Plains CO_2 Reduction (PCOR) Partnership
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THE ROLE OF HYDROGEN SULFIDE (H_2S) IN REPURPOSING CARBON STEEL PIPELINES FOR CARBON DIOXIDE (CO_2) TRANSMISSION

White Paper

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Plains CO_2 Reduction (PCOR) Partnership

Energy & Environmental Research Center (EERC)

THE ROLE OF HYDROGEN SULFIDE (H_2S) IN REPURPOSING CARBON STEEL PIPELINES FOR CARBON DIOXIDE (CO_2) TRANSMISSION

EXECUTIVE SUMMARY

The need for reliable transmission of carbon dioxide (CO_2) streams from various sources for carbon capture and storage (CCS) and carbon capture, utilization, and storage (CCUS) projects is growing rapidly. Repurposing existing pipelines is an attractive option in many cases over the construction of a new pipeline. However, the transmission of scCO_2 requires special design considerations rarely included in the original pipeline design. Moreover, internal scales from previous hydrogen sulfide (H_2S) exposure can interact with certain CO_2 streams to create corrosive conditions. This paper explores considerations for two scenarios: a pipeline that had not previously been exposed to H_2S repurposed for a stream of CO_2 now containing H_2S and a pipeline that had been previously exposed to H_2S repurposed for use with a clean CO_2 stream without H_2S. A more detailed and complete review is provided in the PCOR (Plains CO_2 Reduction) Partnership's "Guideline for Repurposing Existing Carbon Steel Pipelines for CCS and CCUS Projects," Stress Engineering Services, Inc., Document 1256154-MT-RP-02_Rev0, Final Report: December_2022, Rowe and Craig.

THE ROLE OF HYDROGEN SULFIDE (H_2S) IN REPURPOSING CARBON STEEL PIPELINES FOR CARBON DIOXIDE (CO_2) TRANSMISSION

INTRODUCTION

Carbon capture and storage (CCS) and carbon capture, utilization, and storage (CCUS) projects continue to develop as effective initiatives to reduce anthropogenic carbon dioxide (CO_2) emissions. As capture facilities continue to grow and expand, the need for reliable transmission of CO_2 from capture sources to injection wells is expected to increase rapidly. A 2021 Princeton University study estimated that up to 25,000 km of interstate CO_2 trunk pipelines and 85,000 km of spur pipelines would be needed by 2050 to achieve net-zero emission goals (1).

Historically, where possible, repurposing existing underutilized pipelines has been found to be an attractive option over construction of a new pipeline. The oil and gas industry has done this with good success over many decades, converting gas lines to oil lines and vice versa. One of the most common problems for converting pipelines from one service to another is incomplete records. This is a frequent problem in hydrocarbon transport and is expected to be more so for conversion to $scCO_2$ service where fracture toughness is critical to the design.

The change from one product to another, as will more often than not be the case for repurposed CO_2 pipelines, presents additional challenges. Surface deposits and scales left by the previous process may interact with the new process, and it is of critical importance to evaluate the possible reactions and account for them as part of the conversion process.

This paper discusses considerations for two pipeline conversion scenarios: a pipeline not previously exposed to H_2S (sweet) being considered for a stream of CO_2 now containing H_2S and a pipeline previously exposed to H_2S (sour) being considered for use with a clean CO_2 stream without H_2S as an impurity.

This work was completed by Stress Engineering Services, Inc., and the Energy & Environmental Research Center (EERC) through the Plains CO_2 Reduction (PCOR) Partnership. The PCOR Partnership, funded by the U.S. Department of Energy's (DOE) National Energy Technology Laboratory (NETL), the North Dakota Industrial Commission's Oil and Gas Research Program and Lignite Research Program, along with more than 250 public and private partners, is accelerating the deployment of CCUS technology. The PCOR Partnership is focused on a region comprising ten U.S. states and four Canadian provinces in the upper Great Plains and northwestern regions of North America. It is led by the University of North Dakota (UND) Energy & Environmental Research Center (EERC), with support from the University of Wyoming and the University of Alaska Fairbanks.

GENERAL CONSIDERATION FOR REPURPOSING PIPELINES FOR CO_2 TRANSPORT

CO_2 pipeline design is an entire subject in itself. Since the purpose of this paper is to discuss implications related to H_2S, this section will only briefly touch on certain general considerations that apply for both repurposing a "sweet" pipeline to carry $scCO_2$ containing H_2S and repurposing a "sour" pipeline to carry $scCO_2$ without H_2S. While there is currently considerable discussion and work on standards and best practices for repurposing hydrocarbon pipelines for transport of $scCO_2$, many of these efforts are entirely focused on pressures, temperatures, and hydraulics with relatively little mention of potential corrosion and materials issues. Note: $scCO_2$ is defined as dense-phase CO_2 with viscosity similar to gas and a density of a liquid.

In general, modern pipelines with good service history, integrity programs, and well-documented properties are the best candidates for conversion. Pipelines that have had a history of integrity problems (cracking, corrosion, seam failures, manufacturing defects) or pipelines that have historically operated above their maximum allowable operating pressure (MAOP) may be at particular risk if repurposed.

The design review, materials review, and integrity review considerations briefly discussed here are each themselves entire complex topics. Specifically, determining minimum fracture toughness to resist a running ductile fracture is the most significant qualifying determinant for pipeline repurposing. Therefore, it is highly advisable that subject matter experts (SMEs) with relevant experience in their specific areas be contacted for this work.

Pipeline History

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, if available, to better understand the current state of the internal surfaces of the pipe that will be exposed to $scCO_2$. Information should be gathered regarding not only the original design conditions but 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 $scCO_2$ conditions or not. If the pipeline was originally designed for $scCO_2$, 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 $scCO_2$ transport, as will be the case with most oil and gas pipelines, it may be difficult to qualify the pipe 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) (2). Current American Petroleum Institute (API) Specification 5L requirements for petroleum pipelines only require minimum Charpy (metallurgical material properties testing) toughness values which are not typically sufficient to meet the much higher values required for running ductile fracture arrest in $scCO_2$ pipelines. If crack arrestors (short heavy-wall pipe segments) 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. It will also be necessary to perform a risk analysis to consider the proximity of populated areas as well as other risks such as road crossings, to determine application.

Any review of the materials of construction should include all available data regarding the pipe and fitting materials and associated welding procedures. This includes any replacements or repairs made over the life of the pipeline. For scCO_2 pipelines, it is common practice to specify a relatively high-strength grade (i.e., X70 and X80 grade) in order to reduce the total cost of steel and allow for high transport pressures, but certain projects may be limited by the properties of pipelines available for repurposing. The grade of pipe and, more importantly, the microstructure will need to be carefully reviewed since the steel microstructure can have a significant effect on the corrosion from CO_2 when water is present.

As noted in the introduction, incomplete records are expected to be a sizable challenge for repurposing pipelines for scCO_2 service. 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 by nondestructive examination (NDE) methods, 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 NDE services often claim that fracture toughness can be estimated from the test data, this has not gained wide industry acceptance. Destructive testing is still the best method for establishing unknown pipe properties. Because the pipe properties, specifically the fracture toughness, are so critical to scCO_2 pipeline design, destructive testing is worth considering for property verification even in cases where the existing pipe properties are documented.

The compatibility of nonmetallic components, such as seals, gaskets, etc., with scCO_2 streams are outside of the scope of this paper, but it should be noted that seals used for typical hydrocarbon pipelines are not necessarily resistant to scCO_2 and associated impurities and thus may require replacement.

Pipeline Integrity

Prior to transitioning a pipeline to scCO_2 service, it is advisable to run inline inspection to define the status of the pipeline. Pipelines may have accumulated wall loss and pitting corrosion damage over the course of their lives, which can compromise the performance in new service. Mechanical features such as dents and gouges may exist as well, which could put an scCO_2 pipeline at risk. Inspection is critical in order to identify and characterize such damage and 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 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. A large array of pigs are 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). Smart pigs may utilize calipers, magnetic flux leakage (MFL), ultrasonics, other advanced inspection technology, or some combination of these. A suitable combination of techniques should 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. Necessary 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.

New scCO_2 Stream Composition

The stream composition can be defined largely by water content and stream impurities. The effect of the composition on pipeline performance will depend on temperature and pressure.

In recent years, considerable effort has been made to study the role of water content in scCO_2 streams from a corrosion standpoint. Unlike the typical water limits for natural gas pipelines of about 7 lb/MMscf, or 650 ppm (the standard limit for Kinder Morgan natural gas pipelines as example), the solubility of water in scCO_2 is a strong function of temperature, pressure, and impurities. As shown by deVisser and others, water solubility significantly increases when CO_2 goes through a phase change from gas to liquid with increasing temperature and pressure (3). Typical scCO_2 pipeline specifications for water range from 50 to 650 ppm.

In the absence of free water, when water remains completely soluble in the scCO_2 stream and not at risk of breaking out, the fluid will not be corrosive. As proof of this, enhanced oil recovery (EOR) projects have been in operation for at least 40 years utilizing carbon steel pipelines for transport of scCO_2 with essentially no reported problems. It is only when liquid water is present that carbon steel pipelines will corrode, but the severity of corrosion in scCO_2 streams can be severe. Some research has shown that even water mist is sufficient to cause minor corrosion and pitting in scCO_2 streams (4). Water dropping out of the scCO_2 phase will have no buffering of pH, so the resulting pH of such water will be very low. Numerous studies and modeling analyses have shown that the pH will be on the order of 3 (5). Note that pH less than 7 is acidic, corrosive.

A number of compositions of CO_2 streams are slated for current and future CCS and CCUS projects. 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 $CO_2 \geq 95\%$ with no free water present. These examples are not exhaustive and are presented solely for comparison. Some streams may vary substantially from those listed, so only generalizations can be made in this section of the report regarding how detrimental each species may be for a given pipeline.

Table 1. Examples of 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
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

The presence of impurities such as oxygen (O_2), hydrogen sulfide (H_2S), sulfur dioxide (SO_x), and nitrous oxide (NO_x) can further exacerbate corrosion. Because the presence of even a 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.

It is the focus of this paper how H_2S specifically can impact the performance of repurposed CO_2 pipelines, either due to previous exposure or as a contaminant in future CO_2 streams. O_2, SO_x, and NO_x are briefly discussed here for completeness, and H_2S is discussed in further detail below.

SO_2 and NO_2 impurities in the CO_2 cause the pH of a liquid water phase to decrease. Ayello and others found that adding as little as 100 ppm SO_2 to scCO_2 at 1099 psi and 104°F reduced the pH down to approximately 2.5 (6). Pipeline steels will be at greater risk of accelerated corrosion and possibly environmental cracking in lower pH waters resulting from SO_x and NO_x impurities, but the effect is complicated by synergistic interactions.

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 and others (6). However, when they are present together, the corrosivity has been demonstrated by Dugstad and others to be minimal (7). The inclusion of O_2 to this mix can dramatically increase the corrosion rate, as shown by Sun and others (8). The limited work on the role of O_2 is somewhat contradictory. For example, Choi (9) reported an increase in corrosion rate when O_2 was present at 50°C; however, Hua (10) 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 (11). More work is needed to better characterize the effect of these contaminants in scCO_2 on the corrosion of pipelines steels.

SWEET PIPELINES REPURPOSED FOR TRANSPORT OF scCO_2 CONTAINING H_2S

In addition to the general considerations discussed above, certain issues need to be specifically reviewed and accounted for when repurposing a sweet pipeline, a pipeline that had not previously been exposed to H_2S repurposed for a stream of scCO_2 containing H_2S.

Materials of Construction

One 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). Note: NACE, National Association of Corrosion Engineers, was established for corrosion control and prevention standards, and ISO, International Organization for Standardization, is an independent nongovernmental affiliated standard setting entity. The conversion of a nonsour pipeline to one that will transport fluids containing H_2S should at a minimum conform to the requirements of NACE MR0175/ISO 15156. However, this standard is specifically related to the potential for SSC and HIC in upstream petroleum production; it does not address the risk in scCO_2 systems. Craig (13) published a short note raising the issue of whether this standard is applicable to scCO_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). He 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, he 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 scCO_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 scCO_2 systems, but since most pipelines that transport scCO_2 are relatively large diameter, they are typically manufactured with welded longitudinal seams. Modern transmission line pipe is often seam-welded by high-frequency electric welding (HFW), but thick wall pipe may use submerged arc welding (SAW), and older pipe may have been made using low-frequency electric resistance welding (LF-ERW) or other obsolete long seam techniques. Welded steel pipe is known to be more susceptible to HIC than seamless pipe; therefore, the materials of construction should be assessed with this risk in mind for scCO_2 pipelines.

H_2S Concentration

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. However, if there are other impurities such as SO_2, NO_2, and O_2, then additional corrosion concerns may also be present. Pipelines repurposed for scCO_2 need to consider not just the presence or absence of H_2S, but the concentration as well. As shown in Table 1, the range of H_2S that may be present in a stream depends on the source. Peletiri compiled H_2S contents across several streams and showed a wide range of typical H_2S concentrations from less than 0.002% up to 1.5% (15).

A comparatively large number of studies have been performed considering the effect of H_2S on corrosion of steels in $scCO_2$. 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 and others (16) found almost no effect of H_2S contents ranging from 5 to 200 ppm on corrosion from $scCO_2$; however, these authors did not present a base case corrosion rate in the absence of H_2S. Sui and others (17) found that for 1000 ppm H_2S at various temperatures, the corrosion rate depended on the temperature and pressure.

Zhang and others evaluated carbon steel in $scCO_2$ at 1956 psi and 176°F for 96 hours (9). Table 2 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 2. X65 Corrosion Rates vs. H_2S Content

H_2S Concentration, parts per million, ppm	Corrosion Rate, mils per year, mpy
0	614.6
3–5	858.9
300–400	1375.1

Choi and others (18) 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 to 32 mpy when 200 ppm H_2S was present.

The NACE MR0175/ISO 15156 standard sets a threshold partial pressure (thermodynamic activity) 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. $scCO_2$ and impurities such as H_2S are correctly defined by fugacity (fH_2S), a thermodynamic property of H_2S, which must be determined using software. Biswas and others present 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 (19). This analysis shows a significant drop in pH_2S and fH_2S once there is a phase change of the CO_2 from gas to dense phase and suggests that $scCO_2$ containing certain concentrations of H_2S would not strictly follow the 0.05 psia limit in NACE MR0175. $scCO_2$ could, therefore, possibly tolerate higher pH_2S before SSC is a risk, but much more work on this, including parallel SSC tests, needs to be performed in order to define an fH_2S limit.

Effect of Existing 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, 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 paper. As regards to 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. 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 scCO_2 service.

Potential Corrosion Problems after Conversion to scCO_2 Containing H_2S

In the case of H_2S alone as the only impurity in the scCO_2 stream, potentially any number of corrosion/cracking mechanisms can be operative depending on the partial pressure and fugacity, pH_2S (fH_2S). Even small amounts of H_2S in the CO_2 stream can produce an FeS corrosion product on the surface of the steel. Li and others (20) found that 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 (18) 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. More work would be needed to determine whether there is a lower limit of H_2S that would not form a sulfide. It is worth reiterating that such corrosion should not occur so long as any water remains soluble in the stream.

Numerous variables 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 nonprotective 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.

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 because of pH reduction. Because of the complexity of these various interactions between impurities, no means are currently available 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.

SOUR PIPELINES REPURPOSED FOR TRANSPORT OF scCO_2 WITHOUT H_2S

In addition to the general considerations discussed above, certain issues need to be specifically reviewed and accounted for when repurposing a sour pipeline to carry scCO_2 without H_2S as an impurity in the stream.

Materials of Construction

It is important to ensure that a candidate preexisting pipeline that has been exposed to H_2S was correctly designed, constructed, and operated in compliance with NACE MR0175/ISO 15156. This is not so much a requirement for sweet supercritical CO_2, $scCO_2$, as it is a step to mitigate risk that SSC and HIC damage could have been introduced through prior use. Pipelines not designed for H_2S that were exposed to H_2S may have permanent damage that would be difficult to detect. No current inspection method can reliably detect insipient SSC or HIC. For this reason, pipelines not designed for H_2S that were exposed to H_2S may be risky to convert to $scCO_2$ service.

In practical sour applications, this would mean the highest strength pipe would generally be Grade X65 or possibly Grade X70. Sour service pipelines are rarely constructed from Grade X80 pipe and higher, although some may exist. Construction and purchase records confirming the specified minimum yield strength, tensile strength, hardness, and chemical composition should be reviewed to ensure compliance with NACE MR0175/ISO 15156. As noted earlier in the general considerations for all $scCO_2$ pipelines, these records should also include mill test reports (MTRs) documenting the actual Charpy impact toughness of the steel since it will be needed for a running ductile fracture assessment.

Effect of Existing Internal Surface Products

For an existing sour pipeline, it can be expected that the internal surfaces of the pipe will be covered with iron sulfides of some type, and 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. Unlike the single corrosion product from CO_2, a whole host of possible iron sulfides may form from H_2S exposure. For many hydrocarbon pipelines, the corrosion product will be mackinawite, an iron sulfide of the type $Fe_{1+x}S$, commonly written Fe_9S_8 or simply FeS.

The stability of mackinawite in the Fe–H_2S–H_2O system does not significantly change between 25° and 80°C, and it should thus be the dominant iron sulfide formed in H_2S-containing $scCO_2$ pipelines as well. However, this has not yet been confirmed by research data. In some cases where the H_2S concentrations/partial pressures are high, the predominant product will be pyrrhotite ($Fe_{1-x}S$). This latter phase is much more stable than is mackinawite.

Subsequent exposure of FeS scales to various impurities contained in an $scCO_2$ stream may cause a variety of issues depending on the specific impurities. For one, the FeS scale is soluble when the pH decreases to less than about 5. Therefore, the introduction of $scCO_2$ with a separate water phase would result in a pH around 3 and likely cause the FeS scale to dissolve. This can create a serious localized problem. 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 fluid 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 in oil and gas wells when downhole tubulars scaled with FeS are acidized with HCl, resulting in cracking.

Other possible reactions when $scCO_2$ with various impurities is introduced into an existing sour pipeline with FeS scale are numerous. Of special concern is the introduction of $scCO_2$ containing O_2. As Craig has shown (21), mackinawite is especially unstable when exposed to air and will oxidize according to:

$$2Fe_9S_8 + 9H_2O + 27/2\ O_2 \rightarrow 18\ \gamma\text{- } FeO(OH) + 2S_8 \qquad \text{[Eq. 1]}$$

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

$$3\ \gamma\text{-}FeO(OH) + e \rightarrow Fe_3O_4 + H_2O + OH^- \qquad \text{[Eq. 2]}$$

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

However, the elemental sulfur generated, S_8, can induce severe pitting and cause the corrosion rate to escalate to very high values. The reaction between O_2 and FeS may not require the presence of liquid water. The oil and gas industry has numerous examples of scale products from sour pipelines and sour wells bursting into flame on exposure to air due to the immediate oxidation of FeS. This issue has not been thoroughly studied in CCS systems, and it is not yet clear what concentration of O_2 in the $scCO_2$ stream would be needed to cause such a reaction in situ. Therefore, it is recommended that the introduction of $scCO_2$ 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 an $scCO_2$ stream, it is highly recommended that laboratory testing of FeS-scaled pipe be performed using simulated $scCO_2/H_2O$ 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 $scCO_2$ service.

Because of the additional risk of converting a sour pipeline imposed by possible FeS dissolution in low pH water, some operators may choose 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 of the scope of this paper, but if FeS removal can be performed effectively, it may help reduce the risk of H_2S formation when low pH water is present.

GENERAL COMMENTS ON CO_2 PIPELINE INTEGRITY

Regardless of the pipeline history, continuous pipeline maintenance should be largely similar to natural gas transmission pipelines with additional emphasis on water control. Following hydrotesting, it is good practice to thoroughly dewater the pipeline prior to filling with CO_2. It is generally felt in the industry that small amounts of water remaining in the pipeline will be reabsorbed into the dense-phase CO_2 because of its high solubility; however, care should be taken if large amounts of water remain since mixing gaseous CO_2 and water during initial filling of the pipeline can create a very corrosive environment.

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.

The frequency and duration of upsets leading to a separate liquid water phase dropping out can be a corrosion concern if $scCO_2$ 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.

The design and operating temperatures and pressures of $scCO_2$ 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° to 111°F (13°–4°C) and 1232–2174 psi (84.9–149.9 bar) (15). Generally, increasing pressure and temperature increase corrosion rates.

Efforts have been made to develop corrosion inhibitors to deal with free water in contact with $scCO_2$. At present, these inhibitors are not effective nor reliable over the life of a $scCO_2$ pipeline. The most effective methods of corrosion mitigation are sufficient dehydration and prudent operation such that liquid water does not drop out of the supercritical fluid. In both the case of a sweet pipeline being converted to $scCO_2$ with H_2S and a sour pipeline being converted to $scCO_2$ without H_2S, the absence of a water phase will prevent corrosion.

CONCLUSIONS

Repurposing existing pipelines for CO_2 transmission is complicated and requires special engineering considerations, especially when H_2S is involved, either in the previous process or the new CO_2 service. Guidelines for the scenarios discussed in this paper are summarized below. As can be appreciated from the above discussion, this area is very complicated and warrants the assistance of SMEs in several disciplines to assist in navigating all of the many issues. These guidelines alone are not a substitute for review by an SME.

For all pipelines repurposed for $scCO_2$ service:

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, including replacements and repairs.

2. If material property records are incomplete, perform destructive testing on representative pipe in order to establish properties for $scCO_2$ design.

3. 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.

4. Run ILI to determine the status of the pipe, including any existing cracks and pits.

5. Review inspection results, and conduct risk assessments to determine whether conversion to $scCO_2$ service is advisable. Consult relevant SMEs, as needed.

For existing <u>sweet</u> pipelines repurposed for transport of $scCO_2$ <u>containing H_2S</u>:

1. 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 in order to prevent SSC and HIC in the new service.

2. Run scraper/brush pigs to remove as much of any corrosion product layer as possible.

3. Perform laboratory tests with H_2S and all other impurities to determine if SSC and HIC could be an issue.

For existing <u>sour</u> pipelines repurposed for transport of $scCO_2$ without H_2S:

1. 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 in order to mitigate possible SSC and HIC damage from prior service.

2. Scraper/brush pig runs should be specifically engineered to remove as much of the FeS layer as possible. FeS in the pipeline can lead to severe corrosion or cracking if liquid water drops out of the $scCO_2$ stream.

3. Ensure no measurable oxygen is present in the $scCO_2$ stream, which may oxidize FeS to form elemental sulfur. Testing would be needed to establish acceptable oxygen levels.

4. Perform laboratory tests with prescaled FeS pipe under simulated $scCO_2$ conditions to ascertain if the interaction will exacerbate corrosion and if SSC and HIC could be an issue.

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