hardness should be reviewed to ensure such is the case. These records would also include mill test reports (MTRs) that also include the actual Charpy toughness of the steel.

The compatibility of non-metallic components such as seals, gaskets, etc. with CO_2 must also be considered. The non-metallic components used for sour service equipment are not necessarily resistant to SC-CO_2 and thus may require replacement before exposure to SC-CO_2.

5.2 Composition of Transported Fluids

Existing pipelines, particularly older lines, may have transported different fluids at different times in the pipeline's life. The historical record of fluids that have been transported should be reviewed to better understand the current state of the internal surfaces of the pipe that will be exposed to SC-CO_2. However, of more concern is the composition of the SC-CO_2 to be transported in a previously sour pipeline. As discussed below, it can be expected that the internal surfaces of the pipe will be covered with iron sulfides of some type. Subsequent exposure to various impurities contained in the SC-CO_2 stream may cause a variety of issues depending on the specific impurities. These issues are discussed in further detail in Section 5.3.

5.3 Effect of Internal Surface Products

For an existing sour pipeline, the actual composition of the resulting surface corrosion product depends on the transported fluid composition: oil, gas, CO_2 concentration, partial pressure of H_2S, temperature, water chemistry, etc. For many hydrocarbon pipelines, the corrosion product will be $Fe_{1+x}S$ (commonly written FeS) and more specifically Mackinawite, as shown in Figure 8 [36].

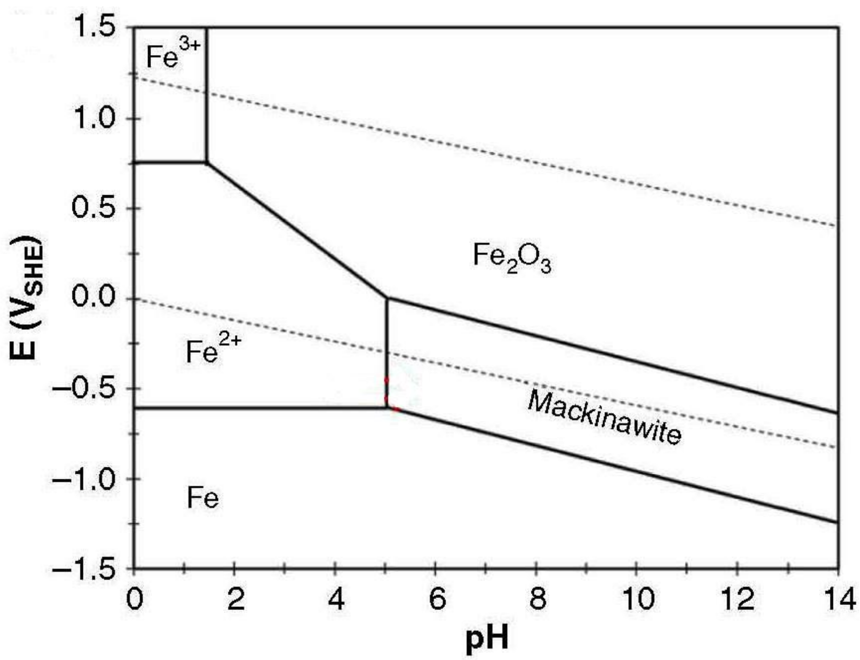

Figure 8. EH-pH diagram for the Fe-H_2S-H20 system at 80 °C

Although this diagram is for a temperature of 80 °C, the boundaries do not significantly change with decreasing temperature down to 25 °C, and thus it would cover most pipelines including SC-CO_2 pipelines. In some cases where the H_2S concentrations/partial pressures are high, the predominate product will be Pyrrhotite. This latter phase is much more stable than is Mackinawite. As should be noted, the FeS scale is soluble when the pH decreases to less than about 5. Therefore, the introduction of SC-CO_2 with a separate water phase would result in a pH around 3 and cause the FeS scale to dissolve. This can create a serious localized problem, as when FeS dissolves in low pH fluids, it will produce H_2S at very low pH, creating a severe sour environment worse than during the original sour fluids exposure. This sudden release of H_2S at pH 3 has the potential to crack even SSC resistant steels. This phenomenon has been observed on a regular basis when downhole tubulars scaled with FeS are acidized with HCl, resulting in cracking.

It may be expected that the possible reactions when SC-CO_2 with various impurities is introduced into an existing sour pipeline are numerous. Of special concern would be the introduction of SC-CO_2 containing O_2. As Craig has shown [37], mackinawite is especially unstable when exposed to air and will oxidize according to:

$$2Fe_9S_8 + 9H_2O + 27/2\ O_2 \rightarrow 18\ \gamma\text{- }FeO(OH) + 2S_8$$

The γ-FeO(OH) is unstable and will quickly transform to magnetite by either of the following reactions:

$$3\ \gamma\text{-}FeO(OH) + e \rightarrow Fe_3O_4 + H_2O + OH^-$$

$$Fe^{+2} + 8\ \gamma\text{-}FeO(OH) + 2e \rightarrow 3Fe_3O_4 + 4H_2O$$

However, the elemental sulfur generated, S_8, can induce severe pitting and cause the corrosion rate to escalate to very high values. Therefore, it is imperative that the introduction of SC-CO_2 into a preexisting sour pipeline not contain any measurable O_2.

As a result of the many unknowns discussed above regarding how the FeS scale will interact with the introduction of a SC-CO_2 stream, it is highly recommended that laboratory testing of FeS scaled pipe be performed using simulated SC-CO_2/H2O conditions to better define the possible results of this planned conversion. This will require the assistance of an SME knowledgeable in the creation of a testing program that will generate the results needed to make an informed decision about using an existing sour pipeline for SC-CO_2 service.

It is worth emphasizing that prior to transitioning a pipeline to SC-CO_2 service, it is advisable to run in-line inspection (i.e., smart pigs) to define the status of the pipeline as regards existing corrosion damage, pits, and cracks. The impact of these findings and the decision whether the pipeline is suitable for SC-CO_2 service is beyond the scope of this guideline

A summary guideline for the repurposing of a sour pipeline to carry SC-CO_2 is provided in Appendix B.

6. Corrosion Mitigation Options

In recent years, efforts have been made to develop corrosion inhibitors to deal with free water in contact with SC-CO_2. At present, these inhibitors are not effective nor reliable over the life of a SC-CO_2 pipeline. The most effective method of corrosion mitigation is sufficient dehydration such that liquid water does not drop out of the supercritical fluid. In both the case of a sweet pipeline being converted to SC-CO_2 with H_2S and a sour pipeline being converted to SC-CO_2 without H_2S, the absence of a water phase will prevent corrosion.

Because of the additional risk of converting a sour pipeline imposed by possible FeS dissolution in low pH water, some operators may be motivated to mitigate this risk through aggressive cleaning of the pipeline internal surface to remove FeS scales. Mechanical removal, such as by heavy duty brush pigs, may not be fully effective since FeS scales can be tenacious. However, partial removal of FeS may still reduce associated risk. Several chemical cleaning solutions have been proposed to dissolve and remove FeS, but such treatments need to be employed carefully to avoid damaging the pipeline and associated equipment, and the chemicals will need to be completely cleared from the pipeline before returning it to service. Evaluation of these cleaning methods is outside the scope of this guideline, but if FeS removal can be performed effectively, it may help reduce the risk of H_2S formation when low pH water is present.

7. Subject Matter Expert (SME) Review

The information detailed in this document provides pipeline repurposing guidance for operators and end users to consider in the design of CCS and CCUS systems. This guideline alone is not a substitute for review by a subject matter expert (SME).

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Appendix A: Guideline Summary for Pipelines Repurposed for Transport of SC-CO_2 Containing H_2S

Guideline Summary for Pipelines Repurposed for Transport of SC-CO_2 Containing H_2S

1. Review all available data from the subject pipeline, including:
    a. Original design basis
    b. Actual operating conditions (MAOP, temperature, water content, etc.)
    c. Integrity (pigging frequency, cathodic protection survey, etc.)
    d. Pipe material properties for each heat of pipe installed
2. If material property records are incomplete, perform destructive testing on representative pipe in order to establish properties for SC-CO_2 design.
3. Confirm that the existing pipeline and ancillary components were all specified and constructed in accordance with NACE MR0175/ISO 15156 or would otherwise meet the requirements of this standard.
4. Perform BTCM analysis to confirm adequate fracture toughness to resist running ductile fractures. If insufficient, then contract an SME to assist with other options such as crack arrestors to limit fracture propagation.
5. Perform laboratory tests with H_2S and all other impurities to determine if SSC and HIC could be an issue.
6. Run scraper/brush pigs to remove as much of any corrosion product layer as possible.
7. Run ILI to determine the status of the pipe including any existing cracks and pits.
8. Review inspection results and conduct risk assessments to determine whether conversion to SC-CO_2 service is advisable. Consult relevant SMEs, as needed.

Appendix B: Guideline Summary for Existing Sour Pipeline for Transport of SC-CO_2 without H_2S

Guideline Summary for Existing Sour Pipeline for Transport of SC-CO_2 without H_2S

1. Review all available data from the subject pipeline, including:
    a. Original design basis
    b. Actual operating conditions (MAOP, temperature, water content, etc.)
    c. Integrity (pigging frequency, cathodic protection survey, etc.)
    d. Pipe material properties for each heat of pipe installed
2. If material property records are incomplete, perform destructive testing on representative pipe in order to establish properties for SC-CO_2 design.
3. Confirm that the existing sour pipeline and ancillary components were all specified and constructed in accordance with NACE MR0175/ISO 15156.
4. Perform BTCM analysis to confirm adequate fracture toughness to resist running ductile fractures. If insufficient, then contract an SME to assist with other options such as crack arrestors to limit fracture propagation.
5. Perform laboratory tests with a pre-scaled FeS pipe under simulated SC-CO_2 conditions to ascertain if the interaction will exacerbate corrosion and if SSC and HIC could be an issue.
6. Run scraper/brush pigs to remove as much of the FeS layer as possible.
7. Run ILI to determine the status of the pipe including any existing cracks and pits.
8. Review inspection results and conduct risk assessments to determine whether conversion to SC-CO_2 service is advisable. Consult relevant SMEs, as needed.