

SECTION 21

Hydrocarbon Treating

There are many methods that may be employed to remove acidic components (primarily H_2S and CO_2) and other impurities from hydrocarbon streams. The available methods may be broadly categorized as those depending on chemical reaction, absorption, adsorption or permeation. Processes employing

each of these techniques are described and a general bibliography for additional reading is included. Because of the diversity of the processes available, and new processes introduced, all possible processes are not discussed.

DEFINITIONS OF WORDS AND PHRASES USED IN HYDROCARBON TREATING

Absorption: A separation process involving the transfer of a substance from a gaseous phase to a liquid phase through the phase boundary.

Acid gases: Impurities in a gas stream usually consisting of CO_2 , H_2S , COS, RSH, and occasionally SO_2 . Most common in natural gas are CO_2 and H_2S .

AGE: Acid Gas Enrichment

AGR/AGRU: Acid Gas Removal / Acid Gas Removal Unit

Acid gas loading: The amount of acid gas, on a molar or volumetric basis, that will be picked up by a solvent.

Adsorption: The process by which gaseous components adhere to solids because of their molecular attraction to the solid surface.

Alkanolamine: An organic nitrogen containing compound related to ammonia having at least one, if not two or three linear or branched alkanol groups where only one or two could also be substituted with a linear or branched alkyl group (e.g., as in methyldiethanolamine, or "MDEA"). The number of hydrogen atoms substituted by alkanol or alkyl groups at the amino site determine whether the alkanolamine is primary, secondary or tertiary.

Antifoam: A substance added to the treating system to reduce the tendency for the solvent to foam.

Chelate: An organic molecule in which a central metallic ion is held in a coordination compound.

Claus process: The process in which one third of the H_2S is burned to SO_2 which is then reacted with the remaining H_2S to produce elemental sulfur.

Degradation products: Impurities in a treating solution that are formed from both reversible and irreversible side reactions.

Doctor sweet: Describes a hydrocarbon stream which has had mercaptans removed to a level that it passes the Doctor Test (GPA-1138).

Grain: A unit of mass where one pound is equivalent to 7,000 grains and a specification of 0.25 grain of H_2S per 100 SCF is equivalent to an H_2S concentration of 4.0 ppmv.

Mercaptan: Any of a homologous series of organosulfur compounds, known as **thiols** that contain a sulfur-hydrogen bond (S-H). Thiols are the sulfur analogue of an alcohol of the general formula RSH where the "R" represents the alkyl group that the S-H bond is attached to in lieu of a H or an O-H bond in the comparable alkane (paraffin) or alcohol. All of the materials possess a foul odor, e.g. methyl mercaptan.

Physical solvent: A liquid capable of absorbing selected gas components by solubility alone without associated chemical reactions.

ppmv: A volumetric concentration of a species in a bulk fluid measured in parts per million.

Residence time: The time period for which a fluid will be contained within a specified volume.

Selective treating: Preferential removal of one acid gas component, leaving at least some of the other acid gas components in the treated stream.

Sour gas: Gas containing undesirable quantities of hydrogen sulfide, other sulfur species (such as mercaptans or COS) and/or carbon dioxide.

Sterically hindered amine: An alkanolamine containing a bulky substituent group close to the amino nitrogen site to lower the stability of the carbamate ion thus inhibiting reactions with CO_2 directly with the amine (e.g., diisopropanolamine, or DIPA, AMP, or FLEXSORB®SE).

SRU: Sulfur recovery unit.

Sweet gas: Gas which has no more than the maximum sulfur content defined by: (1) the specifications for the sales gas from a plant; (2) the definition by a legal body such as the Texas Railroad Commission.

TGCU (tail gas clean-up unit): a process unit that takes tail gas from a SRU and removes additional sulfur.

Threshold limit value: The amount of a contaminant to which a person can have repeated exposure for an eight hour day without adverse effects.

SAFETY PRECAUTIONS

Hydrogen sulfide is a highly toxic gas. At concentrations as low as 10 ppmv irritation of the eyes, nose, and throat is possible. The human nose can detect hydrogen sulfide in concentrations as low as 0.02 ppmv. However, the human sense of smell cannot be relied on to detect hazardous concentrations of hydrogen sulfide. Higher concentrations and extended exposure to hydrogen sulfide will desensitize the sense of smell. The concentrations required for different reactions by the human body are:¹

- Threshold limit value (TLV) for prolonged exposure: 10 ppmv
- Slight symptoms after several hours exposure: 10-100 ppmv
- Maximum concentration that can be inhaled for one hour without serious effects such as significant eye and respiratory irritation: 200-300 ppmv
- Dangerous after exposure of 30 minutes to one hour: 500-700 ppmv
- Fatal in less than 30 minutes: 700-900 ppmv and above.
- Death in minutes: greater than 1000 ppmv

Hydrogen sulfide is highly flammable and will combust in air at concentrations from 4.3 to 46.0 volume percent. Hydrogen sulfide vapors are heavier than air and may migrate considerable distances to a source of ignition.

Gaseous carbon dioxide is a naturally occurring gas that is 50% heavier than air and is colorless and odorless. It is also a principal by-product of combustion. CO₂ is inactive and therefore non-flammable. CO₂ will displace oxygen and can create an oxygen-deficient atmosphere resulting in suffocation. The principal hazard of CO₂ is exposure to elevated concentrations. The atmospheric concentration immediately hazardous to life is 10% (volume).² Because CO₂ is heavier than air, its hazard potential is increased, especially when entering tanks and vessels. "A common but erroneous belief is that CO₂ simply acts as an asphyxiant by lowering the oxygen level below the 16 percent minimum necessary to sustain life (at sea level). Although this is frequently the case in most serious accidents, CO₂ begins to have a noticeable effect on normal body functions at about two to three percent. The concentration of carbon dioxide in the blood affects the rate of breathing, a measurable increase resulting from a level of one percent in the inspired air."²

Anyone engaged in the design or operation of a facility in which H₂S and/or CO₂ are present should seek expert advice for detailed safety precautions and mechanical design considerations.

TYPES OF CONTAMINANTS

Ammonia (NH₃)
Hydrogen sulfide (H₂S)
Hydrogen cyanide (HCN)
Carbon dioxide (CO₂)
Carbonyl sulfide (COS)
Carbon disulfide (CS₂)
Mercaptans (RSH)
Nitrogen (N₂)
Water (H₂O)
Sulfur dioxide (SO₂)
Elemental sulfur
Mercury and arsenic
Oxygen

Removal of these contaminants from hydrocarbon streams is required for reasons of safety, corrosion control, gas and/or liquid product specifications, to prevent freeze-out at low temperatures, to decrease compression costs, to prevent poisoning of catalysts in downstream facilities and to meet environmental requirements. The removal of water (dehydration) is discussed in Section 20. The discussion in this section will deal with removal of some or all of the sulfur-containing compounds and carbon dioxide.

GAS PRETREATMENT

All gas sweetening units should have well-designed pretreatment facilities. Carryover of brine or liquid hydrocarbon (as slugs or aerosol) from upstream production operations can cause problems for gas treating and downstream processing equipment. Also, field facilities are not typically designed to remove troublesome contaminants like gas-phase heavy hydrocarbons. These contaminants can likewise cause operational difficulties in the sweetening process.

Inlet Separation

If gross liquid carryover from an upstream facility is possible, a slug catcher is recommended. It should be sized not only for steady inlet fluid volumes, but for surge capacity to handle slugs of liquid hydrocarbons, water, and/or well treatment chemicals. See Section 17 for options regarding slug catcher design.

If aerosols are a concern, an inlet filter separator is suggested. Selected filter elements if combined with properly designed coalescing devices can remove entrained droplets down to 0.3 microns in diameter. The detailed design of filter separators is described in Section 7. Note that the effectiveness of a filter separator may be enhanced by the injection of a small amount of polymer into the gas stream upstream of the filter.³

In lieu of an inlet filter separator, a water wash column as shown in Fig. 21-1 may be placed ahead of the sweetening unit. Water washing can be particularly effective for removing glycol or methanol mists or fogs as well as reducing the vapor phase concentration present. Of course, stainless steel or other corrosion-resistant alloys should be considered for water washing in a sour environment. Trays can be sieve type, valves or other design as recommended by a vendor. Most of the time weirs are 2.5 to 3 inches high, and a reasonable pressure differential for the gas stream is 1.5 psi. A demister pad is recommended at the gas outlet.

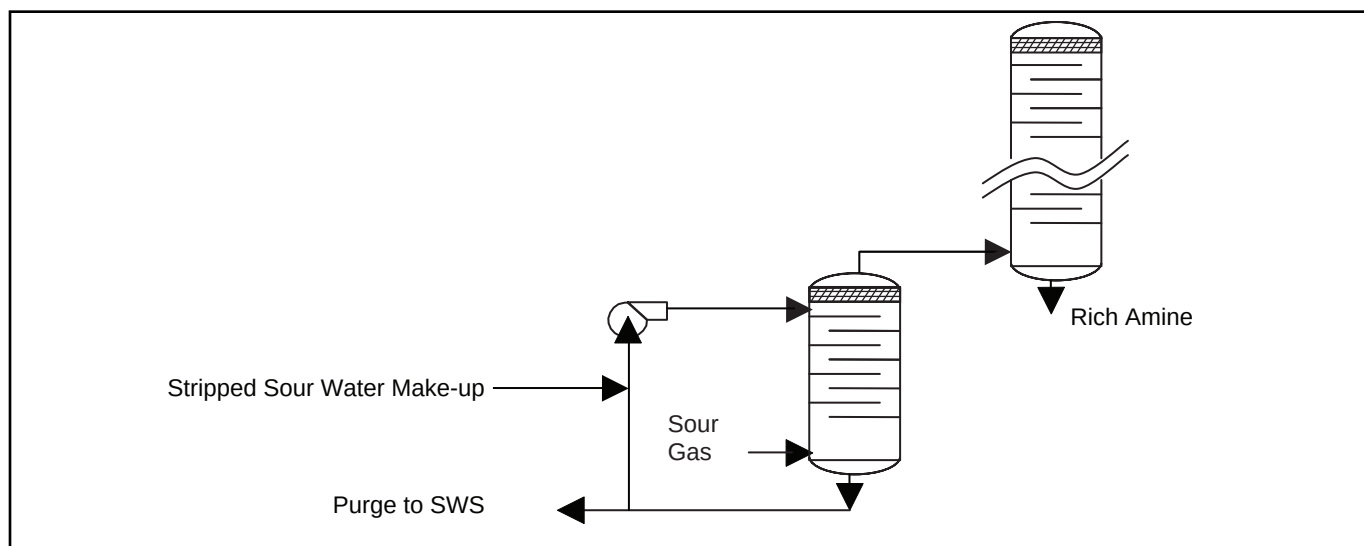
Water circulation rate should be 1 gallon per each 5 to 7 Mscf of gas (or 10 GPM per 80 to 100 MMscfd of gas). The recommended make up rate is 2 to 3% of the circulation, but this figure can be changed based on analytical results. The source of make up water can be stripped sour water, if available in the plant.

A white paper developed by members of GPA's Technical Section A (Facilities Design), titled, "Design Considerations for Water Wash Installations", may be obtained from GPA for a more in depth description of this system and possible design alternatives.

In the case of fine iron sulfide blowing in a dry pipeline, a glycol wash column has been reported to be an effective means of solids removal⁴.

For liquid hydrocarbon treatment, a filter coalescer may be used to remove suspended water or glycol prior to further processing.

FIG. 21-1
Typical Water Wash Schematic



Hydrocarbon Dewpoint Control

Heavy hydrocarbons (C6+) can be absorbed by solvents, which could lead to foaming in the sweetening unit. It is possible to reduce the heavy hydrocarbon content of the incoming gas through cooling (via Joule-Thomson expansion, propane refrigeration, or turbo-expansion as described in Section 16), and subsequent condensation of the heavy components. The condensed liquids are removed, and the gas is warmed above the saturation temperature before going to the sweetening unit.

An alternative means to remove gaseous heavy hydrocarbons is through adsorption. Typically silica gel beds may be used in parallel such that one bed is regenerated while the other is in service. The beds are regenerated by heating and desorbing the hydrocarbons. The heavy hydrocarbons are recovered from the regeneration gas via condensation.

Another alternative is to use a composite membrane where a rubbery polymer provides the selective membrane layer. This technology is used in fuel gas conditioning commercially, and is described in more detail in Section 16, Hydrocarbon Recovery.

Oxygen Contamination

Oxygen entry into a hydrocarbon system is often troublesome. If liquid water is present, severe corrosion may occur. If H₂S or sulfur is present, corrosion by a different mechanism or sulfur deposition and plugging may occur. Oxygen contamination may be addressed by several different approaches, but the first step is to find and correct the source of oxygen entry into the system. This is often the simplest and most cost effective approach. Most oxygen leaks may be traced to compressor suction or pipe fittings.

To eliminate oxygen contamination a number of possibilities exist:

- React the oxygen with chemicals.
- Chemicals such as amines, organics or inorganic compounds may be added to remove free oxygen. Oxygen scavengers are available from many suppliers.

- Use thermal oxidation by using a catalyst to consume the free oxygen by reacting it with the hydrocarbon present to form CO₂ and water.
- Use an iron-based oxidation catalyst that is activated with hydrogen sulfide or other organic sulfur compounds to remove the free oxygen.
- Remove other reactants that cause problems with the presence of oxygen. By removing offending components such as water or H₂S that react with oxygen, the presence of low amounts of oxygen might be tolerated.
- Treat the symptom.
- Corrosion inhibitors, filtration and/or alternate schemes may be utilized to stop or offset any adverse effects of oxygen contamination.

A GPA report (RR-201) reviewing technology for oxygen removal from natural gas is listed at the end of this section.

MERCURY REMOVAL

It is not unusual for gas streams to contain 1 to 10 micrograms/Nm³ (approx. 0.1 to 10 ppbv) of mercury. Some gas streams have been reported to have over 100 micrograms/m³ (approx. 10 ppbv). The mercury can attack aluminum in downstream plate fin heat exchangers used in most modern cryogenic hydrocarbon recovery plants as described in Section 16. In order for the attack to occur, the mercury must be present as a free liquid. This situation cannot occur above -40°F. Technically, mercury containing feedstocks can be handled without aluminum corrosion. Mercury containing equipment, which is kept at low temperature can be decontaminated by carrying out a cold, then warm purge with bone dry gas. However, this is not a practical method to be assured that mercury attack does not occur.

The mercury in the feed gas can be removed with a mercury removal bed. The bed uses a sulfur based trapping material which reacts with the mercury to form cinnabar (HgS) on the bed. The trapping material is carried on activated carbon, zeolite or alumina. The trapping bed is usually located downstream

of the dehydration. In this location, the gas is free of entrained liquids and water. Locating the bed in other locations is very dependent on the material used as recommended by the vendor. Fig. 21-2 designed to remove the mercury to 0.001 micrograms/Nm.³

Each vendor has criteria for sizing beds for their material. Typical sizing criteria used in the industry are to design for a superficial flow velocity of about 50 ft/min and a residence time of 10 seconds. With the rather small mass of mercury which is typically removed, the beds can last many years between change outs.

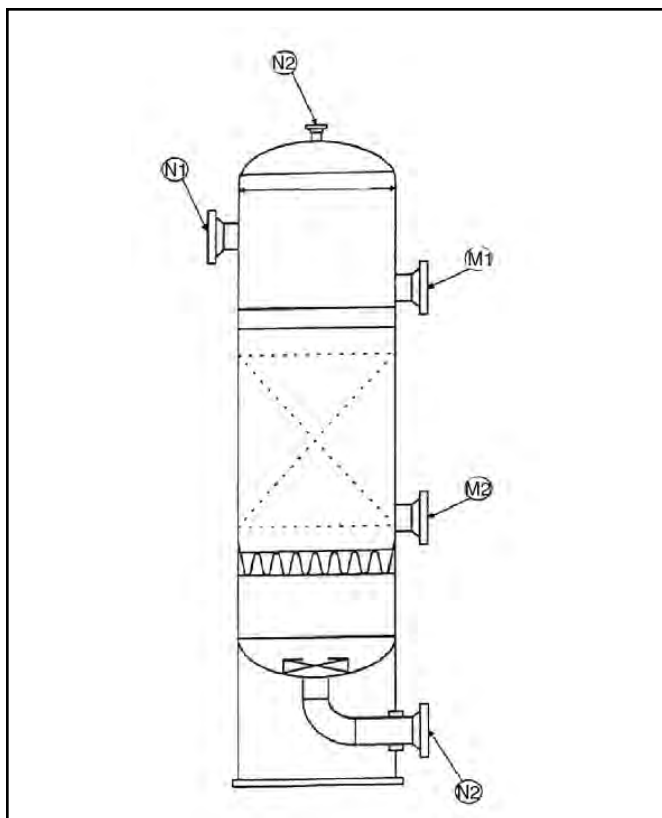
Calgon HGR[®]

Solid adsorbents can remove mercury from gas to produce residuals in the range of 0.01–0.001 µg/Nm.³. Calgon sulfur impregnated HGR[®] (4 x 10 mesh) and HGR[®]-P (4 mm dia.) carbons are used for mercury removal and indicate designs removing mercury down to very low levels. Removal of both inorganic and organic mercury is achieved. By first drying the gas the degree of mercury removal increases. The sulfur impregnate reacts with the mercury to produce a mercury sulfide that is fixed in the carbon microstructure.

Puraspec[®]

Johnson Matthey Catalysts supplies Puraspec[®] fixed bed adsorbents for removal of traces, elemental and organic, of mercury from hydrocarbon liquids and gases. The adsorbents have been shown to be capable of providing the outlet mercury concentration normally specified for LNG production and are in service in several European locations including an offshore oil/gas production platform.

FIG. 21-2
Mercury Removal Bed



Desorex[®]

Activated carbon provides only a limited storage capacity for the strictly physical adsorption of mercury. Desorex[®] HGD2S and HGD4S from Donau Carbon can be employed to bind mercury through the process of chemical adsorption involving oxidation and adsorption in the form of stable compound or fixation in metallic form as an amalgam. These Desorex[®] products have been used to purify natural gases to levels as low as 10 ug/m³ of mercury.

HgSIV[®]

UOP supplies HgSIV[®] adsorbents which are molecular sieves coated with elemental silver. Mercury in the gas is trapped by amalgamation with the silver. The adsorbent also serves the dual function of dehydrating the gas. HgSIV[®] is regenerated thermally, just like molecular sieves for dehydration. This material can be added as a layer to existing molecular sieve dryers⁵. However, one must take care to appropriately handle the regeneration gas in this case, as it will contain mercury, which when desorbed will come off as a concentrated spike.

CMG 271 and 273

Another mercury trapping material, CMG 273 is offered by Axens, which is sulfur supported on a mesoporous alumina. The advantage of this mesoporous alumina based product is its resistance to capillary condensation⁶. The larger pore size of this material, compared to carbon-based trapping materials, permits utilization at near dew point conditions. The trapping component is anchored on the alumina carrier making it completely insoluble in liquid hydrocarbons and water. The material has been subjected at gas plant sites to both DEA and liquid hydrocarbon carry-over with no active phase leaching. This same material has been used to eliminate elemental mercury from LPG and full range condensates.

CMG 271 also offered for use by Axens as a guard bed material used for mercury removal from gas hydrocarbon streams where the active trapping phase is a metal sulfide supported on alumina. This material provides a high efficiency for the removal of mercury from all types of gaseous flows, including natural gas.

Organic Mercury Removal

Removal of all forms of organic mercury compounds from natural gases and liquids requires firstly the conversion of the compounds to elemental metallic mercury followed by trapping materials to remove the metallic mercury formed. This requires in the first stage some hydrogen for organo-mercury hydrogenolysis with a suitable catalyst. The first stage catalyst such as MEP 841 also traps arsenic and lead impurities in the feed. The two stage impurities removal process is called RAM and is available from Axens.

GAS TREATING — PROCESS OPTIONS

The gas treating process can affect the design of the entire gas processing facility including methods chosen for acid gas disposal and sulfur recovery, dehydration, liquids recovery, liquids fractionation and liquid product treating. Some of the factors to be considered in making a gas treating process selection are:

- Air pollution regulations regarding sulfur compound disposal and/or Tail Gas Clean Up (TGCU) requirements.

- Type and concentration of impurities in the sour gas.
- Specifications for the residue gas.
- Specifications for the acid gas.
- Temperature and pressure at which the sour gas is available and at which the sweet gas must be delivered.
- Volume of gas to be processed.
- Hydrocarbon composition of the gas.
- Selectivity required for acid gas removal.
- Capital cost and operating cost.
- Royalty cost for using the process.
- Liquid product specifications.
- Disposal of byproducts considered hazardous chemicals.

Any process which requires disposal of waste chemicals must determine if the chemical is considered "hazardous." The permitting requirements and economic impact of hazardous waste disposal on a project must not be overlooked.

The importance of having an accurate analysis of the inlet gas stream cannot be overstressed. Process selection and economics depend on knowing all components present in the gas. Impurities such as COS, CS₂ and mercaptans (even in very small concentrations) can have a significant impact on the process design of both the gas treating and downstream processing facilities.^{7,8}

If the gas processing facility is to be used in conjunction with liquids recovery, the requirements for H₂S, CO₂, and mercaptan removal may be affected. In liquid recovery plants, varying amounts of H₂S, CO₂, and other sulfur compounds will end up in the liquid product. Failure to remove these components prior to liquids recovery may require liquid product treating in order to meet product specifications. In many instances, liquid treating may be required anyway.

When sulfur recovery is required, the composition of the acid gas stream feeding the sulfur plant must be considered. With CO₂ concentrations greater than 80% in the acid gas, the possibility of selective treating should be considered to raise the H₂S concentration to the sulfur recovery unit (SRU). This may involve a multi-stage gas treating system in which the gas exiting the first stage is enriched by passing it through another absorption solvent loop.

High concentrations of hydrocarbons can cause design and operating problems for the SRU. The effect of these components must be weighed when selecting the gas treating process to be used. Further discussion of this can be found in Section 22.

Decisions in selecting a gas treating process can many times be simplified by gas composition and operating conditions. High partial pressures (50 psi) of acid gases enhance the possibility of using a physical solvent; however, the presence of significant quantities of heavy hydrocarbons in the feed discourages using physical solvents. Low partial pressures of acid gases and low outlet specifications generally require the use of amines for adequate treating. Process selection is not easy and a number of variables must be weighed prior to making a process selection. Fig. 21-3 gives a summary for a number of processes.

Controlling pH is very important in most of the processes discussed in this section. The following is offered to assist in understanding electrolyte solutions and pH.

An electrolyte is a substance or material that will provide ionic conductivity when dissolved in water. Both bases and acids, if they ionize in water, can be electrolytes. In water, acids ionize or split, into H⁺ and the anion. The H⁺ combines with a water molecule to form H₃O⁺ which is usually written as H⁺ and is referred to as a hydrogen ion, or proton. Water-soluble bases, on the other hand, ionize in water to produce hydroxyl or OH⁻ ions and a cation. Pure water ionizes such that the concentration of H⁺ (and OH⁻) in the solution is 10⁻⁷ gram ions/liter.

The method used for measuring hydrogen and hydroxyl ion concentrations uses pH (from the French pouvoir hydrogene), where the pH of a solution is the logarithm (base 10) of the reciprocal of the hydrogen ion concentration (gram mole/liter). For pure water, then, the pH would be:

$$\text{pH} = \log (1/ [\text{H}^+]) = 7$$

When a water molecule dissociates, one proton and one hydroxyl ion are formed. The concentration of OH⁻ in pure water, then, is also 10⁻⁷ mole/liter.

A strong acid (or strong base) is one which ionizes completely in water solution. Typical are HCl or NaOH. At an acid concentration of 0.1 mole/liter, the pH of a strong acid will be 1. The following table will be helpful in understanding the relative concentrations of H⁺ and OH⁻ in solutions of different pH.

FIG. 21-3
Process Capabilities for Gas Treating

	Normally Capable of Meeting 4 ppmv H ₂ S	Removes Mercaptans and COS	Selective H ₂ S Removal	Solution Degraded (By COS & CO ₂)
Primary Amine	Yes	Partial	No	Yes
Secondary Amine	Yes	Partial	No	Some
Tertiary Amine	Yes	Partial	Yes*	No
Hybrid/Mixed	Yes	Yes	Yes*	Some
Physical Solvent	Yes	Yes	Yes*	No
Solid Bed	Yes	Yes	Yes*	N/A
Liquid Redox	Yes	No	Yes	CO ₂ at high conc.
Sacrificial	Yes	Partial	Yes	N/A
* Some selectivity exhibited				

	pH	Concentration, mole/liter	
		H ⁺	OH ⁻
Acid Side (Excess H ⁺)	1	$1.0 \cdot 10^{-1}$	$1.0 \cdot 10^{-13}$
	2	$1.0 \cdot 10^{-2}$	$1.0 \cdot 10^{-12}$
	3	$1.0 \cdot 10^{-3}$	$1.0 \cdot 10^{-11}$
	4	$1.0 \cdot 10^{-4}$	$1.0 \cdot 10^{-10}$
	5	$1.0 \cdot 10^{-5}$	$1.0 \cdot 10^{-9}$
	6	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-8}$
Neutral Solution	7	$1.0 \cdot 10^{-7}$	$1.0 \cdot 10^{-7}$
	8	$1.0 \cdot 10^{-8}$	$1.0 \cdot 10^{-6}$
	9	$1.0 \cdot 10^{-9}$	$1.0 \cdot 10^{-5}$
	10	$1.0 \cdot 10^{-10}$	$1.0 \cdot 10^{-4}$
	11	$1.0 \cdot 10^{-11}$	$1.0 \cdot 10^{-3}$
Basic Side (excess OH ⁻)	12	$1.0 \cdot 10^{-12}$	$1.0 \cdot 10^{-2}$
	13	$1.0 \cdot 10^{-13}$	$1.0 \cdot 10^{-1}$

Example 21-1 — 5,000 gallons of amine solution with a pH of 12 is to be neutralized by the addition of hydrochloric acid (HCl). How many pounds of pure HCl will be required?

Note: This is simply an example calculation; there is no practical reason for doing this in a gas treating plant.

MW of HCL = 36.5 g/gmole

Solution steps

$5,000 \text{ gal.} \cdot 3.79 \text{ (liter/gal)} = 1.9 \cdot 10^4 \text{ liters}$

For each liter of solution the change in OH⁻ (H⁺) required is $(10^{-2}) - (10^{-7}) = 1.0 \cdot 10^{-2} \text{ gram moles/liter}$

The total requirement of HCl is

$(1.9 \cdot 10^4) \text{ liter} \cdot (1.0 \cdot 10^{-2}) \text{ (g mole/liter)} = 190 \text{ g mole}$

or

$$\frac{(190 \text{ g mole})(36.5 \text{ g/gmole})}{454 \text{ (gram/pound)}} = 15.3 \text{ pounds HCl}$$

Note that at a pH of 7, all of a weak acid (base) would probably not be neutralized. The pH required to have all of a weak acid (base) neutralized will vary with the acid but will usually be less (greater) than 7. In the example all of the HCl is neutralized because it is completely ionized in the water solution.

CHEMICAL SOLVENT PROCESSES

Chemical reaction processes remove the H₂S and/or CO₂ from the gas stream by chemical reaction with a material in the solvent solution. The reactions may be reversible or irreversible. In reversible reactions the reactive material removes CO₂ and/or H₂S in the contactor at high partial pressure and/or low temperature. The reaction is reversed by high temperature and/or low pressure in the stripper. In irreversible processes the chemical reaction is not reversed and removal of the H₂S and/or CO₂ requires continuous makeup of the reacting material. Fig. 21-5 shows the process flow for a typical reversible chemical solvent reaction process. Fig. 21-6 is a table of physical properties of pure gas treating chemicals. Figs. 21-7 through 21-9 show vapor pressures at various temperatures and freezing points and specific gravity for some of the treating chemicals.

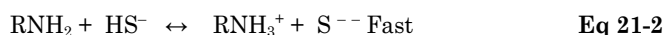
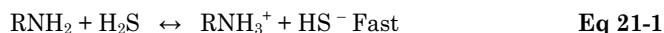
Aqueous Alkanolamine Processes

Originally applied to gas treating in 1930 by Bottoms⁹ alkanolamines have become the most widely used solvents for the removal of acid gases from natural gas streams¹⁰. Triethanolamine (TEA) was the first used commercially for gas treating. It has been displaced for conventional applications by other alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), diglycolamine® (DGA®) and methyldiethanolamine (MDEA). Fig. 21-4 lists approximate guidelines for a number of alkanolamine processes.

The alkanolamine (hereafter amine) solvent processes are particularly applicable where acid gas partial pressures are low and/or low levels of acid gas are desired in the residue gas. Because the water content of the solution minimizes heavy hydrocarbon absorption, these processes are well suited for gases rich in heavier hydrocarbons. Some amines can be used to selectively remove H₂S in the presence of CO₂.

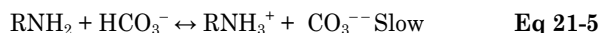
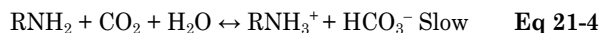
Chemistry — The overall equilibrium reactions applicable for H₂S and CO₂ and primary and secondary amines are shown below with a primary amine.¹¹ A qualitative estimation of the velocity of the reaction is given.

For hydrogen sulfide removal



The overall reactions between H₂S and amines are simple since H₂S reacts directly and rapidly with all amines to form the bisulfide by Equation 21-1 and the sulfide by Equation 21-2.

For carbon dioxide removal



Concerning the chemical reactions with CO₂, primary amines (RNH₂) such as MEA and DGA® agent, and secondary amines (RR'NH) such as DEA and DIPA, differ from tertiary amines (RR'R"N) such as TEA and MDEA.

Primary and Secondary Amines

With the primary and secondary amines, the predominant overall reaction (Equation 21-3) rapidly leads to the formation of a stable carbamate which is slow to further hydrolyze to bicarbonate.

The other overall reactions leading to bicarbonate (Equation 21-4) and to carbonate (Equation 21-5) are slow because they have to proceed through the hydration of CO₂.

Therefore, according to Equation 21-3 there is a theoretical limit to the chemical loading capacity of the primary and secondary amine solutions to 0.5 mole CO₂ per mole of amine, even at relatively high partial pressures of CO₂ in the gas to be treated.

Tertiary Amines

Unlike primary and secondary amines, the nitrogen (N) in tertiary amines (RR'R"N) has no free hydrogen (H) to rapidly form carbamate as per overall Equation 21-3. As a consequence, the removal of CO₂ by tertiary amines can only follow the slow route to bicarbonate by Equation 21-4 and carbonate by Equation 21-5.

The slow rate of the reaction leading to bicarbonate is the underlying reason why tertiary amines can be considered for selective H₂S removal. By adjusting absorption contact time, this selectivity can be used to full advantage when near total CO₂ removal is not necessary.

However the slow route to bicarbonate theoretically allows at equilibrium a chemical loading ratio of one mole of CO₂ per mole of amine. Furthermore, at high partial pressure, the physical solubility of CO₂ in tertiary amines is far greater than in the primary and secondary amines, thus enhancing the CO₂ loading by physical solubility under these conditions. Therefore, in the case of gases to be treated for bulk CO₂ removal, large amounts of CO₂ can be liberated from the rich solvent using a simple flash, and thereby, reducing the thermal regeneration duty with consequent energy savings.

Activated Tertiary Amines

The use of activators mitigates the slow rate of the reaction to bicarbonate for tertiary amines. Activators are generally primary or secondary amines; they are tailored to increase both the hydrolysis of the carbamate, and the rate of hydration of dissolved CO₂, thus making the activated tertiary amines especially suitable for efficient and economic bulk removal when selectivity is not required (see discussion on MDEA).

Amine Process Flow Configuration

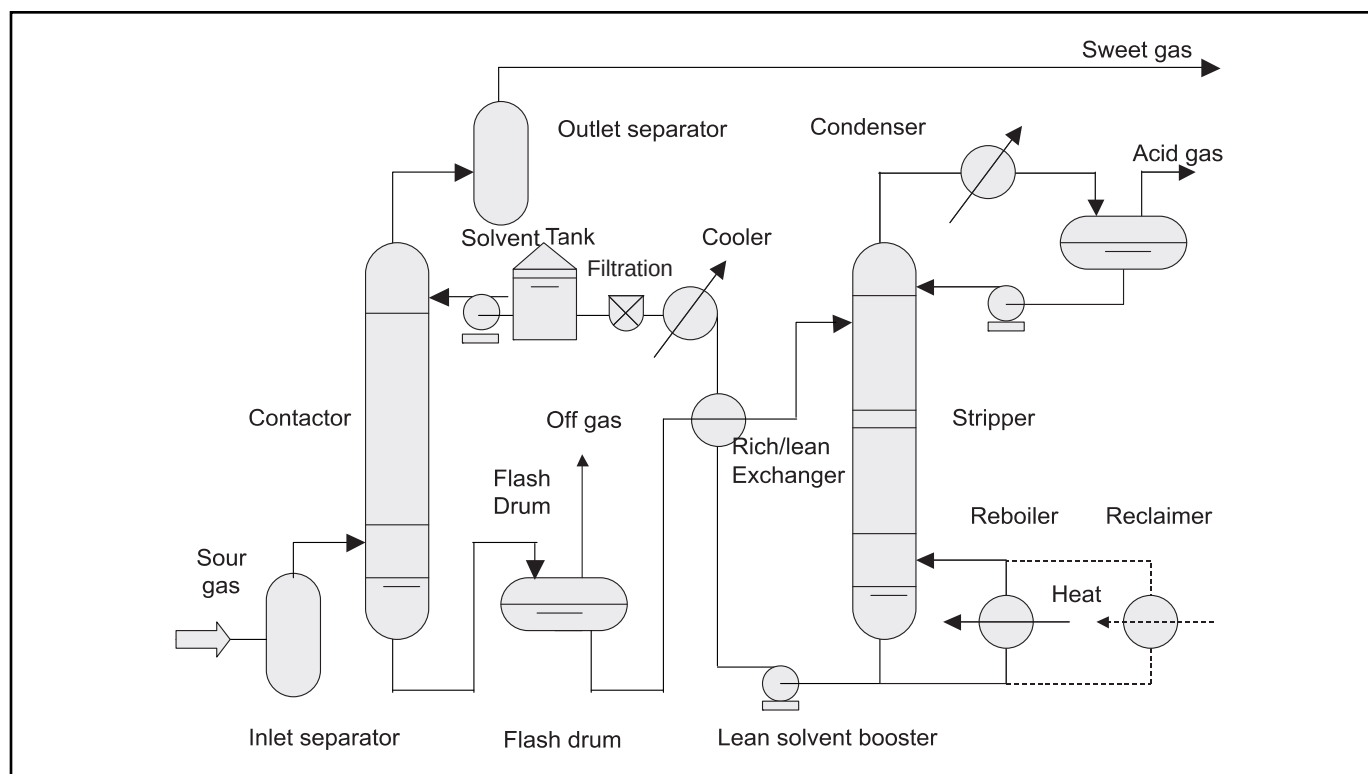
The general process flow for an amine treating plant is shown in Fig. 21-5. The basic flow configuration varies little for different solutions though some designs incorporate multiple feeds and contactor sections. Note that commercially-available process simulators are available to model these solvent processes.

FIG. 21-4

Approximate Guidelines for Amine Processes¹

	MEA	DEA ⁽⁹⁾	DGA [®]	Sulfinol [®]	MDEA
Acid gas pickup, scf/gal @ 100 °F, normal range ⁽²⁾	3.1–4.3	6.7– 7.5	4.7–7.3	4–17	3–7.5
Acid gas pickup, mols/mol amine, normal range ⁽³⁾	0.33–0.40	0.20–0.80	0.25–0.38	NA	0.20–0.80
Lean solution residual acid gas, mol/mol amine, normal range ⁽⁴⁾	0.12±	0.01±	0.06±	NA	0.005–0.01
Rich solution acid gas loading, mol/mol amine, normal range ⁽³⁾	0.45–0.52	0.21–0.81	0.35–0.44	NA	0.20–0.81
Max. solution concentration, wt%	25	40	60	3 comps., varies	65
Approximate reboiler heat duty, Btu/gal lean solution ⁽⁵⁾	1,000–1,200	840–1,000	1,100–1,300	350–750	800–900
Steam heated reboiler tube bundle, approx. average heat flux, Q/A = Btu/hr-ft ² ⁽⁶⁾	9,000–10,000	6,300–7,400	9,000–10,000	9,000–10,000	6,300–7,400
Direct fired reboiler fire tube, average heat flux, Q/A = Btu/hr-ft ² ⁽⁶⁾	8,000–10,000	6,300–7,400	8,000–10,000	8,000–10,000	6,300–7,400
Reclaimer, steam bundle or fire tube, average heat flux, Q/A = Btu/hr-ft ² ⁽⁶⁾	6,000–9,000	NA ⁽⁷⁾	6,000–8,000	NA	NA ⁽⁷⁾
Reboiler temperature, normal operating range, °F ⁽⁸⁾	225–260	230–260	250–270	230–280	230–270
Heats of reaction; ⁽¹⁰⁾ approximate: Btu/lb H ₂ S Btu/lb CO ₂	610 825	555 730	674 850	NA NA	530 610
NA — not applicable or not available					
NOTES: 1. These data alone should not be used for specific design purposes. Many design factors must be considered for actual plant design. 2. Dependent upon acid gas partial pressures and solution concentrations. 3. Dependent upon acid gas partial pressures and corrosiveness of solution. Might be only 60% or less of value shown for corrosive systems. 4. Varies with stripper overhead reflux ratio. Low residual acid gas contents require more stripper trays and/or higher reflux ratios yielding larger reboiler duties. 5. Varies with stripper overhead reflux ratios, rich solution feed temperature to stripper and reboiler temperature. 6. Maximum point heat flux can reach 20,000–25,000 Btu/hr-ft ² at highest flame temperature at the inlet of a direct fired fire tube. The most satisfactory design of firetube heating elements employs a zone by zone calculation based on thermal efficiency desired and limiting the maximum tube wall temperature as required by the solution to prevent thermal degradation. The average heat flux, Q/A, is a result of these calculations. 7. Reclaimers are not used in DEA and MDEA systems. 8. Reboiler temperatures are dependent on solution conc. flare/vent line back pressure and/or residual CO ₂ content required. It is good practice to operate the reboiler at as low a temperature as possible. 9. According to Total. 10. B.L. Crynes and R.N. Maddox, Oil Gas J., p. 65–67, Dec. 15 (1969). The heats of reaction vary with acid gas loading and solution concentration. The values shown are average ¹⁰ .					

FIG. 21-5
Typical Gas Sweetening by Chemical Reaction



Sour natural gas enters through an inlet separator for the removal of liquids and/or solids. From the separator, the gas stream is often heated about 10°F to reduce the potential for hydrocarbon condensation as discussed earlier in this chapter. The gas then enters the bottom of the contactor where it contacts the amine solution flowing down from the top of the column. The acid gas components in the gas react with the amine to form a regenerable salt. As the gas continues to pass up the contactor, more acid gases chemically react with the amine. The sweetened gas leaves the top of the contactor and passes through an outlet separator to catch any solution which may be carried over.

The sweet gas leaving the contactor is saturated with water so dehydration, discussed in Section 20, is normally required prior to sale. If the amine losses are excessive, a water wash section as shown in Fig. 21-10 is typically added to the column to attempt to recover some of the vaporized and/or entrained amine from the gas leaving the contactor. The water wash section generally consists of three or four trays at the top of the contactor. Trays can be sieve type, valves or other design as recommended by a vendor. Weirs are 2.5 to 3 inches high. It is recommended to install a demister pad on the vapor outlet.

Amine vapors and small droplets are dissolved and coalesced in water running in a closed loop with a circulation pump. To control amine concentration from building up in the water, some of the water is purged and made up. The purge is normally routed to the Flash Tank (Drum).

Water circulation rate should be 1 gallon per 7 Mscf of gas (or 10 GPM per 100 MMscfd of gas). The recommended make up rate is the largest of 3% of the circulation or the total system make up flow.

A white paper developed by members of GPA's Technical Section A (Facilities Design), titled, "Design Considerations for Water Wash Installations", may be obtained from GPA for a more in depth description of this system and possible design alternatives.

Note that the lean amine coming into the top of the contactor must be at a sufficiently low loading and temperature such that the vapor pressure of the acid gas above the amine is low enough to meet the treated gas specification (e.g., 4 ppm H₂S, and in the case of LNG, 50-100 ppm CO₂). If the loading/temperature criteria are not met, no amount of solvent will reduce acid gas concentration adequately to meet the required specification. This is known as a "lean end pinch," since there is not sufficient mass-transfer driving force to remove the residual acid gases.

As the solvent moves down the column and reacts with the H₂S and CO₂, the exothermic reactions increase the solvent temperature. Since raw gas coming into the bottom of the contactor cools the solvent, there is usually a temperature "bulge" above the gas inlet. Increased temperatures tend to increase the vapor pressure of acid gases above the enriched solvent, so it is possible that the driving force for mass transfer is reduced to near zero, resulting in a "rich end pinch." In this case, additional solvent will improve the situation by reducing the rich loading and temperature in that portion of the column.

The maximum attainable pure component loading is limited by the equilibrium solubility of H₂S and CO₂ at the absorber bottoms conditions, which may be reached in some high-load applications. Attached as Fig. 21-11 is data from GPA research report RR-104 on MEA, DGA® & MDEA along with the DEA

FIG. 21-6
Physical Properties of Gas Treating Chemicals

	MEA	DEA	TEA	DGA®	DIPA	Selexol®
Formula	HOC ₂ H ₄ NH ₂	(HOC ₂ H ₄) ₂ NH	(HOC ₂ H ₄) ₃ N	H(OC ₂ H ₄) ₂ NH ₂	(HOC ₃ H ₆) ₂ NH	Polyethylene glycol derivative
Molecular Wt	61.08	105.14	148.19	105.14	133.19	280
Boiling point @ 760 mm Hg, °F	338.9	516.2 (decomposes)	680 (decomposes)	430	479.7	518
Freezing point, °F	50.9	82.4	72.3	9.5	107.6	-20
Critical constants						
Pressure, psia	868	474.7	355	547.11	546.8	—
Temperature, °F	662	827.8	957.7	756.6	750.6	—
Density @ 20°C, gm/cc.	1.018	1.095	1.124	1.058 @ 60°F	0.999 @ 30°C	1.031 @ 77°F
Weight, lb/gal	8.48 @ 60°F	9.09 @ 60°F	9.37 @ 68°F	8.82 @ 60°F		8.60 @ 77°F
Specific gravity 20°C/20°C	1.0179	1.0919 (30/20°C)	1.1258	1.0572	0.989 @ 45°C/20°C	—
Specific heat @ 60°F, Btu/lb°F	0.608 @ 68°F	0.600	0.70	0.571	0.69 @ 30°C	0.49 @ 41°F
Thermal conductivity						
Btu/[(hr · sq ft · °F)/ft] @ 68°F	0.148	0.127	—	0.121	—	0.11 @ 77°F
Latent heat of vaporization, Btu/lb	180 @ 760 mmHg	288 @ 73 mmHg	230 @ 73 mmHg	219 @ 760 mmHg	185 @ 760 mmHg	—
Heat of reaction, Btu/lb of Acid Gas						
H ₂ S			-400	-674	—	-190 @ 77°F
CO ₂			-630	-850	—	-160 @ 77°F
Viscosity, cp	24.1 @ 68°F	350 @ 68°F (at 90% wt. solution)	1013 @ 68°F (at 95% wt. solution)	40 @ 60°F	870 @ 86°F 198 @ 113°F 86 @ 129°F	5.8 @ 77°F
Refractive index, N _d 68°F	1.4539	1.4776	1.4852	1.4598	1.4542 @ 113°F	—
Flash point, COC, °F	200	298	365	260	255	304

	Propylene Carbonate	MDEA	Sulfolane®	Methanol	10% Sodium Hydroxide	Flexsorb®SE
Formula	C ₃ H ₆ CO ₃	(HOC ₂ H ₄) ₂ NCH ₃	C ₄ H ₈ SO ₂	CH ₃ OH		Proprietary
Molecular Wt	102.09	119.16	120.17	32.04	19.05	>130
Boiling point @ 760 mm Hg, °F	467	477	545	148.1	217	446
Freezing point, °F	-56.6	-9.3	81.7	-143.8	14	32
Critical constants	—					
Pressure, psia	—		767.3	1153.9		
Temperature, °F	—		1013.8	464		
Density @ 20°C, gm/cc.	1.2057					
Weight, lb/gal		8.68	10.623 @ 30°C/30°C		9.254	7.81 @ 60°F
Specific gravity 20°C/20°C	1.203	1.0418	1.268	0.7917	1.110	
Specific heat @ 60°F, Btu/lb°F	0.335	0.535	0.35 @ 30°C	0.59 @ 5°-10°C	0.897	
Thermal conductivity						
Btu/[(hr · sq ft · °F)/ft] @ 68°F	0.12 @ 50°F	0.159	0.114 @ 100°F	0.124		
Latent heat of vaporization, Btu/lb	208 @ 760 mmHg	204	225.7 @ 212°F	474 @ 760 mmHg		172 @ 760 mmHg
Heat of reaction, Btu/lb of Acid Gas	—					
H ₂ S						
CO ₂						
Viscosity, cp	1.67 @ 100°F	1.01 @ 68°F 33.8 @ 104°F	10.3 @ 86°F 6.1 @ 122°F 2.5 @ 212°F 1.4 @ 302°F 0.97 @ 392°F	0.6 @ 68°F	1.83 @ 68°F 0.97 @ 122°F 0.40 @ 212°F	127 @ 60°F 37 @ 100°F
Refractive index, N _d 68°F	1.4209	1.469	1.481 @ 86°F	1.3286		
Flash point, COC, °F	270	265	350	58		210

FIG. 21-7
Vapor Pressures of Gas Treating Chemicals

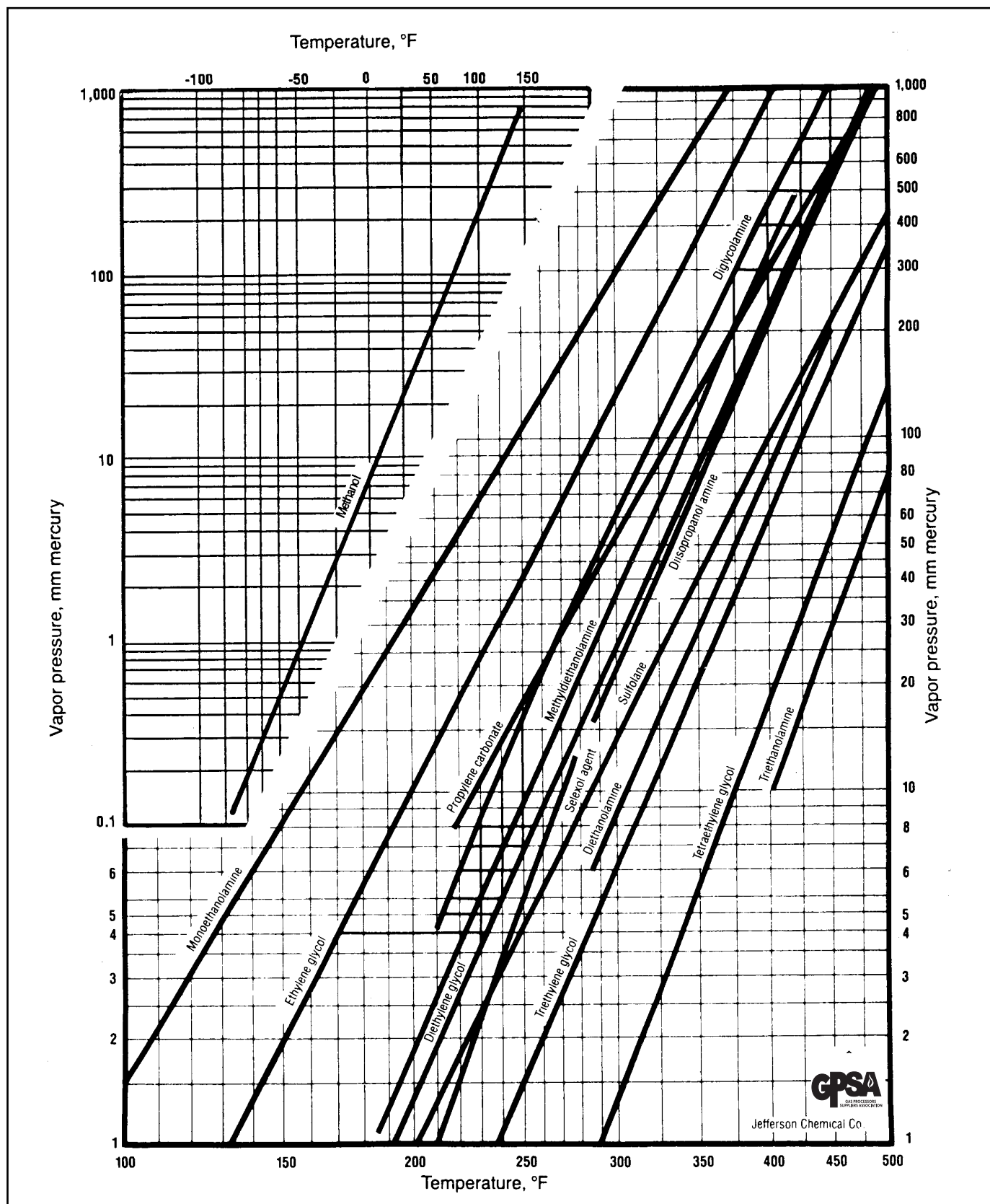


FIG. 21-8
Freezing Points of Aqueous Amine Solutions

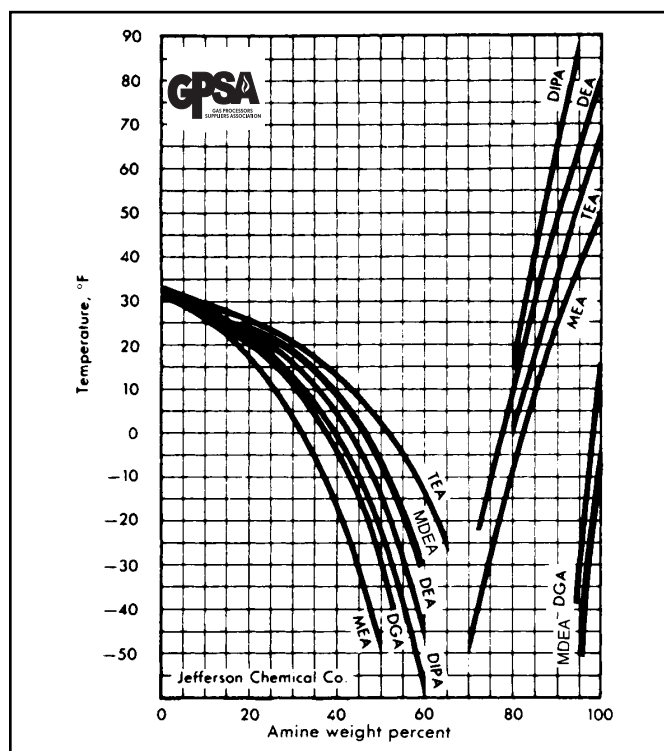


FIG. 21-9
Specific Gravity of Aqueous Amine Solutions

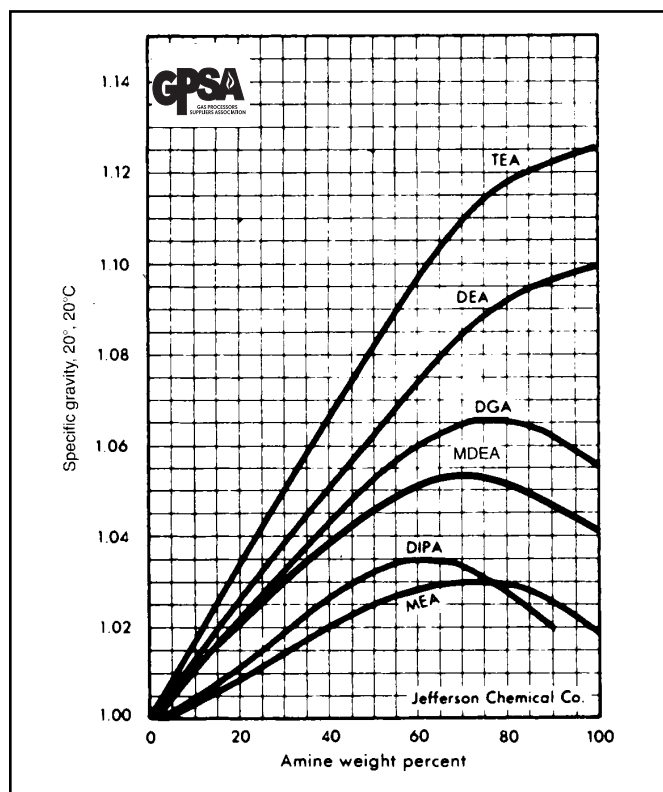
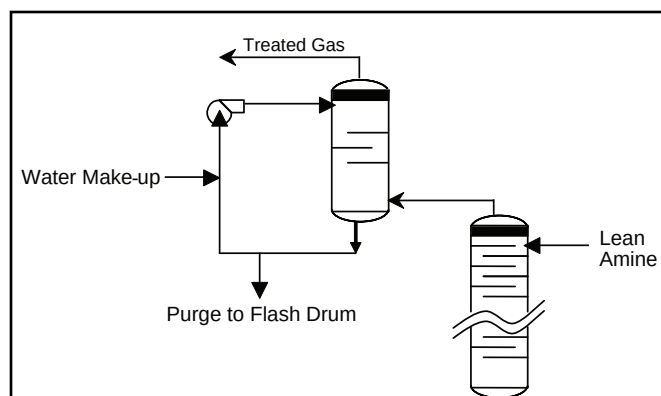


FIG. 21-10
Typical Water Wash for Sweet Gas Leaving Amine Contactor



data from the 12th Edition for the equilibrium solubility of H_2S and CO_2 ; however, it should be noted that both species are usually present, and the equilibrium limit for each species is impacted by the existence of the other.

FIG. 21-11
Maximum Attainable Pure Component Loading

40 wt% DEA @ 190°F

H_2S partial pressure (psia)	45	145	220
mol H_2S /mol amine	0.66	0.8	0.97
CO_2 partial pressure (psia)	45	90	145
mol CO_2 /mol amine	0.49	0.55	0.6

15 wt% MEA @ 176°F

H_2S partial pressure (psia)	0.96	6.87	67.4
mol H_2S /mol amine	0.717	0.995	1.187
CO_2 partial pressure (psia)	36	170	254
mol CO_2 /mol amine	0.636	0.787	0.832

60 wt% DGA® @ 122°F

H_2S partial pressure (psia)	2.8	12.9	58.8
mol H_2S /mol amine	0.435	0.756	0.986
CO_2 partial pressure (psia)	26.6	115	484
mol CO_2 /mol amine	0.5984	0.668	0.773

20 wt% MDEA @ 150°F

H_2S partial pressure (psia)	3.24	26.3	138.1
mol H_2S /mol amine	0.435	0.756	1.178
CO_2 partial pressure (psia)	6.92	24.26	148.4
mol CO_2 /mol amine	0.4433	0.706	0.999

Regardless it is important to note most conventional amine plants operate at significantly lower loadings than the equilibrium limit.

Rich amine solution leaving the contactor flows through a flash drum to flash off light hydrocarbons like methane and to allow heavier hydrocarbons to be skimmed off as a separate liq-

uid phase. From the flash drum, the rich solution passes through the rich/lean exchanger where heat is transferred from the hot lean solution. The heated rich amine goes to the upper portion of the stripper. As the solution flows down the column to the reboiler, it is stripped of H_2S and CO_2 . The amine solution leaves the bottom of the stripper as lean solution. This lean solution is then passed through the rich/lean exchanger and a lean cooler to reduce the lean solution temperature to approximately 10°F warmer than the inlet gas temperature, to stay above the hydrocarbon dew point. At this point, the lean solution is returned to the contactor to repeat the cycle.

Acid gas stripped from the amine passes out of the top of the stripper. It goes through a condenser and separator to cool the stream and recover water. The recovered water is usually returned to the stripper as reflux. The acid gas from the reflux separator is either vented, incinerated, sent to sulfur recovery facilities, or compressed for sale or reinjected into a suitable reservoir for enhanced (see acid gas injection) oil recovery projects or for sequestration.

Reclaimer — A reclaimer is usually required for MEA and DGA® amine-based systems. The reclaimer helps remove degradation products from the solution and also aids in the removal of heat stable salts, suspended solids, acids and iron compounds. The reclaimers in MEA and DGA® systems differ. For MEA, a basic solution helps reverse the reactions. Soda ash and/or caustic soda is added to the MEA reclaimer to provide a pH of approximately 8-9; no addition is required for the DGA® reclaimer system. Reclaimers generally operate on a side stream of 1-3% of the total amine circulation rate.¹³ Reclaimer sizing depends on the total inventory of the plant and the rate of degradation expected.

Reclaimer operation is a semi-continuous batch operation. The reclaimer is filled with hot amine solution and, if necessary, soda ash is added. As the temperature in the reclaimer increases, the liquid will begin to distill. Overhead vapors can be condensed and pumped back into the amine system, but generally the reclaimer is operated at slightly above stripper column pressure and the vapors are returned to the stripper. The initial vapor composition is essentially water. Continued distillation will cause the solution to become more and more concentrated with amine. This raises the boiling point of the solution and amine will begin to distill overhead. Fresh feed is continually added until the boiling point of the material in the reclaimer reboiler reaches 280° to 300°F . At this point, distillation is continued for a short time adding only water to help recover residual amine in the reclaimer reboiler. The reclaimer is then cleaned, recharged, and the cycle is repeated.¹⁴

Reclaimer “sludge” removed during cleaning must be handled with care. Disposal of the “sludge” must be in accordance with the governing regulations.

If needed a reclaiming company may be contracted to remove degradation products or heat-stable salts from the amine. One type of reclaimer performs vacuum distillation on batches of spent amine mixed with sufficient caustic to neutralize the excess acidity. Another type of reclaimer uses ion exchange resin beds to remove heat stable salts.

Amines Used

Monoethanolamine — Gas sweetening with monoethanolamine (MEA) is used where there are low contactor pressures and/or stringent acid gas specifications. MEA removes both H_2S and CO_2 from gas streams. H_2S concentrations well below 4.0 ppmv can be achieved. CO_2 concentrations as low as

100 ppmv can be obtained at low to moderate pressures. COS and CS_2 are removed by MEA, but the reactions are irreversible unless a reclaimer is used. Even with a reclaimer, complete reversal of the reactions may not be achieved. The result is solution loss and build-up of degradation products in the system. Total acid gas pick up is traditionally limited to 0.3-0.35 moles of acid gas/mole of MEA and solution concentration is usually limited to 10-20 wt%. Corrosion inhibitors can be used to allow much higher solution strengths and acid gas loadings. Because MEA has the highest vapor pressure of the amines used for gas treating, solution losses through vaporization from the contactor and stripper can be high. This problem can be minimized by using a water wash.

Diethanolamine — This process employs an aqueous solution of diethanolamine (DEA). DEA will not treat to pipeline quality gas specifications at as low a pressure as will MEA.

Among the processes using DEA is the SNPA-DEA process developed by Societe Nationale des Petroles d'Aquitaine (today Total) to treat the very sour gas which was discovered in Lacq France in the 1950s. The original patents covered very high acid gas loading of 0.9 to 1.3 moles per mole of amine. This process is used for high pressure, high acid gas content streams having a relatively high ratio of $\text{H}_2\text{S}/\text{CO}_2$. The original process has been progressively improved and Total (through Prosernat) uses higher DEA solution concentrations up to 40 wt% and a high acid gas loading with corrosion control by appropriate design and operating procedures.

The process flow scheme for conventional DEA plants resembles the MEA process. The advantages and disadvantages of DEA as compared to MEA are:

- The mole/mole loadings typically used with DEA (0.35-0.82 mole/mole) are much higher than those normally used (0.3-0.4) for MEA.
- Because DEA does not form a significant amount of non-regenerable degradation products, a reclaimer is not usually required. If DEA has to be reclaimed it must be done under vacuum conditions.
- DEA is a secondary amine and is chemically weaker than MEA, and less heat is required to strip the amine solution.
- DEA forms a regenerable compound with COS and CS_2 and can be used for the partial removal of COS and CS_2 without significant solution losses.

Diglycolamine — This process uses Diglycolamine® brand [2-(2-aminoethoxy)] ethanol in an aqueous solution. DGA® is a primary amine capable of removing not only H_2S and CO_2 , but also COS and mercaptans from gas and liquid streams. Because of this, DGA® has been used in both natural and refinery gas applications. DGA® has been used to treat natural gas to 4.0 ppmv at pressures as low as 125 psig.¹⁵ DGA® has a greater affinity for the absorption of aromatics, olefins, and heavy hydrocarbons than the MEA and DEA systems. Therefore, adequate carbon filtration should be included in the design of a DGA® treating unit.

The process flow for the DGA® treating process is similar to that of the MEA treating process. The three major differences are:

- Higher acid gas pick-up per gallon of amine can be obtained by using 50-60% solution strength rather than 15-20% for MEA (more moles of amine per volume of solution).