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(54) Title: PROCESS FOR PROTECTING CARBON STEEL PIPE FROM SULFIDE STRESS CRACKING IN SEVERE SOUR SERVICE ENVIRONMENTS

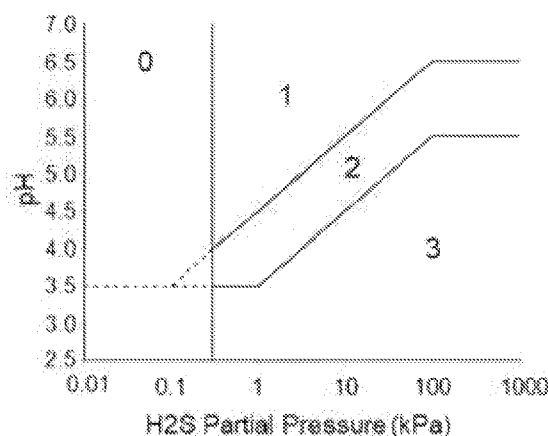


FIG. 1

(57) Abstract: The present disclosure relates to processes and associated equipment for protecting commercial carbon steel pipe and piping components, exposed to sour service environments (high H_2S and low pH) from experiencing sulfide stress cracking (or "SSC") as defined in the ANSI/NACE/ISO International Standard ANSI/NACE MR0175 / ISO 15156-1:2015. In particular, the present disclosure relates to determining operating conditions of a process fluid to determine minimum safe operating temperature to prevent SSC in carbon steel pipe, equipping the carbon steel pipe with an appropriately designed heating supply, and utilizing the heating supply to ensure that the internal wall of the carbon steel pipe (i.e., the face of the inner pipe which is exposed to the process fluid) is maintained at or above the minimum safe operating temperature to prevent SSC from occurring in the carbon steel pipe materials.

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PROCESS FOR PROTECTING CARBON STEEL PIPE FROM SULFIDE STRESS CRACKING IN SEVERE SOUR SERVICE ENVIRONMENTS

FIELD OF DISCLOSURE

5 [0001] The present disclosure relates to processes and associated equipment for protecting carbon steel pipe from sulfide stress cracking (SSC) in high hydrogen sulfide (H₂S) content (i.e., severe sour service) environments.

BACKGROUND

10 [0002] This section is intended to introduce problems associated in the industry and various aspects of the art. This discussion is believed to facilitate a better understanding of particular aspects of the present techniques. Accordingly, it should be understood that this section should be read in this light, and not necessarily as admissions of prior art.

[0003] Many processes and associated piping and transfer pipelines in the petroleum/petrochemical (PPC) industries are exposed to process fluids that have a high content of hydrogen sulfide (H₂S), also referred to as “severe sour service” conditions. A significant amount of pipe and pipeline materials are made from carbon steel plates manufactured by Thermo-Mechanical Controlled Processing (TCMP) processes due to their ease of fabrication, weldability and significantly lower cost as compared to Corrosion Resistant Alloys (CRAs). However, use of carbon steel in severe sour service conditions can be limited by its potential to experience sulfide stress cracking (SSC), due to absorption and trapping of hydrogen leading to embrittlement (see Neeraj, T., Srivastava, V., Hallai, J.F., Ma, N., Sarosi, P. Jun, H.J., Baker, D., 2019, “Hydrogen Permeation, Absorption and Trapping in Carbon Steels: A Comparison of Line Pipe and OCTG Steels”, 29th International Ocean and Polar Engineering Conference (ISOPE), Honolulu, HI, June 16-21).

25 [0004] In these services, the H₂S can lead to acidic conditions in the process streams resulting in corrosion of the carbon steel material. Hydrogen ions (H⁺) dissociate from the H₂S during the corrosion process and can also be generated from the cathodic reaction of steel/Fe corrosion reaction and are small enough to diffuse into the carbon steels. The diffused hydrogen can become trapped in the carbon steel, and accumulate at internal stress centers, and resulting sulfide stress cracking (SSC).

30 [0005] While H₂S content of the fluid is a major factor in the extent of SSC in carbon steel materials, other factors such as pressures, temperatures, water content, and plates or weld defects

(such as hard spots or porosity) can additionally affect the extent of the SSC experienced. Severe sour service conditions can result in the initiation and propagation of SSC in carbon steel and due to the embrittlement nature of the SSC mechanism, can lead to sudden and catastrophic failures prior to detection of the cracking.

5 **[0006]** While improvements have been directed to improving the TCMP steel quality (e.g., reduce defects associated with SSC failures, relieving cold work stresses via thermal treatment, etc.), in processes with severe sour service conditions, generally the use of Corrosion Resistant Alloys (CRAs) has been relied upon in the industry to limit the exposure to SSC in high H₂S environments. These corrosion resistant alloys may be used either as pipeline materials or
10 metallurgically bonded internally CRA clad pipeline materials (“lined pipe materials”), the latter wherein the plate utilized for the pipe is a carbon steel with a layer of CRA which when rolled into a pipe shape, the CRA materials forms the inside liner. The CRA materials are much more resistant to SSCs due to the their lower corrosion rate under severe sour service conditions as compared to convention TCMP carbon steel materials. This results in a lower rate of hydrogen dissociation
15 and these CRA materials can also provide for lower diffusion rates of hydrogen ions into the steel due to their austenitic /face centered cubic crystal structure as well as due to their higher solubility for H, therefore reducing susceptibility to SSC cracking.

[0007] Major drawbacks regarding the use of CRAs include the significant expense of the materials and fabricating processes as compared to these costs associated with the use of carbon
20 steel materials. In contrast with carbon steels, CRAs generally have a significant content of expensive elements such as Chrome (Cr), Nickel (Ni), Molybdenum (Mo), and/or Vanadium (V) (see, for example, US 2014/0352836 A1 to Eguchi et al.). It has also been found that levels of Copper (Cu) included in CRAs can improve resistance to SSC cracking (see, for example, US 5,820,699 A to Asahi et al. and US 2017/0145547 A1 to Saal et al.). Compared with carbon steel,
25 these materials are expensive sometimes increasing the costs of pipe materials by as much as 6 to 8 times over the cost of carbon steel pipe materials. Additionally, these specialty materials can have long lead times for fabrication and delivery as well as significantly increase the cost and reduce the availability in qualified welders and welding equipment and materials. While using carbon steel CRA lined pipe can reduce some of the material costs, these materials can also be
30 expensive and difficult to weld due to their bimetallic nature. Additionally, defects and failures (such as delamination or crack propagation) can occur at the internal interface between these

materials which can be difficult to detect by conventional inspection methods.

[0008] As such, there exists a need in the industry for methods, processes, and associated equipment to allow the use of TCMP carbon steel for piping and pipelines operating in high H₂S environments (i.e., severe sour service conditions) while minimizing the susceptibility of the carbon steel pipe to SSC cracking.

SUMMARY

[0009] In an embodiment herein is a method for preventing sulfide stress cracking (SSC) in carbon steel pipe exposed to a process fluid under operating conditions which include sour service environment conditions, comprising:

a) determining at least one temperature and at least one pressure of the process fluid under the operating conditions;

b) determining at least one H₂S partial pressure and at least one pH of the process fluid under the operating conditions;

c) determining at least one minimum safe temperature of the inner wall of the carbon steel pipe that is high enough to prevent SSC of the carbon steel pipe under the operating conditions;

d) maintaining the temperature of the inner wall of the carbon steel pipe at or above the at least one minimum safe temperature while the carbon steel pipe is under operating conditions;

wherein the at least one minimum safe temperature is substantially the same or greater than the at least one temperature of the process fluid under the operating conditions.

[0010] In an embodiment, the carbon steel pipe meets API 5L specifications. In another embodiment, the API 5L Grade is selected from the group consisting of X52, X56, X60, X65, X70, X80, X100 and X120. In another embodiment, the carbon steel pipe is fabricated from plate manufacture by Thermo-Mechanical Controlled Processing (TMCP).

[0011] In another embodiment, the at least one minimum safe temperature is at least 25 °F (13.9 °C) greater than the at least one temperature of the process fluid under the operating conditions. In another embodiment, the temperature of the inner wall of the carbon steel pipe at least 25 °F (13.9 °C) greater than the at least one minimum safe temperature. In another embodiment, the at least one H₂S partial pressure of the process fluid under the operating conditions is from about 0.01 bar (0.15 psi) to about 20 bar (290 psi), and the at least one temperature of the process fluid under the operating conditions is from about 70 °F (21.1 °C) to

about 300 °F (148.9 °C). In another embodiment, the at least one process fluid further comprises water. In another embodiment, the at least one process fluid further comprises CO₂, chlorides or a combination thereof. In another embodiment, the composition of the process fluid under the operating conditions falls within SSC Region 2 or SSC Region 3 of International Standard
5 ANSI/NACE MR0175/ISO 15156-1:2015.

[0012] The foregoing has broadly outlined the features of the present disclosure so that the detailed description that follows may be better understood. Additional features will also be described herein.

DESCRIPTION OF THE DRAWINGS

10 [0013] These and other features, aspects and advantages of the present disclosure will become apparent from the following description and the accompanying drawings, which are briefly discussed below.

[0014] FIG. 1 is a graph reproduced from International Standard ANSI/NACE MR0175 / ISO 15156-1:2015, showing process conditions defining Region 0 and sulfide stress cracking (SSC)
15 Regions 1, 2, and 3 per the standard.

[0015] FIG. 2 illustrates the effect of temperature on hydrogen flux through carbon steel in severe sour service environment as measured with a Devanathan–Stachurski cell.

[0016] FIG. 3 illustrates measured H₂ concentration in carbon steel as a function of strain at two different temperatures for carbon steel samples subjected to severe sour service conditions.

20 [0017] FIG. 4 illustrates measured stress in carbon steel as a function of strain at two different temperatures for carbon steel samples subjected to severe sour service conditions.

[0018] FIG. 5 shows an embodiment of the methods herein for preventing sulfide stress cracking (SSC) in carbon steel pipe exposed to a process fluid under operating conditions which include severe sour service conditions.

DETAILED DESCRIPTION

25 [0019] For the purpose of promoting an understanding of the principles of the disclosure, reference will now be made to the features illustrated in the drawings and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the disclosure is thereby intended. Any alterations and further modifications, and any further
30 applications of the principles of the disclosure as described herein, are contemplated as would normally occur to one skilled in the art to which the disclosure relates. It will be apparent to those

skilled in the relevant art that some features that are not relevant to the present disclosure may not be shown in the drawings for the sake of clarity.

[0020] At the outset, for ease of reference, certain terms used in this application and their meanings as used in this context are set forth. To the extent a term used herein is not defined below, it should be given the broadest definition persons in the pertinent art have given that term as reflected in at least one printed publication of issued patent. Further, the present techniques are not limited by the usage of the terms shown below, as all equivalents, synonyms, new developments, and terms or processes that serve the same or a similar purpose are considered to be within the scope of the present disclosure.

[0021] The term “carbon steel” as used herein means a ferritic-pearlitic, bainitic, ferritic-bainitic or martensitic steel that contains only limited amount (typically less than 1 to 2 wt%) Corrosion Resistant Alloying (CRA) elements such as Cr, Mo or Ni (may include non-substantial trace/impurities amounts of CRA elements only). Examples of carbon steel materials may be plates manufactured by Thermo-Mechanical Controlled Processing (TCMP) processes or pipe materials meeting API Specification 5L.

[0022] The term “carbon steel pipe” as used herein means pipe or other pipe materials (such as pipe fittings, valves, etc.) that have been fabricated using a carbon steel material.

[0023] The term “Corrosion Resistant Alloys” or “CRA”’s means materials that contain added amounts of alloying materials selected from Aluminum (Al), Chrome (Cr), Cobalt (Co), Copper (Cu), Nickel (Ni), Molybdenum (Mo), Vanadium (V), and/or Titanium (Ti) which have been specifically added (i.e., not trace or impurities) to the steel compositions in significant enough amounts; typically greater 2 wt%, such as >12 wt% Cr and >50 wt% Ni steel alloys, to improve the corrosion resistance of the resulting alloy.

[0024] The term “Direct Electrical Heating of Pipe-in-Pipe” or “DEH- PiP” system or element as used herein refers to a heating system for piping wherein the inner pipe to be heated is located inside the annulus of an outer pipe and an alternating current (AC) is applied between the inner and outer pipes. This makes both the inner and outer pipes electrical conductors and the inner pipe is heated via the Joule resistive effect. The temperature of the inner pipe can be controlled via the amount of current passed through the AC circuit. The outside circumference of the inner and/or outer pipes may be insulated to maintain heat and temperature control.

[0025] The term “Electrical Heat Tracing of Pipe-in-Pipe” or “EHT- PiP” system or element

as used herein refers to a heating system for piping wherein the inner pipe to be heated is located inside the annulus of an outer pipe and an electrical resistive heat tracing system, usually consisting of electrically resistive metal wires, cables or strips (i.e., “tracers”), is installed between the inner and outer pipes. An electrical current is passed through the tracers to heat the inner pipe via electrical resistance produced in the tracers. The temperature of the inner pipe can be controlled via the amount of current passed through the tracers. The electrical current can be either alternating current (AC) or direct current (DC). The outside circumference of the inner and/or outer pipes may be insulated to maintain heat and temperature control. The tracers may be located between outside circumference of the inner pipe and a layer of insulation, or the tracers may be located between multiple layers of insulation that are located on the outside circumference of the inner pipe.

[0026] The term “fluid” or “process fluid” as used herein includes a gas or a liquid and may include, for example, a produced or native reservoir hydrocarbon, an injected mobilizing fluid, hot or cold water, or a mixture of these among other materials. “Vapor” refers to steam, wet steam, and mixtures of steam and wet steam, any of which could possibly be used with a solvent and other substances, and any material in the vapor phase.

[0027] The term “hydrocarbon” as used herein is an organic compound that primarily includes the elements hydrogen and carbon, although nitrogen, sulfur, oxygen, metals, or any number of other elements may be present in small amounts. Hydrocarbon compounds may be aliphatic or aromatic, and may be straight chained, branched, or partially or fully cyclic.

[0028] The term “sulfide stress cracking” or “SSC” as used herein is meant to have the meaning as defined in the ANSI/NACE/ISO International Standard ANSI/NACE MR0175/ISO 15156-1:2015 “Petroleum, petrochemical, and natural gas industries — Materials for use in H₂S-containing environments in oil and gas production” wherein SSC is defined as the “cracking of metal involving anodic processes of localized corrosion and tensile stress (residual and/or applied) in the presence of water and H₂S”.

[0029] The term “severe sour service”, “severe sour environment”, “severe sour conditions” and the like as used herein is meant to have the meaning as stated in the ANSI/NACE/ISO International Standard ANSI/NACE MR0175/ISO 15156-1:2015 “Petroleum, petrochemical, and natural gas industries — Materials for use in H₂S-containing environments in oil and gas production” wherein this term is meant as oilfield environments that contain sufficient H₂S to

cause cracking of materials by the mechanisms addressed by ANSI/NACE MR0175/ISO 15156-1:2015.

[0030] The terms “approximately,” “about,” “substantially,” and similar terms are intended to have a broad meaning in harmony with the common and accepted usage by those of ordinary skill in the art to which the subject matter of this disclosure pertains. It should be understood by those of skill in the art who review this disclosure that these terms are intended to allow a description of certain features described and claimed without restricting the scope of these features to the precise numeral ranges provided. Accordingly, these terms should be interpreted as indicating that insubstantial or inconsequential modifications or alterations of the subject matter described and are considered to be within the scope of the disclosure. These terms when used in reference to a quantity or amount of a material, or a specific characteristic of the material, refer to an amount that is sufficient to provide an effect that the material or characteristic was intended to provide. The exact degree of deviation allowable may in some cases depend on the specific context.

[0031] The articles “the,” “a” and “an” are not necessarily limited to mean only one, but rather are inclusive and open ended so as to include, optionally, multiple such elements.

[0032] As used herein, the phrase “at least one,” in reference to a list of one or more entities should be understood to mean at least one entity selected from any one or more of the entity in the list of entities, but not necessarily including at least one of each and every entity specifically listed within the list of entities and not excluding any combinations of entities in the list of entities. This definition also allows that entities may optionally be present other than the entities specifically identified within the list of entities to which the phrase “at least one” refers, whether related or unrelated to those entities specifically identified. Thus, as a non-limiting example, “at least one of A and B” (or, equivalently, “at least one of A or B,” or, equivalently “at least one of A and/or B”) may refer, to at least one, optionally including more than one, A, with no B present (and optionally including entities other than B); to at least one, optionally including more than one, B, with no A present (and optionally including entities other than A); to at least one, optionally including more than one, A, and at least one, optionally including more than one, B (and optionally including other entities). In other words, the phrases “at least one,” “one or more,” and “and/or” are open-ended expressions that are both conjunctive and disjunctive in operation. For example, each of the expressions “at least one of A, B and C,” “at least one of A, B, or C,” “one or more of A, B, and C,” “one or more of A, B, or C” and “A, B, and/or C” may mean A alone, B alone, C alone, A and

B together, A and C together, B and C together, A, B and C together, and optionally any of the above in combination with at least one other entity.

[0033] As used herein, the term “and/or” placed between a first entity and a second entity means one of (1) the first entity, (2) the second entity, and (3) the first entity and the second entity.

5 Multiple entities listed with “and/or” should be construed in the same manner, i.e., “one or more” of the entities so conjoined. Other entities may optionally be present other than the entities specifically identified by the “and/or” clause, whether related or unrelated to those entities specifically identified. Thus, as a non-limiting example, a reference to “A and/or B,” when used in conjunction with open-ended language such as “comprising” may refer to A only (optionally including entities other than B); to B only (optionally including entities other than A); to both A and B (optionally including other entities). These entities may refer to elements, actions, structures, steps, operations, values, and the like.

[0034] As used herein the terms “adapted” and “configured” mean that the element, component, or other subject matter is designed and/or intended to perform a given function. Thus, 15 the use of the terms “adapted” and “configured” should not be construed to mean that a given element, component, or other subject matter is simply “capable of” performing a given function but that the element, component, and/or other subject matter is specifically selected, created, implemented, utilized, programmed, and/or designed for the purpose of performing the function. It is also within the scope of the present disclosure that elements, components, and/or other recited 20 subject matter that is recited as being adapted to perform a particular function may additionally or alternatively be described as being configured to perform that function, and vice versa.

[0035] As used herein, the phrase, “for example,” the phrase, “as an example,” and/or simply the term “example,” when used with reference to one or more components, features, details, structures, embodiments, and/or methods according to the present disclosure, are intended to 25 convey that the described component, feature, detail, structure, embodiment, and/or method is an illustrative, non-exclusive example of components, features, details, structures, embodiments, and/or methods according to the present disclosure. Thus, the described component, feature, detail, structure, embodiment, and/or method is not intended to be limiting, required, or exclusive/exhaustive; and other components, features, details, structures, embodiments, and/or 30 methods, including structurally and/or functionally similar and/or equivalent components, features, details, structures, embodiments, and/or methods, are also within the scope of the present

disclosure. Any of the ranges disclosed may include any number within and/or bounded by the range given.

[0036] In the illustrative figures herein, in general, elements that are likely to be included are illustrated in solid lines, while elements that are optional may be illustrated in dashed lines.

5 However, elements that are shown in solid lines may not be essential. Thus, an element shown in solid lines may be omitted without departing from the scope of the present disclosure.

[0037] As noted prior, many processes and associated piping and transfer pipelines in the petroleum/petrochemical (PPC) industries are exposed to process fluids that have a high content of hydrogen sulfide (H_2S), also referred to as “severe sour environments” or “severe sour service”.

10 A significant amount of pipe and pipeline materials are made from carbon steel plates manufactured by Thermo-Mechanical Controlled Processing (TCMP) processes due to their ease of fabrication, weldability and significantly lower cost as compared to Corrosion Resistant Alloys (CRAs). However, use of carbon steel exposed to severe sour service conditions can be limited by its potential to experience sulfide stress cracking (SSC), due to absorption and trapping of
15 hydrogen leading to embrittlement and possibly catastrophic (i.e., abrupt) failure.

[0038] There are a multitude of scientific papers, professional journal articles and industry guidelines and standards directed to the problem of SSC in carbon steel materials exposed to severe sour service environments. In particular, for the oil and gas industry, the ANSI/NACE/ISO International Standard ANSI/NACE MR0175/ISO 15156-1:2015 “Petroleum, petrochemical, and
20 natural gas industries — Materials for use in H_2S -containing environments in oil and gas production” (also referred to as “NACE MR0175” or the “NACE standard” herein) is one of the primary standards used in the industry for evaluation, design and analysis of materials severe sour service environments. The NACE standard defines the SSC regions of environmental severity utilizing a graph plotting the H_2S partial pressure vs. the in-situ pH of the process fluid and defining
25 three (3) regions of SSC severity, as well as one (1) Region 0, the latter of which is generally assumed to present little to no exposure to SSC in most carbon steel materials. A copy of this graph is reproduced in FIG. 1 and shows SSC Region 1, SSC Region 2, SSC Region 3, with Region 3 being the highest exposure for SSC in carbon steel materials.

[0039] The NACE standard, as well as other standards and guidelines on SSC mitigation, are
30 generally directed to mitigating SSC under susceptible conditions (such as outlined by NACE in terms of the two variables of the H_2S partial pressure and the in-situ pH of the process fluid)

through proper selection of materials capable of being exposed to the severe sour service conditions without experiencing SSC. By the term “selection of materials”, it is meant these guidelines focus only on the material selection aspect for mitigating SSC, which includes upgraded metallurgies, more stringent quality control of material and welds, and/or increased inspection of materials and welds (the latter including both non-destructive and destructive testing and qualifications). All of these requirements significantly increase the price of the final constructed pipeline as compared using commercial grade carbon steel pipeline materials as well as the use of standard quality control and inspection practices when meeting service requirements for Region 2 and Region 3 of the NACE standard. None of these standards or guidelines are directed to altering the operating conditions of the pipeline material in an effort to minimize or eliminate SSC when operating under Region 2 and/or Region 3 process conditions.

[0040] FIG. 2 shows over time, the effect of temperature on hydrogen flux through carbon steel in a severe sour service environment as measured with a Devanathan–Stachurski cell. It can be observed that higher temperatures lead to higher hydrogen diffusivity in carbon steel, thereby demonstrating a significantly related propensity to decrease the likelihood of “trapped hydrogen” within the carbon steel as a function of an increase in the metal temperature. An increase in “trapped hydrogen” is related to an increased likelihood of carbon steel incurring damage and/or failure as a result of SSC.

[0041] FIG. 3 further illustrates this concept that higher metal temperatures lead to a reduction of hydrogen being trapped in sites such as dislocations, vacancies, and grain boundaries, resulting in lower hydrogen concentration and accumulation at higher temperatures in carbon steels subjected to severe sour service conditions. The data shown in FIG. 3 reflects results from slow strain rate testing (SSRT) tensile tests of carbon steel samples (i.e., test specimens) subjected to severe sour service conditions. The method of this testing is described in NACE Standard TM0198, with the exception that in the experiments herein, a system was utilized wherein the temperature of the test specimens and the severe sour service conditions to which the test specimens were exposed was able to be controlled while the testing was in progress. This was accomplished by exposing the test specimens to a brine solution (at pH of approximately 4) in which 100% H₂S was bubble through a chamber to expose the test samples to severe sour service conditions for a period of approximately 48 hours prior to testing (i.e., a “pre-soak” period) as well as while the samples were being tensile tested. After each tensile test, the test specimen was heated

up to 300 °C to extract and measure the amount of hydrogen in the sample. This process is called “hot extraction”.

[0042] As can be seen in plot **301** of FIG. 3, at a metal temperature of $1.07 \cdot T_0$, in a sample of carbon steel exposed to severe sour service conditions, high amounts of trapped hydrogen were measured in the carbon steel. It is noted that the term “ T_0 ” as used herein is equal to 278 degrees Kelvin (K). In contrast, as can be seen in plot **305** of FIG. 3, at a metal temperature of $1.21 \cdot T_0$, in a similar sample of carbon steel exposed to the same severe sour service conditions, significantly lower amounts of trapped hydrogen were measured in the carbon steel at equivalent levels of strain. Such a reduction in trapped hydrogen with increased temperature occurs even as the amount of plastic strain is significantly increased. These lower hydrogen concentrations can prevent SSC from occurring in commercial grade carbon steel materials, including pipelines and piping materials.

[0043] This concept of utilizing the control of metal temperatures to control the increased hydrogen concentrations induced in carbon steels when subjected severe sour service conditions which result in SSC is further illustrated in the experimental data shown in FIG. 4. As can be seen in plot **401** of FIG. 4, at a temperature of $1.07 \cdot T_0$, in a test specimen of carbon steel exposed to severe sour service conditions, the material failed in a brittle manner indicative of failure due to SSC. This is shown in FIG. 4, wherein in plot **401**, the carbon steel test specimen failed at near maximum applied stress, but at a very low amount of strain. This is clearly indicative of brittle failure due to SSC. The test specimen was further analyzed by a Scanning Electron Microscope (SEM) and was determined to have been subject to SSC with brittle fracturing failure.

[0044] In contrast, a similar test specimen of carbon steel was maintained at a metal temperature of $1.21 \cdot T_0$ and exposed to the same severe sour service conditions, and tested in the same manner for stress vs. strain which results are shown in plot **405** of FIG. 4. Here it can be seen that while this carbon steel second test specimen was maintained at a somewhat elevated temperature than the failed sample of plot **401**, it was at a threshold temperature sufficient to prevent the carbon steel from experiencing SSC. The elongated strain curve clearly shows that the material maintained both strength and ductility similar to a carbon steel that had not been subjected to a severe sour service environment. The test specimen was further analyzed by a Scanning Electron Microscope (SEM) and was determined not to have experienced SSC and experienced no brittle fracturing failure (i.e., the test specimen experienced ductile failure).

[0045] As can be seen from the examples of the testing associated with FIGs. 3 and 4, it has been found that by maintaining a sufficient minimum metal temperature of the carbon steel material, the material (such as pipe) will not experience SSC as the same material would at a temperature below a certain SSC minimum safe temperature. It is believed that at a minimum safe temperature of the carbon steel material, that the H⁺ ions can freely move within the metal framework and grain boundaries thereby removing the mechanism for SSC and thus preventing the carbon steel material for experiencing SSC related damage and/or failures when exposed to a severe sour service environment, including SSC Region 2 or SSC Region 3 environments as defined by the NACE standard.

[0046] An embodiment as disclosed herein comprises a method for preventing sulfide stress cracking (SSC) in carbon steel pipe exposed to a process fluid under operating conditions which include sour service environment conditions, the steps as shown in the method illustrated in FIG. 5. This includes step 505 of determining at least one temperature and at least one pressure of the process fluid under the operating conditions. This can be done either directly, such as analyzing a sample, or a representative sample, of the process fluid or through process simulation. The next step 510 includes determining at least one H₂S partial pressure and at least one pH of the process fluid under the operating conditions. Similarly, this can be done either directly, such as analyzing a sample, or a representative sample, of the process fluid or through process simulation. It should be noted that temperatures, pressures, H₂S partial pressures and/or the pH of the process fluid under the operating conditions may comprise a profile which changes over the length of the pipeline. The next step 515 includes determining at least one minimum safe temperature of the inner wall of the carbon steel pipe that is high enough to prevent SSC of the carbon steel pipe under the operating conditions. This may be performed through either empirical analysis or simulation with appropriate SSC modeling data and/or tools. The final step 520 of this embodiment includes maintaining the temperature of the inner wall of the carbon steel pipe at or above the at least one minimum safe temperature while the carbon steel pipe is under operating conditions; wherein the at least one minimum safe temperature is substantially the same or greater than the at least one temperature of the process fluid under the operating conditions.

[0047] The carbon steel pipe used in the processes herein can be fabricated from plate manufacture by Thermo-Mechanical Controlled Processing (TMCP). The carbon steel pipe used in the processes herein can meet API 5L specifications (commercial TCMP carbon steel pipe). In

preferred embodiments, the API 5L pipe is selected from grades X52, X56, X60, X65, X70, X80, X100 and X120. Generally, it is preferred that the methods herein are utilized to prevent SSC in the carbon steel pipe wherein the composition of the process fluid under the operating conditions falls within SSC Region 2 or SSC Region 3 of International Standard ANSI/NACE MR0175/ISO 15156-1:2015. In embodiments, the at least one H₂S partial pressure of the process fluid under the operating conditions may be from about 0.01 bar (0.15 psi) to about 20 bar (290 psi), and the at least one temperature of the process fluid under the operating conditions may be from about 70 °F (21.1 °C) to about 300 °F (148.9 °C). In embodiments, the at least one pH of the process fluid under the operating conditions may be less than or equal to 5.5, 4.5, or 3.5. In other embodiments, the at least one process fluid further comprises one or more of water, CO₂, and chlorides.

[0048] In embodiments, the least one minimum safe temperature is at least 25 °F (13.9 °C), at least 50 °F (27.8 °C), at least 75 °F (41.7 °C), or at least 100 °F (55.6 °C) greater than the at least one temperature of the process fluid under the operating conditions. In embodiments, the temperature of the inner wall of the carbon steel pipe is maintained at a temperature at least 25 °F (13.9 °C), at least 50 °F (27.8 °C), at least 75 °F (41.7 °C), or at least 100 °F (55.6 °C) greater than the at least one minimum safe temperature. The temperature of the inner wall of the carbon steel pipe is preferentially maintained at least in part by providing at least one heating element along the outer wall of the carbon steel pipe. Alternatively or additionally, the inner wall of carbon steel pipe may be maintained at least in part by providing insulation around the outer circumference of the carbon steel pipe and/or by providing a “pipe-in-pipe” configuration. In the “pipe-in-pipe” configuration, the carbon steel pipe (which is exposed to the sour service environment) is enclosed within the annulus of another pipe. The heating element preferably utilizes an electrical heating element and/or a steam heating element, although other fluids (such as glycol) may alternatively or additionally utilized as a heating fluid, which may also be referred to a Direct Electrical Heating (DEH) element. When a heating fluid is utilized (such as steam or glycol), the heating fluid generally is heated by an external heating device (such as a fired heater or heat exchanger) and the carbon steel piping is heated by passing the heating fluid through tubing which is in direct contact or thermal contact with the carbon steel piping. In embodiments, the temperature of the inner wall of the carbon steel pipe may maintained by a Direct Electrical Heating of Pipe-in-Pipe (DEH- PiP) element or system, or an Electrical Heat Tracing of Pipe-in-Pipe (EHT- PiP) element or system.

[0049] In embodiments, the carbon steel pipe is continuously monitored and used to control

the heating element(s) in order to maintain the inner wall temperature of the carbon steel pipe above the at least one minimum safe temperature. Such temperature monitoring can be done by placing temperature monitoring devices at select intervals or locations along the pipeline, or continuously along the pipeline. Such devices may be selected from thermocouples and Distributed Temperature Sensing (DTS) devices utilizing fiber optic sensor cables. The measurements temperature monitoring devices can be analyzed by systems such as distributed control system (DCS) or programmable logic controller (PLC) and then output provided by these devices to controllers on the heating element systems to maintain the inner wall temperature of the carbon steel pipe above the at least one minimum safe temperature. While these temperature monitoring devices will in most cases be positioned on an external wall of the carbon steel pipe, the inner wall of the carbon steel pipe can easily be determined through the use of appropriate heat transfer equations in the associated control algorithms.

[0050] In the present disclosure, several examples have been discussed and/or presented in the context of flow diagrams, or flow charts, in which the methods are shown and described as a series of blocks, or steps. Unless specifically set forth in the accompanying description, the order of the blocks may vary from the illustrated order in the flow diagram, including with two or more of the blocks (or steps) occurring in a different order and/or concurrently.

[0051] In the event that any patents, patent applications, or other references are incorporated by reference herein and (1) define a term in a manner that is inconsistent with and/or (2) are otherwise inconsistent with, either the non-incorporated portion of the present disclosure or any of the other incorporated references, the non-incorporated portion of the present disclosure shall control, and the term or incorporated disclosure therein shall only control with respect to the reference in which the term is defined and/or the incorporated disclosure was present originally.

Industrial Applicability

[0052] The systems and methods disclosed in the present disclosure are applicable to the oil and gas industry.

[0053] It is believed that the following claims particularly point out certain combinations and subcombinations that are novel and non-obvious. Other combinations and subcombinations of features, functions, elements and/or properties may be claimed through amendment of the present claims or presentation of new claims in this or a related application. Such amended or new claims,

whether different, broader, narrower, or equal in scope to the original claims, are also regarded as included within the subject matter of the present disclosure.

CLAIMS

What is claimed is:

1. A method for preventing sulfide stress cracking (SSC) in carbon steel pipe exposed to a
5 process fluid under operating conditions which include sour service environment conditions,
comprising:

a) determining at least one temperature and at least one pressure of the process fluid under
the operating conditions;

b) determining at least one H₂S partial pressure and at least one pH of the process fluid
10 under the operating conditions;

c) determining at least one minimum safe temperature of the inner wall of the carbon steel
pipe that is high enough to prevent SSC of the carbon steel pipe under the operating conditions;

d) maintaining the temperature of the inner wall of the carbon steel pipe at or above the at
least one minimum safe temperature while the carbon steel pipe is under operating conditions;

15 wherein the at least one minimum safe temperature is substantially the same or greater than
the at least one temperature of the process fluid under the operating conditions.

2. The method of claim 1, wherein the carbon steel pipe meets API 5L specifications.

20 3. The method of any one of claims 1-2, wherein the temperature of the inner wall of carbon
steel pipe is maintained at least in part by providing insulation around the outer circumference of
the carbon steel pipe.

4. The method of claim 3, wherein the temperature of the inner wall of the carbon steel pipe
25 is maintained at least in part by providing at least one heating element along the outer wall of the
carbon steel pipe.

5. The method of claim 4, wherein the heating element comprises an electrical heating
element or a steam heating element.

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6. The method of claim 5, wherein the heating element comprises a Direct Electrical Heating (DEH) element.

7. The method of any one of claims 1-2, wherein the carbon steel pipe is an inner pipe of a pipe-in-pipe configuration.

8. The method of claim 7, wherein the temperature of the inner wall of the carbon steel pipe is maintained by a heating element selected from the group consisting of a Direct Electrical Heating of Pipe-in-Pipe (DEH- PiP) element, or an Electrical Heat Tracing of Pipe-in-Pipe (EHT- PiP) element.

9. The method of any one of claims 4-8, wherein the outer wall temperature of the carbon steel pipe is continuously monitored and used to control the at least one heating element.

10. The method of any one of claims 1-9, wherein the carbon steel pipe is fabricated from plate manufacture by Thermo-Mechanical Controlled Processing (TMCP).

11. The method of any one of claims 1-10, wherein the carbon steel pipe is meets an API 5L Grade selected from the group consisting of X52, X56, X60, X65, X70, X80, X100 and X120.

12. The method of any one of claims 1-11, wherein the at least one minimum safe temperature is at least 25 °F (13.9 °C) greater than the at least one temperature of the process fluid under the operating conditions.

13. The method of any one of claims 1-12, wherein the temperature of the inner wall of the carbon steel pipe at least 25 °F (13.9 °C) greater than the at least one minimum safe temperature.

14. The method of any one of claims 1-13, wherein the composition of the process fluid under the operating conditions falls within SSC Region 2 or SSC Region 3 of International Standard ANSI/NACE MR0175/ISO 15156-1:2015.

15. The method of any one of claims 1-14, wherein at least one temperature, the at least one pressure, the at least one H₂S partial pressure, and the at least one pH of the process fluid under the operating conditions are determined by computational modeling.

5 16. The method of claim 15, wherein the at least one temperature of the process fluid comprises a temperature profile of the process fluid along a section of the carbon steel pipe.

17. The method of any one of claims 1-16, wherein the minimum safe temperature changes over the time that the carbon steel pipe is exposed to the process fluid.

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18. The method of any one of claims 1-17, wherein the at least one H₂S partial pressure of the process fluid under the operating conditions is from about 0.01 bar (0.15 psi) to about 20 bar (290 psi), and the at least one temperature of the process fluid under the operating conditions is from about 70 °F (21.1 °C) to about 300 °F (148.9 °C).

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19. The method of any one of claims 1-18, wherein the at least one pH of the process fluid under the operating conditions is less than or equal to 5.5.

20. The method of any one of claims 1-19, wherein the at least one process fluid further
20 comprises water.

21. The method of any one of claims 1-20, wherein the at least one process fluid further comprises CO₂, chlorides or a combination thereof.

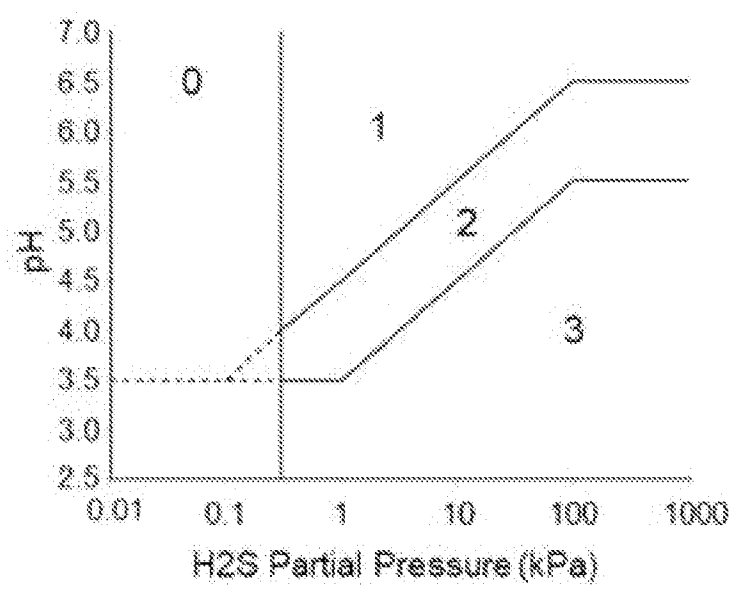


FIG. 1

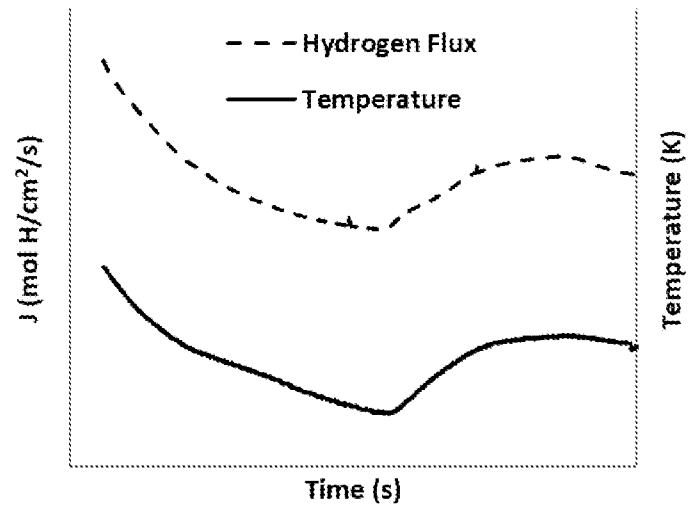


FIG. 2

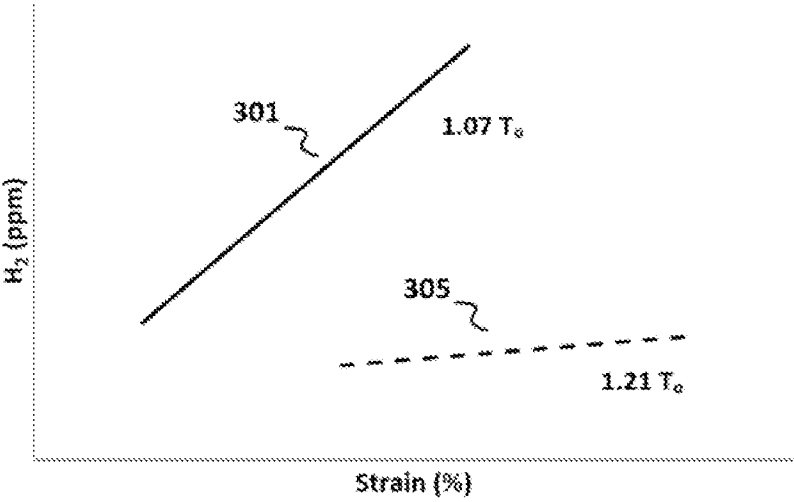


FIG. 3

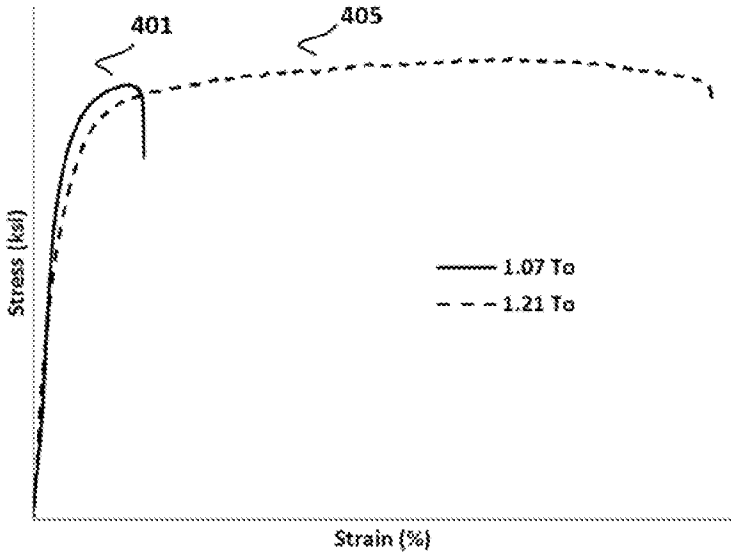


FIG. 4

3 / 3

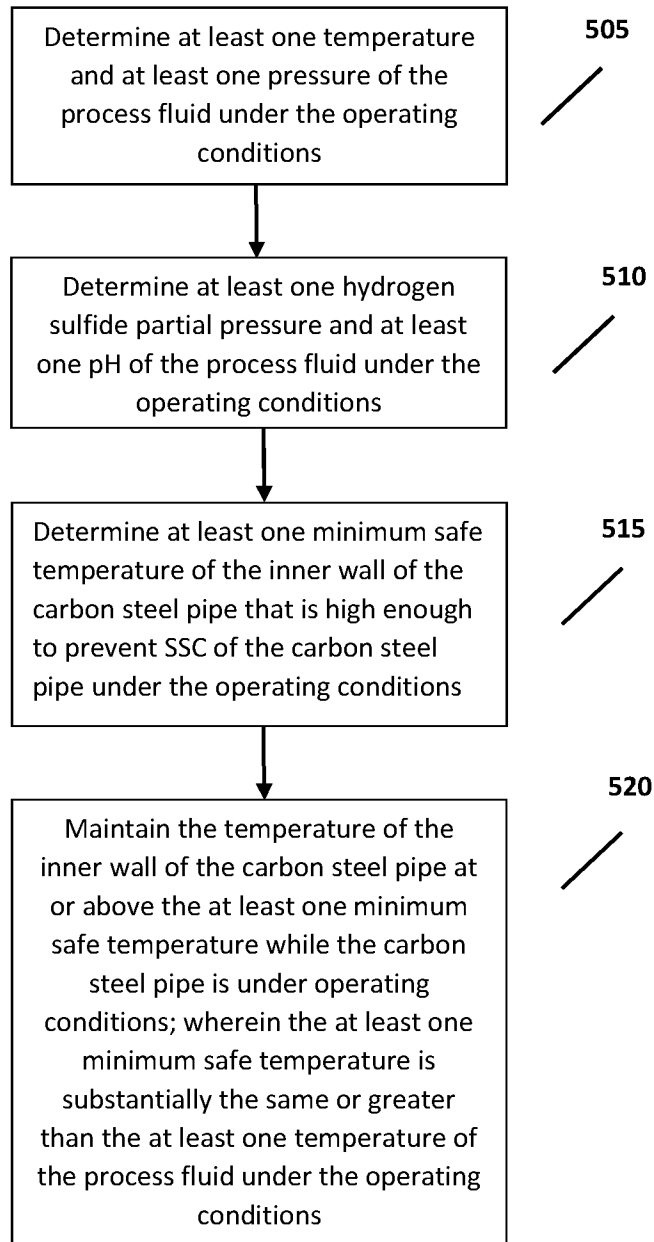


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2021/072892

A. CLASSIFICATION OF SUBJECT MATTER
INV. F16L57/02
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10G B01J F16L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/315276 A1 (BOSCH CHRISTOPH [DE] ET AL) 29 December 2011 (2011-12-29) paragraphs [0001], [0049], [0056], [0057]; tables 1-7 -----	1-21
A	WO 2019/079885 A1 (SAYED AMR MOHAMED [CA]; MOORE ROBERT GORDON [CA]; MEHTA SUDARSHAN [CA]) 2 May 2019 (2019-05-02) the whole document -----	1-21
A	US 2014/148628 A1 (BRADLEY STEVEN A [US] ET AL) 29 May 2014 (2014-05-29) the whole document -----	1-21

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

22 March 2022

Date of mailing of the international search report

30/03/2022

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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