In a process for the exploration for or the production of crude oil and/or natural gas, wherein metal objects are exposed to a gas for a period of time sufficient to produce an aqueous film, a method including introducing a corrosion inhibitor into a fluid in contact with the subject metal under conditions sufficient to introduce the corrosion inhibitor into the aqueous film can be used to prevent excessive corrosion. Useful as the corrosion inhibitor is 2-sulfanylp propane-1-ol, also known as 2-mercapto-ethanol, and 2-mercapto-ethanol substituted with one or two methyl groups, and combinations thereof.

**FIG. 1.**
TITLE: INHIBITING CORROSION IN AQUEOUS FILMS

BACKGROUND OF THE INVENTION

1. Field of the Disclosure
[0001] The invention relates to the prevention or mitigation of corrosion. The invention particularly relates to the prevention or mitigation of corrosion in aqueous films.

2. Background Of The Disclosure
[0002] The problem of corrosion of metal surfaces in contact with air and water is well known. Corrosion and pitting are accelerated in environments in which metal surfaces are in contact with corrosive chemicals such as hydrogen sulfide, carbon dioxide and organic acids, and water having a high electrolyte concentration. Such environments are typical of downwell conditions in oil and gas wells, in which corrosion of metal pipes, pumps and other equipment poses a serious problem requiring monitoring of well sites, frequent maintenance and costly replacement of parts.

[0003] Oil recovery operations in deep-sea oil fields present these corrosion problems in their most extreme form. The downhole metal surfaces are in contact with large quantities of corrosive chemicals such as dissolved acid gases present in the recovered oil, and the metal surfaces are subjected to temperatures of 90°C or higher and pressures of 1000 psig or higher, the extreme conditions of temperature and pressure acting to accelerate corrosion and to intensify the problems of applying and maintaining chemical protection for the equipment. Flow lines that follow the contours of the sea floor often have highpoints where entrapped gas prevent the contact of liquids
passing through the flow lines to contact at least parts of the top of the flowline.

[0004] Corrosion inhibition is particularly difficult when dealing with multiphase fluids. For example, in gas wells, the exposed metal surfaces are often contacted for long periods with hydrocarbon gasses saturated with water. The application of corrosion inhibitors is difficult in these situations. When conditions such as temperature and pressure inside such equipment favors the formation of aqueous films, the resulting aqueous films may selectively absorb or extract hydrophilic compounds, many of which are corrosive, such as carbon dioxide and hydrogen sulfide.

SUMMARY

[0005] In one aspect, the invention is a method for employing a corrosion inhibitor to prevent or mitigate corrosion of metal in an aqueous film.

[0006] In another aspect, the invention is, in a process for the exploration for or the production of crude oil and/or natural gas, wherein metal objects are exposed to a gas for period of time sufficient to produce an aqueous film, introducing a vaporous corrosion inhibitor under conditions sufficient to treat the aqueous film with the vaporous corrosion inhibitor.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Figure 1 is a graph illustrating the effect of various chemical on water condensation; and

Figure 2 is a graph of the Frequency changes that occur with an iron coated quartz crystal when a water film is condensed in a system that contains 100 psi carbon dioxide.
DESCRIPTION

[0008] In one embodiment, the disclosure is directed a method for employing a corrosion inhibitor to prevent or mitigate corrosion of metal in an aqueous film. The corrosion inhibitors useful with method of the disclosure include those selected from the group consisting of:

\[
\text{HS}^+\text{CH}_2\text{CH}_2\text{OH}
\]

2-sulfanylethanol,

\[
\text{H}_3\text{C}\text{CHCH}_2\text{OH}
\]

2-sulfanylpropan-1-ol,

\[
\text{H}_3\text{C}\text{CHCH}_2\text{CH}_3\text{OH}
\]

3-sulfanylbutan-2-ol,

\[
\text{H}_2\text{C}\text{CHCH}_2\text{CH}_3\text{OH}
\]

1-sulfanylpropan-2-ol,

and combinations thereof.

[0009] In another embodiment, the invention is, in a process for the exploration for or the production of crude oil and/or natural gas, wherein metal objects are exposed to a gas for period of time sufficient to produce an aqueous film. In most embodiments, the aqueous film is condensed from water vapor in the gas. In other embodiments, the film may also be the film resulting from a flush or surge of a liquid having an aqueous component present. The method includes introducing a corrosion inhibitor under
conditions sufficient to treat the aqueous film with the corrosion inhibitor. The compounds useful as the corrosion inhibitor include 2-sulfanylpropan-1-ol, also known as 2-mercapto-ethanol, and 2-mercapto-ethanol substituted with one or two methyl groups.

While not wishing to be bound by any theory, it is believed that the corrosion inhibitors work by two processes. In a first process, surprisingly, these mercapto alcohols, despite their relatively low molecular weight, are effective at protecting a metal surface from oxidation caused by acids. In a second process, it is believed that these same alcohols can retard the rate that water can condense into a film on a metal surface. By reducing the volume of the fluid in the film (because the rate of condensation is lower), there is less fluid to solubilize oxidation products and to adsorb corrosive compounds such as carbon dioxide and/or hydrogen sulfide.

The methods of the disclosure may be used with any type of equipment that is subject to corrosion from a gas stream or phase. For example, in one embodiment, the method of the disclosure is used to protect the surface of metal in contact with the production fluid from a gas well. For the purposes of this application, the production fluid from a gas well includes the natural gas, minor amounts of readily condensable hydrocarbons, water, carbon dioxide, and other gases produced from the well.

In such an embodiment, the corrosion inhibitors may be introduced as a vapor or aerosol into a pipeline at a concentration sufficient to allow it to partition into the aqueous film. The concentration of corrosion inhibitor in the production fluid may vary as a function of the composition of the production fluid and can be determined by one of ordinary skill in the art of employing such additives, especially during the collection and transportation of natural gas.

Any equipment that may be exposed to a gas phase for a period sufficient to cause corrosion may be treated using the method of the disclosure. For example, flow lines, which for the purposes of this application are the transfer lines used for offshore production that allow production fluids
to flow between oil and gas wells to reception points often follow the contours of the sea floor. Where the flow line makes an abrupt bend, there is scope for a "bubble" to form where a liquid does not fully fill the flow line. In this gas space, also known as “the top of the pipe,” it is sometimes observed that excessive corrosion may occur.

[0014] This condition may be treated with the method of the disclosure where the corrosion inhibitor is introduced as a vapor or aerosol into this gas space or, in an alternative embodiment, the corrosion inhibitor can be selected such that it may be introduced into the production fluid and then partition out of the liquid into the gas phase.

[0015] The corrosion inhibitors of the application may be introduced using any method known to those of ordinary skill in the art of exploring for or producing oil and gas to be useful. The corrosion inhibitors desirably have a vapor pressure and solubility within the subject aqueous film that they easily and preferentially partition into the films.

EXAMPLES

[0016] The following examples are provided to illustrate the invention. The examples are not intended to limit the scope of the invention and they should not be so interpreted. Amounts are in weight parts or weight percentages unless otherwise indicated.

Examples 1 & Comparative Examples A-CC.

[0017] Corrosion tests were performed using 2-sulfanylethanol, diethyl amine, morpholine, and monoethyl amine. The corrosion tests were done in a hastelloy test apparatus where a quartz crystal microbalance was used to measure corrosion rates. The use of this test apparatus is fully explained in the a publication: Cattanach, K., Jovancicevic, V., Ramachandran and, R., and Sherik, A., “A New Methodology for Monitoring Corrosion under Sales Gas Conditions Using the Quartz Crystal Microbalance”, Corrosion 11, Paper 1185 (Houston, TX: NACE International 2011).
In this study, the following chemicals were tested: volatile amines - S1) 2-sulfanylethanol S2) diethyl amine (DEA), S3) monoethanol amine (MEA) and S4) morpholine (M). The total amount of fluid injected was a mixture of 30 μl chemical and 250 μl distilled water that simulates the typical concentrations of inhibitors used in continuous applications.

Two types of tests were performed. In the experiments determining water condensation rate in the absence and presence of various chemicals a gold coated quartz crystal was used. A gold coated quartz crystal as received is used and placed in the vessel. The vessel is purged with nitrogen until a dew point temperature of -30 °C is attained. This step removes water from the system. The vessel is then pressurized and kept at temperature of 30 °C until a stable baseline frequency is attained. Then 250 μl of solution are injected in the vessel. The frequency of the quartz crystal is monitored for thirty minutes and the crystal temperature is cooled to 5 °C to induce condensation. As condensation occurs, the frequency of the quartz crystal is reduced. When a stable condensation layer is obtained, the crystal is heated back to 30 °C to remove the layer of condensation. If the frequency is essentially the same as the frequency before the condensation, this indicates that the changes in mass were due to condensation. See Figure 2.

The effect of different chemicals on water condensation on gold coated quartz crystal is shown in Figure 1 which is a graph of the effects of various chemical on water condensation. The crystal temperature is 5 °C. The injected solution contains 30 μl of chemical and 250 μl of water. It can be seen from the graph that morpholine and proprietary alcohol exhibit significant effect on condensation rate and subsequent film formation, while DEA and MEA had little/no affect on water condensation. The decrease in frequency occurs due to the formation of an aqueous condensation layer.

In tests that measure the corrosion of iron and the effects of chemicals on the corrosion of iron, an iron coated quartz crystal is used. The iron coated quartz crystal is placed in the vessel. The vessel is purged with nitrogen until a dew point temperature of -30 °C is attained. This step removes water from
the system. The vessel is then pressurized and kept at temperature of 30 °C until a stable base line frequency is attained. Than 250 μl of volatile corrosion inhibitor containing solution are injected in the vessel. The frequency of the quartz crystal is monitored for thirty minutes and the crystal temperature is cooled to 5 °C to induce condensation. As condensation occurs, the frequency of the quartz crystal is reduced. When a stable condensation layer is obtained, the crystal is heated back to 30 °C to remove the layer of condensation. At this point, the vessel is pressurized with 100 psi CO₂. The crystal temperature is then cooled to 5 °C to induce condensation. As condensation and corrosion occurs, the frequency of the quartz crystal is reduced. The crystal is maintained at 5 °C for several hours to allow for corrosion to occur. The crystal is then heated back to 30 °C to remove the condensation layer. At this stage the frequency changes of the quartz crystal microbalance are due to corrosion and the formation of a corrosion product layer.

[0022] The frequency drops were recorded and converted to a corrosion rate as described previously. The results of the experiments are summarized in the Table with experimentally determined as percent corrosion inhibition.

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<th>Sample ID/Inhibitor</th>
<th>Corrosion Efficiency</th>
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<tr>
<td>Ex. 1: 2-sulfanylethanol</td>
<td>80</td>
</tr>
<tr>
<td>Comp. Ex. A: diethyl amine</td>
<td>5</td>
</tr>
<tr>
<td>Comp. Ex. B: morpholine</td>
<td>22</td>
</tr>
<tr>
<td>Comp. Ex. C: monoethyl amine</td>
<td>39</td>
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</table>
What Is Claimed is:

1. A method for employing a corrosion inhibitor to prevent or mitigate corrosion of metal in an aqueous film.

2. The method of Claim 1 wherein the corrosion inhibitor is selected from the group consisting of:
   
   \[
   \begin{align*}
   &\text{2-sulfanylethanol}, \\
   &\text{2-sulfanylpropan-1-ol}, \\
   &\text{3-sulfanylbutan-2-ol}, \\
   &\text{1-sulfanylpropan-2-ol},
   \end{align*}
   \]

   and combinations thereof.

3. The method of Claim 1 wherein the corrosion inhibitor is
   
   \[
   \begin{align*}
   &\text{2-sulfanylethanol}.
   \end{align*}
   \]

4. The method of Claim 1 wherein the corrosion inhibitor is
5. The method of Claim 1 wherein the corrosion inhibitor is

\[
\text{H}_3\text{C} \quad \text{CH} \quad \text{CH}_2 \quad \text{OH} \\
\text{SH} \\
2\text{-sulfanylpropan-1-ol}
\]

6. The method of Claim 1 wherein the corrosion inhibitor is

\[
\text{H}_3\text{C} \quad \text{CH} \quad \text{CH}_2 \quad \text{OH} \\
\text{CH}_3 \\
\text{SH} \\
3\text{-sulfanylbutan-2-ol}
\]

7. The method of Claim 1 wherein the corrosion inhibitor functions to mitigate or prevent the formation of an aqueous film.

8. The method of Claim 1 wherein the metal is a surface within a gas well.

9. The method of Claim 8 wherein production fluid with the gas well includes natural gas, minor amounts of readily condensable hydrocarbons, water, and carbon dioxide.

10. The method of Claim 1 wherein the metal is a surface within a pipeline.

11. The method of Claim 1 wherein the metal is a surface within a flowline.
12. The method of Claim 11 wherein the metal is the top of the pipe within a flowline.

13. The method of Claim 12 wherein the corrosion inhibitor is introduced as a vapor or aerosol into a gas space within a flowline.

14. The method of Claim 9 wherein the corrosion inhibitor is introduced into the production fluid and then partition out of the liquid into the gas phase.

15. A process for the exploration for or the production of crude oil and/or natural gas, wherein metal objects are exposed to a gas for period of time sufficient to produce an aqueous film, introducing a vaporous corrosion inhibitor under conditions sufficient to treat the aqueous film with the vaporous corrosion inhibitor.

16. The process of Claim 15 wherein the corrosion inhibitor is selected from the group consisting of:

\[
\begin{align*}
&\text{2-sulfanylethanol,} \\
&\text{2-sulfanylpropan-1-ol,} \\
&\text{3-sulfanylbutan-2-ol}
\end{align*}
\]
17. The method of Claim 15 wherein the corrosion inhibitor functions to mitigate or prevent the formation of an aqueous film.

18. The method of Claim 15 wherein the metal objects are in contact with a production fluid comprising natural gas, minor amounts of readily condensable hydrocarbons, water, and carbon dioxide.
INTERNATIONAL SEARCH REPORT

PCT/US2012/061458

A. CLASSIFICATION OF SUBJECT MATTER

C23F 11/00(2006.01)i

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)
C23F 11/00; C09D 5/08; B05D 1/36; C23F 11/16; C09K 3/18; CIOM 101/00; C23F 11/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic database consulted during the international search (name of database and, where practical, search terms used)
eKOMPASS(KIPO internal) & keywords: metal, corrosion, corrodiible, oxidation, inhibitor, prevent, mitigate, mercapto, ethyl, propyl, butyl and alkyl

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No.
--- | --- | ---
X | US 2002-0107151 AL (AHN et a$l$.) 8 August 2002 See abstract , paragraphs [0017]-[0025] , and claims 1-4 . | 1-18
A | US 4608191 A (WU, YULIN) 26 August 1986 See abstract , column 2 , lines 13-33 , column 7 , lines 4-17 , and claim 1. | 1-18
A | US 5324347 A (LAWSON, JOHN R.) 28 June 1994 See abstract , column 3 , lines 1-63 , and claim 1. | 1-18
A | US 2008-0216705 AL (HAYES et a$l$.) 11 September 2008 See abstract , paragraphs [0020]-[0023] , and claims 1,4,5. | 1-18

人死亡 documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"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
26 FEBRUARY 2013 (26.02.2013)

Date of mailing of the international search report
26 FEBRUARY 2013 (26.02.2013)

Name and mailing address of the ISA/KR

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Facsimile No. 82-42-472-7140

Form PCT/ISA/210 (second sheet) (July 2009)
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