Process, Method, and System for Removing Heavy Metals from Fluids

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims benefit under 35 USC 119 of US Provisional Patent Application Nos. 61/697867 and 61/697855 with a filing date of September 7, 2012.

TECHNICAL FIELD

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

BACKGROUND

[002] Exploration and production of deeper, lower quality oil and gas reserves has challenged refiners and gas processors with feedstocks having significantly higher sulfur content, increasing corrosion risks and other undesired impurities. Amine units for amine gas treating (also known as "gas sweetening" or "acid gas removal") refers to a group of processes or units that use aqueous solutions of various alkanolamines (commonly referred to simply as amines) for the removal of H_2S and CO_2 from gases. The removal is driven by either required product specification, e.g., natural gas that contains less than 4 ppm H_2S, or by environmental permission requirements, and/or by the minimization of corrosion problem of process equipment.

[003] Amine treating units are commonly used in refineries as well as in petrochemical plants, natural gas processing plants, and other industries, for the removal of H_2S and CO_2 from gases. When volatile mercury is present in the gases to the amine units, it will appear in the products from the units, e.g., the sweetened gas (after removal of H_2S and CO_2) and rich amine containing H_2S and CO_2. Mercury, CO_2 and H_2S are to be removed from the sweetened gas. Mercury in these products can impact the operations downstream from the amine units.

[004] Glycol dehydrators are sometimes used in to dry natural gas, e.g., the sweetened gas from the amine unit, to specifications. The glycol absorbs the moisture forming a dry gas. Wet glycol is recycled by vaporizing water at low pressure and at elevated temperatures. Methane and other hydrocarbons are somewhat soluble in triethylene glycol, particularly at high pressure and ambient temperature. These hydrocarbons are vaporized from the glycol as the pressure is reduced and temperature is increased. If mercury

is present in the natural gas, a portion can appear in either the dry gas or vent to the atmosphere from glycol dehydrators.

[005] Absorbers have been used in the prior art to remove heavy metals such as mercury from the sweetened gas to specifications, e.g., 0.1 $\mu g/m^3$, with the use of an adsorbent bed of carbon, zeolite, or supported metals known in the art. The adsorbents are rather expensive and require disposal as a hazardous waste, or shipped to a re-processing facility.

[006] There is still a need for improved methods and systems to remove volatile mercury from fluids such as natural gas, vent gas or flue gas, allowing for the optimization of plant operations to minimize the equipment corrosion, mercury emission and any HES risks associated with mercury.

SUMMARY

[007] In one aspect, the invention relates to a method to remove mercury from a gas feed. The method comprises: providing a gas feed to a dehydrator, the gas feed containing acid gases, a first concentration of volatile mercury and water, contacting the gas feed with a glycol solution containing a complexing agent in the dehydrator, generating a dehydrated gas stream with a reduced concentration of water and mercury; and wherein mercury and water are concurrently removed from the gas feed for a rich glycol containing at least 50% of the volatile mercury in the gas feed as non-volatile mercury. In one embodiment, the method further comprises: heating the rich amine solution containing mercury and acid gases in a solvent regeneration process employing at least a stripper and a reboiler, generating a lean amine containing non-volatile mercury for recycle in an absorber to remove acid gases.

[008] In a second aspect, a method for removing a trace amount of mercury in a natural gas feed is provided. The method comprises: providing a gas feed containing acid gases, a first concentration of volatile mercury and water, contacting the gas feed with a glycol solution in a dehydrator, the glycol solution containing a complexing agent for the glycol solution to concurrently remove the volatile mercury and water from the gas feed, for a rich glycol containing at least 50% of the volatile mercury in the gas feed as non-volatile mercury, generating a dehydrated gas stream having a reduced concentration of water and mercury, removing the non-volatile mercury from the rich glycol by at least one of filtration, centrifugation, precipitation, stripping, distillation, adsorption, ion exchange, electrodialysis, a hydrocarbon steam and separation step, and combinations thereof, generating a recycled

glycol stream having a reduced concentration of mercury of less than 50% of the non-volatile mercury in the rich glycol.

[009] In a third aspect, a method of removing mercury from a gas feed is provided, the method comprises the steps of: contacting the gas feed with an absorption solution in an absorber, the absorption solution comprising lean amine and a first complexing agent, wherein the absorption solution concurrently removes mercury and acid gases from the gas feed generating a rich amine solution containing mercury and acid gases and a treated gas stream containing water vapor and a reduced concentration of acid gases and a second concentration of mercury, and wherein the second concentration of mercury is less than 50% of the first concentration of mercury; contacting the treated gas stream with a glycol solution in a dehydrator, wherein the glycol solution contains a second complexing agent for the glycol solution to concurrently remove mercury and water vapor from the treated gas stream, generating a rich glycol containing non-volatile mercury and a dehydrated gas stream with a reduced concentration of water and a third concentration of mercury, wherein the third concentration of mercury is less than 50% of the second concentration of mercury.

[010] In yet another aspect, a method for removing mercury from a gas feed is provided. The method comprises: providing a gas feed containing a first concentration of volatile mercury and acid gases; contacting the gas feed in an absorber with an absorption solution comprising lean amine and a first complexing agent comprising volatile cations selected from ammonium polysulfide, amine polysulfides, and sulfanes, wherein the absorption solution concurrently removes mercury and non-volatile mercury and acid gases from the gas feed; generating a rich amine solution containing acid gases and at least 50% of the volatile mercury in the gas feed as non-volatile mercury and a treated gas stream with a second concentration of acid gases and mercury.

DRAWINGS

[011] Figure 1 is a diagram illustrating an embodiment of a gas processing plant.

[012] Figure 2 is a diagram illustrating an embodiment of an amine unit.

DETAILED DESCRIPTION

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

[014] "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 $\mu g/Nm^3$ to up to 30,000 $\mu g/Nm^3$.

[015] "Volatile mercury" refers to mercury that is present in the gas phase of well gas or natural gas. Volatile mercury is primarily elemental mercury (Hg^0) but may also include some other mercury compounds (organic and inorganic mercury species).

[016] "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 an approximate stoichiometric equivalent of one mole of sulfide ion per mole of mercury ion. Mercury sulfide is not appreciably volatile, and not an example of volatile mercury. Crystalline phases include cinnabar, metacinnabar and hypercinnabar with metacinnabar being the most common.

[017] "Sulfane" refers to a hydrogen-sulfur complex of the formula H_2S_x, where x >= 2. For purposes of this disclosure, hydrogen sulfide is not a sulfane.

[018] "Wet gas" refers to natural gas that contains less methane (e.g., less than 85%) and more ethane and other more complex hydrocarbons.

[019] "Amine" refers to amines for use in gas treating, including but not limited to monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), aminoethoxyethanol(diglycoamine) (DGA), triethanolamine (TEA), diisopropylamine (DIPA), proprietary amines known in the art and commercially available, and mixtures thereof. The most commonly used amines are the alkanolamines such as MEA, DEA, and MDEA.

[020] "Acid gas" refers to the product gas from an amine unit that contains acidic impurities, e.g., H_2S, CO_2, SO_2 and SO_2 (SO_x), NO and NO_2 (NO_2), chlorine, etc. In one embodiment, the acid gas is chemically absorbed in the liquid (solution or fluid). In another embodiment, the acid gas is dissolved in the liquid, e.g., an aqueous amine solution.

[021] "Amine unit" refers to a process or a group of processes using aqueous solutions of various amines to remove hydrogen sulfide (H2S) and carbon dioxide (CO2) from gases. Amine unit can be located in refineries, petrochemical plants, natural gas processing plants and other industries. It is also known as "gas sweetening" or "acid gas removal" unit.

[022] "Acid gas" refers to natural gas or any other gas mixture containing hydrogen sulfide (H_2S), carbon dioxide (CO_2), or similar acidic gases.

[023] "Sour gas" refers to natural gas or flue gas prior to treatment, which contains acid gas and trace amounts of mercury as volatile mercury.

[024] "Rich amine" refers to the aqueous amine solution containing absorbed acid gas.

[025] "Lean amine" refers to the amine after being regenerated by steam stripping to remove the absorbed acid gases and produce regenerated amine solution for use in the absorber to treat sour gas.

[026] "Sweetened gas" or "sweet gas" refers to a sour gas stream after treatment in an amine unit, after absorption / removal of acid gas by an amine solution, and flows overhead from the absorber (scrubber or amine contactor).

[027] In the sections that follow, the reference to "amine" is by way of exemplification only for a solute in which an acid gas is chemically absorbed and can be subsequently released. Similarly, the reference to "H_2S" is by way of exemplification only for an acid gas that can be chemically absorbed in a liquid system, e.g., amine, sour water, and can be subsequently released, and does not exclude other acid gases or mixtures thereof, e.g., mixture of H_2S and CO_2, mixture of SO_2, NO_2, chlorine.

[028] 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 is present in natural gas as volatile mercury, including elemental mercury Hg^0, in levels ranging from about 0.01 $\mu g/Nm^3$ to 5000 $\mu g/Nm^3$. The mercury content may be measured by various conventional analytical 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. If the methods differ, ASTM D 6350 is used to measure the mercury content.

[029] The invention relates to an improved method and a system to remove heavy metals such as mercury present in natural gas feedstock, e.g., wet gas feed, in a gas processing plant. The term "gas processing plant" may be used interchangeably with "gas production facility." The mercury removal is carried out in the amine treating unit and / or the gas dehydration unit of with the use of a complexing agent.

[030] Gas Processing Plant: Figure 1 is a schematic diagram illustrating the various processes within a typical natural gas processing plant. Natural gas collected from gas wells is first processed in step 10 for the removal of liquid water and natural gas condensate, generating a gas feed which typically contains acid gases and water vapor, which is typically

referred to as a sour gas. The initial water removal step can be done at the processing plant, or it can be at the collection point.

[031] In amine unit 30, the sour gas feed is purified with the removal of acid gases by absorption with an amine solution, generating a gas stream with reduced concentration of acid gases. The acid gases can be routed into a sulfur recovery unit 15 to recover elemental sulfur. The residual gas is processed in the tail gas treating unit 40.

[032] The sweetened gas having a reduced concentration of acid gases is routed to dehydrator 45, where a solution such as glycol is used to remove water vapor by absorption. In the mercury removal unit (MRU) 50, mercury is then removed by adsorption using activated carbon or other adsorbents known in the art. After the MRU, nitrogen is optionally removed in process step 60 in a cryogenic or adsorption process. The residue gas from the natural gas liquid (NGL) recovery process 20 is the final purified gas which can be pipelined to the end-user market, or optionally sent to a fractionation train 25 with distillation towers to generate various products such as propane, butane, C5+, etc. The various gases can also be sweetened in unit 26 with the removal of mercaptans, prior to being pipelined to the end-user market.

[033] In terms of the average distribution of mercury in a typical gas processing plant as shown in Figure 1, it has been shown that out of 100% of mercury entering the plant, 90% goes to the amine unit as sour gas feed. Of this 90%, proportionally 70% goes to the sour gas product stream (e.g., to the sulfur unit), and 30% stays in the sweetened gas stream. The sweetened gas stream goes to the gas dehydration unit, e.g., a glycol dehydrator, wherein proportionally 20% leaves with the vented moisture stream, and 80% leaves in the dry gas. If not removed with a MRU, mercury can appear in other process streams. It has been recommended that mercury be removed upstream of the process steps in a gas processing plant. The invention relates to the removal of heavy metals such as mercury from feed to a gas processing plant. In one embodiment as illustrated in Figure 1 with the mercury removal unit (MRU) being made optional (as dotted lines), mercury removal is carried out in the amine unit concurrent with the removal of acid gas from the sour gas feed with the addition of a complexing agent to the amine solution. In another embodiment, mercury removal is carried out concurrently with the removal of water in a gas dehydration unit (in addition to or instead of the amine unit), with the addition of a complexing agent to the glycol solution. The complexing agent for the mercury removal can be 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.

[034] Mercury Removal in Amine Unit: In one embodiment for mercury removal in an amine treating unit, (lean) amine scrubbing solution is used to remove acid gases such as hydrogen sulfide (H_2S) and carbon dioxide from the sour feed steam in an absorber, generating a rich amine stream. A sufficient amount of a complexing agent is added to the absorber for the removal of mercury concurrently with the removing of acid gases from the sour feed stream by the amine scrubbing solution. The complexing agent coverts at least a portion of the volatile mercury in the sour gas feed into a non-volatile form, extracted from the gas phase into the amine scrubbing solution.

[035] The amount of amine in the scrubbing solution feed to the absorber depends on the amount of acid gases in the natural gas to be treated (acid loadings), and based on the moles of H_2S (and / or CO_2) per mole of amine in solution. In one embodiment, the ratio of absorbed acid gases to amine ranges from 0.3 to 0.9. Examples of amines suitable for use in the scrubbing solution include but are not limited to MEA, DEA, TEA, DIPA, MDEA, and mixtures thereof. The concentration of amines in the scrubbing solution varies depending on the amine type, and the acid gases for removal, e.g., H_2S and CO_2 or removing CO_2 only, etc. The amine concentration (as wt. % of pure amine in the aqueous solution) ranges from 15-65% in one embodiment, from 20-55% in a second embodiment, and from 25-45% in a third embodiment. In one embodiment, the scrubbing solution further comprises absorption promoters and other additives, e.g., piperazine.

[036] The complexing agent is added to the lean amine feed to the absorber in one embodiment; as a separate feed stream to the absorber in a second embodiment; and as the same feed with the make-up water stream to the absorber in a third embodiment. The complexing agent is added in an amount of less than 5 vol. % of total scrubbing solution in the amine absorber in one embodiment; less than 3 vol. % in a second embodiment; less than 1 vol. % in a third embodiment; and less than 0.5 vol. % in a third embodiment.

[037] In one embodiment to prevent contamination of the amine in the amine absorber, the complexing agent contains little if any non-volatile alkali metals or alkali earth cations (none purposely added), e.g., with no sodium polysulfide or other sodium salts, as the sodium cation will accumulate in the amine recycle and degrade its performance. In one embodiment, the complexing agent is selected from the group of volatile cations, which can be removed in the regenerator. Examples of volatile cations include but are not limited to ammonium, amines and hydrogen cations, e.g., ammonium polysulfide, amine polysulfides, and sulfanes.

[038] Mercury Removal in Dehydrator Unit: In another embodiment, mercury removal is carried out in the dehydrator unit ("dehydrator") in addition to, or in place of mercury removal in the amine unit. The dehydrator can be tray columns or packed columns in one embodiment. In a dehydrator, a liquid desiccant dehydrator such as glycol serves to absorb water vapor from the gas stream. Glycol has a chemical affinity for water, upon contact with a stream of natural gas that contains water in a dehydrator (e.g., a contactor, an absorber, etc.), will serve to 'steal' the water out of the gas stream. Upon exiting the dehydrator, the glycol stream containing water (and mercury) is referred to as "rich glycol."

[039] The glycol solution typically involves either diethylene glycol (DEG) or triethylene glycol (TEG). In one embodiment, the glycol solution is employed in a concentration ranging from 99.1% up to 99.95% wt, in an amount sufficient to strip water at a rate of 0.5 – 6 scf of gas feed / gallon of glycol, for a dehydrated gas having water specifications of less than 1 lb. / MMSCF (Million Standard Cubic Feet).

[040] The dehydrated gas having been stripped of most of its water content has a concentration of less than 100 $\mu g/Nm^3$ mercury in one embodiment; less than 10 $\mu g/Nm^3$ mercury in a second embodiment; less than 1 $\mu g/Nm^3$ in a third embodiment; and less than 0.1 $\mu g/Nm^3$ mercury in a fourth embodiment. The dehydrated gas is further processed, e.g., nitrogen injection, NGL recovery, fractionation, etc.

[041] In one embodiment, the complexing agent is added as part of the glycol solution feed to the dehydrator. In another embodiment, it is added as a separate feed stream to the dehydrator. The complexing agent is added in an amount of less than 5 vol. % of total glycol solution to the dehydrator in one embodiment; less than 3 vol. % in a second embodiment; less than 1 vol. % in a third embodiment; and less than 0.5 vol. % in a third embodiment.

[042] Complexing Agent: "Complexing agent" refers to a material or compound that is capable of extracting volatile mercury in natural gas into the liquid phase, forming non-volatile mercury complexes. Examples of non-volatile mercury complexes include HgS and soluble mercury sulfur compounds (e.g. $HgHS_2^-$ or HgS_2^{2-}).

[043] Examples of complexing agents include but are not limited to water-soluble sulfur species, e.g., sulfides, hydrosulfides, and polysulfides, for extracting mercury in natural gas into the aqueous phase as precipitate (e.g., HgS) or soluble mercury sulfur compounds (e.g. HgS_2^{2-}). Examples of water-soluble sulfur compounds include amine polysulfides, sodium hydrosulfide, potassium hydrosulfide, ammonium hydrosulfide, sodium sulfide, potassium sulfide, calcium sulfide, magnesium sulfide, ammonium sulfide, sodium

thiocarbamate, sodium dithiocarbamate, ammonium thiocarbamate, ammonium dithiocarbamate, and mixtures thereof. Aqueous source containing water-soluble sulfur species can be any of purchased or produced reagent solutions, sulfidic water, sulfidic waste water, kraft caustic liquor, kraft carbonate liquor, etc.

[044] Other examples of complexing agents that can be used for the removal of mercury from the amine unit includes mercaptans, organic polysulfides (compounds of the general formula R-S_x-R' where x is greater than 1 and R and R' are alkyl or aryl groups), sulfanes and combinations thereof.

[045] The amount of complexing agents to be added to the amine scrubbing solution and / or the glycol solution is determined by the effectiveness of complexing agent employed. The complexing agent to be added to the amine scrubbing solution can be the same or different from the complexing agent added to the glycol solution. The amount is at least equal to the amount of mercury in the gas 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. In one embodiment with the use of a water-soluble sulfur compound as a scrubbing agent, a sufficient amount of the complexing agent is added to the amine scrubber 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. If the mercury complexing agent is an organic polysulfide, sulfane or mercaptan, the moles of complexing agent are calculated on the same basis as the amount of sulfur present.

[046] In one embodiment, the complexing agent is an inorganic polysulfide such as sodium polysulfide, for an extraction of mercury from the natural gas according to equation: $Hg\ (g) + Na_2S_x\ (aq) + H_2O \rightarrow HgS_2H^-\ (aq) + Na_2S_{x-2}\ (aq) + OH^-\ (aq)$, where (g) denotes the mercury in the gas phase, and (aq) denotes a species in water. The charges are balanced by other species. Solid HgS is not formed and the mercury remains in solution as an anionic species. In another embodiment, the complexing agent is a compound with a relatively high boiling point, e.g., not too volatile and above 100°C in one embodiment and above 125°C in another embodiment. If not, the complexing agent would be lost in the stripping operation for the removal of adsorbed acid gas from the acid gas scrubbing solution. In yet another embodiment the complexing agent is sodium sulfide. Sodium sulfide and other complexing agents may promote the removal of mercury from gas streams containing high CO_2 concentrations but low H_2S concentrations. In yet another embodiment the complexing agent

is hydrogen sulfide (H_2S) or a combination of hydrogen sulfide and one or more of the above-mentioned complexing agents.

[047] In one embodiment, the complexing agent is added to the absorber (scrubber) and / or the contactor (dehydrator), allowing the extraction of volatile mercury from the sour gas feed into the scrubbing solution of rich amine or the glycol solution, for a sweetened gas stream having a reduced concentration of acid gas as well as a mercury concentration of less than 50% of the mercury originally present in one embodiment (at least 50% mercury removal). In another embodiment, the sweetened gas contains less than 10% of the original mercury level (at least 90% removal). In a third embodiment, less than 5% of the original level (at least 95% removal). The mercury content in the sweetened gas stream will depend on the mercury content of the feed and the percent removal. The mercury content is reduced to below 100 $\mu g/Nm^3$ in one embodiment, less than 10 $\mu g/Nm^3$ in a second embodiment, less than 1 $\mu g/Nm^3$ in a third embodiment, and less than 0.1 $\mu g/Nm^3$ in a fourth embodiment.

[048] In one embodiment with the addition of complexing agent to the dehydrator, the glycol solution leaving the dehydrator unit contains at least 50% of the mercury initially present in the gas feed (to the dehydrator). The solution contains at least 75% of the mercury originally present in a second embodiment; and at least 90% in the third embodiment.

[049] Optional additives: In one embodiment in addition to the complexing agent, at least one of an anti-foam and / or a demulsifier is added to the glycol solution. As used herein, the term anti-foam includes both anti-foam and defoamer materials, for preventing foam from happening and / or reducing the extent of foaming. Additionally, some anti-foam material may have both functions, e.g., reducing / mitigating foaming under certain conditions, and preventing foam from happening under other operating conditions. Anti-foam agents can be selected from a wide range of commercially available products such as silicones, e.g., polydimethyl siloxane (PDMS), polydiphenyl siloxane, fluorinated siloxane, etc., in an amount of 1 to 500 ppm.

[050] In one embodiment, at least a demulsifier is added in a concentration from 1 to 5,000 ppm. In another embodiment, a demulsifier is added at a concentration from 10 to 500 ppm. In one embodiment, the demulsifier is a commercially available demulsifier selected from polyamines, polyamidoamines, polyimines, condensates of o-toluidine and formaldehyde, quaternary ammonium compounds and ionic surfactants. In another embodiment, the demulsifier is selected from the group of polyoxyethylene alkyl phenols, their sulphonates and sodium sulphonates thereof. In another embodiment, the demulsifier is a polynuclear, aromatic sulfonic acid additive.

[051] In another embodiment, in addition to the complexing agent and optionally at least a demulsifier / anti-foam agent, an oxygen scavenger is preferably added to any of the glycol solution, the amine solution, and the absorbent. The oxygen scavenger may be present in an amount ranging from 0.001 to 1 wt. %, based on the weight of the glycol solution, lean amine, or absorbent. As dissolved oxygen in the amine or glycol storage tank would lead to corrosion of iron surfaces, or react with the feed gas making heat stable salts which are difficult to separate in the regeneration step, the oxygen scavenger removes traces of dissolved oxygen present, minimizing corrosion impact.

[052] Examples of oxygen scavengers include bisulfites, metabisulfites, hydrazine salts, hydroxylamine salts, guanidine salts, N,N-Diethylhydroxylamine, oximes, dithionites, ascorbic acid, and isoascorbic acid. The anion salts of these oxygen scavengers can be chlorides, sulfates, and other suitable anions. The cations associated with the oxygen scavengers can be sodium, potassium or volatile cations as described for the complexing agents. Volatile cations are preferred when they are used in an amine unit.

[053] A compatible oxygen scavenger is one that does not react with the mercury complexing agent and reduce its effectiveness for mercury capture. Examples of oxygen scavengers that react with a complexing agent such as polysulfide include bisulfites and metabisulfite. In one embodiment, the oxygen scavenger is selected for compatibility with the mercury complexing agent. Examples of compatible oxygen scavengers include: hydrazine salts, guanidine salts, N,N-Diethylhydroxylamine, oximes, dithionites, ascorbic acid, and isoascorbic acid.

[054] Recovery / Regeneration of Amine Solution: In one embodiment for the concurrent mercury removal from the absorber, the resultant rich amine containing non-volatile mercury and acid gases from the absorber is routed into the regenerator. In the regenerator ((a stripper with a reboiler), a "lean" amine containing non-volatile mercury is regenerated for recycle / subsequent reuse in the absorber to remove acid gases. With the regeneration of the lean amine for use in the absorber unit, mercury will gradually build up over time in the system, along with other known solid and ionic materials which accumulate in acid gas scrubbing solutions and are commonly known as “heat stable salts” or HSS.

[055] In one embodiment, the regenerator overhead gas undergoes further processing in a sulfur unit, e.g., to make sulfuric acid from the acid gas H_2S, or combusted for subsequent venting. Removal of the mercury in the amine absorber gives an acid gas product with reduced mercury. This enables the production of sulfuric acid, or elemental sulfur, with reduced mercury. In another embodiment, the regenerator overhead gas is first routed

through a condenser set up for the removal of water by condensation, then subsequently sent to a mercury removal unit (MRU) for the removal of mercury using processes and equipment known in the art.

[056] In one embodiment, a portion of the mercury-containing amine adsorbent can be continuously or intermittently purged from the amine unit / removed from the scrubber, and replaced with fresh amine. In yet another embodiment, other remediation actions include: a) the contaminated amine solution is purged (bled) on a continuous or intermittent basis and replaced with fresh amine; b) the entire inventory of amine is replaced; and c) reclaiming the solution. Reclaiming the solution to remove non-volatile mercury as removed from the natural gas feed to the amine unit can be done by a variety of processes and systems known in the art for the removal of heat stable salts, including but not limited to filtration, centrifugation, precipitation, reduction to elemental mercury followed stripping, distillation, adsorption, ion exchange, electrodialysis, or transfer to a hydrocarbon steam and separation, and combinations thereof.

[057] Recovery / Regeneration of Glycol Solution: In one embodiment after the concurrent removal of water and mercury in the dehydrator, the rich glycol bearing non-volatile mercury and water stripped from the natural gas, is put through a specialized boiler designed to vaporize only the water out of the solution. While water has a boiling point of 212°F, glycol does not boil until 400°F. This boiling point differential makes it relatively easy to remove water from the rich glycol, allowing it be reused in the dehydration process. Depending on the temperature of the distillation, e.g., below than 150°C, in one embodiment, mercury remains in the rich glycol bottom, with water going overhead in the glycol regenerator. In another embodiment with the distillation at a lower temperature, e.g., above 150°C, mercury can be removed from the bottom stream by techniques known in the art such as ion-exchange or sub-atmospheric pressure distillation.

[058] In another embodiment, residual mercury in the rich glycol can be removed by other processes known in the art, including but are not limited to filtration, centrifugation, precipitation, reduction to elemental mercury followed stripping, distillation, adsorption, ion exchange, or transfer to a hydrocarbon steam and separation, and combinations. Alternatively a portion of the mercury-containing rich glycol stream can be purged from the system. In one embodiment, the non-volatile mercury complexes can be removed from the regenerated / recycled rich glycol with the use of a mercury absorber containing a bed of sulphided absorbent as disclosed in US Patent No. 7435338, the relevant disclosure is incorporated herein by reference.

[059] Reference will be made to Figure 2 of a diagram schematically illustrating an embodiment of a system and process for removing mercury from natural gas / flue gas (sour gas feed) in an amine unit.

[060] In the Figure 2, (lean) amine scrubbing solution 5 is used to remove acid gases from a sour gas feed 1 in absorber 10 generating a rich amine stream. As shown mercury complexing agent 6 is added to the lean scrubbing solution feed to the scrubber. Although not shown, mercury complexing agent can also be provided as any of a separate feed stream, part of the make-up water stream to the scrubber, or combinations thereof. In one embodiment (not shown), different complexing agents can be added to the amine unit as different feed streams. The mercury complexing agent(s) can be added continuously or intermittently. Sweetened gas stream 4 with reduced concentration of acid gas and mercury is removed from the scrubber for subsequent treatment with a glycol dehydrator (not shown). The rich amine solution 31 undergoes steam stripping in stripper 30 for the removal of weak acids such as H_2S and CO_2 as overhead stream 34, wherein the stripping steam is generated from the amine solution in a reboiler 40 that takes its feed 32 from the regenerator tower below the steam stripping section.

[061] In one embodiment, at least a portion of non-volatile mercury in the rich amine is also released from the amine solution in stripper 30 and/or reboiler 40 as volatile mercury that leaves the process with overhead stream 34. In one embodiment (not shown), the overhead stream is directed to a mercury removal unit, e.g., a mercury removal adsorbent bed, for the mercury to be removed by adsorption.

[062] Condensing water from the effluent water / acid gas stream from the top of the regenerator helps minimize water usage. The steam stripping is not complete so residual H_2S and CO_2 remain in the lean amine solution, along with some non-volatile mercury. Many of the acids that are not removed by steam stripping are called Heat Stable Salts (HSS) or, unless otherwise neutralized, Heat Stable Amine Salts (HSAS). Examples include but are not limited to formate, acetate, glycolate, propionate, oxalate, chloride, sulfate, thiosulfate, and thiocyanate. In one embodiment, a portion of the HSS is removed with at least a portion of the non-volatile mercury in the bleed stream 41.

[063] EXAMPLES: The following illustrative examples are intended to be non-limiting.

[064] Example 1: The example was to investigate the retention of mercury in absorbents, a lean amine from a refinery acid gas scrubber was sampled and analyzed, and found to contain 250 ppb mercury. The lean amine was stripped with 300 cc/min nitrogen at

room temperature for one hour. It was found that the mercury content of the lean amine was not changed. The lean amine was centrifuged at 1500 RPM for 10 minutes. The mercury content of the supernatant was analyzed and found to be unchanged.

[065] In the next step, the lean amine containing mercury was filtered through a 0.2 μ filter. The mercury content of the supernatant was analyzed and found to be unchanged. It is concluded that the mercury which is present in the lean amine is a non-volatile mercury species, and is not present in the form of large particles. Since this mercury species was found in the lean amine from the commercial unit, it was not decomposed to solids or volatile elemental mercury by the temperatures, pressures and residence times in the amine regeneration process.

[066] Example 2: In this example, a sample of volatile Hg^0 was dissolved in white oil. This material is used to study the conversion of volatile mercury (Hg^0) into non-volatile mercury (HgS and other forms). First, five grams of elemental mercury Hg^0 was placed in an impinger at 100°C and 0.625 SCF/min of nitrogen gas was passed over through the impinger to form an Hg-saturated nitrogen gas stream. This gas stream was then bubbled through 3123 pounds of Superla® white oil held at 60-70°C in an agitated vessel. The operation continued for 55 hours until the mercury level in the white oil reached 500 ppbw by a Lumex™ analyzer. The simulated material was drummed and stored.

[067] Example 3: In this example, volatile mercury was shown to be absorbed by an aqueous solution of sodium polysulfide. A gas containing volatile mercury was prepared by sparging nitrogen through the white oil of Example 2 and this gas was bubbled through a 10 wt% solution of sodium polysulfide at room temperature. Mercury was transferred from the white oil to the polysulfide solution. The mercury content of the stripped oil was reduced below the limit of detection, while > 70% of the mercury initially in the oil was measured in the polysulfide solution. The extent of mercury capture in this bubbler experiment was not optimized, but the test showed the ability of complexing agents such as sodium polysulfide to capture mercury from a gas stream in a non-volatile form that is soluble in the polysulfide solution.

[068] Examples 4 – 16: To study the conversion of volatile mercury to non-volatile mercury, 20 ml of the material from Example 2 was placed in a series of vials. The mercury analysis of the samples averaged 359 ppbw, indicating some loss of mercury over the years that the sample was stored.

[069] A number of complexing agents were added to the vials and the initial mercury content was measured by Lumex™ mercury analyzer (detection limit of ~ 50 ppbw).

A nylon stopper equipped with a small vent hole was place on top of each vial. The vials were then heated in an oil bath overnight. In the morning each vial is shaken. Then each vial was purged with N_2 for one hour at 90°C with a gas flow to produce a steady bubbling (about 300 ml/hr). The final mercury content in each vial was then measured. The comparison of the initial and final mercury contents were used to judge the conversion of volatile elemental mercury into a non-volatile form (% Hg fixed). Results are summarized in Table 1. These complexing agents convert volatile mercury to a non-volatile form that would be removed from the treated gas when incorporated in an amine scrubber.

[070] Table 1

Example	Agent	Amount added	Temp. °C	Time, Hrs	Final Hg, ppbw	% Hg Fixed
4	None	0	90	24	0	0
5	Di-Phenyl disulfide	0.1 g	90	24	20	6
6	Di-n-propyl disufide	0.1 ml	90	24	0	0
7	Di-tert-nonyl polysulfide	0.1 ml	90	24	2	1
8	1-Hexyl mercaptan	0.1 ml	90	24	243	68
9	Thiophene	0.1 ml	90	24	0	0
10	None	0	90	72	0	0
11	Di-Phenyl disulfide	0.1 g	90	72	48	13
12	Di-n-propyl disufide	0.1 ml	90	72	0	0
13	Di-tert-nonyl polysulfide	0.1 ml	90	72	3	1
14	1-Hexyl mercaptan	0.1 ml	90	72	240	67
15	Thiophene	0.1 ml	90	72	23	7
16	1-Hexyl mercaptan	0.1 ml	20	24	10	3

[071] Example 17: In a three-neck flask with a Teflon stirrer (as glass reactor) was placed a 200 ml of solution of stannous chloride and sulfuric acid, for a concentration of 10% stannous chloride and 5% sulfuric acid. When mercury vapors were to be generated, 0.5 cc of a 209.8 ppm Hg solution of mercuric chloride in water was injected into the reactor via a septum. The stannous chloride rapidly reduced the mercury to elemental mercury. In the glass reactor was a line carrying 300 cc/min of nitrogen which bubbled in the reducing acidic stannous chloride solution. This was used to sweep the evolved elemental mercury to the downstream absorbers.

[072] The glass reactor was connected to two absorbers in series, each of which contained 200 ml of solution. The absorbers were equipped with a glass frit to produce small bubbles. The bubbles contacted the absorbing solution for about one second. The first absorber contained the test solution. The second contained 3% sodium polysulfide in water.

The 3% sodium polysulfide solution was prepared by dilution of a 30% solution of sodium polysulfide. This second absorber was a scrubber to remove the last traces of mercury from the nitrogen to provide mercury mass closures. Analysis of the exit gas from the second absorber by both Lumex and Jerome techniques found no detectable mercury.

[073] Samples of the liquids in the reactor and two absorbers and gas leaving the reactor and leaving the two absorbers were drawn at periodic intervals over a ninety-minute period and analyzed for mercury by Lumex. Mercury balances over 57 runs average 98.6%. The reaction of the mercury chloride in the three neck flask is rapid, and the elemental mercury was stripped rapidly as well. After a typical ninety-minute period the conversion and displacement of mercury in the reactor averaged 94%.

[074] The efficiency of the test solutions was calculated by comparing the amount of mercury taken up in the first reactor absorber to the amount taken up in both absorbers. If no mercury was taken up in the first reactor with the test solution, the efficiency was zero percent. If all the mercury was taken up in the first reactor, the efficiency was 100%. At the end of the experiments no evidence of precipitated HgS was observed in the absorbers. The solutions were clear.

[075] Examples 18 - 21: The experiments were to evaluate the Hg uptake in various solutions without the complexing agent according to the procedures in Example 17. The results are shown in Table 2. A 56% MEG solution was prepared by mixing 56 wt. % monoethylene glycol (MEG) in DI water. MEG solutions are typically used to prevent the formation of hydrates in gas pipelines that also contain water. A 45% MDEA solution was prepared by mixing 45 percent Methyl diethanolamine in DI water. MDEA solutions are typically used in acid gas scrubbers which remove hydrogen sulfide, carbon dioxide and other acidic gases from natural gas. 100% TEG was pure triethylene glycol. TEG is used to dehydrate gases.

[076] Table 2

Example	Solvent	Efficiency %
18	DI Water	0
19	56% MEG	0
20	45% MDEA	0
21	100% TEG	0

[077] These results show that insignificant amounts of mercury were absorbed (0% efficiency) and retained in the test solutions in the absence of mercury capture agents.

[078] Examples 22-38: These experiments are to evaluate sodium polysulfide as complexing agent in the removal of mercury. Sodium polysulfide is highly effective in capturing elemental mercury vapors at 1 second of contact, even when the sulfur to mercury stoichiometric ratio is near 2. Sodium polysulfide was added in varying amounts to the four solvents as listed and tested according to the procedure of example 17. Results are shown in Table 3.

[079] Table 3

Example	Solvent	ppm Na_2Sx	S/Hg Molar ratio	Efficiency %
22	100% TEG	36	0.429	37.99
23	100% TEG	179	2.143	88.93
24	100% TEG	357	4.286	78.04
25	100% TEG	1,786	21.429	83.13
26	100% TEG	3,571	42.858	81.63
27	45% MDEA	357	4.286	38.01
28	45% MDEA	1,786	21.429	76.86
29	45% MDEA	3,571	42.858	79.48
30	56% MEG	36	0.214	17.74
31	56% MEG	179	1.071	30.15
32	56% MEG	357	2.143	31.15
33	56% MEG	357	4.286	46.92
34	56% MEG	893	10.714	67.91
35	56% MEG	3,571	42.858	82.49
36	DI Water	357	4.286	25.81
37	DI Water	893	10.714	33.76
38	DI Water	3,571	42.858	60.31

[080] Examples 39-62: These experiments are to evaluate ammonium polysulfide as complexing agent in the removal of mercury. Ammonium polysulfide and sodium polysulfide are both used in refineries to control cyanides and to moderate corrosion. If ammonium polysulfide is used then the sodium cation can be avoided, such as in amine absorbers. Using the transient method of example 17, the efficiency of ammonium polysulfide in various solvents was explored and results are shown in Table 4.

[081] Table 4

Example	Solvent	Temperature	ppm (NH4)2Sx	S/Hg Molar ratio	Efficiency %
39	100% TEG	Room T	2,429	32.424	86.18
40	100% TEG	Room T	243	3.242	65.45
41	45% MDEA	Room T	2,429	33.510	42.09
42	45% MDEA	Room T	243	3.351	31.97
43	56% MEG	Room T	2,429	33.510	68.86
44	56% MEG	Room T	243	3.351	47.58
45	DI Water	Room T	2,429	33.510	70.49
46	DI Water	Room T	243	3.351	39.05

47	DI Water	70°C	2,429	33.510	68.55
48	DI Water	70°C	243	3.351	55.44

[082] Samples of the solution in the first absorber were filtered through a 0.45μ filter and analyzed for mercury. Within the limits of the Lumex technique there was no significant change in the mercury content. This demonstrated that the mercury was absorbed as a solution and was not forming measurable amounts of HgS precipitate (e.g., less than 50 ppb difference in the concentration of the original and the filtered solutions).

[083] Examples 49 – 56: The experiments are to evaluate the removal of aqueous Hg anions by ion exchange and adsorption, showing that anion mercury can be removed by anion exchange resins or adsorbents. The 10 ml of a solution containing anionic mercury were contacted with approximately 0.1 grams of various adsorbents to study the removal of mercury. The solution was a 56% MEG solution in water with 2439 ppm ammonium polysulfide and 267 ppb mercury. The adsorbents were Darco Carbon (Aldrich 242276), Activated Carbon (Aldrich C2889), and various Siemen's anion exchange resins: A-244OH, A-464OH, A-674OH, A-714OH, and A-284C Resins. The solutions and the solid adsorbents were mixed overnight at room temperature on a rotating wheel, and the mercury content of the aqueous solution was determined in the morning along with the mercury content of the adsorbent. The results are shown in Table 5:

[084] Table 5

Example	Adsorbent	Solution Hg, ppb	Adorbent Hg, ppb	**[0001]** % Removed
49	None	299	-	0.00
50	Darco Carbon	1.97	11,600	99.34
51	Act. Carbon	129	-	56.86
52	A-244OH Resin	0.53	27,150	99.82
53	A-464OH Resin	0.43	36,200	99.86
54	A-674OH Resin	0.89	28,900	99.70
55	A-714OH Resin	156	15,900	47.83
56	A-284C Resin	0.3	21,400	99.90

[085] The efficiency of various oxygen scavengers was evaluated by use of the procedure described in example 17. In each of the following examples, 243 ppm of ammonium polysulfide (APS) was dissolved in a 56% solution of monoethylene glycol in deionized water. Tests were performed at room temperature and the results are summarized in Table 6.

Table 6

Example	Composition	Result
57	243 ppm APS Only	44.16
58	APS + Hydroxylamine HCl	10.16
59	APS + sodium bisulfite	11.91
60	APS + sodium dithionite	38.99
61	APS + Hydrazine sulfate	52.24
62	APS + N,N Diethylhydroxylamine	63.50
63	APS + Guanidine HCl	68.74
64	APS + Acetaldehyde Oxime	79.18
65	APS + D-(-)-Isoascorbic Acid	81.61

Example 57 contained ammonium polysulfide only and is a reference. Examples 58 and 59 show that hydroxylamine and sodium bisulfite suppress the ability of ammonium polysulfide to capture mercury. In contrast examples 60 to 65 show that other oxygen scavengers do not suppress the ability of polysulfides to capture mercury and some increase its ability. These are examples of compatible oxygen scavengers.

[086] For the purposes of this specification and appended claims, unless otherwise indicated, all numbers expressing quantities, percentages or proportions, and other numerical values used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by the present invention. It is noted that, as used in this specification and the appended claims, the singular forms "a," "an," and "the," include plural references unless expressly and unequivocally limited to one referent.

[087] As used herein, the term "include" and its grammatical variants are intended to be non-limiting, such that recitation of items in a list is not to the exclusion of other like items that can be substituted or added to the listed items. The terms "comprises" and/or "comprising," when used in this specification, specify the presence of stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components, and/or groups thereof. Unless otherwise defined, all terms, including technical and scientific terms used in the description, have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs.

[088] This written description uses examples to disclose the invention, including the best mode, and also to enable any person skilled in the art to make and use the invention. The patentable scope is defined by the claims, and can include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims if they have structural elements that do not differ from the literal language of the claims, or if they include equivalent structural elements with insubstantial differences from the literal languages of the claims. All citations referred herein are expressly incorporated herein by reference.

CLAIMS

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

providing a gas feed to a dehydrator, the gas feed containing acid gases, a first concentration of volatile mercury and water,

contacting the gas feed with a glycol solution containing a complexing agent in the dehydrator,

generating a dehydrated gas stream with a reduced concentration of water and mercury;

wherein mercury and water are concurrently removed from the gas feed for a rich glycol containing at least 50% of the volatile mercury in the gas feed as non-volatile mercury.

2. The method of claim 1, wherein the gas feed prior to entering the dehydrator is treated in an absorber with an absorption solution, the absorption solution comprising lean amine and a first complexing agent,

wherein the absorption solution concurrently removes mercury and acid gases from the gas feed, generating a rich amine solution containing mercury and acid gases, and a treated gas stream containing water vapor and a reduced concentration of acid gases and a second concentration of mercury, wherein the second concentration of mercury is less than 50% of the first concentration of mercury; and

wherein the treated gas stream is provided to the dehydrator as the gas feed containing acid gases, a first concentration of volatile mercury and water.

3. The method of claim 2, further comprising

heating the rich amine solution containing mercury and acid gases in a solvent regeneration process employing at least a stripper and a reboiler, generating a lean amine containing non-volatile mercury for recycle in an absorber to remove acid gases.

4. The method of claim 3, further comprising treating the lean amine to remove the non-volatile mercury any of filtration, centrifugation, precipitation, reduction to elemental mercury followed stripping, distillation, adsorption, ion exchange, electrodialysis, transfer to a hydrocarbon steam and separation, and combinations thereof.

5. The method of any of claims 1 - 4, wherein the lean amine in the absorption solution is selected from monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), aminoethoxyethanol(diglycoamine) (DGA), triethanolamine (TEA), diisopropylamine (DIPA) and mixtures thereof.

6. The method of any of claims 1 - 4, wherein the glycol solution is selected from dietheylene glycol, triethylene glycol and mixtures thereof.

7. The method of any of claims 1 - 4, wherein the complexing agent is added in an amount of less than 5 vol. % of the glycol solution to the dehydrator.

8. The method of claim 7, wherein the complexing agent is added in an amount of less than 3 vol. % of the glycol solution to the dehydrator.

9. The method of claim 8, wherein the complexing agent is added in an amount of less than 0.5 vol. % of the glycol solution to the dehydrator.

10. The method of any of claims 1 - 4, wherein the complexing agent is selected from water-soluble sulfur compounds, mercaptans, organic polysulfides, sulfanes, and mixtures thereof.

11. The method of claim 10, 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, sodium polysulfide, ammonium polysulfide, sodium thiocarbamate, sodium dithiocarbamate, ammonium thiocarbamate and ammonium dithiocarbamate, and mixtures thereof.

12. The method of any of claims 1 - 4, wherein at least 50% of volatile mercury is removed from the gas feed as non-volatile mercury in rich glycol.

13. The method of claim 12, wherein at least 90% of volatile mercury is removed from the gas feed as non-volatile mercury in rich glycol.

14. The method of claim 13, wherein at least 95% of volatile mercury is removed from the gas feed as non-volatile mercury in rich glycol.

15. The method of any of claims 1 - 4, wherein the dehydrated gas stream contains less than 100 $\mu g/Nm^3$ mercury.

16. The method of claim 15, wherein the dehydrated gas stream contains less than 10 $\mu g/Nm^3$ mercury.

17. The method of claim 16, wherein the dehydrated gas stream contains less than 1 $\mu g/Nm^3$ mercury.

18. The method of claim 17, wherein the dehydrated gas stream contains less than 0.1 $\mu g/Nm^3$ mercury.

19. The method of any of claims 1 - 4, wherein the glycol solution further comprises at least one of an anti-foam, a demulsifier, an oxygen scavenger, and mixtures thereof.

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

providing a gas feed containing acid gases, a first concentration of volatile mercury and water,

contacting the gas feed with a glycol solution in a dehydrator, the glycol solution containing a complexing agent for the glycol solution to concurrently remove the volatile mercury and water from the gas feed, for a rich glycol containing at least 50% of the volatile mercury in the gas feed as non-volatile mercury,

generating a dehydrated gas stream having a reduced concentration of water and mercury,

removing the non-volatile mercury from the rich glycol by at least one of filtration, centrifugation, precipitation, stripping, distillation, adsorption, ion exchange, electrodialysis, a hydrocarbon steam and separation step, and combinations thereof,

generating a recycled glycol stream having a reduced concentration of mercury of less than 50% of the non-volatile mercury in the rich glycol.

21. The method of claim 20, wherein the dehydrated gas stream contains less than 100 $\mu g/Nm^3$ mercury.

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

providing a gas feed containing acid gases, water vapor and a first concentration of volatile mercury;

contacting the gas feed with an absorption solution in an absorber, the absorption solution comprising lean amine and a first complexing agent, wherein the absorption solution concurrently removes mercury and acid gases from the gas feed generating a rich amine solution containing mercury and acid gases and a treated gas stream containing water vapor and a reduced concentration of acid gases and a second concentration of mercury, and wherein the second concentration of mercury is less than 50% of the first concentration of mercury;

contacting the treated gas stream with a glycol solution in a dehydrator, wherein the glycol solution contains a second complexing agent for the glycol solution to concurrently remove mercury and water vapor from the treated gas stream, generating a rich glycol containing non-volatile mercury and a dehydrated gas stream with a reduced concentration of water and a third concentration of mercury, wherein the third concentration of mercury is less than 50% of the second concentration of mercury.

23. The method of claim 22, wherein the glycol solution further comprises at least one of an anti-foam, a demulsifier, a compatible oxygen scavenger, and mixtures thereof.

24. The method of claim 23, wherein the anti-foam agent is a silicone material.

25. The method of claim 23, wherein the demulsifier is selected from polyamines, polyamidoamines, polyimines, condensates of o-toluidine and formaldehyde, quaternary ammonium compounds, ionic surfactants, polyoxyethylene alkyl phenols, aromatic sulfonic acid additive, and mixtures thereof.

26. The method of claim 23, wherein the compatible oxygen scavenger is selected from the group of hydrazine salts, guanidine salts, N,N-Diethylhydroxylamine, oximes, dithionites, ascorbic acid, and isoascorbic acid , and mixtures thereof.

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

providing a gas feed containing a first concentration of volatile mercury and acid gases;

contacting the gas feed in an absorber with an absorption solution comprising lean amine and a first complexing agent comprising volatile cations selected from ammonium polysulfide, amine polysulfides, and sulfanes, wherein the absorption solution concurrently removes mercury and non-volatile mercury and acid gases from the gas feed;

generating a rich amine solution containing acid gases and at least 50% of the volatile mercury in the gas feed as non-volatile mercury and a treated gas stream with a second concentration of acid gases and mercury.

28. The method of claim 27, further comprising:

contacting the treated gas stream with a glycol solution in a dehydrator, wherein the glycol solution contains a second complexing agent for the glycol solution to concurrently remove mercury and water vapor from the treated gas stream,

generating a rich glycol containing non-volatile mercury and a dehydrated gas stream with a reduced concentration of water and a third concentration of mercury, wherein the third concentration of mercury is less than 50% of the second concentration of mercury.

29. The method of claim 28, further comprising:

removing the non-volatile mercury from the rich glycol by at least one of filtration, centrifugation, precipitation, stripping, distillation, adsorption, ion exchange, electrodialysis, a hydrocarbon steam and separation step, and combinations thereof,

generating a recycled glycol stream having a reduced concentration of mercury of less than 50% of the non-volatile mercury in the rich glycol.

30. The method of any of claims 27 - 29, wherein the lean amine in the absorption solution is selected from monoethanolamine (MEA), diethanolamine (DEA),

methyldiethanolamine (MDEA), aminoethoxyethanol(diglycoamine) (DGA), triethanolamine (TEA), diisopropylamine (DIPA) and mixtures thereof.

31. The method of any of claims 27 - 29, wherein the absorption solution comprising lean amine has a concentration of amine ranging from 15 to 65 wt. %.

32. The method of any of claims 27 - 29, wherein the volatile cation is ammonium polysulfide.

33. The method of any of claims 27 - 29, wherein at least 90% of volatile mercury is removed from the gas feed in the absorption solution.

34. The method of claim 33, wherein at least 95% of volatile mercury is removed from the gas feed in the absorption solution.

35. The method of any of claims 27 - 29, wherein the treated gas stream contains less than 100 $\mu g/Nm^3$ mercury.

36. The method of claim 35, wherein the treated gas stream contains less than 10 $\mu g/Nm^3$ mercury.

37. The method of claim 36, wherein the treated gas stream contains less than 1 $\mu g/Nm^3$ mercury.

38. The method of claim 37, wherein the treated gas stream contains less than 0.1 $\mu g/Nm^3$ mercury.

39. The method of any of claims 27 - 29, wherein the complexing agent is added in an amount of less than 5 vol. % of the absorption solution to the absorber.

40. The method of claim 39, wherein the complexing agent is added in an amount of less than 1 vol. % of the absorption solution to the absorber

41. The method of claim 40, wherein the complexing agent is added in an amount of less than 0.5 vol. % of the absorption solution to the absorber.

42. The method of any of claims 27 - 29, further comprising:

heating the rich amine solution containing acid gases and non-volatile mercury in a solvent regeneration process employing at least a stripper and a reboiler, and

generating a lean amine containing non-volatile mercury for recycle in an absorber to remove acid gases.

43. The method of claim 42, further comprising:

treating the lean amine to remove the non-volatile mercury by processes selected from the group consisting of filtration, centrifugation, precipitation, reduction to elemental mercury followed stripping, distillation, adsorption, ion exchange, electrodialysis, or transfer to a hydrocarbon steam and separation, and combinations thereof.

44. The method of any of claims 27 - 29, wherein the glycol solution further comprises at least one of an anti-foam, a demulsifier, a compatible oxygen scavenger, and mixtures thereof.

45. The method of claim 44, wherein the demulsifier is selected from polyamines, polyamidoamines, polyimines, condensates of o-toluidine and formaldehyde, quaternary ammonium compounds, ionic surfactants, polyoxyethylene alkyl phenols, aromatic sulfonic acid additive, and mixtures thereof.

46. The method of claim 44, wherein the oxygen scavenger is selected from the group of hydrazine salts, guanidine salts, N,N-Diethylhydroxylamine, oximes, dithionites, ascorbic acid, and isoascorbic acid , and mixtures thereof.

47. The method of claim 44, wherein the anti-foam agent is a silicone material.

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

providing a gas feed containing a first concentration of volatile mercury and acid gases; and

contacting the gas feed in an absorber with an absorption solution comprising lean amine and a complexing agent, generating a treated gas stream with a reduced concentration of acid gases and mercury, wherein the absorption solution concurrently removes mercury and acid gases from the gas feed for a rich amine solution containing mercury and acid gases, wherein the complexing agent is selected from ammonium polysulfide, amine polysulfides, calcium polysulfide, sulfanes, and mixtures thereof;

heating the rich amine solution containing acid gases and mercury in a solvent regeneration process employing at least a stripper and a reboiler, wherein at least a portion of the mercury is removed from the rich amine with acid gases as an overhead stream; and

treating the overhead stream containing mercury by adsorption in a mercury removal adsorbent bed.