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(54) Title: PROCESS FOR REMOVING SULFUR DIOXIDE FROM A GAS STREAM

(57) Abstract: A process for removing sulfur dioxide from a feed gas stream, which comprises (i) contacting the feed gas stream with an aqueous lean absorbing medium comprising a chemical solvent comprising a regenerable absorbent, a physical solvent, and one or more heat stable salts. The regenerable absorbent is an amine. The ratio of the wt% of the physical solvent over that of the regenerable absorbent is between 0.05 and 0.45. The pH of the lean absorbing medium is 6 or less. Preferably the lean absorbing medium comprises in the range of from 10 to 18 wt%, preferably 10 to 17 wt%, more preferably from 12 to 14 wt% regenerable absorbent, calculated on the total weight of absorbing medium. With the process S02 can be selectively removed. When the absorbing medium is stripped, a reduced amount of energy is required as compared to known processes.

PROCESS FOR REMOVING SULFUR DIOXIDE FROM A GAS STREAM

Field of the invention

The present invention relates to a process for capturing sulfur dioxide (SO_2) from a feed gas stream. The present invention especially relates to a process suitable to selectively capture sulfur dioxide (SO_2) from a feed gas stream, more especially to remove SO_2 from a gas stream while not at the same time removing CO_2 from the gas stream.

Background to the invention

It is known that SO_2 is more soluble in water than many other components of feed gas streams. For example, measured at 1.013 bar 0°C, the solubility of SO_2 in water is 228 g/L whereas the solubility of carbon dioxide and hydrogen sulfide in water is 3.369 g/L and 7.100 g/L, respectively.

The solubility of SO_2 in many other pure solvents has also been widely studied. See, for example, Fogg and Gerrard, 1991 (Solubility of Gases in Liquids, John Wiley and Sons, Chichester, U.K.) for a summary of the literature solubility data of SO_2.

Regenerable absorbents can be used to remove SO_2 from feed gas streams. Typically, a lean aqueous medium comprising the absorbent is exposed to a SO_2 containing feed gas stream, and then SO_2 is absorbed by the medium producing a SO_2 lean gas stream and a spent absorbing medium. Removal (recovery) of the absorbed SO2 from the spent absorbing medium to regenerate the aqueous medium and to provide gaseous SO_2 is typically effected by gaseous stripping using steam generated in situ.

Amine-based absorbents can be used for SO_2 removal. See, for example, US5019361 which discloses the use of an

aqueous absorbing medium containing a water-soluble half salt of a diamine. US7214358 discloses the use of an aqueous absorbing medium containing a water-soluble half salt of a diamine and an elevated level of heat stable salts (HSS). Physical solvents can also be used as SO_2 absorbents.

Commercially available steam-regenerable SO2 capture technologies include those that rely on chemical solvents or physical solvents, such as Cansolv DSTM (amine-based absorbent-containing chemical solvent), LabsorbTM (inorganic absorbent-containing chemical solvent), ClausMasterTM (non-aqueous physical solvent), and Sea water process (chemical solvent).

Use of a combination of solvents has also been disclosed.

Indian Patent Application No. 2381/DEL/2006 describes a process for the removal of SO_2 using a solvent blend comprising chemical and physical solvents.

US20130039829 describes a process for the capture of sulfur dioxide from a gaseous stream utilizing a regenerable diamine absorbent comprising a diamine and a weak organic acid, such as formic acid.

WO2015066807 describes a process for removing sulfur dioxide from a gas stream using a regenerable absorbing medium comprising a chemical solvent, a physical solvent and heat stable salts. The weight ratio of physical solvent over regenerable absorbent, for example the weight ratio of polyol over amine, is in the range of from 0.5 to 2.5, preferably from 1.1 to 2.2.

The energy required to regenerate an absorbing medium as described in WO2015066807 is relatively low. Nevertheless, there remains a need to further improve the process for removing sulfur dioxide.

Summary of the invention

The invention relates to a process for removing sulfur dioxide from a feed gas stream, which process comprises:

(i) contacting the feed gas stream with an aqueous lean absorbing medium to absorb sulfur dioxide and to form a sulfur dioxide lean treated gas stream and a spent absorbing medium;

wherein the aqueous lean absorbing medium comprises:

(a) a chemical solvent comprising a regenerable absorbent which is an amine preferably a mono amine, a diamine, a polyamine, or a mixture thereof, most preferably a diamine,

(b) a physical solvent, and

(c) in the range of between 0.8 to 1.2 equivalent/amine mole of heat stable salts, preferably 0.9 to 1.2 equivalent/amine mole of heat stable salts;

wherein the ratio of the weight percentage of the physical solvent in the lean absorbing medium over that of the regenerable absorbent is in the range of from 0.05 to 0.45, preferably from 0.05 to 0.30, more preferably from 0.05 to 0.20;

wherein the pH of the lean absorbing medium is 6 or less, preferably 5.6 or less, more preferably in the range of from 4.5 to 5.6, even more preferably in the range of from 5.2 to 5.6.

(ii) stripping, preferably steam stripping, absorbed sulfur dioxide from the spent absorbing medium to produce a regenerated aqueous absorbing medium and a gaseous sulfur dioxide; and

(iii) optionally recycling the regenerated aqueous absorbing medium from step (ii) to step (i).

With the process of the current invention SO2 can be removed selectively, that is, SO2 is removed from gas. CO2 and other components are not or hardly removed from the gas. Furthermore, during step (i) the absorbing medium preferably is present in a single liquid phase; in other words, preferably no liquid-liquid phase separation takes place. Also during step (ii) the absorbing medium preferably is present in a single liquid phase.

It was surprisingly found that the ratio of physical solvent to regenerable absorbent in the lean absorbing medium can be much lower as compared to the ranges disclosed in WO2015066807. The process of the present invention nevertheless proved to result in significantly reduced regeneration energy consumption as compared to a process in which no physical solvent is used.

Detailed description of the invention

The invention relates to a process for removing sulfur dioxide from a feed gas stream, which process comprises:

(i) contacting the feed gas stream with an aqueous lean absorbing medium to absorb sulfur dioxide and to form a sulfur dioxide lean treated gas stream and a spent absorbing medium;

wherein the aqueous lean absorbing medium comprises:

(a) a chemical solvent comprising a regenerable absorbent which is an amine preferably a mono amine, a diamine, a polyamine, or a mixture thereof, most preferably a diamine,

(b) a physical solvent, and

(c) in the range of between 0.8 to 1.2 equivalent/amine mole of heat stable salts, preferably 0.9 to 1.2 equivalent/amine mole of heat stable salts;

wherein the ratio of the weight percentage of the physical solvent in the lean absorbing medium over that of the regenerable absorbent is in the range of from 0.05 to 0.45, preferably from 0.05 to 0.30, more preferably from 0.05 to 0.20;

wherein the pH of the lean absorbing medium is 6 or less, preferably 5.6 or less, more preferably in the range of from 4.5 to 5.6, even more preferably in the range of from 5.2 to 5.6.

(ii) stripping, preferably steam stripping, absorbed sulfur dioxide from the spent absorbing medium to produce a regenerated aqueous absorbing medium and a gaseous sulfur dioxide; and

(iii) optionally recycling the regenerated aqueous absorbing medium from step (ii) to step (i).

The absorbing medium preferably is present in a single liquid phase during step (i) and/or during step (ii).

The feed gas stream used in step (i) comprises sulfur dioxide. Sulfur dioxide is commonly present in effluent streams from a variety of commercial sources. Examples are stack gases from coal fired power plants, from industrial boilers, from smelting, and from metallurgical roasting operations, and tail gas streams from Claus sulfur plants, from refineries and from chemical plants.

A sulfur dioxide comprising gas, for example an effluent stream of a commercial source, may be treated before use in step (i) of the present invention.

For example, the gas may be cooled, for example by quenching, or it may be subcooled. Additionally or alternatively the gas may be de-dusted. Additionally or alternatively the gas may be de-acidified. In one embodiment the gas is (sub)cooled and de-dusted, and

optionally de-acidified before use in step (i) of the present invention.

Optionally sulfur dioxide is removed from a sulfur dioxide comprising gas before use in step (i). In most cases, however, it is not necessary to remove sulfur dioxide from an effluent stream of a commercial source as the process of the present invention is suitable for treating gas streams having a high amount of sulfur dioxide.

The sulfur dioxide concentration in the feed gas stream used in step (i) may vary. Preferably the sulfur dioxide concentration in the feed gas stream used in step (i) is in the range of between 800 ppmv and 45 volume percent, more preferably in the range of between 800 ppmv and 11 volume percent.

The aqueous lean absorbing medium used in step (i) preferably comprises between 25 and 90 wt% water, more preferably between 50 and 85 wt% water, even more preferably between 70 and 85 wt% water, calculated on the total weight of lean absorbing medium.

The aqueous lean absorbing medium used in step (i) preferably comprises in the range of from 10 to 18 wt%, preferably 10 to 17 wt%, more preferably from 12 to 14 wt% regenerable absorbent, calculated on the total weight of lean absorbing medium.

The pH of the lean absorbing medium is 6 or less, preferably 5.6 or less, more preferably in the range of from 4.5 to 5.6, even more preferably in the range of from 5.2 to 5.6.

In step (i) the feed gas stream is contacted with an aqueous lean absorbing medium to absorb sulfur dioxide and to form a sulfur dioxide lean treated gas stream and a spent absorbing medium. The contacting of the absorbing

medium with the SO_2 containing gas stream may be effected within a temperature range from the freezing point of the absorbent up to 75°C, or from 10°C to 60°C, or from 10°C to 50°C. The pressure may be in the range of between 1.0 and 2 bara.

In some embodiments, the lean absorbing medium comprises in the range of from 0.5 to 8 wt%, preferably 0.5 to 7.5 wt% of the physical solvent, calculated on the total weight of lean absorbing medium.

In some embodiments, the sulfur dioxide amine absorbent is a mixture of 4-[hydroxyethyl]piperazine (Hep) and 1,4-bis[hydroxyethyl]piperazine (DiHep).

In some embodiments, the step of stripping absorbed sulfur dioxide, i.e. step (ii), may use steam. With the current invention it proved to be possible to use less steam during stripping than in a corresponding step in a process that does not use a physical solvent. This results in a significant energy reduction.

In some embodiments, the processes as described herein may further comprise a step of removing heat stable salts from the regenerated aqueous absorbing medium before recycling the regenerated aqueous absorbing medium. The step of removing heat stable salts may comprise using a weak base anion resin, ion pairing, crystalisation or precipitation.

In some embodiments, the processes as described herein further comprise a step of recovering the gaseous sulfur dioxide.

With the process of the invention a pure SO2 stream can be obtained that can be used for sulfuric acid make, or for use in a sulfur reduction unit in a Claus application. The pure SO2 stream is not or hardly contaminated with CO2 or mercaptans which would

contaminate sulfuric acid, or which would contaminate a Claus unit.

SO2 removal

In general, a suitable indicator for an appropriate choice of absorbent (e.g., a chemical solvent) for use in the capture of a given gaseous acid gas contaminant (such as SO_2) in a feed gas is the difference in the pK_a values between the acid gas in water and the absorbent.

The pK_a of an acid is defined as the negative logarithm to the base 10 of the equilibrium constant K_a for the ionization of the acid HA (e.g., H_2SO_3), where H is hydrogen and A is a radical capable of being an anion:

$$HA \rightleftharpoons H^+ + A^- \quad (1)$$

$$K_a = [H^+][A^-]/[HA] \quad (2)$$

$$pK_a = -\log 10\ K_a \quad (3)$$

For a basic absorbent B, the pK_a is for the ionization reaction of the conjugate protonated acid of B, the species BH^+:

$$BH^+ \rightleftharpoons B + H^+ \quad (4)$$

The reaction involved in the absorption of the acid gas contaminant HA by the basic absorbent B can be shown as follows:

$$HA + B \longrightarrow BH^+ + A^- \quad (5)$$

Reaction (5) is reversible:

$$BH^+ + A^- \longrightarrow HA + B \quad (6)$$

When SO_2 is dissolved in water, following reaction (1), bisulphite ions (HSO_3^-) and protons are formed. The proton may be ionically associated with the absorbent (for example, when an amine-based absorbent is used, the proton may be ionically associated with the sorbing nitrogen of the absorbent). The absorbed SO_2/desorbed SO_2 equilibrium is illustrated in the above reaction (6). Absorbed SO_2 can be "stripped" from the spent absorbing medium as gaseous SO_2, for example and without limitation, by the application of steam. In this stripping process, desorbed SO2 is released from the spent absorbing medium. "Stripping" is used herein to broadly encompass removal of absorbed SO_2 from the spent absorbing medium, and should be understood as also, more specifically, encompassing releasing desorbed SO2 from the spent absorbing medium.

It has been found that contacting a feed gas stream with a lean absorbing medium comprising a chemical solvent and a physical solvent may reduce the energy consumption for stripping absorbed SO2 from spent absorbing medium, or may reduce the energy consumption for releasing desorbed SO_2 from spent absorbing medium, thereby reducing regeneration energy consumption in a process for removing SO_2 from the gas stream. The reduction of regeneration energy consumption achieved by the methods of the invention is understood to be relative to a method that does not use a physical solvent.

As used herein, regeneration energy relates to the amount of energy required to regenerate an absorbing medium used to absorb SO_2 in a process for removing SO_2 from a feed gas stream. The absorbing medium, according

to the invention, comprises a chemical solvent and a physical solvent.

Stripping

Preferably step (ii) is performed in a reboiler. More preferably step (ii) is performed in a kettle reboiler, forced circulation reboiler, fired reboiler, falling film reboiler, direct steam reboiler, or thermosyphon, most preferably in a thermosyphon.

The reboiler may be heated by hot oil, electricity, hot flue gas or steam, preferably steam. Alternatively, direct steam addition can be utilized.

Preferably at least 97 vol%, more preferably at least 99 vol%, even more preferably at least 99.9 vol% of the spent absorbing medium formed in step (i) is stripped, preferably steam stripped, in step (ii).

Stripping may be performed at a temperature in the range of between 100 and 150 °C.

Stripping may be performed at a pressure in the range of between 1.0 and 3 bara.

Chemical Solvent

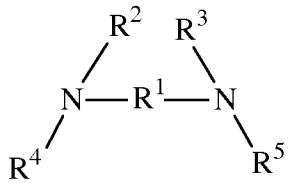
Chemical solvents for use in the invention comprise a regenerable absorbent that selectively absorbs SO2. In some embodiments, the chemical solvent comprises an aqueous medium and the absorbent.

In general, a suitable chemical solvent may have one or more of the following properties: high capacity for the absorption of SO_2; ready and substantially complete release of absorbed SO_2; little tendency to cause oxidation of SO_2; low heat of absorption; high boiling point; low specific heat; and high stability at temperatures required for the release of SO_2.

The chemical solvent is or comprises an amine. The amine may be a mono amine, a diamine, a polyamine, or a

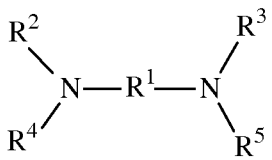
mixture thereof. Suitable amines include, but are not limited to, 1,4-bis[hydroxyethyl]piperazine, 4-[hydroxyethyl]piperazine, 1,4-diazabicyclo[2.2.2]octane (DABCO), 2-[2-aminoethyl]pyridine, 2-aminomethylpyridine, 3-amino 5-methylpyrazole, 3-aminopyrazole, 3-methylpyrazole, N,N,N',N'-tetraethyldiethylenetriamine, N,N,N',N'-tetramethyldiethylenetriamine, 2-piperazinone 1,4-bis[2-hydroxyethyl], or a combination thereof.

The amine-based absorbent may be a diamine represented by the structural formula:



wherein R^1 is an alkylene of two or three carbon atoms as a straight chain or as a branched chain, R^2, R^3, R^4, and R5 may be the same or different and can be hydrogen, alkyl (e.g., lower alkyl of 1 to 8 carbon atoms including cycloalkyls), hydroxyalkyl (e.g., lower hydroxy alkyl of 2 to 8 carbon atoms), aralkyl (e.g., 7 to 20 carbon atoms), aryl (may be, for example, monocyclic or bicyclic), or alkaryl (e.g., 7 to 20 carbon atoms), and any of R^2, R^3, R^4, and R^5 may form cyclic structures.

The diamines may also be tertiary diamines. For instance, the tertiary diamine may be of the formula:



wherein R^1 is as defined above, and R^2, R^3, R^4, and R^5 are as defined above with the exception that none are hydrogen. In an exemplary embodiment, each of R^2, R^3, R^4, and R^5 is the same or different and is an alkyl group (e.g., methyl or ethyl) or a hydroxy-alkyl group (e.g., 2-hydroxyethyl).

Other diamines in which one or both of the nitrogen atoms is primary or secondary and which otherwise meet the parameters discussed herein may also be suitable, provided mild oxidative or thermal conditions exist to minimize side reactions of the solvent, including oxidation.

Suitable diamines, according to some invention embodiments, have one amine with a lower pK_a and the other amine with a higher pKa wherein the higher pK_a is above 6.5 and, in some instances, above 7.5 and the lower pKa is less than 5.0 and, in some instances, less than 4.0. The stronger amine (the one with the higher pK_a) may react to form heat stable salts (HSS). For instance, the stronger amine may react with a strong acid (e.g., sulfuric acid) to obtain a HSS. In some embodiments, the lean amine-based absorbent, which is exposed to the gas stream, is therefore in its half-salt form. Accordingly, only the weaker, more moderate amine is available for reacting with the feed gas stream and releasably absorbing SO_2.

In some embodiments, the diamine in half salt form has a pK_a value for the free nitrogen atom of 3.0 to 5.5 and, in some instances, 3.5 to 4.7 at a temperature of 20 °C in an aqueous medium. The free amine form of the amine salt absorbent may have a molecular weight less than 300 g/mol and, in some instances, less than 250 g/mol.

In some embodiments, the amine salt absorbents have a hydroxyalkyl group as a substituent on an amine group. Without being limited by theory, it is believed that a hydroxy substituent may increase the solubility of the amine salt absorbents in water. Without being limited by theory, it is further believed that a hydroxy substituent may retard the oxidation of sulphite or bisulphite to sulfate, which can result in the formation of HSS. As discussed below, it may be desirable to minimize the formation of HSS.

Suitable diamine compounds may include, but are not limited to, N,N'N'-(trimethyl)-N-(2-hydroxyethyl)-ethylenediamine (pK_a=5.7); N,N,N', N'-tetrakis(2-hydroxyethyl)ethylenediamine (pK_a=4.9); N,N'-dimethylpiperazine (pK_a=4.8); N,N,N',N'-tetrakis(2-hydroxyethyl)-1,3-diaminopropane; and N',N'-dimethyl-N,N-bis(2-hydroxyethyl)ethylenediamine. Useful diamines may also comprise, in some embodiments, heterocyclic compounds, such as piperazine (pK_a=5.8), N-(2-hydroxyethyl)piperazine, N,N'-di(2-hydroxyethyl)piperazine and 1,4-diazabicyclo[2.2.2]octane (pK_a=4.9). The pK_a values identified in the brackets are for the weaker, sorbing nitrogen.

According to some embodiments of the invention, the diamine may be selected from the group comprising hydroxyethyl piperazine, bis-hydroxyethyl piperazine, piperazine, hydroxyethylethylenediamine, bis-hydroxyethylethylenediamine and mixtures thereof. For example, the diamine may comprise 1,4-bis[hydroxyethyl]piperazine, 4-[hydroxyethyl]piperazine, or a combination thereof.

Without being limited by theory, it is believed that use of amine-based absorbents that generate HSS at a

controllable low level may permit an increase in the concentration of the physical solvent in absorbing medium of the present invention, and maintain a one-phase solution of the absorbing medium. One example of such an amine is 2-piperazinone 1,4-bis(2-hydroxyethyl) (Amide-DiHep).

It will be appreciated that, in some embodiments, one or more amines may be used as the absorbent and one or more amines may be used with other heat regenerable sulfur dioxide absorbents.

The amine-based absorbent may be in an amount sufficient to provide a spent absorbing medium containing at least 180 grams of SO_2 per kilogram of absorbing medium. The amount of amine-based absorbent, however, may not be so great as to either (a) unduly increase the viscosity of the absorbing medium such that undesirable pressure drops are incurred in the feed gas stream passing through an absorber vessel or (b) render the absorbing medium difficult to atomize in, for example, a Waterloo scrubber.

In some other embodiments, the chemical solvent may comprise an organic acid. The organic acid may have a pKa such that, at the pH of the lean aqueous medium, the organic acid is substantially in its basic form and, at the pH of the spent absorbent medium, the organic acid is substantially in its acidic form. For example, if the organic acid is formic acid, then at the pH of lean absorbent stream, the formic acid is present as formate and, at the pH of the spent absorbing medium (SO2 rich absorbent stream), the organic acid is substantially in the form of formic acid. By substantially, it is meant that at least 30% or, in some instances, at least 50%, of

the organic acid is in the particular form at the specified pH.

The organic acid may have a pK_a of 1.2-6 and, in some instances, 3.5-5.5.

The organic acid may comprise one or more of formic acid, acetic acid, glycolic acid, malonic acid, propanoic acid, succinic acid, phthalic acid, citric acid, adipic acid, tartaric acid, malic acid, and oxalic acid. In some embodiments, the organic acid comprises one or more of formic acid, acetic acid, malonic acid, malic acid, tartaric acid, citric acid, and adipic acid.

The chemical solvent may comprise a mixture of amine based absorbent and organic acid as described above.

Physical Solvent

Physical solvents for use in the invention may have one or more of the following characteristics: low volatility; water solubility; and low heat capacity.

The physical solvent may have a vapour pressure less than 0.1 mmHg at 20°C with a boiling point equal to or higher than 240°C.

Suitable physical solvents include, but are not limited to, a polyol, a polycarbonate, an N-formyl morpholine, or a combination thereof. The polyol may be a polyethylene glycol or an ether thereof, for instance, of the formula R^6-O-(C_2H_4O)n-R^7, wherein n is 3 to 12, R^6 is hydrogen or lower alkyl (e.g., C_{1-8} alkyl), R^7 is hydrogen or lower alkyl (e.g., C_{1-8} alkyl), or R6 is C_{6-10} aryl (e.g., phenyl) and R^7 is hydrogen or lower alkyl (e.g., C_{1-8} alkyl). For example, the physical solvent may be polyethyleneglycol dimethylether (PEGDME), tetraethyleneglycol dimethylether (TetraEGDME), triethyleneglycol monomethylether (TriEGMME), tetraethylene glycol (TetraEG), or a combination thereof.

The miscibility of some physical solvents such as PEGDME in the absorbing medium may be affected by the concentration of the regenerable absorbent and/or the amount of HSS. For example, the miscibility of PEGDME in an aqueous diamine solution decreases as the concentration of diamine increases and as the amount of HSS increases. In some embodiments, it may be desirable to lower the concentration of the regenerable absorbent and/or the amount of HSS in order to increase the amount of miscible physical solvents in the absorbing medium.

When the physical solvent is PEGDME, without being limited by theory, it is believed that reduction of the amount of HSS and increase of the concentration of PEGDME may reduce hydrogen bonding and/or increase ether-sulfur bridges in the absorbing medium, which renders the absorbing medium more aprotic and potentially reduces the energy consumption for stripping absorbed SO_2.

Without being limited by theory, it is believed that physical solvents may reduce the energy consumption required for releasing desorbed SO_2. Physical solvents may compete with other components of spent absorbing medium to attract SO2. Physical solvents may further reduce hydrogen bonding between SO_2 and spent absorbing medium. Physical solvents may also reduce the polarity of SO_2 in spent absorbent medium or make the medium more aprotic. Physical solvents may even further change the surface tension of spent absorbent medium.

Heat Stable Salts (HSS)

HSS may accumulate in the medium due to, for example, sulfite/bisulfite oxidation or disproportionation, or due to the absorption of acid mist from the feed gas. These salts are too stable to decompose under normal steam conditions for stripping SO_2 from spent absorbing medium.

Examples of such heat stable salts are those salts that are formed from strong acids such as sulfuric acid, nitric acid, or hydrochloric acid. If allowed to accumulate, these heat stable salts would eventually completely neutralize the SO_2 absorption capacity of the absorbent. Therefore, management of HSS in the solution may be an important part of the SO_2 removal process to maintain performance over time

The amount of HSS formed may be affected by the absorbent used and/or the concentration of the absorbent. The amount of HSS for an absorbing medium may be controlled by using conventional means, such as an ion exchange resin, eletrodialysis unit or crystallization. Amine purification units (APU) that are currently used industrially utilize weak anionic resins capable of some selectivity between sulfate (a strong conjugated base) and weaker conjugated bases in the absorbing medium. The performance of such weak base resins varies depending on the concentration of sulfate in solution. These resins do not always perform well if there is a low concentration of HSS.

Ways to control the level of HSS for an organic acid/physical solvent mixture may also include ion exchange with cyclo[8]pyrrole as the functional groups or by crystallization of alkaline sulfate salts (e.g. Na_2SO_4), where the cation can be sodium or potassium, most often sodium. Another way of controlling the level of HSS in the organic acid/physical solvent mixture is precipitation of Ettringite ($Ca_6Al_2(SO_4)_2(OH)_{12}\cdot 26H_20$).

In the alternative, HSS could also be removed by ion pairing. Without being limited by theory, it is believed that a low HSS amount in the absorbing medium, in accordance with some embodiments of the invention, may

reduce the efficiency of the exchange of HSS with a standard anionic weak base resin. In some embodiments, it may therefore be desirable to remove HSS by ion pairing, which may permit a higher rate of removal of HSS even when the amount of salts in solution is low. Ion pairing may be achieved, for example, by using a dual function resin having different ionic functional groups (such as a combination of phenol and quaternary amine functional groups) or by liquid-liquid extraction.

Without being limited to theory, it is believed that a strong base quaternary amine functional group insensitive to suppressed salt concentrations will attract opposite charged anions regardless of their type. During regeneration, the phenolic functional group which is the active exchange site in the above described dual function resin, becomes negatively charged at a pH greater than 10.5, and repels the like charged anions.

The Absorbing Medium

The absorbing medium comprises the physical solvent and the chemical solvent. The absorbing medium is a one phase solution during step (i) and during step (ii). It is aqueous.

The pH of the lean absorbing medium is 6 or less, preferably 5.6 or less, more preferably in the range of from 4.5 to 5.6. Even more preferably the pH of the lean absorbing medium before contacting the feed gas is controlled in the range from 5.2 to 5.6.

The absorbing medium may contain at least one mole of water and usually more for each mole of SO_2 to be removed from the gas stream. The water acts both as a solvent for the amine salt and as for a reactant to produce "sulfurous acid" H_2SO_3 from the SO_2.

The lean absorbing medium may comprise an organic acid and/or an inorganic acid, preferably an inorganic acid, more preferably one or more acids chosen from the group of nitric acid (HNO_3), hydrochloric acid (HCl), sulfuric acid (H_2SO_4) and sulfurous acid (H_2SO_3), even more preferably sulfuric acid (H_2SO_4) and/or sulfurous acid (H_2SO_3).

The viscosity of the absorbing medium may be below 1200 centipoise at 25°C, e.g., between 1 and 500 centipoise, and more specifically between 1 and 50 centipoise, at 25°C. Frequently, the solubility of the amine salt absorbent in water may be at least 0.01, often at least 0.1, mole per liter at 25°C. In some embodiments, the amine salt absorbent is miscible with water under the conditions in the process. However, the amine salt absorbent and water does not have to be miscible under the conditions of the process, nor does the amine salt absorbent have to be liquid under the conditions of the process.

In some embodiments, anti-foam agents known in the art may be used to reduce the foaming tendency of the mixture of the chemical solvent and the physical solvent. Anti-foam agents and amounts can be chosen and optimized in accordance with known practices. It may be desirable to choose an anti-foam agent compatible with the system chosen for HSS removal (e.g., compatible with an anionic resin used in a commercial installation).

Regeneration Energy Consumption

The methods of the present invention may reduce the regeneration energy consumption by 10% or more. In some embodiments, the regeneration energy consumption may be reduced by 15% or more, or even 20% or more.

It has been observed that the level of regeneration energy saving may vary over the concentration of the physical solvent or the ratio of the physical solvent over the regenerable absorbent. The ratio of the weight percentage of the physical solvent in the absorbing medium over that of the regenerable absorbent may be from 0.05 to 0.45. In some embodiments, the ratio may be from 0.05 to 0.30. In some embodiments, the ratio may be from 0.05 to 0.20.

In some embodiments, it may be desirable that the absorbing medium comprises at least 0.5wt% of the physical solvent. In some embodiments, it may be desirable that the absorbing medium comprises up to 8 wt%, preferably up to 7.5 wt% physical solvent.

The amount of heat stable salts (HSS) may also affect the level of regeneration energy saving as it affects the solubility of the physical solvent in the absorbing medium. The presence of HSS may reduce the miscibility of the physical solvent in the absorbing medium.

The lean absorbing medium comprises in the range of between 0.8 to 1.2 equivalent/amine mole of heat stable salts, preferably 0.9 to 1.2 equivalent/amine mole of heat stable salts. In other words, per mole amine, the aqueous lean absorbing medium may comprise in the range of between 0.8 to 1.2 mole equivalent HSS, and preferably, per mole amine, the aqueous lean absorbing medium comprises in the range of between 0.9 to 1.2 mole equivalent HSS. The heat stable salt may be a salt of a monoprotic, diprotic or polyprotic acid.

One way of controlling the amount of HSS in the absorbing medium is a treatment to remove HSS from regenerated absorbing medium. As a result more amine groups are in free base form.

Typically only a slip stream of the regenerated absorbing medium needs to be treated for heat stable salt removal or heat stable anion removal. In one embodiment HSS is removed from a small fraction, preferably less than 10 percent, preferably less than 5 percent, more preferably less than 2 percent of the total amount of regenerated absorbent. The often is sufficient to achieve a substantial increase in absorption capacity for sulfur dioxide.

HSS are preferably removed by means of an ion exchange resin, electrodialysis, crystallization, and/or thermal reclamation.

EXAMPLES

The invention will now be illustrated by the following examples.

Tests were performed using a pilot unit. The pilot unit was equipped with an absorption zone and a regeneration zone, which is also referred to as stripping zone. The regeneration zone was heated with electrically driven elements.

The pilot unit was equipped with several gas and liquid sampling points. The sampling points were used to take accurate measurements of the SO2 concentration in the gas, and to take measurements of the SO2 and the HSS concentration in the liquid samples.

Using the pilot unit, tests according to the process of the invention were performed. The tests according to the invention were performed with a lean absorbing medium having a weight ratio of physical solvent over regenerable solvent in the range of between 0.05 and 0.20.

Additionally comparative tests were performed. The comparative tests were performed with a lean absorbing

medium comprising a regenerable solvent, but no physical solvent.

The tests according to the invention and the comparative tests were all conducted with the same operating conditions in the absorption zone. At the inlet of the absorption zone the sulfur dioxide concentration in the gas was about 1 vol% on a dry basis. In the absorption zone the circulation rate of the absorbing medium was in the range of between 4.5 and 4.8 L/min.

The tests according to the invention and the comparative tests were all conducted with the same operating conditions in the regeneration zone.

The energy input to the regeneration zone was varied. Data were gathered when steady state was reached after each change to the energy input.

Figure 1 shows stripping curves of tests according to the invention and comparative data.

The measured energy reduction of the samples according to the present invention as compared to the comparative samples is summarized in Table 1.

Table 1

Comparative data versus data according to the invention	
kW	Reduction (%)
32	36
27	34
21	31
18	28
15	26

The tests demonstrate that the process of the present invention requires on average 30% less energy to achieve

the same SO2 emissions as compared to the comparative tests.

The non-linearity of the energy-response relationship in Figure 1 implies that the energy differences vary with heat input. The measured energy reduction increases with increasing heat input and vice versa.

C L A I M S

1. A process for removing sulfur dioxide from a feed gas stream, which process comprises:

(i) contacting the feed gas stream with an aqueous lean absorbing medium to absorb sulfur dioxide and to form a sulfur dioxide lean treated gas stream and a spent absorbing medium;

wherein the aqueous lean absorbing medium comprises:

(a) a chemical solvent comprising a regenerable absorbent which is an amine preferably a mono amine, a diamine, a polyamine, or a mixture thereof, most preferably a diamine,

(b) a physical solvent, wherein the physical solvent preferably is a polyol, a polycarbonate, an N-formyl morpholine, or a combination thereof, and

(c) in the range of between 0.8 to 1.2 equivalent/amine mole of heat stable salts, preferably 0.9 to 1.2 equivalent/amine mole of heat stable salts;

wherein the ratio of the weight percentage of the physical solvent in the lean absorbing medium over that of the regenerable absorbent is in the range of from 0.05 to 0.45, preferably from 0.05 to 0.30, more preferably from 0.05 to 0.20;

wherein the pH of the lean absorbing medium is 6 or less, preferably 5.6 or less, more preferably in the range of from 4.5 to 5.6, even more preferably in the range of from 5.2 to 5.6.

(ii) stripping, preferably steam stripping, absorbed sulfur dioxide from the spent absorbing medium to produce a regenerated aqueous absorbing medium and a gaseous sulfur dioxide; and

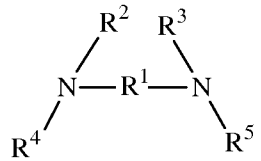
(iii) optionally recycling the regenerated aqueous absorbing medium from step (ii) to step (i).

2. The process according to claim 1, wherein the lean absorbing medium comprises between 25 and 90 wt% water, preferably between 50 and 85 wt% water, more preferably between 70 and 85 wt% water, calculated on the total weight of lean absorbing medium.

3. The process according to claim 1 or 2, wherein the lean absorbing medium comprises in the range of from 10 to 18 wt%, preferably 10 to 17 wt%, more preferably from 12 to 14 wt% regenerable absorbent, calculated on the total weight of lean absorbing medium.

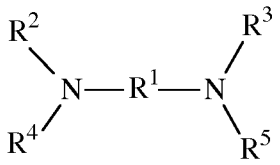
4. The process according to any one of the above claims, wherein the regenerable absorbent is a diamine or polyamine which in half salt form has a pK_a value for the free nitrogen atom of 3.0 to 5.5, preferably 3.5 to 4.7, at a temperature of 20 °C in an aqueous medium.

5. The process according to any one of the above claims, wherein the regenerable absorbent is a diamine represented by the formula:



wherein R^1 is an alkylene of two or three carbon atoms as a straight chain or as a branched chain, R^2, R^3, R^4, and R^5 may be the same or different and can be hydrogen, alkyl, hydroxyalkyl, aralkyl, aryl, or alkaryl, and any of R^2, R^3, R^4, and R^5 may form cyclic structures.

6. The process according to any one of the above claims, wherein the regenerable absorbent is a tertiary amine represented by the formula:



wherein R^1 is an alkylene of two or three carbon atoms as a straight chain or as a branched chain, and R^2, R^3, R^4, and R^5 can be alkyl, hydroxyalkyl, aralkyl, aryl, or alkaryl, and any of R^2, R^3, R^4, and R^5 may form cyclic structures.

7. The process according to any one of the above claims, wherein the regenerable absorbent is piperazine, hydroxyethyl piperazine, bis-hydroxyethyl piperazine, hydroxyethylethylenediamine, bis-hydroxyethylethylenediamine, 1,4-diazabicyclo[2.2.2]octane (DABCO), 2-[2-aminoethyl]pyridine, 2-aminomethylpyridine, 3-amino 5-methylpyrazole, 3-aminopyrazole, 3-methylpyrazole, N,N,N',N'-tetraethyldiethylenetriamine, N,N,N',N'-tetramethyldiethylenetriamine, 2-piperazinone 1,4-bis[2-hydroxyethyl], or a combination thereof.

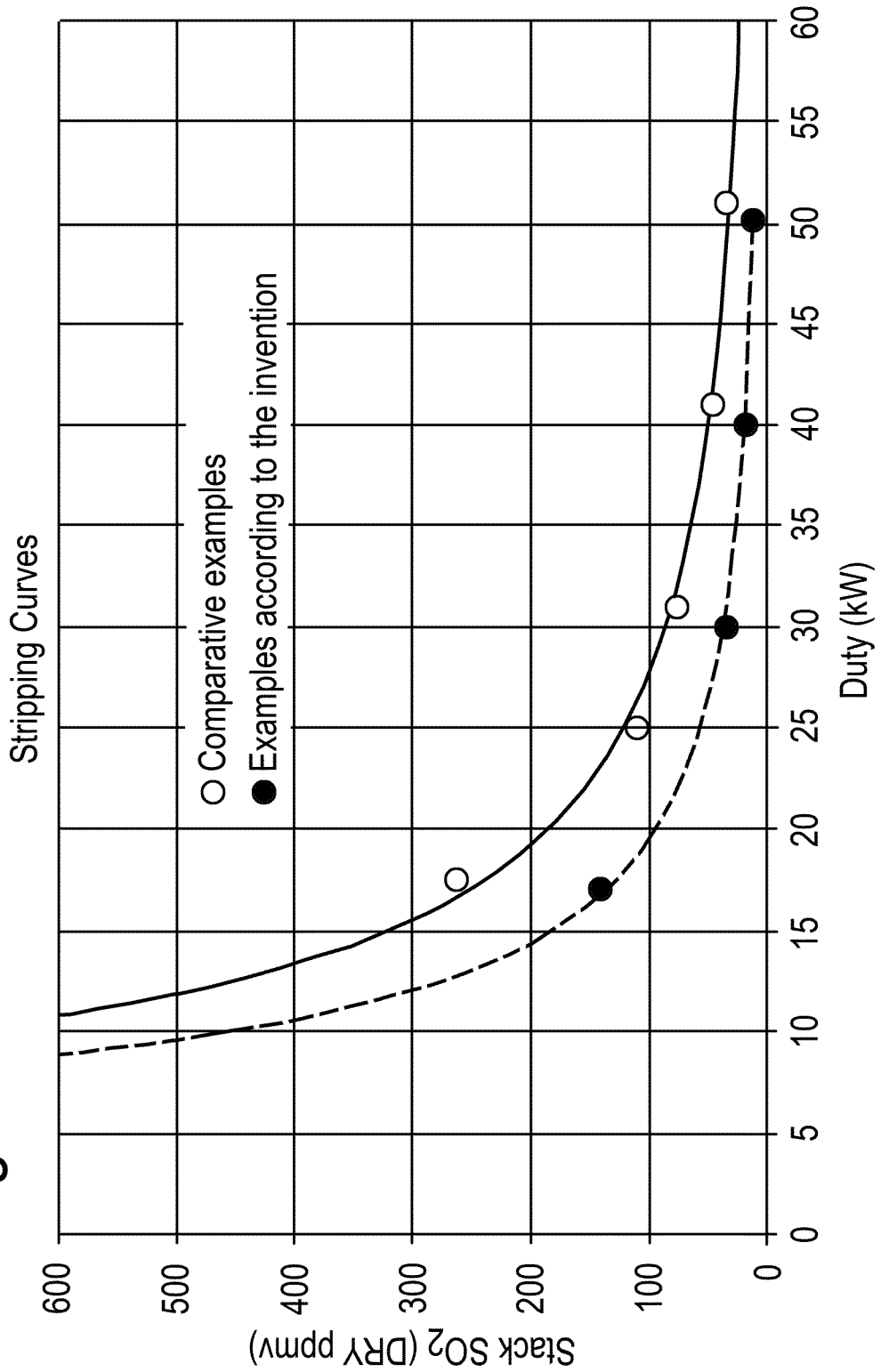
8. The process according to any one of the above claims, wherein the lean absorbing medium additionally comprises an organic acid and/or an anorganic acid, preferably an anorganic acid, more preferably one or more acids chosen from the group of nitric acid (HNO_3), hydrochloric acid

(HCl), sulfuric acid (H_2SO_4) and sulfurous acid (H_2SO_3), even more preferably sulfuric acid (H_2SO_4) and/or sulfurous acid (H_2SO_3).

9. The process according to any one of the above claims, wherein the physical solvent is polyethyleneglycol dimethylether (PEGDME), tetraethyleneglycol dimethylether (TetraEGDME), tetraethylene glycol (TetraEG), triethyleneglycol monomethylether (TriEGMME), or a combination thereof, preferably polyethyleneglycol dimethylether (PEGDME).

10. The process according to any one of the above claims, wherein the physical solvent is polyethyleneglycol dimethylether (PEGDME), and
wherein the regenerable absorbent is
4-[hydroxyethyl]piperazine (Hep), or
1,4-bis[hydroxyethyl]piperazine (DiHep), or
3-aminopyrazole, or
a mixture of 4-[hydroxyethyl]piperazine (Hep) and 1,4-bis[hydroxyethyl]piperazine (DiHep).

Fig.1


Stripping Curves
○ Comparative examples
● Examples according to the invention
Stack SO_2 (DRY ppmv)
600
500
400
300
200
100
0
0
5
10
15
20
25
30
35
40
45
50
55
60
Duty (kW)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/077745

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/14 B01D53/50
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2015/066807 A1 (CANSOLV TECHNOLOGIES INC [CA]) 14 May 2015 (2015-05-14) cited in the application pages 27-35; claims	1-10
A	US 7 214 358 B2 (CANSOLV TECHNOLOGIES INC [CA]) 8 May 2007 (2007-05-08) cited in the application the whole document	1-10

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

☒ See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 December 2017	15/12/2017

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2017/077745

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