

Chapter 1

INTRODUCTION TO GAS TREATING

1.1 INTRODUCTION

The removal of acid gas impurities such as carbon dioxide (CO₂), hydrogen sulfide (H₂S), and carbonyl sulfide (COS) from industrial gases is an essential step in processing sour natural gas, refinery off-gases, and synthesis gas for ammonia production. The removal of acid gases from gas streams, commonly referred to as acid gas treating and also as gas sweetening, is a technology that has been in use for several years in natural gas processing units, refineries, petrochemicals, and fertilizer industries. In 1930 Bottoms (Bottoms, 1930) presented a process to remove CO₂ using alkanolamines.

CO₂ and H₂S concentrations in the sour natural gas streams may vary widely, from several parts per million to 50% by volume of the gas streams. These impurities when present in the gas streams may lead to very serious problems in pipeline transportation and downstream processing of the gas. CO₂ present in natural gas will reduce the heating value of the gas and may cause corrosion in pipelines and equipment in presence of moisture. Moreover, energy is wasted in compressing this extra volume for pipeline transportation of natural gas. The CO₂ specification in the treated natural gas may be about < 1% by volume for pipeline gas, but for natural gas liquefaction plants CO₂ in the treated natural gas must be below 100 ppm to avoid freezing in the cryogenic equipment. The CO₂ specification is < 10 ppm by volume for treated syngas for ammonia manufacture to protect ammonia synthesis catalyst (Astarita *et al.*, 1983). Bio-generated methane from the decomposition of organic material often contains large amounts of CO₂, which must be removed in order to improve its heating value (Ashare, 1981; Zimmerman *et al.*, 1985). The cleanup target for H₂S is particularly stringent, e.g., 4 ppm by volume for pipeline gas, 0.1 ppm for ammonia synthesis and in petrochemical plants (Astarita *et al.*, 1983). In refinery operations, H₂S must be

removed almost completely from the refinery-off gas streams due to its toxicity and corrosivity and to avoid catalyst poisoning. However, the cleanup specifications vary widely from process to process. A comprehensive summary of important industrial gas treating processes and cleanup targets are discussed by Astarita *et al.* (1983).

With massive and sustained growth in natural gas sectors both with respect to its resource and consumption, natural gas is certainly poised to take the leading role in this century in the world energy sector as well as in chemical and petrochemical industries. It is now apparent that fossil fuel will continue to meet the world energy requirements for several years to come. However, to reduce the CO₂ penalty it is essential to shift, as much as possible, from high carbon density fossil fuel, e.g., coal to low carbon density fuel, e.g., natural gas, for energy production. Thus, it is important to recognize that natural gas takes up a unique and strategic position in the hierarchy of energy resource options. Natural gas utilization has been constantly increasing in the last 50 years. Industrial sector accounted for 44 % of world natural gas consumption in 2004 and industrial use of natural gas is projected to increase at an average annual rate of 1.9% for 2004-2030. Consumption of natural gas worldwide is likely to increase from 100 trillion cubic feet in 2004 to 163 trillion cubic feet in 2030 (Energy Information Administration/International Energy Outlook, 2007). However, the trend observed in the discoveries of new gas reserves reveals a growing distance between resources and major consumer markets. Approximately, 3000 trillion cubic feet out of 6183 trillion cubic feet of proved world natural gas resource (Energy Information Administration/International Energy Outlook, 2007) is in stranded reserves, usually located far away from pipeline infrastructure. Consequently, the cost of production, processing and transportation of natural gas remain high and represent a handicap. Hence, extensive R&D activities on more efficient processes and technologies, improved solvents for sweetening to reduce the costs of production and processing is clearly essential to ensure the development and best utilization of available natural gas resources.

In recent years, growing environmental concerns for global warming, climate change and acid rain have motivated extensive R&D activities to develop efficient and economic processes for CO₂ capture and sequestration. A recent report of the

Intergovernmental Panel on Climate Change (IPCC) on Carbon dioxide Capture and Storage (CCS) (IPCC, 2005) states that global emissions of CO₂ from fossil fuel use totaled about 23.5 GtCO₂ per year (6 GtC per year) in 2000. Of this, close to 60% was attributed to large (> 0.1MtCO₂ per year) stationary emission sources like, power plants, gas processing industries, refineries, chemical and petrochemical industries, iron and steel industries and cement industries. As a result of anthropogenic CO₂ emission, atmospheric concentrations rose by 30 % from pre-industrial levels of 280 ppmv to 360 ppmv today and it is predicted that the CO₂ concentration of the atmosphere will increase from its present value of 600 ppmv to 900 ppmv by the year 2050, primarily as a consequence of fossil fuel use. In the IPCC Special Report on Emission Scenarios, the future emission ranges of CO₂ are projected from 29 to 44 GtCO₂ (8-12 GtC) per year in 2020, and from 23 to 84 GtCO₂ (6-23 GtC) per year in 2050. The projected potential of CO₂ capture associated with the above emission ranges has been estimated as 2.6 to 4.9 GtCO₂ per annum by 2020 (0.7 – 1.3 GtC) and 4.7 to 37.5 GtCO₂ per annum by 2050 (1.3 –10 GtC). In view of this situation, developed countries under the Kyoto protocol of the United Nations Framework Convention on Climate Change (UNFCCC), have agreed to reduce their emissions by 5.2 % below the 1990 levels by 2008-2012. Major challenges for CO₂ capture from the flue gas stream of a fossil fuel fired power plant are the large volumetric flow rates of flue gas with large amount of CO₂ at low partial pressures. The flue gas from a power plant mainly consists of N₂, water vapor and CO₂. For coal based thermal power plants the flue gas may also contain SO₂ and NO_x which are known to form heat stable salts with the amines used for CO₂ capture leading to substantial solvent degradation. Hence, appropriate measures need to be taken to reduce thermal and chemical degradation of the solvents for application of alkanolamine solvents for CO₂ capture from the flue gas streams of thermal power plants. Due to the low CO₂ partial pressure and the fact that flue gas compression to high pressure is not economic, application of physical absorption for CO₂ capture is not appropriate. Therefore, potential solvents for CO₂ capture are only those which have high reaction rates and high equilibrium capacities for CO₂. The column diameter of the absorber and the desorber and thus capital cost are mainly determined by the feed gas flow rate. In addition, capital cost is also related to the

column height, which is strongly influenced by the kinetics, especially in the absorber. Operating costs are primarily determined by the solvent circulation rate in the absorber/desorber loop, and the regeneration energy requirement. Thermodynamic equilibrium data for CO₂ solubility determine the most important process parameters e.g., solvent circulation rate and energy requirement. Obviously, these two play an important role in process economics. Absorption/desorption kinetics have strong influence on the height of the columns and thus the capital cost. Solvent properties like water solubility and corrosivity are other important parameters with regard to operational behavior. All these criteria have to be taken into account in the solvent selection process.

1.2 CURRENT TECHNOLOGIES FOR CO₂ REMOVAL

There are several commercial processes which can, in principle, be used for the removal of CO₂ from gas streams. Based on the method of removal, capture technologies can be broadly classified into the following categories (Kohl and Nielsen, 1997; Astarita *et al.*, 1983, IEA, 2001):

- (i) Chemical/Physical Absorption
- (ii) Adsorption
- (iii) Membrane Separation
- (iv) Cryogenic

1.2.1 Chemical/Physical Absorption

Chemical, physical, and hybrid absorption processes are widely used for removal of acid gas impurities from sour gas streams (Astarita *et al.*, 1983; Kohl and Nielsen, 1997). Commercially available CO₂ scrubbing solvents used for sweetening sour gas streams are listed in Table 1.1. Regenerative chemical absorption processes make use of the reversible nature of the chemical reaction of an aqueous solvent with the acid gas component, e.g., CO₂. The most commonly used chemical solvents for the chemical absorption processes are aqueous alkanolamines, aqueous carbonate, etc.

While chemical absorption is preferred for low to moderate CO₂ partial pressures in the primary gas streams, physical absorption processes in which CO₂ can be physically absorbed by a solvent without any chemical reaction, are used when the partial pressure of CO₂ is high (>1.5 MPa). The main point of difference between the chemical absorption and the other CO₂ removal processes is the large energy requirement in solvent regeneration in chemical absorption. In addition, thermal and oxidative degradation of the solvents result in large solvent make-up, besides producing products that are corrosive. Hence, chemical absorption processes with newer amine solvents, such as sterically hindered amines, amine based ionic liquids, and activated amine solvents which have a higher selectivity for CO₂, a higher degradation resistance, and lower energy requirements for regeneration, are presently the subject of global R&D. In hybrid absorption processes, solvents, which offer a combination of chemical and physical absorption, are used.

1.2.2 Adsorption

Adsorbents, such as molecular sieves are used in adsorbing CO₂ from various gas streams (Kohl and Nielsen, 1997; Kapoor and Yang, 1989). Pressure swing adsorption (PSA) and temperature swing adsorption (TSA) are commercially practiced methods of gas separation by adsorption. Adsorption is not yet considered attractive for large-scale separation of CO₂ from natural gas or flue gas streams because the capacity and CO₂ selectivity of available adsorbents is low. However, it may be useful in combination with other capture technologies. The development of a new generation of materials that would efficiently adsorb CO₂ will undoubtedly enhance the competitiveness of adsorption separation for flue gas application.

1.2.3 Membrane Separation

Although various gas separation membranes are developed today, such as inorganic membranes, polymeric membranes, and zeolite based membranes, application of membrane separation has not yet been very successful for bulk removal

of CO₂ from natural gas and also from the flue gas streams of power plants. Because of low CO₂ - CH₄ selectivity of available membranes, the use of membranes in CO₂ removal from natural gas has not been found to be attractive (Kohl and Nielsen, 1997; Maddox and Morgan, 1998). However, with the development of newer membrane materials with high selectivity and permeability for CO₂, membrane separation processes may find successful commercial application in future, since membrane processes are in general less energy intensive.

1.2.4 Cryogenic

Cryogenic separation is another technique used in the industry for the separation of CO₂ from gas streams with high CO₂ concentrations (typically >50%) (Kohl and Nielsen, 1997). But it is not used for dilute CO₂ streams. The advantage of this process is that it produces a liquid CO₂ ready for transportation by pipeline or by ship. The major disadvantages of this technology are the high energy requirement to provide the needed refrigeration for the process, and the need to remove almost completely components that have freezing points above the operating low temperatures of the process to avoid freezing and eventual blockage of process equipment. The most promising applications for cryogenics are expected to be for separation of CO₂ from high-pressure gases, such as in pre-combustion CO₂ capture from natural gas.

1.3 CO₂ REMOVAL USING AQUEOUS ALKANOLAMINES

1.3.1 Major Alkanolamines

Aqueous solutions of alkanolamines are the most widely used solvents for the removal of acid gas impurities, e.g. CO₂ and H₂S, from natural gas and industrial gas streams by the regenerative chemical absorption process. The use of alkanolamines for the removal of acid gases was first suggested by Bottoms (Bottoms, 1930), who discovered that “certain amines and amino compounds have the property of absorbing CO₂ and H₂S, forming pyrolytically unstable carbonates and hydrosulfides which, when

heated to a temperature above 50⁰C, decompose and liberate the carbon dioxide and hydrogen sulfide and release the free base in its original form". The basic amine process was then patented by Bottoms (1930) and by Allen *et al.* (1933). Because of the reactivity, availability, and relatively low cost, the amines have achieved a position of prominence in the gas treating industry. Today, approximately 90% of all acid gas treating processes in operation use alkanolamine solvents.

Industrially important alkanolamines for gas treating processes are monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), N-methyldiethanolamine (MDEA), triethanolamine (TEA) and diglycolamine (DGA). Table 1.2 gives the structural formulas of the commonly used alkanolamines in the gas treating industry. The alkanolamines are categorized by the degree of substitution on the central nitrogen; a single substitution denoting a primary amine, a double substitution, a secondary amine, and a triple substitution, a tertiary amine. Each of the alkanolamines has at least one hydroxyl group (–OH) and one amino group (–NH₂). In general, the hydroxyl group serves to reduce the vapor pressure of the amine and increases its water solubility, while the amino group provides the necessary alkalinity in aqueous solutions to cause the absorption of acid gases (Kohl and Nielsen, 1997). MEA, DEA, and DGA, like other primary and secondary amines, react rapidly with CO₂ to form carbamates of the respective amines. By addition of a primary or secondary amine to a purely physical solvent such as water, the CO₂ absorption capacity and rate is enhanced manifold. However, because there is a relatively high heat of absorption associated with the formation of carbamates, loaded primary and secondary amines require a substantial input of energy for the regeneration of amines. Besides, according to stoichiometry, for the primary and secondary alkanolamines, two moles of the amine react with one mole of CO₂ and thus the equilibrium loadings are limited to a maximum of 0.5 mol of CO₂/mol of amine, while the tertiary amines, which have no hydrogen atom attached to the nitrogen atom, are unable to form carbamates, and hence the stoichiometric loading is 1 mol of CO₂/mol of amine. However, the tertiary amine-CO₂ reaction leading to the formation of bicarbonate in aqueous solution is very slow, which results in low rate of absorption. Because of this, the kinetic selectivity of tertiary amines towards CO₂ is low. On the other hand, the

heat of reaction associated with the formation of bicarbonate ions is much lower than that associated with carbamate formation, and thus the regeneration energy requirement is lower for tertiary amines than that for the secondary and primary amines. Besides, the tertiary amines show a lower tendency to form degradation products than primary and secondary amines. Also, the tertiary amines generally have lower corrosion rates compared to the primary and secondary amines. It may be pointed out that corrosion has been a serious issue in amine processes. It may be noted that alkanolamines themselves are not corrosive to carbon steel, but the acid gas loaded solvents are corrosive particularly at the elevated temperature in the regenerators. The observed corrosivity of CO₂ loaded alkanolamines towards carbon steel is generally in the following order:

Primary Amines > Secondary Amines > Tertiary Amines

Speciality amine molecules are also formulated today to meet specific requirements in chemical absorption, e.g., sterically hindered amines. These amines are claimed to be potential absorbents with high equilibrium capacity and moderately high reaction rate for CO₂ (Sartori and Savage, 1983; Say *et al.*, 1984). Sterically hindered amines are generally primary or secondary amines that do not form stable carbamates. Steric hindrance is introduced in the primary or secondary amine by placing a bulky substituent group adjacent to the amino nitrogen site. A sterically hindered amine can be a primary amine in which the amino group is attached to a tertiary carbon atom or a secondary amine in which amino group is attached to a secondary or a tertiary carbon atom (Sartori *et al.*, 1987). The bulky substituent lowers the carbamate stability. By making the amine carbamate unstable, one can theoretically double the capacity of the solvent. An example of a hindered primary amino alcohol is 2-amino-2-methyl-1-propanol (AMP). 2-Piperidine ethanol (PE) is an example of a hindered secondary amino alcohol. The hindered amines can also be classified as either moderately hindered or severely hindered amines. The moderately hindered amines may be used for bulk non-selective removal of H₂S and CO₂, while severely hindered amines may be employed for the selective removal of H₂S (Sartori and Savage, 1983). Moderately hindered amines form carbamates of intermediate-to-low stability. The reaction with CO₂ proceeds mainly through the production of bicarbonate. Carbamate reversion to

bicarbonate is also a significant reaction. Hence, these moderately hindered amines have a high thermodynamic capacity for CO₂ that approaches one mol of CO₂ /mol of amine, besides having higher rate of absorption. The uses of hindered amines in CO₂ removal and for selective removal of H₂S and for non-selective simultaneous removal of CO₂ and H₂S have been commercialized by Exxon Research and Engineering Company (Goldstein, 1983; Goldstein *et al.*, 1986; Gas Process Handbook'92, 1992) under the broad designation of Flexorb solvents (Flexsorb[®] SE, Flexsorb[®] PS, Flexsorb[®] HP). Besides substantial saving on regeneration energy, the other advantage of using sterically hindered amines is their better stability than conventional amines, since hindered amines have low or no amine degradation.

1.3.2 Mixed/Blended Amines

There is a growing interest in recent times to use mixed amine solvents instead of a single amine solution for gas treating. The blended amine solvents, which consist of a mixture of a primary or secondary amine with a tertiary amine combine the higher equilibrium capacity of the tertiary amine with the higher reaction rate of the primary or secondary amine. The use of blended amines in gas treating can bring about a significant improvement in absorption capacity and absorption rate and also, a great saving in solvent regeneration energy requirements (Polasek *et al.*, 1990; Campbell and Weiland, 1989; Katti and Wolcott, 1987). Besides, these blended amine solutions also offer the advantage of setting the selectivity of the solvent toward CO₂ by judiciously mixing the amines in varying proportions which results in an additional degree of freedom for achieving the desired separation for gas treating (Vickery *et al.*, 1988). This approach could noticeably reduce capital and operating costs, while providing more flexibility in achieving the specific treated gas requirements.

More recently, there is much interest in using a high efficiency absorption and desorption rate accelerator in gas treating processes. One such activated amine system is piperazine (PZ) activated MDEA. Piperazine is used as an activator in the activated MDEA technology of BASF (Appl *et al.*, 1982) and it is claimed that PZ is more effective at much lower activator concentration than the conventional blended amines

(MEA/DEA or DEA/MDEA) for high efficiency removal of CO₂ from gas streams. Meissner (1983) and Meissner and Wagner (1983) reported that activated MDEA process is a low energy process for the removal of CO₂ from high pressure natural gas. They also observed that the capital investment for this process is significantly less than other chemical solvent processes, while energy requirements are about 20 % of other chemical solvent processes.

1.3.3 Basic Flow Scheme of a Regenerative Amine Process for Gas Treating

The general schematic of an amine process for gas sweetening is shown in Figure 1.1. The sour gas containing acid gas impurities enters the bottom of the absorber and flows upward through the packed or plate column counter currently to the lean aqueous amine solution fed to the top of the column. The treated gas leaves the top of the absorber. As the amine solution travels down the absorber, it is loaded with the acid gas constituents from the gas stream and flows from the bottom of the absorber through the amine-amine heat exchanger and then fed to the top of the regenerator, where the absorbed acid gases are removed from the loaded solution and the amine solution is regenerated. The vapor from the reboiler (primarily steam) strips the acid gases from the rich amine solution. The acid gases and steam leave the top of the regenerator column and pass through a condenser, where the steam and amine vapor are condensed. The regenerated lean amine from the bottom of the regenerator is pumped through an amine-amine heat exchanger and then through a water-cooled or air-cooled heat exchanger before being introduced to the top of the absorber column.

Usually, the absorber operates at temperatures in the range 313 – 323 K. It operates at a wide range of pressures depending on the pressure of the feed gas. For flue gas treatment, the absorber pressure is nearly atmospheric, while for natural gas or syngas treating, the absorber operates at about 7 MPa or higher. Typical operating temperature at the regenerator is in the range 383 – 393 K.