

Process, Method, and System for Removing Mercury from Fluids

CROSS-REFERENCE TO RELATED APPLICATIONS

[001] This application claims benefit under 35 USC 119 of US Patent Application
5 Serial No. 61/647,919 with a filing date of May 16, 2012. This application claims priority to
and benefits from the foregoing, the disclosures of which are incorporated herein by
reference.

TECHNICAL FIELD

10 [002] The invention relates generally to a process, method, and system for removing
mercury from hydrocarbon fluids such as natural gas.

BACKGROUND

[003] Mercury can be present in trace amounts in all types of hydrocarbon streams
15 such as natural gas. The amount can range from less than 1 ppbw (parts per billion by
weight) to over a thousand ppbw depending on the source. Methods have been disclosed to
remove mercury from liquid hydrocarbon feed. US Patent Nos. 5,281,258 and 5,223,145
disclose methods of removing mercury from natural gas streams by selective adsorption in
fixed adsorbent beds. U.S. Pat. No. 4,474,896 discloses using polysulfide based absorbents
20 to remove elemental mercury (Hg^0) from gaseous and liquid hydrocarbon streams.

[004] There are also a number of commercially available processes and products for
the removal of elemental mercury Hg^0 from hydrocarbon streams including but not limited to
ICI Syntex's Merespec™ fixed bed absorbents, UOP's HgSIV™ regenerative mercury
removal adsorbents, and Johnson Matthey's Puraspec™ and Puracare™ granulated
25 absorbents for the removal of mercury from gaseous hydrocarbon streams. Adsorption
technology generates a mercury-containing spent adsorbent, which is hazardous solid waste
for disposal.

[005] Production of oil and gas is usually accompanied by the production of water.
The produced water may consist of formation water (water present naturally in the reservoir),
30 or water previously injected into the formation. As exploited reservoirs mature, the quantity
of water produced increases. Produced water is the largest single fluid stream in exploration
and production operations. Every day, U.S. oil and gas producers bring to the surface 60
million barrels of produced water.

[006] There is a need for improved methods for the removal of mercury from gaseous hydrocarbon streams, and particularly methods wherein produced water can be used / recycled.

5 SUMMARY OF THE INVENTION

[007] In one aspect, the invention relates to an improved method to treat a crude oil to reduce its mercury concentration. The method comprises: recovering a mixture of produced water and mercury-containing natural gas from an underground reservoir; separating the mercury-containing natural gas from the produced water; scrubbing the
10 natural gas with an aqueous solution in an absorber, wherein the aqueous solution comprises a water-soluble sulfur compound to react a least a portion of the mercury in the natural gas with the water-soluble sulfur compound to produce a treated natural gas with a reduced concentration of mercury and a mercury containing sulfur-depleted solution; removing at
15 least a portion of the mercury containing sulfur-depleted solution as a purge stream; recirculating at least a portion of the mercury containing sulfur-depleted solution as a recirculating stream; and providing a fresh source of water-soluble sulfur compound as a feed to the absorber for reaction with the mercury in the natural gas.

[008] In one embodiment, the fresh source of water-soluble sulfur compound is generated on-site by reacting elemental sulfur with a sulfidic solution. In another
20 embodiment, at least a portion of the purge stream is disposed by injection into an underground reservoir.

BRIEF DESCRIPTION OF THE DRAWINGS

[009] Figure 1 is a block diagram of an embodiment of a system and process to
25 remove mercury from natural gas, wherein the scrubbing liquid needed for the mercury removal unit (MRU) contains produced water, and wastewater from the system is disposed by injection into an underground reservoir.

[010] Figure 2 is a block diagram of a second embodiment of the MRU, wherein the polysulfide needed for the mercury removal is generated on-site as part of the MRU.

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DETAILED DESCRIPTION

[011] The following terms will be used throughout the specification and will have the following meanings unless otherwise indicated.

[012] “Trace amount” refers to the amount of mercury in the natural gas. The amount varies depending on the natural gas source, ranging from a few $\mu\text{g}/\text{Nm}^3$ to up to 30,000 $\mu\text{g}/\text{Nm}^3$.

[013] “Mercury sulfide” may be used interchangeably with HgS, referring to mercurous sulfide, mercuric sulfide, and mixtures thereof. Normally, mercury sulfide is present as mercuric sulfide with a stoichiometric equivalent of one mole of sulfide ion per mole of mercury ion.

[014] “Flow-back water” refers to water that flows back to the surface after being placed into a subterranean formation as part of an enhanced oil recovery operation, e.g., water flooding or a hydraulic fracturing operation.

[015] “Produced fluids” refers hydrocarbon gases and / or crude oil. Produced fluids may be used interchangeably with hydrocarbons.

[016] “Produced water” refers to the water generated in the production of oil and gas, including formation water (water present naturally in a reservoir), as well as water previously injected into a formation either by matrix or fracture injection, which can be any of connate water, aquifer water, seawater, desalinated water, flow-back water, industrial by-product water, and combinations thereof.

[017] “Polysulfide” refers generally to an aqueous solution that contains polysulfide anions represented by the formula S_x^{2-} . Polysulfide solutions can be made by dissolving in water reagents including cations from alkali metals, alkali earth, ammonia, hydrogen, and combinations thereof, or by reacting elemental sulfur with sulfidic solutions.

[018] “Sulfur-depleted” means that at least a portion of the water-soluble sulfur compound in the solution will have reacted, forming complexes such as HgS, which may be present in the solution either dissolved or in suspension. The sulfur associated with the complexes is not a water-soluble sulfur compound for purposes of defining sulfur depleted.

[019] “Absorber” may used interchangeably with “scrubber,” referring to a device to contact a gas and a liquid, permitting transfer of some molecules from the gas phase to the liquid phase. Examples include but are not limited to absorption columns, fiber film contactors, etc.

[020] The invention relates to systems and processes for the removal of mercury from a natural gas. The system in one embodiment is located at a natural gas production facility, wherein produced water is used in the mercury removal process prior to the liquefaction of the natural gas for transport. The wastewater containing mercury after the removal process can be injected into an underground facility, e.g., a reservoir. In one

embodiment, the reagents needed for the mercury removal is generated on-site, e.g., manufacture of polysulfide solutions from elemental sulfur and sulfidic solutions, or the manufacture of sodium sulfide solutions from sodium carbonate and sulfur sources if available on site.

5 [021] Mercury containing Natural Gas Feedstream: Generally, natural gas streams comprise low molecular weight hydrocarbons such as methane, ethane, propane, other paraffinic hydrocarbons that are typically gases at room temperature, etc. Mercury can be present in natural gas as elemental mercury Hg^0 , in levels ranging from about $0.01 \mu\text{g}/\text{Nm}^3$ to $5000 \mu\text{g}/\text{Nm}^3$. The mercury content may be measured by various conventional analytical
10 techniques known in the art, including but not limited to cold vapor atomic absorption spectroscopy (CV-AAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray fluorescence, or neutron activation.

[022] Method for Removing Mercury: Mercury in natural gas is removed by treatment in a scrubber (absorber) with a solution containing an oxidant capable of oxidizing
15 mercury but not the natural gas itself. In one embodiment, the oxidant is a water-soluble sulfur species, e.g., sulfides, hydrosulfides, and polysulfides, for extracting mercury in natural gas into the aqueous phase as soluble mercury sulfur compounds (e.g. HgS_2^{2-}), wherein very little or no solid mercury complex, e.g., HgS , is formed. Very little or no solid mercury complex means that less than 1% of the mercury in the crude oil after extraction is in the
20 form of a solid such as HgS in one embodiment; less than 0.10% HgS is formed in a second embodiment; and less than 0.05% HgS in a third embodiment. The percent of solid mercury complexes can be determined by filtration, e.g., through a 0.45 micron (or less) filter.

[023] Examples of water-soluble sulfur compounds include sodium hydrosulfide, potassium hydrosulfide, ammonium hydrosulfide, sodium sulfide, potassium sulfide, calcium
25 sulfide, magnesium sulfide, ammonium sulfide, and mixtures thereof. Aqueous source containing water-soluble sulfur species can be any of sulfidic water, sulfidic waste water, kraft caustic liquor, kraft carbonate liquor, etc.

[024] In one embodiment, the water-soluble sulfur species is an inorganic polysulfide such as sodium polysulfide, for an extraction of mercury from the natural gas
30 according to equation: $\text{Hg}(\text{g}) + \text{Na}_2\text{S}_x(\text{aq}) \rightarrow \text{HgS}(\text{aq}) + \text{Na}_2\text{S}_{x-1}(\text{aq})$, where (g) denotes the mercury in the gas phase and (aq) denotes a species in water.

[025] The removal of mercury from the natural gas can be carried out in equipment known in the art, e.g., scrubbers or absorbers (absorption columns) packed with structural packing, although a bubble cup or sieve tray could also be employed. Exemplary equipment

is as described in Air Pollution Training Institute APTI 415, Control of Gaseous Emissions Chapter 5 – Absorption, March 2012, the relevant disclosure is included herein by reference. In another embodiment, the absorption is via the use of fiber film contactors as described in US Patent Publication Nos. US20100200477, US20100320124, US20110163008,
5 US20100122950, and US20110142747; and US Patent Nos. 7326333 and 7381309, which the relevant disclosures are included herein by reference.

[026] By absorption with a scrubbing liquid containing water-soluble sulfur compounds, mercury is extracted from the natural gas feed into the liquid phase, for a treated gas stream having a reduced mercury concentration of less than 50% of the mercury
10 originally present in one embodiment (at least 50% mercury removal); less than 10% of the original mercury level in a second embodiment (at least 90% removal); and less than 5% of the original level in a third embodiment (at least 95% removal). The mercury content in the treated natural gas will depend on the mercury content of the feed and the percent removal. The mercury content is reduced to below $10 \mu\text{g}/\text{Nm}^3$ in one embodiment, less than $1 \mu\text{g}/\text{Nm}^3$
15 in a second embodiment, and less than $0.1 \mu\text{g}/\text{Nm}^3$ in a third embodiment.

[027] The water for use as scrubbing liquid is non-potable water, which can be supplied at cold, heated, or ambient temperature. Depending on the location of the natural gas processing facility, the non-potable water can be any of connate water, aquifer water, seawater, desalinated water, oil fields produced water, industrial by-product water, and
20 combinations thereof. In one embodiment, the water stream consists essentially of produced water. The water for use as the scrubbing liquid can be the produced water from the reservoir producing the natural gas. In this embodiment, a mixture of natural gas and water from an underground reservoir is first separated generating a stream of natural gas to be treated for removal of mercury, and a stream of produced water which can be use for the scrubbing
25 liquid.

[028] In another embodiment for a reservoir that produces dry gas only or with very little water in the produced fluid extracted from the production well, the water for use as the scrubbing liquid can be from a water storage / treatment facility connected to the natural gas processing facility, wherein produced water, seawater, etc., is recovered and prepared with
30 the addition of water-soluble sulfur compounds to generate a scrubbing solution for mercury removal.

[029] The amount of water-soluble sulfur compounds needed is determined by the effectiveness of sulfur compound employed. The amount of sulfur used is at least equal to the amount of mercury in the crude on a molar basis (1:1), if not in an excess amount. In one

embodiment, the molar ratio ranges from 5:1 to 10,000:1. In another embodiment, from 10:1 to 5000:1. In yet another embodiment, a molar ratio of sulfur additive to mercury ranging from 50:1 to 2500:1. A sufficient amount of the sulfur compound is added to the scrubbing liquid for a sulfide concentration ranging from 0.05 M to 10M in one embodiment; from 0.1M to 5M in a second embodiment; from 0.3M to 4M in a third embodiment; and at least 0.5M in a fourth embodiment. The concentration of sulfur in the scrubbing water ranges from 50 to 200,000 ppmw in one embodiment, and from 100 to 100,000 ppmw in a second embodiment; and from 100 to 50,000 ppmw in a third embodiment. The amount of scrubbing solution provided to the absorber in one embodiment is sufficient to wet the packings and distribute the sulfur compounds for reaction with the mercury.

[030] The pH of the water stream containing the sulfur compound is adjusted to a pre-selected pH prior to the absorber to at least 8 in one embodiment; at least 9 in a second embodiment; at least 10 in a third embodiment; and at least 11 in a fourth embodiment. The pH can be adjusted with the addition of amines such as monoethanol amine, ammonia, diethanol amine, or a strong base such as sodium hydroxide, potassium hydroxide, etc.

[031] The scrubber is operated at a temperature of at least 50°C in a second embodiment, and in the range of 20-90°C in a third embodiment. The operating temperature is as high as practical in one embodiment, as HgS precipitation can be enhanced by increasing the temperature of the scrubbing solution. The operating pressure is sufficient to prevent the scrubbing solution from boiling in one embodiment, and in the range of 100 to 7000 kPa in a second embodiment. The scrubber in one embodiment is first purged with an inert gas to remove oxygen, preventing oxidation of the sulfur species. Depending on the equipment employed for the scrubbing operation and the packing materials used, the superficial gas velocity is less than 5 cm/s in one embodiment, and in the range of 2-30 cm/s in a second embodiment.

[032] In one embodiment of the operation of the absorber column, recirculation pumps are used to recirculate the scrubbing liquid from the chamber of the absorber (bottom outlet) into spray headers located in an upper portion of the column for spraying into the gas flowing upwards in the column. The effluent stream exiting the column contains mercury extracted from the natural gas in various form, e.g., precipitates and / or water-soluble mercury compounds. A portion of the mercury-containing sulfur depleted scrubbing liquid is withdrawn on a continuous or intermittent basis as a purge stream for subsequent treatment / disposal. The rest of the scrubbing liquid is recirculated back to the absorber column as a recirculating stream. The ratio of the purge stream to the recirculating stream in one

embodiment is sufficient to prevent solid HgS from precipitating in the mercury-containing sulfur-depleted scrubbing liquid.

[033] A fresh source of sulfur compound is provided to the column on a continuous basis as a make-up source of sulfur, which can be added to the absorber as a separate make-up stream, or directly to the recirculating stream. In one embodiment, the make-up source of sulfur comprises a sulfide containing salt, e.g., sodium sulfide, which is added to the recirculating stream. The amount of make-up stream is sufficient to provide the sulfur needed for the removal of mercury from the natural gas, replacing the sulfur that is removed with the purge stream.

[034] In one embodiment, the make-up stream containing the fresh source of water-soluble sulfur species can be generated on-site as part of the mercury removal unit. In one embodiment, polysulfide is synthesized by dissolving elemental sulfur in a sulfidic solution, e.g., a sulfide reagent such as Na₂S, generating Na₂S_x for the make-up stream. The reactor for the generation of the polysulfide can be at a temperature higher than the temperature of the absorber column, e.g., at least 10°C higher, generating polysulfide at a higher temperature for greater dissolution of the sulfide in the scrubbing solution.

[035] The water for use in the make-up stream can be produced water from the formation, after separation from the produced fluid such as natural gas and / crude oil in the mixture extracted from the production well.

[036] After the scrubbing tower, the natural gas is optionally fed into a dehydrator for water removal. The dried natural gas with reduced mercury concentration can be fed to heat exchangers and other additional equipment necessary, for liquefying the gas prior to transporting. In another embodiment, the treated gas is directed to a fabric filter or an electrostatic precipitator (ESP) for removal of any particulates from the treated gas prior to liquefaction.

[037] In one embodiment, at least a portion of the purge stream containing mercury is disposed by injection underground, e.g., into a depleted reservoir. In another embodiment, the purge stream containing mercury can be first treated before recycling or disposal according to safe environmental practices.

[038] The mercury removal unit and process described herein may be placed in the same location of a production facility, i.e., subterranean hydrocarbon producing well, or placed as close as possible to the location of the well. In another embodiment, the mercury removal equipment is placed on a floating production, storage and offloading (FPSO) unit. A FPSO is a floating vessel for the processing of hydrocarbons and for storage of oil. The

FPSO unit processes an incoming stream of crude oil, water, gas, and sediment, and produce a shippable product with acceptable properties including levels of heavy metals such as mercury, vapor pressure, basic sediment & water (BS&W) values, etc.

[039] Figures Illustrating Embodiments: Reference will be made to the figures with block diagrams schematically illustrating different embodiments of a mercury removal unit (MRU) and process for the removal of mercury from natural gas.

[040] As illustrated in Figure 1, a mixture 101 of produced water and mercury containing natural is extracted from an underground reservoir 100. The mixture is separated in a gas-water separator 20 to recover a mercury-containing gas 21 and produced water 22. The mercury-containing gas is processed in absorber 10, where it flows upwards in contact with a scrubbing liquid 13 containing a water soluble sulfur compound, e.g., a polysulfide-containing solution which flows downwards. In the column, at least a portion of the mercury in the mercury-containing gas is transferred to the scrubbing solution, generating a treated gas 11 with reduced mercury levels along with a mercury-containing sulfur-depleted scrubbing solution 12.

[041] A portion of the mercury-containing sulfur-depleted scrubbing solution is withdrawn as a purge stream 15, and disposed by injection into the underground formation 100. As shown, the produced water 22 is used as the scrubbing liquid for the removal of mercury. Produced water 22 is mixed with a concentrated solution of polysulfur species 14 for a makeup stream which is blended with the mercury-containing sulfur-depleted polysulfide solution 12, forming the scrubbing feed 13 to the column.

[042] It should be noted that crude oil can be produced along with natural gas as part of the produced fluid from an underground reservoir, and that not all of the produced water recovered from a reservoir (after gas / liquid separation) is needed for use in the scrubbing solution.

[043] Figure 2 illustrates another embodiment of the invention, wherein the polysulfide species for the scrubbing solution is generated on-site as part of the MRU. The on-site generation can reduce operating costs by generating polysulfide from less expensive sources such as elemental sulfur and sulfide reagents. As shown, a portion of the mercury-containing sulfur depleted polysulfide solution 12 is recycled to the absorber 10, another portion is optionally recycled by injection to formation directly (not shown), and a portion is sent to a filtration system 40 for the removal of any solid HgS precipitates. The mercury-containing sulfur-depleted polysulfide filtrate 41 with reduced contents of solid HgS can be

used in the polysulfide synthesis reactor 30. In the reactor, elemental sulfur 32 reacts with sodium sulfide in solution 31, generating the makeup sodium polysulfide concentrate stream 14.

CLAIMS

1. A method for removing a trace amount of mercury in a natural gas feed, comprising:

recovering a mixture of produced water and mercury-containing natural gas from an underground reservoir;

separating the mercury-containing natural gas from the produced water;

scrubbing the mercury-containing natural gas with an aqueous solution in an absorber, wherein the aqueous solution comprises a water-soluble sulfur compound to react a least a portion of the mercury in the natural gas with the water-soluble sulfur compound to produce a treated natural gas with a reduced concentration of mercury and a mercury-containing sulfur-depleted solution,

removing at least a portion of the mercury-containing sulfur-depleted solution as a purge stream;

recirculating at least a portion of the mercury-containing sulfur-depleted solution as a recirculating stream; and

providing a fresh source of water-soluble sulfur compound as a feed to the absorber for reaction with the mercury in the natural gas.

2. The method of claim 1, further comprising injecting at least a portion of the purge stream into an underground reservoir.

3. The method of claim 1, wherein less than 1% of the mercury is scrubbed from the natural gas as a solid mercury complex.

4. The method of claim 1, wherein providing a fresh source of water-soluble sulfur compound comprises reacting elemental sulfur with a sulfidic solution.

5. The method of claim 4, wherein the sulfidic solution comprises Na_2S .

6. The method of claim 4, wherein the produced water separated from the mercury containing natural gas is added to the reaction of elemental sulfur with a sulfidic solution to provide a fresh source of water-soluble sulfur compound.

7. The method of claim 1, wherein the produced water separated from the mercury containing natural gas is added to the fresh source of water-soluble sulfur compound as a feed to the absorber.

5 8. The method of claim 1, further comprising filtering the mercury containing sulfur-depleted solution prior to recirculating at least a portion of the mercury containing sulfur-depleted solution.

9. The method of claim 8, further comprising adding the filtered mercury
10 containing sulfur-depleted solution to a fresh source of water-soluble sulfur compound.

10. The method of claim 8, further comprising adding the filtered mercury containing sulfur-depleted solution to a reaction of elemental sulfur with a sulfidic solution to provide a fresh source of water-soluble sulfur compound as a feed to the absorber.

15 11. The method of claim 1, wherein the water-soluble sulfur compound is selected from sodium hydrosulfide, potassium hydrosulfide, ammonium hydrosulfide, sodium sulfide, potassium sulfide, calcium sulfide, magnesium sulfide, ammonium sulfide, and mixtures thereof.

20 12. The method of claim 1, wherein the aqueous solution containing a water-soluble sulfur compound comprises any of sulfidic water, sulfidic waste water, kraft caustic liquor, kraft carbonate liquor, and combinations thereof.

25 13. The method of claim 1, wherein at least 50% of mercury is removed from the natural gas.

14. The method of claim 13, wherein at least 90% of mercury is removed from the natural gas.

30 15. The method of claim 1, wherein the treated natural gas contains less than 10 $\mu\text{g}/\text{Nm}^3$ mercury.

16. The method of claim 15, wherein the treated natural gas contains less than 1 $\mu\text{g}/\text{Nm}^3$ mercury.

17. The method of claim 16, wherein the treated natural gas contains less than 0.1 $\mu\text{g}/\text{Nm}^3$ mercury.

18. The method of claim 1, wherein the aqueous solution comprising a water-soluble sulfur compound has a pH of at least 8.

19. The method of claim 1, wherein the mercury-containing natural gas is scrubbed with an aqueous solution comprising a water-soluble sulfur compound in a molar ratio of 5:1 to 10,000:1 of sulfur to mercury in the natural gas.

20. The method of claim 1, wherein the mercury-containing natural gas is scrubbed with an aqueous solution comprising a water-soluble sulfur compound having a concentration of sulfur in the aqueous solution from 50 to 20,000 ppmw.

21. The method of claim 1, wherein the method is carried out on a floating production, storage and offloading (FPSO) unit.

22. A method for removing a trace amount of mercury in a natural gas feed, comprising:

recovering a mercury-containing natural gas from an underground reservoir;

scrubbing the mercury-containing natural gas with an aqueous solution in an absorber, wherein the aqueous solution comprises a water-soluble sulfur compound to react a least a portion of the mercury in the natural gas with the water-soluble sulfur compound to produce a treated natural gas with a reduced concentration of mercury and a mercury-containing sulfur-depleted solution,

removing at least a portion of the mercury containing sulfur-depleted solution as a purge stream;

recirculating at least a portion of the mercury containing sulfur-depleted solution as a recirculating stream; and

providing a fresh source of water-soluble sulfur compound as a feed to the absorber for reaction with the mercury in the natural gas.

23. The method of claim 22, wherein the aqueous solution is non-potable water selected from connate water, aquifer water, seawater, desalinated water, oil field produced water, industrial by-product water, and combinations thereof.

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24. The method of claim 22, wherein providing a fresh source of water-soluble sulfur compound comprises reacting elemental sulfur with a sulfidic solution.

25. The method of claim 22, wherein providing a fresh source of water-soluble sulfur compound comprises adding elemental sulfur and a sulfidic solution to the recirculating stream.

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